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Basic Research Needs and Opportunities on Interfaces in Solar Materials

Proceedings of a July 1980 Workshop

- Executive Summary
- Overview of Solar Energy Conversion Systems and Designs
- Assessment of the State-of-Interface Science Relevant to Solar Energy Conversion Systems
- Discussion of Interface Research Needs and Opportunities

April 1981

U.S. Department of Energy
Office of Basic Energy Sciences
Division of Materials Sciences

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Washington, D.C. 20545

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PREFACE

These Proceedings document the principal discussions and conclusions arrived at during a Workshop held in July 1980 sponsored by the DOE Division of Materials Sciences. The purpose of this Workshop was to bring together scientists and engineers from academic, industrial, and government laboratories to identify needs and opportunities for basic research on interfaces in solar materials. The participants identified generic problems at materials interfaces in solar energy conversion systems (SECS) and conceived stimulating ideas on interfacial materials research to provide a scientific foundation for the needs of these technologies. With these Proceedings the scientific research community can be exposed to the subject and deliberations of the Workshop.

An Executive Summary for these Proceedings is contained in Chapter I. Overviews of the current status of important topics related to SECS are contained in Chapters II through IX; these are summaries of plenary lectures presented on the first day of the Workshop. The needs and opportunities for research on interfaces in SECS are identified and discussed in Chapters X through XV; these are summaries generated from intensive discussion and analysis of six major problem areas by small working groups of the participants during the last three days of the Workshop.

Acronyms used throughout this document are not defined in each chapter but are given in the Glossary located on pages 235-237. The editors only permitted authors to define acronyms unique to their chapter.

The Solar Energy Research Institute provided assistance in the conduct of this Workshop and the preparation of these Proceedings. The editors express their deep appreciation to all participants for their analytical, creative, and incisive involvement. We especially thank the authors of Chapters II-IX and the chairmen of the working groups corresponding to Chapters X-XV for their cooperation and efforts in producing and/or coordinating the preparation of the written copy. Finally, we gratefully acknowledge the significant administrative, coordinative, and secretarial contributions of Melody Albrandt, Administrative Assistant for the Materials Branch at the Solar Energy Research Institute, before, during, and after the Workshop in helping us produce these Proceedings.

I. EXECUTIVE SUMMARY

R. J. Gottschall* and A. W. Czanderna[+]

Basic research needs and opportunities which pervade solar energy conversion systems (SECS) evolve from four common fundamental considerations:

- The efficiency, degradation in performance, and device lifetime for SECS are interwoven with and dependent on the structural, chemical, and electronic behavior of interfaces. The important interfaces may be grouped into three categories: Solid/Solid (S/S), Solid/Liquid (S/L), and Solid/Gas (S/G).

- The interfaces of concern for SECS are area intensive because solar radiation on the earth's surface is low in energy density. The present energy needs of the United States, approximately 85 quads, would require approximately $7.3\text{x}10^4$ square kilometers ($2.8\text{x}10^4$ square miles) of solar collectors of 50% efficiency. Furthermore, the interfacial area per unit device is significant, and is typically measured in square centimeters up to square meters. Previous developments in interfacial technology have led to the evolution of thin-film microcircuit technology, where the interfacial area per unit device is typically measured in square microns. The technological experience with microcircuits can not be translated to solar devices either linearly or by simply scaling-up however, as there are particular problems associated with the production and behavior of large-area interfaces. In addition, SECS must operate in a hostile environment whereas small area microcircuits are readily encapsulated.

- Economic SECS typically require a high and non-degrading performance lifetime of approximately thirty years. Maintenance needs and lifetime limits of SECS depend upon the design and behavior of the interfaces from which device degradation and failures are initiated. Short time laboratory data and field testing of themselves, are not capable of giving reliable predictions of the required thirty year behavior. A fundamental understanding of interfacial behavior and degradation mechanisms at an atomistic level is necessary to permit valid extrapolation of short-time test data to thirty year behavioral modeling, and to understand and ultimately minimize degradation in real solar environments.

- The behavior of the S/G interface is more accessible to contemporary analytical techniques than are S/L and S/S interfaces. However, studying reactions at the S/G interface at ambient pressures which correspond to normal solar operating environments, can not generally

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be accomplished with existing analytical techniques. Thus required understanding of the behavior of S/L, S/S, and S/G interfacial behavior is presently limited, and progress towards this understanding is being substantially impeded, because real-time in situ analytical techniques for characterization of structural, chemical, and electronic behavior do not exist. Bold, imaginative, forefront analytical device development and application are urgently required to achieve the necessary understanding of interfacial behavior and degradation phenomena at S/L, S/S, and S/G interfaces.

Tutorial information on the current status of important interfacial topics related to SECS is contained in Chapters II through IX, while needs and opportunities in interfacial research in support of SECS are identified and discussed in Chapters X through XV.

OVERVIEW OF SECS AND INTERFACIAL PHENOMENA

A background overview of existing SECS, including both quantum and thermal processes, is provided in Chapter II which identifies some key interfacial issues. Relevant behavioral parameters include reflectance, transmittance, absorptance, emittance, photovoltaic efficiency, adhesion, permeability, diffusion, corrosion, and photo-oxidative stability. Design requirements for interfaces in SECS are discussed in Chapter III where the thirty year lifetime objective and large area device requirements are noted for optical and receiver/converter subsystems. Economic structures to support receiver-converters require that thin films of the active material be incorporated into light-weight, multi-layered stacks for their support and protection. Thus, system costs dictate designs based on supported thin films, and component durability mandates encapsulating the active material. L/S interfacial degradation is discussed for photoelectrolytic systems and is generally attributed to corrosion, dissolution, and diffusion reactions between the semiconductor electrode and the electrolyte.

Fundamental aspects of the general classes of the structure and thermodynamics of interfaces are discussed in Chapter IV. It is noted that an interface is characterized by its own structure, composition, and free energy, which are distinct and separate from these same parameters characterizing the S, L, or G phases adjacent to the interface. Research efforts should simulate as closely as possible realistic ambient environments, i.e. standard atmospheric composition and pressure, and approximate operating temperatures. The wide range of required interfacial properties is also noted. Thus in some circumstances adhesive bonding is desirable, as between a protective encapsulant and the underlying functional components, but in other situations adhesive bonding is not desired such as for dust or soil deposits on protective encapsulants.

S/S INTERFACES

The S/S interface represents combinations of materials classes such as metals, ceramics, glasses, semiconductors, polymers, and amorphous metals. The task here is to relate the mechanical (adhesion, abrasion resistance, etc.), electrical (resistivity, barriers, etc.), chemical (oxidation, corrosion, etc.) and optical (reflectance, emittance, absorptance, etc.) behavior to their structural, defect, chemical, and electronic configurations.

An overview of mechanical stability problems at the S/S interface is given in Chapter V; some associated research opportunities are discussed in Chapters V and XIII. Considerations include the large area of such interfaces, as-fabricated residual-stress states, and in-service exposure to thermal cycling, excursions, and gradients, and to ambient moisture, corrodants, ultraviolet radiation, and wind-driven particulate matter. New techniques are required for the quantitative measurement of adhesion and the microscopic characterization of mechanical behavior together with the application of classical fracture toughness concepts in order to understand interfacial strengths and behavior. Polycrystalline films have a much smaller grain size and a higher crystal defect density than do corresponding materials in bulk form. To attain a reliable thirty year stability of SECS composed of such polycrystalline films requires fundamental understanding at the atomic-level of the behavior of such films under exposure to all of the aforementioned environmental parameters, including their inevitable degradative processes and mechanisms. This understanding should be coupled with nondestructive *in situ* techniques to give a capability to predict remaining useful service lifetime and early warning of impending failure.

Polymeric encapsulation is a promising method of protecting optical surfaces from moisture, corrosion, and particulate abrasion. The compelling necessity to understand bonding degradation mechanisms at interfaces between polymeric and non-polymeric solids is emphasized in Chapter XIII. Concerns include the mechanisms of metal-polymer reactions, adhesion, delamination, and the synergistic roles of environmental species such as H_2O and O_2, thermal cycling, residual stress states, and long-time ultraviolet exposure. The mechanism of polymeric degradation under ultraviolet fluence requires a fundamental level of understanding so that meaningful accelerated tests can be designed and the extrapolation of short time behavior to that anticipated over thirty year durations may become possible. A better understanding of the surface hardening behavior of polymers is required for necessary resistance to particulate abrasion resistance and retention of optical properties.

Problems resulting from diffusion in the S/S interfacial region are expected because most SECS require multilayer, large-area, thin-film, polycrystalline components. The preparation of such multilayered devices leads to a device morphology that uniquely depends on the technique and process parameters by which the device is fabricated. In general, however, such thin film structures will contain high densities of imperfections such as dislocations, grain boundaries, and dissimilar material film interfaces which act both as sources and high mobility paths for diffusing species even at low temperatures. Diffusion between and along these imperfections is sensitive to the device fabrication procedure and the resultant defect state. These multilayered thin-film structures must withstand exposure to fields (electromagnetic, thermal, electrical, and photon) and thermal stresses which may enhance defect mobility over thirty year service lifetimes. Defect mobility will in turn influence or control degradative processes which occur at interfaces in devices and their performance and efficiency *per se* by its effect on optical absorptivity, electron-hole recombination, and minority carrier lifetime in photovoltaics, and on optical absorptivity, infrared emittance, and thermal conductivity in photothermal systems.

Vital research topics in diffusion at S/S interfaces which are discussed in Chapter X include (1) development of microstructure; (2) microstructural stability; (3) dependence of diffusion and nucleation of new structures on external influences such as thermal cycling, electric fields, and radiation fields; (4) acquisition of standard S/S interfacial diffusion and electrical property reference data; and (5) the relationship between microstructure (and its time dependence) and the electrical, optical, and mechanical properties of composite multi-layered solids. The discussion in Chapter X includes recommendations for identification and characterization of diffusion phenomena involved in the formation of multilayer thin-film structures including their substrates, interdiffusion between chemically dissimilar layers under realistic operating conditions, segregation and transport of impurities at grain boundaries coupled with the desire of passivating grain boundaries with respect to photovoltaic device performance, characterization of the electrical activity at grain boundaries, and long-term behavioral stability of non-equilibrium thin-film structures.

The economic manufacture of SECS components requires adapting present large-area, high-speed technologies (e.g., vacuum, chemical vapor deposition, and physical vapor deposition) for producing reliable films and coatings. Thin film and coating research objectives emphasized in Chapter XIV are (1) to understand basic processes involved in thin film fabrication; (2) to understand the relationship between process parameters and thin film properties and behavior; (3) to improve analytical methods for characterizing films or coatings in terms of relevant materials properties and solar device degradation modes; and (4) to develop *in situ* characterization techniques which can be used in feedback modes to provide instantaneous control of deposition parameters. Concerns (1-4) are unique for large area films or coatings which are necessary for solar devices to optimize quality, uniformity, cost, and durability.

Other research needs which are discussed in Chapter XIV include understanding the (1) relationship between minority carrier lifetime and the density of states in amorphous semiconductor layers, (2) various aspects of the molecular beam growth of prototypical photovoltaic devices, (3) deposition processes that are attractive for large area devices such as plasma assisted deposition and chemical vapor deposition, (4) fundamental nucleation and growth phenomena related to both film deposition as well as to their behavior, including stability aspects of metastable films, (5) surface segregation and passivation of alloy reflector surfaces, (6) *in situ* techniques appropriate for characterizing and controlling growth processes and products, (7) material properties relevant to long-term performance and stability for various problems such as photocorrosion of semiconductor surfaces, coating stability under high photon fluence, etc., (8) existing analytical techniques and their application to characterize manufacturing processes and product behavior, and (9) behavior of passivation layers and diffusion barriers. Discussion of photothermal conversion surfaces, reflector surfaces, anti-reflective coatings, and thin-film photovoltaic transducers is contained in the Appendix to Chapter XIV.

S/L INTERFACES

The current status of S/L interface science is overviewed in Chapter VI, and research needs are discussed in Chapters VI and XI. Research opportunities such as (1) new theoretical approaches, including modeling of the double layer and diffuse layer using quantum mechanical and Monte Carlo approaches, (2) elucidating the structure at semiconductor/liquid interfaces and its bearing on photoelectrochemical solar energy conversion processes, and (3) developing new in situ spectroscopic and direct measurement techniques (e.g. ellipsometric spectroscopy, etc.) to investigate the S/L interface are developed in Chapter VI. The need for the development of new techniques for in situ S/L interface analysis and their application to both photoelectrochemistry and solar related degradation phenomena is also discussed in Chapter XI; both in situ and electrochemical analysis techniques could be used to gain an understanding of passivation-depassivation reactions, photochemical effects, and poisoning mechanisms in real (impure) electrolytes. Chapter XI discusses research needs for (1) special real-time in situ analytical techniques in order to probe and study S/L interfaces, (2) theory that incorporates the properties of the S/L interface, (3) new materials for photoelectrochemical conversion systems, (4) photo-assisted synthesis and electrocatalysis, and (5) understanding mechanisms of electrochemical degradation (especially photocorrosion), mechanical degradation (especially corrosion fatigue), and erosion in solar energy systems. The development of microscopic theoretical models is essential in order to understand the behavior of electrochemical photovoltaic cells and photoelectrosynthetic systems and to provide guidance and direction for further research in photoelectrochemistry. Chapter XI also discusses the need for clarification of electrochemical reactions and mechanisms at electrolyte/electrode interfaces, e.g. for local cell formation, active-passive transformations, inhibition mechanisms, photocorrosion mechanisms at semiconductor-solution interfaces, electrochemical phenomena in nonaqueous environments such as fused salts at elevated temperatures, and liquid NH_3 solutions, etc. Corrosion fatigue is also discussed because of thermal-induced stress cycles likely to occur in ocean-thermal energy conversion and wave power systems.

Understanding fouling behavior and deposit formation on S/L heat transfer interfaces requires specialized experiments which are discussed in Chapter XI. Experimental methods need to be developed for determining the states of residual and applied stresses and their effects on the initiation of stress-assisted corrosion, stress-corrosion cracking, corrosion fatigue, and such behavior in aqueous, non-aqueous, high-temperature, metal/polymer, and semiconductor/polymer interfaces. Solid-liquid erosion phenomena of concern include the action of moving fluids on solid surfaces, the role of suspended corrosion products, and the synergistic relationship between erosion and corrosion in S/L systems.

S/G INTERFACES

The principal methods for establishing chemical composition, long range structure, short range structure, and nature of chemical bonding at the S/G interface are reviewed in Chapter VII. Principal analytical methods involve electron and ion spectroscopies, both of which are presently limited in their application by high vacuum requirements. New methods of S/G interfacial characterization that will permit reliable analysis at atmospheric and higher pressures are needed. Both infrared ellipsometry and polarization modulation reflection absorption spectroscopy are discussed in Chapter VII, and offer some possibilities for necessary future development of analytical methods that are not subject to vacuum requirements.

Research opportunities concerning S/G reactions that may occur at surfaces of devices exposed to the normal solar environment (i.e., ambient air, high ultraviolet flux, thermal cycling, etc.) are considered in Chapter XII. Concerns include glass and polymer transmitters and polymer coatings generally, all of which may develop micro-cracks or otherwise fail in SECS at rates far in excess of those for uniform degradation. An equally important class of S/G interfaces are those developed sequentially in the manufacture of multilayer devices, e.g., mirrors and photovoltaic modules and arrays. Thus, it becomes necessary to know how the properties of a particular component layer are affected by the manufacturing environment (air, vacuum, etc.) and especially to know how the overall operation of the device is influenced by the cumulative effect of these various surface reactions. This problem is crucial because solar technologies frequently require using multilayer stacks and long life-time components.

There are a number of important chemical reactions which involve photoconversion and/or photocatalysis. In these processes, S/G interfaces occur on catalysts and their support materials. Major research needs include understanding semiconductor surfaces with and without chemisorbed species, photoconversion and photocatalytic mechanisms, effects of sensitizers, and spill-over phenomena; theoretical modeling; and developing new experimental methods to study S/G interfacial behavior under ambient pressure.

In both thermal conversion and catalytic conversion systems, the transfer of energy occuring at S/G interfaces is of concern, especially under high ultraviolet fluxes and on amorphous and non-metallic systems. This transfer of energy may involve the coupling of translational, vibrational, and rotational modes of gas molecules to excitation modes of the solid surface. In order to optimize the rate and efficiency of energy transfer, it is necessary to understand the microscopic mechanisms of coupling, energy exchange, and relaxation.

Other research opportunities at the S/G interface discussed in Chapter XII concern the chemical stability of glass surfaces exposed to atmospheric species (combined with varying levels of ultraviolet exposure); pitting corrosion; encapsulant polymer degradation mechanisms including the synergistic effects of ultraviolet radiation, and the reactivity and permeation of atmospheric species; chemisorption phenomena on semiconductor surfaces; mechanisms of photoconversion and photocatalytic reactions; the role of sensitizers on photoprocesses; and various problems related to thermoelectric and thermionic behavior.

INTERFACIAL ANALYSES

Progress in all interfacial science discussed in these Proceedings is limited by both the availability and the effective application of analytical techniques. Ideally, one seeks information concerning the absolute value and distribution in three dimensional space in the vicinity of an interface of such fundamental information as chemical identity, crystal structure, nature of bonding, and electrical characteristics. This information is sought with the best possible spatial resolution, and *in situ* under (non-vacuum) environments which coincide with those of manufacture or application. In some instances there is concern for rapid information aquisition and its feed-back to control system environment, as for example, in the manufacture of large-area thin film devices.

Limitations of contemporary experimental techniques for interfacial analysis are discussed in Chapters VIII and IX. Problems associated with electron beam power density effects, sample or substrate destruction, valence identification, and theoretical interpretation are discussed in Chapter VIII. Limitations of ion etching techniques of interfacial analysis are discussed in Chapter IX. Presently, particle probe beams require a vacuum environment which in turn necessitate vacuum compatibility for specimens. The correlation between interfacial characterization in vacuum with that under real ambient conditions is extremely difficult; it might be best accomplished by carefully integrated complementary experiments. Chapter IX discusses advantages and disadvantages of interfacial analysis, and the artifacts which may degrade spatial resolution such as surface roughness, zones of mixing, bulk and surface diffusion, residual gas adsorption, matrix effects, and various consequences of sample sputtering. Various remedies and improvements which are discussed include the use of reactive ion beams, multiple ion beams, sample rotation and special mounting, variable ion energies and angles of incidence, and data deconvolution methods.

Interfaces of many types (S/S, S/G, S/L) occur in most solar devices, often with several in close proximity. Economic considerations mandate that manufacture be reliable, reproducible, and in cost-effective quantities. To extrapolate from short term laboratory behavior to the required thirty year service behavior requires an atomic level mechanistic understanding of the degradation processes occurring at interfaces. The latter in turn requires application of forefront techniques and methods of characterization of localized microstructure and microchemistry.

Microcharacterization yielding structural, chemical, or electronic information with a lateral spatial resolution approaching atomic dimensions is considered in Chapter XV. Comparison of available techniques with these needs reveals major inadequacies. Effort is required on _in situ_ techniques. Much deeper understanding of existing techniques is necessary and totally novel characterization approaches should be encouraged, particularly for _in situ_ interfacial characterization.

Research opportunities for characterizing interfacial microstructure and microchemistry which are discussed in Chapter XV include (1) photon and ion analytical techniques for _in situ_ characterization of S/L and S/G interfaces (e.g., laser, Raman, infrared, and related techniques, Rutherford backscattering spectroscopy, and nuclear reaction analysis), (2) improved depth profiling techniques for S/S interfacial analysis, (3) analytical electron microscopy experiments and techniques appropriate to studies involving diffusion, corrosion, oxidation, grain boundary recombination processes, and defect structures, (4) high voltage (1 MeV) electron microscopy in conjunction with _in situ_ environmental stages with analytical capabilities for S/S, S/L, and S/G interfaces, (5) methods for quantitative surface analysis, characterization of beam artifacts, and improved methods of data analysis for Auger electron spectroscopy, X-ray photoelectron spectroscopy, ion scattering spectroscopy, and secondary ion mass spectroscopy, (6) new and improved techniques for interfacial analysis, including polymers, (7) general electron microscopy techniques (e.g., scanning electron microscopy, scanning transmission electron microscopy, ultra high vacuum reflection electron microscopy, high resolution transmission electron microscopy), (8) correlation of *in situ* S/L interfacial measurements with results of parallel experiments obtained after removal of the fluid, (9) atom-probe field ion microscopy and field desorption spectroscopy, and (10) appropriately integrated theoretical efforts to underpin the optimal design of new experimental systems and make the most effective use of the information they collect. An ultimate goal is to relate the mechanical (adhesion, delamination, creep, abrasion resistance, etc.), chemical (oxidation, phase change, diffusion, etc.), and electrical (resistivity, barriers, etc.) behavior of interfaces to their atomic, defect, and chemical state and configuration.

EPILOGUE

The effective implementation of many of the recommendations contained herein require the use of specialized experimental facilities and a collaborative interdisciplinary effort. Researchers are encouraged to make use of existing user-oriented national facilities for synchrotron radiation, small angle neutron scattering, and high voltage and analytical electron microscopy that are appropriate for the analysis and understanding of interfaces. It is imperative that these basic research recommendations be carried out in an interactive mode involving a balanced integrated mix of different science disciplines as well as a sound cognizance of the realities of technology.

Although there will be many different assessments of this Workshop, a number of positive results can be stated already. It has provided another opportunity for increased communication among basic and applied scientists. The involvement of the academic, industrial, and government laboratory scientific community in planning has also had an important effect in making them aware of the problems and difficulties in setting priorities for the overall field of Materials Science. Their dedicated effort in establishing these priorities and pointing out the most exciting new areas in basic research on interfaces in solar materials for SECS has brought forth this document. The task for all of us now is to carry through on the most important recommendations.

II. OVERVIEW OF SOLAR ENERGY CONVERSION TECHNOLOGIES: QUANTUM PROCESSES AND THERMAL PROCESSES

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ABSTRACT

The conversion of solar energy into heat, fuels, or electricity is accomplished by a wide range of technologies. The sunlight may first interact with the biosphere producing winds, ocean currents, thermal gradients, salinity gradients, moving water or plants to be harnessed by turbines, low temperature heat engines, or biomass processing systems. Alternatively, systems that interact directly with incoming sunlight may provide more cost effective sources of energy in many climates. The purpose of this chapter is to provide an overview of these conversion systems and their critical interfacial problems focussing primarily on direct quantum and thermal systems.

Direct quantum conversion includes the production of fuels from photobiological, photochemical, and photoelectrochemical converters, and the generation of electricity from photovoltaic systems. Key interfacial questions in these systems are related to the efficiency of charge separation and the repression of charge recombination. The electrolyte/semiconductor interface, the metal/oxide/semiconductor interfaces and the photo-oxidative stability of encapsulating layers are also important issues. On a microscopic scale, the effects of grain boundaries, defects, and material inhomogenities in the semiconductor, biological, or chemical complexes are also important.

The thermal conversion of sunlight to useful heat, ranging from low temperature hot water heating to process heat in excess of 1000° C, requires the successful absorption and conversion of photons to phonons with minimum reradiation. For temperatures in excess of 100° C, satisfactory conversion efficiencies require optical concentrators. The optical and mechanical stability of the absorbing and reflecting surfaces in solar thermal concentrators dominate the interfacial problems in these systems. The interaction of the working fluid (used to extract the heat from the receiver and to deliver it to the end use) with the container material of the receiver heat transfer system is also of considerable interest.

Brief discussions of ocean thermal, biomass, and membrane systems are also included.

I. INTRODUCTION

The purpose of this chapter is to provide a broad overview of solar energy conversion technologies, and to identify some key interface issues for systems within these technology categories. The abundant descriptive literature available on individual technologies will be referenced in the appropriate sections and the reader is referred to Refs. [1] and [2] for more thorough general treatments.

A coherent theme for solar energy research and development is the improvement in cost-effectiveness of a diverse set of conversion systems. Such an improvement requires simultaneous consideration of three factors: initial cost, durability/reliability, and performance. Some technologies (e.g., photovoltaics, photoconversion, biomass conversion, and ocean thermal energy conversion) exhibit low conversion efficiencies, and thus a considerable emphasis on performance improvements is warranted. Solar thermal processes, by contrast, show conversion efficiencies in excess of 50%, providing a greater incentive for lowering the cost of components and systems.

In almost every case, durability and reliability issues are poorly quantified and, thus, of considerable interest. However, it is important to analyze the specific system to decide the appropriate emphasis on lowered cost, improved performance, and increased lifetime, because frequently improvements in one of these categories entails sacrifices in one, or both, of the others.

The interfaces between bulk or thin film liquids, gases, and/or solids play an important role in nearly every solar technology. In many cases, the critical issue for these interfaces is the maintenance for up to 30 years of a set of key physical properties of the material(s) which adjoin the interface. These key physical properties may be properties that directly influence solar device behavior, such as reflectance, transmittance, absorptance, emittance, or photovoltaic efficiency; or indirect properties such as adhesion, permeability, interdiffusion, or photo-oxidative stability. These properties must be maintained in a wide variety of environments, often in the presence of high-energy photons and elevated temperature. In some instances, especially for photoconversion systems, new interfaces must be established and characterized to improve the conversion efficiency. Often the desired interfaces require juxtaposition of materials that are inherently incompatible, either physically or chemically, which means that the constraint of cost/performance/durability optimization critical to the cost effectiveness of the ultimate device must be applied to such problems. Overviews of some of the interface issues in various solar technologies can be found in Refs. [3] and [4]. Specific interfaces of interest are discussed in Chapter IV.

II. SOLAR ENERGY CONVERSION SYSTEMS

Solar energy conversion systems can be classifed as either quantum or thermal conversion processes. Quantum processes convert photons into electrical or chemical energy. Thermal processes convert photons to phonons. Either conversion path may be subclassified as indirect, or direct, depending on whether the biosphere provides an intermediate collection step or not. Indirect quantum systems are primarily biological leading to fuel and chemical feedstock. Indirect thermal systems include wind, ocean energy systems (thermal gradients, tides, waves, currents, and salinity gradients), and hydropower. Direct conversion, in either the quantum or thermal case, requires the design and construction of systems to convert solar energy directly to the appropriate end use.

The quantum and thermal pathways lead to various end uses as illustrated in Fig. 1. These end uses are fuels and chemicals, electricity, mechanical work, and heat at temperatures ranging from 60°C to over 1000°C. Fuels and chemicals from solar energy may be obtained from the processing of biomass residues or energy plantation products, from the synthesis of materials using solar thermal or solar electric energy, and from direct conversion using photochemical or photobiological systems. The systems to convert sunlight to electricity (or mechanical work) include photovoltaic, photoelectrochemical, solar thermal-powered heat engines, wind-energy systems, and ocean thermal gradient systems. Solar energy conversion systems that can provide heat include passive

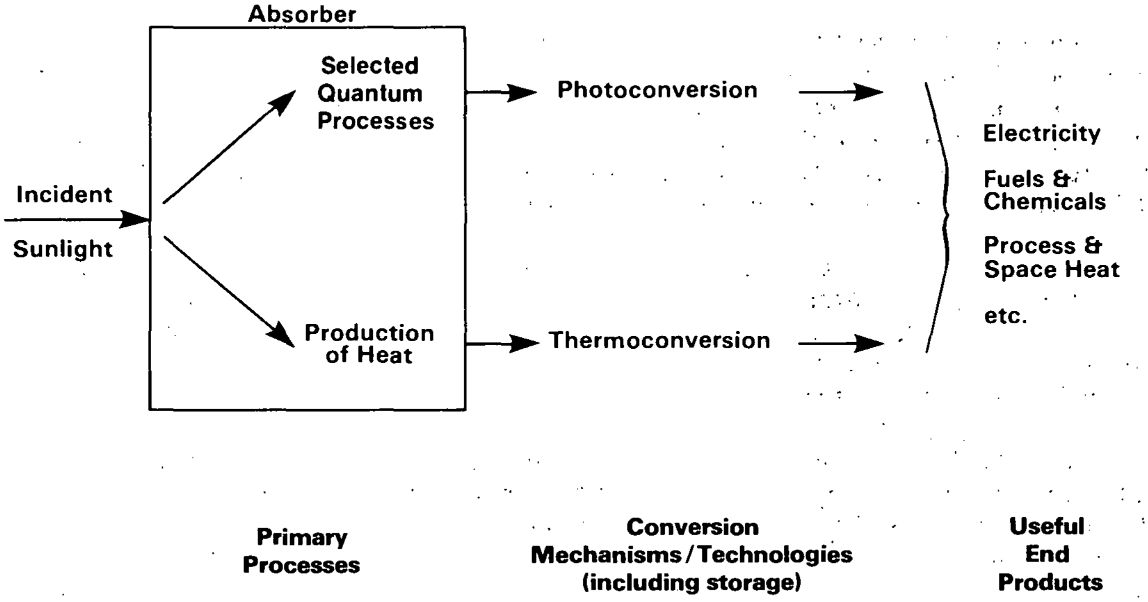

Fig. 1. Solar energy conversion processes (after Claassen and Butler [5]).

buildings, solar ponds, flat-plate collectors, evacuated tube collectors, nonimaging low-concentration ratio collectors, single axis tracking concentrators (Fresnel, parabolic, and hemispherical) and two axis tracking concentrators (parabolic dishes, spherical dishes, and central receivers).

Figure 2 provides some examples of solar energy conversion systems. Some of these systems are modular and can be distributed. Others are large and by necessity centralized. The shallow solar pond concept combines collector and storage in an inexpensive configuration using H_2O and a transparent insulating surface layer. A related concept employs a self-stabilizing inverted thermal gradient obtained through the introduction of salts to the pond and eliminating the need for the transparent insulation. The solar pond is a seasonal storage device allowing the use of thermal energy up to approximately 100° C in the fall and winter heating seasons after collection in the summer. Passive building designs use innovative architectural features to transform building structures into energy conversion systems. Passive designs provide an optical path for light into the structure during the heating season, and a large thermal mass to store energy and deliver heat to the building at low cost and relatively constant temperature. Single axis tracking concentrators reflect light onto an absorbing tube to deliver end use temperatures up to approximately 300° C. The Fresnel design illustrated in Fig. 2 provides for each mirror facet to individually direct the sunlight onto the tube. Parabolic troughs with simpler construction and fewer moving parts have emerged as the leading technology for single axis tracking concentration. Parabolic dishes provide very high temperature thermal energy by allowing extremely high concentration ratios. The maintenance of the optical accuracy of the systems is a critical concern requiring both highly reflecting surfaces and accurate mechanical supports and tracking mechanisms. The external central receiver receives reflected solar energy from a field of Fresnel mirrors (heliostats). The systems are typically large (in excess of 1 MW_e) and have the advantage of minimal fluid handling in contrast to the single axis and dish technologies.

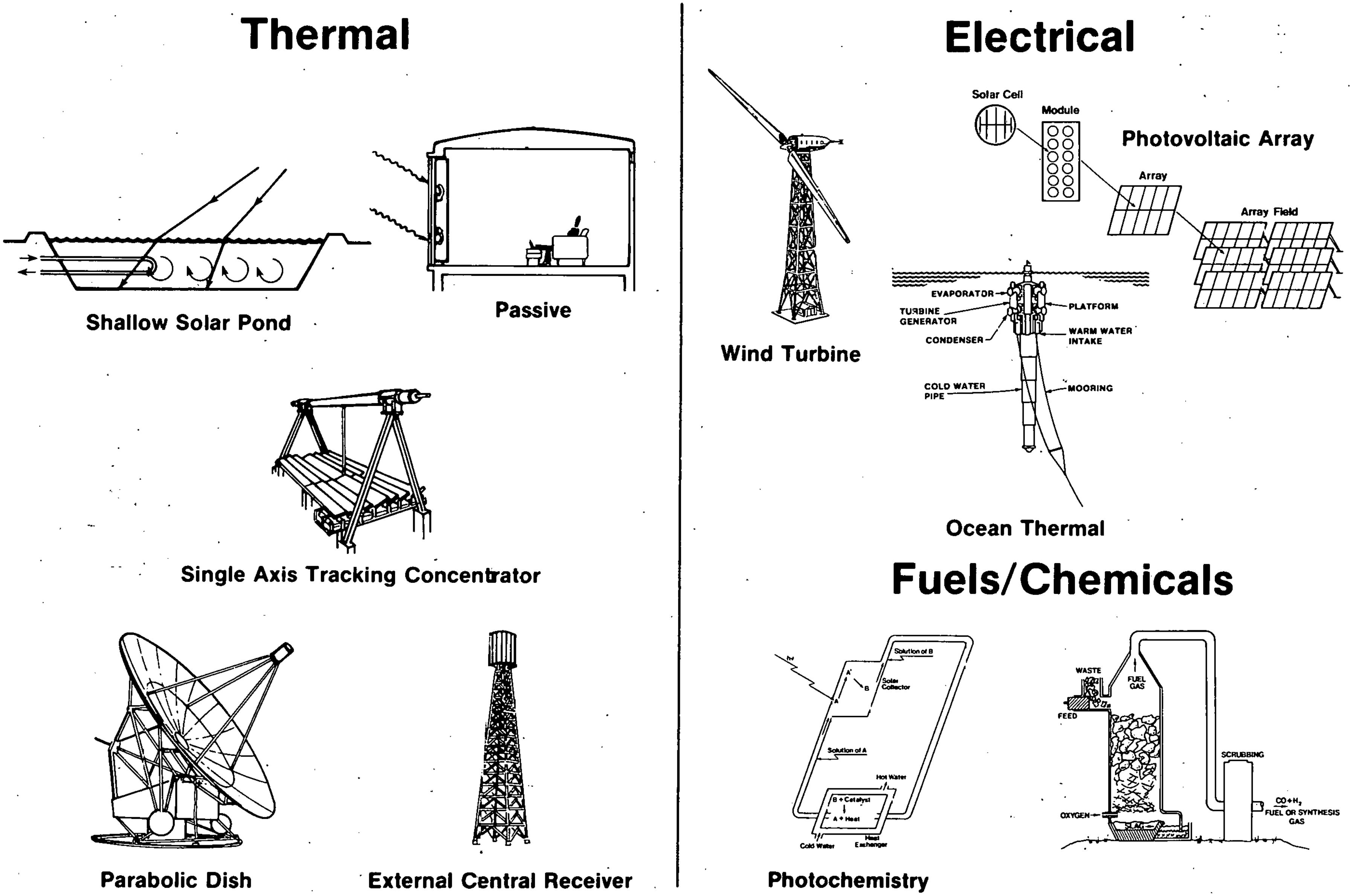

Fig. 2. Selected solar energy conversion systems (after Call [3]).

Wind turbines are being planned and constructed over the size range from a few kW_e to greater than two MW_e in delivered electrical output. Wind energy is one of the most cost-effective, near-term renewable electric options. Ocean thermal energy systems extract electrical power from the small ($< 30°C$) temperature differential existing between the surface and deep water of the tropical oceans. By necessity, ocean thermal systems are large (greater than 10 MW_e) requiring the circulation of large amounts of both warm surface water and cold deep water. The achievement and maintenance of heat transfer surfaces within the low temperature heat engines is critical. Photovoltaic arrays are expected to provide cost effective electrical energy using solid state direct conversion of photons to electrical power. Mass production techniques must be employed to process large areas of semiconductor material very inexpensively. The large number of production steps required to transform raw materials into working devices must be minimized and simplified.

Photochemical systems represent a frontier research area in renewable energy technologies and promise to provide useful fuels and chemicals directly from the interaction of solar photons with solutions containing synthesized organic molecules. The technology employs chemical complexes that act as transitory storage of energy in the form of electrons until a chemical reaction can take place within the solution to produce a useful fuel or chemical. Pyrolysis is one example of a large number of biomass processing technologies that can be used to transform waste or cultivated biological feedstocks into useful fuels and chemicals. Pyrolysis is the anaerobic heating of biomass to produce a higher grade fuel that may be transportable and more widely useful.

The systems illustrated in Fig. 2 are intended to provide a sense of the diversity of solar energy conversion systems. More thorough descriptions of many solar energy conversion technologies are (by topic): photovoltaics [5-10], solar thermal [11-16], biofuels [17-21], wind [22-26], ocean energy systems [27-31], alcohol fuels [32-33], and photoconversion [34-37].

A. Quantum Processes

As shown in Fig. 3, primary quantum processes occur in the photochemical, photosynthetic, and photovoltaic conversion of solar energy. The primary conversion mechanisms and useful end products are also indicated in this figure.

1. Photovoltaics

Photovoltaic devices consist of a series of critical interfaces. As shown in Figs. 4a and 4b, these include air/encapsulant, encapsulant/metallization, metallization/semiconductor, and the junction. Polymer encapsulant materials must resist moisture, thermal cycling, and photo-oxidation to provide impermeable protection to the underlying device and to transmit solar photons effectively. The polymer must not be susceptible to accelerated attack due to the presence of metal ions or atoms. Similarly, ohmic contact to the semiconductor device material must be made by the metal layer while metallic diffusion into the device material must be limited to minimize the number of charge recombination centers. The charge separation region of the photovoltaic junction must also be maintained against the potential interdiffusion of dissimilar semiconducting materials or dopants. Kazmerski [38] has extensively reviewed the research on photovoltaic devices and has classified types of photovoltaic devices by the categories homojunctions, heterojunctions, Schottky barriers, metal insulator semiconductor (MIS) devices,

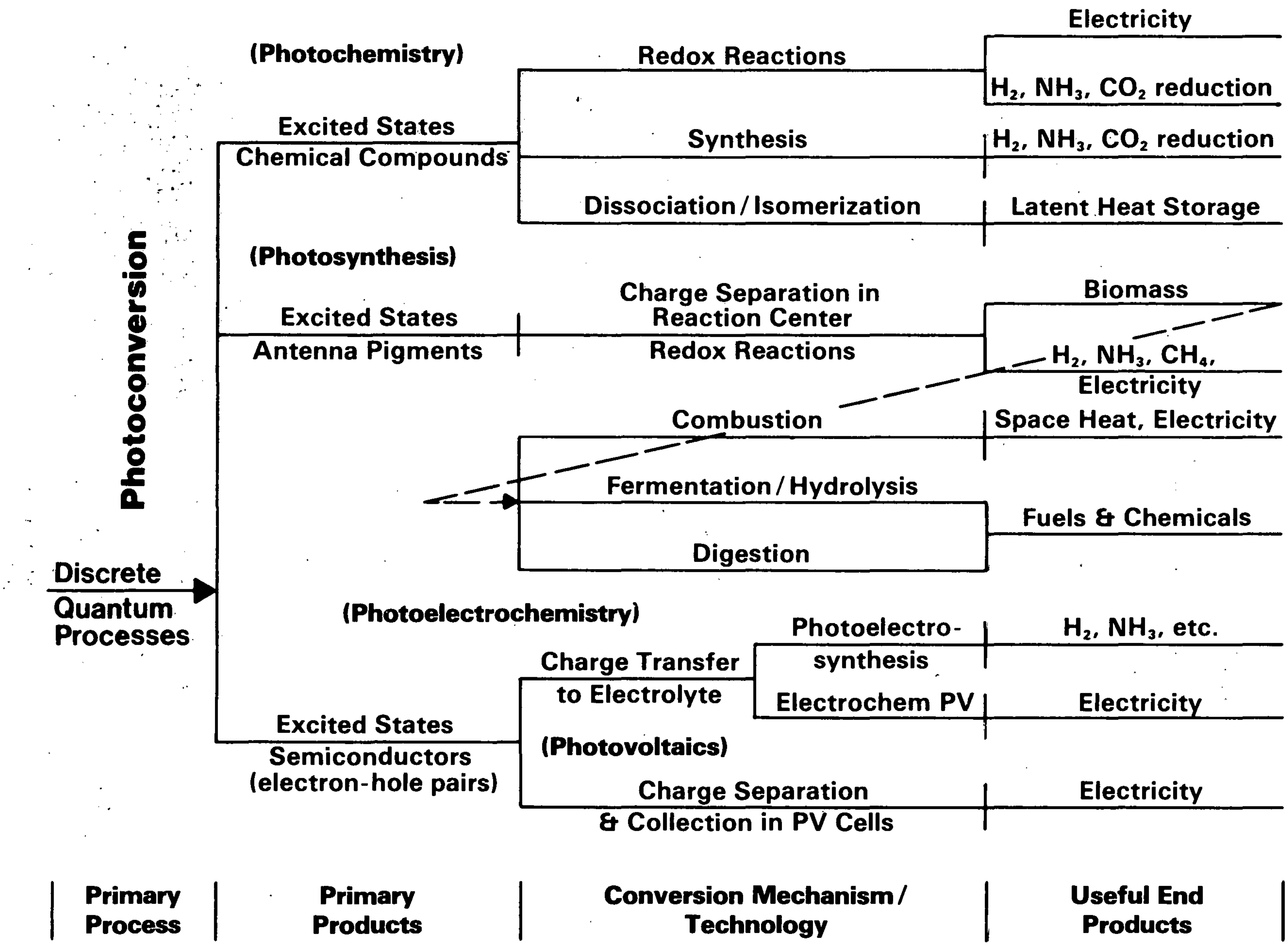

Fig. 3. Detailed framework for photoconversion paths (after Claassen and Butler [5]).

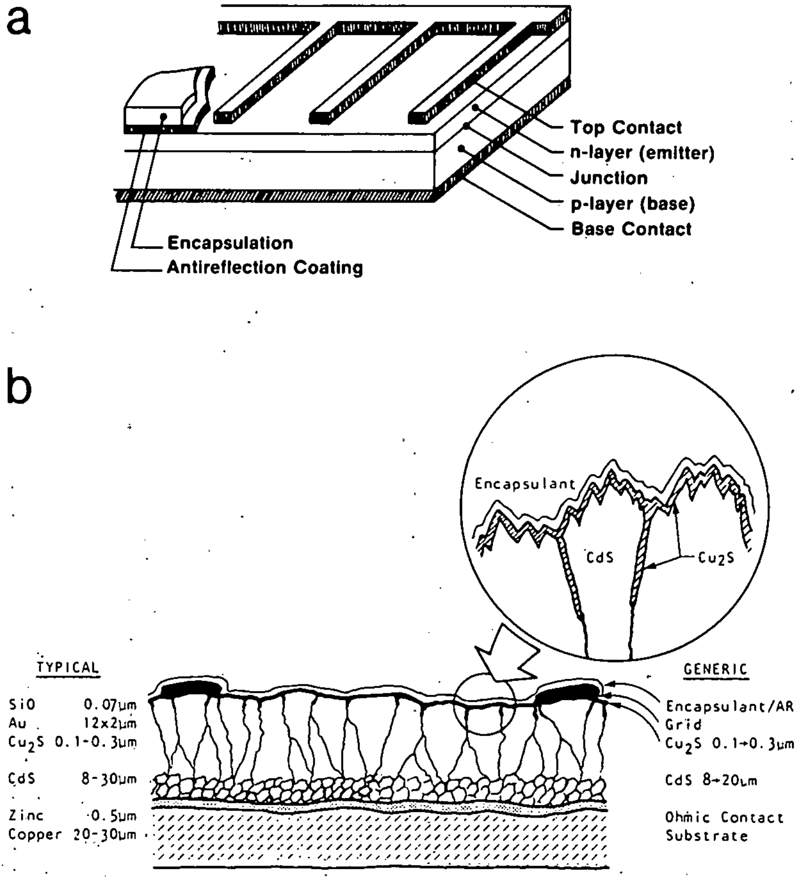

Fig. 4. Solar Cells: (a) generic (after Kazmerski [38]) and (b) thin-film solar cell, illustrating complexity due to microstructure and nonuniformities (after Rothwarf et al. [49]).

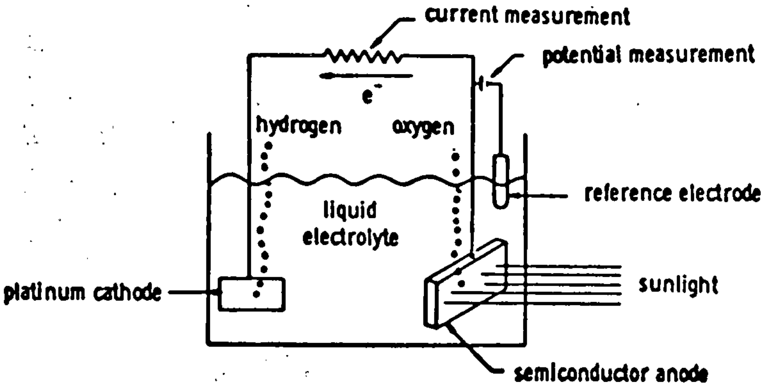

Fig. 5. A photoelectrochemical cell for the decomposition of H_2O into H_2 and O_2. The cell consists of a basic aqueous electrolyte, a photoactive semiconducting anode and a Pt or graphite cathode. Experimentally, potential is measured between the anode and a reference electrode and current between the anode and the cathode (after Ginley et al. [42]).

semiconductor insulator semiconductor (SIS) devices and amorphous devices. Common device examples of each category, respectively, are single crystal Si, CdS/Cu_2S, Au/GaAs, Al/SiO_2/Si, ITO/Si, and amorphous Si. For established devices such as the single crystal Si photovoltaic cell, interface issues are focussed on maintaining excellent performance. For advanced thin film and polycrystalline devices, the challenge is both to obtain and maintain good performance at each interface [39]. The importance of grain boundaries is a pervasive issue for polycrystalline materials and this and other photovoltaic interface issues have been reviewed extensively [40,41].

2. Photoelectrochemical, Photochemical, and Photobiological Systems

In general, photoelectrochemical, photochemical, and photobiological systems have not evolved to an advanced commercial state so that general conceptual configurations for devices are not available in contrast to the situation for photovoltaics. As an example of a potential device, a typical photoelectrochemical cell for decomposing water into H_2 and O_2 appears as shown in Fig. 5. Oxidation occurs at the photo-anode and reduction at the metallic or graphite cathode.

Research and development is progressing along the lines of small particles, colloids, macromolecules, or large synthesized organic molecules entrained in a working fluid. These complexes absorb photons and use the captured energy to convert molecular constituents in the working fluid into more enery-rich fuels and chemicals. The interface issues are predominately ones of geometry: the reactant molecules must be accommodated at a surface in such a way that energy can be transferred through the desired chemical reaction. Additionally, the surface of the complex must play only a transitory role in the chemical reaction preserving the surface for subsequent and repeated synthesis of fuel or chemical molecules. Recent overviews of this rapidly expanding subject are available in Refs. 35 and 43.

B. Photothermal Processes (Systems)

Figure 6 illustrates the framework for thermal conversion paths. Within the category of hot liquids, salts, and gases, the subcategories of thermomechanical, pyroelectric, thermoelectric, thermophotovoltaic, and heat engines require the highest practical temperatures to maximize the Carnot efficiency of the desired output. Most of these applications, therefore, are expected to require concentrating collectors. Within the category of direct heat transfer, however, a broad range of end-use temperatures is needed. The technologies to meet these end uses can be logically divided into concentrating and nonconcentrating systems where the nonconcentrating collectors provide heat primarily below 100° C.

1. Solar Concentrators

In order to obtain heat from direct solar radiation at temperatures greater than 100° C and with acceptable conversion efficiency it is necessary to concentrate sunlight. Although most commonly achieved through reflection, concentrators based on refraction (e.g., Fresnel lens) can also accomplish this task. The conventional reflectors for solar thermal concentrators have been the commercial Ag/glass mirror system (Fig. 7); however, evolving lightweight designs include combinations of Ag or Al with thin glass or polymer supporting layers. Only Ag and Al have a high enough solar weighted

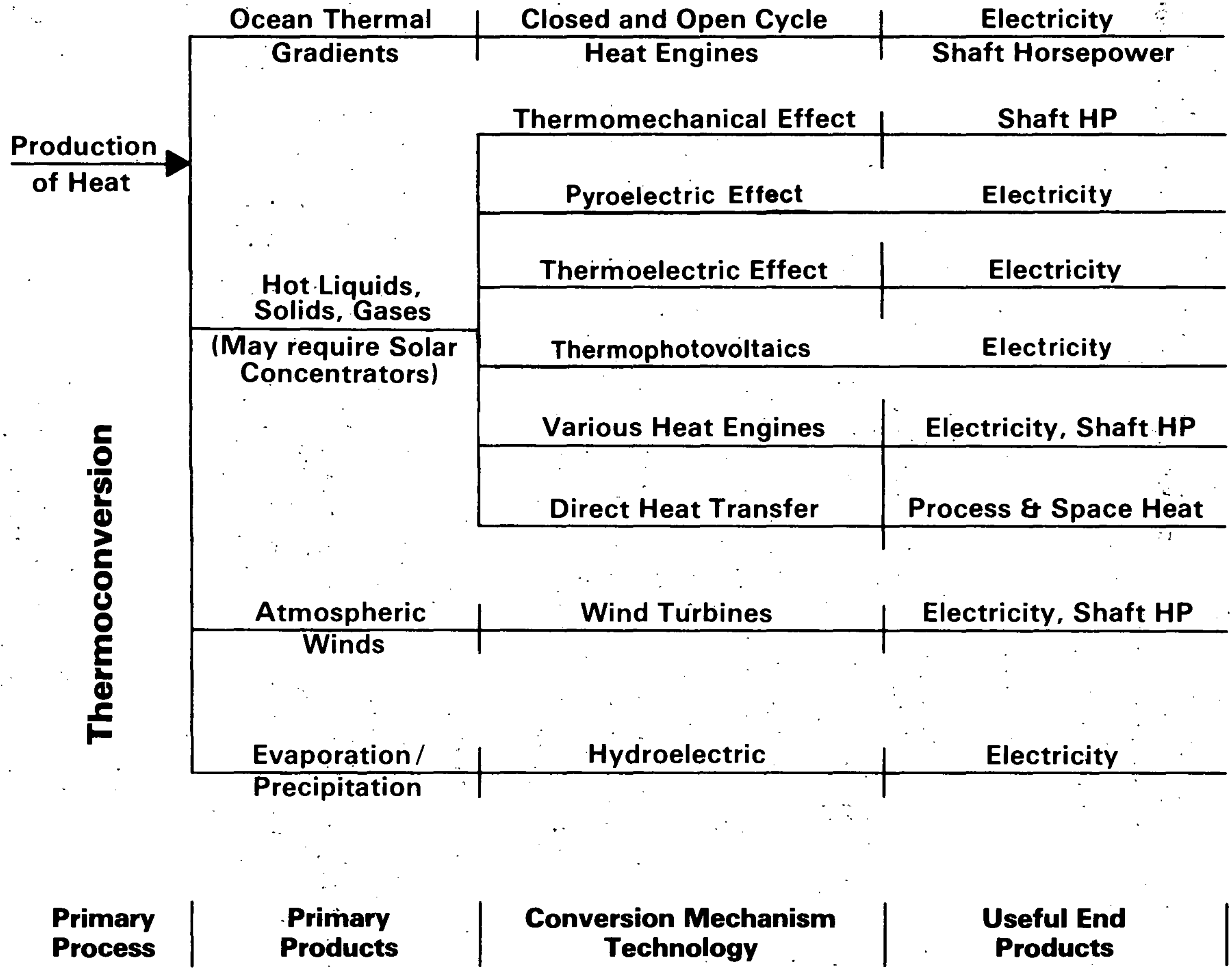

Fig. 6. Detailed framework for thermal conversion paths (after Claassen and Butler [5]).

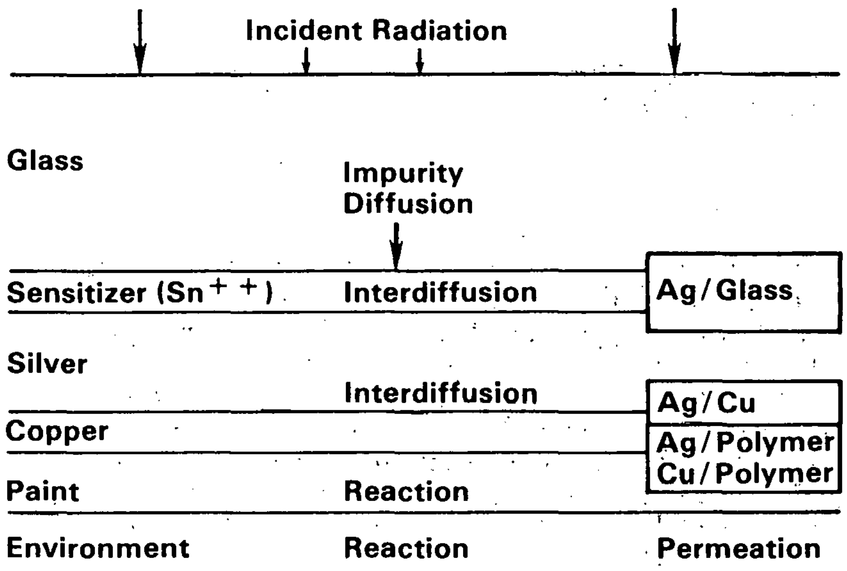

Fig. 7. Interface issues for Ag/glass reflectors (after Czanderna [44]).

reflectance to be considered for cost effective solar reflectors (see Chapter III, Fig. 1). Since the metal reflecting films are extremely thin, protection through the front (glass) and rear surfaces of the reflector is key. The maintenance of the transmittance of the polymer supporting layer in this application is also critical and the photo-oxidative stability of the polymer in the presence of metal atoms and ions must be studied. Solar mirror materials are reviewed in Ref. 45.

Once the sunlight has been reflected, it must be absorbed efficiently by the receiver and the environment/absorber interface becomes another critical issue. The receiver surface ideally would combine excellent solar absorptance with reduced thermal emittance to avoid radiative losses. The absorber stack must resist oxidation from ambient gases at elevated temperatures as well as interdiffusion in multilayer structures. The status of the materials for solar receiver applications has been reviewed extensively [46,47].

The energy from the solar receiver must be transferred to a working fluid and the maintenance of the container/working fluid interface for heat transfer and corrosion durability perspectives is critical. The working fluid may be air or other gases, high pressure water/steam, molten salts or molten metals. Container materials may be steel, stainless steels or advanced ceramic materials (e.g., SiC, but which is difficult to shape or form) for extremely high temperature use. Solar applications introduce extreme thermal cycling which provides a unique aspect to this problem. Overviews of issues at the container working fluid interface are available [48,49].

2. Low Temperature Solar Thermal Systems (< 100° C)

Flat plate collectors, evacuated tube collectors, solar ponds, and passive solar architecture including greenhouses exhibit a common need for inexpensive, highly transmitting glasses and polymers [50]. The interaction of the surface of advanced polymer systems with moisture, pollution, and a photo-oxidative environment make this an extremely important interface issue. The use of direct contact (two fluid) heat exchange for both low and high temperature solar thermal systems also raises the issue of heat and mass transfer in highly dispersed fluid phases.

3. Ocean Thermal Energy Conversion

Ocean thermal energy conversion systems convert the energy stored in the thermal gradient between the cold deep ocean waters and the warm tropical surface water into electricity using a low temperature heat engine. The principal concept seeks to run a large organic Rankine cycle heat engine using this temperature differential. In the heat engine a working fluid such as NH_3 is evaporated by the warm water passes through a turbine and is condensed by the cool water. Critical to the success of this concept is the heat transfer across very large heat exchanger areas. The fouling of the heat exchanger surfaces on the ocean water side by microorganisms and the corrosion of the Ti or Al heat exchanger surfaces in a potentially caustic NH_3/seawater environment due to small leaks are critical concerns.

C. Biomass Energy Conversion Systems

As illustrated in Fig. 8, a very large number of combinations of feedstock, processing, and output variables are potentially available from the conversion of organic biomass residues into more useful fuels and chemicals. Each process must be contained as inexpensively as possible and to select the container material it is important to understand the chemical environment created by the feedstock and products and the physical environment created by the process. In some cases, it is also important to understand the impact of the container on the processing organisms. The interface between the containment and working mixtures is poorly defined for most systems and understanding leading to more cost effective choices for containment has wide ranging implications for biomass conversion systems.

D. Membranes

Membranes may play a critical role in the production of alcohol, in the separation of end products from biomass process mixtures, in some fuel cell and battery systems, and in the extraction of energy from salinity gradients at the ocean/fresh water interface. There is considerable research activity in membrane separation processes which has not yet been directed specifically at solar applications, and with few exceptions has not yielded commercially viable applications. The promise is sufficient, however to spur a continuing research effort, the results of which can guide the solar-oriented work.

Large scale applications using membranes to separate H_2 from petrochemical streams have operated for 15 years. This technology may have application to the separation of H_2 produced by bioprocesses. Separation of O_2 from air using membranes has been applied in medical and other special applications.

Extensions of this technology to upgrading the O_2 content of feed gases to biogasification units is a promising application. Many laboratory scale organic/H_2O separations have been accomplished using membrane processes. Application of membranes to C_2H_5OH/H_2O may eliminate, or reduce, the distillation step which is energy intensive. Reverse osmosis and pervaporation membrane processes to accomplish the separation are illustrated in Fig. 9. The chemistry and morphology of membranes and the long-term

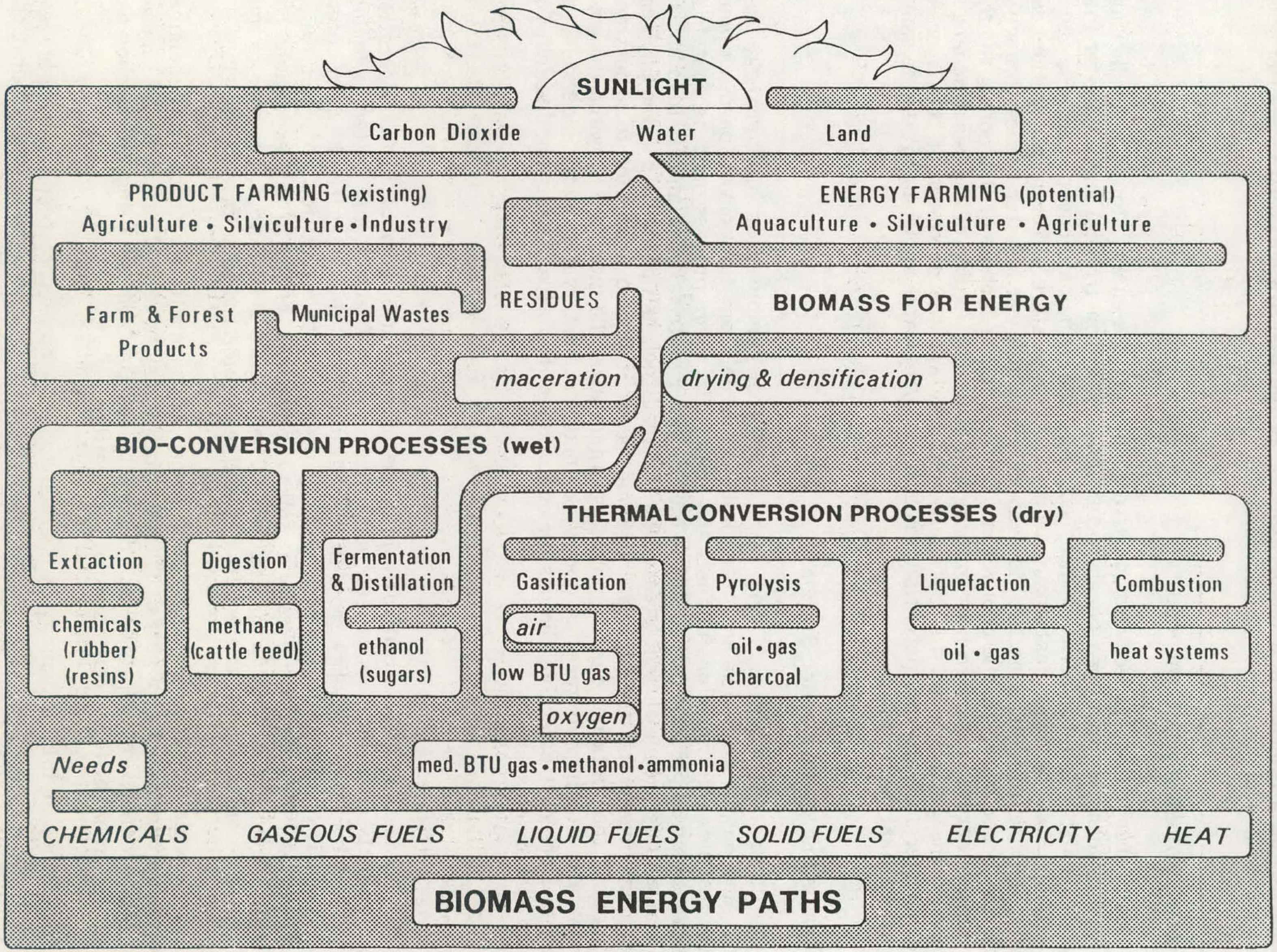

Fig. 8. Biomass energy paths (after Reed [50]).

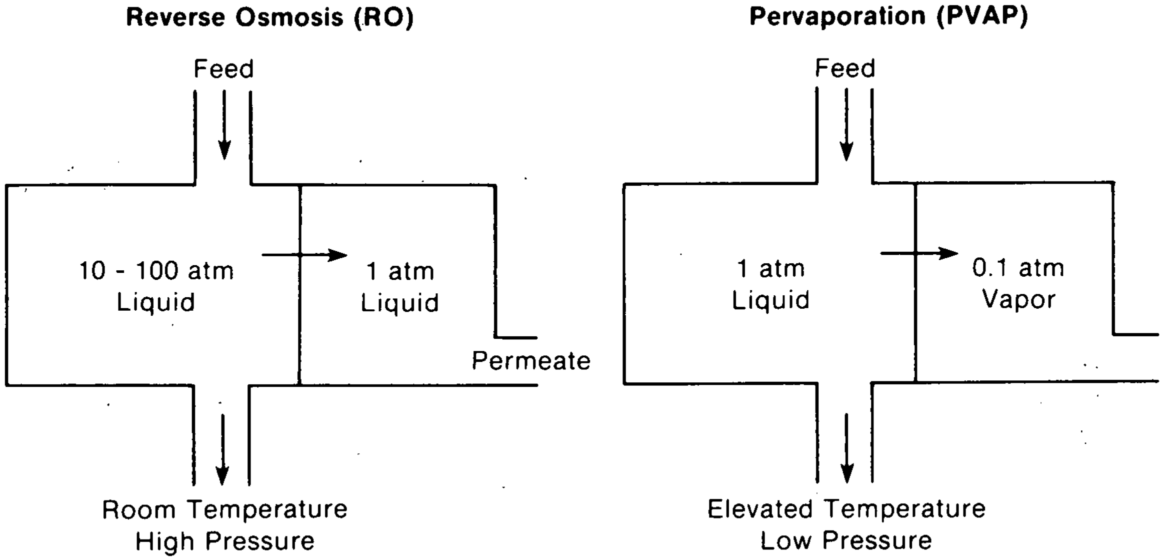

Fig. 9. Two types of membrane separation techniques (after Schissel and Benson [51]).

maintenance of key properties is crucial to their commercial use in the energy sector. Research is needed to find membranes with sufficient through-put, selectivity, and lifetime to make membrane processes economically competitive.

III. CONCLUSION

An attempt has been made to provide an overview of solar energy conversion systems and to illustrate there are numerous key interface issues. It is clear that the diverse technology base in the renewable energy field provides a large number of exciting research opportunities.

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III. DESIGN REQUIREMENTS FOR INTERFACES IN SOLAR ENERGY CONVERSION TECHNOLOGIES

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ABSTRACT

The interface needs of solar energy systems are described according to their role in either optical subsystems or receiver/converter subsystems. Many of the functions performed by these subsystems require large areas of interfaces which must be produced by low cost processes, and result in stable chemical, physical, and optical interfaces. The large areas required, e.g., 2000 m^2 for 1 MW of solar thermal power or approximately 28,000 square miles for the annual U.S. needs of 85 quads, are in marked contrast with the small areas used in the microelectronics industry. Examples of interfaces in solar reflectors, absorbers, and photovoltaic cells are used to illustrate the constraints placed on solar interfaces. The combined requirements posed by the solar radiation, terrestrial weather, and system operating conditions place unique demands on the materials and their interfaces. Basic and applied interface problems must be addressed and solved as solar technologies are developed and deployed.

I. INTRODUCTION

Solar energy conversion systems require large areas of collectors to gather the sun's energy density which is approximately 1.0 kW/m^2 at the earth's surface on a clear day at noon. To supply all the current energy needs of the United States, i.e., about 85 quads, would require approximately 73 x 10^3 square kilometers (28 x 10^3 square miles) of solar collectors [1]. A system capable of producing 1 MW/of thermal peak (noon) power which could be converted to 25 kW of electric power, would require 2000 m^2 of 50% efficient solar collectors. Approximately half of the total system cost is in the optical collector system and the balance in the receiver converter system. Collectors currently weigh between 2.3 kg/m^2 (5 lb/ft^2) and 6.8 kg/m^2 (15 lbs/ft^2) [2]. Thus, using an average collector weight of 4.5 kg/m^2, one can see that 9000 kg of collectors alone must be used to produce 1 MW of thermal power. Thus, solar energy systems are both large area and materials intensive. This makes their initial costs high relative to coal, oil, and gas systems. The life cycle cost of solar systems can be reduced nominally by improving component performance and dramatically by increasing useful component life [3]. Thus, minimum capital cost materials and processes which result in components and interfaces with 30 years expected lives may be required for economic viability [4]. The 30 year lifetime may be necessary, because operation and maintenance costs for large collector arrays are expected to be high, increasing significantly the system payback period. The microelectronic industry has developed and used thin films technology effectively for small areas. The large areas of thin films required by solar energy conversion systems cannot be achieved by directly scaling up present thin film technology. The materials and processes must be adapted to provide long lives in large areas. The processes may be modified to decrease defects per unit area, reducing variations, and by using materials that are more tolerant to processing variables.

The uniquely solar environmental variables that act on materials are related to passage of solar photons without absorbing energy from them, or with the intentional conversion of solar photons to chemical, thermal, electrical or mechanical work. A great deal of work has been done on the interaction of light with optical materials. The art of stabilizing materials for use in solar radiation environments [5] is well developed; however, the basic understanding is not well developed. The economic demands for low capital cost provides incentive for alternative materials and processes, many of which have complex interfaces.

The unique materials problems in solar energy conversion are divided into optical subsystems and receiver converter subsystems (see Table I). The optical materials either transmit or reflect the solar radiation to a receiver/converter. These materials must transfer as much of the radiation as possible, while resisting environmental degradation from UV, wind, water, dust, and cyclic temperature. In addition, they must have minimal chromatic aberration due to the variations in the index of refraction and minimum optical figure distortion (spherical aberration) for focusing applications [6]. The optical transmittance and lens properties and their retention under outdoor environments are the important design considerations for alternative materials choices.

The receiver/converter materials design considerations are specific to the energy conversion systems chosen such as solar/thermal, solar/electric, and solar/chemical. Solar/thermal systems depend on selective absorbers, which absorb radiation and re-emit as little as possible. This generally requires a multilayered stack of materials operating at elevated temperature. In solar/electric converters, the homo- and heterojunctions in photovoltaic cells must provide efficient charge separation while supressing grain boundary and interface diffusion, which would alter the electrical properties of the junction. In solar/chemical systems, catalysts and chemical reaction vessels must not change characteristics which will irreversibly slow the desired chemical reactions.

Reducing the design of conceptual solar energy system to practice requires the selection of appropriate components which are sized for cost effectiveness by system considerations. Once the subsystem components have been selected, then materials choices can be made with regard to providing cost effective subsystem performance. The system optimization criteria for solar energy conversion systems is generally chosen to be life cycle cost. This implies that the elements of life cycle cost for each subsystem must be optimized. Thus, subsystem performance, subsystem capital cost, and subsystem life are the key issues for the development of a cost effective system. For example, the challenge in the optical subsystem is to cover very large areas at low capital cost with highly reliable materials systems. The challenge for receiver/converter systems is to provide a highly efficient path for changing the photon energy into an alternate form, while maintaining low capital costs and high reliability. These requirements translate into the need to understand and characterize surfaces and interfaces in these subsystems, to understand their performance, and how to maintain their performance as a function of time. The design requirements in solar energy systems result in large areas of interfaces. Some of the needs for studying interfaces are highlighted in this chapter.

II. OPTICAL SUBSYSTEMS

Both reflecting and refracting optical subsystems require an optically transparent material which is both weather stable and resistant to changes due to solar photons. Silicate glasses and optical plastics made from polymethylmethacrylates (acrylics), polycarbonates, and polyesters are commonly used as mirror substrates, collector windows (glazings), and refracting lenses. The common glasses used are soda lime (window glass),

Table 1. SUBSYSTEMS REQUIRED FOR VARIOUS TYPES OF SOLAR COLLECTORS

Collector Types	Optical Subsystem		Receiver/Converter Subsystem		
	Reflection	Refraction	Thermal	Electric Photovoltaic	Chemical
POINT FOCUS					
Standard	o Parabolic Dish	o Circular Convex Lens	o Electricity	o GaAs & Multi-junction cells	o Chemical dissociation
Fresnel	o Heliostat	o Circular Fresnel Lens	o Fuels & Chemicals		
LINE FOCUS					
Standard	o Parabolic Trough	o Cylindrical Convex Lens	o Industrial Process Heat	o Si	o Chemical dissociation
Fresnel	o Slat Reflectors	o Linear Fresnel			
FLAT PLATE	o None	o Planar Lens	o Space Heating and Cooling	o Cu_2S/CdS	o $CaSO_4 \cdot 4H_2O$
WIND & OCEAN		o Atmosphere	o Wind & Ocean Waves, Currents and Thermal Gradients		o Photobiology/ Microalgae

borosilicate (Pyrex *) and aluminosilicate (Chemcore *). The chemical, physical, and mechanical properties of the glasses and plastics used vary dramatically. These materials are usually used as substrates or superstrates for composite mirrors or lenses. The selection and use of the transparent materials is governed by the design requirements of the applications. These may require chemical resistance, abrasion resistance, permeability, strength, flexibility, coefficient of expansion, Young's modulus, etc. Examples of several mirrors and lenses will illustrate design constraints.

The reflecting layer in a mirror is normally Ag or Al because of their solar reflectivity, 97 and 92% respectively, as can be deduced from Fig. 1. The next best is Cu at 78% and other materials in the 70% regime are expensive and/or rare. Both Ag and Al react with the atmosphere and will soon lose their high reflectivity if not protected. Aluminum forms continuously growing oxides and hydroxides while Ag can form sulfides and chlorides, and also agglomerate when thin films are used. A typical Ag "bathroom" mirror is shown in Fig. 2-A. It consists of a soda lime glass superstrate, Sn^{++} sensitive (monolayer), a 100 nm layer of wet chemical Ag, a 30 nm Cu base layer, and a polymer paint for added protection. Deploying large areas of this type of mirror has resulted in unacceptable corrosion of the Ag layer and commensurate loss of reflectivity. This composite consists of an electrochemical battery with at least 4 active interfaces. Moisture and ambient temperature cycling combine to provide chemical and mechanical stresses on this mirror system. Silver agglomeration, and Ag chlorides and sulfides have all been identified in degradation of these mirrors. A basic understanding of these interfacial reactions may offer the key to designing a mirror which will resist outside exposure at costs as low as current mirrors designed for bathrooms.

Another important class of mirrors are produced by evaporating Ag or Al layers on acrylic sheets or films. These polymers are permeable to atmospheric contaminants, and Ag layers, which provide almost 10% higher reflectives than Al, are degraded to uselessness after outside exposure for a few days. Aluminum layers are more stable, but they are also subject to degradation after prolonged exposure. The stability of these interfaces, if possible, would make lightweight low cost polymer reflectors based on Ag or Al practical. Polymer films are particularly attractive because they can be used as thin sections and, hence, have very low weights per area of collector. In many instances, these films are composites consisting of a polyester film for tensile strength, a UV attenuating complex polymer film or coating to screen out the high energy solar photons which can cause chemical reactions in hydrocarbon polymer systems, and an inorganic silicate anti-abrasion coating. These composite polymer films must be resistant to abrasion, solar UV degradation, tensile loading, chemical permeability, and thermal expansion mismatch stresses. Composite films allow the materials and interfaces to be tailored to give the best balance between the desired and achievable properties.

These same design considerations also apply to photovoltaic glazing and encapsulating systems (see Fig. 4, Chapter II), except the electrical properties of the Ag contact grid must be maintained with time instead of Ag layer reflectivity. Chemical reactant and product permeability are key issues, as is thermal expansion mismatch stress, with the solar cells. In some instances, the abrasion layer is a thin plate of glass which introduces the glass-plastic interface.

Failures of interfaces in mirror and encapsulant system are often due to delamination or permeability. Delaminations are caused by mechanical stress (shear or tensile)

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*Corning glass trademarks.

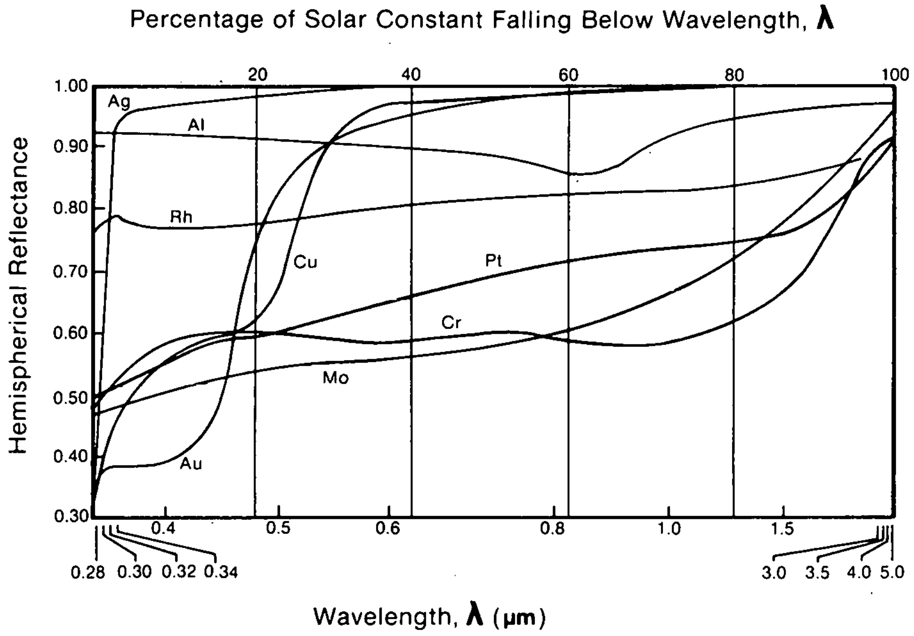
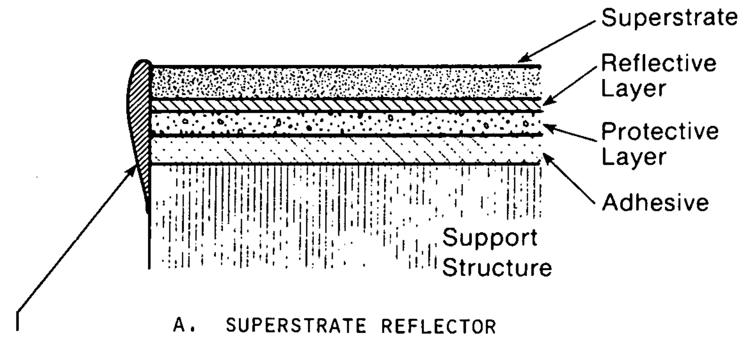
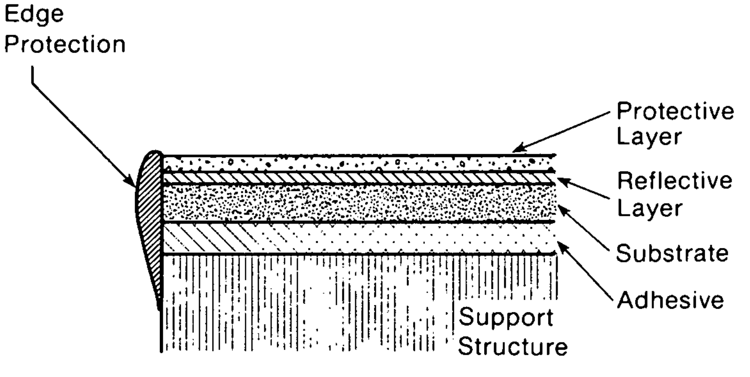


Fig. 1 Hemispherical reflectance of common metals as a function of wavelength over the solar spectrum.



A. SUPERSTRATE REFLECTOR



B. SUBSTRATE REFLECTOR

Fig. 2 Two types of commonly used mirrors. The superstrate mirror is formed by adding the mirror and its protection behind a superstrate. The substrate mirror is built up to the reflecting layer which then has an optically transparent overcoat applied.

which exceed the interfacial strengths (see Chapters V and XIII). These could be derived from thermal expansion mismatches, mechanical stresses, or interfacial bond weakening reactions which alter surface energies or mass transport phenomena. Permeability allows reactants and products to approach and depart from the interface freely. If this affects the interfacial property of interest significantly, it is defined as failure. The key S/S interface stresses result from chemical potentials; from mechanical/thermal strain mismatches resulting from polymer curing, shrinkages, stress gradients, and mismatches in coefficients of expansion; and photon induced thermal and chemical changes. The S/G interfacial stresses are principally derived from the chemical corrosion and mechanical erosion of surfaces which are exposed to the terrestrial environment. These degradation processes can also be changed by photo-induced gaseous and solid state reactions. Airborn dust can abrade the surface or be deposited on it to form a site for moisture condensation and chemical attachment by a surface chemical reaction. A greater understanding of the S/S and S/G interfacial physics and chemistry is required for the development of stable, weatherable optical systems which have 30 year life expectancies with a minimum of cleaning and maintenance expenditures.

III. RECEIVER/CONVERTER SUBSYSTEMS

The most common receiver/converter subsystems convert solar energy into thermal energy, electrical energy, or chemical energy. Some receiver/converter concepts make two or more products out of the incoming solar radiation, to maximize the overall efficiency of the conversion process. For example, solar cells operating at a 100 sun concentration, convert from about 10% (for amorphous or polycrystalline Si) to about 30% (for single crystal GaAs) of the light incident upon them into electricity [7]. The remainder of the light is absorbed in the cells and generates heat, which can be taken away by a transport system to provide thermal energy to the user as well as electricity. In these cases, there are interfaces between the working fluid and its containment walls. The unique aspect of these systems is a daily temperature cycle, which may see 75 to 100°C changes in temperature of the cell surface.

The conversion of solar energy to thermal energy is accomplished by using a black material which has high solar absorptance α_s. Thus, wavelengths from 0.2 to 2 μm should be absorbed. Many materials satisfy this requirement. Black pigments in organic or inorganic binders are used as black paints. The S/G interface is critical because it is where both the photons are absorbed and atmospheric gases/vapors are present. Oxidation or other chemical reactions can change the absorptivity of the surface. Chemical reactions at the paint substrate interface can cause delamination and paint spalling. The spallation process may be accelerated by the expansion and contractions of the solar thermal converter which may cycle between ambient and 100 to 1000°C daily, for nonconcentrating and concentrating systems, respectively (see Chapter II, Fig. 2).

The absorber performance can be improved if the energy absorbed is not reradiated. This can be accomplished by reducing the surface emittance, ε_t. Practically, this can be done by properly selected interference or optical property coating stacks. The theoretical and actual α_s and ε_t values of a black chrome selective absorbers are shown in Fig. 3 [8]. A black chrome selective absorber coating consists of a thin film of a mixed chrome-chrome oxide coating electrodeposited over a thin film of Ni. The solar energy is absorbed by the chrome-chrome oxide coating. This coating is thin so its low bulk IR reflectance and resulting high ε_t does not come into play. Instead the low emittance Ni substrate governs the effective coating emittance. In this and similar systems

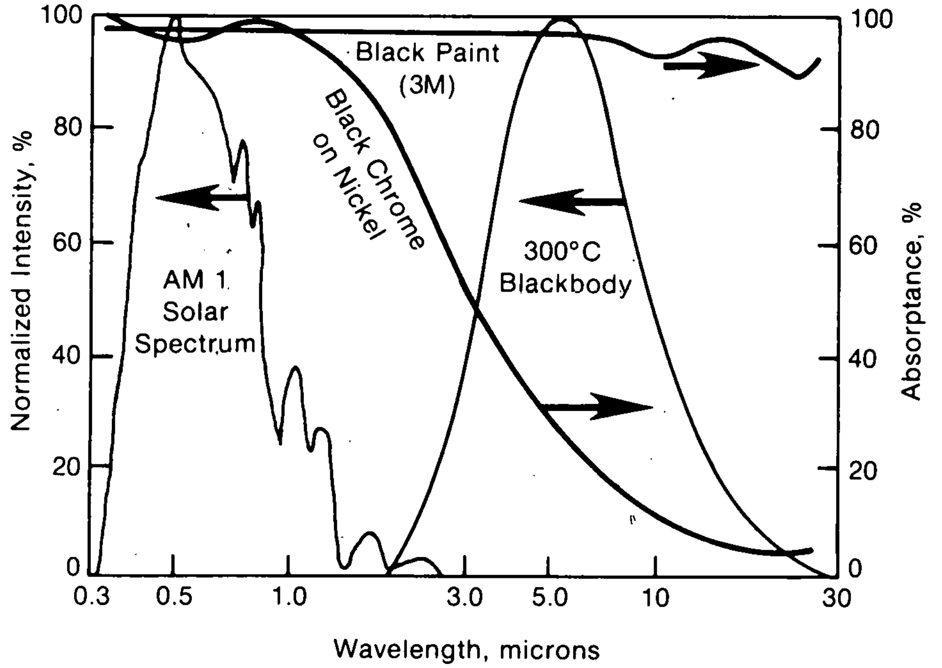


Fig. 3 Normalized intensity versus wavelength for solar radiation which has passed through one atmosphere and for a black body radiating at 300° C. Black chrome on nickel has high solar absorptance ($\alpha_s = 0.95$) and low thermal emittance ($\varepsilon_{300^\circ C} = 0.25$). Black paint has $\alpha_s = 0.91$ but $\varepsilon_{300^\circ C} = 0.90$.

using black Co over Ni, the critical interfaces are absorber/atmosphere and absorber-substrate. Thermal cycling and thermally driven chemical reactions have the greatest effects on the coating's absorptance and emittance and structural integrity. Thermal receivers also have been used to supply hot gases at temperatures up to 930° C [9].

The conversion of solar energy directly to electric energy can be achieved by a number of processes. These include photovoltaic cells or photoelectrochemical cells. The photoelectrochemical cells are sometimes referred to as liquid junction photovoltaic devices. For low concentrations of sunlight, thin film photovoltaic devices based on CdS on a Cu_2S (as illustrated in Chapter II, Fig. 4) are representative of classes of very inexpensive solar cells which could be deployed over very large areas with suitable encapsulation. With the conversion efficiency approaching the 10% goal, the stability of these devices is the major question which needs to be answered [10]. In addition, new films which possess these properties when placed into a photovoltaic diode situation are also being sought. For higher concentrations of sunlight, Si solar cells which can operate up to a 100 sun concentration are being developed and can be obtained by suitably doping wafers of high purity Si. A major objective in the development of Si cells is to provide a technique for making low cost thin-film high purity substrates. Interfaces, and the understanding of them, play a major role in the development of Si solar cells. Impurity segregation at grain boundaries tends to render grain boundaries electrically different from the remainder of the crystal and can provide paths for electron-hole recombination (see Chapter X). Compatibility of these cells with the electrical contacts and encapsulating materials are also important issues. GaAlAs cells may operate at very high concentration ratios in excess of 100, and to high temperature conditions of 100°C. Diffusion and the stability of the materials systems become important considerations. Improved efficiency can be obtained by making multiple junctions such as a GaAlAs cell on top of the Si cell, where certain wavelengths are converted to electric power by the GaAlAs cell, and the remaining wavelengths are passed on to the Si cell where they stimulate the photovoltaic conversion in it. Conversion efficiencies of up to 26% have been demonstrated with these multi-junction cells, which present a new set of unique compatibility problems [11].

The solar to chemical conversion process can be accomplished by a variety of chemical reactions. The desired reaction can be driven thermally or by photon absorption. Thermally driven reactors use the solar energy to heat the reaction vessel. The decomposition of $Ca(OH)_2(l)$ at 400°C to form $Ca_2O(s)$ and $H_2O(g)$ has been demonstrated as a possible closed cycle solar energy storage and transport system. The solid Ca_2O can be transported and stored. The heat of reaction is released when mixed with H_2O at the users site and $Ca(OH)_2$ is shipped back to the collector to be reconverted to Ca_2O. The principal interfaces are those between the solid, liquid and gaseous chemicals and their reactions containers, which may be ceramic, metal or clad or coated materials. The major problems are chemical compatibility and thermal cycling of the chemicals and their reactor. Major materials and surfaces activities which support the thermal chemical conversion of solar energy (Chapter II, Fig. 6) are in catalysis so that the kinetics of the reactions are improved, and in corrosion so the lifetime of the containers can be extended.

Photosynthesis is a photon driven complex chemical reaction which produces complex organic structures from CO_2, H_2O, N_2 and other elements. Photobiological research is focused on enhancing the output of complex chemicals per photon of light absorbed. The past and current emphasis has been placed on understanding the photosynthetic process and the surface and interface challenges will lie in making laboratory results commercially practical [12].

Photoelectrochemical reactions can occur when a solid semiconductor placed in an electrolyte is illuminated with solar radiation and may produce a range of chemicals. Electrode materials such as Si, GaAs, GaP, CdS, and CdTe are commonly used. The electrode solutions used are H_2O if H_2 is to be produced and H_2O plus redox couples if chemicals are to be produced. Ions in solutions such as S_2^-, Te_2^-, Se_2^-, and $Fe,^{+2}$ are commonly used. The major interface problems are associated with stability of the L/S interface which can be degraded by corrosion, dissolution, and diffusion. A potential diagram of this type of junction is given in Fig. 4. A photon passes through the solution and excites an electron into the conduction band, leaving a hole in the valence band. Under the influence of the potential gradient caused by band bending at the interface, the electron moves to the electrode (n-type) and the hole is injected into the solution (n-type). These separated charges can now drive a chemical reaction at the solution/semiconductor interface. For a p-type junction, the electrons are injected into the solution and can reduce $2H^+$ to form H_2 [13]. The electrical and optical character of the interface must be maintained with and without photons present, to maintain the conversion efficiency.

V. SUMMARY

The need for long life, high performance solar energy conversion systems of low capital and maintenance cost poses a crucial challenge to materials and interface scientists. Both the cost and availability of materials must be considered for materials which meet the performance requirements.

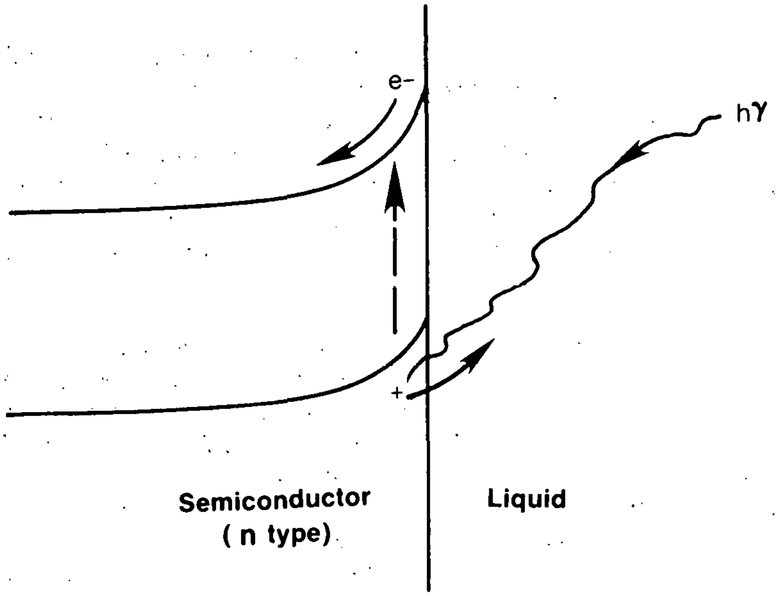


Fig. 4 Potential diagram of electrolyte/semiconductor interface.

Solar conversion systems require large areas to collect the solar energy density of about 1 kW/m^2 at the earth's surface on a clear day at noon. The large areas cause the systems to be materials intensive, resulting in large initial capital costs. Low capital costs mandate using thin films, and the associated preparation techniques, for securing collectors with the desired performance. The large area of optical concentrators required, places stability of thin film stacks and complex glazings as an extremely high priority need. To achieve the optical, chemical, and physical properties of materials for optical conversion systems, different materials are often arranged in many layers resulting in multiple interfaces. Many of these layered systems are unique to solar applications and their durabilities need to be investigated and demonstrated. For example, these materials must collect/transfer as much solar radiation as possible, while resisting environmental degradation from UV, oxygen, ozone, water, other atmospheric pollutants, cyclic temperature, dust, wind, and hail. The materials and component design must avoid problems of permeation, interface reactions, and/or delamination that reduce the performance of the component or system.

The conversion systems, as a whole, are driven by the same type of capital cost constraints. However, the maintenance of the conversion efficiency and high reliability are emphasized by the conversion systems. Unlike an optical system, the solar converter usually operates at temperatures significantly above ambient in a photon flux in the presence of chemical aggressive species. They are also subject to thermal cycling over wider temperature excursions than the optical systems. These stresses require inert outer or barrier layers to prevent or minimize the reactions and transport associated with chemical degradation.

Surfaces and interfaces play an important role in the performance and degradative processes of a wide variety of solar system designs. The solution of the surface and interface problems identified will provide the basis for optimum solar designs which will prove to be cost effective and become a part of our energy future.

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IV. INTERFACIAL PHENOMENA IN SOLAR MATERIALS*

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ABSTRACT

This chapter provides a short review of the fundamental features of general classes of interfaces and interfacial thermodynamics. The energetics and structures of interfaces are reviewed in the context of applications of current understanding of interfacial phenomena to specific materials in several solar technologies. Overviews are presented for interfacial energetics, compositional and chemical analysis of interfaces, and the structure of interfaces and representative illustrations are provided. Numerous examples of interfacial phenomena pertinent to solar materials interface problems are included, and solar materials interface problems are discussed and summarized in a general way. Problems or concerns are tabulated for interfaces in specific solar systems or components, e.g., reflectors, polymers, absorbers, collectors, PV cells, storage systems, and heat transfer materials.

I. INTRODUCTION

"Interfaces, both external and internal, constitute an integral part of the structure of materials, and so they enter directly into the structure/property/performance linkage which forms the central theme of materials science and engineering. These 'boundary aspects' of bulk materials, because of their relatively discontinuous character, are not only difficult to study and elucidate, but they can also exert major influence on the behavior of materials and, hence, dominate their utility in many applications. Furthermore, they may serve as the primary location, where degradative reactions begin. Interfaces are often regarded as two-dimensional imperfections in materials, along with linear-defect dislocations and the point-defect vacancies and interstitialcies, but interfaces play an even deeper and more general role in natures processes". This quotation taken from a foreword by Professor Morris Cohen [1] is certainly appropriate and unsurpassable as a lead-in to the present topic. It is realized that in the context of solar technology, we need to include essentially all materials; polymers, glasses and crystalline ceramics, metals and alloys, semiconductors, as well as complicated systems of all of these materials whose synergism is the epitomy of interfacial phenomena. While this seems overwhelming, it is also realized that in spite of what may appear as a formidable knowledge and understanding of interfaces, in the context of solar materials systems in particular, we know very little. In fact, critical solar developments will depend upon further understanding of specific interfacial phenomena.

While interfacial phenomena have a clear thermodynamic basis, we will not review the basis in detail here except to point out some simple experimental details which are a

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consequence of certain thermodynamic assumptions. It should be pointed out that while the thermodynamic basis, described in detail by Gibbs [2], is fundamentally correct, the assumptions made in interfacial applications are not always correct. For example, certain equilibrium conditions may be met at high temperature which are certainly not met at low temperature. Thus, studies of the kinetics of changes in composition, structure, and electronic properties at interfaces must dominate the materials systems applicable to solar energy devices.

II. INTERFACES AND INTERFACIAL PHENOMENA

Certainly it is now well known that the general classes of interfaces include S/S, S/L, G/S (or vapor/solid (V/S)), G/L, and S/L systems. In all of these systems, we may have the same composition or we can have the same structure and composition, the same composition but different structure, different structure but constant composition or different structure and composition. Useful materials structures, and especially solar structures, may consist of arrays of these systems or classes forming composites as shown by Figs. 4 and 7, Chapter II, and Fig. 2, Chapter III of this volume. In addition to structure and composition characterizing the phases composing an interface, the interface itself possesses a structure and composition. These features also determine the specific surface free energy of the interface. Consequently, the interface is characterized by its structure, composition, and specific surface free energy. To a large extent, basic interface studies are concerned with elucidating these properties. Other measurements or issues, such as surface area, real or clean surfaces, topography, diffusion, adsorption kinetics, adsorbate structure, and chemical bonding at interfaces can be embraced in the major categories of structure, composition, and interface free energy. More detail of how these other issues impact studying solar materials interfaces can be found in a recent book [3].

Normally the structure is observed while the composition and energy are measured. Because of difficulties in resolution, there are not nearly so many examples of interfacial composition as there are of interfacial structure. And while there are numerous measurements of interfacial energies, these are difficult to make in some cases, and in others the accuracy is sometimes questionable because of deviations from equilibrium conditions [1].

A. Energetics

In this subsection, a general background or an overview of interfacial energetics is provided. The reader is cautioned that this cannot be a rigorous treatment of energetics, and the more comprehensive references need to be consulted for a more thorough treatment.

Some simple yet appropriate examples of methods for interfacial free energy measurements are illustrated in Figs. 1-3. In Fig. 1, the "sessile drop" geometry implicit in the Young-Dupré condition allows for an evaluation of the interfacial energy of a "particle" (p) on a solid "substrate":

$$[\gamma_{ps} = F_s + \gamma_p \cos(180 - \Omega_c)]_T \qquad (1)$$

where γ_{ps} is the particle/substrate interfacial free energy, F_s is the substrate surface free energy ($\gamma_{S/G}$), γ_p is the "particle" surface free energy ($\gamma_{S/G}$ or $\gamma_{L/G}$ depending upon

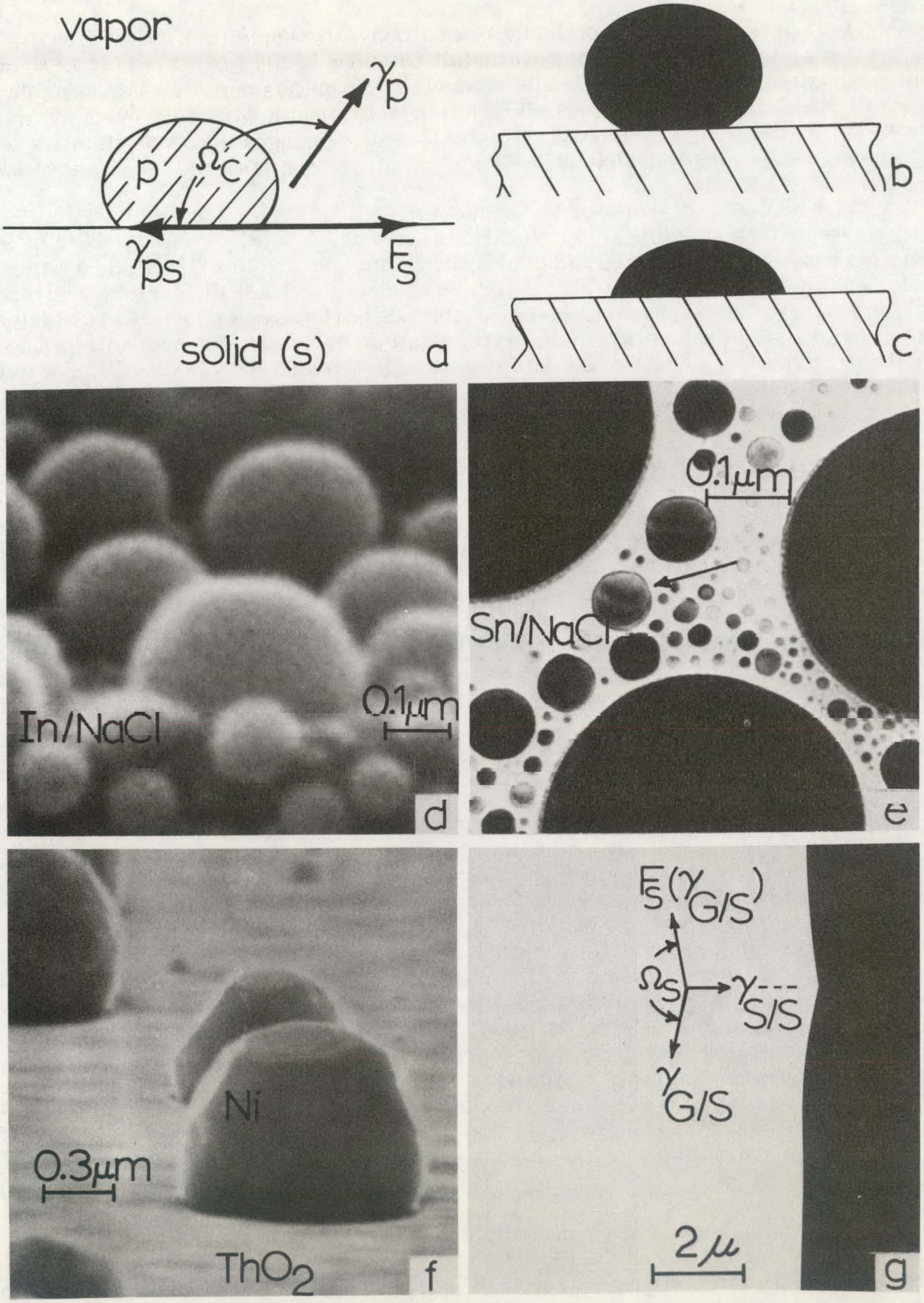

Fig. 1. Examples of simple interfacial energetics and equilibrium geometry. (d) – (f) are SEM images; (g) is TEM image.

whether the "particle" is solid or liquid respectively), and Ω_c is the contact angle. This relationship assumes no mixing or reaction at the interface, and this is frequently not a valid assumption. To measure the interfacial free energy we simply measure the true (dihedral) angle and insert the particle and substrate surface free energies. These must correspond to the temperature and pressure at which γ_{ps}, is to be measured, otherwise there is no common thermodynamic basis.

Figures 1(b) and (c) demostrate the nonwetting ($\gamma_{ps} > \gamma_{S/G}$) and wetting ($\gamma_{S/G} > \gamma_{ps}$) regimes, respectively. While these conditions are more generally characteristic of liquid particles on solid substrates, the examples shown in Figs. 1(d) through (f) illustrate single crystal particles [the arrow in Fig. 1(e) shows uniform crystal diffraction contrast] on single crystal substrates [oriented (001)]. Figure 1(g) extends the geometrical equilibrium conditions to the determination of the ratios of grain boundary free energy ($\gamma_{S/S}$) to surface free energy ($\gamma_{G/S}$) using fine (stainless steel) wires at high temperature where an equilibrium "bamboo" structure develops:

$$\gamma_{S/S}/\gamma_{G/S} = 2\cos(\Omega_S/2) \tag{2}$$

Not all such S/S systems are single crystals. Figures 2(a) and (b) illustrate a polycrystalline "particle" on a polycrystalline substrate. It is interesting to note that in Fig. 2(b) the S/S interfaces meeting the particle surface are low-energy "annealing" twin boundaries. In Figs. 2(c) and (d), additional examples for determining interfacial free energy ratios are shown. The nuclei-cluster of Cr_2O_3 particles on a thin Ni film (0.1 μm thick) shown in Fig. 2(c) differ from the agglomerate of ThO_2 crystals dispersed within a thin Ni film in Fig. 2(d). In Fig. 2(c), an approximation will be identical to Eq. (2) while in Fig. 2(d) all of the energies are S/S interfacial free energies:

$$\gamma_{gb}(ThO_2)/\gamma_{Ni/ThO_2} = 2\cos(\Omega_S/2) \tag{3}$$

where $\gamma_{gb}(ThO_2)$ is the grain-interface energy for the ThO_2 agglomerate.

While situations depicted in Figs. 2(c) and (d) may, indeed be described by Eq. (3), there will, as in Eq. (1), be deviations if chemical reaction of any interface occurs. This is especially true for situations depicted in Fig. 1(a), particularly, when one member of the system is a liquid at any temperature. Where there is any solubility of the solid phase in the liquid, liquid-phase diffusion can allow for rapid distribution of specific elemental species with a concommitant change in the composition of the liquid phase as well as a change in the interfacial structure. Figure 3 depicts some of these features as well as demonstrating the principle concepts of nonwetting and wetting systems. Figure 3(b) illustrates the rapid diffusion of Ni into the Hg drop while Fig. 3 (f) shows that Hg in the liquid drop is not rapidly mixing with the Zn substrate. Figures 3(c) and (d) illustrate the influence of alloying upon the contact angle (and wetting) while Figs. 3(a), (c), and (e) demonstrate this same feature with changes in specific system (substrate) composition.

The basic interfacial energy measurements outlined in Figs. 1-3 have been utilized in the development of a number of systems, such as fiber-reinforced composites and related metal-ceramic systems in recent years. There are a large number of measurements for interfacial free energies and energy ratios available [1], but there are far fewer examples of adhesive energies in complex (composite) systems [4]:

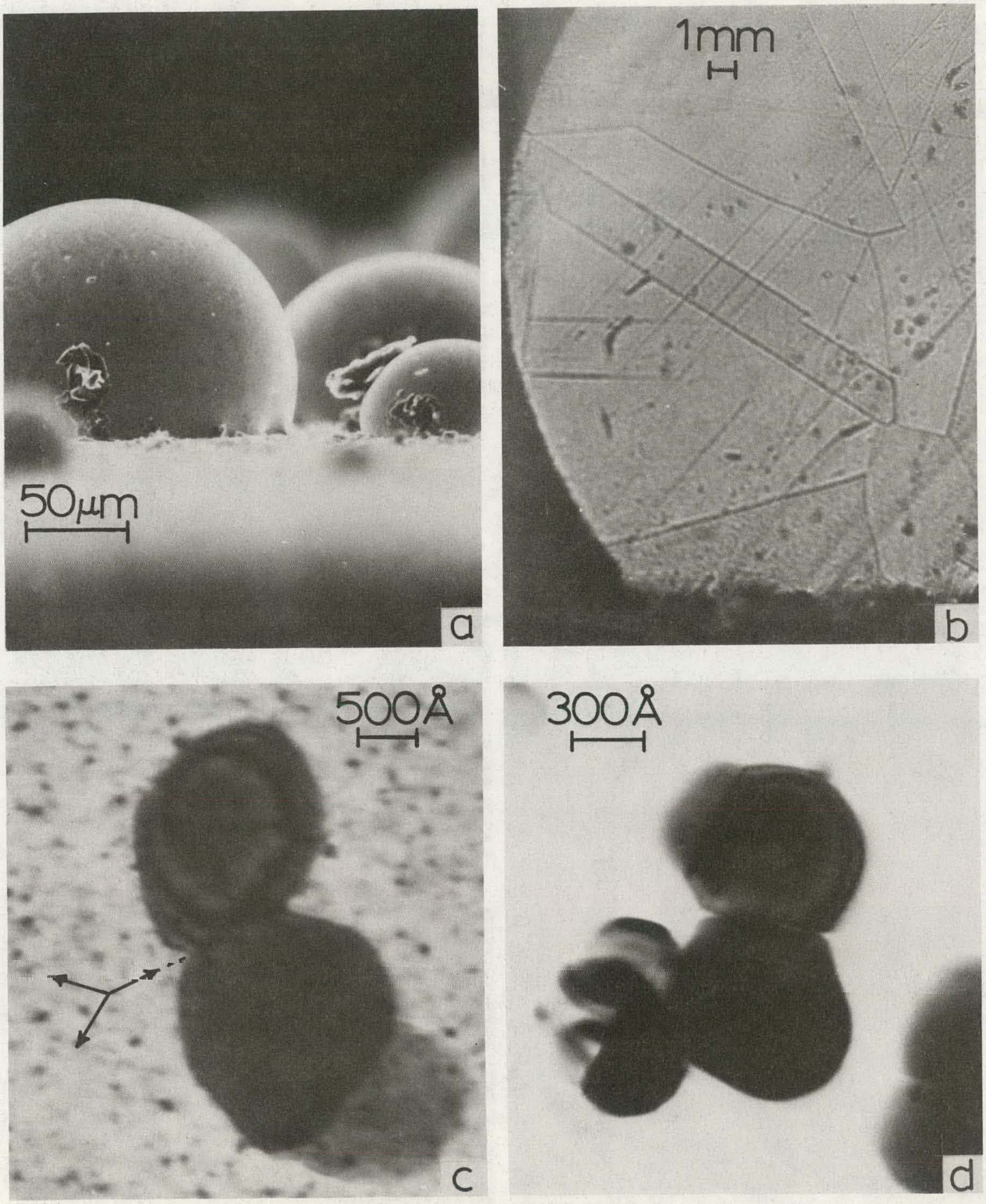

Fig. 2. In (a) and (b), solid, polycrystalline stainless steel on alumina substrates (1400° C); (c) Bicrystal aggregate of Cr_2O_3 electroplated onto a thin (100 nm) Ni film; (d) Bicrystal aggregate of ThO_2 particles dispersed in Ni sheet (dispersion-hardened Ni).

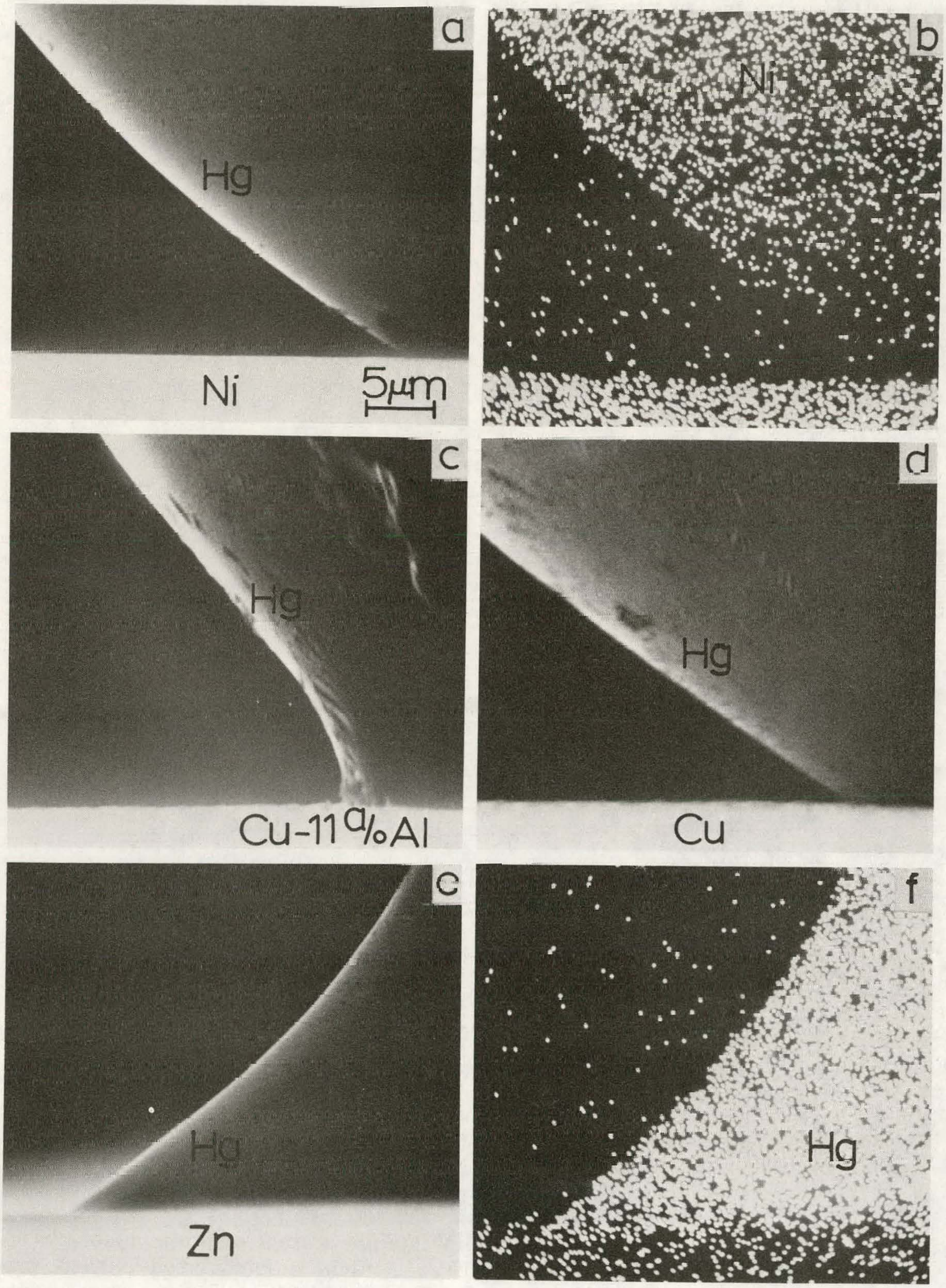

Fig. 3. Examples of interfacial energetics and chemical phenomena effecting wetting and adhesion in liquid metal (Hg)/solid metal (L/S) systems.

$$E_{Ad} = \gamma_{L/G}(1 + \cos \Omega_c) \tag{4a}$$

or

$$E_{Ad} = \gamma_{S/G}(1 + \cos \Omega_c) \tag{4b}$$

where E_{Ad} is the adhesive energy for systems illustrated by Fig. 1(a) - (c) when the sessile "particle" on the solid substrate is a liquid (where $\gamma_{L/G}$ is commonly referred to as the surface tension) or solid respectively. In addition, there are far fewer applications of interfacial phenomena in metal, ceramic, semiconductor, and related composite and more complex systems than liquid organic chemical systems where wetting, spreading, and interfacial reactions are vital to the fields of detergents, rinses, foams, industrial emulsions, and separations, etc. [5,6]. While such systems involve complex molecular interactions, there is a well established and exact thermodynamic basis. Many of these types of interfacial phenomena can be applied in certain solar system fabrications, but a great deal of the interfacial phenomena involved with coating, nucleation, adhesion, stability, degradation, etc. can be understood in terms of the interfacial energetics illustrated in Figs. 1-3. Particularly significant problems will arise in the area of thin photovoltaic device fabrication and a host of related contact, and conductive interconnect problems in the microelectronics areas in general, which will certainly be limited by interfacial energetics as illustrated, for example, in Fig. 4. The principle differences in the thin film continuity shown on comparing Fig. 4(b) with Fig. 4(c) may indeed be simply a matter of interfacial energies, particularly surface energies and the substrate/particle or substrate/overgrowth interfacial free energy.

B. Composition and Chemical Analysis

It is especially important to recognize the difficulty in characterizing the chemical composition of the interface or the interfacial phase associated with the particle/substrate (S/S, S/L) systems shown in Figs. 1-4. While it is possible to attempt some type of destructive or non-destructive depth profiling through the interface [See Chapter IX), this has been rarely attempted. On the otherhand, there are a number of analytical techniques available for determining composition at the G/S interface which are particularly applicable to solar materials [7-12]. In these techniques one normally looks normal to the "plane" of the interface. For very thin films or electron transparent materials systems, a variety of electron optical analytical techniques can be utilized or combined by AEM [13] [also sometimes called the transmission electron analytical microscope (TEAM)]. Resolution, in terms of depth (or interfacial phase "width") can be in the range of 0.1 to 3 nm for LEED, AES, XPS, ISS, and SIMS. For studies where resolution is not particularly critical, XPS and ISS are very promising techniques for the analysis of a wide variety of solar materials and materials systems. However, one of the principal features of these techniques as well as all of the other techniques is that the samples must be examined in a vacuum. In some cases, the vacuum required is very high ($<10^{-8}$ Pa). AEM can also provide compositional data near this range, and electron microdiffraction is also useful in assessing interfacial composition in very thin samples.

Lateral resolution (especially in reference to the interfacial phase width or along a dimension perpendicular to the Gibbs dividing surface), however, is more useful in many applications and this is sometimes difficult to achieve experimentally. That is, it is sometimes difficult to expose and orient interfaces properly for lateral resolution (resolution of composition in the interfacial phase width or along the Gibbs dividing surface line of intersection). In thin films, lattice resolution is possible in the electron

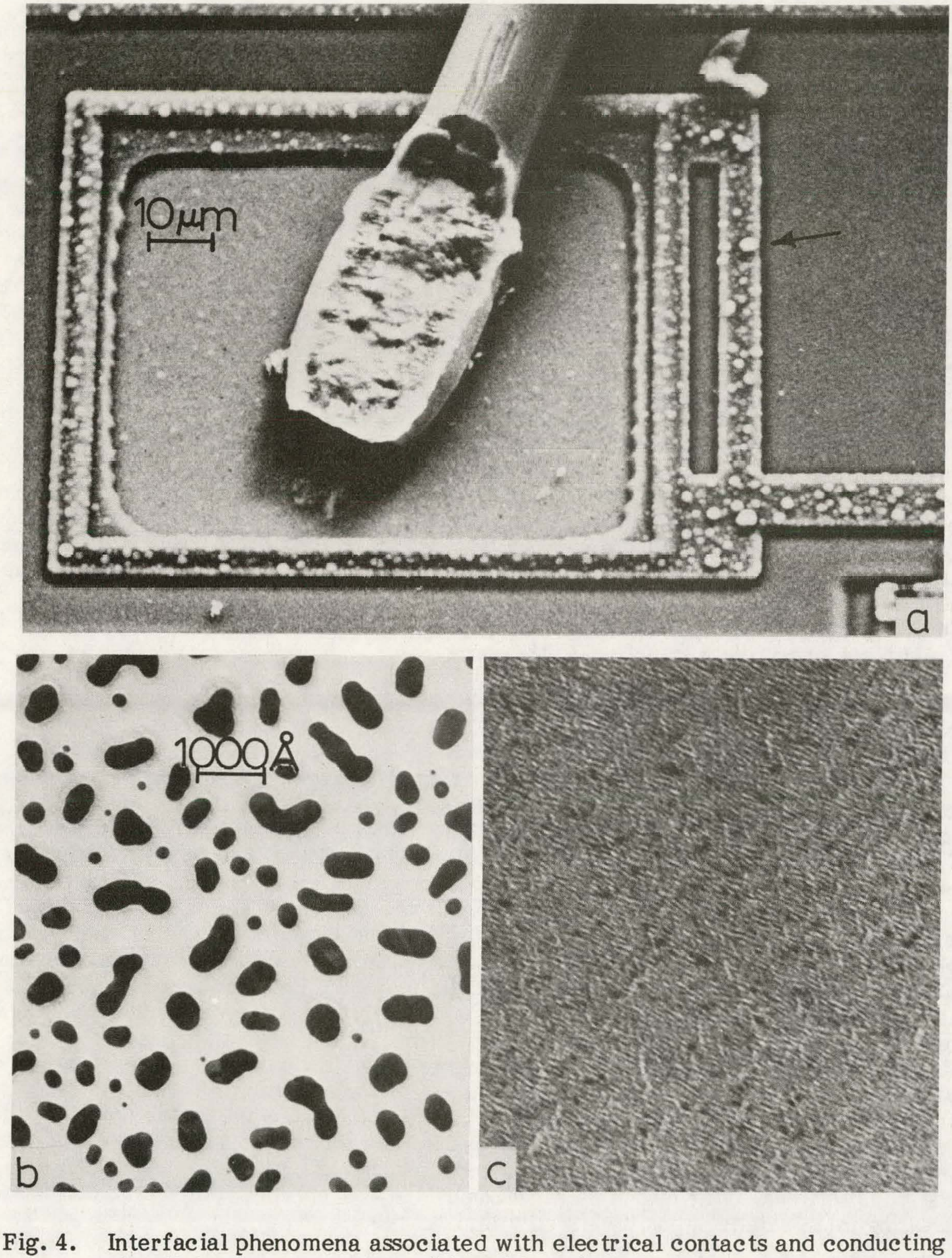

Fig. 4. Interfacial phenomena associated with electrical contacts and conducting circuit interconnect films. (a) IC (silicon) contact; note Al metallization agglomerates (arrow); (b) Au aggregates producing discontinuous film on NaCl; (c) Au-Pd film of same "average" thickness (about 3 nm) as (b) on NaCl.

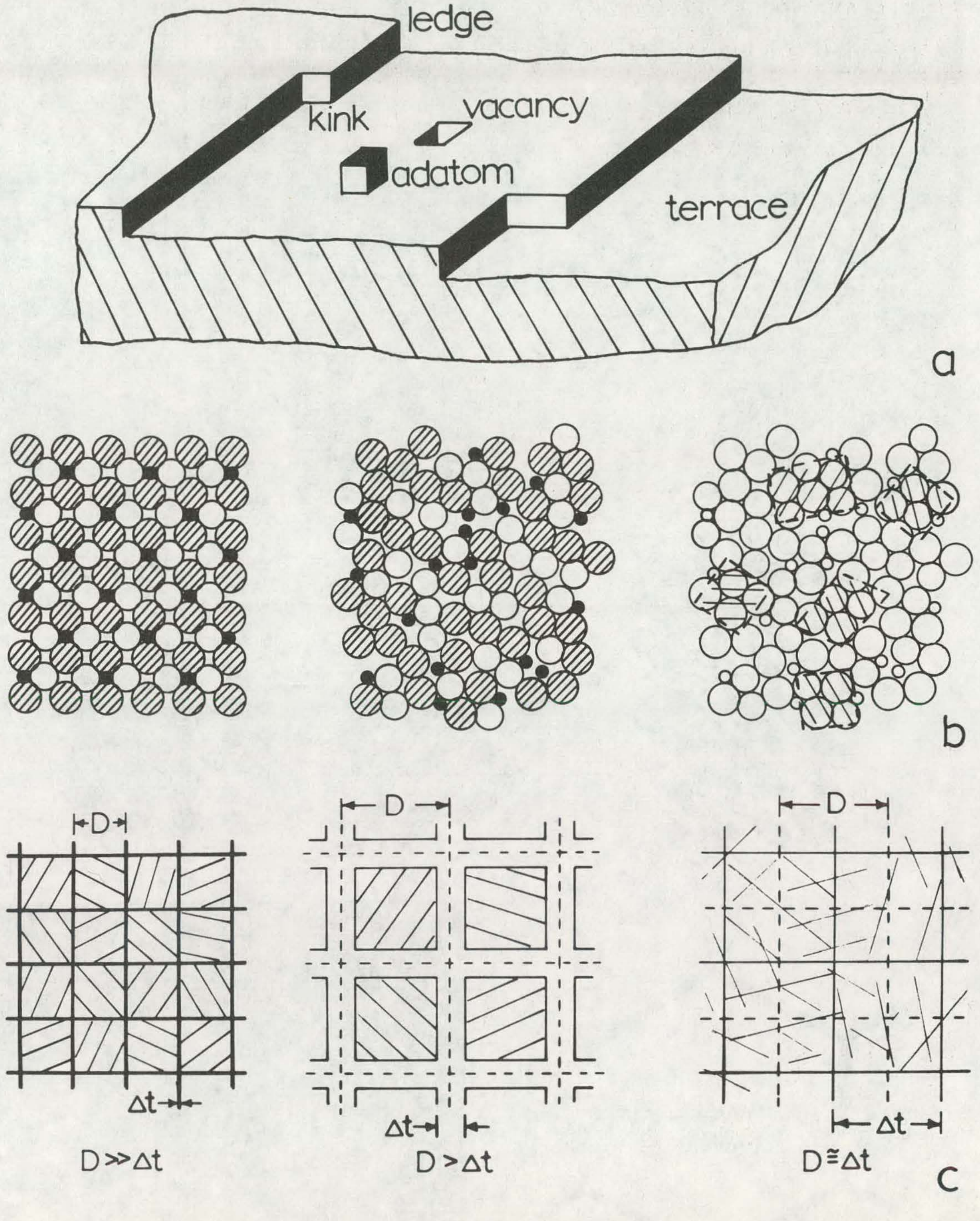

Fig. 5. Interfacial structure. (a) Idealized S/G surface structure; (b) crystalline-to-amorphous structural transition. The amorphous "ternary" characterizes the instantaneous L/G interface or the S/G interface in an amorphous alloy. Regular packing units ("micrograins") are depicted at the right; (c) sequence showing grain boundary (interface) phase effects, where D is the grain size (diam.) and Δt is the boundary (interface) width.

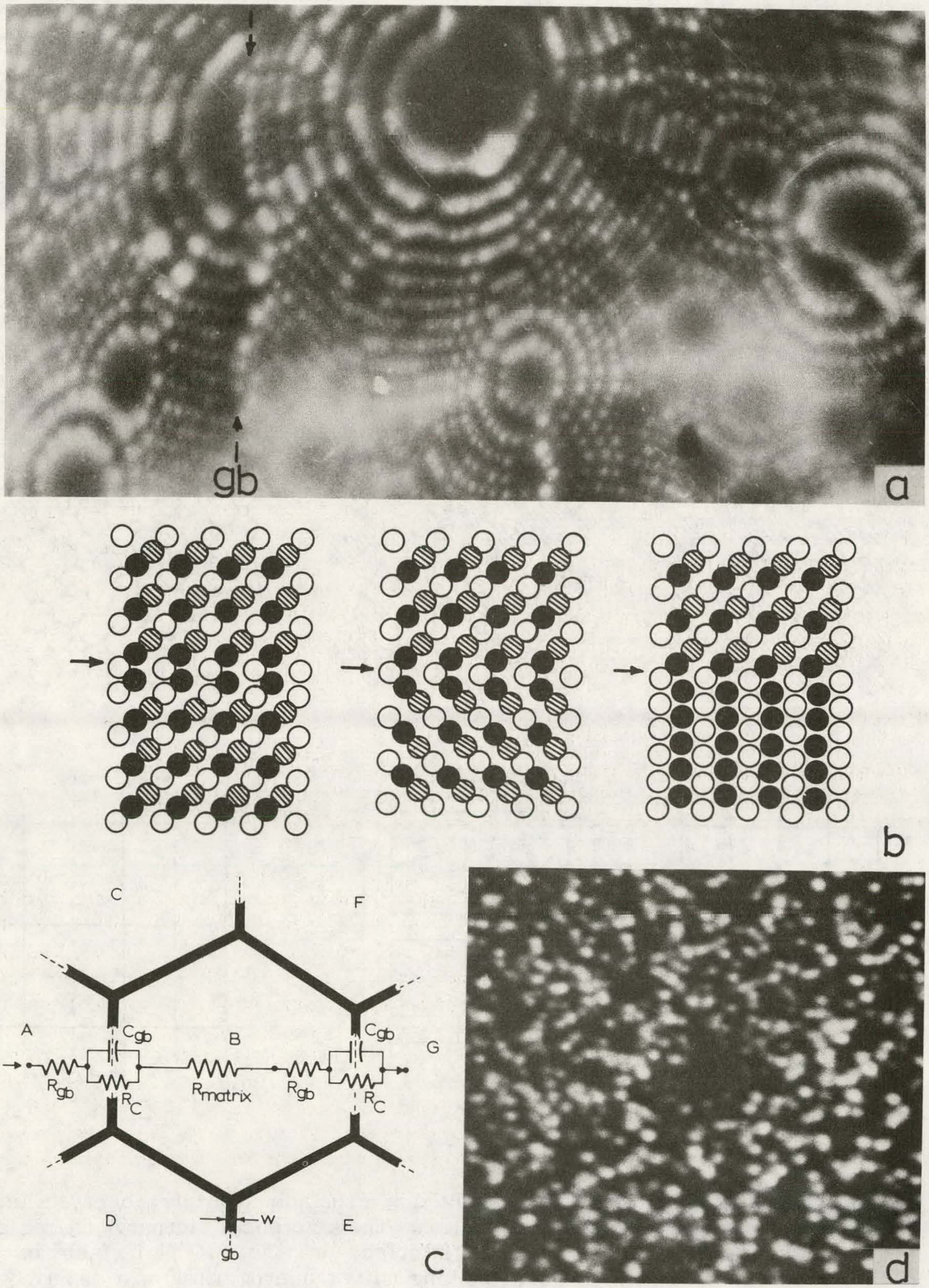

Fig. 6. Interfacial structure. (a) Grain boundary in Ir observed in the FIM; (b) from left: stacking fault, twin, and phase boundary structure in fcc; (c) electrical nature of interface structure; (d) amorphous structure in $Fe_{80}B_{20}$ observed in FIM (Courtesy O.T. Inal).

microscope, but in order to assess accurately the "average" composition near the interface, film thicknesses of about 25 nm are required. This poses special difficulties in preparation, and is applicable only for specialized systems of thin films. The EDX analysis techniques associated with the SEM, as demonstrated to some extent in Fig. 3(b) and (f), have very poor resolution both in depth and in the lateral dimension (in a direction on either side of the interface or the Gibbs dividing surface). Both depth and lateral resolution is determined by the geometry or volume of the interaction zones within the material system. Lateral resolutions are normally an order of magnitude or more smaller than depth resolutions of electron and ion analytical instruments. However, lattice imaging techniques in the TEM are able to demonstrate slight stoichiometry changes accomodating heterojunctions in terms of atom spacings, while specific elemental identity is not possible. Single atom resolution and analysis is, however, possible in very special specimen geometries (whiskers) examined in the atom-probe field ion microscope or by imaging atom-probe mass spectroscopy [13]. This is currently the only available method for actually seeing a Gibbs adsorption layer at an interface such as a grain boundary, or other forms of grain boundary segregation. Unfortunately, the applications have been very limited with regard to interfacial composition and elemental segregation. This would seem to be an ideal technique for investigating the passifying effects of elements at photovoltaic grain boundaries and similar physical and mechanical effects of elemental segregation. Such segregation can and has been deduced from LEED or AES analysis of grain boundary fracture surfaces or other surfaces, but such analyses suffer the uncertainty of not knowing exactly where the fracture surface lies in relation to the Gibbs dividing surface or the interfacial phase thickness.

C. Structure of Interfaces

We know a great deal about the S/G interface especially in the case of single crystals or domains having long-range order. Techniques for the analysis and observation of surfaces are available with resolutions at the atomic level (LEED, FIM, etc.).

In terms of surface perfection, there is really no difference from that of the bulk. However, there are many features of surface structure involving imperfections which are unlike the bulk. Joining two surfaces, while possessing some of the similarities of the surfaces, creates different structures as a result of new bonding, coordinating and relaxations along the "interface". Figure 5(a) illustrates the principal features of a S/G structure [7,14,16]. Figure 5(b) shows a sequence of schematic views depicting a perfect crystal structure on the left, an amorphous structure of the same composition in the center, and a selection of organized units of elements in the amorphous structure shown at the right. Figure 5(c), on the other hand, illustrates the size regimes in a polycrystalline solid where the interface phase thickness Δt becomes commensurate with the grain size D. Figure 5(c) could crudely represent the convergence of a polycrystalline regime to an amorphous regime (or vice versa) if the grain boundary structure (within the phase width Δt) is considered to be essentially amorphous as originally proposed by Ewing and Rosenhain [17] and Quinke [18]. When $D = \Delta t$ as illustrated in Fig. 5(c), there is no longer a distinction between the interface (interfacial phase) and the grain matrix. There is no structural definition in terms of crystal structure.

Figures 6(a) and (b) show some details of crystal structure at the S/G and S/S interfaces. Figure 6(c) illustrates the interfacial (S/S) considerations in polycrystalline semiconductor materials (photovoltaic homojunctions and heterojunctions). The width w shown is indicative of the space-charge region which is usually at least 10 Δt. Figure 6(d) shows the amorphous structure of $Fe_{80}B_{20}$ metallic glass for comparison with Fig. 6(a).

The general structure of grain boundaries is illustrated in Fig. 7. Figure 7(c) is a very general model which includes all of the features shown in Figs. 5(a) and 6(c). In the case of hydrogenated Si, the grain boundary passivation is illustrated as the satisfaction of dangling bonds. Many of these features need to be more thoroughly investigated by analytical TEM schemes which also involve high-resolution TEM. It is especially important to correlate boundary structure in semiconductor junction systems with the electrical response changes caused by hydrogenation, oxygenation, fluorination, and other selective element segregation. Finally, Fig. 8 illustrates some of the more complex features of grain boundary structure and the role of grain boundaries (or grain boundary structure) in deformation and related processes. Since real property evaluation involves dynamic events (degradation of properties), there is an acute need for dynamic observations of grain boundary structure. Furthermore, in processes involving deformation (such as creep, and high-strain phenomena, etc.) the boundary structure itself changes. These changes need to be observed at both room temperature and high temperature in order to really understand mechanical and other property degradation. Finally, these features need to be evaluated in the context of more complex and more common solar materials behavior such as the cyclic differential thermal expansion of materials on stability of the interface.

In summarizing this section, it is appropriate to quote from the recent work of Czanderna [10]: "Broad philosophical guidelines need to be developed in order to narrow the choices of surface analytical facilities required for general study of solar materials surfaces." Indeed, this could be applied more generally to include all interfaces which are so prominent in the development and operation of a wide range of solar devices. "These guidelines should be based on (1) studying the surfaces of long-term interest to solar energy conversion systems; (2) studying surfaces under (actual and simulated) conditions as close as possible to those encountered when operating the system; (3) studying the fundamental processes at the S/S, S/G, and S/L surfaces that impact (1) and (2); (4) employing, initially, those methods where equipment is commercially available or where custom equipment can be used or reproduced quickly because of available expertise; and (5) selecting facilities that will have the optimum impact on problems encountered in thermal, photovoltaic, biochemical, and ocean thermal energy conversion systems."

III. EXAMPLES OF SOLAR MATERIALS INTERFACE PROBLEMS: RESEARCH NEEDS

The important features of interfaces involve their fundamental thermodynamics, characterization, energetics (including modeling and calculations of interfacial energies, adhesion, cohesion, etc.), interfacial formation and reactions at interfaces (including reaction kinetics and thermodynamics), mechanical, electrical, thermal, and optical properties of interfaces, interfacial adhesion and the development of adhesion, and related interfacial phenomena. Typical interfacial systems involve metal/metal, metal/ceramic, ceramic/ceramic, metal/semiconductor, semiconductor/semiconductor, semiconductor/ceramic, metal/polymer, polymer/ceramic, polymer/semiconductor, and related systems representing S/S or S/L phase components. Solid and liquid-phase free surface or S/G and L/G interfaces are also fundamentally important. Adhesion of these systems and adhesion to free, solid surfaces is of the utmost importance in areas involving coatings, or in soiling by dust or other atmospheric particle adhesion, etc.

Solar materials systems, as illustrated in Fig. 9, consist frequently of complicated multilayer, multiphase, multicomponent systems which must meet critical and often contradictory requirements for high performance and reliability, long life, and low cost [see Chapters II and III]. Consequently, the design and fabrication are of great concern in

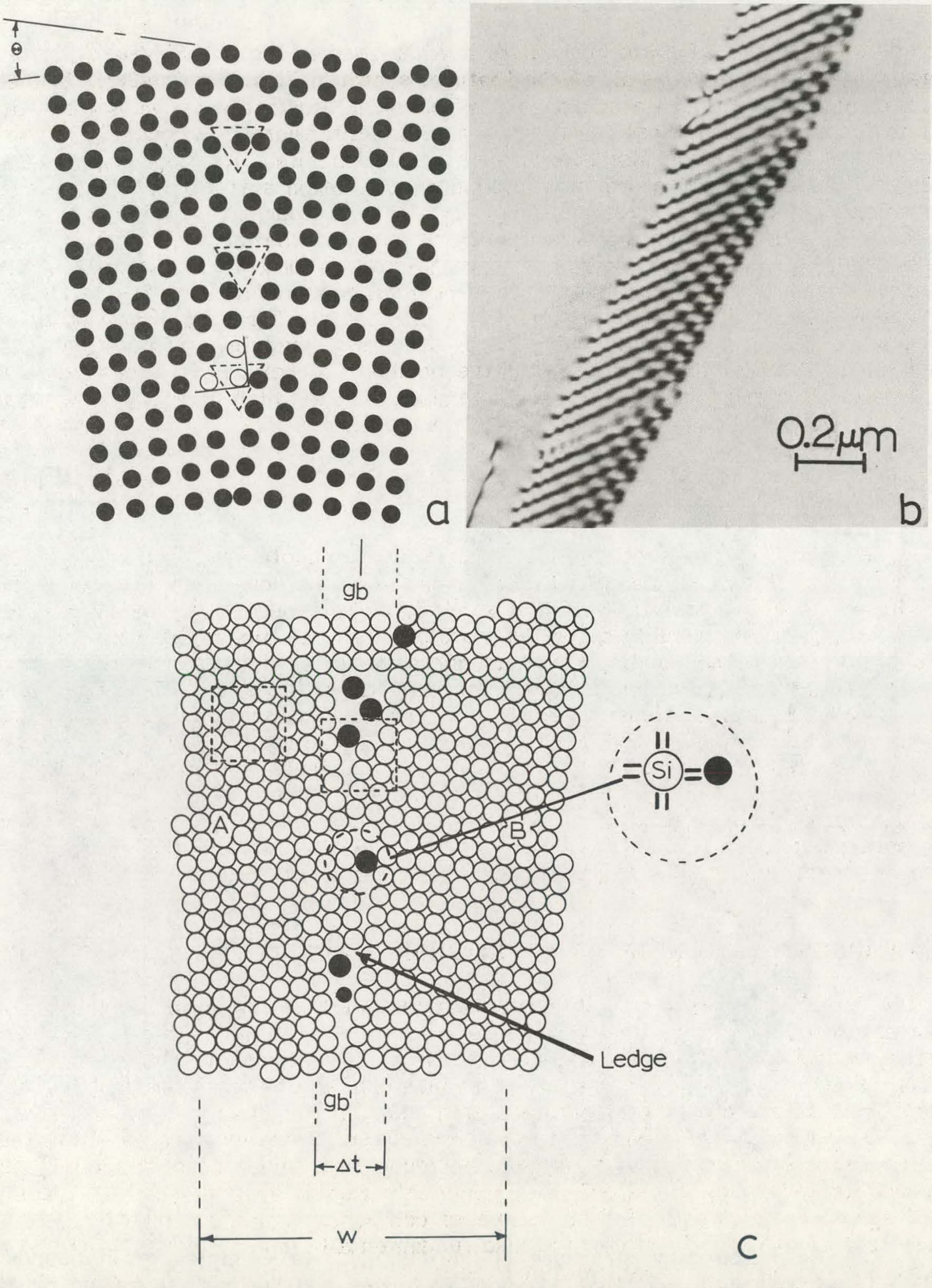

Fig. 7. Grain boundary structure. (a) Simple low-angle boundary; (b) TEM image of low-angle boundary in austenite (dislocation structure); (c) generalized grain boundary schematic where gb denotes the Gibbs dividing surface. Δt is the interface phase width and w is the space-charge width (for semiconductor materials).

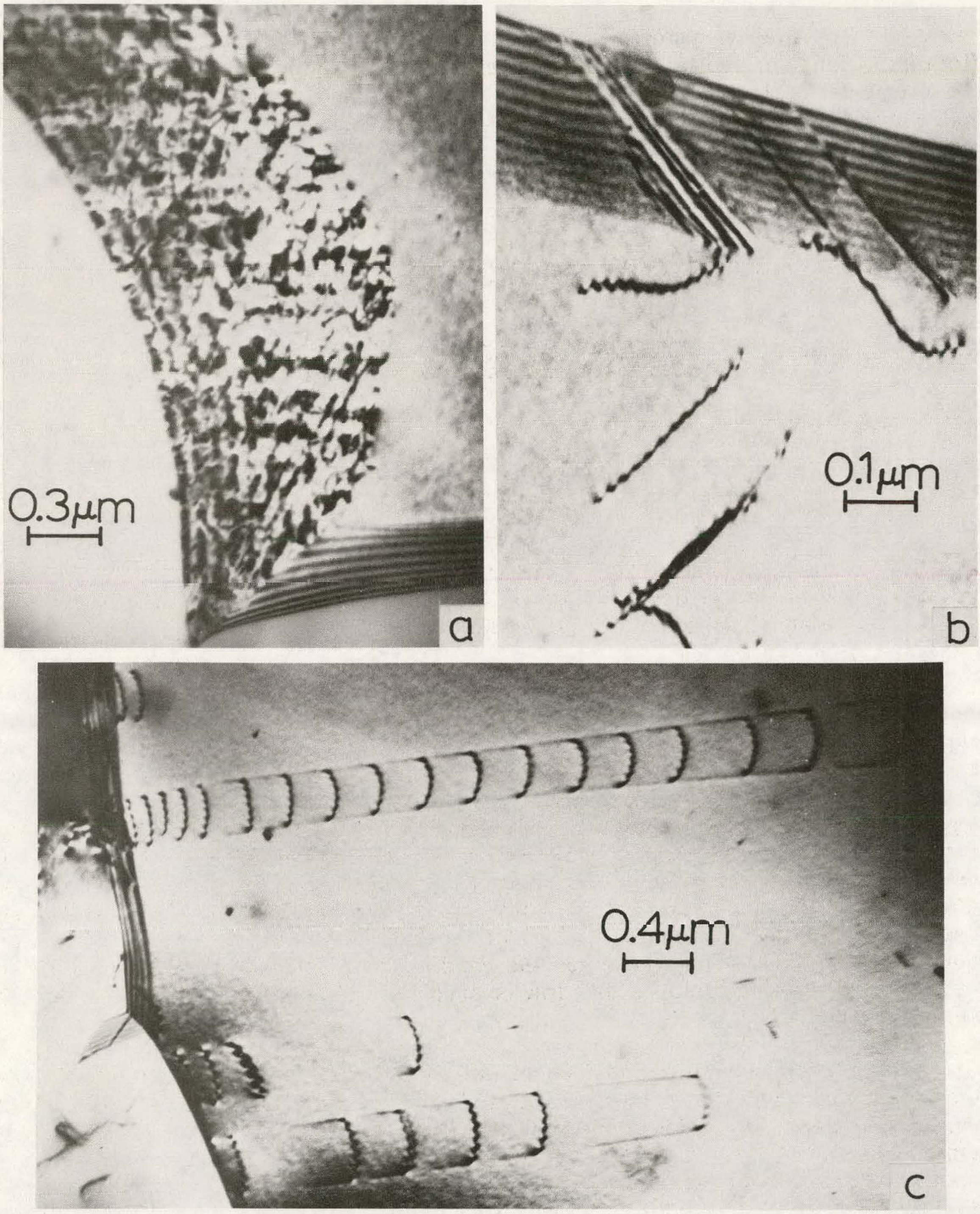

Fig. 8. Grain boundary structure (TEM images). (a) Complex grain boundary structure in annealed Al showing ledges and "debris" swept up by the moving boundary; (b) grain boundary ledges in austenite (304 stainless steel) strained 1.3%; (c) dislocations emanating from grain boundary ledges in austenite while observing in-situ. Electron-beam-induced stresses provide the required driving force.

forming the multilayer systems. The multilayers shown in Fig. 9 are typical of solar reflectors, solar (photovoltaic) cells, solar absorbers, etc. and the interfacial synergism is itself a critical feature of reliable solar components and systems. In actual, practical, working environments, an understanding of, and application of, nonequilibrium and nonlinear thermodynamics is important.

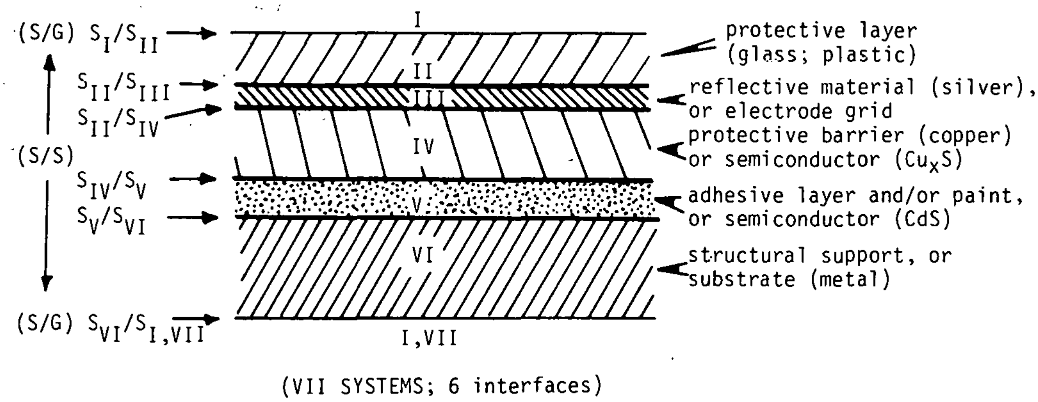

Fig. 9. Idealized construction of a typical solar reflector or thin-film solar cell (photovoltaic device) showing multilayer, multiphase, multicomponent contributions to solid interface formation.

As we noted in the introductory comments, one must be concerned not only with the very fundamental scientific aspects of interfaces in practical solar materials systems, but also with actual applications. As an example, fundamental studies of adhesion and wetting on an Al surface utilizing the techniques illustrated in Figs. 1 and 3 might be criticized from a fundamental viewpoint because the Al surface to be tested would normally contain a thin but tenacious oxide coating. Consequently, one would normally measure the oxide/metal properties. But in a practical sense, this is the property to measure because Al used in any solar application would likely have a thin oxide anyway. Furthermore, fundamental studies and interfacial characterization should relate as near as possible to normal environments (standard pressure and O_2 concentration, often elevated temperatures) because these are the conditions of operation, not HV or UHV, inert gas environments, room temperature, low or cryogenic temperatures, or other "idealized" domains for study.

We have been and must continue to be concerned with degradation of interfaces. This can involve deadhesion or delamination (fracture) and reactions creating interfacial phases; and indeed the characterization of the interfacial phase region as depicted schematically in Fig. 10. In many situations, the interface may not be an interface at all but rather a separate phase which creates additional interfaces. As a consequence, the phase composition, and structure of the presumed interface, may be of no real consequence while the associated interfaces bounding the phase determine the properties and performance of this regime.

Delamination at any interface shown in Fig. 9 may provoke incipient failure of the entire system. Consequently, adhesion is a particularly important feature. There is no wealth of information on adhesion principles, and a fundamental understanding as described in this presentation is lacking. Nothing is known of the dependence of adhesion on phase equilibrium or interfacial microchemistry and microstructure. Indeed, it must be apparent to the reader that the physical and chemical characterization of interfaces

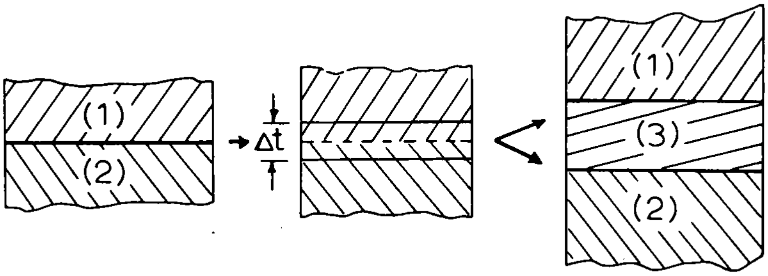

Fig. 10. Idealized interface phase and the evolution of a two-phase system, with one interface, into a 3-phase system [1,2,4] with two interfaces. The dotted line is the Gibbs dividing surface and Δt is the interface phase thickness.

is a necessary if not sufficient feature for understanding its role in the performance of a solar system, and in the synergistic role it may play in determining the physical, mechanical, or electrical properties of the system.

Specific interfaces of significance to solar energy technology obviously span the widest range in character and cannot possibly be treated in a simple summary involving a brief description of principal features and currently recognized research problems and study areas. In Table 1, an overview is given of some interface problems in specific solar materials (systems); this table is not intended to be comprehensive but illustrative. In Table 2, more specific topical areas are listed that are indigenous to solar materials interfaces. There are some redundancies and conceptual overlappings in these two tables, but they will provide at least some points of focus for understanding and addressing fundamental solar materials interfaces problems and concerns, analytical approaches to interfacial characterization, and related features bearing upon solar technology development. When perused collectively, Tables 1 and 2 provide an almost overwhelming perspective of the vast role interfaces must play in the development and implementation of a viable solar technology. This perspective becomes even more vivid in the context of specific and more current solar materials problems when the contents of Solar Materials Science [3] are examined in any detail.

IV. CONCLUSIONS

An attempt has been made here to provide a glimpse of the status of basic and applied interface studies, and especially in the context of solar materials science. Only a few key references have been cited for the reader's convenience. In the main, the principal conclusions to be drawn would not deviate very much from those arrived at during the course of the "Materials Science Workshop in Surface Science" held at the Lawrence Berkeley Laboratory in March of 1977. There is a great deal known about surfaces and interfaces and there are a range of effective tools for characterizing interfaces. What needs to be established is an extensive "case history". The real dilemma and the critical problem in the case of interfaces in solar materials applications stems from the fact that basic knowledge is being taxed far in excess of present understanding in response to the pressing national and international goals to develop alternative energy sources and resources. Consequently, new and innovative research and development priorities must not only be set, but they must be implemented at the earliest possible moment.

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Table 1. EXAMPLES OF CURRENT SOLAR MATERIALS INTERFACE PROBLEMS*

System or Component	Interface (materials)	Problems or Concerns
Reflectors	Polymer/air; glass/air (encapsulant)	Degradative (radiation damage) structural alteration; need to study bond passivation, surface structure, adhesion, soiling, etc.
Reflectors	Silver/glass	Degradation by reactions; delamination; optical degradation; temperature effects; structural and microstructural examination; interdiffusion; impurity diffusion to the interface.
Polymers	Acrylic/air; metal/paint, metal/polymer; polymer/semiconductor	Photodegradation; catalyzed reactions; delamination; temperature effects.
Absorbers	Black chrome/air; metal oxide/air; (ceramic/air): (cermet/air)	Degradation at elevated temperature (> 300° C); composition gradients in Cr.
	Oxide (cermet)/metal (nickel, aluminum, copper)	Adhesion; composition (metal) gradient; nucleation and growth; degradation at high temperature.
	Polymer/oxide; glass/oxide (protective coatings or layers)	Photodegradation; high-temperature degradation.
Absorbers; reflectors	Metal/metal/electrolyte metal/electrolyte (fluid)	Corrosion reactions and degradation, particularly, galvanic effects; microchemistry; microstructure of grain boundaries; interface structure and chemistry.
Absorbers; reflectors; concentrators; collectors	Particle/glass; Particle/polymer	Soiling; particle adhesion; wetting; surface tension phenomena; interfacial energetics; reactions (corrosion, etc.); electrostatic effects (surface charge).

*Based in part upon the contents of Ref. [3].

Table 1. EXAMPLES OF CURRENT SOLAR MATERIALS INTERFACE PROBLEMS (continued)

System or Component	Interface (materials)	Problems or Concerns
Heat transfer materials; mass transport; piping, etc.	Grain boundaries; free surfaces: metal/fluid; metal/steam (gas); ceramic/liquid metal	Creep; low-cycle fatigue microstructural changes associated with deformation; corrosion; stress corrosion; diffusion creep-fatigue interaction; diffusion assisted chemical (microchemical) changes; fretting and wear of metal and ceramic surfaces in contact with liquid or vapor phase materials; caustic cracking of steam generator tube materials; thermomechanical stability of interfaces, e.g., grain boundary structural (microstructural) changes with thermomechanical treatment.
Heat transfer fluids	L/L, L/S	Phase miscibility; wetting and spreading of phases; thermodynamics and thermochemistry; structure of liquid interfaces, etc.
Thermal Storage (Latent Heat)	S/S; (salt)/metal; salt/polymer; liquid salt/solid; ceramic or mineral/salt; etc.	Thermomechanical and thermochemical stability; thermochemical stability; reactions; cycle times; degradation.
Thermochemical energy storage	S/G; S/L; L/G	Corrosion; reactions; microchemical changes; diffusion; segregation (hydrogen embrittlement, etc.).
Ocean thermal energy conversion	S/L; metal/salt; metal/electrolyte; ceramic/electrolyte; interfaces at organic films forming on surfaces; titanium heat exchanger surfaces	Grain boundary and surface corrosion; biofouling (adsorption of living organisms on surfaces); bacterial attachment to surfaces; grain boundary stability in creep of structures.
Solar cell materials (photovoltaic)	Semiconductor/metal; semiconductor/ semiconductor; polymer/semiconductor; semiconductor/ceramic; homojunctions; heterojunctions	Interdiffusion (thin films); role of interfacial defects; elemental segregation; grain boundary passivation; reactions; junction stability; structure of heterojunctions (microstructure); degradation (thermal, microchemical, etc.); adhesion; diffusion; doping, recombination; amorphous structure; amorphous-to-crystalline transitions; grain size effects.
Photoelectrochemical (wet photovoltaic cells)	Metal/semiconductor; semiconductor/electrolyte; metal/ electrolyte	S/L interface characterization; thermodynamics; electrochemistry; corrosion; ion electromigration; electrical nature.

Table 2. EXAMPLES OF SOLAR MATERIALS TOPICAL STUDY AREAS AND RESEARCH PROBLEMS AT SPECIFIC INTERFACIAL REGIMES*

Interface	Topical Study Area or Research Problem
S/S	Adhesion (thin films, including polymer and oxide composites bulk coating; fine powder compaction and consolidation; theoretical models); friction and wear; energetics; diffusion; nucleation and growth; characterization (microstructure and microchemistry, grain boundary structure, modeling, theoretical analysis in metals, semiconductors, ceramics, polycrystal models**); solid-state devices (junction structure, properties, composition, effect of defects, passivation, theoretical analyses); interphase boundary structure (including microanalysis and atomic resolution); effect of temperature and stress on interfacial structure (structural changes at grain boundaries, grain boundaries as sources of dislocations, etc.); basic features of bonding; mixed bonding (e.g., metal/ceramic, metallic/ionic or metal/semiconductor; metallic/covalent, etc.); role of bonding and reaction thermodynamics in degradation of adhesion at interfaces; diffusion and segregation.
S/L	Wetting; spreading; adhesion; friction; lubrication; corrosion reactions (electrochemical); structure (especially the development of analytical techniques to study microchemistry and microstructure at the L/S interface, theoretical studies, and modeling); nucleation and growth; elucidation of degradation and degradation mechanisms.
S/G	Corrosion; oxidation and related surface reactions; diffusion; energetics (including theoretical modeling and energy calculations utilizing appropriate potential theory, etc.); electron emission; thin film deposition (including nucleation and growth on solid surfaces); surface structure and characterization; catalysis and catalyst structure (surface structure); optical properties characterization; elucidation of degradation reactions, etc.; dust adhesion; surface cleaning and protection.
L/G	Surface tension (energetics); diffusion; vapor pressure phenomena; surface structure (analytical and theoretical models for surface structure).
L/L	Energetics (surface tensions, interfacial tensions); wetting and spreading; miscibility and immiscible phases.
General	New materials development; new materials fabrication; instrumentation development for characterizing interfacial microchemistry and microstructure at or near operating environments; modifications to existing materials; materials interfaces in solar technology systems; stability of polycrystalline materials and new concepts of grain boundary structure and properties; composite systems evaluation; theoretical approach to new materials identification (i.e., identifying new materials for solar system applications, including interface characterization, etc.); theory of homojunctions and heterojunctions; amorphous materials research (crystalline-to-amorphous phase interface studies); role of interfaces in optical performance; thermal and optical properties of semiconductors and thermodynamic studies of semiconductors.

*Based in part upon the contents of Ref. 3.

**See also Proc. Conference on Ceramics - "Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems" (Univ. of Calif., Berkeley, July 28-August 1, 1980).

V. OVERVIEW OF THE SOLID/SOLID INTERFACE — MECHANICAL STABILITY

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ABSTRACT

Photothermal and photovoltaic device structures require large area thin film multilayers that must be uniformly processed and will withstand a hostile service environment for long periods without degradation. Our present experience with demanding thin film applications resides in microcircuits and optical applications. Thus little background for predictive capability exists in the case of high, cyclic temperature excursions, oxidation/corrosion ambients, and abrasive winds to be expected for reflectors and collectors.

Long term mechanical stability will be governed by control of the stresses produced during growth followed by stabilization of the microstructure. Low temperature transport has long been known in films but data for many incorporated impurity species including H_2 and OH are not common. The stress relief that accompanies such recovery processes has been studied in detail in only one soft low melting film. Reliable creep data for films do not exist. At high temperatures, even diffusion into the bulks may be an important sink for material originally at interfaces. Surface morphology changes after annealing have been identified.

At fast deposition rates, grain boundaries may become even wider and possess large quantities of impurities. Many dielectric films contain microscopic voids which give rise to reversible and irreversible behavior. Disorder is quenched-in at low effective atom mobility with the formation of amorphous or metastable phases. Even amorphous films have their own scale of structure, lower elastic constants, and doubts about high temperature stabilization. There is a parallel with LASER glazing and near surface modification by ion beams that should be exploited.

The mechanical strains that are produced in a film during growth are a result of the microstructure as well as thermal expansion. Some control is possible, but is often limited as a result of the (gaseous) impurities which may not be stable at high temperatures. Elastic stress distributions may be calculated but are useless without knowledge of plastic flow. Modifications of an interface by grading, stress compensation, and topological interlocking are known to prevent failure. New techniques for the measurement of "adhesion" and the localized characterization of mechanical properties together with the application of fracture toughness concepts are necessary to understand interfacial strengths.

Mechanical integrity requires the solution to many of these problems. Recent developments in high strength films, prevention of grain growth by modulating the structure, and producing a specific microstructure for a desired optical property show that progress is possible. Opportunities for surface science will be to comprehend atomic mobilities in the formation and stabilization of real microstructures in solar environments, to produce new materials, and to develop new techniques, especially in situ and non-destructive, to give early detection and predictive capability of failure.

I. INTRODUCTION

In present applications most thin film-substrate structures, which are rigid because the film to substrate thickness ratio is less than 0.01, are small-area and operate in a controlled environment near room temperature with little temperature cycling. In spite of these generally favorable conditions, spatial and thermal control of film properties is not routine. The edges and interfaces both perpendicular and parallel to the film plane are particularly sensitive regions. For the large areas and hostile ambient required for solar applications, little experience for predictive capability exists. It is the purpose of this paper to identify some of these concerns and the purpose of this workshop to give direction to their solution.

Only passive properties will be examined because of their universal application to the multiplicity of possible structures. It is recognized that severe additional constraints are present for electrically active interfaces, but consideration of the mechanics and mass transport will dominate this discussion.

An idealized structure for solar application (see Fig. 1) demonstrates the many S/S interfaces that must be understood. Because of the large area and economic requirements, the substrate and superstrate may be substantially thinner than our common

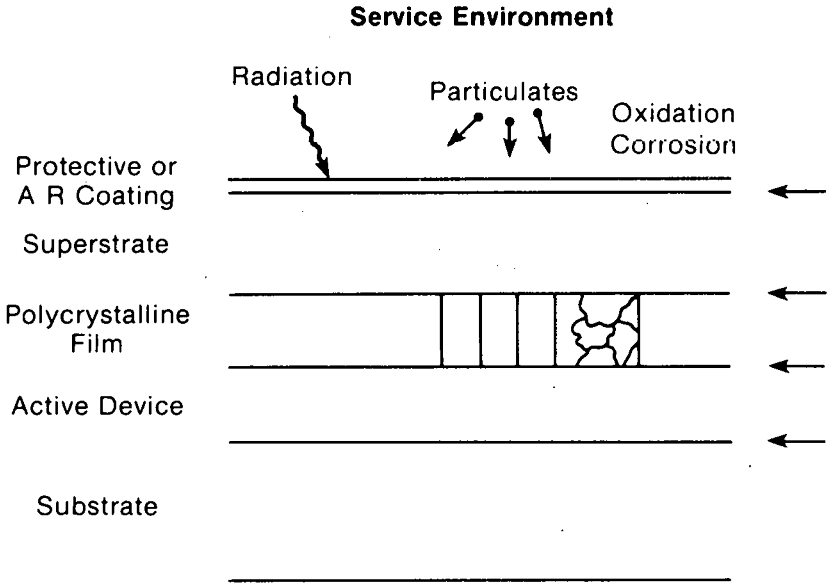

Fig. 1. Model multilayer film structure for solar application. The horizontal arrows indicate interfaces between layers. Each film has microstructure as the grain boundaries shown for the polycrystalline film.

film/substrate experience. The result is an increased sensitivity to mechanical stresses which could deform the structure so that it is no longer able to meet focusing requirements. An active device will require electrodes and very likely transparent conductors. We recognize that multiple materials will be required: polymers, ceramics, insulators, and metals will commonly be appearing as polycrystalline or amorphous films. Photovoltaics may require single crystal techniques. The microstructures existing in these film materials will be highly dependent on the technique used to produce the film, and the properties will be sensitive to this microstructure. In contrast to the operating conditions for a microcircuit where the temperature is controlled and the device commonly encapsulated, solar structures must operate under a hostile environment. A protective coating for the superstrate may be needed to provide UV shielding, a barrier against oxidation and corrosion, and in addition, must be resistant to wind-driven particulates which will erode or abrade the surface. Operating temperatures for flat collectors may reach 150° C, while high performance collectors will operate up to 600° C. Many materials are operating from 1/3 to 2/3 of the melting temperature. Not only are these temperatures cyclic with the time of day but rapid thermal gradients result from cloud motion. As a result, the mechanical compatibility must be the major feature of the design.

We can draw heavily on the information that has been obtained from the study of microcircuits. A status report on that field has just appeared [1]. This enormous background forms the base from which we can extrapolate to solar applications, for it is here that the control of the microstructure has been done in such a way to produce desirable properties. The role of grain boundaries in the low temperature mass transport [2] and the detailed study of the stress relief that accompanies such a recovery process [3] were first encountered here. Furthermore, the introduction of controlled impurities to reduce electromigration and the construction of diffusion barriers gives us a direction for similar approaches, at least for low temperature transport. This background fails, however, in that it is generally concerned with a small-area device of high quality produced in batch processing. In solar applications processing rates must be rapid for economical high area coverage. The vacuum technology exists for the continuous production of rolled stock or batch processing of architectural glass. The production of aluminized mylar and metalized plastics for automobile applications indicates that single layers may be economically produced. Furthermore, some of these applications begin to approach the solar ambient. Figure 1 reminds us that multilayer films will be required with the obvious interfaces which are parallel to the plane of the structure. The polycrystalline films possess many perpendicular boundaries which may act as rapid diffusing paths. At high temperatures, the lattice may even be an important sink for material diffusing from interface sources [see Chapter X]. Several symposia have described the thin film requirements for solar needs [4,5]. The lifetime requirements will require the development of essentially high temperature film materials.

We assume that all the tools of surface science may be brought to bear in order to characterize the interface. We shall not review these but merely comment that many require UHV and have a limited application in a multilayer structure. These techniques will be required to probe an individual interface with improved resolution and quantification.

However, we suggest that it will be important to develop additional techniques for multilayer specimens and report several that are presently in the literature. Angle lapping followed by surface analysis can provide the width, composition, and some structural information. Fracture of the multilayer structure perpendicular to its plane followed by examination of that surface has been used to identify the void and columnar structure of monolayer films. Parallel fractography coupled with surface analysis can localize adhesive failures.

Chemical or radioactive tracers have been used for diffusion studies and the local site information by implanted Mossbauer isotopes or EXAFS. Finally, the measurement of integrated properties, for instance, the mechanical stress or the electrical resistivity may be deconvoluted to relate to growth microstructure as well as information about the interfaces. Other portions of this workshop consider surface analysis studies; from the point of view of the mechanical properties and interfaces, one is struck by how little information exists and often how the test instrumentation is not appropriate.

An example of a multilayer structure analysis is given in Fig. 2 for the 600° C oxidation of Fe at 2.5 kPa of O_2 in an environmental cell of an HVEM [6]. Figure 2 is a result of many TEM and diffraction observations which include blistering and spalling of the outer hematite layer and the observation of microcracks in the magnetite layer below. Extensive plastic deformation occurs in the Fe substrate during the early periods of oxidation. It is clear that stress gradients and enhanced transport result from the oxidation process. In multilayer deposited films similar stresses may be built in.

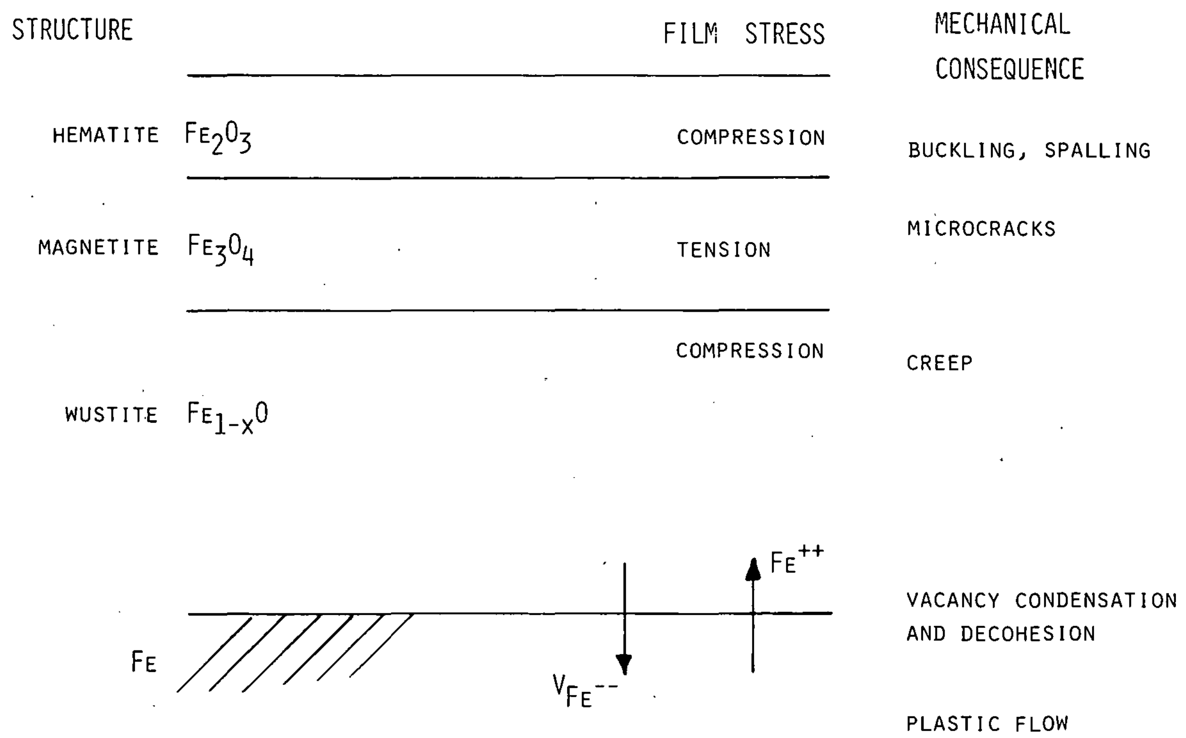

Fig. 2. Consequence of mechanical stresses in multilayer oxidation of Fe. After Voss [6].

II. MECHANICAL CONSIDERATIONS

It is our goal to control the growth of a thin film structure such that no property degradation occurs over its lifetime under the designed environment. This is an ambitious goal and we would like to divide the mechanical considerations into several groups. First of all, there is a microstructure-mechanical property relationship and the possibility that new properties not found in bulk form may be produced to optimize for a particular application. We must consider ways of calculating or measuring the stress distribution and examine the role of the stresses in the failure which we commonly call "lack of adhesion". Finally, having produced the structure we must consider its stability in the operating environment. For solar applications a 30 year lifetime would be desirable without significant degradation of the performance and minimal maintenance. Again the stresses provide a mechanical driving force for mass transport. Rather than a complete review, the purpose of an overview is to indicate some of the important features and provide a guide to the literature.

We identify important mechanical considerations with a particular stage in the deposition of a film. For the substrate itself the elastic constants, thermal expansion, and flow stress are most important. Nucleation is controlled by the surface and interfacial energy. Since interfacial free energies are used to evaluate adhesion [7], we suggest that the energetics of deformed, rather than equilibrium surfaces will be important at temperatures $< T_m/3$ [8]. Interface width, chemistry, and micromechanics play an important role in the adhesion. Stress will produce property changes. Property stability is influenced by a multiplicity of effects which can contribute to the stress relaxation, including grain boundary relaxation and diffusional creep. Finally, the outer surface is important for encapsulation. In the following sections we consider these features in more detail.

III. MICROSTRUCTURE AND MORPHOLOGY

In order to understand the mechanical properties, especially the relaxation and the intrinsic stress, it is vital to have a knowledge of the microstructure. As in problems of bulk mechanical metallurgy, it is our contention that the various contributions to the origin of the stress as well as the mechanisms of flow and relaxation need to be understood. Although a quantitative understanding is far from complete at the present time, specific systems are now studied in enough detail that we are obtaining good insight into the problem. The overall objective is to bring about stress control so that we may obtain the desired final structure in a form in which the performance will not degrade with time.

Detailed differences exist among the various deposition techniques, but we recognize that the single most important parameter in characterizing the structure is the substrate temperature during deposition. In general, forming a film requires a nucleation process which may be three-dimensional if the bonding is different and two-dimensional if similar. Amorphous, polycrystalline, or epitaxial structures result.

For the prototype, consider a medium melting point metal, such as nickel, which is deposited on an amorphous substrate to avoid epitaxial effects. Under these conditions the microstructure can best be described in terms of the zone model [9]. This model, extended by Thornton [10] applies to PVD processes from evaporation to high-rate sputtering. As can be seen in the various portions of Fig. 3, the common structure is a columnar-like growth with either well-defined boundaries between the crystallites at the

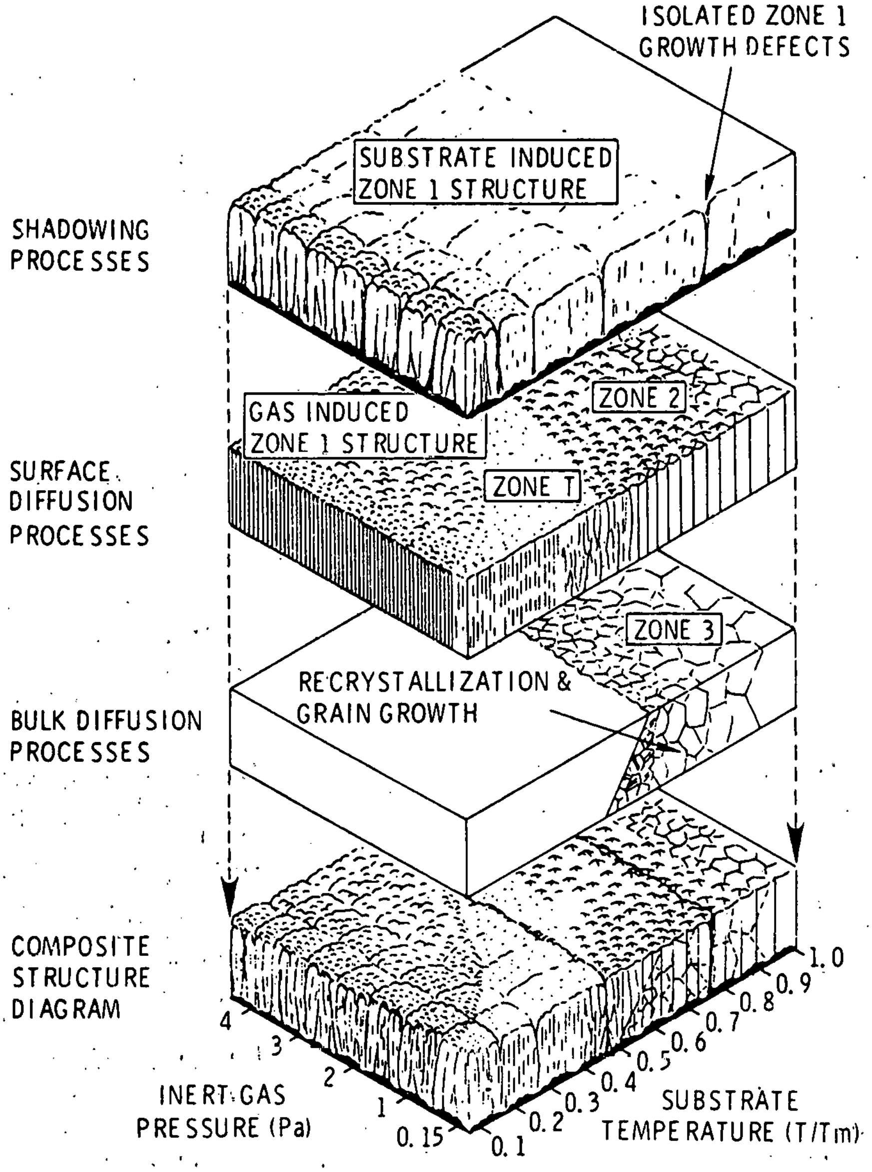

Fig. 3. Representation of physical processes that establish microstructural zones for deposited polycrystalline films. After Thornton [10].

higher temperature, or rather open regions where the mobility has been low. Impurity effects, especially those arising from sweeping and segregation processes, also play an important role in the microstructure. Although this model has been tested primarily with metals, it is applicable to a number of compound materials where the depositing species are essentially molecular rather than atomic.

Compared with corresponding bulk materials, polycrystalline films have a much smaller grain size, higher dislocation density, and more defects. Grain growth is observed upon annealing, but seldom is the diameter larger than 10x the film thickness.

IV. PHYSICAL ORIGIN OF STRESSES

In order to understand the strains generated in the film sample during growth, one requires an atomic rearrangement which attempts to change the volume of the film after it is anchored to the substrate. Such a constrained volume change is the fundamental origin of all the stresses produced. In the case of CVD materials, the substrate temperature is generally extremely high and differential thermal expansion often dominates. In PVD, especially those carried out at lower substrate temperatures, the growth processes dominate. Electrodeposition and solvent drying also produce large stresses; in fact, no processing methods are known that produce stress-free films.

The various contributions that can give rise to growth stresses have been reviewed [11,12,13,14]. As usual in elastic problems, the stress σ is related to the strain ε by an elastic constant. For a biaxial isotropic stress commonly found in films, the relation is $\sigma = \varepsilon E/(1-\nu)$, where E and ν are the Young and Poisson moduli for the material.

During the growth of metal films a net shrinkage at the growth surface [15] or a grain boundary interaction [16] appears to be the mechanism. Incorporation of gases introduces a local expansion (film compressive component) [17]. Compression may also result from self-implantation during magnetron sputtering [14]—a process that is similar to the ion implantation stress effects.

It is important to recognize that the magnitude of the strains may approach 1% and hence the material may plastically deform. Under these conditions, the strain generating mechanism does not determine the final magnitude. In addition, strains may be introduced as a result of oxidation, differential thermal expansion, or other exposure after the film is removed from its deposition environment. Currently, semi-quantitative understanding of growth stresses exists for single metallic layers. Our knowledge for compounds is poor and studies of multilayer structures are rare, but found for optical stacks [18].

Techniques for the measurement of stresses are well known and we shall not review them here. It is important to distinguish, however, between a strain generated at an interface and one which scales with the thickness of the deposited film. In the first case, a mismatch or renucleation in the growth is involved and the strain is localized at the interface and tails off somewhat exponentially. Similar localized strains could, of course, occur as a result of oxidation at the free surface. The volume generated stress is sometimes a more severe condition because the force which must be transmitted across the interface then increases as the film becomes thicker resulting in a critical thickness for failure. In a multilayer structure, some degree of stress neutralization is possible from the point of view of substrate deformation although clearly the local gradients cannot be suppressed [19].

In practice, the most common circumstance is linear growth forces, i.e., a uniform stress generating mechanism. Impurities and substrates make a difference in the nucleation behavior and the stresses in extremely thin films but usually they do not dominate the films with thicknesses greater than 10 nm [20]. At larger thicknesses, the force scales sublinearly, indicating either a change in the growth microstructure or a relaxation in the already deposited material. For low melting point metals, this flow stress limit is often reached for substrates maintained at temperatures less than 100° C during deposition.

V. STRESS DISTRIBUTION

To this point, we have tacitly assumed that the stress is uniformly distributed over the plane of the film. Because of the boundary conditions of no applied forces on the free surfaces, gradients must exist near the film discontinuities. We should recognize that in elastic problems there is a characteristic dimension over which the stress relaxation would take place. For deposited films, it is not surprising to learn this is of the order of the film thickness.

The spatial distribution near the free edge of a film has been calculated [12]. Consider a film that has an isotropic planar stress σ_i in its interior. Assume the stress is uniform in the interior of the film where no other stress components are found. By applying the method of boundary tractions, the stress distribution near the free edge may be calculated. A shear stress of magnitude $2\sigma_i$ is developed near the point determined by the intersection of the edge and the interface. Perhaps more surprisingly a normal force approximately $10\sigma_i$ develops perpendicular to the interface. For a film under tension, the interfacial bonding must be able to support this stress gradient or a fracture at the interface will take place. We treat the propagation of this fracture later but it is obvious and well known that the edges or cracks in a film represent a weak area. Similar analyses have been carried out for adhesive joints in multilayer structures [21] which indicate that the large stresses are found near the outer edges.

The stress distribution in the substrate may also be calculated [22]. For the case of a window etched in an oxidized Si/wafer, the gradients were localized near the window edge but extended into the substrate for a distance of some 50 oxide thicknesses. In submicron structures, stresses will be so nonuniform that the corresponding changes in stress-induced properties will comprise about half the volume. For most solar applications, this geometry is not a concern and the main effect of the gradients would be in the fracture and mass transport.

We should point out the recent application of measuring a thin film strain in the TEM and calculating the corresponding stress by Fourier transform techniques [23]. To date this technique has been used to determine the flow stress and elastic constants of a single craze in polymer materials [24]. The air crazes in polystyrene are a severe degradation. They are localized and have a width of only a few μm; until recently, tensilometers to handle such small samples were not available. Some specialized tensile instruments had been developed [25] but they have fallen out of fashion because they were generally not able to obtain strain rate data. Perhaps this is responsible for the lack of data on the flow stress of films.

VI. MECHANICAL RELAXATION

For bulk materials, thermally activated dislocation recovery and relaxation mechanisms have been identified. It is anticipated that these will also operate in films. The largest difference lies in the huge grain boundary area commonly found in polycrystalline films; hence, the processes are dominated by surface diffusion. Considerable TEM data exists for dislocation motion in thinned samples, presumably representative of the bulk. Dislocation density in films is much higher than in bulk materials and the observation of single dislocation motion in films is difficult. Given the significant effort to carry out a detailed study, the relaxation in film structures may be understood in great detail. We call attention to the papers by Murakami [3,26] for Pb films in which the thermal strain is the only contribution. No relaxation takes place where film thicknesses are less than the critical value but for thicker films dislocation climb seems to be the dominant strain relaxation mechanism. At higher temperatures the grain boundary relaxations are replaced by bulk diffusivity kinetics. To my knowledge, this system represents the best characterized study of a thin film recovery process to date and can serve as a model for future work. An understanding of the processes for "porous" microstructures found in solar films will be more difficult.

The second example involves producing a thin film structure by incorporating a strengthening mechanism. Diffusion hardening is of course commonly known in bulk materials and the Al_2O_3 incorporation has been applied to film structures [27]. Introducing a periodic gas pulse has given a five-fold increase in the fracture strength for Al-Al_2O_3 and Ta-C laminates [28]. The mechanism is felt to be a Hall-Petch type of barrier model and it is this kind of approach which may be useful to produce the high temperature film materials needed for collectors.

Internal friction measurements have served to identify mobile species and are carried out over suitable frequency and temperature ranges. Dynamic measurements have also been made with special instrumentation for films [29]. However, the interpretation may be more difficult because of the uniform stress resulting in a shift of the apparent activation energy.

Microhardness measurements have also been made on thin films although the analysis is complicated by the partial elastic deformation of a relatively thin film on top of a substrate. The importance of such microhardness measurements is the empirical relationship of the hardness number, determined by the indentation, to the flow stress, and the ultimate tensile stress of the material. Special ultramicrohardness apparatus has been developed [30] but has not produced significant improvement. The appearance of cracks in Cr films correlates with the microhardness [31].

VII. ELASTIC CONSTANTS

The isothermal bulk modulus, which is a measure of the stiffness of a crystal, is directly related to the second derivative of the cohesive energy with respect to volume. As a result, elastic constants are generally not considered to be highly dependent on microstructure. Such a statement is true for thin films; however, in some cases the structure is so different from the corresponding bulk material that the constants of different effective material are used. Elastic constants have generally been measured from the linear portion of a stress vs. strain curve under unloading conditions. Tensilometers, the bulge test in which the deformation of a bubble has been measured, and pulse-echo acoustic measurements have been used. With the recent interest in mechanical properties of the implanted, near-surface region, surface wave approaches should appear. We can summarize the data for elastic constants of films as follows: values of elastic moduli are generally within 5% of bulk value under conditions that the film is polycrystalline and relatively free from impurities. Film densities may be low because of the void structure. In such a material, the elastic modulus must be reduced in proportion to film density. Amorphous films may be condensed on low temperature substrates; Young's modulus and especially the shear modulus may be 20%-40% lower in the amorphous state compared to the crystalline one. Periodic compositional variations on a 1-5 nm scale have been reported to increase the elastic constant for certain epitaxial films [32]. This represents a considerable change in the curvature of the cohesive energy vs. interatomic separation and, speculatively, may be a way of tailoring a thermal expansion coefficient.

We call attention to a new tensile device called the nanotensilometer [33] which was developed for examining samples with cross sections as small as 0.1 nm^2. Figure 4 shows the data for a polyethylene single crystal approximately 10 nm thick. The pseudoelastic initial slope corresponds to a modulus of 2 GPa and the decaying portion of the curve at extensions larger than 50 nm corresponds to the pulling of 10 nm diam. microfibrils from the parent crystal and their resultant stretching. On this basis, the structure of these microfibrils can be shown to be folded rather than extended chain configurations [34]. Nanotensilometer data for polystyrene craze material agreed with the flow stress but gave a substantially larger modulus than the TEM technique mentioned earlier. It is suggested that a combination of microscopy and tensile testing using micrometer size specimens (micromechanics) will be a useful way to obtain new mechanical properties for thin films and especially the modified material that may be present as a result of interfacial diffusion and mixing.

VIII. ADHESION AND FAILURE MODES

The role of stress in adhesion is commonly acknowledged but poorly documented. The presence of a stress in a film promotes its failure, and this failure is associated with the propagation of a fracture. The knowledge of the stress and specimen geometry

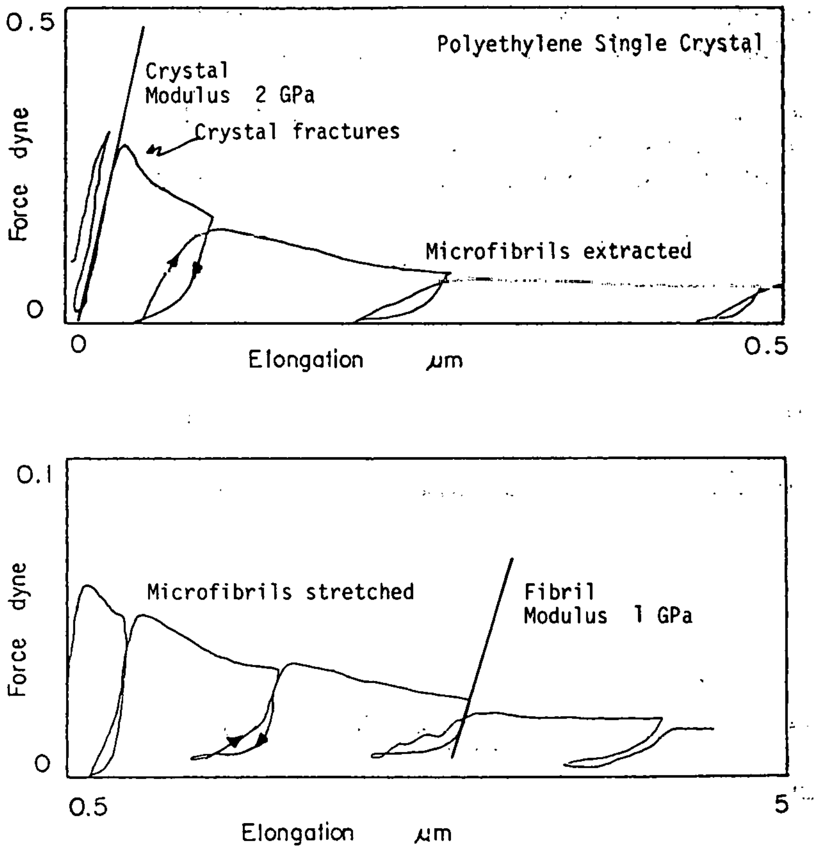

Fig. 4. Deformation of 10 nm thick polyethylene crystals showing microfibril extraction from the fractured crystal. Hagerling and Hoffman [34].

allows the calculation of the stress distribution. Figure 5 indicates the failure in a schematic way. If a tension exceeds the fracture strength, a crack network will appear; if the film material is brittle, such as an epitaxial bubble material [35], the film thickness must exceed the Griffith crack length before the crack will appear. If the normal and shear stresses at the crack on a full edge cannot be supported, then the crack may propagate parallel to the film near substrate interface. It appears as though the propagation is determined by fracture mechanics rather than direct bond failure, although water vapor and other materials will tend to promote a delayed degradation.

Films under compression generally delaminate at the interface with the subsequent lifting of the film in a zigzag pattern where the film tries to expand to reduce its strain energy. Strain models are proposed [36]. In practice, stresses in the range of 1 GPa cause rapid failure, whereas those in the low MPa range are tolerable.

Fracture mechanics concepts have been applied to the analysis of adhesive joints [37] and to metallization of alumina substrates [38]. Their use has been suggested for thin film structures but to date no material constants have been obtained for film geometries. This approach should be expanded, however, because it forms a basis for predicting stress limits.

The recent review [39] of thin and thick films adhesion testing indicates that the scratch and pull test yields numerical information which is at least useful in a relative way to improve material compatibility. We call for the application of surface science techniques to examine the chemistry of the interface [40] and also for ion beam modification of the surface for increasing the adhesion [41].

The second approach is that of functional testing [42] in which a film deposited on the actual substrate used in the application is subjected to a high temperature anneal or immersion in a boiling fluid for a prescribed length of time. This type of accelerated

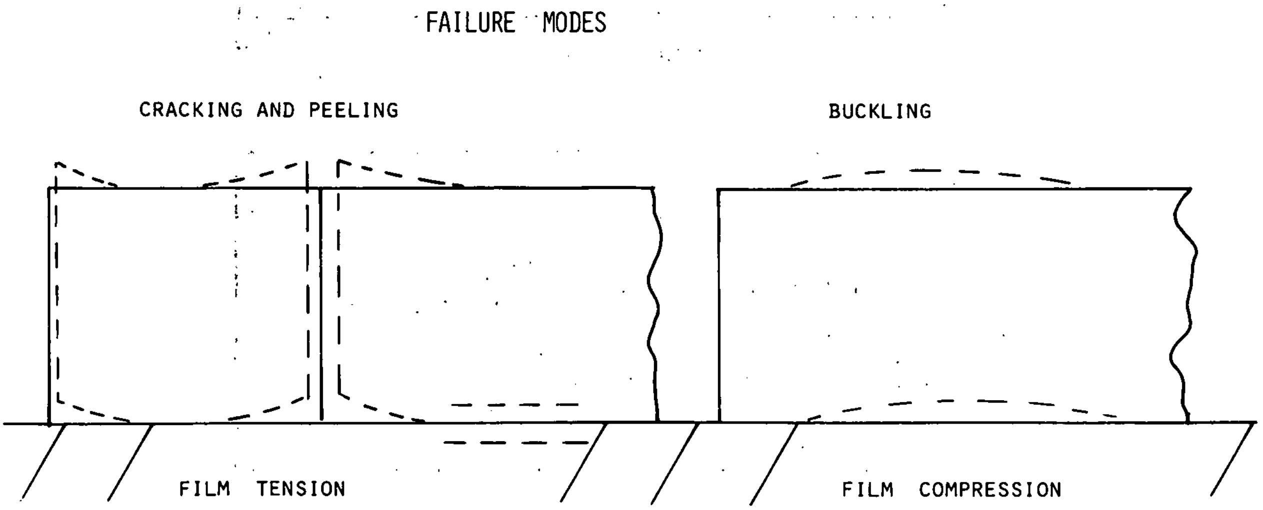

Fig. 5. Simplified model of fracture in the interfacial region. The film edges and defects give stress concentration and promote failure. Interdiffusion may result in brittle intermetallic compounds. After Hoffman [12,13].

testing is useful although each system must be correlated with the ultimate performance on an empirical basis.

A complete description of the mechanical integrity would take account of the stresses both condensed in the film plus any other processing treatments and the relaxation processes to predict a useful lifetime under a given environmental condition. Clearly the models have not been quantitative to this degree but I believe the concepts are developed to the point that the effort would be fruitful.

IX. PROTECTIVE OVERCOAT

Our final concern is to consider techniques by which the film structure may be stabilized. Impurity injection to decrease the grain boundary diffusivity and specialized diffusion barriers have been produced for microcircuitry applications. It is also known that metallic oxides form oxidation and corrosion barriers [43]. The increased temperatures in solar applications will make these problems a difficult challenge.

In response to the requirements of abrasion resistant coatings for wind-driven particulates, I am aware of no published literature which bears on this point. A common empirical test for abrasion resistance is rubbing with an eraser under load and in some cases looking at the wear track. However, the impact of various sized particles with a range of momenta does not appear to be similar. There is some experience with spun glass coatings on plastic eye lenses and a temptation to consider the diamond coordinated plasma deposited C films because of their reported hardness.

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VI. OVERVIEW OF CURRENT STATUS OF SOLID/LIQUID INTERFACE SCIENCE

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ABSTRACT

An overview of the current status of solid/liquid* interface science is presented, along with some comments about its relevance to solar energy conversion technologies. A discussion of the diffuse layer includes past and current perspectives of the structure of H_2O in the double layer and its role on potential changes at the metal/liquid interface. The difficulties of considering the potential changes of semiconductor or insulator/liquid interfaces are related to surface states and dangling bonds. The methods available for investigating the solid/liquid interface are reviewed, i.e., sweep, ellipsometric, radiotracer, AES, XPS, and Mossbauer methods. Frumkin's contributions and the potential at zero charge (p.z.c.) are also discussed. The difficulties and prospects of measuring and/or calculating absolute potentials of solid/liquid interfaces from understanding the p.z.c. are then considered. Organic and ionic adsorption isotherms and the factors limiting their contribution to increasing the understanding of the solid/liquid interface are reviewed.

Future prospects and needs for research on the solid/liquid interface are outlined in the concluding section. Developments in this field are in an early stage, compared with the solid/gas interface, but the subject material has a more practical bearing to real systems. New theoretical approaches, including modeling of the double layer and diffuse layer using quantum mechanical and Monte Carlo approaches are clearly needed. A need for elucidating the structure at semiconductor/liquid interfaces and its bearing on photoelectrochemical solar energy conversion is indicated. The need for applying in situ spectroscopic and direct measurements to study the solid/liquid interface is clearly required for extending our present understanding in this field.

I. INTRODUCTION

In interfacial studies, the historically stressed system has always been the metal-vacuum interface, but, in fact, in practice, the metal (or semiconductor or insulator)-solution contact is that which is most frequently relevant to practical situations. Examples of these interfaces in solar energy-related technologies are in photoelectrochemial converters and in the photoelectrochemical synthesizers. However, the breadth of the application of the interface concerned stretches further, e.g., into electrical storage and conversion devices, and also to conservation problems.

The S/L interface is, in practice, frequently met in solar energy conversion devices. In the following, the various kinds of double layers are overviewed. It is found that although good knowledge exists for that unusual but much studied interface

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*In the rest of the manuscript, "liquid" will be the term used instead of "solution." However, it is essential to understand that all the interfacial situations concern highly heterogeneous structures in which the main entities are ions and electrons.

involving Hg, knowledge of the S/L interface, particularly that involving semiconductors and insulators is limited. Spectroscopic methods have only just begun to be applied in this area. An outstanding lack is the development of ellipsometric spectroscopy. The remainder of this introduction will summarize the status of the theory and models of the S/L interface and methods of experimental investigations.

The Gouy-Layer theory, used in present descriptions and quantitative calculations, suffers from a basic statistical mechanical difficulty because the number of particles in the relevant volume even at high concentrations, is not statistically viable. The principal improvement which has occurred during the last decade in the interpretation of the structural properties of interfaces is the concentration of the H_2O structure, i.e., that part of the impedance which is solvent-dependent. Precise models for this situation are still in competition, and the measurement of the entropy of the solvent at the interfaces seems to be the key for distinguishing between the competing models.

One of the difficulties of a realistic model for the semiconductor/liquid interface is the presence of surface states, either due to dangling bonds belonging to surface atoms, but also to adsorbed entities from the solution, perhaps due to reaction intermediates or charge transfer adsorption from ions which adsorb more strongly on semiconductors than on metals. A weakness is a paucity of methods for determining the concentration level of these surface states, and a lack of application of the 2-3 methods which give some information.

Methods of investigation of the surface radicals on solids in contact with liquids has progressed somewhat since 1970; the major improvement is the better understanding of the sweep rate and its meaning in adsorption determinations. Combinations of these sweep measurements, along with those of radiotracers, are complementary and may lead to the determination of the predominant radical in a reaction sequence.

Optical methods have had a special relevance to systems involving liquids, because it is possible to use reflectance spectroscopy and ellipsometry in the presence of solutions, at least in the visible wavelength range. Although reflectance has been frequently used, it has undoubted drawbacks, in that the Fresnel equations in terms of which the intensity is expressed as a function of adsorption and also of the refractive index and thickness of surface layers. Ellipsometric spectroscopy would be a positive development and could be used in the UV.

The application of electrocapillary thermodynamics to liquids is difficult to apply to solids, but some stretching and turning methods within the elastic limit probably give information concerning the degree of adsorption of entities and the excess surface charge. Frumkin, and particularly Gokstein, have developed such methods with a new thermodynamics, which should take care of the problem of double layer penetration.

The potential of zero charge and the flat band potential are both parameters of great need and immediate applicability, the first to adsorption on metals and the second to identifying electron levels in semiconductors. However, not many experimental systems are among the methods used and the situation resembles that for the metal/vacuum interface and work function determinations of 20 years ago.

Spectroscopic methods are in a general sense the obvious answer to many of the problems of the metal and semiconductor/liquid interface. Although AES and XPS methods can certainly be used in solid/liquid systems, there is a certain reserve concerned with the results referring to the systems which were originally in solution because of the effects of using drying by evacuation. By using low angle XPS, it has recently been possible to show the connection between H_2O binding passive layers in the presence of chloride ions in solution. Mossbauer spectra can also indicate characteristic bonds for oxide films in contact with liquids.

The potential difference (p.d.) at the metal/liquid interface is classically expressed on an arbitrary scale, and this makes often for poor understanding of the p. d. in the double layer. It is increasingly realized that the p.d.'s on these scales can be referred to the vacuum or absolute scale. The breakdown of the p. d.'s across the interface will probably remain model-dependent.

Molecular adsorption at the S/L interface is now subject to molecular model theory. It is probably in better shape than the problems associated with ionic absorption, where the lack of definition of the degree of chemical bonding has begun to interfere with the ability to image well between metal and solution.

Friction plays a part in many semiconductor/solution interfaces, particularly that concerned in photoelectrochemistry, and there is now a theoretical development which interprets the dependence of friction upon the p. d. at the interface.

In summary, the present situation is that electrostatic type models of the solid-liquid interface have reached a plateau of usefulness and await the introduction of a quantum electrochemical viewpoint.

II. THE DIFFUSE LAYER

It is better to start this review by coming in from the direction of the liquid toward the solid. We begin by discussing the diffuse layer, which is part of the well-known double layer. It was derived by Gouy in 1910 [1]. The mode of analysis of the charged cloud at the S/L interface is similar to that used in the Debye-Huckel theory of electrolytes. All chemists know about this theory, and it is often thought to be the parent of the Gouy theory; whereas, in fact, the Gouy theory was derived in 1910, and in 1923 the Debye-Huckel concepts for solution were derived from Gouy's treatment of the metal-liquid (M/L) interface.

The diffuse layer theory is used as a model for considering the M/L interface. For example, in the analysis of the Gibbs surface excess, where the need is to find out how much is adsorbed in the diffuse layer and how much is adsorbed to the electrode, the Gouy theory is used. This is troublesome because, as is well-known, the Debye-Huckel theory is only applicable to dilute solutions, those where ionic interactions are not yet a problem; whereas, the realm of adsorption measurements is at the other end of the scale, in the region of 0.1 M solutions, where the Gouy theory should apply poorly. Hence, there is a doubt in the indirect Gibbsian calculations within the double layer—those pioneered by Grahame [2]—at the basis of the calculation.

Attempts have been made to overcome the approximations in the Gouy treatment of the double layer, but nothing has come of them, because it has been difficult to devise an objective test of what is new [3,4,5].

What is needed is an experimental method of measuring individual ionic concentrations 10 to 100 nm away from the solid surface, and thus, determine the actual concentrations. Perhaps this can be done by some kind of Schlieren pattern measurement, or by the use of ellipsometry where there is negligible specific adsorption.

A. Water Structure in the Double Layer

Before 1952, there was no consideration as to whether H_2O had any structure at the S/L interface, and therefore, contributed to its electrical properties. Bockris and Potter [6] interpreted electrode kinetic data by assuming that H_2O dipoles set up a potential difference (p.d.) at the interface, which varied with the structure of the double layer. Their use of such a contribution applied a view of double layer H_2O, which was first suggested by Lange and Miscenko [7] in 1930. However, the Bockris and Potter model lacked any discussion of the relation of work to the double layer capacitance, which was first taken into account by Mott and Watts-Tobin [5] in 1962. Their model was gas-like, for it did not take into account the lateral interaction between the H_2O molecules at the interface. Bockris, Devanathan, and Muller (DBM) [6] developed the model for H_2O in the double layer in a way which related the H_2O capacitance to the interaction between the H_2O molecules, showing that this greatly increased the capacitance.

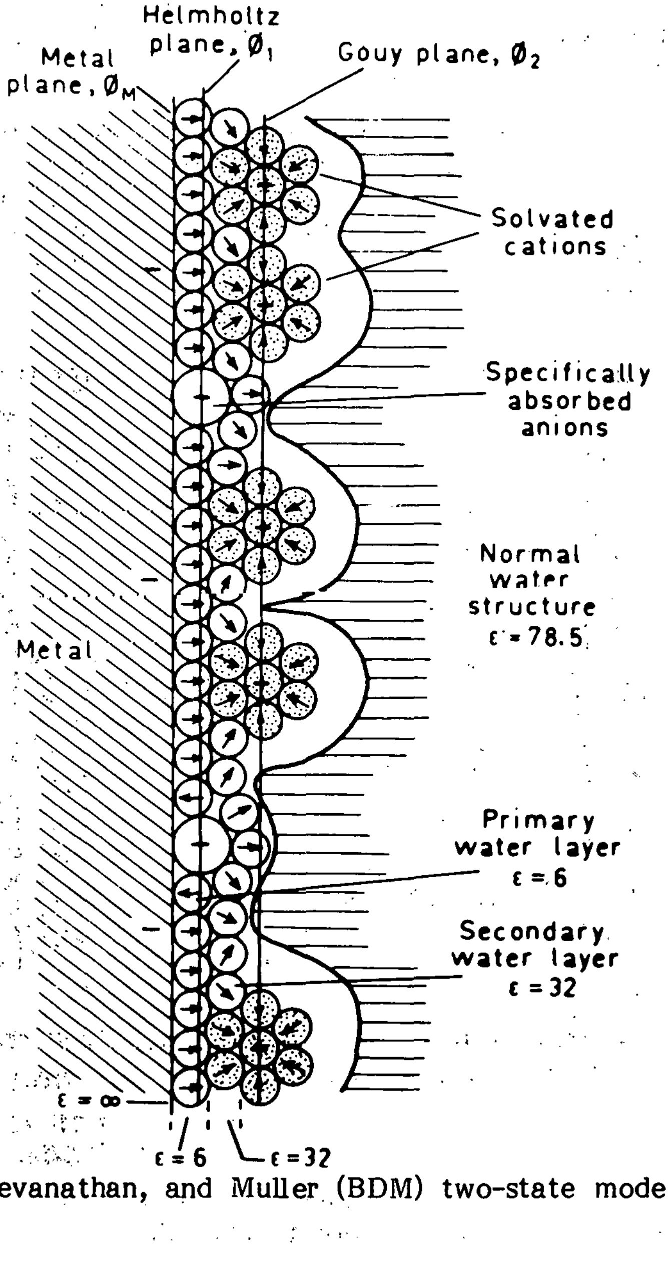


Fig. 1 The Bockris, Devanathan, and Muller (BDM) two-state model of the double layer.

They regarded the ionic and H_2O contributions to the capacitance as being in series (Mott and Watts-Tobin had taken the two capacities in parallel), so that a larger H_2O capacitance means a lesser impact on double layer properties. A well-known model of the double layer has been derived from these ideas (Fig. 1), and since the mid-60's improvements have branched primarily from it.

The double layer structure at the Hg/solution interface is the parent for further interfacial discussions of solids, which we shall carry out below. Because aspects of the H_2O structure in the double layer have come to predominate discussions of double layer structure, we shall present it more in the next section.

B. Some Detail on the H_2O Structure in the Double Layer

In Fig. 2, the basic idea of H_2O in two positions is shown. However, there are new ideas developing about the structure of H_2O. There is evidence that dimers exist in the adsorption of H_2O from the gas phase [8].

A universally observed phenomenon at M/L interfaces is that the fraction of surface covered (when the adsorbent is molecular) is parabolic with respect to potential. It is easy, qualitatively, to understand this trend for adsorption. When the metal interface is strongly charged, positively or negatively, H_2O molecules will be held electrostatically. But, near the potential of zero charge (p.z.c.), there is only a weak bond of H_2O to the surface, so that it is easy for organics to replace H_2O. This is shown in a simple way in Fig. 3.

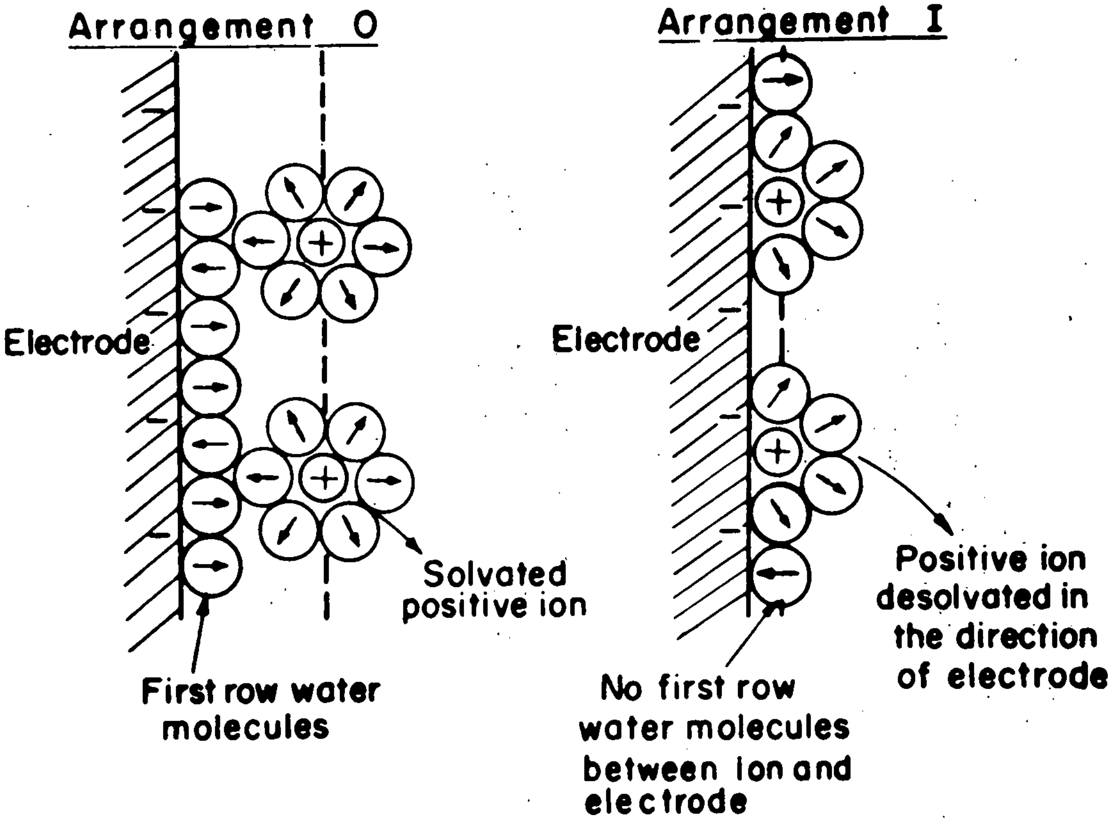
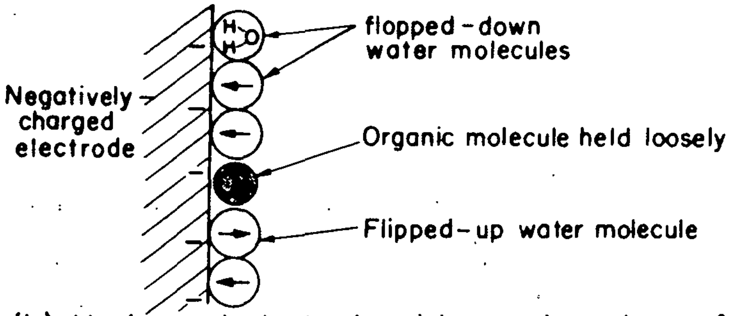
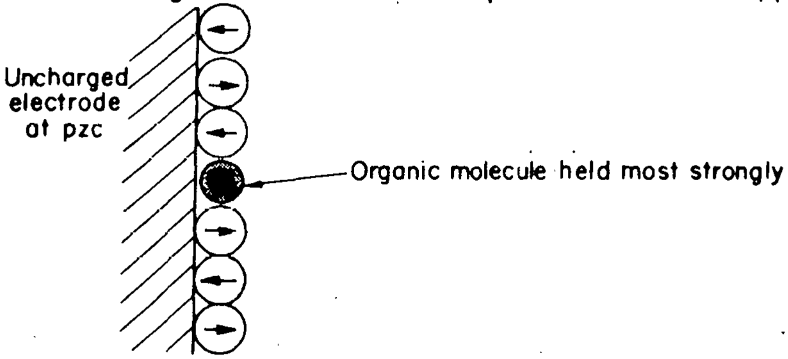


Fig. 2 The two types of arrangement of ions stuck on an electrode (the compensating ions in the diffuse layer are not shown).

(a) Negatively—charged electrode with excess of flopped-down dipoles



(b) Uncharged electrode with equal numbers of flipped and flopped dipole



(C) Postively — charged electrode with excess of flipped-up dipoles

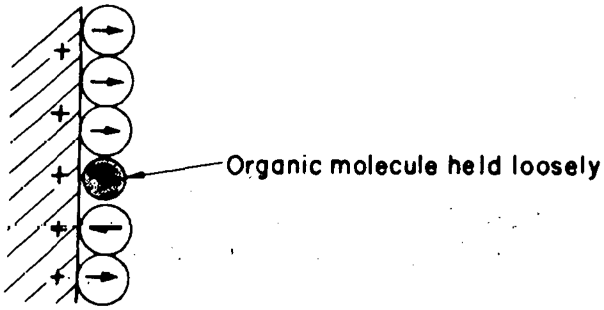


Fig. 3 The relation between the electrode charge and organic adsorption: (a) a negatively charged electrode with an excess of flopped-down dipoles has weak adsorption, (b) an uncharged electrode with equal numbers of flipped and flopped dipoles shows strong adsorption, (c) a positively charged electrode with an excess of flipped-up dipoles has weak adsorption.

Until the mid-70's, there was much opposition to accepting structured H_2O as affecting the electrical behavior of the interface. This opposition diminished after the work of Hills and Payne [9] and Reeve [10], who showed that they could extract, from data of interfacial tension as a function of temperature, the entropy belonging to the H_2O molecules alone. This had a shape which was exactly interpretable in terms of the configurational entropy which one would expect if one had a mixture of H_2O molecules of different types on the surface.

Frumkin [11] regarded H_2O molecules as "largely laying down" on the surface and a model reminiscent of this has been suggested by Parsons [11] in which the H_2O molecules are laying down toward the p.z.c., but stand up to a small extent (they are seen as extensively polymerized) as the excess electrical charge on the metal is made more positive or negative.

Where are advancing frontiers of work in this field? One can learn much from the entropy measurements. They have only been done at a single Hg/liquid interface. Study of interfaces containing aprotic solvents using ellipsometric measurements should give information about the way H_2O adsorbs from this solvent and how it interacts with itself and the surroundings. A more radical suggestion concerns using HVEM in conjunction with a differentially pumped environmental cell. The hope here would be to penetrate about 1 μm of H_2O on the surface to probe adsorbed ions and even the adsorbed H_2O molecules.

III. THE MODEL FOR THE SEMICONDUCTOR/LIQUID (SC/L) AND INSULATOR/LIQUID (I/L) INTERFACES

Although most of the fundamental work on double layers has been done on the structure of the M/L interface, there are in practice more S/L interfaces where the interface involves a semiconductor or insulator. One of the important general developments of electrochemistry in the post-1960 phase is the development of experimental electrode kinetics at SC/L interfaces. Some work was begun by measuring electrode kinetics at I/L interfaces [12].

There is, however, an important difficulty. Physicists, who are familiar with the physics of the interior of the insulator, have contributed to the development but they tend to neglect contact differences between the liquid or electrolyte. Thus, it is generally assumed that there is an identity between the SC/L interface and the Schottky barrier. This seems, at least often, not to be the case. The situation at the SC/L interface is close to that at the M/L interface, because of the adsorption of anions on the semiconductor. These anions provoke surface states on the semiconductor, which change the structure of the model. Thus, instead of the p.d. at the interface being largely inside the conductor, as at the SC/G interface, some of the p.d. projects into the solution and gives a Helmholtz layer, which should be represented in all models in the current literature [13-15].

The I/L interface has received minimal attention, but its importance is great, because it is the nearest approximation for interfaces relevant in biology, many of which are S/L systems.

IV. METHODS OF INVESTIGATIONS FOR SOLIDS

A. Sweep Methods

In spite of the complexity of the S/L interface, the most frequently used device for investigating adsorption as a function of the excess charge density are sweep techniques, of which there are three kinds [16]. In the first, one keeps the current constant and watches the potential vary from 1 ns to 0.1 s [17]. One can do something similar by keeping the potential constant (using a series of these potentials) and recording the currents as a function of time, and finally, one can use the most complicated and widely used of these techniques: the potentiodynamic sweep technique in which there is a steady rate of variation of potential, but one watches current as a function of time. In each of these methods, there are different errors which one has to minimize. For example, if one sweeps too slowly, the material which has been desorbed will diffuse onto the electrode and the measurements will show multilayer adsorption of material. If one sweeps too quickly, one is measuring the capacitance of the interface, because the currents associated with interfacial electron transfer are too small to be observed.

In using sweep methods, a specific electrochemical reaction must be assumed to deduce the coverage from the amount of charge. Because of possibly making incorrect assumptions, at least one totally independent alternative method is needed to close the gap in information which the sweep methods produce.

One of these methods is the radiotracer method [18]. As one measures only the number of tracer atoms present on the surface, one can, by comparing radiotracer with sweep results, obtain an indication of what radicals are present on the surface. In Fig. 4, one sees that for benzene compared with three sweep methods, the latter are in agreement, whereas the radiotracer methods differ on the negative side of the diagram. Thus, in this potential region, there must have been a dissociation of adsorbed benzene to organic radicals, which turn out to be CHO [19].

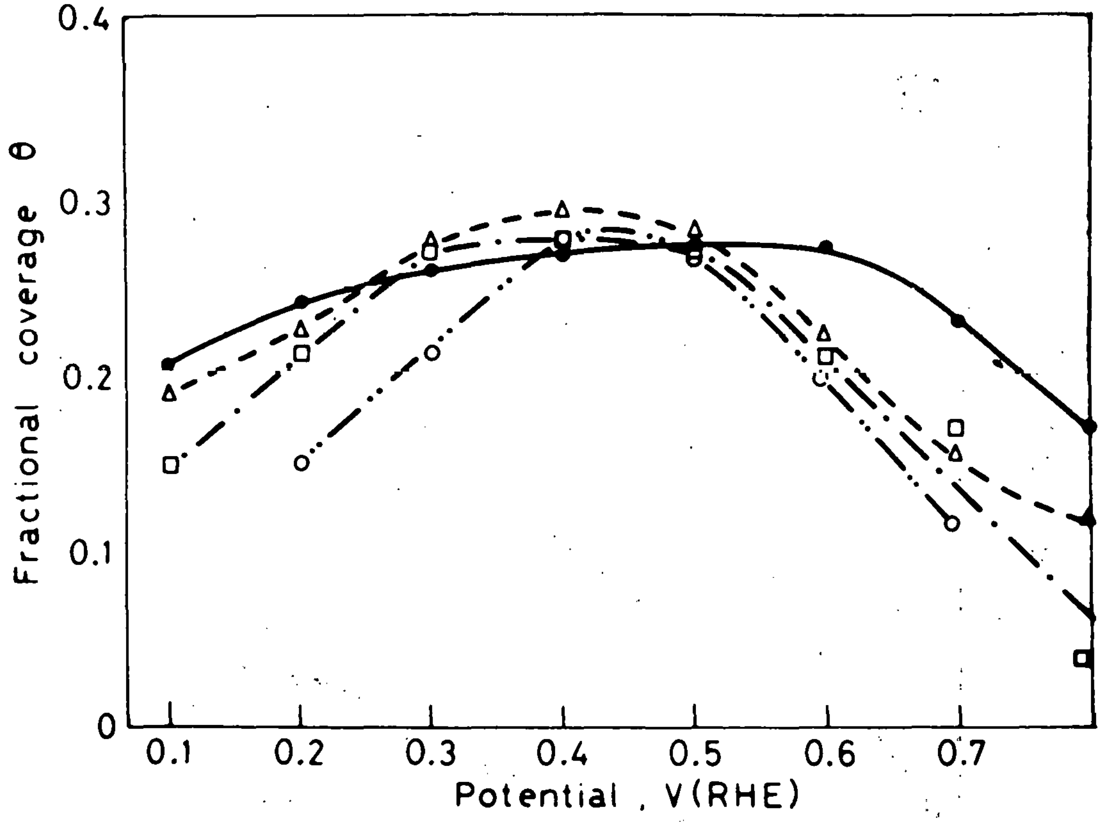


Fig. 4 Potential dependence of electrosorption of benzene—comparison of results obtained by four techniques. 0.50 V (RHE), 50° C; ● radiotracer method, 1.1 µM; △ linear potential sweep method, 1.4 µM; O, potentiostatic method, 1.1 µM; □ galvanostatic method, 1.3 µM.

B. Ellipsometric Methods

Ellipsometry is a technique for studying thin layers of oxides upon surfaces in S/L systems. It has also been used for measuring the adsorption of ions on or near solids in contact with a liquid. One starts by measuring it at the Hg/liquid interface, where one knows the result from independent methods [20]. Assumptions have to be made in the ellipsometric method, e.g., the radius of the adsorbed molecule. Then, it is simple to recover from an ellipsometric measurement of the interface and the molar refractivities of ions and of H_2O, the coverage of the surface with ions.

However, ellipsometry suffers from severe limitations. If the solid begins to dissolve during the measurement of the adsorption of ions on the surface, errors may become catastrophic. Interpretation of ellipsometric data depends on a surface of the metal being polished and smooth, whereas when dissolution begins, there are pits, containing solution, which the ellipsometer mistakes for metal. Another ellipsometric difficulty concerns the variation of the refractive index of the metal surface with potential which can sometimes interfere with results [21].

Nevertheless, useful results have been secured with ellipsometric methods on solids; some for bromide on various metals are shown in Fig. 5. A generalization comes from these results; there is more adsorption of anions on the solid metals than of ions on

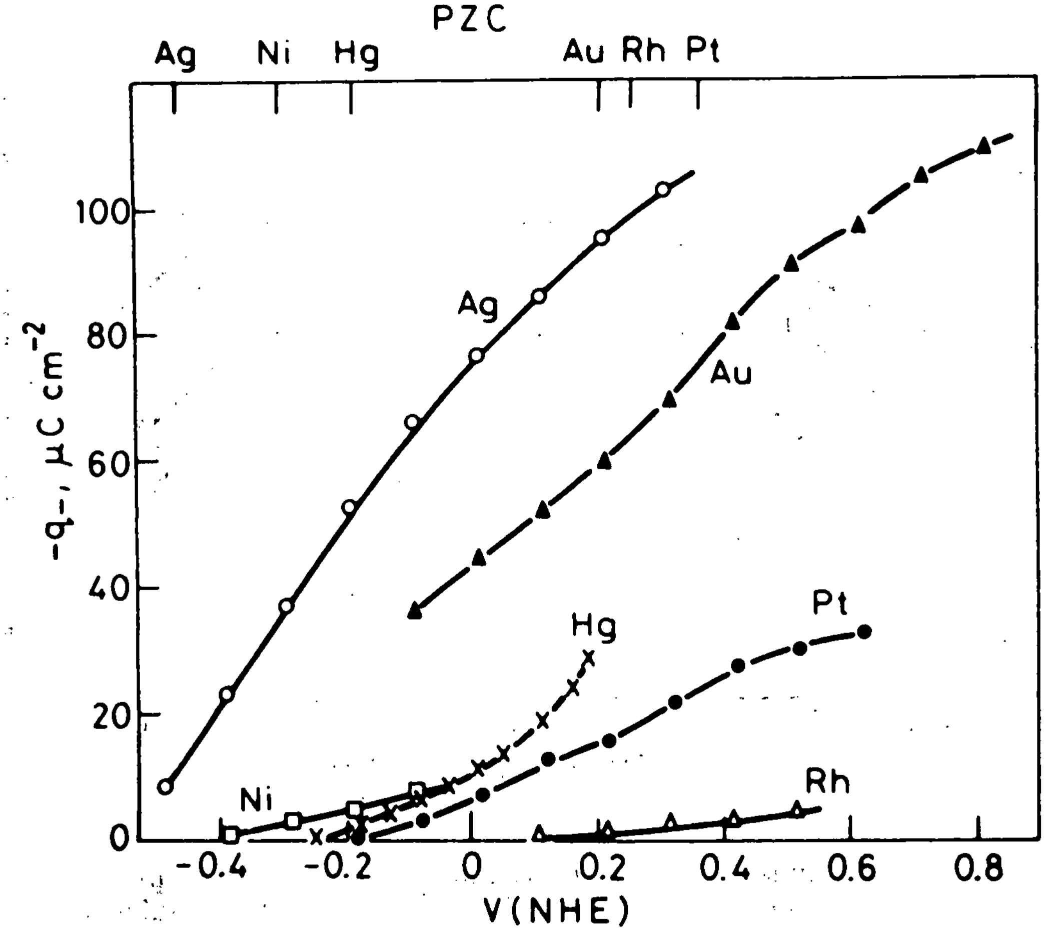


Fig. 5 Adsorption of Br^- ions from 0.01 M Br^- solutions on different metals.

Hg. This suggests charge transfer adsorption occurs. Ten percent of full coverage is a high coverage on Hg, but on the solid metals, it is possible to approach 100%, which would not be possible were the ions fully charged. This is evidence of charge transfer adsorption on metals, but there is little of it on Hg.

Ellipsometry is very sensitive in detecting O_2 adsorption. Oxygen adsorbs on Pt at relatively positive potentials, and then, at more positive potentials, there are inflections in the ellipsometric plots (the adsorption coefficient becomes finite), and there is indication that an oxide is formed (Fig. 6) [22], at first, in clusters.

Investigations with ellipsometry have not continued as well as they should have, due to the introduction of electro-reflectance studies [23]. There seemed advantages, at first sight, because one measures only the more easily obtained intensity ratio of the incident to the reflected beam. However, there are doubts. Thus, it has been assumed that one can regard the plot of the intensity of the reflected beam as a function of wavelength as a spectrum. It has the appearance of one. However, a spectrum involves data on the absorption of light, whereas in electro-reflectance, the effect of absorption is observed in addition to effects of change of refractive index on the interface and its coverage, factors which are in the Fresnel equations for the intensity of the reflected beam [24]. It is therefore better to make examinations of this type with ellipsometry, which evaluates the three variables—coverage, absorption coefficient, and refractive index. Then, one could plot the absorption of light, κ, as a function of wavelength and obtain a real surface spectrum in solution. This has not yet been done. It would seem valuable in the UV, where absorbed organic radicals would be expected to absorb, and would be useful in biochemical conversion schemes. Moreover, there should not be much difficulty in getting response times in the millisecond range, or better, so that one could follow reactions, particularly those involving organic materials on the surface, just after one has tuned in a certain potential, i.e., ellipsometric spectral relaxation.

There would be a learning process to find out what the spectroscopic peaks meant. But after this had been attained, progress in the study of organo-metallic reactions at S/L interfaces could take place. Such an application of ellipsometry would appear to be one of the cutting edges of the field at the present time.

C. Radiotracer Measurements

Blomgren and Bockris [24] were the first to examine isotherms at the S/L interface and to set up measurements for a coverage/potential plot, the parabolic relationship which has been noticed above. One kind of apparatus used in a radiotracer measurement is shown in Fig. 7. The electrode is deposited upon a thin film of Au, which is used to approach the solution, thus measuring the background. One can obtain the increased count due to adsorption on contact and calibrate this by evaporating onto the surface a known weight of the adsorbate.

A different approach with radioactive tracers was developed by Green et al. [25] and is shown in Fig. 8. Here, the counter is outside the liquid, but can detect the signals through it. Thus, it is not possible to carry out measurements when the background is strong. When a material is low in concentration, the count rate indicates what is adsorbed upon the electrode. Figure 9 shows napthalene and its remarkable adsorption upon Cu as a function of potential [25].

The reason for so much data involving Hg and the M/L interface is that it is easy to measure the surface tension of the M/L interface, and therefore, apply the Gibbsian

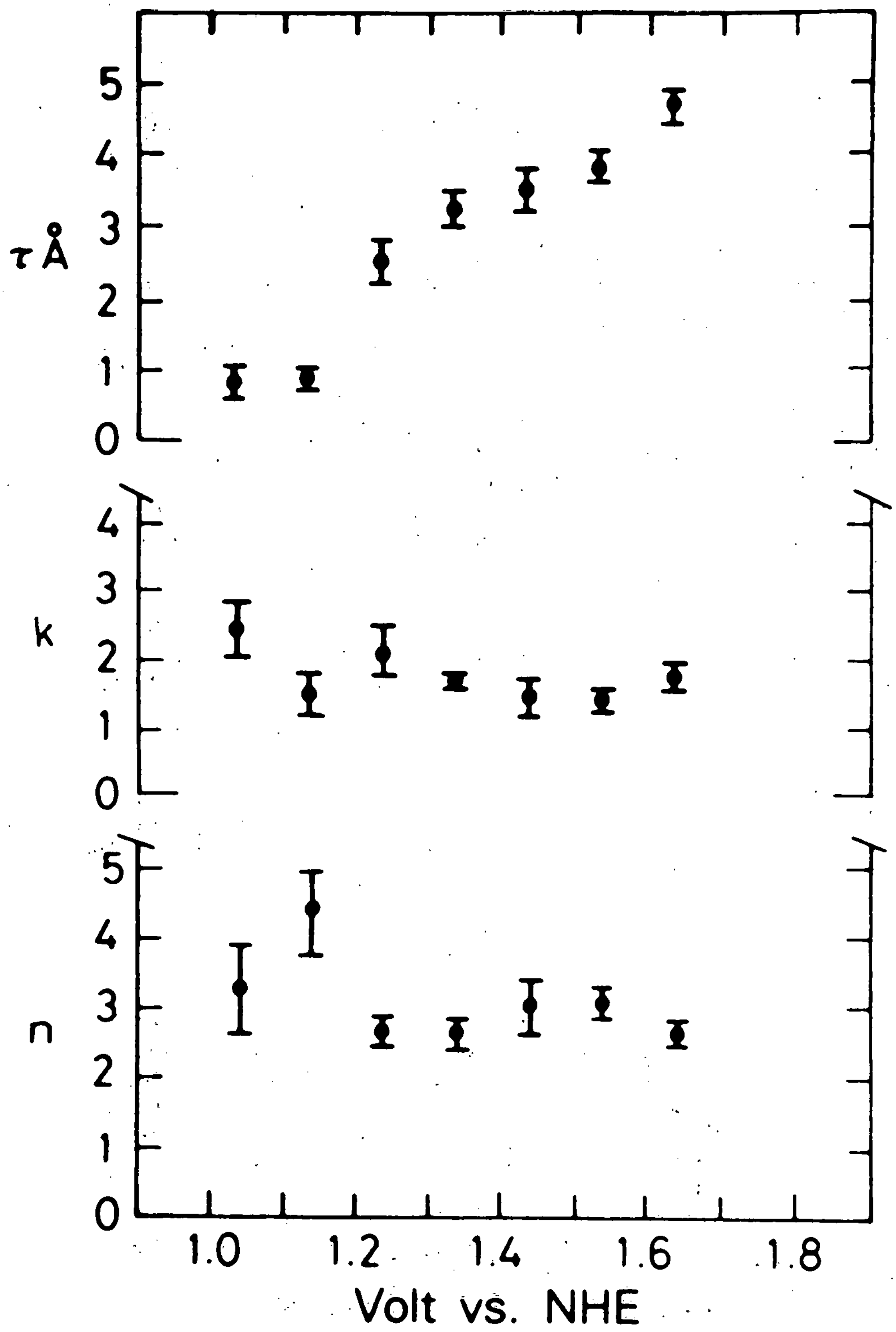


Fig. 6 The calculated values of the oxide thickness, τ, the real and imaginary parts of the refractive index of the film, n and k, at various potentials for a Hg electrode.

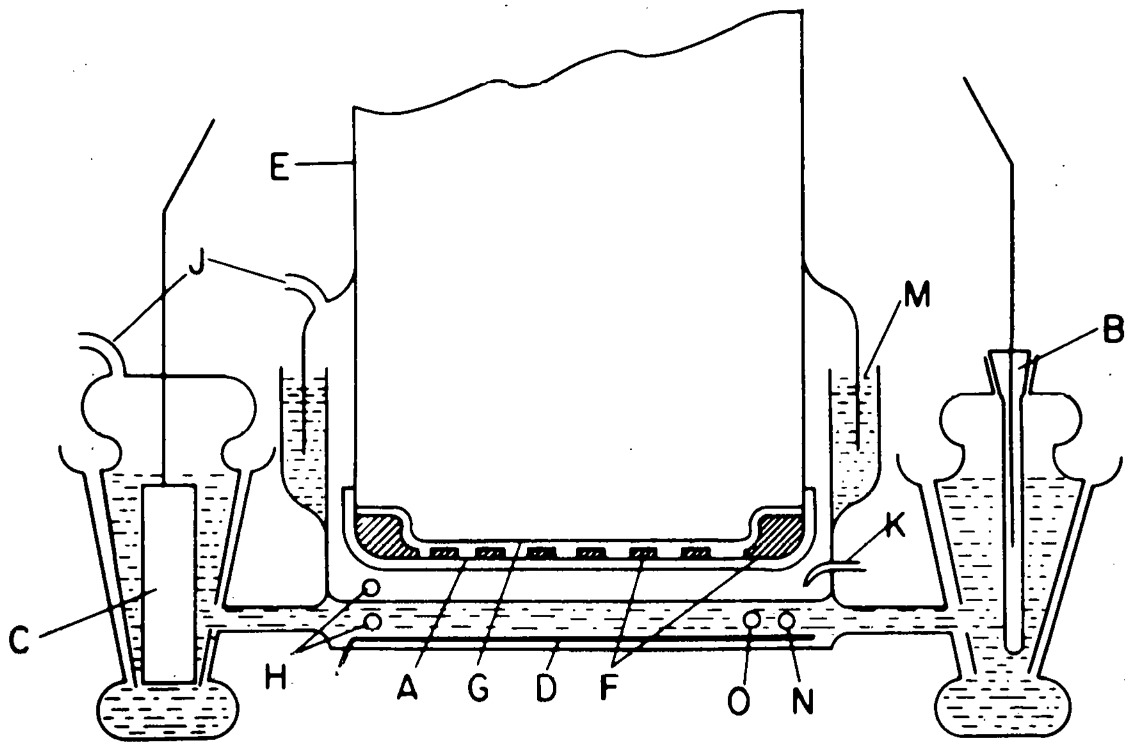


Fig. 7 Scheme of the apparatus for radiotracer measurements of adsorption: A, thin foil of adsorbent; B, reference electrode; C, counter electrode; D, auxiliary electrode; E, body of the counter; F, metal support; G, window; H, gas inlets; J, gas outlets; K, inlet for injecting and sampling; M, H_2O seal; N, thermistor probe for temperature control; and O, heating coil.

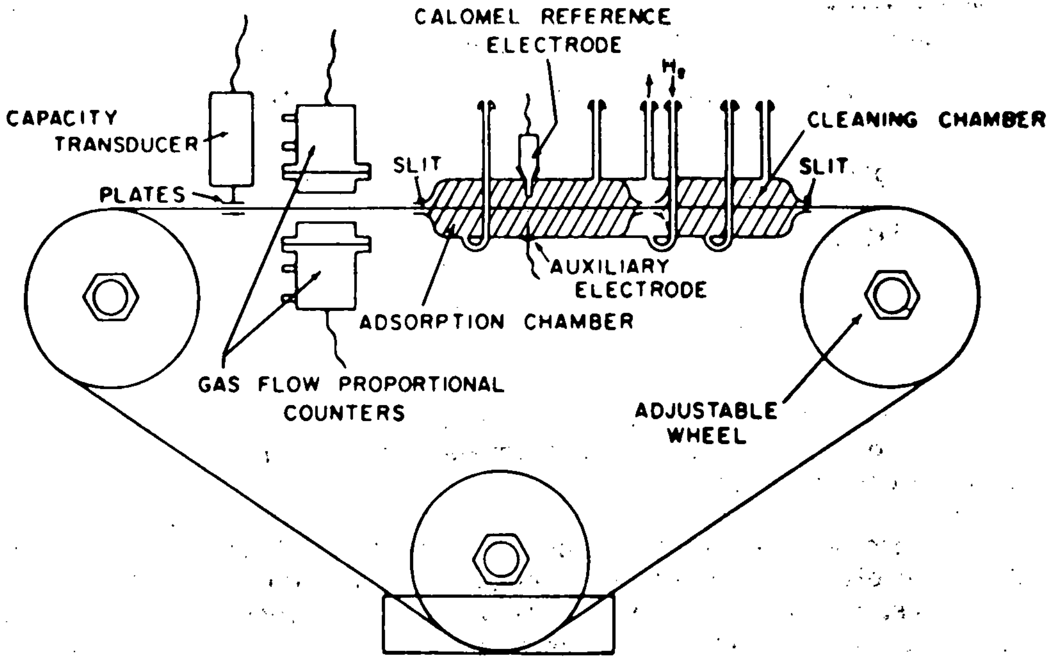


Fig. 8 General arrangement of apparatus for radiotracer measurements.

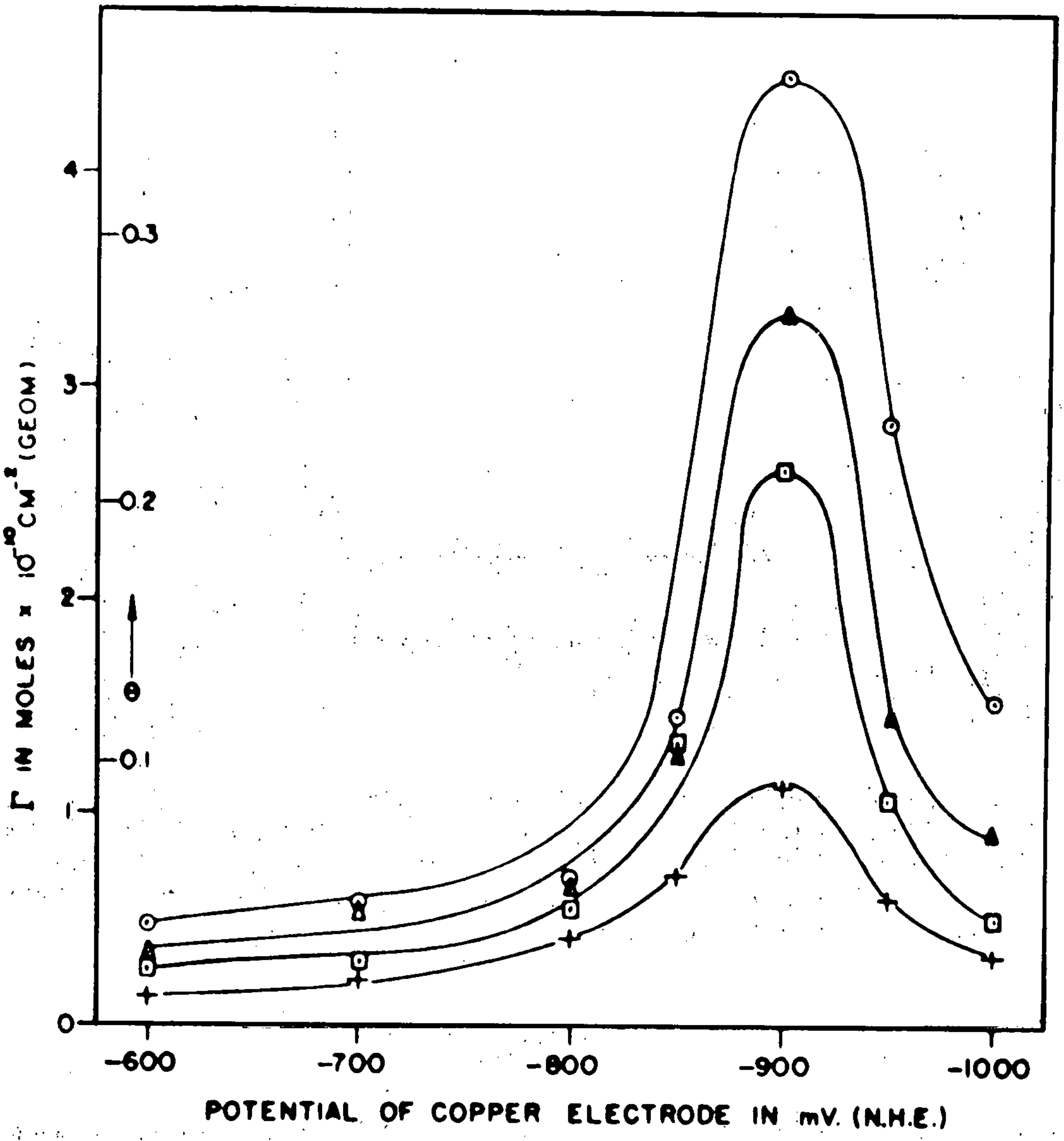


Fig. 9 Adsorption of napthalene on Cu from 1 N $NaClO_4$. O, 10^{-4} M napthalene; Δ, 7.5 x 10^{-5} M napthalene; □, 5.0 x 10^{-5} M napthalene; +, 2.5 x 10^{-5} M napthalene.

electro-capillary thermodynamics. If one could obtain the surface tension of a S/L interface as a function of potential, much progress could be made. However, the measurement of this interfacial tension is difficult.

One method, in which partial success was obtained, was due to a suggestion by Boris Cahan. A diffraction grating was attached to a thin layer of glass, and a laser was directed on this, so that slight movements of the glass allowed one to count the lines in the grating. Thus, a measurement was given of the bending of the glass. If one now evaporates upon the glass (e.g., Pt) and applies an electrochemical circuit so that the Pt is polarized at various potentials, the charge upon the surface of the Pt/L interface changes because of the parabolic relationship between the surface tension and charge [25]. One can measure the change in surface tension, and hence, from data at various concentrations, the amount of adsorption upon it. There are subtleties here, whereby the surface tension in the M/L interface may be confused with the stress resulting from the movement in the surface. Some results of this method are shown in Fig. 10.

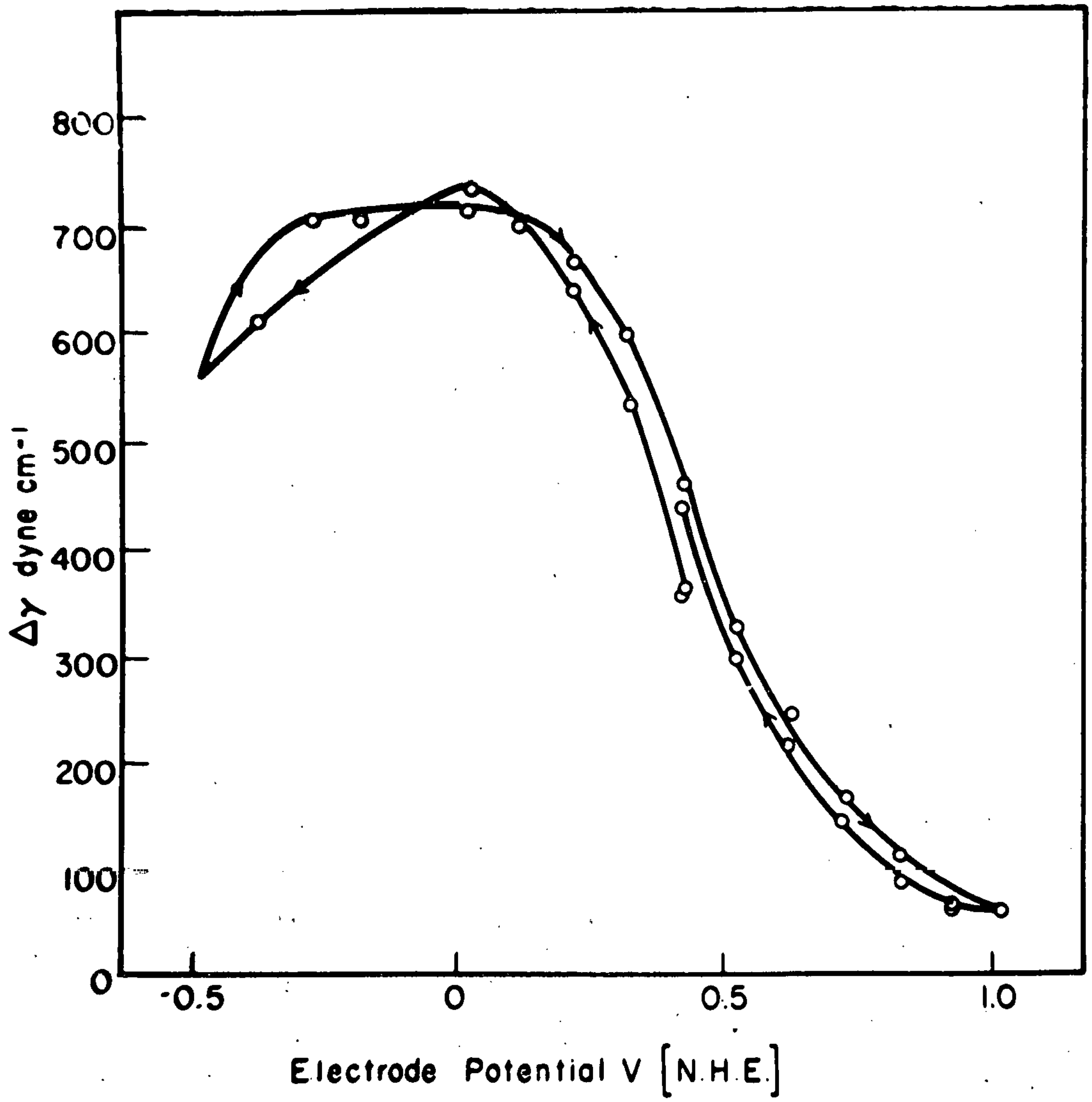


Fig. 10 Change of interfacial tension (Δγ) with potential for a Au electrode in 0.100 M KCl solution.

The extension of a wire has been used to indicate surface tension. If the wire is moved too slowly, creep affects the measurements. But if they are carried out relatively quickly by changing the tension in the wire, the movement of the wire, as a result of the change of weights stretching it, is a function of the surface tension, and one can measure these changes. A result of this kind is shown in Fig. 11. There is no doubt that this is a fairly open area. Even if the heats of wetting on cleavage as a function of potential were determined, the potential value of these measurements still is questionable.

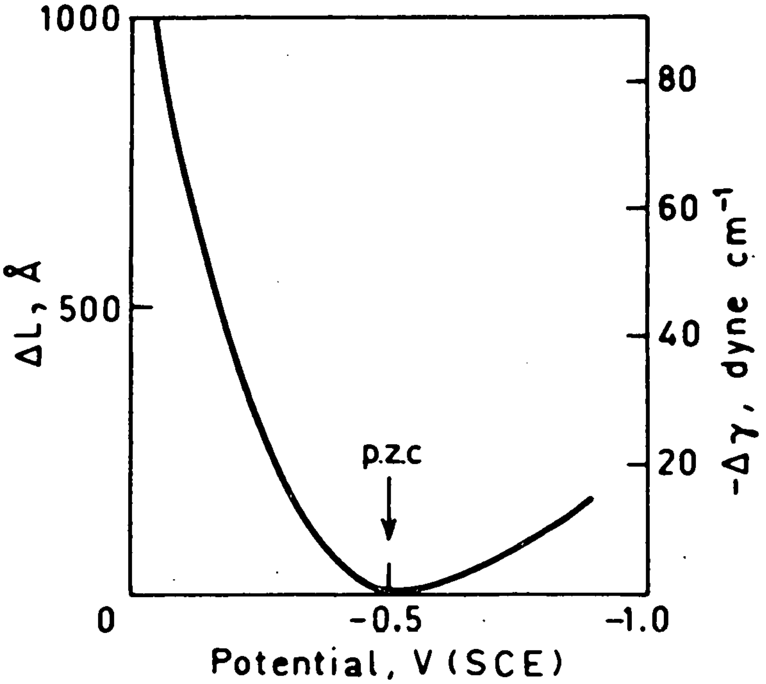


Fig. 11 "Electrocapillary curve" for Au ribbon in 0.1 M KCl (sweep speed = 0.25 V/s).

Russian workers, Gokstein [26] in particular, have measured what is called the estance of the M/L interface. This is a quantity related to, but not equal to, the surface tension where measurement is achieved by sweeping the potential of the electrode over a small amplitude, say 0.1 V, but moving the absolute potential of the region of this amplitude swing over the interior range. Because surface tension is related to potential in a parabolic fashion, one obtains a small change of surface tension with potential during the oscillation of potential far from the p.z.c. Thereafter, one obtains a large change of surface tension with potential as one approaches the p.z.c. and finally, at the p.z.c., zero charge. The electrode is arranged so that only part of it is in contact with the solution. Thereafter, the degree of contact between the electrode and the liquid changes with the surface tension. This effect can be easily measured and the p.z.c. obtained. Bard and Handley [27] have done something similar to this; they found that by stress measurements with an attached piezoelectric detector it is possible to obtain the flat band potential of semiconducting oxides. These are of value for photoelectrochemical applications.

There is much to be done with stress/electrode measurements, although one must come back to the subtlety of the difference between estance and surface tension. Long-term stress measurements can be used to determine the partial molar volume of materials dissolved within the metal at the S/L interface. This is a measurement of interest with respect to the strength of materials.

D. Frumkin's Contributions

It is recognized that Frumkin has contributed as much as any man to the investigations of the S/L interface. Frumkin evaluated the surface tension of the M/L interface by the double integration of the capacitance/potential relationship [28]:

$$C = \partial^2\gamma/\partial\Delta\phi \tag{1}$$

If one double integrates Eq. (1), one should get the surface tension, but there are two integration constants: the p.z.c.—no problem—and the other the surface tension at the electrocapillary maximum. In most cases, one can determine only the change of surface tension with potential. Frumkin and his colleagues have put this capacitance method into the realm of a reliable method for looking at the electrocapillary thermodynamics. They used very smooth electrodes. Earlier, there had been much dispersion of the capacitance with frequency, because of the effects of irregularities and pits, pyramids, and roughness on the surface of the electrode.

A general result came out of this work with capacitance measurements. The main paper by Frumkin et al. [29] is concerned with the disappearance of the Essin-Markov effect at many S/L interfaces. The Essin-Markov effect is the variation of the p.z.c. with concentration. In the simple analysis, not taking into account any breakdown of the double layer nor specific adsorption and is easy to relate to the Nernst coefficient RT/F.

The interpretation of the disappearance of the Essin-Markov effect led Frumkin and his coworkers afar. They realized that in studying a surface, such as Pt in contact with a solution of hydrochloric acid, the description of the adsorption is more complex than at a polarizable interface. Thus, one cannot say that when a new ion is brought up to the L/S interface, it adds one further charge to this surface; it may discharge itself partially across the surface. Thus, the charge Q at a unit area of a S/L interface is not only a function of the number of ions present, but of their discharge reaction rates across the surface.

A special thermodynamics, a development of the Gibbsian electrocapillary thermodynamics, has been developed by Frumkin, but its acceptance is not yet widespread [30].

In looking toward the future of methods for the investigation of S/L interfaces, there is a distinct need for kinetic and structural methods. De-emphasis on the electrocapillary methods is reasonable, because it is often difficult to interpret the data. The introduction of the concept of partial discharge across the surface has added to an already complex situation and suggests that one should probe the surface with spectroscopic methods.

E. The Determination of the Potential of Zero Charge

The p.z.c. for the S/L interface has some analogy in the history of its development to the determination of the work function at the S/G interface. Thus, for years, it was difficult to obtain agreeing data for work functions, and the same was true until the 1970's for potentials for zero charge. The situation is now improved. Many (perhaps one dozen) potentials of zero charge are known by several methods with agreement among the laboratories to about 0.01 V. In Table 1, methods are given for obtaining the p.z.c. Devices for on-line corrosion monitoring of solar liquid heat transfer systems, which involves knowledge of the p.z.c., are being developed.

Table 1. VARIOUS METHODS OF DETERMINATION OF THE POTENTIAL OF ZERO CHARGE ON METALS

Method	Principle	Positive Aspects	Negative Aspects
Surface tension methods contact angle	Maximum in the contact angle versus potential	Basis similar to electrocapillary measurements	Usual objection of formation liquid phase under bubble improbable in aqueous solutions, but magnitude small and hence variation difficult to observe
capillary rise	A minimum in the height of the capillary rise versus potential	Basis similar to surface tension methods	Possible lack of resolution in a position determination
tension vibration measurement	Alternating current superimposed on dc applied to a flexed-beam electrode and vibrations measured by a piezo-element; amplitude proportional to $q \Delta E \cos W$	Possibility of measurement of surface free energy of solid-solution interface	At present, amplitude used to give sufficient sensitivity is 0.1 V
Change of surface area at constant potential (the immersion method)	Charging current proportional to the electrode capacitance and dV/dt	Simplicity of measurement; applied to many systems; possibly several means of exposing fresh metal surfaces	In presence of a Faradaic process, method inapplicable
open-circuit scrape	The potential/time decay curve comes to a plateau at zero charge	Has been used to study ionic specific adsorption on silver and gold	Scraping probably increases active sites and hence interference due to Faradaic processes
Capacitance measurement	A minimum in the C_{dl}/E plots in dilute solutions since diffuse layer capacitance is smallest at zero charge	Applied extensively to many solids; measurement of double-layer capacitance can lead to q_m versus E relationship and electrocapillary thermodynamics; in principle, effects of adsorption and pseudocapacitance can be eliminated by working at high enough frequency; one of the most suitable methods	Applicable only in dilute solutions; pseudocapacitance give difficulty

Table 1. VARIOUS METHODS OF DETERMINATION OF THE POTENTIAL OF ZERO CHARGE ON METALS (cont'd.)

Method	Principle	Positive Aspects	Negative Aspects
Ionic adsorption	Tracer cationic and anionic charges are equal at zero charge	Applied to solid metals	Inapplicable if adsorption of a third ionic species other than the radiotracer species is involved; availability suitable tracers questionable
Organic adsorption	Γ_{org} versus E curves intersect a p.z.c. at various electrolyte concentrations while the concentration of the neutral organic compound is constant	P.z.c. determination in presence adsorption of neutral compounds possible	Absence of specific adsorption of ions of the electrolyte necessary. The contribution of salting out effect must be small; measurement of Γ_{org} on solid metals of limited accuracy
Friction oscillating Herbert pendulum	The friction between the fulcrum of the pendulum and the metal is maximum at p.z.c.	Easy applicability to any solid	Indirect way of measuring friction leads to confusion in interpretation whether friction or hardness is underlaying physical property; experiments cannot easily be carried out under controlled conditions
static friction	Static friction between two surfaces is at a maximum at zero charge	Simple measurements; quantitative interpretation recently given; applicable to many systems	Friction depends upon the mechanical properties of the metal, e.g., plastic yield, hence variation of friction with mechanical properties limits accuracy
Ultrasonic methods ultrasonic potential	Ultrasonic potential is maximum at zero charge	Not clear	Speculatively suggested; no data; difficult apparatus
dispersion of the electrode	Rate of weight loss is at a minimum at p.z.c.	Applied to few systems; possibly applicable to oxides	Method depends on the mechanical properties of the metal; weight loss measurements may be in error due to formation of oxide
Repulsion of diffuse	Repulsion of ions in diffuse layer is at a minimum at p.z.c.	Applied to several systems; possible applicable to "insulators"	Not applicable > 10^{-2} M; apparatus complex, not applicable in presence of specific adsorption

F. Spectroscopic Methods for the Investigation of the S/L Interface

It has been suggested above that the future of much of the S/L interface should lie in the direction of the, as yet, undeveloped ellipsometric spectroscopy. However, it is possible to think of applying methods which have been applied in investigations of the S/L interface. The most obvious ones are AES and XPS. A major difficulty is that a vacuum is needed for the study. This problem was first tackled by Revie et al. [31], who made measurements of Auger spectra. Their apparatus is shown in Fig. 12. The electrochemical work is carried out in the compartment on the bottom, and the magnet is used to raise the electrode out of the solution into an intermediate port where the electrode is washed to remove solute material and subjected to a light vacuum for drying. The electrode material is then raised into a compartment, which is transferred into a high vacuum after the electrode has been placed and cooled to liquid nitrogen temperatures (to avoid the effect of high vacuum upon the stability of the film).

The processes of transfer into vacuum may damage the material which has been prepared electrochemically. If the problem is, for example, the penetration of Cl ions into a passive layer, it is probable that such methods work well. If one wants to examine the effect of adsorbed ions on the surface of a semiconductor, removal of the H_2O layer radically changes the situation.

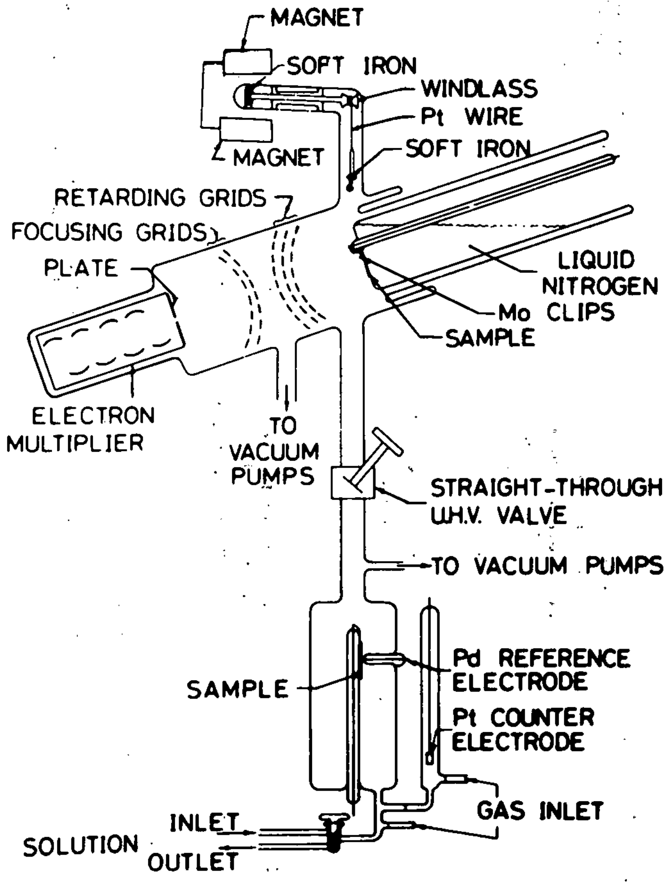


Fig. 12 Apparatus for combined electrochemical studies and AES.

There is also a possibility to examine the S/L interface by HVEM methods with a differentially pumped environmental cell containing the interface of interest, which might be an electrode with a thin layer of solution upon it.

Mössbauer spectra have been used in the study of passive films [32]. The spectra of the common oxides differ from those which are attained through passivation. The latter has a certain Neél temperature which indicates that there may be amorphous layers present on the surface of the electrode and indicates the size of these. It is possible to fit the results to a situation in which H_2O is present as the characteristic component which determines the protective passive layer from other kinds of oxide film layers at the S/L interface. It "sticks the bits together" in amorphous domains, the size of which determines the degree of passivity.

Mössbauer spectra experiments on passive layers give results analogous to those of AES; both indicate the presence of H_2O as the determining entity in the passive layer. Spectroscopic methods (AES) also indicate that breakdown of a passive layer caused by a Cl ion is essentially due to the removal of H_2 by it [33].

V. ABSOLUTE POTENTIALS AT S/L INTERFACES

The absolute value of the p. d. at the S/L interface is impossible to measure. However, calculations of the p. d. at the M/L interface are possible, but in the negative view, they would be worthless because there is no way of checking them. There is now a degree of agreement among electrochemists that something meaningful can be calculated, but the accuracy of the calculations is not better than 0.01 V, and they cannot yet be done for every M/L interface. Interfaces of interest in solar energy are particularly those involving semiconductors, e.g., GaP-NaOH in solution.

Here, the basic contribution made was in understanding the p.z.c. After Frumkin showed there was similarity between the situation of the p.z.c. and the work function [34], Bockris and Argade [35] formed a "theory of zero charge," which led them to calculate the quantity: $\mu_e^\alpha + \alpha_\Delta s_\phi$. Here, the μ_e^α is the chemical potential of the electron in the electrode concerned, e.g., Pt. The sum of μ_e^α and $\alpha_\Delta s_\phi$ is the so-called "absolute electrode potential of the H_2 electrode." This quantity remains constant upon change of substrate for given thermodynamic conditions, and was calculated by Bockris and Argade [35].

It is then possible to write the equation:

$$E_{q=o}^{Hg} = \phi^{Hg}/F - \chi^{s} + \delta\chi^{Hg} - {}^{Na}\Delta\phi_{ref} + \mu e^{Na}/F \tag{2}$$

where $E_{p=O}$ is the p. z. c. on Hg; ϕ^{Hg} is the work function on Hg; χ^{s} is the interfacial potential at the M/L interface; $\delta\chi^{Hg}$ is the change in this brought about by adsorption on Hg; ${}^{Na}\Delta\phi_{ref}$ is the absolute Galvanic potential difference across the Na/L interface; and μe^{Na} is the chemical potential of electrons in the Na electrode, i.e., the Fermi energy.

Note that one utilizes a mixed situation here, where some quantities are for Hg and some quantities are for Na, because it is relatively easy to determine μe^{Na} and light metals, but much more difficult for μe^{Hg}. Thus, the absolute p. d. of the Na/L interface is determined by expressing the p.z.c. for the Hg on the Na scale, i.e., with reference to a Na electrode.

In this way, one can calculate the absolute M/L p.d. at, say, a Na electrode, and it comes to about -1.2 V. Hypothetically, one can determine any S/L p.d., but in practice there are difficulties in doing this with any degree of accuracy. The principal difference is the proper calculation of μe, which is not to be taken as that given by the free electron theory of metals, but the real μe which is difficult to calculate.

Once the idea of "the absolute electrode potential" was accepted, calculating other absolute potentials became fashionable. However, there is an extra difficulty in calculations of the type such as mentioned above for Na, where one calculates the absolute p.d., actually at the interface with the solution, and not the total "electrode potential" (i.e., the sum of the Galvanic potential difference plus the chemical potential of the electron within the electrode). One has to assume a model of the interface to calculate the contribution due to the H_2O molecules at the surface. This can always run one into uncertainty, perhaps as much as ±0.1 V.

Of course, if one can determine an absolute M/L p.d., then, at the p.z.c., it should be possible to calculate the so-called electron overlap p.d. [36]. This little known quantity arises because electrons in the bulk carry over an interface, overlapping or underlapping it and causing a p.d. to arise there, which is part of the surface p.d., independent of the solvent p.d. Calculations of this type are dangerous because they involve a solvent layer calculation which is theoretical and modelistic [37].

Nevertheless, calculations of absolute p.d.'s at M/L interfaces (eventually SC and even I/L interfaces) are part of the future, and by the end of the century, absolute p.d.'s may be used routinely, instead of the reference potentials of classical electrochemistry.

VI. ORGANIC ADSORPTION

In Fig. 13, an example of organic adsorption is seen. The curve is parabolic, in accordance with the predictions of the BDM theory [6].

The "Frumkin Isotherm" which is: $\Theta/(1-\Theta) = BCe^{2a\Theta}$, was deduced in 1926 and is still used by Russian workers to represent the various aspects of organic adsorption at S/L interfaces [38]. To obtain good agreement experimentially, it is necessary to use empirical constants since there are no molecular models used directly in developing the isotherm.

Many other isotherms have been developed for the expression of both ionic and organic adsorption at electrodes [39], as shown in Fig. 14.

Organic adsorption at the S/L interface is a subject which needs direct methods. As measurements were extended to solid metals, in addition to Hg, ample evidence showed that a reaction was often occurring with the organic molecules on the surface, and was in competition with the "reversible adsorption." What is needed here are direct spectroscopic means for characterizing the surface in situ. Resonance Raman spectroscopy might be used to do this, and it can in some cases, such as that of pyridine on Ag [40]. However, in nearly all cases, except for Ag, there is an insensitivity to Raman radiation, so this does not seem to be a generally applicable method. Ellipsometric spectroscopy may provide the methods needed.

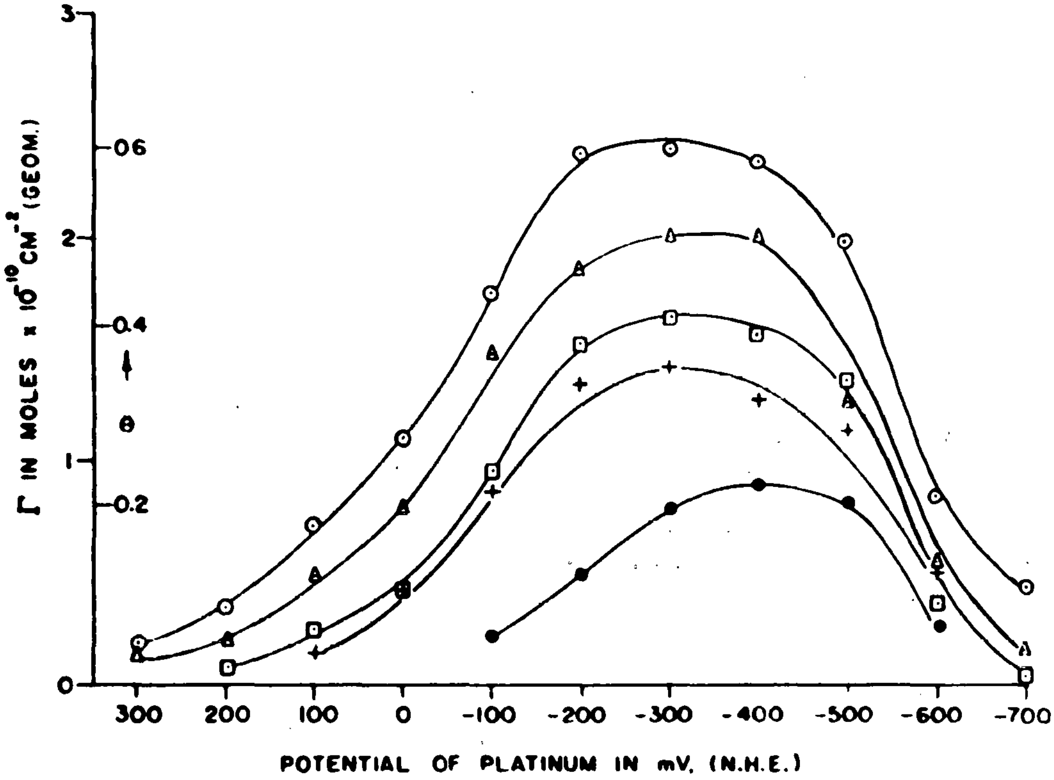


Fig. 13 Adsorption of napthalene on Pt from 0.9 N NaClO$_4$, 0.1 N NaOH. O, 10^{-4} M napthalene; Δ, 5 x 10^{-5} M napthalene; □, 1 x 10^{-5} M napthalene; +, 5 x 10^{-6} M napthalene; ●, 2.5 x 10^{-6} M napthalene.

VII. IONIC ADSORPTION

There are three main topics here, two of which are connected. First, there are forces present in contact adsorption, discussed classically by Anderson and Bockris [41], where an attempt was made to interpret the whole situation on Hg without the use of orbital overlap. Barclay and Caja [42] introduced orbital overlap and showed that, especially for solid metals, there was evidence that this occurred. Schulze [43] has done somewhat similar work.

Secondly, partial charge transfer may occur, which was considered by Schulze, Parsons, and others [44]. Partial charge transfer seems certain to occur. In fact, it has been mentioned that in ionic adsorption measurements, made by ellipsometry, the greater coverage of the electrode by small inorganic ions such as chloride and sulfate makes it likely that there is bonding at the surface. However, the partial charge transfer is awkward for those interested in the S/L interface, because the studies relate back to a Hg situation where the Gibbsian classical thermodynamics has been used, and where it has been assumed that one ion is equal to one charge. If this can no longer be assumed, then there will be numerical changes to be made in the Gibbsian thermodynamics. Little change is probably necessary in the Hg results because there is little overlap. This emphasizes the need for spectroscopic determinations of quantities at the M/L interface (even moreso at the SC and I/L interfaces).

Forms of a Number of Adsorption Isotherms and the Corresponding Reaction Order Factors

Type of isotherm	Form of isotherm	$\left(\frac{\partial \ln \theta}{\partial \ln C}\right)_E$
"Henry's law"	$K(C_R)_b = RT\theta\Gamma_m$	1
Volmer	$K(C_R)_b = RT\frac{\theta\Gamma_m}{1-b\theta}\exp\left(\frac{b\theta\Gamma_m}{1-b\theta}\right)$	$1+\frac{b\theta}{1-b\theta\Gamma_m}+\frac{b\theta\Gamma_m}{1-b\theta\Gamma_m}$
Langmuir	$K(C_R)_b = \frac{\Gamma}{\Gamma_m-\Gamma}=\frac{\theta}{1-\theta}$	$1-\theta$
Flory–Huggins	$K(C_R)_b = \frac{\theta}{x(1-\theta)^x}$	$\frac{1-\theta}{1+(x-1)\theta}$
Virial	$K(C_R)_b = RT\theta\Gamma_m\exp(-r\theta\Gamma_m)$	$\frac{1}{1-r\theta\Gamma_m}$
Frumkin	$K(C_R)_b = \frac{\theta}{1-\theta}\exp(-r\theta\Gamma_m)$	$\frac{1-\theta}{1-r\theta\Gamma_m+r\theta^2\Gamma_m}$
Temkin	$K(C_R)_b = \exp(-r\theta\Gamma_m)$	$-\frac{1}{r\Gamma_m\theta}$

Fig. 14 Forms of a number of adsorption isotherms and the corresponding reaction order factors, where Γ is the surface concentration of adsorbate; Γ_m is the surface concentration corresponding to a monolayer at the surface; $K = \exp(-G^0_{ads}/RT)$; b is the molecular area of adsorbate species; Θ is the degree of coverage of the electrode surface by adsorbate given by Γ / Γ_m; χ is the ratio of relative sizes of adsorbate and solvent molecules in the Flory-Huggins type of isotherm; and r is the interaction parameter characterizing two-dimensional attraction of repulsion in the adsorbed layer in the virial or Frumkin isotherm, or r is a heterogeneity parameter in Temkin's isotherm—units of r depend on how coverage is expressed, i.e., as Γ (= $\Theta\Gamma_m$) or in terms of Θ.

The third subject of interest pertains to the type of isotherm which is deduced. Here, the interest relates to image forces and how one evaluates them [45]. When considering the adsorption of ions at M/L interfaces, one finds it necessary to involve images; otherwise, upon integrating the repulsive field over the whole surface of the electrode, one obtains an impossible answer. However, once one realizes that the image energy of the first layer of ions then gives rise to an image in the solution, etc. the situation becomes more complex. Levine and coworkers [45] have assumed that there was a sharp dielectric image between the Helmholtz layer and the Gouy layer. Their model yields extensive imaging from the liquid, which upsets the much more mathematically tractable picture that one obtains from considering single imaging from the first layer of ions in the electrode. Bockris and Habib [46] have reported calculations which suggest that the Levine view is not numerically cogent. The degree of imaging which comes out of the solution depends upon the sharpness of the boundary between the Gouy and the Helmholtz plane. This boundary can be shown not to be dielectrically sharp. This lack of sharpness of the real boundary diminishes the image energy and gives smaller effects than those which have been anticipated in the work of Levine.

The cutting edge of the classical work on ionic adsorption is generally limited to considering many images, how much and how sharp is the dielectric boundary, etc. But such work lies conceptually in the past, because it is too classical. One needs to add the spectroscopic and quantum basis to the considerations, and a theory of bonding for solid-ion interactions in the presence of solutions.

VIII. FRICTION

Like the Frumkin thermodynamic investigations of S/L interfaces, the study of friction at the S/L interface has been the province of Russian workers and particularly Rehbinder. The "Rehbinder Effect" [47]—the alledgedly variation of hardness with potential—has been used extensively in Russia, e.g., the design of rock drills which have potential control at their tips.

There is a degree of ambiguity between the alleged effects, called by Rehbinder hardness effects (fissures in the surface of the solution varying in "openingness" with potential because of the layers of charge on either side of the fissure, so that the hardness of the surface would vary with potential) and the straight effects of friction. Bockris and Parry-Jones [48] photographed the movements of the wet ball of a Kater pendulum and found that, apart from its oscillitory movements, it slithered over the surface, thus involving friction. By making straightforward measurements of friction alone, rather than the logarithmic decrement of the pendulum which had been used by Rehbinder, they showed that there was a true variation of friction with potential.

The variation of friction with potential at S/L interfaces has been examined theoretically, and an equation has been deduced which gives a degree of agreement with the results [49]:

$$\mu_f = \frac{\rho_T A_o}{w \cos\Theta + (4\pi q_{diff}/t)[e^{-\kappa(x + 1/\kappa)}](A - A_o)} \tag{3}$$

where μ_f is the coefficient of friction; w is the weight of the slider; Θ is the angle of contact; π is the conductance; q_{diff} is the charge on the diffuse layer; $1/\kappa$ is the Debye length; and A_o is the area of microcontact.

The effect of potential on friction could stand more investigation, particularly when the interfaces involve semiconductors and insulators.

IX. FUTURE PROSPECTS

The S/L interface has one positive difference compared with other interfacial subjects. The experiments have a more practical bearing upon reality than those done at, say, the S/G interface. Although workers at the S/L interface do have analogues of UHV (super pure solutions), their experiments are for the most part done under situation not too far from those which would apply in practice.

The field is in an early stage of development. Whereas the S/G interface had excellent experimental work starting about 1940, good electrochemical work on solids did not start until about 10 years later. Thus, solutions were generally dirty and tended to have more variables, so it was difficult to get comparable results in different laboratories.

There is a critical need for theoretical development of the S/L interface. Furthermore, theoretical workers avoid the field, because it is seen as too complex and too practical. Some needs are:

(1) A quantal approach should be attempted for the M/L interface, and then for other kinds of interfaces, e.g., SC/L and I/L. Thus, in principle, it would be possible to consider a one-electron system existing between the solid conductor and the first layer of ions in the double layer.

(2) There is no doubt that the present theoretical treatment of the double layer is one which combines the philosophy of the 19th Century electrostatics with statistical mechanics. There is a lack of reality in many of the molecular considerations made. A considerable weakness arises from the tacit assumption that there is no electron transfer across the interfacial region. Eventually, (i.e., at a certain current density), there must be an effect of such a passage upon ionic distribution laws.

(3) Hypostatization is rife in present double layer models. What kind of connection to reality can be placed on such concepts as "hollow conducting spheres," or "one plate of the condenser" consisting of ions in motion in solution. These weakness must be swept away by treatments in quantum mechanical terms, which deal with the situation as in the rest of chemistry.

(4) The theory of the diffuse layer at present in use should not be applied at concentrations above 0.001 M. It is applied in practice, however, at 0.1 M. This problem is difficult to solve because the volumes of solutions concerned at high concentrations are such that the number of particles are less than the number for which statistical laws apply. A Monte-Carlo approach is needed.

(5) If, when an ion adsorbs at a M/L or S/L interface, there is a charge transfer associated with this, many changes occur in our thinking. For example, a semiconductor exposed to a change of electrode potential changes its potential within a quite different region (in fact, becomes metallized) if these are new surface states of high concentration on the surface, corresponding to high ion-adsorption. Such thoughts have been completely neglected by those dealing with photoelectrochemical energy conversion. No clear idea of the SC/L interfacial structure can be obtained, unless the surface state concentration and its variation with potential can be given. Yet, we do not yet have a good method for such measurements.

(6) A comparison may be made between investigations on the S/G interface. Not being able to use spectroscopic methods is a disadvantage for the S/L interface. However, this interface has one advantage which is little realized by those who work outside it; one can do much by changing the potential, including frequent cleaning of the surface in situ.

In spite of difficulties and indirectness, we know a good deal about the Hg/L interface, and our understanding of the S/L interface is being enlarged. However, spectroscopic and direct methods are necessary to advance the understanding.

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VII. OVERVIEW OF CURRENT STATUS OF SOLID-GAS INTERFACE SCIENCE

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ABSTRACT

The principal methods for establishing chemical composition, long range structure, short range structure, and nature of chemical bonding at the solid gas interface are reviewed. Electron and ion spectroscopies largely developed over the past two decades have vastly improved our ability to establish interface chemical composition, and developments over the past five years have done much to put determination of long range and short range structures on firm ground. The high vacuum requirements of these techniques limit their applications to interfaces whose stability under evacuation can be reasonably presumed. This is a serious limitation for many solar applications, and new methods of characterization not subject to it are badly needed. Some possibilities are indicated.

I. INTRODUCTION

We undertake to assess the current status of techniques for establishing the chemical composition and structure of the S/G interface region, including variations in composition and structure with position in the interface region. We shall discuss some recent developments in fundamental surface science in which new techniques have played important roles, some important areas in surface science needing new or modified techniques for their further development, and some aspects of solar technology in which modern characterization techniques might be employed to advantage. Somorjai's text [1] provides a good introduction to the subject matter; Vol. III of Experimental Methods in Catalytic Research [2] is devoted to characterization of surface and adsorbed species, and has authoritative reviews on the majority of topics covered.

II. DISCUSSION

A. Determination of Chemical Composition

Establishment of interface chemical composition has depended most heavily on XPS and AES. Both involve analysis of kinetic energies of electrons produced in the solid, but since the mean free path of electrons in solids is of the order of molecular dimensions the escape depth of electrons (0.4 to 10 nm) limits those detected to electrons coming from the interface region, and the techniques are therefore surface sensitive. In both cases, the kinetic energy of an emitted electron carriers information as to the kind of atom it came from and so is a qualitative analysis source, and in both cases, for a given stimulation rate, the rate of emission of electrons of a given kinetic energy is proportional to the number of source atoms and so is a quantitative analysis source. In both cases, the kinetic energy of an electron emitted from an atom of a given element will vary slightly with its chemical environment; this chemical shift can be detected at sufficiently high resolution and provides information about the chemical environment (e.g., valence) of the emitting atom. In both cases, the fact that interface composition varies, often considerably over the escape depth, leads to uncertainty in interpretation of analyses. The electron mean free path in a material varies with its kinetic energy; a plot of mean free path against log kinetic energy is roughly parabolic with a broad minimum of about 0.4 nm at about 70 eV and increasing to about 3 nm at 8 and 2000 eV. Kinetic energies of emitted electrons used in analysis are most frequently higher than 70 eV (say 100-500 eV in AES, 500-1200 eV in XPS) corresponding to mean free path 0.4 to 0.8 nm and 0.8 to 2.5 nm, respectively. Plainly both methods generally are sampling more than the outermost layer of atoms; as commonly used, AES is more surface sensitive because of the shorter mean free paths of the electrons sampled. Chang has an excellent discussion of analytical AES [3a] and S. Hercules and D. Hercules of surface characterization by XPS [3b].

AES spectra are most frequently obtained as plots of d^2I/dV^2 vs V, where I is the current due to electrons of kinetic energy equal to or greater than the work function. An Auger transition in such a plot appears as a peak followed immediately by a trough; the voltage at the inflection between the peak and trough is characteristic of the element responsible for the transition, and the peak-to-trough distance (in absence of interferences) is proportional to the amount of that element. The proportionality constant is best obtained by standardization against a known composition (e.g., in alloys, from separate AES spectra of the pure components and in adsorbed overlayers from spectra of overlayers of known structure). Practical sensitivities of the order of 0.001 of a monolayer can be obtained in this way. Interferences result chiefly from incomplete separation of the Auger peak of interest from peaks of other elements (or other peaks of the same element).

AES spectra are obtained under vacuum so surface components which are lost on evacuation are, of course, not detected; conversely, the surface may be easily contaminated during sample preparation by substances not lost upon evacuation (e.g., hydrocarbons, O_2, CO). Subject to those limitations, careful work can provide interesting surface information. Watanabe et al. [4] exploited the difference in escape depths for Auger electrons of different energies to show the surface enrichment of Cu in Cu-Ni alloys in the first four layers from the alloy surface. Use of AES to investigate poisoning of catalysts, composition of corrosion layers, passivating films, surface segregation, and adsorption of strongly-held components is common. Surface layers can be successively sputtered off by Ar ion bombardment with intervening AES analyses to establish composition as a function of depth; this is called depth profiling [3a], and it is useful in studying the effects of surface treatments, the nature of corrosion films, diffusion of embrittling interstitials, etc. (see Chapter IX for a discussion of depth profiling).

An interesting paper by Rye et al. [5] illustrates not only the derivation of chemical shift information from AES but also problems which may arise from overlapping peak in use of AES for quantitative analysis. For example, O (KVV) spectra are compared for H_2O, CH_3OH, and $(CH_3)_2O$. The designation O (KVV) denotes an Auger transition in an oxygen atom in which a valence electron falls into a K vacancy and a second valence electron (whose kinetic energy is measured) is ejected. The energy level of the K electron is unambiguous but there are several molecular orbitals involved in bonding. Hence the O (KVV) spectra involve about 13 transitions spanning a 50 eV range of kinetic energies although there appear to be only about five peaks in the spectra (because of overlapping peaks). Rye et al. have analyzed energy levels and line shapes associated with all 13 transitions to reconstruct the spectra, and have shown that subtle differences in O (KVV) spectra for the three compounds studied provide "fingerprints" that indicate bonding character of the oxygen. Similar studies were conducted for the C (KVV) spectra of CH_4, CH_3OH, $(CH_3)_2O$, C_2H_4, and C_2H_2.

AES is the most widely used technique for qualitative and quantitative surface analysis, but XPS is also extensively used. Three less employed techniques, RBS, ISS, and SIMS, depend on ion scattering or ejection and have special attributes deserving mention.

RBS depends on the scattering of high energy nuclei (typically several MeV He nuclei) by nuclei in the specimen. The scattering is to high degree of approximation a collision between two nuclei in which energy and momentum are conserved, so that knowing the energies of incoming and scattered He^{++} and the scattering angle the mass of the scatterer is established. The method is not particularly surface sensitive (depth resolution 10-20 nm) and is also not very sensitive to light elements. It is correspondingly less sensitive to surface contamination, so requires less stringent vacuum conditions and is hence faster for routine surveys of near surface compositions. The theory of the method is extremely sound, so that qualitative and quantitative analyses can be established based on ab initio theory without calibration. Finally, the fact that He^{++} ions backscattered some depth from the surface lose energy according to a known scheme on passing through a dense medium can be exploited for depth profiling in a (relatively) nondestructive manner. The recent book "Backscattering Spectroscopy" [6] gives a broad and authoritative treatment of the subject.

ISS resembles RBS in that the specimen is bombarded with ions of known energy, usually ions of rare gases such as He^+, Ne^+, or Ar^+, and the energy distribution of scattered (primary) ions at some scattering angle, commonly at 138°, is measured. The energy of the impinging ions is usually chosen in the range 0.5 to 2 keV, and the scattering dynamics are again based on conservation of energy and momentum in a single collision event. Hence the mass of the scattering element can be established. Because of the lower energy of the impinging ion, its ability to penetrate the sample and then escape is much less than in RBS, so that ISS is highly surface sensitive, and can differentiate composition of a surface layer from the immediate subsurface layer. Unlike RBS, however, the scattering cross sections do not follow from ab initio theory, and so quantitative surface analysis by ISS requires calibration of the sort previously described for AES. Buck's review of ISS provides a good coverage of principles and applications [7].

SIMS involves mass spectrometric analysis of ions sputtered from a surface by impinging ions. The impinging ions most frequently used are rare gas ions, e.g., Ar ions, but very great sputtering rates can be obtained if the impinging ions are also reactive (e.g., O_2 ions impinging on metal surfaces). In common practice, the sputtering rate is too great (about a monolayer a second) to qualify SIMS as a true surface sensitive method, but it is very useful for thin film analysis and imaging the near surface region. Benninghoven has pioneered "static SIMS" with a much lower sputtering rate, giving monolayer lifetimes of several hours. This and ISS are probably the most truly surface sensitive methods in current practice. With rare gas ion bombardment, the sputtered ions include clusters, and atoms composing these clusters must have adjoined on the surface. Benninghoven has written a recent review of SIMS in which static SIMS is emphasized [8].

B. Determination of Long Range Structure

Long range structures of interface regions are chiefly determined by LEED, again because the low energy electrons, being unable to penetrate very far into the solid, are surface sensitive probes. Most frequently, LEED is used to produce diffraction patterns characterizing the two-dimensional symmetry of a surface structure and to show changes in symmetry resulting from surface reactions. Such patterns in no way establish surface structures, although if they are particularly simple they may importantly supplement chemical intuition in reaching informed guesses as to structure. Somorjai's text gives photographs of a number of such spot patterns, comparisons of surface structures and diffraction patterns, and recommendations for pattern nomenclature [1]. A well-defined LEED pattern implies that a definite long-range surface structure exists, and these patterns have played important roles in helping investigators in different laboratories to establish whether or not they started with a common surface composition and structure and achieved a common final result.

A rigorous determination of structure by LEED is difficult both experimentally and theoretically. High resolution scattering intensity versus voltage plots must be obtained for as many independent diffraction peaks as can be reasonably obtained, and their analysis, which must carefully include multiple scattering effects, will generally require extensive computation. Duke [9] has analyzed this process carefully with particular reference to semiconductor surfaces, but his comments have general relevance. A proper analysis requires selection of a model for the electron-solid force law, use of this law to calculate the LEED intensities for a set of assumed surface geometries, evaluation of the sensitivities of the intensities to the parameters of the force law and surface geometries, and comparison of calculated and observed intensity-energy curves for as many spots over as wide a range of beam parameters as practicable. Duke analyzed the uncertainties associated with each of these steps, and reviewed work leading to proposed structures for a wide variety of surfaces. The GaAs (110) surface structure evolution makes particularly interesting reading. Duke comments in his synopsis that two disparate regions of structural parameters may give comparable descriptions of a limited data base. This and other problems cited in Duke's review are well illustrated by two recent papers on the structure of C_2H_2 adsorbed onto Pt (111). The first paper [10] proposed a structure in which C_2H_2 molecules "lay down" on the surface, essentially bonded to two Pt atoms and coordinated to a third. When HREELS results [11] made this structure unlikely, the second paper [12], using additional spot intensity data and considering the HREELS results, proposed a new structure, essentially CH_3CPt_3, in which the C_2H_2 had picked up a hydrogen, was perpendicular to the surface, was still coordinated to three Pt atoms but now via only one C atom. In the second paper, it was concluded that the two C_2H_2 configurations, which are markedly different in fact, were poorly resolved by the LEED data alone.

C. Determination of Local (Short Range) Structure

Local structures, for example the nearest neighbor environments of particular atoms, can sometimes be established even if long range structures are unknown or nonexistent. EXAFS is a source of local structure information. If x-ray absorption is plotted against photon energy, there is a steep rise in absorption as the energy of an adsorption edge, e.g., the K edge, of an element is passed, followed by a slow decrease with modulations reflecting coherent backscattering of photoelectrons from neighbors of the emitting atom. The modulations hence contain information similar to that provided by electron diffraction, and analysis of them can provide estimates of distances and numbers of nearest neighbors. It is plainly desirable that other absorption edges be sufficiently separate so as not to interfere with the modulation analysis. In favorable cases, distances to nearest neighbors can be established to about 1 pm and coordination numbers to 20%. Where absorption is the quantity directly measured, the method is not surface sensitive, although it has provided information of surface interest in cases such as supported catalysts in which the material of interest was in the form of particles sufficiently small that all of its atoms were near surfaces. A surface sensitive variant, SEXAFS, depends on Auger electrons emitted following the initial photon absorption. Here, the Auger electrons observed come from a region within an escape depth of the surface; their number is proportional to the number of photons absorbed in this region, and so a plot of Auger emission intensity as a function of photon energy also carries the modulation information. The review by Sandstrom and Lytle [13] provides general background and summarizes work and current status for EXAFS and related techniques. It should be noted that synchrotron radiation sources permit vastly increased rates of data acquisition, and are largely responsible for the substantial amount of work now appearing in the EXAFS area. A new method, extended appearance potential fine structure analysis (EAPFS), depends on fine structure in the excitation probability for core states under electron bombardment. The fine structure origin is similar to that for EXAFS. The second derivative of the elastic yield current is plotted against primary beam voltage and the fine structure is derived (not trivially) from this plot. Since the measurement depends on scattered electrons it is surface sensitive (because of their short mean free paths in a solid). A conventional LEED-Auger system can be adapted rather simply to use of EAPFS—a tremendous advantage likely to stimulate considerable interest in this method [14].

Short range order may also be inferred from clusters sputtered in SIMS, as previously indicated [8]. Angular dependence of scattering in ISS can also provide short range order information through shadowing effects, in which ranges of pathways of a primary ion scattered by one surface atom are blocked by other surface atoms in its neighborhood [7]. This technique is especially useful if combined with LEED; Heiland and Taglauer [15] show the power of this combination in locating oxygen adatom positions in the half-covered ($\theta=0.5$) (2x1) structures on the (110) faces of Ni and Ag. The (110) face is characterized by alternating rows of "top" atoms and "trough" atoms; in Ni the O atoms bridge alternate pairs of Ni atoms along each "top" row, but in Ag they bridge alternate pairs of Ag atoms along each "trough" row. Similar studies could be conducted to advantage on photoconversion materials such as GaAs, to estimate both surface configurations of the base material and configurations of adsorbed species.

D. Inference of Bonding from Vibrational Spectroscopies

A number of spectroscopies may by used to investigate structures of species chemisorbed on surfaces. IR spectroscopies are surveyed in Ref. 2 (chapter by Pritchard and Catterick). Transmission IR spectroscopy is the most familiar, and has long been used for the study of species adsorbed on supported catalysts. As with EXAFS, the method is not inherently surface sensitive, but can provide surface information of interest if the species responsible for the absorption of radiation lies largely on the surface. ATR and RAIR spectroscopies are surface sensitive variants. Polarization modulation reflection absorption spectroscopy (PMRAS) is an interesting recent development offering promise for the investigation of spectra in other than high vacuum systems [16]. It depends on the fact that radiation polarized perpendicular to the plane of incidence interferes on reflection from a metal surface so as to yield no net electric field (and so no vibrational excitation), whereas that polarized parallel to the plane of incidence produces an electric field perpendicular to the surface which is especially strong near glancing incidence. Molecules tumbling in the gas phase absorb both polarizations equally, but surface species having a dipole component perpendicular to the surface absorb only the parallel component. Hence by subtracting intensities of the two beams a difference signal can be obtained which strongly emphasizes surface species. In this way Golden et al. have been able to measure absorption spectra of CO adsorbed on Pt foil in the presence of 13.33 kPa CO ambient pressure [17]. The most extensive and definitive data in recent years have come from HREELS and IETS. Both depend on electrons losing kinetic energy equivalent to specific vibrational transitions; the former detects vibrational transitions involving electric dipoles perpendicular to the surface (a subset of IR active modes), but the latter detects both IR and Raman modes. IETS requires a system of two metals separated by an insulator about 2.5 nm thick; a typical system studied is Al, a thin film of Al_2O_3, something chemisorbed on the Al_2O_3, and a film of Pb evaporated over this configuration. Interpretation carries the presumption that the chemisorbed substance does not change its bonding character as a result of the Pb blanketing process. Both HREELS and IETS are sufficiently sensitive to pick up C-H and C-metal modes at submonolayer coverages on smooth surfaces, which are hard to obtain by other methods. The article by Ibach et al. [11] provides a good review of HREELS; the discussion of structures of C_2H_2 and C_2H_4 on Pt (111) is a particularly interesting contribution to the solution of a significant controversy and should be compared with the moderately different interpretation based on similar evidence by Kesmodel et al. [12]. Weinberg [18] has reviewed IETS; this review and a paper from his laboratory [19] emphasize the spectra of carboxylic acids adsorbed on alumina. Not surprisingly, adsorption is as the carboxylate ion; by comparing IETS spectra with IR spectra of (nonadsorbed) benzoic acid, orientation of the benzoic acid can be inferred from absence of an absorption due to a vibration constrained by the orientation to be parallel to the surface. Preparation of reproducible insulating films 2.5 nm thick may not be possible for all materials of interest and may require considerable experimentation with others, but where it can be used the method is relatively simple and inexpensive to instrument. Comparison of IR and IETS spectra for phenol given in Ref. 18 illustrates one further problem characteristic of a developing field. The IETS spectrum is plainly richer in lines, and intensities do not closely parallel IR intensities. Hence there is not yet a well documented data base for assigning IETS frequencies to particular vibrational modes, and it is therefore prudent, where practicable, to confirm assignments by repeating spectra with isotopically substituted materials.

E. Results, Limitations, and Some Potential Applications in Solar Technology

The methods discussed have served to reveal a variety of properties of the S/G interface, including surface reconstruction, formation of a number of two-dimensional phases of different stoichiometries in chemisorption, preferential concentration of one component of a binary alloy at a surface, surface segregation of minor components in alloy systems, and structural changes in chemisorbed species on heating. So far these methods have not been very successful in detecting minor surface components; such components may be of major importance in reaction pathways. They are largely vacuum methods; surface properties (e.g., those associated with passivating layers, corrosion) depending on adatoms chemically bonded to the substrate can be more reliably investigated using them than others (e.g., wetting, adhesion), which may also be substantially altered by physisorbed species or other species lost on evacuation. Most large scale industrial catalytic processes are carried out under high pressure. In many cases, analogous reactions can be carried out under sufficiently low pressures to permit surface compositions to be established by some of the above methods under these conditions. It cannot safely be assumed that the high pressure reactions proceed under steady state conditions with similar surface compositions, or even that the principal reaction pathways are the same. Methods permitting reliable analysis of S/G interface compositions at atmospheric and higher pressures currently do not exist, and are badly needed. To the extent that vibrational spectra can serve to identify surface species, PMRAS, as previously discussed in Section D, offers some promise in this direction, as does IR ellipsometry [2]. Much information can be obtained up to moderate pressures by gravimetric techniques; vacuum microbalance equipment and techniques have developed substantially over the past decade, and the extensive review by Czanderna and Vasofsky covers both techniques and applications [20]. Microgravimetric methods are particularly useful for studying reaction kinetics in systems where the first 3-100 atomic layers of product are of interest.

While other chapters in this proceedings will deal at greater length with fundamental surface science problems associated with solar technologies, it is appropriate to close this survey with some examples of solar technology problems where G/S characterization techniques of the type reviewed might be helpful. A common "wet" method of preparing mirrors involves "sensitization" of a glass superstrate with $SnCl_2$, deposition of Ag on the sensitized glass surface, and depositing a Cu primer on the Ag, all with S/L methods. After drying, a polymer backing is deposited onto the Cu. Subject to previously mentioned reservations about possible changes in surface conditions on evacuation, it should be possible to characterize the original glass surface, the sensitizing deposit, the Ag surface, and the Cu surface, establish dependence of composition of each on concentrations of potential contaminants (or adhesion modifiers) and establish the dependence of interlayer adhesion for each interface and stability of the whole multi-interface system on these compositions. It may prove possible to block the tarnishing of silver by optically thin overlayers of another phase, possibly a monolayer, stable to attack by sulfur compounds. Compositions and structures of such phases could be established. Electropolished metals are very likely to have surface compositions reflecting the polishing process, and adhesion of other materials to these surfaces will generally depend on this composition. Frictional and wetting properties of glass, and very likely certain mechanical properties, can be markedly altered by appropriate monolayers (placed there deliberately or by contamination); proper investigations of the stability of glass surface in solar environments should include characterizations of surface composition, including change in composition over the investigation period. Passivation of Si devices is very likely to be associated with surface processes which could be revealed by the techniques discussed. Surface characterization must be considered basic to any investigations of photoconversion, photocatalytic, and photocorrosion processes, as further discussed in Chapters VI, XI, and XII.

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VIII. LIMITATION OF EXPERIMENTAL CAPABILITIES FOR INTERFACIAL STUDIES

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ABSTRACT

Solar energy technologies involve components and devices whose operation depend critically on various interfaces. To obtain optimum performance from these devices it is essential to be able to analyze in some detail the characteristics of these interfaces.

In principle, there now exist enough experimental techniques to determine essentially everything that one might want to know about the surface of a solid or the solid-solid interface. In practice, we are clearly not yet at that stage. The reason is not for lack of experimental techniques or theoretical approaches but primarily due to the limitations of these approaches. The variety of techniques presently available indicates that improvement will probably come from alterations in existing techniques rather than in the development of new ones. For characterizing solar interfaces, in situ measurements are critically necessary and because very few probes are available for making relevant measurements, considerable effort should be devoted to developing in situ probes.

The most popular tool for determining the elemental composition at S/G and S/S interfaces is AES in which the electrons resulting from radiationless deexcitation of atoms are energy analyzed. Almost all peaks in an Auger spectrum can be unambiguously identified. However, one must be concerned with various limitations. The sensitivity level under good, normal operating conditions is usually in the 0.1-1% range of the surface (1 nm) region. Insulating surfaces often charge, causing severe and irreproducible shifts in the spectrum of detected elements. Many materials are subject to electron beam effects which can cause irreversible rapid change in the surface being studied. For example, one observes preferential removal of oxygen from many metal oxides, even from apparently very stable materials such as alumina. Another useful approach is to use an ion beam as a probe for surface elemental composition, leading to the techniques of SIMS and ISS. The major limitation of ion probes is the destruction of the substrate, either for the analysis (SIMS) or because of ion bombardment (ISS).

One is also interested in the chemical nature of the various elements, e.g., is the detected Si signal derived from elemental Si, SiO, SiO_2, part of another Si compound, or some combination of these? For some materials, AES can answer some of these questions, but not in every case. In principle, XPS also called ESCA can answer these questions, but in practice the valence state may not be identifiable.

In addition to knowledge about the two dimensional surface lateral spatial distribution of components at the interface, one might wish to know precisely where individual surface atoms are located relative to each other, i.e., specific surface structure. Answers to the latter question might result from using LEED, EXAFS, EELS, etc. However, to make these experimental techniques useful requires the addition of considerable, nontrivial, theoretical calculations. The question of crystallinity can usually be answered

by LEED. Unless detailed current-voltage (I-V) curves are obtained and combined with elaborate theoretical analysis, only limited structural information can be gleaned from the data.

The morphology of the surface is of interest. Here, the SEM is clearly the popular technique being used. It can provide considerable information up to the limit of resolution of the instrument, which is usually about 10 nm under good operating conditions. However, care must be taken in the interpretation of SEM images or photographs to avoid reaching false conclusions.

In all of the approaches mentioned above, the power density effects of the beam probes must always be taken into account and can often be a severe limiting factor. Specific details about limitations of the popular techniques as well as observations about other techniques, are considered.

I. INTRODUCTION

The various solar technologies involve a large number of interfaces including S/S, S/G, and S/L when one considers devices such as mirrors, absorbers, photovoltaics, etc. (as mentioned in Chapters II, III, and IV). There is clearly a compelling need to study these interfaces by exploiting existing experimental capabilities, improving on these techniques, and by devising new ones where required.

The application of a large variety of surface analytical techniques in the study of interfacial problems has provided a considerable amount of useful information. There is no doubt that the continued use of existing techniques and the application of improvements and new developments will continue to provide essential information about interfaces. As with all areas of scientific endeavor, maximum value is obtained from a technique, when, in addition to its advantages, its limitations are understood and appreciated. In this paper we consider a number of the more popular surface analytical techniques presently being used in studying interfaces. In terms of some of the major limitations, where possible, we will try to consider what steps can be taken in future developments so as to reduce the effect of the limiting factors. It should be emphasized that this discussion of limitations in no way indicates a lack of confidence in the use of surface analytical techniques. In organizing the material, a number of specific types of limitations will be considered, and for each category, the limitation to a number of experimental techniques will be related to where it is applicable.

II. GENERAL COMMENTS ON SAMPLES AND PROBES

Before discussing the specific types of limitations in experimental techniques, it is useful to consider some limitations related to the samples to be studied and the probes to be used. If one is to study an interface, one must have access to that interface. In the case of the S/G interface, this problem is minimal and many techniques are available. The S/S and S/L interfaces present much more severe problems, as is discussed in a number of the other chapters. Most probes presently in use involve beams of particles which must be used in a vacuum environment. Samples to be studied must therefore be compatible with HV and UHV environments. One must be concerned with correlating data obtained on a specially prepared sample in UHV with the interface as it might exist in its normal form. This is not a trivial problem and considerable effort must be expended to develop adequate correlations. This effort is necessary since it is quite difficult to study many systems in situ, especially the S/S and S/L interfaces and the S/G interface at atmospheric pressures. For characterizing solar interfaces, in situ measurements are critically necessary and since there are presently a very limited number of probes available for making relevant measurements in this area, considerable effort should be devoted to improving the situation.

III. THERMAL EFFECTS - BEAM POWER DENSITY

Information about interfaces is generally obtained by probing at the interface with a beam of particles such as electrons, photons, ions, etc. One then seeks to obtain specific information by monitoring output signal, some desorbing species, or change in interface property. It would be most desirable if one could obtain a relatively large output signal in a short time, and indeed this can often be achieved if the probe beam has enough intensity. This is quite often possible, but frequently leads to the use of beam power densities that can cause significant thermal effects. One may then significantly change the interface that is being studied, often in an unknown way. To add to the uncertainty, it is generally very difficult to measure temperature changes at the interface. The region under consideration, which not only comprises an extremely small volume and mass but also may sometimes consist of single crystal materials, does not lend itself to the simple attachment of thermocouples or simply using other temperature measuring devices. To further complicate matters, the beam power is generally deposited in a very thin surface region of a substrate held by various types of supports in a vacuum environment. Classical calculations involving macroscopic thermal conductivity values are often not appropriate to this type of situation. In an effort to secure the magnitude of beam power induced thermal effects, we calculated a worst possible situation. We considered that all the power in the beam was deposited in the mathematical surface of the substrate, and that the only heat loss mechanism was by radiation. We considered the sample to be in the center of a vacuum chamber whose walls were at room temperature (300 K). This enabled us to calculate the maximum possible increase in surface temperature due to a specific input beam power density [1]. The results of this calculation are shown in Fig. 1. This curve does not indicate the actual temperature rise, but one can conclude that for a given power density input, the surface temperature rise cannot be larger than the value obtainable from the curve. Thus, if one wishes to be absolutely certain that the probe beam will not cause a temperature rise of more than 1 K, one should use a power density no greater than 1 mW/cm^2. Two points must be very thoroughly emphasized. First, the power density is the important input and its numerical value should be determined in all experiments and should be reported in all publications. Secondly, most experiments include the use of probe beam power densities greater than, and sometimes, much greater than about 1 mW/cm^2. It is essential that the thermal effects of the probe beam be considered, because of possible alteration of the interface under study. The obvious solution to this problem is to perform experiments with the lowest possible power density consistent with obtaining useful reliable data.

IV. NONTHERMAL BEAM EFFECTS

When studying interfaces with various kinds of beams, not only does the probe beam deposit energy, which can cause macroscopic heating effects, but also the probe beam particles themselves (e.g., electrons, photons, ions, etc.) can cause quantum reactions that may modify the surface being studied. A number of these processes have been studied in some detail.

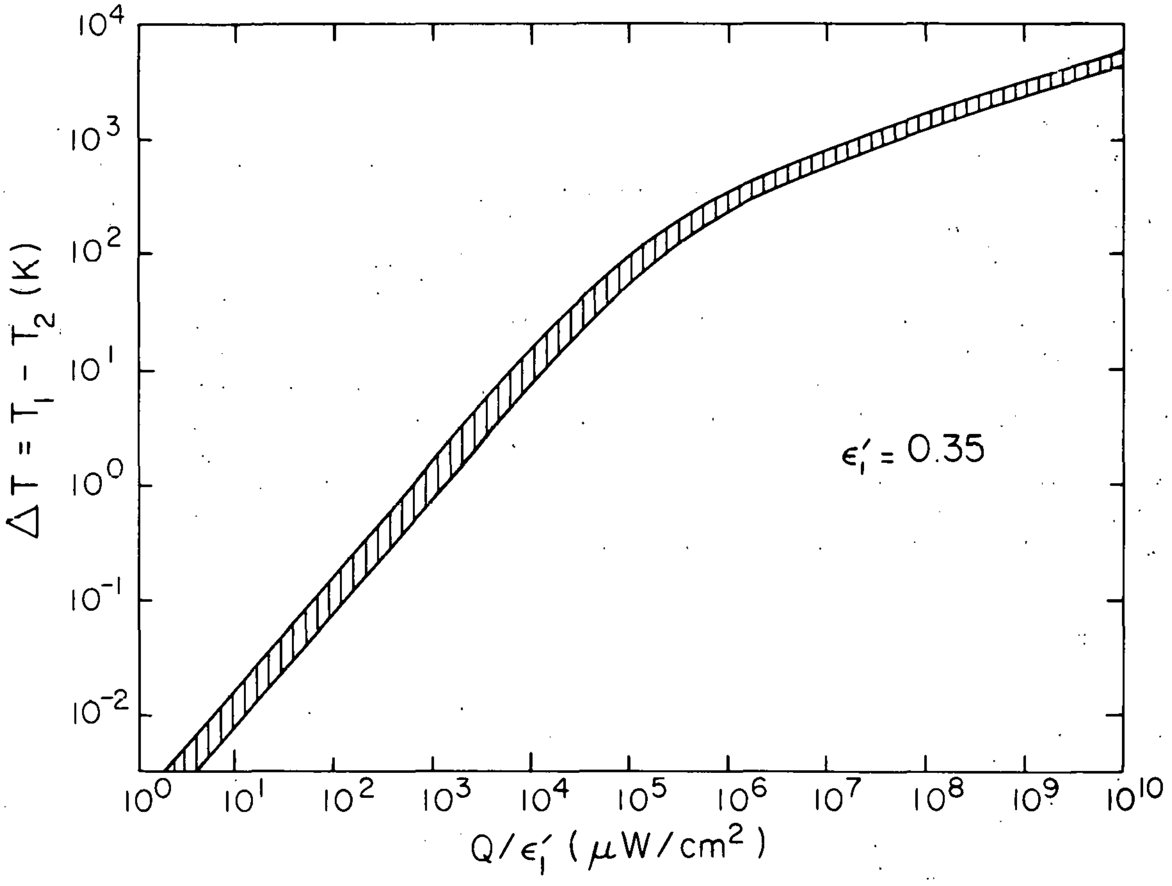

Fig. 1. Plot of theoretical maximum possible temperature increase of surface with emissivity ε_1', bombarded with energy density Q. The width of the line indicates the range of assumptions.

A. Electron Effects

Electrons can interact with surface species in a variety of ways which result in modification of the surface under study. For gases adsorbed on metals, electrons can excite the adsorbed complex via a Franck-Condon transition, resulting in removal of atoms or molecules from the surface [2,3]. Electrons of sufficient energy can also remove core level electrons resulting in deexcitation processes which also lead to the removal of surface components [4,5]. This effect is especially pronounced with a large number of metal oxides in which the electrons cause preferential removal of O_2 atoms, thereby strongly modifying the surface composition. These effects will certainly occur when using electron probe beams associated with AES, LEED, etc. and data can be misinterpreted if this effect is ignored. If one is not careful, data can be obtained for a surface which is quite different from the one originally subjected to study. Since the threshold for these processes are in the range of about 10-30 eV, it is generally not possible to eliminate the effect, but one can reduce it by working with the lowest possible probe beam density. This approach is fortunately consistent with keeping the power density to a minimum.

B. Photon Effects

Photons can also cause dissociation and modification of surfaces by at least three mechanisms. It has recently been discovered that photons of sufficient energy (i.e., 10-30 eV) can cause Franck-Condon transitions and subsequent desorption of surface components in a manner similar to the process of electron stimulated desorption. It has also been established that photons can cause removal of core level electrons similar to the effect caused by electrons of the same energy [4,5]. This again results in the removal of surface components. In a completely different process, band-gap radiation acting on semiconductor substrates often leads to the desorption of neutral CO_2 [6]. It is clear, therefore, that the use of photon beams in the energy range from near UV and up can cause considerable modifications of interfaces being studied. This is, of course, in addition to any power density thermal effects. The increasing use of synchrotron radiation for interface studies will make concern about this problem even more important. The solution, as before, is to be aware of the effects and to use the lowest possible beam density for the shortest possible exposure times.

C. Ion Effects

In the case of electrons and photons, quantum processes are dependent on the specific substrate being studied. In the case of ion probing, virtually all substrates are modified by the probe beams. This entire area is of major concern and is treated in considerable depth in Chapter IX and in the working group in Chapter XV. All the problems and recommendations associated with electrons and photon beams are equally important when using ion beams.

V. ELEMENTAL IDENTIFICATION

Of all the aspects of the interface about which one wishes knowledge, the identification of elemental composition is perhaps in better shape than almost all the other characteristics. A number of techniques exist, such as AES [7,8], SIMS [9,10], ISS [11], XPS [12], RBS [13], etc., which can provide information about the elemental composition. Except for the fairly unusual case where peaks of two or more elements almost overlap exactly, identification is usually obtained directly from the detected signals. The limitations in elemental identification are related primarily to beam effects (as discussed in Sections III and IV above) and sensitivity, i.e., the fractional part of the surface region that can be detected and identified. When one considers sensitivity, one is generally concerned with practical sensitivity, that is, what can be detected in reasonably acceptable time limits and with reasonable effort. Some techniques, such as SIMS, can readily be used to detect elements to parts per million, but the technique, unfortunately, requires destruction of the surface to secure an analysis. Many of the other techniques such as AES, XPS, ISS, etc., usually operate in modes that allow for detection of 0.1 to 1% of the surface atom density. Obviously, the sensitivity level can be reduced if long times and signal processing techniques are utilized. One must remain aware that the elemental identification is made for the area probed by the entire beam and that additional techniques, such as scanning beams are required to specify the exact lateral location where the particular element is found.

VI. CHEMICAL STATE IDENTIFICATION

Since elemental identification is usually obtained directly with a variety of techniques, one quickly desires to obtain information about the chemical state to secure deeper understanding. This is a much more difficult problem, but one which has attracted much more attention in recent years. A number of techniques are being actively used in this area including XPS [12], EELS [14], IR [15], laser raman [16,17], and detailed analysis of AES peak shapes [18]. XPS is the classical technique for chemical state identification. Its limitations are related primarily to establishing suitable calibration data to enable clear cut identification to be made. As work in this area continues, the data base will continue to grow and the technique will become more and more useful.

The main limitation of the other techniques is that they are suitable for specific interface structures only, that is, they will provide results that will allow for chemical state identification for some systems, but are not at all sensitive to many other systems. Thus, for example, AES can be readily used to differentiate between elemental Si and Si in SiO_2, but cannot detect with reasonable effort, the same change for many other metals. The various optical techniques (e.g., IR, laser raman, ellipsometry [19]) can be employed to obtain useful data on an even more selective number of systems. For example, reflection IR absorption has been quite successful in studying CO adsorbed on various solid metal substrates but has had very limited success with almost any other adsorbed gas. This is an overall area in which considerable effort is now being expended to identify chemical states and considerable improvements should evolve in the next few years.

VII. CRYSTALLINITY

In many areas of solar energy research, one is concerned with knowing whether the substrate under study is crystalline or amorphous and, if crystalline, how specific can one determine the details of the crystallinity. The main technique used in this study involves electron diffraction including the family of LEED [20,21], HEED [22,23], RHEED [24,25], etc. There are two levels at which the information is obtained. One can simply obtain a diffraction pattern as an image or a photograph, which will indicate whether there is some degree of order on the surface being studied or no degree of order and it is completely amorphous. One can also reach a number of conclusions about an ordered surface from some of the details of a simple diffraction pattern. This type of experiment is relatively simple but provides only limited information about the substrate. It may well be sufficient for those cases where one only desires to know whether there is order or not. Beyond securing simple diffraction patterns, detailed I-V curves can be obtained for a number of diffraction spots. These data have the possibility of providing specific information about the exact position of the various surface atoms. This approach has had limited application because, first, obtaining good I-V curves is not simple and, secondly, to use the data one must have theoretical curves, which require very extensive effort and computer time to develop. Another experimental approach which has the capability of providing detailed positional information about crystalline surfaces is EXAFS [26,27] and SEXAFS [28,29]. These techniques also are as limited as those just described because, not only is the experimental data more complex than in many other experimental techniques, but also because extensive lengthy computerized calculations are required to use the data. With time there should be some improvement in the ability to obtain experimental data using LEED, EXAFS and ARUPS [30,31] and improvement in obtaining the appropriate theoretical computations. Therefore, these techniques are likely to be used more extensively in their application to a larger number of systems. However, the number of systems for which one will be able to obtain good experimental data, and for which one can afford the time and cost of obtaining the theoretical curves, will be limited. One very important problem in this area is the need to obtain data on real systems which are reasonably close to the theoretical models used in the calculations.

VIII. LATERAL SPATIAL RESOLUTION

The need to learn about the details of practical surfaces with high lateral spatial resolution, is very important. The two basic approaches involve the techniques of FEM [32,33] and FIM [34,35], and the electron microscopies. For several decades, the only instrument with atomic resolution, that is, the ability to clearly discern individual atoms, was the FIM. The major limitation of this technique was that the surface under observation had to be a fine needle point with a tip radius generally less than 100 nm, and made of material which could withstand the electric fields applied. In recent years, improvements in TEM [36] and STEM [37] have brought comparable resolutions to these electron microscopies, but with the important feature of being able to view macroscopically flat surfaces. The limitations in this case are related to the maximum thickness of the sample one can use, i.e., approximately 100 nm for a 100 kV microscope. It is clear that improvements in spatial resolution are probably reaching fundamental physical limitations, but the ability to see individual atoms on many different kinds of materials is now possible. The limitations for both FIM and STEM are related primarily to sample preparation. I expect that there will be considerable improvements in preparing samples in the next few years and significant progress will be made in the ability to observe substrates at atomic level resolution. A detailed discussion of the use of these microscopies is presented in Chapter IV as well as in Chapter XV.

IX. SUMMARY

Interfaces play a very significant role in the development, operation, and lifetime characteristics of virtually all solar energy components and devices. Therefore, knowledge about the interface is essential in order to make significant progress in improving current devices and developing new ones. Perhaps most important is information which will determine the lifetime characteristics of solar energy devices, since this factor will eventually determine the economic feasibility of various solar energy approaches.

In the foregoing sections, I have attempted to consider most of the areas of interest in studying interfaces, the limitations existing in present experimental techniques, and possible solutions to those limitations. Improvements in these techniques and the development of some new ones will be essential in the overall solar energy research and development program. An understanding of the limitations, both fundamental and practical, in present techniques will enable scientists and engineers to obtain the maximum information from their experiments.

I expect that the next decades will see less evolvement of new techniques and more effort related to refinement and improvements in existing techniques as attempts to overcome the limitations indicated are made.

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IX. LIMITATIONS OF ION ETCHING FOR INTERFACE ANALYSIS*

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ABSTRACT

The advantages and limitations of using ion sputtering for interfacial analysis are reviewed. It is concluded that many artifacts may degrade interfacial resolution (e.g., surface roughness, zone of mixing, bulk and surface diffusion, implantation, residual gas adsorption, and matrix effects). Techniques to minimize these limitations are suggested. Some examples are using reactive ion beams, multiple ion beams, sample rotation and special mounting, variable ion energies and incident angles, and deconvolution methods. It is concluded, however, that sputtering may destroy atomic arrangement and chemical state information at the interface. New approaches are needed to determine these interfacial parameters and some are discussed in this chapter as well as in Chapter XV.

I. INTRODUCTION

There are many ways of determining the change of composition versus depth in a solid, or of examining the composition and structure of an interface. The techniques may be loosely categorized as nondestructive or destructive. In the category of nondestructive, optical techniques such as ellipsometry or IR reflection can be used to study L/S or S/S interfaces where the outer layer of material is transparent to the exciting radiation. Electrical properties (e.g., capacitance of a grain boundary in Si may be used for interfacial analysis. At other times, depth profiles of concentration and chemical state may be determined by varying the information depths through variation in primary or detected particle energy (ion or electron) [1,2] or by varying the "take-off" angle between the emitted particle and sample surface [3]. RBS and NRA are fine examples of using varying energy for depth profiling in a nondestructive manner [4].

With respect to destructive interfacial analysis, the sample can be machined and the composition of either the machined chips or of the remaining sample can be analyzed. However, the composition profile is often of interest in very thin samples and in samples with complex shapes. A refinement of the machining technique is to polish the sample. Depth resolution is improved if the surface is polished in a plane approximately one degree from the surface plane. This "angle-lapping" extends the depth features in the plane of the surface to the extent that finely focused primary beams, e.g., electrons, can sometimes be used to measure the composition at various depths [5]. In a similar procedure, Thompson et al. [6] have exposed various depths of a solid by grinding (polishing) with a spherical ball or a circular rod and diamond paste. In other approaches, Adams [7] oxidized thin layers of Si and then preferentially removed the layer by chemical etching.

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However, the above analytical techniques are seldom capable of depth resolution of a few atom layers. For example, even RBS and NRA have depth resolutions of no better than a few hundred Angstroms. Fracture can sometimes expose an interface, but the most common approach is to analyze with a method whose information depth is a few atom layers (using AES, XPS, SIMS, or ISS spectroscopies) and ion sputter down to the interface. The advantages of sputtering for interfacial analysis are several:

(1) It is an atomic process, therefore, near-atomic depth resolution is possible (in principle);

(2) The depth profiling can be performed in situ rather than external to the vacuum system;

(3) Inert gas may be used to produce reactive (clean metal) surfaces and avoid oxidation, etc.;

(4) In most instances, sputtering and analysis can be performed simultaneously; and

(5) Reasonable sputter rates may be achieved (e.g., 0.1 to 100 nm/min.).

However, just as no analytical technique is always the best approach, neither is sputtering a perfect depth profiling technique. A number of problems exist, including:

(1) Surface roughness may develop;

(2) A "zone of mixing" is normally created in which the phenomena of forward scattering ("knock-in" rather than sputter), cascade mixing, preferential sputtering, and destruction of structure and chemical state are observed;

(3) Enhanced adsorption of residual gases may occur;

(4) Bulk and surface diffusion of substrate species may take place;

(5) The sputter gas is implanted into the sample; and

(6) Matrix effects may change the sputter yield and ionization probability of secondary particles.

The sputtering phenomenon itself has been the subject of a number of studies [8,9]. The sputter yields have been measured for most elements using a variety of ions and ion energies [9]. The effects of variables such as surface cleanliness, crystal orientation, residual gas, implantation, incident angle, etc., have been studied in a few systems and generalization should normally be valid [10]. One problem with using sputtering for depth profiling, however, is that these effects are not usually considered in sufficient detail by investigators using the sputtering for surface and interfacial analysis. Many of these effects are discussed by Wehner [11] and Coburn and Kay [12] in their reviews on the use of sputter profiling for surface and thin film analysis.

II. BASIC CONSIDERATIONS

Conventionally, a depth profile is made by combining AES or XPS and sputter removal by an ion beam [13-21]. However, other surface characterization methods such as SIMS [22-29] and ISS [32,33] have frequently been used. It would be relevant here to discuss in short the main features and the fundamental limitations involved in the different methods of surface characterization.

AES and XPS are based on the emission and subsequent energy analysis of secondary electrons produced by high energy (3-5 keV) electron or soft x-ray bombardment, respectively. The energy of a small fraction of the secondary electrons emitted from the sample can be related to the core levels of the target atom and thus the atom can be identified. AES data are usually taken as dN(E)/dE versus E where N(E) is the number of electrons with an energy E. The peak to peak heights in the derivative of Auger spectrum may be proportional to atomic concentration in the surface layer.

In SIMS, energetic ions impinge on a solid and undergo collisions with the lattice atoms. The energy of the particle thus dissipated in the surrounding lattice zone results in the expulsion of atoms and molecules from the surface region. These ejected particles are primarily neutrals, although a fraction come out as ions and excited particles. By mass analyzing the ions (SIMS) or analyzing the photons (SCANIIR) emitted by the deexcited particles, the elemental composition of the solid near the surface can be determined. Sputtering continuously uncovers a fresh surface. Thus, in-depth concentration can be obtained by monitoring the signal. However, quantitative SIMS or SCANIIR analysis is sometimes hindered by the lack of knowledge of the ionization and excitation probabilities, particularly at the interface.

Surface composition during sputtering can also be monitored by ISS. In this case, elastic scattering of low-energy rare gas ions is utilized. From the backscattered energy spectra characteristic of the mass of the scattering centers, one can identify the elements present on the surface. The intensity of a specific scattered peak is proportional to the concentration of a specific element on the surface. Here also, because of the lack of understanding of the ion neutralization mechanisms [34] at the surface, a quantitative interpretation of the spectra may be difficult.

The depth of the sample from which a signal is observed varies with the analysis method. For ISS, the information depth is limited to the outermost atomic layer, while in the case of AES, the "escape depth" of the Auger electrons range from about two to six atomic layers [35]. In SIMS or SCANIIR, the information depth depends to some extent on the penetration depth which in turn depends on the primary ion energy. As an estimate, the escape or information depth amounts to roughly one-quarter of the penetration depth [34]. Thus, for an energy of 3 keV the information depth would be about 1 nm. Clearly, a depth profile may be influenced by the value of the information depth.

Few investigators have compared the depth profiles of a single system simultaneously using all the methods described above. However, Narusawa et al. [36] showed that the depth profiles of Al, Ti, and Ag films on Si obtained by AES and SIMS are different, while the Ni-Cu interface shows very similar profiles (Fig. 1). They attribute differences in the SIMS and AES profiles to changes in the secondary ion energy distribution, work function, and sputtering yield as a function of sample composition. Such matrix effects can severely distort the sputter profiles, as discussed by Coburn and Kay [12]. Furthermore, the effect is different for analysis of material remaining on the surface (SIMS and SCANIIR). These effects are discussed below in more detail.

To characterize the steepness of the change in intensity at the interface, a depth resolution is defined in the literature [37,38] by the ratio of a/b, where a is the time (depth) necessary for the normalized output signal on each leading and trailing edge to vary from 84% to 16%, and b is the time (depth) necessary to reach 50% of the intensity. The width of the interface has also been defined as sputter time (depth) required for the elemental signal to decrease from 90% to 10% [39]. Ho and Lewis [40] have defined the width in terms of a resolution function and expressed it as full width at half maximum of this function.

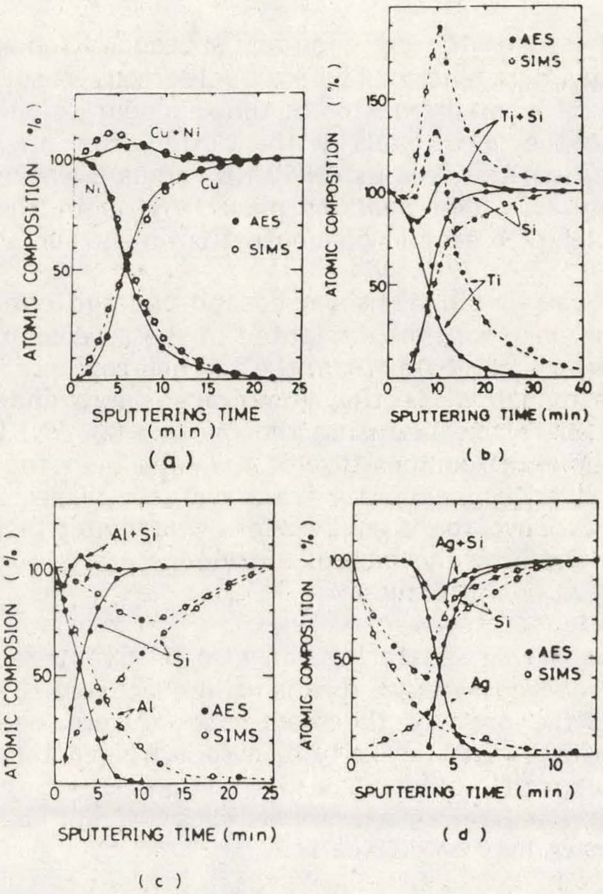

Fig. 1 AES and SIMS depth profiles for: a) Ni-Cu, b) Ti-Si, c) Al-Si, and d) Ag-Si systems [36].

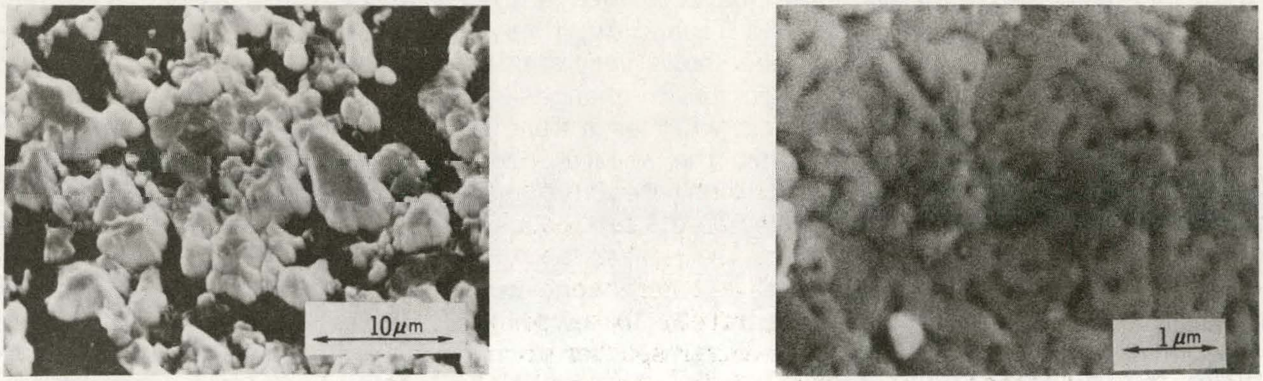

Fig. 2 SEM micrographs of Au on sapphire: a) unsputtered, b) sputtered with 2 keV Ar^+.

III. LIMITATIONS OF ION SPUTTERING

A. Development of Surface Roughness

The development of roughness has been observed on a number of surfaces after ion beam sputtering [41-47]. These ion-induced changes in microtopography are mainly due to variations in sputter yields and rates with crystal orientation, surface contamination, lateral variations in composition and phases, and angle of incidence.

There is a strong dependence of sputtering yield upon the crystalline orientation of the target [8,48]. A polycrystalline surface containing a large number of small crystallites with different crystalline orientation will develop roughness because of yield variations from crystallites. This is illustrated in Fig. 2, where SEM micrographs from 3 μm thick polycrystalline Au films on sapphire are shown. Figure 2 shows that prior to sputtering, the Au surface was extremely smooth and featureless. After sputtering with 2 keV Ar ions, some crystals have been completely removed down to the "interface," while other crystals have sputtered only very slowly. The variation in sputter yield with crystalline orientation can be quite large, as reported previously [8,10].

Beyond crystalline orientation, surface microtopography can result from surface impurities which cause the formation of surface cones [49-52]. These cones result from different sputter yields from covered and uncovered regions of the surface.

Recently, Williams et al. [53] have shown that trace contamination on InP and $In_xGa_{1-x}As_yP_{1-y}$ surfaces cause cone formation during sputter etching with Ar ions. The contaminant originated from the fixtures holding the samples during sputtering, and they were eliminated by mounting samples on a pedestal. The interfacial width decreased from 80 to 25 nm by avoiding the contamination. The interfacial width could further be reduced to 14 nm by sputtering at grazing incidence angles.

Surface roughness may also increase if the sputtered sample has a multi-phase microstructure, and the sputter yield varies from one phase to the next. Increased roughness sometimes results from variations in sputter yield with changes in the ion angle of incidence [54-58]. This is particularly important when the starting surface is rough and the beam is not parallel. Thus, initial surface roughness will grow as the sputtering proceeds.

B. Zone of Mixing

1. Knock-in Effect

The direct transfer of momentum from the bombarding ions to the lattice atoms results in a forward motion of atoms in the lattice. This is often referred to as "knock-on" or "knock-in" process. Many of the sputter depth profiles are broadened because of the forward scattering of atoms at the interface. The broadening due to this effect can be isolated from other broadening effects because of its primary energy dependence. Schwarz and Helms [59] have used Auger sputter profiling to examine the broadening of the Si-SiO_2 interface as a function of Ne^+, Ar^+, and Xe^+ energy. The interfacial width is plotted versus ion energy and mass in Fig. 3. Due to forward scattering during the sputtering process, the interfacial width increased as the ion energy increased or ion mass decreased. A model based on an analogy of thermal diffusion theory predicts

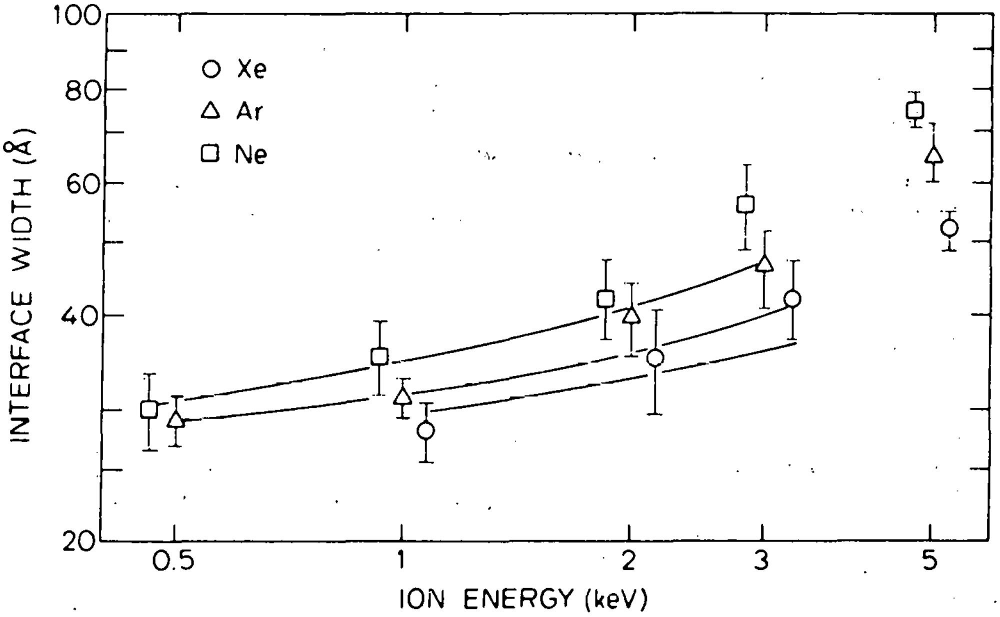

Fig. 3 Average and standard deviation of the measured 10%-90% Si-SiO_2 interface widths as a function of ion energy for Ne^+, Ar^+ and Xe^+ bombardment. Solid curves are the prediction of a mixing model for an original interface width of 2 nm [59].

quantitatively the broadening due to knock-in effect. Schulz et al. [60] have used SIMS to profile B implanted in Si using different sputtering ion energies. The increased tailing of the B at low concentrations as the sputtering ion energy is increased is also attributed to direct momentum transfer processes. Taikang et al. [61] have studied this effect by Monte-Carlo computer simulation. Simulations based on the binary collision model have been applied for a sandwich-type thin B impurity layer in a Si substrate under Ar ion bombardment. The results are consistent with experimental data and show that the B distribution becomes skewed toward the interior of the target, and the position of the peak shifts. The calculation has also suggested that sputter broadening can be affected by the sputter yield; namely, less broadening occurs for a higher sputtering yield.

2. Cascade Mixing

Ion bombardment of a solid results in displacements of the lattice atoms, both by direct momentum transfer and (more probable) by energy cascades resulting from collisions between lattice atoms previously excited and those at rest. This collection of excited atoms spreads around the direction of the primary ion creating a more isotropic mixing, and it is usually referred to as cascade mixing or sputter enhanced diffusion. The extent of cascade mixing depends on the incident ion energy and it can result in sample redistribution by diffusion, broadening of interfaces, and/or broadening of implant distributions. McHugh [62] profiled a 5 nm thick phosphorous rich region in Ta_2O_5, 23 nm below the surface by using SIMS. He found that the full width of the P^+ peak at half maximum increased from 7.8 to 14.8 nm in changing from 1.75 to 7.75 keV O^+ ions. It is inferred that the broadening was a result of cascade mixing because it was not directed preferentially into the solid and also high fractional concentration was involved. Experimentally, such effects are also evident in the work of Ishitani et al. [63,64], Cairns et al. [65], and Zinner et al. [66]. Haff and Switkowski [67] have presented a calculation based on the diffusion model of atomic mixing which shows that the sharp interfaces within a target are smoothed by ion bombardment. Recently, Williams [68] has shown that the rates of removal by sputtering of a variety of surface and interfacial layers on Si vary for different elements. The author proposed that the ion beam causes an efficient mixing of the surface and subsurface layers over a distance of the order of the primary ion range, as has also been demonstrated by Liau et al. [69].

3. Preferential Sputtering

In multi-component solids, sputtering leads to composition changes near the surface. Some of the recent observations have been summarized by Kelly [70]. The normal result is that, irrespective of the mass and energy of the sputtering beam, the target develops a surface layer enriched in the heavier constituent [40,70-77]. A good example of this can be found in the work of Liau et al. [77]. They have sputtered a variety of alloys and compounds, namely, Ag-Au, Cu-Au, Au_2Al, $AuAl_2$, PtSi, Pt_2Si, NiSi, GaP, InP, GeSi, and Ta_2O_5 with 20-80 keV Ne^+, Ar^+, Kr^+, and Xe^+ ions. Surface compositions were studied by the RBS technique.

The spectra of Pt_2Si before and after sputtering are shown in Fig. 4. Platinum enrichment is clearly visible after sputtering. Except for compound semiconductors, all other targets showed enrichment of heavier atoms in a surface layer whose thicknesses correspond to the range of the sputtering ion. The compositions of these enriched surface layers were independent of the mass and energy of the sputtering ions over the ranges tested. The enrichment of heavier atoms in the surface is consistent with the predictions of the linear collision cascade theory of sputtering [78]. However, enhanced diffusion due to ion bombardment must be invoked to explain the change in composition extending over the range of the ions. Also, total sputtering yields of multi-component systems [71,79,80] have been found to be quite different from a linear combination of the yields of the components.

Recently, Sigmund [81] has pointed out that the enrichment of lighter components can be found if the sample is exposed to very high doses. This results from a sequence of events in which a layer rich in light atoms is first created below the surface by forward scattering, then is exposed by subsequent sputtering to cause a surface rich in the light element. The feasibility of such an effect is supported by RBS data, since PtSi bombarded with Ar^+ clearly shows a concentration of light atoms below the surface rich in heavy atoms [82].

4. Structure and Chemical State Changes

As a result of ion bombardment, the atomic arrangement and chemical state of the solid is often changed. For example, high ion doses can completely eliminate low-energy electron diffraction patterns from the surface due to disorder [83]. A similar effect is observed from field ion microscope studies [84]. Therefore, the atomic arrangements of interfaces can seldom be studied by sputter profiling.

In a similar manner, ion bombardment may cause the chemical state of the solid to change. For example, data in Fig. 5 show that Ar^+ bombardment reduced some Ta_2O_5 to Ta on the surface of a thin Ta_2O_5 film [72]. This is apparent from the fact that the Ta 4d photoelectron peaks after sputtering results from a summation of the peak from both

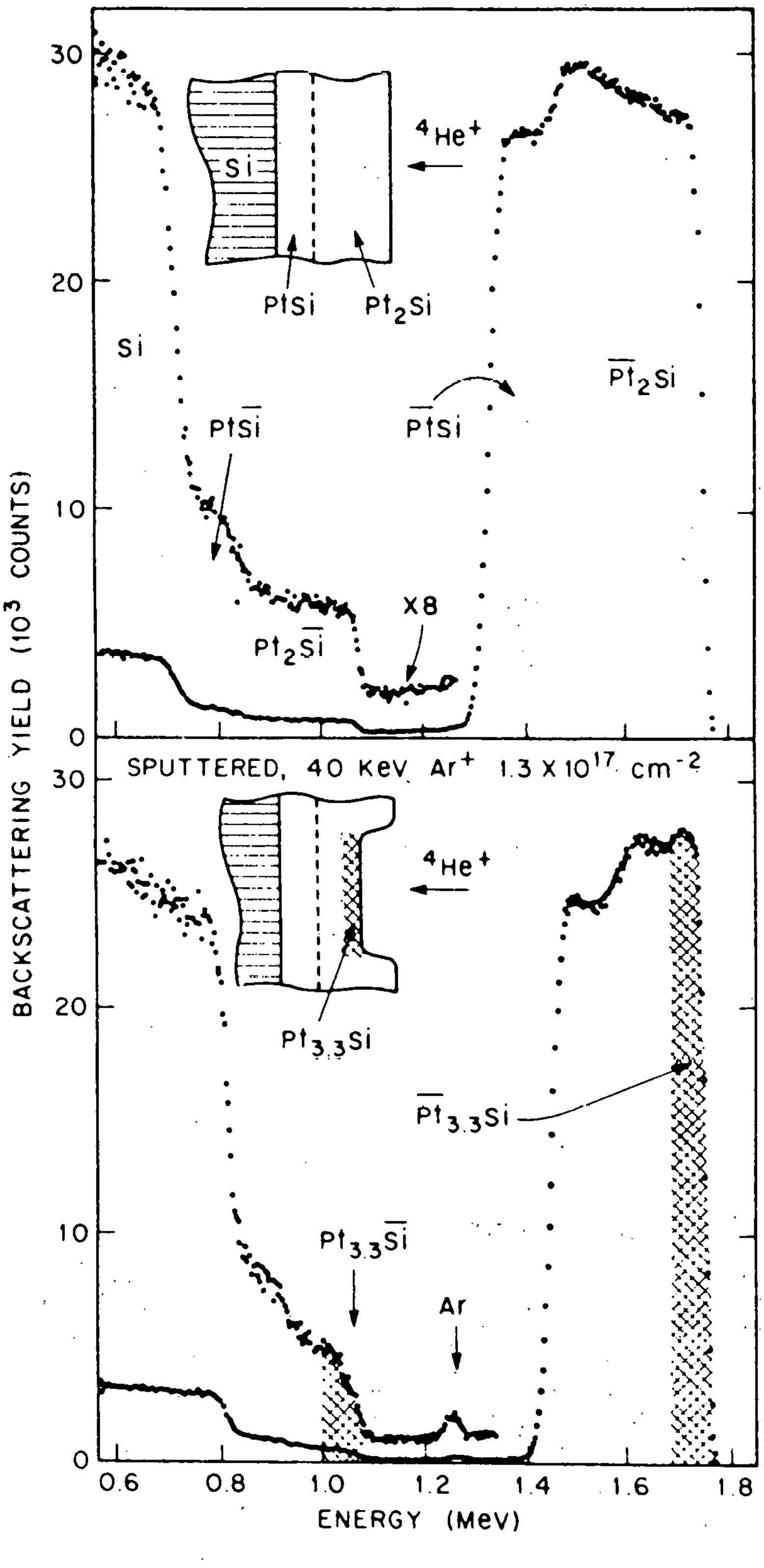

Fig. 4 Backscattering spectra of a Pt_2Si film before and after sputtering. The unsputtered sample has a 250 nm layer of Pt_2Si on the surface and a 135 nm layer of PtSi between the Si substrate and the Pt_2Si. Inside the crater a layer of Pt_2Si of about 100 nm has been sputtered away. A Pt-enriched layer of about 45 nm (shaded region) on the surface is indicated. The Si and Ar signals are magnified (x8) to reveal the layer structures [77].

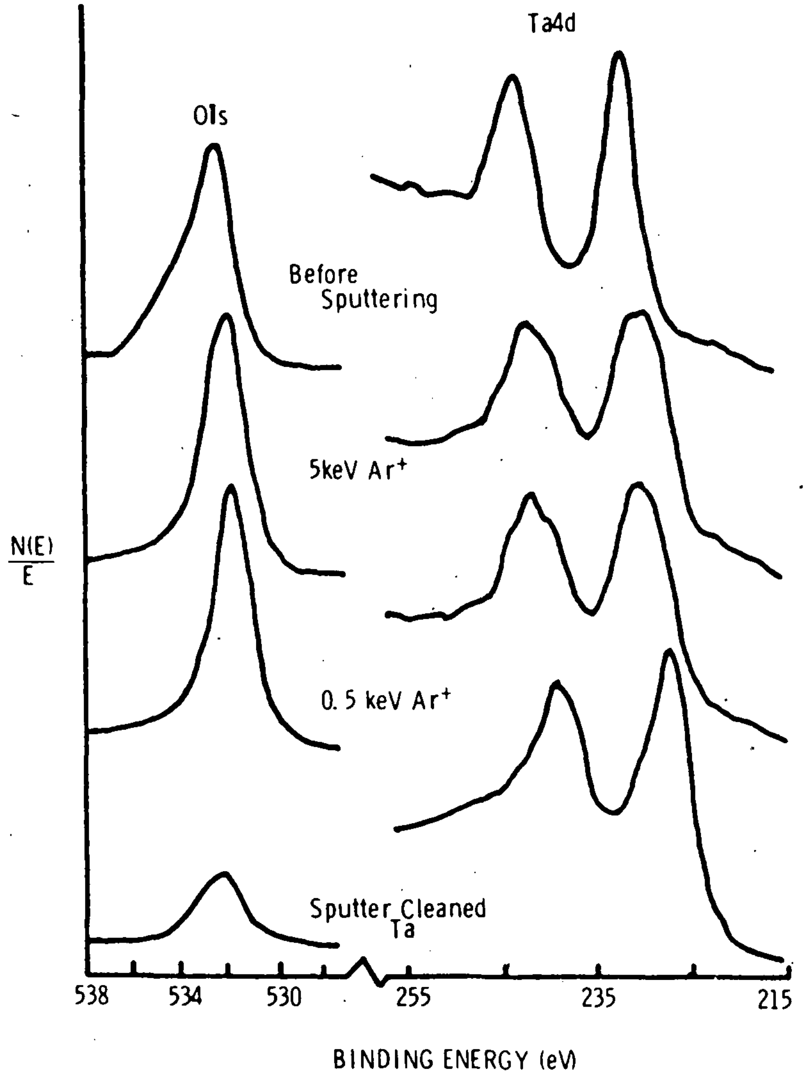

Fig. 5 O ls and Ta 4d x-ray photoelectron peaks from Ta_2O_5 on Ta before sputtering, after sputtering with 5.0 and 0.5 keV Ar^+, and after sputter removal of the Ta_2O_5 [72].

Ta_2O_5 and clean Ta. Therefore, the possibility of a sputter-induced artifact must be considered in measuring the chemical state of atoms at an interface after sputter profiling.

C. Enhanced Adsorption of Residual Gases

If an oxidized surface is cleaned by ion sputtering, that surface may quickly react with impinging residual gases from the vacuum system. Holloway and Stein [85] have examined this effect for C and O impurities on Si and Si_3N_4 samples. They have shown that a steady state is created between adsorption and sputter removal rates, resulting in a finite population of adsorbed impurities. This finite population may interfere with quantitative surface analysis, especially when small concentrations of atoms are important.

D. Bulk and Surface Diffusion

Ion bombardment can cause both bulk and surface diffusion to occur. Figure 6 shows the profile of Na in an SiO_2 layer on Si [86]. Initially, all of the Na was at the SiO_2-air interface, but O^+ ion bombardment caused much of the Na to move to the SiO_2/Si interface. This type of bulk diffusion can destroy the accuracy of the sputter profiles. Another example of this is the experiment of Hart, et al. [87]. They have deposited a fraction of a monolayer of Cu onto a Si wafer. RBS was used to measure the Cu distribution before and after bombardment with 20 keV Ne ions to a fluence sufficient to sputter approximately 9 nm of Si from the surface. Spectra taken after bombardment showed the Cu to be distributed uniformly into the Si to a depth of about 60 nm, which corresponds roughly to the range of the 20 keV Ne ions. The spot previously bombarded with Ne^+ was then bombarded with 800 eV Ar^+ to a dose sufficient to remove 10 nm of Si. This resulted in a concentration of Cu in a 12.5 nm thick layer. Dearnaley [88] has pointed out that high ion doses may induce a large compressive stress gradient and that this can readily result in the migration of certain species away from or back to the surface.

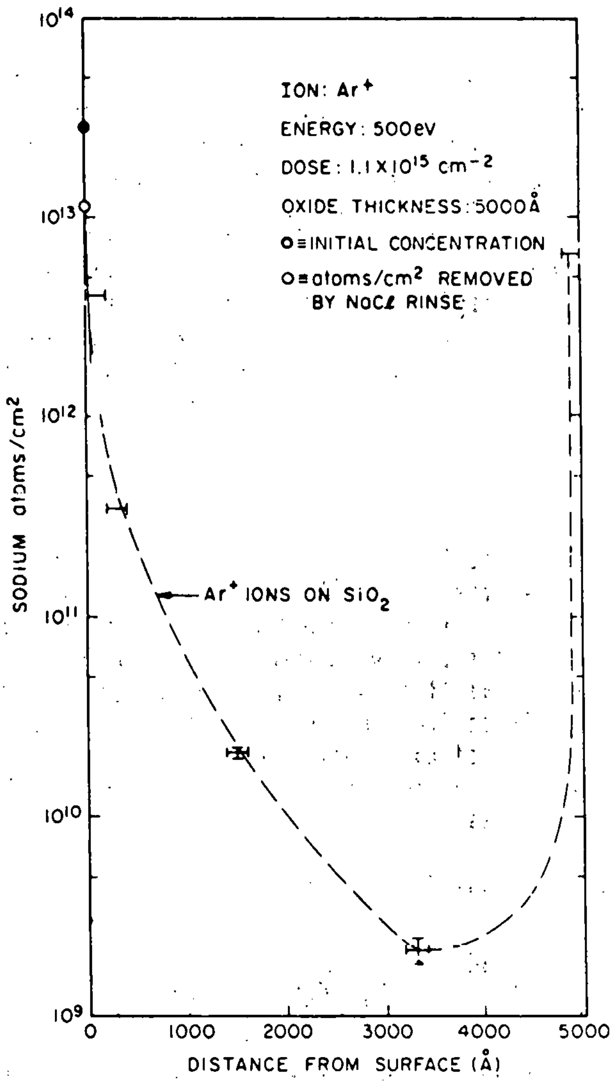

Fig. 6 Profile of ^{22}Na in ion-bombarded SiO_2. Initially all the Na was at the SiO_2-air surface, but was moved to the SiO_2-Si interface by the ion beam [86].

In addition to bulk diffusion, surface diffusion of impurities can also occur in some cases. Tompkins [89] has shown that surface diffusion of Sn on Au can cause contamination of surfaces previously cleaned by sputtering.

E. Implantation of Inert Gases into the Sample

It is a normal practice to sputter etch the sample with Ne or Ar ions. During sputtering the atoms are trapped in the lattice. The number of trapped atoms reaches a maximum at a certain implantation energy as an equilibrium is reached between the ions being implanted and those being re-emitted by diffusion and/or sputtering. These implanted ions dilute the matrix atom concentration in the analyzed region, thus influencing the depth profile. Normally the surface concentration of these implanted atoms increases as the ion energy decreases [90]. McGuire [90] has bombarded GaAs at different Ar ion energies and measured the As/Ga and Ar/Ga intensities. The results show parallel curves which increase slightly at low acceleration voltages, implying that Ar atoms preferentially sputter the Ga atoms.

In addition to the dilution of surface atoms, implantation can influence the depth profile by changing the sputtering yield. Andersen and Bay [91-94] have carried out a detailed study of this phenomenon and found that the sputtering yield decreased at higher doses. For instance, sputtering yields for 45 keV noble gas ions decreased by about 30% during the removal of about 170 nm of Au [95]. This effect has not been studied at lower ion energies. But, since the dose effect is probably a result of changes in both atomic concentration and binding energies of the lattice atoms at the surface, a decreased yield is also expected at lower ion energies. The influence of both ion dose and chemical effect upon sputter yield is demonstrated by the strong disagreement between the experimental data for N_2^+ bombardment of Fe [96] as compared to the theoretical predictions of Sigmund's theory [97].

F. Matrix Effect

It is well known that SIMS and SCANIIR signals are sensitive to the local chemical environment of the target atoms, an effect generally referred to as a matrix effect [32,98,99]. At an interface, the chemical environment is expected to be different from the rest of the film. For this reason, the ion and photon yield from the interface during profiling by SIMS and SCANIIR may not be proportional to the concentration of the element to be profiled. Both ion and photon emission intensities are generally greatly amplified by the presence of oxygen in the collision chamber as well as by O_2^+ bombardment. This property is often used to enhance the positive ion and photon yields during material analysis and profiles.

The ion yield S_A^+ of the element A in a binary alloy, AB, is given by:

$$S_A^{+AB} = \beta C_A S_{AB} I_P P_{AB}^{+A} \qquad (1)$$

where β is the instrumental factor, C_A is the atomic fraction of A in the binary alloy AB, S_{AB} is the sputtering coefficient of the binary alloy, I_P is the primary ion beam current, and P_{AB}^{+A} is the ionization probability of the element A in the binary alloy AB. A similar expression can be written for photon yield. The ion yield for a pure element is written as:

$$S_A^+ = \beta\, S_A\, I_P\, P_A^+ \tag{2}$$

The combination of Eqs. 1 and 2 gives for the ionization probability of element A in the binary alloy normalized to the ionization probability of this pure element target:

$$\alpha_A^+ = \frac{P_{AB}^{+A}}{P_A^+} = \frac{S_A^{+\;AB}}{S_A^+}\,\frac{S_A}{S_{AB}}\,\frac{1}{C_A} \tag{3}$$

This should be unity in the absence of a matrix effect. Yu and Reurter [100] have recently measured α^+ of Cr, Fe, and Cu as a function of Ni composition in the Cr-Ni, Fe-Ni, and Cu-alloys during 15 keV O_2^+ bombardment. The results show large fluctuations in ionization probabilities which causes artifacts in the depth profiling as illustrated in Fig. 7. There is a significant overshoot of the Ni^+ signal close to the interface during

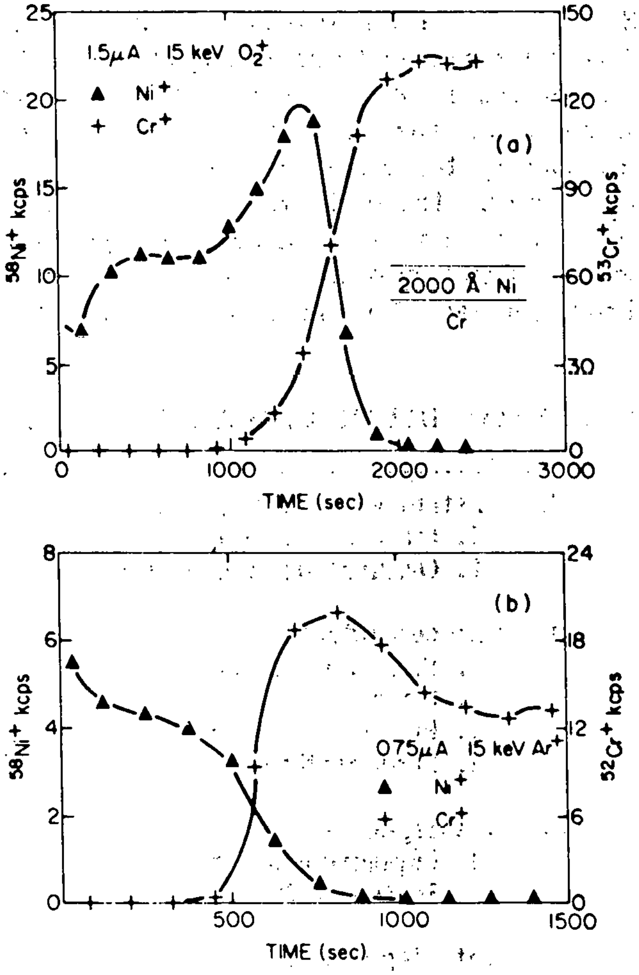

Fig. 7 The Ni^+ and Cr^+ depth profiles of the Ni overlayer on Cr: a) 15 keV O_2^+ beam, b) 15 keV Ar^+ beam [100].

profiling with O_2^+ beam. The use of an Ar^+ beam has eliminated this artifact. However, this is not always the case since an overshoot of Ni^+ was seen in the case of O_2^+ bombarded NiCr while an overshoot of Cr^+ was seen in the case of an Ar^+ bombarded target. Similar effects are expected in the case of SCANIIR.

IV. INTERFACIAL RESOLUTION

All of the above effects can degrade the sharpness of an interface as detected by sputter depth profiling. Hofmann [38] has concluded they are additive according to the following:

$$\Delta Z = \left[\sum_{j=1}^{n} \Delta Z_j^2 \right]^{1/2} \tag{4}$$

where ΔZ is the total interfacial width and ΔZ_j is the width of the interface resulting from the jth factor. Some of the factors causing broadening are shown in Table 1, and are categorized according to their dependence upon sputter time, sputter rate, or sputter depth. The only factors in Table 1 not previously discussed are the basic sputtering process and nonuniform ion beam. The latter refers to a nonuniform density of ion beam over the analyzed area; obviously, this would limit the relative depth resolution ($\Delta Z/Z$) to that of the beam nonuniformity. The basic sputtering process refers to the fact that sputtering is a statistical process and will not proceed layer by layer. Stated another way, some atoms in the second and third layer will be sputter-removed before all atoms in the first layer have been removed. Benninghoven [101] has proposed a simple model of

Table 1. FACTORS LIMITING DEPTH RESOLUTION IN SPUTTER PROFILING

I. Constant with time and depth
    1. Information depth
    2. Original surface roughness

II. Time dependent
    1. Enhanced diffusion
    2. Knock-in
    3. Preferred sputtering
    4. Implantation

III. Rate dependent
    1. Impurity adsorption
    2. Surface diffusion

IV. Depth dependent
    1. Basic sputtering process
    2. Sputter-induced topography
    3. Nonuniform ion beam

this process which predicts that $\Delta Z/Z$ varies as $Z^{-3/2}$. Hofmann compared a number of different measurements from the literature to support his conclusions that the sputter process limited depth resolution for depths varying from 5.0 nm to 1000 nm. However, Hofer and Martin [28] have found $\Delta Z/Z$ to vary as Z^{-1} while Werner [102] found it to be independent of Z. Thus, interfacial resolution is controlled by different factors in different experiments. Hofer and Martin [28] do show, however, that sputtering with a reactive N_2^+ beam did improve their interfacial resolution.

V. HOW TO IMPROVE DEPTH RESOLUTION

Various ways in which sputtering degrades depth resolution have been discussed. It is practically impossible to eliminate all these limitations. However, one can try to minimize some of these effects.

For example, in order to improve on the depth resolution degradation caused by cone formation, one can use N_2^+ beam for sputtering or a high background O_2 pressure (~6.5 x 10^{-3} Pa) in the sputtering chamber and sputter with Ar ions [28,103,105]. Since the development of microtopographical changes also depend on the thickness to be profiled, optimization of the depth resolution in profiling would require an initially polished surface and thinner films. Multiple ion beams and sample rotation also minimize the development of topography. Impurities arriving at the surface from sputtering of the target holder could be avoided by mounting the target on a pedestal.

The degradation of depth resolution resulting from cascade mixing and recoil implantation may be improved by using low primary ion energy, high primary ion mass and high angle of incidence relative to the surface normal [68,106]. This would also reduce the effect of ion implantation because the ions will not be able to penetrate deep enough to remain in the solid. Also, the equilibrium in terms of preferential sputtering and implantation would be reached quickly, thus minimizing their influence in the depth profile.

The other phenomena, like the matrix effect in SIMS and SCANIIR, cause artifacts in depth profiling which are not easily avoided. Quantitative analysis of interfacial impurities may be possible using the "cascade dilution" method proposed by Williams and Baker [26]. This method involves dilution of the interfacial impurities by ion bombardment to such an extent that the ion yield is characteristic of the matrix. If one is interested only in changes in the sharpness of the interface, deconvolution may be used to increase the ability to detect changes [e.g., for diffusion concentration profiles) [107]. However, sputter profiling will not typically allow atomic resolution of interfacial regions and generally destroy structural and chemical state information at the interface. Therefore, new approaches are required to determine these interfacial properties, and improved techniques are desirable to minimize the above limitations. These are emphasized in the conclusions concerned with microstructural and microchemical characterization of interfaces (Chapter XV).

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X. BASIC RESEARCH NEEDS AND OPPORTUNITIES AT THE SOLID/SOLID INTERFACE: DIFFUSION

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ABSTRACT

An attempt is made to identify the basic research needs and opportunities which exist with respect to solid/solid interfaces and diffusion in materials and devices relevant to solar energy. Firstly, the generic problems characteristic of solar energy materials are considered. Secondly, the specific problems involving solid/solid interfaces and diffusion which are peculiar to solar energy materials are described and discussed. Thirdly, the research needs and opportunities associated with these phenomena are identified. General areas of research considered to be either "crucial", "important" or "useful" include the following: (1) development of microstructure; (2) microstructural stability; (3) dependence of diffusion and nucleation of new structures on external influences (especially thermal cycling, electric fields, radiation fields); (4) acquisition of standard reference data (solid/solid interface diffusion and electrical data); and (5) relationship between microstructure (and its time-dependence) and electrical, optical and mechanical properties of composite materials. Finally, priorities are assigned to a number of research areas falling within the above categories.

I. INTRODUCTION

In this chapter, we attempt to identify the basic research needs and opportunities which exist with respect to S/S interfaces and diffusion in materials and devices relevant to solar energy. The chapter is organized along the following lines.

We first (Section II) identify the <u>generic</u> problems which seem to us to be characteristic of solar energy materials in order to put the entire problem in perspective. We then proceed (Section III) to identify specific technical problems involving diffusion at S/S interfaces. Finally, in Section IV, we describe the research needs and opportunities associated with these phenomena and assign priorities to them.

It should be noted at the outset that we deliberately limit our attention to problems which are <u>uniquely</u> related to solar energy. As a result, the focus is mainly on photovoltaic/photochemical/photothermal processes and devices. We do not consider energy storage problems. While such problems are of obvious significance for solar energy, they also are of importance to other energy technologies and, consequently, are receiving widespread attention elsewhere. Furthermore, they have been the subject of other workshops. Also, we do not consider problems associated with more indirect solar technologies such as wind, ocean thermal energy conversion, and biomass. Wind energy technology is involved with the technology of massive high strength structures which is already being pursued by, for example, air frame manufacturers. Ocean thermal technology primarily involves the L/S interface (see Chapter XI) and is intimately related to other technologies presumably being pursued, for example, by the Navy. Similarly, many

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of the elements comprising biomass technology are under active study and development elsewhere, and it therefore seemed unnecessary to consider them separately within the present context.

II. GENERIC PROBLEMS OF PHOTOVOLTAIC, PHOTOCHEMICAL, AND PHOTOTHERMAL SYSTEMS

A. General Characteristics of Solar Collectors

The diffuseness of the solar radiation on the earth's surface requires that solar collectors cover immense areas in order to contribute significantly to the energy requirements of the nation. The size of the collecting arrays and the requirements of low cost and long term operation in hostile and varying environments dictate the fabrication and operation of components which have features unique to the solar energy industry. In the area of photovoltaics, the emphasis in the near future will continue to be on flat plate nonconcentrating collectors composed of cells made from single-crystal Si by conventional techniques, and on high-efficiency single-crystal GaAs cells used with concentrators. The concentrating systems will in all likelihood not be cost effective compared to other energy sources, except in special applications (e.g., remote power peaks). To become cost effective, it is expected that flat plate systems will have to utilize Si cells made from thin film (~50 μm) polycrystalline materials grown on low cost substrates or from semicrystalline materials grown by low cost methods, e.g., ribbon growth, casting, etc., or possibly from organic thin films. Concentrator systems are expected to utilize multi-junction sandwich configurations such as Si/GaAs or spectrum-splitting devices with two or more single-junction cells. In the long term, it may be that thin film (~10 μm) GaAs polycrystalline cells, Cu_2/CdS, and other advanced systems will be developed to the point of economic competitiveness. Indeed, it may be that materials development will lead to a situation in which choices will have to be made between high performance, moderate cost, long lifetime systems and systems of lower performance and moderate lifetimes but extremely low cost.

Photothermal systems are expected to follow a development from flat plate collectors, which are becoming fairly common today, to the immensely more complicated power-tower type systems (Chapter II) that rely on acres of heliostats for solar concentration.

Common to all of these systems, and hence the focus of our attention, is the requirement of the development of multilayer, thin film, polycrystalline components which will operate reliably over long periods of time.

B. Materials Morphology, Chemical Integrity, and Physical Properties

The preparation of large area, multilayered, thin film polycrystalline devices leads to certain morphological problems which vary greatly depending upon the techniques by which the films and layers are made. Diffusion between interfaces and along grain boundaries, and hence, the electrical and thermal properties of the material will undoubtedly depend strongly on this morphology. Moreover, the stability of the device also depends on the morphology, and hence on the fabrication and preparation techniques are employed.

Because of the intrinsic features of thin film fabrication techniques employed, the resulting thin film structures usually contain high densities of imperfections such as dislocations, grain boundaries, and interfaces which act both as sources and high mobility paths for diffusing species. During the long-time operation of thin film components, they may be subjected to high thermal stress, as well as electric and radiation fields. Such operating conditions imply a dynamic chemical environment about which very little is known at present. We may also expect induced defect generation, high mobilities, and reactivities of the various chemical species present, and a concommitant degradation of long-time device performance.

As a consequence of these expectations, we may be certain that severe lifetime problems will be encountered because of the induced changes in the electrical, optical, and thermal properties of the materials. These considerations are, obviously, of vital concern to the component and device designers. Furthermore, the relationships between the morphology, the chemical integrity, and the induced changes in the physical properties are complex, beyond current theories and experience, and can only be gleaned by empirical means.

Specific examples of some typical structure-property relationships are:

(1) dependence on morphology of electrical conductivity changes due to diffusion along grain boundaries;

(2) dependence of optical absorptivity of a composite particle/matrix selective absorber on particle size distribution; and

(3) dependence of contact resistance and junction rectification on the chemical nature of the interface.

Determining the structure-property relationships, as illustrated by examples (1)-(3), demands a close link between basic materials science and the design and development of devices and components.

C. Fabrication and Operation of Solar Devices

Because of the great interest in thin film multilayer devices in the electronics industry, it is useful at this point to introduce the idea of "make or buy" decisions. In other words, what are the key problems in the fabrication and operation of large area, low cost, thin film multilayer components not addressed by manufacturers of nonsolar related components? These are the problems on which the research emphasis must be placed, and hence, are the problems considered herein.

Clearly, photovoltaic applications require the fabrication of inexpensive, uniform, large area layers of prescribed properties such as high optical absorption, low electron-hole recombination, and long minority carrier lifetime. Similarly, photothermal applications require layers of materials with high absorptivity over the solar spectrum and low emittance in the infrared along with satisfactory thermal conductivity properties. For both photovoltaic and photothermal systems, layered materials with suitable reflectivity or refractive properties are needed for solar concentrators.

Once in operation, these systems will be expected to perform without serious degradation for periods of up to 30 years. They will be subjected to corrosive and/or abrasive environments containing moisture, dust, atmospheric pollutants, UV radiation, and chemicals in cleaning agents. They will also be subjected to thermally induced stress, high electromagnetic fields due to static electrical junctions, and dynamic optical effects. In the case of systems utilizing high concentration ratios, radiation damage from high photon fluxes and high temperature cycling may be expected.

III. SPECIFIC TECHNICAL ISSUES PERTAINING TO DIFFUSION AT THE S/S INTERFACE

Having described some of the generic problems in the previous section, we now turn our attention to the description and classification of the range of specific technical issues and scientific phenomena which must be considered in connection with diffusion at S/S interfaces in multilayer thin film solar energy devices.

A. Classification of Relevant S/S Interfaces

We first define an "interface" as the boundary separating two regions with different physical characteristics. A large variety of interfaces may be present in typical solar energy devices. These may be classified according to several different schemes as indicated below:

(1) classification according to electrical properties: in this scheme, a region may consist of metal (M), a semiconductor (S), or an insulator (I). Interfaces may then be of the types: M/M, M/S, M/I, S/S, S/I, etc.;

(2) classification according to the structure of the two regions and the interface: here, a region may be either crystalline (C), or amorphous (A), and the interface structure might be of several types such as the following: C/C (coherent), C/C (semicoherent), C/C (incoherent), or C/A;

(3) classification according to the electrical properties of the boundary itself: included here are p-n junctions; contact interfaces between metals, semiconductors, or insulators which may be either rectifying or injecting; etc.; and

(4) classification according to the change of the refraction at an interface: such a classification is useful, for example, in optically graded transparent materials.

B. Areas of Research Concerned with the Optical and Electrical Properties of S/S Interfaces

The interfaces of interest generally appear in structures which are fabricated by a wide range of techniques (see Chapter XIV) and may be characterized with respect to structure and composition by a variety of high resolution techniques. In recent years, a number of high resolution techniques has become available which are capable of revealing the fine structure of interfaces, often at the atomic level. These include diffraction contrast imaging in the electron microscope [1], direct lattice resolution in the HVEM [2], FIM [3], and analysis of diffraction patterns from the interface region [4]. The chemical composition in the boundary region has been studied by a variety of techniques including STEM [5], AES [5], etc. A detailed consideration of this topic is given in Chapter XV.

Once information is available regarding the structure and chemistry of the S/S interface, a major goal is the determination of the resulting electrical and optical properties and understanding and modeling the atomic processes which might occur at the interface. Typical atomic processes are diffusion, boundary migration, impurity segregation, etc.

In the following, we classify the S/S interface diffusional processes of particular interest with respect to solar energy devices.

C. S/S Interface Diffusional Processes of Major Interest in Solar Energy Devices

1. Major Aspects of the S/S Interface Diffusional Problem

A process of major interest is the rate at which atoms jump in the vicinity of an interface and thereby produce atomic diffusion. Related to this is the change in chemistry and the types of reaction products which may form at interfaces as a result of diffusion. Also of importance are changes in electrical or optical properties which may accompany the diffusion.

2. Classification of Diffusional Processes

The types of diffusional processes which may be of importance include the following:

(1) diffusion through the lattice to/from interfaces: in these processes diffusion occurs through the lattice between interfaces which act as sources or sinks for the diffusing atoms. Of major interest is whether the kinetics are controlled by the diffusion rate of the species through the lattice or by the rate at which the atoms are gained and lost at the interfaces. The process occurs at the maximum possible rate under the "diffusion controlled" condition and at rates which may be much lower if the process becomes "interface controlled". There are many important phenomena in solar energy devices which may be associated with lattice diffusion between interfaces. These include, for example: (1) the growth/dissolution of intermediate layers in initially layered structures; (2) the coarsening ("Ostwald ripening") of fine dispersions of second phase particles; and (3) the precipitation and growth of second phase particles at interfaces;

(2) diffusion along interfaces: it is well established [6,7,8] that atoms generally diffuse more rapidly along grain boundaries and interphase boundaries than in the lattice, and that such diffusional short-circuiting can often predominate at the relatively low temperatures (i.e., $T/T_m < 0.5$, where T_m is the melting temperature) characteristic of solar energy device fabrication and operating temperatures. The activation energy for interface diffusion is usually lower than that for lattice diffusion and, hence, lattice diffusion tends to become "frozen out" relative to interface diffusion as the temperature is reduced. The processes which occur when atoms are involved in diffusion along boundaries are of several different types which have been classified in the literature [9,10]. At low temperatures and relatively short times, atoms diffuse only along the interfaces since they are relatively immobile in the lattice. As the temperature is raised, or the diffusion time is increased, they eventually enter and spread out in the lattice as well as diffuse along the interface. Ultimately, each atom will sample both the lattice and the interface randomly, and therefore execute a random walk through both the lattice and

the interface. These phenomena may be altered if the interface migrates during the diffusion process as it might if the initial interface structure is unstable. In such a case, the migrating interface visits atoms in the lattice as it sweeps through the material and therefore may induce a considerable amount of atomic mobility which might ordinarily be absent in the specimen;

(3) diffusion induced grain boundary migration: it has recently been recognized [11] that a significant amount of bulk alloying/de-alloying can be induced by grain boundary migration in situations where bulk diffusion is essentially frozen out. In this phenomenon, solute atoms diffuse along the boundary and induce the boundary to migrate. The simultaneous interface migration and diffusion along the interface then causes bulk alloying/de-alloying in the wake of the boundary. Such a process could conceivably cause extensive compositional changes in thin film devices over long time periods;

(4) S/S interface migration: grain boundary and interphase boundary migration must occur by the detachment of atoms from one crystal followed by ultimate attachment to the adjoining crystal. This process, therefore, requires some thermally activated atomic motion in the interface. Furthermore, under usual circumstances the rate of migration of the boundary is drastically slowed down by the presence if impurity atoms segregated at the boundary which must be dragged along as the boundary migrates [12]. The overall migration rate of the boundary is therefore dictated by a complex combination of diffusional jumping processes at and near the core of the boundary. It is evident that the rate of this process can be profoundly influenced by the impurity species present;

(5) S/S interfaces as sources or sinks for atoms: there is considerable evidence that grain boundaries generally operate as relatively efficient sources or sinks for atoms at driving chemical potentials as low as 10^{-5} eV. It is now believed [13] that the source or sink operation occurs as a result of the migration of climbing grain boundary dislocations across the interface in a manner analogous to the migration of steps across free surfaces during crystal growth/dissolution. The climb process involves the diffusion of defects to/from the dislocations and, hence, a considerable amount of boundary diffusion is involved. Such source or sink operation is essential for sustaining the Herring-Nabarro and Coble type diffusional creep which might occur in thin film devices in response to applied or internal stresses; and

(6) mechanical relaxation processes at S/S interfaces by diffusional mechanisms: the defect structure produced by mechanical deformation may be relaxed, to a considerable degree, at grain boundaries by grain boundary diffusional processes which are important even at relatively low temperatures. Examples include the dissociation of impinging lattice dislocations [14] at boundaries, and the thermally activated climb and mutual annihilation of dislocation debris in boundaries [15]. These processes could be effective in relieving effects due to mechanical straining in thin film devices generated, for example, by differential thermal expansion (see Chapters XIII and XIV).

D. Key Issues

There is a general need to study the rates of chemical and structural changes brought about by the S/S interface diffusional processes described above. The results should be used to model and understand the kinetics of these processes and ultimately to understand corresponding changes in electrical and optical properties. Such a procedure will be necessary to develop a sufficient level of understanding to make possible lifetime predictions for thin film solar devices. This point is discussed further in the following section.

IV. RESEARCH NEEDS AND OPPORTUNITIES

A. Format

Following the introduction of the scope of our considerations in the preceding sections, we now provide our recommendations for basic research on diffusion at S/S interfaces of importance to multilayer, thin film solar energy conversion devices. A synopsis of our recommendations is given in Table 1. The priority ratings given in this table correspond to:

1 = crucial; indicates basic research required to establish the technical feasibility and unit manufacturing cost of multilayer solar energy converters.

2 = important; indicates basic research required to establish the lifetimes and reliability, and hence the total life cycle cost of multilayer solar energy converters.

3 = useful; indicates basic research expected to be required for lifetime and reliability assessment, but in subject areas about which so little is known that a high degree of uncertainty exists in the expectations.

The text of much of this section consists of a commentary of the entries in Table 1.

B. Research Strategy

It is useful to distinguish clearly between basic research, the result of which is information, and advanced development, the result of which is a working prototype device along with a series of cost and reliability estimates. In this report we consider only basic research, the outputs of which are required as inputs for the generation of accurate cost and reliability estimates by advanced development programs. We envision such useful basic research to consist of the following three necessary and irreducible components:

(1) the selection and characterization of pertinent model systems exhibiting the essential features of the more complex engineering systems. In particular, thorough characterization of the composition, structure, and properties of these model systems is mandatory in order to establish the scope of the phenomena investigated;

(2) the development of characterization techniques capable of measuring phenomena on the time and distance scales and with the precision required to describe the phenomena under examination. In many of the items noted in Table 1, new instrumentation, not yet available, is required to examine the microscopic processes which are involved; and

(3) modeling of the experimental results obtained. Useful models exist at two separate and diverse levels. Phenomenological models are those that contain thermodynamic, kinetic, and macroscopic transport coefficients (e.g., concentrations, activation energies, conductivities, lifetimes, etc.). Microscopic models utilize atomistic structural data as input and seek to predict the various transport coefficients utilized in the

phenomenological models, and to identify the nature and characteristics of the phenomena incorporated in such models. Thus, phenomenological models form the link between basic materials research and engineering device performance, whereas microscopic models constitute the link between materials research and the laws of chemistry and physics. We stress that accurate, tested models of both types of the phenomena listed in Table 1 are rarely available and are absolutely critical to the assessment of the long term reliability of solar energy conversion devices.

Many so-called "basic" studies presumably pertinent to solar energy conversion consist of only fragments of the three requisite activities listed above. Such incomplete studies do not deliver good value to the solar energy program because their output is not cast in a form (i.e., a well understood phenomenological model or standard reference measurements that are directly useful to advanced development programs). Thus, one of our major recommendations is procedural: that the basic research activities that are pursued consist of all three critical ingredients and that their inputs be cast in a form which is directly usable by the appropriate advanced development groups.

1. Development of Microstructure

The first area in which we recommend basic research is the identification and characterization of diffusion phenomena involved in the formation of multilayer thin-film structures. Since most of the processes utilized to produce these structures (e.g., LPE, CVD, sputtering, etc.) involve energetic atomic species, the phenomena associated with the growth of these structures occur in entirely different environments (e.g., higher temperature) than those experienced in the operation of devices based on these structures. The major generic topic of research is the dependence of the microstructure of multilayer devices on the process variables which characterize the fabrication technologies utilized to produce them. Detailed recommendations for studies of specific systems are given by the study group on film formation (see Chapter XIV). We include this topic here to stress our procedural recommendation that sponsored research incorporate adequate characterization and modeling efforts, rather than be confined to empirical property-process correlations.

In addition, we include as a special research topic one which we consider necessary for establishing the technical feasibility of devices built on "low cost" substrates, i.e., the diffusion of impurities either through the bulk or along interfaces from the substrate into the active layers and the diffusion of impurities between the different layers and/or grains characteristic of the composite structure. We emphasize that it is the diffusion, which occurs during the fabrication steps, which most frequently degrades the performance of devices based on "low-cost" technologies. Therefore, for such devices, diffusion studies are required to establish a sound basis for systematically improving initial performance as well as long-term reliability.

2. Microstructure Stability

A critical factor affecting the reliability of a multilayer thin film device is the long term stability of its microstructure under operating conditions. This issue is particularly acute for polycrystalline and amorphous films because they are inherently nonequilibrium structures which are unstable under the thermally induced stresses encountered in solar converter operations. In addition, sharp heterojunction interfaces and steep concentration gradients also degrade under such conditions. The ability to predict the rate of change of impurity concentrations, defect densities, and compositional gradients under realistic time-temperature conditions is the sine qua non of accurate reliability forecasting. Unfortunately, adequate data and models to make such predictions are rarely available, even for common photovoltaic structures based on polycrystalline Si, GaAs, CdS, and Cu_2S, and for common composite selective absorbers for solar thermal devices. Therefore, the acquisition and analysis of suitable data on which to base reliability analysis of such structures is a matter of some urgency to the U.S. solar energy program.

The first major area in which we recommend basic research is the interdiffusion between chemically dissimilar layers. Some requirements for such studies are known from the widely studied model system of metal (Au, Al, In) overlayers on well-characterized (110) surfaces of GaAs. Analytical techniques suitable for determining structure and composition on an atomistic scale with sensitivities of 10^{-2} to 10^{-3} atom fraction are required. Successful applications of LEED for atomic structure and synchrotron radiation photoemission spectroscopy for atomic composition have been made to date, but heavy investments are required to render these techniques utilizable on a routine basis and to develop other techniques like SEM which possess high lateral resolution. The form of the phenomenological models of the diffusion processes involved are known for bulk and grain boundary diffusion in GaAs, and the magnitudes of the relevant parameters in these models are known to an order of magnitude for certain metals (e.g., Au). Expansion and refinement of the work on GaAs, as well as extension of Si, CdS, Cu_2S and other photovoltaic materials, would be appropriate. Microscopic models of the atomic motions involved are virtually nonexistent, so their construction should be encouraged.

The second major area in which we recommend basic research is the study and control of the segregation and diffusion of impurities at grain boundaries. The specific engineering issue motivating the high priority given to this recommendation is the critical need to "passivate" grain boundaries in polycrystalline layers of photovoltaic devices. We utilize the term "passivate" in the engineering sense of rendering these boundaries inconsequential to device performance. In particular, the electrical properties of polycrystalline materials typically require stabilization. Thorough studies of the segregation and diffusion of impurities in grain boundaries in model systems are unavailable even for Si or GaAs. Advances in instrumentation to achieve a spatial volume resolution of $\Delta V \simeq 1\ nm^3$ and a sensitivity of $\sim 10^{-4}$ atom fraction are needed for realistic studies of the dynamics of atomic diffusion along such boundaries.

A particularly pressing theoretical issue is the development of criteria for determining the electrical activity (or lack thereof) of individual grain boundaries. Thus, models of the cogent properties of these boundaries must include their electronic behavior (as traps, recombination centers, etc.) as well as the phenomenology and dynamics of their migration and that of impurities along them.

The final area of microstructure stability in which we recommend basic research is the investigation of the long term stability of nonequilibrium thin film structures. Since systematic work in this area is almost nonexistent and failure mechanisms are not well known, initial studies will, of necessity, be exploratory in character. Important applications abound outside, as well as inside, the solar energy context as, e.g., in the stability of Schottky barrier gates and MOS structures in the micro-electronics industry.

3. Dependence of Diffusion and Nucleation on External Influences Peculiar to Solar Applications

Unique features of the solar converter environment for multilayer thin film structures include the occurrence of thermal cycling and that of a flux of electromagnetic radiation, both effects being relatively large in concentrator systems. Therefore, the life of solar converters depends on the influence of thermally induced stress gradients and of radiation-induced defects, as well as carrier and thermal gradients on the microstructure and properties of thin film structures within these converters. We anticipate that the thermally induced stress fields and internal electrostatic fields will affect the microstructure primarily via modification of the parameters (e.g., activation energies) in the diffusion kinetics, whereas the solar photon flux will generate defects and carriers as well as thermal gradients. Consequently, we list basic research on these two different types of external influences as separate topics in Table 1. It is hoped that the superposition of both types of influence can be described by models in which their effects are treated independently but simultaneously. The crucial importance of embedding the results of experimental studies in phenomenological models embodying a common structure is self evident in those areas in which actual devices are subjected to multiple strong external influences acting in concert. Moreover, these models should also provide the vehicle for the design and evaluation of accelerated life tests—a critically important engineering activity.

4. Acquisition of Standard Reference Data

In addition to the issue of the completeness of basic research studies, dealt with in Section IV (B), the suitability, standardization, and availability of standard reference data used for engineering design are of obvious significance in the planning and funding of basic research pertinent to solar energy. An area in which data of improved accuracy and reproducibility are urgently required is that of "low" temperature S/S interface diffusion (i.e., for $T/T_m < 0.5$). Present data exhibit unacceptable scatter due both to inadequate sample characterization and to differing methods of analyzing the raw measurements.

The acquisition of better low temperature diffusion data is indicated as a special item in Table 1 although the issues of the adequacy and standardization of data acquisition and analysis are obviously more broadly relevant, especially when such data must be used for engineering design and reliability assessment. Data used for these purposes must be widely available in a standard format and for a variety of materials. This issue is listed separately in Table 1. For example, adequate thermal diffusion data for reliability analysis on "newer" materials like GaAs and CdS-based materials is simply not available at the present time. A program involving data acquisition, standardization, storage, and retrieval is needed for accurate assessments of the long term reliability of multilayer thin film components of solar converters.

5. Relationship Between Microstructure and Properties

A major focus in this report has been on the stability of the microstructures of multilayer thin film structures. The reason for this focus is the status of these microstructures as the primary determinant of the electrical, optical, and mechanical properties of the thin film components which are of interest in the operation of solar energy converters. Thus, the final critical area of recommended research is the development of explicit relationships between the microstructure and the physical properties of interest. This activity is indispensable for the evaluation of device reliability, because one must convert data on the spatial and temporal behavior of the material consituents of the device into quantitative measures of its performance over time and under different operating conditions. Specifically, predictive models must be developed which link the time dependent microstructure of a thin film structure to its local thermal conductivity, electrical conductivity, electron-hole recombination coefficient, optical properties, and carrier lifetimes. Some progress along these lines in the area of the optical properties of composite films (used, e.g., as selective absorbers) has been made in recent years. Nevertheless, much remains to be done, especially for the prediction of the electrical properties of polycrystalline materials for photovoltaic applications. Therefore, the development of predictive models of the properties of composite materials is an area of intellectual endeavor of critical importance to the ultimate development of reliable, low-cost solar energy converters.

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Table 1. RECOMMENDATIONS FOR FUTURE RESEARCH ON S/S INTERFACE DIFFUSION

Research Topic	Relevance	Priority*
I. Development of Microstructure		
A. Determine relationship(s) between film microstructure and process variables.	Necessary to improve lifetime and performance of devices but not enough information is available to assess reliably effects on the technical and economic feasibility and lifetime performance of devices.	3
B. Investigate diffusion of impurities through the lattice or along interfaces from and into substrates and between layer grains of composite structures.	Crucial to fabrication of cost effective devices and components.	1
II. Microstructure Stability		
A. Investigate interdiffusion between chemically dissimilar layers.	Required for device stability and performance; basic processes are not understood.	2
B. Investigate grain boundary passivation.	Required for acceptable device performance; basic processes are not understood.	1
C. Investigate stability (long term) of nonequilibrium thin film structures.	Necessary to understand long-term performance of devices but not enough information is available to assess reliably the effects on the technical and economic feasiblity and lifetime performance of devices.	3

Table 1. RECOMMENDATIONS FOR FUTURE RESEARCH ON S/S INTERFACE DIFFUSION (continued)

Research Topic	Relevance	Priority*
III. Dependence of Diffusion and Nucleation on External Influences (especially thermal cycling, electric fields, and radiation fields).		
A. Conduct exploratory research on well defined model systems to identify influence of electric fields and stress fields on diffusion, grain boundary segregation, and kinetics.	Needed to provide information on the stability of devices and as a basis for accelerated life testing procedures. Information is necessary because of severe operational environments of devices.	2
B. Conduct exploratory research on well defined model systems to identify changes in diffusion kinetics due to radiation induced carriers, defects, and local thermal gradients.	Same as IIIA but not enough information is available to assess reliably the effects on technical and economic feasibility and lifetime performance of devices.	3
IV. Acquisition of Standard Reference Data (S/S interface diffusion and electrical data).		
A. Acquire improved data to assess long term stability of standardized and well-characterized systems.	Required to provide technical basis for long-term stability assessment and testing.	2
B. Acquire standardized data base for potentially useful solar energy materials.	Same as IVA but not enough information is available on less-investigated materials systems to ascertain the benefits of substituting new materials for current technological materials.	3

Table 1. RECOMMENDATIONS FOR FUTURE RESEARCH ON S/S INTERFACE DIFFUSION (concluded)

	Research Topic	Relevance	Priority*
V.	Determine Relationship Between Microstructure (and its time-temperature dependence) and the Electrical, Optical and Mechanical Properties of Composite Materials.	Required to provide relationships between research topics I-IV listed in this Table and the measured device performance.	2

*Priority ratings:

1 = CRUCIAL:	Indicates research required to establish the technical feasibility and unit manufacturing cost of multilayer solar energy converters.
2 = IMPORTANT:	Indicates research required to establish the lifetimes and reliability, and hence the total life cycle cost, of multilayer solar energy converters.
3 = USEFUL:	Indicates research expected to be required for lifetime and reliability assessment, but in subjects about which so little is known that a high degree of uncertainty exists in the expectations.

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XI. BASIC RESEARCH NEEDS AND OPPORTUNITIES AT THE SOLID-LIQUID INTERFACE

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ABSTRACT

A panel was convened to deliberate on basic research needs and opportunities at solid-liquid interfaces important in solar energy materials science. The committee concluded that needs exist in two areas, photoelectrochemistry and solar energy-related degradation phenomena. Research is recommended to (1) develop special real-time in situ analytical techniques in order to probe and study solid-liquid interfaces, (2) formulate a theory that incorporates the properties of the solid-liquid interface, (3) generate new materials for photoelectrochemical conversion systems, (4) study photo-assisted synthesis and electrocatalysis, and (5) investigate the mechanisms of electrochemical degradation (especially photocorrosion), mechanical degradation (especially corrosion fatigue), and erosion in solar energy systems. These recommendations, together with their background and justification, are discussed.

I. INTRODUCTION

Our understanding of the properties of interfaces is still in its infancy. Yet, all materials used in existing or emerging solar technologies involve an interface S/G, S/S, S/L, and it is the interactions at this interface that often govern the properties, and thus the usefulness, of the material. With this in mind, the members of the S/L interface panel examined each of the solar energy technologies and attempted (1) to define existing and potential problem areas involving S/L interactions, and (2) to identify generic issues in need of research. The research needs were found to fall conveniently into two major categories -- photoelectrochemistry, particularly in the areas of electrochemical photovoltaics and photoelectrosynthetic devices, and degradation phenomena related to corrosion and erosion.

The major conclusions reached concerning these research topics were as follows:

(1) The development of techniques for in situ S/L interface analysis was identified as crucial to the advancement of our understanding of both photoelectrochemistry and solar energy-related degradation phenomena.

(2) The development of microscopic theoretical models is essential in order to understand the behavior of electrochemical photovoltaic cells and photoelectrosynthetic devices and to provide guidance and direction for further research in the area of photoelectrochemistry.

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* Chairman

(3) Until proven and reliable interface analysis techniques and tractable theoretical methods are in hand, research that involves the exploration of novel electrolytes, solvents, redox couples, semiconductors and surface modification treatments appears to be the best way to advance the field of photoelectrochemistry in the near term.

(4) Degradation phenomena pervade all solar energy technologies. In fact, virtually every generic form of corrosion is found to occur and, in many cases, the corrosion problem is not unique to solar energy. Because of this pervasiveness, research to obtain a basic understanding of corrosion and erosion phenomena is viewed as essential and should be strengthened.

(5) Fundamental studies of corrosion and erosion are being pursued worldwide. It is recommended that this experience be utilized as much as possible in solar energy technology advancement. Nevertheless, there are two areas that are deemed to be special: degradation at photoelectrochemical interfaces and corrosion fatigue. The thermal-induced stress cycles likely to occur in solar power tower, Ocean-Thermal Energy Conversion (OTEC), and wave power systems make corrosion fatigue worthy of special attention. One of the primary factors limiting electrochemical energy conversion devices is the instability of the semiconductor interface towards aqueous solutions.

II. PHOTOELECTROCHEMISTRY

During the last eight years, remarkable progress has been made toward increasing the efficiency of photoelectrochemical devices. Many of the advances that have given rise to this success have occurred by largely empirical approaches to problem solving. However, a plateau in this progress has been reached which now threatens to limit the potential advantages of photoelectrochemical conversion (elimination of S/S junctions, intimate chemical contact between the semiconductor and electrolyte, and the ability to use polycrystalline materials). This plateau is due to the instability of photovoltaic devices toward photoconversion and the unavailability of efficient photoelectrocatalytic electrodes. Advancing beyond this point by empirical methods alone is possible, but establishment of fundamental knowledge about the character of the S/L interface appears essential.

A. Long Term Generic Research Needs and Recommended Research

1. Interface Analysis Techniques

Electrochemistry, in its present state, is equivalent to the study of the solid-vacuum interface before the advent of analytical probes for the study of surfaces. As techniques for probing these surfaces have evolved, significant advances in our understanding of surface physics and chemistry have ensued. The existence of such tools for S/L interface studies would be expected to have a similar impact. There is a need for the development of techniques and for concepts that can be used to determine structure, composition, chemical states, and electronic structures specific to the interfacial region. We recommend that basic research be undertaken to develop tools with which to describe a S/L interface. These tools could involve the following: (a) in situ probes which look at the actual interface such as the optical techniques of IR spectroscopy, optical absorption, modulation spectroscopy (electroreflectance, composition-modulation), Raman spectroscopy, and other methods commonly used for the study of solids and liquids; and (b) techniques and concepts developed for the study of the S/G or solid-vacuum interfaces combined with the use of methods of environmental manipulation.

The availability of reliable methods for S/L interface analysis should contribute significantly to the following: identification of surface states (both intrinsic and extrinsic), elucidation of the structure of the double layer, establishment of charge donating or accepting species as well as the presence and influence of intermediates, and development of microscopic theoretical models of interfaces in photoelectrochemical systems.

2. Theoretical Models

Much of the theory of photoelectochemistry is based on classical statistical and thermodynamic concepts and on solid state physics, without consideration of the microscopic processes often involved in the interfacial region. This has arisen, in large part, because electrochemists have tended not to pay enough attention to the energetics and physics of the solid (e.g., density of states, surface states), while solid state physicists have usually dealt with the theory of solids and have paid little attention to the interface. The interfacial region must be viewed as chemically unique both from the solid and the liquid.

The concepts in current use are largely thermodynamic in nature; yet the processes in the interfacial region predominantly affect the kinetics of electrochemical reactions. A theory of double layer structure has emerged, but it is largely phenomenological in nature. Attempts to approach the double layer and kinetic electrochemistry at interfaces, quantally, have virtually just started [1] and much more needs to be done.

There is a crucial need for basic research on theoretical concepts and models specific to the S/L interface. We recommend that this research include the development of: (a) an understanding of the solid surface and the structural, compositional, and electronic changes which ensue from electrolyte contact, especially,

(1) surface states arising from properties of the solid and their modification by adsorption;

(2) interfacial states arising from chemical interaction of the solution with the solid surface;

(3) electrolyte electronic structure as it relates to charge transfer;

(4) adsorption kinetics and thermodynamics of electrolyte species and the formation and determination of active inorganic and organic intermediates; and

(b) the formulation of a global model of the liquid better suited to extension into the interfacial region.

If one is to understand the problem of charge transfer* across a solid-electrolyte (S/E) interface, it is essential to have available a theory that describes the behavior of the electrons on both sides of the interface in a self-consistent manner. While the solid is well-documented in this respect, the same is not true of the electrolyte. At present, the fluctuating energy mechanism [3] is normally used to model the electronic structure of the electrolyte for charge transfer purposes. Such an approach is limited because it is unable to take account of interface effects and, moreover, requires equating of the energy levels of the fixed-band structure of the solid with the ion levels resulting from temporal fluctuations [3].

To circumvent these limitations, a global rather than local model is needed so that interface states are included in a natural way. While not intending to preclude other possible theoretical methodology, two approaches suggested themselves now. The first is to treat the electrolyte (molten salt) as a lattice gas [4,5] and to develop an electronic theory of a spatially disordered two-component system of positive and negative ions, which is already available from the area of disordered binary alloys. Secondly, the theory of liquid mixtures could be used to provide the appropriate pair correlation function on which to base an electronic theory of the electrolyte in a similar fashion as has been done for the theory of liquid metals [6]. While both these approaches would lead to a band structure of the electrolyte, including interface states, the second approach has an added advantage -- the packing of the ions at the interface could be treated in a more realistic fashion.

In developing an understanding of the structural and electronic factors governing the interaction of electrolyte species with the solid surfaces at the interfacial region, the following factors of paramount importance should be studied: the role of the electrolyte in mediating energy transfer at the interface and its effect on charge transfer rates, the problem of adsorption at the S/E interface, ionosorption and the role of surface states in adsorption processes, direct and indirect interactions between adatoms in an electrolytic environment with the coadsorption of different species (to gain insight into the chemical reactions taking place at the S/E interface), and the role of the liquid structure factor in determining the microscopic features of adsorption and the effect of impurities in the solid on chemisorption.

Theoretical and experimental investigations of double layer structures at solid polymer/solution interfaces also appear to be warranted. Many photoelectrochemical devices may utilize separators made of ion-exchange membranes on porous polymers. While no charge transfer will be occurring at the interface, there will be selective charge and mass transport through the separators which will be strongly influenced by the interfacial region. This will affect the overall efficiency of the devices.

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* Electrons can tunnel through an electric dipole layer which, being thin, does not affect transfer process to any great extent [2].

3. New Materials

The primary factor that can be identified as limiting the practical implementation of photoelectrochemical energy conversion is the instability of the solid toward photon-assisted degradation of the surface. Large band gap semiconductors are available which are relatively stable; however, the low solar efficiency associated with these materials makes them impractical. Whether the eventual goal is electrical power production or the synthesis of transportable products, semiconductor performance and stability and their interrelationship are central to progress.

All currently available semiconductors are susceptible to photo-anodic decomposition, i.e., thermodynamically unstable toward photodegradation in aqueous solutions [7]. Only by introducing kinetic stability, which is accomplished by limiting the decomposition reactions or by competing with them, have useful systems been obtained. Clearly, there is a need for the development of new semiconductor materials that are thermodynamically stable when in contact with H_2O, and we recommend research in this area. This research could take the form of exploring the potential of either compositional modification of the bulk semiconductor or the development of special surfaces designed to eliminate detrimental reactions.

B. Near-Term Research Needs

1. Modified Electrode Materials and Surfaces

The development of interfacial probes and concepts is a long-term goal that will have a general impact on electrochemical science. The application of these concepts and techniques to the engineering of an advanced generation of photoelectrochemical devices, in particular, and of solar energy conversion devices and processes, in general, is a practical, long-term project. In the near term, we are confronted with a variety of options which may have an impact upon solar energy conversion technology but must be developed with the science in hand.

Some of the most viable options appear to be:

(1) GaAs/polyselenide aqueous cells: With suitable surface pretreatment, this cell can achieve up to 12% solar power conversion efficiency [8]. The primary limitation with this system is deterioration of the surface treatment.

(2) WSe_2/triodide aqueous cells: An 8% solar power conversion efficiency has been achieved with this cell system [9]. The primary limitation is the structurally associated defects. These can be reduced by surface treatment but the treatment does not last.

(3) Chemically derivatized Si: Improved stability can be obtained by interposing charge transfer bridge molecules (e.g., ferrocene derivatives) which protect the electrode [10].

(4) Nonaqueous systems: Water plays a dominant role in many photodecomposition reactions. By using organic or room temperature molten salt electrolytes,

many of these reactions can be avoided. Water then becomes a poison and must be rigorously removed, leading to encapsulation problems.

(5) Perovskites as kinetically stable photoelectrochemical materials: The limiting factor in their use is the low efficiency experienced due to the large band gaps involved.

Evidence has accumulated [10,11] which suggests that many of the limitations noted above might be overcome by judicious modification of electrodes and their surfaces. There exist a number of approaches for the manipulation of the properties of materials which have not yet been fully exploited and which could lead to valuable new insights and fruitful avenues for development. Those that appear worthy of further study and exploration are:

(1) doping of surface and near surface regions of the solid for favorable optical absorption properties, chemical stability, enhanced efficiency, and cost savings;

(2) tailoring surface topography for enhanced optical properties, e.g., reduction of the reflection coefficient at the interface;

(3) synthesizing materials for enhanced efficiency, performance properties, and stability;

(4) controlling semiconductor powder catalysis chemistry by special preparation methods (i.e., platinized TiO_2 powders [11]);

(5) developing p-n cells for both enhancement of available energy and better utilization of the solar spectrum by tailoring of both electrodes;

(6) developing novel electrolytes such as nonaqueous media (e.g., organic solvents) and room-temperature molten salts;

(7) exploiting some of the novel fabricative and physical properties of amorphous materials such as amorphous silicon and the chalcogenides; and

(8) modifying semiconductor surfaces by the adsorption of materials such as dyes for tailoring optical absorption, and ions (e.g., Ru^{3+} on GaAs), organics (e.g., tertbutylpyridine on WSe_2 and ferrocene on Si), or metals (e.g., Pt on TiO_2) which inhibit decomposition or enhance kinetics.

2. Thin Film Electrodes

Thin films offer a variety of potentially valuable attributes, e.g., they can be used to fabricate unique physical structures and can result in cost savings. Areas in particular need of study are:

(1) stability and interfacial behavior of thin-film polycrystalline electrodes (significant cost savings should accrue if polycrystalline rather than single crystal materials were to be used in solar devices);

(2) grain boundary chemistry such as impurity segregation and its influence on the S/L interface, grain boundary recombination and its control, and grain boundary diffusion;

(3) preparation techniques such as MBE, evaporation, sputtering, CVD, and LPE;

(4) heterojunction technology development for application to photoelectrochemical cells;

(5) exploration of the effect of solar concentration and the synergism of heat transfer with liquid-junction photovoltaic cells; and

(6) optimization of photoelectrochemical system efficiency which affords several opportunities for S/L interfacial research connected with cell design. These include encapsulation of the electrodes and the electrolyte, which is often harmful to polymers (i.e., polyselenides) for reasons that are not well understood, and development of conducting windows. Although, through the conductivity of the electrolyte, voltages will transmit to the semiconductor regardless of the position of the counter electrode, efficiencies can be increased by reducing the separation of the electrodes. Eventually this gives rise to the need for transparent electrodes which also act as the cell window [11].

3. Photo-assisted Synthesis and Electrocatalysis

The synthesis of C_2H_6 from acetic acid via a PhotoKolbe reaction using a TiO_2 electrode has been reported [12]. Photo-oxidation of methanol, ethanol, isopropanol, hydroquinone, and aromatic amines has also been studied [13,14]. Interest is growing in electrochemical means for separating biomass products and for converting them by electrocatalytic or photocatalytic methods to either chemical feedstock or liquid fuels. The interfacial electrochemistry associated with such electro-organic reactions has been the subject of only limited studies. Not only will electrocatalysis be important in chemical synthesis, but its significance in devices that may be used in connection with the storage of solar energy (e.g., H_2 production) is also unquestionable. Basic research in all aspects of the S/L interfacial science of electrocatalysis would be valuable in solar energy advancement. In particular, there is a need to develop an understanding of the dependence of electrocatalytic activation on electronic and structural properties of catalysts and on interfacial factors. Such studies should be strongly coupled to the development of models and theory. Investigation of electrodes which are modified by the attachment of materials that promote electrocatalysis appears to warrant further attention.

III. DEGRADATION MECHANISMS

As is the case for most energy conversion systems in use today, there is a strong need for a better understanding of the degradation processes at S/L interfaces. All generic forms of corrosion are found to occur in the operation of solar energy devices; and in many cases, these corrosion problems are not necessarily unique to solar energy. There are, however, several corrosion problems which are unique to solar energy due to specific material/fluid combinations currently being considered [15].

Corrosion research is actively being pursued by a great many workers around the world for all types of corrosion phenomena, and we would recommend that this experience be used by the solar energy community as much as possible. Even for widely studied phenomena such as stress-corrosion cracking, many possible mechanisms have been advanced. Since we still do not have a complete understanding of these processes, we recommend that research activities be increased to help advance our basic understanding of the synergistic effects of the many parameters which can be identified in practical engineering systems. Since current models have proved to be deficient in many respects, we feel that experimental techniques need to be developed which can be used to verify existing models or can lead to the proposal of new ones. In general, we lack adequate understanding of initiation processes at the S/L interface, and we need in situ techniques to examine this area.

A. Research Needs

A list of research needs for degradation mechanisms follows. Those related to solar energy devices are indicated by an asterisk (*).

1. Electrochemical Degradation Phenomena

The fundamentals of the electrochemistry at anode and cathode interfaces need greater clarification. This is especially true in the following areas:

(1) Local cell formation, active-passive transformations, and mechanisms of inhibition. An understanding is essential of metallurgical factors including thermochemical processing, segregation, and grain boundary effects as well as device cell behavior, both from mechanical design and from crevices developed by such phenomena as biofouling,* localized corrosion, and stress corrosion cracking.

(2) Photocorrosion* mechanisms at semiconductor-solution interfaces. In this connection, the processes of corrosion initiation, propagation, passivation-depassivation, and inhibition all warrant attention.

(3) Electrochemical phenomena in nonaqueous environments* such as fused salts at high temperatures, liquid NH_3 solutions, and liquid interfaces at very high temperatures ($\sim$1000-2000°C) which may be encountered in solar receivers in power towers.

2. Mechanical Degradation Phenomena

The mechanisms of the effects of mechanical factors (i.e., stress) in materials on their interactions with liquid environment need to be much better understood, especially in the following areas:

(1) stress-assisted general corrosion of materials (often noted in seawater attack or at metal/oxide interfaces where stress initiates spallation);

(2) corrosion fatigue due to variations in sunlight/shadow and diurnal changes, and thermal stress arising from the need to have good thermal transfer characteristics, due to size, wave actions, and variable currents, and due to variations in thermal stresses;

(3) stress corrosion cracking of materials in aqueous environments, in NH_3 and fused salts, and in liquid metals (embrittlement); and

(4) effects of H_2 on photoelectrochemical interfaces*, on passivation-depassivation reactions, and on mechanical properties of materials.

3. Erosion Phenomena

Erosion phenomena are of particular interest in solar energy technology in the following areas[†]:

(1) effects of moving fluids on removal of protective films such as the role of suspended particulates and repassivation kinetics;

(2) physical damage to the underlying material due to cavitation phenomena at high fluid velocities and deformation and buildup of stresses in underlying material; and

(3) dissolution of the solid material due to degradation of glasses and mirrors by rain, effects of acid rain on both metallic and nonmetallic materials, and corrosion of structural materials by salt and liquid metals.

4. Degradation and Heat Transfer

Mechanisms of heat transfer across S/L interfaces need to be studied under conditions of degradation such as biofouling, oxide film formation in solar receivers due to impure liquid metals, formation of condensed liquid deposits due to gas/alloy corrosion processes, etc.

B. Recommended Basic Experimental Research

Based on the above stated needs for a better understanding of the degradation phenomena by S/L interactions, we recommend that the following experimental research be performed.

1. Electrochemical Degradation of the S/L Interface

Local cell formation, inhibition mechanisms, and active/passive transitions should be studied using in situ methods such as scanning ac electrochemistry, potentiodynamic scanning, LRS, and synchotron radiation techniques;

[†] The decrease in reflectance or transmittance in reflectors caused by solid particle impact erosion or abrasion by hail, dust, sand, or particulate detergents constitutes an important subject falling outside the scope of this panel but within the province of the panel on S/S interface science. The reader is referred to Chapter XIII for a discussion of this subject.

and the results should be correlated where possible with ex situ techniques such as LEED, SIMS, ESCA, or AES analysis. These studies should include metallurgical, grain boundary, and crevice effects as determined by STEM or Auger analysis of localized segregations. The electrochemical experiments should be designed to detect the mechanisms of anode and cathode reactions. Measuring techniques need to be developed for use with high temperature metal-fused salt interfaces, and low temperature metal-ammonia reactions. In situ methods need to be developed to advance the science of the degradation mechanisms. Of particular importance is the applicability of electrochemical and in situ surface analysis techniques to studying interfaces between semiconductors and aqueous solutions used in photoelectrochemical devices; these techniques could be used to determine passivation-depassivation reactions and photochemical effects or the nature of these important interfaces. These studies should include determination of the mechanisms of poisoning the surfaces by (impurities in) the electrolyte.

The electrochemistry of reactions in crevices should be studied in detail to determine propagation mechanisms of corrosion in these areas. Existing electrochemical techniques, such as scanning ac and potentiodynamic measurements, may need to be modified to make in situ measurements.

2. Mechanically Assisted Degradation Processes

The corrosion fatigue behavior of materials in various solar energy devices as influenced by thermally developed stresses from sun/shadow and diurnal cycles needs to be studied. Of particular interest is the role of material, composition, surface scales, and environment on the initiation of cracks. These can be studied by electochemical methods such as scanning ac methods used to monitor local areas where depassivation, oxide failure, etc., as precursors of crack formation are likely to develop.

Propagation modes and mechanisms of cracks, once initiated, need to be studied along with the synergistic effects of applied stress and thermal cycles. This research should include the effects of passivation-depassivation kinetics and oxide formation in the crevices on crack propagation. Improved techniques for monitoring environmental effects within propagating corrosion fatigue (or stress corrosion) cracks should be developed for this research.

While both stress-assisted and stress-corrosion cracking have been extensively studied and are ubiquitous problems, both can be anticipated in a number of types of solar devices. Experimental methods should be developed for determining the states of residual and applied stresses and their effects on the initiation of stress-assisted corrosion, stress-corrosion cracking, corrosion fatigue, and the propagation of these phenomena at aqueous, nonaqueous, high temperature, metal/polymer and semiconductor/ polymer interfaces. Of special interest would be studies of stress states which result from the doping of semiconductor surfaces and from the effects of thermal stresses from photovoltaic action on the degradation of these surfaces.

Hydrogen effects on degradation of materials are important to solar energy systems in H_2-producing (photoelectrochemical) devices and in the liquid NH_3 environment proposed for OTEC. Specific research should include measurements of H_2 permeability and H_2 behavior at S/L interfaces in these systems. Hydrogen embrittlement on all materials at corroding interfaces needs to be better understood. Need for research on this topic is not exclusive to solar energy devices.

3. Erosion Phenomena

Recommended research in erosion phenomena[†] includes studies on the action of moving fluids on solid surfaces, the role of formed and suspended corrosion products, the relationship between erosion and the corrosion of surfaces, and the extent of damage to the materials themselves.

Research should be performed on the role of moving fluids in passivation/ depassivation kinetics and on the role of damage to protective oxide films; this research should be done using the in situ and ex situ electrochemical and physical measurement techniques described in Sections II.A and III.A. The role of suspended particles, both previously existing in the fluid or generated by corrosion, needs to be considered in these studies.

Erosion often gives rise to conditions on the surface which tend to accelerate surface corrosion. Studies to understand the synergistic effect that can take place when surfaces are exposed to both erosive and corrosive environments should be done.

Physical damage to the underlying material can cause residual stress to develop which would lead to mechanically assisted degradation processes. Research should be performed to detect the mechanisms and the extent of this damage in proposed solar devices, especially those devices where high-temperature fused salt or liquid metal coolants are used, or where frequent cleaning to remove biofoul may affect the stress patterns in the underlying material.

Research should be performed on mechanisms of attack on metallic and nonmetallic materials by rain, including pollutants such as nitrates or sulfuric acid. Chemical and optical changes in the surface of the nonmetallic or metallic components (in mirrors or wind turbines) need to be studied using surface analytical techniques such as AES and laser beam reflectivity studies studies in both natural and simulated environments. Surface compositional changes that occur in fused salt and liquid metal environments proposed for specific devices should be studied using AES, SIMS, or SEM-EDA techniques.

4. Degradation and Heat Transfer

Specialized experiments need to be conducted to understand the influence of fouling and deposits on heat transfer across S/L interfaces. Thermal cycling conditions and conditions proposed for OTEC and solar receivers should be studied. In situ surface analytical techniques should be widely used in conjunction with the heat transfer measurements.

[†] Particulate impact erosion constitutes an important subject falling outside the scope of this panel, but within the province of the panel on S/S interface. The reader is referred to Chapter 10 for a discussion of research needs and opportunities in particulate impact erosion (e.g., dust, sand, and detergent particles).

IV. SUMMARY AND PRIORITY TABLES

In the preceding sections, we have made an attempt to identify the most important needs in interface science concerning solar materials and to suggest basic research activities which could address these needs. The suggested areas of research and their relevance and priority ranking are summarized in Tables 1 and 2. Priorities were ranked as crucial, important, and useful. They were determined primarily on the basis of fundamental scientific merit and impact with regard to interface science and solar materials development.

TABLE 1. SUMMARY OF RECOMMENDED S/L INTERFACE RESEARCH NEEDS AND PRIORITIES: PHOTOELECTROCHEMISTRY

RESEARCH TOPICS	RELEVANCE	PRIORITY
1. Analytical probes of S/L interface for electronic, compositional, and structural studies	Electrochemical science	Crucial
2. Theoretical models specific to the S/L interface	Electrochemical science	Crucial
3. Novel materials: electrolytes, solvents, semiconductors	Photoelectrochemical energy conversion systems	Crucial
4. Thin film electrodes	Electrochemical photovoltaic cells	Important
5. Photo-assisted synthesis and electrocatalysis	Fuel (e.g., H_2) and chemical feedstock production; photoelectrosynthetic cells	Important
6. Modified electrode materials and surfaces	Electrochemical photovoltaic cells	Useful

TABLE 2. SUMMARY OF RECOMMENDED S/L INTERFACE RESEARCH NEEDS AND PRIORITIES: SOLAR ENERGY RELATED DEGRADATION PHENOMENA

RESEARCH TOPICS	RELEVANCE	PRIORITY
1. ELECTROCHEMISTRY OF CORROSION		
A. Photochemical effects	Photovoltaic-fluid interface mirror degradation	Crucial
B. Development of in situ techniques for studying degradation mechanisms at S/L interfaces	Corrosion science	Crucial
C. Local cell formation	Lifetime and efficiency of heat exchangers	Important
D. Passivation and active-passive transitions	Lifetime and efficiency of heat exchangers	Important
E. Inhibition mechanisms	Lifetime and efficiency of heat exchangers	Important
F. Crevice corrosion	Lifetime and efficiency of heat exchangers and structural members in OTEC systems	Important
G. Nonaqueous environments	Lifetime and efficiency of heat transfers	Important
H. Characterization of thick corrosion product films	Efficiency of heat transfer	Important

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TABLE 2 (Cont'd)

RESEARCH TOPICS	RELEVANCE	PRIORITY
II. MECHANICAL EFFECTS ON CORROSION		
A. Corrosion fatigue	Lifetime of thermal, OTEC, wave, and wind generators	Crucial
B. Stress corrosion cracking	Lifetime of thermal, OTEC, wave, and wind generators	Important
C. Hydrogen effects	Lifetime of thermal, OTEC, wave and wind generators, and H_2 producing photoelectric synthetic devices	Important
D. Stress effects on general corrosion	Lifetime and efficiency of heat exchangers	Useful
III. EROSION		
A. Cavitation damage	Lifetime and efficiency of heat exchangers	Important
B. Removal of protective films by moving fluid	Lifetime and efficiency of heat exchangers	Important
C. Impingement effects	Lifetime and efficiency of heat exchangers and solar reflectors	Important
D. Corrosion/erosion	Lifetime and efficiency of heat exchangers and solar reflectors	Important

XII. BASIC RESEARCH NEEDS AND OPPORTUNITIES AT THE SOLID/GAS INTERFACE

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ABSTRACT

Solid-gas reactions that may occur at surfaces of devices exposed to the normal solar environment (i.e., ambient air, high UV flux, thermal cycling, etc.) are of major concern in solar technology. Surfaces of importance include glass and polymer transmitters and polymer coatings generally, all of which may develop micro-cracks or otherwise fail in solar systems at rates far in excess of those for uniform degradation. An equally important, although less obvious, class of solid-gas interfaces are those developed sequentially in the manufacture of multilayer devices, e.g., mirrors and photovoltaic converters. Thus, it becomes necessary to know how the properties of a particular component layer are affected by the manufacturing environment (air, vacuum, etc.) and especially to know how the overall operation of the device is influenced by the cumulative effect of these various surface reactions. This problem is of special importance in solar applications because of the frequent use of multi-layer technology and the long life-time requirements for components.

There are a number of important chemical reactions which involve photoconversion and/or photocatalysis. In these processes, solid/gas interfaces occur on the catalysts and their support materials. Major research needs include a detailed understanding of semiconductor surfaces, with and without chemisorbed species; and understanding of the photoconversion and photocatalysis mechanisms; effects of sensitizers; understanding of spill-over phenomena; theoretical calculations; and new experimental methods for analysis of the S/G interface under ambient pressure.

In both thermal conversion and catalytic conversion systems, the transfer of energy occuring at solid-gas interfaces is very important. The problem is not simple, especially under high UV fluxes and on non-metallic systems. It is conceivable that useful resonant energy transfers may be predictable.

I. INTRODUCTION

One major area of research, that of surface reactions, occupied the bulk of attention during our discussions of needs and research opportunities at the S/G interface in solar systems. Such reactions are of importance in thermal conversion systems, catalysis, and photovoltaics. They are discussed in the appropriate sections below for each solar technology. Of less pervasive importance, but still of concern, is the question of energy transfer between solids and gases. Also, it is suggested, below, that two methods of direct conversion of solar to electric power, thermoelectric and thermionic conversion, be reconsidered as a result of recent changes in economics and technological progress. Since these technologies are not covered elsewhere in

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this Report, we discuss them briefly in the present Chapter.

As is apparent from the Research Summaries presented in Part I (see especially Chapter VII) of these Proceedings, much is known about S/G interfaces when the solid is a crystalline metal and the gaseous atmosphere is carefully controlled and at low pressures. However, when the solid is an insulator, such as a polymer or a glass, semiconductor, or an amorphous solid, our knowledge is strongly limited. Thus, it is necessary that more attention be given in the future to interfaces involving those classes of materials. Of course their importance also extends to other technolgies, beyond the needs of solar conversion. To that end, substantial advances must be made in analytic methods that can elucidate the microscopic properties of non-metallic S/G interfaces. A number of suitable methods are given in Chapters VIII, IX, and XV, thus they will not be presented in detail in this Chapter. The reader should be able to recognize the necessary experimental methods in what follows. It must be pointed out that the usual approach has been to merely extend surface techniques, which have been effective in studying metal/glass systems, to studies of other classes of solid materials. However, what is needed are analytic techniques which are designed specifically to directly address the important features of the non-metallic systems, e.g., unpaired electrons on polymer surfaces, short-range order in glasses, etc. Furthermore, it is worth emphasizing here that there is an important need for new experimental methods which can examine the S/G interface under ambient pressure.

Current overviews of the status of research and knowledge of the S/G interface are available [1,2,3].

II. THERMAL CONVERSION SYSTEMS

There are a number of solar-thermal conversion components with important S/G interfaces. These are given in sections A through D.

A. Transmitters and Mirrors

1. General Discussion

It may seem that ordinary glass windows could be used in all cases requiring light transmission and these need little further research. Further, double-glazed window arrangements may at present provide adequate and cost-effective insulating capabilities for many applications. However, a reduction in the thermal conductivity and IR transmission of window glass would clearly be beneficial in reducing heat transfer. Furthermore, it is known that corrosion of ordinary glass surfaces does occur under the thermal cycling and moisture conditions to be expected in solar systems; the character of this corrosion should be identified so that its important elements can be addressed.

When more demanding requirements must be met, especially if the economics so dictate, innovative windows of several types will be used. Most will require substantial research on the glass itself, on coatings, and on interfaces. The basic idea will be to provide windows whose properties are "controlled" in one or more of several ways. Since polymeric coatings on glasses must be transparent similar types of polymer/gas interactions must be considered. In order to improve on the performance of "ordinary" mirrors, the combination of transparent materials used in the silvering process must be stable in the solar environment. Metallic mirrors may be suitable for a number of applications.

2. Heat Mirrors and Advanced Transmitters

Schemes and systems are needed whereby the glass is rendered highly reflecting to IR radiation while remaining transparent to shorter wavelength radiation. In this way, heat transfer through the window is sharply reduced, with consequent benefit for both heating and cooling applications. Current systems, generally involve coatings which must be of a character to resist degradation, both physically and in reflecting properties, in normal environments; thermal cycling requirements must be kept in mind. (It would appear meritorious to seek glasses or polymers into which the desired optical reflecting character has been incorporated.) Systems are projected, and in some cases available, which can be attached to existing windows. Such systems will generally involve several interfaces in a multi-layer configuration and must be designed and constructed to retain their integrity in normal operating environments. These conditions must also be met by heat mirrors produced by coating the glass directly. In all such systems, there will be one or more interfaces, one being that with the atmosphere.

Potentially more effective, and certainly more esoteric, would be transmitters that have active character. Exploration of photochromic and thermochromic effects appears to be the most promising avenue of research, the former, via the glass itself, and the latter via the development of suitable phase-change coatings, probably of polymeric character. Encapsulated liquid crystals may also be important in this context. The type of thermochromic system needed is one which converts from highly transmitting to highly reflecting when the external temperature rises above about 25°C. Most desirable for esthetic reasons, especially on homes, would be systems which retain optical acuity through the transformation. This is clearly not essential for all applications. For some climates, photochromic systems, which darken upon exposure to optical band illumination, may be useful. Depending on the types of systems which can be developed, combined use with heat mirrors may be advantageous.

While photochromic systems are already available, cost may be a dominant consideration. Effective thermochromic systems will require a substantial materials science-based developmental effort, some of which is underway. From the interface perspective, all of those systems will require protection from atmospheric degradation with concomitant retention of the desired optical properties and mechanical integrity under thermal cycling.

For mirrors, there is one essential problem at an air/glass or air/polymer interface, i.e., the transmittance character must be maintained while the material is subjected to environmental attack, possibly high illumination intensities, and thermal cycling.

3. Research Needed on the Glass/Air Interface

The necessity of maintaining the optical character of the glass is the paramount consideration in research on the behavior of glass in air. Since the operating temperatures and consequent thermal cycling studies will depend upon the specific application, we will assume that the glass selected for investigation has the macroscopic thermal/mechanical characteristics necessary to satisfy the operating conditions. We recognize that this is a nontrivial matter and that the glass composition ultimately utilized may evolve from an iterative evaluation incorporating thermal/mechanical behavior and degradation behavior to be discussed below. Since mechanical integrity may be reduced by the effects of static fatigue, accelerated testing techniques are necessary.

Starting with a composition satisfying the operating requirements, the resistance of the surface to deterioration in the atmosphere must be determined. This will involve studies of possible deleterious chemical interaction between the surface and the principal constituents of air as well as the minor constituents commonly present, such as S in various forms. These studies must be made with the temperature and thermal cycling conditions adjusted to be consistent with the intended application. Evidence for microcracks and their possible role as localized corrosion sites should be sought and their consequences assessed. Evidence for other localized corrosion sites and their chemical character should also be sought as should chemical effects resulting in the development of inhomogeneities and roughening. Reaction rates and reaction constituents should be determined to permit longevity evaluation. Possible cooperative degradation involving combinations of air constituents must be investigated. All of these studies will require essentially the full spectrum of surface analytical tools currently available.

One phenomenon warranting particular attention is the interaction of water (vapor and liquid) with the glass surface to form a hydrated layer which degrades the optical performance. The inexpensive borosilicate glasses, high in Na content, are particularly susceptible to this problem while soda-lime glasses are much less so.

Once the basic chemical stability of the glass has been established, these studies should be repeated under illumination conditions characteristic of the intended application. Synchrotron radiation sources may be particularly effective for studies of surfaces with high intensity UV. The effects of high intensity light on any deleterious chemistry identified in the earlier work should be examined and allowance made for the possibility that illumination may involve reactions, both general and localized, not occurring without illumination.

Microcracking effects must be considered seriously because they can result from airborne dust and debris. In this connection, reliable methods should be sought for accelerated testing of the effects of dirt deposition and other surface contaminants together with projected cleaning processes. Possible surface treatments should be sought that might provide some protection against contamination by reducing as far as possible the attraction between the surface and airborne contaminates and by rendering the surface more stable against chemical attack and more stable mechanically. Obviously, the surface treatment must be included in the evaluation of degradation resistance.

B. Coatings

1. Technology

Coatings are widely used in solar energy technology in the fabrication of reflecting surfaces, as AR devices and as inert protective coverings for other components. Thus, coatings may be metals (e.g., Ag or Al), semiconductors (both compound and elemental), insulators (e.g., Si, Si_3N_4, GaAs, etc.) or polymers. Coatings are also covered in Chapter XIV. Technological problems arise as a result of environmental interactions that change the composition and/or microstructure of an otherwise protective coating, leading to the degradation of the optical or the electrical properties of the components.

Viewed from the perspective of phenomena occurring at the S/G interface, the three areas of basic research associated with coatings are:

(1) Characterization of the structure and composition of air solid interfaces.

(2) Kinetics and mechanism of polymer degradation.

(3) The development of new reflective materials and the characterization of the reactions of gases (e.g., NO_x, SO_2, etc.) with these materials.

2. Related Basic Research Needs

a. Surface Characterization Studies. The usual mirror is a multilayered device whose fabrication involves the step-wise build up of successive layers, e.g., glass superstrate, sensitizing layer, reflective layer (e.g., Ag or Al), primer layer (Cu), and a polymer backing that serves as a protective coating. The completion of each step produces a new S/G interface whose properties determine the adhesion and, perhaps, other characteristics of the next layer. There is a pressing need to characterize these surfaces in terms of structure and composition in order to provide a basic understanding of the factors governing subsequent adhesion. A variety of surface analytical tools are already available for this purpose: UPS, AES, XPS, EXAFS, etc. (See Chapters VII, VIII, IX, and XV).

Some questions that could be answered by such research are:

(1) What is the nature of the "sensitized" glass surface onto which a reflective Ag coating must be deposited?

(2) Does the presently used $SnCl_2$ sensitizer produce a unique composition/structure on the glass surface?

(3) What is the nature of the bonding of the Ag to that layer? Can the bonding characteristics of a monolayer of Ag be investigated with present techniques, e.g., EXAFS?

(4) What is the effect of solar radiation on this bonding?

(5) What limitations are imposed by current technology, which is based on the needs of the consumer mirror market?

b. Degradation of Polymeric Coatings. Currently, polymer coatings of various sorts are relied upon as the first line of protection for both reflective coatings and for photovoltaic devices. The quality of this protection degrades with time in the ambient environment, leading ultimately to the deterioration of the device. Although considerable research in this field is already in progress, we believe that additional basic investigations of the mechanisms and kinetics of such reactions are essential. This work should stress synergistic effects of solar radiation and various reactive gases (O_2, O_3, NO_x, H_2O, SO_2, etc.). Attention should be given to the electronic trapping properties of polymers being degraded by UV radiation. In addition, the influence of these basically chemical reactions on the mechanical properties of a polymer should be studied. Polymeric degradation is obviously accompanied by an increase in the permeability of polymer coatings to gases that can attack reflectors, photovoltaics, etc. Is this increase in permeability purely mechanical (i.e., due to microcracks), or is the solubility and/or diffusivity in the coating actually changed? Special techniques may need to be developed for some of these studies, although small angle neutron scattering (SANS) has proven valuable in average molecular weight determinations.

c. New Reflecting Materials. The reflectivity of pure Ag cannot be exceeded, and in that regard Ag is the preferred reflector material (Chapter III, Fig. 1). However, its chemical stability, particularly with respect to S attack, leaves much to be desired. Attempts should be made to develop new alloys (possibly based on Ag and Al) that possess acceptably high reflectivity and an improved resistance to oxidation in mixed gases. If a promising system of alloys were identified, basic studies of thin film oxidation-sulfidation mechanisms would be needed with special attention being given to site blocking and other aspects of mass transport across the oxide films formed on such alloys.

3. Self-Cleaning Surfaces

A major source of the degradation of the performance of reflectors is the accumulation of dirt and dust on the surface of the glass superstrate of the mirror. The original properties of the mirror can be largely restored through the simple washing of the glass surface. However, given the very large surface area of the reflectors, the inaccessibility of some systems, and the shortage of H_2O for such purposes in many locations, it would be highly desirable to develop a "self-cleaning" coating for glass. Basic studies of adhesion phenomena are needed (see Chapter XIII). If the factors controlling adhesion were fully understood, a coating could be devised with highly selective surface bonding properties, creating a surface from which dust might be blown with an air jet or be repelled by a suitable surface charge.

C. Absorbers

The thermal conversion of sunlight requires an absorber in the solar spectrum that will retain its properties at relatively high temperatures in a corrosive environment. A broadly based research program in support of an improved absorber technology could be divided into three parts:

(1) Characterization and improvement of existing absorber materials;

(2) A search for new (improved) absorbers; and

(3) An improved understanding of the basic mechanisms of absorption and the development of new absorber concepts.

These three parts will be discussed separately.

1. Current Absorber Materials

Research on existing absorbers should stress the characterization of the material and the identification of its failure modes. These studies on current materials should be limited to projects that can be completed in a relatively short span of time.

The current absorber of choice is "black chrome", that has been shown by XPS studies to contain oxides of Cr and Cr metal. The Cr particles, about 10 nm in diameter, are dispersed in the oxide. A number of laboratories are investigating its properties [4-6]. As presently constituted, black chrome is not stable above 300°C, a limitation that precludes its use in a number of solar applications. Studies of the black chrome/gas interface that would be most likely to result in an improved technology include:

(1) A complete characterization of the material including particle size, composition, morphology, impurities, etc., before and after degradation at elevated temperatures.

(2) A study to determine if sintering of black chrome occurs and, if so, the effect of the ambient environment on the sintering.

(3) The corrosion characteristics of black chrome in environments characteristic of prospective applications, and the dependence of the corrosion on the environment.

2. Alternative Absorbers

The strategic importance and high cost of Cr as well as the degradation of black chrome at elevated temperatures provide ample motivation for seeking alternative absorbers. This search should include:

(1) Alternative metal-metal oxide materials in finely divided form. Of importance are methods for producing such materials as by precipitation, electrochemical deposition, evaporation in the presence of an inert gas, "smoke", etc.;

(2) Textured surfaces, which may have less satisfactory absorbing properties but have offsetting advantages in terms of mechanical properties, heat transfer, fabrication costs, etc. "Black" surfaces often result, for example, even from sputtering reflective materials such as Al at high

temperatures. Of course, care must be taken to optimize the "absorptance-emittance ratio" and stability of such systems;

(3) Encapsulated absorbers in which the particles are held in a transparent matrix to reduce corrosion and sintering, at the cost of degraded heat transfer characteristics; and

(4) Absorbing particles suspended in a transparent heat transfer fluid medium (e.g., india ink).

3. Fundamental Studies

The search for improved absorbers must be guided by what is known about the fundamental processes of absorption of light in the visible spectrum, and IR emissivity. Many of these processes are not sufficiently well understood to offer adequate predictive capability. Accordingly, further theoretical and experimental work on light absorption and emission by particulate matter is needed. This work should incorporate effects due to size, per se, surface morphologies, plasmons in small particles, surface states, multiple scattering effects, refractive index mismatch between adjacent components, and compositional inhomogeneity, among others. A parallel effort dealing with the degradation of finely divided systems must be encouraged further. This work would include studies of surface diffusion and sintering including the role of reactive gases in controlling the kinetics, as well as corrosion characteristics of small particles.

D. S/G Energy Transfer

The transfer of energy from a gas onto a surface is a principal element in developing a system in which a solar heated gas would deposit energy to the solid (or vice versa). In order to optimize the rate and efficiency of the above process, it is of fundamental importance to understand the microscopic mechanisms of coupling, energy exchange, and relaxation.

The transfer of energy may involve the coupling of translational, vibrational, and rotational modes of the gas molecules to excitation modes of the surface. While for metals both phonon excitations and electronic ones (near the Fermi-surface, virtual electron-hole pairs) may play a role, for insulators the electronic elementary excitations will not contribute. Since optimal energy transfer between physical systems occurs when certain resonance, or near resonance, conditions are satisfied, it is suggested that a careful investigation of the conditions of optimal transfer might allow the design of more efficient S/G energy transfer systems. Controlled experiments, perhaps using molecular beams, in which the temperature of the incident and scattered beams are monitored (preferably state selective measurements) for a variety of gases incident upon well characterized surfaces, would provide information needed in order to construct theoretical models and establish criteria for the preparation of such optimal systems. In addition, the effect of irradiation flux on the rate of energy-transfer and thermal accommodation should be explored. The effect of radiation (besides "pumping" energy into the gaseous modes) may be to produce vibrational and/or electronic excitations in the solid. The role of surface defects and morphological characteristics in producing high-frequency vibrational modes could be assessed via HREELS. In this context, careful measurements and calculations of life-time effects, flow rates and state selective measurements (electronic, vibronic, actual molecular species, etc.) should be performed.

It should be emphasized that in addressing this subject, the basic problem is that of matching the partners (solid substrate and gas) so to enhance energy transfer, consequently a systematic study of both components is essential.

III. CATALYSIS AS RELATED TO SOLAR ENERGY

A. Objectives

Plausible long range technical objectives of research at the S/G interface related to solar energy include the catalytic production of H_2, CH_4, other hydrocarbons suitable for fuels, the production of chemical feedstocks, and certain heavy chemicals such as NH_3. In all cases, raw materials must be used that are not dependent on petroleum or natural gas [7]. At present, these processes fall largely into the context of the S/L interface and are described more fully in Chapter XI. The question of biomass conversion is not considered specifically as the catalytic processes needed there are not different from problems in coal conversion.

These objectives involve two distinct classes of photochemical processes, namely:

(1) Photoconversion, in which light energy is used to "drive" a reaction which would not be thermodynamically feasible in its absence. Examples are $H_2O \rightarrow H_2 + 1/2\ O_2$ and $CO_2 \rightarrow CO + 1/2\ O_2$. In these cases, a calculable amount of light energy, generally of the order of a few electron volts, must be absorbed for each molecule of product made.

(2) Photocatalysis, in which light is used, to produce intermediates which catalyze reactions that are thermodynamically favorable but kinetically slow in the absence of catalysts. Examples include $N_2 + 3H_2 \rightarrow 2NH_3$, $CO + 3H_2 \rightarrow CH_4 + H_2O$, and $CO + 2H_2 \rightarrow CH_3OH$.

To the extent that the light-produced intermediates truly serve as catalysts, the number of molecules of product obtained per photon absorbed could be very large (in principle, infinite).

B. Areas Requiring Research

In terms of solar energy usage, both classes of reactions given above will probably involve semiconductor materials with band gaps in the solar spectrum (visible or near UV), and in both cases there may be advantages in also using the semiconductors as supports for metal catalysts (e.g., Pt, Ni, Co, etc.). Hence, there are a number of areas of fundamental investigation that are important to both classes. These are:

(1) Determining the structure and composition of principal crystal planes of semiconductors of major interest. Some excellent studies of this sort have been done on Si and GaAs, emphasizing the use of LEED. For materials not developing long range order, short range chemical environments can be obtained by EXAFS, EAPFS, and/or SEXAFS techniques;

(2) Determining the structures and bonding of species chemisorbed on the semiconductor surface. Potential reactants such as H_2O, CO_2, CO, N_2; potential products or intermediates such as CH_4, NH_3, CH_3OH; and potential poisons such as H_2S are of particular interest. Techniques mentioned in (1) above may be employed, together with NMR, IR, ISS, UPS, and AES. Dependence of coverages or partial pressures should be established, as well as changes in bonding due to irradiation. Reaction intermediates present in very small concentrations may have major roles in the reaction mechanisms. Their presence and concentrations may often be inferred from detailed kinetic studies, but better methods for direct observation are badly needed. In photochemical processes, it is possible that free radicals will be important intermediates, and it may be possible to detect them by ESR. Broadly, methods for establishing steady state concentrations of all significant surface species under steady state reaction conditions are badly needed; this need extends to catalysis in general and is by no means limited to solar energy-related catalysis. Our most surface-sensitive spectroscopies require HV to UHV conditions for their employment, and these are hardly the conditions under which heavy chemicals are likely to be produced.

(3) If a given semiconductor is to accomplish any photochemistry one or more of the chemisorbed reactants or intermediates will trap excited electrons and/or holes, and the reversibility of this trapping will be a factor in the photochemical process. Recombination rates, and their modification by trapping, are thus of central importance in these processes, and their investigation is essential. A number of techniques are applicable, including transient illumination processes (e.g., chopped beam or pulsed light sources).

(4) Catalytic reforming of petroleum is largely accomplished on a compound catalyst consisting of a noble metal (e.g., Pt) supported on a cracking catalyst (SiO_2-Al_2O_3 or zeolite). A spill-over phenomenon, in which species formed on the cracking catalyst migrate to the noble metal without desorbing, is believed by many to be involved in the overall reaction, although the evidence for this is not conclusive. In the photochemical production of methane from CO and H_2O, it would appear reasonable to generate H_2 photochemically on a semiconductor, then let it react with CO on Ni to form CH_4 as Ni is an excellent catalyst for the latter reaction. If the chemisorbed H atoms, presumed to be the initial product of the photodecomposition of H_2O, could simply "skate" to the Ni without desorbing, a significant activation energy might be saved. Research is needed to establish whether or not the spillover phenomenon occurs, if so under what conditions, and what is its microscopic nature. Very recently, Sato and White [8] have found evidence that the photodecomposition of $H_2O(v)$ over Pt supported on TiO_2 proceeds, under circumstances that a monolayer or more of H_2O might be present on the surface, as in a short circuited photoelectrochemical cell, with O_2 formed on TiO_2 and H_2 on Pt.

(5) Systematic investigations of the effects of semiconductor dopants, associated with shallow or deep impurity levels, on photocatalyzed and photoconversion reaction rates are needed.

(6) Systematic investigations of the effects of sensitizers on photocatalyzed and photoconversion reactions are needed, including modes of sensitizer adsorption, excitation, and energy transfer.

(7) In common with other heterogeneous catalysis, there is need for better understanding of reactive chemisorption (e.g., dependence of dissociative chemisorption probability on defect site distributions and coverage) and of surface transport of chemisorbed species (see for example the spillover phenomenon in (4), above). Such understanding may be sought through stochastic modeling and through FIM, flicker-noise field emission, and tracer experiments. Studies should include using clean and systematically contaminated surfaces. For solar energy purposes, modifications of reactive chemisorption and transport processes by light irradiation (including effects of radiation induced surface defects) should be established.

(8) Continued research on theoretical models of chemisorption is needed, and should be extended to include excited states in chemisorption. In the longer range, these models should be developed to provide energetic surfaces for reaction pathways.

IV. PHOTOVOLTAICS

An understanding of the S/G interface is vital to the successful development of inexpensive photovoltaics. Typical cells involve intimate contact between polymers, metals, and semiconductors, often through interfaces whose properties and preparation must be carefully controlled. Among the photovoltaic cell materials which have received the most attention are CdS, Cu_2S, ITO($InSnO_x$), GaAs, Si, etc. The electrical contacts to such cells are typically Cu, Cu-Be, Ag, Ag-Ti or Au-Cu. Degradation of cell voltages with time in the solar environment has been observed, partly due to S/G reactions. The surface reactions in these cells can be divided into attack of the AR coating and encapsulant [9] and then attack of the cell, contacts and interconnects beneath the encapsulant, e.g., a polymer [10].

A. Coatings and Encapsulants

The corrosion of the AR coating and encapsulant polymer needs extensive work. The deleterious effects of O_3 and UV light on polymers is well-known, but the exact mechanism is unknown. It is recognized that embrittlement results from increased crosslinking, and decreases in chain size contribute to the polymer degradation. Spectroscopic techniques and classical chemical kinetics may assist in determining the mechanism of embrittlement. Further work is required to determine the synergistic interactions of O_3 and UV light on the degradation mechanisms. The influence of thermal cycling must also be included. Of primary importance is the transport of O_2 and H_2O through the encapsulant. It is expected that both the diffusivity and solubility of O_2 will be modified by polymer degradation. Studies using permeation and radioactive tracers may assist in determining O_2 diffusion. Coating techniques should also be investigated. The state of residual stress imposed by the polymer coating process may dramatically influence the polymer degradation. Birefringence work will be useful in ascertaining the influence of residual stress on polymer degradation.

Upon degradation of the encapsulant, an O_2 potential far in excess of that anticipated in the cell design may exist at the cell-polymer interface. Under these conditions degradation and rapid destruction of the device may ensue. High temperature corrosion of small particles has been shown to be particularly sensitive to shape and geometry. These effects have been measured only qualitatively, but it has been shown that edges and corners corrode more rapidly than flat surfaces. Enhanced corrosion of this type is expected with most photovoltaic cell configurations. A basic study of the effects of geometry on oxidation rate is needed so as to minimize corrosion through configuration optimization. Such studies can be performed by measuring oxide thicknesses at various controlled interfacial configurations using optical microscopy, TEM, SEM, and ellipsometry, coupled with in-situ TEM.

The influence of electric fields on the oxidation at the cell-polymer interface can be estimated from theoretical studies. However at present, one cannot predict pitting attack from such theoretical studies. Pitting may result in severe localized attack at electrical contact points also. Investigations of pitting phenomena should include the influence of surface geometry and dissimilar metals on the electrical enhancement of oxidation. As an analogy to aqueous corrosion pitting potentials, it may be possible to define threshold O_2 partial pressures and electric fields for pitting. Optical methods for pit detection and monitoring are required.

B. Surface Reactions of the Cell

In the event of the loss of encapsulant integrity, O_2 diffusion may cause the accelerated corrosion of sulfide components. A basic study of the oxidation of both CdS and Cu_2S up to temperatures used in solar applications (> 70°C) must precede the wide-spread use of these materials. The influence of microstructure is particularly important since maximum operating temperatures are well below half the melting point of these compounds. An evaluation of resultant sulfidation of the cell components due to oxidation of CdS and Cu_2S is necessary. Such studies may be able to use standard surface analytical and in-situ electron microscopic techniques because of the low O_2 pressure during operation at the polymer-sulfide interface ($\sim 10^{-2}$Pa). See Chapters VIII, IX, and XV for further details.

At present, Si is the most important photovoltaic cell material. Passivation of Si surfaces has been observed during direct atmospheric contact, the mechanism of which has been the subject of serious debate for many years. Further basic studies are needed to determine the mechanism. It is particularly important to determine the influence of minor amounts of H_2, produced by H_2O decomposition, on the process. Such work would require coordinated studies using all available surface analytical tools, as it is generally recognized that one technique alone is not adequate to determine the passivation mechanism. Such studies should also provide an evaluation of the importance of microstructure on passivation. If a passivated film can be maintained on the Si surface, the need for encapsulation may be eliminated (e.g., by glass or a polymer). Special attention must be paid to polycrystalline and amorphous Si.

C. Production Environment

Between the various stages of the production of a multilayered structure, a particular gaseous environment is present. Generally, ambient air is chosen because of ease and cost, but sometimes clean, dry air is used because the additional cost is rationalized by improved product life-time and/or reliability. In the use of photovoltaic converters over the long times being projected, it may be desirable to use more expensive production environments to obtain a cell which would yield an overall economic improvement. Such approaches are already underway in thin film device preparation (e.g., see Chapter XIV).

It is necessary to understand how simple gases such as moist air, dry air, N_2, and trace quantities of gases present in various low pressure production environments affect the properties of each surface as it is prepared. The interactive effects of various components prepared under various conditions must be determined. As the possibilities for optimal cell characteristics and lifetime are determined, the overall economics must be analyzed.

V. OTHER RESEARCH AREAS

A. Thermoelectric Devices

The bulk of the recent work on thermoelectric materials has been with Bi_2Te_3 and PbTe, which have reasonable figures of merit up to 300 and 600°C, respectively. Even for these existing materials, calculations based on current and projected cost figures show the economic viability of using direct solar-to-electric power conversion by thermoelectric devices [11]. Furthermore, recent materials studies offer the hope that thermoelectric devices with reasonable figures of merit at higher temperatures may be feasible [12-13].

In many ways, these systems are similar to photovoltaic devices when considered from the point of view of S/G interface problems. In both cases, one must consider surface reactions between semiconductors and production and/or environmental gases. These will be most severe at the junctions of the thermoelectrically active materials, as a reaction product at the junction could change the thermoelectric power and ultimately lead to reactive failure.

The type of research needed here also involves studies of reactions between likely materials and environmental gases, oxidation of the junction, decomposition of semiconductor materials possibly leading to enhanced oxidation, and changes in thermoelectric properties with oxidation.

B. Thermionic Devices

Thermionic converters currently use cesiated emitters with high bare work functions (e.g., Ir) and refractory metal oxide collectors sealed in W capsules under a Cs atmosphere. Thus, the S/G interface in this case is different than in the systems considered above. Here, the gas will probably be an alkali metal vapor under reduced pressures. Thus, the techniques used to study systems of interest, e.g., the Cs-Ir system, are the same as those already in use for metal/gas studies in UHV, viz., XPS, UPS, LEED, AES, EELS, etc. Surface reactions of the alkali vapor with the active components (emitters and collectors), insulators and container materials can all lead to degradation of the output voltage and current, and must be studied. Optimization of the various properties may require modeling studies in order to aid in obtaining important information via short-time testing.

VI. RESEARCH TOPICS AND THEIR RECOMMENDED PRIORITIES

A list of research topics relevant to studies at the S/G interface is given in Table 1, along with their applicability to a specific area(s) of solar conversion and the priority(ies) for each conversion technology. They have been grouped in the order given in the text above, and by priority within each group. If a research topic is relevant to more than one technology, it is listed under the first group in which it has its highest priority.

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Table 1. Research Topics and Their Priorities for Solid/Gas Interface Problems in Solar Energy Conversion

Research Topic	Relevance	Priority
Chemical stability of glass surfaces exposed to atmospheric constituents, with and without illumination	Transmitters and Mirrors	Crucial
Surface treatment of glass for improved chemical stability, mechanical stability and reduced attraction to airborne contamination	Transmitters and Mirrors	Crucial
Mechanisms of highly localized corrosion, e.g., pitting	Transmitters and Mirrors Photovoltaics	Crucial Crucial
Stability of glass against static fatigue	Transmitters and Mirrors	Useful
Permeation mechanisms in degraded polymers	Coatings	Crucial
Kinetics of M/G reactions on new reflector materials	Coatings	Crucial
Microstructure of films of new reflector materials	Coatings	Crucial
Synergistic effect of UV radiation and reactive gases on the kinetics and mechanisms of polymer degradation	Coatings	Crucial
Nature of sensitized layers on glasses	Coatings	Important
Nature of the bonding of Ag and other reflectors to sensitized layers	Coatings	Important
Effects of UV radiation on bonding	Coatings	Important
Effect of alloying on thin film oxidation at low temperature ($T < 0.5\ T_M$)	Coatings	Important
Stress effects on oxidation	Coatings	Important
Effect of large electric fields on oxidation	Coatings	Useful
Nature of the mechanical damage associated with the degradation of polymers	Coatings	Useful
Characterization of finely divided materials (size, morphology, composition, etc.)	Absorbers	Crucial
Role of quantum-size states in surface reactions	Absorbers	Crucial

Table 1 (Cont.)

Research Topic	Relevance	Priority
Surface-gas energy transfer mechanisms	Absorbers	Important
Role of ambient gases on surface diffusion and sintering	Absorbers	Important
Corrosion characteristics of ultra-small particles	Absorbers	Important
Alternative absorber concepts (textured surfaces, particle suspensions, etc.)	Absorbers	Important
Fundamentals of absorption by particulate material	Absorbers	Useful
Structure and composition of semiconductor surfaces	Catalysis Photovoltaics	Crucial Crucial
Bonding of species chemisorbed on semiconductors	Catalysis Photovoltaics	Crucial Useful
Effects of sensitizers on photoprocesses	Catalysis	Crucial
Mechanisms of photoconversion and photocatalysis reactions	Catalysis	Crucial
Trapping of charge carriers by chemisorbed species	Catalysis Photovoltaics	Important Important
Reactive chemisorption and surface transport mechanisms	Catalysis	Important
Kinetics of oxidation of non-oxide semiconductor compounds	Photovoltaics	Crucial
Diffusion of gaseous impurities in semiconductors	Photovoltaics	Crucial
Influence of surface geometry and shape on surface reactions	Photovoltaics	Important

XIII. BASIC RESEARCH NEEDS AND OPPORTUNITIES AT THE SOLID/SOLID INTERFACE: ADHESION, ABRASION, AND POLYMER COATINGS

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ABSTRACT

Thirty year service lifetimes are desired for photothermal and photovoltaic devices for use in an environment of moisture, pollutants, abrasive particulates, thermal cycling, and ultraviolet radiation. These devices contain a plethora of solid/solid interfaces of dissimilar materials which are especially vulnerable to degradation induced by this environment. Polymer coatings offer promise for protecting the optical properties and retarding interfacial degradation behavior of solar collectors and glazings. The nature of the bonds that cause adhesion between dissimilar materials such as polymers and semiconductors or polymers and metals, etc., requires identification and a fundamental mechanistic understanding. Present interfacial science is limited by macroscopic experiments which do not permit either a spatial extrapolation to atomic mechanisms, or a time extrapolation from laboratory real times to 30 year service periods.

Mechanistic understanding is required for polymer behavior including surface hardening, stability in an environment of moisture and various airborne contaminants, and degradation under prolonged integrated exposure to ultraviolet. The understanding should result in long time behavioral modeling from short time laboratory data, and the ultimate molecular design of optimal coatings and interfaces in photothermal, photovoltaic, reflector, and concentrator devices.

I. ADHESION AT S/S INTERFACES

Adhesion is a multidisciplinary subject which includes chemical interactions between unlike materials, interfacial structures, and the complex interacting-mechanical and electronic properties of the interfacial region. Optimal adhesion is often dependent on surface cleaning and surface modification processes which introduce very thin interfacial layers which differ from the adjoining phases in chemical, mechanical, and structural properties. Very weak adhesion (release) is sometimes desired but is often achieved accidentally when liquids or weakly-bonded solids are trapped at an interface.

A. Energetics of Adhesion; Intermolecular Forces

Adhesion problems arise when bonded structures fall apart, such as delamination of multilayer structures, or breaking of filler-matrix bonds. Such failures may require strong tensile or shear forces, but sometimes, debonding occurs with little applied mechanical stress, such as when penetrating moisture accumulates at an interface and forces the bonded materials apart. The strength of an adhesive bond is often measured by the force or work required to break the bond. The relationship between the mechanical work of adhesive bond-breaking and molecular properties has been well-enough

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*Chairman

established by Schultz and Gent [1] that one can in general expect that the mechanical work of adhesive bonding is proportional to the thermodynamic work of adhesion W_{12}

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1}$$

where γ_1 and γ_2 are the surface tensions of phases 1 and 2, and γ_{12} is the interfacial tension. The work of adhesion W_{12} is the negative of the Helmholtz free energy of interaction of phases 1 and 2.

Different kinds of intermolecular bonding can be involved in the work of adhesion; these include dispersion force interactions (d), acid-base bonding (ab), covalent bonding (c), and electrostatic contributions (e), i.e.,

$$W_{12} = W_{12}^{d} + W_{12}^{ab} + W_{12}^{c} + W_{12}^{e} \tag{2}$$

The first term is significant at all interfaces and is predictable from

$$W_{12}^{d} = 2\,[\gamma_1^{d}\gamma_2^{d}]^{1/2} \tag{3}$$

where γ_1^{d} is the dispersion force contribution to the surface energy of phase 1 and is typically 0.1 J/m^2 for metals and oxides, or 0.02 to 0.045 J/m^2 for polymers [2].

The second term can be closely approximated by S, the number of acid/base sites per unit area and ΔH^{ab}, the enthalphy of acid-base interaction for the sites of phase 1 and phase 2. The value of ΔH^{ab} is predictable by the Drago equation

$$-\Delta H^{ab} = C_A C_B + E_A E_B \tag{4}$$

in which the C and E are constants related to the covalent and electrostatic contributions, respectively, of the bond strength. The values of C_A and E_A for the acid sites (electron-acceptors) and C_B and E_B for the basic sites (electron-donors) are known for several organic and inorganic acids and bases [3,4]. For example, the adsorption of amines onto Fe_2O_3 involves an acid-base interaction with about two acid sites/nm^2 on the Fe_2O_3, where $C_A = 2$ (kJ/mol)$^{1/2}$ and $E_A = 3$ (kJ/mol)$^{1/2}$; with the known C_B and E_B values for amines, $\Delta H^{ab} = 54.4$ kJ/mole. Then

$$W_{12}^{ab} = S\,\Delta H^{ab}/N = 0.18\ \text{J/m}^2 \tag{5}$$

where N is Avogadro's number.

Covalent bonds are often stronger yet, with bond strengths of about 335 kJ/mole. If one bond per (nm)^2 can be established, this can provide a W_{12}^{c} value as high as 0.5 J/m^2.

Electrostatic bonds originate from electron injection from species with donor states overlapping the energy levels of acceptor sites of the other species. If the charge transferred is Q_s coulombs and the resulting surface potential is V_s, the value of $W_{12}^{e} = V_sQ_s$, and the contribution to the tensile strength F_e is $Q_s^2/2\varepsilon_o$. In all adhesive joints between electron-donor materials and electron-acceptor materials (such as ester-containing polymers on silica), there are appreciable values of W_{12}^{ab}, perhaps 0.05 J/m^2 or more, and though appreciable charge transfer occurs, W_{12}^{e} is usually less than 10^{-3} J/m^2, and F_e, using a value for Q_s of 6 X 10^{-3} C/m^2, is at least 0.23 MPa. Charge transfer between phases is easily measurable by a variety of techniques [5,6] and this allows calculation of the electrostatic contribution to F_e for any interface.

The above principles can be used to evaluate bonding at any interface between liquids or solids. They have been tested at L/L and at L/S interfaces, where W_{12} values are directly measurable, but the principles and calculations apply equally well at S/S interfaces.

B. Covalent Bonding of Organic Materials at Interfaces

As indicated in the previous section, very strong interfacial bonding can be achieved by covalent bonding of polymers to metal oxides; however, aside from certain advertising claims, there have been few proven examples of this approach. It is possible to adsorb reactive species onto metal oxides or modified metal oxides and actually develop covalent bonds between organic and inorganic materials; such adsorption is best done from the vapor phase or by plasma deposition. Adsorption of reactive materials from a solution, especially aqueous solutions, often fails to provide the desired result because the rates of adsorption are very much slower, the solvent competes for surface sites, and often the reactant combines with H_2O and is completely changed chemically.

Glass and silica surfaces can be fluorinated and reacted with phenyl lithium to provide benzene rings directly attached by a Si-C bond. Sometimes silane derivatives can be attached by Si-O-Si bonds, both these are not as stable and can be removed by hydrolyzing.

Bonding of organic polymers to inorganic solids can be promoted by adsorbing polymerizable molecules which can form cross-linked networks at or near the surface. This approach is often quite successful in strengthening adhesive bonds. Many "coupling agents" appear to function in this manner, and epoxy, aziridine or urethane condensation chemistry can be used in this fashion.

C. Multilayer and Stacked Systems

Multilayer structures can be of several types, especially laminar, particulate, or fibrous. Increased mechanical strength results when interfacial bonding is stronger, and the stacked systems are easier to make when interfacial bonds are stronger. In the case of multilayer polymer films, the greatest success has been attained when one layer is an electron-donor and the next is an electron acceptor; a common example is the coating of polyvinylidene chloride films (electron-acceptor) onto polyester film (electron-donor) and in fact most commercial polyester film is so coated. Thin adhesive layers are most successful when a basic adhesive is used between two acidic sheets, as in safety glass.

Similarly, in particulate composites, reinforcement is most often obtained by dispersing an acidic filler into a basic matrix, or vice versa [7].

D. Macroscopic Adhesion Experiments

The thermal and long lifetime requirements for solar applications require a fundamental understanding of the many forms of degradation. A knowledge of both interface and bulk diffusion of impurities, and especially their segregation at interfaces where brittle intermetallics or delamination voids might develop, is necessary in order to design systems with the required long-time adhesion behavior. Development of diffusion barriers may provide a partial solution, and is discussed in Chapter X.

None of the many techniques [8] presently used measures the strength of adhesive bonding quantitatively and reproducibly. Direct pull tests are not reproducible because they are sensitive to alignment and stud bonding nonuniformities. Furthermore, a well "adhering" interface may not be the local point of failure. A statistical variation is expected in "weak-link" models, but the artifacts introduced by the test instrumentation must be brought under greater control and new techniques developed.

Adhesion problems in solar devices are classified in Table 1. In addition to the more obvious interfaces formed by adjacent films of dissimilar materials, it is necessary to understand the structure and behavior of grain boundaries in polycrystalline films, metal-oxide interfaces in absorbers, etc.

Table 1. CLASSIFICATION OF ADHESION PROBLEMS IN SOLAR DEVICES

Interface[a]	Solar Applications
M/M	Reflectors, Absorbers, Heat Exchangers, Photovoltaic Cells
M/S	Photovoltaic Cells, Photochemical Cells
M/I	Reflectors, Absorbers, Photovoltaic Cells, AR Coatings
M/P	Reflectors, Photovoltaic Cells, Heat Transfer Devices
S/I	Photovoltaic Cells, AR Coatings
S/P	Photovoltaic Cells
I/P	Protective Coatings, Fresnel Lenses
P/P	Laminated Polymer Coatings or Structures

[a] M is metal, S is semiconductor, I is insulator, and P is polymer.

The physical extent of the interface must be defined. This includes not only a knowledge of the microstructural and microchemical character as a function of distance from the interface, but also the interface topology and the stress fields that may extend much further than the usual structurally defined interface width. The interface width may be atomically sharp as in the case of $NiSi_2/Si$ [9] or be 20-50 nm as in a graded boundary used to minimize residual stresses [10].

The detailed mechanisms of degradation and failure require identification. In metal-polymer prosthetic joints, the failure has been recently identified as cohesive rather than adhesive as previously assumed [11]. Clearly, atomic depth resolution may be needed in the case of sharp interfaces. The application of Griffith crack models for brittle films [12] and a fracture mechanics approach [13] to take account of the plastic flow has been discussed. However, detailed structural and mechanical data do not exist to allow the application of such ideas for even a model interface.

A mapping of the stress fields is difficult in itself. Finite element analyses are possible, but the incorporation of plastic flow and the long-term relaxation processes for the material that may exist at the interface is not yet possible. In addition, the cyclic thermal stresses will combine with the intrinsic stresses [14] and may produce a fatigue situation involving water vapor and other contaminants of the atmosphere. We anticipate this may be a more difficult limitation for polymers because of the UV flux and the resultant scission of bonds. This underscores the necessity of obtaining a mechanistic understanding of polymeric degradation under UV flux so extrapolation of their long-time behavior can be made with confidence.

Thermal stresses and thermal shock may dominate the high temperature failure mode. It may be possible to change the expansion coefficient by designing composition modulations on a nm scale to give as dramatic an effect as a reported five fold increase in elastic modulus [15].

The stresses in a film and especially in a multilayer structure may not only be large, but of opposing sign in adjacent layers as in the case of the oxidation of Fe [16]. Mechanical driving forces will enhance the mass transport to promote stress relaxation. The atom flux is out of a film under compression [9] and may change the interface and surface topology. Opportunities are obvious in stress control to prevent failure, or with more investigation, to use stress gradients to stabilize a structure or give more desirable near-surface mechanical properties for erosion-abrasion resistance.

Experimental techniques exist for the determination of an integrated stress measurement, and for the localized (0.01 mm resolution) lattice curvature of good single crystals, but there is a need for experimental verification of calculated stress distribution with a higher resolution.

Multilayer arrangements that make up both reflector and absorber assemblies contain numerous interfaces that are believed to control optical, mechanical, and thermal durability properties of these surfaces utilized in solar collection [17,19]. Reflectors are presently glass with $SnCl_2$ sensitizer, 70 nm of Ag backed with 30 nm Cu films, and protected by "paint." Absorbers are carbon steel coated with a metal such as Zn having a surface layer anodized so as to give a black film with small Zn particles in an oxide matrix.

A mechanistic understanding is required in order to model both adhesive and optical behavior and their dependence upon bond and structural parameters. Of the currently available analytical methods, RBS, NRA, and composition in depth profiling (see Chapter IX) offer potential for characterizing the composition of the interface, and, with carefully selected systems, STEM may be utilized for microstructural determinations (see Chapter XV).

There is clearly a need to develop a standardized experimental procedure for evaluating the adhesive strength of interfaces and for characterizing the fracture surfaces on a macroscopic scale. The experiments should lead to a determination of the location of fracture (at the interface or the overgrowth), the type of fracture (ductile, brittle), the role played by the procedure that generates the fracture, and the reproducibility of the adhesive measurement. Developing a quantitative measurement procedure for adhesive strength is a crucial early goal.

While there is a need for developing macroscopic experimental procedures, there is no assurance that these will lead to a mechanistic understanding of adhesive failure. Therefore, longer range research objectives should address the issue of adhesive bonding mechanisms using a microchemical and microstructural approach.

II. ABRASION/EROSION

The large scale use of large-area, high-quality optical surfaces presents new problems due to the effects of the outdoor exposure. This section will be restricted to physical erosion/abrasion problems affecting such optical surfaces; many of these problems are unique to solar technologies. Optical surface damage may occur from wind driven dust, sand gusts (industrial or natural), the action of ice, snow, and rain working independently or in combination with particulate matters, or from cleaning procedures required to remove particulate matter. Specific problems identified at this time include the physical degradation of the front surfaces of reflectors and protective cover materials. The measurable effects include increased optical scatter, reduced transmittance, and the reduction of specular reflectance. The threshold for unacceptable degradation will depend on the application as a result of different requirements, including working distances. The working distances for photovoltaic devices may be as small as 1 mm, but for flat plate collectors the separation may be 25 to 50 mm, and for central receivers the critical distance may be up to 1 km. Degradation effects can be assessed using spectral measurements of optical scatter (specularity), transmittance (specular and diffuse), and reflectance (specular and diffuse). There may be problems associated with artifacts of different manufacturing processes which are not considered here. Corrosion is considered in Chapters XI and XII.

Several topics of research interest are identified:

(1) Abrasion/erosion resistance can be improved by developing harder optical surfaces, possibly by preparing external surfaces in a state of residual compressive stresses, or possibly by synthesizing harder copolymers. Where the economics allow it, glass can be tempered to improve scratch resistance considerably. Coatings and sealants may improve the surface hardness of plastics and it would be useful to understand how they degrade as a consequence of UV flux, moisture, and thermal cycling.

(2) Understanding mechanisms which inhibit particulate deposition and/or reduce the particulate bonding effects caused by moisture is desirable. The ultimate objective is to reduce the frequency of required maintenance. The use of other dust rejection mechanisms may prove cost effective by reducing upkeep costs and degradation performance losses. One potential technique could involve the use of electrostatic fields to repel dust particles from the critical surfaces.

(3) The washing action of detergent solutions for removing deposited matter and the rinsing action of water with nonspotting additives are of concern. The solution of nonprecipitating antistatic agents in wash water is also an area of possible concern.

Other identified needs related to operating and maintenance were not considered as a research opportunity *per se*. These included evaluating field-coating processes, geometric positioning strategies for night-time storage, and the variation in dust, emissions, pollutants, etc., at different terrestrial locations.

III. POLYMERS IN SOLAR ENERGY DEVICES

The use of polymers in solar energy devices ranges from passive applications such as protective coatings, to more direct applications such as membranes for biomass separation or low-cost photovoltaic arrays and flat-plate collectors. Continuous potting or extrusion of completed shapes offers potential cost advantages. For example, low-cost, stabilized, extrudable materials which are compatible with heat transfer fluids are of interest for flat-plate collectors. Polymer technology from other areas of application may be brought to bear here, although new constraints must be considered. Throughout the following discussion, the potential reaction at a polymer/material interface needs to be included with the other variables.

A. Transparent Coatings

Preparing transparent coatings for passive applications that are cost effective is a considerable challenge. It is necessary to produce an integral adhering film that can be maintained over long time periods in the presence of stresses due to thermal cycling of composite materials in an oxidative and photolytic environment, and in the presence of airborne chemicals including water and pollutants. Although much work has been done on the effect of these variables either singly or collectively in other applications [20-23], solar applications place unique constraints on the performance of polymeric materials. The investigation of the effect of particular environmental variables is important, but it should be recognized from the outset that the effects are not expected to be linearly additive. Furthermore, although accelerated testing is essential, it should be realized that scaling may at best be approximate due to a difference in the kinetics of the various processes and their synergistic effect on polymer failure. Finally, since photo-oxidative degradation of polymers can be effected by minor constituents incorporated during synthesis or processing, variable performance of similar materials from different sources must be expected. The staggering magnitude of the problem of stabilizing polymers can be comprehended by studying the effects of various environmental variables on polymers in nonsolar applications [20-29].

Engineering needs in this area can be separated into thin transparent films over flat-plate collectors, and polymeric protectors over photovoltaic devices. Ideally one wants a material which has a hard surface, low water permeability, long-term stability to photo-oxidation and delamination, and remains transparent. It has not been established if any known polymeric material exists today which can meet all of these requirements. For example, materials with known environmental stability (fluorcarbons, silicones) are too expensive for the cost goals for solar applications, but less expensive polymers (polyesters, polycarbonate) may not have sufficient stability for long-term applications, or may abrade readily in solar environments. In some PV applications, polymer AR covers may be used to protect polymer superstrates or pottants (Chapter 5, Fig. 2), but elastomeric mismatches may cause problems. Several areas that require better understanding are:

(1) The influence of UV adsorbers and antioxidant additives, either as dopants or covalently attached to the polymer, needs to be studied to determine if the photo-oxidative degradation mechanism is changed by their presence. This should include a mechanistic

understanding of the behavior of the additives themselves over long periods under oxidative radiation. Ideally, inexpensive commercially available materials, e.g., polyvinyl chloride or polyethylene, should be selected for degradation studies.

(2) The polymeric bonding relationships that are likely to provide photo-oxidative stability and the molecular processes of how such polymers might be prepared (e.g., block and graft copolymerization) need to be elucidated.

(3) The structural relationships of polymer laminates that result in a variation of the surface hardness, permeability of environmental species, and metal or metal oxide adhesion, perhaps made from halogenated polymers or from copolymers of varying composition, should be explored.

(4) Plasma polymerization and other novel gas phase polymer preparation processes should be studied.

(5) The mechanism of catalyzed degradation of candidate polymers caused by contact with materials (Al, Ag, Cu, and Au) planned for use in photothermal and photovoltaic systems needs to be determined.

(6) The mechanism of degradation of inorganic polymers, such as glasses and plasma-deposited refractory materials, needs to be understood when these materials are exposed to solar insolation (radiation).

Regarding (1) to (6) above, there are problems which may only be satisfied by using specific polymers, but which presently are unknown. Using the principles of polymer science, predictions of the behavior and properties can be made for hypothetical polymer structures. Thus, tailor-making polymers, either via new synthetic methods or via modification of presently known polymers, for specific use in solar technologies may be necessary.

Understanding the bonding behavior between polymers of dissimilar structure and how it affects the adhesion and/or environmentally induced degradation of laminates is needed. Polymer/polymer interactions, which may alter the transmittance properties and/or reduce the permeability to invasive foreign materials, and polymer/metal interface stability both require understanding for securing long-term stable laminated structures, such as polymers for application in solar reflectors [see Chapters 2 (Fig. 7) and 3 (Fig. 2)].

Membranes are needed which will selectively separate biomass products, especially alcohols from water. Research is needed to understand the mechanisms controlling the rates of permeation, biofouling, and chemical degradation, and to determine the factors that limit their selectivity and stability.

B. Metallized Polymers for Solar Energy Uses

Some polymers (fluorocarbons and polymethylmethacrylate, etc.) have already demonstrated good resistance to weathering in long-term outdoor tests, sometimes in highly pigmented formulations. It is not known whether these polymers in contact with reflective metals and without pigments will have good resistance to degradation. There is some reason to expect different behavior, since some pigments (semiconducting oxides such as ZnO) and some UV stabilizing additions of paints absorb the energetic UV that should be transmitted for optimum solar performance. In using such UV stabilizers, one must seek an optimum trade-off in efficiency versus lifetime. Furthermore, polymers are generally far more permeable to H_2O, O_2, and other small molecules than are metals, oxides, or glasses; it is not known whether the reflective properties of metals will last under polymer films exposed to outdoor conditions, or how well the adhesion of polymer to metal will survive for 30 years in a terrestrial environment. Fluorocarbons and silicones have some very desirable characteristics but they are much more expensive than vinyl polymers, polyesters, or polyamides, but the latter materials have more limited lifetimes.

Metallized plastics, e.g., Ag or Al on a polymer film, may be useful in either a rigid or flexible mirror array. There is presently a poor understanding of the nature of the adhesive processes which effectively bind the metal to the polymer surface. The present working hypothesis is that acidic or basic sites on the polymer film can form acid-base bonds with the basic or acidic sites on the surface oxide layer of the metal. However, the presence of acidic or basic sites would also attract permeable gases and/or liquids such as O_2 or H_2O. This problem should be thoroughly investigated with the objective being to understand what provides stability at the metal/polymer interface. For example, a reasonable approach to solving this interface problem might be to use a suitable block or graft copolymer at the interface between a nonpolar polymer surface and the metal phase. This approach would utilize the concept of a hydrophobic domain in the block (or graft) copolymer to incorporate O_2 into the nonpolar polymer phase, and an acidic or basic domain to selectively bond with the surface oxide layer of the metal phase. The integrity of the interface might then be maintained even to the extent of the bond association energy of the covalent bonding in the block (or graft) copolymer.

Degradation mechanisms that are initiated at the P/M interface require elucidation. Understanding is required of the synergistic effects of thermal cycling, residual stress states, UV exposure, and environmental species, such as H_2O, O_2, and pollutants (introduced by permeation of the polymer or the metal coating or by interfacial diffusion) on P/M interfacial degradation.

Polymers used to coat the backside of metal/glass mirrors have no optical constraints, but must adhere strongly and prevent the incursion of corrodants. On the other hand when reflective metals are deposited on polymer films, the polymer must not only adhere strongly, but transmit a wide spectrum of light without generating reactive sites which can react with metal, O_2 or H_2O; this latter set of requirements is not trivial.

C. Minimizing Dirt Retention and Cleaning of Polymers

Optical properties can be seriously affected by dust and dirt. Some polymer surfaces are far easier to keep clean than others, and dirt retention can be minimized by several procedures. Soft surfaces entrap dirt particles, so surface hardening of polymers is of help. If the dirt is primarily acidic (clay and other silicates), basic surfaces (esters, etc.) should entrap dirt far more than neutral surfaces (hydrocarbons). A better understanding of mechanisms and surface reactions could lead to cleaning procedures which keep surfaces clean for longer periods, or to the use of "self-cleaning" polymers.

1. Surface Modification to Minimize Dirt Retention and Cleaning

There is ample evidence that the nature of a surface exerts a strong influence on its affinity for foreign materials. Consequently, in a situation where otherwise desirable properties are available, a suitable surface treatment, such as changing the surface density of acidic or basic sites could be an adequate solution of the dirt retention and cleaning problem. Examples of such surface modifications which have been effective are hydrophobic modification to textiles, etching of hydrophobic surfaces to increase hydrophilic character, etc. Problems to be anticipated are possible loss of transmittance properties in certain solar applications and the reduction of efficiency in others.

2. Sacrificial Self-Cleaning

Another viable approach to the problem of cleaning reflecting or transmitting surfaces is to design the component in such a manner that the contaminated portion of the surface is sacrificially removed, e.g., via rain water or via some other natural process such as oxidation. Problems to be anticipated from such an approach are the loss of transmittance in certain applications and eventual erosion and loss of the component. For designs of short-lived duration, the latter problem would perhaps be minimal. In reflector surfaces, the former problem could be enormous whereas for collector surfaces, sacrificial self-cleaning systems could possibly be designed with minimal loss of desirable properties.

D. Polymers for Protecting Photovoltaic Cells

Potting materials for PV cells must be compatible with the other cell material elements. Compatibility studies between the cell materials, the grid metallization, the abrasion-resistant cover and the polymer-pottant are required. The modulus of the pottant must allow stress relief at the interfaces, particularly at the cell interface, over the expected temperature range of operation. Cost/benefit considerations require that the candidate cell materials (inorganic and organic) be identified before long-term research is undertaken to understand the interface problems.

E. Predictive and Nondestructive Polymer Experimental Methods

The experimental approach for identifying and deducing the mechanisms of failure of polymers in the bulk and at interfaces are difficult but very important. In particular, nondestructive experimental methods (Mössbauer, FTIR, ESR, chemiluminescence), and improved analytical/statistical calculational methods are required to deduce mechanisms, which are used to formulate reliable accelerated life-test methods. Then, the accelerated or abbreviated methods need to be verified by comparison with real-time tests to enable prediction of service lifetimes. For example, intimate contact between metal surfaces and polymers may lead to presently unknown mechanisms of polymer degradation and/or loss of light transmittance properties.

IV. SPECIFIC ADHESION AND ABRASION PROBLEMS

A. Photothermal Energy Conversion

1. Absorbers

There are two major methods of photothermal absorption. The first is to use a flat surface, which is sometimes coated with a heat absorbing paint, metal oxide, or with anodically produced wet layers of metal oxide on metal substrates, where the black metal oxide is a 100 nm layer of metal particles in the metal oxide matrix. The second is in a high performance thermal collector, which is a metal pipe coated electrolytically with about 100 nm of a highly selective absorbing layer. In both systems, the black color results from the finely divided metal particles dispersed randomly in the oxide and the layer is quite rough and porous; thermal degradation results in loss of blackness as a consequence of increased surface roughness. Thus, a better understanding of particle ripening and growth processes at elevated temperatures in such metal/metal oxide systems would be useful.

Both absorbers must withstand cyclic thermal stresses as sunshine changes in intensity with the time of day or with clouds. The flat plate absorbers seldom exceed 150° C, but are often tested at 300° C. On the other hand, high performance absorbers often are heated to well over 600° C and their thermal behavior is of great significance.

Degradation mechanisms are of concern. With exposure to elevated temperatures, the black color fades to brown or gold and efficiency decreases, but the reasons are not clearly understood. Perhaps, the adhesion of oxide layer to the metal (in the high performance absorber) has failed. Accelerated test methods are needed; they require a fundamental mechanistic understanding to permit extrapolation to long service lifetimes.

Fundamental research issues include:

(1) understanding the mechanism of adhesion between the above described metals and oxides and how adhesion can be optimized by altering the interfaces, by changing the deposition processes, or by adding species to promote adhesion while not adversely affecting the absorption efficiency.

(2) understanding the equilibrium relations, reaction paths, and interaction between metals and metal oxides in absorbers; the species transport, if further oxidation of the metal particles or the formation of intermetallics occurs; and the effect of time, temperature, and cyclic stresses on interface and particulate morphology. Use of modern interfacial analytical techniques such as a study of fractured or thinned specimens by SEM, SAM, XPS, and ISS, should be considered. Beam effects (see Chapters VIII and IX) and cation injection from the metal into the oxide should not be overlooked.

2. Reflectors (mirrors)

Most reflectors are made by the same wet processes used for household mirrors for the last hundred years, involving reduction of Ag salts in aqueous solutions with organic reducing agents. The glass is first lightly abraded with abrasive powders, dipped into (or sprayed with) a dilute aqueous solution of stannous salts for a few minutes, rinsed, and then dipped into (or sprayed with) an aqueous reducing bath containing Ag salts from which a 70 nm layer is deposited. A 30 nm layer of Cu is then deposited from an aqueous solution of Cu salts onto which Fe powder is added as a reducing agent. Maximum adhesion to the glass is not attained until after a day of drying. The Cu layer is covered with a fairly thick "paint" film, which is typically a thermosetting material. The painted surface is then attached by adhesives to a backing such a polystyrene foam; steel supports are attached to the foam.

Degradation of the mirror sometimes involves poor adhesion of the Ag to the glass, but usually involves an apparent disappearance of the Ag, possibly resulting from reaction with moisture and pollutant gases, from degradation products from polysulfide sealants, or from agglomeration. Failure is less frequently observed when a second layer of glass is used behind the mirror, which is usually bonded with an edge-seal adhesive, but a double layer of glass is considered too expensive. The issues of mirror degradation are manifold, but for this topic, the issue is to determine if deadhesion is the crucial degradation mechanism. Paints or adhesives, which minimize the reaction of the Ag layers, could be applied; silicone rubbers might be considered, but these are quite expensive.

Fundamental research issues include:

(1) understanding and improving the adhesion of the metal layers to glass. Such studies could well include other deposition techniques such as evaporation, sputtering, etc. Condensation and nucleation mechanisms are fundamental to these techniques;

(2) understanding the mechanistic details of degradation of the metal layers caused by the atmosphere and components of the backing;

(3) understanding degradation of the backing material. This task includes studying the adhesion of paints, adhesives, and sealants to each other;

(4) understanding the adhesion of paint to metal layers;

(5) investigating structures, materials, and processes different from those in current usage. Metals can be evaporated or sputtered; they need not be elemental metals but could be compound metals such as titanium nitride or even conductive polymer "metals". Front surface mirrors of refractory metallic compounds such as titanium nitride might be worth consideration; and

(6) investigating the basic phenomena that lead to the adherence of dust, clay, rain, and organic and inorganic contaminants.

B. Windmills

The metal blades of windmills will be subject to erosion and corrosion by sand, dust, salt spray, rain, and hail. Surface coatings to minimize these failure modes are probably limited to some type of polymer coating. In one example, the steel blades (77 m long) are coated first with zinc phosphate (as in conversion coatings), and then coated with a strongly adhesive thermosetting coating with abrasion resistance, and which minimizes attack by water on critical parts of the structure.

Short-range research needs require study of failure modes, developing meaningful accelerated tests for corrosion and abrasion resistance, finding surface coatings optimized to pass the above tests, and developing special protective coatings to minimize pitting corrosion in these parts which get much cyclic stress.

Fundamental research issues include:

(1) understanding the role of zinc phosphate or similar primers; and

(2) optimizing primers and coatings for the special needs of certain geographical locations.

V. SUMMARY AND PRIORITY TABLE

In the preceding sections, the most important needs were identified for our topical area and basic research activities were suggested to meet those needs. The suggested research topics, their relevance, and priority ranking are summarized in Table 2. The priorities were selected on the basis of scientific merit, impact on interface science and solar material relevance.

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Table 2. PRIORITY TABLE FOR ADHESION, ABRASION, POLYMERS

Research Topic	Relevance	Priority
Collectors		
Black coating degradation mechanism	Reduced performance not understood	Crucial
Understanding of adhesion mechanism	Will allow optimization	Crucial
Development of accelerated tests	Necessary for testing optimization	Important
Reflectors		
Replacement technology for metallization	Limited lifetime of state-of-art mirrors	Crucial
Study of degradation mechanisms	Basis for improving mirroring processes	Crucial
Better protective coatings	Present coatings inadequate	Useful
Improve current mirroring processes	Inadequate antiquated processes	Important
Development of accelerated tests	None available now	Important
Understand silver mirror degradation	Silver reacts or agglomerates	Crucial
Improve adhesion of backing materials	Minimize silver corrosion	Crucial
Investigate potential materials options	Replace silver in first surface use	Important
Abrasion Control		
Hardening surfaces	Allow longer use of cheaper materials	Crucial
Cleaning methods	Reduce frequency of cleaning	Crucial
Surface restoration	Minimize abrasion damage	Important
Dust-repellant surfaces	Reduce frequency of cleaning	Important
Polymers		
UV stable polymers	Reduce costs dramatically	Crucial
Improve adhesion to metals	Reduce costs dramatically	Crucial
Improve surface properties	Increase useful lifetime	Crucial
Photovoltaic potting materials	Protect PV devices from atmosphere	Important
Synthesize new polymers	Optimize over present polymers	Important
Membranes for alcohol recovery	Make alcohol separations more cost-effective	Important

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XIV. BASIC RESEARCH NEEDS AND OPPORTUNITIES IN THIN FILMS AND COATINGS

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ABSTRACT

A close link must be established between the Basic Research Community and the Solar Product/User Community in order to maximize our understanding of thin film processing technologies and the principle mechanisms for environmental degradation, as well as to maximize the technology transfer of this necessary understanding into commercial manufacturing operations. To this end we propose objectives for necessary thin-film solar-related research, namely;

(1) to gain a better understanding of basic process involved in thin film fabrication;

(2) to determine process parameters and the relationship of process parameters to thin film properties; and

(3) to develop better methods for characterizing the product film or coating in terms of relevant materials properties and product degradation modes.

Discussion is divided into three areas corresponding to these objectives. In "Fundamental Mechanisms of Film Deposition and Growth," a number of significant basic processes occurring in film growth, all of which need further study, are listed and also the need for analytical techniques to study these processes is discussed. In "Deposition Process Characterization and Control," several deposition techniques are described in some detail ranging from MBE, carried out in a highly controlled UHV environment, to CVD, carried out in a more complex, less well-characterized environment. Advantages and disadvantages of each are discussed. In "Product Characterization," the need for developing clear-cut diagnostic techniques specific to the solar performance of a thin film material is discussed as well as the need for studying mechanisms of environmental degradation of solar films.

The need for in situ characterization during the film or coating process, which can be fed back to control deposition parameters and thus maximize product quality and uniformity, is emphasized.

In a "Summary of Research Needs and Priorities," specific topics of research are presented that were determined by consensus to be of greatest priority to solar thin film devices. In an appendix "Examples of Solar Applications and Needs Related to Coatings and Thin Film Research," we provide the basic researcher with background information about some specific solar thin film problem areas.

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*Co-Chairmen

I. INTRODUCTION

A. Basic Theme

The basic theme of this working group is the importance of establishing a link between the Basic Science Community and the Solar Product and User Community. In order to establish this link, the needs and concerns of the product community will be outlined as related to thin film and coating development, production, and systems application. The Basic Science Community can then strive to help meet these needs and concerns in an environment of mutual interest.

The principle concern of the product community is to obtain high collection efficiency at low initial cost with low maintenance costs and long systems lifetime. In solar components, thin films and coatings are often used in exacting applications such as optical components and as protective layers. In these applications, reproducibility, reliability, and effectiveness are very important. It should be noted that extremely large area production is necessary for solar energy utilization to be a significant contributor to the energy problem.

In the production of reproducible, reliable, and effective components at the lowest possible cost, the production process is as important as the material produced or the product fabricated. Therefore, process reliability and reproducibility is a fundamental goal in any fabrication/utilization scheme. In order to produce a material that meets specifications at the lowest possible cost, it is desirable to have a material that is not process sensitive and a process that has the widest possible tolerances on the process variables.

The Basic Science Community can contribute toward meeting the goals of the Product/User Community by assisting in the characterization and understanding of the processing techniques, materials, and products as these relate to solar applications. This understanding will lead to better reproducibility, higher reliability, increased manufacturing efficiency, and lower cost with a longer product lifetime. The establishment of performance limits and tolerances on processes, materials, and products as a function of cost will allow systems optimization because trade-offs between performance and cost will undoubtedly be necessary.

This group has attempted to establish a link between the Basic Science Community and the Product/User Community by outlining problems of a fundamental nature in the fabrication of films and coatings as these relate to materials properties and fabrication processes. In some cases, specific questions and needs have been presented, while in others, general approaches have been suggested. This is not to imply that these are the only needs or questions!! Most often, the Product/User Community will have to work with the Basic Science Community to determine the most profitable areas and directions of study.

B. The Role of Fundamental Studies in Establishing Solar Thin Film Technology

In the previous section, the vital link between fundamental studies and the proper understanding and control of deposition process parameters was emphasized. In the following discussion, we will deal with the aim and orientation of the efforts that will serve to strengthen this link.

The properties, including the durability of thin films, are largely influenced by processes on the microscopic and submicroscopic scale. Structural, compositional, and chemical effects involving both the film itself and the interfaces on either side of the film play a role. The sum of these effects determines the solar performance of the film. Their sensitivity to degradation establishes the failure modes and limits the durability of the film and the lifetime of devices.

The performance of a film can be improved, and its durability and lifetime increased, if—and perhaps, only if—sufficient attention is paid to the fundamental physical and chemical mechanisms involved in deposition and degradation.

The relationship of these mechanisms to the performance and durability of films may not be fully established in the initial stages of any program; it must be part of the long-term research effort to clarify and understand it. Studies of the basic mechanisms, quantitative product characterization, and process control can all act synergistically to improve further our understanding of the basic mechanisms, which in turn can lead to better and more controlled processes.

The recommendation of this chapter can also be illustrated in negative terms. It is essential that the research effort is not product or performance-oriented in the sense that only work that promises an immediate improvement in performance or durability is performed. Such a trend will lead to a strictly empirical technology that sees its goal in finding a set of process parameters without understanding the fundamental mechanisms involved. In such technologies of which there are many, it is difficult to optimize product performance, to retard in-service product degradation, and to make a reproducibly reliable large-scale fabrication. We cite as an example the use of black chrome for solar absorbers, where the production technology has insufficiently applied the large body of scientific information now available. Another example is the technology of reflector coatings. Being perhaps the oldest optical coatings technology, it has largely retained its empirical character. To reduce or eliminate degradation under solar conditions requires an understanding of the basic processes that govern adhesion, delamination, corrosion, tarnishing, and interfacial stresses induced by differential thermal expansion, to name just a few. Permanent improvements will result if and only if sufficient attention is paid to the understanding of these processes. Judgement on the necessity of basic studies must not be exclusively influenced by their direct and imminent utility for the performance and durability of a particular type of reflecting film.

While the remainder of this report is largely devoted to a rather general discussion of the basic theme presented above, it is important to keep in mind the existing solar applications of coatings and thin films. We have, accordingly, appended a section to the report describing a number of specific applications and needs for improvement.

II. OBJECTIVES

The objectives of the films and coatings report are:

(1) to understand the fundamental mechanisms occurring in the fabrication of a film. These may be further subdivided into

- (a) adsorption kinetics,
- (b) nucleation,
- (c) growth mechanisms, and
- (d) interface formation;

(2) to determine the process parameters and the relationship between process parameters and film structure and properties; and

(3) to characterize products in terms of properties, performance, and durability (lifetime).

III. AREAS FOR STUDY

This discussion is broken down into three major areas following the format of objectives (1), (2), and (3) in Section II.

A. Fundamental Mechanisms of Film Deposition and Growth

1. Goals

A much better fundamental understanding of thin film growth mechanisms is required in order to produce effective and to specify thin film components used in solar technology. Specific areas of research are described below. However, we suggest that the integrated overall goals of research programs in this area should be:

(1) the ability to tailor film properties within the limitations of a given film growth technique;

(2) the ability to specify the film growth environment necessary to meet materials' property requirements, thus providing a rational basis by which to choose a particular film growth technique for a given application;

(3) the development of new materials; and

(4) the development of new processing techniques.

We have chosen to categorize film growth processes into five overlapping areas and have attempted to indicate crucial research needs in each area. In general, an understanding of basic processes is required under nearly-ideal conditions (e.g., UHV for vapor deposition) and systematic studies need to be carried out to determine environmental effects (e.g., ion bombardment during sputter deposition) in order to relate growth variables during deposition to the properties of films deposited under less "ideal" conditions. The latter studies can also lead to new film growth processes. For example, it has been demonstrated recently that with the intentional controlled use of low energy ion bombardment of the growing film during sputter deposition, single crystal metastable alloys such as $InSb_{1-x}Bi_x$ and $(GaSb)_{1-x}Ge_x$ can be grown. Such films have unique properties and exhibit good thermal and long-term stability.

2. Research Objectives

General research objectives are listed below and include studies of:

(1) heterogeneous adsorption kinetics as a function of "ideal" conditions on well-characterized surfaces in UHV; substrate temperature; simultaneous bombardment by

energetic particles (electrons, ions, photons); the chemical state of the impinging adatoms (excited species, metastables, radicals; and substrate contamination;

(2) nucleation kinetics in which adatom surface mobilities, critical nuclei size, island mobility, and island orientation are examined as a function of substrate temperature; substrate microstructure (amorphous, polycrystalline, oriented, lattice matched, etc.) and substrate topography (graphoepitaxy); controlled particle bombardment by energetic photons, electrons, and/or ions during deposition in order to influence adatom mobilities and hence ultimate film microstructure; and contamination;

(3) steady state elemental sticking probabilities (especially high vapor pressure alloying and doping species) as a function of film growth temperature; kinetic energy of impinging species; controlled low energy particle bombardment by electrons, ions, and/or photons during deposition; and contamination;

(4) film growth kinetics including average grain size, grain morphology, preferred orientation, and film density as a function of film growth temperature, deposition rate, controlled low energy ion bombardment during deposition, and contamination;

(5) interfacial diffusion during growth as a function of film growth temperature and controlled low energy ion bombardment during growth; and

(6) post-deposition film processing, especially by laser, electron, or ion beams.

3. Analytical Methods for Studying Fundamental Mechanisms of Film Growth

Very little is understood at present about the fundamental mechanisms of film growth for any processing method. The lack of understanding is in part due to the unavailability of techniques for studying nucleation and growth on solid substrates, as well as the lack of development or application of existing techniques toward this end. We feel that major emphasis should be placed on developing techniques for quantitative studies of fundamental mechanisms.

The types of information desired in such studies can be roughly classified into three categories; structural, chemical or elemental, and electronic or optical. Structural information appears to be the most basic, because most other properties depend on structure. In particular, techniques are required that can elucidate the defect structure, e.g., finite size domains, dislocations, strain, etc. in two or quasi-two dimensions. Techniques need to be developed both for single-crystal substrates and polycrystalline or amorphous materials. Examples of techniques that in our opinion would warrant the attention of researchers are RHEED, LEED, scanning LEED, EXAFS, and FIM. Optical methods such as IR or Raman scattering may also be of aid in identifying structural parameters such as bond lengths and orientations, and should be considered in this respect. Experiments in UHV on such standard electron optical instruments as TEM's and STEM's should be done in order to eliminate questions of contamination inherent in nucleation and growth studies as they are commonly carried out in such devices.

Chemical and elemental analysis must, of course, also be done in situ to characterize the growth process. The availability of good instruments that are readily applicable to this type of research is greater in this area, but few attempts have been made to use these techniques to study fundamental mechanisms of nucleation and film growth, e.g., with respect to stoichiometry, poisoning of nucleation sites, monolayer or submonolayer diffusion barriers, multiple phase formation, etc. It is suggested that, especially, fine-beam instruments used in in situ may provide major advantages in such studies.

Little is at present known about the relation of structure and composition of the film and the interface to the electronic and optical properties of the final material. It is suggested that photoelectron, electron, and optical spectroscopic techniques be developed to assist in determining such relationships, if possible, in conjunction with the structural analysis discussed above. Possible techniques include UPS, XPS, AES, Raman, and IR spectroscopy.

Much important information can be obtained by studying either the equilibrium or a frozen-in state as it relates to nucleation and growth. The dynamics or kinetics of growth will provide different information that may be even more important and certainly will be harder to analyze. We concluded it is important to develop methods that can look at real-time structural, chemical, and electronic properties as these relate to nucleation and growth; in addition to the applications of techniques to study growth modes and interrupted growth, both for single-crystal and polycrystalline substrates. RHEED, LEED, SAM, and STEM in UHV are possible techniques for deducing the structure. The application of the common surface analytical tools for chemical analysis in this type of problem should be considered. The use of new optical techniques should be investigated. Attempts should be made to relate the output of these microscopic techniques to electrochemical measurements of deposition, nucleation, agglomeration, and growth in electrolytic deposition techniques.

To study interface formation and interdiffusion, the additional problem of characterizing a buried interface arises. Typically destructive techniques are used to reach the interface, resulting in poor interfacial resolution and changes in the structure and chemistry. Attention should be focussed on non-destructive structural, chemical, and electronic interface analysis to analyze interfacial effects, e.g., the use of RBS and ion channeling needs to be considered as well as novel applications of electron spectroscopic techniques such as IETS and SEXAFS.

Finally, there may be nontraditional or indirect methods that can aid in the understanding of the basic mechanisms of adsorption, nucleation, growth, and interfacial interactions that have not been listed here.

B. Deposition Process Characterization and Control

1. Introduction

As stated earlier, there is a <u>key link</u> between the process and the product. It is fair to say that while a great deal of attention and energy has been devoted to the detailed characterization of the product in terms of the chemical composition, imperfection content, microstructure, and properties, a detailed study of the process parameters and their influence has been mostly neglected (with a few exceptions such as the MBE and ion beam deposition processes). The tendency is often to establish the process parameters empirically and once the desired product has been achieved no further attempt is made to explore the limits of process parameters which will yield the desired product. This often results in unnecessarily tight process specifications and consequently higher product cost.

It is the opinion of this group that basic studies of processes (i.e., influence of process parameters on the structure and properties of materials) is as important as careful characterization of the product. The two are inextricably linked and only through a better understanding of processes can a higher quality product be produced with the desirable feature of lower cost. This is particularly true for solar energy products where performance and initial cost are both important as contrasted to the microelectronics industry where product cost does not have the same premium.

2. Process Limits

One of the major factors in determining the cost of fabrication and the ability to fabricate an item is the degree of process control that must be exercised during production. An extreme example is MBE, which allows very sophisticated semiconductor devices to be fabricated by careful process control at relatively high cost per unit. An opposite extreme is the vacuum metallization or electroplating of some plastics which can be done at very low unit cost.

Fundamental studies can contribute to determining the limits to process variables in two ways. One way is to define carefully an existing process and then to vary each parameter in a controlled manner to establish tolerances on the deposition variables.

The second way is to produce a new material with desirable properties using precise process control and then to vary the process parameters to establish the relationship between process variables and material properties. An example of the second approach is the fabrication of a semiconductor structure by controlling the thermal flux of depositing atoms and the substrate temperature. Sensitivity of the process to contamination can be evaluated by adding a known flux of contaminants, e.g., O_2.

An example of this approach is the reactive sputter deposition of oxide-metal cermets for high temperature selective solar absorber applications. In order to define the processing, one needs to know the mass and energy of all the species impinging on the substrate surface and the deposition temperature. Subsequently the species, energy, and temperature may be varied to determine process sensitivity.

3. Deposition Processes for Solar Materials

Deposition processes may be classified in various ways. One classification is as follows:

(1) Processes carried out in highly controlled UHV environments. These processes are MBE for evaporation in an UHV environment, and ion beam deposition where the deposition rates are very slow for both processes. However, they offer the possibility of studying in detail the fundamental mechanisms of film formation which may then hopefully be translated to a better understanding and control of the production processes given below.

(2) Processes carried out in a complex (non-UHV) environment which is not closely characterized and controlled. These processes are PVD processes, which include evaporation, sputtering, and ion plating processes; electrodeposition; and spray processes, including thermal spraying, spray pyrolysis, etc.

A detailed discussion of MBE, PVD, and CVD processes along with their advantages, limitations, and research needs is given below.

(a) MBE. MBE is a sophisticated form of vacuum deposition carried out in UHV (typically 10^{-7} to 10^{-9} Pa) utilizing beams of atoms and/or molecules incident upon the growing surface to form an epitaxial, single-crystal film. In recent years MBE has been used to prepare a number of electronic devices with unique properties such as low threshold double/heterostructure lasers, superlattice devices, FET's, and others. While MBE has had small impact as yet in the fabrication of photovoltaic devices, a discussion is included here because the technology involves a high degree of coupling between the fundamental surface mechanisms discussed in the previous section and the ultimate device characteristics. This coupling has been elucidated by the extensive use of analysis techniques such as AES, RHEED, and mass spectroscopy to characterize the surface and its environment before, during, and after growth. This was possible because of the UHV environment and the use of spatially defined beams of film source material. These analysis techniques continue to play a significant role as MBE is extended to new materials.

The most significant feature of MBE is the control it affords at all stages of film growth, both because of the in situ surface analysis, and because the growth rate is slow and low substrate temperatures can be used to minimize bulk and surface diffusion effects. Heterojunctions and superlattices have been grown with virtually single atom layer abruptness. MBE has demonstrated feasibility for producing a number of elemental and compound semiconductors; however, the most extensive studies have been made on GaAs films where the effects of doping and contaminating impurities on the morphology of the film and on the composition of the bulk and surface have been examined. The relationship between surface composition during growth and the resulting bulk defect structure has been determined.

The primary process variables in MBE are the substrate temperature, and the magnitude and time duration of each of the impinging beam fluxes. Secondary parameters that must also be controlled are the initial substrate surface condition and composition, the residual gas pressure, the molecular composition of the beams (e.g., As_2 or As_4), and the magnitude of unwanted impurity beams emanating from the beam sources. An important feature of MBE is that individual beam fluxes can be switched on and off by shutters in times less than that required to grow one atom layer.

As with all film process technologies, there are limitations both to the process and to our understanding of it. The most fundamental limitations to the MBE process are:

(1) the need for extremely clean, ordered substrates with a lattice spacing close to that of the film;

(2) the relatively slow growth rate normally used for high quality films, although faster growth rates have not been extensively studied; and

(3) the relatively high cost of UHV processing.

Some aspects which have not yet been adequately studied are:

(1) the detailed kinetics of incorporating dopants into the growing film;

(2) the adsorption and incorporation of background gas impurities;

(3) the competitive reaction rates of different molecular species, e.g., As_2 and P_2, during the growth of ternary and quarternary compounds; and

(4) the extension of the growth parameter control developed for GaAs to other materials.

It is believed that MBE will have an impact in photovoltaic research not as a production technology but as a method for producing prototype device structures of novel materials for evaluation and testing and for the controlled deposition of polycrystalline metal or oxide films to study other steps in device fabrication. Thus, MBE could serve as a process standard for determining critical structural parameters and tolerances in practical photovoltaic production.

(b) PVD Processes. There are three basic processes, namely evaporation, sputtering, and ion plating. In evaporation and ion plating, thermal energy is used to produce the vapor which subsequently condenses onto the substrate to produce a film. In sputtering, the vapors are produced by positive ion bombardment of the target from a plasma which is biased to a negative potential, i.e., the vapor phase is produced by momentum transfer. A plasma is also present in the ion plating process and positive ions bombard the substrate/coating which is biased at a negative potential; the bombardment produces chemical and microstructural effects at the substrate.

The major advantage of the PVD processes is the great flexibility in selecting materials to obtain different microstructures and properties and deposition rates.

(1) A large variety of materials, i.e., metals, alloys, intermetallic compounds (e.g., GaAs), refractory compounds (oxides, carbides, nitrides), cermets, and some polymers can be deposited.

(2) The composition, microstructure, and properties of a given material can be varied within wide limits by changing the process parameters.

(3) Unusual microstructure may be deposited, e.g., very fine grain size materials, microlaminate composites, or single crystal films.

(4) The deposition rates can be varied from 5 nm/min to 0.075 mm/min; even higher rates have been obtained for special materials such as Zn.

A major limitation of high vacuum PVD processes is that deposition occurs in line-of-sight conditions; this causes poor "throwing power" for coating complex-shaped objects. This problem can be reduced by moving the substrate relative to the vapor source, as is done in coating lenses, tubes or turbine blades. Uniform coating of complex-shaped parts is also achieved by introducing an inert gas into the evaporation chamber, (at pressures exceeding 1.3 Pa) so as to scatter the vapor molecules by increasing the number of collisions. The same scattering process occurs in ion plating. In sputtering, hollow cathode or post cathodic geometries are used to coat the outer and inner surfaces of cylindrical objects.

Variations of the basic PVD processes have been developed for deposition of composite materials or compounds. Alloy deposition using evaporation or ion plating processes can be carried out by multiple source evaporating or from a molten source of constant composition. Sputtering of alloys can be carried out from an alloy target or composite target assembly. Refractory compounds can be deposited by evaporating or sputtering the compound itself, or by reactive evaporation or reactive sputtering in which metal vapors chemically react with an appropriate gas to produce the compound deposit.

Particularly attractive for future solar energy applications is the fact that PVD processes are currently being used in large scale production, e.g., Al on polymeric films, Cr on ABS polymer automobile components, Al on steel strip, etc. Thus, the transition from laboratory studies of a particular solar energy materials system to production for wide-scale applications should be more easily achieved. It is also significant that the deposition technology for producing relatively large areas has been developed.

On the other hand, it is also true that PVD processes are usually carried out in a poorly characterized environment. In particular, this committee identified plasma-assisted PVD techniques such as reactive sputtering, reactive ion plating, and activated reactive evaporation as processes which are not well-characterized and yet which are very powerful deposition techniques for refractory deposits. We believe that studies of the fundamental physical and chemical processes occurring in the plasma and at the surface are crucially needed.

(c) CVD. CVD involves the chemical reaction of one or more vapor species with a heated substrate surface to form the desired film or coating. CVD has been used extensively in semiconductor technology for the production of epitaxial and polycrystalline layers of a wide range of semiconductor materials. Since the growth rates are relatively rapid and large areas can be coated at one time, CVD would seem to have considerable economic value for solar film deposition.

The major process parameters of CVD are the substrate temperature, the composition of the reactant gas phase, its pressure, and its flow rate. Composition, structure, and surface texture of the resulting film can be adjusted within wide limits by variation of these four process parameters.

The principal technological advantage of CVD is that complex structures can be fabricated. Since the composition of the film depends on the composition of the gas phase, heterogeneous structures can be fabricated that are difficult to make with conventional methods. For example, a solar absorber structure can be grown with a reflector layer on the substrate followed by deposition of the absorber and then the antireflection layer using one continuous process simply by varying the composition of the reactant. Specifically, antireflective layers of optimum acceptance angle on Si can be deposited first by adding NH_3 to the SiH_4, producing a Si_3N_4 layer, and then mixing gradually N_2O into the reactant; this produces a graded-index profile of silicon-oxynitrides.

The substrate temperature determines the morphology of the film which can vary from optical smoothness to absorbing-whisker texture. Two-phase composite materials can be produced which utilize scattering mechanisms of the Maxwell-Garnett type.

Examples of using CVD to produce solar coatings include the fabrication of Mo films with the highest reported IR reflectance, and the modification of composition, structure, and grain size to produce "Black Molybdenum" films that combine high IR reflectance with significant solar absorptance. As a third example, we cite CVD amorphous Si absorber films for which the crystallization temperature has been raised from 550 to 1000°C by the co-deposition of C.

4. Techniques for Process Control and Monitoring

In order to evaluate and optimize a given set of process parameters, techniques for on-line, in situ process control and monitoring are required. For example, it would be quite valuable to be able to determine the structural, chemical, electronic and/or optical properties of a film as it is growing, along with the reactant composition, temperature, beam flux, and other parameters that characterize the environment. In the opinion of this group, there has been insufficient development of new techniques and application of existing techniques to process monitoring and control of film deposition. Questions that arise in regard to properties of films are:

(1) Can RHEED, LEED, SEM, STEM, etc. be used in processing environments, and with what limitations, to study structure and morphology?

(2) How can the use of surface compositional techniques be extended to study impurity distributions, phase formation, etc., while the film is growing?

(3) What information can be obtained from in situ electrical and optical measurements and with what limitations?

Greater emphasis should also be placed on characterizing the processing environment. For example, what is the energy distribution of the incident flux? How does the energy distribution affect nucleation and growth and how can such relationship be measured? Can methods be developed that will correlate growth parameters or processing conditions in situ on-line with final materials properties? Research in these and related areas should have a major effect in the development and successful utilization of thin film solar energy materials.

C. Product Characterization

1. Materials Characterization Relevant to Performance in Structures for Solar Applications

Very often research on materials for solar applications is performed in an environment in which it is difficult or not feasible to either fabricate the material into the application structure of interest or to test the specific performance parameters. We believe there is a need to develop both new macroscopic techniques and to utilize those known techniques which will either partially or fully chacterize thin film materials and fabrication techniques with respect to their performance in solar energy device applications. An example of this approach is the measurement of the band edge photoluminescence versus excitation energy to characterize spectral response, e.g., J_{sc} versus $h\nu$, for GaAs solar cells. This technique is easy and rapid and provides accurate information about minority carrier diffusion lengths and surface recombination velocities, when used in conjunction with computer device simulation programs. For research laboratories with limited device fabrication facilities, use of techniques such as the one cited becomes almost mandatory to allow the study of the effects of large parametric variations on materials properties, since the feedback time from direct device measurement would be prohibitive.

- Thus, it is recommended that encouragement be given to the development of new macroscopic methods and/or modification of existing techniques which will easily access materials and interface behavior in terms of their critical performance in solar energy applications.

2. Degradation Phenomena

The study of the degradation and failure of solar energy thin-film materials, material systems, and products is crucial in defining lifetime accurately, improving the durability of products, and in controlled accelerated and abbreviated lifetime testing. It is important that degradation studies be made on well characterized materials or on a statistically meaningful distribution of materials in order to facilitate general conclusions. Although the primary focus of degradation studies is to relate the decline of solar performance parameters (e.g., photovoltaic efficiency, solar reflectance, etc.) to external stresses such as thermal cycling, photon flux, moisture, O_2, or contaminants, in many cases changes in the mechanical and chemical properties not directly related to solar performance may lead to rapid degradation and failure.

Some useful mechanical properties identified by this group for study are:

(1) the plastic flow of interlayers to compensate for thermal mismatch in absorbers;

(2) the stability of amorphous alloys (PV, thermoelectrics); and

(3) the fracture of thin films due to thermal cycling.

Some useful chemical and electrochemical properties identified for study are:

(1) the diffision of H_2O, O_2, and trace contaminants through thin protective films (e.g., PV encapsulants, mirror backing,, AR coatings, switchable optical films);

(2) the electrochemical stability of thin optical and protective films in moist and aqueous environments (e.g., Ag films, PV metallization, heat exchanger coatings);

(3) thermally activated interdiffusion in multilayer structures (e.g., absorbers and PV's);

(4) long term photodegradation; and

(5) the synergistic effects of O_2, H_2O, phonons, and photons.

This list is not intended to be complete, but only to suggest possible areas of study.

IV. SUMMARY OF RESEARCH NEEDS AND PRIORITIES

In Table 1, general topics are presented along with some selected examples which were discussed by this group and thought to be significant areas for research in films and coatings.

APPENDIX: EXAMPLES OF SOLAR APPLICATIONS AND NEEDS RELATED TO COATINGS AND THIN FILM RESEARCH.

Applications for large area thin materials structures are widespread in solar conversion systems. It was thought that a brief summary of the major areas of thin film and coatings applications in contemporary solar collector designs might be helpful in orienting the basic researcher with an interest in using his expertise on the most urgent problem areas. This summary includes a survey of performance parameters and a review of anticipated environmental conditions.

Because the amount of material required by thin films and coatings per unit area is small, one of the major requirements for practical device development, namely reduced cost, is strongly favored. However, the ultimate viability of a particular device or conversion technique depends on its ability to attain acceptable performance levels initially and to maintain those physical characteristics which assure this performance under somewhat extreme environmental conditions for very long times or at least with predictable lifetimes. The discussion below is not meant to be either comprehensive or limiting, but only to indicate examples of practical applications where performance or life time improvement is needed. The examples given are illustrative of two levels of development. The first is for near term applications where materials and methods are already in widespread use in the field in collector systems, but for which improvements in performance, operating range or durability are sought. The second is for advanced technologies where no field applications exist but only prototypical or pre-prototypical systems are under study. Examples of the former are selective photothermal conversion systems, reflector materials, and anti-reflecting coatings. Examples of the latter class are thin film photovoltaic transducers.

Photothermal Conversion Surfaces are tailored to have a high absorptance (α) for the solar spectrum and low emittance (ε) in the IR to suppress radiative thermal losses. Contemporary coatings in widespread use include electroplated "Black Chrome" and "Black Nickel" coatings and various multilayer "interference stacks" and AMA (Alumina/Molybdenum/Alumina) coatings. The solar absorptance for Black Chrome ranges from 92-96% and the emittance from 0.06 - 0.3 depending on the process parameters. For the AMA coatings, lower values of both α (0.78 - 0.88 and ε(0.03-0.08) are typical. These coatings are limited to temperatures below 300° C for practical operation and to temperatures ≤400-450° C for survival. Examples of practical product improvement goals are to increase α for low ε surfaces, and to increase the temperature for both performance and survival to above 400° C.

Other practical requirements that must be considered are the adhesion properties of the coating stack itself relative to a wide variety of possible absorber material substrates, e.g., glass, Au, stainless steel, Al, etc. and absorber shape configurations involving both convex and concave curvature. The extreme range of environmental conditions to which the surface is exposed and the effects on relevant materials properties over a long time needs to be understood. The relatively high operating temperatures occur cyclically with expected lifetimes requiring 5,000-10,000 cycles. In many applications the surface is under concentrated solar illumination with local fluxes from a few hundred ($\sim 10^5$ watts/m^2) to a few thousand ($\sim 10^6$ watts/m^2) suns. Applications for operations in vacuum, in inert atmospheres, and in ambient atmospheres are all probable applications.

Reflector Surfaces are used in solar energy to collect light over large areas and concentrate it on the relatively high cost and/or high thermal loss energy transducers. As such, they must be particularly low cost, and have minimal optical loss. Contemporary reflectors, which almost universally use either Al and Ag as the reflecting surface, are deposited onto a protective transparent superstrate and back-coated with another thin film protective layer or two. Performance (reflectivity) improvements above the 84-90% characteristic of Al films and 94-96% for Ag films are not required so much as an increase in the durability of the reflecting surfaces and their protective films and substrates under direct exposure to the atmosphere and elements. Understanding of the degradation mechanisms for protective superstrates which affect its optical transmittance and specularity is important. The coatings and reflecting surfaces need to be resistant to degradation under long term exposure to one sun level of the UV component of the solar spectrum.

In normal applications the temperature requirements are limited to operation over the range of climatic ambient extremes (e.g., -15° to 45° C). However, there are near term applications for small area secondary reflectors (terminal concentrators) which will be subject to high solar fluxes (typically 50-1000 suns), and probably high temperatures (200°-400° C).

AR Coatings are highly transmitting glazings and required as one of several components in solar converter devices. They are used as thermal barriers against convective heat losses, as vacuum enclosures for high temperature absorbers, as protective covers for mirror arrays, and encapsulant surfaces on photovoltaic cells. In each instance an AR coating can reduce the reflection losses at the glazing air interface by 1 to 3%. This can result in as much as 10-12% improvement in the complete collector system.

The environmental constraints on these coatings range from exposure to solar radiation at one sun up to the highly concentrated fluxes of a few hundred suns. The temperature exposure range would not be expected to be severe in most applications. The operating environment will range from direct exposure to the atmosphere, to a sealed atmosphere to vacuum in some cases.

Thin Film Photovoltaic Transducers are a potentially low cost alternative to thick single crystal Si solar cells, so thin film photovoltaic devices are being developed under a variety of approaches. However, no large scale field deployment or commercialization of any system has occurred. The two most well known techniques are devices based on polycrystalline thin film Si and CdS/Cu_2S thin film solar cells. The performance is typically 9-10% conversion efficiency in small scale laboratory samples. Life times of 3 years have been obtained on 7% cells—and the cells are still being tested—but basic research is urgently needed to help understand and inhibit degradation mechanisms. Investigation of methods for improving the performance through light trapping, built-in fields, and the use of multiple band gap cells is also needed. In general, application involving large area deployment with no concentration will make the most economic sense, so that photon fluxes in excess of one sun and high temperatures are not expected to be a common operating requirement.

TABLE 1. SUMMARY OF RESEARCH NEEDS AND OPPORTUNITIES - FILMS AND COATINGS

Research	Relevance	Priority
1. Relationship between process parameters and material properties	Key item in improvement of products and processes.	Crucial Multi-investigator team approach recommended.
a. Measurements of minority carrier lifetime and density of states in amorphous semiconductor layers		
b. MBE growth of prototypical photovoltaic devices.		
2. New deposition processes for large area device fabrications	A relatively unexplored and potentially highly rewarding area for fabrication of solar components using deposition technology which is new and/or <u>not</u> currently used for this purpose.	Crucial Multi-investigative approach recommended.
a. Energy and species of particles impinging on substrates during plasma assisted deposition		
b. Thermodynamic parameters for CVD.		
3. Fundamental nucleation and film growth studies; effect of surface environment	Essential for basic understanding of fundamental mechanisms in film deposition	Crucial
a. Understanding and control of oxide-semiconductor interfaces states and Schottky barrier heights		
b. Growth and stability of metastable films.		
4. Study of passivation mechanisms	Key to approach of required lifetime in solar products.	Crucial
a. Surface segregation and passivation of alloy reflector surfaces.		

TABLE 1. SUMMARY OF RESEARCH NEEDS AND OPPORTUNITIES - FILMS AND COATINGS (Concluded)

Research	Revelance	Priority
5. Development of in situ techniques for characterization, control, and for studying growth processes and/or the products, a. e.g., development of RHEED analysis or a high resolution microscope operated in situ.	Important methodology to characterize, understand and improve processes and to monitor quality of processing.	Crucial
6. Relation of material properties to long-term performance and stability a. Photocorrosion of semiconductor surfaces b. Stability of coatings with respect to high photon fluxes.	Essential for understanding mechanisms leading to lifetime predictions for solar products.	Crucial
7. Greater application of existing analytical techniques to characterization of processes and products.	Useful and needed item to use all known techniques.	Important
8. Passivating layers deposited onto low-cost substrates (e.g., mild steel) to prevent degradation of active semiconductor element (e.g., GaAs) by diffusion of impurities from the substrate with the active element during processing or use.	Potentially useful for both solar photovoltaic devices and microelectronic devices.	Useful

XV. BASIC RESEARCH NEEDS AND OPPORTUNITIES FOR CHARACTERIZING THE MICROSTRUCTURE AND MICROCHEMISTRY OF INTERFACES

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ABSTRACT

Interfaces of many types (S/S, S/G, S/L) occur in the materials configuration of most solar devices, often with several in close proximity. To make solar devices economically competitive, the manufacturers must make them reliable and reproducible and in cost effective batch quantities. Economic viability also requires that design performance be sustained over long periods of time (e.g., 30 years). To extrapolate from short term laboratory behavior to the required 30 year service behavior requires an atomic level mechanistic understanding of the degradation processes occurring at interfaces. The latter in turn requires application of forefront techniques and methods of characterization of localized microstructure and microchemistry.

Needs were identified for microcharacterization on spatial scales ranging from the macroscopic to the microscopic giving structural, chemical or electronic configurations. Comparison of available techniques with these needs revealed major inadequacies. Much greater effort needs to be invested in "in-situ" techniques. Efforts to extend the capabilities of surface analytical techniques to meet the identified needs are necessary. Recent developments in analytical electron microscopy show promise of complementing the surface technologies and should be developed. Wide use of these techniques in concert is encouraged and wider use of electron microscopy in general is necessary. Much deeper understanding of existing techniques is necessary and totally novel characterization approaches should be encouraged, particularly for "in-situ" characterization of S/L, S/G interfaces.

I. INTRODUCTION

Dominant features of the materials configuration of most solar devices such as mirrors, absorbers, and photovoltaics include S/S, S/G or S/L interfaces with several in close proximity. A mirror, for example, can include ceramic/ceramic, metal/ceramic, metal/metal, metal/polymer and polymer/atmosphere interfaces within a few hundred nanometers thickness. Photovoltaic devices involve semiconductor/semiconductor interfaces and absorbers often are circuits comprising small metallic particles embedded in an insulating matrix. Even prosaic elements such as heat transfer devices will involve S/G or S/L interfaces. To make solar devices economically competitive, the manufacturer must make them reliable and reproducible and in cost effective batch quantities. Economic viability also requires that design performance be sustained over long periods of time (e.g., 30 years). To extrapolate from short term laboratory behavior to the required 30 year service behavior requires an atomic level mechanistic understanding of the degradation processes occurring at interfaces. The latter in turn requires application of forefront

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techniques and methods of characterization of localized microstructure and microchemistry. As understanding of the atomic level behavior develops, development of suitable reliable monitoring procedures during manufacture and in the field becomes possible. Such procedures giving sophisticated atomic-level monitoring may then be developed further to provide feedback control of manufacturing processes.

Exposure of such devices to the atmosphere under ambient conditions of pressure and temperature (which may cycle between wide limits on a daily or seasonal basis) will place extreme demands on the stability requirements for these interfaces. Diffusion into the bulk and along grain boundaries perpendicular to the bulk can convert an initially plane interface into a convoluted profile. Corrosion can be expected to accelerate at the interface, short-circuits or dielectric breakdown can occur due to metallic penetration along defects or grain boundaries,and erosion of the solid surfaces can occur due to chemical reactions or ablation by wind-driven particles. Such phenomena will occur in a wide variety of chemical systems with a wide variety of structural configurations and physical properties on spatial scales extending from the macroscopic (visible by eye) to the atomic (visible only by the most advanced, but still imperfect, means at our disposal).

Needs clearly exist for determination of chemical composition in a direction perpendicular to interfaces in order to assess first whether devices have been constructed as designed, to determine mechanisms causing degradation in performance, and finally to determine suitable monitoring procedures. Profiling parallel to the interface boundary also is needed to deal with the nonplanar surfaces encountered in real devices. Such studies will have to be correlated with physical behavior such as optical properties, strength, adhesion, contact resistance, etc., and will range from large dimensions (e.g., for optical properties one micrometer or more) to the atomic scale to develop an understanding of the underlying atomic mechanisms. Indeed, not only is chemical information needed on a fine scale but also is knowledge of the valence-electronic structure, particularly when electronic devices are in question. The physical atomic structure, i.e., the arrangement and spacing of atoms in the neighborhood of the interface, also is often of considerable importance. The initiation of degradation mechanisms, for example, may well initiate from an unusual atomic arrangement (i.e., defect) in the interface structure. Finally, we note that it is very desirable to develop an understanding of these interfaces, in place and under the conditions in which the device is being used, i.e., "in-situ." Only in these circumstances can one be sure that the underlying mechanisms are correctly identified.

Much progress has been made in microcharacterization techniques in the past twenty years but a comparison of these techniques with the needs outlined in the previous paragraph reveals major inadequacies. "In-situ" techniques have received very little attention and much greater effort must be invested. The most dramatic progress in recent years has been made in surface-analytical techniques as a result of the development of various ion, electron and photon probes and ultrahigh vacuum techniques. Even here, satisfactory interpretation of all the available data has been achieved in relatively few measurements and then only when the sample surface is exposed to a gaseous environment at very low pressures. Profiling of S/S interfaces has been achieved by sputtering techniques but evidence is accumulating of severe modification of the interface during the sputtering process. The surface techniques also are limited in lateral resolution. Clearly, efforts must be made to overcome these limitations. New techniques being developed in analytical electron microscopy offer promise of complementing the surface technologies and should be developed. Electron microscopy techniques in general have not been as widely used as warranted. Wider use of characterization techniques in concert than is currently evident is recommended since all techniques have limitations and provide differing insights; a broad scale attack is more likely to provide reliable information. Reliable use of all techniques requires care. In almost no case is the basis of knowledge of any of the techniques adequate. Theoretical development of the understanding of the electronic mechanisms underlying the probe-response being exploited and background reference data (e.g., cross sections) are badly needed to approach quantitative results. Instrumental improvements and totally novel characterization approaches are also needed, particularly for "in-situ" characterizations of S/L, S/G interfaces.

II. DEVELOPMENT OF MICROCHARACTERIZATION NEEDS/OPPORTUNITIES

This chapter addresses the issue of the structural, chemical,and electronic characterization of interfaces in solar energy conversion technology. By considering examples of the interfaces occurring in solar devices such as mirrors, absorbers, transmitters, and photovoltaic cells, an assessment of the adequacy and limitations of existing, emerging,and needed approaches to the problem was developed.

Specific interfaces of significance to solar energy technology span a wide range in character. Mirror reflectors, for example, as currently manufactured, comprise multilayer structures composed of glass-tin oxide diffusion barrier-silver-copper-protective paint. In this structure S/S interfaces made up of ceramic/ceramic, ceramic/metal, metal/metal and metal/polymer coexist within distances of a few hundred nanometers or less. To be cost effective, solar energy installations need cheap devices with long lifetimes of the order of 30 years under exposure to atmospheric conditions and elevated temperatures. Lifetimes of this length combined with nanometer distance scales place extreme demands on the stability of the microchemistry and microstructure of the system. Indeed, it is already apparent that such systems are susceptible to corrosion and degradation on time scales much shorter than those required and thus improvements of such devices will be necessary. As corrosion and degradation are initiated at the most susceptible interface, it is evident that interface microcharacterization (specifically composition and structure) is required to identify, monitor and control those factors which limit device performance and to develop devices with improved performance, lifetime, or efficiency.

In developing a solar device such as an improved mirror to meet conditions such as those outlined above, a number of distinct needs for microcharacterization are required. These include:

(a) The need to ensure that the device as constructed does indeed meet design specifications. Have the right materials been laid down in the configuration envisioned?

(b) The need to ensure that the device is reproducible. If two devices made under apparently reproducible conditions do not behave identically, the difference will often be related to microcharacteristics. Such differences will then, in many cases, indicate the reproducibility one can achieve.

(c) The need to determine the precise cause of failure of the device from degradation in performance as a result of long term diffusion, corrosion, or other causes from atmospheric exposure. Such degradation will arise from changes in the microchemical structure and accurate determination of such changes will be necessary to identify the underlying mechanisms and to establish corrective actions.

(d) The need to predict lifetimes with confidence over a 30 year period from accelerated bench tests. Extrapolation over such a long period will be dangerous if based solely on empirical tests. Reliable prediction can only be achieved with confidence if an understanding of the underlying atomistic behavior is also achieved so that the progress of degradation can be described with confidence.

(e) The need to develop simple field diagnostic tests to monitor progress of degradation. Such tests will undoubtedly involve measurement of a macroscopic property that can be monitored with simple apparatus on a routine basis. Nevertheless, the validity of such tests will be established with a detailed knowledge of the progress of the microchemical changes of the sample (which might well dictate the need for more than one such procedure).

Similar considerations to the above apply to a number of other solar devices, in particular, to selective solar absorbers and to photovoltaic devices. In the one, the absorptive properties depend in a number of instances on a variation of microstructure involving a cermet (ceramic metal composite) with microchemical variations again on a microscopic spatial scale (~10 nm). In the other, one is dealing either with a heterojunction directly, e.g., CdS/Cu_2S or with questions involving metallization on top of a semiconductor. For these S/S interfaces,additional questions arise concerning the microelectrical properties of the interface. Detailed knowledge of the microchemical and microstructural properties of these interfaces will also turn out to be necessary in improving performance, lifetime,and cost effectiveness.

The oral presentations to the workshops and conclusions of the other working groups have identified many other interfacial problems, not only in S/S but also in S/G and S/L interfaces. The initial stages of nucleation and film growth, for example, are not well understood and it is not now feasible to control deposition conditions adequately so that films with common properties can be prepared in different laboratories; more importantly, film properties usually cannot be adequately predicted based on knowledge of deposition conditions. Relatively simple models have been proposed to describe, for example, the energetics of S/S interfaces and the double layer at solid/electrolyte interfaces, but basic assumptions and deductions have often not been verified due to the lack of adequate structural and chemical characterization methods. An example of an important S/G interface where this applies is the corrosion and degradation of mirrors exposed to the atmosphere. A revolution has occurred recently in our understanding of the solid/vacuum interface as a result of the development of surface spectroscopical and characterization techniques which provided physical insight that completely changed our perspective. It is not too unreasonable to expect a similar change in our thinking should equivalent approaches be generated in studies of the S/L, S/S, and S/G interfaces.

Given the stability requirements outlined above and other considerations, some general conclusions can be drawn:

(1) It is not possible to predict or control many interface properties without detailed knowledge of the composition and structure and without validated theses and models of interfaces and of the chemical and atomic processes occurring there. Measurement of interface properties and processes must usually be made on a scale of atomic dimensions normal to the interface and at least submicron dimensions parallel to the interface.

(2) The ability to design solar devices with improved properties depends on the acquisition of structural and chemical knowledge of interfaces of many classes of materials.

(3) The lack of adequate interfacial characterization methods is a major barrier to solar technologies.

A general basic research goal of microcharacterization studies should therefore be to develop the atomic mechanisms underlying chemical (and associated physical) changes at interfaces coupled with the deliberate development of existing techniques, theoretical understanding, and novel approaches to microcharacterization. In the following sections of the document,we review specific interfaces and identify examples of need, discuss briefly various techniques for microcharacterization,and summarize our recommendations for action with priorities.

III. INTERFACES IN SOLAR ENERGY TECHNOLOGIES

A. S/S Interface

The S/S interface represents combinations of materials classes such as metals, ceramics, glasses, semiconductors, and polymers. In characterizing such interfaces, we are interested in relating the mechanical (adhesion, creep, etc.), electrical (resistivity, barriers, etc.), and chemical (oxidation, phase change, etc.) properties of the interface to their structural (atomic arrangement including defects) and chemical (elemental and chemical compounds) configurations. The terms structural and chemical configuration are meant to be global terms. For example, structural includes the atomic arrangement (e.g., epitaxy), defect structure (e.g., dislocation array in a grain boundary), and the changes in these structures with time and temperature with forces acting on the solid. Chemical configuration includes elemental composition, combination of elements into compounds (e.g., oxides, intermetallics, etc.), and changes in these with time.

There are many specific examples of S/S interfaces in solar materials, for example, the grain boundaries in polycrystalline photovoltaic materials, multilayer metallized reflectors, multilayer selective absorbers, antireflection coatings on transmitters. We have a reasonable array of techniques for studying many of these S/S interfaces, but some areas clearly deserve more attention.

In the case of metal/metal interfaces, the analytical techniques of AES, XPS, ISS, SIMS, RBS, and NRA have proven very useful in characterizing elemental composition. The spectroscopic techniques of AES, XPS, and SIMS can in principle provide the chemical structure at and close to the boundary through the use of depth profiling by sputter etching. Unfortunately, as individual experience with sputter etching has been accumulated [1], so has evidence that the use of sputtering to expose the interface may destroy the intrinsic character of the interface being studied. The reduction in depth resolution that occurs in sputtering lowers significantly the available information at an atomically sharp interface. To the degree that this in fact can be circumvented by modeling or by loss of detail, these techniques can provide a measure of chemical profiles at interfaces. Improvement in these techniques could lead to much better depth profiling and to much improved understanding of interface characteristics.

The atomic arrangement and defect structure at these interfaces have not received comparable attention in spite of the availability of electron microscopy techniques (weak beam, dark field, high resolution) which have been used with considerable effectiveness in the study of grain boundaries. Such studies can be readily tackled with films of grain sizes greater than one micrometer but may encounter complexity of detail at smaller grain sized films. Thus care in instrumental performance (stabilities, etc.), skill in interpretation and exploitation of newly emerging techniques such as convergent beam microdiffraction will all be necessary at this level.

Similar comments may be made about metal/semiconductor, metal/glass, metal/ceramic, semiconductor/ceramic interfaces in solar systems, i.e., the elemental composition can be determined but considerable research is needed in developing our concepts of the interfacial structure and structural evolution. High resolution electron microscopy, for example, has revealed an atomically smooth interface between Si and SiO_2 giving a crystalline to amorphous transition over a very few atomic spacings [2]. Analytical electron microscopy techniques in principle can provide valuable chemical and spectroscopic information on a scale approaching this but has not yet reached the same stage of application.

A particular case in point is the class of interfaces using polymers. For solar systems to be cost effective, extensive use of polymers will be necessary. Polymers are light weight, relatively cheap, and can be impervious to atmospheric corrodents. Therefore, polymers may be used for support materials (such as the base for reflectors or structural members for heliostats) or as protective coatings (such as on the backside of silver reflectors or the outer surface of transmitters containing heat transfer fluids). Presently, profiling of polymer surfaces by XPS can be accomplished in part by varying the photoelectron "take-off" angle and thereby varying the electron escape depth. This is insufficient for profiling over depths of more than 5 nm. Thus, the above discussion calling for improved depth profiling techniques is equally valid for solid/polymer interfaces; i.e., it is critical that techniques be developed which do not disrupt chemical bonds over depth into the solid equal to the detection depth of the analytical technique (i.e., depths of ~2 nm for XPS analysis). Obviously, alternative and even completely novel approaches to these systems (i.e., solid/polymer) should be encouraged.

B. S/G Interface

An understanding of and ability to measure the S/G interface as related to the solar energy area involves two major concerns. One is related to the fabrication of devices and structures and the second concerns the exposure of these devices and structures to gaseous environments during their lifetime.

An example of the fabrication area is the deposition of a thin film in a low pressure (high vacuum) environment which must have certain mechanical, electrical, and/or chemical characteristics. One must know such things as the order, or lack thereof, of the solid surface (using, for example, LEED or RHEED), the elemental composition of the surface (using AES, ISS, static SIMS, etc., for analysis), the chemical state of the surface composition (using XPS, ESCA), the surface morphology (using SEM), and gas composition during the film deposition (using RGA).

An example of the second concern is the exposure of a film (as part of a photovoltaic cell, a passive solar thermal collector, etc.) to the air as it is being used. For example, if the atmospheric oxidation of aluminized reflectors over 30 years is to be understood, the phenomena of low temperature oxidation must be studied. Therefore, the nucleation and growth of oxide islands might be characterized by quantitative LEED analysis, and the influence of surface imperfections upon this process quantified, again by LEED. Quantitative AES and XPS would then be used to study the subsequent chemical states and concentrations of surface elements. By quantitative analysis, the amount of surface hydration could be determined and perhaps related to dust particle adhesion. Adsorption isotherms of trace quantity atmospheric pollutants such as H_2S and H_xSO_y products could be determined.

Polymer systems used as structural members or protective coatings as discussed above can be taken as a second example. Their interface with the atmosphere will be subjected to oxidation both as a result of active radicals from the atmosphere and molecular-bond-breaking and molecular degradation from photon irradiation. Our ability to analyze the polymer/air interface is by itself very limited. Electron beams can be used for high spatial resolution analysis but they generally destroy the polymer molecules. This may be acceptable in some instances such as copper diffusing into polymer protective coatings. In general, though, electron and ion beam techniques tend to modify the polymer material very rapidly and have proven useful only in limited cases under very restrictive conditions (e.g., diffuse beams, extremely low beam currents, and small particle fluence) with techniques such as HVEM, ISS, and SIMS. XPS is the most widely used method currently available for direct nondestructive chemical state and elemental analysis. Multiple reflection infrared spectroscopy (MRIS) can sometimes be used with sufficient surface sensitivity to study polymer/gas interfaces. For "in-situ" analysis, macroscopic property techniques such as wetting-angle measurements are therefore often used for indirect surface characterization. It is critical therefore that techniques be developed which are sensitive to the surfaces of polymeric coating. These techniques must be capable of analyzing the chemical bonds present in the polymer prior to any bond rearrangement induced by the analytical technique, and should be capable of analysis at pressures near atmospheric. Ideally, relatively cheap, reliable and portable instruments using these techniques should become available for "in-situ" measurement of surface conditions. Optical methods do not now have the elemental sensitivity or specificity for routine use although they could be used to monitor changes in surface and interface conditions. Possibly, they can be developed as monitors of large area devices and used as feedback elements in processing control systems.

Analysis of the S/G interface is the most advanced area of research in surface science. Many techniques (such as those listed above) have been developed and used by many people. A fair understanding of these techniques and how to interpret the data obtained from them is available. Improvement of the techniques as such is clearly necessary to provide for further exploitation by generating progress in the areas of quantification, understanding of fundamental scattering, minimization of analytical artifacts and specimen preparation. Even so, in only a few model systems has genuine understanding been achieved such that predictions of long term behavior can be made with confidence. This conclusion is again based on measurements made in extremely low pressure systems and extrapolation from such results to the prediction of behavior over a 30 year time span under atmospheric exposure appears unwarranted without validation with "in-situ" systems. The point can be made succinctly with Fig. 1 giving pressure and temperature scales. The different regimes in which solar devices operate and the available analytical techniques are evident.

C. S/L Interface

The S/L interface also is important to solar energy conversion. For example, photoelectrochemical energy conversion systems are based on a semiconductor/electrolyte interface. Photoelectrolysis cells and photocatalytic cells are also dependent upon S/L interfaces. For the development of new electrolytes, electrodes, and catalysts, and to investigate the degeneration of these systems,knowledge about the chemistry and structure of these S/L interfaces is required. More general S/L systems will also involve the liquid transfer media in heat transfer systems, molten salts, etc., in heat storage systems, and the like. Perhaps the most obvious mechanism of degradation in these systems is corrosion, i.e., chemical attack of the solid at the interface. Studies of micropitting at the interface clearly call for microcharacterization and microanalytical techniques. Identifying the underlying atomic mechanisms and monitoring the progress of the reaction will be necessary both to devise protective measures extending the lifetime and to predict the lifetime with confidence. The study of S/L interfaces is not a new discipline; however, there are almost no studies that determine the atomic structure of the S/L interface nor the chemical or electronic structure on an atomic scale, i.e., there is a lack of spectroscopic methods for characterizing these interfaces. We need approaches to these interfaces that have a similar sensitivity and specificity as those developed for the solid/vacuum interface.

There are two general types of measurement that can be made with these systems. First, there are those wherein the solid electrode surface is removed from the liquid medium and after carefully selected treatments (which may include rinsing, drying, transport) is examined by the usual solid surface analytical methods (SEM, EMPA, AES, XPS, RBS, SIMS, etc.). Such measurements can provide a large amount of information about the chemical and structural properties of these surfaces, and for some systems they represent, at present, the only viable methods. What such measurements cannot provide is assurance that

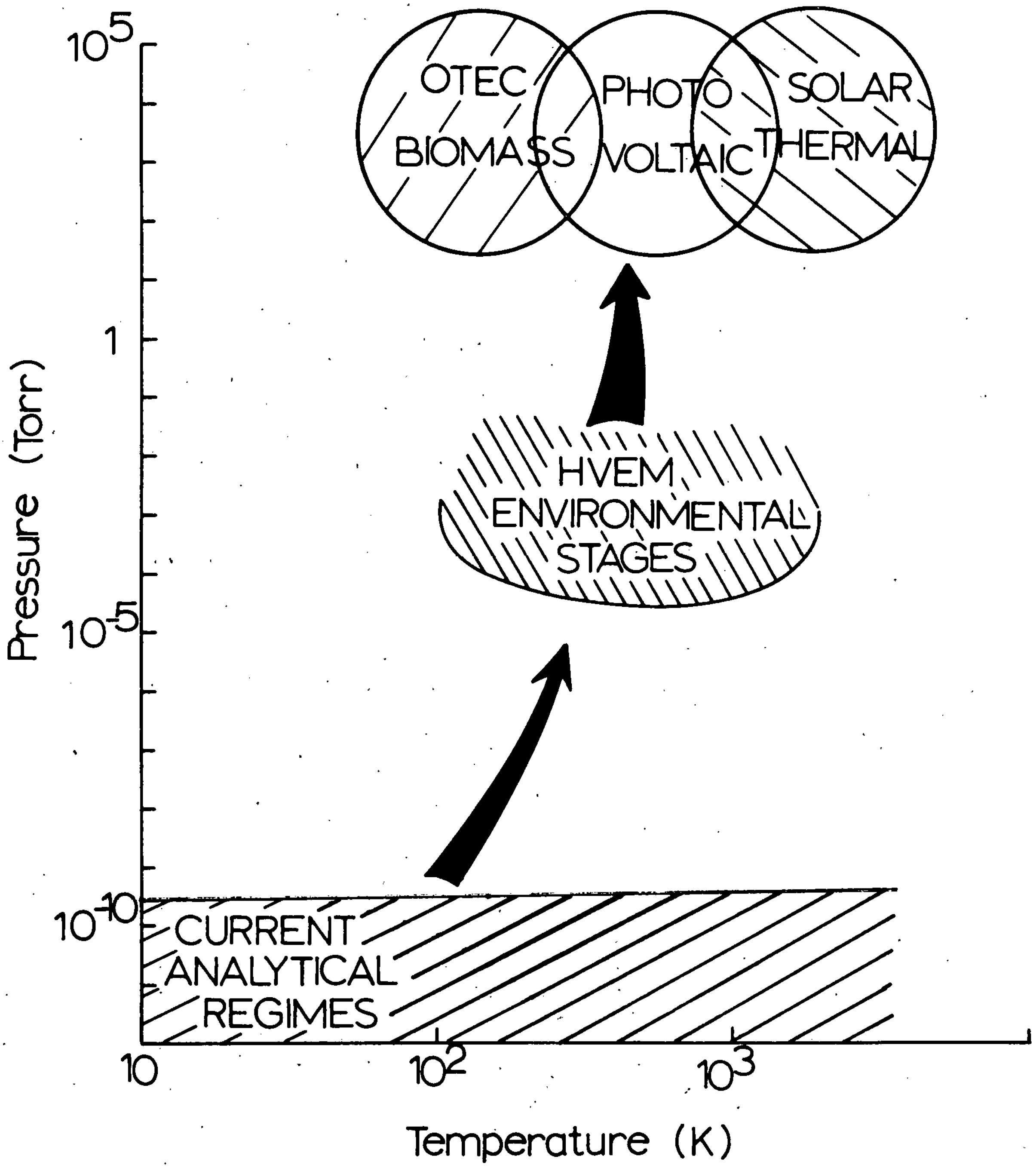

Fig. 1. Regimes of available characterization techniques as a function of pressure and temperature as compared with various solar energy technologies.

the surface so examined is representative of the surface as it existed in the operating cell.

The second general type of measurements are "in-situ" measurements. These "in-situ" measurements are expected to be of critical importance to understanding the interface. Certainly work on "dried out" electrodes and catalysts should be extended, but it must be correlated with "in-situ" measurements to guard against artifacts, etc.

For "in-situ" work, electrochemical measurements can detect very small changes in the interface but they cannot, in general, describe the mechanism of such a change. The "in-situ" methods that can provide such information are the optical spectroscopies such as laser Raman spectroscopy and infrared and multiple reflectance infrared spectroscopies. Novel methods, at least as applied to S/L interfaces, should be investigated. Such novel techniques can include surface enhanced Raman spectroscopy, laser fluorescence, HVEM with liquid cells, nuclear hyperfine structure, etc. These techniques would also be needed to validate "ex-situ" methods.

IV. INTERFACE CHARACTERIZATION

A. General Requirements for Interface Characterization

The interface between two (or more) phases can be identified by the variation of composition or structure with position. Some interfaces may be sharp on an atomic scale (e.g., grain boundaries) while others may be more extended (e.g., interdiffused layers). A given interface property (e.g., mechanical, chemical, or electrical property) may require characterization of the interface on a range of scales ranging from the macroscopic dimensions of a particular device to atomic dimensions, i.e., from concern with physical properties and engineering performance to developing an understanding of chemical and electronic processes at the interface. In all cases, an analysis needs to be made of how the particular interface property depends on the expected or possible variation of structure, elemental composition, or chemical environment with position both normal and parallel to the plane of the interface. An assessment needs to be made of the interface homogeneity or heterogeneity; that is, whether variations of structure or composition in a given region of the interface are similar or different to other regions. Interface characterization with a range of spatial resolutions varying from atomic dimensions to microscopic dimensions is therefore required. Specific needs for the structural and compositional characterization of the many S/S, S/L, and S/G interfaces of interest to solar technologies are given in the reports of the other working groups; some examples are given above. In most cases, the characterizations have to be made on a large variety of interfaces of real devices. In addition, characterization of model interfaces prepared under more ideal conditions should also be used to develop the knowledge required for the prediction and control of interface properties.

B. General Approaches to Interface Characterization

Several different general approaches are now used for interface characterization. First, the S/G interface can be characterized by numerous techniques when the gas pressure is very low (i.e., in UHV) but there are relatively few techniques that can be used for "in-situ" characterization of the S/G interface when the gas pressure corresponds to that in the atmosphere. While gas can be removed at different stages of a S/G reaction, for example, so that the solid/vacuum interface can be characterized, additional diagnostic techniques need to be employed to ensure that changes in gas pressure do not significantly change the measured surface properties. Second, the techniques for "in-situ" characterization of the S/L interface are extremely limited. Attempts are currently being made by several groups to remove the liquid in a vacuum environment with subsequent examination of the solid by "surface" spectroscopies. The general validity and utility of this approach still remains to be demonstrated. Finally, S/S interfaces can be characterized by one or more of the following approaches:

(1) "non-destructive" examination of microscopic thin film devices (e.g., RBS);

(2) removal of solid material by mechanical means or in sputtering in conjunction with "surface" spectroscopies to obtain compositional information as a function of depth from the original surface; and

(3) examination of thinned samples by transmission electron microscopy and diffraction.

These three lead to the following requirements: for non-destructive characterization, the use of the methods with sufficient sensitivity and spatial resolution to characterize composition as a function of depth; the use of material removing techniques which minimize unwanted changes and damage in the sample; and for the characterization of thin samples by analytical electron microscopy, the development of techniques for the preparation of representative samples.

C. Discussion of Interface Characterization Techniques

Table 1 is intended to illustrate the variety of techniques which have been utilized for the structural and chemical characterization of S/S, S/L, and S/G interfaces. It also illustrates where significant improvements of characterization capability are required.

Descriptions and evaluations of the commonly used techniques are given in recent review articles [3-6] and no attempt will be made here to duplicate this material with respect to parameters such as sensitivity, resolution, etc. We do provide the caution that consideration has to be given to the care with which such parameters are specified since different problems often require different approaches and trade-offs; simple blanket comparisons of performance can often be misleading when out of context. A parallel word of caution reflects an apparently often overlooked point, namely, that the quality of the scientific results obtained from an instrument reflects not only the instrument but also the caliber of the scientific staff using the instrument. It is not enough to invest money in an instrument--care must be taken to provide adequate engineering support staff for maintenance, operation and in many cases ongoing development together with appropriately trained scientists able to provide high

Table 1. INTERFACE CHARACTERIZATION TECHNIQUES AND NEEDS

Interface		Present Techniques	Needed
SOLID/ SOLID	Structural Characterization	SEM, optical microscopy, HEED, LEED, XRD, ion channeling, FIM, ellipsometry, EXAFS.	Determination of morphology with atomic resolution. Non-destructive techniques for characterization of polymers.
	Elemental Identification	AES, XPS, SIMS, ISS, RBS, NRA, PIXE, APFIM, laser microprobe analysis, EELS-core levels, EDXA.	Non-destructive depth profiling methods. Methods of "in-situ" observations (e.g., sample under stress and high temperature conditions). Improved interface resolution. Methods of thin film specimen preparation. Non-destructive methods for analysis of polymers.
	Chemical-State Characterization	XPS, SIMS, IR, EELS	Profiling techniques which do not change chemical state of material. Methods with improved spatial resolution. Methods for "in-situ" chemical-state analysis.
SOLID/ GAS	Structural Characterization	IR, Raman spectroscopy, ellipsometry, inelastic neutron spectroscopy, optical microscopy, and "ex-situ" use of LEED, RHEED, ESDIAD, UPS, electron channeling, ion channeling, surface EXAFS, and vibrational EELS.	Methods for "in-situ" structural determination at atmospheric pressures. Methods for structural determination with atomic resolution.
	Elemental Identification	EDXA, RBS, NRA, PIXE, and "ex-situ" use of surface spectroscopies (AES, XPS, SIMS, ISS, APFIM, and EELS-core levels).	Methods for "in-situ" elemental identification.
	Chemical-State Characterization	IR and Raman spectroscopy, inelastic neutron spectroscopy, "ex-situ" use of surface spectroscopies (XPS, ESDIAD), vibrational EELS.	Methods for "in-situ" chemical-state analysis.
SOLID/ LIQUID	Structural Characterization	XRD, ellipsometry, Raman spectroscopy, electrochemical techniques.	Further development and evaluation of Raman spectroscopy. Methods for structure determination with atomic resolution.
	Elemental Identification	Carbometry, laser fluorescence spectroscopy, "ex-situ" use of surface spectroscopies (AES, XPS, ISS, SIMS).	Methods for "in-situ" elemental identification.
	Chemical-State Characterization	IR spectroscopy, laser fluorescence spectroscopy, Raman spectroscopy, "ex-situ" use of surface spectroscopies (XPS, SIMS).	Methods for "in-situ" chemical-state analysis. Characterization of double layer at metal/electrolyte interfaces.

level consulting advice, direction, and interpretation. A scientific staff of the necessary caliber usually requires an active research program.

The techniques shown in Table 1 are in varying stages of development. For some, commercial instrumentation is available. Even with the more widely utilized and available techniques (e.g., AEM and AES), substantial advances in capability are being made. Substantial gaps in supporting knowledge and data still remain (e.g., information on scattering cross sections, reliable methods of data reduction, and relationship of spectral line shapes to chemical environment). It is therefore believed that substantial developments of the newer techniques (e.g., LRS and EXAFS) will be required to permit improvements in their utility and range of applicability over the next few years.

It is also clear from Table 1 that while many of the techniques provide useful diagnostic information, information has often been obtained under circumstances where appreciable modifications could have occurred (e.g., damage by ion sputtering, removal of a solid sample from a liquid or a gaseous environment). There is a clear need for "in-situ" methods of interface characterization. Bearing in mind the complexities which have been found with the commonly used surface spectroscopies (AES, XPS, SIMS, ISS) and known limitations of existing optical methods (e.g., ellipsometry for S/L characterization), it is believed that combinations involving at least two techniques (e.g., ellipsometry, laser fluorescence spectroscopy, Raman spectroscopy) to specify interface composition and structure will be required. New approaches which are more reliable and sensitive for interface characterization are urgently required. Likewise, innovative approaches that minimize the perturbing effects of the incident radiations are also important.

Most of the techniques for microchemical analysis provide data for an "information volume" that will contain the interface and the surrounding medium and do not usually provide data with atomic resolution. It is believed that high resolution analytical electron microscopy and atomic-probe field ion microscopy could provide vital information relating both composition and structure of interfaces with atomic or near-atomic spatial resolution. Such information could provide the key for the understanding and future control of interface properties. The increased use of analytical electron microscopy and atom-probe field ion microscopy will require development of refined methods of specimen preparation.

V. RECOMMENDATIONS

A central theme evident from much of the early part of this chapter, as well as others in this workshop, is the need for "in-situ" studies of "real" systems as well as model systems, i.e., studies of S/S, S/L, or S/G interfaces under conditions that closely simulate if not exactly match conditions met in the field. It is an area that is relatively difficult and not much work has been carried out as a result. Development of a good understanding of atomic mechanisms underlying degradation of these interfaces is considered crucial to the development of reliable predictive capability, and to methods of enhancing device lifetimes. Even if the only result of "in-situ" studies is to provide checks on much more extensive experiments carried out by other means, this validation would be a crucial step in understanding these systems.

However, "in-situ" studies also hold promise of development of methods of monitoring process parameters during film or coating manufacturing procedures. The appropriate feedback of such monitoring so as to control process parameters can be expected to improve considerably the yield of manufactured devices of suitable quality. Accordingly, our recommendations include the following with an assessment of crucial:

- Development of photon and ion analytical techniques for "in-situ" characterization of the S/L and S/G interfaces (e.g., laser, Raman, IR and related techniques, RBS, and NRA).
- Exploitation of "in-situ" environmental stages in high voltage (1 MeV) electron microscopy, preferably with analytical capabilities for S/S, S/L, and S/G interfaces.

Some general comments on these are as follows. Successful achievement of "in-situ" measurements involves the passage of a probe particle through bulk material, interaction with the interface, and then some signal has to propagate out. This often entails use of high energy probe particles, including photons. For example, the energetic ion beams techniques of RBS and NRA are now providing "in-situ" elemental analysis of S/S interfaces and offer some promise of "in-situ" analysis for S/L and S/G (atmospheric pressure) analyses.

With respect to the S/S interface, RBS and NRA have clearly been shown capable of analyzing an interface at a depth from the surface of ≥ 1 μm in many materials. This would prove very useful in solar materials, for example, when applied to interdiffusion of Cu into Ag mirror layers. Another example would be oxidation of Ti adhesion layers under Ag metallization on solar cells. NRA could be used, for example, to measure the amount of H incorporated into the Ti layer under Ag. At high levels of incorporated H, stresses sufficient to cause Ag delamination could result. It is obvious therefore that RBS and NRA can be more extensively used for "in-situ" analysis of the S/S interface.

Since the energetic primary ions used in these techniques will penetrate into a solid ~1 μm, they should penetrate through gases and liquids for distances at least that great. Therefore, it is entirely feasible to envision the use of small windowed reaction cells in which the S/G and S/L interfaces might be studied under "in-situ" conditions. This would clearly be desirable in studies of photoelectrolysis of water, sulfidation of silver reflectors, or surface segregation induced by oxidation of Al-Ag alloys. Therefore, the continued use of RBS should be encouraged for studies of all three types of interfaces.

In electron microscopy, "in-situ" techniques have been developed over a long period of time with the construction of environmental stages providing heating/cooling, straining, specimen orientation changes, etc., within a gaseous environment. A primary limitation has been specimen preparation, but the development of high voltage microscopy (at 1 MeV) reduces this limitation considerably since much thicker samples then become transparent to electrons. Much interesting work has been carried out overseas, at Imperial College, London, for example, where direct observations of the reduction of hematite have been carried out [7]. Development of electron spectroscopy techniques at these voltages (as carried out at Toulouse, France [8], for example) and

X-ray detection capability will add spectroscopic information to the spatial and diffraction capability. The Department of Energy has established HVEM centers at Argonne National Laboratory, Oak Ridge National Laboratory, and Lawrence Berkeley Laboratory. For information on the submission of user proposals to these facilities, the contracts are ORNL: Dr. J. Bentley (615-574-5067); ANL: Dr. A. Taylor (312-972-5005); and LBL: Dr. K. Westmacott (415-486-5663). In addition, the University of Illinois has established a Center for Microanalysis of Materials; for microstructural analysis, the contact is Prof. H. Fraser (217-333-1975) and for microchemical analysis, the contact is Dr. P. Williams (217-333-0386). These facilities should be extensively used in the solar technology thin film problem area.

Finally, we note the promise of photon analytical techniques based on optical spectroscopies (e.g., LRS and IR) for these systems transparent on at least one side to optical radiation. These techniques should be used as probes of such interfaces. Again, however, any novel approaches to these interfaces should be encouraged to the point where serious critical evaluation of potential benefits can be made.

The above recommendations were concerned primarily with the S/L and S/G interfaces. The group also makes the following recommendations,also judged "crucial," with respect to the study of S/S interfaces:

- Improved depth profiling techniques are needed for use in S/S interfacial analysis.
- AEM techniques should be applied for characterizing solar material interfaces.

While surface spectroscopies, such as AES, XPS, ISS, and SIMS have proven to be extremely useful in analyzing interfaces in solar materials, there is considerable room for improvement especially when the interface lies deeper in the sample than the analysis detection depth (i.e., deeper than ~5 nm). For such interfaces, depth profiling is necessary and if ion sputtering is used it is difficult to achieve atomic resolution in depth profiling, or retain chemical state information at the interface. It is critical therefore to develop alternative methods of depth profiling. This is especially true for polymer films. Other examples include the heterojunction region in CdS/Cu_2S photovoltaic devices, passivation layer interface on Si solar cells, the glass/Ag interface on solar reflectors, and the absorber/low emitter interface in selective solar absorber films. In each case, improved techniques are necessary which would allow profiling through the overlying film such that the interface was reached simultaneously over the entire analyzed area, and allow profiling to the interface and still retain metals in the oxide, sulfide, sulfate, etc., state at the interface for chemical state analysis. Possible candidate techniques in this respect are microsection oxidation and chemical stripping, angle lapping, microsection polishing, microsection chemical etching, and modification of sputtering equipment and procedures.

An alternative approach to the S/S interface involves the exploitation of recently emerging developments in AEM. Development of the field emission gun at the University of Chicago [9] made practical STEM which with the addition of microdiffraction, X-ray fluorescence detection,and EELS has extended our capabilities in electron microscopy. Many of the problems identified in Chapter X concern the need for composition profiles as a result of complex diffusion patterns along grain boundaries or through the bulk. For example, diffusion along grain boundaries can rapidly turn an initially flat profile into a convoluted profile with lateral variations on the scale of the grain size. Such patterns can, for example, be expected in multilayer structures such as mirrors and in addition can occur in materials prepared for photovoltaic devices. Since the distance scales are so short (≲100 nm) these represent extremely difficult technical problems. Exploitation of field emission STEM in this area appears promising; this method should be valuable as a complementary tool to the surface spectroscopies in that it provides a point-probe analytical capability as opposed to a surface capability. It should be noted, however, that for this developing technique, attention will need to be paid to the underlying physics of the probe interactions, to improving the instrumentation, and to providing needed data (e.g., interaction cross-sections) if the full potential is to be realized.

The group also regarded as crucial the following recommendation concerning the surface-analysis techniques now in common use:

- Development of methods for quantitative surface analysis, characterization of beam artifacts, and improved methods of data analysis for AES, XPS, ISS, and SIMS.

Although these surface-analysis techniques are in common use for a great variety of applications, most analyses are qualitative, not quantitative. Reliable procedures need to be developed to derive elemental concentrations from observed intensities. More information needs to be obtained on the basic physics of the interactions (e.g., on spectral lineshapes and the origin of satellite features to enable meaningful intensity measurements). Procedures need to be developed to ensure that the instruments are operating correctly (e.g., the transmission function of the analyzer system needs to be determined). Finally, standards are required not only for the different methods of surface analysis but also to calibrate the depth scales when depth profiles are obtained with a surface-analysis technique in combination with sputtering. Quantitative measurement of trace-level impurities, for example, on Si or compound-semiconductor surfaces prior to deposition of a passivation coating could allow a correlation between impurity concentration and electrically active surface-recombination centers in solar cells.

All analytical methods are based on the assumption that the probing particles or radiation do not significantly disturb the sample. The surface-analysis methods derive their surface sensitivities from relatively large scattering or interaction cross section and, as a result, there is often the risk of serious sample damage. The ion methods are inherently destructive unless applied in the "static" mode where the incident ion current density is low and, as a result, the spatial resolution is poor. Progress is being made in documenting the rates of damage to different types of samples exposed to electron, ion, and photon beams but much more data is required as well as an improved understanding of damage (and healing) mechanisms.

The spectra measured by these techniques contain information related to the chemical environment of the particular element. This information is manifested in spectral lineshapes (AES), shifts of peak positions (AES, XPS), positions and strength of satellite peaks (AES, XPS), ion yields (SIMS, ISS), ion fragmentation patterns (SIMS), and changes of ion yield with incident energy (ISS). Information on these phenomena is currently fragmentary but would be extremely worthwhile in, for example, identifying the chemical compounds present in interfaces. Auger peak-shape analysis can provide information on the valence electronic structure localized to specific types of atoms, e.g., dopants in Si solar cells. More data and information on the basic physical mechanisms for each surface-analysis technique are required in order to extract needed chemical information that is now present in the raw data.

Polymers are expected to play a significant role in solar devices. The final crucial recommendation of the group was:

- Develop new and improved techniques for interfaces including polymers.

Polymers are light weight, relatively cheap,and can be impervious to atmospheric corrodents. A prime function will be as protective coatings, for example, as a paint film on the back of a mirror or as the outer surface of a transmitter containing heat transfer fluids. In addition, polymers may be valuable as support members. They are likely to be a significant part of solar devices successful in meeting the requirements of cost effectiveness, reliability,and long lifetime.

Research areas considered as important in furthering solar energy technologies in interface studies included two general areas. First, it is considered that inadequate use of general electron microscopy techniques (i.e., SEM) is made in studies of thin films. The assumption is often made that a surface is planar. In many cases it is not and surface imperfections of various kinds can make interpretation difficult. Such difficulties can often be resolved by use of electron microscopy. Some excellent UHV reflection electron microscopy has recently been reported by Japanese workers [10]. Such techniques may well contribute greatly in the immediate future. Hence, considered as important for progress we recommend:

- Increased application of general electron microscopy techniques to solar materials (e.g., SEM, STEM, UHV reflection electron microscopy, high resolution TEM).

An approach to studies of S/L or S/G interfaces is to permit the process at the interface to proceed and at a selected moment remove the volatile constituent. The solid surface left can then be examined under vacuum by the techniques discussed above. It is important that this approach be validated with whatever "in-situ" methods can be developed. Thus, recommended as important, is:

- Correlation of "in-situ" interfacial measurements with results of parallel experiments obtained after removal of the fluid.

Two areas received recommendations as useful. A method of probing grain boundary structure with atomic resolution has been in existence for a long time but for various reasons primarily including complexity of equipment and difficulty in specimen preparation is not widely used. This is field ion microscopy with atom probe capabilities and may well prove of considerable value, for example, in studies of passivation at grain boundaries in Si. Thus we recommend as useful:

- Use of atom-probe field ion microscopy and field desorption spectroscopy.

The second useful area is in the exploitation of existing national facilities such as synchrotron radiation facilities, small angle neutron scattering, etc., and the developing facilities at SERI uniquely suited to solar technologies. Efforts should be made to make the latter available, adequately staffed and conveniently run so that the contributions that could be made by scientific institutions elsewhere. Such contributions are likely to be useful and also SERI staff may well benefit from the expertise that would then be passing through the laboratory during the course of such interaction. We note that analytical capabilities are available at SERI for SERI photovoltaic contractors. Under certain conditions some of these are also available to others involved in solar related research. For information contact Dr. P. R. Pierce at 303-231-1361.

- Use of national analytical facilities should be greatly encouraged. When possible, SERI fabrication, test and other facilities should be made available to outside users relevant to solar technologies.

The recommendations of the group are summarized in Table 2.

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Table 2. SUMMARY OF RESEARCH NEEDS AND OPPORTUNITIES IN MICROCHEMICAL AND MICROSTRUCTURAL CHARACTERIZATIONS OF INTERFACES

Research Topic	Relevance	Priority
Development of photon and ion analytical techniques for "in-situ" characterization of the S/L and S/G interfaces (e.g., laser, Raman, IR and related techniques, RBS and NRA).	"In situ" S/L interface studies; Polymer interfacial studies; Photoelectrolysis, photoelectrochemical, photocatalysis; System degradation by corrosion and oxidation; Accelerated aging.	Crucial
Improved depth profiling techniques are needed for use in S/S interfacial analysis.	S/S interfacial analysis, e.g., adhesion of reflectors Sputtering results in (i) poor interfacial resolution and (ii) destruction of chemical information; Accelerated life tests.	Crucial
AEM techniques should be applied for characterizing solar material interfaces.	S/S interface with atomic resolution; Interdiffusion, corrosion, oxidation, grain boundary recombination, defect structure; Spatial resolution $\gtrsim$0.5 nm; Composition analysis (2-10 nm area).	Crucial
Exploitation of "in-situ" environmental stages in high voltage (1 MeV) electron microscopy, preferably with analytical capabilities for S/S, S/L, and S/G interfaces.	"In-situ" S/S, S/L, S/G studies; Mechanical structure and integrity; Corrosion and oxidation degradation; Interdiffusion and adhesion; Microstructure; Grain boundary segregation; Growth changes.	Crucial
Development of methods for quantitative surface analysis; characterization of beam artifacts, and improved methods of data analysis for Auger electron, X-ray photoelectron, ion scattering and secondary ion mass spectroscopies.	S/S and S/G interfacial studies; Quantification of data for processing/property correlations; Quantification of data for accelerated life testing; Data for model calculations of efficiencies.	Crucial

Table 2.--continued.

Research Topic	Relevance	Priority
Develop new and improved techniques for interfaces including polymers.	S/S, S/L and S/G interfacial analysis; Sputter depth profiling destroys polymer bonding; Ultraviolet degradation of interfaces; Radical oxidation; Interdiffusion and permeation.	Crucial
Increased application of general electron microscopy techniques to solar materials (e.g., SEM, STEM, UHV reflection electron microscopy, high resolution TEM).	S/S and S/G interface; Topography and structural analysis; Phase changes; Defect Structure; Cost effectiveness of system design.	Important
Correlation of "in-situ" interfacial measurements with results of parallel experiments obtained after removal of the fluid.	S/L interfacial studies; Thermal solar and electrode conversion processes; Passivation of surfaces; System lifetime; Electrode interfacial structures.	Important
Use of atom-probe field ion microscopy and field desorption spectroscopy.	S/S and S/G interfacial studies; Atomic resolution of structure and composition; Depth profiling layer by layer; Segregation; Bombardment and irradiation damage.	Useful
Institutional recommendations:		
National analytical facilities:	Cost savings; Facilities exist; Proper staffing required; Use of solar materials encouraged; e.g., Synchrotron; high voltage electron microscopes; surface science regional instrumentation facilities.	Useful
SERI facilities:	Identify fabrication facilities; Identify environmental test facilities; Disseminate information; Cost savings; Rapid start-up on projects.	Useful

GLOSSARY OF ACRONYMS

AEM	Analytical electron microscopy
AES	Auger electron spectroscopy
APFIM	Atom probe field ion microscopy
AR	Anti-reflection (coating)
ARUPS	Angle resolved ultraviolet photoelectron spectroscopy
ATR	Attenuated total reflection
CVD	Chemical vapor deposition
EAPFS	Extended appearance potential fine structure
EDXA or EDX	Energy dispersive x-ray analysis
ELS or EELS	Electron energy loss spectroscopy (ELS)
EPMA	Electron probe microanalysis
ESCA	Electron spectroscopy for chemical analysis (see also XPS)
ESDIAD	Electron stimulated desorption ion angular distribution
ESR	Electron spin resonance
EXAFS	Extended x-ray fine structure spectroscopy
FDS	Field desorption spectroscopy
FEM	Field emission microscopy
FET	Field effect transistor
FIM	Field ion microscopy
HEED	High energy electron diffraction
HREELS	High resolution electron energy loss spectroscopy
HV	High vacuum
HVEM	High voltage electron microscopy
ITS or IETS	Inelastic tunneling spectroscopy

GLOSSARY OF ACRONYMS (continued)

IR	Infrared
ISS	Ion scattering spectroscopy (see also, LEIS)
LEED	Low energy electron diffraction
LEIS	Low energy ion scattering
LRS	Laser Raman spectroscopy
LPE	Liquid phase epitaxy
MBE	Molecular beam epitaxy
MRIS	Multiple reflectance infrared spectroscopy
MOS	Metal oxide semiconductor
NMR	Neutron magnetic resonance
NRA	Nuclear reaction analysis
PIXE	Proton induced x-ray emission (also PIX)
PMRAS	Polarization modulation reflection absorption spectroscopy
PV	Photovoltaic
PVD	Physical vapor deposition
RA	Reflection absorption
RAIR	Reflection absorption infrared
RBS	Rutherford backscattering spectroscopy
RGA	Residual gas analysis
RHEED	Reflected high energy electron diffraction
SAM	Scanning Auger microscopy
SANS	Small angle neutron scattering
SCANIIR	Surface compositional analysis by neutral and ion impact radiation
SEM	Scanning electron microscopy

GLOSSARY OF ACRONYMS (concluded)

SEXAFS	Surface extended x-ray fine structure spectroscopy
SIMS	Secondary ion mass spectroscopy
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
UHV	Ultra high vacuum
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy (see also ESCA)
XRD	x-ray diffraction

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INDEX

Items which pervade these Proceedings such as degradation, durability, glass, HV, interface, microstructure, photothermal, polycrystalline, PV, RGA, stability, S/G, S/L, S/S, UHV, etc. are not contained in this Index. For all acronyms, the first numbered entry is the page where the acronym is defined.

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