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# THIN POLYCRYSTALLINE FILMS OF INDIUM PHOSPHIDE ON LOW-COST SUBSTRATES

Quarterly Report No. 1,
September 30, 1976—January 1, 1977

MASTER

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Rockwell International
Electronics Research Division
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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

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January 1977

UNDER CONTRACT NO. E(29-2) - 3727

PREPARED FOR THE DIVISION OF SOLAR ENERGY,
RESEARCH AND DEVELOPMENT ADMINISTRATION,

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## ABSTRACT

Plans for the six main technical tasks of this 12-month program are discussed and the activities of the first three months are summarized.

A new reactor system for growing thin films of InP by the metallorganic-hydride chemical vapor deposition (MO-CVD) process has been completed. Experiments using triethylindium (TEI) and phosphine ($PH_3$) reactants in a $H_2$ carrier gas have shown that InP films can be successfully grown over a range of deposition temperatures.

Epitaxial growth of single-crystal films has been obtained on at least two different crystallographic orientations of single-crystal GaAs at temperatures as low as ~525°C, and there is evidence that the process can be utilized at even lower temperatures - perhaps below ~475°C. Films not intentionally doped are n type, with measured carrier concentrations in the $10^{16}$ $cm^{-3}$ range and electron mobilities up to ~2000 $cm^2$/V-sec (room temperature).

Initial investigations involve single-crystal substrates (GaAs, sapphire, InP) but various low-cost materials - glasses, alumina ceramics, metals, and certain composites of these - are being selected and evaluated for subsequent use in the program. Specific candidate materials are discussed.

The program also involves the formation and evaluation of heterojunction photovoltaic device structures using the InP layers formed by MO-CVD and deposited films of CdS, ZnCdS, and similar II-VI compounds and alloys; this work is done at Stanford University. During the first quarter, two techniques for producing ohmic contacts of Au/Zn/Au on p-type InP were successfully developed, with low contact resistances being achieved following annealing in $H_2$ at temperatures up to 475°C.

Planned work for the next quarter is outlined.

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# 1. INTRODUCTION

The long-range objective of the National Photovoltaic Conversion Program is to develop low-cost reliable photovoltaic systems and to stimulate the creation of a viable industrial and commercial capability to produce and distribute these systems for widespread use in residential and commercial applications.

Two of ERDA's specific technical objectives that relate directly to the present program are (1) to conduct research, development, and demonstrations to show a factor of ten reduction in solar array prices and to establish the viability of this technology in the latter half of this decade (i.e., by 1980), and (2) to conduct a focused research and development effort on advanced technologies for photovoltaic devices that show a potential reduction in solar array prices by a factor of 100 or greater.

Specific goals of the national program include establishment of total solar array production capacities of (1) 500 peak Mw per year of solar array modules at a market price of less than $500 per peak Kw by FY 1985, and (2) $5x10^4$ peak Mw per year of solar array modules at a market price of $100 to $300 per peak Kw by FY 2000.

The ERDA strategy behind the program is to use every avenue possible to reduce the cost of efficient photovoltaic production of electrical energy from solar radiation. One of the most interesting conceptual methods of solar energy conversion is to build arrays of extremely low-cost thin-film photovoltaic cells of relatively high efficiency and long life, but a number of practical barriers have to date hindered this approach. This program is intended to help overcome such technical barriers.

It is a goal of the ERDA program that the low-cost photovoltaic cell configuration emerging from research and development programs such as this exhibit solar conversion efficiencies of 10 percent under air-mass-one (AM1) conditions within the next five years. This technical goal may not be achieved during the performance period of a twelve-month contract, but it will provide a continuous guideline for conduct of the program.

## 1.1 CONTRACT OBJECTIVES

The overall objective of this contract is to conduct fundamental studies which lead to a low-cost, high-energy-conversion-efficient, long-life photovoltaic cell using a polycrystalline film of indium phosphide (InP).

The specific technical objectives for the program are as follows:

1. Development of the metalorganic-hydride chemical vapor deposition (MO-CVD) process for growth of good-quality single-crystal or polycrystalline films of InP on selected low-cost substrate materials

2. Evaluation of the structural, electrical, and optical properties of the resulting InP films.

3. Formation of heterojunction device structures by deposition of films of other semiconductors on the InP films, and evaluation of the photovoltaic properties of these composites

4. Analysis and projection of future costs of large-scale quantities of photovoltaic solar cells made by the process.

The following specific activities are required by ERDA in the pursuit of the above objectives: (1) deposition of films of InP on the selected substrate(s); (2) measurement of the pertinent mechanical, electrical, and optical properties of the films, with special emphasis on adherence, morphology, uniformity, doping, carrier concentration, mobility, lifetime, and properties of the electrical contact adjacent to the substrate; (3) determination of the cost, quality, and requirements of the feedstock materials used in preparing the films; (4) performance of studies which include (a) refinement of the selection of appropriate low-cost substrates, (b) deposition of films on the few substrates so selected, (c) determination of the film properties in terms of quantitative physical parameters, and (d) modification of these parameters in a manner aimed toward the production and deployment of high-efficiency photovoltaic solar cells capable of being scaled to an annual production of 50,000 Mw/year by the year 2000 at a selling price of $100-200/peak Kw "without creating inordinate technical and economic problems; " (5) within three months from the inception of contract, begin producing films and supply a minimum of 4 $cm^2$ of current production each month thereafter to ERDA for whatever purpose ERDA deems suitable, the number and shape of the samples to be representative of that month's output; and (6) projection of the results obtained in each quarter into refinement of the conceptual model of the physical system, stating in the required reports the implications of redirection of the on-going study, with the final report stating the Contractor's view of the work which still needs to be done and the approach suggested.

## 1.2 InP AS A SOLAR CELL MATERIAL

Conversion efficiencies well in excess of 10 percent have been demonstrated in solar cells fabricated in single-crystal forms of several semiconductors, but there are only a limited number of semiconductors that offer reasonable likelihood of achieving such efficiencies in thin polycrystalline films deposited on low-cost substrate materials. InP has shown considerable promise as a single-crystal solar cell material, and technical considerations indicate strongly that it is an excellent candidate for successful attainment of the required technical and cost goals in a thin-film configuration.

In the years since the modern era of photovoltaic cell development began in the early 1950's, considerable research and engineering development have gone into achieving improvements in the single-crystal Si solar cell and into developing experimental cells of single-crystal compound semiconductors. The Si cell has become the industry standard, and has received by far the greatest amount of engineering and production effort. Arrays of Si cells have supplied reliable auxiliary power for most of the space vehicles and satellites launched throughout the world in various space programs over the past 15 years.

However, well understood theoretical considerations relating to the two principal processes that take place in the photovoltaic effect in a semiconductor--namely, absorption of incident photon energy to generate charge pairs, and separation and collection of the generated charges across a barrier--indicate that various compound semiconductors should provide significantly higher conversion efficiencies than those available with Si cells.

The efficiency of solar cell operation for maximum power delivered to a matched load is proportional to the product $I_{sc}V_{oc}$, where the proportionality constant is the curve fill factor (CFF), which is a measure of the "squareness" of the I-V characteristic of the cell under illumination. The net result of the increase in light-generated short-circuit photocurrent $I_{sc}$ with decreasing bandgap energy $E_g$ and the increase in open-circuit photovoltage $V_{oc}$ with increasing $E_g$ (because of reverse saturation current decreasing with increasing $E_g$) is a maximum in the efficiency-vs-bandgap energy relationship for values of $E_g$ in the range from 1.2 to 1.8 eV, for normal operating temperatures.

The theoretical relationship between efficiency and bandgap energy, as formalized by Loferski (Ref 1), has provided much of the guidance for solar cell materials research in the past 20 years. Semiconductors such as InP, GaAs, CdTe, AℓSb, and various ternary alloys have bandgap energies at or near the maximum in the $\eta$-vs-$E_g$ curve. The theoretical maximum efficiency predicted for InP for room-temperature operation and ideal junction behavior is in the range 22-26 percent for air-mass-zero (AM0) conditions (Refs 1, 2, 3).

Solar conversion efficiencies up to 13 percent (AM1) were reported for GaAs single-crystal cells as long ago as 1961 (Ref 4), and pilot-line quantities of GaAs cells were fabricated during the same period (Ref 5). However, the performance of experimental arrays in actual space missions was generally disappointing (Ref 6).

The situation is much different for InP. Early experimental cells were made with Zn-doped alloyed junctions in n-type InP crystals (Ref 7), and exhibited efficiencies

of ~2 percent for simulated AM1 illumination. High internal resistances were found in all of the cells. Although interest in InP as a possible solar cell material has continued in the ensuing years (see, e.g., Ref 8), the lack of sufficient single-crystal material of adequate quality has kept solar cell development with this semiconductor to a minimum. The highest reported efficiency for an InP single-crystal junction-type cell prior to 1975 had been about 6 percent (AM1) (Ref 9). In one instance, an efficiency of 6.7 percent was reported in small diffused-junction cells fabricated in n-type InP crystals and illuminated on the surface of the p-type layer, which was <10 μm thick (Ref 10). No attempts to optimize cell design or material parameters were reported in that work, however.

InP shares some of the same advantages over Si for photovoltaic applications that characterize GaAs. These include the following:

1. The bandgap energy (1.34 eV at room temperature) is such that the spectral sensitivity is a better match to the solar spectrum; higher theoretical efficiencies (in excess of 20 percent) than for Si are expected.

2. The decrease of power output with increasing temperature for InP should be much less than that for Si cells, because of the larger bandgap that allows higher-temperature operation of the junction.

3. InP typically has lower carrier lifetimes and shorter diffusion lengths than Si, so InP cells should be less susceptible to radiation damage.

4. The larger bandgap of InP will result in higher output voltage per cell than for Si, although the current per unit area of cell will be smaller.

5. The optical absorption edge in InP is steep (Ref 11) since it is a direct-bandgap semiconductor, so most solar radiation is absorbed very near (within ~1μm of) the surface, eliminating the need for thick cells to capture most of the incident energy. This means that minority carrier diffusion lengths need only be the order of 1μm to assure high charge collection efficiency by the barrier.

However, as with GaAs, some of the disadvantages of InP are consequences of some of its attributes — in particular, the very short absorption length ($\alpha^{-1}$, where $\alpha$ is the absorption coefficient in $cm^{-1}$) for essentially all photons with energies greater than bandgap. Because the absorption and generation of charge pairs occurs so close to the surface, the high surface recombination velocity that is characteristic of most III-V compound semiconductors results in reduced minority carrier collection efficiencies in junction-type devices due to surface recombination losses.

An additional effect of the short optical absorption length and the small minority carrier diffusion lengths is that the very thin layer required on the illuminated side of the junction must be extensively electroded with a fairly dense grid to reduce cell series resistance as much as possible. Even with such measures, losses at the front of cells fabricated as homogeneous junction diodes in crystals of both GaAs and InP have been found to be too high for acceptable solar cell operation under normal conditions.

### 1.2.1 Results Obtained with Single-Crystal Heterostructures

The problem mentioned above was the principal motivation for development of the window-type cell, in which a layer of another semiconductor is applied to the illuminated surface of the active material to remove the junction region sufficiently far from the incident-light surface to reduce recombination losses and at the same time add conductive material that reduces the series resistance of the cell. The window material must provide a sufficiently good interface structurally with the base semiconductor that the interface does not itself become a source of recombination losses. Additionally, the bandgap of the window material must be large enough that there are no significant losses of the incident solar radiation due to absorption in the window material, unless other factors allow the carriers generated in such absorption to be collected by the active junction.

Work with composite GaAs cells involving a front layer of $Ga_{1-x}A\ell_xAs$ serving as a window has been very encouraging (Ref 12) and has removed interest in solar cells of this semiconductor. In these so-called heterostructure cells the active junction is in the GaAs, and efficiencies of over 20 percent (AM1) have been reported by IBM researchers (Ref 13). James and Moon (Ref 14, 15) have reported efficiencies in the range from 19 to 23 percent for this type of cell operated in concentrated sunlight. The heterojunction cell of GaAℓAs and GaAs is similar to the above configuration except that there are only two (instead of three) regions, corresponding to the two materials, and the active junction is coincident with the interface. Alferov et al (Ref 16) have reported efficiencies up to 11 percent in antireflection-coated GaAs-GaAℓAs heterojunction cells of this type.

Similarly, within the past two years composite solar cell structures utilizing single-crystal InP and a deposited CdS layer to form a heterojunction at the interface have been reported by Wagner and Shay and coworkers (Refs 17, 18, 19) and by Ito and Ohsawa (Ref 20). In this configuration the n-type CdS ($E_g \approx 2.4$eV at room temperature) transmits a major portion of the incident solar radiation--for wavelengths to about 0.5 μm--to the p-type InP, which functions as the primary absorber.

Because of the excellent match of lattice parameters of the two semiconductors (5.850Å for wurtzite CdS and 5.869Å for zincblende InP, at room temperature) the interface is expected to be relatively free of inherent defects and thus of recombination centers to trap the light-generated charges. Further, the thermal expansion coefficients of the two materials are very similar in the range at and above room temperature (~$4 \times 10^{-6}$ per deg C for CdS and ~$4.5 \times 10^{-6}$ per deg C for InP), so relatively little stress-induced defect structure would be expected to be introduced upon cooling the composite from the CdS deposition temperature. Finally, the electron affinities of the two semiconductors are such that there is no impeding energy spike in the transition between conduction bands to adversely affect electron transport from the InP base region into the CdS layer under illumination.

Wagner, Shay, et al (Refs 17, 18, 19) reported efficiencies of ~12.5 percent for sunlight conditions close to AM2, for such cells using n-type (excess Cd) CdS epitaxial films 5-10 μm thick grown by vacuum deposition at 200-250°C on the polished "B" face (phosphorus) of (111)-oriented Cd-doped p-type single-crystal InP grown by the liquid-encapsulated Czochralski (LEC) method (Ref 21). SiO antireflection coatings were applied to the cells by vacuum deposition. In a later report of this work Wagner (Ref 22) noted that more consistent results were obtained by depositing the CdS on the

InP "A" face. The CdS films on the "A" face also exhibited lower resistivities. In the most recent descriptions of this work (Refs 23, 24) efficiencies approaching 15 percent (for AM2) have been reported for single-crystal cells if antireflection coatings are used.

Ito and Ohsawa (Ref 20) deposited epitaxial (0001)-oriented n-type CdS layers 10 μm thick by the vapor growth technique in $H_2$ onto p-type (111)-oriented "A" (indium) faces as well as "B" faces of single-crystal InP. A transition layer of mixed composition was found by analysis to be present at the interface in these samples. Despite this, measurements in conditions approximating AM1 indicated efficiencies of ~4 percent for devices formed on the InP "A" face and ~1.7 percent for cells on the "B" face. No antireflection coatings or other optimization procedures were employed in these investigations.

### 1.2.2 Thin-film Polycrystalline Solar Cells of InP

The very large absorption coefficient in InP in the wavelength region to the high-energy side of its fundamental absorption edge is such that most (i.e., 95 percent or more) of the available radiation in the solar spectrum is absorbed within a thickness of about 1 μm (Refs 8, 11). A thickness in excess of 200 μm of Si is required for similar absorption. The fact that InP is a direct-bandgap and Si an indirect-bandgap semiconductor also means that the transition from non-absorbing to absorbing is much more abrupt for InP. Thus, almost any radiation that is absorbed at all is absorbed in an extremely thin region of InP.

The small thickness of InP required for nearly complete absorption of solar radiation immediately suggests the use of deposited films of the material instead of bulk single-crystal wafers. This would clearly help in reducing the cost of the cell, simply by virtue of using less of the expensive active material. It would also assist in reducing the weight of photovoltaic cell arrays (irrespective of whether they are intended for space or terrestrial applications). Whether or not the hoped-for reductions in cost and weight can be realized depends upon the extent of other complications that arise because of adopting the thin-film configuration.

The very short absorption length for solar radiation in InP means that minority carrier diffusion lengths also need only be the order of 1 μm for adequate collection efficiency. Diffusion lengths in deposited films would not be expected to be as large as in high-quality bulk single crystals, but if the restriction is only that they be ~1 μm then there is good prospect of achieving such values providing there are no major defects — such as grain boundaries — more closely spaced than that.

Ideally, single-crystal thin films are most desirable, but the known methods for producing single-crystal (i.e., epitaxial) deposited films of the III-V compounds all require single-crystal substrates (Ref 25), and this does not allow the needed reduction in material costs. Furthermore, if only single-crystal substrate materials are considered then there are real limitations on the maximum area that will be achievable for the basic cell module fabricated by thin-film growth procedures. This leads directly to the need for less expensive substrate materials that are available in relatively large areas. It also leads to the realization that the resulting thin-film cells will almost certainly be polycrystalline, because of the absence of strong ordering forces associated with the substrate surface.

An important consideration for thin-film polycrystalline materials to be prepared for use in solar cells relates to the nature of the crystal grain structure in the film. It has long been recognized that if the individual crystal grains are randomly oriented on the substrate, then - on the average - only those grains that intersect the illuminated surface of the cell will contribute to the collected photocurrent. Carriers generated in other grains, farther from the junction, will tend to be lost by recombination at the grain boundaries that intercept the path between the region of generation and the junction.

A more desirable growth configuration is that in which the grain boundaries are oriented predominantly normal to the film surface (and thus also normal to the junction). In this film structure the carriers generated in the individual grains are far more likely to be collected across the junction (except for those lost due to a lateral diffusion component that still allows them to encounter a grain boundary). This leads to the rule-of-thumb that average grain sizes at least of the same magnitude as the film thickness are required for reasonable thin-film solar cell performance.

The fact that InP thicknesses of only ~1 μm are required to absorb up to 95 percent of the useful solar radiation indicates that InP films with average grain sizes of 1 to 2 μm could be expected to exhibit respectable solar efficiencies. In contrast, for Si polycrystalline film cells the same criterion dictates that average grain sizes approaching 100 μm are required. Calculations of the expected performance of polycrystalline GaAs solar cells were described by Woodall and Hovel (Ref 26). For a 1 μm GaAs layer and a 10 μm Si layer, and assuming that 1 μm average grain sizes could be obtained in both cases, it was found that a 21 percent theoretical efficiency resulted for GaAs and only 6 percent for Si. Using other analyses carried out by Soclof and Iles (Ref 27) for polycrystalline Si solar cells as the basis, Woodall and Hovel found a theoretical efficiency of 11 percent and 1-1/2 percent for GaAs and Si, respectively, for the same dimensional configurations mentioned above. These calculations represent optimistic and conservative predictions, respectively, based on realistic material parameters for GaAs and Si.

Although such predictions must be viewed cautiously, there is enough validity in the analyses to suggest that significantly higher efficiencies can be expected for polycrystalline cells in thin-film GaAs than in thin-film Si, if average grain sizes of 1 μm are obtainable. Furthermore, because of the similarity of many of the characteristics of GaAs and InP, these projections can be taken as an indication of the results that might be anticipated for polycrystalline films of InP with similar grain sizes.

Such dimensions appear to be within the realm of achievement for InP films deposited on non-crystalline substrates by the MO-CVD technique, so there is good prospect for fabricating thin-film solar cells in this program that will meet the 10 percent AM1 goal defined earlier. If grain sizes significantly larger than 1 μm can be achieved, then the chances for success are even brighter.

InP single-crystal material has been very difficult to obtain commercially in recent years. There have been periods when it was not available anywhere on the open market. At the present time it can be purchased, but the cost is very high. These two factors alone--availability and cost--are sufficient to stimulate interest in preparing thin films of the material for solar cell use. The single-crystal substrates required for the cell configurations described in Section 1.2.1 are not consistent with the goal of large-scale low-cost terrestrial use of InP solar cells. However, because

of the relative abundance and the current market prices of the materials involved, it would be expected that--given an equivalent amount of technical development effort--InP solar cells could be less expensive than GaAs cells. Further, depending upon actual junction (or other barrier) behavior in the two materials, it is possible that higher efficiencies could eventually be realized for InP than for GaAs cells.

If these potential advantages of InP over GaAs could be extended to the same materials in the thin-film configuration, then the prospect for InP thin-film cells would be bright indeed. Since the excellent lattice parameter match at the InP-CdS interface is expected to hold for almost any epitaxial relationship that would occur between the two crystal lattices (Refs 17, 18, 19), it appears that an all-thin-film configuration might be expected to exhibit unusually good properties for this particular combination of materials, even in polycrystalline form.

The first good demonstration that this may be the case has been provided recently by the group at Bell Laboratories (Refs 24, 28, 29, 30). Polycrystalline films of p-type InP were grown on Mo and carbon substrates by a CVD process utilizing the InP-HCℓ reversible reaction. Cd and Zn were used as acceptor dopants, and film growth occurred at ~630°C. Grain sizes were the order of 1 μm, and no preferred orientation was observed. By depositing n-type films of CdS on the polycrystalline InP films these investigators obtained photovoltaic structures of <1 $mm^2$ area that exhibited power conversion efficiencies of 2.3 percent under AM1 conditions if used uncoated, and 2.8 percent when an antireflection coating of vacuum-deposited SiO was applied.

## 1.3 GENERAL TECHNICAL APPROACH USED IN THIS PROGRAM

The general technical approach of the program involves application of the metalorganic chemical vapor deposition (MO-CVD) technique, developed by Rockwell for the epitaxial growth of III-V compound semiconductors and their alloys, to the formation of films of InP on both single-crystal and low-cost polycrystalline or amorphous substrates. Scientists at Stanford University then deposit cadmium sulfide (CdS) and/or similar semiconductor compounds or alloys by appropriate methods on the InP films to form heterojunction structures, and evaluate the photovoltaic properties of the resulting solar cell configurations.

During the time that the MO-CVD method is being developed specifically for the InP system--initially on suitable single-crystal substrates--attention is being given to the problem of identifying, preparing, and evaluating potentially inexpensive substrate materials that are (or can be) available in large areas and will tolerate the experimental environment of the MO-CVD process. When adequate substrate materials become available--and after the main CVD parameters required for satisfactory deposition of InP are adequately established--they will be used for growth of polycrystalline films of InP. These films will be doped appropriately to achieve the desired electrical properties for subsequent heterojunction formation.

The first inP films available, irrespective of the nature of the substrate, are being characterized for various material properties at Rockwell and--to some extent--at Stanford. These initial films and others prepared throughout the program are to be used at Stanford for the formation of heterojunction structures by deposition of films of CdS (primarily), ZnCdS, ZnSe, and possibly ZnSSe, using vacuum deposition or chemical spraying techniques. The photovoltaic properties of the resulting heterojunctions will be evaluated at Stanford, using electrical contact methods being developed early in the program both at Stanford and at Rockwell.

Finally, attention will be given to cost analyses of the cell structures as prepared in the contract program, and projections of the possible costs of large quantities of the cells in future years will be periodically adjusted to make use of technical developments in the ongoing work.

The CVD method is believed to be potentially the one best method for achieving large areas of solar cells of reasonable efficiency at sufficiently low cost to meet both the production capacity goal and the cost-per-watt goal of the nation's photovoltaic conversion program. Some of the technical problems that remain to be solved before those goals can be reached are specifically addressed in this program. Once these problems are solved it should then become possible to choose the parameters of the CVD process so that the required properties of the deposited films can be achieved and the efficiency goal of the photovoltaic device (10 percent AM1) realized, subject to the constraints imposed by the properties of the selected substrate material(s).

As it relates to the growth of III-V compound semiconductors, the MO-CVD process involves the mixing of a metalorganic compound of a Group III element with a hydride or metalorganic compound of a Group V element, and pyrolysis of this mixture or its reaction product under appropriate conditions to produce the Group III-Group V semiconductor. Thus, triethylindium (TEI) and $PH_3$ are mixed at room temperature in the gaseous state and pyrolyzed at established temperatures in a cold-wall reactor to form InP according to the following simplified reaction:

$$(C_2H_5)_3\,In + PH_3 \xrightarrow[500-700^oC]{} InP + 3C_2H_6.$$

The organic byproduct (ethane, $C_2H_6$) is stable at film growth temperatures.

The MO-CVD process has several attributes that are important to the application involved in this program:

1. The process is completely free of halides, thus eliminating competing etching reactions, reducing generation of unwanted impurities by reactions with the low-cost substrate materials, and minimizing complication of the heterogeneous film-growth process involved

2. Only a single high-temperature zone is required, greatly simplifying the apparatus and the necessary control systems, and allowing the deposition chamber walls to remain relatively cool because only the pedestal and the samples are heated.

3. The reactants used are either liquid or gaseous at room temperature, facilitating their handling and introduction into the reactor system carrier gas upstream from the deposition chamber, and allowing control of composition of the deposited film by means of flowmeter adjustments

4. Impurity doping of the deposited films can be achieved by introduction of appropriate dopant compounds (liquid metalorganic and/or gaseous hydride sources) into the primary reactant gas stream, again with doping levels controllable by means of flowmeter adjustments

5. The growth process can be observed directly by the operator, since the reactor walls are transparent and unobstructed, thus allowing changes in growth conditions to be made during an experiment if it is desired or necessary.

6. Large-area, uniform surface coverage can be achieved in a single growth sequence, using the same type of commercially-available apparatus that is used for epitaxial growth of elemental semiconductors (e.g., Si)

7. The process requires neither single-crystal InP material nor even semiconductor-grade (ultrahigh-purity) polycrystalline InP for its application, since only compounds of In and of P are used in the reaction, thus eliminating the expensive and energy-wasteful process of producing melt-grown InP source material required for other crystal growth and/or film deposition techniques.

The availability of high-purity reactants is a primary requisite for the ultimate success of the MO-CVD process in the application involved in this contract. This is a matter that needs continuing attention, and requires cooperation of the small number of manufacturers now engaged in supplying the various compounds used in this work, to assure that materials of increasing purity and improved control of quality will become available as needed.

Unfortunately, the situation for InP is not as clear-cut as it is for GaAs with respect to achieving the desired process control and reproducibility of results. This is partly due to the fact that far more development of CVD processes has occurred for GaAs film growth than for InP film growth. There are also other technical factors that are not yet fully understood for the case of InP formation by the MO-CVD technique; these factors require special attention in the contract work.

The highly developed technologies of epitaxial growth of a semiconductor on itself and heteroepitaxial growth on dissimilar materials (especially insulating oxides such as sapphire and spinel) permit growth of films with excellent structural and electrical properties in most cases. The limitations of substrate cost and available substrate size in these two cases place the single-crystal substrate configuration outside the range of the ERDA program goals, so attention must be focused on the problem of identifying a substrate material that is readily available, is inexpensive (or potentially so), and yet permits the formation of InP layers having structural and electrical properties adequate for achievement of reasonable solar cell efficiencies.

Substrate materials that are inexpensive and readily available in large areas are usually not single crystal or even large-grained, so the layer growth process will get relatively little help from the substrate in acquiring the properties important to solar cell performance. This means that after the technical problems associated with achieving satisfactory deposition of InP on substrates that are favorable to epitaxial growth (such as single-crystal InP, GaAs, and sapphire) are under reasonable control, then the more difficult problem of growth on low-cost substrates must be solved.

Thus, the principal technical problems to be solved in the program are (1) establishing preferred CVD process parameters (temperature, reactant concentrations, carrier gas composition, doping impurities, growth rate) for acceptable properties for the films grown on various substrate materials, (2) identifying suitable substrate materials that will survive the environment of the MO-CVD process and be potentially inexpensive and available in large areas, yet be as favorable as possible to InP grain growth, and (3) achieving adequate grain size in the films on inexpensive substrates to provide satisfactory solar cell properties.

To achieve the contract objectives and to progress toward the long-range goals of ERDA's National Photovoltaic Conversion Program, the contract involves work in six main technical tasks plus preparation of required samples for delivery to ERDA, as well as preparation and delivery of required data, reports, and review and presentation information.

The individual technical tasks are as follows:

Task A. Development of MO-CVD Process for InP Film Growth

Task B. Identification, Evaluation, and Development of Inexpensive Substrate Materials

Task C. Growth of InP Films by MO-CVD on Inexpensive Substrate Materials

Task D. Evaluation of InP Film Properties

Task E. Formation and Evaluation of Heterojunction Photovoltaic Device Structures on InP Films

Task F. Analysis and Projection of Cell Performance and Costs

Task G. Preparation and Delivery of Film Samples.

This is the first Quarterly Report for this contract and covers the period 30 September 1976 through 1 January 1977. The contract activities during that period are described by task in the following section.

## 2. TECHNICAL PROGRESS

This section contains a summary of the results obtained during the first three months of the contract. The discussion is arranged by task, but because of the interaction of the activities of the various tasks a distinction is not always easily made. Where this occurs, cross-referencing is used to indicate where additional related discussion is given.

### 2.1 TASK A. DEVELOPMENT OF MO-CVD PROCESS FOR InP FILM GROWTH

The summary of the proposed work of this task, as given in the contract Statement of Work, is as follows:

> The MO-CVD process employing triethylindium (TEI) and phosphine ($PH_3$) will be used to grow films of InP first on suitable bulk single-crystal substrates -- such as InP, GaAs, and sapphire -- or single-crystal films, to identify problem areas and limitations and establish baseline reference data for subsequent experiments with less favorable substrates, and later on selected inexpensive substrates identified in Task B. Initially, a simplified reactor system will be assembled and used, but modifications may be required in the gas-flow system or chamber design because of unique characteristics of the TEI-$PH_3$ reaction. Experiments with formation of the TEI-$PH_3$ addition compound outside the reactor will be carried out to determine if improved InP film nucleation or layer growth rates can be obtained through its direct use. The effects of deposition conditions on the properties of candidate substrate materials and of the resulting InP films will be determined. Experiments to establish effects of CVD parameters on InP grain size will be carried out, and gas-phase doping methods and parameters for achieving the required InP properties will be established, with emphasis on obtaining good p-type properties. Special CVD processing methods -- such as deposition of interface and/or nucleating layers of a metal or another semiconductor to enhance film grain growth, two-step deposition at different rates to improve grain size, and in situ annealing during film growth -- will also be investigated.

The selection of a preferred CVD process for the growth of InP must be based to a great extent on the compatibility of the reactants with the material being investigated as a substrate. For proper nucleation, the process for growth on a foreign substrate should produce InP irrespective of the properties of the substrate. The uniformity of the nucleation process will be controlled by the nature of the substrate surface.

To date only a few CVD processes have been reported for the growth of epitaxial films of InP. These include three halide vapor-phase systems --the In-$PCl_3$-$H_2$ system (Refs 31, 32, 33, 34), the InP-$PCl_3$-$H_2$ system (Ref 33), the In-$HCl$-$PH_3$-$H_2$ system (Ref 35), and the metalorganic-hydride (MO-CVD) process developed in Rockwell's laboratories (Ref 36). Early studies of the halide processes for InP growth used GaAs as the substrate (Refs 31, 32); recent studies have concentrated on homoepitaxy on InP substrates, as single-crystal InP has become more readily available.

The previous exploratory studies of the growth of InP by the MO-CVD technique at Rockwell (Ref 36) were directed mainly at demonstrating the feasibility of achieving epitaxial growth by this method. The major emphasis of the reported work was the growth of InAs and GaInAs films, a result subsequently also confirmed by other researchers (Ref 37).

The limited Rockwell studies showed that changes in reactor chamber design were necessary in order to effect an InP growth rate consistent with single-crystal formation on the single-crystal substrates used. The minor changes that were made in the reactor during these feasibility studies, however, produced a total growth rate of only ~0.1 μm/min or ~6 μm/hr, considerably lower than that obtainable by the MO-CVD growth of GaAs, for example. The growth rate was controlled by the high boiling point of TEI (144°C) and the low volatility of an addition compound which may have been formed at room temperature by the TEI-$PH_3$ reaction. The first factor can be corrected by heating the TEI to increase its vapor pressure and by heating the gas lines into the deposition zone in a similar fashion. The second factor is corrected by introducing the reactants into the chamber in separate lines so that they meet in the vicinity of the substrate, where radiation from the pedestal will produce the desired InP compound in a P-rich atmosphere (when excess P is present).

As an alternative approach the growth of InP might be studied using macro-amounts of the addition compound TEI:$PH_3$ as the direct source of InP, although formation of this addition compound has yet to be demonstrated. The addition compound would be prepared externally and directed into the reaction zone by a carrier gas such as $H_2$ or He. For this procedure to be effective the addition compound must be stable at temperatures necessary to increase its vapor pressure for transporting the complex to the deposition zone and substrate. Once proper conditions are established a significant increase in InP growth rate should result, and improved nucleation phenomena could then be expected on low-cost substrates.

### 2.1.1 Reactor System Design and Assembly

A CVD reactor system has been designed and built for use on the contract work, with subsequent modifications in the deposition chamber or the reactor system itself to be introduced as needed, to achieve best InP growth conditions.

The reactor system incorporates the gas flow lines required for the formation of InP films on substrates supported on an rf-heated pedestal. $PH_3$ is the source of phosphorus and triethylindium (TEI) the source of In. Provision has been made to use either He or $H_2$ as the carrier gas and growth atmosphere. Separate gas-flow lines and source containers are incorporated which provide for either diethylzinc (DEZ) or dimethylcadmium (DMCd) as p-type dopant sources and either $H_2S$ or $H_2Se$ if n-type doping is desired. A schematic diagram of the apparatus is shown in Figure 2-1.

The apparatus presently consists of a single vertical quartz tube 60mm in diameter and about 38 cm long, containing a SiC-covered carbon pedestal 5 cm in diameter which can be inductively heated; stainless steel bubblers containing the liquid metalorganic compounds such as TEI, DEZ/DMCd, and TMG; appropriate flowmeters for monitoring the carrier gas, doping gas, and $PH_3$ flows; a $H_2$ burn-off area, and a manifold made from stainless steel tubing. Provisions are made

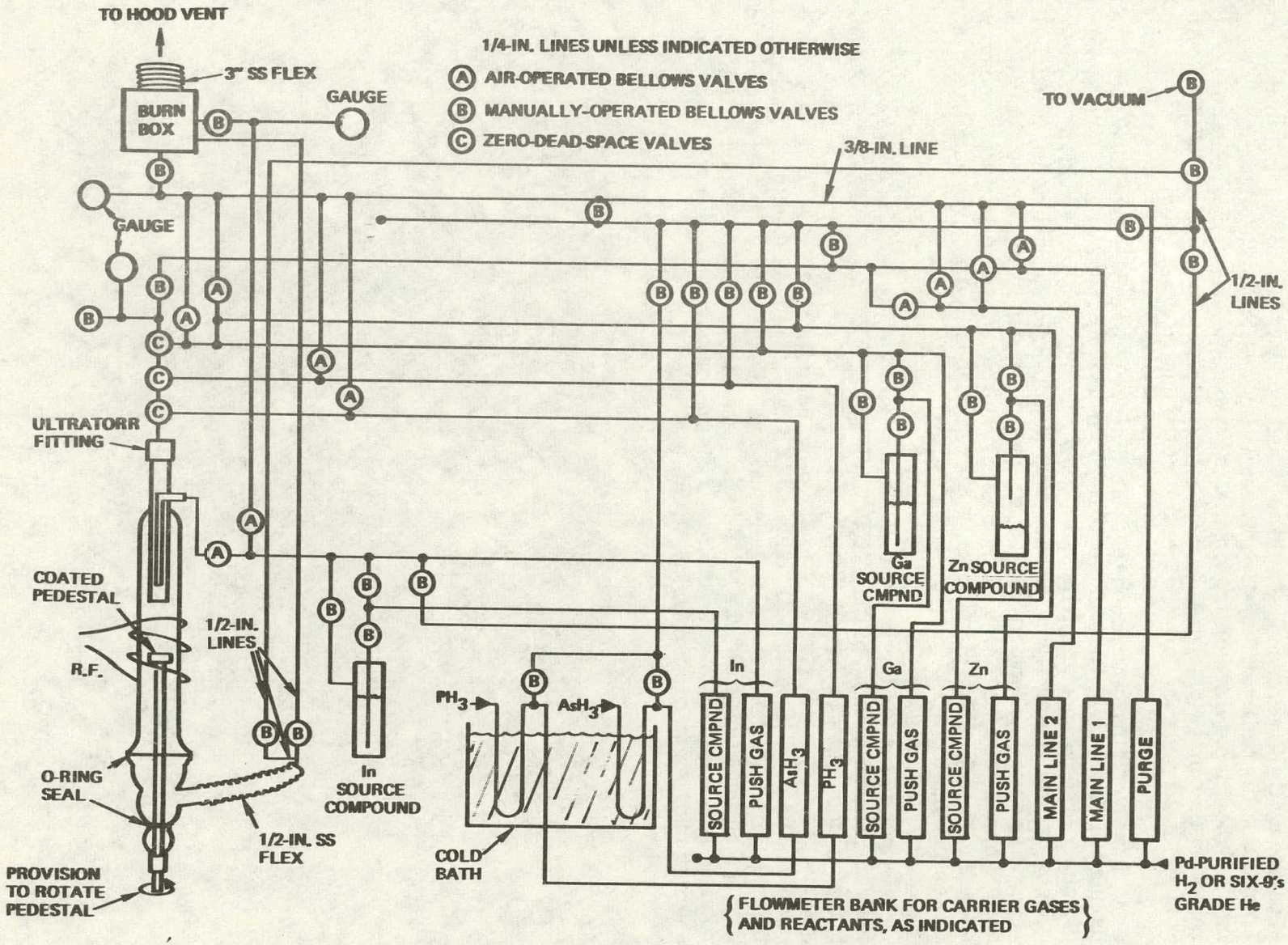



**Figure 2-1. Schematic Diagram of InP MO-CVD Reactor System**

in this apparatus for (1) by-passing the quartz reactor and keeping the reactants separate until the gases are equilibrated and ready to be mixed for film formation, (2) rotating the pedestal, and (3) evacuating all sections of the apparatus. Measurement of the temperature of the substrate is accomplished by means of an infrared radiation thermometer used to sense the apparent temperature of the side (cylindrical) surface of the pedestal through the wall of the quartz reactor tube.

It was originally intended that this reactor system be assembled and tested during the first six weeks of the program. However, there were delays in delivery of some of the components required for the construction, and some modifications had to be made in the electrical and hood-vent facilities in the laboratory housing the reactor system, the latter required for reasons of safety regulations related to the toxic compounds used in this work. As a result, the system was not completed and operable until the third month of the program; deposition experiments thus began late in the quarter.

A photograph of the system now in operation is provided in Figure 2-2. On the right of the central bank of glass rotameters is a cold-bath dewar (with stirrer) for trapping impurities in the $PH_3$ (and/or $AsH_3$) prior to its flow regulation. Above the rotameters are two dewars for later use in regulating the vapor pressure of trimethylgallium (TMG) and diethylzinc (DEZ), which will be used in preparing p-type films of InP. On the far left is a vertical reactor chamber with a T-shaped inlet at the top, an induction coil near the middle, and a water-jacketed joint and glass rotating seal below. The $H_2$ purifier, rf induction unit, gas burn-off box, and source tanks of gas are not visible in this photograph.

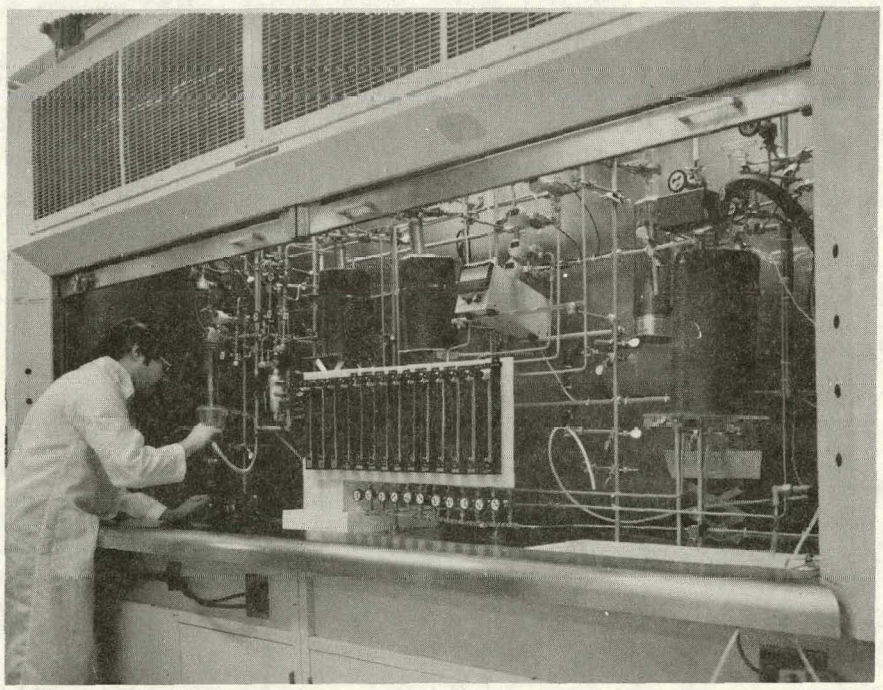


Figure 2-2. Photograph of InP MO-CVD Reactor System

The reactor chambers available at the start of the program were those that had been used in previous film growth studies. The early studies of InP growth by the MO-CVD method at Rockwell (Ref 36) had indicated a white solid is formed at the point of mixing of the TEI and $PH_3$. (See also next section.) With reactor chambers of the type available this solid is formed at the top of the reactor and is directed by a carrier gas (usually $H_2$) to the hot zone (i.e., near the heated pedestal) for InP formation.

It was suggested by the results of the early studies (Ref 36) that a different reactor design -- one that mixes the TEI and $PH_3$ nearer the hot zone -- would be an improvement. Thus, at the start of this contract program, components were ordered for use in constructing such a reactor chamber. The chamber has recently been completed and is shown in the photograph in Figure 2-3. The main reactor section is 75mm in dia and about 45 cm long, from the top to the main O-ring joint (within the large clamp). It connects to an exhaust section, which has a second but smaller O-ring joint at its base. This base in turn connects to a teflon stirrer-bearing. The exhaust port and stirrer-bearing are about 15 cm from the main O-ring joint. The distance from the top of the reactor chamber to the bottom of the concentric tubes in the center of the main reactor portion is ~18 cm. The innermost tube (~8mm dia), which is used for introducing TEI, is about 12mm shorter than the outermost tube (about 18mm dia), through which $PH_3$ and carrier gases flow.

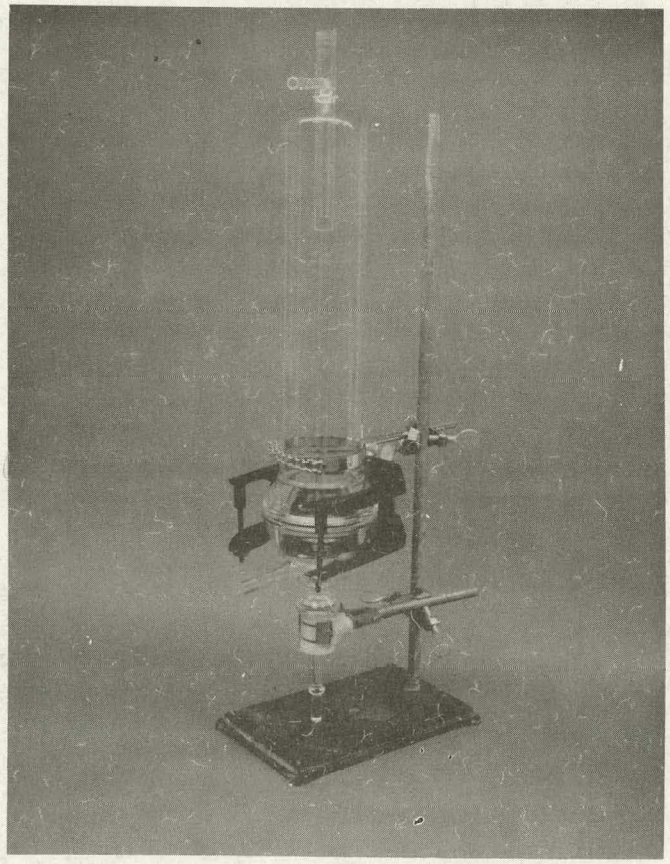


Figure 2-3. Concentric-tube O-ring-sealed Reactor Chamber with Teflon Rotating Seal, for Use in MO-CVD Growth of InP Films

This new reactor chamber will be tested during the second quarter of the program. Its eventual utility may be determined by the uniformity of film thickness and quality that are achieved with it.

The reactor chamber used in the initial experiments late in the first quarter has a square-cross-section center tube 17mm x 17mm, the open end of which extends to a point 10-12mm above the surface of the heated pedestal. The experiments described in the next section were done with that chamber.

At the end of the first quarter of the program, and prior to the availability of the new reactor described above, a second available reactor -- one which does not contain a center tube -- was chosen for further film growth experiments. Studies with this reactor will provide information on film properties over a larger area of growth than provided by the first (center-tube) reactor if the proper gas flow conditions and turbulence are determined. The results of these experiments will be described in later reports.

As the work progresses it may become necessary to change the design of the reactor chamber or of the reactor system gas-line configuration, to achieve proper mixing of the reactants and to effect better coverage of the substrate area. If it is found necessary to enhance the nucleation of InP on the various substrates under investigation the reactor system will be modified to permit deposition of GaAs, InAs, or some other material prior to InP growth. The objective of these changes will be improvement of growth conditions and resulting film characteristics, such as uniformity of thickness and electrical properties, over areas of at least 4 $cm^2$. Included in such changes will be adjustments in orifice-to-substrate spacings, position of the $PH_3$ source relative to the TEI exit tube, and any other changes that will become obvious from the results of the work.

Experimentation with modified reactor chamber designs will probably continue for several months as the investigations of the CVD parameter interrelationships continue. It is anticipated that reactor design changes can be evaluated and a final configuration adopted by the end of the seventh month of the program, so that subsequent CVD experiments with InP growth on various substrate materials will involve the most favorable reactor design.

### 2.1.2 InP Growth Studies

The initially-planned CVD experiments are an extension of the earlier work at Rockwell, and consist of determining the deposition parameters suitable for growth of InP by the metalorganic-hydride process on single-crystal substrates, in order to obtain baseline data on the growth process. The use of substrates that are favorable to epitaxy removes an important uncertainty in experimental conditions that would exist if initial process development were to be undertaken with low-cost (polycrystalline or amorphous) substrates that are of primary interest in the program on a long-term basis.

Single-crystal InP substrates would be preferred for these investigations, but availability and cost as well as utility must be considered. Thus, in the initial baseline experiments single-crystal substrates of sapphire (which is reusable) and GaAs (on which InP epitaxy has been achieved (Refs 31, 32, 36)) will be used, in addition

to some substrates of single-crystal InP. Use of these substrate materials is consistent with the fact that later in the program low-cost polycrystalline oxides--such as alumina ($A\ell_2O_3$)--and metals--which may require nucleating layers of semiconductors for proper InP growth--will be emphasized; the experience obtained in the initial growth studies will be helpful in interpreting later results on similar materials in polycrystalline form.

A deposited thin film of InAs may be used later in place of GaAs if it is found to enhance nucleation of InP on sapphire; its use would simplify the CVD apparatus by requiring the addition of only an $AsH_3$ source rather than both a trimethylgallium (TMG) and an $AsH_3$ source. On the other hand, the TMG-$AsH_3$ reaction does not form an intermediate addition compound, as occurs during mixing of TEI and $AsH_3$, and the GaAs would be easier to grow. At present, it appears that intermediate layers of GaAs would be better for this study.

The deposition parameters being studied include substrate and source temperatures, total gas flow rate, ratio of reactant concentrations, and preferred carrier gas, as they affect InP film growth rate and film properties. Based on the results of these investigations, the preferred growth parameters will then be transferred directly to the work with low-cost substrates.

As soon as the reactor system shown in Figure 2-2 became available for use the growth parameter studies began. During the initial experimentation, however, the radio-frequency (rf) generator unit was found deficient, in that it would not sustain the growth temperature range desired - 550 to 650°C - and would shut off during an experiment. While the rf unit was being repaired, several experiments were made under less-than-desirable conditions, at temperatures dictated primarily by the stability of the rf unit.

These experiments used the reactor with an axial center tube and a side arm at the top for introducing TEI. The reactants TEI and $PH_3$ were first mixed, therefore, at room temperature at the top of the reactor chamber and away from the heated pedestal. A white solid ring was observed to form on the tube wall near the point of mixing of the $PH_3$ and TEI vapors. The ring became more pronounced as the film growth experiment progressed. Film growth was observed on the heated substrates on the pedestal (coated susceptor), with coverage concentrated on those substrates directly below the opening of the center tube. The substrates evaluated in these first experiments were semi-insulating (100) GaAs, (111A) GaAs, (111B) GaAs and (0001) sapphire.

The observed pedestal temperatures at the start of the first three experiments were (arbitrarily) 505, 575, and 518°C, measured with an optical thermometer focused on the side (cylindrical surface) of the pedestal. The unpredictable rf generator shut-off times were 15, 12, and 34 min, respectively, after start. It is estimated that the center of the top surface of the pedestal is typically 10-20 deg C cooler than the side, based on similar measurements made in this temperature range during studies of Si growth on low-cost substrates (Ref 38).

Despite the obviously poor control of growth conditions, optical examination of the highly reflective film-covered surfaces of the GaAs substrates suggested a high degree of order in most of the films grown. Scanning electron microscope (SEM) evaluation of a cleaved portion of a film grown at 518°C (for 34 min) showed the film to be ~1.2 μm thick, and energy-dispersive analysis of x-rays (EDAX) in the SEM qualitatively confirmed In and P to be present in the film. The films on GaAs were found to be conductive, as determined by a simple volt-ohmmeter test. Reflection electron diffraction (RED) examination of two of the films (on (100)GaAs and (111A)GaAs) indicated they were, in fact, single-crystal films; diffraction patterns and Kikuchi lines were in evidence.

In another experiment the surfaces of the substrates were exposed to flowing TEI for about 1-1/2 minutes at 575°C, the TEI flow was stopped, $PH_3$ was introduced into the reactor, and the $PH_3$ flow was then continued for 15 min. Examination of the sapphire surface in the microscope revealed the presence of a triangular network of islands deposited on portions of the substrate, as shown in the SEM photograph in Figure 2-4. Epitaxy was suggested by the geometrical details of the deposit. It might be concluded that In formed by the initial pyrolysis of TEI was converted to InP by the $PH_3$ that was subsequently introduced, and that the InP then crystallized epitaxially on the sapphire.

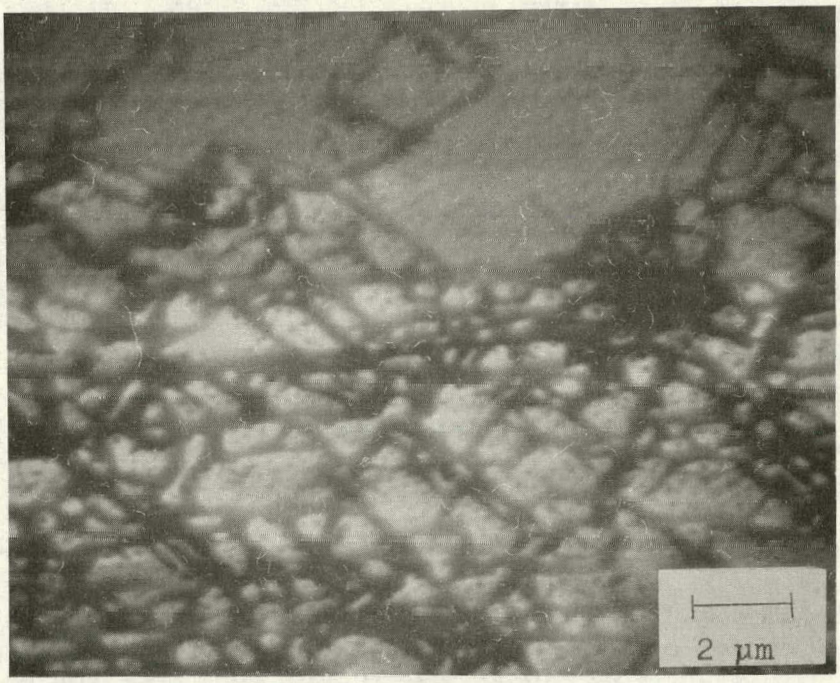



Figure 2-4. SEM Photograph of Crystallographically-symmetrical Triangular Network of Islands of InP Deposited by MO-CVD on (0001)-oriented Polished Sapphire Substrate

EDAX evaluation showed qualitatively that the triangular structures were rich in In and P and that less regularly-shaped islands enclosed by the triangular regions were also In- and P-rich. The result is significant in that InP was, in fact, formed by a procedure such as that used in this experiment. It is thus possible that conditions might be found to produce large grains of InP on amorphous substrates by starting with molten In (m.p. 156.4°C) on the surface (perhaps produced from TEI or some other process) and converting it to InP, and precipitating the InP as large grains.

The results of the first few InP deposition experiments in the new reactor system were very encouraging. It was clear that epitaxial growth could be achieved on single-crystal substrates under the proper conditions -- perhaps by two or more alternative procedures.

Repair of the rf induction unit permitted more intense examination of the growth parameters of InP, mainly on GaAs substrates. The low growth rates (~0.04 μm/min) obtained in earlier experiments prompted an increase in the $H_2$ flow through the TEI to attempt to increase the growth rate. However, it soon became evident that flow conditions would have to be found to minimize the deposit at the tee and carry the white solid into the flow stream leading to the reactor chamber.

This was accomplished by mixing the $H_2$ flow through the TEI with a separate external $H_2$ flow leading to the tee and into the reactor. This external line had been built into the original reactor system, based on previous studies of the formation of In compounds by the metalorganic process and, therefore, was available when needed.

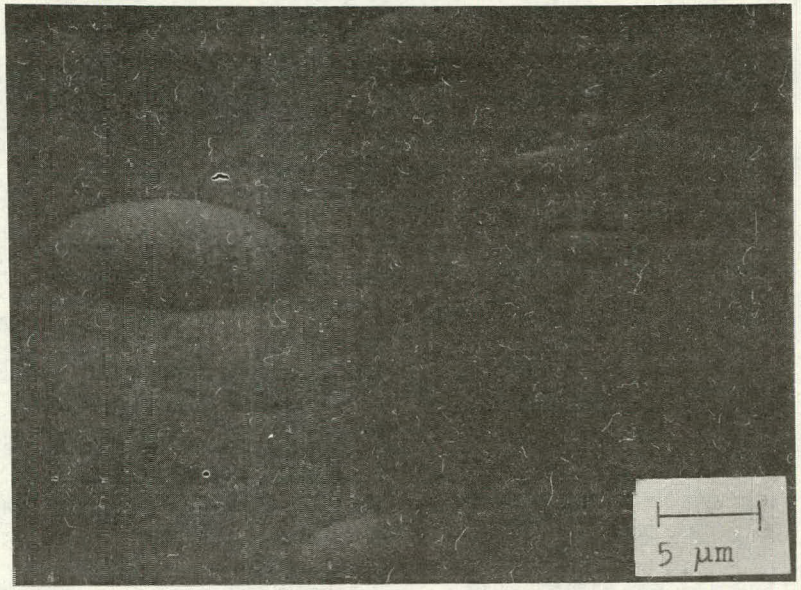
The increased flow rate led to a growth rate increase by a factor of ~3. Epitaxy was consistently obtained on GaAs, the overgrowth of InP on (100)GaAs being quite reflective and smooth; on (111A)GaAs it was relatively smooth, but not so reflective.

Film coverage on the 5 cm-dia pedestal and on the substrates was not uniform, however, and mostly limited to the area below the opening of the center tube. Variations in film thickness during simultaneous growth on the three orientations of GaAs could not be attributed only to the differences in orientations, since the observed variations were not consistent. The $PH_3$ (10 percent in He) flow rate during the above experiments was kept at 250 ccpm; the $H_2$ flow rate through the TEI (at room temperature) was increased in the range from 500 to 1500 ccpm.

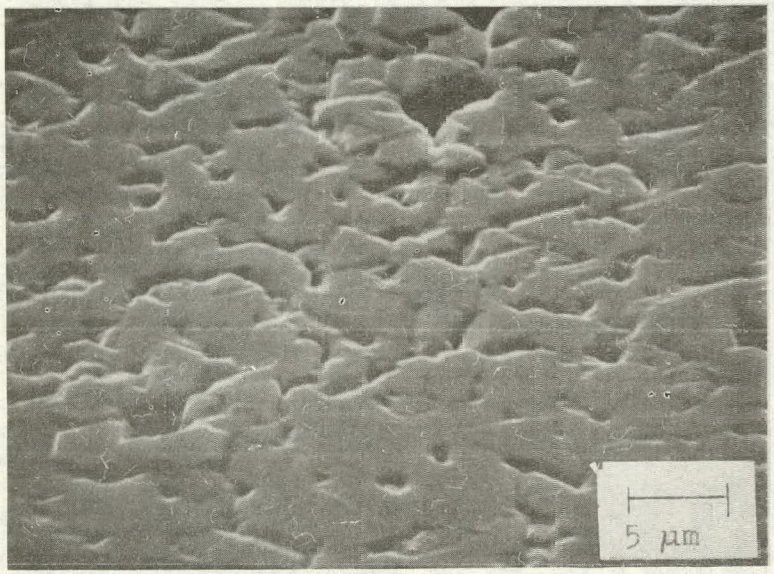
The better looking overgrowths obtained in these experiments had surface characteristics such as those shown in Figure 2-5. Film thickness was measured from photographs taken of cleaved specimens in the SEM. The InP layer could, in most cases, be observed without etching or other processing, as shown in Figure 2-6.

### 2.1.3 Preliminary Experimental Examination of Reaction Leading to InP Formation

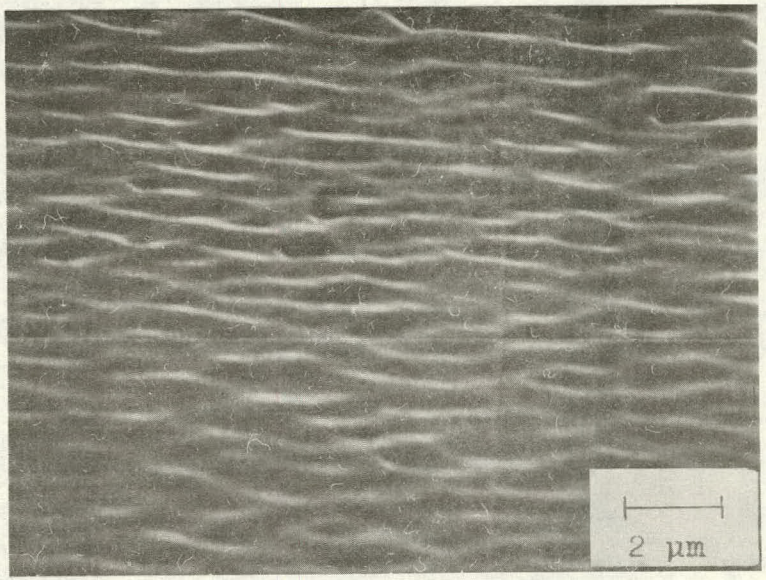
Reference has previously been made to the formation of a white solid ring in the reactor near the point of mixing of the TEI and $PH_3$ at room temperature. This white solid is presumed to be either an addition compound of the reactants or a compound resulting from the presence of impurities, such as oxygen or moisture, in the carrier gases. An attempt was made to eliminate moisture from the $PH_3$ source gas by the use of a low-temperature bath on the $PH_3$ line. A SiC-covered pedestal




(a)




(b)




(c)

Figure 2-5. SEM Photographs of InP Growth on (a) (100)GaAs (film thickness 4.6 μm); (b) (111A)GaAs (film thickness 7.6 μm); (c) (111B)GaAs (film thickness 3.6 μm)

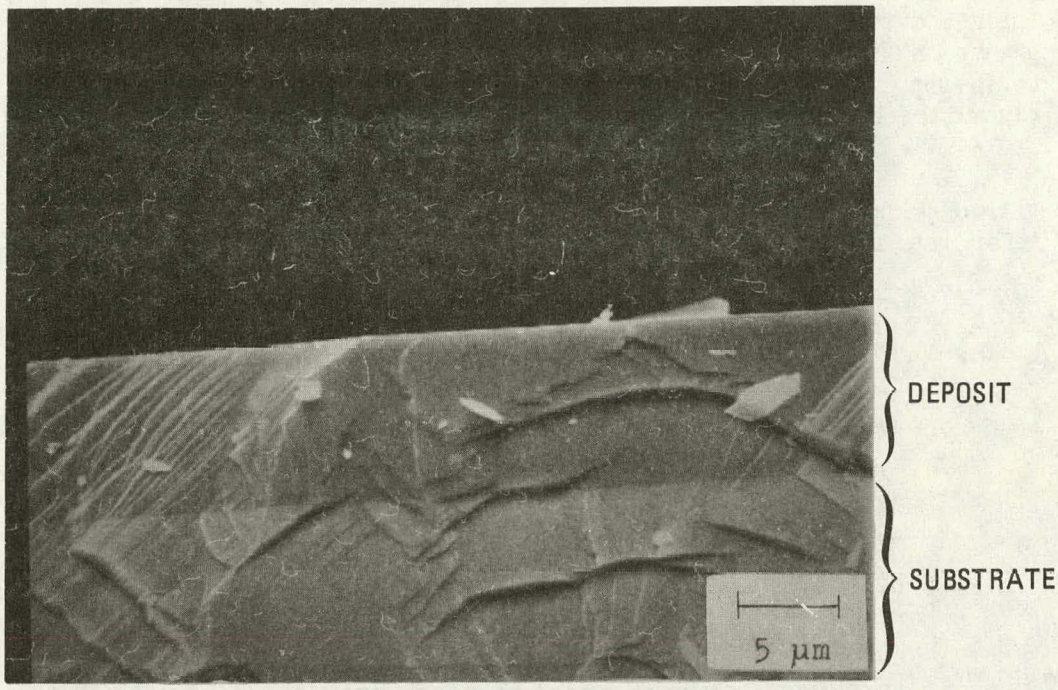



Figure 2-6. SEM Photograph of InP Deposit on High-resistivity GaAs Substrate. (Deposit ~7.5 μm thick.)

and a sapphire substrate were first heated in $H_2$ to ~575°C, to outgas the pedestal and simulate a surface for film growth at this temperature. The rf power was then turned off, and the reactor was cooled to room temperature in flowing $H_2$. TEI and $PH_3$ were then mixed at the intersection of the gas transport tubes just above the main reactor chamber until the white ring was observed (2-3 min). The TEI and $PH_3$ flows were then diverted from the reactor and stopped, but $H_2$ flow was continued.

The white deposit in the clean reactor was found to extend along the length of the center tube, and the formerly shiny and clean sapphire substrate surface had become clouded. A slight shifting in the position of the substrate revealed its outline on the pedestal surface and confirmed that the pedestal was also coated. $H_2$ flow was continued and increased, in an attempt to transport the solid from the point of initial mixing.

After ~35 min it appeared that some of the white solid had been distilled away. Careful warming did not seem to produce major movement of the white solid, but it did cause a yellow cast to develop on the surface of the solid. The reactor was then evacuated. Cooling of several portions of the outside of the reactor with dry ice condensed a white sublimate. A sublimate downstream from the pedestal completely distilled from the walls when the pedestal was subsequently heated in $H_2$.

The reactor was again pressurized with $H_2$, and the pedestal was heated to ~565°C. During heating to temperature, the sapphire surface changed color from yellow to orange to almost black to gray. The temperature was stabilized at an observed reading of ~565°C. $PH_3$ was introduced into the reactor, and this caused the gray film on the sapphire to darken. After 10 min, TEI was introduced into the

reactor together with an additional $H_2$ "push" of 1000 ccpm. The white solid again formed during mixing but was displaced slightly toward the center tube. The InP grown on the substrate had a matte surface. After the film was cooled to room temperature, a dark powder fell on the pedestal from the center tube. This concluded the experiment.

Considerable information of importance was obtained from the above investigation. The principal conclusions -- although preliminary and subject to further interpretation as more experimental data are acquired -- are as follows:

1. The compound that forms on mixing TEI and $PH_3$ vapors has a low vapor pressure, but it is sufficient for the compound to be transported by a carrier gas or by pumping.

2. InP growth can probably be achieved with these reactants at $<465^{o}C$ (the minimum readable temperature of the optical thermometer in use), thus admitting for consideration as possible substrates many glasses with low strain points but reasonable thermal expansion properties.

3. $PH_3$ in excess will be needed to stabilize the InP formed at growth temperatures of ~550-650°C, and probably below, as evidenced by the effect it seemed to have on the gray film (which presumably was InP) produced on the sapphire by decomposition of the TEI-$PH_3$ reaction product which had covered the sapphire surface at room temperature.

4. By manipulating gas flows, it will probably be possible to introduce the room-temperature reaction product into the main gas flow stream, thus minimizing its condensation on the glass tube inlet and maximizing the growth rate of InP for a given TEI concentration.

5. Decomposition of the TEI-$PH_3$ reaction product probably occurs at a low temperature (perhaps as low as 50°C), as evidenced by the discoloration of the white solid on warming as well as by the results of previous film growth experiments in which the hot pedestal caused heating (by radiation) of the glass tube tee where the reactants are mixed. (That part of the apparatus is normally warm to touch, although not hot.)

6. The white condensate produced at -78°C (dry-ice temperature) under vacuum appeared to be volatile without decomposition, and appeared to be a different material from the product of mixing, since it distilled without decomposition from the reactor wall by means of radiation from the hot pedestal. This conclusion, however, is only tentative.

It is expected that these observations will be influential in the planning of future experiments in InP film growth and in optimizing reactor design.

### 2.1.4 Impurity Doping Considerations and Nucleation Studies

During the investigation of CVD parameter interrelationships for InP deposition on various single-crystal substrates, experiments will be undertaken to identify the most satisfactory impurity doping methods for InP films. Although it will be the intention to arrive at satisfactory procedures for producing both n- and p-type films, the emphasis will be on p-type doping because of the later use of n-type semiconductors (e.g., CdS) in forming heterojunction structures. Diethylzinc (DEZ) will be evaluated first as the dopant source for p-type InP.

Film resistivities in the range 0.1-10 ohm-cm are desired for the p-type InP layers to be used in heterojunction formation with CdS or other semiconductors. In terms of single-crystal InP this corresponds to a doping concentration in the $10^{16}$-$10^{17}$ $cm^{-3}$ range, but it remains to be determined what active impurity concentrations of either type can be incorporated into polycrystalline films grown by the MO-CVD method. Doping concentrations and resulting electrical properties are to be determined for epitaxial InP films grown on single-crystal substrates relatively early in the doping studies. This will establish reference levels of active dopant concentrations corresponding to various CVD parameters and added concentrations of appropriate doping compounds. These data will be used in the later studies of doped film growth on low-cost substrates, since the properties of epitaxial films grown simultaneously on companion single-crystal substrates will provide the necessary monitoring information.

In addition, the effects of interface and/or nucleating layers deposited prior to the InP film growth will be investigated later in the program. Previous studies of InP growth on sapphire showed that it was more difficult to control InP growth than InAs growth (Ref 36), so similar problems may occur on low-cost oxide and other substrates. Therefore, the introduction of a foreign layer compatible with InP at the film-substrate interface will be considered. InAs, GaP, and/or GaAs are likely candidates, and can be produced in situ on the substrate surface before the InP film is formed. Both full-coverage layers and partial-coverage layers, consisting of discrete islands, will be examined in this phase of the work.

The effect upon InP film growth of an intermediate layer of CdS will also be examined. Films of CdS will be prepared at Stanford (Task E) on selected low-cost substrates for subsequent use in InP deposition experiments using the MO-CVD technique. The stability of the CdS film at temperatures used for InP deposition may, however, render this configuration impractical.

## 2.2 TASK B. IDENTIFICATION, EVALUATION, AND DEVELOPMENT OF INEXPENSIVE SUBSTRATE MATERIALS

This task is summarized in the contract Statement of Work as follows:

> Samples of both commercially-available and specially-prepared materials -- including high-purity polycrystalline aluminas, special glass-ceramics, some high-temperature glasses, and certain metals--will be evaluated for suitability of physical properties and chemical stability in the MO-CVD environment. The moderate deposition temperatures for InP film growth permit consideration of some glasses not feasible as substrates for CVD growth of other semiconductors. Special attention will be given to Kovar, Mo, and W as growth substrates, both as fabricated sheet and as deposited films. Special substrate preparation procedures--including chemical cleaning and processing, mechanical polishing, surface texturing, and high-temperature annealing--will be investigated and developed to improve surfaces for film growth. Substrate materials will be carefully characterized to provide correlation with film properties, with the final test of suitability being actual use in the InP MO-CVD environment.

Several different types of substrate material – each offering one or more unique advantages – are to be used in this program to optimize the probability of obtaining the needed thin-film InP solar cell properties. The selection of candidate substrate materials is based on a combination of (1) the known required properties of these materials, (2) the availability of either commercially-prepared samples or specially-processed research samples produced specifically for use in this program, and (3) the present-day and probable future costs of the materials when supplied in very large quantities.

The requirements on substrate properties are partially conflicting, and are very difficult to meet without some compromise. General criteria used in identifying possible substrate materials for consideration for this program are as follows: The substrates must be inexpensive, stable, and have desirable mechanical properties for cell support; they may be single- or multi-layered. They must also allow a low-resistance electrical contact to be made to the active layer, must provide no contamination of the active layer over the long term, must be mechanically compatible with the active layer over a wide range of temperature and humidity, and must be transparent to solar radiation if a back-wall configuration is contemplated.

Unfortunately, there does not appear to be a single substrate material that fulfills all of the above requirements. Furthermore, there are additional factors which must be considered in searching for a suitable substrate material to be used with a specific InP film growth method. Consequently, it is more realistic to view the requirements given above simply as technical goals for the characteristics of the substrate materials. On that basis, there are several different kinds of polycrystalline and amorphous substrates that will meet many of the requirements, in combination or alone, and are thus being considered for use in the program.

A substrate characteristic that becomes an essential requirement, especially if the concept proposed for low-cost solar cells involves the use of very large areas of active photovoltaic material without significant concentration of the incident solar radiation, is the availability - or potential availability - of the material in large areas -

as sheets, or plates, or flexible foils, or in other suitable form. This consideration is of relatively less importance for those applications involving the use of small single-crystal bulk or epitaxial photovoltaic cells in conjunction with optical concentrator systems. However, even in those instances the total cost per watt of producing the overall system could be favorably affected by use of a basic processed cell unit that is not restricted in size to the maximum dimensions of available single-crystal wafers.

Additional characteristics that must be considered include the overall compatibility of the substrate material with InP. Its linear thermal expansion behavior should be as close to that of InP as possible, at least from the deposition temperature down to room temperature. If this condition is not met - or closely approached - then the film will be under stress when cooled after growth and - depending upon the magnitude of this stress and whether it is tensile or compressive - may have its electrical and structural properties seriously affected. It is not uncommon to have a film-substrate composite bowed severely as a result of such stresses, and in more extreme cases the film will wrinkle or fracture or separate completely from the substrate. Careful consideration must be given to this factor - one that often has been ignored in selecting substrates for thin-film device design. Figure 2-7 shows the thermal expansion coefficients (TEC) of InP (at one temperature) and several materials that are used as substrates for deposited films in various applications. It can be seen in the figure that several materials have coefficients close to that of InP at room temperature, and are thus of more than passing interest as possible substrates.

In addition, the InP film must be chemically stable with respect to the substrate surface, so that any transition layer at the interface does not cause separation of the two components. Also, the substrate surface must be stable relative to the carrier gas used in the CVD process. This is usually $H_2$, but if necessary He can probably be used with the metallorganic-hydride CVD process to be employed in this program.

The crystalline nature of the substrate is a major factor in the achievement of InP film growth with sufficiently good structural properties to permit fabrication of solar cells meeting the eventual goal of 10 percent AM1 efficiency. At one extreme is a single-crystal substrate, such as InP or GaAs, which results - under proper conditions of temperature, growth rate, and surface preparation - in epitaxial growth of single-crystal InP. At the other extreme is the amorphous substrate, which presents essentially a passive surface to the arriving atoms; the atoms then migrate over the surface and finally congregate at nucleation centers distributed at random. The latter process leads generally to a polycrystalline deposit with a statistical distribution of grain size and orientation, which is then subject to possible modification by various means both during deposition and after growth is complete. This is the main problem area involved in this program.

### 2.2.1 Specific Substrate Materials to be Investigated

The approach used in identifying the most suitable substrate for the purpose is to include several different materials in the investigations, with the intention to identify those potentially inexpensive materials that are (or will be) available in relatively large-area wafers, slices, strips or sheets; that will also withstand the physical and chemical environment of the InP deposition process; and that will either encourage large grain growth in the developing film or have a completely non-influential effect, so that other parameters can dominate the process and enhance natural crystalline growth. Only a few classes of materials now commercially available can be considered as candidate substrate materials, based on cost, availability, and reported properties. These

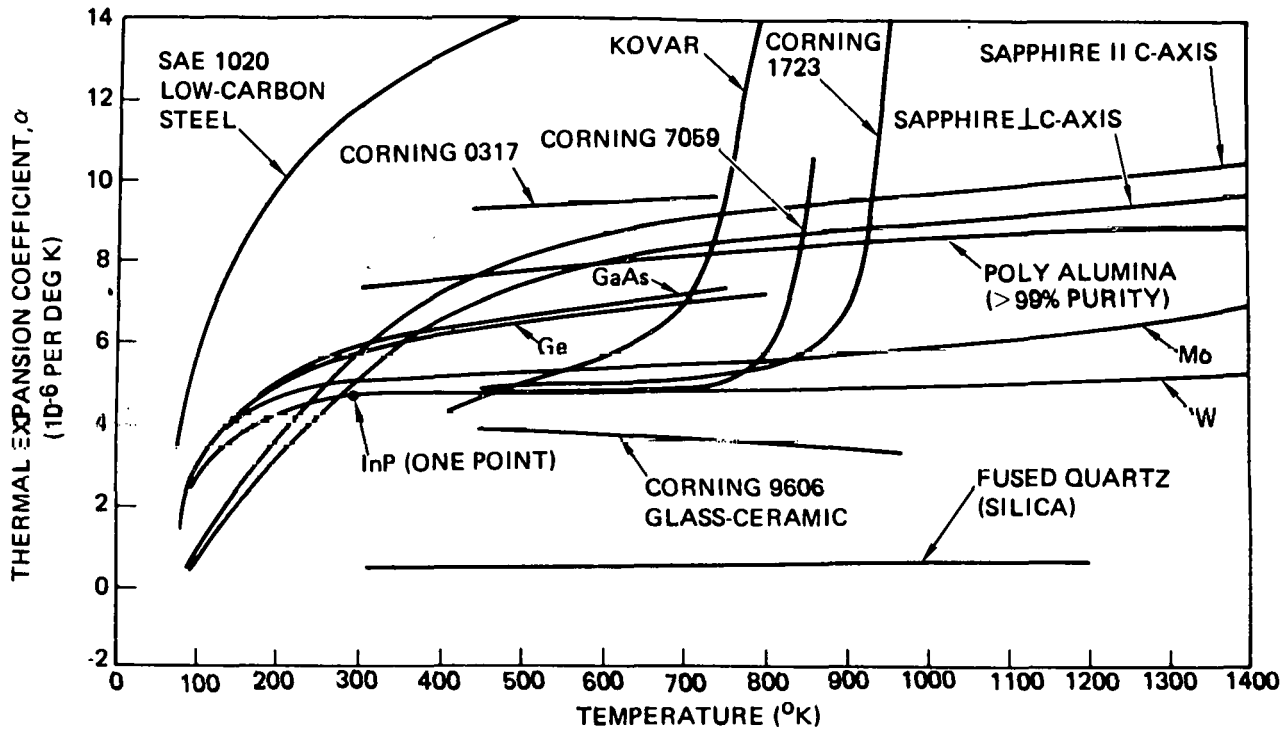



Figure 2-7. Linear Thermal Expansion Coefficients as a Function of Temperature for InP and Several Possible Substrate Materials

include the amorphous glasses, glass-ceramics, polycrystalline ceramics, and certain metals or alloys. Table 2-1 includes some examples of materials that are being used or considered for experimental use in the program; also given are some of the pertinent physical properties and representative costs of these materials in the current market.

2.2.1.1 Single-crystal Substrates

Whereas the primary long-range thrust of this program involves growth of InP films on polycrystalline and amorphous substrates, such as those listed in the table, experiments with single-crystal substrates are also being performed for baseline data and comparative studies of film properties.

The single-crystal substrates being used or planned for use are GaAs, Ge, InP, and sapphire. Investigations with these materials consist mainly of baseline experiments to help in the optimization of film growth parameters and of experimental device configurations, which then will be reproduced on the less-expensive polycrystalline and amorphous substrates.

Single-crystal GaAs and InP are used primarily to establish the CVD parameters that will be required to produce films with properties useful for solar cell fabrication. The single-crystal GaAs used is in the form of both bulk substrates and epitaxial material previously grown on sapphire. Sapphire will be used as a monitor and control substrate during film growth studies with the low-cost substrates. There is a high

Table 2-1. Examples of Materials Considered for Use as Substrates for InP Growth by MO-CVD, with Typical Present Costs

| SUBSTRATE IDENTIFICATION | | MATERIAL/TYPE | AVERAGE THERMAL EXPANSION COEFFICIENT* (TEMP RANGE) ($10^{-6}$ PER DEG C) | SURFACE ROUGHNESS | NOMINAL PURITY (%) | REPRESENTATIVE APPROXIMATE COST FOR RELATIVELY LARGE QUANTITIES |
|---|---|---|---|---|---|---|
| Corning | 0211 | Lime Borosilicate | 7.4(0-300 C) | <1 Microinch | – | $0.031/in.$^2$ (12" x 14" sheet) as drawn |
| | 0317 | Alumina Soda Lime | 8.7(0-300 C) | <0.5 Microinch | – | $0.22/in.$^2$ (10,000 4" x 4") as drawn |
| | 1723 | Aluminosilicate | 4.6(0-300 C) | <0.5 Microinch | – | – |
| | 7059 | Barium Alumino-borosilicate | 4.6(0-300 C) | <0.5 Microinch | (Alkali-free) | $0.11/in.$^2$ (144 sq in.) polished<br>$0.04/in.$^2$ (168 sq in.) as drawn |
| Coors | ADS96F | Alumina | 8.1(25-1000 C) | < 0.6 μm | 96 | $0.05/in.$^2$ (10,000 2" x 2") |
| | ADS995 | Alumina | 7.7(25-1000 C) | < 0.25 μm | 99.5 | $0.10/in.$^2$ (10,000 3¾" x 4½") |
| | Vistal | Alumina | 8.3(25-1200 C) | – | 99.9 | $0.72/in.$^2$ (1000 ½" x ½") |
| MRC Superstrate (Hi Rel) | | Alumina | 7.3(25-800 C) | 4-5 Microinch (max.) | 99.6 | $0.48/in.$^2$ (10,000 3¾" x 4½") |
| 3M | ASM614 | Alumina | 7.9(25-900 C) | – | 96 | $0.06/in.$^2$ (40 x $10^3$ in.$^2$) |
| | ASM772 | Alumina | 7.7(25-900 C) | – | 99.5 | $0.08/in.$^2$ (40 x $10^3$ in.$^2$) |
| | ASM614 w/743 Glaze | Lead Borosilicate on Alumina | ~6.5(40-540 C) | <1 Microinch | – | $0.13/in.$^2$ (40 x $10^3$ in.$^2$) |
| | ASM805 | Alumina | 7.7(25-900 C) | <1–2 Microinch | 99.9 | $0.50/in.$^2$ (40 x $10^3$ in.$^2$) |
| | ASM665 | Steatite | 7.8(25-700 C) | – | – | – |
| Tungsten | | W Sheet | 5.0(25-700 C) | – | 99.95 (min) | $1.23/in.$^2$ (0.020" thick, under 100 Kg) |
| Molybdenum | | Mo Sheet | 6.0(25-700 C) | – | 99.96 (min) | $0.23/in.$^2$ (0.020" thick, under 100 Kg) |
| Kovar | | Ni-Co-Fe Alloy Foil or Sheet | 5.1(25-400 C) | – | ~99.5 | $0.06-0.09/in.$^2$ ($5.50–$8/lb) |
| Ge | | Single Crystal Slice | 6.6(300-650 C)** | Polished one side | Semiconductor grade | ~$2.25/in.$^2$ (~3000 in.$^2$) |
| GaAs | | Single Crystal Slice | 6.9(24-200 C) | Polished one side | Semiconductor grade | $5-8/in.$^2$ |
| Sapphire | | Single Crystal Ribbon | 8.4(25-800 C) | As produced | – | $1/in.$^2$ (1/2 in. wide ribbon)<br>$2.39/in.$^2$ (10,000 in.$^2$ with grains) |
| InP | | Single Crystal Slice | 4.5 ( - ) | As sawed | Semiconductor grade | $110/in.$^2$ (11-25 in.$^2$) |

*Referred to 25 C.

**Referred to temperature at low end of temperature range given.

degree of confidence in the results obtainable by the MO-CVD growth method on (0001)-oriented sapphire. Such substrates provide excellent comparative results for evaluating the success of a given experiment in which films are grown simultaneously on other less-well-known substrates. Furthermore, sapphire can be stripped of films previously grown and then be reused, so its usefulness in this program is considerable, even though in today's market the cost of (0001)-oriented single-crystal sapphire wafers is relatively high.

Consideration will also be given to the use of single-crystal Si and Ge layers as surfaces for InP film growth for solar cells, mainly because of the fairly close match of the thermal expansion coefficients and the lattice parameters in the two cases. The use of such layers will be considered if the grain size of InP films nucleated by GaAs and/or GaP films on the low cost substrates is found insufficient.

2.2.1.2 Low-cost Polycrystalline Ceramic Substrates

Investigations will be made using low-cost insulating polycrystalline ceramic substrates which match the thermal expansion coefficient of InP rather closely, are quite stable at InP film growth temperatures, are readily available, possess relatively smooth surfaces, and are probably chemically compatible with InP.

The literature unfortunately lacks sufficient data on the thermal expansion coefficient of InP at different temperatures. A value of $4.5 \times 10^{-6}$ per deg C is quoted for 300K (Ref 39); this can serve only as a guide in the selection of substrate materials. However, since the CVD growth of InP on sapphire was demonstrated earlier at Rockwell (Ref 36) without any evidence of incompatibility, and the TEC values for sapphire are slightly larger than those of the polycrystalline aluminas, it appears that these relatively low-cost materials should be compatible with InP. They will thus be evaluated as possible substrate materials in this contract work.

Aluminas are available from several manufacturers, in purities from ~94 to 99.9 percent in dense form. Properties of some representative polycrystalline aluminas, samples of which were obtained for use in the Rockwell contract program on Si CVD sheet growth for the JPL/ERDA Low-cost Silicon Solar Array Project (Ref 40), are listed in Table 2-1. Polycrystalline aluminas with purity of 99.5 to 99.9 percent have been fired in $H_2$ to 1250°C for about 15 min at Rockwell without any obvious change in surface structure. It will be established in this program if aluminas of lower purity (and therefore lower cost) are sufficiently stable at InP CVD growth temperatures.

Another class of substrate material of initial interest is the glass-ceramic. These materials have been converted from their original glassy state to polycrystalline ceramics by controlled nucleation and devitrification. Through variations in composition and heat treatment, glass-ceramics offer a wide range of grain size, crystalline orientation, and TEC (from high positive values to negative values, including some that are zero over a limited temperature range). It is anticipated that glass-ceramics with TEC's similar to that of InP will be obtained in the program and evaluated as substrates for the growth of InP. One manufacturer of glass-ceramics (Corning Glass Works) has indicated that a glass-ceramic with TEC of ~6-8 x $10^{-6}$ per deg C can probably be produced in sheet form, with relatively large oriented grains.

Many of the polycrystalline ceramic materials are now available in areas up to about 300 $cm^2$, and the glass-ceramics used today are produced in even larger sheets (the order of square meters). These polycrystalline materials are thus reasonable substrates to consider for larger-scale film growth by the MO-CVD process, especially when TEC matching to InP has been successfully achieved.

2.2.1.3 Low-cost Amorphous Substrates

Glass is an attractive potential substrate material for a number of reasons: It is inexpensive, many varieties are available in large sheet form, it is transparent in the solar spectrum region, and it usually possesses an as-formed surface that is much smoother than the as-fired surfaces of polycrystalline ceramic substrates.

Some representative glasses considered for use as substrates for InP film growth by the MO-CVD process are listed in Table 2-2. These glasses were identified mainly because their softening points are higher than the temperature necessary for InP growth by the metallorganic process. On the basis of present knowledge, it seems clear that only through trial can the possible value of some of these glasses for InP growth be determined. Among available glasses, those with physical properties that appear to be best are Corning Codes 0211, 0317, 1723, and 7059, and Owens-Illinois GS186, i.e., those with the highest annealing points as well as softening points.

Another substrate type being considered for use in InP growth is a combination of the above classes, namely, a glass film produced on a polycrystalline ceramic (i.e., a glazed ceramic). The typical glaze formed on a ceramic offers a surface finish better than that which can be achieved on the ceramic itself (in an as-fired condition) without polishing. The glaze fills in the pores of the surface and can be used with a relatively inexpensive non-smooth substrate of lower purity, for example, <99 percent alumina. Presently, however, the commercial availability of glazed ceramics is very limited, and glazes with low softening temperatures appear to be the rule. This type of composite is attractive, however, and various glazes are being sought for evaluation as substrates for InP growth.

Table 2-2. Examples of Glasses to be Evaluated as Substrates for InP Growth by MO-CVD Process

| Glass Designation | Type of Glass | Average Thermal Expansion Coefficient* in Range 0–300C ($10^{-6}$ per deg C) | Viscosity Data | | | |
|---|---|---|---|---|---|---|
| | | | Strain Point (C) | Annealing Point (C) | Softening Point (C) | Working Point (C) |
| Corning 0211 | Lime Borosilicate | 7.4 | 508 | 550 | 720 | – |
| Corning 1723 | Calcium Aluminosilicate | 4.6 | 665 | 712 | 910 | 1168 |
| Corning 7059 | Borosilicate | 4.6 | 587 | 635 | 842 | 1160 |
| Owens-Illinois GS-186 | Proprietary | 5.4 | – | – | – | – |
| 3M ASM743 Glaze (on ASM614 ceramic) | Lead Borosilicate on Alumina (96% purity) | ~6.5 (40 – 540 C) | – | – | – | – |

*Referred to 25C

2.2.1.4 Metals or Metal Films as Substrates

Certain metals, both in bulk and thin-film form, are being considered for use as substrates for InP growth. Three materials stand out above others - namely, tungsten (W), molybdenum (Mo), and Kovar (a nickel-cobalt-iron alloy*). Based on TEC data (see Table 2-1 and Figure 2-7), the order of preference is 1) W, 2) Mo, 3) Kovar.

These metals are stable in $H_2$, are readily available in sheet and foil form, and are relatively inexpensive compared with single-crystal substrates of most materials. For example, the least expensive - Kovar - presently sells for ~\$0.014 per $cm^2$ (~\$140 per $m^2$) for a single sheet 0.10 cm thick, 33 cm wide, and ~180 cm long. The price drops to ~\$0.0093 per $cm^2$ (~\$93 per $m^2$) for 500 sheets, corresponding to about \$12 per Kg. Mo, on the other hand, sells at ~\$65 per Kg, and W is quoted at ~\$195 per Kg. The availability of these metals in foil form makes a continuous (rather than batch) InP film growth process on such foils as substrates appear feasible. These materials may be compatible with the halide-free MO-CVD process for InP growth.

In addition to the solar cell work reported by the Bell Laboratories group, another account of the successful growth of polycrystalline InP layers on Mo sheet has recently been published (Ref 41). InP was produced by the reaction of In with $PC\ell_3$ in a $H_2$ atmosphere. Pinholes existed in a film grown at 650°C, but homogenous films without pinholes were formed at temperatures below 600°C. Grain size tended to increase with growth temperature and thickness but was not always homogeneous. The mean value of the grain size in a film grown at 600°C was 7 $\mu$m; at 500°C, ~1 $\mu$m. Columnar growth was observed, but "the columns were found not to grow immediately from the substrate and not to exist in layers deposited at temperatures lower than about 500°C." Further, layers "thinner than 5 $\mu$m were random in orientation" if grown at 600°C. The authors also observed that, in the case of thin films (about 1 $\mu$m), relatively random orientation was obtained irrespective of various growth temperatures.

These encouraging results and those of Shay et al (Refs 17-19, 28-30) indicate that the MO-CVD method should be used for growth of InP on Mo substrates and the results compared with those reported by these other investigators. Similar studies should be made on W sheet, to determine if the better TEC match of W to InP changes the properties of the InP.

2.2.2 Substrate Material Acquisition and Evaluation During First Quarter

Although the experiments for the first several months of this program are mainly directed toward developing, understanding and optimizing the MO-CVD process for the formation of films of InP, contacts are being made with various glass, metal, and ceramic manufacturers to encourage their participation in the program. Similar contacts have been made for the purpose of obtaining substrates for other ERDA-funded programs on photovoltaic thin-film materials at Rockwell; in fact, most manufacturers have been encouraged to supply substrates for use in all of these programs. Consequently, evaluations made of substrate properties in the other programs are considered pertinent to this program as well.

*Kovar approximate composition is 29 percent Ni, 17 percent Co, and 54 percent Fe.

Some recent data of that type for several polycrystalline aluminas, obtained on the ERDA thin-film GaAs solar cell contract (Ref 42) and given previously in reports of that work (Ref 43), indicate that none of the alumina materials recently received from several sources new to the program is any better in surface characteristics (i.e., apparent grain size as determined by measurement of surface features in SEM examination) than ASM805, a polycrystalline alumina of 99.9 percent purity supplied by the 3M Co.

An encouraging observation is that considerable improvement in the surface of ASM805 was achieved by a single refiring of the material for 3 hours at ~1600°C; grain sizes as large as 40 μm in one dimension were obtained by this refiring step. These large grains may be found to have a preferred orientation that would be compatible with good-quality film growth; this possibility will be investigated.

Other candidate substrate materials have been received from various other vendors for possible use in this program. Steatite and cordierite substrates have been received from Saxonburg Ceramics (Saxonburg, PA), but the surfaces of these materials are very rough and must be polished before they are used for film growth. The same is true of steatite supplied by Associated Ceramics and Technology, Inc. (Sarver, PA). A group of six different low-cost glasses in slide form has been supplied by Erie Scientific Co. (Buffalo, NY). These glasses have lower softening points than the glasses presently being considered for semiconductor growth, but when the ranges for InP deposition parameters are better established their properties may be compatible, making them worthy of consideration as substrates for InP growth. Amax Specialty Metals Corporatio (Cleveland, OH) has offered to supply some Mo, W, and Mo-W alloy sheet for evaluation u this program. These materials will probably become available early in the second quarte

The specific low-cost substrate materials to be used for initial screening and - depending upon availability and compatibility with InP and the MO-CVD growth process - possible further use in InP solar cell structures have not yet been finally identified. It is expected, however, that the group will include one or more representatives of the following material types: (1) polycrystalline alumina ceramic (e.g., refired ASM805 from 3M Co); (2) glass-ceramic (e.g., Corning Code 9606); (3) glass (e.g., Corning Codes 7059, 0211); and (4) metal sheet (e.g., Mo). Identifications will be made during the second quarter of the program.

The most critical - and most inportant - test of the suitability of a given substrate material is the so-called "use test." Specifically, initial screening will involve the use of procedures yet to be established for growing InP films by the MO-CVD process. Careful attention will be paid to the physical characteristics of the early stages of growth, contamination of a neighboring piece of sapphire during growth, and the stability of the composite film-substrate structure after film growth in evaluating the suitability of a given substrate material. Such tests will begin with the selected candidate materials during the coming quarter.

## 2.3 TASK C. GROWTH OF InP FILMS BY MO-CVD ON INEXPENSIVE SUBSTRATE MATERIALS

This task is summarized in the Statement of Work as follows:

> CVD parameters and procedures developed in Task A with single-crystal substrates will be applied to InP film growth on the inexpensive substrate materials identified in Task B. The TEI-$PH_3$ reaction will be investigated in He carrier gas for use with glasses (or other materials) found to be unstable in $H_2$, the preferred carrier gas. Modifications in other CVD parameters — such as temperature, reactant concentration ratios, and dopant concentrations — will be evaluated in terms of the effect upon film properties achieved in InP grown on polycrystalline and amorphous substrates. Effects of interface layers of metals or other semiconductors on the properties of the InP films will be evaluated. In situ annealing procedures and two-step growth procedures involving changes in deposition rate and temperature cycling over limited ranges will be investigated as possible means for improving the structural and/or electrical properties of the InP films. Similarly, procedures developed in Task B for producing substrate surfaces that are more favorable to large-grain InP film growth will be fully exploited in these investigations.

As indicated in the preceding section, the principal effort on this task will begin later in the program. However, some preliminary growth experiments on inexpensive substrates will be conducted soon for obtaining comparative information on growth processes. Results of these experiments will be discussed in subsequent reports.

The efforts of Task A are devoted to development of appropriate CVD parameter and procedures for InP film growth primarily on single-crystal substrates, to reduce the complications associated with substrate properties to a reasonable minimum while the CVD process itself is examined.

As soon as the principal CVD parameters required for satisfactory InP deposition are established with reasonable certainty, deposition experiments will be undertaken using some of the inexpensive substrate materials identified, acquired, and evaluated under Task B. It is expected that the experiments with these substrates will begin no later than the end of the fifth month of the proposed program, and will continue to the end of the contract performance period.

Special modifications in the MO-CVD process and specific parameters used — such as carrier gas composition, nature of interface layer used (if any), and composition of back-contact conducting grid or layer — may have to be developed for the low-cost substrates selected for study. Experience at Rockwell has shown that the properties of the substrate can dictate which process for film formation is preferred and what growth atmosphere can be tolerated. For example, a substrate unstable in a $H_2$ atmosphere can probably not be used with those CVD methods that require $H_2$, such as the $PC\ell_3$-In-$H_2$, InP-$PC\ell_3$-$H_2$, and In-$HC\ell$-$PH_3$-$H_2$ systems previously referenced. The MO-CVD process for InP film growth, although initially developed in a $H_2$ carrier gas, can be expected to behave like the TMG-$AsH_3$ process which produced GaAs in a He atmosphere (Ref 44) as well as in $H_2$.

If some of the low-temperature glasses are not stable in $H_2$ then growth of InP using the TEI-$PH_3$ process will be studied in a He atmosphere, as is now being done at Rockwell for Si growth from $SiH_4$ on selected glasses. There is no obvious reason at the present time to consider carrier gases other than $H_2$ or He for InP film growth experiments on the other substrates of interest, i.e., the aluminas or the metals.

Other modifications in the CVD process may be required because of special properties of some of the substrates. These modifications can include changes in CVD parameters such as temperature, gas composition and ratio of reactants, dopant concentrations, and other parameters that may affect the growth rates and the film nucleation phenomena. When the substrates are screened and the most promising determined, the CVD parameters previously established for single-crystal substrates will initially be applied to the low-cost substrates. Generally, it is expected that only small modifications in established parameters will be necessary to produce acceptable films with grains large enough for experimental device use. The same approach will probably be valid if interface layers are grown to encourage better InP film characteristics.

The doping conditions and data determined for the growth of single-crystal films of InP using the hydrides and metallorganics as dopant sources will serve as valid references for controlling the properties of polycrystalline films grown by the MO-CVD process. Some differences observed will relate to defects in the films caused by lattice mismatch and other inhomogeneities at the film-substrate interface. However, the principal change in the observed efficacy of a given dopant concentration introduced into the film structure will be caused by the grain boundaries in the polycrystalline films, which may tend to encourage excessive uptake of impurity without measurable effect on the intragrain properties of the film. It will be necessary to conduct a series of experiments with various impurity concentrations added during growth to the polycrystalline InP film and simultaneously to an adjoining epitaxial InP film (grown on a single-crystal substrate), to establish the effective doping behavior of various nominal concentrations of impurity.

If interface layers are used it will then also be necessary to consider heterojunction formation and "autodoping" effects due to the interface layers, and to determine what role these might play in the properties of the InP. In some cases, to effect a better back contact to the active InP layer a heavily-doped p+ layer will be grown prior to the active p-layer. It will be interesting to determine if such a combination leads to improved carrier lifetimes, as was found for Si films on sapphire (Refs 45,46).

Attempts will also be made to improve the properties of the InP films by special substrate surface treatments, film annealing procedures, two-step deposition to enhance nucleation, and the use of intermediate layers of a third material. These and other aspects of this task will be discussed in greater detail in later reports.

## 2.4 TASK D. EVALUATION OF InP FILM PROPERTIES

This task is summarized in the Statement of Work as follows:

A variety of materials characterization methods will be used to evaluate films grown on various substrates in Tasks A and C. Early in the program emphasis will be placed on determination of properties of InP grown on several single-crystal substrates, and on development and evaluation of electrical contacts on p- and n-type InP. Films later grown on inexpensive polycrystalline and amorphous substrates will be evaluated for evidence of film-substrate interactions, preferred orientation tendencies in the films, grain size, and film surface topography. Surface profilometry, X-ray diffraction analyses, scanning electron microscopy examination, reflection electron diffraction analyses, and replica electron microscopy will be used for structural characterization. Auger electron spectroscopy, electron microprobe analysis, and ion-microprobe mass analysis will be employed where appropriate. Electrical properties of the films will be determined by Hall-effect measurements of transport properties, C-V analyses with Schottky-barriers, spreading resistance measurements, EBIC scans in the SEM (for determination of minority carrier properties), and other techniques as required. Optical transmission spectra, reflectance spectra, and surface photovoltage measurements will also be used to supply additional information about film properties.

Characterization of InP properties will constitute a large portion of the total program activity. Analysis by a variety of characterization techniques provides not only useful feedback for the development of the CVD process but also assistance in the selection of substrates for use in device fabrication. Electrical evaluation of film properties and contact properties establishes the suitability of doping levels and contact technology. Interactions of the low-cost substrates and the grown films will be examined carefully. Preferred orientation tendencies in the films, grain size and shape in the films (including any dependence upon distance from the film-substrate interface), and film surface topography are all good indicators of the influence of the substrate on the properties of the film. Measurable improvement in all of these properties must be obtained as the program progresses.

Very little of the program effort expended to date has been devoted to film evaluation, since InP films grown in the new CVD reactor system only recently first became available (see Task A discussion). As a result, most of the work under this task has involved planning and preparation of characterization apparatus. It is expected that many of the techniques being explored and developed, as well as those being routinely used, for characterization of GaAs polycrystalline films on the companion ERDA contact (Ref 42) will also be of use in this program for evaluation of polycrystalline InP. In addition, routine characterization techniques commonly employed for single-crystal materials are also available and will be used in this program as required.

Specifically, the best available X-ray, electron and optical microscopy techniques will be used in conjunction with more conventional metallographic techniques to evaluate the physical and structural properties of the InP films. Analysis of film compositions and impurity content will be used as needed to assist in characterization of the films and evaluation of the MO-CVD process as it is being applied

in this program. Hall-effect, C-V, and spreading resistance measurements will routinely be performed on the InP samples as a guide for future film growth and device design. Development of a low-resistance contact to p-type InP suitable for use with films grown on insulating substrates will be pursued in parallel with film growth studies, to ensure that the CVD development is supported by an adequate contact technology. Also, minority-carrier diffusion lengths in p-type epitaxial and polycrystalline InP films and their spatial variation will be monitored by suitable techniques, development of which must be undertaken early in the program. Finally, certain optical properties of the films will also be measured, to assist in characterization of the films themselves and to provide information important to device design and fabrication.

### 2.4.1 Properties of Films Grown in First Quarter

Some of the first films of InP grown on GaAs substrates have been evaluated using RED and SEM techniques, and the electrical properties of several of these films have been measured. The primary motivation in these early experiments was to determine at what temperatures epitaxy occurs and to determine the growth rates for various flow conditions and reactor configurations. The results show that epitaxy of InP on GaAs occurs at temperatures as low as ~525°C with the MO-CVD technique, as described in the Task A discussion.

The electrical properties of two of the thicker undoped films were determined by van der Pauw measurements of the Hall effect. Ohmic contact was made to the films by means of small dots of In metal pressed onto the film surface. No evidence of rectification was observed for any of the contacts.

The results of these measurements on undoped films are summarized in Table 2-3. The significance of the large difference in carrier mobilities for these films - both of which were epitaxial - is not understood at this time. The carrier concentration typical of the undoped films prepared in this reactor system appears to be consistently the order of $10^{16}$ $cm^{-3}$. Further details of the properties of these and other films will be given in later reports.

Table 2-3. Electrical Properties of InP Films Grown on Single-crystal GaAs Substrates at ~580°C

| SUBSTRATE | FILM COND. TYPE | FILM THICKNESS ($\mu$m) | RESISTIVITY (ohm-cm) | ELECTRICAL PROPERTIES CARRIER CONC. ($cm^{-3}$) | MOBILITY ($cm^2$/V-sec) |
|---|---|---|---|---|---|
| (100) GaAs | n | ~5 | 0.23 | $1.4 \times 10^{16}$ | 1990 |
| (111) GaAs ("A" face) | n | ~7 | 9.4 | $5.6 \times 10^{15}$ | 118 |

### 2.4.2 Characterization Techniques for Evaluation of Single-crystal and Polycrystalline Films of InP

Many of the techniques to be used for evaluation of films being grown in the program have been applied in the current studies of GaAs and Si films on low-cost substrates (Refs 38, 42) and are developed to the point of being routine. Others are still being developed, and the synergism of the ERDA programs in progress at Rockwell should benefit all of the work.

Metallographic techniques have been developed to a high degree at Rockwell and have been successfully employed for the evaluation of thin polycrystalline films of GaAs and Si on low-cost substrates. Though polishing techniques for InP are not as highly developed, it is expected that metallography will be used extensively in examining the films grown in this program.

X-ray diffraction techniques are routinely used in the evaluation of polycrystalline GaAs and Si films to determine grain size and preferred crystallographic orientations. The same methods will be used routinely on the InP and other films being prepared under this contract. A polycrystalline powder sample of InP will be prepared, to serve as a reference standard for X-ray linewidths and intensities for preferred orientation determination and, where grain sizes are small enough to be within the range of the method, particle size measurement by line broadening.

It is expected that SEM techniques utilizing secondary electron images and electron-beam-induced current (EBIC) images will be used extensively to examine the physical characteristics of the films. Techniques for employing the EBIC mode to determine grain boundary locations are being developed and will be applied, if successful, to InP. In addition, energy dispersive X-ray analysis (EDAX) is available on the SEM to determine qualitatively the chemical constituents of substrates, films or interfaces.

The electrical properties of the InP films will be characterized by van der Pauw, Hall bridge, and C-V techniques. These techniques are now in routine use, and near-future capital expenditures for new equipment will provide additional capability in this area. Spreading resistance measurements have been extensively used to characterize polycrystalline Si films, and attempts will be made to apply this technique to polycrystalline InP films, as well.

Minority carrier lifetime properties will be expolored for both single-crystal and polycrystalline InP. In the former case, surface photovoltage measurements can be employed in addition to the EBIC techniques. For polycrystalline films of InP surface photovoltage measurements will provide only an effective diffusion length. All apparatus for making these measurements is now available for these studies.

Apparatus for photoluminescence measurements will soon be available to examine the quality of single-crystal and polycrystalline materials, and will be used where appropriate. Other optical characterization techniques, such as transmittance and reflectance measurements, are readily available and will also be used where necessary.

### 2.4.3 Ohmic Contact and Schottky Barrier Development

As indicated in the Task E discussion, ohmic contact development for InP has already begun at Stanford. As it is further developed, this technology will be used at Rockwell for device and experimental sample preparation.

Optically-semitransparent Au Schottky barriers are being considered for use in InP Schottky-barrier solar cells and for materials evaluation purposes. Barrier heights of 0.8 eV have been determined for Au on p-type InP, a value that should be suitable for initial requirements. Further details of this work will be reported later, as the work progresses.

## 2.5 TASK E. FORMATION AND EVALUATION OF HETEROJUNCTION PHOTOVOLTAIC DEVICE STRUCTURES ON InP FILMS

This task is summarized in the contract Statement of Work as follows:

The properties of electrical charge transport in and electrical contacts to films of InP formed by the MO-CVD method will be investigated, and heterojunction structures will be formed between the InP films and layers of CdS, ZnCdS, ZnSe, and ZnSSe prepared by vacuum deposition or solution spraying, and their properties evaluated. This work will continue throughout the contract period, and will involve activity in five areas: (1) evaluation of the InP CVD layers on both single-crystal and polycrystalline substrates (includes contact development and evaluation, and transport measurements); (2) deposition of CdS films on InP layers by vacuum deposition or solution spraying, and extension of work to include films of ZnCdS solid solutions on the InP, to make heterojunction structures; (3) deposition of ZnSe films on InP layers by vacuum deposition to make wide-window heterojunction cell structures, and extension of work to include ZnSSe solid solutions for wider window; (4) preparation of CdS films on ITO-coated substrates for use as growth surfaces in experimental InP depositions at Rockwell; and (5) characterization measurements to evaluate the photovoltaic properties of the heterojunction structures (including dark and light J-V characteristics, dark and light junction capacitance, minority carrier diffusion lengths in SEM, and spectral dependence of $I_{sc}$).

The work of this task is being carried out by personnel of the Stanford University Department of Materials Science and Engineering, under the direction of Prof. Richard H. Bube as Principal Investigator, on a subcontract from Rockwell. Negotiation of the subcontract was not completed until the third month of the contract, so formal funding has been available for only a short time.

The technical objective of the subcontract work at Stanford is the formation of heterojunction device structures by deposition of films of other semiconductors on the InP films prepared at Rockwell, and the evaluation of the photovoltaic properties of the resulting composites. Emphasis will be on deposition of CdS films, but films of ZnCdS, ZnSe, and ZnSSe will also be utilized. The Stanford work will continue for the remainder of the contract performance period and will include all activities stipulated in the above Statement of Work for this task.

The work in the first quarter was concerned primarily with the characterization of bulk single-crystal InP and with the formation and properties of electrical contacts to this material. These investigations have provided background information and working experience for application to the single-crystal and polycrystalline films of InP being prepared at Rockwell by the MO-CVD technique. Ohmic contacts having low contact resistance have been successfully made during this period.

### 2.5.1 Characterization of Bulk Single Crystals of InP

A small crystal of mostly single-crystal p-type InP (Zn-doped) was obtained, and this was sawed into wafers approximately 5 mm x 3 mm for use in a variety of experiments. A suitable mask was prepared for deposition of an electrode pattern on the samples in order to make Hall-effect measurements as a function of temperature, in both dark and light condition. The surface of each specimen to be measured was polished to a 15 $\mu$m finish, after which Au/Zn/Au contacts were deposited by a vacuum evaporation method (see Section 2.5.2).

A wide range of conductivities was found among the sample crystals of InP examined. The temperature dependence of the conductivity for three such samples is shown in Figure 2-8. Although the conductivity differs by a factor of as much as 50 between sample 1 and sample 3, the general temperature dependence of the conductivity is the same, with a maximum occurring between 110 and 125°K. Sample 3 is a coarse-grained polycrystalline sample obtained from the same parent crystal as samples 1 and 2; grain sizes are the order of 1 mm in average dimension.

The Hall effect was measured as a function of temperature for samples 1 and 2. The variation of hole density with temperature is given in Figure 2-9 and the variation of hole mobility in Figure 2-10. The low-temperature hole density has an activation energy of about 0.02 eV in both samples, and the hole mobility varies with a power of the absolute temperature close to -2. The room-temperature and the 77°K values of hole density and the mobility for the two samples are summarized in Table 2-4. Hall-effect measurements on the polycrystalline sample were not completed before the end of the quarter.

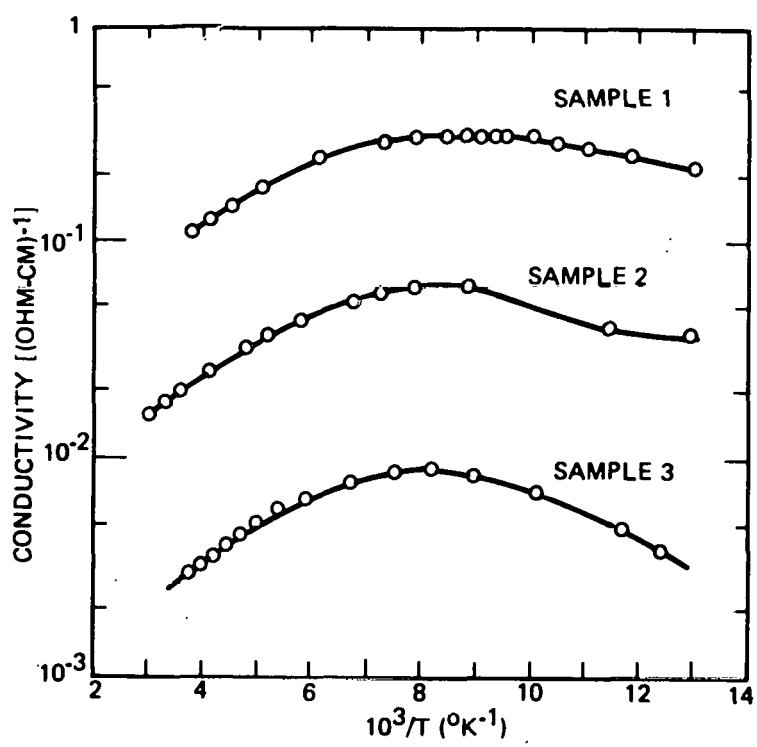



Figure 2-8. Temperature Dependence of Dark Conductivity for P-type InP; Single-crystal Samples (1 and 2) and Coarse-grained Polycrystalline Sample (3) Cut from Same Parent Crystal

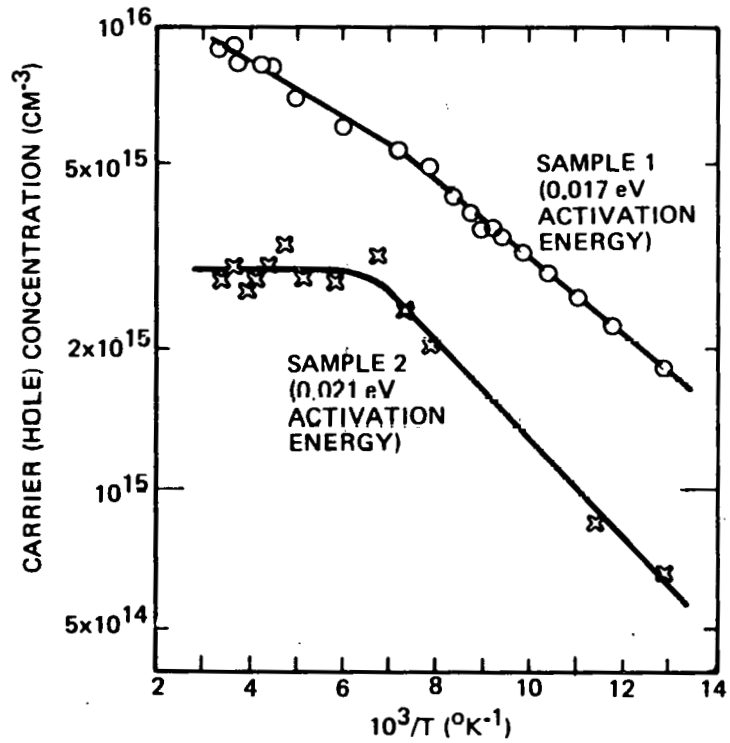



Figure 2-9. Temperature Dependence of Hole Density in Two Single-crystal Samples of Zn-doped InP

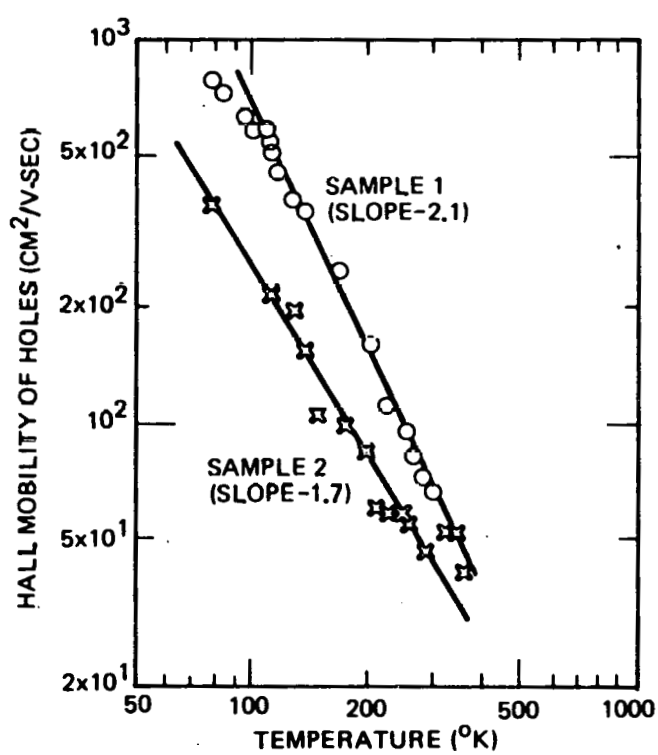



Figure 2-10. Temperature Dependence of Hole Mobility in Two Single-crystal Samples of Zn-doped InP

Table 2-4. Electrical Properties of Single-crystal P-type (Zn-doped) InP* Obtained from Hall-effect Measurements**

| | HOLE CONCENTRATION ($cm^{-3}$) | | HALL MOBILITY OF HOLES ($cm^2$/V-sec) | |
|---|---|---|---|---|
| SAMPLE | 293°K | 77°K | 293°K | 77°K |
| No. 1 (single crystal)† | $9.1 \times 10^{15}$ | $1.9 \times 10^{15}$ | 66 | 783 |
| No. 2 (single crystal)† | $2.8 \times 10^{15}$ | $6.7 \times 10^{14}$ | 42 | 368 |

*Obtained from Varian Associates, Palo Alto, CA.

**Hall-bridge method used.

†Cut from same parent crystal.

2.5.2 Preparation and Evaluation of Contacts on InP

The nature of contacts of Au/Zn/Au on InP has been investigated, both after deposition by vacuum evaporation and after formation by an electrolytic deposition process. Contact resistance at 300°K as well as its temperature dependence have been investigated as a function of InP surface preparation, method of contact deposition, and post-deposition processing.

Contacts were made to samples 1 and 2 (above) and to other samples, as well, by the method of vacuum evaporation. A 300Å-thick layer of Au was covered by a 300Å-thick layer of Zn, which was in turn covered by a 1000-2000Å-thick layer of Au. The InP was polished to a 15 μm finish before deposition of the first layer.

After heat treatment in $H_2$, the contacts to samples 1 and 2, which were used in the Hall-effect measurements, were also used to measure the contact resistance as a function of temperature. The contact resistance varied with temperature in a manner quite analogous to the bulk resistance of the InP, having a minimum value of 0.27 ohm-$cm^2$ for sample 1 and of 4 ohm-$cm^2$ for sample 2 at the temperature where the bulk conductivity is a maximum (cf Figure 2-8). A plot of contact resistance as a function of bulk resistance for samples 1 and 2 is given in Figure 2-11. For both samples the contact resistance varies as about the 3/4 power of the bulk resistivity.

Other samples of single-crystal InP were used to determine the properties of evaporated Au/Zn/Au contacts as a function of heating time and temperature in $H_2$. One set of contacts was heated for a total period of 15 min at 475°C in $H_2$, with testing at 5 min intervals; measurements of the I-V characteristics indicated rectifying properties persisted. A second set of contacts was annealed for a total of 4 min in 1 min intervals; ohmic behavior was observed, with a final contact resistance of 0.15 ohm-$cm^2$.

Measurements of I-V as a function of temperature for the first rectifying contacts showed a family of straight lines on a $\ell n$ I-vs-V plot, with essentially the same slope between 82 and 300°K, suggesting a tunneling mechanism as the dominant process. The magnitude of the current was thermally activated with an activation energy of about 0.05 eV at higher temperatures.

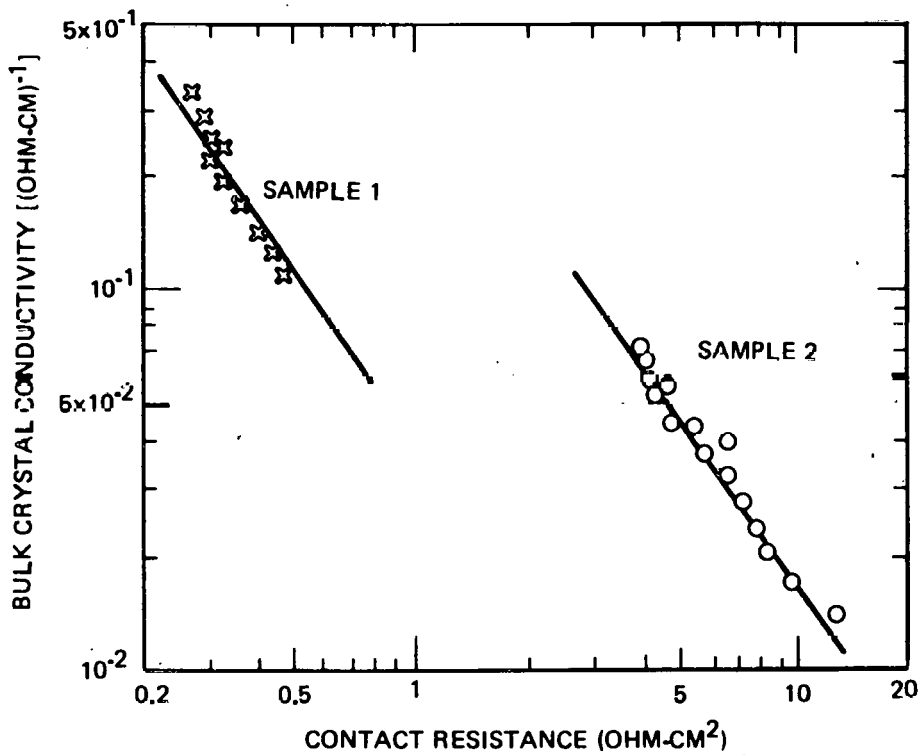



Figure 2-11. Correlation between Contact Resistance and Bulk Conductivity for Two Single-crystal Samples of InP, as Sample Temperature is Varied. (Contacts are evaporated Au/Zn/Au, annealed in $H_2$ at 475°C.)

For the sample with the contact resistance of 0.15 ohm-cm$^2$, the contact resistance and the bulk resistivity were also measured as a function of temperature. The bulk behavior was quite similar to that shown for sample 2 in Figure 2-8. The contact resistance was essentially independent of temperature, maintaining a value of 0.15 ohm-cm$^2$ within 20 percent throughout the range examined.

Contacts of Au/Zn/Au have also been deposited on InP single crystals by an electrodeposition process. These contacts consist of a thin Au layer on the InP surface (previously polished to a 15 μm finish), a thin Zn layer on the Au, and a final thick layer of Au. As deposited, the contact is non-ohmic and of high resistance, but annealing in $H_2$ between 350 and 475°C and for times between 15 sec and 5 min greatly improves the contact quality. The lowest contact resistance obtained to date by this method has been 1.5 ohm-cm$^2$, obtained after annealing for 4 min at 350°C in $H_2$.

The properties of the contacts deposited on the coarse-grained polycrystalline InP sample, the temperature dependence of the conductivity for which is given in Figure 2-8 (sample 3), have not yet been fully evaluated. The temperature dependence of contact resistance on this sample will be examined early in the next quarter. Since the InP films to be grown on the low-cost substrates later in the program will undoubtedly be polycrystalline the results obtained with this sample will be of special interest.

## 2.6 TASK F. ANALYSIS AND PROJECTION OF CELL PERFORMANCE AND COSTS

The summary of this task given in the contract Statement of Work is as follows:

> Early in the program, based on the conceptual cell design to be used as the baseline reference for the technical activities as the contract work progresses, estimates will be made of anticipated photovoltaic performance and of present actual cell costs for experimental quantities. Projections of possible future costs for large-scale production will also be made early in the program. These cost and performance analyses will be updated periodically during the conduct of the program, as technical progress and/or economic factors indicate new influences. During the final two months of the contract, best estimates of future costs for large-scale production of such cells will be projected, based on the analyses of present actual costs of materials, processing costs (including labor), and capital equipment and facilities requirements, compiled from data available from the program, from the Contractor's facilities engineers, from materials and equipment vendors, and other sources.

Since future large-scale terrestrial application of solar photovoltaic power conversion systems will require costs per watt of output power that will be competitive with other alternative power sources, analyses and projections of future costs will be carried out for the InP heterojunction cell design under development in this program to provide an indication of the economic - in addition to the technical - feasibility of the concept. The investigations are intended to lead, within five years at most, to the ability to produce solar cell structures having a 10 percent AM1 power conversion efficiency. Further, the work of the program must be directed toward the long-range goal of production of $5 \times 10^4$ Mw peak power of such cells per year by the year 2000, at a selling price of $100 to $300 per peak Kw.

To provide guidance toward such goals, a tentative conceptual cell design must be adopted early in the program and the costs associated with producing such a photovoltaic cell analyzed in terms of present costs of material, facilities, and labor. At the same time, evaluations must be made of probable photovoltaic performance to be expected in the early stages of the development work. Preliminary projections must also be made of both future performance and future costs, based on reasonable assumptions about technical progress in the program and the usual types of economic factors involved in such analyses.

As technical progress is made in the investigations at Rockwell and at Stanford, and as any new economic factors appear that might influence the analysis, the performance and cost projections will be updated; the results of such updating will be discussed in the contract reports. If necessary, as a result of the technical developments, the conceptual cell design will be appropriately modified from time to time.

Information will be gradually assembled throughout the contract performance period so that a reasonably accurate picture of possible future costs of producing InP thin-film solar cells and arrays by the MO-CVD method can be developed in the last two months of the contract. By that time, many of the important questions about future costs will have been answered in a preliminary way by the experience gained in the program and by continuing discussions with materials and equipment suppliers as well as Rockwell facilities engineering and microelectronic manufacturing

personnel. Consultations with manufacturers of commercial CVD reactors will be included in this activity in order to have useful and realistic guidance in arriving at the long-term cost projection. Best estimates of future costs for large-scale production of such cells will then be projected and the results of the analyses will be discussed in the final contract report, with recommendations given for subsequent actions relative to factors identified during the study.

### 2.6.1 Preliminary Cost Considerations

The future cost (i.e., market price) goals for the National Photovoltaic Conversion Program are \$500 per peak Kw by 1985 and \$100 to \$300 per peak Kw by 2000, with annual production capacities in those years of 500 peak Mw and $5 \times 10^4$ peak Mw, respectively. On the basis of the technical goal of 10 percent efficiency for low-cost polycrystalline solar cells in those same years, it follows that any process to be considered must produce the large areas of cells at total costs not exceeding \$50 per $m^2$ in 1985 and \$10 to \$30 per $m^2$ in 2000.

The 1985 goals of the ERDA/JPL Low Cost Silicon Solar Array Project provide further indication of the significance of these cost figures. The Si material cost goal for 1985 is \$10 per Kg. The cost goal for production of large areas of Si sheet is ~\$17 per $m^2$ (beyond the Si material cost), while the cost goal for fabricating solar arrays (including contacts, bonding, encapsulating, etc) is another ~\$17 per $m^2$ beyond the sheet fabrication cost. The Si cost goal of \$10 per Kg corresponds to \$0.23 per $m^2$ for 10 μm thickness, \$0.47 per $m^2$ for 20 μm thickness, \$2.33 per $m^2$ for 100 μm thickness, and \$4.66 per $m^2$ for 200 μm thickness. Clearly, the Si cost in relatively thin films, layers, or wafers is a small portion of the allowable total cost per $m^2$.

With these 1985 Si cost goals as a guide, some upper limits can be set on materials costs, film formation costs, and cell array fabrication costs for thin-film polycrystalline InP cells in that same time period. Thus, for such InP cells to compete with low-cost Si cells (both presumed to operate at 10 percent AM1 efficiency), the materials costs should not exceed \$16 to \$17 per $m^2$, if the same costs are allowed for film production and for array fabrication in both cases. On a proportional basis, the corresponding figures for the year 2000 - in which the total cost goal is \$10 to \$30 per $m^2$ - would be \$3 to \$10 per $m^2$ for materials, \$3.50 to \$10 per $m^2$ for film formation, and another \$3.50 to \$10 per $m^2$ for array fabrication.

For purposes of projecting possible cost limits the cell design (yet to be developed in detail) will be assumed to be of the heterojunction configuration, with the basic construction as follows, beginning with the back surface (substrate) and progressing toward the front or incident-light surface:

Substrate - Consists of polycrystalline alumina, glass-ceramic, or metal sheet of ~15 mils (375 μm) thickness, or other composite not yet identified.

Backside contact - Consists of deposited (PVD, CVD, or sputtered) or screen-printed metal grid or continuous metal layer the order of 1 μm thick (to be omitted if InP film is grown directly on metal substrate).

Cell base layer - Consists of p-type InP deposited by MO-CVD, ~5 μm thick although variable with design details to be developed.

Cell front layer - Consists of n-type CdS formed by vacuum deposition, probably 1 to 5 $\mu$m thick but subject to design details.

Front-surface contact - Consists of deposited metal grid (or transparent deposited layer of indium tin oxide over entire front surface) having widely-spaced narrow fingers ~1 $\mu$m thick, to provide required contact to individual grains of polycrystalline CdS layer, with low series resistance and high optical transmittance (~90-95 percent).

Antireflection coating - Consists of deposited (PVD or CVD) or spin-on coating of appropriate material to provide reduction of reflection losses and mechanical protection for cell structure.

For purposes of estimating approximate costs of the film production process, only the substrate, the deposited films, and the contacts will be considered, since these are the elements essential to acquiring composites suitable for array fabrication. A total semiconductor thickness of 10 $\mu$m is assumed; a substrate thickness (whatever the composition) of 15 mils (375 $\mu$m) is also assumed.

A rough estimate of the "materials value" of such a configuration can be developed in terms of present market prices for the various key materials involved. For the cell base layer of InP (density 4.8 g $cm^{-3}$) a film 5 $\mu$m thick would contain 24 g of the compound per $m^2$. The CdS window layer, also 5 $\mu$m thick in the cell design assumed, would also contain about 24 g per $m^2$. In terms of approximate prices (Ref 47) for bulk materials (but not in large volume purchases), the InP layer has a materials value of about \$1.53 per $m^2$ and the CdS layer a materials value of about \$0.13 per $m^2$. Thus, the combined materials value of the 10 $\mu$m heterojunction composite is \$1.66 per $m^2$. For comparison, a 10 $\mu$m composite layer consisting of 4 $\mu$m of GaAs and 6 $\mu$m of $Ga_{0.2}A\ell_{0.8}As$, such as is required for one form of the GaAs window-type solar cell, has a materials value of \$9.20 per $m^2$ calculated on the same basis. The main difference in the two configurations is the present high cost of Ga.

A layer of the same total thickness (10 $\mu$m) would have associated with it a materials value of about \$1.40 per $m^2$ if it contained Si at the present price of ~ \$60 per Kg. A 100 $\mu$m layer of Si at present prices would cost about \$14 per $m^2$; this is a more realistic thickness for a Si solar cell, even one consisting of a deposited film.

If the materials value for the CdS/InP composite is calculated in terms of ultrahigh-purity materials, such as are required for most semiconductor synthesis operations, then the amounts become \$5.40 per $m^2$ for the InP layer and \$3.90 per $m^2$ for the CdS, for a total of \$9.30. This amount is similar to that given above for the GaAℓAs-GaAs composite.

If the CdS/InP heterojunction structure is to be formed on an insulating substrate, so that a gridded deposited-metal contact is applied at the InP-substrate interface to contact the p-type base layer, then the materials value associated with that grid must be added. For a dense square grid pattern with 5 percent coverage and consisting of lines 50 $\mu$m wide and 1 $\mu$m thick, the cost will be about \$4 per $m^2$ if the contact material is the Au/Zn/Au composite that has been used for ohmic contact to p-type InP. Similarly, if the same grid pattern is applied to the front surface of the cell (i.e., on the CdS layer) and if ultrahigh-purity In metal is used,

then the associated materials value is \$0.10 per $m^2$. The electroding cost is obviously dominated by the contact containing the Au. A reduction in thickness of the grid lines by a factor of two - to 0.5 μm instead of 1 μm - would lower the associated cost to \$2.10 per $m^2$ instead of \$4.10 per $m^2$ for the two sets of contacts, and appears to be a reasonable alternative.

If the substrate is a high-purity polycrystalline alumina wafer of the type listed in Table 2-1, then its materials value would be ~\$120 per $m^2$ - far too high relative to the other cost factors. Similarly, the metals of interest because of their TEC values - Kovar, Mo, and W - are very high in cost in normally fabricated forms. Kovar, the least expensive of the three, would contribute ~\$37.60 per $m^2$ to the cost total if current prices per gram for large quantities of sheets 0.10 cm thick are used in the calculation. On the other hand, certain low-carbon steels that are available in several thicknesses and large standard sheets are priced as low as ~\$1 per $m^2$, for the thickness considered here.

Thus, the three materials cost elements - semiconductor films, contacts, and substrate - represent a total materials value ranging from about \$12.50 per $m^2$ upward, depending largely upon the particular substrate material involved. The lower end of this range is well below the total cost goal for 1985 and somewhat below the materials cost goal for that period, and it is within the range of the upper and lower limits for total costs for the year 2000 (but above the materials cost goal alone for that year).

Although several factors have been totally neglected, it does appear that the heterojunction configuration proposed for fabrication by the MO-CVD technique has promise of achieving the economic as well as the technical goals of the national photovoltaic program if the problem of identifying a satisfactory substrate material that can be manufactured inexpensively can be solved.

The principal direct materials costs involved in producing the InP layers by the MO-CVD process are those associated with (1) the substrate (simple or composite); (2) the high-purity compounds used as sources of the films deposited on the substrate; (3) the carrier gas, which for some substrates can be $H_2$ but which might in some instances be He; (4) doping gases, to provide necessary impurities to be added to the two layers; and (5) miscellaneoous materials used in the CVD process, such as liquid $N_2$ for condensation traps in gas lines, bulk gas, water, cleaning solvents, etc.

The corresponding direct materials costs associated with producing the CdS films on the InP to form heterojunction structures are related to (1) the ultrahigh-purity compound used for the vacuum deposition process; (2) liquid nitrogen consumed in the cold traps of the vacuum system; (3) doping impurity added to the growing film; (4) miscellaneous source heaters that are gradually "consumed" in the vacuum deposition process; and (5) miscellaneous materials used in the vacuum deposition process and any associated post-deposition treatment of the composite.

To these direct materials costs, of course, must be added appropriate labor costs, overhead costs, and interest and depreciation costs in order to obtain a measure of the total cost per $m^2$ (or per watt) for cells of the type described.

### 2.6.2 Detailed Materials Cost Estimates

Acquisition of detailed cost data for the materials to be used in the growth of InP films by the MO-CVD method began during the first quarter. However, no significant results have yet emerged from this effort; pertinent details will be discussed as appropriate, in subsequent reports.

Details of a preliminary conceptual design for a CdS/InP thin-film heterojunction photovoltaic cell will be developed early in the second quarter in discussions with Stanford personnel. This design will be the basis for the initial detailed cost analysis. Results of these considerations will be given in later reports.

## 2.7 TASK G. PREPARATION AND DELIVERY OF FILM SAMPLES

The contract Statement of Work describes the requirements of this task as follows:

> Within three (3) months from the inception of contract, begin producing films and supply a minimum of 4 $cm^2$ of current production each month thereafter to ERDA, the number and shape of the samples to be representative of that month's output.

As indicated earlier in this report (Task A discussion), the new CVD reactor system was completed in December, and the first InP films were grown by the MO-CVD process in this reactor late in the first quarter.

Selected samples from among the films prepared in those experiments have been identified for shipment to the ERDA Technical Project Officer. These samples meet the requirements specified above.

## 3. CONCLUSIONS AND RECOMMENDATIONS

The results obtained in the first quarter are very encouraging. With relatively few deposition experiments in the new reactor system it has been shown that epitaxial growth of InP films can be achieved by the MO-CVD process on at least two different crystallographic orientations of GaAs at temperatures as low as ~525°C, and perhaps even lower. Films not intentionally doped are n type, with measured carrier concentrations in the $10^{16}$ $cm^{-3}$ range and electron mobilities as high as ~2000 $cm^2$/V-sec.

Substrates of single-crystal GaAs are very useful for the initial investigations under this contract, since the material is readily available and inexpensive compared with single-crystal InP (less costly by a factor of about 20). Thus, with single-crystal GaAs substrates considerable knowledge of the InP CVD growth process under a variety of deposition conditions can be obtained and later be transferred to growth on InP and/or other single-crystal materials with a minimum of further investigation, when those materials become available.

The work to date has also shown that the relatively wide range of deposition conditions that appear sufficient for single-crystal film growth on GaAs is not equally satisfactory for growth on (0001)-oriented sapphire, substrates of which have been used along with the GaAs in most of the experiments to date. Sapphire used in this way, as a comparison substrate for GaAs, serves as a good indicator of how the growth process is proceeding, for the particular deposition conditions being used. Films on single-crystal sapphire substrates will also be a "reference standard" for evaluation of films grown on polycrystalline alumina later in the program. It will be necessary to establish a range of acceptable deposition parameters for InP films grown on sapphire substrates at some time in the future, for use in selecting initial parameters for the experiments with the polycrystalline alumina substrates and in evaluating the properties of the films grown on those materials.

The preliminary studies of the white solid produced in the reactor by mixing $PH_3$ and TEI at room temperature led to the conclusion that the growth rate of InP can be controlled by manipulating gas flow rates and by maximizing the introduction of the solid into the main gas stream. There also are indications that InP can be produced at temperatures below 465°C, thus admitting for consideration as possible substrates many glasses with low strain points but reasonable thermal expansion properties.

Encouraging results have also been achieved in the subcontract work at Stanford (Task E), in which ohmic contacts of Au/Zn/Au have been produced on bulk single-crystal p-type InP by two different deposition methods. Contact resistances as low as ~0.1 ohm-$cm^2$ (after annealing in $H_2$ at 475°C) have been obtained by vacuum deposition methods and ~1 ohm-$cm^2$ (after annealing in $H_2$ at 350°C) by an electrodeposition process.

It is recommended that the CVD experiments during the next quarter be directed toward optimization of the reactor chamber design for the growth of InP films by the metalorganic-hydride method, and toward determining the effects of changes in growth parameters on the properties of films deposited first on single-crystal substrates and then on selected polycrystalline and amorphous substrates.

Studies of the formation of intentionally-doped p-type films will also be initiated and a satisfactory doping procedure will be adopted, so that appropriately doped films can be submitted to Stanford for formation of heterojunction structures. The first such composites will be formed by deposition of CdS on the InP layers supplied by Rockwell. It is anticipated that most of the InP films prepared for this purpose in the coming quarter will be epitaxial layers grown on single-crystal substrates. However, some polycrystalline InP films may be supplied late in the quarter.

## 4. PLANS FOR NEXT QUARTER

The contract work in the coming quarter will consist of (but not be limited to) the following principal activities, arranged by task:

Task A

1. Determine a preferred reactor chamber design for growth of InP films by the metalorganic-hydride process

2. Continue to explore the effects of various deposition parameters on the properties of InP films grown on single-crystal substrates, to identify preferred parameter ranges.

Task B

1. Polish and otherwise prepare surfaces of available candidate low-cost substrate materials, for evaluation in InP deposition experiments

2. Continue to work with various substrate material manufacturers, and encourage them to supply candidate materials for use in this program.

Task C

1. Begin comparative study of growth of InP films on single-crystal and selected low-cost polycrystalline and/or amorphous substrates.

Task D

1. Continue to characterize structural and electrical properties of InP deposits being prepared in MO-CVD reactor system,using routine SEM, x-ray, RED, and classical metallography methods, as well as resistivity and Hall-effect measurements

2. Prepare standard polycrystalline (powder) InP sample, to provide reference x-ray diffraction line intensities and widths for preferred orientation and grain size determinations

3. Utilize and evaluate ohmic contact methods developed at Stanford (Task E) as applied to CVD InP films for purposes of evaluation of electrical properties.

4. Evaluate EBIC mode of SEM for delineating grain boundaries in polycrystalline films of InP.

5. Evaluate spreading resistance measurements as a method for characterizing the electrical (and structural) properties in the interior of polycrystalline InP films

6. Examine possibility of using semitransparent Au Schottky barriers on InP for material evaluation and solar-cell fabrication purposes.

Task E (Stanford Subcontract)

1. Complete study of properties of Au/Zn/Au contacts on p-type InP as function of InP surface preparation, contact deposition method, and post-deposition processing.

2. Evaluate properties and temperature dependence of contact resistance for contacts on bulk polycrystalline InP samples

3. Conduct preliminary investigation of temperature dependence of properties of initial undoped epitaxial InP films prepared in Rockwell CVD reactor system

4. Prepare CdS/InP composite structures on undoped epitaxial InP films prepared in Rockwell CVD reactor system, and evaluate structural properties of these composites

5. Deposit n-type CdS films on p-type bulk crystals of InP, and characterize photovoltaic properties of the heterojunctions

6. Prepare composite CdS/InP structures on doped p-type epitaxial InP films and/or polycrystalline InP films prepared on low-cost substrates at Rockwell, and begin structural characterization of these composites.

Task F

1. Continue accumulation of cost data for materials and processes used in growth of InP films by MO-CVD method

2. Develop preliminary conceptual design for CdS/InP thin-film heterojunction photovoltaic device, for use in preliminary cost analyses

3. Prepare initial projections of possible future costs for large-scale production of CdS/InP thin-film heterojunction photovoltaic solar cells.

Task G

1. Prepare and deliver representative samples to ERDA each month, as required under the contract.

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