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# THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

## Quarterly Project Report No. 1, July 5—October 2, 1976

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November 1976

Work Performed Under Contract No. EY-76-C-03-1202

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

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UNDER CONTRACT NO. E(04-3)-1202

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

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# ABSTRACT

The first quarter of work on the contract is summarized. The metalorganic chemical vapor deposition (MO-CVD) technique is being applied to the growth of thin films of GaAs and GaAℓAs on inexpensive polycrystalline or amorphous substrate materials (glasses, glass-ceramics, alumina ceramics, and metals) for use in fabrication of large-area low-cost photovoltaic device structures. Trimethylgallium (TMG), arsine ($AsH_3$), and trimethylaluminum (TMA) are mixed in appropriate concentrations at room temperature in the gaseous state and pyrolyzed at the substrate, which is heated in a vertical reactor chamber to temperatures in the range ~550-850°C, to produce the desired film composition and properties.

Ten candidate substrate materials have been selected for further experimental investigation, based on a set of qualification criteria and initial experimental tests. To date, only minor differences have been observed in the properties of undoped polycrystalline GaAs films grown on various candidate substrates - including Corning Codes 0317 and 1723 glasses, polycrystalline alumina ceramics ASM805 and ASM838 (from 3M Company), and Mo sheet - with the exception of films deposited on Kovar-type Fe-Ni-Co alloys. Attack of these alloys by $AsH_3$ has been observed at temperatures above 500°C, with resulting formation of an interface compound and Ni-rich inclusions in the deposited GaAs films.

Films on all of the other substrates have typically had growth characteristics in common, with apparent surface grain sizes in the 2-5 μm range and high electrical resistivity ($\geq 10^5$ ohm-cm), with no evidence of chemical reaction with the film or the reactants under the conditions of growth employed. Large-grain (10-20 μm) growth of Ge films on Kovar-type alloy surfaces has also been achieved by $GeH_4$ pyrolysis indicating considerable promise for this composite as a substrate for subsequent, GaAs film growth.

Single-crystal films of Se-doped GaAs, Zn-doped GaAs, Se-doped $Ga_{1-x}A\ell_xAs$ ($x = 0.9$), and Zn-doped $Ga_{1-x}A\ell_xAs$ ($x = 0.9$) have also been grown on single-crystal GaAs:Cr substrates. The resulting carrier concentration dependence on added concentration of dopant has been investigated in each case, providing needed data to be used later in the program.

Construction of a second MO-CVD reactor system was begun and is nearly completed. Two conceptual device designs have been identified for initial cost analyses and future cost projections of thin-film solar cells made by the MO-CVD method, and acquisition of materials and processing cost data has begun.

Plans for the second quarter of work on the contract are outlined.

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## CONTENTS

## CONTENTS (Cont)

# ILLUSTRATIONS

## ILLUSTRATIONS (Cont)

## TABLES

# 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 this program are (1) to conduct research, development, and demonstrations to show a factor of 10 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 of one hundred or greater.

Specific goals of the national program are establishment of a total solar array production capacity of (1) 500 peak Mw/year of solar array modules at a market price of less than \$500/peak Kw by FY 1985, and (2) $5 \times 10^4$ peak Mw/year of solar array modules at a market price of \$100 to \$300/peak Kw by FY 2000.

The overall objective of this contract is the performance of intensive studies that will constitute an initial step in ERDA's program to overcome current problems and deficiencies in design and fabrication of arrays of extremely low-cost thin-film photovoltaic cells of relatively high efficiency and long life. The acquisition of further knowledge of thin-film deposition methods and thin-film technology for polycrystalline GaAs on various substrates is also expected.

In addition, any proposed device configuration should lead, within a period of one or two years at most, to the ability to produce solar photovoltaic cell configurations having 10 percent AM1 efficiency. This technical goal may not be achieved during the performance period of a 12-month contract, but it will provide a continuous guideline for conduct of the program.

Specific studies and/or tasks required by ERDA include (1) selection of appropriate low-cost substrates; (2) deposition of thin films of GaAs, which may be polycrystalline, on the selected substrate(s); (3) conduct of a deposition parameter investigation to optimize the process; (4) determination of the film properties in terms of quantitative physical parameters; (5) alteration of the physical parameters of the film in a manner directed toward production and deployment of high-efficiency photovoltaic solar cells capable of scale-up to an annual production rate of $5 \times 10^4$ Mw by the year 2000, with a selling price of \$100 to \$300/peak Kw, "without creating inordinate technical and economic problems;" (6) the delivery of thin-film samples (minimum 4 $cm^2$/month) to ERDA; and (7) the analysis and projection of cell costs for large-scale production in the future.

## 1.1 ADVANTAGES OF GaAs FOR THIN-FILM SOLAR CELLS

In the years since the modern era of photovoltaic cell development began in the early 1950's, considerable research and engineering work has gone into achieving improvements in the single-crystal Si solar cell and into developing experimental cells of single-crystal GaAs and other 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, theoretical considerations (see, e. g., Ref 1) have shown that various compond semiconductors - especially GaAs and its related alloys - should provide significantly higher conversion efficiencies than are available with Si cells. Although pilot-line quantities of GaAs cells were fabricated several years ago, the performance of experimental arrays in actual space missions was generally disappointing (Ref 2).

Recent work with composite cells involving GaAs and a front layer of another material as a "window" has, however, been very encouraging (Ref 3). These developments have renewed interest in the significant advantages of GaAs as a solar cell material; these advantages include the following characteristics:

1. The bandgap ( ~1.4 eV) is a better match to the solar spectrum; higher theoretical efficiencies (in excess of 20 percent) than for Si are thus to be expected.

2. The decrease of power output with increasing temperature for GaAs is about half of that for Si cells, because of the larger bandgap that allows higher temperature operation of the junction.

3. GaAs cells typically have lower minority carrier lifetimes and diffusion lengths than Si cells, and so are less susceptible to radiation damage.

4. The larger bandgap of GaAs results in higher output voltage per cell than for Si, although the current per cell is smaller.

5. The optical absorption edge in GaAs is steep (it is a direct bandgap semiconductor), so most solar radiation is absorbed very near the surface, eliminating the need for thick cells to capture most of the incident energy.

There are some disadvantages of GaAs relative to Si, not the least of which is related to Item 5 above. Because of the absorption and generation of charge pairs so close to the surface, the high surface recombination velocity that is also characteristic of GaAs (10 to 100 times that found in Si) results in reduced minority carrier collection efficiencies in junction-type devices, due to surface recombination losses.

Additionally, since the minority carrier diffusion lengths in GaAs are typically small compared with those found in single-crystal Si, very thin ( $< 0.5\,\mu m$) layers with extensive electroding (grids) are required on the illuminated side of the junction to reduce cell series resistance as much as possible. Even with these measures, the losses at the front of the cell have been found to be too high for acceptable cell operation under normal conditions.

This problem 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 GaAs to remove the active 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 an interface with the GaAs that is sufficiently good structurally 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 aspects of the design allow the carriers generated by such absorption to be collected by the active junction).

It should also be noted that the costs of GaAs and Si differ by about an order of magnitude for comparable quantity (i.e., "solar grade" single-crystal) material, with GaAs more expensive. The costs of both these materials - especially after they are processed into solar cells - are major factors in the increased interest in thin-film solar cells, as addressed in this program.

The large absorption coefficient of GaAs in the wavelength region to the high-energy side of its fundamental absorption edge is such that most (i.e., 90 percent or more) of the available radiation in the solar spectrum is absorbed within a thickness of 2 μm or less. A thickness in excess of 100 μm of Si is required for similar absorption. The fact that GaAs is a direct-bandgap material and Si an indirect-bandgap semiconductor means that the transition from non-absorbing to absorbing is much more abrupt for GaAs than for Si in progressing from long wavelengths to shorter wavelengths, past the band edge.

The difference in bandgap energy for these two semiconductors means that GaAs responds only to that portion of the total solar spectrum that is to the short-wavelength side of ~0.9 μm, while Si responds to all photons to the short-wavelength side of ~1.1 μm. There is a significant amount of solar energy in the band between these two wavelengths, but the net result of all factors that bear on photovoltaic conversion efficiency is that the theoretical values for GaAs are significantly higher than for Si (Ref 1).

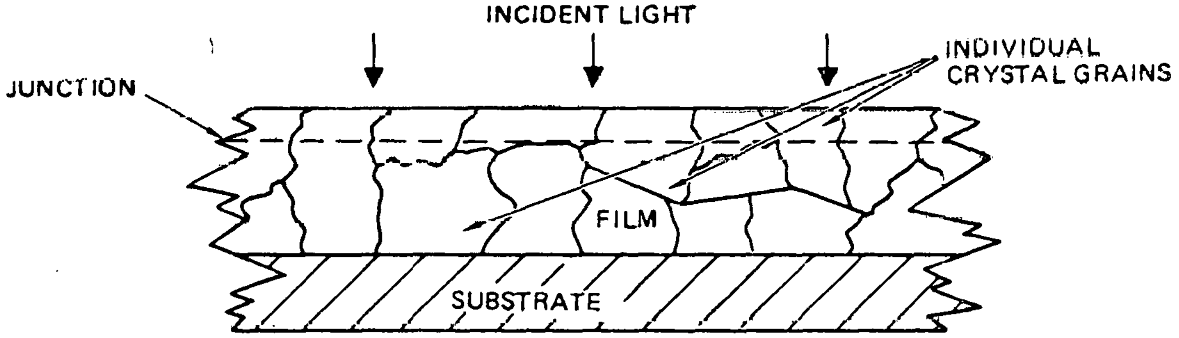
The small thickness of GaAs required for adequate absorption of solar radiation strongly suggests the use of deposited films of the material instead of bulk single-crystal wafers. This would clearly help in reducing the cost of the cell, simply by virtue of using less of the expensive active material; it would also assist in the continuing effort to reduce 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 are realized depends upon the extent of other complications that arise because of the thin-film configuration.

Ideally, of course, single-crystal thin films would be 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 4), and this does not allow the needed extensive reductions in materials costs. Furthermore, if only single-crystal substrate materials are considered then there are serious limitations on the maximum area that can be achieved for the basic cell module to be fabricated by thin-film growth procedures. This reasoning leads directly to consideration of less expensive substrate materials that are available in relatively large areas. It also leads to the realization that the resulting thin-film cells will amost certainly be polycrystalline, because of the absence of strong ordering forces associated with the substrate surface.

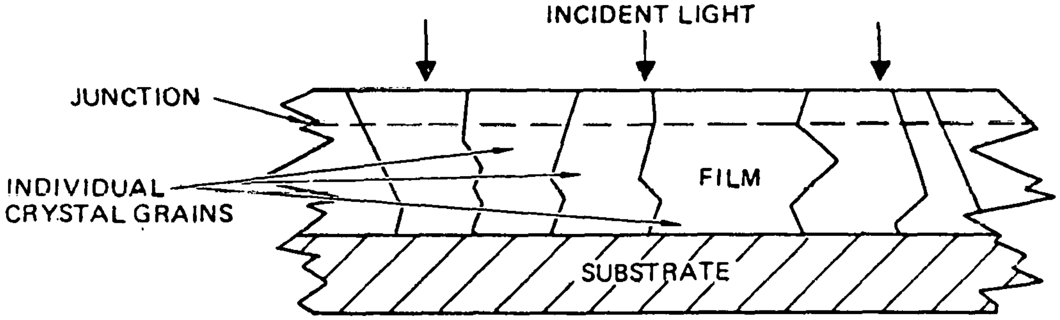
There are several important considerations that are introduced when thin-film polycrystalline solar cells are considered. The first has long been recognized as one of the principal deterrents to the use of polycrystalline thin films for solar cell fabrication, and relates to the nature of the crystal structure in the deposited film. If the individual crystal grains are randomly oriented on the substrate, as shown in Figure 1-1a, 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 shown in Figure 1-1b, in which the grain boundaries are depicted as being 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. The long-standing rule-of-thumb that suggests that average grain sizes at least of the same magnitude as the film thickness are required for reasonable thin-film solar cell performance had its origin in such considerations.

The fact that GaAs thicknesses of only 1 to 2 $\mu$m are required to absorb up to 90 percent of the useful solar radiation (in the proper energy range) indicates that polycrystalline films with average grain sizes of 1 to 2 $\mu$m could be expected to exhibit respectable solar efficiencies, whereas for Si polycrystalline film cells the same criterion dictates that average grain sizes approaching 100 $\mu$m are required.



(a) UNDESIRABLE POLYCRYSTALLINE GROWTH



(b) DESIRABLE POLYCRYSTALLINE GROWTH

Figure 1-1. Two Possible Crystallite Configurations in Polycrystalline Film Solar Cells Grown on Foreign Substrates

Some calculations of the expected performance of polycrystalline GaAs solar cells have been described by Woodall and Hovel (Ref 5). 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 a more conservative analysis carried out by Soclof and Iles (Ref 6) for polycrystalline Si solar cells as the basis, Woodall and Hovel found a theoretical efficiency of 11 percent and 1.5 percent for GaAs and Si, respectively, for the same dimensional configurations mentioned above.

Although such predictions must be viewed with caution, there is enough validity in the analyses to suggest that significantly higher efficiencies may be expected for polycrystalline cells in thin-film GaAs than in thin-film Si, if average grain sizes the order of only 1 μm are obtainable in both cases.

Such dimensions seem well within the realm of achievement for GaAs films deposited on non-crystalline substrates by the chemical vapor deposition technique, so there appears to be good prospect for fabricating thin-film solar cells that will meet the 10 percent AM1 efficiency goal mentioned earlier. If grain sizes significantly larger than 1 μm can be achieved, then the chances for success are even better.

## 1.2 GENERAL TECHNICAL APPROACH USED IN PROGRAM

The general technical approach of the program involves the use of the metalorganic chemical vapor deposition (MO-CVD) technique, pioneered by Rockwell, for the growth of thin films of GaAs, GaAℓAs, and possibly AℓAs on inexpensive polycrystalline or amorphous substrate materials in configurations permitting fabrication of photovoltaic devices. The parameters of the CVD process used will be chosen so that the required properties of the deposited films can be achieved and the efficiency goal of the photovoltaic device (10 percent AM1) can be realized, subject to the constraints superimposed by the properties of the selected substrate material(s).

The CVD method is believed to be potentially the 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 among those specifically addressed in this program.

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, trimethylgallium (TMG) and $AsH_3$ are mixed at room temperature in the gaseous state and pyrolyzed at established temperatures in a cold-wall reactor to form GaAs:

$$(CH_3)_3\,Ga + AsH_3 \rightarrow GaAs + 3CH_4.$$

By mixing TMG in the gas phase with trimethylaluminum (TMA) and $AsH_3$, GaAℓAs is obtained upon pyrolysis at established temperatures. The composition of the alloy is controlled by the ratio of the reactants. The organic byproduct, namely methane ($CH_4$), is stable at film growth temperatures. In similar fashion, AℓAs can be prepared from TMA and $AsH_3$. Many such compounds and alloys have been prepared by the MO-CVD process. (See, e.g., Refs 4, 7, 8, 9.)

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

Clearly, however, 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 relatively small number of manufacturers that are 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.

The other principal technical problems to be solved in this program are (1) 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 GaAs and GaAℓAs grain growth; (2) establishing preferred CVD process parameters (temperature, reactant concentrations, carrier gas composition, doping impurities, growth rate) for optimized intragrain properties of the films grown on various substrate materials; and (3) achieving adequate grain size in the films to provide satisfactory solar cell properties.

To pursue these technical problems and to meet the objectives of the program, the contract work is organized into five main technical tasks, as follows:

Task 1. Substrate Material Selection, Evaluation, and Development

Task 2. CVD Experiments and Parameter Studies

Task 3. Evaluation of Film Properties

Task 4. Experimental Photovoltaic Device Fabrication and Evaluation

Task 5. Analysis and Projection of Cell Fabrication Costs

In addition, the Program Management Task defined in the Statement of Work (Exhibit I) of the contract is carried on in parallel with the above technical tasks.

This is the first Quarterly Project Report for this contract and covers the period 5 July through 2 October 1976. The contract activities during that period are described by task in the following section.

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# 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 1. SUBSTRATE MATERIAL SELECTION, EVALUATION AND DEVELOPMENT

The summary of the proposed work of this task, as given in the original proposal, is as follows:

> Selected samples of both commercially-available and specially-prepared materials--including high-purity polycrystalline aluminas, special glass-ceramics, some high-temperature glasses, and certain metal foils and deposited layers--will be evaluated for suitability of physical properties and chemical stability in the MO-CVD environment. 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.

The highly developed technologies of epitaxial growth of GaAs on single-crystal GaAs substrates and single crystals of dissimilar materials (especially insulating oxides such as sapphire and spinel) permit the growth of films with excellent structural and electrical properties. However, the limitations of substrate cost and available size in these two cases place the configurations outside the range of the ERDA program goals.

Attention must thus be focused on identifying a substrate material that is readily available, is inexpensive (or potentially so), and yet permits the formation of GaAs and GaAℓAs layers having structural and electrical properties adequate for achievement of reasonable solar cell efficiencies. These requirements on the substrate tend to be mutually exclusive: Substrate materials that are inexpensive and readily available in large areas are usually not single crystal or even large-grained, so the GaAs layer growth process will get relatively little help from the substrate in acquiring the properties important to solar cell performance.

As a result, the approach taken in this program is to apply the MO-CVD process to the growth of GaAs and GaAℓAs films on inexpensive substrate materials available in large areas, and then to systematically pursue the achievement of sufficient crystal grain size in the films to permit acceptably high solar conversion efficiencies. Only a few classes of materials now commercially available can be considered as candidate substrate materials, based on cost, availability, and reported properties. These include the amorphous glasses, glass-ceramics, polycrystalline ceramics, and certain metals or alloys, as discussed below.

Although the primary thrust of the program involves the growth by CVD of films of GaAs and GaAℓAs on polycrystalline and amorphous substrates, for baseline and comparative studies of film properties single-crystal substrates are also used. The single-crystal substrates used as GaAs and sapphire. Investigations with these materials consist mainly of experiments to help in the optimization of film growth parameters and experimental device configurations, which are then reproduced on less expensive polycrystalline and amorphous substrates.

Single-crystal GaAs is to be used primarily to establish the CVD parameters and the resulting film properties that are required to produce epitaxial window-type GaAs solar cells equivalent in characteristics to similar structures produced by liquid-phase epitaxy (LPE) or other methods. These studies are planned for early in the program, in parallel with the primary studies of GaAs growth phenomena on low-cost substrates that began at the start of the contract performance period.

Sapphire is used as a monitor and control substrate during film growth studies on the low-cost substrates. Previous experience in Rockwell laboratories with GaAs and GaAℓAs growth on (0001)-oriented sapphire has provided a good level of confidence in the results obtainable with the MO-CVD growth method on this substrate. Comparisons with results obtained simultaneously on other substrate materials provide valuable information, based on this experience.

### 2.1.1 Criteria for Candidate Substrate Material Selection

Practical considerations dictate that the specific criteria used in selection of candidate substrate materials for this program should be based on the following general characteristics:

1. The availability of either commercially-prepared samples or specially-processed research samples produced specifically for use in this program
2. The present-day and probable future costs of the materials when supplied in very large quantities
3. The purity of those materials available to this program
4. The physical and chemical properties of those materials.

A commercially available substrate material that is compatible with the growth process and subsequent device processing and which meets most (or all) of the other selection criteria would be preferred, so that development costs would not be incurred. However, if research samples of one or more specially-prepared materials are made available to the program, and if the properties of the material indicate that it is potentially a useful substrate material for GaAs thin-film solar cells, then the criterion of commercial availability should be temporarily waived. It must be established as soon as possible for such a material if there is realistic prospect for it to be brought from the realm of experimental research-sample quantities to large-scale production quantities within the ERDA time scale for thin-film polycrystalline solar cells.' Unless this can be projected with some certainty - and the element of cost will become a major co-factor here - the advisability of continued experimentation with the material will be doubtful.

Present-day low cost is an obviously desirable characteristic of a candidate substrate material. In the case of some of the commercially-available materials of interest in this program (such as certain glasses) the current cost per unit area (see Table 2-1) certainly qualifies the material as low cost for this application. However, other possible materials - including some now commercially available and others available only in limited (research) quantities - that appear qualified on the basis of their physical and/or chemical properties may offer little hope of becoming adequately inexpensive in the future to justify extended consideration of their possible use as substrates for large-scale terrestrial solar arrays. Such materials may be of great value for experimental use in this program, although not necessarily likely prospects for large-scale use in the future on the basis of economic (or perhaps just mass-producibility) considerations.

As a general guide, it is clear that the projected 1985 cost per unit area of the substrate-and-film cell composite must be less than the 1985 projected cost per unit area of a cell made entirely of the film material (GaAs) in unsupported or bulk crystal form (assuming equivalent power conversion efficiencies in the two cases). The 1985 cost goal of the ERDA/JPL Low Cost Silicon Solar Array Project (LCSSAP) for fabrication of Si sheet material from appropriate Si source material (costing less than \$10/Kg) is no more than \$17/m$^2$, including materials, labor, and all applicable cost elements. This same figure can serve as an upper limit for the projected cost per unit area of the GaAs film and associated materials, including the substrate, before fabrication of the cells and arrays.

The chemical purity of a candidate material will be a very important factor in determining its suitability for use as a substrate for growth of GaAs and GaAℓAs films by the MO-CVD technique. However, it is very difficult to establish a priori a minimum purity level that will be acceptable in this application. In those cases where a given material (and form) is available in several different purities - such as is true for polycrystalline alumina ceramics (see Table 2-1) - the most satisfactory technical choice will be that of highest purity, in nearly all cases. In those areas in which the material is available in only one purity a decision must be made as to the adequacy of that impurity level with respect to the CVD environment, the short-and long-term chemical stability toward GaAs and GaAℓAs and the other materials involved in the cell structures, and the processing to which the composite is subjected in fabricating solar cells and arrays.

Unfortunately, it appears likely that many relatively inexpensive candidate substrate materials that are or have been available commercially have not been manufactured with a consistent and reproducible level of purity. Thus, the probability of non-contamination of the deposited films or non-deterioration of the cell structure and its performance may be quite small. It is the intention in this program initially to use the highest purity materials available in a given class, followed by determination of any adverse effects on film properties or subsequent device properties when substrate materials of reduced purity (and thus lower cost) are used for the same purpose. In general, it is expected that the early experiments with a given material, presumably in its highest purity for the particular form involved, will help to determine the extent to which impurity restrictions can be relaxed without intolerable adverse effects on the resulting films.

The known physical and chemical properties of a given material provide perhaps the most objective measure of its suitability as a possible substrate for the growth of GaAs films for large-area solar cells. Since inexpensive materials are necessarily the ones to be considered, it follows that the candidate materials will almost certainly not be single-crystal materials. Thus, the usual concern (as in epitaxy) over the degree of mismatch of the lattice constants of the substrate material and GaAs (or GaA$\ell$As) disappears, especially where amorphous substrate surfaces are involved. In its place arise two new concerns, related to extremes in the nucleation and growth behavior of GaAs CVD films on substrates that are not single-crystal and thus do not promote large-area epitaxy. The two extremes are (1) a nucleation and growth process that occurs largely spontaneously on a surface, such as the amorphous surface of a glass, that exerts little or no ordering influence on the process but instead provides only a support for random nucleation sites and subsequent extended film growth; and (2) a nucleation and growth process that is influenced strongly and ordered to a high degree in localized regions of the substrate that may have only random crystallographic relationships one to another, yet produce what amounts to good epitaxial growth in confined areas because of good crystal structure in the substrate within those regions.

The concern in the first instance relates to the need for either (1) restricting the incidence (surface density) of nucleation to as few sites as possible, so that the nuclei that do form will have maximum opportunity to grow into large islands or localized single-crystal regions, or (2) modifying the surface in some way to encourage nucleation in a systematic and orderly pattern and to induce a preferred orientation of the controlled nuclei so formed. The concern in the second case is for the need to encourage the area growth of those localized epitaxial regions in the overall polycrystalline deposit that have either identical or twin-related crystallographic orientations, at the expense of the other randomly-oriented regions, and further to encourage the growth of the largest oriented regions at the expense of those that are significantly smaller.

These considerations suggest a substrate surface that is extremely clean, chemically stable, grossly flat, microscopically smooth, and free of defects of all types at one extreme, and at the other a surface that has an orderly array or matrix of nucleation sites or growth regions, such as an array of individual crystallites all oriented crystallographically the same way in a multicrystalline body. There are candidate substrate materials that tend toward these two extremes, but, unfortunately, none that fully meets either specification.

Among the important physical characteristics of a substrate material are its linear thermal expansion coefficient (TEC) and its structural stability over the range of temperatures used prior to, during, and after film growth. The most ideal circumstance would match the TEC of the substrate and the film from growth temperature to room temperature, to minimize stresses in the film. However, such a match is seldom possible, and so a deposited film is often under considerable stress following deposition at elevated temperatures. This can seriously affect both its electrical and its structural properties, depending upon the magnitude of the stress and whether it is tensile or compressive. 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. Unfortunately, the adherence of the film is usually influenced by the type of chemical bonding that is present at the film-substrate interface and this, in turn, probably involves a thin intermediate layer of some material between the substrate and the film with properties that are not readily established or known.

Figure 2-1 shows the linear thermal expansion coefficients of GaAs and several other materials that are often used as substrates for deposited semiconductor films in various applications. It is clear from the figure that none of the materials shown - except for Ge - is a close match for GaAs over the temperature range up to ~700 C, the typical GaAs deposition temperature for the MO-CVD technique. Several materials are close, and there are others (such as tungsten and sapphire) for which the thermal expansion coefficient coincides with that of GaAs at a single temperature. There is also the possibility that other materials to be fabricated specially for use in the program can be tailored in composition so that their coefficients will be reasonably close to that of GaAs. Obviously, there is reason for interest in Ge as a substrate material, but other factors must be considered; these are discussed in more detail in later sections of the report.

The TEC of a glass is affected by changes in viscosity. Fortunately, the TEC's of most glasses are essentially constant and predictable from room temperature up to just below the strain point. Therefore, glasses with strain points near the film growth temperature range may be considered as possible substrate materials in early studies. Additional factors are involved, however, as discussed below.

The physical stability of a substrate and its surface is dependent upon the method used to prepare the material. A dense substrate is expected to provide a more stable surface than a porous substrate that contains pockets of gas that may escape during thermal cycling. The gas may also dislodge particles or grains from the surface, thereby leaving voids and irregular areas for film growth. Based upon observations made in the LCSSAP studies it is recommended that, during the first phase of this program at least, only the most dense, smoothest, and highest purity ( > 99 percent) substrates be considered for film growth experiments.

The stability of the substrate surface in the chemical environment of the deposition process is important to achieving reproducible film nucleation and growth and desirable film properties. For example, if the substrate surface is attacked by $H_2$ prior to film deposition the surface may no longer be smooth and free of defects, the growth atmosphere may be contaminated with undesirable impurities, and the grown film may have incorporated in it material inconsistent with good film properties, both physically and electrically. Since the MO-CVD process used for this program does not necessarily require $H_2$ as the carrier gas, those substrate surfaces adversely affected by $H_2$ can be evaluated in an inert carrier gas, such as He.

In addition, the substrate surface should be chemically stable to the primary reactants used in the growth process. For GaAs formation by the MO-CVD process, non-reactivity with $AsH_3$ or As is probably to be preferred; also, depending on the GaAs growth mechanism involved, nonreactivity with trimethylgallium (TMG) is also probably preferred. On the other hand, it is conceivable that a stable intermediate compound formed at the film-substrate interface due to chemical reactivity with the reactant gases might be useful in influencing enhanced grain growth in the deposited film.

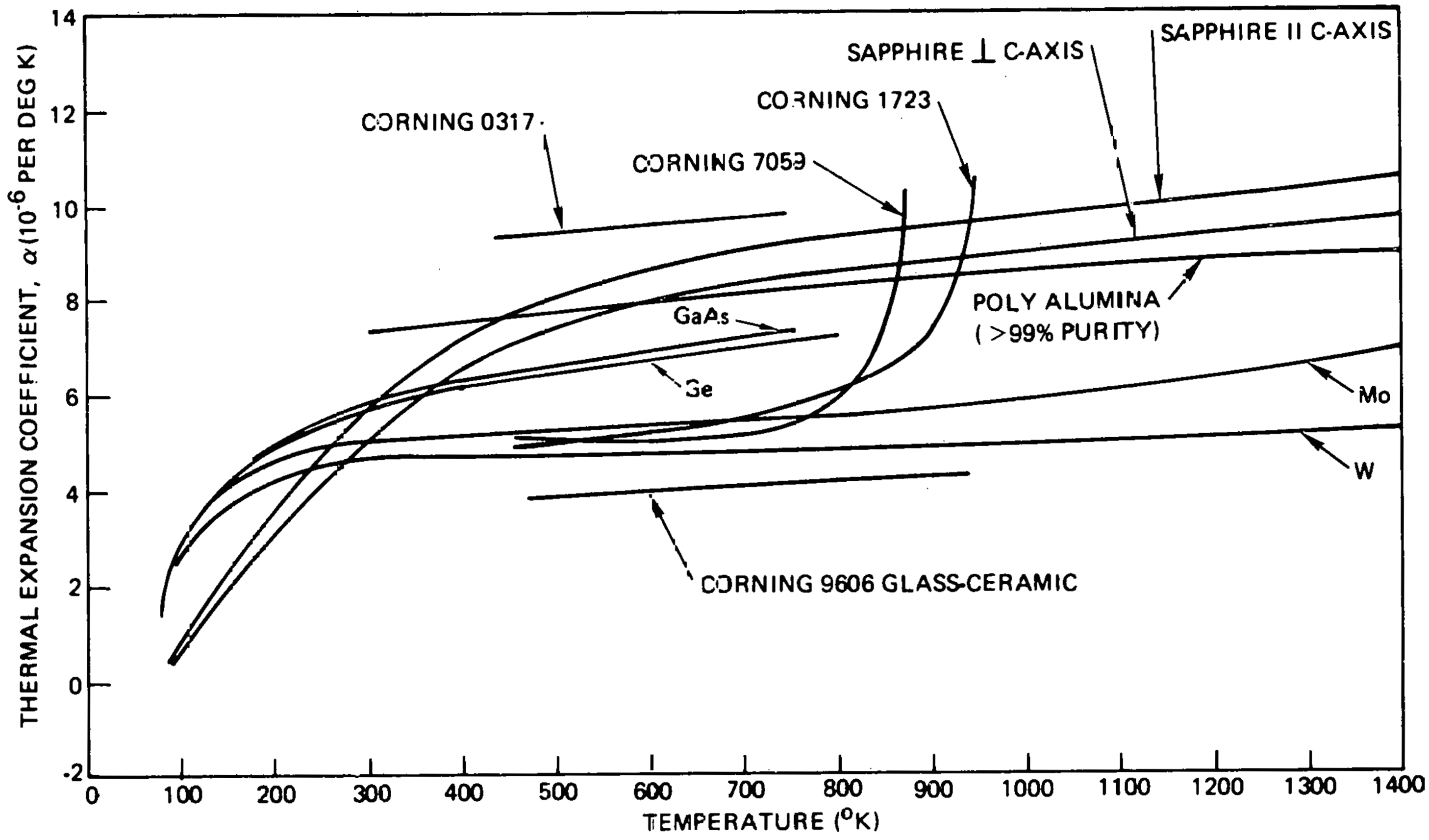

Figure 2-1. Linear Thermal Expansion Coefficients as a Function of Temperature for GaAs and Several Possible Substrate Materials

It is important that any candidate substrate material be at least potentially available in large-area form, to permit large-area growth of GaAs films in order best to meet the cost and production quantity goals established by ERDA. Some materials that are of real interest as possible substrates are already available commercially in large sheet form; these include the metals Mo, W, and some of their alloys. It will be pointed out later that present-day costs indicate these materials to be too expensive for this application if used in available sheet form. Preliminary investigation of these materials will be made with bulk rolled sheet (see Para 2. 2, Task 2), but any consideration of long-term use must be in terms of deposited layers of these metals because of their high cost. It is also necessary to evaluate some materials (especially the polycrystalline ceramics) in both as-manufactured and polished forms to determine if the condition of the surface does, in fact, effect a significant difference in the properties of the film and subsequent devices.

### 2. 1. 2 Candidate Substrate Materials

Consistent with the above criteria, several kinds of low-cost or potentially low-cost substrate materials are being considered for evaluation on this program, including (1) glasses, (2) glass-ceramics, (3) ceramics, and (4) metals and alloys. Representative materials in these four classes are listed in Table 2-1, together with pertinent properties. In addition, thin metallic films and semiconductor films as intermediate layers are also being considered as potential substrate materials.

#### 2. 1. 2. 1 Glasses

Glass is potentially an attractive substrate material for a number of reasons: it is potentially inexpensive, many varieties are available in large-area 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. In combination with the MO-CVD growth process, it is possible to visualize a sheet of glass being rolled to the required thickness in one apparatus and being fed in its as-manufactured state directly into a CVD reactor for GaAs film growth, without contaminating steps intervening. Additional automation of cell formation, fabrication, and testing could then be developed in subsequent process improvements.

In considering the use of an amorphous glass as a substrate, it is necessary to consider the effect of temperature on certain glass properties, notably the TEC and the viscosity. Convention has identified certain viscosity values with some of the physical characteristics recognized as critical in the behavior of glass at elevated temperatures: strain point, $\sim 3 \times 10^{14}$ poises; annealing point, $\sim 10^{13}$ poises; softening point, $\sim 10^{7.6}$ poises; and working point, $\sim 10^{4}$ poises. From room temperature to just below the strain point, which is generally regarded as the upper practical limit for use of an annealed glass, the TEC values for glasses tend to remain nearly constant, increasing only slightly with temperature. However, with further increase in temperature into the annealing range the viscosity decreases and a large and rapid increase in TEC occurs. The reduction in viscosity at temperatures above the annealing point might eliminate a glass from consideration for possible use as a substrate for film growth in that temperature range; however, the problem is much less restrictive for GaAs growth than for Si growth, for example, because the temperature

Table 2-1. Substrate Materials Considered for Use in Program

| SUBSTRATE IDENTIFICATION | MATERIAL/TYPE | AVERAGE THERMAL EXPANSION COEFFICIENT REFERRED TO LENGTH AT 25°C (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 | 5.4(25-670 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 (powder-met.) | 5.0(25-700 C) | – | 99.95 (min) | ~\$0.45/in.$^2$ (0.020" thick) |
| Molybdenum | Mo Sheet (powder-met.) | 6.0(25-700 C) | – | 99.96 (min) | ~\$0.21/in.$^2$ (0.020" thick) |
| Kovar/Rodar | Ni-Co-Fe Alloy Foil or Sheet | 3.1(25-700 C) | – | ~99.5 | \$0.06-0.09/in.$^2$ (\$5.50–\$8/lb) |
| Ge | Single Crystal Slice | 5.6(300-650 C) | Polished one side | Semiconductor grade | \$2.25/in.$^2$ (~3000 in.$^2$) |
| GaAs | Single Crystal Slice | 5.9(24-200 C) | Polished one side | Semiconductor grade | \$5-8/in.$^2$ |
| Sapphire | Single Crystal Ribbon | 3.4(25-800 C) | As produced | – | \$1/in.$^2$ (1/2 in. wide ribbon)<br>\$2.39/in.$^2$ (10,000 in.$^2$ with grains) |

for GaAs growth by the MO-CVD process is much lower than that required for large-grain growth of Si by CVD. Furthermore, very little is known about the effect of glass viscosity on the growth and properties of semiconductors, and it is possible that film growth on a surface having significantly decreased viscosity could produce useful results in the present application.

The principal glasses considered for use as substrates for GaAs film growth are listed in Table 2-2. The glasses listed were selected mainly because their softening points are higher than the temperature necessary for GaAs growth by the MO-CVD process. Although the TEC's listed are in some cases lower than that reported for GaAs (see Figure 2-1), as pointed out above the TEC's change rapidly when the strain point is exceeded. On the basis of the extent of present knowledge it appears that only through trial and error can the usefulness of some of these glasses for GaAs film growth be determined with certainty.

Among the glasses listed in Table 2-2, Codes 0211, 0317, and 7059 are commercially available in plate form; Code 0211 is available in ribbon form, also. Code 1723 (which has properties very similar to Code 1720) was made available in plate form by Corning for the JPL/ERDA LCSSAP Si sheet growth program at Rockwell. Early studies using Code 1723 showed it was not compatible with the Si CVD growth process; thus, samples are immediately available for studies of GaAs growth in this program.

An alternate substrate material for GaAs growth is a glass film produced on a polycrystalline ceramic, i.e., a glazed ceramic. The typical glaze formed on ceramics 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 purity lower than, for example, 99.5 percent alumina ($A\ell_2O_3$). 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 considered for evaluation as substrates for GaAs growth by the MO-CVD process. As a result of a recent trip to present and potential suppliers of substrate materials (August 1976), it is expected that two manufacturers (Chi-Vit Corporation and Ferro Corporation) will submit glazed ceramics for consideration under this program.

### 2.1.2.2 Glass-ceramics

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).

Although no glass-ceramics are now available having TEC's matching that of GaAs exactly, Corning 9606 - with an average TEC of $5.7 \times 10^{-6}$ per deg C in the temperature range 25-300°C (see Table 2-2) - is commercially available and is to be evaluated early in this program (see Para 2.1.3). It is anticipated that other glass-ceramics, with TEC's closer to that of GaAs, will be obtained later in

Table 2-2. Commercial Glasses and Glass-ceramics Considered for GaAs Growth Studies*

| Corning Glass Code | Type of Glass | Forms Usually Available** | Average Thermal Expansion Coefficient (Referred to Length at 25°C) Multiply by $10^{-7}$/°C | Strain Point (°C) | Viscosity Data | | |
|---|---|---|---|---|---|---|---|
| | | | | | Annealing Point (°C) | Softening Point (°C) | Working Point (°C) |
| 0211 | Lime Borosilicate | S (Ribbon) | 74 (0–300°C) | 508 | 550 | 720 | – |
| 0317 | Alumina Soda Lime | S | 87 (0–300° C) | 574 | 622 | 871 | – |
| 1720 | Aluminosilicate | BT | 42 (0–300° C) | 667 | 712 | 915 | 1202 |
| 1723 | Aluminosilicate | BT | 46 (0–300° C) | 665 | 710 | 908 | 1168 |
| 7059† | Barium Alumino-borosilicate | S | 46 (0–300°C) | 587 | 635 | 842 | 1160 |
| 9606 | Magnesium Aluminosilicate | S | 57 (25–300°C) | – | – | – | – |

* From "Properties of Glasses and Glass-Ceramics," Corning Glass Works

** B – Blown ware; S – Plate; T – Tubing and rod

*** Setting point is defined as 5°C above strain point

† From Corning Product Information Sheets or private communication

the program for evaluation in various solar cell configurations. One manufacturer of glass-ceramics (Corning) has indicated to Rockwell that a glass-ceramic with properties compatible with the GaAs MO-CVD process can probably be produced in large-area sheet form with relatively large oriented grains. This prospect is being further pursued.

Many of the polycrystalline ceramic materials now available are produced in areas up to about 300 $cm^2$. 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 large-scale film growth by the MO-CVD process when TEC matching to GaAs has been successfully achieved. The recent visit to substrate suppliers indicated that additional glass-ceramics would also be forthcoming from Schott Optical Glass, Inc., and Owens-Illinois, Inc., in addition to Corning.

### 2.1.2.3 Polycrystalline Ceramics

There are insulating polycrystalline oxide materials which have TEC values matching that of GaAs rather closely, are quite stable at film growth temperatures, are readily available, and are probably chemically compatible with GaAs and the CVD environment. For example, polycrystalline aluminas are available from several manufacturers, in purities from at least 94 percent to 99.9 percent, in dense form. Properties are listed in Table 2-1 for several specific aluminas obtained for the Rockwell contract program on CVD Si sheet for the JPL/ERDA LCSSAP. Several of these materials are being used now in that program to aid in the evaluation of effects of various film growth processes on film properties.

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 must be established in this program if aluminas of lower purity (and therefore, lower cost) are sufficiently stable at GaAs CVD growth temperatures. Other materials, such as steatite (nominally $MgO \cdot SiO_2$), that are considered possible for use in this program because of their TEC values ($7.8 \times 10^{-6}$ per deg C in the range 25 to 700°C for steatite) would also have to be evaluated for their stability in the GaAs CVD growth environment. Those found to react with $H_2$, for example, might still be acceptable as substrates if the MO-CVD process is modified to use He as the carrier gas, a change that has been previously demonstrated as feasible in experiments at Rockwell.

It will be important to determine if the surfaces of the as-produced commercial grades of alumina have properties that are adequate for producing GaAs films with characteristics appropriate for solar cell formation. Commercial aluminas vary considerably in surface roughness due to grain size and method of fabrication. The highest purity materials seem to have the best as-fired surfaces but the smallest grain sizes. Although polishing costs are considered prohibitive in attempting to reach the long-range cost goals of this work, it will be necessary and advantageous during this program to compare the properties of films grown on polished and on as-fired substrates, to assist the study of film growth processes and the evaluation of film properties.

It is intended that some specially-prepared materials (not necessarily low-cost in today's market) be used in such evaluations. These will include polycrystalline alumina materials that have been subjected to special experimental firings beyond those normally used in preparing the materials for the commercial market. Such firings have been undertaken as a means for improving both surface structure and internal grain size.

#### 2.1.2.4 Metals and Metal Films

Certain metals, both in bulk and thin-film form, are also being considered as potential substrates for GaAs growth. Three different materials stand out above others--namely, tungsten (W), molybdenum (Mo), and Kovar (a nickel-cobalt-iron alloy*).

Based on average thermal expansion data (Table 2-1) the preferred substrate order is (1) Kovar, (2) Mo, and (3) W. Ta is another metal with a TEC in the right range, but it is unfortunately reactive with $H_2$ at high temperatures; therefore, its use as a substrate would be considered only if GaAs were to be grown in an inert atmosphere, probably He, by the MO-CVD process. However, the other metals are stable in $H_2$, are readily available in sheet and foil form, and are relatively inexpensive compared with single-crystal substrates of any material. The availability of these metals in foil form makes a continuous (rather than batch) GaAs film growth process on such foils appear quite feasible.

Single-crystal GaAs has been grown on single-crystal W substrates (Refs 10, 11), and polycrystalline GaAs on single-crystal Mo substrates (Ref 11). However, because Kovar is less expensive (~1/5 the cost of polycrystalline Mo and W), it is the first bulk-metal substrate selected for evaluation in this program. Unfortunately, initial investigations have shown that there is a strong reaction between Kovar and $AsH_3$; this is discussed further below and in Para 2.2 and 2.3.

Alternately, the metals of interest can be produced in thin-film form by evaporation, sputtering, or CVD on some other substrate prior to GaAs growth, as a means for (1) better contacting the back of the cell, (2) improving the GaAs nucleating process, (3) sealing and smoothing the substrate surface, (4) acting as a transition bond between the GaAs and a substrate which has a TEC different from that of GaAs, and (5) possibly providing a larger grain structure than is exhibited by the substrate itself.

Both Mo and W thin films have been produced at Rockwell as single-crystal sheets on sapphire substrates by the CVD method (Refs 12, 13). It would be possible to form such films with a nascent surface on another substrate material just prior to GaAs deposition. Experiments of this type may be carried out in this program in an exploratory way, especially if deposition experiments directly on other inexpensive substrates indicate that alternate procedures are necessary. The reactivity that has already been observed between Kovar and $AsH_3$ and/or GaAs indicates that if Kovar is to be used in further film growth studies an intermediate layer will be required to separate the GaAs from the Kovar. Such a layer could be Mo or W, for example, or Ge, as described in the next section.

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

### 2.1.2.5 Ge Films

The data in Figure 2-1 show the similarity in TEC values for GaAs and Ge over a large temperature range. Consideration has often been given to the use of single-crystal Ge as a substrate for GaAs film growth for solar cells, mainly because of the excellent match of the lattice parameters as well as the TEC values in the two cases. The literature has numerous references to composites of these two materials. One special combination of interest is the tandem solar cell, which involves photovoltaic junctions of GaAs and of Ge optically in series, the intention being to make good use of the long-wavelength solar radiation transmitted by the GaAs cell into the Ge cell adjoining it. However, this is not a cell configuration considered for primary attention in this program.

Ge in bulk single-crystal form does not appear to be a likely candidate as a solar cell substrate material, for GaAs growth or other application, for at least two reasons. First, Ge is more brittle than Si. As a result, substrate wafers of Ge would have to be thicker than Si wafers of the same area for equivalent durability in handling during device processing. Si wafers 200 μm thick can be handled readily in large numbers with a high survival rate, and Si wafers (or ribbons) 100 μm thick can survive processing if special handling procedures are used. On the other hand, Ge wafer thicknesses closer to 400 μm are generally recommended for routine device processing.

Second, the available world supply of Ge does not appear adequate to meet the projected future need for the material for solar cells if single-crystal wafers in the thickness range mentioned above were required. Thus, just in terms of the projected annual power-equivalent production that is the goal of the ERDA photovoltaic development program for the year 1985 (i.e., 500 Mw per year), the $5 \times 10^6$ $m^2$ of solar cells required per year would correspond to $6.25 \times 10^6$ Kg of Ge if wafers only 250 μm (10 mils) thick were used, with no allowance being made for material loss in sawing or processing. This figure is approximately 80 times the present world annual production rate of Ge; in fact, it is close to the quantity that has been proposed as the world total recoverable supply between now and the year 2000, and is about one-twelfth of the amount of Ge believed to exist in identified world recoverable zinc resources (Ref 14). In terms of estimated total abundance in the continental crust on the earth (Ref 15) Ge is less than one-tenth as abundant as Ga, for example. Whereas these figures tend to discount the future role of single-crystal Ge wafers in solar cell production, there is interest in the material in thin-film form as an intermediate layer on a low-cost substrate in a GaAs window-type solar cell.

Many of the reasons cited in Para 2.1.2.4 for considering the use of metal films under the GaAs or GaAℓAs active layers apply also to Ge. The additional advantage that Ge so closely matches the TEC and the lattice constant of GaAs might also permit improved GaAs crystal quality within the individual grains of a polycrystalline deposit, depending upon grain size and the effects of the underlayer on which the Ge is deposited. The Ge films would presumably be formed by CVD, by pyrolyzing $GeH_4$ just before the onset of GaAs deposition so that a nascent Ge surface would be provided.

### 2.1.3 Candidate Materials Selected for Detailed Evaluation

Based on the criteria discussed in the foregoing sections, a group of 10 candidate substrate materials has been selected for extensive evaluation in this program. These materials are as follows:

1. Glass: Corning Codes 0317, 7059, 1723, and 0211
2. Glass-ceramic: Corning Code 9606
3. Polycrystalline alumina: ASM805 (3M Co.) and Vistal (Coors)
4. Composite structure: Ge/glass, Ge/Kovar-type alloys, Mo/glass

As additional materials are produced for this program by various manufacturers with properties considered superior to those now available and included in the above group, substitutions may be made. Substitutions may also be made when any of the substrate materials is found to be unsuitable for film growth and/or the properties of the resulting films do not meet the requirements of the program.

### 2.1.4 Procedures Used in Preparing and Evaluating Substrates Experimentally

The procedures used in preparing the substrate materials identified in the preceding section for experimental use in GaAs and/or GaAℓAs deposition studies vary considerably with the material. The condition of the substrate surface when it is placed in the reactor chamber is extremely important to the outcome of the film growth experiment. Experience has shown that the only surface preparation that should be undertaken in early deposition experiments with most substrate materials is that directed at cleaning the substrate, which includes removal of surface oxides if they exist. When film/substrate compatibility is established, then additional and improved surface cleaning procedures can be sought.

For glasses and glass-ceramics, only organic solvents should be used initially; substrates can be cleaned with solvents such as trichloroethane, acetone, isopropyl alcohol, and methyl alcohol. The procedure now being used in preparing glasses for the growth of GaAs includes substrate immersion in warm tricholoroethane followed by immersion in warm acetone, with drying in filtered dry $N_2$. It may be necessary, however, to use Caro's acid* for cleaning if solvent-only cleaning proves to be inadequate.

The cleaning procedure for aluminas has required a more thorough evaluation early in the program, based on recent studies of Si CVD growth on these same materials. Since it is known that the GaAs/sapphire system is compatible and the aluminas to be used early in the program are ~99.5 percent pure $A\ell_2O_3$, it might be assumed that the cleaning procedures acceptable for sapphire could be used for the polycrystalline aluminas. This assumption may be in error, however, so various procedures are being tested and compared with a simple solvent cleaning for each alumina evaluated. Simultaneous growth on substrates cleaned in several different ways helps in the selection of a preferred cleaning procedure. Cleaning steps being evaluated for use on aluminas include the following procedures:

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*Caro's acid consists of 1:1 $H_2O_2$ (30 percent): $H_2SO_4$.

1. Organic solvents only.
2. Organic solvents, HF-$HNO_3$ mixtures, $H_2O$, MeOH.
3. Organic solvents, Caro's acid, $H_2O$, MeOH.
4. Organic solvents, Caro's acid, HF-$HNO_3$ mixtures, $H_2O$, MeOH.

Metals and alloys should initially be used after only a simple solvent cleaning. Fortunately, the metals form oxides that are volatile at relatively low temperatures and/or are reduced by $H_2$. A light oxide acid etch may also be found beneficial in preparing the metal surface for film growth. Solvent- and acid-cleaned substrates should be evaluated early in the program to establish a preferred procedure.

Of the materials identified above as selected for detailed evaluation as possible substrates for use in this program, only the glasses or glass-based materials are considered of questionable stability in the $H_2$ carrier gas normally used in GaAs film growth studies by any CVD method. Some differences in growth habit observed in Si films grown from $SiH_4$ at the same temperature on glass substrates in both $H_2$ and He atmospheres have been arbitrarily attributed to changes in the glass surface caused by the $H_2$. However, Si films are usually grown on glasses at temperatures greater than those needed for GaAs growth, so it is unwise a priori to assert that studies of GaAs growth on glasses will be useless if $H_2$ is used as the carrier gas. However, it will become important to compare films grown in $H_2$ and in an inert atmosphere (probably He) if the properties of films grown in $H_2$ are found to be inadequate.

$H_2$ is considered a satisfactory carrier gas for films to be deposited on the highest purity aluminas and the metals and alloys selected. Comparative studies using He and $H_2$ may become necessary, however, as the purity of the aluminas is reduced to take advantage of the lower costs of such materials.

If the surface of a substrate is found to be attacked chemically by $AsH_3$, or if the As that is formed on pyrolysis alloys into the substrate, then there is probably little chance that the substrate will be useful in this program unless its surface is coated with an intermediate layer that is compatible with $AsH_3$ and/or As. The transparency of the reactor chamber in the MO-CVD process permits observing any major changes in the substrate surface on exposure to $AsH_3$ and before film growth commences. A pre-$AsH_3$ step has been found to be a preferred step in the epitaxial growth of GaAs on single-crystal sapphire; therefore, the high purity aluminas will probably not offer a problem in this respect. It will be determined if any of the other substrates of interest are reactive, particularly the metals and alloys, since As is a product of $AsH_3$ decomposition and alloys of As are known to exist in several metal systems.

The final test of suitability of a candidate substrate material is to use it in one or more GaAs CVD experiments. For the case of most of the materials identified as primary candidates (Para 2.1.3), compatibility of the substrate either with GaAs or with the environment of the MO-CVD process used in its formation has not previously been determined. It is not known if free Ga and As in elemental form reside for a time on the surface following pyrolysis of the source compound, or if the GaAs is formed away from the substrate surface; free Ga could be a good solvent for other metals and is probably very reactive with surface oxides. The presence of excess $AsH_3$, such as is normally provided in the MO-CVD process for GaAs film growth, may help to minimize the reactivity of any liquid Ga on the surface by combining with it to produce GaAs. These and other factors are involved in the details of GaAs film growth on the various substrates of interest, and the results obtained in CVD experiments with these materials will provide the principal measure of their suitability.

Based on the experience gained in the growth of polycrystalline films of GaAs on a number of different substrates--including metals, glasses, and polycrystalline aluminas--a standard MO-CVD evaluation procedure has been established for use in evaluating candidate low-cost substrate materials. This procedure will be a standard MO-CVD run to grow an undoped GaAs film $\sim 5 \mu m$ thick on the substrate material to be evaluated.

The following standard conditions will be employed:

1. $H_2$ atmosphere (carrier gas)
2. $H_2$ flow rate during growth: 3500 sccm
3. Total reactor gas flow rate during growth: 4000 sccm
4. Temperature of substrate for deposition: $725^{\circ}C$
5. Predeposition processing time: 3 min
6. $AsH_3$ flow rate during predeposition process: 75 sccm
7. $AsH_3$ flow rate during growth: 200 sccm
8. TMG carrier gas $H_2$ flow: 20 sccm
9. TMG push $H_2$ flow: 500 sccm
10. TMG source temperature: $0^{\circ}C$
11. 2-in. diameter SiC-coated graphite susceptor.

In general, this test run will include two or more separate portions of the candidate substrate material which have been cleaned by different procedures. A piece of (0001)-oriented single-crystal sapphire ($\alpha$-$A\ell_2O_3$) will also be included as a monitor of the progress of the CVD growth run and the quality of the resulting deposits. The cleaning techniques employed will depend upon the specific candidate material being evaluated, as discussed above.

### 2.1.5 Contacts with Manufacturers and Suppliers

Early in the first quarter of the program a large number of manufacturers and suppliers of possible substrate materials was contacted relative to participation in this phase of the program. Many of these had already been contacted earlier relative to the substrate needs of the ERDA/JPL Si sheet growth program, so it was relatively easy to renew the inquiry in terms of the requirements for GaAs CVD film growth.

In addition to the manufacturers represented by the materials included in Table 2-1--Corning Glass Works, Coors Procelain Co., Materials Research Corp., 3M Company, GTE Sylvania (Precision Metals Group), AMAX Specialty Metals Corp., Wilbur B. Driver Co. (GTE Sylvania), and Carpenter Technology Corp. (Carpenter Steel Division) -- the following companies were contacted during the first month of the program to obtain samples of various ceramics, metals, and glasses: Schott Optical Glass, Inc. (Duryea, PA); American Refractories and Crucible Corporation (North Haven, CO); Star Porcelain Co. (Trenton, NJ); Associated Ceramics and Technology, Inc. (Sarver, PA); Metsch Refractories, Inc. (Chester, WV); Plessey - Ceramics Division (Frenchtown, NJ); General Electric Glass Products and Lamp Division (Cleveland, OH); Ceradyne (Santa Ana, CA); Harbison-Walker Refractories (Pittsburgh, PA); Glass Beads Company (Latrobe, PA); Norton Company (Worcester, MA); and Magneco Electronics (Addison, IL).

Schott Optical Glass showed interest and was sent further information on the program. American Refractories is in the crucible business and has no equipment for processing and/or substrate manufacturing. Star Porcelain indicated it is not ready at this time for this type of development program and has no substrate capability. Associated Ceramics produces $A\ell_2O_3$ and intends to supply some substrates for evaluation. Metsch Refractories will also send samples of materials for evaluation. Plessey presently uses almost exclusively a dry-press process but still has tape-process capability. General Electric is producing Lucalox (large-grained alumina) only for lamp products (and is expanding in that area), and indicated they cannot make a tape product from Lucalox and have no facilities for making flat glass.

Ceradyne was willing to prepare special material for the program, but the cost of the material would have been prohibitive and could not be considered. Harbison-Walker requested further information before determining their position regarding the supply of special materials. Glass Beads Company produces alumina substrates but not high-purity material; future contact might be appropriate when and if the studies indicate low-purity (90-92 percent) alumina should be considered. The Norton Company normally produces only kiln components and prefers not to get involved in substrate manufacture, but considered sending samples of several different materials (carbides and nitrides); a decision was later made not to participate at the present time.

Climax Molybdenum and the AMAX Specialty Metals component of that company indicated a willingness to supply samples of Mo, W, and Mo (70)-W(30) alloy for evaluation. Future participation may involve the preparation of recrystallized alloys for the program. Magneco Electronics submitted some 96 percent alumina substrates for comparative studies with materials of similar purity produced by other vendors.

In the second month of the program the following manufacturers were visited by Rockwell personnel relative to the supplying of substrate materials for the program: (1) Plessey - Ceramics Div.; (2) Schott Optical Glass, Inc.; (3) Corning Glass Works (Corning, NY); (4) Saxonburg Ceramics (Saxonburg, PA); (5) Du-Co Ceramics (Saxonburg, PA); (6) General Electric Co. (Cleveland); (7) Ferro Corporation (Cleveland); (8) AMAX Specialty Metals (Cleveland); (9) Owens-Illinois (Toledo, OH); (10) Chi-Vit Corporation (Cicero, IL); (11) Magneco Electronics; and (12) 3M Co. (St. Paul, MN). With the exception of General Electric (Lamp Division) and Du-Co Ceramics all of the vendors contacted intend to supply some substrates considered potentially useful to this program.

Samples of various substrate materials obtained during this series of visits include the following: (1) "Ceramislik" alumina (Plessey Ceramics); (2) glass-ceramic (Schott Optical Glass); (3) glass-ceramics and $SnO_2$-coated glass (Corning); (4) quartz ribbon (General Electric); (5) dense cordierite (Ferro); (6) W, Mo, and Mo alloy (AMAX); and (7) several aluminas (Magneco). Materials anticipated for receipt in the near future include (1) glazed ceramics (Ferro and Chi-Vit/Magneco); (2) glass-ceramics (Schott, Corning, and Owens-Illionis); and (3) various ceramics, such as steatite, mullite, alumina, and possibly spinel (several vendors).

In the third month another ceramics supplier provided substrate samples for evaluation in this program. Comco, Inc. (Sun Valley, CA), submitted several substrates of 96 percent alumina and 99.5 percent alumina for evaluation and comparison with similar materials produced by other companies. The substrates include material from Tong-Hsing, an associated company located in Taiwan.

### 2.1.6 Substrate Processing at Rockwell

Early in the quarter, several ceramic and metal substrate materials were polished by chemical-mechanical methods developed at Rockwell, to produce an optically smooth surface. This was in anticipation of their use in GaAs and/or GaAℓAs CVD experiments for comparison with unpolished substrates of the same materials, to determine the advantages, if any, that accrue from the additional preparation. The materials polished were ASM805, ASM838, ADS995, ADS96F, and Vistal (all alumina ceramics), and Mo, Kovar, and Rodar* metals.

Several of these polished substrates were examined in the scanning electron microscope (SEM) to evaluate the resulting surfaces. Such analyses revealed some voids in the surfaces of the alumina substrates, either inherently present or caused by the removal of small grains during the lapping and polishing procedure. The number of voids (porosity) seemed to be related to the purity of the substrate, the highest purity aluminas having fewer voids. The variations in shape and reflectivity of the grains in ADS96F alumina (Coors) prompted a preliminary analysis by EDAX** of areas that had dissimilar appearance in the SEM. The regions between grains with well defined shapes were found to be high in Si (probably as $SiO_2$); the grains themselves were high in Aℓ and low in Si. The composite, therefore, appears to consist of alumina grains embedded in a sea of glass rather than a chemically homogeneous material.. Standard cleaning procedures for sapphire ($\alpha$-$A\ell_2O_3$), which use HF mixtures, are thus probably not acceptable for these substrate materials.

Other characterization of the primary substrate materials listed in Para 2.1.3 is in progress and will be described in subsequent reports.

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*Rodar is an alloy of Fe, Ni, and Co similar in composition to Kovar.

**Energy-dispersive analysis by x-ray emission, done in the scanning electron microscope.

## 2.2 TASK 2. CVD EXPERIMENTS AND PARAMETER STUDIES

The summary of the proposed work of this task, as given in the original program proposal, is as follows:

> The MO-CVD process will be used to grow films of GaAs, GaAℓAs, and possibly AℓAs (and/or AℓAsP) on the polycrystalline and amorphous substrates identified in Task 1. The effects of deposition conditions on the properties of candidate substrate materials and of the resulting films will be determined. Experiments to establish the effects of growth conditions on film grain size will be carried out, and optimum film doping methods and conditions will be established for specific desired film properties and photovoltaic device configurations. Special processing methods--such as in situ gas-phase etching and/or annealing and the growth of intermediate nucleating layers--will be investigated, to improve film properties. Early in the program a second CVD reactor system will be assembled to supplement the one initially used for this task.

The experimental investigation of the MO-CVD process for this program began early in the first month of the contract, and employed an existing CVD reactor system that had been used for company-sponsored investigations in the GaAs-GaAℓAs system.

During the first quarter of the contract, 101 MO-CVD experiments were performed. The majority of these can be classifed into two groups: (1) those designed to give data on the doping of GaAs and $Ga_{(1-x)}A\ell_xAs$ (x = 0.9) single-crystal films grown on single-crystal GaAs substrates, and (2) those designed to give information on the growth of polycrystalline GaAs films on a variety of potentially low-cost substrates.

In addition to these CVD experiments the other major task pursued in the first quarter was to design and fabricate a second MO-CVD reactor system which is to become the dedicated reactor for the performance of this contract. Due to delays in the scheduled delivery of some reactor components by suppliers, the completion of the new reactor system has been extended to the end of the fourth contract month.

The reactor system used for the CVD experiments to date is shown schematically in the diagram of Figure 2-2. The diagram is simplified, showing only the main gas lines and the air-operated bellows-sealed valves. The liquid source materials are held in stainless-steel cylinders with dip tubes. The metalorganic source material is carried to the reaction zone by $H_2$ gas which is bubbled through the corresponding liquid source. The gaseous sources are stored in high-pressure cylinders equipped with stainless-steel two-stage pressure regulators. Flow control is provided by flowmeters (Brooks Rotameter type), which will soon be replaced by mass flow controllers.

The reactor chamber is made of quartz, and the SiC-coated graphite susceptor is supported in the rf field by a quartz rod that is rotated during a deposition experiment. The susceptor temperature is monitored by an infrared thermometer. The deposition sequence is controlled by a card-programmable electronic sequencing timer, which controls the air-operated valves and thus the reactant gas flow paths.

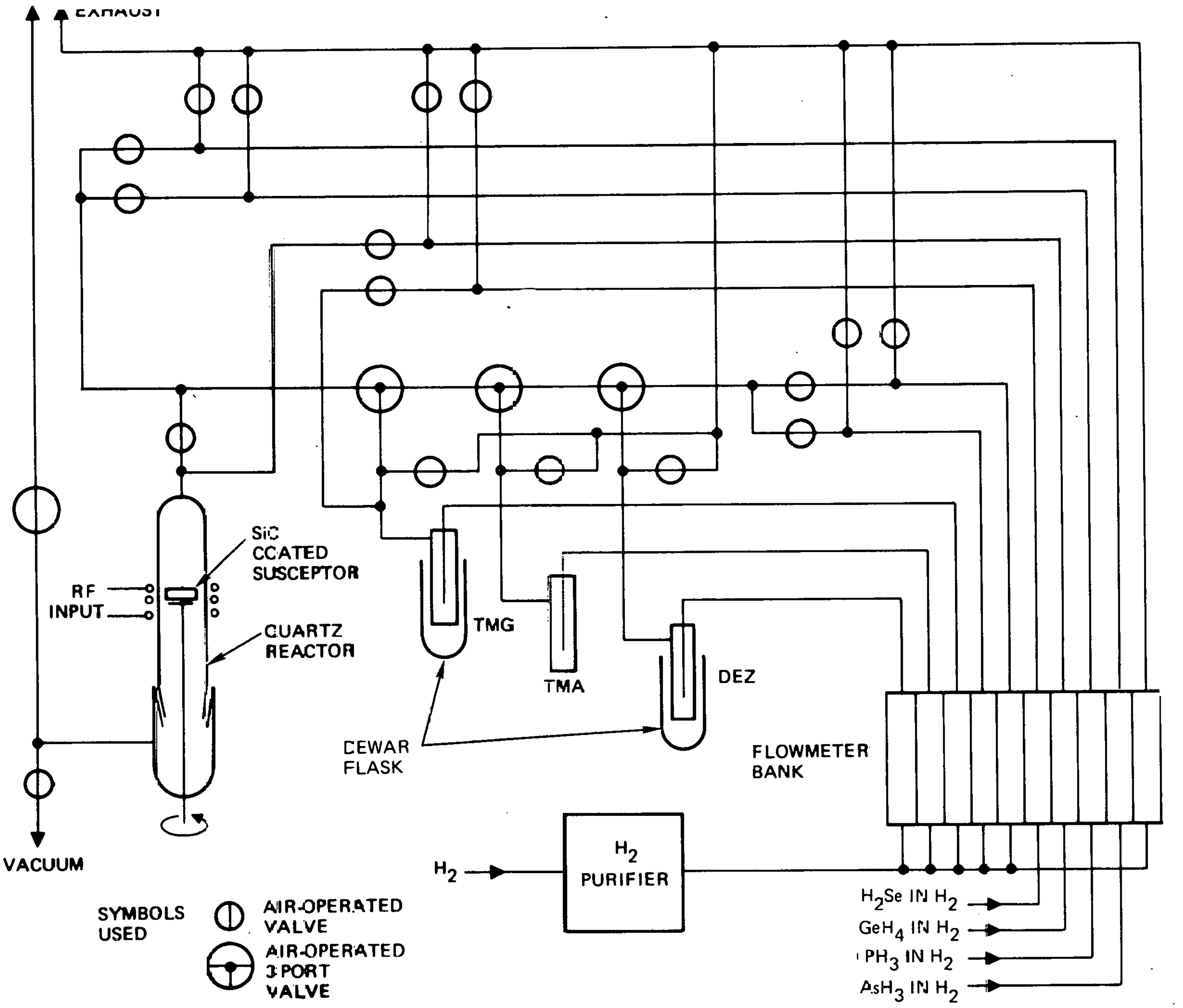


Figure 2-2. Schematic Diagram of MO-CVD Reactor System for Deposition of GaAs and GaAℓAs Films

### 2.2.1 Design and Fabrication of New Reactor System

The design for the new MO-CVD reactor has been completed and a complete scale drawing of its component gas lines has been made. This drawing will aid in the rapid and orderly fabrication of this multicomponent, versatile MO-CVD system. All component parts have been ordered and construction of the reactor and its electronic control system has been started.

The flow rates of the main gas constituents in this MO-CVD reactor are to be controlled by electronic mass-flow controllers (Tylan Corp) having a ±1 percent accuracy and ±0.02 percent full-scale repeatability. The readout unit for these controllers has a 3-1/2 digit display reading directly in standard cc per min (sccm) or standard liters per min (slm) of the corresponding gas. During a growth run the reactant gas flow paths are to be controlled by air-operated bellows-sealed valves which are in turn to be controlled by a card-programmable electronic sequencer. The metalorganic constituents are to be injected into the main reactor manifold by special three-port, low-dead-volume bellows-sealed valves. This will allow abrupt changes in doping and film composition to be made.

The temperature of the SiC-coated graphite susceptor (similar to the arrangement shown in Figure 2-2) will be measured by a thermocouple inserted in the center of the susceptor; the signal will be transmitted to a digital thermometer readout having 0.1$^{o}$C resolution.

The reactor also has a vacuum system using a direct-drive chemical-resistant vacuum pump. This vacuum capability is used to evacuate the quartz reactor chamber prior to each growth run and to aid in leak-checking the reactor gas lines.

The quartz reactor chamber is designed with a quartz baffle which aids in the production of a homogeneous gas mixture and improves the thickness uniformity of the film grown on the substrate, which rests on the susceptor (cf Figure 2-2).

### 2.2.2 Growth of Doped Single-crystal Films

Single-crystal films of GaAs and GaAℓAs have been grown with both Se doping and Zn doping on single-crystal GaAs substrates. $H_2Se$ gas (265 ppm in $H_2$) and diethylzinc (DEZ) are used as sources. These experiments were performed to determine the doping ranges over which these sources would be useful and the dependence of doping levels on source flow rates. This information can then be used in the doping of polycrystalline GaAs and GaAℓAs films. In addition, these data are required for the growth of single-crystal GaAℓAs/GaAs heterostructure solar cells, a stated objective of the planned program, to establish the performance capabilities of cells grown by the MO-CVD process.

#### 2.2.2.1 Zn Doping of GaAs

Doping experiments were begun with the Zn doping of GaAs from a diethylzinc (DEZ) source, which was held at a constant temperature by a low-temperature insulated bath. The partial pressure of DEZ in the reactor was then varied by varying the flow rate of $H_2$ over the DEZ source.

It was determined that with the initial reactor design and with the DEZ source at $0^{o}$C the minimum carrier concentration achieved at a growth temperature of $725^{o}$C and a growth rate of ~0.35 μm/min was $p = 4 \times 10^{18}$ $cm^{-3}$. This value correponds to the lowest flow rate of $H_2$ gas over the DEZ source that could be reproducibly controlled.

The doping of GaAs with lower DEZ source temperatures of -12, -16, -25, -30, -40, and -$48^{o}$C was also studied. Since the melting point of DEZ is -$28^{o}$C, for some of these temperatures the DEZ source was a solid. For a source temperature of -$48^{o}$C, the lowest doping level achieved was $p = 5 \times 10^{16}$ $cm^{-3}$. From detailed studies of the doping behavior with DEZ source temperatures of -28 and -$45^{o}$C it was determined that the doping is not reproducibly controllable with these low DEZ source temperatures.

Modifications were then made to the reactor to allow the use of the DEZ source at $0^{o}$C. These modifications incorporated a gas proportioning system in the DEZ flow control section of the reactor, allowing dilution of the DEZ source $H_2$ flow by up to three orders of magnitude. A portion of this diluted DEZ $H_2$ carrier gas was then injected into the reactor during film growth, resulting in achievement of minimum doping levels of $p \approx 10^{16}$ $cm^{-3}$. The observed dependence of carrier concentration vs the flow rate of $H_2$ gas into the DEZ source cylinder is shown in Figure 2-3. The values of $N_A$-$N_D$ were determined by making van der Pauw measurements at $300^{o}$K on 6-10μm-thick GaAs:Zn films grown on GaAs:Cr substrates oriented in the (100) plane. The observed variation of net carrier concentration with carrier gas flow rate through the DEZ source is approximately a 1.5-power dependence.

### 2.2.2.2 Se Doping of GaAs

Se-doped GaAs films ~6 μm thick were grown on GaAs:Cr (100)-oriented substrates using $H_2Se$ (265 ppm in $H_2$) as a dopant source. The electrical properties of these films were measured at $300^{o}$K by the van der Pauw method.

With the current reactor design, the minimum doping level observed was ~$4 \times 10^{17}$ $cm^{-3}$. The dependence of $N_D$-$N_A$ on the flow rate of the $H_2Se$ gas mixture is shown in Figure 2-4. Approximately 1.3-power dependence of measured net carrier concentration upon the source gas flow rate is found. The corresponding measured electron mobilities ranged from 2744 $cm^2V^{-1}$ $sec^{-1}$ for the lowest-doped film to 1449 $cm^2V^{-1}$ $sec^{-1}$ for the highest-doped film.

Although relatively few Se-doped GaAs films were prepared and evaluated, no additional samples of this type are expected to be prepared in the present reactor system. The data given in Figure 2-4 are adequate to provide the information required for growing composite single-crystal cell structures by the CVD process in the present reactor, as is planned for early in the coming quarter.

### 2.2.2.3 Se Doping of GaAℓAs

All doping experiments of $Ga_{(1-x)}A\ell_xAs$ were performed with $x \approx 0.9$. A gas mixture of 265 ppm $H_2Se$ in $H_2$ was again used as a doping source. GaAℓAs films ~6 μm thick were grown on GaAs:Cr (100)-oriented single-crystal substrates. The measured values of $N_D$-$N_A$ as a function of the flow rate of the doping gas mixture are shown in Figure 2-5. GaAℓAs:Se films with $10^{15} \leq n \leq 10^{18} cm^{-3}$ have been grown. The observed superlinear dependence of n upon the doping gas flow rate is not understood at this time.

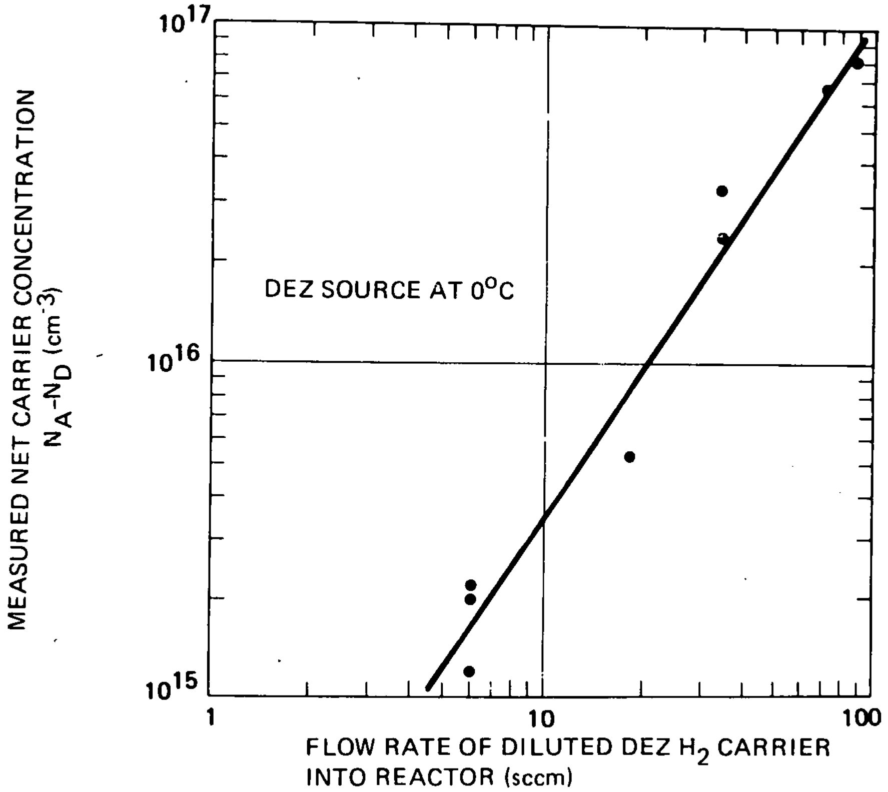


Figure 2-3. Measured Carrier Concentration (van der Pauw method) in Zn-doped Single-crystal GaAs Films on Single-crystal GaAs:Cr Substrates as Function of $H_2$ Flow Rate into DEZ Source Cylinder (at 0°C).

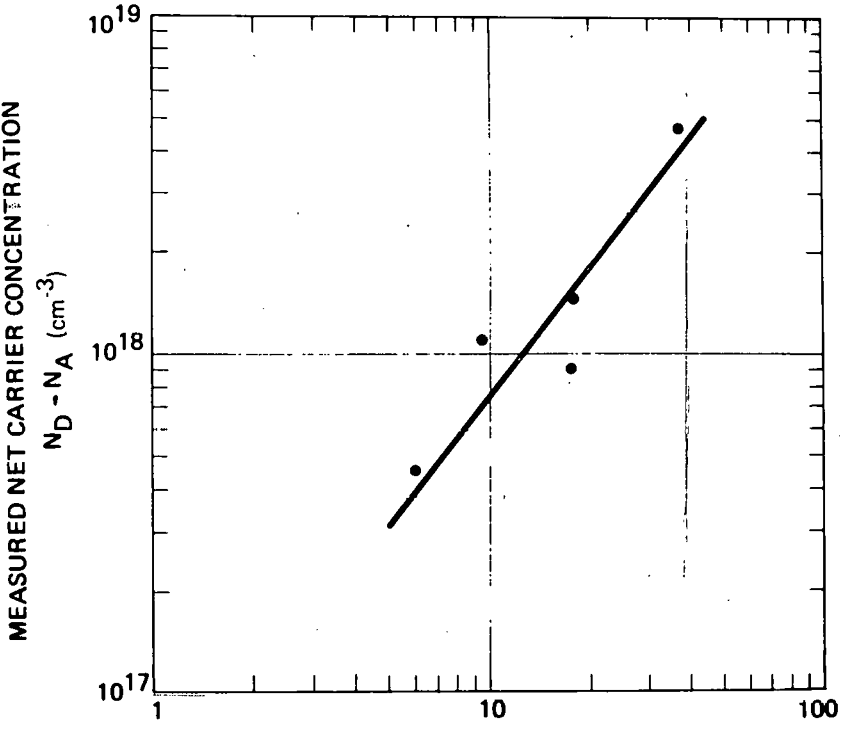


Figure 2-4. Measured Carrier Concentration (van der Pauw method) in Se-doped Single-crystal GaAs Films on Single-crystal GaAs:Cr Substrates as Function of Flow Rate of $H_2$Se Gas Mixture (265 ppm in $H_2$).

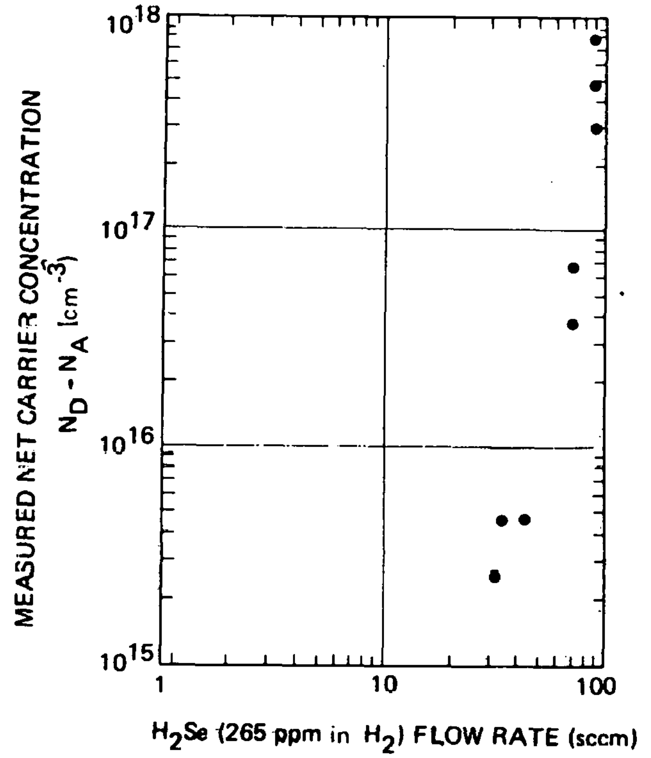


Figure 2-5. Measured Carrier Concentration (van der Pauw method) in Se-doped Single-crystal $Ga_{0.1}A\ell_{0.9}As$ Films on Single-crystal GaAs:Cr Substrates as Function of Flow Rate of $H_2Se$ Gas Mixture (265 ppm in $H_2$)

Some difficulty in making ohmic contacts to $Ga_{(1-x)}A\ell_xAs$ ($x \approx 0.9$) with In has been encountered. In most cases, this problem was most pronounced for the most lightly doped films ($n \leq 4 \times 10^{16}$ cm$^{-3}$). For these films, an extended (~50 min. at 450°C) alloying period was required to produce ohmic contact.

Early in the study of Se-doped GaAℓAs films, difficulty in contacting films was frequently encountered and was observed to be unpredictable, and seemed to occur without any correlation to the doping level of the film. During this early set of doping experiments, it was observed that after a few deposition runs the SiC-coated susceptor exhibited pinholes in the coating and would have to be discarded. It was subsequently determined that the last few lots of SiC-coated susceptors received from the supplier had only one layer of SiC instead of the normal two. This left pinholes in the SiC coating, which then outgassed during the deposition sequence. This affected the film growth, and apparently caused the GaAℓAs layers to become contaminated and thus especially difficult to contact. Any susceptor that showed signs of pinholes was replaced with a new, unused one, but since this occurred frequently, it is difficult to say if any GaAℓAs films grown during these early runs were free of interference from the outgassing of the susceptor in use at the time. Attempts are being made to resolve this difficulty with suppliers of the coated susceptors so that future work can be reasonably free of this obviously serious problem.

### 2.2.2.4 Zn Doping of GaAℓAs

Studies of the Zn doping of $Ga_{1-x}A\ _xAs$ ($x \approx 0.9$) were begun late in the quarter. However, only a few CVD runs were made and no Zn doping data is yet available. Results of these investigations will be described in later reports.

### 2.2.3 Growth of GaAs on Polycrystalline and Non-crystalline Substrates

GaAs films have been grown on a number of polycrystalline and non-crystalline materials during the first quarter by the MO-CVD method. The materials used were considered to be possible candidates for low-cost substrates for thin-film GaAs solar cells. Included in this group of materials were three metals, two polycrystalline alumina ceramics, and two glasses.

#### 2.2.3.1 Polycrystalline GaAs Films on Metals

Three metals — Kovar, Rodar, and Mo — were used as substrates for the MO-CVD growth of thin (~6 μm) GaAs films. The substrates were cleaned in various ways prior to deposition to determine what effect, if any, the cleaning procedure would have on the deposited film. Also, different deposition temperatures were employed to establish the dependence of film properties on the growth temperature.

It was discovered that at high temperatures (i.e., at GaAs deposition temperatures for the MO-CVD process) $AsH_3$ gas attacks the Kovar and Rodar substrates. A run was made in which the $AsH_3$ was injected into the reactor at the same time as the TMG, a departure from the usual deposition procedure. This minimized the attack but did not eliminate it. No $AsH_3$ attack of the Mo substrates was observed. One run was made on a polished Mo substrate; the GaAs film was doped with Se in this case, and the properties of the film did not appear to be influenced by the surface preparation.

Detailed discussion of the results of these experiments is given in Para 2.3.2.1 and 2.3.2.2.

#### 2.2.3.2 Polycrystalline GaAs Films on Polycrystalline Aluminas

Two polycrystalline alumina ceramics manufactured by the 3M Company were also used as substrates in GaAs MO-CVD experiments during the first quarter. These materials — ASM805 and ASM838 — were used with both as-received and polished surfaces (see Para 2.1.6). In one run, the growth rate was increased to ~0.5 μm/min (~0.33 μm/min is normally used) to determine if the nominal size of the surface features observed on the film was dependent upon growth rate. No major differences were observed, however. Different cleaning procedures were then employed to determine if this played any role in the film growth. The usual cleaning procedure for these aluminas includes etching in hot Caro's acid; the etching time was varied in two runs — one set of substrates was etched for 2 min and the other set for 30 min. No prominent differences were observed in the surface structure or preferred orientation of the films grown in these runs.

In one run, a Se-doped GaAs layer was grown simultaneously on polished ASM805 and ASM838 substrates. The films were fully adherent on both substrate materials, and appeared to have a small-grain polycrystalline structure. Detailed evaluations are in progress and will be described in subsequent reports.

#### 2.2.3.3 Polycrystalline GaAs Films on Glasses

GaAs films were also grown on two Corning glasses, viz., Code 1723 and Code 0317 (see Table 2-2). It was determined that these glasses are stable in $H_2$ at the growth temperatures employed. Three runs were made with Code 1723 substrates at three different temperatures up to 750°C, and a GaAs film was grown on Code 0317 glass at 730°C. The polycrystalline films grown on these substrates were adherent, and no bowing of the film-substrate composite was observed. GaAs:Se films were grown on Code 1723 glass, and the resulting polycrystalline GaAs layers exhibited slight conductivity. The properties of these films are discussed further in Para 2.3.2.4.

### 2.2.4 Growth of Materials for Intermediate or Nucleating Layers

It has been suggested that a thin layer of some material deposited on the surface of a substrate might improve the properties or nucleation of GaAs films. As discussed in Para 2.1.2.5 such an intermediate layer might be a thin film of Ge.

To determine if Ge could be grown on Kovar/Rodar, a deposition run was made employing a 5 percent $GeH_4$ source in $H_2$. A control wafer of $(01\bar{1}2)$-oriented sapphire was included in the run. Ge was deposited on both substrates, and no attack of the polished Rodar substrate was observed. Further, SEM studies showed surface features on the film on Rodar that appeared to be individual grains ~20 $\mu$m across. (See Para 2.3.2.5.) The Ge film on the sapphire substrate was measured to be ~4 $\mu$m thick and was n type, with $n \approx 10^{17}$ $cm^{-3}$. This doping could be due to the residual background As in the reactor system. X-ray analysis showed the film to be highly twinned.

A thin film of Ge on Rodar probably would eliminate the opportunity for the $AsH_3$ attack previously observed on this alloy, and might provide a large-grained surface for the growth of GaAs films. This possibility will be explored in additional detail in the coming quarter.

## 2.3 TASK 3. EVALUATION OF FILM PROPERTIES

This task was summarized in the program proposal as follows:

> A variety of materials characterization methods will be used to evaluate the films grown on various substrates in Task 2. Early in the program, emphasis will be placed on determination of film-substrate interactions, preferred orientation tendencies in the films, grain size, and film surface topography. Surface profilometry, x-ray diffraction analyses, scanning electron microscope 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, 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.

The first-quarter activity of this task has been dominated by two main areas of investigation. The first is the electrical characterization of single-crystal GaAs and GaAℓAs films. The other is the electrical and structural evaluation of polycrystalline GaAs grown on a variety of dissimilar substrates. In addition, CVD films of Ge on Kovar have been evaluated, and some characterization technique development has begun.

### 2.3.1 Electrical Characterization of Single-crystal Films of GaAs and GaAℓAs

The electrical properties of the CVD films grown to establish the doping curves shown in Para 2.2.2 were determined using the van der Pauw method (Ref 16). This technique has been found to be reliable for measuring the parameters of interest in single-crystal films, i. e., free carrier concentration, resistivity, and mobility. Furthermore, sample preparation for the use of this technique is less time-consuming than Hall bridge preparation, and since the sample remains intact it can be used for other measurements subsequent to the electrical characterization. For these reasons the technique has been used exclusively in this program up to now. When, later in the program, doped films of polycrystalline material become available, the van der Pauw and Hall bridge techniques will be compared with each other in terms of reproducibility as well as apparent accuracy. C-V analysis of Schottky barriers, four-point probe measurements, and possibly spreading resistance measurements will also be analyzed for their applicability to these polycrystalline materials.

The usual sample preparation for van der Pauw measurements is to apply indium (In) dot contacts to four corners of the as-grown sample. In some cases it has been necessary to etch or abrade the edges of the sample to ensure that any overgrowth on the edges of the sample does not interfere with the accuracy of the measurement. The In contacts are normally alloyed into the sample at 400 - 450$^{o}$C in a reducing atmosphere to achieve ohmic contact. The sample is then mounted in an appropriate holder by soldering contact wires to the In dots.

The use of In as the ohmic contact and the alloying procedure described above has been universally successful for evaluating GaAs over the entire doping range that has been explored in the program to date. GaAℓAs has proven to be more difficult to contact, however, particularly in the Aℓ concentration range of interest for window solar cells ($x \approx 0.9$). For material of this composition it has sometimes been necessary to alloy the In for as long as 60 min to obtain ohmic contact, regardless of the doping level. For n-type doping concentrations below $10^{16}$ cm$^{-3}$ it has not been possible to obtain ohmic contacts on GaAℓAs using In, so the possibility of using In-Te or In-Sn as an ohmic contact material for evaluation purposes is now being explored.

The variability observed in the alloying times necessary to produce ohmic contacts is being ascribed to native oxides on the surfaces of the material. The native oxide on GaAℓAs is known to be difficult to handle adequately, and it is possible that by adding a small amount of Aℓ to the In dopant mixture the oxide will be "dissolved". More reproducible alloying times could then be achieved.

The polycrystalline material which has been evaluated to date has been highly resistive; no measurable Hall effect has been observed. Thus, only the resistivity of the material has been measured. In all cases for polycrystalline material grown on insulating substrates, the resistivity of undoped films has been greater than $10^5$ ohm cm. In one case, for a doped film on glass, the resistivity was the order of $10^3$ ohm-cm.

Three polycrystalline films of GaAs grown on Mo sheet substrates were investigated using the capacitance-voltage characteristics of Aℓ Schottky barriers. Two undoped films were found to have carrier concentrations of $4 \times 10^{16}$cm$^{-3}$, which compares favorably with the background impurity doping level in the system. A Se-doped polycrystalline GaAs/Mo sample showed a carrier concentration of $4 \times 10^{18}$cm$^{-3}$, while a GaAs/sapphire sample grown simultaneously showed a doping level of $\sim 10^{18}$cm$^{-3}$. At the present time, it is not known if this observed difference is significant.

As mentioned above, a thorough comparison of several electrical characterization techniques will be made to determine the correlation, if any, that exists between them for polycrystalline materials. One problem which has been observed for the polycrystalline samples measured to date by C-V analysis is the low breakdown voltage of the Schottky barriers. Even for the undoped samples, breakdown voltages $V_B$ of less than 2V were observed. These low $V_B$ values are most likely occurring because of microplasmas or other leakage mechanisms at the grain boundaries.

### 2.3.2 Evaluation of Polycrystalline Samples

Several materials which are potentially low in cost have been evaluated in a preliminary way as possible substrates for growth of GaAs. These include (1) Kovar and Rodar, (2) Mo, (3) ASM805 alumina, (4) ASM838 alumina, (5) Corning Code 0317 glass, and (6) Corning Code 1723 glass. In addition, preliminary experiments with Ge growth on Rodar were carried out to determine if any interaction occurs between Ge and Rodar in the MO-CVD environment.

#### 2.3.2.1 GaAs Films on Kovar/Rodar

Kovar and Rodar are trade names for an Fe-Ni-Co alloy whose composition is approximately 29 percent Ni and 17 percent Co. As pointed out in the Task 1 discussion, this material has the advantage of being a relatively low-cost metal with average thermal expansion properties to those of GaAs. It thus holds the potential of serving as a conductive substrate for solar cell devices. It has the disadvantage that it is composed entirely of transition elements, which are known to be deep-level impurities in GaAs. As will be discussed, it also has chemical reaction characteristics which make it unsuitable for growth of GaAs unless special additional protective measures are taken.

Most of the analyses of GaAs films grown on Kovar/Rodar were done in the scanning electron microscope (SEM). The SEM used for this work is equipped with an energy-dispersive x-ray analysis system so that qualitative determination of materials compositions can be made.

Initial depositions of GaAs on Rodar were done at 735°C. The surface structure of the films which resulted at this temperature is illustrated in Figure 2-6. Note in Figure 2-6a that the film has crystalline surface features 5-10 $\mu$m in size. X-ray diffractometer studies of these films show them to have strong (111) preferred orientation. However, interspersed on the film surface are "veils" of a second phase of material. Note also that the film has cracks in its surface, visible on the left side of Figure 2-6a. In Figure 2-6b the surface can be seen to be rather smooth, with the surface features apparently 1-2 $\mu$m high.

The composition of the veils of second-phase material was analyzed using the provision for energy-dispersive analysis by x-ray (EDAX) that is an accessory to the SEM. Figure 2-7 shows a magnified region of a GaAs/Rodar sample imaged by two different emission modes. The secondary electron image is shown in (a), while (b) shows an image of the x-ray emission due to the Ni K$\alpha$ line at the same photographic magnification. Note that the veils are very Ni-rich. This is further illustrated by the x-ray spectrum shown in Figure 2-8. The vertical bar display illustrates the spectrum obtained from the prominent crystalline regions while the dotted envelope is from the veil regions. Both are normalized to the Ga K$\alpha$ x-ray line intensity. Note again the large excess of Ni in the veil region. Attempts to remove this veil material from the film with a room-temperature HCℓ etch were not successful.

It was observed that the surface of Rodar underwent a change in the reactor when $AsH_3$ was introduced at high temperatures. Figure 2-9 shows the nature of this change; Figure 2-9a shows a Rodar sample after a standard HCℓ cleaning, while Figure 2-9b shows a film after being exposed to $AsH_3$ at 730°C for 3 min. Note the change in the surface structure and the presence of surface cracking in the latter case. Additionally, As was detected in the surface film by x-ray analysis. The compound formed here is most likely that responsible for the cracking of the GaAs films deposited on these metal surfaces.

Cross-sections of GaAs/Rodar films were prepared by metallographic polishing techniques. A photograph made in the SEM of one of these is shown in Figure 2-10. This figure clearly shows the intermediate compound layer. In addition, voids are present at the interface and sometimes appear to be the cause of film cracks. Note that the veils do not appear to penetrate the film but are only present on the surface.

Attempts were made to grow films at lower temperatures to avoid the $AsH_3$-Rodar reaction, but to no avail, as can be seen in Figure 2-11. At 610°C the veils and cracking of the film are still evident, while at 536°C a filamentary growth has resulted.

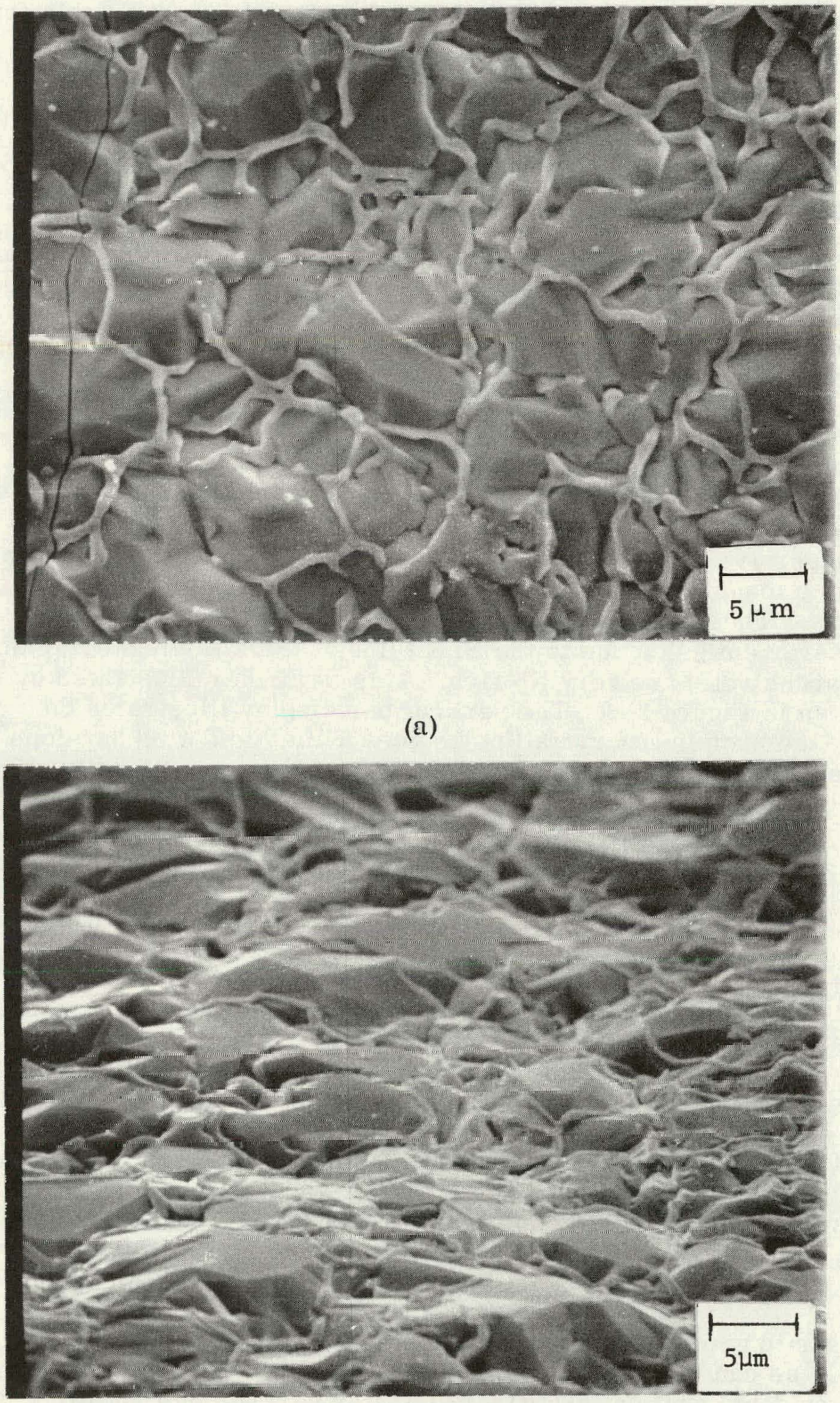
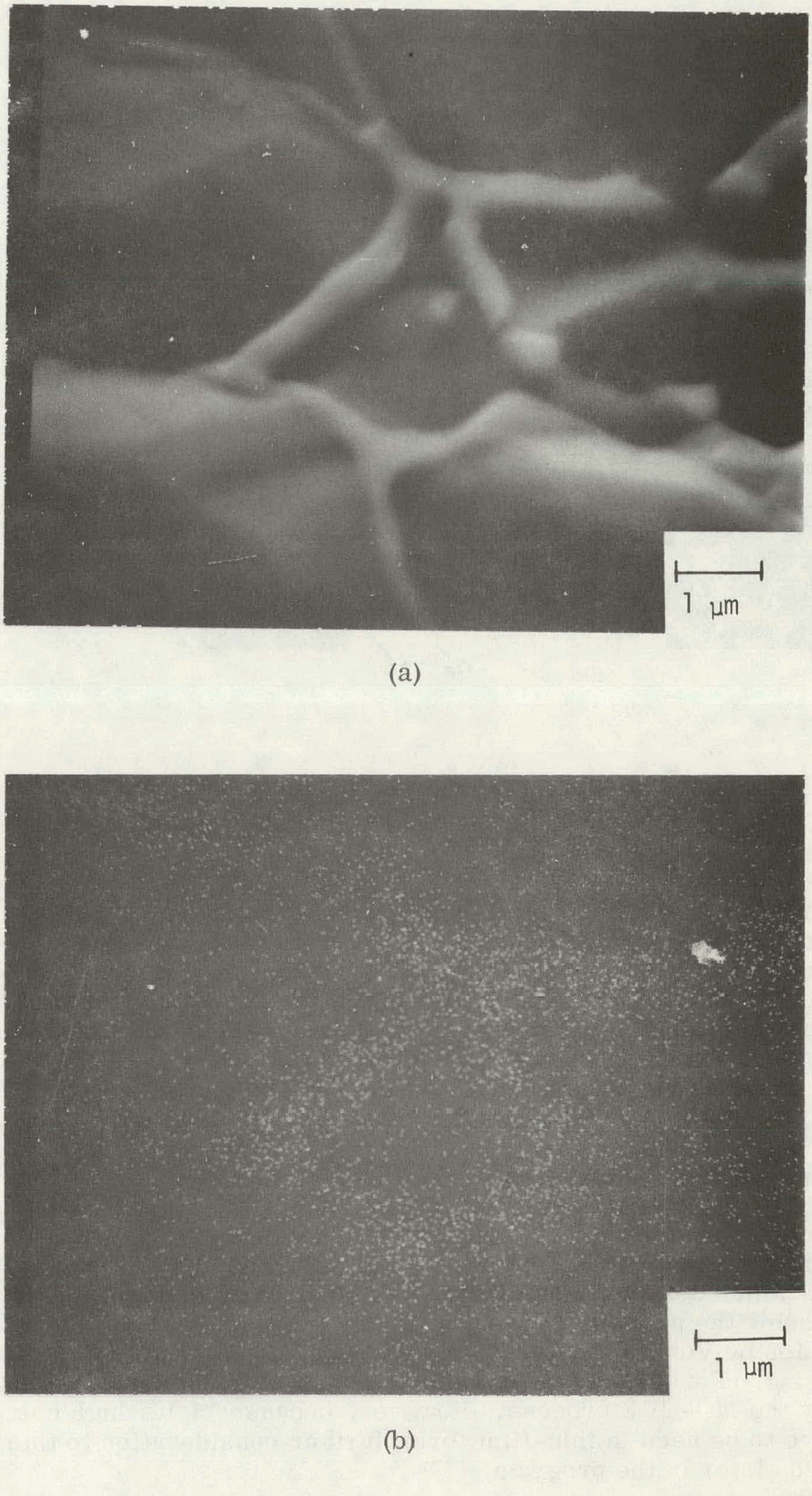


Figure 2-6. SEM Photographs of GaAs Film Grown on Rodar at 725°C. (a) Perpendicular View; (b) View at 30 Deg Angle with Surface.



(a)

(b)

Figure 2-7. SEM Images Obtained from Surface of GaAs Film on Rodar. (a) Secondary Electron Image; (b) Image Formed by Ni K$\alpha$ X-ray Line. (Note amorphous veils are Ni-rich.)

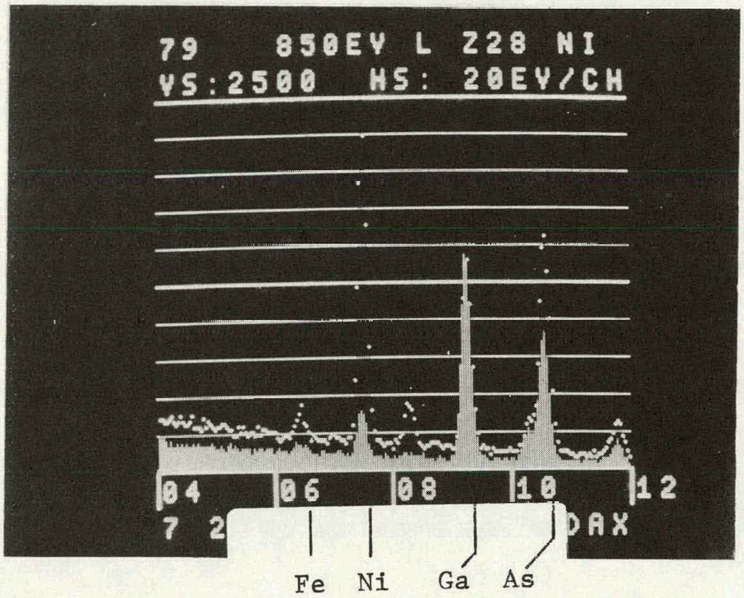


Figure 2-8. X-ray Spectrum of Crystalline Region (Bar Display) and Veil Region (Dotted Envelope) for GaAs Film on Rodar.

It would appear that there are fundamental problems inherent in vapor phase growth of GaAs on Kovar type alloys. The presence of As or of $AsH_3$ causes a compound to form. The formation of this compound is not expected from the binary phase diagrams of As and the individual constituents of the alloy (Fe, Ni, Co). However, the formation of this compound results in cracking of the grown GaAs, contamination with Ni, and formation of veils of amorphous material on the surface of the film. All of these are undesirable characteristics of a substrate material to be used for thin-film solar cell applications.

#### 2.3.2.2 GaAs Films on Mo

MO has a number of features which make it attractive as a substrate for GaAs. Its average thermal expansion properties are close to those of GaAs. It is a single-element refractory metal which does not react with As at the temperatures of interest. Because it is a metal it holds the promise of providing ohmic contact to the deposited film, although early studies by Vohl et al (Ref 17) for evaporated and sputtered GaAs on Mo were not encouraging. For all of these reasons, Mo has been explored as a substrate for GaAs grown by the MO-CVE process. However, because of its high cost it will will eventually have to be used in thin-film form; further consideration to this alternative will be be given later in the program.

A typical surface structure of a GaAs film on Mo is shown in Figure 2-12. Note in these figures that the typical surface feature is ~2 μm in size, with a few as large as 4 μm in principal dimension. The surface features appear to have vertical

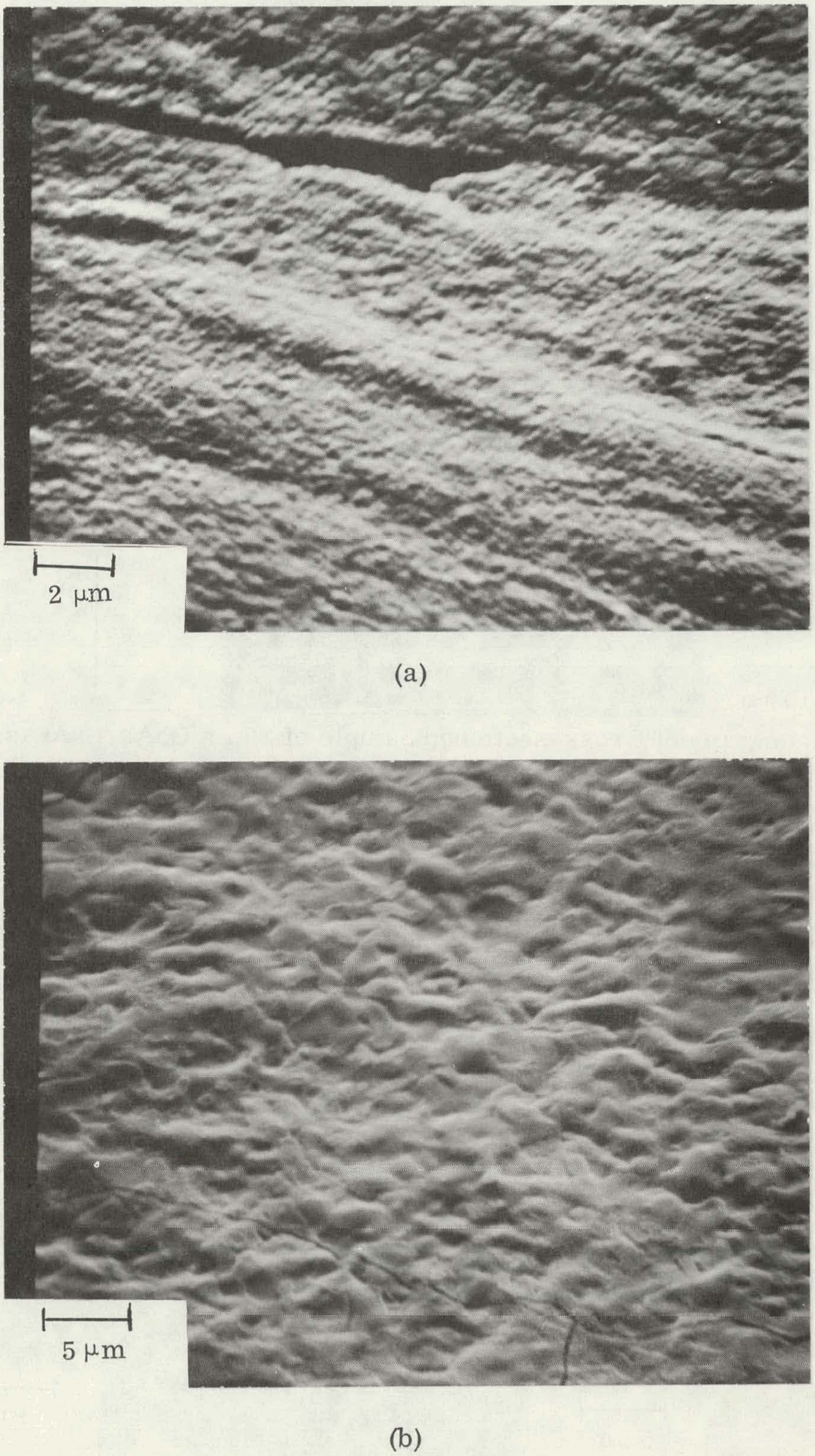


Figure 2-9. SEM Secondary Electron Image of Rodar Substrates after (a) 2 min HCℓ Etch, and (b) 2 min HCℓ Etch and Exposure to $AsH_3$ for 3 min at 725°C.

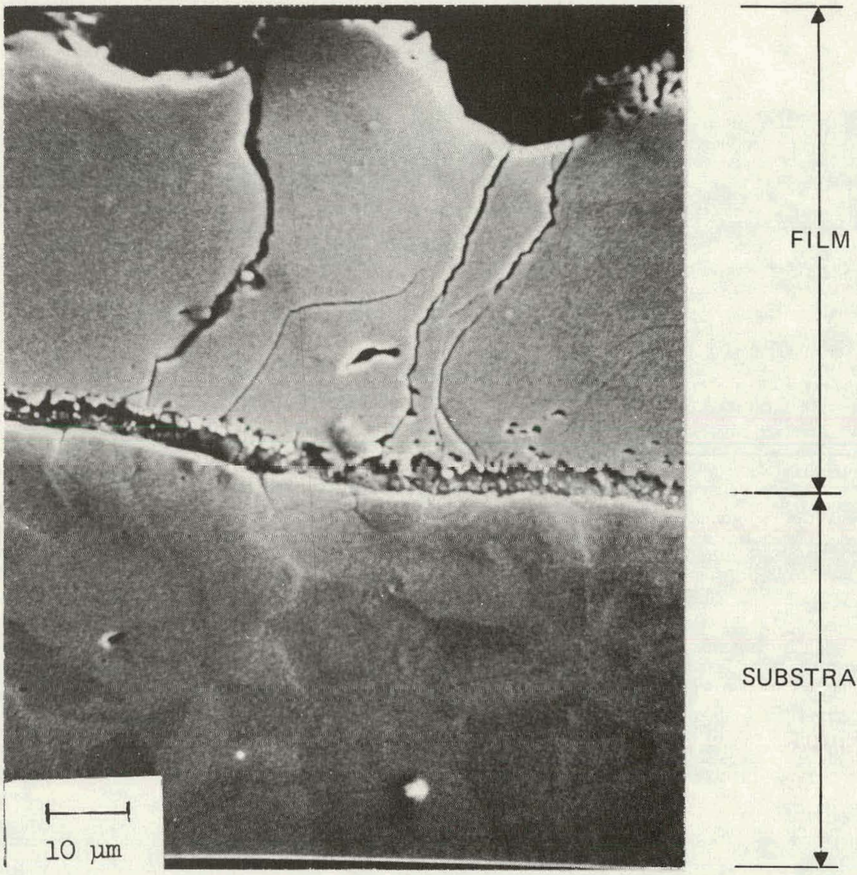


Figure 2-10. SEM Photograph of Cross-sectioned Sample of 20 µm GaAs/GaAℓAs Film Grown on Rodar. (Note interface layer and presence of voids and cracks.)

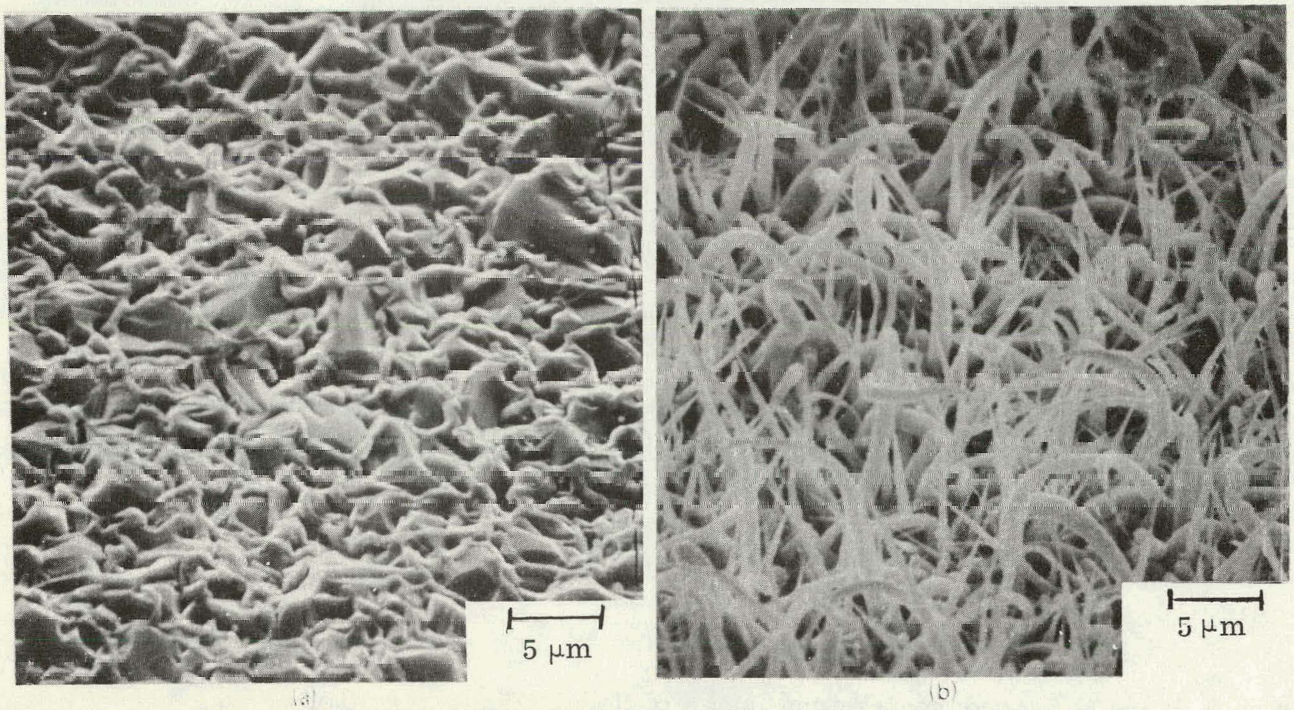
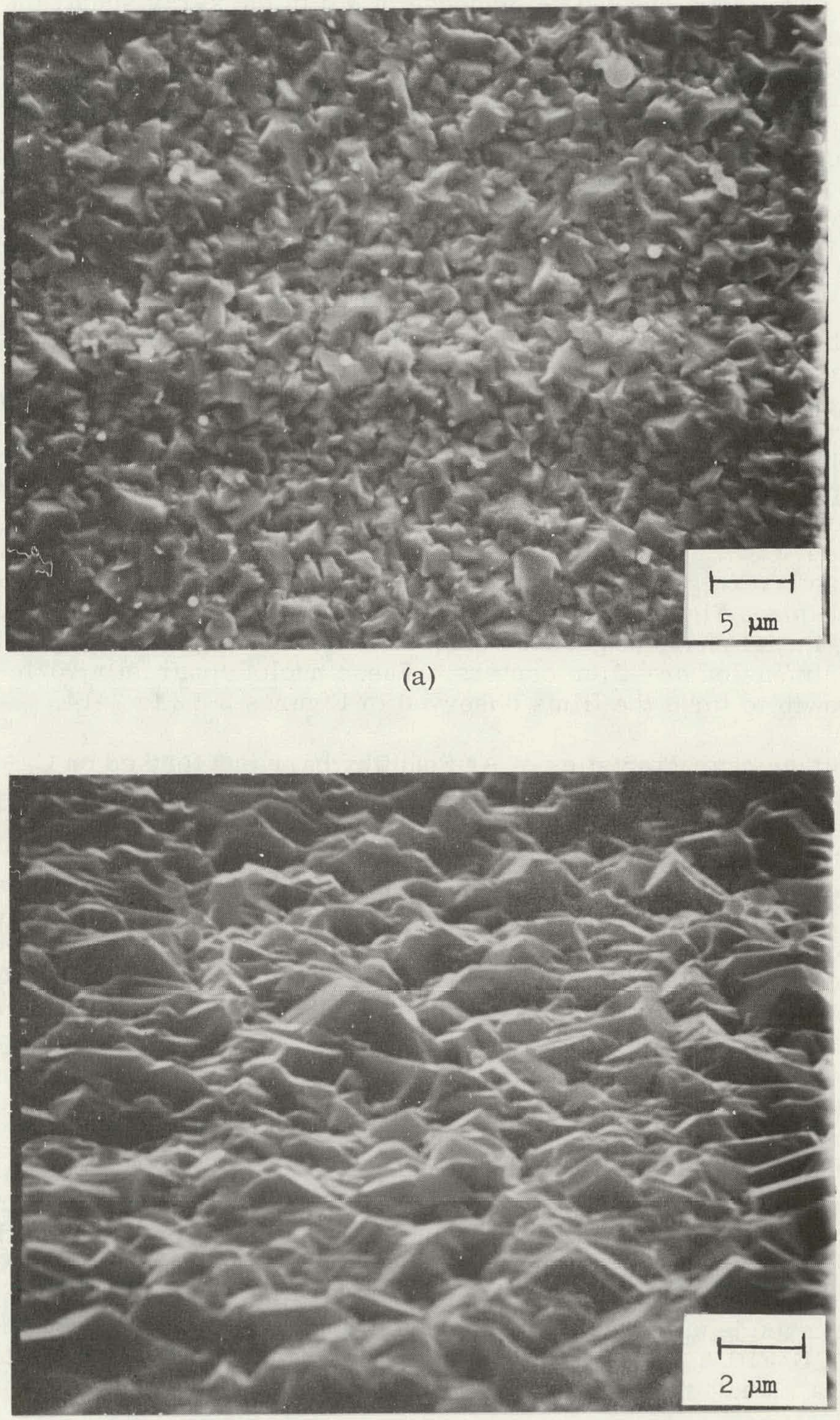


Figure 2-11. SEM Photographs of GaAs Films Grown on Rodar at (a) $610^{\circ}$C, and (b) $536^{\circ}$C.



(a)

(b)

Figure 2-12. SEM Photographs of GaAs Film Grown on Mo at 725°C.
(a) View Perpendicular to Surface; (b) View at Angle of 30 deg with Surface.

dimensions of ~2 μm. This film showed no evidence of Mo in the x-ray spectrum and had strong (111) preferred orientation. This film was grown on Mo that had been degreased and cleaned with HCℓ. No difference was observed for other surface treatments or for films grown on Mo obtained from different suppliers.

Figure 2-13 shows two films of GaAs grown on Mo at 650°C (Figure 2-13a) and 775°C (Figure 2-13b). Both films were grown for the same length of time and with the same flow conditions and thus should be approximately the same thickness. The maximum size of surface features for both is ~4 μm, with the average being ~2 μm. The major difference between the two films is the presence of taller surface features for the film grown at 775°C (Figure 2-13b). This trend is seen to continue in Figure 2-14, in which a film grown at 836°C is shown. Note the presence of much taller surface features than seen in the photographs of films previously shown. Film growth at a higher deposition rate but at 740°C seemed to increase the incidence of larger surface features (~5 μm typical dimension). All of the films showed preferred (111) orientation, although the film grown at 836°C (Figure 2-14) was not as strongly oriented in the (111) plane as the others. No evidence for Mo has been observed in any of the films for any temperature of growth.

Partial-coverage layers grown for very short times illustrate the nucleation morphology of these films. Figure 2-15 shows an SEM photograph of such a partial-coverage layer. The initial phase of growth consists of islands approximately 0.5 - 1.0 μm in horizontal dimension on ~2 μm centers. These nuclei apparently coalesce during subsequent growth to form the films observed in Figures 2-12 to 2-14.

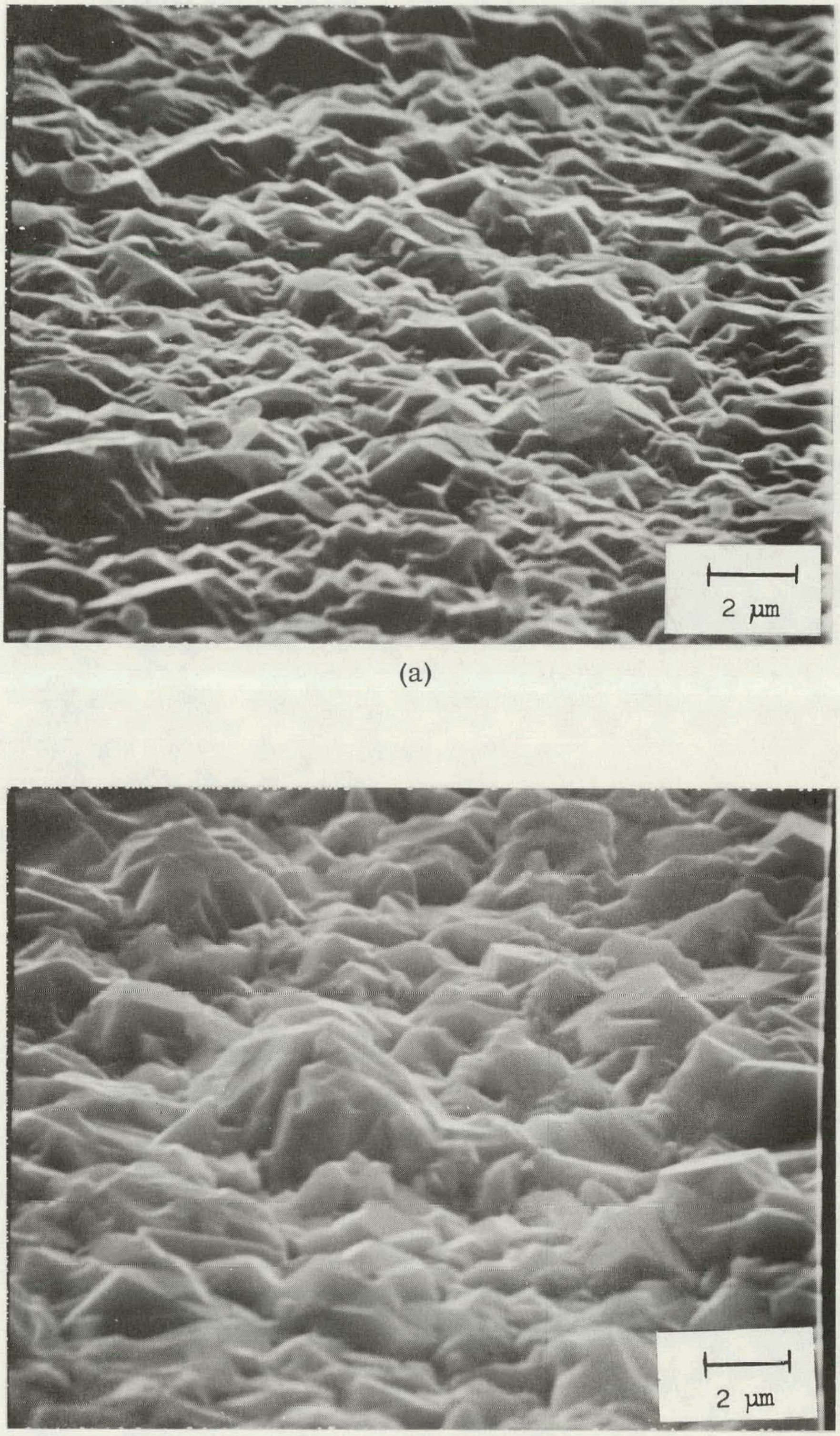
Capacitance-voltage characteristics of Aℓ Schottky barriers formed on GaAs films grown on Mo have been determined. In one case a doped film on Mo was determined to have a net carrier concentration of $4\times10^{18}$ cm$^{-3}$ as compared with $1\times10^{18}$ cm$^{-3}$ for a GaAs film grown on sapphire in the same run. Undoped GaAs films on Mo typically have had a measured carrier concentration of $4\times10^{16}$ cm$^{-3}$. This is somewhat higher than the best background level of the reactor system, but the deposition experiment in question followed several doping runs and this may have caused a somewhat higher carrier concentration. Further analysis of C-V and other measurements will be carried out later in the program and will be described in subsequent reports.

It appears that Mo is a suitable substrate for growth of GaAs by the MO-CVD technique, but it will be necessary to test this conclusion by growing GaAs films on Mo in its practical form for this program - a thin film.

### 2.3.2.3 GaAs Films on Polycrystalline Alumina

GaAs of excellent quality can be grown epitaxially on single-crystal sapphire ($\alpha$-$A\ell_2O_3$) by the MO-CVD method. Polycrystalline aluminas therefore present the possibility of tailoring the film grain structure by proper preparation of the alumina substrate, e.g., by firing at high temperatures to increase the grain size. This has already been accomplished to a degree in the Rockwell contract for large-area Si sheet growth in the JPL/ERDA LCSSAP, in which Si has been grown by CVD on large-grained Vistal alumina manufactured by Coors Porcelain Co.

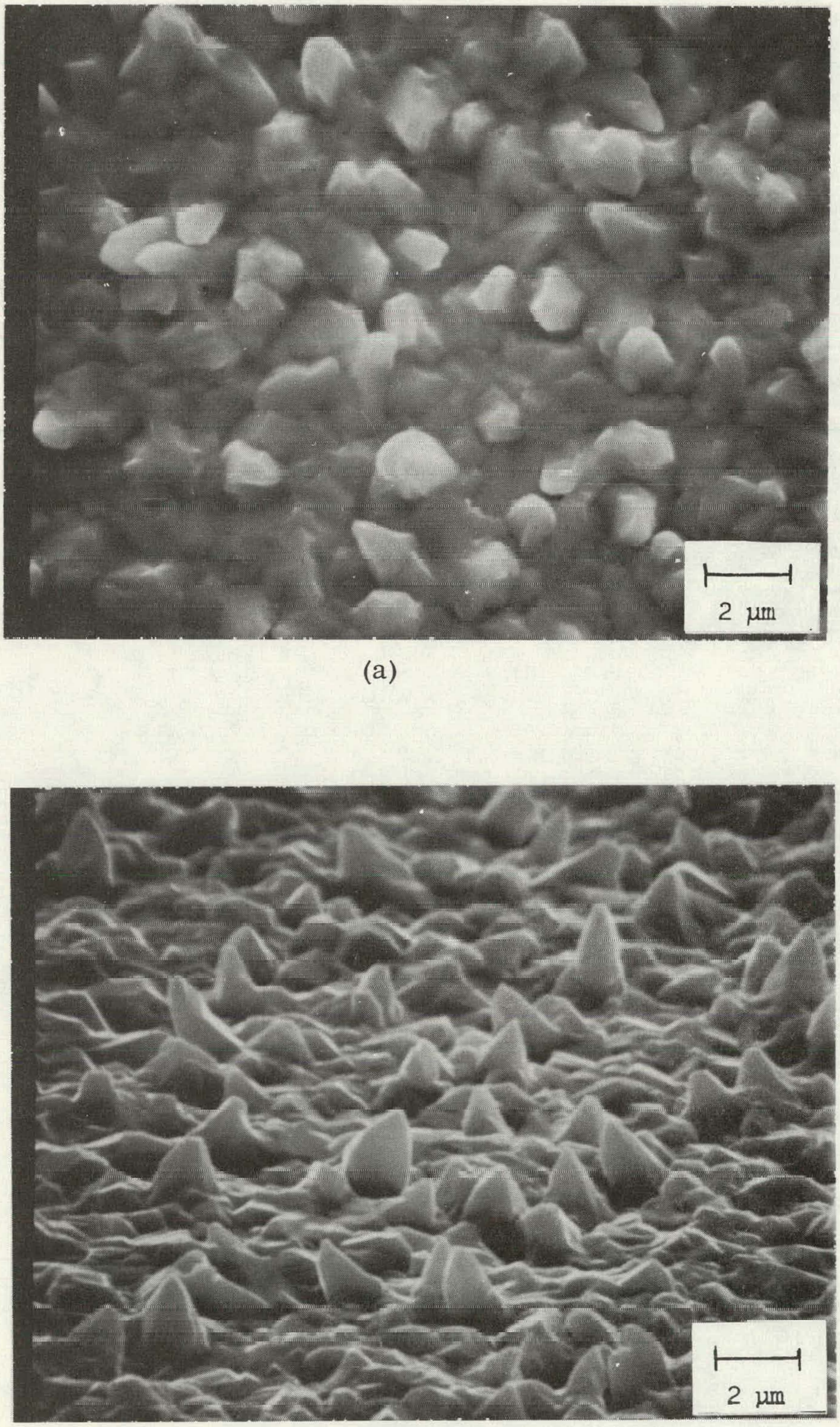
Aluminas tend to be too expensive for long range use. However, it is possible that sufficient motivation to review manufacturing procedures and thus eventually reduce costs could be provided by successful implementation of a high-efficiency solar cell of GaAs on alumina. To date preliminary growth studies have been performed on ASM805 and ASM838 aluminas only; both are manufactured by the 3M Company. The characteristics of these films are discussed below.



(a)

(b)

Figure 2-13. SEM Photographs of GaAs Films Grown on Mo at (a) 650$^{o}$C, and (b) 775$^{o}$C.



(a)

(b)

Figure 2-14. SEM Photographs of a GaAs Film Grown on Mo at 836°C. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.

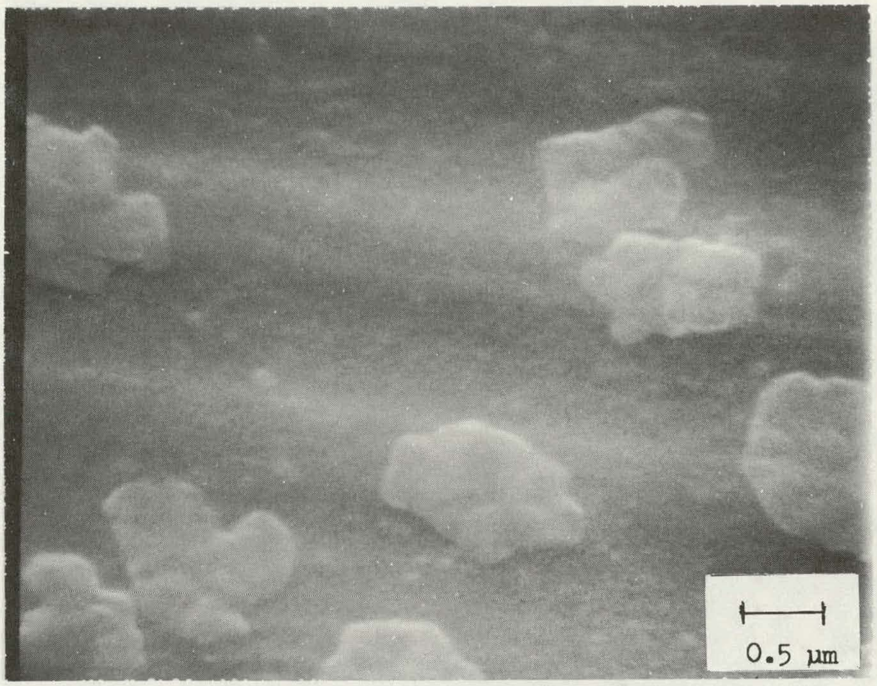


Figure 2-15. SEM Photograph of Partial-coverage Layer of GaAs Grown on Mo Substrate at 735°C

SEM secondary electron images of GaAs films ~5 µm thick grown at 735°C on ASM805 and ASM838 are shown in Figures 2-16 and 2-17, respectively. The film on ASM805 shows surface features the order of 2-3 µm in dimension, with surface roughness (i.e., vertical dimensions) the order ~1 µm. The undoped films grown on this alumina were highly resistive, i.e., $\rho \geq 10^5$ ohm-cm. X-ray diffraction analysis showed the preferred orientation to be (111). A fractured cross-section of the film on ASM805 is shown in Figure 2-18a. Note the abrupt interface between substrate and film. Small grown-over voids in the substrate surface are visible upon close examination. The fracture structure of the grown film as shown in Figure 2-18a does not appear to be columnar, although this is not considered to be necessarily a conclusive indication of grain structure in the film.

The film of GaAs grown on ASM838 alumina and shown in Figure 2-17 is similar in many ways to that grown on ASM805. The major difference is the occurence of some large (5-6 µm) surface features in the film on ASM838. Again the preferred orientation of the film was determined to be (111), and the undoped films had resistivities $\rho > 10^5$ ohm-cm. The fracture structure of this film, shown in Figure 2-18b, again is not columnar. However, few voids are seen at the interface in this case. The interface is again quite abrupt, with no intermediate layers, as expected.

#### 2.3.2.4 GaAs Films on Glass

From an economic point of view glass is nearly an ideal substrate for implementation in large scale. It is inexpensive, available in large areas, and made of abundant materials. From the point of view of crystal growth, however, it is the most difficult to implement because it is amorphous and provides no natural sites for nucleation of crystallites.

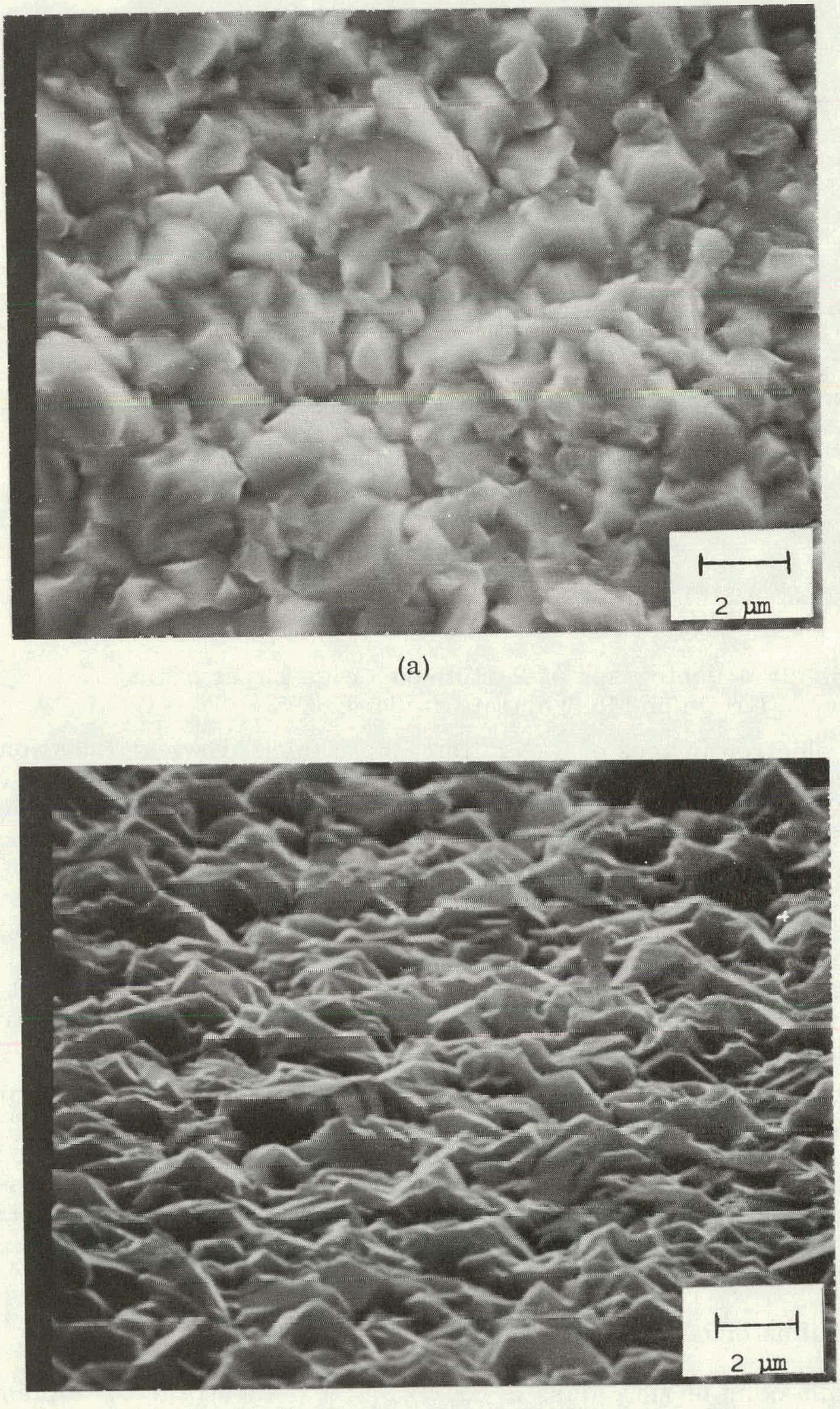
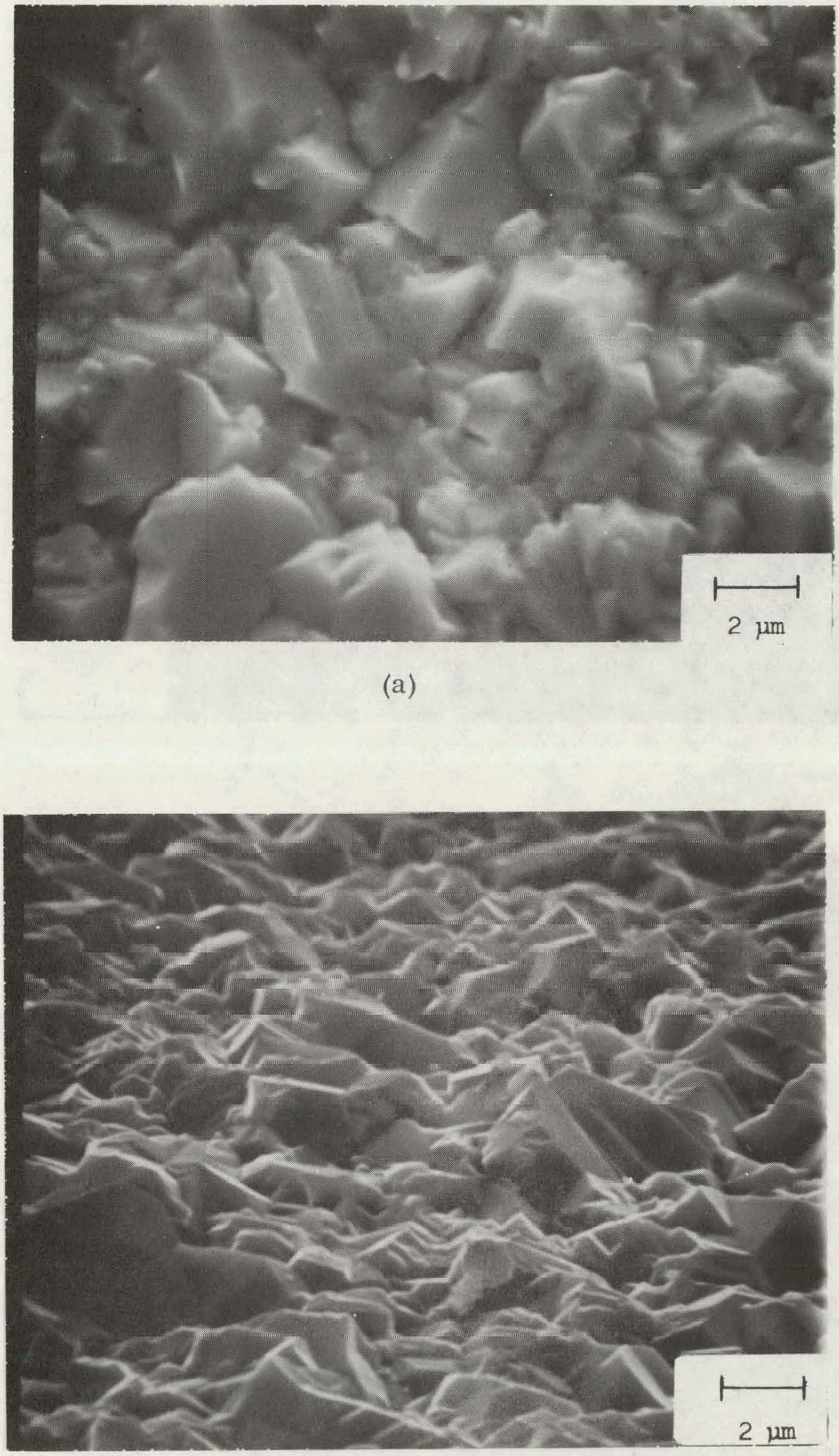


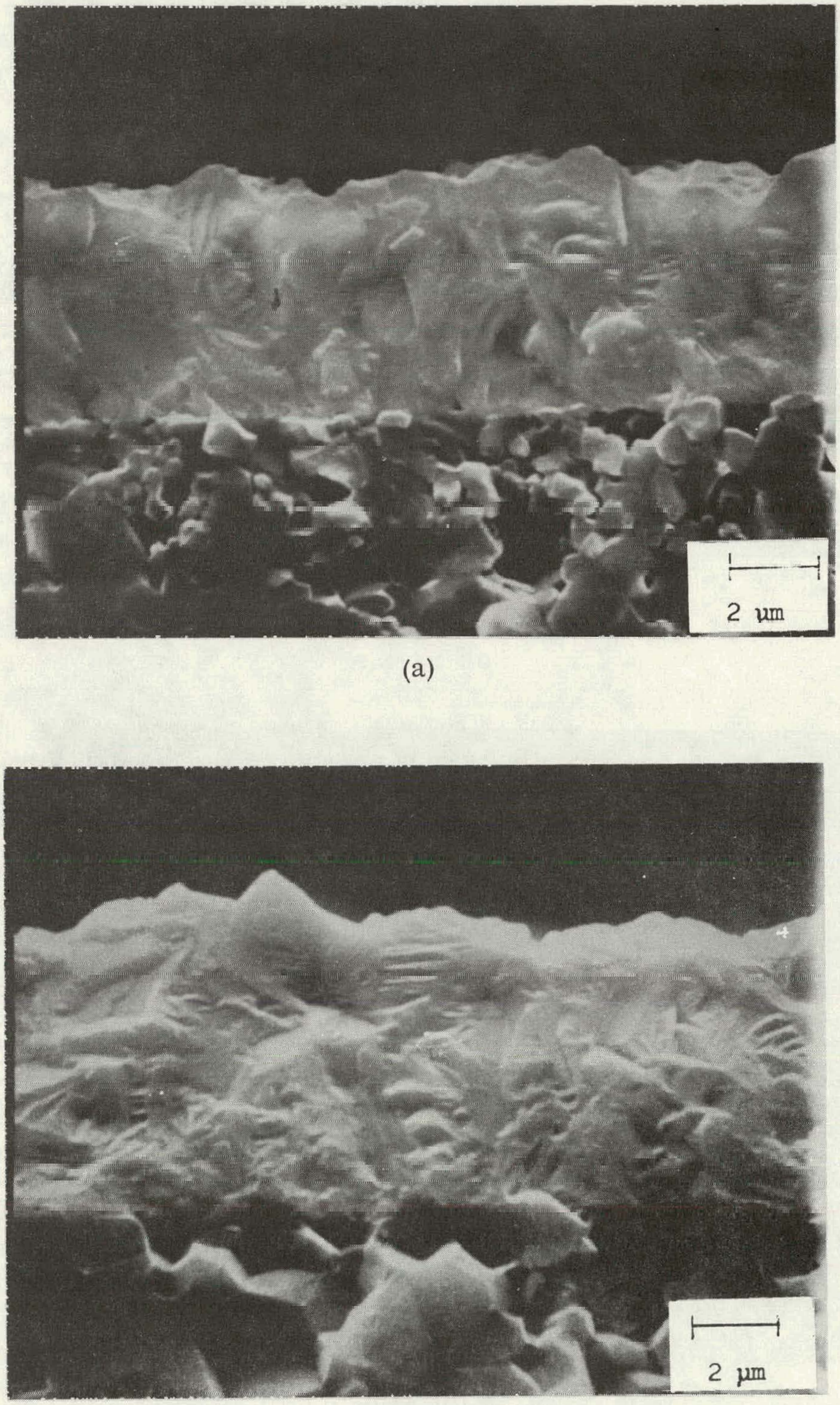
Figure 2-16. SEM Photographs of GaAs Film Grown on ASM805 Alumina at 735°C. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.



(a)

(b)

Figure 2-17. SEM Photographs of GaAs Film Grown at 735°C on ASM838 Alumina. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.



(a)

(b)

Figure 2-18. SEM Photographs of Fractured Cross Sections of GaAs Films of Figures 2-16 and 2-17. (a) Film on ASM805 Alumina; (b) Film on ASM838 Alumina.

Two glasses have been examined in a preliminary way to test their suitability in a high-temperature reducing environment — Corning Codes 1723 and 0317. Growth of GaAs films on both glasses results in high resistivity ($\rho \geq 10^5$ ohm-cm) material with (111) preferred orientation. The surface structure of GaAs grown on 1723 glass is shown in Figure 2-19. Note there are crystallites of dimension 2-4 μm, with ~1 μm height variations. The fractured cross-section of the film (Figure 2-21a) shows an abrupt interface, with no apparent chemical interaction such as would result from compound formation. Similarly, the film fractures in non-columnar configuration.

The structure of a film grown on Corning Code 0317 glass is shown in Figures 2-20 and 2-21b. There are no obvious differences in the general features of films grown on 0317 glass compared with those grown on 1723. The resistivities of these undoped films on 0317 glass are also $\geq 10^5$ ohm-cm, and the films show the same (111) preferred orientation. Again the interface between the film and the substrate is abrupt (Figure 2-21b).

The importance of these feasibility experiments is that the surface of the glass in both cases maintained its integrity at the growth temperature of 700°C in a $H_2$ atmosphere, allowing deposition of GaAs under nearly "ideal" conditions. If this stability continues in future experiments where studies of nucleation phenomena and grain-size enhancement are undertaken, the need for film growth in He may be negated. Furthermore, it is important that there is no apparent cracking of the film, further indicating that growth directly on these high-softening-point glasses may be satisfactory in essentially all important respects.

#### 2.3.2.5 Ge Films on Rodar

The reaction which occurs between $AsH_3$ and Kovar/Rodar makes the growth of GaAs directly on these alloys an unsuitable prospect for solar cell fabrication. To determine the viability of Ge as an intermediate passivating and/or nucleating layer on Kovar/Rodar, the feasibility of depositing Ge by CVD on Rodar was established. Films of Ge with grain sizes of 10-20 μm were grown on Rodar substrates. The surface of such a film is shown in Figure 2-22. Obviously, if GaAs can be grown epitaxially on the many Ge crystallites — some of them quite large — this substrate combination may well be a promising candidate for the application involved in this program.

### 2.3.3 Characterization Technique Development

More detailed characterization of the various thin-film materials prepared in this program will be undertaken in the coming quarter. During the first three months of the contract some attention was given to development of certain specialized procedures that are required for these more extensive evaluations.

#### 2.3.3.1 Grain Size Determination

A widely used method for describing grain size in polycrystalline materials is to measure the dimensions of crystalline surface features. The application of this technique to the films grown to date on this program indicates that the average grain size in most of the films has been 2-5 μm. However, no correlation between true grain size and the dimensions of surface features has yet been established.

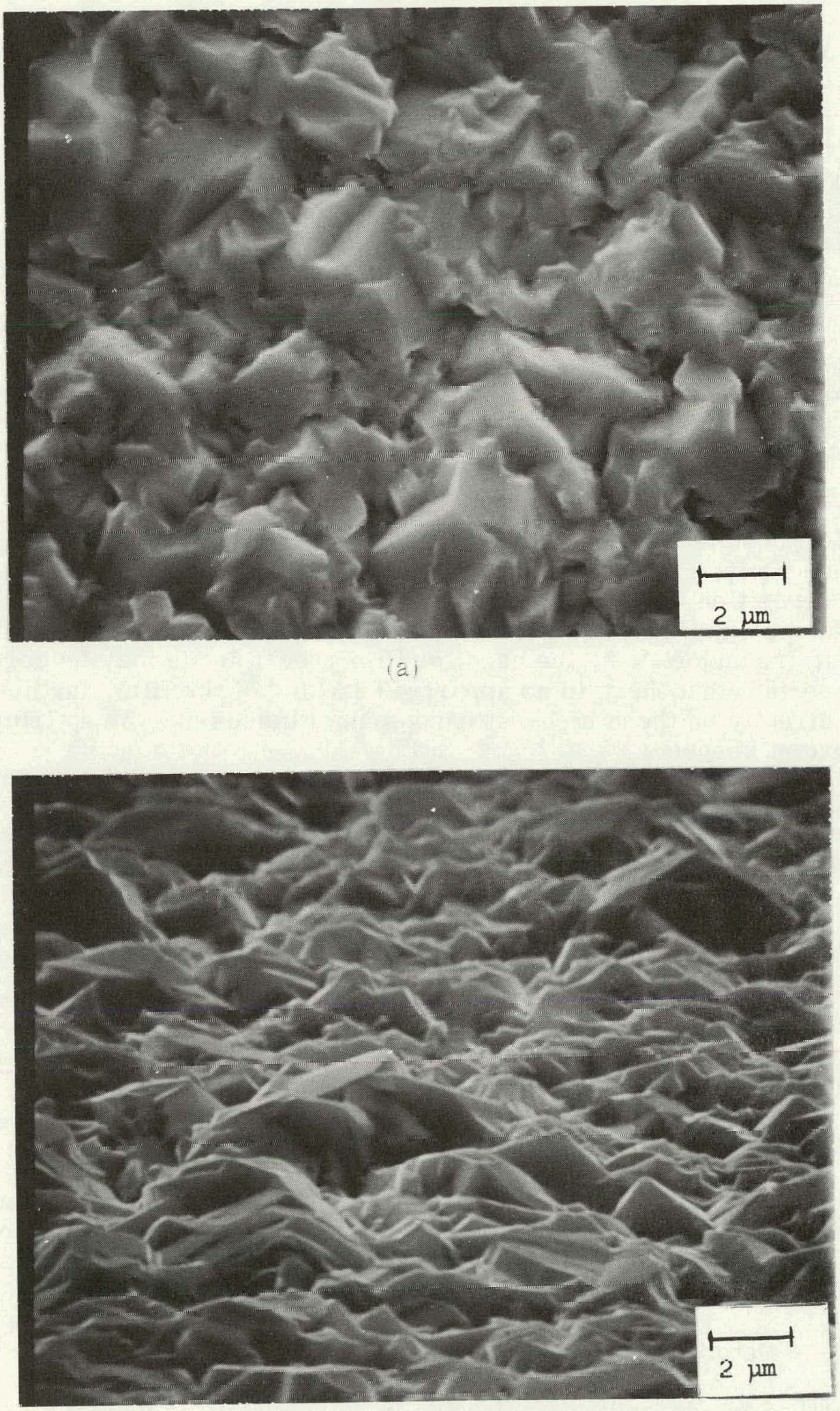


Figure 2-19. SEM Photographs of GaAs Film Grown on Corning Code 1723 Glass. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.

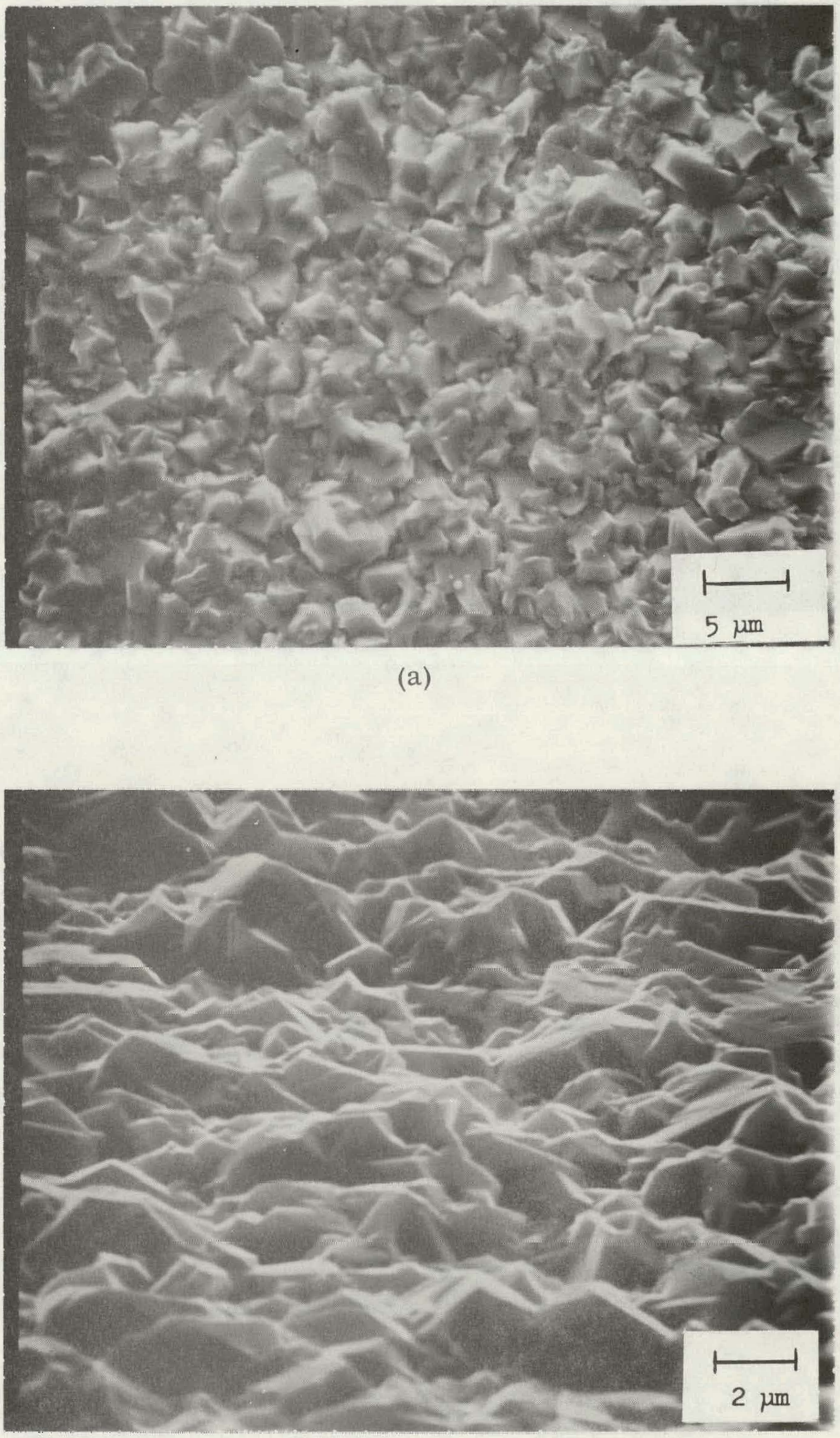
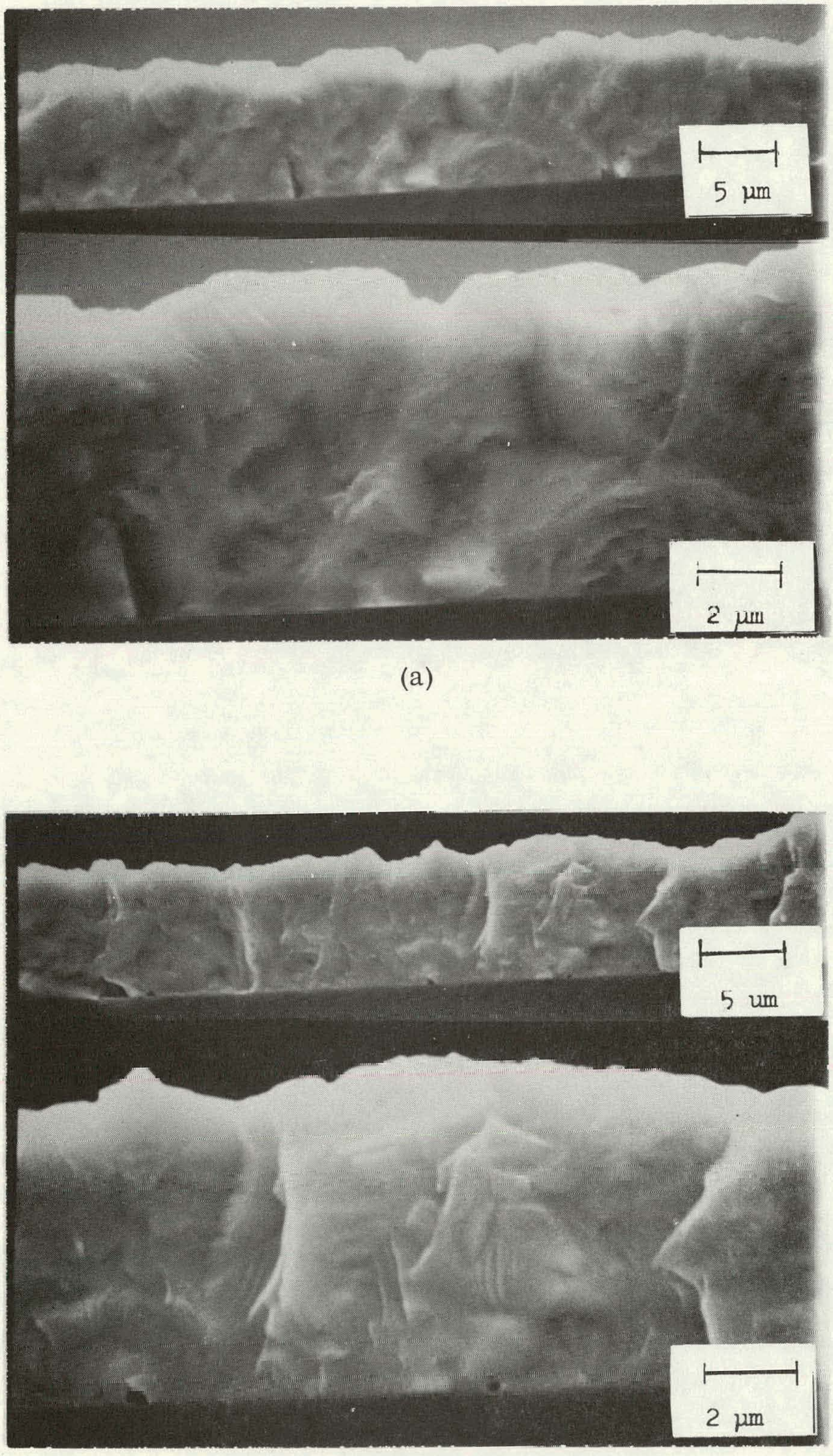


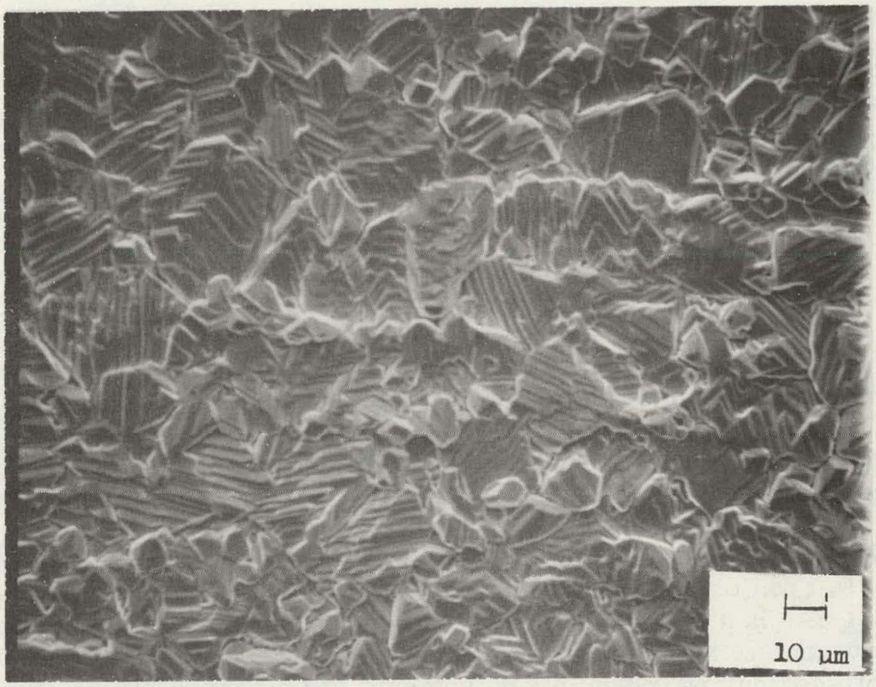
Figure 2-20. SEM Photographs of GaAs Film Grown on Corning Code 0317 Glass. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.



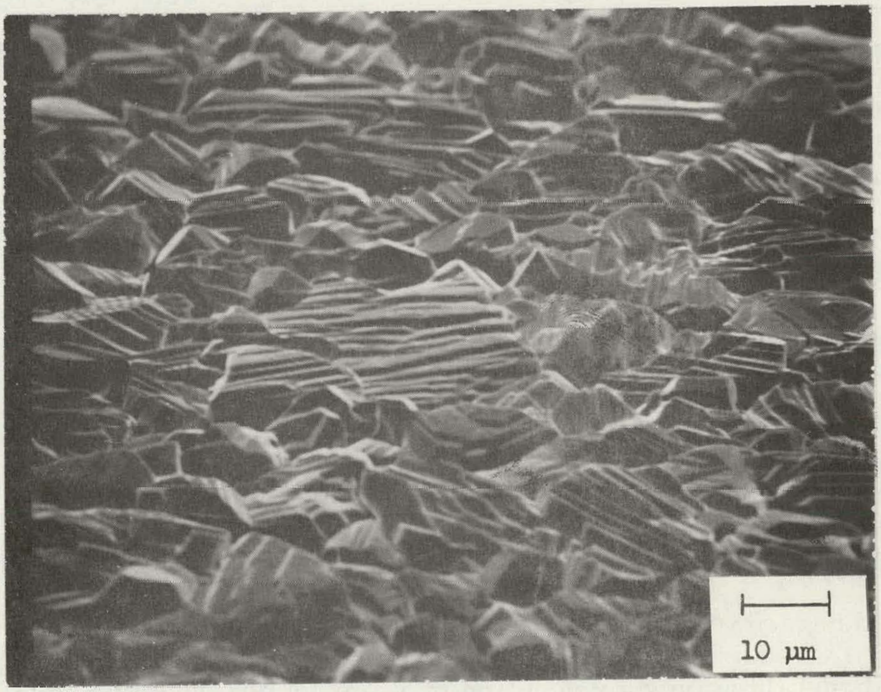
(a)

(b)

Figure 2-21. SEM Photographs of Fractured Cross Sections of GaAs Films on (a) Corning Code 1723 Glass, and (b) Corning Code 0317 Glass.



(a)



(b)

Figure 2-22. SEM Photographs of Ge Film Grown by CVD from $GeH_4$ Source on Rodar Substrate. (a) View Perpendicular to Surface; (b) View at 30 deg Angle with Surface.

Chemical etching, using etches which are selective for dislocations and other crystalline defects, is an applicable technique for determining grain size when the etched feature is small compared with the grain size. For example, a 5 μm-wide etched line at a grain boundary is adequate when the grain size is the order of 100μm. The common dislocation etchant for GaAs - the so-called A-B etch* (Ref 18) - has been applied to the delineation of grain boundaries in slices from a polycrystalline boule of GaAs. The lines etched at grain boundaries were ~5 μm wide when they became distinguishable as features in an optical microscope. The etch features tend not to be sharp chasms, as are developed in Si with the Sirtl etch, but rather V-shaped grooves, the orientation of the V depending on the grain orientation.

Features of this size and shape are not suitable for delineating grains suspected to be less than 5 μm in dimension and with height variations of 1-2 μm. This was borne out by an experiment in which a GaAs film grown on glass was etched lightly in A-B etch. The resultant surface structure showed the surface features to be rounded by the etch, but there was no discernible grain-boundary delineation.

X-ray line broadening can be observed for polycrystalline materials when the grains are the order of 0.1 μm or less in dimension. A standard sample of large-grained polycrystalline GaAs has been prepared to determine the extent of line broadening contributed by instrumentation. Once this has been determined a lower limit on grain size can be established during x-ray measurements of preferred orientation.

Determination of the location of grain boundaries can be accomplished in the SEM using the electron-beam induced-current (EBIC) mode. This is accomplished by measuring the minority-carrier current collected by an electron-transparent Schottky barrier on the surface of the sample as the electron beam of the SEM is scanned across the sample. Grain boundaries are sinks for minority carriers and will appear dark in the EBIC image. The major questions about the applicability of this technique in this program are the effect of surface morphology on the EBIC image and the effect of long intragrain diffusion lengths on the sharpness of grain boundary images. Work is in progress now to determine the utility of this technique.

#### 2.3.3.2 Doping Levels of Multilayer Structures and Depth Profiles of Single-layer Structures

The doping levels of individual layers in a multilayer structure as well as doping profiles for individual layers will have to be determined, to analyze the performance of devices and to study possible impurity diffusion from substrate materials. Determining doping as a function of depth using the reverse-bias capacitance characteristics of Schottky barriers deposited on a beveled surface of a sample provides information at discrete points through the thickness of the layer. The resolution obtainable depends on the angle of bevel, the dimensions of the Schottky barrier, and the uniformity of the doping profile across the sample.

A mask has been designed to define 50 μm-by-300 μm Schottky barriers on a beveled surface in such a way as to give a resolution of 0.438 μm/deg of bevel. For an easily obtainable 2 deg bevel this gives a resolution of 1 μm, which should provide adequate diagnostic resolution for devices. If greater resolution is required for doping profiles near foreign substrate interfaces, more shallow angles can be bevel-polished.

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*Etch consists of 2 mℓ $H_2O$, 8 mg $AgNO_3$, 1 g $CrO_3$, 1 mℓ HF.

However, since the ultimate resolution of the technique requires adjacent Schottky barriers separated by 350 μm to be coplanar to 0.438 μm/deg or better, the planarity and smoothness of the bevel and the accuracy of alignment of the pattern become critical. These problems not withstanding, the technique is judged to be one which will provide a great deal of useful information in this work.

A technique which has proven useful in determining doping profiles in Si films grown by the CVD process is the spreading resistance technique. It is not yet characterized for GaAs but may well provide useful qualitative information for this program. Its possibilities and limitations will be explored in the coming quarter.

## 2.4 TASK 4. EXPERIMENTAL PHOTOVOLTAIC DEVICE FABRICATION AND EVALUATION

This task was summarized in the original program proposal as follows:

> Prototype heterostructure and Schottky-barrier solar cells will be fabricated to provide an ultimate test for the CVD films grown on various low-cost substrates. Appropriate device designs will be developed for both transparent and opaque substrate materials, and experimental structures will be made for each case. In addition to determining the suitability of the films for solar cell applications, detailed characterization of these devices will provide the needed information on various aspects of the device fabrication technology itself--e.g., layer dimensions, doping concentrations, contact materials and processing. Characterization methods will include determination of detailed I-V curves (light and dark) and determination of the usual solar cell properties ($V_{OC}$, $I_{SC}$, curve fill-factor, efficiency) both under laboratory illumination and in an AM1 solar simulator.

The primary activities for this task in the first quarter have been the design of an experimental solar cell contact mask and the verification of single-crystal contact technology for window-type heterojunction solar cell fabrication.

### 2.4.1 Experimental Solar Cell Contact Mask

A mask has been designed to define contacts on the top or window layer of heterostructure solar cells. The mask provides for a square grid of 50 μm lines on 1 mm centers, with every fifth intersection containing a 250 μm x 250 μm square bonding pad. This mask provides for approximately 10 percent contact coverage and allows, with suitable isolation techniques, cells as small as 0.25 $cm^2$ to be evaluated.

The latter capability will be a useful diagnostic tool for evaluating material uniformity. The grid line width was chosen to be the minimum consistent with achieving continuous contact lines after alloying. It is planned that this contact pattern will be used on the window layer of the cell, with a full-surface contact on the back side.

### 2.4.2 Contact Technology for Single-crystal Solar Cells

Single-crystal window-type solar cells will basically require that ohmic contacts be applied to both GaAs and GaA$\ell$As, either of which may be n or p type, depending on whether the structure is n-on-p or p-on-n. However, to assure a low resistance device the GaAs substrate upon which epitaxial layers are grown and the GaA$\ell$As window layer must both have relatively high conductivity. This relieves some of the problems of applying ohmic contacts.

Experiments have been conducted to determine the applicability of ohmic contacts that are commonly used for GaAs and GaA$\ell$As. For contacts to n-type material a Au-12 percent Ge contact is evaporated to a thickness of 6000Å and then alloyed in forming gas at 450°C. This procedure produces ohmic contacts to GaAs with doping concentrations as low as $10^{16}$ $cm^{-3}$. Similarly, this technology has been found applicable to GaA$\ell$As ($x \approx 0.9$) provided the doping level is $n \approx 5 \times 10^{16}$ $cm^{-3}$ or greater.

However, as indicated earlier for the case of In, the native oxide on GaAℓAs makes alloying times somewhat unpredictable for most doping levels. It has been found necessary in some cases to realloy contacts up to 3 times for 10 min each to achieve ohmic contact. This problem will require further attention as the program develops.

Similar experiments for p-type GaAℓAs using In-Ag-Zn contacts are planned for the near future. A possible solution to the general problem of contacting the window layer is to grow a contacting "cap" layer of GaAs on top of the GaAℓAs and then to selectively remove the GaAs except for those regions under the metal contacts. This technique has been used in single-crystal cells, but its applicability to polycrystalline cells is untested.

## 2.5 TASK 5. ANALYSIS AND PROJECTION OF CELL FABRICATION COSTS

This task was summarized in the proposal for the program as follows:

> Present costs for experimental and pilot-line quantities of thin-film GaAs solar cell structures will be analyzed at the start of the program and again during the final month of the contract. Future costs for large-scale production of such cells will be projected during the final month of the contract, 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 this program, from Rockwell facilities engineers, from materials and equipment vendors, and other sources.

The effort on this task in the first quarter has been limited to (1) selection of the conceptual device designs to be used as the basis of cost analyses and projections, (2) acquisition of materials costs from various vendors and the costs of certain facilities and support services from Rockwell personnel, and (3) development of preliminary materials and processing matrices to use in establishing a range of present and projected costs for thin-film GaAs solar cells fabricated by the MO-CVD method.

It had originally been suggested (in the program proposal) that the initial analysis of present device fabrication costs and a preliminary projection of future large-scale production costs be completed during the first six weeks of the program. However, this plan was revised early in the first quarter, and it is now intended that these initial analyses will be completed during the second quarter.

### 2.5.1 Conceptual Device Designs for Cost Analyses

For purposes of the preliminary analysis two different conceptual device designs are being used. These are both heterostructure devices, one involving opaque substrate materials and the other involving transparent substrates and an inverted structure permitting illumination through the substrate. Both involve a p-type GaA$\ell$As window layer in front of a p-type GaAs active layer adjoining an n-type GaAs active base region.

The first design is illustrated in Figure 2-23a, and consists of the conventional GaA$\ell$As/GaAs window-type heterostructure cell, in this case involving layers of p-type GaA$\ell$As, p-type GaAs, and n-type GaAs on an opaque substrate, as shown. . This design involves deposition of n-type GaAs onto the substrate followed by deposition of p-type GaA$\ell$As on the GaAs layer. The p-n junction will be formed in the n-type GaAs layer by diffusion of Zn (the acceptor dopant) from the p-type GaA$\ell$As layer into the initial GaAs layer, during the GaA$\ell$As deposition process. The A$\ell$ concentration must be selected to achieve stable low-contact-resistance devices and good high-energy spectral response, i.e., $x \approx 0.8-0.9$ in $Ga_{1-x}A\ell_xAs$. The thickness of the GaA$\ell$As layer must also be adjusted to provide good spectral transmission and yet allow adequately low series resistance in the cell.

The design employing a transparent substrate is shown in Figure 2-23b; it consists of an inverted GaA$\ell$As/GaAs window-type heterostructure, formed by depositing n-type GaAs on a p-type layer of GaA$\ell$As grown on the transparent substrate; again the active junction will result from Zn diffusion from the p-type GaA$\ell$As

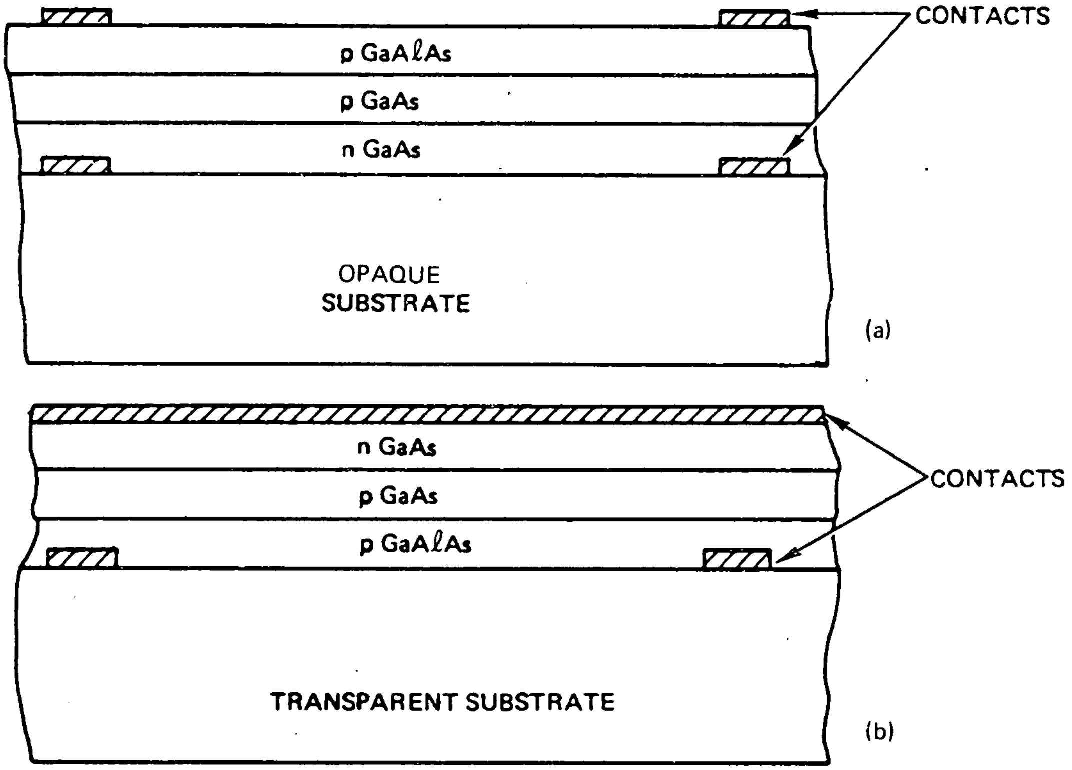

Figure 2-23. Conceptual Designs of Thin-film GaAs Heterostructure-type Solar Cells, Used for Cost Analyses and Future Cost Projections
(a) Conventional Structure with Opaque Substrate; (b) Inverted Structure with Transparent Substrate

into the GaAs layer during deposition of the latter. Here also the A$\ell$ concentration in the alloy layer as well as the layer thickness must be chosen for optimum cell characteristics. In both cases the details of the contact design and the exact A$\ell$ composition and impurity doping levels remain to be determined.

Based on these conceptual designs it is possible to begin compiling materials and processing costs, even though significant details of the designs are not yet resolved. The basic GaAs solar cell components that are being considered in initial cost analyses are (1) substrate; (2) base-region or backside contact; (3) active n-type base layer of cell; (4) front layer of cell (p-type GaAs); (5) window layer (p-type GaA$\ell$As); (6) front surface (incident-light side) contact; and (7) antireflection coating on front surface (optional).

### 2.5.2 Acquisition of Materials and Process Cost Data

Accumulation of information needed for the initial analysis of current costs for experimental and pilot-line quantities of thin-film GaAs solar cells made by the MO-CVD technique is under way. However, the information is not sufficiently complete to permit a useful presentation of the data in this report; results of the preliminary analysis will be given in later reports.

Now that a restricted number of candidate substrate materials has been defined for evaluation in the program (see Para 2.1.3) it will be possible to establish a range of materials costs associated with the substrate component of each of the two conceptual device designs specified above. Also, in the course of obtaining metal-organic compounds - such as trimethylgallium (TMG) - for use in the experimental studies of this contract it has been found that a wide range of prices exists among the few current suppliers (manufacturers) of these materials. Based on discussions with (or visits to) these suppliers, as well as on experience with the use of these materials in the laboratory, there appears to be a similar wide variation in quality (i. e., purity). These variation's must be considered in setting up the materials and processing matrices to be used with the two conceptual device designs.

It appears that the most valuable cost analysis at this stage of the program, when so many aspects of the device design that will be judged most useful at the end of the first-year program are yet undefined, will consist of three parts: (1) analysis of the "materials content value" range for the two conceptual device designs, in terms of present costs and - to the extent now possible - projected future costs; (2) analysis of the total cost of producing a solar cell in each of the two conceptual designs in the laboratory today, accounting for all materials costs, processing costs, labor, and facilities and equipment allowances; and (3) analysis of projected total costs for producing these same two cell designs on a limited pilot-line basis, using current cost factors scaled up to the pilot-line level. This is the approach now being taken.

Details of all three cost analyses will be given in subsequent reports.

# 3. CONCLUSIONS

A large variety of candidate substrate materials has been considered for use in this program. Only a few materials now commercially vailable—including amorphous glasses, glass-ceramics, polycrystalline ceramics, and certain metals and alloys—can meet the stringent requirements of physical and chemical properties, cost, and eventual availability in large areas required for application to low-cost terrestrial solar arrays.

Selection criteria have been developed to serve as the basis for identifying those candidate materials to be extensively evaluated in the program. Ten such materials have been selected: (1) Corning Code 0317 glass; (2) Corning Code 7059 glass; (3) Corning Code 1723 glass; (4) Corning Code 0211 glass; (5) Corning Code 9606 glass-ceramic; (6) ASM805 polycrystalline alumina ceramic (3M Co.); (7) Vistal polycrystalline alumina ceramic (Coors Porcelain Co.); (8) Ge thin film on glass; (9) Ge thin film on Kovar-type alloy sheet; and (10) Mo thin film on glass.

Several of these materials have been evaluated by a standard GaAs film growth procedure using the MO-CVD process. A number of different substrate cleaning procedures have been employed in these investigations. Analysis of the properties of the polycrystalline GaAs films grown on the substrates evaluated to date has shown only minor differences among the films with the exception of those grown directly on Kovar-type alloys. In most cases the films had similar growth characteristics and surface features with typical dimensions of 2-5 μm and high electrical resistivity in the undoped condition. All of the substrate materials, again with the exception of the Kovar-type alloys, were found to be non-reactive with the GaAs film or the reactants used to produce it, under the particular conditions of growth employed.

Growth of GaAs on Corning Code 0317 and Code 1723 glasses did not result in any any detectable bowing of the substrate-film composite. These glasses appeared to be stable in $H_2$ up to ~730°C. Surface features (assumed to correspond to interior grain sizes) averaged about 2 μm across. GaAs films grown on the high-purity polycrystalline aluminas ASM805 (99.9 percent) and ASM838 (99.5 percent) showed similar apparent grain sizes of 2-5 μm.

Kovar and Rodar (essentially identical Fe-Ni-Co alloys) were also used as substrates for GaAs deposition, and attack of the alloy by $AsH_3$ was observed at temperatures above 500°C. The resulting compound formation and the high incidence of Ni-rich inclusions in the deposited GaAs films render these alloys unsuitable as substrates for direct growth of GaAs films by the MO-CVD method. However, the use of an intermediate layer of another material on the alloy could still permit its successful use as an inexpensive supporting underlayer. The achievement of large-grain (10-20 μm) growth of Ge films on Rodar by $GeH_4$ pyrolysis indicates considerable promise for this configuration as a composite substrate for subsequent large-grain growth of GaAs. Additionally, Mo substrates were used for GaAs film growth, and films with surface features 2-5 μm in dimension were again observed. Contrary to the case for the Fe-Ni-Co alloys, no attack of the Mo substrates by $AsH_3$ was observed.

The achievement of polycrystalline GaAs films with apparently adequate grain size, grown by the MO-CVD technique on several potentially low-cost substrates, is an important and encouraging step. However, more detailed analysis of the films and considerably more experimentation — including doping studies, methods for enhancing grain size, and solar cell fabrication — are required before final differentiation among the candidate substrate materials will be possible. The film and device characterization techniques now being developed and used in the program will permit the required analyses to be made on these films and device configurations.

Early in the quarter single-crystal films of Se-doped GaAs, Zn-doped GaAs, Se-doped $Ga_{1-x}A\ell_xAs$ ($x = 0.9$), and Zn-doped $Ga_{1-x}A\ell_xAs$ ($x = 0.9$) were grown on single-crystal Cr-doped GaAs substrates. The dependence of doping concentration (in terms of measured electrical properties, viz., free carrier concentration) upon the flow rate (i. e., concentration) of the doping gas was investigated. The study of the first three doping systems has been completed; the experiments with Zn doping of $Ga_{1-x}A\ell_xAs$ ($x = 0.9$) will be completed early in the coming quarter. The information obtained from these investigations is to be used in the growth of single-crystal GaA$\ell$As/GaAs heterostructure solar cells, planned for the second quarter of the program, and will also provide good groundwork for the subsequent required studies of doping in polycrystalline films of GaAs and GaA$\ell$As on low-cost substrates.

Finally, two conceptual device designs — one involving a conventional window-type GaA$\ell$As/GaAs film structure on an opaque substrate and one involving an inverted structure on a transparent substrate — have been identified for the initial cost analyses of thin-film cells made by the MO-CVD method. Acquisition of meterials and processing cost data has begun, for use in preparing the preliminary cost analyses and in projecting future large-scale production costs later in the program.

# 4. PLANS FOR NEXT QUARTER

The activities of the program in the coming quarter will follow the plans defined in the revised Technical Program Plan and Schedule given in Monthly Letter Report No. 2. By task, these planned activities are as follows:

Task 1

1. Continue characterization of pertinent physical and chemical properties of candidate substrate materials selected for experimental evaluation
2. Conduct standard experimental growth of undoped GaAs film by MO-CVD method on all candidate substrate materials
3. Extend evaluation procedure to include n-type (Se-doped) GaAs films on all selected candidate substrate materials not previously evaluated by standard CVD growth test
4. Continue contacts with substrate manufacturers and suppliers, primarily to obtain specially processed samples of some of the candidate materials selected for further experimental study.

Task 2

1. Continue experimental study of Zn doping of $Ga_{1-x}A\ell_xAs$ ($x= 0.9$) films, using $H_2$ carrier gas, in reactor system in use since start of contract
2. Complete construction and test of new dedicated CVD reactor system
3. Continue and complete experimental study of n-type (Se) doping of single-crystal films of GaAs and $Ga_{1-x}A\ell_xAs$ ($x=0.9$), using new reactor system
4. Continue and complete experimental study of p-type (Zn) doping of single-crystal films of GaAs and $Ga_{1-x}A\ell_xAs$ ($x=0.9$), using new reactor system
5. Grow window-type single-crystal heterostructure solar cells on single-crystal substrates by the MO-CVD method, using doping procedures and data developed in experimental studies
6. Undertake experiments designed to produce large grain growth or enhance initial grain size in polycrystalline films of GaAs and GaA$\ell$As (by means of deposition parameter variations, annealing procedures, substrate surface texturing, deposition of intermediate nucleation layers, or other suitable procedures)
7. Begin experimental study of film nucleation mechanisms and growth habits in the GaAs-GaA$\ell$As system, using selected substrates.

## Task 3

1. Continue evaluation of electrical properties of single-crystal and polycrystalline films of GaAs and GaAℓAs by van der Pauw and other techniques
2. Continue characterization of surface and internal structural and crystallographic properties of polycrystalline films on various selected substrates
3. Establish satisfactory technique(s) for determination of internal grain size in polycrystalline films of GaAs and GaAℓAs (including evaluation of additional etching procedures and of SEM EBIC mode analysis).
4. Establish detailed x-ray diffraction procedure for determination of preferred orientation in polycrystalline films
5. Complete design and assembly of apparatus for surface photovoltage measurements
6. Identify ohmic contact materials and procedures for n- and p-type GaAℓAs
7. Determine applicability of C-V analysis of Schottky barriers for measurement of carrier concentration in polycrystalline films.

## Task 4

1. Complete assembly and test of apparatus for measurement of solar cell properties - including I-V characteristics, spectral response, $V_{OC}$, $I_{SC}$, $\eta$ and CFF
2. Identify suitable contact materials, processes, and designs for fabrication of epitaxial state-of-the-art window-type solar cells on single-crystal substrates using MO-CVD technique
3. Fabricate and evaluate window-type solar cells on single-crystal substrates
4. Design and fabricate buried-contact grid/layer for use with heterostructure cells on insulating substrates.

## Task 5

1. Continue acquisition of various materials and processing cost data for use in initial cost analyses
2. Complete initial analysis of "materials content value" and total cost to produce two conceptual-design cells on laboratory scale
3. Complete initial projection of costs to produce conceptual-design cells on limited pilot-line scale.

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