SAN/1202-77/2

THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

Quarterly Project Report No. 3, January 2, 1977—April 2, 1977

By
R. P. Ruth
P. D. Dapkus
R. D. Dupuis
A. G. Campbell
R. E. Johnson
H. M. Manasevit
L. A. Moody
R. D. Yingling

Date Published—April 1977

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

Electronic Devices Division
Electronics Research Center
Rockwell International
Anaheim, California

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161

5.25
Price: Paper Copy ~~$4.50~~ (domestic)
~~$7.00~~ (foreign) 10.50
Microfiche $3.00 (domestic)
$4.50 (foreign)

C76-1168.3/501

SAN/1202-77/2
Distribution Category UC-63

THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

Quarterly Project Report No. 3

for the period

January 2, 1977 — April 2, 1977

R. P. Ruth, P. D. Dapkus, R. D. Dupuis, A. G. Campbell,
R. E. Johnson, H. M. Manasevit, L. A. Moody, and R. D. Yingling

April 1977

PREPARED FOR THE DIVISION OF SOLAR ENERGY,
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION,
UNDER CONTRACT NO. E(04-3)-1202

ROCKWELL INTERNATIONAL
Electronic Devices Division
Electronics Research Center
3370 Miraloma Avenue
Anaheim, CA 92803

ABSTRACT

The third quarter of work on the contract is summarized. The metallorganic 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 600-800°C, to produce the desired film composition and properties.

Polycrystalline GaAs films have now been grown on all of the low-cost materials on the candidate substrate list. The list has been narrowed as a result of these experiments, which indicate that certain substrates will not be compatible with the growth of GaAs and because certain other materials, such as uncoated glasses and polycrystalline aluminas, do not allow a low-resistance contact to be made to the backside of a polycrystalline solar cell. GaAs films have been grown on Ge deposited on some of these low-cost substrates, the Ge film being employed as a conducting intermediate layer. In addition, thin (2000Å and 1μm) films of Mo have been used as conducting intermediate layers. Polycrystalline GaAs n/n$^+$, p/p$^+$, and p-n junction structures have also been grown on the low-cost substrates.

Single-crystal films of GaAs and $Ga_{(1-x)}A\ell_xAs (x \sim 0.8)$ have been grown to study the Zn and Se doping of these materials and to provide the doping data needed to grow p-n junctions and heterostructure solar cell configurations. Two-layer single-crystal structures, consisting of p-GaAℓAs/p-GaAs on an n-type single-crystal GaAs substrate, and three-layer epitaxial structures, consisting of p-GaAℓAs:Zn/p-GaAs:Zn/n-GaAs:Se on an n-type single-crystal Si-doped GaAs substrate, with very thin (~500Å) GaAℓAs window layers, have been prepared for fabrication of solar cells.

The electrical resistivity of doped p-type polycrystalline GaAs films, determined by van der Pauw measurements, is found to vary with doping in a manner similar to that of Se-doped n-type films; that is, $\rho \propto p^{-3/2}$, where p is the net hole concentration. Resistivities are generally two orders of magnitude greater than that of comparably doped single-crystal material, with the minimum observed resistivity being ~0.07 ohm-cm.

The physical properties of GaAs films grown on a variety of substrates – including Mo/glass, Mo/alumina, and Ge layers on all of the candidate insulator materials – have been studied, and the results of these investigations are described. In most cases the presence of the Ge intermediate layer resulted in more planar growth and, in some cases, in larger grain sizes than obtained for GaAs growth directly on the low-cost substrate material. However, Ge nucleation and growth on all of the glasses was found to be at relatively widely separated sites, with the result that incomplete coverage of the substrate was obtained.

Single-crystal window-type heterostructure solar cells have been fabricated in GaAℓAs/GaAs multilayer structures grown by the MO-CVD process. Devices with no AR coating have been evaluated under simulated AMO illumination and found to have conversion efficiencies as high as 12.8 percent. Devices with all-epitaxial junctions were found to have much higher efficiencies than those with junctions at the film-substrate interface. Open-circuit photovoltages as high as 0.99V, short-circuit current densities as high as 24.5 mA/cm^2, and curve fill-factors up to 0.74 have been achieved. These results clearly show that the MO-CVD process is capable of producing materials with the photovoltaic properties required for high-efficiency GaAℓAs/GaAs solar cells.

Polycrystalline solar cells have also been grown and fabricated. Initial results on Schottky-barrier solar cells formed on films grown on Mo/glass composite substrates indicated efficiencies of ~1.4 percent under simulated AMO illumination. Other composite substrates have also been used for fabrication of Schottky-barrier devices.

Various techniques for characterizing polycrystalline GaAs films have been developed further, and details of these studies are given.

Plans for the fourth quarter of work are outlined.

CONTENTS

CONTENTS (Cont)

ILLUSTRATIONS

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 Photovoltaic Conversion Program include establishment of total solar array production capacities of (1) 500 peak Mw/year of solar array modules at a market price of less than \$500 per peak Kw by FY 1985 and (2) 5 x 10^4 peak Mw/year of solar array modules at a market price of \$100 to \$300 per peak Kw by FY 2000.

The work of this contract is directed toward those goals. The overall objective of the 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. Acquisition of further important knowledge of thin-film deposition methods and thin-film technology for polycrystalline GaAs on various substrates is also expected to occur.

In addition, it is expected that any proposed device configuration will 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 the 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 appropreiate 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 film properties in terms of quantitative physical parameters; (5) alteration of the physical parameters of the films 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 x 10^4 peak Mw by the year 2000, with a selling price of \$100 to \$300 per peak Kw, "without creating inordinate technical and economic problems;" (6) the delivery of thin-film samples (minimum 4 cm^2 per month) to ERDA; and (7) the analysis and projection of cell costs for large-scale production in the future.

The general technical approach of the program involves application of the metalorganic chemical vapor deposition (MO-CVD) technique 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 are 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 and thus meet both the production capacity goal and the cost-per-watt goal of the National 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 is applied in this program, 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 according to the following simplified equation:

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

By mixing TMG in the gas phase with trimethylaluminum (TMA) and AsH_3, GaAℓAs is obtained upon pyrolysis at appropriate temperatures; the composition of the alloy is controlled by the ratio of the reactants. The organic byproduct, 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 (Ref 1).

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 still needs considerable attention; it requires cooperation of the relatively small number of manufacturers now engaged in supplying the various compounds used in this work to assure that materials of increasing purity and improved control of quality will become available. Additional principal technical problems to be solved 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: (1) Substrate Material Selection, Evaluation, and Development; (2) CVD Experiments and Parameter Studies; (3) Evaluation of Film Properties; (4) Experimental Photovoltaic Device Fabrication and Evaluation; and (5) Analysis and Projection of Cell Fabrication Costs. In addition, the Program Management Task defined in the Statement of Work of the contract is carried on in parallel with the above technical tasks.

This is the third Quarterly Project Report for this contract and covers the period 2 January through 2 April 1977. The contract activities during that period are described by task in the following section. Conclusions of the quarter's work are given in Section 3, and plans for the fourth quarter's activities are outlined in Section 4. Section 5 contains references used in the body of the report.

2. TECHNICAL PROGRESS

This section contains a summary of the results obtained during the third quarter of the contract. The discussion is arranged by task, although at times results are referred to in more than one place in the report, for clarity of presentation.

2.1 TASK 1. SUBSTRATE MATERIAL SELECTION, EVALUATION AND DEVELOPMENT

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

> Selected samples of both commerically 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.

During the first quarter a variety of candidate substrate materials was considered for use. Only a relatively small number of materials now commerically available--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 were developed to serve as the basis for identifying those candidate materials to be evaluated. Ten such materials were 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) thin-film Ge on glass; (9) thin-film Ge on Kovar-type alloy sheet; and (10) thin-film Mo on glass.

Several of these materials were evaluated in the first quarter by a standard GaAs film growth procedure using the MO-CVD process. Analysis of the properties of the polycrystalline GaAs films grown on these substrates in the first quarter showed only minor differences among the films. All of the candidate insulating substrate materials tested appeared to be non-reactive with the GaAs film or the reactants used to produce it, under the particular growth conditions investigated. However, it was found that bare Kovar was attacked by AsH_3 at temperatures above 500°C. The resulting compound formation and the high incidence of Ni-rich inclusions found in the deposited GaAs films make these Ni alloys unsuitable as substrates for direct growth of GaAs films by the MO-CVD method. The use of an intermediate layer of another material on the alloy might still permit its successful use as an inexpensive supporting underlayer, and the achievement of large-grain (10-20 μm) growth of Ge films on this alloy by GeH_4 pyrolysis in the first quarter indicated some promise for this configuration as a composite substrate. Mo substrates were also used for GaAs film growth, and contrary to the case for the Fe-Ni-Co alloys, no attack of the Mo substrates by AsH_3

was observed. Growth of GaAs on Corning Code 0317 and Code 1723 glasses did not result in any detectable bowing of the substrate-film composite. These glasses appeared to be stable in H_2 up to ~730°C. The high-purity polycrystalline aluminas ASM805 (99.9 percent) and ASM838 (99.5 percent) also appeared to be completely stable, physically and chemically, in the GaAs CVD environment.

During the second quarter contacts were maintained with various manufacturers of the substrate material types selected for use in the program, to ensure that samples would be available as needed for the CVD experiments (Task 2) and to encourage continuing efforts to identify other materials that might be even more satisfactory than those selected. As a result, additional supplies of the candidate substrate materials were obtained. Although several new sources of polycrystalline aluminas were found, none of the material received from such sources appeared any better in surface characteristics than ASM805 alumina (3M Co.), one of the 10 selected materials. Predeposition characterization of candidate substrate materials continued, with GaAs film growth by the MO-CVD method under a set of standard conditions still used as the critical test of a substrate's suitability. Composite substrates consisting of films of Mo 1-2 μm thick deposited by sputtering onto Kovar and several glasses and polycrystalline aluminas were prepared and tested by GaAs film growth. The effects of H_2 and AsH_3 atmospheres at two different temperatures (625 and 725°C) on the surfaces of the candidate glass substrates were examined, with only one glass (Corning Code 0211) adversely affected. Several substrate surface cleaning procedures were also evaluated. The most effective procedure tested included etching the substrate in Caro's acid (1:1 H_2SO_4:30 percent H_2O_2) as one of the steps. Preliminary examination of the effects on film growth of texturing the surface of a glass substrate indicated that further work with this method of influencing nucleation should be undertaken.

During the third quarter, attempts to obtain additional materials for consideration as substrates were continued, and evaluation of the 10 selected candidate materials also progressed, as described below.

In the third quarter, contacts with various manufacturers of glass, metal, and ceramic substrate materials continued. For example, AMAX Speciality Metals Corp. (Cleveland, OH) recently supplied generous samples of Mo, Mo alloy (TZM), W, and Mo-W alloy sheet for evaluation as substrate material. This now makes it possible to test samples of this class of metals having slightly different compositions and thermal expansion coefficients for their compatibility with the GaAs MO-CVD process, and to determine if differences in film nucleation and growth occur as a result.

GTE Sylvania (Towanda, PA) provided specially annealed Mo sheet for use in comparative studies of GaAs growth on Mo of different grain sizes, to determine the effect of grain size on film properties. Depending on the results obtained with such films, further studies of GaAs growth on specially prepared deposited Mo films on various substrates will be performed. GTE Sylvania has now provided Mo sheets annealed at 950, 1100, and 1725°C. The largest grain sizes were produced in the material annealed at 1100°C; some grains were as wide as 20 μm, but most were 5-10μm in size.

Two of the three Ni-Fe alloys of different Ni composition, and therefore of different thermal expansion coefficients, have been prepared for the program and have been received from Pfizer Metals (Wallingford, CT). One alloy has 42 percent Ni, and the other is Sealvar, A Co-Ni-Fe alloy produced by powder metallurgy. These materials were to be considered for use in achieving thermal expansion coefficient matching to intermediate layers, such as Mo and Ge, in attempting to enhance growth of large-grained GaAs. However, recent experiments with GaAs growth on composite substrates of thick Ge (4 μm) deposited by CVD on Kovar sheet have shown that the strong interaction between the GaAs film and the Ni in the Kovar alloy occurs even when there is an intermediate layer of Ge on the alloy. Because of this adverse effect on film growth and film properties, Kovar and Kovar-like (e.g., Rodar and various Fe-Ni alloys) materials will no longer be used. Specifically, composites of thin-film Ge on Kovar-type alloy sheet will be dropped from the list of 10 candidate substrates used for continued experimentation.

Based on other experimental results obtained to date for GaAs growth on various substrate materials, it is now possible to narrow further the list of 10 candidate substrate materials selected at the end of the second month of the program for experimental evaluation. Because of the high resistivities consistently obtained in polycrystalline films of GaAs or GaAℓAs grown on substrates of the various candidate glasses--irrespective of the conductivity type or the concentration of added dopant--it is clear that a conducting metal layer or grid of large area coverage will be required for adequate contact to the base layer of a polycrystalline solar cell structure.

Consequently, totally bare glasses (Corning Codes 0317, 7059, 1723, and 0211) and totally bare Corning Code 9606 glass-ceramic will no longer be considered candidate substrates. However, Codes 0317, 7059, 1723, and 9606 when accompanied by an appropriate open conducting grid on the growth surface will remain as candidates. Corning Code 0211 glass is being eliminated from further extensive use except when completely coated with Mo or other suitable material, because of its Zn impurity content discussed in previous reports. Arrangements for sputter-coating substrates with thin films of Mo have been made with another group within the Rockwell Electronics Research Center. In addition, a local service laboratory has also been contacted for similar work and is available on a quick-service basis if further requirements develop.

Graphite is being added to the list of candidate substrate materials to be evaluated in this program because of its apparent compatibility with GaAs and with the MO-CVD growth environment. Deposition directly on graphite and on an intermediate metal or Ge layer could lead to films with electrical and physical properties adequate for photovoltaic applications. Later experiments could involve the in situ formation of a carbon film on a low-cost substrate as a means for enhancing grain growth of GaAs and/or as a high-conductivity back contact for solar cell device use. Polished substrates of graphite grade DFP-3-2 (high density, high purity) have been ordered from Graphite Machined Products (Downey, CA), which represents Poco Graphite, Inc. (Decatur, TX); experiments with these substrates will be undertaken in the near future.

ASM805 polycrystalline alumina ceramic from the 3M Co. is also being eliminated from further experimental use, primarily because polycrystalline films grown on it have also exhibited high resistivities that would require extensive contact gridding at the film-substrate interface, and its relatively higher cost compared with that of the glasses renders it non-competitive with them for the present application. One of the reasons for conducting growth experiments with a large-grained polycrystalline alumina substrate is that it provides a useful intermediate crystal structure between single-crystal and fine-grained polycrystalline or amorphous substrates, and permits the study of various aspects of film nucleation and early-stage growth. However, the large-grained Vistal polycrystalline alumina ceramics from Coors fill this need more satisfactorily than does ASM805; the former will thus be retained as an experimentally useful candidate substrate material - at least for the present time - despite its relatively high cost.

2.2 TASK 2. CVD EXPERIMENTS AND PARAMETER STUDIES

This task was summarized in the original program proposal 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.

In the first quarter, experimental investigation of the MO-CVD process began early in the first month, and employed an existing CVD reactor system that had been used for previous company-sponsored investigations in the GaAs-GaAℓAs system. A second MO-CVD reactor system was designed and fabrication was begun, but delays in delivery of some of the essential components prevented its completion before the end of the quarter. The existing reactor system was used in the first quarter for 101 MO-CVD experiments. The majority of these were in 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. 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 upon the flow rate (i.e., concentration) of the doping gas was investigated, and study of the first three doping systems was completed. Polycrystalline GaAs films with apparent grain sizes in the 2 to 5 μm range and high electrical resistivities in the undoped condition were grown by MO-CVD on several of the candidate low-cost substrate materials in the first quarter.

During the second quarter of the contract, 59 MO-CVD experiments were performed in the original reactor (the "A" reactor) and 26 MO-CVD experiments were done in the new dedicated CVD reactor (the "B" reactor), which was completed in the second quarter. The experiments done in Reactor A included (1) growth of GaAℓAs on single-crystal substrates; (2) growth of polycrystalline GaAs on candidate low-cost substrates; (3) studies of the nucleation of GaAs on low-cost substrates; (4) studies of the effects of H_2 and AsH_3 on the candidate glasses; (5) studies of the effect of surface texturing on the growth of GaAs on a selected glass substrate (Corning Code 0211); and (6) studies of the growth of GaAs on Mo films deposited on various low-cost substrates. In addition, 45 other MO-CVD runs were made in Reactor A to study the problem of faulty SiC-coated graphite susceptors. The fact that adequately sealed susceptors were not available from the usual suppliers prevented continuation of the study of doping of GaAℓAs films, and prompted an extensive parallel investigation of various alternative solutions to this problem.* This also delayed the planned fabrication of thin-film GaAℓAs/GaAs heterostructure solar cells by the MO-CVD technique. The experiments done in the new Reactor B were principally the growth of (1) undoped GaAs films on single-crystal substrates and (2) Se-doped GaAs films on single-crystal substrates. The undoped GaAs films were grown to check out the reactor performance, while the doped films were grown to determine the n-type Se-doping characteristics of this new reactor.

During the second quarter polycrystalline undoped and Se-doped films of GaAs were grown on Corning Codes 0211, 0317, 1723, and 7059 glasses and on the polycrystalline aluminas ASM805 (3M Co.) and Vistal (Coors), the latter two in various refired conditions which result in increased grain sizes. All of these substrates except 0211 glass appeared stable in H_2 at 725°C. Grain sizes in films on the glasses were typically in the 1-2 μm range, although some larger grains were found intermixed under certain conditions -- e.g., in films grown on 7059 glass at 675°C and on Corning Code 9606 glass-ceramic at 725°C. Grain sizes in polycrystalline GaAs films on the aluminas were found to be directly related to the grain sizes in the substrates and were quite large in some cases (up to ~100 μm or more).

It was also found that at temperatures above ~600°C the Corning Code 0211 glass begins to discolor and soften in H_2, and at higher temperatures (those used for deposition of GaAs) additional changes occur that result in film properties quite different from those found with other glasses. Relatively large grains (5-10 μm) and p-type carrier concentrations were found in the GaAs films; the apparent acceptor doping is tentatively attributed to Zn impurity in the glass, and the larger grain size is probably associated with a tendency of this glass to induce relatively widely-spaced nucleation of the growing GaAs film -- a tendency also shared, to a much smaller degree, by Corning Code 1723 glass. Some similarities were also observed in the post-nucleation early-stage growth behavior at 725°C of GaAs films on Corning Code 9606 glass-ceramic and polished ASM805 polycrystalline alumina substrates, presumably due to the regions in the surface of the former in which recrystallization has occurred during formation of the glass-ceramic material. Polycrystalline GaAs films grown by the MO-CVD method were found to show a slightly preferred {111} crystallographic orientation on the metals and the aluminas investigated. The films deposited on the various glasses, however, exhibit a marked tendency for completely random crystallographic orientation.

Many of these investigations have extended into the third quarter. During this period 69 MO-CVD experiments were carried out using Reactor A and 61 MO-CVD experiments were performed in Reactor B. In addition, 55 separate experiments were done to examine further the problem of faulty susceptors; as before, these studies were supported largely by separate company funds.

The 130 contract-related MO-CVD experiments performed during this quarter can be grouped into nine categories: (1) growth of polycrystalline GaAs layers on uncoated low-cost substrates (from the candidate list); (2) growth of polycrystalline GaAs layers on low-cost composite substrates of sputtered Mo films that had been deposited on glasses, polycrystalline aluminas and Kovar metal; (3) growth of poly-

---

*Several possible solutions are still being investigated. Because of the nature of the problem and the fact that solution is important to several other programs in progress at Rockwell, these investigations have been supported largely by company (i.e., not contract) funding.

crystalline Ge films on uncoated low-cost substrates; (4) growth of GaAs films on low-cost composite substrates consisting of Ge films on glasses, aluminas, and Kovar metal; (5) growth of polycrystalline GaAs n/n$^+$, p/p$^+$, and p-n junction structures on low-cost substrates; (6) growth of polycrystalline p-type $Ga_{(1-x)}A\ell_xAs$:Zn ($x \approx 0.8$) films on low-cost substrates; (7) growth of doped and undoped single-crystal GaAs and $Ga_{(1-x)}A\ell_xAs$ ($x \approx 0.8$) films on GaAs:Cr single-crystal substrates; (8) growth of single-crystal $A\ell As$ films on single-crystal substrates; and (9) growth of single-crystal $GaA\ell As$/GaAs heterostructure solar cells.

Polycrystalline GaAs films have now been grown on all of the potentially low-cost materials in the candidate list given in Quarterly Report No. 1 (Ref 2). All of the MO-CVD experiments concerning the growth of polycrystalline GaAs films were carried out in Reactor A, the system that has been used since the start of the program. Most of the single-crystal films were grown in Reactor B, the new dedicated reactor; however, some single-crystal films were grown in Reactor A, also.

2.2.1 Growth of Polycrystalline GaAs on Uncoated Low-cost Substrates

Doped and undoped polycrystalline GaAs films have been grown on a number of uncoated candidate low-cost substrates to study the characteristics of n- and p-type doping of polycrystalline GaAs grown on these materials. In addition, undoped films have been grown to study GaAs nucleation and early growth characteristics on certain low-cost substrates.

As discussed in Quarterly Report No. 2 (Ref 3), Se-doped films of polycrystalline GaAs grown on the glass and alumina substrates employed in this program generally exhibit high resistivities. To further study this phenomenon, polycrystalline GaAs:Se films were grown at 725 and 775°C on Corning Code 0317, 1723, and 7059 glasses and on several polycrystalline aluminas — ASM805 with a normal firing history, ASM805 with one additional firing (ASM805-1), and Coors Vistal with five extra firings beyond normal (Vistal-5).

A change was made in the flowmeter tube employed for controlling the H_2Se (265 ppm-in-H_2 mixture) flow rate to allow much higher doping levels to be achieved. Even with this modification, low-resistivity Se-doped GaAs films were not obtained except on the relatively large-grained (and relatively expensive) Vistal-5 alumina. These results are discussed further in Section 2.3 (Task 3).

The growth of polycrystalline GaAs:Zn films on these low-cost substrates was also extensively studied during the third quarter. A diethylzinc (DEZ) source held at 0°C was used to supply the Zn doping, as discussed in Quarterly Report No. 1 for the Zn doping of single-crystal GaAs:Zn films (Ref 2). Polycrystalline GaAs:Zn films were grown at temperatures of 650 and 725°C on Corning Code 0317, 1723, and 7059 glasses as well as on the polycrystalline aluminas ASM805, ASM805-1, and Vistal-5. The measured resistivities of all of these films were high; as with Se-doped material, films on Vistal -5 showed the lowest resistivities. A detailed discussion of these results is also given in Section 2.3.

Undoped films of GaAs were grown on Corning Code 0211 glass to study further the unintentional p-type doping observed in presumably undoped GaAs films grown on this substrate, as reported in Quarterly Report No. 2 (Ref 3). Undoped GaAs films grown at 725°C on 0211 glass exhibit resistivities of $\sim 10^{-2}$ ohm-cm and doping levels of $\sim 10^{18}$ cm^{-3}. To determine if this doping could be controlled, a substrate of 0211 glass was heated at 800°C for 30 min in a H_2 atmosphere. The temperature was then lowered to 725°C and an undoped GaAs film was deposited in the normal manner. Measurements of the electrical properties of this film showed that it was highly resistive and was not p-type, contrary to the case for films deposited on 0211 substrates that had not been fired in H_2 at high temperatures. Unfortunately, this firing process resulted in extensive softening of the glass substrate and, as a result, the surface was quite rippled.

To determine if the p-type doping of GaAs polycrystalline films grown on 0211 glass could be used to advantage in the growth of polycrystalline p-n junctions, a 30 min deposition of undoped GaAs followed by a 15 min deposition of heavily Se-doped GaAs was made at 725°C. Voltage breakdown measurements on the resulting structure showed the top layer to be heavily compensated p-type GaAs. Thus, it appears that the p-type doping provided by the 0211 glass substrate would have to be reduced to permit the formation of a p-n junction in this manner. Although such a reduction might be possible by a high temperature firing sequence as described above, this process results in significant deviations from planarity in the substrate surface and would thus make processing of such p-n junction structures difficult.

Undoped polycrystalline GaAs films were also grown on Corning Code 0317 glass at 550 and 625°C for use as randomly-oriented polycrystalline x-ray standards. In addition, 30-sec undoped GaAs depositions were made on uncoated Corning Code 0211, 0317, 1723, and 7059 glasses to study the nucleation behavior of GaAs on these substrates by observing partial-coverage layers. A similar nucleation experiment was also carried out employing a deposition time of 2 sec and Code 0211, 0317, 1723, and 7059 glass substrates that had been patterned photolithographically and etched with buffered HF. The results of these GaAs deposition experiments are described in Section 2.3.

The results obtained to date on the resistivity of doped GaAs films grown on uncoated glasses and polycrystalline aluminas indicate that some type of conducting back contact is required for the fabrication of polycrystalline GaAs solar cells on these low-cost substrates. For this reason, work during the remainder of the third quarter concentrated upon composite substrates employing a conducting intermediate layer.

2.2.2 Deposition of GaAs Layers on Mo-coated Low-cost Substrates

Nucleation experiments were also performed on Corning Code 0317 and 7059 glasses that had been sputter-coated with a ~ 1 μm-thick Mo film. Undoped GaAs depositions were carried out at 725°C for 2 sec and for 30 sec to study the effects of the presence of the thin Mo intermediate layer on the early growth habits of GaAs films. A description of these results is given in Section 2.3, in the discussion of Task 3 results.

Doped films of GaAs:Se have also been grown at 725°C on Mo-coated 0317, 1723, and 7059 glasses as well as on Mo-coated Vistal with 2 firings beyond normal (Vistal-2) and on Mo-coated Vistal-5. The Mo films employed in these experiments were also ~1 μm thick. The Mo/7059 glass composite substrate curled severely at the growth temperature, indicating a poor match in the thermal exapnsion coefficients of Mo and Code 7059 glass. For this reason this particular composite substrate was not used further in GaAs deposition experiments.

The physical properties of GaAs films deposited on the Mo-insulator composite substrates employed appear to be similar to those of polycrystalline GaAs films deposited directly on bulk Mo substrates, as is expected. However, the substrates consisting of 1 μm Mo films on glass that were studied are much less expensive than is bulk Mo, and are thus much more attractive for use in low-cost solar cells.

A film of undoped GaAs was also grown at 725°C on a Mo-coated polished Kovar metal substrate. The 1 μm-thick Mo coating was intended to eliminate the introduction of Ni into GaAs films grown on Kovar as is observed for the MO-CVD growth of GaAs on bare Kovar metal (Ref 2). SEM examination of the surface of this film indicated that significant Ni incorporation still occurred despite the Mo intermediate layer. Thus, it appears that this technique will not eliminate the substrate-film interaction that results in the Ni incorporation. The use of Mo/Kovar composite substrates was not studied further.

The above results are described further, in terms of the properties of the films produced, in the Task 3 discussion that follows in Section 2.3.

2.2.3 Growth of Ge Films on Uncoated Low-cost Substrates

Undoped Ge films were grown at 725°C on Code 0211, 0317, 1723, and 7059 glasses; the polycrystalline aluminas ASM805, ASM805-1, and Vistal-5; and polished Kovar metal substrates. The Ge films grown on Kovar showed large (~10 μm) surface features, as was found earlier in the program when this combination was first examined (Ref 2). The Ge films grown on the aluminas had surface features that correlated well with the grain structure of the respective substrate, indicating that epitaxy was occurring on individual grains as is observed for growth of GaAs films on these materials. Ge films grown on glasses exhibit somewhat larger surface features than GaAs films grown on the same materials, indicating that it might be possible to enhance the grain size of polycrystalline GaAs films by employing Ge intermediate layers. This was investigated further, as discussed in the following section.

2.2.4 Growth of GaAs on Ge-coated Low-cost Substrates

Polycrystalline GaAs films were grown at 725°C on composite substrates of Ge films deposited on Corning Code 0211, 0317, 1723, and 7059 glasses; the polycrystalline aluminas ASM805, ASM805-1, and Vistal-5; and Kovar metal. The Ge intermediate layer in each case was deposited in the same CVD run, just prior to the growth of the GaAs film (and at the same temperature).

The undoped GaAs films grown on these Ge intermediate layers all exhibited n-type conductivity, as determined by voltage breakdown measurements.

The GaAs/Ge/Kovar films exhibited the phenomenon of Ni incorporation into the GaAs film, as evidenced by strong Ni-rich regions on the top surface that were identified by energy dispersive x-ray analysis performed in the SEM and also by electron microprobe analysis. This phenomenon was also observed in the growth of GaAs films on uncoated Kovar substrates, as described in Quarterly Report No. 1 (Ref 2). To attempt to reduce the Ni incorporation, a GaAs/Ge/Kovar film was grown at 650°C. Energy-dispersive x-ray analysis showed that Ni incorporation was still a problem, even with the lower growth temperature.

It thus appears that Kovar and other related Ni-Fe-Co alloys are incompatible with MO-CVD growth of GaAs films. Further description of these results is given in Section 2.3, in which the properties of the films are summarized.

2.2.5 Growth of Polycrystalline GaAs Solar Cell Structures on Low-cost Substrates

Polycrystalline GaAs thin-film structures have been grown on thin sheets of Mo and W metal and on composite substrates consisting of a thin Mo film on Code 0317 glass, for fabrication of polycrystalline GaAs solar cells. The structures that were grown include GaAs n/n^+ double layers on Mo metal substrates and on composite substrates consisting of a Mo film on Code 0317 glass. Also, a GaAs p/p^+ structure has been grown on a Mo film/0317 glass composite substrate. Polycrystalline GaAs p-n junction structures have also been grown on Mo, W, and Mo film/0317 glass composite substrates.

Some of the n/n^+ structures have been fabricated into Schottky-barrier diode devices by the evaporation of a ~50Å-thick Au metal film upon the top surface. The p/p^+ structure was also processed in this manner, but a short-circuit resulted so Schottky-barrier behavior was not observed. A detailed description of the performance of Schottky-barrier solar cells fabricated in these polycrystalline GaAs films is given in Section 2.4 (Task 4).

Evaporated Au-Zn contacts have been applied to a number of the polycrystalline p-n junction samples. Preliminary results indicate the presence of a p-n junction in these films, but detailed I-V characteristics have not yet been measured.

2.2.6 Growth of Zn-doped GaAℓAs Films on Low-cost Substrates

To study the growth of polycrystalline p-type GaAℓAs films with the properties that would be required for polycrystalline GaAs p-n junction solar cells, Zn-doped films of $Ga_{(1-x)}A\ell_xAs$ ($x \approx 0.8$) were grown at 750°C on the Corning Code 0211, 0317, 1723, and 7059 glasses as well as the polycrystalline aluminas ASM805, ASM805-1, and Vistal-5.

Although p-type doping could be detected by voltage breakdown measurements of the GaAℓAs:Zn films grown simultaneously on single-crystal (0001) sapphire control slices, such measurements of the polycrystalline GaAℓAs:Zn films grown on the glass and polycrystalline alumina substrates simply indicated that these films had high resistivity. These results are expected from previous experience with polycrystalline GaAs:Zn films in this contract.

2.2.7 Growth of Single-crystal GaAs and GaAℓAs Films on GaAs Substrates

Se-doped n-type GaAs films and Zn-doped p-type GaAs and $Ga_{(1-x)}A\ell_xAs$ ($x \approx 0.8$) films were grown on (100)-oriented GaAs:Cr high-resistivity substrates to study the doping characteristics of Reactor B, the new dedicated MO-CVD reactor completed during the second quarter. Some data for the Se-doping of GaAs films grown in this reactor were given in Quarterly Report No. 2 (Ref 3). Both the older data and recent data are shown in Figure 2-1.

It can be seen that the Se doping of GaAs films grown at temperatures of 700 and 750°C follows very nearly the same function of the H_2Se flow rate employed. The line drawn through the data of Figure 2-1 has a slope of unity, showing a linear relationship between the dopant gas flow rate and the measured net donor concentration, as is expected.

Single-crystal GaAs:Zn and GaAℓAs:Zn films have also been grown on GaAs:Cr substrates, to determine the dependence of the Zn doping upon the effective flow rate of the DEZ carrier gas (H_2) into the reactor chamber. Figure 2-2 shows the results obtained by van der Pauw measurements made on the GaAs:Zn films. The line in this figure is also drawn with a slope of unity. The measured values of the net acceptor concentration are seen to follow a linear dependence upon the effective H_2 carrier gas flow rate through the DEZ, as would be expected.

Single-crystal p-type $Ga_{(1-x)}A\ell_xAs$:Zn ($x \approx 0.8$) films have also been grown on GaAs:Cr substrates, to determine the experimental conditions required for the growth of heavily doped p-type GaAℓAs films as will be needed for the window layers for GaAℓAs/GaAs heterostructure solar cells. $Ga_{0.2}A\ell_{0.8}As$:Zn films were grown with a doping of $\sim 10^{18}$ cm^{-3}, required for this window layer.

2.2.8 Growth of Single-crystal AℓAs Films

Because AℓAs has a higher bandgap energy than GaAs or GaAℓAs alloys, it might be the best material for the window layer of a heterostructure GaAs solar cell. Single-crystal films of AℓAs have been grown at 750°C on single-crystal (0001) sapphire and (100) GaAs substrates. Some of the AℓAs/GaAs films were stored in a dry N_2 atmosphere to prevent any oxidation of the epitaxial film. These were subsequently used in x-ray diffraction measurements of the AℓAs lattice parameter. AℓAs films that were exposed to air gradually oxidized over a period of 1-2 weeks.

2.2.9 Growth of Single-crystal GaAℓAs/GaAs Heterostructure Solar Cells

Single-crystal GaAℓAs/GaAs heterostructure solar cells have been grown with a thin (500-1500Å) $Ga_{(1-x)}A\ell_xAs$($x \approx 0.8$) layer as a low-surface-recombination hetero-barrier and transparent window. Two-layer epitaxial structures of p-GaAℓAs:Zn/p-GaAs:Zn and three-layer epitaxial structures of p-GaAℓAs:Zn/p-GaAs:Zn/n-GaAs:Se have been grown on n-type (100)-oriented GaAs:Si substrates. The two-layer structures were grown in Reactor B while the three-layer structures were grown in Reactor A. Films were grown with various doping levels and layer thicknesses at 750 and 775°C.

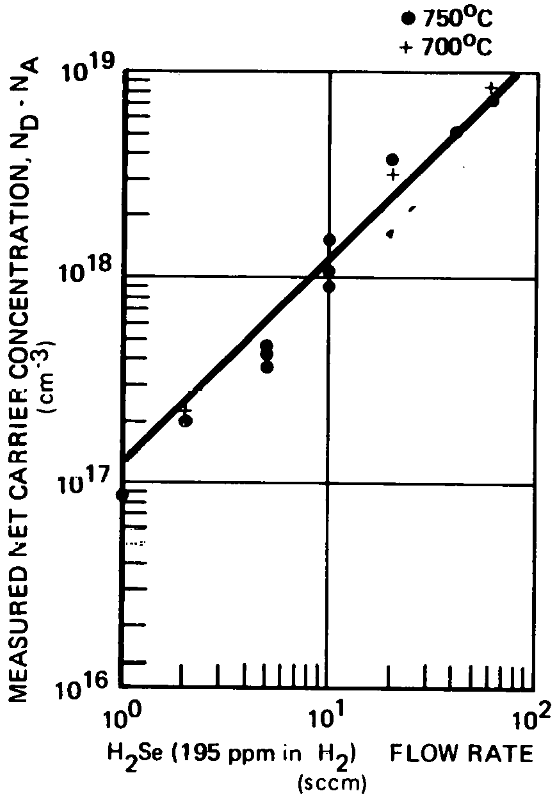


Figure 2-1. Measured Carrier Concentration for Se-doped GaAs Films Grown at 700 and 750°C, as Function of H_2Se Flow Rate

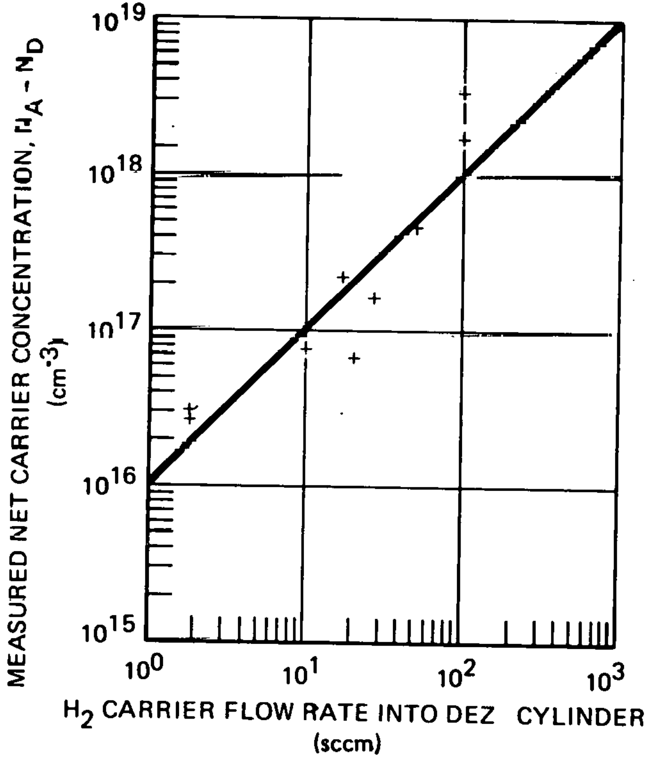


Figure 2-2. Measured Carrier Concentration of Zn-doped GaAs Films as Function of Carrier Gas Flow Rate Through DEZ Source

A number of these structures have been cleaved and chemically stained to define the interfaces between layers. Both stained and unstained cleaved cross-sections have been examined in the SEM to determine layer thicknesses. Figure 2-3 shows an SEM photograph of an unstained cleaved cross-section of one of the three-layer epitaxial structures. The location of the p-n junction is easily seen. The location of the interface between the n-type epitaxial layer and the n-type substrate is not easily seen on unstained cross-sections because the n-type doping concentrations in the two regions are nearly equal ($\sim 10^{18}$ cm^{-3}). The location of this interface was determined for this device by SEM examination of a stained portion of the cleaved piece shown in Figure 2-3.

The 500Å-thick GaAℓAs window layer is not visible in the figure because of secondary electron reflection at the top sample edge. The thickness of this layer is estimated from the results of studies of heteroepitaxial GaAℓAs films grown under the same deposition conditions on single-crystal (0001) sapphire substrates. Surface profilometer measurements of the thicknesses of the GaAℓAs heteroepitaxial films on sapphire are made after a portion of the deposited layer is completely removed from the sapphire substrate. These measurements have shown that good film thickness reproducibility and control can be realized in the reactors now being used in these studies.

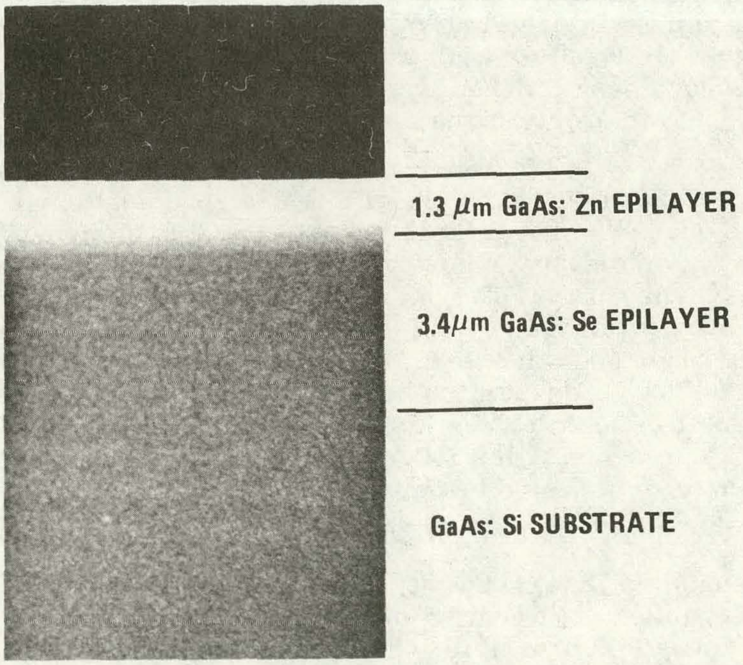


Figure 2-3. SEM Photograph of Unstained Cleaved Cross-section of 3-layer Epitaxial Solar Cell Structure. Thin (~500Å) GaAℓAs Window Layer Masked by Secondary Electron Reflection at Upper Edge of Sample

$Ga_{(1-x)}Al_xAs$ ($x \approx 0.8$) films ~500Å thick have been reproducibly grown over 3.8 cm-diam sapphire substrates (11.4 cm^2 area) in both Reactors A and B. This assures that the GaAℓAs window layer is uniform over even the largest substrate (~6 cm^2) employed to date in these solar cell structure growth experiments. Details of the fabrication of solar cell devices from these structures are given in Section 2.4 (Task 4).

2.2.10 Experimental Evaluation of SiC-coated Susceptors

As discussed in Quarterly Report No. 2 (Ref 3), a significant problem that has affected the progress of certain portions of this program has been the difficulty encountered in attempting to obtain properly coated and sealed SiC-coated graphite susceptors. The products of five of the major suppliers of SiC-coated susceptors used in commercial Si epitaxial reactors have been examined during this quater, with the net conclusion that the problem remains unsolved.

Of the 55 MO-CVD runs made during the quarter to study the susceptor problem all but 2 were made to evaluate SiC-coated susceptors purchased from these manufacturers. A total of 14 different susceptors were used in MO-CVD runs to deposit $Ga_{(1-x)}Al_xAs$ ($x \approx 0.8$) films on (0001) sapphire substrates. As noted previously (Ref 3), the deposition of GaAℓAs films seems to be extremely sensitive to the quality of the SiC coating, probably because of the very reactive Aℓ compound used in the growth of such films.

Of the 14 susceptors examined, only one has proven satisfactory. This susceptor has now been used in over 100 MO-CVD runs, and has been acid-cleaned in a 2:9 mixture of $HF:HNO_3$ after each run. It is still performing satisfactorily. Additional susceptors have been ordered from this supplier in an attempt to obtain duplicate performance, but the order has not yet been filled.

Two alternatives to the use of SiC-coated graphite susceptors were also evaluated during this quarter. The first is the use of a disk of high-purity (and thus high-resistivity) Si as a susceptor. The second is the use of a high-purity (99.97 percent) Mo disk as a susceptor. The Si disk was placed on a SiC-coated graphite susceptor to aid in the coupling of the rf field into the low-conductivity (~158 ohm-cm) Si. Even with this arrangement, it was difficult to attain measured susceptor temperatures greater than 760°C, despite the fact that the full output of the rf generator was used. The GaAℓAs film deposited in this run had poor morphology, but this may have been a result of the presence of the SiC-coated susceptor support used for the Si disk. This susceptor was known to be incompletely sealed, and it was used simply to determine if the use of the Si disk on top would permit the growth of high-quality GaAℓAs films.

The use of a low-resistivity doped Si disk as a susceptor would probably allow the direct coupling of rf energy into the susceptor without the use of a SiC-coated graphite base. This prossibility has not yet been evaluated experimentally, however.

A $Ga_{(1-x)}Al_xAs$ ($x \approx 0.8$) film was also grown on (0001) sapphire at ~775°C employing a high-purity machined Mo disk as a susceptor. The GaAℓAs film grown in this experiment also had poor surface morphology, so this alternative has not been further studied.

2.3 TASK 3. EVALUATION OF FILM PROPERTIES

The activities originally planned for inclusion in this task are summarized 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 was dominated by two main areas of investigation - the electrical characterization of single-crystal GaAs and GaAℓAs films, and the electrical and structural evaluation of polycrystalline GaAs grown on a variety of dissimilar substrates. In addition, some characterization technique development was begun.

The majority of the effort during the second quarter was devoted to characterizing the physical and electrical properties of polycrystalline films of GaAs grown on various potentially low-cost substrate materials - mainly insulators - from the list of candidate substrate materials identified in the first quarter. The rationale for emphasizing the low-cost substrates earlier in the program than originally planned was provided by early measurements of polycrystalline films grown on insulators, which indicated high electrical resistivity for most polycrystalline GaAs films examined. Because of the importance of these electrical properties to eventual cell design, fabrication, and utilization, this part of the planned program was undertaken early in the second quarter.

Unfortunately, all undoped and Se-doped polycrystalline GaAs films on the candidate insulator substrates (other than 0211 glass) were found to have resistivities greater than is desirable for the fabrication of solar cells on these low-cost materials. The lowest resistivity obtained in any Se-doped polycrystalline GaAs film on glass (excluding Corning Code 0211) was about 10 ohm-cm. The lowest resistivity obtained in any Se-doped polycrystalline film on the aluminas was about 2 ohm-cm; in these films the resistivities were found to have an inverse relationship to grain size in the substrate, at all doping levels.

Whereas good correlations were obtained for carrier concentration measurements by C-V analysis and the van der Pauw method for polycrystalline GaAs films on Mo, carrier concentrations in polycrystalline films on aluminas as determined by C-V analysis were at times two to three orders of magnitude lower than that found for the companion epitaxial film on sapphire as determined by van der Pauw measurements.

It was suggested that these discrepancies may be caused by excessive series resistance of the polycrystalline samples, giving erroneous results by the C-V method. The use of thin intermediate layers of Mo on some of the other substrate materials was suggested as a means of improving the base region sheet conductivity in polycrystalline GaAs thin-film cell structures prepared by the MO-CVD process.

These efforts have been continued where appropriate during the third quarter, and the film evaluation activities have been expanded to include determination of the structural and physical properties of GaAs films deposited on conducting and composite substrates and the electrical properties of p-type polycrystalline GaAs films. The composite substrates considered to be the best "first attempt" substrates were (1) Mo films on glass, (2) Ge films on glass, and (3) Ge films on Kovar. The results of growth of GaAs on all of these composites have been evaluated and are discussed below. In addition, the electrical properties of GaAs:Zn p-type material grown on the insulating substrates were also evaluated. This was considered to be of great importance, since the behavior of n-type polycrystalline GaAs was shown to be dominated by grain boundary effects which limited the resistivity of the material to very high values, even at high doping levels.

Development of characterization techniques for polycrystalline materials has continued with some success. However, the very high resistivity of the polycrystalline GaAs has frustrated some of the planned activity, particularly in the area of grain size determination, where suitable Schottky barrier samples for EBIC-mode examination of films on insulators have not been achieved. The various experiments performed and techniques developed to date are described in the following sections.

2.3.1 Electrical Properties of Polycrystalline GaAs:Zn

As described in the second quarterly report (Ref 3), n-type GaAs grown on the candidate insulating substrates was found to be very resistive. The minimum resistivity found was ~2 ohm-cm in a film grown on refired Vistal, with a carrier concentration $n \approx 3 \times 10^{18}$ cm^{-3}. Attempts to reduce the resistivity by increasing the doping to the solid solubility limit and beyond resulted only in higher resistivity films. Films grown on glasses and other ceramics were still higher in resistivity, the lowest being approximately 10 ohm-cm. It seemed clear that resistivities this high would probably not be suitable for a 1 μm-thick layer that was to be contacted by a grid contact, since the resulting device series resistance would be too high. Consequently, it was decided that n-type GaAs would probably not be suitable as the top layer of a p-n junction solar cell made by the MO-CVD method.

These results underlined the differences between polycrystalline and single-crystal materials and the need for complete materials characterization before making a final decision about a solar cell configuration. Consequently, a series of p-type Zn-doped GaAs samples was grown on all of the candidate insulators, under a variety of growth conditions. The doping level and growth temperature, in particular, were varied in a systematic manner; films 5 to 8 μm thick were grown.

The electrical properties were measured by the van der Pauw technique. In most of the polycrystalline films the carrier concentration could not be measured and had to be inferred from the carrier concentration of a film grown on a single-crystal sapphire substrate in the same experiment. In those cases where the carrier concentration could be measured, reasonable but far from good agreement was obtained between the single-crystal and polycrystalline samples.

The data are shown in Figure 2-4, where the resistivity of the p-type polycrystalline samples is plotted as a function of the net carrier concentration as determined by measurement of the carrier concentration of a companion epitaxial GaAs/sapphire sample. Whenever possible, for the samples at high doping concentrations (>10^{19} cm^{-3}), the resistivity is plotted versus the hole concentration measured in the sample itself. The data show that the resistivity decreases monotonically with doping following a relationship which could be roughly described as $\rho \propto p^{-3/2}$. This is particularly true for the samples grown on the various glass substrates. (Corning Code 0211 was omitted from this study owing to its tendency to dope films with residual impurities in the glass, as mentioned earlier.)

The data for p-type films grown on the aluminas show a similar scatter to that obtained for n-type GaAs films on aluminas, as can be seen by examination of Figure 2-5. Note also that the resistivity of films of either type grown on aluminas is consistently lower than those on glass, presumably because of the larger grain size obtained for films grown on the polycrystalline aluminas. The minimum measured resistivity for a p-type GaAs polycrystalline film is seen to be 0.07 ohm-cm at a doping level of ~10^{20} cm^{-3}. This is more than an order of magnitude lower than any resistivity achieved with polycrystalline n-type material, and results primarily from the ability to dope p-type GaAs more heavily. In fact, the data shown in Figure 2-5 for n-type material fall, within acceptable experimental scatter, along the same general curve as do the results for p-type material shown in Figure 2-4. Thus, the dominance of grain boundaries in determining the resistivity of these films is clearly demonstrated.

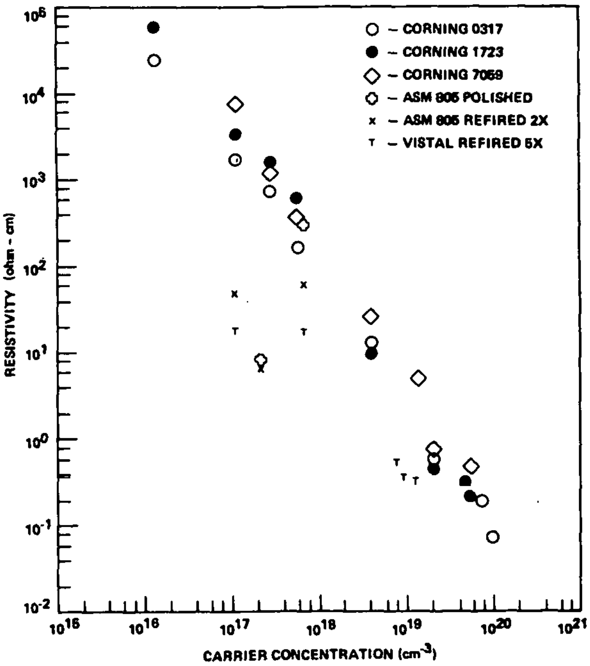


Figure 2-4. Resistivity of Polycrystalline P-type GaAs on Variety of Substrates as Function of Measured or Inferred Carrier Concentration. (Inferred carrier concentrations are those measured on companion sapphire substrates)

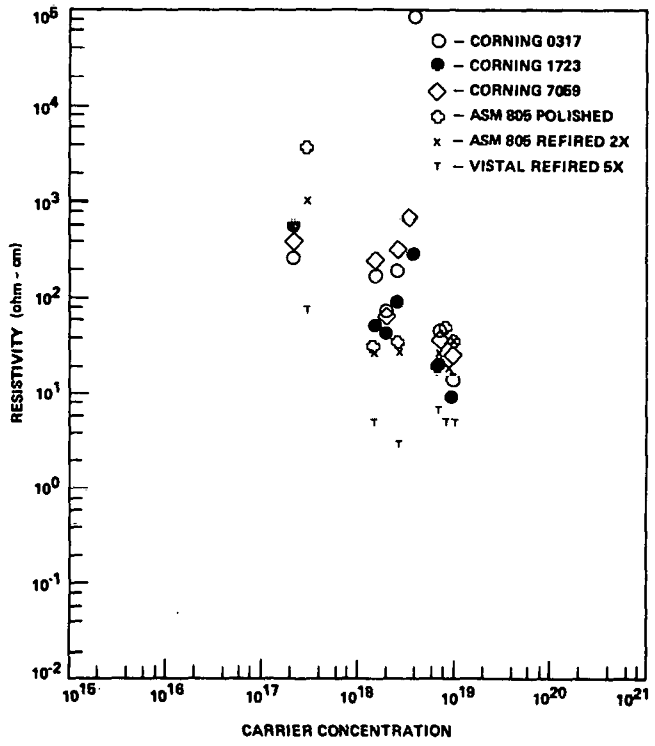


Figure 2-5. Resistivity of Polycrystalline N-type GaAs on Variety of Substrates as Function of Carrier Concentration Measured on Companion Single-crystal Sapphire Substrate

The measured hole concentrations in p-type polycrystalline GaAs films were never found to be lower by more than a factor of three than those found in the companion epitaxial films on sapphire. As a result, impurity segregation at grain boundaries to produce lower-than-expected intragrain doping can probably be discounted as a cause for the high resistivity. This conclusion is supported by the data given in Table 2-1, which includes the measured mobility and carrier concentration values for polycrystalline GaAs films grown on several substrates, along with the same quantities measured on the companion GaAs/sapphire sample.

In all cases the polycrystalline sample has a mobility two orders of magnitude lower than that of the companion epitaxial sample. In addition, the mobilities of the polycrystalline films were found to vary irregularly from sample to sample. The amount of experimental error in the measurements is not known. Although the samples were 5 to 8µm thick the film surfaces typically varied 1 to 2µm in height. In addition, the doping uniformity within the films is unknown. It is thus probable that the carrier concentrations and mobilities as measured are weighted averages of quite variable quantities.

For most of the deposition runs listed in Table 2-1 the carrier concentration is higher by a factor of 3 to 5 in the polycrystalline films than in the epitaxial films. Similar differences have been measured between n-type polycrystalline films and companion epitaxial films by C-V analysis. It is possible that orientation effects are

Table 2-1. Electrical Properties of Polycrystalline and Epitaxial P-type GaAs Films

EXPERIMENT NO.	SUBSTRATE*	CARRIER CONCENTRATION (cm^{-3})	MOBILITY (cm^2/V-sec)
EA70125A	$A\ell_2O_3$	1.2×10^{18}	145
	1723	4.3×10^{17}	1.3
EA70125B	$A\ell_2O_3$	4.8×10^{18}	52
	1723	1.9×10^{19}	0.9
EA70126A	$A\ell_2O_3$	2×10^{17}	207
	Vistal	7×10^{18}	1.3
EA70127B	$A\ell_2O_3$	3.7×10^{18}	70
	Vistal	7.5×10^{18}	2.4
EA70128A	$A\ell_2O_3$	6.9×10^{18}	76
	1723	3.9×10^{19}	0.45
	7059	1.4×10^{19}	0.08
	0317	6.4×10^{19}	0.69
EA70128B	$A\ell_2O_3$	9×10^{18}	62
	1723	4.4×10^{19}	0.70
	0317	9.6×10^{19}	0.98
EA70201B	$A\ell_2O_3$	2.2×10^{19}	53
	Vistal	1.0×10^{19}	2.0
	Refired ASM805	2.7×10^{19}	3.4

*$A\ell_2O_3$ is single-crystal sapphire. Numbers are Corning Code numbers for glasses. Vistal and ASM805 are polycrystalline aluminas.

the cause of this apparent increase in the incorporation of electrically active impurities in polycrystalline GaAs films.

The implications for solar cell design of the data of Figures 2-4 and 2-5 are discussed in Section 2.4 (Task 4).

2.3.2 Physical Properties of GaAs Films on Composite Substrates

During the third quarter, deposition of GaAs on all of the candidate composite substrates was performed and the films analyzed for their physical properties. The composites are all conducting substrates and thus address, to some extent, the requirement for back contacts to thin-film solar cells deposited on them. The substrates in question are Mo-coated insulators (particularly glasses), Ge-coated insulators, and Ge-coated Kovar.

In the last case it was hoped that coating the Kovar with Ge would eliminate the interaction, observed earlier in the program, between AsH_3 and Kovar-type metals. The other two composites were studied separately but may be used in concert with one another, if appropriate, to enhance performance; for example, Ge might be deposited on patterned Mo on glass. The physical properties of GaAs films on these substrates are summarized below.

2.3.2.1 GaAs Films on Mo/Glass and Mo/Alumina Composites

The initial Mo/glass substrates used for experimentation were fabricated by sputtering a Mo layer 1 to 2 μm thick on glass. All of the candidate glasses as well as some of the other candidate insulators were used for initial experimentation. The thick Mo films were chosen to ensure adequate conductivity and to test the mechanical aspects of the three layer system under extreme conditions.

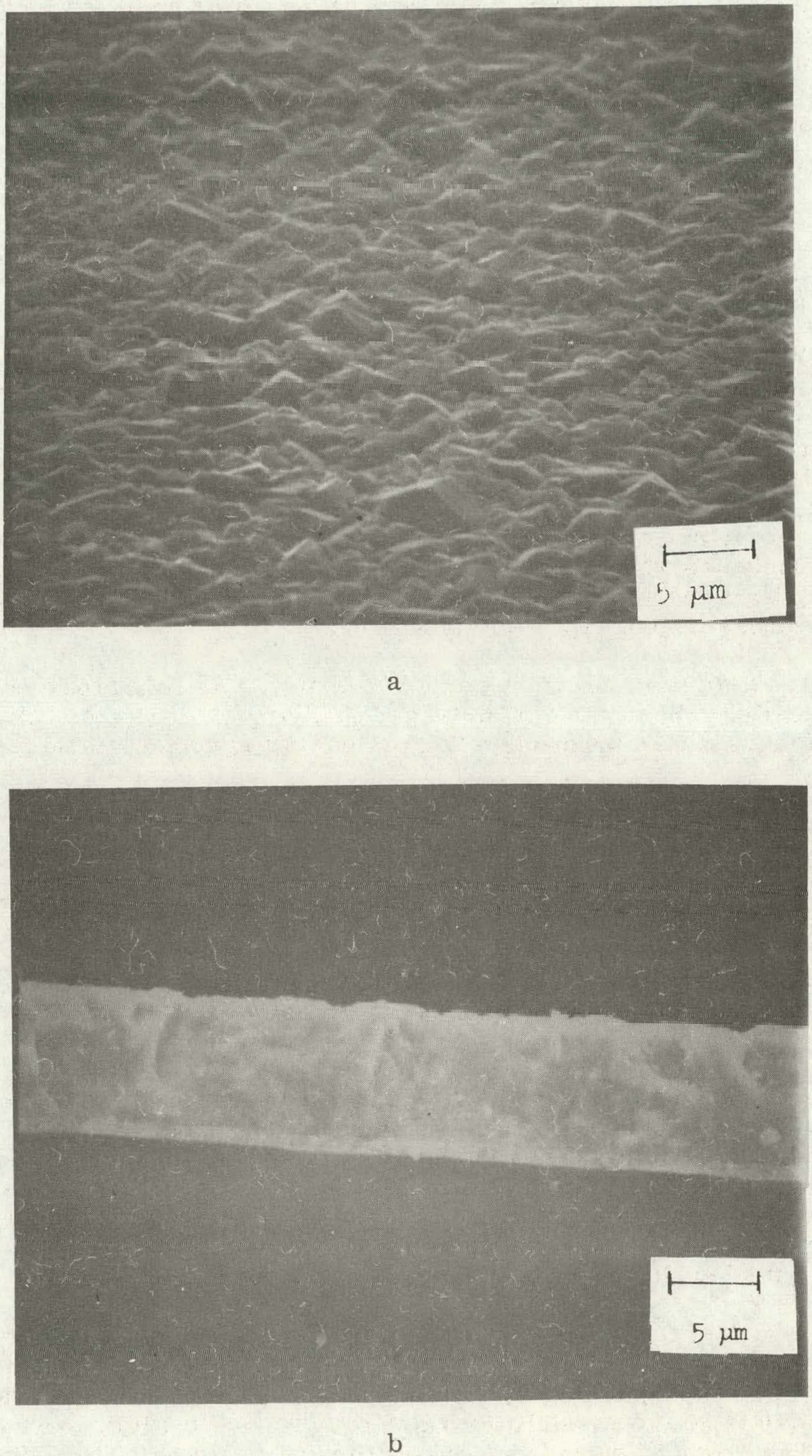
Figures 2-6a and b show the surface and a fracture cross-section, respectively, of a GaAs film grown at 725°C on a Mo/0317 glass composite substrate. The surface features of the film are 2 to 5 μm in lateral dimension, with a height variation of 1 to 2 μm. These surface features are typical of most of the polycrystalline films grown on substrates which do not induce large grain growth. The cross-section photograph shows the apparent integrity of the GaAs/Mo and Mo/glass interfaces. The Mo thickness is about 1 μm in this sample.

Figures 2-7a and b show the same views of a GaAs film grown on a Mo/7059 glass composite. The surface features are similar to those of the film grown on Mo/0317 (Figure 2-6), as expected. Again the film interfaces show good integrity.

Photographs of films grown on Mo/1723 composites showed a tendency toward small (< 0.5 μm) voids at the GaAs/Mo interface. It is not known whether this tendency is significant or simply occurs on all films but was detected only on the Mo/1723 sample. There is no a priori reason to expect any differences in the growth habit of GaAs on Mo that is deposted on different glasses. In fact, the surface features of the films are found to be quite similar. As will be discussed below, there is a tendency for these thick films of Mo to exhibit short cracks after exposure to brief GaAs depositions. It may be that the observed voids are the result of GaAs growth over these cracks.

The morphology of these cracks is shown in Figure 2-8, which is an SEM photograph of the surface of a Mo/0317 composite as it appears after a 2-sec growth of GaAs at 725°C. The cracks are clearly less than 0.5 μm wide and do not appear to affect the nucleation and early growth of the GaAs, which appears to have nucleated in a pattern similar to that observed for growth on bulk Mo. Further examination of these effects will be undertaken with thinner films of Mo, to determine what role the thickness of the Mo film may play in the observed phenomena.

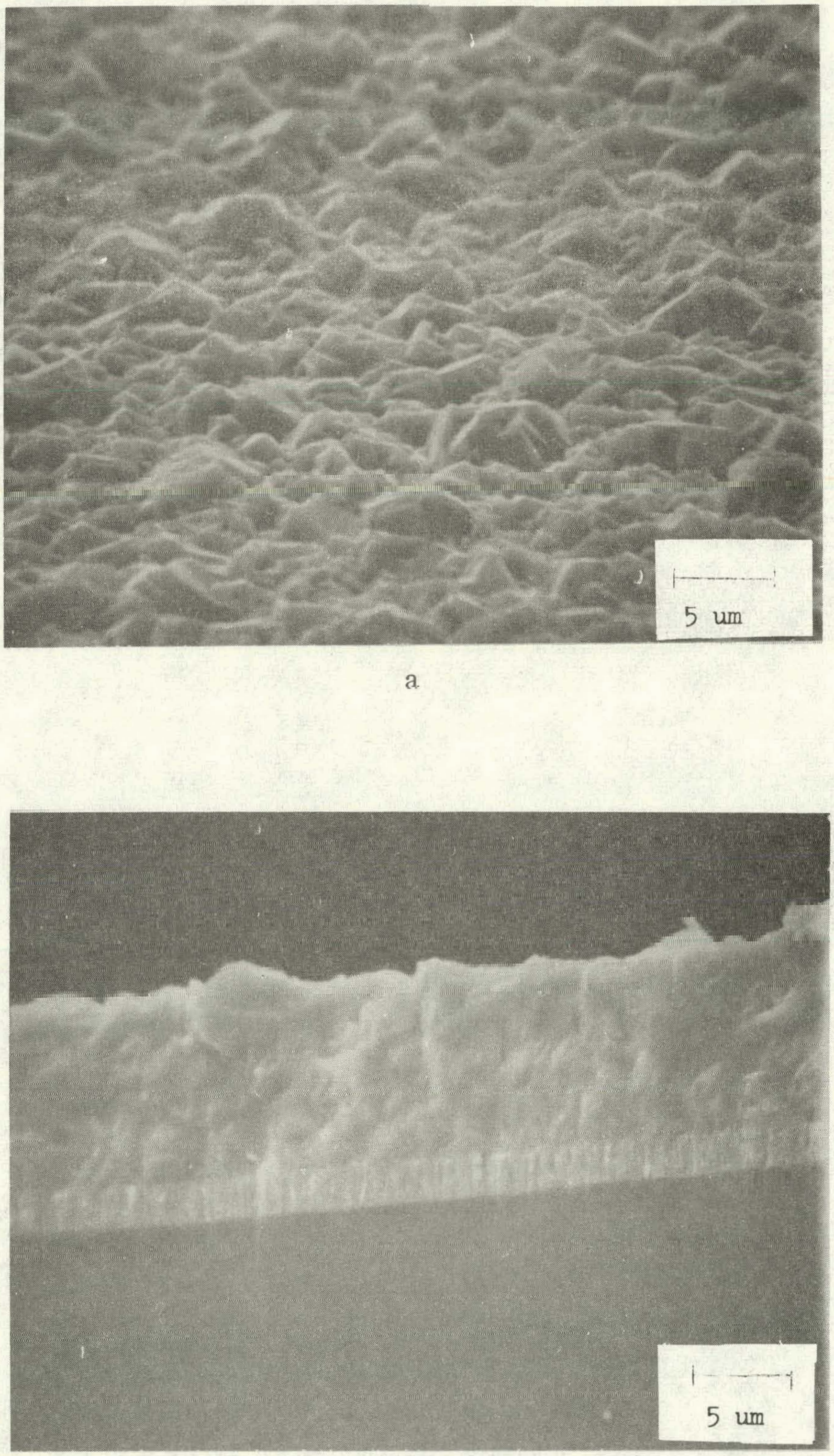
The growth of GaAs films on Mo-coated polycrystalline aluminas resulted in fine-grained (2 to 5 μm) polycrystalline films which followed the contrours of the substrate. In some cases, however, distributed on the top of this fine-grained material were large (10 to 20 μm) crystallites which protruded 5 to 10 μm above the surface of the film. The origin of these large crystallites is not known. They could originate from nucleation and growth in cracks in the Mo films. The aluminas are more conducive to nucleation and oriented growth of GaAs than are the glasses, for example.



a

b

Figure 2-6. SEM Photographs of GaAs Film Grown on Mo/Corning Code 0317 Glass Composite Substrate. (a) Surface Viewed at 45 Deg; (b) Fractured Cross-section



b

Figure 2-7. SEM Photographs of GaAs Film Grown on Mo/Corning Code 7059 Glass Composite Substrate. (a) Surface Viewed at 45 Deg; (b) Fractured Cross-section

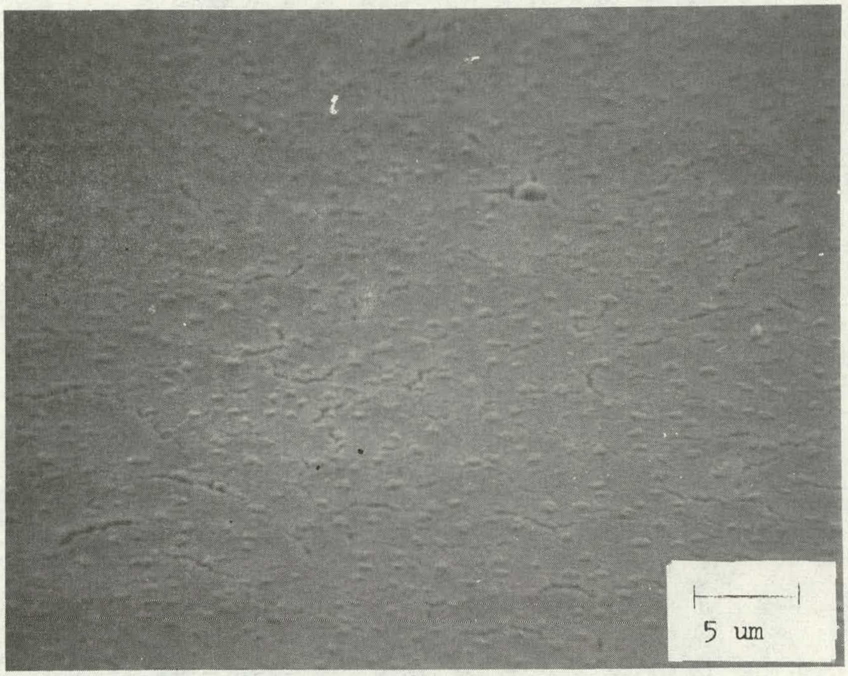


Figure 2-8. SEM Photograph Showing Early-stage Growth of GaAs on Mo/Corning Code 0317 Composite Substrate. (Note presence of ~1 μm growth islands.)

2.3.2.2 GaAs Films on Ge-coated Composites

Ge has been deposited on all of the candidate insulators, and GaAs has been subsequently deposited over the Ge composites. Figure 2-9 shows the surface structure of Ge grown on the candidate aluminas. The surfaces show no evidence of Ge grains larger than 2 to 5 μm; this is true even for refired ASM805 and refired Vistal, where individual $A\ell_2O_3$ grain sizes in excess of 40 μm occur. Note, however, the absence of sharp pointed features on the surface in all three cases shown. This may be indicative of more order and orientation that is initially obvious.

In fact, subsequent growth of GaAs on these composite substrates (Figure 2-10) indicates the existence of considerable order, particularly in the case of the refired aluminas. The film on refired ASM805, in particular, shows large grain growth.

Deposition of Ge on glass has resulted in the formation of incomplete-coverage films for the growth times used to date. Films of Ge grown on all of the candidate glasses for 20 min at 725°C are shown in Figure 2-11. The tendency is to nucleate sparsely and to form generally spherical crystallites having crystallographic facets. These crystallites might serve as excellent nucleation sites for subsequent growth of GaAs, and may well be a possible means of enhancing the grain size in GaAs films.

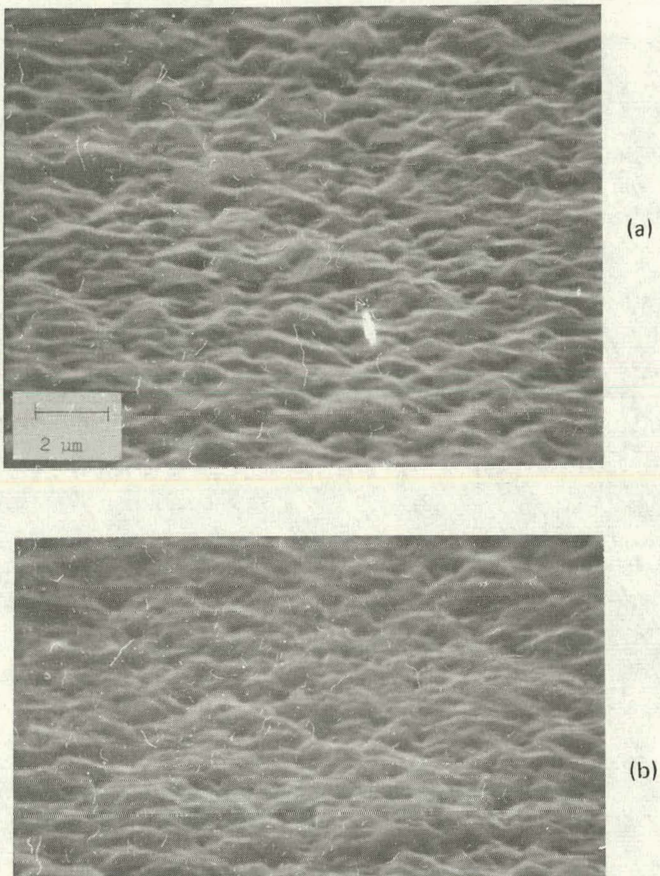


Figure 2-9. SEM Photographs of Ge Films Deposited on Various Polycrystalline Alumina Substrates. (a) Polished ASM805; (b) ASM805 Refired; (c) Vistal Refired

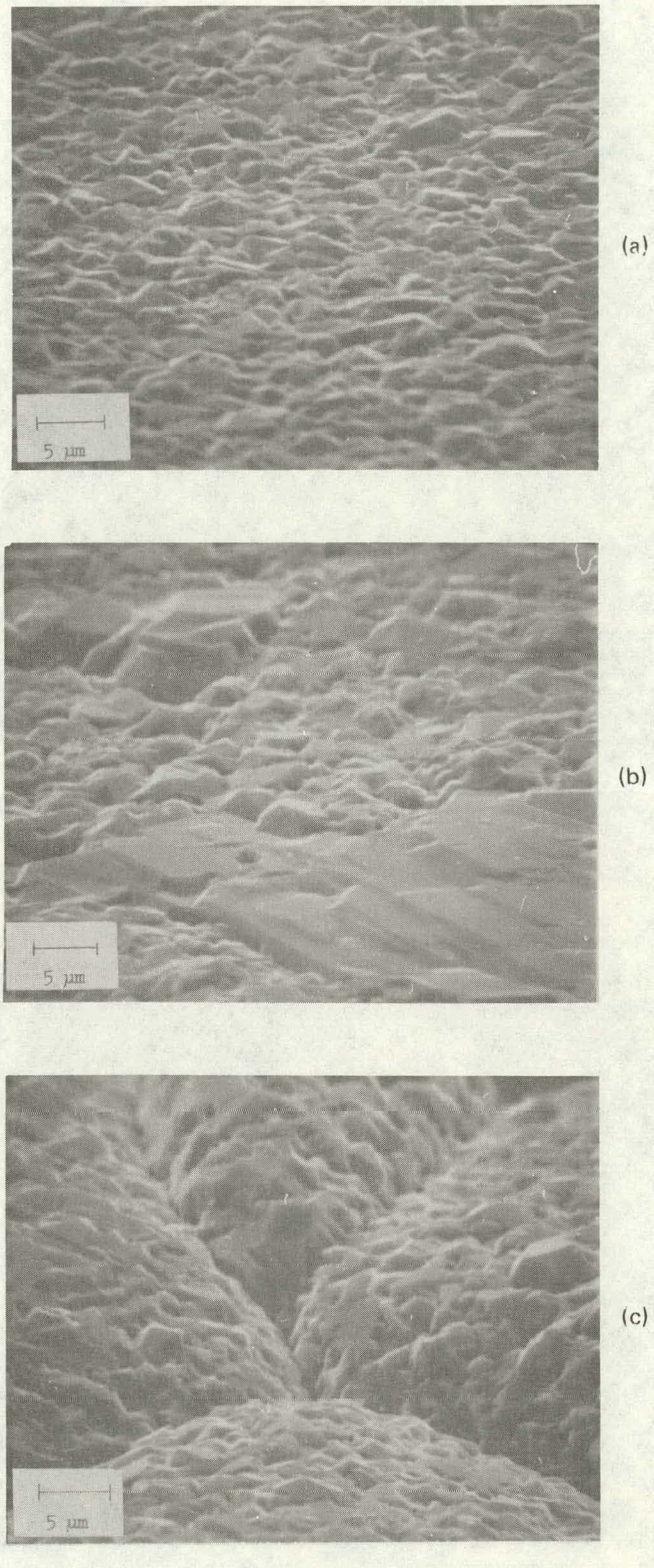


Figure 2-10. SEM Photographs of GaAs Films Grown over Ge Films on Various Polycrystalline Aluminas. (a) Polished ASM805; (b) ASM805 Refired; (c) Vistal Refired

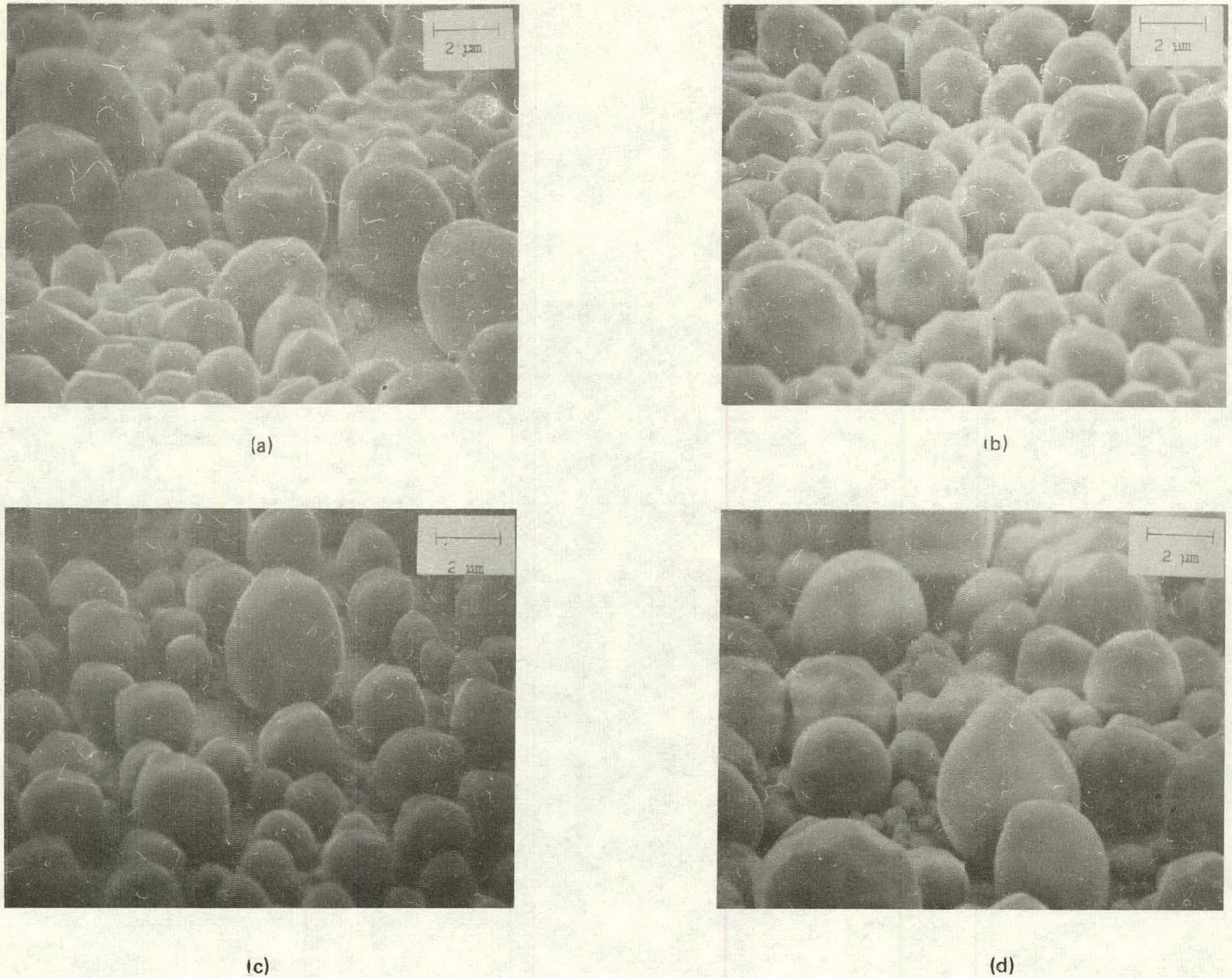


Figure 2-11. SEM Photographs of Ge Deposits Grown at 725°C on Various Corning Glass Substrates. (a) 0317; (b) 1723; (c) 7059; (d) 0211

Figure 2-12 shows the result of growing GaAs films on two Ge/glass composites for a time that would be sufficient to produce 8 μm films directly on glass. The GaAs is seen to grow preferentially on the Ge, which was grown for half the deposition time of those deposits shown in Figure 2-11. The result is the formation of "rosettes" with apparent intervening voids in the GaAs film. The voids are less apparent in the films grown on 0317 substrates, and additional deposition for a short time would probably have resulted in complete coverage. In addition, the rosette features are 10 to 20 μm in diameter in the latter case.

2.3.2.3 GaAs Films on Coated Kovar Substrates

The CVD growth of Ge on Kovar was demonstrated earlier in the program (Ref 2). It resulted in the formation of polycrystalline Ge with grain sizes in the range 10 to 20 μm. Films such as these were thought to be very promising for the growth of GaAs films with large grains.

However, subsequent growth of GaAs on Ge-coated Kovar resulted in the same morphology as that observed for GaAs grown directly on Kovar. Ni was present in amorphous veils at the surface of the film, and extensive cracking of the film occurred (Figure 2-13).

Similarly, Mo-coated Kovar behaved the same as uncoated Kovar when subjected to the environment typical of GaAs MO-CVD (725°C). It is apparent that the interaction between AsH_3 and Kovar noted earlier in the program occurs also in the presence of coatings of either Ge or Mo. It now appears that Kovar is incompatible with the MO-CVD environment, and its use will be discontinued.

2.3.3 Development of Characterization Techniques for Polycrystalline GaAs

During the course of this program efforts have been proceeding to develop pertinent characterization techniques for polycrystalline materials. As discussed in previous reports, parameters of prime interest are grain size and preferred orientation. In addition, a technique for rapid determination of Aℓ concentration in GaAℓAs films (both single-crystal and polycrystalline) is needed. Some progress in all of these areas has been made in this quarter.

2.3.3.1 Measurement Techniques for Preferred Orientation

In the last quarterly report (Ref 3) measurements of the intensities of x-ray diffraction peaks for GaAs films on a variety of candidate substrates under a variety of conditions were reported and compared with the ASTM Standard Card Index intensities for randomly oriented polycrystalline GaAs. However, considerable difficulty had been experienced in producing a randomly oriented sample of polycrystalline material which gave results that agreed with the ASTM data.

It has since been found that work previously reported by scientists at the National Bureau of Standards does not agree with the ASTM data, but does agree with theoretical calculations of expected intensities for GaAs. It has also been found that the polycrystalline GaAs reference standards prepared at Rockwell agree with the NBS work and with theoretical expectations.

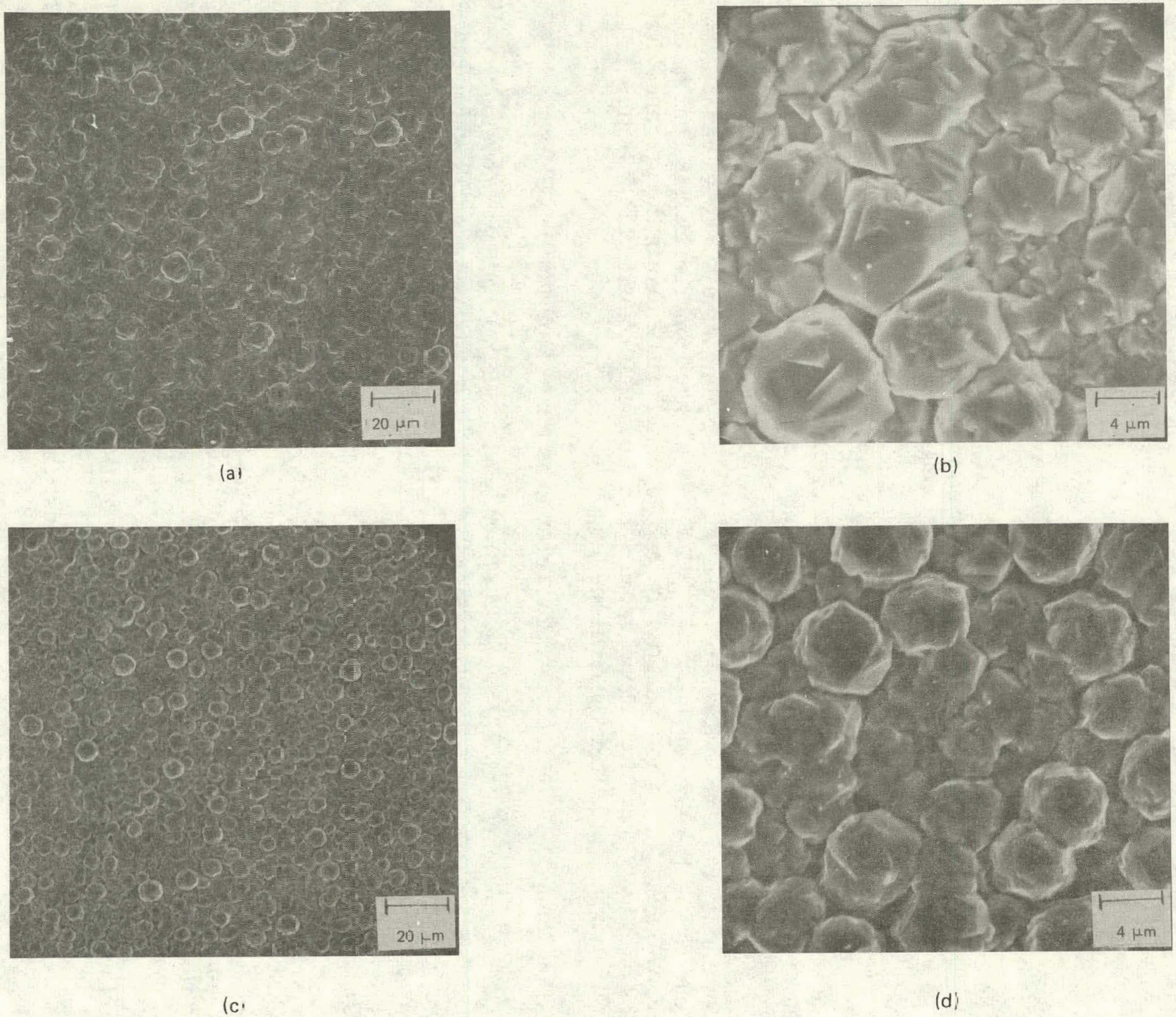
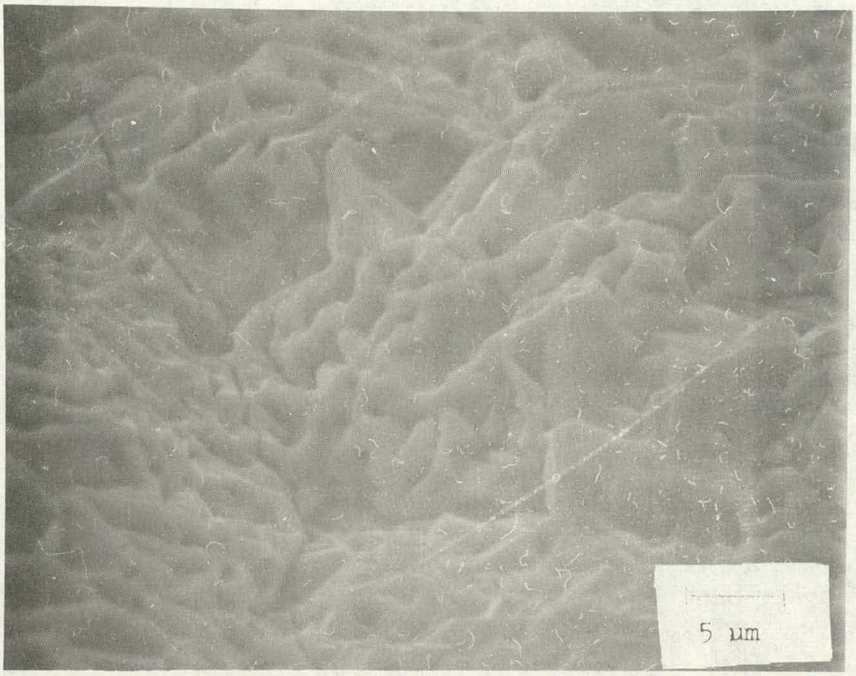
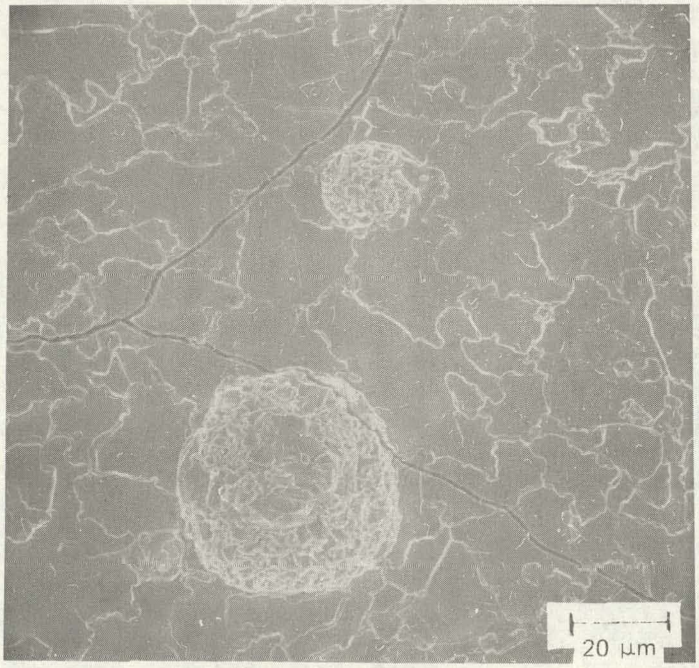


Figure 2-12. SEM Photographs of Composite GaAs-on-Ge-on-glass Films Grown on Two Glasses. (a) and (b) Corning Code 0317; (c) and (d) Corning Code 7059.



a



b

Figure 2-13. SEM Photographs of GaAs on Kovar Composite Substrates. (a) Mo/Kovar; (b) Ge/Kovar. (Note both films show presence of amorphous veil material on surface.)

The standard sample was prepared by grinding single-crystal high-purity GaAs with a mortar and pestle and sieving the resultant powder successively with 20 µm and 5 µm sieves. The powder remaining on the 5 µm sieve was then gently mixed with Krylon which had been sprayed on a glass slide. The resulting slurry was then allowed to dry.

The relative intensities of the principal low-index x-ray diffraction lines for GaAs were obtained using the diffractometer with a focusing monochromator. After locating the positions of the diffraction peaks and taking into account the background correction a step-scanning method was employed. A Philips Model 3181S Angle Mode Programmer system with teletypewriter output was used to obtain the line profile data.

The conditions used for the analysis were to step-scan in Bragg angle in increments of 0.1 deg (for 2Θ) through the peak, counting at each step for a fixed time (10 sec). The data obtained in this manner were simultaneously printed out on the teletypewriter and punched out on paper tape. The programmer would then traverse to the next peak, and the complete process would be repeated until all the required diffraction line profile data had been obtained. The sample was then rotated about an axis normal to its surface, in 90 deg increments, and the data again obtained.

The line peak intensities and the "integrated" (i.e., summed) intensities under the curve were each corrected for background. The values for a given diffraction line were then averaged, and the results were compared with those listed in the ASTM Card No. 14-450 and the National Bureau of Standards Bulletin No. 25, Section 3. The results of this comparison are shown in Table 2-2.

The peak intensities obtained by this procedure are seen to be in good agreement with experimental values reported by NBS and with calculated theoretical values. The data reported in the ASTM Card Index appear to be in error in the intensity listed for the (220) reflection.

As a result of this work a good reference standard is now available with which to compare experimental samples for determination of preferred orientation and grain size. In addition, the experimental technique is now well specified for determination of preferred orientation.

Table 2-2. Comparison of Relative Intensities of X-ray Diffraction Lines for Polycrystalline GaAs

	MILLER INDICES OF DIFFRACTION LINE				
	<111>	<220>	<311>	<400>	<331>
Rockwell Standard Sample					
Peak	100	74	36	7.4	9.8
Area	100	103	49	12	17
ASTM Card Index	100	35	35	6	8
NBS Data	100	61	29	7	11
Theoretical Intensities	100	70	40	10	15

2.3.3.2 Determination of Grain Size in Polycrystalline GaAs

The most widely used technique for specifying apparent grain size in a polycrystalline material is the determination of the dimensions of surface features. In many cases this will accurately indicate grain size, and confidence in the method is bolstered when the surface features are regularly shaped structures with well-defined crystallographic planes. On the other hand, when the surface features are irregularly shaped and randomly spaced, as are those on some of the GaAs films prepared in this program, it is not always evident when a surface feature can be correlated with an individual grain. In these cases a corroborating observation is required to establish the validity of the determination.

Some of the attempts to establish techiques for grain size determination have been described earlier in the program. The two techniques which have been of most interest are chemical etching and electron-beam-induced current (EBIC) imaging in the SEM. It now appears that neither of these techniques can be unambiguously applied to an as-grown crystal. Rather, it appears that some light polishing is required, primarily to provide a smooth surface on which to delineate structural features after etching and from which to reduce spurious electron emission upon examination in the SEM.

Initially, a polished sample was prepared for EBIC-mode examination by beveling the sample to expose the film throughout its thickness. A major problem which has developed in using such samples for the EBIC technique is that the resistivity of the films is high, despite apparent normal intragrain doping levels. Thus, when Schottky barrier samples are prepared on films with sufficiently low resistivity to form a useful device the Schottky barrier is not rectifying. This has prevented more active pursuit of this technique for grain size determination. Recently, however, n/n+ GaAs samples on Mo have been prepared which show rectifying behavior and reasonably low resistance. It is hoped that these samples can now be exploited for EBIC determination of grain size.

The EBIC mode has also been used to examine thin Schottky barriers in GaAs films grown on bulk polycrystalline GaAs. The EBIC images revealed the presence of grain boundaries, but in some instances also delineated surface features which may not have been related to grain boundaries.

Some of the beveled samples described above have been used for etching experimentation under a variety of conditions. Figure 2-14 shows SEM photographs of portions of a beveled GaAs film on refired ASM805 which has been exposed to a 1:1 H_2O:A-B etch solution for 15 sec. Figures 2-14a and b show a region of the bevel near the top of the film and c shows a portion near the bottom of the film. The top portion shows etch features ranging up to 5 μm in dimension. The features appear to be crystallographic and are probably individual grains in the film. The etched features near the bottom of the bevel (Figure 2-14c) are generally smaller in size, with a maximum being about 2 μm.

Whether this difference in etch feature size is a true measure of the change in grain size with thickness is not yet known with certainty. The effect observed may be strongly influenced by variations in intragrain quality or etch rate with film thickness. A variety of other etching conditions were tried with A-B etches, both dilute and concentrated, as well as with the $H_2SO_4:H_2O_2:H_2O$ etch system, but the results shown here are the best achieved to date.

(a)

(b)

(c)

Figure 2-14. SEM Photographs of Etched Angle-lapped Sample of GaAs on Refired ASM 805; Dilute 1:1 H_2O: A-B Etch for 15 sec Used. (Note presence of apparent grains both at top (a) and (b) and bottom (c) of film.)

Work on this problem in the remainder of the program will center on comparing and correlating surface-feature geometry, EBIC images, and etch patterns to establish the relationship between EBIC images of regions of high recombination rate and surface features, and their relationship to individual grains delineated by etching.

2.3.3.3 Determination of Aℓ Concentration in GaAℓAs

The determination of the Aℓ concentration in GaAℓAs films is required to permit correlation of the observed performance of GaAs window-type solar cells with the theoretically predicted characteristics. A routine, easy-to-use, non-destructive technique is required.

One such method is centered on determination of Aℓ concentration in GaAℓAs films by x-ray measurement of lattice constants. The measurement of the relative difference in lattice constant between an epitaxial film and a substrate is a routine measurement at Rockwell commonly used in adjustment of the composition of magnetic bubble films to the correct proportions. The technique is capable of yielding the $\Delta a/a_o$ ratio with sufficient accuracy to determine the Aℓ concentration of GaAℓAs films grown on GaAs. It is hoped that bv establishing a series of standard GaAℓAs films on GaAs that the $\Delta a/a_o$ measurement will provide a routine technique for determining Aℓ concentration in other films. The preliminary work done toward establishing this calibration is described here.

A series of CVD $Ga_{1-x}A\ell_x$ As films was prepared with the Aℓ concentration ranging from 0 to 100 mole percent (i. e., from GaAs/GaAs to AℓAs/GaAs). The AℓAs/GaAs samples were kept in a N_2 atmosphere to prevent any oxidation of the film, and were removed just prior to analysis. The films were studied using electron microprobe analysis, double-crystal x-ray diffractometry, and conventional x-ray diffractometry.

In the electron microprobe analysis, measurements were obtained using the K-alpha x-ray spectrum of the elemental components of the films -- Ga, Aℓ, and As. To date only qualitative results havc been obtained. To obtain the concentration of these elements quantitatively, several methods of correcting the observed x-ray line intensities will be employed.

Rocking curve measurements were made using an x-ray double-crystal diffractometer, a method which permits separation of the diffracted beams from film and substrate. The rocking curve for a particular line then consists of two peaks, with the peak separation being a direct measurement of Δa (i. e., $a-a_o$). Since the first crystal in the experimental arrangement was set for the (888) reflection from Gd-Ga garnet (G^3), the asymmetric (620) line from the (100)-oriented GaAs samples was used in the analysis. Assuming the published value of $a_o = 5.6534$ Å (Ref 4) for the lattice parameter of GaAs, measurements of the lattice parameter a were made on the series of samples. The results obtained for the lattice parameters of the composite films were higher than the reported value for the lattice parameter of AℓAs ($a_o = 5.6622$Å) (Ref 4). Work is continuing with this technique to resolve these differences.

The third technique investigated involves conventional x-ray diffractometry. The experimental arrangement is the same as that used in determining preferred orientation in polycrystalline films. The relative intensities of the (400) and (600) diffraction lines were obtained from the films and the substrates. Using the measured "d" spacings of these diffraction lines, the lattice parameter for each sample could be determined. A standard curve of lattice parameter versus Aℓ concentration was made, using the a_o values for GaAs and AℓAs as the end points and assuming Vegard's Law applies. The Aℓ concentrations in these samples were found to be in the range of 0.3 to 0.8 mole fraction by this method.

Further work will be necessary to extract the composition from the electron microprobe data and to measure the $\Delta a/a_o$ value with a symmetric reflection on the double-crystal diffractometer.

2.4 TASK 4. EXPERIMENTAL PHOTOVOLTAIC DEVICE FABRICATION AND EVALUATION

This task is summarized 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 limited activities on this task in the first quarter involved the design of an experimental solar cell contact mask and the verification of single-crystal contact technology for window-type heterojunction solar cell fabrication.

Relatively little further work was done in the second quarter, primarily because of problems that were encountered in obtaining good quality GaAℓAs films (Ref 3). However, all of the apparatus required for complete characterization of GaAs solar cells was acquired, assembled, and made operational. Also, the ohmic contact technology for both n- and p-type GaAs was tested and found fully satisfactory. For n-type GaAs, contacts of Au-12 percent Ge are used, and contacts to p-type GaAs are either In-Ag-Zn or Au-Zn. The development of a specific contact material for GaAℓAs was hampered by the lack of doped GaAℓAs material of adequate quality in the first two quarters.

However, significant progress has been made in the third quarter toward the goal of producing low-cost GaAs solar cells. Results obtained on single-crystal heterostructure window cells grown by the MO-CVD technique have clearly established that the technique is capable of producing high-efficiency GaAs solar cells. This development was a necessary one to establish confidence that the ultimate goals of the present and later programs directed at low-cost large-area polycrystalline solar cells could be met. In addition to the single-crystal results, initial attempts to produce polycrystalline GaAs solar cells have also been successful.

2.4.1 Single-crystal GaAℓAs/GaAs Heterostructure Solar Cells

The first single-crystal solar cells fabricated in this program are similar in structure to those which have yielded high efficiencies in devices grown by liquid-phase epitaxy (LPE) (Ref 5). The structure is a p/p/n composite of $Ga_{(1-x)}A\ell_xAs$/GaAs/GaAs, with $x \approx 0.8$.

The initial structures were formed by sequentially growing p-type GaAs and p-type GaAℓAs on an n-type single-crystal GaAs substrate, thus forming a p-n junction at the interface of the epitaxial material and the bulk substrate. The best devices, however, had an all-epitaxial junction, involving an n-type GaAs epitaxial layer grown before the p-type layers but during the same CVD run. The typical layer thicknesses were GaAℓAs 500Å, p-type GaAs 1.4 to 1.5 μm, and n-type GaAs 4 to 6 μm.

The cells were fabricated by depositing a Au-Ge (12 percent Ge) contact on the back surface of the device, defining a square grid pattern in photoresist on the top surface, etching the pattern lightly to remove the GaAℓAs where the contact deposition was to take place, depositing a Au-Zn-Au (2 percent Zn) layer over the whole surface, and removing the photoresist to define the grid contact. The structure was then alloyed at 425°C for 1 to 2 min. The samples were then cleaved into portions having a maximum area of 0.5 cm^2. This was done to allow mounting the devices on available headers.

The resulting devices were evluated by measuring the I-V characteristics under illumination by an uncalibrated AMO solar simulator. A Canrad-Hanovita Model 976C-0010 Xe high-pressure arc lamp, powered by an Oriel Model 6117 Universal Arc Lamp Source, was used unfiltered for the measurements. The lamp was operated at 1 Kw, and the resultant illumination at the sample was measured by a calibrated Eppley Bi-Ag thermopile. Incident intensitities in the range 128 to 135 mw/cm^2 were used. The results of measurements on some of the devices were subsequently checked by measurements using a balloon-flight-calibrated AMO solar simulator at the Photoelectronics Group of OCLI (City of Industry, CA) and found to be quite accurate.

Figure 2-15 shows the I-V characteristics, both dark and under simulated AMO excitation, for a heterostructure solar cell with the p-n junction at the film substrate interface. The open-circuit voltage (V_{oc}) and the curve fill factor (FF) are somewhat lower than the best values for these parameters obtained on LPE devices. Similarly, the short-circuit current density (J_{sc}) is about 20 percent lower than expected for the best devices. The CVD device involved here had no antireflection (AR) coating.

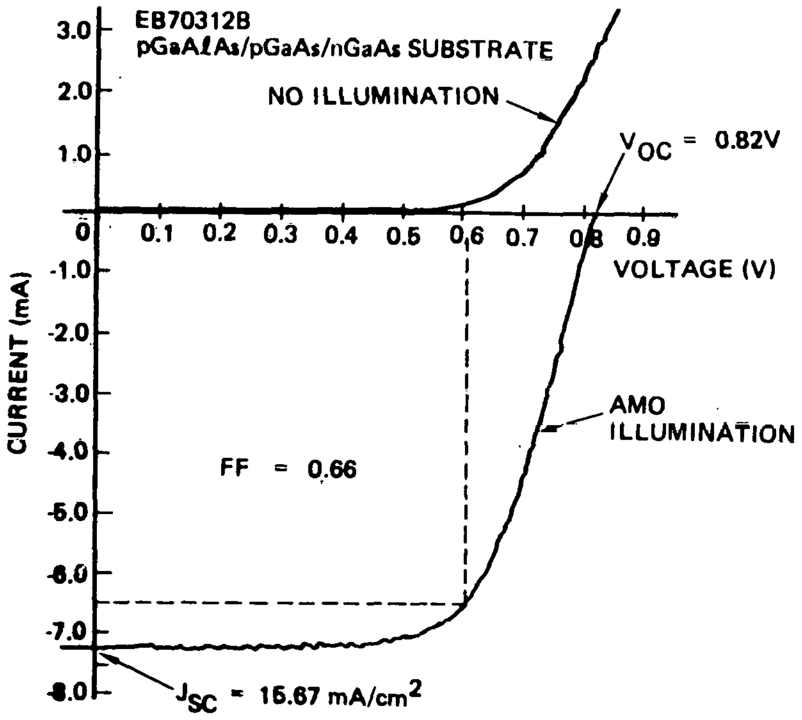


Figure 2-15. Dark and Light I-V Characteristics for MO-CVD GaAℓAs/GaAs Heterostructure Solar Cell with Junction at Film-substrate Interface.

The above device is one of the better devices obtained with the junction at the epitaxial film-substrate interface. Figure 2-16 shows similar characteristics for a device with an all-epitaxial grown junction. Note the increased V_{OC} and J_{SC} values for this device, which is the best of those fabricated to date. The conversion efficiency of the device is 12.8 percent with no AR coating, under simulated AMO conditions. With an appropriate AR coating an efficiency comparable with the best reported values for LPE devices would be expected.

Table 2-3 compares the ranges of properties obtained for an all-epitiaxial-junction device with those obtained for devices with junctions at the film-substrate interface. Note that the devices with all-epitaxial junctions are improved in almost every respect.

These results not only present a strong argument for increased confidence in and effort on polycrystalline solar cells formed by MO-CVD but also indicate a potential high-volume technique for fabrication of high-efficiency cells for use in concentrator systems, such as would be used in either terrestrial systems or orbiting space power supplies.

2.4.2 Polycrystalline GaAs Solar Cell Fabrication and Evaluation

The first step in the fabrication and evaluation of polycrystalline solar cells has been to fabricate Schottky-barrier cells on conducting substrates. The substrates chosen for initial consideration during the past quarter were Mo sheet and glass with a sputtered Mo film.

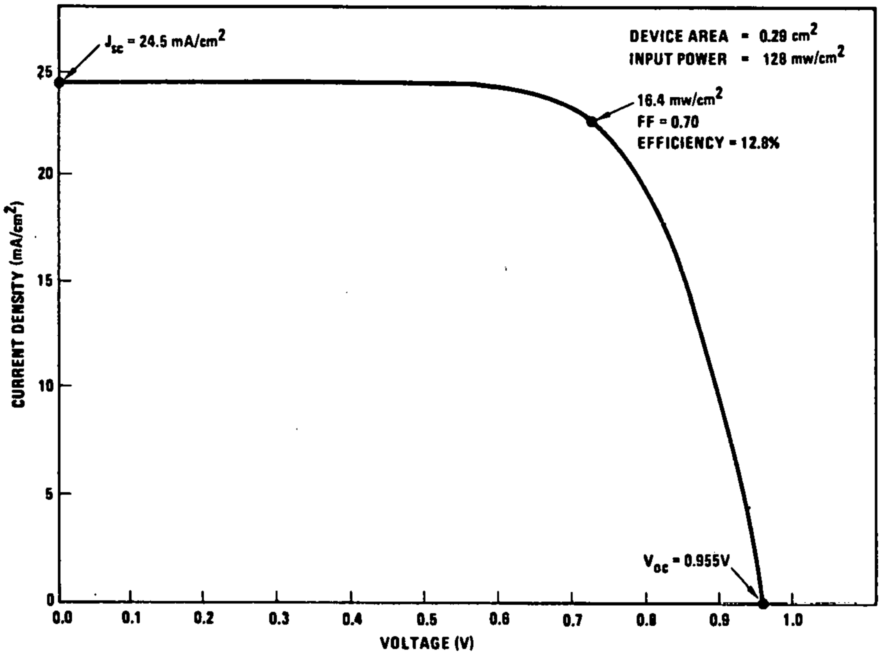


Figure 2-16. Fourth Quadrant of I-V Characteristic of MO-CVD GaAℓAs/GaAs Heterostructure Solar Cell under 128 mw/cm^2 Illumination (uncorrected for contact area or reflection from uncoated GaAℓAs window).

Table 2-3. Comparison of Film-Substrate and All-epitaxial Heterobarrier Solar Cells

Structure	Maximum* Efficiency	V_{oc} (max)*	J_{sc} (max)*	FF (max)*
pGaAℓAs/pGaAs/n Substrate	8%	0.82V	17 mA/cm^2	0.72
pGaAℓAs/pGaAs/nGaAs/n Substrate	12.8%	0.99V	24.5 mA/cm^2	0.74

*Measured under simulated AMO conditions with no AR coating

Two-layer n-on-n$^+$ GaAs films were grown on these substrates, with both the n and n$^+$ layers 5μm thick. The Mo/glass substrates were masked in a small region to allow access to the Mo layer which served as the backside contact. Au Schottky barriers 50Å thick were vacuum-evaporated over a photolithographically defined pattern to produce 50 mil x 50 mil square Schottky-barrier devices. In some cases 10 mil x 10 mil Au bonding pads 2000Å thick were deposited near one corner of the large-area Schottky barriers.

These small-area devices were illuminated in the same way as the single-crystal cells described in the preceding section. The I-V characteristics of the best GaAs/Mo/glass cell are shown in Figure 2-17. This device had an efficiency of 1.35 percent, with V_{oc} = 0.4V, J_{sc} = 10 mA/cm^2, and FF = 0.45.

These results are encouraging first attempts. The cell described is potentially a low-cost device. The remaining problems revolve around increasing grain size, developing techniques for fabricating p-n junction and p-n heterojunction devices, and overcoming by proper design the limitations imposed by the inherent high resistivity of polycrystalline GaAs. These problems will all be further pursued in the coming quarter.

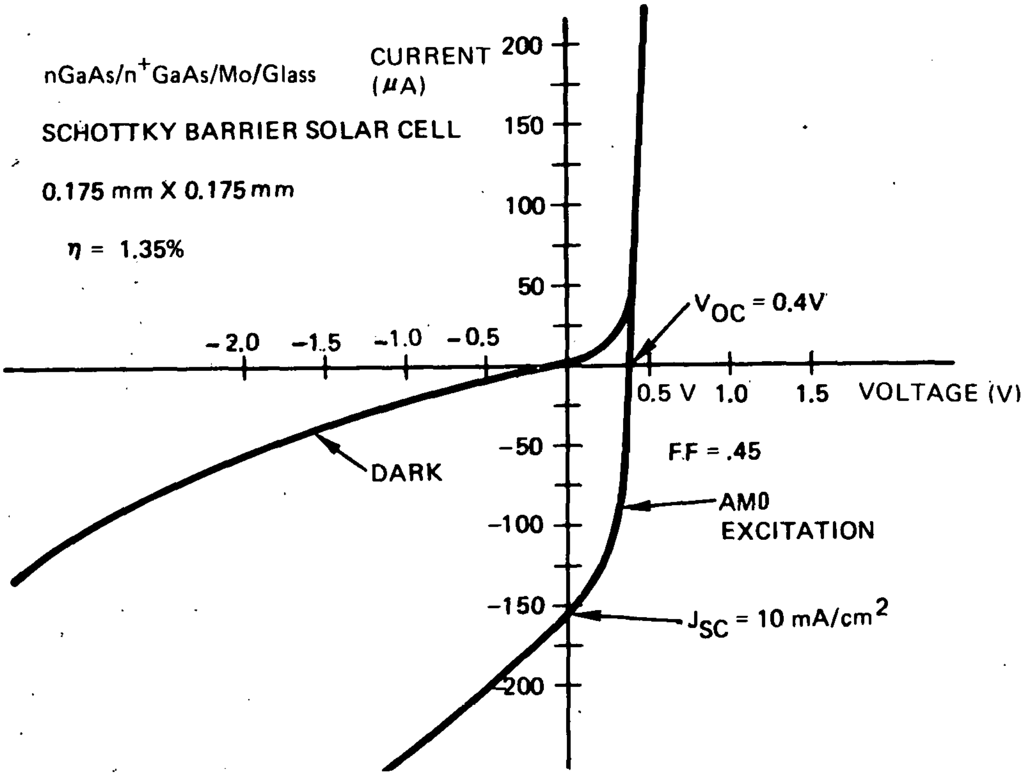


Figure 2-17. Dark and Illuminated I-V Characteristics of Small-area Schottky-barrier Solar Cells Fabricated in Polycrystalline GaAs Deposited by MO-CVD on Mo Film on Glass Substrate

2.5 TASK 5. ANALYSIS AND PROJECTION OF CELL FABRICATION COSTS

This task was summarized in the program proposal 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 was limited to (1) selection of the conceptual device designs to be used as the basis of cost analyses and projections; (2) acquisition of some materials costs from vendors and the costs of certain facilities and support services (from Rockwell facilities personnel); and (3) outlining 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 proposed 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 program, with the intention that the initial analysis be completed during the second quarter. It was suggested that this analysis should consist of three parts: (1) determination of the "materials content value" for the two conceptual device designs, in terms of present costs and - to the extent 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) projection of 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. Two conceptual device designs - one involving a conventional window-type GaAℓAs/GaAs film structure on an opaque substrate and one involving an inverted structure on a transparent substrate - were identified in the first quarter for the initial cost analysis.

During the second quarter some attention was given to identification of materials and processing costs associated with the two conceptual designs, but it was realized that further details of the actual device designs most likely to be adopted should become established before any extensive cost analyses are carried out. However, in very preliminary consideration of current costs of materials used in simplified versions of the two conceptual designs of thin-film GaAℓAs/GaAs heterostructure devices it appeared that there is a probable lower limit of \$43 - \$52 per m^2 for the total cost of just the materials used in the proposed configurations. Despite this, it was concluded that thin-film GaAs cells fabricated by the MO-CVD process can probably meet the future cost goals of the ERDA program (materials costs not exceeding ~\$16 per m^2 by 1985 and \$3-\$10 per m^2 by 2000) provided substrate materials with the necessary properties can be identified and produced inexpensively in practical sizes and very large quantities.

Some further consideration has been given to these matters during the third quarter, although the analyses have not yet been completed. Both conceptual designs involve the following basic solar cell components: (1) substrate (opaque or transparent, simple or composite); (2) base-region or backside contact; (3) active base region of cell (probably n-type GaAs); (4) front layer of cell (probably p-type GaAs); (5) window layer (probably p-type $Ga_{1-x}A\ell_xAs$, with $x \approx 0.9$); (6) front contact, on incident-light surface; and (7) antireflection coating on front surface (optional).

The two configurations of the conceptual design are reproduced in Figure 2-18 for reference. Design No. 1 (Figure 2-18a), involving conventional window-type GaAℓAs/GaAs film structure on an opaque insulating substrate, is shown in a more general form similar to that first given in Quarterly Project Report No. 1 (Ref 2) rather than with a composite substrate, as it was shown in Figure 2-24 of the second quarterly report (Ref 3). In both designs both the front (incident-light surface) contact and the base-region (backside) contact are now shown in a general form as continuous layers in the diagrams. It is understood, however, that these conducting contact layers may in practice take the form of an open gridwork or a continuous layer, in either instance with an associated high degree of optical transparency for the case of the front contact.

The high efficiency all-epitaxial three-layer thin-film $Ga_{1-x}A\ell_xAs$ ($x \approx 0.8$)/GaAs solar cell described in Sections 2.2.9 and 2.4.1 is a special case of Design No. 1 (Figure 2-18a), with a single-crystal wafer of n-type 0.001 ohm-cm (100)-oriented Si-doped GaAs serving as the substrate and the backside contact being applied on the underside of this substrate rather than at the interface of the n-type GaAs base region and the substrate, as shown in Figure 2-18a.

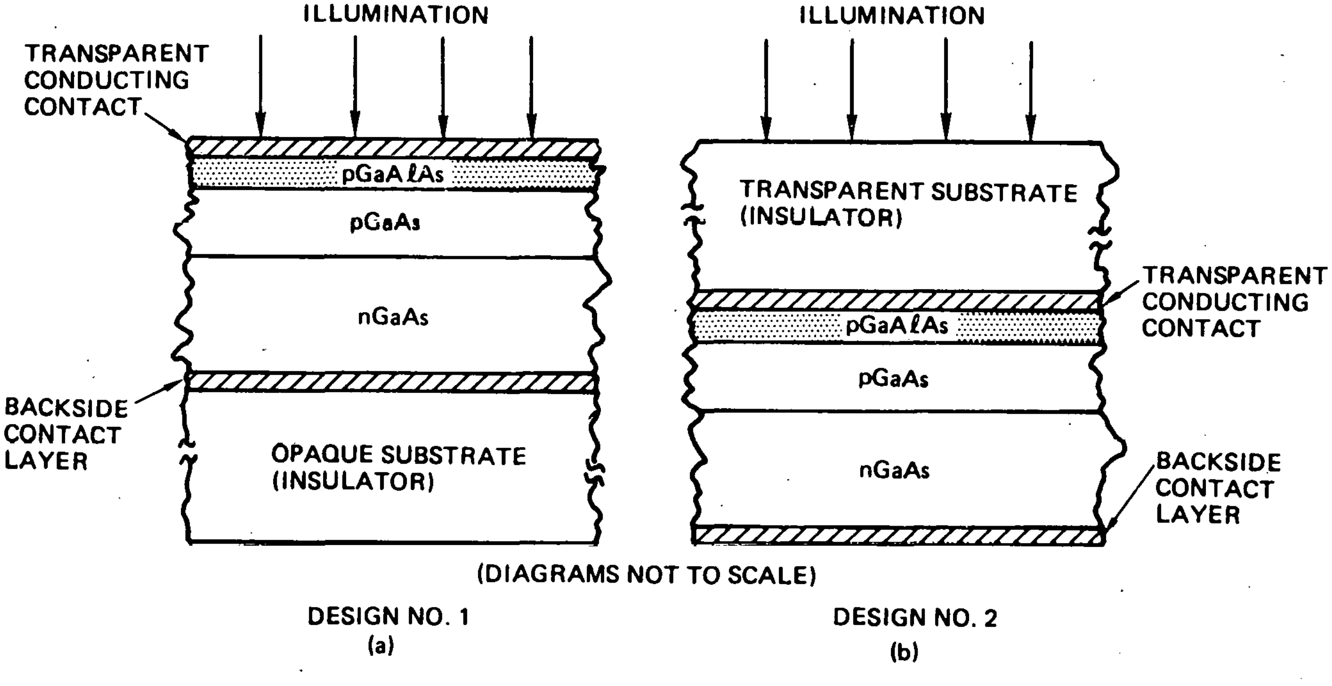


Figure 2-18. Conceptual Designs of Thin-film GaAℓAs/GaAs Heterostructure Solar Cells. (a) Conventional Window Structure with Opaque Substrate; (b) Inverted Structure with Transparent Substrate. (AR coating not shown on either configuration.)

A tabulation of the "materials content values" (per m^2 of cell area) for this single-crystal cell structure, using the dimensions actually involved in the experimental cells, is given in Table 2-4 along with the corresponding figures for conceptual Design No. 1 as given in the last quarterly report (Ref 3). This over-simplified view of materials costs again emphasizes the overwhelming dominance by the current price of single-crystal GaAs wafers and clearly illustrates the importance of developing thin-film cells of adequate efficiency on low-cost substrate materials. If the single-crystal cell is used in a concentrator system with a concentration ration of 1000:1, or if the cost of the single-crystal substrate wafer is reduced by a factor of ~1000, then the substrate material cost per m^2 would be in the range of the glass sheet substrate proposed for conceptual Design No. 1.

Many of the experimental polycrystalline cell structures now being prepared in this program involve the use of Corning Code 0317 glass, an alumina soda lime glass with a strain point of 574°C, an annealing point of 622°C, a softening point of 871°C, and an average thermal expansion coefficient (referred to 25°C) of 8.7×10^{-6} per deg C in the range 0-300°C. This glass has heretofore been made available for experimental purposes at no charge to the program by the manufacturer (Corning Glass Works). However, it is now necessary to purchase the glass in experimental quantities. The price per m^2 is a strong function of the size of the individual pieces that are supplied, but on a minimum-order basis ~\$48 per m^2 represents a realistic current price for moderate quantities in usable form.

This cost is within the range given for glass substrates in Table 2-4. It seems a reasonable assumption that the combination of large-scale production methods, such as are used for certain types of glasses in the glass industry (e.g., glass ribbon production and the float-glass process), and large-volume purchases on a regular basis could result in a drop in the cost per m^2 of this glass by at least one and possibly two orders of magnitude relative to the experimental quantity price given above. A decrease by two orders of magnitude, to ~\$0.50 per m^2, would make such a glass a very practical candidate for use in the low-cost solar cell arrays required for the terrestrial applications of interest here. Such a cost figure for the substrate, the predominant cost-controlling item in the solar cell designs being considered in this program, would make realization of the cost goals of the National Photovoltaic Conversion Program an excellent possibility.

One of the advantages of the MO-CVD process that was emphasized in the original program proposal and in the first quarterly report (Ref 2) is that large-area uniform surface coverage of a substrate can be obtained and that a sequence of layers of various conductivity types and doping levels can be achieved in a single growth sequence, using the same type of commercially available CVD apparatus that is used for epitaxial growth of elemental semiconductors, e.g., Si. This fact distinguishes the MO-CVD process from other methods for growing films of GaAs and related materials.

It also makes it possible to obtain an indication of the extent to which the future annual solar array production goals of the ERDA program can be realized in terms of CVD production equipment available today to the semiconductor device industry. The annual production capacity goal of the national program for 1985, in terms of 10 percent array efficiencies, is 5×10^6 m^2 of solar cell arrays.

Table 2-4. Materials, Dimensions, and Costs of All-epitaxial Thin-film Experimental GaAℓAs/GaAs Solar Cell and Conceptual Cell Design No. 1

	EXPERIMENTAL ALL-EPITAXIAL THREE-LAYER GaAℓAs/GaAs CELL			CONCEPTUAL DESIGN NO. 1 (OPAQUE SUBSTRATE)		
COMPONENT/REGION OF BASIC CELL	MATERIAL	THICKNESS (μm)	COST PER UNIT AREA ($\$/m^2$)	MATERIAL	THICKNESS (μm)	COST PER UNIT AREA ($\$/m^2$)
1. Substrate	GaAs (single-crystal n-type Si-doped wafer)	375	>15,000.**	Glass sheet	500	5.00–60.00†
2. Base Region Contact	Au-12% Ge alloy layer (full coverage, on underside of substrate wafer)	0.2	10.62	Mo layer	10	16.30
3. Active Base Region	GaAs film (n-type, Se-doped)	5	18.55	GaAs film (n-type, Se-doped)	5	18.55
4. Front Layer of Cell	GaAs film (p-type, Zn-doped)	1.5	5.58	GaAs film (p-type, Zn-doped)	0.5	1.86
5. Window Layer	Ga$_{0.2}$Aℓ$_{0.8}$As film (p-type, Zn-doped)	0.05	0.13	Ga$_{0.1}$Aℓ$_{0.9}$As film (p-type, Zn-doped)	0.5	1.22
6. Front Contact	Au-Zn-Au (2% Zn) square grid (10% area coverage)	~0.4	2.12	Ag-2% Zn alloy square grid (5% area coverage)	1.0 (50μm linewidth)	0.08
7. Antireflection Coating* (optional)	–	–	–	–	–	–
TOTALS (Approx)			>$15,000 per m^2			$43–$98 per m^2

* The AR coating is omitted in this preliminary evaluation.

** Based on current price for polished (1 side) single-crystal GaAs wafers purchsed in moderate quantities.

† Lower amount based on untempered window glass costs; higher amount based on Corning Code 7059 as-drawn glass sheets, purchased in moderate quantities.

A specially designed CVD reactor system for use in depositing epitaxial Si by the SiH_4 pyrolysis process on 3-in. diameter Si substrates in large numbers has been constructed by a major supplier of production equipment for the semiconductor industry.* This system is designed to accommodate 300 substrate wafers per run, mounted vertically in a vertical cylindrical deposition chamber which is raised and lowered into and out of a 30 Kw resistance-heated clamshell furnace. The system has a very fast cycle time (30 min for a $20 \mu m$ deposit of Si by SiH_4 pyrolysis in H_2), and is capable of producing 82 m^2 of CVD Si $20 \mu m$ thick in a normal five-day 40-hr week.

On the above basis, 400 such reactors could produce 5×10^6 m^2 of Si annually operating on a three-shift (24-hr day) five-day-week schedule (with no allowance for down-time and assuming 100 percent yield), while 208 such systems could produce the same amount of CVD Si if operated on a 24-hr-day schedule for 365 days, on the same basis. The cost of such a system (complete) is the order of $250,000. An examination of the possibility of using this type of system for producing CVD Si for the ERDA/JPL Low Cost Silicon Solar Array Project (Ref 6) indicated that relatively minor modifications in the deposition chamber and the form and size of the substrates used could reduce the number of such reactor systems required for producing 5×10^6 m^2 per year to somewhere in the range 50-75. This is a more encouraging number, but unfortunately this type of system involves batch processing and all of the attendant severe limitations.

Since the MO-CVD process - even one involving deposition of several different layers in sequence - could be applied equally well in such a production system having the required design changes, the above estimates do provide some preliminary indication of the magnitude of the undertaking required to meet the 1985 production goal for GaAℓAs/GaAs solar cell arrays. A reduction in cycle time per deposition run, which might be possible because of the thinner layers involved in the GaAs cell structure, could further reduce the number of reactor systems required to meet the production goals, but such an improvement would probably be only slight. The main modification required to achieve the necessary production level and yet keep the associated costs within the established limits is the development of continuous (or semi-continuous) processes for formation of the large-area substrates as well as for deposition of the semiconductor layers. This must be the long-term goal of these and other studies directed toward meeting the future needs of ERDA's photovoltaic conversion program.

---

*The manufacturer is the Tylan Corp, Torrance, CA

3. CONCLUSIONS

The candidate substrate list has been narrowed as a result of experiments which indicate that certain substrates will not be compatible with the growth of GaAs and because certain other materials do not allow a low-resistance contact to be made to the backside of a polycrystalline solar cell. In particular, Kovar metal substrates lead to unacceptable levels of Ni incorporation in the GaAs films grown on this material, and Kovar-like metals can be expected to exhibit the same problem. Uncoated insulators, such as glasses and polycrystalline aluminas, have been eliminated because even heavily doped polycrystalline n- and p-type GaAs films grown on these materials are highly resistive and thus not suitable for fabrication of solar cells unless a large-area conducting contact is provided at the film-substrate interface. Thus, much of the effort in the remainder of the program will be devoted to investigations using insulating low-cost substrates with full- or partial-coverage conducting intermediate layers.

Polycrystalline GaAs films have now been grown on all of the low-cost materials on the candidate list. High resistivities have been measured for doped polycrystalline GaAs films grown on all of the uncoated insulating substrates, as indicated above. GaAs films have been grown on Ge deposited on low-cost substrates, the Ge film being employed as a conducting intermediate layer. In addition, thin (2000Å and 1 μm) films of Mo have been used as conducting intermediate layers. Polycrystalline GaAs n/n+, p/p+, and p-n junction structures have also been grown on low-cost substrates, and Schottky-barrier solar cells have been fabricated in some of the n/n+ structures. Development of techniques for preparing polycrystalline layers with improved electrical properties and increased gain sizes will continue.

Single-crystal films of GaAs and $Ga_{(1-x)}Al_xAs$ ($x \sim 0.8$) have been grown to study the Zn and Se doping of these materials and to provide the doping data needed to grow p-n junctions and heteterostructure solar cell configurations. Two-layer single-crystal structures, consisting of p-GaAlAs/p-GaAs on an n-type single-crystal GaAs substrate, and three-layer epitaxial structures, consisting of p-GaAlAs:Zn/p-GaAs:Zn/n-GaAs:Se on an n-type single-crystal Si-doped GaAs substrate, with very thin (~500 Å) GaAlAs window layers, have been prepared for fabrication of solar cells. Deposition experiments with various configurations and doping levels on single-crystal substrates will continue, although the emphasis will be on polycrystalline films of GaAs and GaAlAs in the coming quarter.

The electrical resistivity of doped p-type polycrystalline GaAs films, determined by van der Pauw measurements, is found to vary with doping in a manner similar to that of Se-doped n-type films; that is, $\rho \propto p^{-3/2}$, where p is the net hole concentration. Resistivities are generally two orders of magnitude greater than that of comparably doped single-crystal material, with the minimum observed resistivity being ~0.07 ohm-cm.

The physical properties of GaAs on a variety of low-cost substrates have been examined in the SEM. GaAs grown on Mo/glass composite substrates exhibits surface features similar to those found on many other materials, including bulk Mo metal sheet, with surface features 2-5 μm across and height variations of 1-2 μm. Similar properties have been seen on GaAs films grown on Mo/alumina composites.

The physical properties of GaAs films grown on Ge layers deposited on all of the candidate insulator materials have also been studied. In most cases the presence of the Ge intermediate layer resulted in more planar growth and, in some cases, in larger grain sizes than obtained for GaAs growth directly on the low-cost substrate material. However, Ge nucleation and growth on all of the glasses was found to be at relatively widely separated sites, with the result that incomplete coverage of the substrate was obtained in most instances. This caused the GaAs overgrowth to be similarly discontinuous.

Techniques for characterizing polycrystalline GaAs films have been developed further. The reference standard for polycrystalline GaAs has been prepared and techniques for establishing preferred orientation specified. Efforts are continuing on development of rapid and unambiguous methods for determining grain size. Experiments to determine the $A\ell$ concentrations in $GaA\ell As$ alloys are also in progress, with a comparison of electron microprobe measurements of composition and x-ray determination of lattice parameters being made in an attempt to establish standards of $\Delta a/a_0$ that can be used for composition determination in the future.

Single-crystal window-type heterostructure solar cells have been fabricated in $GaA\ell As$/GaAs multilayer structures grown by the MO-CVD process. Devices with no AR coating have been evaluated under simulated AMO illumination and found to have conversion efficiencies as high as 12.8 percent. Devices with all-epitaxial junctions were found to have much higher efficiencies than those with junctions at the film-substrate interface. Open-circuit photovoltages as high as 0.99 V, short-circuit current densities as high as 24.5 mA/cm^2, and curve fill-factors up to 0.74 have been achieved. These results clearly show that the MO-CVD process is capable of producing materials with the photovoltaic properties required for high-efficiency $GaA\ell As$/GaAs solar cells.

Polycrystalline solar cells have also been grown and fabricated. Initial results on Schottky-barrier solar cells formed on films grown on Mo/glass composite substrates indicated efficiencies of 1.35 percent under simulated AMO illumination. Other composite substrates are in use for fabrication of additional Schottky-barrier devices, and the properties of junction-type pollycrystalline cell structures are also to be evaluated in the coming quarter.

4. PLANS FOR NEXT QUARTER

The activities of the program in the fourth quarter will follow the plans defined in the revised Technical Program Plan and Schedule given in Monthly Letter Report No. 9. By task, these planned activities are as follows:

Task 1

1. Continue attempts to obtain substrate materials - especially glasses and ceramics - with properties satisfactory for use in this program
2. Evaluate polished high-purity graphite as substrate for GaAs thin-film solar cell structures
3. Prepare substrates of Corning Code 9606 glass-ceramic, aluminas, and other potentially low-cost materials with deposited Mo layers for use in GaAs film growth experiments
4. Prepare textured surfaces on selected candidate glass and alumina substrates by various procedures, and continue to test controlled surface cleaning procedures for producing optimized film growth surfaces.

Task 2

1. Continue studies of growth of polycrystalline GaAs on Mo-coated low-cost substrates
2. Conduct deposition experiments to evaluate graphite as possible substrate for growth of polycrystalline GaAs solar cells
3. Study growth of Ge films on various low-cost substrates, for possible use as intermediate layer for GaAs growth
4. Study possible approaches to grain size enhancement of Ge intermediate layers on low-cost substrates
5. Study growth of GaAs films on Ge layers on low-cost substrates
6. Continue growth of single-crystal multilayer structures for use in fabricating solar cells
7. Continue growth of polycrystalline GaAs junction-type and Schottky-barrier solar cell structures
8. Continue efforts to find long-term solution to problem of faulty SiC-covered graphite susceptors.

Task 3

1. Continue routine evaluation of electrical and structural properties of single-crystal and polycrystalline films of GaAs and GaAℓAs on various substrates

2. Continue to investige SEM EBIC-mode measurements and various etching techniques for determining grain sizes in polycrystalline films, and specify preferred method
3. Investigate C-V analysis and other methods for determination of carrier concentration vs depth in single-crystal and polycrystalline films
4. Identify and apply preferred method for determining minority carrier diffusion lengths in single-crystal and polycrystalline GaAs films
5. Complete development of lattice parameter differential measurement as means of determining Aℓ concentration in GaAℓAs films.

Task 4

1. Evaluate electrical properties of p-n junctions in polycrystalline films on conducting substrates
2. Construct and evaluate properties of Schottky-barrier solar cell devices in polycrystalline films on variety of composite substrates
3. Continue evaluation of single-crystal thin-film solar cell structures, including those that have been antireflection coated
4. Fabricate Schottky-barrier and p-n junction solar cell structures in GaAs films on single-crystal sapphire substrates, and evaluate properties of resulting devices

Task 5

1. Complete analysis of cost of producing photovoltaic cells of two conceptual designs on experimental laboratory basis
2. Complete projection of total costs of producing cells of two conceptual designs on limited pilot-line basis
3. Prepare projections of possible future costs of large-scale production of thin-film GaAs solar cells made by MO-CVD process.

5. REFERENCES

1. H. M. Manasevit and W. I. Simpson, J. Electrochem. Soc. 116, 1725 (1969); H. M. Manasevit, J. Cryst. Growth 13/14, 306 (1972); H. M. Manasevit and A. C. Thorsen, Met. Trans. 1, 623 (1970); H. M. Manasevit, J. Electrochem. Soc. 118, 647 (1971).

2. R. P. Ruth, P. D. Dapkus, R. D. Dupuis, R. E. Johnson, H. M. Manasevit, L. A. Moudy, and J. J. Yang, "Thin Films of Gallium Arsenide on Low-cost Substrates," Quarterly Project Report No. 1, November 1976, Rockwell International, Electronics Research Division, Anaheim, CA 92803. Contract No. E(04-3)-1202, Division of Solar Energy, U. S. Energy Research and Development Administration.

3. R. P. Ruth, P. D. Dapkus, R. D. Dupuis, A. G. Campbell, R. E. Johnson, H. M. Manasevit, L. A. Moudy, and J. J. Yang, "Thin Films of Gallium Arsenide on Low-cost Substrates," Quarterly Project Report No. 2, January 1977, Rockwell International, Electronics Research Division, Anaheim, CA 92803. Contract No. E(04-3)-1202, Division of Solar Energy, U. S. Energy Research and Development Administration.

4. GaAs: G. Gieseike and H. Pfister, Acta Cryst. 11, 369 (1958); AℓAs: N.A. Gorgunova, Chemistry of Diamond Like Semiconductors (in Russian) (Izd, LGU, Leningrad, 1963), p. 92).

5. J. M. Woodall and H. J. Hovel, Appl. Phys. Lett. 21, 379 (1972); also R. Sahai, P. D. Edwall, E. Cory, and J. S. Harris, Late News Paper No. 13.13, 12th IEEE Photovoltaic Specialists Conference, Baton Rouge, LA, November 15-18, 1976.

6. Discussed in original program proposal for "Chemical Vapor Deposition Growth," JPL Contract No. 954372 issued to Rockwell International, Anaheim, CA, on December 29, 1975. See, for example, R. P. Ruth, H. M. Manasevit, R. E. Johnson, J. L. Kenty, L. A. Moudy, W. I. Simpson, and J. J. Yang, "Chemical Vapor Deposition Growth," Annual Report, 1 October 1976, Rockwell International, Electronics Research Division, Anaheim, CA 92803. JPL Contract No. 954372, performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U. S. Energy Research and Development Administration, Division of Solar Energy.

☆U.S. GOVERNMENT PRINTING OFFICE: 1977 -743-920/ 4328 REGION NO. 4