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THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

Quarterly Technical Progress Report No. 7 and
Topical Report No. 3, April 2—July 1, 1978

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July 1978

MASTER

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

Rockwell International
Anaheim, California

U.S. Department of Energy

Solar Energy

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QUARTERLY TECHNICAL PROGRESS REPORT NO. 7
AND
TOPICAL REPORT NO. 3

for the period

April 2, 1978 – July 1, 1978

R.P. Ruth, P.D. Dapkus, R.D. Dupuis, R.E. Johnson,
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DEPARTMENT OF ENERGY, UNDER CONTRACT NO. EY-76-C-03-1202

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ABSTRACT

The seventh quarter of work on the contract is summarized. The metalorganic chemical vapor deposition (MO-CVD) technique has been applied to the growth of thin films of GaAs and GaAℓAs on inexpensive polycrystalline or amorphous substrate materials (primarily glasses and metals) for use in fabrication of large-area low-cost photovoltaic device structures. Trimethylgallium (TMG), arsine (AsH_3), and trimethylaluminum (TMAℓ) 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 of 725-750°C, to produce the desired film composition and properties.

The technical activities during the quarter were concentrated on 1) a continuing evaluation of various graphite materials as possible substrates for MO-CVD growth of polycrystalline GaAs solar cells; 2) attempts to improve the quality (especially the grain size) of polycrystalline GaAs films on Mo sheet and Mo/glass substrates by using HCℓ vapor during the MO-CVD growth process; 3) further studies of the transport properties of polycrystalline GaAs films, with emphasis on n-type films; 4) continuing investigations of the properties of p-n junctions in polycrystalline GaAs, with emphasis on the formation and properties of $p^+/n/n^+$ deposited structures; and 5) assembling apparatus and establishing a suitable technique for producing TiO_2 layers for use as AR coatings on GaAs cells.

Success in the use of graphite substrates was found to be still somewhat limited, based on the low photovoltaic conversion efficiencies obtained in Schottky-barrier solar cell structures on polycrystalline GaAs grown on various graphites. Intermediate layers of Ge or Mo appeared to "seal" the graphite surface and permit improved device performance, but the results were still not satisfactory.

The use of HCℓ vapor during growth of polycrystalline GaAs films by the MO-CVD process was shown to increase substantially the average grain size and also to improve the uniformity of the morphology of such films grown on Mo surfaces (either sheet or deposited film on glass). The eventual usefulness of this procedure for improving polycrystalline solar cell performance appears to depend upon the satisfactory solution of several problems that result from the presence of the HCℓ in the reactant gas mixture, including (1) the necessity for cleaning the reactor system more frequently because of additional reaction products that are formed; (2) the increase in net carrier concentration in the film; (3) the need for growing a "sealing layer" of $\sim 2\ \mu m$ thickness without HCℓ before proceeding with HCℓ-accompanied growth if Mo substrates are involved; and (4) the increased temperature sensitivity of the net growth rate.

The transport properties of n-type polycrystalline films of GaAs were investigated and found to be controlled by transport of majority carriers across the grain boundaries in essentially the same way that was observed for p-type films. The height of the barrier to carrier flow in the boundary region was seen to depend upon the impurity doping concentration added to the film during growth, with the barrier height decreasing with increasing doping. The barrier height E_b varies as $\ell n\ (1/N_D)$, where N_D is the nominal doping concentration, instead of simply $(1/N_D)$ as predicted by the model used to describe the behavior of the polycrystalline material. A similar

relationship had been observed in the earlier work with p-type films. The discrepancy between observation and model is attributed to an increasing density of interface trapped charge with increasing doping concentration.

The properties of polycrystalline GaAs p-n junctions were found still to be dominated by the properties of the grain boundary regions, although $p^+/n/n^+$ structures, in which the n layer is undoped and up to 10 μm thick, resulted in somewhat improved electrical characteristics. The need for an adequate model of the electronic structure in the grain boundary regions is again emphasized by these results. Additional work with Au Schottky-barrier devices on polycrystalline GaAs n/n^+ structures demonstrated the apparently major role played by current collection in the depletion layer as well as the doping level in the n layer in determining the overall performance of the device. It was also found that Au layer thicknesses of 75-100Å should be used for best device results, rather than the previously used 50Å, in fabricating Schottky barriers on these polycrystalline GaAs materials.

A simple apparatus was assembled and a satisfactory deposition technique was developed for preparing TiO_2 layers of controllable thickness and index of refraction in the range 1.9 to 2.4. These layers appear to meet the requirements for AR coatings for GaAs solar cells for this program.

Plans for the activities of the next quarter are outlined.

CONTENTS

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ILLUSTRATIONS

ILLUSTRATIONS (Cont)

TABLES

1. INTRODUCTION

The long-range objective of the National Photovoltaic Program is to ensure that photovoltaic conversion systems play a significant role in the nation's energy supply by stimulating an industry capable of providing approximately 50 Gwe of installed electricity generating capacity by the year 2000.

One of the specific shorter-term objectives of the national program is to conduct research and advanced development on thin-film materials, cell structures, and advanced concentrator material systems to show the feasibility of reducing photovoltaic array costs to $300 per peak kwe by 1986, and to establish the viability of this advanced technology by the year 1990.

The Research and Advanced Development activity of the national program has among its specific technical goals the demonstration of at least 10 percent AM1 cell efficiency in more than one thin-film solar cell material or configuration by the end of FY80, with continued emphasis on reaching the longer-term goals. The latter consist primarily of (1) achieving flat-plate module or concentrator array prices (1975 dollars) of less than $0.50 per peak watt (electric) by 1986 with an annual production rate of at least 500 peak Mw of arrays/modules, and (2) achieving flat-plate module or concentrator array prices (1975 dollars) of $0.10 to $0.30 per peak watt (electric) by 1990 with an annual production rate of such arrays/modules of at least 10-20 peak Gw by the year 2000.

The work of this contract is directed toward these goals. The overall objective of the contract is the performance of intensive studies that constitute an initial step in DoE'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 anticipated.

1.1 GENERAL TECHNICAL APPROACH OF CONTRACT WORK

The general technical approach used in this program has involved the metalorganic chemical vapor deposition (MO-CVD) technique for the growth of thin films of GaAs and GaAℓAs on inexpensive polycrystalline or amorphous substrate materials in configurations permitting fabrication of photovoltaic devices. The parameters of the CVD process have been chosen to maximize the chances of achieving the required properties in the deposited films and the efficiency goal of the photovoltaic devices (10 percent AM1), subject to the constraints imposed by the properties of the selected substrate material(s).

As 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:

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4.$$

By mixing TMG in the gas phase with trimethylaluminum (TMAℓ) 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 TMAℓ and AsH_3, if desired. Many such compounds and alloys have been prepared by the MO-CVD process (Ref 1).

The MO-CVD process has several characteristics that are important to the work of this program:

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

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

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

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

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

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

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

The CVD technique is viewed as potentially the best method for achieving large areas of solar cells at sufficiently low cost to meet both the performance goals and the economic goals of DoE's long-range program. The results of the first year's work of this program demonstrated that the MO-CVD technique is capable of producing materials of quality sufficient to meet the technical goals of the photovoltaic conversion program, and that the technique is also a strong candidate for eventual use in fabrication of single-crystal GaAℓAs/GaAs cells for high-efficiency applications (e.g., space power supplies), with or without concentrator systems.

1.2 TECHNICAL TASKS OF PRESENT PROGRAM

The second year of the program is emphasizing improved understanding of the properties and effects of grain boundaries in the polycrystalline films. In addition, further attention is being devoted to junction formation techniques and techniques which yield larger grain size for equivalent Ga content. Further development of solar cell fabrication technology, including contact and AR coatings, is also being undertaken.

To pursue these technical problems and to meet the objectives of the modified contract the work of the second year has been organized into five main technical tasks, as follows:

Task 1.	Experimental Evaluation of Low-cost Substrates and Methods for Obtaining Enhanced Grain Size in MO-CVD Films
Task 2.	Evaluation of Film Properties and Grain Boundary Effects and Correlation with CVD Growth Parameters
Task 3.	Investigation and Development of Barrier Formation Techniques
Task 4.	Development of Photovoltaic Device Designs and Fabrication Techniques
Task 5.	Analysis and Projection of Cell Material Requirements and Fabrication Costs.

In addition, the required program management activity and the preparation of technical reports and documentation, technical data, and review and briefing information, as well as the preparation and delivery of the required representative samples each month, are carried on in conjunction with the above technical tasks.

This is the seventh Quarterly Technical Progress Report (including the Annual Report (Ref 2)) and the third Topical Report for this contract and covers the period April 2 through July 1, 1978. The technical activities for 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 next quarter's activities are outlined in Section 4. Section 5 contains references used in the body of the report.

2. TECHNICAL PROGRESS

The work of the seventh quarter of the program is described by task in this section.

2.1 TASK 1. EXPERIMENTAL EVALUATION OF LOW-COST SUBSTRATES AND METHODS FOR OBTAINING ENHANCED GRAIN SIZE IN MO-CVD FILMS

This task involves the evaluation of glass, glass-ceramic, graphite, or other suitable materials as low-cost substrates, as well as the detailed analyses and experimental studies necessary to grow thin films of GaAs with enhanced grain size on these substrates using the MO-CVD process. Work in these two areas is summarized in the following sections.

Most of the effort during this quarter was devoted to further development of techniques for growing polycrystalline GaAs on graphite substrates by MO-CVD and to investigation of the effect upon polycrystalline grain size of additions of HCℓ to the MO-CVD growth process. The results of the HCℓ studies and the difficulties encountered with the use of HCℓ during growth on Mo substrates, as described below, provide added impetus to the efforts to develop satisfactory graphite substrates and growth techniques using that substrate material.

2.1.1 Evaluation of Graphite as Low-cost Substrate

Graphite is an attractive potential substrate for deposition of GaAs polycrystalline thin-film solar cells. The purity, conductivity and chemical inertness of several potentially low-cost grades of graphite make it an almost ideal substrate for chemical vapor deposition of GaAs polycrystalline films (Ref 3). Early work at Rockwell on this program concentrated on the growth of GaAs by MO-CVD on polished graphite substrates, but these films were generally not adherent. Subsequent work has concentrated on cleaned but unpolished films.

During this quarter the growth of films and device structures on four kinds of graphite was undertaken with the goal of understanding the limitations of this material for this application. In addition, the effects of various cleaning and baking procedures and coatings (e.g., thin films of Ge and Mo) upon the photovoltaic properties of the resultant cells were investigated. The following graphites were used in this work: Carbone-Lorraine Grade 5890 and Poco Grades DFP-3, AXF-9Q and ACF-10Q.

Typical surfaces for GaAs films grown on each of these graphites are shown in the SEM photographs in Figure 2-1. Grain sizes at the surface range from less than 1 μm to ~10 μm, with slightly different crystal growth habit evident for each of the four cases. The films shown in Figure 2-1 were grown simultaneously in a single deposition experiment, with average thicknesses of 4-5 μm and a deposition temperature of 725°C. No further structural analyses had been carried out on these films in the period covered by this report. However, no substantial difference was found in the device performance achieved on films grown on any of the four graphites, as is discussed below. If later evaluation of device structures indicates that significant differences are appearing then attempts will be made to correlate such differences with the results of more extensive analysis of the structure of the films and the substrates themselves.

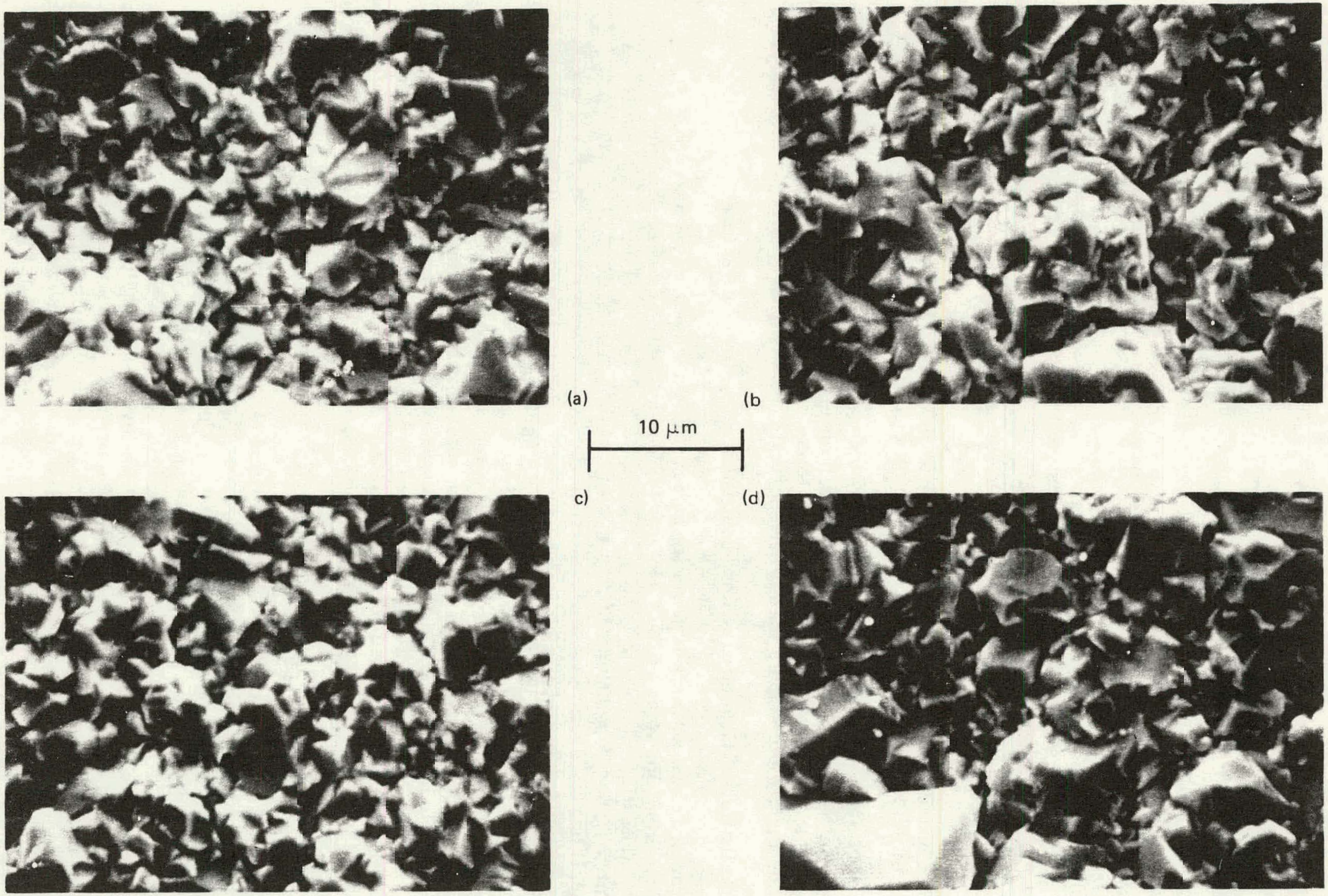


Figure 2-1. SEM Photographs of Surfaces of GaAs Films Grown by MO-CVD on Several Different Graphite Substrates; Substrates Are a) Carbone-Lorraine Grade 5890, b) Poco Grade DFP-3, c) Poco Grade AXF-9Q, d) Poco Grade ACF-10Q.

Evaluation of the photovoltaic potential of GaAs films grown on these substrates was accomplished by the use of n/n^+ structures consisting of n^+ layers doped to $N_D \approx 5\text{x}10^{18}$ cm^{-3} and undoped n layers with N_D-$N_A \approx 2\text{x}10^{15}$ cm^{-3}. The n^+ layer was used to provide adequate ohmic contact to the substrate. The thickness of the layers was varied by varying deposition time. Schottky-barrier solar cells were then fabricated by depositing an array of thin (~ 50-100Å) Au pads 0.05 x 0.05 in. on the surface. The thickness of the Au was controlled during vacuum deposition by a quartz-crystal deposition thickness monitor.

A series of devices of this type was used to provide a comparison of the effects on the quality of the deposited GaAs layer of different surface cleaning procedures used for the graphites. Representative I-V characteristics for these devices are shown in Figure 2-2. The data for films grown on all of the graphite substrates showed no significant or reproducible photovoltaic effect, similar to the situation illustrated in the figure. In most cases any light-induced change appeared to be a modulation of the forward resistance of the device. As indicated in the curves of Figure 2-2 the devices also exhibited substantially higher forward voltages than those typically observed for Schottky-barrier devices. This may be indicative of an interface problem at the GaAs-graphite interface.

The devices illustrated by Figure 2-2 were prepared on substrates that had been solvent-cleaned, dried, and baked at ~1000°C in H_2 for 15 min. Increasing the bake time to 30 min and omitting the solvent cleaning made no substantial change in device performance.

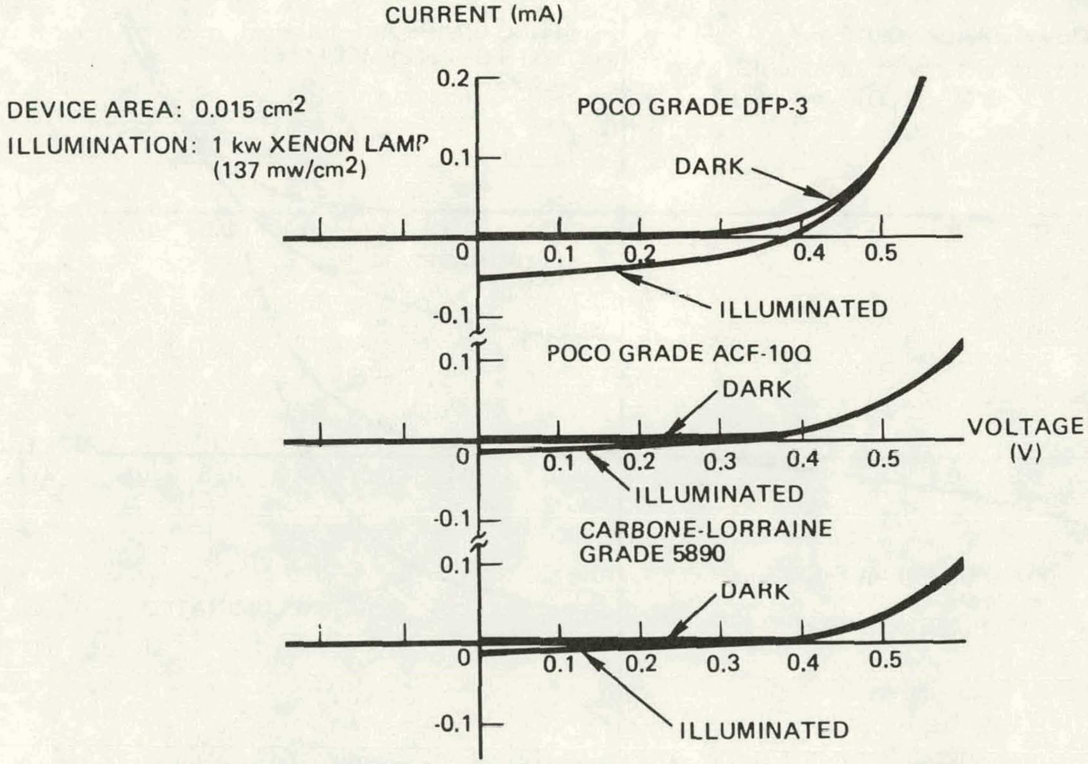


Figure 2-2. I-V Characteristics of Au Schottky-barrier Solar Cells on n/n^+ GaAs Structures Grown by MO-CVD on Three Different Grades of Graphite

To further determine the effect of substrate cleanliness on device performance, samples of GaAs were then grown on graphite substrates that were coated with either Ge or Mo deposited films. The Ge films were prepared by CVD and were approximately 5 μm thick. The Mo films were sputtered by the same process that was typically used for the Mo/glass substrates used in this program. Representative I-V curves for two of these samples are shown in Figure 2-3. Note that substantial photocurrent was generated in these devices - comparable to that seen in the best devices previously grown on Mo or Mo/glass substrates.

However, the I-V characteristics measured across a given wafer showed a great deal more variation and the forward I-V characteristics were generally "softer" than for similar devices in GaAs on Mo or Mo/glass substrates. The Ge and Mo coatings on the graphite either sealed the surface of the graphite (at least in some areas) or perhaps altered the GaAs growth habit so that films with better properties resulted. The added possibility that Ge intermediate films might also enhance grain size in deposited GaAs may warrant further evaluation of Ge films, in particular, later in the program. However, the cause of the low device efficiencies and the variations in device properties observed over a given GaAs/graphite composite sample requires additional investigation. Each of the four graphites used in the above experiments will be examined separately to attempt to determine if cross-contamination among them may have been the cause of the low efficiencies seen to date.

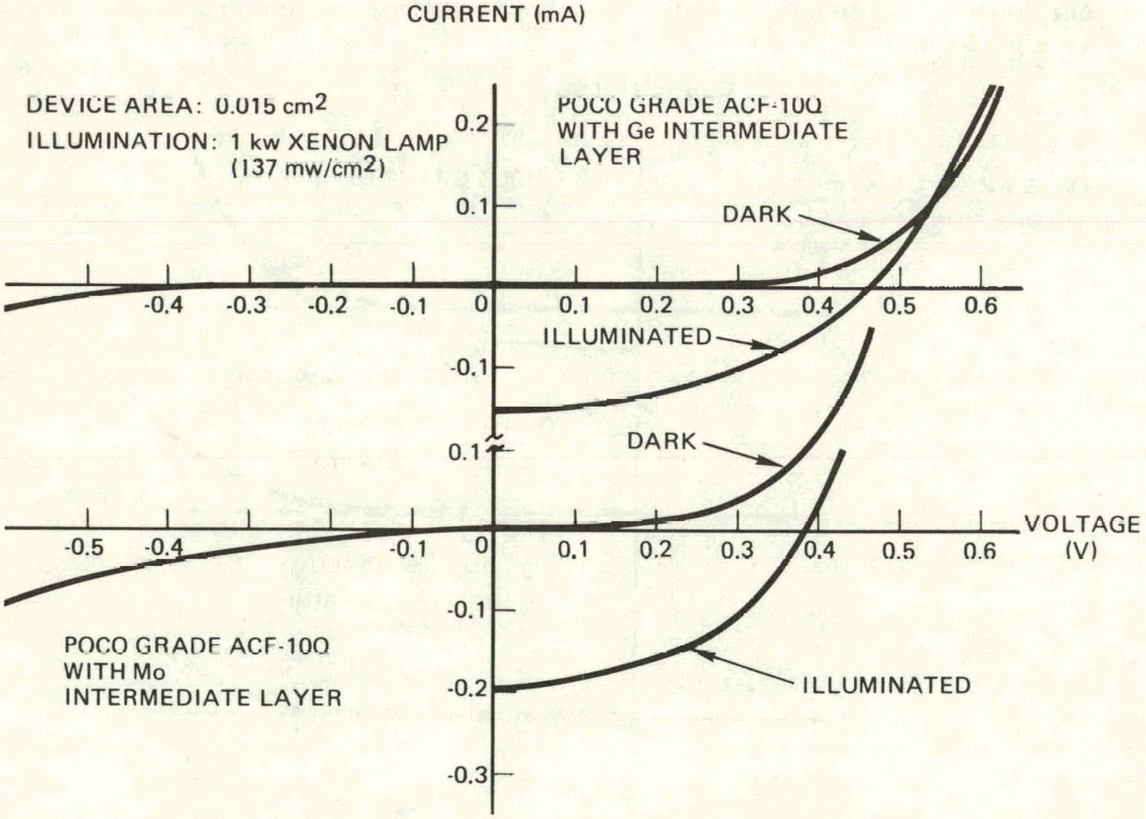


Figure 2-3. I-V Characteristics of Au Schottky-barrier Solar Cells on n/n$^+$ GaAs Structures Grown by MO-CVD on Poco Grade ACF-10Q Graphite Substrates with Ge and Mo Intermediate Layers

2.1.2 Grain Size Enhancement Using HCℓ during MO-CVD Growth of GaAs Films

One of the major advantages of the MO-CVD process for deposition of thin-film solar cells is the unidirectional nature of the pyrolysis reaction, i.e., the absence of a competing reverse or etching reaction during film growth (see Section 1.1). This makes it possible to grow GaAs (or other) films on a wide variety of substrates that might otherwise be subject to severe attack in other CVD processes.

On the other hand, this characteristic also tends to allow virtually unrestricted nucleation and island growth in the early stages of film deposition, and this may - in some cases, at least - lead to smaller average grain size in polycrystalline films than might be obtained on the same substrate material using a CVD process that does contain a chemical etching species.

To evaluate the effects of such etching on the growth of GaAs films by MO-CVD a series of investigations was conducted using HCℓ vapor as a constituent of the reactant gas mixture in a modified MO-CVD process. The HCℓ was added to the gas stream just prior to its entering the top port of the cold-wall deposition chamber. The modified process thus retained many of the advantages inherent in the basic MO-CVD process yet the overall chemistry of the process would be expected to be modified considerably. At the least, a bidirectional reaction was expected, in which the normal MO-CVD pyrolysis that produces film growth would be competing with the etching action of the HCℓ. In practice a more complicated reaction chemistry undoubtedly resulted, with a variety of intermediate compounds probably formed. Irrespective of this, however, it was hoped that the presence of HCℓ would enhance the average grain size in the polycrystalline GaAs films by increasing the definition of certain crystallographic facets and thus increasing growth on those planes and by discriminating against the continued development of smaller nuclei and grains, all as the result of the etching mechanism. It is a well-established experimental fact (Ref 4) that the etching of single-crystal GaAs is highly preferential crystallographically at temperatures below 800°C. Bhat and others (Ref 4) have shown there is a strong tendency toward pitting of $\{100\}$ facets in GaAs and major differences in etch rates for various low-index planes in GaAs at temperatures below 800°C. Above that temperature, however, all low-index planes appear to etch at the same rate and without pitting.

Initial experiments were carried out using a third reactor not previously used in this program. The growth rate and As/Ga ratio were adjusted so that the single-crystal and polycrystalline GaAs films grown in this reactor were generally equivalent to those grown in the other two reactors being used in the program. Initial HCℓ experiments were performed with Mo/glass substrates by adding at first small and then increasing amounts of HCℓ to the growth environment through the gas inlet manifold. As the HCℓ flow rate (and thus partial pressure) was increased an increasing problem of poor adherence of the GaAs film to the substrate was observed. At high HCℓ flow rates ($p_{HC\ell} \approx 0.1\ p_{TMG}$) it became obvious that the HCℓ was attacking the Mo film and thus undercutting the growing GaAs film. Mo sheet substrates were substituted for the Mo/glass composites and showed somewhat better resistance to this effect, but the undercutting still occurred to an undesirable extent.

In an attempt to "seal" the substrate and still allow the influence of HCℓ on film growth, thin layers of GaAs were first deposited on the Mo without HCℓ present and then HCℓ was added for the remainder of the growth. A GaAs thickness of ~2 μm was found necessary to provide the required sealing of the surface for Mo sheet substrates. Thicker layers were required for the Mo/glass substrates. As a result all further experiments were done with thin Mo sheet substrates. It should be pointed out that at times the sealing layer would have a pinhole and the introduction of HCℓ would result in local undercutting of the substrate and subsequent film peeling. However, a pinhole-free sealing layer of GaAs resulted in an adherent uniform film.

A series of runs was then made with increasing HCℓ flow rates, using Mo sheet substrates. The growth rate was determined by measuring the total thickness of the GaAs film, including the sealing layer, and dividing by the total growth time. In most cases the film was grown to a total thickness of 12-16 μm. Figure 2-4 shows the dependence of growth rate upon relative HCℓ flow rate in the reactor. Although there is considerable scatter in the data it can be seen that there is no substantial decrease in the growth rate with HCℓ addition in the range examined. Since etching of GaAs with HCℓ is strongly temperature-activated it is expected that these results could be greatly changed at higher growth temperatures. Most likely, however, higher growth temperatures would also require less HCℓ to produce similar changes in the morphology of growth.

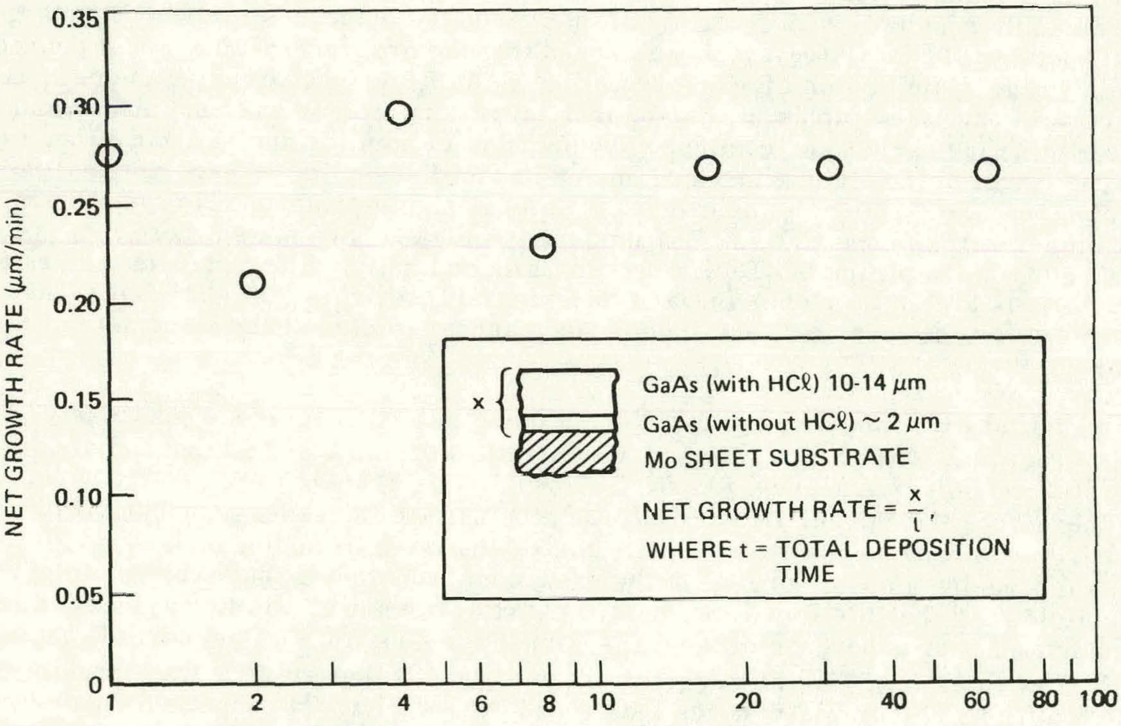


Figure 2-4. Dependence of Net Growth Rate of GaAs Film, Deposited by MO-CVD on Mo Sheet Substrate at 725°C, upon Relative Concentration (i.e., Flow Rate) of HCℓ Vapor Added to Reactant Gas Stream

The change in growth morphology for GaAs deposited by MO-CVD on Mo with no HCℓ added and with the highest flow rate of HCℓ added is shown in Figure 2-5 for thick films (~40 μm) grown at 725°C on a Mo sheet substrate. Note the increase in average grain size and the increased uniformity of grain size that results with the use of HCℓ during growth. If this kind of grain size enhancement can also be induced in thinner films it should then be possible to improve the performance of devices formed in them.

Figure 2-6 shows a series of four GaAs films grown at 725°C on Mo sheet substrates with increasing HCℓ partial pressure. The highest HCℓ flow rate represented is half of that used during deposition of the film shown in Figure 2-5b. It can be seen that the major effects of the HCℓ additions on the film morphology occur in the films deposited with HCℓ flow rates greater than 0.75 ccpm. It is difficult to determine accurately the actual partial pressure of the HCℓ in the vicinity of the substrate since the flow patterns in that region of the deposition chamber are not well known; HCℓ flow rates have thus been used as a measure of the HCℓ concentration in most of this work.

The above results clearly established that the presence of HCℓ in sufficient concentration in the deposition chamber can have a significant effect upon both morphology and grain size in polycrystalline GaAs films grown by MO-CVD. The most effective concentration of HCℓ may be near that for which the etch rate and the normal deposition rate are equal, for a given deposition temperature. Based on these encouraging results additional study of the modified process is planned, with the hope that device results can be improved significantly through the use of HCℓ during growth of multilayer device structures.

Unfortunately, the beneficial effects of HCℓ are apparently not achieved without penalty. Several problems were encountered in association with its use in the MO-CVD process. The most annoying of these was the need to clean thoroughly not only the reactor deposition chamber after every run (the normal procedure) but also the neighboring portions of the reactor system after at most a few runs because of the formation of a black, oily volatile substance that formed in the output lines of the reactor system when HCℓ was used. It is not known at this time if this substance is formed as part of the deposition reaction and merely collects in the lines or if it is formed in place in these cold reactor parts. At any rate, its presence makes the reactor difficult to evacuate during film growth and in the worst cases can impede nucleation and growth on the substrate in subsequent runs. As a result, a policy of cleaning the reactor output section after every other run has been adopted. Also, the HCℓ now is added to a side-arm port of the top of the deposition chamber rather than in the gas manifold.

The other major problem associated with the use of HCℓ is the increase in the net carrier concentration of GaAs films grown with HCℓ present. The cause of this increase is not yet known but its effect is seen in the performance of devices formed in the films. Figure 2-7 shows the dark and illuminated I-V characteristics of two representative Au Schottky-barrier solar cell devices formed on n/n^+ polycrystalline GaAs structures deposited at 725°C on Mo substrates with HCℓ present. Although reasonable short-circuit currents (~9 mA/cm^2) were obtained the I-V characteristics are soft and symmetrical. Whether this was caused by high intragrain doping concentrations or preferential grain-boundary doping is not known at this time. However, since single-crystal GaAs films grown on single-crystal substrates with HCℓ present have been found to be doped to concentrations of $\sim 10^{17}$ cm^{-3} in some cases, it appears that intragrain doping is involved to some degree.

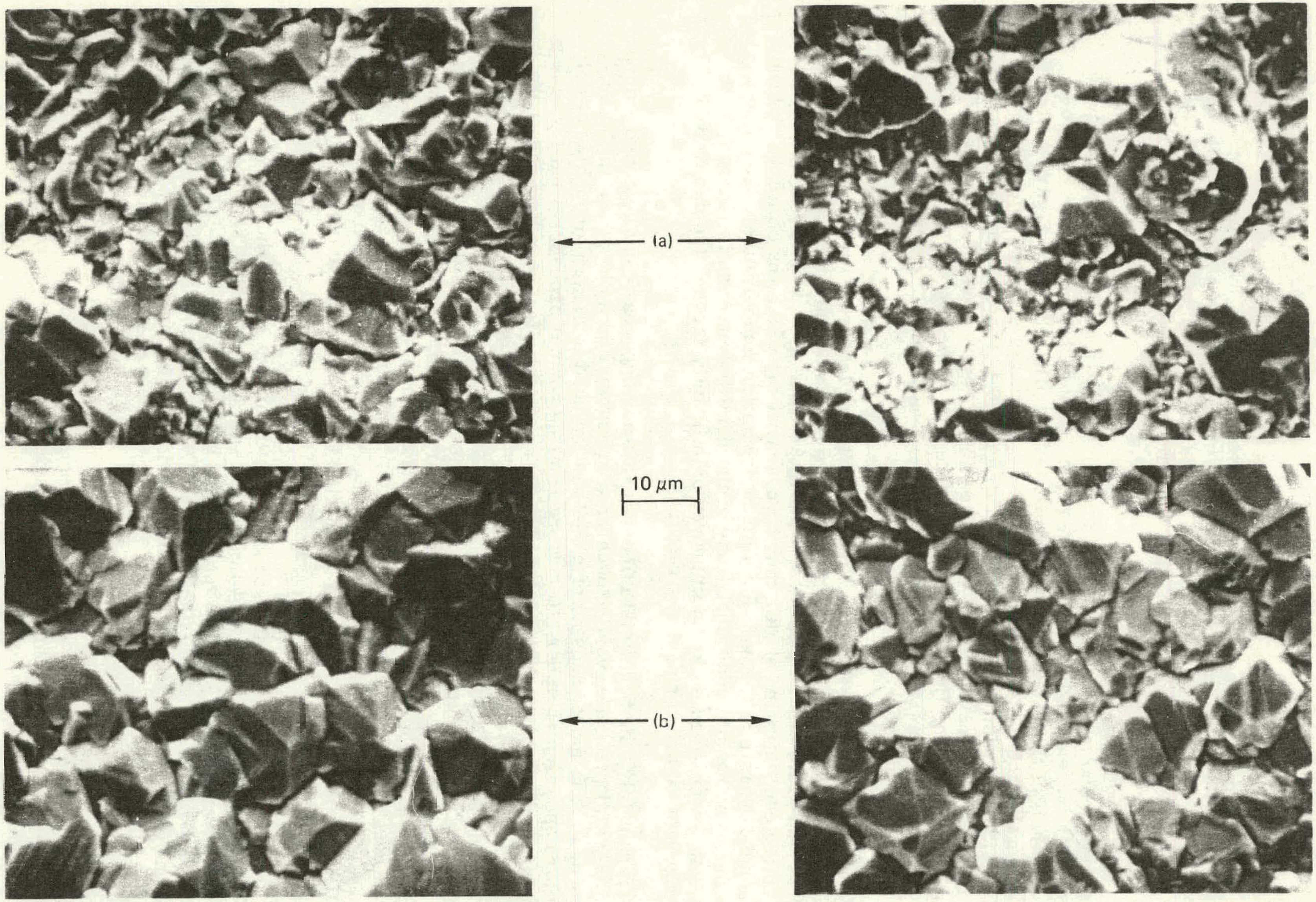


Figure 2-5. SEM Photographs Showing Effect of HCℓ Addition on MO-CVD GaAs Film Growth Morphology on Mo Sheet Substrates. a) No HCℓ; b) High Flow Rate of HCℓ. (Films ~40μm thick, deposited at 725°C.)

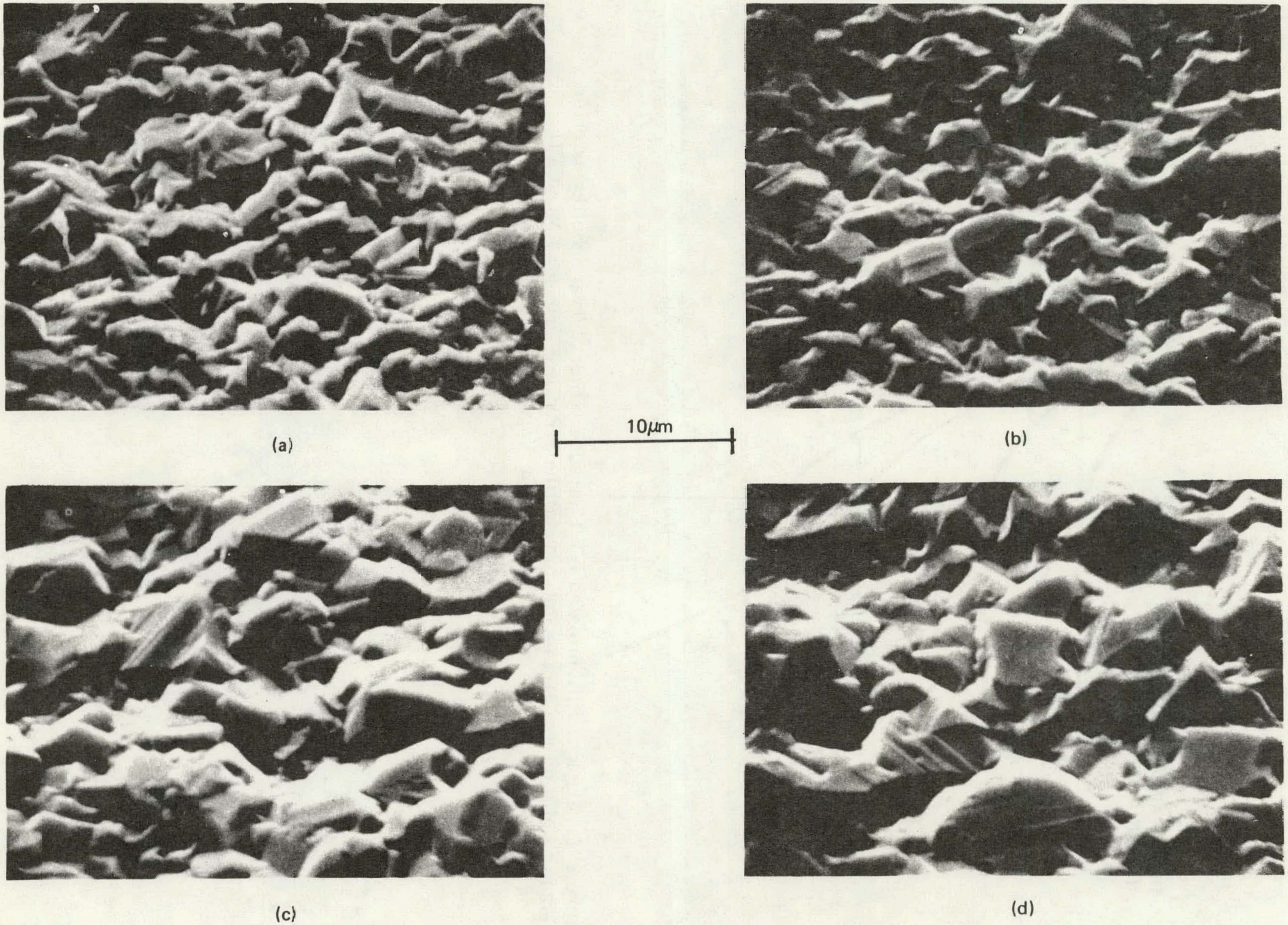


Figure 2-6. SEM Photographs Showing Effect of Increasing HCℓ Partial Pressure (Flow Rate) on Average Grain Size and Surface Morphology of MO-CVD GaAs Films Grown on Mo Sheet Substrates at 725°C. HCℓ Flow Rates a) 0.085 ccpm, b) 0.37 ccpm, c) 0.75 ccpm, d) 1.5 ccpm.

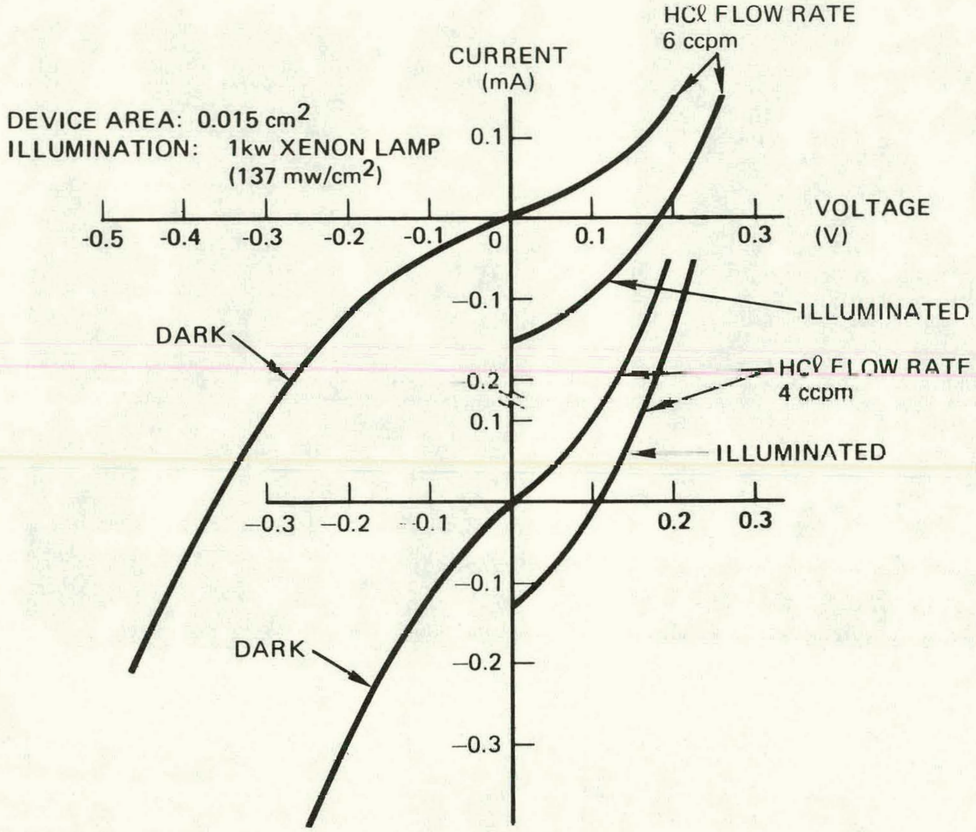


Figure 2-7. Dark and Illuminated I-V Characteristics of Two Schottky-barrier Solar Cells on n/n' GaAs Polycrystalline Structure Grown by MO-CVD on Mo Sheet Substrate at 725°C with HCℓ Vapor Present during Growth.

2.2 TASK 2. EVALUATION OF FILM PROPERTIES AND GRAIN BOUNDARY EFFECTS AND CORRELATION WITH CVD GROWTH PARAMETERS

This task is intended to involve the performance of parametric studies and measurements to determine the pertinent mechanical, electrical, and optical properties of the polycrystalline films — with emphasis on adherence, morphology, uniformity, doping concentrations, carrier concentrations, carrier mobilities and lifetimes, and contact properties (especially for the layer adjoining the substrate) — and the properties of the grain boundaries and the role they have in determining the properties of the films.

The three main activities included in this task are (1) improvement of film growth and doping procedures, (2) routine evaluation of film properties, and (3) study of grain boundary effects in the polycrystalline films grown on various low-cost substrates.

During the quarter covered by this report there was no additional work of significance in the first of these three areas, but considerable effort was devoted to routine evaluation of the properties of polycrystalline GaAs films by techniques discussed in earlier reports. The principal activity, however, was in the study of grain boundary effects in these films and especially in a continuation of the investigation of their transport properties.

Experiments had been initiated in the preceding quarter to examine the transport of majority carriers across grain boundaries in p-type polycrystalline GaAs films deposited by MO-CVD on substrates of large-grained Vistal 5 alumina and amorphous Corning Code 0317 glass (Ref 5). These studies were extended during the period of this report to include n-type Se-doped films.

As in the experiments with p-type films, two sets of polycrystalline GaAs n-type films were prepared, one on Vistal 5 and the other on 0317 glass, each set with Se doping concentrations in the range $\sim 10^{16}$ to $\sim 10^{19}$ cm^{-3} as determined by the flow rate of the H_2Se used as doping source. In each deposition experiment a substrate of (0001)-oriented single-crystal sapphire (α-$A\ell_2O_3$) was also included, resulting in growth of a companion epitaxial GaAs film of $\{111\}$ orientation along with the polycrystalline films. Deposition temperatures of 725°C were used in growing the three sets of films.

The polycrystalline GaAs films on the Vistal 5 substrates contained large numbers of individual crystal grains that had grown epitaxially on certain orientations of the large grains in the alumina substrates, resulting in generally large-grained growth. The GaAs films grown on the glass substrates were relatively small-grained, typically in the range 2-5 μm at the film surface for the film thicknesses (8-10 μm) used in these samples.

As was discussed in the preceding quarterly report (Ref 5), the assumption was made in this investigation that the impurity doping concentrations within the individual grains of the polycrystalline GaAs films on the alumina and on the glass substrates are the same as that in the simultaneously grown epitaxial film on the single-crystal sapphire substrate and that this can be determined by measurement of the electron concentration in the n-type epitaxial film.

The n-type samples were prepared for measurement by alloying In dots on the surface at 450°C for 1 min. Van der Pauw measurements of the Hall effect were performed on the automatic Hall-effect apparatus at several temperatures. The temperature of the sample was controlled manually. The magnet switching and data logging are performed automatically by the system, and the data are stored on tape and listed for subsequent reference. The data can later be retrieved from the tape and plotted on the accompanying plotter.

Figure 2-8 shows the room-temperature resistivity of n-type polycrystalline GaAs on both Vistal 5 and 0317 glass substrates as a function of doping concentration. As in the case of p-type material, the resistivity of polycrystalline n-type GaAs is 2-3 orders of magnitude higher than that of single-crystal material doped to the same nominal concentration. Further, the resistivities of films on Vistal 5 are seen to be considerably lower than those of films of the same nominal doping concentration on 0317 glass.

Resistivity as a function of sample temperature for the n-type polycrystalline films on Vistal 5 substrates and 0317 glass substrates is shown in Figures 2-9 and 2-10, respectively. In the temperature range 250-450°K the resistivity in both cases varies as exp (E_b/kT). The activation energy or effective barrier height E_b increases with decreasing doping concentration in the film. Most of this variation is caused by a variation of the carrier mobility with temperature, as was found to be the case for the p-type films (Ref 5).

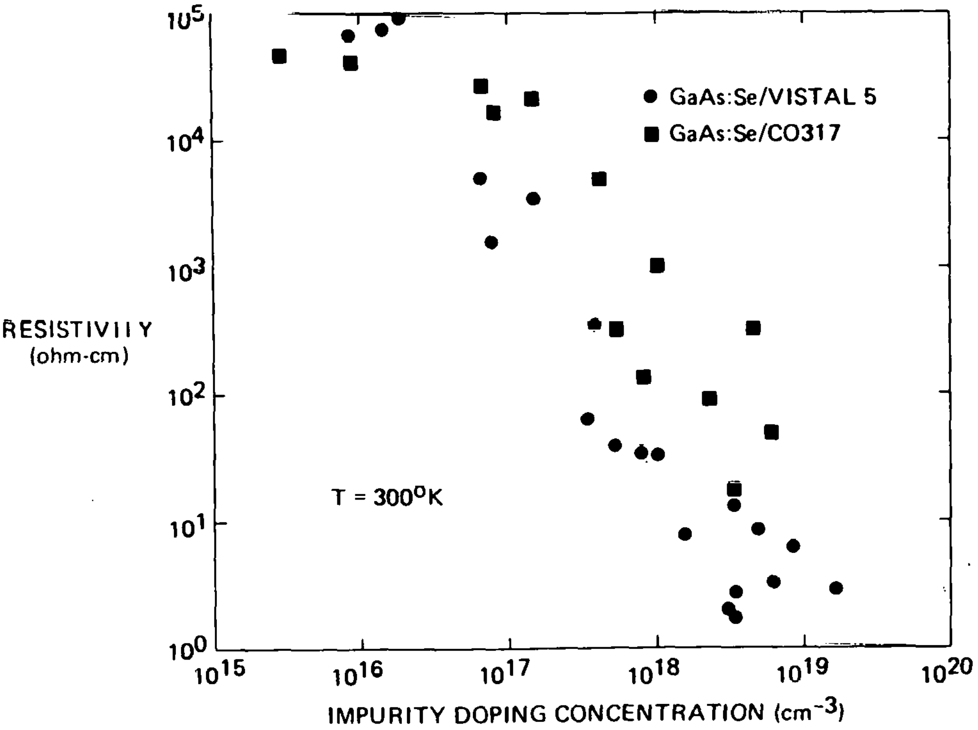


Figure 2-8. Room-temperature Resistivity of n-type Polycrystalline GaAs Films Deposited by MO-CVD on Substrates of Vistal 5 Alumina and Corning Code 0317 Glass, as Function of Se Doping Concentration (see text).

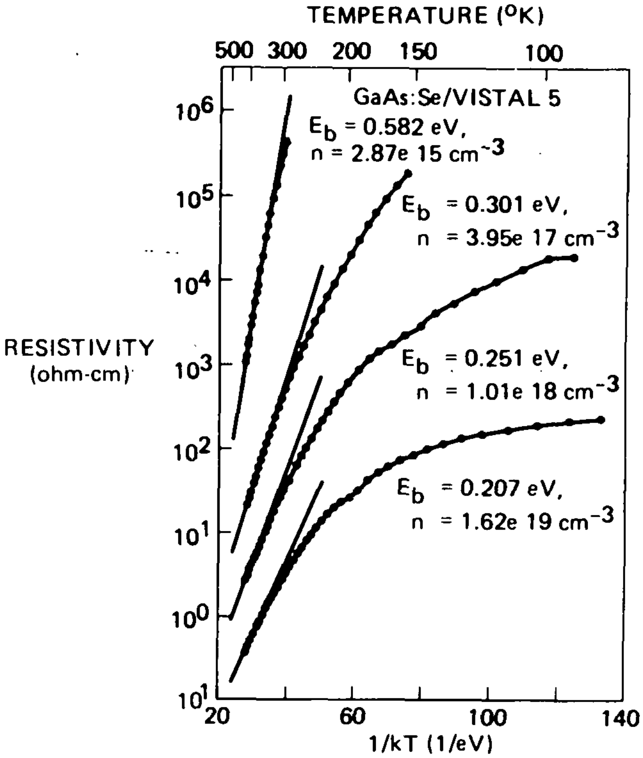


Figure 2-9. Measured Resistivity of n-type Polycrystalline GaAs Films, Deposited by MO-CVD on Vistal 5 Alumina Substrates, as Function of Sample Temperature for Various Doping Impurity Concentrations.

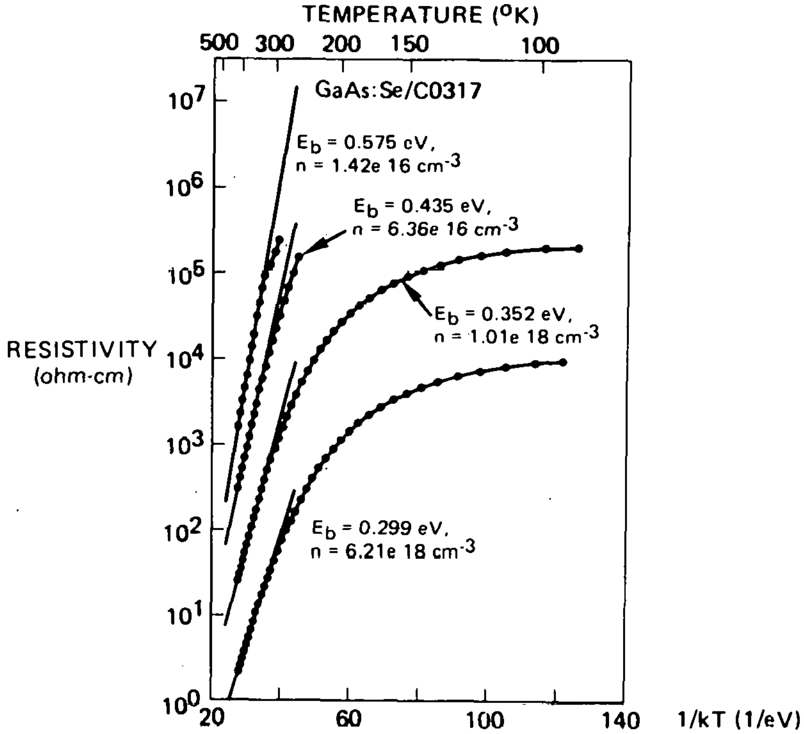
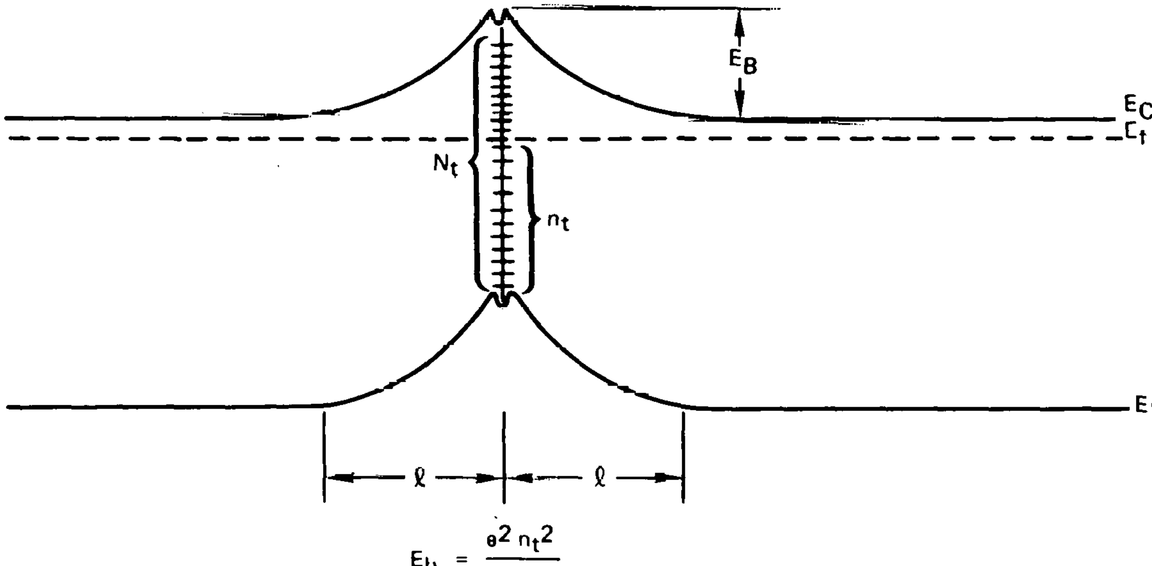


Figure 2-10. Measured Resistivity of n-type Polycrystalline GaAs Films, Deposited by MO-CVD on Corning Code 0317 Glass Substrates, as Function of Sample Temperature for Various Doping Impurity Concentrations.

The same model that was used to explain the behavior of the p-type films is invoked for the n-type material. Figure 2-11 shows a suggested schematic diagram of the energy-band structure near a grain boundary in the n-type polycrystalline GaAs films studied here. The model assumes that the interface between grains is a high-defect interface with N_t neutral traps per cm^2 of interface area. These traps capture majority carriers until n_t per cm^2 are filled. This creates a depletion region of width ℓ around the grain boundary. The resulting dipole layer causes a change in the energy-band structure such that a barrier of height E_b is formed, as shown in Figure 2-11. When ℓ is less than the grain size the barrier height is determined by the number of trapped carriers and the doping concentration N_D in the grain by the following relation:

$$E_b \approx \frac{e^2 n_t^2}{8 \epsilon N_D} , \tag{1}$$

where e is the electronic charge and ϵ is the dielectric constant of GaAs. The transport properties of polycrystalline materials would thus be expected to be temperature-activated owing to the need for carriers to be thermally excited over the barriers at the grain boundaries. The activation energies E_b obtained from the measured data (Figures 2-9 and 2-10) represent the heights of those barriers. As a result, the measured barrier height would be expected to vary as $E_b \propto 1/n$, where n is the electron concentration and $n \approx N_D$.



$$E_b = \frac{e^2 n_t^2}{8 \epsilon N_D}$$

Figure 2-11. Schematic Diagram of Suggested Energy-band Structure near Grain Boundary in n-type Polycrystalline GaAs Film Deposited by MO-CVD (see text).

Figures 2-12 and 2-13 show the variation of E_b with measured electron concentration for the two types of substrate. Also given in each figure are the corresponding data for observed barrier heights as a function of measured hole concentration in the p-type films previously reported (Ref 5). Note that the observed dependence of E_b upon carrier concentration (i.e., doping density)in the n-type films is again of the form $E_b \propto \ell n\ (1/n)$, rather than the expected $E_b \propto 1/n$. Thus, similar behavior is seen in both n- and p-type films on the two substrates.

Since the grain sizes in these polycrystalline films were found to be large enough that the grains would not be fully depleted over their entire dimensions, it appears that the model used provides a reasonable description of the observed barrier height behavior. It is concluded that the density of filled traps n_t must change with the doping concentration in such a manner as to give the reduced dependence of E_b upon N_D that was observed.

The data shown in Figure 2-14 confirm that the measured carrier concentration in these films does increase linearly with the impurity doping density and that the epitaxial GaAs film grown simultaneously on the companion sapphire substrate provides a good measure of the carrier concentrations in the polycrystalline films. In Figure 2-14 the carrier concentrations measured in the polycrystalline films at 400°K are plotted vs the doping concentration of the accompanying epitaxial film at room temperature. Notice that there is a one-to-one correlation and that the carrier concentration increases linearly with doping. The 400°K temperature was chosen as the measurement temperature so so that films in a wider range of doping concentrations could be measured. At this temperature the mobility of the polycrystalline films represented in the figure is high enough to allow the measurement of carrier concentration to be made.

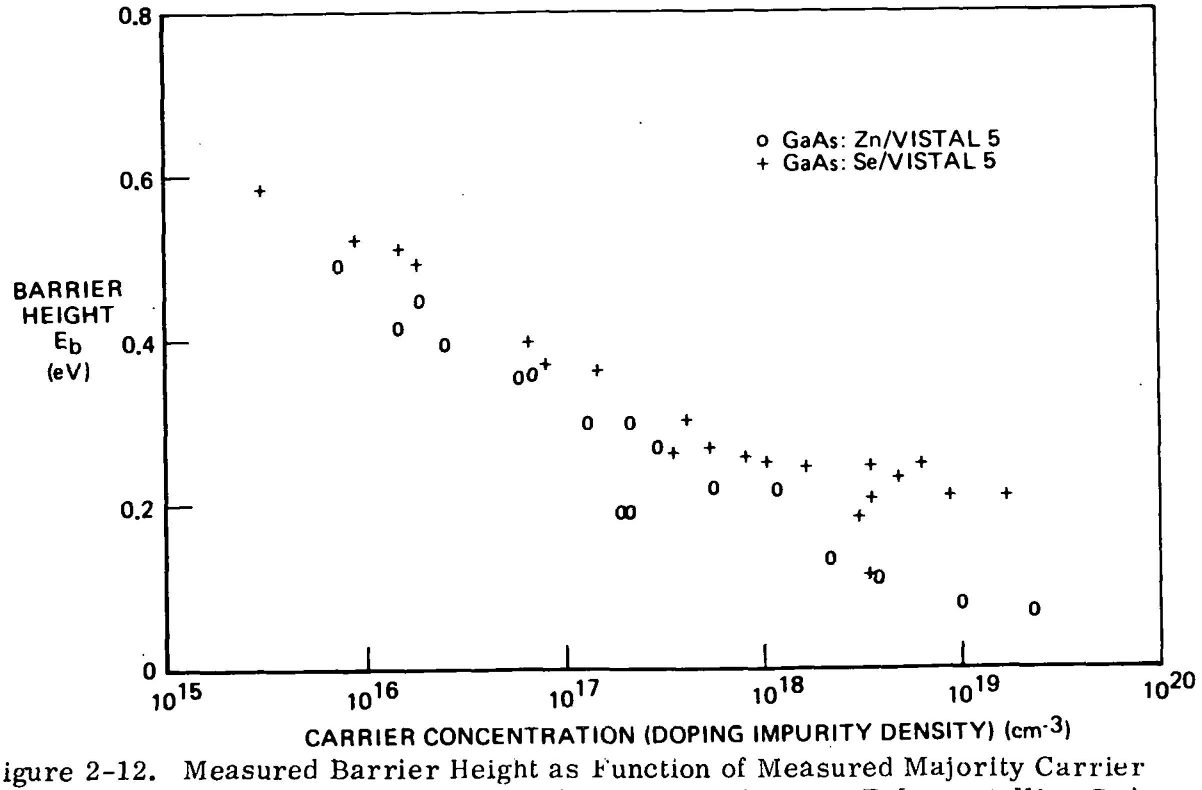


Figure 2-12. Measured Barrier Height as Function of Measured Majority Carrier Concentration (Doping Impurity Density) for n-type and p-type Polycrystalline GaAs Films Grown by MO-CVD on Vistal 5 Alumina Substrates.

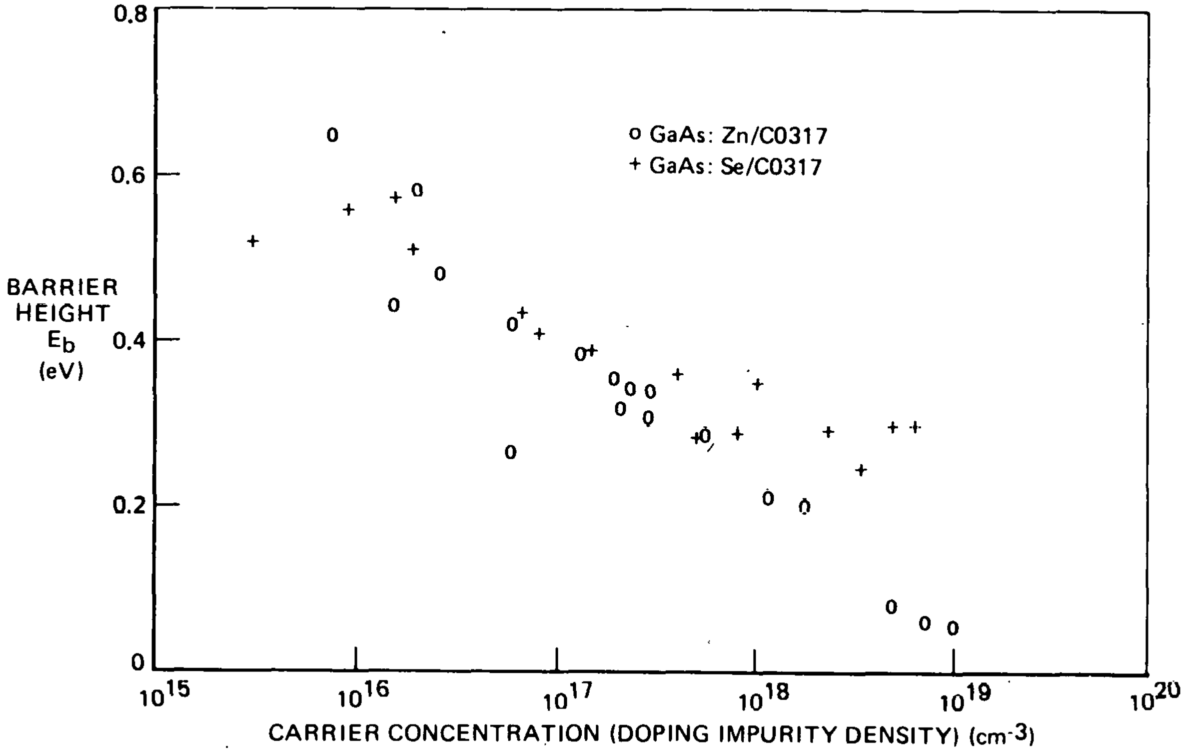


Figure 2-13. Measured Barrier Height as Function of Measured Majority Carrier Concentration (Doping Impurity Density) for n-type and p-type Polycrystalline GaAs Films Grown by MO-CVD on Corning Code 0317 Glass Substrates.

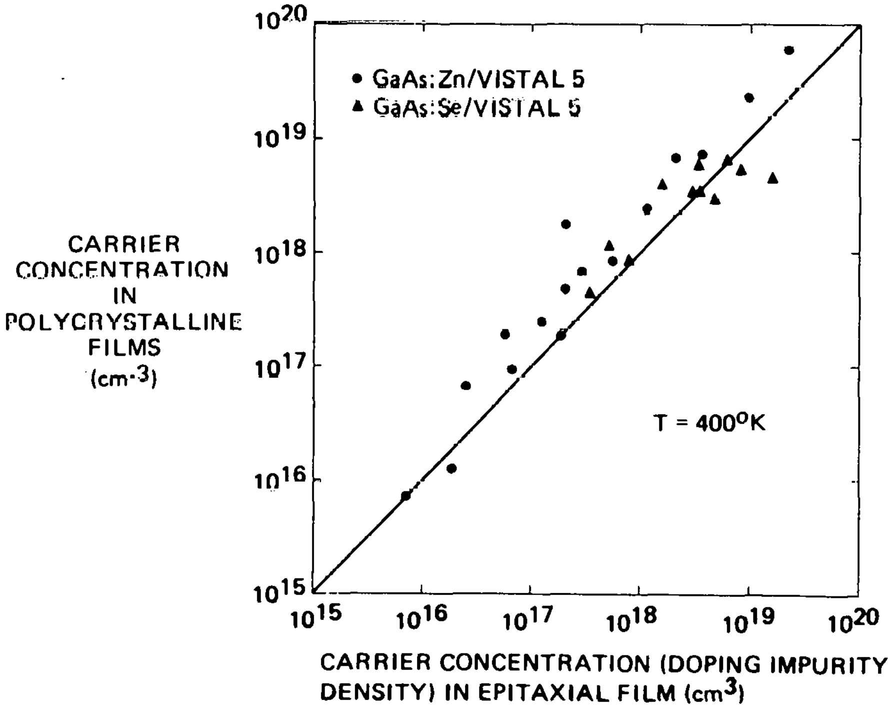


Figure 2-14. Measured Carrier Concentrations in Polycrystalline GaAs Films Grown by MO-CVD on Vistal 5 Alumina and Corning Code 0317 Glass Substrates as Function of Measured Carrier Concentration (Impurity Density) in Simultaneously Grown Epitaxial GaAs Film on Single-crystal Sapphire Substrate.

With an established basis for determining the carrier concentration it became possible to extract from the model and the data the value of n_t with reasonable confidence. Equation (1) was used to obtain values for n_t, the trapped charge density at the grain boundary, for use in plotting this parameter versus the doping density (measured carrier concentration) in the polycrystalline film. The results are shown in Figures 2-15 and 2-16 for the films on Vistal 5 alumina and on Corning Code 0317 glass, respectively. Note that n_t increases monotonically with doping concentration up to a trap density the order of 10^{13} per cm^2. Also note the similarity between n_t values for n-type and p-type material on a given substrate, as well as the similarity for given type films on the two substrate materials.

These similarities occurring in the face of considerably different values for resistivity in the polycrystalline GaAs films on Vistal 5 alumina and 0317 glass substrates (cf Figure 2-2 of Reference 5) indicate that a model with more quantitative detail must be developed to account adequately for the observations. Attempts will proceed in the next quarter to develop such a model and to further improve the understanding of transport processes in these polycrystalline films.

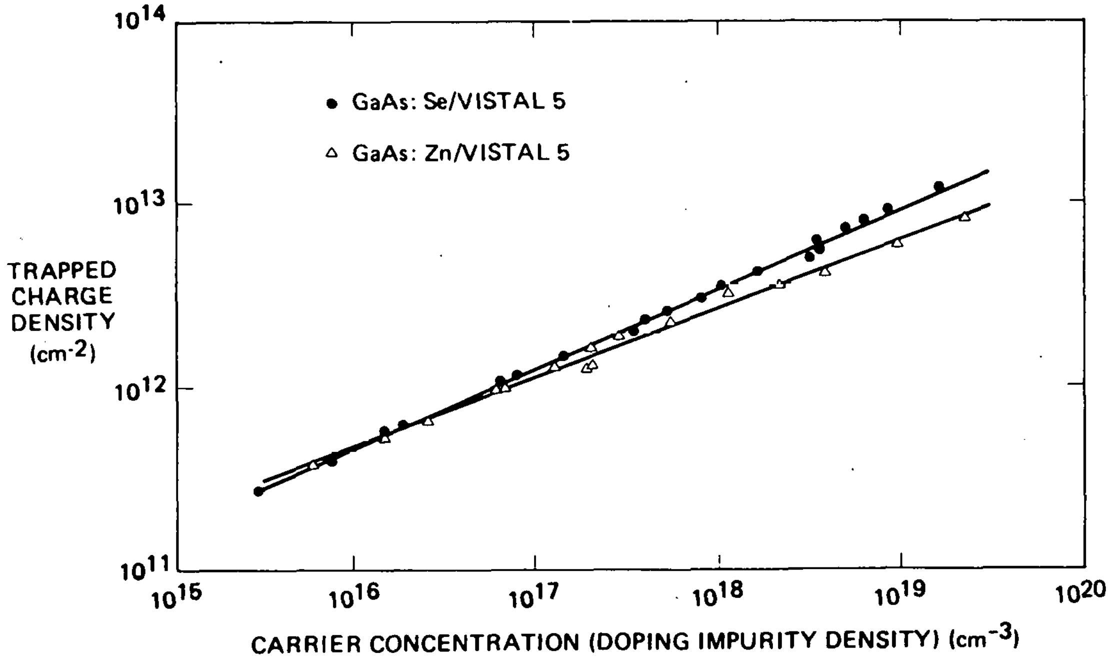


Figure 2-15. Trapped Charge Density at Grain Boundaries as Function of Impurity Doping Density (Measured Carrier Concentration) in n-type and p-type Polycrystalline GaAs Films Grown by MO-CVD on Vistal 5 Alumina Substrates

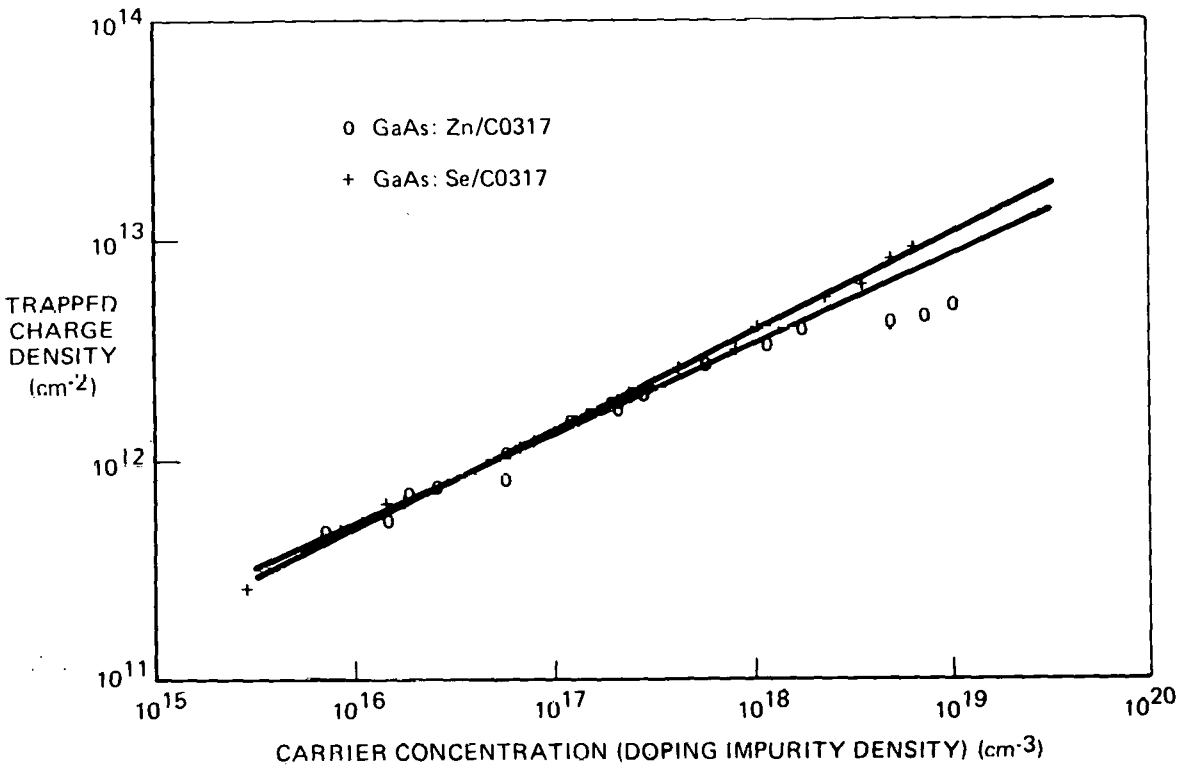


Figure 2-16. Trapped Charge Density at Grain Boundaries as Function of Impurity Doping Density (Measured Carrier Concentration) in n-type and p-type Polycrystalline GaAs Films Grown by MO-CVD on Corning Code 0317 Glass Substrates.

2.3 TASK 3. INVESTIGATION AND DEVELOPMENT OF BARRIER FORMATION TECHNIQUES

This task involves investigation and development of various techniques for the formation of the necessary charge collecting barriers in polycrystalline GaAs thin-film photovoltaic devices. Emphasis is on direct growth of p-n junction structures by the MO-CVD process, but also included can be alternate barrier-forming techniques such as thermal diffusion or ion implantation of impurities, the use of deposited indium-tin oxide (ITO) layers on the GaAs films, or the use of thin Au (or other metal) Schottky barriers at the film surface.

The work on this task during the period covered by this report was concentrated on the formation and investigation of the properties of deposited $p^+/i/n^+$ junction structures and $Au/n/n^+$ Schottky-barrier devices. The results obtained are decribed in the following sections.

2.3.1 Schottky-barrier Solar Cells

Schottky-barrier solar cells employing thin Au layers have been routinely used for evaluation of polycrystalline GaAs films and multilayer structures in this program. Such cells have been successfully fabricated on a variety of materials. The typical device design has involved a vacuum-deposited Au film ~50Å thick to form the Schottky barrier.

The dependence of Schottky-barrier solar cell efficiency upon the doping in the polycrystalline GaAs has been found to be a complicated multivariable problem. The depletion layer depth and diffusion length in n-type material are expected to decrease with increasing doping concentration, thus reducing the short-circuit current. The resistance of the device should decrease but the leakage current in the device should increase with increasing doping. Furthermore, the importance of these effects may be masked or enhanced by the details of the processes occurring at grain boundaries.

A brief study of the effect of n-layer doping upon the performance of Schottky-barrier solar cells on polycrystalline GaAs was carried out by varying the doping of the n layer of an $n/n^+/Mo$ structure. The short-circuit currents derived from these devices under 1 kw xenon lamp excitation of 137 mw/cm^2 intensity are given in Table 2-1. These devices were all fabricated at the same time and had approximately the same Au layer thickness of ~50Å. The doping concentrations were determined indirectly on the basis of the measured properties of similar films prepared with the same deposition parameters at about the same time for the study of transport properties (Section 2.2).

The sharp decrease in short-circuit current for n layer concentration above 10^{16} cm^{-3} was not expected and is not understood. It suggests, however, that in films with this range of grain sizes (~2 μm) the collection of current in the depletion layer plays a significant role in the short-circuit current collection process. The table shows the corresponding depletion depths for single-crystal GaAs doped to the listed concentrations. It appears that there must also be a strong dependence of diffusion length upon doping in these films to account for the effects illustrated by these data. To obtain high conversion efficiencies in Schottky-barrier solar cells in these small-grained materials may require doping concentrations of 10^{16} cm^{-3} or below in the n-type layers.

Table 2-1. Characteristics of Au* Schottky-barrier Solar Cells Fabricated on Polycrystalline GaAs n/n$^+$ Structures Deposited by MO-CVD on Mo Sheet Substrates

Impurity Doping Concentration in n Layer (cm^{-3})	Short-circuit Current under Illumination** (μA)	Depletion Layer Depth at Zero Bias (Å)
10^{15}	185	12,000
10^{16}	170	3500
10^{17}	10	1200
10^{16} (on Mo/glass substrate)	170	3500

*Au vacuum-deposited layer 50A thick

**1 kw xenon lamp illumination of 137 mw/cm^2 intensity

At times, especially when the polycrystalline GaAs films being used were relatively rough, it appeared that the Au metallization was too thin to provide good contact to all of the surface grains. Consequently, a limited study was made of the effect of the Au layer thickness on the resulting performance of Schottky-barrier devices. A set of similar n/n$^+$ GaAs structures deposited on Mo sheet substrates in a single run was used to fabricate a group of Schottky-barrier solar cells. Au layer thicknesses of 25, 50, 75, and 100Å were deposited on these structures in the usual way.

The results obtained are simmarized in Table 2-2. The device with the 25Å Au layer exhibited no photovoltaic response, due probably to inadequate coverage by the metal film. The data indicate that once the barrier metal is thick enough there is only a small change in the collected current with further increase in the Au thickness up to 100Å. Most of the observed change in conversion efficiency in these samples was caused by an increase in the cell fill factor with increase in Au thickness due to the lowered series resistance of the cell. There was some variation observed in open-circuit voltage from device to device on a given sample in this group, and the efficiencies given in the table represent the best obtained among the various individual devices on a given sample.

Based on these results it was determined that Au film thicknesses of 75-100Å would be used thereafter for the Schottky barriers prepared on polycrystalline GaAs films in this program.

2.3.2 Properties of p$^+$/i/n$^+$ Device Structures

The use of a lightly doped n layer in p-n junction structures in polycrystalline GaAs films to improve the I-V characteristics was discussed in the preceding quarterly report (Ref 5). The lightly doped n layer was actually an undoped layer (i layer) which was n type due to the unidentified background doping of the MO-CVD reactor system. However, the forward "turn-on" voltage of the best of such devices was still only 0.5-0.6 V.

Table 2-2. Photoresponse* of Au Schottky-barrier Solar Cells as Function of Thickness of Au Layer

Au Layer Thickness (Å)	Short-circuit Current (μA)	Conversion Efficiency (%)
25	0	–
50	190 - 200	1.9
75	190 - 200	2.1
100	185 - 190	2.2

*Illumination ~AMO (xenon lamp), with no AR coating

To prepare similar devices in polycrystalline GaAs structures having larger grains thicker composite layers were grown on Mo sheet substrates. Structures in the $p^+/n/n^+/Mo$ configuration (actually $p^+/i/n^+/Mo$) were prepared with 10 μm n-type layers and 20 μm n^+ layers. The p layers were only 1 μm thick. The carrier concentration in the undoped n layers was $\sim 10^{15}$ cm^{-3}.

Mesa devices were fabricated on these layers by etching through the p layer to a depth of ~5 μm. The top of the p layer was contacted with Cr-Au to avoid the need for alloying. The I-V characteristics of these devices were not substantially different from those seen on thin samples 5 - 10 μm thick. All were excessively leaky and permitted no worthwhile photovoltaic measurements.

These results suggested several things, including the following: (1) grain sizes in the range 5 - 10 μm are not sufficient to provide reasonable quality p-n junctions in this material, and (2) diffusion of Zn along grain boundaries to provide a shunt path is probably not a significant problem, since the devices of thickness ~30 μm behave in a similar way to devices only 5 μm thick.

To test this latter hypothesis a 5-8 μm thick p+/n/n+ structure with relative layer thicknesses 1:4:1 was evaluated by I-V and C-V analyses. The I-V characteristic showed a turn-on voltage of 0.5-0.6V and shunt leakage across the junction. The C-V characteristics showed an abrupt junction with a built-in barrier of 0.5 V. The p layer was then etched off the sample and Au Schottky barriers were deposited on the n layer. The resultant devices showed good Schottky-barrier characteristics with reasonably low leakage, lower than found for the p-n junction. If Zn were diffused into the grain boundaries the Schottky barrier would be expected to draw a low forward voltage and exhibit considerable leakage. The C-V characteristics showed a non-ideal plot of $1/C^2$ vs V and an extrapolated barrier height of 2.0 eV. These results are not easily explained. It is possible that an m-i-n structure was formed by the inclusion of an inadvertent oxide. This and other possibilities will be considered in further studies of these device structures.

2.4 TASK 4. DEVELOPMENT OF PHOTOVOLTAIC DEVICE DESIGNS AND FABRICATION TECHNIQUES

This task involves development of solar cell design and fabrication techniques for the preparation of thin-film GaAs photovoltaic devices having conversion efficiencies greater than 10 percent, and evaluation of the electrical and optical performance of the cells so fabricated. Further development of appropriate contact materials and procedures for applying them to the various polycrystalline device structures prepared in this program, including the investigation of indium-tin oxide (ITO) films and thin Au layers as transparent ohmic contacts, is part of this task. Also included is investigation and development of suitable antireflection (AR) coatings for polycrystalline GaAs cells; initial attention is to be given to TiO_2 layers deposited by chemical pyrolysis (or other methods). Additional single-crystal thin-film GaAs solar cells, grown by MO-CVD on single-crystal substrate materials, will also be fabricated from time to time to provide baseline reference data against which to compare the performance of the polycrystalline GaAs cell structures that are of primary concern.

In the period covered by this report there was no effort expended on device design and very little work done on cell fabrication techniques as such. Device performance in this period was severely limited by materials and/or grain boundary problems, as discussed earlier in this report.

However, preliminary attention was given to the assembly and performance verification of a system for depositing layers of TiO_2 by means of low-temperature pyrolysis of titanium isopropoxide, for use as AR coatings on GaAs solar cells. The system that was assembled was based on a design described by Hovel (Ref 6).

2.4.1 TiO_2 Deposition Apparatus

The deposition apparatus was constructed entirely of pyrex and used teflon-plug pyrex stopcocks. Joints were clamped pyrex greaseless ball-and-socket joints with elastomer O-rings. The hot stage supporting the sample to be coated was simply the plate of a laboratory-type electric hot plate with a plated Au-over-Ni Cu block on it, for temperature uniformity. Temperature was indicated by a thermocouple embedded in the Cu block. The sample to be coated was placed on the Cu block directly above the location of the embedded thermocouple bead. The titanium isopropoxide was contained in a pyrex bubbler, and a similar bubbler contained distilled H_2O for use if the H_2O vapor content of the laboratory air was found insufficient. Argon gas was directed through both bubblers to carry the reactants into the reaction chamber and to the region of the heated substrate.

The reaction chamber initially was simply a large inverted pyrex flask with sidearm tubes for introducing the gaseous reactants. However, the films deposited with this apparatus were quite nonuniform. Consequently, a reaction chamber incorporating a swivel tube fitting through a ground ball-and-socket joint centrally located in its top was fabricated. The swivel tube was connected to the source bubbler by means of a flexible stainless steel tube. The configuration of this modified apparatus is shown in the simplified schematic diagram in Figure 2-17.

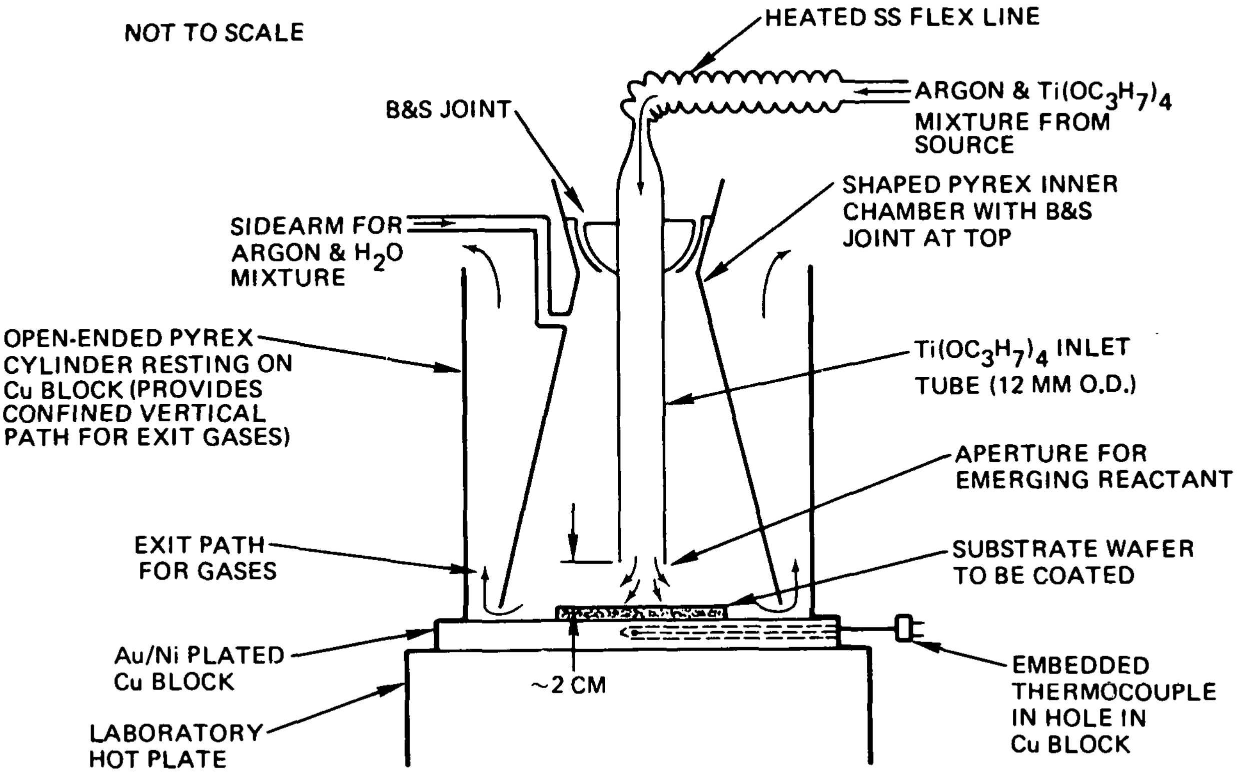


Figure 2-17. Simplified Schematic Diagram of Apparatus for Producing AR Coatings of TiO_2 by Pyrolysis of Titanium Isopropoxide at Temperatures of 50-300°C

Films of TiO_2 were deposited by moving the swivel tube manually in a random motion so that its exit aperture described a back-and-forth "painting" pattern above the substrate surface until a film of the desired uniformity and appropriate color was achieved. Reasonable uniformity of TiO_2 film thickness (±10 percent) was achieved by this technique on 2 in. diameter Si wafers used as test substrates.

2.4.2 Properties of TiO_2 Layers as AR Coatings

The thicknesses of the films deposited in this simple apparatus were measured, along with the indices of refraction, by ellipsometry. This procedure was followed for a variety of film deposition temperatures under various reactant flow conditions which had been found to allow control of film thickness and thickness uniformity.

One of the main advantages of this simple low-temperature process is that it permits the growth of films with a wide range of index of refraction. This makes it possible to prepare single-layer AR coatings for semiconductor devices, which require an AR coating index of 1.8, or for metal-semiconductor devices, which require a coating index of ~2.4 (Ref 7).

The variation of index of refraction with deposition temperature achieved for films prepared in this apparatus is shown in Figure 2-18. The index is seen to increase from ~1.95 for deposition at ~50°C to ~2.45 for deposition at ~275°C. For higher deposition temperatures the index remains approximately constant and then

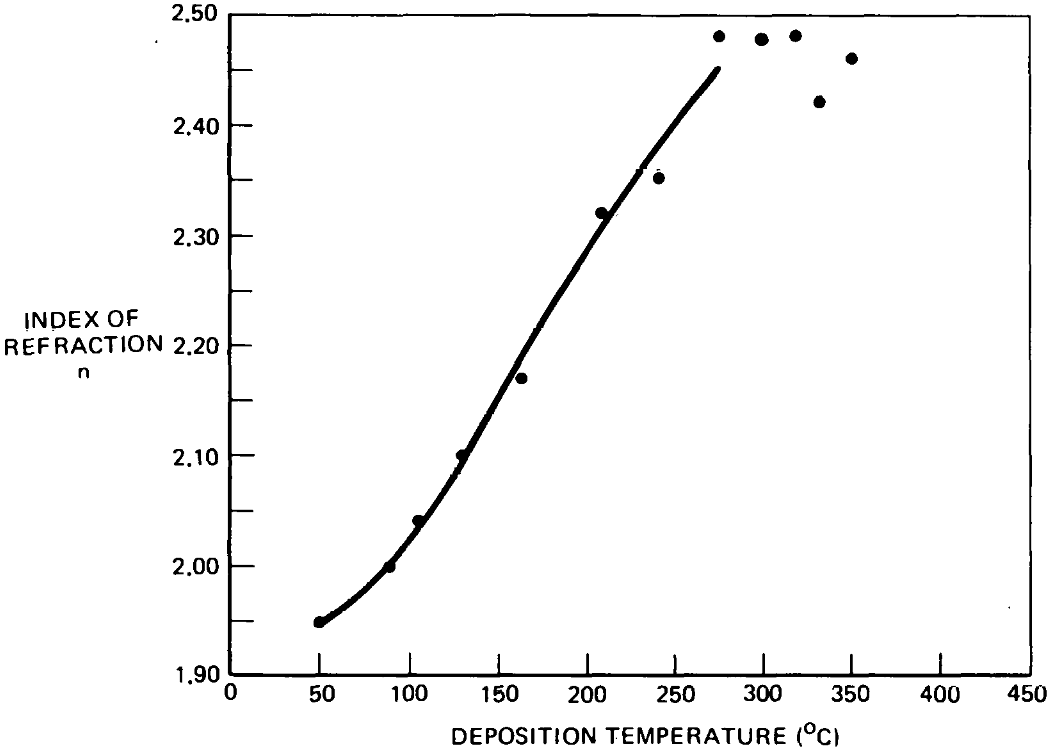


Figure 2-18. Index of Refraction of TiO_2 Layers as Function of Pyrolysis Deposition Temperature

appears to decrease slightly as the temperature is further increased. It is expected that spontaneous gas-phase nucleation and resulting non-uniform films are produced by this process at temperatures above ~275°C. It is evident that this system allows the formation of layers with the necessary range of index values.

The requirements for AR coatings are such that good control of film thickness is necessary. The thickness control method used for these TiO_2 layers was simply visual observation of the color of the depositing film as it developed. A single-layer AR coating on Si should have an index of refraction $n_{AR} \approx \sqrt{n_{Si}} \approx 1.9$ and a thickness $t_{AR} = \lambda_{min}/4n_{AR}$, where λ_{min} is the wavelength where the reflectivity minimum is desired.

TiO_2 layers were deposited in this apparatus at 70°C to produce an index of 1.95 and allowed to grow to a thickness for which a dark blue color was achieved. Figure 2-19 shows the relative reflectance as a function of wavelength for such a film found to be 856Å thick. The reflectance of the TiO_2-coated Si wafer was measured relative to the reflectance of an uncoated Si wafer, and an approximate absolute reflectivity scale - assuming a 30 percent reflectivity for Si - is indicated on the right vertical axis in the figure. The minimum reflectivity is of the order of 0.15 percent, indicating a film of high optical quality and a good interface. Data for a thinner film (667Å) are also shown, and the appropriate shift to shorter wavelengths occurs. These results show that the system is capable of producing the required AR coatings for this program.

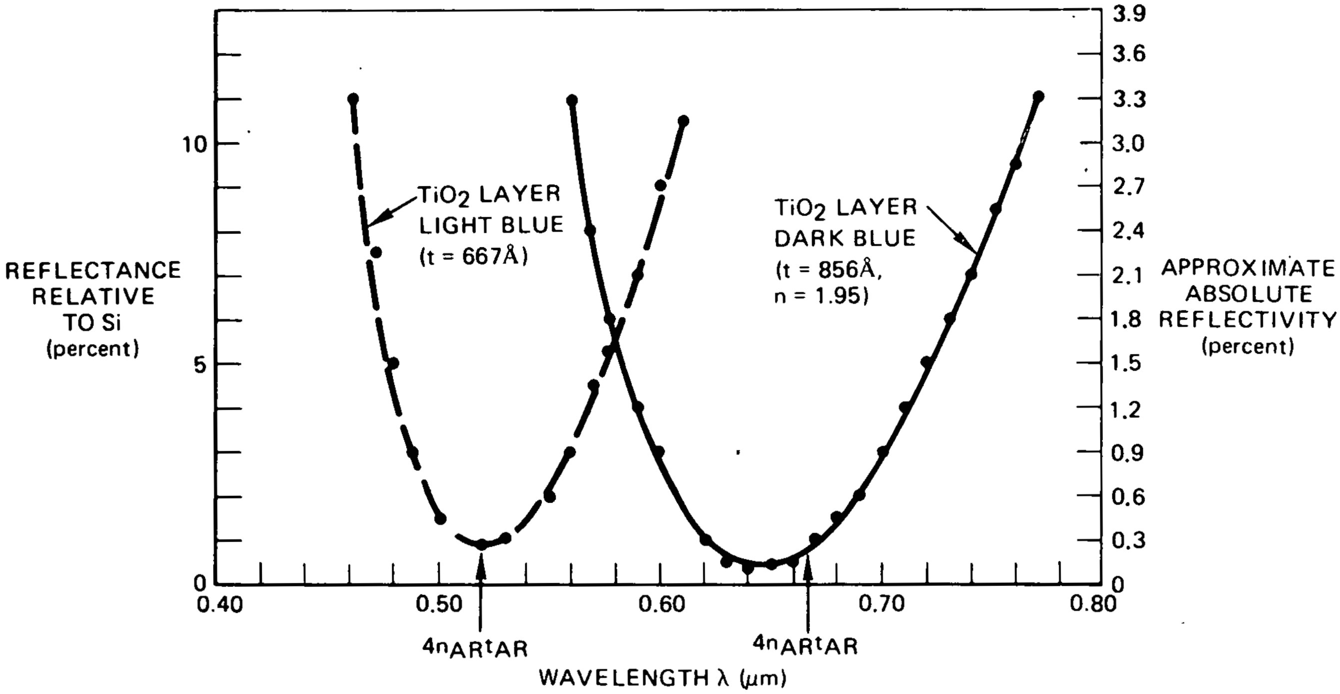


Figure 2-19. Relative Spectral Reflectance and Estimated Absolute Spectral Reflectivity for TiO_2 Layers Deposited on Si Substrates by Pyrolysis of Titanium Isopropoxide. (Calculated wavelengths for minimum reflectivity shown by arrows along horizontal axis.)

2.5 TASK 5. ANALYSIS AND PROJECTION OF CELL MATERIAL REQUIREMENTS AND FABRICATION COSTS

The task is intended to carry out the analysis and projection of estimated costs, material quality, and material quantity requirements associated with scaled-up production of 5×10^4 Mwe (peak) solar array generating capacity per year (the DoE program goal for the year 2000) using the MO-CVD process.

The program plan developed early in the second contract year scheduled activity on this task only in the final month (June) of the quarter covered by this report. That activity was to consist of a reexamination of earlier projections of future costs to fabricate thin-film GaAs solar cells of the current design on low-cost substrates using the MO-CVD process. Although this reexamination was begun it was evident that there had been no changes of significance relative to the situation discussed in earlier reports (Refs 2, 5, 8). Thus, there are no new conclusions or data to report at this time.

3. SUMMARY AND CONCLUSIONS

The technical activities during the quarter were concentrated on 1) a continuing evaluation of various graphite materials as possible substrates for MO-CVD growth of polycrystalline GaAs solar cells; 2) attempts to improve the quality (especially the grain size) of polycrystalline GaAs films on Mo sheet and Mo/glass substrates by using $HC\ell$ vapor during the MO-CVD growth process; 3) further studies of the transport properties of polycrystalline GaAs films, with emphasis on n-type films; 4) continuing investigations of the properties of p-n junctions in polycrystalline GaAs, with emphasis on the formation and properties of $p^+/n/n^+$ deposited structures; and 5) assembling apparatus and establishing a suitable technique for producing TiO_2 layers for use as AR coatings on GaAs cells.

Success in the use of graphite substrates was found to be still limited, based on the low photovoltaic conversion efficiencies obtained in Schottky-barrier solar cell structures on polycrystalline GaAs grown on various graphites. Intermediate layers of Ge or Mo appeared to "seal" the graphite surface and permit improved device performance, but the results were still not satisfactory. Further efforts must be expended to determine improved methods for cleaning and/or purifying graphite substrates.

The use of $HC\ell$ vapor during growth of polycrystalline GaAs films by the MO-CVD process was shown to increase substantially the average grain size and also to improve the uniformity of the morphology of such films grown on Mo surfaces (either sheet or deposited film on glass). The eventual usefulness of this procedure for improving polycrystalline solar cell performance will depend upon the satisfactory solution of several problems that have appeared as a result of the presence of the $HC\ell$ in the reactant gas mixture. Among these problems are (1) the necessity for cleaning the reactor system more frequently because of additional reaction products that are formed; (2) the increase in net carrier concentration (and thus possibly in the incorporation of impurities in the individual grains or the grain boundaries); (3) the need for growing a "sealing layer" of $\sim 2\ \mu m$ thickness without $HC\ell$ before proceeding with $HC\ell$-accompanied growth if Mo substrates are involved; and (4) the increased temperature sensitivity of the net growth rate of the film. Continued attention to both the advantages of $HC\ell$ use and the solutions of these problems is required in the coming quarter.

The transport properties of n-type polycrystalline films of GaAs were investigated and found to be controlled by transport of majority carriers across the grain boundaries in essentially the same way that was observed for p-type films. The height of the barrier to carrier flow in the boundary region was seen to depend upon the impurity doping concentration added to the film during growth, with the barrier height decreasing with increasing doping. The barrier height E_b varies as $\ell n\ (1/N_D)$, where N_D is the nominal doping concentration, instead of simply $(1/N_D)$ as predicted by the model used to describe the behavior of the polycrystalline material. A similar relationship had been observed in the earlier work with p-type films. The discrepancy between observation and model is attributed to an increasing density of interface trapped charge with increasing doping concentration. A model having greater quantitative detail must be developed to account adequately for the observations in both n- and p-type materials.

The properties of polycrystalline GaAs p-n junctions were still found to be dominated by the properties of the grain boundary regions, although $p^+/n/n^+$ structures, in which the n layer is undoped and up to 10 μm thick, result in somewhat improved electrical characteristics. The need for an adequate model of the electronic structure in the grain boundary regions is again emphasized by these results. Additional work with Au Schottky-barrier devices on polycrystalline GaAs n/n^+ strucures during the quarter demonstrated the apparently major role played by current collection in the depletion layer as well as the doping level in the n layer in determining the overall performance of the device. It was also found that Au layer thicknesses of 75-100Å should be used for best device results, rather than the previously used 50Å, in fabricating Schottky barriers on these polycrystalline GaAs materials.

Finally, a simple apparatus was assembled and a satisfactory deposition technique was developed for preparing TiO_2 layers of controllable thickness and index of refraction in the range 1.9 to 2.4. These layers meet the requirements for AR coatings for use on GaAs solar cells, when such coatings are needed later in the program.

4. PLANS FOR NEXT QUARTER

Contract activities in the eighth quarter will follow the Management Plan as given in revised form in the Monthly Technical Status Report forDecember 1977. By task, the planned activities include the following:

Task 1

1. Continue investigation of graphite as substrate material for GaAs MO-CVD
2. Continue experimental study of effects of HCℓ vapor on MO-CVD growth of polycrystalline GaAs films.

Task 2

1. Continue fundamental study of transport properties of polycrystalline GaAs films grown by MO-CVD
2. Continue investigation of electrical and photovoltaic properties of device structures in polycrystalline GaAs as function of grain size
3. Continue routine characterization measurements on polycrystalline GaAs and GaAℓAs films.

Task 3

1. Conduct systematic study of graphite substrate cleaning procedures as they affect properties of Schottky barriers formed on polycrystalline GaAs films grown on the graphite
2. Continue evaluation of effects of Au film thickness on performance of Schottky-barrier devices on polycrystalline GaAs
3. Investigate effects of grain boundaries on I-V characteristics of grown p-n junctions in polycrystalline GaAs films.

Task 4

1. Continue investigation and development of improved contact materials and deposition techniques for use on polycrystalline GaAs devices
2. Fabricate complete window-type GaAℓAs/GaAs and Schottky-barrier polycrystalline solar cells, and characterize their photovoltaic properties
3. Continue development of TiO_2 deposition process, adapting it to low-pressure regime for improved thickness control and uniformity.

Task 5

1. Prepare updated estimate of present costs to fabricate thin-film GaAs solar cells by MO-CVD process.

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APPENDIX A. PROGRAM MANAGEMENT TASK

(Included only in printed copies sent directly to DoE Project Officer and DoE Program Coordinator and copies printed for Rockwell internal distribution).

A.1 ACTUAL MANPOWER AND FUNDING EXPENDITURES FOR QUARTER

During the seventh month of the modified contract, from April 2 through April 29, 1978, a total of 766 engineering and support manhours was expended on this contract. In the same period a total of $32,775 was expended on labor and materials.

During the eighth month of the modified contract, from April 30 through June 3, 1978. a total of 702 engineering and support manhours was expended on the contract. In the same period a total of $34,468 was expended on labor and materials.

During the ninth month of the modified contract, from June 4 through July 1, 1978, a total of 499 engineering and support manhours was expended on the contract. In the same period a total of $24,659 was expended on labor and materials.

From the start of work on the original contract (July 5, 1976) through July 1, 1978, a total of 11,006 engineering and support manhours and a corrected total of $423,274 in funding (excluding fees and commitments) were expended.

A.2 PROJECTED EXPENDITURES FOR EIGHTH QUARTER

The projection of expenditure of funds and manpower (engineering and support manhours) for the three months of the eighth quarter is as follows (exclusive of fees and commitments):

July 1978	180 manhours	$8500
August 1978	580 manhours	$37,000
September 1978	460 manhours	$31,900

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