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THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

Quarterly Technical Progress Report No. 6 and Topical Report No. 2, January 1—April 1, 1978

By

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MASTER

April 1978

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. 6
AND
TOPICAL REPORT NO. 2

for the period

January 1, 1978 – April 1, 1978

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April 1978

PREPARED FOR THE DIVISION OF SOLAR TECHNOLOGY, UNITED STATES
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ABSTRACT

The sixth 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 substrate materials used for experimental studies during the quarter included several grades of graphite (from two different manufacturers), commercial-grade Aℓ alloy sheet, large-grained annealed Mo sheet, sputtered Mo films on Corning Code 0317 glass, uncoated 0317 glass, large-grained polycrystalline alumina (Coors Vistal 5), and large-grained bulk polycrystalline GaAs. Results indicated graphite to be a suitable substrate for GaAs film growth by MO-CVD, although some adherence problems were uncountered with improperly prepared graphite surfaces. No major differences were observed for GaAs growth on the various graphites; films ~10μm thick exhibited apparent grain sizes (indicated by dimensions of surface features) in the 2-5 μm range. Annealed Mo sheet substrate having relatively large grain structure did not appear to produce correspondingly large grains in deposited polycrystalline GaAs films.

Studies were begun to determine the effects of HCℓ vapor additions to the reactant gas stream on the growth habit and properties of polycrystalline GaAs films on low-cost substrates, primarily Mo/glass composites. It was found that grain sizes in polycrystalline GaAs films on both Mo sheet and Mo/glass composites increased with increasing film thickness and were generally larger, for a given film thickness, when the films were grown in the 700-750°C range than in the vicinity of 600°C.

Further investigation of the factors influencing the properties of p-n junctions formed by sequential deposition of polycrystalline GaAs layers confirmed that the deposition parameters employed produced the expected properties for each separate layer in a controlled and reproducible way but that the resulting junction structure still exhibited leaky I-V characteristics. No evidence for impurity diffusion along grain boundaries was observed. Investigation of various p-i-n structures (the undoped i layer is n type), however, showed that significant improvements in the I-V characteristics could be achieved through use of i layers as thick as ~4 μm, although excess leakage still occurred.

Detailed studies of the transport properties of polycrystalline GaAs films grown by MO-CVD on substrates of Vistal 5 alumina and Corning Code 0317 glass were carried out. Emphasis was on p-type Zn-doped films in the 10^{16} - 10^{19} cm^{-3} concentration range, although work was also begun at the end of the quarter on similarly doped n-type films. The large-grained films on alumina exhibited resistivities nearly an order of magnitude lower than those of simultaneously grown small-grained films on glass for a given concentration of added dopant. Measurement of transport properties as a function of sample temperature in the range 77-450°K demonstrated that the presence of barriers to majority carrier flow at the grain boundaries in these films controls the carrier transport process. The height of these barriers (E_b) was shown

experimentally to decrease with increasing impurity doping concentration according to the expression $E_b \propto \ell n\ (1/p)$, where p is the measured hole concentration, for films on both the large-grained polycrystalline and the amorphous substrates. These results were explained in terms of a model for polycrystalline GaAs films that assumes that the intergrain boundaries have a high density of neutral traps that capture majority carriers, produce a depletion region on both sides of the boundary, and thus result in the experimentally observed barrier of height E_b.

A detailed analysis was made of the materials and labor requirements for producing thin-film GaAℓAs/GaAs window-type solar cells by the MO-CVD process in research-type reactors on a laboratory scale. The resulting cost estimates were examined briefly with respect to areas of possible reduction in material and labor costs. Estimates were also made of consumption rates of the three principal reactants (TMG, TMAℓ, and AsH_3) and of the apparent efficiency of the MO-CVD pyrolysis reaction as used in this program.

Other details of the quarter's work are reviewed, and plans for the activities of the seventh quarter are outlined.

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1. INTRODUCTION

The long-range objective of the National Photovoltaic Conversion 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 element 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 those 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 PROGRAM

The general technical approach used in this program involves 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:

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

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 mimimizing 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 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 on this program demonstrated that the MO-CVD technique is capable of producing materials of quality sufficient to meet the 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 contacts 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 sixth Quarterly Technical Progress Report (including the Annual Report (Ref 2)) for this contract and covers the period January 1 through April 1, 1978. The technical activiteies 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.

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2. TECHNICAL PROGRESS

The work of the sixth quarter of the program is described by task in this section. The tasks were identified in the Introduction (Section 1).

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

As specified in the contract Statement of Work, this task involves the evaluation of glass, glass-ceramic, and graphite as low-cost substrate materials, as well as the detailed analyses and the 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.

2.1.1 Investigations of Low-cost Substrate Materials

The growth of polycrystalline GaAs films on several candidate low-cost substrate materials not previously used in these studies was undertaken during the quarter covered by this report. Included were repurified polished and as-sawed grade DFP-3 graphite (Poco Graphite Inc.), as-sawed grade ACF-10Q graphite (Poco), as-sawed grade AXF-9Q graphite (Poco), as-sawed grade 5890 graphite (Carbone-Lorraine Industries Corp.), and commercial grade $A\ell$ alloy sheet (composition not determined). Additional deposition experiments were carried out with substrates of large-grained annealed bulk Mo sheet (GTE Sylvania, Inc.) and with composite substrates involving sputtered Mo films on Corning Code 0317 glass. Finally, a special group of polycrystalline GaAs films was prepared by deposition directly on substrates of 0317 glass and large-grained polycrystalline alumina (Coors Vistal 5); the experiments involving these two substrates are described further in the Task 2 discussion (Section 2.2.3).

The growth of polycrystalline GaAs films on the above graphite substrates at ~725°C by the MO-CVD process typically resulted in films having apparent grain sizes (as indicated by surface features) in the 2-5 μm range for film thicknesses ~10 μm. The as-sawed surfaces of the various graphites were not further prepared mechanically, as a rule, and only degreased in organic solvents prior to use in a deposition experiment. Typically, however, they were baked out at temperature of 900-1000°C for 10-30 min in H_2 in the CVD reactor chamber before GaAs film growth was begun. Only minor differences were seen in the results obtained with the various graphites during the quarter – not sufficient to indicate a preference for any one of them.

Mo sheet material that had been annealed at ~1000°C to produce grain growth (obtained from and heat-treated by GTE Sylvania, Inc.) was used as a substrate in several GaAs film growth experiments. However, no significant difference in apparent grain size of the GaAs films was observed for films grown simultaneously on the annealed Mo sheet and on conventional unannealed Mo sheet.

The deposition of polycrystalline GaAs films on the $A\ell$ alloy sheet substrates had to be carried out at temperatures below 640°C to avoid melting the $A\ell$. The resulting GaAs film appeared to adhere adequately to the $A\ell$ surface and did not flake off. Relatively little was done with this substrate material during the quarter, however.

2.1.2 Experiments to Produce Enhanced Grain Size in Polycrystalline GaAs Films Grown by MO-CVD

Late in the quarter a series of experiments was undertaken to begin a study of the effects of HCℓ additions on the growth habit of polycrystalline GaAs films, using a third reactor system so that the other ongoing studies in the program would not be interrupted. Several calibration runs were first conducted to be sure that the system was operating equivalently to the other two systems being used on the contract; these included investigation of film growth rate and temperature control as well as doping control. The preferred growth temperatures were found to be similar to those in use in the other two reactors, as expected. It was also established that the apparent grain size in polycrystalline GaAs films grown on Mo/glass and on Mo sheet substrates increases almost linearly with film thickness, as discussed in Section 2.2.1.

The experiments done with HCℓ gave preliminary indication of the effects of these additions on the properties of the resulting polycrystalline films. It was observed that the Mo films of the composite Mo/glass substrates are much more susceptible to HCℓ attack than is GaAs itself. In fact, simultaneous injection of HCℓ and TMG usually resulted in severe flaking of the GaAs film from the composite substrate due to undercutting of the metal-glass bond during the GaAs film growth. Similar effects were observed at times for the films grown on Mo sheet. It was thus found necessary to first grow a very thin layer of GaAs over the substrate before admitting the HCℓ to the reactor chamber; this successfully avoided the difficulty.

Additional studies of the effects of HCℓ in the MO-CVD growth environment on the properties (especially grain size) of the GaAs polycrystalline films will continue into the next quarter.

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

This task, as described in the contract Statement of Work, 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, contact properties (especially for the layer adjoining the substrate), and on 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. These are discussed in the following sections.

2.2.1 Film Growth and Doping Procedures

The effect of deposition temperature on GaAs film properties was examined in the first year for growth on several low-cost substrate materials, but but because of the interest in Mo sheet and Mo-coated glass substrates in the current program a series of experiments was undertaken with these substrates to establish the effect of growth temperature. Polycrystalline GaAs films were deposited in the range 600-750°C, with a substrate of single-crystal sapphire used in each experiment to serve as a monitor of the deposition and film growth process. Although this was not a detailed study, there was clear evidence that the film grain size (as indicated by the size of surface features on the film) tends to be larger for films deposited in the 700-750°C range. Only the films grown at 600°C appeared to have significantly smaller grains than the others. Since no appreciable grain size increase was detected for films deposited at other temperatures in the 600-750°C range, the previously identified preferred deposition temperature range of 700-725°C was selected for continued use in other experiments with substrates of Mo sheet and Mo film on Corning Code 0317 glass.

These substrate materials were used in another series of experiments to determine the variation of GaAs film properties with film thickness, for deposition at 725°C and an average growth rate of 0.3 μm/min. Apparent average grain size, as determined by observation of surface features in the SEM, was found to increase with increasing film thickness, although there was considerable variation in the sizes of individual grains on a given film. Figure 2-1 shows the observed trend, with the vertical bars representing the spread in the observed apparent grain sizes on a given sample.

It should be emphasized that an accurate measurement of true grain size distribution was not made in obtaining the data shown in Figure 2-1. In particular, the films were not etched to determine if some of the larger crystallographic features seen at the surface and assumed to be large individual crystallites might actually have consisted of aggregates of smaller individual crystal grains. However, the absence of submicron-size surface features and the increased number of large surface features in the thicker films was clear semiquantitative corroboration of the trend shown by the SEM observations presented in Figure 2-1.

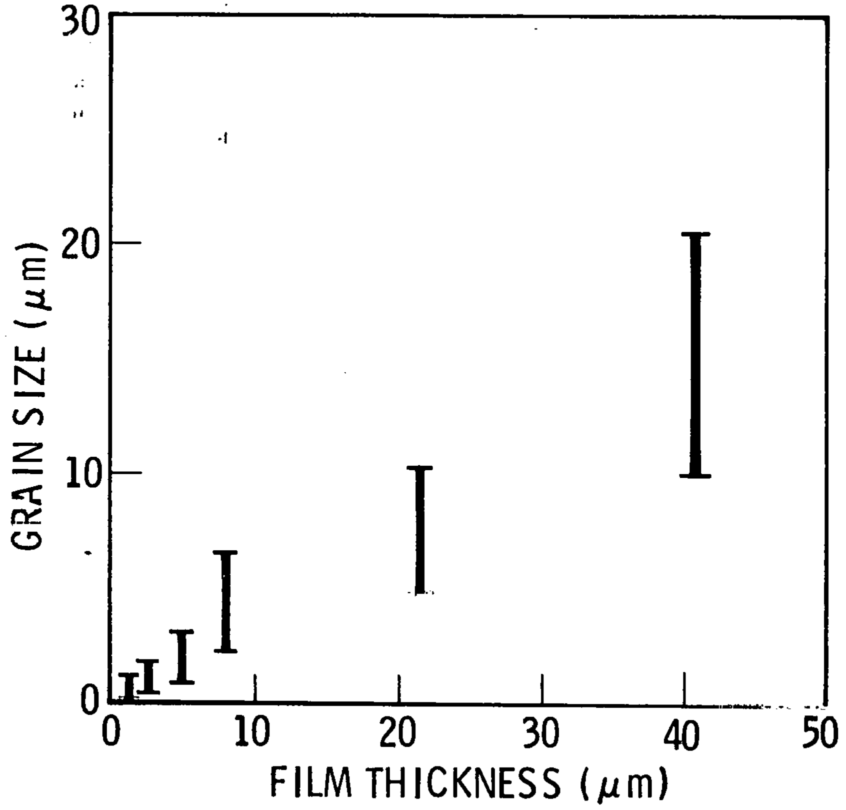

Figure 2-1. Range of Apparent Grain Sizes for Polycrystalline GaAs films Grown by MO-CVD at 725°C on Substrates of Mo Sheet and Mo Film/Corning Code 0317 Glass. (Grain sizes indicated by surface features as observed in SEM.)

These results emphasize the fact that films of comparable thickness must be used if the effects of variations in deposition parameters on film grain size and surface morphology are to be examined. The results also tend to confirm the feasibility of the concept of using thick layers of AℓAs as underlayers for the active GaAs regions of thin-film cells for the purpose of achieving enlarged grain sizes in the cell. Whether the concept actually proves practical will rest on the extent to which the deposition of stable and adequately doped AℓAs layers with good ohmic contact to the substrate can be achieved.

The preliminary experiments with HCℓ added to the reactant gas stream, described briefly in the preceding section, gave strong evidence that significant modifications in the details of the procedures followed in depositing GaAs films by the MO-CVD process will have to be invoked if it is determined by further investigation that the use of HCℓ should be an integral part of an optimized growth process for polycrystalline films. It is expected that the work of the coming quarter will clarify this point.

2.2.2 Properties of GaAs Polycrystalline Films on Low-cost Substrates

As indicated in Section 2.1.1, the deposition of GaAs films on graphite substrates was done under standard MO-CVD conditions for GaAs — that is, a substrate temperature of ~725°C, a reactant concentration ratio (As:Ga) of about 10, and a resulting film growth rate of ~0.3 μm/min. The graphites identified in the earlier section were used either as received from the supplier, with only organic solvent cleaning prior to insertion into the reactor deposition chamber, or with the surface smoothed somewhat by light hand-lapping on fine-grade emery cloth prior to the solvent cleaning. Previous experiments with graphite substrates had shown that fine-polishing of the surface leaves a powder residue in the natural pores of the material that adversely affects the adherence of the film on the substrate. In either case the substrates were baked for periods ranging from 10 to 30 min in flowing H_2 at temperatures ranging from the intended deposition temperature up to about 1000°C .

Examination of the deposited GaAs films (typically ~10 μm thick) in the SEM provided a measure of the approximate grain size (found to be 2-5 μm for all of the films, as indicated previously). The films on Poco ACF-10Q graphite exhibited some tendency to form a few large smooth-faceted crystallites in the 10-20 μm size range, while the films on Carbone-Lorraine 5890 graphite showed some cracking and peeled partially from the substrate in one case.

All of the films on graphite were grown in the n/n^+ configuration so that Schottky-barrier devices could be fabricated on the structures and the photovoltaic properties measured.

The continued difficulties encountered in attempting to prepare p-n junctions in fine-grained polycrystalline GaAs films prompted further efforts to study the properties of the individual layers. To do this, the composite film structures were step-etched using a Br_2-methanol (2 percent) solution, and the individual layers were then probed (tungsten probes) to measure the reverse breakdown voltage, as was done in the earlier studies (Ref 3). In most cases the observed breakdown voltage again agreed with the expected value based on the intended doping of the CVD film. Comparisons were also made of the measured breakdown voltages for n-type layers in $p/n/n^+$ structures before and after growth of the p-type layer and, as reported previously, no differences were observed. These results appear to confirm the earlier conclusion that shunting due to impurity diffusion along grain boundaries is not responsible for the leaky I-V characteristics typically found for the polycrystalline p-n junctions formed in GaAs films in this program.

An exploratory examination of a polycrystalline GaAs film sample containing a p-n junction using the ion microprobe mass analyzer (IMMA)* was not successful in detecting Zn in the junction region of the angle-lapped sample. The intention of the analysis was to determine if Zn, if present in the grain boundaries in sufficiently high concentrations, could be detected and possibly mapped as a function of position in the sample. Zn is one of the more difficult elements to detect by IMMA, however, and none was found in this preliminary investigation.

2.2.3 Electronic Properties of Grain Boundaries in Polycrystalline GaAs Films

The electronic properties of grain boundaries in polycrystalline GaAs are not well understood. Early work in this program demonstrated that both n- and p-type polycrystalline GaAs are highly resistive — from two to three orders of magnitude larger than single-crystal material comparably doped with impurity (Ref 2). Experiments undertaken during this quarter and described below were designed to develop a more detailed understanding of the properties of polycrystalline GaAs, considered essential to maximum exploitation of these properties in photovoltaic devices.

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*The IMMA analyses were conducted at the Aerospace Corporation Research Laboratories, El Segundo, CA.

Measured transport properties of polycrystalline Si were used by Seto (Ref 4) in developing a model to describe the electronic structure of grain boundaries in that material. The model developed in that work is being applied, with appropriate modifications, to the polycrystalline GaAs films grown by MO-CVD in these investigations.

Two sets of polycrystalline film samples were prepared for this study. One consisted of GaAs films deposited on large-grain polycrystalline alumina (Coors Vistal 5) and the other involved similar films deposited on an amorphous glass (Corning Code 0317), prepared simultaneously in pairs and doped with impurity in the range $\sim 10^{16}$ to $\sim 10^{19}$ cm^{-3}. Two full sets of p-type films (doped with Zn) have been prepared, and a number of Se-doped n-type sample pairs have also been grown for measurements to be undertaken in the coming quarter.

In each deposition experiment a substrate of (0001)-oriented single-crystal sapphire was also included. The GaAs growth on the sapphire substrate was epitaxial in each case, of (111) orientation. The assumption has been made that the impurity doping concentration within the individual grains of the polycrystalline films on the alumina and the glass substrates is the same as that in the simultaneously grown epitaxial layer on the sapphire and that this can be adequately represented by the measured hole concentration in the epitaxial film. A similar assumption was made in earlier measurements of the properties of p-type polycrystalline CVD Si films at Rockwell (Ref 5).

The GaAs films on the Vistal 5 substrates consisted of large but variously sized (20-100 μm) individual grains duplicating the grain boundary pattern of the alumina growth surface. The crystallographic orientations of many of the alumina substrate grains were such that epitaxial growth of the GaAs film occurred on those grains, while highly preferred multicrystalline growth occurred on other individual grains. The result was a large-grained GaAs film containing a wide distribution of crystallographic perfection in the individual grains. The GaAs films on the glass substrates, on the other hand, were characterized by only moderately preferred orientation (shown earlier in this program to be mainly in the {111} planes); grain sizes were typically small (2-10 μm) and relatively uniform, with the average size strongly dependent upon details of the nucleation and early-stage growth mechanisms on the amorphous surface. In general, however, the grain size is expected to increase almost linearly with film thickness, as was observed in the films on Mo (see Section 2.2.1), so that the conduction process in these films on glass may be quite inhomogeneous.

The investigations to date have involved mainly the p-type Zn-doped films, although measurements are also to be made on n-type films. Ohmic contact to the p-type films has been achieved by alloying In dots into the surface at ~450°C for 1 min; lightly doped p-type material has been contacted with In-Zn dots. Transport measurements have been made by the van der Pauw technique in the automated Hall-effect apparatus (Ref 3) at sample temperatures from 77 to 450°K. Sample temperature in this apparatus is still controlled manually. Magnetic field switching and logging of the data are performed automatically, with the data being printed and/or stored on tape for subsequent retrieval and automatic plotting.

Figure 2-2 shows the room-temperature resistivity as a function of p-type doping density for polycrystalline GaAs films deposited in pairs simultaneously on substrates of Vistal 5 alumina and Corning Code 0317 glass. The films on alumina are seen to have resistivities nearly an order of magnitude lower than those of the films on glass at a given doping density.

Plots of film resistivities vs 1/T, where T is the sample temperature, are shown in Figure 2-3 for the films on Vistal 5 and Figure 2-4 for the films on 0317 glass. In both instances the resistivity ρ varies as exp (E_b/kT) in the temperature range 250-450°K, where E_b is the effective barrier height and is seen to increase with decreasing nominal doping density in the films.

Figure 2-5 shows the variation of resistivity, carrier concentration, and carrier (hole) mobility in one of the films on Vistal 5 as a function of temperature. In the temperature range where the resistivity exhibits the exponential dependence on barrier height, as noted above, the hole mobility is seen to vary as exp $(-E_b/kT)$ and the carrier concentration remains essentially constant, confirming that the observed resistivity variation with temperature results from the variation of mobility with temperature.

The model invoked to explain these data assumes that the interface between individual grains is highly defected, 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 results in a depletion region of width (thickness) ℓ on either side of the interface (i.e., the grain boundary). The dopole layer associated with this causes a change in the energy band structure such that a barrier of height E_b is formed at the interface, as shown schematically in Figure 2-6.

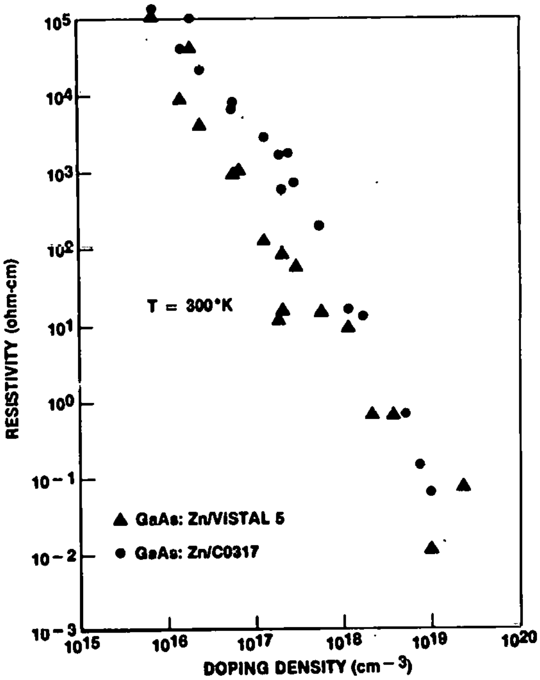


Figure 2-2. Room-temperature Resistivity of p-type Polycrystalline GaAs Films Deposited by MO-CVD on Substrates of Vistal 5 Alumina and Corning Code 0317 Glass, as Function of Zn Doping Concentration (see text).

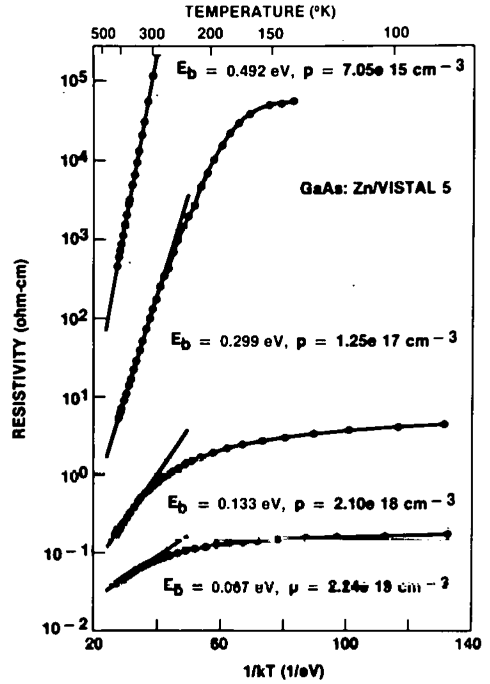


Figure 2-3. Measured Resistivity of p-type Polycrystalline GaAs Films, Deposited by MO-CVD on Vistal 5 Alumina Substrates, as Function of Sample Temperature for Various Doping Impurity Concentrations (see text).

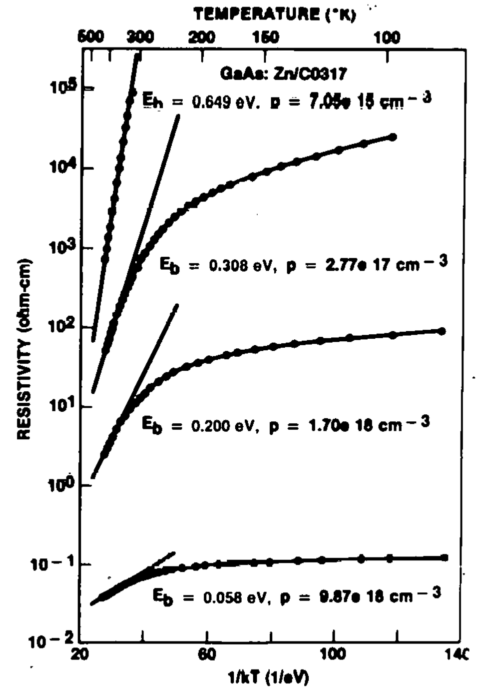


Figure 2-4. Measured Resistivity of p-type Polycrystalline GaAs Films, Deposited by MO-CVD on Corning Code 0317 Glass Substrates, as Function of Sample Temperature for Various Doping Impurity Concentrations (see text).

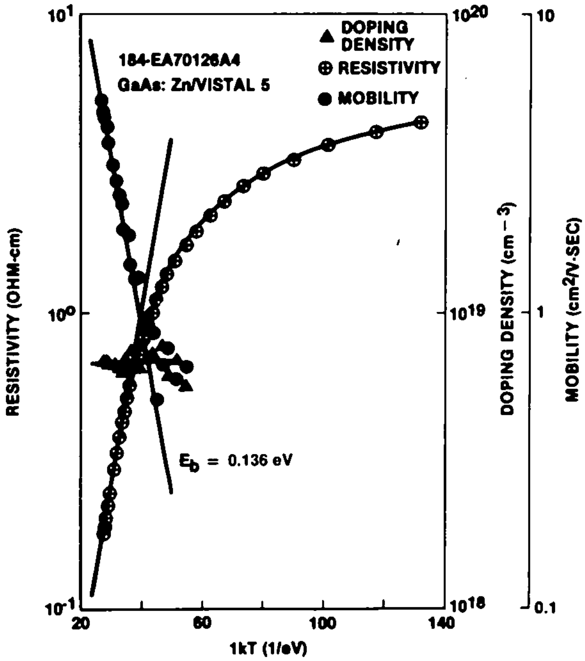
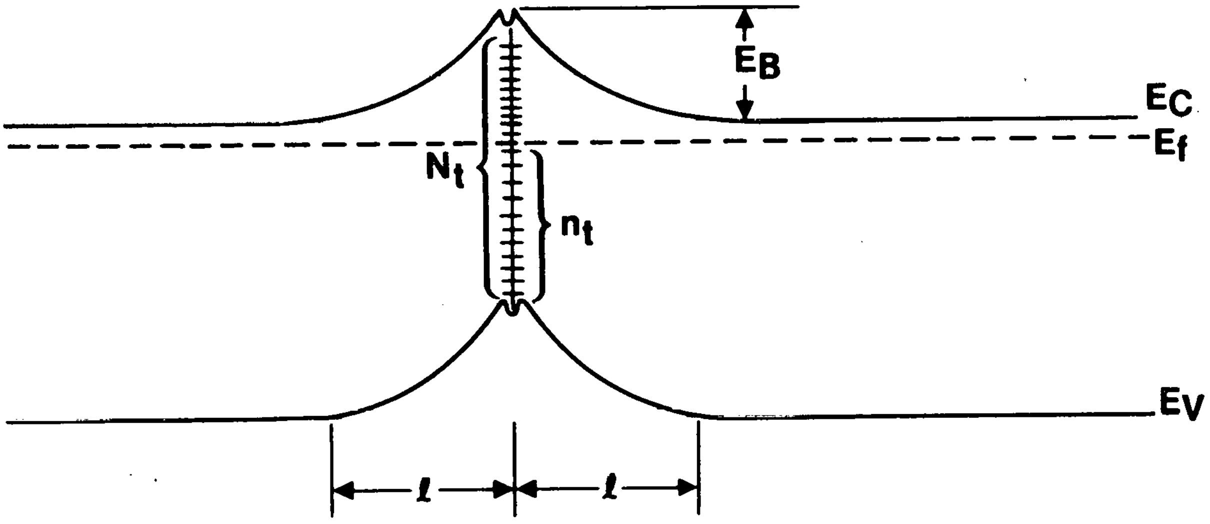


Figure 2-5. Resistivity, Hole Concentration (Doping Density), and Mobility of p-type Polycrystalline GaAs Film, Deposited by MO-CVD on Vistal 5 Alumina Substrate, as Function of Sample Temperature (see text).



$$E_B = \frac{e^2 n_t^2}{8 \epsilon n_D}$$

Figure 2-6. Schematic Diagram of Suggested Energy-band Structure at Grain Boundary in Polycrystalline GaAs Film Grown by MO-CVD (see text).

When the dimension ℓ is much smaller than the size of the grain the barrier height is determined by the number of trapped carriers and the doping density N_D in the grain according to the following relation:

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

where e is the electronic charge and ϵ is the dielectric constant of GaAs. The need for carriers to be thermally excited to surmount the barriers at the grain boundaries leads to the expectation that the transport properties of the polycrystalline GaAs films would be temperature activated. The observed activation energies E_b in the data of Figures 2-3, 2-4, and 2-5 correspond to these barrier heights.

The above expression for E_b indicates an inverse variation with the doping density N_D — i.e., $E_b \propto 1/N_D$. Figure 2-7 shows the observed variation of E_b with measured carrier (hole) concentration for both sets of samples. For the range of doping densities investigated ($\sim 10^{16}$ to $\sim 10^{19}$ cm^{-3}) the variation of barrier height is $E_b \propto \ell n\,(1/p)$, where p is the hole concentration, and not linear with 1/p as the model suggests. This slower observed variation of barrier height with carrier concentration (doping density) is not yet fully understood, although it may be caused by a variation of the trapped carrier density n_t with doping concentration.

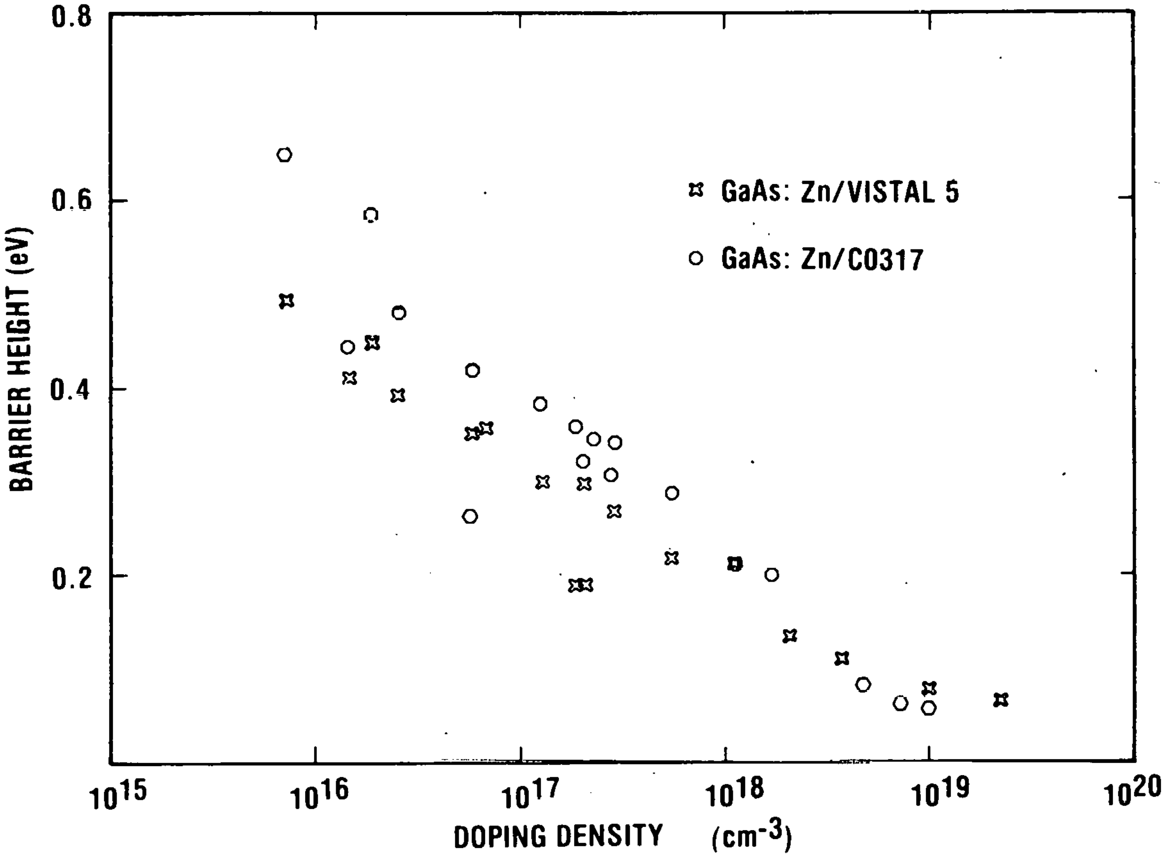


Figure 2-7. Measured Barrier Height as Function of Doping Impurity Density in p-type Polycrystalline GaAs Films Grown by MO-CVD on Vistal 5 Alumina and Corning Code 0317 Glass Substrates (see text).

Further experiments are planned with these p-type polycrystalline films to examine the variation in electrical properties with distance from the film-substrate interface and the variation in electrical properties as a function of post-deposition annealing. In addition, similar investigations with n-type (Se-doped) polycrystalline GaAs films, just begun during this quarter, will be continued in the coming quarter.

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 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 are thermal diffusion, ion implantation, the use of deposited ITO layers on the GaAs films, and the use of thin Au (or other metal) Schottky barriers at the surface as possible alternate barrier formation techniques.

Work during the quarter covered by this report was concentrated on continued study of the effects of impurity doping concentration in the two regions defining a p-n junction upon the electrical properties of the junction, and on initial investigation of the formation of ITO-GaAs heterojunctions and contacts.

It was reported in the preceding quarterly report (Ref 3) than p-n junctions formed in polycrystalline GaAs by using a lightly doped n-type layer were found to have lower leakage currents than other junctions formed previously in this material. The structures that produced these improved results were $p^+/i/n^+$ multilayers, with the nominally undoped i layer actually exhibiting a low concentration of some unidentified donor. It had been speculated that tunneling currents at the grain boundaries, resulting from impurity segregation during growth of the p and n layers, could be the cause of the excessive junction leakage currents observed. The undoped i layer was introduced in an attempt to eliminate the possibility of forming tunnel junctions associated with the grain boundaries.

To investigate this situation further, various polycrystalline GaAs multilayer structures that were modifications of the basic p-i-n structure were prepared early in the quarter. Thus, $p^+/p/i/n/n^+$, $p^+/i/n^+$, and $n^+/n/i/p$ structures were deposited on substrates of bulk Mo sheet and sputtered Mo films on Corning Code 0317 glass, with the thickness of the i layer having various values in the range 1.5-4.0 μm and the impurity doping concentration on both sides of the junction (i.e., the p-i interface) also varied. Typical doping concentrations and thicknesses for the various layers were as follows:

$p^+ \approx 1 \times 10^{19}\ \text{cm}^{-3}$ $t_{p^+} \approx 1.5\ \mu\text{m}$
$p \approx 1 \times 10^{18}\ \text{cm}^{-3}$ $t_p \approx 6\ \mu\text{m}$
$n_i \approx 1 \times 10^{15}\ \text{cm}^{-3}$ $t_i \approx 1.5\text{-}4.0\ \mu\text{m}$
$n \approx 2 \times 10^{18}\ \text{cm}^{-3}$ $t_n \approx 6\ \mu\text{m}$
$n^+ \approx 2 \times 10^{19}\ \text{cm}^{-3}$ $t_{n^+} \approx {\sim}1\ \mu\text{m}$

The n^+ layer, when used, was designed to facilitate ohmic contact to the Mo substrate. The indicated doping concentration in the i layer represents the measured carrier (electron) concentration found to be characteristic of the background doping level being obtained in the MO-CVD reactor system at the time these samples were prepared.

It was found that the structures with the thicker i layers (3.5-4.0 μm) gave significantly better results, although the I-V characteristics were still quite "soft." Also, the structures with reduced doping concentration in the p layer gave slightly less leaky I-V characteristics, but the general junction properties were still inferior. It is evident that more detailed studies of junction properties in polycrystalline GaAs films are still required to understand the source of leakage currents in these structures.

Preliminary investigation of deposited ITO layers for possible use as transparent ohmic contacts as well as a component of heterojunction structures on polycrystalline GaAs films was undertaken during the quarter. The ITO layers were deposited by an rf sputtering process previously developed at Rockwell for use in producing transparent ITO contacts on Si CCD imagers. The polycrystalline GaAs film sample was not heated during the ITO deposition except for the normal slight heating that accompanied the rf sputtering deposition process, but this still allowed the sample to remain near room temperature. The extent of possible surface damage to the GaAs as a result of the deposition process was not known, however.

Unfortunately, the deposition process used in these initial experiments produced ITO with very high resistivity as deposited; annealing at 500°C in air for 1-5 min was required to reduce the resistivity to ~0.05 ohm-cm. Samples of ITO/nGaAs/n^+GaAs and ITO/pGaAs/p^+GaAs prepared for evaluation of the ITO/GaAs heterojunction were not characterized during the period covered by this report, but several samples prepared for examination of ITO as a possible ohmic contact were characterized. It was found that ITO contacts on both n^+ and p^+GaAs layers exhibited very high forward voltages, as seen in the I-V characteristics, indicative of a high contact resistance between the ITO and the GaAs in both instances.

It thus appears at this time that ITO layers deposited by the existing process (developed for another application) will not be satisfactory for achieving ohmic contact to the polycrystalline GaAs films. Modifications in the deposition process used at Rockwell are being considered for the requirements of this program, and the possibility of collaborating with other laboratories actively producing ITO by processes more compatible with the GaAs films will also be investigated.

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 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 this program.

As in the preceding quarter, this task received relatively little emphasis during the period covered by this report, the effort consisting mainly of some further attention to the ohmic contact problem and the preparation and processing of several additional large-area solar cell structures.

The procedures used for preparing large-area ohmic contacts during this report period continued to be unsatisfactory, as evidenced by the fact that the large-area contacts applied to several large-area (~4 cm^2) single-crystal GaAs solar cell structures exhibited excessively high resistance, thus severely limiting cell performance. For example, Au-Zn-Au was used as the contact for p-type GaAs, but when the as-deposited contact was heated to ~500°C to ensure ohmic contact properties it was found that significant balling of the contact metal occurred. A eutectic point was evidently reached at which alloying took place. This resulted in a high contact resistance and excessive junction leakage.

In an attempt to resolve this persistent difficulty an investigation of other contacting procedures was begun, especially for use with p-type material. Various techniques for applying Pd, Ag-Mn, and Cr-Au contact materials were examined, with emphasis on vacuum deposition methods. This work was still in progress at the end of the quarter.

As indicated in the Task 3 discussion (Section 2.3) a preliminary evaluation of ITO as a transparent contact material for polycrystalline GaAs was also undertaken during this report period. All evidence, however, pointed toward a high resistance at the ITO-GaAs interface. Although other processes for depositing the ITO might result in improved contact properties it appears more likely at this time that the solution to this contact problem will be found in one of the other contact materials being evaluated.

Several three-layer and five-layer single-crystal large-area (up to ~4 cm^2) heterostructure solar cell configurations were prepared by MO-CVD during the quarter. The three-layer structures employed a conventional pGaAℓAs/pGaAs/nGaAs epitaxial configuration, with a GaAℓAs window thickness <500Å. The five-layer cell structures were double-heterostructure cells with the configuration pGaAℓAs/pGaAs/nGaAs/nGaAℓAs/nGaAs, grown epitaxially on a single-crystal n-type GaAs substrate.

The n-type GaAs layer in the center of the structure was undoped, with $n < 1x10^{15}$ cm^{-3} so that it would be almost fully depleted. Two different center layer thicknesses and two different pGaAℓAs window layer thicknesses were used in these structures. In addition, two large-area n^+/p shallow-junction GaAs homojunction cell structures were grown by MO-CVD on single-crystal GaAs substrates. However, the contact problems cited above precluded detailed characterization of the photovolatic properties of these cell configurations as well as those of several other large-area cell structures grown in the preceding quarter. The contact resistance and physical integrity problem and the junction leakage problem must be solved before meaningful cell characterizations can be carried out.

Several polycrystalline three-layer cell structures were also grown during this report period - on substrates of bulk Mo sheet and sputtered Mo films on Corning Code 0317 glass. Fabrication of these structures into completed cells was delayed, however, pending resolution of the contact problems. It is anticipated that the photovoltaic properties of all of these cell configurations will be evaluated in the next quarter.

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

This 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.

Effort on this task was resumed during the quarter covered by this report, consistent with the program plan as developed early in the second year of the present contract. The planned activity was to involve further analysis of present fabrication costs for complete thin-film GaAℓAs/GaAs solar cells made by the MO-CVD process on a laboratory scale, as well as updated projections of future materials requirements for fabricating large quantities of cells of the present design by the MO-CVD process on selected low-cost substrates.

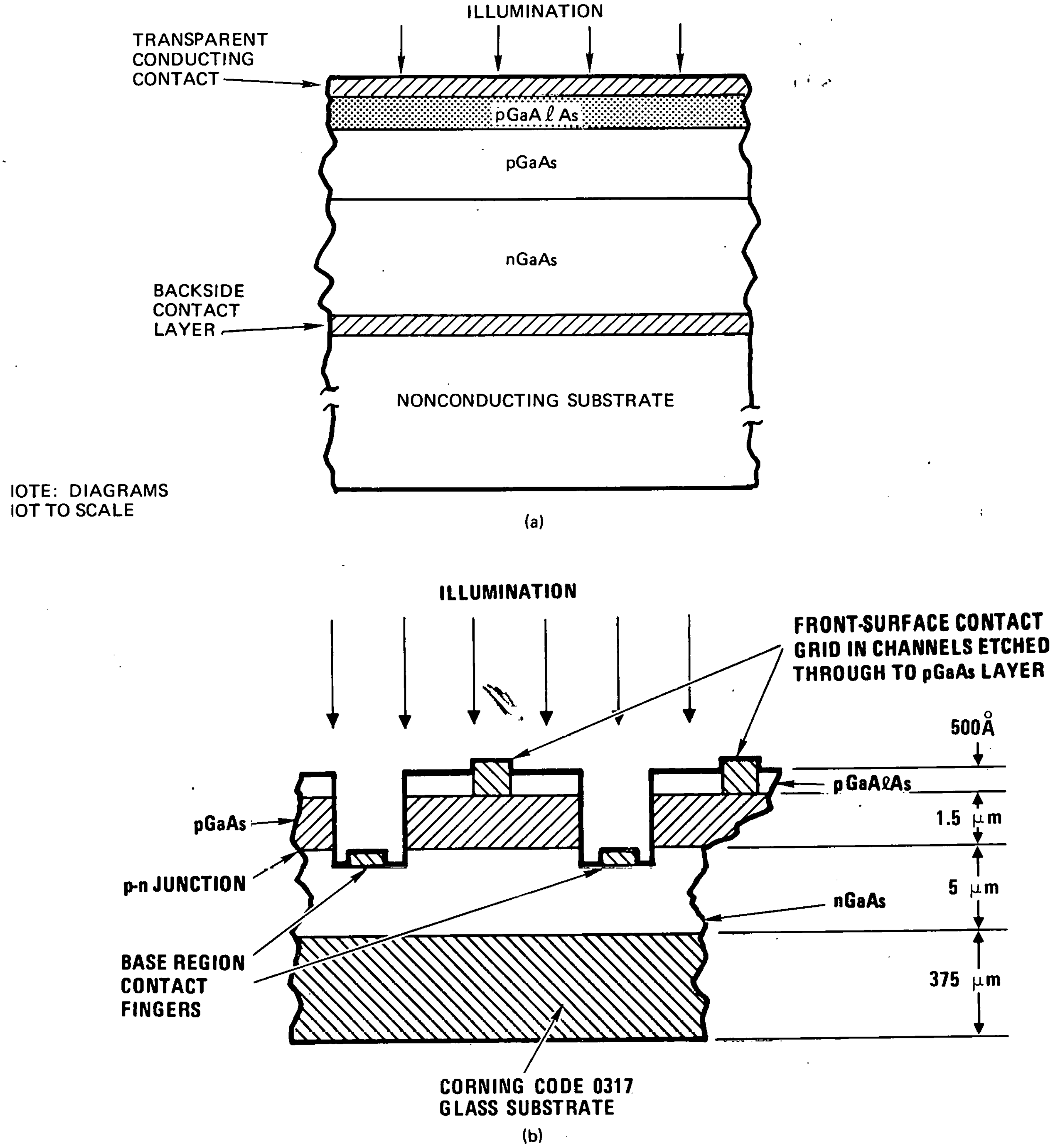
A detailed analysis was made of the materials and manpower required in the step-by-step procedures being used in the laboratory for depositing the required composite film structure and applying the necessary contact structures. This analysis was then used to develop estimates of present costs (in 1978 dollars) for fabricating the cells in the laboratory, using the present research-type MO-CVD reactor system and the associated laboratory procedures. These results are given below.

2.5.1 GaAs Solar Cell Design Used in Analysis

The experimental GaAs thin-film solar cell design used as the basis for the analysis is the conventional window-type GaAℓAs/GaAs p-n junction configuration deposited by the MO-CVD process on a non-conducting substrate, so that contact access to the n-type base region that adjoins the substrate is achieved by etching through the two upper (p-type) layers. The design is thus basically that of conceptual Design No. 1 of Figure 2-35a of Reference 2, reproduced here in Figure 2-8a, which shows the cell design in generalized form. This is one of the two conceptual designs set forth early in the program for use in preliminary cost estimates and as exemplary design concepts for the experimental studies that ensued. The second conceptual design (Figure 2-35b, Reference 2), involves an inverted window-type thin-film cell structure on a transparent substrate such as glass with illumination through the substrate. This configuration is not considered in this discussion.

The thicknesses of the various layers of the completed cell structure are given in Figure 2-8b, which shows a cross-section view of the cell to indicate the way in which the two active regions are contacted. The effective area of the cell is that of a large comb-like mesa, with two sets of interdigitated contacts. Note that no AR coating is included in the design used for this analysis.

Since obtaining fairly detailed estimates of the materials and labor costs involved in fabricating a GaAs thin-film solar cell using the MO-CVD process was the primary objective of this exercise, the actual operating efficiency of the resulting cell was not of major concern at the time. Obviously, the actual power conversion efficiency of the cell is a parameter of first-order importance in any final appraisal of the film growth and cell fabrication techniques under consideration.



IOTE: DIAGRAMS
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Figure 2-8. Thin-film GaAℓAs/GaAs Window-type Heteroface Solar Cell Structure Used as Basis for Analysis of Costs to Fabricate on Laboratory Scale by MO-CVD Process. a) Generalized Configuration; b) Cross-section View, Showing Layer Thicknesses and Method of Contacting.

2.5.2 Costs Involved in MO-CVD Growth of Multilayer Cell Structure in Laboratory-type Apparatus

A typical MO-CVD film-growth experiment in a laboratory-type reactor system such as those used for the work of this contract (shown schematically in Figure 2-4 and photographically in Figure 2-5 of Reference 2) consists of eight main steps or procedures: (1) substrate preparation; (2) reactor chamber loading; (3) reactor pump-down and pre-deposition flush; (4) substrate heating and equilibration; (5) deposition of layer(s); (6) sample cooling and reactor shutdown; (7) sample removal; and (8) reactor system and susceptor cleaning.

Each of these eight procedures was carefully analyzed for the directly consumed materials of all types and the required expenditure of manpower for preparation of the experimental multilayer cell structure shown in Figure 2-8 (exclusive of etching the large mesa and applying the contacts). Specifically, an n-type Se-doped GaAs layer ~5 μm thick is grown on a substrate of Corning Code 0317 glass 15 mils (375 μm) thick, and on that are grown in succession a p-type Zn-doped GaAs layer 1.5 μm thick and a p-type Zn-doped GaAℓAs window layer 500 Å thick.

The susceptor diameter is 2 in. (5 cm), so the effective area of the susceptor (which is also the sample platform) is ~20 cm^2. In this program to date typically only one or two substrates have been used in a given deposition experiment, depending upon the particular purpose of the experiment. Experimental cell structures of the type involved in this analysis have typical lateral dimensions of 2 x 2 cm (area 4 cm^2), but because of the exceptionally good uniformity of film growth in the GaAs materials system in these MO-CVD reactors it is possible to utilize essentially all of the available susceptor area for substrate(s). Thus, in this cost analysis a total usable cell area of 20 cm^2 was assumed.

Table 2-1 lists the eight main steps in the growth of the required multilayer structure by MO-CVD and shows the costs of the various materials consumed in each of the eight steps. Although the analysis was made in terms of every identifiable material used in the overall procedure, only a coarse breakdown into material type is given for each step except for the case of the reactants required for film growth, where the specific materials are listed separately.

The costs for materials as given in Table 2-1 were determined on the basis of current (1978) prices for the highest purity and generally highest quality materials available for research use in the laboratory, in most cases purchased in limited quantities and therefore generally quite expensive. It must be understood that the costs shown do not represent a projection of costs for a production operation nor even for moderately large-quantity preparation in the laboratory: they represent actual costs for preparation of a multilayer cell structure in a single deposition run in the laboratory at this time.

Not included explicitly as a consumed item in this tabulation of costs are the electrical energy required by apparatus used in the eight steps of the growth process and the other miscellaneous consumed utilities (water, gas, lighting, air conditioning, etc.) that constitute significant real cost items. However, such items along with

Table 2-1. Costs of Materials Consumed and Time and Costs* of Labor Required for MO-CVD Growth of 20 cm^2 Multilayer Solar Cell Structure Shown in Figure 2-8 (Work done by research laboratory personnel using research-type reactor system)

Procedure	Cost of Materials Directly Consumed ($)†										Labor Required (min/hr)	Labor Cost ($)†	Total Cost ($)†
	Substrate (Note 1)	Solvents (Note 2)	Acids (Note 3)	Carrier Gas (H_2)	TMG	$TMA\ell$	AsH_3	Dopants (Note 4)	Misc. (Note 5)	Total			
1. Substrate preparation	2.50	10.00	11.00	7.22	–	–	–	–	0.03	30.75	37.0/0.62	21.39	52.14
2. Reactor chamber loading	–	–	–	0.49	–	–	–	–	–	0.49	2.5/0.042	1.45	1.94
3. Reactor pumpdown and predeposition flush	–	–	–	10.53	–	–	–	–	–	10.53	47.0/0.78	26.91	37.44
4. Substrate heating and equilibration	–	–	–	3.20	–	–	5.83	0.0048	–	9.03	11.0/0.18	6.21	15.24
5. Deposition of layers	–	–	–	9.09	2.94	0.02	18.01	0.03	–	30.09	31.0/0.52	17.94	48.03
6. Sample cooling and reactor shutdown	–	–	–	7.31	–	–	0.58	–	–	7.89	32.0/0.53	18.28	26.17
7. Sample removal	–	–	–	0.25	–	–	–	–	–	0.25	1.5/0.025	0.86	1.11
8. Reactor system and susceptor cleaning	–	17.00	13.70	3.22	–	–	–	–	0.02	33.94	16.5/0.28	9.66	43.60
TOTALS (without G&A)	2.50	27.00	24.70	41.31	2.94	0.02	24.42	0.03	0.05	122.97**	178.5/2.98	102.70**	225.67**

*Labor costs are determined by using $11.50/hr. base rate for direct labor and 200 percent overhead (indirect labor) rate, or an equivalent total labor rate of $34.50/hr. See text.

†1978 dollars, without general and administrative (G&A) factor (see text). To obtain "bottom line" costs the tabulated amounts must be multiplied by the 1.20 G&A factor adopted for this analysis.

**Total adjusted cost = ($122.97 + $102.70) x (G&A factor) = $225.67 x 1.20 = $270.80. Capital cost of MO-CVD reactor system of $60,000 amortized (straight line) over 5-year period adds $48 per day (5-day week, 50-week year) or $16 per run (3 runs per 8-hr day) to total cost before G&A, or $19.20 per run for bottom-line cost. Thus, total cost per run = $270.80 + $19.20 = $290.

Notes:
1. Cost used for glass substrate is more than order of magnitude larger than expected actual cost for as-received material, which was obtained from Corning Glass Works for this study at no charge.
2. Solvents consist primarily of highest quality methanol, acetone, and 1-1-1 trichloroethane.
3. Acids consist primarily of highest purity $HC\ell$, H_2SO_4, HF, HNO_3; H_2O_2 is also included here.
4. Diethylzinc (DEZ) is the p-type dopant and H_2Se the n-type dopant.
5. Principal material involved here is high-resistivity deionized water.

other support expenses (miscellaneous supplies and services, management and supervision, building maintenance, etc.) were taken into account in the overhead and the "general and administrative" (G&A) factors that were used in obtaining the "bottom-line" costs that are also shown in the table. A representative G&A rate of 20 percent (i.e., a G&A factor of 1.20) was used in adjusting the base material and labor costs developed in this analysis. The only item that would be considered to be part of an eventual "market price" that was omitted from the tabulated data is a profit or fee, but it was considered inappropriate to attach such an item to a preliminary estimate of costs that are associated with exploratory device fabrication carried out under premium-cost conditions.

The expended labor for each of the eight procedures is also given in Table 2-1. It again must be emphasized that the exploratory nature of this work normally requires relatively close attenition of laboratory personnel in most stages of the processing. Operations that would be unattended or only intermittently checked in a production environment are generally monitored almost constantly in these laboratory procedures. A representative indirect labor or overhead rate of 200 percent was used in this analysis.

A capital equipment amortization cost was added for the MO-CVD reactor alone. On the basis of an approximate market value of $60,000 for the laboratory-type reactor system in use for this work, and assuming a five-year straight-line depreciation, an amortization rate of $48 per day of use was applied (5-day week, 50-week year). Since three runs are typically made per eight-hour day in these research reactors, it follows that a capital amortization cost of $16 per run is applicable. No other capital costs were included in this analysis.

It should be noted that the G&A and the overhead rates used in these cost estimates do not necessarily reflect the values used for these parameters at Rockwell for the period covered by this report or at any other time. However, the net result of this simplified approach is a set of final costs that closely duplicate the actual costs experienced for the work described.

2.5.3 Costs Associated with Fabrication of Solar Cell Contact Structures

Three main steps are involved in formation of the ohmic contacts on the multilayer cell structure prepared by MO-CVD and the procedures itemized in Table 2-1. These are (1) n-type (base region) contact formation; (2) p-type (front layer) contact formation; and (3) contact alloying.

Table 2-2 lists these three steps and the costs of the materials consumed directly in each, adjusted from actual consumption for the typical experimental cell size (2 x 2 cm) to a total assumed cell area of 20 cm^2, as indicated earlier. A relatively coarse breakdown into material type is again given for each step except in the case of the contact metals employed, where the specific materials are separately tabulated. The direct labor involved for each of the three main steps is also shown and the approximate labor cost for each is given, as in Table 2-1.

Table 2-2. Cost of Materials Consumed and Time and Costs* of Labor Required for Preparing Ohmic Contacts on 20 cm^2 Multilayer Solar Cell Structure of Figure 2-8 (Work done by research laboratory personnel using laboratory-type processing equipment)

Procedure	Cost of Materials Directly Consumed ($)†									Labor Required (min/hr)	Labor Cost ($)†	Total Cost ($)†
	Solvents (Note 1)	Acids (Note 2)	Gases (Note 3)	Photoresists (Note 4)	Au-Ge Alloy	Au	Zn	Misc. (Note 5)	Total			
1. Formation of n-type (base region) contact	11.25	0.72	0.02	2.62	1.10	–	–	0.02	15.73	95/1.58	54.51	70.24
2. Formation of p-type (front layer) contact	5.62	–	0.01	1.31	–	0.58	0.01	0.01	7.54	56/0.93	32.08	39.62
3. Contact alloying (at elevated temperature)	–	–	0.99	–	–	–	–	–	0.99	21/0.35	12.08	13.07
TOTALS (without G&A)	16.87	0.72	1.02	3.93	1.10	0.58	0.01	0.03	24.26**	172/2.86	98.67**	122.93**

*Labor costs are determined by using $11.50/hr base rate for direct labor and 200 percent overhead (indirect labor) rate, or an equivalent total labor rate of $34.50/hr. See text.

†1978 dollars, without general and administrative (G&A) factor (see text). To obtain "bottom line" costs the tabulated amounts must be multiplied by the 1.20 G&A factor adopted for this analysis.

**Total adjusted cost = ($24.26 + $98.67) x (G&A factor) = $122.93 x 1.20 = $147.52. No capital costs were included for this processing sequence.

Notes:
1. Solvents consist primarily of highest quality acetone.
2. Acids consist primarily of highest purity H_2SO_4; H_2O_2 is also included here.
3. Gases consist primarily of highest purity H_2 and N_2.
4. Included here are both photoresist and developer.
5. Principal materials involved here are high-resistivity deionized water and liquid nitrogen (coolant for vacuum-system traps).

2.5.4 Discussion of Estimated Costs

It was not the intention in this reporting period to examine the sensitivity of the total cost of fabricating these thin-film cells to specific cost variations in individual materials or procedures; that is considered later in the contract program and will be discussed in a subsequent report. Nor were projections made to future (presumably lower) costs of certain materials (such as TMG) that are now priced extremely high because of small-volume production and relatively low and intermittent market demand. Such projections are also scheduled for consideration later in the program.

However, several observations based on the results of the cost analysis as given in Tables 2-1 and 2-2 can be mde, as follows:

1. Even for the experimental cell fabrication process represented in this analysis the substrate does not dominate materials costs for the deposition sequence (Table 2-1). Substrate costs as high as those of single-crystal GaAs wafers (~20 cm^2 area) could be involved and still be only about equal to that of the H_2 carrier gas consumed in the present laboratory-scale process.
2. Materials costs for the deposition sequence are dominated by those of the chemical solvents, acids, AsH_3, and especially the H_2 carrier gas, the latter accounting for ~1/3 of the total. Of the principal reactants, AsH_3 and H_2 together account for over half of the total deposition sequence materials costs, while TMG is responsible for only about 2 percent.
3. The AsH_3 cost is high because of the large amount used in this process (see Section 2.5.5), rather than the unit cost being particularly high. (The cost per gram of AsH_3 is only about 8 percent of that for TMG and for TMAℓ.)
4. For the eight main steps in the deposition sequence (Table 2-1) materials costs account for ~54 percent of the total and labor costs for ~46 percent (excluding amortization of capital equipment).
5. Substrate preparation and reactor cleaning after deposition and sample removal (steps 1 and 8) together account for 30 percent of the total labor costs for the overall deposition process.
6. Labor costs for the actual multilayer structure deposition (step 5, Table 2-1) represent only about 1/6 of the total for the entire deposition sequence (steps 1 through 8).
7. Constant monitoring by laboratory personnel is probably not absolutely essential for all periods of the eight main steps in Table 2-1, so the labor costs obtained in the analysis represent an upper limit that could be reduced.

8. Use of less-highly-trained personnel than those involved in this contract work, such as would be employed in a pilot line or production facility, would - if assigned to carrying out the same eight procedures as shown in Table 2-1 - reduce the labor cost by only about 30 percent and thus the total cost for the deposition sequence of Table 2-1 by only about half of that percentage if the materials costs remained unchanged.

9. The total materials costs for the contact processing (Table 2-2) are dominated by the solvent costs, which account for ~70 percent of the total. Costs of photoresist and developer are next, amounting to ~16 percent of the total.

10. The labor invested in applying contacts is very nearly as extensive as that required for the multilayer structure deposition sequence. That is, the contact processing is labor-intensive, with ~80 percent of the total cost being attributed to labor costs. That this is the case is partly the result of the two separate vacuum deposition operations (n and p contacts) and separate alloying step, in addition to the usual sequence of mask processing.

11. Formation of the n-type (base region) contact dominates the time (i.e., labor) requirement for the contact processing of Table 2-2, accounting for ~55 percent of the labor costs for that sequence. The need for etching through the p-type GaAℓAs window layer and p-type GaAs front layer to form the large comb-like mesa and expose the base region for contact access contributes heavily to this cost.

12. The use of less-highly-trained labor for all steps of the contact processing sequence could reduce the corresponding labor cost by about 30 percent, as in Item 8 above, but in this case the total cost of the contact processing would be reduced by about 24 percent because of its labor-intensive nature.

There are clearly opportunities for cost reduction in each of the eight steps in the deposition sequence and each of the three main steps in the contacting sequence, both in materials consumed and in labor required. Further, by the obvious expedient of increasing the cell area capacity per deposition run and the contact processing capacity of each step in that sequence the effective cost per unit area of cell could be greatly reduced. The first of these modifications is considered briefly in the next section, and other aspects will be examined in later reports. Until such projections are presented in detail, however, it appears that calculation of a cell cost per unit area (for example, cost per m^2) based on the above analysis alone would be relatively meaningless and probably quite misleading.

2.5.5 Reactant Consumption Rates and MO-CVD Process Efficiency

The MO-CVD reactor chamber design used in this program (Figures 2-4 and 2-5 of Reference 2) involves a rotating susceptor ~5 cm in diameter horizontally disposed in the vertical cylindrical chamber of 8.0 cm inside diameter. The susceptor thus intercepts about 0.4 of the cross-sectional area of the interior of the reactor chamber normal to the cylindrical chamber axis, which is the region through which the reactant gas mixture flows during the MO-CVD film growth process. Pyrolysis occurs at the hot surface of a substrate resting on the heated susceptor and/or on the hot susceptor surface itself in any regions not covered by substrate, resulting in deposition of GaAs or GaAℓAs, depending upon the composition of the reactant mixture.

Based on the assumption that the flow of the reactant mixture downward in the reactor chamber is laminar (i.e., non-turbulent) it follows that 40 percent of the reactants consumed impinge on the surface of the hot substrate (or uncovered susceptor) in the reactor design now in use, with the remaining 60 percent passing through the surrounding annulus and either undergoing spurious reaction downstream or exiting from the chamber into the exhaust line. The present reactor system design does not provide for any recycling or salvage of the unused reactants or of the carrier gas.

From the basic pyrolysis reaction equations for formation of GaAs and GaAℓAs by the MO-CVD process as used in this work (Equations 2-1 and 2-2, Reference 2) the minimum quantities of the reactants TMG, TMAℓ, and AsH$_3$ required for deposition of the experimental cell structure shown in Figure 2-8 can be calculated. For a cell area of 20 cm^2 (the full area of the susceptor surface) these quantities are as follows:

TMG	5.50×10^{-2} g
TMAℓ	2.20×10^{-4} g
AsH$_3$	3.74×10^{-2} g

However, in terms of the actual reactant flow rates used in a single deposition experiment the corresponding quantities of reactants consumed are the following:

TMG	0.294 g
TMAℓ	2.2×10^{-3} g
AsH$_3$	29.4 g

Based on these two sets of numbers the absolute overall efficiency of utilization of each of the three reactants with respect to the theoretical minumum amount required for the 20 cm^2 multilayer structure of Figure 2-8 is found to be

TMG	0.19
TMAℓ	0.10
AsH$_3$	0.0013

When allowance is made for the fact that only 40 percent of the reactant mixture is intercepted by the susceptor (i.e., by the 20 cm^2 substrate in this analysis) an indication of the actual efficiency of the pyrolysis reaction - that is, the efficiency of use of the intercepted reactant flow - can be obtained relative to each reactant. The values are

TMG	0.47
TMAℓ	0.25
AsH_3	0.0032

These results lead to the following preliminary conclusions:

1. The overall efficiency of utilization of the principal reactants could be increased by redesigning the substrate support (susceptor) to intercept a larger fraction of the flowing gas stream. However, as this fraction increases toward unity greater turbulence of the flow in the vicinity of the susceptor surface can be expected, and thus less uniformity of film growth rate and perhaps other film properties is likely.

2. In terms of the intercepted reactants the reaction efficiency is reasonably good (nearly 50 percent) for TMG, the reactant about which there is the most concern relative to cost and general availability. Reaction efficiency with respect to TMAℓ, also quite expensive in the required purity at the present time, is only about 25 percent. This raises questions as to the exact nature of the pyrolysis reactions when TMAℓ is present and as to the molecular state of the compound (i.e., monomer or polymer) when in the vapor phase at elevated temperatures.

3. A very large excess of AsH_3 is used in this process as it has been applied to the GaAs materials system, to maintain the stoichiometric integrity and the surface quality of the deposited films. An AsH_3 mass flow many times larger than that theoretically required for the pyrolysis reaction to proceed to completion has been employed. It is probable that this overpressure could be reduced by a yet-undetermined amount and still retain the required film stability, thus reducing the AsH_3 consumption rate and the associated cost, which is appreciable (see Table 2-1).

The actual consumption of TMG in a series of more than 300 deposition experiments in the program prior to the end of this reporting period was found to correspond to an average consumption of 0.235 g per experiment. On the basis of careful estimates of the weighted average amount of GaAs and/or GaAℓAs deposited per run in this long series of experiments it was determined that the multilayer cell structure of Figure 2-8 corresponds to an adjusted average consumption of approximately 0.19 g of TMG per deposition run. When this is compared with the theoretical minimum amount of TMG required by the pyrolysis reaction (in a reactor chamber of the size used here - 50 cm^2 cross-sectional area) for deposition of the multilayer structure under consideration an average efficiency of utilization of about 73 percent is calculated. The assumptions made in obtaining this figure were relatively risky, however, and it is believed that the lower efficiencies given in the previous paragraphs are more accurately indicative of the actual situation.

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3. SUMMARY AND CONCLUSIONS

The substrate materials used for experimental studies during the quarter included several grades of graphite (from two different manufacturers), commercial-grade Al alloy sheet, large-grained annealed Mo sheet, sputtered Mo films on Corning Code 0317 glass, uncoated 0317 glass, large-grained polycrystalline alumina (Coors Vistal 5), and large-grained bulk polycrystalline GaAs. Results obtained during the quarter indicated graphite to be a suitable substrate for GaAs film growth by MO-CVD, although some adherence problems were again encountered with improperly prepared graphite surfaces. Baking the substrate at elevated temperatures in the reactor prior to deposition appeared to be a requirement for satisfactory results. No major differences were observed for GaAs growth on the various graphites; polycrystalline films ~10 μm thick had apparent grain sizes (based on dimensions of surface features) in the 2-5 μm range, comparable with that obtained on various other non-crystalline low-cost substrates. The use of large-grained annealed Mo sheet substrates did not appear to enhance the grain size of deposited polycrystalline GaAs films with respect to the sizes previously observed for growth on small-grained (unannealed) Mo sheet.

Investigation was begun of the effects of $HC\ell$ addition on the growth habit and properties of polycrystalline GaAs films. Because of the appreciable attack of Mo films on glass by $HC\ell$ it was found necessary to first grow a very thin layer of GaAs over the Mo/glass composite substrates being used before admitting any $HC\ell$ to the reactor chamber. Additional examination of the effects of $HC\ell$ will be continued in the next quarter.

An examination of the effects of deposition temperature and film thickness on the properties of GaAs polycrystalline films on substrates of Mo sheet and Mo films on glass (Corning Code 0317) showed that grain size is larger for growth in the 700-750°C range than for growth at ~600°C, although it is relatively temperature-insensitive within the 700-750°C range. The average apparent grain size on both types of substrate was found to increase with increasing film thickness, with the maximum grain size in a given film approaching the thickness of the film itself (for thicknesses ≤10 μm).

The study of the factors influencing the properties of p-n junctions formed by deposition of polycrystalline GaAs layers by MO-CVD continued. Further investigation of the properties of the individual layers in such junctions provided more confirmation of the earlier conclusion (Ref 3) that the deposition parameters produced the expected properties for each layer in a controlled and reproducible way. However, leaky junction properties, as determined by I-V characteristics, continued to be observed. No evidence for impurity diffusion along the grain boundaries was found.

Examination of various p-i-n structures (the undoped i layer is n type) in polycrystalline GaAs grown on low-cost substrate materials showed that significant improvements in the I-V characteristics could be achieved through use of i layers ~ 4 μm thick. Even in that case, however, the junctions were still somewhat leaky.

Detailed studies of the transport properties of polycrystalline GaAs films grown by MO-CVD on substrates of Vistal 5 alumina and Corning Code 0317 glass were carried out. Emphasis was on p-type Zn-doped films in the 10^{16}-10^{19} cm^{-3} concentration range, although work was also begun at the end of the quarter on similarly doped n-type (Se-doped) films. The large-grained films on alumina exhibited resistivities nearly an order of magnitude lower than those of simultaneously grown small-grained films on glass for a given concentration of added dopant. Measurement of transport properties as a function of sample temperature in the range 77-450°K demonstrated that the presence of barriers to majority carrier flow at the grain boundaries in these films controls the carrier transport process. The height of these barriers (E_b) was shown experimentally to decrease with increasing impurity doping concentration according to the expression $E_b \propto \ln (1/p)$, where p is the measured hole concentration, for films on both the large-grained polycrystalline and the amorphous substrates.

The model used to explain the observed results assumes that the interface between individual grains of these polycrystalline films is highly defected, with a large density of neutral traps in the interface. These traps capture majority carriers, producing a depletion region on both sides of the interface (grain boundary). The resulting dipole layer causes a change in the energy band structure such that a barrier of height E_b is formed at the interface, and this is the barrier height obtained from the experimental data.

Determination of the variation in transport properties with sample temperature for the n-type Se-doped films is to be completed in the next quarter. Variations in electrical properties with distance from the film-substrate interface and variations as a function of post-deposition annealing of the films should also be investigated to complete this phase of the study.

Further attention was given to the ohmic contact problem that had persisted with the GaAs solar cell structures, especially for large-area (~4 cm^2) cells which exhibited excessive contact resistances and thus severely limited photovoltaic performance. In particular, the vacuum-deposited Au-Zn-Au contact used for p-type GaAs had continued to prove troublesome in terms of contact continuity over large areas, so several alternative contact materials for p-type GaAs were prepared and evaluated, including Pd, Ag-Mn, and Cr-Au. This work will be continued until satisfactory reproducible contact materials and procedures are identified. In addition, increased emphasis in the next quarter should be placed on fabrication of complete solar cells, both in polycrystalline films and in epitaxial films grown on single-crystal substrates -- the latter to provide baseline reference data against which to compare the performance of the polycrystalline devices.

A detailed analysis was made of the materials and labor required in the procedures used in the laboratory for depositing the composite film structure and applying the contacts for a complete thin-film $GaA\ell As/GaAs$ window-type solar cell made by MO-CVD. This analysis was then used to develop estimates of costs for fabricating these cells on a laboratory scale using the research-type reactor system and associated procedures employed in this program. Estimates of the consumption rates of the three principal reactants (TMG, $TMA\ell$, AsH_3) were also developed, and the efficiency of the MO-CVD pyrolysis reaction as used in the present reactor system was examined in terms of the consumption of these main reactants. Preliminary suggestions were made of several areas in which material and labor cost reductions appear feasible and increases in efficiency of utilization of the primary reactants appear possible. These preliminary results will be expanded later in the program and will provide part of the basis needed for projection of future large-scale production costs for thin-film GaAs cells made by MO-CVD.

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4. PLANS FOR NEXT QUARTER

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

Task 1

1. Continue evaluation of graphite as substrate material
2. Continue investigation of effects of $HC\ell$ additions during film growth on grain size and other properties of GaAs films
3. Continue evaluation of Ge intermediate layers on various low-cost materials as substrate for GaAs growth
4. Continue attempts to obtain new or improved materials, beyond those already in use, for substrates.

Task 2

1. Extend study of dependence of grain size at film surface on thickness of polycrystalline GaAs films
2. Continue study of transport properties in p- and n-type polycrystalline GaAs films
3. Continue investigation of electrical and photovoltaic properties of various p-n and p-i-n structures in polycrystalline GaAs on low-cost substrates
4. Investigate specific effects of grain size on photovoltaic properties of various multilayer structures
5. Continue routine characterization measurements on polycrystalline GaAs and $GaA\ell As$ films.

Task 3

1. Continue preparation and characterization of Au Schottky-barrier structures on polycrystalline GaAs films with emphasis on n/n^+ structures, and investigate effects of variations in Au layer thickness
2. Study polycrystalline $p^+/n/n^+$ structures to establish barrier heights and look for evidence of diffusion of dopants along grain boundaries
3. Continue preparation and evaluation of polycrystalline GaAs junction devices
4. Resume study of ITO/GaAs heterojunctions on polycrystalline GaAs films.

Task 4

1. Begin fabrication of deposition system for preparing antireflection coatings of TiO_2 for GaAs cells
2. Continue investigation and development of contact materials and techniques
3. Grow additional polycrystalline and single-crystal thin-window GaAs heterostructures and fabricate and evaluate solar cells.

Task 5

1. Begin reexamination of future costs of fabricating large quantities of thin-film GaAℓAs/GaAs solar cells by MO-CVD process.

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