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THIN POLYCRYSTALLINE FILMS OF INDIUM PHOSPHIDE ON LOW-COST SUBSTRATES

Quarterly Report No. 3, April 3—July 2, 1977

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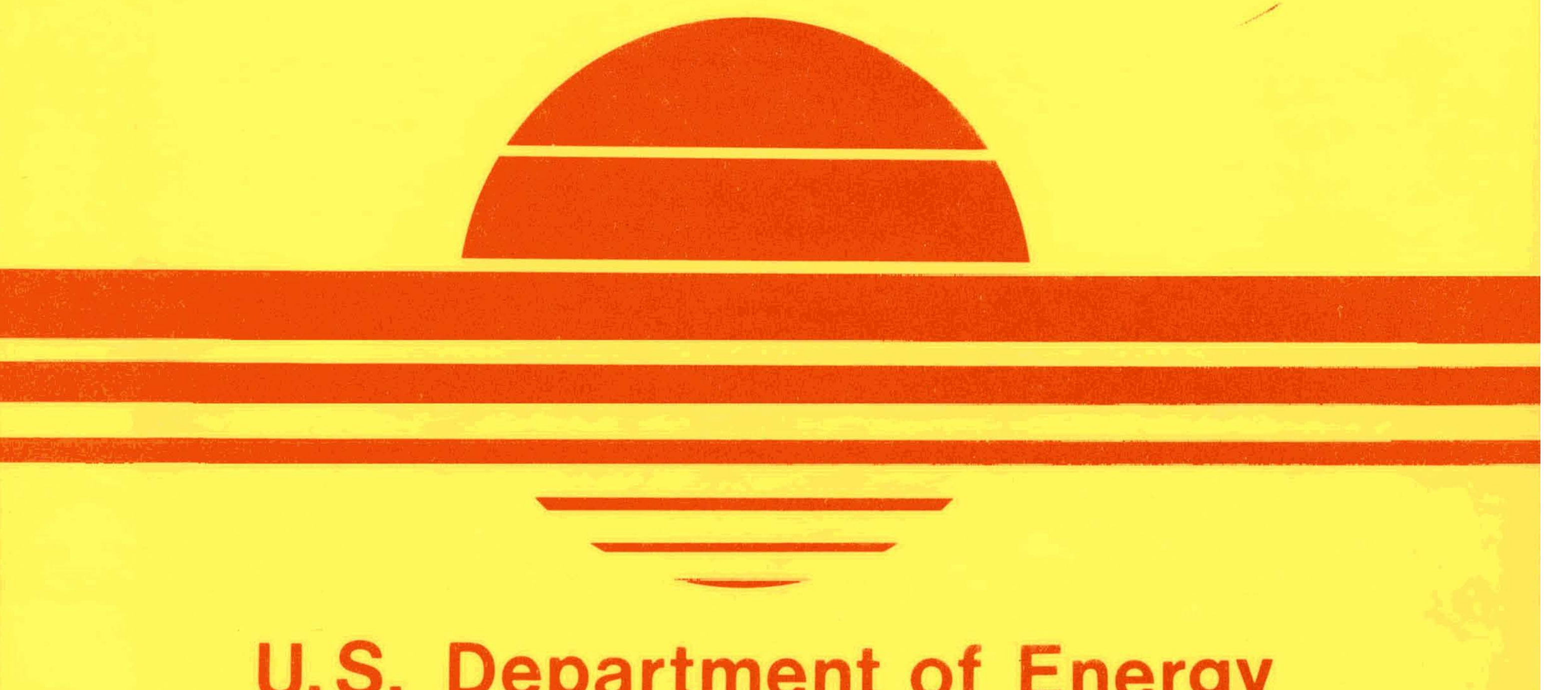
July 1977

Work Performed Under Contract No. EY-76-C-04-3727

Rockwell International
Electronic Devices Division
Electronics Research Center
Anaheim, California



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July 1977

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION,
UNDER CONTRACT NO. E(29-2)-3727

ABSTRACT

The work of the third quarter of the 12-month contract program is described. The program is intended to develop the metalorganic chemical vapor deposition (MO-CVD) process for growth of InP films using triethylindium (TEI) and phosphine (PH_3) reactants in a H_2 carrier gas, and then to prepare such films on inexpensive substrate materials for subsequent fabrication of heterojunction polycrystalline solar cells by deposition of CdS (or other semiconductor) on the InP. The CdS/InP heterojunction device fabrication and evaluation is done on subcontract at Stanford University.

Minor changes in reactor design have permitted achievement of InP film growth rates up to four times larger than those previously obtained. Deposition conditions have been established for obtaining good-quality undoped n-type epitaxial InP films on single-crystal (111A) and (111B) InP substrates, and p-type Zn-doped epitaxial InP films have been produced on both GaAs and InP single-crystal substrates, with doping concentrations in the 10^{16}-10^{18} cm^{-3} range. Experiments have continued on the growth of polycrystalline InP films on various low-cost substrates, including several glasses, metals and metal alloys, and intermediate layers of metals and semiconductors previously deposited on glass substrates; a wide range of InP film properties has been obtained in these studies, results of which are summarized.

Experimental Schottky-barrier device structures, employing thin Au barrier layers, have been fabricated on p-type InP films prepared in various single- and multiple-layer configurations. Short-circuit current densities (under simulated AMO illumination) of up to 12.5 mA/cm^2 were achieved in structures on GaAs substrates, but contact problems have limited the results obtained in various configurations on InP substrates. Some preliminary p-n junction structures have also been fabricated, but excess leakage currents have been found in the devices examined to date.

Detailed characterization of the transport properties in both undoped n-type epitaxial InP films on GaAs:Cr and InP:Fe semi-insulating substrates and Zn-doped p-type epitaxial films on GaAs:Cr substrates has indicated that the heteroepitaxial films exhibit mobility behavior for carrier concentrations below ~10^{16} cm^{-3} consistent with the presence of structure-related potential barriers of heights up to ~0.05 eV, while homoepitaxial films with carrier concentrations above ~10^{16} cm^{-3} are almost identical to good single crystals of InP in their mobility behavior. Mobilities as high as 16,500 cm^2/V-sec at 77°K in films on InP:Fe substrates have been measured.

The first heterojunction photovoltaic solar cell employing a vacuum-deposited n-type CdS film and an epitaxial p-type InP film grown by MO-CVD has been fabricated and characterized. A good short-circuit current density of ~14 mA/cm^2 was obtained in natural sunlight of 90 mw/cm^2 intensity, but the open-circuit photovoltage was ~0.3 V because of a large reverse saturation current in the heterojunction. The power conversion efficiency was only 2.3 percent, but this first result, obtained with non-optimized material parameters and device geometry, is considered to be a successful demonstration of the applicability of the MO-CVD process for growing InP films for solar cell applications.

Planned work for the fourth quarter is outlined.

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1. INTRODUCTION

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

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

Specific goals of the national program include establishment of total solar array production capacities of 500 peak Mw per year of solar array modules at a market price of less than \$500 per peak Kw by FY 1985, and 5×10^4 peak Mw per year of solar array modules at a market price of \$100 to \$300 per peak Kw by FY 2000.

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

1.1 CONTRACT OBJECTIVES

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

The specific technical objectives for the program are as follows:

1. Development of the metalorganic-hydride chemical vapor deposition (MO-CVD) process for growth of good-quality single-crystal or polycrystalline films of InP on selected low-cost substrate materials
2. Evaluation of the structural, electrical, and optical properties of the resulting InP films
3. Formation of heterojunction device structures by deposition of films of other semiconductors on the InP films, and evaluation of the photovoltaic properties of these composites
4. Analysis and projection of future costs of large-scale quantities of photovoltaic solar cells made by the process.

The following specific activities are required by ERDA in pursuit of the above objectives: (1) deposition of films of InP on the selected substrate(s); (2) measurement of the pertinent mechanical, electrical, and optical properties of the films, with special emphasis on adherence, morphology, uniformity, doping, carrier concentration, mobility, lifetime, and properties of the electrical contact adjacent to the substrate; (3) determination of the cost, quality, and requirements of the feedstock materials used in preparing the films; (4) performance of studies which include (a) refinement of the selection of appropriate low-cost substrates, (b) deposition of films on the few substrates so selected, (c) determination of the film properties in terms of quantitative physical parameters, and (d) modification of these parameters in a manner aimed toward the production and deployment of high-efficiency photovoltaic solar cells capable of being scaled to an annual production of 50,000 Mw per year by the year 2000 at a selling price of $100-300/peak Kw "without creating inordinate technical and economic problems;" (5) within three months from inception of the contract begin producing films and supply a minimum of 4 cm^2 of current production each month thereafter to ERDA for whatever purpose ERDA deems suitable, the number and shape of the samples to be representative of that month's output; and (6) projection of the results obtained in each quarter into refinement of the conceptual model of the physical system, stating in the required reports the implications of redirection of the on-going study, with the final report stating the Contractor's view of the work which still needs to be done and the approach suggested.

To achieve the above objectives and comply with the above program directives as established by ERDA, the technical approach described in the following section is being used in this contract.

1.2 GENERAL TECHNICAL APPROACH

The general technical approach of the program involves application of the metalorganic chemical vapor deposition (MO-CVD) technique, developed by Rockwell for the epitaxial growth of III-V compound semiconductors and their alloys, to the formation of films of InP on both single-crystal and low-cost polycrystalline or amorphous substrates. Cadmium sulfide (CdS) or other similar semiconductor compound or alloy is deposited by appropriate methods on the InP films to form heterojunction structures, and the photovoltaic properties of the resulting solar cell configurations are evaluated.

Early in the program, while the MO-CVD method has been further developed for the InP system--initially on suitable single-crystal substrates--attention has been given to the problem of identifying and evaluating potentially inexpensive substrate materials that are (or can be) available in large areas and will tolerate the experimental environment of the MO-CVD process. These substrate materials are used for growth of polycrystalline films of InP, which must be doped appropriately to achieve the desired electrical properties for heterojunction formation.

The InP films prepared in the program have been characterized for various material properties both at Rockwell and at Stanford University, the latter work being done on a subcontract. Films prepared throughout the program are used at Stanford for the formation of heterojunction structures by deposition of films of CdS (primarily), ZnCdS, and possibly ZnSe and ZnSSe, using vacuum deposition or chemical spraying techniques. The photovoltaic properties of the resulting heterojunctions are evaluated at Stanford, using electrical contact methods developed early in the program both at Stanford and at Rockwell.

Finally, some attention is being given to cost analyses of the cell structures being prepared in the contract program; projections of possible costs of large quantities of the cells in future years will be adjusted to allow for technical developments that may occur in the contract work.

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

The particular CVD method being used 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, triethylindium (TEI) and phosphine (PH_3) are mixed at room temperature in the gaseous state and pyrolyzed at established temperatures in a cold-wall reactor to form InP according to the following simplified reaction:

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

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

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

1. The process is completely free of halides, thus eliminating competing etching reactions, reducing generation of unwanted impurities by reactions with 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 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, 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 desired
6. Large-area, uniform surface coverage can be achieved in a single growth sequence, using the same type of commercially available apparatus that is used for epitaxial growth of elemental semiconductors (e.g., Si)
7. The process requires neither single-crystal InP material nor semiconductor-grade (ultrahigh-purity) polycrystalline InP for its application, since only compounds of In and of P are used in the reaction, thus eliminating the expensive and energy-wasteful process of producing melt-grown InP source material, as is required for other crystal growth and/or film deposition techniques.

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

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

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

To achieve the contract objectives and progress toward the long-range goals of ERDA's National Photovoltaic Conversion Program, and to find solutions to these major problems, the contract work is organized into six main technical tasks, plus preparation of required samples for delivery to ERDA and preparation and delivery of required data, reports, and review and presentation information. The contract tasks are as follows: (A) Development of MO-CVD Process for InP Film Growth; (B) Identification, Evaluation, and Development of Inexpensive Substrate Materials; (C) Growth of InP Films by MO-CVD on Inexpensive Substrate Materials; (D) Evaluation of InP Film Properties; (E) Formation and Evaluation of Heterojunction Photovoltaic Device Structures on InP Films (Stanford subcontract); (F) Analysis and Projection of Cell Performance and Costs; and (G) Preparation and Delivery of Film Samples.

This is the third Quarterly Report for this contract and covers the period 3 April through 2 July 1977. The contract activities during that period are described by task in the following section.

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2. TECHNICAL PROGRESS

This section contains a summary of the results obtained during the third quarter of the contract; the discussion is arranged by task.

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

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

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

A new reactor system for growing thin films of InP by the MO-CVD process was completed in the first quarter. Experiments using triethylindium (TEI) and phosphine (PH_3) reactants in a H_2 carrier gas showed that InP films could be successfully grown over a range of deposition temperatures. Epitaxial growth of single-crystal films was obtained on two different crystallographic orientations of single-crystal GaAs at temperatures as low as ~525°C. Films not intentionally doped were n type, with measured carrier concentrations in the 10^{16} cm^{-3} range and electron mobilities up to ~2000 cm^2/V-sec (room temperature).

The work in the first quarter showed that the relatively wide range of deposition conditions that appeared sufficient for single-crystal film growth on GaAs is not equally satisfactory for growth on (0001)-oriented sapphire, substrates of which were used along with the GaAs in most of the experiments. Sapphire used in this way, as a comparison substrate for GaAs, serves as a good indicator of how the growth process is proceeding, for the particular deposition conditions being used.

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

The Task A acitvities in the second quarter were concentrated in four major areas: (1) reactor chamber design evaluation; (2) InP growth on single-crystal GaAs substrates; (3) InP growth on single-crystal InP substrates; and (4) InP growth on various other single-crystal substrates. Heteroepitaxial films of undoped InP were grown on single-crystal GaAs substrates over the temperature range from below 575°C to ~700°C, with growth rates essentially independent of deposition temperature. Electron mobilities as high as 10,500 cm^2/V-sec at 77°K were measured in undoped n-type films less than 3μm thick on (100)GaAs substrates. It was also shown that p-type InP films can be grown on GaAs substrates by doping the film during deposition with Zn from diethylzinc (DEZ) added to the reactant gas stream. The p-type doping concentrations obtained in the second quarter were in the range above 10^{18} cm^{-3}.

Experiments with single-crystal InP substrates in the second quarter also led to a set of experimental conditions, involving the presence of PH_3, that help to preserve the stoichiometry of the substrates before film growth and of the films after growth. Other deposition studies were carried out with single-crystal substrates of sapphire, Ge, and InAs, with oriented InP growth obtained in all three cases.

Development of a low-resistance ohmic contact technology continued at Stanford for p-type InP in the doping range 10^{15} - 10^{18} cm^{-3}, using both vacuum deposition and electrodeposition of the contacts followed (in both cases) by post-deposition heat treatment in H_2. Investigation of transport properties of undoped n-type films indicated that lattice scattering dominates the low-temperature behavior of these films, with appreciably higher electron mobilities being found in films grown on (100)GaAs than on (111A)GaAs surfaces. Photoconductivity measurements were also carried out on these films.

The contract work in the third quarter has emphasized (1) the determination of conditions for producing good quality p-type InP films first on GaAs and then on InP single-crystal substrates, and (2) the modification of reactor chamber and reactor system design for the purpose of improving film growth rates and film thickness (i.e., growth rate) uniformity on the sample pedestal.

2.1.1 Reactor Modifications and Other Apparatus Considerations

During the third quarter two reactor chamber designs - Reactor No. 2, as described in Quarterly Report No. 2 (Ref 1), and Reactor No. 7 — were used. Reactor No. 2 has a tee just above the chamber neck but does not have a center tube. Reactor No. 7 incorporates a small vertical tube extending about 1/2 in. into the upper end of the main part of the reactor chamber, just below the tee where the reactants are mixed.

In addition, the sample pedestal support used in both chambers was modified to help in centering the pedestal in the reactor. This modification consisted of three quartz rod-like spokes, spaced 120 deg apart and projecting from the pedestal support, and bent slightly upward to form a cup-like structure for the pedestal yet not extend above the tope surface of the pedestal.

The reactor gas-handling system was also modified. A second triethylindium (TEI) bubbler was installed in parallel with the TEI bubbler normally used for film growth, thus providing means for at least doubling TEI mass flow rates at room temperature without major system changes or resort to special techniques for increasing the vapor pressure of the TEI. The total gas flow rates employed using the two bubblers are the same as those employed with one bubbler.

As previously shown in Quarterly Report No. 2, Figures 2-1 and 2-2 (Ref 1), total carrier gas flow rate affects the growth-rate profile across the sample pedestal. Profiles for InP growth in Reactor No. 7 for flow rates of 5, 6.5, and 8 ℓpm were determined using single-crystal GaAs substrates rather than sapphire substrates, since the visual quality of the epitaxy (in terms of obvious defect structure and reflectivity) on GaAs would provide some additional information as to growth uniformity across the pedestal. Appropriate masking and removal of part of the InP film with HCℓ (down to the GaAs substrate) provided the step necessary for measuring film thickness.

The results shown in Figure 2-1 are profilometer measurements taken along such an etched step at 2mm intervals. (The GaAs substrates are available for reuse after the InP film is totally removed by HCℓ, which does not attack GaAs.) Better thickness uniformity along with greater film reflectivity was obtained for a flow rate of 6.5 ℓpm. The use of Reactor Design No. 7 resulted in an improved growth rate, usually better than a two-fold increase, over the highest rates realized with Reactor No. 2. The increased rates reduced the growth time sufficiently to permit completion of several additional experiments each week, on the average. Thus, the combined use of two bubblers and Reactor No. 7 has permitted at least a four-fold growth rate increase over the rates obtained with Reactor No. 2.

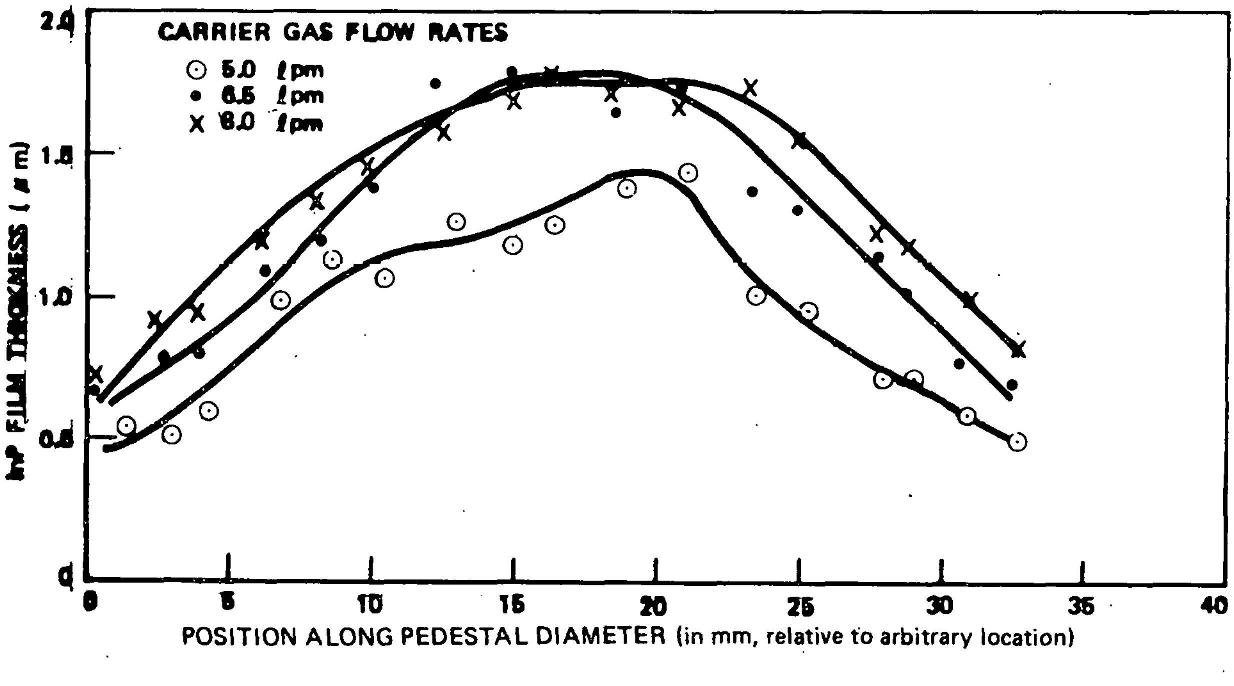


Figure 2-1. InP Growth Rate Profile Measured on (100)GaAs:Cr Substrate for Three Different Carrier Gas Flow Rates

Some slight changes were also made during the quarter in the flow rates used in the deposition studies. When the deposition system was originally assembled (at the start of the program), some of the last components to be received were the glass rotameters. However, the gas flow-rate charts for H_2 and He that were requested from the manufacturers at the time of the original purchase were not supplied with the rotameters. As a temporary expedient, flow-rate charts for other rotameters covering the same total flow-rate range as the purchased models were used in developing the InP growth process. These approximate flow rates used in the early experiments were recorded for later correction to more accurate values when the appropriate "calibration" charts were received. It should also be noted that it was expedient to use rotameter readings corresponding to the pure carrier gases rather than to the correct gas mixtures when flow rates for PH_3-in-He and PH_3-in-H_2 were being determined. The proper charts were finally received for H_2 during this reporting period, but not for He.

To reduce the uncertainties associated with the gas flow rates being used it was decided to undertake a direct calibration of the rotameters then in use. A volumeter (manufactured by George K. Porter, Hatfield, PA) was used for calibration of the appropriate three different flowmeter ranges incorporated in the system for H_2, He, and PH_3-in-H_2. The calibrated flow rates for H_2 were found to be in relatively good agreement with the charts supplied by Applied Materials, Inc. (Santa Clara, CA). All experiments performed in Reactor No. 7 in the third quarter employed the calibrated flow-rate values.

Because of concern for the purity of the reactants, it was decided to purchase two empty stainless-steel bubblers from one vendor, with instructions that they be supplied in the condition they would be in just before being filled with a metalorganic compound. One of these bubblers was disassembled and examined. The valves were found to be lubricated with a black substance. The valve design is such that the vapors of any material stored in the bubbler would be in contact with the lubricant, clearly a likely contaminant. During shipping any liquid material in the container could easily contact this lubricant.

One of these bubblers was subsequently thoroughly cleaned and shipped to Orgmet (E. Hampstead, NH) for filling with TEI. This material has now been received and is available for growth studies, when needed.

2.1.2 InP Growth on Single-crystal GaAs Substrates

GaAs substrates - because of their availability, lower cost, and potential reuse - have continued to play an important role in experiments directed at determining the effect of various growth parameters on film properties during the early part of this quarter. They were used in obtaining the Reactor No. 7 growth profile (as mentioned earlier), for testing old and new sources of TEI, and for further Zn doping studies, which are described in the next section.

At the start of the program two 25 g quantities of TEI were ordered from two different sources - Orgmet and Texas Alkyls (Deer Park, TX). TEI that was available from previous studies in our laboratory was used for film growth experiments while these orders were being filled. When the TEI from Texas Alkyls was received and tested, a leak was detected in the exit valve on the bubbler. Sealing it was evidently not sufficient, since most of the films grown using this bubbler had poor electrical properties. The bubbler and the TEI were recently replaced by Texas Alkyls, but the material has not yet been evaluated.

The other 25 g quantity of TEI (from Orgmet) produced films with properties similar to those of the films grown with the old supply of TEI used early in the program. As this supply began to deplete, as evidenced by a decreased film growth rate, the old TEI was reinstalled in the system and reevaluated by growth of InP on a (100)-oriented Cr-doped GaAs single-crystal substrate. The properties of the resulting undoped film (electron concentration 6.5×10^{15} cm^{-3} and room temperature mobility ~1400 cm^2/V-sec) indicated this TEI source is still acceptable for use.

Earlier investigation (Ref 1) of Zn doping of InP films formed by the MO-CVD method, in which the diethylzinc (DEZ) was maintained at 0°C and at -23°C, led to films with hole concentrations of 10^{18}-10^{19} cm^{-3}. Therefore, the DEZ bath temperature was lowered still further, to -36°C and -45°C, and films were grown on (100)- and (111A)-oriented high-resistivity GaAs single-crystal substrates.

As shown in Table 2-1, with the DEZ at -36°C films with hole concentrations of ~10^{16} cm^{-3} or greater can be prepared, the level of doping concentration appearing to be growth-temperature dependent; e.g., the films grown at ~690°C were more p-type than those grown at ~650°C, at the lower DEZ flow rates.

With the DEZ at -45°C it appears that p-type InP films with perhaps even lower doping concentrations can be grown on GaAs substrates. Thus, with the feasibility of producing InP p-type layers with doping levels in the 10^{16}-10^{18} cm^{-3} range on GaAs substrates demonstrated, studies of the growth of p-type layers on single-crystal InP substrates were subsequently pursued.

2.1.3 InP Growth on Single-crystal InP Substrates

It was reported earlier (Ref 1) that PH_3 is introduced into the reactor at about 500°C to help stabilize the surface of the InP substrates as the deposition temperature is reached, and that PH_3 flow is also maintained after film growth is complete and until the substrate has cooled to about 500°C. A PH_3-in-H_2 flow of 500 ccpm was arbitrarily used initially in the series of experiments described below.

However, during the studies of InP growth on InP a problem in determining the film growth temperature was encountered. Optical thermometer readings of the temperature of the surface of the pedestal slowly decreased with time before the start of deposition, suggesting the walls of the reactor were becoming less transparent - probably due mainly to a fine film of phosphorus produced by the decomposition of the PH_3 and perhaps partially to evaporation of InP and/or In from the substrates onto the reactor wall. After exposure of the InP substrates to PH_3 for 1 hour at 575°C, thermal etching was in evidence even though a high PH_3 flow rate was being used. These results indicate the necessity for achieving the desired film growth temperature in a minimum of time. The PH_3-in-H_2 flow rate was lowered to 50 ccpm in later experiments without an obvious effect on the stability of the InP surfaces.

The instability of the substrates (as evidenced by prolonged thermal etching) may be the prime cause for the increased n-type doping as the growth temperature is increased from 575 to 675°C, suggested by electrical measurements on InP films grown on (100)-oriented Fe-doped InP substrates (Table 2-4, Ref 1). The doping mechanism, however, is not clear.

Table 2-1. Effect of DEZ Bath Temperature and Film Growth Temperature on Properties of Doped* InP Films Grown on GaAs Substrates by MO-CVD Method

Experiment Sequence No.	Substrate Orientation	TEI/PH3 Flow Rates (ccpm)	DEZ Temp (°C)	H_2 Flow Rate over DEZ (ccpm)	Growth Temp† (°C)	Approx Film Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc (cm^{-3})	Mobility (cm^2/V-sec)
90	(111A)	1500/500	-36	**	648	1.4	1.1	1.7×10^{16}	348††
87	(100)	1500/500	-36	10	622	2.3	1.8	8.2×10^{16}	43
	(111A)					2.1	1.1	1×10^{17}	60
89	(100)	1500/500	-36	10	648	1.1	6.6	2.5×10^{16}	38
	(111A)					1.3	26.2	7.2×10^{16}	3.3
125	(100)	2500/500	-36	10	692	1.9	0.12	1×10^{18}	51
	(111A)					1.9	0.03	4.5×10^{18}	47
102	(100)	1500/500	-36	30	656	1.1	1.9	8.2×10^{17}	4.1
	(111A)					1.0	0.09	2.8×10^{18}	24
124	(100)	2500/500	-36	30	688	1.7	0.13	9.2×10^{17}	52
	(111A)					1.9	0.04	3.4×10^{18}	48
101	(100)	1500/500	-36	50	647	1.0	0.27	8.5×10^{17}	27
	(111A)					1.1	0.06	3.3×10^{18}	33
92	(100)	1500/500	-45	**	640	2.0	0.04	1.0×10^{16}	1480††
	(111A)					2.3	0.38	9.3×10^{15}	1770††
91	(100)	1500/500	-45	10	653	1.4	11.3	2×10^{16}	27
	(111A)					1.2	17.8	–	–

* All films p type except as noted

† Observed temperature, measured by sighting optical thermometer on vertical surface of susceptor

†† N-type InP film

** DEZ line open to permit normal vaporization of DEZ, but no carrier gas flowing through DEZ tank

During this report period high-resistivity (111)-oriented Fe-doped InP wafers were received from Imanco (Cambridge Instrument Co., Inc). Both (111A)- and (111B)-oriented surfaces were then polished at Rockwell and subsequently used for film growth studies along with the (100)InP substrates previously prepared. The (111A)InP substrates were polished first, and early experiments using (111A)InP were limited to obtaining comparative data for films grown simultaneously on (100)InP.

When the polished (111B)InP substrates became available the film growth studies utilized both the (111A) and (111B) faces, since it is not known which orientation will be preferred for subsequent growth of n-type CdS and fabrication of solar cell structures. Recent works described in the literature report both the A and B faces useful for cell fabrication. The eventual choice may, however, be determined by the CdS growth process used in this work.

2.1.3.1 Undoped N-type Films

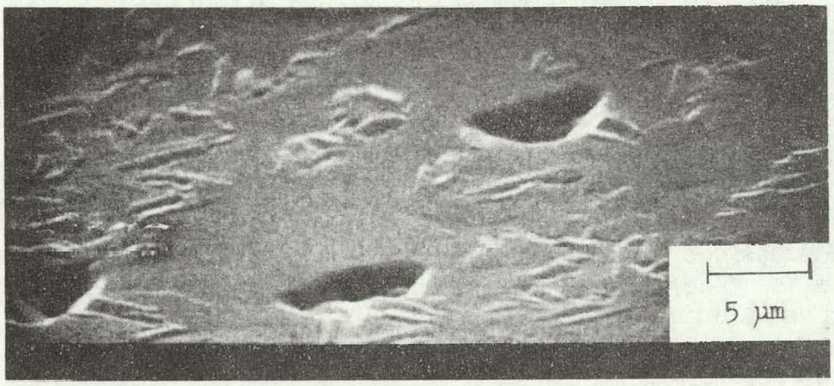
As indicated above, the availability of polished high-resistivity (111B)-oriented Fe-doped InP wafers permitted a study to compare the properties of films grown simultaneously on the (111A) and (111B) faces. For these epxeriments the PH_3-in-H_2 flow rate was kept at 50 ccpm from the time the measured temperature reached 500°C until the desired growth temperature was reached and found to be stable. The flow rate was then changed to 500 ccpm or the value desired during deposition, and film growth commenced with addition of the TEI.

At ~650°C, more reflective InP films were achieved on (111A)InP; at ~710°C and ~735°C both orientations provided reflective films. The surface quality of the films grown at different temperatures is shown in Figures 2-2 and 2-3.

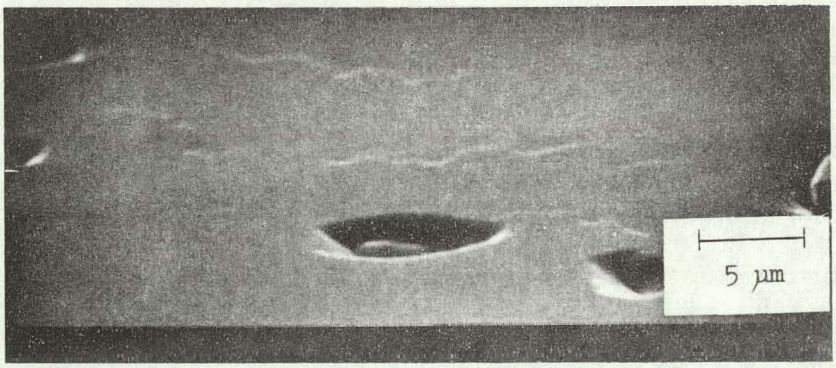
The electrical properties of films grown in the temperature range 618-737°C are recorded in Table 2-2. The films deposited at 713°C and 737°C agree quite well in electrical properties, so an intermediate temperature of ~725°C was selected for the next investigation - that of the effect of PH_3 flow rate, for a constant concentration of TEI, on the properties of the films. For these experiments PH_3 (10 percent in H_2) flow rates from 15 to 1000 ccpm were used. At 15 ccpm the substrates were found to be unstable; at 31 ccpm, the next low flow rate examined, the surface remained reflective during the film growth process.

As shown in Table 2-3, reasonably high mobilities were found in all the films but one, grown over a large span of PH_3 flow rates. No obvious correlation between PH_3 flow rate and measured carrier concentration in the film was in evidence. At the higher PH_3 flow rates ($\geq$500 ccpm) the mobilities of (111A) and (111B) films were quite similar; at lower PH_3 flow rates ($<$250 ccpm) the (111B)InP films appeared electrically superior to the (111A) films.

(100)InP:Fe substrates were also included in the last two experiments, in which high flow rates of PH_3 were used. The electrical properties of the films grown on these substrates are quite surprising, in light of the results reported in Quarterly Report No. 2 (Ref 1), Table 2-4, for films grown at lower temperatures. That is, higher n-type doping levels and/or lower mobilities were expected in the films grown on (100)InP at ~725°C. The results may be related to the higher PH_3 flow rates and/or to the use of Reactor No. 7, which increased film growth rates over those obtained in Reactor No. 2 (without a center tube), as noted earlier in this report.



(a)



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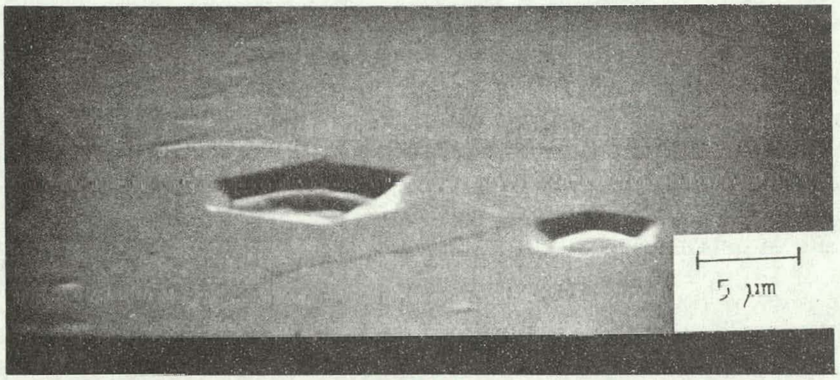
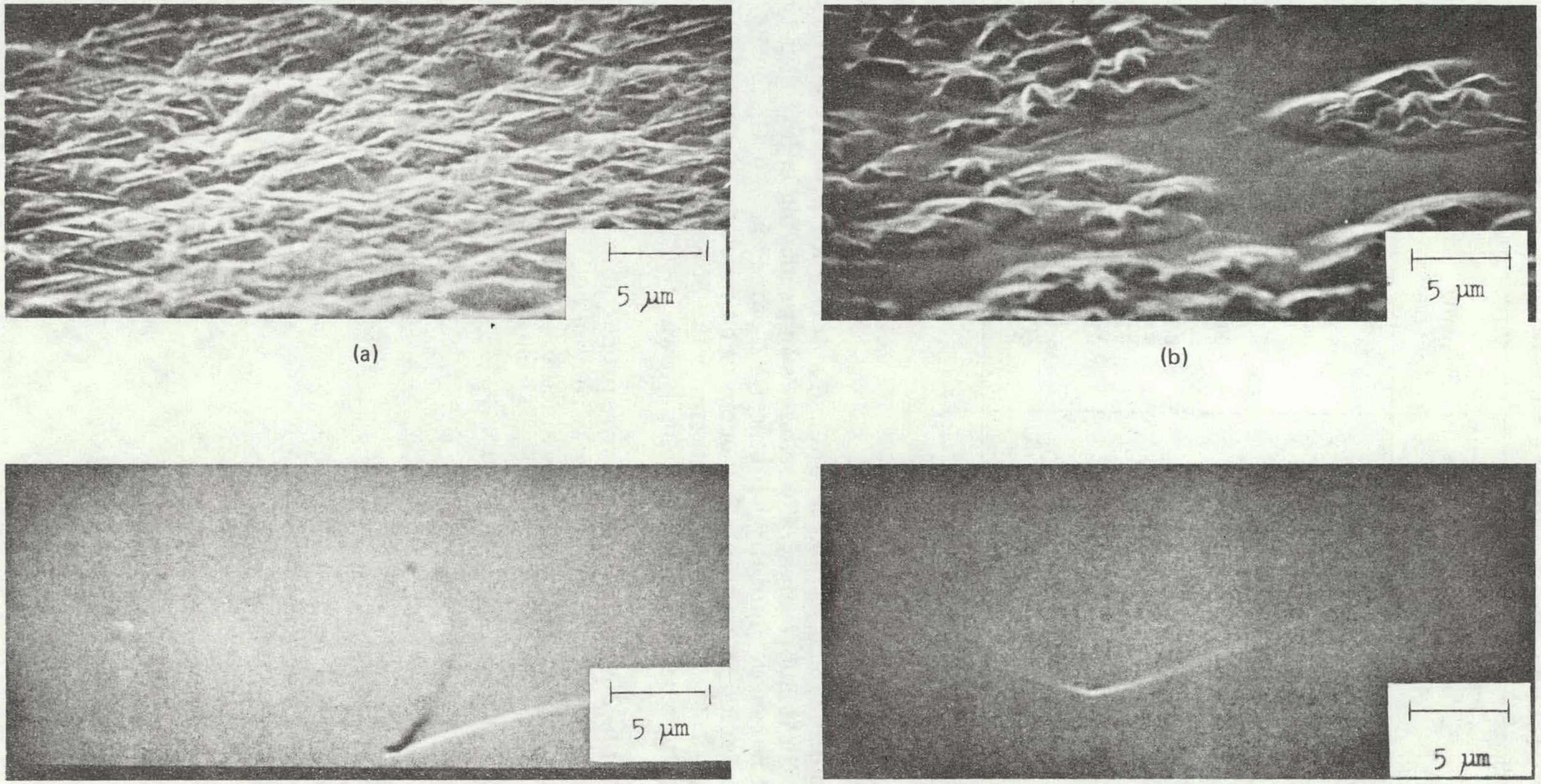


(c)

Figure 2-2. SEM Photographs of InP Growth on (111A) InP:Fe As Function of Growth Temperature. a) 652°C, 3.2 μm Thick; b) 713°C, 3.2 μm Thick; c) 737°C, 2.5 μm Thick. (Viewed at 60 deg angle with surface.)



(a) (b) (c) (d)

Figure 2-3. SEM Photographs of InP Growth on (111B)InP:Fe As Function of Growth Temperature. a) 618°C, 3.2 µm Thick; b) 652°C, 2.5 µm Thick; c) 713°C, 3.2 µm Thick; d) 737°C, 3.0 µm Thick. (Viewed at 60 deg angle with surface.)

Table 2-2. Effect of Growth Temperature on Properties of Undoped InP Films Grown on InP:Fe Substrates*

Expt. Sequence No.	Substrate Orientation	Growth Temp. (^{o}C)	Approximate Film Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Mobility (cm^2/V-sec)
134	(111A)	618	2.8	39	3.6×10^{15}	45
	(111B)		3.2	0.28	2.8×10^{16}	790
135	(111A)	652	3.2	1.5	9.4×10^{15}	450
	(111B)		2.5	0.09	6.6×10^{16}	1060
140	(111B)	678	1.6	0.02	1.4×10^{17}	2100
141	(111A)	701	1.6	0.73	8.6×10^{15}	995
136	(111A)	713	3.2	0.06	5.8×10^{16}	1820
	(111B)		3.2	0.09	2.4×10^{16}	2970
137	(111A)	737	2.5	0.04	8×10^{16}	1930
	(111B)		3.2	0.13	2.2×10^{16}	2160

*TEI flow rate 2500 ccpm; PH_3 flow rate 500 ccpm

2.1.3.2 P-type Zn-doped Films

Using growth conditions and parameters found suitable for producing p-type Zn-doped InP films on GaAs substrates, experiments in producing epitaxial p-type films on InP were next pursued. Initially with the DEZ stored at -36^{o}C, the H_2 flow over the DEZ was varied from only a few ccpm to as much as 60 ccpm. A temperature span of 685-759^{o}C was used to determine the effect of temperature on doping concentration, with most of the films being grown at ~725^{o}.

As indicated in Table 2-4, p-type films were produced in most cases on (111A)InP:Fe substrates, but only n-type films were obtained on (111B)InP:Fe substrates. The DEZ bath temperature was then raised to -23^{o}C, and it because possible to produce p-type films on (111B)InP:Fe substrates, with hole concentrations in the range considered useful for solar cell fabrication.

Table 2-3. Effect of PH_3 Flow Rate on Properties of Undoped InP Films Grown on InP:Fe Substrates*

Expt. Sequence No.	Substrate Orientation	PH_3 Flow Rate (ccpm)	Growth Temp. (°C)	Approximate Film Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Mobility (cm^2/V-sec)
145	(111A)	31	720	2.3	0.27	2.0×10^{16}	1140
	(111B)			2.1	0.09	3.2×10^{16}	2160
144	(111A)	62	726	1.6	0.09	4.5×10^{16}	1580
	(111B)			1.7	0.13	2.2×10^{16}	2090
143	(111A)	125	721	1.3	0.14	4.8×10^{16}	915
	(111B)			1.4	0.05	6.5×10^{16}	2060
142	(111A)	250	728	1.8	0.05	6.4×10^{16}	1850
	(111B)			1.6	0.05	6.1×10^{16}	2240
136	(111A)	500	713	3.2	0.06	5.8×10^{16}	1820
	(111B)			3.2	0.09	2.4×10^{16}	2970
137	(111A)	500	737	2.5	0.04	8.4×10^{16}	1930
	(111B)			3.2	0.13	2.2×10^{16}	2160
160	(100)	750	721	2	0.07	4.2×10^{16}	2160
	(111A)			2	0.07	4.2×10^{16}	2650
	(111B)			2	0.05	5.2×10^{16}	2220
161	(100)	1000	724	2	0.05	5.5×10^{16}	2080
	(111A)			2	0.13	2.0×10^{16}	2470
	(111B)			2	0.09	3.0×10^{16}	2320

*TEI flow rate 2500 ccpm

Table 2-4. Electrical Properties of InP Films Grown on InP·Fe Substrates with DEZ Bath at Two Different Temperatures.

Expt. Sequence No.	Substrate Orientation	DEZ Source Temp. (°C)	H_2 Flow Rate over DEZ (ccpm)	Growth Temp.† (°C)	Approx. Film Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Mobility (cm^2/V-sec)
168	(111A)	-36	0	730	–	–	–	52
152	(111A)	-36	7	727	1.7	0.08	$2.7x10^{18}$	39
155	(111A)	-36	7	729	3.5	0.05	$5.9x10^{16}$	2070††
147	(111B) (111B)	-36	7	685	2 2	0.03 0.06	$5.3x10^{18}$ $4.7x10^{16}$	35 2250††
154	(111B)	-36	7	715	3	0.06	$3.9x10^{16}$	2530††
151	(111B)	-36	7	728	1.5	0.75	$3.9x10^{16}$	215††
146	(111A) (111B)	-36	7	731	2 2	0.04 0.43	$4.5x10^{18}$ $5.9x10^{16}$	36 177††
148	(111A) (111B)	-36	7	759	2 2	0.08 0.11	$1.8x10^{18}$ $3.1x10^{16}$	46 1860††
165	(111A)	-36	30	717	3.4	0.06	$2.6x10^{18}$	38
169	(111A)	-36	30	749	2	0.05	$2.5x10^{18}$	49
166	(111A)	-36	60	727	2.0	0.04	$4.1x10^{18}$	43
179	(111B)	-23	7	695	3.5	0.95	$4.5x10^{15}$	1460††
170	(111B)	-23	30	702	2	0.62	$2.8x10^{17}$	36
171	(111B)	-23	30	729	2	0.49	$4.7x10^{17}$	27

* TEI flow rate 2500 ccpm; PH_3 flow rate 500 ccpm

† Observed temperature, measured by sighting optical thermometer on vertical surface of susceptor

†† N-type InP film; all others are p-type

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

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

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

The selection of candidate substrate materials is based on a combination of (1) the known required properties of these materials, (2) the availability of either commericially-prepared samples or specially-processed research samples produced specifically for use in this program, and (3) the present-day and probable future costs of the materials when supplied in large quantities. The crystalline nature of the substrate is a major factor in the achievement of InP film growth with sufficiently good structural properties to permit fabrication of solar cells meeting the eventual goal of 10 percent AM1 efficiency. At one extreme is a single-crystal substrate, such as InP or GaAs, which results - under proper conditions of temperature, growth rate, and surface preparation - in epitaxial growth of single-crystal InP. At the other extreme is an amorphous substrate, which presents a passive surface to the arriving atmos; the atoms then migrate over the surface and finally congregate at nucleation centers distributed at random. The latter process leads generally to a polycrystalline deposit with a statistical distribution of grain size and orientation, which is then subject to possible modification by various means.

During the first quarter the deposition studies involved the single-crystal substrate materials GaAs and sapphire. Attention was also given to the selection and evaluation of various low-cost materials — glasses, alumina ceramics, metals, and some composites of these materials. Various contacts were made with glass, metal, and ceramic manufacturers to encourage their participation in the program by supplying specially prepared as well as standard materials for experimental evaluation.

Low-cost substrate materials that were tentatively identified as candidates for use in the program included the following: (1) polycrystalline alumina ceramics, such as refired ASM805 from the 3M Co; (2) glass-ceramics, such as Corning Code 9606; (3) glasses, such as Corning Codes 7059 and 0211; and (4) metals, such as Mo, in sheet or deposited film form.

During the second quarter the efforts to obtain samples of suitable candidate materials were continued. The specific materials identified for initial experimentation with InP films deposited by the MO-CVD process were listed in Table 2-1 of

Quarterly Report No. 2 (Ref 1). Because of early difficulties in establishing preferred growth parameters for large-area InP epitaxy on sapphire, any study of InP growth on polycrystalline aluminas has been deferred until later in the program. Sapphire, however, continues to be used as a substrate for monitoring possible cross-contamination among substrates, for comparative growth rate studies, and for growth of GaAs, Ge, and/or metal intermediate layers for subsequent InP growth.

During the third quarter efforts to obtain new samples of suitable candidate low-cost materials were continued. For example, several glazed zircon substrates were received from Ferro Corporation (Independence, OH) for preliminary evaluation on this and other solar cell programs at Rockwell. The glaze RX-3672 (composition not yet released by Ferro) is described as having an average thermal expansion coefficient (TEC) of 4.0×10^{-6} per deg C, approximately equal to that of InP. In addition, Owens-Illinois (Toledo, OH) plans to supply three new glasses with TEC values of $\sim 4.5\times10^{-6}$ per deg C; these will be processed by Rockwell into polished substrates. Corning Glass Works has also supplied additional substrates of Code 0317 glass, even though this glass has been withdrawn from the commerical market at the present time.

Films of In (~2500 Å thick), Au (~1500 Å), and Ge (~2000 Å), in addition to Mo (~2000 Å) previously prepared, have been vacuum deposited on separate substrates of Corning Code 0317 glass for use in determining the effect of intermediate layers on InP film nucleation and growth.

To help in determining the possible influence of substrate impurities on film properties, several glasses from various vendors were sent to Pacific Spectrochemical Laboratory, Inc. (Los Angeles, CA), for semiquantitative analysis by spectrographic means. Because of the proprietary nature of most of these materials, the glasses have been identified by letter code only. Table 2-5 indicates the major constituents found in these glasses, i.e., those elements detected as oxides present in concentrations over 1 percent.

Table 2-5. Major Constituents in Several Glass Substrate Materials

Glass Designation	Major Elements Present*
A	Si, Ca, Aℓ
B	Si, Ca, Aℓ, Mg, Ba
C	Si, Ca, Aℓ, Ti, Pb, Zr
D	Si, Ca, Aℓ, Mg
E	Si, Aℓ, Mg, Ti
F	Si, Na, K, As

*As oxides, in concentrations of 1 percent or more

At least 17 different elements (as oxides) were found in the analyses of these six glasses; some elements major in one glass were not detected at all in others. In addition to the major elements listed in Table 2-5 are other chemical constituents such as Fe, B, Mn, Ga, W, Cu, Ag, Sr and Ni; in several of the glasses Sr, As, B and Fe are present (as oxides) in concentrations between 0.2 and 1.0 percent. Because the MO-CVD process depends on pyrolysis to form the desired compound, the probability of contamination from the substrate is reduced compared with that associated with a halide "etching" process. In fact, there may be little relation between impurities occurring in the substrate and impurities found in the film. Later work with InP film growth on various low-cost substrate materials may help to clarify this question. In the meantime, the results of these analyses will be used in evaluating the suitability of the glasses involved for continued use in the InP film growth studies.

Several polycrystalline ceramics, such as aluminas of various grain sizes and steatite, have been polished in Rockwell laboratories and are new available for substrate use at the appropriate time. Considerable further delay has been encountered in the receipt of the polished graphite substrates of high purity and low porosity ordered over 3 months ago from Poco Graphite, Inc. (Decatur, TX). The latest promised delivery date is the end of July.

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

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

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

As indicated in the program proposal and in the first quarterly report (Ref 2), the principal effort on this task was scheduled to begin during the second quarter, with the first experiments concentrating on comparisons of the growth of InP films on single-crystal and on selected low-cost polycrystalline or amorphous substrates, for given deposition parameters. Because many of the CVD parameters required for the epitaxial deposition of InP were identified early in the program, it appeared practical to use these parameters initially in experimentally testing some of the candidate low-cost substrate(s) for InP film growth. The low-cost materials used for initial evaluation included Corning Codes 1723, 7059, and 0317 glasses and Owens-Illinois EE-2 glass, as well as Mo, Mo alloy, W, and Fe-Ni alloys in sheet form, and sputtered Mo films on 7059 and 0317 glass substrates.

During the third quarter, experiments continued for determining the effect of varying growth parameters on the condition and quality of films grown on selected low-cost polycrystalline and/or amorphous substrates. Growth parameters which had previously given high quality films on GaAs and InP single-crystal substrates were initially used in these experiments and in testing some new candidate substrate materials for compatibility with InP and the CVD environment. Films were grown on glasses, metals and metal alloys, and on intermediate layers of Au, Mo, and Ge. The results are summarized below.

2.3.1 InP Film Growth on Glasses

Films were grown on six additional glasses at temperatures in the range 550-770°C during this report period. In addition to Corning Codes 1723, 0317, and 7059, and Owens-Illinois EE-2 glasses previously used for InP film growth, the following glasses were tested: Corning Code 0211 and Owens-Illinois EE-5, GS238, GS210, GS211, and GS213.

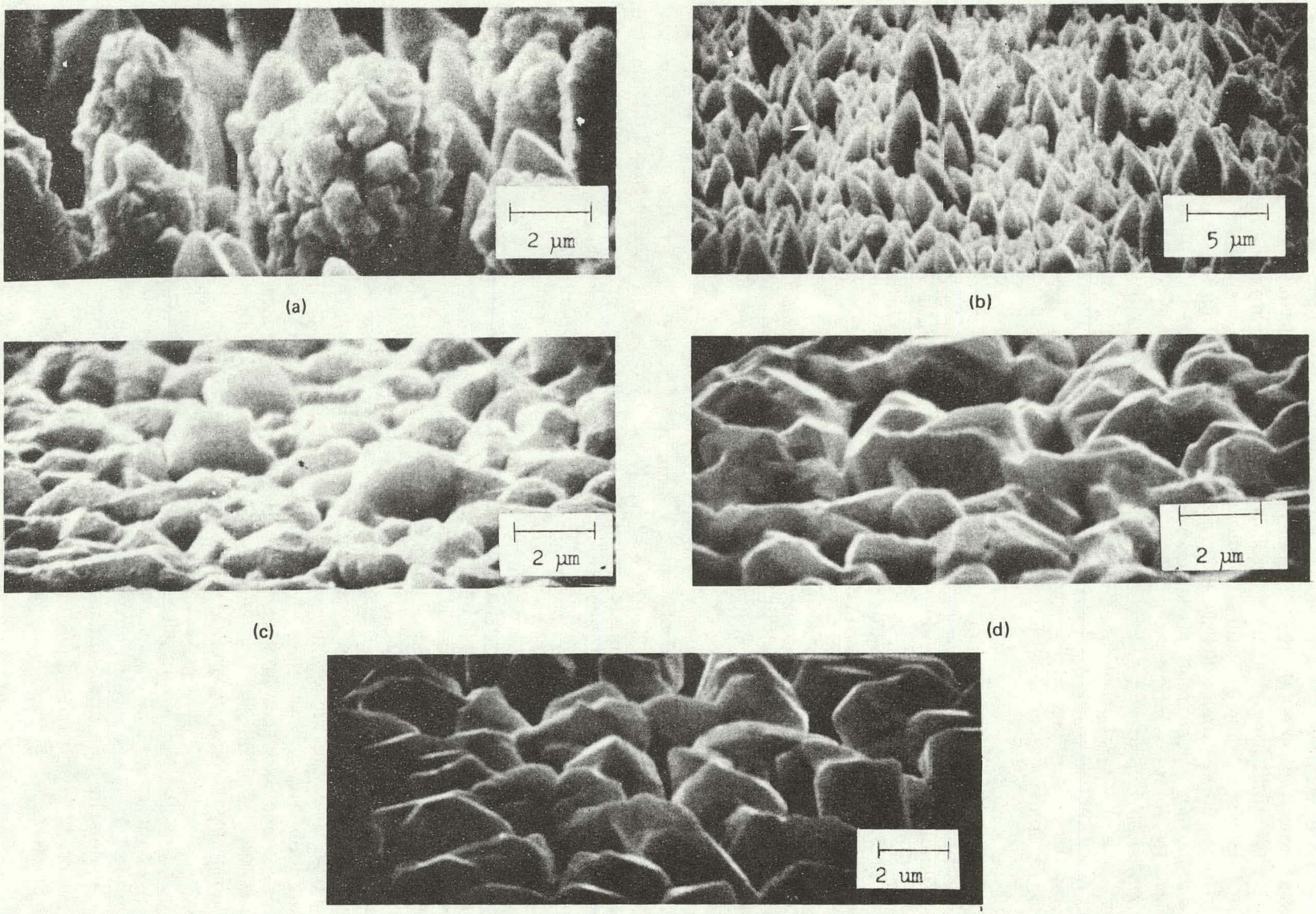
SEM examination of the films indicated that the growths on these glasses were essentially identical for the same growth conditions. The nature of the deposits is shown in Figures 2-4 and 2-5; these photographs show representative film growth on Owens-Illinois EE-5 glass substrates. In Figure 2-4 columnar-type growth of InP appears to be more prevalent for deposition temperatures of 575°C and below, with the crystallite columns initiating at or near the glass surface; at and above 625°C the surfaces of the films appeared crystallographically faceted but still very rugged in texture, when observed at 7000X magnification in the SEM. Photographs taken normal to the surface indicate fewer voids in the films grown at 671°C than in those grown at 704°C (Figure 2-5). These films did exhibit many areas of high reflectivity and crystallographically oriented surface textures.

InP growth on these glasses was observed to occur very slowly. The early growth is in the form of a gray-white deposit that is obvious only after the first few minutes of growth at the typical growth rate of 1-2 μm/hr. If this initial deposit is free In, then it was thought that a thicker molten In layer might enhance surface mobility, result in more rapid surface coverage by In, and perhaps induce a vapor-liquid-solid (VLS) mechanism of needle growth.

To test this hypothesis, a "layer" of In was produced on a glass substrate by pyrolysis of TEI in H_2, annealed in H_2 for about 5 min, then exposed to PH_3 for 15 min; InP deposition was then continued. As shown in Figure 2-6, the deposits of separate vertical columnar-type crystallites on 0317 glass at 548 and 579°C were randomly decorated with "cauliflower-like" structures; at 631°C the continuous film surface was crystallographically faceted, but many of the crystal grains had hollow or depressed central regions. There was no direct evidence for VLS growth during this limited study. It is obviously necessary to explore the early growth process on glasses in more detail, e.g., to examine the nature of the gray-white deposit and its composition as a function of thickness, in order to begin to understand the growth phenomena that are taking place.

Sequential deposition of two InP layers at two different temperatures on a given substrate was also undertaken with these glasses. Layers were grown at 625°C for 10 min and for 30 min in two separate experiments. In the former case a second layer was grown at 675°C for a period of 50 min to form the double layer. In the other experiment the second layer was grown at 675°C for 30 min. No intentional doping was done in either experiment. The double layers were discontinuous in both instances; it appeared that the first-grown layers were probably not continuous. This apparent tendency toward relatively widely separated island growth (and thus probably widely separated nucleation at the onset of deposition) may be characteristic of InP growth on these glasses and may thus be significant in determining eventual grain size in polycrystalline InP films on glasses. Additional investigation of these phenomena will be undertaken later in the program.

After Reactor No. 7 was put into use, additional films were grown on various glasses over the range 625-700°C to take advantage of the higher growth rates possible with Reactor No. 7. Substrate coverage appeared to be at most only about 90 percent complete under the best conditions used with this reactor.

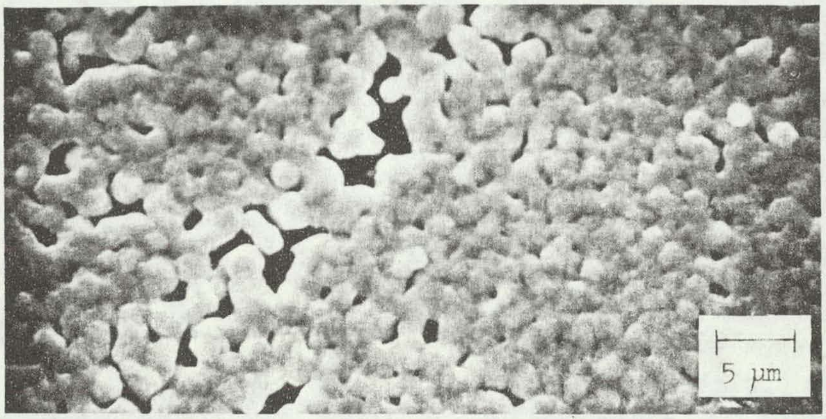


(a) (b)

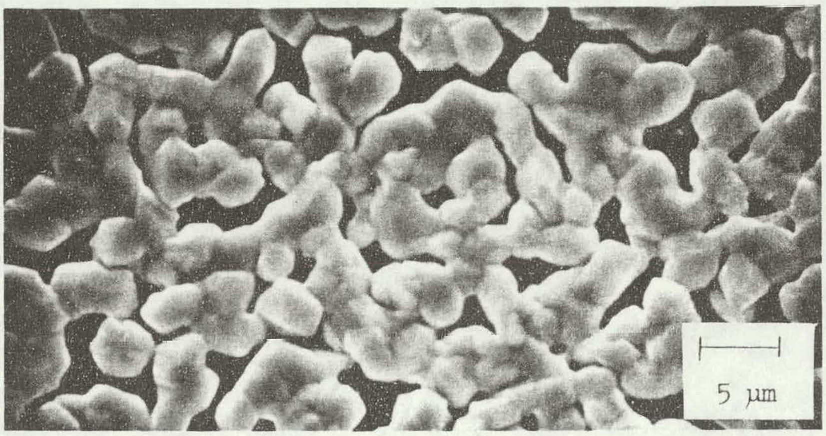
(c) (d)

(e)

Figure 2-4. SEM Photographs of InP Film Growth on EE-5 Glass as Function of Deposition Temperature. a) 549^{o}C, b) 573^{o}C, c) 634^{o}C, d) 671^{o}C, e) 704^{o}C. (Views at 60 deg angle with surfaces.)

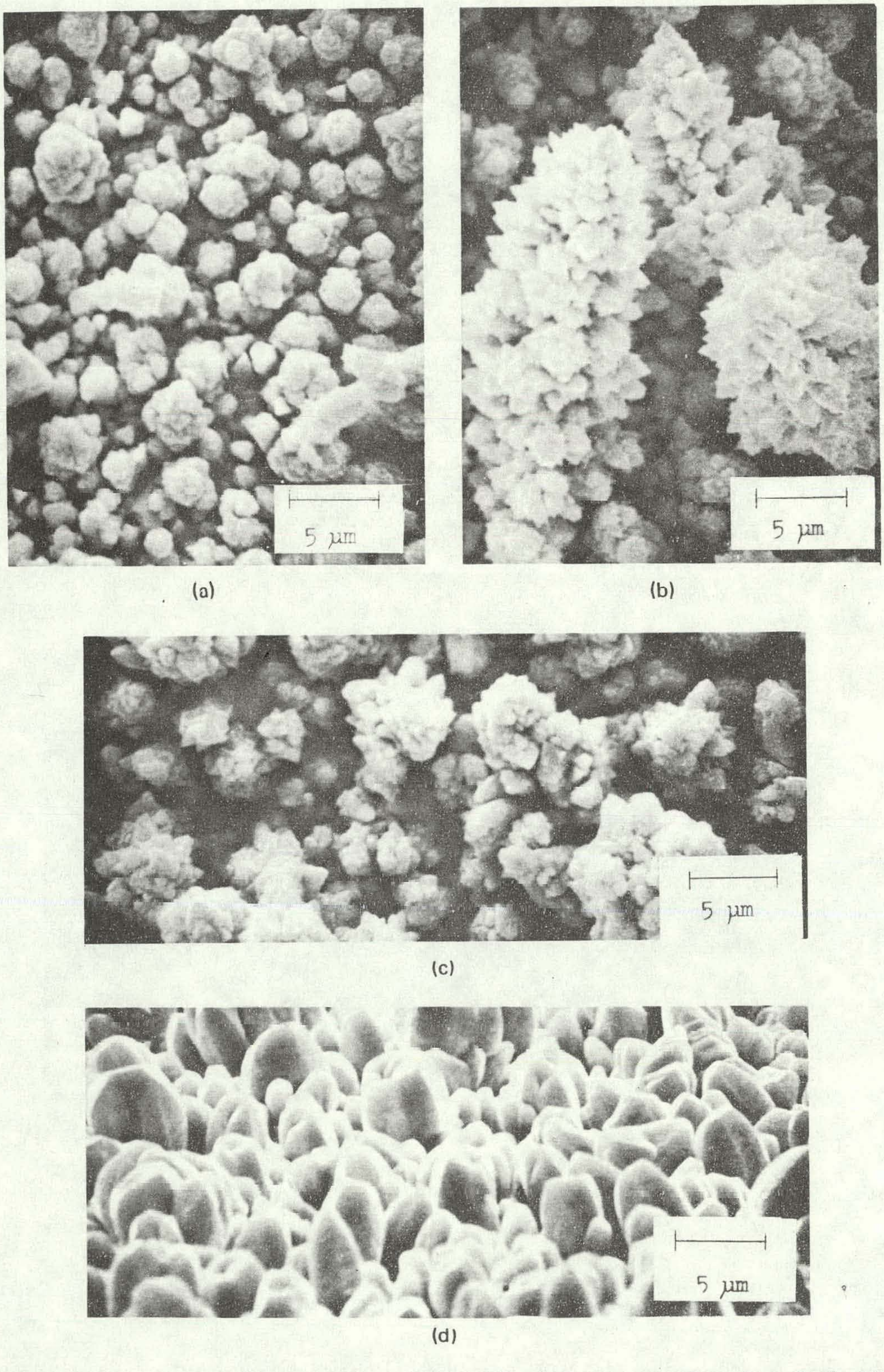


(a)



(b)

Figure 2-5. SEM Photographs of InP Film Growth on EE-5 Glass at a) 671°C and b) 704°C. (Views normal to film surfaces.)



(a) (b)

(c)

(d)

Figure 2-6. SEM Photographs of InP Films Grown on Corning Code 0317 Glass at Several Different Temperatures. a) 551°C, b) 548°C, c) 579°C, d) 631°C. Films in b, c, d Grown with "Pre-In" Treatment - See Text. (Views normal to film surfaces, except d which is at 60 deg with surface.)

For the case of films grown with Reactor No. 2, better surface coverage was achieved at ~625°C, and the films appeared smoother when grown at this temperature, as shown in Figure 2-5 for growth on EE-5. In one experiment, however, for reasons not clear, part of a film grown on glass EE-5 at 606°C separated from the substrate. The lifted portion shown at the left in Figure 2-7 indicates that many voids were present at the film-glass interface, and that changes in the present nucleation and early growth process are necessary to improve InP film growth on these glasses. None of the other film-glass composites grown simultaneously with the above film showed any separation, however.

2.3.2 InP Film Growth on Metals and Metal Alloys

SEM photographs of the polycrystalline films grown on standard Mo, W, and TZM (Mo alloy) materials from AMAX Specialty Metals, various Fe-Ni alloys from several suppliers, and specially annealed Mo from GTE Sylvania are shown in Figures 2-8, 9, and 10. SEM photographs of some of the bare substrates are also included. At these magnifications (see Figure 2-8) the "standard" metal surfaces are seen to be quite variable in quality and roughness; this may be the reason for the variation in film quality obtained. The film growths on Mo, W, and TZM appear to be quite similar (Figure 2-8); similarly, the InP growths on the Fe-Ni alloys (Figure 2-9) are very much alike. The crystallites appear more highly oriented on W, Mo, and the TZM alloy than on the Fe-Ni alloys. When a thicker film was grown on Kovar at 650°C, the film did not adhere well; therefore, the use of Kovar and related alloys as substrates for the direct growth of InP is no longer being considered.

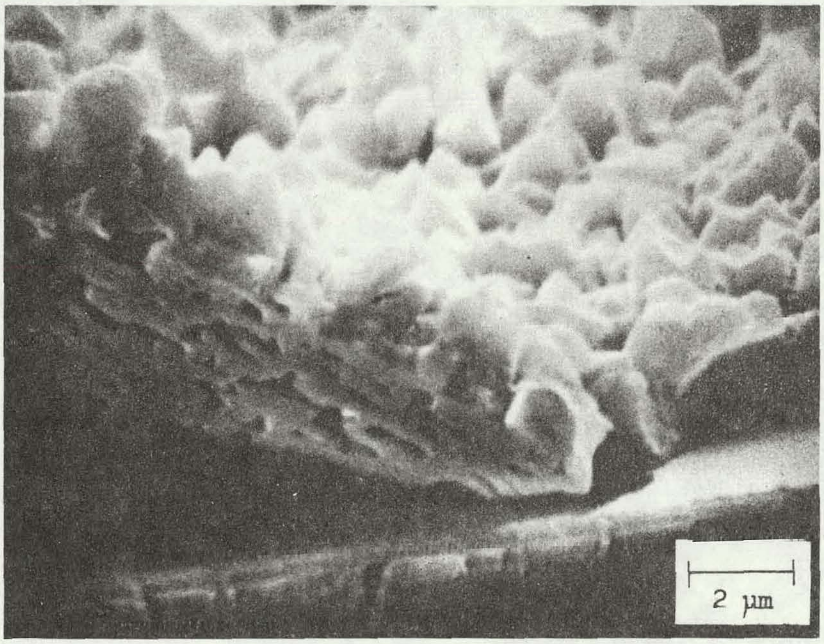


Figure 2-7. SEM Photograph of InP Film Partly Detached from Surface of EE-5 Glass Substrate. (View at 45 deg angle with film surface.)

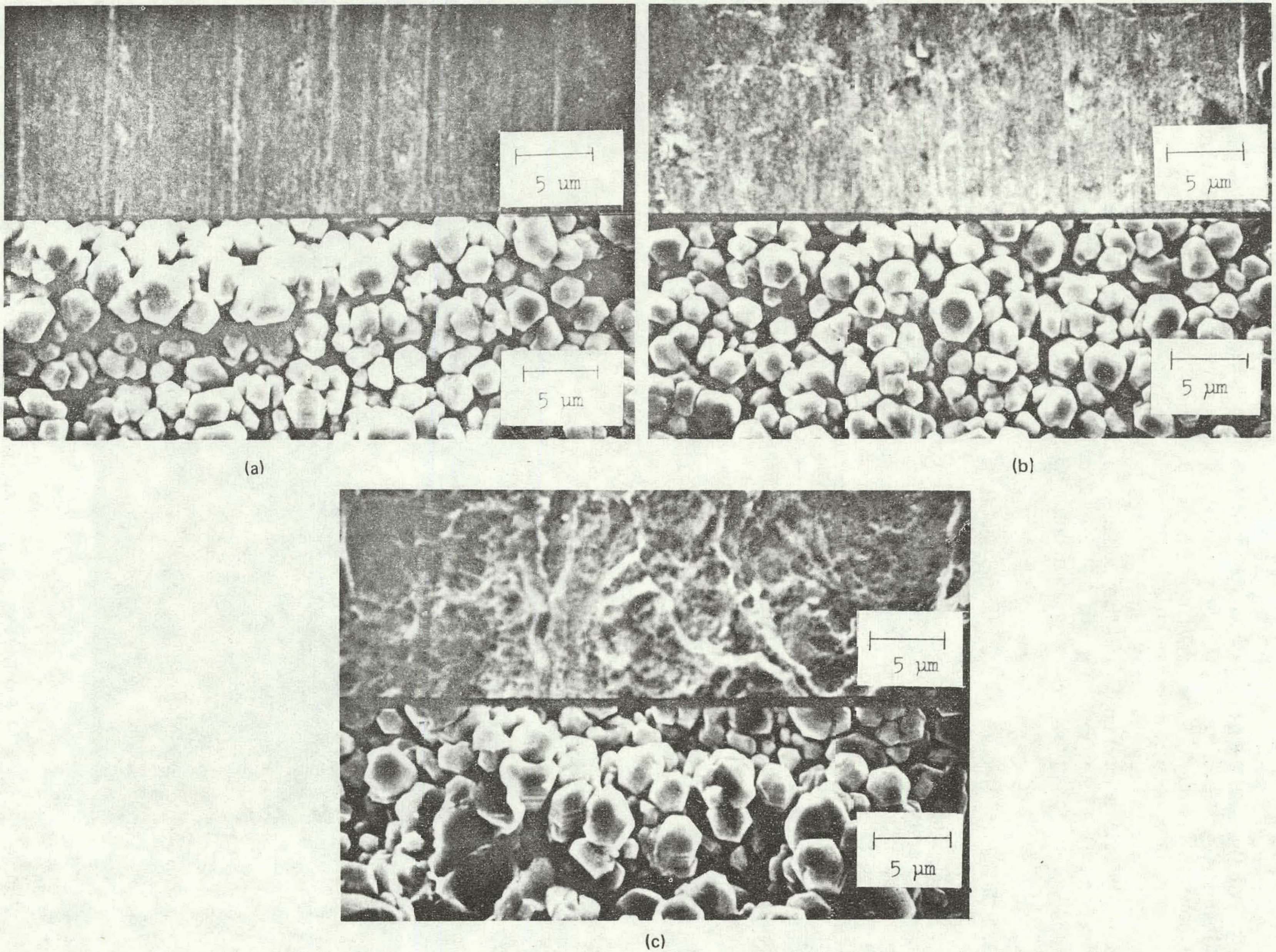


Figure 2-8. SEM Photographs of InP Films (lower portion of photograph) Grown at 624°C on Several Metal Substrates (upper portion of photograph). a) Mo, b) W, c) TZM Alloy.

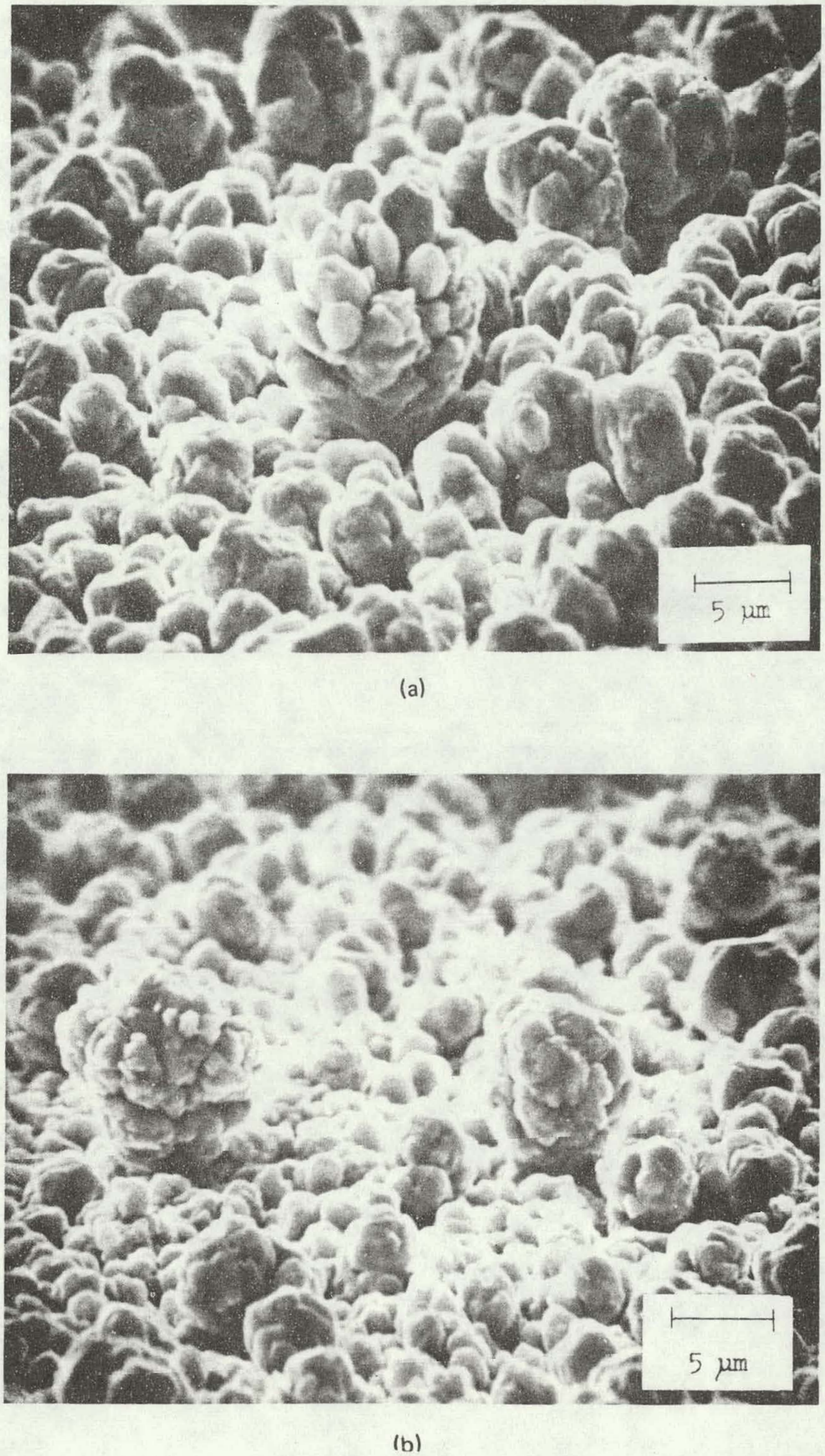
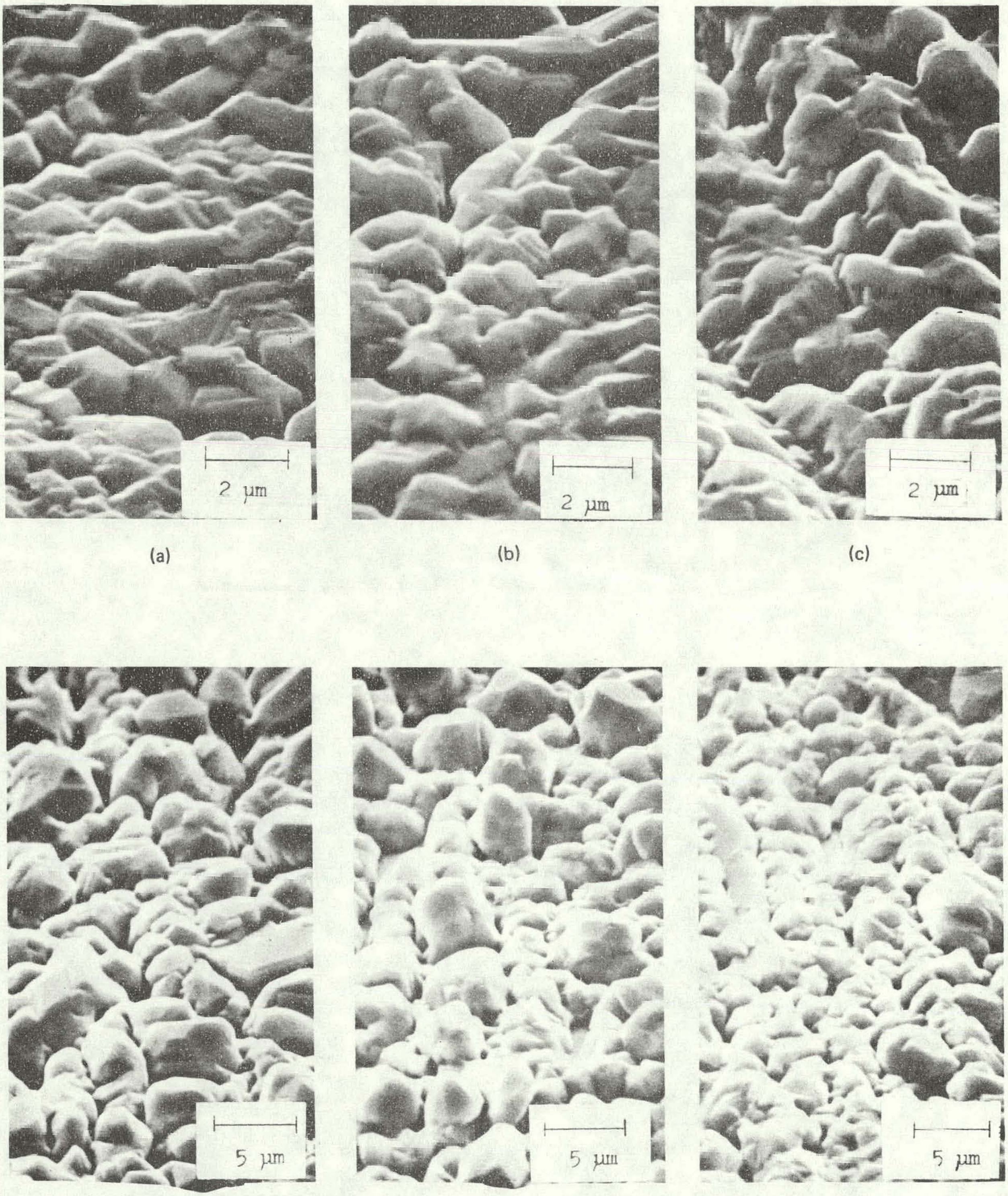


Figure 2-9. SEM Photographs of InP Films Grown at 576°C on Substrates of a) Kovar and b) Niron. (Views at 45 deg angle with film surfaces.)



(a) (b) (c)

(d) (e)

Figure 2-10. SEM Photographs of InP Films Grown on Surfaces of Specially Annealed Mo Substrates at 619°C (a, b, c), and at 704°C (d, e, f). (Views at 45 deg angle with film surfaces.)

InP Films were also deposited on the three annealed Mo substrates supplied by GTE. A comparison of the films grown at 619°C and 704°C (Figure 2-10) indicates a much smoother structure and fewer voids in the films grown at the lower temperature. The reason for the different networks of apparent "grains" in these films is not known. However, it may relate to the annealing processes used by GTE in preparing these substrates. Representative pieces of these annealed materials will be electropolished to prepare a better surface for InP film growth in future experiments.

2.3.3 InP Film Growth on Intermediate Films on Glass Substrates

InP films were grown using established conditions on Mo layers 2000Å and 4000Å thick that had been sputtered onto Corning Code 0317 glass substrates. As shown in Figure 2-11, the films grown on both thicknesses of the Mo at 624°C were needle- or spike-like, somewhat similar to the films grown on EE-5 glass at 573°C (Figure 2-4). Films grown on the Mo layers at 704°C (Figure 2-12) were much more granular. There appear to be fewer voids at the InP-Mo interface than are found at the interface of films grown directly on glass at the same temperature (cf Figure 2-5).

As shown in Figures 2-13 and 2-14, needle- or spike-like growth was also obtained for InP layers grown at 653°C on thin films (2000Å) of Ge deposited on 0317 glass (Figure 2-13) and on a lightly-etched polycrystalline film of GaAs ~6 μm thick grown by MO-CVD on 0317 glass (Figure 2-14). At a higher growth temperature of 693°C the surface of the InP film on Ge was somewhat undulating, with channels 0.5 μm deep. This nonuniformity is probably related to changes that have been observed in the Ge films during the initial heating period and the "H_2 etch." The Ge films are normally heated in H_2 to temperatures in excess of 700°C prior to InP film growth, to remove naturally occurring surface oxides. This causes a change from a dark reflective Ge surface to a crystalline-gray color. The nature of this change has not yet been examined in detail.

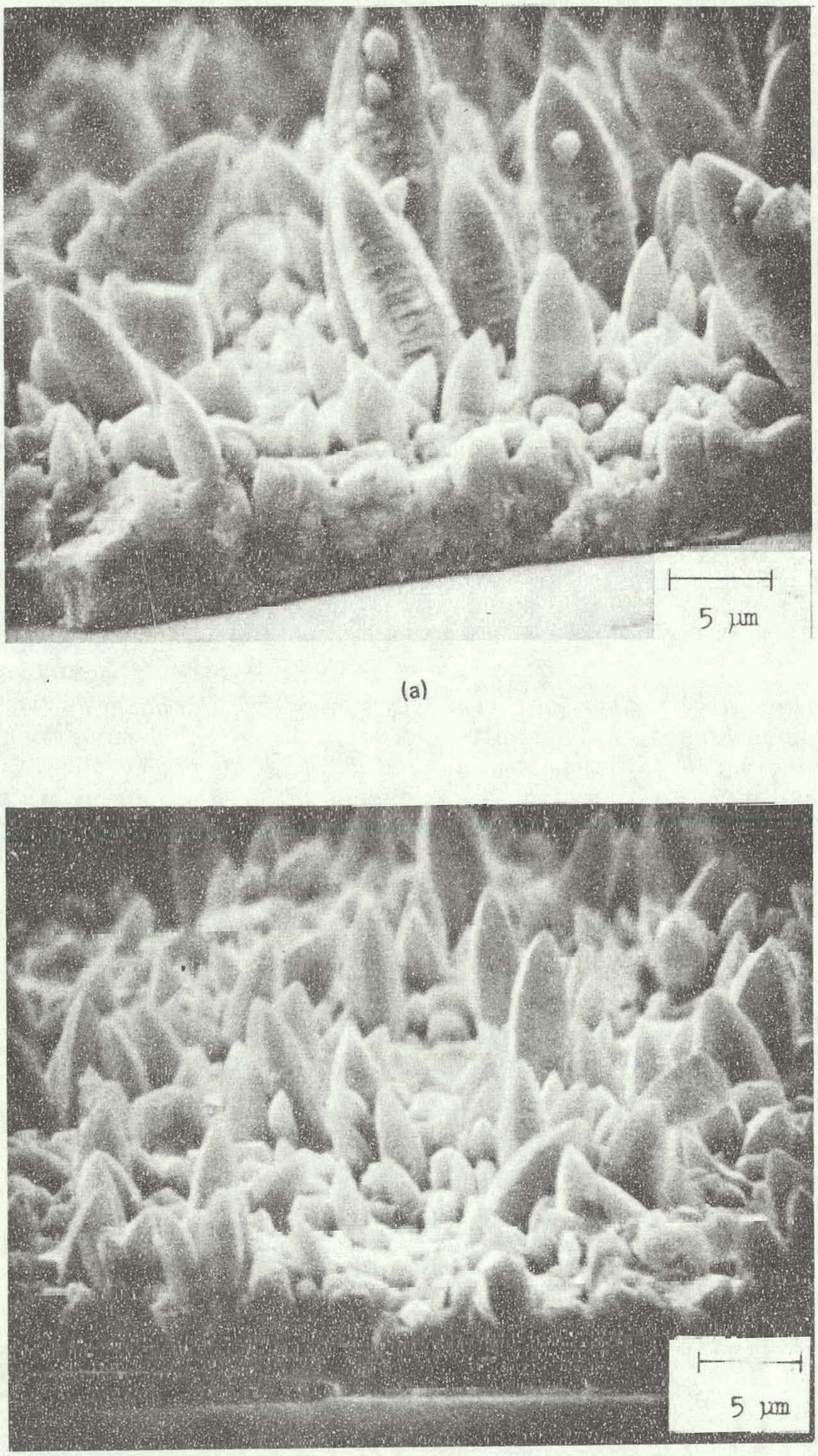


Figure 2-11. SEM Photographs of InP Films Deposited at 624°C on Mo Layers Sputtered onto Corning Code 0317 Glass Substrates. a) Mo 2000Å Thick; b) Mo 4000Å Thick. (Views at 60 deg angle with film surfaces.)

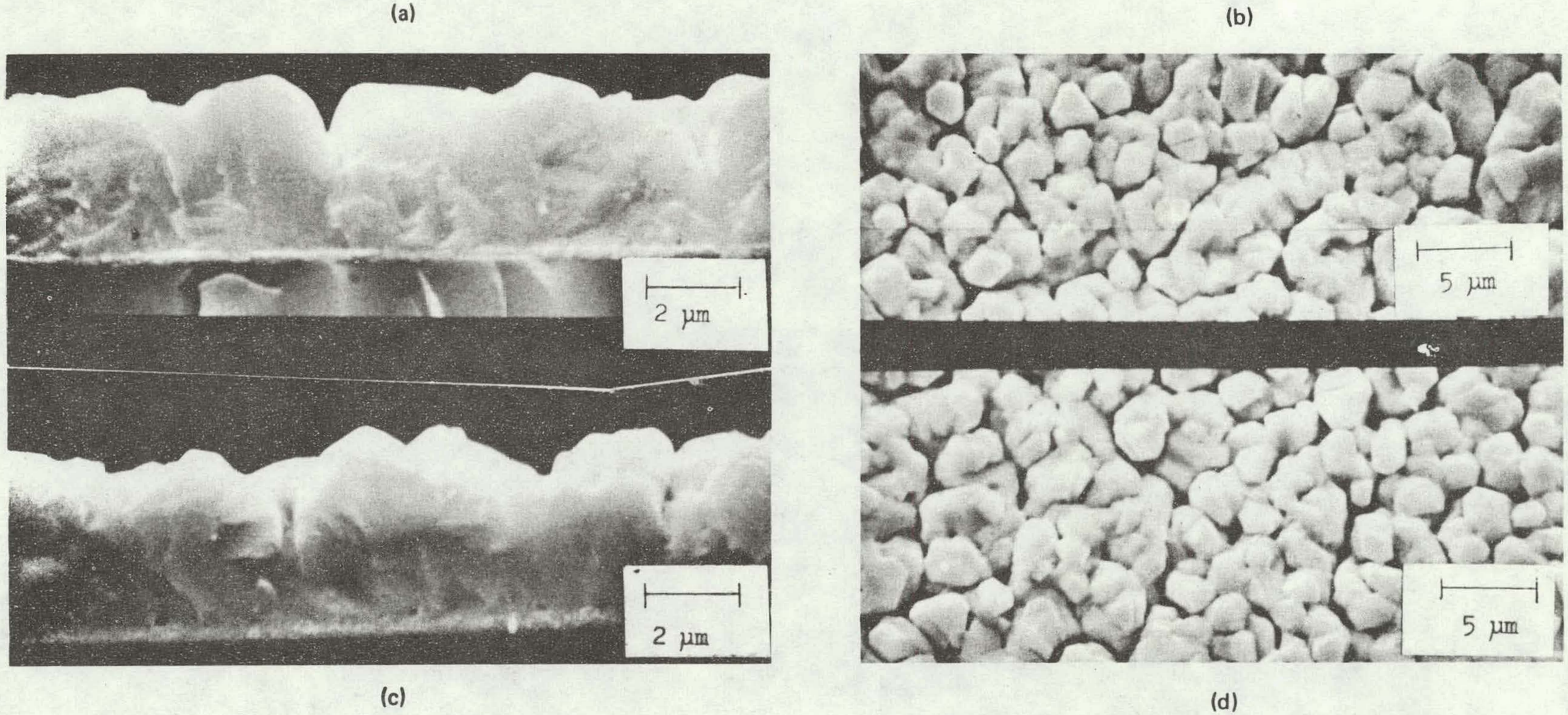
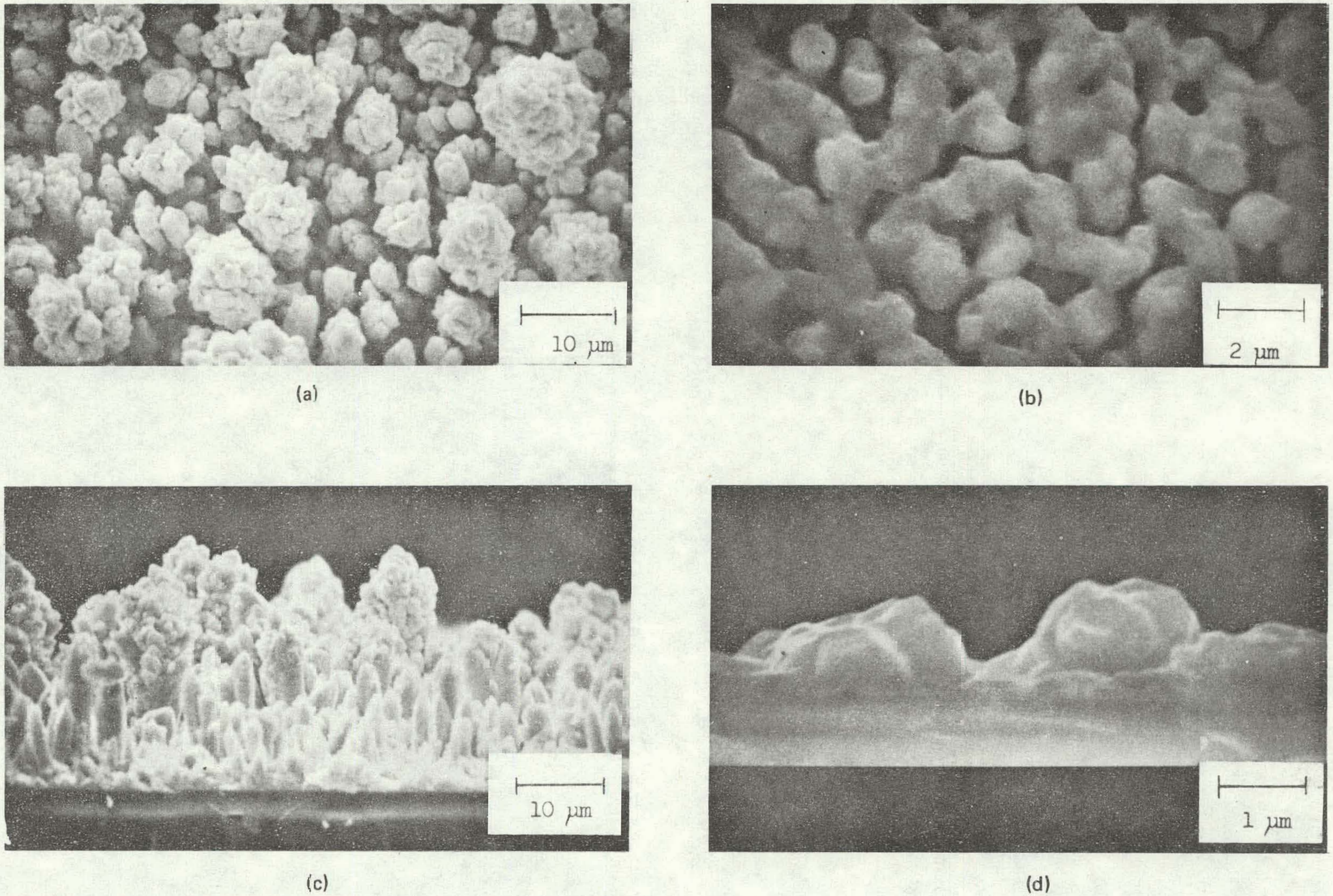
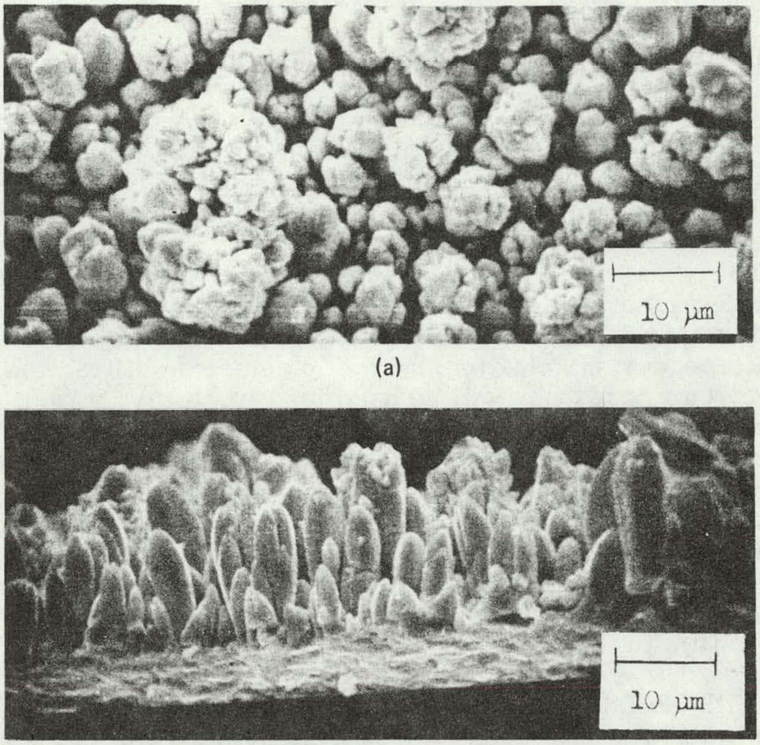


Figure 2-12. SEM Photographs of InP Films Grown at 704°C on Sputtered Mo Layers on Corning Code 0317 Glass. InP Film on 2000Å Mo Viewed a) in Cross-section and b) Normal to Surface; InP Film on 4000Å Mo Viewed c) in Cross-section and d) Normal to Surface.



(a) (b) (c) (d)

Figure 2-13. SEM Photographs of InP Films Grown on Ge Layers 2000Å Thick on Corning Code 0317 Glass. Film Grown at 653°C Viewed a) Normal to Surface and b) in Cross-section; Film Grown at 693°C Viewed c) Normal to Surface and d) in Cross-section.



(a)

(b)

Figure 2-14. SEM Photographs of InP Deposited at 653°C on GaAs Layer ~6 μm Thick on Corning Code 0317 Glass, Viewed a) Normal to Film Surface and b) in Cross-section.

2.4 TASK D. EVALUATION OF InP FILM PROPERTIES

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

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

Relatively little activity occurred on this task in the first quarter since InP films were first grown in the new MO-CVD reactor system quite late in the quarter. Most of the effort was devoted to planning and preparing characterization apparatus and techniques. However, some of the first InP films grown on single-crystal GaAs substrates were evaluated using reflection electron diffraction (RED) and SEM techniques, and electrical properties of several of the films were measured. The undoped n-type films that were grown were found to be epitaxial (i.e., single crystal) on two different orientations of single-crystal GaAs, with measured carrier concentrations in the 10^{16} cm^{-3} range and electron mobilities (measured by the van der Pauw method) up to ~2000 cm^2/V-sec at room temperature.

The effort expended on this task increased greatly during the second quarter. Characterization of InP film properties now constitutes a large portion of the total program activity. Analysis by a variety of techniques provides not only useful feedback for the development of the CVD process but also assistance in the selection of substrates for use in device fabrication. Electrical evaluation of film properties and contact properties establishes the suitability of doping levels and contact technology. Interactions of the low-cost substrates and the grown films are examined carefully. Preferred orientation tendencies in the films, grain size and shape in the films (including any dependence upon distance from the film-substrate interface), and film surface topography are all good indicators of the influence of the substrate on the properties of the film.

Much of the work to date in this task has involved application of routine measurement techniques to the characterization of single-crystal and polycrystalline InP in support of Tasks A, B, and C. Measurements of electrical properties by the van der Pauw technique, of surface physical properties by scanning electron microscopy, and of structural properties by x-ray diffraction analysis have provided the primary indicators of film quality to direct the growth experiments. The latter two techniques are quite standard and are employed in that way.

For electrical measurements the major deviation from standard practice has been in the area of contact formation. While it has been standard practice to alloy small spheres of In into experimental samples to obtain ohmic contact, this procedure has generally not been successful for p-type InP. As a result, the Au-Zn-Au contact technology developed under the subcontract to Stanford (Task E) has been used for these samples. It has proven to be more than adquate, although less convenient than the alloyed-sphere method. In cases where there is doubt over the conductivity type of a layer to be evaluated a voltage breakdown technique is used to determine the type. This technique is based on observing the rectifying behavior of a pressure-type "Schottky barrier". Ohmic contact is first formed by locally "altering" the surface of the sample with a Tesla coil and then touching a mechanical contact probe to the altered area. This technique has proved to be valuable for screening samples for conductivity type.

Since p-type films have now become available as a result of the work on Task A some preliminary device structures have been constructed, both to measure the performance of the devices themselves and to provide models for experimental samples to be fabricated later in the program for use in determining minority carrier diffusion length and grain size.

The first such samples used were p-type films of InP deposited on semi-insulating GaAs single-crystal substrates. One was Zn-doped to produce a measured hole concentration of 8.2×10^{16} cm^{-3}, with a thickness of 2.3 μm. The other was grown to a thickness of 1.1 μm and was Zn-doped to produce a measured hole concentration of 2.5×10^{16} cm^{-3}.

Broad ohmic contact grids (50-mil lines on 100-mil centers) of Au-Zn-Au were deposited on the InP film surface and alloyed. Schottky barriers of 50Å-thick Au 25 mils square were then deposited in the centers of the square contact grid openings, and a 10-mil-square bonding pad of Au was deposited on one corner of each Schottky barrier. The devices were then tested at a probe station to obtain the I-V characteristics.

The ohmic contact metallization on these samples was apparently much thinner than originally intended, and as a result the contacts alloyed deeply into the surface, leaving only a thin resistive contact layer. However, in some regions of the metallization the conductivity was high enough to permit reasonable Schottky-barrier behavior to be observed. The forward resistances of the devices were generally quite high - the order of 2000 ohms - but some of the better devices were nonetheless exposed to simulated AMO illumination (~135 mw/cm^2) to determine their photoresponses.

The best of the devices so tested (see Figure 2-15) showed a short-circuit current density of 12.5 mA/cm^2. This relatively high value is surprising in view of the disorder expected to exist in the lattice of the InP so close to the InP-GaAs interface. These results are encouraging to the further exploration of Schottky-barrier devices on InP films, possibly using the MIS configuration. Additional work will be done in the coming quarter.

Other p-type InP films have become available for device fabrication. These include epitaxial p layers on p-type InP, $n/p/p^+$ structures on InP, $p/n/n^+$ structures on InP, and n/p^+ structures on InP. In the cases of the $p/n/n^+$ and $n/p/p^+$ structures the top epitaxial layer was chosen to be the order of 1 μm thick; the bottom layer is the substrate in these two cases.

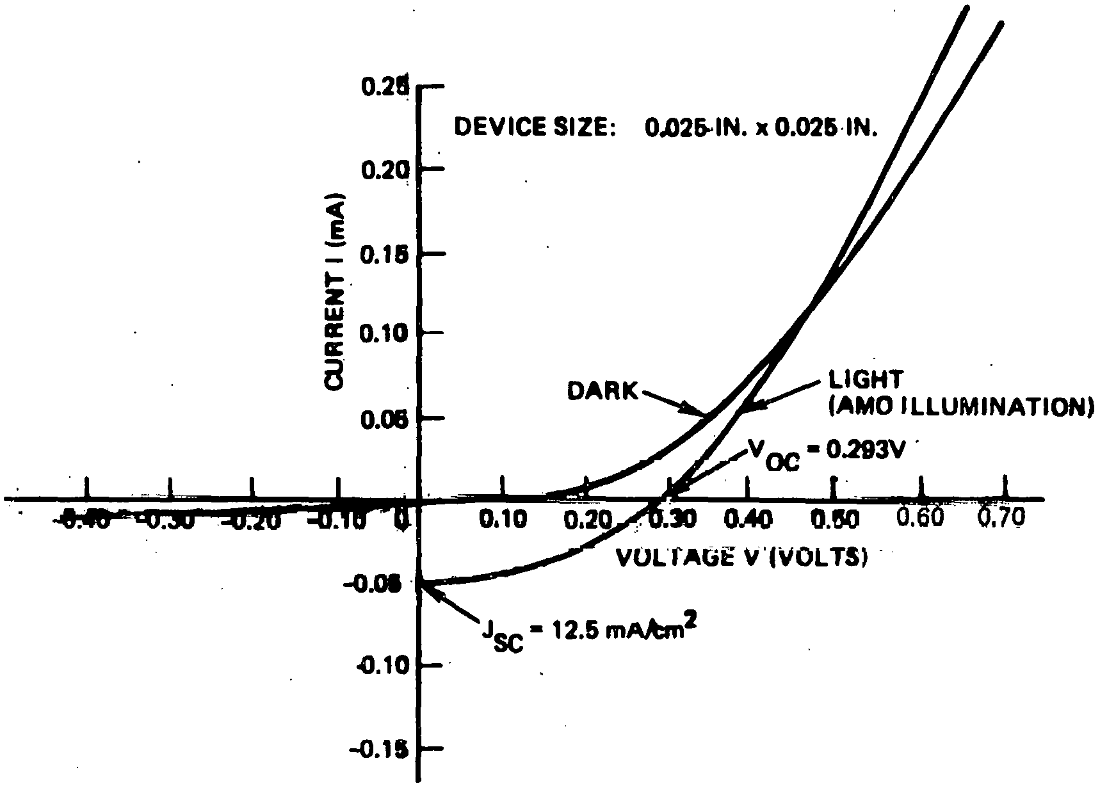


Figure 2-15. Dark and Illuminated I-V Characteristics of 50Å Au Schottky-barrier Diode in Epitaxial InP Film Grown on Single-crystal Semi-insulating GaAs Substrate.

Schottky barriers were formed by depositing Au layers ~50Å thick on the p/p$^+$ samples, and Au-Zn-Au contacts were applied to the back of the sample. The devices so fabricated showed anomalously high forward voltages of greater than 1 V at 1 mA. When the samples were luminated with ~135 mw/cm^2 of AMO illumination the light I-V characteristics showed an anomalous "dip" (see Figure 2-16) in the fourth quadrant. The effect of this inflection is to reduce the short-circuit current from the light induced values observed at negative biases by a factor of about two. The fill factor is reduced to less than 0.25, as a result.

Similar effects have been seen for devices in the n/p/p$^+$ structures fabricated at the same time, so the possibility of a processing-induced problem is suggested. It is postulated that the contact to the p$^+$ InP is rectifying and that, in effect, two barriers exist in series. Such a model might account for the I-V characteristics seen in Figure 2-16.

Most of the junction structures grown to date have shown excess leakage currents, even for devices of area less than 0.1 cm^2. Further work will be necessary to determine the cause of this leakage and to correct the problems.

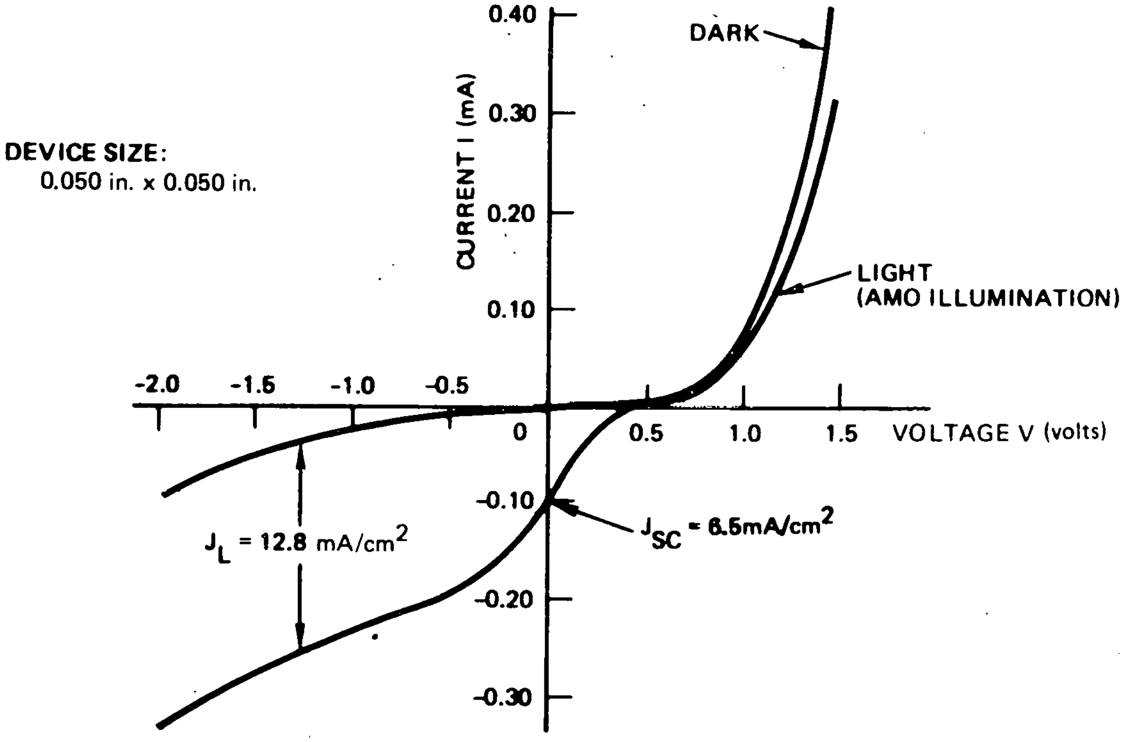


Figure 2-16. Dark and Illuminated I-V Characteristics of 50Å Au Schottky-barrier Diode in 1 μm Epitaxial InP Film Grown on P-type Single-crystal InP Substrate.

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

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

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

The work of this task is being carried out by personnel of the Stanford University Department of Materials Science and Engineering, under the direction of Prof. Richard H. Bube as Principal Investigator, on a subcontract from Rockwell; Dr. A. L. Fahrenbruch is principal research associate on this task at Stanford. The technical objective of the subcontract work is the formation of heterojunction device structures by deposition of films of other semiconductors on the InP films prepared at Rockwell, and the evaluation of the photovoltaic properties of the resulting composites.

The work in the first quarter was concerned primarily with the characterization of bulk single-crystal InP and with the formation and properties of electrical contacts to this material. These investigations provided background information and working experience for application to the single-crystal and polycrystalline films of InP being prepared at Rockwell by the MO-CVD technique. Ohmic contacts having low contact resistance were successfully made during the first quarter; ohmic contacts of Au-Zn-Au were produced on p-type InP by two different deposition methods. Contact resistivities as low as ~0.1 ohm-cm^2 (after annealing in H_2 at 475°C) were obtained by vacuum deposition methods and <1 ohm-cm^2 (after annealing in H_2 at 350°C) by an electrodeposition process.

The work of this task in the second quarter continued the development of low-resistance electrical contacts to p-type InP in the doping range 10^{15}–10^{18} cm^{-3} by vacuum deposition and electrodeposition, and included an analysis of transport in single crystals of n-type and p-type InP and in CVD films of n-type InP as a function of temperature, via the Hall effect. The study of transport properties of undoped n-type CVD films of InP indicated that lattice scattering dominates the low temperature behavior of these films, with appreciably higher mobility observed in films grown on (100) GaAs than in films grown on (111A) GaAs surfaces. Photoconductivity measurements on the InP films indicated a photo-induced increase in both the electron concentration and the electron mobility over the entire temperature range between 77°K and room temperature. Spectral response measurements gave values of 1.34 eV and 1.43 eV for the bandgap of these InP films at 300°K and 77°K, respectively.

During the third quarter of work on this task extensive characterization was carried out on the nature of electrical transport in (1) seven n-type InP films, prepared by MO-CVD at Rockwell on semi-insulating GaAs:Cr substrates; (2) six n-type InP films, prepared by MO-CVD at Rockwell on semi-insulating InP:Fe substrates; and (3) five p-type InP films doped with Zn prepared by MO-CVD at Rockwell on semi-insulating GaAs:Cr substrates. In addition, the first experimental photovoltaic n-CdS/p-InP all-film cell utilizing InP grown by MO-CVD was constructed and evaluated.

2.5.1 Properties of Undoped N-type InP Films on GaAs:Cr Substrates

Seven samples of undoped n-type InP films deposited by MO-CVD on insulating GaAs:Cr substrates at Rockwell were examined by Hall-effect measurements as a function of temperature at Stanford. Results of these measurements are summarized in Table 2-6. Figure 2-17a, b, and c show the temperature dependence of conductivity, electron concentration, and electron mobility, respectively, for these seven samples.

A comparison of the properties of films deposited on (100)GaAs substrates with those deposited simultaneously on (111)GaAs shows that in each case the mobility of the InP film is greater on the (100)GaAs substrate.

The film listed first in the table - that grown on (100)GaAs in experiment 26 - exhibited the highest carrier mobility of the undoped n-type films grown on GaAs substrates to date, throughout the temperature range from 77°K to room temperature. Based on the assumption that this film represents a case in which carrier mobility is totally controlled by scattering processes within the bulk material, that is, is not influenced by any kind of grain boundary effects, it is possible to describe in a useful way the temperature dependence of electron mobility of all the samples measured. Thus, if the mobility as a function of temperature for the reference film is called $\mu_o(T)$, then for all samples of this type it is possible to describe the mobility $\mu(T)$ as follows:

$$\mu(T) = \mu_o(T) \exp(-E_\mu/kT), \qquad \text{for } T > T_c, \tag{1}$$

and

$$\mu(T) = \mu_o(T) R_\mu, \qquad \text{for } T < T_c. \tag{2}$$

The observed value for T_c for this group of samples is about 200°K.

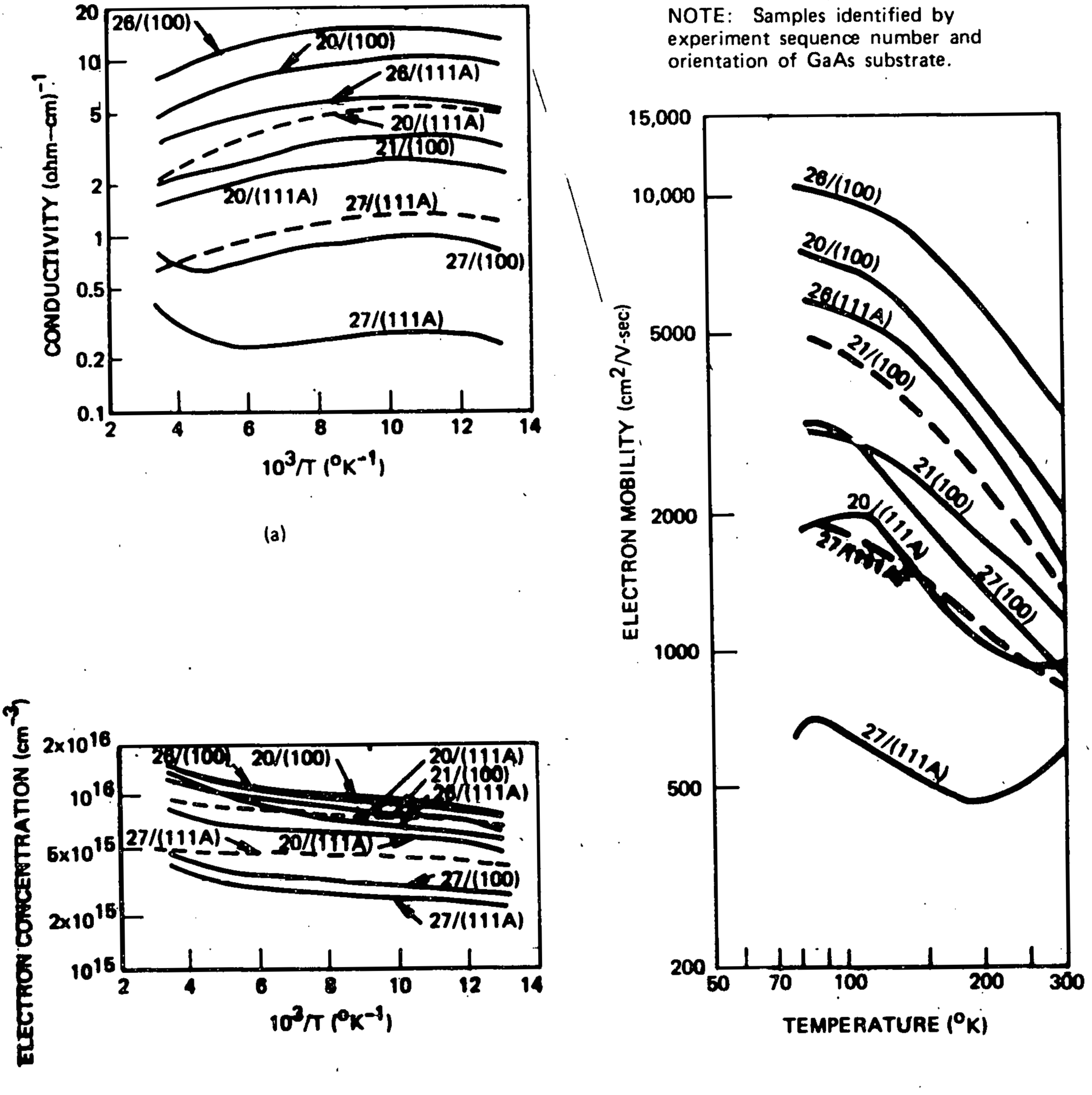
Calculated values of E_μ and R_μ for the samples other than the reference sample are also given in Table 2-6. It is evident that the magnitude of E_μ generally increases with decreasing electron density, and that the magnitude of R_μ generally decreases with decreasing electron density. The parameter E_μ can be interpreted to represent the height of intergrain potential barriers within the layers that impede the normal mobility

Table 2-6. Electrical Properties of Undoped N-type InP Films Grown by MO-CVD on Single-crystal GaAs:Cr Substrates

Experiment Sequence Number	Substrate	Depos. Temp. (°C)	Film Thickness (μm)	Carrier Concentration (cm^{-3})		Carrier Mobility (cm^2/V-sec)		Barrier Height E_μ* (eV)	Mobility Ratio R_μ†	In Contact Resistivity (ohm-cm^2)
				77°K	296°K	77°K	296°K			
26	(100)GaAs	625	2.77	$8.2X10^{15}$	$1.6X10^{16}$	10,500	3100	0.00	1.00	0.6 – 4.0
26	(111A)GaAs	625	2.77	$5.7X10^{15}$	$1.4X10^{16}$	6040	1480	0.00	0.53	0.6 – 5.0
20	(100)GaAs	620	2.40	$7.7X10^{15}$	$1.6X10^{16}$	7730	1880	0.00	0.64	0.7 - 3.5
20	(111A)GaAs	620	2.40	$4.8X10^{15}$	$8.7X10^{15}$	3120	1120	0.0077	0.30	1.2 – 9.5
21	(100)GaAs	626	2.8	$6.3X10^{15}$	$1.3X10^{16}$	3280	968	0.016	0.28	1.3 – 5.6
27	(100)GaAs	649	2.6	$2.7X10^{15}$	$4.9X10^{15}$	1900	1050	0.035	0.19	4.2 – 15
27	(111A)GaAs	649	2.2	$2.4X10^{15}$	$4.2X10^{15}$	657	611	0.049	0.066	14 – 36

*Assuming that carrier mobility varies at higher temperatures ($T > T_c$) as $\mu = \mu_0 \exp(-E_\mu/kT)$ where μ_0 is defined as the measured μ (T) for the film grown on (100)GaAs in experiment 26 (first row of table).

†Assuming that the mobility varies at lower temperatures ($T < T_c$) as $\mu = R_\mu \mu_0$, where R_μ is a temperature-independent parameter (see text) and μ_0 is as defined above.



(a)

(b)

(c)

Figure 2-17. Temperature Dependence of (a) Electrical Conductivity, (b) Electron Concentration, and (c) Electron Mobility for Undoped N-type InP Films Deposited by MO-CVD on GaAs:Cr Substrates. (Dashed curves represent measured properties under illumination for two of the samples; see text.)

of charge carriers above a certain temperature (T_c). The parameter R_μ can be interpreted to represent the temperature-independent mobility behavior in the lower temperature range ($T<T_c$), where tunneling through these intergrain potential barriers dominates.

The mobility ratio $\mu(T)/\mu_0(T)$ for the six samples of Table 2-6 (referred to the mobility of the film on (100)GaAs in experiment 26) is plotted throughout the temperature range in Figure 2-18. The values listed in Table 2-6 for E_μ for these samples are shown, as derived from the slopes of the curves in the high temperature region ($T>\sim200^\circ K$). When the values of R_μ, as listed in Table 2-6, are plotted as a function of the low-temperature (77°K) electron concentration n for the seven samples the result is as shown in Figure 2-19. It is seen that the value of R_μ varies approximately as n^2. It would be expected that the effects of intergrain barriers on electron transport would be greatest in films with the lowest electron concentrations, and hence the largest depletion layer widths at such intergrain boundaries. Both barrier height E_μ and tunneling transmission probability R_μ are seen to take on extreme values for the films of experiment 27 - those with the smallest electron concentrations.

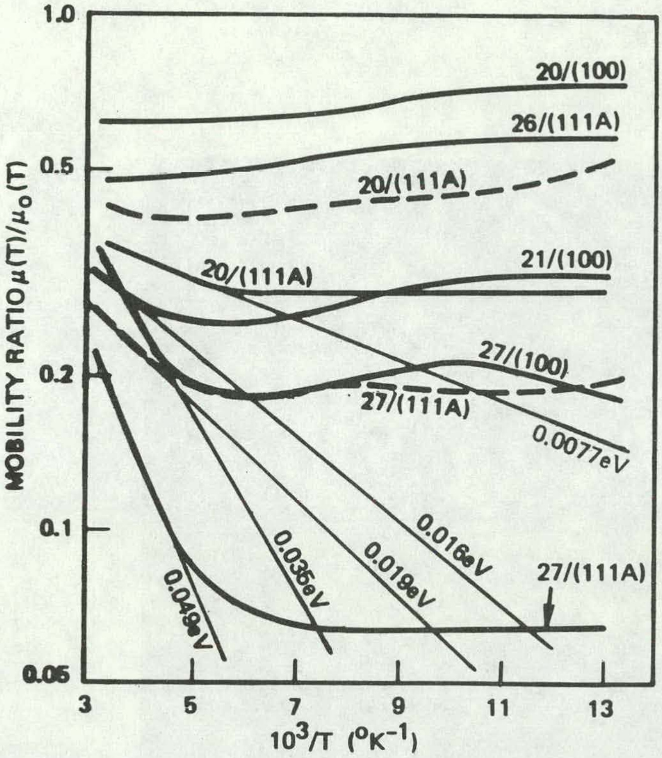
One way of increasing the electron concentration and of affecting intergrain barrier heights through trapping of carriers is photoexcitation of the material. It can be seen in Figure 2-17 that photoexcitation increases both the electron concentration and the electron mobility for two of these films. Figure 2-18 shows that photoexcitation reduces the value of E_μ for film 20/(111A) from 0.0077 eV to zero, and increases the value of R_μ for this film from 0.30 to 0.45. Similarly, for film 27/(111A) photoexcitation reduces E_μ from 0.049 eV to 0.019 eV, and increases R_μ from 0.066 to 0.19.

Such behavior would be expected for a material in which the properties are controlled by intergrain boundaries according to the above interpretation. There is a possibility that low-angle grain boundaries exist in these films on GaAs substrates, and thus might be a factor in the effects discussed above. Some evidence for such defects is seen in the optical photomicrographs shown in Figure 2-20. Both films shown were deposited on (111A)-oriented GaAs:Cr substrates, one at 620°C and one at 649°C; the film grown at 620°C (experiment 20) was deposited with the usual "pre-PH_3" treatment (see Task A discussion), while the sample prepared at 649°C did not have the pre-PH_3 treatment prior to growth. The extent to which these differences might affect the observed properties of these films is not known at this time.

2.5.2 Properties of Undoped N-type InP Films on InP:Fe Substrates

Six samples of undoped n-type InP films deposited by MO-CVD on semi-insulating InP:Fe single-crystal substrates at Rockwell were examined by Hall-effect measurements as a function of temperature at Stanford during this report period. Results of these measurements are summarized in Table 2-7. Figures 2-21a, b, and c show the temperature dependence of the electrical conductivity, the electron concentration, and the electron mobility, respectively, for these six samples.

InP films grown in InP substrates show more uniform dependence of properties upon changes in growth conditions than do the InP films on GaAs substrates that have been evaluated in detail to date. The highest mobility found for any of the MO-CVD InP films is that for the film of experiment 53: 3540 cm^2/V-sec at 296°K, and 16,600 cm^2/V-sec at 77°K. The mobility of this film varies approximately as T^{-2} between 200 and 300°K, as indicated in Figure 2-21c.



NOTE: Samples identified by experiment sequence number and orientation of GaAs substrate

Figure 2-18. Mobility Ratio $\mu(T)/\mu_o(T)$ for N-type Undoped InP Films Deposited by MO-CVD on GaAs:Cr Substrates, Referred to Mobility $\mu_o(T)$ of Film on (100)GaAs in Experiment 26. (Dashed curves represent data for two of the samples under illumination; see text.)

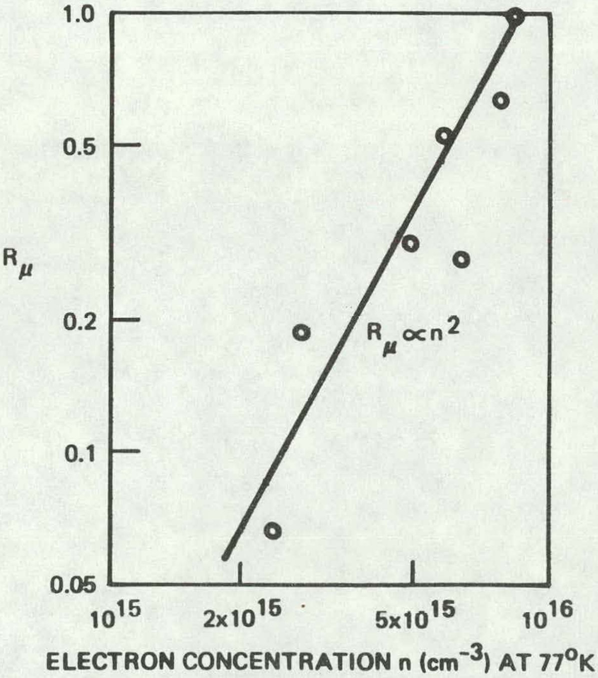


Figure 2-19. Value of Low-temperature Mobility Ratio R_μ as Function of Electron Concentration at 77°K for N-type Undoped InP Films Deposited by MO-CVD on GaAs:Cr Substrates

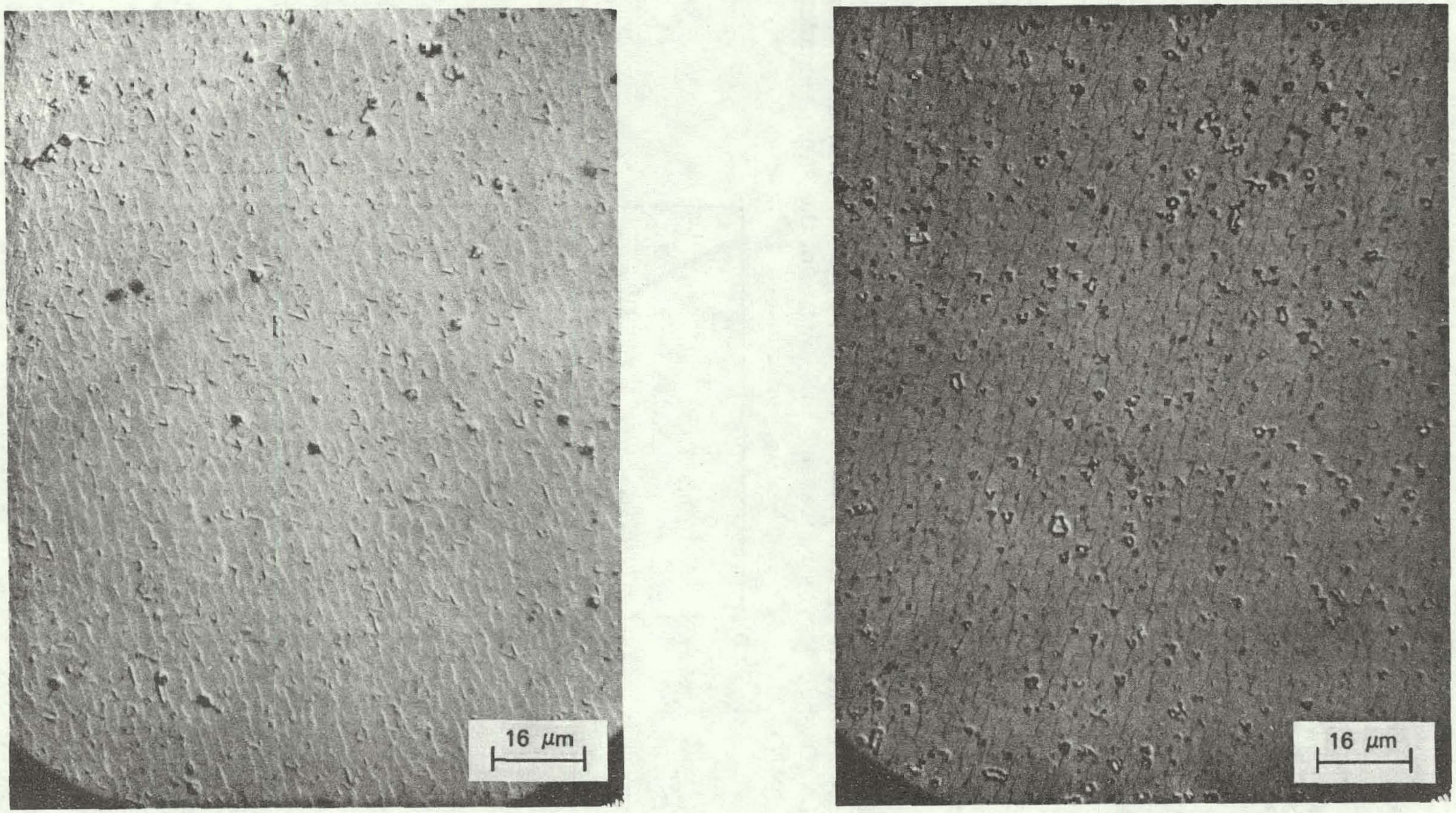


Figure 2-20. Optical Photomicrographs of Surfaces of Two Undoped N-type InP Films Deposited by MO-CVD on GaAs:Cr Substrates. (a) Film Deposited at 620°C on (111A)GaAs in Experiment 20, with Pre-PH_3 Treatment; (b) Film Deposited at 649°C on (111A)GaAs in Experiment 27, without Pre-PH_3 Treatment. (See text.)

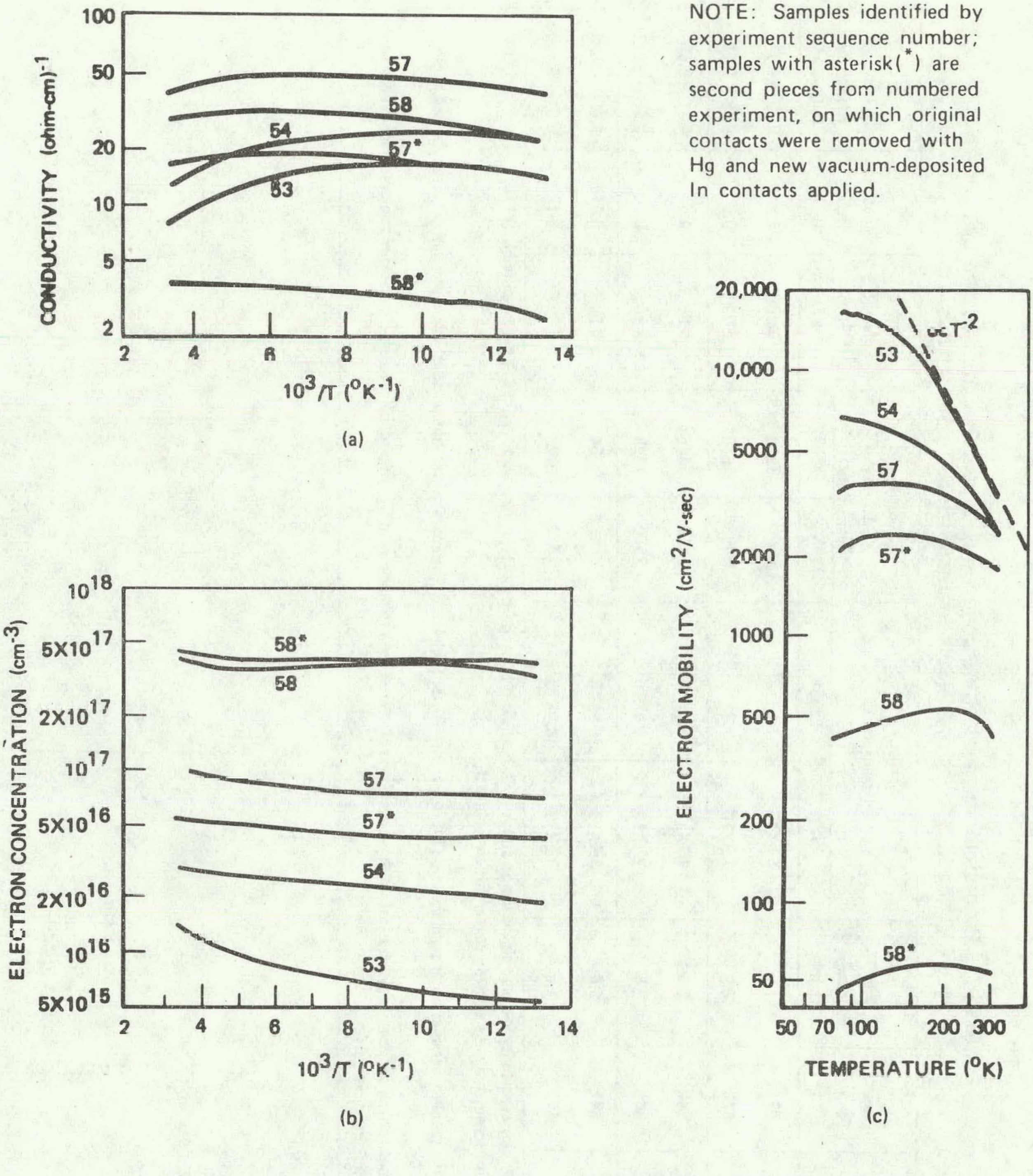
Table 2-7. Electrical Properties of Undoped N-type InP Films Grown by MO-CVD on Single-crystal (100)-oriented InP:Fe Substrates

Experiment Sequence Number	Depos. Temp. (^oC)	Film Thickness (μm)	Carrier Concentration (cm^{-3})		Carrier Mobility ($cm^2/V\text{-}sec$)		Barrier Height E_μ * (eV)	Mobility Ratio R_μ †	In Contact Resistivity (ohm-cm^2)
			77^oK	296^oK	77^oK	296^oK			
53	571	3.7	$5.5X10^{15}$	$1.4X10^{16}$	16,600	3540	0.00	0.8	0.26 – 1.7
54	620	2.9	$1.9X10^{16}$	$3.0X10^{16}$	6960	2660	0.00	0.6	0.08 – 0.98
57**	646	2.5	$4.2X10^{16}$	$5.4X10^{16}$	2150	1840	0.00	0.5	0.11 – 0.92
57	646	2.5	$7.0X10^{16}$	$1.0X10^{17}$	3560	2490	0.00	0.7	0.06 – 0.51
58**	682	1.8	$3.6X10^{17}$	$4.5X10^{17}$	45	54	0.00	0.018	0.006 – 0.26
58	682	1.8	$3.2X10^{17}$	$4.2X10^{17}$	417	423	0.00	0.15	0.01 – 0.89

*Assuming that carrier mobility varies at higher temperatures ($T > T_c$) as $\mu = \mu_0 \exp(-E_\mu/kT)$, where μ_0 is defined as the measured μ (T) for single-crystal InP having the same electron concentration (see text).

†Assuming carrier mobility varies at lower temperatures ($T < T_c$) as $\mu = R_\mu \mu_0$, where R_μ is a temperature-independent parameter and μ_0 is as defined above.

**Contacts applied for van der Pauw measurements on these samples at Rockwell were removed with Hg, after which vacuum-deposited In contacts were applied for six-terminal Hall measurements.



NOTE: Samples identified by experiment sequence number; samples with asterisk(*) are second pieces from numbered experiment, on which original contacts were removed with Hg and new vacuum-deposited In contacts applied.

Figure 2-21. Temperature Dependence of (a) Electrical Conductivity, (b) Electron Concentration, and (c) Electron Mobility for Undoped N-type InP Films Deposited by MO-CVD on Single-crystal (100)-oriented InP:Fe Substrates.

For all six films grown on InP single-crystal substrates, the variation of the mobility with temperature is identical to that reported by Glicksman and Weiser (Ref 3) for single crystals with comparable electron concentration, except that the absolute magnitude of the mobility in the films is slightly smaller. Equation (2) can be used to describe the mobility in these InP films when the mobility for one of the films is compared with the mobility of a single crystal with the same electron concentration. The results of such a comparison are included in Table 2-7. At least for electron concentrations at 296°K between 1.4×10^{16} cm^{-3} and 1.0×10^{17} cm^{-3} the scale factor R_μ is approximately independent of both temperature and electron concentration.

The close correlation between the mobility of these films and the mobility of single crystal InP indicates that severe grain boundary effects are absent. Indication of much improved structural quality in the films grown on InP substrates relative to that of the films grown on GaAs substrates is seen in the optical photomicrograph of the surface of a film on InP, shown in Figure 2-22. Comparison of this with the photomicrographs of Figure 2-20 shows a significantly better surface structure in the film on (100)-oriented InP, which was deposited at 571°C. It should be noted, however, that other factors than just the nature of the substrate may well be involved in producing differences in the structural perfection of the films illustrated in the two figures.

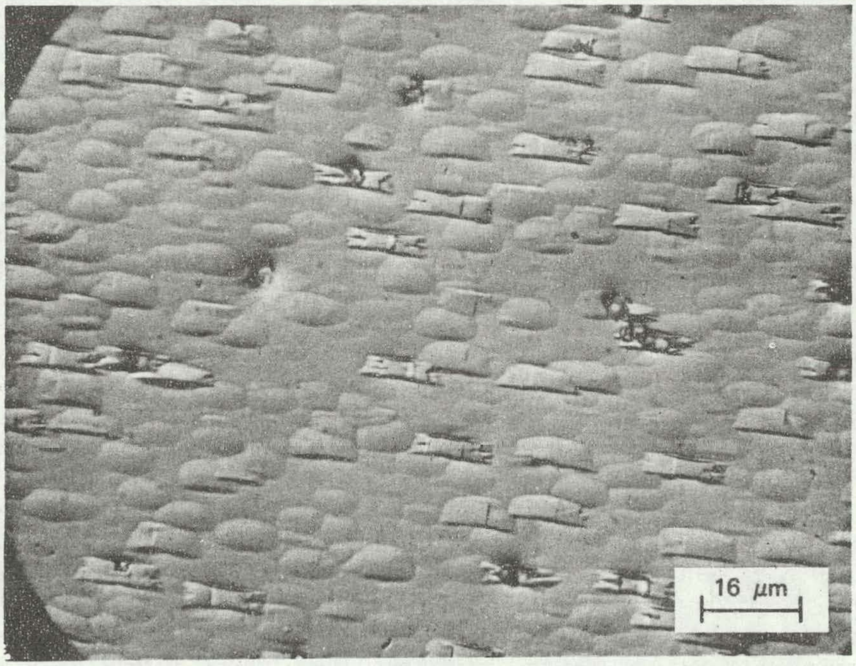


Figure 2-22. Optical Photomicrograph of Undoped N-type InP Film Deposited at 571°C by MO-CVD on InP:Fe Single-crystal Substrate, with Pre-PH_3 Treatment. (See text.)

2.5.3 General Observations on Undoped N-type InP Films

Consideration of the data in Tables 2-6 and 2-7 with regard to variation of electron concentration and electron mobility with various deposition parameters indicates several correlations of interest. It must be noted, however, that these films were not intentionally doped during growth; the measured n-type conductivity and the associated net electron concentration result from effective donor centers that have not yet been identified, nor has it been established if these centers are chemical impurities or physical imperfections.

1. For either InP or GaAs substrates the measured electron mobility increases with increasing InP film thickness. This effect is commonly seen in expitaxial semiconductor films, especially in heteroepitaxial systems, and is attributed to the reduction in interface-related defects that occurs in the film at greater distances from the growth interface.

2. For either InP or GaAs substrates, the measured electron mobility appears to decrease, in general, with increasing film deposition temperature. The data are the most consistent for the layers on InP substrates and suggest that better film structure, correlated with higher electron mobilities, may result for film growth at the lower temperatures.

3. The mobility in films on InP substrates decreases with increasing electron concentration, whereas the mobility in films on GaAs substrates increases with increasing electron concentration. The actual data are shown in Figure 2-23. The fact that the electron concentration values in the films on GaAs substrates have almost no overlap with the values in films on InP substrates makes it difficult to tell whether the major effect is a substrate effect or simply an electron-concentration effect. However, the following interpretation appears to fit the observed facts. When the epitaxial growth is good (films on InP substrates), potential barriers to electron transport are absent and mobility is limited by lattice and charged impurity scattering effects; thus, the highest mobilities are obtained for the lowest electron concentrations. When the epitaxial growth is not so good (films on GaAs substrates), potential barriers to electron transport exist which limit the electron mobility; the height and width of these barriers, however, depends on the electron concentration present, and an increase in electron concentration produces a decrease in height and width of the barriers and hence an increase in the electron mobility.

4. The measured electron concentration averaged over the total film thickness in films on InP substrates decreases with increasing film thickness, whereas the measured electron concentration in films on GaAs substrates increases with increasing film thickness. The variations in electron concentration with thickness are so large (four times greater concentration for an increase in thickness by 25 percent for films on GaAs, and forty times smaller concentration for an increase in thickness by factor of two for films on InP) that it does not appear that the thickness itself can be the primary parameter. It is more likely that the deposition temperature is the primary parameter in this observed variation; in the case of the films on InP substrates the measured electron concentration goes down as the deposition temperature is reduced, while in the films on GaAs the observed electron concentration

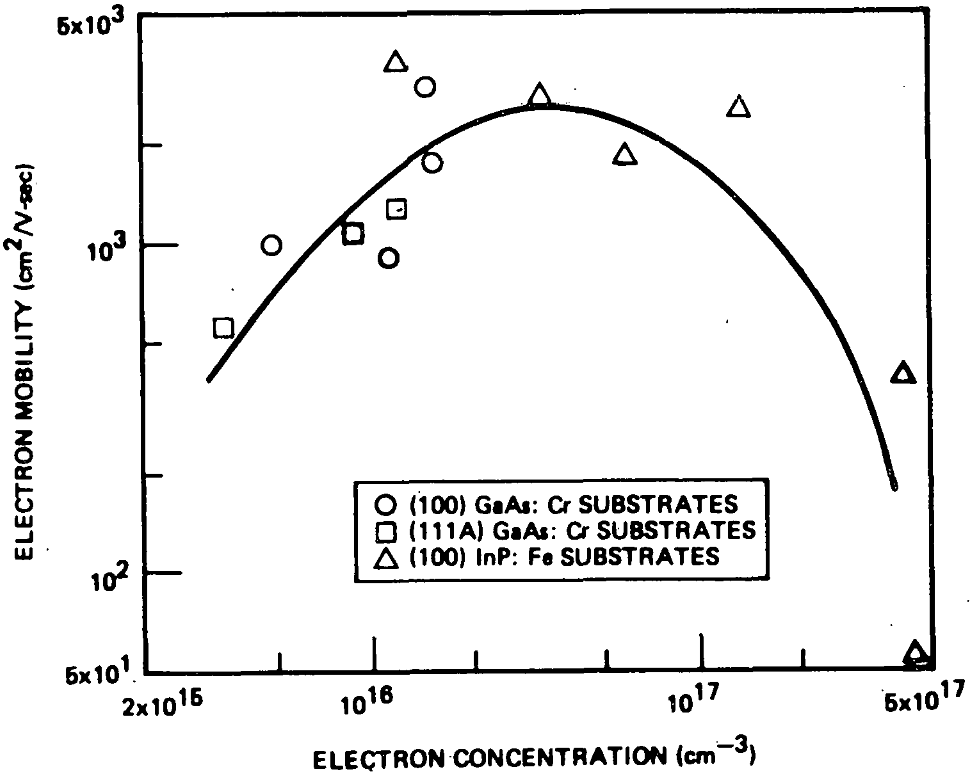


Figure 2-23. Measured Electron Mobility as Function of Electron Concentration for Undoped N-type InP Films Deposited by MO-CVD on Single-crystal Substrates of GaAs:Cr and InP:Fe, from Tables 2-6 and 2-7.

appears to increase with decreasing deposition temperature. The situation here is very complex, however. It is possible that the interfacial defects have associated with them acceptor centers, which occur in significant concentrations at the InP-GaAs interface (i.e., in thin films on GaAs) and only relatively sparsely at the InP-InP interface, and further, that the predominant electrically active donor centers occurring in undoped InP films are related to chemical impurities that may or may not be uniformly distributed through the thickness of the InP film. Since there has also been some evidence of possible out-diffusion or chemical reaction at the intersection of GaAs substrates and the SiC-coated graphite susceptor used as the sample pedestal in these investigations, no further speculation about the significance of this observed correlation will be made until additional data are obtained.

5. The last columns in Tables 2-6 and 2-7 list the measured ranges of the In contact resistivity on these various undoped n-type InP films. A plot of these ranges is given in Figure 2-24. It is evident that there is a close connection between the contact resistivity produced by In contacts and the electron concentration n in the InP film, the contact resistivity varying approximately as $n^{-1.3}$.

2.5.4 Properties of Zn-doped P-type InP Films on GaAs:Cr Substrates

Five samples of Zn-doped p-type InP films deposited by MO-CVD on semi-insulating GaAs:Cr substrates at Rockwell were examined at Stanford by Hall-effect measurements as a function of temperature; results of these measurements are given in Table 2-8. Figure 2-25a, b, and c show the temperature dependence of the electrical conductivity, the electron concentration, and the electron mobility, respectively.

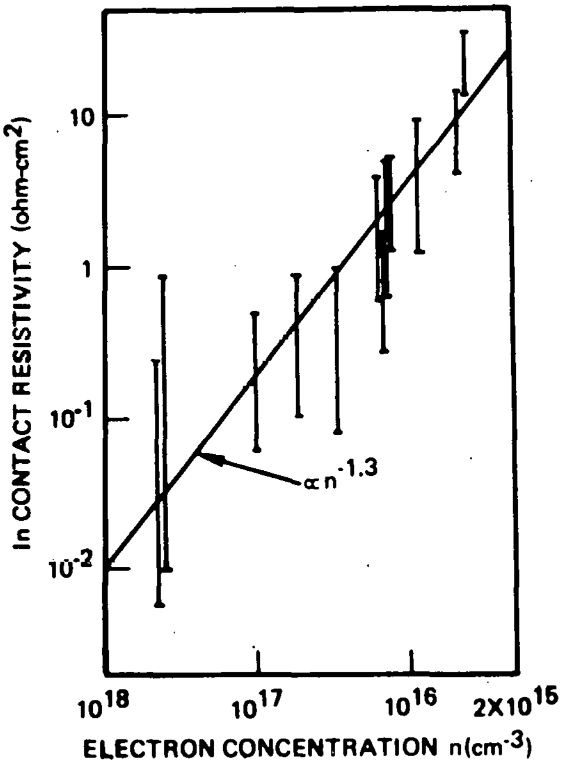


Figure 2-24. Dependence of In Contact Resistivity on Electron Concentration in Undoped N-type InP Films Deposited by MO-CVD on GaAs:Cr and InP:Fe Substrates. (See Tables 2-6 and 2-7.)

Just as for n-type InP films, it appears that for the p-type InP films higher mobilities are found in films on (100)GaAs substrates than on (111A)GaAs substrates. If the film grown on (111A)GaAs in experiment 87 (Table 2-8) is excepted, it appears that increasing hole mobility accompanies decreasing hole concentration over the relatively high values of hole concentration found in these films. Sample 87/(111A) exhibits anomalous behavior in terms of the results of the earlier van der Pauw measurements at Rockwell and six-terminal Hall-effect measurements at Stanford, a factor of 25 decrease in the hole concentration appearing between these two measurements. No explanation for this difference has yet been found.

The mobility plots in Figure 2-25c indicate that there is strong impurity scattering present in the p-type samples (excepting 87/(111A)), as was found characteristic of the undoped n-type films on InP:Fe substrates. The temperature dependence of mobility in sample 87/(111A), on the other hand, is more like that observed in some of the undoped n-type films on GaAs substrates (cf Figure 2-17c), all of which had lower electron concentrations than did those on InP substrates.

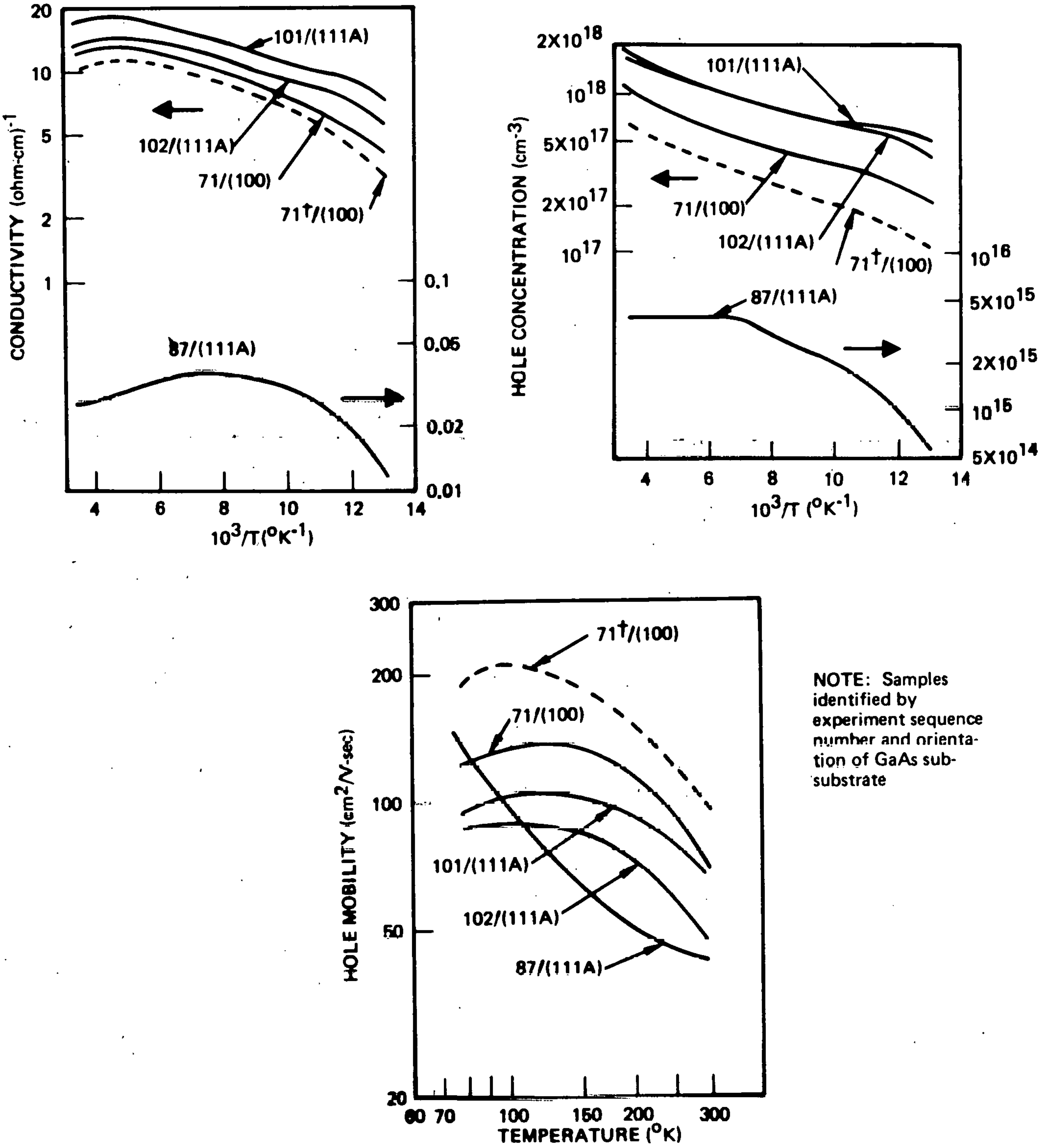
If the ratios of mobility of sample 87/(111A) to that of the highest mobility sample of the group (71/(100)) are obtained at each temperature, as was done for the

Table 2-8. Electrical Properties of Zn-doped P-type InP Films Grown by MO-CVD on Single-crystal GaAs:Cr Substrates

Experiment Sequence Number	Substrate	Deposition Temp. (°C)	Film Thickness (μm)	Carrier Concentration (cm^{-3})		Carrier Mobility (cm^2/V-sec)		In Contact Resistivity (ohm-cm^2)
				77°K	296°K	77°K	296°K	
71	(100)GaAs	650	1.6	$2.1\text{X}10^{17}$	$1.1\text{X}10^{18}$ $(2.5\text{X}10^{18})$*	122	68 (41)*	0.15–0.45
71†	(100)GaAs	650	1.6	$1.0\text{X}10^{17}$	$6.6\text{X}10^{17}$	190	97	0.5–3.0†
87	(111A)GaAs	622	2.1	$5.5\text{X}10^{14}$	$3.9\text{X}10^{15}$ $(1.0\text{X}10^{17})$*	139	42 (60)*	30–91
101	(111A)GaAs	647	1.1	$4.8\text{X}10^{17}$	$1.6\text{X}10^{18}$ $(3.3\text{X}10^{18})$*	95	67 (33)*	0.24–0.29
102	(111A)GaAs	656	1.0	$3.9\text{X}10^{17}$	$1.9\text{X}10^{18}$ $(2.8\text{X}10^{18})$*	90	44 (24)*	0.25–0.57

*Values obtained by van der Pauw measurements at Rockwell.

†On this sample, the Au/Zn/Au contacts exhibited rectifying characteristics and a larger contact resistivity than the normal ohmic contacts.



NOTE: Samples identified by experiment sequence number and orientation of GaAs sub-substrate

Figure 2-25. Temperature Dependence of (a) Electrical Conductivity, (b) Hole Concentration, and (c) Hole Mobility for Zn-doped P-type InP Films Deposited by MO-CVD on GaAs:Cr Substrates. (Dashed curves are for sample with slightly non-ohmic contacts; see Table 2-8.)

undoped n-type samples on GaAs:Cr substrates (cf Figure 2-18), and plotted as a function of temperature the results shown in the upper curve of Figure 2-26 are obtained. (Although the mobility for sample $71^{\dagger}/(100)$ was higher than that of sample 71/(100) at each temperature, the fact that the contacts were slightly non-ohmic suggests that it not be used for this calculation.) Since impurity scattering dominates in sample 71/(100) but not in sample 87/(111A) at low temperatures the ratio is not constant in the low-temperature range, even though behavior like that described by Equation (1) is observed at higher temperatures.

As a further examination of this point the ratios of measured mobility for sample 87/(111A) to mobility of a p-type InP single crystal of hole concentration 3×10^{16} cm^{-3}, as reported by Glicksman and Weiser (Ref 3), are also plotted in Figure 2-26 (lower curve). It is interesting that this produces excellent agreement with the behavior predicted by both Equations (1) and (2) throughout the temperature range, with $E_{\mu} = 0.026$ eV and $R_{\mu} = 0.11$.

Two general observations are suggested by these results:

1. The behavior of the mobility as a function of carrier concentration is quite similar for both n- and p-type InP films. For small carrier concentrations the mobility is dominated by intergrain potential barriers, with barrier heights of a few hundredths of an electron-volt, whereas for large carrier concentrations the mobility is dominated by impurity scattering.

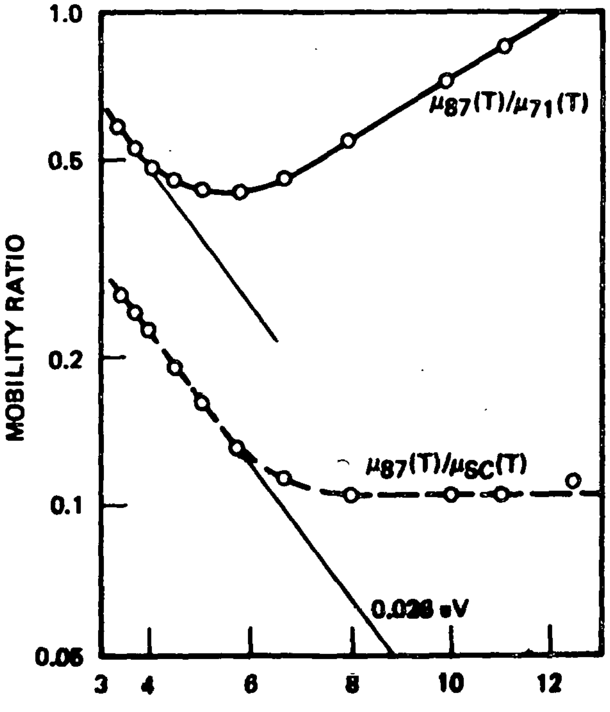


Figure 2-26. Ratio of Mobility for Zn-doped P-type MO-CVD InP Film of Sample 87/(111A) (on GaAs:Cr Substrate) to Mobility of (a) Similar Film of Sample 71/(100), and (b) Single Crystal of P-type InP of Hole Concentration 3×10^{16} cm^{-3}

2. The data on n- and p-type InP films suggest that the curve of Figure 2-23 illustrates a fairly universal behavior that depends primarily on the carrier concentration and only secondarily on the nature of the substrate. That is, p-type InP films with high hole concentration deposited on GaAs substrates behave similarly to n-type InP films with high electron concentration deposited on InP substrates, and p-type InP films with low hole concentration deposited on GaAs substrates behave similarly to n-type InP films with low electron concentration deposited on GaAs substrates.

2.5.5 All-thin-film Photovoltaic Heterojunction Solar Cell of CdS/InP

It is a major goal of this contract to prepare and evaluate heterojunction photovoltaic solar cells made with the InP films deposited by MO-CVD at Rockwell. Initial results with such structures were obtained during the quarter by the vacuum deposition of a film of n-type CdS onto a p-type Zn-doped MO-CVD InP layer that had been grown on a semi-insulating GaAs:Cr substrate (from experiment 73). The details of the cell components and measured properties are summarized in Table 2-9, as measured in natural sunlight (Palo Alto, CA) of 90 mw/cm^2 intensity.

A p-type InP layer on a semi-insulating substrate is clearly not an optimal arrangement for making an efficient solar cell because of the current collection and series resistance problems. In order to test the present films, however, before they are produced on more suitable substrates the simple geometry shown in Figure 2-27 was adopted. This consisted of a stripe of CdS about 1mm wide and 5mm long deposited centrally along a median of the approximately rectangular InP/GaAs sample, with a narrow (~0.1mm) In contact stripe deposited centrally along most of the length of the CdS. Parallel to the CdS stripe and separated from it by ~1.6mm (center-to-center) on either side were two deposited contacts of Au/Zn/Au, each about 0.6mm wide.

An illuminated I-V curve is shown in Figure 2-28. A good short-circuit current density of 14.2 mA/cm^2 was observed. This value is at least two-thirds of that reported for single-crystal InP solar cells, but because of a large reverse saturation current the open-circuit voltage was only 0.32V. The resulting solar efficiency was therefore a relatively low 2.3 percent, as indicated in Table 2-9.

Considering the far-from-optimized parameters involved in this first cell, these measured characteristics can be considered a successful demonstration of the utility of the MO-CVD method for the preparation of p-type InP layers for solar cell applications.

Table 2-9. Data for First n-CdS/p-InP Photovoltaic Cell Fabricated on Epitaxial InP Grown by MO-CVD Technique

p-InP Layer

Zn-doped InP deposited on (100)GaAs:Cr substrate (Rockwell experiment 73)

Growth temperature	645°C
Thickness	1.5μm
Resistivity	0.09 ohm-cm

p = 1.4×10^{18} cm^{-3}

μ_p = 51 cm^2/V-sec

n-CdS Layer

In-doped CdS deposited by vacuum evaporation (at Stanford)

Substrate temperature	300°C
CdS source temperature	840°C
Deposition time	14 min
Film thickness	2.2μm
Resistivity	0.9 ohm-cm

In contact evaporation source temperature 660°C

n-CdS/p-InP Cell Characteristics (illumination in sunlight at 90mw/cm^2)

V_{oc} = 0.32V

J_{sc} = 14.2mA/cm^2

Fill factor = 0.44

J_0 = 2×10^{-5}A/cm^2

A (diode eqn) = 3.9

R_{series} = 71 ohms

R_{shunt} = 1000 ohms

Active area = 0.059 cm^2

Solar power conversion efficiency = 2.3 percent

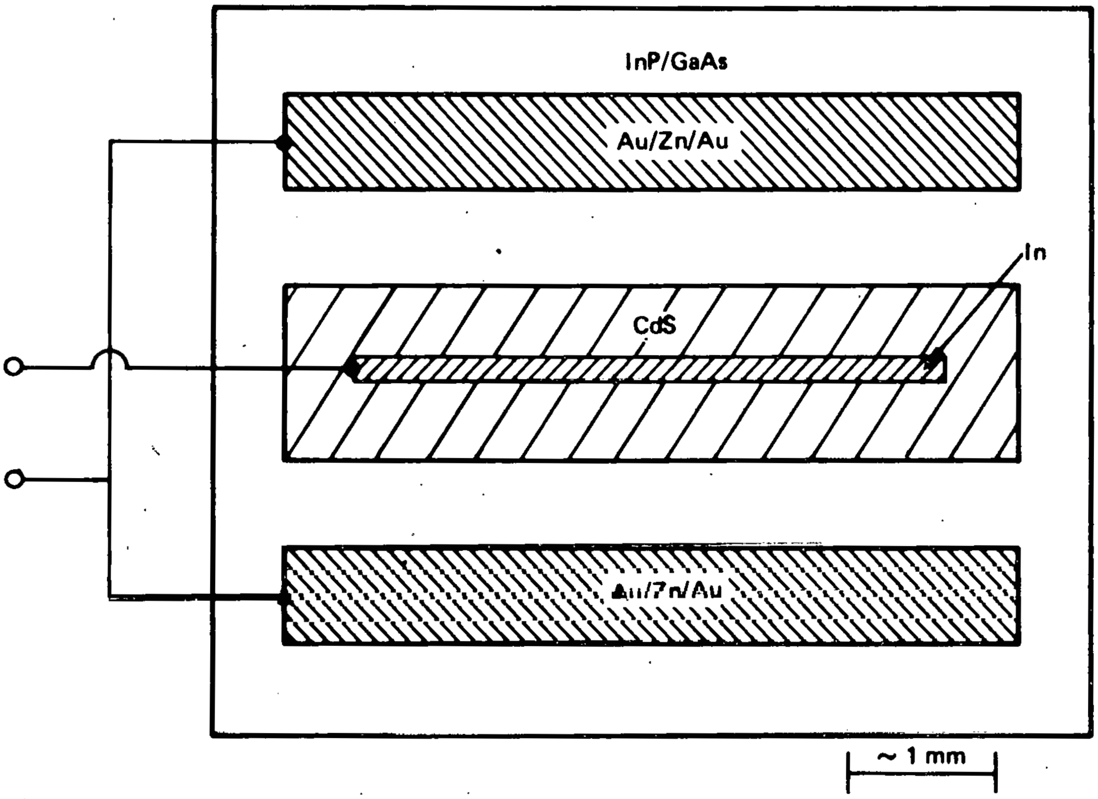


Figure 2-27. Geometry Used for n-CdS/p-InP All-thin-film Heterojunction Photovoltaic Cell

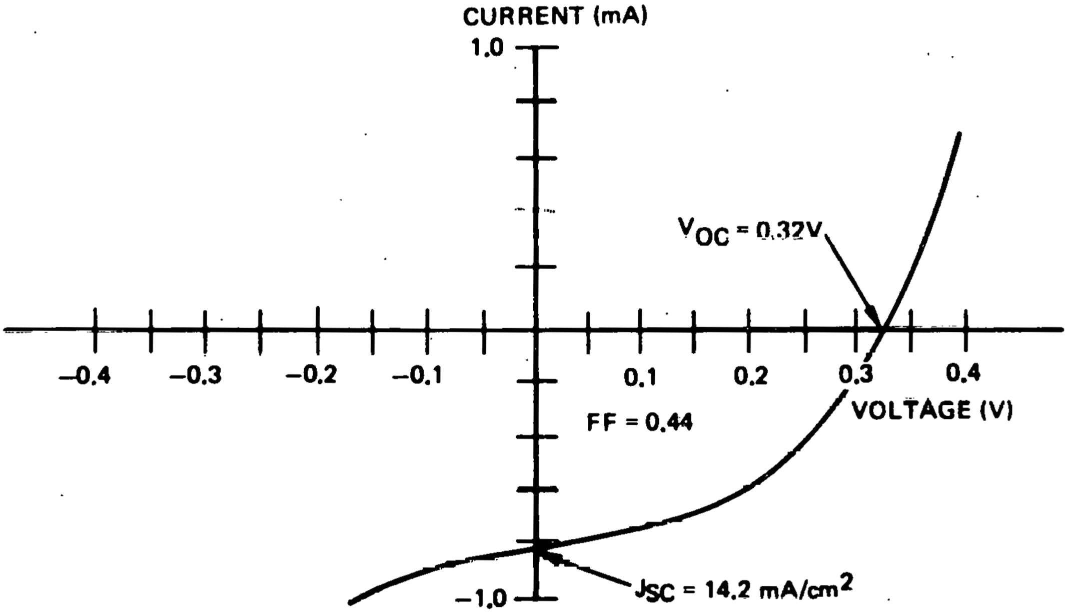


Figure 2-28. Measured I-V Characteristic for All-thin-film n-CdS/p-InP Heterojunction Photovoltaic Cell, under Natural Sunlight Illumination (90 mw/cm^2).

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

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

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

Some preliminary cost estimates for the materials used in a CdS/InP heterojunction solar cell were developed during the first quarter, and some permissible upper limits were identified for materials costs, film formation costs, and cell array fabrication costs for thin-film polycrystalline InP solar cells for the 1985 time period, based on the corresponding goals of the Low Cost Silicon Solar Array Project. Although a number of factors were neglected in these preliminary considerations, it appears that the heterojunction configuration proposed for fabrication by the MO-CVD technique has promise of achieving the economic as well as the technical goals of the national photovoltaic program if the problem of identifying a satisfactory substrate material that can be manufactured inexpensively can be solved.

Relatively little effort was expended on this task during the second quarter. However, a preliminary conceptual design for a CdS/InP heterojunction photovoltaic device to be fabricated by thin-film deposition techniques was developed. It consists of a Mo substrate ~15 mils (375 μm) thick* on which is deposited by the MO-CVD method a double layer of polycrystalline InP of ~5 μm total thickness. The bottom layer of p+ InP is ~1 μm thick and is heavily doped ($>5\times10^{18}cm^{-3}$) with Zn (or Cd) to facilitate ohmic contact between the Mo substrate and the p-type base region of the cell, which is ~4 μm-thick InP doped to $\sim5\times10^{17}$ cm^{-3} with Zn (or Cd) during CVD growth. A layer of n-type polycrystalline CdS ~5 μm thick is deposited (by vacuum deposition methods) on the p-type InP MO-CVD layer, to form the p-n heterojunction at the interface. A transparent conducting layer is deposited on the CdS layer to provide the front-surface (incident-light-side) contact. This generalized front contact layer may be in the form of a transparent continuous layer of indium tin oxide (ITO) or other similar material, or in the form of a deposited metal square-pattern contact grid, with a separate antireflection coating then deposited over the open grid contact.

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*The Mo substrate may be in the form of Mo sheet ~375 μm thick or - preferably - a deposited layer of Mo a few tenths of micrometers thick on a thicker sublayer of another material, such as glass.

There has been essentially no additional effort expended on this task during the third quarter, emphasis being placed entirely on the other (experimental) parts of the program. During the fourth quarter, however, the matter of estimated costs associated with fabricating heterojunction CdS/InP photovoltaic cells by MO-CVD and vacuum deposition techniques will be re-examined.

2.7 TASK G. PREPARATION AND DELIVERY OF FILM SAMPLES

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

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

As indicated in the first quarterly report (Ref 2), the new CVD reactor system was completed late in the first quarter, and the first InP films grown by the MO-CVD process in that reactor were available just before the end of the first quarter. Accordingly, selected samples from those first experiments were delivered to the ERDA Technical Project Officer in January 1977.

Subsequently, samples meeting the contract delivery requirements as specified above have been delivered to ERDA in each succeeding month.

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3. CONCLUSIONS AND RECOMMENDATIONS

Significant additional progress was made during the third quarter on development of the MO-CVD process for growth of InP films. Slight changes in reactor system design and in reactor chamber design resulted in at least a four-fold increase in film growth rate over that previously realized. Preferred deposition conditions were established for producing undoped n-type InP films on both (111A) and (111B) orientations of InP substrates; these are the film orientations expected to be used in fabricating CdS/InP heterojunction solar cell structures. P-type Zn-doped InP films were also obtained on these InP substrate orientations, as well as on GaAs substrates; conditions for achieving p-type dopant concentrations in the range 10^{16} - 10^{18} cm^{-3} were established for GaAs substrates. It was also demonstrated that much higher Zn partial pressures are required in the gas ambient to produce p-type films on (111B) InP substrates than on (111A) InP substrates. It appears that two separate doping curves will have to be developed for producing given doping concentrations in films of the two orientations.

Experiments continued on the growth and properties of InP films grown on glasses, metals and alloys, and intermediate metal and semiconductor layers. At low growth temperatures (below ~600°C) needle or spike-like growth is apparent on glass substrates, irrespective of composition. Films grown at temperatures of 600-625°C are smoother and surface coverage is better than for films grown at higher temperatures, such as 675 - 700°C. Simultaneous growth of InP on W, Mo, and TZM (a Mo alloy) produced films with almost identical structures (at 624°C), indicating there is no preference for substrate, at least for the deposition conditions used. However, there appear to be fewer voids at the InP-Mo interface than at a typical InP-glass interface. Relatively fewer voids were also present in films of InP grown on Mo-coated glasses. The surface characteristics of these InP deposits appear to be similar to those on Mo sheet and on glass substrates for about the same substrate surface temperature. Reflective areas in InP films on annealed Mo substrates were more prominent than in films grown on unannealed Mo, suggesting a correlation between grain size in the Mo sheet and in the film. The instability of the Mo/glass composite at high temperatures, however, limits the prospect of enhancing grain growth in Mo films grown on glass by thermal processes. Ni-Fe and Kovar substrates provided almost identical bulbous InP overgrowths at <600°C, and InP film separation from Kovar substrates was evidenced for a growth temperature of 650°C; consequently, no further studies with Kovar are planned. Encouraging results were obtained for InP films grown on composite substrates consisting of Ge films on Corning Code 0317 glass and GaAs films on this same glass, when deposition occurred at ~700°C, rather than at ~650°C.

In addition to the continued routine evaluation of film properties by van der Pauw measurements some preliminary Au Schottky-barrier device structures have been fabricated on the p-type InP films on GaAs substrates, using the Au-Zn-Au contact technology developed earlier in the program at Stanford. Short-circuit current densities as high as 12.5 mA/cm^2 were measured in these devices, an encouraging result. Au Schottky-barrier devices were also fabricated on p-type layers grown on InP substrates as well as on composite $n/p/p^+$, $p/n/n^+$, and n/p^+ film structures on InP substrates. Anomalous forward I-V characteristics under illumination were observed in the latter group of devices, believed to be caused by the effects of non-ohmic contacts to the p^+ InP. Junction structures were also examined briefly, but most such devices had excess leakage currents, even in small areas (<0.1 cm^2).

Detailed characterization of the electrical transport properties by Hall-effect measurements in both undoped n-type InP films on GaAs:Cr and InP:Fe semi-insulating single-crystal substrates and Zn-doped p-type InP films on GaAs:Cr substrates was continued at Stanford. It was found that for electron concentrations less than 10^{16} cm^{-3} in the samples evaluated, InP films deposited on GaAs:Cr substrates show a general increase in electron mobility with increase in electron concentration, as small structural potential barriers, with barrier heights up to about 0.05 eV, play a significant role in determining the mobility. All films deposited on InP:Fe substrates had electron concentrations greater than 10^{16} cm^{-3} and exhibited behavior virtually identical to that of single crystals of InP. Electron mobilities at 77°K as high as 10,500 cm^2/V-sec on GaAs:Cr substrates and 16,500 cm^2/V-sec on InP:Fe substrates were found in this study. Several observations on the properties of the InP films prepared by the MO-CVD process have been tentatively proposed and discussed, based on correlations of some of the experimental data for this limited set of samples.

The first heterojunction photovoltaic structure involving deposited films of n-type CdS and p-type MO-CVD InP was fabricated and characterized, using a special geometry required by the non-ideal properties of the layers involved. A good short-circuit current density of 14.2 mA/cm^2 was observed in natural sunlight of 90 mw/cm^2, but the open-circuit voltage was ~0.3V because of a large reverse saturation current. The measured power conversion efficiency of this first cell was only 2.3 percent, but the result is considered to be a successful demonstration of the applicability of the MO-CVD technique for producing InP films suitable for solar cell use.

In the coming quarter it will be important to extend the p-type Zn-doping studies of InP films grown on InP substrates so that the doping concentration is readily adjustable and values consistent with the production of good solar cells with n-type CdS films grown on the p-type (111)-oriented InP films can be achieved. At this stage both (111A)- and (111B)-oriented InP substrates are being considered until either the requirements of the CdS film growth process being applied at Stanford or some other factor arises to indicate which orientation is best for cell performance. It will also be necessary to establish conditions for producing p-type polycrystalline InP films on low-cost substrates, using the parameters found best for p-type growth on single-crystal substrates. It will be helpful to explore further the early stages of growth on selected low-cost substrates to determine the effect of various experimental parameters on the nature of the film growth process, and to maximize surface coverage — particularly in the early stages of film growth — by surface conditioning methods of various kinds. By the end of the coming quarter there should be increased emphasis on the growth of polycrystalline p-type InP layers on low-cost substrate materials of various configurations.

Additional work is required on preparation of Schottky-barrier devices in both simple and composite single-crystal InP film structures (on GaAs as well as on InP substrates). Further attention to the contact problem in these devices is needed, and determination of proper doping levels in the InP layers for best characteristics of both Schottky-barrier devices and p-n junction devices is required. Since most of the junction structures fabricated to date have been leaky, the cause of that problem must be investigated and corrected.

Additional p-type epitaxial films, on both GaAs and InP single-crystal substrates, will be sent to Stanford for use in preparing heterojunction device structures. The effort on vacuum deposition of n-type CdS, occasionally involving single-crystal InP substrates but mainly emphasizing the MO-CVD films prepared at Rockwell, should be accelerated so that a measure of the upper limits of performance that might be expected of the CdS/InP heterojunction system involving polycrystalline films on low-cost substrates can be obtained at an early date. In addition, some preliminary investigation of the heterojunction system involving indium-tin-oxide (ITO) and InP should be undertaken, with single crystals of InP used initially but epitaxial MO-CVD films employed in later experiments.

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4. PLANS FOR NEXT QUARTER

The contract work in the coming quarter is expected to consist of the following principal activities, arranged by task:

Task A

1. Determine growth conditions for producing p-type InP films of controlled doping concentrations on (111B)-oriented InP:Fe single-crystal substrates.
2. Prepare p-type InP films in 10^{16}-10^{17} cm^{-3} doping range on Zn-doped InP substrates for use in photovoltaic cell fabrication
3. Conduct experiments to examine stability of compound formed upon mixing TEI and PH_3
4. Prepare various single-crystal multilayer film structures of InP for film evaluation and device fabrication.

Task B

1. Continue efforts to obtain suitable low-cost substrate materials from various manufacturers.

Task C

1. Investigate deposition parameters required for preparation of p-type doped polycrystalline InP films on selected low-cost substrate materials, with emphasis on composite substrates involving Mo and Ge intermediate layers
2. Investigate effects of various substrate surface conditioning procedures (polishing, etching, cleaning, etc) on film growth and resulting film properties, using selected low-cost substrates.

Task D

1. Continue characterization of structural and electrical properties of InP deposits prepared in MO-CVD reactor system, using routine SEM, x-ray, RED, and metallography methods, as well as resistivity and Hall-effect measurements
2. Prepare and evaluate Schottky-barrier devices on epitaxial p-type InP films
3. Prepare and evaluate p-n junction solar cell structures in epitaxial InP films on various substrates
4. Investigate properties of Schottky barriers on polycrystalline InP films grown on selected low-cost substrates.

Task E (Stanford Subcontract)

1. Continue investigation of temperature dependence of electrical and optelectrical properties of doped and undoped epitaxial InP films prepared in Rockwell CVD reactor system
2. Prepare heterojunction CdS/InP structures on p-type InP films prepared by Rockwell and on single-crystal p-type InP wafers, and evaluate photovoltaic properties of these structures
3. Investigate photovoltaic properties of ITO/InP heterojunction system, initially with single-crystals of InP and later with MO-CVD InP films.

Task F

1. Prepare estimates of current costs of producing (on laboratory scale) CdS/InP heterojunction device structures of design now being used, allowing for efficiency of deposition processes.

Task G

1. Prepare and deliver representative samples of InP films to ERDA, as required by contract.

5. REFERENCES

1. R. P. Ruth, P. D. Dapkus, H. M. Manasevit, A. G. Campbell, K. L. Hess, R. E. Johnson, and L. A. Moudy, "Thin Polycrystalline Films of Indium Phosphide on Low-cost Substrates," Quarterly Report No. 2, April 1977, Rockwell International, Electronics Research Division, Anaheim, CA 92803. Contract No. E(29-2)-3727, Division of Solar Energy, U.S. Energy Research and Development Administration.

2. R. P. Ruth, P. D. Dapkus, H. M. Manasevit, K. L. Hess, R. E. Johnson, and L. A. Moudy, "Thin Polycrystalline Films of Indium Phosphide on Low-Cost Substrates," Quarterly Report No. 1, January 1977, Rockwell International, Electronics Research Division, Anaheim, CA 92803. Contract No. E(29-2)-3727, Division of Solar Energy, U. S. Energy Research and Development Administration.

3. M. Glicksman and K. Weiser, J. Electrochem. Soc. 105, 728 (1958).

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APPENDIX A. MANPOWER AND FUNDING EXPENDITURES

(To be included only in printed copies sent directly to ERDA Technical Project Officer and ERDA Contracting Officer and in printed copies used for Rockwell internal distribution).

During the third quarter of this contract — from April 3, 1977, through July 2, 1977 — a total of 1549 engineering and support manhours and a total of \$53,793 in funding (excluding fees and commitments) were expended at Rockwell. These figures do not include the subcontract effort at Stanford University.

The projection of expenditure of manpower (engineering and support manhours) at Rockwell and of contract funds at Rockwell and at Stanford (subcontract) for the next three months, exclusive of fees, is as follows:

July 1977	420 manhours (Rockwell)	\$19,500 (total)
August 1977	305 manhours (Rockwell)	\$19,600 (total)
September 1977	250 manhours (Rockwell)	\$10,800 (total)

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