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THIN FILMS OF InP FOR PHOTOVOLTAIC ENERGY CONVERSION

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Second Quarterly Technical Progress Report, September 29—December 28, 1979

By
Harold M. Manasevit
Ralph P. Ruth
Lavada A. Moudy
Jane J. J. Yang
Richard E. Johnson

January 1980

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Rockwell International
Electronic Devices Division
Electronics Research Center
Anaheim, California

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ABSTRACT

A research study is being conducted for the purpose of developing a low-cost high-efficiency thin-film InP heterojunction solar cell based on InP films grown by the metalorganic chemical vapor deposition (MO-CVD) process on suitable substrates. Heterostructure devices of CdS/InP (and possibly indium-tin oxide/InP) are to be prepared at Stanford University under subcontract, using the MO-CVD InP films grown at Rockwell. The work of the second quarter of the program is summarized.

Growth parameters have been established using new triethylindium, diethylzinc (DEZn), and PH_3 sources for the formation of Zn-doped p-type InP films in the modified MO-CVD reactor system. Appropriately doped films have been prepared and sent to Stanford for use in deposition of CdS layers.

An investigation of the properties of grains and grain boundaries in polycrystalline InP films was begun using several polycrystalline film/substrate combinations, including tungsten (W) layers produced by roller coating and screen-printing on polycrystalline alumina, and mechanically abraded surfaces of single-crystal bulk InP:Fe wafers. Growth quality on the W layers was generally very poor, and in no case were highly conducting InP:Zn films produced directly on low-cost insulators in the samples prepared during this reporting period. Only when the substrate was a metal or had a metal or GaAs:Zn coating layer was measurable conductivity in the grown film indicated by point-contact rectification probe testing. Growth on the mechanically disturbed single-crystal InP:Fe substrates proved to be interesting; depending upon the surface treatment, significant differences were observed in the electrical and crystallographic properties of the films relative to those of epitaxial layers. The p-type films formed on mechanically abraded surfaces were higher in resistivity and carrier concentration and lower in mobility than those grown on polished substrates.

An investigation was also undertaken into the use of GaP as an alternative intermediate-layer material to GaAs on low-cost substrates for subsequent growth of InP films. Heteroepitaxy was found to occur on companion single-crystal substrates of InP and (0001) Al_2O_3 when the appropriate deposition conditions were established. Epitaxial GaP:Zn films exhibited hole concentrations as high as $\sim 10^{19}$ cm^{-3}, while direct growth on Corning Code 0317 glass produced p-type films with hole concentrations in the 10^{17} cm^{-3} range. Coverage on the glass was complete and relatively smooth for a film thickness less than 2μm. The GaP film appeared to reduce the incidence of discontinuities typically formed at the substrate-semiconductor interface in InP growth.

Auger electron spectroscopy analysis done on a group of specially prepared Zn-treated films of polycrystalline InP indicated the presence of Zn at surfaces of InP:Zn films grown on Al and/or heat-treated in high concentrations of DEZn at ~600°C. However, no Zn was detected in polycrystalline films grown under deposition conditions that would be expected to produce highly doped p-type epitaxial fims if single-crystal substrates were used.

Plans for work in the third quarter are outlined.

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1. INTRODUCTION

The Electronics Research Center of Rockwell International is undertaking a one-year research study to develop a low-cost high-efficiency thin-film InP heterojunction solar cell, using the metalorganic chemical vapor deposition (MO-CVD) technique for InP film growth on suitable substrates. Heterostructure devices of CdS/InP and indium-tin oxide (ITO)/InP are to be prepared and characterized by the Department of Materials Science and Engineering of Stanford University, under subcontract.

The contract work is directed toward achievement of the Department of Energy goals for thin-film polycrystalline solar cells on low-cost substrate materials - namely, AM1 photovoltaic conversion efficiencies of 10 percent or greater by 1980 and cost feasibility of $0.30 per peak watt (electric) by 1986.

The research effort involves three major technical tasks:

I. Materials Growth
II. Materials Characterization
III. Device Fabrication and Characterization.

The principal subtasks for each of these are defined in the contract Statement of Work as follows:

Task I - Materials Growth

1. Investigate further the growth of thin films of InP on low-cost substrates by the standard MO-CVD process

2. Select substrates which will promote the growth of InP with the required photovoltaic properties

3. Investigate growth in a He carrier gas and growth at reduced pressures in terms of the properties of polycrystalline InP

4. Investigate nucleation and early-stage growth of InP films on low-cost substrates

5. Investigate the use of Cd as a suitable p-type dopant for MO-CVD InP and the use of <u>in situ</u> diffusion/annealing processes for improved doping.

<u>Task II - Materials Characterization</u>

1. Measure structural, electrical and optical properties of films grown by the process of Task I and provide definitive information regarding the photovoltaic potential of the various alternate processes

2. Investigate by x-ray, TEM and SEM techniques the preferred orientation, grain size, grain perfection and other structural properties of the films grown by the various processes described above. Determine transport properties of the polycrystalline films and their relation to preparation techniques

3. Determine by SEM and optical techniques the photovoltaic properties and potential of the InP films.

<u>Task III - Device Fabrication and Characterization</u>

1. Make state-of-the-effort CdS/InP and/or ITO/InP solar cell devices and characterize them by taking I-V curves under solar or simulated solar irradiation.

In addition to carrying out the three main technical tasks, Rockwell will deliver representative experimental solar cells and associated photovoltaic performance data to DoE quarterly beginning with the third quarter, as specified in the contract Statement of Work.

This constitutes the second Quarterly Technical Progress Report for this program and covers the period from September 29, 1979, through December 28, 1979. Technical progress during this period is described by task in the next section. Section 3 gives a summary of the work, with appropriate conclusions, and Section 4 an outline of work planned for the third quarter. Section 5 lists the references used in the report.

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2. TECHNICAL PROGRESS

The activities of the three main technical tasks during the second quarter of the program are summarized in this section.

2.1 TASK I - MATERIALS GROWTH

During the second quarter 67 InP deposition experiments were carried out. These included 1) the deposition of undoped films for the purpose of evaluating the background doping level in the reactor system at several appropriate times during the investigation; 2) the deposition of doped films for the purpose of achieving suitable p-type electrical properties in epitaxial films to be sent to Stanford - although work was also begun on deposition of polycrystalline Zn-doped InP films on several different types of substrate; 3) an investigation of the properties of grains and grain boundaries in polycrystalline films grown by MO-CVD on mechanically disturbed single-crystal surfaces; and 4) an investigation of p-type GaP formed by the MO-CVD process for evaluation as a possible interface or intermediate layer material for the subsequent growth of p-type InP:Zn.

2.1.1 Growth of Undoped Epitaxial InP Films

Typical electrical properties of undoped epitaxial InP films grown during this quarter to determine the system background doping concentration are recorded in Table 1. The results on the (100)-oriented substrates are fairly consistent with those reported in the first quarterly report (Ref 1). The data indicate the background level for the (111B)-oriented films to be as much as an order of magnitude higher than that in films grown on (111A)- and (100)-oriented substrates. The results on (111B)-oriented films grown at the preferred growth temperature of ~730°C are also about an order of magnitude greater than previously reported for this orientation (Ref 1).

These differences in background donor doping concentration at a given temperature are consistent with the previously observed and reported (Ref 2)

Table 1. Electrical Properties of Undoped Homoepitaxial InP Films as Function of Growth Temperature*

Expt. Seq. No.	Substrate Orientation	Growth Temp. (°C)	Approx. Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Room-temperature Mobility (cm^2/V-sec)
57	(100)	654	8	0.18	1.4×10^{16}	2520
36	(100)	676	5	0.11	2.5×10^{16}	2217
37	(100)	676	10	0.16	1.6×10^{16}	2431
	(111A)			0.48	1.3×10^{16}	1036
	(111B)			0.04	9.1×10^{16}	1651
34	(100)	730	10	0.07	4.0×10^{16}	2344
	(111A)			0.25	1.9×10^{16}	1303
	(111B)			0.02	1.4×10^{17}	1990
35	(100)	732	10	0.07	4.1×10^{16}	2370
	(111A)			0.18	1.8×10^{16}	1990
	(111B)			0.02	1.8×10^{17}	1964
75	(100)	732	6	0.05	4.1×10^{16}	3317
76	(111B)	732	6	0.02	1.5×10^{17}	1812

*TEI flow rate 2500 ccpm, PH_3 (~ 10% in H_2) flow rate 500 ccpm.

differences in Zn uptake in films of these orientations grown in the presence of DEZn. Whether the differences in ease of producing Zn-doped p-type films of the three orientations result directly (and only) from this background doping effect or are caused by additional factors has not been determined. Further, the cause of the orientation dependence of the background donor doping concentration has also not been established.

2.1.2 Growth of Zn-doped p-type Epitaxial InP Films

During the first quarter the diethylzinc (DEZn) available at that time for doping was found to be of poor quality, and it was not until late in the third month of the program that the DEZn ordered at the start of the contract was received from the vendor and installed on the reactor system. An immediate improvement in film quality was observed, indicating that the subsequent experimental investigations of p-type films should be more significant than those done early in the program.

The first Zn doping experiments performed with the new DEZn source tank were with (100) and (111B) InP substrates in the 715-730°C temperature range, with emphasis on use of (111B)-oriented InP substrates. The latter orientation had been found in the previous Rockwell/Stanford studies to result in good quality InP films made by the MO-CVD process and in high-efficiency CdS/InP heterojunction solar cells, at least in part because of the relatively good lattice-parameter match of the two semiconductors in that crystallographic plane (Ref 2).

Numerous experiments were carried out to attempt to find the deposition conditions that would result in the desired film properties with reasonable reproducibility. The properties sought for the epitaxial InP films to be supplied to Stanford were acceptor concentrations (i.e., hole concentrations) in the 10^{16}-10^{17} cm^{-3} range, with p^+InP:Zn substrates ($p \approx 2 \times 10^{18}$ cm^{-3}) of (111B) orientation being preferred, based on the earlier work in the CdS/InP and ITO/InP systems at Rockwell and elsewhere (Refs 2, 3).

Several such samples were successfully prepared and sent as a group to Stanford in mid-quarter. These samples were intended for use in preparing CdS/InP heterostructure devices as part of the Task III effort (see Section 2.3).

When the supply of (111B)-oriented InP:Zn p-type substrate material in this high conductivity range became almost depleted most of the epitaxial p-type InP films were prepared on Fe-doped (high-resistivity) InP substrates of the three orientations (100), (111B), and (111A). Although these configurations are much less useful for preparation of heterostructure cells, they do facilitate measurement of the electrical properties of the InP films, an important advantage at this stage of the program. In addition, they will provide an opportunity for comparison of the properties of vacuum-deposited CdS layers on (100) and on (111B) InP substrates as well as the properties of CdS/InP heterojunction solar cells on the two orientations.

The procedure of "proportioning" the H_2 gas stream passing through the DEZn source tank to achieve sufficiently dilute concentrations of DEZn in the deposition chamber was used in the more recent Zn doping experiments. It was found, however, that proportioning relatively high flow rates of the H_2-DEZn gas mixture did not provide the control necessary to achieve the required film properties. Despite that fact, total gas flow rates lower by 15-25 percent, when proportioned, did make it possible to achieve p-type epitaxial InP films with hole concentrations in the 10^{17}-10^{18}cm^{-3} range on (100) InP and (111B) InP substrates, in over 50 percent of the experiments in which that was the goal.

Figure 1 summarizes the measured data for net hole concentration vs DEZn-H_2 flow rate for the p-type films grown on the three orientations of InP, with the DEZn source at 0°C. Growth sequence numbers appear adjacent to the data points to permit comparison of properties of films grown in the same experiment. The effect of orientation on film properties (ease of doping) is as previously observed: (111A)>(100)>>(111B) InP. Only at and above an effective flow rate of 5.5 ccpm was it possible to produce p-type InP:Zn on (111B) InP:Fe; at 0.2 ccpm films were n type on (100) InP:Fe; at 0.1 ccpm they were n type as well on (111A) InP:Fe. Clearly, there are variations in the achieved

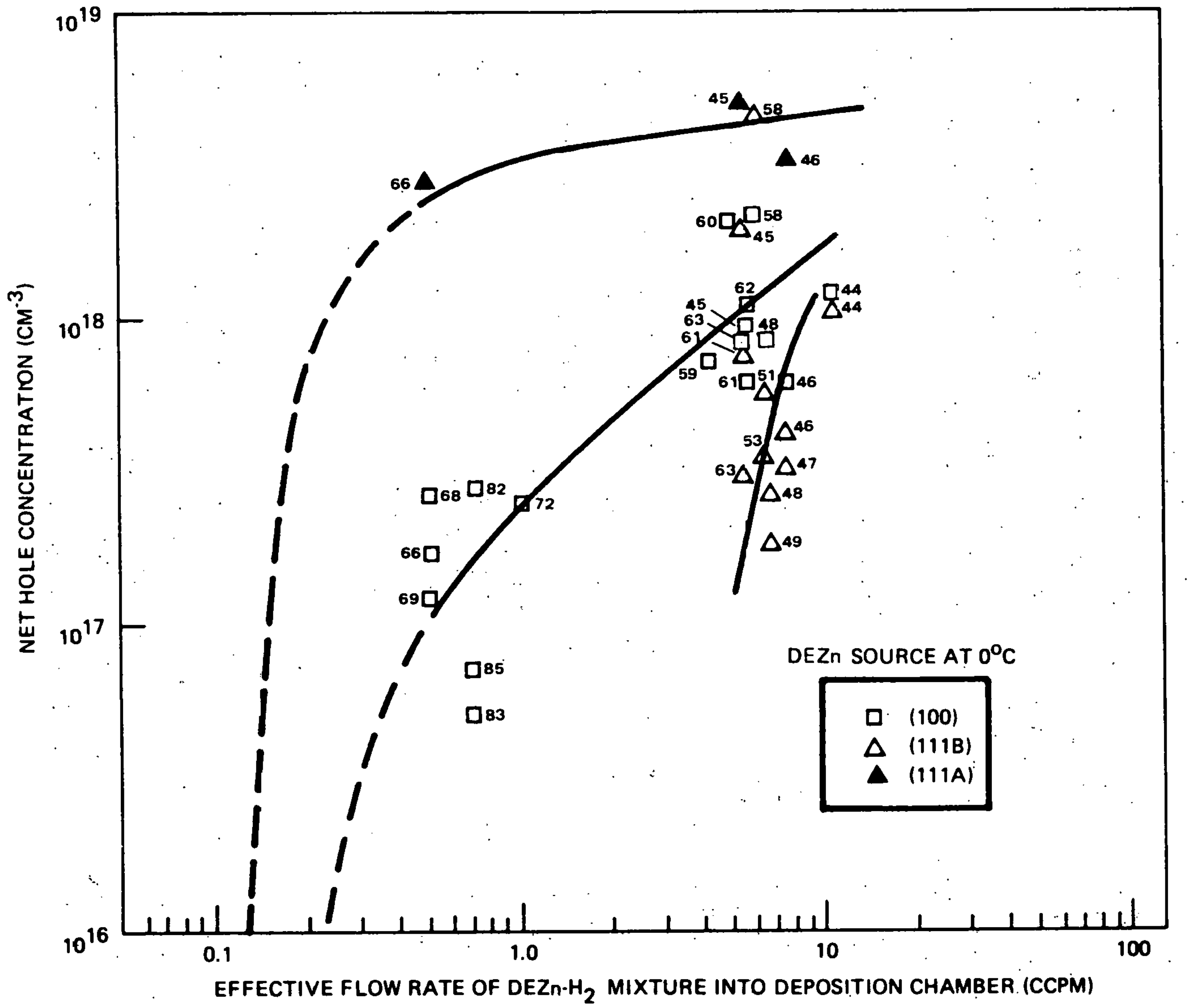


Figure 1. Net Hole Concentration in Epitaxial Zn-doped MO-CVD InP Films as Function of Effective Added Zn Concentration.

film properties relative to the properties expected on the basis of the nominal experimental conditions.

2.1.3 Investigation of Properties of Grains and Grain Boundaries

The investigation of the properties of grains and grain boundaries in polycrystalline InP films grown by MO-CVD was begun using several different substrate surfaces/materials to induce polycrystalline growth, including 1) p^+ polycrystalline GaAs:Zn film on sputtered Mo film on Corning Code 0317 glass; 2) screen-printed polycrystalline tungsten on sintered polycrystalline alumina (94 percent purity); 3) similar structures but with the tungsten applied by hot roller-coating; and 4) mechanically abraded surfaces of single-crystal bulk InP:Fe wafers.

The first of these substrates was shown in the earlier DoE-sponsored contract at Rockwell (Ref 2) to permit the successful growth of continuous p-type Zn-doped polycrystalline InP layers. The fourth type of substrate listed was investigated as a possible alternative (and readily prepared) surface for achieving similarly continuous yet polycrystalline and successfully doped InP layers. The intention was to disturb the InP wafer surface sufficiently to assure entirely (or at least largely) polycrystalline growth of the deposited film due to the introduction of randomly oriented crystallographic growth facets at the nominal growth surface. The second and third substrates listed above were new low-cost materials obtained from Ceramic Products, Inc. (Newburyport, MA).

The nominal Zn doping concentration added to the polycrystalline InP film grown on the p^+GaAs:Zn/Mo/0317 composite substrate was found to be $\sim 2 \times 10^{18}$ cm^{-3} by measurement of the transport properties of a companion epitaxial film grown simultaneously on a single-crystal GaAs:Cr substrate. The polycrystalline InP film on the composite substrate exhibited p-type conductivity detectable by the point-contact rectification method, although van der Pauw measurement of transport properties was not undertaken.

Both the screen-printed and the roller-coated tungsten/alumina substrates had high densities of voids and surface pits, and the resulting deposited InP films showed the effects of the poor surfaces in their high defect density. These are shown in Figure 2. No further experiments are planned for these substrate materials in their present forms because of these unsatisfactory results.

InP films deposited simultaneously (at ~ 730°C) on InP:Fe substrates having the usual highly polished (and lightly etched) surfaces for epitaxial growth and on companion substrates of the same material but having surfaces mechanically disturbed by various procedures were found, in general, to have surprisingly similar properties. The less disturbed the crystallographic surface of the substrate, the more the resulting film properties resembled those of the companion film grown on the polished surface, as would be expected.

A pair of undoped films grown on polished and on lapped (600-grit SiC paper using glycerine vehicle) (100)-oriented substrates exhibited essentially the same carrier (electron) concentration ($\sim 4 \times 10^{16}$ cm^{-3}), but the defective n-type film had a carrier mobility of ~ 1400 cm^2/V-sec compared with ~ 3300 cm^2/V-sec for the n-type epitaxial film, and a consequent resistivity over twice that of the epitaxial film. X-ray diffraction analysis of the defective film showed evidence of polycrystalline growth as well as some single-crystal growth, indicating that the damaged surface had some of the desired effect but had not successfully prevented all epitaxial growth. The fact that the measured electron concentrations were nearly the same is not surprising for material in this high doping concentration range; that the other properties did not differ more indicates that the dominant features of the defective film were still the bulk crystal grains and the epitaxial regions, rather than the grain boundaries.

A pair of undoped films grown at ~ 730°C on polished and on lapped single-crystal (111B) InP:Fe substrates exhibited similar carrier (electron) concentrations of $\sim 1 \times 10^{17}$ and $\sim 8 \times 10^{16}$ cm^{-3}, respectively. The higher electron concentration found in this pair of undoped InP films than in the (100)-oriented pair is consistent with earlier observations on film and

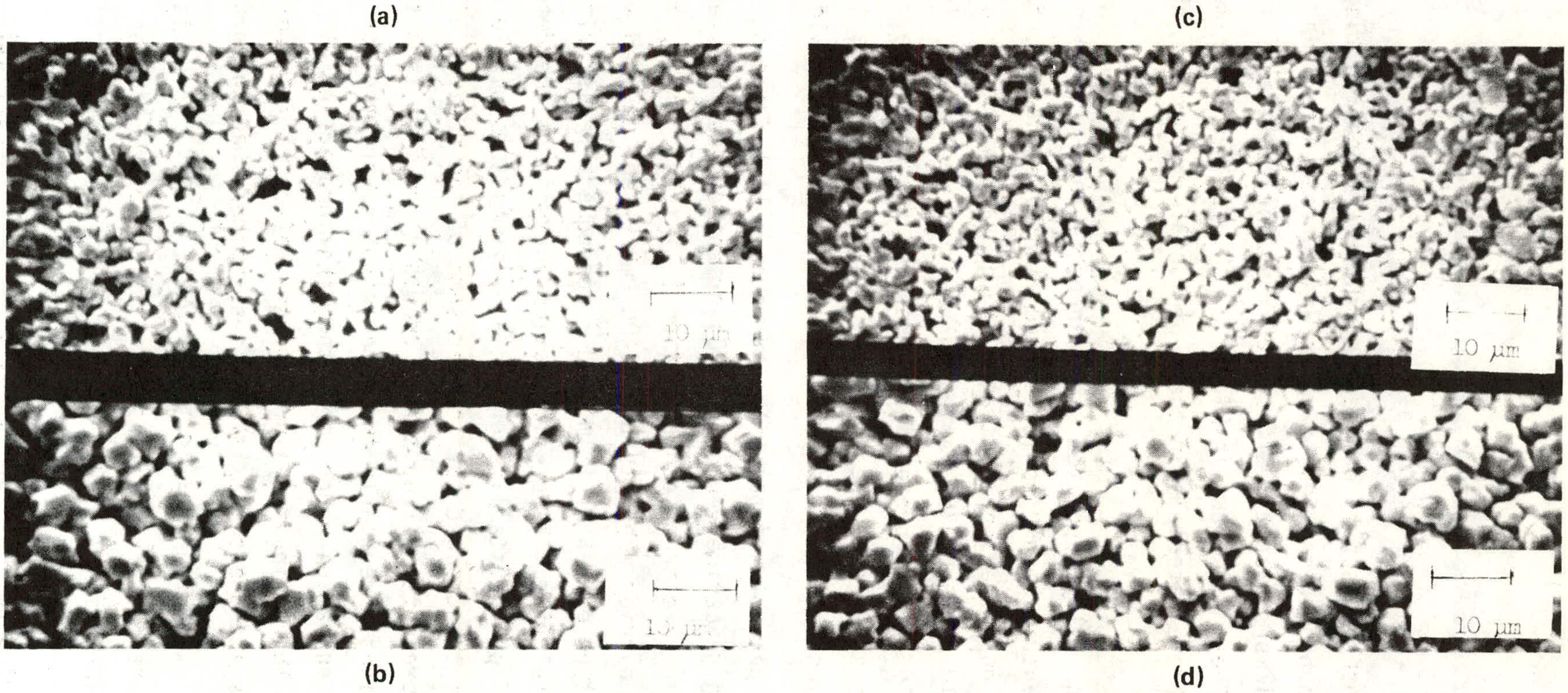


Figure 2. SEM Photographs of $W/A\ell_2O_3$ Surfaces and of 5μm InP Films Grown on Those Surfaces at 694°C. a) Bare Roller-coated $W/A\ell_2O_3$ Substrate; b) InP Film on Substrate a; c) Bare Screen-printed $W/A\ell_2O_3$ Substrate; d) InP Film on Substrate c.

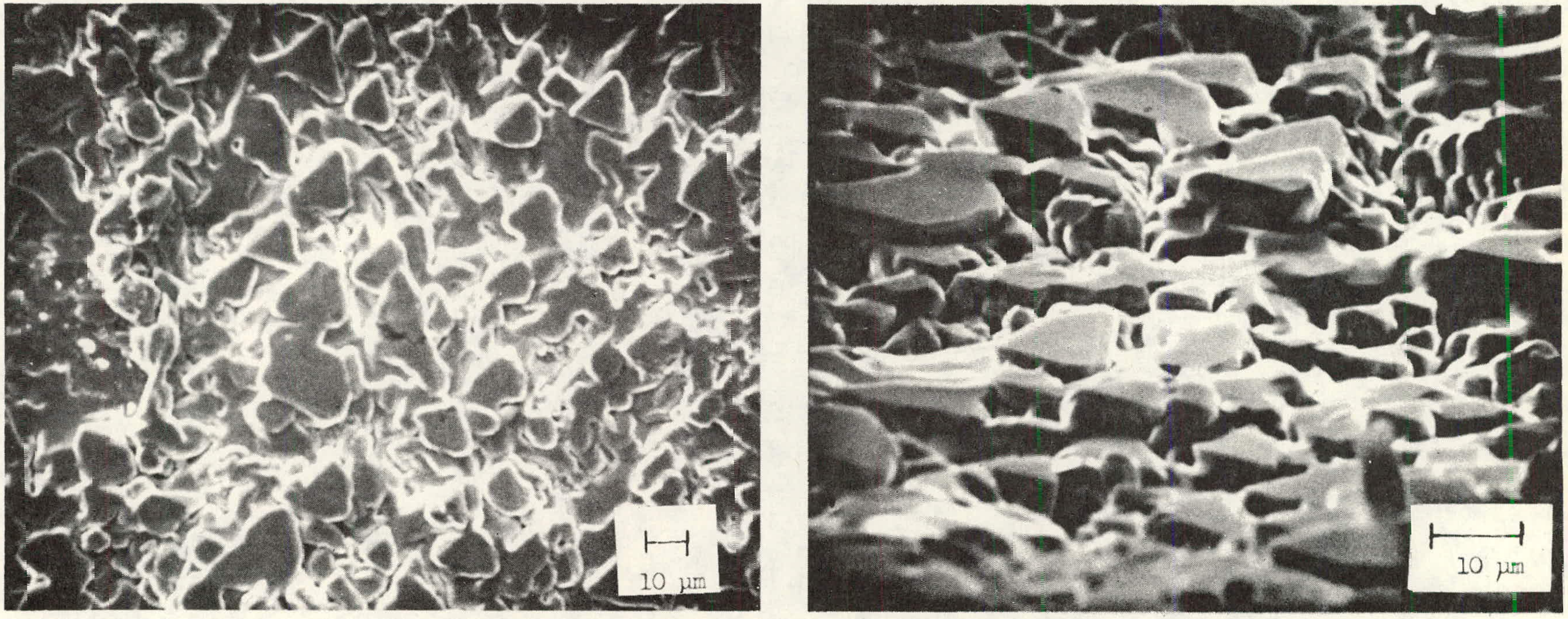
substrate orientation. The carrier mobility in the defective (111B) film was only about 1/5 of that in the epitaxial (111B) film, whereas that in the defective (100) film had been found to be about 0.4 of that in the epitaxial (100) film. The resistivity of the defective (111B) film was thus about an order of magnitude larger than that of the epitaxial companion film. X-ray diffraction examination (Task III) of both sets of films showed clearly the polycrystalline content of the defective films, and the effect was approximately the same for the two orientations prepared under similar conditions.

Similar pairs of Zn-doped films were also grown at ~ 730°C simultaneously on polished surfaces and on either unpolished as-sawed (or as-lapped) or freshly lapped (600-grit SiC paper, glycerine vehicle) surfaces of InP:Fe. Both (100) and (111B) orientations were examined, and in each case the abraded surface was etched (dilute bromine-methanol for ~ 30 sec) as a cleaning procedure just before placement in the reactor chamber. Lightly doped p-type pairs (DEZn flow rate 0.5 ccpm, $\sim 1 \times 10^{17}$ cm^{-3} hole concentration in p-type epitaxial layer) again exhibited similar hole concentrations, with significantly lower mobilities (and thus higher resistivities) in the defective partly polycrystalline layers. More heavily doped p-type pairs (DEZn flow rates 1 to 5.5 ccpm, $\sim 3 \times 10^{17}$ cm^{-3} hole concentration in p-type epitaxial layer) were quite dissimilar, with significantly higher hole concentrations ($1 - 2 \times 10^{18}$ cm^{-3}) and again lower mobilities in the defective layers, resulting in resistivities not very different for the two simultaneously grown layers.

Three pairs of Zn-doped InP films were also grown at ~ 730°C in separate experiments on polished and on sandblasted companion substrates, (100) orientations being used in two of the runs and (111B) in the other. The sandblasting procedure resulted in a more severely but more uniformly damaged substrate surface than that generated by the hand-lapping procedure used on the previously prepared substrates. A very lightly doped pair of (100) films (DEZn flow rate 0.2 ccpm) both remained n type, with similar carrier (electron) concentrations of $\sim 9 \times 10^{16}$ and $\sim 1 \times 10^{17}$ cm^{-3} on the polished and sandblasted surfaces, respectively, but with the mobility in the defective (polycrystalline) layer only about 1/60 of that in the epitaxial film. The second pair of (100) films was doped somewhat more (DEZn flow rate 0.3 ccpm), and the epitaxial film was partially converted to p type although some regions remained n type. The defective film, however, appeared to be entirely p type by the point-contact rectification (PCR) test.

The third, more heavily doped, pair (DEZn flow rate 5.1 ccpm) of (111B) films still exhibited mixed conductivity type in the epitaxial film on the polished substrate but distinct p-type conductivity, with a hole concentration of ~ 2 x 10^{18} cm^{-3} and a very low carrier mobility (~ 5 cm^2/V-sec), in the defective film. It thus appears that generally similar results were achieved for growth on both the hand-lapped surfaces and the sandblasted surfaces. X-ray diffraction analyses (Task III) showed that the films grown on sandblasted InP surfaces were not quite as extensively polycrystalline as those grown on hand-lapped surfaces (a somewhat surprising result), but in both instances, as shown in Figure 3, there was considerable evidence that single-crystal layer growth had persisted to a significant degree in all films grown on the damaged surfaces. The diffractometer data for the partially polycrystalline growths indicated very strong preferred orientations in planes corresponding to those of the nominal substrate surfaces - either (100) or (111B) - as would be expected. There did not appear to be any significant difference in the apparent amount of polycrystallinity for the two growth orientations.

A final experiment with InP growth on damaged surfaces was carried out using a pair of (100) GaAs single-crystal substrates, one in the as-sawed condition and the other as cut but then heavily etched (10 min) in 1-1/2 percent bromine-methanol to provide an "etch-polished" surface. Deposition was done at ~ 730°C, with relatively low doping (DEZn flow rate 0.7 ccpm) employed. Both resulting (100) InP films were p type, with the hole concentration ~ 4 x 10^{17} cm^{-3} and mobility 55 cm^2/V-sec on the etched-substrate sample and 2 x 10^{18} cm^{-3} and ~ 7 cm^2/V-sec on the as-sawed substrate. These properties are somewhat similar to those obtained for films grown on polished and hand-lapped InP surfaces with roughly the same doping conditions.



(a)

(b)

Figure 3. SEM Photographs of InP Film Grown on Sandblasted Surface of (111B) InP Single-crystal Wafer. a) Viewed Normal to Surface; b) Viewed at 45 deg Angle with Surface. Considerable Triangular Faceting Is in Evidence in Both Views.

The properties of several of the films grown during the above study and described above are summarized in Table 2. They tend to show that heavily etched surfaces resulted in p-type films with higher resistivity and lower mobility than in films grown simultaneously on polished InP wafers; lapped surfaces showed increased hole concentrations as well as lower mobility; and a sandblasted surface resulted in a film with low mobility (in this case n type because of the low flow of DEZn used). As indicated above, growth of InP on the as-sawed surface of GaAs showed the same trend in electrical properties as was obtained on the disturbed InP surfaces.

Whereas the approach of physically damaging the single-crystal semiconductor substrate surface did induce partially polycrystalline InP layer growth that was indeed continuous (one of the main goals of the exercise), the procedure as used to date has not resulted in essentially complete polycrystalline growth to the exclusion of epitaxy (single-crystal growth). Thus, further experiments of this nature will probably not be carried out at this stage of the program. However, several of the partially polycrystalline InP films were sent to Stanford late in the quarter for further evaluation and for use in fabricating polycrystalline CdS/InP heterojunction structures.

2.1.4 Investigation of GaP as Intermediate Layer for InP Growth

An investigation of GaP layers formed by the MO-CVD process was undertaken late in the quarter, for several reasons. If it continues to appear that intermediate layers are necessary for achieving continuous polycrystalline InP films of adequate quality on various low-cost substrate materials, then GaP is a potentially attractive alternative material for this purpose to GaAs, which has been used successfully in preparing composite substrates for InP film growth (Ref 2). Since P is common to both InP and GaP, sequential growth of the two could occur without concern for contamination by As. Further, GaP is a better match for InP in thermal expansion properties than is GaAs, so less thermally induced stress would be expected in the film-substrate interfacial region. Finally, GaP might also serve as a large-bandgap window-layer material and possibly even a top-contact material in certain InP cell configurations.

Table 2. Effect of Surface Treatments on InP:Zn Film Properties*§

Expt. Seq. No.	Substrate Material and Orientation	Substrate Surface Finish	Est. Film Thickness (μm)	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Room-temperature Mobility (cm^2/V-sec)
69	InP:Fe(100)	Polished	6	0.68	1.6×10^{17}	56
		Heavily Etched	6	2.3	1.3×10^{17}	21
71	InP:Fe(111B)	Polished	4	0.98	2.5×10^{17}	25
		Lapped†	4	0.35	1.9×10^{18}	9.6
72	InP:Fe(100)	Polished	5	0.35	2.6×10^{17}	18
		Lapped†	5	1.7	1.5×10^{18}	2.5
79	InP:Fe(100)	Polished	3	0.05	8.9×10^{16}	1414**
		Sandblasted	3	1.9	1.4×10^{17}	24**
84	GaAs:Cr(100)	Polished	3	0.31	3.6×10^{17}	55
		As-sawed	3	0.42	2.0×10^{18}	7.4

*For CdS deposition to form heterostructure solar cells.

†Hand-lapped on 600-grit SiC paper.

**Films n type, low addition of DEZn.

§Films grown at ~ 730°C.

Therefore, it appeared desirable to determine if GaP 1) is at least as compatible as InP with various low-cost substrate materials, 2) can be doped heavily (p^+) in polycrystalline layers, and 3) might in some way encourage larger grain growth in subsequently deposited InP layers than would otherwise occur if the InP were deposited directly on the low-cost substrate.

A number of GaP growth experiments were thus caried out using trimethylgallium (TMG) and phosphine (PH_3) in the InP MO-CVD reactor system. Substrate materials used included Corning Code 0317 glass, Mo films on 0317 glass, Mo sheet, Mo films on polycrystalline alumina (MRC HiRel), Al films on 0317 glass, single-crystal InP:Fe, and (0001)-oriented single-crystal sapphire. The latter was used to provide expected epitaxial growth of the GaP and thus allow measurement of film thickness and electrical properties as means for monitoring the process and establishing upper limits on film quality to be expected on the low-cost substrates. Both undoped and Zn-doped films were deposited, at temperatures ranging from ~ 650°C to ~ 775°C.

Undoped GaP films desposited at ~ 730°C on several of the above substrates all had high resistivities. The films on (100)InP:Fe and basal-plane sapphire were found by x-ray analysis to be single crystal, while on (111B)InP:Fe mixed single-crystal and preferred-orientation polycrystalline growth resulted.

Addition of Zn to the deposition process, using DEZn added to the gas stream as for InP film growth, at deposition temperatures of ~ 725°C produced p-type GaP films on (100)InP:Fe and (0001)-oriented sapphire substrates that were nearly equivalent in electrical properties, despite the fact that GaP growth on this sapphire orientation is probably (111A) oriented. When (111B)InP:Fe substrates were used the resulting GaP films consistently had lower hole concentrations, lower mobilities, and higher resistivities than those grown simultaneously on the other single-crystal substrates.

Table 3 summarizes the electrical properties and crystallinity of Zn-doped GaP films grown on sapphire, InP, and Corning 0317 glass. It was found that epitaxial GaP films heavily doped with Zn (DEZn flow rate ~ 10 ccpm) and

Table 3. Electrical Properties of GaP:Zn Films Grown by MO-CVD on Various Substrates

						Electrical Properties of Film		
Expt. Seq. No.	Substrate Material and Orientation	Growth Temp. (°C)	DEZn Flow Rate (ccpm)	Approx. Film Thickness (μm)†	Film Crystallinity*	Resistivity (ohm-cm)	Hole Conc. (cm^{-3})	Hall Mobility (cm^2/V-sec)
90	InP:Fe(100)	656	0.5	(9)	poly + pref.	2.1	1.9×10^{17}	15.6
	InP:Fe(111B)			(9)	poly + pref.	36	-	-
	Al_2O_3(0001)			9	poly + pref.	3.2	5.0×10^{18}	0.39
89	InP:Fe(100)	727	0.5	(9)	Sx	0.35	3.3×10^{17}	54.0
	InP:Fe(111B)			(9)	Sx+ pref.(slight)	2.7	4.1×10^{17}	5.7
	Al_2O_3(0001)			9	Sx	0.38	6.9×10^{17}	23.6
88	InP:Fe(100)	727	5.5	(9)	Sx	0.034	6.8×10^{18}	27.5
	InP:Fe(111B)			(9)	Sx+ pref.	0.12	2.6×10^{18}	19.5
	Al_2O_3(0001)			9	Sx	0.033	8.4×10^{18}	22.4
97	Al_2O_3(0001)	750	10	0.5	NM	0.035	2.8×10^{19}	6.5
	0317 glass			(0.5)	poly.	high	-	-
98	Al_2O_3(0001)	760	10	1.8	NM	0.048	1.3×10^{19}	10
	0317 glass			(1.8)	poly	57	-	-
96	Al_2O_3(0001)	756	10	8.6	Sx	0.024	1.3×10^{19}	20.4
	0317 glass			(8.6)	poly.	109	$\sim 5.0 \times 10^{17}$	~0.1

*Sx = Single-crystal; poly = polycrystalline; pref. = preferred orientation; NM = not measured.

†Measured thickness for film grown on sapphire assumed also to be thickness of other simultaneously grown films.

deposited at 750-760°C on (0001) sapphire exhibited hole concentrations as high as 1 - 3 x 10^{19} cm^{-3} for thicknesses from ~ 0.5 to ~ 9μm. Polycrystalline films grown on 0317 glass simultaneously with the thicker (~ 9μm) films on sapphire were also p type, with hole concentrations ~ 5 x $10^{17} cm^{-3}$; the resistivities were high, however, because of very low effective carrier mobilities (<1 cm^2/V-sec).

Figures 4 through 6 show the nature of polycrystalline GaP:Zn growth on four potentially low-cost substrates as a function of thickness, i.e., after 7, 14, and 60 minutes of growth (see Seq. Nos. 96-98 in Table 3). Incomplete coverage was observed only on the bare 0317 glass after the first 7 minutes of growth. Discontinuities at the substrate-semiconductor film interface are evidently "corrected" by the GaP film, which appears to be relatively smooth even at a thickness of ~ 2 μm.

These early results were considered encouraging. It became obvious that the effect of deposition temperature on resulting film properties and the effect of DEZn flow rate on the doping concentration in GaP films deposited directly on 0317 glass substrates should be examined next. This will be undertaken in the coming quarter.

2.2 TASK II - MATERIALS CHARACTERIZATION

The principal techniques used for materials characterization continued to be 1) Hall-effect measurements by the van der Pauw method, 2) conductivity-type determination by the PCR probe method, 3) surface morphology and structure characterization by SEM examination, and 4) crystallographic characterization by x-ray and electron diffraction analyses.

The room-temperature transport properties of the various InP films grown during the quarter were determined, as previously, by measurement of the Hall effect using the van der Pauw technique. Difficulties have persisted, however, in making accurate determination of film thickness when InP substrates are involved because the A-B etch* used for staining fractured and cleaved cross-

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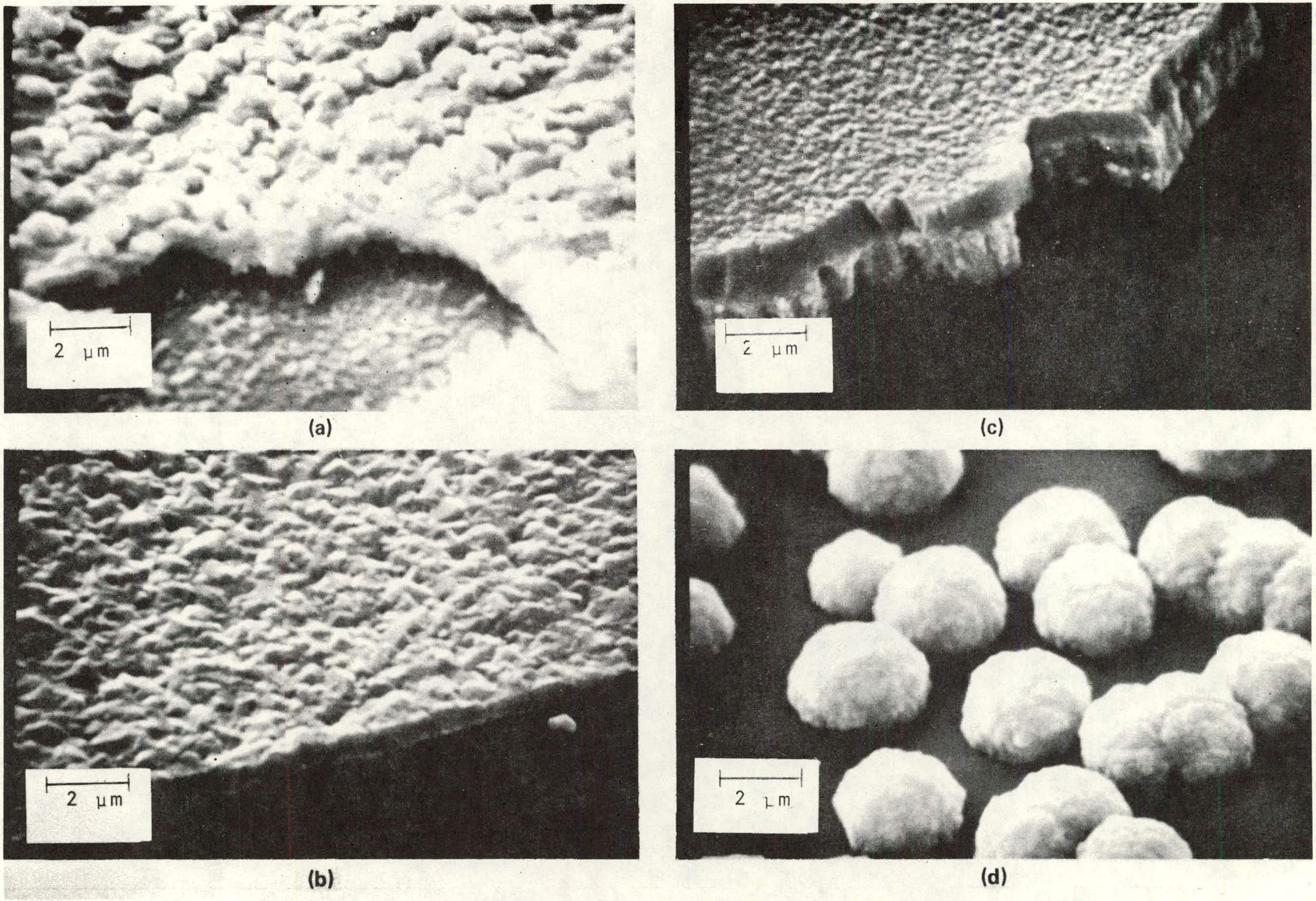
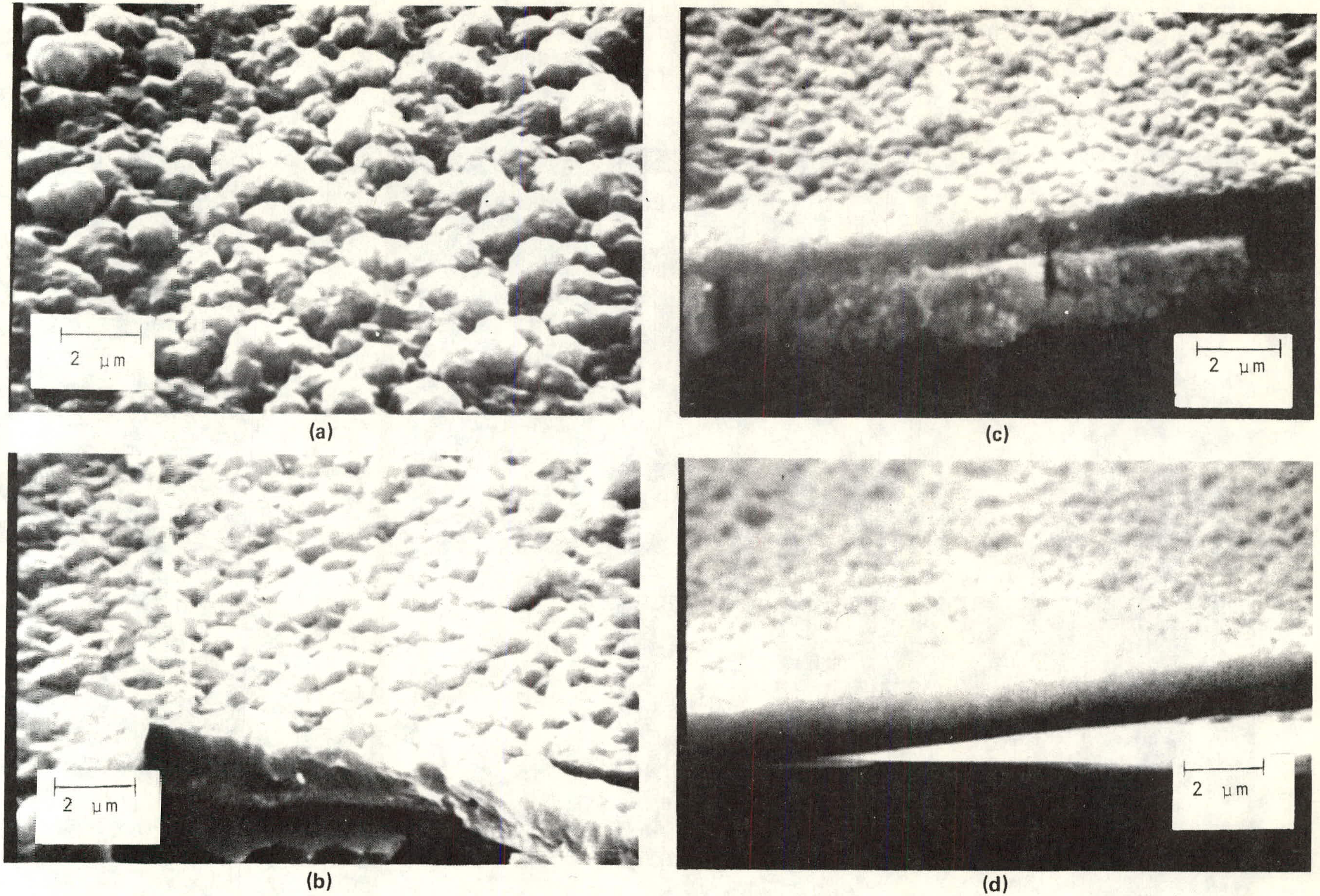
*1:1 mixture of 40cc H_2O + 0.3g $AgNO_3$ + 40cc HF and 40g CrO_3 + 40cc H_2O.



(a) (c)

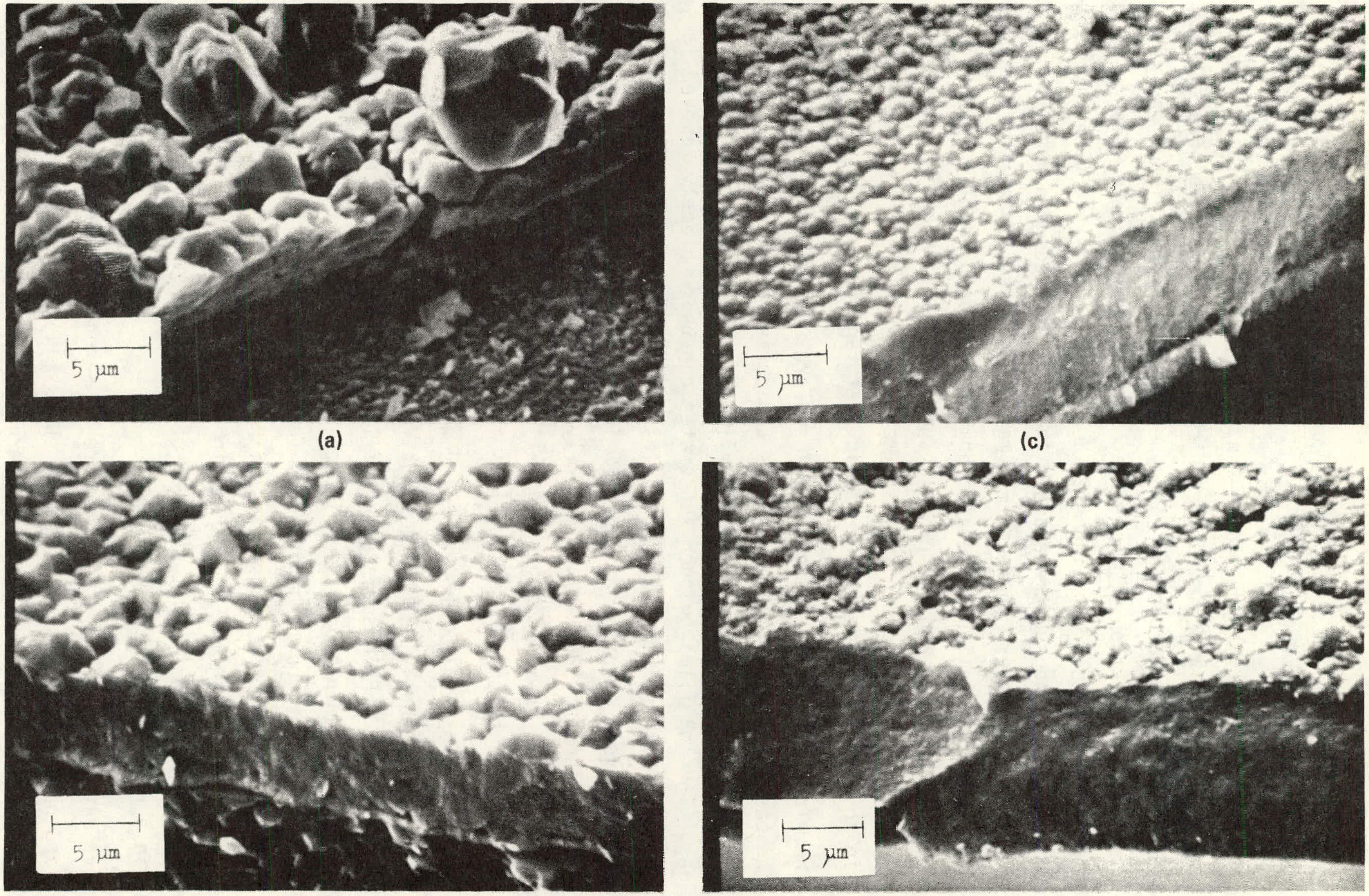
(b) (d)

Figure 4. SEM Photographs of Polycrystalline GaP after 7 min Growth, Viewed at 45 deg Angle with Film Surface a) on Bulk Mo Sheet; b) on 5000Å Mo Film Grown on Polycrystalline Alumina (MRC HiRel); c) on 2µm Mo Film Deposited on Corning Code 0317 Glass; d) on 0317 Glass (directly).



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

Figure 5. SEM Photographs of Polycrystalline GaP after 14 min Growth, Viewed at 45 deg Angle with Film Surface a) on Bulk Mo Sheet; b) on 5000Å Mo Film Grown on Polycrystalline Alumina (MRC HiRel); c) on 2μm Mo Film Deposited on Corning Code 0317 Glass; d) on 0317 Glass (directly).



(a) (c)

(b) (d)

Figure 6. SEM Photographs of Polycrystalline GaP after 60 min Growth, Viewed at 45 deg Angle with Film Surface a) on Bulk Mo Sheet; b) on 5000Å Mo Film Grown on Polycrystalline Alumina (MRC HiRel); c) on 2μm Mo Film Deposited on Corning Code 0317 Glass; d) on 0317 Glass (directly).

sections does not reproducibly delineate the film-substrate interface. When delineation is successfully achieved the thickness measurement follows directly, using the SEM or a light microscope. At other times a small chip of InP wafer has been placed on one portion of the surface of an InP substrate to serve as a mask, and the height of the resulting step between the deposited film surface and the covered portion of the substrate under the chip provides a direct measure of the film thickness. However, whereas this method appears simple and direct it has been found not very reliable, because some film growth usually appears on the substrate beneath the chip and the reactant gas flow pattern at the substrate surface is disturbed sufficiently in the immediate vicinity of the edge of the masking chip to alter the deposition rate in that region.

Therefore, film thicknesses on InP substrates have been most often deduced on the basis of deposition parameters and periodic verification of deposition rates using those parameters for InP film growth on substrates of single-crystal GaAs. The InP films on such substrates can be completely removed in selected regions by etching with HCl, which leaves the GaAs substrate undisturbed and produces an abrupt step the height of which can be accurately measured with the surface profilometer (Dektak). Similarly, straightforward determination of InP film thickness on low-cost substrates will depend on the chemical differences between the InP and the substrate materials involved.

Film thicknesses for the GaP films were determined by etching a step in a film grown simultaneously on (0001) sapphire and measuring the step height with a Dektak profilometer. Film surfaces and film-substrate interfaces were examined in the SEM. These examinations (see Figures 4, 5, 6) showed that the GaP films were, for the most part, quite smooth even for thicknesses of $\sim 9 \mu m$ on all of the polycrystalline and amorphous substrates with the single exception of bulk Mo sheet. On the latter material the GaP grain sizes appeared to be larger than on the other substrates, but the distribution of grain sizes was nonuniform, resulting in a rougher surface overall.

Evaluation of the crystal structure of several of the InP films, both epitaxial and polycrystalline, was carried out using x-ray diffraction techniques; the results of those analyses are discussed in Section 2.1.3.

X-ray diffraction analysis of a number of the GaP polycrystalline films was undertaken late in the quarter. Both back-reflection Laue patterns and diffractometer scans using the angle-mode programmer were employed. Films deposited on 0317 glass in the temperature range ~ 700°C to ~ 780°C were found to be polycrystalline with strong {111} preferred orientation, which was reduced somewhat at the higher growth temperatures. Films deposited on annealed bulk Mo sheet in the same temperature range also showed strong {111} preferred orientation, although not as strong as that observed in the films on glass.

The preferred orientation was diminished somewhat in the films grown at the upper end of the temperature range, as the (220) and (311) diffraction line intensities became relatively stronger than at the lower temperatures. A GaP film grown at ~ 780°C on a substrate consisting of a sputtered Mo film on a polycrystalline alumina (MRC HiRel) wafer appeared to be even more strongly preferentially oriented in the {111} planes than were the films on 0317 glass or annealed Mo sheet that were prepared at the same high temperature.

Additional examination of these orientation characteristics in GaP films to be prepared in the future may provide some evidence of a controllable orientation effect that might be useful in inducing preferred-orientation InP film growth on the GaP intermediate layer.

Several polycrystalline InP films were analyzed by Auger electron spectroscopy (AES) at the Rockwell Science Center (Thousand Oaks, CA), to attempt to map the distribution of Zn in the doped films. These analyses gave the following results:

1) Zn was detected in a polycrystalline InP:Zn film grown on Al sheet at ~ 600°C in a high DEZn flow rate (~ 3 atomic percent at surface; ~ 0.1 atomic percent at 400Å from surface).

2) Annealing a polycrystalline InP:Zn film on Mo sheet at ~ 620°C for 30 min in a high DEZn flow rate produced ~ 1 atomic percent Zn at the surface, but none was detected at 100Å below the surface.

3) No Zn was detected on the surface of a polycrystalline film of InP:Zn grown at 727°C with DEZn flow rates that would be expected to produce highly doped p-type epitaxial films.

The results in (2) above indicate that annealing in DEZn at relatively low temperatures can enhance the surface concentration of Zn; thus, further studies might lead to a technique for controlling the doping of InP (and other III-V semiconductors). How polycrystalline films would behave under such experimental conditions is not clear, however.

The differences observed in (1) and (2) may be temperature-related, substrate-related, and/or Zn-concentration-related. Al may enhance alloy formation with Zn and InP, and if Al had diffused to the InP surface it may have influenced the high concentration of Zn found there. In (3) the detection limits of Zn by AES may have been reached.

Further work of this nature with both single-crystal and polycrystalline substrates and films is necessary to help clarify the question of Zn distribution in these MO-CVD materials.

2.3 TASK III - DEVICE FABRICATION AND CHARACTERIZATION

Personnel of the Department of Materials Science and Engineering at Stanford University are responsible for most of the effort on this task. The subcontract with Stanford was executed during the quarter, with an effective performance period extending for the full duration of the one-year Rockwell contract.

A group of six samples of Zn-doped p-type epitaxial InP films grown on p^+(111B)InP:Zn substrates ($\sim 1.8 \times 10^{18}$ cm^{-3}) was delivered to Stanford in mid-quarter for use in fabricating CdS/InP heterojunction solar cell structures. The hole concentration in these films ranged from 3.0×10^{17} to 1.8×10^{18} cm^{-3}, as measured on companion films grown simultaneously on InP:Fe substrates.

Late in the quarter two additional separate groups of samples were prepared for delivery to Stanford. The first consisted of 11 p-type InP films grown (with one exception) on pairs of polished and damaged single-crystal substrates, as described in the Task I discussion. CdS was to be deposited on most of these samples to prepare pairs of CdS/InP heterojunction solar cells, for comparison of cell properties for epitaxial and partially polycrystalline InP layers. The second group consisted of seven epitaxial n- and p-type InP films grown on an assortment of InP:Fe substrates of (100), (111A), and (111B) orientations. The carrier concentration range was $\sim 1 \times 10^{16}$ to $\sim 5 \times 10^{18}$ cm^{-3}. These samples were also intended for fabrication of CdS/InP heterojunction structures and evaluation of their properties as a function primarily of crystallographic orientation.

It is expected that the first results with these samples will be obtained at Stanford early in the next quarter.

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3. SUMMARY AND CONCLUSIONS

Growth parameters have been established using new triethylindium (TEI), diethylzinc (DEZn), and PH_3 sources for the formation of p-type InP films in the modified MO-CVD reactor system. Appropriately doped films have been prepared and sent to Stanford for use in deposition of CdS layers; some of the CdS/InP composites will be returned to Rockwell for evaluation and some will be retained at Stanford for subsequent fabrication of solar cells.

An investigation of the properties of grains and grain boundaries in polycrystalline InP films was begun using several polycrystalline film/substrate combinations - tungsten (W) layers produced by roller coating and screen-printing on polycrystalline alumina, and mechanically abraded surfaces of single-crystal bulk InP:Fe wafers. In no case were highly conducting InP:Zn films produced directly on low-cost insulators in the samples prepared during this reporting period. Only when the substrate was a metal or contained a metal or a GaAs:Zn interface layer was conductivity in the grown film indicated by point-contact rectification probe testing.

Growth on the W layers was generally very poor, mainly due to the initial condition of the W layers - a high density of voids and surface pits was found on all samples used. Growth on the mechanically disturbed single-crystal InP:Fe substrates proved to be the most interesting. Depending upon the surface treatment - heavily etched, hand-lapped, or sandblasted - differences were observed in the electrical and crystallographic properties of grown films when they were compared with InP layers grown on polished InP substrates. Orientation effects were also noted. The p-type films on mechanically abraded surfaces in general were higher in resistivity and carrier concentration and lower in mobility than those on polished substrates. The same trend was found for a p-type InP film grown on an as-sawed GaAs:Cr (100) surface.

An investigation was also initiated into the use of GaP as an intermediate layer on low-cost substrates for subsequent growth of InP films. GaP would presumably be preferred to GaAs for this purpose because P is common to both materials, its thermal expansion coefficient is a better match to that of InP, and its larger bandgap may make it useful in a configuration using a low-cost transparent substrate as the top layer of a solar cell. Heteroepitaxy was found to occur on companion single-crystal substrates of InP and (0001) Al_2O_3 when the appropriate deposition conditions were established. Epitaxial GaP:Zn films exhibited hole concentrations as high as 1-3 x 10^{19} cm^{-3}; in a limited study, direct growth on Corning Code 0317 glass produced a p-type film with a hole concentration ~ 5 x 10^{17} cm^{-3}. Coverage on the glass was complete and relatively smooth for a film thickness less than 2μm. The GaP film appeared to correct discontinuities at the substrate-semiconductor interface and seemed adequate for use as a surface for the subsequent growth of InP.

Characterization of various films prepared during the quarter was generally limited to (1) Hall-effect measurements by the van der Pauw method; (2) conductivity-type determination by a point-contact rectification probe test; (3) surface morphology examination in the SEM; and (4) crystallographic characterization by x-ray techniques. Film thicknesses on InP substrates were often deduced from deposition parameters because of a lack of an appropriate stain; on other substrates, measurements were made from SEM photographs of cleaved or broken sections, or a profilometer (Dektak) measurement was made at a step produced by etching part of the film to the substrate (GaAs, sapphire, glass).

Auger electron spectroscopy analysis was done on specially prepared Zn-treated films of polycrystalline InP. The results indicated the presence of Zn at surfaces of InP:Zn films grown on Al and/or heat-treated in high concentrations of DEZn at ~600°C. However, no Zn was detected in polycrystalline films grown under deposition conditions that would be expected to produce highly doped p-type epitaxial films.

Three groups of samples were submitted to Stanford during the quarter. These included films on p^+ (111B)InP:Zn substrates, on polished and mechanically damaged single-crystal InP substrates, and on an assortment of InP:Fe substrates of (100), (111A), and (111B) orientations. Device results obtained with these samples will be described in the next quarterly report.

4. PLANS FOR NEXT QUARTER

The planned activity for the third quarter includes the following:

Task I Continue the preparation of p-type InP polycrystalline films on suitable substrates; investigate means for preparing high-conductivity p-type GaP on low-cost substrates; evaluate the use of DMCd for Cd-doping of single-crystal and polycrystalline InP films; prepare polycrystalline films on suitable substrates for solar cell fabrication and evaluation at Stanford; being study of nucleation and early-stage growth phenomena.

Task II Continue routine characterization of structural and electrical properties of InP films on various substrates; evaluate the structural quality of CdS/InP composites prepared at Stanford.

Task III Prepare CdS/InP heterojunction solar cell structures on single-crystal and polycrystalline films, and characterize their photovoltaic properties; demonstrate reproducible properties in doped and undoped CdS films produced in the above structures.

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3. See, for example, K. Ito and T. Ohsawa, Japan. J. Appl. Phys. 14, 1259 (1975); also S. Wagner, J.L. Shay, K.J. Bachmann, and E. Buehler, Appl. Phys. Lett. 26, 229 (1975); J. Appl. Phys. 47, 614 (1976).

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