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THIN FILMS OF InP FOR PHOTOVOLTAIC ENERGY CONVERSION

Third Quarterly Technical Progress Report for the Period December 29, 1979—March 28, 1980

By
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April 1980

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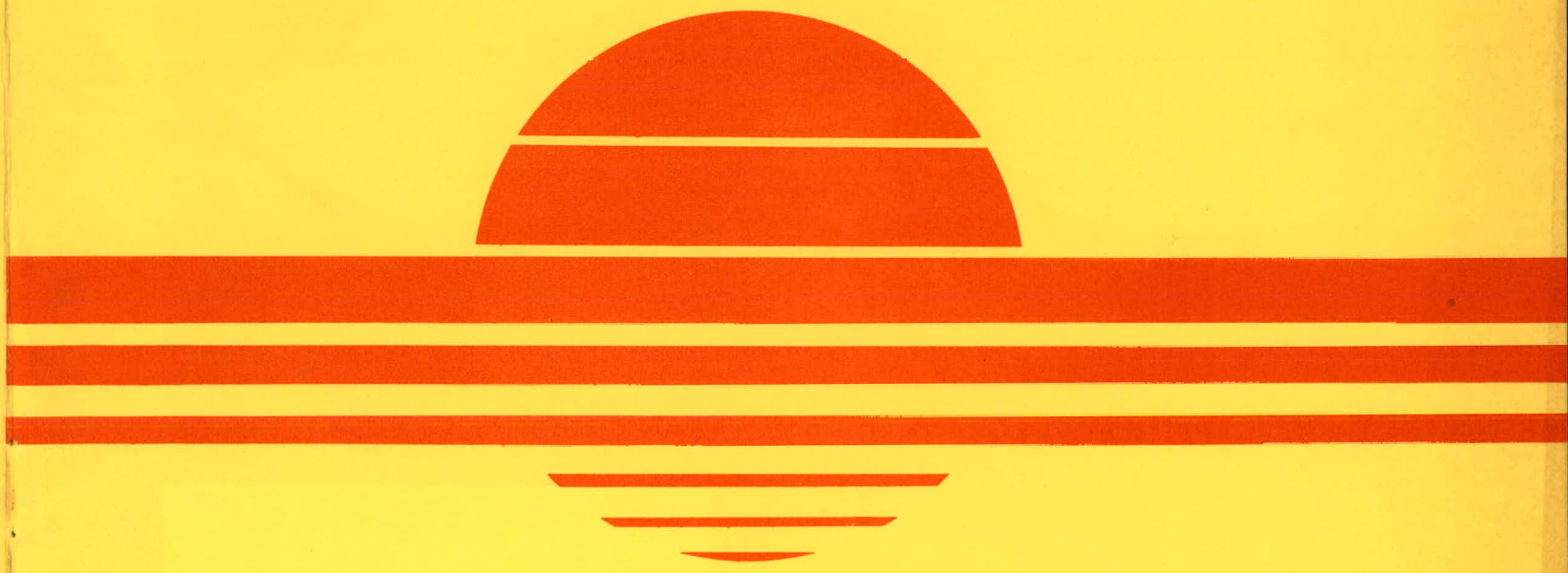
Rockwell International
Anaheim, California



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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 third quarter of the program is summarized.

Experiments continued on evaluation of GaP as an intermediate layer material for subsequent growth of InP films on various substrate materials, and Cd (obtained from dimethylcadmium) was evaluated as a p-type dopant (an alternative to Zn obtained from diethylzinc) for InP films made by the MO-CVD process. Despite various approaches tested in attempting to find a means for obtaining polycrystalline low-resistivity p^+GaP layers directly on low-cost substrates this did not occur, so the work with GaP intermediate layers was discontinued. Cd was found to behave much like Zn in InP films made by the MO-CVD process, with an exponential dependence of achievable Cd doping concentrations upon the reciprocal of the InP deposition temperature, as if the Cd vapor pressure is a contributing controlling factor. The same dependence of dopant incorporation upon crystallographic orientation of the InP growth as was found earlier for Zn has been observed for Cd: most effective for (111A) growths, less effective for (100) growths, and the least effective for (111B) growths. However, at any given deposition temperature Zn is more effectively incorporated into InP than is Cd.

Since Cd doping appeared to offer no clear advantages over Zn doping - especially for polycrystalline InP films - the experiments with Cd-doped layers were not pursued further except for a brief investigation of the possibility that Cd_3P_2 formation during the growth of Cd-doped InP films might be occurring in such a way as to adversely affect the film growth process. The latter investigation was not conclusive and would have to be carried further to fully resolve the question.

A preliminary x-ray diffraction analysis was conducted of the crystallographic structure of the vacuum-deposited CdS films prepared at Stanford as part of the process of fabricating CdS/InP heterojunction solar cells. Polycrystalline hexagonal CdS was found to be present in films deposited on single-crystal InP surfaces of three different crystallographic orientations, raising the question of the extent to which CdS/InP heterojunction solar cells previously fabricated in various laboratories have actually consisted of single-crystal structures having true heterojunction properties.

A group of CdS/InP heterostructure cells involving vacuum-deposited CdS and p-type epitaxial InP films grown by MO-CVD was prepared and evaluated during the quarter. High J_0 values and low fill factors were observed in all of the cells, resulting in AM1.5 efficiencies in the 2-5 percent range.

Plans for the fourth quarter's work 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 possibly indium-tin oxide (ITO)/InP are 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 *in situ* diffusion/annealing processes for improved doping.

Task II. Materials Characterization

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 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.

Task III. Device Fabrication and Characterization

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 is to 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 third Quarterly Technical Progress Report for this program and covers the period from December 29, 1979, through March 28, 1980. 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 fourth quarter. Section 5 lists the references cited in the report.

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2. TECHNICAL PROGRESS

The activities of the three main technical tasks during the third quarter of the program are summarized in this section. The work is summarized in Section 3.

2.1 TASK I. MATERIALS GROWTH

During this quarter a total of 46 InP deposition experiments was carried out. These included (1) deposition experiments to test the quality of two new batches of TEIn and evaluate the background level and growth rate profile obtained with each; (2) deposition experiments to continue the evaluation of GaP as an intermediate layer material for InP:Zn growth on low-cost substrates; (3) evaluation of dimethylcadmium (DMCd) as a potential source of p-type dopant for InP layers on low-cost substrates; and (4) growth of InP/GaP multilayer structures on low-cost substrates, for characterization and possible use in experimental cell fabrication.

These deposition experiments are summarized in the following paragraphs.

2.1.1 Growth Of Undoped Epitaxial InP Films

The first InP growth experiments carried out early in the quarter indicated that the film deposition rate was slowly decreasing. Since this is often an indication of depletion of a reactant source, it was decided to replace the TEIn source with a new and previously untested 90g source from Ventron.* However, the subsequent experiments produced undoped n-type films with doping levels of ~ 2-4 x 10^{18} cm^{-3} on both (100)- and (111B)-oriented substrates of InP:Fe. No improvement on film properties was achieved using the TEIn (at 0°C) after pumping on it for 60 min. Cleaning and reassembling of the TEIn lines leading to the deposition chamber also had no appreciable effect on the properties of films grown using the new TEIn.

*Alfa Division of the Ventron Corporation, 152 Andover St., Danvers, MA 01923.

It was concluded that the new TEIn was unsatisfactory from the standpoint of purity, and arrangements were made with Ventron to replace the new batch with other material. The old source tank was reinstalled on the system, and it was then found to produce a (100)-oriented film with acceptable properties. No explanation for the reduced InP growth rate, which persisted when the old TEIn source was installed, was found.

2.1.2 Investigation of GaP as Possible Intermediate Layer Material for Subsequent InP Film Growth

This investigation was begun late in the second quarter and was continued during this report period.

Following the experiments with the TEIn source tanks as described above, an exploratory deposition run was made to check the overall system performance with a source material other than TEIn. Films of GaP:Zn, using trimethylgallium (TMGa) as the source material, were grown simultaneously on substrates of sapphire and Corning Code 0317 glass. The film on sapphire was found to be p type, with a hole concentration of 4×10^{18} cm^{-3}; the film on glass had high resistivity (>75 ohm-cm) and the carrier concentration could not be measured.

The next three experiments were done to evaluate the quality of an InP:Zn layer grown on a layer of GaP first grown on a low-cost susbtrate. These experiments were done at deposition temperatures of 700, 715, and 725°C. A companion sapphire substrate was used in each experiment, in addition to substrates of bare 0317 glass, Mo/0317 glass, and Mo/alumina (polycrystalline MRC HiRel Superstrate). The GaP layers were grown nominally 4 μm thick (30 min deposition time) and the InP layers about 3 μm thick, except for the first experiment of the three in which the run was terminated with ~ 1.5 μm of InP deposited because of apparatus problems.*

*Following the first experiment of the three the deposition chamber was modified to replace its large ground taper joint with a butt-type O-ring joint, to facilitate assembly and disassembly between runs.

The smoothest composite films were those on sapphire, as would be expected, and on the Mo/alumina (HiRel) composite substrate. Film morphology was progressively worse on Mo/0317 and on bare 0317 and as the deposition temperature decreased. Point-contact rectification tests indicated high resistivity for the InP:Zn films on the 0317 glass but good conductivity for the films on sapphire, with intermediate conductivities suggested for the films on Mo intermediate layers.

Several experiments explored the effect of temperature on GaP film properties; subsequently, ~ 750°C was chosen over 770 and 700°C for further study, even though all three temperatures yielded p^+ films (~ 5×10^{18}-10^{19} cm^{-3}) on sapphire. The best homogeneous coverage seemed to be on sapphire and Mo/HiRel composite substrates; Corning Code 0317 glass substrates were only partially covered and/or displayed small spherical structures. Coverage on Mo substrates (obtained from GTE Sylvania) appeared to be complete, but the film had many orange-colored crystallites embedded in it.

The next three experiments explored the effects on the properties of thinner (up to 3.5 μm thick) films of <u>in situ</u> annealing in PH_3-DEZn atmospheres for ~ 30 minutes under "standard" doping conditions. The results of electrical measurements on GaP films on sapphire were about as expected (~ 3-6 $\times 10^{18}$ cm^{-3}, p type), but voids were present in the films on Corning 0317 glass and the films were not p type. The final experiment of the three involved growth at ~ 750°C and annealing at a lower temperature, ~ 680°C. The noncontinuous film on the 0317 glass proved to be conductive but appeared to be n type, with a net carrier concentration of ~ 1.5×10^{17} cm^{-3}.

These rather discouraging results with amorphous (and/or microcrystalline) substrates prompted a series of deposition experiments using polycrystalline alumina substrates of various grain sizes. Included among the substrates used were single-crystal sapphire; large-grained Vistal (99.9

percent purity) alumina substrates, manufactured by Coors and refired four times at high temperature (≥ 1800°C) to produce enlarged grains; large-grained high-purity aluminas from 3M Co. (ASM805), also refired four times; and standard pure aluminas (99+ percent) from Materials Research Corporation (HiRel) and/or from Coors (ADS995). The other parameters varied in the experiments were the growth temperature and the PH_3 flow rate.

Preliminary measurements on these films using the point-contact rectification (PCR) probe indicated some conductivity in the films on the aluminas and high conductivity in those on sapphire. The properties of these films, described in more detail in the Task II discussion (Section 2.2), were not encouraging, however.

Fused quartz was also tested as a possible low-cost substrate material for the growth of p^+ GaP. One substrate was cleaned in organic solvents and aqua regia and another in organic solvents and hot HF. Films grown at 750°C were found to be crazed on both quartz substrates and partially nonadherent on the HF-treated surface.

In another experiment Zn-doped GaP was grown at ~ 730°C on six different glasses obtained from Owens-Illinois (Toledo, OH). The glasses were designated GS-186, GS-210, GS-211, GS-213, GS-238, and EE-5. The first four glasses are Owens-Illinois proprietary high-temperature glasses. Types EE-5 and GS-238 are both calcium-magnesium-barium-aluminosilicate glasses.

Needle growth occurred mainly on the first four glass substrates, and the PCR test indicated essentially no conductivity in the films. The other two did show slight conductivity, but electrical measurements indicated the film on GS-238 was highly resistive (85 ohm-cm) and n type (carrier concentration ~ 4×10^{17} cm^{-3}), while the film on EE-5 was ~ 160 ohm-cm in resistivity and p type (carrier concentration ~ 1×10^{16} cm^{-3}). Such results, obtained with DEZn flow rates that produced a p-type GaP film with a carrier concentration of ~ 7×10^{18} cm^{-3} and resistivity of ~ 0.07 ohm-cm on a companion sapphire wafer discouraged any further work with these glasses at this time.

In an isolated experiment, a piece of galvanized iron sheet was also tested as a possible source of Zn dopant for converting a nonconducting GaP layer on 0317 glass into a p^+ layer. After 60 minutes at ~ 600°C part of the iron sheet (situated on top of the film) was found to have fused to the GaP layer at its edges, but no major change in conductivity was observed in that part of the film not fused to the iron sheet. A heavy metallic deposit was apparent on the quartz walls of the reactor after the experiment; it was assumed that this was Zn. No further work was done with this approach.

2.1.3 Evaluation of Cd as p-type Dopant for InP Films

Earlier studies at Rockwell (Ref 1) demonstrated that dimethylcadmium (DMCd) is effective as a dopant for producing p-type GaAs films grown by the MO-CVD process. Its use for producing p-type InP had not been previously investigated, however. The compound is a liquid at room temperature (mp = -2.4°C, bp = 105.5°C), with a reasonably high vapor pressure of ~ 20 mmHg at 16°C and ~ 40 mmHg at 30°C.

Since incorporation of Zn (from DEZn) in polycrystalline InP layers has not produced electrically active acceptor centers in a predictable and controllable way it was hoped that Cd incorporation might proceed differently and more favorably. It was thus necessary to determine first the doping characteristics of Cd in epitaxial layers of InP as a function of DMCd flow rate and InP deposition temperature and then to use that information to produce Cd-doped polycrystalline InP films for evaluation.

2.1.3.1 Growth of Epitaxial InP:Cd Films

Initial experiments established the doping level in epitaxial films of several different orientations as a function of temperature and flow rate of H_2 over the DMCd, maintained at a temperature of 0°C by an external bath. The properties of the films grown in these experiments are described in the Task II discussion (Section 2.2). The data given there indicate that the same orientation dependence of doping efficiency was obtained with DMCd as with

DEZn. That is, the effectiveness of Cd incorporation was greatest for (111A) films, next for (100) films, and much poorer for (111B) films.

A H_2 flow rate of 50 ccpm over the DMCd was more than sufficient to produce Cd saturation in the (111A)-oriented InP films over the temperature range ~ 650-730°C. Even when saturation has been reached for (111A)InP at 730°C (a useful temperature for producing p-type films of the three orientations using DEZn) only n-type films were produced on (100)InP and (111B)InP.

These results indicated Zn to be generally preferred over Cd for producing good quality p^+ epitaxial layers of InP. On the other hand, better doping control may be obtained experimentally in producing p-type (100)-oriented InP films with carrier concentrations in the ~ 10^{16}-10^{17} cm^{-3} range by using DMCd, since no further dilution of the DMCd-H_2 mixture is required.

2.1.3.2 Growth of Polycrystalline InP:Cd Films

Polycrystalline InP films were grown on a number of low-cost substrate materials using DMCd as the source of acceptor impurity. The substrates used included various polycrystalline aluminas, Corning Code 0317 glass, Mo sheet, deposited Mo films on alumina and on glass, and GaAs/0317 glass composites.

High flow rates (50 ccpm) of H_2 over the DMCd source (held at 0°C) were used in a group of four separate experiments at three different temperatures - nominally 650, 675, and 700°C.

At ~ 650°C, after 60 min of deposition time only partial coverage was obtained on 0317 glass, films on the aluminas were nonconducting (as indicated by the PCR probe), and some needle growth was observed on Mo films on alumina and 0317 glass substrates. A film on a bulk Mo sheet substrate was relatively smooth, however, and showed slight conductivity by the PCR probe test. At a growth temperature of ~ 675°C some triangular structure was obtained in films on 0317 glass and on Mo/0317 glass, but the conductivity was quite low. At ~ 700°C films grown on GaAs/0317 and on bare 0317 were essentially nonconductive.

One growth experiment was performed on a thin, highly oriented ZnO layer that had been grown on a glass microscope slide in a separate Rockwell program. The ZnO film did not survive the heating process, having virtually disappeared from the substrate (possibly by H_2 transport) before the pedestal temperature had reached 650°C. InP:Cd growth on the surface of the slide and a companion 0317 glass substrate was poor, with flaking of the deposit occurring on the glass slide.

2.1.3.3 Study of Cd_3P_2 Formation as Factor in InP Film Growth

It was considered possible that some of the problems associated with poor film nucleation and some of the subsequent doping problems in the films on low-cost substrates might be related to the co-formation of Cd_3P_2 and InP, the former perhaps being accommodated by a single-crystal surface but not by an amorphous one for which the chemistry and bonding are so different. There has, in fact, been a tendency toward rougher film surfaces when high concentrations of dopant (either Zn or Cd) are present in the growth atmosphere, even on single-crystal substrates.

Therefore, it was decided to determine if it is possible to produce Cd_3P_2 during the growth of InP in an atmosphere of H_2 that is rich in Cd and P. The H_2 flow rate over the DMCd was increased to 100 ccpm (at least ten times that necessary to produce a p-type InP film doped to $\sim 10^{18}$ cm^{-3} on InP) with PH_3 flow rate at 100 ccpm - sufficient to grow InP if TEIn had been admitted into the reactor. Sapphire and 0317 glass, both of which are transparent, were used as substrates to aid in establishing if film growth was occurring.

The reaction was examined first at 600°C and then at ~ 450°C. At both temperatures heavy wall deposits were observed; some discoloration of the substrates occurred at 600°C but none at ~ 450°C, suggesting the reaction was limited by the pyrolysis temperature of PH_3. These results were therefore not conclusive that Cd_3P_2 can be generated by pyrolyzing mixtures of DMCd and PH_3. They did, however, indicate further studies are warranted at

temperatures greater than 450°C at higher concentrations of DMCd and PH_3 to determine if the darkening of the substrates at 600°C was due to the formation of Cd_3P_2 or was impurity related.

2.2 TASK II. MATERIALS CHARACTERIZATION

Materials characterization continued on various thin-film samples during the quarter, using the following principal techniques: (1) Hall-effect measurements by the van der Pauw method; (2) conductivity-type determination by the point-contact rectification (PCR) probe method; (3) surface morphology and structure characterization by SEM examination; and (4) crystallographic characterization by x-ray and electron diffraction analyses. Some of the results obtained in these activities are summarized in this section.

2.2.1 GaP:Zn Films Grown on Polycrystalline Alumina Substrates

As indicated earlier (Section 2.1.2), the lack of success realized in attempting to obtain highly conducting p-type films of GaP:Zn on amorphous substrates prompted a series of experiments to grow GaP:Zn films on polycrystalline substrates of various average grain sizes and evaluate their properties.

The results of measurements of the electrical properties of these films are given in Table 1. Only for the epitaxial film on the sapphire substrate in each of the runs were valid measurements of carrier concentration (and thus of Hall mobility) obtained, and in those cases the transport properties obtained were consistent with the deposition conditions used. The resistivity values obtained for the polycrystalline GaP films on the polycrystalline alumina substrates, however, were also valid and properly indicative of the film properties. Values ranging from 20 to 260 ohm-cm were obtained, and conductivity type in the polycrystalline films was observed to vary greatly

Table 1. Electrical Properties of GaP:Zn Films Grown on Various Substrates

Expt. Seq. No.	Substrate Material	TMGa Flow Rate (ccpm)	PH_3-in-H_2 Flow Rate (ccpm)	DEZn Flow Rate (ccpm)	Depos. Temp (°C)	Film Thickness (μm)	Conductivity Type	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Mobility (cm^2/V-sec)
121	α-Al_2O_3[1]	50	200	20	697	6.9	p	35.7	7.1×10^{17}	0.25
	ASM805[2]						-	32.0	-	-
	HiRel[3]						-	45.2	-	-
	Vistal 4[4]						-	25.6	-	-
120	α-Al_2O_3[1]	50	200	20	724	5.4	p	0.10	6.3×10^{18}	9.5
	ASM805[2]						-	21.5	-	-
	HiRel[3]						-	60.0	-	-
	Vistal 4[4]						-	25.8	-	-
122	α-Al_2O_3[1]	50	100	20	725	7.1	p	0.11	7.0×10^{18}	8.2
	ASM805[2]						-	54.9	-	-
	HiRel[3]						-	110.2	-	-
	Vistal 4[4]						-	69	-	-
119	α-Al_2O_3[1]	50	200	20	760	7.3	p	0.07	7.5×10^{18}	12
	ADS995[3]						-	104	-	-
	ASM805[2]						-	47	-	-
	HiRel[3]						-	259	-	-

1. (0001)-oriented sapphire.
2. Large-grained high-purity alumina manufactured by 3M Co. (refired 4 times).
3. Commercial high-purity aluminas; HiRel manufactured by Materials Research Corp., ADS995 manufactured by Coors.
4. Very-large-grained high-purity alumina manufactured by Coors (refired 4 times).

among films in a given deposition run as well as among various regions of a single film on a given substrate. Clearly, the effectiveness of Zn incorporation in these polycrystalline GaP films is neither very high nor very reproducible - similar to the situation encountered for Zn doping in polycrystalline InP films.

There was some indication that the films prepared in Run No. 122 - in which a lower flow rate of PH_3-in-H_2 was used - were more extensively and uniformly p type, suggesting that lower PH_3:TMGa concentration ratios might be influencing the conductivity type (that is, the Zn doping efficiency) as is observed for changes in the AsH_3:TMGa concentration ratio and the properties of GaAs films grown by MO-CVD on sapphire and GaAs single-crystal substrates. However, it is not clear if this tendency in Run No. 122 was related to such deposition parameter relationships or simply to influences from the substrates. There was no observable effect of the reduced PH_3 concentration on the properties of the epitaxial film on sapphire, for example.

It is also somewhat surprising that the properties of the films grown on the refired large-grained aluminas (Vistal 4 and ASM805) did not more closely approach those of the epitaxial films on sapphire. Studies at Rockwell of the properties of other polycrystalline films as a function of average grain size have shown that polycrystalline films grown on Vistal 4 substrates, especially, tend to have properties that approach those of epitaxial films on sapphire for high doping concentrations, i.e., $>10^{18}$ cm^{-3} (Refs 2,3).

2.2.2 Epitaxial InP:Cd Films on Single-crystal Substrates

The electrical properties of a series of InP:Cd films grown on different orientations of InP:Fe substrates, with variations in dopant flow rates and growth temperatures, were measured by the van der Pauw method. The data are shown in Table 2 and depicted graphically in Figures 1 and 2.

The effect of temperature on the achieved doping concentration is readily apparent in Figure 1. Exponential relationships are seen to exist between the measured hole concentrations (and thus, presumably, the actual

Table 2. Properties of InP:Cd Epitaxial Films Grown by MO-CVD on Various InP:Fe Single-crystal Substrates

Expt. Seq. No.	Substrate Orient.	Depos. Temp (°C)	H_2 Flow Rate over DMCd* (ccpm)	Cond. Type	Resistivity (ohm-cm)	Carrier Conc. (cm^{-3})	Mobility (cm^2/V-sec)
125	(100)	731	25	n	0.021	1.6×10^{17}	1758
	(111B)			n	0.020	1.5×10^{17}	2161
	(111A)			p	0.174	8.1×10^{17}	44
127	(100)	730	50	n	0.014	2.3×10^{17}	1941
	(111B)			n	0.017	1.9×10^{17}	2012
	(111A)			p	0.254	7.3×10^{17}	33
133	(100)	680	10	n	11.1	8.0×10^{15}	71
	(111A)			p	0.23	1.0×10^{18}	26
134	(100)	678	25	p	0.97	1.1×10^{17}	59
	(111B)			n	0.50	1.7×10^{16}	739
	(111A)			p	0.20	1.2×10^{18}	26
128	(100)	684	50	p	2.79	4.0×10^{16}	56
	(111B)			n	0.252	1.6×10^{16}	1557
	(111A)			p	0.129	1.5×10^{18}	33
132	(100)	652	10	p	0.69	1.3×10^{17}	71
	(111A)			p	0.20	1.5×10^{18}	21
136	(100)	645	25	p	0.26	3.4×10^{17}	72
	(111B)			p	0.62	5.6×10^{18}	2
	(111A)			p	0.08	2.7×10^{18}	29
131	(100)	650	50	p	0.14	7.2×10^{17}	64
	(111A)			p	0.066	3.4×10^{18}	28

*TEIn flow rate 2500 ccpm; PH_3 flow rate 200 ccpm; DMCd at 0°C.

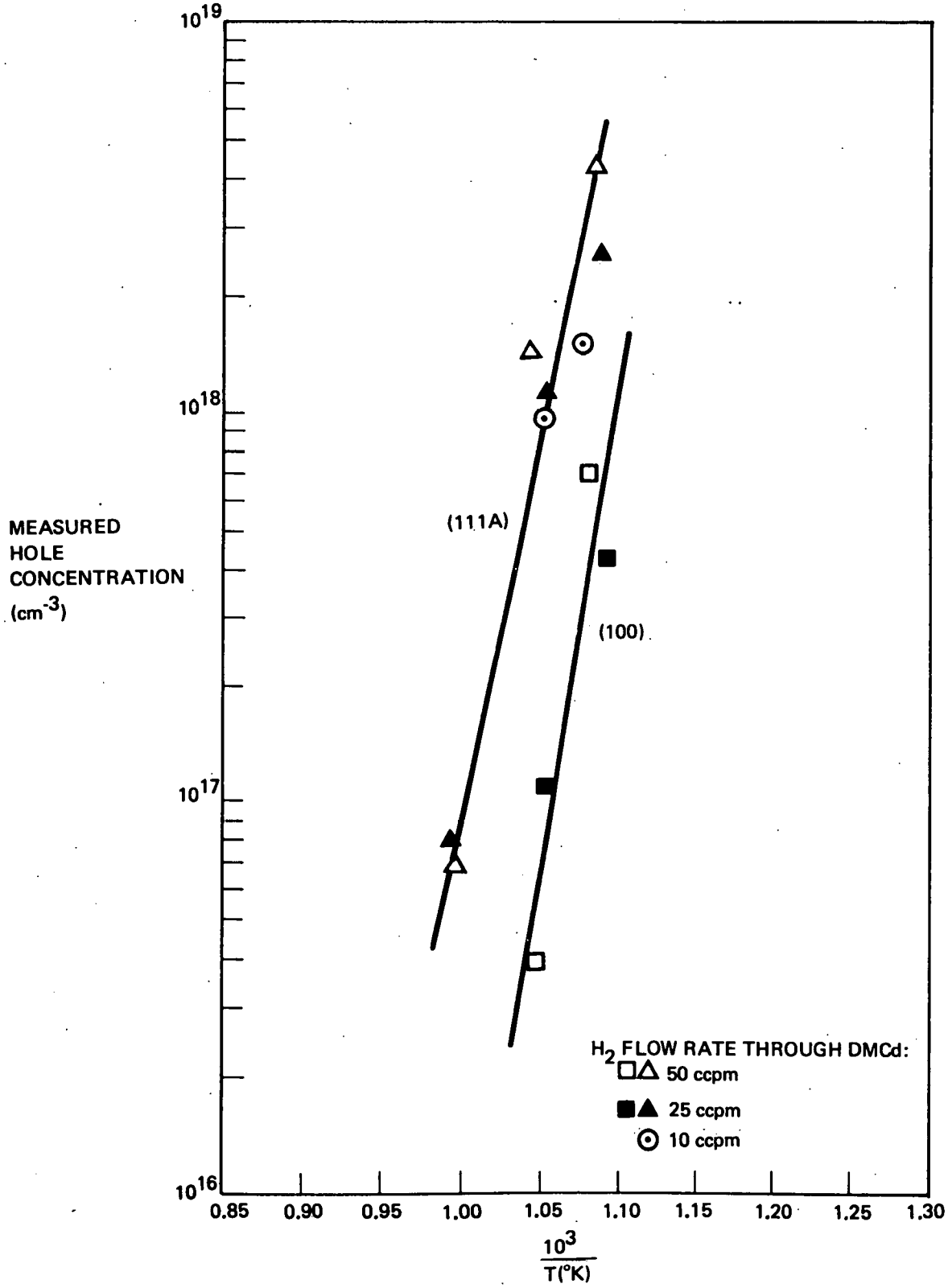

Figure 1 Measured Hole Concentrations in Epitaxial InP:Cd Films Deposited by MO-CVD on Single-crystal InP:Fe Substrates of Two Different Crystallographic Orientations, as Function of Deposition Temperature.

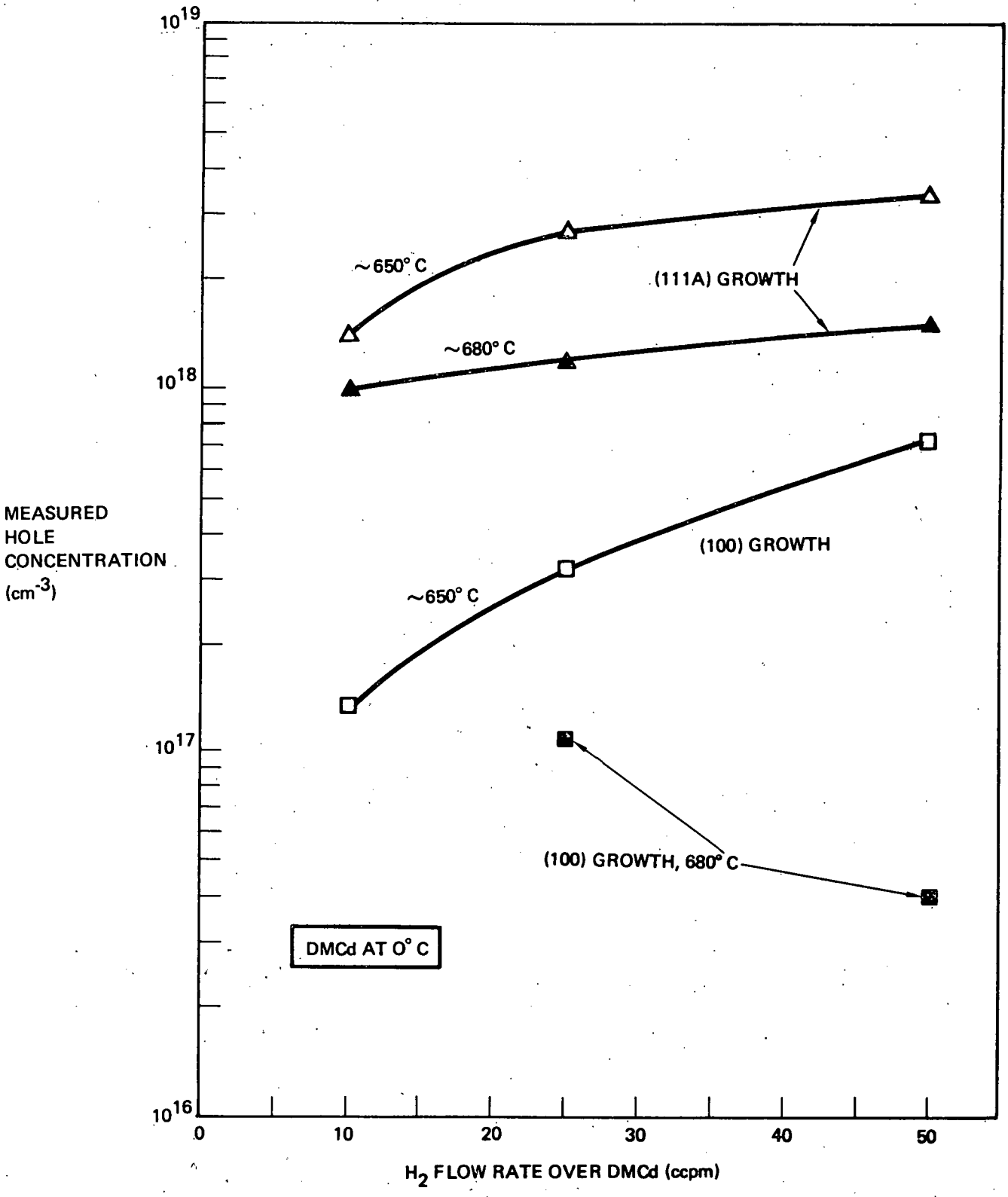

Figure 2. Measured Hole Concentrations in Epitaxial InP:Cd Films Deposited by MO-CVD on Single-crystal InP:Fe Substrates of Two Different Crystallographic Orientations and at Two Different Deposition Temperatures, as Function of H_2 Flow Rate over DMCd (maintained at 0°C).

active Cd concentrations) and the reciprocal of the deposition temperature for film growth on both the (100) and the (111A) orientations of InP. A similar relationship was reported in the earlier studies of Cd (as well as Zn) doping of (111A)-oriented GaAs films grown by MO-CVD on sapphire substrates (Ref 1) although a considerably stronger temperature dependence is found in Figure 1 (slope corresponding to ~ 4 eV) for both orientations than was observed for either Cd (~ 2.8 eV) or Zn (~ 2.1 ev) in the GaAs films.

The highest Cd doping concentrations (mid-10^{18} cm^{-3}) were obtained at the lowest temperature used - about 650°C. At ~ 725°C Cd-doped films were n type on (100) and (111B) InP, with doping levels more typical of background (donor) doping. At ~ 675°C p-type films were obtained on (100) InP:Fe, but they were still n type on (111B) InP. At 650°C the films were p type on all three orientations, but the film quality on the (111B) plane was poor, as expected for this orientation at this growth temperature. As previously indicated, the doping efficiency for Cd was as found earlier for Zn - very orientation dependent and highest for (111A), next for (100), and lowest for (111B).

From Figure 2 it is clear that a gradual doping concentration increase occurs in p-type (111A)-oriented films as the DMCd concentration (flow rate) is increased from 10 ccpm to 50 ccpm for a given growth temperature. The measured values appear to approach saturation for (111A)-oriented films at DMCd flow rates ≥ 25 ccpm. For (100)-oriented films much higher flow rates (even greater than 50 ccpm) are evidently needed to reach saturation. Better doping control is suggested at lower growth temperatures by the limited data shown in Figure 2.

2.2.3 Crystallographic Properties of InP and CdS Films

X-ray diffraction analysis of one of the InP:Zn films grown on a GaP/sapphire composite substrate as described in Section 2.1.2, using the angle-mode programmer with the diffractometer, indicated single-crystal structure in the InP. Polycrystalline InP with no preferred orientation was

obtained on GaP/Mo/alumina, GaP/Mo/0317 glass, and GaP/0317 glass composite structures, however.

SEM photographs of sequentially grown composite structures of InP:Zn/GaP on several substrates (InP deposited at ~ 725°C) are shown in Figure 3. The substrates involved were Mo/0317 glass, Mo/HiRel alumina, and bare 0317 glass. Holes at the GaP/Mo interface are readily apparent in the first two cases, with the apparent grain size on the Mo/HiRel substrate being slightly larger. Simultaneous growth on bare 0317 glass (Figure 3c) produced a very rough surface, with only little indication of any problem at the GaP-glass interface. However, the InP overgrowth appears very disordered on this substrate, and visible voids seem to extend at least to the GaP surface.

In Figures 3a and b the InP-GaP interface is discernible and appears to be relatively flat. Although it is difficult to detect the interface in the photograph, previous examinations of GaP films deposited on 0317 glass substrates have indicated relatively smooth surfaces on the GaP films. It is thus believed that the rough surface seen on the InP films in Figure 3 is a characteristic primarily of the InP:Zn growth itself.

A group of vacuum-deposited CdS films prepared at Stanford (Task III) on various InP surfaces supplied by Rockwell were returned to Rockwell for structural analysis during the quarter. The samples and the conditions of growth are described in the Task III discussion. InP orientations represented were (100), (111A), and (111B). Back-reflection Laue patterns and x-ray diffractometer traces were obtained for all of the samples.

The diffractometer traces showed diffraction lines associated with both the film and the substrate in all cases. The patterns produced by the films on all three orientations indicated the presence of polycrystalline hexagonal CdS.

However, it has not yet been possible to determine with certainty if the films are composed of single-phase hexagonal CdS or of a mixture of the hexagonal and cubic phases, since diffraction lines for cubic CdS (film) are

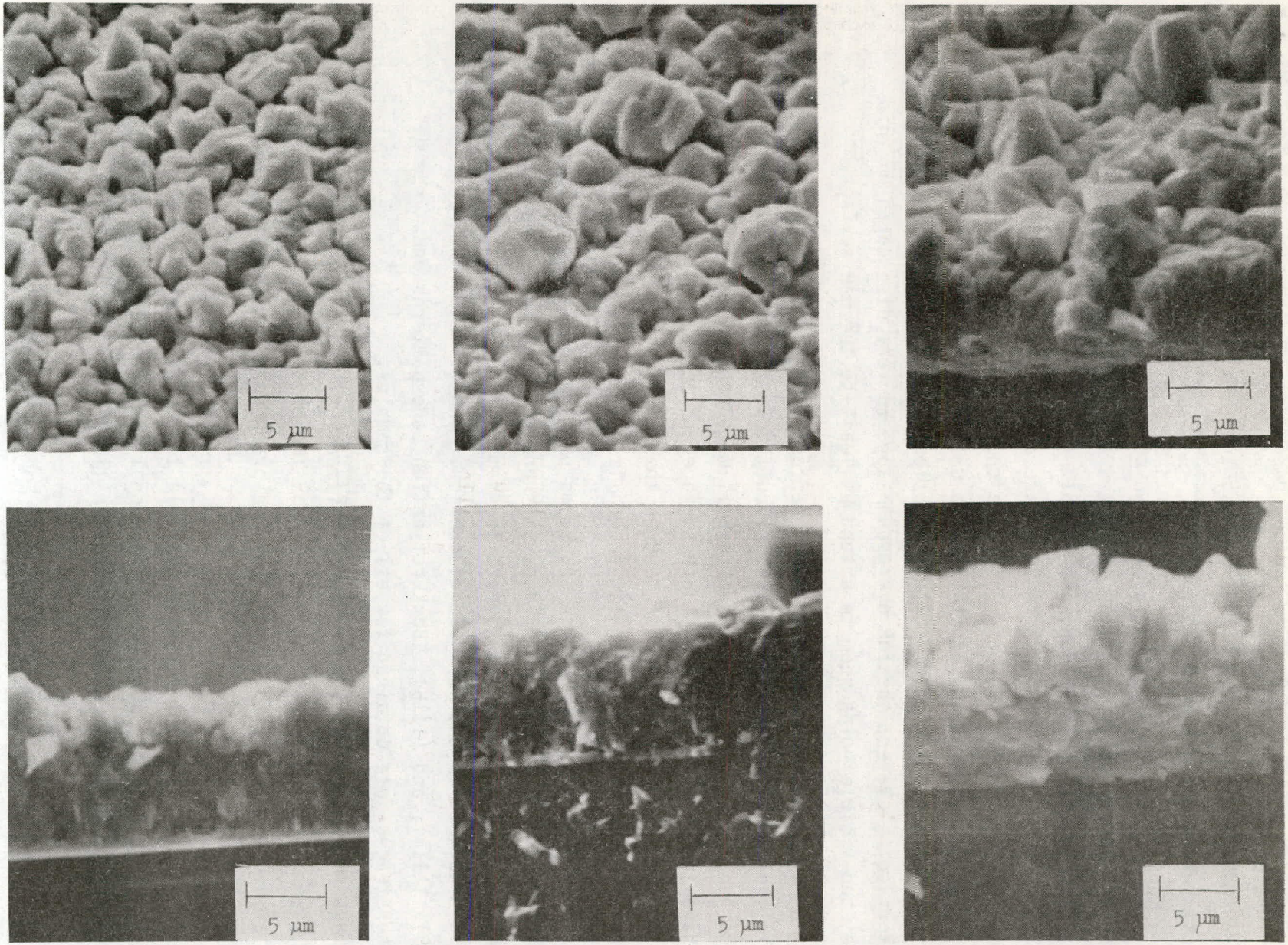

Figure 3 SEM Photograph of Sequentially Grown Multilayer InP:Zn/GaP Structures Deposited by MO-CVD at ~725°C on (a) Mo/0317 Glass (top, 45 deg to surface; bottom, cross-section); (b) Mo/HiRel Alumina (top, 45 deg to surface; bottom, cross-section); (c) Bare 0317 Glass (top, 30 deg to surface; bottom, cross-section).

coincident with diffraction lines for InP (substrate) and are thus indistinguishable without special techniques. Further investigation using such techniques is planned, however, to allow identification of the CdS phases present. Also, reflection electron diffraction analyses of these films will be undertaken to assist in this identification.

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, on the basis of a subcontract extending to the end of the one-year Rockwell contract.

A group of samples of vacuum-deposited CdS films on InP single-crystal wafers and InP films deposited by MO-CVD was prepared at Stanford during the quarter and returned to Rockwell for structural analysis of the CdS (see Section 2.2.3).

The InP substrates (wafers and films) used for the CdS deposition were separated into two groups. A 2-μm-thick film of CdS was deposited on the first group with deposition at a rate of 0.2 μm/min using a substrate temperature of 300°C. Seven InP samples were included in this deposition: two consisted of InP:Fe polished single-crystal substrates with orientations of (111B) and (100); the others were (100)-, (111A)-, and (111B)-oriented InP films grown by MO-CVD on InP substrates at Rockwell.

For the second group of samples, In was coevaporated with the CdS to grow films 3 μm thick at a rate of 0.3 μm/min with a substrate temperature of 300°C. Four InP film samples representing the three different orientations were included in this run. The resistivity of a film of CdS evaporated on a glass slide during this deposition was measured to be 3×10^{-3} ohm-cm, indicating a carrier density of about 10^{19} cm^{-3}. This is higher than would have been predicted from previous experiments done under what was believed to be the same conditions, probably due to difficulties that had been experienced with one of the thermocouples in the deposition apparatus.

The principal contract activity at Stanford during the quarter involved the processing and characterization of a group of CdS/InP heterojunction solar cell structures, using vacuum-deposited CdS and p-type epitaxial InP films previously deposited by MO-CVD at Rockwell on p^+InP:Zn single-crystal substrates.

Six nCdS/pInP/p^+InP cell structures were fabricated, utilizing InP film samples identified by Rockwell deposition experiment numbers 48, 49, 53, and 63. Each sample had an ohmic Au/Zn/Au contact deposited onto the back surface and then was annealed in H_2 for 2 min at 475°C to "form" the contact. The samples were prepared for CdS evaporation by etching in 1 percent Br-methanol for about 30 sec (except for sample 53-1, which was etched for about 1 min).

The samples were separated into two groups. Samples in the first group (49-2, 53-1, 63-2) were heated to 300°C in a vacuum of 3×10^{-7} torr, and CdS was vacuum-evaporated onto them. Two layers of CdS were deposited; the first layer was deposited at a rate of about 0.3 μm/min for 10 minutes and was doped with In, with the intention of providing an electron density of about 10^{18} cm^{-3}. A second thinner layer was then deposited with a greater In density, about 10^{19} cm^{-3} being intended. Indium front contacts were then deposited onto the CdS.

The CdS deposition for samples in the second group (48-1, 49-1, and 63-1) was similar to that described above for the first group of samples, but the substrates were held at 250°C during the deposition. Optical measurements of the thickness of CdS layers deposited on glass slides at the same time indicated a thickness of 3 μm for the first CdS layer and 1.8 μm for the second CdS layer.

A summary of room-temperature photovoltaic properties obtained for these cells is given in Table 3. The high values of J_0 and the low values of fill factor found in all these cells resulted in efficiencies in the 2-5 percent range.

Table 3. Photovoltaic Properties of nCdS/pInP/p^+InP Heterojunction Solar Cells Fabricated* at Stanford

Cell No.†	Substrate Temp. (°C)	V_{oc} (volts)	J_{sc} (mA/cm^2)**	Fill Factor	Solar Efficiency (AM1.5) (percent)**	J_o (A/cm^2) (300°K, dark)	Diode Factor (300°K, dark)
49-2	300	0.46	15.8	0.43	3.6	4.9×10^{-5}	3.77
53-1	300	0.34	15.4	0.38	2.3	6.2×10^{-5}	3.14
63-2	300	0.43	11.4	0.40	2.3	2.1×10^{-5}	3.64
48-1	250	0.53	15.1	0.49	4.6	5.3×10^{-5}	4.55
49-1	250	0.47	16.6	0.43	4.0	4.9×10^{-5}	3.77
63-1	250	0.45	10.2	0.44	2.4	1.1×10^{-5}	2.99

*For substrates at 300°C, CdS layer 3.0 μm thick with resistivity of 12 ohm-cm was covered with CdS layer 1.8 μm thick with resistivity of 0.6 ohm-cm. For substrates at 250°C, CdS layer 3.0 μm thick with resistivity of 2 ohm-cm was covered with CdS layer 1.8 μm thick with resistivity of 0.5 ohm-cm. Values of CdS resistivity for first layer obtained from measurements of layers on glass slides.

**Active cell area used in calculating J_{sc} and efficiency.

†Data on pInP:Zn layers (measured at Rockwell) as follows:

Deposition Sequence No.	Film Thickness (μm)	Carrier Conc. (cm^{-3})	Carrier Mobility (cm^2/V-sec)
48	7	3.7×10^{17}	25
49	3	1.4×10^{18}	12
53	8	3.7×10^{17}	14
63	8	3.0×10^{17}	14

The cells will be more fully characterized in the coming quarter, and the effects of various heat treatments will be investigated. Other heterojunction cell structures, especially using polycrystalline InP films grown by MO-CVD, will also be fabricated and characterized.

3. SUMMARY AND CONCLUSIONS

Experiments continued in the third quarter on development of the MO-CVD process for use in preparing device-quality polycrystalline InP films on low-cost substrate materials. The main emphasis of these studies was on continuation of the evaluation of GaP as an intermediate layer material for the subsequent growth of InP films on various substrate materials and on examination of Cd, obtained from dimethylcadmium (DMCd), as a p-type dopant for InP films made by the MO-CVD process.

The experiments relating to GaP as a possible intermediate layer material were mostly directed at finding means for producing a p^+GaP layer directly on a low-cost substrate. Various approaches were tested, including (1) direct deposition in a Zn-containing atmosphere, as a function of various deposition parameters; (2) annealing a previously grown film in a H_2 atmosphere containing DEZn; and (3) even the use of a sheet of galvanized iron as a possible solid source of Zn dopant. Conditions that produced epitaxial p^+GaP films ($p \sim 5 \times 10^{18} - 1 \times 10^{19}$ cm^{-3}) on single-crystal sapphire did not produce conductive GaP films on amorphous substrates, however. The results of GaP:Zn growth on polycrystalline alumina substrates of various grain sizes were somewhat more encouraging in terms of conductivity type determinations by the PCR probe test, but van der Pauw measurements showed the films to be too high in resistivity (20-100 ohm-cm) to be useful as conducting intermediate layers. In the case of the attempt at doping GaP by contact with galvanized iron sheet at elevated temperature, there was no indication of enhanced conductivity except in areas where the sheet had actually stuck to the GaP layer as the result of local melting or similar localized interaction. It was decided that the investigation of GaP should not be continued further in this program.

In the evaluation of Cd as an acceptor dopant for InP it was found that Cd from DMCd behaves in epitaxial InP films much as it was found to do as an acceptor in GaAs films. That is, the effective doping concentration varies

exponentially with the reciprocal of the deposition temperature, in a manner suggesting that the Cd vapor pressure in the environment of the growing InP film may be a controlling factor, although the dependence of incorporated active dopant upon temperature is considerably stronger than that of the vapor pressure of Cd, so this is clearly not the only controlling factor. It was also found that at temperatures that permit the formation of good quality (111B)InP (i.e., 675-730°C), only n-type films were obtained on (111B)InP, but p-type films could be generated on (111A)InP over the entire temperature range studied (650-730°C), while p-type films were obtained on (100)InP only at intermediate temperatures (650-680°C) and not at 730°C. The same relative ease of dopant incorporation for various growth orientations was obtained for Cd doping as had been found for Zn doping in InP: (111A)>(100)>>(111B). However, at any given deposition temperature Zn appears to be more extensively incorporated into InP films than does Cd, again possibly due to the relative vapor pressures of the two metals at the deposition temperatures. It has been concluded, therefore, that Cd offers no clear advantages over Zn as an acceptor dopant. In particular, since Cd did not result in highly conducting polycrystalline InP films on low-cost substrates the experiments with Cd-doped layers were discontinued.

Some further examination of possible mechanisms involved in the Cd doping process was undertaken briefly during the reporting period. At high doses of DMCd in the growth stream some deterioration of the surface structure of the films had been observed. To test if this could be due to the formation of Cd_3P_2, for example, during the growth of Cd-doped InP, two experiments were carried out in which concentrations of DMCd ~ 10 times higher than normal for doping were pyrolyzed with PH_3 at temperatures of 600°C and ~ 450°C. At 600°C some darkening of a sapphire wafer occurred; at ~ 450°C, a sapphire substrate viewed under normal optical magnifications appeared to be essentially free of any deposit. The deposit at 600°C was very sparse, and it was not clear whether it was due to a DMCd-PH_3 reaction or to pyrolysis of residual contaminants in the reactants or in the reactor system. A heavy deposit formed on the chamber wall at temperatures even as low as 450°C, suggesting

the wall deposit to be Cd; failure to produce a deposit on the substrate may have been due to the limited amount of phosphorus produced at that temperature in a kinetic system. These results indicated further studies of such growth are probably warranted using larger amounts of DMCd in the gas stream, that is, with a carrier gas saturated with DMCd vapor rather than one that only passes over the liquid and sweeps up the vaporized compound.

An examination of the crystallographic structure of the vacuum-deposited CdS films prepared at Stanford for use in forming CdS/InP heterojunction solar cells was undertaken by x-ray diffraction analysis during the quarter. Films grown on both single-crystal InP wafers and single-crystal InP films grown by MO-CVD at Rockwell were characterized. The initial results indicate the presence of polycrystalline hexagonal CdS on all three crystallographic orientations of InP involved - (100), (111A), and (111B). If the CdS films examined are typical of those that have been used in producing the high-efficiency CdS/InP solar cells obtained in the earlier Rockwell-Stanford contract work (Ref 4) or in other investigations of this particular cell configuration (in other laboratories), then the question again is raised of the possible formation of a very shallow homojunction - caused perhaps by diffusion of S from the polycrystalline CdS into the p-type InP - rather than a true heterojunction of good structural quality, as has been previously thought to be the case.

A group of CdS/InP heterostructure cells, using vacuum-deposited CdS and p-type epitaxial InP films grown by MO-CVD, was prepared at Stanford during the quarter. High J_o values and low fill factors were obtained in all of this group of cells, so that efficiencies (~ AM1.5) of only 2-5 percent were realized. More complete characterization of these cells and fabrication and characterization of additional single-crystal cells and new polycrystalline cells will be undertaken in the coming quarter.

It now appears that other techniques must be examined for inducing p-type polycrystalline InP film growth directly on low-cost substrates. A return to the use of heavily doped p^+GaAs:Zn intermediate layers on various

substrates, shown in earlier studies (Ref 4) to be effective in permitting the achievement of doped p-type polycrystalline InP films, may be indicated. The results obtained during this quarter have provided a better understanding of the MO-CVD process for InP growth for the present application, but the discouraging results indicate that fabrication of good quality polycrystalline CdS/InP solar cells using this process will be further delayed.

4. PLANS FOR NEXT QUARTER

The planned activities for the fourth quarter include the following:

Task I Continue study of techniques for preparing p-type InP polycrystalline films on suitable low-cost substrates; explore various growth techniques for encouraging better nucleation and growth of polycrystalline InP layers on low-cost substrates; prepare InP:Zn films on GaAs:Zn intermediate layers for subsequent CdS/InP solar cell fabrication and evaluation; evaluate He as carrier gas in this MO-CVD system.

Task II Continue routine characterization of structural and electrical properties of InP films on various substrates; complete evaluation of structural quality of CdS/InP composites prepared at Stanford and attempt to relate this to solar cell performance.

Task III Explore techniques for improving quality of CdS/InP heterojunction structures; prepare and characterize heterojunction solar cell structures on InP films grown by MO-CVD.

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5. REFERENCES

1. H. M. Manasevit and A. C. Thorsen, J. Electrochem. Soc. 119, 99 (1972).

2. R. P. Ruth et al, "Chemical Vapor Deposition Growth," JPL Contract No. 954372, Final Report (for period December 19, 1975, to August 31, 1977); Rockwell International, Electronic Devices Division, Electronics Research Center, Anaheim, CA 92803; also, R. P. Ruth et al, 19th Electronic Materials Conference, Ithaca, NY, June 29-July 1, 1977, Paper No. H7.

3. R. P. Ruth et al, "Thin Films of Gallium Arsenide on Low-cost Substrates," DoE Contract No. EY-76-C-03-1202, Final Report (for period July 5, 1976, to December 5, 1978); Rockwell International, Electronic Devices Division, Electronics Research Center, Anaheim, CA 92803; also J. J. J. Yang, P. D. Dapkus, R. D. Dupuis, and R. D. Yingling, to be published in Journal of Applied Physics, 1980.

4. R. P. Ruth, P. D. Dapkus, H. M. Manasevit, K. L. Hess, A. G. Campbell, R. E. Johnson, L. A. Moudy, and J. J. J. Yang, "Thin Polycrystalline Films of Indium Phosphide on Low-cost Substrates," Final Report, April 1978, Rockwell International, Electronics Research Center, Anaheim, CA 92803. Contract No. EY-76-C-04-3727, Division of Solar Technology, U. S. Department of Energy.

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