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INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

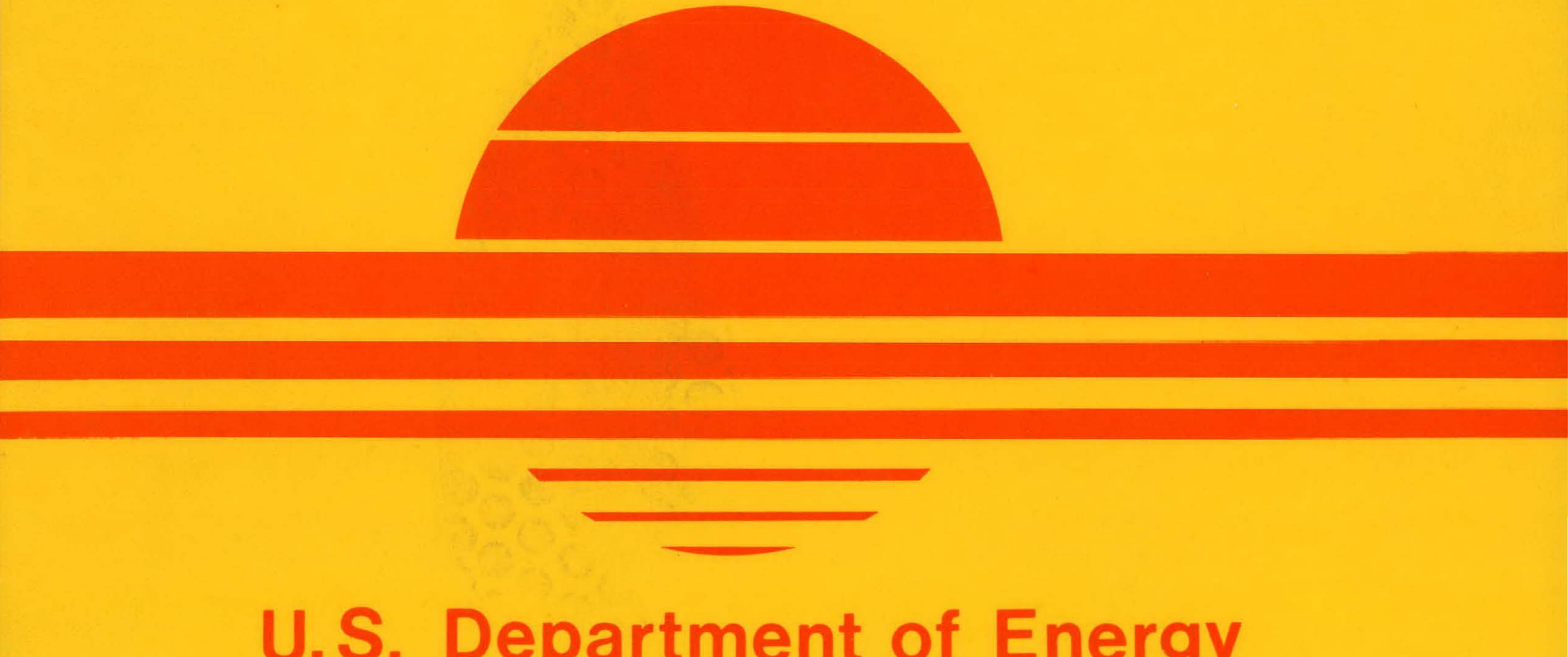
Quarterly Technical Progress Report No. 2, September—November 1979

By
K. Zanio

March 1980

Work Performed Under Contract No. EG-77-C-01-4042

Hughes Research Laboratories
Malibu, California



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March 1980

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FOREWORD

This report was prepared by Dr. Kenneth Zanio of the Hughes Research Laboratories (Malibu, California), a division of Hughes Aircraft Company, for the Photovoltaic Branch of the Division of Solar Energy of DOE under contract XJ-9-8170-1. The technical monitors were Drs. Kim Mitchell and Richard Nottenburg at SERI in Golden, Colorado.

The program is being undertaken by personnel in the Chemical Physics Department under the supervision of Mr. M. Braunstein, Dr. R. Knechtli, and Dr. G.S. Picus. The program manager is Dr. Zanio. Principal investigators are Dr. Zanio and Mr. F. Krajenbrink. Important contributions to the program were made by Messrs. P. Hoberg and H. Montano.

ABSTRACT

Thin-film InP/CdS structures were prepared by depositing, in sequence, ITO on a low-cost glass substrate, CdS on the ITO by thermal evaporation, and InP on the CdS by planar reactive deposition (PRD). Films of CdS, 15 μm thick, were recrystallized in flowing H_2/H_2S at 500°C. Lateral dimensions of typical grains were 50 μm with values up to 200 μm. The sheet resistance of the recrystallized CdS (RXCdS) was lowered from greater than 10^5 Ω/□ to values as low as 16 Ω/□ by annealing in either H_2 or Cd atmospheres. Epitaxy of InP was undertaken on (100) InP at a substrate temperature of 320°C. Room-temperature electron mobilities of about 2000 cm^2/V-sec were found. Mobilities and hole concentrations of 60 cm^2/V-sec and 10^{17} cm^{-3}, respectively, were achieved with Be-doped films. P-type films with hole concentrations as high as a few times $10^{18} cm^{-3}$ were achieved with increased doping.

Be-doped InP was deposited onto the RXCdS/ITO/GLASS substrate to form a thin-film cell. However, p-type InP could not be prepared with CdS as a substrate, presumably due to interdiffusion or vapor transport of sulfur. Consequently, blocking action and a photovoltage could only be achieved using a gold Schottky barrier on the InP/RXCdS/ITO/GLASS structure. Plans for the next quarter include determining whether n-type doping from the CdS occurs by either interdiffusion or vapor transport, characterizing InP epitaxy on the RXCdS, and preparing additional thin-film structures.

SECTION 1

INTRODUCTION

The InP/CdS system is interesting to investigate because air mass two (AM2) efficiencies of 15% have been obtained for the single-crystal system. Although efficiencies of only 5% have been obtained for the polycrystalline thin-film system, studies directed toward passivating the grain boundaries and enhancing the grain size may prove successful and may result in increased efficiencies. Normally, the all-thin-film structure is prepared by depositing InP on either Mo or graphite and subsequently depositing the CdS on the InP. Recently, it has become clearer that the effect of the substrate (which has to be low cost) on the photovoltaic properties of semiconductor layers grown on top of it is critical. Our approach in developing the InP/CdS thin-film system is to deposit CdS on a low-cost ITO/GLASS substrate and replicate larger recrystallized CdS grains with a 1-μm-thick InP layer. Advantages of this reverse approach include a minimum use of InP and a reduced grain boundary surface density. Introducing this approach required the development of a technique for depositing InP at low temperatures to prevent the dissociation of CdS. The planar reactive deposition (PRD) technique was developed under contract EY-76-C-0403717 with the Department of Energy to meet this need. In that program, we prepared single-crystal CdS-on-InP cells using PRD-prepared InP as the light-absorbing layer. Efficiencies of up to 10% were obtained. In this program, we are continuing these studies, the primary goal being to prepare the InP-on-CdS-on-glass thin-film structure. Polycrystalline CdS serves as the basis of this structure. During this quarter, we prepared large-grained, low-resistivity CdS on ITO/GLASS substrates. The properties of these films are discussed in Section 2. Because severe interdiffusion occurs when InP is vacuum evaporated on polycrystalline CdS at elevated temperatures, it is desirable to lower the substrate temperature but yet achieve single-crystal epitaxy with good transport properties. During this quarter, we prepared single-crystal InP films at substrate temperatures of 320°C. In Section 2, we also discuss the transport properties of the unintentionally doped and Be-doped films as well as our first thin-film-cell results using recrystallized CdS. During our studies this quarter, we encountered n-type doping of our p-type InP films, presumably due to the incorporation of S. Plans for alleviating S-doping and further developing the all-thin-film structure are discussed in Section 3.

SECTION 2

TECHNICAL PROGRESS

A. RXCdS/ITO/GLASS SUBSTRATE

During the last quarter, CdS films were thermally deposited on ITO/GLASS substrates. Films were recrystallized, but the lateral dimensions of the recrystallized grains were less than 10 μm. During this quarter, we achieved a significant increase in the grain size and a significant decrease in the resistivity of the grains. Figure 1(a) shows an optical photograph of a 15-μm-thick undoped CdS film thermally evaporated onto an ITO/GLASS substrate at 200°C. The reflection of unpolarized light shows the grain size to be about 1 μm. The structure was then heat treated in flowing H_2S for 30 min at 525°C. The average grain size of this sample increased to about 30 μm (Figure 1(b)) with some grains having lateral dimensions up to 0.1 mm. Figure 1(c) shows another photograph of the RXCdS film with reflected polarized light. Again, the average grain size is seen to be about 30 μm. In some of our more recently recrystallized CdS layers, we have been able to observe even larger grain sizes than those shown in Figure 1. Presently, the lateral dimensions of the grains range from 20 to 200 μm, which meets the original objective of this program.

The optical properties of these recrystallized films have not yet been evaluated. However, from a visual inspection, the optical properties of the RXCdS/ITO/GLASS structure are quite good. At present, the mechanism of recrystallization is not well understood. It is not known whether or not impurities play an important role in the recrystallization process. Therefore, Auger analysis of the grain boundaries may prove helpful.

Electrical measurements subsequent to recrystallization showed these films to have resistivities of about 10^5 Ω-cm. Subsequent annealing of the films in 10% H_2/90% Ar at 500°C for about 30 min reduced the resistivity only an order of magnitude. However, resistivities of less than 1 Ω-cm were achieved by annealing in pure H_2. Because of the danger of annealing in pure H_2, we investigated the alternative method of lowering the resistivity by annealing RXCdS films at 500°C in Cd overpressures.

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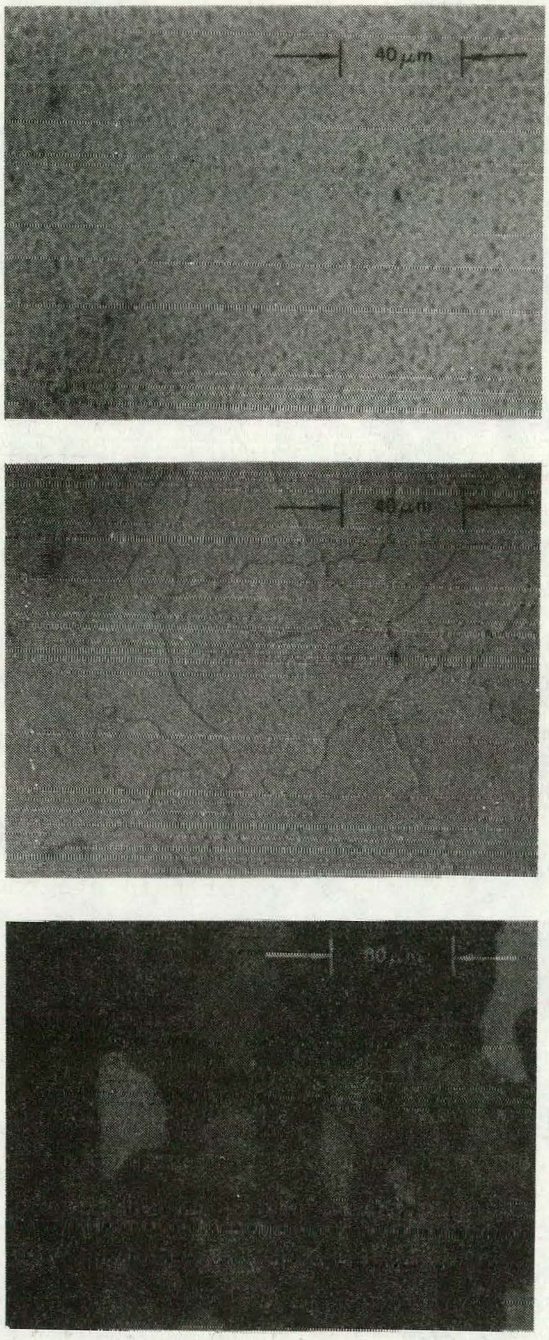


a) THERMALLY DEPOSITED (UNPOLARIZED LIGHT)

b) RECRYSTALLIZED (UNPOLARIZED LIGHT)

c) RECRYSTALLIZED (POLARIZED LIGHT)

Figure 1. Optical photographs of CdS films (a) thermally deposited and viewed with reflected unpolarized light, (b) recrystallized and viewed with reflected unpolarized light, and (c) recrystallized and viewed with reflected but polarized light.

The sheet resistance of the annealed films again dramatically decreased to values ranging between 15 and 150 Ω/□. Although the resistance of these films is no lower than the resistance of films annealed in flowing H_2, low-resistivity material is more consistently obtained.

The lowest resistivity and corresponding sheet resistance for a 15-μm-thick film were, respectively, 0.023 Ω-cm and 16 Ω/□. Typical sheet resistances were 40 Ω/□. Three H_2 and three Cd-overpressure runs were undertaken to lower the resistivity of the RXCdS; all were successful. We also measured the sheet resistance of the ITO both after the recrystallization process and after reducing the resistivity of the RXCdS films. After recrystallization, the resistivity of the ITO exposed directly to the H_2S is extremely high. However, the sheet resistance under the CdS cap is relatively unchanged and increased by less than a factor of two, from about 100 Ω/□ to less than 200 Ω/□. The resistance of the ITO films does not appear to change appreciably after the resistivity of the CdS is lowered. Table 1 summarizes the processing steps that result in low-resistivity RXCdS films. The locations where resistance measurements are made on the films are shown in the structure at the bottom of the table. The RXCdS films peeled severely from the glass during one of the runs. Since peeling might be due to water vapor in the system, we took precautions in subsequent runs to drive water vapor out of our system before annealing. Although peeling did not occur again, we have not yet confirmed that water vapor caused the peeling in the prior run.

B. InP LAYERS

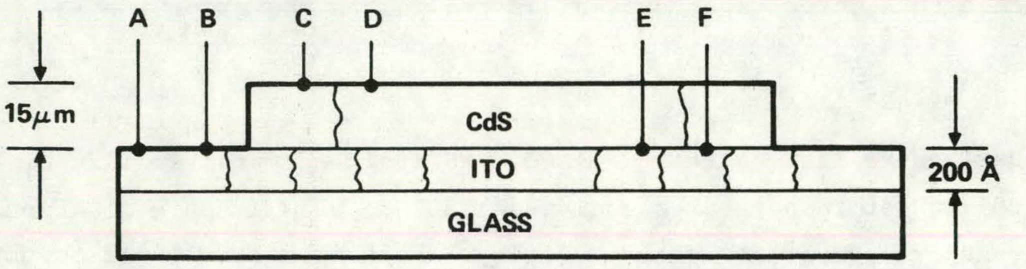
During the last quarter, we achieved single-crystal epitaxy of InP on (100) InP at temperatures as low as 260°C. We began an evaluation of the transport properties of these films. Further measurements on unintentionally doped and Be-doped films were made during this quarter.

The transport mobilities for our unintentionally doped InP films prepared by PRD are plotted in Figure 2 along with the electrical properties of other unintentionally doped InP films prepared by other vacuum technologies. At 260°C, the highest electron mobilities were 1500. At 315°C, the mobilities increased to 2000 cm^2/V sec. In agreement with

Table 1. Processing Steps Used to Prepare Low-Sheet-Resistance RXCdS/ITO/GLASS Substrates

9319–3 R1

STRUCTURE	Ω/□	LOCATION OF MEASUREMENT	PROCESS	PROCESS °C
ITO/GLASS	80	ITO (A-B)	REACTIVE E-BEAM EVAPORATION OF ITO	400
CdS/ITO/GLASS	≈ 100	CdS (C -D)	THERMAL EVAPORATION OF UNDOPED CdS	200
RXCdS/ITO/GLASS	4×10^5	CdS (C-D)	ANNEAL IN FLOWING H_2/H_2S	500
	≈ 150	ITO (E-F)		
	$> 10^7$	ITO (A-B)		
RXCdS/ITO/GLASS	4×10^4	CdS (C-D)	ANNEAL IN FLOWING 10% H_2/Ar	450
	≈ 150	ITO (E-F)		
	$> 10^7$	ITO (A-B)		
RXCdS/ITO/GLASS	15–1000	CdS (C-D)	ANNEAL IN PURE H_2	450
	≈ 150	ITO (E-F)		
	$> 10^7$	ITO (A-B)		
RXCdS/ITO/GLASS	15–150	CdS (C-D)	ANNEAL IN Cd	500
	≈ 150	ITO (E-F)		
	$> 10^7$	ITO (A-B)		



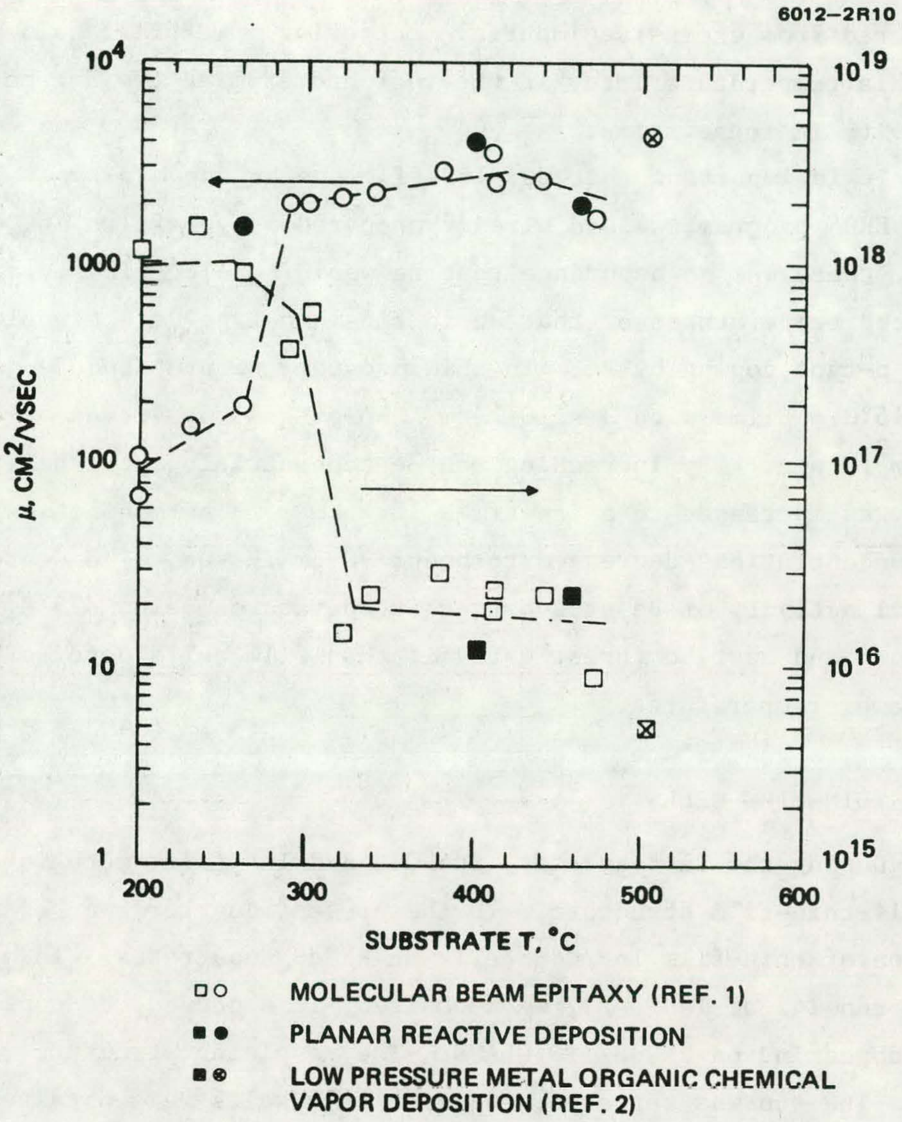


Figure 2. Electrical properties of unintentionally doped InP films prepared by vacuum technologies on InP substrates.

results from molecular beam epitaxy,[1] the mobility increases with increasing substrate temperature except for our measurement at 460°C. This latter measurement was performed early in our program and may have suffered from excessive impurity scattering. We will again prepare films at this temperature later in the year and examine the degree of electrical activity in these films.

It is important that our InP film can be doped p-type. In an earlier ERDA program, we had already prepared p-type films at 340°C. However, there was no assurance that Be would be electrically active at reduced temperatures or that an intrinsic n-type defect would not override p-type doping by Be. In this program, we prepared Be-doped films at 315°C. Films with 3×10^{17} cm^{-3} holes had mobilities of about 60 cm^2/V sec. By increasing the Be concentration, the hole concentration was increased to a few times 10^{18} cm^{-3}. The mobilities at higher Be concentrations decreased to about 20 cm^2/V sec. The degree of electrical activity of Be at substrate temperatures below 315°C is still unknown and must be investigated if thin-film cells need to be prepared at lower temperatures.

C. THIN-FILM CELLS

During the last quarter, the CdS and InP films were integrated into an all-thin-film structure. In the present quarter, we began the fabrication of thin-film InP/CdS cells on RXCdS substrates. In our first run (see run 142 of Table 2), we deposited, in sequence, Be-doped InP and Be^+ doped InP on RXCdS/ITO/GLASS. The resulting structure was nonblocking. The run was repeated, and similar results were obtained. Suspecting contamination of the deposition system, we replaced the sources. We replaced the Be-doped right-hand source with an undoped source. On the right-hand side (RHS), InP was deposited on semiinsulating InP. As expected, the layers were n-type. We also replaced the Be-doped left-hand source with a similar Be-doped source. On the left-hand side (LHS), InP was deposited on semiinsulating InP and RXCdS. The layers on the InP and presumably those on the RXCdS were also n-type. Sulfur from the CdS apparently overcompensated the Be, resulting in n-type InP. As

Table 2. Summary of Processing Results for InP Deposited on RXCdS and High-Resistivity InP by PRD

9422–4

RUN	DEPOSITION POSITION	InP DOPANT	SUBSTRATE	HALL MEASUREMENTS			I – V RESULTS
				TYPE	cm^{-3}	$(cm^2/Vsec)$	
141	RHS	Be	Hi ρ InP	p	3×10^{17}	64	
	LHS	Be^+	Hi ρ InP	p^+	2×10^{18}	20	
142	LHS/RHS	Be^+/Be	RXCdS/ITO/GLASS				NON-BLOCKING
143	LHS/RHS	Be^+/Be	RXCdS/ITO/GLASS				NON-BLOCKING
145	RHS[a]	NONE	Hi ρ InP	n	4×10^{17}	1957	
	LHS[b]	Be	RXCdS/ITO/GLASS				NON-BLOCKING (In SCHOTTKY)
		Be	Hi ρ InP	n	6×10^{17}	875	
146	RHS	NONE	Hi ρ InP	n	3×10^{17}	1925	
	LHS[b]	Be	RXCdS/ITO/GLASS				NON-BLOCKING (In SCHOTTKY)
		Be	Hi ρ InP	n	7×10^{17}	837	
147	RHS	NONE	Hi ρ InP	n	3×10^{17}	2101	
	LHS	Be	RXCdS/ITO/GLASS				BLOCKING (Au SCHOTTKY)
		Be	Hi ρ InP	n	8×10^{17}	703	

a - CHANGED TO UNDOPED SOURCE

b - REPLACED Be DOPED SOURCE

+ - $> 10^{18}$ Be/cm^3

expected, blocking action was not found when In Schottky barriers were deposited on the InP. Similar results were found in two subsequent runs. However, blocking action occurred when Au Schottky barriers were used (Figure 3). As expected, the light and dark characteristics for this Schottky diode are poor because holes must diffuse from the InP/CdS interface to the Schottky barrier, and the high p-type doping in the InP probably results in excessive tunneling currents at the junction.

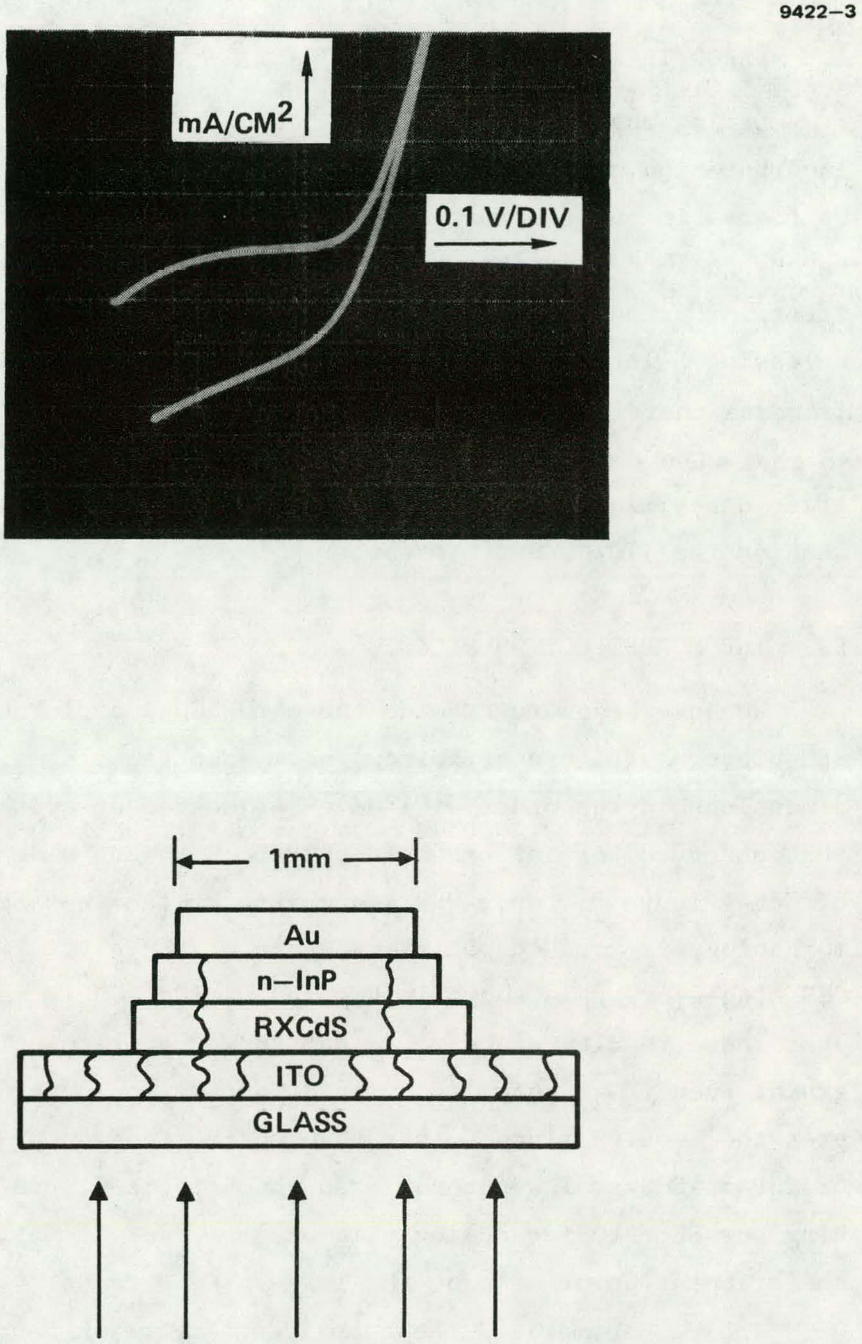


Figure 3. Dark and light I-V characteritics (top) of Au (Schottky barrier)/n-InP/RXCdS/ITO/GLASS device (bottom).

SECTION 3

FUTURE WORK

A. VAPOR TRANSPORT OF SULFUR

During the next quarter, we intend to concentrate on preventing the incorporation of sulfur via vapor transport into our p-type InP films. Up to now in our fabrication of thin-film cells, we deposit an InP film through a 1-cm-diameter mask onto a larger 1.5-cm-diameter RXCdS substrate. During InP deposition, the shielded CdS outgasses, presumably releasing S into the deposition chamber. In our future runs, we will decrease the diameter of the RXCdS substrate on the ITO/GLASS substrate so that when deposition occurs it will cap the RXCdS as shown in Figure 4. After deposition, the structure will be etched, leaving an InP/RXCdS mesa on the ITO/GLASS substrate.

B. InP MORPHOLOGY ON RXCdS

We have begun to examine the morphology of InP on RXCdS. The first SEM pictures (Figure 5, bottom) show some faceting with characteristic dimensions on the order of 1 μm. The degree of epitaxy is inferior to that observed for InP prepared by PRD on the Cd side of single crystals of CdS (Figure 5, top), where complete epitaxy has been achieved. The morphology is more compatible to that of the partial epitaxy of InP on CdS single crystals shown in Figure 5, middle. It is difficult to interpret these results since we do not know the orientation of this RXCdS grain. Even if we knew its orientation, we would not know how to interpret the results since, other than on the Cd-face of CdS, the morphology of InP on CdS grains has not been characterized. In addition to continuing our SEM studies during this program, we will attempt to determine the orientation of some of the large RXCdS grains.

Table 3 summarized the epitaxy of InP on InP and CdS substrates by PRD. It is evident that little is known regarding the epitaxy on RXCdS. We anticipate continuing these studies during next quarter.

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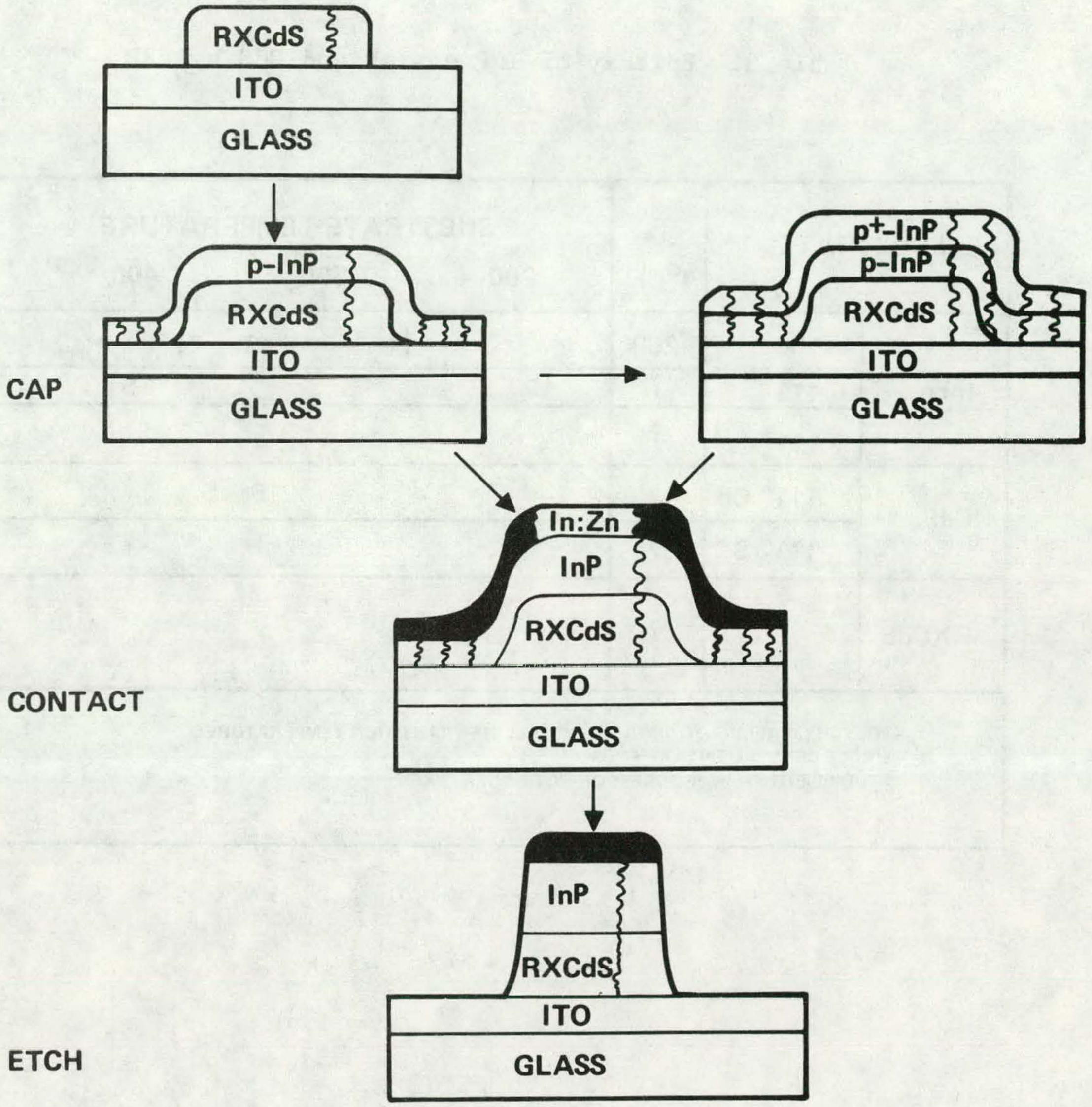

Figure 4. Capping/etching scheme to eliminate sulfur doping via vapor transport.

Table 3. Epitaxy of InP on InP and CdS by PRD

9422–23

SUBSTRATE		T_R (^{o}C)	SUBSTRATE TEMPERATURE		
			200	300	400
InP	100	260		|← S →|	
	$\overline{111}$	?			S
	111	?			
CdS	"111" Cd	?		S	
	"111" S	?			
RXCdS		?		?	

T_R – POLYCRYSTALLINE TO SINGLE CRYSTALLINE TRANSITION TEMPERATURE
S – SINGLE CRYSTAL EPITAXY FOUND
? – STUDIES EITHER IN PROGRESS OR NOT UNDERTAKEN

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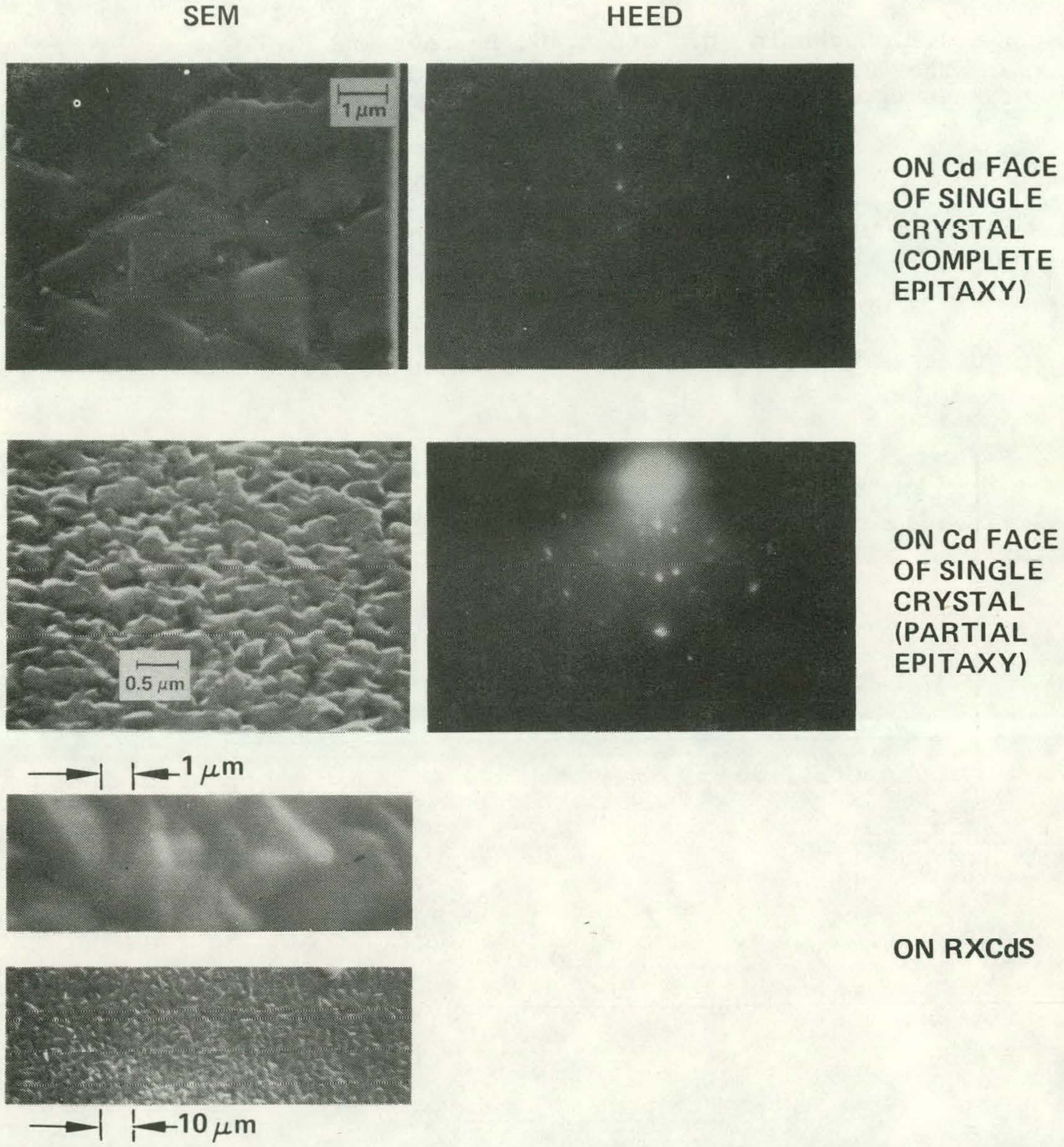

Figure 5. SEM and HEED photographs of InP films prepared by PRD on the Cd face of CdS single crystals (top and middle) and RXCdS (bottom).

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