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SERI/TR-8170-1-T2

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

Final Report for Period May 1979—July 1980

By
K. Zanio

September 1980

Work Performed Under Contract No. AC02-77CH00178

Hughes Research Laboratories
Malibu, California

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U.S. Department of Energy

Solar Energy

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September 1980

Contract XJ-9-8170-1

Final Report
May 1979 through July 1980

Prepared for
DEPARTMENT OF ENERGY
Division of Distributed Solar Technology
Washington, DC 20545

Monitored by
SOLAR ENERGY RESEARCH INSTITUTE
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Golden, CO 80401

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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.

This program is being undertaken by personnel in the Optical Physics Department under the supervision of Mr. M. Braunstein, Dr. R. Knechtli, and Dr. R.L. Abrams. 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, H. Montano, R. Turk, and A. Timper.

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ABSTRACT

Thin-film InP/RXCdS/ITO/GLASS devices were prepared by depositing ITO on low-cost glass substrate, depositing CdS on the ITO by thermal evaporation, increasing the CdS lateral grain size by recrystallization, and depositing p-type InP by planar reactive deposition (PRD) on the recrystallized CdS (RXCdS). Yields of the RXCdS/ITO/GLASS substrates were increased to 90% with lateral dimensions of the RXCdS grains as large as 0.3 mm. P-type InP layers were obtained with Be doping. S-doping via vapor transport from the CdS was eliminated by capping the entire RXCdS substrate with InP. For InP deposited on RXCdS at 380°C, devices showed blocking action with a barrier height of about 0.5 V but no light response, possibly due to an intermediate $\sim 3\text{-}\mu\text{m}$ -thick n-InP layer from diffusion of S from the RXCdS. These results were achieved despite poor InP epitaxy due to an $\sim 0.5\text{-}\mu\text{m}$ -thick In-Cd-S transition layer between the InP and the RXCdS. InP films were subsequently deposited on RXCdS at the reduced substrate temperature of 280°C to reduce S-diffusion and improve the quality of the epitaxy. Complete InP epitaxy on RXCdS was achieved with the lateral dimensions of the InP ($\sim 40\text{ }\mu\text{m}$) replicating that of the RXCdS. Given the increase in the concentration of n-type native defects as substrate temperature is decreased, the present lower limit for obtaining p-type InP by vacuum technologies appears to be about 300°C. A 300 to 350°C range of substrate temperature appears to be feasible for preparing large-grained p-type InP for both frontwall and backwall cells. However, if the thickness of the n-type layer due to S diffusion cannot be kept to less than a few thousand Angstroms, then development must be restricted to the frontwall cell.

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SECTION 1

INTRODUCTION

Single-crystal CdS/InP* solar cells have achieved AM2 efficiencies of 15%.¹ However, all-thin-film CdS/InP solar cells have shown efficiencies of only about 6%. To achieve even this 6% efficiency, the all-thin-film structure requires at least a 40- μ m-thick layer of InP, a layer much too thick to make the all-thin-film structure economical. This report summarizes our efforts to develop a more efficient and more economical all-thin-film InP/CdS solar cell.²

Our structures consist of a 1- μ m-thick film of InP epitaxially deposited on recrystallized CdS (RXCdS). Figure 1 shows both front- and backwall approaches. The lateral dimensions of the RXCdS grains are about 40 μ m. When the InP grain boundaries replicate the CdS grain boundaries, the lateral dimensions of the InP grains are also about 40 μ m. As the grain boundary surface density is decreased, the grain boundary leakage currents should also decrease, thus potentially improving the cell efficiency. Presently, our efforts are directed towards the backwall structure. In an earlier Department of Energy (DOE) program (EY-76-C-04-3717), we demonstrated that the planar reactive deposition (PRD) technique was capable of preparing semiconductor-grade InP for solar cells. The purpose of the present program was to integrate these films into a potentially low cost all-thin-film structure. Section 2 discusses the development of the low-cost RXCdS substrate. Section 3 summarizes the PRD method of preparing InP. Section 4 discusses the epitaxial deposition of InP on single-crystal InP and RXCdS. Section 5 considers the electrical properties of InP on single-crystal InP and RXCdS. Initial InP/RXCdS/GLASS device operation is discussed in Section 6. The final section summarizes the work performed on this contract and discusses the further efforts required to make the InP/RXCdS/GLASS structure useful.

* CdS/InP refers to a structure in which CdS has been deposited on InP; similarly, InP/CdS refers to InP deposited on CdS.

Figure 1. All-thin-film InP/CdS solar cells utilizing the backwall (left) and frontwall (right) structures.

SECTION 2

THE RXCdS/GLASS SUBSTRATE

A. BACKGROUND

The high efficiencies obtained with GaAs single-crystal solar cells and the wealth of established GaAs processing technologies made this material the most likely candidate for a high-efficiency all-thin-film solar cell. But unfortunately, a suitable low-cost substrate is not available. Consequently, we considered other direct-gap materials. One of these materials is InP, and all-thin-film cells of CdS/InP have been prepared by depositing InP on various substrates. These cells required film thicknesses of at least 40 μm to obtain 5.7% efficiencies, and even then the lateral dimensions of the grains were only about 4 μm . The open-circuit voltage was only 0.4 V and was possibly limited by grain boundary leakage currents. To make a more efficient but yet economical thin-film cell requires simultaneously reducing the grain boundary surface density and the thickness of the InP.

CdS is lattice matched to InP, can be made highly conductive and is transparent to most of the solar spectrum. Grains with lateral dimensions up to 40 μm had been prepared at HRL in an early light valve program.³ One objective of this program was to routinely prepare large grains of low-resistivity, optically transparent CdS on glass. This section discusses our preparation of these structures. The RXCdS/GLASS structure is not without disadvantages. Because of the volatility of CdS, a special low-temperature PRD technique (discussed in Section 3) was developed. Another disadvantage is that interdiffusion between InP and CdS results in an unwanted doping effect; that problem is discussed in Section 5.

B. RXCdS PROCESSING

The CdS films are prepared by the thermal evaporation of bulk polycrystalline CdS onto a substrate having a temperature of about 200°C at growth rates of several micrometers per hour and at a background

pressure of 10^{-6} Torr. The CdS is undoped and commercially available from Eagle Pitcher. The substrate consists of about 1000 to 2000 Å of indium-tin-oxide (ITO) on a soda lime glass. The ITO/GLASS substrates are commercially available from both Optical Coating Laboratories and Pittsburg Glass. The Exploratory Studies Department of Hughes Research Laboratories also routinely deposited ITO on glass; these films have also proven satisfactory.

From 10 to 30 μm of thick films of CdS are deposited on the ITO. The lateral dimensions of these grains are less than 1 μm . The CdS/ITO/GLASS structure is then heated in flowing H_2S for about 30 min at about 500°C. The average size increases to about 40 μm , with some grains having lateral dimensions up to 0.3 mm.⁴ Figure 2 shows optical photographs of typical CdS films (1) thermally deposited on ITO/GLASS and viewed with unpolarized light, (2) recrystallized and viewed with unpolarized light, and (3) recrystallized and viewed with polarized light.

Before recrystallization, the films have sheet resistances of about 100 $\Omega/\square$, which is approximately the same as the sheet resistances of the ITO. Electrical measurements subsequent to recrystallization show these films have resistivities of about $10^5 \Omega\text{-cm}$. Subsequent annealing of the films in 10% H_2 /90% Ar at 500°C for about 30 min reduces the resistivity only an order of magnitude. However, resistivities of less than 1 $\Omega\text{-cm}$ are achieved by annealing in pure H_2 . Because of the explosive nature of H_2 , we chose the alternative method of lowering the resistivity by annealing RxCdS films at 500°C in Cd overpressures. With Cd overpressures, the sheet resistance of the annealed films again dramatically decreased to values ranging between 10 and 30 $\Omega/\square$. Although the resistance of these films is no lower than the resistance of films annealed in flowing H_2 , low-resistivity layers are more consistently obtained.

The lowest resistivity and corresponding sheet resistance for a 15- μm -thick film were 0.014 $\Omega\text{-cm}$ and 10 $\Omega/\square$, respectively. Typical sheet resistances for a 15- μm -thick film are 20 $\Omega/\square$. The sheet resistance of the ITO exposed directly to the H_2S is extremely high. However, the resistance of the ITO films under the CdS does not appear

**a) THERMALLY DEPOSITED
(UNPOLARIZED LIGHT)**

**b) RECRYSTALLIZED
(UNPOLARIZED LIGHT)**

**c) RECRYSTALLIZED
(POLARIZED LIGHT)**

Figure 2. Optical photographs of CdS films: (a) thermally deposited and viewed with the reflected unpolarized light, (b) recrystallized and viewed with transmitted unpolarized light, and (c) recrystallized and viewed with transmitted but polarized light.

to change appreciably (the largest resistance increase observed was by a factor of two) after the resistivity of the CdS is lowered. Table 1 summarizes the processing steps that we have undertaken to obtain low-resistivity RXCdS films. Positions on the films where resistance measurements are made are shown on the bottom part of the table.

C. X-RAY AND OPTICAL EVALUATION

To obtain additional information regarding the quality and orientation of the grains of RXCdS, we supplement the optical photographs with X-ray Read photographs. In this technique, X-rays are incident on the film at a low angle (typically 7°) to increase the interaction of the beam with the thin film and minimize the effect of the substrate. The beam consists of a dominant $\text{Cu}_{K\alpha}$ line and a subordinate $\text{Cu}_{K\beta}$ line superimposed on a background of white radiation. As in a powder pattern, the $\text{Cu}_{K\alpha}$ and $\text{Cu}_{K\beta}$ beams interacting with fine grains of random orientation result in rings on the X-ray film. The white radiation from the source interacting with fine grains of random orientation results in a uniform darkening of the X-ray film. Figure 3 (top) shows (left) an optical photograph in unpolarized light and (right) the corresponding X-ray Read picture of a thermally deposited CdS film. The rings on the X-ray Read picture are not continuous but consist of arcs. These arcs indicate that the c-axis of the grains prefers to be aligned normal to the substrate. The effect of this preferred orientation on the white radiation is to generate rays at right angles to the arcs. As grain growth occurs during recrystallization, the grains tend to adopt a random orientation. After grain growth, optical films were taken in polarized light. The CdS film in Figure 3 (middle) illustrates incomplete recrystallization. The recrystallized grains have both preferred and random components, the preferred orientation having the c-axis normal to the substrate. The bottom picture shows a fully recrystallized* film. Although only discrete spots are visible, there evidently is also some degree of preferred

* A fully recrystallized film is defined here as one which shows only spots on our X-ray film as examined with the unaided eye.

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

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STRUCTURE	$\Omega/\square$	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)

OPTICAL

X-RAY READ

THERMALLY DEPOSITED CdS

INCOMPLETELY RECRYSTALLIZED CdS

FULLY RECRYSTALLIZED CdS

Figure 3. Optical (left) and X-ray Read (right) pictures of (top) a thermally deposited and unrecrystallized CdS film, (middle) an incompletely recrystallized CdS film, and (bottom) a fully recrystallized CdS film. Photographs of the thermally deposited films were taken in unpolarized light, whereas photographs of the recrystallized films were taken in transmitted polarized light.

orientation. Generally, the degree of recrystallization is more complete with larger grain sizes. The comparison between Figure 3 (middle) and Figure 3 (bottom) might be considered to be an exception to the general behavior. However, the larger grains in Figure 3 (middle) show small inclusions, which might be unrecrystallized CdS having a preferred orientation.

Low-resistivity thermally deposited CdS, high-resistivity RXCdS, and low-resistivity Cd-fired RXCdS were examined in transmitted light with a microscope. The transparency was highest for the high-resistivity RXCdS and lowest for the low-resistivity thermally deposited RXCdS. Unfortunately, more quantitative transmission studies were undertaken only on the thermally deposited CdS. It is assumed that the following measurements on the low-resistivity thermally deposited CdS represent the lower limit of optical quality of the low-resistivity RXCdS which is used as the substrate for the InP.

Most of the thermally deposited CdS/GLASS structures examined with the Cary spectrometer transmitted from 40% to 70% of the incident light over the wavelength 0.6 to 0.9 μm . CdS film thicknesses ranged from about 1 to 10 μm . Without an antireflection (AR) coating, 70% transmission is expected. As expected, poorer transmission was found with the thicker films. With our experimental arrangement, it was difficult to determine whether the poor transmission was due to absorption or scattering. Therefore, we decided to check the transmission properties of our CdS films on sapphire substrates using a Si detector. We isolated the effect of scattering by varying the distance between the CdS film and the detector, as shown in Figure 4. Figure 4 shows transmission spectra for two situations; with no CdS and with a 0.6- μm CdS film on sapphire in the 0.6- to 0.9- μm -wavelength range. Considering a 30% reflection from the CdS sapphire structure, the scattering was negligible. The degree of transmission of the 6- μm -thick CdS film was poorer. To determine if this transmission loss was due to light scattered out of the beam by the CdS window, the detector-to-film distance was increased. Although results for the 0.6- μm -thick film and the substrate without CdS were equivalent, there was a significant

Figure 4. Transmission characteristics of CdS films on sapphire for film-detector separations (S) of 4 cm (top) and 1 cm (bottom).

decrease in the percentage transmission for the 6- μ m-thick film. This particular scattering effect would not have a significant effect on the quantum efficiency of the InP/CdS cell for forward-scattered light because of the direct contact of InP with CdS. These results indicate that the absorption losses of our thermally deposited CdS films less than 1 μ m thick are insignificant, whereas up to 10% of the light is lost for films about 10 μ m thick. To what extent the absorption centers anneal out during the recrystallization process of Cd firing is not known.

D. YIELDS

The yield of RXCdS/GLASS substrates has been substantially improved. In January 1980, yields were only about 25% (see Table 2). But in the last month of the program, 33 of the 36 substrates processed (92%) were acceptable for thin-film devices. An acceptable structure is defined as one with an average RXCdS grain size of at least 20 μ m and with X-ray Read pictures that predominately show spots and only weak continuous lines. The yields have been limited by peeling of the films, incomplete recrystallization, and process equipment failure. The factors that cause peeling and the degree of recrystallization have not been studied in detail. However, as expected, a clean ITO/GLASS substrate and vacuum system for depositing the CdS is essential. There is some evidence that peeling is due to the presence of water vapor during either recrystallization or Cd-firing. Therefore, we take precautions to drive water out of the system before either step. At present, the mechanism of recrystallization is not well understood. For example, we do not know whether impurities play an important role in our recrystallization process. Auger analysis of the grain boundaries may prove helpful. Several RXCdS/GLASS structures have been sent to SERI for their evaluation.

Table 2. RXCdS/GLASS Processing Summary

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PERIOD	INITIAL STRUCTURES	ACCEPTABLE STRUCTURES	YIELD (%)	AVERAGE GRAIN SIZE (μm)
JAN → MAY	74	20	27	30
JUNE	16	12	75	40
JULY	36	33	91	50

SECTION 3

PLANAR REACTIVE DEPOSITION

A. DESCRIPTION OF THE SYSTEM

High-quality InP thin films have been prepared by chemical vapor deposition (CVD) methods by several groups^{5,6} at temperatures in excess of 600°C. However, the InP-on-CdS sequence requires a low-temperature deposition process (250 to 350°C) to prevent the decomposition of the CdS substrate. Single-crystal thin films of InP have already been prepared at temperatures as low as 200°C by molecular beam epitaxy (MBE).⁷ Unfortunately, the MBE approach is not economical, because of the requirement of an ultra high vacuum ($<10^{-10}$ Torr), and does not provide large-area films of uniform thickness.

The PRD technique was supported under DOE program EY-76-C-04-3717 to prepare InP films at reduced substrate temperatures. Because of its importance to the present program, we describe it here. The PRD process combines the features of both CVD and MBE. Figure 5 shows the PRD system. A stainless-steel chamber is evacuated to 10^{-7} Torr by a turbomolecular pump located directly under the chamber. Entry ports for reactant and dopant gases and for LN_2 are also located at the bottom of the chamber. Figure 6 is a schematic top view of the vacuum chamber. A substrate plate rides on three bearings, which permits several substrate arrays to be successively positioned above PRD deposition units. Below the substrate plate are two deposition units which deposit films of different composition. The substrate plate also has three positions, allowing different structures to be prepared during the same run without breaking vacuum. A cross-sectional view through one of the two deposition units is shown in Figure 7. The source-substrate assembly is enclosed within a liquid-nitrogen-cooled shroud forming a CVD-type growth chamber. The shroud protects the source-substrate deposition region from condensable gases streaming into this region. As in MBE, indium is melted in a Knudsen cell. The vapor pressure of the indium controls the film growth rate and is determined by the source temperature, which is held

Figure 5. PRD apparatus for preparing InP.

Figure 6. Schematic top view of the vacuum chamber in the PRD system.

Figure 7. Cross section of PRD source/substrate assembly.

at about 800°C. A PH_3/H_2 gas mixture is bled through a Tylon mass flow controller at a rate of about 30 cm^3/min . Phosphine is introduced into the Knudsen cell from below and decomposes. The indium vapor and P_2 stream onto the substrate to form InP. Since an In atom has a sticking coefficient on the substrate of near unity, whereas a phosphorus ad atom's sticking coefficient is near unity only for an indium-stabilized surface (excess In) and near zero for a phosphorus-stabilized surface (excess P), near stoichiometric films are produced by allowing an excess of P_2 in the growth chamber.

The hydrogen gas provides a reducing atmosphere in the deposition chamber. The H_2 is pumped out of the chamber by a Leybold-Heraeus turbomolecular pump. The use of a turbomolecular pump instead of a diffusion or an ion pump is necessary to maintain an oil-free system while allowing good pumping speeds at chamber pressures on the order of 10^{-4} Torr.

B. THE DEPOSITION PROCEDURE

After the samples are loaded onto the substrate plate, the chamber is pumped down to below 10^{-6} Torr. During pump down, the quality of the vacuum is monitored by a residual gas analyzer (RGA). During the pump-down stage of a typical run, the RGA shows predominately water vapor. Figure 8(a) shows the H_2O peak and a subsidiary peak associated with air. Adding LN_2 to the shrouds eliminates the H_2O peak. The residual pressure (Figure 8(b)) is an indication of the quantity of residual N_2 (used for backfilling) or air remaining in the system. After the total pressure drops to about 10^{-7} Torr, the source is turned up to 800 to 900°C for outgassing while the substrates are being preheated in the 300 to 400°C range in an adjacent position not over the source. When the source is outgassed, H_2 out diffuses from the carbon crucible, and H_2O reacts with the crucible to form CO (Figure 8(c)). After 1 hr of getter cleaning, the source temperature is reduced to the 600 to 700°C range, where In evaporation is negligible, and the substrates are rotated into position above the source for thermal etching. For InP substrates, the substrates are held at $\sim 425^\circ\text{C}$ for thermal cleaning in the presence of phosphorus

Figure 8. Residual gas spectra in vacuum chamber after (a) sample loading, (b) filling LN_2 shroud assembly, (c) source outgassing, (d) $\text{H}_2 + \text{PH}_3$ gas shutoff at end of film deposition, and (e) LN_2 shroud emptied at end of deposition.

vapor for about 1 hr. The phosphorus vapor stabilizes the InP surface against indium droplet formation. For deposition on CdS, the substrates are held at a lower temperature. After the substrates are thermally cleaned, the substrate is cooled to the temperature desired during deposition, and the source is heated to about 50°C below the outgas temperature used during film deposition at about 10^{-4} Torr. The source temperature required to obtain a specific deposition rate also depends on the diameter of the four holes in the sapphire plate at the top of the Knudsen cell. For an aperture diameter of 1/8 in. and a source-to-substrate distance of 12 cm, source temperatures of approximately 790 and 840°C result in In deposition rates of 0.2 $\mu\text{m/hr}$ and 2 $\mu\text{m/hr}$, respectively. The source temperature refers to the temperature of a Mo-capped Pt/Pt(Rh) thermocouple located directly beneath the Knudsen cell. After deposition, the source is turned off. Then, to prevent phosphorus depletion of the InP, the substrates are cooled to below 300°C before the phosphorus source is turned off.

For the case where the second source chamber is to be used for preparing a multilayer structure, the bakeout procedure is repeated, but the subsequent deposition is undertaken without thermal etching. PH_3 and its dissociated forms are apparent on the RGA spectrum (Figure 8(d)) after PH_3 is introduced into the hot cavity. After the deposition is complete and the shrouds have been emptied of LN_2 , different forms of phosphorus vaporize from the warmer chamber walls (Figure 8(e)).

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SECTION 4

EPITAXY OF InP

A. BACKGROUND

From earlier work on DOE contract EY-76-C-04-3717, it was evident that severe interdiffusion occurs between polycrystalline InP and CdS at CdS substrate temperatures above 400°C. However, for cleaved structures examined by SEM, interdiffusion was not evident at 300°C. Even though good epitaxy of InP was achieved on CdS single crystals at 350°C, it was not evident that interdiffusion would not inhibit epitaxy on the RXCdS grains.* Even if epitaxy could be achieved on RXCdS, it was not evident that p-type films could be produced. The restrictions in doping comes from overriding n-type doping by sulfur via diffusion from the CdS and intrinsic native defects.

B. ON InP SINGLE CRYSTALS

To determine the lowest temperature of InP epitaxy while simultaneously minimizing interfering effects from interdiffusion, InP was grown on single-crystal (100) InP substrates. InP was prepared at substrate temperatures ranging from 225 to 410°C. X-ray Read pictures were used to characterize the layers. As in a Laue photograph, the white radiation incident on a single crystal results in spots where the Bragg condition is satisfied. White radiation interacting with a polycrystalline film results in a continuous exposure of the film. As in a powder pattern, the monochromatic lines of $Cu_{K\alpha}$ and $Cu_{K\beta}$ interacting with the polycrystalline film result in rings. Figure 9(a) shows a Read photograph of an InP film grown on a sapphire substrate at 320°C. The rings are characteristic of the polycrystalline InP, the spots of the sapphire substrate. Figure 9(b) is a Read photograph of InP grown on a (100) semiinsulating InP substrate at 320°C during the same run. The spots are characteristic of the single-crystal epitaxial film and the single-crystal substrate.

* InP epitaxy was achieved on the Cd-face of single crystals of CdS. However, the RXCdS is randomly orientated. There, the single-crystal experiments do not ensure epitaxy on RXCdS because the degree of epitaxy on RXCdS may be orientation dependent.

(a) InP/SAPPHIRE
AT 320°C

(b) InP/(100)InP
AT 320°C

(c) InP/(100)InP
AT 260°C

Figure 9. Read photographs of (a) polycrystalline InP deposited on sapphire at 320°C, (b) epitaxial InP deposited on (100) InP at 320°C, and (c) epitaxial InP deposited on (100) InP at 260°C.

Rings characteristic of polycrystalline InP were not observed. In the next run, the substrate temperature was lowered to 260°C. Growth on the (100) InP substrate resulted in a Read photograph (Figure 9(c)) that is identical to Figure 9(b) and is characteristic of epitaxial growth.

Since no single-crystal films could be grown below 260°C, 260°C is assigned the single-crystal to polycrystalline transition temperature for films grown at deposition rates of about 1 $\mu\text{m/hr}$ on (100) substrates by PRD. This transition temperature is slightly lower than that obtained earlier by the MBE group at Bell Laboratories.⁸ Our results were obtained in the fall of 1979. In concurrent MBE studies, Norris and Stanley⁷ demonstrated that InP films could be epitaxially grown by MBE at substrate temperatures as low as 150°C. Our PRD and the recent MBE results are interesting for they indicate that III-V compounds might be grown at low temperatures to alleviate the diffusion problems that degrade terrestrial solar cells. However, it is important that the transport properties of these films be adequate.

C. ON RXCdS

1. At 380°C Substrate Temperature

Complete epitaxy of InP had been achieved on single crystals of CdS at a substrate temperature of 350°C on DOE program EY-76-C-04-3717. Epitaxy of InP on RXCdS was begun on this program. Initial depositions of InP on RXCdS began at a substrate temperature of 380°C. Attempts to deposit a 0.35- μm -thick InP layer on RXCdS at a substrate temperature of 380°C were unsuccessful. Instead, the deposition was transparent and identical in color and texture to the RXCdS. Microprobe measurements of the layer on the RXCdS indicated an In-S-Cd compound. Only a trace of P was found. These results are consistent with earlier studies on polycrystalline CdS which showed that an In-Cd-S transition layer exists when InP is deposited on polycrystalline CdS in vacuum at substrate temperatures of about 400°C. In subsequent runs, we deposited 4.5- μm -thick InP layers at a substrate temperature of 380°C.

Figure 10 shows InP deposited on (top) ITO/GLASS and (middle) RXCdS. The X-ray pictures of InP deposited on ITO/GLASS show only the continuous rings characteristic of polycrystalline InP. However, a careful examination of the X-ray picture of InP deposited on RXCdS shows the rings to be composed of discrete spots.* Unfortunately, due to the loss of resolution in reproducing the original X-ray film, the discrete spots appear as broad rings in this report. However, discrete reflections from the background radiation indicate more clearly that the InP film contains grains larger than submicrometer size. It is not straightforward to determine the typical grain size of this InP layer on RXCdS. From a comparison with the RXCdS grains in Figure 3, we estimate the InP grain size to range from 1 to 10 μm . From these SEM pictures of InP on RXCdS, it is not evident that any degree of epitaxy was achieved. However, there is a definite increase in the characteristic dimensions of the prominent features of the InP on the RXCdS as compared to the InP on ITO/GLASS.

We expected the InP to either exhibit faceting or to replicate the contours of the RXCdS. To preserve the cleanliness of the RXCdS on which we had deposited the InP, we took no pictures of the RXCdS surface even though it would have been helpful if we had had such pictures. Instead, we examined RXCdS films prepared under conditions as similar as possible. An examination of an SEM picture of another RXCdS substrate (Figure 10, bottom) shows a smoother but not entirely featureless surface. A close examination of the polarized light pictures of the RXCdS also shows surface roughness. In addition, the surface is decorated with submicrometer-sized particulate matter. Since the InP deposition should follow the contours of the RXCdS, smooth or even uniformly faceted InP cannot be expected.

The quality of the InP epitaxy can be underestimated from SEM pictures. We have included from an earlier study (Figure 11) SEM and HEED pictures of InP deposited on the Cd face of single crystals of CdS.²

* Since the InP layer is at least a few micrometers thick, the spots are characteristic of InP and not CdS.

Figure 10. SEM (left) and X-ray Read (right) pictures of (top) InP on ITO/GLASS, (middle) InP on partially recrystallized CdS, and (bottom) partially recrystallized CdS.

SEM

HEED

Figure 11. SEM and HEED photographs showing (top) complete and (bottom) partial epitaxy for InP films prepared by PRD on the Cd-face of CdS single crystals.

As expected, the HEED pictures show that the faceted and "wormy" looking layers are, respectively, characteristic of complete and partial epitaxy. However, the degree of epitaxy of the inferior layer is much better than expected from the SEM.

Although the X-ray Read pictures indicate that the InP grain size was increased from submicrometer dimensions to the 1- to 10- μm size range, SEM pictures leave us disappointed since they show that faceted InP was not obtained. The presumably inferior quality of the InP could be due to the presence of the thick intermediate InCdS layer, which is at least 0.35 μm thick. It probably is not more than 1 μm thick because, if it were, then device measurements (see Section 6) and hot probe measurements (see Section 5) of the InP on the RXCdS would not have indicated p-type.

2. At 280°C Substrate Temperature

When InP is deposited on RXCdS at reduced temperature, the degree of epitaxy significantly improves.⁴ Grains with lateral dimensions of 40 μm are observed. Figure 12 (top) shows SEM pictures of InP deposited on a single RXCdS grain at 280°C. Only at higher magnifications can the facets of the grains be resolved. It is evident that the facets are aligned over the entire photograph. The middle picture shows InP epitaxy covering two adjacent grains of RXCdS. The orientations of the facets are distinctly different across the grain boundary. In the bottom picture, this grain boundary is delineated to better contrast the orientation of the two grains. The X-ray Read picture (Figure 13, top) shows the characteristic discrete spots seen also for the RXCdS film. There is some indication that the InP film contains submicrometer grains with the preferred orientation. However, these submicrometer grains are believed to replicate regions of the CdS that are not completely recrystallized. These results are important because it is the first time that a large-grained but thin film of a III-V compound has been prepared on a low-cost substrate.

INP ON SINGLE
RXCdS GRAIN

INP ON TWO
RXCdS GRAINS

INP ON TWO
RXCdS GRAINS
(GRAIN BOUNDARY
DELINEATED)

Figure 12. InP deposited by PRD at 280°C on (top) a single RXCdS grain, (middle) two RXCdS grains, and (bottom) the same two RXCdS grains but with the grain boundary delineated.

**X-RAY READ OF
InP/RXCdS**

**X-RAY READ OF
CdTe/RXCdS**

Figure 13. X-ray Read pictures of InP (top) and CdTe (bottom) deposited on RXCdS.

It is inevitable that even at lower substrate temperatures intermediate phases will form at the InP/CdS interface. In the epitaxial growth⁹ of CdS on InP single crystals at about 650°C, there is a 1- μ m-thick transition region having composition gradients for In, Cd, S, and P. Regardless of whether or not this transition region is present, good epitaxy of CdS on InP is obtained. More importantly, good solar cell efficiencies are obtained with this transition layer present. In the reverse structure (i.e., InP deposited on CdS), transition regions exist even at low temperatures. In the vacuum deposition of a few hundred Angstrom thick InP films on CdS at 300°C, Dhere and Parikh¹⁰ encountered in some instances two new hexagonal structures and also a cubic superstructure. It is likely that a thin transition layer also exists in our InP/RXCdS structure. However, from our results it appears that thin transition layers will not seriously interfere with the replication of InP grains on RXCdS grains.

Within each of the InP grains, it is likely that there are stacking faults.¹¹ During heteroepitaxial growth of InP on CdS, periodicity may not be preserved. For example, along the c-axis of CdS, the ABAB structure of the CdS may transform to either an ABAB/ABCABC or ABAB/CABCBAB structure. (Here the CdS-to-InP transition is indicated by the slash.) The lateral coalescence of nuclei having different stacking sequences should result in a boundary with a high degree of periodicity. We have been concerned about the effect of these boundaries on the electrical properties of the InP/RXCdS device. Although the boundaries may be quite periodic, the degree of disorder might result in a high density of deep levels. Such stacking faults have recently been observed¹⁰ in the deposition of several hundred Angstrom thick InP films vacuum deposited on CdS/NaCl. However, in our earlier etching studies of twin and grain boundaries in InP, we found the twin boundaries to be relatively inert to etchants.¹¹ The relative inertness of the twin boundaries might indicate the twin boundaries to have a low density of additional electronic levels.

D. PARALLEL CdTe/RXCdS STUDIES

The poor epitaxy of InP on RXCdS at a substrate temperature of 380°C left us disappointed. Consequently, we began a parallel effort of depositing CdTe on RXCdS to eliminate the effects of the severe inter-diffusion of elements from different columns of the Periodic table. Figure 14 shows SEM pictures of 20- μ m-thick CdTe films that we deposited on (top) RXCdS and (bottom) ITO/GLASS substrates at 460°C by physical vapor deposition. For the CdTe grown on the RXCdS, the average grain size is about 40 μ m. For CdTe grown on the ITO/GLASS substrate, the grain size is about an order of magnitude less. The more direct comparison in the middle figure at a lower magnification shows CdTe grown both on and off the RXCdS. Compared to InP, the CdTe grains have larger facets. Under similar growth conditions, the CdTe facets would be expected to be larger than the InP facets due to differences between their growth properties. However, the growth conditions were such as to enhance even further the CdTe facet size. The higher temperature for the CdTe substrate enhances surface mobility and consequently enhances facet size. In addition, the CdTe film is about an order of magnitude thicker; as growth proceeds, the larger grains appear to crowd out the smaller ones. The X-ray Read pictures (Figure 14, bottom) confirm the presence of the large CdTe grains. Although only a limited number of CdTe experiments were undertaken, surprisingly good results were achieved. In contrast, an extensive effort has been undertaken to achieve comparable results with InP on RXCdS. It has become even more obvious that the lattice mismatch between compound semiconductors formed from different chemical species but similar columns of the Periodic table is a lesser barrier to good epitaxy than is the chemical interaction between chemical species of semiconductors found by different columns of the Periodic table. These results strengthen the requirement that the substrate temperature be reduced to promote the growth of epitaxial InP on RXCdS.

CdTe/RXCdS/ITO/GLASS

CdTe/RXCdS/ITO/GLASS

CdTe/ITO/GLASS

CdTe/ITO/GLASS

Figure 14. SEM pictures of CdTe deposited on (top) RXCdS and (bottom) ITO/GLASS. The middle picture directly compares the grain size of CdTe deposited on RXCdS to that on ITO/GLASS.

SECTION 5

ELECTRICAL PROPERTIES OF InP EPITAXIAL FILMS

A. ON InP SINGLE CRYSTALS

Preliminary electrical measurements of the single-crystal films grown at lower temperatures on semi-insulating InP substrates indicated that the highest room-temperature mobility achieved for a growth temperature of 260°C was about $1500 \text{ cm}^2/\text{Vsec}$. Our best mobilities at higher substrate temperatures on undoped n-type InP films have been about $4000 \text{ cm}^2/\text{Vsec}$. Only three runs were made at 260°C, and the deposition environment probably is not yet as clean as it could be. Our highest mobilities normally are not realized until about the sixth or seventh run. The fact that our best mobility for a growth temperature of 260°C was achieved in the latest run was consistent with this explanation.

Our electrical measurements are in qualitative agreement with MBE results. For example, Norris and Stanley^{7,12} report a drastic decrease in the Hall mobility of the layers below 300°C. Whereas room-temperature electron mobilities of about $3000 \text{ cm}^2/\text{Vsec}$ were typical at a substrate temperature of 350°C, they decreased to $1500 \text{ cm}^2/\text{Vsec}$ at a substrate temperature of 150°C. The transport properties of unintentionally doped InP films prepared by the vacuum technologies PRD, MBE, and low-pressure metal-organic CVD are summarized in Figure 15.

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 330°C. Films with $3 \times 10^{17} \text{ cm}^{-3}$ holes had mobilities of about $60 \text{ cm}^2/\text{Vsec}$. 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 $20 \text{ cm}^2/\text{Vsec}$. The degree of electrical activity of Be at substrate temperatures below 330°C is still unknown and must be

Figure 15. Unintentionally doped InP films prepared on InP substrates by vacuum technologies.

investigated if thin-film cells need to be prepared at lower temperatures. Even if Be is electrically active at lower temperatures, it may be compensated by n-type native defects. In our best undoped films, our free electron concentration increases from 10^{16} cm^{-3} to 10^{18} cm^{-3} for a decrease in the substrate temperature from 360 to 260°C. MBE data^{7,8,12} show that at about 310°C the free electron concentration increases over several decades with decreasing substrate temperature. Associated with the increase in the free carrier concentration is a strong attenuation in the luminescence for substrate temperatures below 300°C. The source of native defects responsible for the increase in electron concentration and degradation of the electrical and optical properties is not known. Norris¹² suggests that the dimer P_2 cannot readily dissociate at the lower temperature growth interface, causing a change in the growth mechanism and an increase in native defects.

One problem with using Be as a p-type dopant is that it becomes inactive (presumably oxidized) after 4 or 5 runs, and p-type doping can no longer be achieved. Each time the Be-source is replaced, the system must be baked out. Since improved system cleanliness is achieved in subsequent runs, ultimate system cleanliness with Be-doped films is never achieved. Besides not achieving improved system cleanliness, it is time consuming to replace the source and difficult to obtain the same level of p-type doping when the source is replaced. An alternative to Be doping is doping with Zn via metal organics. Although the vapor pressure of Zn at 300°C is 10^{-3} Torr, Zn_3P_2 is more stable than InP in vacuum, and the sticking coefficient of Zn in the presence of excess P may be much less than one. The use of Zn doping via metal organics has been proposed but never undertaken in DOE contract EY-76-C-04-3717.

B. CAPPING THE CdS

When Be-doped and presumably p-type InP layers were deposited onto semi-insulating substrates with RXCdS in an adjacent deposition position, electrical measurements indicated the films to be n-type rather than p-type. For example, in Run 141 of Table 3 Be-doped InP was deposited onto InP at 380°C without RXCdS present. As expected,

Table 2. Effect of Sulfur Doping via Vapor Transport on InP Thin Films

RUN	DEPOSITION POSITION	InP DOPANT	SUBSTRATE	HALL MEASUREMENTS			I vs 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/cm³

the layers were p-type. However, in Run 142 and subsequent runs when Be-doped InP was deposited onto InP and RXCdS in an adjacent deposition position, the layers were n-type. Hot probe measurements of both the single-crystal layer and the InP on the RXCdS also both indicated n-type.

Sulfur is presumed to outgas from the exposed CdS and become incorporated in the InP films. In the deposition of an InP film onto a CdS/ITO/GLASS substrate, the diameter of the CdS film was about 1.5 cm, whereas the diameter of the InP film was about 1.0 cm. We reduced the diameter of the CdS to about 7 mm and, in subsequent depositions, capped the CdS. P-type films could be prepared on semi-insulating InP only when the RXCdS in adjacent deposition positions was capped.

Figure 10 (middle) shows a p-type InP film deposited on RXCdS at 380°C. The type was determined by hot probe measurements. The InP film deposited on a semi-insulating substrate was also p-type, as determined by Hall and hot probe measurements. The type of the film on RXCdS could be influenced by grain boundaries. Although the hot probe measurement might indicate p-type, the intragrain quality could be n-type. However, device type measurements discussed in Section 6 support the view that at least the top of the layer is p-type. We are certain that there is an n-type InP transition layer between the p-InP and the RXCdS.

To reduce the thickness of the transition layer between the InP and the RXCdS and thus enhance the quality of the InP epitaxy, we lowered the substrate temperature to 280°C. We achieved excellent epitaxy (see Figure 12), but the films were n-type. The n-type behavior is presumably due to the increase in the concentration of native defects and not to S doping via either vapor transport or diffusion.

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SECTION 6

InP/RXCdS DEVICES

Under DOE contract EY-76-C-04-3717, we had prepared 10% single-crystal CdS on InP solar cells using an intermediate p-type PRD layer as the light absorber. In the present program, we concentrated on the all-thin-film structure which uses the reverse InP on CdS approach. After we had prepared p-type InP and p^+ InP on separate semi-insulating substrate (Run 141 of Table 3), we undertook the deposition of a p^+ -InP/p-InP double layer on RXCdS. As outlined in the PRD deposition procedure (Run 142 of Table 3 and Section 3), in the right hand deposition position we first deposited lightly doped InP and presumably p-type InP onto both the RXCdS and the semi-insulating InP. The substrates were rotated to the left deposition position and heavily doped InP and presumably p^+ InP were subsequently deposited onto both the RXCdS and semi-insulating InP. As discussed in the last section, the layers were n-type due to S from the CdS via vapor transport overcompensating the Be. As expected, blocking action was not found when In Schottky barriers were deposited on the InP. However, blocking action occurred when Au Schottky barriers were used (Figure 16). 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.

At the end of this program, we deposited p-InP on RXCdS/GLASS at a substrate temperature of 380°C. As a first step in preparing devices from these structures (Figure 17), we contacted the InP with Ag paste. These samples exhibited blocking action, with a barrier height of about 0.5 V. We were disappointed by the absence of light response. However, there can be various reasons for the absence of a light response. It is likely that an intermediate n-InP transition light-blocking layer exists, and the holes may be generated tens of diffusion lengths from the p-n junction. As discussed earlier, there is an intermediate In-Cd-S transition layer between the InP and the CdS. However, its transparency

Figure 16. Dark and light I-V characteristics (top) of Au (Schottky barrier)/n-InP/RXCdS/ITO/GLASS device (bottom).

Figure 17. Dark I vs V (top) of p-InP/RXCdS device (bottom) prepared by depositing p-InP on RXCdS at 380°C .

is similar to CdS and is not light blocking. It is also possible that, for photovoltaic response to occur, the CdS surface must be etched prior to the InP deposition. In the preparation of CuInSe_2 on CdS,¹⁴ if the initial CdS surface was exposed to the environment, no photovoltaic effect was observed. A photovoltaic effect was observed if the CdS layer was etched just prior to CuInSe_2 deposition. No special treatment was given to our CdS prior to loading the RXCdS/GLASS substrates in the PRD system.

Regardless of the lack of photoresponse, our results are encouraging for several reasons. These results indicate that a p-type InP layer has been deposited on RXCdS. In earlier devices consisting of n-type InP films on RXCdS, high leakage currents with Ohmic behavior were observed. Blocking action with n-InP could only be achieved if Schottky barriers were prepared by carefully etching the InP and depositing Au. Hot probe measurements on the InP thin film and Hall measurements of single-crystal InP deposited on adjacent semi-insulating InP substrates substantiate that the InP on this all-thin-film structure is p-type.

Considering the small grain size and assuming the forward characteristics in Figure 17 to be determined by a buried homojunction, it is encouraging that a respectable barrier height was obtained. X-ray Read pictures indicated that the lateral dimensions of the InP grains were of the order of a few micrometers. (The poor epitaxy of InP on RXCdS is presumably due to the intermediate In-Cd-S transition layer which interferes with the replication of the InP epitaxy from the RXCdS substrates.) A value of 0.5 V would be high for an InP/CdS polycrystalline cell dominated by grain boundary leakage currents. The electrical state of and consequently the leakage current at the grain boundary might be different for films prepared by PRD versus films prepared by CVD because of the different processing conditions. A depleted high-resistance grain boundary is likely for p-type InP. The Fermi level at the surface of bulk InP is easily pinned near the conduction band due to surface states. If the surface states at the grain boundary behave in a similar fashion to those at the surface, then the grain boundaries in p-type InP should be in a depleted state with a corresponding reduction in grain boundary leakage currents.

SECTION 7

SUMMARY AND FUTURE WORK

In this program, we accomplished three things. First, we demonstrated that RXCdS/GLASS substrates could be produced with low resistivity grains, with grains having large lateral dimensions, and with good yields. The availability of these low-cost substrates lay the groundwork for the development of an economical and efficient InP/CdS solar cell. Second, we prepared large area but only micrometer thick grains of InP on these substrates. This is an important step in preparing an economical (i.e., minimal use of In) as well as efficient (i.e., reduction in grain boundary density) all-thin-film solar cell from a III-V compound. One of the question marks on the development of this cell has been whether S-doping could be overcome by preparing a p-type InP layer on an RXCdS substrate. As a third accomplishment, we did prepare p-type material; unfortunately, we did not simultaneously prepare the p-type and large-grained InP layers necessary for a useful device. However, we did define the processing conditions where large-grained layers and p-type layers are likely to be produced simultaneously. The most important processing variable controlling the properties of the InP is substrate temperature. Although large grains of Be-doped InP can be deposited on RXCdS at 280°C, the films are n-type due to over-compensation by n-type defects (see Figure 18). The concentration of n-type defects increases with decreasing substrate temperatures and is about 10^{17} cm^{-3} at 300°C. Therefore, 300°C is presently the lowest temperature where it is possible to prepare p-type films. The highest temperature at which p-type large-grained film can be prepared is more uncertain. At 380°C and above, the InCdS transition layer is too thick to promote large-grained epitaxy. However, high-quality epitaxy of InP on single crystals of CdS has been achieved at 350°C. And 350°C is certainly a temperature low enough to promote single-crystal epitaxy on RXCdS. Then, within the temperature range of from 300°C to 350°C, as indicated on Figure 18, large-grained p-type InP layers can be produced.

Figure 18. Summary of InP/RxCdS thin-film solar cell development.

The key question is what will be the resulting thickness of the n-type layer due to sulfur doping. If the n-type layer can be kept to within a thickness of a few thousand Angstroms, then the development of the backwall cell (Figure 1) is feasible. However, if the n-type layer cannot be kept within this thickness, then the development of the all-thin-film cell must proceed along the guidelines of a frontwall cell with a buried tunnel junction. At the present stage of research, the backwall cell still remains feasible. At a substrate temperature of 380°C, overcompensation due to S diffusion extends about 3 μm into fine-grained InP. The preparation of larger-grained InP films on RxCdS should significantly reduce sulfur diffusion down grain boundaries. The degree to which it is reduced will depend on the degree of intragrain twinning or mosaic structure (see Section 5).

Because of the difficulty in predicting the extent of S-doping, the next step in the development of the InP/CdS thin-film cell is to deposit large grains of Be-doped InP on RxCdS substrates over the temperature range of 300 to 350°C, prepare devices from those structures, and estimate S penetration from the light response and sputter Auger techniques.

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Appendix A

Large Grains of InP and CdTe on Recrystallized CdS Substrates

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Abstract

Thin films ($\sim 1 \mu\text{m}$) of large-grained ($\sim 40 \mu\text{m} \times \sim 40 \mu\text{m}$) InP were epitaxially deposited on low-cost recrystallized CdS substrates at 280°C by planar reactive deposition. Large grains of CdTe ($\sim 40 \mu\text{m}$) were also deposited on similar substrates at 460°C by physical vapor deposition. Typically, the recrystallized CdS grain size is about $40 \mu\text{m}$. However, grains with dimensions up to $300 \mu\text{m}$ were observed.

InP,¹ GaAs,² and CdTe³ are promising semiconductors for all-thin-film solar cell systems. Unfortunately, the development of these systems, especially those using III-V compounds, is inhibited by the unavailability of a low-cost substrate. We have suggested the use of recrystallized CdS on indium tin oxide on glass (RXCdS/ITO/GLASS) as a low-cost substrate.⁴ In this letter, we report a substantial increase in the grain size and further development of the RXCdS substrate. More importantly, we report for the first time the epitaxial deposition of large area but thin films of a III-V compound on a low cost substrate. We also describe the preparation of large grains of CdTe on the same substrates by low-temperature physical vapor deposition.

As described in earlier publications,^{4,5} about 20 μm of CdS is thermally deposited on ITO/GLASS. The CdS is then recrystallized. Figure 1 shows optical (left) and X-ray Read (right) pictures of three different CdS films at different stages of processing. The thermally deposited films consist of submicrometer size grains. The orientation of the grains are such that the c-axis is preferably aligned normal to the substrate. The preferred orientation results in arcs rather than continuous rings on the X-ray Read picture.

As the recrystallization process proceeds in flowing H_2S at 500°C. (as previously described),⁵ the grain size increases and the grains adopt a more random orientation. The Read picture of the incompletely recrystallized film (middle) contains both arcs characteristic of submicrometer grains of preferred orientation and random discrete spots characteristic of large grains of randomly oriented CdS. Clusters of discrete spots also indicate a small fraction of the large grains to have a preferred orientation.

OPTICAL

X-RAY READ

THERMALLY DEPOSITED CdS

INCOMPLETELY RECRYSTALLIZED CdS

In these Read pictures, the discrete spots due to the $\text{Cu}_{K\alpha}$ and $\text{Cu}_{K\beta}$ radiation are superimposed on a background of discrete spots due to white radiation. Only discrete spots are found in the picture (bottom) for the fully recrystallized film. It is generally — but not always — true that the recrystallization as indicated by the X-ray film is more complete with increasing grain size. However, an exception is demonstrated here. The Read picture for the film having the larger grains (middle) shows arcs, which are characteristic of submicrometer size grains having a preferred orientation. The average grain size of our films has increased from 30 μm in earlier work to 50 μm . Grains with lateral dimensions up to 0.3 mm have been observed. No quantitative reason for the increase in grain size is known. However, our substrate temperature of 180°C for thermal deposition is about 50°C higher than previously used. As expected, we also found that the yield of recrystallized films improves as the cleanliness of the deposition system and the ITO/GLASS substrates improves. After films are recrystallized, the sheet resistance is in excess of $10^5 \Omega/\square$. However, by firing RXCdS in a Cd overpressure at 500°C, the sheet resistivity is reduced to a typical value of about 20 $\Omega/\square$. Values as low as 10 $\Omega/\square$ have been obtained. Absorption losses are about 10% over wavelengths ranging from 0.5 to 1.0 μm .

InP was deposited on RXCdS by planar reactive deposition (PRD)⁴ at substrate temperatures of 280 to 380°C at a rate of about 2 $\mu\text{m/hr}$. No special preparation was given to the RXCdS film. After firing in Cd overpressures, they were stored in air. Before the InP deposition, they were thermally etched in PH_3 for 30 min at a temperature 50°C above the deposition temperature. At a substrate temperature of 380°C,

there is about a 1- μ m-thick In-Cd-S transition layer between the InP and CdS. X-ray Read pictures of these InP/RXCdS films show rings composed of fine spots. For these films, scanning electron microscope (SEM) pictures show a "wormy" looking surface. The characteristic dimension of these films is several times larger than the characteristic dimension of polycrystalline films deposited on ITO/GLASS. A casual examination of X-ray Read pictures of the "wormy" looking surfaces shows continuous rings. However, a more careful examination shows the rings to be composed of discrete spots, which indicates that the degree of epitaxy is superior to that indicated by the SEM. However, the dimensions of the InP grains are much smaller than those of the RXCdS. At the 380°C substrate temperature, there is a 1- μ m-thick In-Cd-S transition layer between the InP and CdS, which presumably degrades the quality of the epitaxy. Unintentionally doped films are always n-type. Films doped with Be are p-type when the RXCdS is capped (i.e., when the diameter of the InP deposition is larger than the diameter of the RXCdS substrate). When the RXCdS is not capped, the films are always n-type, presumably due to sulfur doping via vapor transport.

Complete epitaxy occurs at 280°C on the RXCdS grains, which have dimensions of about 40 μ m. Figure 2 (top) shows SEM pictures of InP epitaxy on a single RXCdS grain. Only at higher magnifications can the facets of the grains be resolved. It is evident that the facets are aligned over the entire photograph. The middle picture shows InP epitaxy covering two adjacent grains of RXCdS. There is a distinct difference in the orientation of the facets across the grain boundary.

**InP ON SINGLE
RXCdS GRAIN**

**InP ON TWO
RXCdS GRAINS**

**InP ON TWO
RXCdS GRAINS
(GRAIN BOUNDARY
DELINEATED)**

Figure 2. InP deposited by PRD at 280°C on (top) a single RXCdS grain, (middle) two RXCdS grains, and (bottom) the same two RXCdS grains but with the grain boundary delineated.

In the bottom picture, this grain boundary is delineated to better contrast the orientation of the two grains. The X-ray Read picture (Figure 3, top) shows the characteristic discrete spots also seen for the RXCdS film. There is some indication that the InP film contains submicrometer grains with preferred orientation. However, these submicrometer grains are believed to replicate regions of the CdS that are not completely recrystallized. It is likely that, for a substrate temperature of 280°C, a thin In-Cd-S transition layer also exists in our InP/RXCdS structure. Dhare and Parikh⁶ occasionally found two new hexagonal structures and also a cubic superstructure when they vacuum deposited InP films of a few hundred Angstroms on CdS/NaCl at 300°C. However, it appears from our results that thin transition layers will not seriously degrade the replication of InP grains on RXCdS grains. Unintentionally doped films prepared at 280°C are n-type. Be-doped films prepared at 280°C are also n-type, presumably due to a rapid increase in the n-type nature defect concentration below a substrate temperature of 320°C.

CdTe was also deposited on RXCdS at 460°C in a physical vapor deposition (PVD) system. This system is a modification of an earlier system⁷ for growing CdTe by PVD. Growth was undertaken in a 2-in.-diameter flat-bottomed vertical quartz ampoule with the RXCdS substrate located at the bottom of the ampoule. A CdTe source at ~600°C was located 1 in. above the substrate. Samples were loaded through a 2-in.-diameter stainless-steel flange located at the top of the ampoule. The ampoule containing the source and the substrate were first outgassed at 100°C and 10^{-7} Torr. Then the source and substrate were brought up to the growth temperature, and CdTe was deposited at a rate of ~30 $\mu\text{m/hr}$.

X-RAY READ OF
InP/RXCdS

X-RAY READ OF
CdTe/RXCdS

Figure 3. X-ray Read pictures of InP (top) and CdTe (bottom) deposited on RXCdS.

Figure 4 shows SEM pictures of $\sim 30\text{-}\mu\text{m}$ -thick CdTe films deposited on (top) RXCdS and (bottom) ITO/GLASS substrates. For the CdTe grown on the RXCdS, the average grain size is about $40\text{ }\mu\text{m}$. For CdTe grown on the ITO/GLASS substrate, the grain size is about an order of magnitude less. A more direct comparison in the middle figure at a low magnification shows CdTe grown both on and off the RXCdS. The X-ray Read picture (Figure 3, bottom) confirms the presence of the large CdTe grains. Thin films of CdTe with grains as large as $70\text{ }\mu\text{m}$ have recently been prepared by CVD at 620°C on unrecrystallized CdS.⁸ However, the lower growth temperatures possible with physical vapor deposition are preferred in preparing CdTe thin-film solar cells, as vacuum processing is more likely to result in smooth, continuous films and to be a more economical technology.

The morphologies of the CdTe and InP layers are quite different. Compared to InP, the CdTe grains have larger facets. Enhanced facet size is due in part to the higher substrate temperature for the CdTe, as a higher substrate temperature enhances surface mobility. However, even under similar growth conditions, the CdTe facets should be larger than the InP facets due to differences between the binding energies of crystal planes. Unlike the InP, it is not evident that the CdTe replicates the RXCdS. In the CdTe growth, the larger grains appear to crowd out the smaller ones.

The preparation of large grains of InP on a low-cost substrate lends support to further development of the InP/CdS system. These results rule out the possibility that an In-Cd-S transition layer would prevent the epitaxial deposition of large grains of polycrystalline InP on CdS. Potential problems do not exist, however. A high concentration of n-type native defects at lower substrate temperatures may interfere with intentional p-type doping. The

CdTe/RXCdS/ITO/GLASS

CdTe/RXCdS/ITO/GLASS

CdTe/ITO/GLASS

CdTe/ITO/GLASS

Figure 4. SEM pictures of CdTe deposited on (top) RXCdS and (bottom) ITO/GLASS. The middle picture directly compares the grain size of CdTe deposited on RXCdS to that on ITO/GLASS.

extent of sulfur diffusion and consequently n-type doping in the p-type InP will determine whether the development of this device will be directed towards a backwall or frontwall device.

An increase in the grain size of the CdTe for solar cells is not as important as for the III-V compounds because the leakage currents at the grain boundary in the wide bandgap II-VI materials are not as severe. Difference in device performance between the single crystal and polycrystalline CdTe/CdS systems are not expected to be as extreme as in the InP/CdS systems because the lattice mismatch between the CdTe and CdS will affect device performance regardless of grain size.

The authors thank Ken Miller and Art Timper for the X-ray Read pictures, Jerry Meldrum for the SEM pictures, and Roger Turk for the optical photographs. This work was administered by SERI on DOE Contract XJ-9-8170-1.

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