291
11-12-80
MR

Dr. 2021
SERI/PR-8170-1-T1

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

MASTER

Quarterly Technical Progress Report No. 3, December 1979—April 1980

By
K. Zanio

June 1980

Work Performed Under Contract No. AC02-77CH00178

Hughes Research Laboratories
Malibu, California

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$5.00
Microfilm \$3.50

INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

K. Zanio

Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265

June 1980

Contract XJ-9-8170-1

Quarterly Technical Progress Report No. 3
For period December 1979 through April 1980

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

Monitored by
SOLAR ENERGY RESEARCH INSTITUTE
Photovoltaic Program Office
Golden, CO 80401

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

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 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 and H. Montano.

ABSTRACT

Thin films ($\sim 1 \mu\text{m}$ thick) and large grains ($\sim 40 \times 40 \mu\text{m}$) of InP were epitaxially deposited on low-cost recrystallized CdS (RXCdS) substrates at 280°C by planar reactive deposition. At 380°C , a 0.4- to $1.0\text{-}\mu\text{m}$ -thick In-Cd-S transition layer between the InP and the RXCdS degrades the quality of the InP epitaxy. However, p-type InP films were prepared at this temperature by Be-doping and capping the entire RXCdS substrate with InP. Large grains of CdTe ($\sim 40 \mu\text{m}$) were also deposited on RXCdS substrates at 460°C by physical vapor deposition. The grain size of the RXCdS is typically $40 \mu\text{m}$. However, during this period we prepared RXCdS with grains having dimensions up to $300 \mu\text{m}$.

TABLE OF CONTENTS

SECTION		PAGE
	LIST OF ILLUSTRATIONS	6
1	INTRODUCTION	7
2	EPITAXY OF InP ON RECRYSTALLIZED CdS	8
	A. Recrystallized CdS.	8
	B. Capping the Recrystallized CdS	8
	C. In-Cd-S Transition Layers	10
	D. InP on Recrystallized CdS at Reduced Temperatures	15
3	EPITAXY OF CdTe on Recrystallized CdS	19
4	FUTURE WORK AND SUMMARY	22
	REFERENCES	23

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Polarized light microscope (left) and X-ray Read (right) pictures of fully recrystallized (top) and incompletely recrystallized (bottom) CdS films	9
2	Sulfur doping in InP via vapor transport	11
3	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	12
4	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	14
5	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	16
6	X-ray Read pictures of InP (top) and CdTe (bottom) deposited on RXCdS	17
7	SEM pictures of CdTe deposited on (top) RXCdS and (bottom) ITO/GLASS	20

SECTION 1

INTRODUCTION

This report summarizes the efforts at Hughes Research Laboratories during the third quarter under Contract XJ-9-8170-1 to develop the InP/CdS system as an all-thin-film solar cell. During this quarter, we successfully deposited large-grain thin films of InP on low-cost recrystallized CdS (RXCdS) substrates. This is an important achievement because it is the first time that large-area but thin grains of a III-V compound have been deposited on a low-cost substrate. At higher temperatures, the quality of the epitaxy degrades because an n-type In-Cd-S transition layer forms between the InP and the CdS. Although films prepared at elevated temperature exhibited poor epitaxy, we were able to prepare p-type InP layers. In the future preparation of our InP/CdS thin film devices the upper substrate temperature will be limited by the extent of n-type sulfur doping in the InP due to diffusion from the CdS. The lower substrate temperature will be limited by the increase of n-type native defects in the InP. Consequently, there is a range of substrate temperatures where preparation of the all-thin-film InP/CdS backwall cell should be feasible. These results are discussed in Section 2.

The availability of RXCdS prompted us to deposit CdTe on these substrates. This resulted in a significantly larger CdTe grain size, as discussed in Section 3.

During the next quarter, we intend to prepare devices on our all-thin-film p-InP/RXCdS/ITO/GLASS structures. These and other plans are discussed in Section 4.

SECTION 2

EPITAXY OF InP ON RXCdS

A. RXCdS

In the second quarter, we reported the preparation of RXCdS having grains with lateral dimensions up to 40 μm . During this quarter, we prepared films with grains having dimensions up to 300 μm . However, the quality of these recrystallized films is not apparent from optical microscope pictures. X-ray Read pictures are the best presently available technique for evaluating the films. We will discuss our use of the X-ray Read camera to evaluate the quality of RXCdS. The left side of Figure 1 shows polarized light pictures of 15- μm -thick RXCdS films having grains with dimensions of approximately (top) 30 μm and (bottom) 100 μm . The right hand side shows X-ray Read photographs for comparison with the optical photographs. Only discrete spots characteristic of a fully recrystallized film* are found in the X-ray Read picture of the film containing the smaller grains. In these Read pictures, a background of discrete spots due to white radiation is superimposed on the discrete spots due to the $\text{Cu}(K_\alpha)$ radiation. It is generally true that the degree of recrystallization is more complete with larger grain sizes. This comparison in Figure 1 is an exception to the general behavior. The Read picture for the film having the larger grains also shows arcs, which are characteristic of submicrometer-size grains having a preferred orientation with the axis normal to the substrate.

B. CAPPING THE RXCdS

When Be-doped and presumably p-type InP layers were deposited in the second quarter onto semiinsulating InP substrates, Hall measurements indicated that films were n-type rather than p-type. These results were obtained with CdS/ITO/GLASS substrates in adjacent deposition positions. Sulfur is presumed to outgas from the exposed CdS and become

* Fully recrystallized CdS films are those films which show only discrete spots and no rings on our X-ray Read pictures.

POLARIZED LIGHT

X-RAY READ

FULLY RECRYSTALLIZED CdS

INCOMPLETELY RECRYSTALLIZED CdS

Figure 1. Polarized light microscope (left) and X-ray Read (right) pictures of fully recrystallized (top) and incompletely recrystallized (bottom) CdS films.

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 at substrate temperatures of 380°C, capped the CdS. As indicated in Figure 2, p-type films can be prepared on semi-insulating InP only when the CdS is capped.

C. In-Cd-S TRANSITION LAYERS

Earlier studies indicated that an In-Cd-S transition layer exists when InP is deposited on polycrystalline CdS at substrate temperatures of about 400°C. Studies in the third quarter provide information regarding the thickness of the transition layer for InP deposited on RXCdS. Attempts to deposit a 0.35- μ m-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. Hall measurements of the InP deposited on an adjacent semi-insulating InP substrate indicated an n-type layer, which is not surprising since the transition layer was never capped and sulfur could dope the InP film via vapor transport.

In subsequent runs, we deposited a 4.5- μ m-thick InP layer on the InP substrate, also at a substrate temperature of 380°C. This time, InP covered the In-Cd-S and RXCdS. Hall measurements on the semi-insulating InP substrate indicated p-type. Hot probe measurements on the RXCdS indicated p-type. Both X-ray Read and SEM pictures were taken of the InP/RXCdS structure. Figure 3 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

		InP ELECTRICAL PROPERTIES	
		RXCdS	hi ρ InP
EXPOSED CdS		n-TYPE	n-TYPE $10^{17} - 10^{19}$ cm^{-3}
CAPPED CdS		p-TYPE ON n-TYPE	p-TYPE $10^{17} - 10^{19}$ cm^{-3}

Figure 2. Sulfur doping in InP via vapor transport.

Figure 3. 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.

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 1, 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 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 3, 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 4) SEM and HEED pictures of InP deposited on the Cd face of single crystals of CdS. 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.

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

SEM

HEED

Figure 4. 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.

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 Hall measurements of the InP on the semi-insulating substrate and hot probe measurements of the InP on the RXCdS would not have indicated p-type. Although we deposited InP on an InCdS transition layer and not directly on the RXCdS, we achieved some degree of epitaxy. The exact composition and crystal structure of the InCdS transition layer are not known. Possible compounds are In_2S_3 doped with Cd and CdIn_2S_4 . Both the In_2S_3 and CdIn_2S_4 sulfur lattices are smaller than the sulfur lattices for CdS. It is not clear what effect the InCdS layer has on the degree of InP epitaxy on solar cell performance. The effect of a thin transition layer may not be catastrophic. It is inevitable that at least several monolayers of InCdS exist in the 15% CdS/InP single-crystal solar cell prepared by depositing CdS on InP at 600°C.

D. InP ON RXCdS AT REDUCED TEMPERATURES

When InP is deposited on RXCdS at reduced temperature, the degree of epitaxy significantly improves. Grains with lateral dimensions of 40 μm are observed. Figure 5 (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 6, 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

INP ON SINGLE
RXCdS GRAIN

INP ON TWO
RXCdS GRAINS

INP ON TWO
RXCdS GRAINS
(GRAIN BOUNDARY
DELINEATED)

Figure 5. 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 6. X-ray Read pictures of InP (top) and CdTe (bottom) deposited on RXCdS.

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.

SECTION 3

EPITAXY OF CdTe ON RXCdS

The CdTe/CdS system is also being considered by DOE for an all-thin-film solar cell. Figure 7 shows SEM pictures 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 6, bottom) confirm the presence of the large CdTe grains. Although only a single CdTe deposition was 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.

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 severe. Differences in device performance between the single-crystal and polycrystalline CdTe/CdS systems are not expected to be as

CdTe/RXCdS/ITO/GLASS

CdTe/RXCdS/ITO/GLASS

CdTe/ITO/GLASS

CdTe/ITO/GLASS

Figure 7. 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.

extreme as in the InP/CdS systems because the lattice mismatch between the CdTe and CdS will affect device performance regardless of grain size. However, an increase in the grain size of the CdTe is important if a lower bandgap HgCdTe layer with potentially higher leakage currents is used to increase the efficiency of the thin film structure. Thin films of large grains of CdTe have recently been prepared by CVD at 600°C on CdS.¹ However, the lower growth temperatures possible with physical vapor deposition² are preferred in the preparation of CdTe thin-film solar cells as the latter vacuum processing (1) is more likely to result in smooth, continuous films; (2) represents a more economical planar technology; and (3) is more adaptable to subsequent preparation of HgCdTe.

SECTION 4

FUTURE WORK AND SUMMARY

The preparation of large grains of InP on a low-cost substrate lends further enthusiasm to the development of the InP/CdS systems. These results rule out the possibility that an In-Cd-S transition layer would prevent the preparation of large grains of InP epitaxial layers on CdS. However, the extent of sulfur diffusion and consequently of n-type doping in the p-type InP will determine whether the development of this device will be directed towards a back wall or front wall device. During the next quarter, efforts will be directed towards preparing devices on our p-InP/RXCdS/ITO/GLASS backwall structures. Contacts will be made by depositing p^+ Be doped on the p-InP. Light and dark current versus voltage will be examined as a function of the temperature at which the p-InP is deposited on the RXCdS substrate. We anticipate that it will not be possible to prepare p-type InP films below 300°C because of an intrinsic n-type defect. We anticipate that excessive leakage currents will occur for layers prepared above 360°C because of extensive growth of the In-Cd-S transition layer and excessive sulfur diffusion. Therefore, a substrate temperature of about 330°C should be near optimum for the preparation of the p-InP layer.

REFERENCES

1. M. Bettini and C. Brandt, J. Appl. Phys. 54, 869 (1979).
2. W. Akutagawa and K. Zanio, J. Crystal Growth 11, 191 (1971).