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INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

Quarterly Report for Period July--October 1980

By
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MASTER

January 1981

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Hughes Research Laboratories
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INDIUM PHOSPHIDE/CADMIUM SULFIDE THIN-FILM SOLAR CELLS

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July 1980 through October 1980

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PREFACE

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 SERI contract XZ-0-9196-1. 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. K. Miller, P. Hoberg, H. Montano, and A. Timper.

ABSTRACT

InP thin films were deposited by planar reactive deposition on recrystallized CdS (RXCdS) and semi-insulating (100) InP substrates and evaluated as potential layers for an all-thin-film solar cell. One objective of this period was to grow InP on RXCdS at a substrate temperature which is high enough to permit the growth of p-type material but yet low enough to permit the epitaxial growth of large grains. Films prepared on RXCdS at approximately 330°C contained a mixture of grains having both large and submicron lateral dimensions. Be-doped epitaxial films, deposited on semi-insulating InP at 330°C, showed both n- and p-type behavior. Films prepared at higher temperatures with a freshly Be-charged indium source were p-type. However, at these temperatures, layers prepared after several runs with the same source were n-type. Analyses of the indium source and films were initiated to determine the cause of the transient doping.

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SECTION 1.

INTRODUCTION

This report summarizes the efforts at Hughes Research Laboratories (HRL) for the first quarter on this contract to develop InP/CdS as a thin-film solar cell. An important step in the development of this system is to deposit epitaxial thin films of p-type InP with large lateral grain size on a low-cost substrate. By the end of DOE contract XJ-9-8170-1, we had deposited epitaxial n-type InP thin films with large lateral grain size ($\sim 40 \mu\text{m}$) on recrystallized CdS (RXCdS) substrates at 280°C . Films were not p-type. We prepared p-type films on RXCdS at 380°C , but the quality of the epitaxy was poor. The first objective of the present study is to prepare p-type films at an intermediate substrate temperature with good crystal perfection.

SECTION 2

EXPERIMENTAL RESULTS

A. InP EPITAXY ON RXCdS

We prepared several films of InP on RXCdS at about 330°C. The quality of the epitaxy was intermediate between that at 280°C and at 380°C. Figure 1 shows scanning electron microscope (SEM) and X-ray Read pictures of InP films prepared on RXCdS at 280°C, 330°C, and 380°C. The results at 280°C, obtained in the previous program, show the best crystal perfection. Average lateral grain size was about 40 μm . In the SEM picture, the grain boundary between two large grains is delineated. The X-ray picture is dominated by spots rather than rings, which is characteristic of large rather than submicrometer size grains. At the other extreme, the results at 380°C are characteristic of poor crystal perfection. The SEM shows no faceting. The X-ray Read picture is dominated by rings rather than spots. Our crystal perfection at 330°C is of intermediate and unacceptable quality. The X-ray Read still shows rings due to a large fraction of submicrometer size grains. It was not clear whether the InP crystal perfection is limited by either a contaminated RXCdS surface, an improper phosphorus to indium flux ratio, or a poor RXCdS/InP interface due to interdiffusion between the CdS and the InP. Determining the degree of interdiffusion at this substrate temperature was the first step we took to solve this problem. In this period, we delivered to SERI two InP/RXCdS structures prepared at 340°C and 380°C for SIMS or Auger/sputter analysis. We hope to report these results in the next quarterly.

B. ELECTRICAL PROPERTIES OF Be-DOPED InP

In these studies, InP was also deposited on semi-insulating substrates to determine the type and electrical properties of the films. Although most of the In sources were charged with Be for p-type doping, p-type films were not obtained. Under contract XJ-9-8170-1, we successfully established a procedure to cap the RXCdS to prevent n-type

Figure 1. Scanning electron microscope and x-ray Read pictures of InP deposited on RxCdS at different substrate temperatures.

doping of the InP by sulfur via vapor transport. However, we continued InP deposition without the presence of the RXCdS to avoid the possibility of inadvertent n-type doping by sulfur. N-type films were still obtained, even at high substrate temperature, where severe n-type doping by native defects is not observed. After incorporating a new Knudsen cell in the system, we found that p-type films could be obtained. Apparently, the Knudsen cell contained residual contaminants after outgassing. In contract XJ-9-8170-1, we had established a procedure for outgassing used cells in a vacuum at 1500°C . Apparently this cell had not been outgassed adequately.

After incorporating the new Knudsen cell, p-type doping with Be was obtained. Figure 2 shows the general behavior of the type and carrier concentration for several runs subsequent to charging In sources to similar levels of Be. The degree of p-type electrical activity is strongly dependent on the substrate temperature. At a substrate temperature of 380°C , the films are strongly p-type for the first few runs. After the fourth or fifth deposition, the films are n-type. The films become either weakly compensated (solid line) or, less frequently, highly compensated (dashed line). At a substrate temperature of 300°C or below, p-type films are never obtained. Inconsistent results are obtained at 330°C .

Two problems are apparent. The first is associated with the source, the second with the substrate.

1. Source Problem

The source either does not deliver a constant flux of Be atoms or it delivers Be plus an impurity such as oxygen. It is therefore necessary to know the concentration and distribution of Be atoms in the source and in the films as a function of the number of runs after charging the source. We undertook an analysis of several Be-doped films with our microprobe but it was not sensitive enough to Be. However, Al was detected in some of our films at about 1% (see Figure 3). When our film, indicated by the dots, is compared against an InP reference sample, an Al peak becomes apparent to the left of the phosphorus peak.

Figure 2. Type and carrier concentration of InP films prepared at various substrate temperatures versus the number of depositions after charging the In source with similar levels of a 5%/95% by weight Be/Al alloy.

Figure 3. Microprobe analysis of Be doped InP film showing about 1% Al.

Al is present on our films because Be is incorporated in the In source as a 5%/95% by weight Be/Al alloy. At high levels of Al and presumably also of Be, the quality of the epitaxy degrades. Figure 4 shows SEM and corresponding selective area electron diffraction (SAD) pictures of a layer containing ~1% Al. This figure also contains SEM and SAD pictures of a layer having less than 1% Al. The SEM shows the surfaces to be rougher for the more heavily doped layer. There is no difference in the channeling pattern between the substrate and the film for the film containing less than 1% Al. However, for the film containing 1% Al, the channeling pattern of the substrate is superior to that of the film. For more sensitive analysis, we sent Be-doped films to SERI for SIMS and Auger analyses. We also sent an undoped In source to Charles Evans & Associates. Figure 5 shows the results from Charles Evans & Associates for oxygen bombardment analysis of an undoped In source. A mass spectrum (from mass 1 to 250) was obtained from the surface region and from the bulk of a high-purity In foil. The relative ion intensities between the two In samples are different because of extraction efficiencies resulting from changes in sample topography. For example, the ^{115}In intensity which was measured with a Faraday cup is 6.0×10^6 for the In foil and 6.0×10^5 for the In source. The Faraday cup was inserted into the secondary ion beam for ^{113}In through ^{115}In because the In^+ signal was too intense to be placed on the electron multiplier. The intensity measured by the Faraday cup needs to be multiplied by 1200 to be on the same scale as the remaining ions which were measured on the electron multiplier. When comparing impurity ion intensities between the two In samples, the ratio of the impurity intensity to the In matrix ion intensity should be used. The impurities which were found to be more abundant in the In source over the In foil are ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe , and ^{69}Ga . A depth profile (Figure 6) of these ions in the In source was then made. The abrupt change in ion intensity four-fifths of the way through the profile resulted when the sputtering rate was increased four fold. Each element shows a gradual decrease in intensity versus depth. Surprisingly, the SIMS shows high levels of Be and Al in the undoped source. This is thought to be due to Al and Be in residual

SEM

SAD

Figure 4. Scanning electron microscope (SEM) and corresponding selective area electron diffraction (SAD) pictures of Be/Al doped InP films prepared at 330°C containing (top) less than 1% and (bottom) approximately 1% of Al by microprobe analysis.

Figure 5a. SIMS analysis of surface of In source and pure In foil for mass 1 through 50.

Figure 5b. SIMS analysis of surface of In source and pure In foil for mass 51 through 100.

Figure 5c. SIMS analysis of surface on In source and pure In foil for mass 101 through 150.

Figure 5d. SIMS analysis of surface of In source and pure In foil for mass 151 through 200.

Figure 5e. SIMS analysis of surface of In source and pure In foil for mass 201 through 250.

Figure 6. SIMS depth profile of ^9Be , ^{27}Al , ^{40}Ca , ^{56}Fe and ^{69}Ga in In source.

indium in the PH_3 inlet line which subsequently dopes the new source. Regardless, this level of Be does not dope the films p-type. InP prepared with this source was n-type.

An oxide layer of BeO may suppress the flux of Be to the films. We have not observed such transient doping effects with Sn. An Auger analysis at the surface of the above source for P, C, and O is being done at Charles Evans & Associates. These results should be helpful in resolving this problem and will be included in the report for the next period.

2. The Substrate Problem

At substrate temperatures of 300°C and lower, p-type doping is not achieved even for the initial run. There are several possibilities why p-type doping cannot be achieved. First Be may either not be electrically active, due to association with oxygen or native defects, or it may be compensated by these species. Second, the films may contain higher levels of oxygen at lower substrate temperatures than at higher substrate temperatures due to a lesser degree of interaction with H_2 . The overriding effects of n-type native defects are the most likely reason why we cannot make the material p-type at low substrate temperatures. We consider the n-type doping effects of O in the films to be of secondary importance because MBE systems, which operate at a lower background pressure and in a cleaner environment, produce the same concentrations of n-type carriers and presumably of native defects. Interaction of native defects with fluctuating levels of Be and O probably results in inconsistent doping at intermediate substrate temperatures. The concentration and type of native defects are affected by the ratio of the flux of indium to phosphorus atoms $[\text{In}]/[\text{P}]$. We have not undertaken studies to determine the effect of $[\text{In}]/[\text{P}]$ on doping. The primary difficulty in solving the doping problem in the substrate is the unavailability of a reproducible flux of Be atoms. Therefore, we must solve this problem first.

SECTION 3

DISCUSSION

Figure 7 shows two possible all-thin-film InP/RXCdS structures. In the first structure, a p-type InP film is deposited directly on the RXCdS substrate. Light is incident on the glass. Whether this structure is viable depends on whether a suitable temperature can be found that is simultaneously low enough to permit good InP epitaxy and high enough to permit p-type doping. At a substrate temperature of 330°C, there are presently $\sim 10^{18} \text{ cm}^{-3}$ n-type defects present in InP. This background concentration is too high to permit good transport properties by overcompensation with p-type doping. The only solution is to vary the growth conditions (e.g., [InP]/[P], source temperature) to reduce the native defect concentration. Raising the growth temperature will not solve this problem if good epitaxy cannot be achieved at the present growth temperature. These other alternatives should be investigated before abandoning growth at 330°C.

If either the background concentration of native defects cannot be reduced to 10^{17} cm^{-3} at 330°C or good crystalline perfection cannot be achieved at higher substrate temperatures, then the alternate approach in Figure 7 must be used. In this structure, an n^+ InP epitaxial layer is prepared at 280°C as in Figure 1. This buffer layer will permit the growth of a p^+ layer at a higher temperature of 350°C. A p-type layer would be deposited on the p^+/n^+ tunnel junction at the same temperature. Light is incident in an ITO or CdS transparent top contact.

Figure 7. All-thin-film InP/CdS solar cells utilizing the backwall (left) and frontwall (right) structures.

SECTION 4

FUTURE WORK

Plans for the next quarter include achieving more reliable p-type doping in InP at low substrate temperatures. More specifically, we intend to either determine the cause of transient Be doping or use an alternate p-type dopant. We intend to examine the electrical properties of undoped InP films at low substrate temperatures as a function of $[In]/[P]$ to reduce the concentration of n-type native defects.