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PHOTOVOLTAIC MECHANISMS IN POLYCRYSTALLINE THIN-FILM
SOLAR CELLS

Quarterly Technical Progress Report No. 2 for Period January 27—April 27, 1979

By
K. Zanio

August 1979

Work Performed Under Contract No. ET-78-C-01-3412

Hughes Research Laboratories
Malibu, California

U.S. Department of Energy

Solar Energy

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Quarterly Technical Progress Report No. 2
For period 27 January 1979 through 27 April 1979

Prepared for

DEPARTMENT OF ENERGY
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Washington, D.C. 20545

Monitored by

SOLAR ENERGY RESEARCH INSTITUTE
Photovoltaic Program Office
Golden, CO 80401

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 ET-78-C-01-3412. The technical monitor was Dr. Kim Mitchell at SERI in Golden, Colorado.

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

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ABSTRACT

Indium phosphide films were prepared at reduced temperatures on InP by the planar reactive deposition technique. For substrate temperatures as low as 260°C and growth rates of 1 $\mu\text{m/hr}$, single-crystal epitaxy was obtained on (100) semi-insulating substrates. These results are preliminary steps in the process of achieving clean polycrystalline layers and preparing p-n junctions containing grain boundaries. In parallel studies to eventually passivate grain boundaries by etching beyond the p-n junction to form isolated single-crystal mesa structures, a 3 $\text{HNO}_3\text{:HCl}$ etch was found to preferentially attack selected InP grain boundaries and produce grooves.

SECTION 1

INTRODUCTION

This report summarizes efforts at Hughes Research Laboratories (HRL) during the second quarter under Department of Energy Contract ET-78-C-01-3412 to investigate the effects of grain boundaries on solar cells and to develop approaches for alleviating the adverse effects of grain boundaries. Our program includes preparing thin-film InP p-n junctions with and without grain boundaries under growth conditions as nearly identical as possible in order to isolate the effect of grain boundaries on the p-n junction. During the first quarter, our deposition equipment was modified with the intent of eventually preparing p-n junctions at lower temperatures so that the resulting thin-film structures will contain grain boundaries. This report discusses our results for InP films grown at temperatures as low as 260°C.

We expect the leakage currents to be higher and the open-circuit voltages to be lower for polycrystalline p-n junctions than for single-crystal p-n junctions. Although we are certain of these results through our experience and from the literature, it is necessary to prepare reproducible baseline polycrystalline p-n junctions for subsequent studies directed towards reducing the grain boundary leakage currents. Studies begun during the first quarter to passivate the grain boundaries were continued. Such studies are normally made to counteract the adverse effects of foreign atoms that have diffused along the grain boundary to the p-n junction from the substrate, windows, or contacts. During this quarter we demonstrated that single-crystal InP can be epitaxially prepared at temperatures below 300°C. This is important because it suggests that the passivation required to counteract unwanted impurities may not be as extensive if structures can be prepared at reduced temperatures.

Our technique of low-temperature InP growth is discussed in Section 2. Sections 3 and 4 will, respectively, discuss our passivation studies and future plans.

SECTION 2

INP THIN-FILM GROWTH

A. SUBSTRATE ASSEMBLY MODIFICATION

During the first quarter, we redesigned the substrate assembly to allow the substrate to be cooled to below 300°C (Figure 1, top). Introducing a cooled gas into the welded bellows section at atmospheric pressure expanded the bellows. The heating/cooling plate then made pressure contact with the Mo substrate holders. To rotate the Mo substrate holders either into or out of the molecular beam, the heating/cooling plate was retracted from the substrates by evacuating the bellows. However, the welded bellows developed a crack during our initial run. This restricted the background pressure in the deposition chamber to above 10^{-5} Torr and prevented the deposition of clean films. Rather than risk a recurrence of this problem and further interruption of our studies, a more reliable method of coupling the heating/cooling plate to the Mo substrate holders was implemented (Figure 1, bottom). With this method, the heating/cooling plate is positioned by manipulating a flange located exterior to the chamber walls. The flange is coupled to the chamber walls through a more rigid but more durable flexible coupling. A gimbal assembly between the flange and the chamber walls allows manual positioning of the heating/cooling plate. The depositions reported in Section 3 were undertaken with this assembly.

B. INP MORPHOLOGY

During this quarter, we began growing InP at temperatures below 300°C with the modified substrate assembly. Surprisingly, single-crystal epitaxial films were obtained on InP single-crystal substrates. Figure 2(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 2(b) is a Read photograph of InP grown on a (100) semi-insulating InP substrate during the same run at 320°C. The spots are characteristic of the single-crystal

Figure 1. Initial (top) and modified (bottom) substrate assemblies for coupling the heating/cooling plate to the Mo substrate holders.

Figure 2.
 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.

epitaxial film and the single-crystal substrate. 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 2(c)) that is identical to Figure 2(b) and is characteristic of epitaxial growth.

These are interesting results — 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.

Our preliminary electrical measurements on these grown-at-lower-temperature films 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 $4000 \text{ cm}^2/\text{Vsec}$. Because we have only made three runs with the new substrate assembly, the deposition environment probably is not yet as clean as it is possible of becoming. 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 our most recent run is consistent with this explanation. We have included this tentative mobility data point on Figure 3; the figure summarizes mobility data for undoped n-type InP films grown by vacuum technology at Hughes Aircraft and other laboratories. In contrast to our results, InP films grown below 320°C by molecular beam epitaxy (MBE) are polycrystalline.¹ Since the mobilities reported for the polycrystalline films are characteristic of the grain boundary rather than the intragrain material, it is not surprising that our mobilities are higher. Whether or not intentionally Be-doped p-type films with these background transport properties will be adequate for solar cells is not known. However, before preparing p-type films, we intend to determine if undoped films with improved transport properties can be prepared at these temperatures. Under a new InP/CdS program with DOE, we will be preparing CdS/InP cells with Be-doped single-crystal and polycrystalline InP films.

Figure 3. Electrical properties of InP films deposited on InP single-crystal substrates by vacuum technologies.

Our single-crystal results at low substrate temperatures are not unique: single-crystal GaAs,² GaInP,³ and GaInAs³ have been epitaxially grown on single-crystal GaAs substrates at temperatures as low as 200°C by MBE. However, since most of the films deposited at 260°C by MBE and by other vacuum techniques have been polycrystalline (see Table 1 in the first quarterly report), we are examining reasons for this difference. The wide range of temperatures for epitaxy summarized in Table 2 in the first quarterly report may be due to variations in the temperature. The temperature that we refer to is that of the Mo substrate holder and not of the InP. Because the InP is heated from below by radiation and cooled from above by conduction from the Mo block at 260°C, the temperature of the InP should be higher than that of the Mo. However, the difference should not be large because the InP is bonded to the Mo block with In. A second reason for differences in the temperature of epitaxy is that our films are prepared in a reactive atmosphere, whereas in MBE they are not. Hydrogen on the surface might catalyze reactions, resulting in a lower growth temperature.

SECTION 3

PASSIVATION STUDIES

The ability to prepare single-crystal epitaxial layers of InP at a lower temperature is a pleasant surprise with respect to the preparation of the all-thin-film InP-on-CdS-on-glass solar cell. The reduced growth temperature should alleviate grain boundary interdiffusion problems. These results give us additional confidence in preparing improved structures in our new InP/CdS thin-film program. Regardless of these encouraging results, the intrinsic material of the InP grain boundary is likely to degrade cell performance. Consequently, we have continued to examine methods of reducing leakage currents. One general approach to reducing leakage current at the grain boundaries in polycrystalline solar cells is to etch the grain boundary beyond the intersecting junction and passivate the exposed surfaces. None of the etchants used during the first quarter preferentially attacked grain boundaries in InP. However, we found that $3\text{HNO}_3:1\text{HCl}$ can preferentially attack InP grain boundaries. Figure 4 shows a grain boundary and adjacent bicrystals from a wafer that was etched for 1 min. The focus in the bottom picture is trained at the bottom of the groove. The focus in the top picture is trained approximately $8\text{ }\mu\text{m}$ higher on the surface of the two adjacent bicrystals. There is approximately a $1\text{-}\mu\text{m}$ difference between the height of the two crystal planes; this difference is due to differences in the etch rates for different crystal planes.

This etch does not always produce grooves. As discussed in the last quarterly report, steps always occur. The type of grain boundary attack is presumably associated with crystallite orientation. These results encourage us to examine other etchants and modify the present etch and processing so as to attain stronger preferential grain boundary attack. It is also important to determine the orientation conditions for preferred attack (i.e., the orientation between the bicrystals and their orientation with respect to the surface). Preferred growth of crystallites, including CdS, occurs on amorphous substrates. In the case of CdS, the c-axis normal to the substrate is the preferred orientation.

→ | ← 10 μm

→ | ← 10 μm

Figure 4. (Center) cross section of InP bicrystal preferentially attacked at grain boundary by HNO_3 : HCl etch. Top view of bicrystal with plane of focus (indicated by arrow) at (top) surface and in (bottom) groove.

Consequently, InP in the InP-on-CdS structure will grow with the [111] axis also preferred normal to the substrate. It is therefore important to determine the degree of preferential etching for InP grain boundaries with crystallites of such an orientation.

SECTION 4

FUTURE PLANS

During the third quarter, we will continue work toward inducing the polycrystalline growth of InP on InP substrates. Several steps will be taken, including lowering the growth temperature, increasing the growth rate, altering the substrate orientation, and undertaking growth on lattice mismatched substrates. P-N junctions prepared from single-crystal and polycrystalline structures will be compared. A longer range goal of this program is to reduce the leakage currents in these polycrystalline structures by incorporating results from our parallel passivation studies. Studies planned for the next quarter to achieve this goal include defining the crystallographic orientation of adjacent grains whose grain boundary is selectively attacked and continuing to search for etchants that will provide a more universal attack of the grain boundaries. Studies directed towards the preferred anodic oxidation of grain boundaries were initiated in the final quarter. These parallel passivation studies will be continued in the next quarter.

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