EMERGING MATERIAL SYSTEMS FOR SOLAR-CELL APPLICATIONS

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MASTER

Technical Progress Report No. 3
For Period 17 October 1979 to 16 January 1980

Contract No. DE-AC04-79ET23003

July 23, 1980

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ABSTRACT

This is the third quarterly report on a program to develop an InP/CdS polycrystalline thin film solar cell. During this quarter, the plasma deposition was completed and a number of depositions of InP were made with the indium transported into the reaction zone via the vapor phase transport of indium chloride.

Amorphous films of InP were obtained when the substrate was at room temperature. Substrate temperatures above approximately 200°C resulted in polycrystalline films. Plans for the next quarter include the use of single crystal InP as the substrate in an attempt to grow epitaxial film.

1. INTRODUCTION

The planned program for thin film InP as a solar cell material entailed five tasks: 1) Modelling 2) Film Growth 3) Film Characterizations 4) Cell Preparation and 5) Cell Evaluation. The major task was to demonstrate a low temperature film growth of InP using a plasma process. The other tasks were dependent, to some degree, on the success of the film growth task.

During this quarter, the plasma induced deposition (PID) system was completed and a number of depositions of InP were made using the chloride transport of indium. Amorphous films of InP were deposited at room temperature and polycrystalline films were obtained at elevated temperature. In addition, junctions were formed in n-type InP by diffusion of Cd using a sealed tube technique.

2. PROGRESS

2.1 InP Growth by Plasma Induced Deposition (PID)

The final version of the tube system is shown in Figures 1, 2, and 3. It is a 2" O.D. closed quartz tube. One end has a glass-to-metal seal which connects to the remainder of the system. The plasma is generated inductively by a 2-turn winding around the tube. The power supply is a 1 KW Varian double-ended system with its own matching network. The substrate heater was fabricated from Kanthal wire, running parallel to the tube to reduce loading on the RF supply.

Initially the system was tried using capacitive coupling of the RF supply since design considerations were simpler. Coupling was achieved using two plates outside the tube. Severe non-uniformities in the deposition were encountered. It appears that the discharge region

Figure 1 Tube System for PID of InP Films Using In Source

Figure 2. Photograph of Plasma Tube System

Figure 3 Photograph of Source Furnace for Plasma Tube System

is similar to the positive column of a d-c discharge, which tends to be electrically noisy and unstable. The uniformity and reproducibility of the deposition were improved by changing to inductive coupling. Alternate methods exist for producing the discharge which appear more controllable but there was insufficient time to investigate them.

The transport of the indium to the substrate was by the vapor phase as InCl . The InCl which was produced by flowing HCl over metallic indium was converted to indium chloride by the reaction: $\text{In} + \text{HCl} \rightarrow \text{InCl} + 1/2\text{H}_2$. If the walls of the system are maintained above $\sim 100^\circ\text{C}$, the InCl will not condense on the walls and will be carried to the plasma region. Conventional CVD reactors, operating at room pressure, normally obtain virtually complete conversion of the HCl (i.e., each molecule of HCl converts to InCl) at temperatures of 750°C . In this system, it was necessary to operate the indium source at 1000°C before an appreciable transport of indium occurred.

Measurements on the total amount of indium transported over a number of runs indicated a conversion of approximately 15%. Such a conversion is probably due to the combination of high gas flow and low pressure, resulting in a low residence time for the HCl over the In source. An increase in this ratio is probably desirable since excess chlorine can have a number of side effects such as etching of the InP film, and could be accomplished by a redesign of the source and/or raising the source temperature. Limitations on the present furnace prevented use at temperatures over 1000°C .

The gas flow was controlled by individual rotometers located near the cylinders. The gases were mixed prior to entering the source tube; HCl gas was supplied as 15% HCl in argon (Matheson UHP) and a flow rate of 25 sccm/min was used. The PH_3 was also provided as 15% PH_3 in argon (Matheson UHP) and its flow rate was set at 40 sccm/min. The indium source was held at 1000°C . The mechanical pump was valved off to give a total pressure of 0.2 torr as measured by a Bariton MKS gauge located at the exhaust side of the tube.

An unusual development was a strong substrate temperature dependence of the thickness. This can be seen in Figure 4, which plots the thickness obtained vs. the substrate temperature (all runs lasted 20 minutes) and indicates an upper temperature limit of about 400°C. There are a number of possible mechanisms for such a temperature dependence. If the growth process involves absorption of an InCl molecule followed by capture of a phosphorus atom to yield InP, the InCl absorption-evaporation process would be strongly temperature dependent. A more likely explanation is a temperature activated etching of the growing film with the chlorine via the mechanism

Evidence of this reaction include some single crystal samples which had a weight loss during an attempted deposition at a substrate temperature of 450°C. In addition, there is a large excess of chlorine present due to the low conversion ratio involved in the transport of the indium. Further work would be required to determine if this 400° limit is basic to the process or simply a result of the chosen deposition condition.

Films were deposited at substrate temperatures from 100°C to 400°C. Films deposited below 170°C were amorphous as determined both by reflection electron (RED) and X-ray diffraction. These films were also insulating ($\rho > 10^{11} \Omega\text{-cm}$). Films deposited on glass or quartz substrates above 170°C were polycrystalline.

Figure 5 shows the X-ray diffraction pattern of films deposited at temperatures from 170°C to 420°C. The rings at 170°C are diffuse while the rings at 420°C are much sharper indicating a larger grain size. There is no evidence of any preferred growth pattern in the film nor any indication of other phases present in the film.

RED photographs of films deposited at various temperatures are shown in Figure 6 and Figure 7. Figure 8 shows SEM photographs of the sample T18. This sample (substrate temperature of 180°C) had some micron-size spherical growth patterns sitting on a relatively featureless

Figure 4 Thickness of InP Films vs. Substrate Temperature (all Depositions were for 20 Minutes).

T18
275°C Substrate Temperature
Quartz Substrate

T19
400°C Substrate Temperature
Quartz Substrate

T20
420°C Substrate Temperature
Quartz Substrate

Figure 5 X-ray Patterns for InP on Quartz

T18

T19

Figure 6 RED Patterns of InP Films on Quartz. Sample T18 was Deposited at 180°C and T19 at 340°C.

Figure 7 RED Patterns of InP Films on Quartz (T20) Deposited at 400°C.

T18 (2400X)

T18 (24,000X)
Background Area

Figure 8 SEM Photograph of Sample T18, Deposited on Quartz at 180°C.

background. EDAX measurements (Figure 9a and b) indicated InP in both the spheres and the background. It is possible that poor control of the deposition produced this type of growth pattern since it was not found in other samples. Figure 10 shows SEM views of sample T20 deposited at a substrate temperature of 400°C. It has a more textured surface than the lower temperature sample (consistent with the higher growth temperature) but there are no large irregularities.

2.2 Junction Formation in InP

Some diffusion experiments were tried in order to dope the InP p-type. This would allow device studies on single crystals as well as junction formation on the n-type thin films produced by the various deposition techniques.

The junctions in InP were fabricated by Cd diffusion according to the technique developed by Tien and Miller.¹ This permits the use of high diffusion temperatures to obtain reasonable, controllable diffusion depths and yet avoid the high Cd pressures which would cause degradation of the InP surface by alloying. Instead of Cd as a diffusion source, CdP or CdP plus P is used since this gives much lower equilibrium Cd pressures at a given temperature. The source and InP were sealed in an evacuated quartz ampoule, heated for the desired time and temperature and the ampoule was then air quenched.

The p^+n junction depths were measured by cleaving the diffused wafer and staining it in a 50/50 ferricyanide/KOH solution for 10 sec at room temperature.² This solution etches the junction region preferentially as shown in Figures 11 (a) and (b). In the first test diffusion a deep junction was desired to calibrate the system and allow for easy junction depth measurement. The diffusion conditions were 681°C for 4 hours and the junction depth was measured as 8.5 μm (see Figure 20 (a)) compared to a predicted value of 9 μm . The temperature was then lowered to 615°C for the same 4 hours. The resulting junction depth was 0.9 μm , compared to a predicted 1.9 μm .

T-18

PR= S 100SEC 0 INT

V=2048 H=10KEV 1:30 AQ=10KEV 10

Figure 9a EDAX Measurements of Sample T18 — Background

T-18

PR= S 41SEC 0 INT

V=2048 H=10KEV 1:30 AQ=10KEV 10

Figure 9b EDAX Measurements of Sample T18 - Sphere.

T20 (2400X)

T20 (24,000X)

Figure 10 SEM Photographs of Sample T20, Deposited on Glass at 400°C.

(a)

(b)

Figure 11 InP p^+n Junctions. (a) $681^\circ\text{C} - 4 \text{ hrs.}$, $x_j = 8.5 \mu\text{m}$; (b) $615^\circ\text{C} - 4 \text{ hrs.}$, $x_j = 0.9 \mu\text{m}$. The Dark Line is the Actual Junction.

These experiments show that shallow junction devices can be fabricated by this diffusion technique in single crystal InP starting material. However, when the same technique was applied to deposited InP films, we were unable to convert the layers. At the higher temperatures the films peeled while at lower temperatures they did not convert, even when using a Cd source.

3. FUTURE WORK

During this period, the PID system was used to deposit films of InP on quartz and glass substrates. The films were amorphous when the substrate were at room temperature and polycrystalline for substrate temperatures above 200°C. During the next quarter, single crystal InP will be used as a substrate with an attempt to grow the films epitaxially. If time permits, this will be followed by depositions using single crystal CdS as the substrate.

REFERENCES

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