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**ZnSe WINDOW LAYERS For
GaAs and GaInP₂ SOLAR CELLS**

Final Report

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ABSTRACT

This report concerns studies of the use of ZnSe as a window layer for GaAs solar cells. Well-oriented crystalline ZnSe films on (100) single crystal GaAs substrates were grown by MOCVD. In particular, ZnSe films were grown by reacting a zinc adduct with hydrogen selenide at temperatures in the range of 200°C to 400°C. X-ray diffraction studies and images obtained with an atomic force microscope determined that the films were highly oriented but were polycrystalline. Particular emphasis was placed on the use of a substrate temperature of 350°C. Using iodine as a dopant, n-type ZnSe films with resistivities in the range of .01 to .05 ohm-cm were grown on semi-insulating GaAs. Thus procedures have been developed for investigating the utility of n-type ZnSe window layers on n/p GaAs structures. Studies of recombination at n-ZnSe/n-GaAs interfaces in n-ZnSe/n-GaAs/p-GaAs cell structures are planned for future work.

1. INTRODUCTION

This report concerns the first years effort to investigate the use of ZnSe as a window layer for GaAs solar cells. GaAs solar cells are typically fabricated with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (AlGaAs) heteroface layers. There are two particular problems with the use of AlGaAs. First, it is difficult to grow high quality Al containing compounds consistently because Al is so reactive with oxygen and water vapor. Another problem arises because it is preferable to grow AlGaAs at relatively high temperatures such as 800°C . Since an AlGaAs heteroface is grown after most of a cell structure has been formed, growth of AlGaAs can lead to interdiffusion effects that can degrade junction properties. ZnSe is a potential replacement for AlGaAs since it has a bandgap of 2.67 eV and the lattice mismatch with GaAs is only 0.23 %. Furthermore, ZnSe can be grown at much lower temperatures than AlGaAs which may allow the fabrication of GaAs solar cells with improved current-voltage characteristics.

The ultimate objective of this work is to fabricate a n/p GaAs cell with an n-type ZnSe window layer. Work this first year has involved development of procedures for growing ZnSe on GaAs, characterizing ZnSe films grown on GaAs, and determining approaches to doping ZnSe n-type. These subjects are discussed in the following sections.

2. MOCVD GROWTH OF ZnSe

Growth of ZnSe is accomplished in a SPIRE 500XT reactor housed in the Electronic Materials Laboratory at WSU Tri-Cities by reacting a zinc adduct with H_2Se . The zinc adduct is formed (by a vendor) by reacting triethylamine (TEN) and dimethylzinc (DMZn). The triethylamine is mixed to give a vapor pressure of 16 torr at 20°C. Growth rate of ZnSe is controlled by adjusting the flow of hydrogen through a metalorganic bubbler. The growth rate varies linearly with the flow of hydrogen through the DMZn/TEN bubbler. Typical growth conditions that result in a ZnSe growth rate of 1 Å/s and a VI/II ratio of 5 are as follows: a total pressure of 65 torr, 6000 sccm of palladium-diffused hydrogen; 25 sccm hydrogen bubbled through the DMZn/TEN bubbler at 20°C; and 270 sccm hydrogen selenide (1% in H_2); and a substrate temperature of 250°C. Substrates are placed on a pancake shaped, SiC-coated graphite susceptor which is heated by RF induction. All gas flows and RF power are computer controlled.

3. GROWTH Of ZnSe ON GaAs

3.1 GaAs Surface Preparation

High quality ZnSe films can be grown on as-received GaAs wafers from Sumitoma. For wafers from other sources or for ones that have been taken out of their jacket, we find that it is preferable to etch the wafer before film growth. The best results were obtained with the so-called slow etch combined with a NH_4OH pre-etch. After eight microns were removed at a rate of $0.4 \mu\text{m}/\text{minute}$, the samples were specular and looked very similar to as-received wafers from Sumitoma. The procedure used for etching and cleaning GaAs wafers is described in Table 1. Incorporation of this etching procedure resulted in consistent results for ZnSe films grown on GaAs substrates.

Table 1. Procedure for Etching and Cleaning GaAs Wafers

- (1) Etch wafer with NH_4OH (5 %);
- (2) Solvent clean as 2" wafers, in a ultrasonic cleaner (USC) in each of TCE, acetone, MeOH, at room temperature in teflon beakers, blow dry from MeOH;
- (3) Notch and cleave into quarters;
- (4) Squirt notch dust off with MeOH, N_2 blow;
- (5) Etch > 1 minute with NH_4OH (5 %);
- (6) Etch 20 or 32 minutes with sulfuric peroxide at RT on a stirrer;
- (7) Double rinse and N_2 blow;
- (8) Just prior to MOCVD load dip > 15 seconds in NH_4OH (5 %), rinse in overflow tank, and N_2 blow.

3.2 MOCVD Growth Of ZnSe On GaAs

ZnSe films were grown on GaAs with substrate temperatures varied between 200 °C and 500°C. Most work was carried out with a substrate temperature of 350°C, since it was also appropriate for doping studies. X-ray diffraction studies determined that (100) oriented crystalline ZnSe films were grown on (100) GaAs substrates. A typical x-ray spectrum for a ZnSe film grown by MOCVD on (100) GaAs is shown in Figure 1. The $K\alpha_1$ (400) and $K\alpha_2$ reflection peaks are shown for GaAs, while only the $K\alpha_1$ peak is visible for ZnSe. The ZnSe peak is hidden by the GaAs $K\alpha_1$ peak. Although this set of data was taken prior to this program, it is representative of films grown for this effort.

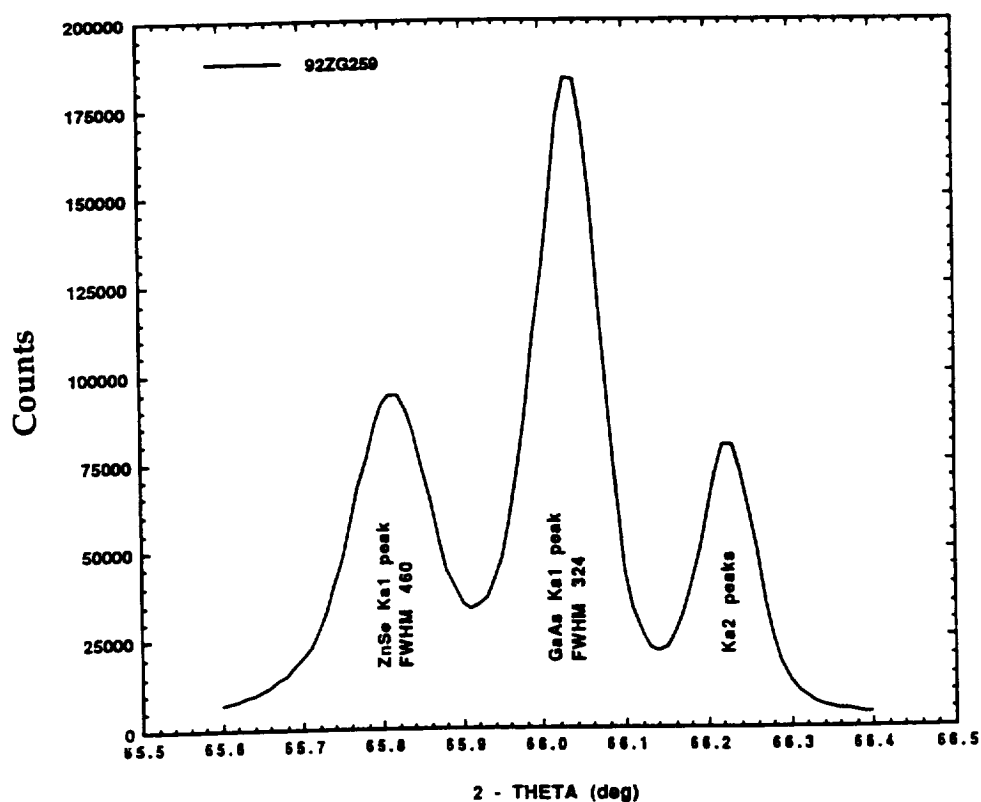


Figure 1. X-Ray reflection intensity vs 2-Theta for a ZnSe film grown on (100) GaAs by MOCVD .

Although X-ray diffraction studies established that (100) oriented ZnSe films can be grown on (100) GaAs substrates, they do not clearly determine that single crystal layers are grown with such an approach. To further characterize the ZnSe films grown on GaAs, films were examined with an atomic force microscope (AFM). Figure 2 shows an AFM image taken for a 1000 Å ZnSe film grown on single crystal GaAs at 350 °C. The film is polycrystalline with a typical grain size on the order of 0.1 μm, or 1000 Å the film thickness.

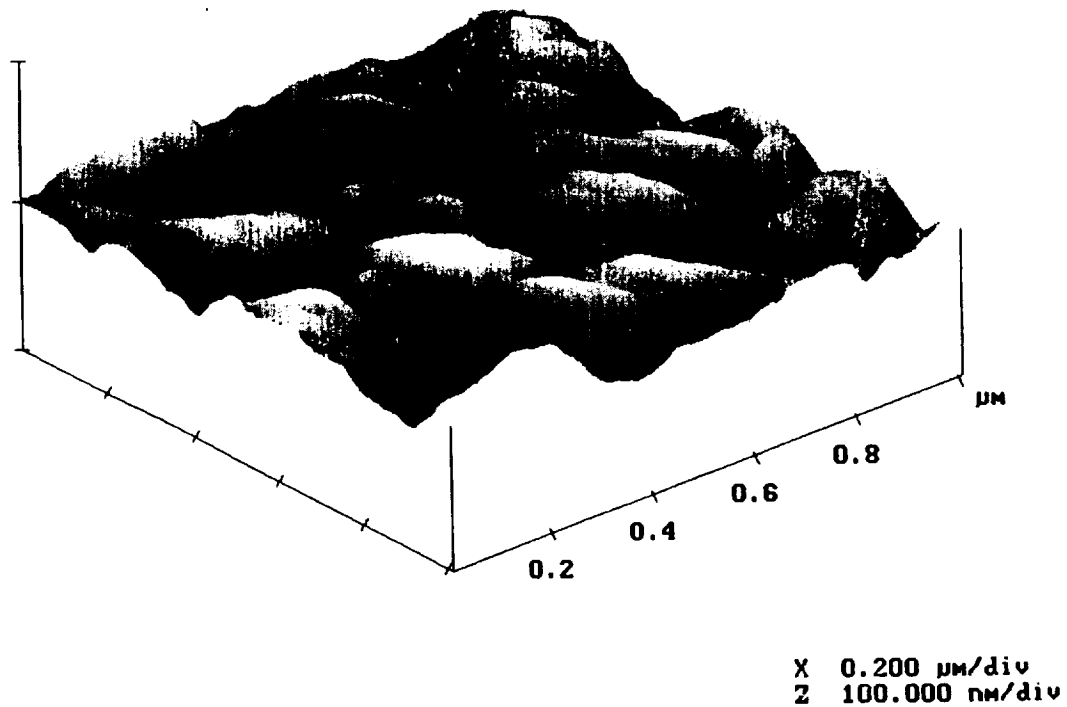


Figure 2. AFM image for a 1000 Å ZnSe film grown on single crystal GaAs at 350 °C.

3.3 Growth Of N-Type ZnSe

In order to utilize ZnSe effectively as a window, one must be able to dope the material. Doping studies were carried out with emphasis placed on the use of iodine as a dopant. Iodine doping was achieved using ethyliodide mixed with helium (1000 ppm) as a source. These studies were carried out by growing doped ZnSe films on semi-insulating GaAs substrates. The following growth parameters typically give ZnSe films with a resistivity in the range of .01 to .05 ohm-cm:

GaAs Substrate Temperature :	350 °C
ZnSe Film Thickness :	1000 Å
Zn Adduct Flow:	185 $\mu\text{mol}/\text{min}$
H ₂ Se Flow :	370 $\mu\text{mol}/\text{min}$
Ethyliodide Flow:	8 $\mu\text{mol}/\text{min}$
Growth Rate:	7 to 8 Å/s

4. CONCLUSIONS

An approach to growth of specular, well-oriented polycrystalline ZnSe films on (100) single crystal GaAs substrates has been developed. ZnSe films are grown by reacting a zinc adduct with hydrogen selenide at temperatures in the range of 200°C to 400°C. Particular emphasis was placed on the use of a substrate temperature of 350°C. Using iodine as a dopant, n-type ZnSe films with resistivities in the range of .01 to .05 ohm-cm were grown on semi-insulating GaAs. Thus procedures have been developed for investigating the utility of n-type ZnSe window layers on n/p GaAs structures. Studies of recombination at n-ZnSe/n-GaAs interfaces in n-ZnSe/n-GaAs/p-GaAs cell structures are planned for future work.