A Study of Polycrystalline Cd(Zn, Mn)Te/CdS Films and Interfaces

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Polycrystalline films of Cd₁₋₀xZnxTe (x = 0–0.4) and Cd₁₋₀.₂₅MnxTe (x = 0–0.25) were grown by MBE and MOCVD, respectively, on CdS/SnO₂/glass substrates to investigate their feasibility for solar cell applications. The compositional uniformity and interface quality of the films were analyzed by x-ray diffraction, surface photovoltage, and Auger depth profile measurements to establish a correlation between growth conditions and lattice constant, atomic concentration, and bandgap of the ternary films. MBE-grown polycrystalline Cd₁₋₀xZnxTe films showed a linear dependence between Zn/(Cd + Zn) beam flux ratio, Zn concentration in the film, and the bandgap. Polycrystalline Cd₁₋₀xZn₀.₈₅Te films grown at 300 °C showed good compositional uniformity in contrast to compositionally non-uniform Cd₁₋₀.₄₅Mn₀.₅₅Te films grown by MOCVD in the temperature range of 420–450 °C. The MBE-grown Cd₁₋₀xZnxTe/CdS interface also showed significantly less interdiffusion compared to the MOCVD-grown Cd₁₋₀.₂₅MnxTe/CdS interface, where preferential exchange between Cd from the CdS layer and Mn from the Cd₁₋₀.₂₅MnxTe film was observed. The compositional uniformity of MOCVD-grown polycrystalline Cd₁₋₀xMnxTe films grown on CdS/SnO₂/glass substrates was found to be a strong function of the growth conditions as well as the Mn source.

Key words: CdZnTe/CdS, CdMnTe/CdS, MBE, MOCVD

I. INTRODUCTION

In recent years, CdTe has become a strong candidate for photovoltaic applications due to its optimum bandgap, high absorption coefficient, and ease of deposition. Cell efficiencies of ~13% have been reported for single crystal CdTe solar cells¹ and greater than 12% for polycrystalline thin film CdTe cells.² It has been projected³ that thin film cell efficiencies in the range of 15–20% can be obtained by a tandem cell design consisting of two cells of different bandgap semiconductors on top of each other (1.7 eV on 1.1 eV). Semiconducting alloys such as Cd₁₋₀xZnxTe and Cd₁₋₀.₂₅MnxTe are good candidates for the top cell since their bandgaps can be tailored between 1.45 eV (CdTe) and 2.26 eV (ZnTe) or 3.0 eV (MnTe) by adjusting the film composition. However, very few attempts have been made to grow these films in polycrystalline form⁴-⁸ and hence little is known about the properties of such films, particularly when grown on coated glass substrates that are suitable for solar cells. Good control of bulk composition and reduced or no interdiffusion at the Cd(Zn, Mn)Te/CdS interface is important for high performance devices based on these materials.

In this work, polycrystalline Cd₁₋₀xZnxTe and Cd₁₋₀.₂₅MnxTe films were grown by molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), respectively, on CdS/SnO₂/glass substrates to form frontwall solar cell structures. X-ray diffraction (XRD), electrochemical surface photovoltage (SPV), and Auger electron spectroscopy (AES) measurements were performed to determine the proper growth conditions for obtaining a uniform bandgap and composition throughout the film and an abrupt film/CdS interface. In this paper we report growth-induced variations in the composition and interface quality of the heterojunctions formed by MBE and MOCVD grown polycrystalline ternary films.

II. GROWTH AND CHARACTERIZATION OF FILMS

Polycrystalline Cd₁₋₀xZnxTe and CdTe films were grown by MBE using a Varian Gen II MBE system. Elemental sources with a purity better than 5N were used for all constituents. The films were grown on CdS/SnO₂/glass and glass substrates which were cleaned by standard degreasing procedures. The substrates were baked in a vacuum of ~1 x 10⁻⁷ Torr at 250 °C for 2 hr prior to film growth. During film growth, the substrate temperature was kept at 275 °C for 30 min to commence film growth and increased to 300 °C for the remainder of the run. Growth rates were typically ~1 μm/hr for both the Cd₁₋₀xZnxTe and CdTe films.

Polycrystalline Cd₁₋₀.₂₅MnxTe films were grown by MOCVD on CdS/SnO₂/glass substrates using a Cambridge Instruments MR102 MOCVD system. The source materials for Cd and Te were dimethylcadmium (DMCd) and diisopropyltellurium, respectively. Two different Mn sources were used, tricarbonyl methylcyclopentadienyl manganese (TCPMn) and Bis (isopropylcyclopentadienyl) manganese (BCPMn) to study the effects of different sources on...
the film properties. Cadmium and tellurium source temperatures were maintained at 0°C and 20°C, respectively, while the manganese source temperature was varied in the range 80°C to 100°C for both TCPMn and BCPMn. In order to investigate the effects of the growth conditions, the reactor pressure was varied in the range of 50 to 250 Torr and the substrate temperature was varied from 420°C to 450°C for C_{1-x}Mn_{x}Te films. The substrate temperature was kept at 400°C for CdTe films. Typical growth rates for C_{1-x}Zn_{x}Te and CdTe films were 0.5 μm/hr and 1.5 μm/hr, respectively.

X-ray diffraction studies were performed to estimate the film composition using a Phillips PW1800 automatic diffractometer with 1.504Å Cu-Kα radiation. The lattice constants, a, of the C_{1-x}Zn_{x}Te films were determined from the XRD data by plotting the lattice parameter, a(θ), against its angular dependence (θ) and determining the intercept according to

\[ a(\theta) = 0.5[(\cos^2 \theta/\sin \theta) + (\cos^2 \theta/\theta)] \]  

where 2θ is the diffraction peak position. The film composition (x) was determined from the lattice constant according to \(^6,9\)

\[ a(x) = 6.481 - 0.381x \text{ (Å), for C}_{1-x}Zn_{x}Te \]  

and

\[ a(x) = 6.487 - 0.149x \text{ (Å), for C}_{1-x}Mn_{x}Te \]  

where x is the atomic concentrations of Zn and Mn in the C_{1-x}Zn_{x}Te and C_{1-x}Mn_{x}Te, respectively.

The absorption edge or bandgap of the films was estimated by a nondestructive electrochemical SPV measurement in which an electrolyte composed of 0.2M NaOH and 0.1M EDTA (ethylenediaminetetraacetic acid) forms a Schottky barrier contact with the film surface. This barrier separates the photo-generated carriers to produce an open circuit voltage as a function of incident wavelength. This technique is also capable of providing information about bandgap variations within the film because the electrolyte/semiconductor junction can be biased so that controlled etch-steps can be made between SPV measurements. Hence, compositional variations in the direction of film growth can be monitored. This technique has been discussed in more detail elsewhere.\(^10,11\) Bandgaps of the films were estimated from the wavelength (λ) at the midpoint of the absorption edge \((E_g(eV) = 1.24/\lambda(\mu m))\) in the SPV response. It should be noted that in certain cases, the sharpness of the absorption edge can be influenced by the diffusion length and film thickness.

To gain further confirmation on the compositional uniformity of the ternary films, AES profile measurements were performed using a Physical Electronics Model 600 Scanning Auger Multiprobe. The angle between the sample normal and the electron beam was 45°. All AES data were taken using a 3 keV electron beam with a current of 1.0 μA. Sputter profiling was performed using a normally incident 2 keV Ar ion beam at a current density of 28 μA/cm².

III. RESULTS AND DISCUSSION

A. MBE-Grown Polycrystalline C_{1-x}Zn_{x}Te and CdTe Films

In order to achieve optimal composition (x = 0.3-0.4) or bandgap (1.65-1.75 eV) for tandem solar cell applications, MBE films were grown with various Zn/(Cd + Zn) ratios. Figure 1 shows a comparison of XRD spectra of a CdTe film and a C_{1-x}Zn_{x}Te film grown with a Zn/(Cd + Zn) beam flux ratio of 0.4 on CdS/SnO₂/glass substrates. A comparison of the peak positions and relative amplitudes in each diffraction pattern with the tabulated values\(^10\) suggests that in both cases the CdTe cubic structure is the only detectable phase. By determining the lattice parameter (a(θ)) associated with each major C_{1-x}Zn_{x}Te diffraction peak, the lattice constant (a) of the film was determined according to Eq. (1). By combining this information with the measured bandgap from the SPV (Fig. 3) for several films grown with various Zn/(Cd + Zn) beam flux ratios, a correlation was established between the growth conditions (Zn/(Cd + Zn) beam flux ratio), film composition, and bandgap.

\[ \text{Fig. 1} -- \text{X-ray diffraction spectra of MBE-grown polycrystalline (a) C}_{1-x}Zn_{x}Te \text{ and (b) CdTe.} \]