

Effect of Thermal Annealing on Zinc Diffused- CdTe Thin Film

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CdTe films covered with thin layer of Zn were deposited by thermal evaporation technique. Zn interdiffusion in CdTe was studied by annealing the prepared films at different temperatures (T_{an}) and for different time interval (t_{an}). The effect of thermal annealing temperature (T_{an}) and time of annealing (t_{an}) on the optical bandgap energy (E_g), diffusion length (L) and the corresponding diffusion coefficient (D) is discussed. Results revealed that during thermal annealing process at 100 °C and after a time of 30 min, a thin layer of CdZnTe mixed structure have been formed on the top of CdTe films with variable bandgap between 1.74 and 2.05 eV. The formation of this mixed structure is attributed to the diffusion process of Zn atom to the top surface of CdTe film.

Introduction

Cadmium based binary and ternary II – IV compound semiconductors have attracted considerable interest because of their wide applications in optoelectronic devices [1]. CdTe properties make it a prime candidate for terrestrial photovoltaic applications [2,3]. Doping CdTe thin films with transition metals such as titanium, vanadium and indium [2,4] produced considerable change in the optical, electrical and mechanical properties of the thin films materials. There is a lack of reports on the possibility of obtaining variable bandgap films of CdZnTe using the diffusion process of Zn into CdTe. This ternary structure is one of the important semiconductor compounds, as a top device in a high efficiency tandem solar cell structure, due to its tunable physical parameter [5]. Although much research efforts has been focused primarily on the properties of bulk CdZnTe, very little attention was paid to its thin film structure particularly on the understanding of Zn impurity diffusion effects on the fundamental absorption of CdTe.

This paper analysis the effect of Zn diffusion on the absorption edge of CdTe layers grown by thermal evaporation on glass substrates.

Experimental

The samples used in the present investigation of Zn diffusion in CdTe films were prepared by thermal evaporation CdTe films were prepared by the thermal evaporation CdTe film under a vacuum of 10^{-5} torr, with thickness $\sim 1.5 \mu\text{m}$. A very thin layer of Zn, of thickness $\sim 0.1 \mu\text{m}$, was deposited on the top surface of CdTe film by thermal evaporation technique. The obtained samples were annealed, in air atmosphere, at different temperatures (T_{an}) ranging from room temperature to $500 \text{ }^\circ\text{C}$ for different annealing times (t_{an}) up to 360 min.

The optical transmission spectra of the prepared samples were recorded, at room temperature, by UV-VIS Unicam double beam spectrometer in the wavelength range from 200 to 1000 nm. A photocurrent response was measured by Keithley 610 electrometer at the ambient atmosphere using 100 W tungsten lamp light source. For the spectral response curves measurements, the thin films were deposited on a glass substrate coated with SnO_2 as a transparent electrode. A finger-shaped upper electrode was obtained by evaporating a high purity copper (Cu) through a appropriate mask. The photocurrent spectral response was recorded using CM110 monochromator in the rang of 200-1200 nm.

Results and discussion

The optical transmission spectra of CdTe samples coated with thin layer of Zn element, were found to exhibit a high dependence on the thermal annealing temperature (T_{an}) and annealing time (t_{an}). The optical absorption coefficient (α) calculated from the optical transmission spectra can be used to determine the corresponding energy gap (E_g) from the optical transition theory [6,7],

$$(\alpha h\nu)^2 = B (h\nu - E_g) \quad (1)$$

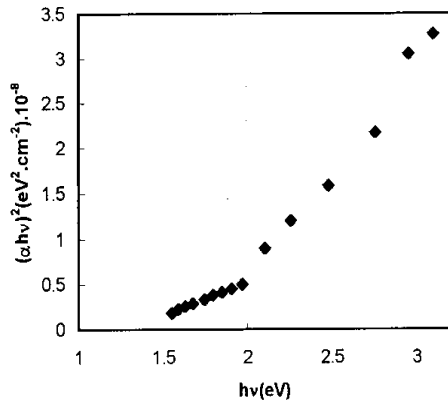


Fig. (1): The relation between $(\alpha h\nu)^2$ and the incident photon energy ($h\nu$) for CdTe:Zn as deposited film.

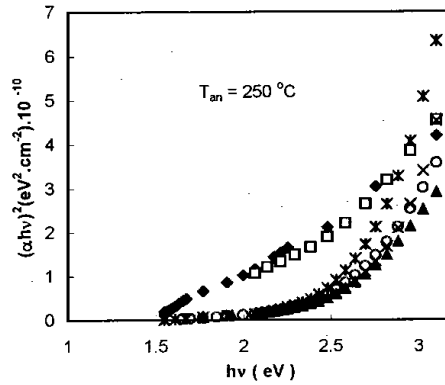


Fig. (2): The dependence of $(\alpha h\nu)^2$ on the incident photon energy ($h\nu$) for CdTe:Zn film annealed at 250 °C for different annealing times : (■) 5 min, (□) 15, (▲) 30, (×) 90, (*) 180 and (○) 360 min.

where $h\nu$ is the incident photon energy in eV and B is a parameter depends on the transition probability. A plot of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for CdTe: Zn thin films, as deposited, is shown in Fig. (1), indicating that the samples under investigation are characterized by a direct interband transition. The corresponding energy gap (E_g) was obtained from the intersection of the linear part at both high photon energy (1.75 eV) and at low photon energy (1.4 eV). These different values are corresponding to the optical energy gap of CdTe [8]. In the present work, the value of 1.75 eV can be taken as an evidence for the formation of different structures formed at the upper surface of the CdTe thin film. Therefore, a mixed structure of CdZnTe was formed, at the top surface of CdTe, with an energy gap of 1.75 eV, where CdZnTe mixed structure could have a bandgap energy varying from ~ 1.45 eV for CdTe to ~ 2.26 eV for ZnTe films according to its stoichiometry [8].

Fig. (2) represents the relation between $(\alpha hv)^2$ and the photon energy (hv) for samples at a temperature 250 °C for different annealing times. The same dependence for samples annealed for 90 min. at different annealing temperatures is illustrated in Fig. (3). The corresponding bandgaps as a function of both annealing time ($t_{an} = 90$ min.) and annealing temperature ($T_{an} = 250$ °C) have been illustrated in Fig. (4). These results showed that the optical bandgap (E_g) is depending on both the temperature and time of thermal annealing. It is also observed that as the annealing time increases up to 15 min (at $T_{an}=250^\circ\text{C}$), the corresponding E_g varies from 1.78 to 2.15 eV (see Fig 4a). These bandgap variations were found to be in agreement with that previously reported for graded CdZnTe mixed structure [8,9] at the top surface of CdTe. For annealing time more than 15 min, bandgap energies between 2.5 and 2.75 eV have been obtained. A high dependence of E_g on the thermal annealing temperature has been found. As the T_{an} increased from 100 °C to 500 °C, with constant annealing time (90 min.), the corresponding optical gaps were raised from 2.05 to 3.80 eV (Fig 4b).

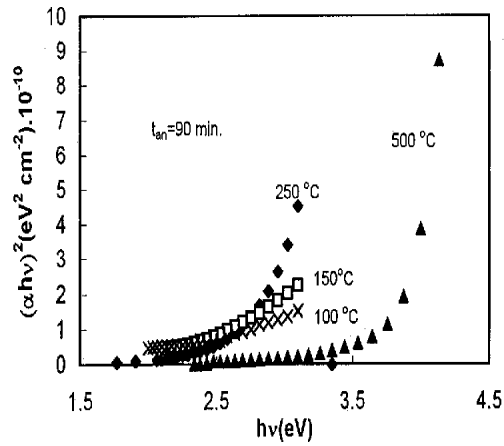


Fig. (3): The relation between $(\alpha hv)^2$ and the incident photon energy (hv) for CdTe:Zn films annealed for 90 min. at different annealing temperatures.

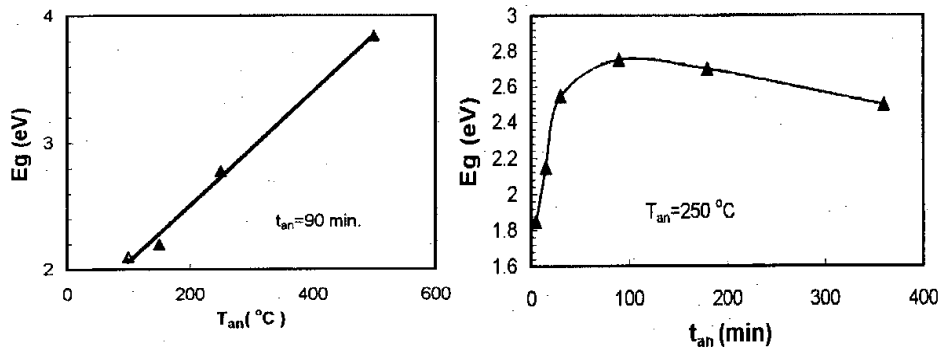


Fig. (4): The bandgap (E_g) dependence, of CdTe:Zn films, on both
 (a) The annealing time (t_{an}) at $T_{an} = 259$ °C and
 (b) The annealing temperature (T_{an}) for 90 min.

Oxygen description accompanying annealing, in air atmosphere, at longer times and higher annealing temperatures resulting in the production of another structure formed at the upper surface of CdTe. Under these conditions, the upper metallic film (Zn) is partially converted into its oxide form (ZnO) while the remaining part of Zn can be removed from the top of metallic surface layer and give a chance of oxygen to diffuse into CdTe where oxidation has taken place.

The dependence of energy gap (E_g) on the time of annealing at lower thermal treatment (100 °C) is shown in Fig. (5). It is noticed that E_g values range between 1.78 and 2.05 eV. These results supported the idea, that during thermal annealing process, the temperature is the predominant factor affecting on the diffusion process and consequentially the optical properties of the films under investigation. At lower annealing temperatures (less than 100 °C), a CdZnTe structure has

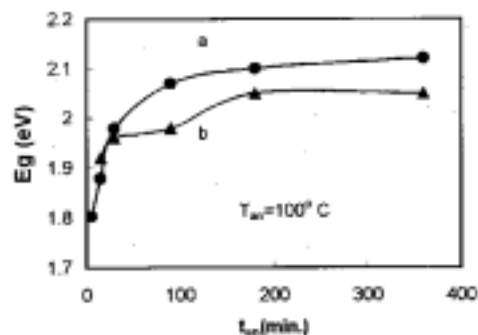


Fig. (5): The optical bandgap (E_g) variation as a function of annealing time of CdTe:Zn annealed at 100 °C, calculated from transmission spectra response (curve b).

been formed at the top of CdTe surface due to Zn diffusion process. While at higher annealing temperature ($T_{an} > 100$ °C) a structure modification has been formed at the surface of CdTe film, with high E_g . This is due to the elevation process of Zn elements from the metallic layer and the oxidation process of the residual Zn atoms associated with the oxygen diffusion through CdTe matrix.

On the other hand, films isothermally annealed at 100 °C were found to exhibit a high resistivity in the dark and show a detectable photocurrent response (I_{ph}) under illumination. The spectral response of the photocurrent, for samples illuminated from the Zn deposited film (curves 1a, 2, 3, 4, 5 and 6) annealed at 100 °C for different time of annealing are shown in Fig. (6). An abrupt increase in the photoresponse curves in the lower photon energy, reveals the absorption edge related to the CdTe matrix at ~ 1.5 eV. A boarding and shifting of the spectra toward the higher photon energy regions were observed as the annealing time increased. The existence of CdZnTe mixed structure with variable bandgaps, corresponding to the maximum value of spectra, was also expected and in agreement with that calculated from transmission spectra and shown in fig. (5) curve (b).

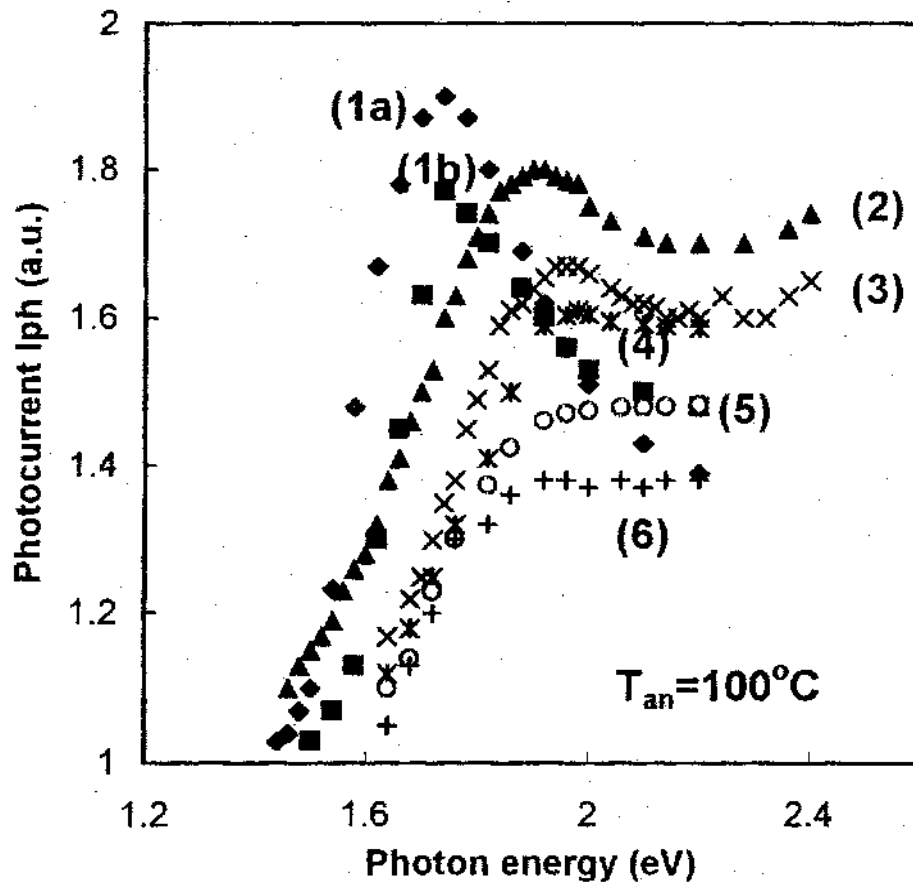


Fig. (6): Photocurrent spectral response curves as a function of the incident photon energy of CdTe:Zn samples, illuminated from Zn side, annealed 100 °C for different times (t_{an}):
 1a) as deposited 2) 15, 3) 30, 4) 90, 5) 180 and 6) 360 min.
 1b) as the deposited film illuminated from CdTe (or glass substrate) side under the same conditions of annealing.

The average absorber thickness (L) of mixed structure CdZnTe layer, formed on the outer surface of CdTe films, due to the diffusion process of Zn atoms, at $T_{an} = 100$ °C, could be obtained from the relation [9-11],

$$L = \ln R/\alpha \quad (2)$$

Where α is the absorption coefficient of CdZnTe and $R = I_{ph}/\Gamma_{ph}$, and I_{ph} and Γ_{ph} are the maximum photocurrent intensity for illuminating the sample from CdZnTe layer side [curve 1(a), Fig 6] and the glass substrate side [curve 1 (a), Fig 6] and the glass substrate side [curve 1(b), Fig 6], respectively. The dependence of the diffusion length of Zn into CdTe to form a mixed structure

of CdXnTe, at $T_{an}=100^{\circ}\text{C}$, on the time of annealing is illustrated in Fig (7a). An abrupt increase in L has been detected for annealing time up to 30 min and a nearly constant diffusion length L, has been obtained for higher annealing times ($t_{an} > 30$ min). These results revealed that when Zn interdiffusion into CdTe, the absorber layer is of great concern. Moreover, the diffusion coefficient (D) of Zn through CdTe to form mixed structure of CdZnTe on the top of CdTe surface during isothermal annealing (at $T_{an} = 100^{\circ}\text{C}$), can be estimated from the relation [12 – 14],

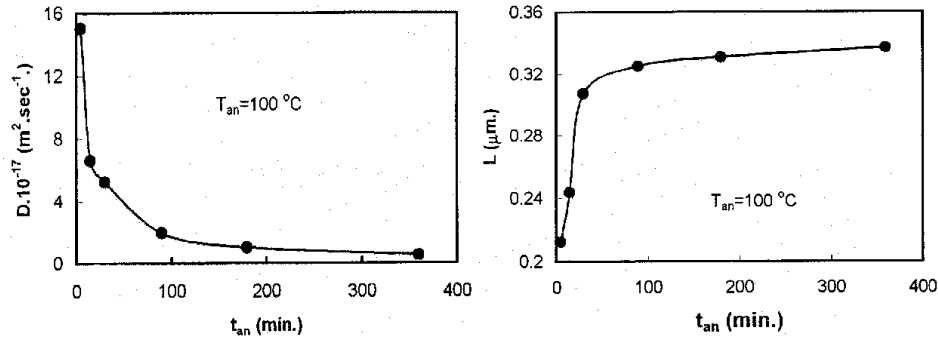


Fig.(7): The dependence of :a) the diffusion length (L) and b) the diffusion coefficient (D) on the annealing time at 100°C .

$$L = (D \cdot t_{an})^{1/2} \quad (3)$$

The effect of isothermal annealing at 100°C on the diffusion coefficient (D) is shown in Fig 7b. Inspection of figures 5 & 7 (a,b) revealed that the Zn atoms diffuse through the top surface of CdTe, forming CdZnTe mixed structure with variable bandgap (in the range 1.78 ~ 2.10 eV) till annealing times of 90 min and at annealing temperature $T_{an} < 100^{\circ}\text{C}$. After these conditions, L, D and E_g are independent of both the annealing time and temperature.

Conclusion

Transmission spectra of the samples under investigation have been measured at room temperature. From the analysis of the data, it has been demonstrated that at annealing temperature $T_{an} > 100^{\circ}\text{C}$, the atmospheric oxygen was found to play a significant role on the properties of the samples. Oxidation of Zn at the top surface of CdTe and the oxygen diffusion into the CdTe matrix lead to a structure modification with higher bandgap values. For lower thermal treatment process ($T_{an} < 100^{\circ}\text{C}$ and $t_{an} < 90$ min) the formation of CdZnTe variable bandgap has been detected from the transmission spectra and

photocurrent spectral response data. It is suggested that, under these conditions, Zn atoms could be interdiffuse through the upper surface of CdTe with a diffusion length in the range from 0.21 to 0.34 μm and diffusion coefficient of order $10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$.

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