

Structural, electronic transport and optical properties of Zn-doped CdTe thin films

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Non-doped and Zn-doped CdTe thin films were deposited by thermal evaporation under vacuum onto unheated glass substrates, using staked layer method. Zn content in the samples was controlled by Zn source temperature that varied in 670 K – 770 K range. The CdTe source temperature was 925 K and was kept constant during deposition of all samples. The XRD studies revealed that the non-doped CdTe films present a cubic oriented (111) polycrystalline structure whereas the as-deposited Zn-doped films are quasi-amorphous. The influence of Zn doping on the electrical conductivity and its temperature dependence and optical absorption spectra of CdTe thin films was investigated. Depending upon Zn content, the electrical conductivity at room temperature for as deposited films varied in the $10 \Omega^{-1}\text{m}^{-1} - 10^4 \Omega^{-1}\text{m}^{-1}$ range and was about of six to ten orders of magnitude higher than those of non-doped CdTe films. The annealing up to 800 K determines an important irreversible decrease of doped film conductivity. Also, an increase of the optical band gap (from 1.49 eV for non-doped CdTe films) to 1.67 eV (for Zn-doped annealed samples) was observed.

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1. Introduction

In the recent years, there was an increasing interest in the preparation and study of the physical properties of CdTe thin films and its alloys due to their great potential applications in optoelectronic devices. The doping of CdTe thin films with different metal atoms produces considerable changes in their structural and physical properties that make it useful in the technology of thin film devices [1 – 5]. From such CdTe doped films, the CdZnTe (CZT) alloys in thin films are intensively studied due to their important applications in technology of thin film tandem solar cells and of X-ray and gamma ray detectors [6 – 8].

In present paper, the effect of Zn-doping on the electronic transport properties (electrical conductivity and its temperature dependence) and optical properties (absorption spectra) of CdTe thin films are investigated.

2. Experimental

A variety of preparation techniques have been reported for CZT thin films as chemical vapor deposition, close spaced vapor transport, molecular beam epitaxy, r.f. sputtering, evaporation under vacuum etc. [9 – 13]. Due to non-uniform distribution of Zn into the film during the deposition process, an important problem in preparing of CZT films is the control of their homogeneity. From this reason, in order to assure a uniform doping of the CdTe films studied in present paper, a stacked layer method [14] was used. During the deposition process, the film substrates, placed to a rotating disk, passed successively with constant rotating rate, r , of 120 rpm, over the separated evaporation sources for CdTe and Zn respectively. Metallic Zn and CdTe powder were used as

source materials. Two vertical Pyrex cylinders separate the respective sources and ensure a quasi-closed volume for deposition of each component. So, multilayered CdTe/Zn structures with uniform thickness of component sub-layers have been deposited. The main advantage of the used method is the possibility to assure the doping uniformity and to control the sub-layer thickness of each component, hence the dopant contents, by varying of source temperatures.

Our previous studies [15 – 17] revealed that the structural and physical properties of the CdTe films evaporated onto unheated glass substrates by quasi-closed volume technique are strongly influenced by CdTe source temperature. From this reason, for preparation of Zn-doped CdTe samples, a CdTe source temperature of 925 K was selected and was kept constant during deposition of all samples. The Zn content in the samples was modified by varying the Zn source temperature between 670 K and 770 K. For comparison, Zn and CdTe reference samples were deposited onto glass substrates, fixed above the each source, in the same preparation conditions as Zn-doped CdTe films. The interferometrically measured thickness of as doped samples ranged between 450 nm and 750 nm.

After the preparation, some samples were heat-treated under ambient conditions at different temperatures and for various times. The isochronal annealing arrangement was used.

The film structures were investigated by standard X-ray diffraction (XRD) technique, using CoK_α radiation ($\lambda = 0.1790 \text{ nm}$) in the 2θ range $20^\circ - 60^\circ$.

For electrical measurements, cells both with planar and sandwich geometry have been prepared using deposited indium thin film as contact electrodes. The temperature dependence of electrical conductivity was studied in the temperature range of 300 K – 800 K. The absorption spectra were studied in the wavelength range of the fundamental absorption edge for CdTe.

3. Results and discussion

3.1. Structural characterization

In Fig. 1, typical diffraction patterns for doped films before annealing (pattern a), after heating up to about 700 K (pattern b) and at the end of second cooling (pattern c) are shown. For comparison, the XRD patterns for both as-deposited CdTe and Zn reference samples are shown in Fig. 2.

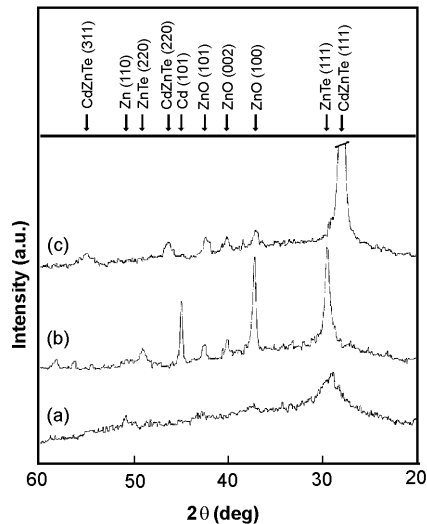


Fig. 1. The XRD patterns ($\text{CoK}\alpha$ radiation) for Zn-doped CdTe film (sample S.3.2): (a) as-deposited; (b) after first heating-cooling cycle; (c) after second heating - cooling cycle.

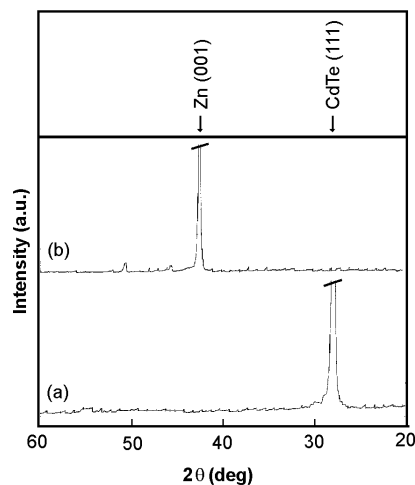


Fig. 2. The XRD patterns ($\text{CoK}\alpha$ radiation) for as-deposited reference films: (a) CdTe; (b) Zn.

Strong textures (111) for CdTe sample and (001) one for Zn sample respectively, from Fig. 2 indicate a good crystallinity of respective samples. On the contrary, the as deposited Zn-doped CdTe films present a quasi-amorphous structure (Fig. 1a). This can be due to the Zn

sublayers which limit the growth of large CdTe crystallites. The annealing of doped samples up to temperature of about 700 K determines the film crystallization with segregation of ZnTe phase as consequence of Zn diffusion in CdTe layers. The peaks at $2\theta = 29.6^\circ$ and 49.3° from pattern (b) correspond to reflection on (111) and (220) planes respectively of cubic ZnTe structure [18] and confirm this assumption. The diffraction peaks, at $2\theta = 37.0^\circ$, 40.2° and 42.3° , from pattern (b), are characteristic for cubic ZnO structure [19] and indicate the formation of zinc oxide on the film surface due to greater affinity of Zn for oxygen [20]. The diffraction peak at $2\theta = 44.8^\circ$, visible in pattern (b), can be associated with (101) plane of metallic cadmium [21], which precipitate in crystalline form during annealing process. When the film temperature increases over 720 K, other structural changes in the doped films occur. The appearance of diffraction peaks at $2\theta = 27.7^\circ$, 46.1° and 54.7° , respectively and the decrease of peak intensity corresponding to Cd at $2\theta = 44.8^\circ$ (Fig. 1, pattern c) indicate the formation of cubic phase of CdZnTe alloy with strong (111) texture. The decrease of the intensity of ZnO diffraction peaks after annealing at high temperature reveals that a part of metallic Zn is removed from the film due to high temperature of annealing.

3.2. Electrical properties

Depending on the preparation conditions, the electrical conductivity at room temperature, σ_c , of the as-deposited Zn-doped CdTe films ranged between $10 \Omega^{-1}\text{m}^{-1}$ and $10^4 \Omega^{-1}\text{m}^{-1}$. For some representative samples, the values of σ_c and other characteristic parameters are summarized in Table 1. For comparison, the electrical conductivity both of reference CdTe and Zn samples are also presented.

Table 1. The deposition parameters and electrical conductivity for the typical studied samples (T_{CdTe} – CdTe source temperature, T_{Zn} – Zn source temperature, d – film thickness, σ_c – electrical conductivity at room temperature for as-deposited film, σ_t – electrical conductivity after heating-cooling cycles).

Sample	T_{CdTe} (K)	T_{Zn} (K)	d (nm)	σ_c ($\Omega^{-1}\text{m}^{-1}$)	σ_t ($\Omega^{-1}\text{m}^{-1}$)
S.1	925	670	710	8.5×10	3.6×10
S.3.1 S.3.2	925	720	460	5×10^3	1.2×10^{-1}
S.5	925	770	530	1.2×10^4 (planar type cell)	3.5×10^{-2}
				7.8×10^{-11} (sandwich type cell)	5.9×10^{-11}
CdTe sample	925	–	750	9.2×10^{-6}	6.2×10^{-5}
Zn sample	–	770	210	9.1×10^4	1.4

As it can observe from Table 1, the Zn-source temperature, hence the Zn content in the film, strongly influences the values of σ_c . The films deposited at Zn source temperature of 770 K, hence with the greater Zn content, have an electrical conductivity with ten orders of magnitude higher than those of non-doped CdTe films. On the other hand, the value of electrical conductivity of a Zn-doped sample determined in direction perpendicular to the plane substrate, using sandwich type cell, is considerable lower (about 10^{14} times) than that measured in direction parallel to the substrate, using planar cell. This indicates that in the case of planar-type cell, the charge transport in as-deposited doped sample is mainly through Zn sub-layers. This explains the higher value of respective film conductivity. The extremely low ($\cong 10^{-11} \Omega^{-1} \text{m}^{-1}$) electrical conductivity in direction perpendicular to the multilayered structure may be related to large barrier height between Zn and CdTe sub-layers.

It is known that the study of the temperature dependence of the electrical conductivity of thin films may offer many information about the correlation between the structure and the electrical properties of the film. Moreover, when this study is carried out *in situ* during successive heating and cooling cycles, one may reveal possible changes in the film structure during the annealing process [17,22]. From this reason, for some samples prepared in different deposition conditions, the temperature dependence of σ during successive heating-cooling cycles has been studied within the temperature range 300 K – 800 K, using planar cells (Fig. 3). For comparison, the analogous dependences for reference CdTe and Zn samples, respectively, are shown in Fig. 4.

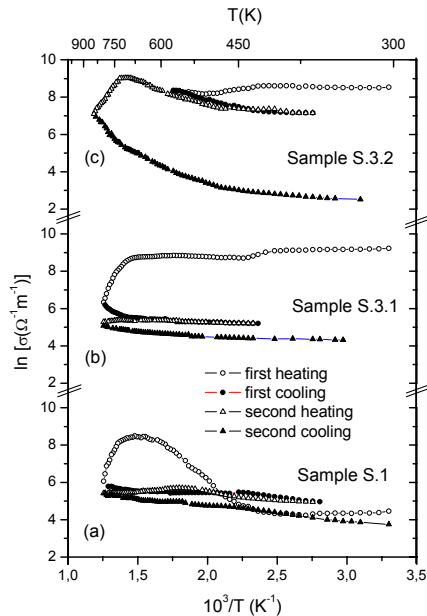


Fig. 3. Typical temperature dependences of σ during of the heating-cooling cycles: (a) for Zn-doped CdTe films deposited at lower Zn source temperature ($T_{Zn} = 670$ K); (b), (c) for two Zn doped CdTe films simultaneous deposited at 720K; (c) when the first heating is stopped at temperature lower than 720 K.

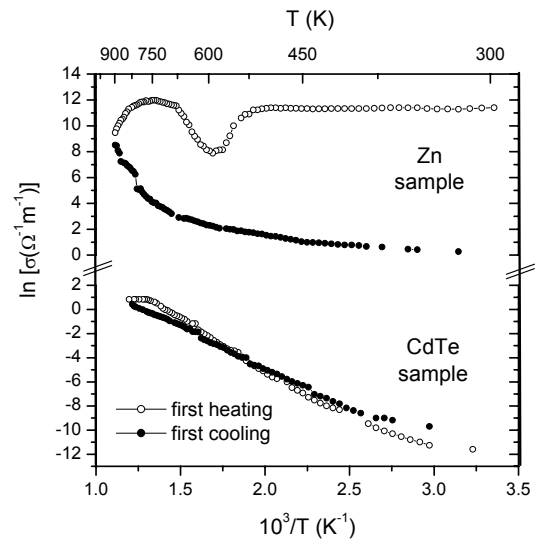


Fig. 4. Temperature dependences of electrical conductivity during heating-cooling cycle of as-deposited reference films: CdTe (bottom), Zn (top).

One can see that the presence of Zn in CdTe films determines an irreversible temperature dependence of electrical conductivity during heating-cooling cycles. At the beginning of the first heating cycle, up to a temperature which depends on amount of Zn contents, the electrical conductivity remains practically constant. Then, in the case of doped samples deposited at lower Zn source temperature, σ begins to increase (Fig. 3, curve a). At greater temperature, of about 720 K, the electrical conductivity considerably decreases. If the annealing is stopped at this temperature, σ continues to decrease quickly. In the next cooling-heating cycle, σ varies reversibly with temperature only up to the about 720 K then again decreases (Fig. 3, curve b). The annealing time, τ_a , in the 720 K – 820 K temperature range influences the decrease of σ . It was observed that for greater τ_a , the decrease of σ is more significant. The influence of both temperature and time of thermal annealing on the physical properties of CdZnTe alloys have been also reported by other researchers [23 – 25].

The observed irreversible temperature dependence of σ may be correlated with changes that take place in the film structure during annealing process. The removal of Zn atoms from doped CdTe film at greater annealing temperature explains the decrease of electrical conductivity in respective temperature range. This assumption is in concordance with the aspect of temperature dependence of electrical conductivity for Zn films plotted in Fig. 4.

The reversible $\ln \sigma = f(1/T)$ dependence in the second heating up to temperature of 720 K indicates the stabilization of the sample structure in respective temperature range. The exponential increase of σ in this temperature range is specific both for ZnTe and ZnO semiconducting polycrystalline films [22,26]. For doped

films with lower Zn content, such exponential increase of σ take place even at first heating cycle (Fig. 3, curve a).

3.3. Optical properties

The presence of Zn atoms in as-doped CdTe films and the post-deposition heat-treatment also influence the value of the optical band gap of respective films. In Fig. 5, the dependences $(\alpha h\nu)^2 = f(h\nu)$ in domain of CdTe fundamental absorption edge for as-deposited (curve 1) and heat-treated doped sample (curve 2) are presented. For comparison, the similar dependence for non-doped CdTe sample was plotted in Fig. 6.

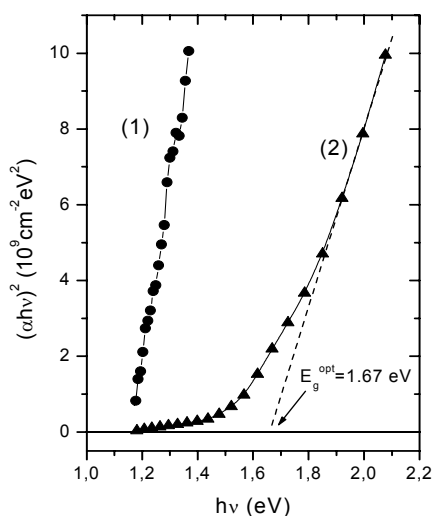


Fig. 5. The dependence $(\alpha h\nu)^2 = f(h\nu)$ for Zn-doped CdTe film (sample S.3.2): (1) as-deposited; (2) after second heating-cooling cycle.

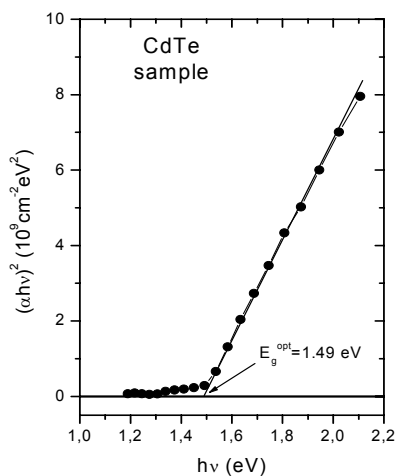


Fig. 6. The dependence $(\alpha h\nu)^2 = f(h\nu)$ for non-doped CdTe film.

By assuming allowed direct inter-band transitions [27], the optical band-gap, E_g^{opt} , of respective samples

were evaluated by extrapolating the linear portion of these plots to $(\alpha h\nu)^2 = 0$. The lower value of about 1.2 eV obtained for E_g^{opt} of unheated Zn-doped CdTe sample may be related to the existence of the high density of defect levels within the band-gap, determined by quasi-amorphous structure of respective sample [28]. The higher value of E_g^{opt} (of about 1.67 eV) obtained for heat-treated doped films, in comparison with those of 1.49 eV calculated for non-doped CdTe sample, proves the formation of CdZnTe alloy as consequence of thermal annealing. Both values of E_g^{opt} obtained for heat-treated Zn-doped CdTe films and non-doped CdTe films respectively are in good agreement with those found by other researchers for CdZnTe thin films and bulk CdTe, respectively [12,13,27].

4. Conclusions

Zn-doped CdTe thin films were deposited onto unheated glass substrates by thermal evaporation under vacuum using stacked layer method. The as-deposited films present a quasi-amorphous structure. The annealing determines the film crystallization with formation of CdZnTe phase. The increase of amount of Zn content in doped films determines an increase of electrical conductivity of CdTe films with about ten orders of magnitude. *In situ* measurement of the electrical resistance of doped films during the heating-cooling cycles revealed that the heat treatment at temperature higher of about 720 K determines an irreversible decrease of electrical conductivity. This is correlated both with presence of Zn in the doped films and crystallization process during film annealing. The values of optical band-gap calculated from absorption spectra were found to be of 1.49 eV for non-doped CdTe films and of 1.67 eV for the heat-treated Zn-doped CdTe films, respectively. The shift of the band edge toward higher photon energy for heat-treated doped films indicates the formation of CdZnTe alloy during film annealing at temperature higher than about 720 K.

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