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Studies on morphological change and optical properties for various Zn concentrations in CdTe thin film prepared by stacked elemental layer method

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ABSTRACT

Te/Cd/Zn stack was prepared using stacked elemental layer (SEL) method. XRD results showed the effect of Zn concentration on the growth of CdTe in their preferred orientations. Optical studies revealed a reduction in band gap from 1.35 to 1.42 eV as well as low transmittance for higher Zn concentration. Improved surface morphology was the evidence of effects of Zn concentration on micro structural damage and the grain growth. Significant change on particle size, grain size and porosity was attributed to the influence of Zn concentration presented in the stack. *ImageJ* software also used to identify the presence of nano size particles in the annealed stack. EDAX studies revealed the presence of desired compositions in the annealed stacks.

1. Introduction

CdTe is a near perfect material for PV application with a direct band gap of 1.5 eV that is closely matched to the terrestrial solar spectrum and a high optical absorption coefficient where less than 1 μm thickness is adequate to absorb the incident light. The optical and morphological properties of chemically synthesized CdTe and electron beam deposited ZnTe thin films were reported by different authors [1–3]. Recently, advancements in two-junction solar cell technology have indicated that CZT thin films may be successfully used in the fabrication of polycrystalline thin film tandem solar cells [4]. For a high efficiency of such devices, the band gap of the top cell should be in the range of 1.5–1.8 eV [5].

CdZnTe ternary compounds also have a great potential in opto-electronic devices, such as solar cells, optical windows, light-emitting diodes, neutron detectors [6], X-ray detectors [7] and gamma detectors [8]. The direct energy band of $Cd_{1-x}Zn_xTe$ (CdZnTe) ternary compounds can be continuously tuned from the CdTe energy gap (1.50 eV) to the ZnTe one (2.3 eV) by varying the Zn concentration. This could be achieved by diffusion of Zn into CdTe using various techniques and growth methods [9–12]. Alikhanian et al. have reported the first experimental investigation of the solid–vapor equilibrium in the CdTe–ZnTe system at 525 °C and 505 °C over the whole composition range [13]. The micro structural defects of MBE deposited $Cd_{1-x}Zn_xTe$ thin films with $x \approx 0.04$ using HRTEM have been reported by different authors [14].

To achieve perfect ternary CdTe-based compounds such as CZT, it is essential to understand the atomic and electronic structure and the incorporation kinetics of Zn doping in CdTe [15–17] and the contact performance depends strongly both on the electrode metal and semiconductor surface preparation before metallization [18]. This led to an increasing interest in the development of wide band gap absorbers based on the alloys of ZnTe and CdTe, with a variety of advantageous properties.

Among the various physical vapor deposition methods, SEL method is one among the best method to achieve desired compositions. SEL technique was originally developed to produce $CuInSe_2$ thin films [19]. It has also been used to produce CdTe films [20]. Cruz et al. have reported the influence of post deposition treatment on CdTe prepared by SEL method. It is particularly suitable for deposition of compound semiconductor films, as it provides good control of composition; also, it seems to be a promising method for producing highly efficient CdTe/CdS solar cells [21]. We have recently reported the morphological and electrical studies of 0.15% Zn doped CdTe thin films prepared by SEL method [22]. In this paper, the optical and surface properties of the Te/Cd/Zn stack annealed at 500 °C for various Cd and Zn concentrations have been reported. In addition, the influence of Zn on grain growth and particles size has been analyzed using the *ImageJ* Software.

2. Experimental techniques

Zn layered Te/Cd stacks with various Zn layer thicknesses were prepared at room temperature by SEL method using PVD unit supplied by Hindhivac, Ban-

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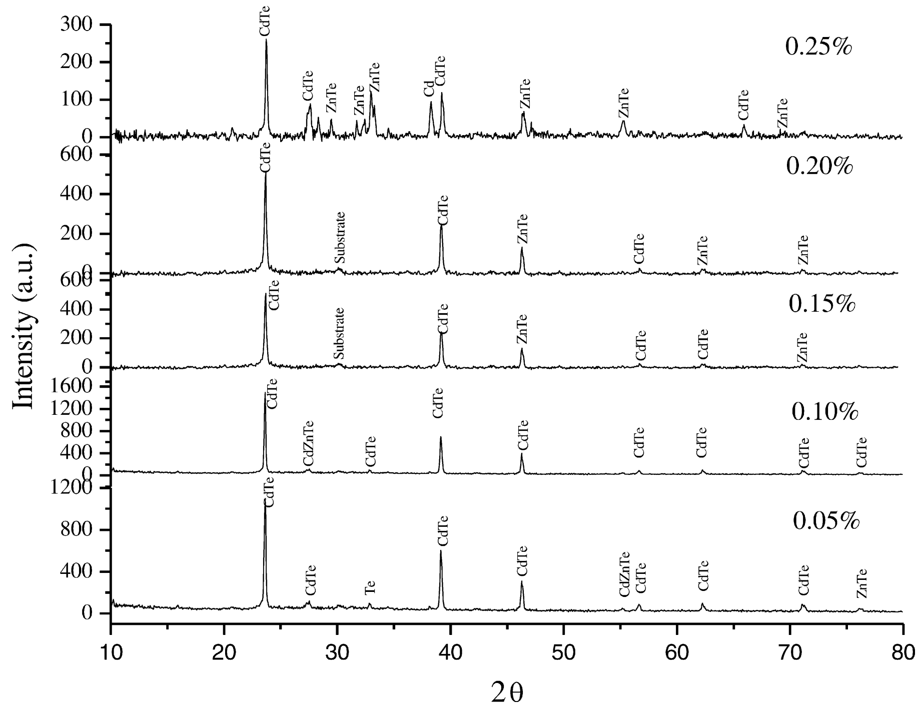


Fig. 1. XRD spectra of Te/Cd stack annealed at 500 °C for various Zn concentrations.

galore (model BC 300). We have already reported the procedure of SEL method for Sb doping to CdTe in another work [22,23]. The same methodology has been adopted in this paper. To achieve the stochiometric and to alter the Zn concentration in the stack, thickness of Zn and Cd elemental layers were adjusted while Te layer thickness was fixed as constant. The ratio of the thickness of elemental layers was maintained as $t_{Te}/t_{Cd} = 1.53$ (Te and Cd) and $t_{Te}/t_{Zn} = 1.95$ (Zn) and the coated thickness of (Te, Zn and Cd) elemental layers are presented in Table 1.

The stacked layers (Te/Cd/Te/Zn/Cd) were allowed to isochronal annealing at 500 °C for about 1 h in Ar gas atmosphere in a separate vacuum furnace. The XRD spectra were recorded using Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.5406 Å). To study the optical properties, the transmittance spectra were recorded by using a Double Beam Shimatzu UV 160A spectrophotometer in a wavelength range from 400 to 1100 nm. The SEM with EDX analysis was performed using a HITACHI S-3400N model equipment to study the surface properties as well as the particle size of the annealed films. To elucidate the observation, *ImageJ* software was used to analyze the grain growth and porosity by processing the SEM images.

3. Results and discussion

3.1. XRD analysis

Zn layered Te/Cd thin films deposited on corning glass were found to be uniform, semi transparent and strongly adherent to the substrate after annealed at 500 °C. XRD spectra of all annealed stacks (Fig. 1) showed reflections corresponding to CdTe, CdZnTe, ZnTe structures which indicate the effect of Zn atoms on the growth of (1 1 1), (2 2 0) and (3 1 1) orientations considerably. In addition, few elemental peaks related to Te and Cd is observed with Zn concentration of 0.05 and 0.25% respectively. Fig. 1 also shows that the predominant (1 1 1) oriented peak with high intensity is observed for 0.05 and 0.10% Zn doped Te/Cd stacks when compared with other Zn concentrations. It is also observed that there is no improve-

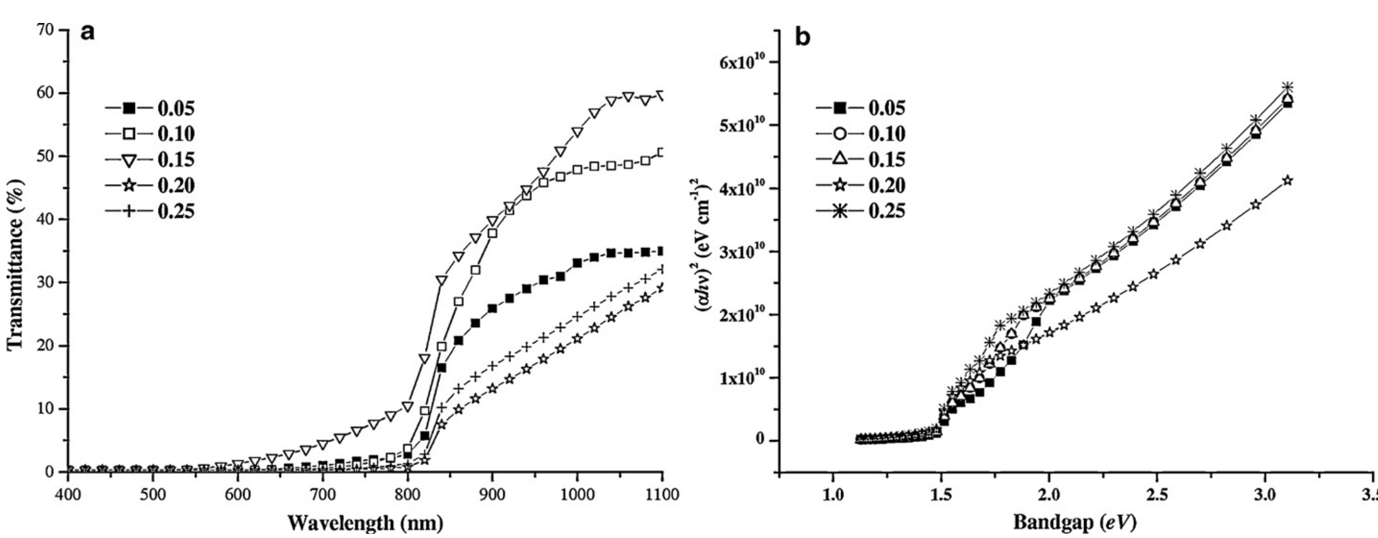


Fig. 2. Transmittance spectra (a) and band gap of annealed CdTe stack (b) for different concentrations of Zn.

ment on the intensity of preferred CdTe peaks as well as ZnTe peaks with increase of Zn concentrations from 0.15% to 0.20% in the stack. Meanwhile the phase conversion from CdTe to ZnTe could be identified at these concentrations. It is found that the XRD spectrum of 0.25% Zn doped Te/Cd stack shows the presence of more ZnTe peaks and also it seems to be the effect of Zn concentration on the growth of CdTe phase at this concentration.

3.2. Transmittance studies

The transmittance spectra were recorded for all stacks and presented in Fig. 2(a). The spectra show the interference pattern for all films with a sharp fall of transmittance at the band edge for various concentrations which is an indication of good crystallinity.

Fig. 2(a) reveals that the presence of non-reacted Zn in the stack reduces the transmittance of pure CdTe prepared by SEL method. The spectra also show the influence of Zn concentration on transmittance of the annealed Te/Cd/Zn stacks. It is also observed that the transmittance decreases considerably with an increase of Zn concentration. The absorption edge is found to shift towards the lower wavelength region as with increasing zinc content (about 0.15%) in the films. But the shift was also observed towards the higher wavelength for higher Zn concentration (i.e. Zn = 0.20% and 0.25%). It is contrary for the reported results [24]. However, the peak sharpness is found to decrease with increasing zinc content. It attributes to the decrease of grain size with increasing Zn content.

From Fig. 1, it is also observed that the increase in optical transmittance for low (0.05–0.15%) Zn concentration is the evidence of improvement on film crystallinity [25]. At high Zn concentration,

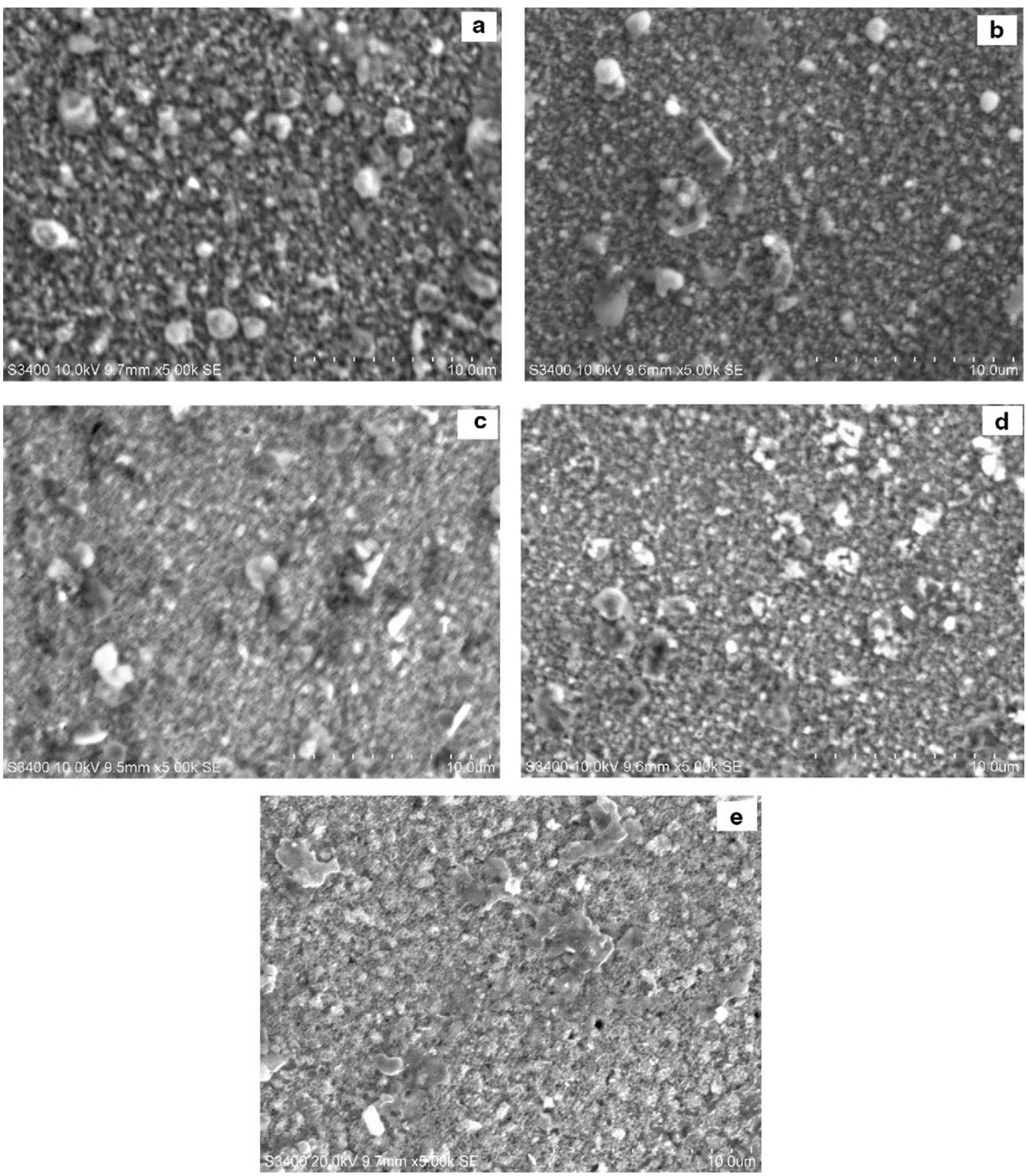


Fig. 3. SEM images of Zn doped CdTe thin film for different Zn concentrations: (a) 0.05%, (b) 0.10%, (c) 0.15%, (d) 0.20% and (e) 0.25%.

the presence of non-reacted Cd particles is identified in the stack which is the reason for the reduction of the film transmittance due to the strong optical absorption of Cd in this wavelength range. It is mainly due to the difference in diffusion coefficients of Zn and Cd. There may be a chance to the presence of Zn–Cd alloy on the surface since the top surface was fully covered by Zn and Cd layer. The increased absorbance of doped films may be due to either larger grain size or the presence of a preferred (1 1 1) orientation.

The optical band gap of all films were analyzed by using the relation

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2} \quad (1)$$

where A is a constant. The variation of $(\alpha h\upsilon)^2$ with photon energy $h\upsilon$ for the prepared Zn doped CdTe thin films is shown in Fig. 2(b). It is observed that the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for all films are mostly linear over a wide range of photon energies indicating the direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis $[(\alpha h\upsilon)^2 = 0]$ give the energy band gap.

Fig. 2(b) shows that the band gap varies from 1.35 to 1.42 eV and it is lower than that of pure CdTe (1.5 eV). The observed value is in good agreement with the reported value [26]. It is also observed that a small decrease in band gap from 1.42 to 1.38 eV with increase of Zn concentration. This decrease in band gap is also observed for $Cd_{0.2}Zn_{0.8}Te$ thin films as annealing temperature increases [17], but it is contrary for the results reported by Prasada Rao et al. [27]. This may occur due to the following reasons: According to the band structure of ZnTe and CdTe non local pseudo-potential method [28,29] there is unlikely to be any indirect optical energy gap less than the direct gap. It is known that at lower photon energy transitions, transitions rules are relaxed in the presence of a high density of defects, charge impurities and disorders at the grain boundaries may cause the decrease in the direct band gap. There is another reason for the decrease of direct band gap, which is likely to be

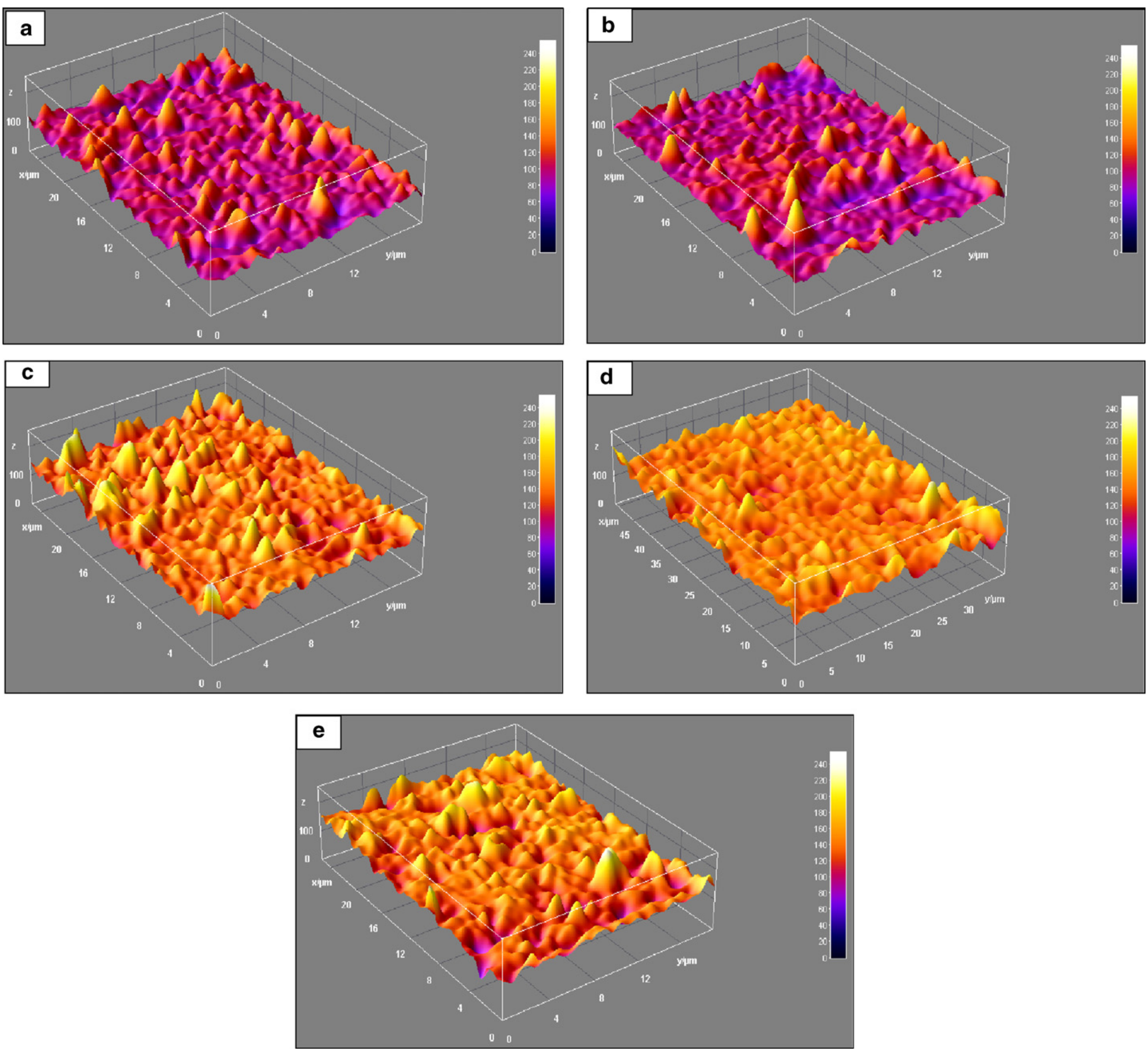
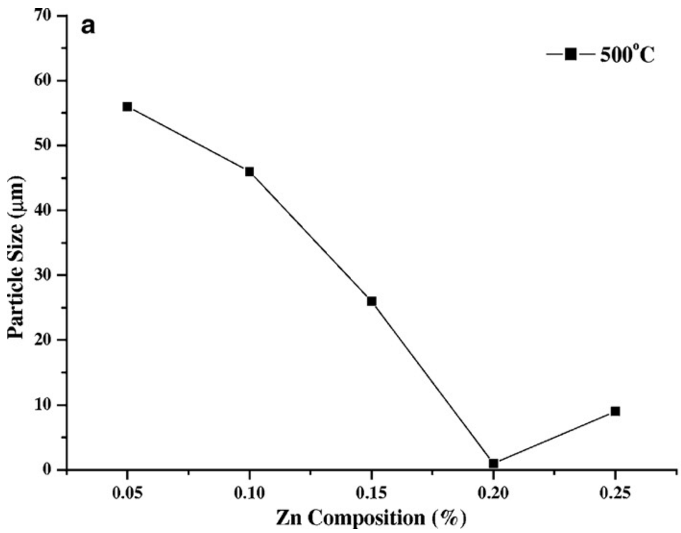


Fig. 4. 3D images of Zn doped CdTe thin film for different Zn concentrations: (a) 0.05%, (b) 0.10%, (c) 0.15%, (d) 0.20% and (e) 0.25% processed by *ImageJ* software.



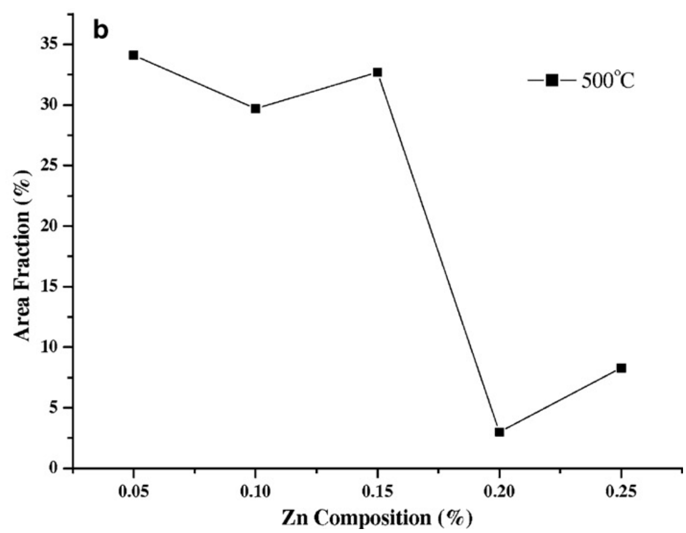


Fig. 5. Change in grain size (a) and area fraction (b) of the annealed stack for different concentrations of Zn in Te/Cd stack.

attributed to an increase in particle size and decrease in RMS strain, leads to decrease in band gap energy [30]. This is confirmed by studying the grain size analysis of the annealed stack and reported in the consecutive section.

Another fact on the further decrease of the optical band gap may be due to the presence of free tellurium atom on the film surface. Their unsaturated bonds and other structural defects can introduce localized states in the forbidden band that can be responsible for narrowing of the band gap. Such lower values for E_g for the Te-rich CdTe films have also been reported in other papers [26,30,31]. It suggests that the higher Zn concentration attributes the Te rich CdTe surface while using SEL method. It is confirmed by observing high Te concentration in EDS analysis and the observed results for all stacks are presented in Table 1.

3.3. Morphological characterization (SEM and ImageJ)

SEM images were recorded to understand the effect of Zn concentration on surface morphology at Te/Cd stack and presented in Fig. 3(a)–(e). It is observed that the surface morphology of the film is improved with increased Zn concentration and shows the grain growth for high Zn content in the stack. From the SEM figures, it shows some white particles on the surface at concentration of about 0.20% reveal the presence of non-reacted Cd particles since the sequence of elemental layers are Te/Cd/Te/Zn/Cd. Hence it is possible to prepare the Cd rich Zn doped CdTe thin film as well as Te rich CdTe thin film by using the proposed SEL method.

To know more in detail about the influence of Zn concentration on the microstructure of the film surface, SEM images were processed with *ImageJ* software and presented as 3D surface plot in Fig. 4(a)–(e). It gives clear picture about the effect of Zn concentration on surface roughness and grain growth. The grain sizes of the annealed stack were analyzed and presented in Fig. 5(a). It shows that the Zn concentration suppress the grain growth when the stack annealed at 500 °C. Using *ImageJ* software, the area fraction of the annealed stack was also measured and plotted for various Zn concentrations in Fig. 5(b). Area fraction is one of the factors to affect the porosity of the thin film. It unwraps that the porosity decreases drastically as Zn concentration increases. It also reveals the behavior of Zn on reducing the porosity at high Zn concentration in the annealed stack.

The EDS spectra for all stacks were observed to know the composition of the elements present in the stack and also to understand the diffusion behavior of Zn in to the Te/Cd stack at high temperature. The observed values are summarized in Table 1. The observed spectra show the presence of only Cd, Zn and Te elements in the stack which elaborates that the synthesis conditions were perfect.

Table 1
Thickness and composition of Zn doped CdTe thin film prepared by SEL method for different concentrations of Zn.

Doping concentration by SEL method	Thickness of elemental layer (nm)	Element present	Atomic%
0.05	400 (Te)	Cd	65.73
	239 (Cd)	Te	26.83
	9 (Zn)	Zn	7.45
0.10	400 (Te)	Cd	49.08
	227 (Cd)	Te	35.38
	18 (Zn)	Zn	15.54
0.15	400 (Te)	Cd	55.79
	214 (Cd)	Te	26.69
	27 (Zn)	Zn	17.52
0.20	400 (Te)	Cd	38.41
	202 (Cd)	Te	35.71
	36 (Zn)	Zn	25.88
0.25	400 (Te)	Cd	43.98
	189 (Cd)	Te	44.60
	45 (Zn)	Zn	11.42

4. Conclusions

CdTe thin films doped with different Zn concentration were prepared by SEL method. The transmission spectra revealed the influence of Zn concentration on the optical properties of the annealed stack and observed that the high Zn concentration at above 0.20% helps to reduce the transmittance due to the grain size variation as a result of Zn diffusion in to CdTe structure. The decreasing behavior of band gap suggests that the decrease in particle size and strain value in the presence of high Zn concentration. This could be verified by analyzing the annealed films surface using SEM and observed some noticeable improvement in both grain growth and surface roughness. All observed results encourage the synthesis of Zn doped CdTe thin film with significant properties using the proposed SEL method.

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