

Synthesis and properties of 10% Zn doped CdTe thin films

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Te/Cd/Te/Zn/Cd stacked layers were prepared for 10% Zn doping. All stacks were annealed from 200 °C – 500 °C and confirmed as polycrystalline nature. CdTe and ZnTe cubic/hexagonal phases were identified at high annealing temperature. Transmittance against wave length emphasized the significance of 10% Zn in Te/Cd stack. The optical constants n and k were calculated as $n = 1.52-2.45$ and $k = 0.07-0.36$. The band gaps (E_g) were observed between 1.38 and 1.44 eV at above 350 °C. A uniform surface morphology could be observed at high annealing temperatures.

(Received September 24, 2010; accepted October 14, 2010)

Keywords: Multilayer, Physical vapor deposition (PVD), Structural properties, Topography, Surface properties

1. Introduction

Cadmium Telluride (CdTe) is one of the most promising polycrystalline materials for producing solar cells because of its high absorption coefficient ($>10^5 \text{ cm}^{-1}$) and optimum band gap (1.5 eV). To date, about ten methods have been developed for fabricating CdTe thin films [1–3]. A considerable change in the optical, electrical and mechanical properties was observed for CdTe thin films doping with transition metals such as titanium, vanadium and indium [4, 5]. There is a lack of reports on the possibility of obtaining the variable band gap films of CdZnTe using the diffusion process. This 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 [6].

Stacked Elemental Layer method was originally developed to produce CuInSe₂ thin films [7] and also used to produce CdTe films [8-10]. Since the method 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 [9]. Latterly, this method was used for Sb doping [11]. This work reports the structural, optical and morphological properties of 10% Zn doped CdTe thin films produced by this proposed method.

2. Experimental work

10% Zn doped CdTe thin films were prepared at room temperature by SEL method using PVD unit supplied by M/s HINDHIVAC, Bangalore (model BC 300). The 5N purity Te, Zn and Cd powders from M/s Sigma Aldrich were used for film preparation. Sequential layer of Te, Cd followed by Zn were coated on soda lime glass substrates. The deposition rates of 3 Å/s and 1.5 Å/s were maintained for Cd & Te and Zn films respectively. To achieve the

desired stoichiometry, the ratio of the thickness of Te, Zn and Cd elemental layers was adjusted and maintained as $t_{\text{Te}}/t_{\text{Cd}} = 1.53$ (Te & Cd) and $t_{\text{Te}}/t_{\text{Zn}} = 1.95$ (Zn). To achieve the 10% Zn doped CdTe thin film, the thickness of Te, Zn and Cd elemental layers was maintained as 400nm, 18nm and 227nm respectively. The distance between the substrate and source was fixed at 10 cm. Rotary drive assembly was used to enhance the film uniformity.

The stacked layers (Te/Cd/Te/Zn/Cd) were allowed to isochronal annealing from 200 °C – 500 °C for about an hour in Ar gas atmosphere in a separate vacuum furnace. The structural properties were analyzed by X-ray Diffraction (XRD) technique using CuK α radiation [$\lambda = 1.5406 \text{ \AA}$] in Bruker D8 Advance diffractometer. The lattice parameter ' a ' can be evaluated from the relation

$$a^2 = d^2 (h^2 + k^2 + l^2) \quad (1)$$

where h, k, l are Miller indices. In order to investigate the possibility of preferred orientation, the Harris analysis [15] was performed using the following relationship for the Texture Coefficient (P_i).

$$P_i(TC) = \frac{N(I_i/I_0)}{\sum_{i=1}^N(I_i/I_0)} \quad (2)$$

where P_i is the Texture Coefficient of the plane I , I_i is the intensity of the peak observed from XRD technique, I_0 is the intensity of the peak observed from JCPDS powder diffraction pattern of the corresponding peak and N is the number of reflections considered for the analysis. P_i is the unity for each reflection in the case of a randomly oriented sample and values of P_i greater than the unity indicate preferred orientation of the crystallites in that particular direction.

The transmittance spectra were recorded using a Double Beam Shimadzu UV 160A Spectrophotometer in

the wavelength range from 400 to 1100 nm. The spectral refractive index (n) of the films was calculated from the transmittance data using the simple and straightforward method developed by Manifacier's [18]. The refractive index of the films was calculated from the formulae.

$$n = \{N + (N^2 + n_o^2 n_1^2)^{1/2}\}^{1/2} \quad (3)$$

Where n_o is the refractive index of air, n_1 is the refractive index of the substrate and

$$N = (n_o^2 + n_1^2) / 2 + 2 n_o n_1 (T_M - T_m) / T_M T_m \quad (4)$$

where T_M and T_m is the upper and lower extreme transmittance values for a given wavelength obtained from the envelope curves. The transmittance T varied with wavelength according to the relation [19]

$$T = \frac{16 n_a n_g n^2 \exp(-\alpha t)}{R_1^2 + R_2^2 \exp(-2\alpha t) + 2 R_1 R_2 \exp(-\alpha t) \cos 4\pi n t / \lambda} \quad (5)$$

Where

$$R_1 = (n + n_a) (n + n_g) \quad (6)$$

$$R_2 = (n - n_a) (n_g - n) \quad (7)$$

Here n_a , n_g and n are the refractive indexes of the air, substrate and film respectively. α is the absorption coefficient and t is the thickness of synthesized film. Iterations were carried out until the desired convergence was achieved. The relation between the absorption (α) and the incident photon energy ($h\nu$) can be written as

$$\alpha h\nu = C_1 (h\nu - E_g^d)^{1/2} \quad (8)$$

$$\alpha h\nu = C_2 (h\nu - E_g^i)^2 \quad (9)$$

for direct allowed and indirect allowed transitions respectively, where C_1 and C_2 are two constants, E_g^d and E_g^i are the direct and indirect band gaps, respectively. The optical band gap of all films was analyzed by using the relation:

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \quad (10)$$

where, A is a constant. The absorption coefficient (α) was calculated from the transmittance spectra using the relation [25]

$$\alpha (h\nu) = 4\pi k_f / \lambda \quad (11)$$

The extinction coefficient k_f coming out from experimental measurements was then calculated from the relation.

$$k_f = \frac{2.303 \lambda \log (1 / T_o)}{4\pi t} \quad (12)$$

where T_o is the transmittance, t is the film thickness and λ is the wavelength of the incident radiation.

The surface morphology of annealed stack was analyzed using HITACHI make Scanning Electron Microscope (SEM) coupled with Energy dispersive X-ray spectroscopy (EDAX) analysis (Model S-3400N). S.I.S. ULTRAObjective AFM and ImageJ software have been used to analyze the 3D morphology and grain size of the annealed films.

3. Results and discussions

3.1 Structural studies

The XRD spectra of annealed (Te/Cd/Te/Zn/Cd) stacks are presented in Fig.1 and shown that the structures are in polycrystalline nature. It also reveals the presence of mixed phases (Cubic and Hexagonal) of both CdTe and ZnTe at high annealing temperature. The figure also shows that the elemental peaks related to Cd with high intensity are dominated at 200 °C since the top of the stack is covered by Cd layer and the intensity of elemental peaks get reduces slowly as Cd layer diffuses into the Te/Zn stack as the temperature increases. This may be due to because of thermal activated diffusion process. The figure also depicts that the formation of binary compounds like ZnTe and CdTe start even at low temperature due to the difference in diffusion coefficients of Cd and Zn atom [12]. As a result, number of peaks related to ZnTe was observed at 200 °C.

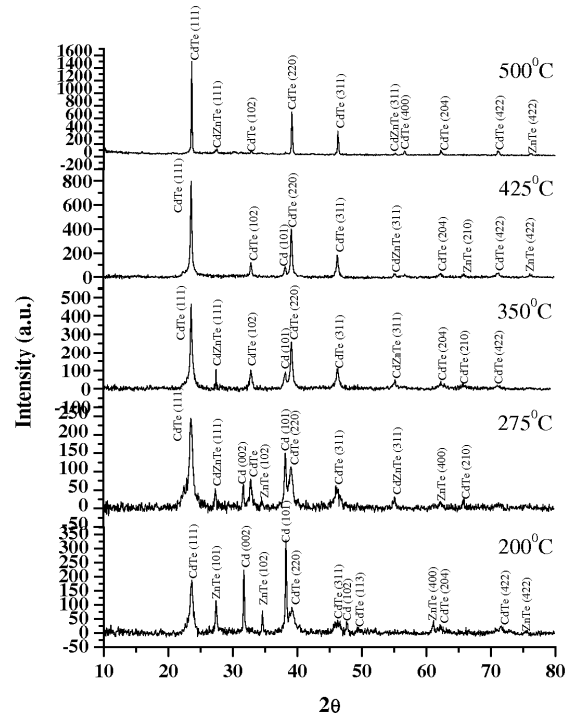


Fig. 1. XRD spectra of 10% Zn doped CdTe thin film for different annealing temperature.

The behavior of decreased intensity of elemental peaks as the temperature increases reflects the compound formation. The peaks related to cubic CdTe with (111), (220) and (311) orientations could be observed at 275 °C and also be observed that the intensity increases as the temperature increases. In addition to that, the diffraction peaks at $2\theta = 27.7^\circ$ and 54.7° were observed in the higher annealing temperature which indicate the formation of

cubic phase of CdZnTe alloy with (111) and (311) orientations. It is in good agreement with results observed in ref. [13]. From the figure, it could be observed that the annealing temperature at above 350 °C helps to increase the crystalline quality of the annealed stack. It suggests that the higher annealing temperature helps to crystallize the CdTe in (111) orientation in presence of Zn atoms introduced by SEL method [14].

Table 1. Structural parameters of Zn doped CdTe thin film by SEL method.

Treated Temp. (°C)	(h k l)	Lattice parameter (a) Å	Cell volume (Å) ³	Texture Coefficient (TC)	FWHM (2θ)
200	(111) c	6.53	279	1.54	0.587
	(311) c	6.52	276	0.71	2.229
	(422) c	6.51	276	0.75	4.000
275	(111) c	6.54	279	1.40	0.681
	(220) c	6.50	275	0.45	0.345
	(311) c	6.53	277	0.60	1.735
350	(111) c	6.52	277	1.59	0.364
	(220) c	6.51	275	0.23	0.263
	(311) c	6.50	275	0.16	0.424
	(331) c	6.48	272	0.06	1.709
	(420) c	6.41	262	4.30	2.585
425	(111) c	6.53	278	1.69	0.245
	(220) c	6.51	275	1.44	0.216
	(311) c	6.51	275	1.19	0.316
	(331) c	6.52	276	0.16	4.000
	(422) c	6.50	274	0.53	0.282
500	(111) c	6.51	277	1.76	0.112
	(220) c	6.51	275	1.18	0.127
	(311) c	6.50	275	1.25	0.118
	(400) c	6.50	274	0.93	0.139
	(331) c	6.50	274	0.65	0.131
	(422) c	6.49	273	0.63	0.204

Table 1 summarizes the calculated values of the texture coefficients and reveals that the texture coefficient value of (111) peak increases as the temperature increases. It suggests that the Zn doped CdTe thin film by SEL method helps to grow the film in their preferred

orientation. It also suggests that the Zinc helps to promote the (111) orientation of CdTe peak and also the crystallinity of the film. The observed results are in well matched with the results published in ref. [16].

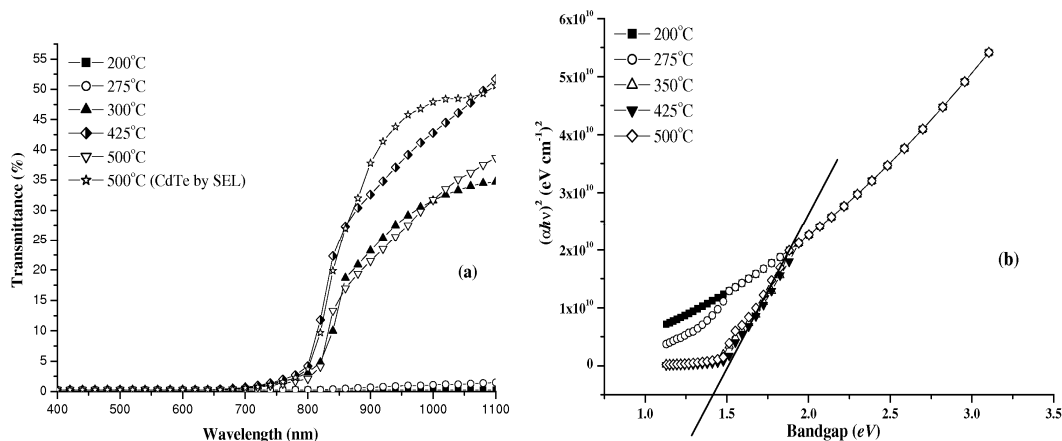


Fig. 2. Optical properties (a) Transmittance Spectra and (b) band gap of 10% Zn doped CdTe thin film for different annealing temperature.

Additionally, the influence of Zn on CdTe thin films is explained by calculating the lattice parameter and the cell volume from the XRD spectra and given in Table 1. The increased lattice parameter and the cell volume disclose the occupancy of Zn atom at the interstitial sites of CdTe lattice. Hence the calculated lattice parameter value is higher than that of pure CdTe [$a_{\text{CdTe}} = 6.48 \text{ \AA}$ and $a^3_{\text{CdTe}} = 272.1 \text{ \AA}^3$]. The higher value of 'a' is due to the recrystallized lattice in the grown films and also influence of compressive stress as a result of introduction of Zn in to CdTe lattice. This is also due to the lattice mismatch and/or differences in thermal expansion coefficient between the doped film and substrate.

To confirm the effect on crystalline size, the observed Full Width Half Maximum (FWHM) for plane (111) and (311) were given in Table 1. It reveals that the FWHM value of both (111) and (311) peaks decreases as the temperature increases and hence the crystallite size of the annealed films increases. It attributes in decreasing RMS strain values as with temperature. Such an increase of crystallite size with increasing annealing temperature is in good agreement with the reported value [17].

3.2 Optical studies

Transmittance spectra against wavelength were recorded and presented in Fig. 2 (a). The spectra show that the small interference pattern with a sharp fall of transmittance at the band edge is the sign of good crystallinity. It also reveals that the increase in transmittance at high annealing temperature validates the compound formation from the elemental stack. The films annealed at low temperature show a poor transmittance behavior which reflects the presence of non reactive elements (Cd) on top surface of the stack (Glass/Te/Cd/Te/Zn/Cd).

The variation of $(ah\nu)^2$ with photon energy $h\nu$ for the prepared 10% Zn doped CdTe thin films are shown in Fig. 2(b). It is observed that the plots of $(ah\nu)^2$ verses $h\nu$ 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 [$(ah\nu)^2 = 0$] give the band gap energy.

Table 2 shows that the observed band gap is between 1.35 and 1.44 eV. It also depicts that the band gap value at about 350 °C is slightly lower than that of pure CdTe (1.45 eV) when annealed at above 350 °C. The same behavior was observed elsewhere [19]. It could be seen that the higher E_g value of about 1.44 eV is with the stack annealed at 425 °C.

Table 2. Bandgap of 10% of Zn doped CdTe thin film by SEL method annealed at different temperature.

Annealing temperature	Bandgap (eV)
350	1.43
425	1.44
500	1.38

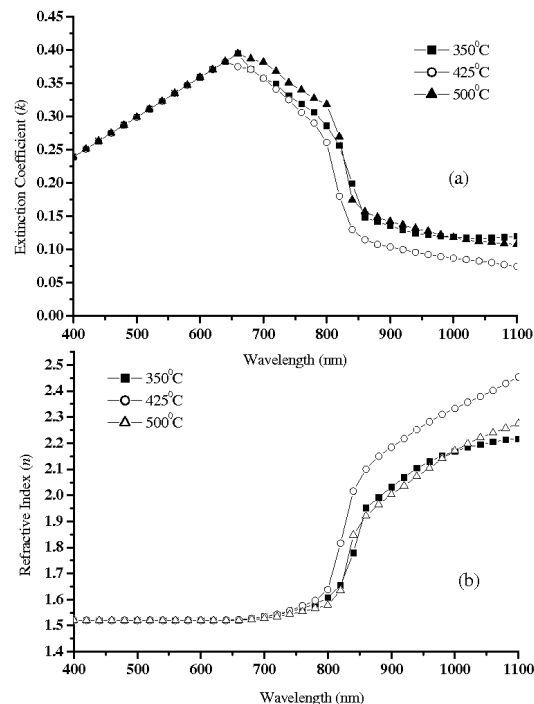


Fig. 3. Variation of extinction coefficient (k) [a] and Refractive Index (n) [b] with wave length for Zn doped CdTe by SEL method.

But it is low when compared with the results observed by other researchers and this is attributed to the formation of CdZnTe alloy at high annealing temperature [13]. It is also confirmed by the XRD results.

From the Fig. 2(b), A small decrease in band gap from 1.44 to 1.38 eV could be observed while increasing the annealing temperature from 425 °C-500 °C according to the band structure of ZnTe and CdTe nonlocal pseudo potential method [20,21], 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 attributed to an increase in particle size and a decrease in rms strain as observed from the XRD, leads to decrease in band gap energy [21].

The another fact that the further decrease of the optical band gap beginning at an annealing temperature of about 327 °C may be attributed to the remaining free tellurium in the films. 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 E_g values for the Te-rich CdTe films have also been reported in other papers [22, 23].

In addition to that the bandgap shift was observed at absorption edge towards lower photon energies for the heat treated layers. It is attributed to the change in the grain size and the stoichiometry due to loss of Cd resulting

formation of shallow acceptor levels. This behavior shows that the Cd evaporation is possible during the annealing process at above 500 °C [24]. Fig. 3(a) shows the variation of k value with wavelength for the annealed films and reveals that the extinction coefficient varies between 0.07 and 0.375 with annealing temperature.

The calculated refractive index (n) of the annealed films were plotted against wavelength and given in Fig. 3(b). It shows that the n value increases for 425 °C and

decreases as the temperature increases to 500 °C. This may be due to the smaller grain in these films resulting in significant amount of voids [26]. The observed very low n and k value and variation at the fundamental band gap region may be due to the surface effect and volume imperfection on the micro scale [27]. It could also be seen in the SEM studies. This behavior is in good agreement with the observed results by Chattopadhyay et al. [28].

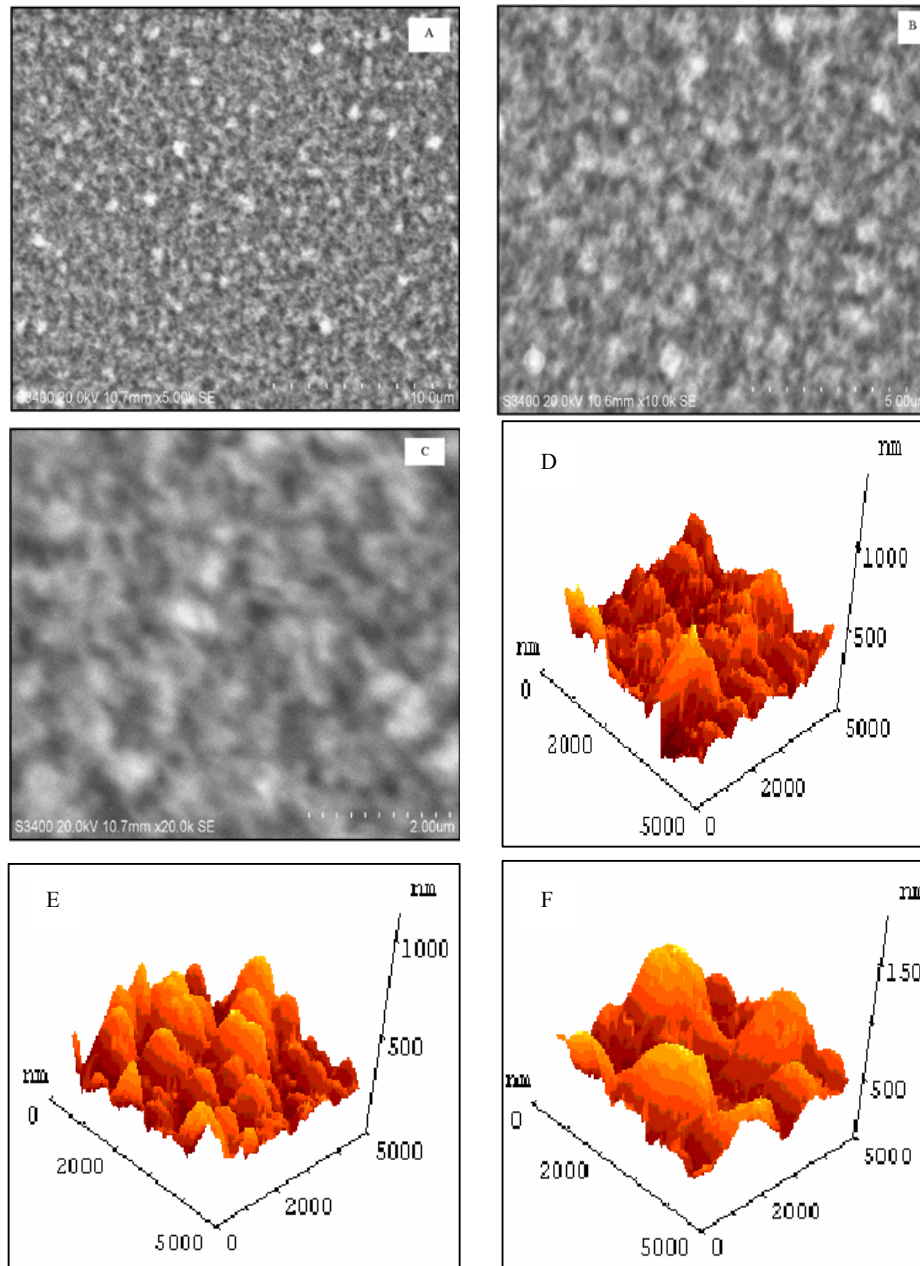


Fig. 4. SEM image of 10% Zn doped CdTe thin film annealed at 500°C for (A) 60min, (B) 90 min & (C) 120min and 3D AFM images of the surface of the same film for (D) 60 min, (E) 90 min & (F) 120 min.

3.3 Morphological studies

Morphological nature of the film annealed at 500°C for different annealing time (60 min, 90 min and 120 min) was analyzed by using Scanning Electron Microscope and presented in Fig. 4(A-C). In order to investigate more on surface of the stack, the same samples were analyzed by AFM tool and their 3D images presented in Fig. 4 (D-F). The figures reveal that the considerable morphological change exists as the annealing time increases and seems to be grain growth. It also exposes the influence of annealing time on the surface roughness of the film. It may be the evidence of thermal diffusion of Zn into the stack Te/Cd as with temperature. From the 3D image, it could also be seen that the surface roughness of the films is quite high and also could visualize the grain growth in higher annealing time.

By using the ImageJ software, the average particle size of the samples annealed at 500 °C have been evaluated and plotted against annealing time in Fig. 5. It could be observed that the particle size reduces as the annealing time increases from 60 min to 120 min.

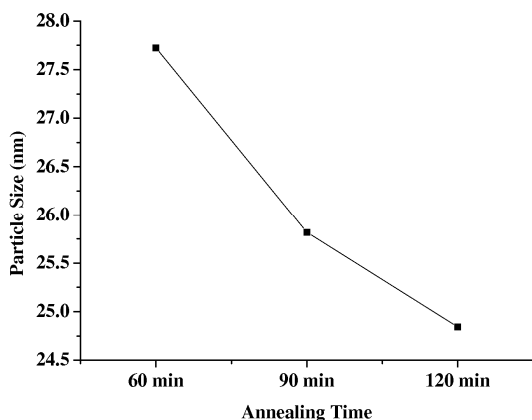


Fig. 5. Particle size variation for plane (111) and (311) with different annealing time.

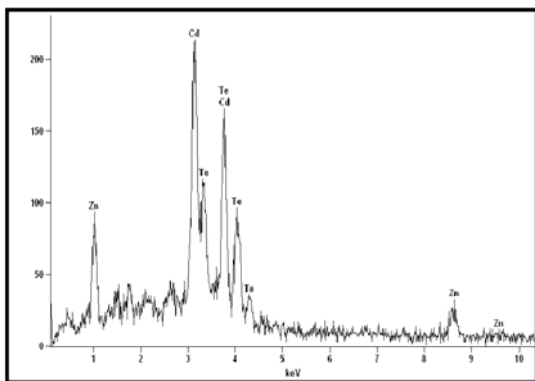


Fig. 6. EDS spectrum of Zn doped CdTe thin film annealed at 500°C for 60 min.

EDAX spectrum of 10% Zn doped CdTe thin film annealed at 500 °C for 60 min was also recorded and given in Fig. 6 and the atomic percentage of the elements is summarized in Table 3. The EDAX spectrum shows the presence of only Cd, Te and Zn elements in the annealed stack. The atomic percentage of Cd, Te and Zn may vary as the annealing temperature increases since the elemental layers are stacked like Te/Cd/Te/Zn/Cd. This behavior depicts the inter diffusion process as a result of increase in annealing temperature. From the observed results, it is suggested that the CdZnTe alloy exists in the annealed stack which is attributed for the surface changes.

Table 3. Composition of 10% of Zn doped CdTe thin film by SEL method annealed at 500°C for 60 min.

Element present	Atomic %
Cd	49.08
Te	35.38
Zn	15.54

4. Conclusion

10% Zn doped CdTe films were prepared by SEL method and confirmed as polycrystalline nature. Highly oriented (111) peak related to cubic CdTe along with mixed structure of ZnTe and CdZnTe alloy were observed at high annealing temperature. The calculated lattice parameter (6.53 Å) was the evidence of Zn doping in Te/Cd stack. As a result of Zn diffusion, increased crystallite size and noticeable change in surface properties have been observed at high annealing temperature as well as time. The calculated band gap values were between 1.38 and 1.44 eV. Appreciable optical constants k and n were suggested that the proposed SEL method alleviate the controllable doping of Zn in to CdTe.

Acknowledgements

The authors gratefully acknowledge The Management of Thiagarajar College of Engineering, Madurai for their full support and providing the facilities to carry out the research.

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