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SUBSTRATE TEMPERATURE DEPENDENT OPTICAL AND STRUCTURAL PROPERTIES OF VACUUM EVAPORATED CdTe THIN FILMS

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Abstract

Substrate temperature dependent optical and structural properties of Cadmium Telluride (CdTe) thin films were studied. Films were grown onto glass substrate by thermal evaporation method in high vacuum (10^{-6} Torr) with varying thickness (200 ~ 500 nm). All the films were characterized optically by UV-VIS-NIR spectrophotometer in photon wavelength range (300 nm ~ 2500 nm). The optical transmittance and reflectance were utilized to compute the absorption coefficient, refractive index and band gap energy of the films. The calculated band gap energy was found to increase (1.49eV ~ 1.55eV) with varying thickness and to decrease (1.56eV ~ 1.46eV) with varying substrate temperature. The X-ray diffraction (XRD) patterns exhibited the zinc-blende structure of CdTe films with (111) preferential orientation. The lattice parameters, grain size, average internal stress, micro strain, dislocation density in the films were calculated. The grain size was varied from 32nm to 52nm with variation of substrate temperature. Micro strain and dislocation density were also found to vary between 0.69×10^{-3} ~ 1.12×10^{-3} and 3.59×10^{10} cm^{-2} ~ 9.49×10^{10} cm^{-2} respectively.

Keywords: CdTe thin films, Thermal evaporation, Optical properties, XRD, Structural properties

Introduction

Cadmium Telluride (CdTe) is an important compound semiconductor of II-VI group. It is a potential candidate for having suitable applications in the areas of polycrystalline thin films, IR detector, photovoltaic and optoelectronic applications. The direct band gap 1.45 eV and the high optical absorption coefficients for visible light makes CdTe suitable for fabrication of thin film solar cells. In addition, CdTe is a material of low cost and also a stable absorber which makes it possible for processing a high efficiency solar cell. Several deposition methods such as electron beam evaporation (Rigana et al., 2013), closed space sublimation (Britt et al., 1993), sputtering (Gupta et al., 2003), spray pyrolysis (Vamsi Krishna et al., 2004) and vacuum evaporation (Patil et al., 2012) were employed for the deposition of CdTe thin films. Among various other techniques, thermal evaporation technique is simple and economical. This tehnique was utilized to study the effect of thickness on the optical properties of GaAs thin films (Das et al., 2013). Also structural and optical properties were investigated on undoped and Iodine doped Tin Oxide (SnO_2) thin films (Chowdhury et al., 2011) and Cadmium doped ZnS ($Zn_xCd_{1-x}S$) thin films (Biswas et al., 2007) by this same technique.

Effect of substrate temperature on structural and optical properties of nanocrystalline CdTe thin films by electron beam evaporation was studied by (Rigana et al., 2013). The effects of annealing on structural and optical properties of CdTe thin films by thermal evaporation method were investigated (Geethalakshmi et al., 2012). It was seen that the energy band gap increased with film thickness and decreased with substrate temperature. Thermally evaporated CdTe thin films were fabricated on quartz and glass substrates to investigate the structural, optical, photoluminescence, dielectric and electrical studies (Khan et al., 2012).

In this present work, various optical and structural properties of thermally evaporated CdTe thin films have been reported. CdTe thin films of different thicknesses and also at different sbstrate temperatureshave been prepared. Photometric measurements (transmittance, and reflectance) of CdTe films were carried on to characterize the material in the wavelength range 300 ~ 2500nm. X-ray diffraction pattern of the annealed CdTe films was investigated and various structural parameters were calculated from the XRD analysis. The effect of substrate temperature and thickness of thermally deposited CdTe thin films is investigated to optimize the growth condition for a good quality film which will be suitable for optoelectronic devices.

Experimental:

The samples were prepared by thermal evaporation method using a vacuum evaporation unit (Edwards 306A, UK), in high vacuum (10^{-6} Torr). Glass slides were used as substrates which were cleaned chemically and ultrasonically. Powder form of CdTe was used as source material. The rate of evaporation for CdTe thin film was 0.2 nm /sec measured *in situ* by the FTM5 quartz crystal thickness monitor (Edwards, UK). Cadmium Telluride thin films of various thicknesses (200, 300, 400 and 500nm) were prepared keeping substrate temperature at 100°C. CdTe samples were also prepared at various substrate temperatures (100°C, 150°C and 200°C) where annealing temperature was kept fixed at 100°C and annealing time was 60 minutes.

A PHILIPS PW 3040 X' Pert PRO X-ray diffraction system was used to get X-ray data for the samples. The powder diffraction technique was used with a primary beam power of 40 KV and 30 mA for Cu-Kα radiation. All the data of the samples were analyzed using "X PERT HIGHSCORE" computer software.

The variations of optical transmittance (*T %*) and reflectance (*R %*) of the films with wavelength of light incident on them were measured using a dual-beam UV-VIS-NIR recording spectrophotometer (Shimadzu, UV-3100, Japan) in the photon wavelength range from 300-2500 nm. An integrating sphere was used to detect the light signals coming from the samples. By infrared interference method the thickness of a film is given by

$$d = \frac{\Delta m}{2\sqrt{n_1^{\,2} - \sin^2\theta}} \frac{1}{(1/\lambda_1) - (1/\lambda_2)} \qquad (1)$$

where, n_1 is the refractive index of the film, θ is the incident angle of light to the sample, λ_1 and λ_2 are the peak or valley wavelengths in the reflectance spectrum and Δm is the number of peaks or valleys between λ_1 and λ_2, where, $\lambda_2 > \lambda_1$.

For transmittance *(T %)* at normal incidence and reflectance *(R %)* at near-normal incidence of light on the films, expressions for the multiple reflected systems have been given by (Heavens, 1965). (Tomlin, 1968) simplified these equations as

$$\frac{1+R}{T} = \frac{1}{4n_2(n_1^2+k_1^2)}\left[\begin{array}{l}(1+n_1^2+k_1^2)\{(n_1^2+n_2^2+k_1^2)\cosh 2\alpha_1 + 2n_1n_2\sinh 2\alpha_1\} \\ +(1-n_1^2-k_1^2)\{(n_1^2-n_2^2+k_1^2)\cos 2\gamma_1 - 2n_2k_1\sin 2\gamma_1\}\end{array}\right] \qquad (2)$$

$$\frac{1-R}{T} = \frac{1}{2n_2(n_1^2+k_1^2)}\left[\begin{array}{l}n_1\{(n_1^2+n_2^2+k_1^2)\sinh 2\alpha_1 + 2n_1n_2\cosh 2\alpha_1\} \\ +k_1\{(n_1^2-n_2^2+k_1^2)\sin 2\gamma_1 + 2n_2k_1\cos 2\gamma_1\}\end{array}\right] \qquad (3)$$

where, n_1 *and* n_2 are the refractive indices of the film and substrate, respectively, k_1 is the extinction-coefficient of the film, $\alpha_1 = \frac{2\pi k_1 d}{\lambda}$ and $\gamma_1 = \frac{2\pi n_1 d}{\lambda}$, where λ is the wavelength of light and *d* is the thickness of the film. The above two equations were solved for k_1 and n_1 utilizing a computerized iteration process. The absorption coefficient α was then calculated using $\alpha = \frac{4\pi k_1}{\lambda}$.

The optical band gap E_g can be estimated from the following relation known as the Tauc relation (Tauc, 1974):

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

where A is a constant, ν is the transition frequency and the exponent n characterizes the nature of band transition. $n = 1/2$ and $3/2$ corresponds to direct allowed and direct forbidden transitions and $n = 2$ and 3 corresponds to indirect allowed and indirect forbidden transitions, respectively. For all the films the best straight line is obtained for n equal to ½, which is expected for direct allowed transition.

The lattice parameter 'a' was evaluated from the relation

$$a = d\sqrt{(h^2 + k^2 + l^2)} \qquad (3)$$

where, d is atomic spacing and h, k, l are the Miller Indices.

The grain size (D) was determined using Debye Scherrer formula (Warren, 1969),

$$D = k\lambda/\beta_{2\theta}\cos\theta \qquad (4)$$

here constant k is a shape factor usually taken as 0.94 for cubic structure, λ the wavelength of X-ray (1.5406Å) used, θ is the Bragg's angle and $\beta_{2\theta}$ the full width at half maximum of [111] peak of XRD pattern.

The micro strain (ε) was calculated by the formula

$$\varepsilon = \beta_{2\theta}\cos\theta/4 \qquad (5)$$

The dislocation density (ρ) defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula (Lalitha, 2006)

$$\rho = \frac{1}{D^2}$$

Result:

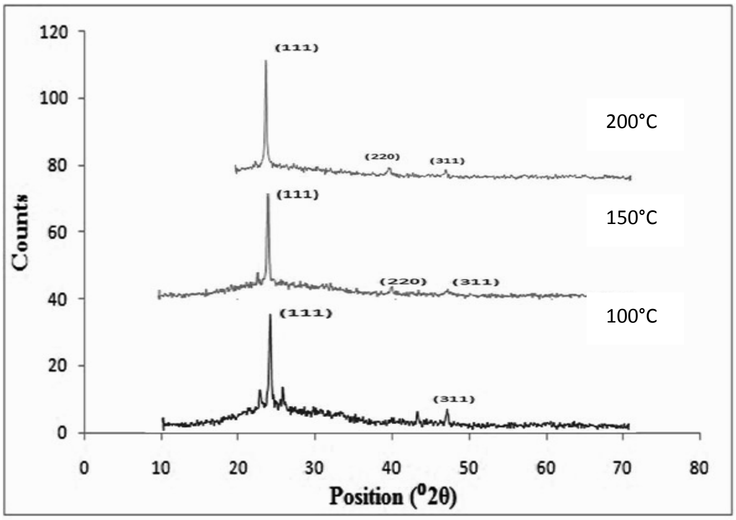


Figure 1. X-ray diffraction pattern of annealed CdTe thin films at various substrate temperatures

All the XRD pattern shows in Figure 1 the preferential (111) direction which is the close packing direction of the zinc blende structure and this type of ordering is often observed in polycrystalline films (Kokate et al., 2007) grown on heated amorphous substrates. It can be seen that the (111) diffraction plane is localized at approximately 23.8º and the weak other twos are at approximately 39.4º and 46.5º match with the (220) and (311) diffraction plane of cubic phase CdTe films which is in good agreement with (Sathyamoorthya et al., 2003). However, in all the cases the intensities of the (220) and (311) peaks are extremely low in comparison with the (111) peak. This indicates that a preferential orientation of the crystallites in the (111) direction perpendicular to the substrate (Qi, 1996). From these results it can be concluded that the elevated substrate temperature (100ºC-200ºC) are the suitable optimum growth conditions to prepare good quality polycrystalline thin film.

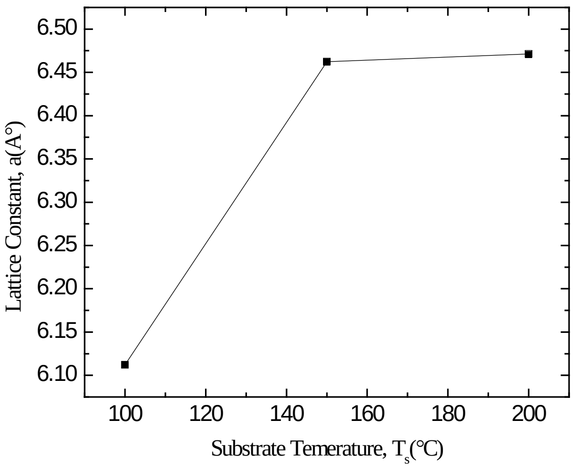


Figure 2. Variation of lattice constant with substrate temperature for annealed CdTe thin films

From Figure 2, it can be observed that lattice parameter of the films increased from 6.11Å to 6.47Å when the substrate temperature of the films increased from 100ºC to 200ºC. The increase in the lattice constant with the increase of substrate temperature may be due to development of internal stress in the film grains which triggers the prolongation (Rigana et al., 2013).

Figure 3 shows that the grain size of CdTe thin films are small and are within the range 32-52nm. Increase in annealing temperature increases the average grain size. As the substrate temperature increases the adatom mobility also increases and the FWHM decreases. This is the indication of improvement of crysallinity due to annealing (Sathyamoorthya et al., 2003).

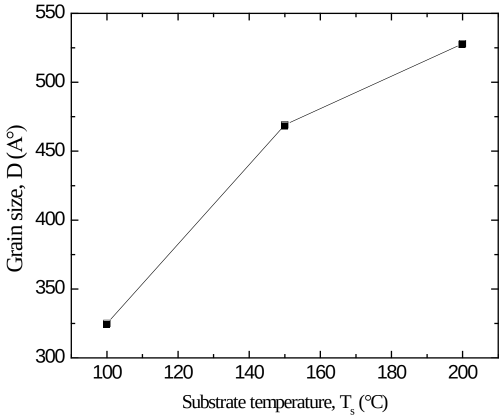


Figure 3. Variation of grain size with substrate temperature for annealed CdTe thin films

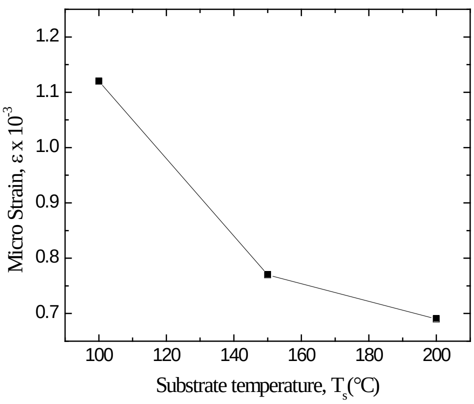


Figure 4. Variation of micro strain with substrate temperature for annealed CdTe thin films

It is observed from Figure 4 that there is decrease in micro strain with the increase of substrate temperature. This may be due to the difference in the temperature coefficient of expansion of the glass substrate and CdTe thin films (Rigana et al., 2013).

Figure 5 exhibits decreasing trend of dislocation density similarly as micro strain with substrate temperature .The dislocation density and micro strain both are the indication of dislocation network of the films. The decrease of dislocation density at higher substrate temperature may be due to the movement of interstitial Cd atoms from inside the crystallites to its grain boundary which dissipate leading to reduction in the concentration of lattice imperfection. Further the number of crystallites decreases with increasing substrate temperature (Kalita et al., 2000). The decrease in the dislocation density and strain indicates the formation of higher quality films at higher substrate temperature (Chaliha et al., 2008).

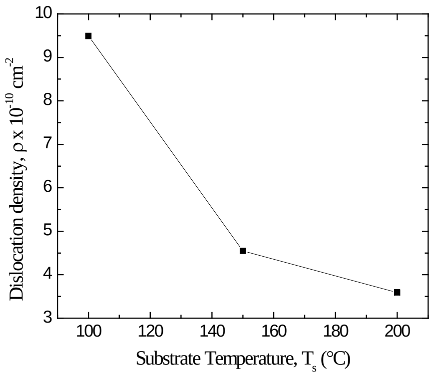


Figure 5. Variation of dislocation density with substrate temperature for annealed CdTe thin films

From Figure 6, it can be observed that the film of thickness 500nm shows good interference pattern which indicates better homogeneity and good quality. High transmittance in a higher wavelength region and a sharp absorption edge were observed in the films. All the samples show optical transparency exhibiting interference pattern in the spectral region between 850 nm to 2500 nm and display a clear explicit absorption edge interrelated to the optical band gap which agrees with (Patil et al., 2012). Such behavior of the transmission spectra is an evidence of the increase in the thickness and uniformity of the films. The transmittance falls steeply with decreasing wavelength (300–850 nm) (Sathyamoorthy et al., 2003). The appearance of maxima and minima result from their interference effect (El-Kadry et al., 1995). The rise and fall in reflectance is observed by other workers (Miah et al., 2010). Interference pattern with rise and fall is observed in the reflectance spectra of the films.

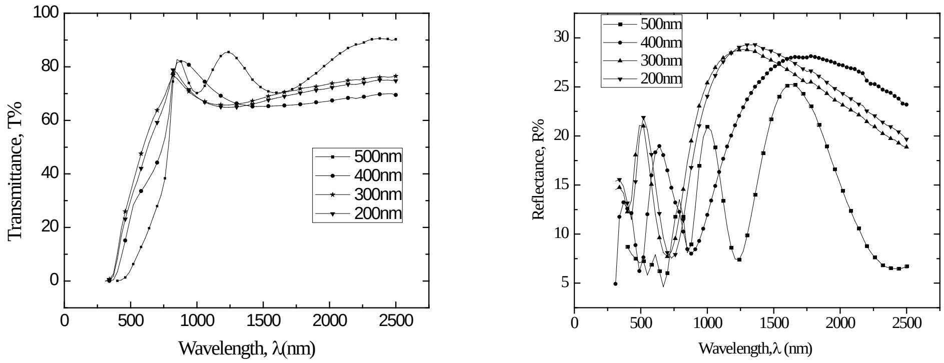


Figure 6. Dependence of transmittance and reflectance on photon wavelength of CdTe thin films having different thicknesses

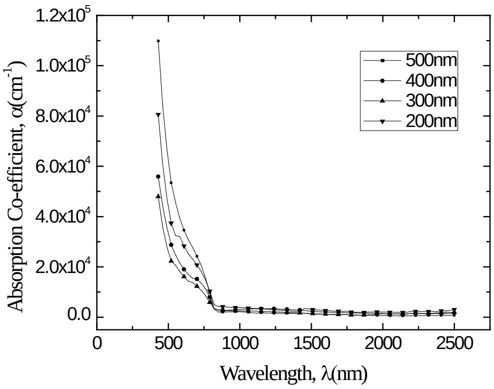


Figure 7. Dependence of absorption coefficient on photon wavelength of CdTe thin films having different thicknesses

It is observed from Figure 7 that absorption co-efficient decreases as the film thickness increases. It can also be seen that in the shorter wavelength the absorption co-efficient exhibits higher values, these values of α (>10^4) means there is a large probability of the allowed direct transition which agrees with (Mott, 1979), then α decreases with increasing λ and remains consistent at higher wavelength.

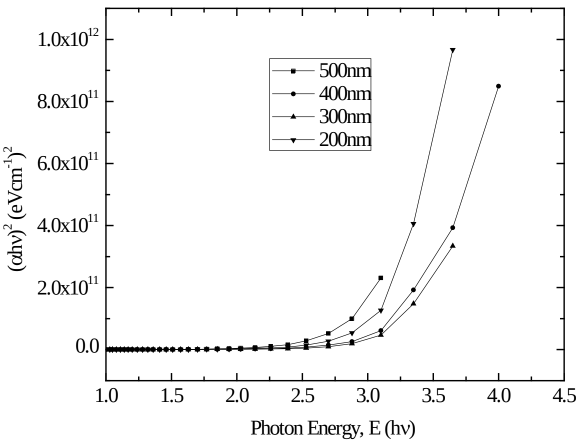


Figure 8.Variation of band gap with photon energy of CdTe thin films having different thicknesses

From Figure 8 the values of band gap energies of the samples of different thicknesses of 200nm, 300nm, 400nm and 500nm is obtained 1.52eV, 1.525eV, 1.53eV and 1.55eV respectively. The optical band gap increases with increase in the film thickness. Higher band gap energy is found when film thickness is 500nm. The increase of E_g with film thickness was attributed to the improvement of the crystallinity of the films (Ikhmayies, 2008). That is the grain size increases with film thickness. This clearly indicates the dependence on thickness of the films.

It can be seen from Figure 9 that refractive indices of the samples first increases, then decreases abruptly. The initial sharp decrease on n with wavelength indicates a rapid change in the absorption energy of the materials, which depends on the surface and volume imperfections. The gradual decrease of refractive index with wavelength implies that the normal dispersion occurred before the absorption edge followed by anomalous dispersion. Low refractive index occurs due to successive internal reflections or due to the trapped photon energy within the grain boundary (Ong et al., 2000).

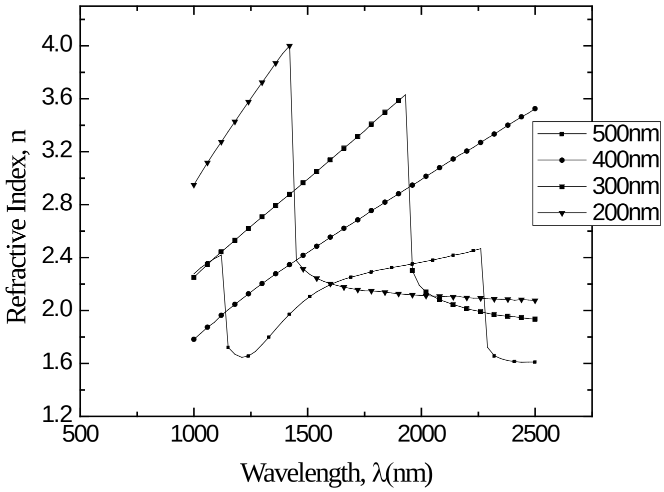
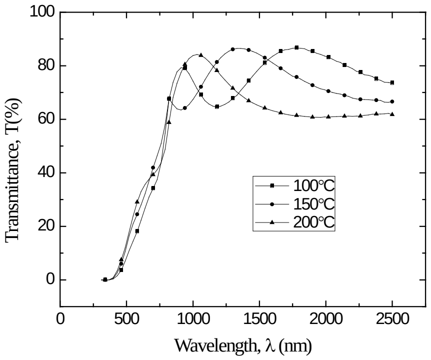


Figure 9. Dependence of refractive index with photon wavelength of CdTe thin films having different thicknesses

From Figure 10 it is seen that transmittance increases smoothly from a very low value to a maximum value in the wavelength region 300 nm to about 1000 nm and becomes low and almost consistent in the wavelength region 1200 nm – 2500 nm. There is some rise and fall in the wavelength region for the films having substrate temperature 100ºC and 150ºC, which may be due to annealing (Popa et al., 2011).The interference pattern in the transmittance manifests a fairly smooth surface and relatively good homogeneity of the film. The transmission of the films in the spectral range of 1000-2500nm is found to be high which is a confirmation of semiconducting properties of the films (Nowak, 1995). The reflectance spectra shows interference pattern with distinct peaks and valleys.



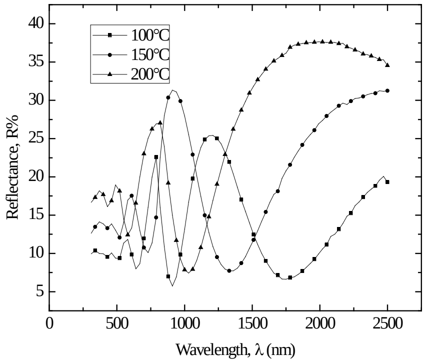


Figure 10. Variation of transmittance and reflectance with wavelength in the range 300 nm-2500 nm for annealed CdTe thin films at different substrate temperature

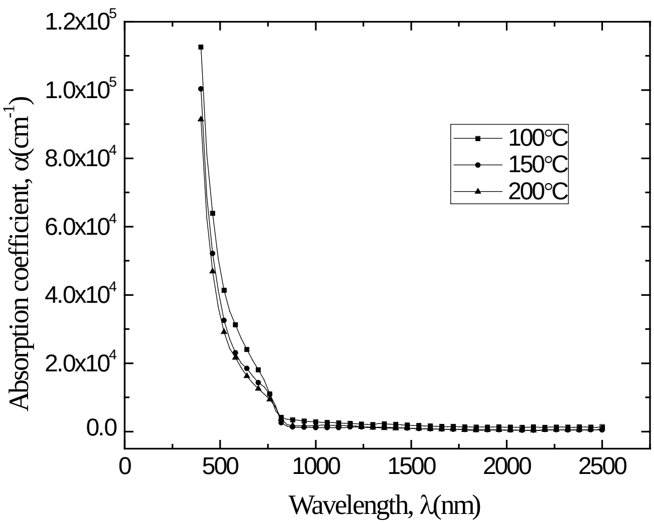


Figure 11. Variation of absorption co-efficient (α) with wavelength in the range 300 nm-2500 nm for annealed CdTe thin films having different substrate temperature

It is observed from Figure 11 that absorption co-efficient (α) exhibits higher values in the shorter wavelength. The value also decreases with the increase of substrate temperature. These values of α ($>10^4$) means there is large probability of the allowed direct transition (Mott, 1979), then α decreases with increasing λ and remains consistent at higher wavelengths. The absorption co-efficient variation is the highest in case of substrate temperature 100ºC. This may be due to the presence of thermal lattice vibrations and imperfections.

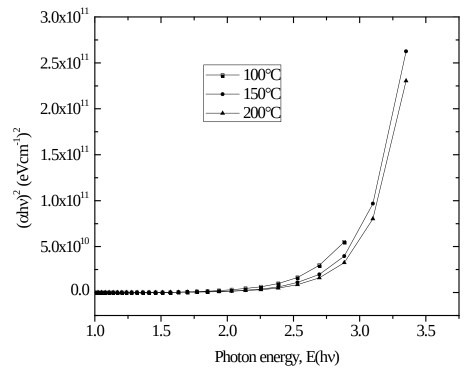


Figure 12: The plot of $(\alpha h\nu)^2$ vs photon energy for CdTe thin films having different substrate temperature

The evaluated band gap energy values are 1.56eV, 1.52 eV and 1.49eV for the films having substrate temperature 100ºC, 150ºC and 200ºc respectively. Increase of annealing temperature continuously decreases the band gap. This is because grain size increases with annealing temperature which decreases the band gap and enhances the optical property of the film. Decrease of band gap with increase in annealing temperature has been reported by (Garadkar et al., 2010).

From Figure 13 it is seen that refractive indices first increases gradually, attaining a maximum peak they decrease abruptly and finally at higher wavelength range they increases. The sharp decrease depends on the surface and volume imperfections. Low refractive index occurs due to successive internal reflections or due to the trapped photon energy within the grain boundary (Ong et al., 2000).

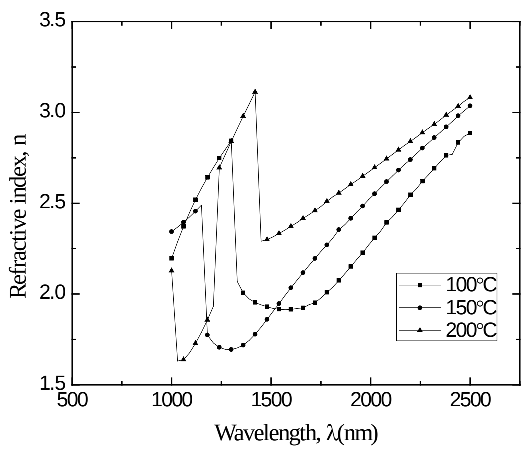


Figure 13. Variation of refractive index with wavelength in the range 300 nm-2500 nm for annealed CdTe thin films having different substrate temperature

Conclusion:

CdTe thin films were deposited on to chemically and ultrasonically cleaned glass substrates at different thicknesses and different substrate temperatures. The transmittance decreases and optical band gap increases with the increase of thickness which is a proof of improvement of crystallinity. The films showed high absorption in the UV region and the optical band gap value of the films decreased with the increase of substrate temperature. The as-deposited films showed amorphous structure in XRD analysis, but the XRD pattern of the annealed CdTe films showed polycrystalline f.c.c. zinc- blende structure with a preferred orientation along the (111) plane. The crystalline quality increased with increasing substrate temperature which was understood by studying the micro structural properties. It can be said that higher substrate temperature is very much suitable for deposition of CdTe thin films to have better optical and structural characteristics.

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