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STUDY OF STRUCTURAL PROPERTIES AND EFFECT OF SUBSTRATE TEMPERATURE ON OPTICAL PROPERTIES OF SPRAY PYROLYTICALLY DEPOSITED $CdZnSe_{2x}Te_{2(1-x)}$ THIN FILMS FOR X=0.75

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ABSTRACT

Spray pyrolysis is a simple, inexpensive and economical method to produce a thin film on large substrate area. Semiconducting thin films of $CdZnSe_{2x}Te_{2(1-x)}$ with composition parameter x=0.75 have been deposited onto preheated glass substrate by varying substrate temperature from 250°C at an interval of 25°C to 325°C. The optimized deposition temperature is around 300°C. From optical transmission and reflection spectra, absorption coefficient(α) was calculated at various wavelengths ranging from 350 nm to 1100 nm and was of the order of 10^4 cm^{-1}. Band gap energy were determined from absorbance measurement in visible range using Tauc theory. It shows that the main transition at the fundamental absorption edge is a direct allowed transition. At the temperature of 300°C, the optical band gap is found to be 2.47 eV. At the temperatures less than or greater than 300°C, the optical band gap goes on increasing. The refractive index(n) and extinction coefficient(k) both decreases as wavelength increases which shows that the optical constants are most suitable for many scientific studies and technological applications such as heat mirrors, transparent electrodes and solar cells. SEM study provide the information regarding the morphology of the material which confirms the formation of nano sized, nanotubes. From the TEM study it is clear that formation of crystals is cubic in nature which is also confirmed from XRD studies. The value of lattice parameter 'a' is 6.1451 A° for $CdZnSe_{2x}Te_{2(1-x)}$ thin films deposited at substrate temperature 300°C with composition parameter 'x=0.75.'

KEYWORDS: $CdZnSe_{2x}Te_{2(1-x)}$, thin films, spray pyrolysis, optical band gap, refractive index, extinction coefficient, SEM, TEM, lattice parameter.

INTRODUCTION

Thin films play a vital role in the development of microelectronics, optical coatings, integrated optics, etc.Due to the limitations of crystalline silicon, in solar cells, other absorber materials have been studied extensively. CdTe,ZnTe,CdZnTe,CdZnSe,CdZnS etc. are the semiconductors with direct band gaps and high absorption coefficients, and consequently they can be used in thin film form. Thin film solar cells have several advantages over crystalline silicon cells.[1] Recently renewed interest in II–VI semiconductor materials is attributed to their wide spread use for the optoelectronic devices as well as solar cells fabrication process.[2-4] Cd and Zn based chalcogenides (S, Se, Te) are technologically important materials due to their direct & rather larg band gap.[5] Chalcogenide alloys are applicable materials in modern optoelectronics& conventional storage devices applications.[6-7] These alloys in binary or multi-component systems based on sulfide, selenide and telluride alloys are very promising materials for various optical and photonic applications in the spectral range 0.6 to 15 mm. They also found important optical applications in the infrared region due to their high optical transparency in IR region.[8]

Several researchers studied properties of II-VI semiconductor films using the variety of methods such as thermal evaporation,[9] vapour phase deposition,[10] r.f.sputtering,[11] spray pyrolysis,[12-15] electrodeposition,[16] chemical deposition.[17]

We have chosen spray pyrolysis due to simple, inexpensive and produce a thin film on large substrate area and it is suitable for scientific studies and for many technological and industrial applications. The advantage of the technique is that just by varying the concentration of precursor and substrate temperature, it is possible to control stoichiometry of the deposits. The present study deals with the study of structural properties and effect of substrate temperature on optical band gap of spray pyrolitically deposited $CdZnSe_{1.5}Te_{0.5}$, thin films.

Nanotubes including II-VI compound semiconductors, such as binary CdTe, ZnO, ZnSe, ZnS and ternary CdZnTe, HgCdTe and HgZnTe are used in many scientific applications including biological labeling,[18] light-emitting devices,[19] and solar cells.[20] Nanotubes of CdZnTe and CdZnSehave been fabricated and studied in the last decade due to their importance in a large

number of potential applications. They have extensively been used in nano electronics, nanodevices, alternative energy sources and security.[21]

2.***Experimental Details***

The aquous solutions of Cadmium chloride($CdCl_2$), of Zinc chloride($ZnCl_2$), Selenium dioxide (SeO_2) and Tellurium tetrachloride($TeCl_4$) each of 0.02 M were prepared using ,in double distilled water. Chemicals used were of AR grade. The solutions are mixed in the proportion 1:1::3:1 by volume. The film shows a tellurium and selenium deficiency.[22,23] if the ratio of proportion of solution was taken as 1:1::1.5:0.5 by volume. Sprayer was mechanically moved to and fro to avoid the formation of droplets on the substrate and insure the instant evaporation from the substrate. The distance between the sprayer nozzle and substrate was kept at 30 cm. The spraying was done in the atmosphere at the spray rate 3.5 ml/min. with a maintaining pressure of 12 Kg/cm^2. The temperature of substrate was maintained at 250°C, 275°C, 300°C, 325°C and was measured by pre-calibrated copper constantan thermocouple. The thicknesses of the films were measured by weighing method on unipan microbalance and were of the order of 0.1703μm at substrate temperature 300°C. It was found that the thin films had whitish colour owing to the presence of more amount of selenium. Optical transmittance and reflectance was taken on UV-1800-Shimandzu Spectrophotometer in the wavelength range 350 nm to 1100 nm. Analytical method of indexing the X-ray diffraction pattern was used. The copper K_α (λ=1.5418A^o) radiation was used for recording the diffraction pattern. In spray pyrolysis technique aqueous solutions of required material are mixed in proper proportion and then sprayed onto preheated substrate. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater and temperature controller as shown in **fig.1.**

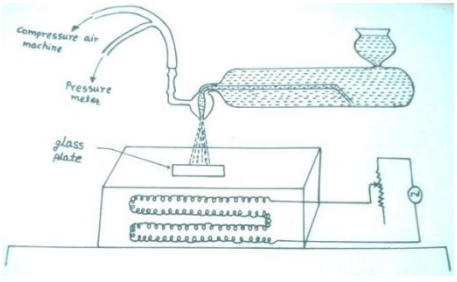

Fig. 1: Experimental set- up for the preparation of the films.

When droplets of sprayed solution reach the hot substrate, owing to pyrolytic decomposition of the solution, well adhered and good quality films are formed on the surface of the

substrate. It was observed that the thickness of the as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films increases with temperature, attains the maximum value at 300°C.

3. RESULTS AND DISCUSSION

In spray pyrolysis technique aqueous solutions of required material are mixed in proper proportion and then sprayed onto preheated substrate.When droplets of sprayed solution reach the hot substrate, owing to pyrolytic decomposition of the solution, well adhered and good quality films are formed on the surface of the substrate.

3.1 Thickness variation

The thickness of $CdZnSe_{1.5}Te_{0.5}$ thin films deposited at various substrate temperatures was measured and the graph was plotted between the thickness of the films and substrate temperature as shown in **fig.2**

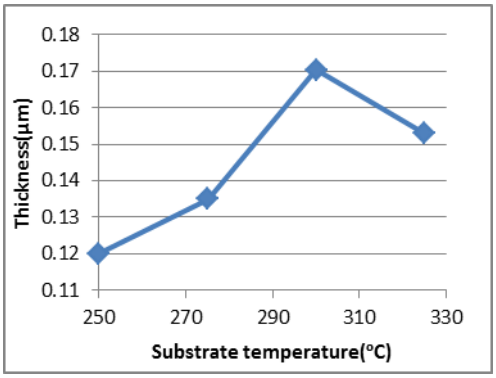

Figure 2: Variation of film thickness of $CdZnSe_{1.5}Te_{0.5}$ thin films with substrate temperature.

It was observed from **fig.2** that the thickness of the as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films increases with substrate temperature, attains the maximum value i.e. 0.1703 µm at 300°C and then decreases with further increase in substrate temperature. At low temperatures (<300°C), the temperature may not be sufficient to decompose the sprayed droplets from the solution and hence the deposits results into low thickness. At substrate temperature 300°C, deposition occurs at optimum rate resulting in terminal thickness of 0.1703µm. At higher substrate temperatures (>300°C) film thickness decreases due to higher evaporation rate of initial ingredients.[24]

3.2 Optical study

The optical transmission spectra of, $CdZnSe_{1.5}Te_{0.5}$ thin films deposited at different substrate temperature was taken on UV-1800-Shimandzu spectrophotometer in the wavelength range 350 nm to1100 nm.**Fig.2**.Shows the variation of transmission versus wavelength of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films at different substrate temperatures.

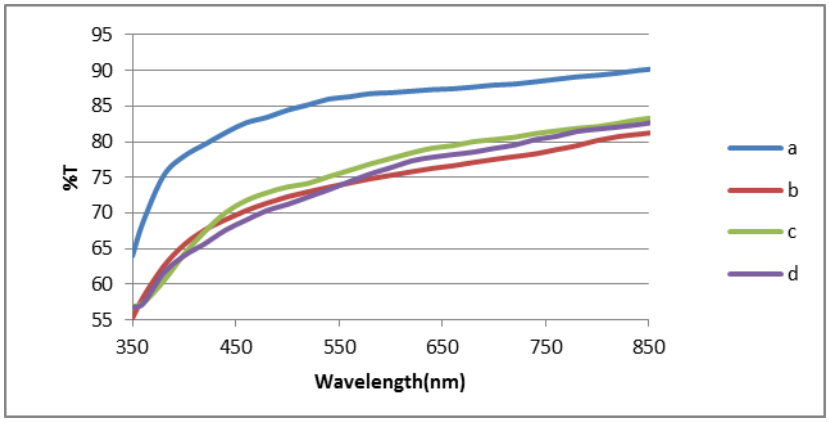

Fig. 3: Transmission versus wavelength of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films at different substrate temperatures. a.250°C, b.275°C, c.300°C, d. 325°C.

It was observed that onset of decrease of transmission gives the optical absorption edge. The optical coefficients were calculated for each wavelength given by relation,

$\alpha = (1/t)*[\ln(1/T)]$ ..... (1)

Where, t- thickness of the films, T- transmittance of the film.

Reflectance can be calculated using above values of %transmittance and graph is plotted between reflectance(R) and wavelength in nm.

Fig. 4 represents the reflectance spectra of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films at different Substrate temperatures.

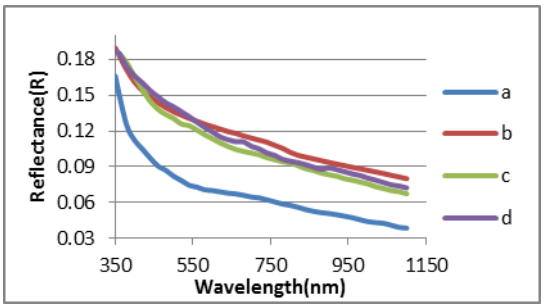

Fig. 4: Reflectance spectra of $CdZnSe_{1.5}Te_{0.5}$ thin films at Substrate temperatures a.250°C,b.275°C,c.300°C,d.325°C

The absorption coefficient "α" is related to the optical transmission "T" and reflectance "R" by the relation,[25]

$T = (1-R)^2\exp(-\alpha t)/1-R^2\exp(-2\alpha t)$ ……(2)

Equation (2) is valid in the vicinity of fundamental absorption edge when $R^2 \exp(-2\alpha t) \ll 1$ and it is used to calculate the absorption coefficient "α".

From **fig. 4** it was observed that as the wavelength increases there is sharp decrease in the reflectance. The onset of decrease of reflectance gives the approximate value of band gap.[26]

Knowing the approximate region of band gap from reflectance curve, α is calculated by using equation (2), from the knowledge of T, R and t. An analysis of the spectrum showed that the absorption at the fundamental absorption edge can be described by the Taue relation [27],

$\alpha = (A/hv)\,(hv-Eg)^n$ …… (3)

Where hv –photon energy, A-constant which is different for different transitions, n = 1/2 for direct allowed transition and

n = 2 for indirect allowed transition.

To calculate the exact value of band gap, a graph is plotted between $(\alpha hv)^2$ versus hv of as deposited $CdZnSe_{1.5}Te_{0.5}$thin film at different substrate temperatures as shown in **fig.5.** The linearity of each graph showed the direct allowed transition, indicating the semiconducting nature of the films. The linear portion of the plot was extrapolated to meet on hv axis yield, the value of band gap energy.

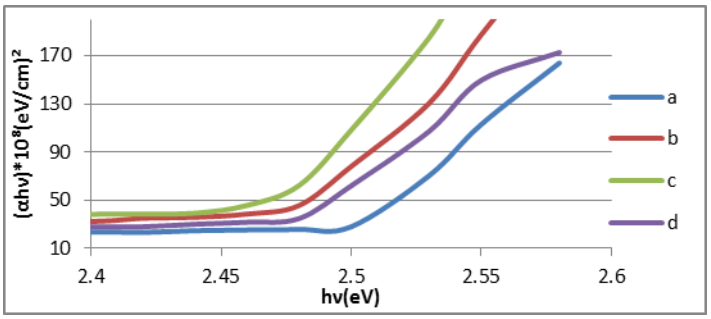

Figure 5: Variation of(αhv)² in (eV/cm)² versus hv in eV for as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films at substrate temperatures a)250°C,b) 275°C,c)300°C,d)325°C.

The variation of optical band gap energies with substrate temperature for as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films at different substrate temperatures are shown in **Fig. 6.**

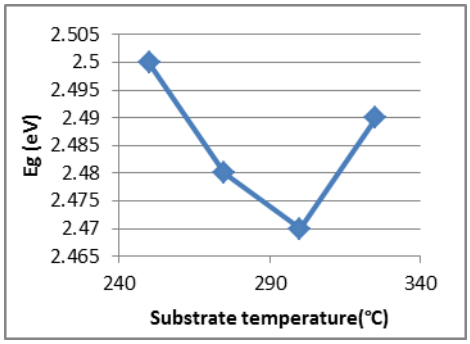

Figure 6: Variation of optical band gap energy (Eg) with substrate temperature of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films.

It is observed that optical band gaps of $CdZnSe_{1.5}Te_{0.5}$ thin films decreases from 2.50eV to 2.47eV as substrate temperature increases from 250°C to 300°C which is due to increase in grain size with increase in substrate temperature and beyond 300°C, the optical band gap again increases with increase in substrate temperature and attains the value 2.49eV at substrate temperature of 325^0C as shown in fig.4. These results are found to be in good agreement with that obtained by Umeshkumar *et al*. and Murali *et al*.[28-29]

Extinction coefficient and refractive index

The extinction coefficient ‘ k’ is related to absorption coefficient ‘α’ by the relation.[30-32]

$K = \alpha \lambda / 4 \pi$…… (3)

And Refractive index ‘n’for the $CdZnSe_{0.5}Te_{1.5}$ thin films at different substrate temperatures are calculated using the relation,

$n = (1 + \sqrt{R})/(1 - \sqrt{R})$……. (4)

where ‘α’ is the absorption coefficient, ‘λ’ the wavelength and ‘R’ the reflectance. The calculated values of extinction coefficient (k) and refractive index (n) at the wavelengths in the range 350 nm -1100nm are plotted as a function of wavelength as shown in figs.7 and 8 respectively. Figures shows that both k and n decreases with increasing wavelength but at higher wavelengths remains approximately constant. The same results have been also reported byPankove et.al.[33]

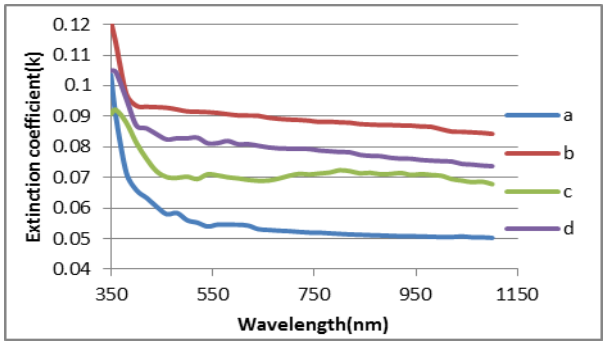

Fig. 7: Variation of refractive index as a function of wavelength for $CdZnSe_{1.5}Te_{0.5}$ thin films at Substrate temperatures a.250°C,b.275°C,c.300°C,d.325°C.

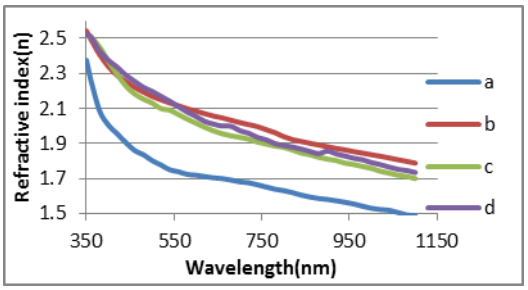

Fig. 8: Variation of extinction coefficient as a function of wavelength for $CdZnSe_{1.5}Te_{0.5}$ thin film at substrate temperatures. a.250°C,b.275°C,c.300°C,d.325°C.

3.3. SEM and TEM study

The surface morphologies, microstructure of the films, and compositions of deposited films can be investigated by SEM and TEM. TEM is a high resolution tool, able to analyze a t high resolution at nano level. It is used to measure nano particles size, measurement of grain size, crystallite size, atomic arrangement in material. Figs.9 & 10 shows the SEM and TEM images of as deposited $CdZnSe_{2x}Te_{2(1-x)}$ thin films with composition parameter x= 0.75.respectively.

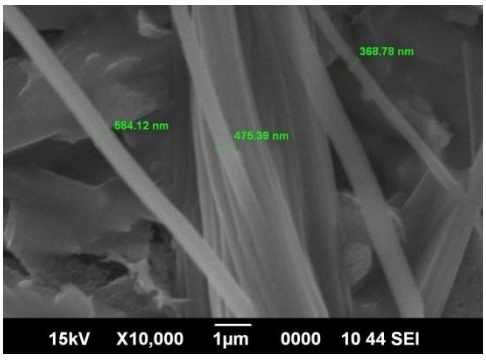

Fig. 9: SEM image if as deposited$CdZnSe_{1.5}Te_{0.5}$ thin film at the substrate temperature of 300^0C.

From the SEM image it is clear that the films shows the presence of nanosized tubes. The size of nano tubes of the films was about 368 nm. This also indicates that the crystallanity of the film. From the TEM study it is clear that formation of crystals is cubic in nature which is also confirmed from XRD studies.

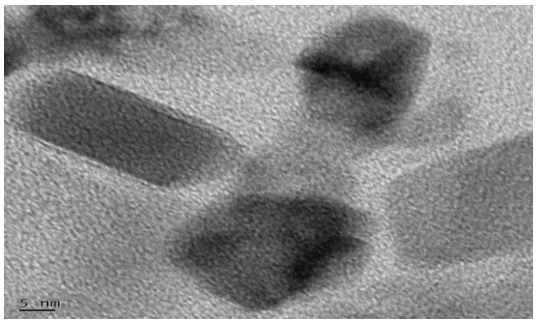

Fig. 10: TEM image if as deposited$CdZnSe_{1.5}Te_{0.5}$ thin film at the substrate temperature of 300^0C.

3.4. XRD STUDY

Phase analysis of deposited thin films is carried out by X-ray diffraction method using C_uK_α radiation (λ=1.5406A.U.) with 2θ=20° to 80°. XRD study of all samples were taken at room temperature. X-ray diffraction (XRD) spectra of as deposited $CdZnSe_{2x}Te_{2(1-x)}$ thin films deposited on glass substrate at the substrate temperature 300°C for the composition parameter x= 0.75, is shown in **Fig9**.The XRD pattern shows number of peaks indicating that the films are polycrystalline in nature. The analysis of spectrum indicated that the ternary films are having throughout cubic structure It is observed that two main peaks corresponds to (111) and (220) planes. The experimental d-values for $CdZnSe_{0.5}Te_{1.5}$ thin films are calculated using Bragg's relation, by taking θ values from the peaks of XRD pattern; these d-values are compared with the results of other workers.[34-40]

$$2d_{hkl} \sin\theta = n\lambda, \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

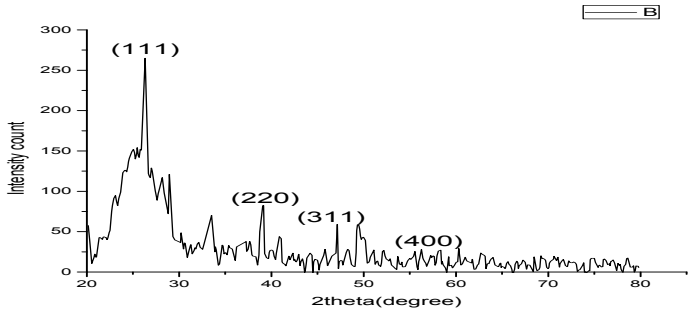

Fig. 9: XRD of as deposited $CdZnSe_{2x}Te_{2(1-x)}$ thin film with x=0.75.

The films shows the preferred orientation along (111) direction. The value of lattice parameter 'a' is found to be 6.1451 A° for for $CdZnSe_{2x}Te_{2(1-x)}$ thin films deposited at substrate temperature 300°C with composition parameter x=0.75 Hankare et. al.[41] prepared Cd_{1-x} Zn_xSe thin films by chemical route method and reported that the films have cubic structure with lattice parameter varying from 6.07 A.U. to 5.66A.U. as composition parameter changes from 0 to 1.

Ibrahim[42] also studied the physical properties of vacuum deposited $Cd_{0.5}Zn_{0.5}Te$ ternary solid solutions also reported the cubic phases with lattice parameter a=0.629 nm. The results are in good agreement with the results of Nevesha et.al.[43] who prepared $Zn_xCd_{1-}xSe$ thin films with various compositions by thermal vacuum evaporation technique and reported lattice parameter a to vary from 0.5676 nm to 0.5875 nm for x=1 to 0.39.

CONCLUSION

Spray pyrolysis is a simple and inexpensive method to produce a thin film. At substrate temperature 300°C, deposition occurs at optimum rate resulting in terminal thickness of 0.17030 μm. At low temperatures (<300°C), the temperature may not be sufficient to decompose the sprayed droplets from the solution and hence the deposits results into low thickness. At higher substrate temperatures (>300°C) film thickness decreases due to higher evaporation rate of initial ingradients. Optical band gap of $CdZnSe_{1.5}Te_{0.5}$ thin film was of 2.47 eV at substrate temperature 300°C, which was calculated from $(\alpha h\nu)^2$ versus (hv) plot. The linearity of the plot shows the direct allowed transition. It is observed that optical band gaps of $CdZnSe_{0.5}Te_{1.5}$ decreases from 2.5eV to 2.47eV as substrate temperature increases from 250°C to 300°C which is due to increase in grain size with increase in substrate temperature and beyond 300°C, the optical band gap again increases with increase in substrate temperature and attains the value 2.49eV at substrate temperature of 325^0C. SEM study provide the information regarding the morphology of the material which confirms the formation of nano sized, nanotubes. From the TEM study it is clear that formation of crystals is cubic in nature which is also confirmed from XRD studies. The XRD pattern shows number of peaks indicating that the films are polycrystalline in nature. The analysis of spectrum indicated that the ternary films are having throughout cubic structure(sphalerite). The value of lattice parameter 'a' is 6.1451 A° for $CdZnSe_{2x}Te_{2(1-x)}$ thin films deposited at substrate temperature 300°C with composition parameter 'x=0.75.'

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