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STUDY OF OPTICAL AND ELECTRICAL 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. Thin films of $CdZnSe_{2x}Te_{2(1-x)}$ for composition parameter 'x'=0.75 at a substrate temperature of 300^0Care prepared by spray pyrolysis technique. From the optical transmission and reflection spectra, absorption coefficient (α) was calculated and was of the order of 10^4 cm^{-1}..Band gap energy were determined from absorbance measurement in visible range as 2.47 eV using Tauc theory. It shows that the main transition at the fundamental absorption edge is a direct allowed transition. 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. The activation energy increases at higher temperature may be due to attributed to the increase of band gap. Hence the grain size of the films increases. This effect reduces the grain boundry effect. The XRD pattern shows number of peaks indicating that the films are poly crystalline in nature. The analysis of spectrum indicated that the ternary films are having throughout cubic structure. The value of lattice parameter ' a ' is 6.1451 A°.

KEYWORDS: $CdZnSe_{2x}Te_{2(1-x)}$ thin films, spray pyrolysis ,optical and electrical properties, lattice parameter.

1. INTRODUCTION

Binary semiconductor compounds of II-VI group and their ternary alloys crystallizes in chalcopyrite structures. These compounds were of great importance due to their applications in opto-electronic devices. The properties of these compounds have been investigated for crystalline form and also thin film form. There are several binary and ternary semiconductors, such as GaAs, GaP, $CuInSe_{2,}$ CdZnTe, CdZnSe, etc. which have band gaps in the required range(suitable for photovoltaic conversion). It was known from the Vegard's law for solid solutions, that the lattice constant for a solid solution of binary or ternary semiconductors varies linearly with composition and the band gap is quadratic function of composition. Hence in case of solid solutions of two or more ternaries, the band gaps and lattice constants can be varied independently by a mere choice of proportions and this makes them ideal for use in solar cells. In order to have many semiconductors of the same lattice constants but different band gaps,many workers.[1-4] have studied solid solutions of ternary sulphides,selenides, and tellurides of the type, $A^{II}{}_{X}B^{II}{}_{1-X}C^{VI}{}_{2Y}D^{VI}{}_{2(1-Y)}$ for various values of composition parameters.

Thin films are crystalline or non-crystalline materials developed two dimensionally on a substrates surface by physical or chemical methods. They play vital role in nearly all electronic and optical devices. They have been used as electroplated films for decoration and protection.[5-6]

In order to achieve higher efficiencies attempts have been made to make tandem solar cells using ternary, III-V and II-VI semiconducting alloys whose theoretical efficiencies are high (86%),[7] Chander et.al.[8] prepared CdZnTe thin films by electron beam vacuum evaporation method on glass and ITO substrates followed by thermal treatment at 150 °C, 300 °C and 450 °C. They have shown that from XRD study it is revealed that the films have cubic structure and polycrystalline nature along with predominant reflection(111) and structural parameters found to be affected by substrates. Muraliet. al.[9]

deposited CdxZn1xSe (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) thin films by pulse plating technique and have shown that thin films, grown on Titanium and conducting glass substrates have Cubic structure with (1 1 1) phase; XRD peaks shifted toward CdSe side with increased CdSe content in mixture; band gap varied from 1.72 to 2.70 eV with variation of x; surface roughness became higher due to larger grain size. Rekha G.Solanki.[10] also prepared CdZnTe thin films by electro deposition technique and investigated structural, compositional and optical properties of these thin films. She has shown that thin films of CdZnTe have cubic structure with (111) orientation. Sivaramanand Bensalah et. al.[11-12] have stated that the lattice constant for alloy $Cd_{1-x}Zn_xTe$ thin films varies between 6.495 $A^0$to 6.287 A^0 for x=0.05 to 0.5.

Very less work has been found on CdZnSe2x Te2(1-X) thin films. So our aim is to study optical, electrical and structural properties of CdZnSe2xTe2 (1-x) thin films with x=0.75 prepared by spray pyrolysis technique.

2. Experimental Details

The aqueous 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 one in the proportion 1:1:3:1 by volume. The film shows a selenium and tellurium deficiency.[13,14] 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 300^0C and was measured by pre-calibrated copper constantan thermocouple. The thicknesses of the films were measured by weighing method on unipan microbalance and was of the order of 0.1703 µm. 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. Electrical conductivity was measured by using four probe methods.[15] Analytical method of indexing the X-ray diffraction pattern was used. The copper Kα (λ=1.5418A0) radiation was used for recording the diffraction pattern.

3. Optical Study

3.1 Transmission spectra

The optical transmittance (T) of the film was recorded at room temperature using UV-1800-Shimandzu spectrophotometer. Variation of transmittance with wavelength of the incident beam was recorded for the range of wavelength 350 nm to 1100 nm. And then the graph is plotted between % transmittance and wavelengths in nm. .Fig.1. Shows the transmission versus wavelength of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films.

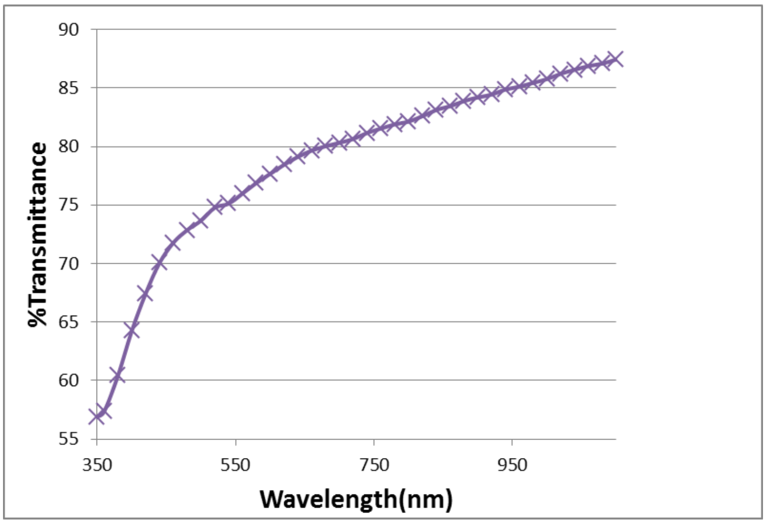

Fig. 1: Transmission versus wavelength of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films.

It was observed that the transmittance started decreasing after a particular wavelength, depending upon composition parameter (x) and remains constant for higher wavelengths. It was also observed that onset of decrease of transmission gives the optical absorption edge. The optical coefficients were calculated for each wavelength given by relation,[16]

$\alpha = (1/t)*\ln(1/T)$ …………..(1)

Where, "t" thickness of the film, and "T" is the transmittance.

3.2 Reflectance spectra

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

Fig. 2 represents the reflectance spectra of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films.

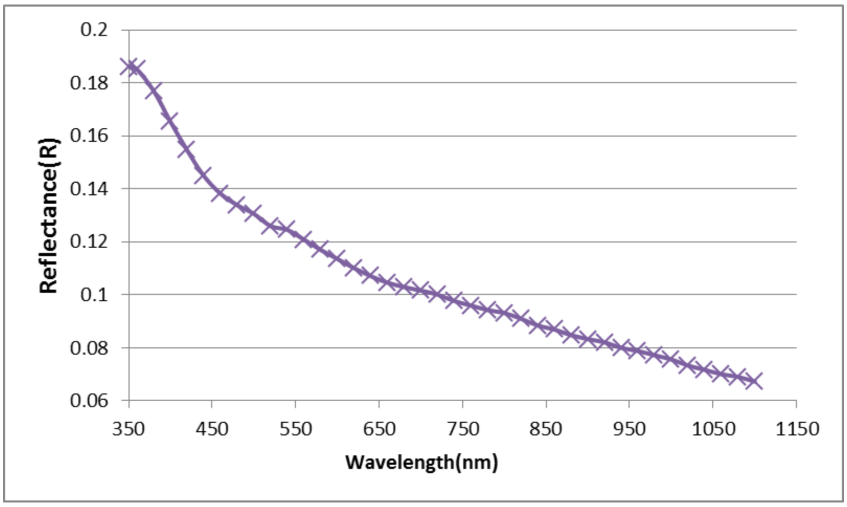

Fig. 2: Reflectance spectra of as deposited $CdZnSe_{1.5}Te_{0.5}$thin films.

The absorption coefficient "α" is related to the optical transmission "T" and reflectance "R" by the relation.[17]

$T = (1-R)^2 \exp(-\alpha t)/1-R^2 \exp(-2\alpha t)$ ………………(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. 2** 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.[18]

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.[19]

$\alpha = (A/h\nu) \times (h\nu-E_g)^n$ ………………………(3)

Where hν –photon energy, A-constant which is different for different transitions, n = 1/2 for direct band gap transition and n = 2 for indirect band gap transition.

To calculate the exact value of band gap, we plotted the graph between $(\alpha h\nu)^2$ versus hν of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin film of as shown in fig.3.

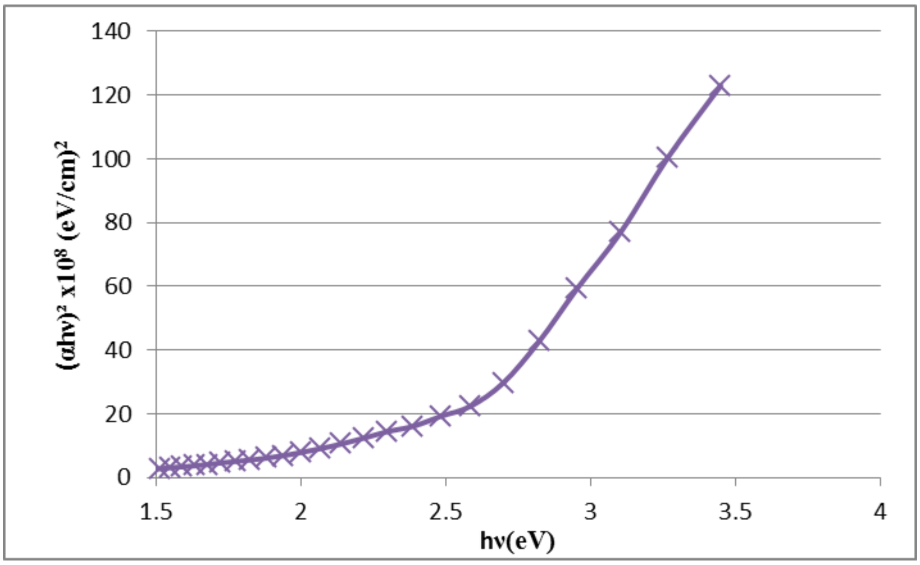

Fig. 3: Graph between $(\alpha h\nu)^2$ versus hν of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin film.

The linearity of the 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 which was found to be 2.47 eV.

These results are found to be in good agreement with that obtained by Umeshkumar *et al*. and Murali *et al*.[20-21]

The optical transmission spectrum of the films under study shows that the transmission spectra mechanism is due to the direct allowed transition.[22]

The linear plot of $(\alpha h\nu)^2$ versus hv over wide range of photon energies shows thin film $CdZnSe_{1.5}Te_{0.5}$ has a direct allowed transition.

3.3 Optical constants (n and k)

The refractive index was obtained from the relation,[23]

$$n = [(1+R)/(1-R)] + [(4R/(1-R)^2)-k^2]^{1/2} \text{ ……….(4)}$$

Where k –is the extinction coefficient which is related to the absorption coefficient α and wavelength λ as,

$$K=\alpha\lambda/4\pi \text{ …………………………..(5)}$$

The value of refractive index (n) and extinction coefficient (k) were calculated using relations (4) and (5). The calculated values of refractive index (n) and extinction coefficient (k) at the wavelengths in the range 350 nm -1100nm are plotted as a function of wavelength in nm as shown in figs.4 and 5 respectively.

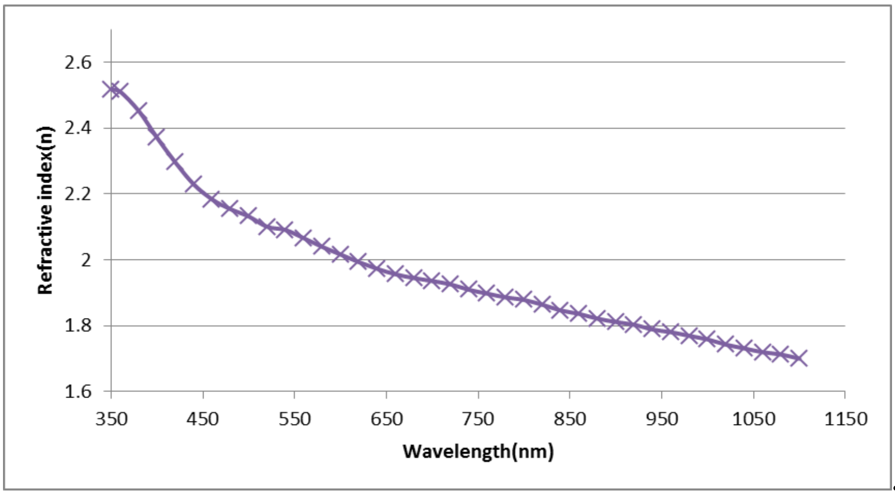

Fig. 4: Graph of refractive index (n) versus wavelength (λ).

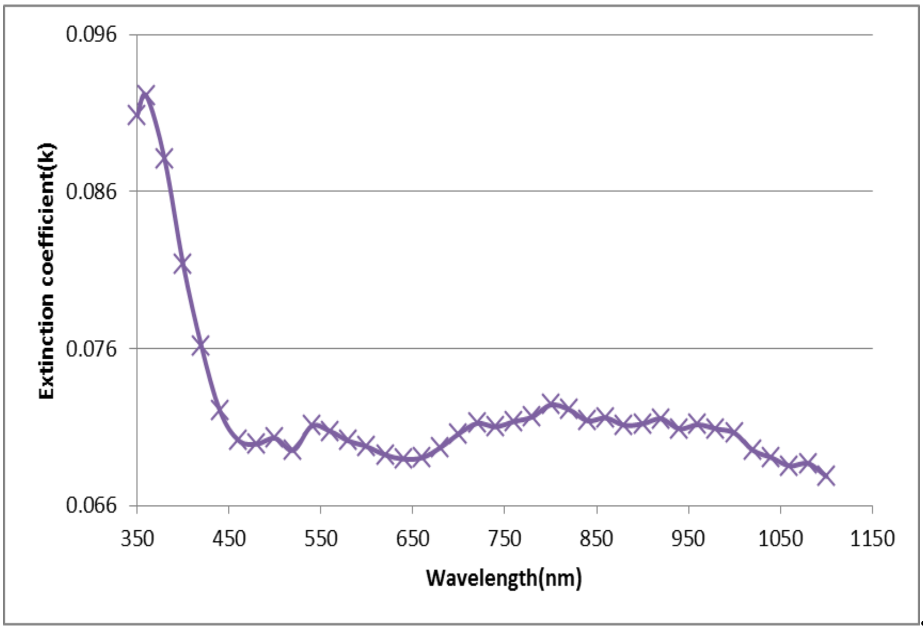

Fig. 5: Graph of extinction coefficient (k) versus wavelength (λ).

Figures 4 and 5 shows that both k and n decreases with increasing wavelength but at higher wavelengths remains approximately constant. Our calculated values of n and k are well agree with the Saliha Ilican et.al.[23] for spray pyrolitically deposited some ternary semiconducting $CdZnS_{(1-x)}Se_{2x}$ thin films and other workers.[24-25] also for ternary group of semiconducting materials.. Quijada and Ross Henry.[26] reported the refractive index for CdZnTe material to be 2.6.This shows that optical constants are most suitable for many scientific studies and technological applications, such as sensors, heat mirrors, solar cells transparent electrodes and piezoelectric devices.

3.4 Real and imaginary parts of dielectric constant

The real (ε_1) and imaginary(ε_2) parts of dielectric constant are given by the relations.[27]

$\varepsilon_1 = n^2 - k^2$.............................. (6)

$\varepsilon_2 = 2nk$ ………………………………(7)

We also calculated real and imaginary parts (ε_1 and ε_2) of dielectric constants at several wavelengths ranging from 350nm-1100nm as it is directly related to the density of states within the energy gaps of the films. Fig 6 and 7 shows the variation of real and imaginary parts of dielectric constant for $CdZnSe_{1.5}Te_{0.5}$ thin films at substrate temperature 300°C.

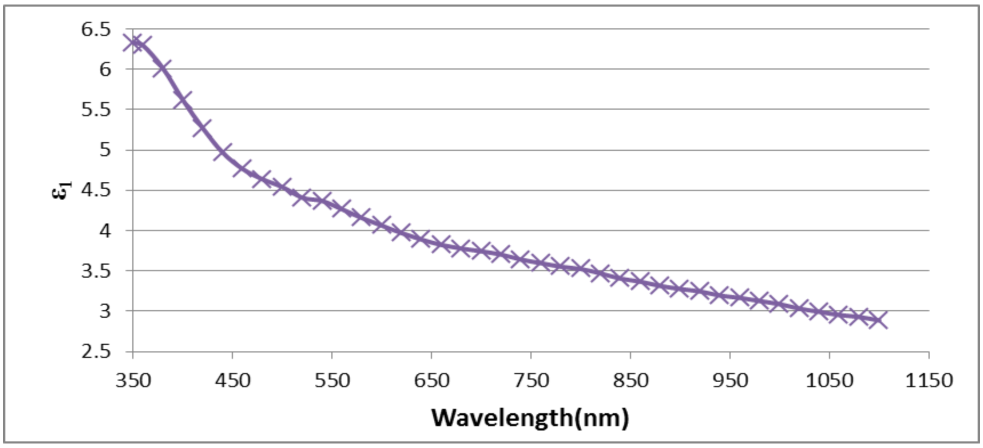

Fig. 6: Variation of real part of dielectric constant for $CdZnSe_{1.5}Te_{0.5}$ thin films at substrate temperatures 300°C.

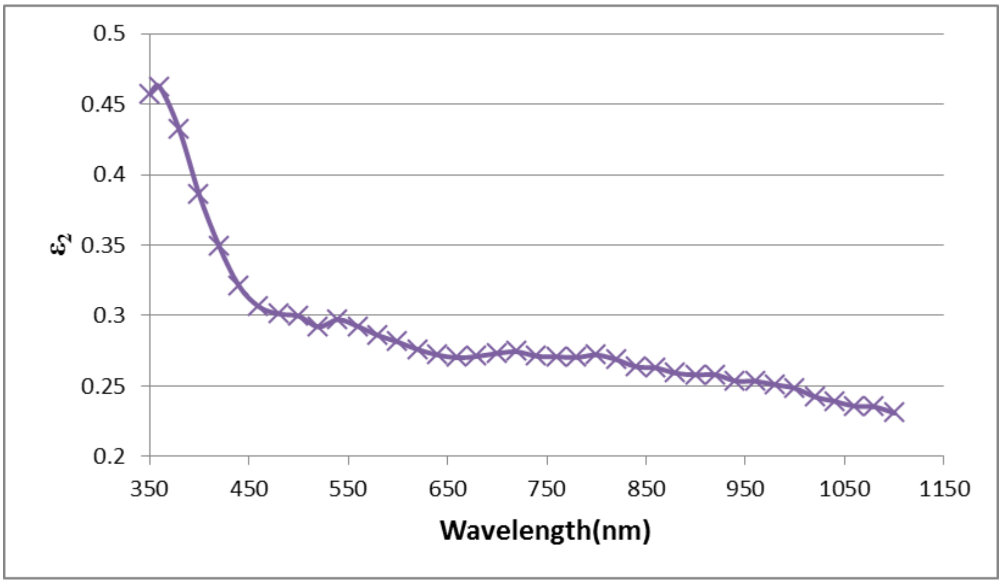

Fig. 7: Variation of imaginary part of dielectric constant for $CdZnSe_{1.5}Te_{0.5}$ thin film at substrate temperatures 300°C.

It is observed from the graph that both real and imaginary parts of dielectric constant decreases with increasing wavelength. The nature of curves for both ε_1 and ε_2 are found to be same, the only difference is that the values of real parts are higher than those of imaginary parts.

4. ELECTRICAL PROPERTIES

The temperature dependence of conductivity was studied in the temperature range 300 K to 573 K. The resistivity were measured by four- probe method [28] given by the relation,

$\rho = [(V/I) * (2\pi S)] / [G_7(t/S)]$…………… …(8)

And

$G_7(t/S) = [2S/t] * \ln(2)$………………………. (9)

Where S-the distance between the probes, t- the thickness of the film, I- the current generated from the constant current source between the inner probes, V- the voltage developed between the outer probes. Fig.8 Shows the Arrhenius plot of conductivity versus inverse temperature of as deposited $CdZnSe_{1.5}Te_{0.5}$ thin films.

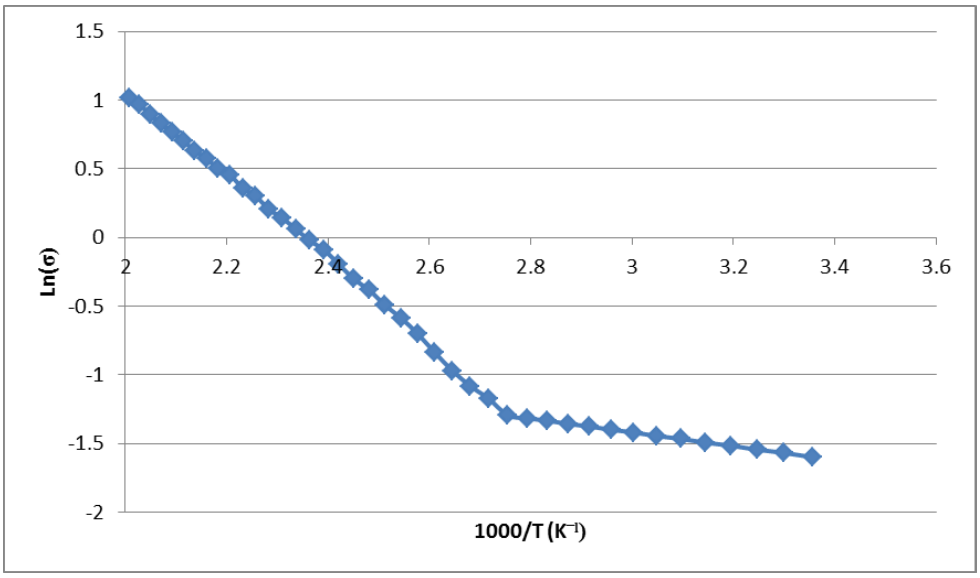

Fig. 8: Arrhenius plot of conductivity versus inverse temperature of as deposited $CdZnSe_{0.5}Te_{1.5}$ thin film.

The activation energy was calculated from Arrhenius plot using the relation.[29-31]

$\sigma = \sigma_0 \exp\{-E_a/kT\}$……………..(10)

Where ' σ_0 ' is the pre-exponential conductivity, ' E_a ' is the activation energy and 'k' Boltzmann constant and 'T ' is the absolute temperature.

The plot shows two segments i.e. two conduction regions. Region I(lower part of graph) between the temperature 298 K to 363 K and region II(upper part of graph) between the temperatures 364K to 498 K. These two segments correspond to two values of activation energy. The temperature dependence is weak at lower temperature which confirms the low activation energy. The slope increases at high temperature which reveals the possibility of conduction due to the extended state. This indicates semiconducting nature of the films. The polycrystalline $CdZnSe_{1.5}Te_{0.5}$ thin films of do have the electrical and optical properties similar to those of single crystal. At the same time, the deposition conditions have been found to have significant effect on the electrical properties.[32-33]

The activation energy increases at higher temperature may be due to attributed to the increase of band gap. Hence the grain size of the film increases. This effect reduces the grain boundary effect .Thus it is evident that $CdZnSe_{0.5}Te_{1.5}$ thin films the possibility of shallow trapping state due to the interstitials of Cd/Zn or telluride vacancies are expected to dominate the extrinsic conductivity near the room temperature. Whereas at higher temperature deep traps states influence are probable appears. Similar results are also reported by the other workers.[34-35] for same group of ternary compounds.

5. 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 Fig8..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 $CdZnSe_{1.5}Te_0$ thin films are calculated using Bragg's relation,

$2d_{hkl}\sin\theta = n\lambda$,………………..(11)

By taking θ values from the peaks of XRD pattern; these d-values are compared with theresults of other workers.[36-42]

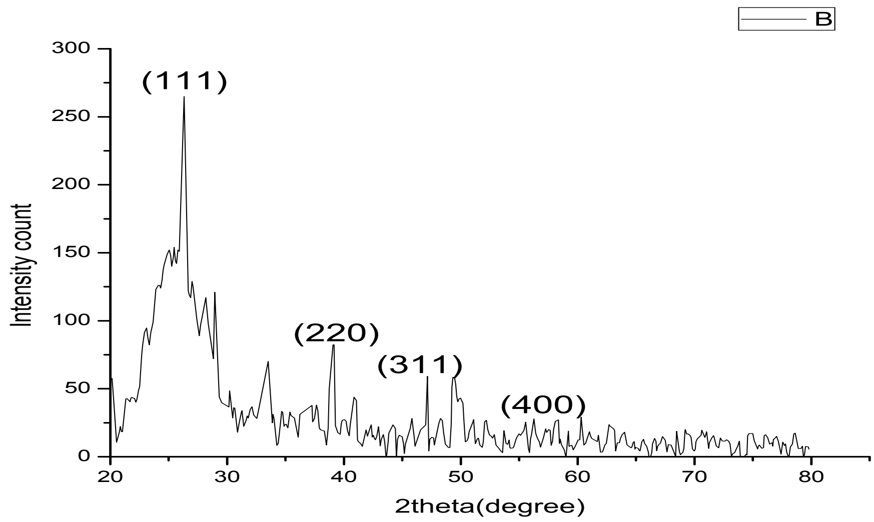

Fig. 9: XRD of as deposited $CdZnSe_{2x}Te_{2(1-x)}$ thin film with x=0.75.

The value of lattice parameter ʽ a ʼ 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 ʽx=0.75ʼ.

CONCLUSION

Spray pyrolysis is a simple and inexpensive method to produce a thin film. Optical band gap of $CdZnSe_{1.5}Te_{0.5}$ thin film was of 2.47 eV .which was calculated from $(\alpha hv)^2$ versus (hv) plot. The linearity of the plot shows the direct allowed transition. Arrhenius plot shows the two segments i.e. two conduction regions. Higher the conductivity value at low temperature is an evidence of the adsorption-distortion phenomenon The XRD pattern shows number of peaks indicating that the films are polycrystalline in nature. The analysis of spectrum indicated that the $CdZnSe_{1.5}Te_{0.5}$ thin films are having throughout cubic structure. The value of lattice parameter ʽ a ʼ is 6.1451 A° for $CdZnSe_{2x}Te_{2(1-x)}$ thin films deposited at substrate temperature 300°C with composition parameter ʽx=0.75.ʼ

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