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Optical and Electrical Properties of spray pyrolitically deposited $CdZnTe_2$ thin films

S.A. Gaikwad[1], Y.D. Tembhurkar[2] and C.M. Dudhe[3]

[1]Department of Physics, Guru Nanak Science College, Ballarpur-442701, M.S., India.
[2]Department of Physics, S.K.Porwal College, Kamptee-441002, Maharashtra, India.
[3]Department of Physics, Institute of Science, Nagpur, Maharashtra, India.
[1]Corrosponding Author

Abstract

Spray pyrolysis is a simple, inexpensive and economical method to produce a thin film on large substrate area. 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 2.04 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. Type of conductivity tested by hot-probe method was of n-type semiconductor. 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 .$CdZnTe_2$ 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. But at higher temperature deep traps states influences are probably appears. SEM study provides the information regarding the morphology of the material which confirms the formation of nano sized, nanotubes.

Keywords:- $CdZnTe_2$ thin films, spray pyrolysis ,optical and electrical properties.

1. INTRODUCTION

In the recent years much more attention has been paid in semiconducting II-VI compounds because of their optoelectronic properties and their possible applications in switching and memory devices, photodiodes and solar cells. The ternary compounds including Cadmium zinc telluride have attracted much more attention in the field of solar cells due to their interesting properties of band gap. For example, the band gap values of $CdZnTe_2$ ternary semiconductor was of 2.04 eV. The evaluation of any material for application is complete and meaningful only when its structure and composition are precisely known. The reliability factor, which is the most important one for device application, can only be assured through a systematic and detailed study of the structural, electrical and zinc ditelluride is unit among II-VI series of semiconducting compounds as it shows both n- and p-type conductivity. The growth of ternary compound is a opens up the possibility of their application for novel optoelectronic devices such as light emitting diodes, photo electrodes, blue green lasers etc.[1] the visible region of electromagnetic radiation [2]. The research of the optical and electrical properties of CdZnTe system forms a basis of the active region of laser and LED. Most of the work has been done on $Cd_{1-x}Zn_xSe$ system. To the best of our knowledge, very less work has been reported on tellurium rich $CdZnTe_2$ polycrystalline material. Thus the present study is aimed at investing the optical and electrical properties of $CdZnTe_2$ in the form of thin films.

Several researchers studied properties in the II-VI semiconductor films using the variety of methods such as flash evaporation, chemical vapour deposition, r.f. sputtering, chemical bath deposition, electrodeposition [3-5] and spray pyrolysis [6-7].

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.

2. EXPERIMENTAL DETAILS:-

Aqueous solutions of cadmium chloride, zinc chloride and Tellurium tetrachloride of 0.02 M of each were prepared in double distilled water. Chemicals used were of AR grade. The solutions are mixed in one in the proportion 1:1:3.2 by volume. The film shows a tellurium deficiency [8-9] if the ratio of proportion of solution was taken as 1:1:2 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 ^{0}C and was measured by pre-calibrated copper constantan thermocouple. The thicknesses of the films were measured by weighing method on unipan microbalance and Michelson interferometer. The thicknesses of the films found by both the methods were found to be approximately same. The difference was of the order of 0.003 μm. 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 [10].

3. OPTICAL STUDY

3.1 Transmission spectra

Fig.1. Shows the transmission versus wavelength of as deposited $CdZnTe_2$ thin films.

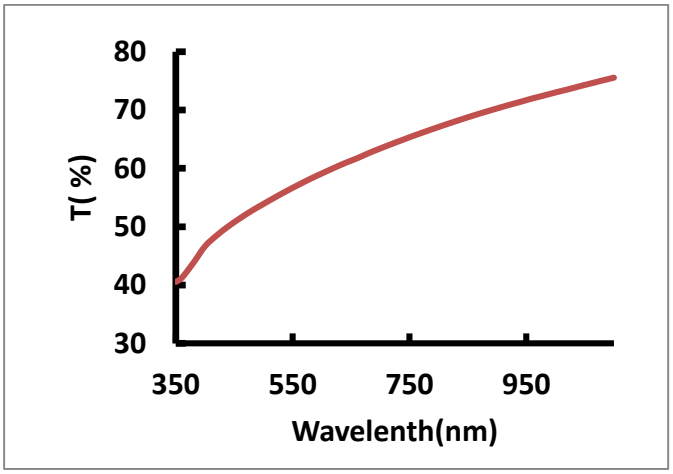

Fig.1 Transmission versus wavelength of as deposited $CdZnTe_2$ thin films

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,

$$\alpha = 1/t \ln(I_0/I) \quad (1)$$

Where, "t" thickness of the film," I_0" and " I" the intensity of incident and transmitted radiations respectively.

3.2 Reflectance spectra

Fig. 2 represents the reflectance spectra of as deposited $CdZnTe_2$ thin films.

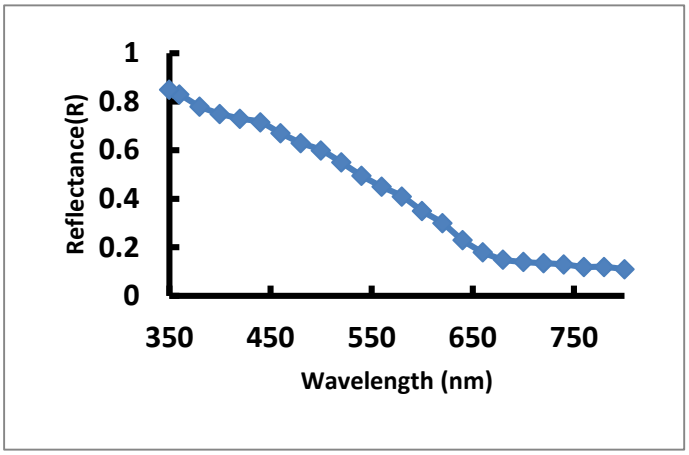

Fig. 2 Reflectance with wavelength of as deposited $CdZnTe_2$ thin films

The absorption coefficient "α" is related to the optical transmission "T" and reflectance "R" by the relation [11],

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

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 [12]. 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 [13],

$$\alpha = (A/hv) \times (hv-E_g)^n \quad (3)$$

Where hv –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, plotted the graph between $(\alpha hv)^2$ versus hv of as deposited thin film of $CdZnTe_2$ as shown in fig.3.

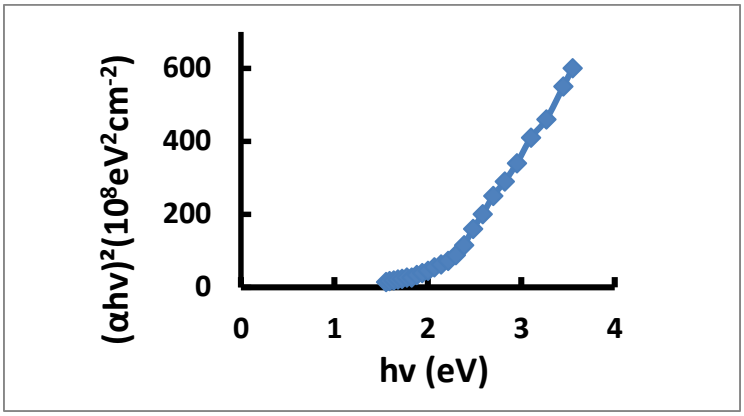

Fig.3 Graph between $(\alpha hv)^2$ versus hv of as deposited $CdZnTe_2$ thin film

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 was found to be 2.04 eV. These results are well agreed with the Alex Zunger et.al [14]. They have reported the band gap value of 1.99 eV by modern epitaxial growth technique. M. Bilal Faheem et.al [15] have also reported optical band gap value vary from 1.48 to 2.26 eV.of $Cd_{1-x}Zn_xTe$ thin films by varying the Zn content prepared by thermal evaporation technique. The optical transmission spectrum of the films under study shows that the transmission spectra mechanism is due to the direct allowed transition.

Our calculated value of optical band gap 2.04 eV are less than the value reported as 2.2748 to 2.2226 eV by M. Becerril et.al.[16] by r.f. sputtering method to prepare Zn rich $Zn_{1-x}Cd_xTe$ thin films on 7059 corning glass substrate at room temperature. This shows that spray pyrolysis produce a good stoichiometric in semiconducting nature. The linear plot of $(\alpha hv)^2$ versus hv over wide range of photon energies shows $CdZnTe_2$ thin film has a direct allowed transition.

3.3 Optical constants (n and k)

The refractive index was obtained from the relation [17],

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

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

$$K = \alpha\lambda/4\pi \quad (5)$$

The value of refractive index (n) and extinction coefficient (k) were calculated using relations (4) and (5). We also plotted the graph of refractive index (n) versus wavelength (λ) in nm as shown in fig.4 and a graph of extinction coefficient(k) versus wavelength (λ) in nm. As shown in fig.5.

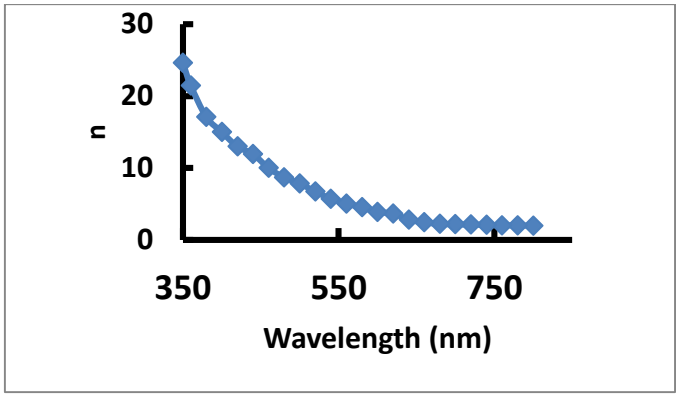

Fig. 4 Graph of refractive index (n) versus wavelength (λ)

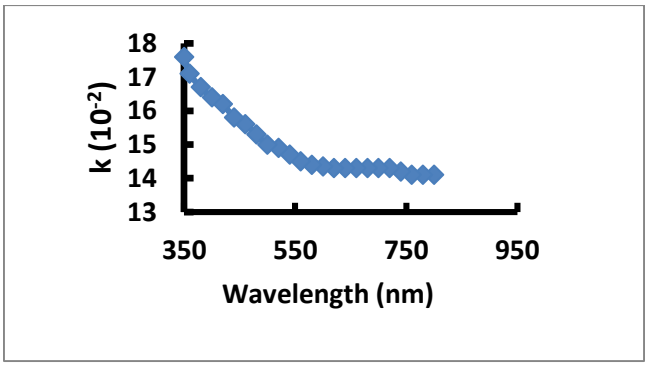

Fig. 5 Graph of extinction coefficient (k) versus wavelength (λ)

It was observed that refractive index (n) and extinction coefficient (k) both decreases as wavelength increases. Our calculated values of n and k are well agree with the Saliha Ilican et.al [17] for spray pyrolitically deposited some ternary semiconducting $CdZn(S_{1-X}Se_x)_2$ thin films and other workers [18-19] also for ternary group of semiconducting materials. 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.

4. ELECTRICAL PROPERTIES-

Conductivity of the films tested by hot- probe method was of n-type semiconductor. The temperature dependence of conductivity was studied in the temperature range 300

K to 573 K. The resistivity were measured by four- probe method [19] given by the relation,

$$\rho = [(V/I) \text{ x } (2\pi S)] / [G_7(t/S)] \quad (6)$$

And

$$G_7(t/S) = [2S/t] \text{ x } \ln(2) \quad (7)$$

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.6 Shows the Arrhenius plot of conductivity versus inverse temperature of as deposited $CdZnTe_2$ thin films

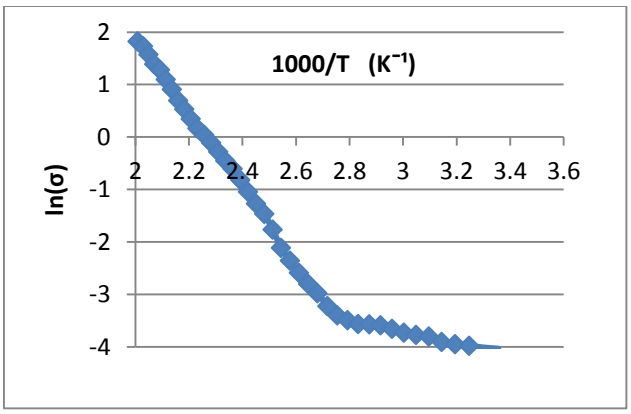

Fig. 6. Arrhenius plot of conductivity versus inverse temperature of as deposited $CdZnTe_2$ thin film

The activation energy was calculated from above graph using the relation,

$$\sigma = \sigma_0 \exp(-E_a/2kT) \quad (8)$$

where σ_0-pre-expontial conductivity, E_a - the activation energy, k- Boltzmann constant, T-absolute temperature.

The plot shows two segments i.e. two conduction regions. Region I(lower part of graph) between the temperature 298 K to 368 K and region II(upper part of graph) between the temperatures 369K 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 films of $CdZnTe_2$ 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 [20-21]. The higher the conductivity value at lower temperature is an evidence of the adsorption-desorption phenomenon whereas the saturation of conductivity value at higher temperature is a consequence of homogeneous nucleation and diffusion controlled process. 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 $CdZnTe_2$ 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 [22-23] for same group of ternary compounds.

5. SEM AND TEM STUDY-

Fig.7 & 8 represents TEM and SEM of as deposited $CdZnTe_2$ thin films respectively.

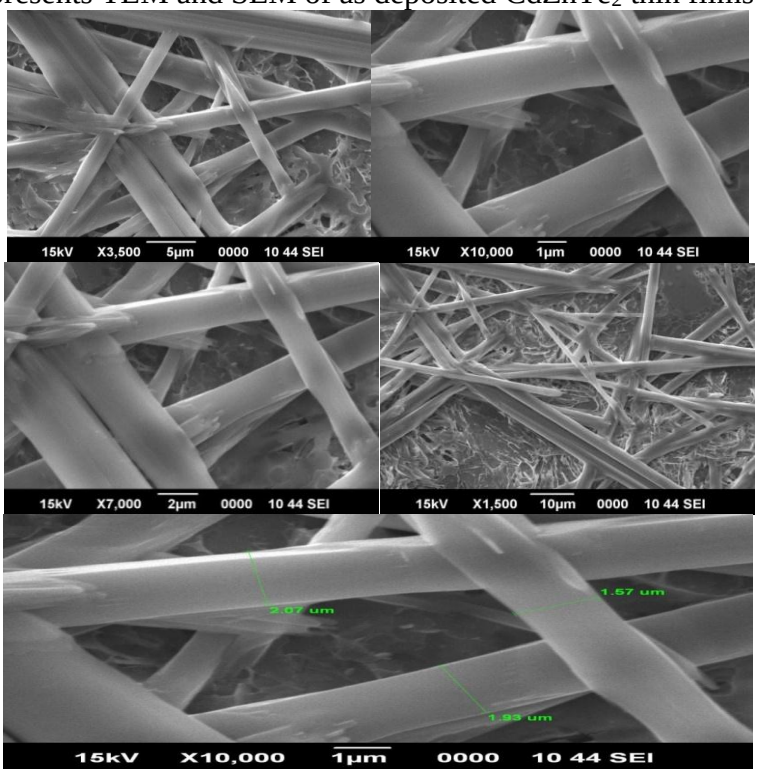

Fig. 7 SEM of as deposited $CdZnTe_2$ thin films

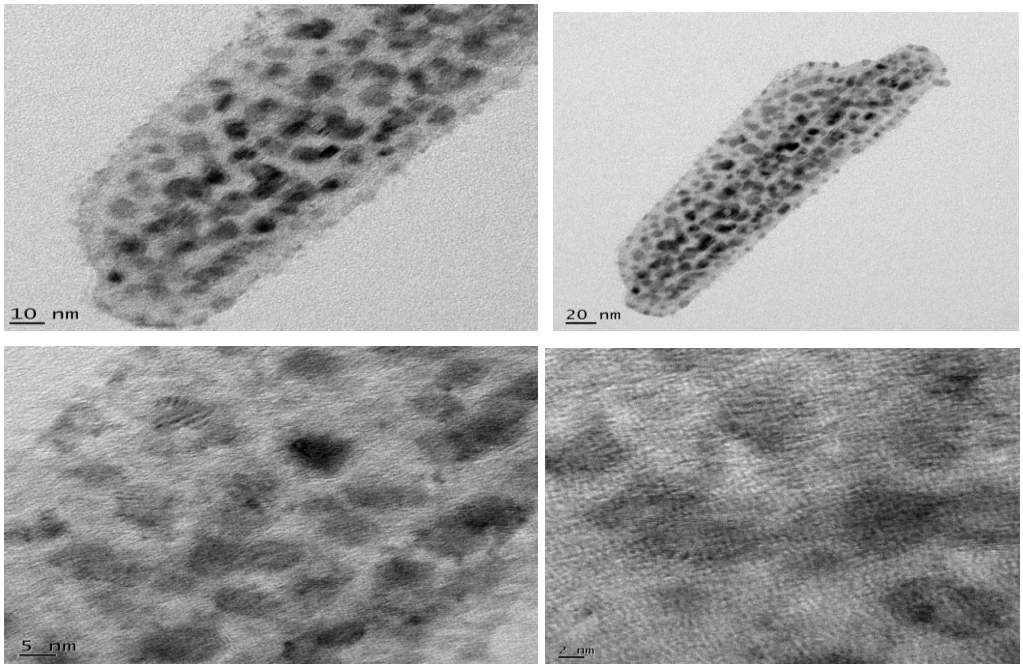

Fig. 8 TEM of as deposited $CdZnTe_2$ thin films

The SEM images provide the information regarding the morphology of the material which confirms the formation of nanosized, nano-tubes has the smooth surface of the films.

CONCLUSION

Spray pyrolysis is a simple and inexpensive method to produce a thin film. Optical band gap of $CdZnTe_2$ thin film was of 2.04 eV .which was calculated from $(\alpha h\nu)^2$ 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 whereas the saturation of conductivity value at higher temperature is a consequence of homogeneous nucleation and diffusion controlled process. This may be attributed to the increase of band gap and hence grain size of the film increases which reduces the grain boundary effect. TEM and SEM study confirm the formation of nanosized which is in the form like nanotubes.

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