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Research Article

STUDY OF ELECTRICAL PROPERTIES AND EFFECT OF SUBSTRATE TEMPERATURE ON OPTICAL BAND GAP OF SPRAY PYROLITICALLY DEPOSITED $CdZnSe_2$ Thin Films

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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 $CdZnSe_2$ 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 vary from 2.52 – 2.6 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

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 selenide 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 $CdZnSe_2$, ternary semiconductor varies from 2.52 - 2.6 eV at substrate temperature 300°C. The evaluation of any material for application is complete and meaningful only when its structure and composition are precisely known. The growth of ternary compound is a opens up the possibility of their application for novel optoelectronic devices [1-4], solar cells [5], light emitting diodes [6-7], field effect transistors [8], photo electrodes, blue green lasers etc.[9]. The research of the optical properties of $CdZnSe_2$, system forms a basis of the active region of laser and LED. Most of the work has been done on $CdZnS_{2X}Se_{2(1-x)}$ system. To the best of our knowledge, very less work has been reported on selenium $CdZnSe_2$, polycrystalline material. With this idea in mind we present a detailed study of bandgap energies of $CdZnSe_2$, in the form of thin films at different substrate temperatures and electrical conductivity of the films.

Several researchers studied properties of II-VI semiconductor films using the variety of methods such as thermal evaporation [10], vapour phase deposition [11], r.f.sputtering [12], spray pyrolysis [13-16], electrodeposition [17], chemical deposition [18]. 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 electrical conductivity and the effect of substrate temperature on optical band gap of spray pyrolitically deposited $CdZnSe_2$, thin films.

Experimental Details

Aqueous solutions of cadmium chloride, zinc chloride and selenium dioxide of 0.02 M of each were prepared in double distilled water. Chemicals used were of AR grade. The

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solutions are mixed in one in the proportion 1:1:3.2 by volume the film shows a selenium deficiency [19-20] if the ratio of proportion of solution was taken as 1:1:2 by volume. In order to find optimized condition for deposition of thin films, the deposition was carried out by varying one of the parameters as substrate temperature and keeping others at fixed value.

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, 375°C, 300^{0}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 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.

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.

It was observed that the thickness of the as deposited $CdZnSe_2$ thin films increases with temperature, attains the maximum value 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 0.1730µm. At higher substrate temperatures (>300°C) film thickness decreases due to higher evaporation rate of initial ingradients[21].

Optical study

The optical transmission spectra of $CdZnSe_2$, thin films deposited at different substrate temperature was taken on UV-1800-Shimandzu spectrophotometer in the wavelength range 350 nm to 1100 nm. Fig.1. Shows the transmission versus wavelength of as deposited $CdZnSe_2$ thin films at different substrate temperatures.

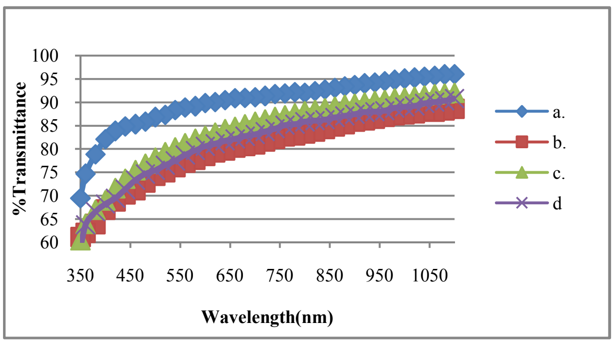

Fig 1 Transmission spectra of $CdZnSe_2$ thin films deposited at substrate temperature of a)250°C, b)275°C, c)300°C, d)325°C.

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,

$$\alpha = 1/t \ln(1/T) \quad (1)$$

Where, t- thickness of the films, T- transmittance of the film. An analysis of the spectrum showed that the absorption at the fundamental absorption edge can be described by the Taue relation [22],

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

Where hν –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 $(\alpha h\nu)^2$ versus hν of as deposited $CdZnSe_2$thinfilm at different substrate temperatures as shown in fig.2 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 hν axis yield, the value of band gap energy was found to be 2.52 eV. K.Y.Rajpure *et.al* [23] have also reported optical band gap value vary from 1.73 to 2.58 eV of $Cd_{1-}xZnxSe$ thin films by varying the Zn content prepared by electrodeposition technique.

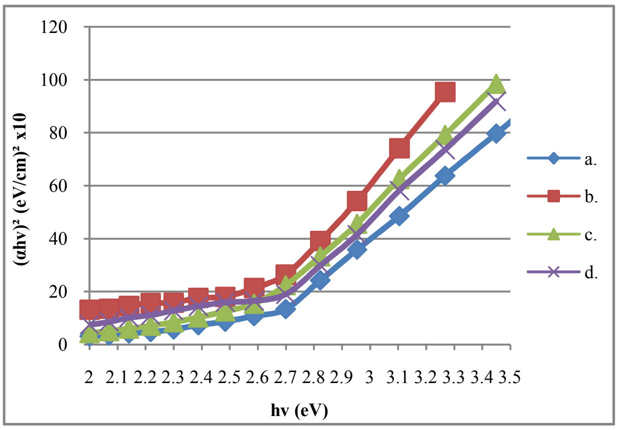

Fig.2 Variation of($\alpha h\nu)^2$ in $(eV/cm)^2$ versus hν in eV for as deposited $CdZnSe_2$ thin film deposited at different substrate temperatures a)250°C, b)275°C,c)300°C,d)325°C

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 2.52 eV are less than the value reported as 2.20 to 2.67 eV by S.D.Chavhan. *et.al*.[24] for pseudobinary $CdZn(S_{1-X}\,Se_X)_2$ by low cost solution growth technique. This shows that spray pyrolysis produce a good stoichiometric in semiconducting nature. The linear plot of $(\alpha h\nu)^2$ versus hν over wide range of photon energies shows $CdZnSe_2$ thin film has a direct allowed transition.Fig.3 shows the variation of optical band gap of $CdZnSe_2$ thin films deposited at different substrate temperatures. From fig.3. it is observed that optical band gap energy of $CdZnSe_2$ thin film is 2.6 eV at substrate temperature 250°C.

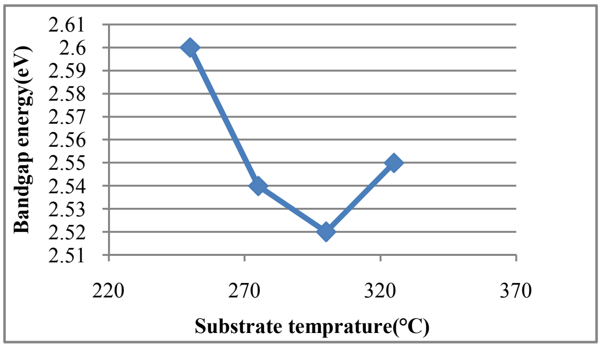

Fig 3 Variation of optical band gap energy (E_g) with substrate temperature of as deposited $CdZnSe_2$ thin films

The band gap energies determined for the samples decreases from 2.6 to 2.52 eV with increase in substrate temperature upto 300°C and it further increases with increase in substrate temperature. This shows that 300°C is the most suitable substrate temperature for depositing $CdZnSe_2$ thin film with optical band gap value which is most suitable for many scientific studies and technological applications, such as sensors, heat mirrors, solar cells transparent electrodes and piezoelectric devices.

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 [25] given by the relation,

$$\rho = [(2\pi S)V/I] / G_7(t/S) \qquad (3)$$

$$G_7(t/S) = [2S/t] \times \ln(2) \qquad (4)$$

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.4 Shows the Arrhenius plot of conductivity versus inverse temperature of as deposited $CdZnSe_2$ thin film deposited at substrate temperature 300°C. 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.

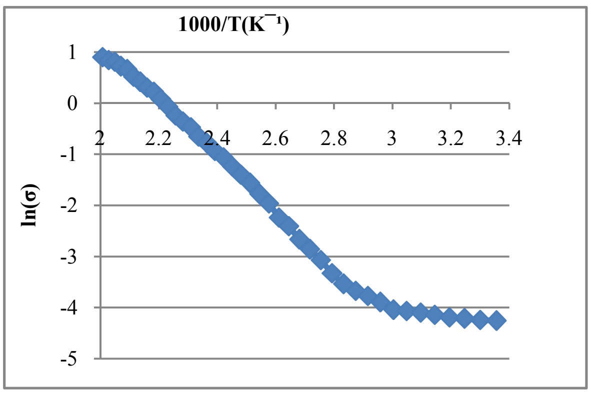

Fig 4 Arrhenus plot of conductivity versus inverse of temperature of as deposited $CdZnSe_2$ thin film

It was found that at room temperature the film posses resistivity of the order of $10^7 \Omega$ cm. The electrical conductivity of the film increases with increase in temperature that indicates semiconducting nature of the thin film material. The break in curve occurs at the temperature of 368 K. The variation of ln(σ) with 1/T is linear in two regions of temperature showing the well known exponential law

$$\sigma = \sigma_0 \exp(-E_a/2kT) \qquad (5)$$

where σ_0-pre-expontial conductivity, E_a - the activation energy, k- Boltzmann constant, T-absolute temperature. The activation energy values have been calculated from above graph using above relation .This shows that activation energy for conduction is lesser for low temperature region than that for higher temperature region. This low temperature conductivity is considered to be extrinsic (impurity dominated) while conduction in higher temperature region can be regarded as intrinsic [26-27] Even small amount of impurity can drastically modify electrical properties of semiconductors. At higher temperatures these impurity atoms gets ionized and do not show their effect.

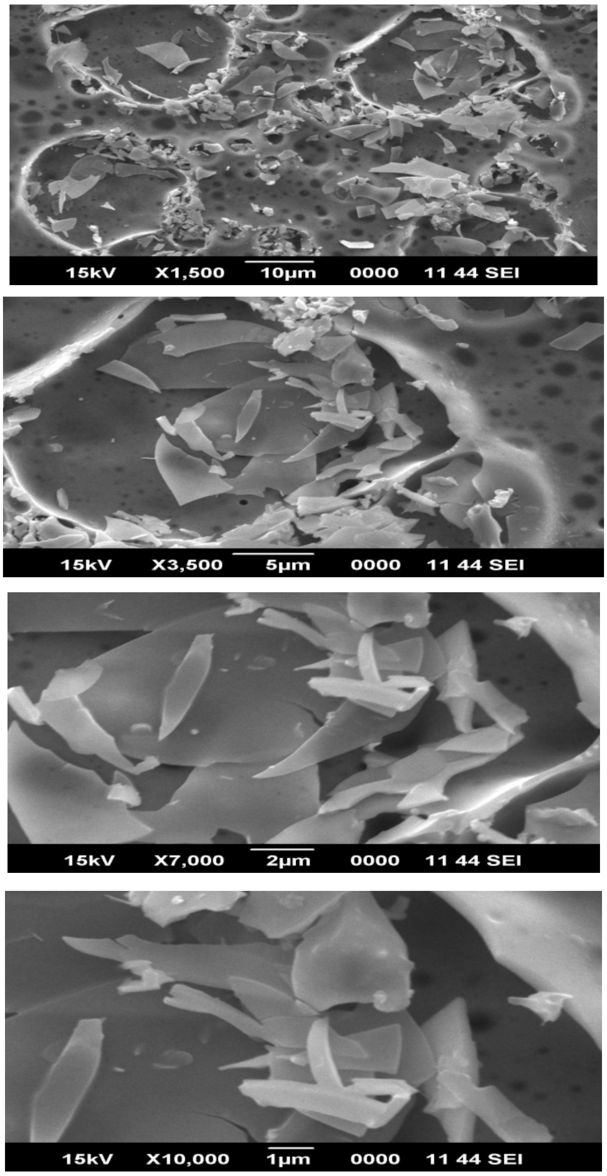

Fig 5 SEM of as deposited $CdZnSe_2$ thin films

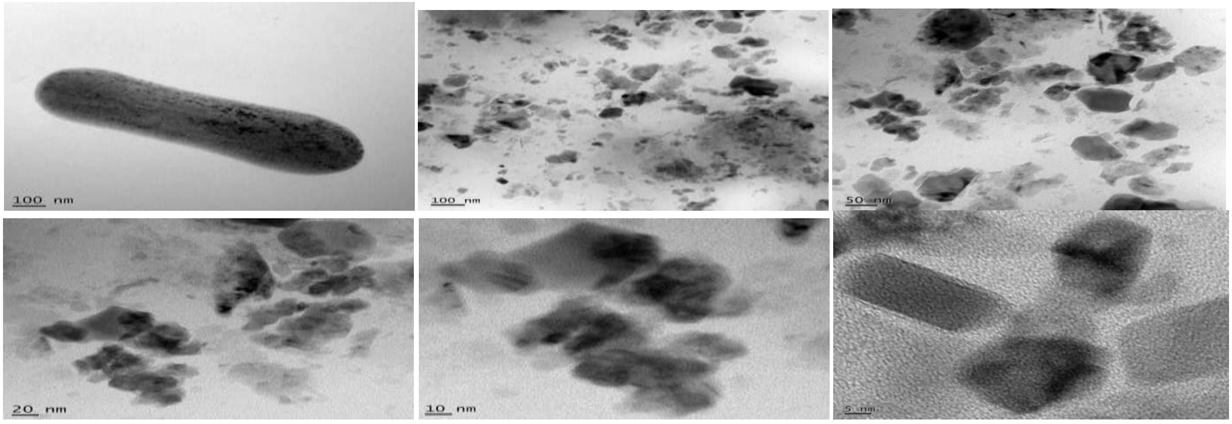

Fig 6 TEM of as deposited $CdZnSe_2$ thin films

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 $CdZnSe_2$ thin films the possibility of shallow trapping state due to the interstitials of Cd/Zn or selenide 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 [28-29] for same group of ternary compounds.

SEM and TEM study- Fig.5 & 6 represents TEM and SEM of as deposited $CdZnSe_2$ thin films respectively

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 $CdZnSe_2$ thin film was of 2.52 eV. which was calculated from $(\alpha h\ )^2$ versus (hv) plot. The linearity of the plot shows the direct allowed transition. The plot of optical band gap energies vs. substrate temperature is parabolic in nature which shows that at substrate temperatures less than or greater than300°C, band gap energy values goes on increasing. 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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