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RESEARCH ARTICLE

STUDY OF EFFECT OF SUBSTRATE TEMPERATURE ON OPTICAL AND ELECTRICAL PROPERTIES OF $CdZnSe_2$ THIN FILMS DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE

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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 CdZnSe2 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 10^4-10^5 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 2.52 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 .Electrical conductivity was measured by four probe method. Arrhenius plots shows the semiconducting nature of films. EDAX analysis reveals the formation of thin films.

INTRODUCTION

Elements of II–VI group are attracting a great deal of attention because of their potential abilities in the wide spectrum optoelectronic devices such as solar cells light emitting diodes, field effect transistors, photo electrodes, blue green lasers etc. (Sharma, 1979; Burger, 1984; Bassam, 1988; Nasibov, 1989; Gupta, 1995a and Deshmukh, 1998). High absorption coefficient, high efficiency of radiative recombination and nearly matching band gaps with the visible region of the solar spectrum are the root causes of the popularity of II–VI group semiconductors. Ternary materials provide a possibility of tailoring their properties as per requirements and hence project themselves as important semiconducting materials for further advancements in the field of device fabrication. $CdZnSe_2$ is wide band gap material and plays a dominant role in modern technology (Bassam, 1969). There are many methods of depositing II-VI alloy compounds such as thermal evaporation (Venugopal, 1996 and Korostelin, 1996), vapour phase deposition of high quality II-VI alloy crystals (Krishna Kumar, 2004; Hirde, 1990), spray pyrolysis (Tembhurkar, 1992, 1994& 1992), electrodeposition (Atef Y.Shenouda 2015, Rashwan, 2007), chemical bath deposition (G.Wary, 2016). Spray pyrolysis technique is most simple and economical method. The advantage of the technique is that just by varying the concentration of precursors and substrate temperature, it is possible to control stoichiometry of the deposits (Tembhurkar, 2016; Chavhan, 2009; Kale, 2007). Hence the thin films of $CdZnSe_2$ have been prepared by spray pyrolysis technique. Most of the work has been doneon $SeCd_{1-x}Zn_x$ system. So far no work has been reported on selenium rich $CdZnSe_2$ polycrystalline material. It has been reported that microstructures and morphologies of thin films are highly affected by substrate temperature. The grain size and crystallinity of the films can show variations at different substrate temperature. Therefore, the effect of the substrate temperature is important in fabrication of high-quality thin films and should be studied in detail.Hence the present study deals with the effect of substrate temperature on optical and electrical properties of spray pyrolitically deposited CdZnSe2, thin films.

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Experimental Details

Aqueous solutions of cadmium chloride, zinc chloride and selenium dioxide each of 0.02 M 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 selenium deficiency (Tembhurkar, 2016, Tembhurkar2016) 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. The sprayer was mechanically moved to and fro to avoid 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 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 1100nm.Electrical conductivity was measured by four probe method and formation of alloys was confirmed by EDAX analysis.

RESULTS AND DISCUSSION

Optical studies

Optical band gap

The optical transmission spectra of $CdZnSe_2$, thin films deposited at different substrate temperature was taken in the wavelength range 350 - 1100 nm. Fig.1Shows the transmission versus wavelength of as deposited $CdZnSe_2$ thin films at different substrate temperatures. 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.An analysis of the spectrum showed that the absorption at the fundamental absorption edge can be described by the Taue relation []. J.Tauc 1974],

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

Where hν –photon energy, A-constant which is different for different transitions, n = 1/2 for direct 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 energies. From graph it was found that optical band gap energy decreases from 2.60eV to 2.52 eV as substrate temperature increases from 250°C to 300°C beyond which band gap energy again increases with increase in substrate temperature.

b) Extinction coefficient (k) and refractive index(n)- The knowledge of the optical parameters such as refractive index (n), extinction coefficient (k) and dielectric constant (ε), over a wide wavelength range and optical band gap values of semiconducting films is quite important to predict the photoelectrical behaviour of a device. The extinction coefficient (k) is directly related to absorption of light. In the case of polycrystalline films, extra absorption of light occurs at grain boundaries (Mahalingam1988). This leads to non-zero value of 'k' for photon energies smaller than the fundamental absorption edge (Metin, 2003).

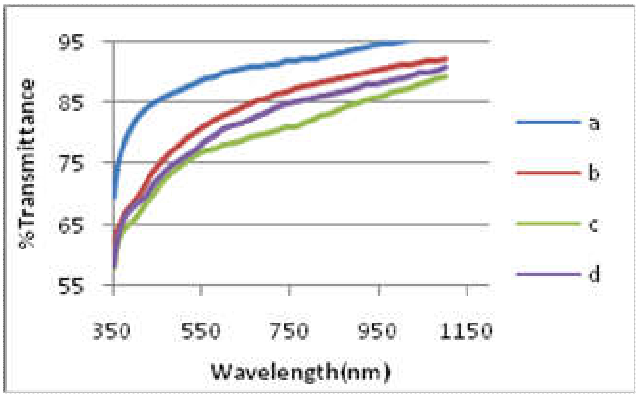

Fig. 1. Transmission spectra of CdZnSe2 thin films deposited at Substrate temperature of a)250°C, b)275°C, c)300°C, d)325°C.

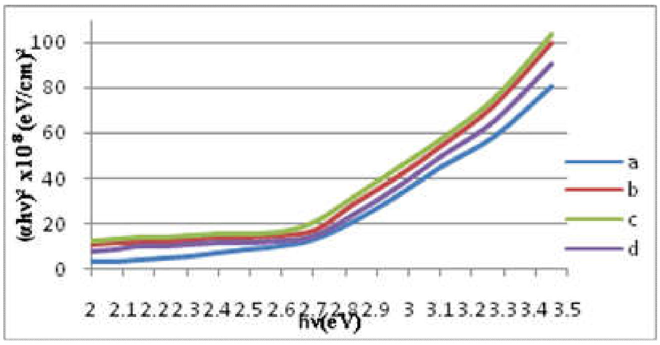

Fig. 2. Variation of (αhν)² as a function of photon energy in eV for of CdZnSe2 thin films deposited at Substrate temperature of a)250°C, b)275°C, c)300°C, d)325°C

Extinction coefficient (k) is related to absorption coefficient (α)' by the relation,

$K = \alpha \lambda / 4 \pi$. --(3)

Refractive index 'n' for the film is 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.

Fig. (5) shows the variation of extinction coefficient(k) of as deposited $CdZnTe_2$ thin film deposited at substrate temperatures 250°C,275°C, 300°C and 325°C as a function of wavelength in the wavelength range 350nm-1100nm. From graph it is clear that 'k' goes on decreasing with increasing wavelength and for higher wavelengths remains approximately constant at each substrate temperature. It is also observed from graph that extinction coefficient is minimum for substrate temperature 300°C, above and below this substrate temperature, it goes on increasing.

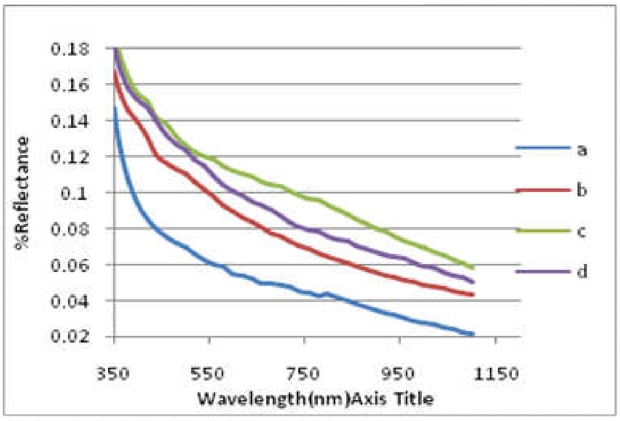

Fig. 3. Reflectance spectra of as deposited $CdZnSe_2$ thin films at Substrate temperatures a)250°C, b)275°C, c)300°C, d)325°C

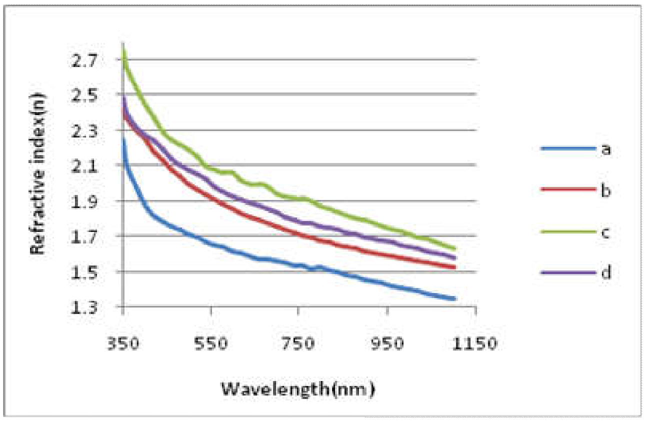

Fig. 4. Variation of refractive index(n) of $CdZnSe_2$ thin films at Substrate temperatures a)250°C, b)275°C, c)300°C, d)325°C

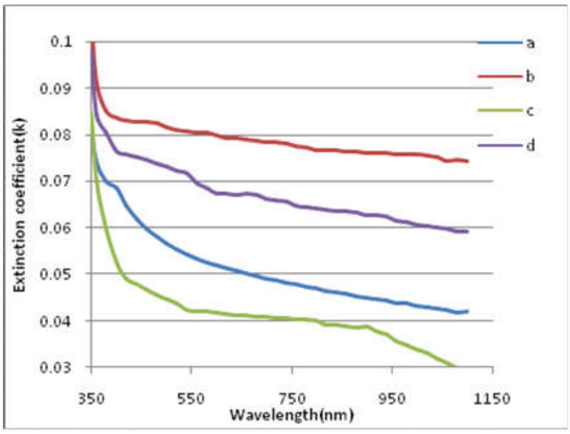

Fig. 5. Variation of extinction coefficient (k) as a function of of wavelength for as deposited $CdZnSe_2$ thin films at temperatures a. 250°C,b.275°C, c.300°C ,d.325°C

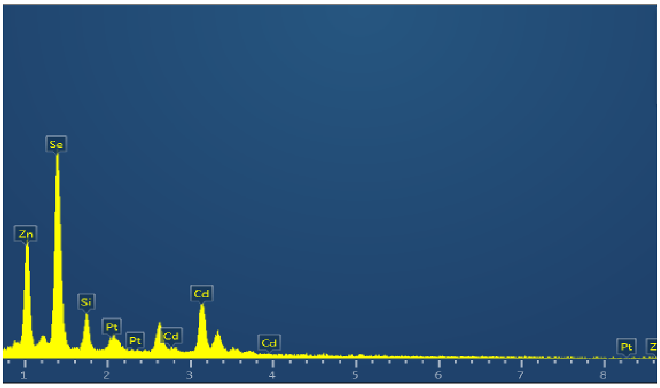

Fig. 6. EDAX spectra of as deposited $CdZnSe_2$ thin film at substrate temperature 300 °C

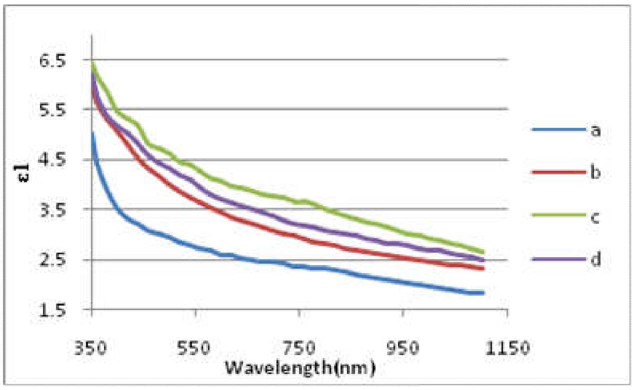

Fig. 7. Variation of real part(ε_1)of dielectric constant as a function of wavelength for as deposited $CdZnSe_2$ thin films at substrate temperature a. 250°C,b.275°C, c.300°C ,d.325°C.

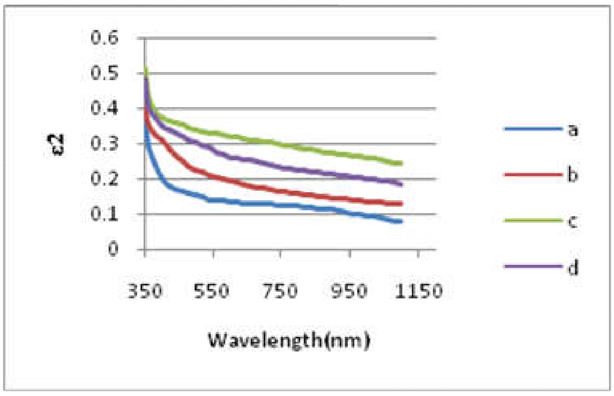

Fig. 8. Variation of imaginary part(ε_2)of dielectric constant as a a function of wavelength for as deposited $CdZnSe_2$ thin films at substrate temperature a. 250°C,b.275°C, c.300°C ,d.325°C.

Fig.(3 &4) shows the reflectance spectra and variation of refractive index of as deposited $CdZnSe_2$ thin film deposited at substrate temperatures 250°C,275°C, 300°C and 325°C as a function of wavelength in the wavelength range 350nm-1100nm.Figurs 4 shows that refractive index goes on decreasing with wavelength and at the substrate temperature 300°C,it attains maximum value of 2.7 than its corresponding values at other temperatures. At higher wavelengths(n)remains approximately constant. These results are in fairly good agreement to that given by Castiblanco at.el. and Akaltun at.el. (Castiblanco, 2014 and Akaltun, 2011).

Real and imaginary parts of dielectric constant-

Real and imaginary parts of dielectric constant(ε_1 and ε_2) are related to extinction coefficient(k) and refractive index(n) by the relation,

$$\varepsilon_1 = n^2 - k^2 \quad \text{--(5)}$$

$$\varepsilon_2 = 2nk \quad \text{--(6)}$$

Figs.7&8 represents the variation of real(ε_1) and imaginary(ε_2) parts of dielectric constants as a function of wavelength for as deposited $CdZnSe_2$ thin films for substrate temperatures 250°C,275°C,300°C,and 325°C. From fig. it is very much clear that variation of both real and imaginary parts of dielectric constant follow the same nature of curves and as wavelength increases, both $\varepsilon_1$and ε_2 goes on decreasing. Also it is observed that values of real parts are higher than the values of imaginary parts of dielectric constants and values of both (ε_1) and (ε_2) are higher for films at substrate temperatures 300°C.

Compositional studies

EDAX analysis is carried out to study the composition of the films in the binding energy region between 0 to 16keV. The typical EDAX patterns of as deposited $CdZnSe_2$ thin films are presented in Fig. 6.The presence of Cd, Zn and Se elements in the deposited $CdZnSe_2$ thin films is observed in the EDAX patterns. The silicon peak is also observed which may be due to the glass substrate.Platinum peak is due to platinum contact for EDAX analysis.

Surface morphology studies

SEM is one of the most useful techniquefor the invention of surface topography, microstructural features etc. because such properties of films influence their optical studies.Fig.9 shows the surface morphology of as deposited $CdZnSe_2$ thin film deposited at substrate temperature 300°C.SEManalysis shows the presence of nanotubes.

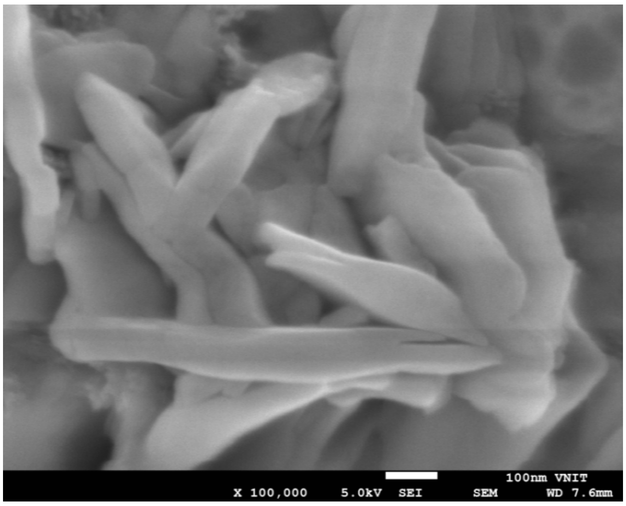

Fig. 9. SEM picture of as deposited $CdZnSe_2$ thin film at substrate temperature 300°C

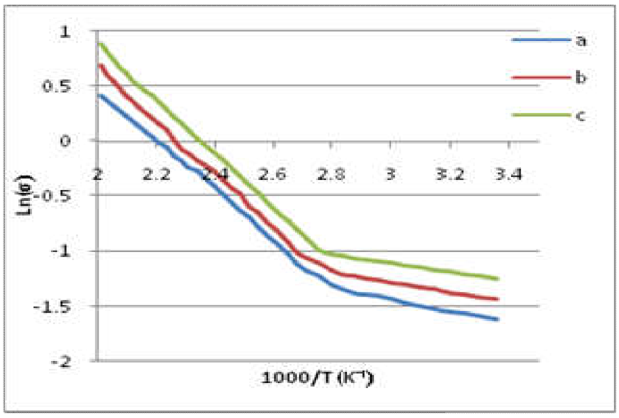

Fig.10. Arrhenius plots of as deposited $CdZnSe_2$ thin films at substrate temperatures a.250°C, b.275°C, c.300°C

Electrical studies

The conductivity of $CdZnSe_2$ thin films was measured by four probe method. Arrhenius plots of as deposited $CdZnSe_2$ thin films at substrate temperatures 250°C, 275°C and 300°C are as shown in Fig. 10. It was observed that conductivity increases with increasing substrate temperature which may be due to higher crystallanity (Garadkar, 2010). Fig. shows two distinct conducting regions indicating more than one conduction mechanisms due to localized states responsible for this conduction process are the direct consequence of imperfections associated with the films (More, 2003). The activation energies in two regions were calculated using the relation,

$$\sigma=\sigma_0 \exp(-E_a/kT) \quad \text{-------------------------------------}(7)$$

where 'k' is Boltzman constant, 'σ' is conductivity of thin film at temperature T, 'σ_o' is a constant and 'E_a' is the activation energy and 'T' absolute temperature. Activation energy represents the location of trap levels below the conduction band. It is found that activation energy in low temperature region is 0.0714 eV and in high temperature region 0.442eV.

Conclusion

$CdZnSe_2$ thin films were successfully deposited on glass substrate by spray pyrolysis technique and effect of substrate temperature on optical and electrical properties was studied successfully. Optical studies shows that films are highly absorptive in nature having high absorption coefficient. The optical band gap was found to be 2.52 eV at substrate temperature 300°C bolow and above which optical band gap increases. EDAX analysis shows the presence of Cd, Zn and Se elements [illegible] of nanotubes [illegible] of $CdZnSe_2$ thin films increases with substrate temperature as well as working temperature confirming semiconducting nature of the films.

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