Bandgap tuning of optical and electrical properties of zinc selenide

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Zinc Selenide (ZnSe) as an important II-VI semiconductor and one of the first semiconductors discovered with a band gap of around 2.7 eV at 25 °C. ZnSe thin films have been deposited by e-beam evaporation method with different thicknesses from 50 nm to 150 nm and effects of annealing temperature on optical and electrical properties of thin films have been investigated at room temperature (RT), 100^0C and 200^0C. It has been found that the energy bandgap of semiconductor thin films tend to decrease as the temperature increases. Optical properties of the synthesized films were investigated by UV-VIS spectrometer in the wavelength range of 400-1000 nm. Energy band gap of films were calculated and variation due to variation in the thickness were observed. The least band gap value was found to be 1.92 eV for 150 nm thin at 200^0C.The band gap results show the semiconducting nature of films grown. XRD technique was used to study the structural properties and the Hall measurement and I-V characteristics were used to study the electrical properties of the thin films. Hall characteristic of the ZnSe thin films for 150 nm at room temperature show that the material has p-type semiconducting nature which remains same if annealed to 200^0C.

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1. Introduction

In recent years, the II–VI family of compound semiconductors including, cadmium selenide (CdSe), zinc selenide (ZnSe), cadmium telluride (CdTe) and zinc telluride (ZnTe) have been studied due to their low cost and high absorption coefficients for applications to photovoltaic and photoelectrochemical cells. Zinc Selenide (ZnSe) is II-VI direct semiconductor having optical bandgap of around 2.7 eV at room temperature and is generally produced as an n-type semiconductor like most of the other II-VI compounds. [1-3]. ZnSe is an important promising material for optoelectronic devices such as red, blue and green light-emitting diodes [4], Lenses and prisms [5], photovoltaic [6], sensors and laser screens [7], thin film transistors [8], photo electrochemical (PEC) cells [9], etc. Recently, ZnSe thin films have been used as an n-type window layer for thin film heterojunction solar cells [10]. Currently, nanotechnology and nanomaterials have attracted a number of researchers across the world from different fields due to their unique properties and potential applications in diverse areas such as photocatalysis, display panels, solar cells, light-emitting diodes, and color-converted solid-state lighting devices [11-13]. Owing to these properties different methods have been adopted to prepare the ZnSe crystals as well as thin films. Thin films of ZnSe material can be deposited by using a variety of methods,

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including electrodeposition technique, Chemical Vapour Deposition, Inert Gas Condensation method , evaporation method, Thermal Evaporation , Vacuum Evaporation ,Chemical Bath Deposition (CBD), Molecular Beam Epitaxy, Successive Ionic Layer Adsorption and Reaction, Cyclic Voltammetry method [10-13]. The effect of annealing on the structural and optical properties of ZnSe thin films were studied by H. Amrollahi Bioki et al [1]. It was observed that the energy gap decreases with the increase in the film thickness and increases with the increase in the annealing temperature.

The Hall Effect has been used for analyzing the semiconductor thin films [14]. The Van der Pauw method is one of the most important methods for the evaluation of electrical properties in semiconductor materials such as resistivity, carrier density and mobility as reported by S. Thirumavalavana et al [14, 15]. Effect of the deposition conditions and post-deposition heat treatment on the structural and optical characteristics of ZnSe has also been reported [16].

In the present work ZnSe powder was used to deposit ZnSe thin films on the glass substrate by electron beam evaporation method with different thicknesses and analyzing the optical band gap of ZnSe at different temperatures. Due to annealing of films at different temperatures the optical bandgap variation has been determined. Prepared films were characterized for their structural, electrical and optical properties.

2. Materials and methods

ZnSe powder has been purchased from Alfa Aesar: having 99.999% purity. Glass substrates were washed by acetone. ZnSe was deposited on glass substrate by electron beam evaporation method in a vacuum of 3.75×10^{-2} Torr. The ZnSe thin films were annealed at room temperature (RT), 100°C and 200°C in a muffle furnace. The structural analysis of prepared samples was carried out by XRD and the optical properties were studied using UV-VIS spectrophotometer. The conductivity of this thin film was determined by current–voltage measurement while Hall measurements were done to find out whether films have semiconducting nature or differs from it. X-ray diffractometer of Make Broker X8 at MRC, MNIT Jaipur (India) was used for structural characterization. Optical properties of the films have been studied using UV-VIS spectrophotometer (make Perkin Elmer, Lambda, 750) at MRC, MNIT Jaipur (India). I-V Characteristics of various samples have been studied using Semiconductor Device Analyzer (Agilent Technology, B1500A, Malaysia) at MRC, MNIT Jaipur (India). Hall characteristics of various films have been studied by using (HMS 5000, Ecopia corp, (Korea) at MRC, MNIT Jaipur (India).

3. Results and discussion

3.1. Structural characterization using X-ray diffraction pattern.

XRD patterns of ZnSe thin films for a thickness of 150 nm at room temperature (RT), 100°C and annealed at 200°C of the substrate were studied. No peaks have been found in the XRD Spectra as shown in Fig.1. Thus, the obtained XRD pattern brings out that the deposited thin films are amorphous in nature. Poulopoulos et al [17] reported the influence of thickness of electron beam deposited ZnSe thin films on their properties. They also reported that the film with thickness of 36 nm is amorphous. Due to this much low thickness, ZnSe thin films are not showing any diffraction peaks. Further, the amorphous nature structures are non-crystalline and having a glass-like structure therefore, having a good electrical conductivity [18].

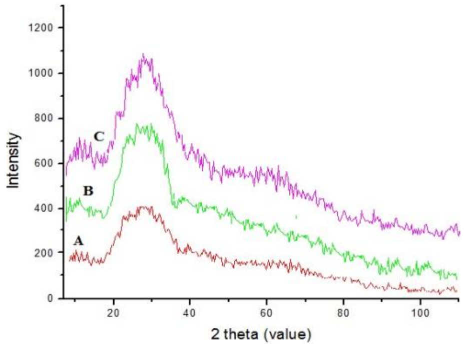

Fig. 1. XRD pattern of ZnSe thin film (100 nm) at (A) room temperature (RT), (B) 100°C and (C) 200°C.

3.2. Optical studies of ZnSe thin films

Optical absorption spectra of the as deposited films at 50 nm thickness at different substrate temperatures are recorded in the 400-1000 nm range to investigate the optical absorbance properties of the as-grown films and are presented in the Fig. 2 (A). Absorption spectrum of ZnSe at different substrate temperatures shows a remarkable difference in the optical absorbance. This difference may be attributed to structural changes due to surface roughness and scattering in the films [19]. The film prepared at RT and 200^0C has highest absorbance and least for 100^0C as the substrate temperature increases. Optical absorption spectra of deposited film at 100 nm and at different temperatures are shown in Fig.2 (B). It is evident from the figure that the optical absorption is very high at 100 nm and is least at 200^0C. Further, optical absorption spectra of deposited film at 150 nm and at different temperatures are shown in Fig. 2 (C), which shows that the optical absorption is remarkably high at 150 nm as compared to 50 nm and 100 nm. From all these findings, it can be concluded that the optical absorption of the annealed ZnSe film is highest at 150 nm with substrate temperature of 200^0C. Thus, ZnSe films indicate a gradually increasing transmittance (less absorbance) throughout the visible region, which makes it possible for this material to be used in photoelectrochemical cell [20]

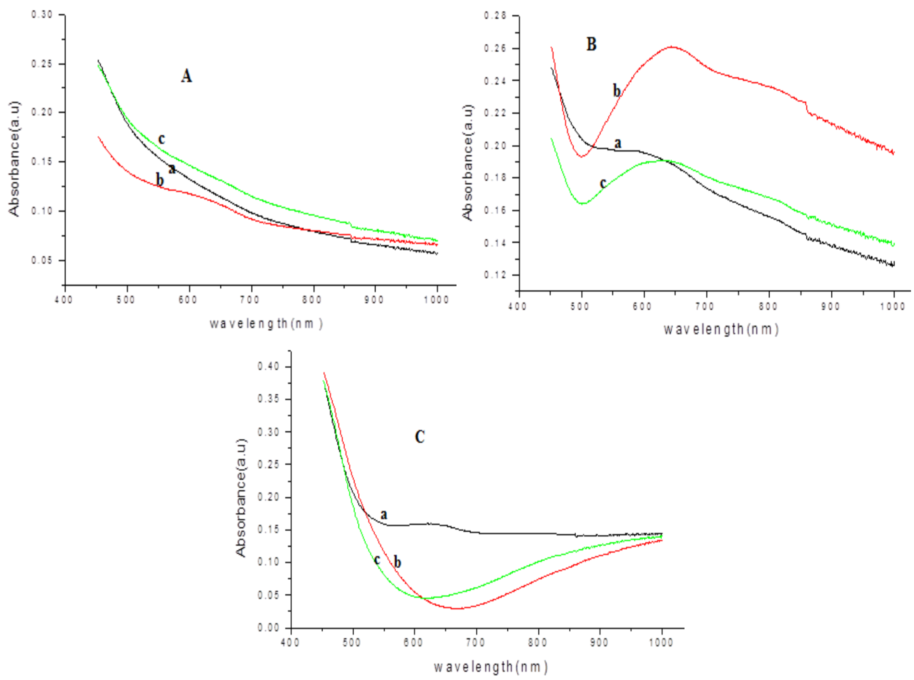

Fig. 2. Plot of absorbance (a.u) vs. wavelength (nm) for (A) ZnSe thin films of 50 nm at (a) RT, (b) 100°C and (c) 200°C. (B) ZnSe thin films of 100 nm at (a) RT, (b) 100°C and (c) 200°C. (C) ZnSe thin films of 150 nm at (a) RT, (b) 100°C and (c) 200°C.

From the above mentioned absorbance data, the absorption coefficient was calculated using Lambert law: $\alpha = 2.303 \times A_{bs}/d$, A_{bs} is optical absorbance, α is absorption coefficient and *d* is thickness of the films (cm). Optical Energy band gap (*Eg)* was determined by analyzing the optical data with the expression for the optical absorption coefficient (α) and the photon energy (hv) using the relation.

$$\alpha hv = C(hv-E_g)^{n/2}$$

where E_g is the energy band gap, C is constant which is dependent on the structure of sample, h is a plank's constant and α is the absorption coefficient which is obtained using Beer-lambert's law [21], the value of *n* is equal to one for a direct-gap material, and four for an indirect-gap material.

Plots of (α*h*ν)2 versus *h*ν were drawn using the above equation The energy bandgap plot of $(\alpha hv)^2$ vs E(eV) for 50 nm is shown in Fig. 3 (A), for 100 nm ZnSe film in Fig. 3(B) and for 150 nm ZnSe film in Fig. 3(C). Extrapolation of the linear portion of the plot to the energy axis yielded the direct band gap value and the linear natures of the curve indicate direct nature of transition as shown in Fig. 3.Theoretical band gap energy values (in eV) determined from this analysis for 50 nm ZnSe film Fig. (3A), 100 nm ZnSe film (Fig. 3B) and 150 nm ZnSe film (Fig. 3C) at RT, 100^0C and 200^0C respectively, were calculated and shown in table 1. It is observed that the energy band gap values obtained are less than as reported by the earlier workers which shows that the present thin films are more conducting in nature. Further, the ZnSe thin film formed at 150 nm and annealed at 200^0C has least energy band gap value of 1.92 eV. This is because at higher annealed temperature absorption spectra of the annealed films exhibit increase in the optical absorbance with its absorption edge shifting gradually towards lower wavelength and shrinks the band gap.

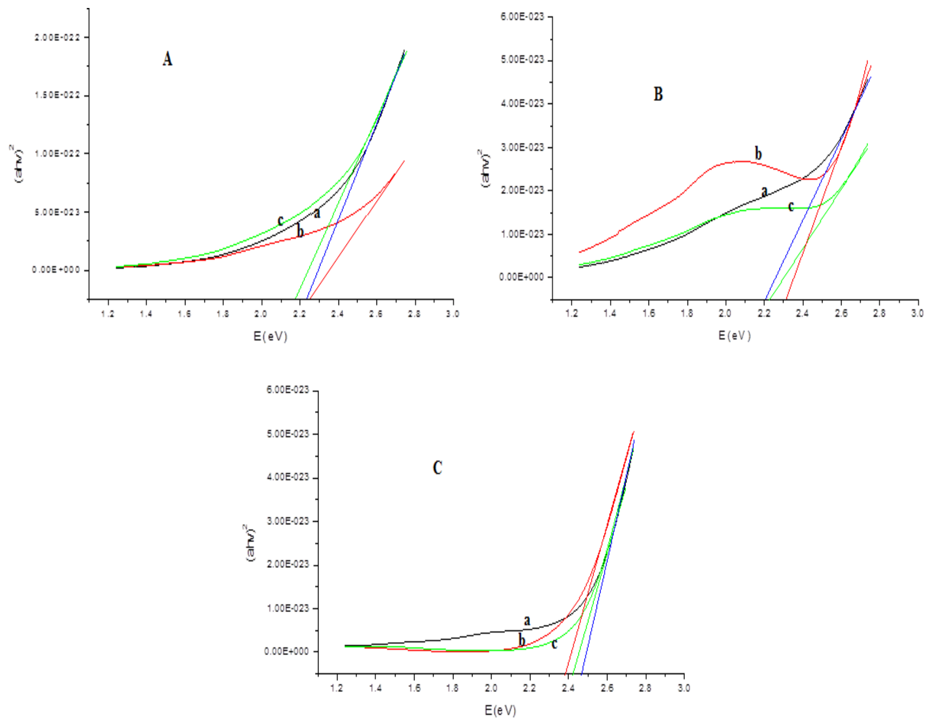

Fig. 3. Plot of $(ahv)^2$ vs. E(eV) for (A) ZnSe thin films of 50 nm at (a) RT, (b) 100°C and (c) 200°C. (B) ZnSe thin films of 100 nm at (a) RT, (b) 100°C and (c) 200°C. (C) ZnSe thin films of 150 nm at (a) RT, (b) 100°C and (c) 200°C.

Table 1. Energy band gap values of ZnSe of 50 nm, 100 nm and 150 nm thin films at different temperatures (RT, 100^0C and 200^0C).

ZnSe	Thickness (nm)	Room temperature	100^0C	200^0C
Energy band gap (eV)	50	2.21	2.05	1.98
	100	2.30	2.11	2.0
	150	2.40	2.10	1.92

3.3. Electrical properties of ZnSe

3.3.1. Current voltage (I-V) characteristics of ZnSe

The current-voltage (I-V) characteristics of ZnSe thin film for thickness 150 nm at as deposited room temperature and annealed at 200^0C is shown in Fig. 4. The current-voltage behaviour revealed the ohmic nature of the contacts which is formed between the surface of the film and the glass substrate. The electrical conductivity of the film annealed at 200^0C (Fig. 4B) is seen to be more than at lower temperature. This increase in conductivity or decrease in resistivity may be due to the reorientation of grains or reduction in the grain boundary domains or thermal excitation of charge carriers. This decrease in the resistivity and increase in conductivity with the increase in-temperature can also be understood on the basis of the semi-conducting temperament of ZnSe thin films.

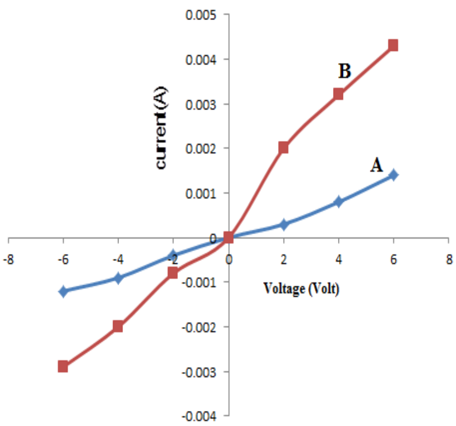

Fig. 4. Transverse current-voltage behaviour of as-deposited and thermally annealed 150 nm ZnSe thin film at room temperature (A) and at 200^0C (B).

3.3.2. Hall measurements of ZnSe thin films.

Electrical properties of the deposited 150 nm thin films were studied by employing Hall measurement setup in van der Pauw configuration (ECOPIA HMS-5000) at room temperature and at 200^0 C. The results show that the deposited ZnSe thin films belong to p-type semiconductor which remains the same if annealed to 200^0C (Table 2). Further, ZnSe thin films have high resistivity [22, 23]. However, after comparing the resistivity values with the literature values, the resistivity decreases by few orders. The electrical parameters measured for ZnSe thin films are compared with the corresponding value of the previous works in table 2. The results show that the resistivity of the amorphous ZnSe films deposited in this work is reduced very much when compared with corresponding values of the other reports. Further, the conductivity of the ZnSe films in this work at RT and 200^0 C are 9.92×10^1 Sm^{-1} and 9.802×10^2 Sm^{-1} , respectively. The high resistivity makes ZnSe suitable as buffer layer in thin film technology and also it is a semiconductor that has large potential applications in thin films like photo luminescence and electroluminescent devices [23].

Table 2. Hall measurement of ZnSe 150 nm thin film at RT and 200^0C and the comparison of its electrical properties with the literature values.

Substrate Temperature	**Resistivity Ωm**	**Conductivity S/m**	**Magneto Resistance**	**Avg Hall m^3/C**	Reference
Room temperature	1.01×10^{-2}	9.92×10^{1}	1.61×10^{3}	1.61×10^{-3}	Present work
200°C	1.02×10^{-3}	9.802×10^{2}	1.674×10^{2}	6.771×10^{-2}	Present work
Room temperature	3.35×10^{2}	2.98×10^{-3}	--	2.95×10^{6}	Murali et al. [20]
Room temperature	3.15×10^{4}	-	-	-	Okereke and Ekpunobi [23]

4. Conclusions

Zinc selenide thin films were successfully deposited by Electron Beam Evaporation method at different thicknesses from 50 nm to 150 nm at varying substrate temperatures of RT, 100^0C and 200^0C. XRD results show that the materials are amorphous in nature. Optical properties were studied using UV-Vis study and the band gap values were found to decrease and the least value was found to be 1.92 eV for 150 nm thin at 200^0C.

The electrical studies carried out using Hall measurement and I-V characteristics show that the zinc selenide thin films belong to p-type semiconductor and possess relatively low resistivity compared to that of other reports.

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