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Thermal induced changes on optical and electrical properties of zinc selenide thin films

Jeewan Sharma^{1*}, S.K.Tripathi²

¹Department of Physics, Maharishi Markandeshwar University, Mullana, Ambala - 133 207, (INDIA)

²Centre of Advanced Study in Physics, Panjab University, Chandigarh - 160 014, (INDIA)

E-mail : jeewansharma29@gmail.com

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ABSTRACT

ZnSe thin films have been prepared by inert gas condensation method at argon gas partial pressure of 2×10^{-1} mbar and room temperature (298 K). The influence of thermal annealing in vacuum, on optical and electrical properties of ZnSe films have been investigated using optical transmission and conductivity measurements. The absorption coefficient (α) and band gap (E_g) are calculated using transmission curves. Optical transmittance measurements indicate the existence of direct allowed optical transition with a corresponding energy gap in the range of 2.80-3.00 eV. The dark conductivity (σ_d) and photoconductivity (σ_{ph}) measurements, in the temperature range 253-358 K, indicate that the conduction in these materials is through an activated process having two activation energies. σ_d and σ_{ph} values increase with the increase in the crystallite size on annealing. The values of carrier life time have been calculated and are found to increase with the increase in the crystallite size on annealing. Results show that the above properties change appreciably after the thermal treatment.

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INTRODUCTION

ZnSe is one of the group II-VI semiconductors and has a direct optical band gap of 2.58 eV^[1,2]. It has been regarded as material with many attractive properties, such as large band gap, low resistivity, remarkable photosensitivity etc., which makes it suitable material for a variety of the optoelectronic applications in the blue green wavelength region, including light emitting diodes and lasers^[3-8]. Because of wide band gap and transparency over a wide range, it is suitable for window layer for solar cells^[9]. ZnSe is used for production of optical elements (windows, lenses, prisms) for IR range including the passive laser optics elements. It has superior optical transmission with extremely low bulk

losses from scattering and absorption. ZnSe is the first choice for high power laser windows and multispectral applications with useful transmitting range^[10]. The effect of different deposition parameters such as pressure, substrate temperature, pH and annealing on properties of ZnSe is an area of interest these days^[11,12]. Because of their interesting physical properties and device applications a variety of techniques have been used for the deposition of ZnSe films, such as MOCVD^[13], RF magnetron sputtering^[14], molecular beam epitaxy^[15], MOVPE and vacuum evaporation^[16]. The knowledge of structural, optical and electrical properties of ZnSe films is very important for such applications. Indium is a very good contact material for this ZnSe thin film. It is used as an ohmic contact for this ZnSe thin-film struc-

ture. The vacuum evaporation technique is used to prepare the ZnSe thin films, because the vacuum evaporation technique is relatively simple, inexpensive and convenient, in particular for large area deposition. In this paper, we report the structural, optical and electrical properties of ZnSe thin films deposited at different Ar gas pressures.

In the present work, the optical and electrical properties of ZnSe thin films deposited by inert gas condensation method have been studied. The absorption coefficient (α) and band gap (E_g) are calculated using transmission curves. Dark- and photo-conductivity (with temperature and intensity) measurements have been done on these films. Also, transient photoconductivity behaviour is studied using rise and decay analysis. The present paper describes the effect vacuum annealing on optical and electrical properties of ZnSe films.

EXPERIMENTAL

The semiconducting $Zn_{25}Se_{75}$ was prepared from its constituents (5N pure) by melt-quenching technique as described earlier^[17]. Thin films of this material were grown in a conventional vacuum coating system on well degassed chemically cleaned Corning 7059 glass substrates. The vacuum chamber was evacuated to 2×10^{-6} mbar and Ar gas was introduced through specially designed inlet tube having a jet of diameter ~ 0.5 mm. This jet was kept adjacent to the evaporation boat pointing towards the glass substrates. The vacuum chamber was purged several times with spectroscopic grade Ar gas to remove any residual gas impurities. Thermal evaporation of the material was carried out from the Mo boat. This film is then annealed at 473 K for one hour. Annealing is done in vacuum of 2×10^{-3} mbar. A double beam spectrophotometer [HITACHI-330] was used to study the optical transmission in ZnSe thin films. The electrical measurements of these thin films were carried out in a specially designed metallic sample holder where heat filtered white light of intensity 8450 Lux (200 W tungsten lamp) was shown through a transparent glass window. A vacuum of about 10^{-3} mbar was maintained throughout these measurements. Light intensity was measured using a digital luxmeter (MASTECH, MS6610). Planar geometry of the films (length ~ 1.0 cm; electrode gap $\sim 8 \times 10^{-2}$ cm) was used for the elec-

trical measurements. Pre deposited thick Indium electrodes were used for the electrical contacts. The electrical conductivity in thin film has been calculated using two probe methods. The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the current measured in the presence of light. For transient photoconductivity measurements, light was shone on the thin film and, the rise and decay of photocurrent was noted manually from a digital picoammeter (DPM-11 Model). The accuracy in I_{ph} measurements was typically 1 pA.

RESULTS AND DISCUSSION

Optical properties

Figure 1(i) shows the transmission spectra of as-deposited and annealed thin films. From the transmission data, nearly at the fundamental absorption edge, the values of absorption coefficient (α), are calculated in the region of strong absorption using the relation,

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (2)$$

and are shown in figure 1(ii).

To see the nature of transition in n-ZnSe, the variation of $d\{\ln(\alpha hv)\}/d(hv)$ w.r.t. hv is studied as described elsewhere^[18]. Figure 2(i) shows the plots of $d\{\ln(\alpha hv)\}/d(hv)$ vs. hv , for as-deposited and annealed thin films, with discontinuities at 2.95 eV and 2.21 eV respectively. Taking these values as the optical gap of ZnSe thin films, $\ln(\alpha hv)$ vs. $\ln(hv/E_g)$ graphs are plotted. From the slopes of these straight line graphs (Figure 2(ii)), values of n have been calculated to be 0.45 and 0.35 respectively, which are close to 0.5 indicating that the transition is direct. The values of optical gap are calculated by extrapolating the straight line portion of $(\alpha hv)^{1/n}$ vs. hv graphs to hv axis taking $n = 0.5$. Figure 3 shows the plots of $(\alpha hv)^2$ vs. hv for as-deposited and annealed thin films. The correct values of the optical gap calculated from the figure are found to be (3.00 ± 0.01) eV for as-deposited and (2.80 ± 0.01) eV for annealed thin films. There is a red shift of 0.20 eV in the optical gap after annealing the film at 473 K in vacuum for one hour. This shows that the improvement in crystallinity is followed by a shift in the optical absorption edge of the films towards lower energy values. Samatilleke et al.^[19]

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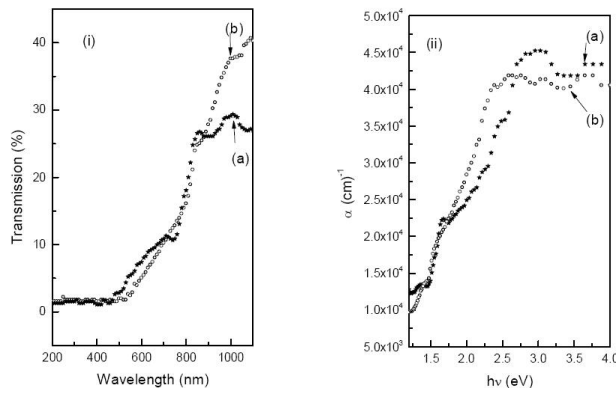


Figure 1 : (i) Transmission spectra and (ii) absorption coefficients of (a) as-deposited and (b) annealed ZnSe thin films

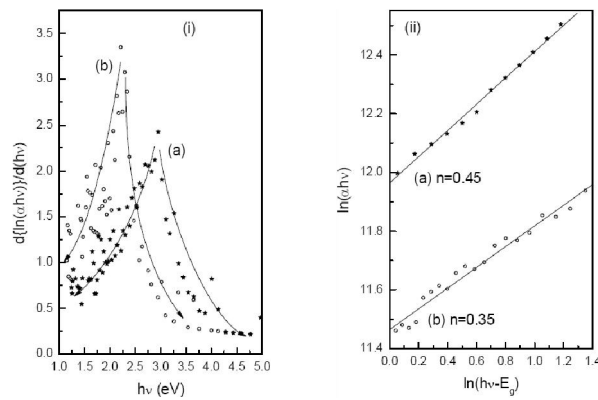


Figure 2 : (i) Variation of $d\{\ln(\alpha hv)\}/d(hv)$ with energy and (ii) plots of $\ln(\alpha hv)$ vs. $\ln(hv-E_g)$ for (a) as-deposited and (b) annealed ZnSe thin films

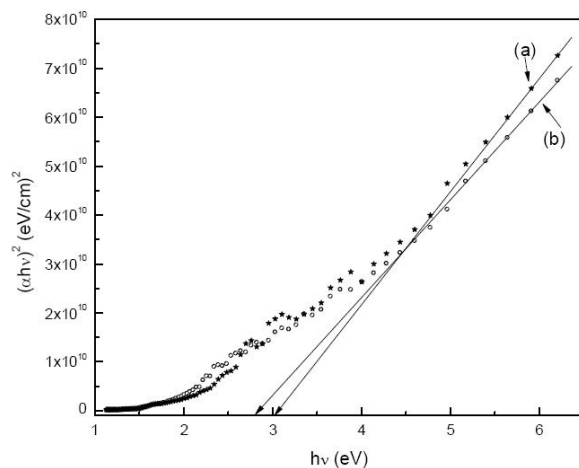


Figure 3 : Variation of $(\alpha hv)^2$ with energy for (a) as-deposited and (b) annealed ZnSe thin films

also reported the increase in crystallinity on annealing ZnSe thin films at 473 K for 15 minutes.

Electrical properties

Figure 4(i) shows the current vs. voltage plots for

as-deposited and annealed ZnSe thin films. The I-V curves are found to be symmetric and linear upto the operating range of applied voltage. The electrical conductivity shows typical Arrhenius type of activation,

$$\sigma_d = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \quad (6)$$

where ΔE is the activation energy for conduction and k is the Boltzmann's constant. The values of σ_d for as-deposited and annealed ZnSe thin films are found to be $(2.19 \pm 0.02) \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ and $(4.23 \pm 0.02) \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ respectively at 298 K.

These values of conductivity are in good agreement with earlier reported values^[20,21]. Figure 4(ii) shows the temperature dependence of dark conductivity for as-deposited and annealed ZnSe thin films in the temperature range 250-370 K. The plots of $\ln\sigma_d$ vs. $1000/T$ have two linear portions. First in the lower temperature range (250-315 K), characterized by a small slope and second in higher temperature range (315-370 K) having large slope. The activation energies for dc conduction has been calculated from the slopes of $\ln\sigma_d$ vs. $1000/T$ curves for both lower and higher temperature ranges. The values of σ_d and ΔE_d are given in (TABLE 4.6). The value of σ_d increases and ΔE_d decreases on annealing ZnSe thin film. This type of behaviour has also been observed by others for semiconductors^[22,23]. The increase in electrical conductivity and activation energies after annealing may be due to the change in structural parameters, improvement in crystallite and grain size, decrease in inter-crystallite boundaries (grain boundary domains) and removal of some impurities (adsorbed and absorbed gases). Excess atoms of compound are also possible^[24] due to a small change in stoichiometry after annealing.

Figure 5 (i) shows the temperature dependence of photoconductivity for as-deposited and annealed ZnSe thin films. The values of photoconductivity are calculated to be $(9.42 \pm 0.02) \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$ and $(2.85 \pm 0.02) \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ for as-deposited and annealed ZnSe thin films at 298 K. Clearly, the value of σ_{ph} increases on annealing. The photo activation energy has been calculated using the slopes of figure 4.22 (i) and is found to decrease from $(0.22 \pm 0.01) \text{ eV}$ to $(0.10 \pm 0.01) \text{ eV}$ on annealing (TABLE 4.6). The activation energies for photoconduction are much smaller than for the dark conduction. No maximum in the steady state

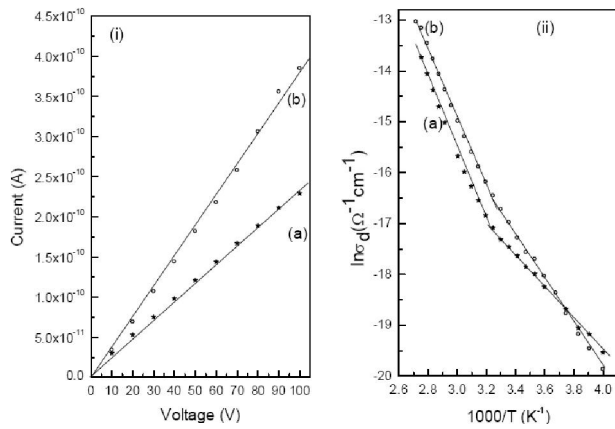


Figure 4 : (i) I-V plots and (ii) temperature dependence of dark conductivity for (a) as-deposited and (b) annealed ZnSe thin films

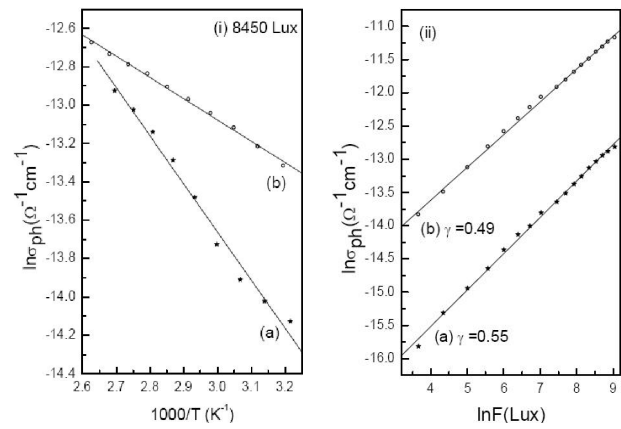


Figure 5 : (i) Temperature and (ii) intensity dependence of photo conductivity for (a) as-deposited and (b) annealed ZnSe thin films

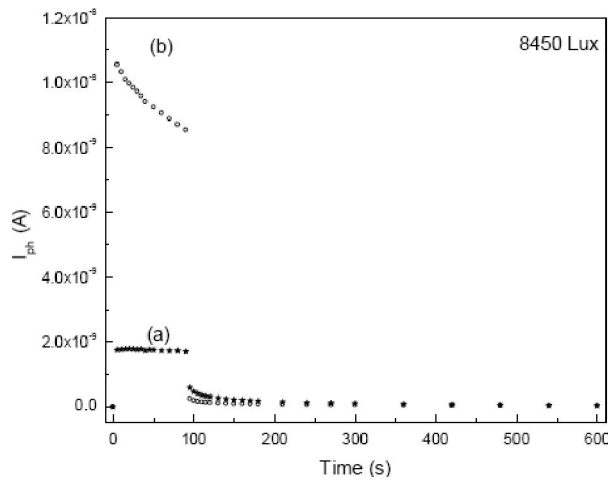


Figure 6 : Rise and decay of photocurrent for (a) as-deposited and (b) annealed ZnSe thin films

photoconductivity with temperature has been observed in the measured temperature range. Photosensitivity is found to increase after annealing. Figure 5 (ii) shows the intensity dependence of σ_{ph} for as-deposited and annealed ZnSe thin films. It is clear from the figure that $\ln\sigma_{ph}$ vs. $\ln F$ curves are straight lines indicating that the σ_{ph} follows a power law with intensity (F), i.e., $\sigma_{ph} \propto F^\gamma$. In as-deposited and annealed ZnSe thin films, the values of γ are found to be in between 0.5 and 1.0, indicating that the resulting recombination mechanism is bimolecular^[25], where the recombination rate of electrons is proportional to the number of holes.

Photosensitivity (σ_{ph}/σ_d) of the order of 10-10² has been found in ZnSe thin films.

Figure 6 shows the rise and decay curves of I_{ph} for as-deposited and annealed ZnSe thin films. I_{ph} rises to

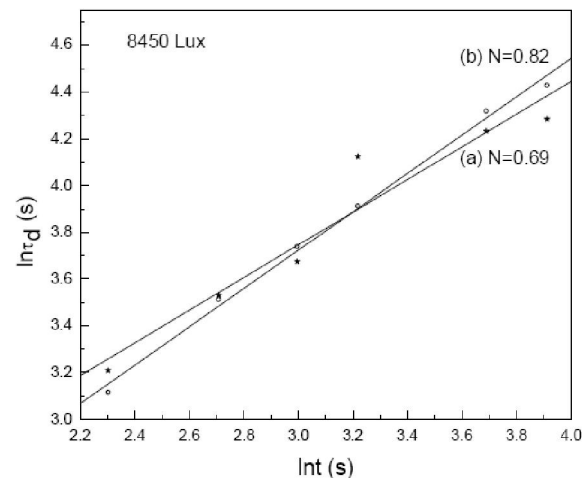


Figure 7 : Plots of lnτ_d vs. lnτ for (a) as-deposited and (b) annealed ZnSe thin films

a steady state value and no peak is observed for as-deposited film while a peak is observed in rise curve of annealed ZnSe film. It is evident that decay of I_{ph} is slow. In materials, having traps in the mobility gap, the recombination time of carriers is same as carrier life time when free carrier density is more than trapped carrier density^[26]. If the free carrier density is much less than the trapped carriers, then the recombination process is dominated by the rate of trap emptying and is much larger than carrier life time, resulting in a slow decay. During decay, the photocurrent does not reach zero for a long time after the incident light is switched off. A persistent photocurrent is observed in all the cases. This type of photoconductive decay has also been reported in various other semiconductors^[27-29]. In the present case, non-exponential decay of photocurrent is

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observed. The values of τ_d at different times have been calculated using following eq. (15).

$$\tau_d = - \left[\frac{1}{I_{ph}} \left(\frac{dI_{ph}}{dt} \right) \right]^{-1} \quad (15)$$

Eq. (15) for as-deposited and annealed ZnSe thin films from the slopes (at different times) of decay curves of Figure 6.

The decay times observed for ZnSe thin films are found to be time dependent. The value of τ_d increases with time, which confirms the non-exponential decay of photocurrent. Figure 7 shows the plots of $\ln \tau_d$ vs. $\ln t$ for as-deposited and annealed ZnSe thin films at a temperature 298 K and intensity 8450 Lux. The extrapolation of the curves at $t = 0$, give the values of the carrier life time^[30] and are found to be 1.6 and 1.3 seconds for as-deposited and annealed ZnSe thin films respectively. Clearly, the carrier life time decreases on annealing the film. The straight lines in Fig. 4.24, obey a power law of the form t^{-N} , with $N = d(\ln \tau_d / \ln t)$ and the values of N are 0.69 and 0.82 for as-deposited and annealed ZnSe thin films.

CONCLUSIONS

The ZnSe thin films were deposited on well degassed corning glass substrates using inert gas condensation technique. The transition in the films was found to be direct. The optical band gap value decreases after annealing. The value of σ_d increases and ΔE_d decreases after thermal annealing. I-V curves are symmetric and linear up to the operating range of applied voltage. Steady state photoconductivity studies indicate that there is continuous distribution of localized states. Decay of photocurrent is non-exponential and slow which may be due to the presence of deeper localized states in this material. The value of decay time constant increases with time, confirming the non-exponential decay of photocurrent. The carrier life time is found to increase annealing.

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