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Electrical characterization of nanocrystalline zinc selenide thin films

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Abstract

In the present paper, we have studied the effect of photo-illumination on electrical properties of nanocrystalline ZnSe thin films. The ZnSe thin films with different grain sizes (coherently diffracting domains) have been prepared. The semiconducting material with the composition $Zn_{25}Se_{75}$ has been prepared using melt-quenching technique. Thermal evaporation technique has been used to prepare nanocrystalline ZnSe thin films on highly cleaned glass substrates at different partial pressures of Ar gas. The grain size has been controlled by the partial pressure of inert gas. The grain size has been calculated using X-ray diffraction plots. Mobility activation has been studied from the photocurrent decay curves. The effective density of states (N_{eff}), frequency factor (S), and trap depth (E) have been calculated for all the films having different grain sizes. Three different types of trap levels have been found in these films. There is a linear distribution of traps having different energies below the conduction band. The increase in photoconductivity is explained in terms of built in potential barriers (φ_b) at the grain boundaries.

Keywords: Effective density of states, Trap depth, Potential barrier
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Background

Recently, nanocrystalline materials are being investigated largely because of their potential for new technological applications as well as their scientific interest. Their size-dependent properties make it possible to change the wavelength of band-to-band transitions permitting emission in the green, blue, or even UV region of the light spectrum [1]. ZnSe is an interesting II-VI semiconducting material, widely used in optoelectronic devices, because its bandgap (2.7 eV) belongs to the visible region [2]. ZnSe is a highly photosensitive semiconductor, so great attention has been given to investigate its photoelectronic properties in order to enhance the performance of different devices and their applications. Nanocrystalline ZnSe can be synthesized by many methods such as chemical vapor deposition [3], molecular beam epitaxy, atomic layer epitaxy, pulsed laser, metalorganic chemical vapor deposition, and sputtering [4]. All of these techniques, besides being expensive, are not entirely able to control the size of the nanoparticles obtained. Inert gas condensation (IGC) is the method by which one can deposit films with high purity as deposition is done in vacuum. Also, IGC has many other advantages over other nano-processing methods including (1) the potentially very large number of pure metals, alloys, and composite materials which can be deposited with grain sizes less than 100 nm, (2) few shape and size limitations, (3) high production rates, (4) low initial capital investment requirements, and (5) most importantly, easily controllable processing parameters.

Results and discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of the ZnSe film deposited on the glass substrates at different pressures of Ar gas [5]. The spectrum in Figure 1 shows the diffraction peaks at 2θ values of 27.3°, 45.6°, and 53.8° at different pressures. The highest intensity reflection peak is at 2θ = 27.3° (111), with two another small intensity peaks at 2θ = 45.6° (220) and 53.8° (311), indicating that (111) is the preferred direction. The intensity of these peaks decreases as the pressure of Ar increases. The comparison of observed d values with standard d values [6] confirms the zinc blende type

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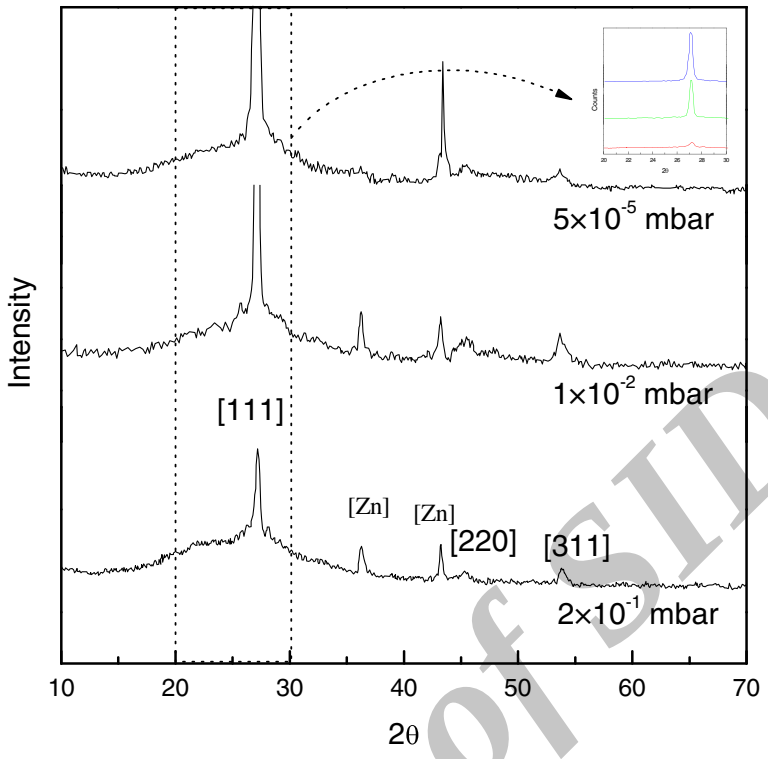

Figure 1 XRD plots for ZnSe thin films deposited at different pressures. Inset: relative intensity of (111) peak for the same plots.

nanocrystalline structure of ZnSe thin films. As described earlier, information on crystallite size is obtained from the full width at half maximum (FWHM) of the diffraction peaks using the relation [5]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{L} + \frac{\epsilon\sin\theta}{\lambda}, \tag{1}$$

where β is FWHM, ϵ is the strain, and L is grain size. The average grain sizes obtained are approximately 22.24, 18.52, and 6.65 nm for films deposited at different pressures.

Figure 2 shows the rise and decay of photocurrent for ZnSe thin films with different crystallite sizes. The trap depth (E) in nanocrystalline ZnSe thin films has been calculated using the relation

$$E = \left[\ln S - \ln\left\{\frac{\ln(I_0/I_t)}{t}\right\}\right], \tag{2}$$

where I_0 is the photocurrent when the illumination is stopped, I_t is the photocurrent at any subsequent time, t, after the termination of illumination, and S is the frequency factor (defined in terms of the number of attempts per second that quanta of photons are making to eject the electrons from the trap multiplied by the probability of transition of electron to the conduction band) [7]. The frequency factor can be calculated using

$$S = N_{\text{eff}}\nu_{\text{th}}S_t, \tag{3}$$

where N_{eff} is the effective density of states in the conduction band, ν_{th} is the thermal velocity, and S_t is the capture cross section of electrons. Now, the probability that an electron escapes from a trap depth E at temperature T is given by

$$p = S\exp\left(\frac{-E}{kT}\right). \tag{4}$$

N_{eff} is calculated by conductivity data with an assumption that the number of occupied energy levels in the conduction band is identical as N_{eff}. For the calculation of S, the values of mobility, thermal velocity, dielectric constant, and effective mass of an electron in ZnSe are considered from [8]. The calculated values of N_{eff} and S are represented in Table 1.

For the films with larger crystalline size, the value of S was found to be much greater than that with smaller size. Figure 3 presents the $\ln(I_0/I_t)$ vs. time plots for ZnSe thin films with different crystallite sizes. The trap depths for these films are calculated using the slopes of $\ln(I_0/I_t)$ vs. time plots and S. The different values of trap

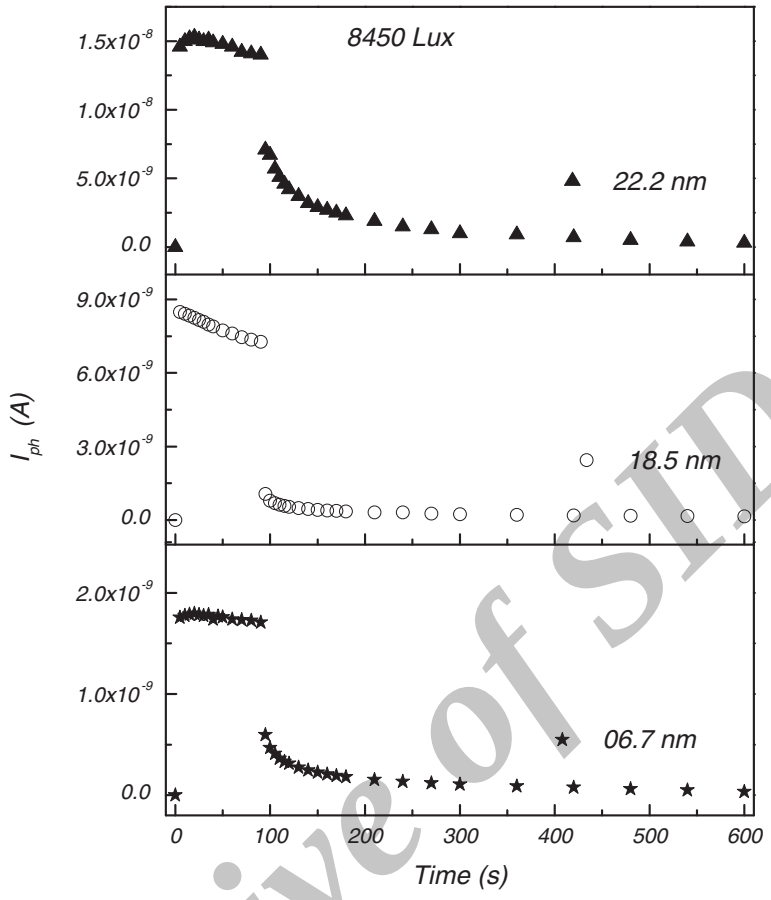

Figure 2 Decay of photocurrent at 298 K for ZnSe thin films having different crystallite sizes.

depths are also systematically presented in Table 1. There exist three different slopes in $\ln(I_0/I_t)$ vs. time plots, which indicates the existence of three distinct trap levels: E_1, E_2, and E_3, in all the films.

Due to the absorption of illuminating radiation, free electron–hole pairs are generated. The photo-generated electrons and holes in excess to the thermal equilibrium carriers are responsible for photoconduction process. The polycrystalline films are reported to have some built in potential barriers (ϕ_b) at the grain boundaries [9]. One part of the photo-generated carriers recombines with respective opposite charges localized at grain boundary depletion regions, thereby reducing the grain boundary potential barriers and the rest take part in the photoconduction process. As a result of the reduction of ϕ_b, the effective mobility of the carriers increases. This process is known as barrier modulation. The decrease in ϕ_b also leads to increase in effective mobility, thereby increasing the conductivity of the sample. Thus, the increase in photoconductivity has two main contributors, *viz.* one from the resultant increase in the photo-generated carriers and the other from the increase in the effective mobility.

Table 1 Some electrical parameters for ZnSe thin films with different crystallite sizes

Grain size	N_{eff}	S	E (eV)		
(nm)	(cm^{-3})	(s^{-1})	E_1	E_2	E_3
22.2	6.68×10^{11}	1.68×10^{7}	0.48	0.47	0.46
18.5	1.79×10^{9}	4.50×10^{4}	0.27	0.26	0.25
06.7	1.17×10^{10}	2.96×10^{5}	0.32	0.31	0.30

Conclusions

The nanocrystalline ZnSe thin films have been deposited in the presence of Ar gas. The partial pressure of gas governs the crystallite size. In these films, the photoconductivity is mainly due to two main factors, *viz.* resultant increase in the photo-generated carriers known as carrier modulation and increase of effective mobility known as barrier modulation. In the present case, trapping centers are responsible for controlling the photocurrent. Both shallow and deep traps are found to be available in these films. The observed trap depths are not single valued, and there is a quasi-continuous distribution of various traps.

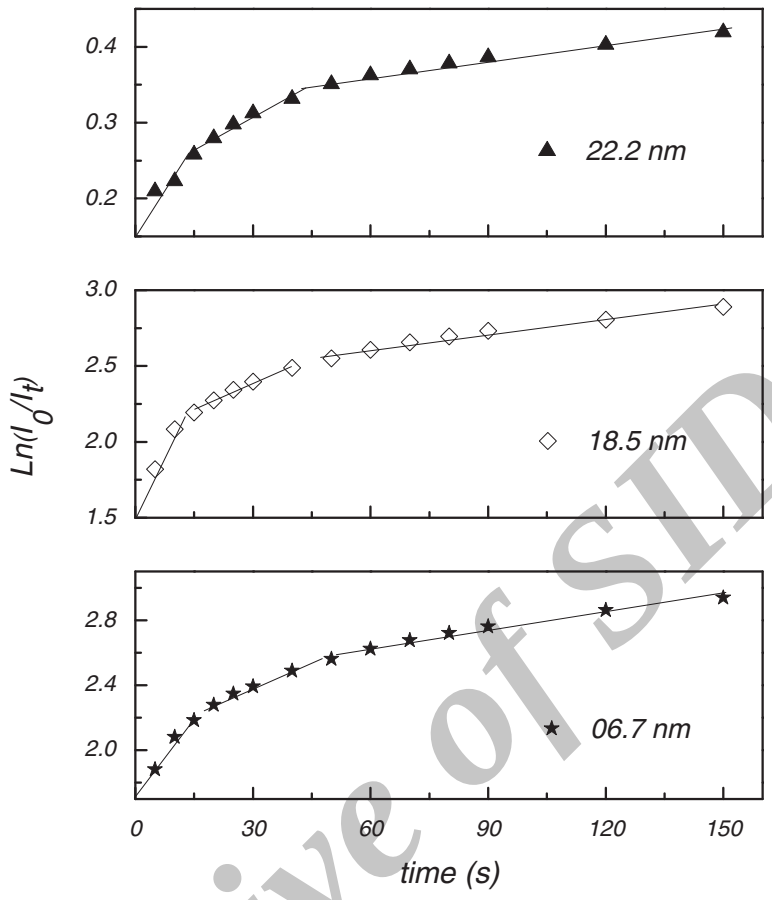

Figure 3 ln (I_0/I_t) vs. time plots for ZnSe thin films with different crystallite sizes.

Methods

The semiconducting zinc selenide with the composition $Zn_{25}Se_{75}$ is prepared from 5N pure constituents using melt-quenching technique as described earlier [10]. Thin films of this material are deposited on well-degassed, chemically cleaned Corning 7059 glass substrates (Corning, NY, USA) in a conventional vacuum coating system in the presence of argon gas. Thermal evaporation of the material is carried out from the Mo boat at different pressures (5×10^{-5}, 1×10^{-2}, and 2×10^{-1} mbar) of argon gas. A planar geometry of the film (length approximately 1.0 cm and electrode gap approximately 8×10^{-2} cm) is used for the electrical measurements. The photocurrent measurements are carried out in a metallic sample holder in order to avoid noises. Heat-filtered white light of 8,450-lx intensity (200-W tungsten lamp) is directed on the sample through a transparent glass window. Pre-deposited thick indium electrodes are used as ohmic contacts. A vacuum of about 10^{-3} mbar is maintained throughout these measurements. Light intensity is measured using a digital luxmeter (MS6610, MASTECH, Shenzhen, China). Crystallographic study is carried out with a Philips PW-1610 X-ray diffractometer (Amsterdam, The Netherlands) using CuKα radiation (λ = 1.54056 Å).

Abbreviations

FWHM: Full width at half maximum; IGC: Inert gas condensation.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

JS carried out the preparation of thin films, recorded the XRD spectra and electrical observations of these films, and also analyzed the spectra. He also participated in the sequence alignment and drafted the manuscript. DS carried out the analysis of electrical parameters of these films. SKT helped analyze the results and supervised this work to complete successfully. All authors read and approved the final manuscript.

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