

EFFECT OF DEPOSITION PARAMETERS ON THE OPTICAL AND ELECTRICAL PROPERTIES OF NANOCRYSTALLINE CdSe

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Nanocrystalline semiconductor offers a wide variety of possible applications in electronics, optoelectronics and photonics. CdSe ($E_g = 1.7$ eV), a direct band gap semiconductor, is chemically grown in an aqueous alkaline medium using sodium selenosulphate as Se^{2-} source. The formation of CdSe nanocrystals has been confirmed with the help of infrared (IR) spectroscopy by observing bands corresponding to the multi phonon absorption. n-CdSe thin films have been deposited at different temperatures of bath solution. Electrical, optical and structural studies have been done on these thin films. The shift in E_g (~ 0.5 eV) and the variation of grain size of CdSe crystallite from 30 Å to 40 Å has been observed when the temperature of the bath varies from 26 °C to 80 °C. These changes are attributed to the quantum size effect in nanocrystalline semi conducting films.

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1. Introduction

The synthesis of binary metal chalcogenides of II-VI semiconductors in nanocrystalline form has experienced an enormous development in the recent years owing to their interesting size dependent optical and electrical properties [1, 2]. In particular, nanostructures of CdSe have received considerably more attention due to its great fundamental [3], experimental and applied interests. CdSe nanocrystals are useful in understanding the phenomenon of quantum confinement effect and are used in the fabrication of devices like PV cells [4], lasers [5], TFTs [6], Light-emitting diodes [7] and other nanoscale devices [8]. Blue shift in the band gap of this material, with decreasing grain size, has lead to many applied investigations. CdSe nanocrystalline films have been prepared by various techniques including chemical bath deposition (CBD) [1]. CBD is a well known method for preparing semiconductor layers and has been used mainly for metal selenides. Chemically deposited films found their sound application in photovoltaics. The films prepared by CBD are usually composed of closely spaced nanocrystals [9]. The band gap engineering of films is possible by tailoring of the NC size, which can be done by changing the parameters of deposition [10, 11]. To deposit a film, it is necessary to slow down the rate of chemical reactions to such an extent that CdSe is either directly formed on the substrate or small particles of CdSe are formed in the solution and subsequently adhere to the growing film, rather than aggregate into large particles in the solution and precipitate out. In CBD, this rate control is accomplished by a slow generation of Se^{2-} ions in the deposition (e.g., by alkaline hydrolysis of sodium selenosulphate (Na_2SeSO_3) [1]. Some of the authors distinguish two regimes for the formation of CdSe films. In the ion-by-ion deposition mechanism, CdSe is grown by ionic reaction between Cd^{2+} and Se^{2-} , while in cluster deposition mechanism, CdSe is formed by conversion of $Cd(OH)_2$ in the deposition solution by selenide ion[1]. Both mechanism can, in principle coexist- their relative importance is affected by the concentration of individual components in the deposition solution, by the solution pH, by temperature, etc. This leads to a large number of free parameters that can be adjusted in the procedure of CBD. The deposition parameters are usually optimized to obtain specularly reflecting films with a good adherence to the substrate [9-11].

In this paper, we report on the preparation of highly reflecting CdSe films in the alkaline medium. We describe the effect of temperature on the optical and electrical properties of CdSe nanocrystalline films.

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2. Experimental

Substrate cleaning plays an important role in the deposition of thin films. Commercially available glass slides were boiled in chromic acid for 2 h, washed with detergent, rinsed in acetone and finally cleaned with double distilled water before use. Cadmium selenide thin films were deposited on glass substrates by the method of chemical bath deposition (CBD). The basic idea of deposition is a reaction between a slowly released selenide anion with a free metal cadmium cation (Cd^{2+}). As precursor of selenide ions (Se^{2-}), sodium selenosulphate (Na_2SeSO_3) was used. The pH value of the reaction system is of prime importance for the chemical deposition of CdSe thin films. The precursor of selenide ions, sodium selenosulphate, was used in the form of solution, which has been obtained by adding selenium powder to a hot solution of sodium sulphite, magnetically stirring this mixture for several hours at 80 °C and filtering the excess of selenium. This solution is relatively unstable and therefore it must be freshly prepared prior to thin film deposition process. The optimal chemical composition of reaction system for preparation of photoconductive CdSe thin films were obtained by mixing the following solutions: 10 ml of 0.5 M cadmium acetate solution was taken in a 100 ml capacity glass beaker and to it, 5 ml of triethanol amine, 10 ml of 25% ammonia and 15 ml of sodium selenosulphate was slowly added with constant stirring. The final pH of the chemical bath was 10 ± 0.1 . The solution was stirred for few seconds and then transferred into another beaker containing cleaned glass substrate inclined vertically at 20° to the walls of the beaker. The bath solution was formed at different temperatures at constant pH. After about 6 h the deposited films were thoroughly washed with double distilled water and dried in air. The CdSe thin films were uniform, well adherent to the substrates and red-orange in color.

Crystallographic study was carried out before and after annealing using a Phillips PW-1710 X-ray diffractometer using CuK_α radiation in the 2θ range from 10° to 70°. To study the optical properties of n-CdSe thin films, the transmission spectra were recorded using Monochromator-spectrograph [*SOLAR III*, MS 2004] in the transmission range 400-1000 nm for all samples. FTIR spectra have been recorded using Perkin Elmer PE-RX 1 FTIR spectrophotometer. The spectral resolution of the IR spectrophotometer was 1 cm^{-1} throughout the experiment. 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 ~ 2.38 cm; electrode gap 8×10^{-2} cm) was used for the electrical measurements. Thick In electrodes were used for the electrical contacts. The film thickness was measured to be ~ 100 nm with the commonly used weight difference method. The photocurrent (I_{ph}) was obtained after subtracting the dark current (I_d) from the current measured in the presence of light. The dark- and photo- current was noted manually using a digital picoammeter (DPM-11 Model). Accuracy in I_{ph} measurements was typically 1 pA.

3. Results and discussion

3.1 Structural and Optical Properties

Fig. 1 shows the diffraction spectrum of n-CdSe thin film. In this spectra, there is a highest intensity reflection peak at $2\theta = 25.3^\circ$ [111], with two small another intensity peaks at $2\theta = 41.8^\circ$ [220] and 50° [311]. The comparison of observed 'd' values with standard 'd' values [12,13] confirms that the deposited film is having sphalerite cubic (zinc blende type) nanocrystalline structure.

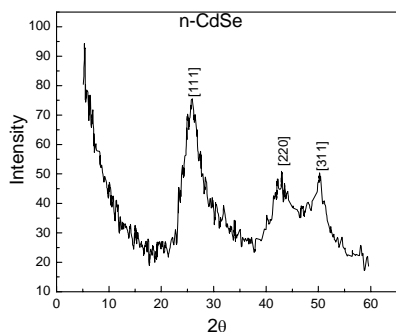


Fig.1. The XRD pattern of CdSe thin films deposited at 300 K at pH 8

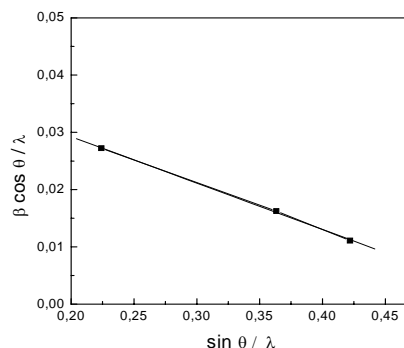


Fig. 2. Plot of $\sin\theta/\lambda$ vs. $\beta\cos\theta/\lambda$ for CdSe thin film.

Information of the strain and the particle size are obtained from the full width at half maximum (FWHMs) of the diffraction peaks. The FWHMs (β) can be expressed as a linear combination of the contributions from the strain (ε) and particle size (L) through the following relation [19]

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon \sin \theta}{\lambda} \quad (1).$$

Fig. 2 represents the plots of $(\beta \cos \theta)/\lambda$ versus $(\sin \theta)/\lambda$ for n-CdSe thin film which is a straight line. The slope of the plot gives the amount of residual strain, which turns out to be -8.11×10^{-2} for n-CdSe thin film. The reciprocal of intercept on the $(\beta \cos \theta)/\lambda$ axis gives the average particle size as ~ 3.3 nm. The negative value of residual strain for the as-deposited film indicates the compressive strain. If the film is deposited free from impurities, the compressive strain is generated at the thin film substrate interface, when the very small crystallites are bonded to substrates due to surface tension effect.

Fig. 3. shows the FTIR spectrum of CdSe nanocrystals. The presence of the band at 1387 cm^{-1} and 1561 cm^{-1} confirms the presence of capping agent trisodium citrate used for above study. The former band can be assigned to symmetric stretching of COO^- , while the later band can be assigned to the asymmetric COO^- [15]. Another band at 3368 cm^{-1} can be assigned to OH stretching of trisodium citrate. The presence of above mentioned bands shoulders around 1420 cm^{-1} shows that trisodium citrate is bounded to the CdSe nanocrystals and it is arresting the growth of bulk crystals of CdSe.

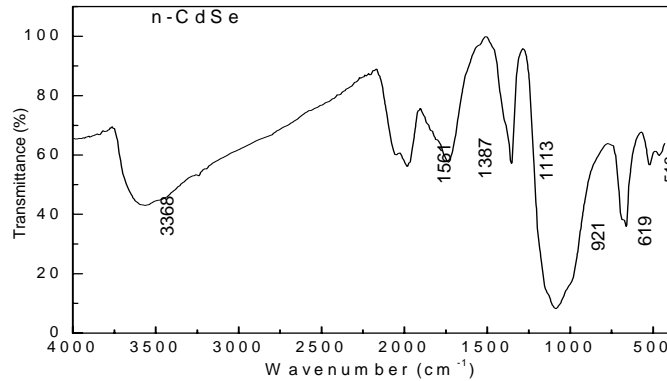


Fig. 3. FTIR spectrum of CdSe nanocrystals.

Optical properties are studied by recording the transmission spectra of the films. Fig. 4 shows the transmission data of n-CdSe thin films deposited at different temperatures of bath solutions i.e., 300 K, 323 K, 353 K. 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

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

The fundamental absorption, which corresponds to the transition from valence band to conduction band, can be used to determine the band gap of the material. The relation between α and the incident photon energy ($h\nu$) can be written as [16]

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (3)$$

where A is a constant, E_g is the band gap of the material and the exponent n depends on the type of transition. The n may have values $1/2$, 2 , $3/2$ and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

The value of E_g is calculated by extrapolating the straight line portion of $(\alpha h\nu)^{1/n}$ vs $h\nu$ graph to $h\nu$ axis taking $n = 0.5$. Fig. 5 shows the plots of $(\alpha h\nu)^2$ vs $h\nu$ for as-deposited and annealed thin films. The correct values of the optical gap calculated from the plots are (2.25 ± 0.01) eV, (2.00 ± 0.01) eV and (1.90 ± 0.01) eV for the films deposited at different temperatures. The value of E_g is found to decrease with the increase in the deposition temperature. These values of optical gap are inserted in Table 1. Clearly, the observed values of E_g are higher than the value of bulk optical gap of CdSe $[(1.74 \pm 0.01)$ eV] [17] due to quantum confinement in the CdSe nanocrystallites.

From the blue-shift of the band gap (E_g), we can calculate the average diameter of the particles using relation [18, 19], since change in the value of E_g suggests weak confinement of the exciton:

$$\Delta E_g = E_g(\text{film}) - E_g(\text{bulk}) = E_{\text{shift}} = \frac{\hbar^2 \pi^2}{2\mu R^2} \quad (4)$$

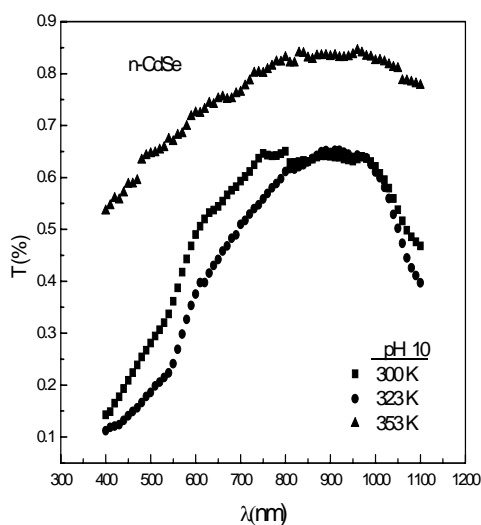


Fig. 4. Plot of transmission vs. wavelength for n-CdSe thin films deposited at different temperatures

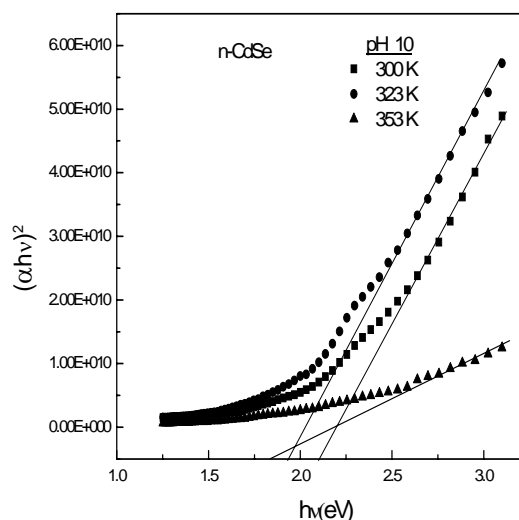


Fig. 5. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for n-CdSe thin films

where E_{shift} is the shift in the band gap, μ the translation mass ($m_{\text{hole}} + m_{\text{electron}}$) and R the radius of the nanoparticles. This formula is applicable in our case as we are well below the strong confinement regime and hence observe the effects due to weak confinement of the exciton only. We have calculated the average diameter of the particles using Eq. (4) as ~ 2.3 nm, 2.9 nm and 3.6 nm for films deposited at 300 K, 323 K and 353 K respectively. These values are very close to the values obtained from XRD data. Infact, the experimentally measured crystalline size in the small size regime does not agree well with the size estimated from the blue shift using effective mass approximation [20]. The disagreement in size estimated by XRD and the blue shift can be assigned, therefore, to the non-spherical geometry of nanoparticles.

Table 1.

Temperature (K)	E_g (eV) (± 0.01)	Particle size(nm) optical	σ_d ($\Omega^{-1}\text{cm}^{-1}$)	E_a (eV) (± 0.01)	σ_{ph} ($\Omega^{-1}\text{cm}^{-1}$)	σ_{ph}/σ_d
303	2.25	2.3	$(2.2 \pm 0.02) \times 10^{-9}$	0.74	$(5.9 \pm 0.02) \times 10^{-8}$	26.8
323	2.00	2.9	$(2.8 \pm 0.02) \times 10^{-9}$	0.69	$(6.4 \pm 0.02) \times 10^{-8}$	22.8
353	1.90	3.6	$(4.4 \pm 0.02) \times 10^{-9}$	0.66	$(7.7 \pm 0.02) \times 10^{-8}$	17.5

3.2 Electrical Properties

Fig. 6 shows the temperature dependence of dark conductivity (σ_d) for n-CdSe thin films deposited at different temperatures. The electrical conductivity shows typical Arrhenius type of activation

$$\sigma_d = \sigma_o \exp\left(\frac{-\Delta E}{kT}\right) \quad (5)$$

where ΔE is the activation energy for conduction and k is the Boltzmann's constant. The values of σ_d , calculated using Eq. (5), are $(2.2 \pm 0.02) \times 10^{-9} \Omega^{-1}\text{cm}^{-1}$, $(2.8 \pm 0.02) \times 10^{-9} \Omega^{-1}\text{cm}^{-1}$ and $(4.4 \pm 0.02) \times 10^{-9} \Omega^{-1}\text{cm}^{-1}$ for films deposited at 300 K, 323 K, 353 K respectively. The value of σ_d increases as the particle size of n-CdSe increases. Fig. 7 shows the temperature dependence of photoconductivity (σ_{ph}) for films deposited at 300 K, 323 K and 353 K. The values of σ_{ph} are found to be $(5.9 \pm 0.02) \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$, $(6.4 \pm 0.02) \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$, $(7.7 \pm 0.02) \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ respectively. The value of σ_{ph} increases on increasing the deposition temperature of n-CdSe thin film. The activation energy for photoconduction is much smaller than dark conduction. No maximum in the steady state photoconductivity with temperature has been observed in the measured temperature range.

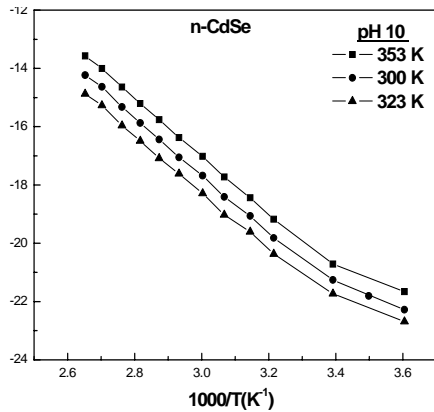


Fig. 6. Plot of $\log \sigma_{\text{dark}}$ vs. $(1000/T)$ of n-CdSe thin films.

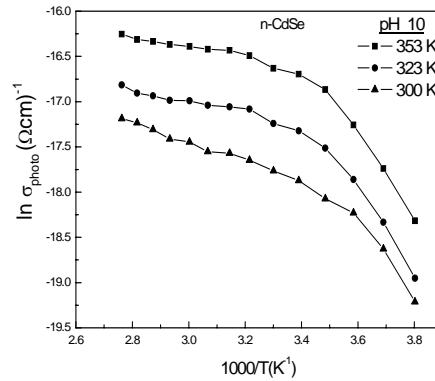


Fig. 7. Plot of $\log \sigma_{\text{photo}}$ vs. $(1000/T)$ of n-CdSe thin films.

4. Conclusions

From above studies, it is concluded that the n-CdSe thin films deposited by aqueous alkaline medium at different temperatures (303 K, 323 K and 353 K) grow with nanocrystalline phase with band gap varying from 2.25 eV to 1.9 eV and the electrical conductivity also increases. The optical study shows that the CdSe thin films are size-quantized i.e., nanocrystals behave as quantum dots with blue shifted band gap energy of 0.5 eV in comparison to the bulk value. By controlling the temperature of the reaction solution, the presented method permits to design optoelectrical properties of highly photoconducting n- CdSe films.

Acknowledgements

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