

Effect of UV- irradiation on chemically deposited nanocrystalline CdSe films

Charita Mehta¹, G.S.S. Saini², S.K. Tripathi³

^{1,2,3} Department of Physics

¹GGN Khalsa College Ludhiana-141004 India

^{2,3} Panjab University, Chandigarh-160 014 (INDIA)

Abstract- Nanocrystalline films and nanocrystals of cadmium selenide are chemically deposited from an alkaline bath using sodium selenosulphate as Se^{2-} ion source. The formation of CdSe has been confirmed with the help of infrared spectroscopy by observing bands corresponding to the multiphonon absorption. The samples characterized by optical spectroscopy and X-ray diffraction have the nanocrystal radii 2-4 nm. Optical gaps (E_g) higher (up to 0.5 eV) than in single crystal samples are observed and explained in terms of quantum size effect. Increase in E_g depends strongly on deposition temperature with a greatest increase obtained at lowest temperature. Structural studies of as-deposited layers showed them to be composed of nanocrystalline cubic CdSe depending on deposition temperature. We demonstrate the effect of UV- irradiation on the optical properties of nanocrystalline films.

I. INTRODUCTION

Nanocrystalline materials have opened new chapter in the field of electronic application since they exhibit scientifically interesting phenomena and desirable engineering characteristics. Properties of the materials in the nanometer scale could be changed by changing the crystallite size and/or shape of the film. Semiconductor nanoparticles have attracted great interest in both theoretical and applied research areas [1-2]. CdSe an important member of luminescent II-VI family having luminescence in the visible range of optical spectra, has shown potential to be used in nanocrystalline form in biological field [3], TFTs [4], diodes and lasers [5], solar cells [6], and other nanoscale devices [7]. By appropriate choice of CdSe nanocrystal (NC) size, the absorption edge can thus be made to fall anywhere in the visible region. In recent years, major attention have been given to the investigation of electrical and optical properties of CdSe thin films in order to improve the performance of the devices and also for finding new applications [8].

CdSe nanocrystalline films have been prepared by various techniques including chemical bath deposition (CBD) [9]. CBD aside of its industrial use, is also a cheap technique for preparation of semiconductor crystallites with dimensions

of a few nanometers. Under certain preparation conditions, the chemically deposited films are nanocrystalline and exhibit quantum size effect (confinement of carriers within individual NCs). The quantum confinement effects strongly the optical properties of the film in the same way as in the case of individual nanocrystals. The optical properties of NCs can be changed by varying the parameters of chemical bath deposition and/or by subsequent heat or chemical treatment of the films [9, 10-11]. The ability to control the optical properties of NCs has made this field of material science very interesting for fundamental understanding and technological applications. CdSe thin films investigated in this paper consist of closely spaced NCs, properties of which show many similarities with those of isolated NCs.

II. 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 CBD. In this method, the solution chemistry is chosen such that a spontaneous reaction from liquid phase is possible. When the ionic product exceeds the solubility product, precipitation occurs and ions combine on the substrate and in the solution to form nuclei which result in thin film formation on the substrate and the precipitation in the solution. 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 highly reflecting CdSe nanocrystalline films were obtained by mixing the following solutions; 10 ml of 0.3M cadmium acetate solution taken in 100 ml capacity glass beaker and to it, 10 ml of 0.13M sodium citrate, 10 ml of sodium selenosulphate and 20 ml of double

distilled water was slowly added with constant stirring. The final pH of the chemical bath was 8.0 ± 0.1 . The solution was stirred for sometime and then transferred into another beaker containing cleaned glass substrates. The glass substrates were held vertically in the bath by placing them against the walls of beakers containing the deposition mixture. The bath solution was also 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 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 TII, 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.

III. RESULTS AND DISCUSSION

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 without an interfacial layer. 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 [14].

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

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.

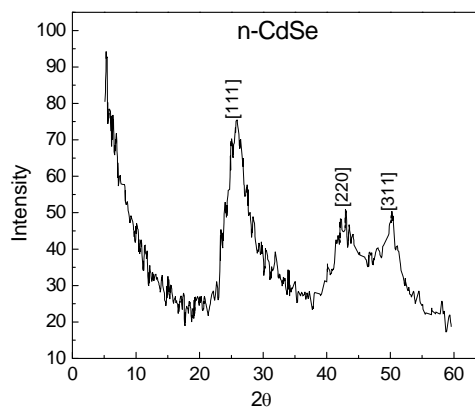


Fig.1 The XRD pattern of CdSe thin films deposited at 300 K at pH 8.

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.

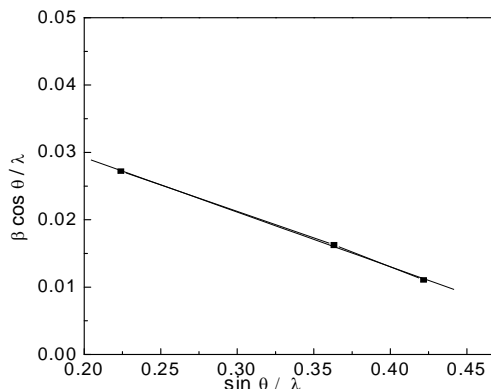


Fig. 2 Plot of $\sin \theta / \lambda$ vs. $\beta \cos \theta / \lambda$ for CdSe thin film.

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].

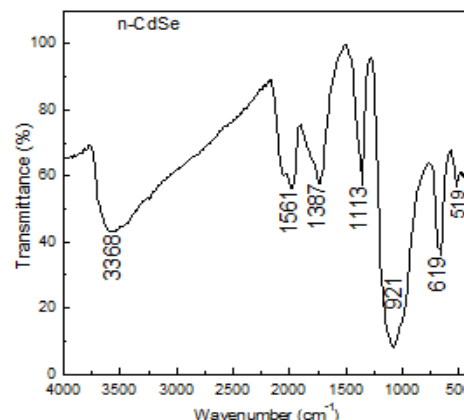


Fig. 3 FTIR spectrum of CdSe nanocrystals.

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.

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.

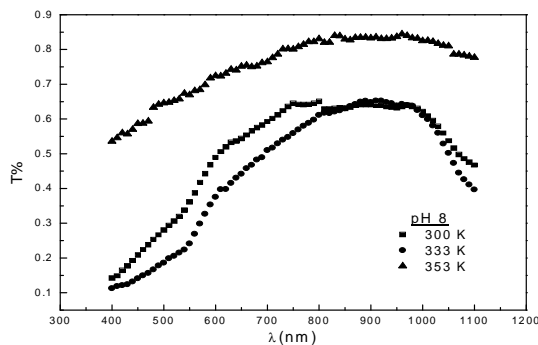


Fig. 4. Plot of transmission vs. wavelength for n-CdSe thin films deposited at different temperatures.

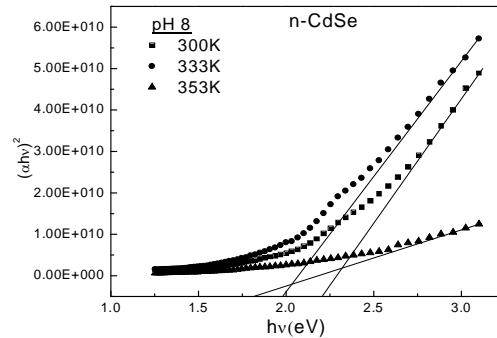


Fig. 5. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for n-CdSe thin films.

The value of E_g is found to decrease with the increase in the deposition temperature. Clearly, the observed values of E_g are higher than the value of bulk optical gap of CdSe [1.74 ± 0.01 eV] due to quantum confinement in the CdSe nanocrystallites.

In order to explore further the properties of CdSe NC films, we studied the effect of UV irradiation at different time intervals on the optical properties of the same. Fig. 6 shows the transmission data of n-CdSe thin films irradiated by UV light at different time intervals of 1 h, 4 h, and 5 h.

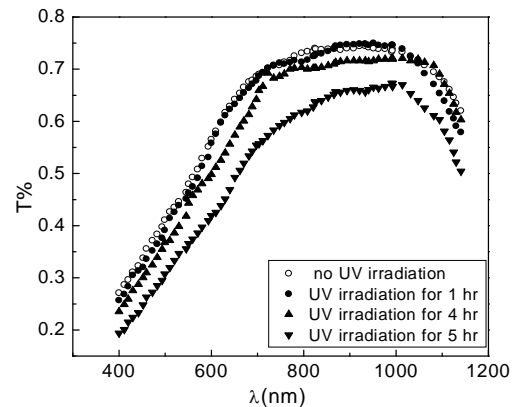


Fig. 6 Plot of transmission vs wavelength for CdSe NC films irradiated with UV light at different time intervals.

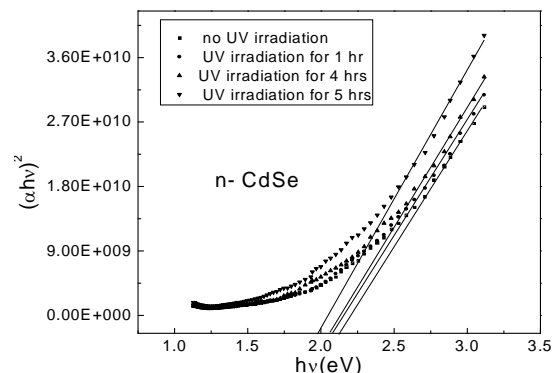


Fig. 7 Variation of energy with $(\alpha h\nu)^2$ for n-CdSe films.

Fig. 7 shows the plots of $(\alpha h\nu)^2$ vs energy for n-CdSe films. Band gap decreases from (2.17 ± 0.01) eV, (2.1 ± 0.01) eV, (2.07 ± 0.01) eV and (2.0 ± 0.01) eV when UV light is irradiated for time intervals of 1 h, 4 h and 5 h respectively. Thus on irradiating UV light at increasing time intervals particle size of CdSe NCs increases.

III. CONCLUSIONS

We have observed that the n-CdSe films deposited by chemical bath technique at different temperatures grow with nanocrystalline phase. 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. Further on irradiating UV light at different time intervals over n-CdSe films band gap decreases.

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