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Synthesis, microstructure study and optical characterization of chemical bath deposited nanocrystalline CdSe thin films

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We report on the preparation of high-quality nanocrystalline CdSe thin films, which have been deposited successfully by the chemical bath deposition method using triethanolamine as a complexing agent. The effect of various process parameters, such as deposition time and temperature, concentration of species, speed of magnetic stirring, reflux time in condenser for the preparation of selenium precursor, pH of bath etc. on the growth and quality of the films are studied experimentally. Structural morphology is observed by scanning electron microscope (SEM). Band gap measurements for the prepared films have been done with the help of optical transmission spectra using UV-VIS-NIR spectrophotometer (190-1100Å). The action spectra showed displacement in the absorption edge towards lower wavelength side after formation of nano phase material at room temperature. The energy gap increased from 1.74 eV (bulk-CdSe) to 2.65 eV (nano-CdSe) for 0.4M concentration in 24 hour deposition. This substantial improvement of the properties of the prepared films was accomplished by a modification of the chemical bath deposition procedure. The values of some important parameters of the studied films (extinction coefficient, refractive index, dielectric constant and optical conductivity) are determined from transmission spectra. The size of the nano particles is calculated using Effective Mass Approximation method.

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Keywords: CdSe thin films, optical studies, nanocrystalline, SEM, band gap

1. Introduction

The advent of thin-film technology contributed to a prediction of greatly reduced costs for thin film solar cells that has yet to be achieved. An advantage of thin-film technology theoretically results in reduced mass so it allows fitting panels on light or flexible materials, even textiles. A key aspect of semiconductors in a nano crystalline thin film form is the modification of the energy levels and the density of states owing to the confinement of the charge carriers. The charge carriers are localized in nano crystals and this leads to a blue shift in the band gap [1]. The physical properties of nanostructures are substantially influenced by the synthesis route and have a strong bearing on the structure and microstructure of the specimens. Nano-crystalline thin films of semiconductors have been the subjects of intensive studies from fundamental, experimental and applied interests.

Cadmium selenide solid is a semi conducting material, but has yet to find many applications in manufacturing. Much current research on cadmium selenide has focused on controlled syntheses of CdSe nano particles. In addition to synthesis, scientists are working to understand the properties of cadmium selenide, as well as apply these materials in useful ways. Whatever be the method of synthesizing of the nano particles, it is essential to avoid the coalescence of particles into larger particles and achieve mono dispersity and chemical stability over a long period. At nanometer scale the properties of the material becomes size-dependent and hence can be tailored by changing the size [2]. Nano size effect occurs even if only one dimension of the bulk material is of nanometer size. The relationship between the size of a structure and the energy quanta that interact with it is very important in the control of light by molecules and by nanostructures viz. 0-D, 1-D & 2-D. Characterization involves determining the shapes and sizes of nano particles, their structure and understanding of the inter-particle interaction.

CdSe is an important material for the development of various modern technologies of solid-state devices such as solar cells [3], high-efficiency thin-film transistors [4], light-emitting diodes [5] & opto-electronics applications etc. [6]. Compounds from (II-VI) group viz. $A^{II}.B^{VI}$ show high efficiency of radiative recombination, high absorption coefficients ($=10^6$ cm^{-1}) and direct band gaps corresponding to a wide spectrum of wavelengths from ultraviolet to infrared regions. The evaluation of optical band gaps and refractive indices of semiconductors is of vital importance for the design of integrated optic devices such as switches, filters, modulators and heterostructure lasers etc [7]. The potential of cadmium chalcogenides for low cost photovoltaic power generation has stimulated many efforts around the world to develop such devices. The control of film composition and properties has proven difficult in CdSe film, and a deeper study of deposition technique is needed. In recent year major attention have been given to the investigation of electrical and optical properties of CdSe thin films in order to improve the performances of the devices and also for finding new applications [8-10]. CdSe thin films have been prepared using a variety of methods including electro deposition [11], physical vapor deposition[12], sonoelectrochemically deposition [13], laser ablation technique [3], brush plating [14], low pressure metal organic chemical vapour deposition [15], hot wall deposition [16], sputtering, spray pyrolysis [8, 17] etc. In the present work, we have prepared by chemical bath deposition (CBD) technique and studied pure CdSe thin film because of its high photosensitivity and suitable intrinsic band gap=1.74 eV [18].

The experimental procedure has been presented and results are discussed in the next sections. The last section deals with the conclusions of this work.

2. Experimental

2.1 Film preparation

Though difficult, we have successfully prepared the CdSe thin films using chemical bath deposition technique. Ours CBD technology is based on the controlled release of the ions in a bath containing aqueous solution of $(CH_3COO)_2Cd.2H_2O$ (A.R. 99%) and freshly prepared and filtered selenium precursor solution (Na_2SeSO_3) under reflux in condenser along with magnetic stirring and without reflux for a period between three and four hours. Different baths are used to obtain films of various concentration (0.1M -0.5M) and thickness. The high purity (99.99%) selenium pellets of analytical reagent grade are used here. 25% ammonia solution and triethanolamine was used to adjust pH of the reaction mixture and to increase the film adherence. To obtain good quality films, time, temperature of deposition and pH of the solution were optimized. These optimum values were observed to be 24hrs, room temperature and 11±0.3 respectively. The pH value is of prime importance. All the depositions were made and samples were dried at room temperature. The reason for drying the samples at lower temperature was to avoid the cracks in the samples. In this technique the deposition is based on the principle of precipitation followed by condensation in a glass slide of dimension 75 mm x 25mm x 1mm. Before immersing the glass substrate into the reaction bath, it is normally degreased in nitric acid for 48 hours, cleaned in ultrasonic cleaner with distilled water, washed with detergent and then allowed to dry in open air at room temperature. This process is to ensure a clean surface, which is necessary for formation of nucleation centers, required for thin film deposition. In present paper the influence of the preparation conditions on the optical properties of CdSe thin films and its microstructure is investigated. Different concentrations are checked for maximum band gap enlargement

2.2 Measuring instruments

Characterization of nanostructures requires extreme sensitivity and accuracy with atomic level resolution. Novel tools and instruments are needed for proper results. The size quantization effects of nano particles of pure CdSe are studied using UV-visible absorption spectra. Optical transmission & absorption spectra of the films were recorded at room temperature in the wavelength range of 300-1100 nm using UV-VIS-NIR double beam spectrophotometer CHEMITO SPECTRASCAN-2600. A sample holder was mounted in front of the monochromator, which has two sample positions. The first position has the sample film and the other has a clean glass substrate as a reference. Characterization of the sample using other experimental tools such as scanning electron microscope is also given. SEM studies for microstructure of the prepared films, using JEOL-JSM 5600 model has been performed at Inter University Consortium - Department of Atomic Energy (IUC-DAE), Indore.

3. Results and discussion

3.1 Growth kinetics

The deposits are smooth well adherent to the substrate, uniform, densely packed and reproducible over the entire range of the composition parameter. Initially the color of the sample was orange and it turns to orange- red with increase in time. This might be due to the increased rate of release of Se from sodium selenosulphite. The reactant concentration, pH, deposition temperature, reflux and rate of agitation were found to influence significantly the quality and thickness of the films. Absorption spectra of film specimens have shown blue shift in absorption edge as compared to their bulk counterpart indicating increased band gap energy due to quantum confinement effect. This paper reports on an investigation of the optical properties of chemical bath deposited cadmium selenide thin film. The optical properties investigated include the Absorbance (A), Transmittance (T), and Reflectance (R), which were used to calculate the other properties such as refractive index (n), extinction coefficient (k), dielectric constant (ε), and optical conductivity (σ).

Table 1. Technological parameter of composition and optical properties of CdSe films.

S. No.	Sample Name	Molar Concentration	Thickness	Band Gap (eV)	Band Gap Shift (eV)	Particle Size (nm) (Effective Mass Approximation)
1	CdSe 18	0.1 M	2280 nm	1.90	0.16	1.80
2	CdSe 30	0.2 M	902 nm	1.75	0.01	7.20
3	CdSe 34	0.2 M	394 nm	2.18	0.44	1.09
4	CdSe 36	0.2 M	526 nm	2.16	0.42	1.11
5	CdSe 22	0.3 M	701 nm	1.75	0.01	7.20
6	CdSe 26	0.3 M	902 nm	2.18	0.44	1.09
7	CdSe 62	0.4 M	166 nm	2.65	0.91	0.75
8	CdSe 63	0.4 M	541 nm	2.60	0.86	0.78
9	CdSe 64	0.4 M	360 nm	2.62	0.88	0.77
10	CdSe 66	0.4 M	341 nm	2.62	0.88	0.77
11	CdSe 68	0.4 M	350 nm	2.62	0.88	0.77
12	CdSe 69	0.5 M	315 nm	2.05	0.31	1.29
13	CdSe 71	0.5 M	323 nm	2.13	0.39	1.15

3.2 SEM analysis

Surface morphology of the films was observed by the SEM images. Some representative CdSe films of thicknesses (166 nm and 341 nm) and molar concentration 0.4M are given (in fig. 1 & 2) each at a magnification of 750x, 3,300x and 10,000x. In general, films are smooth, homogeneous, continuous and well covered to the substrate. Figures show the small spherical nano sized grains, which indicate the nano crystalline nature of CdSe films. Also some overgrowth of particles was observed at few places.

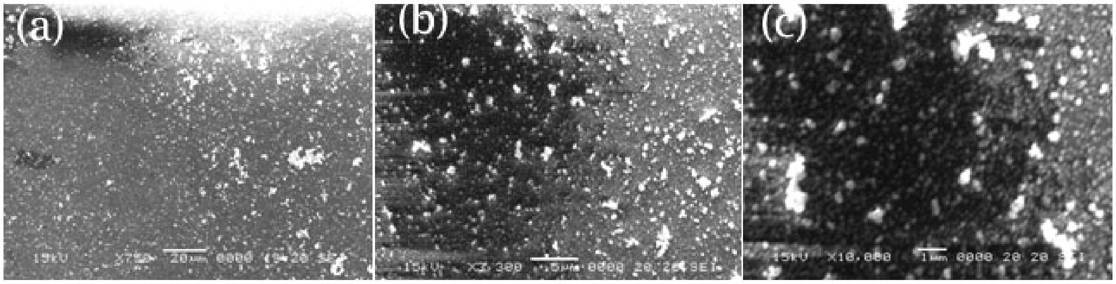

Fig. 1. SEM micrograph of the CdSe film (molar concentration=0.4M, thickness – 166nm) (a) × 750, (b) × 3300, (c) × 10000.

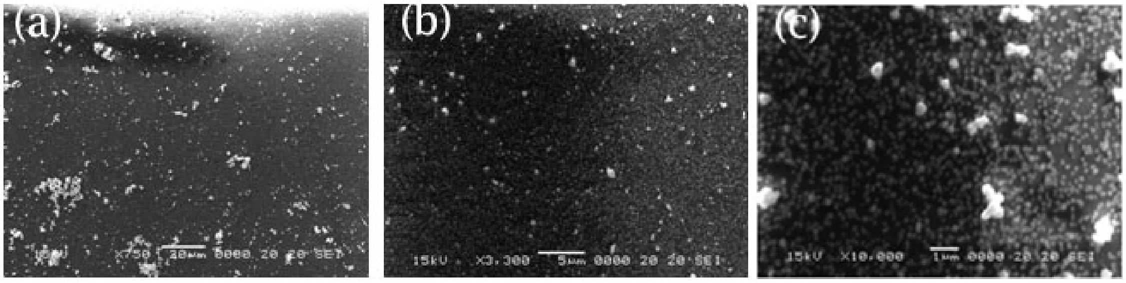

Fig. 2. SEM micrograph of the CdSe film (molar concentration=0.4M, thickness – 341nm) (a) × 750, (b) × 3300, (c) × 10000.

3.3 Absorption spectra/transmission spectra

Different materials absorb photons of different energies, so the color of different materials is different and measurements of the absorptivity 'A' (fraction of intensity of electromagnetic radiation that is absorbed) as a function of photon energy provides useful information on the electronic properties of the material. Absorption losses occur when the frequency of the light is resonant with oscillations in the electronic or molecular structure of the material. Various ions and functional groups have characteristic absorption peaks at well-defined frequencies.

Optical absorption is commonly used in characterization of size of semiconductor nano crystals. Photons of energy ($h\nu$) less than the forbidden energy gap (E_g) of the crystals are not absorbed. Absorption starts at $h\nu = E_g$ and then increases rapidly. It is known that reduction in size of crystals to nanometer range causes increase in effective forbidden gap of crystals due quantum confinement effect. In case of nano crystals absorption starts at higher energy. In small mono dispersed nano crystals stepwise absorption or absorption peaks are obtained. Optical absorption studies of CdSe films were carried out in the wavelength (λ) range 300-1100 nm at room temp. The variation of absorbance with wavelength (λ) shows presence of sharp peaks (1D nano tubes) & an absorption increase (most 3D solids).

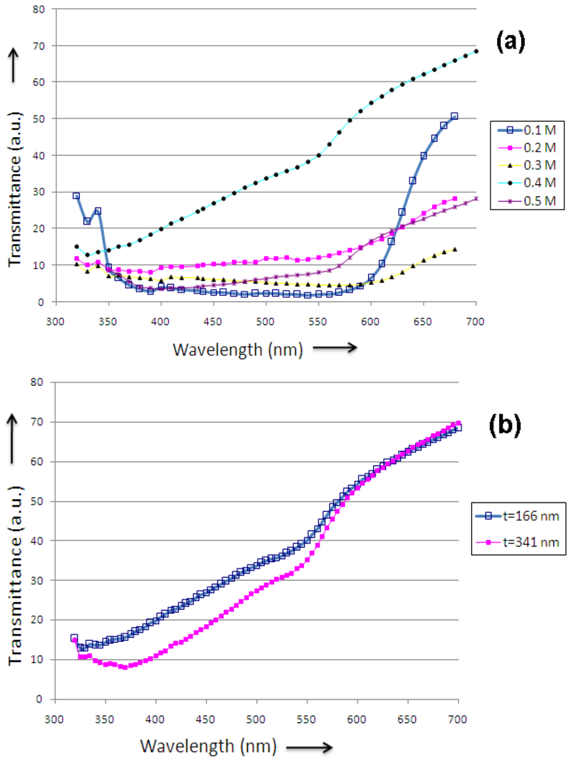

Fig. 3. Variation of Transmittance with wavelength for (a) Molar concentration 0.1M-0.5M and (b) Molar Concentration 0.4M.

The films have high fundamental absorption in the ultraviolet (0.30 μm - 0.40 μm) region, in the visible (0.39 μm - 0.77 μm) region of the electromagnetic spectrum and also wide energy gap. A steep absorption rise was observed on the shorter wavelength side. This optical data was analyzed in terms of the expression for near edge optical absorption in semiconductors. The thickness of the films was determined by the weight difference method in which area and weight of the film were measured. The thickness is again confirmed by interference method. The optical absorption spectra show a strong blue shift. In case of band edge luminescence, it is seen that absorption edge and luminescence peak are at the same energy. Both shift towards higher energy as particle size of nano crystals is reduced. The photoluminescence study of the above samples is in progress.

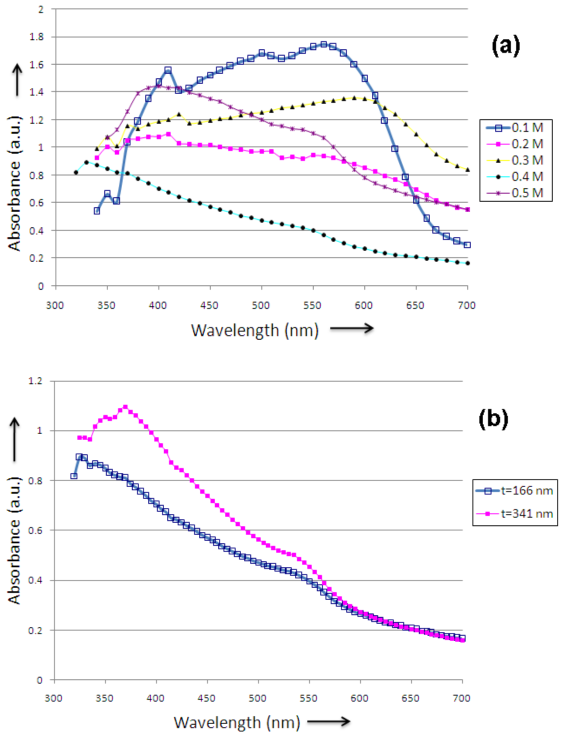

Fig. 4. Variation of Absorbance with wavelength for (a) Molar concentration 0.1M-0.5M and (b) Molar Concentration 0.4M.

3.4 Optical studies

The optical properties of the films are determined from the transmission spectra. The Transmittance is very low in the UV-region but increases rapidly within the visible region of the spectrum. The values of optical absorption coefficient (α) are of the order of 10^6 to 10^7 (m^{-1}) for near edge absorption given by

$$\alpha = \frac{-\ln T}{t} \qquad (1)$$

where 'T' is transmission and't' is the thickness of the film. The values of α have been calculated at different wavelengths, from transmission spectra. For a highly absorbing material, reflectivity R (fraction of intensity that is reflected) is usually measured instead of the absorptivity. The law of the conservation of energy indictates that the fraction absorbed (A), the fraction reflected (R) and the fraction transmitted (T) must add up to 1, i.e. $A + R + T = 1$. The reflectivity of a semiconductor decreases abruptly as the photon energy is increased beyond the energy gap (i.e. as the wavelength is decreased below that corresponding to the energy gap), because of increased absorptivity.

$$T = \frac{(1 - R^2)\exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \tag{2}$$

Extinction coefficient is calculated by

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

where k =extinction coefficient and λ = wavelength of incident light.

The refractive index η is a very important physical parameter related to the microscopic atomic interactions. From the theoretical point of view, there are basically two different approaches to this subject: on the one hand, considering the crystal as a collection of electric charges, the refractive index may be related to the density and the local polarizabilty of these entities [19]. On the other hand, considering the crystalline structure represented by a delocalized picture, the refractive index may be closely related to the energy band structure of the material. The refractive index of a material (speed of electromagnetic radiation in this material, $n = c / v$ or $v = c / n$) is the key parameter for device design. The refractive index of a material varies with the wavelength. In general 'n' decreases with increasing wavelength. The optical constants such as refractive index n, extinction coefficient k, real and imaginary part of dielectric constant are calculated in the visible region and plots of samples (Molar concentration 0.4M) are shown (in fig. 6,7,8). It has been observed that these plots are linear in the high energy region indicating the band to band direct type of transitions in these films. Figure 7(b) of refractive index vs wavelength shows a peak value of 2.6 for most of the films. This means that electromagnetic radiation is 2.64 times slower in CdSe films than in free space. This peak value occurs within the visible region of the electromagnetic spectrum. Real dielectric constant (ε') has been calculated by the following Kramers-kronig relationship,

$$\varepsilon' = n^2 - k^2 \tag{4}$$

While the imaginary dielectric constant (ε'') is calculated by the following equation,

$$\varepsilon'' = 2nk \tag{5}$$

The optical conductivity can be calculated using absorption coefficient as follow:

$$\sigma = \frac{\alpha n c}{4\pi} \tag{6}$$

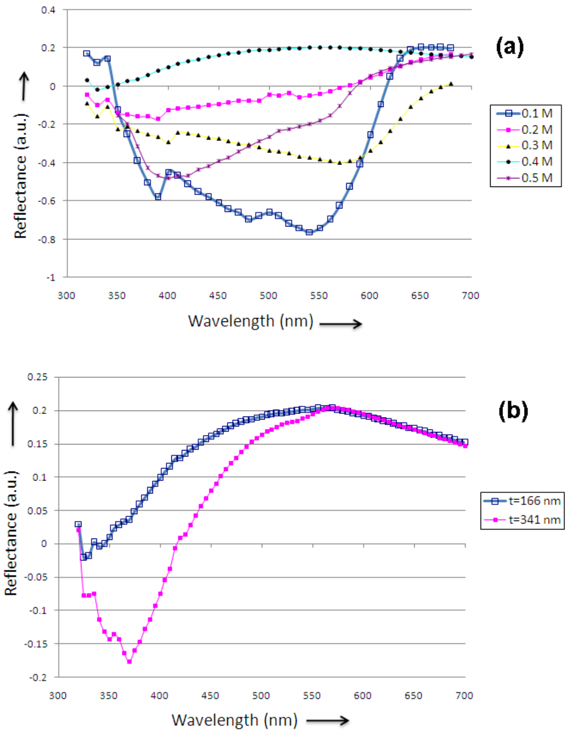

Fig. 5. Variation of Reflectance with wavelength for (a) Molar concentration 0.1M-0.5M and (b) Molar Concentration 0.4M.

3.5 Band gap measurement

The optical data were analyzed from the following classical relation (Tauc relation)

$$\alpha = A(h\nu - E_g)^n / h\nu \tag{7}$$

where '$h\nu$' is the photon energy, E_g is the band gap energy, A and n are constant. A is related to the effective masses associated with the valence and conduction bands. n may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transmissions respectively [20]. Fig. 6 shows plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) of the CdSe films (Tauc plot). Since the variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for the film is a straight line, it indicates that the involved transition is direct one. Band gap energy E_g was determined by extrapolating the straight-line portion to the energy axis for zero absorption coefficients (α). The energy band gap increases typically from 1.74 eV to 2.65 eV as deposition time is increased from 20hrs to 24hrs.

For CdSe–62 (0.4M, t=166nm), sample sudden increase in the absorption occurred at about 325 nm similarly onset of absorption is obtained at 350 nm, 370 nm, 370 nm and 360 nm for CdSe–63 (0.4M, t=541nm), CdSe–64 (0.4M, t=360nm), CdSe–66 (0.4M, t=341nm) and CdSe–68 (0.4M, t=350nm) samples, respectively. The values of E_g are obtained as 2.65 eV, 2.60 eV, 2.62 eV, 2.62 eV & 2.62 eV, respectively for the samples CdSe–62 to CdSe–68 (Molar concentration - 0.4M & thicknesses 166nm, 541nm, 360nm, 341nm, 350nm respectively) corresponding to the absorption edge. The band gap decreases with increase in thickness. The effective mass has important effects on the properties of a solid, including everything from the efficiency of a solar cell to the speed of an integrated circuit.The particle size of the nano particles are studied using Effective Mass Approximation [2]

$$\Delta E_g = E_g(film) - E_g(bulk) = E_{shift} = \frac{\hbar^2 \pi^2}{2\mu R^2} \qquad (8)$$

Where E_{shift} is the shift in the band gap, μ the translation mass $(m_{hole} + m_{electron})$ and R the radius of the nanoparticles. Their sizes were tunable between 1.0 and 2.0 nm.

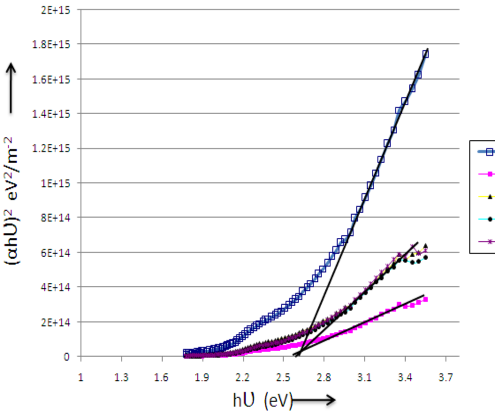

Fig. 6. Dependence of $(\alpha h\nu)^2$ on the photon energy $h\nu$ for the CdSe films having Molar concentration 0.4M.

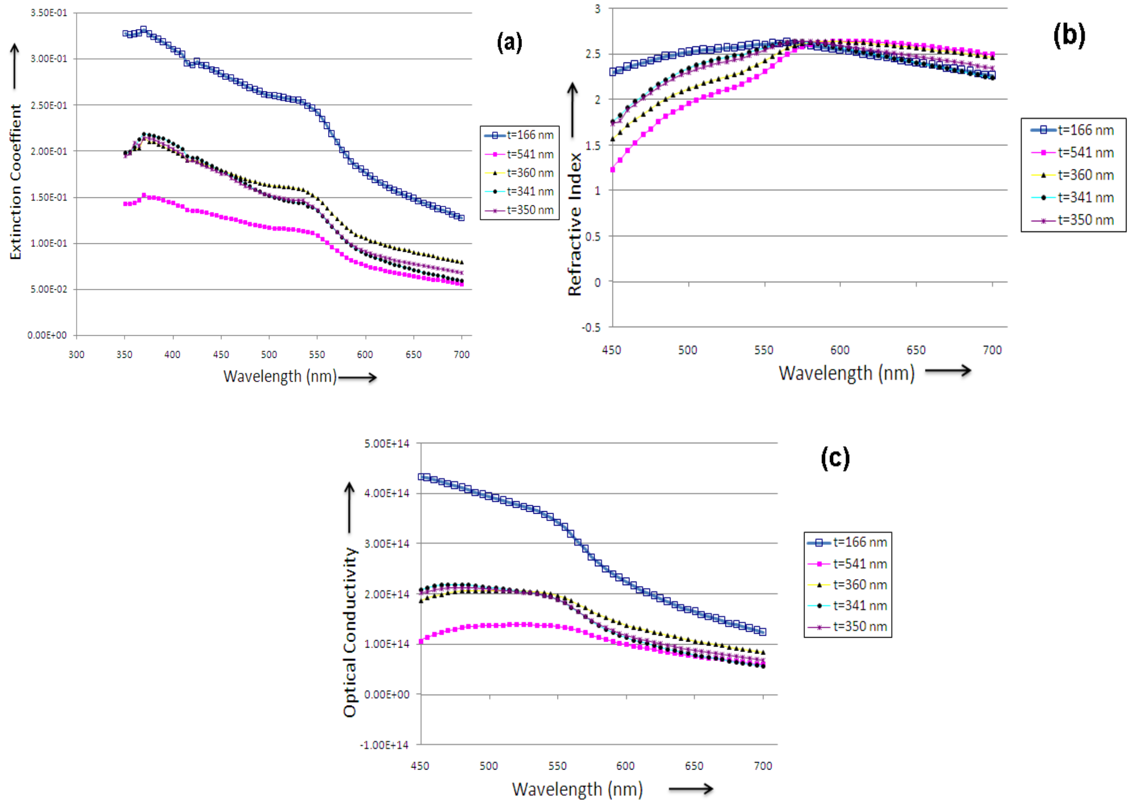

Fig. 7. (a) Variation of Extinction coefficient with wavelength for Molar concentration 0.4M. (b) Dependence of refractive index with wavelength for the CdSe films having Molar concentration 0.4M and (c) Variation optical conductivity with wavelength for Molar concentration 0.4M.

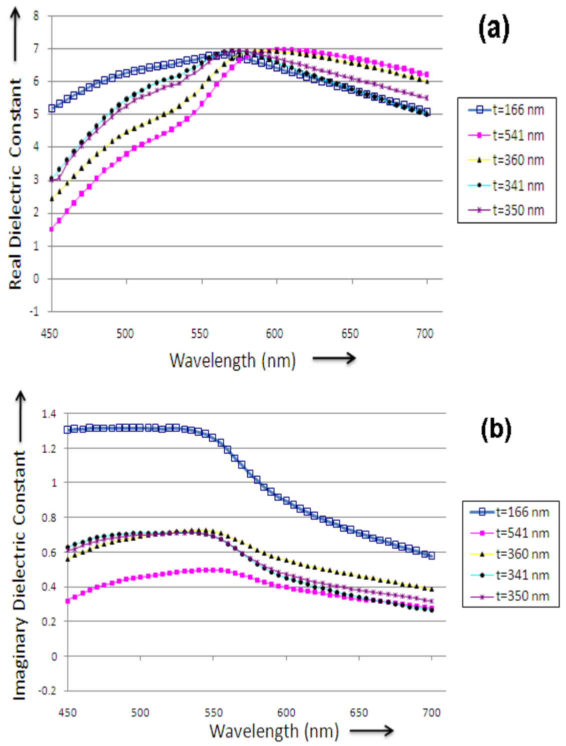

Fig. 8. Variation of (a) Real dielectric constant and (b) Imaginary dielectric constant with wavelength for Molar concentration 0.4M.

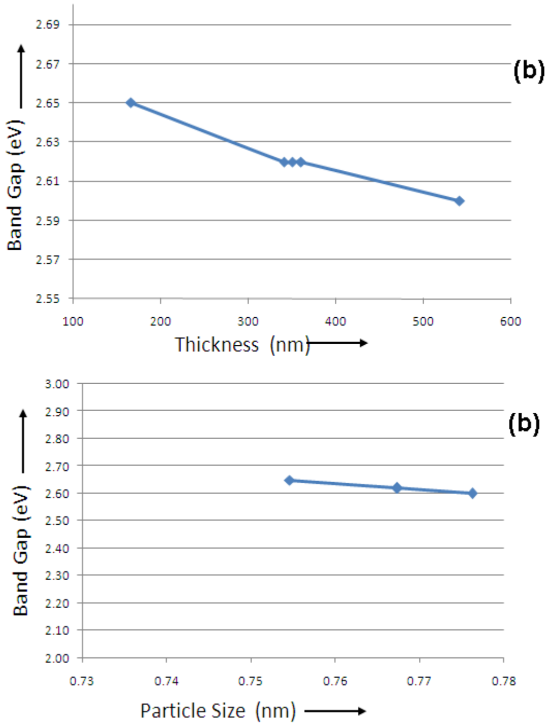

Fig. 9. Variation of Band gap with (a) Thickness of the films and (b) Particle size of the films for Molar concentration 0.4M.

4. Conclusions

Cadmium selenide thin films have been successfully deposited using chemical bath deposition technique. Solutions of Na_2SeSO_3, Cadmium acetate and NH_3 formed the reaction bath. This technique seems to be an inexpensive, low temperature method that could produce good quality films for device applications. The attractive features of this method are the convenience for producing large area devices and possibility to control the film thickness, morphology and stochiometry of the film by adjusting the deposition parameters and concentration of precursors. The final products were characterized by UV–VIS absorption spectra and SEM micrograph exhibited that the NCs were nearly monodisperse and relatively uniform. SEM studies show ball type structures, which may be due to layered growth. Diposited films are found to have nanocrystalline nature. Their sizes were tunable between 1.0 and 2.0 nm (for the samples having Molar Concentration - 0.4M) depending on reflux time & coalesceness of particles is avoided in this preparation process. The optical spectra revealed a high co-efficient of absorption of the order of 10^{6} to 10^{7} and a shift in absorption edge to a shorter wavelength side with corresponding band-to-band type of transition. The increase of the direct energy gaps is probably due to the formation of nano phase in these films. The bandgap of the CdSe films is enlarged upto 2.65 eV (bulk CdSe =1.74 eV). The band gap decreases with increase in thickness. The refractive index of the films has a peak value of 2.6 within the visible region of the electromagnetic spectrum. The optical transmittance is proportional to the wavelength of electromagnetic spectrum within the visible and near infra-red region. In the visible region, the reflectance rises slightly to a peak value and falls again. The films were observed to have highest optical conductivity (σ) and the film having thickness 166 nm showed maximum optical conductivity, Average extinction coefficient (k) value of 0.564. The highest values of real (ε') and imaginary (ε'') parts of dielectric function were found to be 7 and 1.4 respectively for CdSe thin film (0.4M & 166nm). All these optical and solid-state properties made this semiconducting material to be a good candidate for electroluminescent, photovoltaic and photoconductor devices applications.

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