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QUANTUM SIZE EFFECT IN CHEMOSYNTHESIZED NANOSTRUCTURED CdS THIN FILMS

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Nanostructured thin films of cadmium sulphide (CdS) with different thickness were prepared by chemosynthesis method. The films were deposited at various time intervals at <100^0C using low precursor concentration. These films were characterized for their structural, optical and surface morphological studies by using X-ray diffraction, UV-visible spectroscopy and scanning electron microscopy techniques respectively. The X-ray diffraction spectra reveal cubic crystal structure. With increase in film thickness the optical band gap was found to be decreased from 2.98 to 2.44 eV. An increase of 0.56 eV over the bulk band gap of CdS is found, this attributed due to the quantum size effect in CdS films. The transmittance of the films is found to be in the ranges between 55 to 75%. The CdS thin films show the particles sizes in the range of 4-19 nm in diameter.

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1. Introduction

Cadmium sulphide (CdS) has been used in various potential applications like light emitting diodes, solar cells, opto-electronics devices, photo catalyst, X-ray detectors, and in display devices [1-4]. It is a common material used as a buffer layer in the formation of solar cell devices based on CIS, CIGS, CdTe [5-7]. Recently, CdS nanoparticles are applied to Semiconductor Sensitized Solar Cells (SSSC) to improve the performance of wide band gap semiconductor materials [8].

CdS thin films preparation by the chemical deposition route is attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. It is a slow process which facilitates better orientation of crystallites with improved grain structure. The film growth can take place by ion-by-ion condensation on the substrates or by adsorption of the colloidal particles from the solution onto a substrate. It depends on the deposition conditions such as the bath temperature, pH, solution concentration, etc. [9].

2. Experimental details

All chemical were purchased from s. d. fine-chemicals and used without any further purification. The cadmium sulfate ($CdSO_4{\cdot}H_2O$) and thiourea ($H_2N{\cdot}CS{\cdot}NH_2$) were used as cadmium (Cd^{2+}) and sulphur (S^{2-}) precursors. Ammonia (NH_3) was used as a complexing agent. For the deposition of CdS thin films, 1mM $CdSO_4$ solutions were prepared in 15 ml double distilled water. Then 2 M NH_3 were added to form a clear solution, which was kept under stirred condition for 10 min. 1 mM thiourea ($H_2N{\cdot}CS{\cdot}NH_2$) is added to the above solution as S^{2-} precursor. The bath temperature was 70^{o}C. The CdS thin films were deposited by dipping the substrates in to the above solution for 50, 100, 150, 200, 250 and 300 min, and samples are denoted as C50, C100, C150, C200, C250 and C300 respectively. The deposited CdS films were

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rinsed with double distilled water, and allowed to dry at room temperature.

The structural properties of the CdS thin films were studied with X-ray diffraction (XRD) using an X-ray diffractometer (Philips, PW 3710, Almelo, Holland) operated at 25 kV, 20 mA with CrKα radiation. The UV–Visible absorbance spectra of CdS thin films were recorded using a UV–visible spectrophotometer (UV3600, Shimadzu, Japan). The surface morphology of the films were examined by analyzing the scanning electron microscopy (SEM) (Model JEOL-JSM-6360, Japan), operated at 20 kV. The film thickness was determined by surface profiler (Ambios, XP-1 model) and thicknesses of the CdS samples were found to in the range 54 to 139 nm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CdS thin film samples C50, C100, C150, C200, C250 and C300 deposited on soda-lime glass substrates. The presence of a broad XRD peaks is an indication of nanocrystalline nature of the CdS thin films. The comparison of the observed XRD patterns with the standard (JCPDS data 80-0019) confirms the deposited CdS thin films are polycrystalline having cubic crystal structure with diffraction peaks along (111), (200), (220) and (311) planes at 39.90, 46.34, 67.67 and 81.03 degree respectively. The C50 and C100 exhibit amorphous nature.

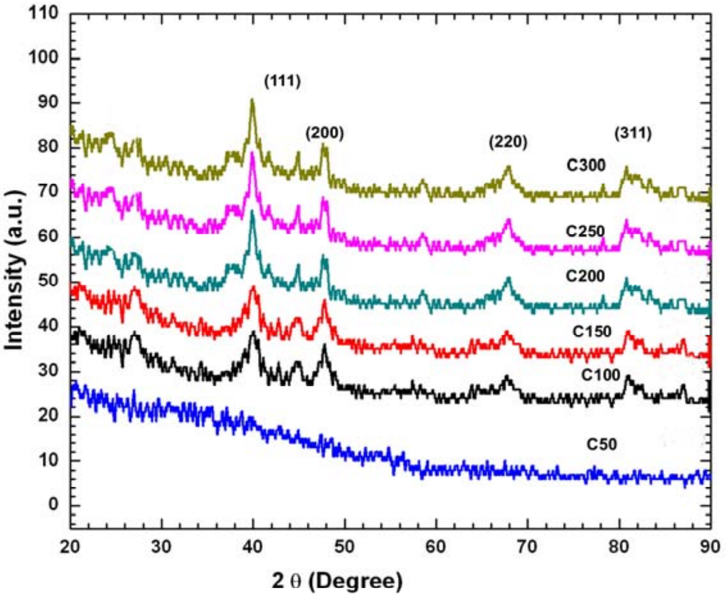

Fig. 1. XRD spectrum of CdS samples.

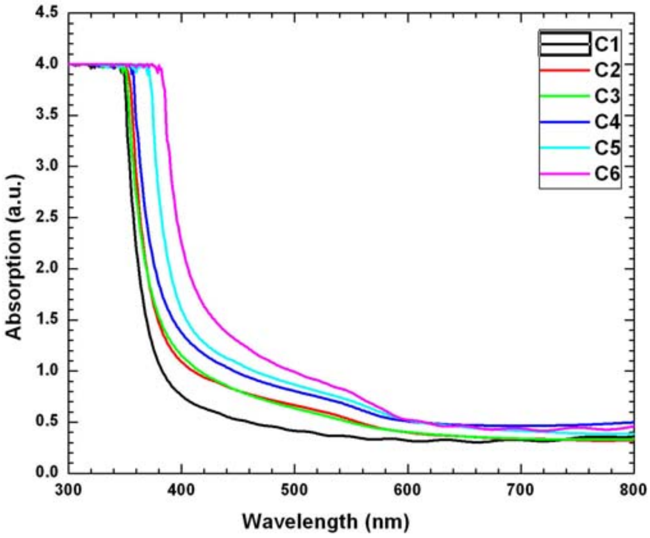

Fig. 2. Plots of optical absorption for CdS samples.

The UV-Vis spectroscopy has become an effective tool in determining the size and optical properties of the nanocrystalline thin films. In the present study, optical absorption in CdS films with different film thicknesses were studied over 300 to 800 nm. Fig. 2 show optical absorption spectra for the CdS films with different thicknesses. The optical absorption edge showed a blue shift indicating a change in the band gap compared its bulk. The nature of the transition (direct or indirect) is determined by using the relation:

$$\alpha = \frac{\alpha_0 (h\upsilon - E_g)^n}{h\upsilon} \tag{1}$$

where 'Eg' is the separation between bottom of the conduction and top of the valence band, hν is the photon energy, 'n' is constant and is equal to 1/2 or 3/2 depending on whether transition is allowed or forbidden and α_0 is a constant depending upon the transition probability for direct transition. For allowed direct transitions n =1/2 and for allowed indirect transition n = 2. Thus if the plot of $(\alpha h\nu)^2$ against hν is linear then the transition is direct allowed. The band gap energy Eg is determined by extrapolating the linear portion of the curve to the energy axis at α=0. The plots of $(\alpha h\nu)^2$ against hν are shown in Fig. 3 for CdS films for different thicknesses. The nature of the plots indicates the existence of the direct transitions. CdS is direct band gap semiconductor with a band gap of 2.42 eV in the bulk form [10]. Fig. 4 shows variation of deposition time with film thickness for CdS films. The band gap values were obtained as 2.98, 2.74, 2.58, 2.54, 2.52 and 2.44 eV for samples C50 to C300 respectively. Similar blue shift in the band gap energy with smaller thicknesses for chemically deposited chalcogenide thin films have been reported [11-13]. The optical transmittance of CdS samples C50 to C300 are shown in Fig. 5. The CdS samples exhibit transmittance in the range of 55 to 75 %

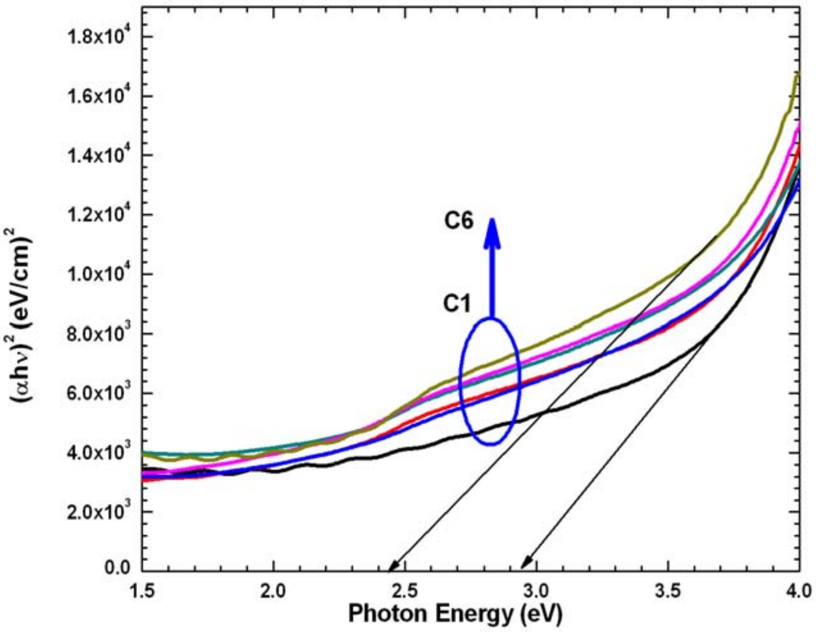

Fig. 3. Plots of $(\alpha h\nu)^2$ *against* $h\nu$ *for CdS samples.*

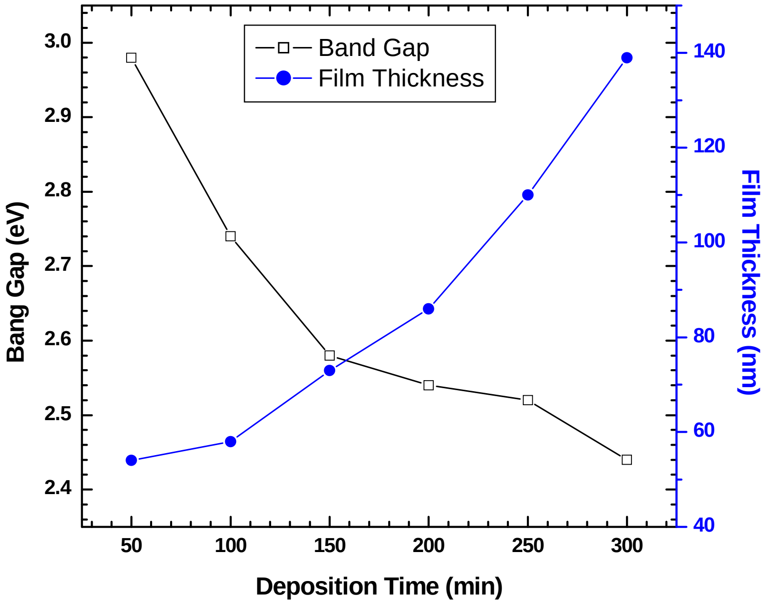

Fig. 4. Variation of CdS films thickness and Band Gap with deposition time.

The size of the CdS nanoparticles has been estimated using hyperbolic band model [14]. It is the inclusion of the effect of electron and hole band non-parabolicity. Hyperbolic model has been used to explain the change of band gap energy as a function of particles radius as shown in eq.(2)

$$\Delta E_g \cong E_{g(nano)} - E_{g(bulk)} = \frac{h^2}{8MR^2} \tag{2}$$

where, M is effective mass of the system and h is Planck's constant. The results were obtained using equation 2 are summarized in Table 1.

Table 1. The comparative study of the band gap energy and the deposition time with the film thickness.

Sr. No.	Sample	Deposition time (min)	Film thickness (nm)	Band gap energy (eV)	Particle size (nm)
1	C50	50	54	2.98	3.51
2	C100	100	58	2.74	4.60
3	C150	150	73	2.58	6.57
4	C200	200	86	2.54	7.61
5	C250	250	110	2.52	8.37
6	C300	300	139	2.44	18.80

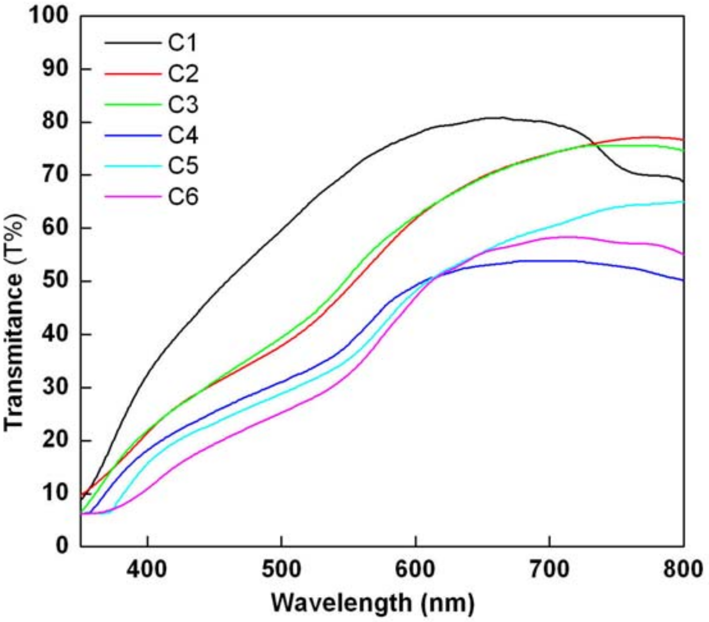

Fig. 5. Plots of optical transmittance for CdS samples.

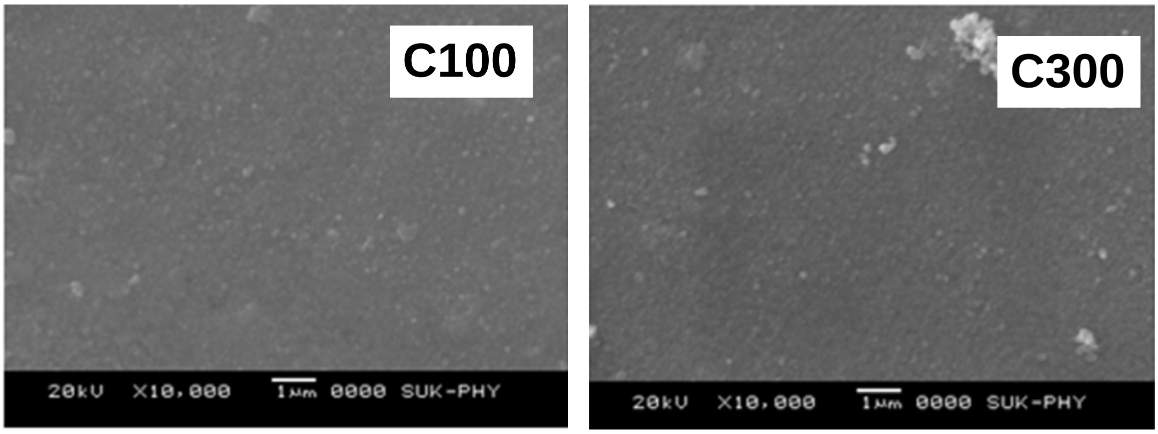

Fig .6. SEM images for CdS samples C100 and C300.

Scanning electron microscopy (SEM) is a suitable method for the analysis of nanostructured thin films. Fig. 6 represents the SEM micrograph of as-grown CdS samples C100 and C300, onto glass substrate fabricated by CBD at 70^{o}C. It was observed from the images that the as-deposited CdS films were homogeneous and covered the substrate well without cracks. The morphology of CdS semiconductor materials depends on the deposition time.

4. Conclusions

As the size of the semiconductor particle decreases to the nanoscale the absorption peaks of the prepared CdS samples appear to be blue shifted as compared to that of the bulk CdS. It can be easily understood that quantum confinement effect is present in the prepared CdS thin films. This make the physical properties of the thin films evidently different from those of the bulk and have potential applications for nanotechnology.

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