Experimental and Theoretical NANOTECHNOLOGY
http://etn.siats.co.uk/

Optical and structural of Nanocrystalline CdS

*A. Kumar, R. Vasantha**

School of Mechanical Engineering, Kalinga Institute of Industrial Technology (KIIT),
Deemed to be University, Bhubaneswar 24, Odisha, India
*) Email: vasaritha@yahoo.co.in

Received: 3/3/2020 / *Accepted:* 4/7/2020 / *Published:* 1/9/2020

Nanocrystalline CdS thin films have been deposited using precursors with different thiourea concentration onto glass substrates by sol-gel spin coating method. The crystalline nature of the films has been observed to be strongly dependent on thiourea concentration and annealing temperature. The CdS films are found to be nanocrystalline in nature with hexagonal structure. The grain size is found to be in the range of 7.6 to11.5 nm depending on the thiourea concentration and annealing temperature. The high-resolution transmission electron microscopy (HRTEM) results of the CdS films prepared using cadmium to thiourea molar ratio of 0.3:0.3 indicate the formation of nanocrystalline CdS with grain size of 5 nm. Fourier transform infrared (FTIR) analysis shows the absorption bands corresponding to Cd and S. The optical study carried out to determine the band gap of the nanostructured CdS thin films shows a strong blue shift. The band gap energy has been observed to lie in the range of 3.97 to 3.62 eV following closely the quantum confinement dependence of energy on crystallite radius. The dependence of band gap of the CdS films on the annealing temperature and thiourea concentration has also been studied. The photoluminescence (PL) spectra display two main emission peaks corresponding to the blue and green emissions of CdS.

Keywords: Sol-gel; CdS; HRTEM, Nanocrystalline.

1. INTRODUCTION

CdTe thin film solar cells are usually fabricated as hetero-structures because of the short absorption length and difficulty in forming a shallow thin film junction with a high conductivity surface layer [1]. The hetero-junction partner or the window material to CdTe should have a large band gap and good lattice and electron affinity match to minimize interface states and avoid deleterious conduction band spikes. Among the various heterojunction window materials available today, CdS is the one, which is most extensively studied and is best suited for CdTe solar cells [2]. Capoen et al. [3] have reported that CdS nanoparticles have low refractive index compared to the bulk due to the quantum confinement effect and have also stated that the CdS layers exhibit wave guiding properties. CdS is one of the most important II-VI semiconductor compounds possessing excellent optical properties. A tremendous amount of effort has been de- voted to the synthesis and study of optical properties of CdS related nanoparticles and quantum dots [4]. The quantum dots are considered as promising candidates for optoelectronic applications including light emitting diodes [5] and optically pumped high power blue lasers [6]. Various concepts have been proposed for the use of nanostructured materials in solar energy conversion [7] Quantum dots can be used as frequency converters to match the spectrum of the incoming radiation to the spectral efficiency of the solar cell [8]. Devi et al. [9] have reported that the grain size and band gap of CdS depend on the molar ratio of Cd and S used in the preparation of CdS. Ramaiah et al. [10] have reported that higher sulphur concentration in- creases the grain size and decreases the band gap of CdS. The behavior of CdS quantum dots depending on the quantum confinement effect presents in the material. The quantum size effect is theoretically classified into two types: one is the exciton confinement effect and the other is the independent confinement effect of electron and hole. When the radius of the microcrystal is sufficiently larger than the exciton Bohr radius, the exciton confinement effect occurs. On the other hand, when the radius is comparable or smaller than the exciton Bohr radius, the independent confinement of electrons and holes takes place [11].

CdS thin films have been prepared by different workers using various techniques such as brush plating [12], pulsed laser deposition [13], physical va- por deposition [14], chemical bath deposition [15], spray pyrolysis [16], successive ionic layer adsorption and reaction [17], screen printing [18]. The sol-gel technique is extensively studied as a matrix material method to produce nanocomposites because it gives a higher specific surface area, superior homogeneity and purity, better microstructural control of metallic particles, narrow pore size and uniform particle distribution. In addition, the sol-gel method also offers several other advantages, such as low temperature process- ing, possibility of coating on large area substrates and most importantly cost-effective. In this paper, we re- port about the effect of thiourea concentration and annealing temperature on the structural properties, surface morphology and optical properties of the CdS nanocrystalline thin films prepared using sol gel spin coating method.

2. EXPERIMENTAL

In the present study, CdS particles were embedded in polyethylene glycol-based solution. A polyethylene glycol (PEG 400, Merck) sol was prepared by mix X-ray diffraction (XRD) studies were carried out on the prepared CdS films using Panalytical x-ray diffractometer (Netherlands), and high-resolution transmission electron microscopy (HRTEM) images of the prepared CdS films were recorded using a Philips TECNAI F20 microscope (USA). The surface morphology of the films was studied by scanning electron microscopy (SEM) using a Hitachi S-500 microscope (Japan). The chemical composition of the samples was determined using an energy dispersive x-ray analysis (EDX) spectrometer attached to the scanning electron microscope, and Fourier transform infrared (FTIR) spectrum was recorded using a Shimadzu spectrometer (Japan). The optical properties were studied using the absorbance spectrum recorded by spectrophotometer (JASCO V-570), and the photoluminescence spectra were recorded using the Cary Eclise WinFLR photoluminescence device (USA).

3. RESULTS AND DISCUSSION

In the preparation of CdS thin films by solution growth method, the film growth can take place by one of the following methods [19,20]. One is the cluster by cluster mechanism described as follows: in the ammonia-thiourea system, S^{2-} ions are released by the alkaline hydrolysis of thiourea and Cd^{2+} ions are released by dissociation of the corresponding ammonia complexes. As soon as the product of the free S^{2-} and Cd^{2+} ion concentration exceeds the solubility product of CdS, the precipitation of CdS takes place. The other method is the ion by ion mechanism which consists of the following three steps: (i) the reversible adsorption on the substrate surface of dihydroxo-diamino cadmium, (ii) the adsorption of thiourea by the formation of a metastable complex, (iii) the formation of CdS and site regeneration by the metastable complex decomposition. Generally, the formation of CdS films is observed to take place by ion mechanism.

Table 1 Interplanar distance (d) values of (002) crystal plane of CdS thin films.

Solution Cd:S	Thin film Cd:S	Annealing temperature/˚C	Experimental, d/nm	CdS hexagonal (JCPDS 6-314) d/nm	CdS hexagonal (JCPDS 6-314) (hkl)
0.3:0.3	1.0:0.66	250	0.336	0.336	(002)
		450	0.339		
0.3:0.4	1.0:0.75	250	0.338		
		450	0.339		
0.3:0.6	1.0:0.92	250	0.336		
		450	0.336		

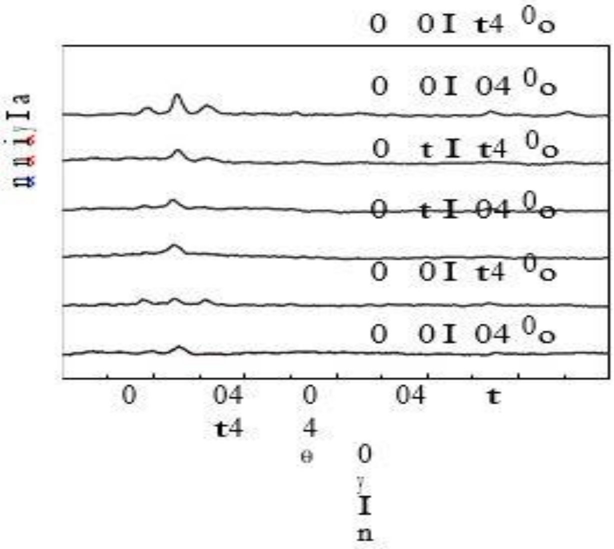


Figure 1 XRD patterns of annealed CdS films deposited Cd:S molar ratio of 0.3:0.3, 0.3:0.4 and 0.3:0.6.

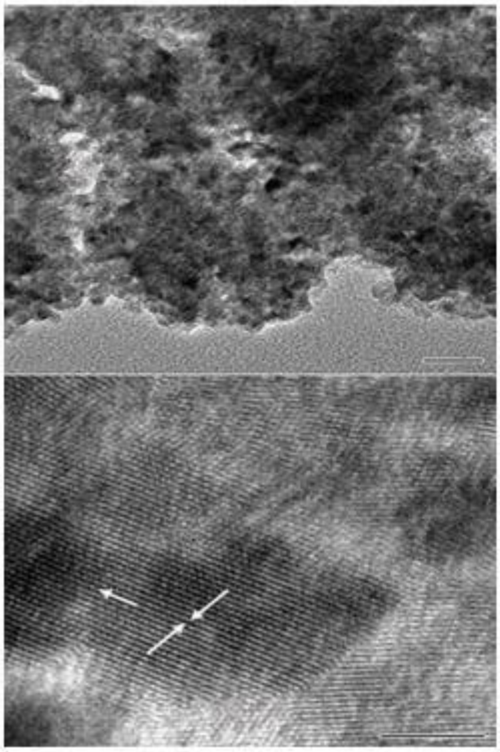


Figure 2 HRTEM images of annealed CdS film prepared using Cd:S molar ratio of 0.3:0.3.

CuK α radiation. Figure 1 shows the XRD patterns of CdS thin films prepared using three different thiourea concentrations (0.3, 0.4 and 0.6 mol/L) and annealed at 250 and 450◦ C for 45 min. Peaks are observed at 24.63, 26.26, 28.02 and 43.5 deg. corresponding to the (100), (002), (101) and (110) planes of the hexagonal phase of CdS. The intensity of the peaks is observed to increase as the ratio of Cd/S is decreased. Additional peak corresponding to unreacted Cd or S has not been observed. For comparison, the obtained interplanar spacing (d) values of CdS films along with Joint Committee on Powder Diffraction Standards (JCPDS) data are given in Table 1. The lattice para- meter values a and c have been calculated to be 0.441 and 0.672 nm, respectively, and these values are in agreement with the JCPDS data (6-314). The crystallite size has been determined from the width of the XRD peak at 26.26 deg. using Scherrert s equation [22] and is listed in Table 1. With the increase of temperature and thiourea concentration, there is an increase in the intensity of the peak, and this is due to the improvement in the crystalline nature of the films. The grain size is found to be in the range of 7.6 to 14.5 nm.

Figure 2 shows the HRTEM images of CdS prepared using a sulphur concentration of 0.3 mol/L and annealed at a temperature of 250◦ C. The image clearly shows lattice fringes corresponding to hexagonal CdS phase. The interplanar lattice spacing of the planes seen is 0.357 nm corresponding to the (100) plane of hexagonal phase. The HRTEM image gives a grain size of about 5 nm and this is in agreement with XRD results. This confirms the formation of nanocrystalline CdS films with particle size lying in the quantum dot range.

SEM is a convenient technique to study the sur- face morphology of thin films. Figure 3 shows the surface morphology of CdS thin films prepared us- ing three different thiourea concentrations (0.3, 0.4 and 0.6 mol/L) and annealed at 250◦ C. A large num- ber of cavities seen in the images may be due to the prolonged drying resulting in the evaporation of the solvent. Evaporation of the solvent from the gel film affects the film morphology. A sol film is required to have a sufficient fluidity for some time during the drying process to form macroporous structure. Evaporation rate of the gel film is determined mainly by transport rate of the top surface of the film and is in dependent of the film thickness [23]

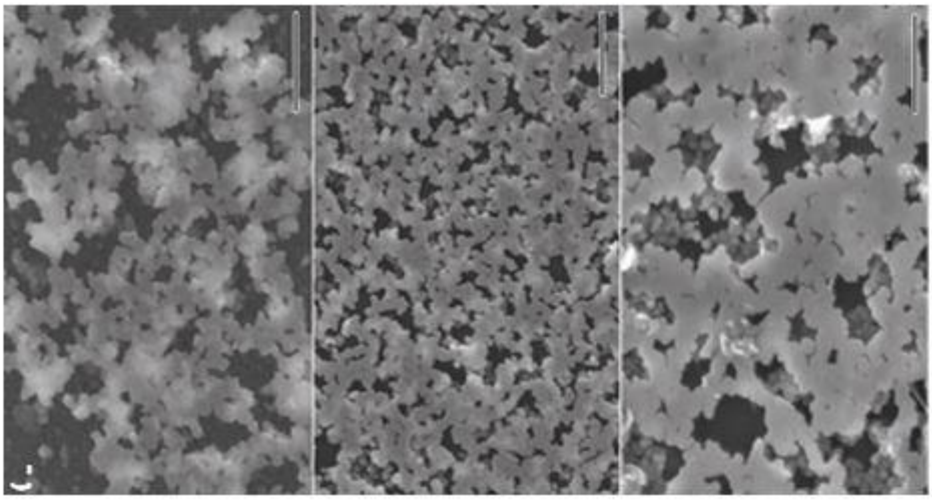


Figure 3 SEM images of 250◦ C annealed CdS films pre- pared using Cd:S molar ratio 0.3:0.3 (a), 0.3:0.4 (b) and 0.3:0.6 (c).

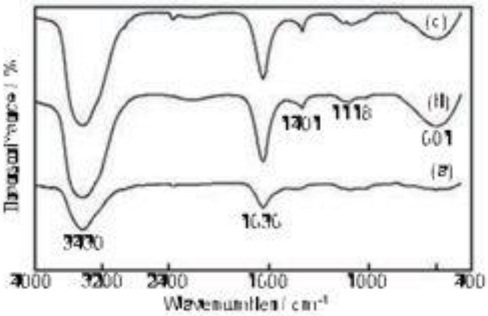


Figure 4 FTIR spectrum of 450◦ C annealed CdS films: (a) Cd:S=0.3:0.3, (b) Cd:S=0.3:0.4, (c) Cd:S=0.3:0. 6

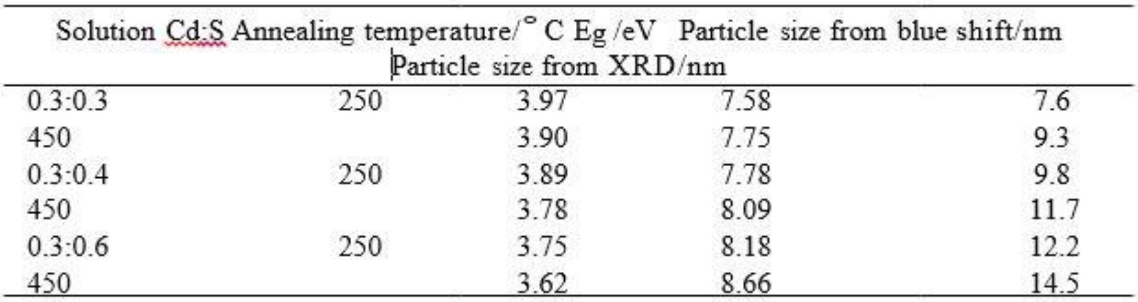
Generally during the film formation, PEG interacts with Cd2+ ions and self-assembles through cross-linking and polymerization to form ordered inorganic/polymer composites. As a result, in the SEM pictures, we see the nanostructured inorganic matrix with CdS nanoparticles and their agglomerates. The distribution of Cd2+ cations in the polymer chains is a result of the interaction of the Cd2+ ions with the functional groups of PEG. The morphology observed may be due to the rearrangement of the polymer chains at molecular level that occurs due to the interaction between lone electron pairs belonging to oxygen atoms from the functional groups of PEG and the metal ions. Kajihara and Yao [24] have reported that decomposition of PEG is the reason for the variation of macroscopic morphology.

EDX analysis carried out to study the composition of the films revealed that the Cd/S ratio in the grown films increased with increasing Cd/S concentration ratio in the solution as expected. The com- position of the prepared CdS films is shown in Table 1. Figure 4 shows the FTIR spectrum of 450◦ C annealed CdS films (Cd:S=0.3:0.3, 0.3:0.4, 0.3:0.6). The absorption band present at 3430 cm−1 is due to OH stretching vibration of water molecules. The band at 1636 and 1401 cm−1 results from aromatic C-C stretches. The γ(SO2) stretching mode at 1118 cm−1 is also observed, confirming the successful incorporation of the sulfonic group [25]. The band at 601 cm−1 corresponds to the Cd-S stretching.

Optical absorbance spectra of the CdS thin films have been recorded in the wavelength range 300–1800 nm. It is well known that for semiconductor particles with radius less than the bulk Bohr exciton radius, there is a blue shift in the absorption edge due to the quantum size effect [22]. Excitons have an average physical separation between the electron and hole, referred to as the exciton Bohr radius, and this physical distance is different for each material. In bulk, the dimension of the semiconductor crystal is much larger than the exciton Bohr radius, allowing the exciton to extend to its natural limit.

However, if the size of a semiconductor crystal becomes small enough, i.e., it approaches the size of the materials exciton Bohr radius, then the electron energy levels can no longer be treated as continuous and they must be treated as discrete. This situation of discrete energy levels is called quantum confinement, and under these conditions, the semiconductor material ceases to resemble bulk, and instead can be called a quantum dot. This has large repercussions on the absorptive and emissive behavior of the semiconductor material. Because the electron energy levels of quantum dots are discrete rather than continuous, the addition or subtraction of just a few atoms to the quantum dot has the effect of altering the boundaries of the band gap. Changing the geometry of the surface of the quantum dot also changes the band gap energy due to the small size of the dot and the effects of quantum confinement. The band gap in a quantum dot will always be energetically larger; therefore, we refer to the radiation from quantum dots to blue shift reflecting the fact that electrons must fall a greater distance in terms of energy and thus produce radiation of a shorter and therefore a blue wavelength. The size dependence of the electronic structure of the lowest exciton states in CdS quantum dots is mainly determined by two terms: the spin-orbit interaction and the electron- hole (e-h) exchange interaction. Matrix elements of the spin-orbit interaction are constant and the e-h ex- change interaction increases as the quantum dot radius decreases. Two opposite limits can be considered: small and large dots. For small quantum dots, the e-h exchange interaction is much larger than the spin-orbit coupling, and for large quantum dots, the e- h exchange interaction is much smaller than the spin-orbit coupling.

Table 2 Particle size of CdS films obtained from XRD pattern and blue shift of optical band gap



Solution Cd:S	Annealing temperature/° C	Eg /eV	Particle size from blue shift/nm	Particle size from XRD/nm
0.3:0.3	250	3.97	7.58	7.6
450		3.90	7.75	9.3
0.3:0.4	250	3.89	7.78	9.8
450		3.78	8.09	11.7
0.3:0.6	250	3.75	8.18	12.2
450		3.62	8.66	14.5

4. CONCLUSION

Nanostructured CdS thin films have been deposited using different Cd/S concentration ratio. The XRD analysis indicates that the films are nanocrystalline in nature with hexagonal structure and the grain size is found to be less than 10 nm indicating the formation of CdS quantum dots. The particle size has been cal¬culated using the blue shift of the optical band gap caused by quantum confinement and is shown in Table 2. The particle size is found to lie in the range of 7.58 to 8.66 nm. The strong and weak confinements occur from the small and large grains present in the sample, respectively. The blue shift suggests strong quantum confinement. The optical band gap values of 3.97 to 3.62 eV obtained from strong confinement could be due to the small size of grains. The formation of CdS nanoparticles can be also confirmed by photoluminescence (PL) spectroscopy, because CdS nanoparticles exhibit light-emitting due to quantum confinement effects arising due to the formation of very small CdS particles. The next stage of work is the optimization of the size of CdS particles for quantum dot solar cell applications.

References

[1] Bisma Bilal, Suhaib Ahmed, Vipan Kakkar, Experimental and Theoretical NANOTECHNOLOGY 3 (2019) 33

[2] C. Ferekides and J. Britt: Sol. Energy Mater. Sol. Cells 35 (1994) 255

[3] C. Capoen, T. Gacoin, J. M. Nedelec, S. Turrell, M. Bouazaovi, J. Mater. Sci., 36 (2001) 2565

[4] A. Blanco, C. Lopez, R. Mayoral, H. Miguez, F. Meseguer, A. Mitsud, J. Herrero, Appl. Pbys. Lett. 73 (1998) 178

[5] V. Tasco, M.T. Todaro, M.D. Giorgi, R. Cingolani, P. Passaseo, J. Ratajczak, J .W. Katcki, Appl. Pbys. Lett. 84 (2004) 4155

[6] Q. Darugar, W. Qian, M.A. EI-Sayed, Appl. Pbys. Lett. 88 (2006) 261108

[7] P. Oelhafen, A. Schuler: Sol. Energy 79 (2005) 110

[8] W.G.J.H.M. Va n Sark, A. Meijerink, R.E.I. Schropp, J.A.M. Van Rroosmalen, E.H. Lysen, Sol. Energy Mater. Sol. Cells 87 (2005) 395

[9] R. Devi, P. Purkayastha, P.K. Kalita, B.K. Sarma: Bull. Mat. Sci. 30 (2007) 123

[10] K.S. Ramaiah, A.K. Bhatnagar, R.D. Pilkington, A.E. Hill, R.D. Tomlinson, J. Mater.

Sci. Mater. Elec- tron. 11 (2000) 269
[11] H. Nasu, J. Matsuoka, Kamiya: J. Non-Cryst. Solids 178 (1994) 148
[12] K.R. Murali, S. Kumaresan and J. Joseph Prince, J.Mater. Sci. Mater. Electron. 18 (2007) 487
[13] X.L. Tong, D.S. Jiang, W.B. Hu, Z.M. Liu, M.Z.Luo, Appl. Phys. A, 2006, 84, 143.
[14] R.W. Birkmire, B.E. McCandless, S.S. Hegedus, Sol. Energy, 1992, 12, 45.
[15] B. Pradhan, A.K. Sharma, A.K. Ray, J. Cryst.Growth, 2007, 304, 388.
[16] P. Raji, C. Sanjeeviraja, K. Ramachandran, Bull.Mater. Sci., 2005, 28, 233.
[17] Y.A. Kalandaragh, M.B. Muradov, R.K. Mammedov, A. Kaodayari J. Cryst. Growth 305 (2007) 175
[18] D. Patidar, R. Sharma, N. Jani, T.P. Sharma, N.S. Saxena, Bull. Mater. Sci. 29 (2006) 21
[19] J.M. Dona, J. Herrero, J. Electrochem. Soc. 144 (1997) 408
[20] R. Ortega-Borges, D. Lincol, J. Electrochem. Soc. 140 (1993) 3464
[21] I. Kaur, D.K. Pandya, K.L. Chopra, J. Elec- trochem. Soc. 127 (1980) 943
[22] M. Maleki, M.S. Ghamsari, Sh. Mirdamadi, R.Ghasemzadeh, Semicond. Phys., Quantum Electron. Optoelectron. 10 (2007) 30
[23] K. Kajihara, K. Nakanishi, K. Tanaka, K. Hirao, N. Soga, J. Am. Ceram. Soc. 81 (1998) 2670
[24] K. Kajihara, T. Yao, J. Sol-Gel Sci. Technol. 17 (2000) 173
[25] T.P. Martin, H. Schaber: Spectroc. Acta Pt. A- Molec. Biomolec. Spectr. 38 (1980) 655