STUDIES ON NANO-CRYSTALLINE PROPERTIES OF CHEMICALLY DEPOSITED CdSe FILMS

R. S. SINGH[*], S. BHUSHAN[a], A. K. SINGH[b]
Dept. of Physics, Govt. D. T. College Utai, Durg-491107 (C. G.), India
[a]Dept. of Physics, SSCET Bhilai, Durg-490020 (C.G.), India
[b]Dept. of Chemistry, Govt. VYT PG College Durg-491001 (C.G.), India

Results of SEM, XRD, optical absorption spectra and photoluminescence (PL) emission spectra are presented for chemically deposited bulk and nano-crystalline CdSe films prepared on microscopic glass substrates. Nano-crystalline CdSe films were prepared with two concentrations of capping agents thiophenol and methanol (TPM). SEM studies show spherical shaped morphology. XRD studies show the hexagonal structure with a preferred orientation along the (002) direction of films. The average grain size decreases with increasing TPM volume. Blue shift in the absorption edge with increase in TPM volume is seen from optical absorption studies which also indicate increase in its band-gap. The grain sizes determined from such studies also lie in nano-range. The PL emission spectra show shift of peaks in the lower wavelength side due to reduction in grain size.

1. Introduction

Considerable attention has been paid to semiconductor nanostructures in the past decade. The attention they received stems from either their unique physical properties or potential applications in nanoscaled electronics and photonics [1,2]. Great efforts have been spent in growing and characterizing the nanostructures. As a result of these efforts, quantum dots, nanotubes, nanowires, nanoribbons, nanoneedles and nanorods have been fabricated and studied [3,4]. The nanostructures can be grown from many semiconducting materials. Reports on the nanostructures grown from II-VI compound semiconductors have mushroomed recently [5-8]. CdSe has long been studied because it has a suitable band gap, a high absorption coefficient and photosensitivity [9]. It finds potential applications in light emitting devices [10], solar cells [11], photodetectors [12] and laser [13]. More importantly, the band gap of CdSe in the form of nanocrystals can be varied to cover the whole visible spectrum just by varying its crystal size. [14]. These nanocrystals are potentially useful as biological labels [15] and have attracted considerable interest from researchers in many fields. It is important that the improvement of material properties requires a closer inspection of preparation conditions. From this point of view, a large number of techniques [16-18] for preparing CdSe films were employed. Some of the above mentioned methods have some drawbacks. Used precursors are unstable causing environmental hazards and require very high temperature. These methods are also not cost effective. Hence, the chemical bath deposition methods have been widely used for the growth of thin films [19, 20]. In the present paper, the morphological, structural and optical properties of the chemically deposited CdSe films have been investigated.

---

[*]Corresponding author: rss.bhilai@gmail.com

2. Experimental details

Substrates used in the present work were commercial quality microscopic glass slides of dimensions 24mm x75mm, which were first cleaned with HCl, acetone, distilled water and ultrasonic cleaner. They were then dried and dipped vertically into a mixture of solutions of 1M cadmium acetate, triethanolamine (TEA), sodium selenosulphate (prepared by heating sodium sulphite with selenium at 90^0C for 5 hrs.), 30% aqueous ammonia. All solutions were prepared in double distilled water. TEA was used as a complexing agent to form Cd[TEA]$^{2+}$ complex for controlling the growth rate. The capping agents thiophenol and methanol in 1:1 ratio were then added to the above said mixture of solutions, for preparing the nanocrystalline films. The films were then formed on glass substrates by dipping them vertically in the solution, kept in a constant temperature water bath for 60 minutes. The deposition of films is based on precipitation followed by condensation. After deposition, the films were washed with double distilled water and then dried at room temperature.

The structural parameters of the CdSe films were characterized by using X-ray diffractometer (Rigaku RUZHR, CuKα radiation) and JEOL (JSM-5600) scanning electron microscope respectively. The fundamental optical property which has been investigated here is the reflection of light at various wavelengths using Shimadzu (UV-VIS) Pharma Spec-1700 spectrophotometer and PL studies were made by Shimadzu fluorospectrophotometer (RF 5301) under 365nm excitation.

3. Results and discussion

3.1 SEM studies

Scanning electron microscopy (SEM) is a convenient technique to study microstructure of thin films. Figs. 1-(a), (b) and (c) show the SEM pictures of the different CdSe films. Role of capping agents is to avoid the coalescence of particles and thus particle size reduces. As the concentration of capping agents increases, particle size is expected to reduce further because of the more avoidance of coalescence of different particles in presence of capping agents and this obviously can be seen from the micrographs.

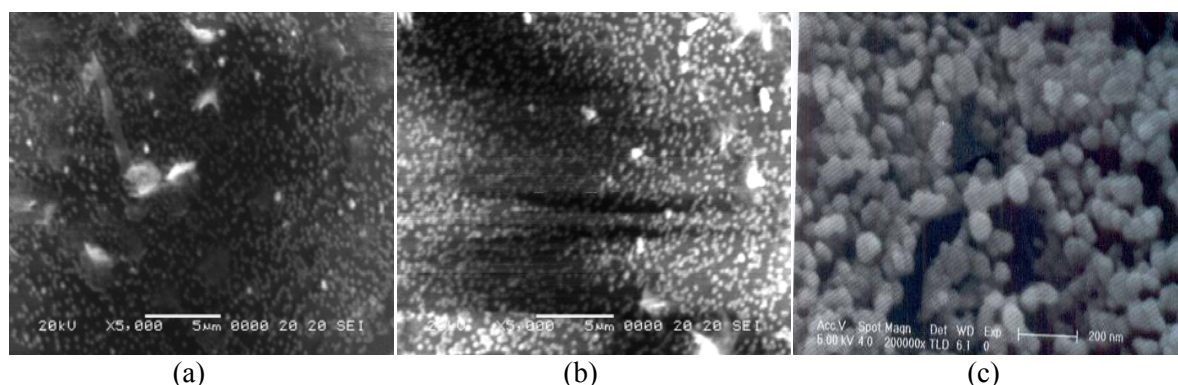| (a) | (b) | (c) |

Fig. 1. SEM micrographs of different films : (a) bulk CdSe film without using capping agent (sample A), (b) nanocrystalline CdSe film using 0.5 ml capping agent (sample B), (c) nanocrystalline CdSe film using 1.0 ml capping agent (sample C).

3.2 XRD studies

CdSe can form hexagonal, wurzite-type structure or cubic, zinc blende-type structure (JCPDS files no 8-459 and 19-191). The X-ray diffractograms of the different CdSe films are shown in figs 2-(a), (b) and (c), respectively.
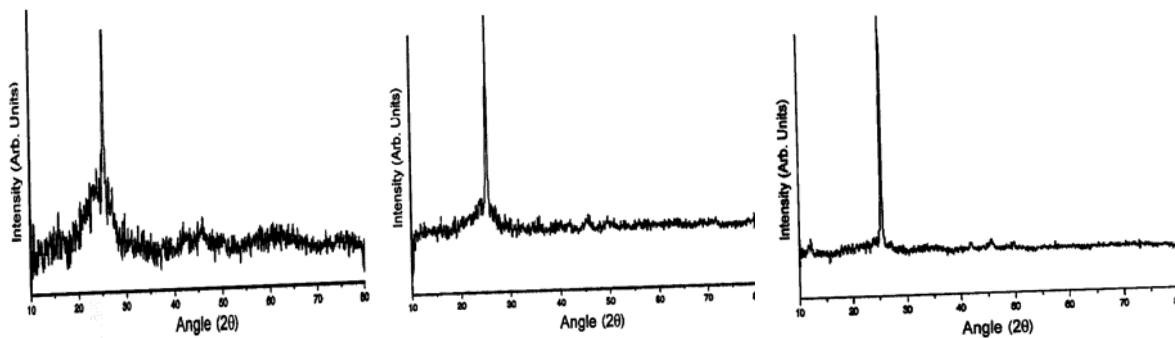
Fig. 2. X-ray diffractograms of different films : (a) bulk CdSe film without using capping agent (sample A), (b) nanocrystalline CdSe film using 0.5 ml capping agent (sample B), (c) nanocrystalline CdSe film using 1.0 ml capping agent (sample C).

The strong X-ray peak at (002) plane indicates the preferred orientation of the crystalline grains with c-axis perpendicular to the plane of the substrates that makes the (002) peak relatively stronger than the other peaks. The crystalline size (grain diameter 'D') of the crystallites can be determined using the Scherrer's formula from the full width at half maximu (FWHM) β [21],

$$D = 0.94 \, \lambda / \beta \cos\theta$$

where λ is the wavelength of X-ray used and θ the angle between the incident and scattered X-ray. The strain values 'ε' can be evaluated by using the following relation

$$\varepsilon = \beta \cos\theta / 4$$

The lattice spacing 'd' is calculated from the Bragg's formula

$$D = \lambda / 2 \sin\theta$$

The lattice parameter 'c' is determined for hexagonal structure by the following expression

$$1/d^2 = (h^2 + k^2 + l^2) / c^2$$

where h, k and l represent the lattice planes. The dislocation density 'δ' has been calculated by using the formula [22]

$$\delta = 15 \, \varepsilon / aD$$

The grain size and dislocation density of the CdSe films are calculated and given in table-1.

Table 1. Structural parameters of the different CdSe films.

Sample	Grain size D (nm)	Strain $\varepsilon \times 10^{-4}$ (lin^{-2}m^{-4})	Dislocation density $\delta \times 10^{14}$ (lin m^{-2})
A	96	3.31	5.35
B	42	9.88	11.38
C	24	16.61	14.75

The intense and sharp peaks in the XRD pattern reveal good crystallinity of the films and also confirm the stoichiometric nature of the CdSe films. Table-2 gives the comparision of observed 'd' values with the standard JCPDS data files. The lattice constant 'c' calculated using the XRD data for the different CdSe films are in close agreement with the ASTM data.

Table 2. Structural parameters of the different CdSe films.

Sample	2θ (deg.)	h k l	Lattice spacing d (Å)		Lattice parameter c (Å)
			Experimental	Standard	
A	25.4619	0 0 2	3.4983	3.5050	6.996
B	25.4319	0 0 2	3.4994	3.5050	6.998
C	25.3947	0 0 2	3.5074	3.5050	7.014

3.3 Optical absorption studies

The optical absorption spectra of chemically deposited CdSe films were taken at room temperature with Shimadzu (UV-VIS) Pharma Spec-1700 spectrophotometer in the wavelength range 300-700nm and are shown in fig. 3. A slight shift in the absorption peak is observed in the spectra near 450 nm which is indicative of quantum confinement effect in nanocrystalline materials in which the electrons, holes and excitons have limited space to move and their motion is possible for definite values of energies. Thus, their energy spectrum is quantized. As a result, the continuum of states in conduction and valence bands are broken down into discrete states with an energy spacing relative to band edges which is approximately inversely proportional to the square of the particle size and reduced mass [23]. The highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively resulting in the widening of band gap, which leads to the effective band gap larger than its bulk value. Thus, there will be a blue shift in the absorption spectra with reduction in particle size as observed in the present case. The energy band gaps of these films were determined from the absorption spectra. Almost all the II-VI compounds are direct band gap semiconductors. According to Tauc's relation, the absorption coefficient for direct band material is given by [24]

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where $\alpha h\nu$ is the photon energy, E_g the band gap and A a constant which is different for different transitions.
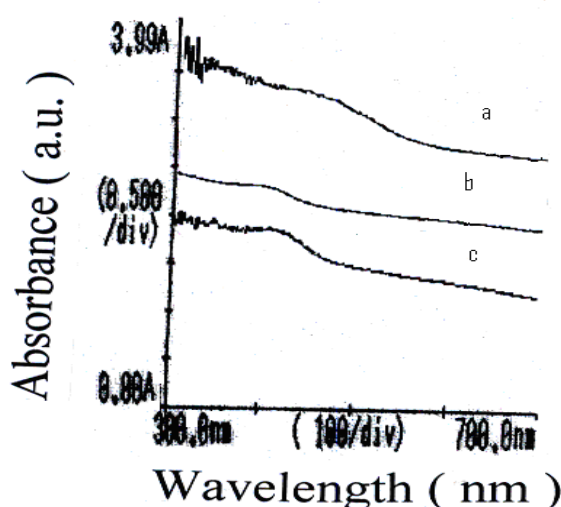

Fig. 3 Absorption spectra of different films : (a) bulk CdSe film without using capping agent (sample A), (b) nanocrystalline CdSe film using 0.5 ml capping agent (sample B), (c) nanocrystalline CdSe film using 1.0 ml capping agent (sample C).

The extrapolation of the nonlinear plot of $(\alpha h\nu)^2$ vs $h\nu$ gives the band gap of the corresponding material. Such plots for the bulk and the nanocrystalline films studied at two volumes of the capping
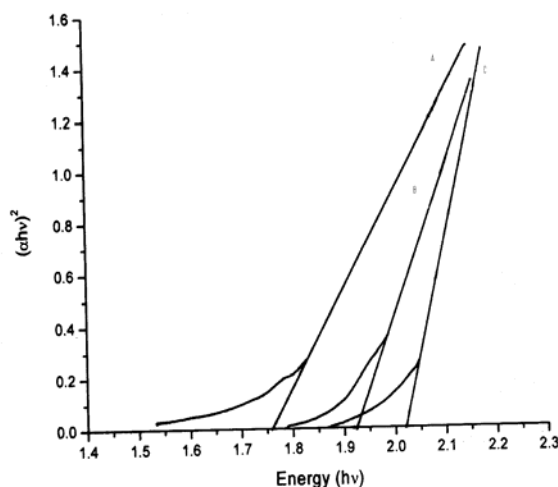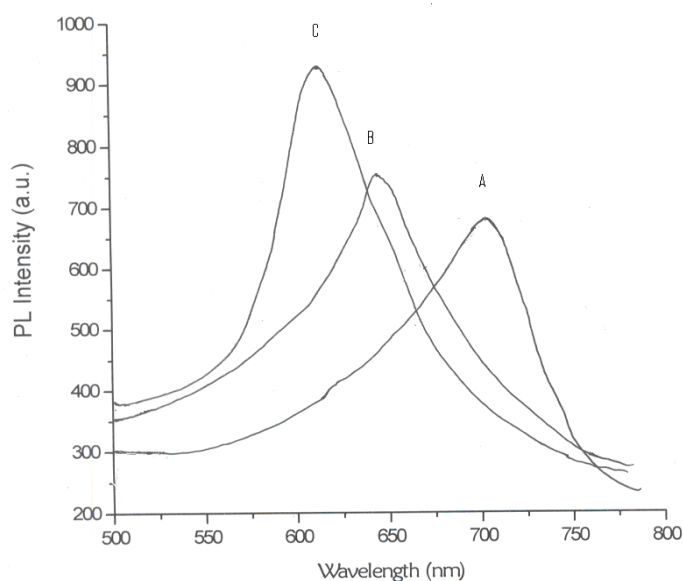

Fig. 4 Tauc's plots for different films : (a) bulk CdSe film without using capping agent (sample A), (b) nanocrystalline CdSe film using 0.5 ml capping agent (sample B), (c) nanocrystalline CdSe film using 1.0 ml capping agent (sample C).

agents are shown in fig. 4. The evaluated values of the band gaps are 1.76 eV for the bulk film; and 1.92 eV and 2.02 eV for the nanocrystalline films at the two volumes of capping agents. Thus, as expected, the band gap of the materials increases with increasing concentration of the capping agent, since the particle size then decreases.

3.4 Photoluminescence studies

The photoluminescence studies of the CdSe films A, B and C under the excitation of 365nm radiation are shown in fig. 5. The spectrum of the samples A, B and C contains peaks at 704, 647 and 615 nm respectively. The peak at 704 nm in sample A may be attributed to the band to band transition. The peak positions in samples B and C are found to shift towards lower wavelength side due to increase in concentration of capping agents. This indicates particle size reduction (quantum confinement) due to which the band gap increases and the emission peaks shift correspondingly on the lower wavelength side. The strong peak at 615 nm was considered due to band to band transition with increased band gap occurring due to nanocrystalline effect. This confirmed the quantum confinement effect also. As is known, under nanocrystalline effect two prominent changes are observed : (i) increase in band gap with reduced particle size and (ii) discreteness in the continuum of valence and conduction band states. Thus, apart from the band emission, due to discreteness, the transitions at higher levels may cause emission in the shorter wavelength side as observed in the present case. Manna et al [25] also reported a sharp peak in nanocrystalline CdSe film at 615 nm.

Fig. 5 Photoluminescence emission spectra of different films : (a) bulk CdSe film without using capping agent (sample A), (b) nanocrystalline CdSe film using 0.5 ml capping agent (sample B), (c) nanocrystalline CdSe film using 1.0 ml capping agent (sample C).

4. Conclusions

Results of XRD and optical absorption spectra support particle size reduction in CdSe films prepared with the capping agents. SEM studies show spherical morphology and irregular distribution of particles. Optical absorption spectra show increasing band gap with reduction in particle size. Photoluminescence emission spectra are seen to have blue shift in presence of capping agents, which again support particle size reduction as compared to the bulk materials, due to enlargement of the band gap.

Acknowledgement

References

[1] M. S. Gudiksen, L. J. Lauhon, J. F. Wang, D. C. Smith and C. M. Leiber, Nature (London) **415**, 617 (2002).
[2] N. A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P. M. Petroff and J. R. Heath, Science **300**, 112 (2003).
[3] X. T. Zhang, Z. Liu, Y. P. Leung, Quan Li and S. K. Hark, Appl. Phys. Lett. **83**, 5533 (2003).
[4] S. Bhunia, T. Kawamura, Y. Watanabe, S. Fujikawa and K. Tokushima, Appl. Phys. Lett. **83**, 3371 (2003).
[5] J. Q. Hu, Y. Bando, J. H. Zhan, F. F. Xu, T. Sekiguchi and D. Golberg, Adv. Mater. (Weinheim, Ger.) **16**, 1465 (2004).
[6] L. W. Yin, Y. Bando, Y. C. Zhu, D. Golberg and M. S. Li, Appl. Phys. Lett. **84**, 3912 (2004).
[7] W. I. Park, D. H. Kim, S. W. Jung and G. C. Yi, Appl. Phys. Lett. **80**, 4232 (2002).
[8] X. F. Duan and C. M. Lieber, Adv. Mater. (Weinheim, Ger.) **12**, 298 (2000).
[9] R. J. Waldau, N. Stücheli, M. Braun, M. L. Steiner, E. Bucher, R. Tenne, H. Flaisher, W. Kerfin, R. Braun and W. Koschel, J. Appl. Phys. **64**, 2601 (1988).

[10] N. Matsumura, H. Endo and J. Saraie, Phys. Status Solidi B **229**, 1039 (2002).

[11] K. W. Frese, Jr., Appl. Phys. Lett. **40**, 275 (1982).

[12] C. F. Hermandez, D. J. Suh, B. Kippelen and S. R. Marder, Appl. Phys. Lett. **85**, 534 (2004).

[13] M. Klude, T. Passow, H. Heinke and D. Hommel, Phys. Status Solidi B **229**, 1029 (2002).

[14] M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, Science **281**, 2013 (1998).

[15] A. Ubieta, P. Fernádez and J. Piqueras, J. Appl. Phys. **96**, 2210 (2004).

[16] J. Hambrock, A. Birkner, R. A. Ficher, J. Mater. Chem. **11**, 3197 (2001).

[17] J. E. Bowen Katari, V. L. Colvin, A. P. Alivisatos, J. Am. Chem. Soc. **115**, 8706 (1993).

[18] M. A. Malik, N. Revaprasadu and P. Oʹ Brien, Chem. Mater. **13**, 913 (2001).

[19] R. S. Singh & S. Bhushan, Chalcogenide Letters **5** (12), 377-388 (2008).

[20] Kusumanjali D., S. Bhushan & M. Mukherjee, Chalcogenide Letters **7** (1), 11-19 (2010).

[21] A. P. J. Wilson, Mathematical theory of X-ray powder diffractometry (New York : Gordon and Breach) p.62 (1963).

[22] C. K. De and N. K. Mishra, Indian J. Phys. **71**, 530 (1997).

[23] A. L. Afros, A. L. Afros, Sov. Phys. Semicond. **16**, 722 (1990).

[24] A. L. Dawar, P. k. Shishodia, J. Chouhan, G. Kumar, A. Mathur, Mat. Sci. Lett. **9**, 547 (1990).

[25] A. Manna, R. Bhattacharya and S. Saha, Chalcogenide Letters **6** (11), 611-616 (2009).