

Photoluminescence Studies of Nanocrystalline Films of Cadmium Sulphide

U. S. PATLE

*Department of Physics,
Govt. Narmada P.G. College, Hoshangabad (M.P.) - India.*

Abstract

Films of cadmium sulphide nanocrystals of various sizes have been prepared on glass substrate by chemical bath deposition method. These have been characterized by scanning electron microscope their absorption spectra and photoluminescence have been studied. Absorption indicates increased forbidden band gap due to quantum confinement. Two PL peaks have been observed at energies lower than effective band gap. Peak A near 680 nm and peak B near 920 nm. Both the peaks shift towards blue by decreasing the crystal size. Intensity of peak A increases by reducing the size, whereas that of peak B remains practically unchanged. The results are explained by considering that the energy levels are produced within the band gap by surface states and due to excess Cd, and only the density of surface states increases by reducing the particle size.

Keywords: Nanocrystalline, Photoluminescence, Cadmium Sulphide, Energy band gap.

INTRODUCTION

During the past decade, the preparation and characterization of materials on the nanometer scale has provided not only new physics in reduced dimensions, but also the possibility of fabricating novel material. The change in the properties of nanoparticles are driven mainly by two factors, namely the increase in the surface to volume ratio and drastic changes in the electronic structure of the materials due to

quantum confinement effects with decreasing particle size. Very often it is an interplay of these two effects that is responsible for the change in the properties [1] for size as small as a few nanometers, the surface atoms, which can be neglected for a bulk solid material, play a major role in determining the electronic properties. Apart from the effect of a large surface area, the material properties undergo drastic changes in their optical and electronic properties as a function of the size below a certain critical size. The physical properties of semiconductor nanoparticles exhibit distinctive changes compared to the bulk for sizes below the exciton Bohr radius (α_B), of the bulk semiconductor. At sizes comparable to and less than α_B , the exciton binding energy and the oscillator strength increases due to the enhanced overlap between the electron and hole wave function [2]. An interesting consequence of changes in the electronic structure is seen in the variation of the band gap with size in semiconductor nanoparticles. The studies of optical properties of nanocrystals have become the topic of both theoretical and experimental interest because of their tailorable properties and wide applications [3].

Recent reports suggest that nanoparticles can be used to produce light of various colors by band gap tuning using particles size effects [4]. Experimental evidence for quantum size effect was obtained by Ekimov and Onushchenko [5] for microcrystalline CuCl and CdS dispersed in a silicate glass. A blue shift in the absorption threshold and excitonic confinement effect resulted in theoretical development in these areas by Efros and Effros [6]. Consequently large experimental activities spurted up to confirm quantum confinement effect using size controlled nanocrystalline semiconductors. Among II-VI compounds, CdS is one of the most studied materials. Different methods have been employed to synthesize CdS nanoparticles and to study optical characteristics [7-8]. Attempts have also been made to study the optical properties of nanoparticles in polymer matrix. The nanoparticle polymer composite films can directly and surface passivation of the quantum dots is easily achieved. Firth et al [9] have reported blue emission from CdS - polymer composite.

In the present work, films of CdS nanocrystals of different sizes have been prepared by chemical bath deposition method and their optical absorption and photoluminescence (PL) have been investigated.

EXPERIMENTAL

Films of CdS nanocrystals were deposited on glass substrate using chemical precipitation technique as described by Nanda et al. [10]. 1 M aqueous solution of CdSO₄ was prepared and 1.9 M NH₄OH solution was added to it till it becomes transparent. Then 0.33 M solution of thiourea was added stirring the mixture for about 15 to 20 minutes, which precipitated CdS crystals. The mixture was kept in constant temperature bath at 300 K and CdS was deposited on glass plates by dipping them in the mixture for different time- duration which gave nanoparticles of different sizes. After deposition the samples were washed in running water and dried.

In order to investigate the surface morphology and crystalline size, the films were analyzed by scanning electron microscope (SEM) using nanoscope II. The absorption spectra of the samples in UV-VIS region were recorded with the help of Perkin Elimer Lemda -12 spectrometer in the wavelength range from 300 to 700 nm. The photoluminescence of the samples was investigated using grating monochromator HM 104 and photomultiplier tube RCA-931. Mercury lamp was used for excitation and PL intensity was measured in the range 400 to 1000 nm.

RESULTS

A Typical scanning electron microscope photograph of CdS nanocrystalline film is shown in Fig. 1. The particle sizes of the samples obtained by various dipping times were estimated by SEM and these are given in Table 1. It is observed that the particles size increases with the dipping time.



Fig. 1: SEM of CdS nanocrystalline Film (a) and experimental setup (b).

Table 1: Photoluminescence of CdS Nanocrystalline Films

S. No.	Sample	Deposition Time (in minutes)	Crystal Size (in nm)	PL Peak A		PL Peak B	
				Intensity (in a. u.)	λ (in nm)	Intensity (in a. u.)	λ (in nm)
1.	I	20	21	120	670	100	903
2.	II	30	26	80	680	100	911
3.	III	40	31	50	685	97	923
4.	IV	60	88	75	695	100	940

Reduction in particle size below a particular value causes increase in band gap due to quantum confinement. Hence optical absorption starts at higher energies. Fig. 2 shows a typical absorption spectrum of CdS nanocrystalline film for deposition time of 20 minutes. It is evident from the figure that absorption slowly increases in the wavelength range 600 - 400 nm; it suddenly decreases at 387 nm and then again

increases from 382 nm for lower wavelength giving peak at 329 nm. The absorption edge is obtained at 382 nm revealing that band gap is 3.25 eV. It is greater than band gap of bulk CdS (2.4 eV) by 0.85 eV indicating quantum confinement effect. In order samples also similar results have been obtained.

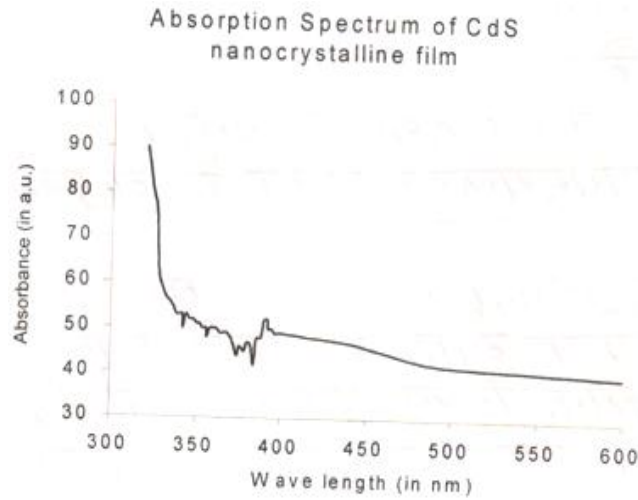


Fig. 2: Absorption Spectrum of CdS nanocrystals.

The photoluminescence studies of the CdS nanocrystalline films show two emission-peaks at energies lower than band gap (Fig.3). The peak intensities and corresponding wavelengths are shown in Table 1. It is observed that the intensity of band A increases as the particles size is decreased, whereas that of band B remains practically the same. Slight blue shift is seen in both the bands with decreasing crystalline size.

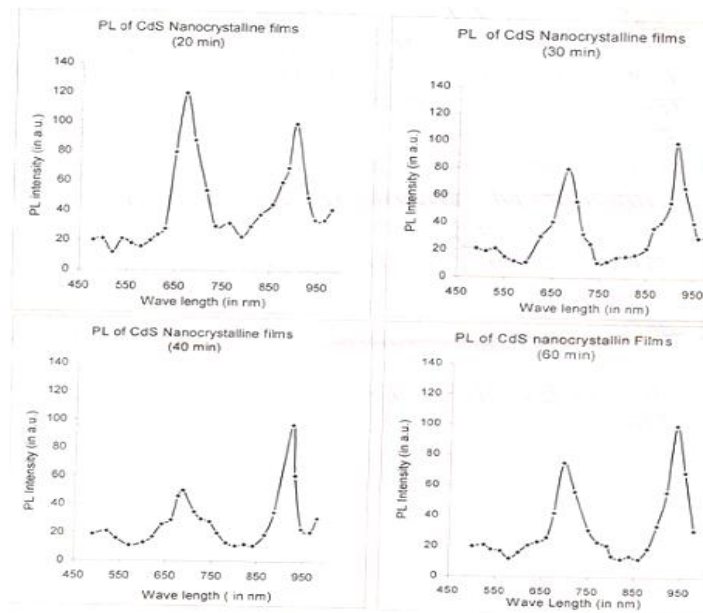


Fig. 3: Photoluminescence Spectra of films of CdS nanocrystals of various sizes.

The variation of particle size and shifting of PL peaks with the deposition time are shown in Fig. 4. It can be seen that the blue shift in both the PL peaks A and B is nearly same.

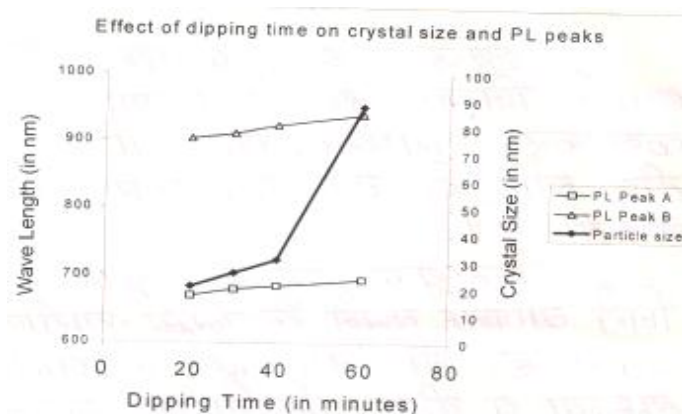


Fig. 4: Variation of particle size and shifting of PL peaks with deposition time

DISCUSSION

Scanning electron microscopy (SEM) is a very powerful tool to observe the surface morphology. Fractal features are observed by SEM, which, under high magnification, reveals particle size. In the chemical bath deposition method used presently, the growth of particles is slow in the beginning and it is fast after an hour, as can be seen from the Table I. This may be due to increased reaction rate as ammonia is reduced from the solution.

Optical absorption spectrum provides a technique to determine E_g of the material. At low energies photons are not absorbed. Absorption starts at $h\nu = E_g$ and increases with photon energy giving a broad peak. Hence E_g can be estimated from the starting edge of absorption (α) or from the slope of $(\alpha h\nu)^2$ versus $(h\nu)$ curve [3]. In case on nanoparticles, absorption starts at higher energies due to increased E_g and sometimes shows steps also. The simplest and easiest method to determine size dependence of electronic states in semiconductor nanoparticles is to study the absorption as a function of wavelength. The slow increase in the absorption as the wavelength is reduced below 500 nm can be attributed to defect states or levels due excess Cd as discussed later. Low absorption in the range 387 to 382 indicates discretization of states in nanocrystals and sudden increase in the absorption for wavelengths below 382 nm may be caused by band to band transitions.

Photoluminescence (PL) is a process in which an electron, excited by monochromatic photon beam of certain energy undergoes radiative recombination either at valence band (band edge luminescence) or at traps/surface states (normally red shifted luminescence) within the forbidden gap. Hence, PL provides an estimation of band gap and levels within the gap. Attempts have been made to study PL properties of

nanocrystalline semiconductors [11-12], which show that with decreasing crystalline size, the band edge luminescence or excitonic recombination yield decreases. The red shifted band intensity, in general, is found to increase with reduction in crystalline size. The increase in PL yield of red shifted band is ascribed to the increase in the surface state density. The photoluminescence (PL) intensity, in general, is found to increase with decreasing crystalline size. However, both the band edge and red shifted emission shift towards blue with decreasing crystalline size.

In the present studies, the energy of both PL bands are at quite low energy as compared to the band gap showing that the photo-excited electrons decay non-radiatively to deep traps. This is also supported by small shift in the bands with decreasing size. Nanda et al [8] have reported that nanocrystalline CdS films prepared by similar method are Cd-rich. The excess Cd, being electro-positive, will give rise to occupied levels below Fermi level, which can trap holes. A model is proposed in order to explain our PL spectra (Fig.5).

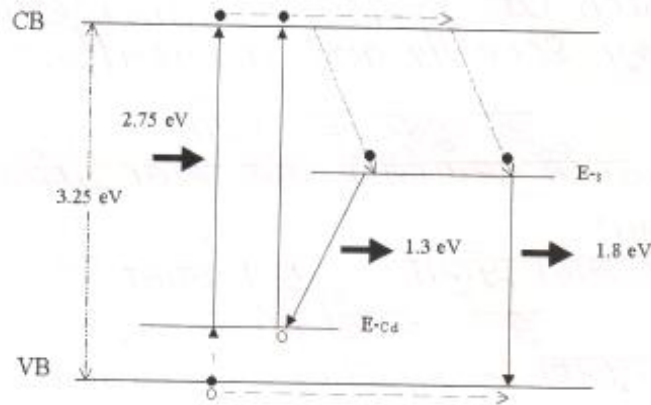


Fig.5 Proposed Model for photoluminescence in CdS nanocrystalline films.

The energy states within the band gap of nano-sized CdS are produced by surface states and due to excess Cd. Since excitation is by visible mercury light, the exciting photons have energy less than the effective band gap ~ 3.25 eV as obtained by absorption spectra. Therefore these excite the electrons from excess Cd levels near the valance band to conduction band. These excited electrons decay non-radiatively to surface states and recombine with holes in valance band giving rise to PL band A at ~ 680 nm or ~ 1.8 eV. With decrease in the particles size, the surface to volume ratio increases, increasing the density of surface states, which causes increase in PL intensity of band A. the PL band B may be attributed to transitions from surface states to Cd levels giving a peak at ~ 920 nm or ~ 1.3 eV. Since the concentration of the reacting agents is kept same for all the samples, numbers of excess Cd level do not change with the particle size and the intensity of this peak remains practically constant. Narrow peaks clearly indicate narrow size distribution of nanoparticles. The blue shift by about 0.06 eV in both the peaks by decreasing particle size can be

understood by considering downward shift of valance band edge due to quantum size effect.

REFERENCES

- [1] S. A. Majetich, A.C. Karter, "Surface effects on the optical properties of cadmium selenide quantum dots". *J. Phys. Chem.*, vol. 97, pp 8727, 1993.
- [2] Y. Wang, N. Herron, "Nanosized semiconductor clusters: materials synthesis, quantum size effect and photophysical properties". *J. Phys. Chem.*, vol. 95, pp 525, 1991.
- [3] S. N. Sahu, K. K. Nanda, "Nanostructure semiconductors: physics and applications". PINSA, Vol. 67A (1), pp 103, 2001.
- [4] R. Seigel, "Creating nanophase materials. Scientific American", 74, 275, 1996.
- [5] A.I. Ekimov, A. L. Efros, A. A. Onushchenko, "Quantum size effect in semiconductor micro crystals". *Sol. Stat. Comm.*, 56 (11) 921, 1985.
- [6] A.I. Efros, A. L. Efros "Interband absorption of light in a semiconductor sphere". *Sov. Phys. Semiconductor*. 16, 772, 1982.
- [7] A. F. G. Monte, N.O. Dantas, P. C. Morais, D. Rabelo, "Synthesis and characterization of CdS nanoparticles in mesoporous copolymer template". *Braz. J. Phys.* 36, 2a. 2006,
- [8] Chu Yuan-Chih, Wang, Cheng-Chien, Haung, Yao Hui, Chen Chun- Yung, Preparation and characterization of luminescent CdS nanoparticles immobilized on poly (St-co-GMA-IDA) polymer microspheres. *Nanotechnology*, 16, 376, 2005.
- [9] A.V. Firth, S.W. Haggata, P. K. Khanna, S. J. Williams, J. W. Allen, S. W. Magennis, I. D. W. Samuel, D. J. Hamilton "Cole., Production and luminescence properties of CdSe and CdS nanoparticles polymer composites". *J. of Lumi.* 109, 163, 2004 .
- [10] K. K.Nanda, S. N. Sarangi, S. Mohanty, S. N. Sahu, "Optical properties of CdS Nanocrystalline films prepared by precipitation technique" . *Thin Solid Films*, 322, 21, 1998.
- [11] T. Arai, H. Fujumura, I. Umez, T. Ogawa, A. Fiji, "Effect of size confinement on the electronic states of CdS cluster in germanium oxide matrix". *Jpn. J. Appl. Phys.* 28, 484, 1989.
- [12] W. Chen, Y. Xu, Z. Lin, Z. Wang, L. Lin, "Formation, Structure and fluorescence of CdS clusters in a mesoporous zeolite". *Solid State Commun.*, 105,129, 1998

