

Electrical and optical properties of CdS nanocrystalline semiconductors

Shikha Tiwari¹ and Sanjay Tiwari*²

¹ State Forensic Science Laboratory, Raipur (C.G.), India

² S.O.S. in Electronics, Pt Ravishankar Shukla University, Raipur (C.G.), India

Received 20 April 2004, revised 25 May 2004, accepted 15 July 2004

Published online 15 December 2005

Key words nanocrystalline, cadmium sulphide.

PACS 68.60.-p

II-VI semiconductor nanoparticles have recently attracted a lot of attention due to the possibility of their application in various devices. In the present study, chemical method has been used in synthesis of CdS nanoparticles and thiophenol was used as capping agent. X-ray diffraction studies of both samples were done. The dc conductivity of CdS increases at a lower rate or is approximately constant upto 500K and thereafter the conductivity increases at a rapid rate. Beyond T_c it is seen that the portion of the σ_{dc} versus $1000/T$ is almost a straight line showing an Arrhenius behaviour. The dielectric constant of nanoparticles of CdS is found to be larger than the corresponding values of CdS crystals. It is clearly observed that at lower wavelengths nanocrystalline samples show a blue-shift. The three peaks of sample (S2), A, Band C can be ascribed to the transition from Cd-O complex donor formed by adsorbed oxygen to the valance band, Cd - excess acceptor and the surface states, respectively.

© 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Nanostructured materials especially II-VI semiconductors have become a subject of intensive research for their extraordinary properties compared to their bulk counterparts [1-3]. Blue shift of the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength, nonlinear optical effect are some examples of the interesting properties exhibited by these nanoparticles. Particularly, semi conducting materials in the nanostructured form offers the possibility of possessing large optical nonlinear susceptibility and ultra fast response [4]. Also they are very attractive for the realization of thermally stable and frequency selective lasers and photodetectors [5, 6], whose performance have been. found to be modulated drastically by the shape and sizes of the nanocrystallites

All these properties are various manifestations of the so called quantum size effect which arises due to the increasing quantum confinement of the electrons and holes with diminishing size of the crystallites and the consequent changes in the electronic structures. The crucial barrier between a micron and nanometer was scaled at the laboratory level in the early eighties. Operational economy and the reliability trimmed the microns but the erosion of nanometers is mainly resulting from functional, material and swiftness requirements.

However, when the dimensions of the crystallites become comparable or less than the Bohr radius of the exciton wave function, there is a significant change in the properties. In molecular terminology, this corresponds to the widening of the energy gap between the highest occupied molecular orbits as the size decreases.

In CdS, such quantum size effect is observed for crystallite dimensions below 50Å which is approximately the Bohr exciton diameter in CdS. This ability to tune the band gap of semiconductor to suit any specific application by tailoring the size of the particles has many exciting technological implications. However in order to optimize the properties, the nanocrystallite sizes should have a narrow distribution in size and shape.

* Corresponding author: e-mail: sanjay_t63@yahoo.com, sanjaytiwarijbp@rediffmail.com

Different chemical routes have been followed in the literature to control the particle shape and more importantly their size distribution. These include the uses of surface clipping ligands [7, 8, and 9], reverse micellar method [10, 11], polymers [12, 13], glasses and crystalline hosts such as zeolites [14]. Here we will concentrate on electrical and optical properties of CdS nanoparticles with thiophenol as capping agent.

2 Experimental

Sulphide nanoparticles like CdS are potential candidates for optoelectronics devices. Controlled size tuning of the particles can lead to properties tuning which can have important consequences in the device fabrication. The details of the synthesis and passivation method may vary to some extent from one laboratory to other, but the underlying idea is similar.

Here CdS nanocrystallites with thiophenol capping were synthesized as follows: Stock solutions were prepared as: 0.1M cadmium salt solution [Cd^{2+}] was made by dissolving cadmium acetate in methanol and 0.1 Na_2S solution [S^{2-}] was made by dissolving 80gm of sodium sulphide in 50ml of methanol. 0.2M solution was made from 2.2ml of thiophenol in 100ml of methanol. From these stock solutions, 50ml of sodium sulphide solution and 50 ml of thiophenol solution was mixed and stirred, to which 100ml of cadmium acetate solution was added while stirring the solution. This results in a cloudy yellow solution. Then the solution was stirred for some more time, filtered and suction dried. Dry yellow powder was obtained by this process. By changing the relative ratio of sulphide to thiophenol, clusters of different sizes can be obtained. For smaller size clusters the S: Ph = 1:2, (sample S1) and for larger size crystals it was 2:1, (sample S2) (where S stands for sulphide and Ph stands for thiophenol).

Organic capping agent inhibits the coalescence of the particles. After the reaction is completed the nanoparticles can be precipitated, washed and dried as the free standing powder. Powders can be used as precursors for thin films. The crystal structure of the particles was determined by X-ray diffraction. The diffraction peaks of the nanoparticles were found to be shifted slightly to larger angles than expected for the corresponding bulk crystals suggesting a possible lattice contraction.

D.C. conductivity was determined by measuring the resistance of the sample using an electrometer in the V/I mode. Dielectric constant ϵ and ac conductivity σ_{ac} , of the samples were determined using an impedance analyzer over a frequency range 10kHz to 13MHz. In order to study the optical properties of CdS nanocrystallites we have characterized these samples through optical absorption, photoluminescence, luminescence decay and photovoltaic measurements.

3 Results and discussion

Variation of dc conductivity σ_{dc} and ac conductivity σ_{ac} of CdS with temperature is shown in figure 1. The log σ_{dc} vs $1000/T$ graph of CdS shows two distinct regions, the first region indicating a slow increase of conductivity with temperature and the second one indicating a rapid increase beyond this temperature. σ_{ac} of CdS samples is found to increase linearly with frequency. ac conductivity σ_{ac} increases at a low rate with temperature initially and more rapidly beyond about 425K. The σ_{ac} versus $1000/T$ graphs of the samples at low frequencies show a maximum around almost the same temperature.

The variation of dielectric constant ϵ and the ac conductivity σ_{ac} of the CdS samples as function of temperature is shown in figure 2.

Figure 3 shows the room temperature absorption spectra. The absorption edges of the nanocrystalline samples are observed at lower wavelengths signifying a blue shift. Figure 4 shows the size dependence of the band gap, clearly showing a blue shift with decreasing crystalline size. It is clear from the figure that a change in band gap could be achieved in the band gap from 2.405eV to 2.97eV as we narrow down the crystalline size.

Figure 5 shows the photoluminescence (PL) studies of CdS nanocrystals at room temperature. It is clear from this figure that PL spectra shows three peaks at 670nm, 915nm, and 1180nm. These spectra were recorded using 488nm Ar^+ laser. Figure 6 shows the Cd 3d core level spectrum of CdS nanocrystallite sample, suggesting a single environment for all C sites in the cluster and bonding around Cd sites similar to the bulk.

Table 1 shows the open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) as a function of band gap for different CdS samples for photoelectrochemical solar cells with configuration Ti/CdS/ Na_2SO_3 /Pt. The intensity of illumination used was $60\text{mW}/\text{cm}^2$. It is clear from the table that photovoltage increases for nanocrystalline sizes.

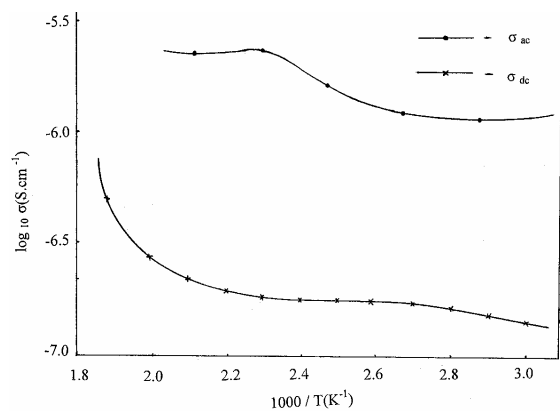


Fig. 1 Variation of log of dc conductivity σ_{dc} and ac conductivity σ_{ac} of CdS with $1000/T$.

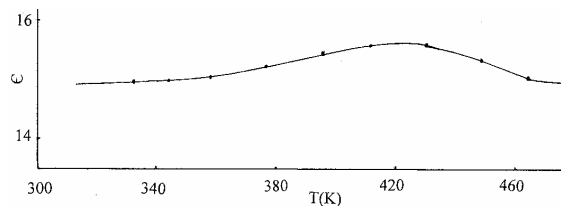


Fig. 2 Variation of dielectric constant ϵ of CdS samples with temperature.

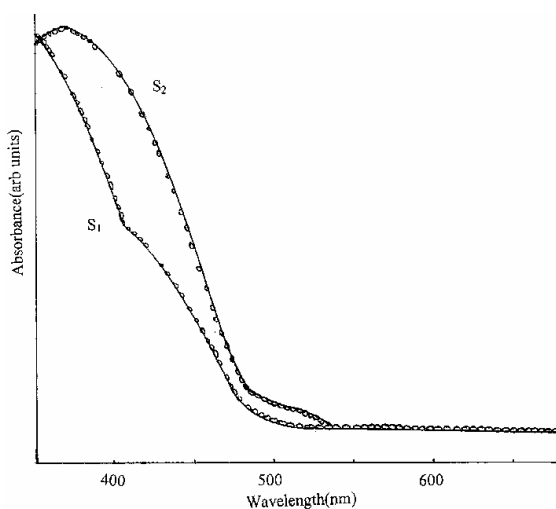


Fig. 3 Room temperature absorption spectra of CdS samples.

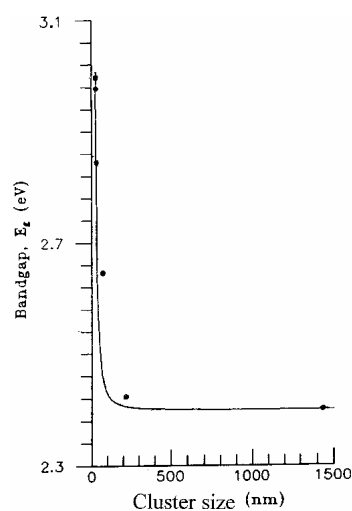


Fig. 4 The size dependence of the band gap.

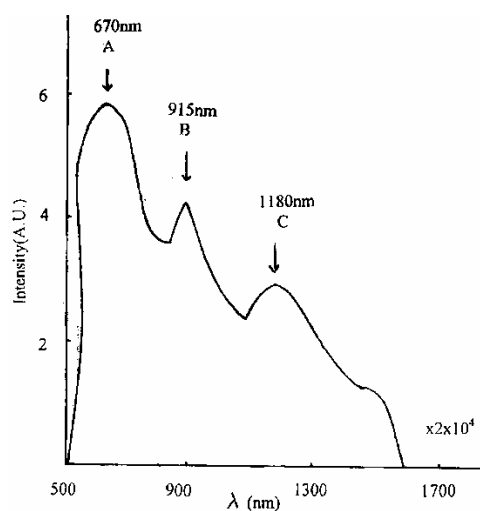


Fig. 5 Photoluminescence (PL) studies of CdS nanocrystals at room temperature.

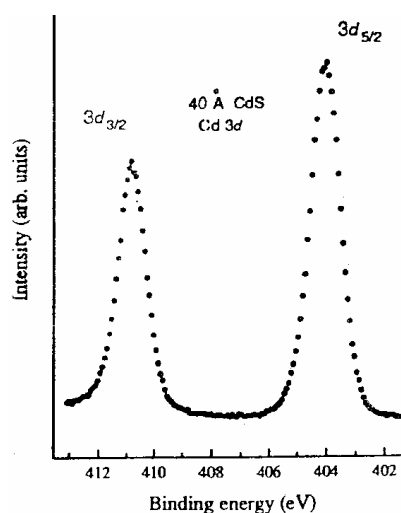


Fig. 6 Cd 3d core level spectrum of CdS nanocrystallite sample.

Table 1 Open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) as a function of band gap for different CdS samples for photoelectrochemical solar cells.

Thickness(nm)	Band-gap	V_{oc} (mV)	J_{sc} ($\mu\text{A}/\text{cm}^2$)
40	2.95	679	458
20	3.01	686	458

It is clear from the present study that the dc conductivity of CdS increases at a lower rate or is approximately constant upto 500K and thereafter the conductivity increases at a rapid rate. Beyond T_c it is seen that the portion of the σ_{dc} versus $1000/T$ is almost a straight line showing an Arrhenius behaviour. The lack of dependence of conductivity on temperature up to T_c may be attributed to the large band gap (nanosize), due to which the charges are not released from the particles by thermionic emission are not available for tunneling. The conductivity above T_c is due to both thermionic emission and tunneling of charge carriers across the barrier. Because of the small size of the particles, the charge carriers reach the surface of the particles more easily enabling easy electron transfer by thermionic emission, or tunneling or both, enhancing the conductivity [15].

The dielectric constant of nanoparticles of CdS is found to be larger than the corresponding values of CdS crystals [16, 17]. Also σ_{ac} of CdS is much larger than that of the bulk crystals [18, 19]. Unlike the case of ionic crystals, where the effective field CdS nanocrystalline were synthesized using thiophenol as capping agent. By changing the relative ratio of sulphide to thiophenol, clusters of different sizes were obtained. Electrical and optical properties of CdS nanocrystallites exhibit extraordinary behavior over that of bulk.

$$E_{\text{eff}} = E + (4/3) \pi P,$$

For semiconductors E_{eff} should be essentially equal to the macroscopic field E , i.e. $E_{\text{eff}} = E$.

This leads to an expression for ϵ of the form $\epsilon - 1 = 4\pi\alpha/V$ where V is the volume. The large value of ϵ of pallets of nanoparticles of CdS compared to the corresponding bulk values may be due to the small of V in the above expression. The very large value of σ_{ac} of CdS may be attributed to the defect structure of the particles [20, 21].

It is clearly observed that at lower wavelengths nanocrystalline samples show a blue-shift. The sample (S1) is expected to be of smaller size, as it was prepared with a relatively higher proportion of the capping agent. This is supported by the shift of the absorption band edge to still lower wavelength compared to that of sample (S2). This clearly demonstrates a progressive increase of the band gap with decreasing cluster size in CdS nanocrystallites. In more qualitative terms, the sample of larger clusters (S2) has an absorption edge at 461nm (2.69eV) and another one with smaller clusters (S1) has an edge at 396nm (3.13eV). Thus the shift in the band gaps are 0.3eV and 0.73eV for clusters (S2) and (S1) respectively. These shifts corresponds to 40\AA and 20\AA diameter particles for these two nanocrystallite samples, when analyzed on the basis of experimental results as well as tight binding calculations reported by Wang and Herron[22]. However the excitonic feature is not pronounced in any of these samples. This may be due to a large size distribution of particles

We know that the PL spectrum is due to the radiative recombination of the lowest lying excited states of the nanocrystallites, the semi quantitative estimation of the dependence of peak position on the average grain radius can be done. In general, the carrier confinement effect in the semiconductor nanocrystallites stabilizes both excitons and corresponding luminescence due to excitonic recombinations even at room temperature. With the gradual decrease of the sizes of the nanocrystallites, the luminescence has been found to be dominated by the band impurity and surface state transitions over the excitonic luminescence. However, the relative intensities depend on the excitation intensity, the transitions associated with the band to band free electron and hole would dominate in the PL spectra even for samples with smaller (5.7nm) grain size.

The three peaks of figure 5 of sample (S2), A, B and C can be ascribed to the transition from Cd-O complex donor formed by adsorbed oxygen to the valance band, Cd - excess acceptor and the surface states, respectively. These peaks are marked as A, B and C respectively. The two peak structure in Cd 3d core level arises from the spin-orbit interaction with the Cd $3d_{5/2}$ peak position at 404.0eV and the $3d_{3/2}$ at 410.8eV. We have expanded a narrow energy range around the $3d_{5/2}$ feature in the inset. It is clear from these spectral features that Cd 3d exhibits narrow, well defined, single peak feature for each of the doublet structure. This suggests that specifically Cd atoms appear to bond only to S atoms and not directly with the capping agent. Apart from the s-p splitting corresponding to the S 2p signal, there is a clear evidence of another spin orbit

doublet feature superimposed. Thus, it appears that a second S species present in this sample alone has S2p_{3/2} feature overlapping the S2p_{1/2} feature arising from CdS; this enhances the intensity in this energy range relative to the S 2p signal from the bulk.

4 Conclusions

CdS nanocrystalline were synthesized using thiophenol as capping agent. By changing the relative ratio of sulphide to thiophenol, clusters of different sizes were obtained. Electrical and optical properties of CdS nanocrystallites exhibit extraordinary behavior over that of bulk.

References

- [1] H. Gleiter, *Nanostruct. Mat.* **1**, 1 (1992).
- [2] M. G. Bawendi, P. J. Corroll, W. L. Willson, and L. E. Brus, *J. Chem. Phys.* **96**, 946 (1992).
- [3] R. P. Andres, R. S. Nverback, W. L. Brown, L. E. Brus, W. A. Goddard, A. Kaldor, S. G. Louie, M. Moscovits, P. S. Perry, S. J. Riley, R. W. Siegel, F. Spaepen, and Y. Wang, *J. Mater. Res.* **4**, 704 (1989).
- [4] L. Brus, *Appl. Phys.* **A53**, 465 (1991).
- [5] W. T Tsang, *Semiconductors and semimetal*, Ed. by R. K. Willardson and A. C. Beer **24**, P397, Academic Press, New York.
- [6] S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, *Adv. Phys.* **38**, 89 (1989).
- [7] T. Vossmeier, L. Katsikas, M. Giersig, I. G Popvik, K. Diesner, A. Chemseddine, and H. Weller, *J. Phys. Chem.* **98**, 7665 (1994).
- [8] N. Herron, Wang Ying, and Eckert Hellhmut, *J. Am. Chem. Soc.* **112**, 1322 (1990).
- [9] C. B Murray, D. J. Norris, and M. G Bawendi, *J. Am. Chem. Soc.* **115**, 706 (1993).
- [10] C. Petit, *J. Phys. Chem.* **94**, 598 (1990).
- [11] L. Molle, F. Billoudet, and M. P. Pileni, *J. Phys. Chem.* **99**, 16425 (1995).
- [12] Y. Wang, A. Suna, W. Mahler, and R. Kasowski, *J. Phys. Chem.* **87**, 7315 (1987).
- [13] W. Stephen, Xiaochang Haggatta, and David Li, *J. Mater. Chem.* **6**, 1771 (1996).
- [14] Wei Chem, *Solid State Commun.* **100**, 101 (1996).
- [15] J. H. Fendler, *Chem. Rev.* **87**, 877 (1987).
- [16] J. Nanda, B. A. Kuruvilla, K. V. P. M. Shafi, and D. D. Sharma, *Phys. Sem. Nanostruct.* **25** (1997).
- [17] K. K. Nanda, S. N. Sarangi, and S. N. Sahu, *Phys. Sem. Nanostruct.* **217** (1997).
- [18] C. Elbaum, *Phys. Rev. Lett.* **32**, 376 (1974).
- [19] P. Merchant and C. Elbaum, *Solid State Commun.* **26**, 73 (1978).
- [20] K. Shahi and K. Wagner, *J. Electrochem. Soc.* **128**, 6 (1981).
- [21] K. Shahi and J. B. Wagner, *J. Electrochem. Soc.* **42**, 107 (1982).
- [22] Y. Wang and N. Herron, *J. Phys. Chem.* **95**, 525 (1991).