Surface morphology based optical properties of chemically deposited CdS nano crystalline thin films

Ruby Das [a,*], SumanPandey[b]

[a]*Department of Applied Physics, Bhilai Institute of Technology, Durg (C.G.) 491001, India*

[b]*Deprtment of Physics, Rungta College of Engineering and Technology, Bhilai (C.G.) India*

**E-mail: ruby.das@bitdurg.ac.in*

Abstract

Nano crystalline thin films of CdS with varied concentrations of capping agents thioglycerol and methanol (TGM) were prepared on suitably cleaned glass substrate by chemical bath deposition technique. The thickness of the films decreases with increasing concentration of TGM. The effect on surface morphology and optical properties of the deposited films has been discussed. The surface morphology of the deposited films was characterized by SEM. SEM micrographs suggest smooth, uniform and cabbage type structure which may due to layered growth of material. After increasing concentration of TGM the densification of the particles was observed. UV-Vis Spectroscopy and photoluminescence (PL) studies have been carried out to characterize the prepared materials. Optical absorption spectra shows a shift in the absorption edge to shorter wavelength side in comparison to that of the bulk material which may be due to quantum confinement effects. The values of some important parameters such as transmittance, absorption coefficient (α) and band gaps of the films were successfully calculated by UV-VIS spectrophotometer. It is varying from 2.90eV to 2.80eV for concentration change of capping agents from 0.2ml to 0.8ml respectively. From the shift in optical bandgap, particle sizes were also calculated using Effective Mass Approximation (EMA) method. PL spectra showed enhancement in intensity in blue region which suggests that the host lattice of CdS absorbs energy from capping agent and transfers it to visible radiation. Thus, nano crystalline CdS can be used as an effective UV filter.

***Keywords:**Nanocrystalline,chemical bath deposition, quantum confinement,SEM.*

1. Introduction

Nanometer-scale electronics have opened the new area of application in device technology. Quantum confinement effect modifies the electronic structure of nano crystals when the sizes of the nanoparticles are comparable to that of Bohr excitonic radius of those materials. Hence depending upon the sizes of the materials, the nano scale semiconductors show interesting properties, and great efforts have been imposed on controlling their sizes [1]. The most evident manifestation of such properties is the optical light emission in the blue – red spectral region characterized by a blue-shift at smaller crystallite dimensions [2]. Such properties make semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings to bioelectronics and light emitting devices [3]. Nanotechnology has strongly driven the development of recent electron microscopy, with demands not only for increasing resolution but also for more information from the sample. In any molecule, the more atomic orbitals take part in bonding, the less energy gap will be between the molecular orbitals. The particle's physical properties are extremely important to their performance and the performance of any product into which they are ultimately incorporated [4-8].

The behavior of NPs is critically dependent on several particle characteristics, including size, shape, surface area and surface reactivity, and that risk assessments for both human health and the environment have to be based on these characteristics [9, 10]. Materials with suitable optical properties, appropriate band gap, and suitable dielectric constants can be used effectively to transmit solar radiation within crucial wavelength regions for various applications. CdS is one of the most promising materials as its band gap corresponds closely to the visible spectra and also band to band transitions occur in these materials, making it suitable for applications in many electro-optic devices [11, 12]. Although there are a variety of techniques for the preparation of CdS like vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy etc., and chemical bath deposition method is the simplest and the least expensive [13-15]. This method requires very economical experimental facilities and is highly suitable for large scale preparations, usually in film form. Chemical bath deposited films are now being developed to be utilized in converting solar radiation into electricity.

Whether the reduced thickness influences the nanoparticle shape and the crystal structure is not yet well understood. The present paper concerns with the nano crystalline effect on UV-Vis-NIR spectra and photoluminescence spectra of CdS films prepared by chemical bath deposition (CBD) method using thioglycerol and methanol (TGM) as capping agents. We present a comparative study of photoluminescence and its relation to the morphology of cadmium sulphide (CdS) thin films.

2. Materials and Method

2.1 Preparation of CdSnano crystalline thin films

The Films were prepared on microscopic glass slides of dimension 24 mm × 75 mm. The substrates were previously degreased in nitric acid for 48 hours, cleaned in ultrasonic cleaner with distilled water and then allowed to dry in air.The dried glass slides were dipped vertically into a mixture of solutions of 1M cadmium acetate, TEA, 30% aq. ammonia and 1M thiourea. All the solutions were prepared in triple distilled water. TEA was used as a complexing agent to from [Cd(TEA)+2] complex for controlling the growth rate. The capping agents' thioglycerol with methanol (TGM) in 1:1 ratio were then added to the above said mixture of solutions, since this gave better results. Alls chemicals were AR grade and used without further purification. The liquid ammonia was used to adjust the pH up to 8.5 to avoid precipitate formation of cadmium hydroxide. The adjusted solution was kept under moderate stirring before filming. The CdS films were deposited at a constant temperature of water bath at 70°C for 60 minutes. The deposition of films is based on precipitation followed by condensation. The principle behind the formation of precipitate is based on slow release of Cd^{2+} and S^{2-} ions in aqueous basic bath. The obtained yellow-reddish films were washed with triple distilled water for several times to remove the excessive thiourea and ions possibly remaining in the films. The final ones were dried at room temperature.

2.2 Characterization Techniques

The deposited films were characterized by studying mainly structural and optical properties. The surface morphology investigations of the CdSnano crystalline thin films were carried out using a scanning electron microscope (SEM) of EVO 18.UV-VIS spectrophotometric measurement was performed by using a double beam Spectrophotometer, spectra scan software 6.51 (Chemito, SPECTRASCAN-UV-2600) at room temperature in the wavelength range 400–1100 nm with a resolution setting of 2 nm. The spectrum was recorded by taking a similar glass as reference and hence transmission due to the film only was obtained. The photoluminescence spectra of the films were taken in the range 400–700 nm by using a constant deviation spectrometer. The PL excitation source was a UV source with filters of wavelength 235nm. For detection of emitted light, an RCA 931A photomultiplier tube, operated by a highly regulated power supply (EHT-11, Scientific Instruments, Roorkee, India) was used. The integrated light output in the form of current was recorded by digital Pico-ammeter (DPM-121, Scientific Instruments, Roorkee).

3. Results and Discussion

The resulting thin films have a yellow colour, reflective, smooth, homogeneous and well adhered to the glass substrate. The thicknesses of the films were estimated by gravimetric weight difference method. For this, a sensitive microbalance was utilized. The variations of the thickness with TGM concentration are represented in Fig.1.The thickness of the films was found to decrease and finally becomes more transparent with increasing concentration of TGM.

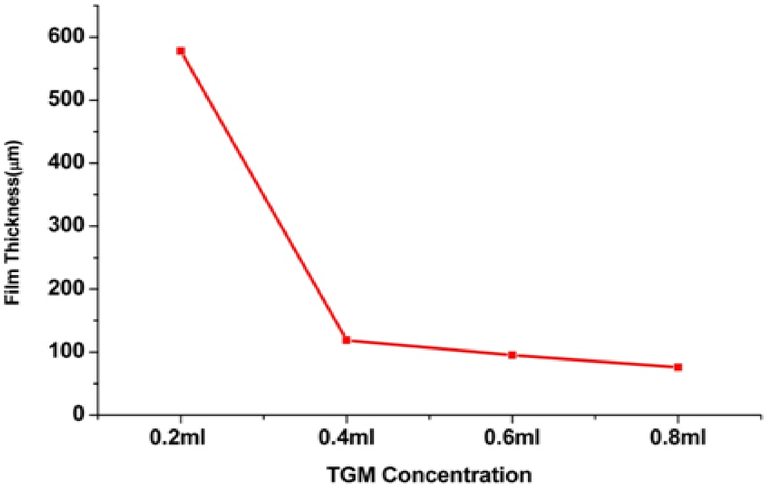

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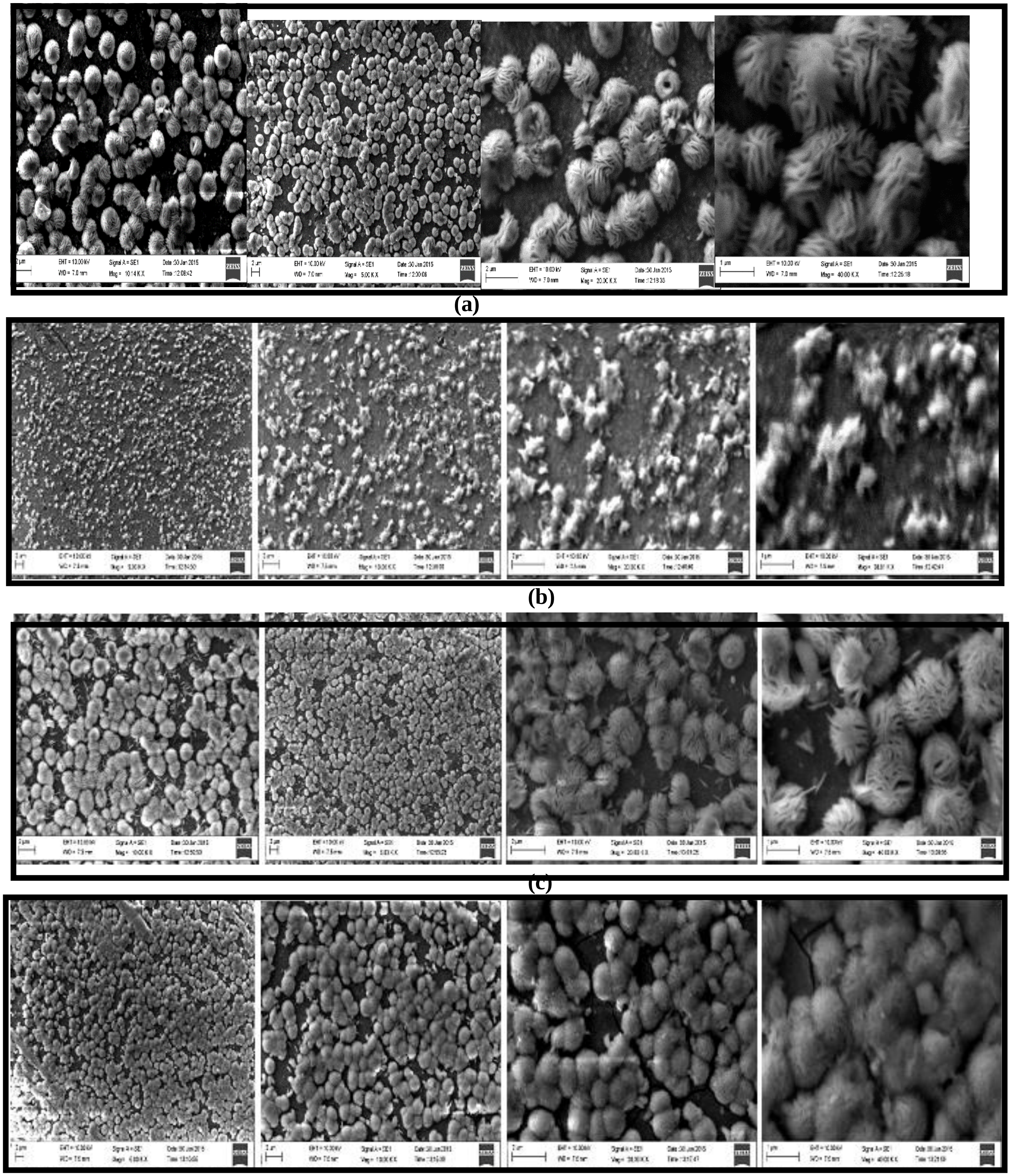
Fig.1.The variation of thickness of CdS thin films with TGM concentration.

3.1. Scanning Electron Microscope (SEM)

Fig. 2 represents the SEM micrograph of nanoCdS thin films with various concentrations of capping agents at magnification of 5KX, 10KX, 20KX and 40 KX at 10 KV. The surface morphologies of the CdS films were obviously changed under various concentrations of TGM. At a very low concentration, it is evident from the SEM photographs that the CdS film is consisting of close packed round grains and aggregates of grains that heaped up together. It reveals that the contribution of the cluster-by-cluster deposition is considerably in the filming. For 0.2ml (Fig.2a), nanoparticles of spherical shaped with small void observed while on adding capping agents for 0.6ml and 0.8ml (Fig.2c) and (Fig.2d) the surfaces becomes dense due to diffusion or coalescence of nanoparticles and the nanoparticles converted into bigger clusters. With 0.4ml TGM the accumulations of clusters of CdS into the aggregates of CdS were collapsed. Thus, the surface morphology of the film (Fig. 2b) just consists of close linked fibrils and some slabs of CdS covered between them, which indicated that particle have been splitted into smaller nanoparticles but did not diffuses together, produces more voids at the surface morphology (Fig.2b).These mention evidence that there exist various linkages of cadmium species and TGM and effect on the mechanism of two deposition processes, cluster-by-cluster and ion-by-ion [15-18].



(a)

(b)

(c)

(d)

Fig.2 SEM micrographs of (a)CdS(0.2ml TGM) film, (b) CdS(0.4ml TGM) film, (c) CdS(0.6ml TGM) film and (d) CdS (0.8ml TGM) film.

3.2. Optical Absorption and Transmission Spectra

Aiming to the role of TGM, UV-visible absorption spectroscopy was employed on the CdS films that were prepared under different conditions (Table 1). Optical studies were performed by measuring the absorbance and transmittance of the films deposited on glass substrates in the wavelength range 400–1100 at room temperature. The optical transmission spectra show high transmission for higher concentration of capping agents (0.8ml with denser surface) which will be appropriate window layer for photovoltaic applications [5,15-16,18]. Figure 3 shows the optical absorption spectra of the CdS films prepared at different concentrations of TGM. As seen the onset of optical absorptions are red-shifted as the concentration of TGM increases. However, the features at 470, 488 and 482nm, respectively for 0.2ml, 0.4ml and 0.6ml, reveal considerably blue-shifted relative to the absorption peak of bulk CdS, at 515 nm, indicating quantum size effect. At low concentrations of TGM, the absorption spectra also exhibit that a steadily increasing absorption tail as the wavelengths as smaller, oppositely to the one at high concentration of TGM (0.8ml). These mentions reveal that the presence of TGM has a positive effect at grain boundaries, leading to a detrimental reduction of the band bending towards the absorber surface and increasing the population of optical absorptions.

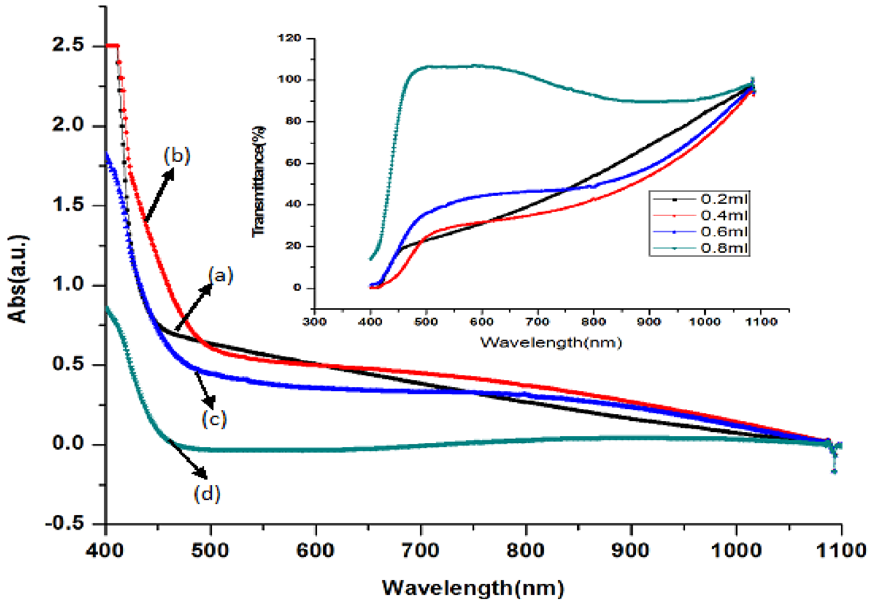


Fig.3 The optical absorption and transmission spectra of nanoCdS for varying concentrations of capping agents: (a) 0.2ml ,(b) 0.4ml ,(c) 0.6ml and (d) 0.8ml.

As the energy spacing of these states is approximately inversely proportional to the square of the particle size and reduced mass consequently, the highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively thereby resulting in the widening of band gap. The optical absorption coefficient α and band gap $E_g$are calculated by the equations

$$\alpha = -\frac{1}{t}\ln(T) \quad (1)$$

$$(\alpha h\nu)^{\frac{1}{n}} = A\left(h\nu - E_g\right) \quad (2)$$

Where α is the absorption coefficient, (hν) is the photon energy , A is a coefficient and n gets the values of ½,2,3/2 and 3 for allowed direct , allowed indirect , forbidden direct and forbidden indirect transitions respectively. Additionally, in a crystalline or polycrystalline material, both direct and indirect transitions can occur depending on the band structure of the material. To determine whether the films have allowed direct, allowed indirect , forbidden direct or forbidden indirect gap, plots of $(\alpha h\nu)^2$ versus $h\nu$, $(\alpha h\nu)^{1/2}$ versus $h\nu$, $(\alpha h\nu)^{2/3}$ versus $h\nu$ or of $(\alpha h\nu)^{1/3}$ versus $h\nu$ were drawn respectively[not shown].The straight line portions were extrapolated to the energy axis at $\alpha = 0$, to obtain band gaps of the CdS thin films. It was seen that better linearity was observed in the former case and determined that all films have a direct band gap transition. The variation of $(\alpha h\nu)^2$ versus hν for different films is a straight line which confirms the direct transition. It is found that the direct band gap E_g of as-deposited films increased from 2.82eV to 2.90eV with decreasing TGM concentration. This may be due to change in crystallinity with TGM concentration. Such high values of band gap can be attributed to quantum confinement effect, due to the small grain size of the polycrystalline films. The properties of nano crystalline materials change from their corresponding bulk properties, because the crystallites sizes become comparable to the Bohr excitonic radius. The variation of band gap of the different as-deposited thin films with TGM concentration is represented in Fig. 4.

The particle sizes were calculated using the Effective Mass Approximation (EMA) method and the following equation

$$E_{gn} = E_{gb} + \frac{\hbar^2\pi^2}{2m^*R^2} \quad (3)$$

Where E_{gn}&E_{gb} are the band gaps of nanocrystallites, and bulk semiconductor (2.4eV) respectively, R is the particle radius and m* is the effective mass of electron. Substituting the values of E_{gn} determined from eq. (2) and standard values of other parameters, the particle sizes were found to be 1.86nm to 2.10nm.

Table.1 Values of Band Gap and Radius of Particle for different films.

System	Band Gap (eV)	Radius of particle (from Effective Mass Approximation EMA)(nm)
($CdS_{0.2ml\ Capping\ Agent}$)	2.90	1.86
($CdS_{0.4\ ml\ Capping\ Agent}$)	2.87	1.95
($CdS_{0.6\ ml\ Capping\ Agent}$)	2.80	2.10
($CdS_{0.8ml\ Capping\ Agent}$)	2.82	2.05

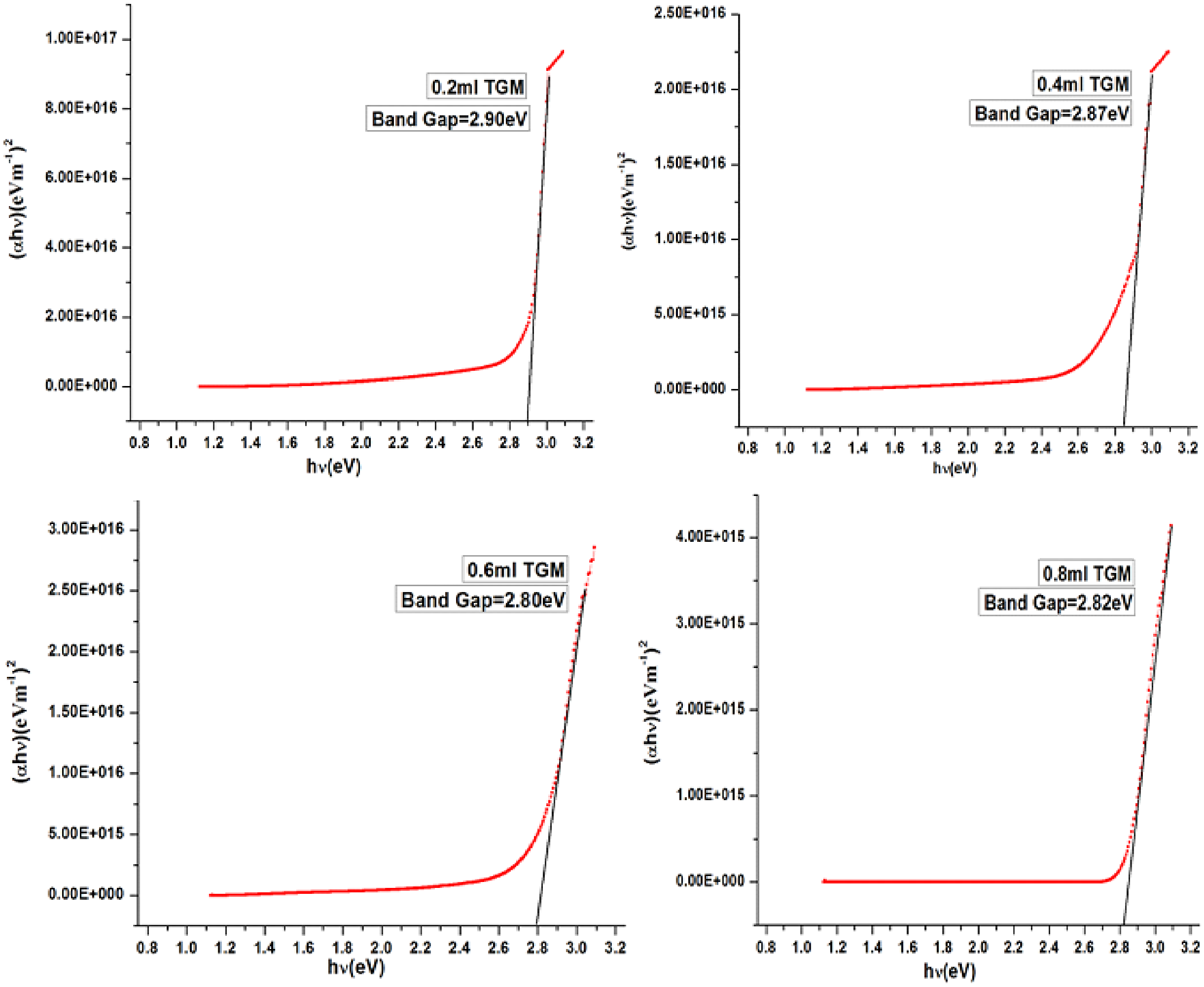


Fig.4 Tauc's plots for the films studied at four volumes of capping agents (TGM): (a) 0.2ml (b) 0.4ml, (c) 0.6ml and (d) 0.8ml.

The exact reason for increase of the band-gap for nanoscale materials is related to the overlap of the atomic orbitals involved in a specific material. In the bulk state, the numbers of atoms involved in bonding are high and each atom shares some atomic orbitals in bonding to overlap. Therefore, we will have many molecular orbitals (ignoring the orbitals with low energy) half of them are bonding molecular orbitals (valence band) and the other half are anti-bonding orbitals (conduction band) and the gap between these two will be small. In the nanoscale materials, however, the number of atoms and also atomic orbitals involved in the overlap are much less than the bulk counterpart and the band- gap will increase. Our results are in agreement with and higher as compared with available literatures [3-4,13,19].

3.3. Photoluminescence Studies

The photoluminescence emission spectra of nanoCdS at four volumes of capping agents are shown in the Fig.5. In CdS, the peak positions observed with 0.2ml TGM were at 410 nm , 450 nm,500nm and 590nm. With 0.4ml TGM similar peaks were resolved with the same potions but with high intensity values at 500nm and 590nm. Taking into account that the physical properties of CdS thin films depend upon the growth technique and the optimization of the deposition conditions, we show that the best crystal perfection occurs for CdS films with 0.2ml TGM since the main photoluminescence peak at low wavelength is due to bound excitons (2.90 eV). For semiconductor nano crystals, luminescent mechanisms are originated from both of the quantum confinement size effect and the radiative centers associated to surface states /defects [1, 2]. This diminution in PL intensity is explained on the basis of effect of particle size reduction on optical properties of nano phosphors. Due to their small sizes and relative large surface to volume ratio, more and more surface defects act as quenching centers, the luminescence centers near the surfaces are quenched and fluorescent lifetime decreases. As a result, the most efficient luminescence may be observed at a certain size in nano-scale.

Table.2Values of Wavelength and Intensity for different films.

Wavelength(nm)	(Intensity) 0.2ml TGM	(Intensity) 0.4ml TGM	(Intensity) 0.6ml TGM	(Intensity 0.8ml TGM
410	269	225	151	205
450	328	273	156	195
500	289	476	160	212
590	385	625	194	205

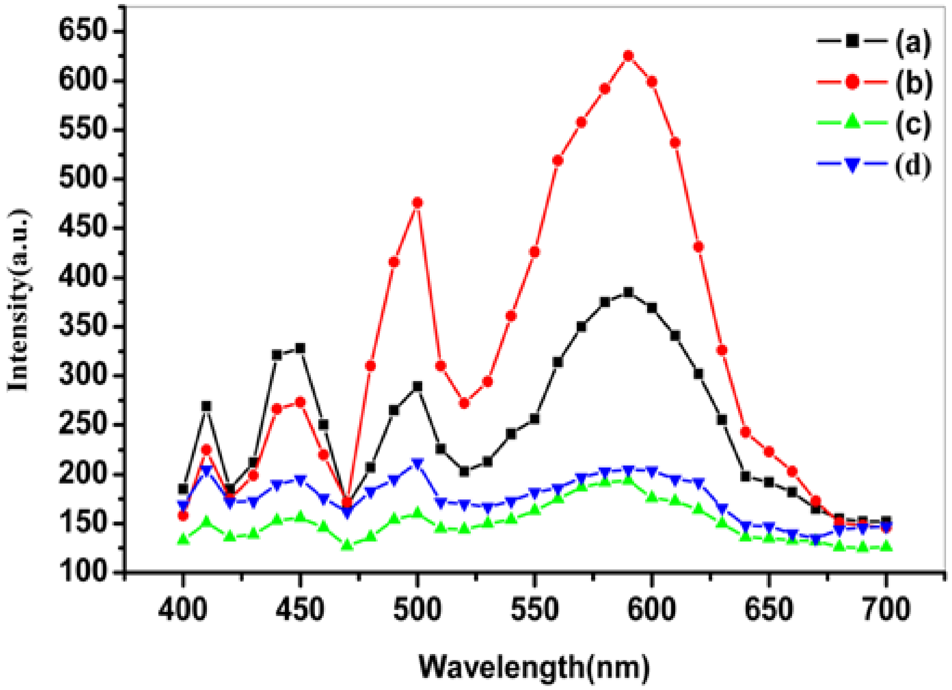


Fig. 4.Combined PL study of Nano CdS for different concentrations of capping agents (a) 0.2ml (b) 0.4ml, (c) 0.6ml and (d) 0.8ml.

4. Conclusions

We have deposited thin layers of cadmium sulphide (CdS) nanoparticles with elevated optical transparency and nanoparticles have quasi-spherical shape without evident microstructural defects. A SEM image showed the cabbage like structure due to layered growth and becomes dense by varying capping agents for 0.2ml to 0.8ml. Due to the presence of TGM, the morphology can be transformed from fibrous structure to regular shaped grains. The size of the CdS nanoparticles depends on the concentration of TGM and is about 1.86-2.05 nm. Optical absorption show shift due to decrease in particle size with decreasing TGM concentration i.e. due to enlargement of band gap. Our studies on PL of CdS nanocrystalline films has shown blue shift in PL peak and a rapid increase in intensity as the volume of TGM is increased. From the PL spectra of nanoCdS films deposited on glass substrate, it is found that the emission intensity of blue peak (~ 450 nm) with 0.2ml TGM is enhanced prominently and hence such system can be used for protection from UV. It can also be used as a window material as blue phosphors for display devices.

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References

1. Jungang He et al , Effect of ligand passivation on morphology, optical and photoresponse properties of CdS colloidal quantum dots thin film, Mater Sci: Mater Electron (2014) 25:1499–1504.
2. YongqianWang, Preparation of hierarchical CdS structures and effect of sodium dodecyl benzene sulfonate (SDBS) on the morphologies , Journal of Materials Science: Materials in Electronics, July 2016, Volume 27 , Issue 7 , pp 6750-6756.
3. ArfatFirdous, D. Singh, M. M. Ahmad, Electrical and optical studies of pure and Ni-doped CdS quantum dots, ApplNanosci (2013) 3:13–18.
4. Chander, S. Dhaka, M. S. Optimization of substrates and physical properties of CdS thin films for perovskite solar cell applications, J Mater Sci: Mater Electron (2017) 28: 6852–6859.
5. M.L. AlborAguileraa et al, Influence of CdS thin films growth related with the substrate properties and conditions used on CBD technique, Energy Procedia, 44 (2014) 111 – 117.
6. Xi Chang, et al, Application of ultra-thin CdS film as buffer layer in non-doped blue organic light emitting diodes, Journal of Materials Science: Materials in Electronics, August 2016, Volume 27, Issue 8, pp 7839–7844.
7. K. Gowrish Rao, V.K. Ashith, Influence of deposition parameters on the structural and optical properties of CdS thin films obtained by micro-controlled SILAR deposition, Journal of Physics and Chemistry of Solids 77 (2015) 14–22.
8. Ravi Kant Choubey, Dipti Desai, S. N. Kale, Sunil Kumar, Effect of annealing treatment and deposition temperature on CdS thin films for CIGS solar cells applications, Journal of Materials Science: Materials in Electronics, August 201 6, Volume 27, Issue 8, pp 7890-7898.
9. Mohammadikish, M. &Hajisadeghi, H. Hierarchical crystal growth of sheaf-like CdS by microemulsion/hydrothermal route, J Mater Sci: Mater Electron (2017) 28: 1455.
10. EntidharAlkuamMuatez Mohammed Tar-Pin Chen, Fabrication of CdS nanorods and nanoparticles with PANI for (DSSCs) dye-sensitized solar cells, Solar Energy Volume 150, 1 July 2017, Pages 317-324.
11. H. I. Salim, O. I. Olusola, A. A. Ojo, K. A. Urasov, M. B. Dergachev, I. M. Dharmadasa, Electrodeposition and characterisation of CdS thin films using thiourea precursor for application in solar cells, Journal of Materials Science: Materials in Electronics, July 2016, Volume 27 , Issue 7 , pp 6786-6799.
12. Y.S. Lo , R.K. Choubey, W.C. Yu , W.T. Hsu , C.W. Lan ,Shallow bath chemical deposition of CdS thin film, Thin Solid Films 520 (2011) 217–223.
13. Sandhya Pillai and S. Bhushan, Preparation of nanocrystalline CdS photoconductive cell in pellet form and its characterization, Proceedings of NanoThailand 2012, (2012) 21-25.
14. Abdullah M.A. Al-Hussam , Salah Abdul-Jabbar Jassim ,Synthesis, structure, and optical properties of CdS thin films nanoparticles prepared by chemical bath technique Journal of the Association of Arab Universities for Basic and Applied Sciences (2012) 11, 27–31
15. Moualkia, H. Rekhila, G. Mahdjoub, A. Trari, M. The semiconducting properties of CdS nanocrystalline thin films prepared by chemical bath deposition. Application to the eosin photodegradation, Journal of Materials Science: Materials in Electronics, December 2017, Volume 28, Issue 24, pp 19105–19112.
16. M.A. Islama, M.S. Hossainb, M.M. Aliyub, P. Chelvanathana, Q. Hudaa, M.R. Karimc, K. Sopiana, N. Amina, Comparison of Structural and Optical Properties of CdS Thin Films Grown by CSVT, CBD and Sputtering Techniques, Energy Procedia 33 (2013) 203 – 213.
17. Kusumanjali D, Bhushan S. and Mukherjee M., “Studies on Nano-crystalline Properties of Chemically deposited Pr doped CdSfilms”,Chalcogenide letters, (2010),7(1): 11.
18. F. Lisco, P.M. Kaminski, A. Abbas, K. Bass, J.W. Bowers, G. Claudio, M. Losurdo, J.M.Walls, The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering,Thin Solid Films, 582 (2015) 323–327.
19. Samir Pandya, Kamlesh Raval, Investigation of structural, morphological and optical properties of cadmium sulphide (CdS) thin films at different Cd/S concentration deposited by chemical technique, J Mater Sci: Mater Electron (2017) 28:18031–18039.