

Effect of Capping Agents on the Structure, Surface Morphology and Optical Properties of Chemically Deposited CdS Nanocrystalline Thin Films

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Abstract - Nano crystalline CdS thin films has been prepared by chemical bath deposition technique on glass substrates with varied concentrations of capping agents thioglycerol and methanol(TGM). Results of optical absorption spectra, Photoluminescence (PL), SEM and TEM studies are reported for CdS thin films for a uniform sample can be obtained in the form of thin films. UV-Vis Spectroscopy and photoluminescence (PL) studies have been carried out to characterize the materials prepared. 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. From the shift in optical band gap, particle sizes were calculated using Effective Mass Approximation (EMA) method and were found to be in nano range. PL spectra show 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 at 590nm. Thus, nanocrystalline CdS can be used as effective UV filter. SEM micrograph shows cabbage type structure which may due to layered growth of material.

Keywords: Photoluminescence, chemical deposition, nanocrystalline, quantum confinement effects.

1. INTRODUCTION

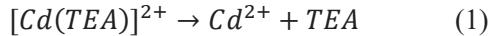
Thin films now occupy a prominent place in basic research and solid state technology. Due to their low production costs, the use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. The II -VI semiconducting materials in nanocrystalline form has been a rapidly growing area of research due to their nonlinear optical properties [1], luminescence properties [2], quantum size effects [3], and other physical and chemical properties making them suitable for applications in photodetectors, LED's, thin film transistors, heterojunction solar cells etc. CdS is one of the most promising materials as its bandgap 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 [4]. Although there are a variety of techniques for the preparation of CdS like vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy

etc.[5], chemical bath deposition method is the simplest and the least expensive. This method requires very economical experimental facilities and is highly suitable for large scale preparations, usually in film form. The utility of chemical deposition method in the deposition of metal chalcogenide thin films was reviewed by Mane and Lokhande [6]. The present paper concerns with the nanocrystalline effect on uv-spectra and photoluminescence spectra of CdS films prepared by chemical bath deposition (CBD) method using thioglycerol and methanol (TGM) as a capping agents. Results of optical absorption and photoluminescence spectral studies are included in this paper. Although many workers [7-10] have studied the role of capping agents on PL of CdS films. 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.

2. SAMPLE PREPARATION

The Films were prepared on substrates of 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. Then 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 double distilled water. TEA was used as a complexing agent to form $[Cd(TEA)]^{+2}$ 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. The films were then formed on glass substrate by dipping the substrate in the solution, kept in a constant temperature of water bath at 70^0C for 60 min. 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 slow release of Cd^{2+} ions is achieved by the

dissociation of a complex species of Cd such as $[Cd(TEA)]^{2+}$. The availability of Cd^{2+} is governed by the following reaction:



The S^{2-} ions are also provided by the dissociation of thiourea $[Sc(NH_2)_2]$ in the aqueous alkaline or ammonical medium-



After deposition the films were then washed with double distilled water and dried at room temperature. The thicknesses of the films were estimated by gravimetric weight difference method. For this, a sensitive microbalance was utilized and the film density was assumed as the bulk density of CdS (4.82gcm^{-3}).

3. RESULTS AND DISCUSSION

The resulting thin films have a yellow colour, reflective, smooth, homogeneous and well adhered to the glass substrate. The thickness of the films was found to vary from 638 to 265 nm by varying capping agent (TGM) concentration from 0.2ml to 0.8ml. This may be due to the increase in the number of Cd^{2+} ions, which leads quick precipitation. The variation of the thickness with TGM variations are represented in Fig.1

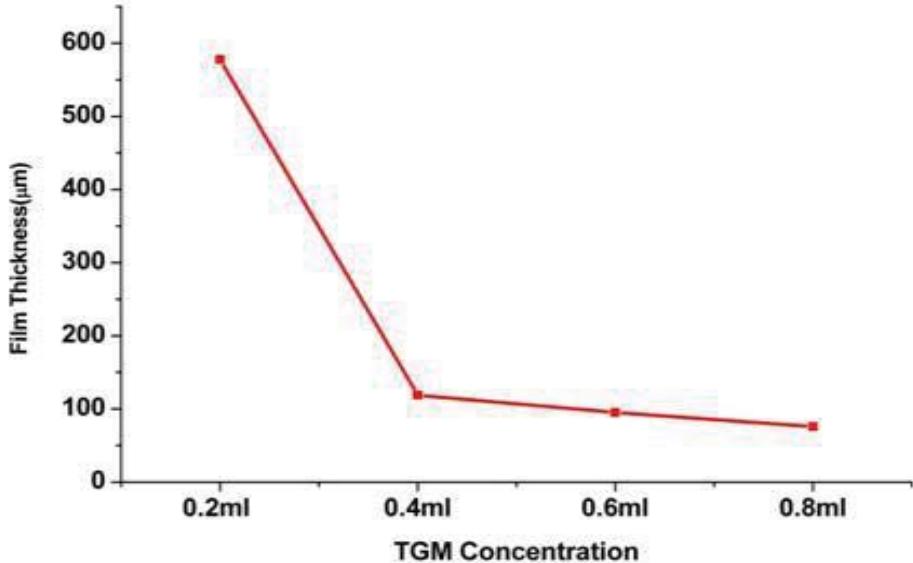


Fig.1. The variation of thickness of CdS thin films with TGM concentration.

3.1. Optical Absorption and Transmission Spectra

Optical studies were performed by measuring the absorbance and transmittance of the films deposited on glass substrates in the wavelength range 200–1100 nm at room temperature. The results of optical absorption and transmission spectra for different values of capping agent are shown in Fig.2. A slight shift in absorption peaks 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 [11]. 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 with decreasing TGM as observed in the present case.

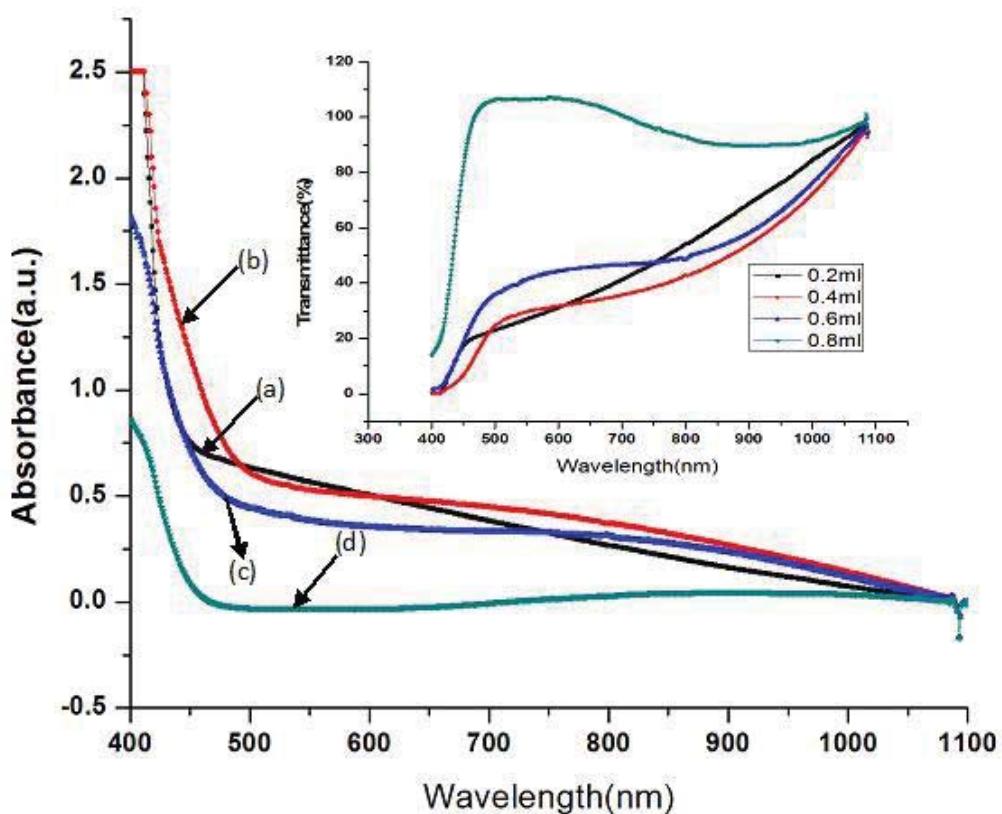


Fig.2. The optical absorption and transmission spectra of nano CdS at four concentrations of capping agents: (a) 0.2ml ,(b) 0.4ml ,(c) 0.6ml and (d) 0.8ml.

As the energy spacing of these states is approximately inversely proportional to the square of the particle size and reduced mass [11]. 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.

$$\alpha = -\frac{1}{t} \ln(T) \quad (4)$$

Thus, the effective band gap in the presence of different concentrations of TGM correspondingly a blue shift (to the shorter wavelength side) in the absorption spectra is observed. The optical absorption coefficient α and band gap E_g are represented by the equations [12].

$$(\alpha h\nu) = A(h\nu - E)^n \quad (5)$$

Where α is the absorption coefficient, $(h\nu)$ is the photon energy, A is a coefficient and n gets the values of $\frac{1}{2}, \frac{2}{3}, \frac{3}{2}$ 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 $(h\nu)^2$ versus $h\nu$, $(h\nu)^{1/2}$ versus $h\nu$, $(h\nu)^{2/3}$ versus $h\nu$ or of $(h\nu)^{1/3}$ versus $h\nu$ were drawn respectively [not shown]. The straight line portions were extrapolated to the energy axis at $= 0$, 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 $h\nu$ for different films is a straight line which confirms the direct transition [13]. It is

found that the direct band gap E_g of as-deposited films increased from 2.86 eV to 2.91 eV 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 nanocrystalline materials change from their corresponding bulk properties, because the crystallites sizes become comparable to the Bohr excitonic radius. The variation of band gap at crystallite diameters around 40 nm arising from quantum confinement of excitons in PbS is well documented and solar cells have been developed based on this behavior [14]. The variation of band gap of the different as-deposited thin films with TGM concentration is represented in Fig. 3.

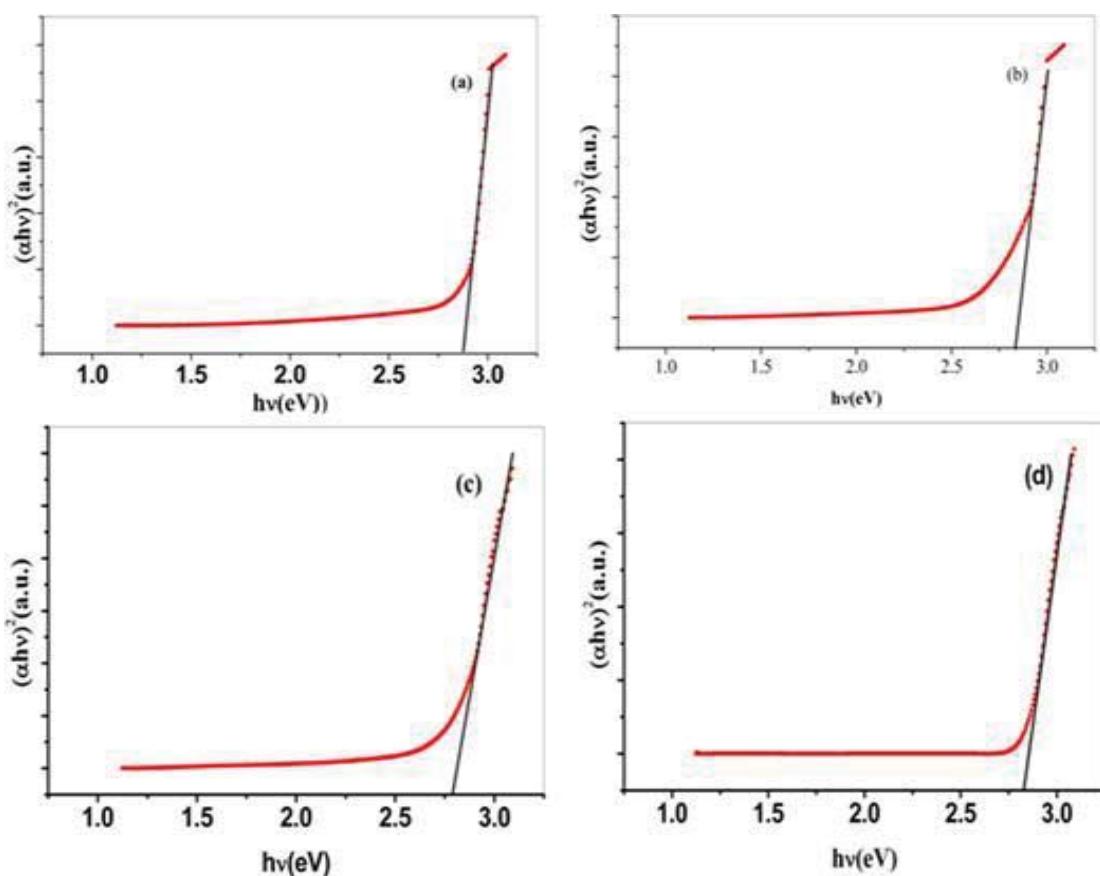


Fig.3 Tauc's plots for the films studied at four volumes of capping agents (TGM): (a) 0.2ml (b) 0.4ml, (c) 0.6ml and (d) 0.8ml.

The particle sizes were calculated using the Effective Mass Approximation (EMA) method and the following equation [15].

$$E_{gn} = E_{gb} + \frac{\hbar^2 \pi^2}{2m^* R^2} \quad (6)$$

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

System	Band Gap (eV)	Radius of particle (from Effective Mass Approximation EMA)(nm)
(CdS 0.2ml Capping Agent)	2.91	4.89
(CdS0.4 ml Capping Agent)	2.87	4.93
(CdS0.6 ml Capping Agent)	2.80	4.99
(CdS0.8ml Capping Agent)	2.86	4.94

Where E_{gn} & E_{gb} are the band gaps of nanocrystallites, and bulk semiconductor (2.42eV) respectively, R is the particle radius and m^* is the effective mass of electron. Substituting the values of E_{gn} determined from eq(5) and standard values of other parameters, the particle sizes were found to be 4.89nm to 4.99nm. Thus, the particle sizes lie in the nanocrystalline range.

3.2. Photoluminescence Studies

The photoluminescence emission spectra of nano CdS at four volumes of capping agents are shown in the Fig.4. 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 posions but with high intensity values. The strong peak at 590nm was considered due to band to band transition with increased band gap occurring due to nanocrystalline effect. This actually confirmed the quantum confinement effect also. As is known under nanocrystalline effect two prominent changes are observed: (i) change in band gap i.e. decrease in band gap with enlarged particle size and (ii) discreteness in the continuum of valence and conduction bands 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 [15].

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

Wavelength(nm)	(Intensity) 0.2ml TGM (10 ³ mA)	(Intensity) 0.4ml TGM (10 ³ mA)	(Intensity) 0.6ml TGM (10 ³ mA)	(Intensity) 0.8ml TGM (10 ³ mA)
410	269	225	151	205
450	328	273	156	195
500	289	476	160	212
590	385	625	194	205

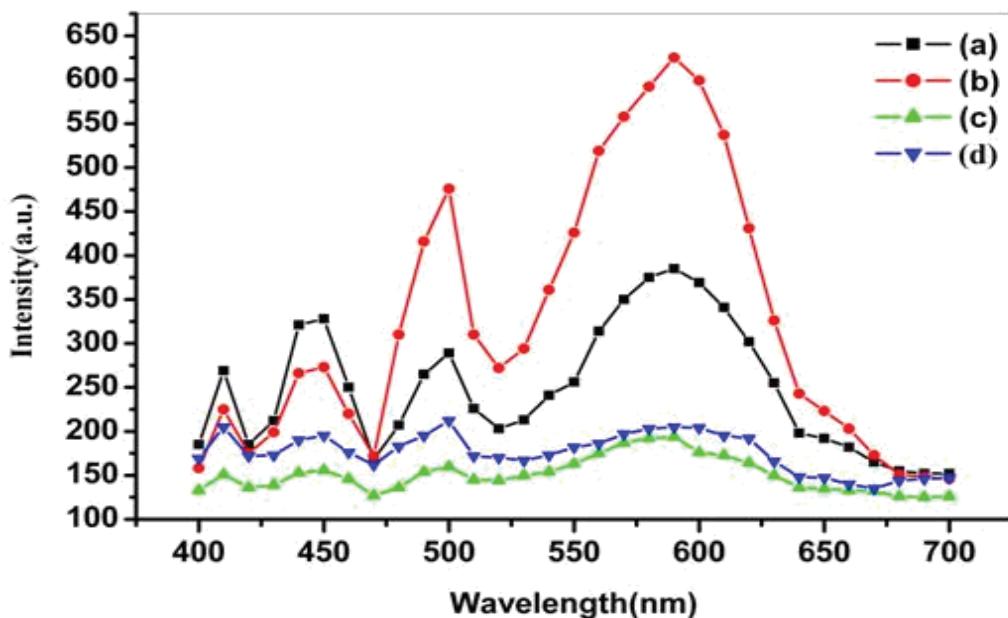


Fig. 4. Combined PL study of Nano CdS for different concentrations of capping agents

As also reported by Maleki et al [16], the peak at 363nm was attributed to higher level excitonic transition and its energy was calculated to be 3.38eV. Devi et al [17] also reported a peak in nanocrystalline CdS at 376nm with similar explanation. Maleki et al also observed a peak at 340nm under 220nm excitation which was related to higher level transitions. According to them this kind of band edge luminescence is caused by recombination of excitons and/or shallowly trapped e-h pairs [16], it should be noted that PL edge emission in CdS was extensively investigated by a

number of workers [18-20] and was associated with excitonic transitions or defect exciton complexes [21].

3.3. Surface Electron Morphology (SEM)

The SEM micrograph of nano CdS thin films are presented in Fig.5 with magnification of 10,000x. Each consists of cabbage like structures which is due to overlap of different layers formed under continue growth convert into cabbage structure[22]. Voids are seen of smaller concentration of capping agent. Densification of particles is observed with adding capping agent. SEM micrograph of CdS(0.2ml), CdS(0.4ml) and CdS(0.8ml) films are shown in figure.

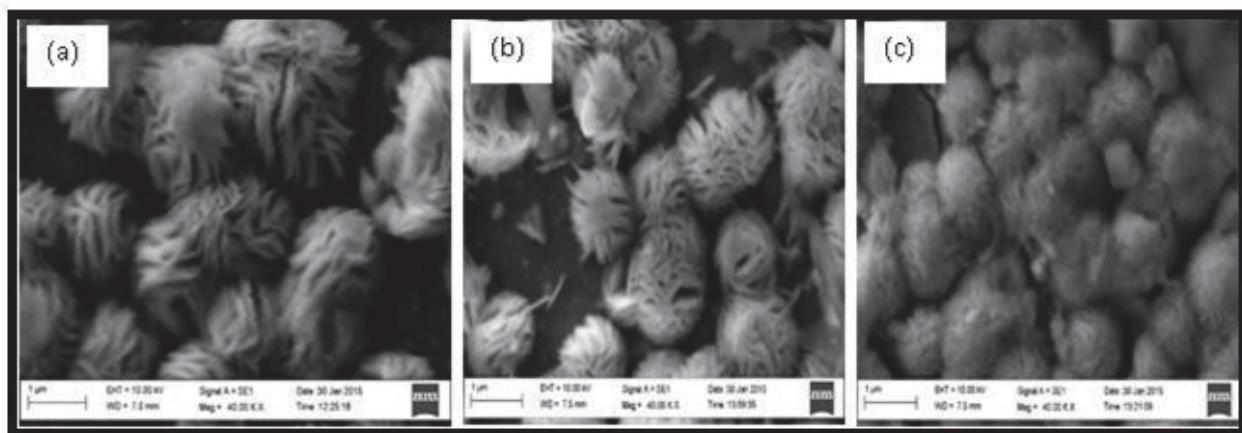


Fig.5. SEM micrographs of (a) CdS (0.2ml TGM) film, (b) CdS (0.4ml TGM) film and (c) CdS(0.8ml TGM) film.

3.4. Transmission Electron Microscopy(TEM)

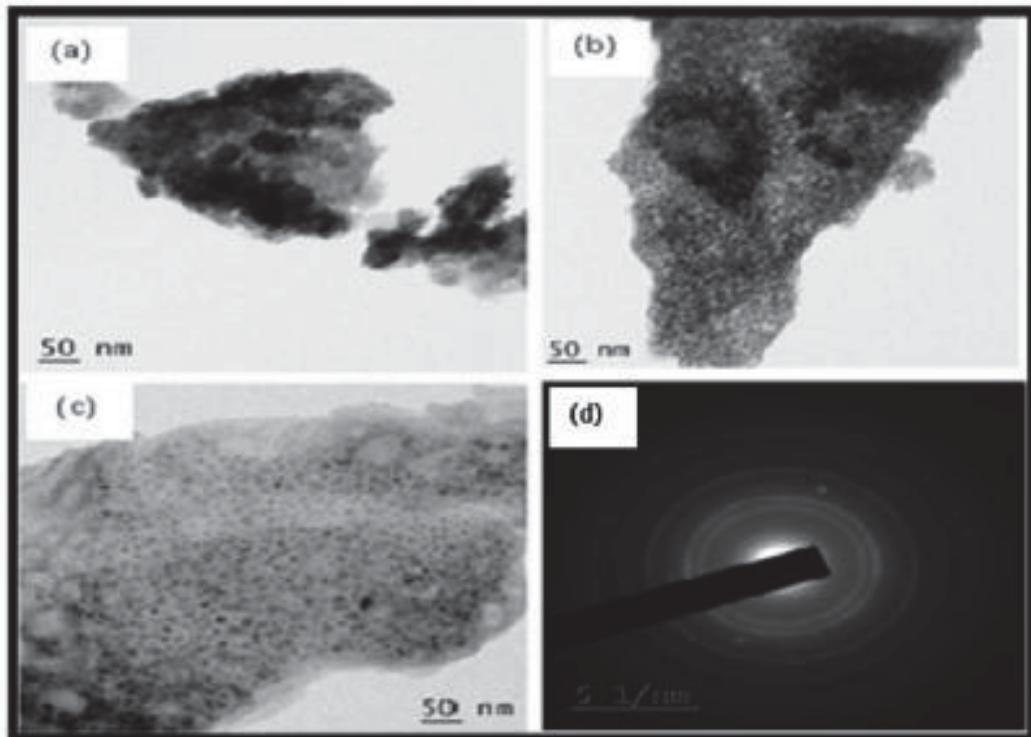


Fig.6. TEM micrographs of (a) CdS (0.2ml TGM) film, (b) CdS (0.4ml TGM) film and (c) CdS(0.8ml TGM)

The TEM micrographs of CdS films with varying capping agents are shown in Fig.6(a), (b) and (c). It can be seen many nanosphere (light black) of 5 to 6 nm diameter are entrapped. The selected area diffraction pattern (SAED) in Fig.6(d) show characteristics diffraction rings of cubic CdS. The bright portion shows crystalline whereas the ring pattern shows polycrystalline nature[22]. The concentric rings with some bright spots in the SAED patterns are assigned to the diffraction from (111), (220) and (311) planes of fcc-CdS as measured from the radius of these concentric rings. The film with 0.2ml capping agents shows scattered crystal atoms and becomes dense with increasing concentrations of capping agents which also agrees with SEM images. It is clear from the Fig, the crystallite size decreases with increasing concentration of capping agents which also agrees with increasing energy band gap due to decrease in particle size from UV spectra.

CONCLUSIONS

From UV spectra of optical absorption show shift due to decrease in particle size with decreasing TGM concentration i.e. due to enlargement of band gap. Particle sizes determined from absorption study lies in the nanocrystalline range. From the PL spectra of nano CdS films deposited on glass substrate, it is found that the emission intensity of blue peak (~ 590 nm) 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. SEM studies show cabbage type structures, which may be due to layered growth.

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