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Effect of Capping Agents on Structural, Morphological and Optical Properties of CdS Nanocrystalline Films

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Abstract: - CdS nanocrystalline films were prepared by chemical bath deposition method (CBD) on glass substrates at 70^0c for 1 hour. Mercaptoethanol, Thioglycerol, and water-soluble PVP have been used as capping agents for the synthesis of these films. The effect of capping agents on the structural, morphological and optical properties of the films was investigated and discussed. The films were characterised by XRD, SEM and UV-VIS absorption spectral studies. XRD studies shows prominent diffraction lines of CdS with maximum orientation towards (111) plane of the cubic phase. Sharp peaks were observed in PVP capped CdS in comparison to Mercaptoethanol and Thioglycerol capped films. Particle sizes calculated from XRD studies were found to be in nano range. Distinctly different morphology is observed in the films capped with Mercaptoethanol, Thioglycerol and PVP in comparison with the bulk films. CdS films show large sized clusters of particles while Mercaptoethanol and PVP capped films show spherical particles forming clusters and a cabbage like layered structure is seen in Thioglycerol capped films.EDX spectra confirms the presence of Cadmium and Sulphur with excess Cadmium. Absorption spectral studies show a blue shift in absorption edge in all the capped films compared to the bulk suggesting quantum confinement effect. The studies suggest that the properties of the nanocrystalline CdS films can be tuned by using different capping agents.

Keywords: **CdS, capping agents Mercaptoethanol, Thioglycerol, PVP.**

I. INTRODUCTION

Nanoscale particles have been a subject of great interest in recent times, in terms of both their fundamental and technological importance [1][2]. Chalcogenide based semiconductor nanoparticles are quite promising materials for application in optoelectronics [3][4][5]. CdS, a binary chalcogenide semiconductor has a band gap of 2.43eV. The various advantages of CdS semiconductors are its size dependent optical properties, tunable band gap, good chemical stability and easy preparation techniques. [6] CdS nanocrystalline thin films have wide applications in piezo electric transducers, laser materials, photovoltaic cells and window materials in hetero-junction solar cells. [7][8]

Although a variety of techniques have been employed for the preparation of these materials like vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy etc [9]. Chemical bath deposition (CBD) method is the simplest and the least expensive.[10] This method requires very economical experimental facility and is highly suitable for large scale preparation, usually in film form. The utility of chemical deposition method in the deposition of metal chalcogenide thin film was reviewed by Mane and Lokhande [11]. The semiconductor nanoparticles agglomerate very rapidly in the absence of capping agents [12] and hence a bonding of the capping agents to these nanoparticles is required to provide chemical passivation and improve the surface state which directly affects the structural and optical properties of these materials. Hence Mercaptoethanol, Thioglycerol and water-soluble PolyVinyl Pyrrolidone (PVP) have been used as capping agents in the present work and methanol has been used to dissolve the capping agents. The present paper reports the effects of these capping agents on the structural and optical properties of CdS nanocrystalline films, not reported earlier. For the characterization of the films, results of XRD, SEM and Absorption spectra are presented and discussed.

II. MATERIAL AND METHODS:

2.1 Film Preparation

The films were prepared by vertically dipping cleaned substrates of microscopic glass slides in a mixture of Cadmium Acetate, Triethanolamine, Thiourea, 30% aqueous Ammonia, Mercaptoethenol (MEL), Thioglycerol and PVP as capping agents (CA) and Methanol (for dissolving the capping agents). All the chemicals were of analytical grade (minimum purity 99%). In the beginning when precipitation started, stirring was done using a magnetic stirrer for 5 min. After that, the deposition was made in static condition in water bath at 70˚C. After deposition, the films were cleaned with distilled water, and then dried by keeping them in open atmosphere at room temperature. [13] Film thicknesses were determined by optical interference method and were found to lie in the range of 0.2 µm to 0.3 µm.

2.2 Measuring Instruments

The Optical Absorption Spectra were recorded using Ellico SL 210 UV-Vis Spectrophotometer in the range 300-800 nm. The SEM and XRD Studies were carried out at NIT Raipur using for structural characterization XRD was done with a PANalytical 3kW X'pert powder Multifunctional X-ray diffractometer in the range $10^0 < 2\theta < 80^0$ with a step of 0.02^0 and ZEISS EVO 18 Scanning Electron Microscope (SEM), 30kV of acceleration voltage with Quorum SC7620 sputter gold coater.

III. RESULTS AND DISCUSSION

3.1.1 Structural Studies

X-Ray diffraction analysis data is used to determine the lattice parameter, crystallite size and for phase identification. The X-ray diffractograms of the different CdS films are presented in figure 1. The corresponding data are presented in Table 1a, 1b, 1c and 1d. The assignments were made by comparison with ASTM data and the lattice constants were calculated and compared with the reported values.[F] Prominent peaks of CdS have been observed with maximum intensity at $(111)_c$ plane in the case of all films. Sharp diffraction peaks are seen in bulk and PVP capped CdS while broadening of peaks is observed in Mercaptoethanol capped and Thioglycerol capped CdS. Particle sizes were calculated using Scherrer's formula

$$d = 0.9\lambda / \beta \cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, d is the average crystallite size, λ is wavelength of CuKα (1.5418 Aº), θ is the angle between the incident beam and the lattice plane, β is the full width at half maximum (FWHM) in radians [15].The particle sizes were found to be in the nanorange. The values of particle size, strain and dislocation density for the different CdS films are presented in table 2.

The strain, ε was calculated by using the formula [16]

$$\varepsilon = \beta \cos\theta/4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The dislocation density, δ of the CdS thin film is defined as the length volume of the crystal, was calculated from the formula [16]

$$\delta = 1/ D^2 \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

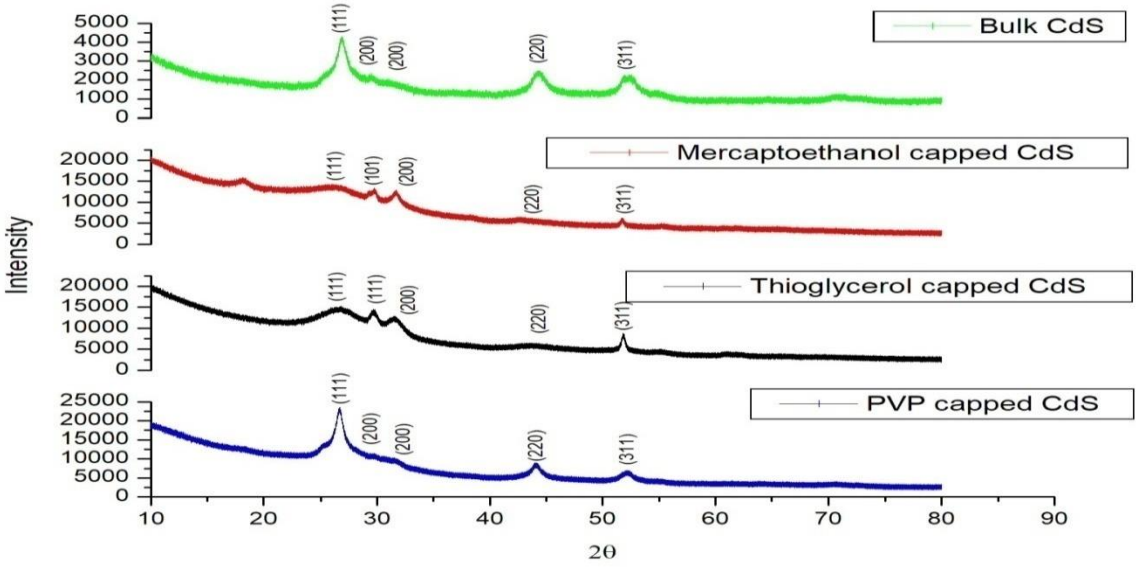

Fig. 1 X-Ray Diffractograms of different CdS films prepared on glass substrate a) Bulk CdS, b) Mercaptoethanol capped CdS, c) Thioglycerol capped CdS, d) PVP capped CdS.

Table 1a: XRD data of Bulk CdS film prepared on glass substrate.

d Value(A^0)		Relative Intensity		hkl	Lattice Constant (A^0)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.316	3.36	100	100	$(111)_c$	a=5.7434	a=5.818
3.02	2.90	53.46	40	$(200)_c$	a=6.04	a=5.818
2.88	2.90	46.35	40	$(200)_c$	a=5.76	a=5.818
2.038	2.058	56.9	80	$(220)_c$	a=5.7643	a=5.818
1.759	1.753	51.7	60	$(311)_c$	a=5.8339	a=5.818

Table 1b: XRD data of Mercapthoethanol capped CdS film prepared on glass substrate.

d Value(A^0)		Relative Intensity		hkl	Lattice Constant (A^0)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.424	3.36	100	100	$(111)_c$	a=5.9305	a=5.818
3	3.1608	83.4	100	$(101)_h$	a=4.2426, c=6.8962	a=4.1354, c=6.7120
2.82	2.705	80.4	10	$(200)_c$	a=5.64	a=5.4060
2.114	2.058	38.6	80	$(220)_c$	a=5.9792	a=5.818
1.765	1.753	36.8	60	$(311)_c$	a=5.8538	a=5.818

Table 1c: XRD data of Thioglycerol capped CdS film prepared on glass substrate.

D Value(A^0)		Relative Intensity		hkl	Lattice Constant (A^0)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.322	3.36	100	100	$(111)_c$	a=5.7538	a=5.818
3.011	3.123	94.6	100	$(111)_c$	a=5.2152	a=5.4060
2.832	2.90	83.5	40	$(200)_c$	a=5.664	a=5.818
1.763	1.753	55.7	60	$(311)_c$	a=5.8472	a=5.818
1.665	1.68	30.3	10	$(222)_c$	a=5.7677	a=5.818

Table 1d: XRD data of PVP capped CdS film prepared on glass substrate.

d Value(A^0)		Relative Intensity		hkl	Lattice Constant (A^0)	
(Obs)	(Rep)	(Obs)	(Rep)		(Obs)	(Rep)
3.338	3.36	100	100	$(111)_c$	a=5.7815	a=5.818
3.00	2.90	47.13	40	$(200)_c$	a=6.00	a=5.818
2.83	2.90	42.30	40	$(200)_c$	a=5.66	a=5.818
2.053	2.058	36.37	80	$(220)_c$	a=5.8067	a=5.818
1.751	1.753	27.49	60	$(311)_c$	a=5.8074	a=5.818

Table 2 Values of particle size, Strain and Dislocation density for different CdS films.

Sample	Particle Size D (nm)	Strain Value ε (10^{-4})	Dislocation density δ ($10^{14}cm^{-1}$)
Bulk CdS	4.80	75.38	4.34
Mercapthoethanol capped CdS	3.19	113.51	9.82
Thioglycerol capped CdS	3.62	99.95	7.63
PVP capped CdS	4.12	87.81	5.89

3.1.2 SEM Studies: The SEM micrographs of the different CdS films are presented in Fig 2a, 2b, 2c and 2d at a magnification 50000X. The bulk CdS film shows clusters of large spherical particles suggesting agglomeration. Films capped with Mercaptoethanol, Thioglycerol and PVP show different morphology. Smaller sized spherical particles are seen in Mercaptoethanol and PVP capped films. It can be seen that agglomeration has reduced after capping the films. A layered structure resembling a cabbage is observed in Thioglycerol capped films.

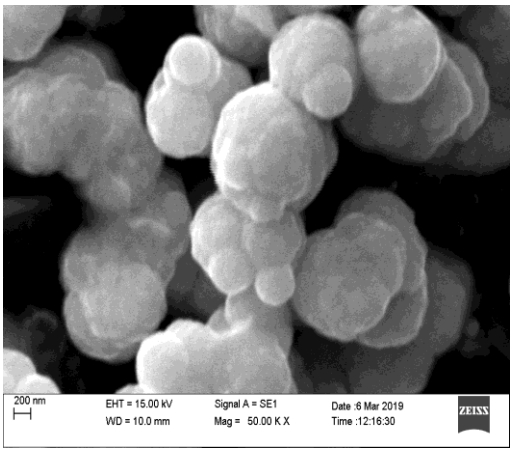

Fig: 2a

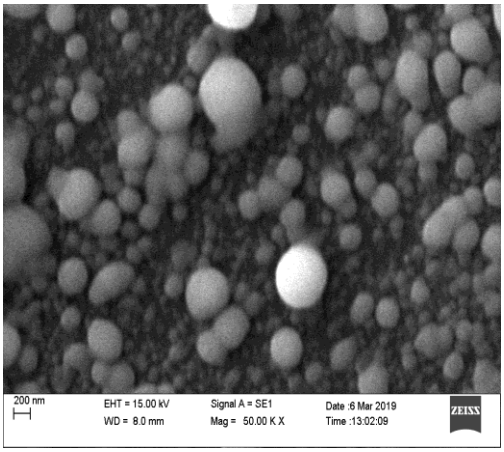

Fig: 2b

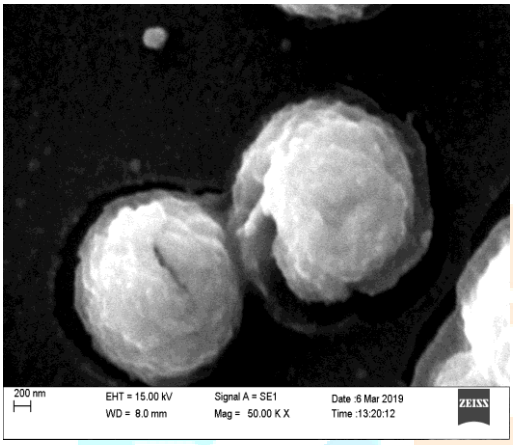

Fig: 2c

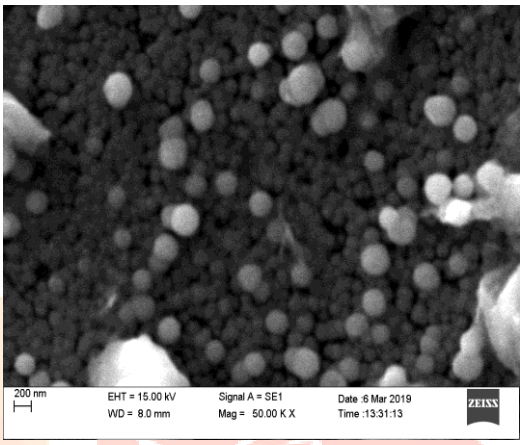

Fig: 2d

Fig. 2 SEM Micrograph of different CdS nanocrystalline films a) Bulk CdS, b) Mercaptoethanol capped CdS, c) Thioglycerol capped CdS, d) PVP capped CdS

3.1.3 EDS analysis: Figures 3a, 3b, 3c and 3d shows the EDX spectra of different CdS films. The EDS analysis confirms the presence of Cadmium and Sulphur with excess Cadmium.

Element	Weight %	Atomic %
S K	19.59	46.07
Cd L	80.41	53.93
Totals	100.00	

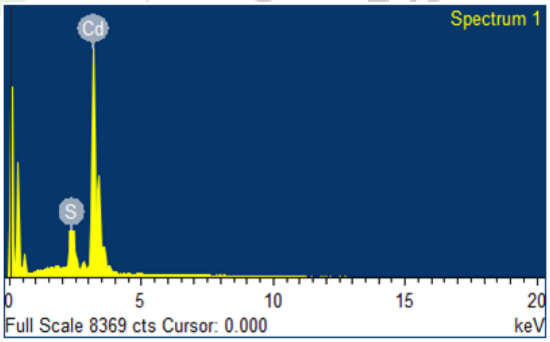

Fig. 3a

Element	Weight %	Atomic %
S K	13.79	35.92
Cd L	86.21	64.08
Totals	100.00	

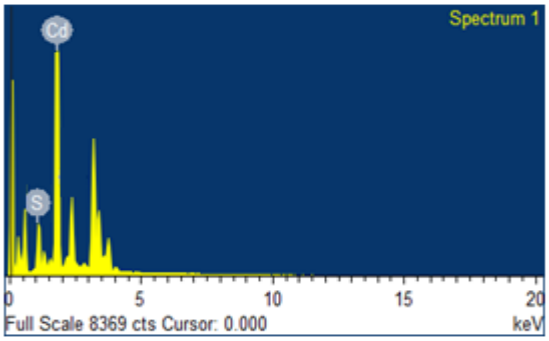

Fig. 3b

Element	Weight %	Atomic %
S K	20.44	47.39
Cd L	79.56	52.61
Totals	100.00	

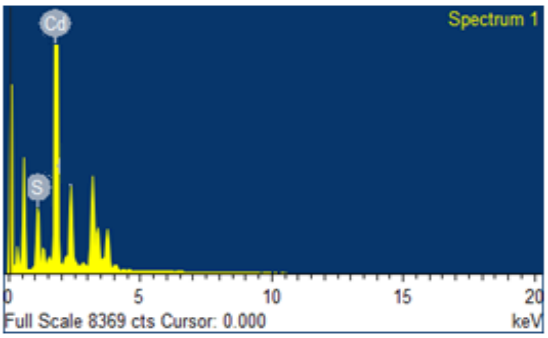

Fig. 3c

Element	Weight %	Atomic %
S K	19.39	45.75
Cd L	80.61	54.25
Totals	100.00	

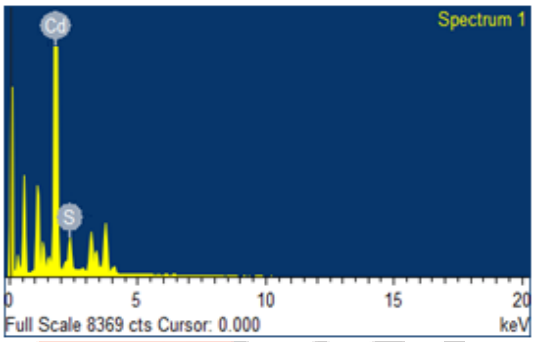

Fig. 3d Fig. 3 EDX spectra of different CdS nanocrystalline films, a) Bulk CdS, b) Mercaptoethanol capped CdS, c) Thioglycerol capped CdS, d) PVP capped CdS

3.2 Optical Spectral Studies:

The optical absorption spectra of different CdS films are shown in fig 4. It is observed that, as compared to the bulk film, nanocrystalline films show a shift in absorption edge to the shorter wavelength side. This may be attributed to the well known Quantum Confinement Effect in which the motion of electrons, holes and excitons is possible only for discrete values of energies thereby resulting in the quantisation of their energy spectrum and the continuum of states in the conduction and valence bands are broken down into discrete states. The energy spacing of these states is approximately inversely proportional to the square of the particle size and reduced mass [17]. 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. [18] Thus, the effective band gap in the presence of capping agents is larger than its bulk value and correspondingly a blue shift (to the shorter wavelength side) in the absorption Spectra is observed.

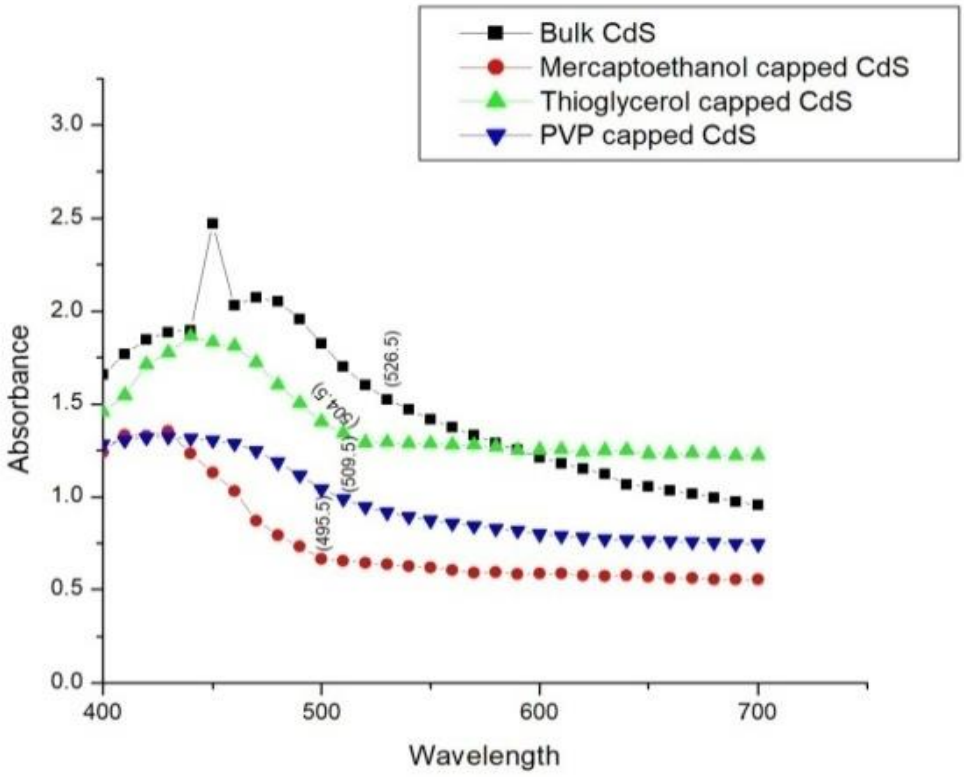

Fig: 4 Absorption Spectra of different CdS films of Bulk CdS, Mercaptoethanol capped CdS, Thioglycerol capped CdS, PVP capped CdS

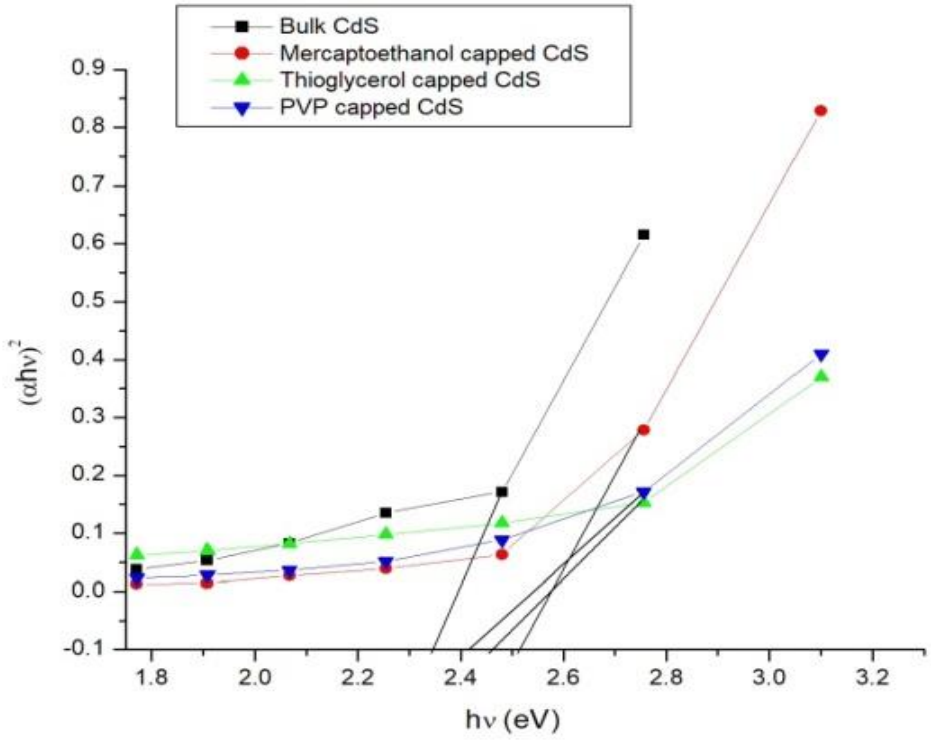

Fig: 5 Tauc's plot of different CdS films of Bulk CdS, Mercaptoethanol capped CdS, Thioglycerol capped CdS, PVP capped CdS

The Optical Absorption Coefficient α and band gap E_g (for direct band gap materials) are represented by the equation:

$$\alpha = c\,(h\upsilon - E_g)^{1/2}/h\upsilon \qquad \text{.....(1)}$$

Where, E_g is the optical band gap and c is a constant. Thus a plot between $(\alpha h\upsilon)^2$ vs $h\upsilon$ (Tauc's plot) gives the band gap value E_g of the material. The Tauc's plot of the different CdS samples are shown in fig.(5).The values of optical band gap obtained from these plots are presented in table 3.

Table 3: Optical band gap variation of CdS nanoparticles with different concentration of capping agents.

S. no.	Sample	Absorption edge (nm)	Optical Band-gap Eg (eV)
1	Bulk CdS	526.5	2.35
2	Mercaptoethanol capped CdS	495.5	2.50
3	Thioglycerol capped CdS	504.5	2.45
4	PVP capped CdS	509.5	2.43

The particle sizes were calculated using the Effective Mass Approximation (EMA) Method using the following equation [19]:

$$E_{gn} = E_{gb} + (h^2\pi^2/2m^*R^2) \quad \text{... (2)}$$

Where, E_{gn} and E_{gb} are the band gap of nanocrystalline, and bulk semiconductor respectively, R is the particle radius and m^* is the effective mass of the electron.[20] Substituting the values of E_{gn} and E_{gb} from table 3, the particle sizes were calculated and are presented in table 4.

Table 4: Particle sizes of different CdS films from absorption spectra

xS no.	Sample	Particle Size(nm)
1	Mercaptoethanol capped CdS	22.80
2	Thioglycerol capped CdS	27.93
3	PVP capped CdS	31.22

IV. CONCLUSION

CdS nanocrystalline films were prepared by chemical bath deposition method (CBD) using Mercaptoethanol, Thioglycerol, and water-soluble PVP as capping agents. The films were characterised by XRD, SEM and UV-VIS absorption spectral studies and the effect of capping agents on these films were studied. Prominent diffraction lines of CdS with maximum intensity at (111) plane of the cubic phase of CdS is seen from XRD patterns. Particle sizes, strain and dislocation densities were calculated for the films. SEM studies show different morphology in the films capped with Mercaptoethanol, Thioglycerol and PVP in comparison with the bulk films. Clusters of large spherical particles are seen in bulk films. Mercaptoethanol and PVP capped films show smaller spherical particles forming clusters and a layered structure is seen in Thioglycerol capped films. The presence of Cadmium and Sulphur with excess Cadmium is observed from EDX studies. Quantum confinement effect is observed from absorption spectral studies.

V. ACKNOWLEDGEMENTS

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