

Structural and optical characterization of CdS nanorods

M. Dinendra Singh, K. Kunjabali Singh

Abstract— CdS films have been chemically deposited on glass substrates at room temperature at varying molarity from $0.05M \leq x \leq 0.2M$ by Chemical Bath Deposition technique. The study of crystallinity of the films by XRD, without annealing the films, is observed to improve with increasing molarity at $0.2M$ with particle size $10nm$ and prominent reflection along (200) plane in cubic Zinc blend structure. The SEM micrographs of the films at $0.1M$ and $0.2M$ show the formation of CdS nanorods with diameter within the range $471.2 - 668.7nm$. The band gaps in the films are determined from UV absorption spectra which show lowering from the bulk value at $0.05M$ but increase above $2.4eV$ with increasing molarity. The absorption spectra shows blue shift at around $435nm$ wavelength.

Index Terms— Cadmium sulphide, CBD technique, Nanostructure, Nanorods, optical absorption, Ionic concentrations

I. INTRODUCTION

A variety of physical and opto-electronic properties of nanoparticles have been reported by several research workers due to their unique size dependant for fabrications of electronic devices¹⁻⁸. Such novel properties of nanoparticles have been enhanced non-linearly due to quantum confinement effect^{9,10}. Cadmium sulphide is reported as an important n-type material for thin film heterojunction solar cells and can be prepared by different techniques viz. chemical bath deposition (CBD)¹¹⁻¹⁴, electro-deposition¹⁵, sol-gel spin coating¹⁶, vacuum evaporation¹⁷. However, the basic problem with CdS is to obtain uniform and stoichiometric film over large area relative to less time consumption and less expensive. The CBD technique is found to be relatively simple, inexpensive method for synthesis of homogeneous films with controlled composition. The paper presents the synthetic study of the growth of nanocrystalline CdS films from nearly amorphous state with increasing molar concentration from $0.05 - 0.2M$ deposited on ultra fine cleaned glass substrates ($25 \times 20 \times 1.30 \text{ mm}^3$) by CBD technique at RT without annealing, using AR grade cadmium sulphate, $CdSO_4$ and thiourea, $CS(NH_2)_2$ in liquid ammonia solution with p^H value adjusted at 10 and study the change in microstructures, particle size, band gaps, optical absorption at different molars.

II. MATERIALS AND METHODS

Synthesis of nano-composite CdS films has been carried out by CBD technique on ultra fine cleaned micro-glass slides at

different equimolar solutions (EM) $0.05M \leq x \leq 0.2M$ using cadmium sulphate, thiourea and ammonia solution. The films of $0.05M$ were prepared by dissolving $3.8gm$ of $CdSO_4$ in 100 ml of doubled distilled (DD) water and stirred vigorously for 15 min with a magnetic stirrer for homogeneity of the solution. Then, ammonia solution was added drop-wise to the precursor till the solution turned into a white turbid. Excess ammonia was again added till the solution became clear with the production of $Cd(NH_3)_4^{2+}$ ions in the solution. The p^H of the solution was maintained at 10 using a digital p^H -meter. An EM solution of thiourea was prepared into $100ml$ of DD water at RT and then stirred for 15 min . The precursor was then added to the alkaline cadmium sulphate solution in the ratio 1:4 while the matrix was kept on stirring for 1.30 hr at $70^\circ C$. After cooling the solution at RT, the chemically and ultrasonically cleaned substrates were immersed vertically into the reaction bath for 24 hr using a suitably designed substrate holder properly clamped. The substrates were removed from the bath when we obtained CdS thin films deposited, which were then kept for 30 min in a desiccator for stabilization, washed several time with running DD water after which were dried in an oven at $10^\circ C$ above RT for 30 min for better adhesive with the substrate. Similarly, we synthesized CdS films of different molars $x = 0.1M, 0.15M$ and $0.2M$ by dissolving appropriate amount of $CdSO_4$ and thiourea in DD water. XRD technique was used for particle size determination and SEM for nano-structural analysis. The optical absorbance, transmittance and energy band gaps at different molars in the films were determined using UV-vis-spectrometer. The average thickness of the films were measured by microbalance method.

III. RESULTS AND DISCUSSIONS

(3.1) Effects of molarity on microstructures of the CdS thin films

The as deposited CdS films at RT substrates of molar, $x = 0.05M, 0.1M, 0.15M$ and $0.2M$ were taken X-ray diffractions (Phillips X'pert Pro-Automated Powder X-ray, model APP 1700) with CuK_α radiations ($\lambda = 1.572\text{\AA}$) at Sophisticated Analytical Instrumentation Facility (SAIF) in USIC, Gauhati University, Assam. The spectral analysis of the CdS films prepared at EM solution of $CdSO_4$ and $CS(NH_2)_2$ at $0.05M$ shows almost amorphous state with a negligible peak (111) ($2\theta = 25.8^\circ$) as shown in Fig.1(A). It may be interpreted as to low concentrations of cadmium and sulphur ions in the growth of CdS thin films. The crystalline growth of CdS thin films is found to enhance with increasing molar of the precursor as observed in Fig.1(B) ($x = 0.1M$), Fig.1(C) ($x = 0.15M$) and Fig.1(D) ($x = 0.20M$). The X-ray profile analysis of the CdS films grown at $x = 0.20M$ reveals a maximum peak at (200) plane at $2\theta = 31^\circ$ with some small peaks corresponding to the planes (100) at $2\theta = 17.5^\circ$, (111) at $2\theta = 25.8^\circ$, (210) at $2\theta =$

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38° , (220) at $2\theta = 44.9^\circ$ and (311) at $2\theta = 52.1^\circ$ and (400) at 61.9° with lattice parameters evaluated using the relations

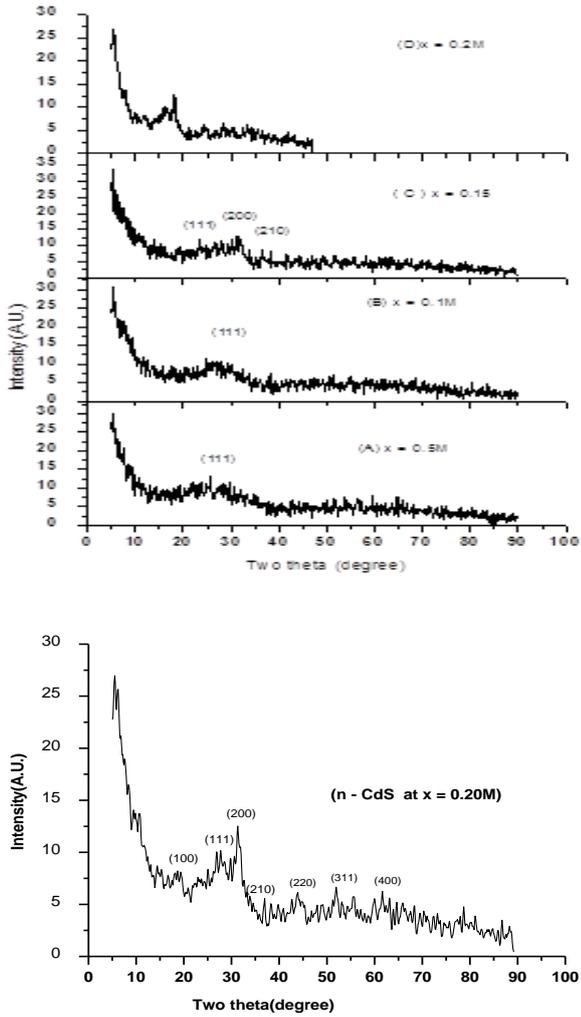


Fig. 1— XRD pattern of n-CdS films

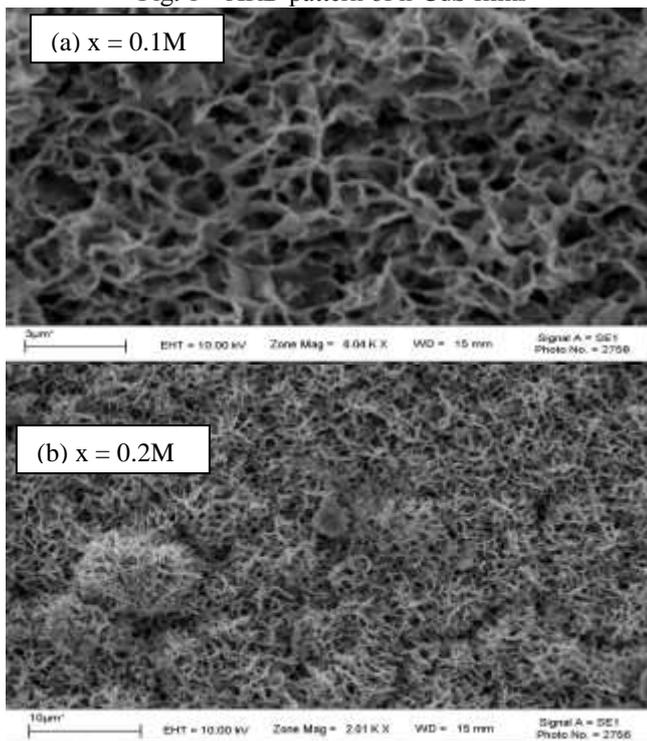


Fig.2 (a & b)— SEM images of n-CdS films ($x = 0.1M$ and $0.2M$)

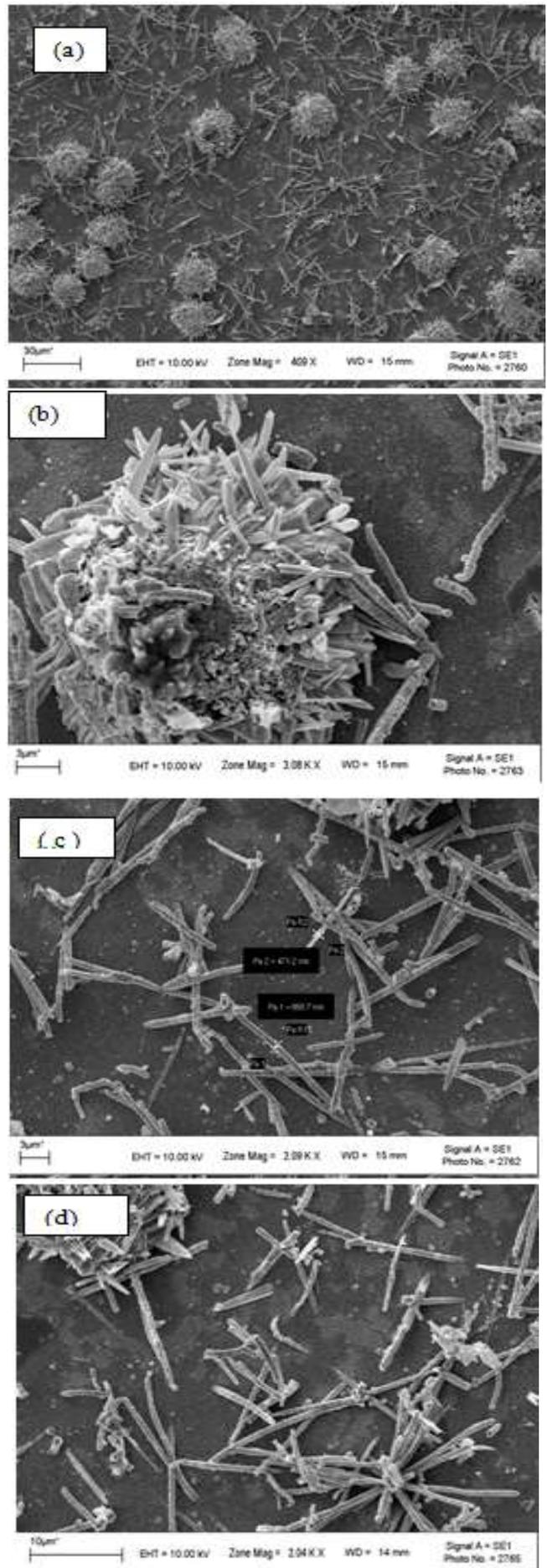


Fig. 3 (a, b, c & d)— SEM images of CdS nano-pencils at different zone magnifications ($x = 0.2M$).

$$a_{cal} = \frac{\lambda}{2\sin\theta} \sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

and

$$d_{cal} = \frac{a_{cal}}{\sqrt{(h^2 + k^2 + l^2)}} \quad (2)$$

as shown in Table-1.

Table1—Lattice parameters of n-CdS films at 0.2M

hkl	JCPDS	a - value (bulk) - value (Å)	a _{cal} - value (Å)	d _{ca} (Å)
100		5.630	5.072	5.072
111	3.362	5.630	5.984	3.455
200		5.830	5.775	2.887
210		5.830	5.299	2.370
220	2.069	5.830	5.714	2.020
311	1.756	5.830	5.837	1.760
400		5.830	6.000	1.500

The observed X-ray diffraction pattern at $2\theta = 31^\circ$ exhibits cubic zinc blend¹⁸ as confirmed from JCPDS Table-5(1970). The crystal has 4 atoms per unit cell with unit cell dimension $a = 5.763\text{Å}$, $A = 144.47\text{gm}$ and $\rho = 4.8\text{gm/cc}$ which reveals the f.c.c. zinc blend structure. The $\sin^2\theta_1/\sin^2\theta_2$ value corresponding to the adjacent planes (200) and (111) in the diffraction spectra is found 0.8 which also corresponds to the f.c.c. cubic zinc spharalite structure. Similar results were also obtained by other workers^{19,20}. The particle size in the films is determined from FWHM of peak corresponding to $2\theta = 31^\circ$ using Scherrer's relation

$$d = k\lambda/\beta_{2\theta} \cos\theta \quad (3)$$

with k value ≈ 0.94 and λ (wavelength of X-rays used) $\approx 1.542\text{Å}$ and $\beta_{2\theta} \approx 0.8542^\circ$. The estimated average grain sizes of the films ($x = 0.1M$ & $0.2M$) is found to be 10nm showing nanocrystalline growth. The particles agglomerate to the formation of CdS nanorods (NRs) as observed in Fig. 2(a&b). Figure 3 (a, b, c & d) show SEM micrographs of CdS-NRs ($x = 0.2M$) at zone magnifications 409x, 2.09Kx, 3.08Kx and 2.04Kx respectively. Figure 3(c) shows a flower like structure of micrometer size of the NRs formed as a result of agglomeration of small CdS-NRs. The average diameter of the NRs lies in the range 471.2 – 668.7nm (Pa-1 & Pa-2) as observed in Fig. 3(b). These one dimensional nanorods will be useful for fabrication of efficient field emitters in low field and low current density. Similar reports are also available in from other workers.^{21,-23}

(3.2) Study of optical properties in the films

CdS is a direct band gap semiconductor. Figure 4 (a, b, c & d) show the absorbance vs. wavelengths curves in the films obtained from UV-vis. spectrometer (model: Lamda 35 LS 35, PARKIN ELMER 2008). The absorption coefficient, α in the films can be correlated to the photon energy as

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (4)$$

where E_g is the energy band gap between the valency and the conduction bands, A is a constant being different for different transitions, and n is a constant being equal to 1 for direct band gap semiconductor .

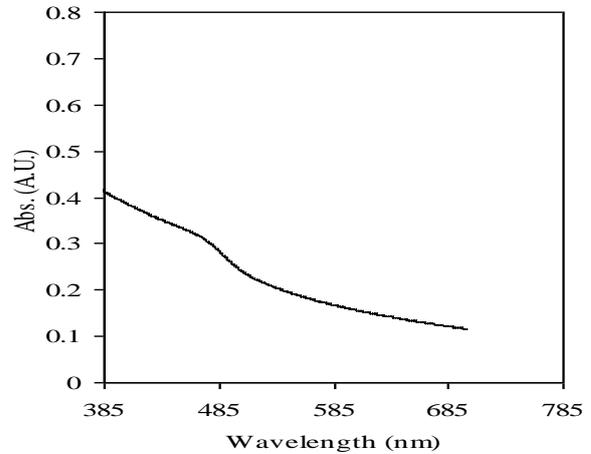


Fig. 4(a) — Abs vs. wavelength (nm) of CdS nanocomposite films ($x = 0.05M$).

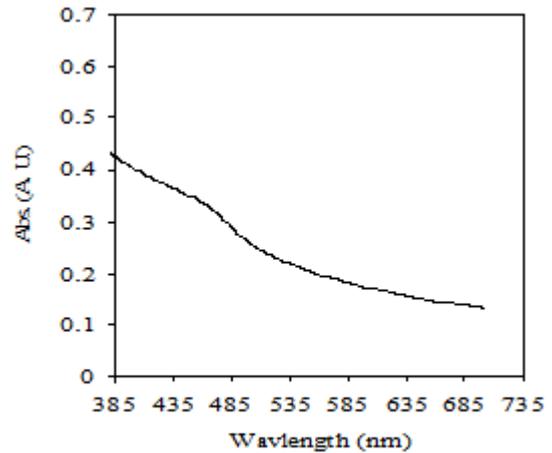


Fig 4(b) — Abs. va wavelength curve of n-CdS films (0.1M)

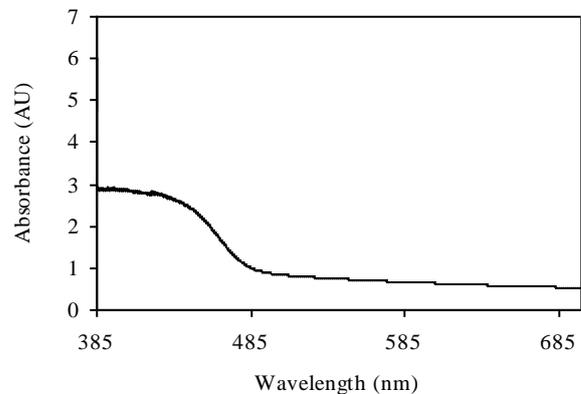


Fig. 4(c) — Abs. Vs. wavelength curve of n-CdS films($x = 0.15M$).

where A is a constant, E_g the energy band gap. The band gaps determined from the $(\alpha h\nu)^2$ vs. $h\nu$ (photon energy) curves of the films with extrapolation to zero absorbance as shown in Fig.5(a, b, c & d) have been shown in Table-2

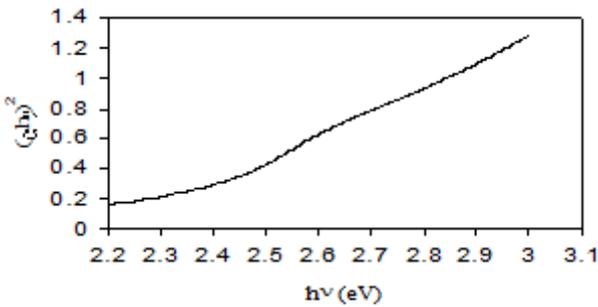


Fig.5(a) — Estimation of energy gap in-CdS film (x = 0.05M).

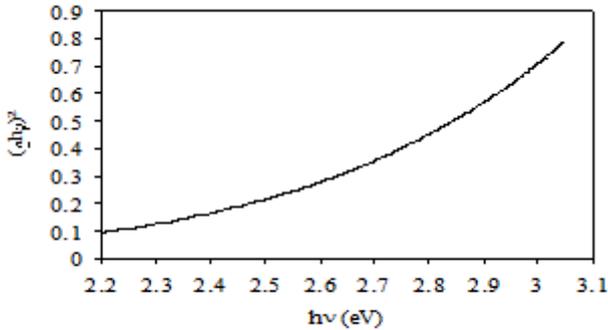


Fig.5 (b)— Estimation of energy gap in n-CdS film (x = 0.1M).

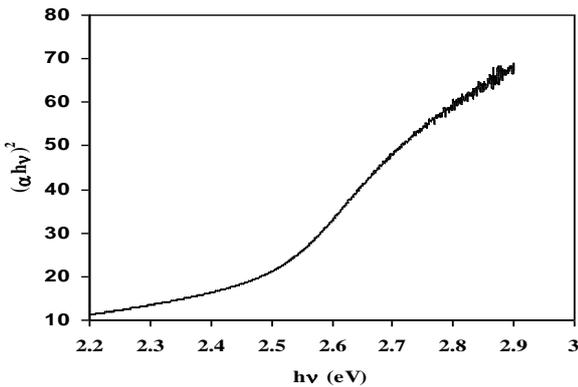


Fig.5 (c) — $(\alpha h\nu)^2$ vs. $h\nu$ curve of n-CdS film (x = 0.15M).

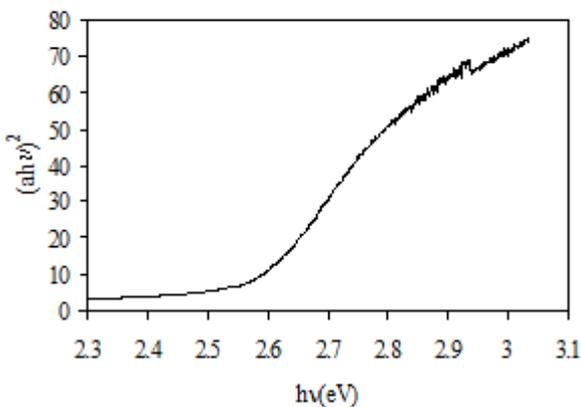


Fig.5 (d)— Estimation of energy band gap in n-CdS film(x=0.2M)

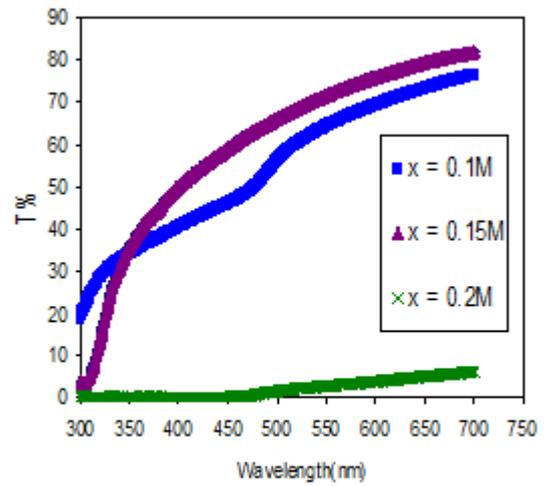


Fig. 6- Trans. vs. wavelength (nm) in n-CdS films.

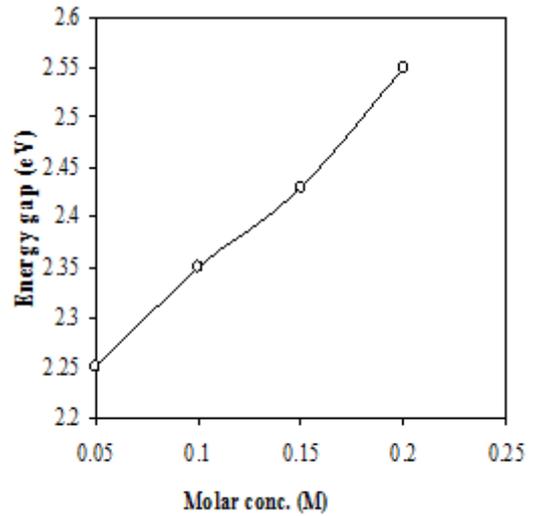


Fig.7— Energy gap vs. molar concentration.

Table2— Band gaps at different molars of CdS films (0.4-0.8μm thick)

Molarity (M)	Substrate temperature (°C)	Band Gap (eV)
0.05	27	2.25
0.10	27	2.35
0.15	27	2.43
0.20	27	2.58

The absorption coefficient, α is found to enhance with increasing molar within 385 – 700 nm wavelength range. The enhancement of the absorption in lower wavelength ranges may be attributed due to increase of agglomeration of nanorods under quantum size effect which absorb more photons of lower wavelengths with less transmissions. The study of the optical absorption spectra shows absorption peak at 435 nm which exits in the lower blue spectral side. The blue shift of the absorption edge indicates decreasing the grain sizes in the films¹⁴. The study of the optical band gaps with different molar concentration in the films shows an increase in band

gap with increasing molars. The increase in band gap in the films is a consequence of decreasing the crystallite sizes in the films. The change in the energy gap as function of crystallite or particle size in the films may be defined by a hyperbolic band model²⁴ given by

$$E_{gn} = \sqrt{[E_{gb}^2 + 2h^2 E_{gb} (\pi/R)^2/m^*]} - (5)$$

where E_{gn} is the band gap in nano-crystal films, E_{gb} the band gap in the bulk semiconductor, h the Plank constant, R the particle radius and m^* is the effective electron mass. The eqn. (5) shows that energy gap increases with reduction in particle radius. Figures 6(a & b) show the corresponding transparency co-efficient vs. wavelength curves of n- CdS films in the visible spectrum. The curves reveal that transition of photon energy is high in films with lower cadmium and sulphur ion concentration as shown at intercepts from $(22 - 4)\% T$ ($\lambda = 300\text{nm}$). As the continuum of the Cd^{2+} and S^{2-} ion concentration increased in the growth of n- CdS films, the quantum of photon transparency decrease as a result of increasing absorption of photon energy due to quantum size effects. The change in energy gaps with molar concentrations of Cd^{2+} and S^{2-} ions is shown in Fig.7. This mechanism of the optical analysis in chemically deposited CdS films will find significant contributions in the photo – electrical transport mechanism in fabrications of solar cells, solar detectors, photo-electrical cells etc. for different nano-technology device and applications in near future.

IV. CONCLUSION

The crystal growth of chemically synthesized CdS films by CBD technique under control of: p^H value of the solution, deposition time, film thickness at varied concentrations of Cd^{2+} and S^{2-} ions in the solution is found to improve with increasing concentration of Cd^{+2} and S^{2-} ions in the solution. The phase analysis of the film is found to possess f.c.c. cubic zinc sulphide with highly oriented along (200) direction. The Scanning Electron Micrographs of the CdS films show formation of agglomerated CdS –nanorods which have higher absorption co-efficients in lower wavelengths with blue shift peak at 435nm. The study of UV-spectra of the samples ($x = 0.5 - 0.2\text{M}$) show enlargement of optical band gap as a result of increasing concentration of cadmium and sulphur ions.

ACKNOWLEDGEMENT

The author (KKS) wishes to thank the University Grants Commission, New Delhi for granting a Major Research Project *F. No. F. No.34-19/2008 (SR) dated 29th Dec., 2008*. We wish to thank the authorities of the Central Instrumentation Facility (CIF), IIT, Guwahati, Assam for providing SEM and USIC, Guwahati University, Assam for XRD facilities of the samples and lastly, Department of Chemistry, Manipur University for optical data analysis of the films.

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