Abstract: CdS films have been chemically deposited on glass substrates at room temperature at varying molarity from 0.05M ≤ x ≤ 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.

Keywords: 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 devices. Such novel properties of nanoparticles have been enhanced non-linearly due to quantum confinement effect. 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), electro-deposition, sol-gel coating, vacuum evaporation. However, the basic problem with CdS is to obtain uniform and stoichiometric film over large area relative to less time consumptions 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 by CBD technique at RT without annealing, using AR grade cadmium sulphate, CdSO\textsubscript{4} and thiourea, CS(NH\textsubscript{2})\textsubscript{2} in liquid ammonia solution with pH 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 ≤ x ≤ 0.2M using cadmium sulphate, thiourea and ammonia solution. The films of 0.05M were prepared by dissolving 3.8gm of CdSO\textsubscript{4} in 100 ml of doubled distilled (DD) water and stirred vigorously for 1.30 hr at 70°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 100°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\textsubscript{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.

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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).

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).
1700) with Cukα-radiations (λ=1.572Å) at Sophisticated Analytical Instrumentation Facility (SAIF) in USIC, Gauhati University, Assam. The spectral analysis of the Cds films prepared at EM solution of CdSO₄ and CS(NH₂)₂ at 0.05M shows almost amorphous state with a negligible peak (111) (2θ = 25.8°) 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 2θ= 31° with some small peaks corresponding to the planes (100) at 2θ = 17.5°, (111) at 2θ = 25.8°, (210) at 2θ = 38°, (220) at 2θ = 44.9° and (311) at 2θ = 52.1° and (400) at 61.9° with lattice parameters evaluated using the relations

\[
a_{\text{calc}} = \frac{\lambda}{2 \sin \theta} \sqrt{(h^2 + k^2 + l^2)}
\]  

(1)

and

\[
d_{\text{calc}} = \frac{a_{\text{calc}}}{\sqrt{(h^2 + k^2 + l^2)}}
\]  

(2)
as shown in Table-1.

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<th>100</th>
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<td>JCPDS</td>
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The observed X-ray diffraction pattern at 2θ = 31° exhibits cubic zinc blend as confirmed from JCPDS Table-5(1970). The crystal has 4 atoms per unit cell with unit cell dimension a = 5.763Å, A = 144.47gm and ρ = 4.8gm/cc which reveals the f.c.c. zinc blend structure. The sin²θ/sin²2θ 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. The particle size in the films is determined from FWHM of peak corresponding to 2θ = 31° using Scherrer’s relation

\[
d = \frac{k\lambda}{\beta_{2θ} \cos θ}
\]  

(3)

with k value ≈ 0.94 and λ (wavelength of X-rays used) = 1.542Å and β2θ =0.8542°. 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 (Pa1 & Pa2) 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.

(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: Lambda 35 LS 35, PARKIN ELMER 2008). The absorption coefficient, α in the films can be correlated to the photon energy as

\[
a = \alpha = \frac{A(h\nu - E_g)^n}{2}
\]  

(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.
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 absorption as shown in Fig.5(a, b, c & d) have been shown in Table-2.
The absorption coefficient, $\alpha$ 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 films. 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 model given by

$$E_{\text{gn}} = \sqrt{E_{\text{gb}}^2 + 2\hbar^2 E_{\text{gb}} (\pi/R)^2} / m^*$$

where $E_{\text{gn}}$ is the band gap in nano-crystal films, $E_{\text{gb}}$ the band gap in the bulk semiconductor, $\hbar$ the Planck 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 coefficient 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 (λ = 300nm). 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: pH 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 ($x = 0.5 – 0.2$M) show enlargement of optical band gap as a result of increasing concentration of cadmium and sulphur ions.
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Reference

[18]. Powder Diffraction Data from Joint Committee of Powder Diffraction Standard Associateshipt at the National Bureau of Standards (Table-5) 314 43 1970.