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EFFECT OF pH VARIATION ON SIZE AND STRUCTURE OF CdS NANOCRYSTALLINE THIN FILMS

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The interrelation between particle size, crystal structure and optical properties in semiconductor nanocrystalline thin films has wide spread interest. We report here an attempt to relating the size and structure of cadmium sulphide (CdS) nanocrystalline thin film with variation of pH of the solution. CdS particle sizes between (3.5 to 5.3nm) were obtained by varying the pH between 1.6 to 2.2 and using polyvinyl alcohol as a capping agent in a chemical route. X-ray diffraction (XRD), UV-Visible spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to characterize the samples.

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Keyword: Cadmium sulphide, Nanocrystalline, Structural, and optical properties

1. Introduction

Currently there is a great deal of interest in optical and structural properties of nanometer sized semiconductor particles or thin films [1]. Nanocrystalline thin film of II-VI semiconductor have attracted particular attention, because they are relatively easy to synthesis in the size range required for quantum confinement They show significant departures from bulk optical and structural properties when scale of confinement approaches to excitonic Bohr radius(r_B), which sets the length scale for optical process[2]. Reduction in particle size strongly influences the crystallinity, melting point and structural stability. CdS is a wide band gap semiconductor with Eg ≈2.42 eV[3]. The optical properties of CdS have been extensively studied [4].Quantum size effects are quite pronounced because CdS has r_B (≈3nm) [1]. CdS nanoparticles are attractive candidate for optoelectronic application as it is possible to tailor the band gap over wide spectral range (visible to UV).CdS is a technologically useful material, as many devices based on CdS, including sensors have come up in the recent years. The thin film cadmium sulphide solar cell has for several years been considered to be a promising alternative to the more widely used silicon devices. Bulk CdS has a hexagonal wurtize type crystal structure with a=0.4160nm and c=0.6756nm. Again as the size of CdS nano particle decreases the equilibrium crystal structure tends to change from the hexagonal to cubic phase. The size dependence CdS nanocrystalline thin film is one of the subjects of present study. CdS thin film have been fabricated using several deposition technique such as screen printing[2], electro deposition[3], molecular beam epitaxy (MBE)[1], physical vapor deposition(PVD)[4]. All these technique require high sophisticated instrument and mismatch of thermal expansion co-efficient between the film and substrate causes micro cracks. One of the most promising techniques for producing large areas of inexpensive CdS film is chemical route and here we followed this method to synthesize the CdS films.

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Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were used to analyze the surface morphology and shape and size of the sample. The present work represents the preparation of CdS nanocrystalline thin film using polyvinyl alcohol (PVA) as capping material and their subsequent characterization by UV-Visible spectrometer, XRD and TEM.

2. Experimental

CdS nanocrystalline thin films are synthesized in the polymer matrix by an ion exchange reaction. The detailed preparation procedure is as follows. Aromatic solids like PVA, being good solute to multiple phase system and it provides uniform gaps that are very close to each other and distributes in the form of array.5 wt% solution of PVA ,2wt% $CdCl_2$ was mixed with various concentration (2,3,4 wt%) under a high stirring rate (200rpm) condition. The constant temperature 70^0C for 3 hours was maintained during the process of stirring.. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. To this solution 2 wt% Na_2S was added till the whole solution turns into yellow color. The CdS nanoparticle containing PVA were caste over glass slides to produce thin film form and successive experiments for characterization were carried out. The chemical reaction occurs as follows

$$CdCl_2+Na_2S \longrightarrow CdS + 2NaCl \qquad (1)$$

For characterization Philips X'pert XRD, double beam spectrometer, TEM (JEOL JEM-100cx) have been used. Thickness of the films have been measured using gravimetric method.

3. Results and discussion

3.1 Size and structural transformation

To identify the structure and phase, the diffraction patterns of as prepared sample were taken by (Philips X'pert) operating at 40kV-30 mA. The radiation source used was CuKα (λ =1.542Å) and a Nickel filter was used to block K_β radiation. The samples were synthesized by above technique and differs only in pH from 1.5 to 2.The XRD patterns are as shown in Fig1.

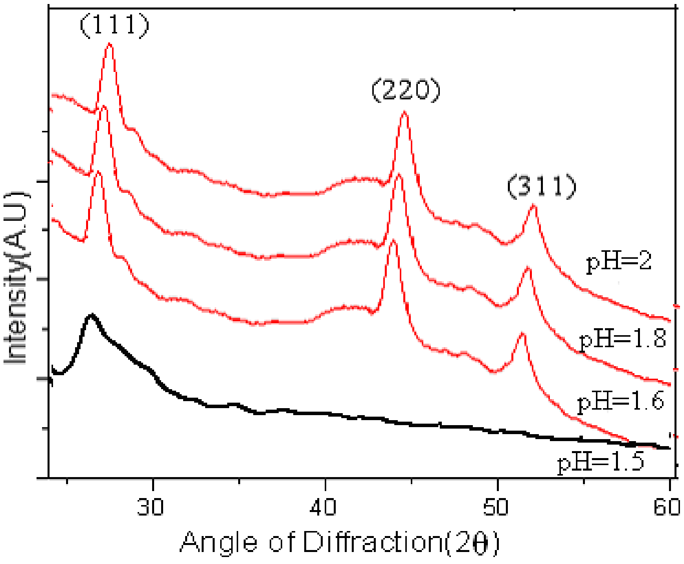

Fig. 1. XRD pattern of CdS nanocrystalline thin film at different pH

It is observed that XRD peaks are broaden to the reflecting plane of cubic phase [JCPDS 89-0440] (111), (220), (311) at pH 1.8 and 2. The XRD pattern within pH 1.5 apparently exhibits only one broad peaks at $2\theta \approx 26.3$ Again it is observed that when pH increases the peak position of the sample are shifted to higher diffraction angle suggesting lattice contraction with respect to bulk. The lattice contraction occurs because of higher surface to volume ratio [4]. Again broadening of peak represent the increase in FWHM and reduction of particle size .The reduction of grain size is a indicator of change in crystal structure from hexagonal to cubic. The size of the samples at different pH is calculated by using Sherer formula [5]

$$D_{hkl} = K\lambda / w\, \mathrm{Cos}\theta \qquad (2)$$

w being FWHM & θ is the Braggs angle and shape factor K=0.89 for spherical shape(confirmed by TEM image). From the calculation it is found that when pH increases the particle size decreases (Table1). pH controlled the rate of reaction due to the common ion effect[6,7]. At higher pH the solubility product increases and as a result no formation of CdS particle is formed. The lattice constant was calculated by following relation

$$a_{cal} = d(h^2+k^2+l^2)^{1/2} \qquad (3)$$

and found that when pH increases from 1.5 to 2 the lattice constant decreases from0.58201nm to 0.56889nm (Fig2) .

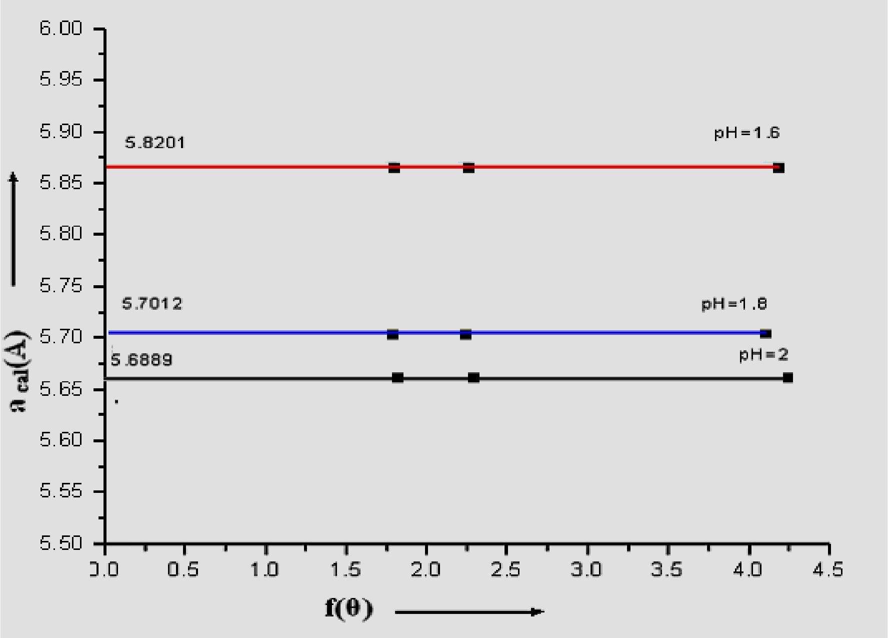

Fig. 2. Nelson Riley plot.

The systematic error 2θ was eliminated by applying Nelson Riley plot [5] for films having three prominent peaks as shown in Fig2. A straight line is obtained as shown in Fig2 .The corrected value of lattice constant a is then obtained by extrapolating the function $f(\theta)$ to zero .

3.2 Optical observation

The optical absorbance of the samples were observed using double beam automated spectrophotometer (HITACHI-U3210).

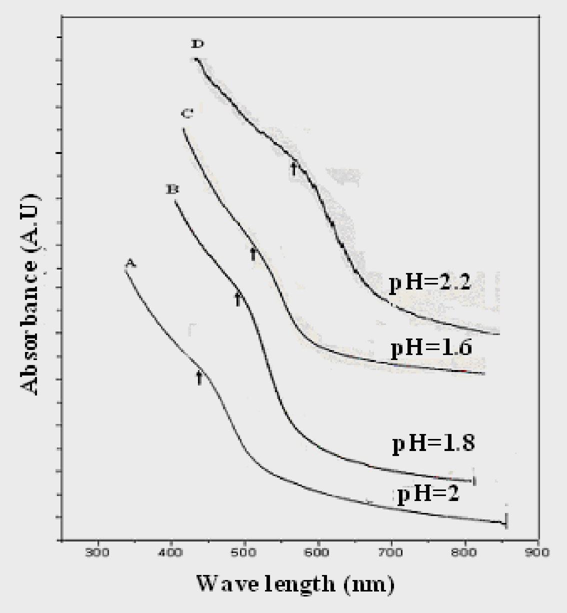

Fig. 3. Absorption spectra of CdS nanoparticles at different pH.

It is evident from the Fig3 that all samples exhibit absorbance edges which are blue shifted with respect to bulk CdS, arising from quantum confinement effect in nano particles. The band gap of the corresponding to pH 1.6 to 2 was calculated by plotting $(\alpha h\nu)^2$ vs hν using the relation(Fig4)

$$\alpha h\nu = \text{const}\,(h\nu - E_g)^n. \qquad (4)$$

The value of α is obtained from relation

$$\alpha = 2.3026(A/\,t) \qquad (5)$$

where A is absorption and t is the thickness of the sample .The Fig4 shows maximum blue shift is observed at pH=2 corresponding to wave length 380 nm., which is expected to be 1S-1S quantum particle as suggested by Brus[3].

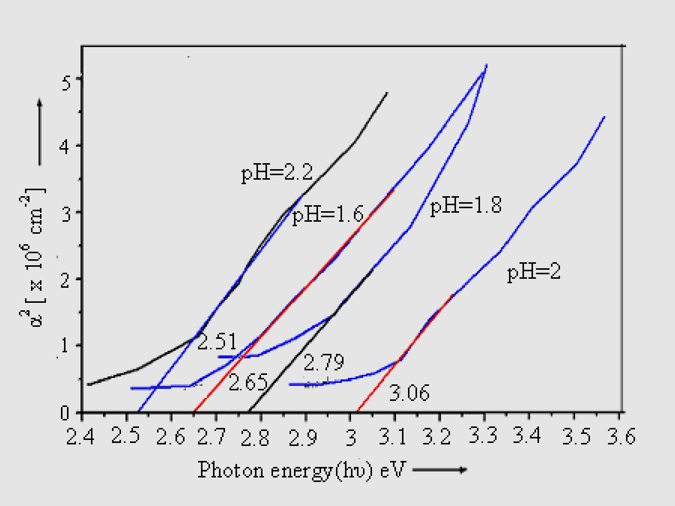

Fig. 4. Determination of energy gap.

The band gap increases when pH increases from 1.5 to 2. The highest blue shift energy is found to be 0.64 eV .From the band gap information the size of the CdS quantum dots were calculated using effective mass approximation (EMA) method and hyperbolic band model(HBM) using the following equation[8]. For EMA

$$E_{gn} - E_{gb} = [(\hbar^2 \pi^2 /2R^2)1/ m^*] \tag{6}$$

and for HBM

$$E^2_{gn} = [E^2_{gb}+2\hbar^2 E_{gb}(\pi/R)^2 / m^*]. \tag{7}$$

In the above two equations m* is the effective mass of the specimen, E_{gb} is bulk band gap and E_{gn} is the band gap of sample. From the calculation it is found that when pH increases from 1.6 the particle size decreases up to pH=2 and then the particle size again increases beyond pH value2. The observations are shown in Table1. From the TEM photo graph Fig6 the dots are seen to be spherical and symmetrical.

Table 1. Variation of size with pH from different method

pH	Band gap(eV)	Blue shift energy(eV)	EMA(nm)	HBM(nm)	Sherer size(nm)
1.6	2.65	0.23	5.70	12.6	3.8
1.8	2.79	0.37	4.50	9.82	3.6
2	3.06	0.64	3.41	7.27	3.5
2.2	2.51	0.09	9.1	15.8	5.1

The size calculated from Sherer formula (equation 2) for three prominent peaks are also found to be almost of same size. TEM observation of sample also indicate nearly same value of quantum dots. Again absorption spectra show that samples are of single phase because the sample exhibits only one absorption edge [9-16].

3.3 SEM and TEM studies

SEM observations of the CdS nanocrystals were performed by using LEO 1430VP brings microscopic information of the surface structure and roughness (Fig5). In this work, it appears to be a helpful technique to specify the growth mode via the study of a surface roughness, and to determine the effect of the pH on the film morphology. Fig5 shows surface topography of CdS layers obtained at two different pH. Semispherical grains are uniformly distributed at the surface. A slight increase of the grain size follows the pH decreasing but does not improve the surface roughness. Concerning the nucleation stage film growth proceeds by nucleation of crystallites, then forming grains which coalesce to cover the entire substrate surface and to show a dense structure.

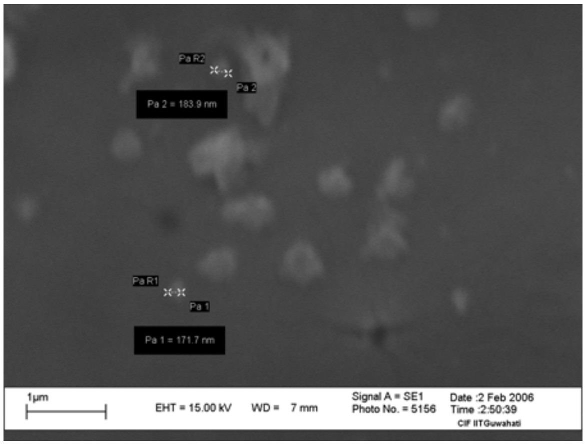

Fig5.SEM image of CdS thin film at pH=2

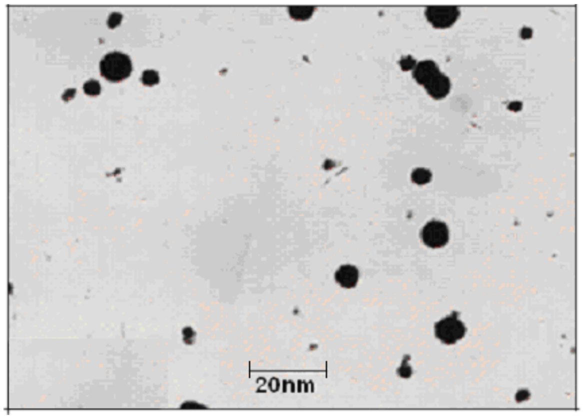

Fig. 6.TEM image of CdS thin film at pH=2.

TEM observations of the CdS thin films were performed by using (model JEOL JEM-100cx) transmission electron microscope, operating at 400 kV accelerating voltage. TEM images of CdS thin films show that all particles of thin films exhibited spherical shape, and the crystal sizes are estimated to be 4 nm(Fig. 6).

3.4 Energy Dispersive X-ray Spectroscopy (EDS):

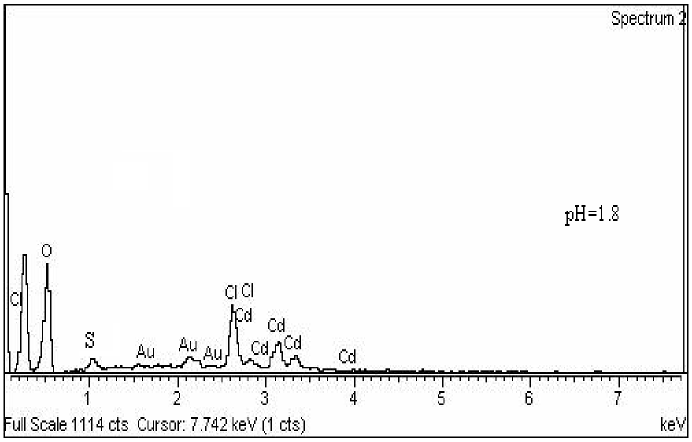

Fig7.EDS spectrum CdS thin film at pH=1.8.

Fig7 shows the composition of the CdS nanocrystalline thin film with the help of Energy Dispersive X-ray Spectroscopy (EDS). Fig7 shows the clear peaks of Cd and S, but some additional peaks are also present. The extra peaks are expected to occur from capping material. Si peak is due to the amorphous glass substrate (Silica Sio_2). The sample contains higher percent of oxygen because the samples are kept in ambient condition so formation of CdO is not surprising.

4. Conclusions

The reduction of particle size with variation of pH in CdS nanocrystalline thin film growth as well as transformation from bulk hexagonal (w) type structure to cubic zinc blende type structure (zb) have been observed . The result indicates that particle sizes are symmetric in nature and are of spherical in shape. Optical properties of nanocrystalline CdS are governed by quantum confinement effect. The particle sizes can be controlled by the amount of polymer stabilizer, pH variation and temperature of the solution. XRD, optical absorbance shows that samples are of single cubic phase, which is important for device performance.

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