SYNTHESIS OF CdS QUANTUM DOTS USING WET CHEMICAL CO-PRECIPITATION METHOD

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Size tunable Cadmium sulphide (CdS) quantum dots have been synthesized through wet chemical co-precipitation method, at three different temperatures 35^{o}C, 50^{o}C and 65^{o}C for varying pH values of 9 and 10.5 respectively. The solution was prepared using Cadmium chloride and thiourea as material precursors, ammonium hydroxide as precipitating agent and mercaptoethanol as surfactant. Thin films of these nanoparticles were deposited by dip coating technique on glass substrate. The formation of CdS quantum dots was confirmed through their structural characterization using X-Ray diffraction (XRD) technique. Photoluminescence (PL) spectroscopy was used to investigate the optical behaviour of as synthesized CdS quantum dots. XRD analysis reveals that these quantum structures have single phase hexagonal- cubic structure. It has also been found that the particle size depends on both temperature and pH. The PL spectra shows the large stoke shift for CdS bulk as compared to CdS nano particle which implies reduction of particle size.

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1. Introduction

In recent years semiconductor nanoparticles and their thin film has got great emphasis due to their wide range of application [1]. II-VI semiconductor group based nanocrystalline thin film utilize expertise in synthetic crystal materials growth, optics fabrication, electronic component manufacture, and more to create high-tech products for a wide range of applications in industries. This is because they are relatively easy to synthesis in the size range required for quantum confinement .The particle size reduction influence the crystallinity, melting point and structural stability. CdS is a wide band gap semiconductor with Eg ≈2.42 eV[2]. Cadmium sulfide can be prepared by the precipitation from soluble cadmium (II) salts with sulfide ion and this has been used in the past for gravimetric analysis and qualitative inorganic analysis. Quantum size effects are quite pronounced because CdS has rB (≈3nm) [1]. For optoelectronic devices CdS has been one of the main material of choice as it has the property to tailor the band gap over wide spectral range. CdS has up come with several applications in solar cells, sensors etc. Bulk CdS has a hexagonal wurtize type [3]. CdS thin films have been fabricated using wet chemical co-precipitation method which is one of the most promising techniques with low cost reduction. The present work represents the preparation of CdS nanocrystalline thin film and their subsequent characterization by X-ray diffraction and photoluminescence.

2. Experimental techniques

The deposition of cadmium sulfide films was carried out on glass substrates under identical conditions. Prior to deposition glass substrate was ultrasonically cleaned in a neutral detergent solution, washed with HCL and then triple distilled water prior to the deposition.

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Cadmium sulphide films were deposited using wet chemical synthesis. The reaction matrix employed in our study consisted of LR grade $CdCl_2$, NH_4Cl and thiourea in 1:3:7 molar ratios. The reaction matrix was prepared in two parts. In part A, $CdCl_2$ and NH_4Cl with molar ratio 1:3 were dissolved in distilled water. In part B, an aqueous solution of thiourea was prepared. The pH of the electrolyte was maintained at 9.0 using ammonia solution. The cleaned substrates were dipped in this solution , following which part B of the solution containing thiourea was injected into the reaction matrix. Particle size control in the deposited CdS layer was attained by adding mercaptoethanol as a surfactant. The total volume of the electrolyte was always maintained 80 ml. Synthesis process was performed at three different temperature 35 ^oC, 50 ^oC, 65 ^oC. The chemical reaction occurs as follows:

$$CdCl_2+2H_2O \rightarrow Cd(OH)_2+2HCl$$

$$Cd(OH)_2 \rightarrow Cd_2{+}{+}2(OH).2(NH)_2CS+OH\_ \rightarrow 2CH_2N_2+H_2O+HS\text{-}HS^-+OH^- \rightarrow H_2O+S^{2-}$$

$$Cd^{2+}+S^{2-} \rightarrow CdS$$

For characterization PANalytical X'pert HRXRD machine is used to study the structural properties of CdS thin films and for optical analysis photoluminescence was carried out.

3. Result and discussion

3.1 Structural and Optical Transformation

The X-ray diffraction profile is characterized for CdS sample (Figure 1) at 35^oC by one prominent peak at 26.325 and one relative weak peak at 2θ =43.78, Similarly for sample CdS at 50 ^oC , 65 ^oC the most prominent peak at 27.24 , 26.929 respectively and at and one relative weak peak at 44.27 , 46.40. Both the peaks of the X-ray diffraction pattern clearly indicates the formation of single phase cubic CdS quantum dot (JCPDS Card No.- 75-1546) with estimated particle size 0.8 nm , 1.1 nm and 1.3 nm as calculated by using debye Scherrer's formula.

$$d = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

Where θ is the Braggs angle, B is FWHM, λ is incident X-ray wavelength and d is particle size.

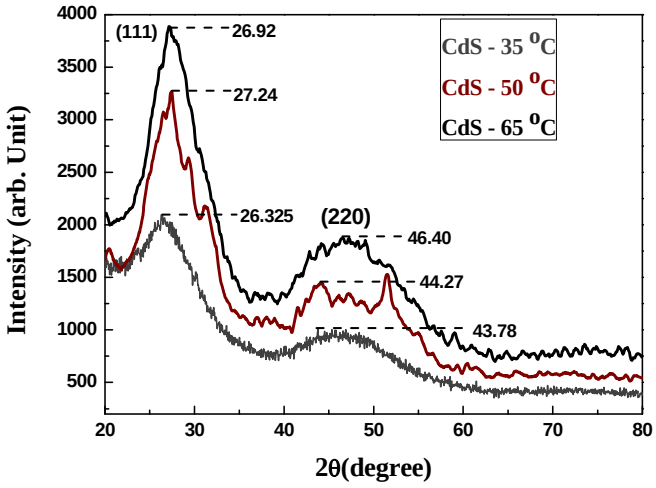

Fig 1. XRD diffraction pattern of a typical nanocrystalline CdS Quantum Dots

In Fig. 1 the dotted lines indicates the observed 2θ values for both prominent peak and relative weak peak. The peak position 2θ (observed and standard value) along corresponding full width half maxima (FWHM), Miller indices (hkl), particle size d (in nm), relative intensity and phase assignment for different temperatures have been summarized in table 1. It is clear from table

1 that there is modification in particle size with change in temperature i.e with increase in temperature particle size of CdS quantum dots also increases.

Table 1. The value of 2θ (Observed, standard), d, FWHM, Relative intensity, hkl, phase assignment with temperature variation for CdS samples

Sample Specification	2thetha(degree)	d(nm)	FWHM (degree)	Relative Intensity (arb. unit)	hkl	Phase assignment
CdS: 35 °C	26.325 26.505 43.78 43.969	0.8	9.14	2100	111 220	Cubic
CdS: 50 °C	27.24 26.505 44.27 43.969	1.1	7.28	1122	111 220	Cubic
CdS: 60 °C	26.929 26.505 46.40 43.969	1.3	6.02	998	111 220	Cubic

The X-ray diffraction profile for CdS samples with pH-9 and pH-10.5 has been plotted in figure 2. It is clear from the figure that prominent peaks are observed at 26.325 and 27.16 respectively, however one relative weak peak at 43.78 and 44.00 respectively has also been observed. Both the peaks of the X-ray diffraction pattern for CdS at pH-9 clearly indicates the formation of single phase cubic CdS quantum dot (JCPDS Card No.- 75-1546) where as for CdS at pH-10.5 the peak position is displaced which indicates the formation of Complex phase CdS quantum dot, with estimated particle size 0.8 nm and 1.3 nm resp. as calculated by using debye Scherrer's formula. The peak position 2θ along corresponding FWHM & Miller plane assignment have been summarized in table 2.

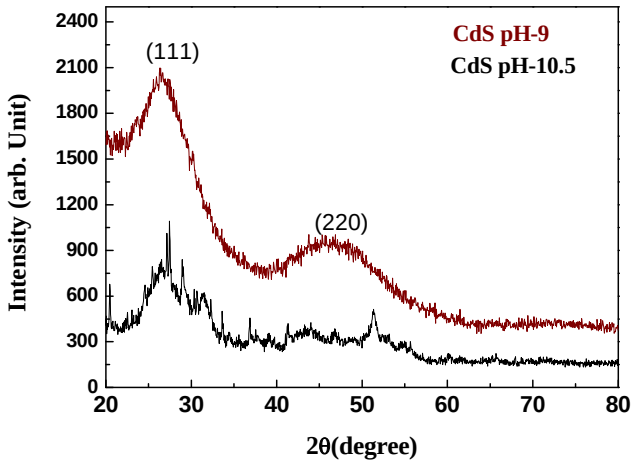

Fig. 2. XRD For nanocrystalline CdS quantum dots by pH variation

Generally, several factor can contribute to the broadening of diffraction peaks. Among these, instrumental factors, sample factors, Crystalline size broadening and Strain broadening contribute significantly.

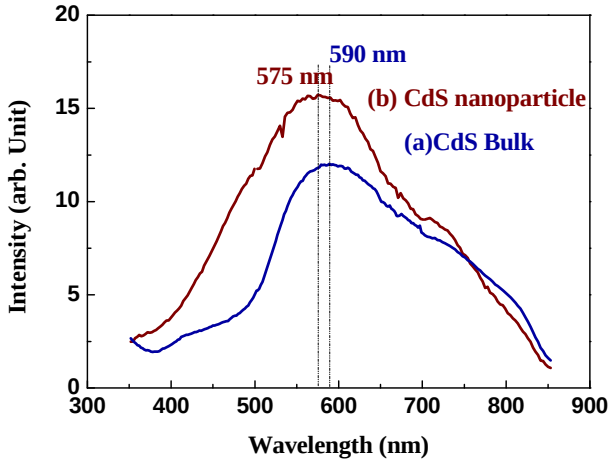

Fig. 3. Photoluminescence spectra for CdS thin film

Table 2. The value of 2θ (Observed, standard), d, FWHM, Relative intensity, hkl, phase assignment with pH variation for CdS samples

Sample Specification	2thetha(degree)	d(nm)	FWHM (degree)	Relative Intensity (arb. unit)	hkl	Phase assignment
CdS: ph-9	26.325 26.505 43.78 43.969	0.8	9.14	2100	111 220	Cubic
CdS: ph-10.5	27.16 26.505 44.00 43.969	1.3	6.084	1095	111 002 220 110	Cubic Hexagonal Cubic Hexagonal

The PL spectra for CdS nanoparticle is shown in figure 3 at an excitation wavelength of 266 nm .In the PL spectra emission peak due for CdS bulk is at 590nm where as emission peak due for CdS nanoparticles is at 575.22 nm. The observed peak position in PL spectra exhibited blue shift i.e PL spectra shows the large stoke shift for CdS bulk as compared to CdS nano particle which implies that particle size reduces. Energy band gap of bulk is 2.09eV (590nm) where as energy band gap of CdS nanoparticle is 2.15eV (575.22 nm) , which indicate that as the particle size reduces as energy band gap increases.

4. Conclusion

The reduction of particle size with variation in temperature in CdS nanocrystalline thin film growth. The x-ray peak in pH variation indicates the formation of single phase cubic CdS quantum dots which is important for device performance. The PL spectra exhibit blue shift. From PL spectra one can conclude that as the particle size reduces the energy band gap increases .The particle sizes can be controlled by the amount pH variation and temperature of the solution.

References

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