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Preparation Of Cds Nanocrystalline Thin Film By Chemical Method: The Effect Of Molarity On Structural And Optical Properties

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Abstract:

CdS Nanocrystalline Thin Films are prepared on cleaned glass substrate by Chemical Bath Deposition (CBD) method using polyvinyl alcohol (PVA) as matrix solution at room temperature. Structural characterization performed by X-Ray Diffraction (XRD) exhibits that the films are polycrystalline and cubic structure and the size of nanoparticles are within 7 nm. The size and distribution of the crystallites are controlled by varying the molarities of the solution. The surface morphology of the films have been observed by TEM. The optical investigation performed by means of UV Spectrophotometer shows a blue shift of energy compared to its bulk value due to quantum confinement effects of electrons and holes.

Keywords*: Chemical Bath Deposition, PVA, Blue shift*

1.Introduction

II-VI semiconductor Nanocrystalline thin films have attracted much attention in recent years because of their potential applications in various fields [1-8] such as in Electronics, Optics, Information Technology, Biology, etc. Cadmium Sulphide(CdS) is a typical wide direct band gap II-VI semiconductor having a bandgap = 2.42 eV at room temperature. CdS nanocrystals deposited as thin films are being extensively studied for their wide range applications such as in solar cells [9-10], nonlinear optical material [11], lasers, light-emiting diodes, luminescence devices [12-14], Biological Labels, etc. It has been shown that the particle size and distribution play an important role in application [15]. CdS thin films have been prepared by various methods such as sputtering [16], vacuum evaporation [17], spray pyrolysis [18], electrodeposition [19] and chemical bath deposition (CBD) [20]. Among these various techniques, CBD is a simple, low-cost method that provides uniform, adherent and reproducible large area thin films for solar-related technologies. In the present study we report the chemical deposition of CdS nanoparticles and their characterization by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and UV-absorption spectrometry. The objective of our work is to study the effect of molarity on structural properties, the grain size changes and optical properties of the samples.

2. Experimental Method

CdS Nanocrystalline thin films were synthesized in the polymer matrix by an ion exchange reaction. Aqueous solutions of $CdCl_2$ of various molarities are prepared in distilled water and stirred at a rate of 200 rpm at constant temperature 70^0C for 3 hours. Next 4% wt. solution of PVA is prepared under the same rate of stirring and at same temperature. The solutions of $CdCl_2$ and PVA were kept overnight inside a dark chamber at room temperature for complete dissolution to get transparent solution. The matrix solution is obtained by adding the two solutions in equal proportion. Na_2S solution of 0.5M was added to the above matrix solution till the whole solution turns into yellow colour. The CdS nanoparticle containing PVA solution was casted onto the properly cleaned glass substrates and are allowed to dry in a closed chamber at room temperature. The chemical reaction mechanism for the formation of CdS nanoparticle is:

$$CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$$

3. Results And Discussion

3.1.XRD Study

X-Ray Diffraction method is used to study the structural and size formation of the CdS samples. CdS nanocrystalline thin films peapared were found to be mainly in cubic phase. The highest intensity peak (111) plane of CdS with other smaller intensity peaks at (200), and (311) were observed.

3.1.1.Structural Study

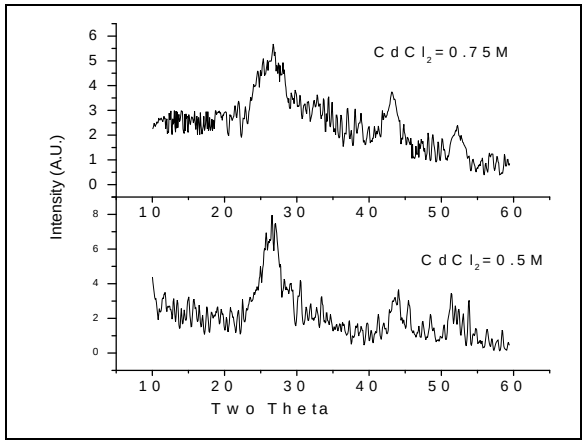

Figure 1: XRD spectra of CdS samples with 0.5M $CdCl_2$ and 0.75M $CdCl_2$

The interplanar spacing (d) and lattice constant (a) for cubic phase structure of CdS samples with different molarities of $CdCl_2$ were determined which is very close to the reported values (a=5.798 A^0, JCPDS 75-2023). The values of lattice constant 'a' and 'd' spacing at different molarities of $CdCl_2$ are given in Table 1.

Sample No.	PVA and $CdCl_2$	hkl	d value (A^0)	2θ (degree)	a_{cal} (A^0)
CdS_1	4Wt% PVA and 0.5M $CdCl_2$ (equal volume)	111	3.3039	26.9544	5.7225
		220	2.0718	43.6357	5.8599
		311	1.7701	51.57	5.87087
CdS_2	4Wt% PVA and 0.75M $CdCl_2$ (equal volume)	111	3.33112	26.73	5.7697
		220	2.09276	43.1767	5.9192
		311	1.74574	52.3447	5.78998

Table1: Values of lattice constant and Interplanar spacing

3.1.2.Grain size studies

With increase of molarities of $CdCl_2$ the broadening of the peaks is observed. The broadening of the peaks can be associated with the decrease in the particle size. The X-ray peaks are found to shift to lower diffraction angle with increasing molarity which indicates lattice contraction. The lattice contraction occurs due to higher surface to volume ratio resulting decrease in cryatallite size. The crystallite sizes of the same sample were also calculated from different peak position corresponding to different planes and they are found to be almost same which indicates that particles are of symmetrical shape. The crystallite size of CdS samples at different molarities of $CdCl_2$ are calculated by using Deby-Scherrer formula [21]

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad \text{.....(1)}$$

Where β is the Full Width Half Maxima (FWHM) in radian, θ is the Bragg's angle, K is a constant taken to be 0.94 and λ is the wavelength of X-Ray used which is $1.54A^0$. The various values of FWHM for different peak positions along with grain sizes of CdS sample with different molarities of $CdCl_2$ are given in Table 2 and Table 3.

Position (2θ)	**FWHM(2θ) in degree**	**FWHM (in Radian) $\beta_{2\theta}$**	**Grain Size (nm)**	**Average grain size (nm)**
26.9544	1.8893	0.0329877	4.512555	6.3045
43.6357	1.2595	0.0219912	7.090504	
51.5700	1.2595	0.0219912	7.31049	

Table 2: Particle Size from Scherer formula of CdS sample with 0.5M $CdCl_2$

Position (2θ)	**FWHM(2θ) in degree**	**FWHM (in Radian) $\beta_{2\theta}$**	**Grain Size (nm)**	**Average grain size (nm)**
26.73	2.7280	0.04763	3.12385	5.3441
43.1767	1.5257	0.02663	5.84419	
52.3447	1.3077	0.02283	7.06422	

Table 3: Particle Size from Scherer formula of CdS sample with 0.75M $CdCl_2$

3.2.TEM Study

TEM photograph of CdS film sample is presented in Figure 2. The TEM photographs clearly indicate the morphology of the particles are nearly spherical and homogeneous. The crystallite sizes are found to be within 12nm. The overlapping of nanoparticles in some areas of TEM image may be due to preparation method for the TEM sample.

Figure 2: TEM photograph of CdS sample in PVA matrix (1cm=37 nm)

3.3.Optical Properties

The optical absorption of prepared CdS nanocrystalline thin films were recorded at room temperature using UV-Absorption Spectrophotometer (HITACHI spectrometer, U-3210). The CdS nanocrystalline thin films prepared in PVA matrix show good optical absorption and sharp increase beyond its band edge wavelength 550 nm. The absorption spectra of CdS/PVA thin films for different molarities of $CdCl_2$ taken at room temperature are shown in Figure 3.1- Figure 3.2. A sharp absorption edge is observed in the visible region, indicating good crystallinity and low defect density near the band edge. From the spectrograph it is clear that, the absorption edges of the samples are found to take place in the range 425-525 nm. The optical absorption edge of the nanoparticles is shifted towards the longer wavelength region with the increase of the molarity of $CdCl_2$.

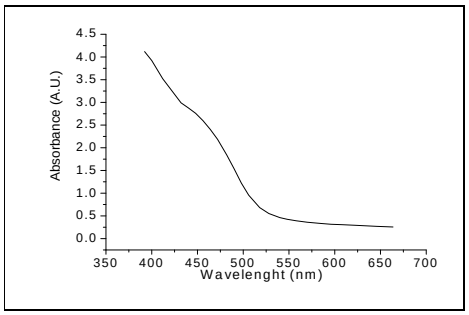

Figure 3.1: UV Absorption spectra of CdS sample with 0.5M $CdCl_2$

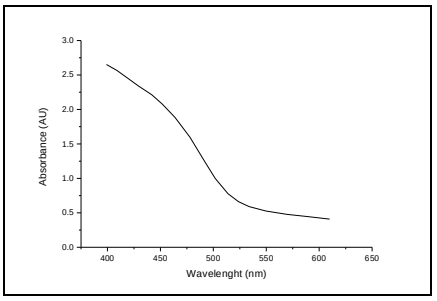

Figure 3.2: UV Absorption spectra of CdS sample with 0.75M $CdCl_2$

CdS is a typical direct band gap semiconductor. According to Tauc relation, the absorption coefficient for direct band material is given by [22]

$$(\alpha h\upsilon)^{1/2} = C(h\upsilon - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where α is absorption co-efficient, hυ is incident photon C is a constant and E_g is the band gap of the material. The extrapolation of linear portion of the graph on hν axis at $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap. The direct band gap values of CdS samples with different molarities of $CdCl_2$ have been obtained from hν vs $(\alpha h\nu)^2$ plot as shown in Figure3.3- Figure 3.4.

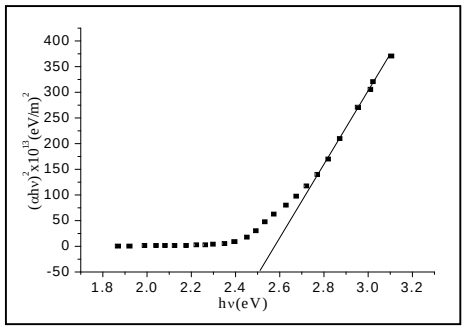

Figure 3.3: Plot to determine direct band direct band gap energy of CdS film with 0.5M $CdCl_2$

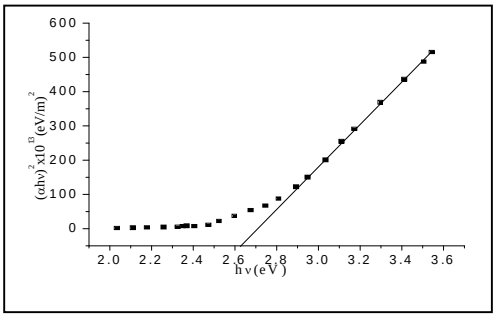

Figure 3.4: Plot to determine gap energy of CdS film with 0.75M $CdCl_2$

Molarity of $CdCl_2$	**Energy Band Gap (eV)**	**Blue Shift (eV)**
0.5M	2.512	0.092
0.75M	2.624	0.204

Table 5.1: Variation of band gap and blue shift of CdS nanocrystalline thin films with molarity of $CdCl_2$

The experimental values of direct band gap are found to be 2.5 eV and 2.55 eV respectively for CdS samples with 0.5M and 0.75M $CdCl_2$ which are larger than the value of bulk material which is 2.42 eV. So, there are Blue shifts of energy of 0.092 eV and 0.204 eV respectively for CdS sample with 0.5M and 0.75M $CdCl_2$. This is attributed to size quantization in nanocrystalline material. The sizes of the nano particles decrease with the increase of molarity. The size quantization occurs due to confinement (localization) of electrons and holes in an extremely small volume of space of the nanocrystalline materials. So, the Band gap increases with the increase of molarity or decrease of crystallite size.

4.Conclusion

CdS films were successfully deposited on suitably cleaned glass substrates by chemical bath deposition method. The structural characterization of the nanomaterial observed by XRD reveals that the films are polysrystalline in cubic structure with preferred orientation in (111) direction. The XRD patterns show the formation of cubic face centered structure of CdS. The phase shift to cubic is an indication of decrease of particle size. The crystallite sizes measured by XRD studies are found to be within 7 nm and from TEM, it is found to be within 12 nm. The TEM photographs clearly indicate the morphology of the particles are nearly spherical and homogeneous. The UV absorption studies on films clearly show an increase in band gap which supports the formation of nanocrystallites in these films. A spectral response study was made to determine the band gap which reveals that there is increase of band gap with the decrease in crystallite size. The overall deposition method clearly shows that higher molarity facilitates the growth of nanocrystallite in CdS films in PVA matrix.

5.Reference

1. Brus, L. (1986). J. Phys. Chem. 90, 2555.
2. Kayanuma, (1988). Phys. Rev. B 38, 9797.
3. Alivisatos, A. P. (1996). Science 271, 933.
4. Henglein, A. (1989). Chem. Rev. 89, 1861.
5. Trindade, T. (2001). Chem. Matter 13, 3843.
6. Woggon, U. (1997). Optical properties of semiconductor quantum dots. Springer-Verlag, Berlin-Heidelberg. New York.
7. Alivisatos, A. P. (1996). J. Phys. Chem. 100, 13226.
8. Kalandaragh, Y. A., Muradov, M. B., et al, (January, 2008). Structural, Compositional and Optical Characterization of Water Soluble CdS Nanoparticles Synthesized by Ultrasonic Irradiation. Optoelectronics and Advanced materials – Rapid Communications. Vol. 2, No. 1. p. 42 – 45.
9. Norris, D. J., Sacra, A., Murray, C.B. & Bawendi, M.G. (1994). Phys. Rev. Lett 72, 2612.
10. Britt, J. & Ferekides, (1993). Appl. Phys. Lett. 62, 2851.
11. Norris, D. J., Sacra, A., et al, (1994). Phys. Rev. Lett 72, 2612.
12. Hyeong, L.J. (2003). Thin Solid Films 431, 344.
13. Dhumure, S.S. & Lokhande, C.D.(1993). Indian J. of Pure & Appl. Phy. 31, 512.
14. Devi, R., Purakayastha, P., Kalita, P.K., Sarma, R., Das, H.L & Sarma, B.K. (2007). Indian J.of Pure & Appl. Phy., 45, 624.
15. Barman, B., Mochahari, P.K. & and Sarma, K.C. (2012). Synthesis of ZnS Nanoparticles in Acidic Media and their Luminescence Properties. International Journal of Networks and Applications. ISSN 0976-5859 Volume 3. Number 1. pp. 1-6 @ International Research Publication House.
16. El-Akkad, F. & Abdel Naby, M. (1989). Sol. Energy Mater. 18, 151.
17. Chamseddine, A. & Fearkeily, M.L. (1994). Thin Solid Films 247, 3.
18. Martinuzzi, S. (1982). Sol. Cells 5, 243.
19. Baranski, A.S., Bennet, M.S., & Fawcett, W.R. (1983). J. Appl. Phys. 54, 6390.
20. Lincot, D., Froment, M. & Cachet, H. In R.C. Alkire & D.M. Kolb (Eds.). Advances in Electrochemical Science and Engineering. Vol. 6, (pp. 165–235). Wiley-VCH, Weinheim.

21. Klug, H.P., & Alexander, L.E. (1954). X-ray diffraction procedures for polycrystalline and amorphous materials. 2nd edition, John Wily and Sons: New York, p491.
22. Tauc, J. (ed.) (1974). Amorphous and liquid semiconductors (New York: Plenum) pp. 159