Synthesis of nanocrystalline CdS thin films in PVA matrix

R DEVI*, P PURKAYASTHA†, P K KALITA† and B K SARMA

Department of Physics, Gauhati University, Guwahati 781 014, India
†Department of Physics, Guwahati College, Guwahati 781 021, India

Abstract. Nanocrystalline thin films of CdS are deposited on glass substrates by chemical bath deposition technique using polyvinyl alcohol (PVA) matrix solution. Crystallite sizes of the nanocrystalline films are determined from broadening of X-ray diffraction lines and are found to vary from 5·4–10·2 nm. The band gap of the nanocrystalline material is determined from the UV spectrograph. The absorption edge is shifted towards the lower wave length side (i.e. blue shift) and are found to be within the range from 2·48–2·8 eV as grain sizes decrease from 10·2–5·4 nm. This is also supported by the spectral response curves. An increase of molarity decreases the grain size which in turn increases the band gap.

Keywords. Chemical method; UV spectra; spectral response; energy band gap.

1. Introduction

Thin films now occupy a prominent place in basic research and solid state technology. The use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. Cadmium sulphide (CdS) is one of the most promising II–VI compound materials because of its wide range of application in various optoelectronic (Iyechika et al 1988; Dhumure and Lokhande 1993; Lee et al 2003), piezo-electronic (Kerk and Kelly 1964; Stefko 1991) and semiconducting devices. The thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cells (Chu et al 1992; Britt and Ferekids 1993). In recent years nanocrystalline thin films of different II–VI compound semiconductors have been widely synthesized and studied. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Many properties of nanocrystalline materials are found to deviate from those of coarse grained polycrystalline materials with the same average chemical composition. These deviations result from dimensionality of nanometer sized grains and numerous interfaces between adjacent crystallites (Tong and Zhu 2006). A major research goal of recent years is to understand the size dependent properties of nanocrystalline materials and as a result considerable amount of work on synthesis and characterization of nanocrystalline thin films are being carried out (Nandakumar et al 1997; Breen et al 1998; Behera et al 2000; He et al 2003).

Out of several methods for deposition of nanocrystalline thin films, chemical bath deposition technique in polymer matrix is relatively simple, cost effective and suitable for deposition of film on large area substrate. In the present communication, results of preparation and characterization of nanocrystalline thin films of CdS within the self organized pores of PVA via a CBD process are reported.

2. Experimental

Nanocrystalline thin films were deposited on glass substrates by CBD technique. The deposition was carried out in a mixture of matrix solution and thiourea. The matrix solution was prepared by adding cadmium sulphate to an aqueous solution (2%) of PVA with constant stirring at a constant temperature (70°C) maintained for 90 min. Five different concentrations of cadmium sulphate (0·1 M, 0·25 M, 0·5 M, 0·75 M and 1 M) were used to get five different matrix solutions. The solution was then left for 24 h to get a transparent liquid indicating complete dissolution of cadmium sulphate. The pH of the solution was maintained at around 11 by slowly adding NH_4OH solution. Then the equimolar solution of thiourea was added to the mixture solution and glass substrates were introduced vertically into the solution with the help of a substrate holder. Within a few minutes colour of the solution changed to yellow. The substrates were kept in the solution for 18–24 h at room temperature for deposition of films. After deposition, the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air. Grain sizes of the films were then measured by X-ray diffractometer (Philips X-pert Pro diffractometer (PW 1830)) at room temperature with CuKα radiation. Surface morpho-

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*Author for correspondence (kuhkhal@yahoo.com)

logical study of the CdS thin films were done using scanning electron microscope (SEM) operating with an accelerating voltage of 20 kV. Grain sizes of the films were determined from SEM photographs at different magnifications. IR spectra were recorded using Perkin-Elmer instrument series II (2400-CHNS/0). Samples were prepared by mixing the dried CdS nanoparticles with KBr and pressing them into pellets. Optical absorption spectra at 300 K were obtained using a UV visible spectrophotometer (VARIAN CARY 300 scan) in the wavelength range 300–700 nm. For spectral response studies, the current measurement was done with the help of a high impedance ($\sim 10^{14}\ \Omega$) ECIL (electrometer amplifier (EA815)). A series of highly stable dry cells each of emf 9 V was used for providing the applied bias. A tungsten halogen lamp with a parabolic focusing mirror was used as the light source. A set of metal interference filters was used to get the monochromatic radiations of different wavelengths. The intensity of illumination is measured with a sensitive APLAB luxmeter.

3. Results and discussion

All the measurements were done at room temperature for the films with different molarity deposited by chemical route. The thickness of the films were 1500–1800 Å, measured by the multiple beam interferometry method.

3.1 *XRD studies*

The X-ray diffractogram of CdS films show broadened diffraction profiles (figure 1). It is observed that XRD patterns show a preferred orientation along (002) plane. The crystallite size of the nanocrystalline films is estimated using the Scherrer formula

$$D = K\lambda/\beta_{2\theta}\cos\theta, \tag{1}$$

where K is a constant taken to be 0·94, λ the wavelength of X-ray used (λ = 1·54 Å) and $\beta_{2\theta}$ the full width at half maximum of (002) peak of XRD pattern, Bragg angle, 2θ, is around 26·5°. The values of crystallite sizes of the films are shown in table 1. The crystallite sizes were found to be within the range 5·4–10·2 nm. It is observed that crystallite size decreases with increase in molarity.

3.2 *SEM analysis*

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 2 shows the surface morphology of CdS thin films deposited at room temperature for five different molarities observed by SEM. From the micrographs, it is observed that the 'as-deposited' films are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. From the figure, we clearly
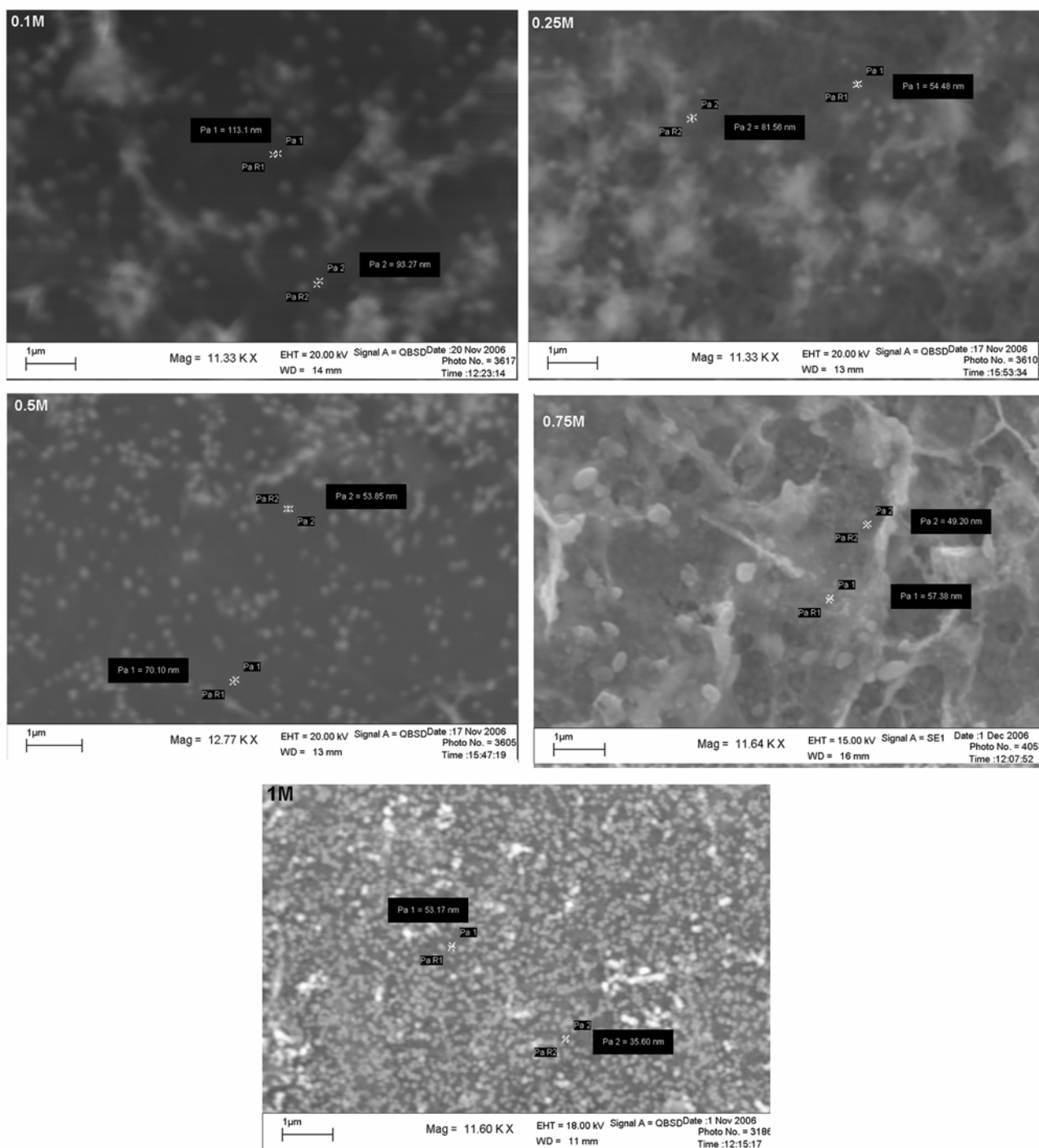
observe the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films. From these images, it can be seen that the grain sizes of the films are not uniform. Therefore, average grain sizes were estimated from different grains within the film and found to be about 44·4–103·2 nm. The values of grain sizes measured from SEM pictures are presented in table 1. It is quite clear from the results that the average grain
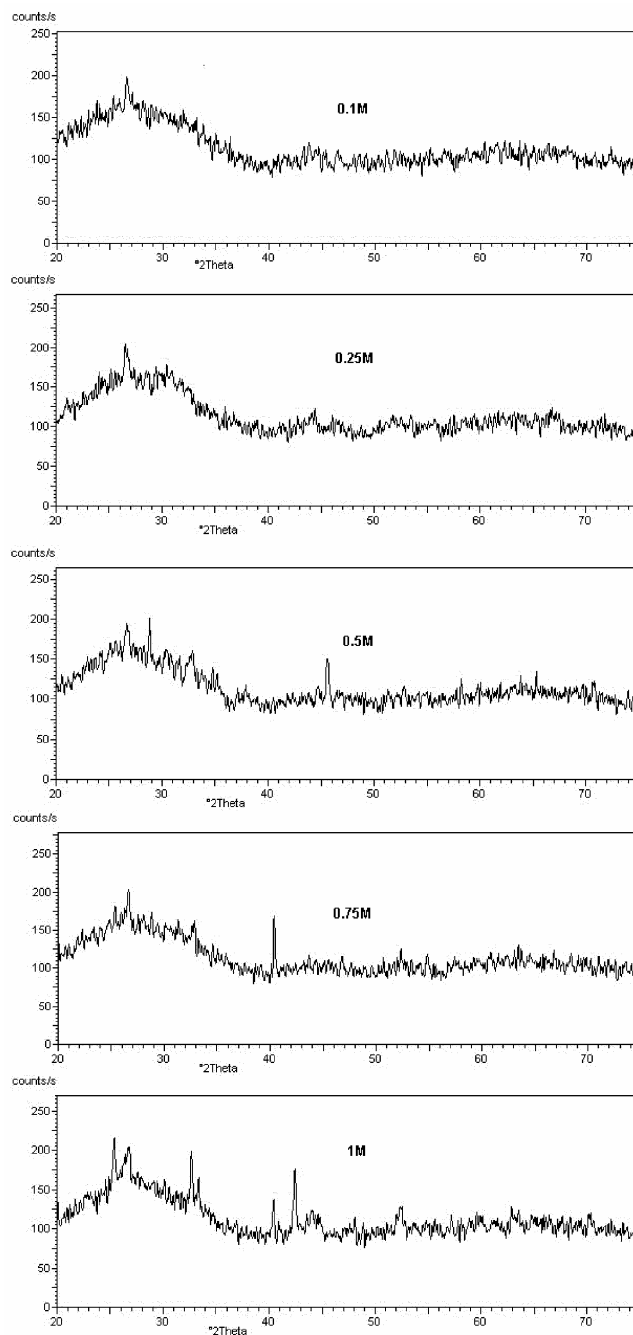
Figure 1. XRD patterns of CdS nanocrystalline films for different molarities.

Table 1. The values of crystallite sizes and band gaps for CdS nanocrystalline films having different molarities.

Film no.	Molarity	Grain size (nm) from XRD	Grain size (nm) from SEM	Band gap (eV) from UV	Band gap (eV) from spectral response
1	0·1 M	10·2	103·2	2·48	2·53
2	0·25 M	8·2	68	2·52	2·61
3	0·5 M	7·0	61·9	2·6	2·66
4	0·75 M	5·8	53·3	2·7	2·75
5	1 M	5·4	44·4	2·8	2·89

Figure 2. SEM photographs of CdS nanocrystalline films for different molarities at almost equal magnifications.
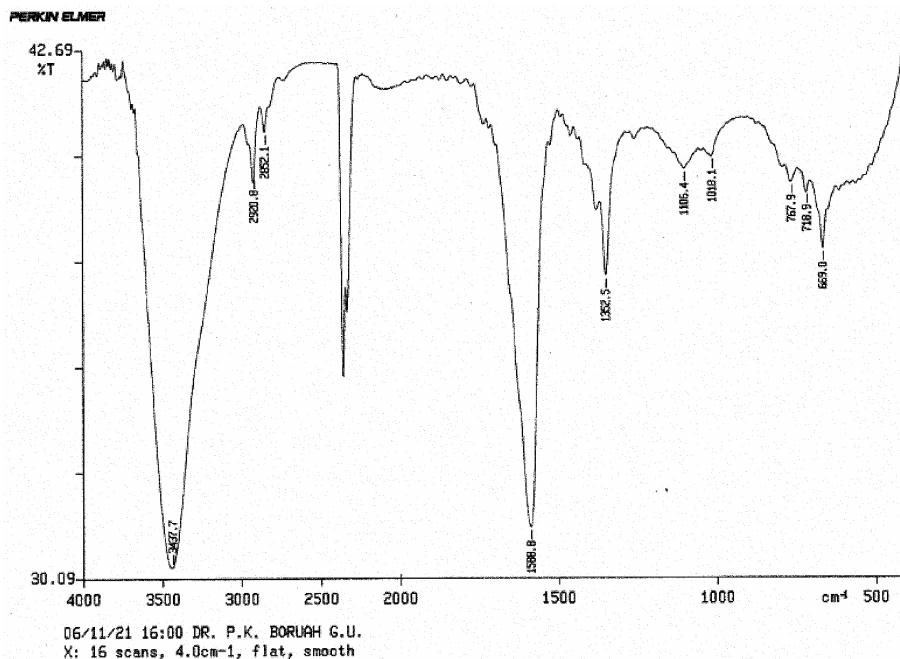
Figure 3. IR spectra of CdS nanoparticles for 0·5 M molarity.

Table 2. Vibrational assignments of CdS nanomaterials with positions and intensities of absorption shown by IR spectra for a typical film (0·5 M).

Positions (cm^{-1})	Intensities	Assignments
3437·7	Strong	OH stretching, ν_1 ν_3 H$_2$O
2920·8 2852·1	Doublet	C–H stretching
1588·8	Strong	C–C stretching
1352·5	Medium	C–O stretching, ν_2 H$_2$O
1106·4 1018·1	Weak	SO$_4^-$ as trace
669·0 718·9	Medium	Cd–S stretching

size estimated by SEM is quite larger than the average grain size measured by XRD.

3.3 *IR spectra*

IR spectra of CdS nanoparticles for different molarities were similar, hence one graph of a typical deposition (0·5 M) is presented in figure 3. The IR frequencies along with the vibrational assignments for CdS nanoparticles are given in table 2. The band at 3437·7 cm^{-1} are due to OH stretching vibrations of water molecules. The bending vibrations of water molecules appeared at 1588·8 cm^{-1}, C–C stretching, and a COO-unsymmetrical stretching at 1352·5 cm^{-1} appeared, which were induced by the trace
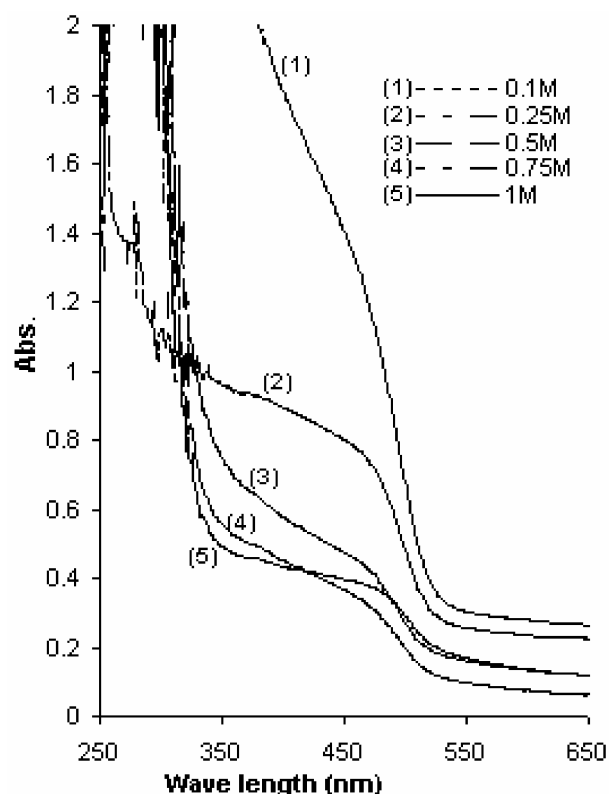

Figure 4. UV-absorption spectra of CdS nanocrystalline films for different molarities.

amount of PVA present as impurities bound to the CdS core. CdS particles showed two stretching bands, asymmetric and symmetric, at 2920·8 cm^{-1} and 2852·1 cm^{-1}, associating with C–H stretching (Tang *et al* 2005). Trace
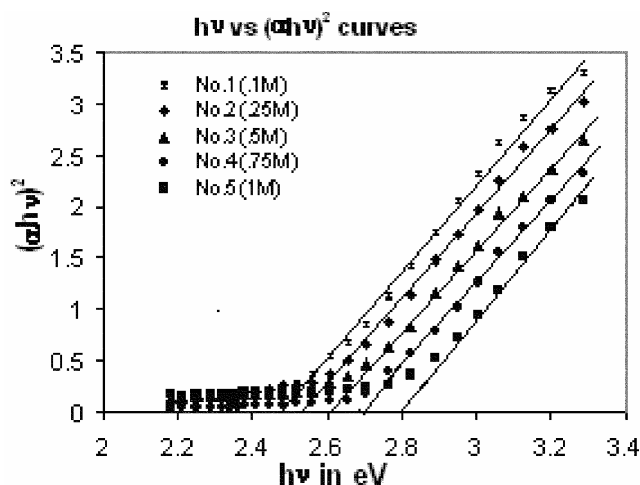
amount of SO_4 as impurity is seen as there are small absorptions around 1105 cm^{-1}. Absorptions at 1106·4 cm^{-1} and 1018·1 cm^{-1} were assigned to SO_4^- (Williams and Fleming 2004). At 669·0 cm^{-1} and 718·9 cm^{-1}, there are medium to strong bands which have been assigned to Cd–S stretching (Periasamy *et al* 1997). The vibration absorption peak of the Cd–S band, which should be at 405 cm^{-1} and 265 cm^{-1}, as reported by other workers (Martin *et al* 1982; He *et al* 2003) could not be observed since it was beyond the extent of our measurement.

3.4 *Absorption studies*

The UV absorption spectra of CdS/PVA thin films for different molarities taken at room temperature are shown in figure 4. From the spectrograph the absorption edge of the samples are found to occur in the range 350–450 nm for nanocrystalline films. Absorption spectrum shows a clear shift to the lower wavelength side over bulk crystallites at ~ 515 nm. This blue shift of the absorption edge indicates decrease of the crystallite sizes of the samples. CdS is a typical direct band gap semiconductor. According to Tauc relation, the absorption coefficient for direct band material is given by (Tauc 1974; Sharma *et al* 1992)

$$\alpha = c(h\nu - E_g)^{1/2}/h\nu, \tag{2}$$

where α is the absorption coefficient, c a constant, $h\nu$ the photon energy and E_g the band gap. The spectrographs were studied using the standard relation (2). A graph between $h\nu$ vs $(\alpha h\nu)^2$ is plotted and shown in figure 5. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of film materials. The band gap of the films are determined from the plots which are found to be within 2·5–2·8 eV. The band gap increases with the decrease of crystallite size. This observation of increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation (Brus 1986).

3.5 *Study of spectral response (optical band edge)*

By investigating the spectral response properties of thin film semiconductor for light of energy greater than the forbidden energy gap, it is possible to obtain information on its band structure (Kisiel *et al* 1976). Photoconductive materials generally exhibit spectral distribution curve having more or less sharp peaks in the vicinity of the absorption edge. The variation of photocurrent due to monochromatic radiation is observed at different applied biases in the chemically deposited CdS thin films and a typical curve at applied bias, 27 V, for different molarity is shown in figure 6. Here the photocurrent density is defined as

$$J_{ph} = J_L - J_D, \tag{3}$$

where J_L is the current density due to monochromatic radiation and J_D the corresponding dark current density. During the measurements, a constant photon flux density for each selected wavelength is used by keeping the intensity fixed at 100 lx (normalized intensity). From the plots of photocurrent vs wavelength of monochromatic radiation ($\lambda = 350$–600 nm) shown in figure 6, it is observed that there is a maximum absorption peak at 425–491 nm. The band gaps were determined from the absorption peak. From this absorption edge the corresponding band gap is found to be 2·89–2·53 eV. For different molarities the amount of absorption is different. The band gap increases with the increase in molarity. It is to be noted that the difference of band gap determined by UV absorption spectra and spectral response studies reduces significantly along

Figure 5. Energy band gap determination of CdS films for different molarities from the $h\nu$ vs $(\alpha h\nu)^2$ graph.
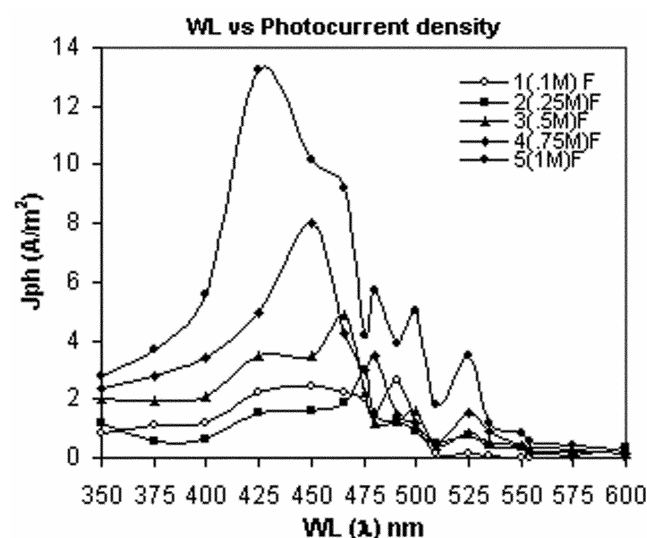
Figure 6. Photocurrent density (J_{ph}) vs wavelength (λ) plots for CdS films. (Intensity of light normalized at 100 lux.)

higher molarity. The additional absorption peaks along longer wavelength side is attributed to defects in the films.

4. Conclusions

Thin films of CdS prepared by CBD technique in PVA matrix are found to be nanocrystalline. The crystallite sizes measured by XRD studies are found to be within 5·4–10·2 nm, and from SEM, are within 44·4–103·2 nm. 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 also made to determine the band gap which also reveals similar facts of increase of band gap with the decrease in crystallite size. The overall deposition technique clearly observed that higher molarity facilitates the growth of nanocrystallite in CdS films in PVA matrix.

Acknowledgement

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