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Synthesis and Physical Properties of nanocrystalline CdS Thin Films – Influence of sol Aging Time & Annealing Temperature

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Abstract: Nanocrystalline Cadmium Sulphide (CdS) thin films have been deposited onto the microscopic glass substrates by sol-gel spin coating method using cadmium nitrate and thiourea as precursor solutions. The influence of sol aging time and annealing temperature on the structural, surface morphological and optical properties were studied by X-Ray Diffraction method (XRD), Field Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive X-ray Analysis (EDAX), Photoluminescence (PL) study and UV-Visible spectroscopy. The XRD study reveals that CdS films have crystalline hexagonal structure with dominant (0 0 2) orientation and that the crystallite size increases with increase in annealing temperature. The aging time of the starting solutions was also found to have an evident effect on the crystallite sizes. FESEM studies reveal that the grains are spherically shaped and distributed uniformly over the entire surface of the substrate. The elemental compositions of the films were observed by EDAX spectrum. The UV-Visible spectral analysis showed that the calculated direct band gap values were found to decrease with increase in annealing temperature. These results suggest that the appropriate aging of CdS sol is an important parameter for the improvement of structural quality of CdS thin films derived by sol – gel method and it could be a good potential candidate for optoelectronic devices.

Keywords: CdS Thin Films, Sol - Gel, Spin Coating Technique, XRD, FESEM, EDAX, UV-Visible, PL.

1. Introduction

In recent years extensive research has gone into the area of preparation and characterization of CdS thin films owing to its promising applications in the field of photovoltaic devices. CdS thin film is a direct semiconducting material with a fundamental band gap of 2.42 eV [1] and has been used as a window material in heterojunction solar cells together with several narrow band gap semiconductors like Cu_2S, InP, $CuInSe_2$, CdTe *etc*., [2, 3].

The CdS thin films have been prepared by various methods, including vacuum evaporation [4], spray pyrolysis [5], sputtering [6], electro deposition [7], molecular beam epitaxy [8], photochemical deposition [9], metal organic chemical vapour deposition [10], chemical bath deposition [11], screen printing [12] and sol- gel spin coating method [13]. Among these techniques, the sol – gel method gives higher specific surface area, superior homogeneity and purity, better micro structural control of metallic particles, narrow pore size and uniform particle distribution compared with those prepared by traditional methods. The main advantage of the sol – gel method is its simplicity, low cost and its ability to obtain uniform films with good adherence and reproducibility in a relatively shorter processing time at lower temperatures [14].

It is well known that that the sol – gel method is a wet chemical technique; the properties of the sol have important effect on the physical properties of CdS thin films. The present paper discusses the effect of sol aging time and annealing temperature

on structural, surface morphological and optical properties of nanocrystalline CdS thin films coated by sol-gel spin coating method.

2. Experimental Procedure

The sol – gel spin coating method is basically a chemical deposition technique where the desired material is spread onto the substrates by spin coating. Prior to deposition the substrates were washed with soap solution, acetone and then heated in chromic acid and kept in distilled water. Finally the substrates were ultrasonically cleaned for 30 minutes. After deposition, annealing of the samples was carried out for the removal of solvent and residual organics. The spin coating method was used to prepare CdS thin films on the glass substrates using cadmium nitrate and thiourea as precursor solutions. The flowchart to prepare CdS thin films was shown in figure 1.

In the process of aging, some properties of the sol will change. Annealing temperature is one of the parameters, which may influence the stiochiometry and structural properties of the films. Therefore, to study the effect of sol aging time and annealing temperature on the CdS films is important.

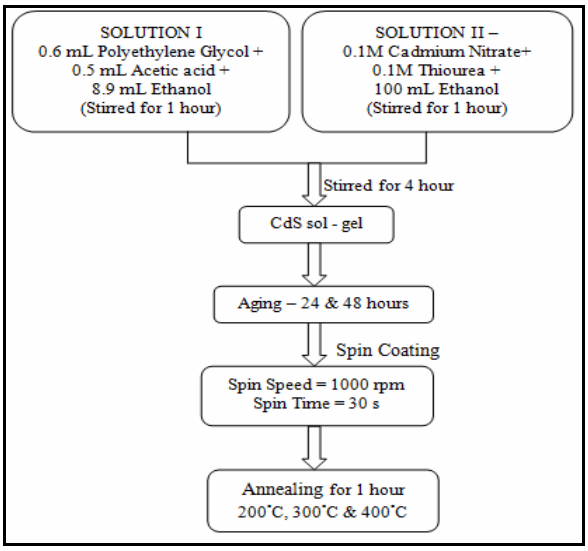


Figure 1: Flowchart for the preparation of CdS thin films

For the obtained CdS thin films X-ray Diffraction (XRD) patterns were obtained with X'Pert Pro X – ray diffractometer, using CuKα_1 radiation. The surface morphological study and the elemental analysis were carried by Quanta SEG - 200 FESEM and Bruker EDAX respectively. The Photoluminescence (PL) study was carried out with a xenon lamp as light source using Schimadzu RF-5301 luminescence spectrophotometer. Optical transmission spectra were recorded in the range of 200 – 800 nm using Schimadzu 1800 UV – VIS – NIR spectrophotometer.

3. Results and Discussion

3.1 XRD analysis

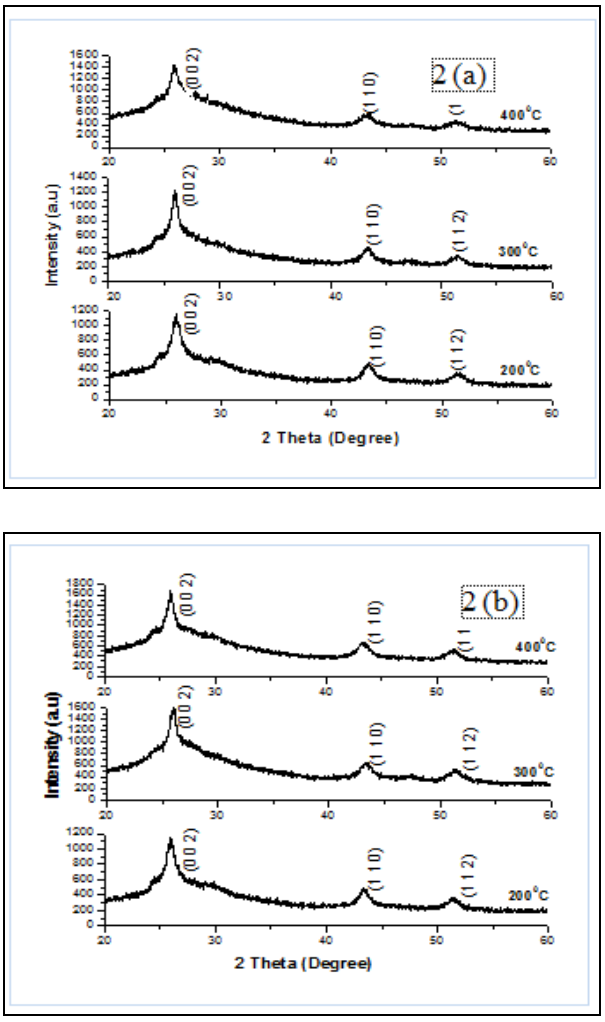


Figure 2: XRD patterns of CdS thin films with sol aging of (a) 24 hour and (b) 48 hour

The comparative XRD patterns of CdS films grown by spin coating method on glass substrates after 24 hour and 48 hour sol aging time were shown in figure 2(a) and (b) respectively for different annealing temperatures such as 200°C, 300°C and 400°C.

From the XRD pattern, it is observed that the CdS thin films have a preferred orientation along (0 0 2) plane with hexagonal phase structure. The observed XRD pattern is in good agreement with standard data JCPDS File No: 06 – 0314 and reported literature [15]. The crystallite sizes (D) of the films are estimated using the Debye-Scherrer formula [16]:

$$D = \frac{0.9\,\lambda}{\beta \mathrm{Cos}\theta}\ (\mathrm{nm}) \qquad (1)$$

where D is the average crystallite size, λ is the X – ray wavelength (CuKα_1 = 1.54060 Å), β is the full width at half maximum (FWHM) of the dominant peak and θ is the Bragg angle. It is found that the crystallite size of 24 hour and 48 hour sol aged films vary as 7.8 nm, 9.6 nm & 14.2nm and 11.4nm, 15.5nm & 21.8nm for the annealing temperatures 200°C, 300°C, 400°C respectively. Thus the aging time of the starting solutions was found to have an evident effect on the crystallite sizes. Also the crystallite size was found to increase with increase in annealing temperature. Similar results have been shown by earlier literature Bilgin *et al*., [17]. It is well known that the ultrafine particles in the semiconductor films lead to the unusual properties arising from the quantum confinement effect and high surface area. The dislocation density δ, which represents the amount of defects in the film, was determined from the formula [17],

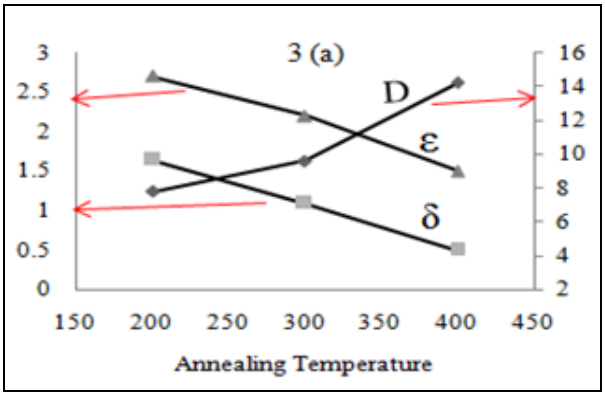
$$\delta = \frac{1}{D^2}\ \mathrm{lines/m^2} \qquad (2)$$

As the annealing temperature increases the dislocation density (δ) decreases which may lead to reduction in the concentration of lattice imperfections.

The strain (ε) of the spin deposited CdS thin films was evaluated according to the relation [18].

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (3)$$

The calculated crystallite size, dislocation density and strain values have been summarized in table 1. Figure 3 (a) and (b) show the effect of annealing temperature on the crystallite size, dislocation density and the strain for 24 hour and 48 hour sol aged CdS thin films respectively. At a higher annealing temperature the crystallite size of the CdS thin film was bigger whereas the dislocation density and the strain values were small.



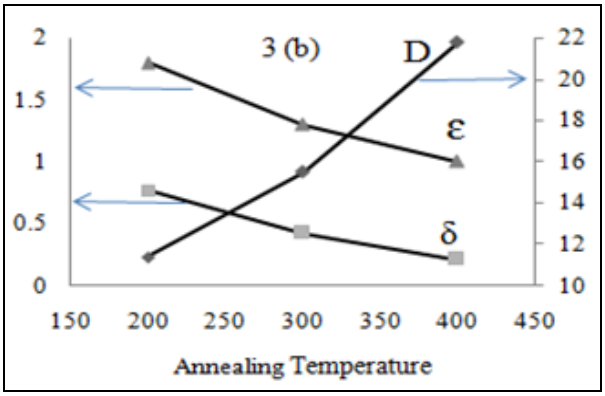


Figure 3: Variation of crystallite size (D), dislocation density (δ) and strain (ε) for (a) 24 hour and (b) 48 hour sol aged CdS thin films

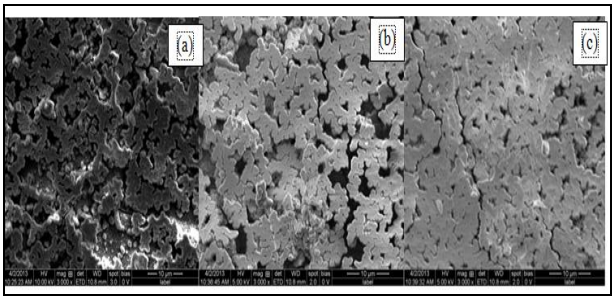
Table 1: A summary of the x – ray diffraction data of the CdS thin films

		24 hour Aging Time			48 hour Aging Time		
		200 °C	300 °C	400 °C	200 °C	300 °C	400 °C
	Miller Indices						
2 Theta	(0 0 2)	25.90	25.95	25.97	25.88	25.91	25.91
(Degree)	(1 1 0)	42.85	43.24	43.12	43.14	43.07	43.14
	(1 1 2)	51.04	51.37	51.88	51.16	51.06	51.13
Crystallite Size D (nm)		7.8	9.6	14.2	11.4	15.5	21.8
Dislocation Density δ ($x10^{16}$) (lines/m^2)		1.64	1.09	0.50	0.77	0.42	0.21
Strain ε ($x10^{-4}$)		2.66	2.17	1.46	1.83	1.34	0.95

3.2 Surface Morphology with Elemental Analysis

The surface morphology of spin-deposited CdS thin films was investigated using FESEM technique. FESEM has been proved to be a unique, convenient and versatile method to analyze surface morphology of thin film and to determine the grain size. Figure 4 (a - c) and (d - f) shows the FESEM image of CdS thin films with sol aged at 24 hour and 48 hour respectively. From FESEM image 4 (a – c), it is observed that the deposited CdS film is uniform, without cracks with dense surface morphology covering entire substrate surface area.

The FESEM image of 48 hour aged sol film show small nano sized perfect spherical grains with uniform grain boundaries. It can be easily understood that the shape and arrangement of the grains are highly influenced by the growth mechanism.



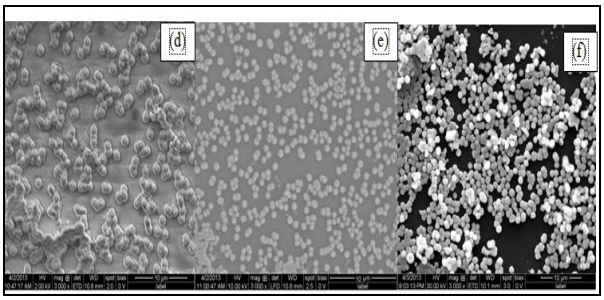
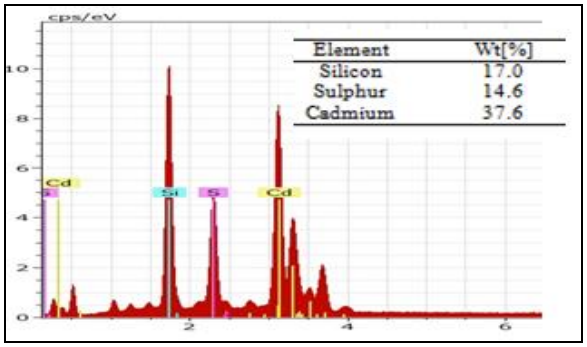


Figure 4: FESEM image of CdS thin films



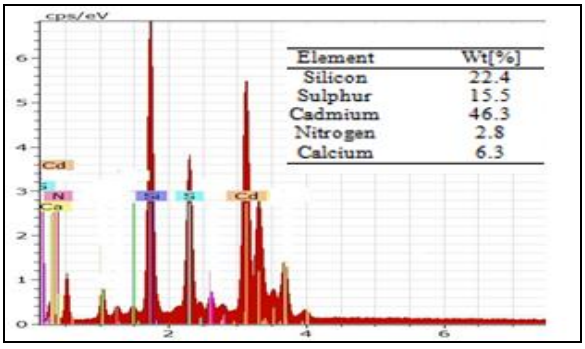
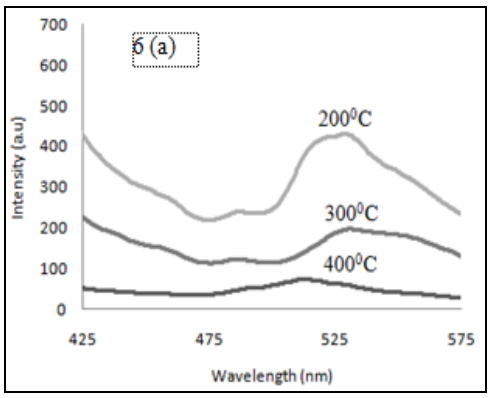


Figure 5: EDAX spectra of CdS thin films

To study the stoichiometry of the spin deposited CdS thin film, quantitative analysis of the film was carried out by using the EDAX technique. The spectra reveal that the films deposited using sol – gel technique contains the Cd and S as expected and the corresponding spectra is shown in figure 5.

3.3 Photoluminescence Analysis

PL spectra have been recorded at room temperature with an excitation wavelength of 380 nm. PL spectra of the CdS film samples are shown in figure 6 (a) & (b). Each PL spectrum is characterized by two emission weak bands. A blue band emission with a peak centered at around 488 nm, which can be attributed to excitonic transitions. Typically, in semiconductors like CdS, excitonic peak appears at energies lower (wavelengths larger than 500 nm) than the band gap energy. A possible explanation for the band at 488 nm is that it is related to the confinement effects and the direct inversion of the fundamental absorption edge for the nanometric dimensions of the crystallite [19].



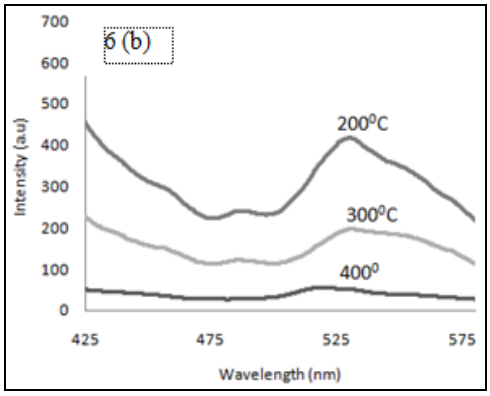
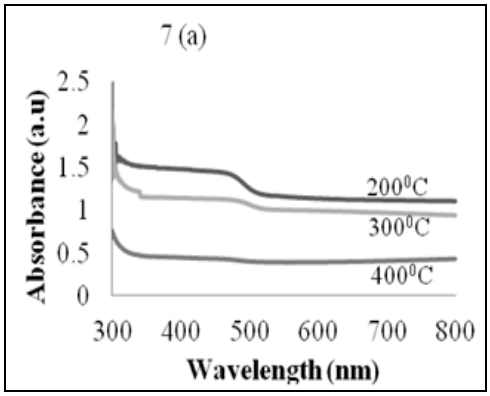


Figure 6: PL spectra of CdS thin films aged at (a) 24 hour and (b) 48 hour

at around 526 nm, originated from radiative recombination [20], which was related to the grain size distribution. As the size of the grains was decreased, the ratio of surface to volume of the grain was increased and thus led to enhancement of the green band intensity. It should be noted that there is a decrease in the intensity of the PL peak with increase in annealing temperature. The bigger the crystalline, the smaller the number of surface states induced is, and so defects are lower.

3.4 Optical Analysis

Optical absorption spectra of 24 hour and 48 hour aged sol CdS thin films are shown in figure 7 (a) and (b). It is well known that the absorption edge is related to the size of the nanoparticles. It is seen from the optical spectra the absorption edge shifts on annealing towards the higher wavelength side indicating the increases in crystallite size and hence reduction in the band gap values. This matches well with the XRD study.



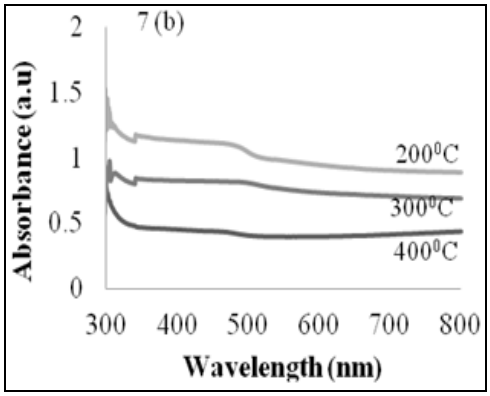


Figure 7: Optical absorbance of CdS thin films aged at (a) 24 hour and (b) 48 hour

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the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. CdS is a direct band gap material and for a direct allowed transition, the absorption coefficient is given by [5],

$$\alpha h\nu = k(h\nu - E_g)^m \quad (4)$$

where k is a constant related to the effective masses associated with the bands and m = 1/2 for direct transition, α the absorption coefficient, hν the incident photon energy and E_g the optical band gap. The optical band gap is obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus hν to α = 0. Figure 8(a) and (b) shows the $(\alpha h\nu)^2$ versus hν plot for the 24 hour and 48 hour sol aged CdS thin films respectively for three different annealing temperatures.

Table 2: Optical band gap of 24 hour and 48 hour sol aged CdS thin films

Annealing Temperature	Optical Band gap (eV)	
	24 hour aging Time	48 hour aging Time
200°C	3.4	3.1
300°C	3.0	2.7
400°C	2.6	2.5

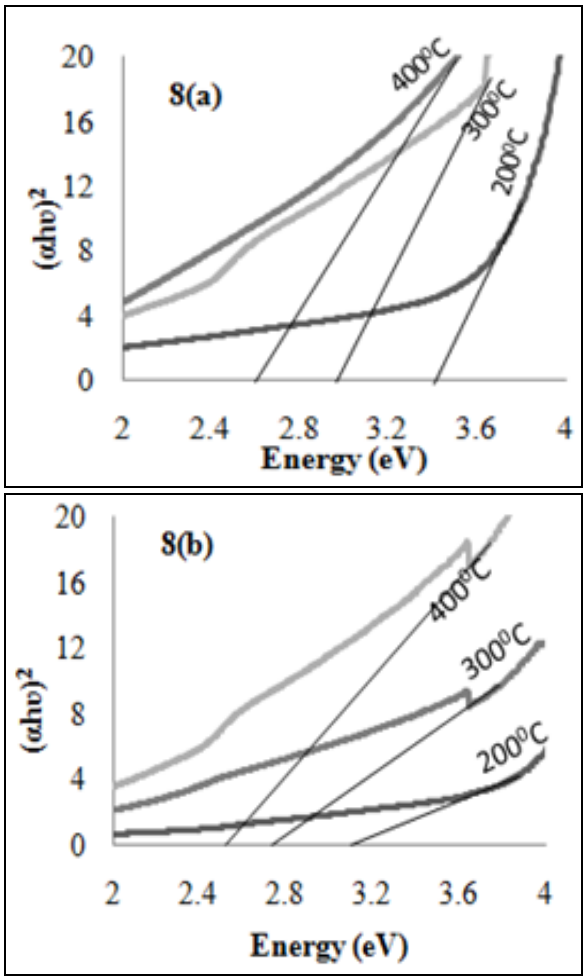


Figure 8: Optical band gap of CdS thin films at aging time of (a) 24 hour, (b) 48 hour

The optical band gap values calculated using the absorption spectra is greater than that of the bulk CdS (2.42 eV) and it was shown in table 2. On annealing, the size of the crystallite increases resulting in a decrease of the band gap. The change in band gap with temperature is attributed to the quantum size effects [21].The size of the particles can also be estimated from the band gap values, using the Brus equation [22],

$$E_{th} = E_g + \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{\varepsilon R} \quad (5)$$

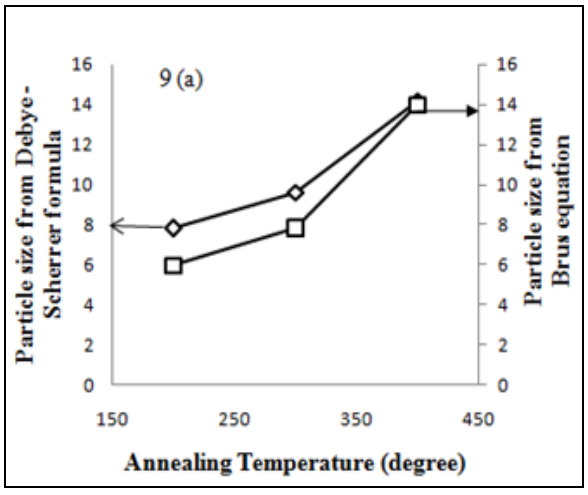
where E_{th} is the band gap of the CdS thin film, E_g is the band gap of bulk CdS (2.42 eV), h is the Planck's constant, m_e* is the effective mass of electron (0.9 m_e), m_h* is the effective mass of hole

($0.8\ m_e$), ε is the dielectric constant and R is the radius of the grains. The second term of equation (5) represents the kinetic energy of the confined exciton and the third term indicates the coulomb interaction of the electron with the hole. Here the coulomb interaction is negligible.

The particle size values obtained using the optical band gap caused by quantum confinement are shown in table 3. The variations in particle size with Debye-Scherrer formula & Brus equation for 24 hour and 48 hour sol aging time with annealing temperature are shown in figure 9 (a) and (b) respectively.

Table 3: Particle size values of 24 hour and 48 hour sol aged CdS thin films

Annealing Temperature	Particle size from Band gap (eV)	
	24 hour aging Time	48 hour aging Time
200°C	6.0	7.2
300°C	7.8	11.2
400°C	14.0	20.9



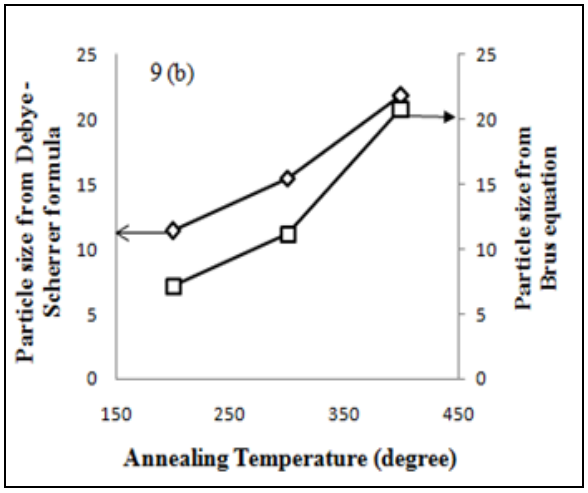


Figure 9: Variation in particle size with annealing temperature at sol aging time of (a) 24 hour, (b) 48 hour

The wide band gap and the high optical transparency in the visible range observed for the deposited CdS films make them possible window layers in solar cells.

4. Conclusion

CdS thin films have been successfully prepared by sol – gel spin coating method and the effect of sol aging time and annealing temperatures on the structural, optical and surface morphological properties were studied. All of the CdS films have crystalline in nature and showed a preferential orientation along (0 0 2) with hexagonal phase structure. Crystallinity levels became better at higher annealing temperature. FESEM image revealed that the grains are spherically shaped and distributed uniformly over the entire surface of the substrate. The photoluminescence spectra show that the intensity of PL emission peaks found to decrease in intensity, with increase in annealing temperature. Using the optical investigations, it was determined that the 24 hour sol aged CdS films having larger band gap than the 48 hour sol aged films. On annealing, the size of the crystallite increases resulting in a decrease of the band gap. These results suggest that the method of spin coating technique for the deposition of CdS thin films with the effect of sol aging time and annealing

temperature should be further investigated for applications towards the optoelectronic devices especially solar cells.

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