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OPTICAL AND STRUCTURAL PROPERTIES OF SPIN COATED CADMIUM SULFIDE THIN FILMS

D.M.C.U. DISSANAYAKE AND P. SAMARASEKARA *

Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka.

ABSTRACT

Thin films of cadmium sulfide have been synthesized using the spin coating technique. Films were fabricated on inexpensive amorphous glass substrates at spin speeds of 1500, 2200 and 2400 rpm for 30 seconds. Films were subsequently annealed at 200, 300 and 400 ^{0}C for one hour in air in order to crystallize the phase of CdS. Films were characterized using X-ray diffraction patterns (XRD) and UV-visible spectroscopy. According to XRD patterns, the phase of CdS was crystallized without any secondary phases. The particle size, dislocation density and strain were also estimated using XRD patterns. All the films indicate a strong orientation in (002) direction. The optical band gap was determined using UV absorption spectroscopy. Tauc model was employed to determine the optical band gap. According to our data, the optical band gap decreases with the particle size.

Keywords: CdS, XRD, optical band gap, particle size, Tauc model

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INTRODUCTION

CdS is one of the most important II-VI group semiconductors with a direct band gap of 2.42 eV. CdS thin films belong to the Chalcogenide family and there is an extensive research work carried out with CdS mainly due to its potential applications in solar cells, especially as a window material for CdS/CdTe solar cells because of its suitable band gap and stability (Olopade *et al.,* 2013). Also, CdS thin film is one of the important materials for applications in light emitting diodes, sensors, photoconductors, optical mass memories

* Corresponding author Email: pubudus@pdn.ac.lk

and solar selective coatings (Olopade *et al.,* 2013). Nanostructures have attracted a great interest in recent years because of their unique chemical, physical, optical, electrical and transport properties which are different from those of either the bulk materials or single atoms. Due to the vast surface area, all nanostructured materials possess a high surface energy and thus, are thermodynamically unstable or metastable. CdS nanoparticles are considered as a capable applicant for their applications in future opto-electronic devices, nanodevices and biological labeling due to availability of discrete energy levels, tunable band gap, size dependent chemical and physical properties, better chemical stability and easy preparation techniques.

There are many methods of fabricating CdS thin films. These include spray pyrolysis (Yadav *et al.,* 2010), chemical bath deposition (Lisco *et al.,* 2015), electro deposition (Takahashi *et al.,* 2002), screen printing (Kumar *et al.,* 2011), physical vapor deposition and sol-gel spin coating. Among various deposition methods, sol-gel spin coating technique is extensively studied as a matrix material method to produce nanocomposites because it gives a higher specific surface area, superior homogeneity and purity, better microstructural control of metallic particles, narrow pore size and uniform particle distribution. The main advantages of the sol-gel method are 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.

In addition to optical and electrical properties, magnetic properties of films are also important. CdS possesses some magnetic properties (Rasu *et al.,* 2006). The Heisenberg Hamiltonian was used to describe the magnetic properties of ferromagnetic and ferrite films by us previously (Samarasekara, 2006, Samarasekara, 2006, Samarasekara & Silva, 2007). Thin films of Lithium mixed ferrite (Samarasekara, 2002), multi walled carbon nanotubes (Samarasekara, 2009), Cu_2O/CuO layers (Samarasekara, 2010), Nickel ferrite (Samarasekara, 2003) and copper oxide (Samarasekara & Yapa, 2008) have been fabricated. Previously electrical properties of semiconductor particles doped with salts have been investigated by us (Tennakone *et al.,* 1987). In this manuscript, the optical and structural properties of CdS films containing nano-particles will be described.

EXPERIMENTAL

For the deposition of CdS thin films two solutions have been prepared. Polyethylene Glycol (PEG) was dissolved in ethanol (CH_3CH_2OH), and acetic acid

(CH_3COOH) was added to ethanoic solution under stirring which was continued for 1 hour (Solution 1). Cadmium nitrate ($Cd(NO_3)_2$) and thiourea ($CS[NH_2]_2$) were dissolved in ethanol under stirring which was continued for 1 hour (Solution 2). Solution 2 was mixed with Solution 1 and stirred again for 4 hours to obtain the final sols for deposition of thin films. CdS thin films were deposited on ultrasonically cleaned glass substrates by sol-gel spin-coating technique. Solution was dropped onto the glass substrates at speeds of 1500, 2200 and 2400 rpm for 30 seconds. After deposition, the glass substrates were dried on hot plate at 120 ^{0}C for 1 hour and then annealed at temperatures of 200 ^{0}C, 300 ^{0}C, and 400 ^{0}C in air for one hour.

Structural properties of film samples were determined using X ray diffraction (XRD) with Cu-K_α radiation of wavelength 1.54060 Å. UV-visible spectrometer was employed to investigate optical properties of samples.

RESULTS AND DISCUSSION

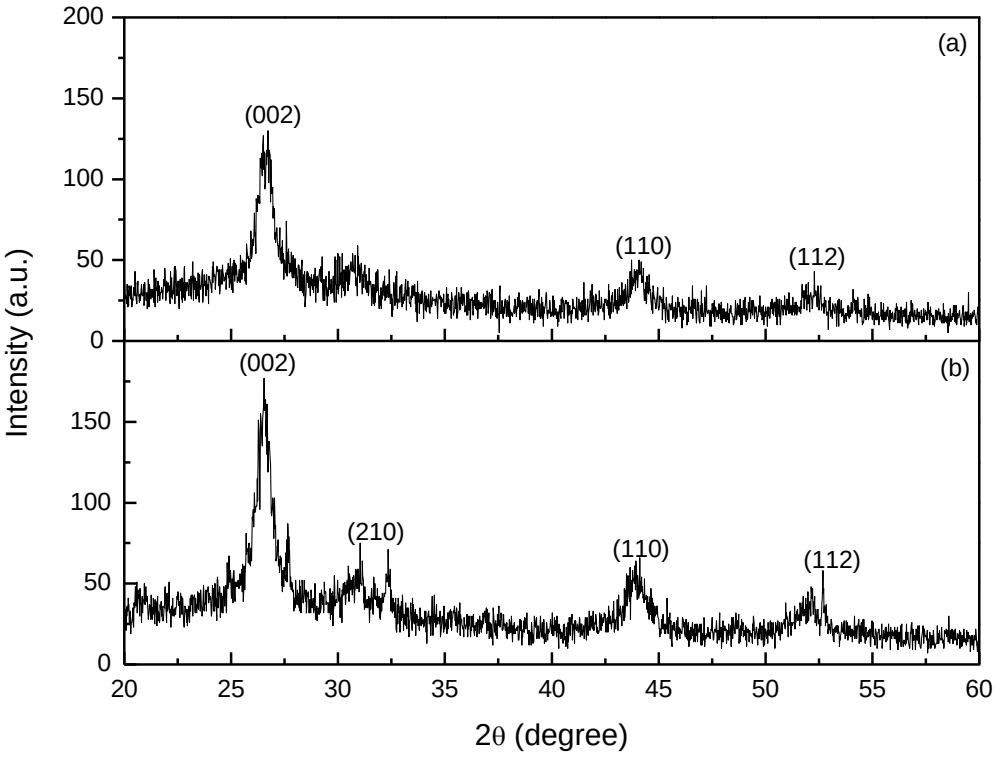

Figure 1: XRD of CdS thin films annealed at (a) 200 ˚C and (b) 400 ˚C coated at 2200 rpm

Figure 1 shows the XRD patterns of CdS films spin coated at 2200 rpm and annealed at 200 and 400 ^{0}C. The relationship between diffraction angle and the distance between parallel atomic planes (d) is given by the Bragg's law $2d\sin\theta = m\lambda$, where θ is the Bragg angle, m is an integer equals to one, and λ is the wavelength of the incident X-ray beam. The crystallite size (D) of the films is estimated using the Debye-Scherrer formula (Rathinamala *et al.,* 2014) $D = \frac{0.91\lambda}{\beta\cos\theta}$, where λ is the X –ray wavelength (CuK_α = 1.54060 Å), β is the full width at half maximum (FWHM) of the dominant peak and θ is the Bragg angle. The dislocation density (δ) and strain (ε) of CdS nanostructures were determined using these XRD results and following relations, respectively. $\delta = \frac{1}{D^2}$ and $\varepsilon = \frac{\beta\cos\theta}{4}$. In addition, the lattice parameters *a* and *c* were calculated by following relations, respectively. $a = \frac{\lambda}{\sqrt{3}\sin\theta}$ and $c = \frac{\lambda}{\sin\theta}$.

Table 1: XRD results of CdS thin films spin coated at 2200 rpm and annealed at different temperatures

Annealing temperature (^{0}C)	Peak (deg)	Particle Size (nm)	Dislocation density (δ) (10^{16} lines/m^2)	Strain (ε)	Interplanar distance (d) (Å)	Miller indices (hkl)	Lattice parameters a and c (Å)
200	26.62	6.09	2.70	0.0304	3.34	(002)	a=0.8861 c=1.5464
	44.03	3.31	9.13	0.1680	2.05	(110)	a=0.0473 c=28.9503
	52.32	6.42	2.43	0.1676	1.75	(112)	a=0.7874 c=1.7402
300	26.56	9.00	1.23	0.3424	3.35	(002)	a=0.8802 c=1.5568
	43.90	5.00	4.00	0.4459	2.06	(110)	a=0.0725 c=18.8889
400	26.54	10.85	0.85	0.0323	3.36	(002)	a=0.8773 c=1.5619
	31.15	5.82	2.95	0.3577	2.87	(210)	a=0.2308 c=5.9370
	43.95	6.53	2.34	0.3427	2.06	(110)	a=0.0298 c=45.9554
	52.06	6.48	2.38	0.0776	1.76	(112)	a=0.8681 c=1.5785

Table 1 shows the values of particle size, dislocation density, strain and interplanar distance calculated using XRD patterns given in figure 1 for different XRD peaks. Calculated results shows that the crystallites of the CdS thin films were larger at higher temperatures.

The absorbance of film samples versus wavelength was measured using UV-visible spectroscopy. Hence the absorption coefficient at different wavelengths was calculated. Figure 2 indicates the graph of $(\alpha hv)^2$ versus (hv) for CdS thin film coated at 2200 rpm and annealed at 300^0C. The optical band gap (E_g) was determined using Tauc model by plotting $(\alpha hv)^2$ versus (hv) and selecting the linear part in the relation of $(\alpha hv)^{1/n}=A(hv- E_g)$. Here A is a constant, α absorption coefficient, hv the photon energy and n is equal to 2 for direct transitions.

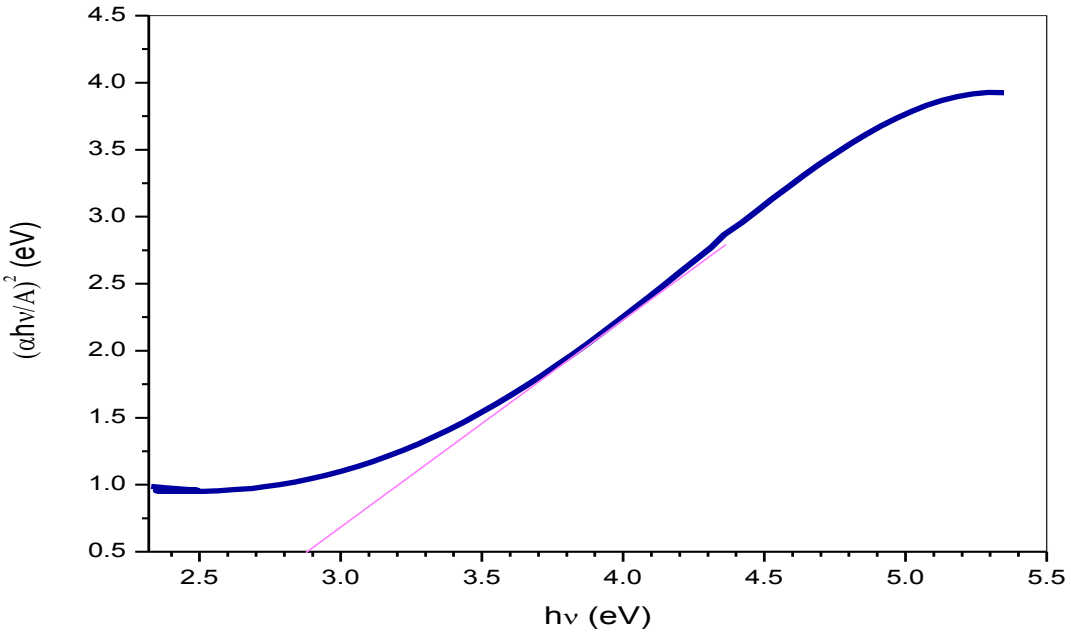

Figure 2: $(\alpha hv)^2$ versus (hv) plot of CdS thin film coated at 2200 rpm and annealed at 300^0C

The calculated band gap values are greater than that of the bulk CdS as shown in Table 2**.** The optical energy gap decreases with increasing temperature and it indicates a slight increase with increasing spin speed. This indicates the formation of nanoparticles of CdS and quantum confinement effect.

Table 2: Optical band gaps of CdS thin films spin coated at different spin speeds and annealed at different temperatures

Annealing Temperature (^{0}C)	**Band gap(eV)**		
	1500 rpm	**2200 rpm**	**2400 rpm**
200	3.061	3.063	3.065
300	2.885	2.886	2.887
400	2.752	2.753	2.753

The relation between particle radius and the band gap is given by Brus equation as follows.

$$E_g = E_{bulk} + \frac{h^2}{8r^2}\left(1/m^*_e + 1/m^*_h\right) - \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_r r^2} \quad (1)$$

Where E_g and E_{bulk} are the band gaps of CdS thin film and bulk, respectively, h is the Planck's constant, m^*_e and m^*_h are the effective masses of electron and hole, respectively , ε is the dielectric constant and r is the radius of the grains. The third term stands for the columbic interaction energy and often can be neglected due to high dielectric constant of semiconductor materials. Second term represents the additional energy due to quantum confinement having r^{-2} dependence on the band gap energy. If the sphere is too small, the movements of the electron and hole are restricted and so they feel confined which raises the energy required to excite the electron into the conduction band.

CONCLUSIONS

CdS nanostructures have been successfully prepared by the sol-gel spin coating method. Compared to the powder diffraction pattern of CdS, (002) peak of XRD pattern of our CdS film becomes dominant. All CdS thin films exhibit a favored direction along (002), and crystalline size increases with the annealing temperature. However, the dislocation density gradually decreases with the annealing temperature. This is related to the fact that the dislocation density decreases with the improvement of crystallization. The

strain initially increases and then decreases with the annealing temperature. Lower strains can be observed at lower and higher annealing temperatures. Higher strains were observed at intermediate annealing temperatures. Strain mostly takes place in the film sample when the sample is cooled from annealing temperature to the room temperature. Due to that reason, when the sample is cooled from a lower annealing temperature to the room temperature, the strain is not that high. On the other hand, the strain will be lower at higher annealing temperatures due to the improvement of crystallization. In other words, because the particles are compact at higher annealing temperatures, any free space (or voids) required for strain is not available. The absorption studies revealed a strong blue shift indicating the presence of quantum confinement effect. As a matter of fact, the optical band gap decreases when the particle size increases. Furthermore, CdS nanostructures prepared at this range of annealing temperatures and spin coating speeds can be recommended for photovoltaic and optoelectronic applications.

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