UDC: 538.9 Condensed matter Physics, Solid state Physics, Theoretical Condensed matter Physics

## EFFECT OF NUMBER OF LAYERS ON STRUCTURAL AND OPTICAL PROPERTIES OF SPIN COATED CdS FILMS

D. M. C. U. Dissanayake and P. Samarasekara

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

#### Abstract:

Films of CdS were synthesized using spin coating technique starting from a solution with cadmium nitrate and thiourea. Number of layers was changed from 2 to 14. Structural properties were determined by X-ray diffraction method. XRD patterns indicate the crystallization of single phase of polycrystalline CdS. Lattice spacing, texture coefficient, particle size, lattice parameters, strain and dislocation density were calculated using XRD patterns. Peak intensity and particle size increase with the number of layers. However, the strain and dislocation density decrease with the number of layers. Optical properties were measured using UV-visible spectroscopy. Absorbance increases with the number of layers. Due to the decrease of number of localized states, the optical band gap increases with the number of layers.

*Keywords:* Spin coating, XRD patterns, optical band gap, particle size, texture coefficient

#### 1. Introduction:

CdS is a potential candidate in the applications of light emitting diodes, sensors, photoconductors, optical mass memories and solar selective coatings. CdS is a II-IV type semiconductor with a high band gap around 2.42 eV. Owing to the high band gap, CdS films are employed as a window material in CdS/CdTe solar cells. CdS is a n-type semiconductor with yellowish color. Nanostructures have attracted a great interest in recent years because of their unique chemical, physical, optical, electrical and transport properties. Owing to the high surface area, all nanostructured materials posses a high surface energy and thus, are thermodynamically unstable or metastable. CdS nanoparticles are considered to be a prime candidate in the 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.

Fabrication techniques of CdS thin films include spray pyrolysis [1], chemical bath deposition [2, 7,], electro deposition [3], screen printing [4], physical vapor deposition, vacuum evaporation [5], electron beam evaporation [6] and sol-gel spin coating. Among many deposition methods, sol-gel spin coating technique is extensively applied 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 sintering temperatures. Influence of sol aging time and annealing temperature on nanocrystalline CdS thin films has been investigated [8]. Previously, structural and optical characterization of sol-gel spin- coated nanocrystalline CdS thin film have been investigated [9].

Previously we have prepared film samples using chemical vapor deposition [10] and sputtering techniques [11, 12, 13] incorporated with expensive vacuum machines. However, spin coating technique was found to be low cost compared to above methods. CdS possesses some magnetic properties [14]. The Heisenberg Hamiltonian was used to describe the magnetic properties

of ferromagnetic and ferrite films by us previously [15, 16, 17, 18, 19]. Previously band gap of semiconductor particles doped with salts have been investigated by measuring electrical properties [20]. In this manuscript, the variation of optical and structural properties of CdS films with number of layers will be described.

### 2. Experimental:

Initially two solutions have been prepared as following. Polyethylene Glycol (PEG) was dissolved in ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), and acetic acid (CH<sub>3</sub>COOH) was added to ethanoic solution under stirring which was continued for 1 hour. Cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>) and thiourea (CS[NH<sub>2</sub>]<sub>2</sub>) were dissolved in ethanol under stirring which was continued for 1 hour. Two solutions were mixed and stirred again for 4 hours to obtain the final sols for deposition of thin films. CdS thin films were deposited on ultrasonically cleaned amorphous glass substrates by solgel spin-coating technique. Solution was applied onto the glass substrates at speeds of 1500, 2200 and 2400 rpm for 30 seconds. Thereafter, the samples were dried on a hot plate at 120  $^{\circ}$ C for 1 hour, and annealed at 350 and 400  $^{\circ}$ C in air for one hour. This procedure was repeated several times to synthesize multilayers.

Structural properties of film samples were determined using X ray diffraction (XRD) with Cu-K<sub> $\alpha$ </sub> radiation of wavelength 1.54060 Å. UV-visible spectrometer Shimadzu UV1800 was employed to investigate the optical properties of samples.

### 3. Results and discussion:

Figure 1 shows the XRD patterns of CdS thin films with 6 and 10 layers and annealed at 400  $^{0}$ C for one hour. All the samples described in this section were spin coated at spin speed of 2200 rpm for 30 s. These were found to be the optimum deposition conditions after varying spin speed and spin time. The XRD patterns of crystalline CdS thin films reveal that the CdS films are in polycrystalline nature, and the existence of a CdS single-phase with a hexagonal wurtzite structure. The sharp and well defined intense peak patterns are well agreed with standard ICDD data (ICDD-PDF file 772306). Furthermore, the intensity of XRD peaks increases with number of layers. Peak positions, corresponding reflections, interplanar distances (d) and texture coefficients (C<sub>hkl</sub>) of CdS thin films with 6 and 10 layers are given in Table 1. Here d was calculated using the Bragg's law. The texture coefficient of a certain crystal plane (hkl) in a polycrystalline thin film is given by the relation,

$$C_{hkl} = \frac{I(hkl)/I_0(hkl)}{(1/N)[\Sigma_N I(hkl)/I_0(hkl)]}$$

(1)

Where, h,k,l = Miller indices corresponding to the diffraction peak

I(hkl) = Measured intensity

 $I_0(hkl) = JCPDS$  standard intensity of the corresponding powder

N = Number of reflections



Figure 1: XRD pattern of CdS thin films with (a) 6 layers and (b) 10 layers annealed at 400 <sup>o</sup>C for 01 hour.

No. of Layers	hkl	20 (deg)	d (Å)	C <sub>hkl</sub>
6	(1 0 0)	24.88	3.579	1.19
	(0 0 2)	26.58	3.353	1.04
	(101)	28.25	3.159	0.99
	(1 0 2)	36.73	2.447	0.35
	(1 1 0)	43.77	2.068	0.81
	(1 0 3)	47.88	1.900	0.55
	(1 1 2)	51.91	1.761	0.90
	(201)	52.96	1.729	2.16
10	(1 0 0)	24.86	3.582	1.23
	(0 0 2)	26.54	3.358	0.99
	(101)	28.22	3.162	0.88
	(1 0 2)	36.65	2.452	0.93
	(1 1 0)	43.74	2.070	0.99
	(1 0 3)	47.87	1.900	0.45
	(1 1 2)	51.89	1.762	0.83
	(201)	52.88	1.731	1.69

Table 1: Miller indices (hkl), angle of diffraction ( $\theta$ ), interplanar distance (d) and texture coefficient (C<sub>hkl</sub>) of CdS thin films of layers 6 and 10.

As seen from above table, interplanar distances increase with the number of layers. Each plane exhibits a higher interplanar distances value for thin films with 10 layers than that of thin films with 6 layers. The texture coefficient measures the enhancement of the *hkl* reflection in comparison to a completely randomly oriented sample. According to table 1, the (2 0 1) plane has the highest  $C_{hkl}$  value for both 6 layers and 10 layers of CdS.

The crystalline size, lattice parameters (a and c), strain and dislocation density of CdS thin films of layers 6 and 10 were determined from the full width at half maximum (FWHM) of the most intense peak (1 0 1) and presented in Table 2. The lattice constants for hexagonal CdS film reported in ICDD-PDF file 772306 are, a=4.136 Å and c= 6.713 Å. Even though, the c value is bit higher than the standard value, the calculated values in table 2 are in agreement with standards. This suggests that the fabricated films are under compressive stress.

No. of Layers	D (nm)	a(Å)	c(Å)	ε (x 10 <sup>-4</sup> )	$\delta (10^{14} \text{ lines/m}^2)$
6	38.035	4.129	6.743	9.222	6.912
10	40.586	4.133	6.749	8.643	6.071

Table 2: Crystalline size (D), lattice parameters (a and c), strain ( $\epsilon$ ) and dislocation density ( $\delta$ ) of CdS thin films of layers 6 and 10.

The crystallite size (D) of the films is estimated using the Debye-Scherrer formula [8].

 $D = \frac{0.91\lambda}{\beta\cos\theta}$ , where  $\lambda$  is the X –ray wavelength (CuK<sub>a</sub> = 1.54060 Å),  $\beta$  is the full width at half

maximum (FWHM) of the dominant peak and  $\theta$  is the Bragg angle.

The dislocation density ( $\delta$ ) and strain ( $\epsilon$ ) of CdS nanostructures were determined using these XRD results and following relations respectively  $\delta = \frac{1}{2}$  and  $\epsilon = \frac{\beta \cos \theta}{2}$ 

XRD results and following relations, respectively. 
$$\delta = \frac{1}{D^2}$$
 and  $\varepsilon = \frac{1}{4}$ .

In addition, the lattice parameters a and c were calculated by following relations, respectively.

$$a = \frac{\lambda}{\sqrt{3}\sin\theta}$$
 and  $c = \frac{\lambda}{\sin\theta}$ .

A noticeable observation from Table 2 is that the strain and dislocation density decrease with number of layers whereas crystalline size increases. The decrease of stress with film thickness is caused by the reduction of cohesive force between thin film and substrate and hence can conclude that there is a reduction of lattice imperfections which give rise to crystalline size.

Figure 2 shows the graph of absorption versus wavelength measured using UV-visible spectrometer for films with 2, 4, 6, 8, 10, 12 and 14 layers annealed at  $350 \,^{0}$ C for 01 hour. The absorption of UV radiation by thin films increases slowly at the higher wavelength region, and then increases sharply near the absorption edge (around 500 nm). In the meantime, the absorption increases with the number of layers of the film strongly demonstrating that the film property is thickness dependent because in the case of more atoms are present, more states will be available for the photons to be absorbed.



Figure 2: Absorption spectra of thin films with layers 2, 4, 6, 8, 10, 12 and 14 annealed at 350 <sup>o</sup>C for 01 hour.

Figure 3 shows the transmittance versus wavelength for thin films with layers 2, 4, 6, 8, 10, 12 and 14 layers. The films are highly transparent in the visible range (above 80%) and a sharp fall can be observed below 500 nm in all films. This is due to the strong absorbance of the films in this region and confirmed by the absorption spectra as well. Below the absorption edge, the transmittance decreases with the number of layers due to the increase of film thickness and continues just above the absorption edge. Eventually, this sequence disappears at higher wavelength region and originates a sinusoidal form. The sinusoidal behavior in the transmission spectra indicates the interference phenomena between two wave fronts from air and substrate. Furthermore, excellent surface quality and homogeneity of the film were confirmed from the presence of interference fringes in the transmission spectra.



Figure 3: Transmittance spectra of thin films with layers 2, 4, 6, 8, 10, 12 and 14 and annealed at 350 °C for 01 hour.

Optical band gap values calculated using Tauc plots are given in table 3 and these values are in the range (2.34-2.43) eV. The estimated values are in agreement with reported values by other researchers.

No of Layers	Bandgap (eV)
2	2.344
4	2.387
6	2.406
8	2.414
10	2.423
12	2.424
14	2.430

Table 3: Optical band gap values at different number of layers.

Figure 4 shows the variation of optical band gap with the number of layers. It is clear that optical band gap increases with number of layers. In amorphous chalcogenide thin films, the numbers of unsaturated bonds are higher due to insufficient number of atoms and it leads to increase the number of defects. When the film becomes thicker, these defects are eliminated with the presence of more atoms and thus create a homogeneous network with low density of defects. As a result, the numbers of localized states are minimized and thereby, increase the optical band gap. Hence, film thickness is an important parameter for band structure modification.



Figure 4: Optical band gap variation with number of layers.

# 4. Conclusion:

According to XRD patterns, single phase of polycrystalline CdS can be crystallized in thin film form under the preparation and annealing conditions given here. Lattice spacing, texture coefficient, particle size, lattice parameters, strain and dislocation density were calculated using XRD patterns. Peak intensity increases with the number of layers. The texture coefficient measures the enhancement of the *hkl* reflection in comparison to a completely randomly oriented sample. The (2 0 1) plane has the highest texture coefficient value for both 6 and 10 layers of CdS. Particle size increases from 38.035 to 40.586 nm as the number of layers is increased from 6 to 10 layers. However, the strain decreases from  $9.222x10^{-4}$  to  $8.643x10^{-4}$ , and dislocation density decreases from  $6.912x10^{14}$  to  $6.071x10^{14}$  lines/m<sup>2</sup> as the number of layers is increased from 6 to 10 layers. Optical properties were measured using UV-visible spectroscopy. Absorbance increases with the number of layers. Due to the decrease of number of layers is increased from 2 to 14. These optical band gap values are fairly close to the standard value of band gap of CdS (2.42 eV).

# **References:**

- 1. A.A. Yadav, M.A. Barote and E.U. Masumdar, Solid sate sciences (2010), 12(7), 1173.
- P. Lisco, P.M. Kaminski, A. Abbas, K. Bass, J.W. Bowers, G. Claudio, M. Losurdo and J.M. Walls, Thin solid films (2015), 582, 323.
- 3. M. Takahashi, S. Hasegawa, M. Watanabe, T. Miyuki, S. Ikeda and K. Iida, Journal of applied electrochemistry (2002), 32, 359.
- 4. V. Kumar, D.K. Sharma, M.K. Bansal, D.K. Dwivedi and T.P. Sharma, Science of sintering (2011), 43(3), 335.
- 5. 1. K. Yilmaz, Journal of Ovonic Research (2014), 10(6), 211.
- 6. Yang Dingyu, Zhu Xinghua, Wei Zhaorong, Yang Weiqing, Li Lezhong, Yang Jun, and Gao Xiuying, Journal of Semiconductors (2011), 32(2), 023001 1-4.
- 7. Be Xuan Hop, Ha Van Trinh, Khuc Quang Dat, Phung Quoc Bao, VNU journal of science, mathematics –Physics (2008), 24, 119.
- 8. I. Rathinamala, J. Pandiarajan, N. Jeyakumaran and N. Prithivikumaran, International Journal of Thin Films science and Technology (2014), 3(3), 113.
- 9. M.A. Olopade, A.M. Awobode, O.E. Awe and T.I. Imalerio, International journal of research and reviews in applied sciences (2013), 15(1), 120.
- 10. P. Samarasekara, Chinese Journal of Physics (2009), 47(3), 361.
- 11. P. Samarasekara, Georgian Electronic Scientific Journals: Physics (2010), 2(4), 3.
- 12. P. Samarasekara and N.U.S. Yapa, Sri Lankan Journal of Physics (2007), 8, 21.
- 13. P. Samarasekara, A.G.K. Nisantha and A.S. Disanayake, Chinese Journal of Physics (2002), 40(2), 196.
- 14. X.G. Zhao, J.H. Chu and Z. Tang, The journal of physical chemistry (2015), 119(52), 29075.
- 15. P. Samarasekara and Udara Saparamadu, Georgian electronic scientific journals: Physics (2012), 1(7), 15.
- 16. P. Samarasekara and N.H.P.M. Gunawardhane, Georgian electronic scientific journals: Physics (2011), 2(6), 62.
- 17. P. Samarasekara, Electronic Journal of Theoretical Physics (2008), 5(17), 227.
- 18. P. Samarasekara and Udara Saparamadu, Research & Reviews: Journal of Physics-STM journals (2013), 2(2), 12.
- 19. P. Samarasekara and B.I. Warnakulasooriya, Journal of science: University of Kelaniya (2016), 11, 11.
- 20. K. Tennakone, S.W.M.S. Wickramanayake, P. Samarasekara and, C.A.N. Fernando, Physica Status Solidi (a) (1987), 104, K57.