### PREPARATION AND CHARACTERIZATION STUDY OF CADMIUM SULFIDE DOPED ZINC THIN FILMS BY THERMAL EVAPORATION TECHNIQUE \*Suganthi J<sup>a</sup>, Elangovan M<sup>a</sup>, Johnsonjeyakumar S<sup>b</sup>

<sup>a</sup>Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya University, Enathur, Kanchipuram-631561, TamilNadu, India, E-mail: <u>sugimaya2@gmail.com</u>

<sup>b</sup>Department of Physics, Trenquebar Bishop Manikkam Lutheran Arts and Science College, Porayar – 609307, TamilNadu, India

### **ABSTRACT:**

In this present study, the Zinc and Cds material is deposited on glass substrate by thermal evaporation method. Thin film preparation is very important process of control the particle size, particle shape and morphology. Zinc [Zn] thin films were deposited on glass substrates using Physical vapour deposition. The substrate temperature is varied in the range of 100°C to 150°C. The structural and optical properties of Zn thin films were characterized with X-ray diffraction [XRD], scanning Electron Microscope (SEM). The XRD analyses indicate that Zn films have Zinc blonde structures with (111) preferential orientation, whereas the diffraction patterns sharpen with the increase in substrate temperatures. The SEM data also reveal that the films have nano-size grains with a grain size of approximately 69 nm. The films grown at 150°C exhibit a relatively high transmittance of 80% in the visible region, with an energy band gap of 3.79ev.

### **KEYWORDS:**

Physical vapour deposition, Scanning Electron Microscope, XRD, Zn films

### Introduction

Thin films can be prepared from a variety of materials such as metals, semiconductors, insulators or dielectrics etc. and for these purpose the various preparative techniques have also been developed newer methods are also being evolved to improve the quality of the deposits with maximum reproducible properties and minimum variation; in their compositions<sup>[1]</sup>. One of the major barriers met in the thin film deposition is the ability to coat large dimension substrates while obtaining high precision results with mono or multi-layer depositions. Cadmium sulfide has, like zinc sulfide, two crystal forms. The more stable hexagonal wurtzite structure (found in the

mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite). In both of these forms the cadmium and sulfur atoms are four coordinate.<sup>[20]</sup> There is also a high pressure form with the NaCl rock salt structure.<sup>[2]</sup>.

## Material and Methods

In the present study, the Zinc doped Cds thin films are deposited on glass substrate of length 7.6 cm and breadth 2.6 cm by thermal evaporation method (PVD). The Zinc doped Cds thin film deposition was done by Vacuum coater model 12A4D (Hind High Vacuum in Bangalore). Glass substrate is cleaned gently using an acetone and loaded in substrate holder. Evaporant source material Zinc & Cds is loaded in the molybdenum boats in a source holder. Initially diffusion pump is evacuated by rotary pump and low pressure is maintained to avoid oxidation of silicone oil in the pump. Diffusion pump is heated then vacuum chamber is evacuated and the vacuum  $(5x10^{-5})$  is maintained. glass substrate is heated by substrate heater. HT (High tension) ion bombardment was done to clean the substrate. LT (low tension) voltage is applied to the source holder, Zinc & Cds material is heated and evaporation occurs. The zinc atoms are deposited first then Cadmium Sulphide deposited on the glass substrate, and thin film is formed. Thickness of the film is maintained by thickness monitor. The Zinc and Cds deposition was done at different temperatures in 12A4D vacuum coating unit finally the vacuum coater is shut down properly.

### PHYSICAL VAPOUR DEPOSITION

The material to be deposited is placed in an energetic, entropic environment. So that particles of material escape its surface. Facing this source is a cooler surface<sup>[9]</sup> which draws energy form these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particle to travel as freely as possible. Since particle tends to follow as straight path., films deposits by physical means are commonly directional, rather than conformal. Examples of physical deposition include.

### **RESULT AND DISSCUSION**

In this present study, the Zinc and Cds material is deposited on glass substrate by thermal evaporation method. Thin film preparation is very important process of control the particle size,

particle shape and morphology. The deposited Zinc with Cds thin films were characterized by Xray diffraction and field emission scanning electron microscope studies. XRD study is the most important tool in thin film technology. From X-ray diffraction spectrum film morphology, FWHM (Full Width at Half Maximum), Diffraction angle, intensity, diameter of the particle, dspacing has been calculated. The X-ray diffraction results shows the particle size is less than 100 nm at 100°C . Scanning electron microscopy (SEM) demonstrates spectacular changes in morphology of zinc and Cds thin films deposited on glass substrate at 100°C temperature. Using the fractional dimension of the assembly of nanostructures in the thin films has been estimated. The effects of thin films surface morphology and fractal dimension, structure, composition have been discussed.

**Table 1** 2θ values of zinc in (degree) and Height in (cps)

2θ(degree)	d(angle)	Height(cps)	FWHM(degree)
36.4446	2.45711	26393	0.1210
37.78	2.3792	249	0.13
43.409	2.08291	17425	0.162

Table 2 20 values of Zinc with cus in (degree) and neight in (c)	Table 2	$2\theta$ values of	Zinc with cds i	in (degree) a	nd Height in (cr	)s)
------------------------------------------------------------------	---------	---------------------	-----------------	---------------	------------------	-----

2θ(degree)	d(angle)	Height(cps)	FWHM(degree)
54.557	1.6807	614	0.104
70.249	1.33807	1497	0.118
77.266	1.23380	895	0.120

Table.1 shows the XRD results of zinc thin film on copper substrate at  $100^{\circ}$ C. The different 20 values, d-spacing values in angle, Height values in (cps) and Full width at half maximum values in (degree) are tabulated. In the table the 2 theta values are increases continuously between the range from 36.4446(deg) to 77.266 (deg) at the same time the d-spacing values are decreased. Height of the peak is decreased, increased corresponding 2 Theta values, but the full width at half maximum values are increased.

# Table 3 Miller Indices, d-spacing values of zinc thin film at 100°C

2θ of the intense peak (degree)	Miller indices (h k l)	d-spacing (nm)
54.5453	102	0.1682
70.3911	103	0.1336
70.9202	110	0.1327
77.4246	004	0.1231

## Table 4 Miller Indices, d-spacing values of zinc with cds thin film at 100°C

2θ of the intense peak (degree)	Miller indices (h k l)	d-spacing (nm)
36.4446	002	0.2459
39.1380	100	0.2381
43.3866	101	0.2084

The d-spacing (decreased) value in nano meter is calculated from the Bragg's law  $2d\sin\theta = n\lambda$  are shown in table-2. The 2 $\theta$  values from 36.4446 (degree) to 70.4246(deg) and corresponding Miller Indices is (002) - (004) are also tabulated.

Table 5 Size of the Zinc Particle and FWHM	(β)	values in radians
--------------------------------------------	-----	-------------------

FWHM of intense peak β(radians)	Size of the particle (nm)	d-spacing(nm)
0.00211	69.26	0.2459
0.00226	64.90	0.2381
0.00282	52.855	0.2084

### Table 6 Size of the Zinc with Cds Particle and FWHM $(\beta)$ values in radians

FWHM of intense peak β(radians)	Size of the particle (nm)	d-spacing(nm)
0.00181	86.07	0.1682
0.00205	82.79	0.1339
0.00340	51.13	0.1280

The scherrer equation is used to calculate, the grain size of zinc thin films from X-ray diffraction results. The scherrer equation for particle size as follows,

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

The calculated values of FWHM in radians, size of the particle in nm and the d-spacing values in nm are and tabulated in table.3. The grain size is increases from 51.13, 52.855, 64.90, 69.26, 82.79, nm 84.88 to 86.07nm.



XRD Pattern of Zinc WITH Cds Thin Films at 100°C

2θ(degree)	d(angle)	Height(cps)	FWHM(degrees)
43.348	2.0857	23974	0.172
45.289	2.4625	25982	0.176

# Table.7 Zinc Thin Films at 100°C 20 values in (degree) and Height in (cps)

# Table.8 Zinc with Cds Thin Films at 100°C 2θ values in (degree) and Height in (cps)

2θ(degree)	d(angle)	Height(cps)	FWHM(degrees)
50.461	1.8071	3317	0.207
74.024	1.2796	778	0.186

In the Debye-Scherrer photographic method, a film was wrapped around the inside of Xrays camera. The powder, sealed in a glass capillary tube, diffracts the X-rays (Bragg's law) to produce cones of diffracted beams. These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film. The film can be removed and examined. Using the radius of the camera and the distance along the film from the center, the Bragg angle  $2\theta$  and therefore the d-spacing for each reflection can be calculated.

Table 9 Miller mulces, u-spacing values in zinc (iiii) at 100 (	Table 9	Miller	Indices,	d-spaci	ng values	s in zino	c (nm)	at 100°	°C
-----------------------------------------------------------------	---------	--------	----------	---------	-----------	-----------	--------	---------	----

$2\theta$ of the intense peak (degree)	Miller indices (h k l)	d- spacing (nm)
43.348	111	0.2087
49.456	200	0.1398

# Table 10 Miller Indices, d-spacing values in Zinc with Cds (nm) at 100°C

$2\theta$ of the intense peak (degree)	Miller indices (h k l)	d- spacing (nm)	
50.461	200	0.1808	
74.024	220	0.1280	

The d-spacing (decreased) value in nano meter is calculated from the Bragg's law  $2d\sin\theta = n\lambda$  are shown in table-5. The increased 2 $\theta$  values from 43.348 (degree) to 74.024 (deg) and corresponding Miller Indices is (111) - (220) are also tabulated.

# Table 11 Zinc Thin Films at 100°C Size of the Particle and FWHM $(\beta)$ values in radians

FWHM of intense peak β(radians)	Size of the particle (nm)	d-spacing(nm)
0.00300	49.77	0.2087
0.00361	42.48	0.1808

# Table 12 Zinc with Cds Thin Films at 100°C Size of the Particle and FWHM ( $\beta$ ) values in radians

FWHM of intense peak β(radians)	Size of the particle (nm)	d-spacing(nm)
0.00324	56.53	0.1280
0.00312	49.98	0.2465

The Scherrer equation is used to calculate, the grain size of zinc thin films from X-ray diffraction results. The calculated values of FWHM in radians, size of the particle in nm and the d-spacing values in nm are and tabulated in table.6. The grain size is increases from 49.77, 42.48, 56.53nm.

The results confirm zinc thin films, uniformed size at 100°C less than 92 nm. Seven peaks at  $2\theta_{-}$  values of 36.4446(degree) ,d-spacing values is0.2459nm, Miller Indices is (002) to  $2\theta$  values is 77.4246(degree),d-spacing values is 0.1234(nm), Miller Indices is (004), the zinc is

(HCP) Hexagonal Closed Packed structure standard powder diffraction. The XRD study confirms / indicates that the resultant particles are (HCP) Zinc Nano particles. In addition to these 100°C&200°C, the diffraction pattern confirms the (HCP) structure is presented.

# SEM CDS IMAGE AT 100°C



## SEM ZINC IMAGE AT 100°C



## Table 13 Shape and Size of Zinc Thin Films at Different Temperatures

Substrate	Substrates Temperature(°C)	Shape	Size(nm)
Zinc	100°C	Hexagonal	39 nm - 92nm

# Table 14 Shape and Size of Zinc and CdsThin Films at DifferentTemperatures

Substrate	Substrates Temperature(°C)	Shape	Size(nm)
Zinc with Cds	100°C	Hexagonal	69 nm - 150 nm

The zinc doped cds thin films prepared by thermal evaporation method at 100°C. The grain size is observed by XRD results and the shape of the zinc andcds molecule is Hexagonal is confirmed by SEM results. At 100°C the shape of zinc and Cds is hexagonal; the grain size is 39-92 (nm).

# Conclusion

Cadmium Sulhide is an important and useful material for photovoltaic applications. In this study, pure CdS and Zn-doped CdS (CdS:Zn) thin film were fabricated on glass substrate using physical vapour deposition (PVD) method. Cadmium sulphide (CdS) has generated a lot of interest among scientists because of its extensive use in the fabrication of solid state devices such as solar cells, thin film transistors and electroluminescent displays.

In the present work Zinc with Cds thin films were deposited employing the simple and economic experimental set up known as Physical Vapour deposition (PVD) method.

The Zinc with cadmium sulfide film was prepared at 100<sup>o</sup>C temperature. Zinc with Cds thin films thus deposited on a glass substrate was observed to be good in appearance and hence the analysis with the X-ray diffraction investigation observed crystalline structure of CdS and CdS:Z films have (polycrystalline) structure. The doping with Zn did not effect on the nature of crystal structure of CdS. The average crystallite size estimated from XRD data indicate that the crystallite size within the structures of the nanoparticles, as well as crystallite size decrease with increasing the doping ratio.

The SEM analysis for the samples was carried out and the thin film morphology was reported. Analyzing the SEM image it is found that it is much continuous and smooth film is attained. The EDAX analysis is good agreement with the zinc molecule analysis reported earlier.

TEM and DSC will be much useful tool in the surface characterization is suggested for the future study.

### **REFERENCES:**

- [1] A. Antony, K. V. Mirali, R. Manoj and M. K. Jayaraj, Mater. Chem. Phys. 90, 106 (2005).
- [2] E. Hichou, M. Addou, J. L. Budendor\_, J. Eboth\_e, E.Idrissi and M. Troyon, Semicond. Sci. Technol. 19, 230(2004).
- [3] B. Elidrissi, M. Addou, M. Regragui, A. Bougrine, A.Kachouane and J. C. Bern\_ede, Mater. Chem. Phys. 68,175 (2001).
- [4] N. fathy, R. Kobayashi and M. Ichimura, Mater. Sci.Eng. B 107, 271 (2004).
- [5] J. A. Ru\_ner, M. D. Hilmel, V. Mizrahi, G. I. Stegemanand U. Gibson, Appl. Opt. 28, 5209 (1989).
- [6] U. Gangopadhyay, K. Kim, D. Mangalaraj and J. Yi, Appl. Surf. Sci. 230, 364 (2004).
- [7] M. Tonouchi, S. Yong, M. Tarsuro, S. Hirosh and O.Masaki, J. Appl. Phys. 2, L2453 (1990).
- [8] T. B. Nasr, N. Kamoun, M. Kanzari and R. Bennaceur, Thin Solid Films 500, 4 (2006).
- [9] X. D. Gao, X. M. Li and W. D. Yu, Thin Solid Films468, 43 (2004).
- [10] T. Dedova, M. Krunks, O. Volobujeva and I. Oja, Phys.Stat. Sol. (c) 2, 1161 (2005).
- [11] S. D. Sartale, B, R. Sankapal, M. Lux-Steiner and A.Ennaoui, Thin Solid Film 480, 168 (2005).
- [12] S. M. Kim, K. Kyhm, H. S. Yang and K. S. Hong, J.Korean Phys. Soc. 49, 688 (2006).
- [13] J. W. Kim, J. J. Han, J. G. Choi, D. K. Kim, K. C. Je, S.H. Park, J. I. Yun and T.
- Frangh• omel, J. Korean Phys.Soc. 49, 135 (2006).
- [14] J. S. Park, S. W. Mho, J. C. Choi, H. L. Park, G. C.Kim, S. H. Lee and J. S. Kim, J. Korean Phys. Soc. 50,3 (2007).

- 1. Advincula R and Knoll-Wiley W, "Functional Polymer Films Eds" ISBN 978-3527321902, (2011)
- Optical inhomogeneity of ZnS films deposited by thermal evaporation;Xiaochun Wu, Fachun Lai, Limei Lin, Jing Lv, Binping Zhuang, QuYan, Zhigao Huang; Applied Surface Science 254 (2008) 6455–646067
- **3.** ZnS thin films grown on Si(100) by XeCl pulsed laser ablation: K.T. Hillie, C. Curren, H.C. Swart; Applied Surface Science 177 (**2001**) 73-77
- Helmersson U, Lattemann, M. Bohlmark, J.; Ehiasarian, A. P Gudmundsson, J. T. "Thin Solid Films" 513, 1, (2006).
- Porter Alan L, Youtie Jan, Shapira Philip, Schoeneck David J. Refining search terms for nanotechnology, J Nanopart Res; 10:715–728(2008).
- Mattox, Donald M. and Vivivenne Harwood Mattox (editors)"50 Years Of Vacuum Coating Technology and the Growth of the Society of Vacuum Coaters", Society of Vacuum Coaters (2007).

7. Helmersson U, Lattemann, M. Bohlmark, J.; Ehiasarian, A. P Gudmundsson, J. T. "Thin Solid Films" 513, 1, (2006).

S. D. Sartale, B, R. Sankapal, M. Lux-Steiner and A.Ennaoui, Thin Solid Film 480, 168 (2005). [20]

S.

M. Kim, K. Kyhm, H. S. Yang and K. S. Hong, J.Korean Phys. Soc. 49, 688 (2006).

[21] J. W. Kim, J. J. Han, J. G. Choi, D. K. Kim, K. C. Je, S.

H. Park, J. I. Yun and T. Frangh• omel, J. Korean Phys.

Soc. 49, 135 (2006).

[22] J. S. Park, S. W. Mho, J. C. Choi, H. L. Park, G. C.

Kim, S. H. Lee and J. S. Kim, J. Korean Phys. Soc. 50,

1. 3 (2007).