IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861. Volume 3, Issue 3 (Mar. - Apr. 2013), PP 41-47
www.iosrjournals.org

Study of structural, Morphological and Electrical Properties of $Cd_xZn_{1-x}S$ Thin Films

Ravangave L. S.[1], Biradar U. V.[2]
[1](Department of Physics, Shri Sant Gadge Maharaj College, Loha, Dist. Nanded, (MS), India)
[2](Departmen tof Physics , M. B. College, Latur, (MS), India)

Abstract: *The $Cd_xZn_{1-x}S$ (x=00, 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared by using Chemical Bath Deposition (CBD) Technique. The prepared $Cd_xZn_{1-x}S$ thin films were characterized by X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). The structural and morphological properties have been investigated. XRD pattern exhibits the hexagonal crystal structure of $Cd_xZn_{1-x}S$. The dark electrical resistivity measurement was carried out in the temperature range 298 to 383 K by using two point probe method. The dark resistivity measurement shows that the prepared $Cd_xZn_{1-x}S$ thin films have high resistivity. The dark resistivity at room temperature was found to be of the order of $\geq 10^5$ Ω cm for pure CdS and $\geq 10^6$ Ω cm for $Cd_xZn_{1-x}S$ thin films. The dark resistivity was observed increased with Zn content.*

Keywords *– Chemical Bath Deposition, $Cd_xZn_{1-x}S$ thin films, Electrical resistivity, Structural properties, and morphological properties.*

I. INTRODUCTION

Thin films are crystalline or non-crystalline and play vital role in all optoelectronic devices. They have been used as electroplated films for decoration and protection [1]. In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other optoelectronic devices with much interest shown in the use of CdS window layer in solar cell architecture. However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of solar cells [2].

The $Cd_xZn_{1-x}S$ films have more advantages for application in solar cell because they also offer a wider band gap (larger than 2.5 eV) as compared to the CdS films [3]. The higher band gap of ternary CdZnS has led to less window absorption loss, which makes it an effective replacement for CdS in thin film solar cell systems [4].

The limited reports were found on study of electrical properties of $Cd_xZn_{1-x}S$ system therefore the attempt have been made to synthesis the $Cd_xZn_{1-x}S$ thin films to study the structural and electrical properties.

There are many report on the deposition of CdZnS thin films with different concentration of Zn^{+2} deposited by using different deposition techniques [5-8]. A number of thin film deposition techniques are used for deposition of the thin films. Chemical Bath Deposition Technique (CBD) is a simple technique in which no high quality substrates are required; also it is a non vacuum system. The method is more suitable for large area coatings. Therefore, in present research work an attempt was made to deposit the Cd_xZn_{1-x} S thin films by CBD technique.

II. EXPERIMENTAL

In order to prepare $Cd_xZn_{1-x}S$ thin films, cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$) and thiourea (NH_2CSNH_2) were used as Cd^{+2}, Zn^{+2} and S^{-2} ions respectively. The stock solutions of $CdCl_2$ (0.25M), $ZnCl_2$ (0.25M) and NH_2-CS-NH_2 (0.3M) were prepared. The experimental solutions with different proportion were taken in reaction beaker for deposition of $Cd_xZn_{1-x}S$ thin films as shown in table1.

Table 1 The experimental solution with different proportion in chemical bath

Composition x	$CdCl_2$ (ml)	$ZnCl_2$ (ml)	NH_2CSNH_2 (ml)
0.0	0	10	10
0.2	2	8	10
0.4	4	6	10
0.6	6	4	10
0.8	8	2	10
1.0	10	0	10

The pH of the solution was adjusted to 11 by adding the aqueous NH_3. The reaction beaker was kept in temperature bath, maintained at 80° C. Glass substrates were cleaned by 24 hr immersion in chromic acid, rinsed with acetone and distilled water. The experimental glass substrates were mounted on substrate holder and immersed in the reaction beaker. The substrate holder was rotated at slow speed (45 rpm) by means of DC geared motor for 25 to 27 minutes. The thin, uniform $Cd_xZn_{1-x}S$ films were obtained at the end of the reaction process.

Mechanism $Cd_xZn_{1-x}S$ Thin Film Formation: The method which is used to prepare cadmium Zinc sulphide (CdZnS) includes the reaction of Cd^{2+}, Zn^{2+} ions and S^{2-} ions were found in solution from thiourea is as:

$$(NH2)2\ CS + OH^- \leftrightarrow SH^- + CN_2H_2 + H_2O \quad \text{----------(1)}$$

$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O \quad \text{----------(2)}$$

Dissolving $CdCl_2$ and $ZnCl_2$ in water made both cadmium and zinc ions available in the solution and formation of complexes of those ions as: In case of NH_3 as complexing agents, the Cd^{2+} and Zn^{2+} exist predominantly in the form of ion complex. The rates of ZnS and CdS formation are determined by the concentration of Zn^{2+} and Cd^{2+} provided by $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$, and the concentration of S^{2-} from the hydrolysis of $SC(NH_2)_2$, respectively. The general reaction can be expressed as :

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$[Zn(NH_3)_4]^{2+} \leftrightarrow Zn^{2+} + 4\ NH_3$$

$$[Cd(NH_3)_4]^{2+} \leftrightarrow Cd^{2+} + 4\ NH_3$$

$$_x[Cd(NH_3)_4]^{2+} + (_{1-x})[Zn(NH_3)_4]^{2+} + S^{2-} + NH_3 \rightarrow Cd_xZn_{1-x}S + \text{Remaining product.} \quad \text{--------(3)}$$

The prepared $Cd_xZn_{1-x}S$ thin films were rinsed with deionized water to remove the loosely bound particles and annealed at 100 ^{0}C. The synthesized $Cd_xZn_{1-x}S$ films are subjected to different characterizations to study the effect of Zn content on structural, morphological, compositional, electrical properties.

Film thickness is an important parameter in the study of the film properties. Amongst different methods for measuring the film thickness, the weight difference method is simple and convenient and thickness 't' is measured using the relation(4).

$$t = \frac{m}{A\rho} \quad \text{-------(4)}$$

where, m is the mass of the film deposited on area A of the substrate and ρ is the density of the material in the bulk form.

III. RESULTS AND DISCUSSION

Structural study :

The chemically deposited $Cd_xZn_{1-x}S$ (x=0., 0. 2, 0.4, 0.6, 0.8, and 1.0) films were characterized by X-ray diffractometer. The XRD pattern was presented in fig. 1. The XRD spectra of the $Cd_xZn_{1-x}S$ films exhibit the hexagonal crystal structure with preferential orientations at (100), (002), (101), (203), (102), (110), (200) and (004) planes, at 2θ = 25.31, 26.756, 29.59, 31.20, 37.9, 52.10 and 55.60. The observed diffraction patterns are in good agreement with the standard JCPDS card data: 49-1302. Rajathi S. et al. (2012) and Kumar T. et al., (2009) reported similar hexagonal structure of $Cd_xZn_{1-x}S$ [9, 10]. As Zn content in the composition was increased, XRD peaks corresponding to (100), (101), (203), (102), (110) and (200) reflections significantly disappeared and only (002) was found significant. The (002) peak gives the lattice matching to the chalcogenide semiconductor such as CuInGaSe2 and CuIn(SexS1-x)2 which are used in solar cell devices for better solar cell efficiency [11]. In the composition x=0.4 and X=0.2 the polycrystalline nature of prepared $Cd_xZn_{1-x}S$ thin films was increased with Zn content. However in the film composition x=0.0 (ZnS) shows amorphous crystal structure with broad hump at at 26.70^0 due to glass substrate. In the x=0.0 composition the film exhibits (100) and (002) reflection at an angle of diffraction 2θ=34.32 and 36.144 respectively which was well fitted with JCPDS card No. 12-0688 of ZnS.

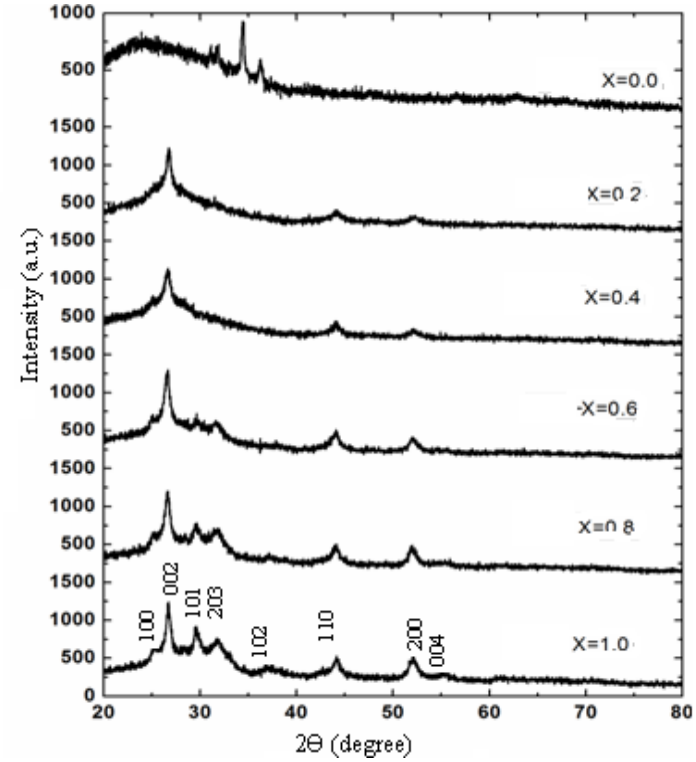

Fig.1 XRD pattern of $Cd_xZn_{1-x}S$ thin films

The average grain size calculated by using scherrer's relation (5):

$$D = \frac{0.94\lambda}{\beta Cos\theta} \quad \text{------ (5)}$$

Where λ= 1.54 ^{0}A, θ is the angle of diffraction and β the full width at half maximum. The variation of average grain size verses composition (x) was shown in table 2 and presented in fig. 2. The average grain size for x=0.2 composition was observed to be 4.19 nm.

The values of lattice constants a and c are calculated from XRD data by using relation (6).

$$1/d^2 = 4/3\,(h^2+hk+k^2)/a^2 + l^2/c^2 \quad \text{------- (6)}$$

The variation of lattice constant with composition (x) was shown in fig. 3 and displayed in table 2.

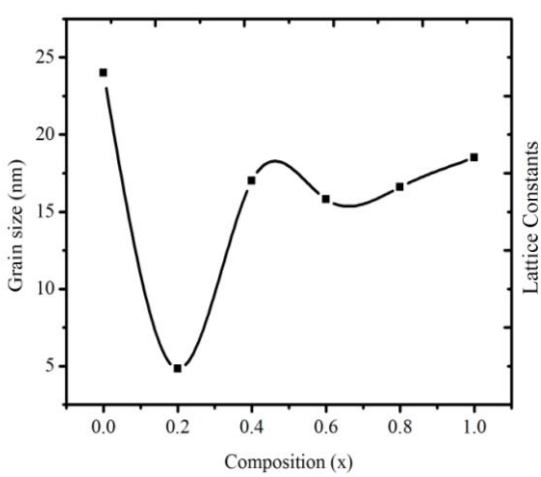

Fig. 2 Grain size Verses Composition (x)

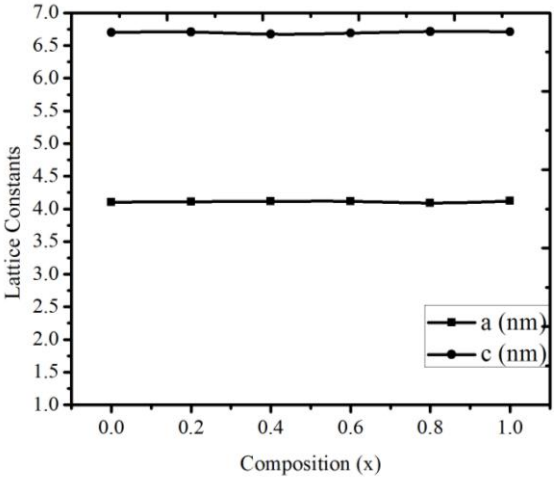

Fig. 3 Lattice constants a and c verses Composition (x)

Table 2 Film Thickness, Grain Size, Lattice constant and optical band gap of different composition of $\mathbf{Cd_XZn_{1-x}S}$

Composition of $Cd_XZn_{1-x}S$ film	Thickness µm	Grain Size nm	Latice Constants nm	
			a nm	c nm
0.0	1.13	24	4.1017	6.701
0.2	1.67	4.82	4.110	6.706
0.4	2.13	17	4.114	6.676
0.6	2.13	15.8	4.115	6.691
0.8	2.43	16.6	4.0911	6.715
1.0	2.63	18.5	4.121	6.712

3.2 Morphological study

In order to investigate the effect of Zn content on the surface morphology of the prepared $Cd_xZn_{1-x}S$ thin film the selected film were scanned by using Scanning electron microscopy (SEM Model: Quanta 200 ESEM). The SEM micrographs five different $Cd_xZn_{1-x}S$ thin films were presented in fig. 4 (A through E). All the films were scanned at 15 KX magnifications. The micrograph shows that the films deposited cover the whole substrate with uniform surface morphology.

SEM image of $Cd_{1.0}Zn_{0.0}S$ (fig. 4 A) shows the porous fibrous network consisting of regularly arranged matrix over which regular shaped fine particles systematically distributed. The larger size spherical granules were observed on the scan image due to aggregation of spheroid structure of S^{-2} ions.

The effect of increase of Zn content in $Cd_xZn_{1-x}S$ thin films clearly understood from the improvement in the microstructure of the surface morphology from figures 4 (A through E). The micrograph of $Cd_{0.0}Zn_{1.0}S$ shows spherical granules of ZnS particles irregularly distributed over the substrate. The SEM study confirms that even low Zn content was effectively changes the microstructure $Cd_xZn_{1-x}S$ thin films.

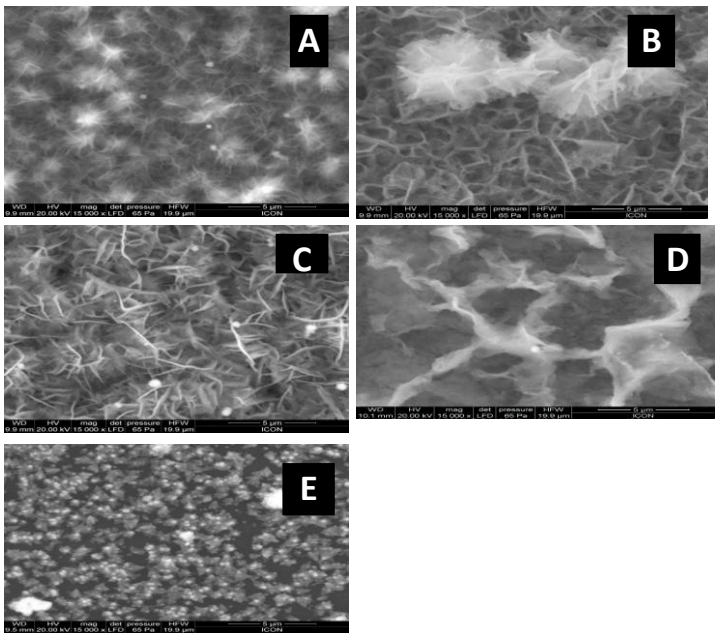

Fig. 4 The SEM micrographs of $Cd_xZn_{1-x}S$ thin films [A) for x=1.0, B) for x=0.8, C) for x=0.4, D) for x=0.2 and E) for x=0.0]

4. Electrical characterization of $Cd_xZn_{1-x}S$ thin films

In order to study the electrical characterization of $Cd_xZn_{1-x}S$ thin films, dc two point probe technique was used. The dark electrical resistivity measurement was carried out in the temperature range 298 to 383 K. The dark resistivity measurement shows that the prepared $Cd_xZn_{1-x}S$ thin films have high resistivity. The dark resistivity at room temperature, was found to be of the order of $\geq 10^5$ Ω cm for pure CdS and$c \geq 10^6$ Ω cm for $Cd_xZn_{1-x}S$ thin films. The plot of dark resistivity at different temperature was shown in fig. 5. The plot shows that the resistivity decreased with temperature. The decrease of resistivity with increasing temperature shows that the prepared $Cd_xZn_{1-x}S$ thin films are semiconducting. The variation of resistivity at room temperature verses composition (x) was shown in figure 6. It was observed from fig. 6 that resistivity at room temperature increased with Zn content of the films. The similar findings were reported by S. Jiyon et al.,(2005) in their work [12]. The variation (log ρ) with (1000/T) (K^{-1}) has shown in fig. 7.

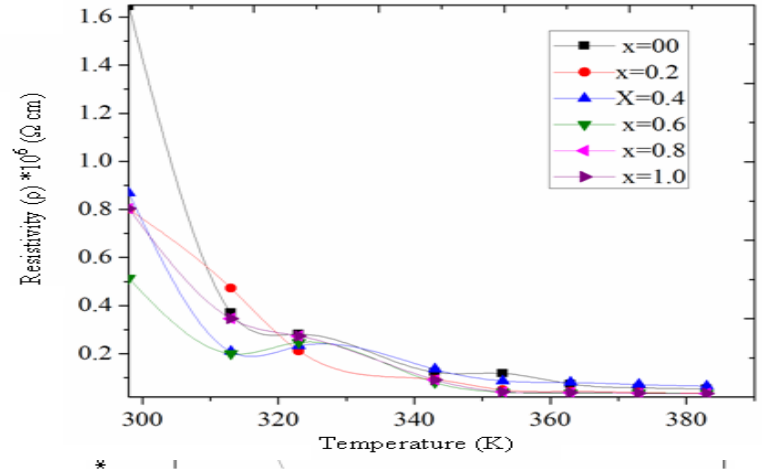

Fig.5 Electrical resistivity plotted verses temperature (K)

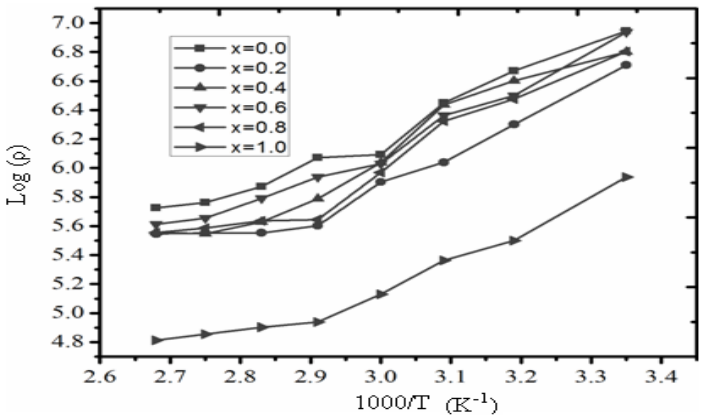

Fig. 7 The variation (log ρ) plotted verses (1000/T) (K^{-1})

The thermal activation energy estimated from the slopes of the curve in fig. 7 and by using relation (7).

$$\rho = \rho o \exp(-\Delta E / KT) \quad \ldots (7)$$

The activation energy was found to be in the range of 0.215 to 0.336 eV. Similar finding were reported by different researchers for CdS thin films [13,14]

Thermoemf Measurement of $Cd_xZn_{1-x}S$ Films.

The termoemf of the prepared thin films was measured by using two point probe method in the temperature range 298 K to 383 K with the interval of 10 K. Fig. 8 shows the variation of thermoemf plotted as function of temperature difference.

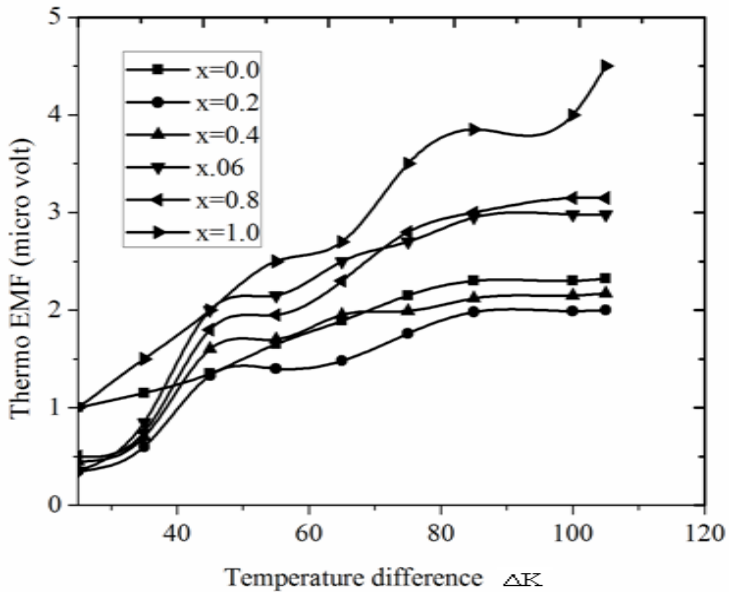

Fig. 8 Plot of thermoemf verses temperature difference (Δ K)

It is observed that thermoemf increases with in temperature difference. This may be attributed to increase the mobility of charge carriers and carrier concentration with increase in temperature. From the sign of the terminal connected towards hot end the sign of predominant charge carriers can be deduced. In this case the hot end is connected to the positive terminal, the films shows n-type conductivity**.**

IV. CONCLUSION

The $Cd_xZn_{1-x}S$ thin films prepared by simple chemical deposition exhibits hexagonal crystal structure. The crystallity of $Cd_xZn_{1-x}S$ was observed increase with Zn Content. In the x=0.2 composition grain size observed was 4.19 nm. Incorporation of Zn ions in the CdS, only (002) peak was found significant which gives the lattice matching to the chalcogenide semiconductors used in solar cell devices. The SEM study confirms that even low Zn content was effectively changes the microstructure $Cd_xZn_{1-x}S$ thin films. The dark resistivity at room temperature was found to be of the order of $\geq 10^5$ Ω cm for pure CdS and $\geq 10^6$ Ω cm for $Cd_xZn_{1-x}S$ thin films. The effect of Zn doping increases the dark resistivity of CdS thin films. The decrease of resistivity with increasing temperature shows that the prepared $Cd_xZn_{1-x}S$ thin films were semiconducting. . The activation energy was found to be in the range of 0.215 to 0.336 eV. The TEP measurement concluded that the prepared $Cd_xZn_{1-x}S$ films show n-type conductivity.

ACKNOWLEDGEMENTS

The corresponding Author is acknowledges to UGC India, for providing financial assistant under Minor Research Project , Prof Khairnar , Director School of Physical Sciences, SRTM University, Nanded, India, for providing XRD and other Laboratory Facilities.

REFERENCES

[1] O. S. Heavens, *Thin Film Physics*, (Methuen and Co,Ltd. London,.1970),
[2] S. Ilican, Y. Caglar and M. Caglar, Effect of the Sustrate Temperatures on the Optical Properties of the $Cd_{0.22}Zn_{0.78}S$ Thin Films by Spray Pyrolysis Method, *Physica Macedonica* 56, 2006 43-48
[3] J. Zhou, X. Wu, G. Teeter, B.To, R. G. Dhere and T. A. Gessert, CBD Deposited $Cd_xZn_{1-x}S$ Thin Films and Their Application in CdTe Solar Cell, *Phy. Stat. Sol., 24 (13)*, 2004, 775-778.
[4] Ragesh. chandran, G. Suresh, A comparative studyof physical and optical properties of CdZns and CdNiS nanocrystalline films deposited by Chemical Bath Method, *Chalconised Letters, 8(11)*, 2011,689-694,.
[5] Y.J. Chang, C. L Munsee, G. S.Herman, J. F. Wager. P.Mugdur, D. H. Lee, C. H. Chang, Growth, Characterization and application of CdS thin films deposited by chemical Bath Deposition', *Chem Eur J, 8*, 2002, 29.
[6] Lee Jae-Hyeong, Song Woo-Chang, Yi Jun-Sin , Yoo Yeong-Sik, Characteristics of the CdZnS thin Film Doped by Thermal Diffusion of Vacuum Evaporated Indium Films., *Solar Energy Materials & Solar Cells ,759*, 2003, 227-234.
[7] L.C. Burton, T. L. Hetch, $Zn_xCd_{1-x}S$ Films for use in Hetrojunction Solar Cells, *.Appl.phys,Lett . 29*, 1976, 612.
[8] M. P. Valkonen, T. Kanniainen, S. Lindroos, M. Leskela and E. Rauhala, Growth of Zns, CdS and multilayer ZnS/CdS Thin Films by Silar Technique, *Applied Surface Science*, *115*, 1997 386-392.

[9] S, Rajathi, N. Sankarasubramabian , K. Ramanataan, M. Senthamizhselvi, Structural and optoelectrical properties of paralytically sprayed CdZnS thin films, *Chalcogenide Letters,* **9** *(12),* 2012, 495 – 500.

[10] T. Premkumar, K. Shankarnaryanan, Growth and Characterization of CdZns thin films by short duration microwave assisted-Chemical Deposition Technique, *Chalcogenised Letters 6(10),* 2009, 55-262.

[11] S. V. Borse, S. D. Chavan, R. P. Sharma, Growth, structural and optical properties of $Cd_{1-x}Zn_xS$ alloy thin films grown by solution growth technique (SGT), *Journal of Alloys and compounds, 436,* 2007, 407-414.

[12] Growth and Characterizations of CdZnS Thin films Buffer Layer by Chemical Bath Deposition, *IEEE 31st IEEE PVC Specialists Conf. Dept. of Electr. & Comput. Eng., Florida Univ Univ., Gainesville*, FL, USA, 2005, 7803-8707.

[13] M. A. Barote, A.A. Yadav, E.U. Masumdar, Synthesis, characterization and photoelectrochemical properties of n-CdS thin films, *Physica B, 406,* 2011, 1865–1871.

[14] B. Vidhya, S. Velumani, J. Arenas-Alatorre, V.S. Resendiz, J. A. C. Carvayar, R. Asomoza, Y. Kudriavtsev, Structural, Photoluminescence and Electrical Properties of MW-CBD CdZnS Thin films, 7Th Int. Conf. Dept. of Electr. Eng., CINVESTAV, Mexico City, Mexico, 2010, 569 - 573