2010 7th International Conference on Electrical Engineering, Computing Science and Automatic Control (CCE 2010)
Tuxtla Gutiérrez, Chiapas, México. September 8-10, 2010.

Structural, Photoluminescence and electrical properties of MW-CBD CdZnS thin films

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Abstract — **Thin films of CdZnS have found extensive applications in various optical, electrical and optoelectronic devices. A simple method of microwave assisted chemical bath deposition (MW-CBD) has been used to deposit CdZnS (Cadmium Zinc Sulphide) thin films. The bath solution is composed of Cadmium Sulphate, Zinc Sulphate, thiourea, ammonium Sulphate and ammonia. The concentration of bath solution is varied as Y=0.1, 0.3 and 0.5 where Y= [$ZnSO_4$]/ {[$CdSO_4$] + [$ZnSO_4$]}. Deposition has been carried out for 120s microwave irradiation time. X-ray diffraction (XRD) indicates the hexagonal structure (002) reflection for the as-deposited CdZnS thin films. Grain size, dislocation density and strain in the deposited films have been determined. High resolution scanning electron microscopy (HRSEM) image gives the morphology, size and shape of particles in the deposited CdZnS thin films. Secondary ion mass spectrometry (SIMS) results show that composition is uniform throughout the entire film thickness. Band gap of deposited films as determined by photoluminescence (PL) studies is found to increase from 2.40 eV to 2.47eV with the increase in Y from 0.1 to 0.5. Ohmic conduction and space charge limited conduction (SCLC) has been observed in the deposited films.**

Keywords — **CdZnS, microwave, PL, SCLC**

I. Introduction

CdZnS thin films have become the subject of considerable interest due to their use in solar cells [1]. CdZnS have attracted technological interest because the energy gap can be tuned and lattice parameters can be varied [2]. The common techniques which have been adopted for preparation of CdZnS films are vacuum evaporation [3], chemical solution spray [4], Chemical bath deposition [5] etc. In the present work CdZnS thin films have been prepared by microwave assisted chemical bath deposition. Microwave irradiation as a heating method has found a number of applications since 1986 [6]. The effect of heating is created by the interaction of dipole moment of molecules (solvent and solute) with high frequency electromagnetic radiation (2.45 GHz). Therefore a polar solvent such as water is preferred for microwave assisted reactions.

MW-CBD is essentially based on microwave heating of the precursor solution. Microwave heating is a quite fast, simple and efficient method to prepare nano-sized inorganic materials [5, 7, 8]. Although the exact nature of interaction between microwaves and reactants during synthesis of materials is somewhat unclear and speculative; energy transfer from microwave to the material is believed to occur either through resonance or relaxation, which results in rapid heating. Interaction between dielectric materials and microwaves leads to dielectric heating. Electric dipoles present in such materials respond to applied electric field leading to dipole interaction. MW-enhanced chemistry is based on the efficiency of interaction of molecules in a reaction mixture (substrates, catalyst and solvents) with electromagnetic waves generated by a "microwave dielectric effect" [5]. This process mainly depends on the specific polarity of molecules where a constant reorientation creates friction and collisions between molecules, which subsequently generates heat. Hence, compared to conventional heating in bath, which is realized mainly by heat conduction, microwave heating is more efficient and rapid.

By applying microwave irradiation in chemical bath, nucleation on surface of substrate results in a preferential adsorption of negative and positive ions, over the rest of the sub-products of chemical reaction [9, 10]. Consequently substrate–ion interaction during growth process can be modified; that is, ion-by-ion heterogeneous growth on substrate can be promoted. In this way uniformly deposited CdZnS thin film is obtained in few seconds compared to some minutes or hours by the conventional chemical bath deposition. In the present work we discuss about the effect of Zn/Cd concentration on the structural, PL and electrical properties of CdZnS thin films. To the best of our knowledge this is the first study which gives the SIMS depth profile of elements in CdZnS thin films and explains the transport mechanisms of ternary semiconductor compound CdZnS (thin films) deposited by microwave assisted CBD.

II. Methodology

The chemicals used in this work consist of aqueous solutions of $5.8x10^{-3}$mol/l $3CdSO_4.5H_2O$, 0.037mol/l

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ISBN: 978-1-4244-7314-4
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NH_3SO_4, 0.065mol/l H_2NCSNH_2, 1.738x10^{-3}mol/l $ZnSO_4.7H_2O$ and 1.5 mol/l NH_3. The value of Y = 0.3 and. We define Y = $[ZnSO_4]/([ZnSO_4] + [CdSO_4])$. Thin films of CdZnS were deposited on well cleaned glass substrates. Microwave assisted bath temperature of solution was kept in the temperature range between 90°C to 95°C. Deposition time is maintained for 120s.

In this case, the advantages of microwave such as rapid reaction, small particle size and narrow particle size distribution are taken into account [11]. At the same time to have a controlled deposition of thin film, a cyclic microwave radiation(duty cycle) is applied to the bath solution, where the microwave is on for first 30 seconds; by this time, chemical bath temperature reaches around 70 degrees and color of solution changes to yellow (formation of the product). After this microwave is switched OFF and ON, for every 5 seconds (so that the temperature is maintained below 95 degrees) until the desired time. By this way we tried to control the deposition process to achieve small particle sizes–with narrow size distribution. Reaction procedure for the formation of CdZnS has been described in our previous report [12].

Thicknesses of the deposited films were measured by Dektak stylus profilometer. Structure of the films were analyzed using a Grazing Incidence X-ray diffractometer (Siemens D5000, using Cu-Kα radiation with λ = 1.5406 Å). Measurements were made for 2θ values over 20-70° in steps of 0.03° with a count time of 5 s and a grazing angle equal to 1.5º. Surface morphology and particle size of deposited films were analyzed by Zeiss High resolution Scanning Electron Microscope (HRSEM). HRTEM analysis was performed in a JEOL JEM-2010 FEG instrument with a point resolution of 1.9 Å. Composition over the depth profile of deposited CdZnS thin films was analyzed by SIMS, ims-6f CAMECA at room temperature. PL studies were done at room temperature, using a SPEX double monochromator, at 325nm excitation wavelength.

For electrical studies, CdZnS samples were cut in square shape 1cmx1cm and sufficiently small contacts were made at four corners of the sample with silver conducting paint. Hall studies were carried out to determine the carrier concentration and mobility of deposited films. For I-V measurement, a current of 50 nA was applied and the voltage has been measured at room temperature. Transport properties of deposited films have been studied by analyzing the different regions of I-V plot.

III. RESULTS

Structural

Several analytical techniques such as XRD, SEM and TEM are available for the analysis of structure. These techniques are also useful in identifying the aggregation effect of nanoparticles, particle size, plane of orientation etc. In general II-VI chalcogenide semiconductors can be formed as either spharlite (cubic, zinc blend type) or Wurtzite (hexagonal type). X-ray diffraction patterns of deposited films show (0 0 2), (110) and (201) reflection which correspond to CdZnS hexagonal crystalline phase (JCPDS card no: 40-0835) [3, 5] as given in figure 1. Value of 2θ shifts to a slightly higher angle with the increase in Zn concentration. Lattice parameter 'c' has been calculated using the below equation and given in table 1.

$$1/d^2 = 4/3[(h^2+hk+k^2)/a^2] + [1/c]^2 \quad (1)$$

It is observed that lattice parameter decreases with the increase in Y which is due to the Substitution of Cd^{2+} ions (r_{Cd2+} = 0.92 Å at tetrahedral sites) with the smaller radius Zn^{2+} ions (r_{Zn2+} = 0.74 Å at tetrahedral sites) [13].

Micro structural parameters crystallite size (D), dislocation density (δ) and strain (ε) of deposited CdZnS thin films have been determined by the relations (2-4) given below and the values are tabulated. Crystallite size is found to decrease where as dislocation density and strain are observed to increase with the increase in Y from 0.1 to 0.5.

$$D = (0.94\lambda)/(\beta\cos\theta) \quad (2)$$

$$\beta = [\lambda/(D\cos\theta)] - \varepsilon\tan\theta \quad (3)$$

$$\delta = 1/D^2 \quad (4)$$

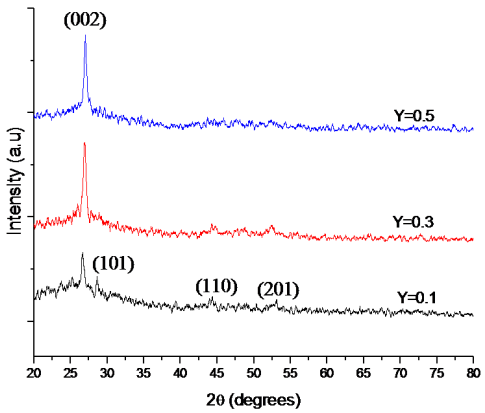

Figure 1. XRD pattern of MW-CBD CdZnS thin films.

TABLE 1. STRUCTURAL PARAMETERS OF MW-CBD CdZnS THIN FILMS

Y= $[ZnSO_4]/\{[CdSO_4]+[ZnSO_4]\}$	c Å	(D) nm	δx10^{15} lines/m^2	εx10^{-3}
0.1	6.694	21.2	2.225	2.796
0.3	6.637	20.3	2.426	1.978
0.5	6.589	19.52	2.624	3.273

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ISBN: 978-1-4244-7314-4
978-1-4244-7314-4/10/$26.00 ©2010 IEEE

Morphology and Composition

Many approaches have been used to control the growth process such as microwave irradiation [14], magnetic field [15], ultrasonic vibration [16] etc. Among this microwave irradiation has shown very rapid growth due to its unique reaction effects such as rapid heating and the consequent effective increase in reaction rates. A preferential adsorption of negative and positive ions induced by electromagnetic interaction results in nucleation and heterogeneous growth on the surface as shown in figure 2 [9, 10]. Uniform sized clusters of around 100-125nm which are made up of closely packed nano particles is observed. The size of these nanoparticles is determined by HRTEM analysis as discussed below.

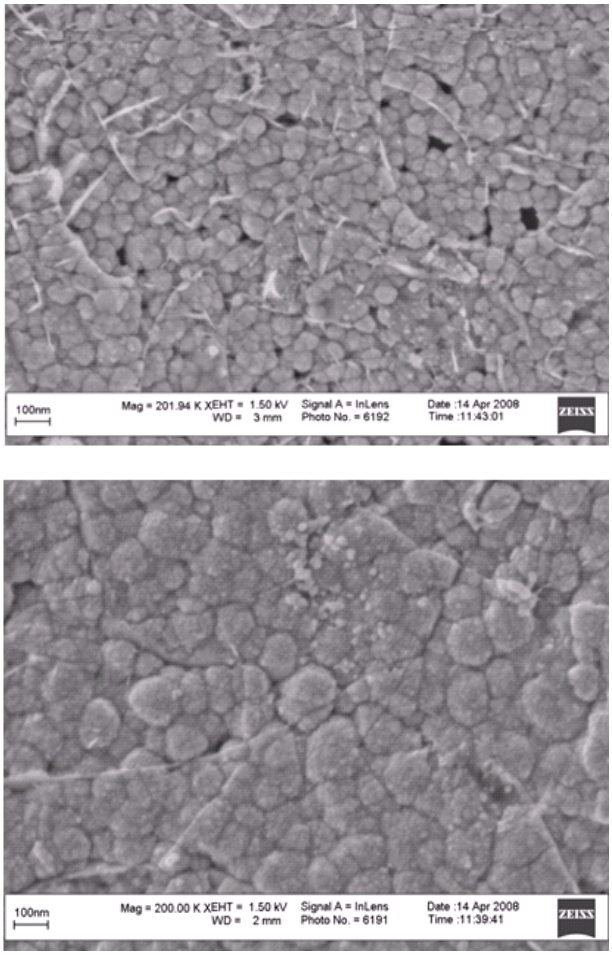

Figure2.HRSEM images of CdZnS thin films Y=0 and Y=0.3.

HRTEM

From HRTEM analysis in figure 3, CdZnS nanoparticle of size 12nm and several particles with strong aggregation having different orientations has been identified.

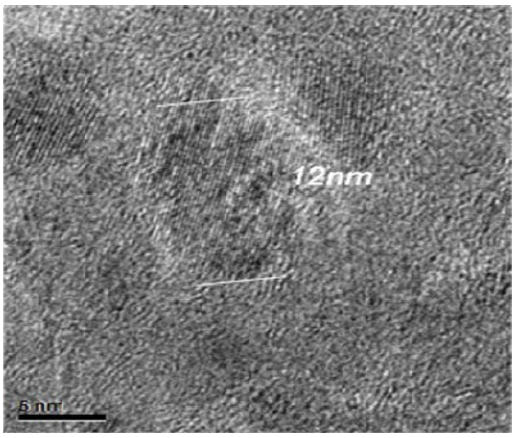

Figure3. HRTEM image of CdZnS thin film with Y=0.3.

SIMS analysis

In order to confirm the presence of Zn throughout entire film thickness, SIMS analysis has been carried out and results are given in figure 4a and b. It is observed that with the increase in Zn concentration in bath solution Y=0.3 and 0.5, percentage of Zn in film also increases. This analysis confirms the uniformity of Cd, Zn and S present throughout entire film thickness.

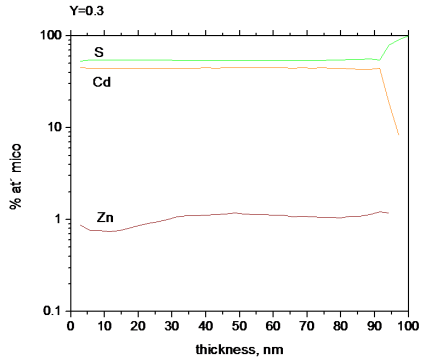

Figure 4. a)SIMS depth profile of deposited film with Y=0.3.

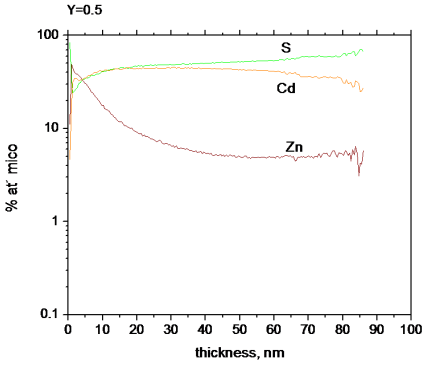

Figure 4. b)SIMS depth profile of deposited film with Y=0.5.

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ISBN: 978-1-4244-7314-4
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Photoluminescence

Room temperature Photoluminescence (PL) emission spectra of CdZnS thin films following the 325 nm excitation wavelength is given in figure 5. PL spectra of CdZnS thin films shows broad green emission peak in visible range at 516, 511 and 503nm for Y=0.1, 0.3 and 0.5 concentrations in the chemical bath. From spectral peak position the band gap energy has been calculated and found to be 2.40eV, 2.43eV and 2.47eV. For higher concentrations (Y) films with poor crystalline quality and increased structural and morphological disorders are observed, which causes broadening and asymmetry in PL peaks. Broad PL peak exhibited a trend of shifting towards higher energies with increasing Zn^{2+} content in films [17].

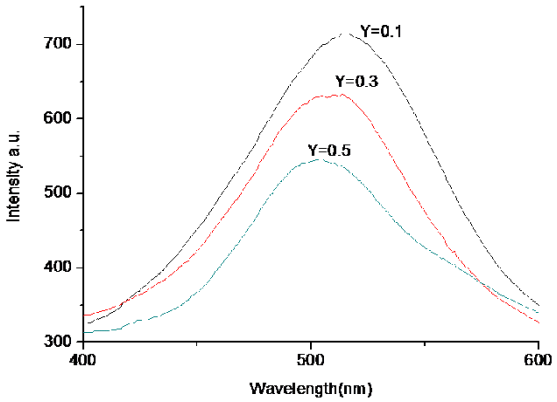

Figure 5. PL spectra of CdZnS thin films

Hall Studies

Hall studies has been carried out at room temperature and it has been determined that carrier concentration of deposited films vary from $6.04x10^{16}$ to $7.53x10^{16}cm^{-3}$, which is in accordance with the results reported by Oztas and Bedir [18], where they have reported that the carrier concentration varied from $1.5x10^{17}$ to $3.9x10^{17}$ cm^{-3} for $Zn_xCd_{(1-x)}S$ ($0.0<=x<=0.6$). Deposited films were found to be n-type with electrons as majority carriers. Variation of mobility and carrier concentration for Y=0.1 to 0.5 is given in table 2. It is also observed that carrier densities are quiet high, of the order of 10^{16} and increased with the increase in Y. Observed mobility values were low, but increased with the increase in Y. These values are in accordance with reported results , where the variation in carrier density and mobility values for $Cd_{1-x}Zn_xS$ thin films (where x=0.0, 0.05, 0.08, 0.12 and 0.18) from $2.8x10^{17}$ to $6x10^{17}cm^{-3}$ and 2 to $4.8cm^{-2}/Vs$ respectively has been observed by Khefacha et al[5]. Therefore concentration of Zn in the films plays a vital role in determining its electrical properties.

TABLE 2. HALL PARAMETERS FOR MW-CBD CdZnS THIN FILMS

Y	Carrier concentration (cm^{-3})	Mobility(cm^{-2}/Vs)
0.1	$6.04x10^{16}$	39.1
0.3	$6.99x10^{16}$	48
0.5	$7.53x10^{16}$	52.4

Transport mechanism

Study on I–V characteristics is a matter of importance for properly analyzing the conduction mechanism in films. A non-linear curve often may reveal the existence of different kinds of conduction mechanisms. In the present work non-linear I–V characteristics of films are examined and explained on the basis of space charge limited conduction (SCLC). Figure 6 clearly shows two distinct slopes for each of curves within the applied bias. The value of slopes are determined from log I-log V plot, and are found to be n=0.996 in lower voltage region and n= 2.145 in higher voltage region for film with Y=0.3. Thus I–V curves show two regions of conduction, viz. (i) nearly ohmic and (ii) non-ohmic conduction in these CdZnS films. For lower bias the injected charge carrier density is lower than thermally generated carrier density and that leads to ohmic behavior. At higher bias, as the slopes are ~2 it clearly suggests that conduction in this region is dominated by space charge limited conduction mechanism [3, 19]. Similar plots were obtained for films with Y=0.1 and 0.5. In addition, disorder originating from surface defects and charge traps may also play a role which has been reported for GaAs and CdS [20, 21].

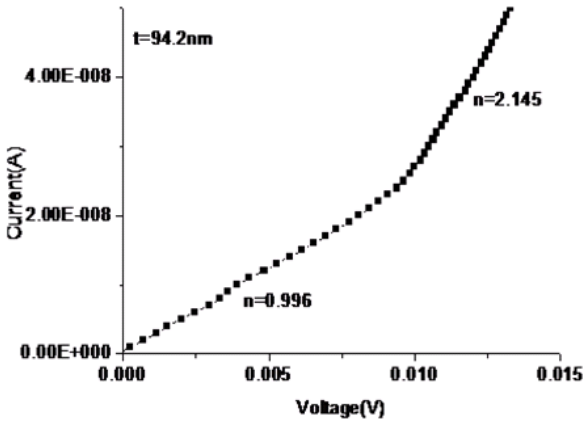

Figure 6. I-V plot of MW-CBD CdZnS thin film with Y=0.3.

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ISBN: 978-1-4244-7314-4
978-1-4244-7314-4/10/$26.00 ©2010 IEEE

IV. CONCLUSIONS

Without sacrificing the simplicity and versatility of CBD, good quality CdZnS thin films were prepared in short duration by MW-CBD. Small particle size and uniform particle distribution is achieved by MW-CBD. From XRD analysis, the structural parameters like crystallite size, dislocation density and strain were calculated for all the deposited films. Strong aggregation of nanoparticles has been confirmed by HRSEM analysis. Presence of nanoparticles with different orientations has been confirmed by HRTEM analysis. Uniform distribution of Cd, Zn and S throughout the entire film thickness has been verified by SIMS analysis. Increase in band gap with the increase in Y has been observed, which confirms the tunability of band gap, that can be used to decrease the window layer absorption loss and hence an increase in short circuit current in PV device. Hall studies revealed that deposited CdZnS thin films are of n-type and the carrier concentration and mobility increased with the increase in Y, which shows that mobile charge carriers can be modified based on the concentration of Zn. A transition from nearly ohmic to SCLC conduction mechanism is observed for the deposited films. Thus we conclude that MW-CBD can be used as an efficient technique to deposit a variety of binary and ternary semiconductors in short duration.

ACKNOWLEDGMENT

The authors would like to acknowledge the Solid State Physics group, Department of Physics, CINVESTAV for the XRD analysis. We thank Ing. Miguel Avendaño for PL measurements. One of the authors B.Vidhya is thankful for the scholarship provided by CONACYT to pursue the Doctorate programme.

REFERENCES

[1] Isaiah O. Oladeji, Lee Chow, Christos S. Ferekides, Vijay Viswanathan , Zhiyong Zhao, "Metal/ CdTe/ CdS/ $Cd_{1-x}Zn_xS$/ TCO/ glass: A new CdTe thin film solar cell structure", Solar Energy Materials & Solar Cells, vol.61 ,pp. 203-211, 2000.

[2] J.M.Dona and J.Herrero , "Chemical bath codeposited CdS-ZnS film characterization", Thin Solid Films, vol.268 , pp.5-12, 1995.

[3] Pawan Kumar, Aparna Misra,D.Kumar ,Neeraj Dhama,T.P.harma and P.N.Dixit , "Structural and optical properties of vacuum evaporated $Cd_xZn_{1-x}S$ thin films" ,Optical Materials, vol.27, pp.261-264,2004.

[4] Idris Akyuz, Salih Kose, Ferhunde Atay and Vildan Bilgin, "Some physical properties of chemically sprayed $Zn_{1-x}Cdx_S$ semiconductor films" , Materials Science in Semiconductor Processing ,vol.10, pp.103-111,2007.

[5] Zoubeida Khefacha,Zohra Benzarti, Mohamed Mnari,Mohamed Dachraoui, "Electrical and Optical properties of $Cd_{1-x}Zn_xS(0<=x<=0.18)$ grown by chemical Bath deposition" , Journal of crystal growth ,vol.260, pp.400-409, 2004.

[6] D.M.P. Mingos and David R. Baghurst "Applications of microwave dielectric heating effects to synthetic problems in chemistry", Chem. Soc. Rev., vol.20, pp.1-47, 1991.

[7] J.J.Zhu, O.Palchik, S.G.Chen and A.Gedanken, J. Phys. Chem. B, 104(2000)7344.

[8] E.Vigil, L.Saadoun, J.A.Ayllon, X.Domenech, I.Zumeta and R .Rodriguez-Clemente, "TiO_2 thin film deposition from solution using microwave heating", Thin Solid Films, vol.365, pp.12, 2000.

[9] O.Palchik, J.J.Zhu and A.Gedanken, "Microwave assisted preparation of binary oxide nanoparticles", J. Mater. Chem., vol.10, pp.1251, 2000.

[10] J.J.Zhu, O.Palchik, S.G.Chen and A.Gedanken, "Microwave Assisted Preparation of CdSe, PbSe, and $Cu_{2-x}Se$ Nanoparticles", J. Phys. Chem. B, vol. 104, pp.7344, 2000.

[11] Yu Zhao, J.M.Hong and J.J.Zhu, "Microwave-assisted self-assembled ZnS Nanoballs", Journal of crystal growth, vol.270, pp.438-445, 2004.

[12] B.Vidhya and S.Velumani, Effect of thickness on the structural, optical and electrical properties of MW-CBD CdZnS thin films, 6th International Conference on Electrical Engineering, Computing Science and Automatic Control(CCE), Toluca, Mexico, November 10-13,2009, ISBN:978-1-4244-4689-6, 649-652.

[13] Dae Sung Kim, Yong Jae Cho, Jeunghee Park, Jungbum Yoon, Younghun Jo and Myung-Hwa Jung, "(Mn, Zn) co-doped CdS nanowires", J. Phys. Chem. C., 111(2007)10861–10868.

[14] Ran Zhai, ShuBo Wang,HaiYan Xu,Hao Wang and Hui Yan , "Rapid formation of CdS,ZnS thin films by microwave –assisted chemical bath deposition" ,Materials Letters ,vol.59,pp.1497-1501,2005.

[15] J. Vidal, O. de Melo, O. Vigil, N. López, G. Contreras-Puente and O. Zelaya-Angel, "Influence of magnetic field and type of substrate on the growth of ZnS films by chemical bath",Thin Solid Films ,vol.322,1998.

[16] Ortega-Lopez M., Avila-Garcia A., Albor-Aguilera M.L., Resendiz V.M.S., "Improved efficiency of the chemical bath deposition method during growth of ZnO thin films", Materials Research Bullettin ,vol.38,no.7, pp. 1241-1248(8),June 2003.

[17] T.Prem Kumar and K.Sankaranarayanan, "Growth and characterization of CdZnS thin films by short duration micro wave assisted- chemical bath deposition technique", Chalcogenide Letters, vol.6, pp.555 – 562, 2009.

[18] M.Oztas, M.Bedir and R Kayali, " Some Properties of $Zn_xCd_{(1-x)}S$ and $Zn_xCd_{(1-x)}S$(In) Thin Films Prapared by Pyrolytic Spray Technique", Pakistan Journal of Applied Sciences, Vol.1, No.4, pp. 534-537, 2001.

[19] R.Sathyamoorthy, J.Dheepa and S.Velumani, "Space charge limited current conduction in Bi_2Te_3 thin films", Materials Characterization, vol. 58, pp.842–846, 2007.

[20] A.D.Schricker, F.M.Davidson, R.J.Wiacek and B.A.Korgel, "Space charge limited currents and trap concentrations in GaAs nanowires", Nanotechnology, vol.17, pp.2681, 2006.

[21] Y.Gu and L.J.Lauhon, "Space-charge-limited current in nanowires depleted by oxygen adsorption", Appl. Phys. Lett., vol.89, pp.143102, 2006.

IEEE Catalog Number: CFP10827-ART
ISBN: 978-1-4244-7314-4
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