

# Synthesis and Characterization of Non-Aqueous Electrodeposited ZnSe Thin Film

S. R. Kumar, Shashikant Rajpal

**Abstract**—A nanocrystalline thin film of ZnSe was successfully electrodeposited on copper substrate using a non-aqueous solution and subsequently annealed in air at 400°C. XRD analysis indicates the polycrystalline deposit of (111) plane in both the cases. The sharpness of the peak increases due to annealing of the film and average grain size increases to 20 nm to 27nm. SEM photograph indicate that grains are uniform and densely distributed over the surface. Annealing increases the average grain size by 20%. The EDS spectroscopy shows the ratio of Zn & Se is 1.1 in case of annealed film. AFM analysis indicates the average roughness of the film reduces from 181nm to 165nm due to annealing of the film. The bandgap also decreases from 2.71eV to 2.62eV.

**Keywords**—Electrodeposition, Non-aqueous medium, SEM, XRD.

## I. INTRODUCTION

A considerable effort has been put forward in recent years for the development of new generations photodiodes. In this regard, the most suitable materials are the semiconductor materials (CdS, CdSe, ZnSe, etc.) which fall in the group of II-VI family of the compounds. Zinc Selenide (ZnSe) is one of the most promising binary semiconductors exhibiting a wide direct band gap. It has potential application in the fabrication of blue light emitting diodes, blue lasers, low cost solar cells, nuclear detector and several optoelectronic devices [1], [2]. Due to its large band gap it can be used as a substitute for CdS material in photovoltaic cell devices [3], [4]. Other significant uses of ZnSe include application in protective and anti-reflection coating for infrared operating electrochemical thermal control surfaces since a large number of photons can reach the absorber layer due to wide band gap [5]. A number of techniques [6]-[11] have been employed in the synthesis of high quality thin films such as, chemical vapor deposition, molecular beam epitaxy, pulse laser evaporation, sputtering and electrodeposition. Electrodeposition is a low cost viable method of synthesizing good quality films suitable for device applications [1], [6], [12]. There are many scientific reports available on the electrodeposition of ZnSe from aqueous solution [13]-[17]. However, the research report on the development of ZnSe thin film through electrodeposition from non-aqueous solution is limited [18]. The formation of ZnSe thin film by electrodeposition from aqueous bath is

difficult due to wide difference in reduction potential of Zn and Se ions. Moreover the electrodeposition from aqueous bath is associated with hydrogen evolution problem that leads to porosity or pin holes defects. Besides the non-aqueous bath provides the flexibility to conduct electrodeposition at higher temperature (even above 150°C) [19], [20]. Higher temperature accelerates the electrodeposition process of ZnSe and also improves the quality of the film [21].

## II. EXPERIMENTAL PROCEDURE

Non-aqueous electrolytic bath of ethylene glycol based solution consisting of 1.6M of ZnCl<sub>2</sub> and 0.045M of H<sub>2</sub>SeO<sub>3</sub> was prepared. These chemicals used were of analytical reagent grade. The bath was aged for 48 hours before use. The copper sheet (substrate) of about 1mm thickness with a surface dimension of 1.5x1.0 cm<sup>2</sup> was at first polished by 400 grit carborandum paper. Thereafter it was cleaned with soap solution and water and finally was dried in an oven. For electrodeposition, 40 ml solution was taken into a predried borosil glass beaker. The electrodeposition was carried out cathodically using a scanning potentiostat (model 680, CH Instruments, USA). A standard three electrode system comprising of copper substrate (Cathode/working electrode), counter electrode (graphite), and reference electrode (platinum wire) was used for electrodeposition of the film. The temperature of the non-aqueous electrolyte was maintained at 160°C. The deposition was carried out at a potential of -1.0V for 2 minutes duration. The deposition potential (-0.1V) was selected on the basis of cathodic polarization characteristics as well as several trials to obtain proper deposit. Thereafter the deposited film was annealed at 400°C with 5 minutes holding. The as deposited and annealed films were characterized by XRD, SEM, EDS, AFM, Optical properties, etc.

## III. RESULTS AND DISCUSSIONS

Figs. 1 (a) and (b) show the XRD patterns of as deposited and annealed at 400°C ZnSe thin film respectively. It is clear from both the patterns that polycrystalline deposits are there with preferred (111) plane orientation. Reflections due to (111), (200), (220) planes of the substrate are also observed. The sharpness of the peak increases due to annealing of ZnSe film. The average grain size increased from 20 nm to 27 nm. In this regard it is important to note that annealing is often required to improve the film quality, crystallinity, etc. [16], [17].

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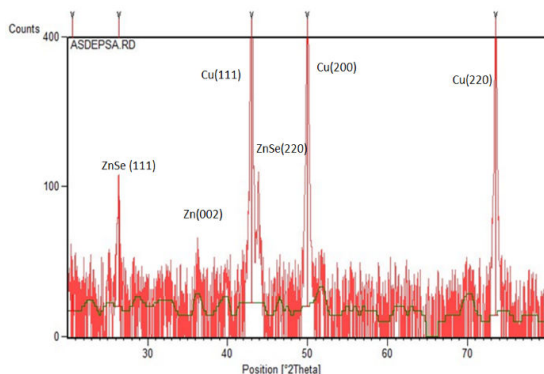


Fig. 1 (a) XRD Spectra of as deposited ZnSe film

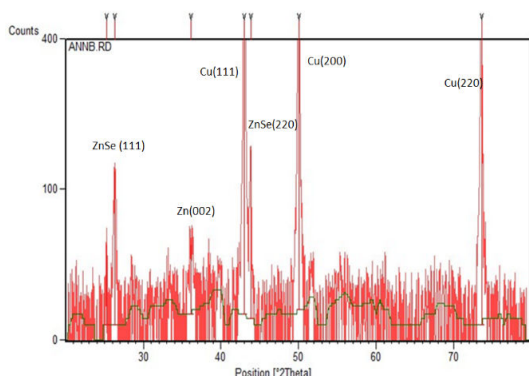


Fig. 1 (b) XRD Spectra of annealed ZnSe film

Figs. 2 (a) and (b) show the SEM photograph of as deposited and annealed films. It is clear from the photograph that grains are uniform and densely distributed over the surface. The contrast of the photograph indicates that some charging effects are seen on the as deposited film. Charging effects are due to loosely bound semiconducting grains. In the annealed sample the grains are of bigger size and spherical due to fusion. The grain size increases by around 20%. The peaks of Zn and Se are observed in both the films as it is evident from EDS spectra in Figs. 3 (a) and (b).

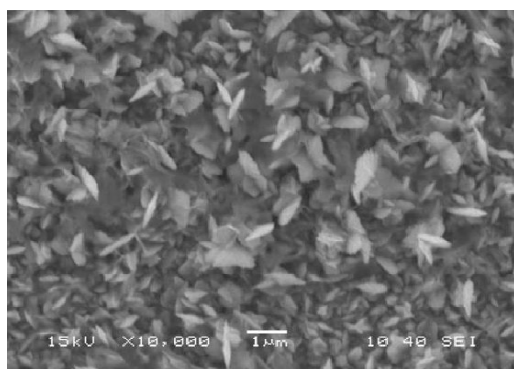


Fig. 2 (a) SEM photograph of as deposited ZnSe film

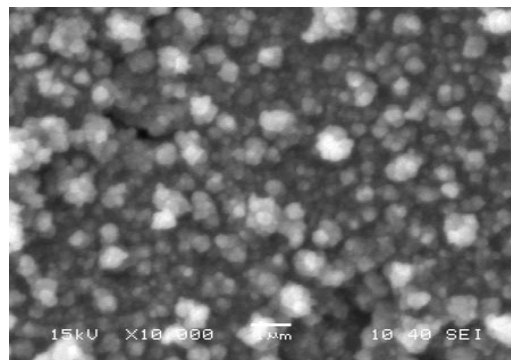


Fig. 2 (a) SEM photograph of annealed ZnSe film

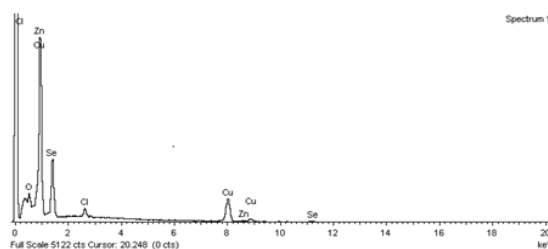


Fig. 3 (a) EDS spectra of as deposited ZnSe film

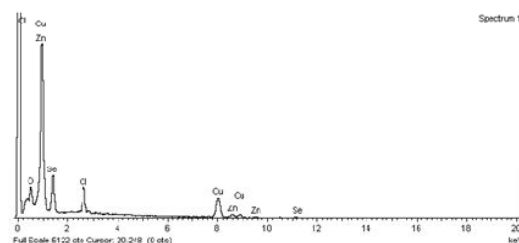


Fig. 3 (b) EDS spectra of annealed ZnSe film

In the As deposited films the atomic percentage are non-stoichiometric but in annealed case it is stoichiometric as given in Table I.

TABLE I  
THE ATOMIC AND WEIGHT PERCENTAGE OF AS DEPOSITED AND ANNEALED ZINC SELENIDE FILMS

Element	As deposited		Annealed	
	Weight%	Atomic%	Weight %	Atomic %
OK	5.45	19.21	7.28	23.51
Cl K	2.29	3.64	6.49	9.46
Cu L	63.98	56.77	55.21	44.88
Zn L	1.29	1.11	13.64	10.78
Se L	26.99	19.27	17.38	11.37
Total	100	100	100	100

The three dimensional images of as deposited and annealed films show the polycrystalline granular morphology of the film as shown in Figs. 4 (a) and (b). The average roughness of the film reduces from 181 nm to 165nm respectively.

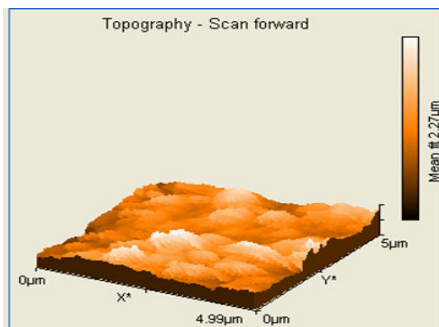


Fig. 4 (a) AFM photographs of as deposited ZnSe

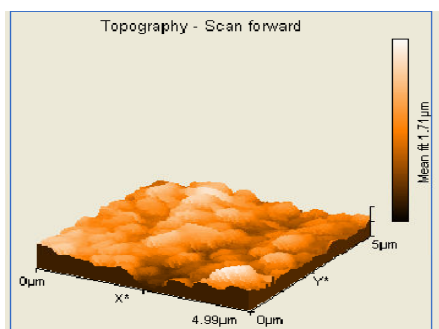
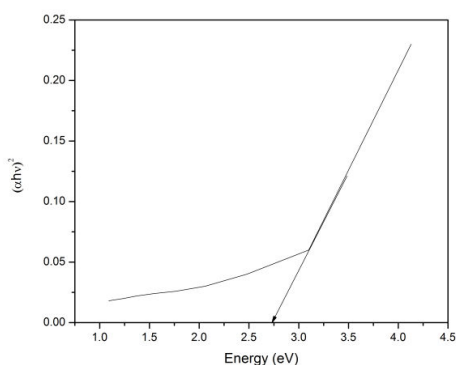
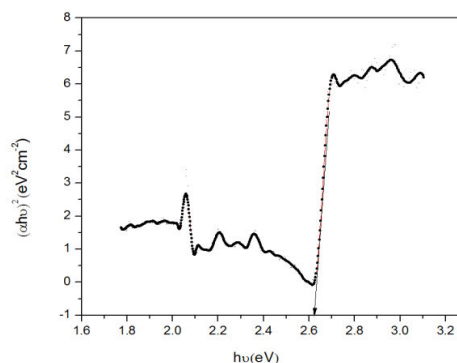


Fig. 4 (b) AFM photographs of annealed ZnSe

The semiconductor with direct bandgap follows the relationship  $\alpha h\nu = A (h\nu - E_g)^{1/2}$  for  $h\nu > E_g$ , where  $\alpha$ ,  $h\nu$ ,  $E_g$ ,  $A$  are absorption coefficient, photon energy, bandgap and proportionality constant respectively. The  $(\alpha h\nu)^2$  is plotted against  $h\nu$  for both the films. The straight line of the plot is extrapolated to zero absorption  $\{(\alpha h\nu)^2 = 0\}$  in order to obtain the bandgap as shown in Figs. 5 (a) and (b). In this work the band gap of the film decreases from 2.71 eV to 2.62 eV.

Fig. 5 (a)  $(\alpha h\nu)^2$  vs  $h\nu$  spectra of as deposited ZnSe filmFig. 5 (b)  $(\alpha h\nu)^2$  vs  $h\nu$  spectra of annealed ZnSe film

#### IV. CONCLUSIONS

ZnSe thin film can be electrodeposited on Copper substrate using a non-aqueous ethylene glycol based solution containing 1.6M of  $ZnCl_2$  and 0.045M of  $H_2SeO_3$ . The as deposited and annealed films are crystalline in nature. Annealing helps the loosely bound, poor adherent grains to spherical, well connected and good adherent film. It changes the film from selenium rich to stoichiometric. The roughness and bandgap of the film reduces due to annealing and it confirms the deposition of semiconducting material.

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#### REFERENCES

- [1] R. Chandamohan, A. Kathalingam, K. Kumar, D. Kalyanaraman, and T. Mahalingam, "Studies on Electro synthesized Semiconducting Zinc Selenide Thin Films," *Ionics*, vol.10, pp.297, 2004.
- [2] H. Morkoe, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, and M. Burns, "Large bandgap SiC, III-V nitride and II-VI ZnSe-based semiconductor device technologies," *J. Appl. Phys.*, vol. 76, pp 1363, 1994.
- [3] K.R. Murali, S. Dhanapandiyana, and C. Manoharana, "Pulse Electrodeposited Zinc Selenide Films and Their Characteristics," *Chalcogenide Lett.*, vol. 6, pp-51, 2009.
- [4] J.M. Dona, and J. Herrero, "Chemical-Bath Deposition of ZnSe Thin Films: Process and Material Characterization," *J. Electrochem. Soc.*, vol. 142, pp-764, 1995.
- [5] N.J. Suthan Kissinger, N. Velmurugan, and K. Perumal, "Substrate-temperature-dependent Structural and Optical Properties of ZnSe Thin Films Fabricated by Using an Electron Beam Evaporation Technique," *J. Korean Phys. Soc.*, Vol. 55, pp- 1577, 2009.
- [6] T. Mahalingam, A. Kathalingam, S. Lee, S. Moon, and Y.D. Kim, "Studies of electro synthesized Zinc Selenide thin films," *J. New Mater. Electrochem. Sys.*, Vol. 10, pp-15, 2007.
- [7] M.C. Harris Liao, Y.H. Chang, Y.F. Chen, J.W. Hsu, J.M. Lin, and W.C. Chou, "Fabrication of ZnSe Quantum Dots Under Volmer-Weber Mode by Metalorganic Chemical Vapor Deposition," *Appl. Phys. Lett.*, Vol. 70, pp-2256, 1997.
- [8] H. Li, and W. Jie, "Growth and characterizations of bulk ZnSe single crystal by chemical vapor transport," *J. Cryst. Growth*, Vol. 257, pp-110, 2003.

- [9] N. Sankar, and K. Ramachandran, "On the thermal and optical properties of ZnSe and doped ZnSe crystals grown by PVT," *J. Cryst. Growth*, Vol. 247, pp-157, 2003.
- [10] E. Guzewicz, M. Godlewski, K. Kopalko, E. Lus-akowska, E. Dynowska, M. Guzewicz, M.M. Godlewski, and M. Phillips, "Atomic layer deposition of thin films of ZnSe—structural and optical characterization, *Thin Solid Films*, Vol. 446, pp-446, 2004.
- [11] A. Rizzo, M. A. Tagliente, L. Caneve, and S. Scaglione, "The influence of the momentum transfer on the structural and optical properties of ZnSe thin films prepared by r.f. magnetron sputtering," *Thin Solid Films*, Vol. 368, pp-8, 2000.
- [12] R.K. Aloney, J.K. Dongre, B.E. Chandra, and M. Ramrakhi-ani, "Photoelectrochemical Solar Cells Based on Electro-codeposited CdSe/ZnSe Double Layer Photoelectrodes," *Chalcogenide Lett.*, Vol. 6, pp-569, 2009.
- [13] K. Singh, and J.P. Rai, "Electrosynthesis and photoelectroactivity of polycrystalline p-zinc selenide," *Phys. Status Solidi*, Vol. A 99, pp-257, 1987.
- [14] C. Natarajan, M. Sharon, C. Levy-Clement, and M. Neu-mann-Spallart, "Electrodeposition of zinc selenide," *Thin Solid Films*, Vol. 237, pp-118, 1994.
- [15] A. P. Samantilleke, M. H. Boyle, J. Young, and I. M. Dharma-dasa, "Electrodeposition of n-type and p-type ZnSe thin films for applications in large area optoelectronic devices," *J. Mater. Sci. Mater. Electron.*, Vol. 9, pp- 2891998.
- [16] G. Riveros, H. Gomez, R. Henriquez, R. Schrebler, R.E. Marotti, and E.A. Dalchiale, "Electrodeposition and characterization of ZnSe semiconductor thin films," *Sol. Energy Mater. Sol. Cells*, Vol.70, pp-255, 2001.
- [17] M. Bouroushian, T. Kosanovic, Z. Loizos, and Z. Spyrellis, "Electrochemical formation of ZnSe from acidic aqueous solutions," *J. Solid State Electrochem.*, Vol. 6, pp-272, 2002.
- [18] Dori. Gal, and G. Hodes, "Electrochemical Deposition of ZnSe and (Zn,Cd)Se Films from Nonaqueous Solutions," *J. Electrochem. Soc.*, Vol. 147, pp- 1825, 2000.
- [19] K.R. Murali, S. Kala, and P. Elango, "Characteristics of ZnS films pulse plated using non-aqueous electrolytes," *J. Mater. Sci. Mater. Electron.*, Vol. 21, pp- 1293, 2010.
- [20] R. Kowalik, P. Zabinski, and K. Fitzner, "Electrodeposition of ZnSe," *Electrochim. Acta*, Vol.53, pp-6184, 2008.
- [21] G. Riveros, H. Gomez, R. Henriquez, R. Sshrebler, and R. Cordova, "Electrodeposition and characterization of ZnX (X=Se,Te) semicond. Thin Films," *Bol. Soc. Chil.Quim.*, Vol. 47, pp-411, 2002.
- and S.K Sharma, *J. Advanced Science Letter* 20(3-4), March 2014 P 686-688.

## Book

1. "Non Aqueous Electrodeposition of Cu-In Alloy", Shyam Kumar, Lap Lambert Academic Publishing GmbH and Co. KG, Germany, 2010.

"Structure, Composition and Surface roughness of CIGS nanocrystalline Films", S.R Kumar and P.K Mishra, presented and awarded best paper in oral presentation in International Conference on Advances in Engineering and technology- 2011 was held at EGS Pillai Engineering College, Nagapattinam, Tamil Nadu, India from 27th and 28th May 2011.

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## Paper(s):

1. "Development of Nanocrystalline ZnSe Thin Film through Electrodeposition from Non aqueous Solution", Shyam Ranjan Kumar, Mohan N. and Joydeep Maity, *J. Scripta Mat.* 67 (2012) 396-399.
2. "Electrodeposition of CdSe Nanocrystalline Thin Film using Non aqueous", S.R. Kumar, Binod Kumar, *Int. J. of Nanotechnology and Applications* 6 No 3 (2012) 258-263.
1. 3. "Effect of Zn as Nanofilm of CdS deposited by Chemical Bath Method in Non aqueous Medium", S.R Kumar, Suresh Kumar, S. Sahu, D. Roy