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 material are the semiconductor material (CdS,CdSe, ZnSe, etc.) which fall in the group of II-VI family of the compounds. Zinc Selenide (ZnSe) is the 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 use of ZnSe include application in protective and anti-reflection coating for infrared operating electrochemical thermal control surfaces since a large number of photon 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 film such as, chemical vapor deposition, molecular beam epitaxy, pulse laser evaporation, sputtering and electrode position. Electrode position 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 electrode position of ZnSe from aqueous solution [13]-[17]. However, the research report on the development of ZnSe thin film through electrode position from non-aqueous solution is limited [18]. The formation of ZnSe thin film by electrode position from aqueous bath is difficult due to wide difference in reduction potential of Zn and Se ions. Moreover the electrode position 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 electrode position at higher temperature (even above 150°C) [19], [20]. Higher temperature accelerates the electrode position process of ZnSe and also improves the quality of the film [21].

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II. Experimental Procedure

Non-aqueous electrolytic bath of ethylene glycol based solution consisting of 1.6M of $ZnCl_2$ and 0.045M of H_2SeO_3 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^2 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 electrode position 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 electrode position 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 trails to obtain proper deposit. There after 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 surfaces of as deposited and annealed at 400°C ZnSe thin film respectively. It is clear from both the surfaces that a 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].

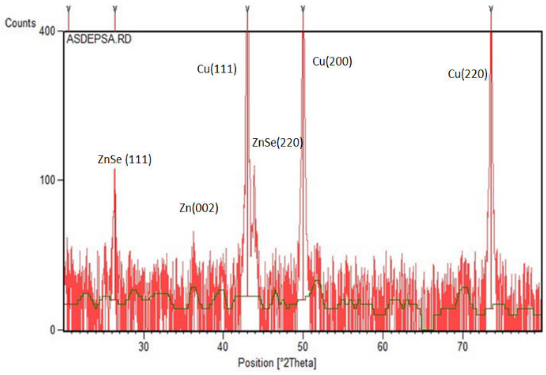

Fig. 1 (a) XRD Spectra of as deposited ZnSe film

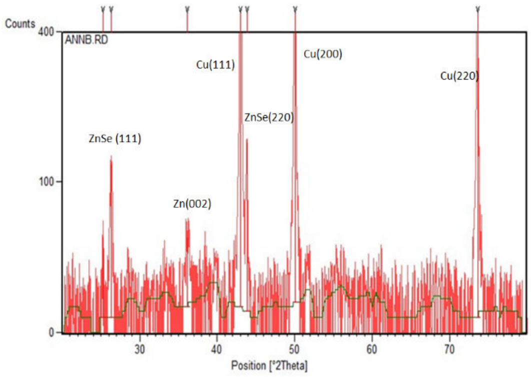

Fig. 1 (b) XRD Spectra of annealed ZnSe film

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).

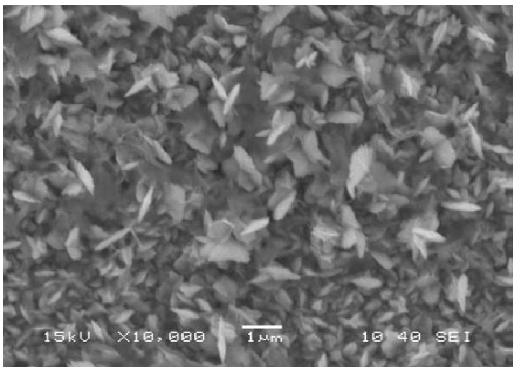

Fig. 2 (a) SEM photograph of as deposited ZnSe film

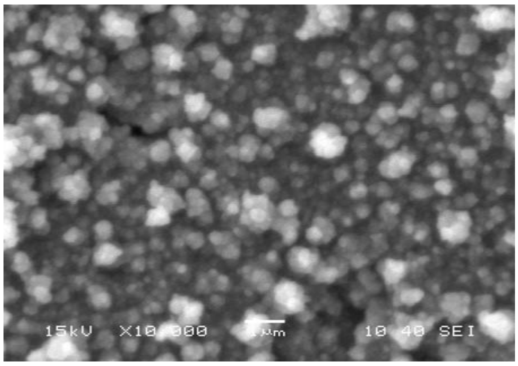

Fig. 2 (a) SEM photograph of annealed ZnSe film

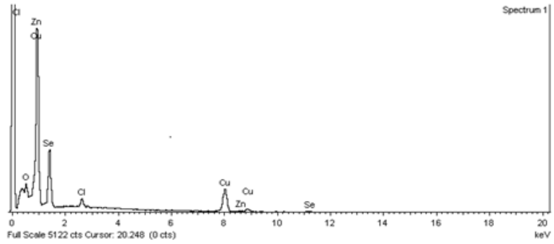

Fig. 3 (a) EDS spectra of as deposited ZnSe film

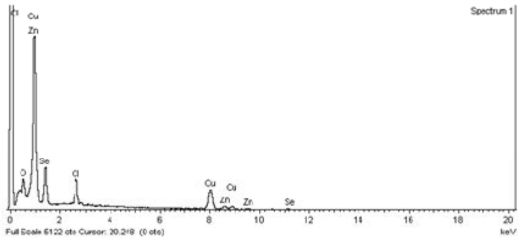

Fig. 3 (b) EDS spectra of annealed ZnSe annealed film

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 %
O K	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.

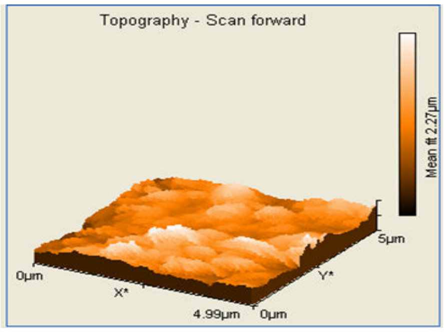

Fig. 4 (a) AFM photographs of as deposited ZnSe

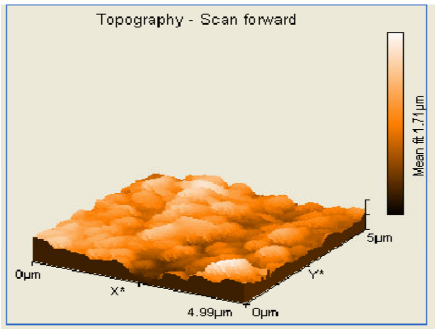

Fig. 4 (b) AFM photographs of annealed ZnSe

The semiconductor with direct bandgap follows the relationship $\alpha h\nu = A\,(h\nu\text{-}Eg)^{1/2}$ for $h\nu>Eg$, where α, $h\nu$, Eg, 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.

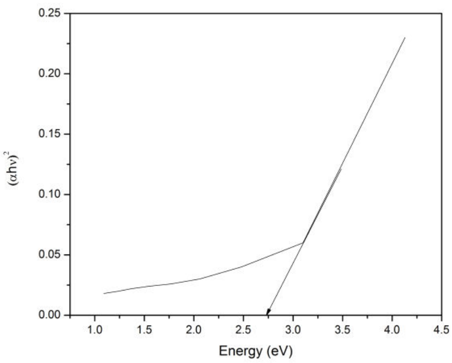

Fig. 5 (a) $(\alpha h\nu)^2$ vs $h\nu$ spectra of as deposited ZnSe film

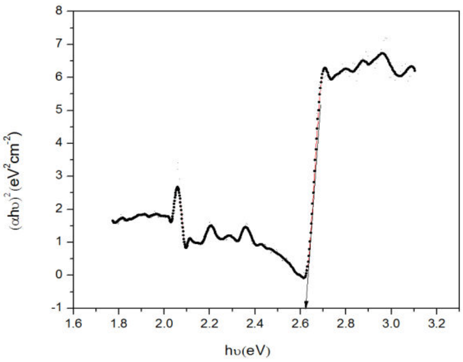

Fig. 5 (b) $(\alpha h\nu)^2$ vs $h\nu$ spectra of annealed ZnSe film

IV. Conclusions

ZnSe thin film can be electrodeposited on Copper substrate using a non-aqueous ethylene gylcol 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 stoichicmetric. The roughness and bandgap of the film reduces due to annealing and it confirms the deposition of semiconducting material.

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