Electrodeposition Of Zinc Selenide Films On Different Substrates And Its Characterization

C.I. Nweze, A. J. Ekpunobi

Abstract: Zinc Selenide (ZnSe) thin films have been successfully deposited on two different substrates using electrodeposition method at different time intervals under direct voltage of 3V. XRD pattern of the films deposited on metallic zinc substrates are indexed to cubic crystal structure at all deposition times. The dominant orientation lies on (111) plane of reflection and also more planes of reflection are formed at high deposition time which shows that polycrystalline films were deposited. XRD pattern of the films deposited on the conducting glass (Indium doped Tin Oxide (ITO)) are indexed to wurzite (hexagonal) crystal structure. Investigation reveals that both the film thickness and the grain size of the deposited ZnSe thin films increase with the deposition time for the films deposited on the two substrates. Electrical analysis of the deposited ZnSe thin films showed that the films deposited on the metallic Zinc substrate has lower electrical resistivity than the films deposited on the ITO and the resistivity increases with the increase in the thickness of the deposited films.

Keywords:, Cubic Structure, Grain Sizes, ITO, XRD, Wurzite Structure

1. INTRODUCTION

In recent years, synthesis of materials, thin films, has attracted great interest. Also these materials have been widely studied for their unique properties, both physical and chemical. The preparation of materials with controlled sizes, morphologies and size distribution is always potentially important in the synthesis of materials suitable for optoelectronics and luminescent applications.[1-3]As one of the most important II – V group semiconductors, Zinc Selenide (ZnSe) with a room temperature bulk bandgap of 2.7eV, is a good candidate for short wavelength lasers and other photoelectronics devices such as blue-green diode lasers and tuneable mid – IR laser sources.[1,3-5]Dimensionality, size and size distribution are known to play important roles in determining the physical and chemical properties of ZnSe thin film materials.[6] Because of the novel properties and various potential applications, ZnSe thin film materials, with typical grain size less than 10nm are attracting increasing attention from researchers all over the world.[7] Thin film materials with grain size less than 10nm exhibit properties that are often superior and sometimes completely new, in comparison with those of conventional coarse grained materials because of their small size and consequently the large volume fraction of atoms in or near the grain boundary.[7,8] Some outstanding properties of ZnSe thin film materials of smaller size include, increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, increased corrosion and wear resistance.

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2. EXPERIMENTAL

All reagents were used as purchased and solvents were distilled prior to use. ZnSe films were deposited on indium doped tin oxide (ITO) (conducting glass) and Zinc metallicsubstrates by electrodeposition method. Prior to use, the substrates were cleaned with detergent solutions, rinsed with distilled water and then rinsed with acetone, methanol and distilled water and dried before use. An area of about 6.25 cm^2 of the substrate was dipped into the electrolyte (solution). The electrodeposition bath system is composed of Zinc tetraoxosulphate VI Heptahydrate($ZnSO_4.7H_2O$)as source of cation (Zn^{2+}), Selenium IV Oxide (SeO_2) as source of anion (Se^{2-}), Tetra-oxo Sulphate VI acid (H_2SO_4) as pH control, Potassium tetraoxo Sulphate VI (K_2SO_4) as inert electrolyte and distilled water.

2.1. Preparation of solution

0.14M solution of $ZnSO_4$.7H2O was prepared by dissolving 20g of it in 500ml of distilled water and it dissolved completely. 0.054M solution of SeO_2 was prepared by dissolving 3g of it in 500ml of distilled water and when thoroughly shaken, it dissolved completely in water with clear solution. Again 0.1M solution of H_2SO_4 was prepared by dissolving 3ml of it in 500ml of distilled water and it dissolved completely. Finally 0.092M of K_2SO_4 was prepared by dissolving 8g of it in 500ml of distilled water and it dissolved completely with a clear solution.

2.2. Electrodeposition

Deposition of ZnSe on conducting glass(ITO) and Zinc metallic substrates was carried out using electrodeposition technique. 28ml, 28ml, 5ml, and 4ml solutions of $ZnSO_4.7H_2O$, SeO_2, H_2SO_4, and K_2SO_4 respectively were measure in 100ml beaker and stirred to achieve uniformity and the resultant solution was used for the deposition. The substrates (ITO and Zinc) were used as the cathode while a copper electrode was used as the anode. The deposition was done under 3V at room temperature (26^{0}C) and the pH of 1.8 and the deposition took place for 30secs. The same process was repeated for 60 and 90secs and in each case metallic Zinc and ITO substrates were separately used. The possible reaction mechanism is shown below:

$$Zn^{2+} + 2e^- \rightarrow Zn$$

$SeO_2 + H_2O \rightarrow H_2SeO_3$

$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$

$Zn + Se \rightarrow ZnSe$

At the end of deposition, the coated substrates were washed well with distilled water and air dried at room temperature. The thickness of the deposited films was determined gravimetrically. The deposited films were taken for structural characterization using Cu-Kα (λ = 0.154nm) on an MD-10.3 diffractometer. The samples were mounted flat and scanned between 10^o and 80^o in a step size of 0.05 and with a count rate of 9s. Electrical characterization of the samples was done using a four point probe.

3. RESULTS AND DISCUSSION

Figures 1-3 show the X-Ray Diffraction (XRD) pattern of the films deposited on Zinc metallic substrate under the experimental optimum conditions for 30, 60 and 90secs respectively. For the samples deposited at 30 and 60secs, the prominent planes of reflection are indexed to (111), (220), (311), and (400) (**figures 1 and 2**) while the sample deposited at 90sec shows five prominent plans of reflection indexed to (111), (220), (311), (400) and (331) (**figure 3**). These planes of reflection show that cubic structure of ZnSe was formed on the zinc metallic substrate and the number of planes of reflection shows that the polycrystalline nature of the deposited films increased as the time of deposition increases.As the time of deposition increases, the dominant orientation in the (111) plane increase, this shows that the preferred orientation of the thin film deposited lies along (111) plane.Again it is also observed that the broaden of the peaks decreases as the time of deposition increases (**figures 1, 2 and 3**), this shows that the film deposited at 30secs has smaller grain size compared to the films deposited at 60 and 90secs. The average crystalline grain size calculated were 1.68Å, 2.04Å and 2.28Å for films deposited at 30, 60 and 90sec respectively. The film thickness of 0.13µm, 0.26µm and 0.33µm were calculated for the film deposited at 30, 60 and 90secs respectively.The ZnSe thin film deposited at 90secs has highest resistivity at room temperature (26^o), with a value of 12.10 x 10^4 Ωm, while the ZnSe film deposited at 60secs has resistivity of 6.54 x 10^4 Ωm and 4.93 x 10^4 Ωm for the film deposited at 30secs.

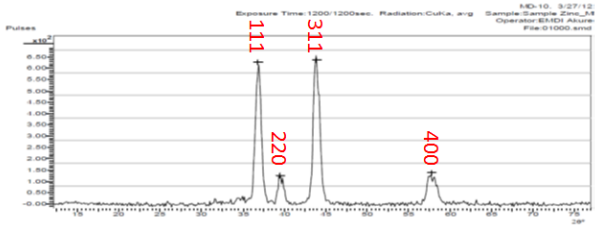

Figure 1:X-ray diffraction pattern of ZnSe thin film deposited on Zinc metallic substrate for 30secs under optimum experimental conditions.

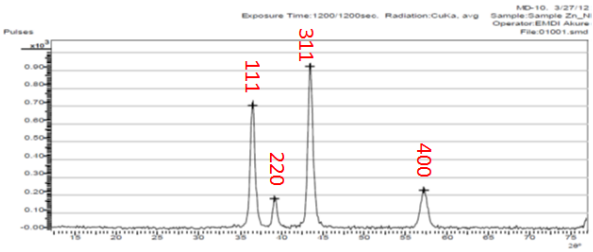

Figure 2:X-ray diffraction pattern of ZnSe thin film deposited on Zinc metallic substrate for 60secs under optimum experimental conditions.

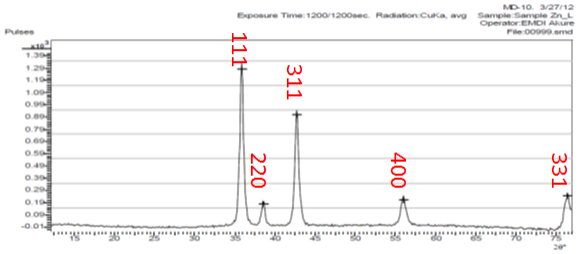

Figure 3:X-ray diffraction pattern of ZnSe thin film deposited on Zinc metallic substrate for 90secs under optimum experimental conditions.

Figures 4 – 6 show the XRD pattern of the films deposited on ITO under the experimental optimum conditions for 30, 60 and 90secs respectively. The observed diffraction peaks in these patterns can be indexed to wurzite (hexagonal) structure. The several peaks of hexagonal phase of ZnSe have been obtained due to diffraction from (002), (101), (110), (103), (112), (202), (203), (210) and (105) planes of ZnSe. The calculated grain size increased with the deposition time and the average crystalline grain size of 1.55Å, 2.40Å and 2.88Å were obtained at deposition time of 30, 60 and 90secs respectively. The thickness of the film deposited on ITO was 0.10µm, 0.18µm and 0.26µm at 30, 60 and 90secs respectively. The resistivity of the deposited films at room temperature was 1.01 x10^9 Ωm, 6.91 x 10^7 Ωm and 1.32 x 10^8 Ωm for the films deposited on conducting glass at 30, 60 and 90secs respectively.

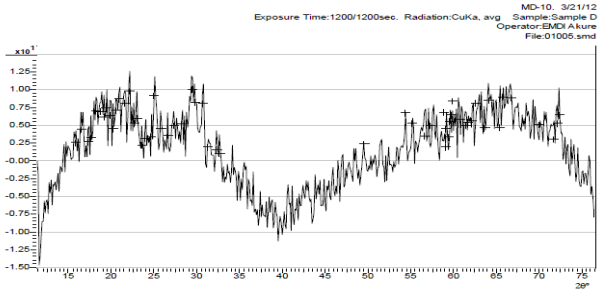

Figure 4:X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 30secs under optimum experimental conditions

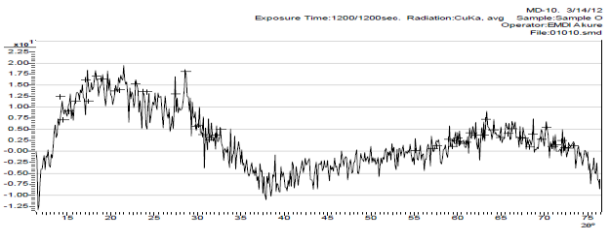

Figure 5:X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 60secs under optimum experimental conditions

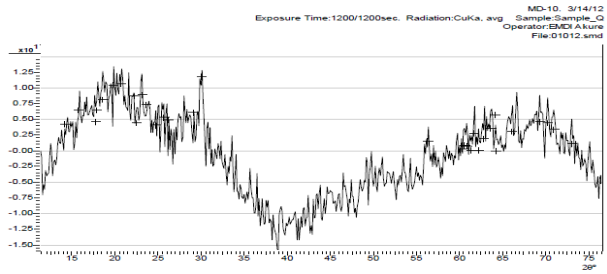

Figure 6:X-ray diffraction pattern of ZnSe thin film deposited on conducting glass (ITO) substrate for 90secs under optimum experimental conditions

4. CONCLUSION

Electrodeposition technique has been used to deposit polycrystalline of ZnSe thin filmon two different substrates. Investigation reveals that the crystal structure of the deposited films depend on the nature of the substrate used. Cubic crystalline structure of ZnSe was deposited on the metallic zinc substrate with preferred orientation in (111) plane at high deposition time while hexagonal crystalline structure of ZnSe was deposited on the conducting glass (ITO). Both the crystalline grain size and the thickness of the films deposited on the two different substrates increased with deposition time. The resistivity of the films deposited on the metallic substrate is lower than that of the films deposited on ITO and this might be as a result of the conductivity of the metallic substrate used, again the semiconductor-metallic interface must have played a significant role in increasing the conductivity of the ZnSe thin films.

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REFERENCE

1. Yang J., Wang G., Liu H., Park J., and Chen X. (2009). Mater. Chem. Phys. 115, 204-208.

2. Zawani E.L. and Shabani E.L. (2004). J. Solids. 27, 223-232.

3. Jana S., Baek I.C., Lim M.A., and Seoki S.I. (2008). J. Colloid interface Sci. 322, 437 – 477.

4. Cheng C.L. and Chen Y.F. (2009). Chem. Physics. 115, 158-160.

5. Jiang C, Zhang W., Zou G., Yu W., and Qian Y. (2005). Nanotechnol. 16, 551-554.

6. Monajjemi M. Khaleghian M., Tadayonpour M., and Mollaamin F. (2010). Int. J. Nanosci. 9, 517-529.

7. Gurrappa I and Binder L. (2008). A review, Sci. Technol. Adv. Mater. 9, 1-11.

8. Desphande V.V., Chandra B., Caldwell R., Novikov D.S., Hone J., and Bockrath M. (2008). Science 323, 106 – 110.

9. El-Sherik A. M, Erb U, Palumbo G and Aust K T (1992). Scr. Metall. Mater. 27, 1185– 1192.

10. Cheung C, Palumbo G and Erb U 1994 Scr. Metall. Mater. 32, 735– 741.

11. Wong L, Ostrander D, Erb U, Palumbo G and Aust K T 1994 Nanophases and Nanocrystalline Structures ed R D Shull and J M Sanchez (Warrendale, PA: TMS) p 85

12. Erb U, Palumbo G, Zugic R and Aust K T (1996). Proceedings and Properties of Nanocrystalline Materials ed C Suryanarayana, J Singh and F H Froes (Warrendale, PA: TMS) p 9

13. Anuar K., Tan W.T., Dzulkefly K.A., Jelas H., Ho S.M., Shanthi M. and Sarvanan N. (2010). Journal. Kimia. 4, 1 – 6

14. Ezenwa I.A, Okereke N.A. and Umeokwonna N.S. (2010). Journal of Basic Physical Research 1, 9 – 12.

15. Okereke N.A. and Ekpunobi A.J. (2011). Journal of Non-oxide glasses. 3, 31-36.

16. Molloamin F., Gharibe S., and Monajjemi M. (2011). International Journal of the Physical science. 6, 1496-15500.