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Characterization Studies on Field Assisted-Electrostatic Spray Pyrolysis Deposition of Zns Thinfilms for Optoelectronic Applications

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Abstract We investigated the properties of zinc sulphide thinfilms deposited using a field assisted electrostatic spray pyrolysis deposition apparatus at an optimized substrate temperature, time, pressure and flowrate of 300°C, 10minutes, 1atm and 0.5ml/min respectively. The ZnS thin films were there-after annealed at 350°C for 3hours. The influence of process parameters on the properties of the ZnS thinfilms were investigated using x-ray diffractometry, uv-spectrophotometry and profilometry. The morphology of the films and the nano-mechanical properties of the optimized thinfilms were also investigated using nano-indentation technique. The optimized films obtained were transparent, homogeneous, uniformly dispersed with an average surface thickness of 500nm and roughness of 206.65nm. It had a polycrystalline hexagonal structure and a relative optical transmittance in the visible spectrum of more than 60%. The morphology of the film revealed a highly oriented nanostructure composed of uniformly and evenly distributed pore materials. The pores; inevitably influencing the optical properties of the films. The films would find applications in dielectric filters, electroluminescent and solar cells devices.

Keywords Field assisted, Electrostatic spray pyrolysis, Zinc sulphide films, Characterization, Optoelectronics

1. Introduction

Zinc sulphide thinfilms are used in several optoelectronic devices which include UV light emitting diodes, blue light emitting diodes, emissive flat screens, electroluminescent devices and antireflection coatings in solar cell technology [1-3]. Being a known semi-conductor and with its wide band gap, it can be used as a transparent material in the visible light region as dielectric filters. ZnS occurs mainly in two phases which are α-phase and β-phase [1].

Different techniques have been employed in the preparation of ZnS thinfilms. These include thermal decomposition, sol-gel, precipitation, forced hydrolysis, sputtering, vacuum evaporation, spin coating, electrodeposition, chemical bath deposition (CBD) and spray-based (aerosol) production [4-9]. Amongst these methods, spray pyrolysis enables both kinetic (nucleation/ growth) and thermodynamic control through the fine tuning of deposition parameters giving rise to enhanced tailored materials for specific applications [10-11].

The technique of field assisted electrostatic spray pyrolysis of ZnS thinfilms offers the possibility of depositing layered films and films with homogeneous composition gradients over a large area of the substrate through changing of the composition of the spray solution and deposition parameters [10-16]. This method which is a one –step can be used to produce thinfilms which are highly homogeneous, uniformly shaped and of high purity in large quantities [17]. It is a relatively cheap and dry deposition process with adequate control over deposition rate [8].

In spite of the fact that ZnS has been extensively investigated in the light of its structural and optical properties, many issues still remain to be understood on the applicability of the films in optoelectronics.

In this paper, production of homogeneous and uniformly dispersed ZnS thinfilms is undertaken using field assisted electrostatic spray pyrolysis deposition apparatus. The influence of the optimized molar concentrations of the zinc acetate and thiourea precursors on the ZnS thinfilms produced is studied. X-ray diffraction, uv-visible spectroscopy, nano-indentation studies and profilometry techniques are used to evaluate the influence of the process parameters on the properties of the ZnS thinfilms.

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2. Experimental

The ZnS thinfilms were deposited on glass slides by the spray pyrolysis technique described in previous works [5-7]. The temperature at which deposition was carried out was varied using 300°C, 350°C and 400°C respectively to ascertain the influence of process temperature and the optimized temperature was found to be 300°C. In the same manner, the deposition time was varied from 5min, 10mins and 20mins respectively and it was observed that uniformly deposited films was obtained at 10minutes deposition time. The deposition process was carried out at an optimized substrate temperature, time, pressure and flowrate of 300℃, 10minutes, 1atmoshphere, and 0.5ml/min respectively followed by annealing at 350°C in open air for 3hrs, taking into effect the influence of the following parameters on the film thickness: the spray nozzle- substrate distance, the substrate temperature, the concentration of the precursor solution, and the amount of sprayed precursor solution.

Essentially, the chemical reaction in the formation of ZnS thinfilms from Zinc acetate and thiourea in an aqueous medium is given as follows:

$$Zn\ (CH_3COO)_3 \rightarrow Zn^{2+} + 3CH_3COO^- \quad (1)$$

From thiourea, the sulphide ions are liberated as follows:

$$SC(NH_2)_2 + OH^- \rightarrow SH^- + CH_2N_2 + H_2O_2 \quad (2)$$

$$SH^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (3)$$

The overall redox reaction therefore for the formation of ZnS thinfilms is:

$$Zn^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow ZnS + CH_2N_2 + 2H_2O \quad (4)$$

The formation of the ZnS thinfilms is a reaction between the Zn^{2+} and S^{2-} ions of the zinc acetate and the thiourea in aqueous solution of acetic acid, deionized water and absolute ethanol in a defined ratio. The initial solution was prepared using 100ml of zinc acetate (0.1M $Zn(CH_3COO)_3$) and 100ml of thiourea (0.1M $SC(NH_2)_2$) in aqueous solution of acetic acid, deionized water and absolute ethanol in the ratio of 2:3:5 respectively. The precursor was atomized electrostatically in high voltage of about 17KV. The glass substrates were thoroughly cleaned with acetone to remove any impurities before being used. The ZnS thinfilms were thereafter annealed at 350℃ for three (3) hours. The thickness and roughness of the films were measured using a Veeco Dektak 150 Stylus Surface Profiler. The transmittance and absorbance of the films was measured using a UV-Vis Spectrophotometer (Avantes) in the wavelength range 200-900nm. The morphology of the films and the nano-mechanical properties of the optimized ZnS thinfilms was investigated using a nano-indenter equipped with AFM capability (HYSITRON INC, TI 750 Ubi System), while the structural analysis of the deposited and annealed films was performed using a PANalytical XPERT PRO MPD X-ray diffraction PW 3040/60 system with CuKα monochromatic radiations. The wavelength, accelerating voltage and current were 1.54060A, 45KV and 40mA respectively. The data was collected over a scanning range of angle 2Θ = 10℃ to angle 2Θ = 100℃ using a step size of 0.0840° and an acquisition scan step time of 92.0750secs. The interplanar distance, lattice parameters, preferential growth orientation and grain sizes was evaluated from the spectra.

3. Results and Discussions

3.1. Structural Analysis

The X-ray diffractogram of ZnS thinfilms obtained by the field assisted electrostatic spray pyrolysis deposition technique at the three operating temperatures of 300°C, 350°C and 400°C process parameters is shown in Figure 1 below.

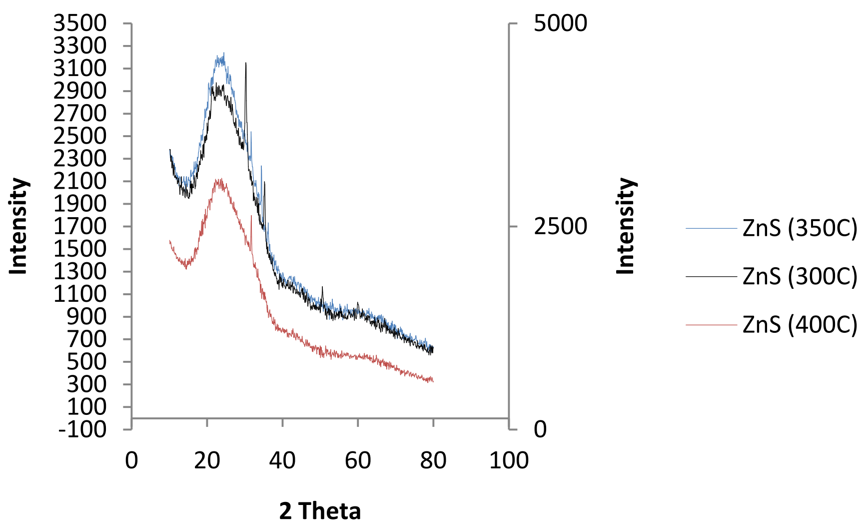

Figure 1. X-ray diffraction pattern of ZnS thinfilms deposited at 300C, 350C and 400C and annealed at 350C process parameter

XRD analysis revealed that the sample deposited at 300°C gave the optimal result. The spectra showed the presence of three pronounced peaks at 2Θ positions of 30.2335˚, 35.1872˚ and 50.5514˚ for the sample deposited at 300°C. This is indicative of a highly preferential growth which is oriented towards the [111] direction/plane with reference to the more pronounced peak position 30.2335˚ thereby exhibiting a polycrystalline combination of hexagonal and cubic structures though the hexagonal phase predominates. This is in agreement with several authors who had reported singly; cubic and hexagonal structures and combinational; cubic and hexagonal phases for ZnS films deposited by both chemical vapour deposition and spray pyrolysis techniques [19, 20]. The structural parameters such as interplanar spacing, lattice constant and grain size were determined from the XRD software and by the use of appropriate equations. At the substrate temperature of 300 ℃, the structural parameter of ZnS films formed at the highest pronounced peak gave a peak position 2Θ of 30.2335˚, Full Width at Half Maximum (FWHM) of 0.3306, d-spacing of 2.95620A, calculated lattice constant, 'a' of 5.378A, orientation plane/direction of [111] and grain size, 'D' of 243.65nm.The identification and assignments of the observed diffraction patterns were found to be in good agreement with International Center for Diffraction Data (ICDD) reference values. In essence, cubic and hexagonal structures were obtained by the field assisted- electrostatic spray pyrolysis deposition technique employed. This is in agreement with reports of several authors [21-26]. However, the structural parameters were obtained with reference to the more pronounced [111] peak position while Scherrer's formula was used to determine the crystallite size and this was found to be 243.65nm.

3.2. Optical Properties

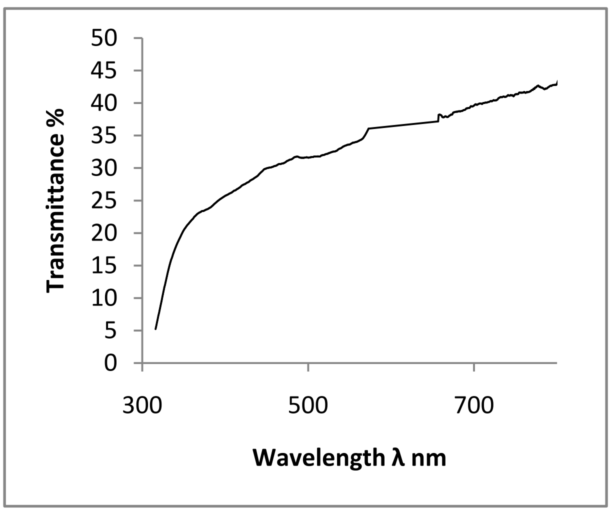

Figure 2. Optical transmittance spectra of the ZnS thinfilm

Figure 2 and Figure 3 above shows the transmittance and absorbance spectra in the wavelength range of 200-900nm for the ZnS thinfilms deposited at the optimized process parameters of temperature of 300°C and annealed at 350℃ for 3hours. From the figures, it was observed that at the optimized process parameters, there was an improvement in the optical transmittance as well as absorbance of the thinfilms which were attributable to the surface thickness of the films. Generally, the transmittance of the deposited thinfilms increased with wavelength between 350nm to 800nm which indicated that the region of absorbance lies below the wavelength. It was also observable that as the ZnS thinfilms were annealed, there was a general increase in the average transmittance and absorbance. This was because of the decrease in the defect density caused by the annealing process. The relative optical transmittance in the uv-vis spectrum was observed to be more than 60% indicative of a good material for optoelectronic devices. The ZnS thinfilms had excellent absorption at relatively short wavelength regions. However, it was observed that increasing the wavelength resulted in decreased absorption. In all cases, the absorption coefficient α and absorption index (extinction coefficient) K_f were obtained from the transmittance, T, as follows.

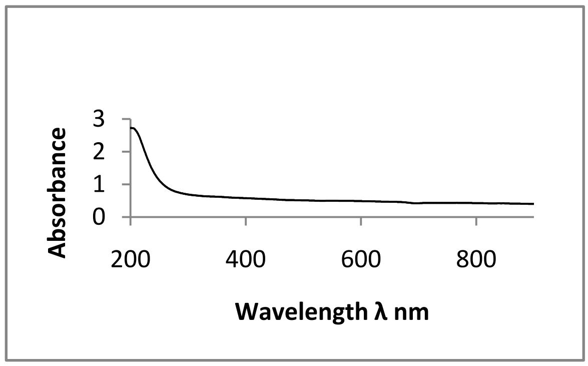

Figure 3. Optical absorbance spectra of the ZnS thinfilm

$$K_f = [2.303 * \log (1/T)\ \lambda]/4\pi t \quad (5)$$

Where't' is the thinfilm thickness. Generally, absorption coefficient 'α' and absorption index, K_f, are related by,

$$\alpha = 4\pi t/\lambda \quad (6)$$

Estimation of the optical energy gap of the ZnS thinfilms was done from the uv-spectrophotometry and this was found to be 3.436eV. The optical study of the ZnS thinfilms prepared at 300 ℃ had the following parameters: Film thickness- 500nm, absorption coefficient ($10^6 m^{-1}$) – 4.54, absorption index – 0.18058 and estimated energy gap (eV) of 3.436.

3.3. Surface Profilometry

The average surface thickness and roughness of the optimized ZnS thinfilms was obtained using a Veeco Dektak 150 Stylus Surface Profiler. It was observed that at the optimized process condition, the average surface thickness and roughness were 500nm and 206.65nm respectively. The films were observed to be homogeneous and uniformly dispersed on the substrates.

3.4. Nano-indentation Morphology

The nanographs of the deposited ZnS thinfilms show that the films have highly oriented nanostructures. The pores inevitably influenced the optical properties of the thinfilm. The morphology of the film revealed a highly oriented nanostructure composed of uniformly and evenly distributed pore materials. The films showed a flat, dense, evenly and uniformly distributed thin film surface. This is shown in figures 4, 5 and 6 below.

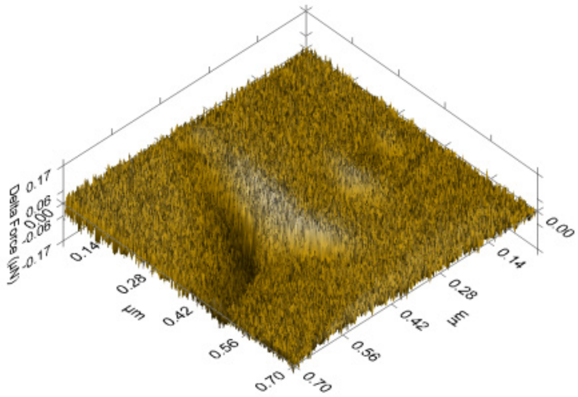

Figure 4. Nanograph of ZnS sample annealed at 350°C

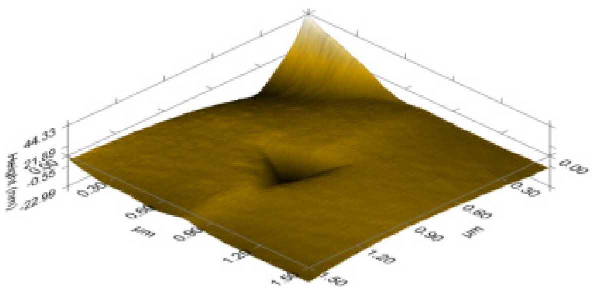

Figure 5. ZnS annealed 3D morphological depth indentation of thinfilm

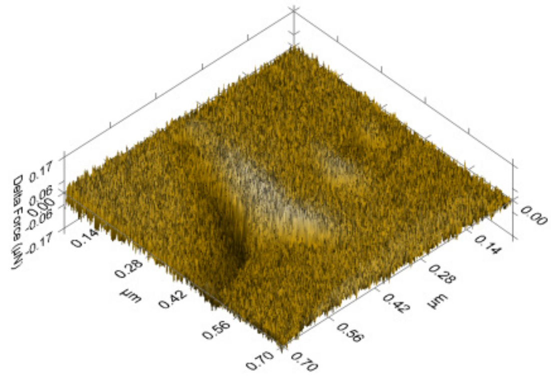

Figure 6. Unannealed ZnS nanograph of sample deposited at 300C

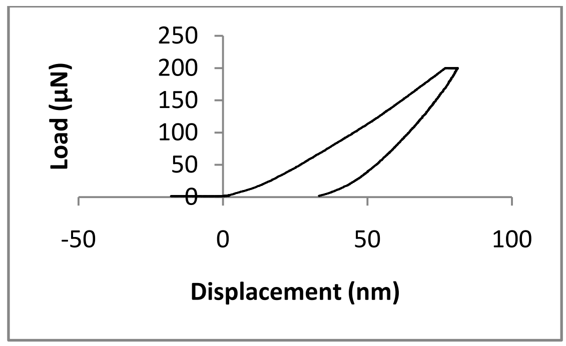

Figure 7. Actuation- Displacement graph for unannealed ZnS sample

From figures 7 and 9 above, it can be observed that the maximum load applied was 200µN. The Reduced Modulus of the annealed films was 33.04GPa with a hardness of 1.62GPa. The unannealed films had a Reduced Modulus of 15.22GPa and a hardness of 1.39GPa. The maximum force achieved at this point in all situations was 200µN. The strain rate shown in figure 6 above for the unannealed sample was observed to be 8.89nm/sec while that shown in figure 8 above of the annealed sample was 6.67nm/sec implying a constant applied strain to both annealed and unannealed samples. This shows the depth profile of the film deposited at the boundary point between the film and the substrate.

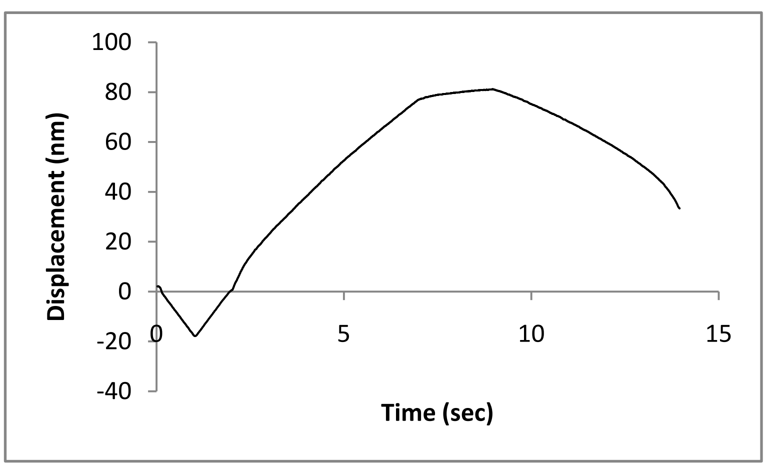

Figure 8. Constant strain rate for the unannealed ZnS samples

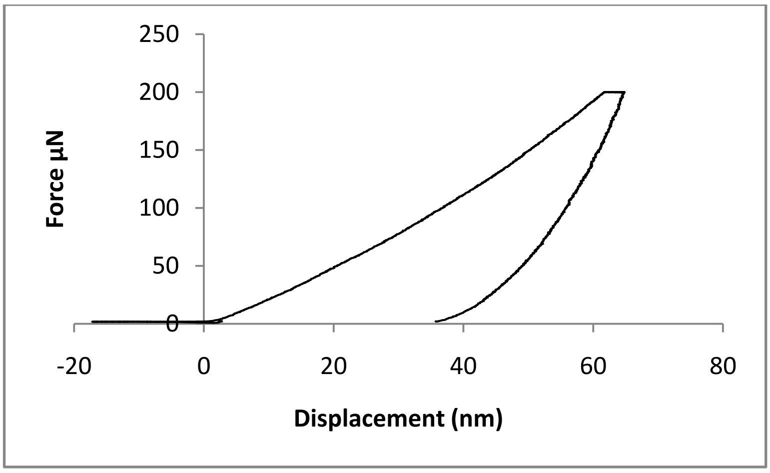

Figure 9. Actuation- Displacement graph for annealed ZnS sample

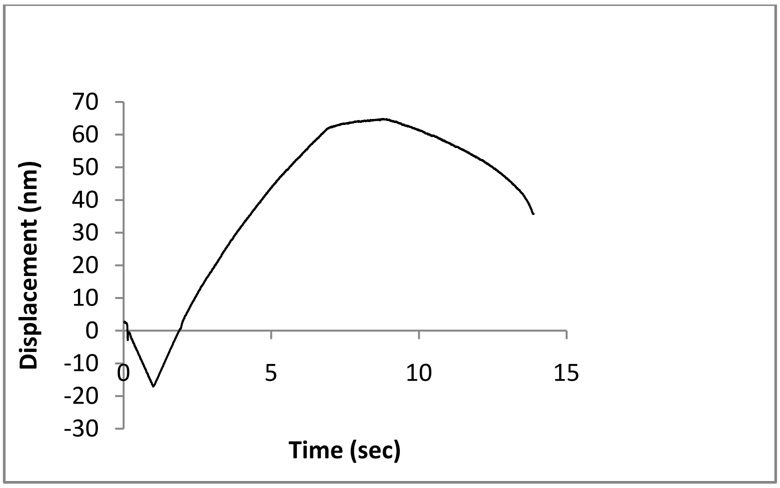

Figure 10. Constant strain rate for the annealed ZnS samples

4. Conclusions

Transparent, homogeneous and uniformly dispersed ZnS thinfilms were successfully deposited using field assisted – electrostatic spray pyrolysis apparatus at the optimized substrate temperature, time, pressure, and flowrate of 300℃, 10minutes, 1atmosphere and 0.5ml/min respectively. Polycrystalline ZnS films with reference to the more pronounced (111) plane at 2Θ peak position of 30.2335° was obtained at the deposition temperature of 300 ℃ and annealed temperature of 350 ℃ for 3hours. The nano-mechanical indentation studies of the thinfilms showed the films have highly oriented nanostructures whose influences on the optical properties of the films are significant. The films showed a flat, dense, evenly and uniformly distributed surface. The optical properties of the thinfilms showed an improvement in optical transmittance occasioned by the decrease in the defect density due to the annealing process. Relatively, optical transmittance in the uv-vis spectrum was more than 60% with surface properties of thickness and roughness obtained as 500nm and 206.65nm respectively. Estimation of the optical energy gap of the thin films was observed to be 3.436eV. The films can be utilized in dielectric filters, electroluminescent and solar cell devices.

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