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Effect of Post Annealing Temperature on Structural Properties of ZnS thin films Grown by Spray Pyrolisis Technique

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ABSTRACT: ZnS thin films were grown on soda lime glass substrates using spray pyrolisis method at a substrate temperature of 573K. The films were then subjected to a rapid thermal annealing at different temperatures. X-ray diffraction carried out on the films revealed a single peak which increase in intensity with increase in annealing temperature. The patterns of the ZnS thin films showed that the full width at half-maximum (FWHM), micro-strain and dislocation density of the films decreased with increase in annealing temperature, indicative of an improvement of the crystal quality of ZnS films. Similarly the calculated grain size of the films exhibited an increase with increase in annealing temperature which is a clear indication of an improvement of the crystal quality of the ZnS films. The values of lattice constant '**a**' agree with the standard and reported values.

KEYWORDS: ZnS, Spray Pyrolisis, annealing, XRD, Structural property.

1 INTRODUCTION

II – VI semiconductors, such as Zinc Sulphide (ZnS) have attracted growing interest owing to their possible applications in Photovoltaics and optoelectronics [1]. It is important semiconductor material for the development of various modern technologies of solid – state devices (laser diodes, solar cells). Zinc Sulphide have wide direct band gap of about 3.50 eV in the UV region [2]; it is used as a key material for blue light emitting diodes and other optoelectronic applications such filters, photoelectric cells, display devices and materials for LEDs and lasers [2], [3]. ZnS exist in two forms, an α-phase (hexagonal Wurtzite structure) and β-phase (cubic Zinc blende structure); a cubic crystal structure is its most stable state. Many deposition techniques have been used to prepare ZnS thin films, such as spin coating [4], chemical vapor deposition [2], and chemical bath deposition [6], [6]. Among these methods, Spray Pyrolisis is the most common method in producing thin film because the advantages of spray pyrolisis are its convenience for the deposition of semiconductor thin films and has the several advantages in comparison with other deposition techniques such as low cost of the source materials, producing high quality films using comparatively simple deposition equipment, moderate substrate temperatures, deposition scaled for large area and uniform deposition with very thin layers with specific composition, morphology, good adhesion between the deposited film and controlling the shape and sizes. Usually, as-deposited films require a thermal treatment to improve stability and reduce the possible undesirable influence of the substrate. Thermal annealing is a widely used method to improve crystal quality and to study structural defects in materials. During an annealing process, dislocations and other structural defects will move in the material and adsorption/decomposition will occur on the surface, thus the structure and the stoichiometric ratio of the material will change. Such phenomena can have major effects on semiconductor device properties, light emitting devices being particularly affected. For ZnS films, many research groups have investigated the effects of annealing temperatures on the structure properties of ZnS films [7]. In this paper, we report deposition of ZnS thin film on soda lime glass substrates by spray pyrolisis technique at temperature of 573K. The thin films were subsequently annealed in two different batches at 573K and 673K. The samples were further investigated for their structural properties.

2 EXPERIMENTAL

All the chemicals used for the deposition of ZnS thin films were 4N grade, soda lime glass was used as substrate, and film thickness was measured using Profilometer (Stylus Taylor Hobson model). Zinc sulfide thin films were prepared on soda lime glass substrates using KM 150 spray pyrolisis deposition machine. Before deposition the substrates were cleaned using trichloroethylene methanol and acetone sequentially. The dried substrate was rubbed gently with cotton. Solution containing Zinc Chloride ($ZnCl_2$) and Thiourea ($SC(NH_2)_2$) of molar concentration 0.1 M/L were used to prepare ZnS thin films. The precursor solution was sprayed for about 10 minutes. When zinc sulphide started depositing on the substrate, flow rate was maintained at 0.8ml/min. The substrate temperature was fixed at 300^{o}C. Similarly, the film thickness and nozzle to substrate distance were kept at 100nm and 11.0cm respectively. After deposition, samples were removed from the spray chamber and were subjected to a thermal annealing at different temperatures under nitrogen atmosphere. The ramp rate was 6□/s and the dwell time was 1 h. After annealing, the samples were taken out for characterization. Three samples were grown one sample was marked as as-deposited and did not undergo thermal annealing while the other two samples were annealed under nitrogen atmosphere at 573K and 673K respectively.

In order to investigate the crystallographic properties of ZnS thin films , X-ray diffraction analyses were carried out using PANALYTICA XPERT-PRO Diffractometer with Cu-Kα radiation (λ = 1.54056Å). The X-ray tube was typically operated at a voltage of 45 kV and a current of 40 mA. XRD patterns were recorded in the range of 20^{0}-80^{0} with a scan speed of 2^{o}/min, step size of 0.2000^{o} and scan step time of 1.10 seconds for all deposited thin films.

2.1 FORMULATION OF STRUCTURAL PARAMETERS

The grain sizes **D** were calculated through the Scherer's formula [8]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where β is full width at Full width half maximum (FWHM) of the preferential plane, θ is Bragg angle and λ is the wavelength of Cu-K_{α} radiation. The Dislocation density of thin films **δ** was calculated by employing Williamson and Smallman's relation [9]:

$$\delta = \frac{n}{D^2} \qquad (2)$$

Where n is a factor which equals unity giving minimum dislocation density and D is the grain size. The micro strain **ε** developed in thin films was calculated from the relation [10]:

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (3)$$

Where β =FWHM (Full width at half maximum intensity and θ is the Bragg's angle. The lattice parameters '**a'** value for tetragonal crystallographic system was calculated from the following equation using *hkl* parameter and the inter planer spacing d [11]

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (4)$$

3 RESULTS AND DISCUSSIONS

3.1 XRD RESULTS

Fig. 1, 2, and 3 represents the XRD pattern for as deposited ZnS thin film, ZnS annealed at 300°C under N_2 and ZnS annealed at 400°C under N_2 respectively. It can be observed that All films shows a diffraction peak centered at 26.5 corresponding to the (111) lattice plane of zinc-blende phase (International Centre for Diffraction Data ICDD, Card No. 01-089-4245). The XRD pattern for as-deposited ZnS films in figure 1 is characterized by a very small peak with orientation at 2θ=26.5°C. Figure 2 illustrate ZnS thin film annealed at 573K under Nitrogen atmosphere. It can be observed that the position of peak is still at 2θ=26.5°C but its intensity stronger than that of as deposited films. Furthermore, as the annealing temperature is increased to 673K under N_2 atmosphere as displayed by figure 3 the peak intensity is observed to further increase and its position is still at 2θ=26.5°C. This implies that annealing enhances crystallinity of thin film. Improvement in crystal structure could be attributed to the increase in crystallite size as the small crystallites join each other in the planes by increasing heat treatments. Similar observation was reported by [12], [13], [14], [15] on ZnS thin films as well [16], [17], [18], [19] made related observation but for ZnO thin films.

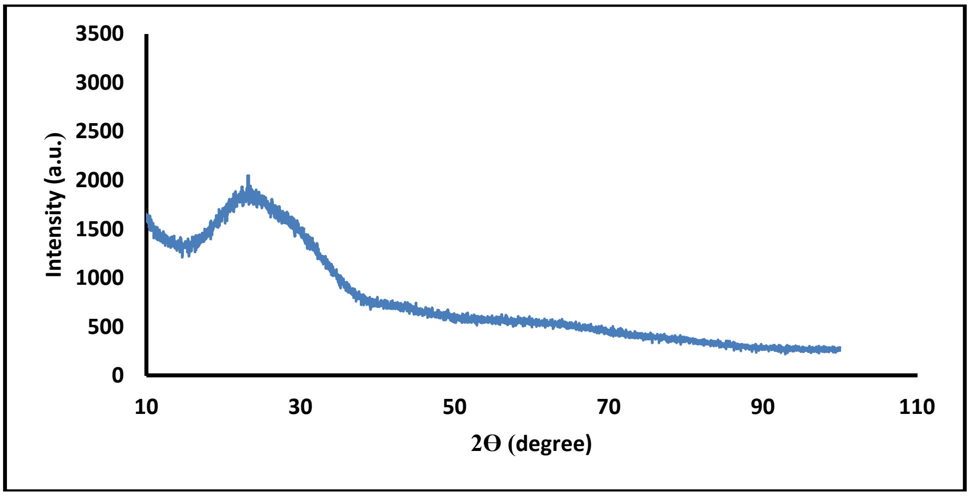

Fig. 1. XRD patterns for as deposited ZnS thin films

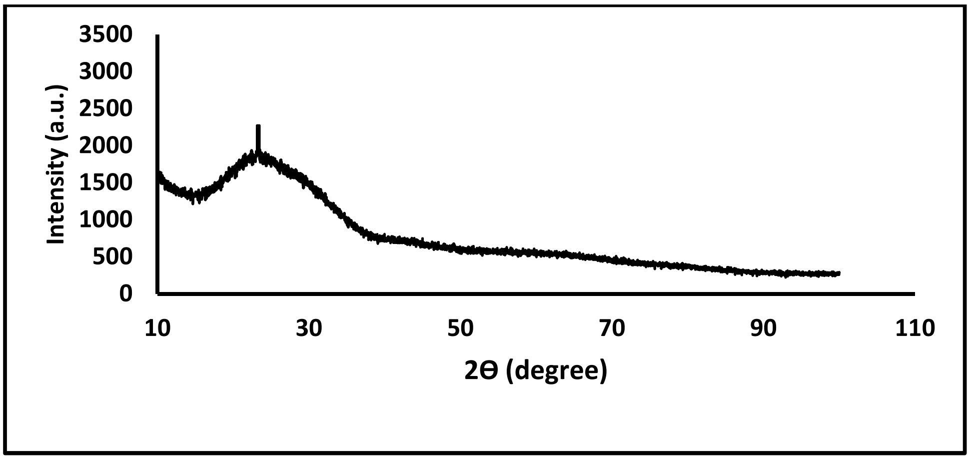

Fig. 2. XRD patterns for ZnS thin films annealed at 573K

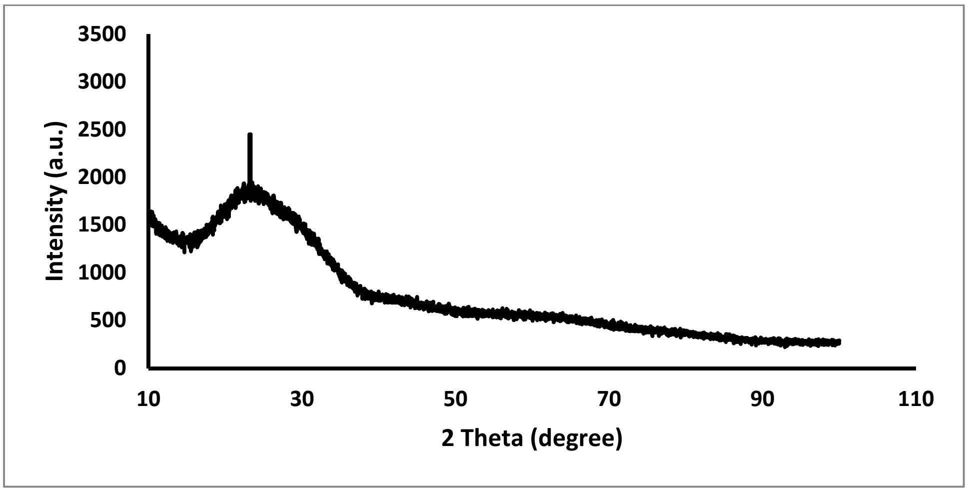

Fig. 3. XRD patterns for ZnS thin films annealed at 673K

3.2 STRUCTURAL PARAMETERS

Table 1.0 display the lattice parameters for three samples namely: - as deposited, annealed at 573K and annealed at 673K all grown at substrate temperature of 373K. It is observed from the table that for all the films the grain size D increases with increases in annealing temperature. In other words, sample annealed at 673K has the largest grain size, and hence should exhibit the most crystallinity. This is due to the small grains coalesced together to produce larger grains. It can also be seen in Table 1 that, the dislocation density **δ** and micro strain ε values decreases exponentially with increase in annealing temperature. This is because when films are annealed they become less strained. Our calculated values of dislocation density δ and micro strain **ε** are close to those reported by [3], [12] and [13]. In the same manner it should be observed from table 1.0 that FWHM decrease as annealing temperature increase; implying that as annealing temperature increase thin films becomes more crystalline. The value of the FWHM is inversely proportional to the grain size. That is, a narrower FWHM and a larger grain size imply better crystal quality. It is clear from the table that the lattice constant **a** decreases with the increase in annealing temperatures, this occurs because the strain decrement in the films treated at different annealing temperature as well as dislocation density values are found to decrease with increase in annealing temperatures. These values of lattice constant agree with those reported by [14].

Table 1. Calculated structural parameters of ZnS thin films deposited at 573K and annealed at different temperatures.

Sample thickness (nm)	Annealing temperature (K)	Grain size D (nm)	Micro strain Ɛ $x10^{-3}$	Dislocation density (δ) $x10^{14}$lines/m^2	Lattice Constant 'a' (nm)	FWHM B (degrees)
100	As deposited	35.68	94.80	7.85	5.40	0.412
100	Annealed at 573K	41.79	80.90	5.72	5.39	0.352
100	Annealed at 673K	44.30	76.40	5.09	5.38	0.332

4 CONCLUSION

Single crystalline ZnS films were deposited on Soda lime glass substrates by Spray Pyrolisis method. The structure of the films deposited at 573K substrate temperature and annealed at different temperatures under nitrogen environment was investigated by X-ray diffraction XRD. From the experimental results, it is clear that, the films grown at these temperatures exhibited polycrystalline structure. However the crystallinity is apparently improved as annealing temperatures increases. The grain sizes increase with increase in annealing temperatures while dislocation density, micro-strain, lattice constant and FWHM decrease with increase in annealing temperature.

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