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STRUCTURAL ANALYSIS FOR A NANO-CRYSTALLINE FILM (ZnS) BY AEROSOL SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT

Nano thin film materials play an indispensable role in modern electronics and other field of material sciences especially in a photovoltaic technology. The scope of this research is to grow Zinc Sulphide (ZnS) thin film and characterize structurally to understand the benefits of the study choosing chemical deposition method (The aerosol spray pyrolysis), the chemical combination analysis and the annealing temperature. Specifically on the film strength and its applications. In the light of this work, Nano crystalline ZnS thin films was grown by carefully dissolving 1.48g of Zinc Acetate ($Zn(CH_3CO_2)_2$) in 15ml of a distilled water (H_2O), Followed by the deposition of 50, 5, and 30ml of acetone (CH_3COCH_3), acetic acid (CH_3COOH) and ethanol (C_2H_6O) to the solution respectively, all in molar concentration of 0.1 M per ml. The solution was allowed to spray for 10 minutes on a soda lime glass substrate (SLG) at 300^oC. The process was repeated for the sample annealed at 300^oC and 400^oC under Nitrogen gas (N_2) environment for 60 minutes. The X-ray diffraction pattern of all the films deposited shows a cubic crystal type with mean crystallite size in the range 0.35nm as deposited, 0.4179 nm and 0.44nm at 300^oC and 400^oC annealing temperature respectively. Patterns of the sprayed film after performing the phase analysis reveal peaks corresponding to the (111) planes of reflection, which indicate the suitability of the deposition process and chemical combination. Furthermore, it is also concluded that the strength of the material depends on the annealing and substrate temperature.

Keywords: Aerosol Spray Pyrolysis, Chemical Combinations, Annealing, X-ray Diffractometer (XRD)

INTRODUCTION

ZnS thin film is among the few semiconductor compounds that received greater attention in the recent time (Al-Diabat et al., 2019). It is the most sought-after semiconductors, sulfides in fabricating infrared sensors/detectors, lasers, solar cells, LEDs, photochemical cells, resistance switches, catalysts, and non-volatile memory devices. Typically, various techniques such as molecular beam epitaxy, chemical vapor deposition, sputtering, thermal evaporation, chemical bath deposition andspray pyrolysis are usedfor preparation of ZnS films (Asif et al., 2012). Spray pyrolysis has been shown to be the most appropriate method for producing ZnS thin films is reliable, inexpensive and good large-scale capability production. ZnS has been adjudged as a potentially important material for anti-reflection coating for hetero junction solar cell light emitting diode, photo voltaic cells etc (Al-Diabat et al., 2019). However, in this research, we study ways on how to produce a material that will be cost effective and environmental friendly. This research work aims to use spray pyrolysis method for good homogeneity with high crystalline ZnS thin films by exploring some of the advantages of this technique in relation to the chemical combination analysis, substrate/annealing temperature, Grain size/Diffraction peak and as well as the crystallinity of the film.Also with exposure to electromagnetic radiatiions, Researchers have shown that ZnS are transparent to visible light, opaque to ultra violet radiation and near infra-red radiations (Liu et al., 2014 & Moreh et al., 2014).

According to Ebrahimi et al. (2017), Zinc Sulfide (ZnS) films were deposited through a simple and low cost spray pyrolytic technique by using mixed aqueous solutions of zinc nitrate and thiourea. The structural and optical properties of films were investigated as a function of initial (Zn:S) molar ratio in the precursor solution which varied between (1:1) and (1:3). X-ray diffraction (XRD) analysis revealed cubic ZnS phases formed in the prepared film of substrate temperature 400^oC by the equal molar ratio of zinc to sulfur ions and only single cubic ZnS phase was appeared by increasing sulfur content in the precursor solution, it shows the same amounts of the solution were used to deposit films with thicknesses of about 600 nm. The films grown from solutions with the molar ratio of (Zn:S)= (1:1) and (1:2) demonstrate poor crystallinity and contain zinc oxide (ZnO) as a secondary phase. The observed diffraction peaks at 31.9°, 34.5° and 36.4° match well with the wurtzite phase of ZnO crystal (JCPDS card No. 01-079- 0205) for their intensity and peak position. For all the patterns, the results exhibit broad diffraction peak at the 2θ position of 29.5° related to the (111) refraction of the ZnS cubic phase. The peak has been indexed with the JCPDS card No. 01-079-0043. (Ebrahimi et al., 2017).

Asif et al. (2012), reported on deposition of zinc sulfide (ZnS) by chemical spray technique using mixed aqueous solutions of zinc sulfate ($ZnSO_4$), and thiourea ($SC(NH_2)_2$). The effect of various deposition parameters on the thin film formation has been investigated and the deposition parameters such as volume of the solution, substrate temperature, substrate to nozzle distance, nozzle diameter, spray rate etc. have been optimized. In the present work, effect of molar concentration of the starting solution on structural characteristics of the films (crystallinity, phases and preferred orientations) has been studied using X-ray diffraction for films synthesized at substrate temperature 500^oC. The X-ray diffraction pattern of all the films deposited shows hexagonal wurtzite crystal type with mean crystallite size in the range 25nm to 35 nm under the optimized condition of substrate temperature, spray rate, nozzle diameter, etc. The observed diffraction peaks at the substrate temperature is 31.9°. The film exhibits increasing c-axis orientation along (002) with change in molar concentration of spray solution. Microstructure has been analyzed using scanning electron microscope. The films have been characterized using structural and optical measurements (Asif *et al.,* 2012).

Manjulavalli et al. (2015) reported in their study titled Structural and optical properties of ZnS thin films prepared by chemical bath deposition methodshows XRD pattern of ZnS films on glass substrate prepared using differentmolar concentration (0.5 M, 1 M and 2 M) at the deposition temperature of 333 K. The XRD pattern showspreferential orientation at 2θ equal to 28.30 indicating nano crystalline nature. The diffraction peaks becomeslightly sharper and their intensity is relatively enhanced on increasing the molar concentration, while theirlocation did not change significantly. The lattice parameters deduced using these 'd' values is found to be in good agreement with some literatures conforming that the film prepared using chemicalbath deposition is hexagonal in structure. From the h k l values, the lattice constants are evaluated using most prominent orientation along (0 0 2) direction.Preferential orientation at 2θ equal to 28.3 indicating nano crystalline nature The number of crystallites per unit area decreases, which is evident from the increase of grain size with concentration. The XRD analysis shows that all the grown films are nanocrystalline. The lattice parameters calculated are in good agreement with the standard data confirming that the ZnS films are hexagonal in structure (Manjulavalli et al., 2015; Nielsen et al., 2021 & Liang et al., 2013)

Khatri *et al.* (2018) reported on the properties of ZnS thin films deposited on glass substrate by using CBD technique at 70 ^{0}C bath temperature with the effect of post annealing at 350^{0}C temperature for 1 h. XRD confirmed hexagonal phase for both as-grown and annealed ZnS thin films. The average crystallite size was 331 nm for as-grown and 643 nm for annealed thin films using Debye-Scherrer equation. TGA analysis has shown that 350 ºC is suitable for annealing process of ZnS thin film and for the patterns, the results exhibit broad diffraction peak at the 2θ position as depositedas 29.1° and finally, they investigated that the materials can be potentially used in electroluminescence devices and photovoltaic cells. For doping on ZnS, as-prepared thin films have been developed for huge number of applications. Doped ZnS may have either cubic or hexagonal structure as Zinc Blende (ZB) or WurtZite (WZ), which depends on its synthesis conditions like sample prepared temperature, precursor type and concentration (Khatri *et al.,* 2018).

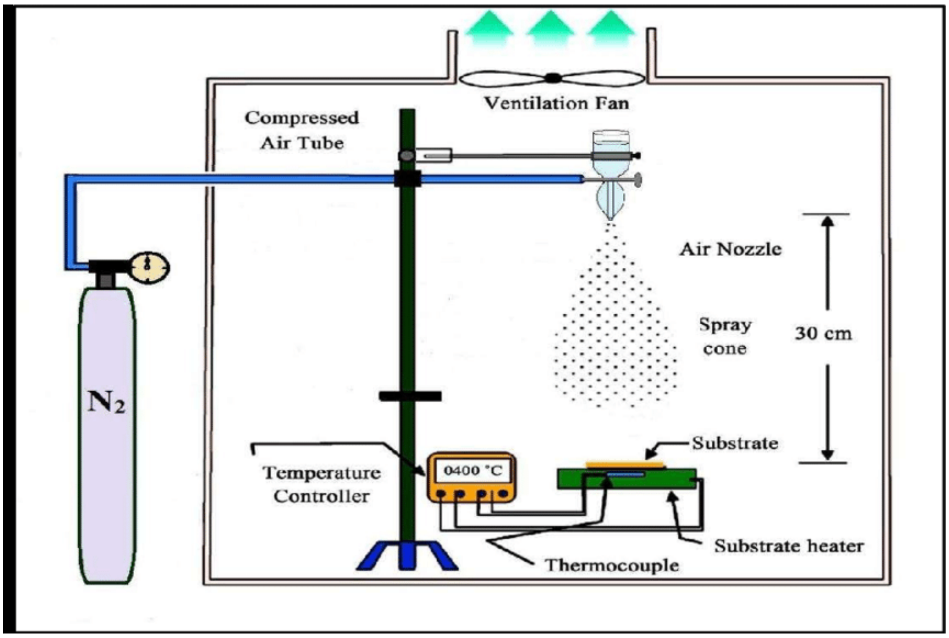


Figure 1a: schematic diagram of the spray pyrolysis technique

Figure 1b: Homemade Spray pyrolysis Machine Front View

Figure 1c: Homemade Spray pyrolysis Machine Side View

MATERIALS AND METHODS

Materials

Chemicals

Solid: Zinc Acetate ($Zn(CH_3CO_2)_2$)

Liquid and Gas: distilled water (H_2O), acetone (CH_3COCH_3), acetic acid (CH_3COOH), ethanol (C_2H_60), and Nitrogen Gas Environment (N_2)

Machineries

X-ray Diffractometer (XRD) PAN analytical (model, Xpert PRO) using Cu–Kα_1 (λ = 1.5418 Å) with the Pixel detector at 45kV/40mA, Homemade Spray pyrolysis machine (Fig.1b), 4N grade Soda lime glass substrate (SLG), Profilometer (Stylus Taylor Hobson model) and 5ml Syringe.

Method

Experimental; Preparations of the Zns thin film

The soda lime glass (SLG) substrate was cleaned with detergent and also with ethanol in an ultrasonic cleaner in order to remove contaminants on the glass surface. The substrates were then washed thoroughly with deionized water and dried with a blower containing dry air.Nano crystalline ZnS thin films was formed after carefully dissolving 1.10g of Zinc Acetate ($Zn(CH_3CO_2)_2$) in 15ml of a distilled water

(H_2O), Followed by the deposition of 50ml of acetone (CH_3COCH_3), 5ml of acetic acid (CH_3COOH), 30ml of ethanol (C_2H_6O) to the solution and finally adding a 0.38g of the solid $Zn(CH_3CO_2)_2$, in order to establish a total solubility.

Experimental; Deposition of the ZnS thin film on SLG

1ml of the mixture was placed in a 5ml syringe attached to spraying chamber with nozzle at a distance of 11cm. The SLG was measured by Profilometer (Stylus Taylor Hobson model), then the solution was allowed to spray for 10 minutes on the substrate (SLG) with a compressed air at 300°C. The deposited thin films was allowed to cool for 5 minutes and then the process was repeated for the sample annealed at 300°C and 400°C under Nitrogen gas (N_2) environment for 60 minutes.The machine used and the schematic picture of the synthesis are depicted in Figure1a and 1b & c above. All the characterization process areperformed at room temperature. The structural characterization was carried out by X-ray Diffractometer (XRD) PAN analytical (model, Xpert PRO) using Cu–Kα_1 (λ = 1.5418 Å) with the Pixel detector at 45kV/40mA. Below is an equation that represents the chemical balance in the deposition process.

$$Zn(C_4H_6O_4) + C_2H_5OH + C_3H_6O + C_2H_4O_2 + H_2O + (SC(NH_2)_2) \rightarrow 5CH_2O_4 + 2C_4H_6O + 3H_2O + ZnS \quad (1)$$

The above was heated by the compressed air at 300°C and the thiourea of 0.1 Mole per 1 $Cm^3$was added as S^{2-}Leading to the relation below

$$Zn^{+2} + S^{2-} \rightarrow ZnS$$: ZnS Was formed. (2)

RESULTS AND DISCUSSION

XRD Analysis on Sample as deposited and After Annealing

XRD patterns of the films (as deposited, 300°C and 400°C respectively). One peak (111) was significantly observed for all the films with diffraction angle 2θ of (22.967 for sample as deposited, 23.018 for a sample after annealing at 300° and 23.052 for a sample after annealing at 400°) respectively .The intensity of the peaks increased with increase in annealing temperature under the influence of N_2 gas. The highest peak was found from the sample annealed at 400° Cwhichindicates better crystallinity among the deposited thin films (Bashar et al., 2020 & Khadayeir et al., 2020).

The crystallite sizes (D) of the films can be calculated using Scherrer relation, by substituting values of Full Wave Half Maximum (FWHM) in the well-known Debye-Scherrer formula (Jones *et al.,* 1938):

$$D_{hkl} = \frac{0.9\lambda}{\beta cos\theta} \quad (3)$$

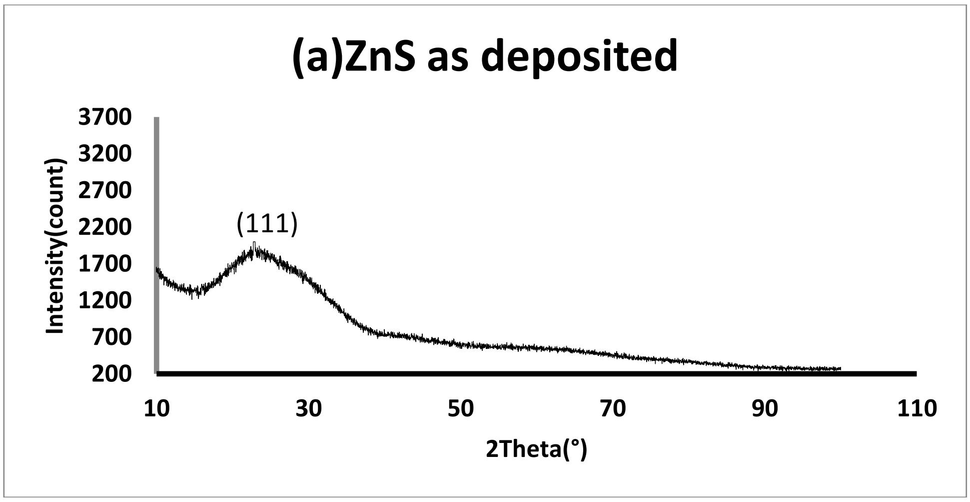
Where λ is the X-ray wavelength of 0.15406nm, β is the full width at half maximum (FWHM) of the film diffraction at 2θ, θ is the Bragg diffraction angle and 0.9 is the constant.

From table 1, the crystallite sizes are found to increase from as-deposited to annealed samples which increase with increase in annealing temperature. Also, the micro-strain (Ɛ) in the thin films can be evaluated using the relation:

$$\varepsilon = \frac{1}{D_{hkl}^3} \quad (4)$$

Where D is the crystallite size.

It is evident that FWHM of an XRD peak reliant on the crystallite size and micro-strain caused by the defect and or dislocations. The evaluated value shows maximum crystallite size of 19.206 corresponding to minimum micro-strain and dislocation density of 76.40 x 10^{-3} and 50937 x10^{14} lines/m^2 respectively for the sample annealed at 400°C.



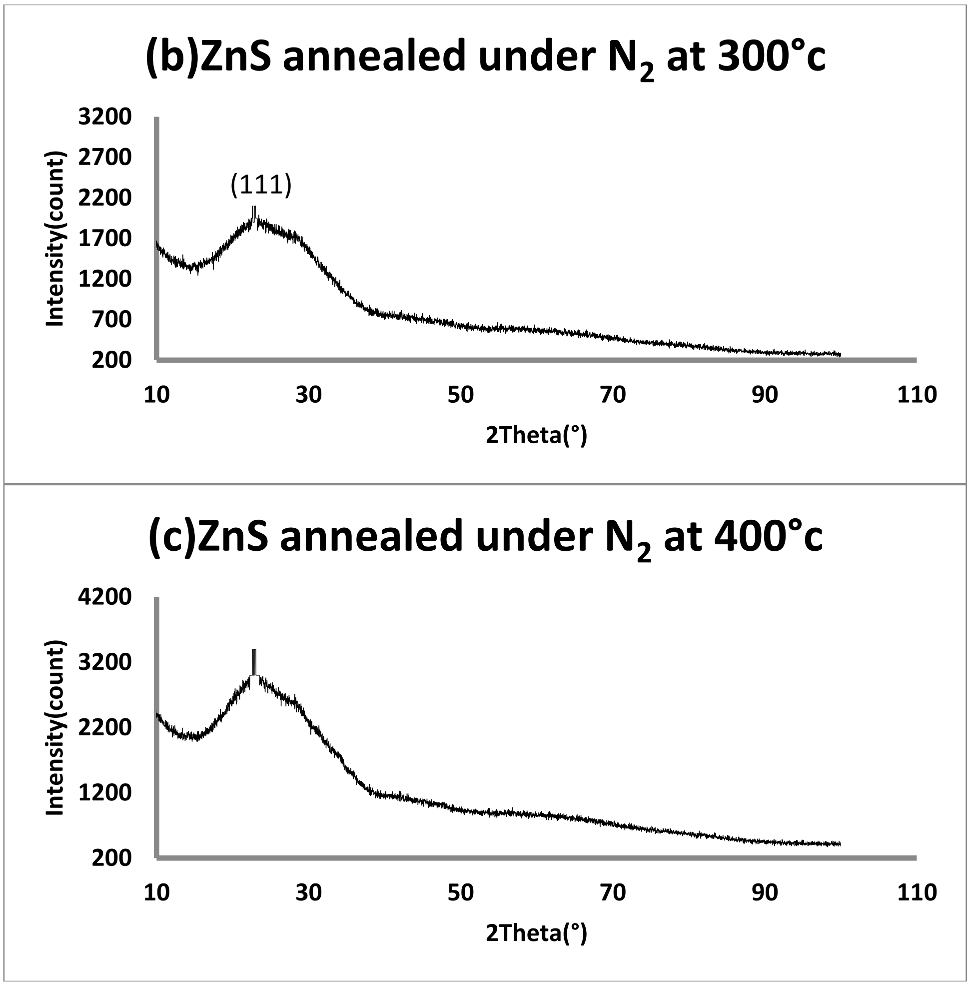


Figure 2:(a) XRD Diffractograms for ZnS thin film as deposited, (b) annealed under N_2 at 300°c, and (c) annealed under N_2 at 400°c.

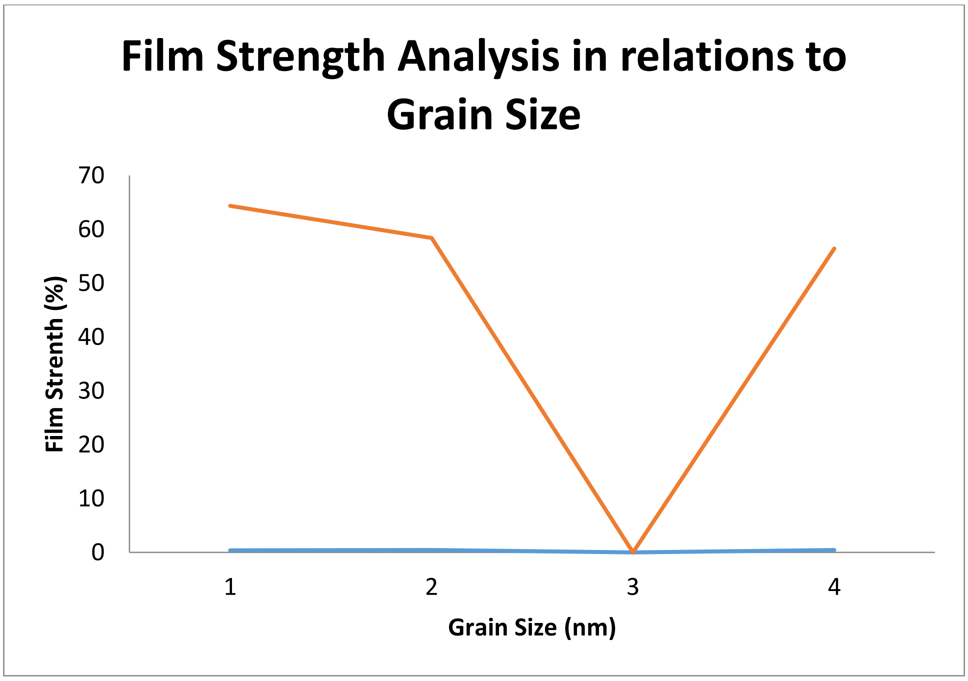


Figure 3: Film Strength Analysis as deposited by spray pyrolysis and after annealing

Table 1: Structural parameters of ZnS thin films annealed at different temperatures

Sample name/Anealing temperature	Grain size D (nm)	D Spacing (nm)	Number of crystallite $x10^{21}$	Micro strain ε $X10^{-3}$	Dislocation density(δ) $x10^{14}$lines/m^2	FWHM β (degrees)	*Peak values* 2θ (°)
ZnS as deposited	*0.3568*	*19.272*	*2.216*	*94.80*	*78518*	0.412	*22.967*
ZnS annealed under N^2 at 300°c	*0.4179*	*19.232*	*1.379*	*80.90*	*57261*	0.352	*23.018*
ZnS annealed under N^2 at 400°c	*0.4430*	*19.206*	*1.150*	*76.40*	*50937*	0.332	*23.052*

Table 2: Film Strength Analysis in relations to Grain Size

Absolute temperature absorbed by the film (℃) Before and After Annealing	Annealing Temperature (℃)	Grain size D (nm)	Film Strength (%)
300°c	*As deposited*	*0.3568*	*64*
600°c	annealed under N^2 at 300°c	*0.4179*	*58*
700°c	annealed under N^2 at 400°c	*0.4430*	*56*

Table 3: Deposition method, Substrate Temperature and Peak values relationships

S/N	ZnS from the research experiment	Deposition Methods	Substrate Temperature	Peakvalues 2Ѳ (°)
1	Current work	Aerosol Spray Pyrolysis	300 ºC	*22.967*
	ZnS Study from Reviews	**Deposition Methods**	**Substrate Temperature**	**Peakvalues 2Ѳ (°)**
2	Ebrahimi*et al., 2017*	Aerosol Spray Pyrolysis	400ºC	29.500
3	Asif*et al., 2012*	Aerosol Spray Pyrolysis	500 ºC	31.900
4	Manjulavalli*et al.,* 2015	Chemical Bath	60 ºC	28.300
5	Khatri *et al.,* 2018	Chemical Bath	70 ºC	29.100

Structural parameter's relationship

From the result in the table 1above, an increase in annealing temperature decreases the micro strain, dislocation density, the number of the crystallites, lattice parameters and increases the size of the crystallites (grain size), the distance between atomic planes parallel to the axis of the incident beam (d-spacing), and the intensity of the peak hence the crystallinity also increased, forming a cubic (Zinc blende) structure of ZnS thin film stable at room temperature. However, based on the above analysis, a cost effective and environmentally friendly material is produced by a spray pyrolysis method and the chemical volumes and weight applied in the deposition process have also been justified to have a good homogeneity with high crystalline ZnS thin films. From (Table 2) and (figure 2) above, the film strength increases with decreased in grain size and annealing temperature.

Also from (Table 3) above the substrate temperature required for a proper Chemical bath deposition is much lesser than the substrate temperature required for a proper spray pyrolysis technique, and according to the findings in Table 1, the grain size increases with a decrease in a peak values (2 theta). Since higher grain size influences plastic deformation due to a larger grain boundary, as indicated in (Table 2), this directly designate a formation of a weaker material. Therefore the literature and research experiment in (Table 3), shows with the spray pyrolysis deposition technique, the higher the substrate temperature the higher the Peak values (2Ѳ) which will equally higher the grain size (Table 1) by lowering the material mechanical strength (Table 2). The same applies to the chemical bath deposition which indicates that the deposition method only plays a little role in the material quality but due to low-cost, versatility of the aerosol spray technique, the method is said to be widely preferred.

CONCLUSION

In this work, ZnS thin films were synthesized by the ultrasonic aerosol spray technique onto soda lime glass substrate to reveal the nano-crystalline structure. The effect of thermal annealing of 300^0C and 400^0C on the preparation of the films, the structural parameters, the chemical combination and the deposition techniques was also studied. Results of X-ray diffraction indicated that the sprayed ZnS films crystallized structure with strong (1 1 1) peak parallel to the substrate surface as the preferred orientation. The intensity peak of the (1 1 1) plane for ZnS annealed at 400^0C deposited was higher than the other two samples. This translates into bigger and better crystallites among the deposited films. The films grown at these temperatures exhibited cubic structure. The average grains size increase from 0.3568nm to 0.4430nm as the annealing temperature increased. Therefore, it is found that the crystallinity is apparently improved as the annealing temperatures increases and even better than the improvement gained with the CBD method from the literature, and we concluded that annealing and the substrates temperature in both aerosol spray pyrolysis and chemical bath deposition of ZnS thin films reduces lattice strain, thereby producing a more perfect crystallite and decreasing the number of micro voids, which indicates the suitability of the deposition process and chemical combination. Furthermore, it is also concluded that the strength of the material depends on the annealing and substrate temperature while the technique plays a little role in the material quality.

RECOMMENDATION

From the breakthrough of the study as regards to the thermal annealing in the deposition of ZnS thin film, it will be worthwhile to use ZnS film synthesized by high annealing temperature in optoelectronic device as it produces a better crystallinity.

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CONFLICT OF INTEREST

The authors declare no conflict of interest

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