

The Influence of Annealing on Electrical and Optical Properties of ZnS Thin Film.

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ABSTRACT

Thin films of ZnS have found extensive applications in various optical, electrical, and optoelectronic devices. In this present work ZnS thin films have been deposited by simple and inexpensive Successive Ionic Layer Adsorption and Reaction (SILAR) technique on glass substrates at room temperature. The precursor solution is composed of ZnCl₂ and Na₂S. The annealing effects on the optical and electrical properties of the films have been investigated. X-ray diffraction technique was used to investigate the structural properties of films. The XRD shows that the films exhibit polycrystalline cubic structure oriented in (111) direction.

The crystallite size was found to be 26.75nm. From the optical absorption measurements, the band gaps energies at room temperature, 100°C, 150°C, 200°C and 250°C were found to be 3.74eV, 3.66eV, 3.57eV, 3.5eV and 3.46eV respectively. The band gap decreased as the temperature increases. The two point probe method was used for the investigation of electrical properties of the films and it was found that current decreased as the temperature increases, thus, the annealed films were found to be more resistance than the as-grown films. The optical transmission measurement revealed that the films exhibit good transmission of 95% in the infrared region for ZnS annealed.

(Keywords: ZnS, thin film, annealing effect, optical and electrical properties, SILAR, successive ionic layer adsorption and reaction)

INTRODUCTION

The ZnS thin films have been grown by Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The solution growth techniques are simple, cheap and convenient for large area deposition and have easy controllable

parameter. The SILAR method is an aqueous solution method based on sequential reactions at substrate-solution interface for the deposition of the thin films. It involves the alternate dipping of the substrate into aqueous solution containing ions of each component.

In the SILAR technique, quality films are obtained by optimizing some parameters such as concentration, temperature and pH of the precursor solutions and the time duration for adsorption, reaction and rinsing (Yildirim et al., 2009). The thin films have mechanical, electrical, magnetic and optical properties which may differ from those of the bulk material and are used commonly in the form of a deposit on a suitable substrate for integrated circuits, resistors, capacitors, transistors and superconductors to name some (Thewlis, 1979).

ZnS thin films have been found useful in various devices. The applications of ZnS thin films which cover a wide area of interest are: antireflection coating for the solar cell (Bloss et al., 1988), environmental friendly buffer layer as compared to CdS layer in CIGS based thin film solar cell (Katsumi et al, 1995), wide band gap material for electroluminescent and opto-electronic devices (Tong et al., 1996), photosynthetic coatings (Ndukwe, 1996), blue light emitting laser diodes (Hasse et al., 1991) and as α - particle detector (Kashani, 1996).

Zinc sulphide (ZnS) belongs to the II-VI compound of semiconductor material with an energy band gap of 3.75eV which is the largest value of all II-VI compound semiconductors. ZnS is an n-type semiconductor with a wide direct band gap. Thus, it could be use for the fabrication of optoelectronics devices, such as blue light emitting diodes, Mn-doped electroluminescent devices, electro-optical modulator and n-window layers of solar cells.

ZnS films prepared by Nadeem et al., (2000) using resistive heating technique had high transmittance (60 – 99%) in the visible and near infrared region. ZnS thin films coated on Ge (Yamanishi et al., 1985) using ionized cluster beam (ICB) method were found to have a transmittance of 96%. So they are useful as an antireflection coating for the optical transmission window. ZnS thin films have been grown on various substrates like silicon, glass, ITO and GaAs (Yan et al., 2008).

The annealing temperature effect on optical band gap and the light effect on the electrical properties of ZnS thin films has been reported and it was found that the optical band gap decreased with increasing annealing temperature, therefore, the annealed films was found to be more than the resistant than the as-grown films (Ates et al., 2007). Hollow structures show a lower density, higher surface area and distinct optical property.

ZnS is an efficient window material in solar cell. It can be a partner of different polycrystalline absorber semiconductor material such as SnO₂/ZnS/CdTe and Cd/ZnS/CuInSe₂ solar cells. It has also been studied with useful applications as phosphors and catalysts (Zhu et al., 2003). The optical study shows that ZnS has a direct band gap of 3.68eV (Sooklal et al., 1996). ZnS has a low exciton Bohr radius (2.5nm) making its nanoparticle interesting as small bimolecular probes for fluorescence and laser scanning microscope. ZnS is also currently used as a shell or capping layer in core/shell nanopropes such as CdSe/ZnS core/shell structures (Thakur et al., 2005).

Optimal annealing temperature of 200°C - 250°C has been reported renders the ZnS films smoother and grains larger. The optical properties are enhanced as well. Due to large lattice mismatch between the structure of ZnS and GaAs, the thin films deposited on these kinds of substrates are characterized as having small grains.

MATERIALS AND METHOD

In this study, ZnS thin films were grown on glass substrates by SILAR technique at room temperature. The adsorption, reaction and rinsing time were chosen experimentally to obtain a layer wise deposition and homogeneous thin films

structure. One SILAR cycle involves four steps. The substrates were first cleaned using distilled water and later dried in air. The substrates were immersed in the first reaction beaker containing 0.1M zinc chloride (pH 5.0). After 40 seconds, the substrates were moved to the rinsing beaker where they were washed with purified water for 30s to remove superfluous Zn²⁺ that might interact very weakly.

The substrates were removed from rinsing water and moved to reaction beaker containing 0.05 M sodium sulphide solution (Na₂S) with pH 12 where sulphide ions were adsorbed to the substrates for 40 seconds. After anion adsorption, the substrates were moved to another beaker containing water where they were rinsed for second time for 30s. Hence, the first SILAR cycle is completed. Repeating these cycles 100 times, film with desired thickness were obtained.

The substrates were cleaned for 10 min in acetone, dried and stored in desiccators. The samples were annealed at 100°C, 150°C, 200°C, and 250°C to examine the annealing effect on the optical and electrical properties of the films. The thickness was measured using gravimetric method. The optical absorption spectra were measured using Janway 6405 UV/VIS spectrophotometer and the structural measurements were done using X-ray diffraction techniques.

RESULT AND DISCUSSION

The optical properties of ZnS thin films were determined from absorbance measurement in the range 300-900 nm. The energy band gaps were calculated with the help the optical absorption spectral. To determine the energy band gap, we plotted (αhν)² against hν. Absorption coefficient (α) associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation,

$$\alpha = 2.303A/t \quad (1)$$

The theory of interband absorption shows that at the optical absorption edge, the absorption coefficient α varies with the photon energy hν according to:

$$\alpha (h\nu) = A(h\nu - E_g)^n \quad (2)$$

where E_g is the optical band gap, A is a constant and the exponent $n = \frac{1}{2}, 1, 2, 3$, depending on the types of electronic transition in k -space. To determine the optical band gap of the ZnS thin films, taking $n = \frac{1}{2}$ gives the best fit for the films.

The optical band gap, E_g , was determined by extrapolating the linear part of the optical absorption spectral. The band gap energy of the as-grown film at room temperature is 3.74eV, film annealed at 100°C, 150°C, 200°C, and 250°C showed the energy band gaps of 3.66eV, 3.57eV, 3.50eV and 3.48eV, respectively. The energy band gaps ranging from 3.48eV to 3.74eV obtained in this work compare favourably with 3.73-3.57eV obtained by Yildirim et al., 2009, 3.51-3.84eV by Nadeem et al., 2000, 3.68eV by Biswas, 1986, 3.5eV by Nomura et al., 1995, 3.68eV by Sooklal et al., 1996, and 3.44eV by Lindroos et al., 1996.

It could be observed that for each annealing temperature, the optical band gap was decreasing with increasing annealing temperature as shown in Figure 3 and Table 1.

The decrease in band gap of the films after annealing could be attributed to improvement in the crystals and change grain sizes of the films with annealing temperature. Due to the high optical band gap of the ZnS film, it could be useful as buffer layers in CIGS thin film solar cells. CdS has been using as buffer layer in CIGS thin film solar cells but due to its toxicity, alternative means has been investigated. This therefore leads to the study of ZnS. ZnS is having advantage over CdS due to wider band gap it possessed more than CdS. Therefore, using ZnS in solar cell devices could lead to increase in high energy photons at the junction and decreases the window absorption losses. This could therefore lead to the improvement in the short circuit current of the cell. The ZnS is very useful as a window layer in heterojunction photovoltaic solar cells, because the high band gap energy will decrease the window absorption losses. This also leads to the improvement of the short circuit current. ZnS has very high optical conductivity.

Figure 1 shows the optical transmittance of ZnS films at different temperatures in the wavelength range of 300nm to 900nm. The optical studies shows that the transmittance of the ZnS films increases as annealing temperature increases. All the samples of ZnS films shows very high transmittance in VIS and NIR region and low

transmittance in the UV region. The relatively high transmittance in the IR regions could be exploited in glazing applications for space heating. The optical spectral of 523K annealed sample of ZnS films exhibit the highest transmittance of about 95% in NIR region at wavelength of 900 nm. The film is actually an efficient transmitting and antireflective material.

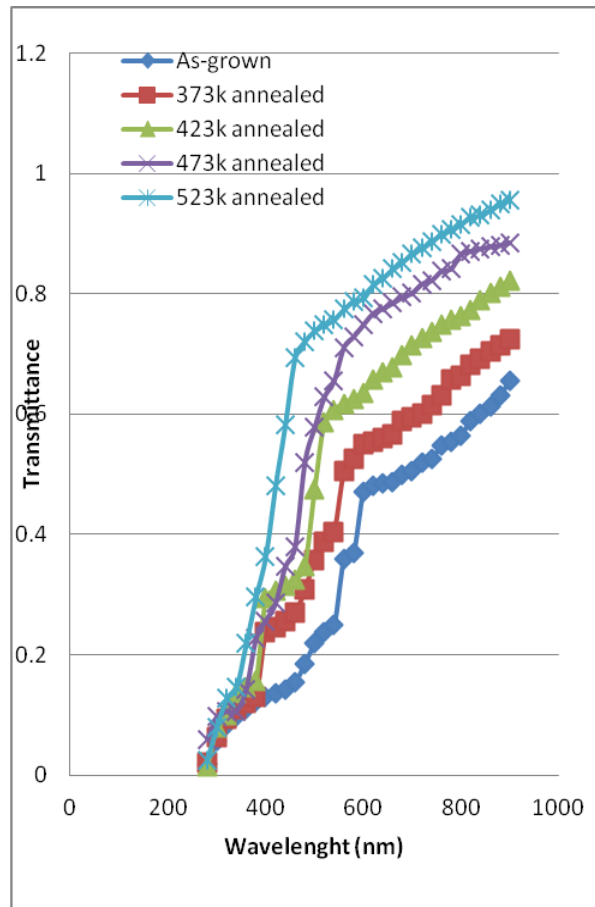


Figure 1: Transmittance Spectral of ZnS film at Various Temperatures.

Because of the high optical transmission and anti-reflective properties of ZnS film, ZnS may play an important role in photovoltaic devices. The film is practically non-absorbing in NIR region. The 373k annealed ZnS film show maximum transmittance of 87% in the NIR region at 900nm. The lowest transmittance of about 65% in NIR was shown by as-grown ZnS film. These results obtained compare favourably with high transmittance (60 – 99%) in the visible and near infrared region obtained by Nadeem et al., (2000) and 96% obtained by Yamanishi et al., 1985. So they are

useful as an antireflection coating for the optical transmission window.

Figure 2 shows the optical absorbance of ZnS films at different temperatures. From the studies, it shows that all the samples of the ZnS films exhibit high absorbance in UV regions and low absorbance in the IR regions. In the visible regions, it absorbs only slightly. This make the material to be useful in windscreen coating and driving mirror to prevent the effect of dazzling light into driver's eyes from oncoming vehicle and following vehicle. The result obtained by Nadeem and Ahmed (2000) and Ndukwe (1996) on the optical absorbance of ZnS thin films for wavelength in the infrared region showed that ZnS is practically non-absorbing in these regions which compares favourably with the result obtained in this present work. Similar behaviour was observed by Hammer (1943).

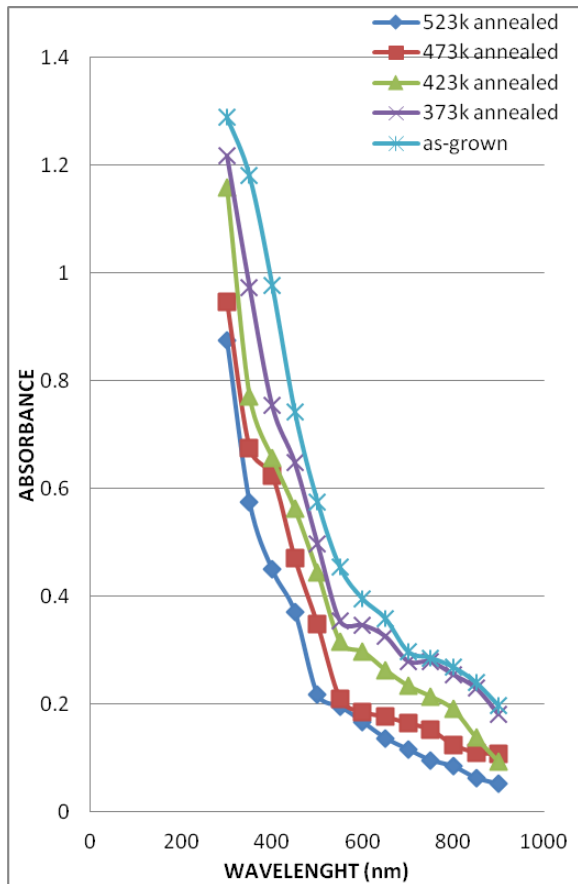


Figure 2: Absorbance Spectral of ZnS Films at Various Temperatures.

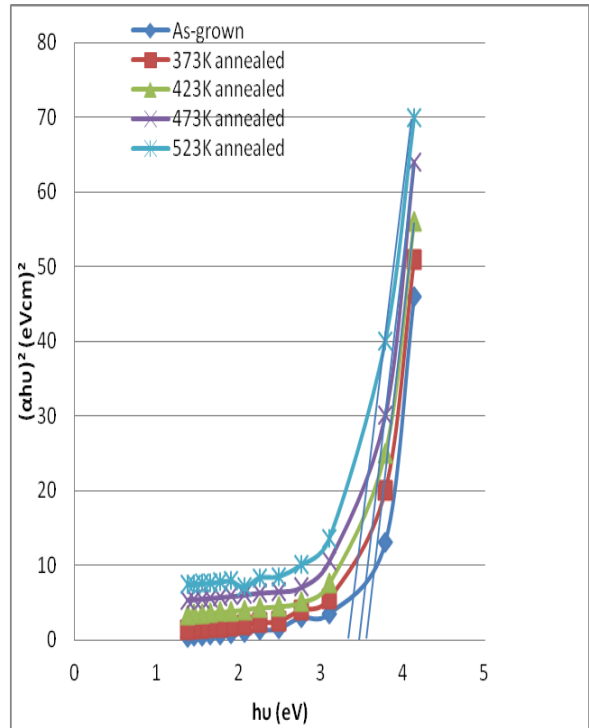


Figure 3: Optical Spectral of ZnS Films at Various Temperatures.

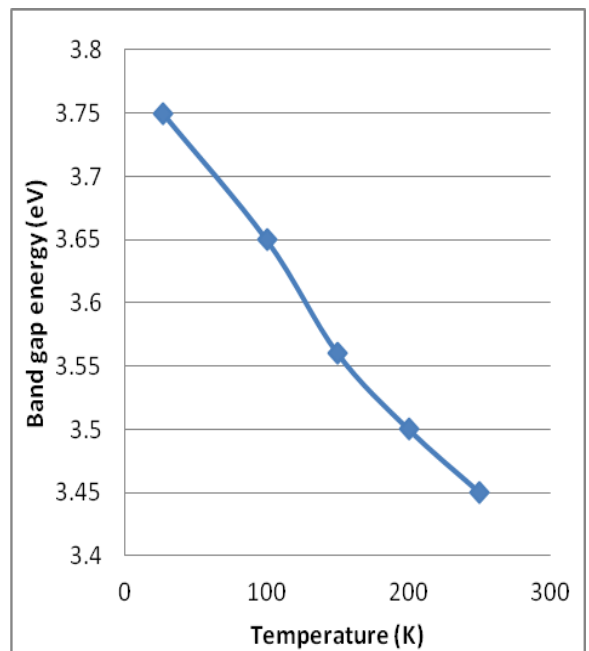


Figure 4: Band Gap Energy of ZnS Thin Film as a Function Temperature.

The refractive indices of the ZnS thin films at various temperatures were determined using Moss rule:

$$n^4 E_g = 77 \quad (3)$$

where n is the refractive index, E_g is the energy band gap. The ZnS films showed refractive index of 2.16 for film grown at room temperature, 2.17 for film annealed at 100°C, 2.15 for film annealed at 150°C, 2.14 for film annealed at 200°C and 2.12 for film annealed at 250°C, respectively.

The I-V behavior for as-grown and annealed ZnS films at 373k, 423k, 473k and 523k were shown in Figures 5 to 9.

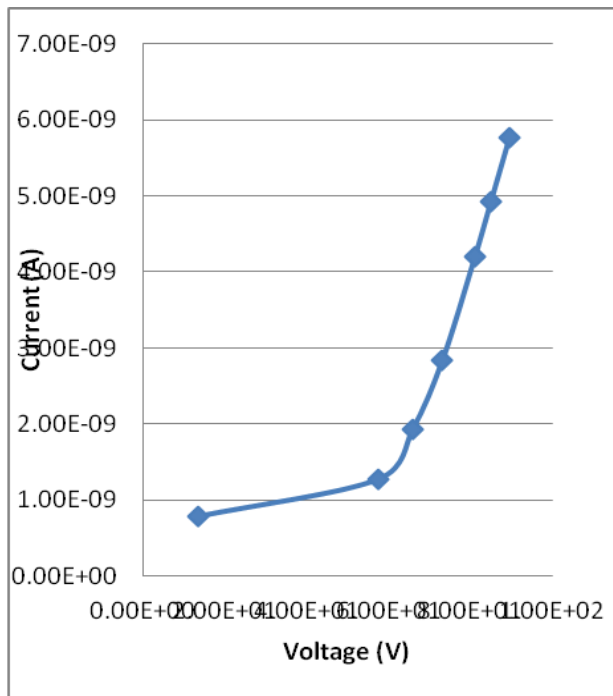


Figure 5: The I-V Behavior of As-Grown ZnS Films.

The current values are about 10^{-10} A. This value compares favorably with the result obtained by Ates et al, 2007. Current of 3.1E-09A was recorded for as-grown film, 1.7E-09A for 373k annealed ZnS film, 3.02E-10A for 423k annealed film, 2.26E-10A for 473k annealed ZnS film and 4.71E-11A for 523k annealed ZnS film.

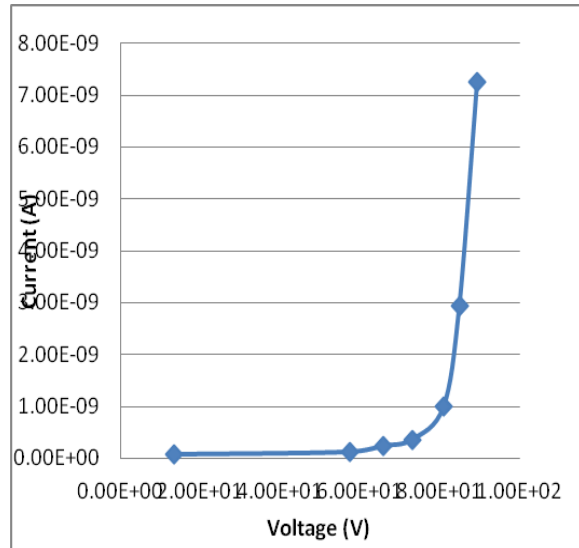


Figure 6: The I-V Behavior of 373k Annealed ZnS Films.

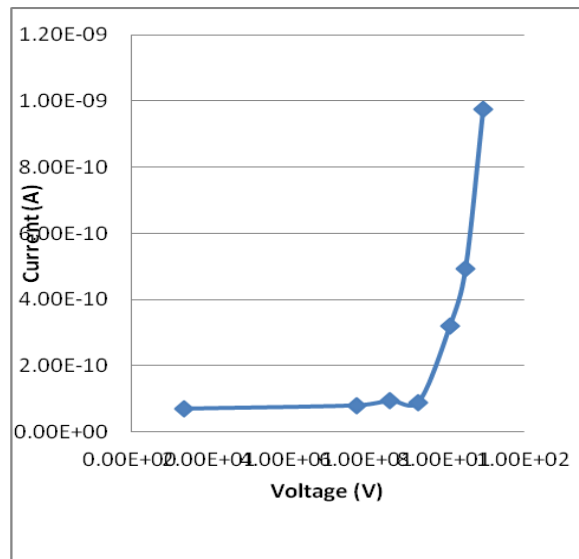


Figure 7: The I-V Behavior of 423k Annealed ZnS Films.

It was found that the current values decreased with increasing temperature. Therefore the annealed films were more resistance than as-grown films. This could be explaining by the presence of elemental Zn in the as-grown film. This metal Zn can act as a shunt path in the electrical measurements and the elemental Zn has the chance to combine with elemental sulphur to form ZnS and causes loss of Zn (Ates et al., 2007).

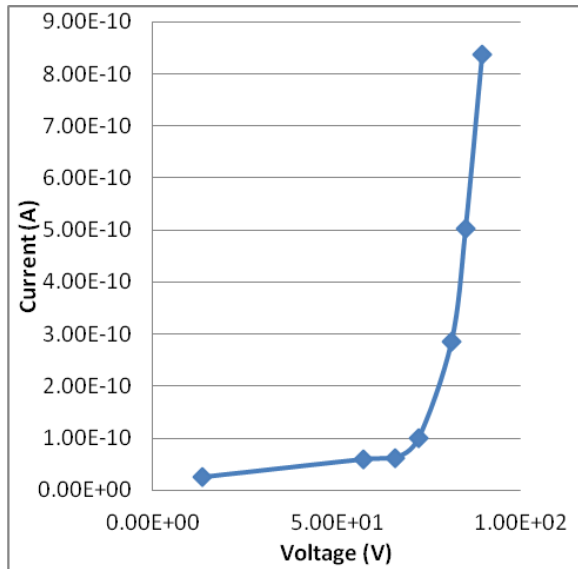


Figure 8: The I-V Behavior of 473k Annealed ZnS Films.

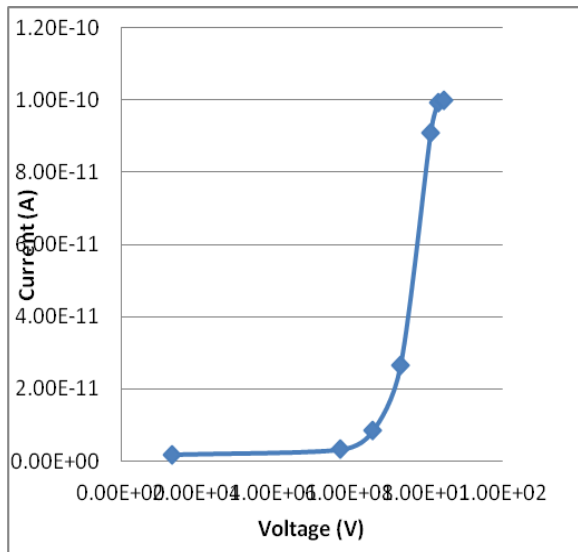


Figure 9: The I-V Behavior of 523k Annealed ZnS Films

The as-grown film was more conductive than the annealed films due to high current value possessed by the sample. The average voltage measured for all samples is 4.66E+02. The sheet resistance is determined using the formulae:

$$R_s = \frac{\pi}{\ln 2} \frac{V}{I} \quad (4)$$

Where R_s is the sheet resistance, V is the voltage and I is the current.

$$K = \frac{\pi}{\ln 2} = 4.53 \quad (5)$$

Factor k is a geometric factor.

Table 2 shows the values of the sheet resistance and the current of ZnS film as a function of temperature. As the temperature increases the sheet resistance increases while the current decreases. This result obtained is in agreement with the literature.

Table 1: Annealing Temperature and Optical Band Gap Values of ZnS Thin Films.

Temperature (°C)	ZnS band gap (eV)
Room temperature	3.74
100	3.66
150	3.57
200	3.50
250	3.48

Table 2: The Values of Current and Sheet Resistance as a Function of Temperatures.

Temperature (k)	Current (A)	Sheet Resistance ()
Room temperature	3.1E-09	6.81E+11
373K	1.7E-09	1.24E+12
423K	3.02E-10	6.99E+12
473K	2.26E-10	9.34E+12
523K	4.71E-11	4.48E+13

The structural analysis of ZnS thin films was carried out using X-ray diffractometer varying diffraction angle 2θ from 16.4° to 72.5° . Figure 10 shows the X-ray diffraction pattern of the ZnS thin film. It was observed that ZnS film has polycrystalline cubic structure oriented towards (111), (220) and (220). In the XRD obtained from the aqueous solvent, the highest intensity peak corresponds to (111) preferred orientation.

The (111) peak is stronger than other peaks. In general, the preferential orientation of the films is along the (111) direction. However, the XRD spectrum of the ZnS layer deposited by SILAR technique from aqueous only exhibit the (111) direction. The grain size of the film was calculated

from XRD pattern by using Debye Scherer's formulae:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (6)$$

Where D is the grain size, λ is the X-ray wavelength, β is the full width at half maximum and θ is the Bragg's angle. The crystallite size is 2.67nm and the inter-planar spacing is 3.655 nm.

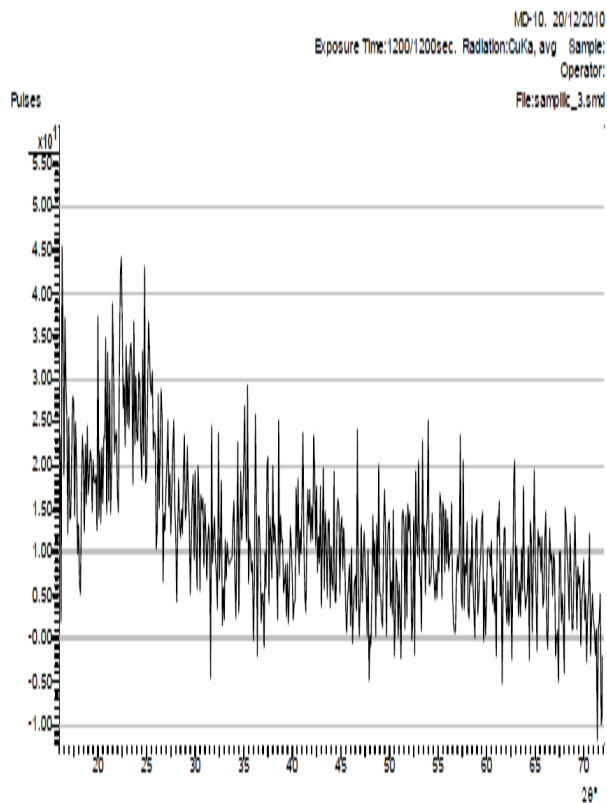


Figure 10: The XRD Pattern on ZnS Thin Films.

CONCLUSION

The Successive Ionic Layer Adsorption and Reaction (SILAR) technique was used to prepare thin films of ZnS. The optical band gap was found decreasing from 3.74 to 3.46eV as the temperature increases. The annealing effect on the electrical properties revealed that the annealed films were more resistant than the as-grown film. The current was found decreasing as the temperature increases. The current value was about 10^{-10} A. The structure of the film is basically a polycrystalline cubic structure oriented towards (111) direction. The results obtained were in agreement with the literature.

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