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Optical Properties of Silver Aluminium Sulphide Ternary Thin Films Deposited by Chemical Bath Method

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Abstract

Ternary thin films of Silver Aluminium Sulphide ($AgAlS_2$) have been prepared by chemical bath deposition techniques. Aqueous solution of 41.5 mls containing $AgNO_3$, $Al_2(SO_4)_3$, thiourea and EDTA was used, where $AgNO_3$, $Al_2(SO_4)_3$, thiourea were the source of Ag^+, Al^+ and S^- respectively and EDTA was used as a complexing agent. NaOH served as pH adjuster. The films were deposited at 300K of temperature. The deposited film properties were studied using a Janway UV – VIS spectrophotometer. From the spectral analysis of absorbance and transmittance, the optical and solid properties were obtained. The properties studied include the reflectance, absorption coefficient, thickness, refractive index, extinction coefficient, optical conductivity and band gap energy. The films show high absorbance in the UV *region and high transmittance in the VIS – NIR regions, while reflectance is generally low. The films showed direct band gap energy range of 2.15 eV – 2.40 eV and a refractive index of 2.64.*

Key words: Chemical Bath, Ternary Thin Film, Optical Properties, Surface Morphology, Compositional properties

Introduction

In recent years, interest on the preparation and study of physical properties of ternary chalcogenide compounds has increased. This is because of their possible applications in solar cells, light emitting diodes and non – linear optical devices (Ortega et al, 2003). Ternary compounds are found to be promising materials for optoelectronic device applications such as green emitting devices and are also suggested to be possible materials for window layer of solar cells (Woon – Jo et al, 2003). The optical and solid state properties of ternary chalcogenide thin films of $AgAlS_2$ make them potential semiconductor materials for electronic applications (Okoli et al, 2006).

Ternary chalcogenide thin films had been deposited by various deposition techniques (Uhuegbu, 2011) deposited FeZnS and (Mohammed et al, 2009) deposited PbCdS thin films by chemical bath method, (Noriyuki et al., 2013) deposited CuZnS and (Ortega et al, 2003) deposited $AgInS_2$ thin films by spray pyrolysis. (Sunyoung et al., 2008) deposited CdZnSe thin films by photoelectrochemical method. In these work, the chemical bath method was used to deposit $AgAlS_2$ ternary thin film. The spectral properties considered in this research work are; absorbance (A), transmittance (T), reflectance (R), thickness (t), refractive index, extinction coefficient, dielectric constants, optical conductivity and band gap energy. The consequence of exposing such a surface to solar radiation is that only certain wavelengths of the incident radiation are transmitted, absorbed or reflected (Uhuegbu et al., 2008 and Ezema, 2005). In other words, the values of these spectral properties become wavelength dependent, varying over the spectral regions, especially (300nm – 3000nm) of solar radiation spectrum. The transmittance, absorbance and reflectance are calculated using equations found in literatures (Majumdar et al, 2003).The grown films were characterized using a Janway UV – VIS spectrophotometer to determine the optical and solid state properties. Surface and compositional characterization of the films was also carried out.

Materials and Method

Chemical bath deposition technique was used to deposit silver aluminium sulphide thin films on glass substrate. Prior to the deposition, the substrates were degreased by dipping them in concentrated HNO_3 for 42 hours, washed with detergent, rinsed with distilled water and died in air. The degreased and cleaned substrate surfaces have the advantage of providing nucleation centres for the growth of the films, hence yielding highly adhesive and uniform deposited films. The deposition of $AgAlS_2$ thin films by chemical bath method was based on the reaction between aqueous solutions of silver nitrate, aluminium sulphate and thiourea as precusors of silver, aluminium and sulphur ions using EDTA as the complexing agent and sodium hydroxide as a pH stabilizer. The reaction baths constitute a mixture of 5 mls of 0.1M aluminium sulphate solution, 5mls of 1.0 EDTA, 5mls of 0.1M of silver nitrate solution, 1.5mls of 2.0Mof sodium hydroxide solution, 5mls of 1.0M of thiourea and 20mls of distilled water. The mixture was stirred with stirrer until it became a homogeneous mixture.

The cleaned subrates were immersed vertically into the reaction baths and were allowed to stay for 18 hours, 26 hours, 36 hours and 48 hours. After each hour, the substrate was rinsed with distilled water after removal and allowed to dry in air.

Results and Discussions

Fig. 1: Plot of Thickness of $AgAlS_2$ Thin Films against Deposition Time

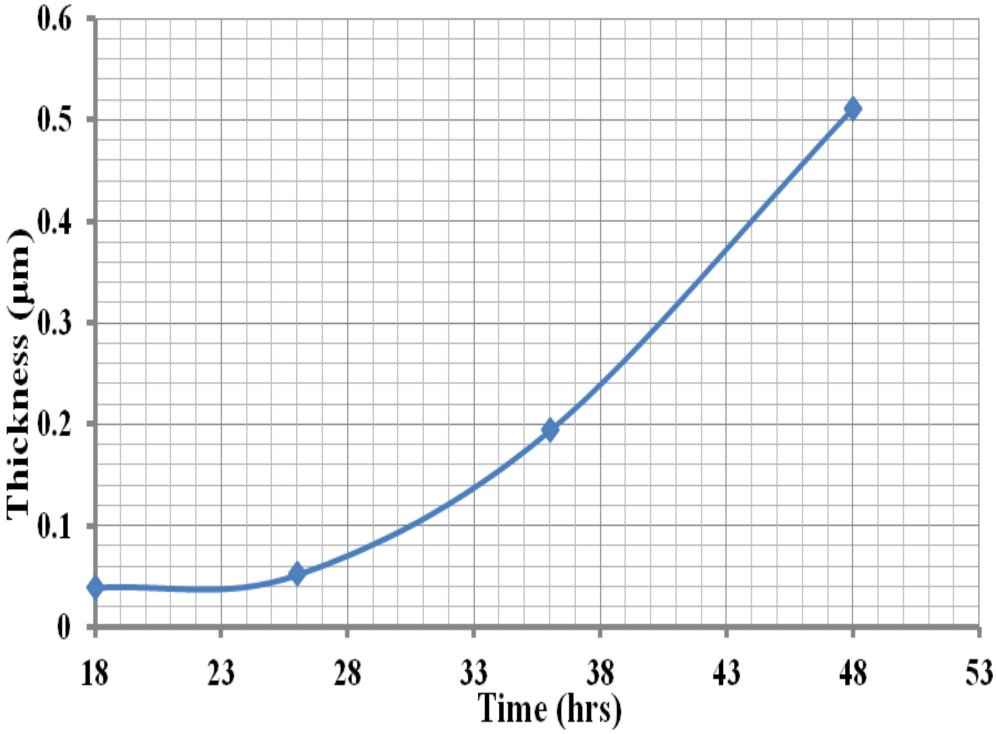

Fig. 2: Plot of Absorbance of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

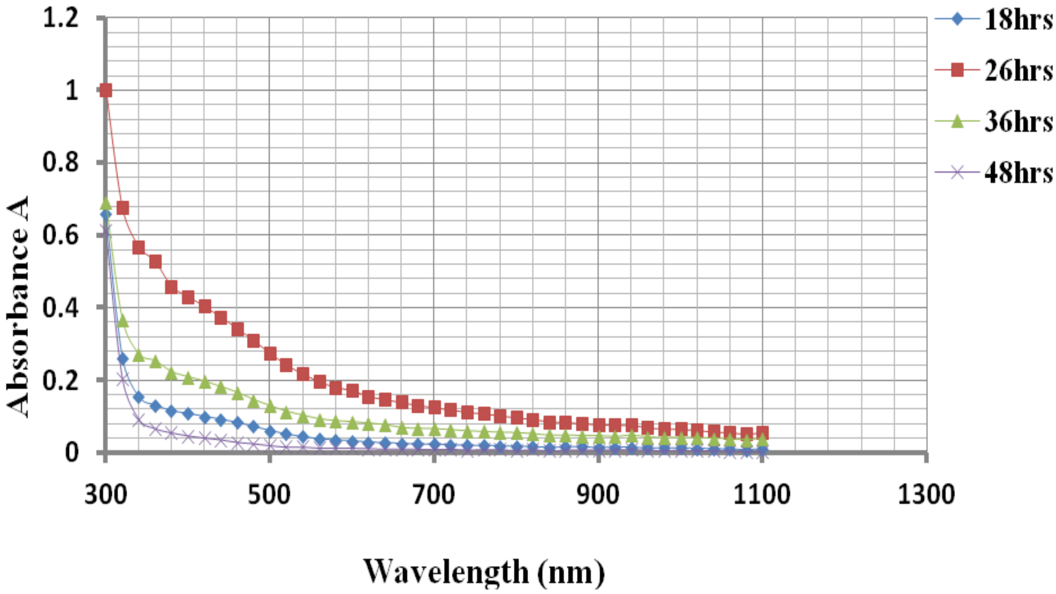

Fig. 1 is a plot of thickness versus time. The thickness of the deposited films increased from a value of 0.03 µm for film grown for 18 hours to a maximum value of 0.52 µm for film grown for 48 hours. The thickness remains nearly constant between 18 – 25 hours of deposition time. Fig. 2 shows the variation of absorbance with wavelength. The absorbance decreased sharply from high value at about 300nm to low values in the visible region and gradually decreased further in the NIR region. It can be seen that spectral absorbance decrease with increase in the time of deposition. The films show average absorbance of 0.51 which is in accordance with the value of 40% – 51% obtained by (Okoli et al, 2006). Fig. 3 shows the variation of transmittance with wavelength. The transmittance increased rapidly from a very low value at 300nm to very high value in the VIS – NIR region of the spectrum. The films show transmittance value of 98% in the NIR region with average transmittance of 75% in the VIS – NIR region. Transmittance increases with increase in deposition time. The properties of high absorbance in the UV region screen off UV radiation while the high transmittance in the VIS–NIR regions admits visible and infrared radiation. These properties make the film good material for the construction of poultry roofs, walls for the protection of the young chicks and coating of eye glasses for protection of the skin the skin around the eye due to UV radiation, while admittance of infrared radiation helps to warm the inside of the poultry house which is needed for the young chicks. The properties of high transmittance also make the film good material for thermal control window coating for cold climates.

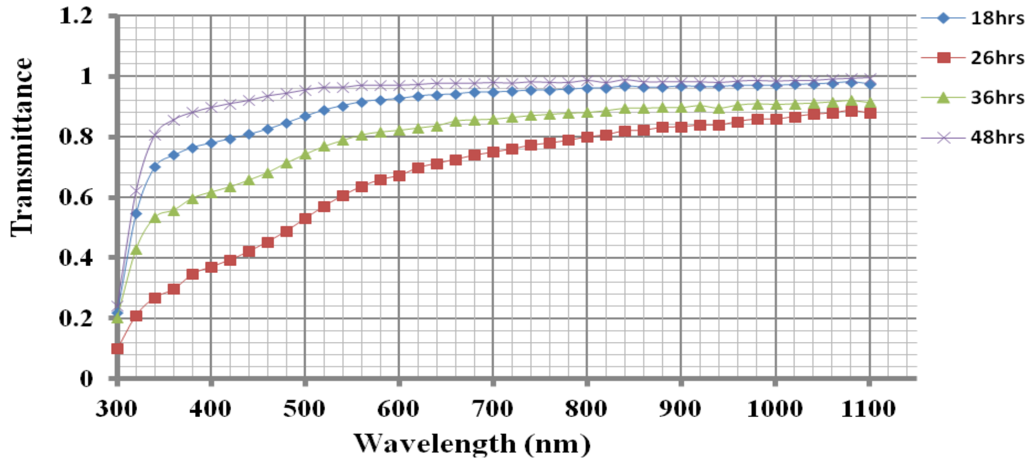

Fig. 3: Plot of Transmittance of $AgAlS_2$ Thin Films against Wavelength for various deposition time

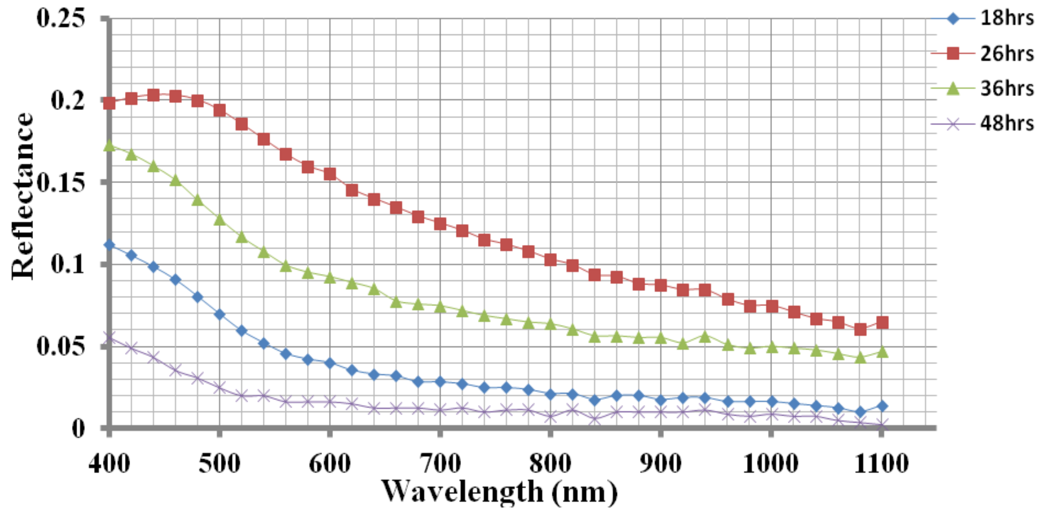

Fig. 4: Plot of Reflectance of $AgAlS_2$ Thin Films against Wavelength for various deposition time

Fig. 4 shows the variation of reflectance with wavelength. The films do not reflect electromagnetic radiation in the UV region and is generally low in the VIS – NIR regions. The reflectance values lies within 7% to 20%(for film grown for 26hrs).

The properties of low reflectance make the films good materials for anti – reflection coating.

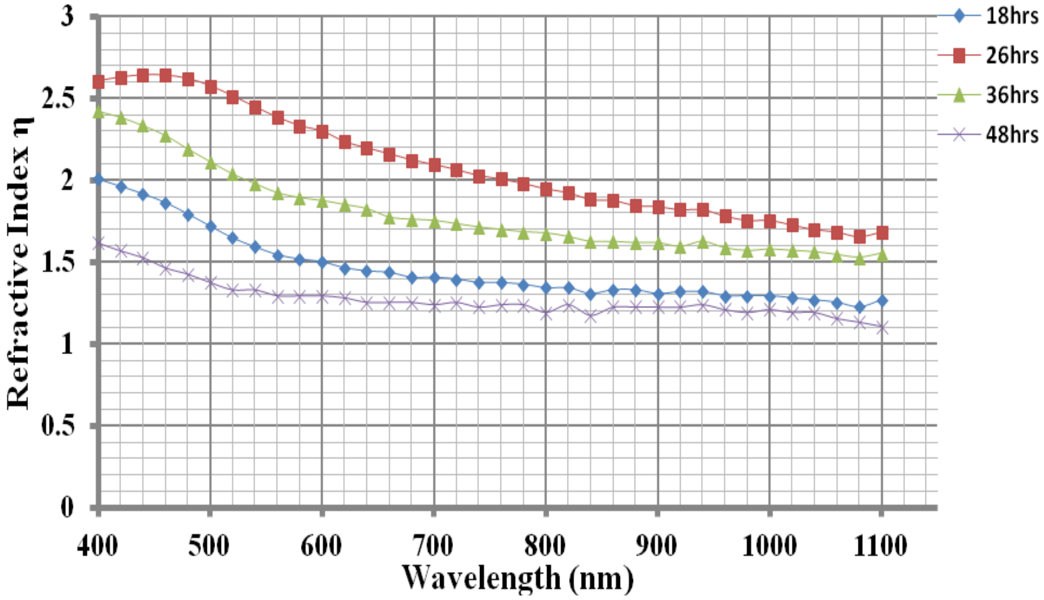

Fig. 5: Plot of Refractive of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

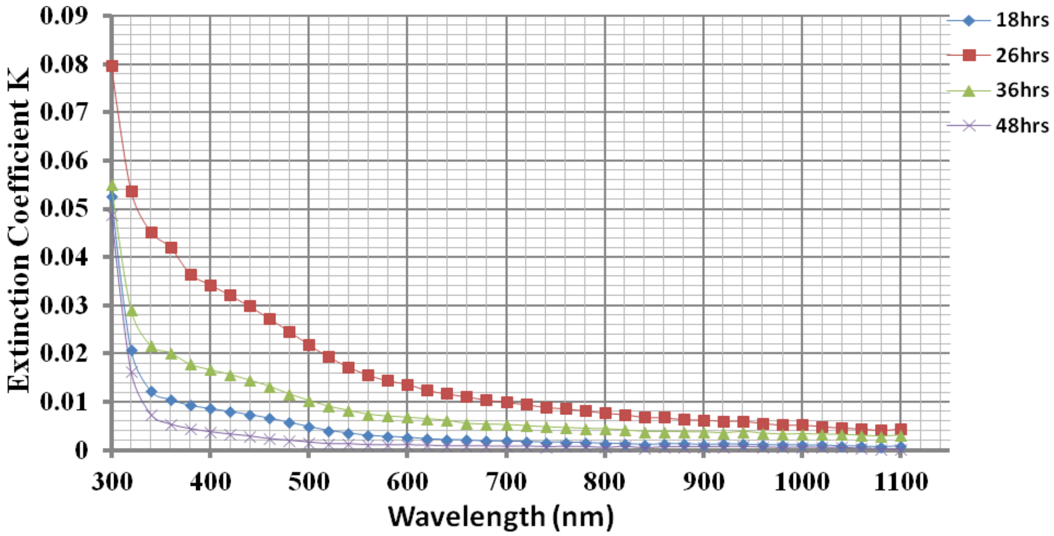

Fig. 6: Plot of Extinction Coefficient of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

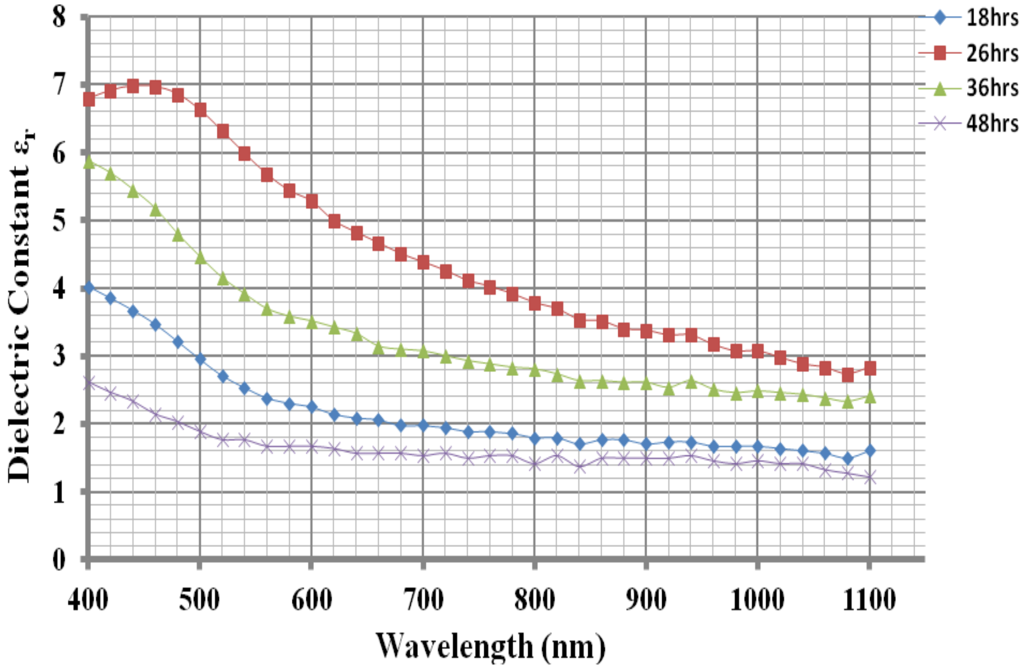

Fig. 7: Plot of Real Dielectric Constant of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

Fig. 5 shows the variation of refractive index with wavelength. The refractive index of the films was studied in the VIS – NIR regions due to the fact that the films did not reflect in UV region. From the graph, it is observed that refractive index decreases with increase in wavelength. The highest refractive index was found to be approximately 2.60 in the VIS region (for the film grown for 26yrs). High refractive index of 2.60 makes the films potential semiconductor materials for photovoltaic applications and solar thermal conversion.

Fig. 6 shows the variation of extinction coefficient with wavelength. Extinction coefficient of the grown films decreased from various peak values at 300nm to very low values in the VIS – NIR regions. Its value ranged from 0.08 in the UV region to 0.05 in the NIR region (for the film grown for 26 hrs). Fig. 7 shows the plotted graph of real dielectric constant versus wavelength. The real part of the dielectric constant was studied in the VIS – NIR region of the spectrum. The values ranged from 6.98 at 400nm to 1.2 at 1100nm. The real dielectric constant of the grown films decreases with wavelength and deposition time.

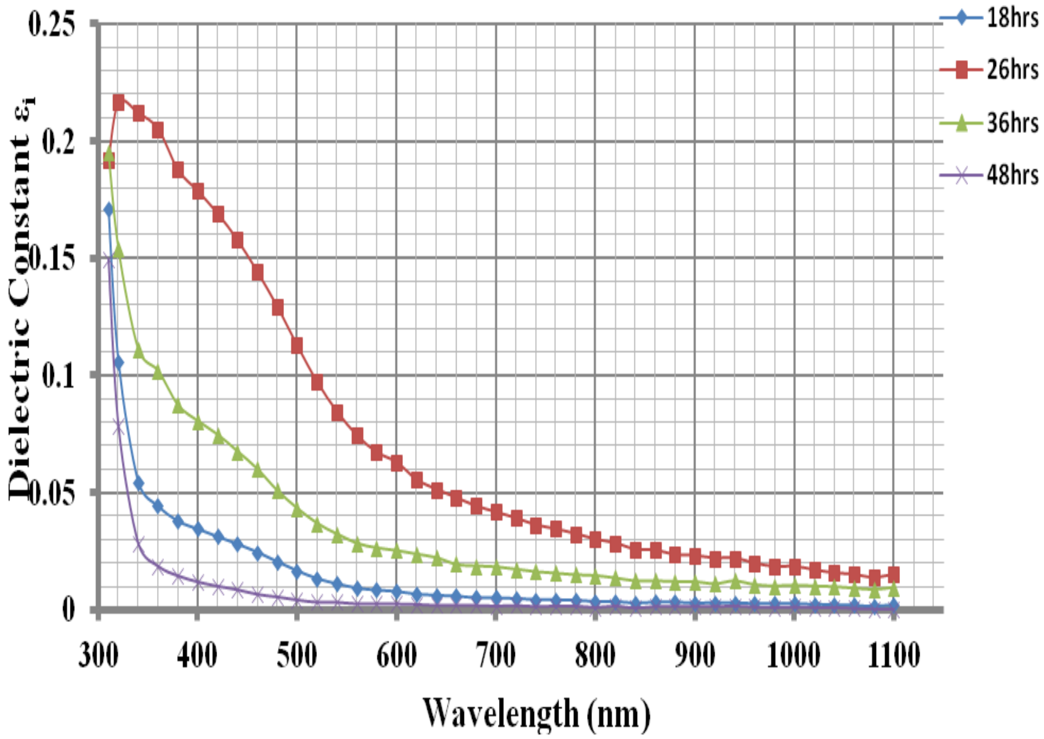

Fig. 8: Plot of Imaginary Dielectric Constant of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

Fig. 8 shows the variation of imaginary dielectric constant with wavelength. The imaginary dielectric constants of the films decrease with increase in wavelength. The values ranged from peak value of at 300nm to at 11oonm.The optical conductivity of $AgAlS_2$ decreases with wavelength as shown in figure 9. Optical conductivity decreased from peak values at 300nm to very low values at 1100nm. The optical conductivity ranged from to $100\ x\ 10^{12}(s^1)$ at 300nm and $5\ x\ 10^{12}(s^1)$ at 1100nm (for the film grown for 26hrs). The graph of absorption coefficient squared against photon energy is shown in figure 10. The optical band gap energy (E_g) of the film was estimated from the graph. The straight nature of the plots indicates the existence of direct transition. The direct band gap energies of the grown films were determined by extrapolating the straight part of the graph to a point where $\alpha^2 = 0$. The values obtained ranged from 2.15 eV to 2.40 eV. These are comparable with values obtained by (Okoli et al, 2006). The direct band gap range of 2.15 eV to 2.4 eV makes the film suitable for solar cell fabrication.

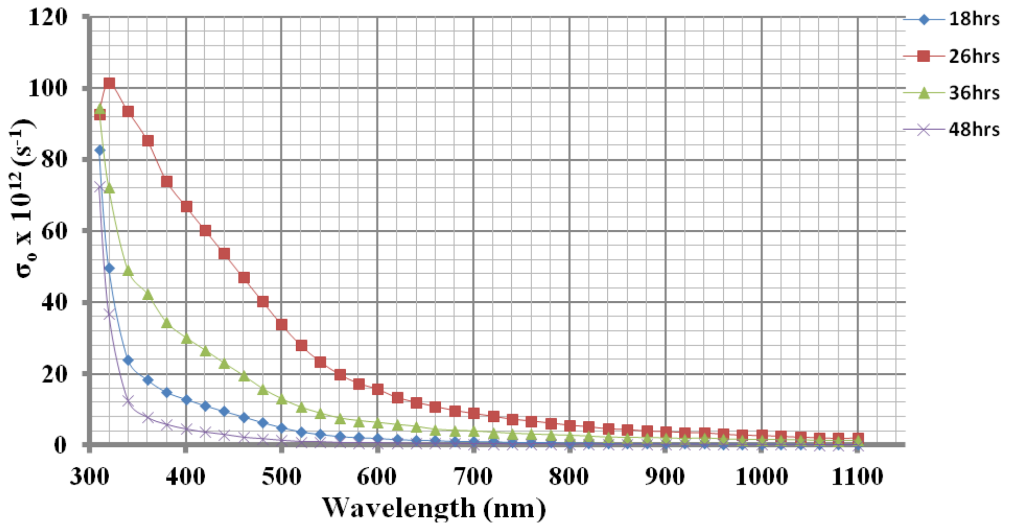

Fig. 9: Plot of Optical Conductivity of $AgAlS_2$ Thin Films against Wavelength for various Deposition Time

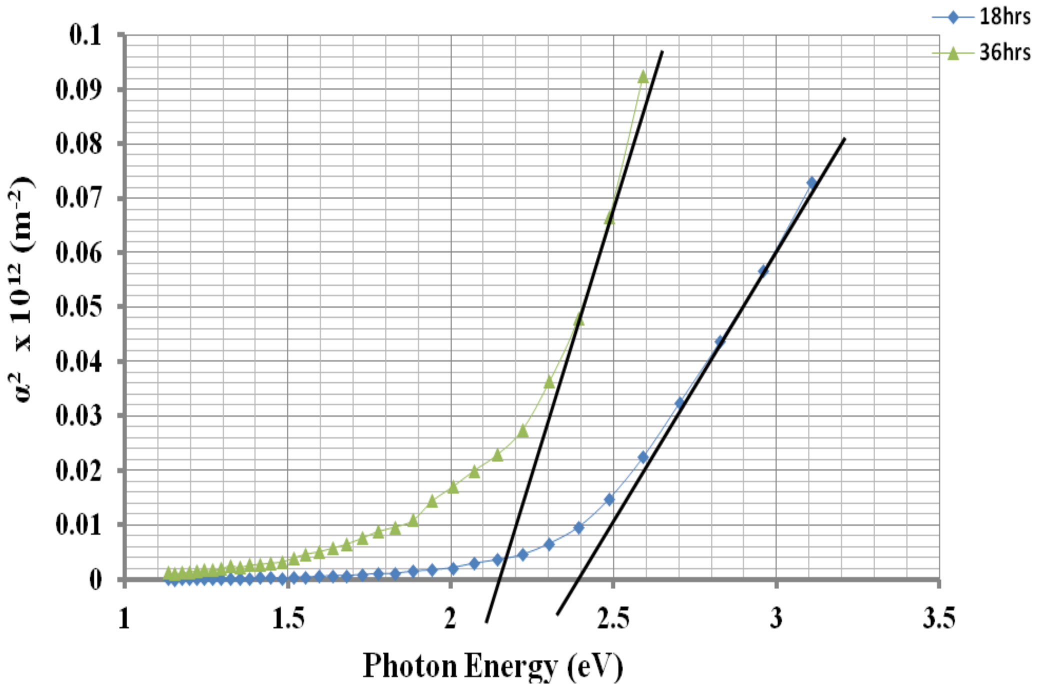

Fig. 10: Plot of Absorption Coefficient Squared of $AgAlS_2$ Thin Films against Photon Energy for various Deposition Time

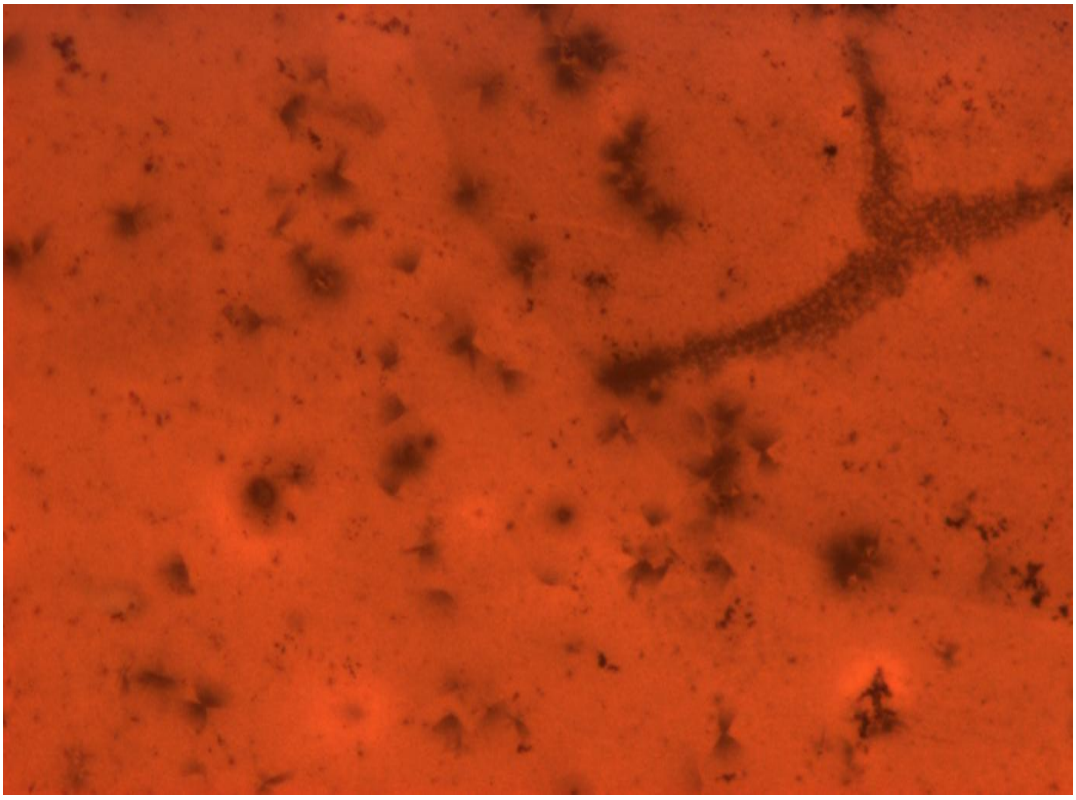

Fig. 11: Micrograph of the Deposited Thin Film

Fig. 11 shows the micrograph of $AgAlS_2$ thin films. Critical observations of the micrographs reveal that the films are crystalline in nature and have small grain sizes.

The compositional characterization of the films was done in Ife, Osun State, Nigeria. Figure 4.12 represents the XRF of $AgAlS_2$ thin film. Figure 13 represents the RXF of degreased substrate without thin film on it. The results as shown in tables 2 below reveal the percentage composition of the elements in the deposition. From our result we can conclusively say that our as- deposited film is $AgAlS_2$ thin film.

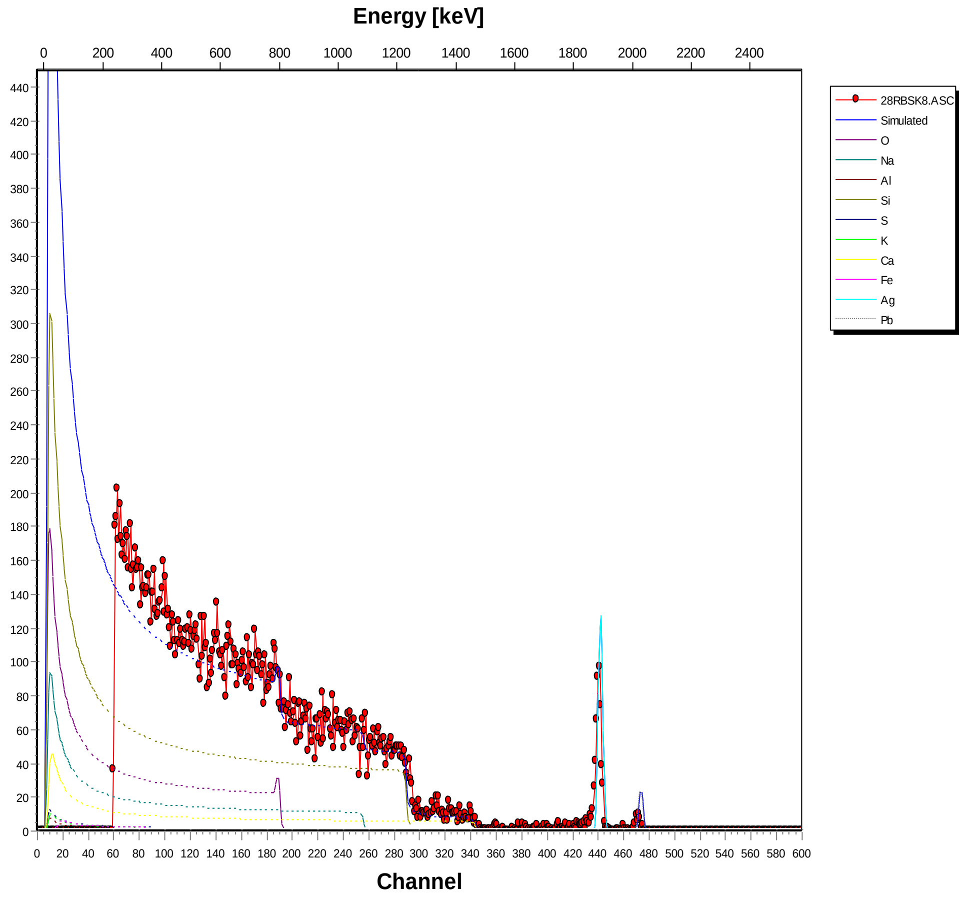

Fig. 12: Elemental Composition of AgAlS Thin Film

LAYER 1: THICKNESS 200.00 (1 E15 Atoms/cm^2) (~ 66.94 nm)

Elements	Percentage Composition
Ag	39.66%
Al	28.40%
S	31.94%

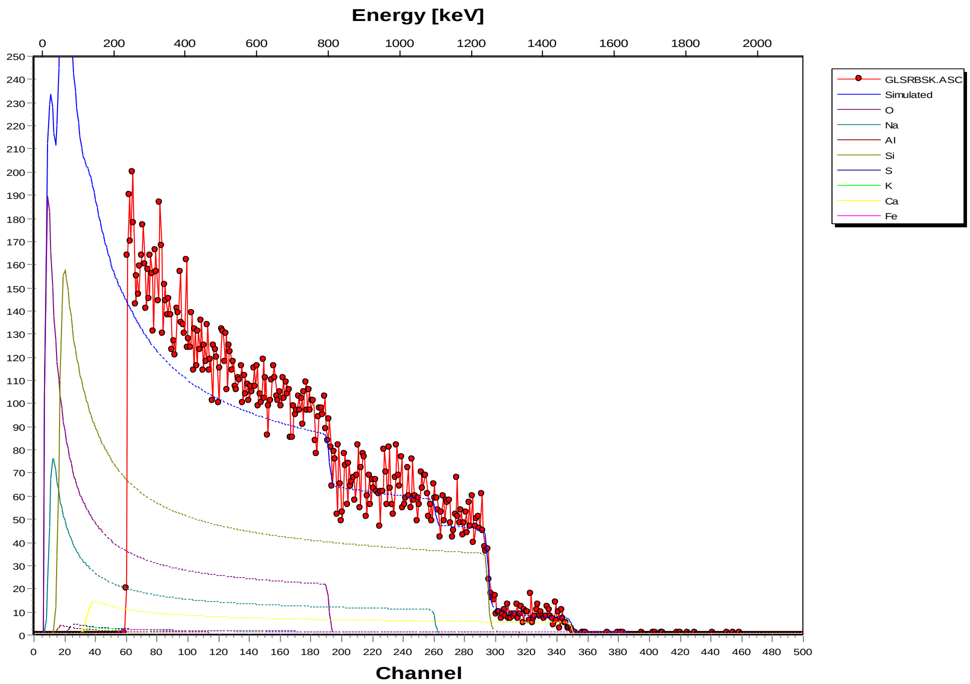

Fig. 13: Elemental Composition of Degreased Substrate used for Deposition

LAYER 1: THICKNESS 17000 (1 E15 Atoms/cm^2)

Elements	Percentage Composition
Si	27.33%
S	0.8%
O	54.23%
Fe	0.27%
Na	14.00%
Al	0.77%
K	0.50%

Conclusion

Silver Aluminum Sulphide ($AgAlS_2$) ternary thin films were successfully deposited on glass substrates using chemical bath deposition technique. $AgAlS_2$ shows average absorbance of 0.51 in UV region, which decreases further as wavelength increases. The films show average transmittance of 75% in the VIS – NIR regions of electromagnetic spectrum. The reflectance is generally low. A refractive index of 2.60 was obtained while the extinction coefficient ranged from 0.08 in the UV region to 0.05 in the NIR region. Optical conductivity of $100\ x\ 10^{12}(s^1)$ at 300nm and $5\ x\ 10^{12}(s^1)$ at 1100nm was obtained. The band gap energy ranged from 2.15 eV to 2.4 eV.

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