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

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Abstract

Lead Silver Sulphide (PbAgS) thin films on glass substrate have been deposited by chemical bath deposition technique with EDTA and TEA as complexing agents, while ammonium solution served as pH adjuster. The films were deposited at room temperature of 300K. The deposited films were characterized using UV – VIS spectrophotometer. From the spectral analysis of the absorbance / transmittance values, the optical and solid state properties were deduced. The optical properties studied include reflectance, absorption coefficient, thickness, refractive index, extinction coefficient, optical conductivity and band gap energy. The films showed very high absorbance in the UV region, moderate in the VIS region and low in NIR region. Transmittance is low in the UV region and high in the VIS – NIR region, while reflectance is generally low in all spectral region studied. The films showed a

direct band gap range of 2.20 eV – 2.40 eV, refractive index range of 2.1 – 2.60, while the thickness of the films increases with deposition time.

Introduction

Ternary chalcogenide semiconductor thin films have been investigated extensively by (Chopra et al, 1983), because the films have properties suitable for fabrication of solar cells (Pawar et al, 1986). Ternary compound have been found to be promising materials for optoelectronic device application such as green light emitting devices and are also suggested to be possible materials for window layers of solar cells (Woon – Jo et al, 2003). The optical and solid state properties of ternary chalcogenide thin film of PbAgS make it a potential semi-conductor material for electronic applications (Uhuegbu, 2007).

In this study, we adopted chemical bath deposition technique. This method has been found to be an inexpensive and simple low temperature method that could be used to produce good quality films for device applications (Wang et al, 1999). The grown films were characterized using a Janway UV – VIS spectrophotometer to determine the optical and solid state properties. The surface and compositional characterization of the films was also carried out.

Materials and Methods

The preparation of Lead Silver Sulphide (PbAgS) thin films was done under normal atmospheric pressure at room temperature (300K). The reaction bath constitute of mixture of 5mls of 0.1M of lead nitrate solution, 5mls of 0.1m of silver nitrate, 5mls of 0.1 mole of EDTA, 5mls of 7.4M of TEA, 5mls of 14.0M of ammonium solution, 10mls of 1.0M of thiourea and 20mls of distilled water. The mixture was stirred with stirrer for 5 minutes to form a homogenous mixture. EDTA and TEA served as complexing agents to prevent spontaneous precipitation of transition metal ions of Pb^{2+} and Ag^{2+} in the mixture. Ammonium solution was used as a pH adjuster, to provide alkaline medium needed for the deposition. The substrates were immersed vertically into the reaction baths with the help of synthetic foams. The substrates were allowed to stay for 6 hours, 12hrs, 24hrs, 36hrs and 48hrs in the deposition baths. After each deposition time, the films were rinsed with distilled water and dried in air.

Before the deposition, the substrates were degreased by dipping them in concentrated HNO_3 for 42 hours, after which they were brought out, washed with detergent, rinsed with distilled water and allowed to dry in an open air. The degreased and cleaned surface has the advantage of providing nucleation centre for the growth of the films, hence yielding highly adhesive and uniformly deposited films. The deposited films were characterized for optical and solid state properties. The surface and compositional characterization of the films was also carried out.

The reaction mechanism is of the form:

$$Pb(NO_3)_2 + EDTA \rightarrow [Pb(EDTA)] + 2NO_3^-$$

$$[Pb(EDTA)] \rightarrow Pb^{2+} + EDTA^{2-}$$

$$AgNO_3 + TEA \rightarrow [Ag(TEA)]^+ + NO_3^-$$

$$[Ag(TEA)]^+ \rightarrow Ag^+ + TEA$$

$$(NH_2)_2CS + OH^- \rightarrow (NH_2)_2CO + HS^-$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$

$$Pb^{2+} + Ag^+ + S^{2-} \rightarrow PbAgS$$

Results and Discussion

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

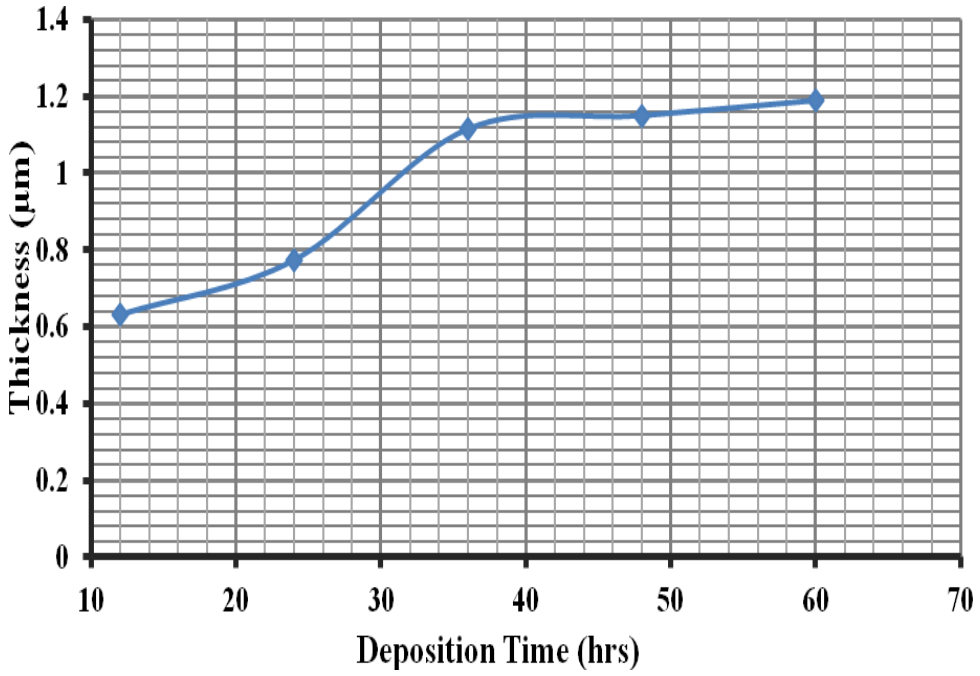
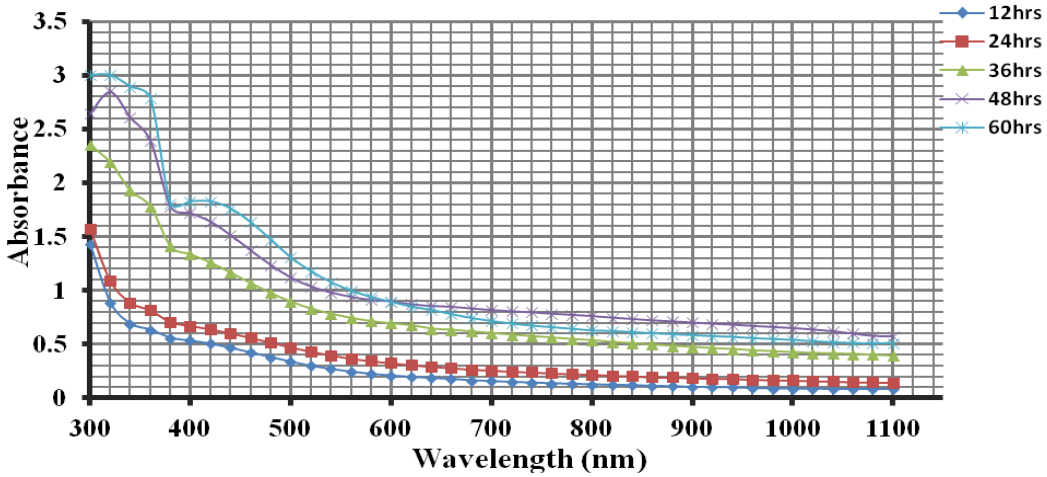


Fig. 1 is a plot of thickness versus time. The thickness of the films increases with deposition time. The lowest film thickness of 0.62µm at 6 hours deposition time and highest film thickness of 1.18µm at 48 hours deposition time was obtained.

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



The absorbance of the films plotted against wavelength is presented in figure 2. The spectral absorbance was very high in UV region, moderate in VIS region and low in NIR region. It is observed that the absorbance of the films increases with deposition time. This could be because of the increase in thickness of the films with deposition time.

Fig. 3: Plot of Transmittance of PbAgS Thin Films against Wavelength for various Deposition Time

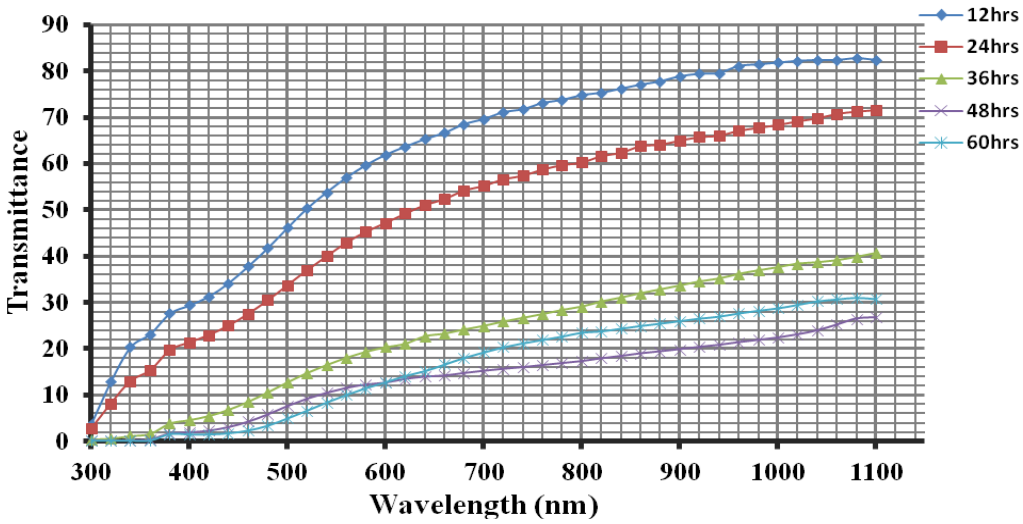
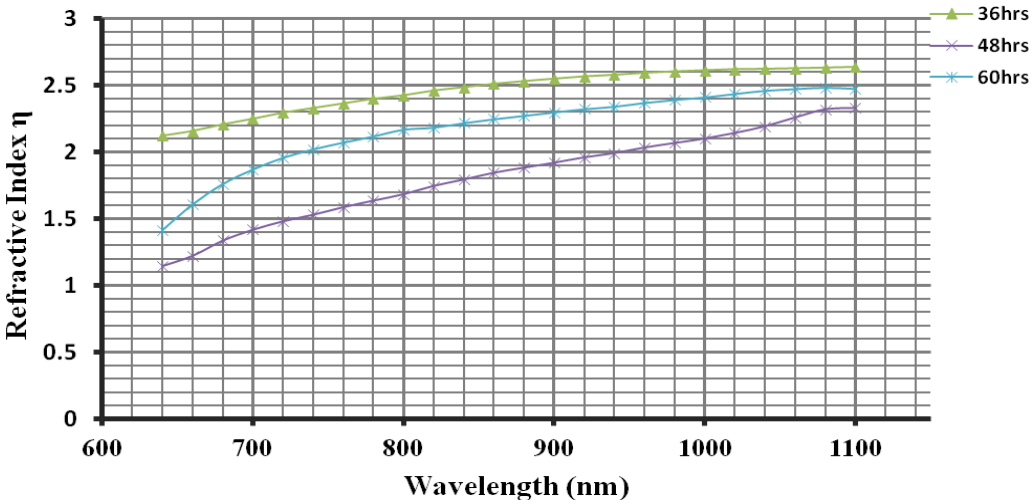


Fig. 3 shows the plot of transmittance against wavelength. Transmittance is very low, as low as 2% in UV region due to high absorbance. Transmittance increases as wavelength increases through VIS to NIR regions. The highest value of 82% in NIR region was recorded for films grown at 12hours deposition time.

Fig. 4: Plot of Reflectance of PbAgS Thin Films against Wavelength for various Deposition Time



Transmittance decreases with increase in deposition time. The reflectance of as – grown films was plotted against wavelength as shown in figure 4. The reflectance of the films is generally low in VIS – NIR regions and does not reflect in the UV region due to high absorbing nature of the as – grown films in UV region. This property makes PbAgS thin films potential materials for anti – reflective coating which can be used on lenses of photographic objectives, on ophthalmic glasses, on lenses and prism of binoculars, microscopes, rangers and periscopes.

Fig. 5 shows the variation of refractive index with wavelength. The refractive index of the films increases with increase in wavelength. The highest refractive index of these films lies in the range of 2.1 – 2.64 (for the film grown for 36hrs). This value of refractive index makes the films good materials for photovoltaic applications.

Fig. 6 shows the variation of extinction coefficient with wavelength. The extinction coefficient of the films decreases as the wavelength increases. The highest extinction coefficient of 0.24 in UV region (300nm) and lowest value of 0.06 in NIR region (1100nm) were obtained for the films grown for 60hrs.

Fig. 5: Plot of Refractive Index of PbAgS Thin Films against Wavelength for various Deposition Time

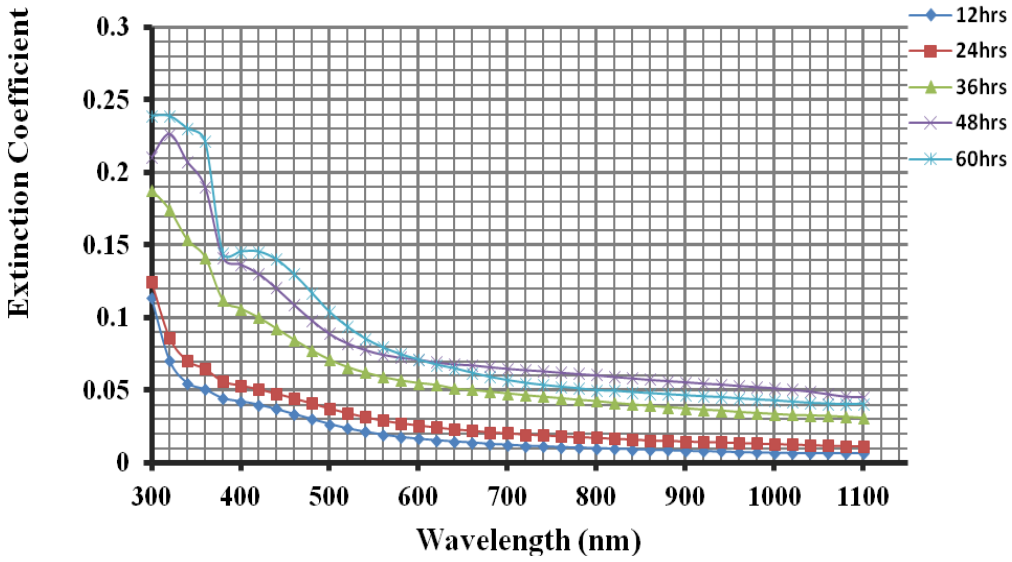


Fig. 6: Plot of Extinction Coefficient of PbAgS Thin Films against Wavelength for various Deposition Time

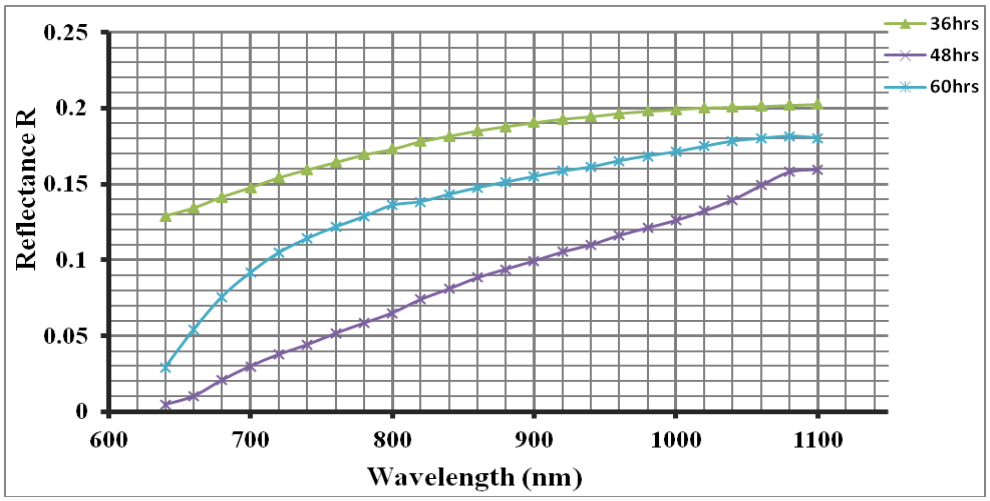


Fig. 7: Plot of Real Dielectric Constant of PbAgS Thin Films against Wavelength for various Deposition Time

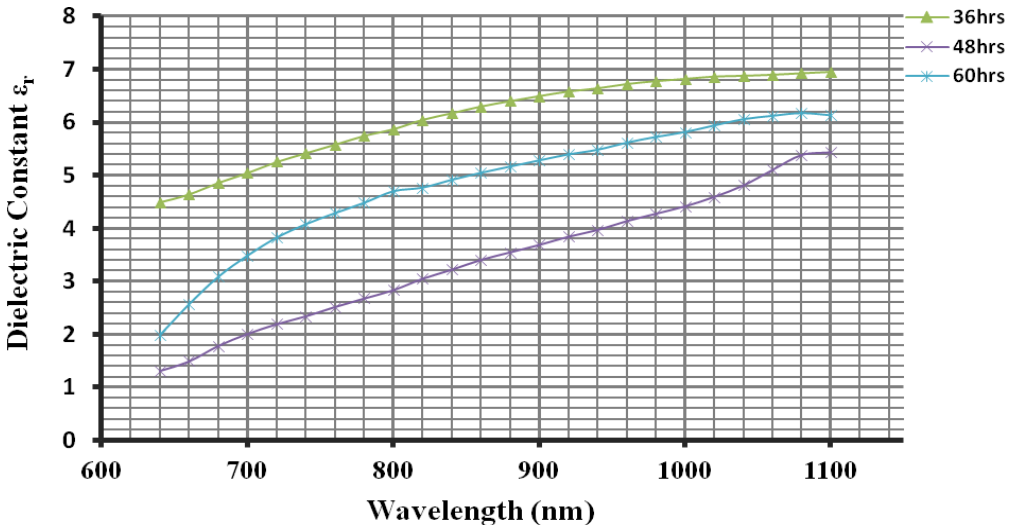


Fig. 7 shows the variation of real part of dielectric constant with wavelength. The values of real part of dielectric constant increase with increase in wavelength and decrease as deposition time increases. The real dielectric constant ranged from 1.31 to 4.40 (for the film grown for 60hrs) and 4.44 to 6.9 (for films grown for 36hrs).

Fig. 8: Plot of imaginary Dielectric Constant of PbAgS Thin Films against Wavelength for various Deposition Time

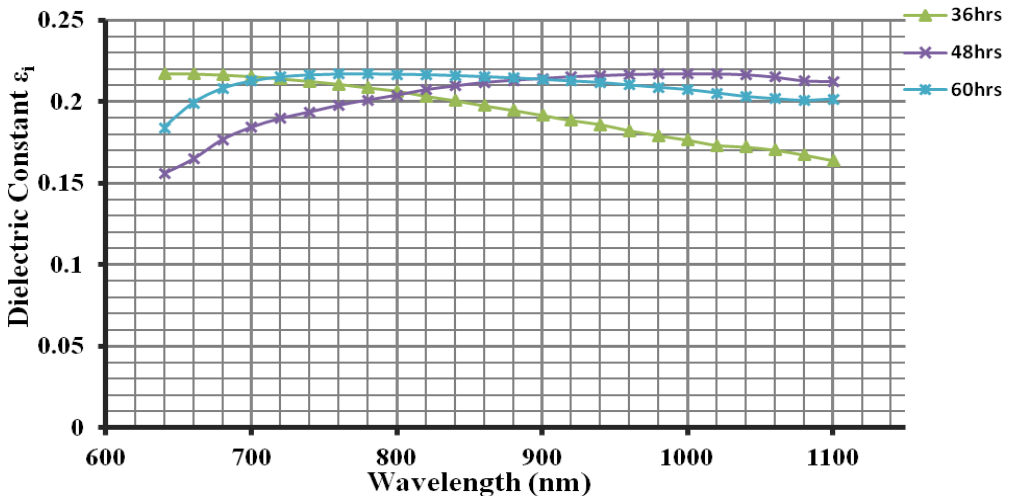


Fig. 8 shows the variation of imaginary part of the dielectric constant with wavelength. The imaginary dielectric constants are generally low with the highest value of 0.22 at 640nm. From the graph, it is seen that imaginary dielectric constant increases with increase in deposition time.

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

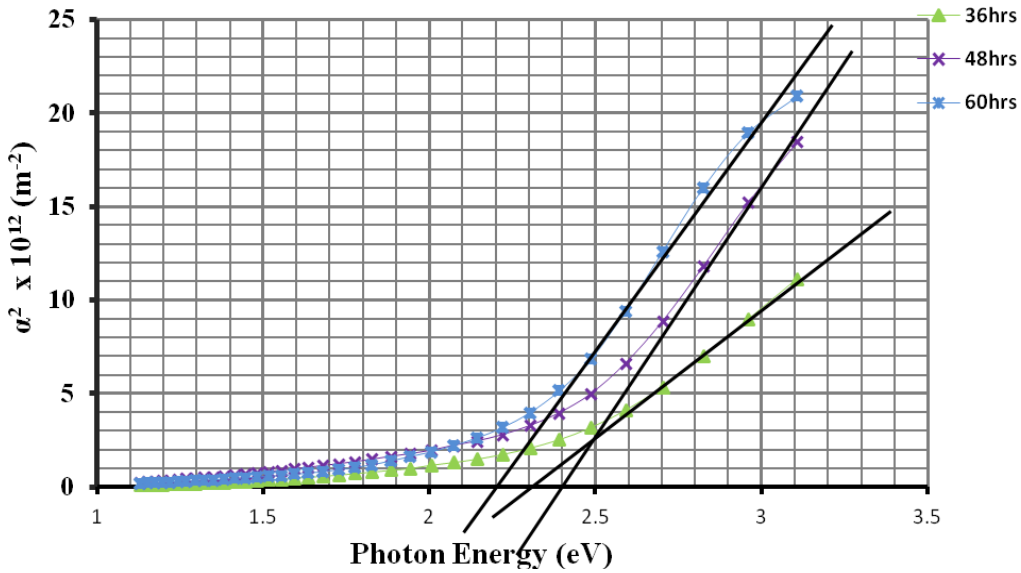


Fig. 9 shows the variation of optical conductivity with wavelength. The optical conductivity of the grown films increases as wavelength increases and increases as deposition time increases. Highest value of $50\,x\,10^{12}(s^{-1})$ at 640nm and lowest value of $22\,x\,10^{12}(s^{-1})$ at 1100nm (for the films grown for 36hrs).

Fig.10 below shows the plot of absorption coefficient squared versus photon energy for PbAgS thin films. 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 2.20 eV to 2.4 eV. This is in agreement with 2.1 eV obtained by (Uhuegbu, 2007). The direct band gap range of 2.2eV to 2.40 eV makes these thin films suitable for solar cell fabrications.

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

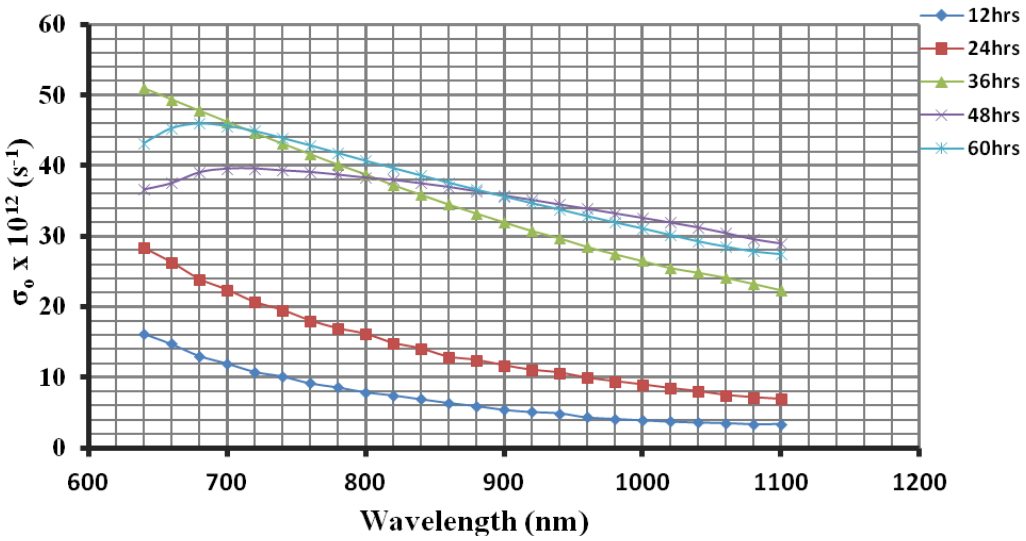


Fig. 11: Micrograph of the Deposited Thin Film

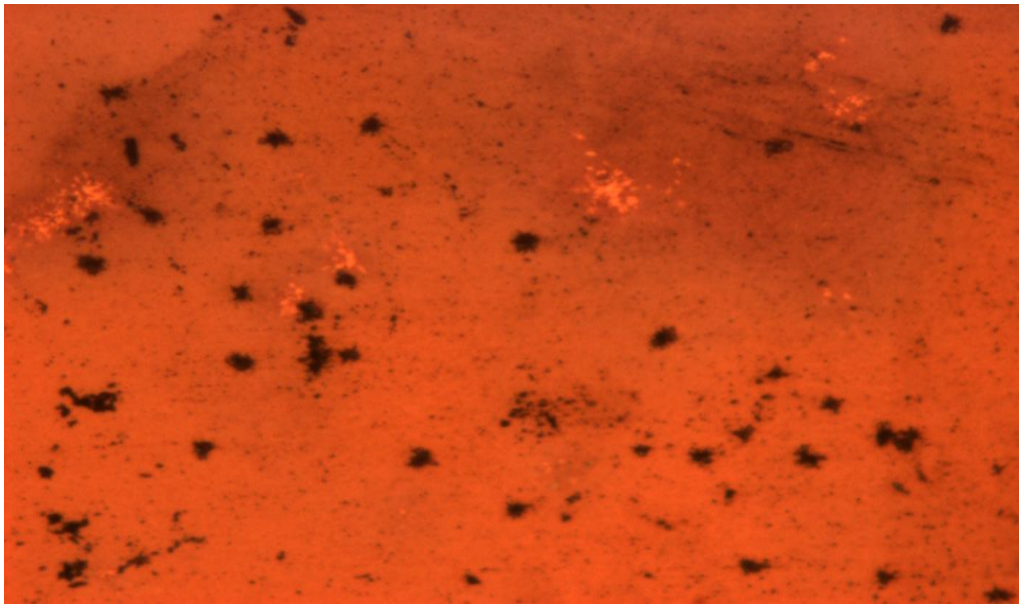
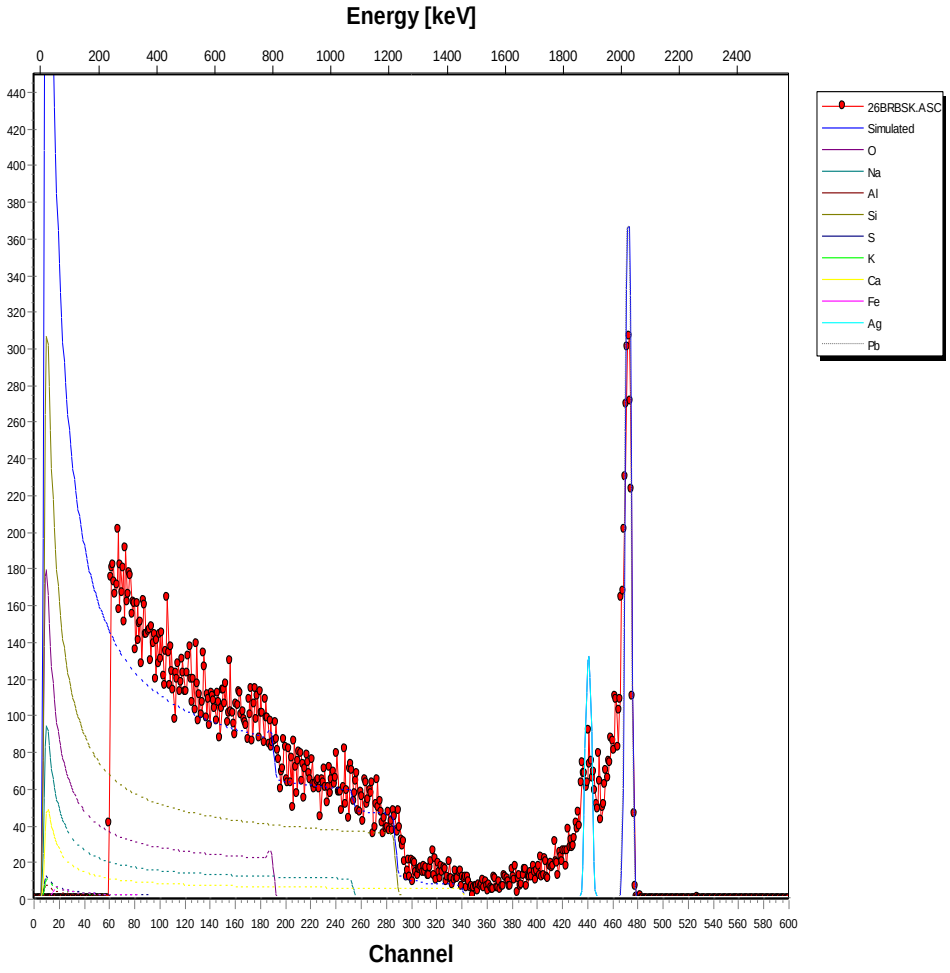


Fig. 11 shows the micrograph of PbAgS thin films. Critical observations of the micrographs reveal that the films are crystalline in nature and have small grain sizes.

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

Fig. 12: Elemental Composition of PbAgS Thin Film



LAYER 1: THICKNESS 268.88 (1 E15 Atoms/cm^2) (~90 nm)

Elements	Percentage Composition
Pb	43.02.03%
Ag	22.00%
S	34.98%

Conclusion

We have successfully deposited ternary thin films of PbAgS by chemical bath deposition techniques using glass substrates. These films have average absorbance of 0.64 NIR region. They show average transmittance of 36% in the VIS – NIR region while reflectance is generally low. The refractive index ranged from 2.1 to 2.60 and highest extinction coefficient of 0.24 in UV region and lowest value of 0.06 in NIR region were obtained. The real dielectric constant ranged from 1.31 to 4.40 (for the film grown for 60hrs) and 4.44 to 6.9 (for films grown for 36hrs) while the imaginary dielectric constant is generally low with the highest value of 0.22 at 640nm. The optical conductivity has highest value of $50\ x\ 10^{12}(s^{-1})$ at 640nm and lowest value of $22\ x\ 10^{12}(s^{-1})$ at 1100nm (for the films grown for 36hrs). The band gap energy ranged from 2.20 eV to 2.40 eV.

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