



Original Research article

Synthesis and Characterization of Aluminium Sulphide (Al₂S₃) Thin Films



I. Lucky Ikhioya^{a,b,*}, B.O. Ijabor^c, G.M. Whyte^{a,b}, F.I. Ezema^{a,b}

^a Crystal growth/Material Science Laboratory, University of Nigeria, Nsukka, Nigeria

^b Department of Physics and Astronomy, University of Nigeria, Nsukka, Nigeria

^c Department of Science Laboratory Technology, Delta State Polytechnic Ogwashi-Uku, Nigeria

ARTICLE INFORMATION

Received: 12 April 2019

Received in revised: 26 April 2019

Accepted: 12 June 2019

Available online: 29 July 2019

DOI: [10.33945/SAMI/CHEMM.2019.6.4](https://doi.org/10.33945/SAMI/CHEMM.2019.6.4)

KEYWORDS

Aluminium

ITO

Temperature

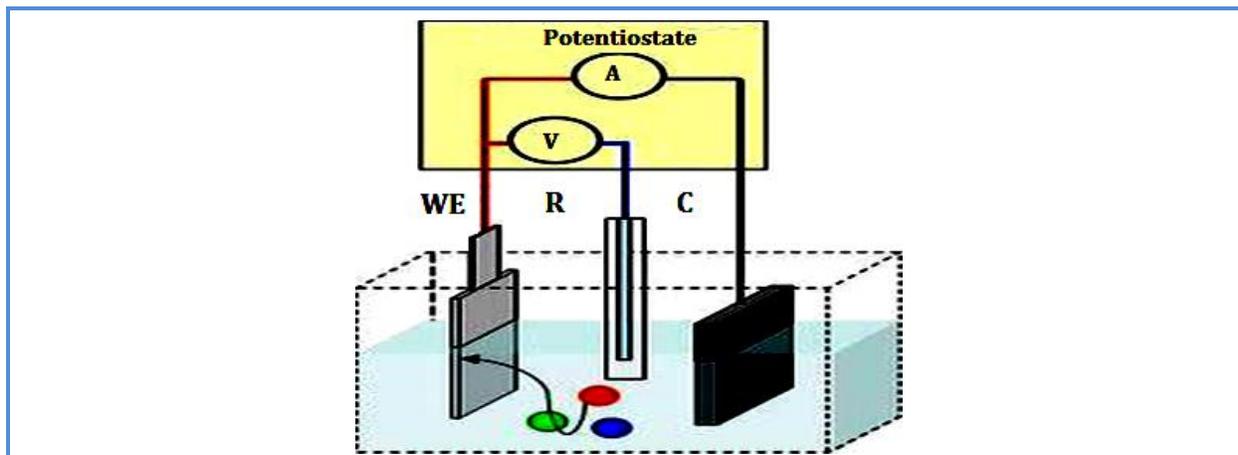
Structural and optical

ABSTRACT

The synthesis of Al₂S₃ thin film was carryout using electrodeposition technique. The electrodeposition bath system is composed of a source of cation (*i.e.* AlSO₄·17H₂O for Al²⁺) and a source of anion (*i.e.* Na₂SO₄ for S²⁻). Indium doped Tin Oxide (ITO) was used as the cathode while the anode was carbon and fluorine electrode. The temperature was varied by heating the entire precursor using a standard heating mantle with temperature ranges from 20 °C- 120 °C and the growth of Al₂S₃ thin films was carried out using the temperature range from 50 °C-80 °C at interval of 10 °C which later was converted to Kelvin. The XRD was found to be of wurtzite-like structure as hexagonal crystal structure that corresponds to 100, 110 and 111 plane. All the samples deposited at different temperature are crystalline in nature with lattice constant, (*a* = 5.829Å). Scanning electron microscopy (SEM) was carried out to reveal the micro-structural properties of aluminium sulphide thin films material. It was observed that as the wavelength of the incident radiation increases the absorbance of the material decreases. The sample deposited at 353 K recorded the highest absorbance at 380 nm. The sample deposited at 333 K recorded the highest transmittance at 1180 nm. Al₂S₃ film has a low transmittance less than 30% in the visible wavelength 520–720 nm and less than 60% transmittance in the near infrared wavelength 760–1200 nm which showed that as the wavelength of the incident radiation increases the transmittance of the films increases. The resistivity of the material decreases as the temperature and thickness of the materials increases while the conductivity of the material increases as the temperature and thickness of the material increases. The band gap energy of Al₂S₃ thin films deposited at (323 K-353 K) as obtained from the plot is given as 2.4-3.0 eV.

*Corresponding author: E-mail: Imosobomeh.ikhioya@unn.edu.ng, Crystal growth/Material Science Laboratory, University of Nigeria, Nsukka Department of Physics and Astronomy, University of Nigeria, Nsukka.
Tel: +2348038684908

Graphical Abstract



Introduction

Semiconductor materials play an important role in our modern day electronics; including, transistors, diodes, integrated circuits and other solid-state devices [1-3]. Such devices have been found to possess wide applications due to their numerous advantages such as compact sizes, reliability, power efficiency, and low cost [4-6]. As discrete components, they have been found to be of use in power devices, optical sensors, and light emitters, including solid-state lasers [7-8]. More importantly, they can be easily incorporated into the easily manufactural microelectronic circuits [9]. They are, and will continue to be one of key elements for almost all electronic systems in the foreseeable future [10]. Thin films are crystalline or non-crystalline materials developed two dimensionally on a substrates surface by physical or chemical methods [11]. They play a vital role in nearly all electronic and optical devices. They have been used as electroplated films for decoration and protection. They have long been used as anti-reflection coatings on window glass, video screens, camera lenses and other optical devices [12]. These films are more than 100 nm thick, made from dielectric transparent materials and have refractive indices less than that of the substrate [13]. Aluminium sulphide (Al_2S_3) has a wurtzite-like crystal structure, existing in several forms [14]. The thin films of aluminium sulphide can be use in optoelectronic industries and for solar cell production and other applications in electronic industries. Aluminium sulphides are versatile materials and can exhibit exceptional electrical, optical, and structural properties [15-16], aluminium sulphides have been incorporated into abroad range of devices; including, heterogeneous catalysts, energy conversion and energy storage devices, transistors, photodetectors, and gas sensors [17-18]. Thin films have been prepared by several techniques; including, molecular beam epitaxy (MBE) vacuum evaporation, radio frequency sputtering and

electrodeposition. Among these techniques, electrochemical deposition offers several advantages: it is relatively economical and can be used on a large scale [19-20, 24-31].

Experimental

Materials and methods

Analytical grade chemicals were used for this study. The chemicals used in the synthesis of aluminium sulphide (Al_2S_3) thin films material included aluminium sulphate ($\text{AlSO}_4 \cdot 17\text{H}_2\text{O}$), sodium sulphate (Na_2SO_4), K_2SO_4 and H_2SO_4 . Electrochemical deposition technique (EDT) was used in this work which involves the deposition of any substance on an electrode as a result of electrolysis which is the occurrence of chemical changes owing to the passage of electric current through an electrolyte. This process involves oriented diffusion of charged growth species through a solution when an external field is applied and reduction of charged growth species at the growth or deposition which also serves as an electrode.

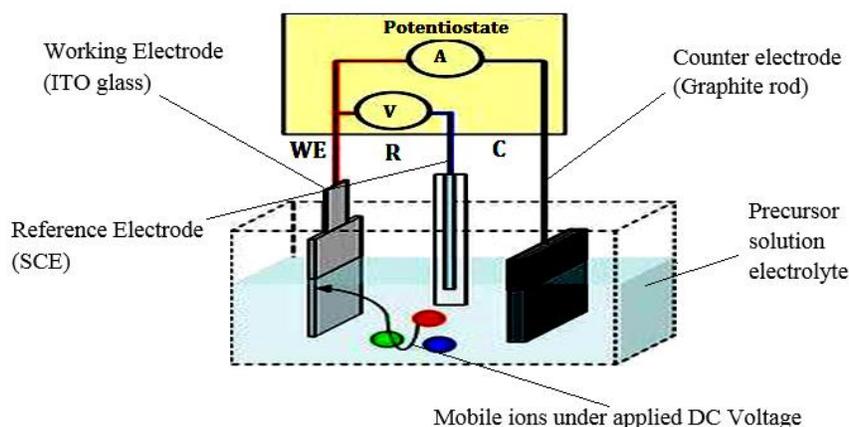


Figure 1. Schematic diagram of electrodeposition setup

Substrate cleaning procedure

Transparent Indium doped tin oxide (ITO) coated glass substrates with a sheet resistance of about $14.42 \Omega/\text{m}$ was used as substrate for deposition. The glass substrates were coated only on one side which was detected by the use of a digital multimeter. Moreover, it gave reading as the non-conducting side which did not give any reading for the deposition of thin films materials. Hand gloves were used to handle the substrates to avoid contamination. The substrates were dipped in acetone, methanol, rinsed with distilled water and later ultrasonicated for 30 min in acetone solution

after which they were rinsed in distilled water and kept in an oven at 333 K to dry. All the prepared substrates were kept in air-tight container.

Synthesis of Al₂S₃ thin films

The synthesis of Al₂S₃ thin films materials was carried out using the cationic precursor which was an aqueous solution of 0.1 M AlSO₄.17H₂O while the anionic precursor was 1 M Na₂SO₄ solution. This was to ensure a uniform deposition. The electrodeposition bath system is composed of a source of cation (*i.e.* AlSO₄.17H₂O for Al²⁺), a source of anion (*i.e.* Na₂SO₄ for S²⁻), distilled water all in 100 mL beaker, and a magnetic stirrer which was used to stir the reaction bath. A power supply was used to provide electric field (DC voltage), a Indium doped tin oxide (ITO) was used as the cathode while the anode was carbon and fluorine electrode. Different temperatures were applied by heating the entire precursor using a standard heating mantle with temperature ranges from 10 °C-120 °C. The growth of Al₂S₃ thin films was carried out using the temperature range from 50 °C-80 °C at an interval of 10 °C which later converted to Kelvin bath parameter. Moreover, they were determined with respect to the different bath parameters which include time and voltage of deposition and substrate for the deposition. In this sense, the concentration of the solution was kept constant throughout the experiment. The concentration of the compounds was maintained as prepared. 10 cm³ of AlSO₄.17H₂O and (Na₂SO₄) were measured into 100 mL beaker using burette. 5 cm³ of K₂SO₄ and H₂SO₄ were measured into the same 100 mL beaker containing AlSO₄.17H₂O and (Na₂SO₄), respectively, to serve as the inert electrolyte helping to dissociate the Al from the AlSO₄.17H₂O and S from the (Na₂SO₄) to form the required AlS film on the substrate. The entire mixture was stirred with the magnetic stirrer to achieve uniformity. In each of the prepared reaction baths, a substrate (ITO) and carbon and fluorine electrode were connected to a DC power supply source and the time and voltage were maintained at 1 min and 10 V with different deposition temperature, respectively.

Characterization technique

The synthesized films were characterized for their optical properties, electrical properties, Scanning electron microscope and structural properties. The structural properties were obtained using X-ray diffractometer (XRD) with scanning range of 10–80° and with CuKα 1 radiation of λ=1.5406 Å. Zeiss scanning electron microscope (SEM) was used to observe the surface morphology of the synthesized films and four point probes were used for I/V analysis. Finally, the optical properties of the deposited films were investigated using Shimadzu UV-1800 spectrophotometer.

Results and discussion

Structural studies

XRD pattern of the deposited aluminium sulphide thin film was characterized using (JCPDS card No. 36-1451) as shown in Figure 2. and it was found to be wurtzite-like structure as hexagonal crystal structure that corresponds to 100, 110 and 111 plane see (Table 1) for the structural parameters of the material. The obtained results were compared to other authors who used different techniques in carrying out their research as reported in [17-19]. All the samples deposited at different temperature are crystalline in nature with lattice constant, ($a = 5.829\text{\AA}$). The crystallite size was determined by means of the X-ray line broadening method using Scherer equation [23].

$$\beta_{size}(2\theta) = \frac{k\lambda}{L\cos\theta}$$

Where β is the FWHM of the peak profile (corrected for instrumental broadening), L volume is average of crystal thickness in direction normal to reflecting planes, K is constant of proportionality and is equal to (0.94), θ is diffraction angle of the reflection and λ is the wavelength of the material; the grain size of the material is shown in Table 1.

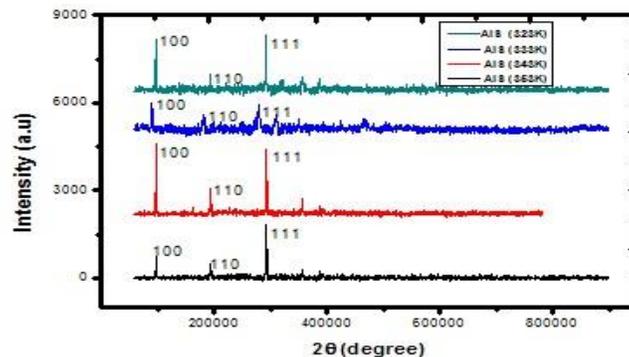


Figure 2. XRD pattern of Al_2S_3

Table 1. Structural parameters of Al_2S_3 thin film

| Sample | 2θ (degree) | d (spacing) \AA | Lattice constant (\AA) | (β) FWHM | (hkl) | Grain Size(D) nm | Dislocation density, σ lines/ m^2 |
|------------|--------------------|--------------------------|-----------------------------------|------------------|-------|------------------|---|
| AIS (323K) | 16.85 | 5.261 | 5.829 | 0.7624 | 100 | 3.514 | 0.080 |
| | 19.94 | 4.451 | | 0.7624 | 110 | 2.221 | 0.202 |
| | 23.10 | 3.850 | | 0.7624 | 111 | 3.592 | 0.077 |
| AIS (333K) | 16.87 | 4.786 | 5.829 | 0.5849 | 100 | 4.491 | 0.111 |
| | 20.11 | 4.414 | | 0.5849 | 110 | 3.051 | 0.163 |
| | 21.89 | 4.315 | | 0.5849 | 111 | 4.876 | 0.102 |
| AIS (343K) | 16.57 | 3.988 | 5.829 | 0.6723 | 100 | 5.133 | 0.097 |
| | 21.14 | 4.660 | | 0.6723 | 110 | 5.194 | 0.096 |
| | 25.41 | 3.564 | | 0.6723 | 111 | 2.165 | 0.230 |
| AIS (353K) | 16.16 | 4.417 | 5.829 | 0.7400 | 100 | 8.694 | 0.057 |
| | 21.84 | 4.069 | | 0.7400 | 110 | 2.580 | 0.019 |
| | 25.42 | 3.282 | | 0.7400 | 111 | 1.967 | 0.254 |

Morphological Studies

The surface morphologies of the samples were carried out using scanning electron microscopy (SEM) and, consequently, the micro-structural properties of aluminium sulphide thin films material was observed. This was done using the LEO (Zeiss) 1540 field emission at high resolution voltage of 15 kV. The morphologies of the deposited aluminium sulphide thin films at different temperature were analysed and the result is shown in Figure 3 (a-d) [17-19].

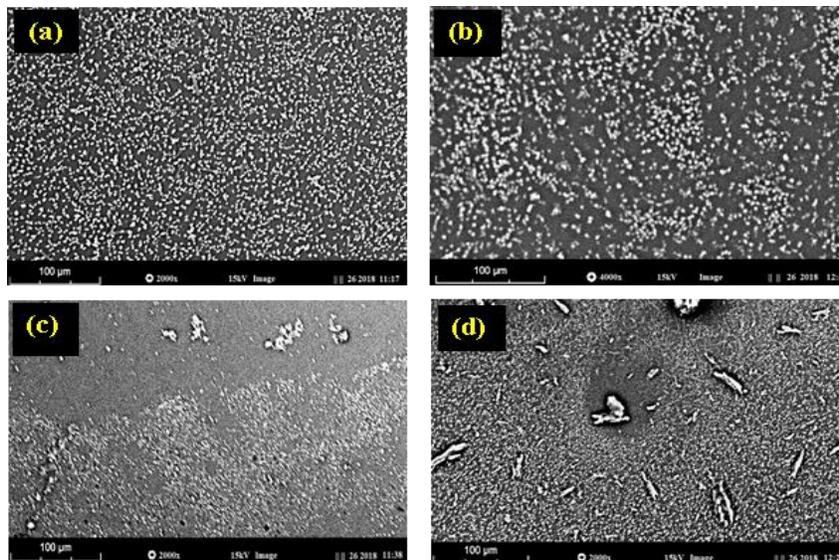


Figure 3. SEM image of aluminium sulphide deposited at different temperature

Electrical studies

The resistivity and conductivity of Al_2S_3 deposited using electrochemical deposition technique was characterized by four point probe. The resistivity of the material decreases as the temperature and thickness of the materials increases while the conductivity of the material increases as the temperature and thickness of the material increases as shown in Table 2.

Table 2. Electrical studies

| SAMPLES | THICKNESS, t (nm) | RESISTIVITY, ℓ (Ω/cm) | CONDUCTIVITY, σ (Ω/cm) ⁻¹ |
|------------|----------------------------|--|---|
| ALS (323K) | 195 | 5.655×10^2 | 1.768×10^{-4} |
| ALS (333K) | 217 | 5.255×10^2 | 1.902×10^{-4} |
| ALS (343K) | 223 | 5.156×10^2 | 1.939×10^{-4} |
| ALS (353K) | 232 | 5.089×10^2 | 1.965×10^{-4} |

The resistivity of Al_2S_3 thin films decreases as the thickness of the films increases and as the conductivity of the material increases the thickness of the Al_2S_3 thin films increases while the varies

deposited temperature increases the thickness of the materials increases which shown that the deposited material can act as a semiconductor material (see Figures 4-5) [17-19].

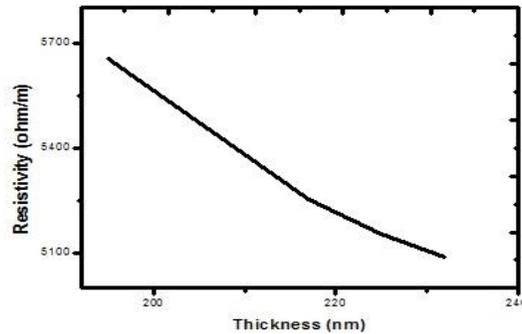


Figure 4. Resistivity Verse Thickness

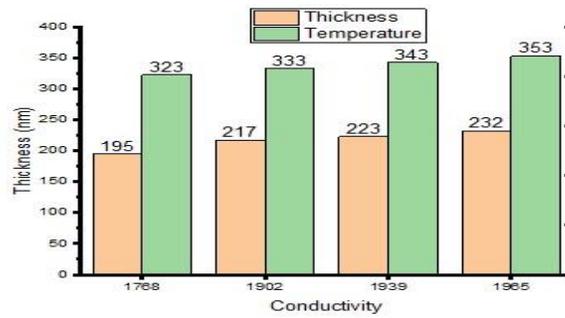


Figure 5. Temperature and thickness Verse Conductivity

Optical studies

The absorbance spectra of Al₂S₃ thin films deposited at 323 K, 333 K, 343 K and 353 K as shown in Figure 8 clearly indicate significant increase in absorbance for all the samples. From Figure 8, it was observed that as the wavelength of the incident radiation increases the absorbance of the material decreases. The sample deposited at 353 K recorded the highest absorbance at 380 nm which shown that at this temperature Al₂S₃ thin films can produce good films for solar cells and photovoltaic applications [8, 17-19].

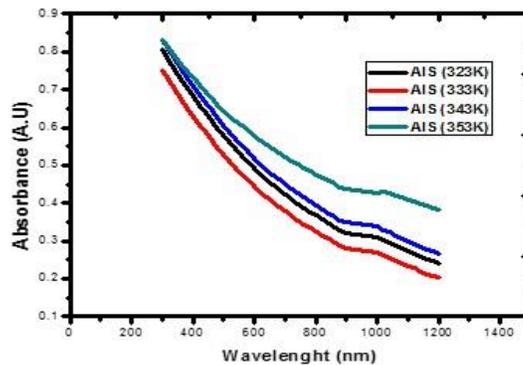


Figure 8. Absorbance verse wavelength

The transmittance spectra of Al_2S_3 thin films deposited at 323 K, 333 K, 343 K and 353 K as shown in Figure 9 clearly indicate significant increase in transmittance for all the samples. The sample deposited at 333 K recorded the highest transmittance at 1180 nm. Al_2S_3 film has a low transmittance less than 30% in the visible wavelength 520–720 nm and less than 60% transmittance in the near infrared wavelength 760–1200 nm which shown that as the wavelength of the incident radiation increases the transmittance of the films increases. From Figure 9 high temperature will influence the transmittance of Al_2S_3 thin films because as the temperature increase the transmittance of the material decreases [8, 17-19].

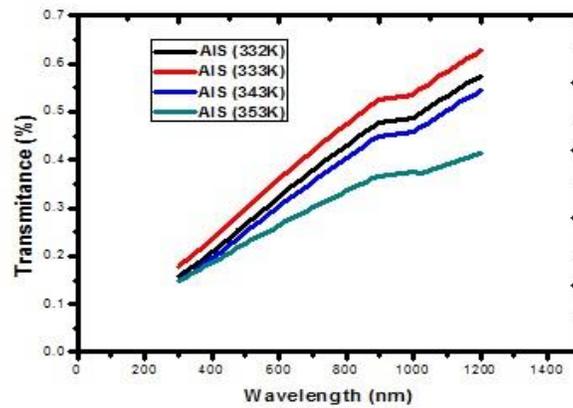


Figure 9. Transmittance verse wavelength

The reflectance spectra of Al_2S_3 thin films deposited at 323 K, 333 K, 343 K and 353 K as shown in Figure 10 clearly indicate significant increase in reflectance for all the samples. From Figure 10, it was observed that as the wavelength of the incident radiation increases the reflectance of the material also increases. The sample deposited at 353 K recorded the highest reflectance at 1200 nm which indicated that at this temperature Al_2S_3 thin films can produce good films for solar cells and photovoltaic applications [8, 17-19].

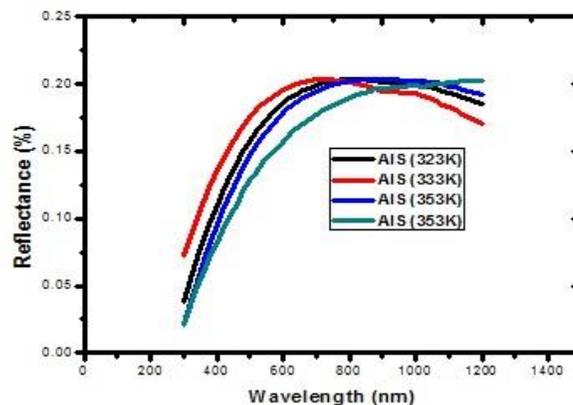


Figure 10. Reflectance verse wavelength

It has been established that Al₂S₃ thin film is the direct band gap semiconductor and therefore, the optical band gap energy was calculated using the following equation [16].

$$\alpha hv = A(hv - E_g)^n$$

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a parameter that depends on the transition probability, h is Planck's constant, and the exponent n depends on the transition during the absorption process. The value of n is 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively. The band gap energy of Al₂S₃ thin films deposited at (323 K-353 K) as obtained from Figure 11 is given as 2.4-3.0 eV, respectively [8, 17-19].

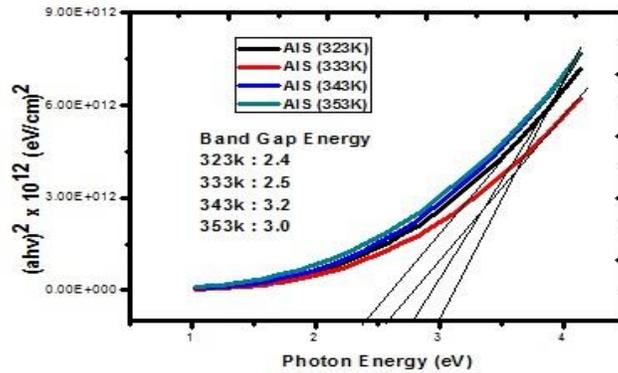


Figure 11. $(\alpha hv)^2$ verse photon energy

The optical conductivity spectra of Al₂S₃ thin films deposited at 323 K, 333 K, 343 K and 353 K as shown in Figure 12 clearly indicate a significant increase in optical conductivity for all the samples. From Figure 12, it was observed that as the photon energy of the material increases the optical conductivity of the material increases. The sample deposited at 333 K recorded the highest optical conductivity at 1200 nm which showed that at this temperature Al₂S₃ thin films can produce good conducting films for solar cells and photovoltaic applications [8, 17-19].

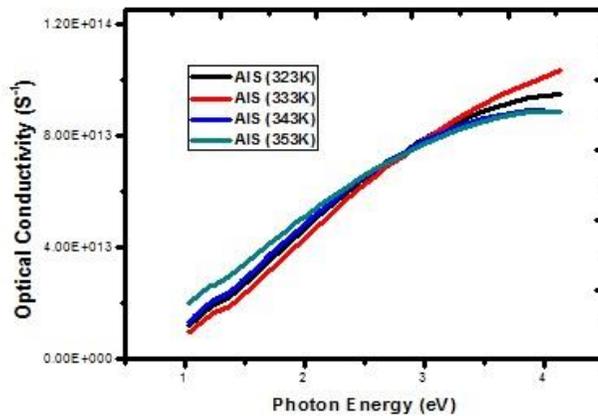


Figure 12. Optical conductivity verse photon energy

Conclusions

Synthesis and characterization of aluminium sulphide (Al_2S_3). Thin films was carried out using electrodeposition technique. The electrodeposition bath system was composed of a source of cation (*i.e.* $\text{AlSO}_4 \cdot 17\text{H}_2\text{O}$ for Al^{2+}) and a source of anion (*i.e.* Na_2SO_4 for S^{2-}), as the Indium doped tin oxide (ITO) was used as the cathode while the anode was carbon and fluorine electrode. The temperature varied by heating the entire precursor using a standard heating mantle with temperature ranges from 20 °C- 120 °C and the growth of Al_2S_3 thin films was carried out using the temperature range from 50 °C-80 °C at interval of 10 °C which later converted to Kelvin. The XRD was found to be wurtzite-like structure as hexagonal crystal structure that corresponds to 100, 110 and 111 plane. All the samples deposited at different temperatures are crystalline in nature with lattice constant, ($a = 5.829\text{\AA}$). Scanning electron microscopy (SEM) was carried out to reveal and observe the micro-structural properties of aluminium sulphide thin films material. It was observed that as the wavelength of the incident radiation increases the absorbance of the material decreases. The sample deposited at 353 K recorded the highest absorbance at 380 nm. The sample deposited at 333 K recorded the highest transmittance at 1180 nm. Al_2S_3 film has a low transmittance less than 30% in the visible wavelength 520–720 nm and less than 60% transmittance in the near infrared wavelength 760–1200 nm clarifying the fact that that as the wavelength of the incident radiation increases the transmittance of the films increases. The resistivity of the material decreases as the temperature and thickness of the materials increases while the conductivity of the material increases as the temperature and thickness of the material increases. The band gap energy of Al_2S_3 thin films deposited at (323 K-353 K) as obtained from the plot is given as 2.4-3.0 eV.

Acknowledgments

The author is thankful to all researchers for their immense contribution leading to the success of this article.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

- [1] Tritsarlis G.A., Malone B.D., Kaxiras E. *J. Appl. Phys.*, 2013, **113**:233507
- [2] Steichen M., Djemour R., Gutay L., Guillot J., Siebentritt S., Dale P.J. *J. Phys. Chem. C*, 2013, **117**:4383
- [3] Miles R.W., Ogah O.E., Zoppi G., Forbes I. *Thin Solid Films*, 2009, **517**:4702

- [4] Devika M., Reddy K.T.R., Reddy N.K., Ramesh K., Ganesan R., Gopal E.S.R., Gunasekhar K.R. *J. Appl. Phys.*, 2006, **100**:023518
- [5] Reddy K.T.R., Reddy P.P., Datta R., Miles R.W. *Thin Solid Films*, 2002, **403**:116
- [6] Banai R.E., Lee H., Motyka M.A., Chandrasekharan R., Podraza N.J., Brownson J.R.S., Horn M.W. *IEEE J. Photovolt.*, 2013, **3**:1084
- [7] Cheng S.Y., Conibeer G. *Thin Solid Films*, 2011, **520**:837
- [8] Letters C., Guneri E., Gode F., Ulutas C., Kirmizigul F., Altindemir G., Gumus C., Thin P.O.P.T.S., *Chalcogenide Lett.*, 2010, **7**:685
- [9] Guneri E., Ulutas C., Kirmizigul F., Altindemir G., Godeand F., Gumus C. *Appl. Surf. Sci.*, 2010, **257**:1189
- [10] Tanusevski A. *Semicond. Sci. Technol.*, 2003, **18**:501
- [11] Khel L.K., Khan S., Zaman M.I. *J. Chem. Soc. Pak.*, 2005, **27**:24
- [12] Sato N., Ichimura M., Arai E., Yamazaki Y. *Solar Energy Mater. Solar Cells*, 2005, **85**:153
- [13] Takeuchi K., Ichimura M., Arai E., Yamazaki Y. *Solar Energy Mater. Solar Cells*, 2003, **75**:427
- [14] Hartman K., Johnson J.L., Bertoni M.I., Recht D., Aziz M.J., Scarpulla M.A., Buonassisi T. *Thin Solid Films*, 2011, **519**:7421
- [15] Holleman A.F., Wiberg E. *Inorganic Chemistry*. Academic Press: San Diego, 2001
- [16] Ikhioya, I.L. *Int. J. Innovat. Appl. Stud.*, 2015, **12**:369
- [17] Meng X., Cao Y., Libera J.A., Elam J.W. *Chem. Mater.*, 2017, **29**:9043
- [18] Lai C.H., Lu M.Y., Chen L.J. *J. Mater. Chem.*, 2012, **22**:19
- [19] Eijsbouts S., Mayo S.W., Fujita K. *Appl. Catal. A General.*, 2007, **322**:58
- [20] Chianelli R.R., Siadati M.H., De la Rosa M.P., Berhault G., Wilcoxon J.P., Bearden R., Abrams B.L. *Catal. Rev. Sci. Eng.*, 2006, **48**:1
- [21] Cabana J., Monconduit L., Larcher D., Palacin M.R. *Adv. Mater.*, 2010, **22**:5435
- [22] Sinha S., Mahuli N., Sarkar S.K., *J. Vac. Sci. Technol.*, 2015, **33**: 01A139
- [23] Abeles F., *Optical Properties of Solid*, North-Holland Pub. Co. Amsterdam, 1988, 234-236
- [24] Lucky I.I. *Int. J. Res. Chem. Environ.*, 2015, **5**:28-32
- [25] Lucky I.I., Simon E., Okeoghene I.B. *Asian J. Chem. Sci.*, 2018, **3**:1. DOI: 10.9734/AJOCs/2017/40415
- [26] Ehika S., Lucky I.I. *Nigerian Annal. Nat. Sci.*, 2017, **16**:066
- [27] Ehika S., Lucky I.I. *Nigerian Annal. Nat. Sci.*, 2017, **16**:057
- [28] Udofia K.I., Lucky I.I. *Asian J. Phys. Chem. Sci.*, 2018, **5**:1, DOI: [10.9734/AJOPACS/2018/40383](https://doi.org/10.9734/AJOPACS/2018/40383)

- [29] Lucky I.I., Orji P.O., Osolobri B.U., Ijabor B.O., P. N. Okanigbuan P.N. *Phys. Sci. Int. J.*, 2018, **19**(1) 9-18, [DOI: 10.9734/PSIJ/2018/43238](https://doi.org/10.9734/PSIJ/2018/43238)
- [30] Lucky I.I., Ehika S., Omehe N.N. *J. Mater. Sci. Res. Rev.*, 2018, **1**(3), 1-11 [DOI: 10.9734/JMSRR/2018/44355](https://doi.org/10.9734/JMSRR/2018/44355)
- [31] Lucky I.I. *Int. J. ChemTech Res.*, 2015, **8**:655

How to cite this manuscript: I. Lucky Ikhioya*, B.O. Ijabor, G.M. Whyte, F.I. Ezema, Synthesis and Characterization of Aluminium Sulphide (Al_2S_3) Thin Films. *Chemical Methodologies* 3(6), 2019, 651-662. [DOI:10.33945/SAMI/CHEMM.2019.6.4](https://doi.org/10.33945/SAMI/CHEMM.2019.6.4).