Synthesis and Characterization of Aluminium Sulphide (Al$_2$S$_3$) 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

**ABSTRACT**

The synthesis of Al$_2$S$_3$ thin film was carried out using electrodeposition technique. The electrodeposition bath system is composed of a source of cation (i.e., AlSO$_4$.17H$_2$O for Al$^{3+}$) and a source of anion (i.e., Na$_2$SO$_4$ for S$^{2-}$). 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 Al$_2$S$_3$ 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 = 5.829 Å). 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. Al$_2$S$_3$ 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 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 Al$_2$S$_3$ thin films deposited at (323 K-353 K) as obtained from the plot is given as 2.4-3.0 eV.

**KEYWORDS**

Aluminium
ITO
Temperature
Structural and optical

*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
Synthesis and Characterization of Aluminium...
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 (Al(SO_4).17H_2O), 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](image-url)

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 Al$_2$S$_3$ thin films**

The synthesis of Al$_2$S$_3$ thin films materials was carried out using the cationic precursor which was an aqueous solution of 0.1 M AlSO$_4$.17H$_2$O while the anionic precursor was 1 M Na$_2$SO$_4$ solution. This was to ensure a uniform deposition. The electrodeposition bath system is composed of a source of cation (*i.e.* AlSO$_4$.17H$_2$O for Al$^{2+}$), a source of anion (*i.e.* Na$_2$SO$_4$ for S$^2-$), 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 Al$_2$S$_3$ 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 cm$^3$ of AlSO$_4$.17H$_2$O and (Na$_2$SO$_4$) were measured into 100 mL beaker using burette. 5 cm$^3$ of K$_2$SO$_4$ and H$_2$SO$_4$ were measured into the same 100 mL beaker containing AlSO$_4$.17H$_2$O and (Na$_2$SO$_4$), respectively, to serve as the inert electrolyte helping to dissociate the Al from the AlSO$_4$.17H$_2$O and S from the (Na$_2$SO$_4$) 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 $\lambda$=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 Shumabzu 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, \( a = 5.829 \text{Å} \). 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 \( \beta \) 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), \( \theta \) is diffraction angle of the reflection and \( \lambda \) is the wavelength of the material; the grain size of the material is shown in Table 1.

![Figure 2. XRD pattern of Al\(_2\)S\(_3\)](image)

<p>| Table 1. Structural parameters of Al(_2)S(_3) thin film |
|---------------------------------|-----|-----|-----|-----|-----|-----|</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>2(\theta) (degree)</th>
<th>d (spacing) (\text{Å})</th>
<th>Lattice constant ((\text{Å}))</th>
<th>((\beta) FWHM)</th>
<th>(hkl)</th>
<th>Grain Size(D) nm</th>
<th>Dislocation density, (\sigma) lines/m(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlS (323K)</td>
<td>16.85</td>
<td>5.261</td>
<td>5.829</td>
<td>0.7624</td>
<td>100</td>
<td>3.514</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td>19.94</td>
<td>4.451</td>
<td>0.7624</td>
<td>110</td>
<td>2.221</td>
<td>0.202</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.10</td>
<td>3.850</td>
<td>0.7624</td>
<td>111</td>
<td>3.592</td>
<td>0.077</td>
<td></td>
</tr>
<tr>
<td>AlS (333K)</td>
<td>16.87</td>
<td>4.786</td>
<td>5.829</td>
<td>0.5849</td>
<td>100</td>
<td>4.491</td>
<td>0.111</td>
</tr>
<tr>
<td></td>
<td>20.11</td>
<td>4.414</td>
<td>0.5849</td>
<td>110</td>
<td>4.491</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.89</td>
<td>4.315</td>
<td>0.5849</td>
<td>111</td>
<td>4.876</td>
<td>0.102</td>
<td></td>
</tr>
<tr>
<td>AlS (343K)</td>
<td>16.57</td>
<td>3.988</td>
<td>5.829</td>
<td>0.6723</td>
<td>100</td>
<td>5.133</td>
<td>0.097</td>
</tr>
<tr>
<td></td>
<td>21.14</td>
<td>4.660</td>
<td>0.6723</td>
<td>110</td>
<td>5.194</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.41</td>
<td>3.564</td>
<td>0.6723</td>
<td>111</td>
<td>2.165</td>
<td>0.230</td>
<td></td>
</tr>
<tr>
<td>AlS (353K)</td>
<td>16.16</td>
<td>4.417</td>
<td>5.829</td>
<td>0.7400</td>
<td>100</td>
<td>8.694</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td>21.84</td>
<td>4.069</td>
<td>0.7400</td>
<td>110</td>
<td>2.580</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.42</td>
<td>3.282</td>
<td>0.7400</td>
<td>111</td>
<td>1.967</td>
<td>0.254</td>
<td></td>
</tr>
</tbody>
</table>
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].

![SEM images of aluminium sulphide deposited at different temperature](image1)

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

Electrical studies

The resistivity and conductivity of $\text{Al}_2\text{S}_3$ 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>
<thead>
<tr>
<th>SAMPLES</th>
<th>THICKNESS, $t$ (nm)</th>
<th>RESISTIVITY, $\ell$ ($\Omega/cm$)</th>
<th>CONDUCTIVITY, $\sigma$ ($\Omega/cm$)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlS (323K)</td>
<td>195</td>
<td>$5.655 \times 10^2$</td>
<td>$1.768 \times 10^{-4}$</td>
</tr>
<tr>
<td>AlS (333K)</td>
<td>217</td>
<td>$5.255 \times 10^2$</td>
<td>$1.902 \times 10^{-4}$</td>
</tr>
<tr>
<td>AlS (343K)</td>
<td>223</td>
<td>$5.156 \times 10^2$</td>
<td>$1.939 \times 10^{-4}$</td>
</tr>
<tr>
<td>AlS (353K)</td>
<td>232</td>
<td>$5.089 \times 10^2$</td>
<td>$1.965 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The resistivity of $\text{Al}_2\text{S}_3$ thin films decreases as the thickness of the films increases and as the conductivity of the material increases the thickness of the $\text{Al}_2\text{S}_3$ 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](image1)

**Figure 4.** Resistivity Verse Thickness

![Figure 5. Temperature and thickness Verse Conductivity](image2)

**Figure 5.** Temperature and thickness Verse Conductivity

**Optical studies**

The absorbance spectra of Al$_2$S$_3$ 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 Al$_2$S$_3$ thin films can produce good films for solar cells and photovoltaic applications [8, 17-19].

![Figure 8. Absorbance verse wavelength](image3)

**Figure 8.** Absorbance verse wavelength
The transmittance spectra of Al$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ thin films because as the temperature increase the transmittance of the material decreases [8, 17-19].

![Figure 9. Transmittance verse wavelength](image)

The reflectance spectra of Al$_2$S$_3$ 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$_2$S$_3$ thin films can produce good films for solar cells and photovoltaic applications [8, 17-19].

![Figure 10. Reflectance verse wavelength](image)
It has been established that Al$_2$S$_3$ thin film is the direct band gap semiconductor and therefore, the optical band gap energy was calculated using the following equation [16].

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

where $\alpha$ 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 Al$_2$S$_3$ 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. $(\alpha h\nu)^2$ verse photon energy

The optical conductivity spectra of Al$_2$S$_3$ 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 Al$_2$S$_3$ 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 \((\text{Al}_2\text{S}_3)\). Thin films was carried out using electrodeposition technique. The electrodeposition bath system was composed of a source of cation \((\text{i.e. AlSO}_4.17\text{H}_2\text{O for Al}^{2+})\) and a source of anion \((\text{i.e. Na}_2\text{SO}_4 \text{for S}^{2-})\), 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\(_2\)S\(_3\) 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, \((a = 5.829\text{Å})\). 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\(_2\)S\(_3\) 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 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\(_2\)S\(_3\) 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


**How to cite this manuscript:** I. Lucky Ikhioya*, B.O. Ijabor, G.M. Whyte, F.I. Ezema, Synthesis and Characterization of Aluminium Sulphide (Al₂S₃) Thin Films. Chemical Methodologies 3(6), 2019, 715-726. DOI: 10.33945/SAMI/CHEMM.2019.6.4.