ANALYSIS OF ELECTRICAL AND MICRO-STRUCTURAL PROPERTIES OF ANNEALED ANTIMONY SULPHIDE (Sb$_2$S$_3$) THIN FILMS.

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Samples of antimony sulphide (Sb$_2$S$_3$) thin films synthesized by CBD technique at room temperature and in an oven at 55 °C were annealed at temperatures of 100 °C, 200 °C and 400 °C. Surface micro-structural and electrical properties of the thin films were analyzed using Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), and a Surface Profiler. Results revealed that some of the films are crystalline while others are amorphous. The film samples deposited at 55 °C and annealed at 400 °C have crystallite sizes ranging from 0.68 nm – 2.96 nm and inter-atomic spacing that ranged from 1.68411 Å – 6.52829 Å for varying angles of diffraction. Other measurements reported in this paper include high dielectric constants, film thickness and sheet resistance exhibited by the thin films.

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Keywords: Dielectric constants, Sheet resistance, Surface profiler, Inter-atomic spacing, Film thickness

1. Introduction

Chalcogenide thin films have a number of applications in various fields including protective coatings, solar cells, photoconductors, IR detectors, microelectronics etc. [1-6]. This has led to increased research in this area culminating in a large body of reports in literature on optical, solid state, structural and electrical properties of chalcogenide thin films of sulphides, tellurides and sellinides [7-10]. Sustained research work is required in order to broaden the specificity of their applications. In this paper we report the effect of annealing on structural and electrical properties of antimony sulphide.

2. Experimental details:

Stoichiometric quantities of antimony trichloride (SbCl$_3$), sodium thiosulphate (Na$_2$S$_2$O$_3$) and a complexing agent, acetone (CH$_3$CO) were prepared in a solution bath followed by the film deposition as follows: 1.3 g of SbCl$_3$ was dissolved in 5ml of acetone in a 50 ml beaker, and then 25 ml of 1M sodium thisulphate was added and stirred before 20ml of H$_2$O was added to the bath. Degreased glass slides were inserted vertically into the bath with a synthetic foam which partly covered the top of the bath. Deposition in different baths were formed and left for different hours undisturbed to check the effect of deposition time. The reaction kinetics for the formation of Sb$_2$S$_3$ thin film are as follows:

\[
2\text{SbCl}_3 + \text{CH}_3\text{CO} \rightarrow 2\text{Sb}[	ext{CH}_3\text{CO}]^{3+} + 3\text{Cl}_2 \\
\text{Sb}_2[	ext{CH}_3\text{CO}]^{3+} \rightarrow \text{Sb}_2^{3+} + \text{CH}_3\text{CO} \\
\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{Na}^+ + \text{S}_2\text{O}_3^{2-} \\
6\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{S}_4\text{O}_6^{2-} + 6e^-
\]

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 Measurements following the film deposition were performed at Sheda Science and Technology Complex (SHESTCO), Gwagwalada, Abuja with the assistant of technicians. The XRD patterns were obtained using X-pert Panalytical X – Ray Diffractometer using Cu K-Alpha ($\lambda = 1.54060 \text{Å}$) operated at 30mA and 40KV. The microstructural analysis was performed with a Scanning Electron Microscope (SEM), while the film thickness was measured with a surface profiler.

3. Results and discussion

X-Ray Diffractometer (XRD) was used to ascertain a wide variety of structural information of the thin films. The maximum crystallite sizes of the films were estimated using Sherrer’s formula

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength used ($1.54060 \text{Å}$), $\beta$ is the angular width at half maximum intensity in radians and $\theta$ is the Bragg’s angle. Values of the XRD measurements are contained in table 1. Figures (1-2) show XRD peaks for Sb$_2$S$_3$ thin films deposited at room temperature for unannealed and 100 °C annealed samples. The SEM micrographs of the surface images of the Sb$_2$S$_3$ thin films deposited at room temperature for as grown sample and sample annealed at 200 °C are shown in figures (3,5) while figures (4,6) are surface images for samples deposited at 55 °C and annealed at 200 °C and 400 °C respectively. It is evident that amorphous and crystalline forms of the thin film are produced by the effect of annealing. The sample annealed at 200 °C has large crystallite size of 7.49 nm measured at a diffraction angle of 15.8462 degrees.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Temp (°C)</th>
<th>Angle $\theta$ (degrees)</th>
<th>FWHM $\beta$</th>
<th>Inter-atomic Distance $d$ (Å)</th>
<th>Constant $K$</th>
<th>Crystallite Size D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB3</td>
<td>200</td>
<td>15.8462</td>
<td>0.09120</td>
<td>2.82104</td>
<td>0.9</td>
<td>7.49</td>
</tr>
<tr>
<td>CB5</td>
<td>400</td>
<td>6.7820</td>
<td>0.04725</td>
<td>6.52829</td>
<td>0.9</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.7623</td>
<td>0.06300</td>
<td>3.24068</td>
<td>0.9</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.968</td>
<td>0.06300</td>
<td>2.80226</td>
<td>0.9</td>
<td>2.23</td>
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<td></td>
<td></td>
<td>22.9352</td>
<td>0.12595</td>
<td>1.97834</td>
<td>0.9</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.2190</td>
<td>0.23040</td>
<td>1.68411</td>
<td>0.9</td>
<td>0.68</td>
</tr>
</tbody>
</table>
Fig. 1. XRD pattern for Sb$_2$S$_3$ thin film deposited at room temperature and unannealed.

Fig. 2. XRD pattern for Sb$_2$S$_3$ thin film at room temperature and annealed at 100 °C.

Fig. 3: SEM micrograph of Sb$_2$S$_3$ thin film deposited at room temperature and unannealed.

Fig. 4: SEM micrograph of Sb$_2$S$_3$ thin film deposited at 55 °C and annealed at 200 °C.

Fig. 5. SEM micrograph of Sb$_2$S$_3$ thin film deposited at room temperature, annealed at 200 °C.

Fig. 6. SEM micrograph of Sb$_2$S$_3$ thin film deposited at 55 °C and annealed at 400 °C.
Figures (8, 9) show plots of crystallite size and inter-atomic spacing respectively for varying diffraction angle for the film sample deposited at 55 °C and annealed at 400 °C. The crystallite size and inter-atomic spacing decrease with increase in diffraction angle while figure 7 shows that the FWHM increases with increase in diffraction angle.

The film thickness was calculated from the lower part of the X-Y charts of the surface profiler shown in figures (10-13). The film resistance, R and sheet resistance, Rs were also calculated using value of V/I given by the surface profiler as follows:

\[
\text{Angle (degrees)} \quad R = k \frac{V}{I} \quad (2)
\]

where \( k \) is a constant (4.523)

\[
R_s = R t \quad (3)
\]

Where \( t \) is film thickness
Fig. 10. Surface profile for Sb$_2$S$_3$ thin film deposited at room temperature and unannealed (sample AB1)

Fig. 11. Surface profile for Sb$_2$S$_3$ thin film deposited at room temperature and annealed at 100 °C (sample AB2)

Fig. 12. Surface profile for Sb$_2$S$_3$ thin film deposited at 55 °C and annealed at 200 °C (sample CB3)

Fig. 13. Surface profile for Sb$_2$S$_3$ thin film deposited at 55 °C and annealed at 400 °C (sample CB5)
Fig. 14. Real dielectric constant as a function of photon energy for room temp deposition and annealed Sb$_2$S$_3$ thin film samples AB1 (unannealed) AB2 (100 °C) and AB3 (200 °C)

Fig. 15. Imaginary dielectric constant as a function of photon energy for room temp deposition and annealed Sb$_2$S$_3$ thin film samples AB1 (unannealed) AB2 (100 °C) and AB3 (200 °C)

Figures (14,15) show that the real and imaginary dielectric constants, $\varepsilon_r$ and $\varepsilon_i$ of the Sb$_2$S$_3$ thin films increase with annealing. Measurements of other electrical properties and thickness obtained for the thin films are contained in table 2.
Table 2: Electrical properties and thickness of Sb₂S₃ thin film samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Temp (°C)</th>
<th>Annealing Temp (°C)</th>
<th>Resistance R x 10⁶(Ω)</th>
<th>Sheet Resistance Rₛ (Ωμm)</th>
<th>Thickness t (μm)</th>
<th>εᵣ</th>
<th>εᵢ</th>
</tr>
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<tbody>
<tr>
<td>AB1</td>
<td>Room Temp</td>
<td>-</td>
<td>1225733</td>
<td>416.75</td>
<td>0.34</td>
<td>6.0x10⁵</td>
<td>1580</td>
</tr>
<tr>
<td>AB2</td>
<td>Room Temp</td>
<td>100</td>
<td>1243825</td>
<td>298.52</td>
<td>0.24</td>
<td>2.2x10⁶</td>
<td>3800</td>
</tr>
<tr>
<td>AB3</td>
<td>Room Temp</td>
<td>200</td>
<td>1225733</td>
<td>220.63</td>
<td>0.18</td>
<td>2.4x10⁶</td>
<td>3800</td>
</tr>
<tr>
<td>CB3</td>
<td>55 °C</td>
<td>200</td>
<td>1239302</td>
<td>334.61</td>
<td>0.27</td>
<td>2.2x10⁶</td>
<td>3000</td>
</tr>
<tr>
<td>CB5</td>
<td>55 °C</td>
<td>400</td>
<td>1230256</td>
<td>492.10</td>
<td>0.40</td>
<td>3.8x10⁶</td>
<td>3000</td>
</tr>
</tbody>
</table>

4. Conclusions

The synthesis and characterization of electrical and structural properties of antimony sulphide thin films have been successfully carried out and qualitative and quantitative results presented. The effects of deposition and annealing temperatures on the properties of Sb₂S₃ thin films were investigated. The variations of inter-atomic spacing and crystallite size with diffraction angle for the thin films have also been presented. The results provide basis for specific applications in such areas as protective coatings, solar cells, photoconductors, IR detectors, microelectronics etc.

References