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ABSTRACT
The effect of deposition time on the bandgap of copper sulphide thinfilms deposited on a glass substrate was studied. The CuS thin films were deposited using chemical bath method. The bath for the deposited CuS films was composed of copper (II) chloride dihydrate (CuCl$_2$.2H$_2$O), thiourea, Triethanolamine (TEA) as the complexing agent and ammonium hydroxide as pH adjuster. The deposition was maintained at room temperature of 300K in alkaline medium. The bandgap energy obtained was found to decrease from 2.50 to 1.85eV with increased deposition time of 3 to 15 hours. The thickness was directly proportional to the deposition time.

Keyword: Chemical Bath, Bandgap, Copper Sulphide, Thinfilm

INTRODUCTION
The process of thin film deposition involves the deposition of materials, atom by atom, molecules by molecules, ions by ions or cluster of species by cluster of species condensation (Chopra and Kaur 1983). Thinfilm technology is the base of astounding development in solid state electronics and has great technological importance in recent years. This is because of its widening sphere of applications in sciences and industries. Some examples of the application of thinfilms are microelectronic integrated circuits, magnetic storage systems, optical, solar coatings, solar cells, photoconductors, sensors, anti-reflection coatings, interference items, polarisers, narrow and band filters, Infrared (IR) detectors waveguide coatings, temperature control of satellite, photothermal coatings etc. (West, 2003).

Copper is stable in media and resists high temperatures. These inherent material properties make copper one of the most important materials for industrial applications. One of these is copper sulphide (CuS) thinfilms. CuS thinfilms have chemical stability, their absorption coefficient is high, and are widely used as semiconductors and or absorber materials with application in electronics, photovoltaic cells and solar collectors. Copper Sulphide (CuS) at room temperature forms five stable phases: (i) Covellite (CuS), (ii) anilite (Cu$_{1.7}$S) (iii) digenite (Cu$_{1.8}$S), (iv) djurtite (Cu$_{1.95}$S) and (v) chalcocite (Cu$_2$S). Copper sulphide (Cu$_x$S) has different crystal structures depending on the value of X such as hexagonal, orthorhombic, pseudo-cubic and tetragonal (Pathan, and Lokhande, 2004; Evan, 1981). For example, Cu$_x$S has hexagonal structure and Cu$_2$S may be present in both the crystal structures, i.e. orthorhombic and hexagonal$^3$. Among these CuS (covellite) thinfilms are known to exhibit metal – like electrical conductivity and to possess near ideal solar control characteristics (Cruz –Vasquez et al., 1999).

The Chemical Bath Deposition (CBD) technique has become very popular in recent decades especially for thinfilm deposition due its low cost since no expensive and sophisticated vacuum technique is required. The method requires only a source of chalcogen anions and metal ions to deposit on the substrates. This technique has found applications in many compounds of sulphides, oxides and selenides which include ZnS, CdS, PbS, CuS, ZnO, CdO, BaBrO, CdSe, PbSe, CuSe$^3$ etc. The bandgap of Copper Sulphide (CuS) lies between 1.8eV-2.9eV (Anuar et.al 2010; Santos et.al., 2012).
In this present work, the effect of deposition time on the bandgap of CuS thinfilm was investigated using copper chloride solution as a source of copper ion, thiourea as a source of sulphide ion, Triethanolamine (TEA) (N(CH₂CH₂OH)₃) as a complexing agent and ammonium hydroxide (NH₄OH) as pH adjuster at room temperature.

**EXPERIMENTAL DETAILS**

In this study, CuS thinfilms were grown on glass substrates by Chemical Bath Deposition (CBD) technique at room temperature. Prior to deposition, the glass substrates were degreased in trioxonitrate (v), washed with detergent, rinsed with distilled water and dried in air. The deposition of CuS thinfilm was based on the reaction between aqueous solution of copper chloride (CuCl₂.2H₂O), thiourea (SC(NH₂)₂), in an alkaline medium of NH₄OH and TEA (N(CH₂CH₂OH)₃) as a complexing agent. For deposition, five reaction baths (100mls beaker) were used. 10.0mls of CuCl₂ were measured into a 50ml beaker using burette, 2.0mls of TEA were then added to it, 3.0mls of thiourea were then added to the solution. 5.0mls of ammonium hydroxide solution were then added. The mixture was then topped to 60mls level by addition of distilled water and stirred gently to ensure uniformity of the mixture. Copper chloride and thiourea were the sources of Cu²⁺ and S²⁻, respectively. The deposition process was carried out at different deposition times of 3, 6, 9, 12 and 15 hours in order to determine the optimum condition for the deposition of CuS thinfilm. The experiment was conducted at room temperature. Five cleaned glass substrates were vertically immersed into the chemical baths with the help of the synthetic foam. After the deposition, the films were washed with distilled water and kept for analysis. Optical and morphological characterization of the films were carried out using, a Janway 6405 UV/VIS spectrophotometer and an Olumpus optical microscope. The absorbance spectra data of the films were obtained from the spectrophotometer. Thickness of the films were calculated using optical parameters in the formular: 

\[ t = \frac{\ln \left( \frac{1-R^2}{T} \right)}{\alpha} \]

where \( t \) = thickness of the film, \( R \) = reflectance, \( T \) = transmittance and \( \alpha \) = absorption coefficient of the film.

The equations governing the reaction and deposition of CuS films are as follow:

\[
\begin{align*}
\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + \text{TEA} & \rightarrow \text{Cu(TEA)}^{2+} + 2\text{Cl}^- \\
\text{Cu(TEA)}^{2+} & \rightarrow \text{Cu}^{2+} + \text{TEA} \\
\text{Sc(NH}_2)_2 + \text{OH} & \rightarrow \text{CH}_3\text{N}_2 + \text{H}_2\text{O} + \text{HS}^- \\
\text{HS}^- + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{S}^{2-} \\
\text{Cu}^{2+} + \text{S}^{2-} & \rightarrow \text{CuS}
\end{align*}
\]

**Table 1.0: Bath constituents for the deposition of copper sulphide thin film**

<table>
<thead>
<tr>
<th>Reaction bath</th>
<th>Volume of CuCl₂.2H₂O (mls)</th>
<th>Volume of TEA(mls)</th>
<th>Volume of Thiourea(mls)</th>
<th>Volume of NH₄OH(mls)</th>
<th>Volume of H₂O (mls)</th>
<th>Time of deposition(hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₁</td>
<td>10.00</td>
<td>2.00</td>
<td>3.00</td>
<td>5.00</td>
<td>60.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Cu₂</td>
<td>10.00</td>
<td>2.00</td>
<td>3.00</td>
<td>5.00</td>
<td>60.00</td>
<td>6.00</td>
</tr>
<tr>
<td>Cu₃</td>
<td>10.00</td>
<td>2.00</td>
<td>3.00</td>
<td>5.00</td>
<td>60.00</td>
<td>9.00</td>
</tr>
<tr>
<td>Cu₄</td>
<td>10.00</td>
<td>2.00</td>
<td>3.00</td>
<td>5.00</td>
<td>60.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Cu₅</td>
<td>10.00</td>
<td>2.00</td>
<td>3.00</td>
<td>5.00</td>
<td>60.00</td>
<td>15.00</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**

Ezenwaka, Laz., Aniefuna, Nnaemeka K., Umekwonu, N.S.
Effects of Deposition Time on the Bandgap of Copper Sulphide Thinfilms Fabricated by Chemical Bath Deposition Method

Ezenwaka, Laz., Aniefuna, Nnaemeka K., Umeokwonna, N.S.

Figure 1: \((\text{Absorption Coefficient})^2\) versus energy for 3 hours deposition time thin film

Figure 2: \((\text{Absorption Coefficient})^2\) versus energy for 6 hours deposition time thin film

Figure 3: \((\text{Absorption Coefficient})^2\) versus energy for 9 hours deposition time thin film

Figure 4: \((\text{Absorption Coefficient})^2\) versus energy for 12 hours deposition time thin film
Figure 5: (Absorption Coefficient)$^2$ versus energy for 15 hours deposition time thin film

Figure 6: Band gap versus thickness

Figures 1-5 show the relation between absorption coefficient square and photon energy. The linear nature of the plot indicates the existence of the direct transition. The bandgaps were determined by extrapolating the straight portion to the energy axis at $\alpha^2 = 0$. The band gap energy decreased from $2.50 \times 1.85$ eV as the time of deposition increased. This is consistent with (Anuar et al. 2010; Santos Cruz et al. 2012) and is evident in figures 1-5. This implies that CuS has high bandgap energy and can be used as an absorber layer of a solar cell.

Figure 6 reveals that the band gap is inversely proportional to the thickness of the deposited
CuS film. This is as a result of grain size effect. This implies that as the film thickens, the grain size increases and it narrows the bandgap. The film with the lowest thickness of 0.64\(\mu\)m has the highest bandgap energy of 2.50eV while the CuS film with the highest thickness of 1.02\(\mu\)m has the lowest bandgap energy of 1.85eV.

Figure 7 shows that the bandgap is also inversely proportional to the time of deposition. The deposition time of 3 hours has the highest bandgap energy of 2.50eV while CuS thin film with the longest deposition time of 15 hours has the lowest bandgap energy of 1.85eV. Figure 8 is the graph of thickness on time of deposition. From the graph, thickness is directly proportional to time of deposition. CuS film with 15 hours deposition time has the highest thickness of 1.02\(\mu\)m while CuS film with 3 hours deposition time has the lowest thickness of 0.64\(\mu\)m.

**CONCLUSION**

The effect of deposition time on copper sulphide thin films deposited on a glass substrate was studied. The CuS thin film was deposited using chemical bath method. The bandgap energy obtained was found to decrease from 2.50 to1.85eV with increased deposition time of 3 to 15 hours. The bandgap was inversely proportional to thickness of the film. The deposition time was directly proportional to the thickness.

**REFERENCES**


