ABSTRACT
The chemical bath deposition technique was used to deposit four thin films of magnesium sulphide. Magnesium sulphate (MgSO₄·7H₂O) was the source of Mg²⁺ while sodium thiosulphate served as the source of S²⁻. Ethylene diamine tetra acetic acid (EDTA) was used to slow down the reaction rate.

The bandgap and optical properties like absorbance (A), transmittance (T), reflectance (R), extinction coefficient (K), refractive index (n), absorption coefficient (α), and optical conductivity (σ_{op}) were determined. The results revealed that the absorbance range is 0-0.05 at the visible and near IR range. The transmittance range is 92 –100%, while the reflectance range is 2-4.5%. The bandgap for the magnesium sulphide generated through this study is 3.9eV. The average value of n is ~ 1.5 while the range of K is ~ 2.5 x10⁻³ – 3.51 x10⁻³. Optical conductivity (σ_{op}) and absorption coefficient (α) have ranges ~ 2.20 – 4.49 x10^{12} S⁻¹ and 0.06 – 0.10, respectively.

(Key words: thin film, chemical bath deposition, absorbance, transmittance, reflectance, extinction coefficient, refractive index, absorption coefficient, optical conductivity).

INTRODUCTION
Thin films are formed by the process of atom-by-atom, molecule–by-molecule, ion-by-ion, or cluster-by-cluster condensation (Udeajah, 1996). Thin film technology is extensively applied in the manufacture of photocells. Apart from this, thin films could be used in optical coatings, microelectronics, and surface science engineering and technology.

Unaogu and Okeke (1990) are of the view that thin films of silicon are found to be very important for photovoltaic devices, such as solar cells, while amorphous silicon solar cells offer improved performance at a very reduced cost. However, recent developments in integrated circuits, which require individual devices to be electrically isolated from one another, have necessitated the growth of silicon, germanium, and gallium arsenide thin films.

The techniques for the deposition of thin films are categorized into two broad groups namely: (a) The physical deposition technique and (b) the chemical deposition technique.

Again, the physical deposition technique is categorized into several types, namely: (i) chemical vapor deposition, (ii) spray pyrolysis, (iii) electro-chemical deposition (ECD), (iv) anodization, and (v) chemical bath or solution growth technique.

The chemical bath deposition technique was the method employed in the deposition of thin films in this work, but in all these techniques, three major steps are involved. The creation of the species required for film formation; the transport of these species through a medium and the condensation of the species on a substrate; and subsequent coalescence to form the film.

Cashatan (1996) used this method to deposit thin films of PbS in 1946 for infrared application followed by Robert and Baines (1958) who used it to deposit PbSe. Biswas, et al. (1986) deposited ZnS film on glass substrates at room temperature while Padam and Rao (1986) used the same method to deposit ternary compound films of CuInS₂. Recently Ezema (2004, 2005) used the same technique to deposit ZnO and BiO.

The method of chemical bath deposition is based on a controlled precipitation of the desired compound from a reaction solution. The condition is that ionic product (IP) must exceed its solubility product constant K_{sp} (Barnes and Czeeny, 1931). An ionic, slightly soluble substrate MₙNₙ dissociates in a saturated solution according to the following equation:

\[ K_{sp} = [M^{n+}] [N^{n+}] \]

The condition for the deposition of thin films is that the concentration of MₙNₙ exceeds its solubility constant K_{sp} in the solution.
The dissociation and crystallization of M\textsubscript{i}N\textsubscript{j} produces iM\textsuperscript{+} + jN\textsuperscript{-}

where i and j are integers showing the number of ions of each molecule.

\[ \text{I.P} = (M^+)^i(N^-)^j \]

where M\textsuperscript{+} signifies the molar concentration of ion M\textsuperscript{+}. At equilibrium and at a given temperature, I.P = K\textsubscript{sp}. At that temperature, K\textsubscript{sp} is obtained from standard tables (Gray, 1963).

**EXPERIMENTAL DETAILS**

In the deposition of magnesium sulphide the following compounds were present in the reaction bath: Magnesium sulphate (MgSO\textsubscript{4}.7H\textsubscript{2}O) which was the source of Mg\textsuperscript{2+}; Sodium thiosulphate which served as a source of S\textsuperscript{2-}; and EDTA which served as the complexing agent. All solutions were made to the desired volume with distilled water. The reaction details are shown below.

\[
\begin{align*}
\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{EDTA} & \leftrightarrow [\text{Mg(EDTA)}]^ {2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \\
[\text{Mg(EDTA)}]^ {2+} & \leftrightarrow \text{Mg}^{2+} + \text{EDTA} \\
\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2 & \leftrightarrow \text{Na}_2\text{O}_3 + 5\text{H}_2\text{O} + \text{S}^{2-} \\
\text{Mg}^{2+} + \text{S}^{2-} & \leftrightarrow \text{MgS} \\
\end{align*}
\]

By varying the molarities and volumes of MgSO\textsubscript{4}.7H\textsubscript{2}O, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}.5H\textsubscript{2}O, EDTA, and the volume of water, four different solution baths were prepared as shown in Table 1.

A Pye-unican SP8-100 model of spectrophotometer was used to measure the absorbance of the thin films developed in this study, in the ultraviolet and visible regions of the electromagnetic spectrum.

The percentage transmittances in the infrared region were also measured directly with an infrared spectrophotometer. The films were measured to be a non-absorbing film on a non-absorbing substrate, A<0.1, therefore the following expression was used to calculate the thickness of the films deposited.

\[
t = \frac{\left( \tan^{-1} \left( \frac{\left( \frac{n_o + n_s}{n_s - n_o} \right)^2 R - \left( \frac{n_o - n_s}{n_s + n_o} \right)^2 \lambda}{2 \Pi n} \right) \right)^{1/2}}{\lambda}
\]

Where n\textsubscript{o} is the refractive index of the medium of the incident light, which in this study is air; n\textsubscript{s} is the refractive index of the substrate (glass in this case); and n is the refractive index of the thin film.

**Table 1: Preparation of Magnesium Sulphide Thin Films.**

<table>
<thead>
<tr>
<th>Reaction bath</th>
<th>Dip time (hr)</th>
<th>Temp °C</th>
<th>pH</th>
<th>MgSO\textsubscript{4}.7H\textsubscript{2}O</th>
<th>Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}.5H\textsubscript{2}O</th>
<th>EDTA</th>
<th>H\textsubscript{2}O Vol. (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{19}</td>
<td>48</td>
<td>Room</td>
<td>5.0</td>
<td>0.5</td>
<td>5</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>C\textsubscript{20}</td>
<td>48</td>
<td>Room</td>
<td>5.4</td>
<td>0.1</td>
<td>5</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>C\textsubscript{24}</td>
<td>48</td>
<td>Room</td>
<td>4.8</td>
<td>2.0</td>
<td>5</td>
<td>2.0</td>
<td>5</td>
</tr>
<tr>
<td>C\textsubscript{25}</td>
<td>48</td>
<td>Room</td>
<td>6.2</td>
<td>1.0</td>
<td>5</td>
<td>2.0</td>
<td>2</td>
</tr>
</tbody>
</table>
Other optical properties calculated for the thin films were transmittance (T), reflectance (R), absorption coefficient (α), refractive index (n), extinction coefficient (K), and optical conductivity (σ_{opt}). The energy bandgaps were determined by the extrapolation of the straight portion of the graphs of α^2 = 0.

RESULTS AND DISCUSSION

Figure 1 shows the spectra absorbance of films C_{19}, C_{20}, C_{24}, and C_{25}. The absorbance of the films are generally low with a range of ~ 0 – 5%. The transmittance characteristics of MgS in the UV, visible, and near infrared regions are displayed in Figure 2.

A close observation of this figure reveals that the range of transmittance of these films is 92-100%. At certain wavelengths of the ultraviolet range, the transmittance of these films dropped to about 40%. Figure 3 shows the infrared transmittance curve of MgS (C_{20}). It shows enhancement of transmittance at far infrared region.

Figure 1: Spectral absorbance of Magnesium Sulphide (MgS) – C_{19}, C_{20}, C_{24}, and C_{25}.

Figure 2: Spectral transmittance of Magnesium Sulphide (MgS) – C_{19}, C_{20}, C_{24}, and C_{25}.

Figure 3: Infrared transmittance curve of Magnesium Sulphide (MgS) – C_{20}.
The reflection of the MgS prepared in this work is low near the infrared region of the electromagnetic spectrum; the range is \( \sim 2 \sim 4.5\% \). As shown in Figure 4, there are series of points of inflexion with peak values for C_{19}, C_{20}, C_{24} and C_{25} occurring at about 300nm. Figure 5 is the plot of \( \alpha^2 \) vs. photon energy where the bandgaps were determined to be 3.9eV.

![Figure 4: Spectral reflection of Magnesium Sulphide (MgS) – C19, C20, C24, and C25.](image)

Figures 6 and 7 show the plots of extinction coefficient and refractive index with photon energy (\( h\nu \)). K has a peak value of about 0.02 while n has average value of about 1.5. This is in close agreement with the value of 1.4 reported by Ballard et al., 1972.

The optical conductivity (\( \sigma_{op} \)) vs. photon energy plots for C_{19}, C_{20}, C_{24} and C_{25} are displayed in Figure 8. They have peak values of \( 55 \times 10^{12} \text{ S}^{-1} \) at photon energy of 4eV.

The average values of the bandgap, thickness and optical properties of the films grown are summarized in the Table 2.
Figure 7: Plot of refractive index against photon energy for Magnesium Sulphide (MgS) – C20, C24, and C25.

Figure 8: Plot of optical conductivity against photon energy for Magnesium Sulphide (MgS) – C19, C20, C24, and C25.

Table 2: Bandgap, thickness, and optical properties of MgS films grown under varying conditions at 300K.

<table>
<thead>
<tr>
<th>Rxn. bath</th>
<th>Dip time (hr)</th>
<th>n</th>
<th>K 10^{-3}</th>
<th>\sigma_{op} 10^{12} (S^-1)</th>
<th>\alpha x 10^6 (m^-1)</th>
<th>Bandgap (eV)</th>
<th>t (\mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C19</td>
<td>48</td>
<td>1.47</td>
<td>3.14</td>
<td>3.81</td>
<td>0.09</td>
<td>3.9</td>
<td>2.63</td>
</tr>
<tr>
<td>C20</td>
<td>48</td>
<td>1.48</td>
<td>3.34</td>
<td>3.98</td>
<td>0.09</td>
<td>3.9</td>
<td>2.55</td>
</tr>
<tr>
<td>C24</td>
<td>48</td>
<td>1.53</td>
<td>3.51</td>
<td>4.49</td>
<td>0.10</td>
<td>3.9</td>
<td>2.47</td>
</tr>
<tr>
<td>C25</td>
<td>48</td>
<td>1.49</td>
<td>3.31</td>
<td>4.03</td>
<td>0.09</td>
<td>3.9</td>
<td>2.58</td>
</tr>
</tbody>
</table>

From Table 2, it is shown that the concentration of the reagents, which is the only varying growth parameter, has little effect on n, k, \sigma_{op}, \alpha and t.

The bandgap of the MgS deposited in this study is 3.9eV. The growth kinetics is similar to that given by Chopra and Das (1979) where the rate of growth which is very high initially slowed down as the terminal thickness is approached.

CONCLUSION

The chemical bath deposition technique has been used to deposit four thin films of magnesium sulphide (MgS). The bandgap of the deposited material was determined to be 3.9eV while the range of thickness is 2.47\mu m to 2.63\mu m. These films, because of their low reflectance and high transmittance in the ultraviolet, visible, and infrared regions, are suitable for coatings on different types of solar collectors. They could also be used as anti-reflection coatings because they all have very low reflectance across the entire range of the electromagnetic spectrum.

REFERENCES


**ABOUT THE AUTHOR**

M.N. Nnabuchi, Ph.D. serves on the faculty of the Department of Industrial Physics at Ebonyi State University in Abakaliki, Nigeria. Dr. Nnabuchi’s research interest center on the application of chemical bath deposition techniques and the characterization of novel materials for solar cells and other optical applications.

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