STRUCTURAL AND OPTICAL CHARACTERIZATION OF BARIUM SULPHIDE THIN FILMS GROWN BY SOLUTION GROWTH TECHNIQUE.

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Abstract
Three thin films of barium sulphide were deposited on glass slides using solution growth technique. The bath compositions include barium chloride (BaCl$_2$) which was the source of Ba$^{2+}$, sodium thiosulphate (Na$_2$S$_2$O$_3$·5H$_2$O), source of S$^{2-}$ and EDTA served as a complexing agent. The structural compositions of these films were examined using the microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) at magnification of x400. Fourier transform infrared (FTIR) spectroscopy and spectrophotometer were used to determine the optical properties like absorbance, transmittance, reflectance, refractive index, extinction coefficient and optical conductivity. The results of characterization show that these films have poor absorbance and reflectance. The transmittance range of the films from UV-NIR is 60-90%. The range of the refractive index is 1.3-1.6; extinction coefficient has range of 0.001-0.012 while optical conductivity has a range of 1.0 x10$^{12}$ s$^{-1}$ - 2.5 x10$^{12}$ s$^{-1}$.

Keywords: Barium sulphide, Fourier transform infrared (FTIR) spectroscopy, optical properties, thin films, solution growth technique.

INTRODUCTION
Solar energy is a source of free, natural and non polluting energy that man can harness for useful applications. Thin films have been found important for various solar energy devices such as mirror filters, anti reflection coating photosynthetic coating, thermal and solar control coatings [Tabor 1979, Meinel and Meinel 1979]. Some are moderately selective while others are non-selective. Those films whose optical properties such as absorbance, transmittance, emittance, reflectance etc. are dependent on wavelength are said to be spectrally selective films. For such films, the optical or radiative properties vary quantitatively with different parts of the electromagnetic spectrum.
Several methods for the deposition of thin films include thermal evaporation, electron beam evaporation, activated reactive evaporation epitaxy and ion plating [Campbel 1967, Duta 1985]. Other techniques include chemical vapor deposition.

In this work chemical bath deposition (solution growth technique) was adopted to deposit three thin films on glass substrates at varying parameters. The structural characterization of these films was done using microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) at magnification of x400. The optical properties of the films examined are absorbance, reflectance, transmittance, extinction coefficient, refractive index and optical conductivity. Also in addition the thicknesses of the films were calculated.

MATERIALS AND METHODS

The reaction bath for the deposition of barium sulphide (BaS) thin films in this work includes barium chloride (BaCl$_2$) sodium thiosulphate (Na$_2$S$_2$O$_3$.5H$_2$O), EDTA and distilled water. BaCl$_2$ was the source of Ba$^{2+}$, Na$_2$S$_2$O$_3$.5H$_2$O was the source of S$^{2-}$ while EDTA was the complexing agent. The three films were obtained from the variation of bath compositions and concentration as shown in Table 1 below:

<table>
<thead>
<tr>
<th>Reaction bath</th>
<th>Dip time (hr)</th>
<th>Temp (K)</th>
<th>pH</th>
<th>BaCl$_2$</th>
<th>Na$_2$S$_2$O$_3$.5H$_2$O</th>
<th>EDTA</th>
<th>H$_2$O (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_7$</td>
<td>48</td>
<td>Room</td>
<td>6.0</td>
<td>0.10</td>
<td>2</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>D$_{10}$</td>
<td>48</td>
<td>Room</td>
<td>6.2</td>
<td>0.01</td>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>D$_{11}$</td>
<td>20</td>
<td>Room</td>
<td>6.0</td>
<td>0.10</td>
<td>2</td>
<td>1.0</td>
<td>2</td>
</tr>
</tbody>
</table>

The ionic equations for the reaction are:

\begin{align*}
\text{BaCl}_2 + \text{EDTA} & \leftrightarrow [\text{Ba(EDTA)}]^{2+} + 2\text{Cl}^- \\
\text{BaCl}_2 + \text{TEA} & \leftrightarrow [\text{Ba(TEA)}]^{2+} + 2\text{Cl}^- \\
[\text{Ba(EDTA)}]^{2+} & \leftrightarrow \text{Ba}^{2+} + \text{EDTA} \\
[\text{Ba(TEA)}]^{2+} & \leftrightarrow \text{Ba}^{2+} + \text{TEA} \\
\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O} & \leftrightarrow \text{Na}_2\text{O}_3 + 5\text{H}_2\text{O} + \text{S}^{2-} \\
\text{Ba}^{2+} + \text{S}^{2-} & \leftrightarrow \text{BaS}\downarrow
\end{align*}

As shown in Table 1, three samples were prepared using EDTA as complexing agent.

The spectral absorbance of the films was obtained using PYE-UNICAM UV SP8-100 spectrophotometers in the UV-VIS-NIR regions. The percentage transmittance in the infrared region was measured directly with infrared spectrophotometers. Other optical properties were calculated using the appropriate formula. Structural characterization was carried out using microscope (HUND WETZLAR H600) and camera (RICOH 35mm SLR, XR-X300) to produce micrographs at magnification of x400.

Transmittance, $T=I/I_o$ (where $I$ is the transmitted flux and $I_o$ is the incident flux. Reflectance, $R$ and absorption coefficient $\alpha$ were calculated using $R = 1 - A - T$.
and $\alpha = \ln(1/T) \times 10^6 \text{ m}^{-1}$ respectively. Other optical properties are refractive index.

$$N = \frac{1-R^{1/2}}{1-R^{-1/2}}$$

Extinction coefficient, $K = \frac{\alpha \lambda}{4\pi}$ [Pankove 1971]

and optical conductivity $\sigma_{op} = \frac{\alpha mc}{4\pi}$, where $c$ represents velocity of light.

Fig. 1: Spectral absorbance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.
RESULTS AND DISCUSSION

The spectral absorbance of barium sulphide films D₇, D₁₀, and D₁₁, are shown in Fig. 1. The absorbance is generally low throughout the ultraviolet, visible and infrared regions. The value ranges from 0.02 to 0.04. The range of spectral transmittance of the same set of films is 60-90% as shown in Fig. 2. This implies that it transmits greatly throughout the UV, VIS and IR regions. The shapes of the graphs are dissimilar showing that dip time and varying concentration of the reagents affected the transmittance spectra.

Fig. 2: Spectral transmittance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.

Fig. 3 shows the reflectance spectra of films D₇, D₁₀ and D₁₁. The difference in the molarities of BaCl₂ and Na₂S₂O₃·5H₂O reagents and time of deposition were responsible for the large difference between the shapes of D₇ reflectance spectra on one side and D₁₀ and D₁₁ on the other side. The plots of K vs. hν for D₇ and D₁₁ are shown in Fig. 4. The extinction coefficient for D₁₀ and D₁₁ decreases as the photon energy increases except at 4eV where there are sharp rise and fall. The refractive index N vs. hν plots for D₁₀ and D₁₁ are displayed in Fig. 5. The
range of refractive index for $D_{10}$ and $D_{11}$ is $\sim 1.32-1.55$. Concentration of the reagents has significant effect on the shape of the graphs. Optical conductivity, $\sigma_{op}$ vs. $h\nu$ for $D_7$ is displayed in Fig. 6. The peak value is recorded at 3.8 eV. Fig. 7 shows the same for $D_{10}$ and $D_{11}$. The range is $\sim 1.0 \times 10^{12} \text{s}^{-1} - 3.4 \times 10^{12} \text{s}^{-1}$. The minimum values are recorded at about 3.4 eV. Table 2 below is a display of the average values of these optical properties and thicknesses of BaS films. Fig. 8 shows the photomicrographs of BaS films deposited at 300K showing the structure of these films.

![Fig. 3: Spectral reflectance of barium sulphide (BaS): a) D7, b) D10, c) D11 thin films.](image)

<table>
<thead>
<tr>
<th>Reaction Bath</th>
<th>Dip time (hrs)</th>
<th>Average $N$ $\times 10^3$</th>
<th>Average $K$ $\times 10^3$</th>
<th>Average $\sigma_{op}$ $\times 10^{12} \text{s}^{-1}$</th>
<th>Average $\alpha$ $\times 10^6 \text{m}^{-1}$</th>
<th>Average Thickness $t$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_7$</td>
<td>48</td>
<td>1.82</td>
<td>6.90</td>
<td>8.34</td>
<td>0.18</td>
<td>1.81</td>
</tr>
<tr>
<td>$D_{10}$</td>
<td>48</td>
<td>1.43</td>
<td>2.44</td>
<td>2.06</td>
<td>0.06</td>
<td>2.59</td>
</tr>
<tr>
<td>$D_{11}$</td>
<td>20</td>
<td>1.48</td>
<td>2.94</td>
<td>2.52</td>
<td>0.07</td>
<td>2.44</td>
</tr>
</tbody>
</table>
Fig. 4: Plots of extinction co-efficient against photon energy of barium sulphide (BaS): 
a) D7, b) D10, c) D11 thin films.

Fig. 5: Plots of refractive index against photon energy for barium sulphide (BaS): 
a) D10, b) D11 thin films.
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Fig. 6: Plot of optical conductivity against photon energy for BaS D7 thin film.

Fig. 7: Plots of optical conductivity against photon energy for BaS:
   a) D10 and b) D11 thin films.
Fig. 8a: Photomicrographs of barium sulphide BaS - D11 thin films prepared at 300K.

Fig. 8b: Photomicrographs of barium sulphide BaS - D10 thin films prepared at 300K.

From Table 2 it is clear that $N$ has not much variation despite the variation in dip time for the different films. $K$ and $\sigma_{op}$ show great variations especially by D7 film. Increase in bath concentration increases the thickness of the films very little.

**CONCLUSION**

It is possible to deposit three films of BaS thin films on glass substrates. The characterization shows that they have poor absorbance and reflectance. The transmittance range of the films from the UV to NIR is 60 to 90%. The range of the refractive index is 1.30-1.60, extinction coefficient has a range of 0.001-0.012, while optical conductivity has a range of $1.0\times10^{12}\text{s}^{-1}$ to $25.0\times10^{12}\text{s}^{-1}$. They are found suitable in so many solar applications such as solar energy collection, antireflection and photosynthetic coatings.

**References**


