Chemical Bath Deposition of Bismuth Chloride Oxide (BiClO) Thin Film and its Applications

F.I. Ezema, Ph.D.

Department of Physics and Astronomy, University of Nigeria, Nsukka, Enugu State, Nigeria
School of General Studies, Natural Sciences Unit, University of Nigeria, Nsukka, Enugu State, Nigeria
E-mail: fiezema@yahoo.com

ABSTRACT

Bismuth chloride oxide (BiClO) thin films were prepared on glass slide using chemical bath deposition from solutions of Bismuth Nitrate, triethanolamine (TEA), and potassium chloride with TEA as a complexing agent. The films were characterized using energy dispersive x-ray fluorescence (EDXRF) and Fourier transform infrared (FTIR) spectroscopy for composition while spectrophotometers were used to study other properties such as absorbance/transmittance and reflectance spectra. Film thicknesses in the range of 0.116 and 0.693μm with energy band gaps between 2.20 and 3.80 have been deposited. Some of the films deposited are poor transmitters of radiation in the VIS–NIR region with ranges between 25 - 47%, and IR transmittance in the mid infrared regions ranges between 3 - 42%, while some are good transmitters and show transmittances that are greater than 90% in the UV-VIS-NIR regions. Some of the films show high absorbance in the VIS-NIR region but moderate transmittances in the NIR and mid infrared regions; hence they have potential applications in the fabrication of absorbers for solar cells. Those with high transmittance in the VIS region and wide band gaps could be employed as window layers for solar cells.

(Key words: chemical bath deposition, bismuth chloride oxide, optical properties, solar cells).

INTRODUCTION

Thin film processes, technology, and devices are well known for their applications in a host of physics-based industries. Chemical bath deposition techniques have been suggested as a low deposition cost technique to realize economic and large area devices [1-4]. There have been a number of published work on various aspects of chemically deposited thin films [5-24].

The effect of varying growth parameters such as deposition rates, bath composition, and bath temperature on the various properties of thin films have been reported by several researchers [3, 7, 17, 18]. This paper is concerned with optimizing the chemical bath reaction conditions, such as pH, and starting material concentrations at constant dip times and at room temperature to produce BiClO films that would be adequate for solar cells applications. These films were then characterized using optical methods. Optical studies using transmittance and reflectance data from samples prepared using chemical bath deposition have been reported in the literature [5, 6].

THEORETICAL CONSIDERATIONS AND CALCULATIONS

In both crystalline and amorphous semiconductors, near the fundamental absorption age there is the dependence of the absorption coefficient on the photon energy. In high absorption regions, the form of the absorption coefficient with photon energy was given in a more general term by [25] as:

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

(1)

Where $\nu$ is the frequency of the incident photon, $h$ is Plank's constant, $A$ is a constant, $E_g$ is the optical energy gap, and $n$ is the number which characterizes the optical processes. The variable $n$ has the value $\frac{1}{2}$ for the direct allowed transition and has the value 2 for the indirect allowed transition. When the straight portion of the plot of $\alpha^2$ against $h \nu$ is extrapolated to $\alpha^2 = 0$, this gives the direct energy band gap of the material. For semi conductors and insulators (where $k^2 << n^2$) there exist a relationship between $R$ and $n$ given by [26-27]:
There is also a relationship between $k$ and $\alpha$ given by [25, 27]:

$$k = \frac{\alpha \lambda}{4\pi} \quad \text{(3)}$$

where $\alpha$ = absorption coefficient of the film, $\lambda$ = wavelength of electromagnetic wave. The relationship between $\varepsilon$ and $k$ is given by [25]:

$$\varepsilon = \varepsilon_r + \varepsilon_i = (n + ik)^2 \quad \text{(4)}$$

where $\varepsilon_r$ and $\varepsilon_i$ are real and imaginary parts of $\varepsilon$ respectively.

Optical conductivity ($\sigma$) is given by [25, 27]:

$$\sigma = \frac{\alpha nc}{4\pi} \quad \text{(5)}$$

where $c$ is the velocity of light.

The optical method as discussed [28-30] was used to estimate the thickness of the film.

**EXPERIMENTAL DETAIL**

A chemical bath deposition technique was employed in the deposition of bismuth chloride oxide (BiClO) films on glass slides at room temperature. The substrates were previous degreased in hydrochloric acid and nitric acid for 48 hours, cleaned with detergent in cold water, rinsed with distilled water and allowed to drip dry in air. To produce BiClO thin films an alkaline solution of bismuth salt and potassium chloride were prepared. The reaction baths for the deposition contain solutions of triethanolamine (TEA) complex of bismuth and potassium chloride in cold water. The reaction baths were made up of given volumes of Bi(NO\textsubscript{3})\textsubscript{3} 5H\textsubscript{2}O, TEA and KCl solutions added into 50ml beakers in that order, then stirred thoroughly using a glass rod at each stage to obtain a homogenous mixture of the solutions. Each bath was made up to 40ml with distilled water and allowed to stay for 24 hour dip times. The reaction baths were tested for pH values and found in the alkaline medium before the substrates were introduced in the solutions.

The variation of the bath composition and concentration is shown in Table 1.

In cold water, BiCl\textsubscript{3} decomposes to produce the ions required for the deposition [31]. The film growth takes place through ion–by–ion condensation [1, 5, 6, 24]. The deposition of the film was achieved through the chemical reaction of TEA complexing method in the following steps:

$$\text{Bi(NO}_3\text{)}_3 \text{5H}_2\text{O + TEA} \rightleftharpoons [\text{Bi(TEA)}]^+ + 3\text{NO}_3^-$$

$$\text{Bi[TEA]}^+ \rightarrow \text{Bi}^+ + \text{TEA}$$

$$\text{KCl + H}_2\text{O} \rightarrow \text{K}^+ + \text{Cl}^- + 2\text{OH}^-$$

$$\text{Bi}^{3+} + \text{Cl}^- + 2\text{OH}^- \rightarrow \text{BiClO} + \text{H}_2\text{O}$$

After the films were grown, their properties were studied to determine the composition of the film. Energy dispersive x-ray fluorescence (EDXRF) and Fourier transform infrared (FTIR) spectroscopy were used for this purpose. In the case of EDXRF, a cross-section of the film was analyzed by using a focused electron beam.

The elements present in the film were identified by the mean pulse heights (photon energies) at which peaks occurred, and the concentration of the constituent elements were estimated from the peak heights (intensities). These were carried out using radio isotopes 25mCi Cd-109.

### Table 1: Variation of the Bath Composition and Concentration.

<table>
<thead>
<tr>
<th>Reaction bath</th>
<th>Bi(NO\textsubscript{3})\textsubscript{3} 5H\textsubscript{2}O</th>
<th>Triethanolamine</th>
<th>Potassium chloride</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC3</td>
<td>0.1</td>
<td>10.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>BC4</td>
<td>0.1</td>
<td>10.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>BC9</td>
<td>0.1</td>
<td>10.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>BC12</td>
<td>0.1</td>
<td>8.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>BC13</td>
<td>0.1</td>
<td>8.0</td>
<td>1.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

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and 25mCi Am-241 excitation sources.

The use of FTIR spectroscopy involves mulling the film in nujol. The nujol background was run to determine the baseline and then the nujol mull was run to determine peaks resulting from the film in the far infrared regions. The films were further studied using PYE UNICAM UV SP8-100 models of spectrophotometers to determine the absorbance, transmittance, and reflectance characteristics in the UV-VIS-NIR regions.

RESULTS AND DISCUSSION

The EDXRF showed that the bismuth peak was recorded at 10.83 keV with intensity of 0.610 c/s while the fractional concentration of 3.72E-04 and error of 2.83E-05 (372±9 ppm) was achieved. The blank background of infrared spectroscopy for nujol (Figure 1) showed peaks at 1377 cm\(^{-1}\), 1461 cm\(^{-1}\), 2855 cm\(^{-1}\), 2924 cm\(^{-1}\), 2953 cm\(^{-1}\) and 3436 cm\(^{-1}\) with a percentage transmittance which ranged between 5-57%. When the film was dissolved in nujol, it modified the nujol peaks and showed other peaks at 1152 cm\(^{-1}\), 1054 cm\(^{-1}\), 876 cm\(^{-1}\), 655 cm\(^{-1}\) and 534 cm\(^{-1}\) with percentage transmittance ranging between 59-72%. These resulted from the dissolving of the BiClO film.

Comparing the nujol peaks to those obtained after dissolving of the film in the nujol; a shift resulting from a transmittance increased was observed. As a result of the nujol peak shift, the percentage transmittance of IR radiation due to the film in the mid infrared region therefore ranged between 15-54%.

Szatran et al. [32] reported that peaks between 780 and 400 cm\(^{-1}\) are due to bonds of the heavier element O–Cl, hence the peaks 655 cm\(^{-1}\) and 534 cm\(^{-1}\) (Figure 1) are attributed to the O–Cl of the bismuth film. According to Conley [33], ClO\(_3\) characteristic absorption bands occur from 985 – 923 cm\(^{-1}\), 662 – 646 cm\(^{-1}\) and 539 – 477 cm\(^{-1}\) while ClO\(_4\) occur at 1108 – 1062 cm\(^{-1}\). These were not incorporated in the film.

Additionally, nitrogen from bismuth nitrate was not introduced into the film as reported [33] for its compounds; NO\(_2\) has absorption bands between 1385 and 1323 cm\(^{-1}\), 1262 and 1231 cm\(^{-1}\), and 862 and 815 cm\(^{-1}\) while NO\(_3\) has absorption bands between 1400 and 1354 cm\(^{-1}\), and 808 and 869 cm\(^{-1}\). The water of crystallization absorption bands, which occurs between 3554 and 3139 cm\(^{-1}\) and 1692 and 1600 cm\(^{-1}\), was not incorporated into the film.

Figure 2 shows the combined effect of film-glass system on transmittance of infrared radiation for BiClO thin film when compared with uncoated glass. This was carried out using a single beam Fourier transform spectrometer. Uncoated glass showed transmittance of 43% at 3508 cm\(^{-1}\), 41% at 2864 cm\(^{-1}\), and only about 2% transmittance at 2000 cm\(^{-1}\). By about 1999 cm\(^{-1}\), no radiation at all is transmitted through the glass. Coated glass showed transmittance of 45% at 3508 cm\(^{-1}\), 48% at 2898 cm\(^{-1}\), and only about 2% transmittance at 2000 cm\(^{-1}\). No radiation at all is transmitted through the film-glass system by about 1999 cm\(^{-1}\).

These films are capable of allowing solar radiation (0.3 – 3.0 \(\mu\)m) to be transmitted into a building but preventing thermal re-radiation out of the building through the glassing system. It is observed that the film-glass system improves transmission of IR over plain glass.
The spectral absorbance of bismuth chloride oxide grown under varying conditions at 300K is displayed in Figure 3. The samples absorb heavily throughout UV-VIS-NIR regions. It is observed that absorbance decreases with increasing wavelength immediately after the fundamental absorption for all the samples. The spectral transmittance-reflectance of BiClO is shown in Figures 4 and 5. It is generally observed that the samples in Figure 4 are poor transmitters of radiation in the VIS-NIR regions. The samples in Figure 5 are generally good transmitters of radiation. The transmittances exhibited by samples BC7 and BC11, show that they are greater than 93% in the VIS regions. It can be seen that these samples have high transmittance throughout UV-VIS-NIR. This property of high transmittance throughout solar spectral region makes the film a good material for solar thermal control in cold climates where maximum transmission is required to warm the environment. The film can also be employed as an anti-reflection coating since the reflectance in these regions is quite below 10%.

The variation of refractive index (n) and extinction coefficient (k) as a function of photo energy (hν) are plotted in Figure 6. The observed maximum value of n was 14.61 at 3.10eV and it decreases with increasing wavelength at the lower energies to a minimum value of 1.33 at 1.55eV.
The observed maximum value of \( k \) was \( 163.67 \times 10^{-3} \) at \( 3.10\text{eV} \) and decreases with increasing wavelength at the lower energies to a minimum value of \( 30.48 \times 10^{-3} \) at \( 1.55\text{eV} \). The maximum \( n \) and \( k \) values occurred at \( 3.10\text{eV} \), which is in agreement with the findings of Greenaway and Harbeke [34], which stated that for semiconductors, it is expected that the maximum in the refractive index \( (n) \) will occur at the energy near that at which the maximum change in \( k \) occurs.

The refractive index of a semiconductor reaches a constant value at wavelengths significantly greater than that corresponding to the fundamental transitions, therefore semiconductors are characterized by un-dispersed value of the index of refraction \( (n_o) \) or by \( (n_o)^2 \), which is known as the high frequency dielectric constant. A plot of \( 1/(n^2-1) \) against \( 1/\lambda^2 \) to obtain value refractive index \( (n_o) \) as shown in Figure 7. The value obtained for the intercept at \( 1/\lambda^2 = 0 \) suggested a value of 2.40 for \( n_o \).

A plot of optical conductivity \( (\sigma_o) \) against \( h\nu \) is shown in Figure 8. \( \sigma_o \) has a maximum value of \( 17.93 \times 10^{14} \text{s}^{-1} \) at \( 3.10\text{eV} \) with a minimum value of \( 0.28 \times 10^{14} \text{s}^{-1} \) at \( 1.55\text{eV} \).

Table 2 shows the average optical properties and thickness of the film prepared at 300k.

The thickness of the film increased as pH increased to pH 8.5 and then decreased as pH increased. Although there is no established correlation between the thickness and pH, the most favorable condition for the deposition of the film has been demonstrated [29] to be in an alkaline medium. The maximum and minimum of thickness of 0.693\( \mu \text{m} \) and 0.116\( \mu \text{m} \) occurred at maximum and minimum absorbance corresponding to 0.784 and 0.158, respectively.

The absorbance of the film depends on the thickness of the film [6,29] hence the absorbance increased as thickness increased as expected.
Figure 7: Plot of $1/(n^2 - 1)$ against $1/\lambda^2$ for BiClO Sample in the region of near Infrared.

Table 2: Average Optical Properties and Thickness of BiClO Films.

<table>
<thead>
<tr>
<th>Samp No</th>
<th>pH</th>
<th>A</th>
<th>n</th>
<th>$k \times 10^{-2}$</th>
<th>$\sigma x 10^{14}$</th>
<th>$t_{\mu m}$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC3</td>
<td>8.3</td>
<td>0.723</td>
<td>1.96</td>
<td>7.67</td>
<td>1.68</td>
<td>0.665</td>
<td>2.40</td>
</tr>
<tr>
<td>BC4</td>
<td>8.6</td>
<td>0.729</td>
<td>2.03</td>
<td>7.23</td>
<td>1.55</td>
<td>0.671</td>
<td>2.40</td>
</tr>
<tr>
<td>BC7</td>
<td>9.8</td>
<td>0.158</td>
<td>1.71</td>
<td>0.87</td>
<td>0.06</td>
<td>0.116</td>
<td>3.80</td>
</tr>
<tr>
<td>BC9</td>
<td>8.2</td>
<td>0.428</td>
<td>2.24</td>
<td>3.81</td>
<td>5.54</td>
<td>0.348</td>
<td>3.00</td>
</tr>
<tr>
<td>BC12</td>
<td>8.8</td>
<td>0.643</td>
<td>2.10</td>
<td>6.10</td>
<td>1.74</td>
<td>0.550</td>
<td>2.20</td>
</tr>
<tr>
<td>BC13</td>
<td>8.5</td>
<td>0.784</td>
<td>1.97</td>
<td>8.18</td>
<td>1.23</td>
<td>0.693</td>
<td>2.80</td>
</tr>
</tbody>
</table>

The plots of $\varepsilon_r$ and $\varepsilon_i$ against $h\nu$ are displayed in Figure 9. $\varepsilon_r$ and $\varepsilon_i$ observed a minimum value of 213.42 and $4783.40 \times 10^{-3}$, respectively, and decreases with increasing wavelength at the lower energies to minimum values of 1.77 and $208.86 \times 10^{-3}$, $\varepsilon_r$ and $\varepsilon_i$ increases, slightly becoming constant with increasing wavelength. The very large values of $k$ and $\varepsilon_i$ indicate that BiClO is a semiconductor [24].

The plot of $\log \alpha$ against $h\nu$ (Figure 10) shows that the film satisfies the exponential behavior of the absorption edge. The slopes remain unchanged which agrees with the finding of Fayek et al. [35] on crystalline and amorphous materials. The plots for the location of energy band gaps of the films are displayed in Figures 11 - 13. The values are as shown in Table 2 above.

The wide band gap exhibited by sample BC7 together with its high transmission in the visible region make the sample a good candidate for transparent conducting material and could be employed as a window in fabrication of solar cells.

**CONCLUSION**

BiClO thin films with thickness ranging between 0.150 and 0.611 $\mu$m and with energy band gaps between 2.20 and 3.80 eV have been successfully deposited in alkaline medium using chemical bath deposition techniques. An EDXRF analysis showed that the film contain bismuth and chloride peaks while FTIR spectroscopy showed O–Cl bonding peaks and the percentage transmittance that ranged between 3 and 42% in the far infrared regions.
Figure 9: Plots of Real $\varepsilon_r$ and Imaginary $\varepsilon_i$, Parts of Dielectric Constants against $h\nu$ for BiClO Sample.

Figure 10: Plots of Log $\alpha$ against $h\nu$ for BiClO Samples.

Figure 11: Plots of $\alpha^2$ against $h\nu$ for BiClO Samples.

Figure 12: Plots of $\alpha^2$ against $h\nu$ for BiClO Samples.
Figure 13: Plot of $(\alpha h\nu)^2$ against $h\nu$ for BiClO Sample.

The deductions from the spectrophotometer analysis showed that average values ($n$) ranged from 1.96 to 2.40, $k$ ranged from $3.81 \times 10^{-2}$ to $8.18 \times 10^{-2}$, and $\sigma_0$ ranges from $1.23 \times 10^{14}$S$^{-1}$ to $5.54 \times 10^{14}$S$^{-1}$.

Some of the films were found to have high absorbance in the UV-VIS regions, but moderate absorbance in the NIR regions, hence, they could be effective as solar radiation absorbers for solar cell fabrications, while some have high transmittances within the UV-VIS-NIR and could employed for thermal and antireflection coatings as well window layers for solar cells.

REFERENCES


ABOUT THE AUTHOR

F.I. Ezema, B.Sc., M.Sc., Ph.D. serves as a lecturer in the School of General Studies, Natural Sciences Unit and Department of Physics/Astronomy at the University of Nigeria, Nsukka. He also serves on the faculty of the Department of Physics and Astronomy at the University of Nigeria, Nsukka. His research interests are in the areas of thin film deposition, solar energy/solar radiation, and meteorology.
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