

Preparation and Optical Properties of Chemical Bath Deposited Beryllium Chloride (BeCl₂) Thin Films.

F. I. Ezema, Ph.D. ^{1,2} and P.U. Azogwa, Ph.D. ^{1,2}

¹Department of Physics and Astronomy,
University of Nigeria, Nsukka, Enugu State, Nigeria

²School of General Studies, Natural Science Unit,
University of Nigeria, Nsukka, Enugu State, Nigeria

E-mail: (Ezema) fiezema@yahoo.com; (Azogwa) misunn@aol.com

ABSTRACT

Beryllium chloride (BeCl₂) thin films were prepared on glass slides using aqueous solutions of beryllium nitrate, potassium hydroxide, and potassium chloride in a chemical bath deposition technique. The optical properties of the film deduced from spectrophotometric analysis included absorbance, transmittance, and reflectance from which other properties such as refractive index (n) were obtained. Refractive indexes for the films prepared in this study had a maximum value range of 1.70 to 2.24; extinction coefficients (k) ranged from 3.13 x 10⁻³ to 8.82 x 10⁻³; and optical conductivity σ ranged from 0.04 x 10¹⁴S⁻¹ to 0.16 x 10¹⁴S⁻¹. The thickness of the films deposited ranged between 0.044 and 0.055 μm. The direct and indirect transition energy band gaps ranged between 1.80 – 3.00 eV and 0.30 – 0.80 eV respectively. The films were found to have high transmittance in the UV-VIS-NIR regions; consequently they show potential in applications for thermal coatings for cold climates and antireflection coatings.

(Key words: Chemical bath deposition, BeCl₂, thermal coatings, antireflection)

INTRODUCTION

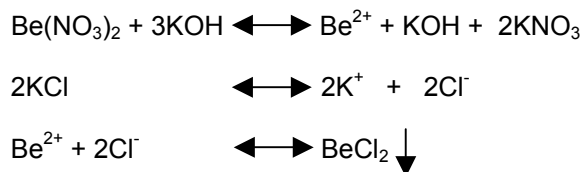
The use of a chemical bath deposition technique for the production of halide and halogenate thin films has not been well documented [1]. The conventional methods for the deposition of halide and halogenate thin films involve chemical vapor techniques and spray pyrolysis [1].

To produce BeCl₂ thin films via chemical bath deposition, the reaction bath consists of

beryllium nitrate and potassium hydroxide as a complexing agent, in addition to potassium chloride and distilled water. The film growth takes place via ion-by-ion condensation of Be²⁺ and Cl⁻ ions on the glass substrate when the ions progress over the solubility limit [2]. The chemical bath deposition of BeBr₂ thin films has been reported in the literature [3].

The deposition of beryllium chloride was based on the reaction between KOH as a complexing agent of Be²⁺, and KCl, which additionally serves as a pH stabilizer.

The reactions involved in the deposition process are as follows:



The optical properties of the films examined in this study include absorbance, transmittance, and reflectance, which in turn, were used to calculate other properties such as the refractive index, extinction coefficient, dielectric constant and optical conductivity. The optical properties and band gap of the film were deduced from equations given in the literature [4, 5, and 6]. In order to estimate the thickness of the films, optical methods [7] were used whereby the films were treated as non-absorbing films on non-absorbing substrate. In this case the reflectance is given by:

$$R = \frac{(n_a - n_g)^2 \cos^2 \beta + (n_a n_g / n_f - n_f)^2 \sin^2 \beta}{(n_a + n_g)^2 \cos^2 \beta + (n_a n_g / n_f + n_f)^2 \sin^2 \beta} \dots \dots \dots (1)$$

where n_a is the refractive index of the medium of the incident light (air), n_g is the refractive index of the substrate (glass), n_f is the refractive index of the thin film and,

$$\beta = \frac{2\pi n_f t}{\lambda} \dots\dots\dots (2)$$

Where t is the thickness of the film and λ is wavelength of light.

After rearranging, substituting, and simplifying, the expression for film thickness was given as:

$$t = \frac{\lambda}{2\pi n_f} \left(\tan^{-1} \left\{ \frac{(n_a + n_g)^2 R - (n_a - n_g)^2}{[(n_a n_g / n_f) - n_f]^2 - [(n_a n_g / n_f) + n_f]^2 R} \right\}^{1/2} \right) \dots\dots\dots (3)$$

This expression was used to calculate the thickness of the films with absorbance A of less than 0.10 that approximates non-absorbing films. For a weakly absorbing film on a non-absorbing substrate, the transmittance T is given by [5]:

$$T = (1-R)^2 \exp(-\alpha t) \dots\dots\dots (4)$$

where R is the reflectance and α is the absorption coefficient. Taking the natural logarithm on both sides of equation 4 and transforming gives the following:

$$t = 1/\alpha \{ \ln(1-R)^2 / T \} \dots\dots\dots (5)$$

This expression was used in this work to calculate the thickness of the experimental films where absorbance A is greater than or equal to 0.10.

EXPERIMENTAL DETAILS

The deposition of the beryllium chloride thin films on glass slides at room temperature was performed using a chemical bath that consisted of beryllium nitrate, potassium hydroxide, potassium chloride, and distilled water. The substrates (glass slides) were previous degreased in nitric acid for 48 hours, cleaned with detergent in cold water, rinsed with distilled water, and allowed to air dry. The nitric acid treatment caused the oxidation of the halide ions in the glass slides (halide glass) used as substrates, thereby introducing functional groups called nucleation and/or epitaxial centers. These functional groups form the foundation

upon which the thin film growth can occur. The reaction baths for the deposition of BeCl_2 thin films contain alkaline solutions of beryllium salt and potassium chloride in cold water. The reaction baths were made up of given volumes of $\text{Be}(\text{NO}_3)_2$, KOH and KCl solutions added into 50ml beakers in that order, with thorough stirring at each stage using a glass rod to obtain a homogenous mixture of the solutions. The reaction baths were made up to a 40ml volume with distilled water and allowed to rest for 6 and 24 hour dip times. The reaction baths were tested for their pH value and they were determined to be in the alkaline range before the substrates were introduced to the solutions. The reaction was a hydrolysis reaction [8] occurring at room temperature with KOH acting as a complexing agent and a pH stabilizer in the alkaline medium. Table 1 shows the variation in reaction baths and the different dip times.

After the films were deposited, they were withdrawn from the reaction baths, rinsed in distilled water, and allowed to air dry. The characterization of the films show the spectral absorbance/transmittance characteristics of the films obtained using PYE UNICAM SP8-100 UV spectrophotometers in the UV-VIS-NIR regions.

RESULTS AND DISCUSSION

The spectral absorbance of the beryllium chloride film prepared at 300K is displayed in Figure 1.

Samples I4 and I33 showed peak absorbance in the UV region between 300 and 300nm with maximum absorbance of 0.158nm and 0.076nm respectively. Immediately after the peak value, absorbance decreased with increasing wavelength towards the NIR regions.

All of the thin films grown in this study were found to exhibit poor absorbance throughout UV-VIS-NIR regions.

The transmittance/reflectance spectra for the thin films are displayed in Figure 2.

All of the films exhibited high transmittance, between 69 and 95%, throughout UV-VIS-NIR regions while exhibiting low reflectance within the same regions. The property of high transmittance throughout the UV-VIS-NIR region makes these films good material for thermal

Table 1. The Preparation of Beryllium Chloride

Reaction Bath	Dip Time (hr)	Be(NO ₃) ₂ .5H ₂ O		KOH		KCl		H ₂ O	pH
		Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Mol. (M)	Vol. (ml)	Vol. (ml)	
I2	24	0.1	2	1.0	4	1.0	2	32	11.4
I4	24	0.5	5	1.0	10	1.0	5	20	13.7
I33	18	1.0	5	1.0	10	1.0	5	20	13.0

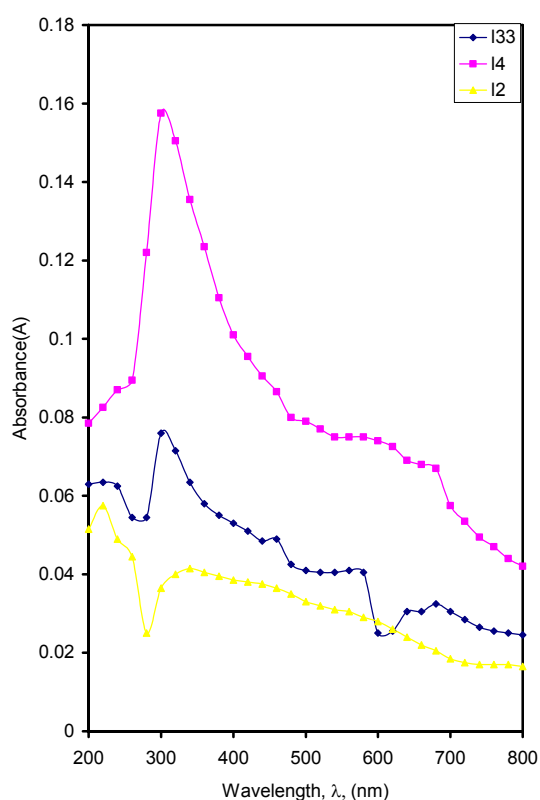


Figure 1: Spectral Absorbance of BeCl₂ Films prepared at 300k

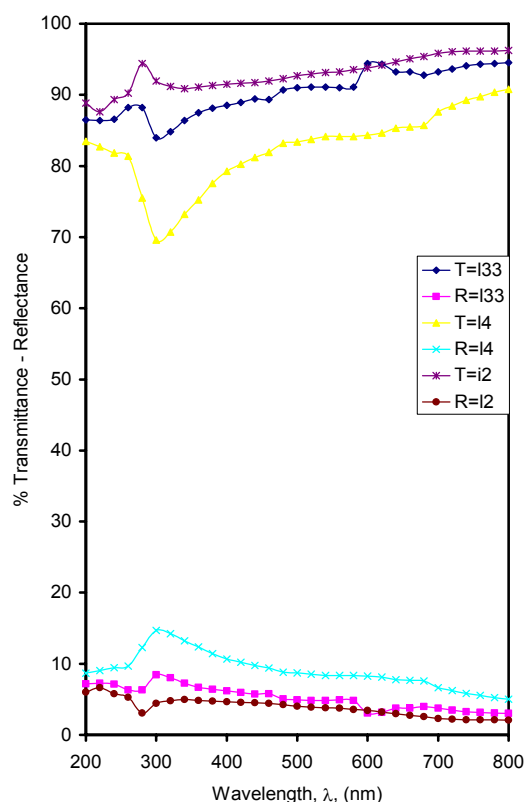


Figure 2: Spectral Transmittance - Reflectance of BeCl₂ Film prepared at 300K.

control window coatings for cold climates and for antireflection coating applications. All of the films were found to have high visible transmissions, of greater than 79% throughout the visible range.

Figure 3 is the plot of absorption coefficient α against $h\nu$ for BeCl₂ thin films. Samples I4 and I33 showed peak values between $0.175 \times 10^6 \text{ m}^{-1}$ and $0.363 \times 10^6 \text{ m}^{-1}$. The samples had average

values that ranged between $0.074 \times 10^6 \text{ m}^{-1}$ and $0.194 \times 10^6 \text{ m}^{-1}$.

The plots of $(\alpha h\nu)^2$ against $h\nu$ for direct transition of BeCl₂ thin films are shown in Figure 4. These reveal a band gap range between 1.80 and 3.00eV with an optimum value of 3.00eV exhibited by sample I33.

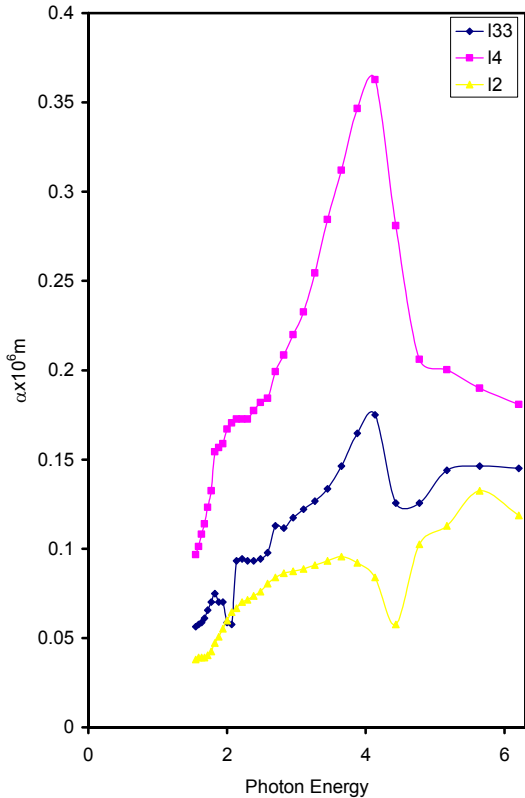


Figure3: Plots of absorption coefficient against Photon Energy for BeCl₂ Film.

The plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ for indirect transition of BeCl₂ thin films are shown in Figure 5.

This reveals a band gap range between 0.30 and 0.80eV with an optimum value of 0.80eV exhibited by sample I4.

The variation of n with $h\nu$ for samples of BeCl₂ is shown in Figure 6. It was observed that the refractive index (n) of I4 and I33 reached peak values between 1.40 and 1.81 at 4.14eV in the samples, with I4 showing the optimal value of 1.81. The samples produced average values that ranged between 1.49 and 1.86.

The variation of k with $h\nu$ for samples of BeCl₂ are shown in Figure 7. All of the study samples produced maximum values between 3.12×10^{-3} and 8.82×10^{-3} with sample I4 showing an optimal value of 8.82×10^{-3} . The samples produced average values that ranged between 2.06×10^{-3} and 7.01×10^{-3} .

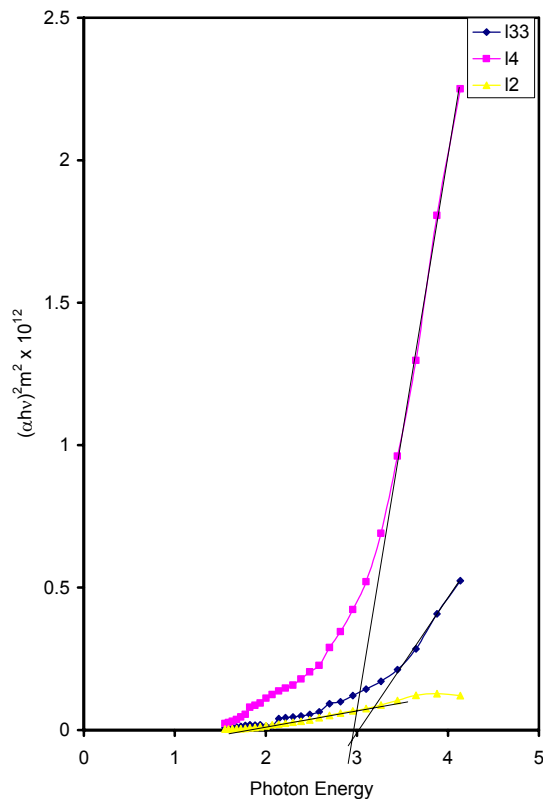


Figure 4: Plots of $(\alpha h\nu)^2$ against Photon Energy for BeCl₂ Samples.

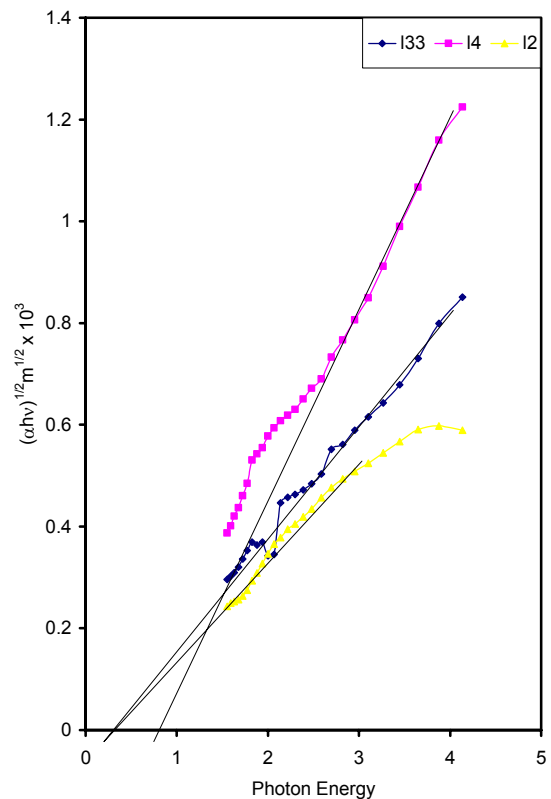


Figure 5: Plots of $(\alpha h\nu)^{1/2}$ against Photon Energy for BeCl₂ Samples.

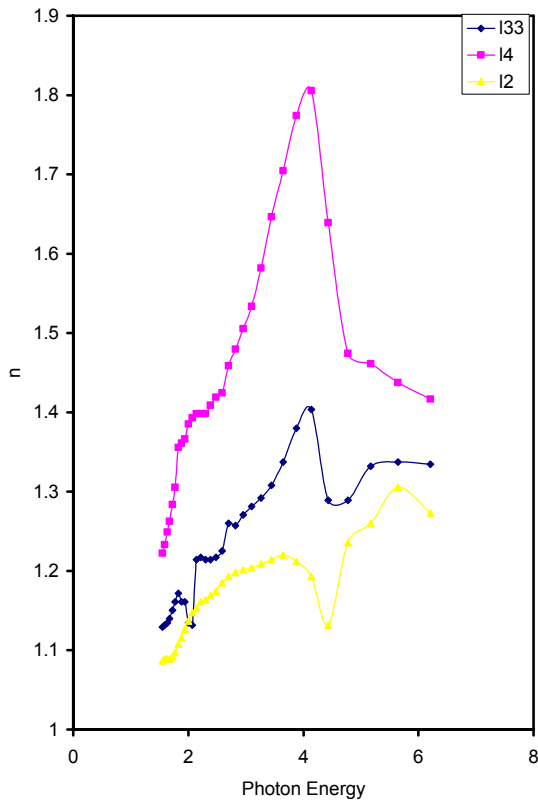


Figure 6: Plots of Refractive Index n against Photon Energy for BeCl_2 Samples.

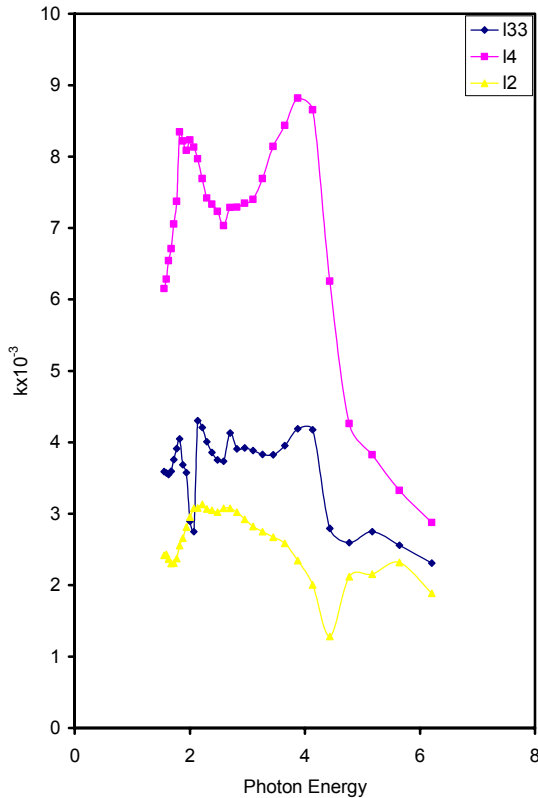


Figure 7: Plots of Extinction Coefficient k against Photon Energy for BeCl_2 Samples.

The plots of ϵ_r against $h\nu$ are displayed in Figure 8. Samples I4 and I33 showed peaks for ϵ_r between 1.97 and 3.26 at 4.14eV. An optimal value of 3.26 was observed in sample I4. The samples produced average values that ranged between 2.22 and 3.48.

The plots of ϵ_i against $h\nu$ are displayed in Figure 9. All of the samples of ϵ_i displayed maximum values between 7.10×10^{-3} and 3.13×10^{-2} with an optimal value observed in sample I4. The samples produced average values that ranged between 7.73×10^{-3} and 2.62×10^{-2} .

The plots of optical conductivity σ_o against $h\nu$ are shown in Figure 10. The films show optical conductivities with peak values between $0.06 \times 10^{14}\text{S}^{-1}$ and $0.16 \times 10^{14}\text{S}^{-1}$ at 4.14eV for samples I4 and I33, with sample I4 having an optimal value of $0.12 \times 10^{14}\text{S}^{-1}$. The samples produced average values that ranged between $0.03 \times 10^{14}\text{S}^{-1}$ and $0.09 \times 10^{14}\text{S}^{-1}$.

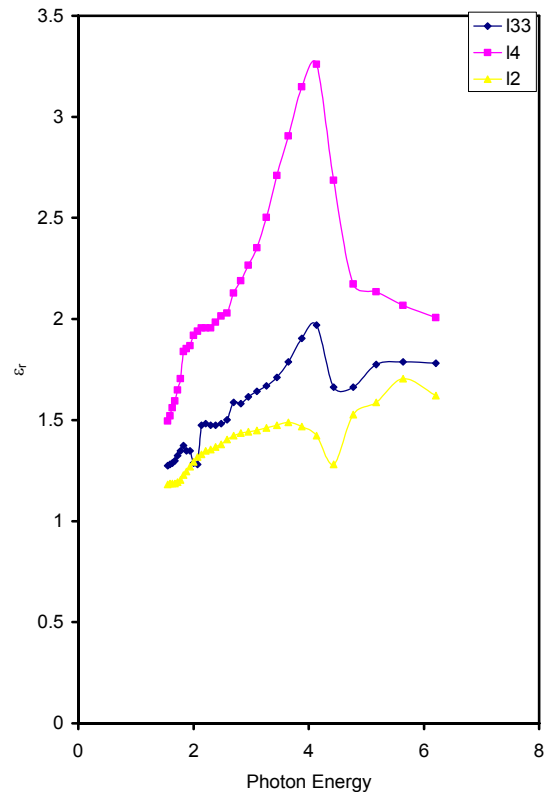


Figure 8: Plot of Real ϵ_r parts of Dielectric Constant against Photon Energy for Samples of BeCl_2 Film.

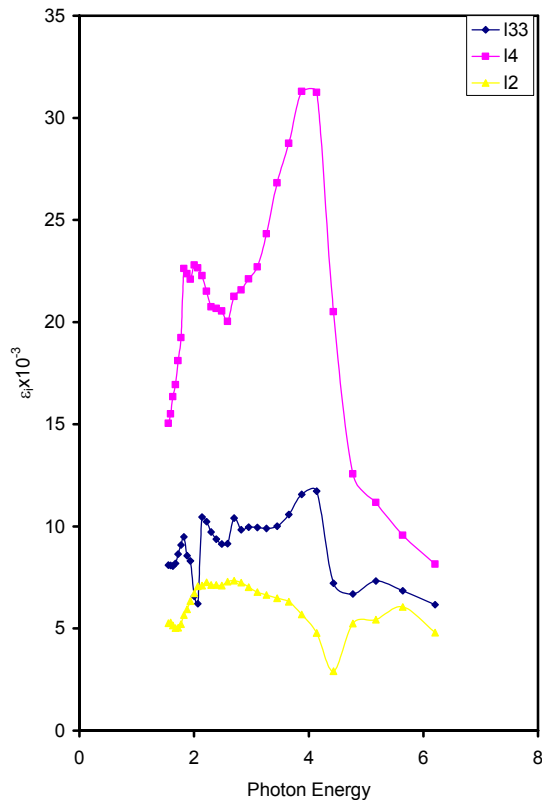


Figure 9: Plots of Imaginary ϵ_i parts of Dielectric Constant against Photon Energy for Samples of BeCl_2 Film.

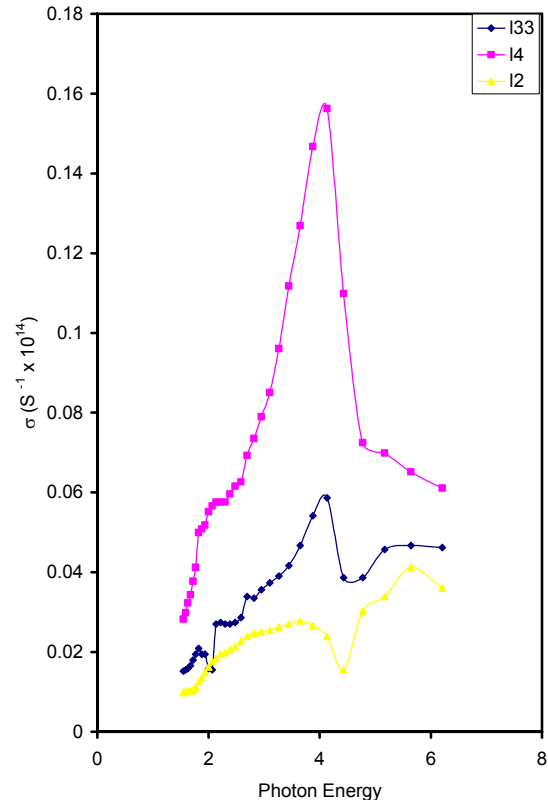


Figure 10: Plot of Optical Conductivity against Photon Energy for BeCl_2 Samples.

It can be seen that the shapes of the spectral curves for n (Figure 6) and that of ϵ_r (Figure 8) and σ_o (Figure 10) are strikingly similar.

Table 2 shows a summary of the maximum optical properties, band gap, and thickness of BeCl_2 films prepared at 300K.

It was observed that as the pH increased, the absorption coefficient as well as other optical properties increased, while the thickness of the thin film decreased. The most favorable condition for the deposition of the film was demonstrated to occur in an alkaline medium.

There was no observed correlation between the thickness of the film and the band gap. The maximum and minimum thicknesses produced during this study were $0.055\mu\text{m}$ and $0.044\mu\text{m}$. These occurred at average maximum and minimum absorption coefficient corresponding to $0.194 \times 10^6\text{m}^{-2}$ and $0.074 \times 10^6\text{m}^{-2}$ respectively.

The values for the refractive index, real dielectric constant, and optical conductivity for samples in this study (Figures 6, 8 and 10) increased from the minimum values at lower energy regions to maximum values at the higher energy regions.

CONCLUSIONS

BeCl_2 thin films with thickness ranging between 0.044 and $0.055\mu\text{m}$, energy band gap between 1.80 and 3.00eV , and indirect transitions between 0.30 and 0.80eV were successfully deposited in an alkaline medium using the chemical bath deposition technique.

Results from the spectrophotometric analysis showed that maximum values of n ranged between 1.70 and 2.27 , ϵ_r ranged between 2.87 and 5.02 , k ranged between 3.13×10^{-3} and 8.82×10^{-3} , and σ_o ranged between $0.05 \times 10^{14}\text{S}^{-1}$ and $0.19 \times 10^{14}\text{S}^{-1}$.

Table 2: Maximum Optical Properties, Band Gap and Thickness of BeCl₂ Films

Sample No	Dip time (hr)	pH	α $\times 10^6 \text{m}$	n	$k \times 10^{-3}$	ϵ_r	$\epsilon_i \times 10^{-2}$	$\sigma_o \times 10^{14}$ S^{-1}	Eg (eV)	t (μm)
I2	24	11.4	0.096	1.70	3.13	2.87	0.94	0.05	1.80	0.055
I4	24	13.7	0.363	2.24	8.82	5.05	3.90	0.19	2.98	0.044
I33	18	13.0	0.175	1.81	4.19	3.13	1.52	0.08	3.00	0.052

The films were found to have high transmittance between 74 and 94% in the UV-VIS-NIR regions; hence, they could be effective as thermal control window coatings for cold climates and antireflection coatings.

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ABOUT THE AUTHORS

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. His research interests are in the areas of thin film deposition, solar energy/solar radiation, and meteorology.

P.U. Asogwa, 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 is member of the solar energy society of Nigeria. His research interests are in the areas of thin film deposition, Crystal Growth, and all aspects energy.

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