Investigation of Optical Properties of Chemical Bath Deposited Beryllium Oxide (BeO) Thin Film and its Applications

F.I. Ezema, Ph.D.

Department of Physics and Astronomy, University of Nigeria

Nsukka, Enugu State, Nigeria

ABSTRACT

Beryllium oxide (BeO) thin films were prepared on glass slides using chemical bath deposition techniques from aqueous solutions of beryllium nitrate and potassium hydroxide. The effects of parametric variations on the film characteristics and their influence on the film growth rates were studied. It is shown through this investigation, that the reasonably inexpensive, simple, and highly reproducible chemical bath deposition technique is suitable for obtaining thin films with satisfactory optical properties. The film properties studied include optical transmission, optical constants, dielectric constants, optical conductivity, and band gap. Films with fairly high transmission rates ($>$ 85% between 400 and 800) and band gaps between 3.60eV and 4.00eV were obtained. Such films could be used transparent conducting oxides for window layers in solar cell fabrications. The films show poor absorbance in the UV-VIS-NIR regions; hence they have potential applications in the thermal control coatings for cold climates and antireflection coatings.

(Key words: chemical bath deposition, thermal coatings, bismuth oxide)

INTRODUCTION

The chemical bath deposition technique has been frequently used for the deposition of metal oxide thin films [1-2]. This technique has become part of new, intensively studied, thin film deposition methods for the synthesis of various functional coatings [3-4]. Metal oxide thin films that are transparent and conducting, have assumed importance in research and technology for their use in various applications [5]. The most extensively researched and used transparent conducting oxide thin films are SnO_2 and ZnO, which are deposited using highly advanced techniques [5-6]. Many of these methods are expensive and require high vacuum and controlled formation conditions [7]. Chemical bath deposition has its own as a large area of thin film can be deposited in a short time with simple and low cost instruments using this method [1, 8].

This paper reports on an investigation of the optical properties of chemical bath deposited beryllium oxide thin film and its applications. The optical properties investigated include the Absorbance (A), Transmittance (T), and Reflectance (R), which were used to calculate the other properties such as refractive index (n), extinction coefficient (k), dielectric constant (ε), and optical conductivity (σ). These optical properties and the band gap of the films were deduced from equations given in literature [2, 9-11] while the film thicknesses were obtained by optical methods [12].

EXPERIMENTAL DETAIL

The deposition of the beryllium oxide thin films on glass slides at room temperature was done using chemical baths that consisted of beryllium nitrate, potassium hydroxide, and distilled water. The substrates (glass slides) were previously degreased in nitric acid for 48 hours, cleaned with detergent in cold water, rinsed with distilled water, and allowed to drip dry in air. 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, which formed the framework on which the thin film growth can adhere. The reaction baths for the deposition of BeO thin films contain alkaline solutions of beryllium salt and potassium hydroxide in cold water. The reaction baths were made up of given volumes of $Be(NO_3)_2$ and KOH solutions added into 50ml beakers, in that order. They were stirred thoroughly using a glass rod at each stage to obtain a homogenous mixture of the solutions. The reaction baths were bought to 40 ml volume with distilled water and allowed to stay between 6 and 24 hours for dip times. The reaction baths were pH tested and found in the alkaline range before the substrates were introduced in the solutions. The reaction was a hydrolysis reaction [1, 5] and occurred at room temperature with KOH acting as complexing agent and a pH stabilizer in alkaline medium. Table 1 shows the variation of reaction bath and the dip times.

The basic reaction involved is stated below :

$$Be(NO_3)_2 + 3KOH + H_2O \Leftrightarrow 2KNO_3 + 2H_2O + BeO + KOH$$

Table 1. The Preparation Of Bismuth Oxide.

Reaction Bath	Dip. Time	$Be(NO_3)_2\ 5H_2O$		KOH		H_2O	pH
	(hr)	Mol. (m)	Vol. (ml)	Mol. (m)	Vol. (ml)	Vol. (ml)	
Bx2	24	0.01	2	1.0	4	34	11.4
Bx13	18	0.1	2	1.0	4	34	11.6
Bx12	12	0.1	2	1.0	4	34	11.6
Bx11	6	0.1	2	1.0	4	34	11.6

After the films were deposited, they were rinsed with distilled water and allowed to drip dry in air. The films were then characterized using FTIR spectroscopy and spectrophotometers. The spectral absorbance/transmittance characteristics of the films were obtained using PYE

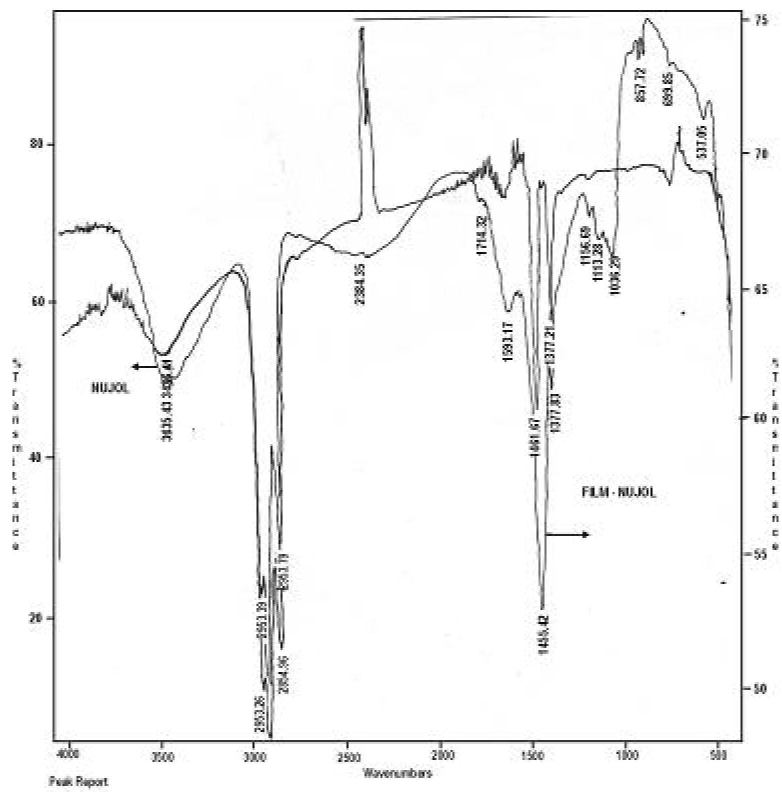
UNICAM HEλ IOS α spectrophotometers in the UV-VIS-NIR regions, while FTIR spectrometer analysis was applied in the far infrared regions.

RESULTS AND DISCUSSION

Figure 1 shows the combined effects of the film-nujol system on transmittance of infrared radiation for BeO when compared with nujol alone. The blank background of infrared spectroscopy for nujol indicates peaks at 1377cm^{-1}, 1461cm^{-1}, 2855cm^{-1}, 2924cm^{-1}, 2953cm^{-1} and 3436cm^{-1} with percentage transmittance between 5 and 57%.

When the film was dissolved in nujol, it showed additional peaks (Figure 1) at 1157cm^{-1}, 1114cm^{-1}, 1036cm^{-1}, 858cm^{-1}, 700cm^{-1}, and 537cm^{-1} with transmittance between 66 and 74%, which resulted due to the dissolved film. However dissolving the film in nujol modified the nujol peaks with those modified peaks showing transmittance that ranged between 44 and 66%. The transmittance of the film with regard to nujol peaks before dissolving the film and the new peaks after dissolving the film shows transmittance ranging between 17 and 61%. Comparing the nujol spectra to that dissolved film in nujol (nujol-film spectra), the percentage transmittance after dissolving the film is higher than that before dissolving of the film. This indicates that the film enhances transmittance within the far infrared regions.

Figure 1. Spectral Transmittance for Nujol/Combined Film-Nujol System.



Peak Report

Nujol

cm - 1	%T	cm - 1	%T	cm - 1	%T
1377.21	56.71	1461.07	45.33	2854.96	15.85
2924.35	4.49	2950.26	10.73	3436.41	53.09

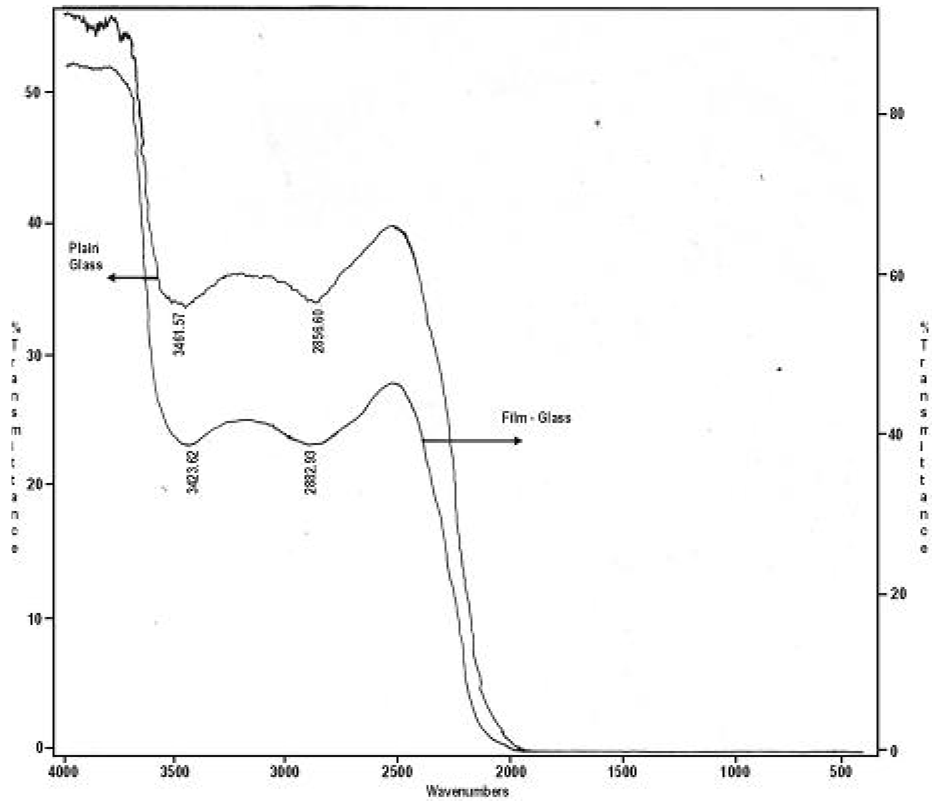
Film-Nujol

cm - 1	%T	cm - 1	%T	cm-1	%T
537.05	71.30	699.85	73.49	857.72	73.65
1036.29	66.26	1113.28	66.88	1156.69	67.72
1377.83	61.23	1456.42	53.11	1593.17	64.21
1714.32	68.24	2384.35	66.43	2853.79	55.57

Fig. 1: Spectral Infrared Transmittance for Nujol / Combined Film- Nujol System for BeO Sample

Nitrogen from beryllium nitrate as reported for its compound [13] has the following absorption bands; NO_2^- has absorption band between 1385-1323 cm^{-1}, 1262 - 1231 cm^{-1} and 862 - 815cm^{-1} while NO_3^- has between 1400-1354 cm^{-1} and 869-808 cm^{-1}. The 858cm^{-1} peak in the range 869 - 808cm^{-1}, could be attributed to an incorporation of nitrogen from beryllium nitrate into the films as reported [13] for its compound NO_3^- in the range 869 - 808cm^{-1}, as can be seen from the Figure 1. However, the absence of the peaks for water of crystallization [13] (3554 - 3139 cm^{-1} and 1692 - 1600 cm^{-1}) from the films confirms the films to be oxide with impurities due to the incorporated nitrogen from NO_3^- of the beryllium nitrate. Figure 2 shows the combined effects of film-glass system on transmittance of infrared for BeO when compared with uncoated glass.

Figure 2. Spectral Transmittance of Plain Glass/Combined Film-Glass System.



Peak Report

Plain Glass

cm - 1	%T	cm - 1	%T	cm - 1
3461.57	33.99	2856.60	34.09	

Film-Glass

cm - 1	%T	cm - 1	%T
3423.62	38.47	2882.93	38.40

Fig. 2: Spectral Infrared Transmittance of Plain Glass / Combined Film-Glass System for BeO Sample

This anlysis was carried out using a single beam Fourier transform spectrometer. Uncoated glass reduced transmittance to 33.99% at 3462cm^{-1}, to 34.09% at 2857cm^{-1}, and finally to about 2% transmittance in the 1896cm^{-1} to 2000cm^{-1} range. By about 2001 cm^{-1}, no radiation is transmitted through the glass.

Using coated glass with the film reduced transmittance to 38.42% at 3424cm^{-1}, 38.40% at 2883cm^{-1}, and about 2% transmittance in the 1896cm^{-1} - 2000cm^{-1} range. By about 2001cm^{-1}, no radiation is transmitted through the film-glass system.

These films are capable of allowing solar radiation (0.3 - 3.0μm) 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 enhances transmittance of IR more than plain glass just as the film-nujol system enhances transmittance of IR more than nujol alone. The spectral absorbance of beryllium oxide film prepared at 300k is illustrated in Figure 3.

Figure 3.

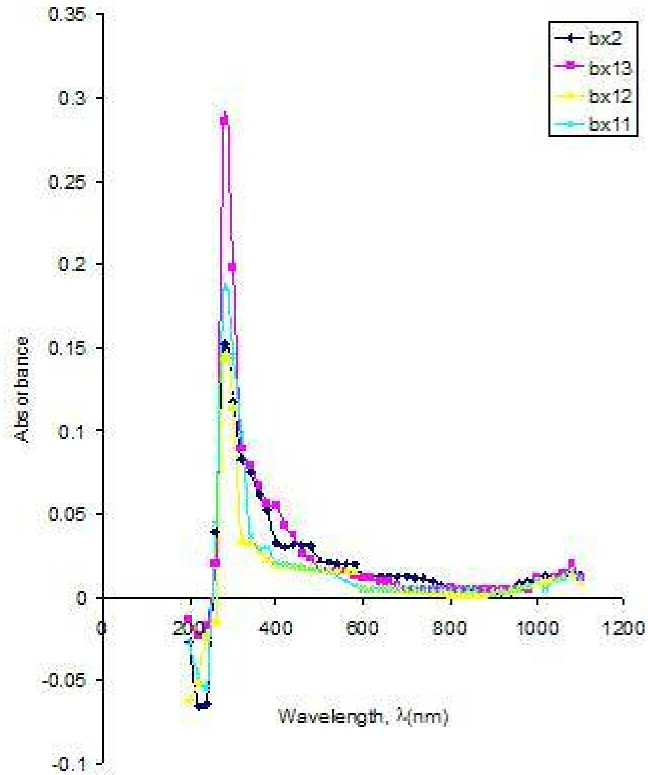


Fig. 3: Spectral Absorbance of BeO Films prepared at 300k.

All samples bx2, bx13, bx12, and bx11 show negative absorbance at UV regions between 200 and 260nm with minimum absorbance of -0.066, -0.023, -0.05, and -0.055 respectively. Samples bx2, bx13, and bx11 observed their own negative minimum absorbance at 220nm with absorbance of -0.066, -0.023, and -0.050 respectively. The phenomenon of negative absorbance of films were described in the work of Ezema and Okeke [2,11].

All the samples of the films grown in this work exhibit poor absorbance all through UV-VIS-NIR regions. The transmittance-reflectance spectra are displayed in Figure 4.

Figure 4.

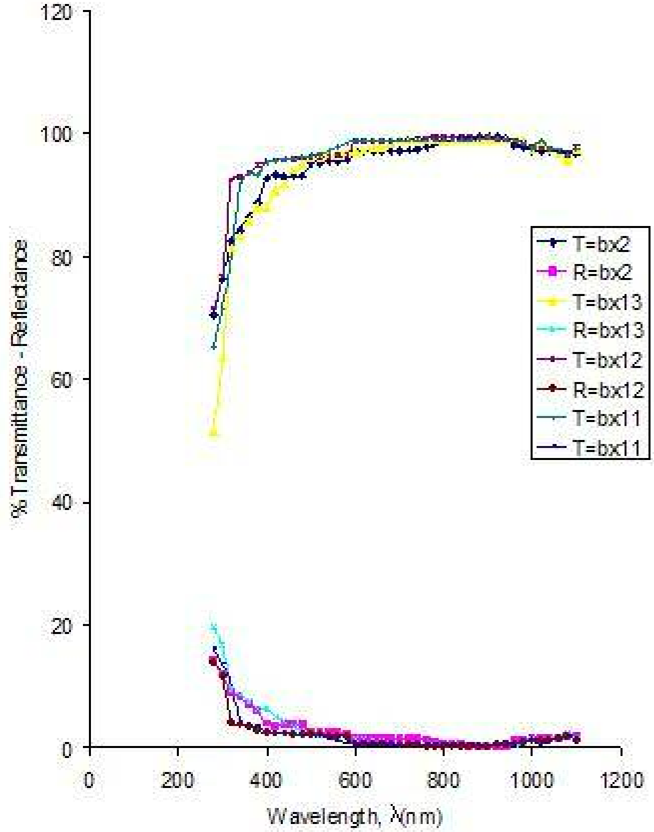


Fig. 4: Spectral Transmittance - Reflectance of BeO Films prepared at 300k.

All the films exhibit high transmittance, between 51and 99%, throughout UV-VIS-NIR regions while exhibiting low reflectance the same regions. All of the films have high visible transmission, $>$ 88%. The properties of high transmittance throughout UV-VIS-NIR make the films good materials for thermal control window coatings for cold climates and antireflection coatings. The variation of n with $h\nu$ for samples of BeO is shown in Figure 5.

Figure 5.

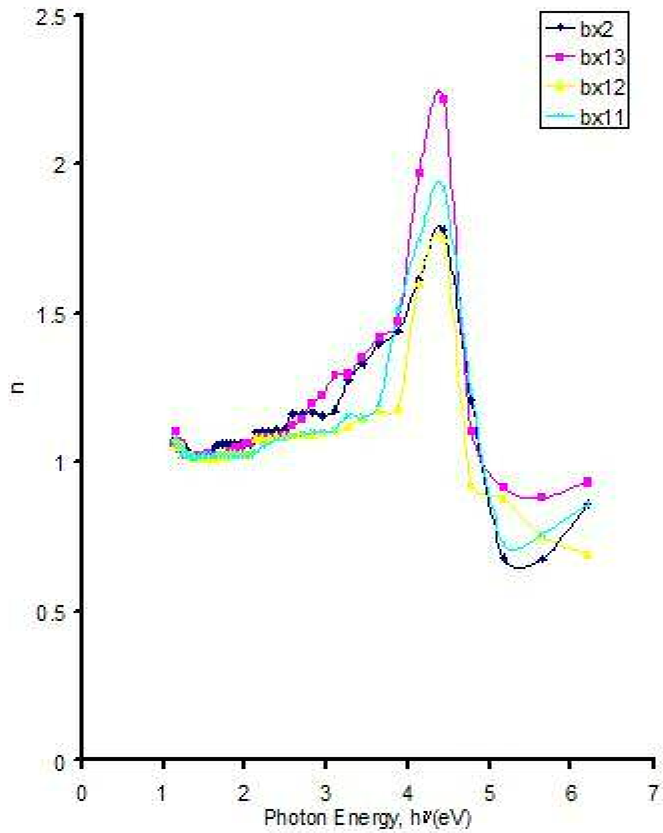


Fig. 5: Plots of Refractive Index (n) against Photon Energy for BeO Film prepared at 300k.

It is observed that n reached peak values between 1.72 and 2.22 at 4.43eV for all of the samples with bx13 having the optimal value at 2.22. The variation k with hν for samples of BeO is shown in Figure 6.

Figure 6.

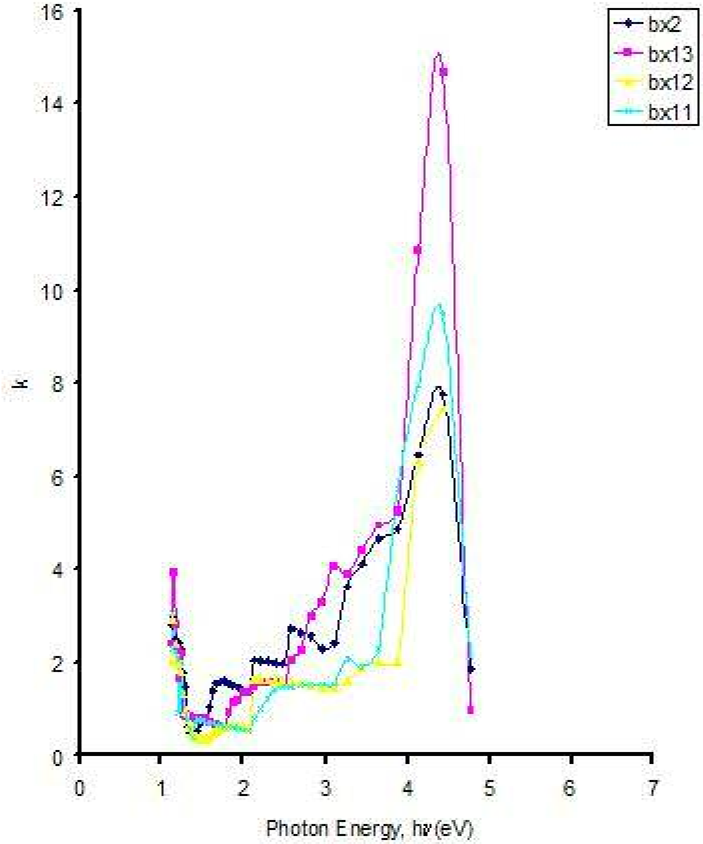


Fig. 6: Plots of Extinction Coefficient (k) against Photon Energy for BeO Film prepared at 300k.

All the samples observed peak values between 0.75 x 10^{-2} and 1.47 x 10^{-2} at 4.43eV and sample bx13 showed an optimal value of 1.47 x 10^{-2}. The BeO thin films prepared in this work are observed to be semiconductors since the maximum in the refractive index (n) occurred at the energy near that at which the maximum change in k occurred [14] as can observed from Figures 5 and 6. The plots of ε_r against hν are displayed in Figure 7.

Figure 7.

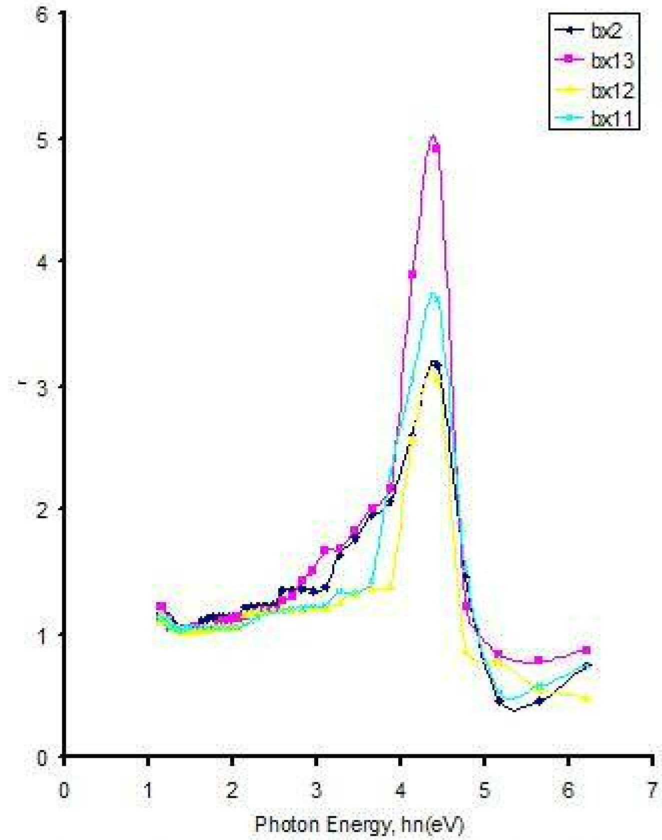


Fig. 7: Plots of Real Dielectric Constant (ε) against Photon Energy for BeO Sample.

All of the samples of ε_r observed peak values between 3.07 and 4.91 at 4.43eV and an optimal value of 4.91 observed in sample bx13. The plots of ε_i against $h\nu$ are displayed in Figure 8.

Figure 8.

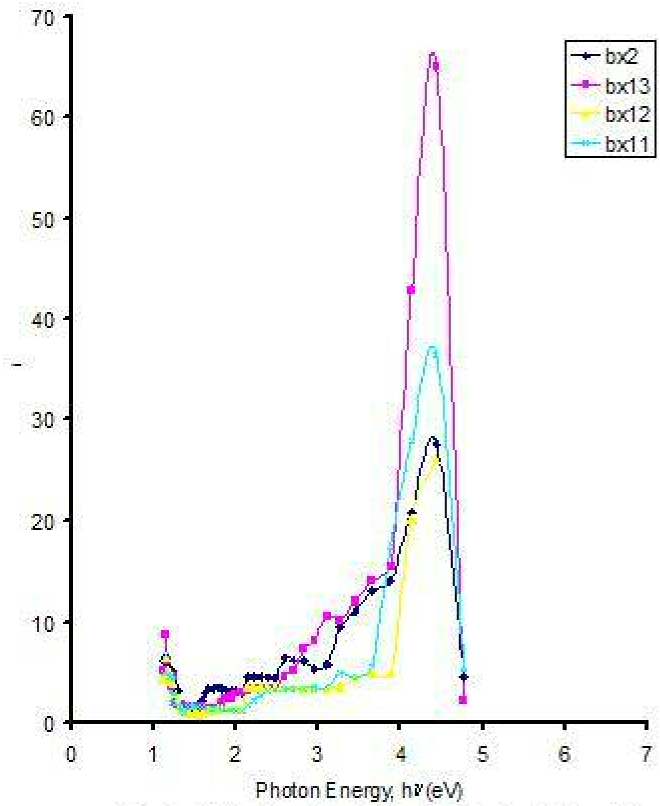


Fig. 8: Plots of Imaginary Dielectric Constant (ε_i) against Photon Energy for BeO Sample.

All of the samples of ε_i observed peak values between 2.61 x 10^{-2} and 6.50 x 10^{-2} with optimal value observed sample bx13. It can be seen that the shapes of the spectral curves for n and k (Figures 5 and 6) and for ε_r and ε_i (Figures 7 and 8) are strikingly similar. The plots of optical conductivity σ_o against hν are shown in Figure 9.

Figure 9.

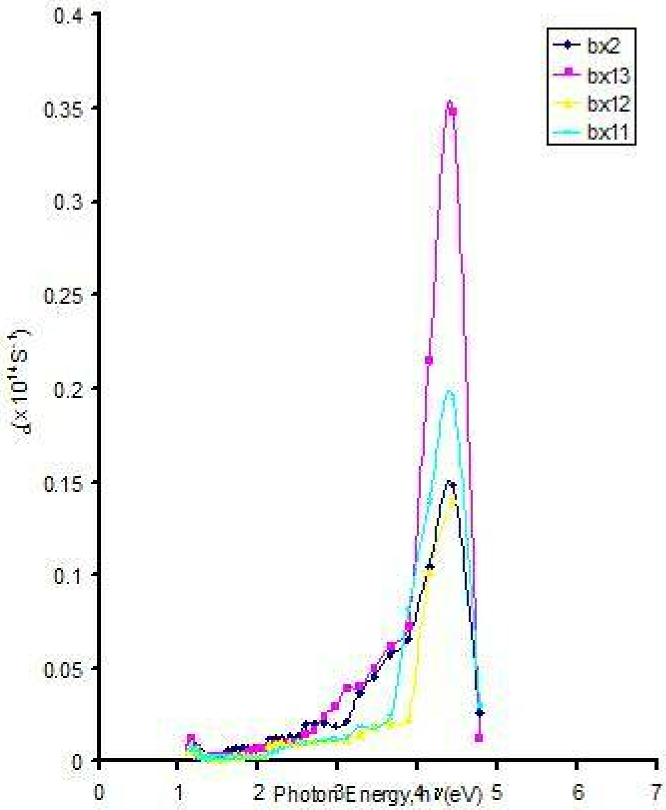


Fig. 9: Plot of Optical Conductivity, σ_o against Photon Energy for BeO Film prepared at 300k.

Peak values are seen between 0.15 x $10^{14}S^{-1}$ and 0.35 x $10^{14}S^{-1}$ at 4.33eV and an optimal value of 0.35 x $10^{14}S^{-1}$ is observed for sample bx13. The plots of α^2 against hν for the BeO films are shown in Figure 10.

Figure 10.

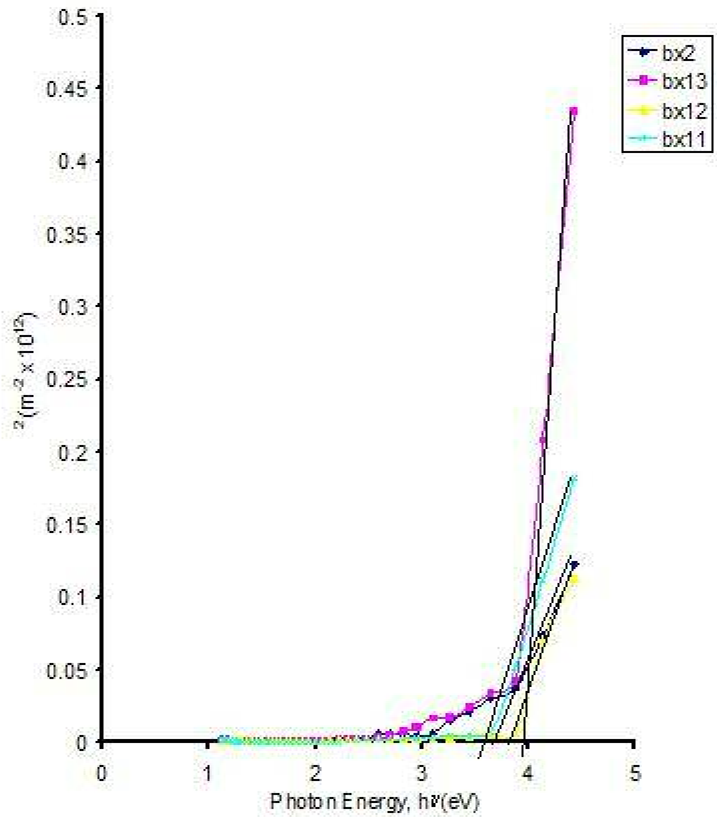


Fig. 10: Plot of α^2 against hν for BeO Sample.

This plot reveals that the band gap ranges between 3.60 and 4.00eV with an optimum value of 4.00eV exhibited by Sample bx13. The high visible transmission, together with the large band gap, makes these films good material for the fabrication of window layers for solar cells.

All the values for complex refractive index, dielectric constant, and optical conductivity increase from the minimum values at low energy regions to peak values at 4.43eV in the higher energy regions, and then decrease to low values in the same regions. Table 2 presents a summary of the peak optical properties, band gap, and thickness of BeO films prepared at 300k.

Table 2. Peak Optical Properties, Band Gap and Thickness of BeO Films.

Samp. No	Dep. Time (hr)	pH	n	kx10^{-2}	ε_r	ε_i x 10^{-2}	σ_o $10^{14}S^{-1}$	Eg(eV)	t (μm)
bx2	24	11.4	1.78	0.78	3.16	2.76	0.15	3.70	0.063
bx13	18	11.6	2.22	1.48	4.91	6.50	0.35	4.00	0.077
bx12	12	11.6	1.75	0.75	3.07	2.61	0.14	3.90	0.071

bx11	6	11.6	1.92	0.95	3.69	3.65	0.20	3.60	0.067

Table 2 shows that as the dip times increased, the thickness as well as the band gap increased. However, a slight variation in the composition of the starting solutions altered the growth kinetics, which shows that a slight decrease in the pH in an alkaline medium caused a decrease in both the thickness and the band gap. This slight variation also affected the peak optical properties as seen from this table. The absorbance of the films depends on the thickness of the film, hence the absorbance increased as thickness increased, as expected [2,11]. It is also observed that as the absorbance increases for this film the band gap increases.

CONCLUSIONS

BeO thin films have been successfully deposited in alkaline medium using chemical bath deposition technique. FTIR spectroscopy showed the bonding peaks and the percentage transmittance that ranged between 17% and 61% in the far infrared regions. The thickness of the film deposited increases with dip times at the same pH, but for slight variation in the starting solutions, the thickness decreased as a result of a change in pH. The band gap and the peak optical properties were found to follow the same pattern.

The films were found to have high transmittance in the range between 51% and 100% in the UV-VIS-NIR regions; hence, they have potential application as thermal control window coatings for cold climates and antireflection coatings. The large band gap (3.60 - 4.00eV) and high visible transmission (> 88%) also make the films suitable for window layers of solar cells.

REFERENCES

1. Chopra, K.L. and S.R. Das. *Thin Film Solar Cells.* Plenium Press: New York. (1983).

2. Ezema, F.I. and C.E. Okeke. Chemical Bath Deposition Of Bismuth Oxide (Bi2O3) Thin Film And Its Applications. *Greenwich Journal of Science and Technology*. 3,2 (2003):90-109.

3. Eze, F.C. and C.E. Okeke. Chemical Bath Deposited Cobalt Sulphide Films; Preparation Effects. *Materials, Chemistry and Physics.* 47(1997): 31- 36.

4. Sabestian, P.J. and H. Hu. Identification of the Impurity Phase in Chemically Deposited CdS Thin Films. *Adv. Mater. Opt. Electron*. 4 (1994):407 - 412.

5. Unaogu, A.L. and C.E. Okeke. Characterization of Antimony Doped Tin Oxide Film Prepared by Spray Pyrolysis. *Sol. Energy Mater*. 20 (1990): 29 - 36.

6. Bahadur, L., M. Hamdani, J.F. Koenig, and P. Chartier. Studies on Semiconducting Thin Films Prepared by the Spray Pyrolysis Technique for Photoelectrochemical Solar Cell Applications: Preparation and Properties. *Sol. Ener. Mater.* 14(1986):107- 120.

7. Pushparajah, P., A.K. Arot, and S. Radhakrisna. Physical Properties of Spray Pyrolysed Pure and Doped ZnO Thin Films. *J. Phys. D: Appl. Phys.* 27(1994):1518- 1521.

8. Choi J.Y., K.J. Kim, J.B. Yoo, and D. Kim. Properties of Cadmium Sulphide Films Deposited by Chemical Bath Deposition with Ultrasonication. *Solar Energy.* 64 (1-3) (1998):41- 47.

9. Ndukwe, I.C. Solution Growth, Characterization and Applications of Zinc Sulphide Thin Films. *Sol. Ener. Mater. Sol. Cells.* 40(1996):123 - 131.

10. Pankove, J.I. *Optical Processes in Semiconductors*. Prentice-Hall: New York. (1971).

11. Ezema, F.I. and C.E. Okeke. Characterization Of Bismuth Fluoride (BiF_3) Thin Films Prepared by Solution Growth Technique And Its Applications. *Nig. Journ. Phys.*14 (2) (2002):77 -85.

12. Theye, M. In: *Optical Properties of Thin Films*. K.L. Chaopra and L.K. Malhota, eds. Thin film technology and Applications. Tata McGraw-Hill: New Delhi. (1985).

13. Conley, R.T. *Infrared Spectroscopy*. Allyn and Bacon, Inc.: Boston. (1966).

14. Greenway, D.L. and G. Harbeke. *Optical Properties and Band Structures of Semiconductors*. Pergamon Press: New York. (1969).

About the Author:

Dr. 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.

Cite As: Ezema, F.I. 2003. Investigation of Optical Properties Chemical Bath Deposited Beryllium Oxide (BeO) Thin Film and its Applications. *Greenwich Journal of Science and Technology*. 3(2):110-122.

Return to GJST Home Page