

CHEMICAL BATH DEPOSITION OF BERYLLIUM SULPHIDE (BeS) THIN FILM AND ITS APPLICATIONS

F.I. EZEMA AND C.E. OKEKE

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

ABSTRACT

Beryllium sulphide (BeS) thin films on glass slide using chemical bath deposition technique were prepared and characterized using Fourier transforms infrared (FTIR) spectroscopy and spectrophotometers. Thickness of the film in the range between 0.068 and 0.095 μm with energy band gap between 2.30 and 4.40eV has been deposited. The deductions from the spectrophotometers showed that average values n range between 1.45 and 2.07, k range between 2.79×10^{-3} and 10.23×10^{-3} , and σ_0 range between $0.028 \times 10^{14}\text{S}^{-1}$ and $0.143 \times 10^{14}\text{S}^{-1}$. Some of the films are good transmitter of radiation in the UV - VIS - NIR that ranges between 77 and 96%, while in the far infrared regions it ranges between 4 and 42%. The films show poor absorbance in the UV - VIS - NIR regions; hence it has potential applications in the thermal control coatings for cold climates and antireflection coatings.

INTRODUCTION

Thin films are well known for their applications in many physics based industries as materials for many semiconductor devices. Chemical deposition of thin films has advantage as a low deposition cost technique to realize economic and large area devices (Choi et al 1998, Sabestian and Hu 1994). Several authors have reported (e.g. Choi et al 1998, Eze and Okeke 1997, Ndukwe 1996, Ortega and Lincot 1993, Nair and Nair 1992, Nair et al, 1990) on various aspects of chemically deposited thin films. Some workers (e.g. Eze and Okeke 1997, Sabestian and Hu 1994) have been studied the effect of varying the growth parameters such as deposition rates, bath compositions and bath temperature on the properties of thin film. The effects of solar radiation and ultrasonification on the various properties of thin films have also been reported (e.g. Choi et al 1998, Eze and Okeke 1997). This paper reports the chemical bath deposition BeS film that would be adequate for solar and industrial applications, which were characterized using optical method. Optical studies using transmittance and reflectance data from samples prepared using chemical bath deposition have been reported (Ndukwe 1996).

THEORETICAL CONSIDERATION and CALCULATIONS

In both crystalline and amorphous semi conductors, near the fundamental absorption age there is the dependence of absorption coefficient on the photon energy. In high absorption region, the form of absorption coefficient with photon energy was given in a more general term by (Pankove, 1971) as

$$\alpha=A (\alpha h\nu - E_g)^n \dots\dots\dots 1$$

Where ν is the angular 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 characterises the optical processes. 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 α^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 $k^2 \ll n^2$) there exist a relationship between R and n given by (Ndukwe, 1996, Janai et al 1979)

$$R = (n-1)^2 / (n+1)^2 \text{ ----- 2}$$

There is also a relationship between k and α given by (Ndukwe, 1996, Pankove 1971).

$$K = \alpha\lambda / 4\pi \text{ ----- 3}$$

where α = absorption coefficient of the film, λ = wavelength of electromagnetic wave. The relationship between ϵ and k is given by (Ndukwe, 1996, Pankove 1971).

$$\epsilon = \epsilon_r + \epsilon_i = (n + ik)^2 \text{ ----- 4}$$

where ϵ_r and ϵ_i are real and imaginary parts of ϵ respectively.

Optical conductivity σ is given by (Ndukwe, 1996, Pankove 1971).

$$\sigma = \alpha nc / 4\pi \text{ ----- 5}$$

where c is the velocity of light.

Optical method as discussed by Theye (1985), and Ezema (2000) was used to estimate the thickness of the film.

EXPERIMENTAL DETAIL.

The preparation of BeS thin films on glass slide was carried out using solution growth technique, the glass substrates were previously degreased in HNO_3 for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air. The degreased

cleaned surface has the advantage of providing nucleation centres for the growth of the films, hence yielding highly adhesive and uniformly deposited films.

The deposition of Beryllium sulphide thin films is done using potassium hydroxide (KOH) and/or ethylene diamine tetra acetic acid (EDTA) as complexing in a bath consisting of Beryllium Nitrate ($\text{Be}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), thiourea $[(\text{NH}_2)_2\text{CS}]$ and distilled water. The basic reaction equations are :

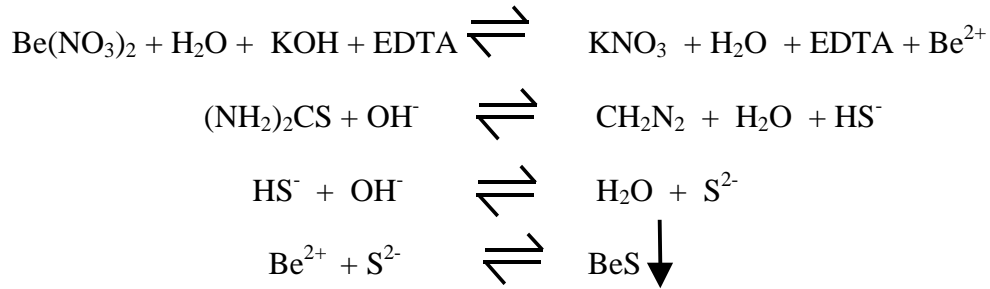


Table 1 shows the reaction bath for preparation of BeS thin films and the details of the molar and volume concentrations of the reagents as well as the dip times of the various reaction baths.

Table 1 : the preparation of beryllium sulphide

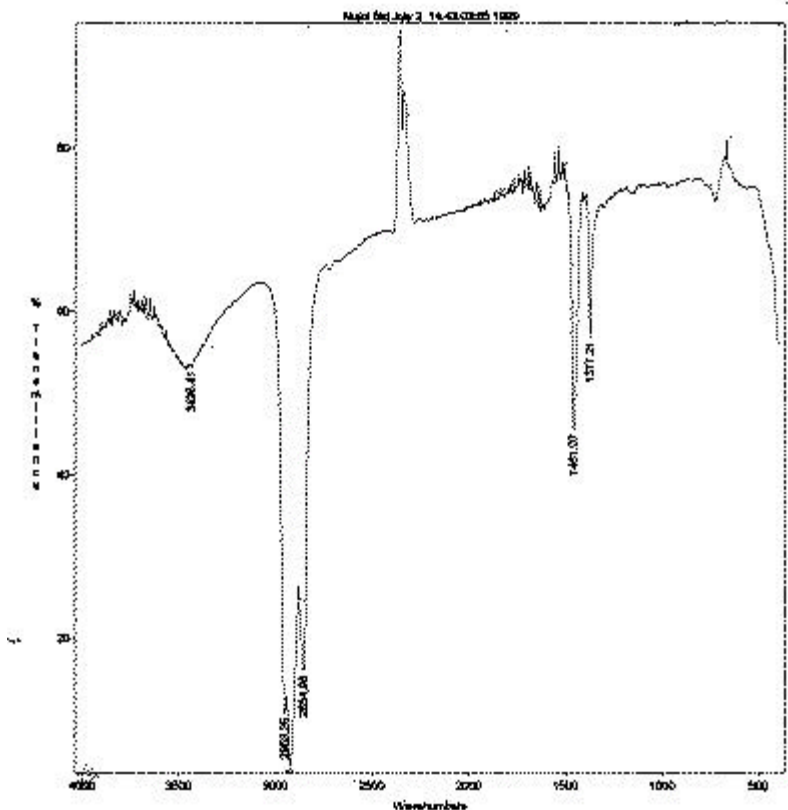
| Reaction Bath | Dip. Time (hr) | $\text{Be}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ | | EDTA | | $(\text{NH}_2)_2\text{CS}$ | | KOH | | H_2O | pH |
|------------------|----------------|---|-----------|----------|-----------|----------------------------|-----------|----------|-----------|----------------------|------|
| | | Mol. (m) | Vol. (ml) | Mol. (m) | Vol. (ml) | Mol. (m) | Vol. (ml) | Mol. (m) | Vol. (ml) | Vol. (ml) | |
| BU ₂ | 24 | 0.1 | 2 | | | 1.0 | 2 | 1.0 | 4 | 32 | 11.3 |
| BU ₃ | 24 | 1.0 | 5 | | | 1.0 | 5 | 1.0 | 10 | 20 | 13.3 |
| BU ₄ | 24 | 0.5 | 5 | | | 1.0 | 5 | 1.0 | 10 | 20 | 13.6 |
| BU ₅ | 24 | 0.1 | 2 | | | 1.0 | 5 | 1.0 | 10 | 23 | 13.7 |
| BU ₁₃ | 18 | 1.0 | 2 | | | 1.0 | 2 | 1.0 | 4 | 32 | 11.3 |
| D ₃ | 23 | 1.0 | 2 | 0.1 | 2 | 1.0 | 5 | 1.0 | 7 | 21 | 3.95 |

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

were obtained using PYE UNICAM UV SP8-100 spectrophotometers in the UV-VIS-NIR regions while FTIR spectrometer were used in the far infrared regions. The optical properties studied 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).

RESULTS AND DISCUSSION

The blank background of infrared spectroscopy for nujol (Fig.1) indicates the peaks at 1377cm^{-1} , 1461cm^{-1} , 2855cm^{-1} , 2924cm^{-1} , 2953cm^{-1} and 3436cm^{-1} with percentage transmittance between 5 – 57%. When the film was dissolved in nujol (Fig.2), it showed peaks at 1600 , 1072cm^{-1} , 858cm^{-1} , 697cm^{-1} and 537cm^{-1} with percentage transmittance between 63 and 74%, which resulted due to the dissolved film. However the new nujol peaks show percentage transmittance ranged between 47 and 61%. The transmittance of the film with regard to nujol peaks before dissolving the film and new nujol peaks after dissolving the film show percentage transmittance ranged between 4 and 42%. Comparing the nujol spectra to that after dissolving of the film in the nujol, that is the nujol – film spectra, the percentage transmittance after dissolving of the film is higher than that before dissolving of the film. This means that the film enhances transmittance within the far infrared regions.



Peak Report
 File: c:\data\data\spec\10221.rtf
 Yfile: nujol.dtl July 2 14:43:03.95 1995
 Filter: Three-Point Center of Gravity

| cm-1 | %I | cm-1 | %T | cm-1 | %T |
|---------|-------|---------|-------|---------|-------|
| 1377.21 | 86.71 | 1461.07 | 45.59 | 2854.08 | 15.85 |
| 2924.35 | 4.49 | 2923.25 | 10.73 | 3424.41 | 13.59 |

Fig. 1: Spectral Infrared Transmittance for Nujol

The peak 537cm^{-1} (Fig. 2) falls within 600 and 500cm^{-1} which is as a result of S – O bonds (Szafran, et al 1991). The sulphur from thiourea was incorporated into the film from recorded vibrations bands reported (Conley, 1966) for its compound HSO_4^- $1200 - 1154\text{cm}^{-1}$, $1092 - 1046\text{cm}^{-1}$, $600 - 569\text{cm}^{-1}$ $\text{S}_2\text{O}_3^{2-}$ $1146 - 1108\text{cm}^{-1}$, $1015 - 969\text{cm}^{-1}$, $692 - 646\text{cm}^{-1}$, $554 - 524\text{cm}^{-1}$.

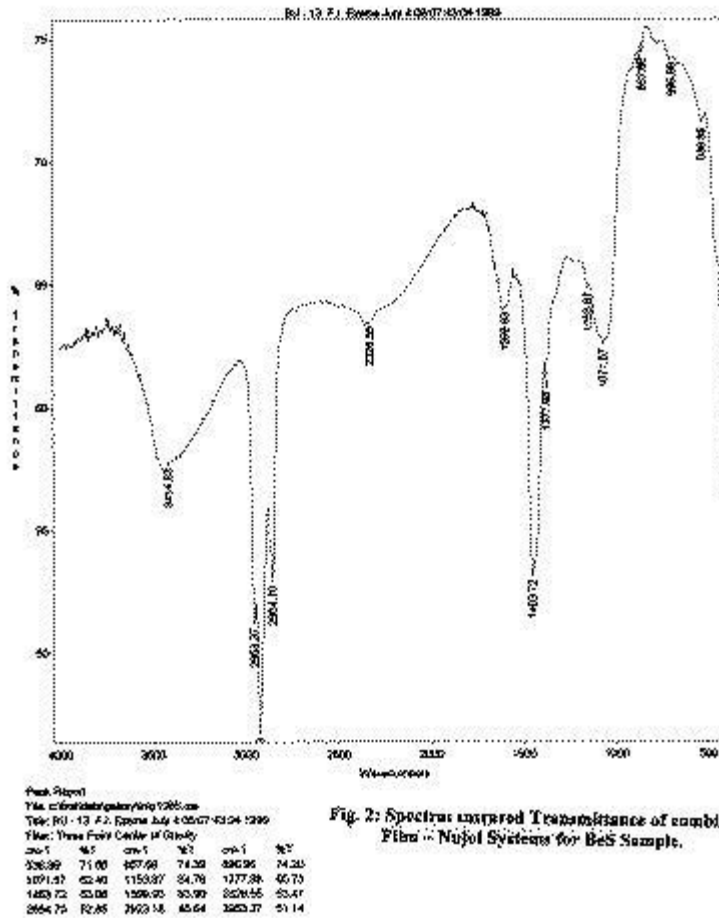


Fig. 2: Spectral infrared Transmittance of combis Film - Nujol System for BeS Sample.

However there is no incorporation of Nitrogen from the Beryllium Nitrates in the films from recorded vibration bands reported (Conley, 1966) for its compound.

There is the possibility of water of crystallization band at 3367cm^{-1} and 1600cm^{-1} , which confirms the hygroscopic nature of the film under different preparation conditions.

Figs. 3 and 4 show the combined effect of film – glass system on transmittance of infrared for BeS when compared with uncoated glass. This was carried out using a single beam Fourier transform spectrometer. Uncoated glass (Fig.3) reduced transmittance to 33.99% at 3462cm^{-1} then to 34.09% at 2857cm^{-1} and then finally dropped to only about 2% transmittance at 1896cm^{-1} to 2000cm^{-1} .

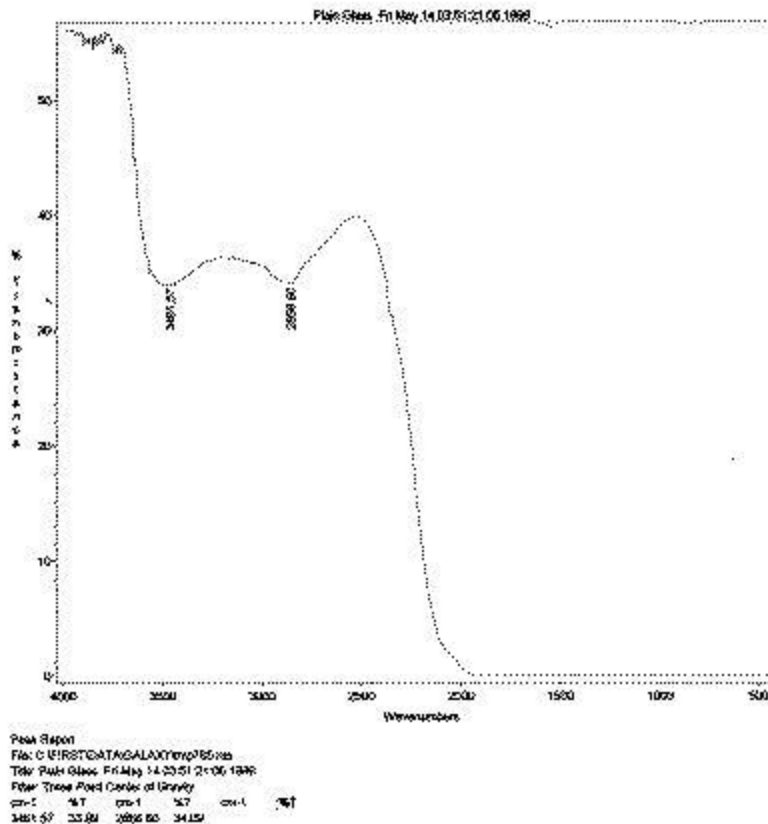


Fig. 3: Spectral Infrared Transmittance of Plain Glass

By about 2001 cm^{-1} , no radiation at all is transmitted through the glass. The coated glass (Fig.4) reduced transmittance to 42.44% at 3442 cm^{-1} then to 41.74% at 2886 cm^{-1} and then finally dropped to only about 2% transmittance at $1896\text{--}2000\text{ cm}^{-1}$.

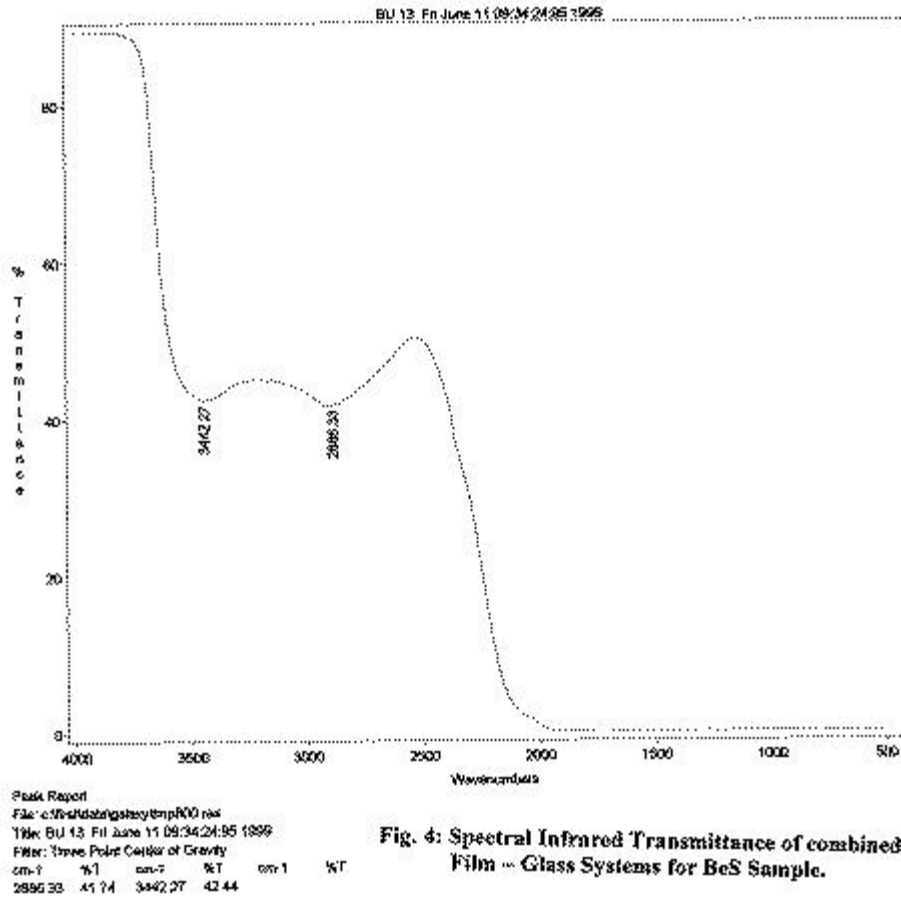


Fig. 4: Spectral Infrared Transmittance of combined Film - Glass Systems for BeS Sample.

By about 2001cm^{-1} , no radiation at all is transmitted through the film-glass system. This film is capable of allowing solar radiation ($0.3 - 3.0\mu\text{m}$) to be transmitted into a building but prevents thermal re-radiation out of the building through the glassing system. It is observed that film-glass systems transmit the IR more than the plain glass. The property of high transmittance throughout UV-VIS-IR makes the film a good material for thermal control window coatings for cold climates and antireflection coatings.

The spectral absorbance of Beryllium Sulphide films prepared at 300K is displayed in Fig. 5.

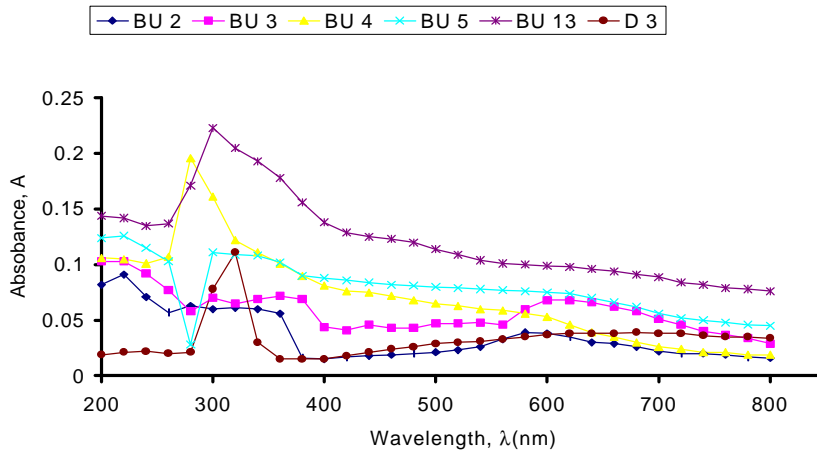


Fig. 5: Spectral Absorbance of BeS Films prepared at 300k.

Sample BU₁₃ shows moderate absorbance at UV region but poor absorbance throughout VIS-NIR regions. Samples BU₂, BU₃, BU₄, BU₅ and D₃ exhibit poor absorbance throughout UV-VIS-NIR regions.

The Transmittance – Reflectance spectra are shown in Fig 6 – 7. It is observed generally that some of the samples show high transmittance throughout UV-VIS-NIR regions, which range between 77 and 96%. However BU₁₃ show moderate transmittance which range between 60 and 84%. BU₁₃ and BU₄ show maximum reflectance of 18% and 17% at 300nm and 280nm respectively and each decreases with wavelength to a minimum of 8% and 2% at 800nm.

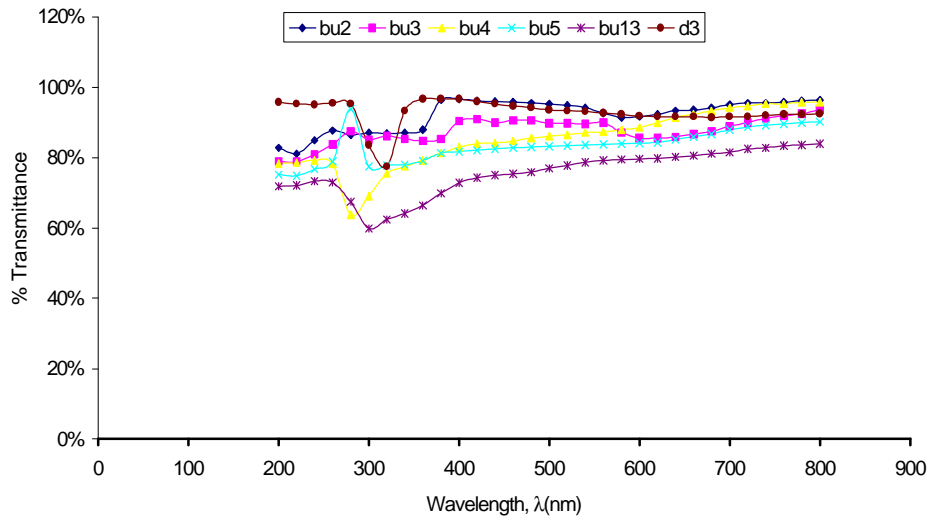


Fig. 6: Spectral Transmittance for BeS Films prepared at 300k.

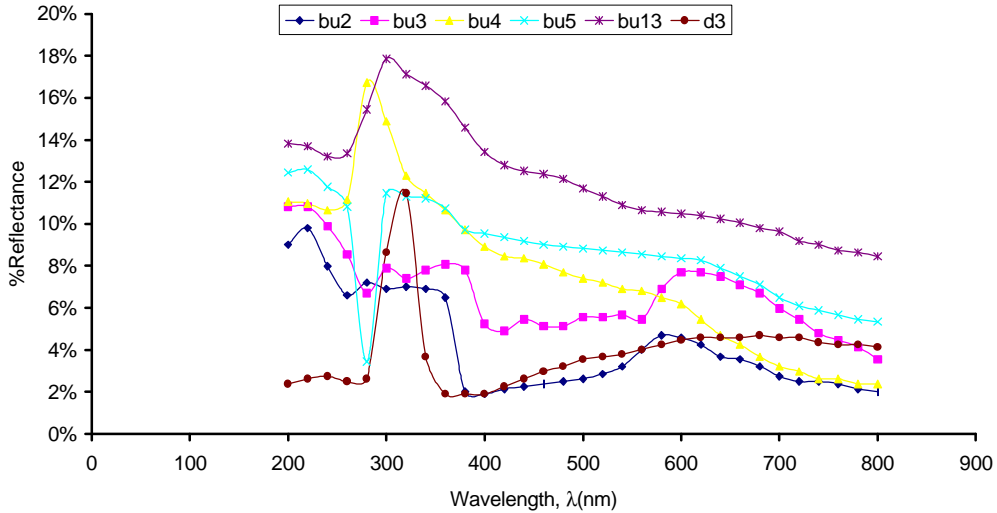


Fig. 7: Spectral Reflectance for BeS Films prepared at 300k.

The variation of n and k with $h\nu$ for sample of BeS are shown in Fig 8. n and k show peaks around 12.2534×10^{-3} and 2.4638 respectively which is at the same photon energy. The maximum n and k values which occurred at the photon energy is in agreement with

the findings of Greenaway and Harbecke (1969), 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. At the lower energies, n decrease with increasing wavelength while k decreases to a minimum around 9.9236×10^{-3} and increases slightly with increasing wavelength. At the high energies, n and k decreases with decreasing wavelength.

A plot of $1/(n^2-1)$ against $1/\lambda^2$ for a sample of BeS is shown in Fig. 9.

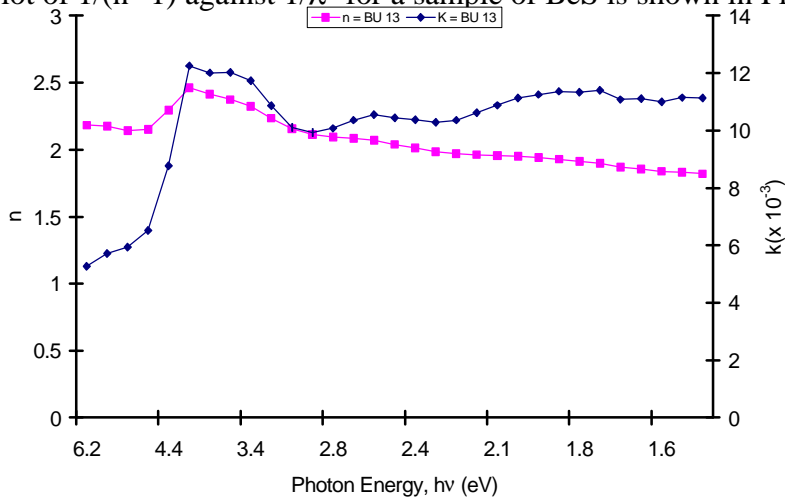


Fig. 8: Plots of Refractive Index n and Extinction Coefficient k against Photon Energy for BeS Film prepared at 300k.

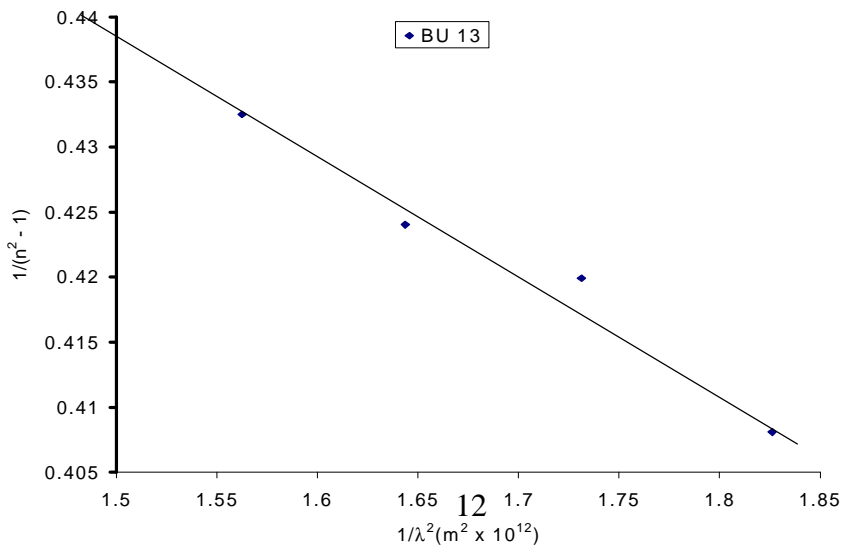


Fig. 9: Plot of $1/(n^2 - 1)$ against $1/\lambda^2$ for BeS Sample in the region of near

The value obtained for the intercept at $1/\lambda^2=0$ is 1.8150 which is called a high frequency dielectric constant n_o .

A plot of optical conductivity σ_o against $h\nu$ is shown in Fig. 10.

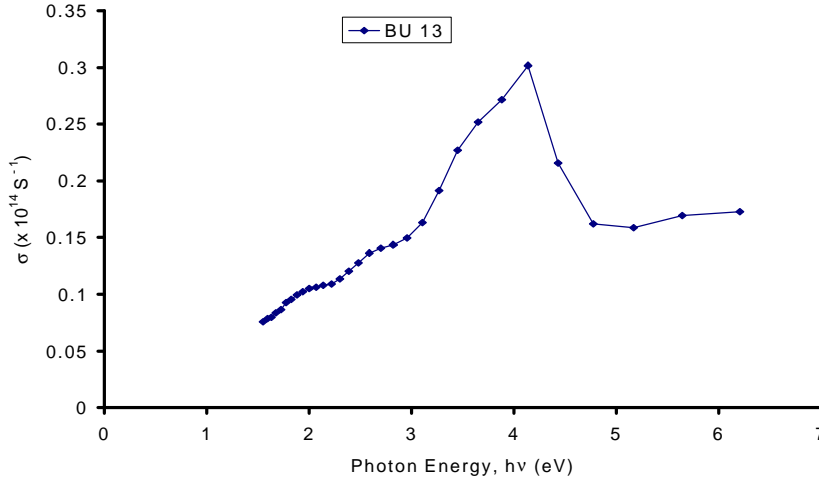


Fig. 10: Plot of Optical Conductivity, σ against Photon Energy for BeS Film prepared at 300k.

It has a peak value of $0.3019 \times 10^{14} \text{ S}^{-1}$ at 4.1367eV a minimum value at $0.0760 \times 10^{14} \text{ S}^{-1}$ at 1.5513eV. It has a maximum value of $104.118 \Omega^{-1} \text{ m}^{-1}$ at 2.5854eV and a minimum value of $39.9562 \Omega^{-1} \text{ m}^{-1}$ at 2.2981eV.

Table 2 is the average optical properties and thickness of BeS films prepared at 300k.

Table 2: average optical properties and thickness of BeS films

| Samp. No | Dep. Time (hr) | pH | Aver. $\alpha \times 10^6 \text{ m}^{-2}$ | Aver. n | Aver. k $\times 10^{-3}$ | Aver. $\sigma_o \times 10^{14} \text{ S}^{-1}$ | Aver. t (μm) |
|------------------|----------------|------|---|---------|--------------------------|--|---------------------------|
| BU ₂ | 24 | 11.3 | 0.0832 | 1.510 | 2.7929 | 0.0320 | 0.085 |
| BU ₃ | 24 | 13.3 | 0.1338 | 1.692 | 4.9082 | 0.0553 | 0.070 |
| BU ₄ | 24 | 13.6 | 0.1640 | 1.754 | 5.3112 | 0.0746 | 0.080 |
| BU ₅ | 24 | 13.7 | 0.1835 | 1.832 | 6.6720 | 0.0823 | 0.068 |
| BU ₁₃ | 18 | 11.3 | 0.2832 | 2.066 | 10.228 | 0.1433 | 0.095 |
| D ₃ | 23 | 3.95 | 0.0758 | 1.488 | 3.0743 | 0.0283 | 0.083 |

The plots of ϵ_r and ϵ_i against $h\nu$ is displayed in fig. 11. ϵ_r and ϵ_i show peaks around 6.0701 and 60.380×10^{-3} . At the low energies both ϵ_r and ϵ_i decrease with increasing wavelength while at the high energies they decrease with decreasing wavelength.

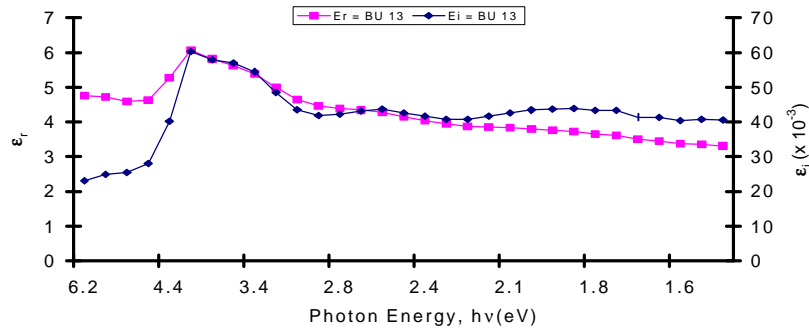


Fig.11: Plots of Real ϵ_r and Imaginary ϵ_i parts of Dielectric Constant against Photon Energy for BeS prepared at 300k.

The optical absorption coefficient α is plotted against $h\nu$ in Fig.12.

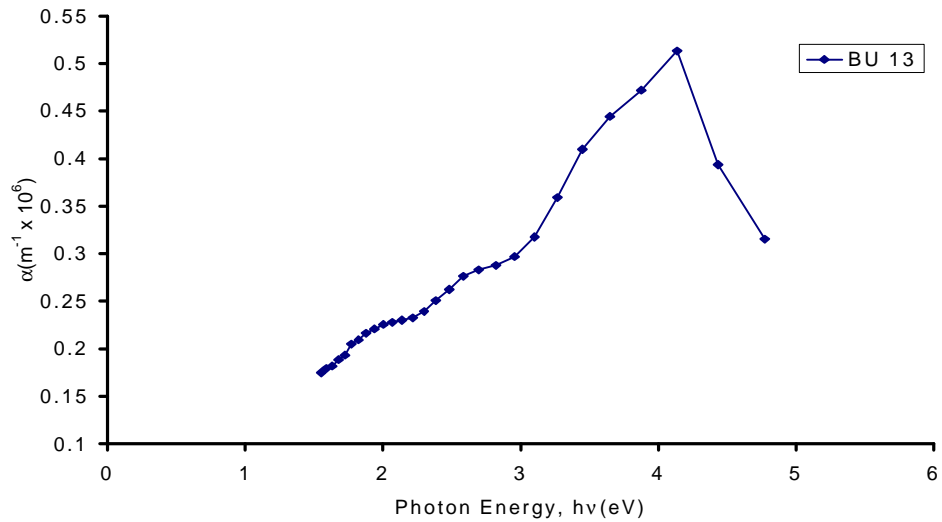


Fig. 12: Plots of Absorption Coefficient α against Photon Energy for BeS Films prepared at 300k.

It has a peak around $0.5135 \times 10^6 \text{m}^{-1}$ and a minimum value of $0.1750 \times 10^6 \text{m}^{-1}$ at 1.5513eV . It shows a straight line around absorption edge. The plots of α^2 against $h\nu$ for BeS films are shown in Fig. 13-14. These reveals band gap range 2.50 and 3.50eV with optimum value of 3.50eV .

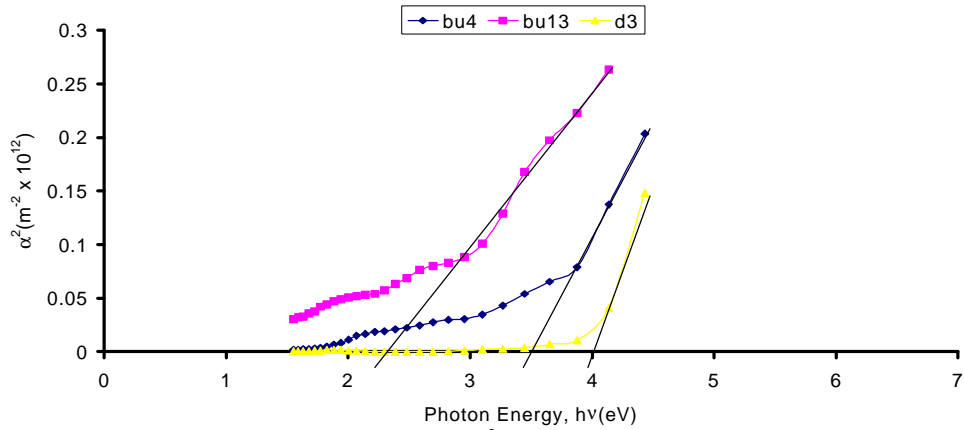


Fig. 13: Plot of α^2 against $h\nu$ for BeS Samples.

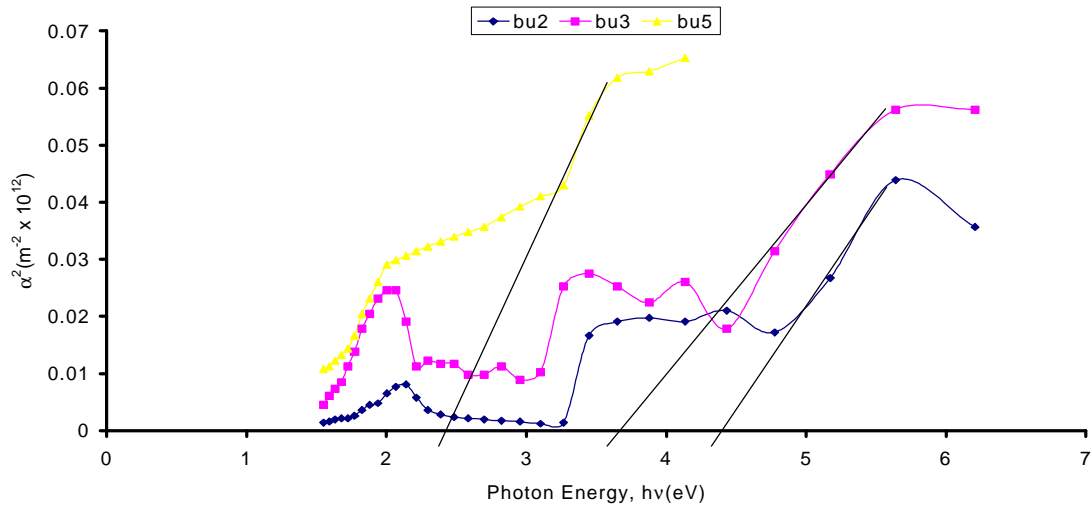


Fig. 14: Plot of α^2 against $h\nu$ for BeS Samples.

Table 3 is the summary of the average solid state properties with thickness for BeS films prepared at 300K.

Table 34: average solid state properties and thickness for bes film

| Samp. No | Dep. Time (hr) | pH | Aver. α $\times 10^6 \text{m}^{-2}$ | Band Gap (eV) | Aver. ϵ_r | Aver. ϵ_i ($\times 10^{-3}$) | t(μm) |
|------------------|----------------|------|--|---------------|--------------------|---|--------------------|
| BU ₂ | 24 | 11.3 | 0.0832 | 4.40 | 2.3100 | 8.6281 | 0.085 |
| BU ₃ | 24 | 13.3 | 0.1338 | 3.60 | 2.8776 | 16.625 | 0.070 |
| BU ₄ | 24 | 13.6 | 0.1640 | 3.50 | 3.1459 | 19.367 | 0.080 |
| BU ₅ | 24 | 13.7 | 0.1835 | 2.40 | 3.3816 | 24.436 | 0.068 |
| BU ₁₃ | 18 | 11.3 | 0.2832 | 2.30 | 4.2999 | 42.169 | 0.095 |
| D ₃ | 23 | 3.95 | 0.0758 | 4.00 | 2.2331 | 9.5220 | 0.083 |

CONCLUSION

BeS thin film with thickness ranging between 0.068 and 0.095 μm with energy band gap between 2.30 and 4.40eV has been successfully deposited in alkaline medium using chemical bath deposition technique. The EDXRF showed that the film contain sulphide peaks while FTIR spectroscopy showed the bonding peaks and the percentage transmittance that ranged between 4 and 42% in the far infrared regions. The deductions from the spectrophotometers showed that average values n ranged from 1.45 and 2.07, k ranged between 2.79×10^{-3} and 10.23×10^{-3} , and σ_0 ranges from $0.028 \times 10^{14} \text{S}^{-1}$ and $0.143 \times 10^{14} \text{S}^{-1}$. Some of the films were found to have high transmittance in the range between 82 and 100% in the UV-VIS-NIR regions; hence, they could be effective as thermal control window coatings for cold climates and antireflection coatings.

REFERENCES

- Choi J.Y., K.J. Kim, J.B. Yoo and D. Kim (1998), Properties of Cadmium Sulphide Films Deposited by Chemical Bath Deposition with ultrasonication, *Solar Energy* 64 (1-3), 41.
- Conley, R.T. (1966), *Infrared spectroscopy*, Allyn and bacon Inc, Boston.
- Eze, F.C. and C.E. Okeke (1997), "Chemical Bath Deposited Cobalt Sulphide Films; Preparation Effects", *Materials Chemistry and Physics* 47, 31
- Ezema, F.I. (2000), *Solution Growth and Characterization of Binary and Ternary Halide and Chalcogenide Thin Films for Industrial and Solar Energy Applications*, Ph.D Thesis, Department of Physics/Astronomy, University of Nigeria, Nsukka.
- Greenway, D.L. and G. Harbeke (1969), *Optical properties and band structures of Semiconductors*, pergamon, New York.
- Janai, M., D.D. Alfred, D.C. Booth and B.O. Seraphin (1979), *Optical Properties and Structures of Amorphous Silicon Films Prepared by CVD*, *Sol. Ener. Mater.* 1, 11.
- Nair, P.K. and M.T.S. Nair (1992), "Chemically Deposited Zinc Thin Films: Applications as substrates for Chemically Deposited Bi_2S_3 , Cu_xS and PbS Thin Films", *Semicond. Sci. Technol.* 7, 239.
- Nair, P.K., M. Ocampo, A. Fernandez and M.T.S. Nair (1990), "Solar Control Characteristics of Chemically Deposited PbS Films for Solar Control Applications", *Sol. Ener. Mater.* 20, 235.
- Ndukwe, I.C. (1996), "Solution Growth, Characterization and Applications of Zinc Sulphide Thin Films", *Sol. Ener. Mater. Sol. Cells* 40, 123.
- Ortega – Borges R., and D. Lincot (1993), "Chemical Deposition of Cadmium Sulphide Thin Films in the Ammonia Thiourea System", *J. Electrochem. Soc.* 140,3464.
- Pankove, J.I. (1971), *Optical processes in semiconductors*, Prentice-Hall, New York.
- Sabestian, P.J. and H. Hu, (1994), "Identification of the Impurity Phase in Chemically Deposited CdS Thin Films", *Adv. Mater. Opt. Electron.* 4, 407.
- Szafran, Z.N., R.M. Pike, and M.M. Sigh (1991), *Microscale inorganic Chemistry, A Comprehensive Laboratory Experience*, John Wiley and Sons Inc. New York.
- Theye, M. (1985), In "Optical Properties of Thin Films", K.L. Chaopra and L.K. Malhota, eds, *thin film technology and Applications*, Tata McGraw-Hill, New Delhi.

Technical College - Bourgas,
All rights reserved, © March, 2000