COMPARATIVE STUDY OF SOLUTION GROWN STRONTIUM FLUORIDE (SrF_2) AND BERYLLIUM IODIDE (BeI_2) THIN FILMS AND THEIR POSSIBLE APPLICATIONS

P. A. Ilenikhena
Department of Physics,
University of Benin, Benin City, Nigeria

ABSTRACT
Semi conducting halide thin films of strontium fluoride (SrF_2) and berylium iodide (BeI_2) were successfully deposited on glass slides at 320K and pH of 8, 9, 10 and 12 using solution growth technique. A complexing agent, ethylenediamine-tetra acetate (EDTA), with pH opposed that of bath constitutions, was used to bath reagents to enhance control and stabilize the deposition pH at different values suitable for film growth. X-ray diffraction method was used to confirm the depositions. Electron micrographs of the films reveal uniform surface depositions. Absorbance (A) spectra data were measured by a single beam spectrophotometer (Pharmacia LKB Biochrom 4060) at wavelength range 200nm to 900nm. Other optical and solid state properties were calculated from the data and compared with other deposited thin films. The average optical and solid state properties of strontium fluoride thin films include absorbance ranging from 0.034 to 0.086, transmittance 0.820 to 0.925, refractive index 1.51 to 1.88, electrical conductivity 0.40 to 0.49$(ohm\text{-}cm)^{-1}$, film thickness 0.013 to 0.074μm and band gap 2.65 to 2.75 ± 0.05eV. For berylium iodide films the absorbance ranges from 0.204 to 0.302, transmittance 0.499 to 0.625, refractive index 2.41 to 2.61, electrical conductivity 0.62 to 0.68$(ohm\text{-}cm)^{-1}$, film thickness 0.202 to 0.362μm and band gap 2.20 to 2.75 ± 0.05eV. Films with refractive index lower than 1.9 could be employed in antireflection coatings, eyeglass coating and solar thermal control coatings. Those with refractive index greater than 1.9, could be useful in construction of poultry houses, solar cells and anti dazzling coatings.

Keywords: *Comparative study, solution growth, halide thin films, possible applications*

INTRODUCTION
Solution growth technique (SGT) is a simple and cheap method of depositing high quality compound semiconductor thin films (Chandra et al; 1980, Campe et al; 1985, Ilenikhena and Okeke, 2001; 2002, Osuji, 2003). Films produced by this technique have comparable structural and optoelectric properties to those produced using other sophisticated thin film deposition tech-

niques such as chemical vapour deposition and sputtering. The method has added advantages of depositing films on large surface area of both metallic and non-metallic substrates. The technique has also been applied in producing emerging materials for solar cells, protective coating and solar thermal controls in buildings. It is now being adopted by some industries (Ilenikhena and Okeke, 2001 and 2002, Ezema and Okeke, 2003, Osuji, 2003). The deposition technique could be improved to overcome the initial tedious and wasteful combinations of bath constitutions to obtain suitable deposition pH values by adding another complexing agent with pH opposed to that of bath constituents to the bath reagents to enhance control and stabilize the deposition pH at different suitable values for film deposition (Ilenikhena and Okeke, 2005).

Not much work has been done on the preparation of metal halide films using various deposition techniques. The deposition of magnesium fluoride was reported by Chopra and Das (1983). Okujagu and Okeke (1997) produced metal halide thin films using solution growth technique. Ilenikhena and Okeke (2001, 2002) produced strontium iodide and beryllium fluoride thin films using chemical bath deposition and solution growth techniques respectively.

This paper reports the deposition of high quality semi conducting thin films of strontium fluoride (SrF_2) and berylium iodide (BeI_2) on glass substrates using solution growth technique at 320K and at pH of 8, 9, 10 and 12 for 3hours. Ethylenediamine-tetra acetate (EDTA), a complexing agent with pH opposed to that of bath constitutions, was added to bath reagents to enhance control and stabilize the deposition pH at different values suitable for film growth. The optical and solid-state properties of the films were calculated and compared with other deposited films. Possible applications of the films are also discussed.

EXPERIMENTAL DETAILS

The deposition of strontium fluoride (SrF_2) and berylium iodide (BeI_2) thin films on glass substrates were successfully carried out using solution growth technique at temperature of 320K and pH of 8, 9, 10 and 12. The glass substrates were cleaned by degreasing them in concentrated nitric acid (HNO_3) for 3 days, thoroughly washed in detergent solution, rinsed in distilled water and dried in air. The cleaned glass surfaces provided nucleation centres for growth, good adhesion and uniform deposition of the films. Reaction baths were 50ml glass beakers containing different molar solutions and volumes of deposition bath constituents. The bath constituents for the deposition of strontium iodide thin films were strontium nirate [$Sr(NO_3)_2$] as source of strontium ions (Sr^{2+}), sodium fluoride (NaF) as a source of fluoride ions (F^-), sodium hydroxide (NaOH) as complexing agent while ethylenediaminetretra acetate (EDTA) (another complexing agent) was used to vary pH values of the deposition solutions. Distilled water was added to raise the volume of the bath solutions to a certain level. For the deposition of berylium iodide thin films, berylium nitrate - 4 - water [$Be(NO_3)_2 . 4H_2O$] was used to replace strontium nitrate [$Sr(NO_3)_2$] in a similar reaction bath. Details of bath constituents for the preparation of the metal halide (YX) thin films are shown in table 1.

Table 1: Bath constituents for preparation of SrF_2 and BeI_2 thin films

Initial Bath pH	0.3M $Y(NO)_3 . 4H_2O)^r$ Vol. (ml)	2.5M NaOH Vol. (ml)	0.8M ZX VoL. ml	H_2O Vol (ml)	0.2M EDTA Vol (ml)
8	8	3	8	21	15
9	8	4	8	20	14
10	7	4	9	20	13
12	6	5	10	19	10

The symbols Y = Sr and r = O for $Sr(NO_3)_2$ and Y = Be and r = 1 for $Be(NO_3)_2 . 4H_2O$, Z = Na and X = F for NaF; Z = K and X = I for KI

The symbol Y represents Sr and Be while X represents F and I in the deposition of SrF_2 and BeI_2 respectively. The complexing agent sodium hydroxide (NaOH) formed complex ions with

Y^{2+}. It slowly released Y^{2+}, ensured ion by ion condensation of Y^{2+} and X^-, controlled the growth rate of the deposited thin films and eliminated spontaneous precipitation of the chemical reagents in the bath. The solution baths were stirred with a glass rod and their initial pH values noted. The baths were placed in a hot water bath that was maintained at a steady temperature of 320K by a Stuart magnetic stirrer hot plot. A cleaned glass slide was suspended in each reaction bath for 3 hours. After deposition time, the coated glass slides were rinsed with distilled water and dried in air. Pretest runs were carried out to determine the optimum deposition parameters such as deposition time, pH and volumes of bath constituents. The most probable reaction equation for the deposition of SrF_2 thin films is $Sr(NO_3)_2 + 2NaOH + 2NaF \rightarrow SrI_2^{--} + 2NaOH + 2NaNO_3$.

The basic reaction equation for deposition of BeI_2 thin films is

$Be(NO_3)_2 . 4H_2O + 2NaOH + 2KI \rightarrow BeI_2^{--} 2NaOH + 2KNO_3 + 4H_2O$

A computerized single beam spectrophotometer (Pharmacia LKB Biochrom 4060) was used to obtain the absorbance spectra data of deposited thin films in the ultraviolet -visible - near infrared (UV - VIS - NIR) regions at wavelength range of 200nm to 900nm. The reference and coated glass slides were mounted on a rotating holder at the reference and sample compartments respectively and scanned to obtain the absorbance spectra data. Other optical and solid-state properties were obtained from the spectra data by calculations based on the theory. Structural characterization of the films was determined with x- ray diffraction technique using Diano cooperation x-ray diffractometry (model XRD 2100E*) using copper target (CuKa) with wavelength 1.540502 Å, current 30mA and voltage 45 kV. The surface microstructure of the films was viewed using electron microscope at magnification 100x.

RESULTS AND ANALYSIS

The absorbance spectra data obtained for the deposited strontium fluoride (SrF_2) and berylium iodide (BeI_2) thin films were used to determine other optical and solid state properties based on existing theory. The spectra absorbances are displayed in figures 1 and 2 for strontium fluoride (SrF_2) and berylium iodide (BeI_2) respectively.

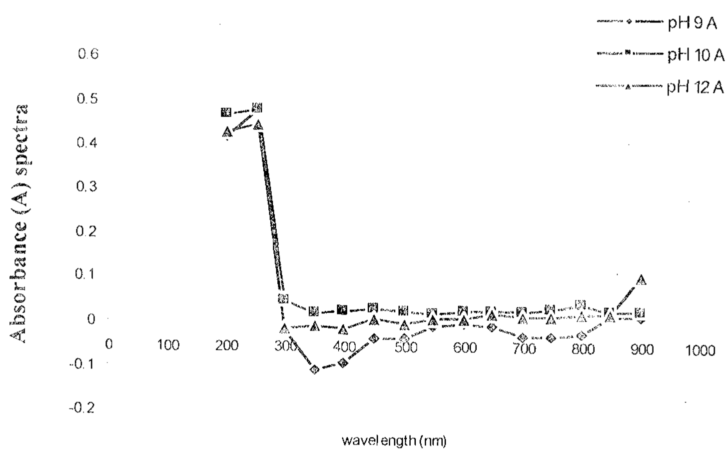

Fig. 1: Absorbance (A) spectra for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

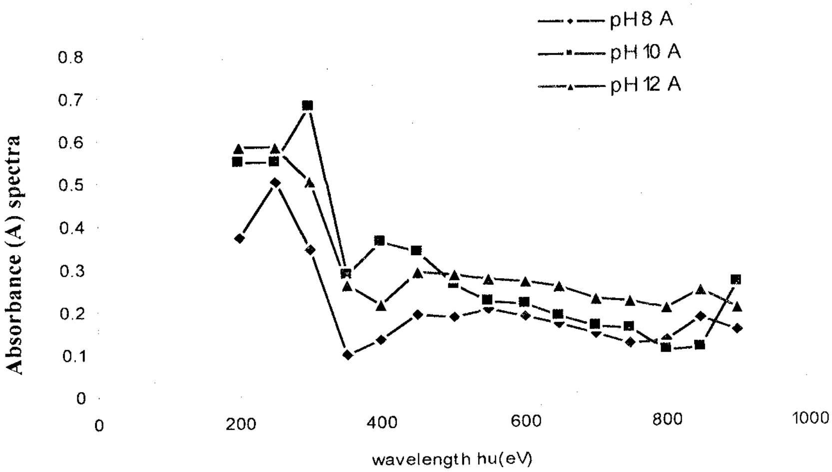

Fig. 2: Absorbance (A) spectra for BeI_2 thin films produced at 320k and pH of 8, 10 and 12

Figure 1 shows that strontium fluoride (SrF_2) thin films have high absorbance for wavelengths lower than 300nm and low absorbance for wavelength range 350 – 850nm.

The strontium fluoride thin film produced at pH of 9 has negative absorbance at wavelength range of 300nm to 800nm. Similarly, the thin film produced at pH of 12 has negative absorbance at 300nm to 500nm. The film has a minimum absorbance of -0.108 at wavelength of 350nm at pH of 9. The film produced at pH 10 has positive absorbance. Fig 2 shows that berylium iodide thin films have a high absorbance in the ultraviolet, visible and near infrared regions of electromagnetic regions. This high absorbance could be used in production of p-n junction of solar cells (Osuji, 2003) for photovoltaic generation of electricity. The transmittance (T) and reflectance (R) spectra of strontium fluoride and beryllium iodide thin films are shown in fig, 3 and 4 respectively.

Both thin films have low transmittance for wavelengths lower than 300nm and high transmittance for wavelength range 350nm to 850nm. For strontium fluoride thin films in figure 3, the transmittance varies from 0.333 to 0.384 for wavelength lower than 300nm and from 0.912 to 1.282 for wavelength range 350 to 850nm. Film produced at pH of 9 has the highest transmittance. For berylium iodide thin films in figure 4, the transmittance varies from 0.263 to 0.429 for wavelength lower than 300nm and from 0.440 to 1.798 for wavelength range 300nm to 850nm. Figures 3 and 4 also show the reflectance of the deposited strontium fluoride (SrF_2) and beryllium iodide (BeI_2) thin films. Strontium fluoride (SrF_2) thin films exhibited high reflectance (R) of 0.190 to 0.200 for wavelengths lower than 300nm and low reflectance of -0.174 to 0.048 for wave length range 350 to 850nm. The film with negative absorbance also exhibited negative reflectance. The BeI_2 thin films have high reflectance of 0.157 to 0.203 for wavelengths lower than 300nm and reflectance of 0.104 to 0.203 for wavelengths range from 350 to 850nm. The high transmittance and low reflectance characteristics exhibited strontium fluoride thin films produced

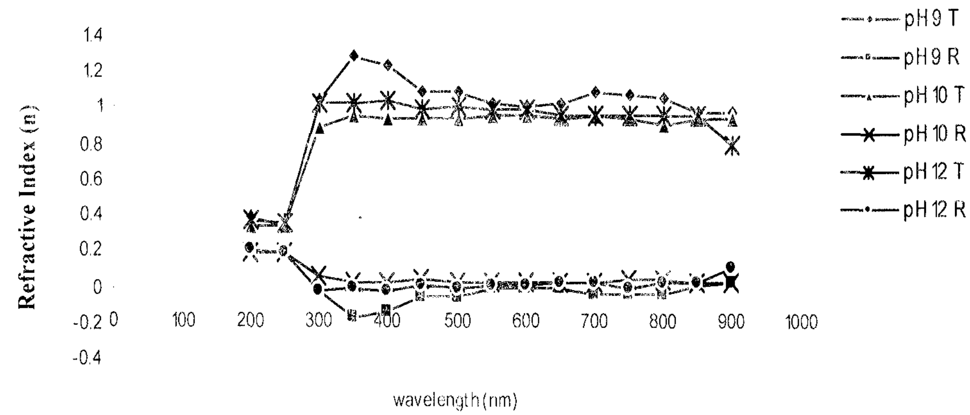

Fig. 3: Transmittance (T) Reflectance ® for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

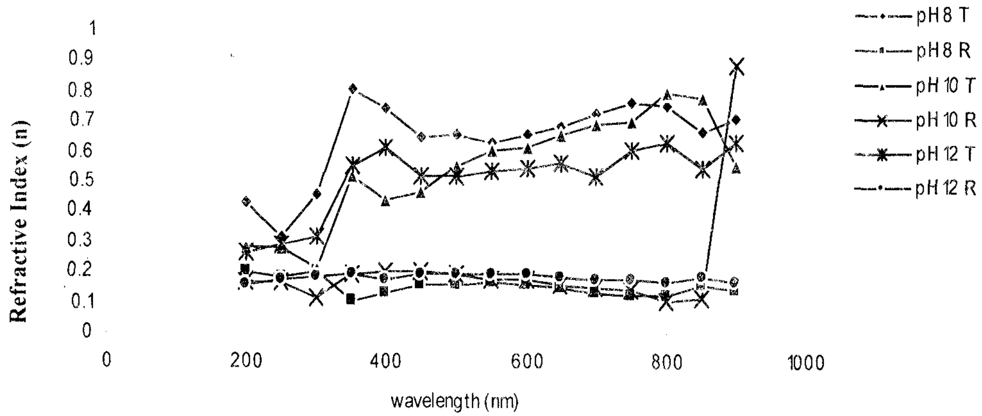

Fig. 4: Transmittance (T) Reflectance ® spectra for BeI_2 thin films produced at 320K and pH of 8, 10 and 12

at pH of 9 and 12 could be employed in antireflection coatings for solar thermal devices and eye glass coatings to reduce solar reflectance, increase the transmittance and improve their efficiencies. The high transmittance and low reflectance properties of strontium fluoride thin films produced at pH of 10 in the visible and near infrared regions are desirable characteristics for ideal solar control glazing to avoid glare problems (Nair *et al*, 1989) and could be employed in solar thermal control coatings. The thin films of beryllium iodide with relatively lower transmittance and higher reflectance could be useful in construction of poultry houses to allow enough infrared radiation to warm the very young chicks (a day to about 5 weeks old)

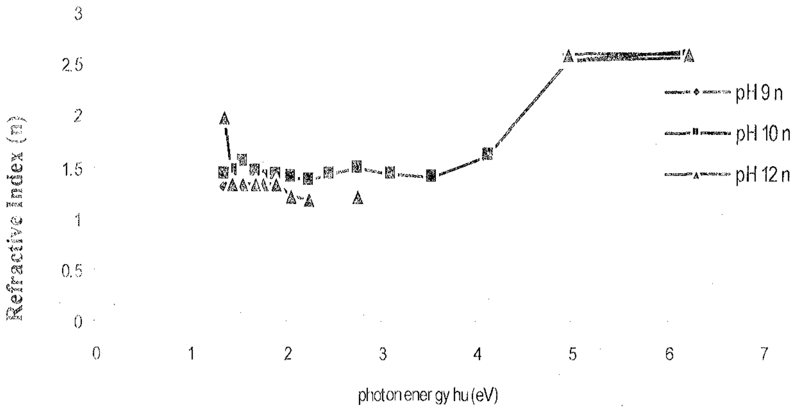

Fig. 5: Variation of refractive index (n) against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

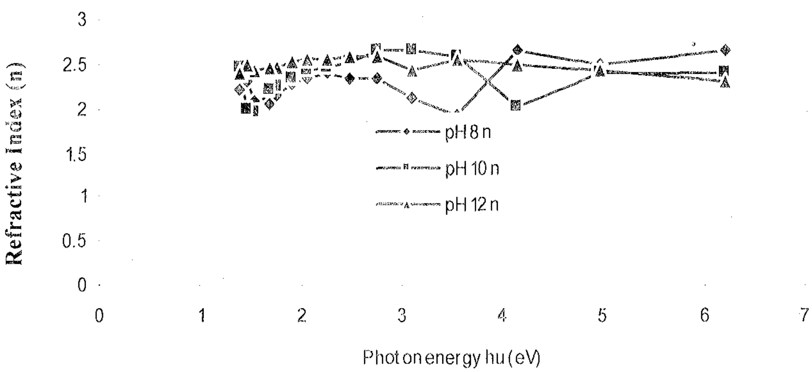

Fig. 6: Variation of refractive index (n) against photon energy for BeI_2 films product at 320K and pH of 8, 10 and 12

which have little or no insulating feather during the day. This could also reduce the cost of energy consumption through the use of stoves, heaters, electric bulbs, etc and the hazards associated with them while at the same time protecting the chicks from ultraviolet radiation. The application of solar energy as a source of heat in chick breeding is environmentally acceptable and promotes sustainable development (Oladipo, 1999). Solar energy technologies are also applicable to egg incubation and to the drying of chicken manure (Okonkwo *et al*, 1992). These films could also be used in photocells (Osuji, 2003), thin films solar cells (Markvart, 2000) and in anti dazzling coatings for car windscreens and driving mirrors to reduce the dazzling effects of light at night. The variation of refractive index (n) with photon energy for SrF_2 and BeI_2 thin films are shown in figures 5 and 6 respectively.

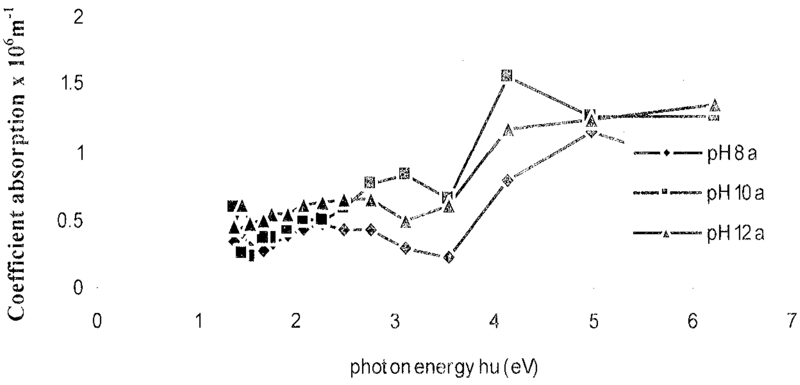

Fig. 8: Variation of coefficient of absorption against photon energy for BeI_2 thin films produced at 320K and pH of 8, 10 and 12

The magnitude of the coefficient of absorption $\alpha = 10^6$ m^{-1} is within the α range 10^6 to 10^7 m^{-1} for semi-conductor thin films suitable for polycrystalline thin film solar cell (Meakin, 1989). The coefficient of absorption method is the simplest and perhaps the most direct method of determining the band gap of semiconductors. Values of band gap for the deposited strontium fluoride thin films vary from 2.65 to 2.75eV. For the beryllium iodide thin films, the band gap varies from 2.20 to 2.75eV. These values compare well with the values 2.34 and 2.50eV for strontium iodide and 2.22 to 2.66eV for beryllium fluoride thin films (Ilenikhena and Okeke, 2001; 2002) and could be used in solar cells. Both films have good photo response with average optical conductivity (σ_o) of 10^{13}s^{-1}. The magnitude of average electrical conductivities of both thin films is 10^{-1} (ohm-cm)$^{-1}$ within the electrical conductivity range 10^{-12} to 10^2 (ohm – cm)$^{-1}$ for semiconductors (Paushkin et al, 1974; Phol, 1962 and Webber et al 1974). The thickness of SrF_2 thin films varies 0.013 to 0.074μm. For BeI_2 thin films, the thickness vary from 0.202 to 0.362μm. Other properties include extinction coefficient (k), real dielectric constant ($\hat{I}_r$) and imaginary dielectric constant ($\hat{I}_i$). Average optical and solid-state properties at wavelength of 550nm for SrF_2 and BeI_2 thin films are shown in tables 2 and 3 respectively.

Table 2: Average optical and solid-state properties for strontium fluoride thin films

pH	T	n	k x10^{-2}	α x 10^6 (m^{-1})	$\hat{I}_r$	S_o x 10^{13} (s^{-1})	σ_e (ohm-cm)$^{-1}$	t (μm)	E_g ± 0.05 (eV)
9	0.925	1.51	0.34	0.078	2.28	0.28	0.40	0.074	2.75
10	0.820	1.88	0.87	0.198	3.54	0.89	0.49	0.013	2.65
12	0.855	1.77	0.69	0.157	3.12	0.62	0.46	0,023	2.70

Table 3: Average optical and solid-state properties for berylium iodide thin films

pH	T	n	k x 10^{-2}	α x 10^{6} (m^{-1})	$\hat{I}_r$	S_o x 10^{13} (s^{-1})	σ_o $(ohm\text{-}cm)^{-1}$	t (μm)	E_g ±0.05 (eV)
8	0.625	2.41	2.06	0.470	5.80	2.70	0.63	0.202	2.20
10	0.509	2.60	2.96	0.675	6.77	4.19	0.68	0.347	2.60
12	0.499	2.61	2.77	0.695	6.82	3.94	0.62	0.362	2.75

The x-ray diffraction patterns of the uncoated glass and deposited strontium fluoride (SrF_2) thin film on glass are shown in Figure 9. Figure 10 shows electromicrograph of (SrF_2) films at a magnification of 100x. The diffraction patterns reveal diffraction peaks at some 2 – theta (2q) values. Similarly, X-ray diffraction patterns of the uncoated glass and deposited beryllium iodide (BeI_2) thin films on glass shown in figure 11 reveal diffraction peaks at some 2-theta (2q) values. Electronmicrographs of the beryllium iodide (BeI_2) thin films at magnification of 100x are shown in Fig.12.

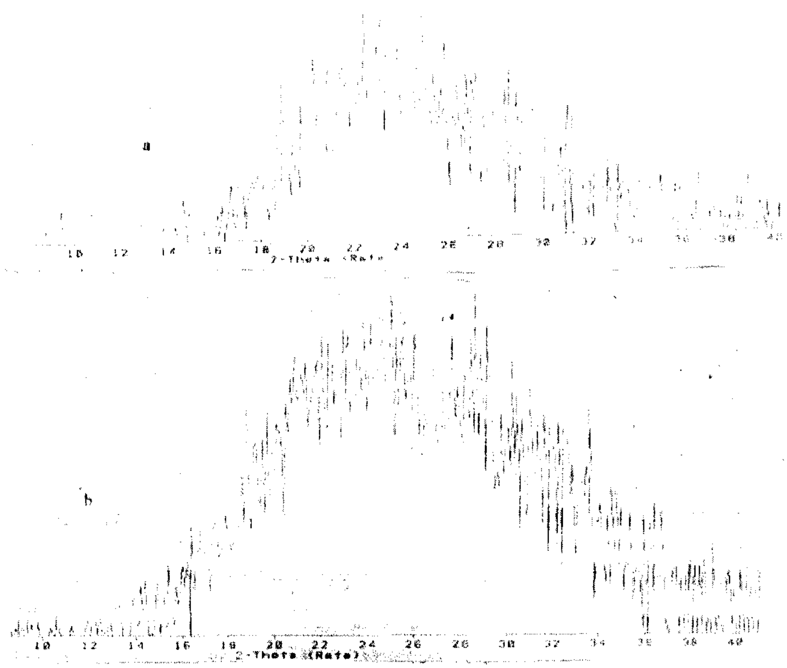

Fig. 9: X-ray diffraction results for (a) uncoated glass slide and (b) SrF_2 thin films at 320K.

Fig. 10: Electron micrograph of SrF_2 thin films at 320K.

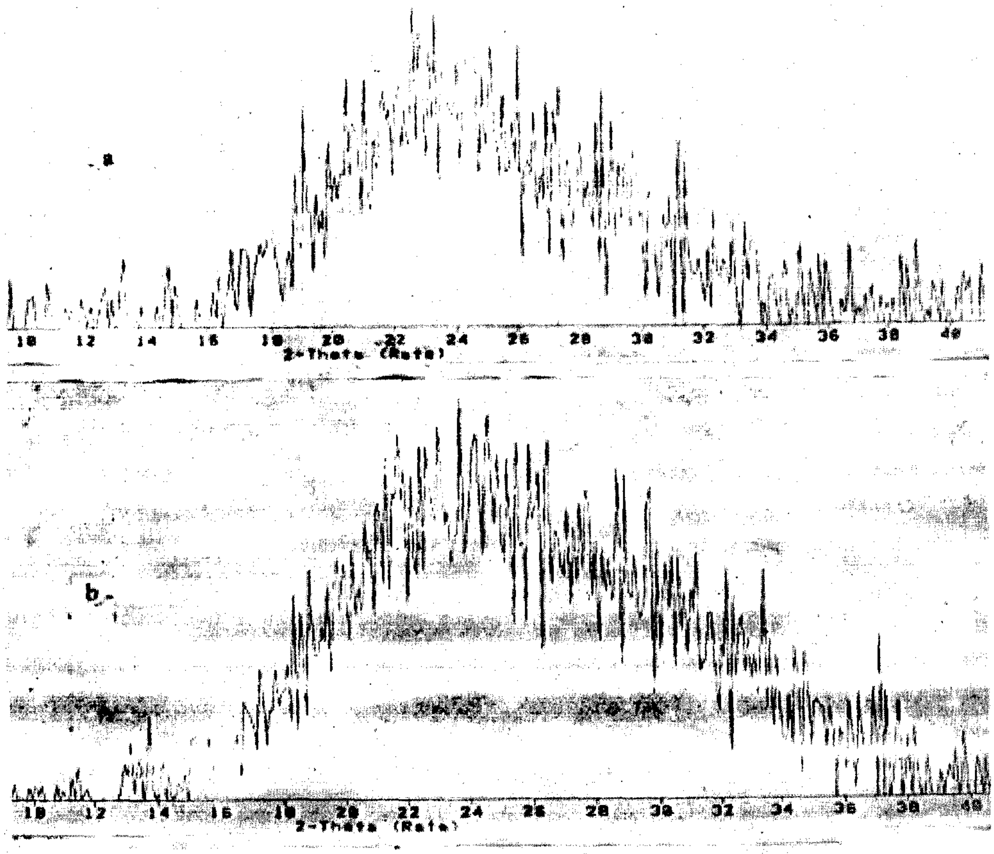

Fig. 11: X-ray diffraction results for (a) uncoated glass slide and (b) BeI_2 thin films produced at 320K.

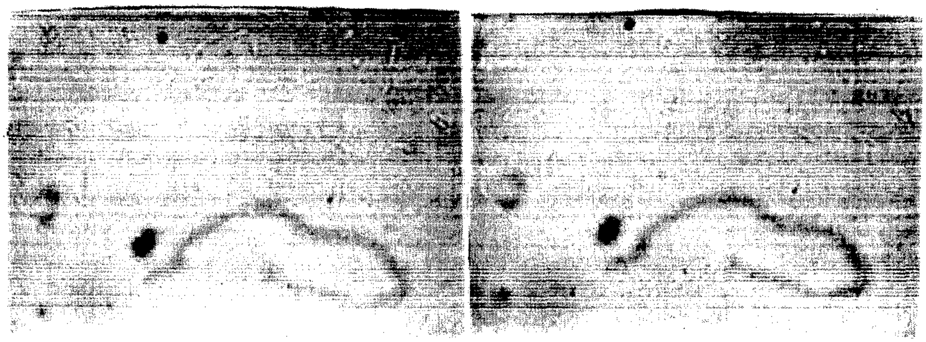

Fig. 12: Electron micrograph of BeI_2 thin films produced at 320K.

CONCLUSION

Semi conducting thin films of strontium fluoride (SrF_2) and berylium iodide (BeI_2) were successfully deposited on glass substrates at 320K and pH values of 8, 9, 10 and 12 by solution growth technique. A complexing agent, ethylenediamine-tetra acetate (EDTA), with pH opposed to that of deposited bath constitutions was used to enhance control and stabilize the deposition pH at different values suitable for film growth. X-ray diffraction method was used to confirm the depositions. A single beam spectrophotometer (Pharmacia LKB Bichrom 4060) was used to obtain the spectra absorbance data. Other optical and solid-state properties of the films were obtained by calculations based on existing theory. These properties include transmittance, refractive index, extinction coefficient, optical conductivity, electrical conductivity, film thickness, coefficient of absorption, energy gap, etc. The films with refractive index lower than 1.9 could be used in antireflection coatings, eyeglass coatings and solar thermal control coatings. Those with refractive index greater than 1.9 could be useful in poultry production, antidazzling coatings and solar cells.

REFERENCES

Brinker, C.J. and Harringston, M.S. (1981). Sol-Gr Derived Antireflection Coatings for Solicon. *Solar Energy Materials*, 52, 159.

Campe, H.V., Hewig, G.H., Hoffman, W. Huschka, H., Schlurick, D. and Worner, J., (1985). 6th E.C. Photovoltaic Solar Energy Conf., 778.

Chandra, S., Pandey, R.K. and Agrawal, R.C., (1980). *Jour. Phys. D. Appl. Phys.*13. (9), 1757 - 1960.

Chopra, K.L. and Das, S.R., (1983). Thin film Solar Cells. New York: Plenum Press; Chaps. 2 and 5.

Ezema, F.I. and Okeke, C.E., (2003). Fabrication and Characteristization of Palladium Sulphide (PdS) Thin Films for Solar Energy Applications using Solution Growth Technique. *Nig. Jour. of Solar Energy*, 14, 66 -72.

Ilenikhena, P.A. and Okeke, C.E., (2001). Chemical Bath Deposition and Characterization of Strontium Iodide (SrI_2) Thin Films and Their Possible Applications. *Nig. Jour. Phys. Mathematical Sciences, 1*, (1), 51-58.

Ilenikhena, P.A. and Okeke, C.E, (2002). Solution Growth, Characterization and Possible

Applications of Berylium Fluoride Thin Films Deposited at 320K and pH of 7-12. *Nigerian Jour. of Pure and Applied Phys.* 2, (1), 21-27.

Ilenikhena, P.A. and Okeke, C.E. (2005). Comparative Studies of Cobalt Oxide (CoO) and Copper Oxide (CuO) Thin Films Deposited by Improved Electroless Chemical Bath Technique at 320K. *Jour. of the Nigerian* Association of Mathematical Physics, 9, 519-528.

Markvart, T. (Ed.), (2000). Solar Electricity, UNESCO Engineering Series, New York:John Wiley and Sons Ltd, 3, 21-71.

Meakin, J.D., (1989). Polycrystalline Thin Fill Solar Cells, Furlain, G., Nobili, D., Sayigh, A.M. and Seraphin, B.O. (Eds.), Workshop on Materials Science and Physics of Non Conventional Energy Sources, Singapore: World Scientific Pub. Co. Ptc; Ltd.

Nair, P.K., Nair, M.T.S., Femaardex, A and Ocampo, M. (1989). *J. Physis. D Appl. Phys.* 22, 829.

Okonkwo, W.I., Anazodo, U.C.N., Echiogu, E.A., Akubuo, C.O. and Iloeje, O.C. (1992). The Passive Solar Poultry Chick Brooder - Further Improvement and Preliminary Testing, *Nig. Jour. of Solar Energy*, 11, 32 - 40.

Okujagu, C.U. and Okeke, C. E. (1997). Growth Characteristics of Chemically Deposited Halide Thin Films, *Nig. Jour. of Renewable Energy*, 5 (1, 2), 125 – 130.

Oladipo, E. (1999). Energy Efficiency for Sustainable Development. National Workshop on Energy Conservation in Commercial/ Institutional Buildings, the Nigerian Society of Engineers and Energy Commission of Nigeria, Lagos.

Osuji, R.U., (2003). Analysis of Chemically Deposited CdSe and CdS Thin Films, *Nig. Jour. of Solar Energy* 14, 90 - 99.

Paushkin, Ya. M. Vishnyakova, T.P., Lunin, A.F. and Nizova, S.A. (1974). Organic Polymeric Semiconductors, New York: John Wiley and Sons Inc.,

Petit, R.B. and Brinker C.J. (1986). Use of Sol. – Gr. Thin Films in Solar Energy Applications, *Solar Energy Materials*. 14 and 269.

Pohl, H.A. (1962). Modern Aspects of Vitreous State, Semiconductor in Polymers, 2. London: Butterworths, 72.

Webber, R.L., Muning, K.V., White, M.W. and Weygand G.A. (1974). College Physics. USA: Mc Graw-Hill Book Company Inc. , 641.