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SOLUTION GROWTH, CHARACTERIZATION AND POSSIBLE APPLICATIONS OF BERYLLIUM FLUORIDE (BeF_2) THIN FILMS DEPOSITED AT 320K AND AT pH of 7 - 12

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Abstract. Solution growth technique (SGT) was successfully used to deposit good quality BeF_2 thin films on glass slides at 320K for 3 hours and at pH of 7 – 12. The bath constituents were beryllium nitrate-4-water, and sodium fluoride as starting materials, sodium hydroxide as complexing agent and ethelenediamine tetra-acetate to vary the pH values. Effects of pH and bath constitutions were also investigated. Our numerous investigations reveal that beryllium flouride thin films were produced only in alkaline medium. The deposited thin films modify the optical properties of the glass substrates at various wavelength regions. Average transmittance (T) values ranges from 0.615 – 0.904, reflectance (R) from 0.052 – 0.175, coefficient of absorption (α) (0.106 – 0.486) x10^{-4} cm^{-1} and refractive index (n) from 1.59 – 2.43. Values of solid-state properties such as bandgap (E_g) range from 2.22-2.66 eV, electrical conductivity (σ) from 0.73 – 1.26) X10^{-5} $(\Omega\text{-cm})^{-1}$ and film thickness (t) from 465 – 2140 Å. Films with refractive index (n) lower than 1.8 have high transmittance (T) and low reflectance (R) while those with refractive index (n) greater than 1.8 have low transmittance (T) and high reflectance (R). The possible applications of the deposited beryllium fluoride (BeF_2) thin films in optical, architectural, agricultural and electronics industries were also discussed.

1. INTRODUCTION

The deposition of thin films by solution growth technique (SGT) was predominantly employed in the field of commercial production of silver mirrors [1]. This technology is one of the intensively studied thin film deposition techniques for the preparation of various metal chalcogenide films [2,3,4,5,6,7,8,9]. Advantages of this technique over the conventional thin film deposition methods include low cost, convenient, reproducible and easy coating of large surfaces. The technology is based on the controlled release of the cations and anions in an aqueous solution into which the substrates are immersed [4]. Films produced by solution growth technique (SGT) are now being developed for use in solar energy and other photonic applications such as photothermal and photovoltaic conversions [10,8], energy efficient glazing including decorative and protective coatings [11,12] and in imaging techniques [13,14]. Properties of films produced by solution growth technique depends on some complex and chemical processes of bath constitutions, formation of films and on heat treatment of the films. For example, any change in the relative rates of complexation and precipitation in the bath has significant effect on the growth and structure of the films.

In this paper, we present results for the solution growth of beryllium fluoride (BeF_2) thin films at 320K for 3 hours and at pH of 7–12. These films are characterized and their possible applications discussed.

2. EXPERIMENTAL DETAILS

2.1 *Preparation of Sample*

Beryllium fluoride (BeF_2) thin films were successfully produced on glass slides by solution growth technique (SGT) at 320K for 3 hours and at pH of 7-12. The chemical baths were 50 ml glass beakers. This was achieved by optimizing the chemical bath constitutions, complexing agent and deposition time. The bath constitutions were 0.36M beryllium nirate-4-water [$Be(NO_3)_2$,$4H_2O$], 2.5M sodium hydroxide (NaOH). 0.8M sodium fluoride (NaF), 0.25M ethelenediamine-tetra acetate ($C_{10}H_{16}O_8N_2$) or EDTA solutions and distilled water H_2O). Sodium hydroxide [15,4] was employed as the complexing agent while, EDTA was used to vary the pH values of the initial bath solutions. All the reagents were of the analytical reagent (A.R.) grade. Several bath constitutions were employed by varying the volume ratio of $Be(NO_3)_2$, $4H_2O$, NaOH, NaF, H_2O and EDTA. The bath mixtures were stirred using a glass rod. The pH values of 5-12 of the initial bath solutions were determined using Kent EIL 3055 digital pH/Temperature meter. All the solution baths were arranged in an aluminum pot water bath for 3 hours at 50^0C (320K). The water bath was heated electrically at a constant rate and maintained at that temperature by means of Stuart magnetic stirred

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hot plate.

Finally, a commercial-quality glass microscope slide (76 mm x 26mm x 1mm) was suspended vertically at the centre of each of the freshly prepared bath solution from synthetic foam cover and clamped at the top with a plastic peg for chemical deposition. Prior to deposition, the glass slides were thoroughly cleaned by degreasing them in concentrated hydrochloric acid (conc. HCl) for three days, washed in detergent solution, rinsed in distilled water, drip dried in air and were weighed by means of Mettler AE166 analytical balance. After deposition, the films were rinsed in distilled water, drip dried in air and reweighed. The deposited films on glass slides were obtained in alkaline medium at pH of 7-12. The details of the deposition bath constitutions of the various BeF_2 thin film samples are shown in Table 1.

Table 1: Details of bath constitution of various BeF_2 thin film samples.

Bath Solution PH	Volume ratio of bath solutions					Bath Temp (K)	Deposition Time (hrs)
	$Be(NO_3)_2$ $4H_2O$	Na0H	NaF	H_2O	EDTA		
5	1.00	0.20	0.60	2.20	2.00	320	3
6	1.00	0.22	0.78	2.44	2.00	320	3
7	1.00	0.33	0.78	2.33	1.78	320	3
8	1.00	0.38	1.00	2.63	1.88	320	3
9	1.00	0.50	1.00	2.50	1.75	320	3
10	1.00	0.57	1.29	2.86	1.86	320	3
11	1.00	0.71	1.29	2.71	1.71	320	3
12	1.00	0.83	1.67	3.17	1.67	320	3

2.2 *Film Characterization*

The spectral absorbance (A) and transmittance (T) of the uncoated glass slide and the deposited thin firms on glass were obtained by a single beam CECIL CE1010 spectrophotometer in the ultraviolet (UV), visible (VIS) and near infrared (NIR) regions of electromagnetic spectrum. Spectral reflectance (R) was obtained from the relationship between these quantities [16] which allows for conservation of energy:

$$A + T + R = 1 \qquad (1)$$

The coefficient of absorption (α) was calculated [17] from the equation:

$$\alpha = \ln (T^{-1}) \times 10^4 cm^{-1} \qquad (2)$$

Refractive index (n) was computed [18] from the expression:

$$n = (1 + R^{1/2}) / (1 - R^{1/2}) \qquad (3)$$

The values of the bandgap (E_g) were computed [18,19] from the expression:

$$\alpha = A (h\nu - E_g)^{1/2}$$
$$\alpha^2 = A^2 (h\nu - E_g) \qquad (4)$$

where $h\nu$ is photon energy. The values of E_g were obtained from the straight-line portion of plots of α^2 Vs $h\nu$ when extrapolated to the portion $\alpha^2 = 0$. The electrical conductivity (σ) of the films was obtained from the expression:

$$\sigma = 1/\rho = d/Sr \qquad (5)$$

where ρ is electrical resistivity, d is thickness of microscope glass slide m, S is area of the film and r is electrical resistance of the film. The value of film electrical resistance was determined by universal bridge B 150/3. Average film thickness (t) obtained by the optical method for films with absorbance (A) > 0.1 [18,19] at wavelength, λ = 660 nm is given by equation:

$$t = \ln [(1 - R)^2/T] / \alpha \qquad (6)$$

while the average thickness (t) of films with absorbance (A) < 0.1 [20] at wavelength, λ = 660nm is given by the equation:

$$t = \frac{\left\{ Tan^{-1} \left[\frac{(n_o + n_s)^2 R - (n_o + n_s)^2}{\left({}^{n_o n_s}/_{n} - n \right)^2 - \left({}^{n_o n_s}/_{n} + n \right)^2 R} \right]^{1/2} \right\} \lambda}{2\pi n} \qquad (7)$$

where n_o is the refractive index of the medium of incident light, n_s is the refractive index of the substrate, n is the refractive index of the film, R is the reflectance and λ is the wavelength of light. The surfaces of the deposited thin films were observed using electron microscope Leitz Periplan Diaplan SE 2344 at a magnification of 400 x. The X – ray diffraction patterns of uncoated glass and deposited films on glass were obtained by Diano Corporation X – ray diffractometry model XRD 2100* E which uses a copper target (Cuk_α=1.540502, current 30 mA and accelerating voltage 45kV).

3 RESULTS AND DISCUSSION

3.1 *Effects of pH and complexing agents*

It was observed that BeF_2 films were deposited on glass only in alkaline medium. The chemical reaction for the deposition is given by the equation:

$$Be(NO_3)_2.4H_2O + 2NaOH + 2NaF \rightarrow BeF_2 + 2NaNO_3 + 2NaOH + 4H_2O \tag{8}$$

The molecules of beryllium fluoride (BeF_2) produced were deposited on glass slides in the bath solutions as single molecules which gradually developed into clusters, islands and finally into continuous layers of thin films. The sodium hydroxide (NaOH) solution used as the complexing agent [4,7,15] formed fairly stable complex ion with beryllium ions (Be^{2+}) by dative bounds and provides the controlled number or slow release of the free metal ions. It also regulated the concentration of the anions or fluoride ions (F^-) by adjusting the ionic product (I.P.) in equilibrium with the solubility product constant (K_{sp}) of BeF_2 compound. For example, very high concentration of fluoride ions (F^-) in the bath solution will disturb the chemical equilibrium or the stability in the bath solution because the I.P. will be greater than the K_{sp} of BeF_2 compound. This will cause the slow release of more Be^{2+} from the metal complex ion formed with hydroxide to react with the excess F^- and produce BeF_2 deposit until equilibrium is restored. On the other hand, if the concentration of F^- is low and the I.P. is greater than the K_{sp}, little Be^{2+} will be released from the metal complex ion to react with the F^- and produce BeF_2 film otherwise no film will be formed when I.P. is lower than the K_{sp} [4,7].

The complexing agent acting in this way helps to maintain the slow and steady deposition of BeF_2 films and controls the stability of the bath solution.

The level of concentration of the complexing agent is of vital importance in the deposition of film. When there is low concentration of the complexing agent, there will be incomplete formation of the complex ion of the Be^{2+}. This will cause spontaneous recipitation of the salt materials in solution and no deposition of the films. In some cases, powdery or amorphous films will be obtained. If the concentration of the complexing agent is too high, it will significantly reduce the concentration of the metal ions due to the formation of the metal complex ions instead of the metal halide [21]. The excess fluoride ions (F^-) may react with the complexing agent (NaOH) to form either the gas (fluoride gas) or acid (hydrofluoric acid). Optimum concentration of the starting materials, complexing agents and deposition time are therefore required to produce slow and steady controlled release of the cations (Be^{2+}) for normal reaction with the anions (F^-) to deposit uniform thin films of the BeF_2 that have good quality [4,7].

3.2 *Optical Properties*

The spectral transmittance (T) and spectral reflectance (R) of the uncoated glass slide and beryllium fluoride (BeF_2) thin films deposited on glass at pH of 7 – 12, in Fig. 1, shows that BeF_2 films have high transmittance (T) and low reflectance (R). The deposition of BeF_2 films on glass slides modifies the spectral transmittance (T) and reflectance (R) properties of the glass at different wavelength regions, depending on the film

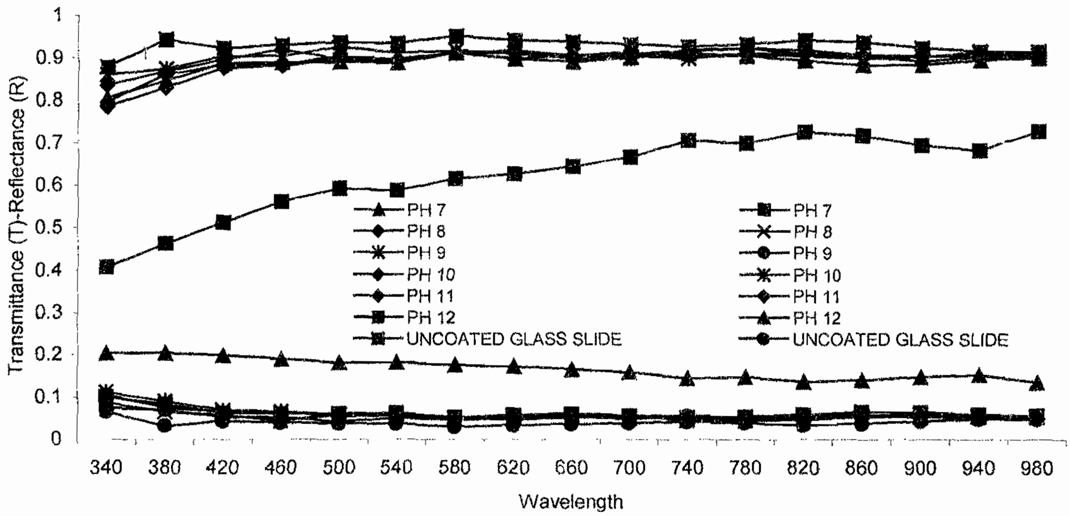

Fig. 1: Transmittance-Reflectance spectra of uncoated glass slide and Bef2 thin films deposited on glass by solution growth technique at PH 7-12 and 320K for 3 hours.

thickness, and thus making it spectrally selective. The spectral transmittance (T) of the films deposited on glass at pH of 7 – 11 rises sharply with increasing wavelength (λ) fom ultraviolet (UV) to some values at about λ = 860nm and later increases slowly in the visible (VIS) region, then increases slightly at about λ = 860 nm and later increases slowly in the near infrared NIR) region, depending on the film absorbance (A). The transmittance spectra conform to the spectra transmittance of some halide films such as NaCl, KBr, CsI, and BaF_2 [22,23,24]. The values of transmittance (T) range from 0.782 – 0.896 in the UV and from 0.878 – 0.925 in the VIS and NIR regions. The spectral reflectance (R) of the films deposited on glass at pH of 7 – 11 is generally low and decreases sharply with increasing wavelength (λ) from the ultraviolet (UV) to some values at about λ = 420 nm in the visible (VIS) region, decreases very slowly in the VIS region, then increases slightly at about λ = 860 nm and later decreases slowly in the near infrared (NIR) region, depending on film absorbance (A). The values of spectral reflectance (R) range from 0.056 – 0.111 in the UV and from 0.044 – 0.065 in the VIS and NIR regions. The film produced at pH of 12 has a relatively low spectral transmittance (T) and high reflectance (R). The values of transmittance (T) range from 0.412 – 0.438 in the UV and from 0.562 – 0.727 in the VIS and NIR regions. Values of reflectance (R) is about 0.203 in the UV and range from 0.134 – 0.189 in the VIS and NIR regions. Average values of coefficient of absorption (α) ranges from 0.101 – 0.486 x 10^4 cm^{-1}. This large α value is within the α range of 10^4 - 10^5 cm^{-1} for semiconductor thin films desirable for the production of polycrystalline thin film solar cells [25]. The variation of refractive index (n) with photon energy (hv) of the deposited BeF_2 thin films on glass at pH of 7 – 12 and 320K for 3 hours is shown in Fig 2. It is observed, from Figs 1 and 2, that the deposited BeF_2 thin films with n lower than 1.8 have high spectral transmittance (T) and low spectral reflectance (R). Films with n greater than 1.8 have low spectral transmittance (T) and high spectral reflectance (R). The average optical properties of the deposited BeF_2 at wavelength, λ = 660 nm is shown in Table 2.

Table 2: Optical properties of uncoated glass slide and BeF_2 thin films deposited on glass by SGT

Average Optical Properties	Uncoated Glass slide	Deposition time	temp.	Bath solution pH					
		(hrs)	(K)	7	8	9	10	11	12
A	0.033	3	320	0.052	0.046	0.044	0.051	0.048	0.211
T	0.927	3	320	0.887	0.899	0.904	0.889	0.895	0.615
R	0.040	3	320	0.061	0.055	0.052	0.060	0.057	0.175
$\alpha x10^4 cm^{-1}$	0.076	3	320	0.120	0.106	0.101	0.117	0.111	0.486
N	1.50	3	320	1.65	1.61	1.59	1.65	1.62	2.43

The deposited BeF_2 thin films with high transmittance, low reflectance and low refractive index could find useful applications in: (i) thermal control window coatings for cold climates. (ii) heat mirror coatings for temperate regions with very cold winter. (iii) antireflection coatings on transparent covers or windows of solar thermal devices and (iv) as transparent contacts or electrodes for photoactivated devices and photoelectrochemical cells (P.E.C.). The films with low transmittance, high reflectance and high refractive index could find useful applications in the: (i) construction of poultry houses to allow enough infrared radiation to warm the very young chicks during the day and reduce the high cost of energy consumption through lamps, stoves, electric bulbs, etc. and the hazards associated with them while at the same time protecting the chicks from ultraviolet radiation. (ii) production of eyeglass coatings to protect the skin around the eye from UV radiation. (iii) production of antidazzling coatings for car windscreens and driving mirrors to reduce the dazzling effect of light at night. (iv) production of cold mirror coatings for tropical and temperate regions with very hot summer to cool the interior by increasing thermal losses from the heated interior to exterior and screening the interior from excessive thermal energy from incoming solar radiation during summer and (v) in the manufacture of this film transistors [16, 26, 27, 28]. The values of bandgap (E_g) of the deposited thin films range from 2.22 – 2.66. The bandgap values, which are within the light energy range (~1.5 – 3.0eV) of the electromagnetic spectrum could be employed in the production of solar electricity for rural electrification and communication. Electrical conductivity of the film, which varies from 0.73 – 1.26 x 10^{-5} (ohm – cm)$^{-1}$ is within the electrical conductivity range of 10^{-12} – 10^2 (ohm – cm)$^{-1}$ for semi conductors [29,30,31,32]. The average film thickness (t) obtained by optical method at wavelength, λ = 660 nm vary from 465 – 2140 Å. These low values of film thickness compare favourably to little film layer of few hundreds angstrom required for active semiconductor materials with large α value used in thin film solar cells [33]. The values of the solid-state properties shown in Table 3 could be employed in solar energy and other photonic applications. The surfaces of the deposited BeF_2 thin films observed under electron microscope reveal the presence of some granular particles. X-ray diffraction patterns of the uncoated glass and the deposited BeF_2 thin films on glass substrates sho some peaks in the coated samples and hence the crystalline nature of the deposited films.

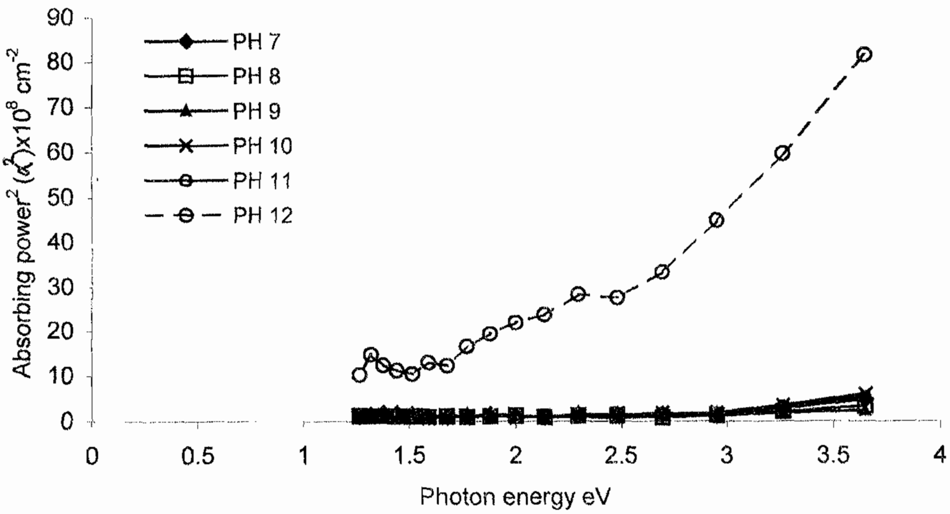

Fig 2: Variation of n with hv for BeF_2 thin films deposited on glass by solution growth technique at pH of 7-12 and 320 K for 3 hours

Table 3: Solid-state properties of BeF_2 thin films deposited on glass slide by SGT.

Solid State Properties	Deposition Time (hrs)	Temp (K)	Bath solution pH					
			7	8	9	10	11	12
E_g(eV)	3	320	2.64	2.56	2.56	2.66	2.64	2.22
σ x 10^{-5} $(\Omega\text{- cm})^{-1}$	3	320	0.73	0.79	0.96	1.15	1.19	1.26
T(Å)	3	320	465	487	495	468	479	2140

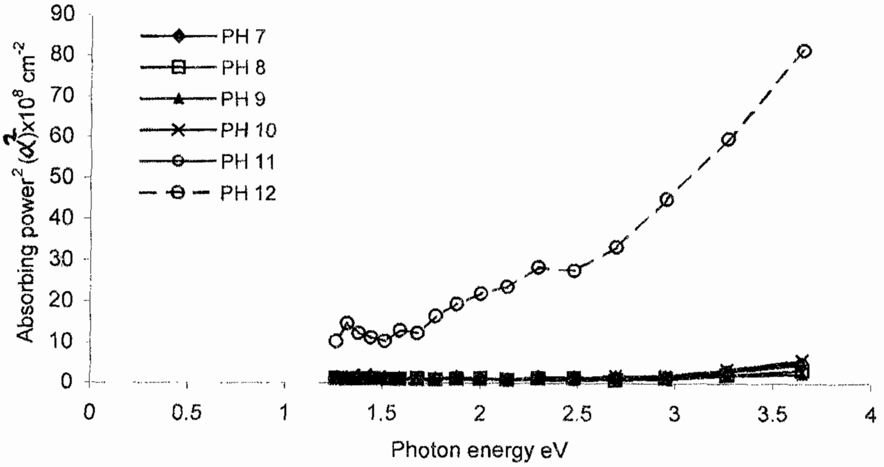

Fig 3: Plots of α^2 vs hv for BeF_2 thin films deposited on glass at pH of 7 – 12 and 320 K for 3 hours

The values of bandgap (E_g) of the deposited thin films range from 2.22 – 2.66. The bandgap values, which are within the light energy range (~1.5 – 3.0eV) of the electromagnetic spectrum could be employed in the production of solar electricity for rural electrification and communication. Electrical conductivity of the film, which varies from 0.73 – 1.26 x 10^{-5} (ohm – cm)$^{-1}$ is within the electrical conductivity range of 10^{-12} – 10^{2} (ohm – cm)$^{-1}$ for semiconductors [29,30,31,32]. The average film thickness (t) obtained by optical method at a wavelength, λ = 660 nm vary from 465 – 2140 Å. These low values of film thickness compare favourably to little film layer of few hundreds angstrom required for active semiconductor materials with large α value used in thin film solar cells [33]. The values of the solid-state properties shown in Table 3 could be employed in solar energy and other photonic applications. The surfaces of the deposited BeF_2 thin films observed under electron microscope reveal the presence of some granular particles. X-ray diffraction patterns of the uncoated glass and the deposited BeF_2 thin films on glass substrates show some peaks in the coated samples and hence the crystalline nature of the deposited films.

4. CONCLUSION

Good quality uniform thin films of beryllium fluoride (BeF_2) were successfully deposited on glass slides at 320K for 3 hours and at pH of 7 – 12 by using solution growth technique (SGT). Advantages of this technique include simple deposition method, convenient, low cost, easy reproducible and can be used for high and low temperature deposition techniques. The deposited thin films with refractive index (n) lower than 1.8 has high spectral transmittance (T) and low reflectance (R). Those with refractive index greater than 1.8 have low spectral transmittance (T) and high reflectance (R). Films with high transmittance (T) and low reflectance (R) could be employed in thermal control window coatings and heat mirror coatings in architectural industries and also antireflection coatings for solar thermal devices. The films with low transmittance (T) and high reflectance (R) could be used in the construction of poultry houses, manufacture of eyeglass coatings, thin film transistors and in production of solar electricity.

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