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Fabrication and optical characterization of improved electroless chemically deposited strontium fluoride (SrF_2) thin films at 320K

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Abstract

Thin semi conductor films of strontium fluoride* (SrF_2) *were successfully deposited on glass microscope slides using simple and cheap electroless chemical bath deposition methods at* 320K *and pH values of* 9, 10 *and* 12. *Controlled addition of ethylenediamine tetra acetate (EDTA), another complexing agent with pH to oppose that of bath constitutions, was used to vary the deposition pH values. X-ray diffractometry technique was used to confirm the depositions. Absorbance spectra data of the films were obtained by a single bean spectrophotometer (Pharmacia LKB Biochrom* 4060) *at wavelength range* 200 *to* 900*nm. Other optical and solid state properties were calculated from the data and compared with other deposited thin films. Average optical and solid state properties include absorbance ranging from* 0.034 *to* 0.086, *transmittance* 0.820 *to* 0.925, *reflectance* 0.041 *to* 0.094, *refractive index* 1.51 *to* 1.88 *absorption coefficient* 0.078 *to* 0.198x $10^6 m^{-1}$, *electrical conductivity* 0.40 *to* 0.49 *(ohm cm)*$^{-1}$, *film thickness* 0.013 *to* 0.074*μm and bandgap* 2.55 *to* 2.75 *eV. The deposited thin films could find applications in antireflection coatings for eyeglass, solar thermal control devices and solar cells

Keywords: improved electroless chemical bath deposition, strontium fluoride thin films, optical characterization, application in antireflection coatings.

1.0 Introduction

Electroless chemical bath deposition method of producing thin films was well employed in the commercial production of silver mirrors (Chopra and Das, 1983 [2], Eze and Okeke, 1997 [3]). The method is simple, convenient, cost effective, reproducible and intensively studied for preparation of thin films on both metallic and non-metallic substrates. Films produced by this technique are now being developed for solar energy and other photonic applications such as energy-efficient glazing, decorative and protective coatings and in imaging technique (Chopra and Das, 1983 [2], Eze and Okeke, 1997 [3], Okujagu and Okeke, 1997 [13], Osuji, 2003 [14],).

The technology depends on the controlled release of cations and anions in an aqueous solution into which the substrates are immersed (Chopra and Das, 1983 [2]). Properties of the film produced depend on some complex physical and chemical processes in bath constitutions, formation of films and heat treatment (Eze and Okeke, 1997 [3]). A ligand or complexing agent acting as a catalyst is usually employed to control the reaction in a suitable medium as indicated by the pH to obtain crystal growth. Otherwise, spontaneous reaction and sedimentation of materials will be obtained. The condition for compound to be deposited from a solution bearing its ions is that its ionic product (I.P) should be greater than the solubility product (Ksp) (Chopra and Das, 1983 [2], Lange, 1992 [10]). The complexing agent of a metal in solution forms a fairly stable complex ions of the metal and provides a controlled release of free ions according to an equilibrium reaction of the form: $M(A)^{2+} \Leftrightarrow M^{2+} + A$, where M^{2+} is the metal ions and A is the complexing agent. The concentration of an ion at any temperature is given by $[M^{2+}][A]/M(A)^{2+} = K_d$, where K_d is the dissociation or instability constant of the complex ion. The negative ions required for the precipitation of the compound are also generated slowly by suitable complex compounds bearing them (Chopra and Das, 1983[2]). The deposition method can be improved to overcome the tedious and wasteful combinations of various bath reagents by controlled addition of another complexing agent with pH oppose to that of bath constitutions to vary the initial deposition conditions at different pH values (Ilenikhena and Okeke, 2005 [6], Ilenikhena 2007 [8]).

Metal halide films, of which strontium fluoride (S_rF_2) is one, have generally high transmittance and low refluence in the visible and near infrared regions of electromagnetic radiation.. Materials with such optical properties and low refractive Index could be employed in antireflection coatings (Lampert, 1987 [9]). Not much work has been reported on the deposition of metal halide films. The deposition magnesium fluoride was reported by Chopra and Das (1983) [2], Okujagu and Okeke (1997 [13]) produced metal halide thin films using solution growth technique, Ileniklena and Okeke (2001, [5] 2003) [6] deposited strontium iodide and beryllium fluoride thin films using chemical bath deposition and solution growth technique respectively. Ilenikhena (2007) [8] also prepared beryllium iodide thin films using improved electroless chemical bath deposition method.

This paper reports the deposition of strontium fluoride (SrF_2) thin films by a cheap, convenient and improved electroless chemical bath deposition (ECBD) method at different pH values and 320K. Controlled addition of ethylenediamine - tetra acetate (EDTA) was used to vary the deposition conditions at different pH values. X-ray diffractometry method was used to confirm the deposition. Optical and solid state properties of the deposited films were obtained and compared with those obtained using some other sophisticated thin film deposition techniques. Possible applications of the deposited strontium fluoride thin films in antireflection coatings are also discussed.

2.0 Experimental details

2.1 Film Preparation

Glass microscope slides (76 x 26 x 1 mm^3) were cleaned by degreasing them in concentrated nitric acid (HNO_3) for two days, washed in detergent solution, rinsed in distilled water and dried in air. Reaction baths were 50ml glass beakers containing different molar solutions and volumes of deposition reagents. The bath constitutions were strontium nitrate [$Sr(NO_3)_2$] as source of strontium ions (Sr^{2+}), sodium hydroxide (NaOH) as complexing agent and sodium fluoride as source of fluoride ions (F). Distilled water was added to raise the volume of the bath solution to a certain level as shown in Table 1. Controlled addition of ethylenediamine tetra acetate (EDTA), another complexing agent with pH oppose to that of bath constitutions, was used to vary initial deposition pH values. They were placed in a hot water bath that was maintained at a steady temperature of 320K by a Stuart magnetic stirrer hot plate. A cleaned glass microscope slide was suspended in each reaction bath for 3 hours. After the deposition time, the coated glass microscope slide were rinsed with distilled water and dried in air. Pretest runs were carried out to determine the optimum deposition parameters. The complexing agent (NaOH) formed complex ions with Sr^{2+}. It slowly released Sr^{2+}, ensured ion by ion condensation of Sr^{2+} and F^+ ions, controlled the growth rate of strontium fluoride (SrF_2) films and eliminated spontaneous precipitation of the chemical reagents in the bath. The most probable reaction equation for the deposition of strontium fluoride (SrF_2) thin films is

$$Sr(NO_3)_2 + 2NaOH + 2NaF \rightarrow (SrF_2) \downarrow + 2\ NaOH + 2\ Na\ NO_3$$

Table 1: Bath constituents for preparation of strontium fluoride (S_rF_2) thin films

Initial Bath pH	**0.36M $S_r(NO_3)_2$ Vol. (ml)**	**2.5M NaOH Vol. (ml)**	**0.8M NaF Vol. (ml)**	**H_2O Vol. (ml)**	**0.2 M EDTA Vol. (ml)**
9	8	4	8	20	14
10	7	4	9	20	13
12	6	5	10	19	10

2.2 Film characterization

The absorbance spectra of the films were obtained by a computerized single beam spectro photometer (Pharmacia LBK Biochrom 4060) at wavelength range 200nm-900nm in the ultraviolet - visible – near infrared (UV-VIS-NIR) regions. The reference and coated glass microscope slides were mounted on a rotating holder at the reference and sample compartments respectively and scanned to obtain the absorbance spectra. Other optical and solid-state properties were calculated. Structural characterization was obtained by x-ray diffractometry method using Diano cooperation x-ray diffractometer (model XRD 2100 E*) and copper target (CuKα) with wavelength 1.540502$\acute{A}$**,** current 30*mA* and voltage 45*kV*.

3.0 Theory and calculation

Following Pankove (1971) [, the a absorbance (*A*) of a semiconductor thin film is given by:

$$A = \log (1/T) \tag{3.1}$$

where *T* is the transmittance

The transmittance, the reflectance (*R*) and the absorbance further satisfy the equation:

$$A + T + R = 1 \tag{3.2}$$

The refractive index (n) may be obtained from the expression:

$$n = \frac{\left(1 + R^{1/2}\right)}{1 - R^{1/2}} \tag{3.3}$$

while the absorption coefficient (α) is related to *T* by the equation:

$$\alpha = In\ (1/T) \times 10^6 m^{-1} \tag{3.4}$$

α is also related to the coefficient of extinction (*k*) and the wavelength (λ) by the equation :

$$\alpha = 4Лk/\lambda \tag{3.5}$$

Near the absorption edge absorption coefficient is related to band gap (*Eg*) by the equation:

$$\alpha = (h\gamma - Eg)^b \tag{3.6}$$

where $h\gamma$ is photon energy and *b* is a constant for a given transition (Chopra and Das, 1983) [2]. For allowed direct transitions, $b = ½$, and the band gap is obtained from allowed direct transitions by plotting α^2 against h γ and extrapolating the graph to the pont where $\alpha^2 = 0$

Again, following Pankove (1971), the film thickness (*t*) is given by:

$$t = In\ \left[(1 - R)^2/T\right]/\alpha \tag{3.7}$$

The complex dielectric constant (ε_c) is given by $\varepsilon_c = (n + ik)^2 = \varepsilon_r + i\varepsilon_i$) (3.8)

From equation (3.8) we obtain, for the real dielectric constant ε_r and the imaginary dielectric constant ε_i the relations:

$$\varepsilon_r = n^2 - k^2 \tag{3.9}$$

and $\varepsilon_{li} = 2nk$ (3.10)

The optical conductivity (σ_0) is given by:

$$\sigma_0 = \alpha nc/4Л \tag{3.11}$$

where *c* is the speed of light in vacuum, and it is also related to the electrical conductivity (σ_e) via the equation (Ezeokoye and Okeke, 2003) [4]:

$$\sigma_e = 2Л\sigma_e/\alpha \tag{3.12}$$

4.0 Results and discussion

Results of the absorbance spectra for the deposited strontium fluoride (SrF_2) thin films at 320K and pH of 9, 10 and 12 are displayed in Figure 1. The films have high absorbance (*A*) of 0.416 to 0.477 for wavelengths lower than 300nm (0.3*μm*) and low absorbance (*A*) of range - 0.108 to 0.040 for wavelengths range 350 to 850nm. Film produce at pH of 9 has negative absorbance (*A*) in the spectral range 300nm to 800nm with a minimum value of -0.108 at 350nm. Similarly, film produced at pH of 12 has negative absorbance (*A*) values in the wavelength range 300nm to 500nm with a minimum value of -0.16 at 400nm. Film produced at pH value of 10 has positive absorbance (A) values. Transmittance (*T*) - reflectance (*R*) spectra of the films are displayed in Figure 2. The films have low transmittance (T) of 0.333 to 0.384 for wavelengths lower than 300nm and high transmittance (*T*) of 0.791 to 1.282, depending on the film absorbance, for wavelengths greater than 300*nm*. The highest transmittance of 1.282 was obtained at wavelength of 350nm for film produced at pH value of 9. Figure 2 also show that the films have high reflectance (*R*) ranging from 0.19 to 0.200 for wavelengths lower than 300nm and low reflectance of -0.174 to 0.048 for wavelengths greater than 300nm. The high transmittance (*T*) and low reflectance (*R*) properties of the strontium fluoride (SrF_2) thin films in the ultraviolet (350- 400*nm*), visible (390-770*nm*) and in the near infrared (700-850*nm*) regions of the electromagnetic spectrum could be employed in the production of antireflection coatings for transparent covers of solar thermal devices and eyeglass coatings. The properties of high spectral transmittance (*T*) and low reflectance (*R*) exhibited by strontium fluoride (SrF_2) film produced at pH of 10 in the visible region could be employed in solar thermal control coatings and solar control glazlings (Nair et al, 1989 [12]). Variation of the reflective index (n) of the films with photon energy is displayed in Fig. 3. It shows high values of the refractive index of 1.61 to 2.61 for photon energy (*hv*) higher than 4.14 eV and low refractive index of 1.17 to 1.56 for photon energy (*hv*) lower than 4.14 eV in the ultraviolet (UV), visible (VIS) and near infrared (NIR) regions. These low values of the refractive index (*n*) of SrF_2 films in the UV - VIS - NIR regions could be used in antireflection coatings (Brinker and Harrington, 1981[1], Petit and Brinker, 1986 [16]). Such films with refractive index (*n*) lower than 1.9 ($n < 1.90$) could be employed to reduce reflectance of photovoltaic from 0.36 - 0.04 and improve transmittance of glass from 0.91 to 0.96 (Brinker and Harrington, 1981 [1], Petit and Brinker, 1986 [16]). Figure4 shows the variation of extinction coefficient (k) with photon energy (*hv*). Values of extinction coefficient range from 1.5 x 10^{-2} to 2.2 x 10^{-2} for photon energies higher than 4.14 *eV* and from - 6.92 x 10^{-3} to 5.86 x 10^{-3} for photon energy (*hv*) range 1.46 to 4.14 eV. Film produced at *pH* of 10 exhibited only positive values of *k*. The variation of absorption coefficient with photon energy is displayed in Figure 5. 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 [11]). The band gap values obtained by the method of absorption spectra range from 2.55 to 2.75eV. These values compared well with 2.22 to 2.64eV for beryllium fluoride (llenikhena and Okeke, 2003) and 2.34 to 2.56eV for strontium iodide thin films (llenikhena and Okeke, 2001 [5]) and could be employed in solar cells. The variation of real dielectric constant ($\in_r$) and imaginary dielectric constant ($\in_i$) are displayed in Figs. 6 and 7 respectively. The variation of optical conductivity (σ_o) is displayed in Figure 8. Its magnitude of $10^{13}s^{-1}$ shows that the thin films have good photo response. Average optical and solid state properties are shown in Table 2. The electrical conductivity (σ_e) of the films range from 0.40 to 0.49 $(\text{ohm-cm})^{-1}$ which is within electrical conductivity range of 10^{-12} - 10^2 $(\text{ohm -cm})^{-1}$ for semiconductors (Paushkin et al, 1974 [15], Phol, 1962 [17] and Webber et al, 1974 [18]). The film thickness (*t*) at wavelength 550nm (5500Å) varies from 0.013 to 0.074μm. which is within the film thickness of 630Å at wavelength (λ) of 5500Å for materials with refractive index less than 1.94 use in antireflection coatings (Chpora and Das, 1983) [2]. The x-ray diffraction patterns of the uncoated glass and deposited strontium fluoride (SrF_2) films on glass are shown in Figures. 9 and 10 respectively. The diffraction patterns reveal diffraction peaks at some 2 – theta (2θ) values.

Table 2: Average optical and solid state properties of SrF_2 thin films

pH	T	n	$K \times 10^{-3}$	$\alpha \times 10^6\ (m^{-1})$	$\in_r$	$\in_i \times 10^{-2}$	$\sigma_0 \times 10^{13}$	$\sigma_e (ohm - cm)^{-1}$	$t (\mu m)$	E_g (eV)
9	0.925	1.51	3.41	0.078	2.28	1.03	0.28	0.40	0.074	2.75
10	0.820	1.88	8.69	0.198	3.54	3.27	0.89	0.49	0.013	2.65
12	0.855	1.77	6.86	0.157	3.12	2.43	0.62	0.46	0.023	2.70

5.0 Conclusion

Semiconductor thin films of strontium fluoride (SrF_2) were produced at 320K and *pH* values of 9, 10 and 12, using simple, cheap and reproducible improved chemical bath deposited method. Controlled addition of ethylenediamine-tetra acetate (EDTA), a complexing agent with pH oppose to that of bath constitutions was used to vary the deposition pH values. X-ray diffractometry technique was used to confirm the deposition of the films. A single beam spectrophotonmeter (Pharmacia LKB Biochrom 4060) was used to obtain the spectra absorbance data. Other optical and solid state properties were calculated. These properties include transmittance (*T*), reflectance (*R*), refractive index (*n*) extinction coefficient (*k*), dielectric constants ($\in_r$ and $\in_i$), electrical conductivity (σ_e), coefficient of absorption (*k*), optical conductivity (σ_o), film thickness (t), band gap (E_g), etc. The deposited films could find applications in antireflection coatings for solar thermal control devices, eyeglass and solar cells.

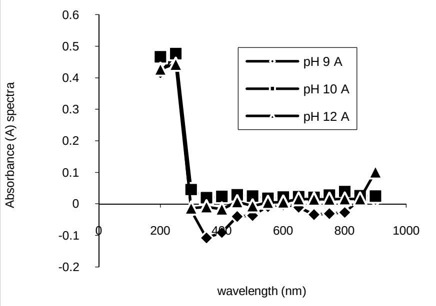


Fig 1: Absorbance (A) spectra for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

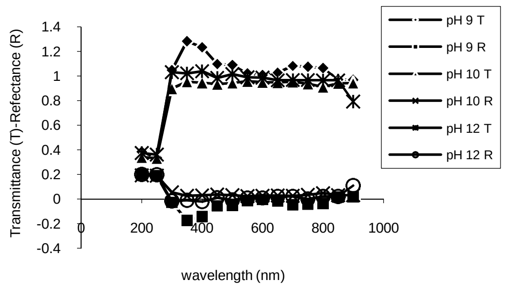
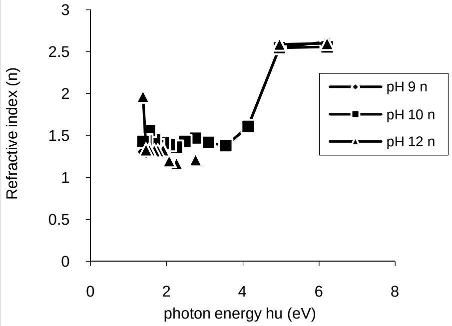
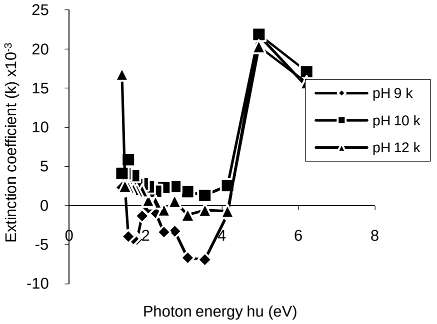


Fig 2: Transmittance (T)-Refectance (R) for SrF_2 thin films produced at 320K and pH of 9, 10 and 12



Fi g 3: variation of refractive index (n) against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12



Fi g 4: variation of extinction coefficient (k) against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

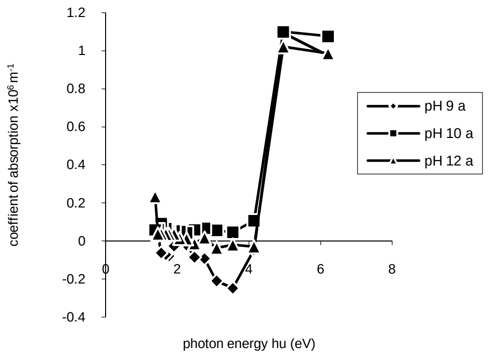


Fig 5: Variation of coefficient of absorption against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

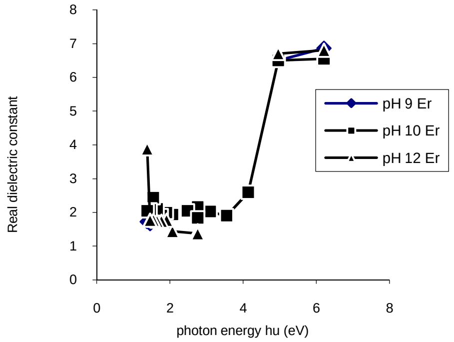


fig 6: Variation of absorbing power against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

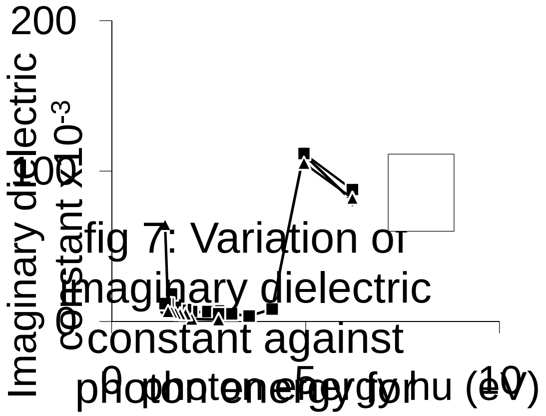


fig 7: Variation of imaginary dielectric constant against photon energy for SrF_2 thin films…

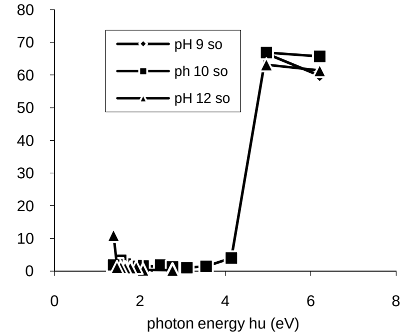


fig 8: Variation of optical conductivity (so) against photon energy for SrF_2 thin films produced at 320K and pH of 9, 10 and 12

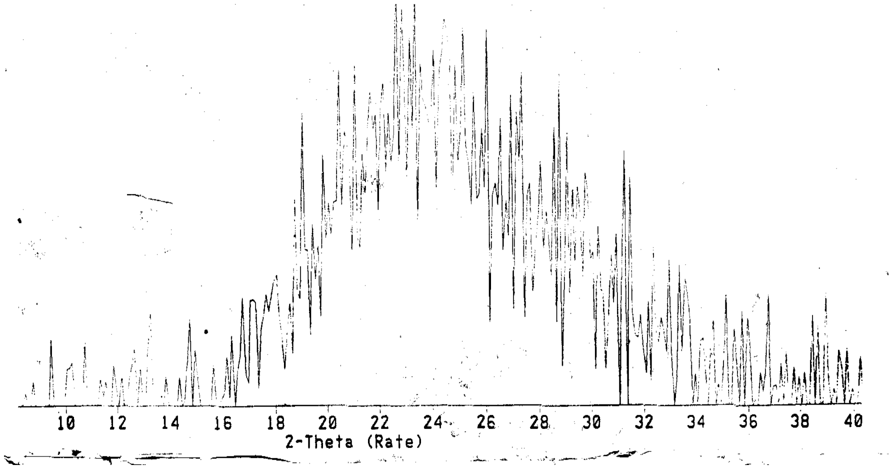


Figure 9: X-ray diffraction for uncoated glass slide

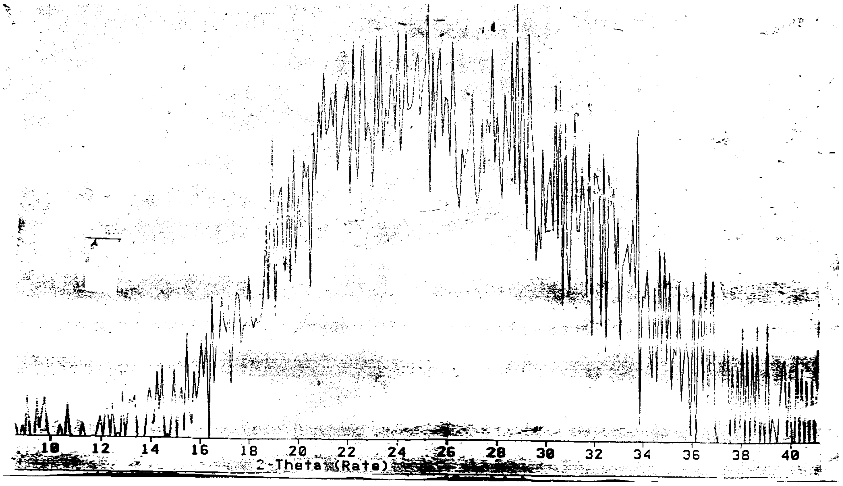


Figure 10: X-ray diffraction for deposited strontium fluoride (SrF_2) thin films on glass slide at 320K

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