Effects of Deposition Period on the Optical Properties of Nano Crystallised Al/Pb-Oxide and Sulphide Films

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Abstract

Oxides and Sulphides of Al/Pb at deposition periods of 2.5, 3.5, 4.5 and 5.5 hours were prepared using the Chemical Bath Deposition (CBD) technique. Nano crystalline films of thickness 100-470nm were produced in the study. Optical characterisation of the films was carried out using the Jenway 6405 UV-VIS model spectrometer. The absorbance decreases with increase in wavelength and has relatively low values in the InfraRed (IR) region of the electromagnetic spectrum. Highest absorbance where observed at a period of 3.5 hours for PbO, 3.5 and 5.5 hours for PbS, 2.5 hours for Al_2O_3 and 5.5 hours for Al_2S_3 at wavelength range 270-400 nm, hence, the films possess potential applications within this region. The transmission increases as the wavelength increases, values greater than 85% were obtained for transmittance spectra of PbO, while the PbS gives high transmittance in the range 10-35%. The high transmission in the visible region suggests the suitability of the films for solar energy collector and aesthetic window glaze materials. On the other hand, the low reflectance values of the thin films revealed their importance as materials for anti-reflectance coating. These indicate that, thin films of Al/Pb oxide and sulphide can be used as optical sensors. The direct band gap energy of the films deposited ranges between 1.8 and 3.4 eV. The result of the studyrevealed that optimum performance of the materials could be achieved by varying the period of deposition.

Keywords: Al/Pb oxide and sulphide, period of deposition, optical properties, energy band gap.

1.0   Introduction

Lead(II) oxide, also called lead monoxide, is the inorganic compound with the molecular formula PbO. PbO occurs in two polymorphs, one having a tetragonal crystal structure and the other having an orthorhombic crystal structure. Modern applications for PbO are firstly in lead-based industrial glass and industrial ceramics, including computer components.

PbO is a traditional n-type semiconductor material, and it has many advantages such as low growth temperature, simple preparation methods, high photoconductivity and corrosion resistance. These properties enable the use of PbO thin films in the manufacture of camera tube, photoconductive detectors, electrode materials, gas sensors etc. A number of authors have deposited thin films of PbO using different techniques [1-3]. PbO can also be prepared with other compounds such as GeO_2[4].

Lead sulphide belongs to IV–VI compound semiconductor materials. The colour of the film is greyish-black. Lead sulphide (PbS) has direct narrow band gap at room temperature. It has anexciton Bohr radius of 9nm and optical cut-off at 3020nm [5]. This narrow band gap makes it useful in several applications like solar control coatings, electroluminescent devices, infrared detection application, diode lasers and display devices [6]. Many properties of PbS thin films have been investigated [7]. The electrical resistivity of the film is of the order of 10^5–10^6 cm. Its absorption coefficient continuously increases from the infrared through the visible region and has been used in infrared detectors since mid 1940s [8]. Several methods such as Solgel, Paulse layer deposition, spray pyrolysis, Successive ionic layer absorption and reaction have been employed by various researchers in the preparation of PbS thin films [9-11]. In solar energy research, PbS thin films had been investigated for photothermal conversion application either independently on metallic substrates [12] or in stacked multilayer [13],and chemical bath deposition [14, 15].

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2.0 Materials and Methods

Sample Preparation

Chemical bath deposition (CBD) technique was employed in the deposition of Al/Pb-oxide and sulphide thin films. The reaction bath was constituted in 50ml beaker. The constituents of the chemical bath included 20ml of 0.05M lead nitrate [Pb $(NO_3)_2$] which served as the precursor for Pb^{2+} ion, 20ml of 0.05M thioacetamide (CH_3CSNH_2) which is the source of the S^{2-} ion, 1.0 ml of 1Mtriethanolamine (TEA) which served as the complexing agent and 1 ml of 25% ammonia[$NH_3(aq)$] which was used to modify the pH of the solution. The $Pb(NO_3)_2$ solution was found to be colourless and transparent until TEA and NH_3 solutions were introduced into the solution, making the mixture to turn white. On addition of CH_3CSNH_2 solution, the resulting solution turned light brown and the colour gradually changed to silvery-black. The microscopic glass slides of dimensions76 mmx26 mmx1mm which were used as substrates and supported vertically at the center of the beaker, were dipped into the solution, while the time of deposition was varied from two and half hours to five and half hours. For the deposition of PbO, the precursor were replaced with $Pb(NO_3)_2$and NaOH. In the same manner, the Al_2O_3 and Al_2S_3 were deposited with $Al(NO_3)_3$ and NaOH as precursors, while Ethylene Diamine Tetra Acetate(EDTA) served as the complexing agent. The concentrations were obtained stoichometrically. The pH values of the samples were obtained and period of deposition determined by a digital stop watch.

3.0 Theoretical Formulation

The optical properties studied in this work include: Absorbance (A), Transmittance (T), Reflectance (R), Absorption coefficient ( ), energy band gap and the absorption edge.
The transmittance (T) of a specimen is defined as the ratio of the transmitted flux (I_t) to the incident flux (I_o), that is,

$$T = I_t/I_0 \tag{1}$$

If a specimen has a thickness d, an absorption coefficient and a reflectivity R, the radiation reaching the first interface is $(1 - R)I_0$, the radiation reaching the second interface is $(1 - R)I_0 \exp(-\alpha)$ and only a fraction emerges. The portion internally reflected eventually comes out considerably attenuated. The end result is that overall transmission is given by [16, 17] as:

$$T = I_t/I_0 = (1 - R)^2\exp(-\alpha)/(1 - R^2)\exp(-2\alpha) \tag{2}$$

Equation 2 accounts for the effect of multiple reflections in the film. When the product α is large, the second term in the denominator becomes negligible and the transmittance is expressed as

$$T = I_t/I_0 = (1 - R)^2\exp(-\alpha) \tag{3}$$

Giving the values for R and d,α can be obtained.
The absorbance (A) is defined as the fraction of radiation absorb from the radiation that strikes the surface of the materials. Alternatively, A is the logarithm to base 10 of the transmittance, i.e,

$$A = l_{10} I_t/I_0 = l_{10} T \tag{4}$$

It follows from equation 5 that the transmittance and absorbance are related by

$$T = 10^A \tag{5}$$

The reflectance is the fraction of the incident radiation of a given wavelength that is reflected when it strikes a surface. A relation between transmittance (T), spectra absorbance (A) and spectra reflectance (R), according to the law of conservation of energy is given by

$$A + T + R = 1 \tag{6}$$

The band gap Energy E_g is the energy needed to move a valence electron into conduction band. For a semiconductor, it is the energy needed to free an electron from the nucleus of the parent atom. It is expressed as

$$E_g = h\upsilon \tag{7}$$

Where h is plank's constant and υ is the frequency of the radiation.
When an electron undergoes transitions from an upper part of the valence band to the lower part of the conduction band, it causes dispersion near the fundamental absorption edge and gives the shape of the absorption spectrum. This could happen without phonon participation and without a change in the crystal in which case, it is called direct transition. But when there is a change in the crystal momentum and interaction with phonon which results to changes in electron energy, this is referred to as indirect transition. Both direct and indirect transitions give rise to different frequency dependency to the absorption coefficient near the fundamental absorption edge. The absorption coefficient for direct transition is given by [18, 19, 20]as

$$\alpha = (h\upsilon - E_g)^n \tag{8}$$

where n = ½ if the transition between the upper part of the valence band and the lower part of the conduction band is allowed by the selection rules, as is in the case of this study, hence,

$$\alpha = (h\upsilon - E_g)^{\frac{1}{2}} \tag{9}$$

Thus a plot of ^{2} against $h\upsilon$will gives a curve with straight line at certain portion. This is attributed to the fact that at the region of the absorption edge, the absorption values fall such that the path due to band-to-band transition becomes difficult to measure. Experimental loses in specimen or other incidental absorptions are contributions to such low values at the region of absorption

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on… *Oluyamo and Adebayo* *J of NAMP*

294

edge[21, 22]. The plot of α^2 against $h\upsilon$ in this region deviates from being straight. Extrapolation of the straight portion of the graph to a point at which $\alpha^2 = 0$ gives the energy band gap E_g.
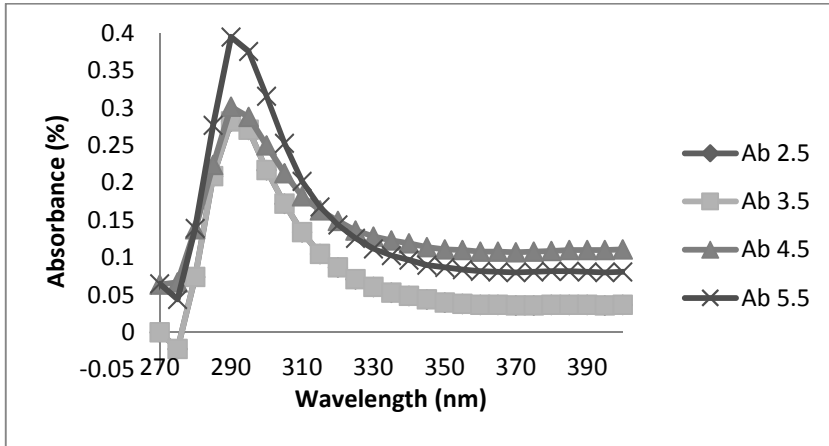

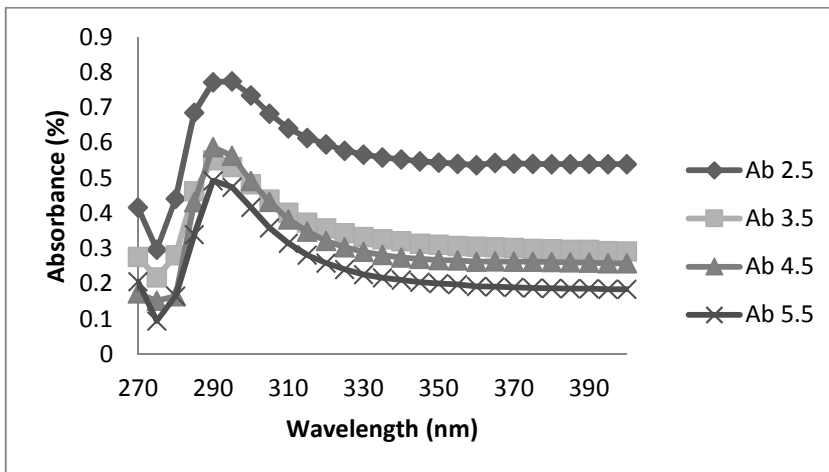**Fig 1:** Graph of Absorbance (%) against Wavelength (nm) for Al_2O_3

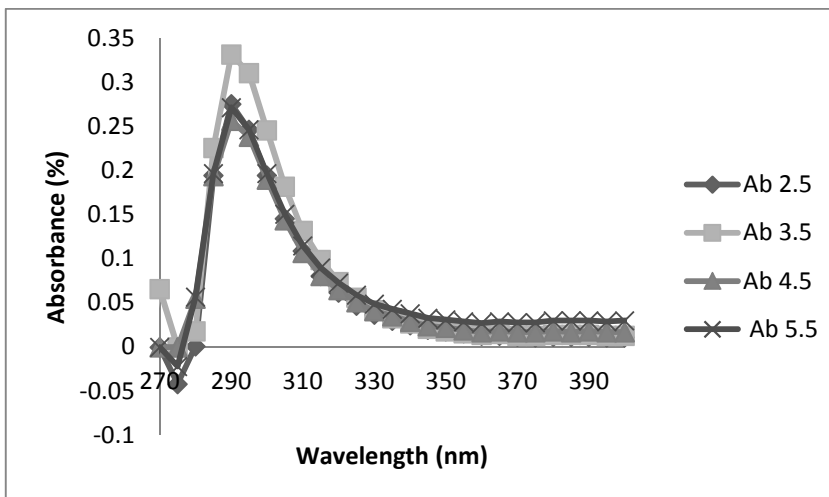**Fig 2:** Graph of Absorbance (%) against Wavelength (nm) for Al_2S_3

Fig. 3: Graph of Absorbance (%) against Wavelength (nm) for PbO

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on…   *Oluyamo and Adebayo*   *J of NAMP*
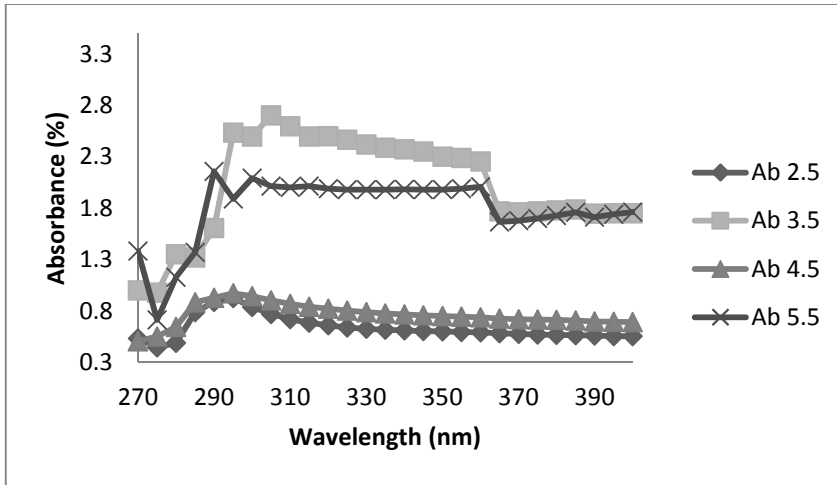
295

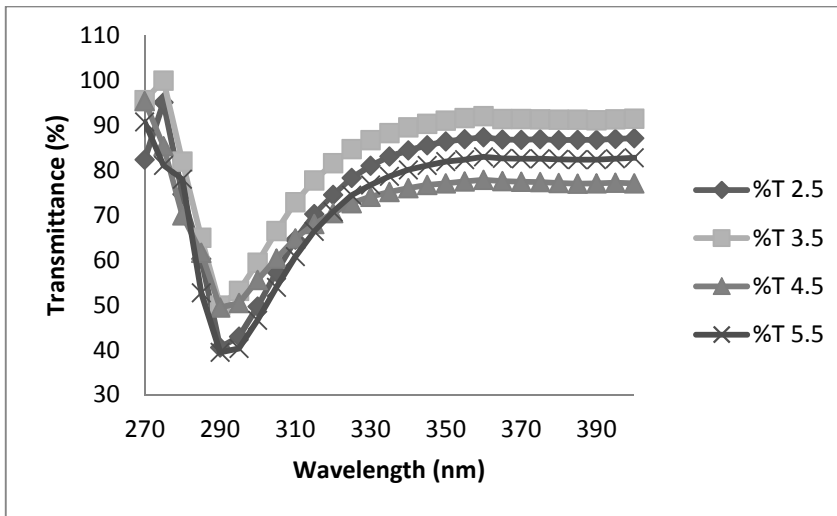**Fig. 4:** Graph of Absorbance (%) against Wavelength (nm) for PbS

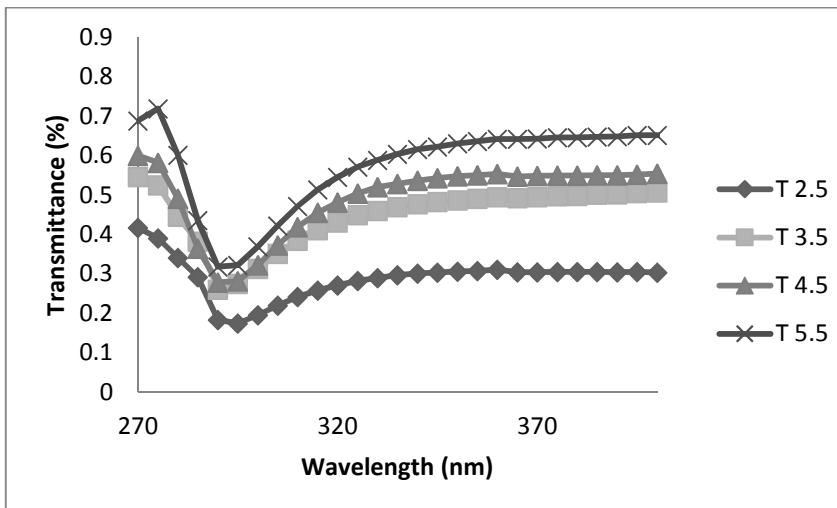**Fig. 5:** Graph of Transmittance (%) against Wavelength (nm) for Al_2O_3

Fig. 6: Graph of Transmittance (%) against Wavelength for Al_2S_3

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on…   *Oluyamo and Adebayo*   *J of NAMP*
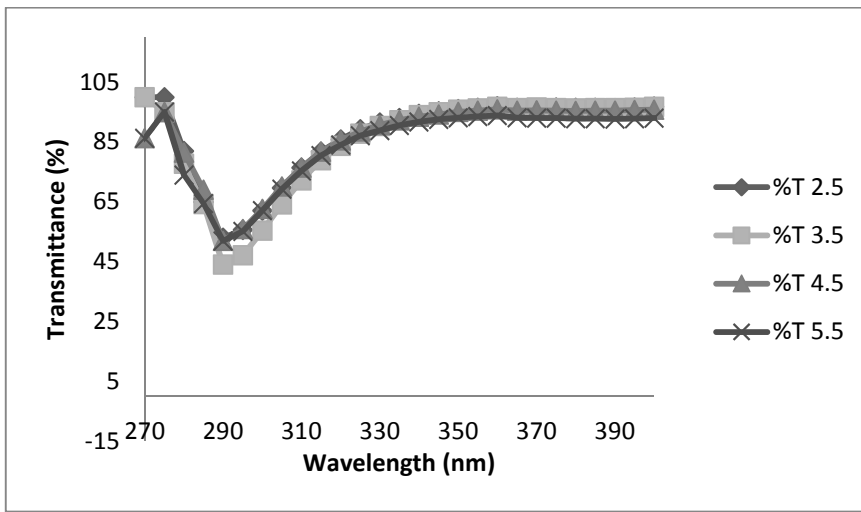
296

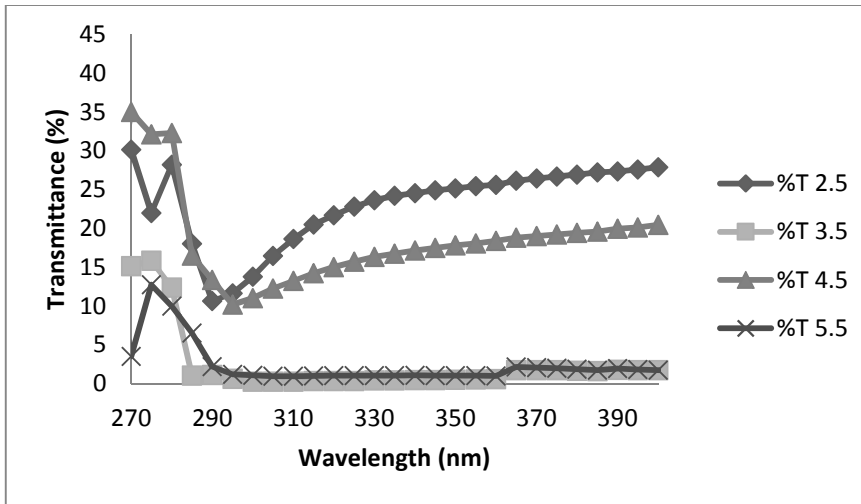**Fig. 7:** Graph of Transmittance (%) against Wavelength (nm) for PbO

Fig. 8: Graph of Transmittance (%) against Wavelength (nm) for PbS

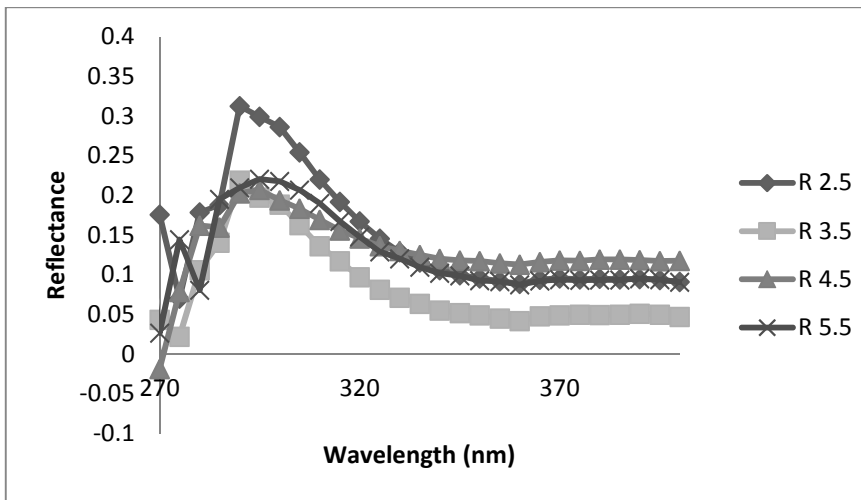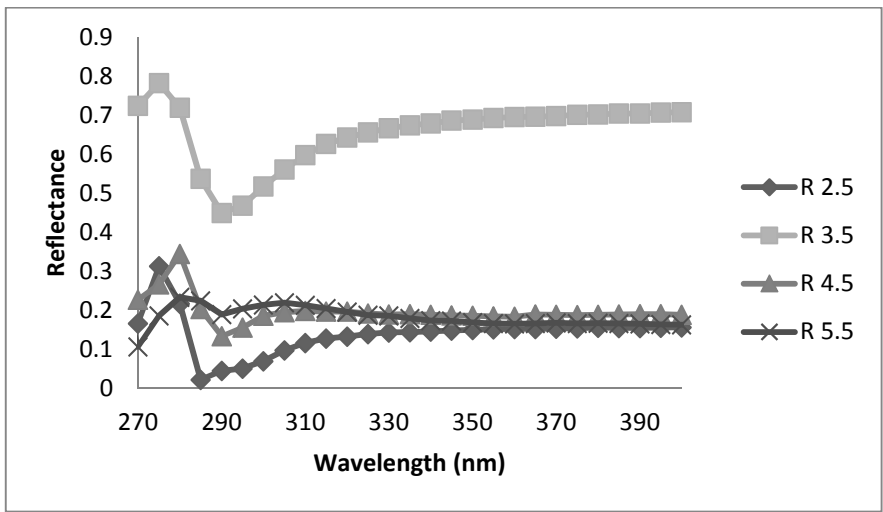**Fig. 9:** Graph of reflectance against wavelength (nm) for Al_2O_3

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on… *Oluyamo and Adebayo J of NAMP*

297

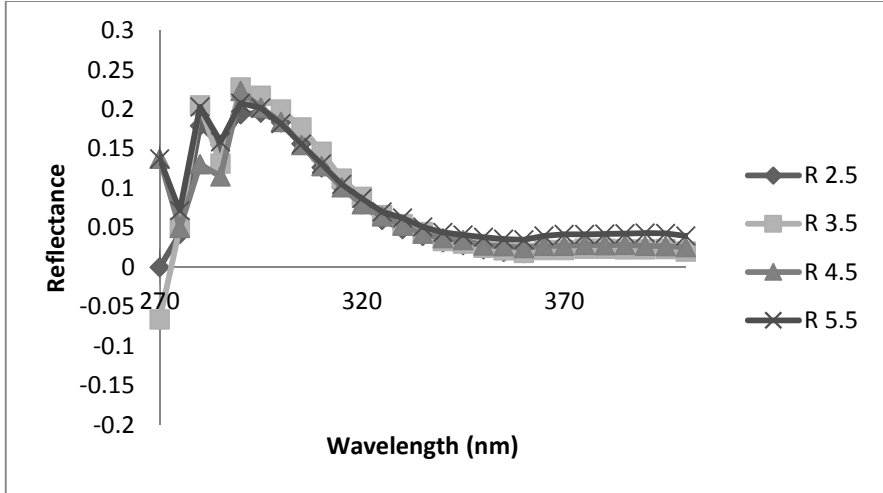**Fig. 10:** Graph of Reflectance against Wavelength (nm) for Al_2S_3

Fig. 11: Graph of Reflectance against Wavelength (nm) for PbO

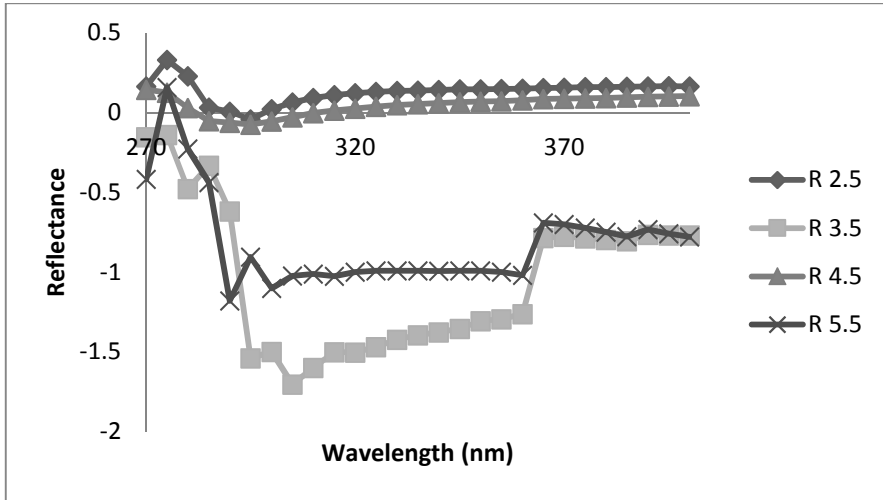**Fig 12:** Graph of reflectance against wavelength (nm) for PbS
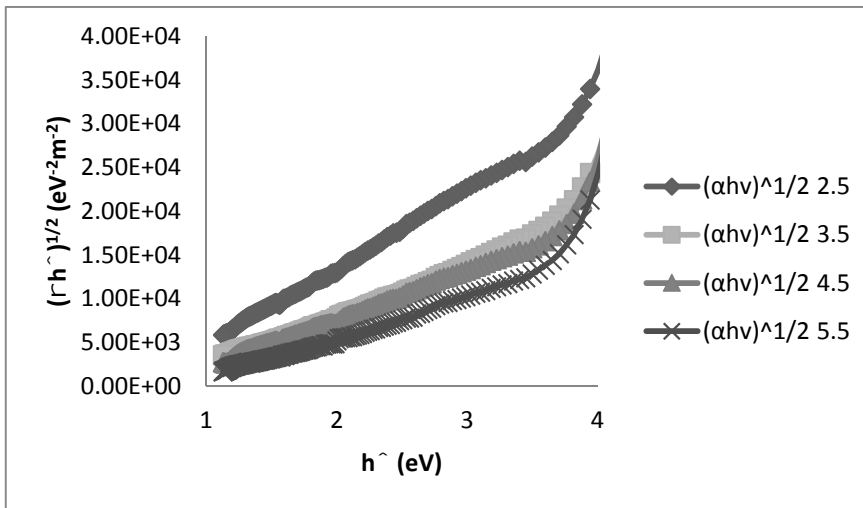
Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on… *Oluyamo and Adebayo* *J of NAMP*

298

Fig. 13: Graph of $(\alpha \upsilon)^{1/2}$ against hυ for Al_2O_3

Fig. 14: Graph of $(\alpha \upsilon)^{1/2}$ against hυ for Al_2S_3

Fig. 15: Graph of $\alpha \upsilon)^{1/2}$ against hυ for PbO

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on…   *Oluyamo and Adebayo*   *J of NAMP*
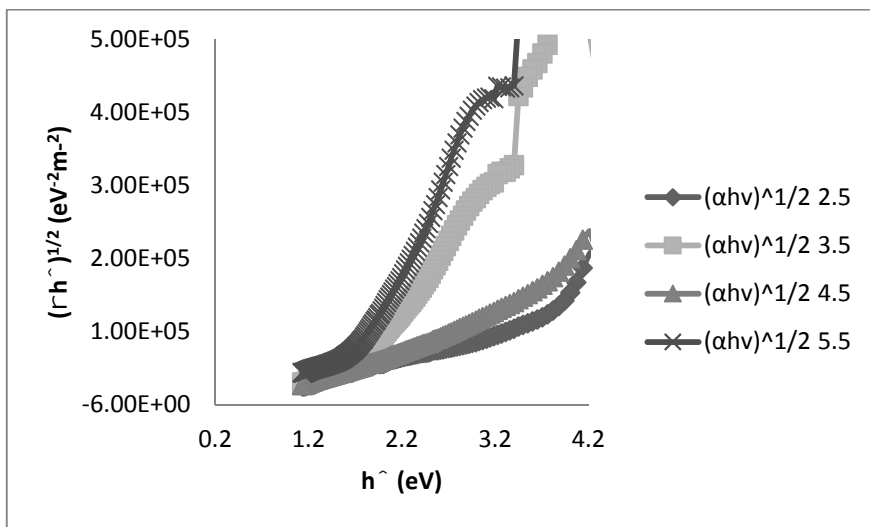
299
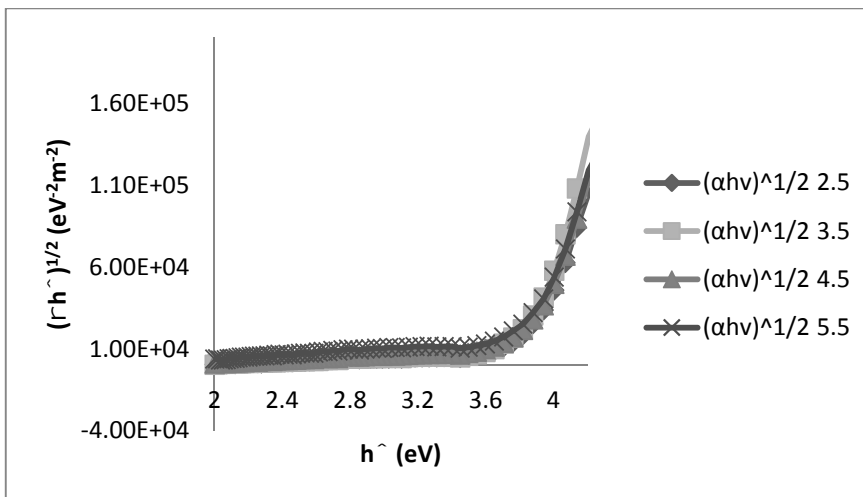
Fig. 16: Graph of $(\alpha \upsilon)^{1/2}$ against $h\upsilon$ for PbS

Table 1: Optical properties of the deposited Al/Pb-sulphide and oxide films

Sample	Period of Deposition (Hours)	Energy Band Gap (eV)	Average Absorbance (A)x10^{-2}	Average Transmittance (T)x10^{-2}	Average Reflectance (R) x10^{-2}	Film Thickness (nm)
`Al_2O_3`	2.5	3.3	1.50	90.51	7.99	440
	3.5	3.4	1.59	94.61	3.80	470
	4.5	2.8	6.37	86.74	6.89	420
	5.5	2.1	5.37	88.63	6.00	380
Al_2S_3	2.5	2.2	46.36	36.40	17.24	780
	3.5	2.4	24.84	56.79	18.37	710
	4.5	2.6	21.91	61.21	16.88	660
	5.5	2.4	14.53	71.90	13.57	610
PbO	2.5	3.2	0.80	98.00	1.20	120
	3.5	3.2	1.08	97.66	1.26	110
	4.5	3.2	1.21	97.27	1.52	110
	5.5	3.0	2.25	95.11	2.63	100
PbS	2.5	2.4	53.62	28.88	17.50	220
	3.5	1.8	101.70	16.65	-18.35	210
	4.5	2,2	56.40	28.46	15.13	200
	5.5	1.8	96.77	17.70	-14.47	150

4.0   Results and Discussion

Figures 1, 2, 3 and 4 show the plots of absorbance against wavelength for the Al/ Pb oxide and sulphide films deposited at room temperature with varied period of deposition. The absorbance of the films increases initially to a maximum within the wavelength range 270-400 nm with distinct peaks at 0.4% for Al_2O_3, 0.8% for Al_2S_3 and 0.35% for PbO respectively with relatively low values in the infrared region of the electromagnetic spectrum. These peaks are highest around 290 nm and thereafter tails off with increasing wavelength. The PbS samples show more absorption within the wavelength range with different peaks and maximum absorbance at 3.02 % and 3.03% at deposition periods of 5.5 and 3.5 hours.

Figures 5, 6, 7 and 8 show the plots of transmittance versus wavelength. The spectra show an initial decrease in curves to a minimum value of about 290 nm with a corresponding sharp increase with wavelength. The highest transmittance of about 100% was noticed at a deposition period of 3.5 hours at 275 nm. The transmission spectra displayed in the figures show decrease in transmittance as the wavelength increases, the samples have about 83% transmittance throughout the UV/VIS/IR region. The high transmittance in the visible region suggests that the thin film could be useful as aesthetic window glaze materials and also suitable for solar energy collection.

Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on…   *Oluyamo and Adebayo   J of NAMP*

300

Figures 9-12 show the plots of reflectance against wavelength. A gradual increase in reflectance with wavelength was observed in Figures 9 and 11 while for Figures 10 and 12, the reflectance decreases to a minimum and then rises gradually before tailing off. Generally, all the films show low reflectance throughout the UV/VIS/IR region. This low reflectance makes the samples important materials for anti-reflection coating and transparent conducting oxides. The materials can also be useful for coating eye glasses for the protection of sunburn as a result of UV radiation. The summary of the optical properties of the films is shown in table 1.

The energy band gaps of the samples were determined using Figures 13-16. The values of the band gap were determined by extrapolation of the straight-line portion to zero. The range of values of the band gap obtained for Al_2O_3 thin films is 2.10-3.40 eV, 2.20-2.60 eV for Al_2S_3, 3.0-3.20 eV for PbO and 1.80-2.40 eV for PbS. In previous research, a band gap range of 1.85-2.60 eV had been reported for PbO [23]. The high value of the energy gap $Eg \geq 3.0$ in this research could be attributed to high pH values of the reactants [24]. The optical properties and thickness of the deposited films are shown in Table 1. The samples in the study exhibit direct band transition. In this type of transition, there is the dependence of absorption coefficient on the photon energy at the vicinity of the absorption edge which corresponds to direct transition (25-27). The band gap energy was also found to decreases with decrease in the film thickness. The result also indicated that optimal performance of the thin films could be achieved by appropriate variation of the period of deposition in the CBD technique.

5.0 Conclusion

Nano crystalline thin films of Al/Pb oxide and sulphide materials were produced and analysed within wavelength range 270-400 nm in the study. Films obtained were found to perform optimally within the ultraviolet and visible region of the electromagnetic spectrum depending on the period of deposition with band gap energy in the range 1.8-3.4 eV. This confirms the materials useful applications in solar device fabrication, aesthetic window glaze materials, antireflection coating and optical sensor devices.

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Journal of the Nigerian Association of Mathematical Physics Volume 29, (March, 2015), 293 – 302
Effects of Deposition Period on…   *Oluyamo and Adebayo   J of NAMP*

301

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