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# Electro-thermal and Optical Properties of SILAR Synthesized PbO Thin Films at Varying Times of Annealing and Constant Temperature

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**ABSTRACT**
PbO thin films were prepared by SILAR method deposition on glass substrates by SILAR method using KOH solution with ammonia ($NH_3$) as a complexing agent. The films were subjected to annealing at the same temperature 250°C using annealing machine. The samples were firmly adhered to the substrate. The samples of PbO have thicknesses of 145nm to 115nm. The transmittance is found to be in the range 0.19 to 0.86 for $B_{25}$ and 0.13 to 0.81 for $B_{26}$ while for absorbance has a sharp fall from about 0.69 to 0.06 for $B_{25}$ and 0.86 to 0.09 for $B_{26}$ as wavelength increases from 250nm to 1080nm. The band gaps obtained under constant thermal treatment and varying times is between 3.7± 0.05eV to 3.6± 0.05eV. The average band gap of PbO is 3.65± 0.05eV. The properties of the PbO thin film makes it suitable for applications in a number of solid state devices such as photo-electrochemical, photovoltaic, photoconductive cells.

Keywords: Transmittance, Absorbance, Band gap, Optical Conductivity, Reflectance

## 1. INTRODUCTION

In future, the applications of nanotechnology in renewable energy technology will be needed in order to ensure a steady and stable electricity generation. This will enable a move away from the existing sources like the nuclear energy and fossil fuels, which have about 90-95% of the world energy budget with a small contribution from the solar energy. And here demands the science and technology of nanotechnology which deals with the development of smaller and smaller devices with a higher speed and greater performance (Chopra and Das, 1983). These materials include CuO, $Cu^2O$(Chandrasekaran, 2013). ZnO, CuS, CuO, ZnS, CdS, CdO etc which are a group of inorganic compounds.

Lead oxide is a toxic, abundant, and an absorber well matched for solar absorption, it has band gap of about 2.26eV to 2.50eV and a melting point of 327$^o$C (Daniel-Umeri *et a*l 2016). Common lead oxides include; lead (II) oxide, PbO, litharge, massicot, lead (II) (V) oxide $Pb_3O_4$, minimum, red lead, lead dioxide (lead (IV) oxide) $PbO_2$. Lead oxide occurs in two polymorphs, one having a tetragonal crystal structure and the other having an orthorhombic crystal structure. Modern applications for PbO are firstly used in lead- based industrial ceramics, including computer components (Grene *et al,* 2003). PbO may be prepared by heating lead metal in air at approximately 600$^o$C. In this work, SILAR deposition method will be adopted in the preparation of PbO thin films.

## 2. MATERIALS AND METHOD

For effective, accurate and adherent results of the deposition of lead oxide thin film on glass slide, by which certain factors were considered before proceeding the deposition process. In this process, the raw materials are in the right measures varied the time of deposition, pH and temperature of the final mixture to see how they will affect the deposition of the film and the properties of the film.
The compound used in the experiments include lead nitrate $Pb(NO_3)_2$, Potassium Hydroxide (KOH), concentrated Hydrochloric acid (HCl) and Nitric acid ($HNO_3$), Ammonia ($NH_3$) which was used as the complexing agent (Substance that moderate the flow of cation in the solution).

The glass substrates were vertically immersed in the beaker containing the solution so that the deposition could be observed. 50ml beaker was used, the substrates were held vertically in the solution.
The substrate were soaked in aqua regia which is the combination of concentrated Hydrochloric acid (HCl) and Nitric acid ($HNO_3$) in the ratio of 3:1 for twenty four hours which should be handle with care. After twenty four hours we throw away the substance, wash the substrate with detergent and rinsed with distilled water. And hang in a slanting order to dry off the water.

## 3. DEPOSITION PROCEDURES

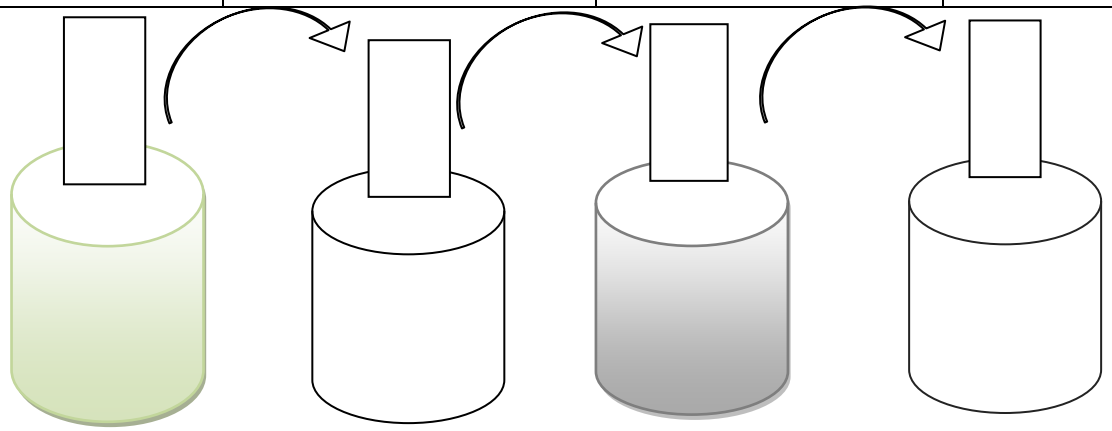
This system does not require any power supply for operations, hence it is economical. in this system, four glass beakers of typically 50ml capacity containing Lead complex solutions for beaker 1 which is 0.5M and deionized water for beaker 2, Potassium Hydroxide for beaker 3 which is 1.6M and deionized water for beaker 4.

The immersion and rinsing of substrates are done manually; the substrate is soaked in beaker 1 for 10 seconds and for beaker 2 for 3 seconds, beaker 3 for 10 seconds and beaker 4 for 3 seconds. Finally this will undergo various cycles with each substrate sample and optimum deposition was observed on the substrates $B_{25}$, $B_{26}$, $B_{27}$, $B_{28}$, $B_{29}$ and $B_{30}$ were dried in air as shown in Fig. 3.1 and the results in Table 3.1.

Table 3.1 Showing deposition time and cycles

| SAMPLE | DIP TIME OF $[Pb(NH_3)_4]^{2+}$ & KOH | DIP TIME OF $H_2O$ | NUMBER OF CYCLE |
|---|---|---|---|
| $B_{25}$ | 10 | 3 | 9 |
| $B_{26}$ | 10 | 3 | 10 |
| $B_{27}$ | 10 | 3 | 8 |
| $B_{28}$ | 10 | 3 | 9 |
| $B_{29}$ | 10 | 3 | 10 |
| $B_{30}$ | 10 | 3 | 8 |





(1) $[Pb(NH_3)_4]^{2+}$ (2) De-ionized $H_2O$ (3) KOH (4) De-ionized $H_2O$

Fig. 3.1 Set up for SILAR method (Pathan and Lokhande, 2014)

## 4. REACTION MECHANISM

$$Pb(NO_3)_2 + 4NH_3 \longrightarrow [Pb(NH_3)_4]^{2+} + 2NO_3^-$$

$$[Pb(NH_3)_4]^{2+} + KOH \longrightarrow PbO + 2K^+ + 4NH_3 + H_2O$$

## 5. POST DEPOSITION PROCESS

The samples after deposition are dried in an annealing machine with the aim of removing water of crystallization. The annealing is done at the same temperature 250°C and with varying annealing time (1hour and 1hour:30min) deposition ending on the complexing agent used.

## 6. RESULTS AND DISCUSSION

The deposition process which are, deposition time, annealing temperature, pH of solution and annealing time were considered, and changes in the properties of the films were observed. But to known the effect of one, all others had to be kept constant. All samples were deposited under the same conditions which are temperature, dip time and PH. Two samples $B_{25}$ and $B_{26}$ were chosen as representative samples. They were deposited at room temperature of $23^0$C, with pH values of 10.6.

Annealing temperature of $250^0$C for all the samples and annealing time of 1hour and 1hour 30min were varied respectively. The thicknesses of the films are 145nm and 115nm for sample $B_{25}$ and $B_{26}$ respectively the thickness as measured by optical method using Rutherford Backscattering (RBS) equipment. The transmittance of the samples were measiured using double beam Spectrophotometer with serial number UV- 1800 series of wavelength ranging from 190nm-1100nm.
The elemental compositions of the samples were determined using Rutherford Backscattering (RBS) : 2.25MeV α-particles IONIX 1.7 MU Trandetron, with a surface barrier detector with energy resolution <15keV.

## 7. COMPOSITION ANALYSIS AND THICKNESS MEASUREMENTS

Table 7.1 Showing composition analysis

| LAYER 2 GLASS $B_{25}$ Before Deposition | | LAYER 1 $B_{25}$ After Deposition | |
|---|---|---|---|
| Ca | 1.83% | Pb | 10.57% |
| Si | 28.0% | O | 89.43% |
| O | 56.0% | - | - |
| Fe | 0.52% | - | - |
| Na | 12.6% | - | - |
| Al | 0.53% | - | - |
| | | Thickness layer 1 $B_{25}$ = 145nm | |

Table 7.1 and Fig. 7.1 show the composition of deposited element of sample $B_{25}$ of layer 2 and layer 1, $Pb^{2+}$ is 10.57% and Oxygen (O) is 89.43% which shows truly that lead oxide thin films were deposited on the substrate with thickness measurement of 145nm. The deposited samples have high percentage of oxygen, which may be due to hydrolysis or hydration (Onwuemeka *et al*, 2014).

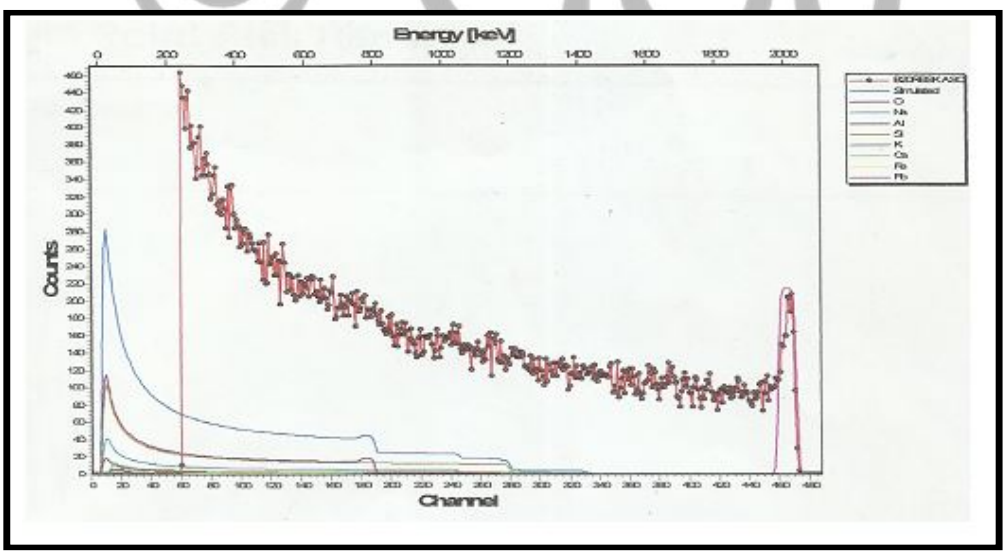



Fig 7.1. Rutherford Backscattering (RBS) of Sample $B_{25}$

Table 7.2 Showing composition analysis

| LAYER 2 GLASS $B_{26}$ Before Deposition | | LAYER 1 $B_{26}$ After Deposition | |
|---|---|---|---|
| Ca | 1.83% | Pb | 12.42% |
| Si | 28.0% | O | 87.58% |
| O | 56.0% | - | - |
| Fe | 0.52% | - | - |
| Na | 12.6% | - | - |
| Al | 0.53% | - | - |
| | | Thickness layer 1 $B_{26}$ = 115nm | |

Fig. 7.2 and Table 7.2 show the composition of deposited element of sample $B_{26}$ of layer 2 and layer 1, b $Pb^{2+}$ is 12.42% and Oxygen (O) is 87.58% which shows that lead oxide was deposited on the substrate with thickness measurement of 115nm.

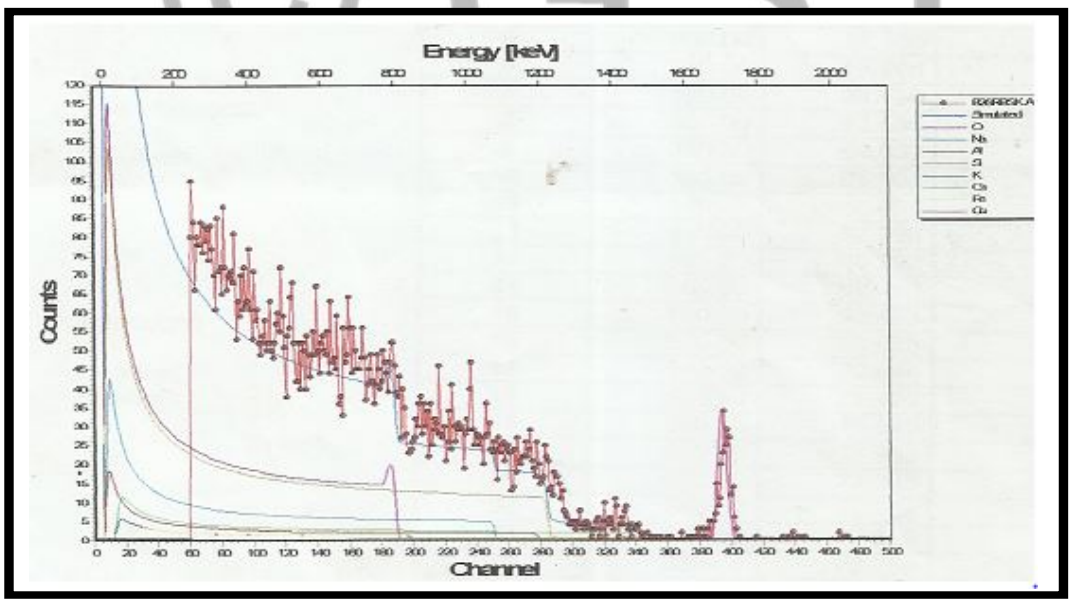



Fig. 7.2. Rutherford Backscattering (RBS) Of Sample $B_{26}$

## 8. OPTICAL CHARACTERIZATION OF PbO THIN FILMS

Optical characterization of the samples, the transmittance which is the ratio of the incident intensity to the transmittance intensity of the radiation was taken as the default. The samples were scanned for transmittance from UV (ultraviolet), through visible down to near infrared region of electromagnetic spectrum. This was from 300nm to 1080nm in wavelength. Absorbance, reflectance, absorption coefficient, refractive index, extinction coefficient, real part of dielectric constant, imaginary part of dielectric constant, optical conductivity, electrical conductivity, thermal conductivity and energy band gap. The transmittance was measured by UV 1800 double beam spectrophotometer.

### TRANSMITTANCE

The transmittance of $B_{25}$ and $B_{26}$ sample of PbO were obtained from the UV double beam spectrophotometer, series 1800. Fig. 8.1 shows the transmittance of $B_{25}$ and $B_{26}$ samples of PbO thin films and their thicknesses. Sample $B_{25}$ has high transmittance which increase from 0.19 to 0.86 as the wavelength increased from UV region (250nm – 400nm) to Visible region (400nm – 700nm) and to (700nm – above) near infrared region of electromagnetic spectrum. Sample $B_{26}$ has low transmittance which increases from 0.13 to 0.81 as the wavelength increases.

Sample $B_{25}$ with high transmittance can be used as windows in infrared optics because of its high transmittance in infrared region. Sample $B_{26}$ with low transmittance at the UV can be used as optical coatings a (Onwuemeka and Nwulu, 2017), smart windows and ornamental coatings.

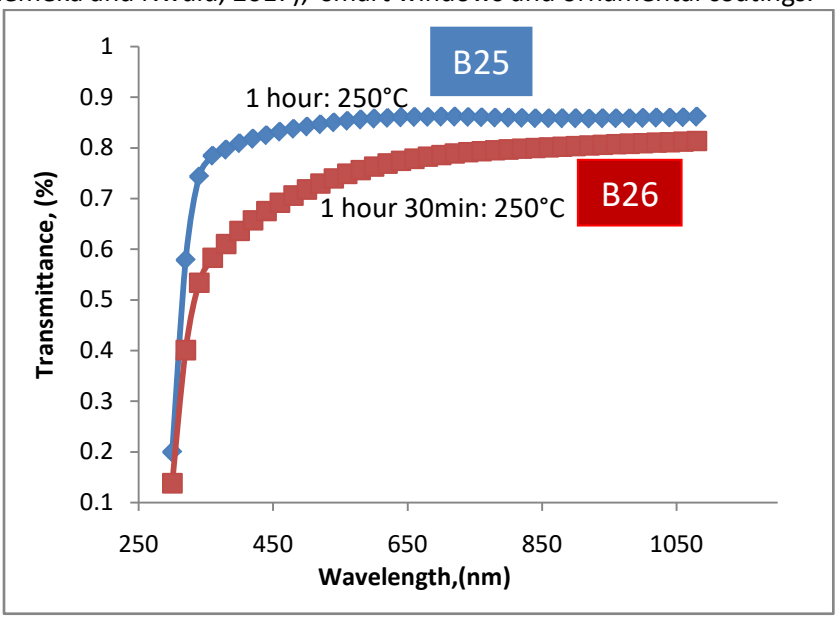



Fig. 8.1 Transmittance of $B_{25}$ & $B_{26}$ sample of PbO thin film against Wavelength

**ELECTRICAL CONDUCTIVITY**

The electrical conductivity $\delta_e$ of $B_{25}$ and $B_{26}$ sample of PbO were obtained from Eqn

$$\delta_e = y\lambda\alpha^2 \qquad (8.1)$$

where y is a constant, $\lambda$ is wavelength and $\alpha$ is the absorption coefficient.

For sample $B_{25}$ decreases from $4.97x10^{+12}\Omega^{-1}m^{-1}$ to $1.04x10^{+12}\Omega^{-1}m^{-1}$ in electrical conductivity and increases from 250nm to 1080nm in the electromagnetic spectrum. For sample $B_{26}$ decreases from $7.49x10^{+12}\Omega^{-1}m^{-1}$ to $2.59x10^{+12}\Omega^{-1}m^{-1}$ and increases from 250nm to 1080nm in the electromagnetic spectrum which is in line with Jiang *et al, 2002.*

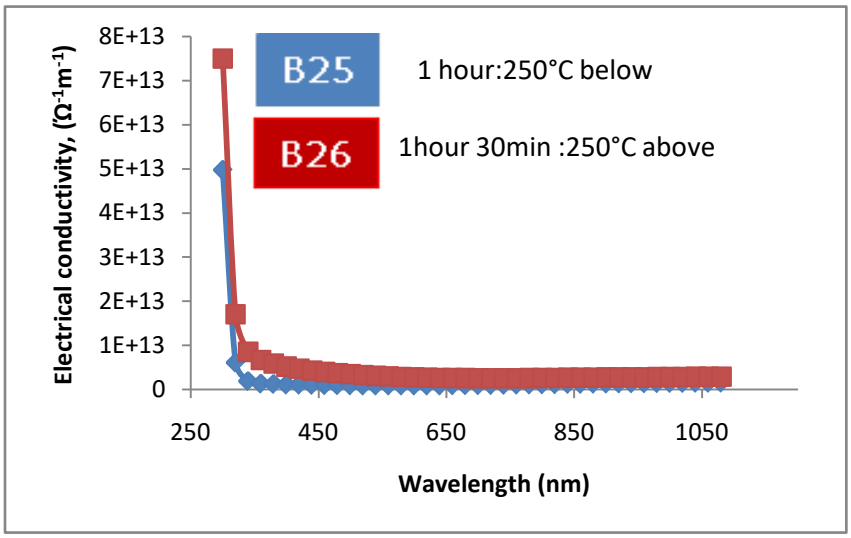



Fig. 8.2 Electrical conductivity of $B_{25}$ & $B_{26}$ sample of PbO thin film against Wavelength

**THERMAL CONDUCTIVITY**

The thermal conductivity k of $B_{25}$ and $B_{26}$ samples of PbO were obtained based on the relation between electrical conductivity as given in Equation (8.2)

$$\kappa = [\delta_e T]1.49 \times 10^{-8} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.2),$$

where T is the temperature and $\delta_e$ is electrical conductivity

For sample $B_{25}$ decreases from $2.09x10^{+6}\Omega^{-1}m^{-1}$ to $306x10^{+5}\Omega^{-1}m^{-1}$ in thermal conductivity with increasing wavelength 250nm to 1080nm in the electromagnetic spectrum. For sample $B_{26}$ decreases from $2.56x10^{+7}\Omega^{-1}m^{-1}$ to $8.85x10^{+5}\Omega^{-1}m^{-1}$ with increasing wavelength from 250nm to 1080nm in the electromagnetic spectrum in Fig 8.3.

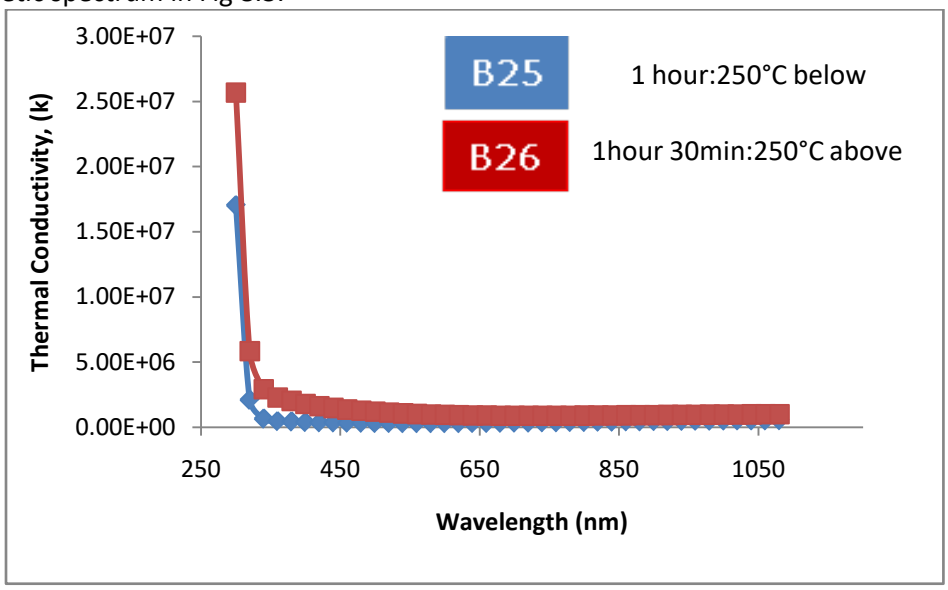



Fig. 8.3: Thermal conductivity of $B_{25}$ & $B_{26}$ sample of PbO thin film against Wavelength

**ENERGY BAND GAP**

The band gap is obtain from the graph of $(\alpha h\upsilon)^2$ against $h\upsilon$ as shown in Fig 8.4 where $h\upsilon$ is the photon energy. The extrapolation of the linear portion of the graph where $(\alpha h\upsilon)^2 = 0$. The values of band gap for samples $B_{25}$ and $B_{26}$ are 3.7 ± 0.05eV and 3.6 ± 0.05eV respectively and in average 3.65 ± 0.05eV. The band gap value of PbO thin films reported in the work by Radhakrishnan et al is 2.16eV which is different from the band gap values obtained in this work with a wide band gap of 3.65eV in average. Since it exhibits p-type semiconductor material, it is a promising material for solar energy conversion. With this wide band gap it is highly suitable for many applications in a number of solid state devices such as photo-electrochemical, photovoltaic, photoconductive cells (Ownuemeka and Ekpunobi, 2018).

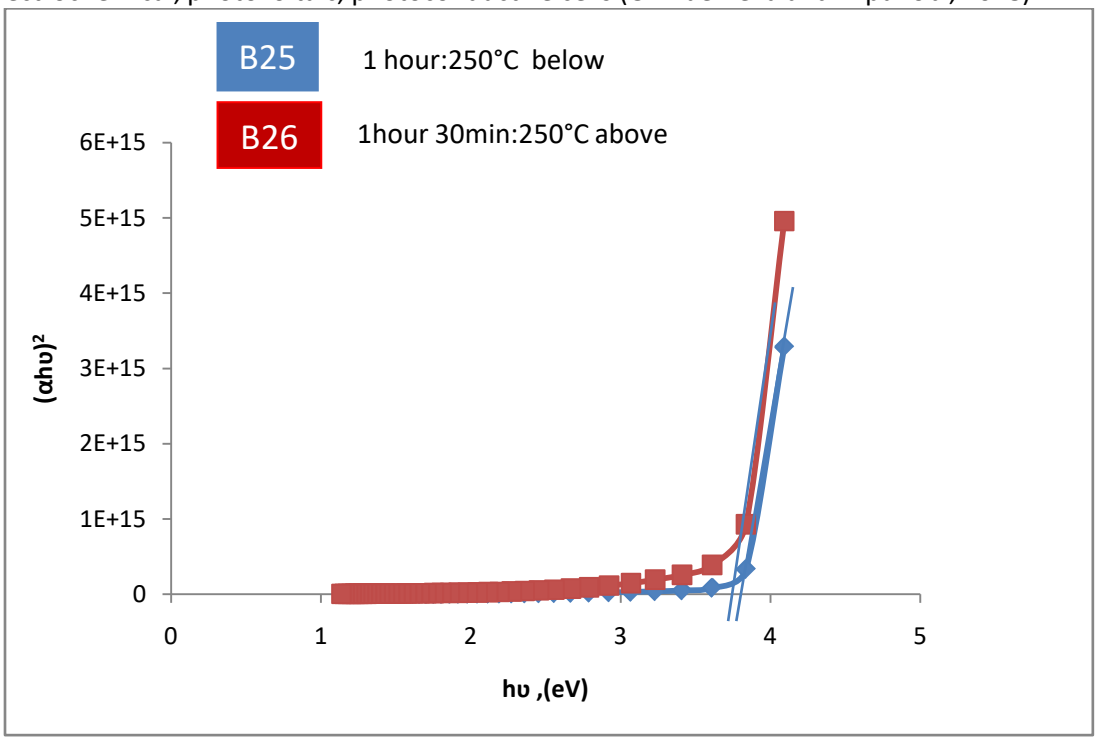



Fig. 8.4 Energy band gap $(\alpha h\upsilon)^2$ against $h\upsilon$

## 9. CONCLUSION

The PbO thin films have successfully been deposited on glass substrates. This was achieved using SILAR method which was preferred over all over other solution deposition techniques because it is cheap, effective, accurate and easy to execute procedure. The substrates were prepared in aqua regia before been use for deposition to achieved an efficient results. The complexing agent used is ammonia ($NH_3$) while $[Pb(NH_3)_4]^{2+}$ were used as the source of cation and KOH as source of anion.

The deposition of PbO was carried out at room temperature of 23°C. The samples were then annealed at 1hour and 1hour:30minute at constant temperature of 250°C. The transmittance was measured using UV doule beam spectrophotometer of Serial number 1800 series of the wavelength range of 190nm to 1100nm.

The values were then used as default to calculate other values of the Optical properties, thermal and electrical conductivity. The graphs of the optical characterization were then plotted against wavelength for two samples produced. The energy band gap was determined from the graph of $(\alpha h\upsilon)^2$ against $h\upsilon$ by extrapolation of straight portion of the curves to $h\upsilon$ axis where $(\alpha h\upsilon) = 0$. The band gap was observed to be of the average 3.65 ± 0.05eV. As a material with wide energy band gap, it can effectively be used as photo–electrochemical, photovoltaic, photoconductive cells.

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