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# Electroless Deposition of Thin Film of Lead Sulphide (Pbs) and Measurement of Its Physical, Electrical and Optical Properties

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## *Abstract*

***The Electroless deposition of the thin films of lead sulphide (PbS) was successfully conducted. Properties of the films which include the thickness, absorbance, transmittance, reflectance, band gap energy, conductivity type and charge carrier mobility were studied using UV–visible spectra photometer model 6405, four point probe and hot probe, pH meter, and meter toledo (AB0084) electric beam balance with four decimal places . The study revealed the thickness of the film to be in the range 0.71µm–3.34µm, absorbance (0.02A –1.105A), Transmittance in the range (0.9% - 99%), reflectance in the range, (0.11% - 98%) within wavelength of the radiations (400nm – 1000 nm),Where energy band gap in the range (1.6 eV – 2.70 eV), charge carrier mobility on average is 7803 $cm^2/Vs$ and the deposited thin film Lead Sulphide is a p-type semi-conductor material.***

**Keywords:** Thin film, Electroless deposition, lead sulphide (PbS)

## 1.0 Introduction

A thin film is a layer of material deposition whose thickness is of the order of a given wavelength of an electromagnetic radiation. The layers of materials are coated on substrates which could be plastics, glasses or metal to accomplish a desirable effect. Thin films are crystalline or non-crystalline materials developed on a substrates surface by physical or chemical method [1]. The significances of thin film cannot be over emphasized among which are in the production of camera lenses, diachronic mirrors, solar cells, solar thermal system, photovoltaic power system, etc. Lead Sulphide had been used in infra-red detectors since mid 1940s [2] and it was for this application that the chemical bath deposition technique for Lead Sulphide thin films known since 1910 was initially developed in the late 1940s.it is well known that Chemical Bath Deposition (CBD) is an "electroless" technique that is attractive as a simple and low cost method[3]. Typical deposition process involves the immersion of glass substrate in alkaline. Lead thiourea solution yielded Lead Sulphide (PbS) thin films of various thickness [4]. Many techniques have been reported for the deposition of PbS thin films such as electrodeposition (ED) [5], chemical spray deposition (CSD) [6], and thermal evaporation techniques [7]. Of the various techniques the chemical bath deposition (Electroless deposition) is an attractive method because good uniformity films can be grown at a low cost [8]. In this work, an attempt has been made to study the physical ,electrical and optical properties of the PbS thin films with different thicknesses ranging from 250 to 700 nm grown by Chemical bath deposition technique on glass substrate. Hence, this research is to measure the physical, electrical and optical properties of thin films of lead Sulphide (PbS), since a low cost, less sophisticated techniques is used compared to the literature reviewed.

## 2.0 Methodology

### 2.1 Substrate Preparation

A microscopic glass slide of dimension 25.4mm x 76.2mm and 1mm thick were used as substrate. The glass slides were decreased in concentrated nitric acid ($HNO_3$) for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air.

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## 2.2 Solution Preparation

The solution for deposition of lead sulphide thin film on both surfaces of glass substrates (microscopic glass slides) were constituted from aqueous solution of 1.0 mole tri-ethanol Amine (TEA) and 1 mole of sodium hydroxide (NaoH). The equivalent mass concentrations of solid reagents were measured using meter toledo (AB 0084) electric beam with four decimal places.

## 2.3 Deposition of Lead Sulphide

In this research the chemical bath deposition contains 37.9340g lead dissolved in 100ml of distilled water, 7.6120g of thiourea dissolved in 100ml of distilled water, 13.7325ml of Tri ethnol amine 100ml in distilled water; 4g of sodium hydroxide dissolved in 100ml of distilled water. The various solutions of the reagents are poured together in a chemical bath and stirred until the solid components of the solution dissolved completely before the substrates were immersed vertically using a peg and tied to a clamp on a retort stand. The temperature of the solution was at room temperature. Sodium hydroxide solution was added to increase the pH level of the solution to 9 which was measured by using a sumtex sp – 70/pH.MV/temperature.

The formation of the Lead Sulphide (PbS) thin film on the glass substrate can be explain by the following chemical reaction:

$Pb\ (N0_3)_2 + TEA \rightleftharpoons (PbTEA)^{2+} + 2N0_3$ (1)

$Pb\ (TEA)^2 \rightleftharpoons pb^{2+} + TEA$ (2)

$(NH_2)_2\ CS \rightleftharpoons CH_2N_2 + H_20 + HS$ (3)

$HS + 0H \rightleftharpoons H_20 + S^{2-}$ (4)

$Pb^{2+} + S^{2-} \rightleftharpoons PbS$ (5)

The presence of the $S^{2-}$ from the hydrolysis of thiourea and $Pb^{2+}$ from lead acetate produce the PbS layer.

## 2.4 Thickness Measurement

The mass of the deposited PbS was obtained by measuring the empty substrate before deposition and re-measured after deposition using Metter Toledo (AB 0084) electrical beam balance.

## 2.5 Conductivity Type Measurement

The hot probe method was used to determine the conductivity type of the deposited lead sulphide thin-films. The two identical stainless steel soldering equipment connected to a voltmeter were placed on the surface of the lead sulphide thin film. One of the probes was heated while the other was at room temperature. The hot probe heated the PbS sample under it, which led to an increase in the kinetic energy of the free carrier. The carrier diffused from the hot to the cold region creating an electric field that opposed the diffusion. The electric current produced a potential which was detected by milliammeter. For n-type semi conductor electrons flew away from the hot probe leaving a positive charge donor and it caused the hot end to have a positive potential with respect to cold probe. In the p-type semi conductor, the current flow will be in reverse [9].

## 2.6 Band Gap Energy Measurement

The optical absorption spectra of lead sulphide thin film deposited by the use of the chemical bath method were obtained using JEN WAY 6405 UV – VIS spectro photometer. An empty glass slide of 1cm width was cut and used to take the base line, which cancelled the effect of absorption of the glass slide. The deposited thin-films of PbS were scanned within the range of 250 – 700nm wavelength between UV and visible spectrum. Other optical and solid properties were obtained from the spectra data by calculations based on the theory.

## 2.7 Measurement of Charge Carrier Mobility (μ)

The Hall Effect measurement is one of the variable ways of characterizing semi conductor materials, whether silicon based compound semi conductor, thin film materials for solar cell or nano scale materials. The first step in determining carrier charge mobility is to measure the Hall voltage. The hall voltage of lead sulphide deposited on glass substrate was measured by placing the sample on a powerful magnet perpendicular to the sample in order to create the magnetic field and a current through sample. This combination creates a transverse current. The resulting potential was measured across the device.

## 3.0 Results and Discussion

Four different samples were deposited during the *exp*eriment, equal volume of solution; the same temperature (room temperature) and pH were also used for all the samples. The time taken for deposition was varied; sample $A_{12}$ for one day, $B_{12}$ for two days, $C_{12}$ for three days, $D_{12}$ four days respectively.

## 3.1 The Thickness Calculation

The thickness of the deposited lead sulphide was obtained as follows

Density $\rho$ is defined as

$$\rho = \frac{m}{V} \tag{6}$$

But $V = At$ (where A = Area and t is thickness)

Thus, rearranging (6) yields

$$t = \frac{m}{\rho A} \tag{7}$$

Where, $m$ is the mass of deposited PbS and $V$ is the volume

Table 1 Shows the relation between the thickness of the samples deposited and the time taken. From the relation it shows that the thicknesses of the films were 0.71µm, 0.83µm, 2.92µm and 3.34µm for samples $A_{12}$, $B_{12}$, $C_{12}$, and $D_{12}$ respectively. Thus, the thickness of the films increases as the number of day increases.

Table 2 shows the wave length in ($\mu$m), Transmittance, Reflectance and Absorbance. Absorbance was obtained from machine while transmittance and reflectance were calculated. From the calculations, it shows that the absorbance is directly proportional to the transmittance and inversely proportional to the reflectance, that is, the higher the absorbance, the higher the transmittance and the lower the reflectance. This relation shows that thin film of Lead Sulphide deposited will be a reliable material for solar cell fabrication as an anti- reflectance material.

## 3.3 Charge Carrier Mobility Calculations

The charge carrier mobility of the sample was calculated using equation (8)

$$\mu = \frac{slope}{(W/L)B} \tag{8}$$

Where the slope was obtained from a graph of $V_H$ (mV) against $V_L$ (Volt)

$$slope = \frac{V_H}{V_L} \tag{9}$$

$W$ and $L$ are the width and length of the substrate samples

$W$ = 2.54 x $10^{-2}$ m $L$ = 7.62 x $10^{-2}$ m

The magnet used has a magnetic field strength B = 0.03T

Table 3: Shows the load voltage $V_L$ and Hall voltage $V_H$ obtained from the samples. The relation was used to plot the graph that obtains the slope needed for the calculation of the electron mobility. It is observed that the mobility of electron in lead sulphide samples are (7273, 7879, 7979, 8081) $cm^2 V^{-1} s^{-1}$ as calculated and the average mobility for the lead sulphide sample is calculated to be 7803 $cm^2 V^{-1} s^{-1}$ which can be compared with the average value of 7850 $Vm^2 v s^{-1}$ obtained in [10].

## 4.0 Discussion

The cations $Pb^{2+}$ and anions $S^{2-}$ in the deposition solution reacts to become neutral atoms called thin films of lead sulphide which is deposited on the glass substrates. The precipitation could be spontaneously fast or proceed slowly. Fast precipitation implied that thin films could not be formed on the substrate immersed in the solution [8]. The complexing agents, tri ethanol amine (TEA) slowed down the precipitation action for the thin film of neutral atom PbS to form. The addition of sodium hydroxide solution served as pH stabilizer.

Figures 1-4 show a graph of $(\alpha E)^2$ against the energy (photon energy) of samples $A_{12}$, $B_{12}$, $C_{12}$, and $D_{12}$ respectively. The energy band gap values were obtained by extra polation of linear portion of the graph to X-axis. The particular point where the straight line or tangent touches the X-axis gives the energy band gap. The linear dependence of $(\alpha E)^2$ with (hv) indicates that the films have a direct band gap[11]. The nature of the graph plotted shows the presence of band to band direct transition. From the graph, energy band gap were estimated to be 1.6 eV for sample $A_{12}$, 1.9 eV for sample $B_{12,}$ 2.45 eV for sample $C_{12}$, and 2.7 eV for sample $D_{12}$, Range (1.6 eV-2.7 eV). The results of the energy band gap can be compared with 1.9 eV reported in [12]. The result is also in a good agreement with the range of 1.88 eV-2.28 eV reported in [8].

The conductivity type of the films was determined by hot probe to be P-type. The transmittance and reflectance in percentage were obtained as $A_{12}$ (0.9%-13%) and reflectance $A_{12}$ (86% - 99%) for wavelength of radiations ranging from 400nm-

1000nm, $B_{12}$ transmittance was in range (2% - 98%) and reflectance (98%- 0.11%), $C_{12}$ transmittance (9%-55%) and reflectance (43% -91%) with wavelength ranging from 400nm – 1000nm. $D_{12}$ transmittance (29%-81%) and reflectance (18% -77%) with wavelength ranging from 400nm – 1000nm.

## 5.0 Conclusion

The optical properties of the thin films of lead sulphide (PbS) such as absorbance, energy band gap, transmittance, reflectance and the charge carrier mobility (μ) of the materials were studied. The study revealed the absorbance to be in the range (0.02A-1.105A) transmittance in the range (0.9%)-99%) reflectance in the range (0.11%-98%) within the wave length of the radiations (400nm- 1000nm) energy band gap in the range (1.6eV – 2.70eV) and the charge carrier mobility on average is $7803 cm^2/Vs$ which is in agreement with values obtained by other researchers in the field of lead sulphide.

**Table 1**: Shows the relation between the thickness of the samples deposited and the time taken.

| Sample | Deposition time (day) | Thickness Of the deposited layer ($\mu$ m) |
|---|---|---|
| $A_{12}$ | 1 | 0.71 |
| $B_{12}$ | 2 | 0.82 |
| $C_{12}$ | 3 | 2.95 |
| $D_{12}$ | 4 | 3.43 |

**Table 2**: Shows the wavelength, absorbance, transmittance and reflectance of deposition of thin film lead Sulphide (PbS) from day 1 to day 4

| | Day 1 Deposition | | | | Day 2 Deposition | | | | Day 3 Deposition | | | | Day 4 Deposition | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S/No | Wave Length(nm) | Absorbance( A) | Transmittance (%) | Reflectance (%) | Wave Length(nm) | Absorbance (A) | Transmittance (%) | Reflectance (%) | Wave Length(nm) | Absorbance( A) | Transmittance (%) | Reflectance (%) | Wave Length(nm) | Absorbance( A) | Transmittance (%) | Reflectance (%) |
| 1 | 400 | 1.105 | 13 | 86 | 400 | 1.991 | 98 | 0.11 | 400 | 1.740 | 55 | 43 | 400 | 1.906 | 81 | 18 |
| 2 | 450 | 0.726 | 5.0 | 94 | 450 | 1.981 | 96 | 2.0 | 450 | 1.374 | 24 | 75 | 450 | 1.815 | 65 | 33 |
| 3 | 500 | 0.454 | 2.0 | 97 | 500 | 1.921 | 83 | 15 | 500 | 1.209 | 16 | 83 | 500 | 1.789 | 62 | 36 |
| 4 | 550 | 0.285 | 1.0 | 98 | 550 | 1.904 | 80 | 18 | 550 | 1.167 | 15 | 84 | 550 | 1.685 | 48 | 50 |
| 5 | 600 | 0.140 | 1.0 | 99 | 600 | 1.888 | 77 | 21 | 600 | 1.110 | 13 | 86 | 600 | 1.623 | 42 | 56 |
| 6 | 650 | 0.052 | 0.9 | 99 | 650 | 1.533 | 34 | 64 | 650 | 1.085 | 12 | 87 | 650 | 1.641 | 44 | 54 |
| 7 | 700 | -0.076 | 0.9 | 99 | 700 | 1.085 | 12 | 87 | 700 | 1.027 | 11 | 88 | 700 | 1.620 | 42 | 56 |
| 8 | 750 | -0.054 | 0.9 | 99 | 750 | 0.754 | 6.0 | 93 | 750 | 0.987 | 10 | 89 | 750 | 1.611 | 41 | 57 |
| 9 | 800 | -0.040 | 0.9 | 99 | 800 | 0.289 | 2.0 | 98 | 800 | 0.701 | 5.0 | 94 | 800 | 1.338 | 22 | 77 |
| 10 | 850 | -0.036 | 0.9 | 99 | 850 | 0.320 | 2.0 | 98 | 850 | 0.874 | 7.0 | 92 | 850 | 1.411 | 25 | 73 |
| 11 | 900 | -0.026 | 0.9 | 99 | 900 | 0.253 | 2.0 | 98 | 900 | 0.888 | 8.0 | 91 | 900 | 1.444 | 28 | 71 |
| 12 | 950 | -0.023 | 0.9 | 99 | 950 | 0.229 | 2.0 | 98 | 950 | 0.895 | 8.0 | 91 | 950 | 1.418 | 26 | 73 |
| 13 | 1000 | -0.022 | 0.9 | 99 | 1000 | 0.302 | 2.0 | 98 | 1000 | 0.963 | 9.0 | 90 | 1000 | 1.459 | 29 | 70 |

**Table 3**: Shows the Load Voltage ($V_L$) and Hall Voltage relation for the samples $A_{12}$ to $D_{12}$ .

| | Sample $A_{12}$ | | Sample $B_{12}$ | | Sample $C_{12}$ | | Sample $D_{12}$ | |
|---|---|---|---|---|---|---|---|---|
| s/n | $V_L$ (Volts) | $V_H$ (mV) | $V_L$ (Volts) | $V_H$ (mV) | $V_L$ (Volts) | $V_H$ (mV) | $V_L$ (Volts) | $V_H$ (mV) |
| 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2 | 0.50 | 3.90 | 0.50 | 4.20 | 0.50 | 4.00 | 0.50 | 3.50 |
| 3 | 1.00 | 7.80 | 1.00 | 8.10 | 1.00 | 7.90 | 1.00 | 7.10 |
| 4 | 1.50 | 11.8 | 1.50 | 12.2 | 1.50 | 12.0 | 1.50 | 10.7 |
| 5 | 2.00 | 15.7 | 2.00 | 16.1 | 2.00 | 15.9 | 2.00 | 14.3 |
| 6 | 2.50 | 19.7 | 2.50 | 20.2 | 2.50 | 20.0 | 2.50 | 17.9 |
| 7 | 3.00 | 23.6 | 3.00 | 24.1 | 3.00 | 23.9 | 3.00 | 21.5 |
| 8 | 3.50 | 27.5 | 3.50 | 28.1 | 3.50 | 27.8 | 3.50 | 25.1 |
| 9 | 4.00 | 31.4 | 4.00 | 32.0 | 4.00 | 31.6 | 4.00 | 28.7 |

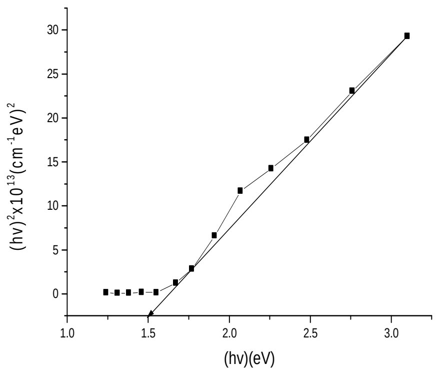


Fig1:Graph of $(hv)^2$against energy for sample $A_{12}$

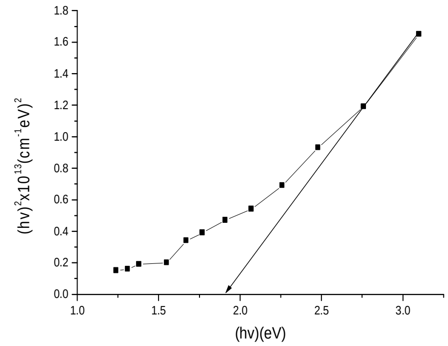


Fig 2: Graph of $(hv)^2$ against energy for sample $B_{12}$

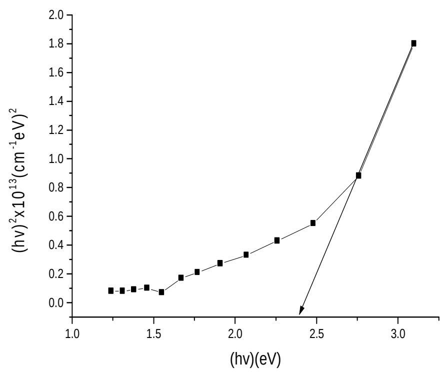


Fig 3:Graph of$(hv)^2$ against energy of sample $C_{12}$

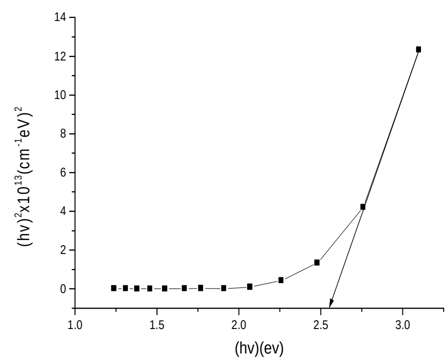


Fig 4: Graph of $(hv)^2$against energy for sample $D_{12}$

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