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Effects of the Composition of Reaction Bath on Growth, Optical and Electrical Properties of PbS Thin Films

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Abstract

The role of deposition conditions and parameters had been subject of concern in thin film fabrication as they constitute essential factors for optimum utilization and applications of the thin films materials. Lead Sulphide thin films have been deposited onto glass substrates from Lead trioxonitrate (V) [$Pb(NO_3)_2$], 1M solution of Thiourea [$SC(NH_2)_2$], 1M solution of sodium hydroxide [NaOH] as the basic medium and 1M solution of triethanolamine (TEA) as the complexing agent in an aqueous solution by chemical bath deposition technique. In this work, the volume compositions of the precursors were varied. The deposited samples were characterized using a Jenway 6405 spectrophotometer, and the effects of the reaction conditions on the properties of the Lead Sulphide [PbS] thin films deposited were observed. The optical and electrical properties of the thin films were found to be thickness dependent. The presence of direct transition with band gap energy ranging between 3.30 eV-3.80 eV was also observed. This range of value indicates the applications of the films as antireflective materials and their use in the fabrication of solar cells. The study however, revealed that the composition of the reaction bath has effect on the properties of the deposited films.

Keywords: Lead Sulphide, Chemical bath deposition, Optical and Electrical properties

1.0 Introduction

Thin films technology had become significant in everyday life due to the numerous applications in various facets of human utilization. The range of such utilization and applications cannot be overemphasized. Thin films had found applications in the fabrication of electronic displays, optical coatings, magnetic films and data storage devices.

Lead Sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate bulk energy band gap of 0.4 eV at 300K and a relatively large excitation Bohr radius of 18 nm [1]. These properties make PbS very suitable for infrared detection application [2, 3]. PbS, which is also known as galena, is the principal ore and most important compound of lead. Intensive research has been performed in the past to study the fabrication and characterization of these compounds in the form of thin films [4 - 6]. PbS is one of the oldest and most common detection element materials in various infrared (IR) detectors. As an IR detector, PbS functions as a photon detector, responding directly to the photons of radiation, as opposed to thermal detectors, that respond to a change in detector element temperature caused by the radiation. A number of methods for the preparation of PbS thin films have been reported, but chemical bath deposition is found to be attractive due to the low cost method of fabrication. Although chemical bath deposition has been used as a technique for preparing films for decades, utilization of CBD semiconductors in photovoltaic devices is much more recent [7 - 9]. Large number of materials that can be prepared by CBD and their prospective applications in solar energy conversion, mainly in the area of thin-film solar cells had been identified. This has increased the research interest in chemically deposited semiconductor thin films. It has been found that the microstructure and the electrical properties of thin films are different from the properties reported for the bulk material with the same composition. Pardo et al [10] have studied the electrical conductivity of epitaxial thin films of $Sr_4Fe_6O_{13-\delta}$deposited on single crystal $NdGaO_3$ and the dependency of the conductivity on the film thickness.

Recently, the effects of deposition parameters on electrical and structural characterization of PbSe thin films were investigated. The study revealed that the pH and time of deposition have influence on the solid state properties of the films [11]. In a similar vein, Oluyamo et al [12] examined the optical properties of Copper (I) Oxide thin films using two different precursors in the Successive Ionic Layer Adsorption and Reaction Technique (SILAR). The research aimed at ascertaining the best anionic precursors that could generate better quality films for solar device applications.

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This paper reports the effect of variation of the deposition parameters on the growth, optical and electrical properties of PbS thin films prepared by chemical bath deposition technique. The possible applications of the material in solar device technology will also be examined.

2.0 Materials and Method Used for the Deposition of PbS Thin Film

In the deposition of PbS, glass slides of dimension 75m x 25mm x 1mm, were used as substrates. The slides were adequately degreased by boiling in a concentrated hydrochloric (HCl) acid for 24hours, followed by a thorough wash in detergent, rinsed in plenty of distilled water and dried in a dust free environment. The materials used are 1M Solution of Lead trioxonitrate (v) [$Pb(NO_3)_2$] as pb^{2+} ions source, 1M solution of Thiourea [$SC(NH_2)_2$] as the S^{2-} ions source, 1M solution of sodium hydroxide [NaOH] as the basic medium and 1M solution of triethanolamine (TEA) as the complexing agent. Three different reaction bath compositions (labeled B, D and E) were made in a beaker, by varying the volumes of precursors and distilled water was added to the solution to achieve a total volume of 50ml. the resulting solution was thoroughly stirred with the aid of a glass rod stirrer for about sixty seconds, to obtain homogeneous solution. The chemical equations for the reactions are as follow;

$$Pb(NO_3)_2 + TEA \longrightarrow [Pb(TEA)]^{2+} 2NO_3 \quad (1)$$

$$[Pb(TEA)]^{2+} \longrightarrow Pb^{2+} + TEA \quad (2)$$

$$SC(NH_2)_2 + OH^- \longrightarrow CH_2N_2 + H_2O + SH^- \quad (3)$$

$$2SH^- + 2OH^- \longrightarrow S^{2-} + 2H_2O \quad (4)$$

The presence of Pb^{2+} and S^{2-} ions led to the formation of PbS, as follows;

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

The cleaned sides were clamped vertically in the reaction bath with the aid of a synthetic cover, which also help to screen off dust and other impurities from getting into the reaction bath. The spectra absorbance (A) and transmittance (T) of the samples at various pH and 300K for 24 hours were obtained with a Jenway 6405 spectrophotometer.

3.0 Theoretical Consideration and Calculations

The Spectral Reflectance (R) was obtained from the law of conservation of energy,

$$A + T + R = 1 \quad (6)$$

The absorption coefficient (absorbing power) (α) is calculated from the equation [13];

$$I = I_0 exp(-\alpha L) \quad (7)$$

where $\alpha = Ln(T^{-1})/L$, I_0 is the incident flux, I is the flux at a distance L in the medium and $T = 1/I_0$ T is the transmittance.

The refractive index (n) is obtained by the expression [14]

$$R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2] \quad (8)$$

where k^2 is the extinction coefficient. For semiconductors and insulators,$k^2 \ll (n-1)^2$. so that the expression is reduced to;

$$R = (n-1)^2/(n+1)^2 \quad \text{and}$$

$$n = (1+R^2)/(1-R^2) \quad (9)$$

The dielectric constant is given by the expression[15, 16]

$$\varepsilon = \varepsilon_r + \varepsilon_i \quad (10)$$

$$\varepsilon = (n+ik)^2 \quad (11)$$

where ε_r and ε_i are the real and imaginary parts respectively of ε and $(n+ik)$ is the complex refractive index. Hence,

$$\varepsilon_r = n^3 - k^2 \quad (12)$$

and

$$\varepsilon_i = 2nk \quad (13)$$

where $k = \alpha\lambda/4\pi$

The energy band gap E_g was computed from the expression[17]

$$\alpha \propto (h\upsilon - E_g)^n \quad (14)$$

where $h\upsilon$ is the photon energy, $n = 1/2$ for direct allowed energy transitions of electrons between valence and conduction bands and $n = 3/2$ for direct forbidden transition. Near the absorption edge,

$$\alpha \propto (h\upsilon - E_g)^{1/2}$$

$$(\alpha)^2 = h\nu - E_g \quad (15)$$

Values of the bandgap (E_g) were obtained from the straight line portion of the plots of $(\alpha)^2$ against $h\nu$ as shown in Fig. 4.0 when extrapolated to the portion where $(\alpha)^2 = 0$.

The electrical conductivity (σ_e) of the films was deduced using the equation [18]

$$\sigma_e = \frac{E_c^2}{\omega} = \frac{E_c^2}{2\pi f} = \frac{E_c^2}{2\pi}\lambda \quad (16)$$

where E_c is wave number and ω is the angular frequency or

$$\sigma_e = 2\lambda_0\sigma_0/\alpha = \frac{2\lambda\alpha nc}{4\alpha\pi} = \lambda nc/2\pi \quad (17)$$

4.0 Result and Discussion

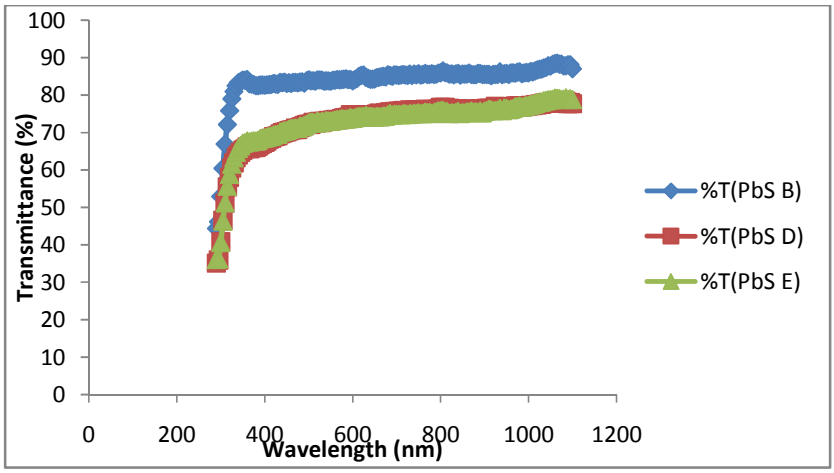

Figure.1.0: Graph of transmittance as a function of wavelength for different composition of PbS thin films.

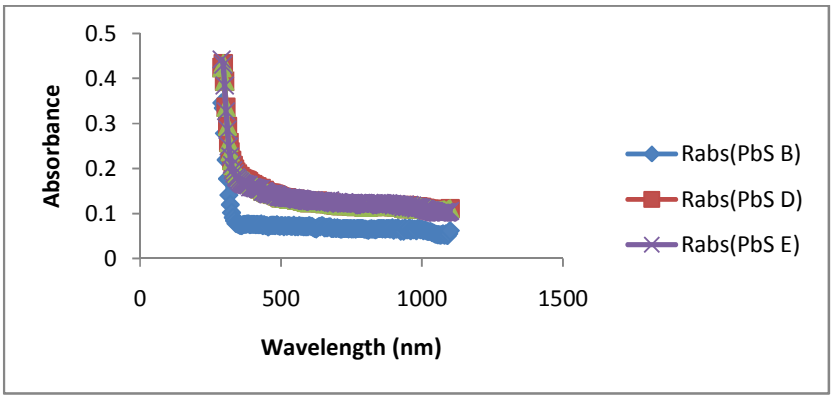

Figure. 2.0: Graph of optical Transmittance as a function of wavelength for different volumes of precursor of PbS thin films.

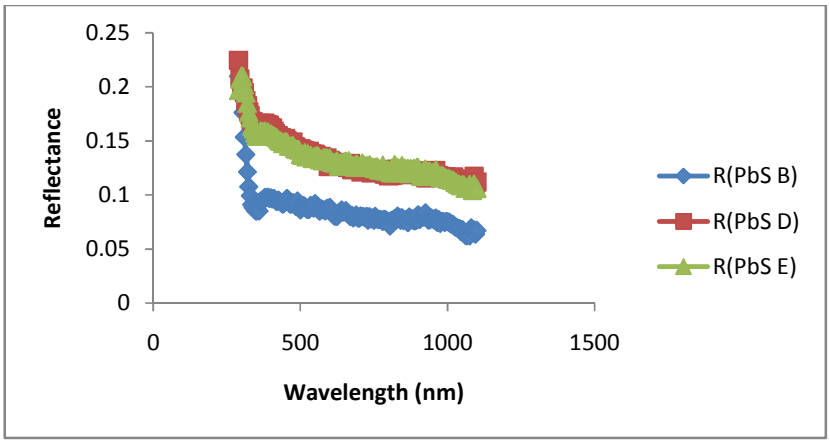

Figure.3.0: Graph of reflectance as a function of wave length of PbS thin films for different volumes of precursor.

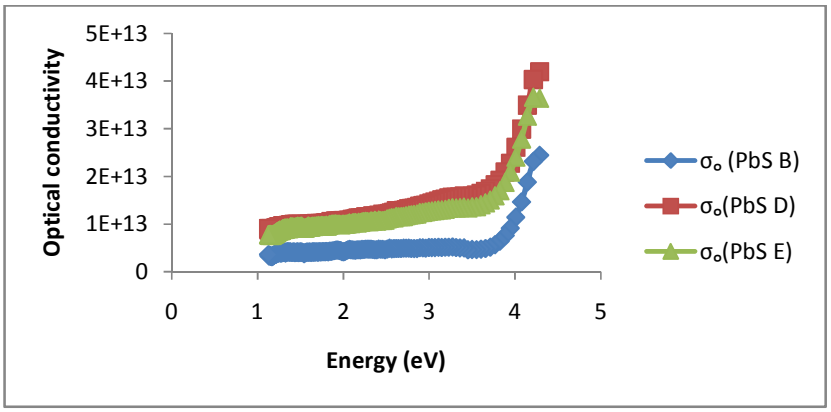

Figure. 4.0: Graph of optical conductivity as a function of energy for different composition of PbS thin films

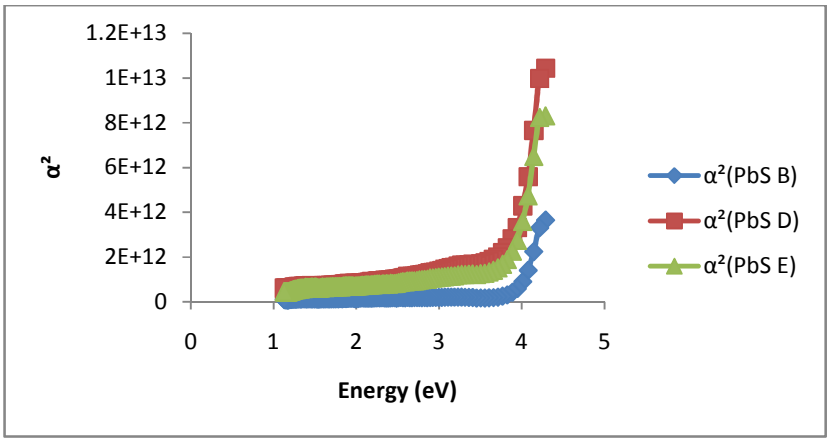

Figure. 5.0: Graph of α^2 as a function of energyfor different composition of PbS thin films.

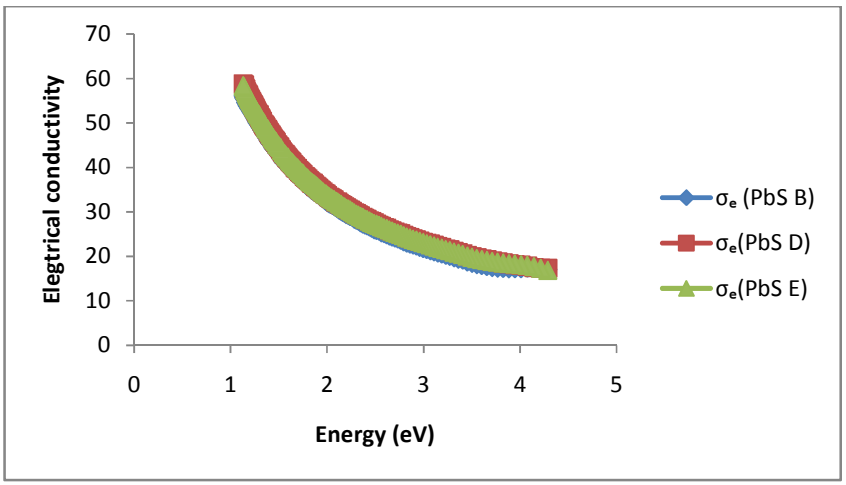

Figure 6.0: Graph of electrical conductivity as a function of energy for different composition of PbS thin films.

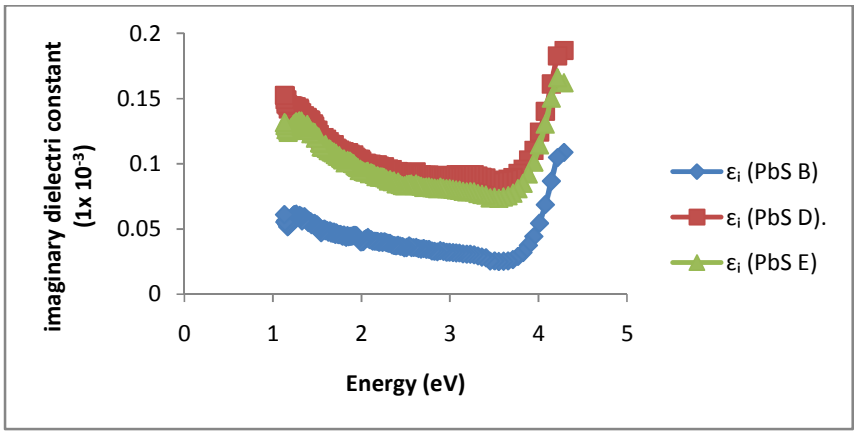

Figure 7.0: Graph of ε_i as a function of $h\upsilon$ for PbS thin films.

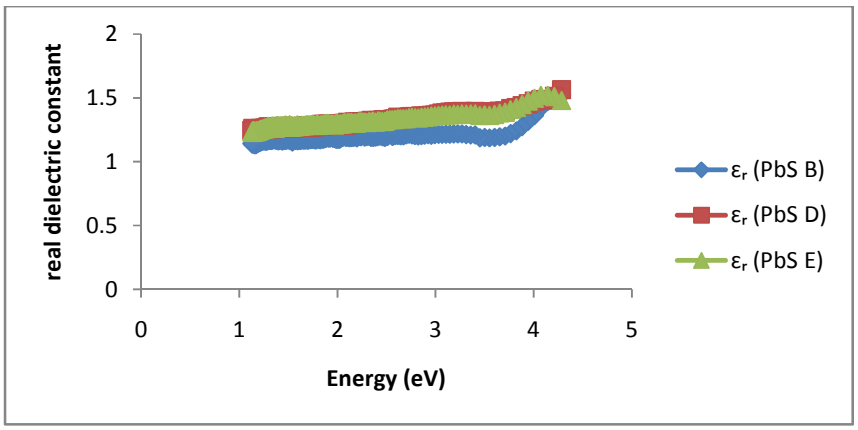

Figure. 8.0: Graph of ε_r as a function of $h\upsilon$for PbS thin films.

Table 1: Average optical properties of PbS thin films deposited at room temperature

Samples	**Absorbance (A)**	**Transmittance (T)**	**Reflectance (R)**	**Refractive index (n)**	**Absorption coefficient (α) x 10^{-5}**	**Extinction coefficient (K)**	**Optical conductivity (σ_o) x 10^{-13}**
PbS B	0.07	0.84	0.09	1.10	4.30	0.020	1.11
PbS D	0.07	0.85	0.08	1.10	2.60	0.012	1.52
PbS E	0.14	0.73	0.13	1.14	9.10	0.047	2.51

Table 2: Solid state properties of PbS thin films deposited at room temperature

Samples	**Thickness (Å)**	**Energy Gap E_g (eV)**	**Electrical conductivity, (σ_e) ($1x10^{-4}(\Omega m)^{-1}$**	**Real dielectric constant (ε_r)**	**Imaginary dielectric constant (ε_i) ($1x\ 10^{-5}$)**
PbS B	7491	3.80	33.72	0.044	1.20
PbS D	5641	3.30	33.33	0.025	1.17
PbS E	9791	3.40	35.26	0.099	1.30

The spectral absorbance of the films is shown in Figure 1.0 while the spectral transmittance and reflectance of the films are shown in Figures 2.0 and 3.0. All the films show strong absorption at wavelength range of 300nm – 400nm. The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. The spectra revealed that the PbS films have low absorbance inthe visible region.

The transmittance spectra displayed in Figure 2.0 shows increase in transmittance as the wavelength increases. It is observed from the figure that the transmittance varies with wavelength in similar manner for all of the samples.The transmittance decreases with increase in volume composition of the precursors. The very high transmittance in the visible region makes Lead Sulphide films useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.

The plot of the spectral reflectance against wavelength for PbS thin films deposited shows that the reflectance of the film decreases with wavelength. It was observed that the films show low reflectance all through the spectra region. The low values observed make PbS thin films very good material for anti-reflection coating[19].

The variations of the optical conductivity of PbS thin films deposited at different compositions of precursors are shown in Figure 4.0. Generally, it is observed that the conductivity increased with increasing frequency of radiation.

The energy band gap $E_g$which varies between 3.30-3.80 eV, was determined from Tauc's plots (Figure 5.0). The energy at the point where the absorption coefficient (α) is zero represents the energy gap, E_g,which can be determined by extrapolation. Values of absorption coefficient α recorded in this work ranges from 2.60-9.80x10^5 cm^{-1}. These values fall within the range of absorption coefficient (i. e. $10^4 – 10^5$ m^{-1}) for semiconductor thin films desirable for the production of polycrystalline thin films solar cell[20].

Figure 6.0 shows the graphs of the electrical conductivity of PbS thin films deposited at different compositions of precursors. All the films conduct well at low frequencies, i.e. the conductivity of the material decreases with increasing frequency of incident radiation.

The graphs of the imaginary part of the dielectric constant against the photon energy are presented in Figure 7.0. It is observed that the dielectric constant decreases from maximum value to a minimum and rises from around 0.031 x 10^{-3} at 3.76eVto maximum value of 0.108 x 10^{-3} at 4.28 eV. Similarly, the dielectric constant of the samples (Figure 8.0) vary in similar manner; increasing linearly from minimum to a maximum value.However, slight decrease was noticed between energies 3.00 and 4.00 eV for all the samples.

Table 1 shows the average optical properties of the deposited PbS thin films. The optical parameters in the study were affected by the composition of the samples. The variation of the solid state properties of the films deposited with different volumes of the compositions of precursors is as shown in Table 2. As the thickness increased the electrical conductivity (of the order 10^{-4}) decreased. The real dielectric constant and the imaginary dielectric constant of the films were also foundto increase with thickness. The electrical conductivity of PbS thin films vary between 33.33 x 10^{-5}- 35.26 x 10^{-5} $(\Omega m)^{-1}$ which is within the electrical conductive range for semiconductors (i.e. 10^{-12} to 10^2 $\Omega^{-1}m^{-1}$).These properties also revealed the suitability of the films in solar cell fabrication.

5.0 Conclusion

Lead Sulphide thin films were deposited by Chemical Both Deposition (CBD) technique with different volumes of individual precursors. The variations in volumes of precursorswere found to affect the thickness of the films deposited. Optical parameters like absorbance, transmittance, reflectance, absorption coefficient, and extinction coefficient as well as the band gap of both films were found to be affected by variations in volume of individual precursors. The films were observed to have direct band gap transition whose range compare favorably well with available literature values for application as antireflection and solar cell fabrication. The electrical conductivities of both films which were found in the order of $10^{-5}(\Omega cm)^{-1}$ were observed to be directly proportional to the films thickness.

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