Journal of Materials Science Research and Reviews

Volume 10, Issue 4, Page 16-31, 2022; Article no.JMSRR.94668

Influence of Ligand on the Morphological, Electrical, Optical and Solid State Properties of Chemical Bath Deposited Lead Sulphide Thin Film

Oluwatobi Adewale Adeyeba [a*], Emmanuel Ifeanyi Ugwu [a] and Rafiu Adewale Busari [a]

[a] *Department of Physics, Nigerian Army University Biu, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/94668

Original Research Article

Received: 20/10/2022
Accepted: 28/12/2022
Published: 29/12/2022

ABSTRACT

Lead sulfide (PbS) thin films with different concentrations of ligand have been deposited on the glass substrate at room temperature using Chemical Bath Deposition (CBD) technique. The influence of ligand on the Optical, Solid State, Morphological and Electrical properties of the deposited thin films has been investigated. The results show that, the absorption coefficient of the films was found to increase as the concentration of Ligand decreases towards longer wavelength region and the energy band gap was observed to increase from 1.61eV to 3.71eV as the concentration of Ligand increases. Surface morphology shows that the deposited thin films are of polycrystalline and the particle grains are evenly distributed across the substrates' surface. The

**Corresponding author: Email: adeyebaoluwatobi@gmail.com;*

electrical properties of the films as deduced using Four-Point Probe (FPP) technique also shows that there is a consistent increase in the electrical conductivity $\geq 10^{43}(\Omega m)^{-1}$ and sheet resistance $(\sim 10^{24}\Omega)$ as the concentration of Ligand increases.

Keywords: Lead Sulphide (PbS); thin film; chemical bath deposition (CBD) technique; Ligand; Properties.

1. INTRODUCTION

In this current dispensation, oxide based and chalcogenide type of compounds/ thin films have attracted the interest of many researchers due to their anticipated applications of these thin films as they are observed to have some unique characteristics Apart from their multipurpose applications they have characteristic of crystallization with the perovskite structure coupled with their unique behavior in gas solid interface, heterogeneous catalysis and also their susceptibility in partial substitution in A and B position [1]. They can also be synthesized easily with given extensive range of their amenability of their chemical and physical properties lots of applications However, based on our work we are focusing more on chalcogenides based thin films which have also attracted lots of researchers' interest because many minerals and ores are monosulfides [2]. "Metal dichalcogenides have the formula ME_2, where M = a transition metal and E = S, Se, Te" [3]. "The most important members are the sulfides. They are always dark diamagnetic solids, insoluble in all solvents, and exhibit semiconducting properties. Some are superconductors" [4]. "Several metals, mainly for the early metals (Ti, V, Cr, Mn groups) also form trichalcogenides. These materials are usually described as $M^{4+}(E_2^{2-})$ (E^{2-}) (where E = S, Se, Te). A well-known example is niobium triselenide. Amorphous MoS_3 is produced by treatment of tetrathiomolybdate with acid" [5]. "These electropositive element thin films combined with chalcogens (S, Se and Te) usually have an exceptional capacity of glass forming, a high refractive index, and photonic energy lower than the standards, high photosensitivity, and excellent transmission over the infrared region. These characteristics make them ideal for manufacturing various civil, medical and military applications such as infrared detectors, infrared lens, planar optics, photonics integrated circuit lasers etc" [6]. "Chalcogenide thin films have attracted a great of attentions for decades because of their unique properties such as earth abundance, environmental friendly, excellent structural, optical and electrical properties. For these reasons, chalcogenide materials are considered excellent absorption coefficient and suitable band gap value to absorb the maximum number of photons from sun radiation" [7].

Thin chalcogenide films are of particular interest for the fabrication of large area, photodiode arrays, solar selective coatings, solar cell, photoconductors, sensors etc. Examples of thin film materials that belong to chalcogenide group are:

Binaries chalcogenide such as CdS, CdSe, Bi_2S_3, PbSe, PbS, As_2S_3, Ag_2S, Cu_2S, Sb_2Se_3 ZnS, CaS, PbTe, MnS. Some of which have been grown using CBD technique [8]. And also pulsed laser technique has been used to grow PbS thin film by [9]. Therefore, so many techniques have been implemented by many researchers in the growth of this group of thin film.

Ternaries chalcogenide like CdZnS, CdSSe, $CuInSe_2$, PbHgS, CdPbSe etc. and Quaternary chalcogenide. Some of which have also been grown by [10,11] etc. Among the aforementioned chalcogenide groups of thin films, many researchers have studied, synthesized and characterized the behaviors of various properties of binary chalcogenide thin films. For instance, the growth and optical characterization of Antimony Selenide (Sb_2Se_3) thin film using CBD technique has been carried out by [12]. In which the work established that the behavior of the film shows that Sb_2Se_3 thin film has high absorbance and low transmittance. Also in the same manner, CBD has been used to grow Cu_2S thin film for which the optical property was studied within UV, Visible, and near infrared region (NIR) of radiation [13].

Theoretically, mathematical approach has also been used to study and analyze the properties of some of these binary based chalcogenide thin film materials in order compare the experimental and theoretical analysis and it has been that results almost consequently tally with each other.

As in case of analytical study of Antimony selenide and manganese sulfide by [14], due to the high cost of experimental analysis involved in the characterization of the grown thin films and sometimes non- availability of the machine especially in some part of our third world countries because of their cost. However, he did a work which is based on the use of theoretical concept to study the optical properties of chalcogenide manganese sulfide (MnS) thin film in order to circumvent the use of experimental analysis and characterization.

Continuing on quest for search on the optimized chalcogenide based thin films for applications in harnessing solar energy and for other device applications in this work, we intend to examine the influence of the ligand on the morphological, electrical and optical properties of chemically bath developed binary PbS thin film.

2. EXPERIMENTAL PROCEDURE

Prior to the deposition, the glass slide substrates were cleaned by scrubbing thoroughly with cleaned cotton wool and soap solution, rinse with running tap water, then ultrasonicate using ultrasonic bath of acetone, methanol and distilled water at room temperature for few hours. Then they were rinsed with de-ionized water. The substrates were dried in an open furnace at moderate temperature. All these cleaning processes were taken to remove possible impurity (organic or inorganic) substances from the surface of the substrate which is very important for adherence of the films to the surface of the glass substrate.

The chemical bath was prepared by sequential addition of 2.5 ml(0.5 M) of lead acetate trihydrate ($Pb(CH_3COO)_2.3H_2O$), 2.5 ml (2 M) of sodium hydroxide ($NaOH$) to neutralize the acidity of the solution, 3 ml (1 M) of thiourea (CH_4N_2S), while tri-ethanolamine (TEA) as ligand was varied from 0.5 M, 0.8 M to 1.0 M according to Table 1. At room temperature (27 ^{o} C), distilled water was added until the volume of the solution reached 70ml and the PH of the solution was measured using digital PH meter and kept constant at 11. The bath solution was then thoroughly stirred on a magnetic stirrer for 30 minutes to aid homogeneity. The cleaned and dried substrate was clamped vertically using retort stand and clip and then lowered into the 100 ml beaker containing the CBD solution with aluminum foil as a cover for the top of the beaker in order to prevent dust or unwanted particles from entering the solution. The deposition time was kept constant throughout for 24hours for each of the samples labelled T_1, T_2 and T_3 for TEA concentration is 0.5 M, 0.8 M and 1.0 M respectively. The three samples were taken out of the bath, rinsed in distilled water and dried in an open furnace at room temperature for 3 minutes to remove residual water content and other possible adsorbed surface impurities. The films were observed to be homogeneous and well adhered to the substrate. Table 1 gives the details of the concentration of the ligand (TEA) used for different samples but with the same time of deposition (24.00 hours) and at room temperature.

Table 1. Concentration of the ligand used for the deposition of thee three samples

Samples	Concentration of Ligand (M)
T_1	0.5
T_2	0.8
T_3	1.0

3. RESULTS AND DISCUSSION

The optical, solid state, morphological, and electrical properties of the deposited film were characterized using various characterization techniques. UV-VIS spectrophotometer was used for determining the optical and solid state properties were deduced from the results of the optical properties and morphological done using scanning electronic microscope (SEM) while Four-point probe (FPP) technique was used to investigate the electrical property of the deposited thin films. All these were carried out at the Center for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun state.

Reaction Equations:

$$\left[Pb(CH_3COO)_2.3H_2O + 2NaOH\right] \longrightarrow Pb(OH)_2 + 2Na(CH_3COO) + 3H_2O$$

$$CH_4N_2S + 2H_2O \xrightarrow{:OH^-} H_2S_{(g)} + CO_{2(g)} \uparrow + 2NH_{3(g)} \uparrow \xrightarrow{:OH^-} S^{2-} + H_2O$$

$$2Pb(OH)_2 + 2\left[C_6H_{15}NO_3\right]_n \longrightarrow 2\left[Pb(TEA)_n\right] + 2H_2O + O_2$$

$$\left[Pb(TEA)_n\right] \longrightarrow Pb^{2+} + n(TEA)$$

$$Pb^{2+} + S^{2-} \longrightarrow PbS \qquad (1)$$

3.1 Optical and Solid State Properties

The influence of Ligand concentrations on the optical and solid state properties of lead sulphide (PbS) thin films using a cost effective chemical bath deposition (CBD) technique at room temperature would be discussed in this section. The ligand influence on Absorbance, Transmittance, Absorption coefficient, Energy band gap, Skin depth, Urbach energy, Refractive index, Dielectric constants and Optical conductivity at photon wavelength region of 200 to 900 nm are sequentially studied using a UV-VIS double beam Spectrophotometer.

3.2 PbS Thin Film Absorbance Study

The absorption behavior of the grown thin films in the wavelength range of 200 to 900 nm is shown in Fig 1. The figure shows the absorbance spectra of the PbS thin films samples of different concentrations of Ligand. It is observed from the graph that sample T_1 indicates higher absorption property followed by T_2. The films show no absorption from spectra range of 200 nm to 550 nm for T_2 and from 200 nm to 700 nm for T_1 due to the considerably high thickness of the films which may be attributed to the concentration of Ligand. However, the absorption spectra increase as the wavelength deceases considerably for T_1 and T_2, which implies that the absorption increases as the concentration of Ligand decreases for the three samples and sample T_3 has the lowest absorption because it has highest concentration of Ligand. As observable, the absorption edge is shifted towards longer wavelength as shown in the figure there is observed variation with decrease in the concentration of Ligand and this phenomenon is called Red- Shift (or Bathochromic) effect which is related to decrease in the direct band gap. And this result is in line with the result obtained by [15]. Absorbance is commonly logarithm of the reciprocal of the transmittance according to the equation 2.

$$\log_{10}\left(\frac{I}{I_{\circ}}\right)=\log_{10}\left(\frac{1}{T}\right)=2-\log T\,(\%) \tag{2}$$

3.3 PbS Thin Film Transmittance Study

The transmittance spectra of PbS thin films for the three samples are shown in the plot of transmittance against wavelength in Fig 2. It can be deduced from the plot that there was no transmittance between the wavelength range of 200 nm to 620 nm for T_1 and T_2, the transmittance increases exponentially as the wavelength increases from 620 nm upward due to the lower concentration of Ligand thus resulted to the high thickness of the films. In comparison to T_3 which has the excellent result for transmittance at about 50 %, this is attributed to the high concentration of Ligand used in the preparation [9].

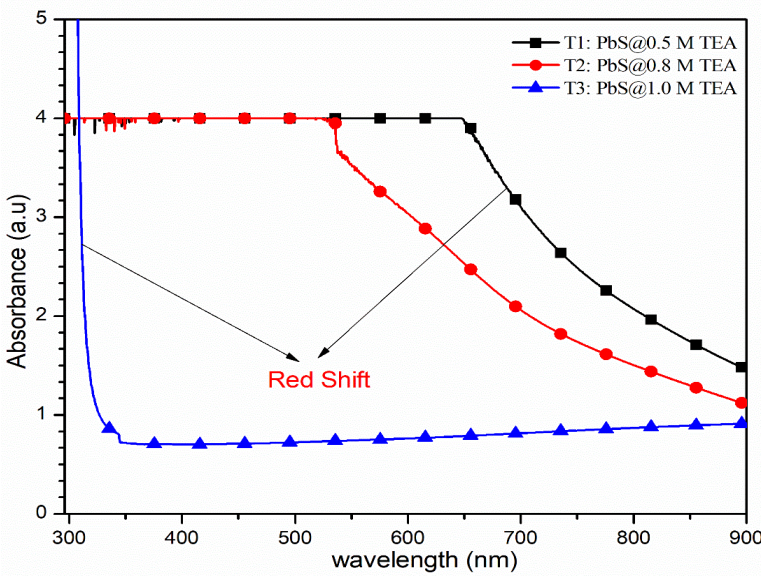

Fig. 1. The absorbance spectral of the three samples

However, the transmittance spectra of PbS thin films shows an increase behavior as the concentration of Ligand increases, and this may be attributed to the thickness of the films. This result is close the result obtained by [16]. It can be concluded that Ligand increases the optical transmission spectra of a chemical bath deposited PbS thin films. This amazing property makes the films for sample T_3 a suitable material for antireflection coatings and solar thermal application in flat- plat collector [16].

3.4 PbS Thin Film Absorption Coefficient Study (∝)

Absorption coefficient or edge of the films correspond to the transition or excitation of electrons from the valence to the conduction band which is usually utilized in determining the nature of the optical band gap of the films. The optical absorption coefficient of PbS thin film with different concentrations of Ligand at room temperature is plotted as a function of wavelength in Fig 3. The figure shows a similar behavior to that of the absorption spectra discussed earlier. It is observed that the films with lower concentration of Ligand (T_1 and T_2) are more thicker compared to T_3 which has thinner films. For this reason, samples T_1 and T_2 shows no absorption within the wavelength range of 200 nm – 520 nm. T_1 and T_2 exhibit absorption edge at wavelength 540 nm and 650 nm respectively and T_3 has the highest absorption coefficient value ($\propto > 10^6$ cm^{-1}) in the UV-VIS region due to its high concentration of Ligand. It shows from there that, ∝ increases as radiation shifts to a longer wavelength. Also, it has been established by [9,16] that the thinner films usually have a high value of α in the band absorption region.

Hence, the result obtained is relatively close to the values of absorption coefficient obtained by [9,16]. Thus, the increase in absorption coefficient increases the transition occurrence of electrons in the bands, then reduces the energy gap of the films. From the absorbance data, the absorption coefficient was calculated in the fundamental absorption region using Lambert law equation below:

$$\ln \frac{I}{I_\circ} = 2.303A = \alpha d \tag{3a}$$

Where $T = \frac{I}{I_\circ}$

$$\alpha = \frac{2.303A}{d} \tag{3b}$$

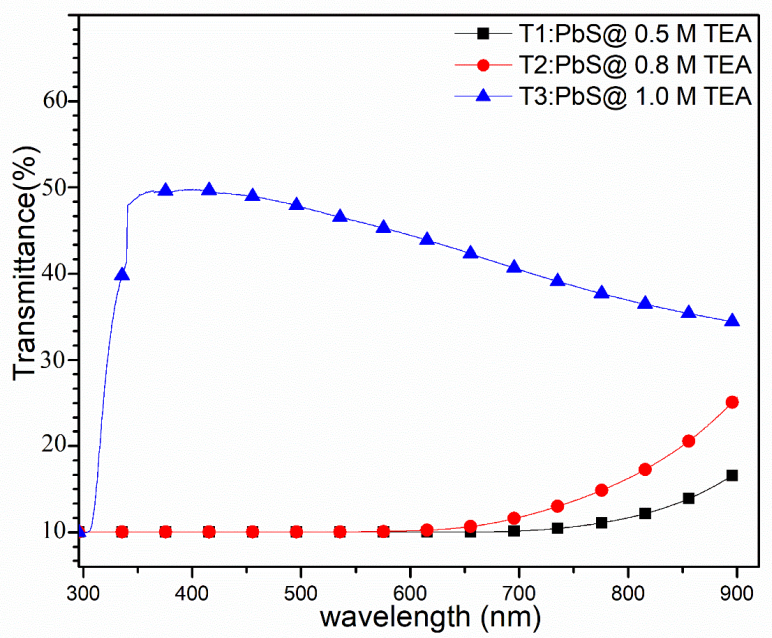

Fig. 2. The transmission spectra of the three samples of PbS thin film

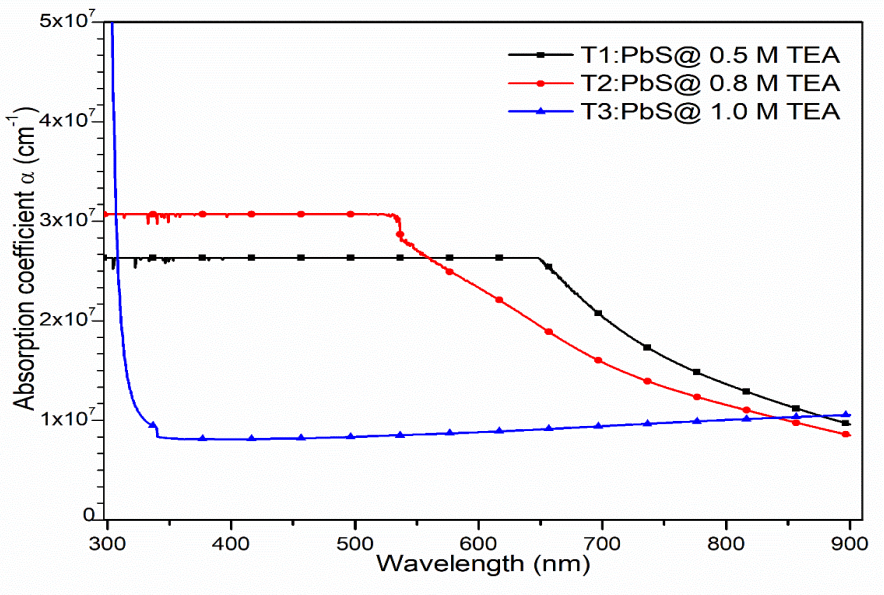

Fig. 3. The plot of absorption coefficient of the three samples of PbS thin films against wavelength

3.5 Energy Band Gap (Eg)

The energy band gap of the thee samples T_1, T_2 and T_3 of the deposited PbS thin films was estimated using Tauc. plot as shown in Fig. 4. In the figure, $\propto$ dependent value of $(\propto h\nu)^2$ were plotted against the photon energy in accordance to expressions for direct band gap estimation. The respective band gap for each sample at different concentration of Ligand was determined by extrapolating the linear region or portion of each plot to the photon energy axis at a point where the term $(\propto h\nu)^2$ is zero. The obtained results for the three samples are tabulated in Tables 2. It is observed from this result that, the energy band gap reduces linearly with the photon energy and thus, the energy band gap reduces or narrows as we increase the concentration of Ligands.

It can then be deduced from this result that Ligands especially, TEA reduces the optical energy band gap of chemically deposited PbS thin film material. The observed energy band gap of 1.61 eV – 3.71 eV is slightly close to the results obtained by [17]. Though, the reported band gap energy of bulk PbS thin film ranges from 0.4 – 0.6 eV, and this may be due to the nanocrystalline nature of the material [9] and can also be attributed to the effect of quantum confinement (i.e. after a certain limiting size of particle size which is associated with the excition radius, thus the space between the band levels of the material changed) [15]. However, this shows that PbS thin film with lower concentration of Ligand like sample T_1 can be used as a good material for solar cell fabrication. Direct energy gap was obtained using the relation equation 4:

$$(\alpha h\upsilon)^2 = A\left[h\upsilon - E_g\right] \quad (4)$$

Where A is the absorbance and υ is the frequency dependent of α near the absorption edge. h is the Planck's constant.

Table 2. Energy Band Gap for The Three Different Samples of PbS Thin Films

Samples	Energy band gap (eV)
T_1	1.61
T_2	1.71
T_3	3.71

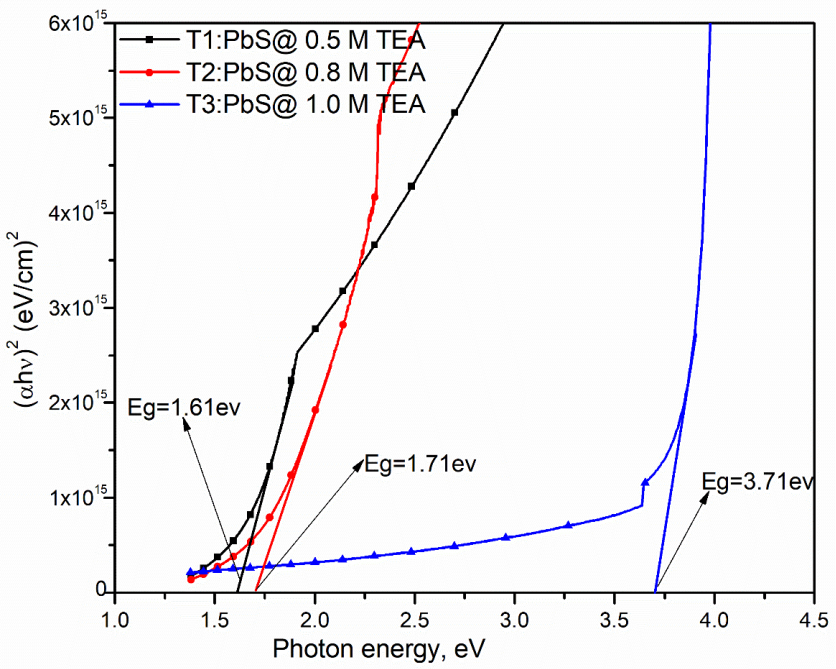

Fig. 4. The plot of energy gap of the three samples of PbS thin films as a function of photon energy

3.6 Skin Depth

Skin depth or penetration depth of a material is described as the measure of the maximum distance to which radiation can propagate or penetrate through a material before the absorption effect vanishes or dies off. Fig.5 shows the plot of skin depth on the incident photon energy of the radiation of the three samples. It can be deduced from the figure that the penetration depth of the samples T_1, T_2, T_3 decreases as photon energy increases or as the wavelength of radiation decreases. It is observable that the skin depth of T_1 with the photon energy or wavelength until it reaches a point 1.80 eV where the effect of absorption vanishes and reduction in the amplitude of the light wave is observed, this region is called a cut-off wavelength. As observable, the cut-off wavelength for Tis lower than that of T_2 (2.4 eV) and T_3 (4.2 eV) which is the highest. This has shown that Ligand increases the skin depth of a chemically deposited PbS thin film, which implies that the penetration depth of the films increases as we increase the concentration of Ligand. This occurrence is attributed to the decrease in the film thickness as the concentration of Ligand increases, thus increases the skin depth of the films. The skin depth is related to the absorption coefficient in the relation in equation 5:

$$\delta = \frac{1}{\alpha} \quad (5)$$

3.7 Urbach Energy (Eu)

Urbach energy represents the degree of disorder and defects in semiconductor materials. It corresponds to the band tail width of the localized states in the energy gap. From the relation shown for absorption coefficient in equation (2), the plot of ln $\propto$ as a function of the photon energy is presented in Fig. 6. The urbach energy in the energy gap were obtained from the graph by taking the reciprocal of the slope of each of the plots for T_1, T_2 and T_3 respectively. It is observed that the values of Eu increases as the concentration of Ligand increases which is attributed to the increase of the defect and the localized state in the energy band gap [16]. It can thus be deduced from here that Ligands increases the defects and localized states in the energy gap of chemically deposited PbS thin film.

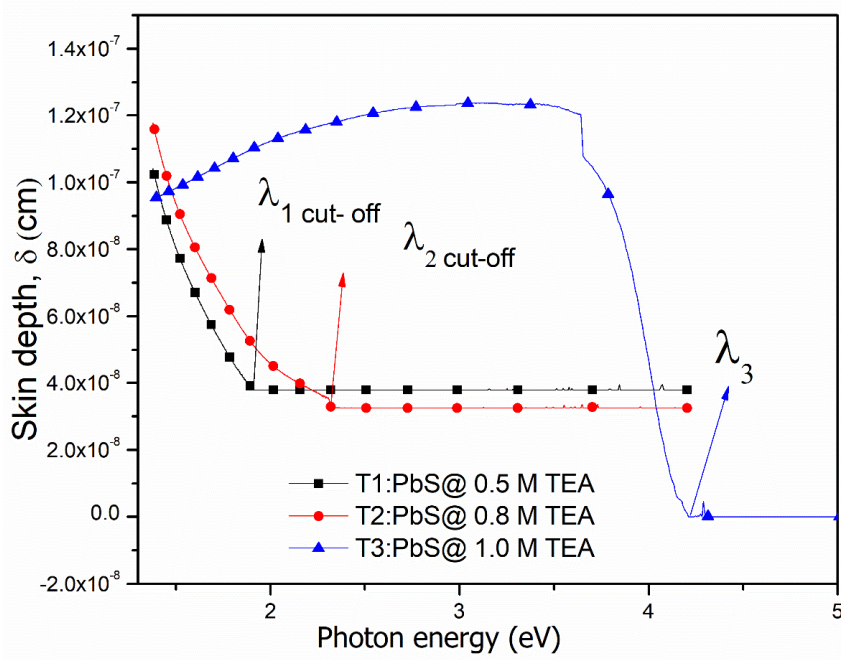

Fig. 5. The variation of skin depth as a function of the photon energy for the three samples

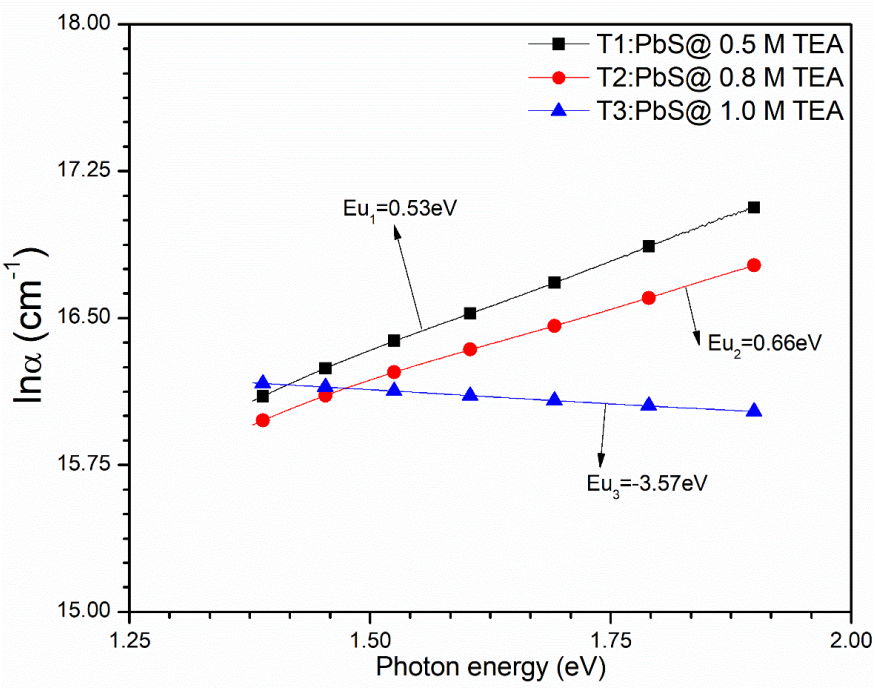

Fig. 6. The variation of ln α as a function of photon energy for T_1, T_2, T_3 of PbS thin film

3.8 Extinction Coefficient (K)

Extinction coefficient is a measure of light loss due to scattering and absorption per unit volume of a material. Fig.7 shows the plot of k as a function of wavelength of PbS thin films deposit at different concentration of Ligands at constant time frame (24 hours). It has been noticed from the graph that the extinction coefficient increases in the UV region with increasing wavelength. As observable, the increase in k at wavelength below 700 nm, 550 nm and 350 nm for T_1, T_2, T_3 respectively. And this is due to the high absorption within those regions which is ascribed

to the smoothness of the surface of the films. It can thus be deduced that increase in Ligands decreases the extinction coefficient from the absorption edge of the visible region of the PbS thin films and k is approximately constant at the visible range in the longer wavelength above 900 nm. samples T_1, T_2, T_3 shows a dominant peak around 800 nm. Extinction coefficient k of a prepared thin film was obtained by using the relation in equation 6:

$$k = \frac{\alpha\lambda}{4\pi} \tag{6}$$

Where λ is the wavelength of the incident photon

3.9 Refractive Index (n)

The refractive index is the rate at which light is slowed down in a material. It is one of the significant properties for an optical material in optoelectronics. The spectral dispersion of the samples was generated. The plot of refractive index as a function of photon energy for the three deposited samples of PbS thin films is shown in Fig. 8. It is observed from the graph that n for sample T_1 and T_2 is high (about 1.80) within the visible region of the films, which is attributed to the increase in the thickness of the films as a result of the smaller concentration of Ligands used in the preparation. In comparison with T_3, which exhibit the lowest value of refractive index (about 0.8) in the UV region, this may be ascribed to its small thickness due to the fact that it has the highest concentration of Ligand. The implication here is that, the scattering of light within this small thickness is attributed to its smaller and uniform grain distribution [15].

Therefore, it can be deduced from this observation that, increasing the concentration of Ligand in the chemical deposition of PbS thin films consequently decreases the refractive index of the films within the UV region. From the transmittance result analysis, the refractive index n of the sample can be calculated using the relations following equation below:

$$n = \frac{1}{T} + \left(\frac{1}{T-1}\right)^{1/2} \tag{7}$$

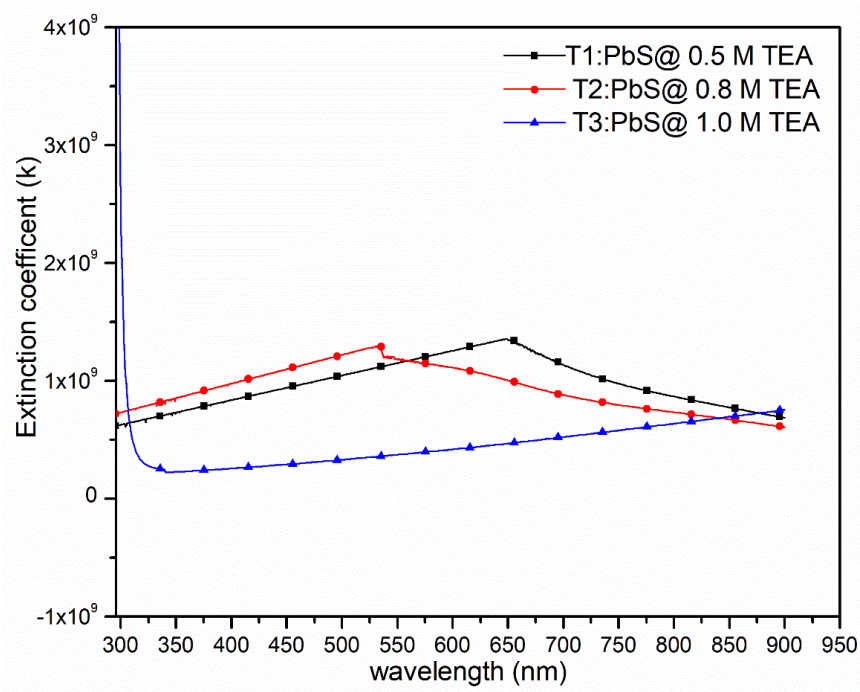

Fig. 7. The variation of K as a function of wavelength for the three samples T_1, T_2, T_3

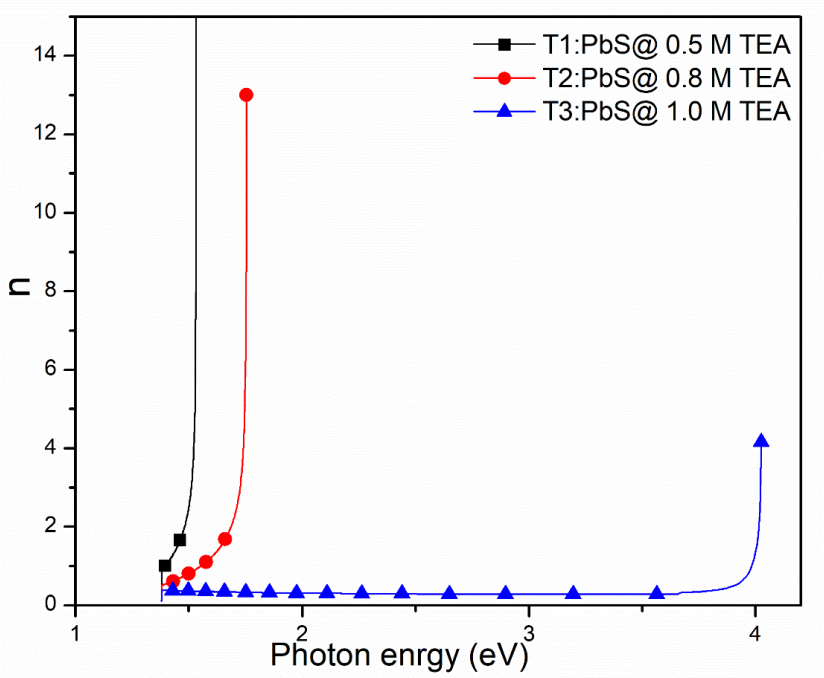

Fig. 8. The plot of the Refractive index (n) against the photon energy for sample T_1, T_2 andT_3

3.10 Optical Conductivity (δ_{opt})

Optical conductivity is a measure of the frequency response of a material when irradiated with light [18]. The optical conductivity of the three samples of the deposited PbS thin films is calculated from an expression which is strictly dependent on $\propto$ and n only. The plot of δ_{opt} against the photon energy is presented in Fig.9 below. It is observed from the plot that, δ_{opt} displays the same trend as that of n discussed above. As shown in the graph, the three samples of the film have a considerably high value of δ_{opt} ($\geq 10^{15}s^{-1}$). T_1 is said to have the highest optical conductivity ($\sim 7.0 \times 10^{15}s^{-1}$), followed by T_2 ($\sim 4.50 \times 10^{15}s^{-1}$), and T_3 shows the lowest value of δ_{opt} ($\sim 2.10 \times 10^{15}s^{-1}$). This indicates that the optical conductivity of PbS thin film materials decreases sequentially as we increase the concentration of Ligand. It is also interesting to know that the sample T_1 with the lowest concentration of Ligand responds quickly and sharply to the frequency of the incident radiation compared to sample T_2 and T_3. Thus, it can be concluded from the sight of this result that Ligand decreases the optical conductivity of chemically deposited PbS thin films. And the result of δ_{opt} obtained in this work is similar to that obtained by [16]. Optical conductivity was determined using equation 8:

$$\sigma = \frac{\alpha nc}{4\pi} \tag{8}$$

Where c is the speed of light.

3.11 Dielectric Constant (ε)

Real and imaginary part of dielectric constant parameters were obtained from an expression in equation 9(a) and 9(b) which are purely n and k dependent. Fig.10 (a) shows the graph of real dielectric constant against the wavelength range 300 nm – 900 nm of PbS thin film at different concentration of Ligand. As observable from the graph, all the three samples exhibit the same behavior as that of the refractive index because, the respective values of K^2 is more smaller compared to n^2 [9,15,16]. This implies that ε_r mainly depend on n. In comparison to ε_i in equation (9a), which is mainly dependent on K. The obtained value of the real dielectric constant ($\geq 10^{10}$) is considerably higher than that of the imaginary part (approx. zero) as observed in Fig.10 (b).

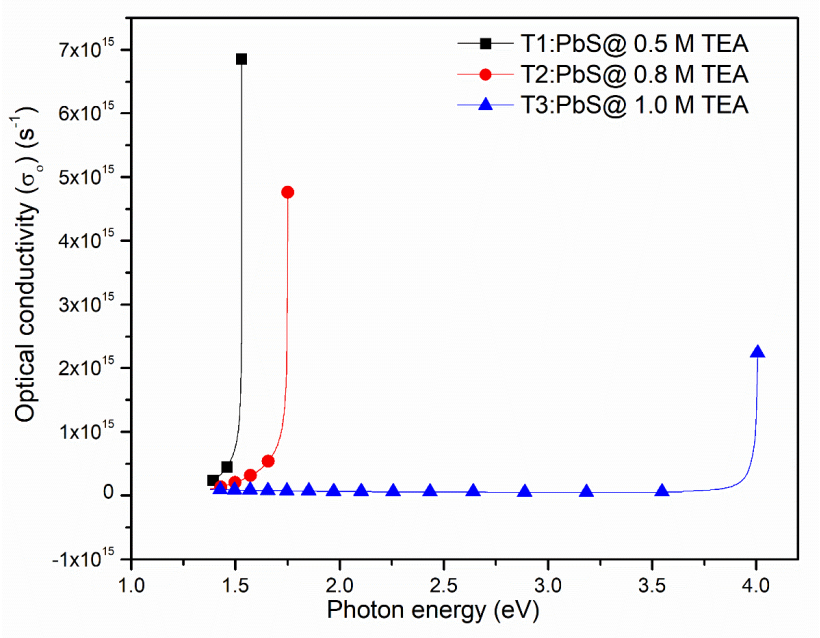

Fig. 9. The variation of δ_{opt} with the photon energy for the three samples T_1, T_2 andT_3 of PbS thin film

Furthermore, it is observed that ε_r and ε_i decreases as the concentration of Ligand increases, also the both the dielectric constants increase as the wavelength of the incident radiation decreases. The implication here is that, the ε_r and ε_i decreases as the Ligand increases and the oscillatory behavior of ε_i appears in the transparent region and a sharp increase in ε_i with the photon energy is observed at the absorption edge. Therefore, Ligand influences the behavior of the real and imaginary part dielectric constants of chemically deposited PbS thin films. Real and imaginary parts of the dielectric constant are related to refractive index n and extinction coefficient k values by the following relations:

$$\varepsilon_1 = n^2 - k^2 \quad (9a)$$

$$\varepsilon_2 = 2nk \quad (9b)$$

Where ε_1 and ε_2 are the real and imaginary parts of the dielectric constants respectively.

3.12 Surface Morphology

The surface morphology and the grain structure of chemically deposited PbS thin film at different concentration of Ligand was studied using Scanning Electron Microscope (SEM). The micrographs of the three samples of deposited PbS thin films are presented in Fig.11,12 and 13. The microstructure revealed that the films are well-adhered to the surface of the substrate and greyish-black in color with a black background. It shows that all the deposited films are nanocrystalline and compact with no voids or pinholes [19]. It can be observed from the micrograph that the films grains distributions are found to be uniform, larger, oriented and densely packed for sample T_1, indicating fast growth rate and size of the nano grains [20]. In comparison with sample T_2 whose grains are less dense and uniform, T_3 shows the lowest density and also irregular grains. It can be deduced from here that the grain sizes are found to be irregular in shape and less dense as the concentration of Ligand increases in PbS thin film preparation. The implication is that the regularity, density and uniformity of the grain sizes of the films decreases as we increase the concentration of Ligand. Also, a decrease in the numbers of facets at the surface of the microstructure of the films is observed from T_1 to T_3, which can be attributed to the increase in the concentration of Ligand and resulting non-homogeneity of the film [19].

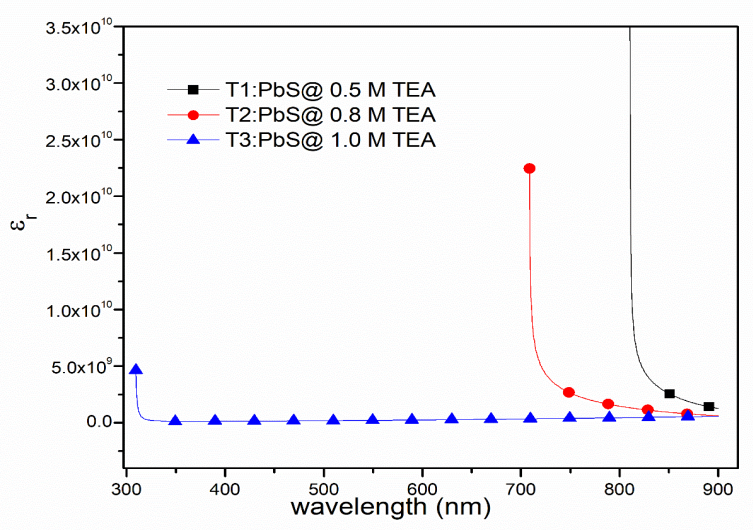

Fig.10 (a). The Plot of ε_r against the wavelength of sample T_1, T_2 andT_3 of PbS thin film

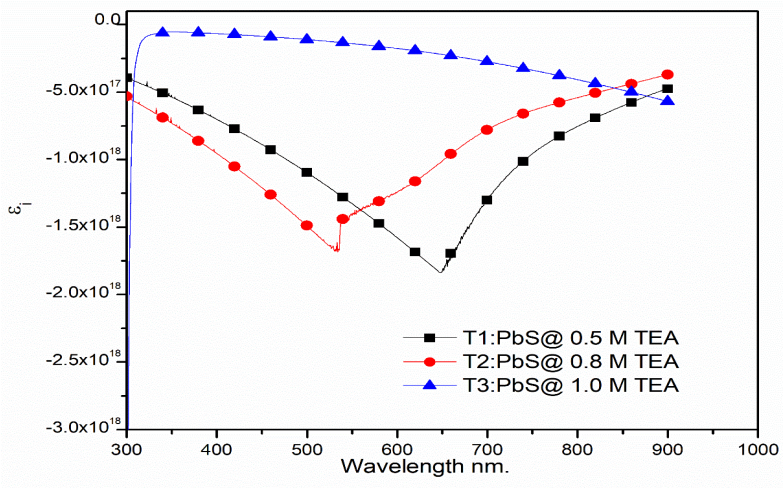

Fig.10 (b). The Plot of ε_i against the wavelength of sample T_1, T_2 andT_3 of PbS thin film

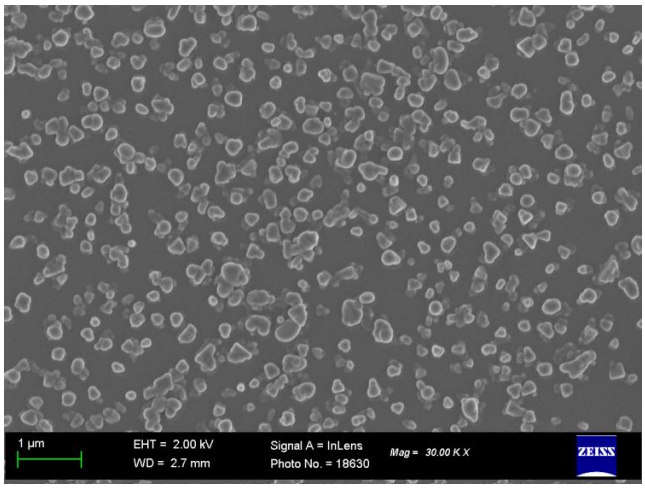

Fig. 11. The Morphology of PbS for 0.5M of Ligand

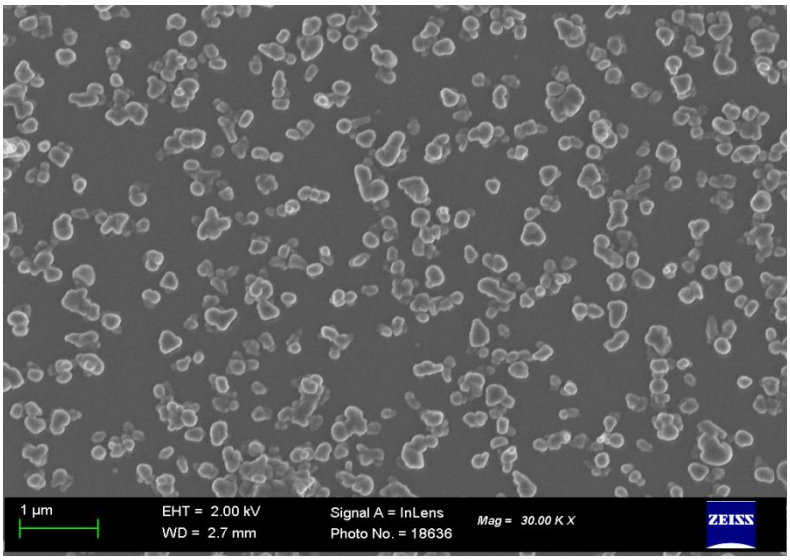

Fig. 12. Morphology for 0.8M of Ligand

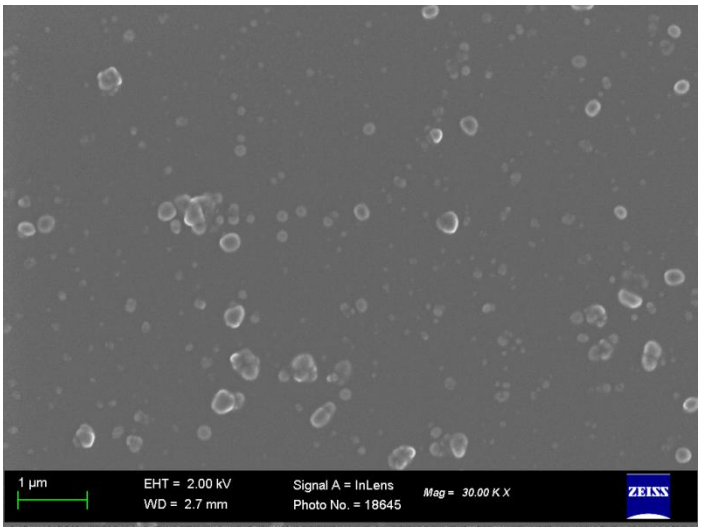

Fig. 13. Morphology of PbS for 1.0M of Ligand

Therefore, increase in the concentration of Ligand changes the grain sizes of a chemically deposited PbS thin film. Hence, sample T_1, which has the lowest conc. of Ligand exhibit a larger and uniform grain size, thus can be used in the improvement of Photovoltaic device performances [21].

3.13 Electrical Characterizations

The electrical analysis of chemically prepared PbS thin films was obtained using Four-Point Probe (FPP) technique. Fig.14, 15 and 16 illustrate the plot of I-V characteristics of sample T_1, T_2 and T_3 respectively. As observable form the plot, currents flow through the films linearly with the applied outer voltage. This is an implication that PbS thin film exhibits ohmic characteristics with higher conductivity. It can also be observed from the graph in Fig.14 that T_1 shows the poorest linear behavior of I-V characteristics compared to T_2 and T_3 in Fig.15 and 16 respectively. The linearity improves and increases as the concentration of Ligand increases. The obtained results of the average electrical conductivity, Resistivity and Sheet resistance of the three samples of PbS thin film are presented in table 3 below. It can be easily deduced from the table that, the average conductivity of the films increases as the concentration of Ligand increases, thus increases the average resistivity and decreases

the average sheet resistance of the films. The consistency in the increase in electrical conductivity $(\geq 10^{43}(\Omega m)^{-1})$ and increase in the sheet resistance $(\sim 10^{24}\Omega)$ as the concentration of Ligand increases in as showcased in graphs Fig.14,15 and 16 is enough to suggest that, PbS thin film deposited at a lower concentration of Ligand can be suitable for so many applications in photoconductor detectors. And those with considerably high sheet resistance have good application in solar control system [22]. The obtained results are almost in agreement with those obtained by [22, 23]. Since negligible constant and spreading resistance are associated with the voltage probes, one can obtain a fairly accurate estimation of sheet resistance R_{sh} using the following relation in equation 10. [23]:

$$R_{sh} = 4.532\left(\frac{V}{I}\right) \quad (10)$$

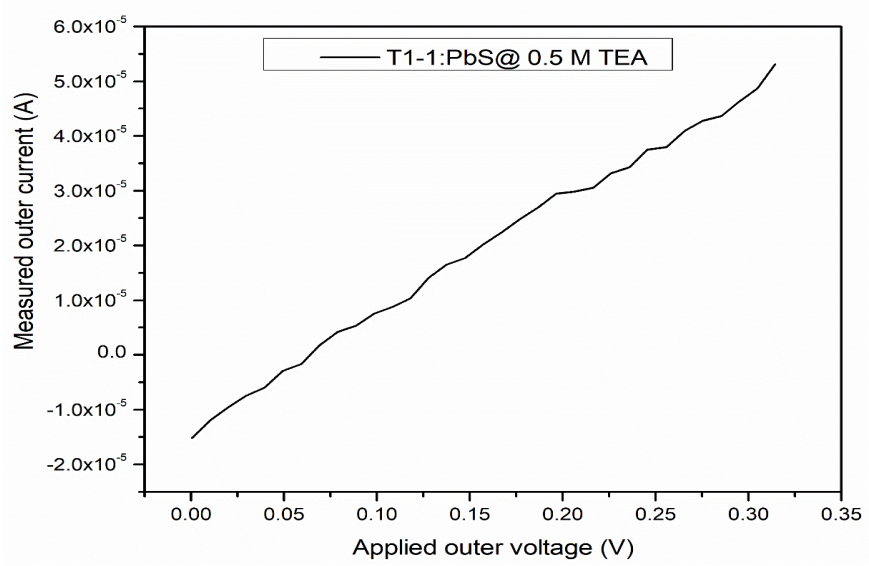

Fig. 14. I-V characteristics for T_1

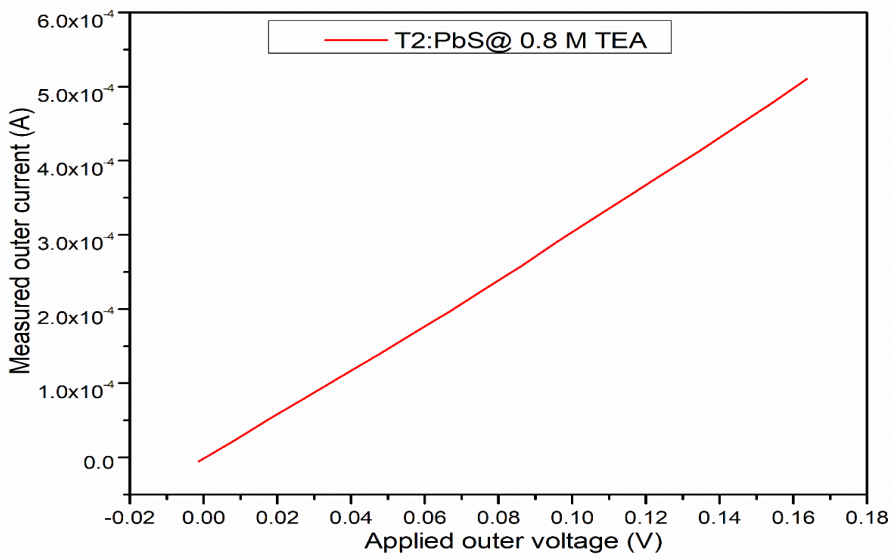

Fig. 15. I-V characteristics for T_2

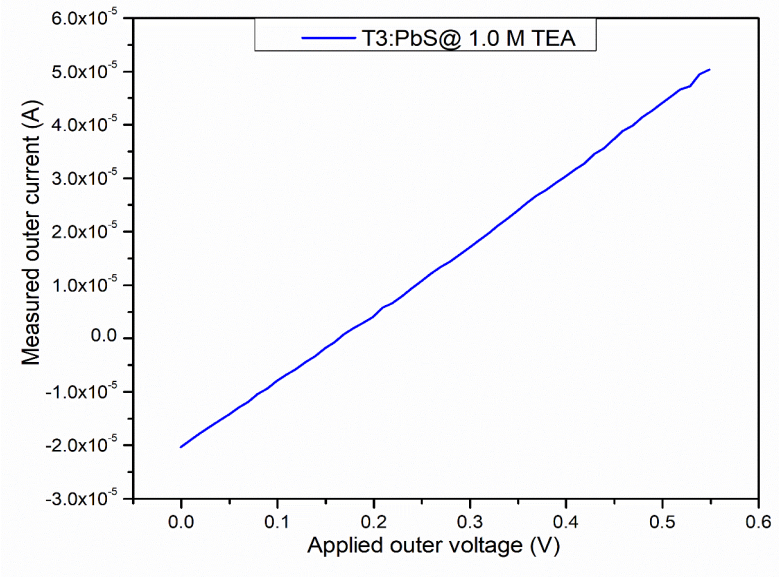

Fig. 16. I-V characteristics for T_3

Table 3. I-V characteristics of chemical bath deposited PbS thin film

Samples	R_{sheet} (Ω)	Resistivity (Ωm)	Conductivity $(\Omega m)^{-1}$
T_1	6.21986E+35	6.21986E-35	1.60775E+32
T_2	1.86591E+30	1.86591E-40	5.3593E+37
T_3	3.90842E+24	3.90842E-46	2.55858E+43

4. CONCLUSIONS

The influence of ligand on the properties of PbS thin film deposited using chemical bath deposition technique has been studied as presented and from the results, it was observed that there were slight variations in some of these properties as analyzed here occasioned by different concentration of the ligand. For instance, there is variation in refractive index, real and complex dielectric constant with the photon energy with the ligand concentration as indicated in figures as presented. In a similar manner, it was clearly revealed that the energy band gap of the thin film widened while the transmittance also increased with increase in the concentration of the ligand coupled with obvious indication of variation of grain sizes as indicated in the surface morphology as obtained from the SEM analysis.

ACKNOWLEDGEMENT

The authors gratefully acknowledge members of staff of the chemistry laboratory, Department of Chemistry, Nigerian Army University Biu for providing us with enabling environment during the synthesis of this work. The authors are also thankful to the materials science research laboratory, Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife for their assistance on electrical characterization.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Luis G. Tejuca, Jose Luis G. Fierro and Juan M.D. Tascon. Structure and Reactivity of Perovskite-Type Oxide. Advance in Catalysis. 1989;36:237-238.
2. Greenwood NN, Earnshaw A. Chemistry of the Elements (2nd Edn.), Oxford: Butterworth-Heinemann; 1997. ISBN 0-7506-3365-4.
3. Wells AF. Structural Inorganic Chemistry, Oxford: Clarendon Press; 1984. ISBN 0-19-855370-6.
4. Wood, Charlie. Physics Duo Finds Magic in Two Dimensions". Quanta Magazine; 2022. Retrieved 2022-08-22.

5. Vaughan DJ, Craig JR. Mineral Chemistry of Metal Sulfides, Cambridge University Press, Cambridge; 1978. ISBN 0521214890.
6. Priyanka P, Das S, Naik. Various Optoelectronic Properties for Different Applications. Engineering and Technology Journal; 2022.
7. Soonmin H, Paulraj I, Kumar M, Sonker RK, Nandi P. Recent Developments on the Properties of Chalcogenide Thin Film; 2022.
8. Ugwu EI, Onah DU. Optical Characteristics of Chemical Bath Deposited CdS Thin Film Characteristics with UV, Visible, and NIR Radiation. Pacific Journal of Science and Technology. 2007;8(1):155-161.
9. Kadhim A. Aadim, Abdul-Majeed E. Ibrahim, and Jassim M. Marie, Structural and Optical Properties of PbS Thin Films Deposited by Pulsed Laser Deposited (PLD) Technique at Different Annealing Temperature. International Journal of Physics. 2017;5(1):1-8.
DOI: 10.12691/ijp-5-1-1
10. Mane RS, Lokhande CD. Chemical deposition method for metal chalcogenide thin films Materials. Chemistry and Physics. 2000;65.
11. Busari RA, Taleatu BA, Adewinbi SA, Adewumi OE, Omotoso E, Oyedotun KO, Fasasi AY. Synthesis and surface characterization of electrodeposited quaternary chalcogenide Cu2ZnxSnyS1+x +2 y thin film as transparent contact electrode, Bull. Mater. Sci. 2020;43:83.
12. Owoh B, Ugwu EI. Growth, Optical characterization of Antimony selenide Cu_2S thin film using chemical bath deposition technique. Metallurgy and Material Engineering. 2009;4(1): 38-41.
13. Nwali NP, Ugwu EI. Optical properties of chemical bath deposited Cu_2S thin film within UV-VIS, and NIR radiation. Metallurgy and material engineering. 2009;4(2):26-30.
14. Emmanuel Ugwu Optical and Solid State Properties of Manganese Sulphide (MnS) Thin Film, Theoretical Analysis, Int. Jnl. of Multiphysics Volume 11 · Number 2 · 2017
15. Fouda AN, Marzook M, Abd El-Khalek HM, Ahmed S, Eid EA, El Basaty AB. Structural and Optical Characterization of Chemically Deposited PbS Thin Films; 2016.
16. Abbas MM, Shehab A Ab-M, Al-Samuraee AK, Hassan NA. Effect of Deposition Time on the Optical Characteristics of Chemically Deposited Nanostructure PbS Thin Films. Energy Procedia. 2011;6: 241–250.
17. Ikhioya IL, Ehika S, Ijabor, Okeoghene B. The Influence of Deposition on Lead Sulphide Thin Film Using Electrodeposition Techniq. Asian journal of chemical sciences. 2017;3(4).
18. Rajathi S, Kirubavathi K, Selvaraju K. Structural, Morphological, Optical and Photoluminescence Properties of Nanocrystalline PbS Thin Films Grown by Chemical Bath Deposition. Journal of chemistry; 2014.
Available:http://dx.doi.org/10.1016/j.arabjc.2014.11.057
19. Zaman Z, Mehmood SK, Mansoor M, Asim MM. IOP Conf. Ser. Mater. Sci. Eng. 2014;60:012057.
20. Preetha KC, Deepa K, Dhanya AC, Remadevi TL. Role of complexing agents on chemical bath deposited PbS thin film characterization. IOP Conf. Ser. Mater. Sci. Eng. 2015;73:012086.
21. SOONMIN. Orient. J. Chem. 2014;30(3):1009-1012.
22. Tavakkol, Tohidi, Kazem, Jamshidi-Ghaleh, Abdolrahman.Namdar and RezaAbdi-Ghaleh(2013) Matrials Science in Semiconductor Processing; 2013.
Available: http://dx.doi.org/10.1016/ j. mssp.2013.11.028
23. Benhaoua A, Rahal A, Benhaoua B. Effect of fluorine doping on the Structural, Optical and Electrical properties of SnO_2 thin films prepared by spray ultrasonic. Superlattices and Microstructures. 2014; 70:61-69.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/94668