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Electrochemical Deposition of Lead Sulphide (PbS) Thin Films Deposited on Zinc Plate Substrate

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Authors' contributions

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

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ABSTRACT

Lead sulphide (PbS) thin films were deposited at different times on a zinc plate substrates using electrodeposition technique at room temperature. The results showed that PbS thin films resistivity has a direct proportionality with time. The optical properties of the thin film were measured using M501 UV-visible spectrophotometer in the wavelength range of 300 nm-1500 nm. The highest and lowest optical absorbance value of 0.253 and 0.219 at 5 mins and 1min respectively were recorded. The transmittance value of 0.582% and 0.966% at 3 mins were recorded in the infrared and ultraviolet regions respectively. The peak reflectance value was attained at 5 mins in both regions, while the minimum was obtained at 1min in the near infrared and visible regions. Refractive index, optical conductivity, extinction coefficient, real dielectric constant and imaginary dielectric constant were examined as a function of the photon energy. Further analysis revealed the band gap to be in the energy range of 1.9eV-2.6eV. These results show that lead sulphide can be used for mass production of solar cells and others photovoltaic devices.

Keywords: Thin films; PbS; electrodeposition and optical analysis.

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1. INTRODUCTION

Lead sulphide (PbS) is an important semiconductor with a narrow band gap. Due to its unique photoconductive properties, PbS is applied as an infrared detector and for mid infrared lasers [1]. PbS has promising photosensitive properties and is a good photo-catalyst [2]. The nanoclusters based on sulphur compounds also have great potential as quantum dots. For these applications, PbS with different particle sizes is required. Particle diameters should vary from a few micrometers for infrared detector applications to several nanometers for quantum dots [1]. Semiconductor materials are always the focus in material science due to their outstanding electronic and optical properties and have potential application in various devices such as light emitting diodes [3] single electron transistors [4] and field effect thin film transistors [5]. In principle, the electronic and optical properties of semiconductor materials are tunable by varying their shapes and sizes [6]. So it is one of the desired goals in material science to have precise control of the morphology of semiconductor materials. The phenomenal rise in thin film researches is due to their extensive applications in the diverse fields of electronics, space science, optics, aircrafts and other industries. These investigations had led to numerous forms of active and passive components, piezoelectric devices, rectification and amplification, magnetic memories, superconducting films. Because of compactness, better performance and reliability coupled with low cost of production and low package weight, thin film components are preferred over the bulk counterparts [7-8]. The lead Sulphide thin films are mostly used in photography, ion selective sensors, solar absorption, photoresistants, humidity and temperature sensors and diode lasers [9-13]. Due to its physical properties, PbS is considered a prime candidate for a photovoltaic (PV) material and has generated great interest in its use. The PbS material is characterised by a direct band gap (1.5eV) with a high absorption coefficient another great advantage of PbS is that it can be deposited by a number of techniques including evaporation, sublimation, sputtering and chemical methods. The growth of PbS films by electrodeposition is a simple and low cost process of producing high-quality material for PV device fabrication. Thin film PbS has attracted a great deal of interest for low-cost, high-efficiency photovoltaic energy conversion applications. Among the various techniques that are available for PbS thin film deposition, electrodeposition is a non-vacuum technique and has the advantage of low cost, efficient utilisation of raw material, and scalability for high-volume production. At the same time, additional research is still needed to improve upon the process reproducibility and performance levels achieved to date. Among the significant issues are interface carrier recombination and top-layer photon absorption which presently limit the short circuit current, junction recombination which limits the open-circuit voltage, and series-resistance losses which suppress the fill-factor [14]. In this research paper, we are interested in the deposited of PbS thin films semiconductor by looking at the effect of the deposition period on the electrical and optical properties of the material deposited.

2. MATERIALS AND METHODS

Lead Nitrate $Pb(NO_3)_2$, Sodium Sulphate Anhydrous (Na_2SO_4), Potassium tetraoxosulphate VI (K_2SO_4) and H_2SO_4were used as the reaction bath.In this current work, deposition period (time) was varied and the growth of PbS films and others bath parameter were determined with respect to the different bath parameters which includes voltage of deposition and substrate for the deposition. The concentration of the solution was kept constant throughout the experiment. The concentration of the following compounds was maintained as prepared: 0.1M $Pb(NO_3)_2$, 0.1M -(Na_2SO_4), 0.092M K_2SO_4 and 0.1M H_2SO_4. A volume of 20 cm^3 each of $Pb(NO_3)_2$ and (Na_2SO_4) was measured into 150 ml beaker using burette. 10 cm^3 of K_2SO_4 was measured into the same 150 ml beaker containing $Pb(NO_3)_2$ and (Na_2SO_4) respectively to serve as the inert electrolyte which helps to dissociate the Pb from the $Pb(NO_3)_2$ and S from the (Na_2SO_4) to form the required PbS film on the substrate and 5 cm^3 of $H_2SO_4$was added to acidified the solution. The entire mixture was stirred with the glass rod to achieve uniformity. In each of the reaction baths prepared, a metal substrate (Zinc plate) and carbon electrode were connected to a DC power supply source and the voltage was maintained at 7V. The absorbance spectral of the films was measured in UV- visible NIR using M501 UV-visible spectrophotometer. UV-visible spectrophotometer uses the principle that when a beam of electromagnetic radiation of initial flux I is incident on a transparent object, it is transmitted. Some part of the incident flux could be absorbed for an absorbing medium while some part could be reflected. Various other parameters from the absorbance include: Transmittance, Reflectance, Refractive index, Optical Thickness, Coefficient of absorption, Extinction coefficient, Optical conductivity and dielectric constants.

3. THEORETICAL BACKGROUND

From the law of conservation of energy we obtained,

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

Where A is the absorbance, R is the Reflectance, and T is the transmittance, by

$$T = 10^{-A} \tag{2}$$

Refractive index n and the 0ptical thickness t are given in [15]

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{3}$$

$$t= \frac{In(\frac{1-R^2}{T})}{\alpha} \tag{4}$$

Coefficient of absorption α and photon energy E are given by

$$\alpha = \frac{A}{\lambda} \tag{5}$$

$$E = \frac{hc}{\lambda} \tag{6}$$

Extinction coefficient k and Optical conductivity σ are given by

$$k = \frac{\alpha\lambda}{4\pi} \tag{7}$$

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

Real dielectric constant and Imaginary dielectric constant [16] are

$$\varepsilon_r = n^2 - k^2 \tag{9}$$

$$\varepsilon_i = 2nk \tag{10}$$

The electrical (I/V) was obtained using four point probe (Model T345) and the resistivity and conductivity were calculated for various thickness as the deposition time is varied (See Fig. 1). The values of the resistivity for the films deposited at room temperature were investigated. The four point probes were connected to a current supply and the inner probes to a volts meter. As current flows between the outer probes, the voltage drop across the probes is measured. If the spacing between the points is constant, and the conducting film thickness is less than 40% of the spacing, and the edges of the film are more than 43 times the spacing distance from the measurement point, the average resistance of the film or the sheet resistance is given by: [15]

$$R_s = k\alpha\frac{V}{I} \tag{11}$$

Where $K = 4.53\ which\ is\ just\ \frac{\pi}{In2}$

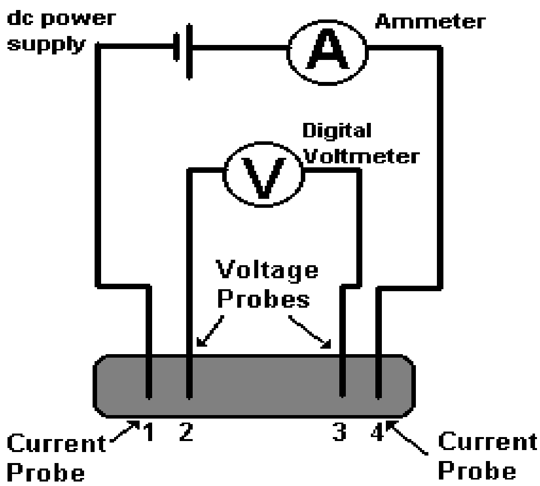

Fig. 1. Schematic of four-point probe

4. RESULTS AND DISCUSSION

4.1 Electrical Analysis of PbS Thin Films

The electrical (I/V) characterisation analysis where the sheet resistivity and conductivity of the films were studied using a four point probe instrument (Model-T345). The arrangement was made in such a way that the voltage across the transverse distance of the films and the values of the current were measured using silver paste to ensure good ohmic contact to the film. Table 1 shows the calculated results for the sheet resistivity and electrical conductivity with their corresponding time and thickness. The results showed that PbS thin films resistivity increases as the time increases and conductivity of the material increases as the thickness of the material decreases. The high resistivity and conductivity of the deposited films makes the material suitable for mass production of PV solar panel and other electronics devices. It is a semiconductor that has large potential applications in thin films technology like photo luminescence and electroluminescent devices [17-23].

4.2 Optical Analysis of PbS Thin Films

Fig. 2 shows the plot of absorbance as a function of wavelength of PbS thin films deposited at different deposition period (time) at constant voltage (7V). From Fig. 2, it was observed that as the wavelength of the films increases the absorbance of the films radiation decreases. From Fig. 2, it was noticed that all the samples deposited at different deposition period follow the same trend. Sample LSE deposited at 5 mins was found to record the highest absorption value of 0.253 at incidence wavelength of 360 nm and sample LSA deposited at 1min recorded the lowest absorption value of 0.219 at incidence wavelength of 320 nm. However, absorbance of the films was found to be high in the both regions, in agreement with refs [1,19-23].

Table 1. Electrical properties of PbS thin films

Samples	Time (Min)	Thickness (t) (nm)	Resistivity (ℓ) $(\Omega m)^{-1}$	Conductivity (σ) $(\Omega m)^{-1}$
LSA	1.00	259	$3.875\text{x}10^{8}$	$2.580\text{x}10^{-9}$
LSB	2.00	302	$3.987\text{x}10^{8}$	$2.508\text{x}10^{-9}$
LSC	3.00	325	$4.222\text{x}10^{8}$	$2.368\text{x}10^{-9}$
LSD	4.00	339	$4.257\text{x}10^{8}$	$2.349\text{x}10^{-9}$
LSE	5.00	347	$4.677\text{x}10^{8}$	$2.138\text{x}10^{-9}$

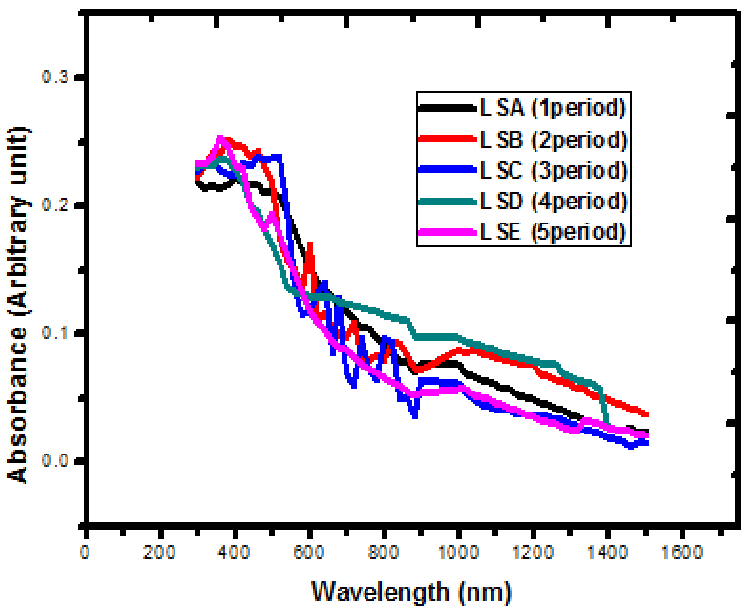

Fig. 2. The plot of absorbance as a function of wavelength

Fig. 3 shows the plot transmittance (%) as a function of wavelength of PbS thin films deposited at different deposition period at constant voltage (7V). From Fig. 3, it was observed that as the wavelength of incident radiation increases, the transmittance increases as well. From Fig. 3, it was noticed that all the samples deposited at different deposition time followed the same trend. It was also observed that sample LSC deposited at 3 mins recorded the transmittance of 0.582% in the infrared region and transmittance of about 0.966% in the ultraviolet region. However, all the samples deposited recorded transmittance above 50% in agreement with refs. [19-23,1].

Fig. 4 shows the plot of reflectance as a function of wavelength of PbS thin films deposited at different deposition period at constant voltage (7V). From Fig. 4, a slight increase in the reflectance as wavelength of incident radiation increases from 200 nm to 400 nm was observed. Beyond this range, the reflectance decreases as wavelength increases. It was observed that sample LSE deposited at 5 mins recorded the highest reflectance with a value of 0.167, while sample LSA deposited at 1 min recorded the lowest reflectance with a value of 0.163 in the near infrared and visible region [19-23,1].

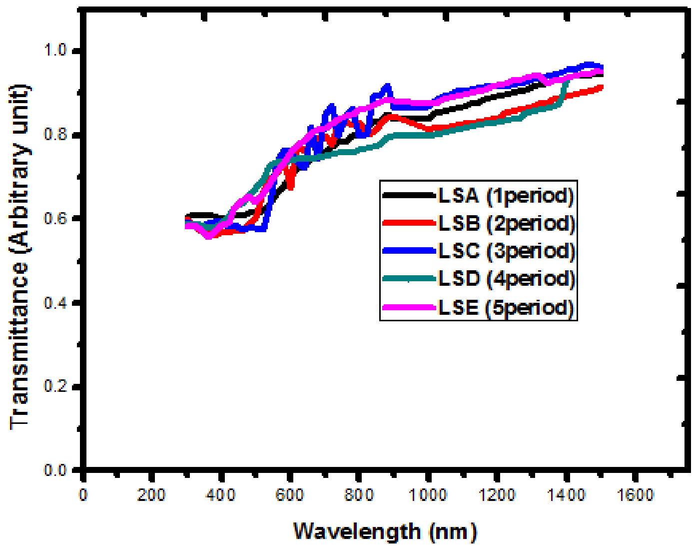

Fig. 3. The plot of transmittance as a function of wavelength

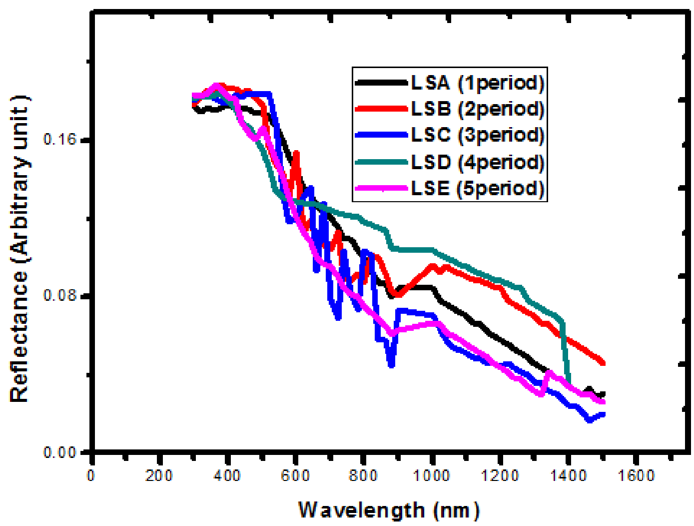

Fig. 4. The plot of reflectance as a function of wavelength

Fig. 5 shows the plot of refractive index as a function of photon energy of PbS thin films deposited at different deposition period at constant voltage (7V). From Fig. 5, it was observed that the refractive index increases as the photon energy increases. It was observed that sample LSE deposited at 5 mins recorded the highest refractive index of 2.494 with photon energy value of 4.137, while sample LSB deposited at 2 mins recorded the lowest refractive index of 2.461 with photon energy value of 4.137 [19-23,1].

Figs. 6-7 show the plot optical conductivity and extinction coefficient as a function of photon energy of PbS thin films deposited at different deposition period at constant voltage (7V). From Figs. 6-7, it was observed that the optical conductivity and extinction coefficient increases as the photon energy increases [19-23,1].

Figs. 8-9 show the plot of real and imaginary dielectric constant as a function of photon energy of PbS thin films deposited at different deposition period at constant voltage (7V). From the Figs. 8-9, it was observed that the real and imaginary dielectric constant increases as the photon energy increases [19-23,1].

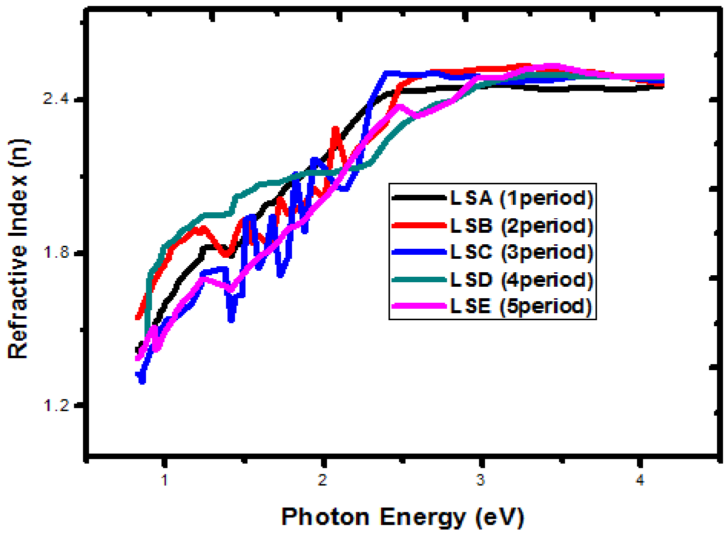

Fig. 5. Plot of refractive index as function of photon energy

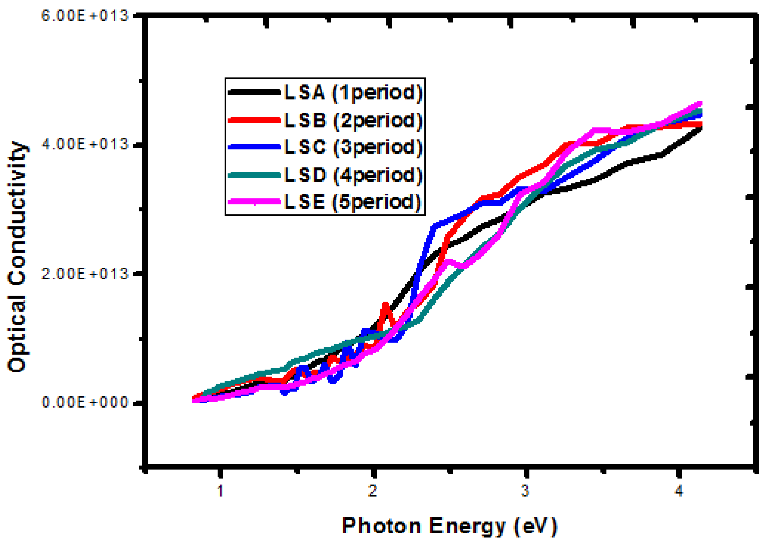

Fig. 6. Plot of optical conductivity as function of photon energy

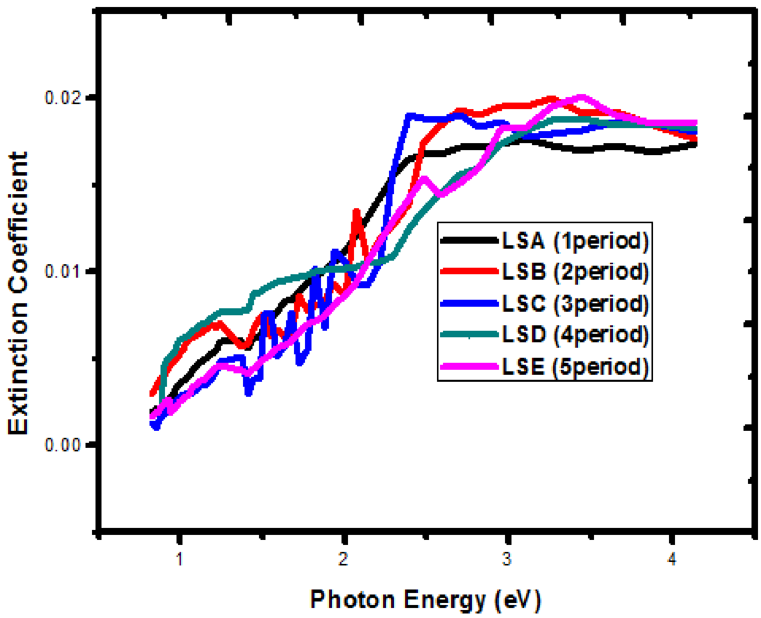

Fig. 7. Plot of extinction coefficient as function of photon energy

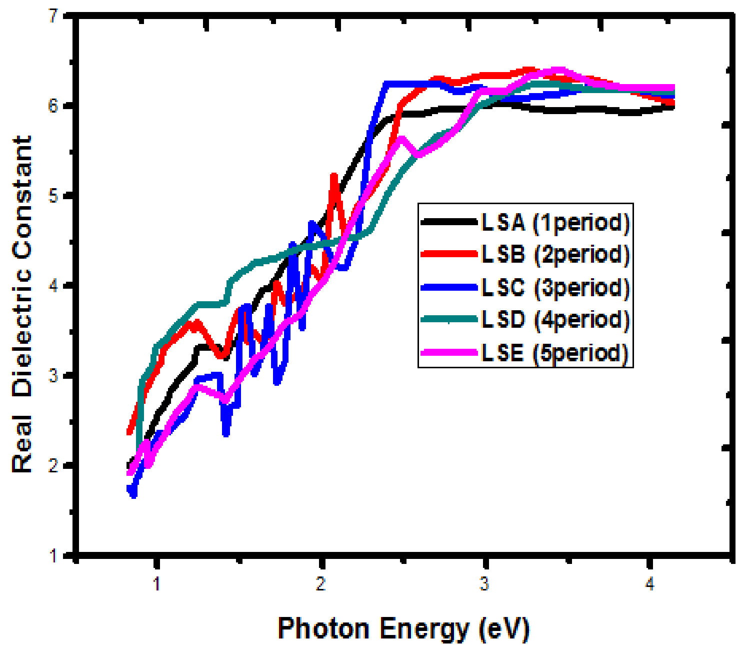

Fig. 8. Plot of real dielectric constant as function of photon energy

The band gap energy and transition types were derived from mathematical processing of the data obtained from the optical absorbance versus photon energy with the following relationships for near edge absorption [1,19].

$$\alpha = (hv - E_g)^{n/2} \quad (12)$$

Where υ is the frequency, h is the Planck's constant, while n carries the value of either 1 or 4. The band gap E_g could be obtained from a straight line plot of α^2 as a function of hυ. An extrapolation of the value of α^2 to zero will give the band gap. If a straight line graph is obtained from n=1, it indicates a direct transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained from n = 4. The band gap energy of 1.9eV-2.6eV was obtained with a direct transition shows in Fig. 10, in agreement with refs. [1,19-23].

Figs. 11-12 show the plot of period as a function of resistivity and thickness. From these figures, it was notice that the deposition period influences the resistivity and the thickness. From the plot, it was observed that as the deposition period increases, the resistivity and the thickness increases as well. This show that deposition period can affect rate of deposition of PbS thin films semiconductor material, the higher the deposition period the higher the resistivity and the thickness of the deposited material.

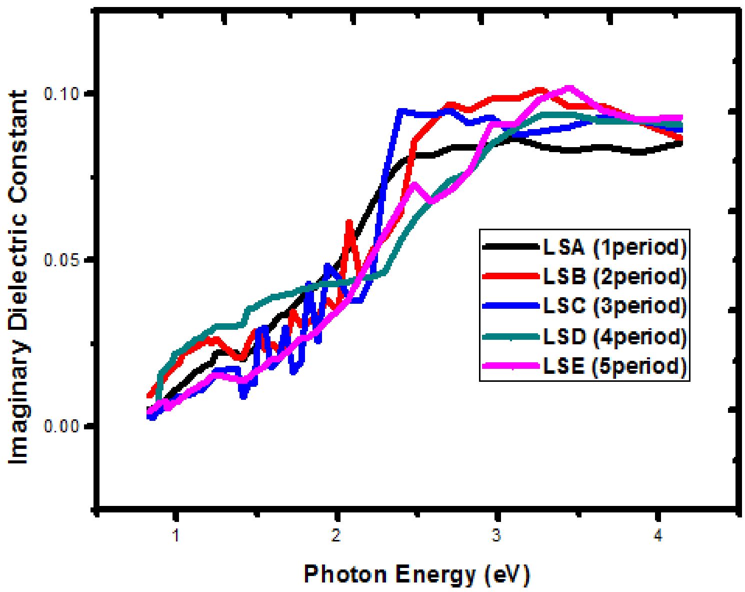

Fig. 9. Plot of imaginary dielectric constant as function of photon energy

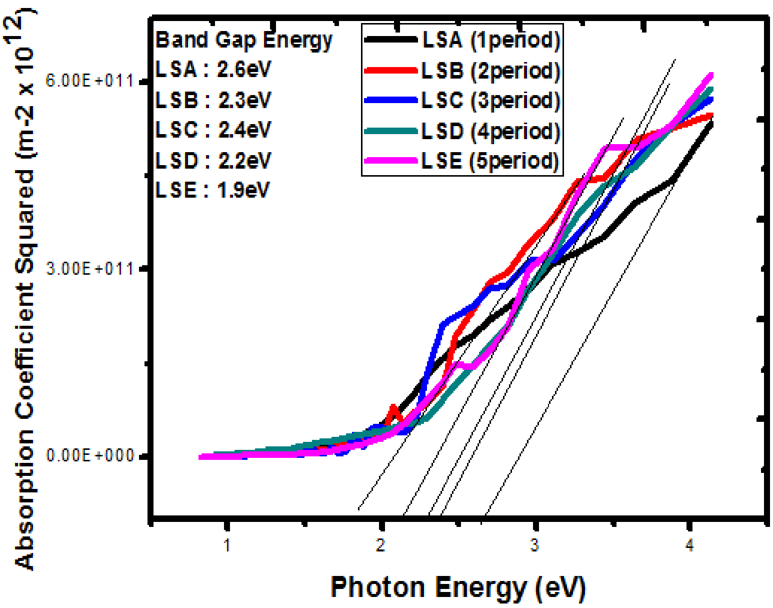

Fig. 10. Plot of absorption coefficient square as a function of photon energy

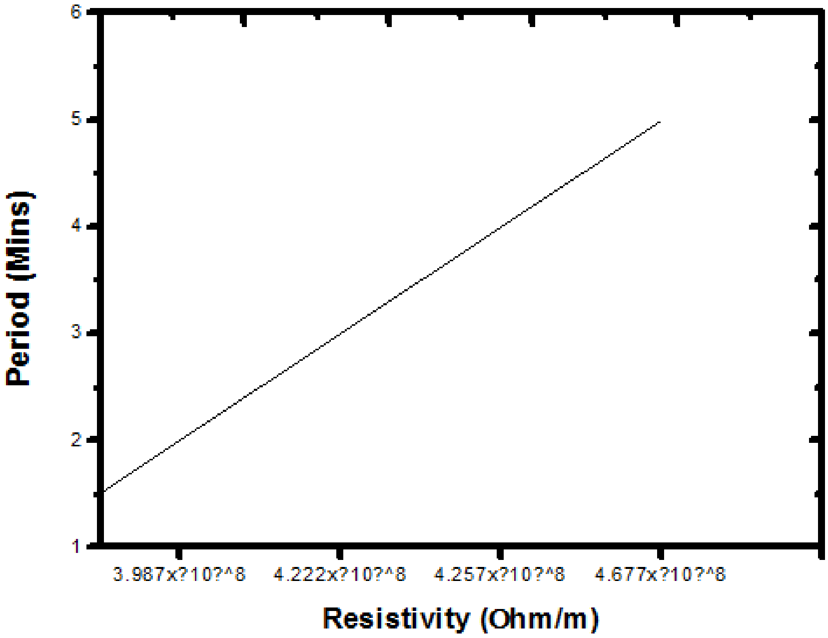

Fig. 11. Plot of Period as a function of resistivity

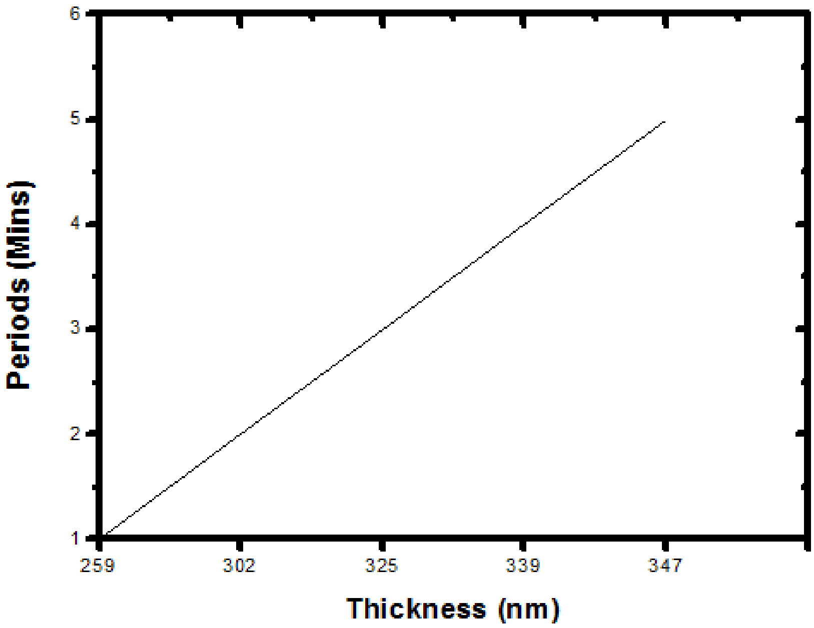

Fig. 12. Plot of Period as a function of thickness

5. CONCLUSIONS

Electrochemical deposition techniques have been used to grown PbS thin films in this paper. It was observed that the thickness of the material as deposited depend on deposition period. The resistivity and conductivity of the films increases as the thickness of the films increases. It was observed that as the wavelength of the films radiation increases, the absorbance of the material decreases. It was noticed that all the samples deposited at different time interval follow the same trend. Sample LSE deposited at 5 min was found to record highest absorption value of 0.253 at incidence wavelength of 360 nm and sample LSA deposited at 1 min recorded the lowest absorption value of 0.219 at incidence wavelength of 320 nm. The transmittance was observed to increase with the wavelength of the incident radiation. Sample LSC deposited at 3 min recorded the transmittance of 0.582% in the infrared region and transmittance of about 0.966% in the ultraviolet region).A slight increase in the reflectance with wavelength in the range 200 nm to 400 nm was observed. Beyond this range, the reflectance decreases rapidly as wavelength increases. It was observed that sample LSE deposited at 5 min recorded the highest reflectance in both region while sample LSA deposited at 1 min recorded the lowest reflectance in the near infrared and visible region. From the result analysis, it was observed that the refractive index, optical conductivity, extinction coefficient, real dielectric constant and imaginary dielectric constant were increased as the photon energy of the material was increased.It was notice that the deposition period influences the resistivity and the thickness of thin film. From the plot, it was observed that as the deposition period increases the resistivity and the thickness increases as well which shows that deposition period can affect rate of deposition of PbS thin films semiconductor material.

CONTRIBUTION TO KNOWLEDGE

We have been able to carried out the deposition of PbS thin films semiconductor on zinc plates using electrochemical deposition technique by varying the deposition period. To the best of our knowledge the deposition of PbS thin film on a metallic substrate such zinc has not been previously done. This is the salient contribution of this work to already existing knowledge.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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