

Characterisation of Nanostructured Lead Selenide (PbSe) Thin Films for Solar Device Applications

Oluyamo, S. S.¹, Ojo, A. S.², Nyagba M. S.³

^{1,2} (Department of Physics, School of Science, Federal University of Technology Akure, Nigeria)

³ (Department of Physics, Faculty of Science, Benue State University, Makurdi, Nigeria)

Abstract: The effects of pH of the reaction baths on the structural, optical and electrical properties of PbSe thin films have been investigated in the study. The thin films were deposited using the Chemical Bath Deposition technique and the samples were analyzed using X-Ray Diffraction (XRD) and UV-VIS-NIR spectrophotometry. The different sample thicknesses observed due to the variation of the deposition parameter are reported. The study revealed that the electrical conductivity and band gap energy of the samples decrease with thickness while the dielectric constant increased with thickness. This indicates that the solid state properties of the material can be controllably adjusted to achieve a desired function by variation of the deposition parameter in the deposition technique. Thus, by influencing the deposition of PbSe thin films through variation of its deposition parameters, it is possible to fabricate nanostructured materials with properties that can play significant roles in the production and utilization of thin films for solar system devices.

Keywords: Band gap, Characterization, PbSe, pH, Solar devices, Thin film.

I. Introduction

Semiconductors based on selenium are an important class of semiconducting systems which have been widely studied due to their fundamental electronic and optical properties. Intensive research has been performed in the past to study the fabrication and characterization of these compounds in the form of thin films [1]. A number of methods for the preparation of PbSe 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 since 1910 [2], utilization of CBD semiconductors in photovoltaic devices is much more recent [3, 4, 5]. The 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 [6], 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. [7] have studied the electrical conductivity of epitaxial thin films of $\text{Sr}_4\text{Fe}_6\text{O}_{13-\delta}$ deposited on single crystal NdGaO_3 and the dependency of the conductivity on the film thickness. Lead Selenide (PbSe) thin films are important materials for applications such as IR detector photographic plates, and photo resistors [8, 9]. Lead Selenide film is used as a target material in infrared sensor, grating, lenses and various optoelectronic devices [10]. PbSe thin films have a direct band gap of 1.30 eV at room temperature. This paper reports the effect of the deposition parameter on the electrical properties of PbSe thin films prepared by chemical bath deposition technique. The possible applications of the material in solar device technology will also be determined.

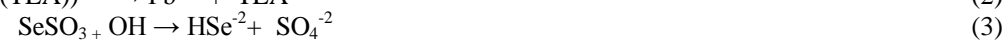
II. Material And Experimental Procedure

PbSe thin films of varying thicknesses were deposited on glass substrates using the chemical bath deposition (CBD) method. The basic principle of the CBD technique consists of the controlled generation of the metal and chalcogenide ions in an alkaline medium and their precipitation on the substrate. The AR reagents used for the thin film preparation are Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$), Selenium Sulphate (SeSO_3), Triethanolamine (TEA), Ethylene diamine tetra acetate (EDTA), 25% Ammonia and microscope glass slides ($76 \times 26 \times 1 \text{ mm}^3$) are used as substrates.

Table 1.0. Different Constituents for the Preparation of PbSe Thin Film at varied pH

Sample	pH	Time (hour)	Pb(NO ₃) ₂		EDTA	SeSO ₃		NH ₃	H ₂ O
	(m)		Mol. (M)	Vol. (mL)	Vol. (mL)	Mol. (M)	Vol. (mL)	Vol. (mL)	Vol. (mL)
T ₁	8.78	24	0.5	10.0	1	0.5	5.0	5.0	20.0
T ₂	8.84				2				
T ₃	8.95				3				
T ₄	9.43				4				
T ₅	9.58				5				

The Lead ion (Pb²⁺) was generated by the decomposition of (Pb(EDTA)²⁺) complex. The Se²⁻ ions were obtained in alkaline medium by decomposition of the Selenium precursor which is SeSO₃. The pH of the solution was adjusted by the use of 25% ammonia (NH₃). The deposition bath was prepared as shown in Table 1.0 : 10 ml of 0.5 M Pb(NO₃)₂ solution was measured into 5 different 50ml beakers and this was added to 5ml of 0.5 M of SeSO₃, various volumes of 1 M EDTA disodium salt was then added. The mixture was made up to the required volume with addition of water. The resulting solution was stirred for a few seconds with a glass rod stirrer and the pH of the solutions were determined using a Jenway 3015 pH meter. Well cleaned and degreased glass slides were clamped in the reaction baths and held vertically. The deposition process lasted for 24 hours at a deposition temperature of 27 °C. The slides were taken out, rinsed with distilled water and allowed to dry in laboratory air. The thickness of deposited thin films was determined using gravimetric weight method with a sensitive digital Mettler AE 166 microbalance. The equation governing the reaction and deposition of PbSe thin films are as follows:



The presence of the Pb⁺² and Se⁻² ions led to the formation of PbSe.



The samples were run on an X'pert Pro MD diffractometer which uses a Copper target (CuKα = 1.540502 Å, Current 40mA and a.c. Voltage 45kV) [11]. The thin films were scanned continuously within the 2θ range from 20° to 50° at a step size of 0.002 and a time per step of 0.05s. The optical absorption spectra were recorded at room temperature using a Jenway 6045 UV-VIS-IR spectrophotometer [11].

III. Theoretical Consideration And Calculations

The theoretical considerations of the optical and electrical properties of the films are as discussed in [12-21].

From the XRD analysis the inter-planer distance (d) and lattice constants (a) as were calculated. The crystallite (grain) size (D), dislocation density (ρ) and the micro strain (ε) were also calculated using the expressions below:

Grain size (D) was calculated using Scherrer's formula

$$D = K\lambda / \beta \cos\theta \quad (6)$$

where λ is wavelength of x-ray, β is FWHM (full width half maximum), θ is the diffraction angle and K is 0.9 which varies with (hkl) and crystallite shape.

The lattice constant (a) was calculated with:

$$a^2 = (\lambda^2 / 4 \sin^2\theta) (h^2 + k^2 + l^2) \quad (7)$$

The dislocation density, (ρ) = aD (8)

where a is the lattice constant.

Micro strain, (ε) = βcosθ / 4 (9)

IV. Result And Discussion

Fig. 1.0 shows the plot of thickness versus pH of the reaction baths. It was observed that varying the volume of complexing agent, EDTA, affects the rate of deposition of the films. The thickness of the films increased initially to a maximum of 1.592 μm and dropped gradually to 0.517 μm. The PbSe thin films were observed to grow optimally in an alkaline medium with a pH range of 8.7-8.93. This indicates that the rate of deposition depends on the pH of the reaction bath.

The XRD diffraction patterns of CBD PbSe thin films deposited for 2ml and 4ml (EDTA) are presented in Fig.2.0. Phase identification was then made from an analysis of intensity of peak versus 2θ. The PbSe deposited with 2ml (EDTA) peaks at 36.02° which gives rise to a structure with lattice constant a = 4.315 Å and (111) preferred orientation. The peak for 4ml deposition was observed at 36.49° with lattice

constant $a=4.261 \text{ \AA}$. The diffraction peak was observed to become much broader with increasing pH values and tends to disappear for higher pH values. Similar effect was observed in previous study by [22]. As the pH of chemical bath increased, the diffraction peak intensity decreased as shown in Fig. 2. It can be seen that the crystal structure of the films was affected strongly by the pH values of the chemical bath. The low intensity peak observed in the XRD pattern of the 4ml sample under study shows that the film is nanocrystalline. The broad hump in the displayed pattern could be due to the amorphous glass substrate [23] and also possibly due to some amorphous phase present in the PbSe nanoparticle thin films. The structural parameters of the PbSe thin film are shown in Table 2. It reveals that lattice constant, the crystal size of the film and the dislocation density increases with film thickness, but micro strain decreases with the increased film thickness. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain of the material indicates the formation of higher quality films. This effect had also been noted by [24] in previous work. This may be due to the decrease in imperfections and dislocations of the films with increasing film thickness.

Transmission measurements are performed at normal incidence over a large spectral range (200 to 1100 nm). The transmission spectra of PbSe thin films obtained at different pH are displayed in Fig. 4. The broad cut off towards short wavelengths indicates the onset of intrinsic inter-band absorption in the PbSe. An increase of the transmission values over the whole spectral range is observed with increasing pH values. In the transparency region, transmission is as high as 70% for pH=9.43; 60% for pH=9.58, about 50% for pH=8.84 and at pH=8.78 transmission varies from 20% to 46% at the near infrared region. However there is no detectable variation of the short wavelength absorption edge with the pH. The decrease of the transmission coefficient with decreasing pH can be interpreted by an increase of the film thickness as reported in Fig. 1. Films grown at pH=8.93 appear to have the best crystallinity but also the smallest transmission in the transparency region.

Table 2.0: Structural Parameters of PbSe Thin Films Deposited varying pH

Sample	Thickness (Å)	hkl	2θ (deg)	d (Å)	Lattice constant, a (Å)	FWHM,B	Grain size, D (Å)	Dislocation density, δ 10^{-20} lines/m ²	Micro strain, ϵ 10^{-3}
2ml	15030	111	36.02	2.491	4.315	0.4224	3.4516	14.8940	0.1004
4ml	11903		36.49	0.921	4.261	0.9216	1.5841	6.7505	0.2188

Table 3.0: Average Optical Properties for PbSe Thin Films Deposited varying pH

Samples with pH (m)	Time (hours)	Temp. (K)	Absorbance (A)	Transmittance (T)	Reflectance (R)	Refractive Index (n)	Absorption coefficient ($\alpha \times 10^4$)
Uncoated Glass slide	24	300	0.003	0.9975	-0.0005	1.0815	22.68
8.78			0.43	0.37	0.20	2.61	1.70
8.84			0.35	0.46	0.19	2.59	1.20
8.93			0.50	0.35	0.18	2.49	1.63
9.43			0.23	0.61	0.15	2.57	1.06
9.58			0.29	0.54	0.17	2.56	3.07

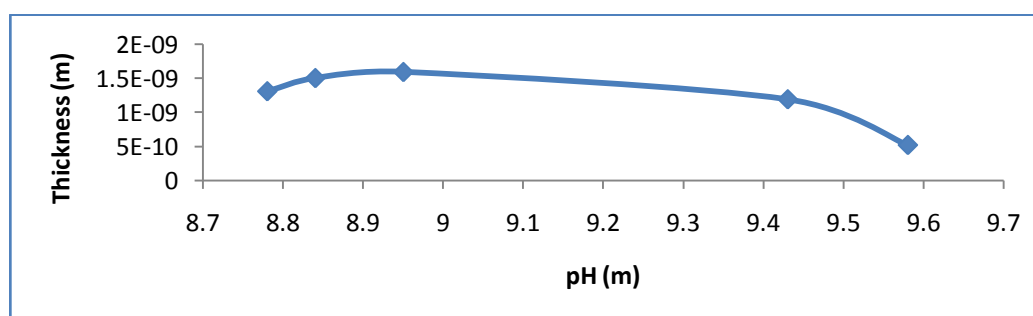


Figure 1: graph of thickness vs.pH (m) of the chemical baths for PbSe thin films deposited at 27°C

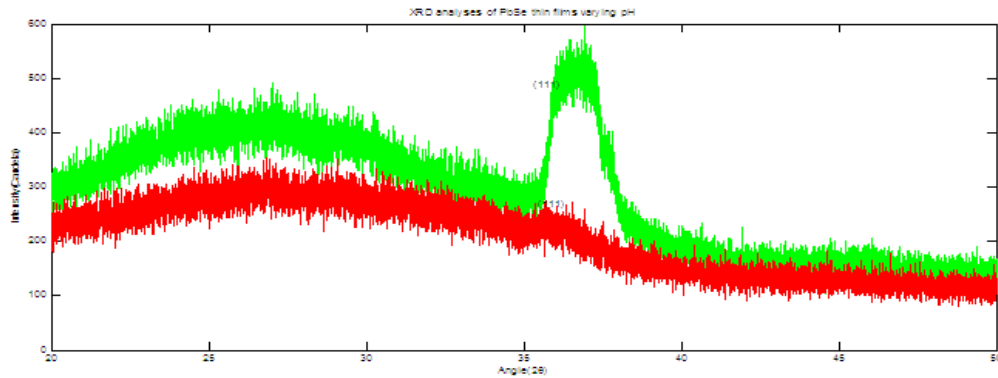


Figure 2.0: X-ray diffraction patterns of samples 2ml and 4ml of PbSe thin films at 27 °C

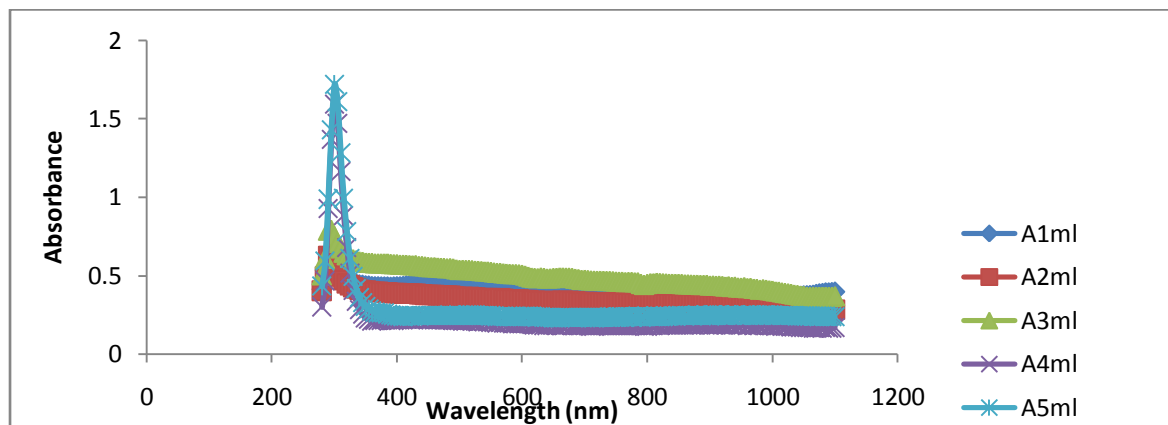


Figure 3.0: graph of Absorbance vs. wavelength (nm) for PbSe thin films deposited at 27°C varying pH

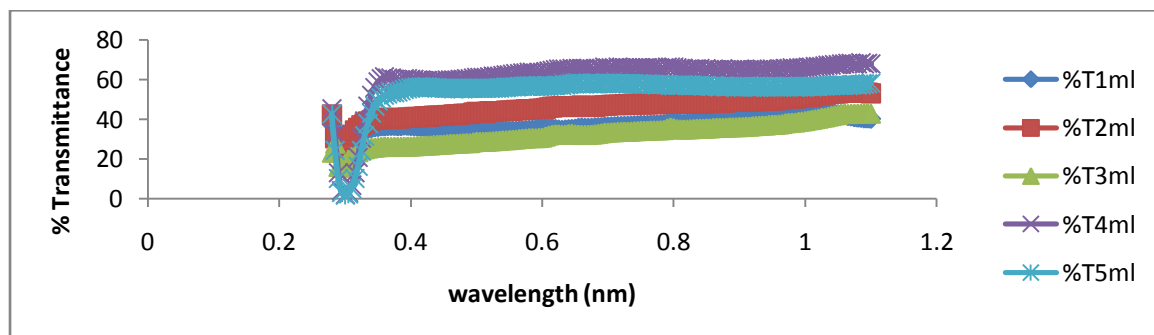


Figure 4.0: graph of % transmittance vs. wavelength (nm) for PbSe thin films deposited at 27°C varying pH

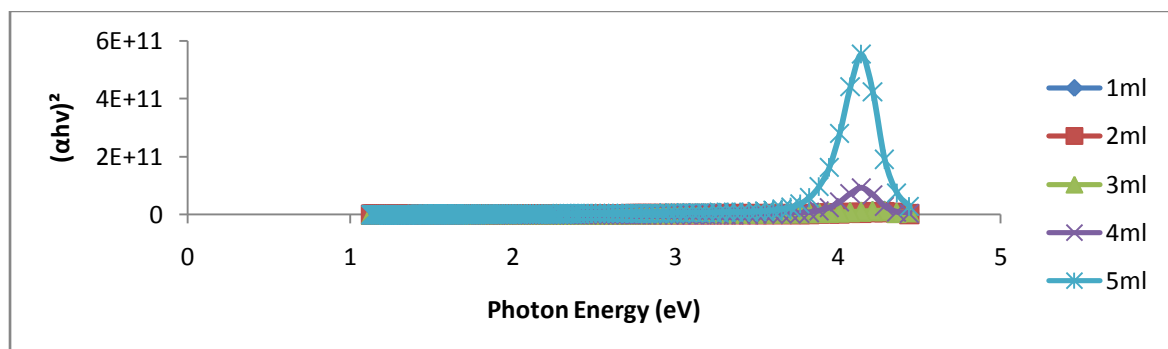


Figure 5.0: graph of $(\alpha h\nu)^2$ vs. photon energy (eV) for PbSe thin films deposited at 27°C varying pH

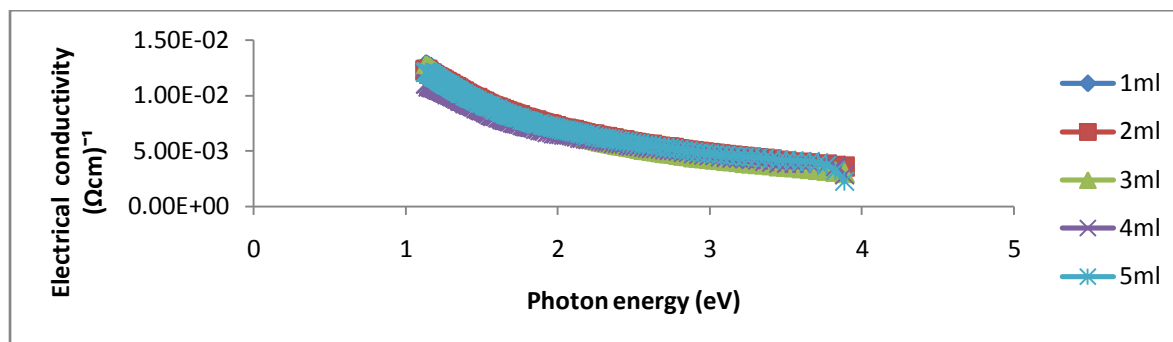


Figure 6.0: graph of electrical conductivity(σ_e) vs. photon energy (eV) for PbSe thin films deposited at 27°C varying pH

Fig.3 shows the plots of absorbance versus wavelength of PbSe thin films deposited in this work. The absorbance generally decreased with increase in wavelength and has relatively low values in the infrared region of the spectrum. A strong absorption was observed at wavelength range of 300nm – 500nm, hence the film has potential application in the fabrication of solar cell.

The transmittance spectra Fig. 4, displayed shows increase in transmittance as the wavelength increases. The very high transmittance in the visible region makes Lead Selenide films useful aesthetic window glaze materials. The films could also be 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 value of α is determined from transmittance spectra. These absorption spectra which are perhaps the simplest method for probing the band structure of semiconductors are employed in the determination of the energy gap, E_g . The value of α determined from transmittance spectra was found to vary from an average of $3.0 \times 10^4 - 1.6 \times 10^4$. This large α -value is within the α -range 10^4 - 10^5 cm^{-1} for semiconductor thin films desirable for production of polycrystalline thin film solar cell [25]. The energy band gap E_g was obtained from Fig. 5.0. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g , which is determined by extrapolation. The values of the energy gap for the films are recorded in table 4.0. The variation of energy gap with thickness is also shown in the Table 4. It is observed from figure5.0 that PbSe thin film exhibits direct band transition and its band gap energy decreases with increase in film thickness. Hence the variations of band gap in the films are due to the changes in the lattice constant.

Table 4.0 Solid State Properties of PbSe Thin Films deposited on glass varying pH

pH (m)	Time (hours)	Temp. K	Energy Gap E_g (eV)	Electrical conductivity $\sigma_e(1 \times 10^{-4}(\Omega\text{m})^{-1})$	Real dielectric constant (ϵ_r)	Imaginary dielectric constant ($\epsilon_i \times 10^{-5}$)	Thickness d (μm)
8.78	24	300	2.20	0.73	7.13	3.56	1.31
8.84			1.73	0.78	6.76	3.07	1.50
8.93			1.50	0.77	6.45	4.07	1.59
9.43			3.20	0.73	5.83	2.12	1.19
9.58			3.30	0.71	6.62	6.77	0.517

Fig. 6.0 shows the graph of the electrical conductivity of PbSe thin films deposited at different pH. All the films are found to conduct well at low frequencies, i.e. the conductivity of the material decreases with increasing frequency of incident radiation. It is observed that, the conductivity of the material decreases with frequency of the incident radiation. So, the material conducts better at photon energy $(h\nu) \leq \text{UV-VIR}$ energy. The electrical conductivity of the films vary from an average of 0.78×10^{-4} - $0.71 \times 10^{-4} (\Omega\text{cm})^{-1}$ within the electrical conductivity range of 10^{-12} to $10^2 (\Omega\text{cm})^{-1}$ for semiconductors [26- 30]. The thickness of the material is also found to influence the conductivity, as the thickness increases the conductivity decreases.

The variation of the solid state properties of the films deposited with different volume of the complexing agent i.e. different pH values is as shown in table 4. It indicates that as the pH increased, the energy band gap, the electrical conductivity (of the order 10^{-4}) decreased. The real dielectric constant of the films decreased while the imaginary dielectric constant increased with pH. These properties also reveal the suitability of the films for solar cell fabrication.

V. Conclusion

Lead selenide thin films were successfully prepared varying pH by chemical bath deposition technique on glass substrates. The variations were found to affect thickness of the deposited films. The structural and electrical properties of the films were found to be thickness dependent. The X-ray diffraction studies revealed that all films had FCC crystal structure with a (111) preferred orientation. Optical studies indicated that the band gap decreased with increasing thickness of the films. The electrical conductivity decreases with thickness while the dielectric constant increases with thickness. The values of bandgap E_g which fall within the light energy range of the electromagnetic spectrum could find applications in solar devices useful for generating electricity especially for rural electrification, communication, remote monitoring and control. Also, the possibilities of fabricating Lead Selenide thin films with adaptable microstructural and electrical properties gives it many prospects in various technological fields. The deposited thin films with high transmittance (T) and low reflectance (R) could find applications in thermal control window coatings and heat mirror coatings in architectural industry and also in antireflection coatings for solar-thermal devices.

References

- [1]. J. Herrero, M.T., Gutierrez, C., Guillen, J.M. Donato, M.A. Martonez, A.M Chaparro and R Bayo. Photovoltaic windows by chemical bath deposition. *Thin Solid Films* 361-362, (2000), 28-33.
- [2]. O. Houser, E. Beisalski, *Chem-Zeitung* 34, (1910),1079.
- [3]. T.L. Chu, S.S. Chu, J. Britt, C. Ferekides, C. Wu, J. Britt and C. Wang. *J. Appl. Phys.* 70, (1991), 7608.
- [4]. I. Grozdanov. *Semicond. Sci. Technol.* 9, 1234, (1994).
- [5]. P.K. Nair, M.T.S Nair, V.M. Garcia. *Sol. Energy Mater. Sol. Cells* 52, (1998), 313.
- [6]. D. Linco, J.F Guillemoles, P. Cowache. *Proc. 2nd World Conf. on Photovoltaic Solar Energy Conv.* JRC-European Commission, Vienna, (1998), 440.
- [7]. J.A Pardo, J. Santos, C. Solis, G. Garcia. A. Figueras and M.D. Rossell. *Solid State Ionics*, 177, (2006), 423-428.
- [8]. R.B. Kale, S.D. Sartale, V. Ganessan, C.D. Lokhande, L. Yi-Feng and Shih-Yuan. Room temperature and Chemical synthesis of Selenide Thin films with preferred Orientation. *Appl. Surf. Sci.* 253, (2006), 930.
- [9]. J.M. Peitryga, R.D. Schaller, D.J Werder, M.H. Stewart, V.I. Klimov and J.A. Hollingsworth. Mid-infrared emitting Colloidal PbSe Quantum dots. *J. Am. Chem. Soc.* 12, (2004), 11752.
- [10]. M.S. Ali, K. A. Khan and M.S.R. Khan. Temperature Effect on Electrical Properties of Lead Selenide. *Phys. Status Solidi (a)* 149, (1995), 611.
- [11]. S. S. Oluyamo, O. A. Abdulsalam and A.S. Ojo. Effects of the Composition of Reaction Bath on Growth, Optical and Electrical Properties of PbS Thin Films. *Journal of the Nigerian Association of Mathematical Physics*, 28, (1), (2014), 309-316.
- [12]. S. S. Oluyamo, M. S. Nyagba and A.S. Ojo. Optical Properties of Copper (I) Oxide Thin Films Synthesized by SILAR Technique. *IOSR Journal of Applied Physics (IOSR-JAP)*, 6, (3), (2014)102-105.
- [13]. G.F. Cothiam. *Treatise on Solar Energy*, Wiley-Interscience Publication, New York, (1984).
- [14]. J.I. Pankova. *Optical Processes in Semiconductors*, Dover Publications Inc. New York. (1971).
- [15]. Fredrick Wooten. *Optical properties of solids*, Academic Press, New York, (1972).
- [16]. B. Mahrov, G. Boschloo, A. Hgfeldt, L. Dloczuk, and Th. Dittrich. Photovoltage study of charge injection from dye Molecules in transparent hole and electron conductors, *Appl. Phys. Lett.* 84(26), (2004), 5455-5457.
- [17]. T.J. Coutts, J.S. Ward, Young, D.L Dessent and R. Noufi. The search for and potential impact of improved transparent conducting oxides on thin film solar cells, *Technical digest of the 12th international photovoltaic science and engineering conference*, Jeju Korea, (2001).
- [18]. G. Harbeke, *Optical Properties of Semiconductors*, Abeles, F.(Ed). *Optical Properties of Solid*, North-Holland Pub. Co., Amsterdam, 28, (1972).
- [19]. F. J. Blatt. *Physics of electronic conduction in solids*, McGraw-Hill Book Company, (1968).
- [20]. P. A. Cox. *The electronic structure and chemistry of solid*, Oxford University Press Oxford. (1987).
- [21]. J. P. Suchet. *Electronic conduction in solid materials (physicochemical bases and possible applications)*, Pergamon Press, New York. (1976).
- [22]. B. Kavitha and M. Dhanam. The effects of pH adjustments on the structural and optical properties of CIAS (Cu (In Al) Se₂) thin films. *Revue des Energies Renouvelables*, 13(4), (2010), 603 – 612.
- [23]. T.B. Nasr, N. Kamoun, M. Kanzari, R. Bennaceur. Effect of pH on the properties of ZnS thin films grown by chemical bath deposition. *Thin Solid Films* 500(4) (2006), 335-350.
- [24]. S. Lalitha, R. Sathyamoorthy, S. Senthilarasu A. Subbarayan and K. Natarajan. Characterization of CdTe Thin Film-Dependence of Structural and Optical Properties on Temperature and Thickness, *Solar Energy Materials and Solar Cells*, 82,(1-2), (2004), 187 – 199.
- [25]. J.D. Mearkin. *Polycrystalline Thin Film Solar Cells*, (G Furlan, D Nobili, A.M. Sayigh. and Seraphin, B.O. (Eds)), *Workshop on Materials Science and Physics of Non-conventional Energy Sources*, World Scientific Pub. Co., Pte. Ltd., Singapore, (1989), 259-262.
- [26]. R.L. Webber, Muning, K.V., White, M.W. and Weygand, G.A. *College Physics*, McGraw-Hill Book Co. Inc., USA 461, (1974).
- [27]. H.A. Pohl. *Modern Aspect of the Vitreous State (Semiconductor in Polymers) Vol.2*, Butterworths, London, (1962), 82.
- [28]. A.A. Dulov. *Usp. Khim*, 35, No. 10, (1963), 1853.
- [29]. V.S. Myl'nikov, *Usp. Khim*, 37(1) (1968), 78.
- [30]. Y. Paushkin, T.P. Vishnyakova, A.F. Lunin and S.A. Nizova, *Organic Polymeric Semiconductors*, John Wiley and Sons Inc., New York, (1974).