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Experimental Evidence of Quantum Confinement Impairment In The Optical Properties of Annealed Lead Sulphide Thin Film

Uno E. U.[1], Emetere M.E.[2], Faluyi E.S.[1], Gbenga B.A.[1]
Department of Physics, Federal University of Technology, Minna, Nigeria.
Department of Physics, Covenant University, Ota, Nigeria.
uno_essang@yahoo.co.uk, moses.emetere@covenantuniversity.edu.ng

Abstract

Recent characterizations of compounds are undoubtedly one of the avenues for the emergence of new semiconducting-light emitting diode (LED) devices. The industrial application of the lead sulphide thin film has been proposed. The lead sulphide thin film was grown by Chemical Bathe Deposition Technique (CBDT) and annealed at four temperatures of 100^{o}C, 150^{o}C, 200^{o}C and 250^{o}C. The samples were analyzed via the 6045 U-V spectrometer. The results shows that PbS thin film has a low transmittance value ranging from 0.204709% to 0.85722%; absorbance value ranging between 3.026% and 3.564%; reflectance value ranging from 81% to 114%; direct band gap was between 1.66eV to 1.78eV. Hence, the calculated refractive index ranges from 1.67 to 1.669. The evidence of quantum confinement impairment in each annealed samples was proofed. This shows that the optical tuning of the lead sulphide is dependent on the thermal control of its constituent's diameter.

Keywords: lead sulphide thin film, optical properties, quantum confinement, impairement, chalcogenide

Introduction

The sectional discoveries about the lead sulphide may be inciting and most importantly connotes that its importance to the industry is unprecedented. Since the 1930s, the lead sulphides are known as infrared detector and have wide range of application in military operations. The lead sulphides also have a wide range of industrial application in recent times. For example, it is used as wave guides switches modulators or laser detectors in integrated optics for measuring gas chemical specie in the laboratory and the lower atmosphere. Also, lead sulphide is used as gas spectrometer (Karami et al., 2013). Asides its use as flame/gas/smoke detector or infrared photo detector, lead sulphide (PbS) is a semiconducting chalcogenide. It is used for fabricating thin film integrated circuits and computer memories. Lead sulphide has a direct bandgap of 0·41 eV and thus serves as a good transducer in many optical-electrical devices e.g. photovoltaic modules. Hence, we propose that the wide range of lead sulphide is directly proportional to its industrial or laboratory preparation techniques.

The most prominent preparation technique for growing lead sulphide is the chemical bath deposition (CBD) method. This method is easy to handle and less expensive. It enables the easy deposition of films on various substrates and sizes. Scientist have discovered that the CBD is dependent on the duration of deposition, composition of compound-constituent, temperature at which the film is deposited on substrate, different molar concentration and chemical nature of the substrate (Bhatt et al., 2012; Uno et al.,2014a,b; Emetere et al., 2013; Devi et al, 2007; Obaid et al.,2012). Other methods e.g. spray pyrolysis, chemical vapour deposition (CVD) and magnetic sputtering can be used to prepare lead sulphide samples. Significant among the conditions for successful CBD is the systemic variation of the molar concentration. Obaid et al., (2012) proofed that the optical band gap of the films decreases from 0.470 ± 0.004 eV to 0.400 ± 0.003 eV with increasing molarity. This results have been adduced to quatum size effect (Mahdi et al., 2012), positional doping effect (Uno et al., 2014) e.t.c.

In this paper, we propose that the optical properties of lead sulphide depend on the systemic variation of the annealed temperature of lead sulphide. Soonmin et al.,(2013) had worked closely to this concept i.e. investigating the effect of bath temperature on the thickness of lead sulphide thin films. Our concept seeks to improve on the quantum confinement induced by the annealed samples to improve the electronic band structure and the band gap in lead sulphide semiconductor nano-crystals (Rosetti et al., 1985; Kang et al., 1997). Quantum confinement occurs in a semiconductor crystallite when its excitons are squeezed via its diameter reduction i.e. lower than the size of its exciton Bohr radius. Generally, there are weak and strong confinement regimes. Hence, the electronic and optical properties are highly tunable at this regime. During this state, continuous energy state may keep the band gap at its original energy except there is a change in size. Figure 1 expresses the expected quantum confinement in nano sturcture and bulk materials. PbS exhibit strong quantum size effects below excitonic Bohr radius (Tang et al., 2010). Hence its energy band gap (of its nanocrystals) can be tuned to anywhere between 0.41 (bulk) to 4 eV. The bandgap width of lead sulphide (PbS) is very sensitive to finite-size effects. Hence, it manifests high increase of optical absorption energy via its particulate size i.e. quantum dot or bulk PbS. Its optical bandgap in the PbS quantum dot increases up to 5.2 eV compared to the 'bulk' PbS value which is given as ~0.4 eV at room temperature (Hoffmann et al., 2000). In this paper, we propose that there exist a quantum confinement impairement which is initiated by the anneal thermal effect on both the structure and interplane of the PbS.

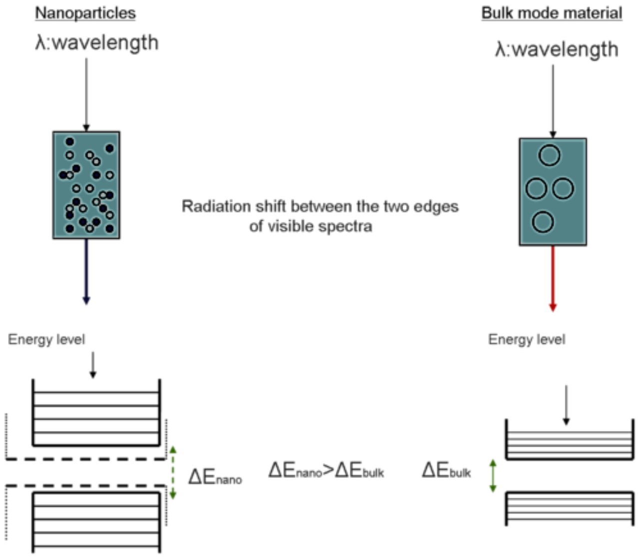


Figure 1: Quantum Confinement Effects On The Energy Difference Between Energy States And Band Gap (Retrieved From Wikipedia)

Laboratory Preparation of Samples

The purification of all reagents were graded analytically. In this experimentation, 22.4g of KOH was used, 15.2g of thiourea was used and 6.6g of lead nitrate. Subsequently, 0.2 mole of Thiourea ($Sc(NH_2)_2$) was measured with the digital weighing balance and placed in 200ml of distilled water. This solution was stirred vigorously by using magnetic stirrer. Also, 0.1 mole of lead nitrate ($Pb(NO_3)_2$) was also measured with the digital weighing balance and placed in 200ml of distilled water. Then, 1 mole of Potassium Hydroxide (KOH) was measured and placed in 400ml of distilled water. All individual solutions were stirred vigorously by using magnetic stirrer. The deposition of lead sulphide (PbS) thin film by Chemical Bathe Deposition Method is based on the reaction between lead nitrate ($Pb(NO_3)_2$) and thiourea ($Sc(NH_2)_2$) using KOH as a complexing agent. Thiourea is used as the sulphide ion source and lead nitrate as the lead ion source. The deposition process is based on the slow release of Pb^{2+} and S^{2-} ions in the solution. 22.4g of potassium hydroxide solution was titrated against the 6.6g of lead nitrate solution until it reached its end point. The end point of the solution is when it turns colourless. The end-point solution was then added to 15.2g thiourea solution and rapidly stirred. The 7 x 5 x 4 glass slide was immediately dipped into this solution and stirred with the electric stirrer until the solution becomes black. The time it took for the solution to turn completely black was about 10 minutes. PbS was created by the stains on the glass slides. The thin film was then divided into four samples i.e. A, B, C and D. These samples were placed in the electrical oven and set to the desired annealed temperature which was 100^oC, 150^oC, 200^oC and 250^oC. The annealing time for each of the samples was for 1 hour each, hence all the samples were annealed at a constant time. Optical property characterizations were conducted using the 6045 U-V Spectrophotometer while the thickness of the film was carried using surface profilometry.

Results and Discussion

The experimental analysis of the thermal controlled quantum confinement monitored via an integrated transmittance, reflectance and absorbance curves against wave length for the PbS thin films annealed at 100^{O}C (Sample A), 150^{O}C (Sample B), 200^{O}C (Sample C) and 250^{O}C (Sample D) is shown below. Here figure 2 represents the transmittance of each sample with respect to its imposed wavelengths, figure 3 represents the reflectance of each sample with respect to its imposed wavelengths, figure 4 represents the reflectance of each sample with respect to its imposed wavelengths. From the figure 2, it is observed that the value of the transmittance increases with increase in annealing temperature. Here, the samples A, B and C were consistent with the observation of Prakash et al.,(2004) when he deposited zinc suphide. This signifies that its quantum confinement as noticed in the sulphide-sample quantum dots are almost alike. Hence, have the same industrial application. The revelation of this study was the characteristic behaviour of the transmittance for sample D. This shows that higher annealed temperature, the quantum confinement of lead sulphide is altered. From figure 3, there was an increase in the reflectance with increasing annealing temperature i.e. showing that PbS has a very high reflectance. This agrees with Prakash et al., (2004) that PbS are very good reflecting semiconductor. The reflectance of sample D further proved that its quantum confinement enables high reflectivity. However, Sample C showed an inverse behaviour to sample D. This affirms the Bauschinger effect which is responsible for thermal gradient truncation in some heterogeneous compounds (Emetere, 2014) may be also affect the quantum confinement of PbS. This may also be that the anneal temperature transited the quantum confinement into the dichroic bleaching state where the electrons are in a non-equilibrium state (Emetere et al., 2014).

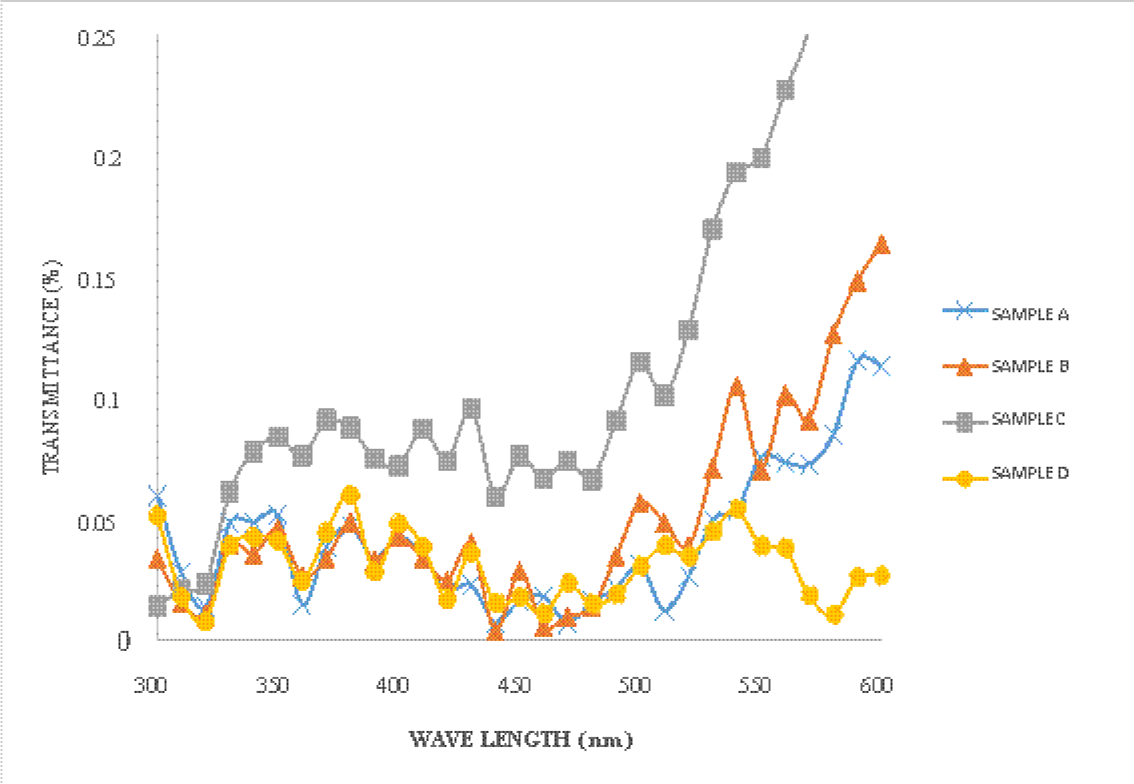


Figure 2: Experimental shift of sample transmittance with respect to wavelengths

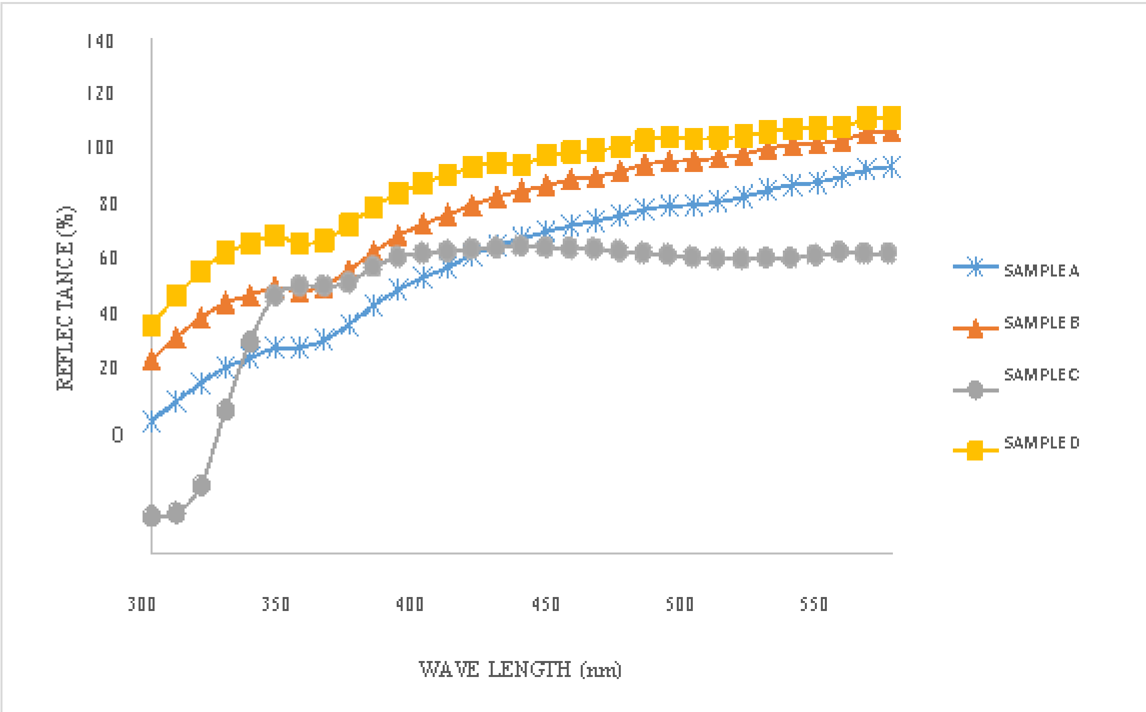


Figure 3: Experimental shift of sample reflectance with respect to wavelengths

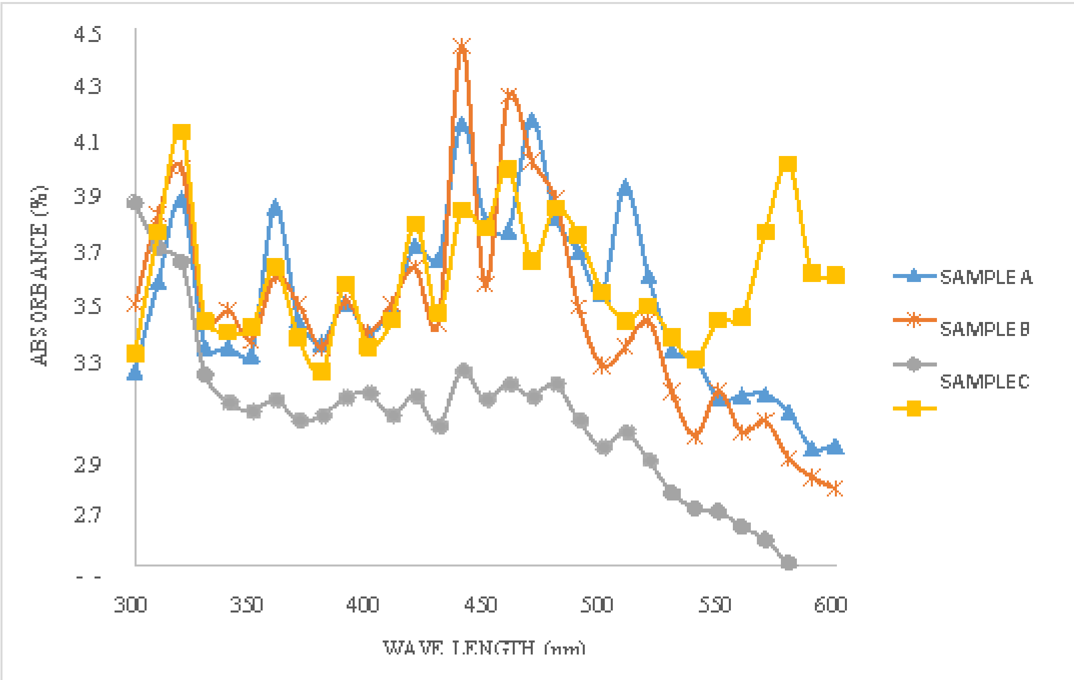
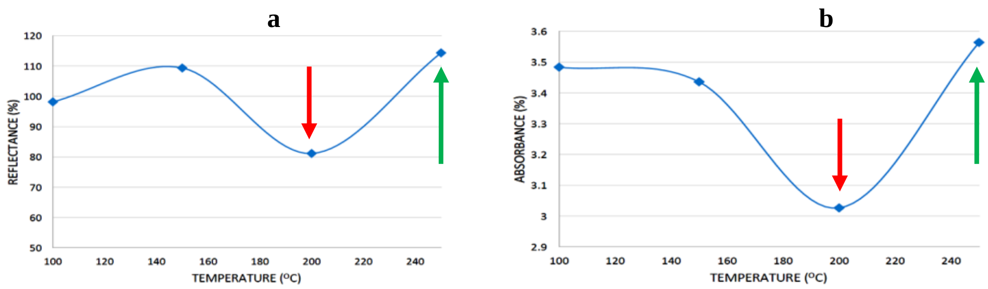


Figure 4: Absorption spectra for Samples A, B, C and D

In figure 4, the films show a marginal decrease in absorbance after annealing. Sample C further shows that its specific trend cannot be attributed to an improved crystallinity only. Rather, it could be attributed to quantum confinement impairment which initiates fewer states within the band gap available for photon absorption. Hence, we affirmed the quantum confinement impairment noticed in the PbS samples by plotting its transmittance, reflectance and absorbance curves against annealed temperature as shown in figure 5a-i below. Specific attention is on samples C (illustrated in red arrow) & D (illustrated in green arrow). .



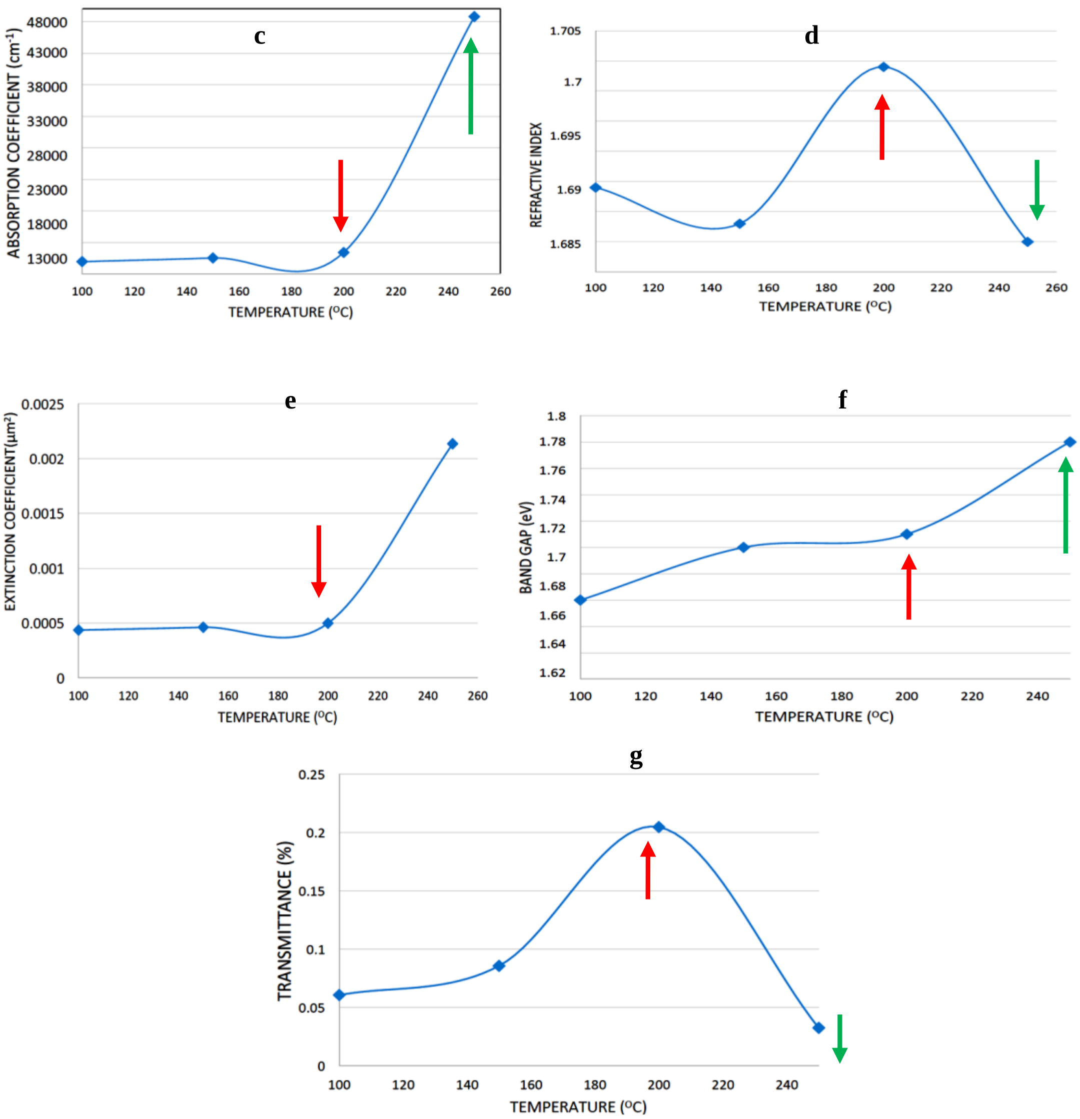


Figure 5 a-g: Pictorial Analysis Quantum Confinement Impairment Effects on The Optical Properties of Pbs

Conclusion

The annealed films at specific temperatures (in this case 100^{O}C, 150^{O}C, 200^{O}C and 250^{O}C) do not only decrease the density of localized states i.e. it improves the crystallinity of the films. This occurrence creates an impact on the quantum confinement of the sample. However, the initiated Bauschinger effect which is responsible for thermal gradient truncation in some heterogeneous compounds opens-up the concept of quantum confinement impairment. Quantum confinement impairment makes the Lead Sulphide sample to mimic several sub-atomic states. This may be advantageous for PbS industrial applications. For example, at very high reflectance value, PbS cannot serve as anti-fire coating, but rather good solar cell candidate. However, the individual sample performance shown by figure 5 reveals that the annealed temperature is directly proportional to the formations of various quantum confinement. When the results are compared with past research on PbS, the quantum confinement impairment are more evident. Hence, the preparation or growing technique of PbS defines the dimension of the quantum confinement impairment.

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Reference

[1] Devi R, Purkayastha P, Kalita P K and Sarma B K . Synthesis of nanocrystalline CdS thin films in PVA matrix *Bull. Mater. Sci*. 30, 123(2007).

[2] Ho SM, Anuar K. Tan, WT. Thickness Dependent characteristics of chemically deposited tin sulphide films. *Universal Journal of Chemistry.* 1(4), 170-174 (2013).

[3] Hassan Karami, Mina Ghasemi, Sara Matini. Synthesis, Characterization and Application of Lead Sulfide Nanostructures as Ammonia Gas Sensing Agent, *Int. J. Electrochem. Sci.*, 8, 11661 - 11679 (2013)

[4] Hoffmann, E., P. Entel. Structure And Dynamics Of Heterogeneous Systems. *From Solids to Clusters*, 148–155 (2000) DOI: 10.1142/9789812793652_0014.

[5] Kang, I.; Wise, F.W. Electronic structure and optical properties of PbS and PbSe quantum dots. *J. Opt. Soc. Am. B-Opt. Phys. 14*, 1632-1646 (1997).

[6] Moses E Emetere. Modeling the Non-Single Exponential photoluminescence Decay Using the Boubaker Polynomial Expansion Scheme. *Journal of Advance Physics*, 2(3), 213-215(2013).

[7] Moses E Emetere. Profiling Laser Induced Temperature Fields for Superconducting Materials Using Mathematical Experimentation. *Journal of Thermophysics and Heat Transfer* 28(4), 700-707 (2014). ;doi: 10.2514/1.T4407

[8] Moses E Emetere and B. Nikouravan. Femtosecond Spin Dynamics Mechanism Probed By the Bloch NMR -Schrödinger Mainframe. International Journal of Fundamental Physical Sciences 4(4): 105-110 (2014). DOI:10.14331/ijfps.2014.330073

[9] Mahdi,M.A., J.J. Hassan, S.S. Ng, Z. Hassan. Growth of CdS nanosheets and nanowires through the solvothermal method, *J. Cryst. Growth*, 359, 43-48 (2012).

[10] Obaid,A.S., M.A Mahdi, Z Hassan, M Bououdina, Characterization of

nanocrystalline PbS thin films prepared using microwave-assisted chemical bath deposition, Materials Science in Semiconductor Processing 15, 564–571(2012) .

[11] Prakash V, Jumate N, Popescu G, Moldovan M, Prejmeriean C. Studies of some electrical and photoelectrical properties of PbS films obtained by sonochemical methods. *Chalcogenide Lett.* 7:95-100 (2004).

[12] Sandip V. Bhatt, M.P. Deshpande, Bindiya H. Soni, Nitya Garg, Sunil H. Chaki. Chemical Bath Deposition of Lead Sulphide (PbS) Thin Film and their Characterization.*Solid State Phenomena*, 209, 111-115 (2013)

[13] Tang,J., X. Wang, L. Brzozowski, D. Aaron, R. Barkhouse, R. Debnath, L. Levina, E.H. Sargent. Schottky Quantum Dot Solar Cells Stable in Air under Solar Illumination, *Adv. Mater*. 22, 1398 (2010)

[14] Uno E. Uno, Moses E. Emetere, Mathew Aplha. Crystalline Grain Size Effects On The Conductivity Of The Doped Tin Dioxide (SnO_2) With Zinc (Zn). *Journal of Ovonic Research,* 10 (3), 83-88 (2014).

[15] Uno E. Uno, Moses E. Emetere, Akhpelor A. Ohiozebau, Enebeli C. Benaiah, Onogu A. Williams. Evidence Of Positional Doping Effects On The Optical Properties Of Doped Tin Dioxide (SnO_2) With Zinc (Zn). *Journal of Ovonic Research* 10 (4),141-147 (2014)