

Growth and Characterization of Lead Sulphide Thin Film for Solar Cell Fabrication

Uhuegbu, Chidi C

Department of Physics: Covenant University, Ota, Ogun State, Nigeria.

Abstract

Lead Sulphide thin film was deposited on glass substrate prepared from lead acetate and thiourea solution using solution growth technique. XRD studies show that, films prepared are in nanocrystalline range. Also the diffraction peaks are found to be in good agreement with standard ASTM data. Optical studies show that the band gap energy is in the range of 0.75eV – 1.98eV. SEM studies show that the film surface have uniform grains and the grain size obtained are of the order of 15-20 nm and this is in agreement with the calculated values from the XRD result. Electrical resistance is in the range of 150 Giga Ohms. Vicker's Hardness value was found to be 74.

Keywords: Growth and Characterization, PbS thin films, Solar Cells

INTRODUCTION

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 [1], single electron transistors [2] and field-effect thin-film transistors [3]. In principle, the electronic and optical properties of semiconductor materials are tunable by varying their shapes and sizes [4], So it is one of the desired goals in material science to have precise control of the morphology of semiconductor materials. As an important IV-VI group semiconductor, Lead sulphide (PbS) has attracted considerable attention due to its small direct band-gap (0.41 eV at 300 K) and a large excitation Bohr radius of 18nm [5]. This has been widely used in many fields such as Pb²⁺ ion-selective sensors [6], photography [7], IR detector [8], and solar absorber [9]. As a consequence of its carrier confinement, an exceptional third-order nonlinear optical property of PbS nanoparticles has been found, which may be useful in optical devices such as optical switch [10]. Also it is predicted that,

compared with GaAs or CdS with a given particle size, the nonlinear properties of PbS will be the best [11]. Usually, PbS was precipitated via the reaction between dissoluble lead salt and H₂S gas in aqueous media. With the development of material science, PbS has been deposited on glass substrate [12], polymers [13, 22], zeolites [14], block copolymer nanoreactors [15], inverse micelle [16], micro emulsion [17] and in ethanol system through gamma-irradiation [18]. However, most of the above methods produced near-spherical PbS particles. Recently, rectangular and rod-like PbS nanocrystals have been successfully prepared in the system containing the organic polyamines with N-chelation property such as triethylenetetramine [19] and ethylenedimine [20]. 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, piezo electric devices, rectification and amplification, magnetic memories, super conducting films. Because of compactness, better performance and reliability coupled with low cost production and low package weight, thin film components are preferred over the bulk counterparts [21, 22]. The lead Sulphide thin films are mostly used in photography, ion selective sensors, solar absorption, photoresistants, humidity and temperature sensors and diode lasers [29-34].

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 [35]. 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 [35]. For the deposition of PbS, different methods are used at present, namely, chemical deposition, electro-deposition, and molecular beam epitaxy. Among these methods, solution growth technique deposition from aqueous solutions has some advantages. Indeed, it permits the routine creation of semiconductor nanocrystals. The size of deposited

nanocrystals is also much smaller than what can be realized using molecular beam epitaxy and lithographic methods [36].

2 Theory

The transmittance (T) was obtained using the equation given by [37]. Reflectance (R) and absorbance (A) were computed using the expression given by [38 -46]. The extinction coefficient (k) and refractive index (n) were obtained with equations in [47 - 49] while the dielectric constant (ϵ) and the optical conductivity (σ_o) were calculated using the expression given by [50, 51]. The relationship between the absorption coefficient and photon energy is given by [52 - 64] from this, energy band gap was extrapolated.

3 Experiment and Materials

The chemical deposition of the thin film onto the glass substrate was carried out by using a The chemical bath deposition technique was used to prepare the PbS thin film on glass substrate (slide) which had been previously degreased in concentrated nitric acid HNO_3 for 48 hours, cleaned in cold water with detergent, rinsed with distilled water and dried in air. The degreased-cleaned surface provide nucleation centre for growth of the film, hence yielding highly adhesive and uniformly deposited films. Mixture of 1M Sodium thiosulphate, 0.1M Ethylenediaminetetraacetic (EDTA), 0.1M lead nitrate 7.4M Triethanolamine (TEA), 14M ammonia, 1M Thiourea, distilled water, microscopic glass slides inside a beaker.

The mixture was thoroughly stirred with a glass rod before the glass slide was vertically introduced into the beaker. The dip time of about 20 - 48 hours, at pH between 9 and 11 was observed for the deposition process, which took place at room temperature. The grown samples were removed from the reaction baths, rinsed with distilled water and allowed to dry. They were then annealed at 423 K for 1 hour to obtain adherent transparent thin films.

During deposition, cations and anions in the deposition solution reacted to become neutral atoms, which either precipitated spontaneously or proceed slowly. Fast precipitation implied that thin films could not be formed on the substrate immersed in the solution. However, with the addition of TEA and EDTA, the reaction proceeded slowly for thin film of neutral atom to be formed on the substrate. The complexing agents slowed down the precipitation action for formation of PbS, while the NH_3 solution served to stabilize pH of the mixture. Sulphide ions were

released by hydrolysis of thiourea, complexes adsorbed onto the glass substrate when heterogeneous nucleation and growth took place by ionic exchange reaction of S^{2-} ions. By the process of ion-by-ion exchange, PbS was deposited on the glass substrate in the form of transparent, uniform and adherent thin film. The experiment was carried out at Covenant University Ota Ogun State. The characterization were carried out at University of Nigeria Nsukka and Covenant University Ota

Discussion and results

The thin film was characterized using UNICO UV-2102 PC spectrophotometer to determine the spectral absorbance, Transmittance and reflectance of the thin film on the glass substrate with blank substrate as a reference glass slide.

The optical absorption measurement of the lead sulphide thin films was measured at room temperature. The absorption co-efficient were calculated using the lamberts law $\alpha = (2.303A)/t$, Where t is the film thickness calculated by using the loss of weight method and A is the absorbance of the material. The band gaps were extrapolated from graphs of $(\alpha h\nu)^2$ vs $(\alpha h\nu)$, $(\alpha h\nu)^{3/2}$ Vs $(\alpha h\nu)$ and $(\alpha h\nu)^{1/2}$ Vs $(\alpha h\nu)$ shown in figures 2, 3, 4 with the values: 1.98eV, 1.81eV and 0.75eV. absorption edge is determined by plotting a graph between (α) Vs $(h\nu)$ in figure(1), it has a energy values of 1.09eV.

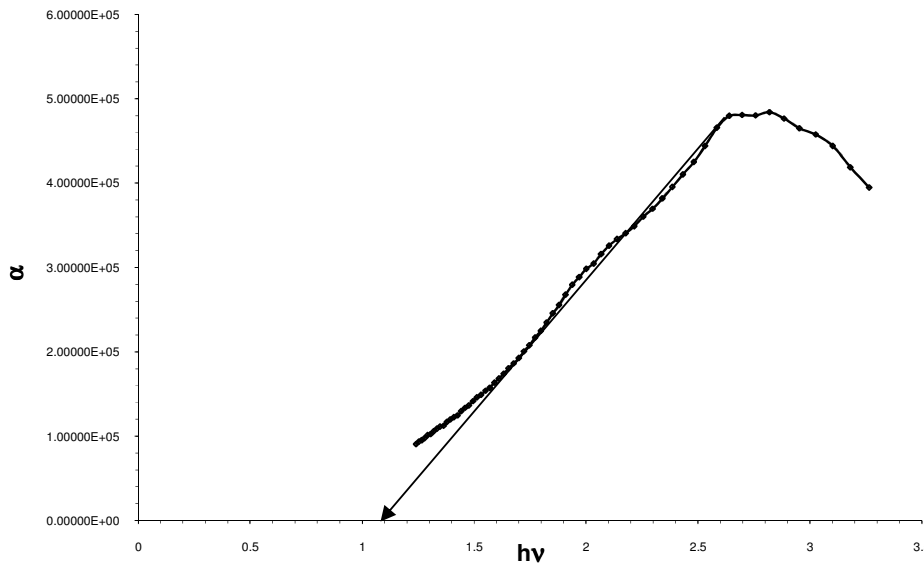


FIG.1. ABSORPTION CO-EFFICIENT OF LEAD SULPHIDE THIN FILM

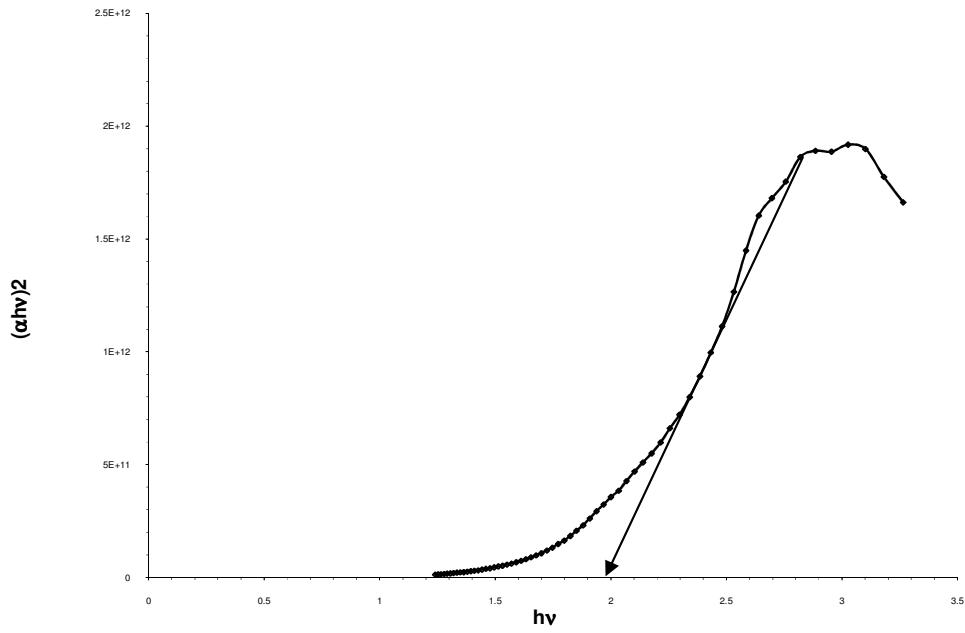


Fig 2 Plot of $(\alpha h\nu)^2$ Vs $(h\nu)$ of Lead Sulphide Thin Film

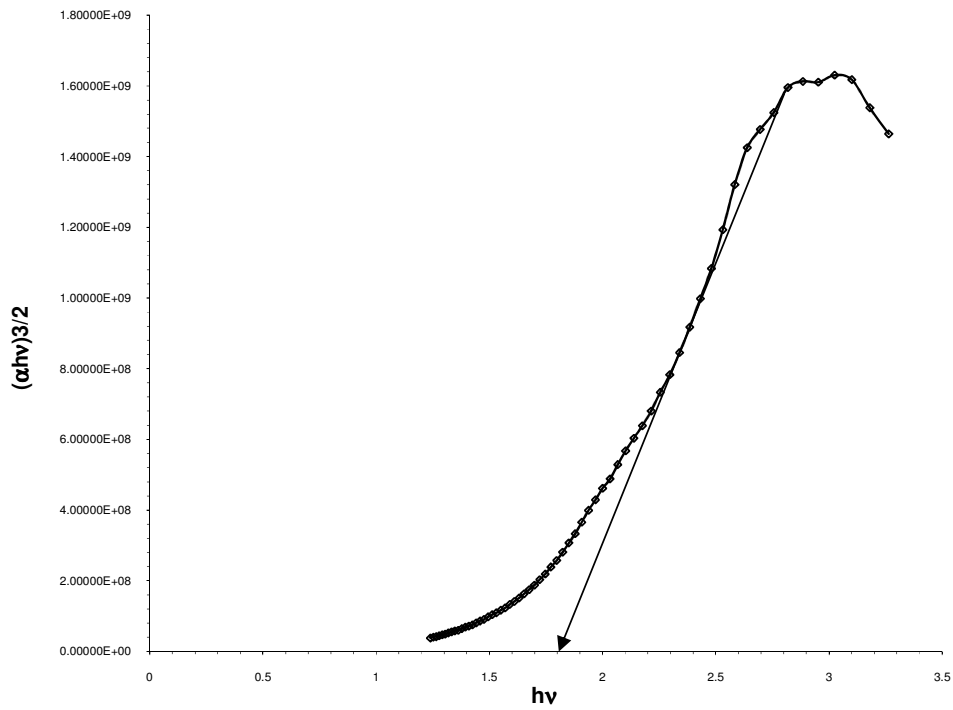


Fig. 3 Plot of $(\alpha h\nu)^{3/2}$ Vs $(h\nu)$ of Lead Sulphide

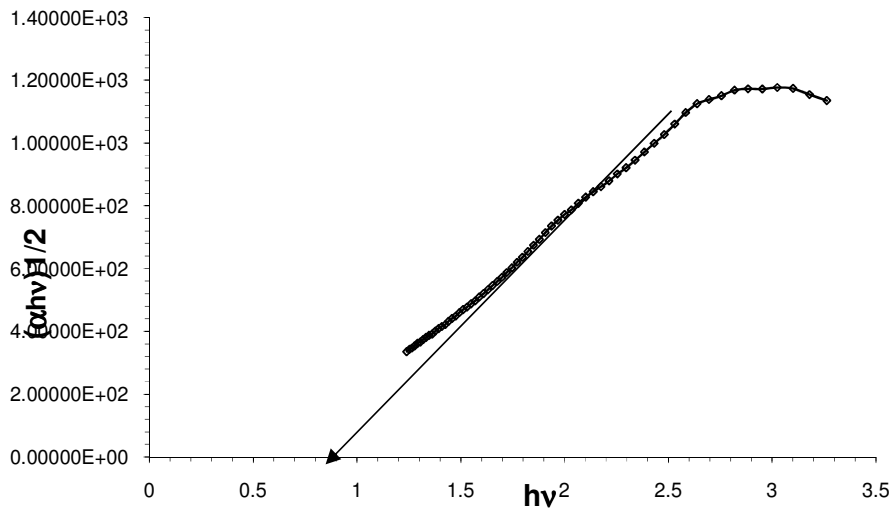


Fig. 4 Plot of $(\alpha h\nu)^{1/2}$ Vs $(h\nu)$ of Lead Sulphide Thin Film

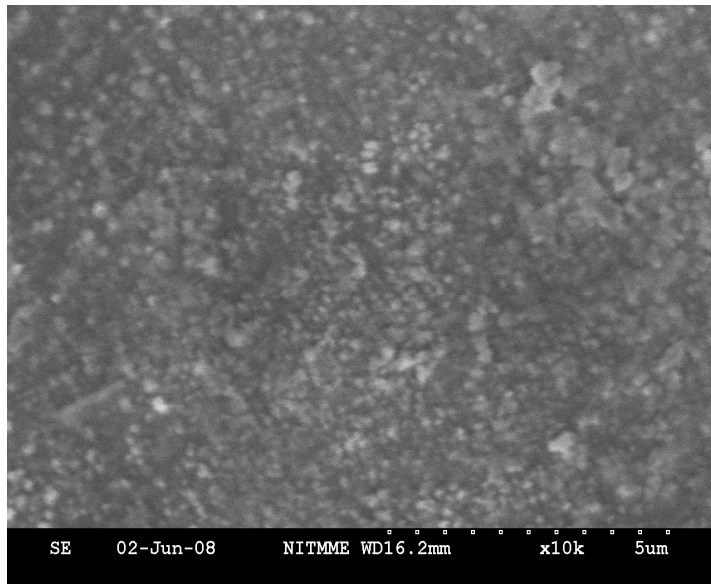


Fig. 5 SEM picture of Lead Sulphide Thin Film

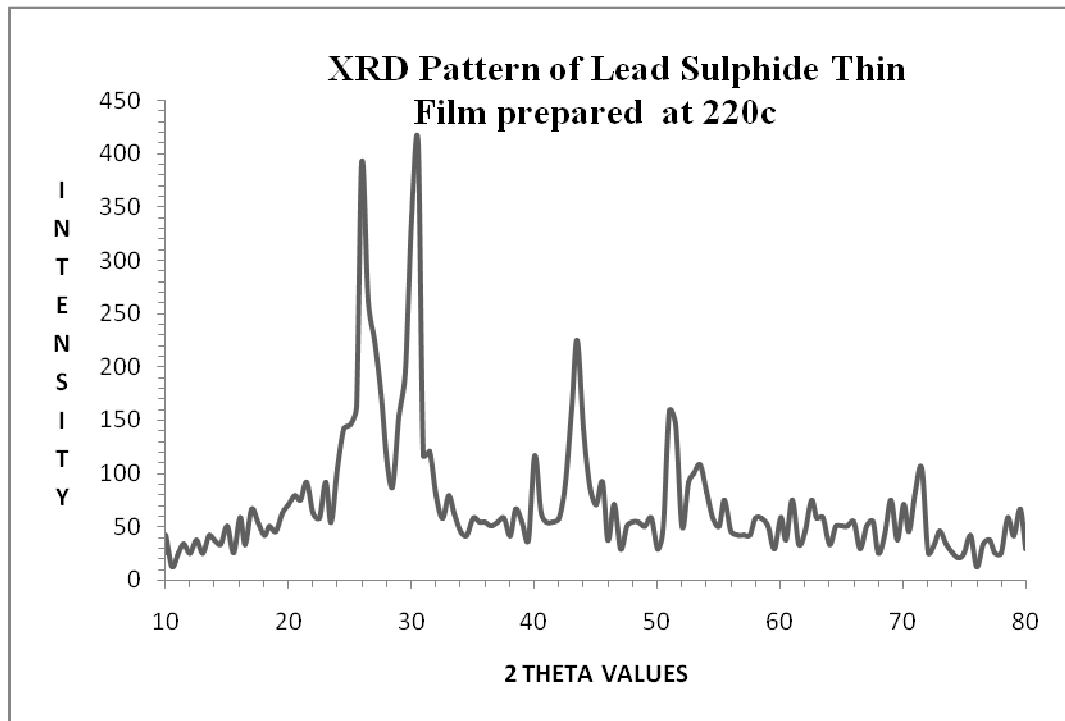


Fig.6.XRD Pattern of lead Sulphide Thin Film

Thin films of lead sulphide were prepared for different molarity such as 0.1M, 0.02M and 0.025M. Film thickness is measured using microbalance method giving 6.03 μ m, 65.26 μ m, and 6.14 μ m respectively.

X-ray diffraction patterns were carried out on the lead sulphide films with the molarity of 0.01M. The XRD patterns of lead sulphide thin films are shown in the fig. 6. All the peaks in the diffraction patterns correspond to the structure of lead sulphide, which were found to be in good agreement with the standard ASTM data. The XRD pattern of the prepared films shows crystalline nature, chosen for characterization study. X-ray diffraction line broadening was used to measure the grain size of film using the scherrer's formula by Full Width Half

Maximum method. The grain size of the film is found to be in the order of (15 – 22) nanometre. The crystallite size indicated that the film is nanocrystalline.

Nanotechnology deals with nanometer size objects. Size dependent new physical aspects have been generating a continuous thrust for new practical applications [65]. Lead sulphide (PbS) nanocrystals with dimension in the range of 1–20 nm are of technological interest for advanced optoelectronic applications. They show a strong quantum confinement effect when the crystallite size is equal to the dimension of Bohr exciton [66, 67]. Earlier investigations into the fundamental limits of the performance of PbS nanoparticle based devices confirmed their ability to become a versatile technological platform for the creation of better optoelectronic devices [65 - 67]. A variety of different methods have been employed to grow the PbS nanoparticles on different substrates [68]. Growth of the nanoparticle films for device applications is still an emerging field of research. XRD studies show that, films prepared are in nanocrystalline range. Electrical resistance is in the range of 150 Giga Ohms. Vicker's Hardness value was found to be 74.

CONCLUSION

The photoconductivity property of lead sulphide is an intrinsic characteristic of the material and not the result of thermal vibration, impurity or crystal defects. Photoconductivity is, however, greatly enhanced by the introduction of impurity ions or crystal defects into the lattice. It has long been known that polycrystalline lead sulphide films might be used as the basic useful photo detector. The lead sulphide photo detector was brought to the manufacturing stage of development in Germany about 1943. After five decades, lead sulphide detectors are still in great demand as sensors for major military systems, as well as industrial, commercial and medical applications [69, 70]. In order to prepare the PbS infrared detector, two primary methods: vacuum sublimation and chemical deposition have been used. In both methods, PbS is prepared as a polycrystalline thin film deposited on a glass, quartz, and sapphire or strontium titanate substrate.

In the present study the nanocrystalline lead sulphide thin film has been successfully deposited using solution growth technique. This method is proved to be simple, cost effective, accurate and reproducible for the preparation of nanocrystalline thin films.

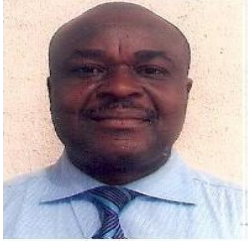
REFERENCES:

- [1] V. L. Colvin, M. C. Schlamp, A. P. Alivisatos, (1994): Nature 370, 354.
- [2] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, P. L. McEuen, , (1997): Nature 389, 699.
- [3] B. A. Ridley, B. Nivi, J. M. Jacobson, (1999): Science 286, 746.
- [4] P. D. Yang, C. M. Lieber, (1996): Science 273, 1836.
- [5] J. L. Machol, F. W. Wise, R. C. Patel, D. B. Tanner, (1993): Phys. Rev. B 48, 2819.
- [6] H. Hirata, K. Higashiyama, Bull. (1971) : Chem. Soc. Jpn. 44, 2420.
- [7] P. K. Nair, O. Gomezdaza, M. T. S. Nair, (1992) : Adv. Mater. Opt. Electron. 1, 139.
- [8] P. Gadenne, Y. Yagil, G. Deutscher, (1989) : J. Appl. Phys. 66, 3019.
- [9] T. K. Chaudhuri, S. Chatterjes, (1992) : Proc. Int. Conf. Thermoelectr. 11, 40.
- [10] R. S. Kane, R. E. Cohen, R. Silbey, (1996) : J. Phys. Chem. 100, 7928.
- [11] M. A. Olshavasky, A. N. Goldstein, A. P. Alivisatos, (1990): J. Am. Chem. Soc. 112,, 9438
- [12] M. Mukherjee, A. Datta, D. Chakravorty, (1997) : J. Mater. Res. 12, 2507.
- [13] Y. Wang, A. Suna, W. Mahler, R. Kasowski, (1987) : J. Chem. Phys. 87, 7315.
- [14] Y. Wang, N. Herron, (1987): J. Phys. Chem. 91, 257.
- [15] R. S. Kane, R. E. Cohen, R. Silbey, (1996): Chem. Mater. 8, 1919.
- [16] V. T. Liveri, M. D. Rossi, G. Arrigo, D. Manno, G. Micocci, , (1999): Appl. Phys. A 69, 369.
- [17] J. P. Yang, S. B. Qadri, B. R. Ratna, (1996): J. Phys. Chem. 100, 17255.
- [18] Z. Qiao, Y. Xie, J. Xu, Y. Zhu, Y. Qian, (1999) : J. Colloid Interface Sci. 214, 459.
- [19] T. Sugimoto, S. H. Chen, A. Muramatsu, (1998) : Colloid Surf. A, 135, 207.
- [20] M. Chen, Y. Xie, Z. Yao, Y. Qian, G. Zhou, (2002): Mater. Res. Bull. 37, 247.
- [21] P. Jiang, Z. F. Liu, S. M. Cai, (2002): Langmuir 18, 4495.
- [22] S. Wang, S. Yang, (2000: Langmuir 16, 389.)
- [23] Murugavel, Nenedict and A.R. Raju, (1986): Bull.Mater. Sci., 18 (3), 385-389.
- [24] C.S. Uma, L..K. Malhotra, K. L. Chopra, (1986): Bull Mater.Sci,18(3),. 385-389
- [25] Y.D.Tembhurkar, Bull. (1996): Mater. Sci ., 19 (1), 155-159.
- [26] P.S.Patil and R.S. Patil, Bull. (1995): Mater. Sci., 18 (7), 911-916.
- [27] P.S. Patil Bull. (1992): Mater. Sci., 15 (5), 459-465.

- [28] Mejia-Garcia. E. Diaz-Valdes, G. Contreras- Puente, J.L.Loper-Lopez and M.Jergel, (2002): Thin Solid Films , 414, 123-128.
- [29] I.Pop, C. Nascu,V. Ionescu,E. Indrea,I.Brateau, (1997) : Thin Solid Films 307, 240.
- [30] C. Nascu, V. Vomir, I. Pop, V. Ionescu, R. Grecu, (1996) : Mater. Sci. Eng. B 841, 235.
- [31] P.K. Nair, M.T.S. Nair, A. Fernandez, M Ocampo, (1989) : J. Phys. D: Appl. Phys. 22, 829.
- [32] P.K. Nair, G.M.Garcia, A.B.Fernandez, M.T.S. Nair, , (1991) : J.Phys. D: Appl Phys.241, 446-1472.
- [33] N.I. Fainer, M.L. Kosinova, Yu.M. RumyansteV, E.G. Salman, F.A. Kuznetsov, (1996): Thin Solid Films 280, 16.
- [34] P.K. Nair, M.T.S. Nair, J. (1990): Phys..D: Appl Phys. 23, 150.
- [35] M. Gunasekaran, and M. Ichimura, (2005) : Jap. J. Appl. Phys., 44, 7345.
- [36] J. J. Peterson and T. D. Krauss, , (2006) : Nano Lett. 6510.
- [37] Theye, M. (1985): Thin Film Technology and Applications in Optical Properties of Thin Films, ed. K.L.Chopra and L.K. Malhotra, Tata McGraw-Hill, New Delhi, Pp.163
- [38] Pentia, E., Draghici, V., Sarau, G., Mereu, B., Pintillie, L., Sava, F., Popeseu, M. (2004): *Journal of Electrochem. Society*, **151 (1)**, Pp.729-733
- [39] Salem, A. M. (2002): *Appl. Phys.* **A74**, Pp.205-211
- [40] Majumdar, A., Xu, H. Z., Zhao, F., Jayasinghe, L., Khaosravani, S., Lu, X., Kelkar, V. Shi, Z. (2003): *Mater. Res. Soc. Symp. Proc.*, Pp.**770**
- [41] Quijada, M., Ceme, J., Simpson, J. R., Drew, H. D., Ahn, K. H., Millis, A. J., Shreekala, R., Ramesh, R., Rajeswari, M., Venkatesan, T. (1998): *Phy. Review*, **B 58 (24)**, Pp.99-102
- [42] Ramesh, D., Gessert, T., Zhou, J., Asher, S., Pankow, J., Moutinho, H. (2003): *Mater. Res. Soc. Symp. Proc.*, **763**, Pp.1-6
- [43] Shwarsstein, A. K., Jaramillo, T. F., Baeck, S., Sushchikh, M., McFarland, E W.(2006): *Journal of Electrochem. Soc.* **153 (7)**, Pp.483-487
- [44] Ezema, F. I. (2004): *J. University of Chemical Technology and Metallurgy*, **39 (2)**
- [45] Elliot, S. R. (1984): *Physics of Amorphous Materials*, Longman London, Pp.255
- [46] Chen, J., Shen, W. Z., Chen, N. B., Qin, D. J., Wu, H. Z. (2003): *J. Phys. Condens. Matter* **15**, Pp. 475-482
- [47] Mitsuaki, Y., Ogata, K., Yan, F., Koike, K., Sasa, S. (2003): M. Inoue, *Mat. Res. Soc. Symp. Proc.* **744**, Pp.1-12
- [48] Rodrigo del, R., Basaure, D., Schrebler, R., Gomez, H., Cordova, R. (2002): *Phys. Chem.*, **B 106 (49)**, Pp.12684-12692

- [49] Ezema, F. I, Asogwa, P. U (2004): *Pacific Journal of Sci. and Technol.* **5 (1)**, Pp.33
- [50] Blatt, F. J. (1968): *Physics of Electronic Conduction in Solids*, McGraw-Hill Book Co. Ltd. New York, Pp.335-350
- [51] Tsidilkovski, I. M. (1982): *Band Structure of Semiconductors*, Pergamon Press Oxford
- [52] Ndukwe, I. C. (1996): *Solar Ener. Mater. And Solar Cells*, **40**, Pp.123
- [53] Osuji, R. U. (2003): *Nigeria Journal of Solar Energy*, **14**, Pp.90-99
- [54] Ezekoye, B. A., Okeke, C. E. (2003): *Nigeria Journal of Solar Energy*, **14**, Pp. 82-89
- [55] Soliman, H. S. (1998): *J.Phys. D. Appl. Phys.* **31**, Pp.1516-1521
- [56] Chopra, K. L., Kainthla, R. C., Pandya, D. K., Thakoor, A. P. (1982): *Physics of Thin Film*, 12, Academic Press, Pp.169-235
- [57] Hass, G. (1972): *Optical Properties in Metals in American Institute of Physics Handbook*, McGraw-Hill Book Co. New York, Pp. 118
- [58] Pramanik, P. S., Bhattacharya, R. N., Busu, P. K. (1987) *Thin Solid Films*, **149**, Pp.181
- [59] Kittel, C. (1977): *Introduction to Solid State Physics* 5th edn. John Wiley and Sons Inc
- [60] Rodriguez-Lazcano, Y., Nair, M. T. S., Nair, P. K. (2001): *J. Crystal Growth*, **23 (3)**
- [61] Rodriguez-Lazcano, Y., Guerrero, L., Daza Gomez, O., Nair, M. T.S., Nair, P. K. (1999): *Superficies Vacio*, **9**, Pp.100
- [62] Numez Rodriguez, A., Nair, M. T. S., Nair, P. K. (2002): *Mat. Res. Symp. Proc.* **730**, v5.14.1
- [63] Ezema, F. I., Nnabuchi, M. N (2005): *Journal of Applied Science and Technology*, **10 (1&2)**, Pp. 53-59
- [64] Ezema, F. I. (2004): *Academic Open Internet Journal*,
- [65] S.B. Qadri, J. Yang, B.R. Ratna, F.E. Skelton, J.H. Hu, (1996): *Appl. Phys. Lett.* 69 2205
- [66] R. Thielsch, T. Bo`hme, R. Reiche, D. Schla`fer, H.D. Bauer, H. Bo`ttcher, (1998) : *Nanostruct. Mater.* 10 131.
- [67] Y. Wang, A. Suna, W. Mahler, R. Kawoski, (1987) : *J. Chem. Phys.* 87 7315
- [68] K.K. Nanda, S.N. Sahu, (2001) :*Appl. Phys. Lett.* 79, 2743
- [69] *State Transducers and the 9th UK Conference on Sensors and their Applications*, 2,(2000) 941-944.
- [70] Lee, A. (1998): *Miniature PbS sensor for NIR spectroscopy. SPIE*, 3857, 92 - 97

Biography:



Dr. Uhuegbu Chidi C was born on March 20th 1960 at Obioluru Mbano Imo Stae and currently a Senior Lecturer in the Department of Physics of Covenant University Ota. He had his B.Sc, M.Sc and P.G.D.E at University of Nigeria, Nsukka in 1985, 1990, and 1995 respectively and Ph.D at Covenant University, Ota in 2007. His current research interest is in the area of thin film growth and Renewable energy. He belongs to following professional

bodies MNIP, MIEEE, MSESN, MMSN, MSAN.