

# Effect of Annealing on Optical and Electrical properties of Magnesium Sulphide (MgS) Thin Film Grown by Chemical Bath Deposition Method

R.A. Babatunde<sup>1\*</sup>, Y.I. Bolanle<sup>2</sup>

<sup>1,2</sup>Department of Science Laboratory Technology, The Federal Polytechnic, Ilaro, Nigeria

\*Corresponding Author: [rasaq.babatunde@federalpolyilaro.edu.ng](mailto:rasaq.babatunde@federalpolyilaro.edu.ng), Tel : +2348053238648

Available online at: [www.isroset.org](http://www.isroset.org)

Received: 30/May/2020, Accepted: 05/June/2020, Online: 30/June/2020

**Abstract** – This study investigated the effect of annealing on optical and electrical properties of MgS deposited by chemical bath deposition method onto glass substrates, the transmittance of the film was obtained from AVANTEX UV spectrophotometer in the wavelength range from 239.534 nm to 999.495 nm. Also, the electrical characteristics of the thin films were investigated using KEITHLEY four-point probe techniques. The films exhibit low reflectance, low absorbance and high transmittance in the visible region, the bandgap energy reduces from 2.4 eV before annealing to 2.2 eV after annealing. The resistivity decreases as annealing temperature increases. Therefore the MgS thin film can be used as a replacement for CdS which contains toxic element.

**Keywords**- MgS, annealing, bandgap, transmittance, resistivity

## I. INTRODUCTION

Currently, about 80% of the world energy source is from burning fossil fuels, such coal, oil, and natural gas but this energy cannot meet the increase in demand for energy [1]. But, the use of fossil fuels has several disadvantages. One of the problems is limited in the availability of fossil fuels. Although different mechanism have been developed to keep the fuel available for future use, the finite supply will ultimately compulsorily restrain the use of fossil fuels [2]. The second negative aspect is the danger of climate change due to releasing of CO<sub>2</sub> from fossil fuels is considered to be the foremost environmental hazard from the convectional energy source [3]. In view of the factors of continuous use of energy for the long run, it is possible to have sustainable energy by sources which are replaced naturally or controlled vigilantly and can, therefore, be used without the risk of finishing it all which is called renewable energy [4]. The most significant feature of renewable energy is finite in supply. Among the renewable energy, solar energy is standing out because is the energy generated from the sun and sun gives out every day a great amount of energy in the form of heat and radiations at no fee [5]. This energy is available in plenty [6] Photovoltaic (PV) materials and devices exchange sunlight into electrical energy and PV cells are generally known as solar cells [7]. Photovoltaic can exactly be translated as light-electricity. First utilized in about 1890, "photovoltaic" has two parts: photo, obtained from the Greek word for light, and volt, concerning electricity pioneer Alessandro Volta. And this is often what photovoltaic materials and devices translate light energy into electricity, as French physicist Edmond Becquerel discovered as early as 1839 [8].

A solar cell or photovoltaic cell is nothing but a p-n junction. When photons with energy greater than or adequate to the bandgap of absorber material hit the cell, electrons are jumped from the valence band to the conduction band within the absorber [9]. Once electron-hole pairs are generated, the electrons cross the junction to travel from p to n region while the holes move from n to p region, releasing their energy before recombining with one another [10]. In other words, the electron-hole pairs, which are within one-diffusion-length from the built-in field of the junction, are separated giving rise to a 'photo voltage' and photocurrent [9]. Solar cells are made from semiconducting materials [11]. Semiconductors materials are the materials that have electrical conductivities between metals and insulators and they exist in either elemental form or compound form. The elemental forms are silicon and germanium because they are composed of single species of atoms. Others are binary compounds [III-V (e.g. GaAs), II-VI (e.g. CdTe), [12], [13], ternary compounds (e.g. In<sub>x</sub>Ga<sub>(1-x)</sub>As), and quaternary compounds (e.g. CuInGaSe<sub>2</sub>, Cu<sub>2</sub>ZnSnS<sub>4</sub>) [14], [15]. Solar cells made from silicon are called a first-generation solar cell, they have high efficiency but the major problem of these cells is relatively expensive to produce [16]. The second-generation cell is known as thin-film solar cell which has some advantages over first-generation solar cell. These advantages include having a very thin thickness and minimum material usage which reduce the cost of the cell [17]. Thin-film solar cells require at least two kinds of semiconducting layers; a wide bandgap window material and a narrow bandgap absorber material. The window materials such as CdS, ZnS, ZnTe, ZnSe, CuS, MgS, etc. serve as an n-type material, while the narrow bandgap such as CdTe, CIGS, CZTS are absorber layer to form

heterojunction solar cell [18]. Different thin film deposition techniques have been employed by Scientists to produce thin films of II-VI semiconductor compounds like Magnesium Sulphide (MgS). Thin films of II-VI semiconductor compounds like Magnesium Sulphide (MgS) have been prepared using the electrodeposition method [19], [20]. Chemical bath deposition (CBD) method was used to prepare the MgS film by [21], [22]. Cadmium sulphide (CdS) thin film grown by CBD method is the most used as a window layer for heterojunction solar cell but the toxicity of cadmium make a reason for its substitution hence necessitated this study. Some related are mentioned in section II, section III discusses the material and method for this study, section IV of this paper contains the results and discussion while conclusion is mentioned in section V.

## II. RELATED WORKS

Some researchers have worked on MgS thin film, these include [19], they fabricated MgS thin film on FTO substrates by electrodeposition method, the optical and structural properties of the films were studied. They found that MgS thin film has direct band gap energies were between 2.25 eV and 2.75 eV. The films have high transmittance in a range of 55% - 85%. Also, Magnesium sulphide (MgS) thin films were deposited by electrochemical deposition process at room temperature [23]. X-ray diffraction studies showed that the films have distinct properties of crystallinity. Surface morphology revealed that the grain sizes of the films ranging between 15 and 17 nm were homogeneously distributed across the substrate. Also, [21] deposited MgS thin-film ferritic stainless steel using CBD method and effect of polishing treatment on the substrates was carried out.

## III. MATERIALS AND METHOD

Magnesium sulphide thin films were deposited on glass substrates which were previously cleaned by soaking them in HCl acid for 24 hours after which they were washed with detergent and rinsed with distilled water. The substrates were allowed to dry and were weighed with an analytical balance to determine their mass before deposition. The bath was formed by sequential addition of 20ml of 1.0M of magnesium chloride ( $MgCl_2 \cdot 7H_2O$ ) as a source of magnesium, 20ml of 1.0M thiourea ( $SC(NH_2)_2$ ) solution as a source of sulphur and 20ml of 1.0M Ethylene Diamine Tetraacetate (EDTA) as a complexing agent. The resulting solution was stirred, vigorously for several minutes with a magnetic stirrer, initially the solution was milky and later turn to colourless. The mixture was then poured in a 100 ml chromatography tank and four cleaned substrates were inserted vertically. The tank was placed in a water bath which has been previously set to 65° C and stayed there for 1 hour. At the end of the deposition times, the substrates were took out and rinsed with distilled water and allow to dry naturally. After the deposition, one side of each of the substrates was cleaned using cotton wool

with hydrochloric acid (HCl) and later with distilled water and weighed again for a change in mass before and after deposition. Three of the samples were annealed for 1 hour in an oven at 100° C, 150° C and 200° C respectively while the last one was not annealed. The thickness of the films was obtained by double weigh method using the equation below

$$t = \frac{m_2 - m_1}{A \cdot \rho} * 10^4 \mu m \quad (1)$$

where:

$m_1$  is the mass of the substrate before deposition

$m_2$  is the mass of the s substrate after deposition

A is the area of the glass substrate covered by the film

$\rho$  is the theoretical density of MgS.

All the four samples have the same values for change in mass before and after deposition since they are prepared under the same condition and the same concentration, therefore all the samples have the same thickness of 1.93  $\mu m$

The transmittance of the thin films was measured using Avantex UV Spectrophotometer in the wavelength range from 239.534 nm to 999.495nm. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was used as a indication casing. The transmittance data was got directly from the spectrophotometer and other parameters such as absorbance, reflectance, photon energy and optical band gap energy were calculated using the relevant known equations.

$$E = hf \quad (2)$$

Where h is Planks constant with the numerical value of  $6.63 \times 10^{-34}$  Js

$$f = \frac{c}{\lambda} \quad (3)$$

where f is the frequency of radiation, c is the speed of light with numerical value  $3 \times 10^8$  ms<sup>-1</sup> while  $\lambda$  is the measured wavelength

$$E = \frac{hc}{\lambda} \quad (4)$$

By substituting all the constant and convert the energy to eV, the energy then becomes

$$E = \frac{1243}{\lambda} \quad (5)$$

The absorbance of the films was obtained from the relation below

$$A = \log\left(\frac{1}{T}\right) \quad (8)$$

The reflectance (R), was calculated using the relation below.

$$R = 1 - (A + T) \quad (9)$$

The absorption coefficient ( $\alpha$ ) was calculated using

$$\alpha = -\ln \frac{T}{t} \quad (10)$$

Where T is the transmittance and t is the film thickness

The bandgap energy of the film is extrapolated from the plot of  $(\alpha hv)^2$  against the photon energy in eV according to the equation below

$$(\alpha hv)^2 = A(hv - E_g)^2 \quad (11)$$

The electrical characteristics of the as-deposited as well as annealed MgS thin films were examined using a KEITHLEY four-point probe technique. The connection

was made in such a way that the voltage across the transverse distance of the films and the corresponding values of the current was measured. The sheet resistivities  $\rho$  of the films at room temperature were calculated using the expression below.

$$\rho = (\pi t l n 2) \frac{V}{I} = 4.53 R t \tag{12}$$

where V is the potential difference (voltage) across the transverse distance of the film. I is the current and t is the thickness of the film deposited

The conductivities were calculated using

$$\sigma = \frac{1}{\rho} (\Omega m)^{-1} \tag{13}$$

#### IV. RESULTS AND DISCUSSION

##### The Optical properties

The transmittance, reflectance, absorbance and band gap energy of MgS thin film were depicted figure 1, figure 2, figure 3 and figure 4 respectively. The transmittance spectral illustrates that the MgS thin films have high transmittance in the visible region, the graphs show that the unannealed film has maximum transmittance percentage of 40 while annealed at 100<sup>0</sup> C, 150<sup>0</sup> C and 200<sup>0</sup> C have almost the same percentage of about 80%. Such high transmittance in visible region have recorded by [22] This shows that the annealing affects transmittance. The transmittance is constant in the infrared region of the electromagnetic spectrum. The reflectance spectral is shown in figure 2, the spectral shows that the same percentages of films transmitted were reflected in the opposite direction. This shows the films have very little reflectance even lower than the reflected reported by [24]. The absorbance spectral in figure 3 shows that the unannealed film has a maximum value of 2.5% while the annealed films have the same value of 1.5% ultraviolet region. The spectral in the visible region of electromagnetic is negative with the absorbance of 1.5% and 2.0% for unannealed and annealed films respectively. The optical band gap energies were extrapolated from figure 4 and found to be 2.4 eV for unannealed (control) while films annealed at 100<sup>0</sup> C, 150<sup>0</sup> C and 200<sup>0</sup> C have the same bandgap of 2.2 eV. The value matched with the reported band gap of 2.25 - 2.75 eV reported by [19]. This result shows that annealing reduces the bandgap from 2.4 eV of unannealed to 2.2 eV which similar to report by [23], [25].

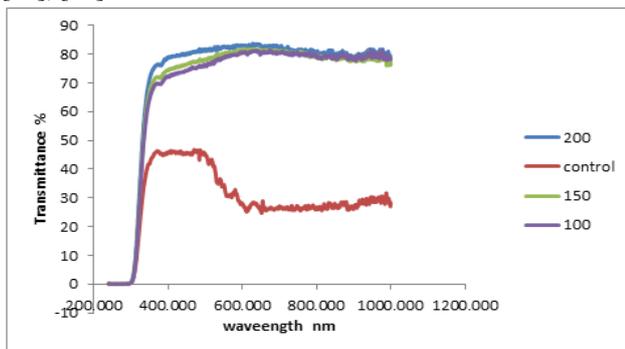


Figure 1: The transmittance spectral of MgS films against wavelength

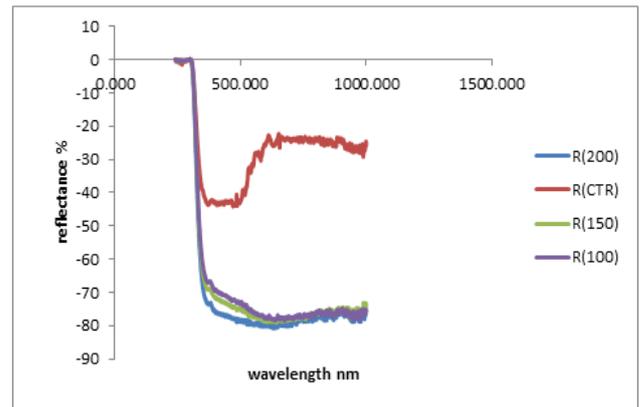


Figure 2: The reflectance spectral of MgS films against wavelength

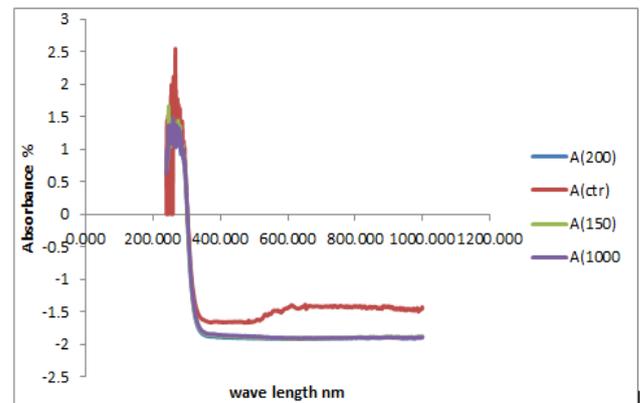


Figure 3: The absorbance spectral of MgS films against wavelength

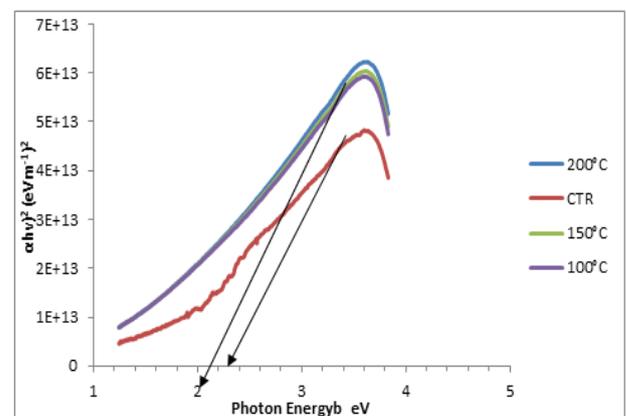


Figure 4 Energy band gap of MgS films using Tauc's plot

##### The electrical properties

The resistivities and conductivities of the MgS thin films as-deposited and annealed are presented in table 1. The resistivity decreases as annealing temperature increases this is in agreement with findings of [26], [27]. This shows that the MgS thin film exhibits semiconductor properties, the annealing temperature made some electrons travel from valence band to conduction band that is the reason why conductivity increases with increase in annealing temperature.

Table 1 : Electrical properties results

samples	V/V	I/A	R/ $\Omega$	P / $\Omega$ m	$\sigma / (\Omega\text{m})^{-1}$
control	2.50E-01	1.36E-05	1.84E+04	1.61E-01	6.22E+00
100 <sup>o</sup> C	2.80E-01	1.76E-05	1.59E+04	1.39E-01	7.19E+00
150 <sup>o</sup> C	1.85E-01	1.79E-05	1.03E+04	9.04E-02	1.11E+01
200 <sup>o</sup> C	1.00E-01	2.25E-05	4.44E+03	3.89E-02	2.57E+01

## V. CONCLUSION

MgS thin film was successfully deposited onto soda-lime glass using a chemical bath deposition method and effect of annealing was investigated on optical and electrical properties of the film. It was found that the transmittance of the film increases as annealing increases, the bandgap energy decreased from 2.4 eV of un annealing (control) to 2.2 eV after annealing. The resistivity of the film decreases as annealing temperature increases. The MgS thin film can be used as a replacement of CdS as a window layer of a thin-film solar cell having exhibits high transmittance and bandgap energy.

## ACKNOWLEDGEMENT

The authors are grateful to Mr. Abdulazeez Oderinde and Mr. Opeyemi Adegboyo of Chemistry unit of Science Laboratory Technology Department, Federal Polytechnic, Ilaro for assistance rendering during the laboratory work. Also, we say thanks to the technical staff of Material Engineering Department, Kwara State University, Malate, Nigeria for characterization of samples

## REFERENCES

- [1] R. M. G. Rajapakse, "Depletion of nonrenewable energy resources, entropy crisis and nanotechnology solutions," *J. Natl. Sci. Found. Sri Lanka*, vol. 35, no. 2, pp. 59–61, 2007, doi: 10.4038/jnsfr.v35i2.3669.
- [2] H. Mitwallyová, "The potential of the usage of renewable energy in the Czech Republic Vukica Janković," *Int. J. Soc. Sci.*, vol. III, no. 4, pp. 39–48, 2014.
- [3] M. Balat, "Usage of energy sources and environmental problems," *Energy Explor. Exploit.*, vol. 23, no. 2, pp. 141–168, 2005, doi: 10.1260/0144598054530011.
- [4] C. N. Ezugwu, "Renewable Energy Resources in Nigeria : Sources , Problems and Prospects," *J. Clean Energy Technol.*, vol. 3, no. 1, pp. 68–71, 2015, doi: 10.7763/JOCET.2015.V3.171.
- [5] S. Sharma, K. K. Jain, and A. Sharma, "Solar Cells: In Research and Applications—A Review," *Mater. Sci. Appl.*, vol. 06, no. 12, pp. 1145–1155, 2015, doi: 10.4236/msa.2015.612113.
- [6] A. Ayeshamariam *et al.*, "Optical Characterisation of ZnSe Thin Films by Using Electro Deposition Technique," *Int. J. Emerg. Technol. Adv. Eng.*, vol. 4, no. 5, pp. 584–590, 2014.
- [7] I. Pujotomo and R. Aita Diantari, "Characteristics Surface Temperature of Solar Cell Polycrystalline Type to Output Power," *E3S Web Conf.*, vol. 73, pp. 8–11, 2018, doi: 10.1051/e3sconf/20187301008.
- [8] B. Soediono, "Photovoltaic (PV) materials and devices," *J. Chem. Inf. Model.*, vol. 53, p. 160, 1989, doi: 10.1017/CBO9781107415324.004.
- [9] C.-P. Fluieraru, G. Preduşcă, H. Andrei, E. Diaconu, P. A. Cotfas, and D. T. Cotfas, "Determination of Technological Features of a Solar Photovoltaic Cell Made of Monocrystalline Silicon P + PNN +," *Int. J. Photoenergy*, pp. 1–14, 2019, doi: 10.1155/2019/7945683.
- [10] A. H. Chander, M. Krishna, and Y. Srikanth, "Comparison of Different types of Solar Cells – a Review," *IOSR J. Electr. Electron. Eng. Ver. I*, vol. 10, no. 6, pp. 151–154, 2015, doi: 10.9790/1676-1061151154.
- [11] D. M. . Bharathidasan, "Solar Cells and Nanotechnology," *IOSR J. Electr. Electron. Eng.*, pp. 473–476, 2003, [Online]. Available: www.iosrjournals.org.
- [12] R. G. Kadhu, B. Y. Kadhum, and M. K. Abd, "Electrical and Optoelectronic Characterization of CdTe 1- x Se x / ZnTe Heterojunction," *J. Kerbala Univ. Sci.*, vol. 9, no. 3, pp. 353–362, 2011.
- [13] K. K. Subedi *et al.*, "Nanocomposite (CuS)<sub>x</sub>(ZnS)<sub>1-x</sub> thin fi lm back contact for CdTe solar cells: Toward a bifacial device," *Sol. Energy Mater. Sol. Cells*, vol. 186, pp. 227–235, 2018.
- [14] M. Jiang, "Cu<sub>2</sub>ZnSnS<sub>4</sub> polycrystalline thin films with large densely packed grains prepared by sol-gel method," *J. Photonics Energy*, vol. 1, no. 1, pp. 501–507, 2011, doi: 10.1117/1.3628450.
- [15] V. Asokan and D. Velauthapillai, "Solar cells of Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films prepared by chemical bath deposition method," *Indian J. Pure Appl. Phys.*, vol. 52, pp. 620–624, 2014.
- [16] M. T. Kibria, A. Ahammed, S. M. Sony, and F. Hossain, "A Review : Comparative studies on different generation solar cells technology," in *Proceedings of 5th International Conference on Environmental Aspects of Bangladesh I*, 2014, pp. 51–53.
- [17] S. Fajardo, García-Galvan, F. R., V. Barranco, J. C. Galvan, and S. F. Batlle, "New Materials for thin film solar cells," *Intech*, vol. i, pp. 208–221, 2016, doi: http://dx.doi.org/10.5772/57353.
- [18] I. M. Dharmadasa, A. E. Alam, A. A. Ojo, and O. K. Echendu, "Scientific complications and controversies noted in the field of CdS/CdTe thin film solar cells and the way forward for further development," *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 23, pp. 20330–20344, 2019, doi: 10.1007/s10854-019-02422-6.
- [19] Ezenwaka, I.A., Ezenwaka.L.N, and N. Egwunyenga, "OPTICAL AND STRUCTURAL CHARACTERISTICS OF MGS THIN FILMS FABRICATED BY," *Asia Pacific J. Res.*, vol. 1, no. 21, pp. 32–37, 2015.
- [20] B. A. Taleatu, E. Omotoso, E. A. A. Arbab, R. A. Lasisi, W. O. Makinde, and G. T. Mola, "Microstructural and optical properties of nanocrystalline MgS thin film as wide band gap barrier material," *Appl. Phys. A Mater. Sci. Process.*, vol. 118, no. 2, pp. 539–545, 2014, doi: 10.1007/s00339-014-8753-0.
- [21] P. Akinyemi, O. L. Ojo, O. T. Kolebaje, and C. I. Abiodun, "Effects of polishing treatment and chemical bath deposited magnesium sulphide ( MgS ) thin films on ferritic stainless steel 430," in *This paper is part of the Proceedings of the 2 International Conference on High Performance and Optimum Design of Structures and Materials*, 2016, vol. 166, pp. 479–485, doi: 10.2495/HPSM160441.
- [22] D. . Okoli, "Optical Properties of Chemical Bath Deposited Magnesium Sulphide Thin Films," *Chem. Mater. Res.*, vol. 7, no. 2, pp. 61–68, 2015.
- [23] B. Taleatu, E. Omotoso, E. Arbab, and A. R. Lasisi, "Microstructural and optical properties of nanocrystalline MgS thin film as wide band gap barrier material Microstructural and optical properties of nanocrystalline MgS thin film as wide band gap barrier material," *Appl. Phys. A Mater. Sci. Process.*, vol. 118, pp. 539–545, 2015, doi: 10.1007/s00339-014-8753-0.
- [24] I. A. Ezenwa, L. N. Ezenwaka, and N. Egwunyenga, "Optical and Structural Characteristics of Mgs Thin Films Fabricated By," *Asia Pacific J. Res.*, vol. 1, no. XXI, pp. 32–37, 2015.
- [25] T. G. Abdullah, S. A. Sami, and M. S. Omar, "Temperature dependence of the energy band gap of CuSi<sub>2</sub>P<sub>3</sub> semiconductor using PSOPW method," *Mater. Sci. Pol.*, vol. 36, no. 4, pp. 553–562, 2018, doi: 10.2478/msp-2018-0085.

- [26] W. Sripumkhai, S. Porntheeraphat, B. Saekow, W. Bunjongpru, S. Rahong, and J. Nukeaw, "Effect of Annealing Temperature on Platinum Thin Films Prepared by Electron Beam Evaporation," *J. Microsc. Soc. Thail.* 2, vol. 24, no. 1, pp. 51–54, 2010.
- [27] W. Sripumkhai, S. Porntheeraphat, B. Saekow, W. Bunjongpru, S. Rahong, and J. Nukeaw, "Effect of Annealing Temperature on Platinum Thin Films Prepared by Electron Beam Evaporation," *J. Microsc. Soc. Thail.*, vol. 24, no. 1, pp. 51–54, 2010.

#### **AUTHORS PROFILE**

Mr. R.A. Babatunde had B.Sc Physics with Electronics in 2009 and M.sc Solid State Physics in 2017 both from Olabisi Onabanjo University, Ago-Iwoye, Nigeria.. Babatunde has been teaching Physics in Department of Science Laboratory Technology, Federal Polytechnic,Iaro Ogun State Since 2012. He is currently a P.HD student in Physics Department Olabisi Onabanjo University, Ago –Iwoye, Ogun State. Nigeria.



Mr. Y.I Bolanle graduated from Physics Department University of Ilorin in 2005; he had M.sc Physics in 2012 from University of Lagos. He has been lecturing Physics courses in the Department of Science Laboratory Technology, The Federal *Polytechnic*, Ilaro , Ogun State. Nigeria.. Since 2012

