Effect of Film Thickness on the Efficiency of an Electroless Deposited Cu$_2$O Based Solar Cell

*I. I. Ibrahim[1], I. M. Musa[1] & I. Sa'adu[1]

[1]Department of Physics, Federal University Dutse,
Jigawa State, Nigeria.
Email: idowuaraba@gmail.com

Abstract

The fabrication of n-Cu$_2$O/p-Cu$_2$S was successful. The n- Cu$_2$O layer was deposited on a copper foil using the immersion technique of the electro less chemical deposition method. The prepared n-type Cu$_2$O samples were grouped into two: the "as-grown" and the annealed; various deposition time and concentration of 0.001M and 0.01M with a pH 9.83 of deposition time 10, 15, 20,25,30,35 and 40 days respectively was used in the same deposition process. At lower deposition time, the samples shows no reaction with both concentrations. The deposition was observed to have begun at the deposition time of 25 days at the 0.001M Conc. and at 20 days for 0.01M Conc. while the formation of the n-type cuprous oxide (n- Cu$_2$O) was at the deposition time of 30 days for both concentrations. However, at 35 to 40 days the n-type cuprous oxide (n- Cu$_2$O) layer turned into cupric oxide (CuO). Afterward, the n- Cu$_2$O was sulphided using Na$_2$S to create the p-Cu$_2$S thereby fabricating the n-Cu$_2$O/p-Cu$_2$S solar cell. Annealing treatment was given to the solar cell at temperature T= 300°c for time t= 15 minutes for each of the concentrations. The dependence of efficiency of the solar cell on the oxide film thickness was established. The efficiency was found to increase as the oxide film- thickness decreases up to a limiting thickness of 4.50μm after which the efficiency decreases with decrease in the oxide film thickness.

Key Words: Deposition Time, Electroless, n-type Cu$_2$O, p-Cu$_2$S, Efficiency, Annealing

1.0 Introduction

Despite the complicated fabrication process and high cost, the majority of solar cells fabricated today are silicon-based solar cells which are single crystalline, large-grained poly crystalline and amorphous forms and they dominated PV market by taking 85% of share (Wang *et al.,* 2007). Silicon is an abundant material, however the purification of the starting material is highly expensive. Therefore to have more cost effective solar cells, silicon should be replaced by other materials. The quest for solution to these problems has led researchers to synthesize and characterize copper oxide materials that are readily available, non-toxic and of low cost of fabrication compared to the silicon based solar cells (Abdul *et al.,*2009). The current debate over copper oxides semiconductors is the low efficiency records of the solar cells fabricated with the cuprous oxide based material (Mateen, 2008; Yunusa *et al.,* 2014).Several authors have prepared and studied copper oxides materials to fabricate solar cell devices using different methods, such copper oxides includes Cuprous oxide (Cu_2O) and Cupric oxide (CuO) (Kidowaki, *et al.,*2011; Abdul *et al.,*2009; Mittiga, 2006; Ibrahim *et al.,* 2015).

Author for Correspondence

In this research, the Electroless Chemical Deposition method which involves the use of immersion technique will be employed to synthesize n-type Cu$_2$O which is an absorber layer for the fabrication of p-n homojunction solar cell. Deposition is performed in solution; the pH of the solution determines conduction type of the formed film. The research investigates the effect of deposition time on thickness of an electroless n-type Cu$_2$O and consequently determine the dependence of the efficiency of the solar cell on the oxide film thickness. Several chemical methods for the deposition of Cu$_2$O layers are available. Of the various techniques the electroless deposition or autocatalytic method is an attractive method that involves the presence of a chemical reducing agent in solution to reduce metallic ions to the metal state, (Awodugba *et al.*, 2011). The name electroless is somewhat misleading, however, there are no external electrodes present, but there is electric current (charge transfer) involved. Instead of an anode, the metal is supplied by the metal salt and a substrate serves as the cathode, while the electrons are provided by a reducing agent. The process takes place only on catalytic surfaces rather than throughout the solution (if the process is not properly controlled, the reduction can take place throughout the solution, possibly on particles of dust or of catalytic metals, with undesirable results) (Mordechay, 2010). Electroless deposition possesses several characteristics not shared by other methods, and that accounts for its ever-growing popularity. Experience shows that each substrate requires its own specific technique and surface preparation (i.e. cleaning process) which requires very careful selection and application. It must be stressed that cleaning may affect the porosity of the metal deposit (Abdel *et al.*, 2007). Residues from cleaners and deoxidizers may create inactive spots that will not initiate electroless deposition. This may result in the necessity to have a thicker deposit before continuity is achieved. In extreme cases continuity is never reached. In general, deposition requires one or more of the following steps (1) Cleaning, (2) Surface modification, (3) Sensitization, (4) Catalyzing, (5) Activation (acceleration). Rinsing is required between the steps. If the metal to be deposited electrolessly can be reduced by the sensitizing ion, then it is not necessary to reduce the active metal first. Instead, the substrate is immersed in the electroless bath immediately after sensitizing and rinsing, (Heaven, 1970).
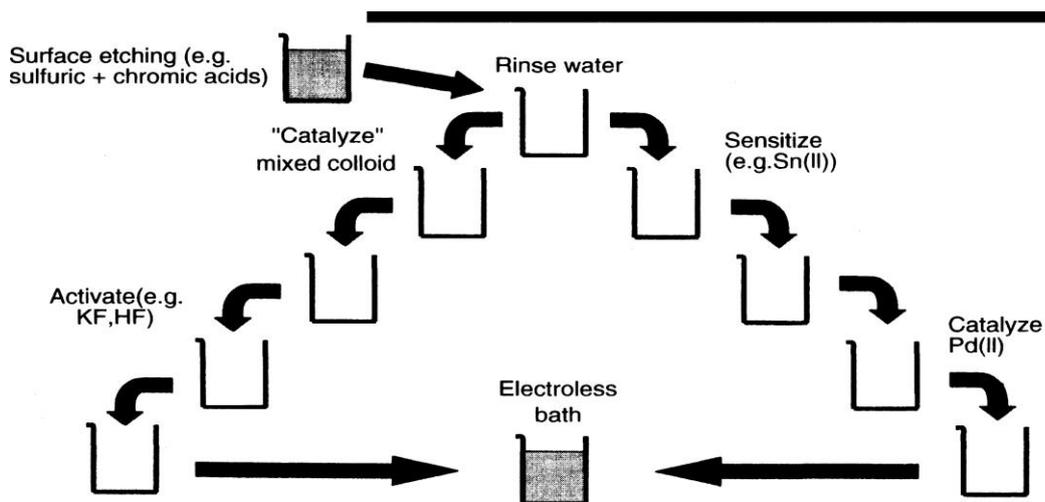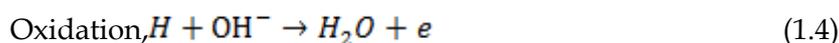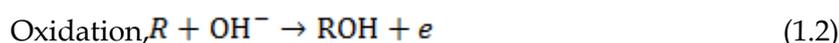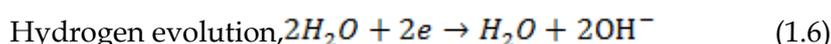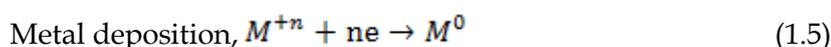

Figure 1.1: Schematic representation of the electroless deposition process. (Abdel *et al.,* 2007)
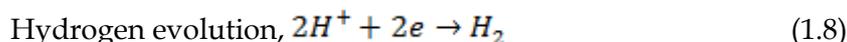
According to Van Den Meerakker and Paunovic (2010), electroless deposition processes may be viewed and understood by what is referred to as a universal electrochemical mechanism regardless of the nature of the many possible reducing agents R. Each process can be viewed as made up of a series of elementary anodic and cathodic reactions. The first anodic stage is the dehydrogenation of the reductant. Thus the following four anodic stages are recognized in the case of alkaline media:

$$\text{ehydrogenation,} RH \rightarrow R + H \qquad (1.1)$$

$$\text{Oxidation,} R + OH^- \rightarrow ROH + e \qquad (1.2)$$

$$\text{Recombination, } H + H \rightarrow H_2 \qquad (1.3)$$

$$\text{Oxidation,} H + OH^- \rightarrow H_2O + e \qquad (1.4)$$

In the case of alkaline media the following two cathodic stages are recognized:

$$\text{Metal deposition, } M^{+n} + ne \rightarrow M^0 \qquad (1.5)$$

$$\text{Hydrogen evolution,} 2H_2O + 2e \rightarrow H_2O + 2OH^- \qquad (1.6)$$

In acid media stages 4 and 6 are to be written as follows:

$$\text{Oxidation, } H \rightarrow H^+ + e \qquad (1.7)$$

$$\text{Hydrogen evolution, } 2H^+ + 2e \rightarrow H_2 \qquad (1.8)$$

Various approaches have been used in depositing n - Cu_2O layer, some of which include the boiling technique (Yunusa et $al.$, 2014), the heating or chemical bath techniques (Ibrahim et $al.$, 2016), the electrochemical deposition technique (Kunhee et $al.$, 2009; Longeheng et $al.$, 2007). In this research work the approach used is the Electroless Chemical Deposition method via the immersion technique, with an attempt to study the effect of varying the concentration of the metal salts and to determine the dependency of efficiency of the solar cell on the oxide film thickness.

2.0 Experimental Procedure

Electroless Deposition Method was used. A good quality copper foil was used as the substrate, the copper foil surface was first conditioned in accordance with the existing procedure (Musa et $al.$, 1998). This eliminates any grease or dirt from the surface of the copper foil. The copper sheets (0.1mm thickness, and 99.99% purity) were cut into samples of 1cm x 1cm size, and were then smoothened and washed in dilute nitric acid then rinse in a solution of sodium persulphate for 20secs and finally rinsed again in deionized water.

Anhydrous copper II sulphate of purity 99.0% (BDH-GPR), and molecular weight of 159.60 was used to make $CuSO_4$ solution of concentrations 0.001M and 0.01M respectively. Adventurer Ohaus analytical balance was used to weigh the copper II sulphate, which was dissolved in 500cm³ of distilled water. The formation of the n-type Cu_2O layers was achieved following the method reported in literature (Yunusa, 2011) which is based on the immersion techniques of the electroless deposition method. In this techniques 100cm³ each of the 0.001M and 0.001M $CuSO_4$ solution, at pH = 9.83, was taken in a beaker for uniformity of the deposition condition. The copper plates were then placed into the solution and left for

the deposition time of 10,20,30,35 and 40 days respectively. At the end of the stated number of days, the copper foils were removed and washed severally in deionized water and finally dried between tissue papers.

2.1 Annaeling

The n- Cu$_2$O layers were given heat treatment according to Abdu and Idowu (2014). This heat treatment is called annealing. The annealing process was performed to achieve the following objectives: healing defects created during the deposition, lowering the resistivity of the layers and improving on the grain size of the crystals. The Vecstar furnace heating chamber, Model Spch12 was used for the annealing process. The sample layers were annealed at the same time of t=15min and temperature T=300^{0}C to determine the effect of annealing of the samples.

2.2 Formation of the p-Cu$_2$S Layer

To form a heterojunction solar cell, the formation of the Cu$_2$S is necessary to make up with the n-type Cu$_2$O formed. Cu$_2$S is a p-type material and it's formed on the n-Cu$_2$O surface by immersing in Na$_2$S for some seconds. The surface of n-Cu$_2$O appear black due to the formation of Cu$_2$S and the reaction that took place is

$$Na_2S + H_2O + Cu_2O \rightarrow Cu_2S + 2NaOH \tag{2.1}$$
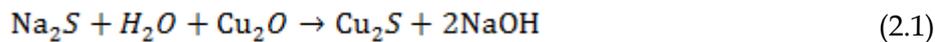
## 2.2 Maximum Power Point Determination

The solar cell fabricated was connected in a circuit as shown in figure 2.1
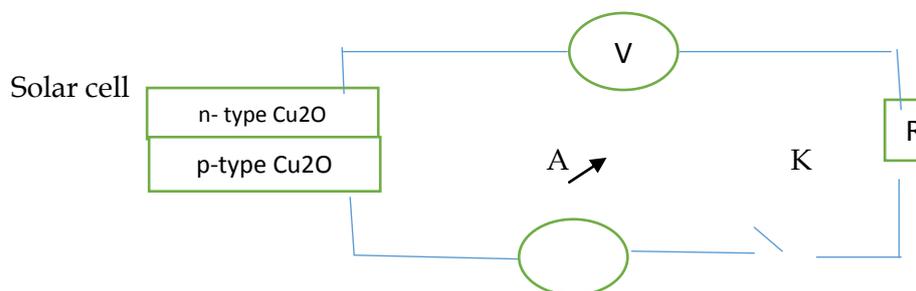
R was set to zero resistance and the microammeter and Voltmeter readings were noted. This was repeated for values of R= 20Ω, 27Ω, 56Ω, 82Ω, 120Ω, 150Ω, 160Ω and ∞. The experiment was repeated with each of the remaining seven cells connected in place.

2.3 Thickness Measurement

The gravimetric method of measurement was used in the setup. In this method the cell samples were weighed on a digital meter balance to obtain the initial mass of the Cu$_2$O/Cu which is recorded as M$_1$ for the different cells. After the initial measurement the Cu$_2$O of the cell sample were washed away using concentrated hydrochloric acid to obtain the Cu. The cell samples were re-weighed and recoded as M$_2$. The chemical reaction is expressed as

$$2Cu_2O_{(s)} + 4Hcl_{(aq)} = 2CuCl_{2(aq)} + 2H_2O_{(L)} + 2Cu_{(s)} \tag{2.2}$$
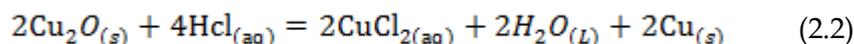
The difference in mass $M_d = M_1 - M_2$ was calculated for all the samples. Equation (2.2) was used to obtain the thickness of Cu$_2$O deposited.

$$t = \frac{M}{A\rho} \qquad (2.3)$$

Where t = thickness of the deposited Cu_2O on Cu, M = mass of Cu_2O ρ = density of Cu_2O which is 6.0gcm⁻³, and A = surface area of the samples which is 0.0001m²,

3.0 RESULT AND DISCUSSION
3.1 Results

Depending on the deposition time and the concentration of the solution, the physical appearance of the films deposited ranged from blackish-brown to reddish brown and black. Tables 3.1 and 3.2 show the 0.001M and 0.01M concentration of $CuSO_4$ solution and the measurement of the weights of the sample with the thicknesses after deposition for the annealed and unannealed samples respectively.

Table3.1a: Time of deposition, weight difference and thickness of the un-annealed n- Cu_2O layer

Cell Sample	Deposition Time(days)	M_1(g)(weight of Cu_2O/Cu)	M_2(g)(weight of Cu)	M_d(g) =(M_1-M_2)	Thickness(μm)	Observation
A_{11}	10	-	-	-	-	Shows no Deposition
A_{12}	15	-	-	-	-	Shows no Deposition
A_{13}	20	-	-	-	-	Shows no Deposition
A_{14}	25	0.2250	0.2220	0.0030	5.000	Cu_2O layer formed
A_{15}	30	0.2951	0.2932	0.0019	3.166	Cu_2O layer formed
A_{16}	35	0.2287	0.2237	0.0045	7.500	CuO layer formed
A_{17}	40	0.2922	0.2886	0.0036	6.000	CuO layer formed

Table 3.1b: Time of deposition, weight difference and thickness of the annealed n- Cu_2O layer

Cell Sample	Deposition Time(days)	M_1(g)(weight of Cu_2O/Cu)	M_2(g)(weight of Cu)	M_d(g) =(M_1-M_2)	Thickness (μm)	Observation
A_{11}	10	-	-	-	-	Shows no Deposition
A_{12}	15	-	-	-	-	Shows no Deposition
A_{13}	20	-	-	-	-	Shows no Deposition
A_{14}	25	0.3070	0.3044	0.0026	4.333	Cu_2O layer formed
A_{15}	30	0.2890	0.2825	0.0065	10.83	Cu_2O layer formed
A_{16}	35	0.2593	0.2552	0.0041	6.833	CuO layer formed
A_{17}	40	0.3186	0.3137	0.0049	8.166	CuO layer formed

Table 3.2a: Time of deposition, weight difference and thickness of the un-annealed Cu$_2$O layer

Cell Sample	Deposition Time(days)	M$_1$(g)(weight of Cu$_2$O/Cu)	M$_2$(g)(weight of Cu)	M$_d$(g) =(M$_1$-M$_2$)	Thickness (μm)	Observation
B$_{11}$	10	-	-	-	-	Shows no Deposition
B$_{12}$	15	-	-	-	-	Shows no Deposition
B$_{13}$	20	0.3015	0.2999	0.0016	2.666	Cu$_2$O layer formed
B$_{14}$	25	0.2734	0.2696	0.0038	6.333	Cu$_2$O layer formed
B$_{15}$	30	0.2664	0.2632	0.0032	5.333	Cu$_2$O layer formed
B$_{16}$	35	0.2813	0.2781	0.0032	5.333	CuO layer formed
B$_{17}$	40	0.3307	0.3276	0.0031	5.166	CuO layer formed

Table3.2b: Time of deposition, weight difference and thickness of the annealed n- Cu$_2$O layer

Cell Sample	Deposition Time(days)	M$_1$(g)(weight of Cu$_2$O/Cu)	M$_2$(g)(weight of Cu)	M$_d$(g) =(M$_1$-M$_2$)	Thickness (μm)	Observation
B$_{11}$	10	-	-	-	-	Shows no Deposition
B$_{12}$	15	-	-	-	-	Shows no Deposition
B$_{13}$	20	0.2818	0.2805	0.0013	2.166	Cu$_2$O layer formed
B$_{14}$	25	0.2938	0.2911	0.0027	4.500	Cu$_2$O layer formed
B$_{15}$	30	0.2941	0.2911	0.0030	5.000	Cu$_2$O layer formed
B$_{16}$	35	0.2888	0.2854	0.0034	5.666	CuO layer formed
B$_{17}$	40	0.2608	0.2578	0.0030	5.000	CuO layer formed

Table 3.3: Maximum Power Point for annealed cell sample A$_{15}$ with the concentration of 0.001M and deposition time of 30days

R(Ω)	I(μA)	J(μA/cm^2)	V(mV)	P(μW)
0	349	87.25	0.0	0.0000
27	280	70.00	30.0	8.4000
56	279	69.75	44.0	12.276
82	206	51.50	38.0	7.8280
120	205	51.25	45.0	9.2250
150	198	49.50	47.0	9.3060
∞	0	00.00	60	0.0000

3.2 Energy Conversion Efficiency
3.2.1 Energy conversion efficiency
The electrical power conversion efficiency η of a solar cell is the ratio of the power out, P_{max} to the total power input, P_{in} of the light incident on the cell. This is expressed as:

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \frac{FF \cdot J_{SC} \cdot V_{OC}}{P_{in}} \times 100\% \qquad (3.1)$$

where P_{max}= maximum power point, V_{OC}= Open circuit voltage, I_{SC}= Short circuit current, P_{in}= Input light irradiance (1000 W/m²), FF= Fill Factor and η= Efficiency of the solar cell.

$$FF = \frac{P_{max}}{J_{sc}V_{oc}} = \frac{V_{max}I_{max}}{J_{sc}V_{oc}} \qquad (3.2)$$

The Fill Factor (FF) is calculated to be **0.40** using the formula above.

Table 3.4 Variation of the energy conversion efficiency with the thickness of the solar cells for the n-type Cu₂O layer formed

Cell Sample	Deposition Time (days)	Efficiency (%)x 10⁻²	Thickness (μm)
B₁₃	20	1.00	2.133
A₁₄	25	0.78	4.333
B₁₄	25	8.40	4.500
B₁₅	30	0.92	5.000
A₁₅	30	2.09	10.17

Figure 3.1: Plot of energy conversion efficiency against the thickness of Cu₂O.
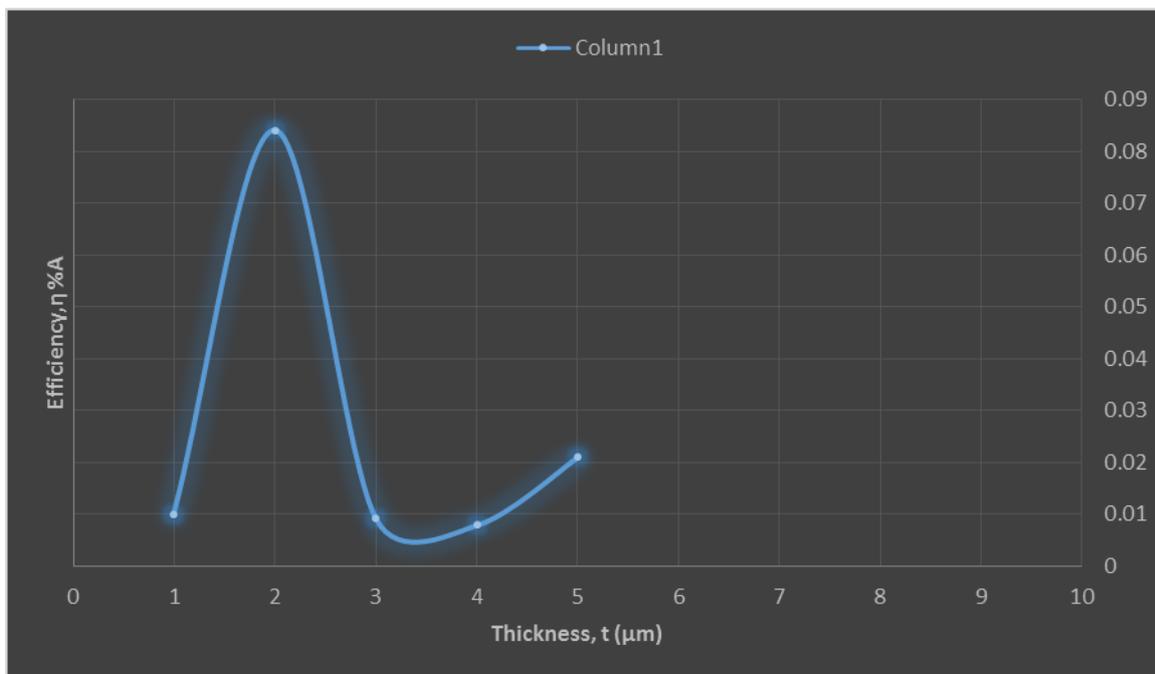
3.3 Discussion
After all the deposition processes, it was observed that, at deposition time of 10,15 and 20 days there were no deposition for the concentration of 0.001M, while deposition took place at deposition time of 20,and 25 days for the concentration of 0.01M. It is clear from the result that concentration plays an important role with respect to time.

It was observed that n-type Cu₂O were formed at the deposition time of 20, 25 and 30days for both concentrations while all deposition formed beyond 30 days shows CuO formation. Table 3.4 and figure 3.1 shows that the efficiency of the solar cell increase as the thickness of the Cu₂O decreases up to a limiting thickness of 4.50μm, after which the efficiency decreases as the thickness further decreases.

The limiting thickness of 4.50μm belongs to the cell sample deposited at concentration of 0.01M with deposition time of 25days. The best deposition condition for Cu_2O on Cu is 0.01M concentration at deposition time of 25days. The short circuit current (I_{sc}),the Open circuit voltage (V_{oc}), maximum power point (P_{max}), Fill Factor (FF), and Efficiency of this solar cells are 280μm,30mV,8.400μW, 0.4 and 0.0840%, respectively.

However, the result obtained from the deposition growth, are similar to the result obtained by Yunusa and Idowu (2014). The photo responses of this process depends strongly upon the thickness and concentration of the Cu_2O solution which have been extensively considered in this work. The method describe is capable of producing an n-type Cu_2O absorber layer for the fabrication of an efficient homojunction solar cell.

4.0 CONCLUSION

It was determine that the efficiency of n-Cu_2O/p-Cu_2S solar cell depends on the thickness of the Cu_2O film layer. This shows that the higher the thickness the higher the resistivity and the less efficiency or photo response. In this result the limiting film thickness is 4.50 μm, after which the efficiency decreases as the thickness decreases. This is in line with the theoretical support that the efficiency of a solar cell is a function of the number of created electron-hole pair that are able to migrate to the space charged region where they are separated, also the ability of an electron-hole pair to get to the space charged region without recombination depends on the proximity of the creation point to the space charged region.

References

A. Mittiga, , 2006. Heterojunction solar cell with 2% efficiency based on Cu2O substrate.. *Journal of Applied Physical. Letter., ,* Volume 88, p. 163502.

Abdel. Z, Hamid. S, El Badry .A, and Abdel. A., , 2007. Electroless Deposition and Characterization of Ni– P–WC Composite Alloys,. *Surface Coating Technology.,,* Volume 201, pp. 594-595.

Abdu, Y and Ibrahim, M.M., 2016. "Fabrication of p-Cu2 S/n -Cu2 O for photovoltaic Application". *Journal of the Nigerian Association of Mathematical Physics,* Volume 33, pp. 271-276.

Abdul,.Y; and A,. Musa, 2009. Copper (1) Oxide (Cu2O) Based Solar cells - A Review.. *Bayero Journal of Pure and Applied Sciences,,* 2(2), pp. 8-12.

Awodugba, A.O, and Adedukun, O., 2011. The physical and optical characteristics of Cds Thin Film Deposited by CBD Techniques.. *Pacific Journal of Science and Technology,* 12(2), pp. 334-341.

H. Kidowaki, T. Oku, T. Akiyama, A. Suzuki, B. Jeyadevan, and J. Cuya, , 2011. "Fabrication and Characterization of CuO-based Solar Cells,. " *Journal of Material Science.,,* 1(1), pp. 138-143.

Heaven S.O.,, 1970. *Thin Films physics,.* ,London.: Methuen and Co. Ltd..

I. I. Ibrahim, N. Yunusa, and C. E. Ndikilar, , 2015. "Electroless Deposition of Thin Film of Lead Sulphide (PbS and Measurement of its Physical, Electrical and Optical Properties,". *Journal of Nigerian Association of Mathematical Physics,,* Volume 32, pp. 465-470.

Ibrahim I.I, Musa I.M and Yunusa .N ., 2016. Comparative Study of the Structural Properties of n-Cu2O thin Produced by Boiling and Immersion Techniques,. *Dutse Journal of pure and applied Sciences* 1, pp. 133-119.

Kunhee, H, and Meng, T. , 2009. Electrically Deposited p-n Homojunction Cuprous Oxide Solar cells.. *Journal of Solar Energy and Solar Cells,,* Volume 93, pp. 21-27.

Longeheng, W. and Meng, T. , 2007. Fabrication and Characterization of p-n Homojunctons in Cuprous oxide by Electrochemical Deposition.. *Electrochemical and Solid State letter,* 10(9), pp. 11248-11250.

Mateen, A., 2008. Some Methodologies Used for the Synthesis of Cuprous Oxide : a Review.. *Journal of Pak Mater Soc,* 2(1), pp. 40-48.

Mordechay S, , 2010. Electroless Deposition of Nikel ,Modern Electroplating. 4(3), pp. 447-458.

Musa, A. O., Akomolofe, T. and Carter, M. J. , 1998. Production of Cu¬2¬O Solar Cell Material, by Thermal Oxidation and Study of its physical and electrical Properties.. *Journal of solar Energy Materials and Solar Cells.,* Volume 51, pp. 3-4.

Olsen,.L.,C ; F. W. Addis, and W. Miller, , 1982. "Experimental and theoretical studies of Cu2O solar cells,. *Journal of solar cells,* 7(3), pp. 247-279.

Paunovic,. M , 2010. "Electroless deposition of copper,". *Journal of Mod. Electroplat.,* Volume 1, pp. 433-446.

Wang,. L and Meng., 2007. Preparation and Characterization of Properties of Electrodeposited Copper Oxide.. *Solid State Letters,,* Volume 10, pp. 248-250.

Yunusa, A. , 2011. *Fabrication and Study of the Physical and Electrical Properties on n-type Copper (I) Oxide/p-type Copper (I) Sulphide (n-Cu2O/p-Cu2S) Heterojunction Solar Cell.,* Kano: Bayero University, Kano.

Yunusa,. A and I. I. Idowu, , 2014. "Optimization of the annealing time and temperature of n- Cu2O /p- Cu2S solar cell,". *Journal of Nigerian Association of Mathematical Physics.,,* Volume 26, pp. 486-489.