Journal of the Nigerian Association of Mathematical Physics
Volume26, (March, 2014), pp 486 – 489
© J. of NAMP

Optimization of the Annealing Time and Temperature of n-Cu_2O/p-Cu_2S Solar Cell

Abdu Yunusa and Ibrahim I. Idowu

Bayero University, Kano

Abstract

Solar cells of n-Cu_2O/p-Cu_2S were fabricated. The n-Cu_2O layers were formed using Electroless chemical method which involved immersing of copper plates in 0.001M CuSO4 solution of pH 9.83, approximately. A uniform layer of n-Cu_2O was formed on the copper plates within 30 days in solution, later some of these samples were subjected to annealing treatment at various times and temperatures. This treatment was aimed at optimizing the annealing time and temperature. The annealed and unannealedn-Cu_2O samples were then immersed in 0.5M Na_2S solution to form the p-Cu_2S layer thereby creating the required n-Cu_2O/p-Cu_2S solar cell. Annealing treatment was also given to the n-Cu_2O/p-Cu_2S solar cell with annealedn-Cu_2O layer, to ascertain the stage at which the annealing treatment canimprove the performance of the cell better. The best results of open circuit voltage V_{oc} = 60mV, short circuit current density, J_{sc} = 87.12μAcm^{-2} and a fill factor, ff = 0.52 were obtained for annealing of n-Cu_2O before and after sulphidation at temperature,T= 300$^oC$and time, t = 15minutes and temperature, T = 250$^oC$and time, t =15minutes, respectively. These results are higher than previously reported experimental values for this solarcell.

Keywords: n-Cu_2O/p-Cu_2S solar cell, Electroless deposition,Annealing time and temperature

1.0 Introduction

Electrical power obtained through solar energy conversion, using photovoltaic (PV) solar cells is regarded the most promising alternative to the conventional energy sources. The conventional energy sources, mainly of fossil fuels, are fast being depleted through high demand despite the attendant consequences of their usage due to pollution. The use of the solar cell to augment the conventional sources is mainly based on their being, among other things, cost effective in areas where extending utility power line is very expensive, requiring little maintenance and production of electricity without polluting the environment. Photovoltaic cells that areused presently in commercial quantities are silicon pn-junction solar cells, cadmium sulphide/copper sulphide (CdS/Cu_2S), gallium arsenide (GaAs) and amorphous silicon (a-Si) solar cells. But the future development of these PV cells is predictably going to be lowered by high cost of material and fabrication methods. For large scale power generation using these cells, there should be a drastic reduction in the cost of the cells. One of the cheapest solar cells now being investigated worldwide are the Cu_2O-based solar cells due to the availability of the starting material which is copper, the material being non-toxic and having simple and cheap fabrication methods. In the past, n-type Cu_2O was not produced, since an approach to achieving n-type doping has not yet been fully developed. Without it, the early studies had to rely on Schottky junctions and p-n heterojunctions for photovoltaic devices. The p-n heterojunction solar cells have the highest electrical conversion efficiency of 3.83 % [1]. However, Fernando and Wetthasinghe[2] have reported the possibility of obtaining n-type photo- responses from clean copper plates, immersed in $CuSO_4$ solution for a few days. Subsequently, Fernando et al[3] reported the n-type Cu_2O produced by heating copper sheets in $CuSO_4$ solution. The formation of the n-type Cu_2O on copper surface, by heating copper sheets in $CuSO_4$ solution, can be explained by the following chemical reaction:

$$Cu^{2+} + Cu + H_2O \rightarrow Cu_2O + 2H^+ \text{..........................} (1)$$

Another approach ofproducingn-Cu_2O was reported by Longchen and Meng[4], their experimental results showed thatboth p- and n-Cu_2O formation can be achieved by varying solution pH. This enables p-type and n-type Cu_2O to be deposited

Corresponding author: ***Abdu Yunusa,*** E-mail: yunusa_abdu@yahoo.com, Tel.: +2348061192954

electrochemically in sequence to form a p-n homojunction of Cu_2O. However, the first homojunction solar cell of Cu_2O using the electrochemical method was made by Kunhee and Meng[5].
This work investigates the effect of annealing temperature and annealing time on the performance of n-Cu_2O/p-Cu_2S solar cell. The fabrication of the cell was in accordance with the procedure reported by Abdu[6]. The motivation for this work is that the method is simple and the materials used are very cheap.

1.1 Experimental

2.1 Copper Preparation

A good quality Cu_2O material was obtained by first conditioning the copper surface according to an existing procedure [7]. This eliminates any grease or dirt from the surface of the copper foil. High purity copper sheets (0.1mm thickness, and 99.99% purity) were cut into samples of 2cm x 2cm size, and were then smoothened. The copper sheets were then washed in dilute nitric acid for about 20secs, and finally rinsed in deionized.

2.2 Solution Preparation

Anhydrous copper II sulphate of purity 99.0% (BDH-GPR), of molecular weight 159.60 was used to make $CuSO_4$ solution of 0.001M concentration. Adventurer Ohaus analytical balance was used to weigh the copper II sulphate and dissolved it in 1000cm^3 of distilled water.

2.3 Growth of Cu_2O Layers

The formation of the n-type Cu_2O layers was achieved according to the method reported by Abdu[6], which is based on the modification of the immersion methodearlier used by Fernando[2]. In this method 100 cm^3 of the 0.001M $CuSO_4$ solution,pH = 5.5, was taken in a beaker in every trial, for uniformity of the deposition condition. The pH of the $CuSO_4$ solution was then adjusted to 9.83, and later copperplates were then placed into the solution and left for 30 days. This was done to achieve a uniform layer of the desired n-Cu_2O material. 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

2.4 Formation of p-Cu_2S Layer

To achieve the formation ofthe p-Cu_2S 0.05M Na_2S solution was used. The solution was prepared by weighing theNa_2S; using Adventurer Ohaus balance, and dissolved in 1 liter distilled water. Then the substrate, Cu/n-Cu_2O was immersed in the Na_2S solution for about 5-10 seconds and finally removed and dried in air.

2.5 Annealing

The Cu_2O and Cu_2S layers were given heat treatment according to report in the literature [8], this heat treatment is called annealing. The annealing process was performed to achieve the following objectives: healing defects created during layer formation, 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. Annealing at various times and temperatures were carried out to determine the point of optimum performance of the cell.

3.0 Results And Discusion

3.1 Formation of the n-Cu_2O Layer

At the expiration of the stated number of days in solution, the copper plates were noticed to have been covered by a uniform reddish-brown layer of the n-Cu_2O material.This n-Cu_2O formation resulted in the creation of Cu/n-Cu_2O structure. It was observed that only at pH of 9.83 that the Cu_2O layer was obtained, at any other pH value, from pH 5.5 and above, either a mixture of Cu_2O and cupric oxide, CuO was formed or pure CuO was formed [9]. The sample was removed and washed in deionized water and dried between tissue papers. Several other samples were produced in the same manner as described above (section 2.3). Some of the Cu/n-Cu_2O samples were later annealed at some selected times and temperatures as shown in Table 1.

3.2 Formation of the Cu_2S Layer

The formation of the Cu_2S is necessary because being a p-type material it is used with the n-Cu_2O material to form the heterojunction n-Cu_2O/p-Cu_2S solar cell. After the immersion in Na_2S, the surface of the n-Cu_2O appears black due to the formation of Cu_2S. The reaction predicted to have taken place [6] is:

$$Na_2S + H_2O + Cu_2O \rightarrow Cu_2S + 2NaOH \qquad (2)$$

Some of the n-Cu_2O/p- Cu_2S solar cells formed were finally annealed. The various annealing timesand temperatures used were considerably low to avoid the formation of CuO on the Cu_2S layer, as reported by Varkey [10]. The annealing times and temperatures considered for the solar cells are presented in Table 1.

3.3 Measurement of Voc and Jsc for the n-Cu_2O/p-Cu_2S Solar Cells

After the annealing process, the open circuit voltage, V_{oc} and the short circuit current, J_{sc} of the n-Cu_2O/p-Cu_2S solar cells were measured. The values for V_{oc} and J_{sc} for all the cells considered are given in Table 2. It is clear from the results that annealing plays an important role towards improving the values of the V_{oc} and J_{sc} of the solar cell. The Unannealed cell A has low values of these parameters compared with those of B_1 down to C_3. The values for cell sample C_4 appears to have over been annealed due to the annealing time used. The annealing time for the solar cell sampleC_4 is a bit higher, and it appears to have affected the performance of the cell. The best result is that of cell sample C_1, having V_{oc} and J_{sc} values 60mV and 87.12μAcm^{-2}, respectively. These values are better than for the cell reported in literature [6] having V_{oc} and J_{sc} value of 45mV and 75 μAcm^{-2}, respectively. Generally, the results show that for better performance of the n-Cu_2O/p-Cu_2S solar cells the n-Cu_2O should be annealed first at 300^{o}C for 15 minutes and when the cell is formed by the formation of the p-Cu_2S, the cell should again be annealed at 250 ^{o}C for 15 minutes.

3.4 The Current-Voltage (J-V) Characteristic of the n-Cu_2O/p-Cu_2S Solar Cell

The current-voltage, J-V characteristic of then-Cu_2O/p-Cu_2S solar cell sample C_1 under illumination, Fig. 1, was used to determine the maximum power point, P_M and the Fill Factor, ff. The values of P_M and the ff obtained are 2.72x10^{-6}Wcm^{-2} and 0.52, respectively. The Fill Factor was evaluated using equation (3):

$$FF = \frac{P_{\max}}{J_{SC}V_{OC}} = \frac{V_{\max}J_{\max}}{J_{SC}V_{OC}} \qquad (3)$$

4.0 Conclusion

Generally, efficient solar cell should have high short circuit current density, J_{sc}, a high open circuit voltage, V_{oc} and a Fill Factor, ff, as close as possible to 1. Therefore,the n-Cu_2O/p-Cu_2Ssolar cell fabricated having values of the V_{oc}, J_{sc} and ff of 60mV, 87.12μAcm^{-2} and 0.52, respectively is concluded to represent an improvement over previously reported experimental values of Jsc, Voc and ff of 75μAcm^{-2}, 45mV and 0.39, respectively [6]. Further work on this cell concerning optimum thickness and use of antireflection coating mayfurther improve the results presented in this work.

Table 1. Annealed layers and their corresponding times and temperatures

Cell Sample	Annealed Layer	Unannealed Layer	n-Cu_2O		n-Cu_2O/p-Cu_2S	
			Annealing Temp	Annealing Time	Annealing Temp	Annealing Time
A		n-Cu_2O n-Cu_2O/p-Cu_2S				
B_1	n-Cu_2O	n-Cu_2O/p-Cu_2S	300^{0}C	30min		
B_2	n-Cu_2O	n-Cu_2O/p-Cu_2S	300^{0}C	15min		
B_3	n-Cu_2O	n-Cu_2O/p-Cu_2S	200^{0}C	15min		
C_1	n-Cu_2O n-Cu_2O/p-Cu_2S		300^{0}C	15min	250^{0}C	15min
C_2	n-Cu_2O n-Cu_2O/p-Cu_2S		300^{0}C	30min	200^{0}C	15min
C_3	n-Cu_2O n-Cu_2O/p-Cu_2S		300^{0}C	15min	150^{0}C	15min
C_4	n-Cu_2O n-Cu_2O/p-Cu_2S		300^{0}C	35min	200^{0}C	15min

Table 2. V_{oc} and J_{sc} values of the n-Cu_2O/p-Cu_2S solar cells under bright sunlight.

Cell Sample	**V_{oc} (mV)**	**Jsc (μA/cm^2)**
B_1	20.3	37.77
B_2	40.5	45.20
B_3	24.5	42.4
C_1	60	87.12
C_2	47	72.35
C_3	58.9	74.88
C_4	4.8	20.81

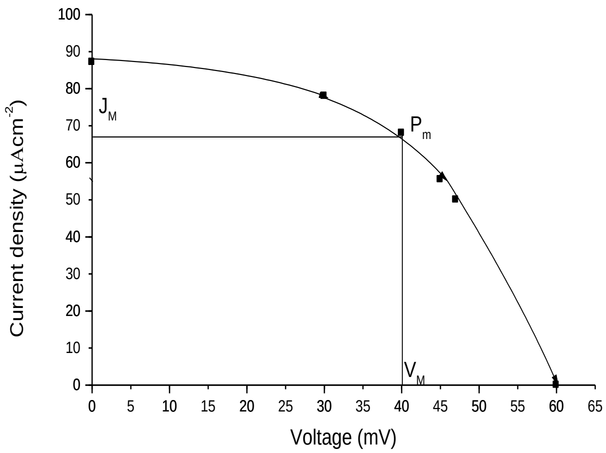

Fig. 1.The J-V characteristic of the n-Cu_2O/p-Cu_2S solar cell under bright Sunlight.

References

[1] Minami, T., Nishi, Y., Miyata, T., and Nomoto, J; (2011): High efficiency Oxide Solar Cells with ZnO/ Cu_2O Heterojunction Fabricated on Thermally Oxidized Cu_2O Sheets. The Japan Society of Applied Physics, Vol. 4 (6)1-3

[2] Fernando, C.A.N. and Wetthasinghe, S.K. (2000): Investigation of photoelectrochemical characteristics of n-type Cu2O Films. Solar Energy Materials and solar cells, 63: 299-308.

[3] Fernando, C.A.N**,** de Silver, P.H.C. Wethasinha, S.K, Dharmadasa, I.M. Delsol, T. and Simmonds, M.C. (2002): Investigation of n-type Cu2O Layers Prepared by Low Cost Chemical Method for Use in Photovoltaic Thin Film Solar Cells. Renewable energy, 26: 521 – 529

[4] Longcheng, W. and Meng, T. (2007): Fabrication and Characterization of p-n Homojunction in Cuprous Oxide by Electrochemical Deposition. Electrochemical and Solid State Letters, 10 (9): H248-H250

[5] Kunhee, H, and Meng, T. (2009): Electrically Deposited p-n Homojunction Cuprous Oxide Solar cells. Solar Energy and Solar Cells, 93: 153-157

[6] Abdu, Y.; (2011): Fabrication and Electrical Characterization of n- Cu_2O/p-Cu_2S Solar Cells. Bayero Journal of Physics and Mathematical Sciences. 4(1): 227-234.

[7] Musa, A. O. Akomolafe, T. and Carter, M. J. (1998): Production of Cu_2O Solar Cell Material, by Thermal Oxidation and Study of its Physical and Electrical Properties. Solar Energy materials and solar cells, 51: 3-4.

[8] Musa, A.O. (1995): Development of Thin Film Copper (I) Oxide for Backwall Schottky Barrier Solar Cells, Ph.D. Thesis, University of Ilorin, Nigeria.85-87, 185.

[9] Yunusa, A., Musa, A. O. and Darma, T. H.; (2012): Electroless Deposition and Electrical Characterization of n- Cu_2O Layer. Bayero Journal of Pure and Applied Sciences. 5(2): 1-10.

[10] Varkey, A.J.; (1990): Photovoltaic Effect of Chemically Deposited Cu_xS/C-Si Heterojunctions. Solar and Wind Technology, 5(619-621).