PREPARATION AND CHARACTERIZATION OF COPPER (I) OXIDE/COPPER (I) SULPHIDE HETEROJUNCTION FOR PHOTOVOLTAIC APPLICATIONS

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Abstract

This paper presents the formation of n-copper (I) oxide/p-copper (I) sulphide (n-Cu_2O/p-Cu_2S) heterojunction. Firstly, the formation of n-Cu_2O layer was carried out by heating copper foil in 0.1M$CuSO_4$ solution at 80°C for 1hour and subsequently annealed at 250°C for 2 hours. The particle morphological and mineralogical phase of the developed n-Cu_2O layer was examined using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD). It was physically observed from the SEM micrographs that the grain sizes of the material appear to be larger after annealing. X-ray Diffraction (XRD) analysis reveals the formation of Cu_2O (111) plane at $2\theta = 36.4^o$, Cu_2O (110) plane at $2\theta=29.5^o$, Cu_2O (200) plane at $2\theta=42.3^o$ and Cu_2O (220) plane at $2\theta=61.3^o$. Secondly, the n-Cu_2O/p-Cu_2S heterojunction was formed by partial sulphidation of the n-Cu_2O in 0.5MNa_2S solution. The n-Cu_2O/p-Cu_2S heterojunction formed, when exposed to sunlight, produced a short-circuit current density, J_{sc}, and open-circuit voltage, V_{oc}, of 77 $\mu A/cm^{-2}$ and 45mV, respectively. Finally, manual formation of grids on the p-Cu_2S layer enhanced the values of J_{sc} and V_{oc} to 96 $\mu A/cm^{-2}$ and 52mV, respectively. These results are an improvement over previously reported values on this heterojunction.

Keywords: *n-Cu_2O, chemical heating, n-Cu_2O /p-Cu_2S heterojunction.*

Introduction

Solar cells are devices that convert sunlight into electrical energy and for this they are called Photovoltaic (PV) devices (Green, 1982). There are presently few PV cells that are widely used in commercial quantities. These are silicon pn-junction solar cells, cadmium sulphide/copper sulphide (CdS/Cu_2S), gallium arsenide (GaAs) and amorphous silicon (a-Si) solar cells. However, it has been predicted that the future development will be hampered 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 by researchers across the globe is the cuprous oxide-based (Cu_2O-based) solar cells. Cuprous oxide is one of the early semiconducting materials whose photovoltaic effects were discovered in 1904 (Musa, 1998). It has promising theoretical electrical power conversion efficiency of about 20% with a very cheap starting material, which is copper. Other unique features that make Cu_2O attractive for photovoltaic applications are, availability of copper, its non-toxicity and having a direct bandgap of about 2.1eV (Siripala et al., 1996 and Mahalingam et al., 2000). Researchers have reported different methods of depositing Cu_2O layers such as electrodeposition (Economou, *et al.*; 1982, Mahalingam *et al.*, 2005, Wijesundara *et al.*, 2000, Santra, *et al*; 1999), thermal oxidation (Musa *et al.*, 1998, Minami, *et al*; 2016), reactive magnetron sputtering (Akimoto *et al.*, 2006, Mugwang, 2013, Herion *et al.*, 1980, Pearson, *et al*; 2003, Reddy, *et al*; 2008), chemical-bath (Fernando *et al.*, 2002), amongst others. On the other hand, Cu_2O layers deposited via these methods were found to be p-type. Furthermore, the low efficiency of the Schottky solar cell of 1.2% (Tanaka, *et al.*, 2004) and 1.8% (Olsen, *et al*, 1982), which proved to be higher than other types of the Cu_2O-based solar cells have led to the establishment that the best approach to improve Cu_2O solar cell efficiency is the production of both p-type and n-type Cu_2O and thus forming a p-n homojunction of Cu_2O. This homojunction will, not only provide a better lattice matching between the layers equally reduce loses due to charge carrier recombination. Conversely, a p-n homojunction of Cu_2O layers was fabricated and solar cell based on this was found to have efficiency of 0.1% (Longchen & Meng, 2007; Kunhee & Meng, 2009). The low efficiency of the cell was attributed to high series resistance of the oxide layers. Thus, it became imperative to identify or possibly develop methods of reducing the high series resistance for the purpose of improving the efficiency of the homojunction. However, electrical power conversion efficiencies of 2% (Mittiga, *et al.*; 2006) and 3.83% (Minami, *et al*, 2011) were reported, using Cu_2O p-n heterojunction solar cells. It is worthy of note that up to the time of this report, the highest efficiency obtained is 3.83%, using Cu_2O heterojunction. This served as a motivation for the present work. Earlier, Fernando and Wetthasinghe, (2000) 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*, (2002) reported the n-type Cu_2O produced by boiling copper sheets in $CuSO_4$ solution. This work focuses on the formation of heterojunction with n-Cu_2O layer based on a heating method using copper in $CuSO_4$ solution to produce the n-Cu_2O layer (Musa & Abdu, 2016). The heterojunction will be formed using a p-type copper (I) sulphide (p-Cu_2S) layer.

Experimental Procedure

Sample Preparation

The starting material, copper foil sheet (0.1mm thickness and 99.99% purity) was cut into 1cm x 2cm sample sizes. The samples were then polished to ensure smooth surface of the copper foil. They were finally washed to remove any possible dirts on their suface and and then dried between tissue papers.

Physical, Structural and morpholgical analysis of the deposited n-Cu_2O layer was carried out using Scanning Electron Microscope (SEM) (model phenom, Pro X). Identification of the material deposited was done using X-ray Diffractometer (XRD) (model Empyrean difractometer DY 674).

Solution Preparation

Anhydros copper (II) sulphate of purity 99.0% (BDH-GPR) of molecular weight 156.60 was used. To prepare 0.1M $CuSO_4$ solution, 0.0157g of the anhydros copper sulphate was dissolved in 1litre of de-ionized water. The partial sulphidation of the Cu_2O requires Na_2S solution. The preparation of 0.05M Na_2S was done by dissolving 0.0039g of the anhydros Na_2S, molecular weight 78.04, in 1000 litres de-ionized water.

Deposition of n-Cu_2O

The deposition of the n-type Cu_2O layer was done using chemical bath deposition method.The deposition was carried out by taking 100cm^3 of the 0.1M $CuSO_4$ solution in a beaker. The beaker containing the solution was put into a water bath and heated at 60^{o}C for 1 hour. The same process was repeated for temperatures of 65^{o}C, 70^{o}C, 75^{o}C and 80^{o}C. One copper sample was considered at a time for each setup and was heated in the solution for about one hours.

The sample was finally, removed and washed in distilled water severally and then dried between tissue papers. The procedure was repeated for solution concentrations of 0.001M, 0.006M, 0.01M and 0.04M under the same temperature conditions as above.

Annealing

The annealing process was carried out in a VECSTAR furnance for 30 minutes at 250^{o}C. The sample was then removed, quenched and finally dried in air. The annealing process was carried out in order to achieve healing of defects created during the deposition, lowering the resistivity of the layer and improving on the grain size of the crystals. It is well known that opto-electric materials perform better when their resistivity is low.

Formation of p-Cu_2S Layer

It has been established that Cu_2S is a p-type semiconducting material with a band-gap of 1.2-1.93eV (Varkey, 1990 & Fajinmi, 2000). This makes it suitable for use as a window material. It is used, in this work, with an n-type Cu_2O material to form a p-n heterojunction.

The formation of Cu_2S was carried out using 0.05M Na_2S solution. The Cu/n-Cu_2O substrate was immersed in the Na_2S solution for about 5-10 seconds and finally removed and dried in air. The samples were annealed at a temperature of 250^oC for 30 minutes.

Grids Formation

Grid patterns serve the purpose of providing contact to the cell for current collection as well as reducing the contribution of the sheet resistance to the series resistance of the cell (Musa *et al.*, 1998). Gold and silver have lower contact resistance compared to aluminum because of their higher conductivity values. Silver paste paint is used in forming grids in this work for the above reasons. The grids pattern is made manually formed, in a comb shape, on top of the p-Cu_2S layer which serves as a window for the sunlight reaching the n-Cu_2O/p-Cu_2S heterojunction.

Determination of Conductivity Type of the Cu_2O Layer

The conductivity type was determined using the hot probe method (Bar-lev, 1979) figure 1.

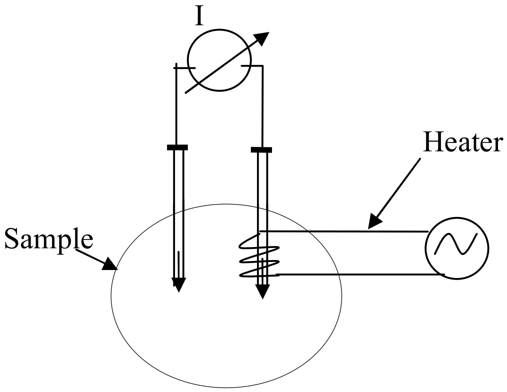

Fig.1 Hot probe method

The conductivity type measurement was carried out using the hot probe method. The surface of the sample was touched by two identical probes of soldering equipment connected to a galvanometer. One of the probes was heated while the other was left at room temperature, Fig. 4.1. The Hot probe heated the sample immediately under it; this increased the kinetic energy of the free carriers. The heated carriers then moved with higher velocity than their cooler neighbors. The carriers therefore, diffused out of the hot region faster than their slower neighbors can diffuse back into it from the vicinity. This resulted in the hot region becoming slightly depleted of majority carriers and acquiring the potential of the ionized impurities there, while the vicinity of the cold probe remained neutral. Current, therefore, flowed in the galvanometer, the direction of which relied on the sign of the charge of the ionized impurity. Thus, on an n-type semiconductor, the hot probe is the more positive one, while on a p-type it is the more negative. The cold probe polarity therefore, indicates the type. The direction of current flow was found to be consistent with that ofan n-type material. Also, Schottky effect was tested to confirm the conductivity type of the material. There was no any photo-voltage detected at the metal-semiconductor junction and no current was recorded flowing through the junction. If the material deposited were p-type, there would have been voltage and current to confirm the existence of the Schottky effect between the metal-semiconductor.

Results and Discussion

Copper samples heated at temperatures below boiling point, in solutions having concentrations of 0.001M, 0.006M, 0.01M and 0.04M Cu_2SO_4, have not shown any sign of material deposition on them at the various time intervals considered. However, the copper samples heated in 0.1M$CuSO_4$ solution, below the boiling point at 80^oC had reddish brown deposits on them but non-uniform.

Increase in the heating time above 2hrs did not show any visible change in the appearance of the deposited films. There was no layer dissolution observed throughout the exercise unlike in the reported boiling method (Fernando *et al*, 2002). However, the best sample was that obtained by chemical heating at 80^oC for 1 hour and thereby considered for analysis in this work. This sample has a very uniform layer deposited.

Sem Micrographs Analysis

The surface morphology of the deposited layer, before and after annealing, was displayed in the SEM micrographs of figure. 2(a) and 2(b), respectively. Physical examination of the SEM micrographs revealed that the n-Cu_2O layer is composed of grains of different sizes and also there exist some black spots, which are predicted to be crystal defects, which, after annealing, were healed and disappeared. Physically, the crystal grains are smaller in figure, 2(a) than when the sample was annealed in figure. 2(b), showing an improvement in the grain size.

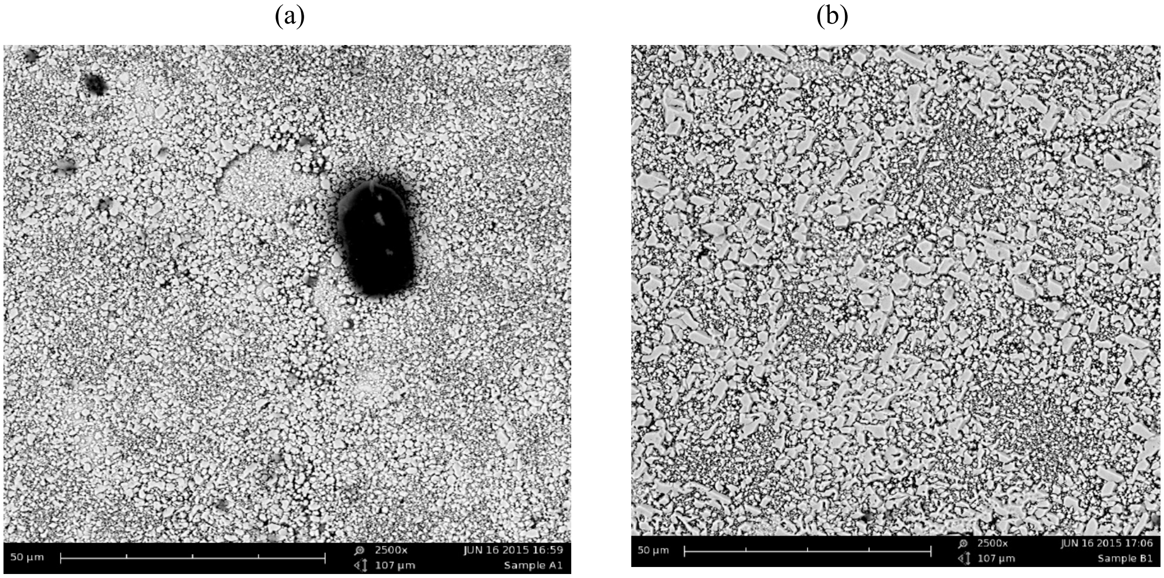

Fig.2: SEM micrographs of n-Cu_2O obtained by heating copper in 0.1M$CuSO_4$ solution at 80^oC (a) before annealing (b) after annealing, at x 2500 magnifications

X-Ray Diffraction Spectra Analysis

The structural and phase identification for the deposited n-Cu_2O were studied using XRD. The XRD spectra are shown in the figure. 3. These diffraction peaks at 2θ value of 36.4°, 29.5°, 42.3° and 61.3° corresponds to crystal plane (111), (110), (200) and (220), respectively.

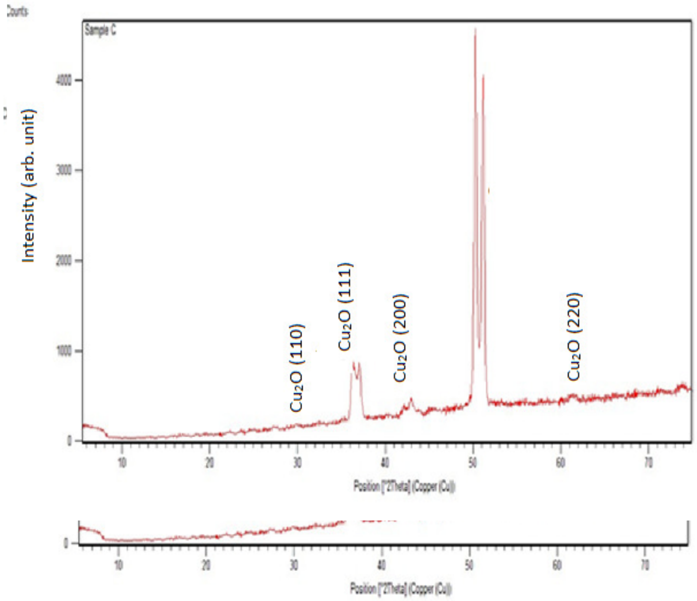

Fig 3: XRD spectra of n-Cu_2O obtained by heating copper in 0.1M$CuSO_4$ solution at 80°C.

Sulphidation of n-Cu_2O

The immersion of n-Cu_2O in Na_2S solution made its surface appears dark due to the formation of Cu_2S. The reaction predicted to have taken place is:

$$Na_2S + H_2O + Cu_2O \rightarrow Cu_2S + 2NaOH$$

Measurement of the Short Circuit Current Density (J_{sc}) and Open Circuit Voltage (V_{oc})

The highest values for the short circuit current density, J_{sc} and the open circuit voltage, V_{oc} measured, for the n-Cu_2O/p-Cu_2S heterojunction formed without grids are 77μAcm^{-2} and 45mV, respectively. However, after the grids were formed, the best junction has J_{sc} and V_{oc} values of 96 μAcm^{-2} and 52mV, respectively. This clearly shows that the grids enhanced the performance of the junction. These values are an improvement over the reported values for J_{sc} and V_{oc} of 75 μAcm^{-2} and 45mV, (Abdu, 2011) and 87.12 μAcm^{-2} and 60mV (Abdu & Ibrahim, 2014), respectively. The n-Cu_2O layers for the reported results were formed by the chemical boiling and immersion methods, respectively.

Conclusion

The formation of Cu_2O layer by simple chemical method of heating copper plates in 0.1M Cu_2SO_4 solution at 80°C for one hour was achieved. The hot probe experiment confirmed that the Cu_2O film obtained is n-type. Formation of the heterojunction was achieved by sulphiding the Cu_2O top layer thereby partially converting it into Cu_2S, which is p-type. The heterojunction formed exhibited photovoltaic effect on exposure to sunlight. It has been observed that grids formation enhanced the values of J_{sc} and V_{oc}; the highest values obtained are 96 μAcm^{-2} and 52mV, respectively. These values are an improvement over reported results for n-Cu_2O/p-Cu_2S heterojunction with n-Cu_2O deposited using different methods.

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