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ORIGINAL RESEARCH ARTICLE

Comparative Analysis of the Photovoltaic Properties of Copper (I) Oxide/Copper (I) Sulphide [N-Cu_2O/P-Cu_2S] Heterojunction Solar Cells Fabricated by Immersion and Heating Techniques

Ziya'ulhaq Sagir[1], and Abdu Yunusa[2]
[1]Department of Physics, Isa Kaita College of Education Dutsin-ma, Katsina State, Nigeria
[2]Department of Physics, Bayero University Kano, Kano, Nigeria

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ABSTRACT
Cuprous oxide (Cu_2O) is a promising semiconductor material for photovoltaic devices due to its low cost, non-toxicity, and high absorption coefficient. This study successfully deposited n-type Cu_2O layers using two electroless methods: immersion and heating. The heating method involved annealing the sample in a copper sulfate solution at 80^0 for one hour. As the second layer, the p-type copper (I) sulphide was formed on an n-Cu_2O substrate by sulfidation using 0.05M Na_2S to form the desired n-Cu_2O/p-Cu_2S heterojunction solar cell. The morphological and structural analyses of the materials were carried out using a Scanning Electron Microscope (SEM) and X-ray diffractometer (XRD), respectively. The SEM shows that the n-Cu_2O layer is composed of grains of different sizes, which were improved by annealing the sample at 300^oC. The results showed that the immersion method produced a solar cell with improved photoresponse, yielding an open-circuit voltage (Voc) of 77 mV and a short-circuit (I_{sc}) of 16 μA, compared to the heating method, which gives a response of: V_{oc} = 40 mV and I_{sc} = 8 μA.

INTRODUCTION
Solar cell technology has emerged as a vital source of renewable energy, but its widespread adoption has been hindered by high costs (Muhammad, 2012). Costly materials and production processes largely drive the expense of solar panels. This has turned researcher's attention to new and low-cost materials and simple production techniques (Zhigang *et. al.,* 2013). One promising area of research is photovoltaic technology, which has the potential to significantly reduce material requirements and energy consumption (Ohajianya *et al.,* 2013). This technology can greatly reduce the quantity of materials required for a cell and the high heat energy required for cell production (Tuama *et al.,* 2020). Solar power stands out as a promising option as the world seeks alternative energy sources, given the sun's projected lifespan of over 10 billion years and consistent energy output (Abdu and Musa, 2009).

Photovoltaic technologies are well known as a method for generating electric power using solar cells to convert energy from the sun into a flow of electrons. This process, known as the photovoltaic effect, occurs when photons from sunlight energize electrons, enabling them to carry an electric current (Miyata *et al.,* 2019). The term "photovoltaic" describes the unbiased operating mode of a photodiode in which current through the device is entirely due to the transduced light energy (Kazuya *et al.,* 2012). Essentially, all photovoltaic devices rely on some type of photodiode technology. Miyata et al. (2019) used AZO/p-Cu2O heterojunction solar cells to investigate the photovoltaic properties of Cu_2O-based heterojunction solar cells. The highest efficiency was obtained, which was 3.21%. The success was attributed to a reduction in deficiency levels at the boundary between the AZO thin film and the Cu2O piece. A lot of work on Cu_2O solar cells brand was published; regrettably, unresolved charge recombination at the crystal boundary and, indeed, the barrier properties of Cu_2O, their efficiencies seem to be very low (Salisu *et al.,* 2022)

Photovoltaic (PV) systems offer numerous benefits, including cost-effectiveness in remote areas, minimal maintenance requirements, and environmentally friendly electricity generation (International Energy Agency, 2022). Currently, several PV cell types are widely used, such as silicon pn-junction solar cells, cadmium sulphide/copper sulphide (CdS/Cu_2S), gallium arsenide (GaAs), and amorphous silicon (a-Si) solar cells (National Renewable Energy Laboratory, 2022). However, the high cost of

Correspondence: Ziya'ulhaq Sagir. Department of Physics, Isa Kaita College of Education Dutsin-ma, Katsina State, Nigeria.
✉ ziqsag1@gmail.com.
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materials and fabrication methods may hinder their future development (Abdu and Musa, 2009).

Copper oxide (metal-semiconductor) is one of the earliest photovoltaic cell development (Hafsa *et al.,* 2012). Copper (I) Oxide (Cu_2O) has been extensively synthesized using electro-deposition from solutions near room temperature (Abdu and Musa, 2011). Copper oxide exhibits dual basic semiconductor phases, namely cuprous oxide (Cu2O) and cupric oxide (CuO), with cubic and monoclinic structures, respectively (Salisu *et al.,* 2022). The Cu_2O unit cell consists of copper and oxygen ions belonging to the space group Pn_3m (Kara *et al.*, 2018). In the 1980s, advancements in efficiency and cost made PV systems a popular power source for small electronic devices (Minami *et al.,* 2016). Moreover, photovoltaic systems can convert approximately 10% of solar energy into electricity, demonstrating their potential as a viable renewable energy source (International Energy Agency, 2022).

Solar energy is the origin of our current fossil fuel resources, as a result of chemical energy conversion processes in living organisms many millions of years ago (Bushra *et al.,* 2014), (Shahadan *et al.,* 2011). Moreover, the global potential for harnessing solar energy is vast, as the amount of solar energy that reaches the Earth's surface annually is approximately 10,000 times greater than the total global energy consumption (Abdu and Musa, 2009).

This research focuses on direct sunlight conversion into electricity using photovoltaic cells. A solar cell serves two primary purposes: it generates charge carriers through light absorption and separation of the charge carriers to a conductive contact that will transmit the electricity (Winkler *et al.,* 2018). At its core, a solar cell consists of a simple junction between two types of semiconductors: n-type and p-type.

MATERIALS AND METHODS

The materials used for this research are: Anhydrous copper II Sulfate of purity 99.0% (BDH-GPR), Copper sheets (0.1mm thickness and 99.99% purity), Nitric acid, Deionize water, and tissue paper.

Samples Preparation

To produce high-quality Cu_2O materials, the surface of the copper foil was carefully cleaned and prepared. High-purity copper sheets of 0.1mm thickness and 99.99% purity were used and cuts into a 3cm x 2cm sample. The samples were then washed in 30% nitric acid for 20secs, rinsed in deionized water several times, and dried between tissue papers.

Formation of copper Sulfate Solution

Highly-purity anhydrous copper (II) Sulfate of 99.0% purity, with a molecular weight of 159.60, was used to prepare $CuSO_4$ solutions of 0.001M and 0.1M concentration. A Metler B154 analytical balance was used to weigh 0.1596g of the copper (II) sulfate and dissolved in $1000cm^3$ of de-ionized water in making 0.001M solution and 15.96g in $1000cm^3$ for 0.1M concentration.

Cu_2O Layer Formation

The n-type Cu_2O layer was formed using two electroless chemical methods: Heating and immersion. In each trial, 100 cm^3 of the solution 0.001M and 0.1M $CuSO_4$ were taken separately in beakers for uniformity of the deposition process.

Heating Method

This method took 100 cm3 of 0.1M CuSO4 concentration in a beaker with a pH 4.6. The beaker was placed into the water bath and heated to 60℃, 70℃, and 80℃, and One sample was dipped into the heated solution and continuously heated for one hour. The sample was removed, washed in de-ionized water, and dried between tissue papers.

Immersion Method

In this method, 100 cm^3 of 0.001M $CuSO_4$ solution was taken in a beaker with a pH of 6.4. the samples were then placed into the solution and left for 36 days. The process was repeated for solutions of the same pH but different lengths of times; 30, 40, and 45 days. At the end of each number of days, the samples were removed and washed severally in deionized water and finally dried between tissue papers.

Deposition of Cu_2S

The Cu_2S deposition process involved using a 0.05M Na_2S solution prepared by dissolving 4.8g of Na_2S in 1 liter of deionized water. The Cu/n-Cu_2O substrate was immersed in the Na_2S solution for 30 seconds to 1 minute, then removed and air-dried. Subsequent trials were made using different samples for different times of; 2, 3, and 4 minutes.

Characterization of the n-Cu_2O Layer

The Physical characterization of the deposited n-Cu_2O layer involved examining its structural and morphological properties. X-ray diffraction (XRD) studies were carried out using an EMPYREAN model X-ray diffractometer to determine the type of film deposited and its crystalline structure. Surface morphological studies were also carried out using "Phenom (Pro X)" Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM) Analysis

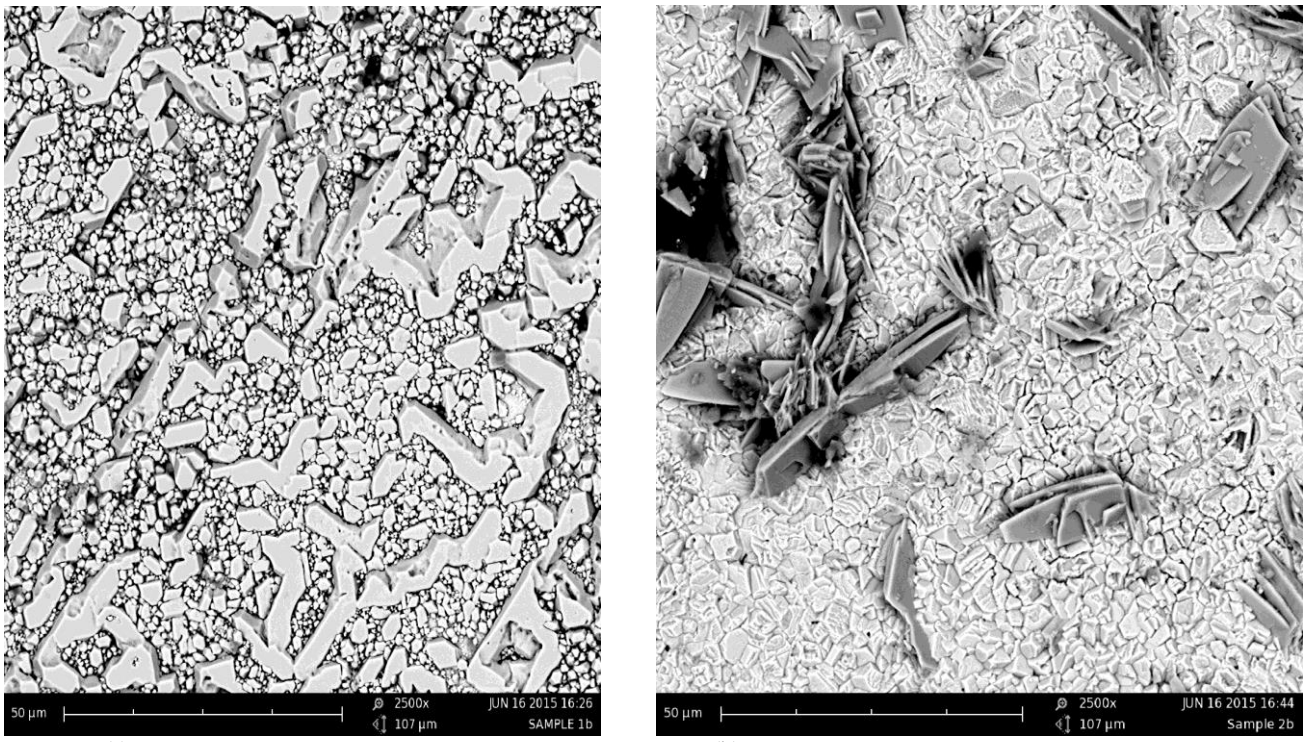
The SEM micrograph, Plate 1 and Plate 2 shows the surface morphological structure of both heating and immersion methods. The micrograph of Plate 1(a) has wide gap crystals; these wide gaps imply that annealing is

required to improve the packing of the crystals. The shape of Cu_2O is generally octahedral due to its cubic crystal structure.

The SEM of the annealed sample, Plate 1b shows that the crystals are more compact than that of the un-annealed sample Plate 1(a). The micrograph also indicates that plate 1(a) crystals' grain size is larger than Plate 1(b).

Plate 2 shows that the crystals have having more compact and smaller grain size than that of the annealed sample obtained by the heating process, Plate 1b. Also, the SEM of the un-annealed sample prepared by heating, "Plate 1a" shows that the crystals are less compact compared to the un-annealed sample of the immersion method Plate 2 by looking at the grain size of the crystals. The SEM micrograph, Plate 3, shows the surface morphological structure of the sample immersed in 0.05M of Na_2S on an n-Cu_2O substrate.

The SEM of the un-annealed sample prepared on immersed Cu_2O substrate (Plate 3c) shows crystals are more closely packed than that of un-annealed sample prepared on the heating Cu_2O substrate Plate 3a, which means that the grain size of the crystals is improving with an increase in time; also more response of both current and voltage goes to the sample with more closely packed crystals (small grain size).



(a) (b)

Plate 1: SEM image of samples prepared by Heating for solution of 0.1M $CuSO_4$ (a) un-annealed sample. (b) Annealed sample.

Plate 2: SEM micrographs of the un-annealed sample prepared by immersion with a solution of 0.001M $CuSO_4$ for a period of 36 days.

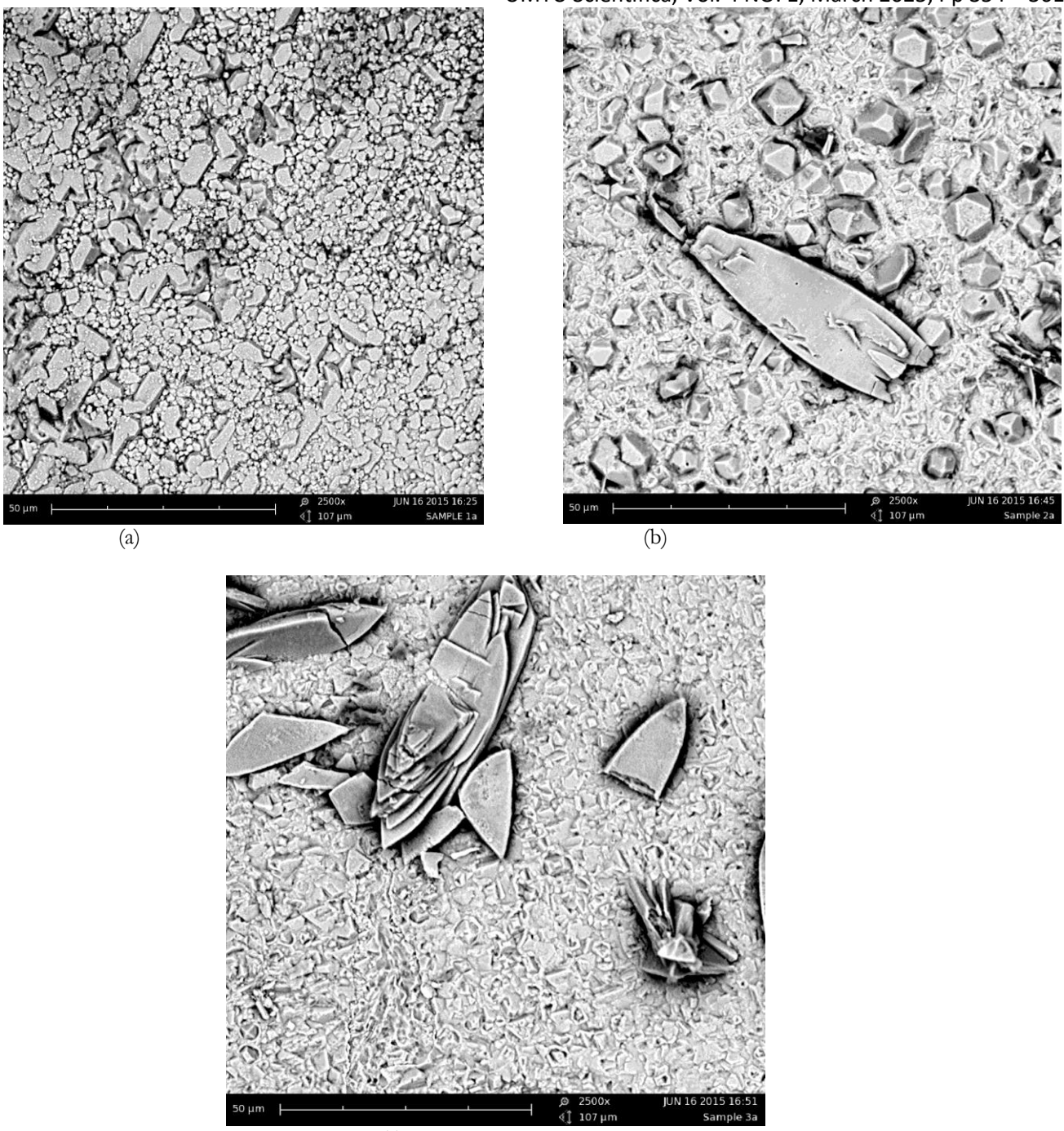


Plate 3: SEM of the sample prepared by sulphiding method on n-Cu_2O substrate; (a) Un-annealed sample, sulphide for 2:20 minutes. (b) annealed at 300°C for 60 minutes. (c) Un-annealed sample, sulphide for 3:00 minutes.

X-ray Diffraction (XRD) Analysis

The XRD analysis of the samples prepared using the immersion method revealed the existence of multiple copper oxide phases, specifically Cu_2O and CuO. This indicates that both phases were deposited simultaneously via the immersion method. In contrast, the heating method at 80°C resulted in the deposition of only Cu_2O, as shown in Figure 1. The XRD analysis of the films immersed for 36 days (Figure 1a) confirmed the presence of both Cu_2O and CuO phases. The characteristic peaks for Cu_2O were observed at: $2\theta = 35.7^o$ (111), $2\theta = 41.5^o$ (200), and $2\theta = 60.9^o$ (220). While the CuO (112) plane was detected at $2\theta = 51.1^o$.

The spectra on Figure 1 above show the presence of the Cu_2O (110) plane at $2\theta = 30.3^o$, Cu_2O (111) plane at $2\theta = 36.5^o$, Cu_2O (200) at $2\theta = 43.4^o$, and Cu_2O (220) plane at $2\theta = 62.2^o$. This shows that Cu_2O films have been successfully deposited using heating method at a temperature below boiling point of water, as indicated by the spectra.

X-ray spectra of sample E obtained for 33 days show that the cupric oxide that appeared on sample D now

disappeared, which were all obtained by the same method but at different lengths of time. This shows that variation in time has affected the existing CuO plane. The peak of the Cu_2O (111) plane is at 2θ=36.3°, while Cu_2O (220) planes appear at 2θ=61.2°.

The XRD spectra for the sample prepared by immersion at pH 12.30 and left for 27 days are shown in Figure 3. It observed the presence of CuO only at 2θ = 51.3°.

Photo Response Of Heterojunction Solar Cells

Observation revealed that when a solar cell was exposed to radiation, both current and voltage were detected using a microammeter. Notably, the current increased with the increase in illumination intensity and decreased with falling illumination intensity. This photo response shows the deposited films exhibit high sensitivity to light. The solar cell fabricated using an n-Cu_2O layer prepared by immersion process at the solution of 0.001M $CuSO_4$, pH 6.06, gives a higher response than that of the heated sample at pH of 4.2 in 0.1M $CuSO_4$ solution. The V_{oc} of 40 mV and I_{sc} of 8 μA were recorded for the solar cell formed using n-Cu_2O layer prepared by heating method at a temperature of 80°C as recorded in the daytime, and the V_{oc} of 77 mV and I_{sc} of 16 μA were recorded for the solar cell obtained with n-Cu_2O layer prepared by immersion method. By comparing these results, it can be seen that fabricated solar cell with the immersion method gives a higher response than that of a new method of heating at 80°C.

It was observed that the larger the number of days the sample was kept in the solution, the more uniform layer was achieved, but as it reached 40 days, the layer started degrading compared to the sample kept for 36 days. However, an increase in temperature from 80°C reduced the uniformity of the layer for a solution of 0.1M $CuSO_4$, as shown in the Table 1 & 2 below:

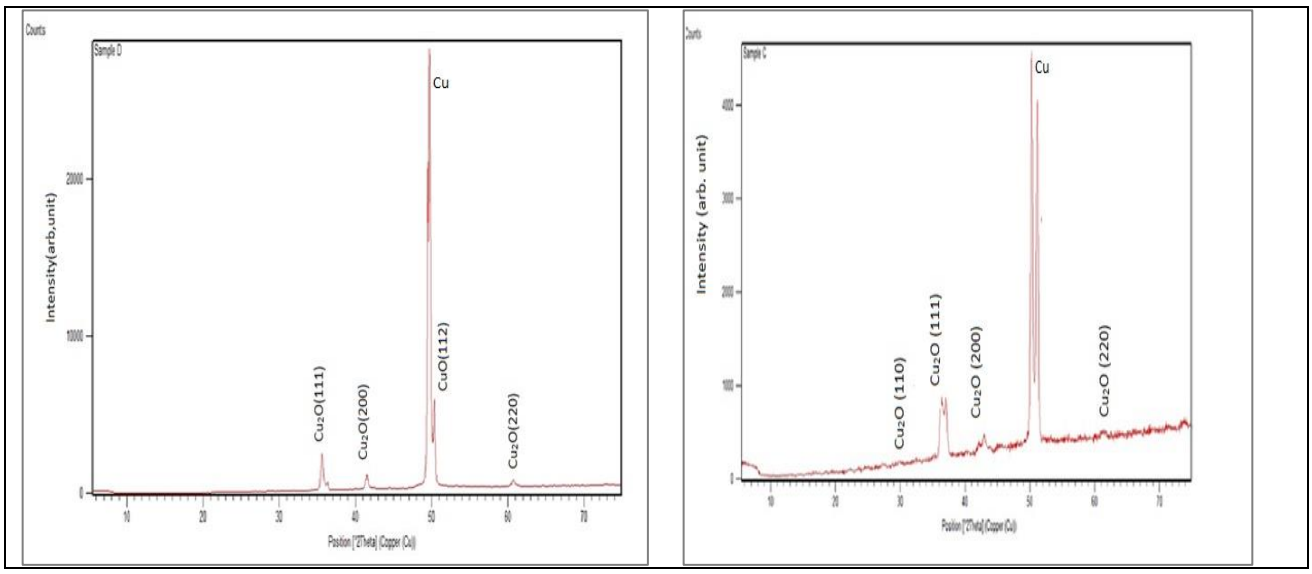


Figure 1: (a) XRD spectra of the immersed sample for 36 days (b) XRD of the sample prepared by heating at 80°C for 60 minutes.

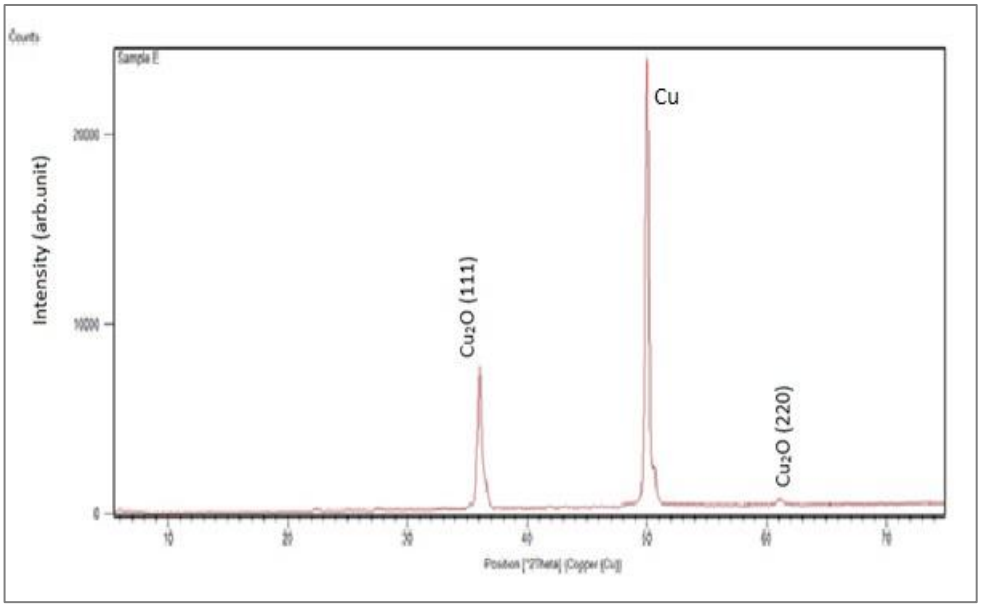


Figure 2: XRD of the immersed sample for 33 days

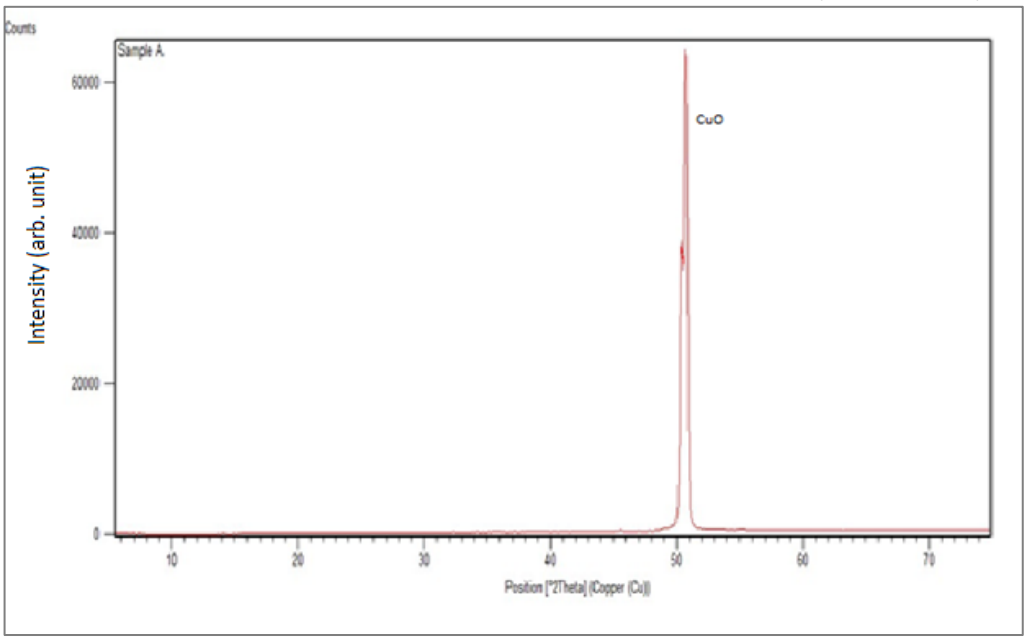


Figure 3: XRD of the sample prepared by the immersion with pH of 12.30

Table 1: Photo response of the cells prepared by immersion method

S/N	Number of Days	V_{oc} (mV)	I_{sc} (μA)
1.	28	54	10
2.	30	58	11.4
3.	33	68	13
4.	36	77	16

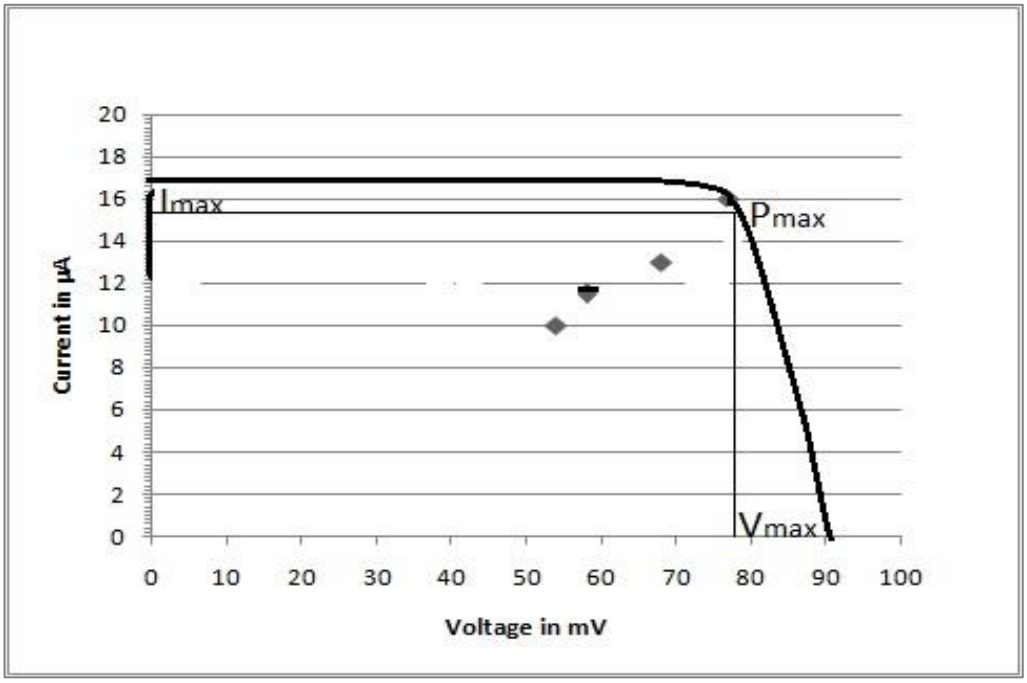


Figure 4: I-V characteristic curve of the cell prepared by Immersion Method

Table 2: Photo response of the cells prepared by heating method

S/N	Temperature (°C) Used	Voc (mV)	Isc (μA)
1.	80	40	8
2.	83	35	6
3.	85	30	5
4.	88	27	3.8

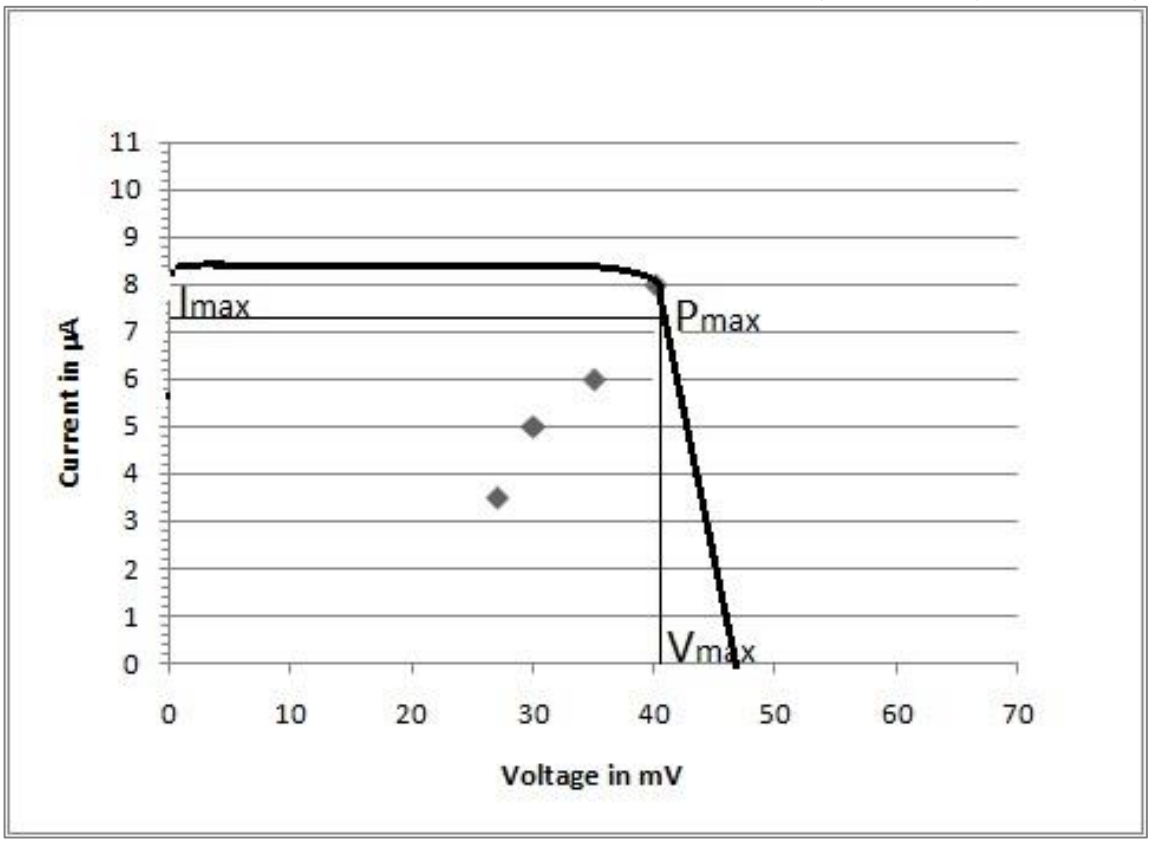


Figure 5: I-V characteristic curve of the cell prepared by heating Method

The following parameters I_{max}, V_{max} and P_{max} were obtained as: For the cell prepared by immersion method (Figure 4), the maximum current I_m = 15.7μA and maximum voltage V_m = 77.5 mV, hence the maximum power $P_m = 1.22x10^{-6}$W and the Fill Factor of 0.99 was obtained, the efficiency of the cell was found to be 0.002% and for the cell prepared by heating method (Figure 5), the maximum current I_m = 7.4μA and maximum voltage V_m = 41 mV, hence the maximum power $P_m = 0.303x10^{-6}$ W and the Fill Factor of 0.95 was obtained, the efficiency of the cell was found to be 0.0005%.

CONCLUSION

This study successfully deposited n-Cu_2O layers using a modified electroless deposition method, which involved boiling and immersion in 0.001M and 0.1M $CuSO_4$ solutions. Additionally, pure n-Cu_2O layers were obtained by heating samples in 0.1M $CuSO_4$ solution at a temperature of 80°C. While in the immersion method the layer was obtained by dipping the sample in 0.001M $CuSO_4$ at the pH of 6.4 for 36 days. The two methods are low-cost and non-toxic. The deposited layers' morphological studies and structural measurements were carried out using a Phenom (Pro X) SEM machine and an Empyrean XRD machine. Fabrication of n-Cu_2O/p-Cu_2S solar cells was also achieved successfully. The photo response of the n-Cu_2O/p-Cu_2S solar cell formed by the immersion method gives an I_{sc} of 16 μA and V_{oc} of 77 mV, which is higher than that of the heating method, which gives an I_{sc} of 8 μA and V_{oc} of 40 mV.

RECOMMENDATION

- The results of this work indicate the need for more investigation into both the heating and the immersion methods in order to have optimum conditions for uniform layer deposition and appropriate thickness of the n-Cu_2O. This is to have a layer of moderate resistivity value. The heating method shows non-uniformity in the layers deposited for most time, with a better layer obtained for the 60 minutes of heating.
- There is also the need for further investigation into the effect of change in concentration of the Na_2S on the formation of the Cu_2S to obtain a better layer. The immersion time of the n-Cu_2O substrate into the Na_2S solution needs optimization, too.

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