



ELECTROLESS DEPOSITION AND ELECTRICAL CHARACTERIZATION OF n-Cu₂O LAYER

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ABSTRACT

This work describes the preparation of n-Cu₂O layer by the electroless methods of boiling and immersion of copper plates in 0.001M CuSO₄ solution. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been used to characterize the oxide films deposited. XRD studies show, for the first time, that cuprous oxide (Cu₂O) and cupric oxide (CuO) were deposited by the two methods. The dissolution of the oxide layer for boiling above the 60 minutes time was found to be due to the turbulent nature of the boiling solution. There was no dissolution of the oxide layer in the case of the immersion method. The thickness of the films deposited for 60 minutes boiling and that obtained by the immersion method at the solution pH of 9.83 are approximately 4.8 μm and 3.8μm, respectively. The resistivities of the oxide layers were found to be 75.64 Ωcm and 61.32 Ωcm, respectively. Annealing of the sample for 60 minutes by boiling, changes the mixed oxides (Cu₂O-CuO) into the single phase Cu₂O.

Keywords: n-Cu₂O deposition, boiling and immersion methods.

INTRODUCTION

Some of the methods used in the deposition of Cu₂O layers include electrodeposition (Economou, et al.; 1982, Mahalingam et al., 2005, Wijesundara et al., 2000), thermal oxidation (Musa et al., 1998), reactive magnetron sputtering (Akimoto et al., 2006, Darma, 2011, Herion et al., 1980), schemical-bath (Fernando et al., 2002), etc. However, the Cu₂O layers deposited using these methods were mostly found to be p-type. This semiconductor has interesting characteristics such as low cost of fabrication, non toxic, material abundance and having a direct band-gap of 2.00eV for the Cu₂O layer (Siripala et al., 1996 and Mahalingam et al., 2000). The highest electrical power conversion efficiency reported of Cu₂O p-n heterojunction solar cells is 2% (Mittiga, et al.; 2006). Slow development of Cu₂O based solar cells has over the years, been attributed to poor understanding of the intrinsic point defects and difficulty in doping the material n-type as a result of which early studies relied on Schottky junctions and p-n heterojunctions for photovoltaic devices. It is generally believed that the best approach to improve Cu₂O solar cell efficiency is to find a means of producing both p-type and n-type Cu₂O and thus forming a p-n homojunction of Cu₂O. A p-n homojunction of Cu₂O layer was recently fabricated (Longchen and Meng, 2007) and also solar cells based on this p-n homojunction were also fabricated (Kunhee and Meng, 2009) but efficiency of this cell is around 0.1%. The low efficiency of the cell is attributed to high series resistance of the oxide layers. Efforts are, therefore required in finding methods of reducing the high series resistance with a view to

improve the efficiency of the homojunction and heterojunction Cu₂O solar cells. In this work a modified electroless method of deposition of n-Cu₂O layer for the fabrication of photovoltaic heterojunction solar cell was investigated.

MATERIALS AND METHODS

Copper Preparation

To prepare a good quality Cu₂O material, the copper surface is conditioned according to an existing procedure (Musa, et al; 1998). 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 2 cm x 2 cm size, and were polished afterwards. The copper sheets were then washed in 30% nitric acid for 20secs, and then later rinsed in deionized water severally and, finally, dried between tissue papers.

Solution Preparation

Anhydrous copper II sulphate of purity 99.0% (BDH-GPR) of molecular weight 159.60 was used to prepare the CuSO₄ solution of 0.001 M concentration. A Metler B154 analytical balance was used to weigh 0.1596 g of the copper II sulphate and dissolved in 1000 cm³ distilled water.

Growth of the Cu₂O Layers

The deposition of the n-type Cu₂O layer was done in two ways: by the boiling and immersion methods. In both methods 100 cm³ of the 0.001M CuSO₄ solution was taken in a beaker in every trial, for uniformity of the deposition condition.

Boiling Method

For the boiling method, 100 cm³ of CuSO₄ solution was taken in a beaker and its pH was measured to be 5.50 ± 1, using TES 1380 pH meter. The beaker containing the solution was heated to boiling using 78HW-1 magnetic heating stirrer. Later, one copper foil was dipped into the boiling solution and heating continued for 60 minutes. The sample was removed at the end of the time, washed in distilled water severally and finally dried between tissue papers. Another trial was made using the same amount of the solution but for a different time. Boiling of different samples was carried out for 50, 40, 30, 20 and 10 more minutes. Oxide films were formed on the copper foils as a result of the boiling. The sample for 60 minutes boiling was annealed at a temperature of 300°C for 30 minutes after the boiling. X-ray diffraction (XRD) studies were carried out on the samples, using the Siemens D-5000 diffractometer, to ascertain the type of films deposited. Surface morphological studies were carried out using the Hitachi S-4100 model Scanning Electron Microscope (SEM). The resistivity of the film for the 60 minutes boiling was also determined.

Immersion Method

For the immersion method, 100 cm³ of the CuSO₄ solution was taken in a beaker. Copper plates were then placed into the solution and left for 30 days, for each trial, using solution pH 5.50, 9.83, 12.01 and 12.30. At the end of 30 days, for each setup, the copper foils were removed and washed severally in deionized water and finally dried between tissue papers. XRD studies were carried out on the samples in order to find out the type of films formed. Surface morphological studies were also carried out using the SEM.

RESULTS AND DISCUSSION

Variation of the Boiling Time for the Boiling Method

The boiling method using copper foil in CuSO₄ solution produced blackish-brown films. The physical appearance of the films was found to be independent of the boiling time. Variation in the boiling time affects the uniformity and amount of the films deposited which is in agreement with an existing report (Fernando, *et al*, 2002). The best layer formed was by the 60 minutes boiling.

Effect of Variation of pH of the Boiling Solution

It was observed that changing the pH of the solution produced no deposition for all pH values except that of the solution as prepared (pH 5.50). This observation holds for all the boiling times considered. Boiling at any other time above 60 minutes caused the dissolution of the layer formed.

Effect of VARIATION OF pH OF THE IMMERSION SOLUTION FOR THE IMMERSION METHOD

The physical appearance of the films deposited ranged from blackish-brown to reddish brown and black, depending on the pH of the solution. The layers obtained for the solution of pH 9.83 appear purely reddish brown. The layers deposited for the pH 12.01 and 12.30 appear black. There was no layer dissolution after deposition for all the pH values considered. All pH values below pH 5.50 did not produce any layer deposition.

THE SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

The SEM micrograph for the boiling method, Fig. 1 shows the existence of large crystals having wide-gaps between them for the unannealed sample. These wide gaps imply that annealing of the sample is required to cement the gaps of the crystals so as to lower the resistivity of the Cu₂O layer.

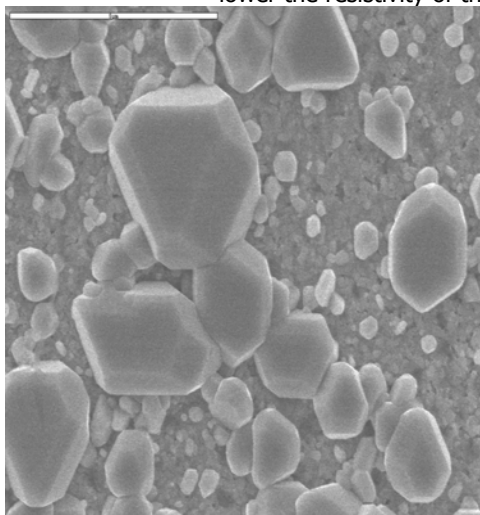
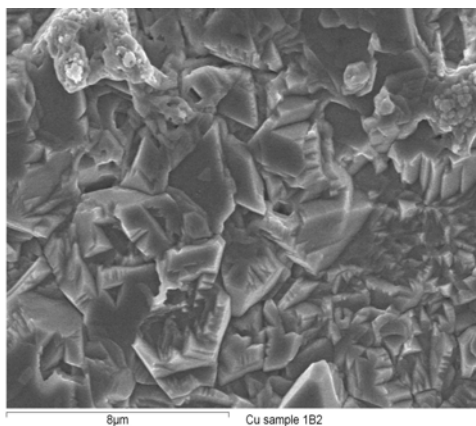
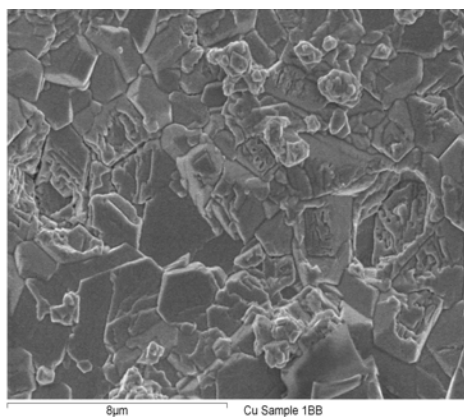


Figure 1: The SEM micrograph of the 60 minutes boiled unannealed sample.



(a)



(b)

Figure 2: SEM micrographs of the sample prepared by the immersion method for solution pH 5.50 (a) unannealed sample. (b) annealed sample

Unlike for the boiling method, the SEM micrographs obtained by the immersion method suggest that the nature of the crystals is pH dependant. The SEM micrograph of the unannealed sample obtained by the immersion method for the

solution pH 5.50, Fig. 2a, shows the crystals of the material being more closely packed together than that of the boiling method. The SEM micrograph for the annealed sample, Fig. 2b, appears even better in texture.

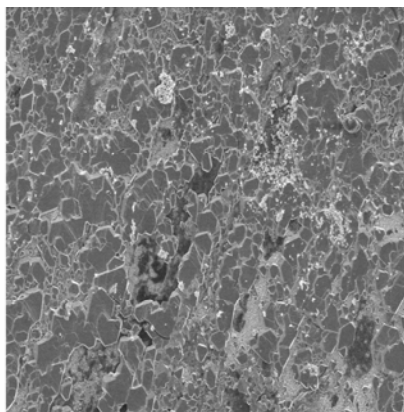


Figure 3: SEM micrograph of the unannealed Sample prepared by the immersion method for Solution pH 8.05

The SEM micrographs for the solution pH 8.05 and 9.83, Fig. 3 and Fig. 4, show that the crystals also have less compaction than that of the

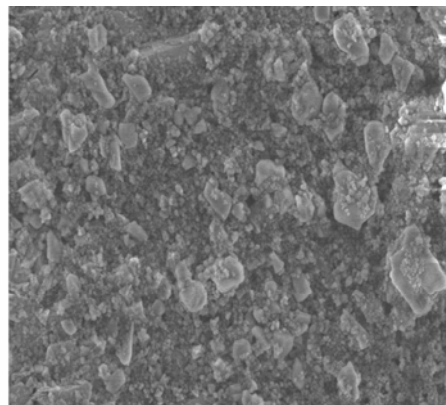


Figure 4: SEM micrograph of the unannealed sample prepared by the immersion method for solution pH 9.83

annealed sample for pH 5.50. There are voids between the crystals.

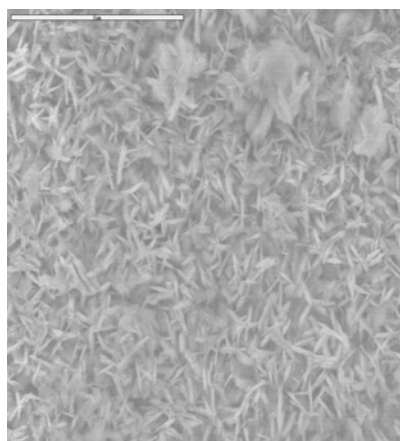


Figure 5: SEM micrograph of the unannealed sample prepared by the immersion method for solution pH 12.01.

The sample for pH 12.01 has hair-like (jelly-like) crystals as can be seen from its SEM micrograph, Fig. 5. The existence of voids between the crystals is also evident. The voids between the crystals serves as traps for charge carriers which shorten the lifetime of the carriers thereby increasing the resistivity of the materials deposited. It is to reduce the volume of these voids that annealing was carried out.

X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) studies of the samples show the existence of one or more phases of oxides of

copper. This shows that for the first time that both Cu_2O and CuO films have been formed simultaneously using the boiling and immersion methods as indicated by the XRD spectra. The diffraction peaks are in agreement with those from the Joint Centre for Powder Diffraction standard (JCPDS) in Table 1 and 2.

XRD analysis of the films for 60 minutes boiling shows the presence of a mixture of Cu_2O and CuO phases on the spectra, as can be observed in Fig. 6. The Cu_2O (211) plane is at $2\theta = 52.5^\circ$, while the CuO (112) plane is at $2\theta = 51.6^\circ$.

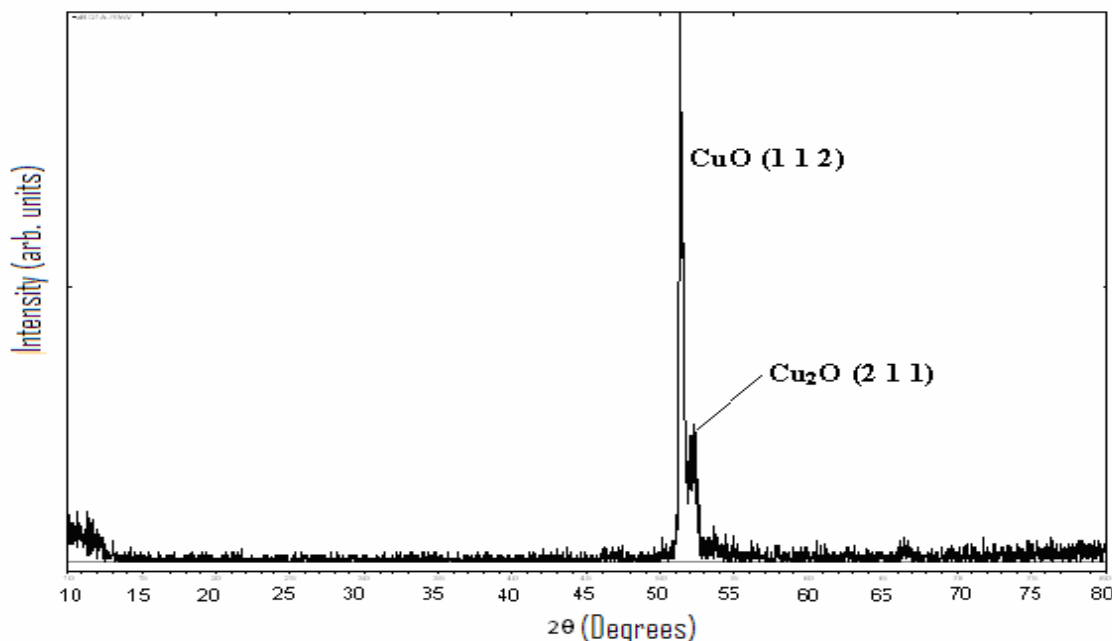


Figure 6: XRD spectra of the unannealed sample obtained by the boiling method for the 60 minutes boiling time.

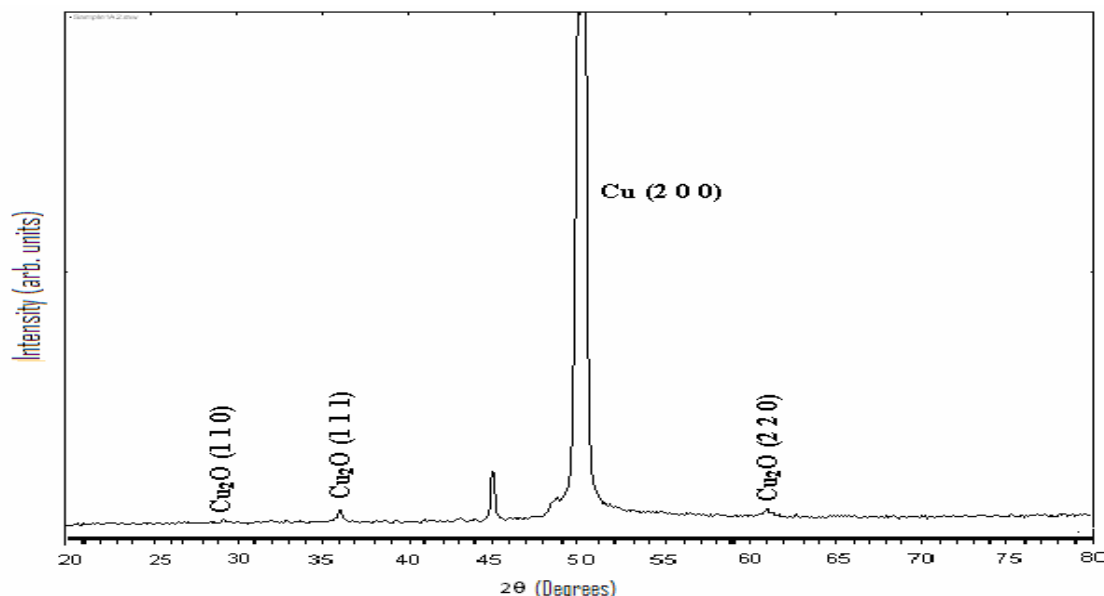
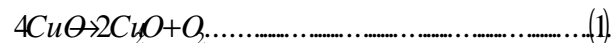


Figure 7: XRD spectra of the annealed sample obtained by the boiling method for the 60 minutes boiling time.

XRD spectra of the annealed sample are shown in Fig. 7. The cupric oxide that appeared on the unannealed sample now disappear on the annealed sample and instead, peaks of Cu₂O (110), (111) and (220) planes appear at 2θ = 29.16°, 36.02° and 61.01°, respectively and an additional Cu (200) plane peak is also shown at 2θ = 50.31°. The possible mechanism for the phase change is given in eqn. 1:



The result of the annealed sample suggests that there was a phase change of the cupric oxide to cuprous oxide as a result of the annealing at 300°C for 30 minutes. This result agrees with the report of Darma, (2011) in which phase change of the oxide films was noticed as a result of annealing at temperature range of 150-300°C. The strong peak of

Cu (200) plane is likely to be an exposure of the substrate due to the annealing process.

In the immersion method, the suspected films of the oxide material were seen to have been deposited on the copper foils. The physical appearance of the films ranged from blackish-brown to reddish brown and black, depending on the pH of the solution. XRD studies of the samples show the existence of one or more phases of oxides of copper depending on the pH of the solution.

Fig. 8 shows the XRD spectra for the sample prepared by immersing copper into the CuSO₄ solution of pH 5.50 and left for 30 days. The spectra show the presence of Cu (111) plane at 2θ = 43.43° and CuO (202) plane at 2θ = 48.62°, the sample of Fig.8 was not annealed.

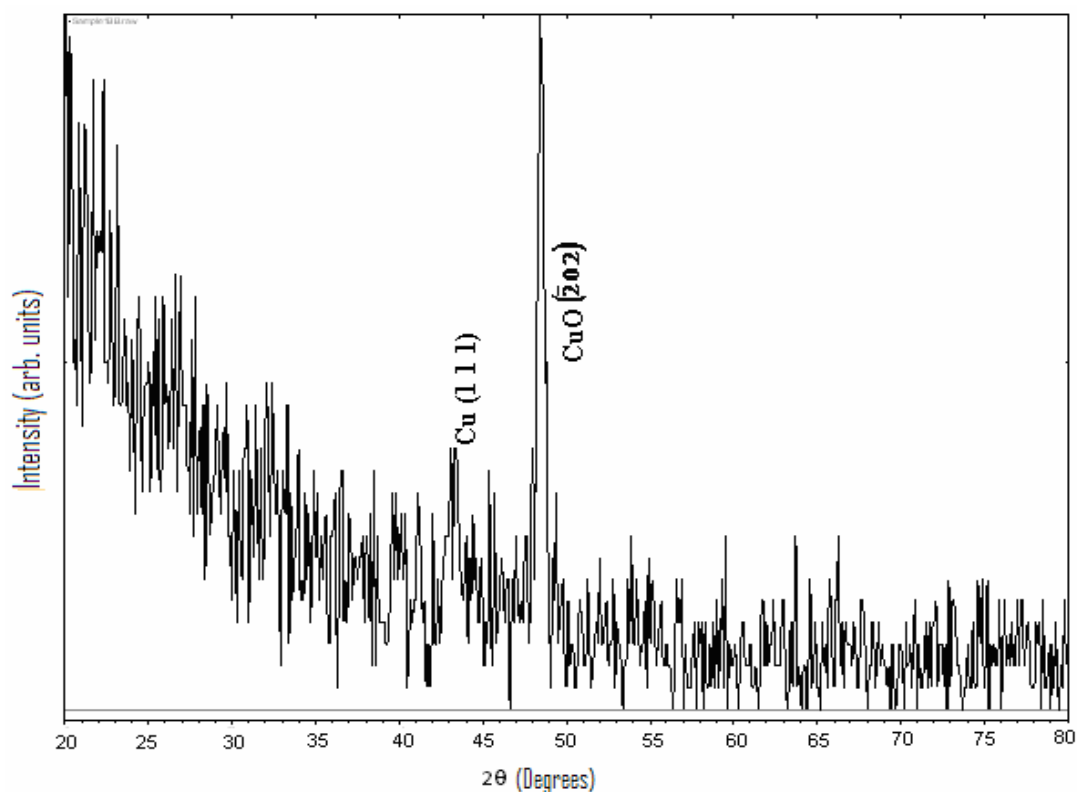


Figure 8: XRD Spectra of the unannealed sample prepared by immersion in CuSO₄ at pH 5.50 showing the presence of CuO and Cu.

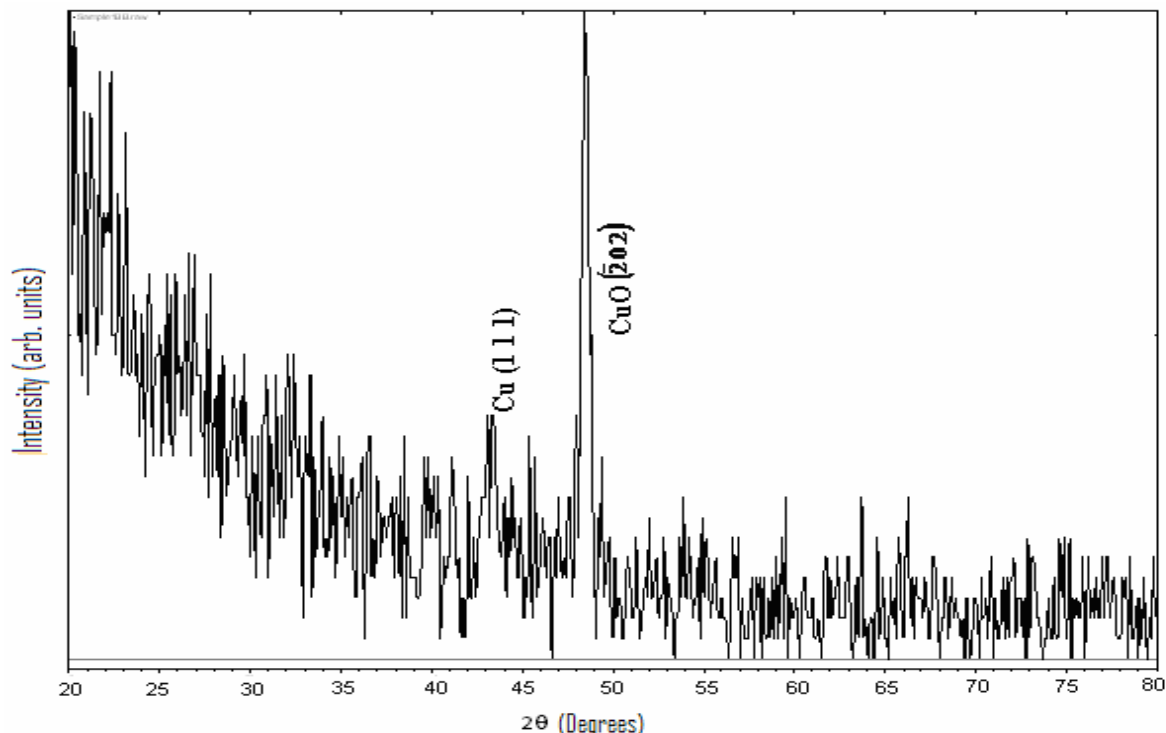


Figure 9: XRD Spectra of the annealed sample prepared by immersion in CuSO_4 at pH 5.50 showing the presence of CuO and Cu .

Unlike for the boiling method, annealing of the sample did not change the type of the oxide materials formed, as both the CuO and Cu materials appear on the annealed sample as can be observed from the XRD spectra of Fig. 9. However, annealing affects the diffraction angles slightly, Cu at $2\theta = 43.40^\circ$ and CuO at $2\theta = 48.52^\circ$, respectively. Annealing was made at 300°C for 30 minutes. The

colour of the sample was observed to be slightly blackish brown.

At higher solution pH of 8.05 with the sample prepared and unannealed, the XRD of the sample is as shown in Fig. 10. The film deposited consists of Cu_2O (111) plane at $2\theta = 36.64^\circ$, Cu (111) plane at $2\theta = 43.24^\circ$, CuO ($\bar{2}02$) plane at $2\theta = 48.36^\circ$ and Cu (220) plane at $2\theta = 74.37^\circ$.

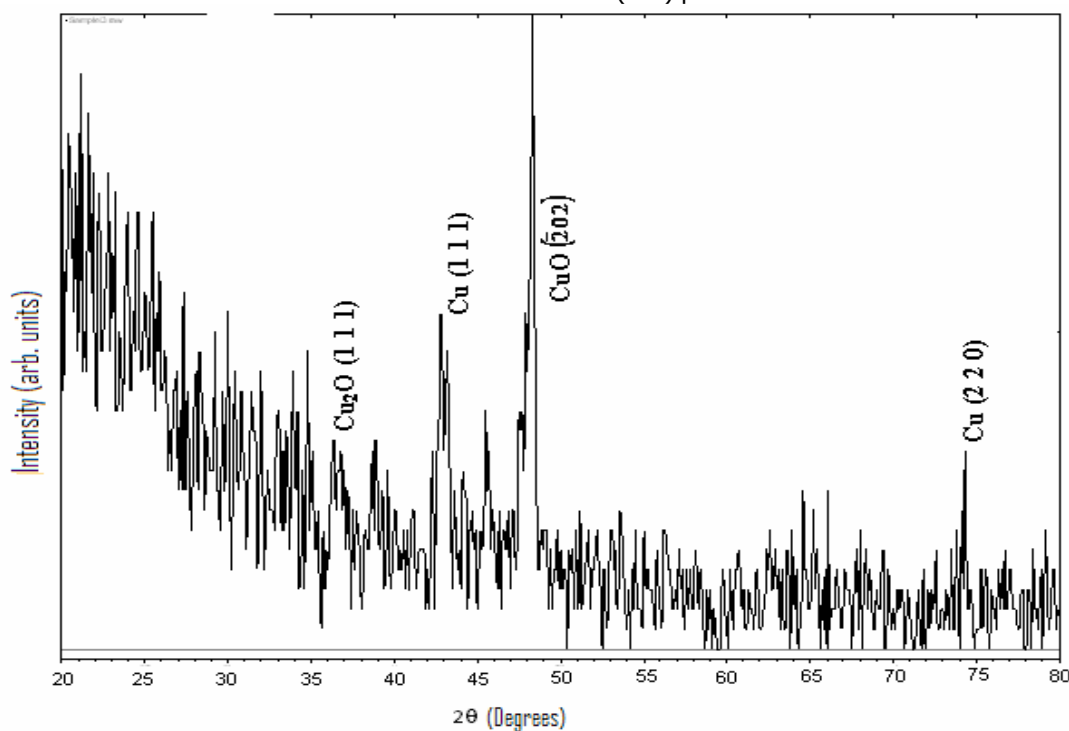


Figure 10: XRD spectra of the annealed sample prepared by the immersion method at pH 8.05.

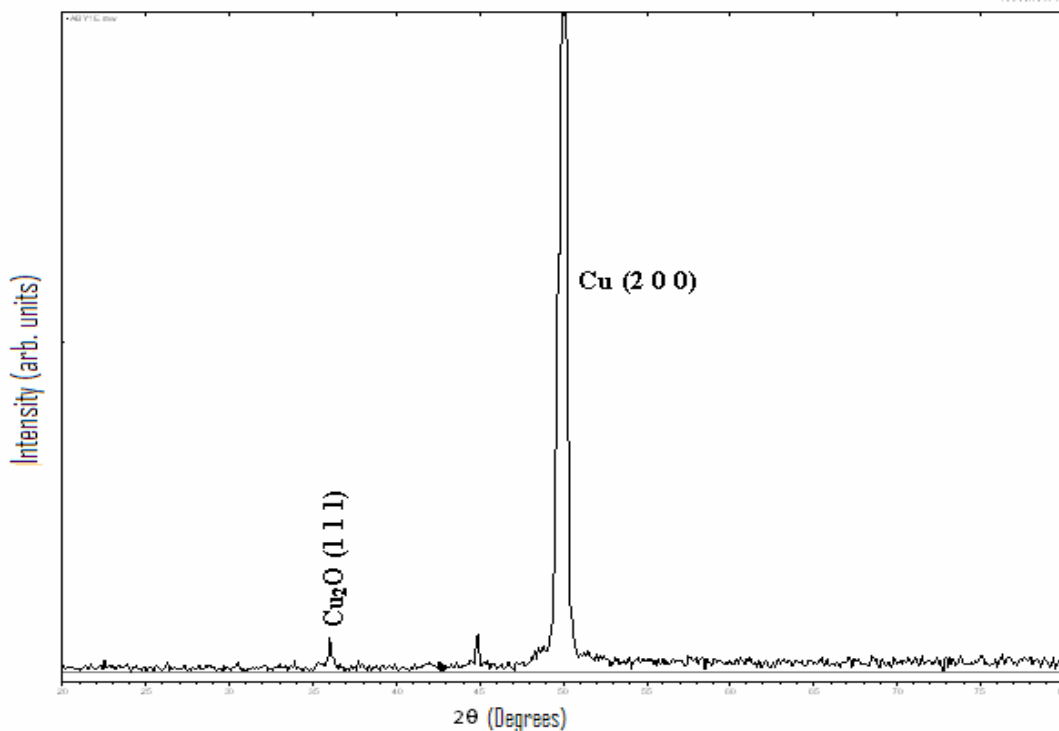


Figure 11: XRD spectra of the unannealed sample Prepared by the immersion method at pH 9.83.

As the pH of the solution was further increased to 9.83, the film deposited consists of Cu_2O (111) plane at $2\theta = 36.13^\circ$ and Cu (200) plane at $2\theta = 50.51^\circ$, as shown in Fig. 11, the sample was not annealed.

For unannealed sample left for 30 days in the solution of pH 12.01, the film consists of Cu_2O (211) plane at $2\theta = 52.50^\circ$ and CuO (112) plane at $2\theta = 51.60^\circ$ was deposited, as shown in Figure 12.

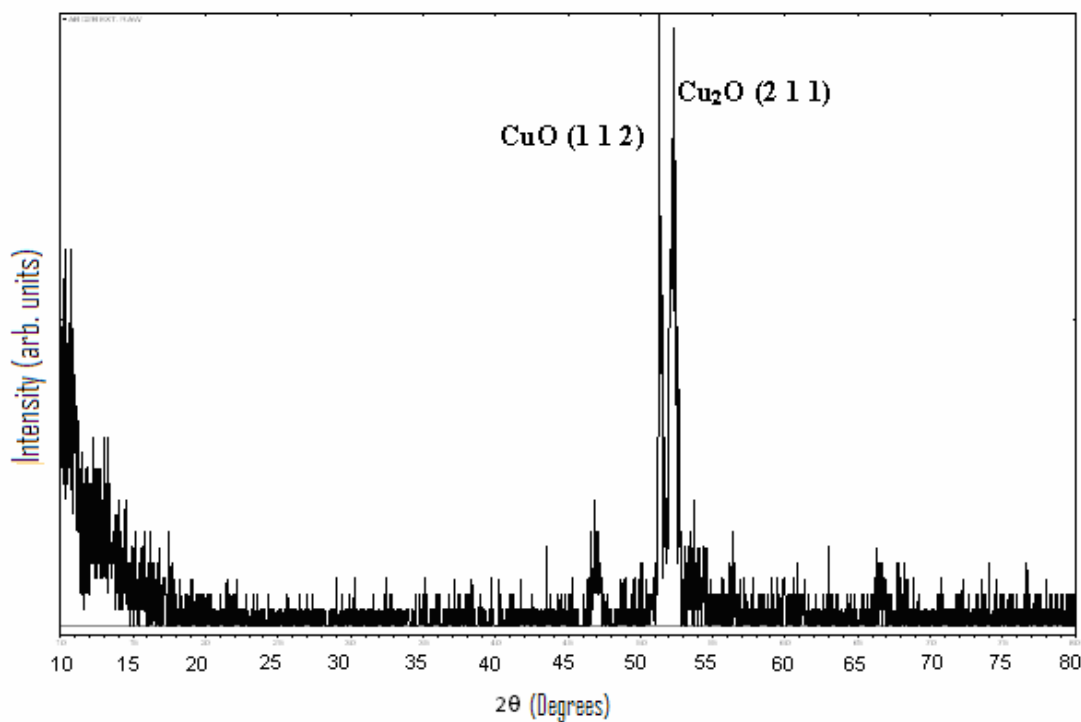


Figure 12: XRD spectra of the unannealed sample prepared by the immersion method at pH 12.01

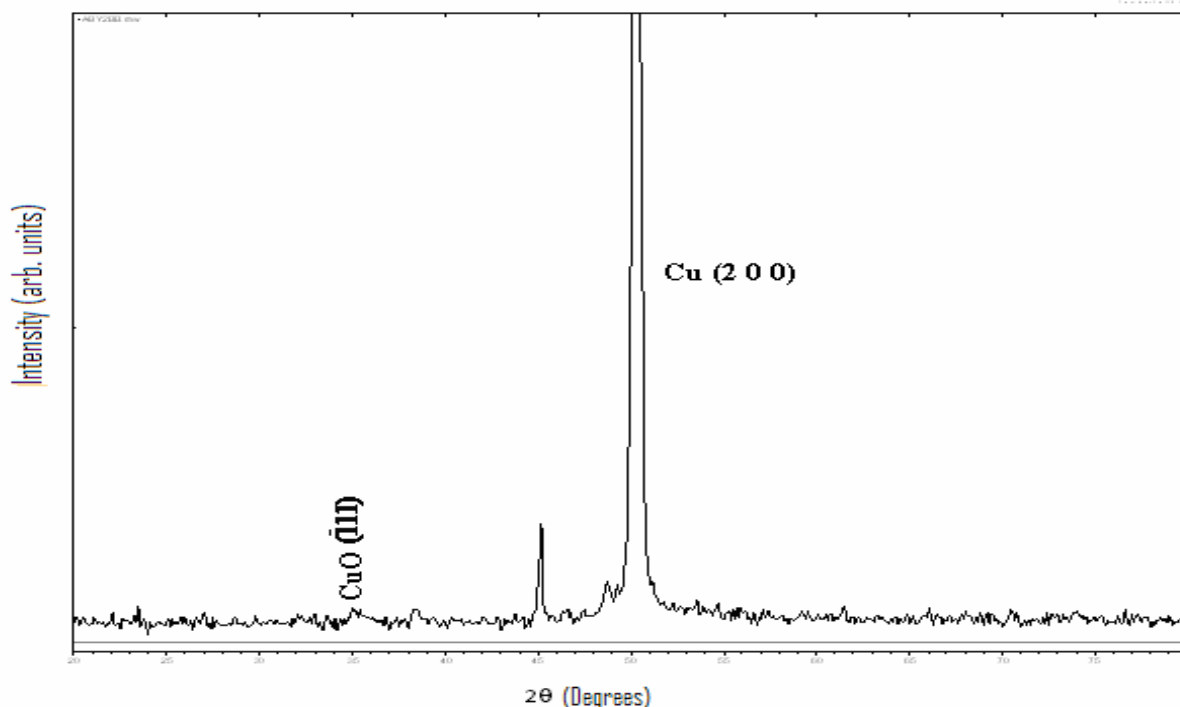


Figure 13: XRD spectra of the unannealed sample prepared by the immersion method at pH 12.30

As the solution pH was slightly adjusted to 12.30, the film deposited changed composition to CuO (111) plane at $2\theta = 35^\circ$ and Cu (200) plane at

$2\theta = 50.51^\circ$, Fig. 13. The colour of the samples in both cases is black.

The general observation for the boiling and immersion methods is that the Cu seen on the XRD spectra might be the substrate which is copper.

Table 1: Observed X-ray diffraction values for copper oxides deposited by boiling method, compared with Diffraction standard ICSD No. 063281 of Cu₂O and Diffraction standard ICSD No. 069758 of CuO

Film Deposited	Observed values		Corresponding JCPDS Values	
	2θ	h k l	2θ	h k l
Cu ₂ O	52.50°	2 1 1	52.53°	2 1 1
CuO	51.60°	1 1 2	51.44°	1 1 2
Cu ₂ O	29.16°	1 1 0	29.61°	1 1 0
Cu ₂ O	36.02°	1 1 1	36.47°	1 1 1
Cu ₂ O	61.01°	2 2 0	61.46°	2 2 0

Table 2: Observed X-ray diffraction values for copper oxides deposited by Immersion method, compared with Diffraction standard ICSD No. 063281 of Cu₂O and Diffraction standard ICSD No. 069758 of CuO

Film Deposited	Observed values		Corresponding JCPDS Values	
	2θ	h k l	2θ	h k l
Cu ₂ O	36.64°	1 1 1	36.47°	1 1 1
Cu ₂ O	36.13°	1 1 1	36.47°	1 1 1
Cu ₂ O	52.50°	2 1 1	52.53°	2 1 1
CuO	48.62°	$\bar{2}02$	48.70°	$\bar{2}02$
CuO	48.36°	$\bar{2}02$	48.70°	$\bar{2}02$
CuO	51.60°	1 1 2	51.44°	1 1 2
CuO	35.00°	$\bar{1}11$	35.53°	$\bar{1}11$

The difference in 2θ might be as a result of contamination of pure crystals due to impurities and crystal defects.

Growth Rate of the Oxide Layer

The general growth rate observed under the boiling method follows the trend shown in Fig. 14. The curve shows that deposition is continuous from 10 minute

up to 60 minutes and above this time the layer deposited was observed to have dissolved completely in solution.

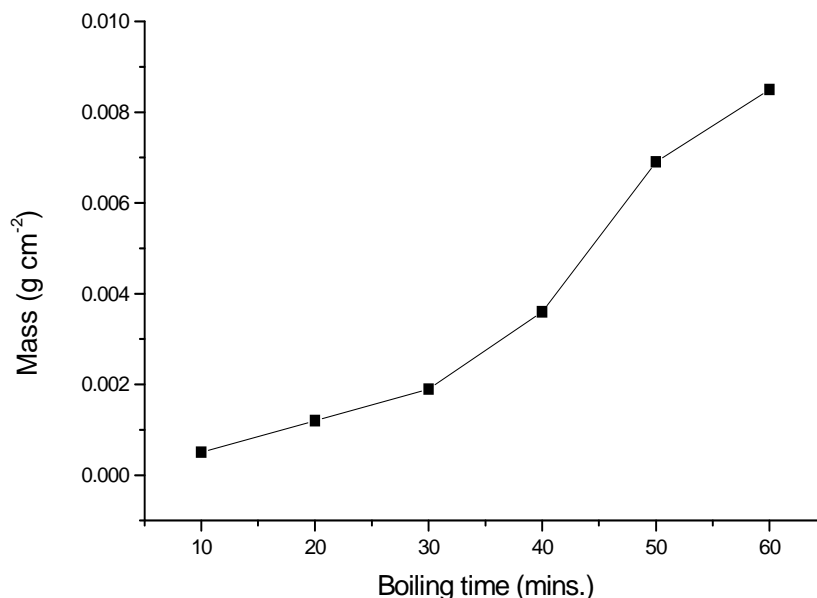


Figure 14: Growth rate of Cu₂O layer.

The growth rate for the immersion method was found to be dependent on the solution pH.

Resistivity Measurement

Resistivity of the oxide layers was calculated using eqn. 2 after the determination of the thickness of the oxide layers.

$$\rho = 4.53 \frac{V}{I} t \dots\dots\dots (2)$$

where *V* is the voltage, *I* is the current and *t* is the thickness of the material.

The values of the voltage and current were measured using the four-point probe method. The thickness of the sample was calculated by first, determining the mass of the oxide deposited. The density of the Cu₂O, 6.0 gcm⁻² was used. The thickness of the sample obtained by the 60 minutes boiling was found to be about 4.80 μm and its resistivity value was calculated to be 75.64 Ωcm.

In the same manner as above, for the sample prepared using the immersion method at solution pH 9.83, a thickness of about 3.80 μm and resistivity of 61.32 Ωcm were calculated for the sample.

Determination of the Conductivity Type

The conductivity type was determined using the hot-probe method (Bar-lev, 1979). The direction of current flow was found to be consistent with that of an n-type material. However, this observation was made for both the 60 minutes boiled and annealed

sample and the unannealed sample for immersion method of solution pH of 9.83.

Conclusion

In this research, n-type Cu₂O layers were successfully deposited using the modified Fernando electroless deposition method involving boiling and immersion in chemical solution of 0.001M CuSO₄. It is reported for the first time, that cuprous and cupric oxides were deposited by both methods. There was layer dissolution in the boiling method above the 60 minutes boiling time. For the immersion method, the oxide layers deposited was found to be pH dependent. There was no dissolution of the oxide layers deposited for all the pH values considered in the immersion method. Therefore, the oxide layer dissolution was concluded to be due to the turbulent nature of the boiling solution, contrary to previous reports attributing the dissolution to the increase in solution pH. The layer deposited for the solution pH of 9.83 is the only layer that appears reddish brown. Layers deposited for other solution pH appear either blackish-brown or black, depending on the pH of the solution. The results indicated that, there has been gradual formation of the Cu₂O layer from the CuO at pH5.50 to Cu₂O at pH 9.83 and then as pH increases, the process is reversed from Cu₂O back to CuO. Annealing changes the cupric phase to cuprous phase for the sample obtained by the 60 minutes boiling.

The thickness and resistivity of both samples obtained at 60 minutes boiling and that obtained by the immersion method for the solution pH 9.83 were found to be 4.8 μm and 75.64 Ωcm and 3.8 μm and 61.32 Ωcm , respectively. This shows that the films

deposited by the immersion method for the solution pH 9.83 have lower resistivity than those obtained by the 60 minutes boiling and would, therefore, be a preferred material growth method for fabrication of Cu_2O based solar cells.

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