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Synthesis with Structural and Morphological Study of n-Cu_2O Layer Produced by Immersion, Boiling and Chemical Bath Heating Techniques of Electroless Deposition Method

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Abstract: ***Cuprous oxide (Cu_2O) thin films with n-type conductivity are prepared on copper plate using $CuSO_4$ solution by the immersion, boiling and the chemical bath heating techniques of Electroless Chemical Deposition Method of Depositing n-Cu_2O. The films produced were analyzed using SEM and XRD machines. The results shows that the film produced by chemical bath method is purely Cu_2O layer with peaks at different diffraction angles ranging from 2 $\theta = 10° - 50°$ without any CuO impurity and is composed of grains of different sizes which were improved by annealing the samples at 250 ^{0}C. On the other hand the film produced by boiling method has larger grains size with CuO impurity at 2 $\theta = 52.5°$. while the film produced by immersion techniques has Grain sizes larger than that of chemical bath techniques and smaller than that of boiling technique with CuO impurity at $2\theta = 48.62^o$. The implication of varying the deposition time in the boiling and chemical bath heating technique with the variation in the pH level of the immersion technique were analyzed. The result shows that there was dissolution of the oxide layer for boiling at boiling time above one hour in the boiling method while there was no dissolution of the oxide in the case of the immersion and chemical bath heating method. However, it was discovered that the growth rate is dependent on the solution pH .Its was also found that at pH 12.30 there was formation of CuO on the sample deposited by immersion technique and show no reaction on that of boiling and chemical bath heating technique. These ensure the true deposition of purely Cu_2O layer without any CuO impurities in chemical bath heating techniques only.***

Keywords: Thin film, Electroless deposition, pH, n-Cu_2O, SEM, XRD, Boiling, chemical bath and Immersion method

1. Introduction

Copper(I)oxide (Cu_2O) was one of the earliest known (since 1904) semiconductor and photovoltaic material which serves as an attractive starting material for low cost terrestrial conversion of solar energy to electricity and the first in which photovoltaic effect was successfully explained[1-5]. It potential in photovoltaic are due to its non-toxicity, availability and relatively low cost of the starting material (copper), simple processing techniques, fairly high minority carrier diffusion lengths, high absorption coefficient in the visible region and large exiting binding energy with a direct band gap of about 2.1eV, transmittance of 20% which reaches 90% for high wavelength in the visible region with 2 to 2.5 refractive index values and an optimum theoretical conversion efficiency of 12-20%[6-14] which makes it an attractive material alternative to silicon, germanium and other semiconductors for use in catalysis applications, lithium-copper oxide electrochemical cells, photoelectrochemical solar cells, photocatalytic degradation of organic pollutants under visible light, photoelectrochemical decomposition of water into O_2 and H_2 under visible light irradiation low cost photovoltaic power generators, gas sensors and as an active material for fabricating of cheaper solar cells for terrestrial applications[14-17].

Several deposition techniques have been used by various researchers to fabricate cuprous oxide thin film such as Electroless deposition techniques [3,6-8], electrochemical deposition [18-22], Thermal oxidation [23-24], sputtering [25 and 27], solution based methods [27-29] and many other deposition techniques like atomic layer deposition, SILAR technique, thermal evaporation, coatings, anodic oxidation, chemical vapour deposition, chemical bath deposition etc. [13-15 and 30-33] but requires either sophisticated equipment, complex method, costly or temperature above 100 ^{0}C and contain cupric oxide impurities.

Electroless deposition method possesses several characteristics which are not shared by other methods, these 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 [34]. 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 electroless 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 [35, 36]. Various approaches have been used in depositing n-Cu_2O layer ,some of which include the boiling technique [6] ,the immersion technique[7], the heating or chemical bath techniques [8], and the electro chemical deposition technique[37].

This paper presents an analytical study of n-Cu_2O thin films deposited by Immersion, boiling and chemical bath heating techniques of the Electroless Chemical Deposition Method at low temperature below 100^0C with it structural and morphological studies and effect of some deposition conditions.

2. Synthesis Techniques

The n- Cu_2O layers were deposited using three different techniques; first with the immersion followed by boiling and then with the chemical bath heating Methods of the Electroless Chemical Deposition techniques. Both techniques were carried out under the same condition of material used, metal salt and same specification for preparing the solution. The main difference in the three techniques under investigation is that, there was variation in the PH level, heating temperatures and deposition time. The immersion techniques was achieved at room temperature while the boiling technique was achieved through boiling at 100°C and in chemical bath it involves heating at various temperatures ranging from 60°C to 80°C.

Copper preparation

To prepare good quality Cu_2O material on Cu, the copper surface condition is very important especially for thin oxide. Copper surface was conditioned according to an existing procedure by [23]. In this method the copper foil was streghtenned and folish this eliminate any grease or dirty from the surface of the copper foil. High purity sheet (0.1mm thickness and 99.99% purity) were cut sample of 1cm x 2cm size and were polished afterwards. The copper sheets were then diffed into the solution of sodium per sulphate ($Na_2S_2O_8$) and washed for three minutes then latter rinsed in distilled water for 20 seconds several times and finally dried between tissue papers and finally in air.

Solution preparation

Anhydros copper (II) sulphate of purity 99.0% (BDH-GPR) of molecular weight 156.60 was used to make $CuSO_4$ solution of different concentration using distilled water according to [6, 7, and 8] .

The Immersion Techniques

This technique is in accordance to [7]. During this process 100cm^3 $CuSO_4$ solutions of pH 5.5 was taken in a beaker and a well-conditioned copper foil was then dipped into the solution and left for 30 days. The process was repeated for different pH of 8.05, 9.83, and 12.30 for the same length of time. At the end of each number of days, the copper foils were removed and washed severally in deionized water and finally dried between tissue papers. The surface morphological studies using Scanning Electron Microscope (SEM) and X- ray diffraction (XRD) were carried out on the sample to ascertain the type of films deposited.

The Boiling Techniques

The n-type cuprous oxide produced is in accordance to [6]. 100cm^3 $CuSO_4$ solutions was taken in a beaker and its pH was measured to be 5.5 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 deionized water severally and finally dried between tissue papers. Subsequent trials were made by taking fresh amount of the solution with varied boiling time of 50,40,30,20 and 10 minutes. Surface morphological studies and X- ray diffraction (XRD) studies were carried out on the sample to ascertain the type of films deposited.

The chemical bath heating techniques

This technique is in accordance to [8]. 100cm^3 of the 0.1M $CuSO_4$ solution prepared from anhydrous copper II sulphate of purity 99.0% (BDR-GPR), of molecular weight 159.60 was taken in a beaker and its PH was measured to be 4.62 using PHS-25 pH meter which. the beaker containing the solution was taken to water bath and heated to (60, 65, 70, 75 and 80) ^{0}C respectively, One copper foil was dipped in to the heated solution and heated for about (one and two)hour in each case. The sample was removed after that hour, washed in deionized water severally and finally dried between tissue papers and finally in air.

ANALYSIS

The SEM and XRD results of the n-Cu_2O obtained by both techniques were analyzed and presented in three parts: the result of the immersion method, boiling method and then that of the chemical bath heating method.

Immersion Technique

In the immersion techniques, the physical appearance ranged from blackish –brown to reddish brown and black, depending on the pH level of the solution which dictates the effect of varying the pH level upon depositing. Based on the pH level adopted, it was observed that the formation of n-Cu_2O started its phase from pH 5.5 through pH 8.05 and finally formed at pH 9.83 which appeared purely reddish brown. The deposition observed at pH 12.30 appeared black which confirms the presence of CuO while the pH level below pH 5.5 did not produce any layer deposition.

Boiling Technique

In the boiling techniques, the physical appearance of the films appeared blackish- brown and it was also found to be independent of the boiling time. Only the variation in the boiling time affects the uniformity and amount of the films deposited . Based on the range of boiling time adopted by [6] the films deposited from 40-60 minutes were said to be more uniform and the best deposition was achieved at 60 minutes boiling with pH 5.5. The variation of the pH level show no deposition for all the boiling time adopted and for the boiling time above 60 minutes it was observed that, there is weakening and later dissolution or washing away of the layer deposited.

Chemical bath heating Technique

The copper foil heated in 0.1M concentration of $CuSO_4$ with pH range between 4.20 to 4.80 produces reddish brown (liver red) colour films on the two surfaces of the copper foil. It was found to be independent of the heating time, but affects the uniformity and the amount of the film deposited. It was observed that the films deposited on heating from one to two hours has higher uniformity and is the best deposition then the one deposited below that. And there is no layer dissolution on staying above two hours. Also the physical appearance of the deposited layer does not change with change in temperature, but the morphology (uniformity) of the layer increases with increase in temperature within the range (60^0C to 85^0C). It was observed that the thin films layer deposited at range 60^0C -75^0C is not uniform throughout the surface but has some uniformity in some part of the surface of the foil. The best layer was the one deposited at 80^0C to 85^0C which is uniform throughout the surface of the foil.

3. Discussion

Scanning Electron Microscope (SEM)

The SEM micrographs obtained by the immersion techniques show that the nature and the grain size of the crystals is pH dependent as shown in Figure 1. The SEM for the boiling techniques shows the existence of large crystals having wide gap between them as shown in Figure 2. These wide gaps imply that annealing of the sample is required to improve on the packing of the crystals so as to lower the resistivity of the Cu_2O layer. It was observed from the SEM result of chemical bath heating techniques that the layer is composed of a grains with different sizes and also there are some crystal defects shown by black spots in the deposited n-Cu_2O layer and the grain sizes of the crystals are very small which was healed and disappears on annealing at 250 ^{0}C and there is also an improvement in the grain size of the crystal Figure 3

X-ray Diffraction Analysis (XRD)

The structural and phase identification for the deposited n-Cu_2O without annealing were studied with XRD model empyrean diffractor meter DY 674 (2010). Using Scherrered equation.

$$D= \frac{K\lambda}{\beta cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, D is the grain size, K is a dimensionless shape factor with a value (0.9) which varies with the actual shape of the crystallite, λ is the wavelength of the X-ray used (1.5402A). β is the full width of the half maximum of the most intense peak, θ is the Bragg angle corresponding to maximum X-ray diffraction peak. The angle of diffraction (2 θ) is varied from 05-75^o as shown in the Figures. The XRD spectra for the sample prepared by immersion techniques at pH 5.5 for 30 days (Figure 4) shows the presence of Cu_2O along (111) plane at $2\theta = 35.50^o$, (200) plane at $2\theta = 41.3^o$ and (220) plane at $2\theta = 61.0^o$ and CuO (112) plane at $2\theta = 50.5^o$ As the pH further increases to 12.30 the deposition changed composition to CuO (111) plane at $2\theta = 50.51^o$ (Figure 5) and the colour is black. In the X-ray diffraction analysis (XRD) the films for 60 minutes boiling (figure 6) shows the presence of a mixture of Cu_2O and CuO phases on the spectra, as can be observed in Figure 3. The Cu_2O plane is at $2\theta = 52.5^o$, while the CuO (112) plane is at $2\theta = 51.6^o$. The XRD pattern for chemical bath heating techniques (Figure 7) shows the presence of purely cuprous oxide with its prominent reflections along (111) plane at $2\theta = 36.4^o$ and other reflections along (110) plane at $2\theta = 29.5^o$, (200) plane at $2\theta = 42.3^o$ and (220) plane at $2\theta = 61.3^o$. Also there exist some reflections from a metallic copper whose plane was not indicated at $2\theta = 50^o$. The presence of these planes ensures the true deposition of Cu_2O layer.

4. Conclusion

This paper presents the deposition of n-Cu_2O layer using Electroless deposition method of Immersion, boiling and chemical bath heating techniques. All the techniques employed the same material used, metal salt and same specification for solution preparation. The formation of a uniform n-Cu_2O thin film with high morphology and n-type conductivity was achieved. The method is cheap, simple, requires no sophisticated set up and is operated at lower temperature. It can also be used to coat large surface area. Another advantage of these techniques is that it can coat both side of a material including inner and outer surfaces for hollow materials. In the analysis it was observed that, there was layer weakening and dissolution in the boiling techniques due to overheating and increased in acidity of the solution as a result of evaporations which does not occurs in immersion and chemical heating techniques. The result also shows that there is formation of cupric oxide CuO impurity in immersion and boiling method and purely cuprous oxide with no impurity in chemical bath heating techniques. It was also observed that there is formation of purely CuO thin film at PH 12.30 in immersion techniques which does not occurred in boiling and chemical bath heating techniques. Based on the analysis it can be concluded that chemical bath heating method is more reliable in deposition of cuprous oxide thin film than the immersion and boiling method because there is no CuO impurity, weakening of the layer and also no layer deposition on staying longer than one hour in chemical bath technique. It was suggested that more analysis can be made on this layer like resistivity measurement, U.V analysis, and optical (reflectance, transmittance and absorptance) study.

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Figure 1(b): Annealed Cuprous Oxide layer produced by Immersion techniques at pH 5.5

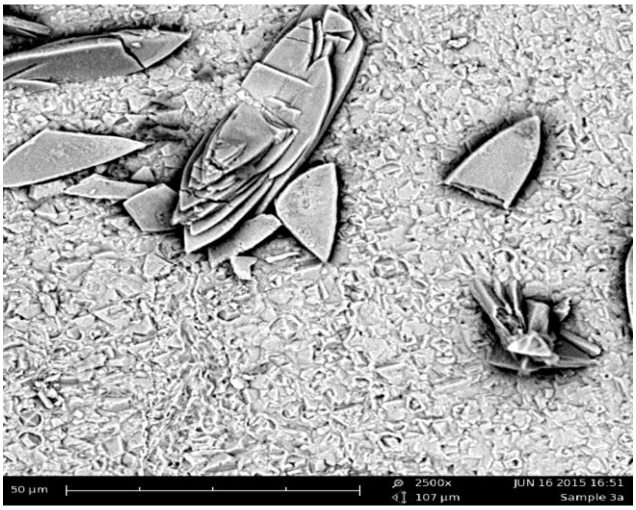

Figure 1(a): Unannealed Cuprous Oxide layer produced by Immersion techniques at pH 5.5

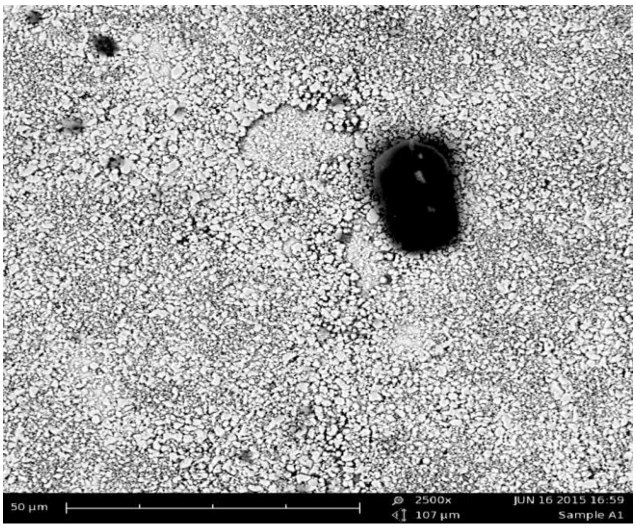

Figure 3(a): Unannealed Cuprous Oxide layer produced by chemical bath heating techniques at pH 4.6

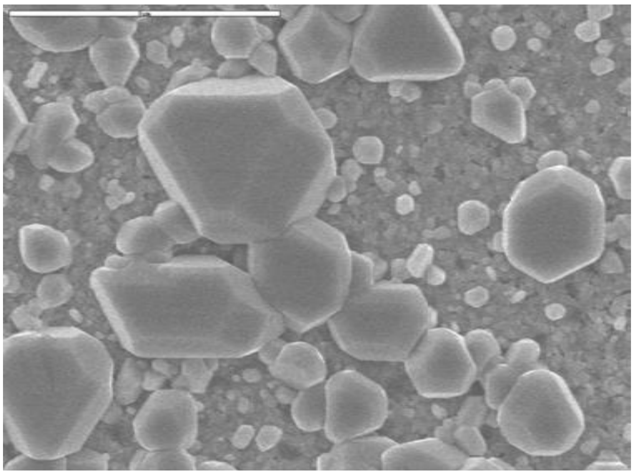

Figure 2: The SEM micrograph of the 60 minutes boiled unannealed sample prepared by boiling techniques with pH 5.5

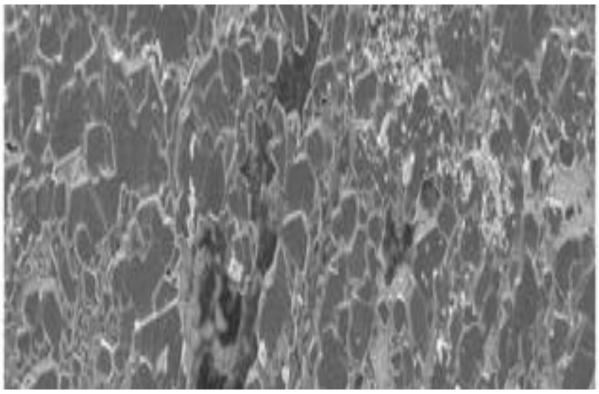

Figure 1(C): Unannealed Cuprous Oxide layer produced by Immersion techniques at pH 8.05

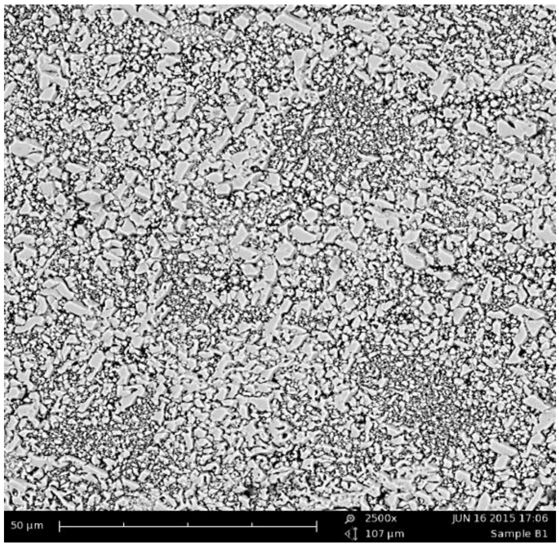

Figure 3(b): Annealed Cuprous Oxide layer produced by chemical bath heating techniques at pH 4.6

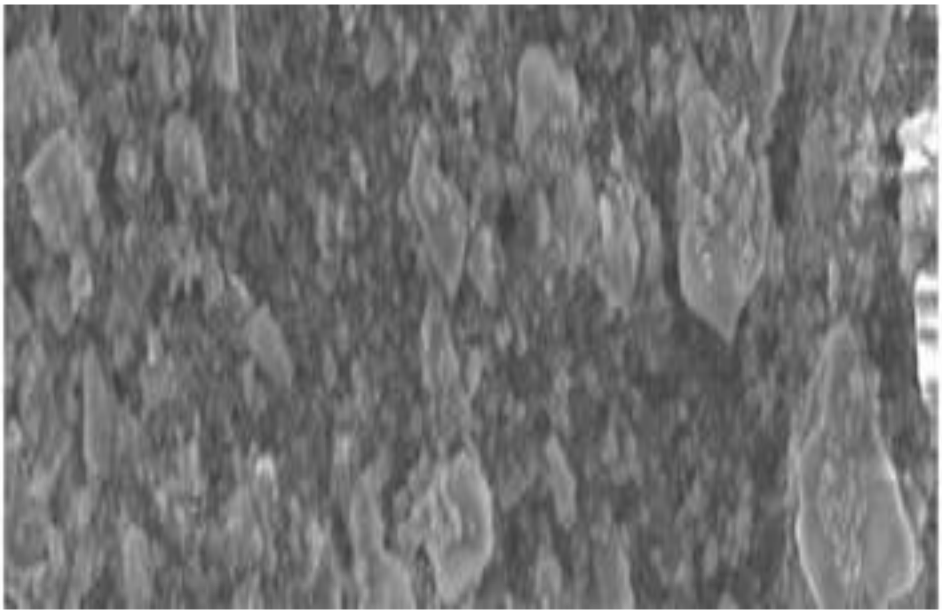

Figure 1(d): Unannealed Cuprous Oxide layer produced by Immersion techniques at pH 9.8

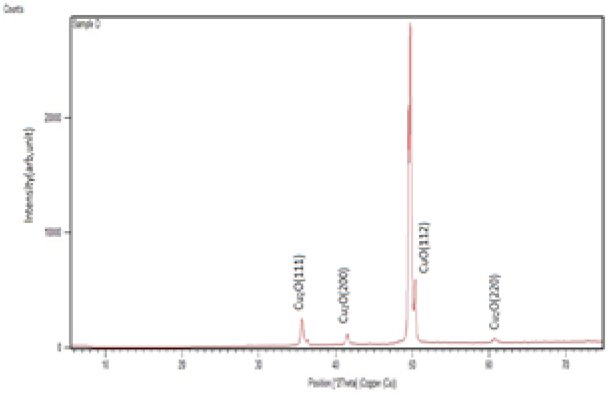

Figure 4. XRD spectra for unannealed Cuprous Oxide layer produced by Immersion techniques at pH 5.5

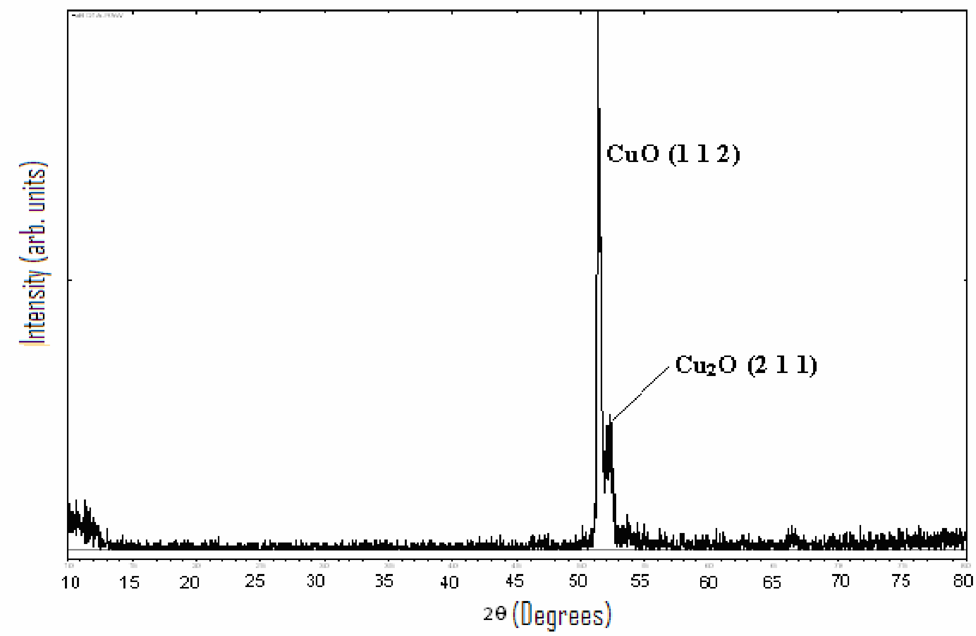

Figure 6: XRD spectra for unannealed Cuprous Oxide layer produced by boiling techniques at pH 5.5

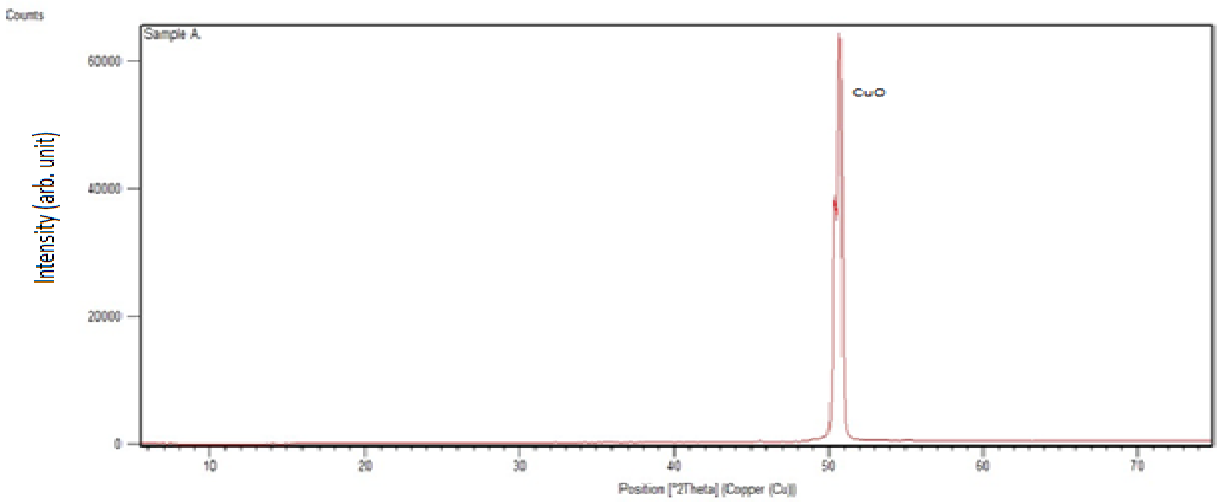

Figure 5: XRD spectra for unannealed Cuprous Oxide layer produced by Immersion techniques at pH 12.30

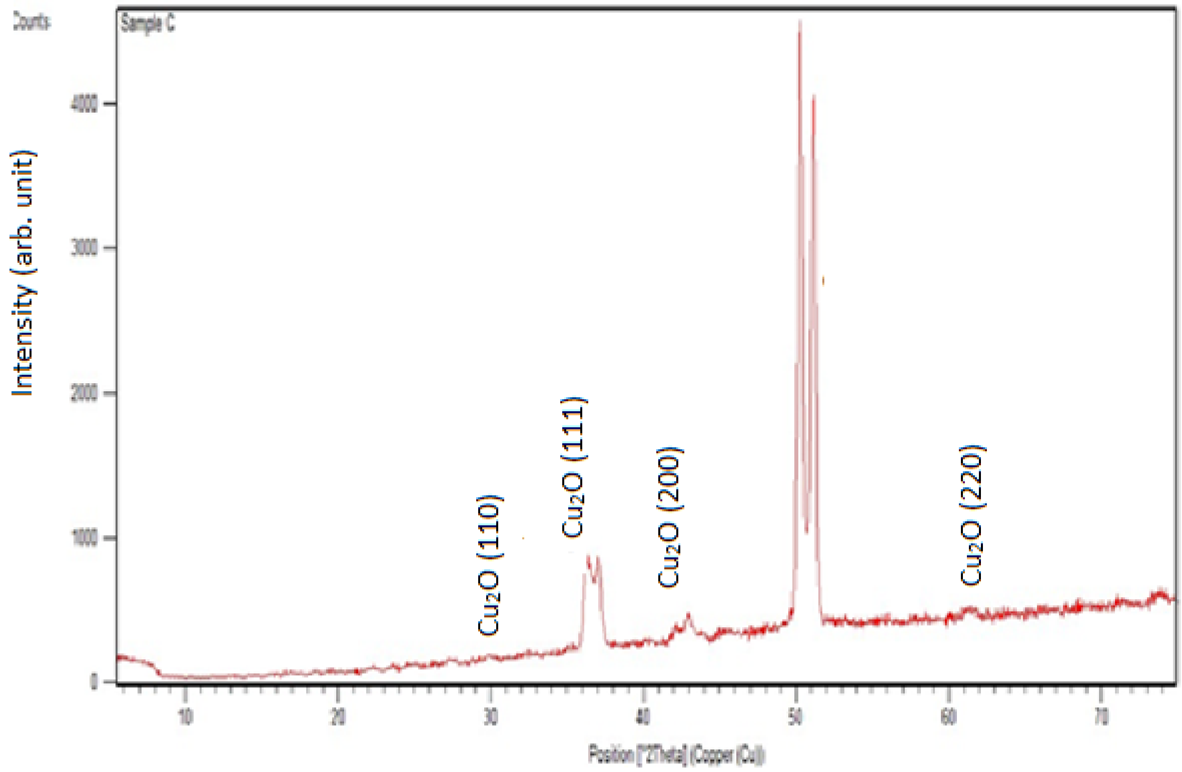

Figure 7: XRD spectra for unannealed Cuprous Oxide layer produced by chemical bath heating techniques at pH 4.6

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