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Analytical Study of n-Cu_2O layer produced by Boiling and Chemical Bath Heating Techniques

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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 boiling and chemical bath heating techniques for one hour followed by annealing at 250℃ for two hours. The films produce were analyzed using SEM and XRD machines. The results shows 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 impurity, However it is observed that the films producedis composed of grains of different sizes which were improved by annealing the samples at 250℃. On the other hand the films produced by boiling method has larger grains size with CuO impurity at $2\theta = 52.5°$. it was also observed that there is weakening and washing away of the deposited layer on extending the deposition time longer than 60minutes in boiling method.

1.0 Introduction

Due to the depletion of fossil fuels, renewable energy sources such as solar and wind energies are of wide interest. Most solar cells are based on polycrystalline silicon and have a relatively high cost price determined by the costs of the starting material and the expensive manufacturing process. In the last few years, the development of solar cells based n-Cu_2O[1-5] has progressed rapidly which are a good alternative for the silicon-based solar cells due to its low cost, abundance of the starting material (Cu) on earth, nontoxicity, cheap and simple processing technique, fairly high minority carrier diffusion lengths, high absorption coefficient in the visible region, and large exciting binding energy with a direct energy gap of 2.1eV and optimum theoretical efficiency of over 20% [6-14].

Several chemical methodsare available for the deposition of Cu_2O layers, amongst which are chemical vapour method, thermal oxidation method, Sputtering, electroless chemical deposition, dip-coating techniques, electrochemical deposition and many other techniques.of all the various techniques the Electroless chemical deposition also called autocatalytic method is an attractive method that involvesthe presence of a chemical reducing agent in solution to reduce metallic ions to the metal state. The approaches involve in the Electroless Chemical Deposition of n-Cu_2O includes the Boiling technique, the immersion technique, the heating techniques or chemical bath technique[15].The name electroless is somewhat misleading, however, there are no external electrodes present, but there is electric current (charge transfer) involved. Instead of an anode, the metal is supplied by the metal salt and a substrate serves as the cathode, while the electrons are provided by a reducing agent. The process takes place only on catalytic surfaces rather than throughout the solution (if the process is not properly controlled, the reduction can take place throughout the solution, possibly on particles of dust or of catalytic metals, with undesirable results) [16].

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 [17]. 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.

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Instead, the substrate is immersed in the electroless bath immediately after sensitizing and rinsing [18, 19]. Various approaches have been used in depositing n-Cu_2O layer ,some of which include the boiling technique [1] ,the immersion technique[2], the heating or chemical bath techniques [3], and the electro chemical deposition technique[4,5,20]. This paper presents an analytical study of n-Cu_2O thin films deposited by boiling and chemical bath heating techniques of the Electroless Chemical Deposition Method.

2.0 Synthesis Techniques

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

The Boiling Techniques

The n-type cuprous oxide produced by boiling techniques is in accordance to [21].In this process the elimination of any grease or dirt from the surface of the copper foil was achieved by conditioning the copper surface according to an existing procedure [22]. In which $CuSO_4$ solution of 0.001M concentration was prepared from anhydrous copper II sulphate of purity 99.0% (BDR-GPR), of molecular weight 159.60 where 100cm^2 $CuSO_4$ 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.

The Chemical Bath Heating Techniques

In this method 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)℃ 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.The surface morpholgical analysis of the deposited n-Cu_2O thin films werecarried out using Scanning Electron Microscope (SEM) model phenom (Pro X) at Umaru Musa yar'aduwa University Katsina State in Biology research Lab . And the phase and crystalline structure of the deposited films was analysed using X-ray Diffractometer (XRD) model Empyrean difractometer DY 674 (2010) at National Geosciences Research Lab NGRL Kaduna.

3.0 Analysis

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

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 [12]. 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℃ to 85℃). It was observed that the thin films layer deposited at range 60℃-75℃ 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℃ to 85℃ which is uniform throughout the surface of the foil.

4.0 Discussion

Scanning Electron Microscope (SEM)

The scanning Electron Microscope (SEM) for the boiling techniques shows the existence of large crystals having wide gap between them as shown in Figure 1. 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 [12]. 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℃ and there is also an improvement in the grain size of the crystal as shown in Figure2

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). UsingScherrered equation.

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

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 (2θ) is varied from 05-75^o as shown in the Figure 4.In the X-ray diffraction analysis (XRD) 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 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 shows prominent reflections along (111) plane at $2\theta = 36.4^o$ and other reflections along (110) plane at 2θ=29.5^o, (200) plane at 2θ=42.3^o and (220) plane at 2θ=61.3^o, Also there exist some reflections from a metallic copper whose plane was not indicated at 2θ=50^o. The presence of these planes ensures the true deposition of Cu_2O layer.

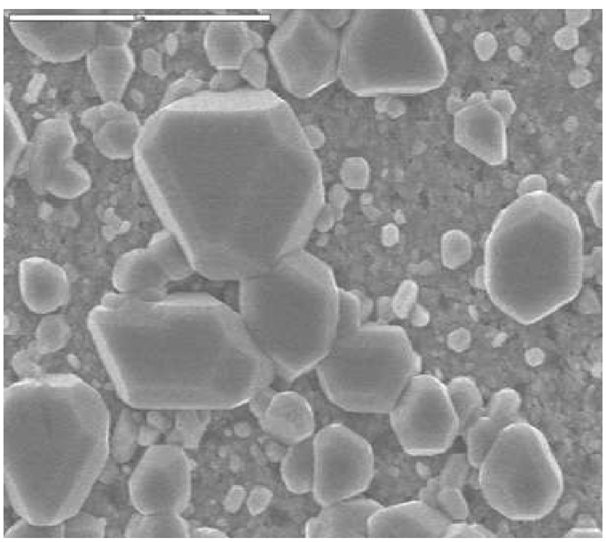

Figure 1: The SEM micrograph of the sample prepared by boiling method with pH 4.6

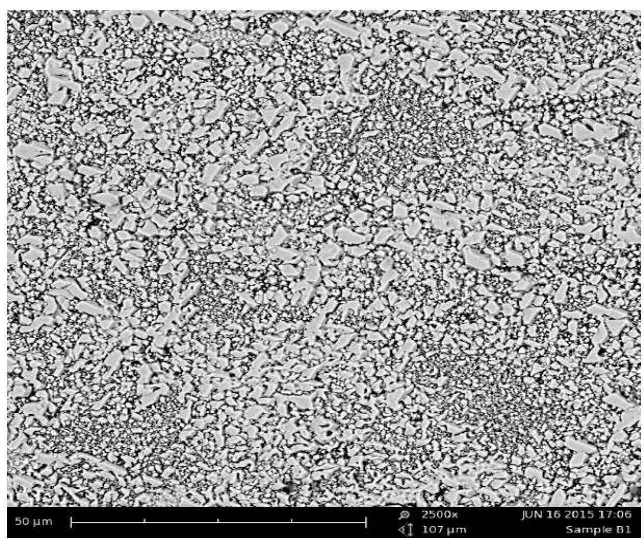

Figure 2: The SEM micrograph of the sample prepared by chemical bath method with PH 5.5

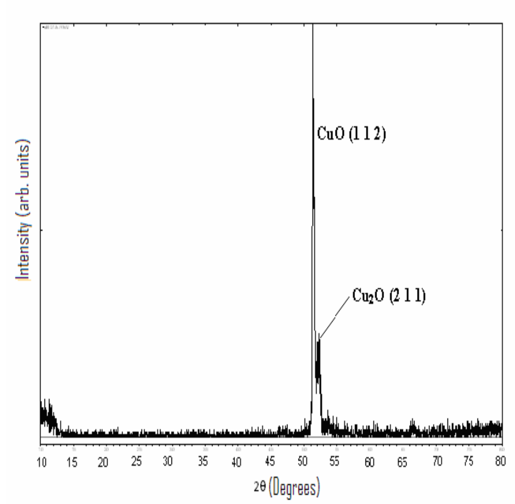

Figure 3: XRD spectra of the unannealed sample obtained by the boiling method

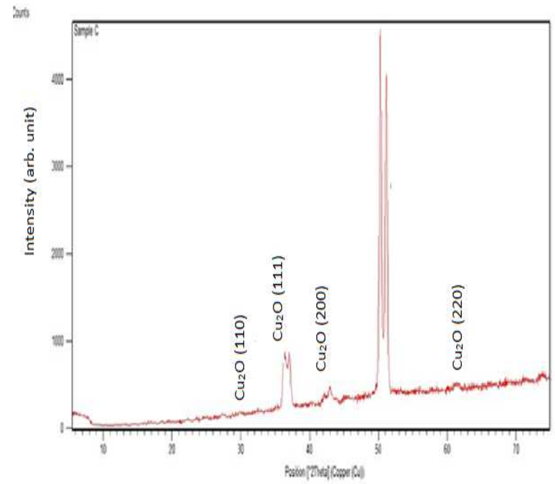

Figure 4: XRD spectra of the annealed sample obtained by chemical bath method

5.0 Conclusion

This paper presents the deposition ofn-Cu_2O layer by boiling techniques andchemical bath heating techniques. All the techniques employed the same material used, metal salt and same specification for solution preparation. The formation of n-Cu_2O layer was achieved and a uniform Cu_2O thin film with high morphology and n-type conductivity was obtained. 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 chemical heating techniques. The result also shows that there is formation of cupric oxide CuO impurity in boiling method and purely cuprous oxide with no impurity in chemical bath heating techniques. Based on the analysisit can be concluded that chemical bath heating method is more reliable than the 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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