Fabrication of Homojunction Cuprous Oxide Solar Cell by Electrodeposition Method

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Abstract: Thin films of p-Cu2O and n-Cu2O were controllably prepared using electrochemical deposition method by using different conditions for each type with different thickness. Photocurrent measurement show that the Cu2O thin films synthesized in acid and alkaline media present n-Cu2O and p-Cu2O semiconductor character, respectively. The morphology and orientation have been investigated. Thin film of p-Cu2O show pyramid shape with orientation (111) and n-Cu2O show dendritic shape with orientations (111) and (200). Optical characteristics of p-Cu2O and n-Cu2O were slightly affected. Homojunction Cu2O solar cells were successfully prepared by consecutively depositing an n-Cu2O layer on a p-Cu2O layer. Then, evaporate gold on n- Cu2O by thermal evaporator. The best performance of the cell fabricated in this study was short-circuit current density 12.7mA/cm², open-circuit voltage 31.5mV, fill factor 35%, and conversion efficiency 0.14% under standard test condition for thickness 2µm and 0.7µm for n-Cu2O and p-Cu2O, respectively. High short-circuit current density due to the pyramid surface structure of p- Cu2O caused the increase of the light path in the solar cell that could facilitate the photons to absorb more effectively. Low open-circuit voltage was due to energy band bending influence by interface states. The main limiting factor for the Cu2O cell efficiency was the high resistivity of both n-Cu2O and p-Cu2O. Doping of Cu2O will be necessary to improve the efficiency of the homojunction Cu2O solar cells further.


Keywords: Solar cell, Cuprous oxide, Electrodeposition, p-Cu2O, n-Cu2O and Homojunction

1. Introduction

Cuprous oxide (Cu2O) is a very promising semiconductor for the fabrication of solar cells due to the theoretical efficiency approximately 20% [1], the direct band gap semiconductor ≈ 2 eV, abundant, nontoxic, prepared with simple methods at very low cost and relatively high absorption coefficient over the wavelength range of the solar spectrum [2,3]. Cu2O can be prepared by many methods, including thermal oxidation, anodic oxidation, sputtering, and electrochemical deposition [4]. Different kinds of Cu2O solar cells have been fabricated [5,6]. The efficiencies of the prepared solar cells were usually around 1%. Fabrication of heterojunction Cu2O/ZnO solar cells made by deposition of transparent conducting oxide films on Cu2O substrates reported by Mittiga et al.[7], and the best conversion efficiency of solar cell is 2%. This is the highest efficiency obtained with a p-n heterojunction, which is still much lower than the theoretical efficiency 20% of the Cu2O solar cell. So, it may be the best way to improve the efficiency is to fabricate a p-n homojunction of cuprous oxide due to the reduction of strain due lattice matching at the interface. But, due to the intrinsic p-type conductivity of Cu2O, creating a p-n homojunction Cu2O has been considered challenging [8]. There have only been a few reports of p- n homojunction Cu2O to date due to the previous lack of synthesis methods to make n-Cu2O. Han et al. [9] fabricated Cu2O homojunction Cu2O solar cells by electrodeposition and optimized the resistivity of film with a result of a conversion efficiency of 0.1%. Recently, the effect of morphology of junction on the performance of Cu2O solar cells was been studied [10]. More recently, Wei H.M. et al fabricate series of homojunction Cu2O solar cells and found the best performance parameters are short-circuit current density 3.97mA/cm², open-circuit voltage 120mV, fill factor 22.6%, and conversion efficiency 0.104% under standard test condition [11].

In this study, a preparation and investigation of p-Cu2O and n-Cu2O by electrochemical deposition method have been done, in order to better understand p-n homojunction solar cell. Then fabricate homojunction Cu2O solar cells with different thickness and characterize the performance of cells using solar simulator.

2. Experimental

(1) Cyclic voltammetry

Before any deposition, cyclic voltammetry is performed in the same cell as for deposition to figure out parameters needed for the deposition of cuprous oxide.

In Figure 1, a typical IV is shown with the corresponding conditions for p-type and n-type cuprous oxide thin film.
Therefore, the samples of p-Cu$_2$O were deposited at the different voltages between -0.23 V and -0.496 V. A constant potential of -0.4V was used for deposition of p-type Cu$_2$O for a reasonable deposition rate to avoid deposition of metallic copper.

According to the IV curve Figure (b), two reduction reactions were observed due to the presence of cupric ions in the electrolyte. The first reduction that took place between -0.02 V and -0.22 V (vs. Ag/AgCl/saturated NaCl) contributes to the formation of Cu$_2$O by Equations (1, 2). The second reduction that occurred after ~ -0.22 V contributes to the formation of Cu by Equation (3).

The corresponding current is much lower than that of p-type cuprous oxide deposition, which results in a much lower deposition rate of n-type cuprous oxide. The potential window for the Cu$_2$O deposition in acetate bath is very narrow, so a constant potential of -0.15 V was used for deposition of n-type Cu$_2$O for a reasonable deposition rate to avoid deposition of metallic copper.

(2) Photocurrent measurements

Photocurrent measurements were carried out using a home-built system, which includes a light source, an illumination switch, three-electrode cell and a controlling system. A 150W tungsten lamp is used to provide broad spectrum light. The illumination switch is actually a manually controlled light chopper with certain time intervals (5 sec), while the potentiostat is used to control the applied potential and scan rate.

Photocurrent measurements were performed on electrodeposited samples at 0V (vs. Ag/AgCl) to verify their conduction type. Figure 2 represents zero bias photocurrent measurements of Cu$_2$O samples. These results revealed anodic photocurrent for sample deposited at bath pH of 5.7, indicating n-type conductivity. For Cu$_2$O sample deposited at bath pH 5.7 we found that they produce cathodic current which means p-type conductivity. Since, electrodeposition of Cu$_2$O involves two steps: The first step of the reaction would be the formation of Cu$^+$ ions at the electrode surface due to the cathodic reaction and the second step will be the formation of Cu$_2$O by reacting Cu$^+$ with OH$^-$ according to Equations (1, 2).

It noted that the chemical reaction is strongly dependent on the concentration of [OH$^-$], in other word, bath pH. At low pH values the rate of reaction is low and presence of excess Cu$^+$ ions favors the formation of Cu rich or O deficient (i.e. having O vacancies) Cu$_2$O thin films. Thus high density of donors can be expected and therefore the film becomes n-Cu$_2$O. This good agreement with the result shown in Figure 2(b). Where at low pH values films grown are n-Cu$_2$O. However, when the electrolyte pH is higher, rate of reaction will be higher and insufficient Cu$^+$ ion concentration might yield Cu$_2$O.

![Figure 1](image1.png)

Figure 1: IV curves for solution containing
(a) 0.4M CuSO$_4$ and 3M lactic acid
(b) 0.02M copper acetate and 0.1M sodium acetate

According to the IV curve Figure (a), two reduction reactions were observed due to the presence of cupric ions in the electrolyte. The first reduction that took place between -0.23 V and -0.496 V (vs. Ag/AgCl/saturated NaCl) contributes to the formation of Cu$_2$O by the following reaction.

$$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \quad (1)$$

$$2\text{Cu}^+ + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} \downarrow + \text{H}_2\text{O} \quad (2)$$

The second reduction that occurred after ~ -0.65 V contributes to the formation of Cu by the following reaction.

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \downarrow \quad (3)$$
thin films with Cu deficiency. In other word, acceptor density will be higher and the thin film will be p-Cu$_2$O. This agrees with the result shown in Figure 2(a). From these results, it found that bath pH has massive role in controlling the type of conductivity for the prepared Cu$_2$O thin films.

![Figure 2: Photocurrent of (a) p-Cu$_2$O (b) n-Cu$_2$O.](image)

### (3) Solar cell fabrication

Cu$_2$O thin films were electrodeposited using a three-electrode setup consisting of platinum wire as a counter electrode, Ag/AgCl as a reference electrode, while FTO-coated glass substrate was employed as a working electrode. The size of the working electrode was 1.6x2.5cm$^2$. Prior to the film deposition, substrate was cleaned by successive sonication in acetone, isopropanol and finally DI water for 10 minutes, respectively and then dried in oven at 105°C for at least 30 min.

To make a p-n homojunction, p-type and n-type Cu$_2$O films were sequentially deposited in two different electrolyte solutions. A p-type Cu$_2$O Film was first electrochemically deposited on a FTO-coated glass substrate using electrolyte consists of 0.4M copper sulfate anhydrous (CuSO$_4$, 99.5%, BDH) and 3M lactic acid (C$_3$H$_6$O$_3$, 90%, Appli Chem). Bath pH value of the electrolyte were adjusted carefully by addition of 4M Sodium hydroxide (NaOH, 99%, Oxford) to the deposition electrolyte to be 13 (varying pH from 9 to 13 and optimized pH 13 from SEM where sample at pH 13 have maximum grain size [1]) which decrease recombination in the cell and have maximum cathodic current].

The temperature of the electrolyte was maintained at 60 °C. Electrodeposition was carried out under a potentiostatic condition of -0.4V vs. Ag/AgCl using Bio-LogicSb-50 potentiostat. After deposition the film was good cleaned by distilled water and dried with air flow.

A n-type Cu$_2$O film was directly deposited on a p-type Cu$_2$O using electrolyte consist of 0.1M sodium acetate anhydrous (C$_2$H$_3$NaO$_4$, ADWIC) and 0.02M cupric acetate monohydrate (CuH$_2$CuO$_4$•H$_2$O). Bath pH value of the electrolyte were adjusted carefully by addition of 0.08M acetic acid glacial (C$_2$H$_4$O$_2$, 99%, El Salam for Chemical Industries) to the deposition electrolyte to be 5.7 (varying pH from 5.2 to 6.4 and optimized 5.7 from photocurrent where samples prepared after pH 5.7 transfer to p-Cu$_2$O and before pH 5.2 formed copper metal [13]).

The temperature of the electrolyte was maintained at 60 °C. Electrodeposition was carried out under a potentiostatic condition of -0.15V vs. Ag/AgCl using Bio-LogicSb-50 potentiostat. After deposition the film was good cleaned by distilled water and dried with air flow. The size of the deposited Cu$_2$O layer was 1.6x1.9 cm$^2$. After deposition, gold (Au) top contact was deposited on the n-Cu$_2$O using thermal evaporator operated at 10$^{-5}$Torr and 80A DC with an Au target (Purity 99.99%). The device fabrication was finished by evaporating of Au for top contact.

The finished device was 1x1 mm$^2$ in size. The performance of the solar cell was investigated with a solar simulator calibrated at standard test condition. The I-V curves were obtained with a Keithley 2400 SourceMeter.

### 3. Results and discussion

#### (1) p-Cu$_2$O and n-Cu$_2$O properties

The morphologies of the prepared Cu$_2$O samples by the electrodeposition processing under different optimum conditions are shown in Figure 3(a, b). The SEM images show that the p-Cu$_2$O samples formed in a three-faced pyramid shape as illustrated in Figure 3(a) which is similar to the textured surface structure of crystalline silicon solar cells [14, 15]. Whereas a dendritic shape was observed and shown in Figure 3(b) for n-Cu$_2$O. A dendritic shape [16] of n-Cu$_2$O appear due to the lateral crystal growth is faster than vertical growth. It was shown that the branches grown on the substrate are significantly longer than the
branches grown out of the substrate, which indicates faster lateral growth than vertical growth. This was mainly because the FTO substrate is much more conductive than the nucleated semiconductor Cu$_2$O, resulting in growth on the conductive substrate faster than the growth out of the substrate. The shape formation of the Cu$_2$O deposition was attributed to the crystal growth with the presence of [H$^+$] or [OH$^-$] under different pH values, which affect the electrochemical reaction [17].

Figure 3: SEM of (a) p-Cu$_2$O (b) n-Cu$_2$O.

The Cu$_2$O crystal structure was characterized using XRD measurements for the prepared films as shown in Figure 4 (a, b), the diffraction peak with asterisks from the FTO conductive film on glass. These measurements indicated that electrodeposited films are polycrystalline and the crystallographic phase of the films is cubic as it is clear from the well-defined peaks. Also Cu$_2$O films deposited at the selected optimum conditions for p-type and n-type are pure cuprous oxide and there is no metallic copper. For n-Cu$_2$O, spectral peaks at 36.45° (111) and 42.33° (200) are detected from the XRD tests; whereas a prominent peak is demonstrated at 36.45° (111) for p-Cu$_2$O. This indicates that the crystal growth of p-Cu$_2$O and n-Cu$_2$O deposition orientation was significantly influenced by pH value [18].

Figure 4: XRD patterns of (a) p-Cu$_2$O (b) n-Cu$_2$O (* refers to FTO substrate)

From these results, it possible to conclude that pH controls the orientation and grain size of Cu$_2$O films by affecting the growth rate of different crystallographic planes with different O density. For more understanding, in Cu$_2$O deposition, Cu$^+$ comes from the reduction of Cu$^{2+}$ and O$^{2-}$ comes from OH$^-$ in the solution. Because [Cu$^{2+}$] is kept constant throughout the deposition, [OH$^-$], i.e., the pH will determine the growth rate of different crystallographic faces and thus control the orientation and grain size.

Optical characterization of Cu$_2$O thin film is performed with a Jasco V630 UV-Vis spectrophotometer. For p-Cu$_2$O, Significant increase of absorption for Cu$_2$O films is observed at
wavelengths shorter than 640 nm corresponding to a band gap of 2.0 eV [12], which is close to the values in the previous report [19]. It was shown that incident light above 570 nm [13] can reach throughout the whole p-Cu$_2$O film, while the transmittance of incident light below 570 nm is close to zero. This demonstrates that the absorption coefficient of p-Cu$_2$O is extremely large at wavelength below 570 nm [12], which corresponds to a small penetration depth [20]. For n-Cu$_2$O, the transmittance of incident light below 475 nm is close to zero. This demonstrates that the absorption coefficient of n-Cu$_2$O is extremely large at wavelength below 475 nm [13].

To analyze the spectrum, the Tauc equation [21] is used:

$$\alpha h\nu = A(h\nu - E_g)$$ (4)

Where $\alpha$ is the absorption coefficient, $h\nu$ represents the photon energy, $E_g$ is the band-gap and $A$ is a constant. $n$ depends on the nature of the band-gap ($n = 1/3$ for indirect forbidden transition, $n = 1/2$ for indirect allowed transition, $n = 2/3$ for direct forbidden transition, and $n = 2$ for direct allowed transition), which indicates that electrodeposited Cu$_2$O has a direct band-gap. The intercept of the plot with the $h\nu$ axis shows that Cu$_2$O has a band-gap of 2.08 eV [12] and 2.055eV [13] for p-Cu$_2$O and n-Cu$_2$O respectively, which is consistent with the reported band-gap values for Cu$_2$O. The band gap energy shows that no effect on the optical properties of p-Cu$_2$O and n-Cu$_2$O thin films.

(2) Device characterization

The prepared Cu$_2$O p-n homo junction solar cell is shown in Figure 5.

There are three junctions formed in this structure:
(1) hetero-junction between the FTO and p-Cu$_2$O
(2) p-n homojunction between the p-Cu$_2$O and the n-Cu$_2$O.
(3) Schottky junction between the n-Cu$_2$O and the Au.

Before J-V characterization of the solar cells, the behavior of junction 1, 3 were investigated in advance to confirm the formation of a Cu$_2$O p-n junction. In order to check the junction 1, a different structure with Au/ p-Cu$_2$O/ Au structure, shown in Figure 6(a), were prepared. Square Au electrode was thermally deposited on the top surface of p-Cu$_2$O. J-V measurements were performed between two Au electrodes. As shown in Figure 6(b), the interface between Au and p-Cu$_2$O shows nice ohmic behavior.
Table 1. Photovoltaic performance parameters of a p-n homojunction Cu$_2$O solar cell with different thickness under standard test condition are shown in Figure 8(b). When deposition time increase lead to thickness increase lead to efficiency decrease due to recombination increase. The best performance of the cell fabricated in this study was short-circuit current density 12.7 mA/cm$^2$, open-circuit voltage 31.5 mV, fill factor 35%, and conversion efficiency 0.14% is shown in Figure 8(b) under illumination intensity 1 Sun and temperature 25°C.
interface states. The main limiting factor for the cell efficiency was the high resistivity of both p- and n-Cu$_2$O, and only a weak internal electrical field is established.

4. Conclusion

Cuprous oxide (Cu$_2$O) is a very promising semiconductor for the fabrication of solar cells due to the theoretical efficiency is approximately 20%, the direct band gap semiconductor ± 2 eV, abundant, non-toxic, prepared with simple methods at very low cost and relatively high absorption coefficient over the wavelength range of the solar spectrum. Thin films of p-Cu$_2$O and n-Cu$_2$O were controllably prepared using electrochemical deposition method by using optimum condition for each type. Photocurrent experiments show that the Cu$_2$O thin films synthesized in acid and alkaline media present n- Cu$_2$O and p- Cu$_2$O semiconductor character, respectively. The morphology and orientation were changed where p-Cu$_2$O show pyramid shape with orientation (111) and n-Cu$_2$O show dendritic shape with orientation (111) and (200). Optical characteristics of p-Cu$_2$O and n-Cu$_2$O were slightly affected. Homojunction Cu$_2$O solar cells were electrochemically fabricated by consecutively depositing an n-Cu$_2$O layer on a p-Cu$_2$O layer. Then, evaporate gold on n- Cu$_2$O. The best performance of the cell fabricated in this study was short-circuit current density 12.7mA/cm$^2$, open-circuit voltage 31.5mV, fill factor 35%, and conversion efficiency 0.14% under standard test condition. Thickness increase lead to efficiency decrease due to recombination of charge carriers’ increase. High short-circuit current density due to the pyramid surface structure of p-Cu$_2$O caused the increase of the light path in the solar cell that could facilitate the photons to be absorbed more effectively. Low open-circuit voltage was due to energy band bending influence by interface states. The main limiting factor for the cell efficiency was the high resistivity of both p-Cu$_2$O and n-Cu$_2$O. Doping studies will be necessary to improve the performance of the homojunction Cu$_2$O solar cells further.

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