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Fabrication and Characterization of p-n Homojunctions in Cuprous Oxide by Electrochemical Deposition

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The conduction type (n- or p-type) of electrochemically deposited cuprous oxide (Cu_2O) can be controlled by solution pH. It was found that cuprous oxides deposited at solution pH below 7.5 are n-type semiconductors, while cuprous oxides deposited at a solution pH above 9.0 are p-type semiconductors. A two-step process was adopted to deposit p-type and n-type cuprous oxides in sequence for the formation of a p-n homojunction in cuprous oxide. Photocurrent and current-voltage measurements demonstrate the successful formation of a p-n homojunction of cuprous oxide.

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Cuprous oxide (Cu₂O) is known as a p-type semiconductor¹⁻⁴ with a bandgap of around 2.0 eV.⁵⁻⁹ In the 1970s and 1980s, major efforts were dedicated to Cu₂O-based photovoltaic devices.^{5,10-14} The best conversion efficiency reported to date on Cu₂O-based photovoltaic devices is around 2%.¹⁵ The low efficiency can be attributed to the lack of n-type cuprous oxide. Without it, the early studies had to rely on Schottky junctions and p-n heterojunctions for photovoltaic devices, which do not provide high efficiency. The long-held consensus is that the best approach to improve cell efficiency in Cu₂O-based photovoltaic devices is to achieve both p-type and n-type cuprous oxides and thus p-n homojunctions of cuprous oxide.⁷

The purpose of this work was to find a systematic method for controlling the conduction type of cuprous oxide and thus fabricate p-n homojunctions of cuprous oxide. Copper vacancies are believed to be the cause for the p-type conductivity in cuprous oxide.^{2-4,16,17} Our previous study¹⁸ suggests that solution pH can control the amount of oxygen incorporated into cuprous oxide films during electrochemical deposition. This means that by reducing the amount of oxygen vacancies in cuprous oxide. If so, the conduction type of cuprous oxide may change from p-type to n-type. This paper reports our experimental results in achieving both conduction types in electrochemically deposited cuprous oxide by varying solution pH. Moreover, p-type and n-type cuprous oxides have been electrochemically deposited in sequence to form a p-n homojunction of cuprous oxide. This is, to the best of our knowledge, the first p-n homojunction of cuprous oxide by a wet-chemical method.

Note that there has been a report on n-type conductivity in electrochemically deposited cuprous oxide.¹⁹ The paper did not explain in detail how n-type conductivity was achieved, but it did speculate that the n-type conductivity was due to oxygen vacancies. In addition, no p-n homojunction of cuprous oxide has been reported in the literature.

Experimental

A standard three-electrode electrochemical cell was used for cuprous oxide deposition, which contained a platinum foil as the counter electrode, a silver/silver chloride/saturated sodium chloride reference electrode (without further notice, all the applied potential is referred to this electrode), and a copper foil (99.9% pure) as the working electrode. Before deposition, the copper foil was degreased in acetone, etched in diluted nitric acid, and rinsed in deionized water. Cuprous oxide films were electrochemically deposited from a solution containing 0.4 M copper(II) sulfate and 3 M lactic acid.^{20.21} The solution pH was adjusted between 6.5 to 12.0 by careful addi-

tion of 4 M sodium hydroxide. Linear-sweep voltammetry was performed on solutions with different pH. The voltammetric results (data not shown) indicated that the potential for cuprous oxide deposition is between -0.15 and -0.25 V for solution with pH of 7.0. For solution with pH of 9.0, the deposition potential is between -0.35 and -0.55 V.²¹ Therefore, for samples deposited at pH below 7.5, a constant potential of -0.20 V was applied, while for samples deposited at pH above 9.0, a constant potential of -0.40 V was applied. Deposition time was 30 to 60 min for each sample. The solution temperature was kept constant at 60°C by a Precision 280 water bath. All of the chemicals used were reagent grade.

After deposition, photocurrent and capacitance-voltage (C-V) measurements were performed to characterize the conduction type of the cuprous oxide films. C-V measurements were performed in a three-electrode cell, in which a cuprous oxide film was the working electrode, and the reference electrode was silver/silver chloride/ saturated potassium chloride. The nonaqueous solution contained 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile.² Photocurrent characterization was carried out in a three-electrode cell, in which the working electrode was a cuprous oxide film facing the light source (a broad-spectrum 100 W tungsten/halogen lamp), the counter electrode was a platinum foil, and the reference electrode was silver/silver chloride/saturated potassium chloride. The solution contained 0.5 M sodium sulfate and 0.1 M sodium formate. A Princeton Applied Research 264A polarographic analyzer/ stripping voltammeter was used to control the applied potential and scan rate.

A two-step process was adopted to deposit p-type and n-type cuprous oxides sequentially to form a p-n homojunction of cuprous oxide. Photocurrent measurements were performed to ensure the formation of a p-n junction. Aluminum was deposited through a shadow mask with a circular dot area of 3.6×10^{-4} cm² as top electrical contacts for current-voltage (*I-V*) characterization, which was performed with a HP 4145A semiconductor parameter analyzer.

Results and Discussion

It is suggested that cuprous oxide electrochemical deposition proceeds in two steps.²³ The first step involves the reduction of copper(II) (Cu^{2+}) ions to copper(I) (Cu^{+}) in the solution, which breaks the copper-lactic complex

$$Cu^{2+} + e^- \rightarrow Cu^+$$

 $E^{\circ} = 0.153 \text{ V} [\text{standard hydrogen electrode (SHE)}] [1]$

The Cu⁺ ions undergo a hydrolysis reaction

$$2\mathrm{Cu}^{+} + 2 \mathrm{OH}^{-} \rightarrow \mathrm{Cu}_{2}\mathrm{O} \downarrow + \mathrm{H}_{2}\mathrm{O}$$
^[2]

The fact that the deposition potential is pH sensitive (-0.2 V for pH of 7.0 and -0.45 V for pH of 9.0, or 125 mV/pH) suggests that the following reaction is possible

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Figure 1. Mott–Schottky plots of cuprous oxide films deposited at pH (a) 6.8, (b) 7.25, (c) 7.5, and (d) 11.0.

$$2\mathrm{Cu}^{2+} + 2 \mathrm{OH}^{-} + 2\mathrm{e} \rightarrow \mathrm{Cu}_2\mathrm{O}\downarrow + \mathrm{H}_2\mathrm{O} \quad E^\circ = 0.7019 \mathrm{~V} \text{ (SHE)}$$
[3]

Even this reaction does not explain the large pH dependence of deposition potential. It is possible that Reaction 1 is only valid in base solutions and for neutral solutions (pH around 7.0), a different reaction, such as Reaction 3, takes place. During deposition, the concentration of Cu^{2+} ions is kept constant. The concentration of OH^- , i.e., solution pH, has been suggested to control the amount of oxygen incorporated into the cuprous oxide film,¹⁸ and possibly the nature of native point defects in cuprous oxide. A series of samples have been prepared at different solution pH from 6.5 to 11.0 with an increment of 0.2–0.5 to verify the hypothesis that the conduction type of the cuprous oxide film changes with solution pH.

After deposition, C-V and photocurrent measurements were applied to determine the conduction type of the cuprous oxide films. C-V data was analyzed with the Mott–Schottky theory as follows²⁴

n-type:
$$\frac{1}{C_{\rm sc}^2} = \frac{2}{e\varepsilon\varepsilon_{\rm o}A^2N_{\rm D}} \left(V - V_{\rm FB} - \frac{kT}{e}\right)$$
 [4]

p-type:
$$\frac{1}{C_{\rm sc}^2} = -\frac{2}{e\varepsilon\varepsilon_0 A^2 N_{\rm A}} \left(V - V_{\rm FB} + \frac{kT}{e} \right)$$
 [5]

where $C_{\rm sc}$ represents the capacitance of the space charge region, ε is the dielectric constant of the semiconductor, ε_0 is the permittivity of the free space, A is the area of the working electrode, $N_{\rm D}$ and $N_{\rm A}$ are the donor and acceptor concentrations, V is the applied potential, and $V_{\rm FB}$ is the flatband potential. Apparently, the conduction type of a cuprous oxide film can be identified by the sign of its Mott–Schottky plot $(1/C^2 \text{ vs } V \text{ plot})$. A positive slope indicates an n-type semiconductor, while a negative slope points to a p-type semiconductor. Mott-Schottky plots for samples deposited at solution pH of 6.8, 7.25, 7.5, and 11.0 are presented in Fig. 1. As shown, samples deposited at solution pH below 7.5 show positive slopes, indicating that these cuprous oxide films are n-type semiconductors. The sample deposited at solution pH of 11.0 has a negative slope, suggesting a p-type semiconductor. It has also been found that all of the samples deposited at solution pH above 9.0 are unambiguously p-type. However, the conduction type of samples deposited at solution pH of around 8.0 is amphoteric by C-V.

The flatband potential for the four samples in Fig. 1 varies from -0.026 V for the p-type sample to 0.038, 0.046, and 0.026 V for pH of 6.8, 7.25, and 7.5, respectively. By adding the flatband potentials



Figure 2. Photocurrent response of cuprous oxide films deposited at pH (a) 6.8, (b) 7.25, (c) 7.5, and (d) 11.0.

from n-type and p-type, it was found that the Fermi level moved by up to 0.072 eV between p-type and n-type, which is smaller than the cuprous oxide bandgap, 2.0 eV. The smaller-than-expected movement in Fermi level can be attributed to the low carrier concentrations in these cuprous oxide films or high densities of surface states. Surprisingly, Fig. 1 suggests that the donor (or accepter) concentration for these samples is between low 10^{18} to low 10^{19} cm⁻³, with an estimated area of 2 cm² and a dielectric constant of 6.3 for cuprous oxide. However, other electrical measurements indicate that asdeposited cuprous oxide films are more resistive and should have lower carrier concentrations.

Photocurrent characterization also verifies the conduction types of these cuprous oxide films. Photocurrent generated upon illumination has opposite directions for n-type and p-type semiconductors. Samples deposited at solution pH of 6.8, 7.25, 7.5, and 11.0 were selected for photocurrent characterization and the results are shown in Fig. 2. As shown, samples deposited at pH below 7.5 show anodic photocurrents, indicating n-type conductivity. The sample deposited at pH of 11.0 shows a cathodic photocurrent, indicating p-type semiconductor behavior. It was also found that samples deposited at solution pH above 9.0 are p-type semiconductors. These photocurrent results are consistent with the C-V results and demonstrate that solution pH can control the conduction type of cuprous oxide.

With both p-type and n-type cuprous oxides, a two-step deposition process was used to form a p-n homojunction of cuprous oxide. First, p-type cuprous oxide was deposited at pH of 11.0 on a copper substrate, and then n-type cuprous oxide was deposited directly onto the p-type cuprous oxide film at pH of 6.8, 7.25, or 7.5. Photocurrent measurements were performed after deposition at pH of 11.0 and after subsequent deposited at pH of 6.8, 7.25, or 7.5. As shown in Fig. 3, cuprous oxide deposited at pH of 11.0 shows a typical p-type photocurrent response. However, after deposition of another cuprous oxide film at pH of 7.5, the photocurrent response shows n-type semiconductor behavior. This demonstrates that n-type cuprous oxide has been successfully deposited on p-type cuprous oxide and a p-n homojunction of cuprous oxide has been formed.

Aluminum top contacts were deposited through a shadow mask on the p-n homojunction samples and I-V characterization was performed to investigate the rectification behavior of the p-n homojunction of cuprous oxide. For I-V characterization of the structure in Fig. 4a, there are three junctions which can result in rectifying I-Vbehavior: the Schottky junction between n-type cuprous oxide and top aluminum contact, the p-n junction between n-type and p-type cuprous oxides, and the Schottky junction between p-type cuprous



Figure 3. (a) Photocurrent of cuprous oxide deposited at pH of 11.0 and (b) photocurrent of two-layer cuprous oxide deposited first at pH of 11.0 and then at pH of 7.5.

oxide and copper substrate. Two additional sets of samples were prepared: p-type cuprous oxide on copper substrate with top copper contacts and n-type cuprous oxide on copper substrate with top aluminum contacts. Both sets of samples show linear I-V relations in the current and potential ranges studied, as shown in Fig. 4b and c. Therefore, any rectifying behavior from the structure in Fig. 4a should come from the p-n homojunction of cuprous oxide itself.

I-V results of cuprous oxide p-n homojunctions before and after breakdown are shown in Fig. 5. In Fig. 5a, the I-V curve displays a rectification effect of a p-n junction. The forward current through the junction increases quickly as the applied potential increases. Under reverse bias, the current through the junction becomes much smaller before breakdown. As the reverse potential passes around -6 V, the p-n junction breaks down. The I-V characteristic after breakdown no longer displays any rectification effect and becomes linear, as shown in Fig. 5b. This I-V characterization demonstrates the successful formation of a p-n homojunction in cuprous oxide.

Conclusion

Based on the hypothesis that solution pH can control native point defects in electrochemically deposited cuprous oxide, both p-type and n-type cuprous oxides have been successfully obtained with different solution pH. For cuprous oxide films deposited at pH below 7.5, they show n-type semiconductor behavior, while those deposited at solution pH above 9.0, cuprous oxide is a p-type semiconductor. Furthermore, a two-step process was used to deposit p-type and n-type cuprous oxides in sequence for the formation of a p-n homojunction in cuprous oxide. Photocurrent measurements demonstrated the successful deposition of n-type cuprous oxide on p-type cuprous oxide, and I-V characterization showed typical rectification behavior of a p-n junction for the fabricated structure, indicating that a p-n homojunction of cuprous oxide has been achieved.



Figure 4. (a) Schematic of the p-n homojunction structure of cuprous oxide for I-V characterization. (b) I-V characteristic of an aluminum/n-type cuprous oxide Schottky junction. (c) I-V characteristic of a copper/p-type cuprous oxide Schottky junction.



Figure 5. I-V characteristics of an aluminum/n-type cuprous oxide/p-type cuprous oxide/copper structure (a) before and (b) after breakdown.

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