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## Effect of bath pH on the electrodeposition of cuprous oxide and copper thin films for photovoltaic applications

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### Abstract

The electrodeposition of cuprous oxide (Cu<sub>2</sub>O) and copper (Cu) thin films at 29 °C on the ITO/glass substrates from cupric acetate aqueous solution is reported. The electrodeposition mechanism was investigated by cyclic voltammetry. The effect of pH on the electrodeposition of cuprous oxide and copper thin films was studied. The X-ray diffraction (XRD) analysis shows that Cu<sub>2</sub>O films has a cubic structure and the preferred growth orientation is the (111) direction. The photocurrent characterization indicated that the films deposited at pH = 6.2 has n-type electrical conductivity.

**Keywords:** Electrodeposition; thin film; cuprous oxide; copper; cyclic voltammetry; photovoltaic solar cells.

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### 1. Introduction

The quest and need for clean and economical energy source have increased interest in the development of solar applications. In particular, direct conversion of solar energy to electrical energy and chemical energy using semiconductor photoelectrodes has attracted attention for many decades. Among the various metal oxide materials for solar energy application, a promising material is cuprous oxide (Cu<sub>2</sub>O), one of the oldest known semiconductors [1]. It is an interesting and nontoxic semiconducting material with a band gap of 2 eV at room temperature suitable for solar cell application and high absorption coefficient.

In the recent past Copper (Cu) thin films are used for various applications particularly preparation of ternary I-III-VI<sub>2</sub> semiconductors and fabrication of interconnections in semiconductor industry. Cuprous oxide and Cu thin films are prepared by various methods like reactive sputtering, vacuum evaporation, chemical and thermal oxidation [2] and electrodeposition [3-11].

Among the various deposition techniques available for the preparation of cuprous oxide and Copper thin films, method of electrodeposition is an attractive technique because of its simplicity and the possibility in making large area thin films [12].

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It has been reported previously that good quality  $\text{Cu}_2\text{O}$  films can be electrodeposited using an acetate bath [13-14]. In the present work, we report on the preparation of  $\text{Cu}_2\text{O}$  and Cu thin films on ITO/glass substrates by cathodic electrodeposition in aqueous solution at different pH. Electrodeposition thin films were characterized using X-ray diffraction (XRD), photo-current.

## 2. Experimental

### 2.1. ITO/glass electrode pre-treatment

Optically transparent indium tin-oxide (ITO,  $12 \Omega/\square$ ) coated glass plate was used as the substrate. Prior to deposition, it was ultrasonically rinsed in acetone, ethanol and distilled water first, and then etched in the diluted hydrochloric acid (5-6%) for 15 s, and finally rinsed in distilled water [15, 16].

### 2.2. Preparation of $\text{Cu}_2\text{O}$ and Cu thin films

Electrodeposition of  $\text{Cu}_2\text{O}$  and Cu thin films on ITO/glass substrates was studied using a three electrode electrochemical cell containing an aqueous solution of sodium acetate and cupric acetate at different pH (3,6,2) (pH was adjusted by adding diluted  $\text{CH}_3\text{COOH}$ ). Cupric acetate was used as  $\text{Cu}^{2+}$  source while sodium acetate was added to the solution making complexes releasing copper ions slowly into medium allowing a uniform growth of  $\text{Cu}_2\text{O}$  thin films.

The counter electrode was a platinum wire of 1 mm diameter and reference electrode was saturated calomel electrode (SCE). Electrolytic solutions were prepared with distilled water and reagent grade chemicals. Temperature of bath was maintained to  $29^\circ\text{C}$  and the electrolyte continuously stirred using a magnetic stirrer. Electrodeposition was carried out under Potentiostatic mode using Princeton Applied Research Model 273 A Potentiostat/ Galvanostat, coupled to a personal computer with power suite software for data acquisition and potential control. The experimental device for the electrodeposition of thin films is shown in Fig. 1.

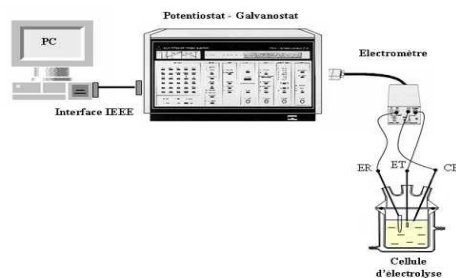


Fig. 1. Experimental device.

### 2.3. Characterization

The crystallographic structure of the films was determined by X-ray diffraction (XRD) using a RIGAKU RAD-2R diffractometer with  $\text{Cu K}\alpha$  radiation. The photo-current characterization was studied using *Current-Voltage* technique. Photocurrent characterization is carried out in a custom-built system (Fig. 2), which includes a light source, an illumination switch and three-electrodes: the counter electrode

is platinum, the reference electrode is SCE and a working electrode is ITO/glass immersed in an electrochemical cell containing an electrolyte of 0.1 M sodium acetate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ). A 100W tungsten/halogen lamp is used to provide broad spectrum light, the working electrode is as-deposited cuprous oxide film facing the light source. The photo-current characterization will be realized by cyclic voltammetry, once, in the dark and the next time under illumination.

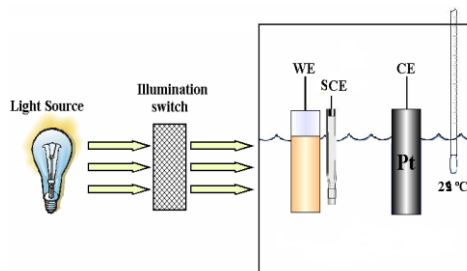
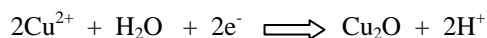


Fig. 2. Arrangement of photocurrent Characterization system.

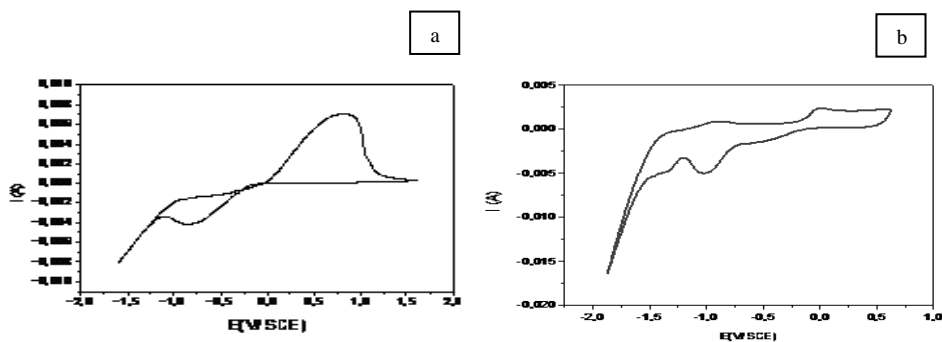
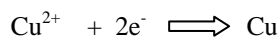
### 3. Results and discussion

#### 3.1. Electrochemical studies

Fig. 3 shows the cyclic voltammogram of ITO-coated glass for the solution containing 0.01M cupric acetate + 0.1M sodium acetate. The sweep is measured at a scan rate of  $50 \text{ mV s}^{-1}$  over the potential range from 2 to  $-2 \text{ V}$ . In curve (a), there is formation only of copper at  $-0.8 \text{ V/ECS}$  in cupric acetate at  $\text{pH} = 3$  [1]. But in curve (b) at  $\text{pH} = 6.2$ , we can observe two cathodic peaks at  $-0.5 \text{ V vs. SCE}$  and  $-1 \text{ V vs. SCE}$  due to the presence of cupric ions in the electrolyte. First cathodic peak at  $-0.5 \text{ V vs. SCE}$  attributes to the formation of  $\text{Cu}_2\text{O}$  on the substrate according to the following reaction [12].



Second cathodic peak at  $-1 \text{ V vs. SCE}$  attributes to the formation of  $\text{Cu}$  on the substrate according to the following reaction.



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Fig. 3. Cyclic voltammogram of ITO-coated glass for the solution containing 0.01M cupric acetate + 0.1M sodium acetate. (a) at pH = 3, (b) pH = 6.2, Scan rate 50 mV s<sup>-1</sup>.

### 3.2. X-ray diffraction analysis

Fig. 4 represents the X-ray diffraction spectra of the films deposited on ITO-coated glass substrate at pH = 6.2. This fig show five peaks at 2θ values of 21.30°, 30.30°, 50.60° and 60.30° corresponding to the reflections from (110), (111), (200) and (220) atomic plans of Cu<sub>2</sub>O in addition to the ITO peak and three additional peaks at 2θ values of 37.25°, 45.25° corresponding to the reflections from (111), (200) atomic plans of Cu.

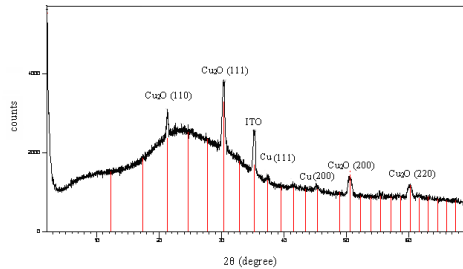


Fig. 4. X-ray diffraction spectra of the films deposited on ITO-coated glass substrate at pH = 6.2.

The intensity of the (111) diffraction is much stronger than that of other peaks, indicating that the Cu<sub>2</sub>O film has a cubic structure.

### 3.3. Photocurrent characterization

Fig. 5. Shows *Current-Voltage* characterization of cuprous oxide (Cu<sub>2</sub>O) deposited at -0.250 V vs. SCE for the solution containing 0.1M sodium acetate (CH<sub>3</sub>COONa.3H<sub>2</sub>O), in the dark and under illumination. In the dark, we observe a low intense anodic current on the other hand, under illumination of the surface of cuprous oxide; there is appearance of a more intense anodic current in that observed in the darkness. This indicates that the cuprous oxide thin film behaves as a semiconductor of type n [17, 18].

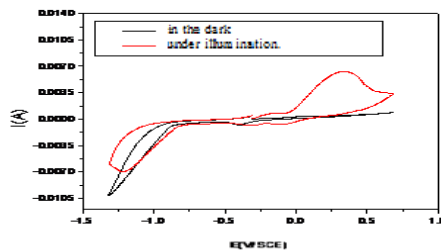


Fig. 5. *Current-Voltage* Characterization of cuprous oxide (Cu<sub>2</sub>O) deposited at -0.250 V vs. SCE for the solution containing 0.1 M sodium acetate (CH<sub>3</sub>COONa.3H<sub>2</sub>O) in the dark and under illumination.

#### 4. Conclusion

Electrodeposition of Cu<sub>2</sub>O and Cu thin films can be carried out in aqueous solution containing sodium acetate and cupric acetate. The results of electrochemical studies show that there is formation only of copper at  $-0.8$  V/ECS in cupric acetate at pH=3. There is formation simultaneously of cuprous oxide (Cu<sub>2</sub>O) at  $-0.5$  V/ECS and the copper (Cu) at  $-1$  V/ECS, respectively at pH=6.2. The XRD measurements revealed that Cu<sub>2</sub>O films has a cubic structure and the preferred growth orientation is the (111) direction. The photocurrent revealed that the films deposited at pH = 6.2 has n-type electrical conductivity.

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