

Donor and Acceptor Density Variations in Electrodeposited Cuprous Oxide Thin Films

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ABSTRACT

Cuprous oxide thin films were electrodeposited in a cupric acetate bath and resulting films were investigated in a photoelectrochemical cell for determining the intrinsic defects density variations. Depth profiles of the current carrier generation in the thin films were studied using the variation in the absorption depths of incident photons. Magnitudes and sign reversal of the photocurrents generated by the incident monochromatic light were used for this purpose. It was observed that by controlling the pH value of the deposition bath density of both Cu and O vacancies, which are responsible for acceptor and donor levels respectively, can be controlled and thereby it is possible to electrodeposit either n-type or p-type cuprous oxide thin films.

1. INTRODUCTION

Cuprous oxide is a potentially attractive material for applications in solar energy converting devices[1] and gas and humidity sensors[2]. It is a low-cost and non-toxic material satisfying the environmental and economical requirements needed for large-scale applications. As a semiconductor, this material has been studied since early fifties and found that it is a p-type semiconductor due to the presence of Cu vacancies in the crystal lattice, owing to an acceptor level at 0.4 eV above the valance band[3]. All the previous investigations were limited to the thermally grown cuprous oxide and there the growth mechanism of oxide restricted only to the formation of Cu vacancies in Cu₂O. However, recently considerable interest has been grown on electrodeposited cuprous oxide thin films[4] and, particularly, on their n-type behavior in photoelectrochemical cells[5]. It has been reported that n-type conductivity in electrodeposited cuprous oxide thin films is due to the presence of a donor level at 0.38 eV below the conduction band, originated from O vacancies[6]. Also, previous studies have shown that n-type films can be electrodeposited in various deposition baths[5] or can be obtained by dipping copper electrodes in cupric ions containing aqueous electrolytes[7]. Moreover, electrodeposition technique was able to produce both n- and p-type Cu₂O thin films and proper control over this behavior has not been reported earlier, however.

In this investigation we have studied the electrodeposition of Cu₂O thin films in an acetate bath and obtained the conditions required for deposition of n- type or p-type films. With the spectral response measurements we have shown that during the electrodeposition, diffusion

of Cu atoms causes the creation of Cu vacancies in the crystal lattice leading to p-type films.

2. EXPERIMENTAL

Cu₂O thin films were deposited on Ti substrates by the electrodeposition method. Prior to the film deposition substrates were cleaned with detergent, diluted HNO₃ and finally with distilled water. Electrodeposition of Cu₂O thin films on Ti substrates was accomplished in a three-electrode electrochemical cell containing aqueous solutions of 0.1M sodium acetate and 0.01 M cupric acetate[8]. The temperature of the electrolyte was maintained at 60 °C and the electrolyte was continuously stirred using a magnetic stirrer. The counter electrode was a platinum plate and a saturated calomel electrode (SCE) was used as the reference electrode. Electrodeposition was carried out under a potentiostatic condition of -200 mV vs. SCE for 45 minutes. pH of the electrolyte was adjusted by adding a dilute sodium hydroxide solution to the bath. The Cu₂O electrodes were investigated in a photoelectrochemical cell containing 0.1M sodium acetate solution with a platinum counter electrode. The spectral response of the electrode was measured using phase sensitive detection method to monitor the photocurrent signal produced by a chopped monochromatic light beam. The chopping frequency was 63 Hz. A monochromator (Sciencetech - 9010), a potentiostat (Hukoto Donko HAB-151), a lock-in amplifier (Stanford Research- SR 830 DSP), and a chopper (Stanford-SR 540) were used with a pc for the spectral response measurements.

3. RESULTS AND DISCUSSION

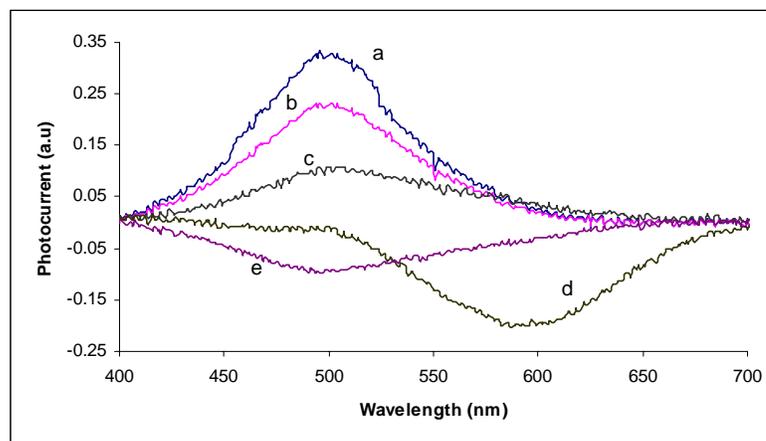


Figure 1: Spectral photoresponses of Cu₂O thin films deposited potentiostatically at - 200 mV vs. SCE at 60 °C for 45 minutes in the depositing baths of pH (a) 5.4, (b) 6.3 , (c) 6.6,(d) 6.9 (e) 7.9

Figure.1 shows the spectral responses of the Cu₂O thin films deposited on Ti substrates in the cupric acetate baths of various pH values. It is very clearly seen that slightly acidic conditions resulted the n-type (positive) photosignals in the entire spectral range. When the pH value of the bath is higher the photoresponse of the films becomes p-type (negative). In the acetate bath possible variations of the pH value is very limited to a narrow range because at higher pH values high precipitation is evident while in acidic solutions Cu deposition can not be avoided.

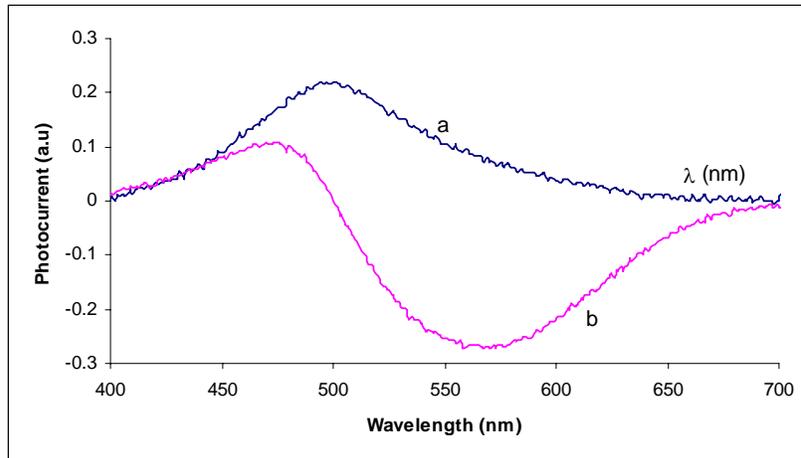
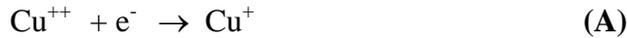


Figure 2. Spectral photoresponse of an n-type Cu₂O thin film deposited in a bath of pH=6.3 (a) and that after depositing another Cu₂O film in a bath of pH=7.9 (b).

Figure 2 shows the spectral response of a thin film Cu₂O electrode which was made by first depositing an n-type film on Ti substrate, followed by the electrodeposition of Cu₂O film in a bath where a p-type film would be deposited. However, as shown in Figure 2 the shorter wavelengths produce n-type photosignals while longer wavelengths produce p-type signals. If the p-type film is grown on the n-type film, one would expect a p-type photoresponse of shorter wavelengths because the absorption depth of shorter wavelengths is small and then the photoresponse will be due to the p-type layer. As long wavelengths have longer absorption depths, more photons can reach the interior of the films. Therefore, according to our result shown in Figure 2, the interior of the films close to the substrate must be p-type, although it was originally an n-type film. Thus, during the Cu₂O film growth in the bath having high pH, Cu ions of the film must have diffused to the surface creating Cu ion vacancies in the inner layers. The Cu ion vacancies are accumulated at the far end (closer to the substrate) because there are no Cu atoms to flow from the substrate to the film. Therefore in the situation depicted in Figure 2, there is a p-type layer on the Ti substrate and an n-type layer grown over it.

Above explanation can be justified if we examine the film growth mechanism during the electrodeposition of Cu₂O. The first step of the reaction would be the formation of Cu⁺ ions at the electrode surface due to the cathodic reaction (A) given below [9].



The second step will be the formation of Cu₂O by reacting Cu⁺ with OH⁻, as given by the reaction (B).



It is clearly seen that reaction (B) is highly dependent on the [OH⁻] concentration, in other words, pH of the bath. At low pH values the reaction rate is low and presence of excess Cu⁺ ions favors the formation of Cu rich or O deficient (i.e. having O vacancies) Cu₂O films. Thus high density of donors can be expected and therefore the film becomes n-type. This agrees with the result shown in Figure 1 where at low pH values films grown are n-type. However, when the pH of the electrolyte is higher, reaction rate will be higher and insufficient Cu⁺ ion concentration might yield Cu₂O films with Cu deficiency. In other words, acceptor density will be higher and the film will be p-type. This agrees with the result shown in Figure 1. When the electrodeposition is performed on an originally n-type film in a bath of high pH value, the reaction (B) will proceed at a higher rate but Cu atoms in the n-type films will also be consumed creating Cu ion vacancies in the film. Then a p-type layer is gradually grown, starting from the substrate side, as explained above.

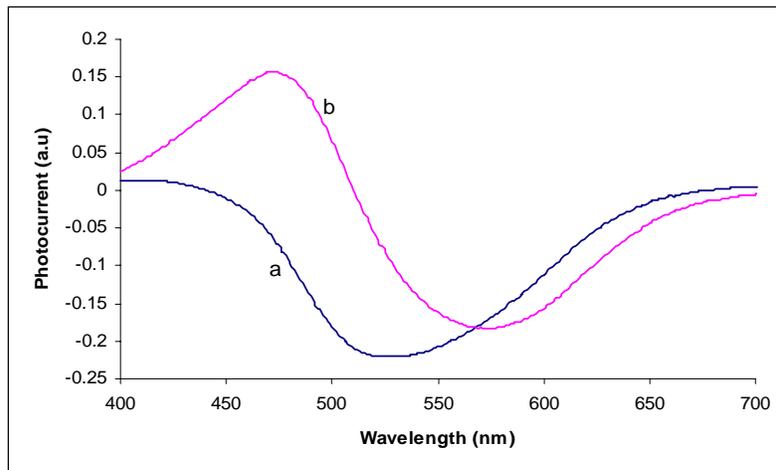


Figure 3. Spectral photoresponse of an p-type Cu₂O thin film deposited in a bath of pH=7.9 (a) and that after depositing another Cu₂O film in a bath of pH=6.3 (b).

This explanation is further supported by the results shown Figure3 where a second Cu₂O film has grown on an originally p-type film in a bath of low pH value. The n-type layer is grown on the p-type films as shown in Figure.3 where short wavelength response is n-type while still the long wavelength response is p-type. There the original p-type layer is unchanged because still the dominant defects are Cu vacancies.

4. CONCLUSIONS

It can be concluded that the pH value of the depositing acetate bath of Cu₂O determines the conductivity type of the resulting films. Diffusion of Cu ions to the surface of the film during the film growth result in the formation of Cu vacancies, producing p-type films at higher pH values. At low pH values reaction rates are low and Cu rich or oxygen deficient Cu₂O films are produced having n-type conductivity.

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