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Research article

Electrodeposition of p-type, n-type and p-n Homojunction Cuprous Oxide Thin Films

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Abstract

Potentiostatic electrodeposition of cuprous oxide (Cu₂O) thin films in aqueous acetate baths was investigated to study the conduction type, n-type or p-type, and the p-n homojunction formation of the films, using photocurrent spectral response and capacitance-voltage measurements to determine the conduction type. The study reveals that not only the pH value but also the cupric ion concentration of the acetate bath determines the conduction type of the films. Electrodeposition of p-n homojunction of Cu₂O is possible with a single or a two step electrodeposition. Both parameters of the deposition bath, pH and cupric ion concentration, can be adjusted to control conduction type and p-n homojunction formation of Cu₂O films.

Keywords: cuprous oxide, electrodeposition, n- and p-type, spectral response, p-n homojunction

1. INTRODUCTION

Cuprous oxide is an attractive material for applications in low cost solar energy converting devices [1, 2]. It is a stoichiometry defect type semiconductor and is generally a p-type material due to an acceptor level at 0.4 eV above the valence band created by copper ion vacancies [3, 4]. A Donor level has also been observed in Cu₂O [4, 5]. Cu₂O has a direct band gap of 2 eV, which is in the appropriate range for solar energy applications. Abundance of the starting material copper, availability of inexpensive processing techniques and non-toxicity made this semiconductor material as an attractive material for low cost solar energy applications.

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As a semiconductor, Cu_2O has been studied since early fifties. These studies mainly concentrated on thermally grown Cu_2O and found that the growth mechanism restricted only to the formation of dominant Cu vacancies in Cu_2O . However, recently considerable interest has been shown on Cu_2O films produced by other techniques, particularly the electrodeposition and the dipping of copper electrodes in aqueous electrolytes (6-13). Films produced by electrodeposition using alkaline lactate baths were more common and there the resulted Cu_2O films were p-type [6, 7, 9-11]. However, studies have shown that n-type films can also be obtained by the electrodeposition [8, 14] or by dipping copper electrodes in cupric ions containing aqueous electrolytes [8, 12, 13]. The recent work of Wang and Tao [12] demonstrates that the conduction type of the electrodeposited Cu_2O can be controlled by pH of the bath. The possibility of deposition of n-type films has attracted much attention because the importance of growing p-n homojunction of Cu_2O for applications in thin film solar cell devices [1, 12]. Indeed, Wang and Tao [12] have already demonstrated the possibility of electrodeposition of p-n homojunction of Cu_2O using a lactate bath. In developing the electrodeposited Cu_2O as a solar energy material, it is very important to identify the parameters that could control the conduction type of the films in the electrodeposition process.

In this work, dependence of the conduction type of the electrodeposited cuprous oxide thin films on the deposition bath parameters, cupric ion concentration and pH, was investigated using spectral response and capacitance - voltage measurements. Further, p-n homojunction formations of Cu_2O in acetate baths of different pH and cupric ion concentrations were also studied. It is revealed that, for the first time to our knowledge, not only the pH but also the cupric ion concentration determines the conduction type of electrodeposited Cu_2O films. Also, p-n homojunction of Cu_2O can be formed by a single step as well as a two step electrodeposition process.

2. EXPERIMENTAL

Cu_2O thin films were deposited on Ti substrates. Prior to the film deposition substrates were cleaned with detergent, diluted HNO_3 and finally with distilled water. Films were deposited in a three-electrode electrochemical cell containing aqueous solutions of 0.1M sodium acetate and various concentrations of cupric acetate. 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 [14]. Different pH values of the electrolyte were obtained (5.4 to 7.9) by adding a dilute sodium hydroxide solution or acetic acid to the bath. Different concentrations of cupric acetate solutions (0.0005 M to 0.01 M) at various pH values (5.4 to 7.9) were used to electrodeposit Cu_2O films to study the n- and p-type behavior of the films and the p-n junction formation. Further, a sequential deposition method was adopted to investigate the p-n junction formation. First a Cu_2O film was deposited in a bath

suitable for producing a p-type film and then a second film was deposited on the first film using a second bath which produces n-type films. The two baths were different from each other in respect of concentration (0.0005 M to 0.01 M) and/or pH value (5.4 to 7.9). Distilled water and reagent grade chemicals were used.

All Cu₂O films were investigated in a three electrode photoelectrochemical cell containing a 0.1 M sodium acetate solution. The contact area of the film with the electrolyte was 4 mm². The counter electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE). Spectral responses of the electrodes were measured using a 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. In capacitance –voltage measurements of the thin films, experimental set up consisted of a potentiostat (Hukoto Donko HAB-151), a lock-in amplifier (Stanford Research- SR 830 DSP) and a signal generator. A constant a.c. current of 1 μA at 1 kHz was passed through the working electrode and the counter electrode while keeping the potential of the working electrode constant with respect to the reference electrode. Variation of the imaginary part of the a.c. signal was measured and the capacitance (C) values were obtained at various applied potentials to obtain the Mott-Schottky ($1/C^2$ vs potential) plots. X-ray diffraction measurements were obtained using a SHIMADZU (XD-D1) X-ray diffractometer. The surface Morphology of the films was determined by scanning electron microscope (Philips XL40).

2. RESULTS AND DISCUSSION

Fig.1 shows the photocurrent spectral responses of the Cu₂O thin films prepared by potentiostatic electrodeposition at pH (a) 5.4, (b) 6.3, (c) 6.6, (d) 6.9 and (e) 7.9 in a deposition bath containing 0.1 M sodium acetate and 0.01 M cupric acetate. It is very clearly seen that films produced at acidic conditions, curves (a), (b) and (c) in Fig. 1, resulted the positive (n-type) photosignals. As shown by curves (d) and (e) in Fig.1, the films produced at higher pH values resulted negative (p-type) photosignals. It is interesting to note that a slight variation of the pH (from 6.6 to 6.9) of the depositing bath, curves (c) and (d), the films produced are changed the conduction type from n-type to p-type. This sensitivity of the pH value of the depositing bath on the conduction type of the film may be the reason why previously reported Cu₂O films deposited using different acetate baths produced n- type as well as p-type films [14, 15].

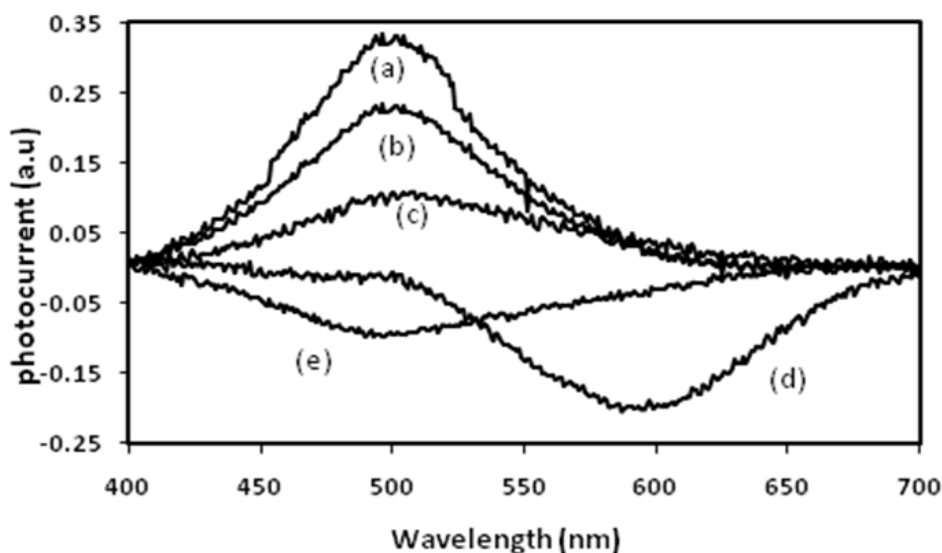


Fig. 1 Spectral photoresponses of Cu_2O thin films deposited potentiostatically at -200 mV vs SCE at 60°C for 45 minutes duration in baths containing 0.1 M cupric acetate and 0.1 M sodium acetate at pH values (a) 5.4 , (b) 6.3 , (c) 6.6, (d) 6.9 and (e) 7.9.

Furthermore, it can be noted in Fig. 1 that the photocurrent maximum of curve (d) has shifted significantly towards the longer wavelength side as compared that with the curves (a), (b), (c) and (e). This enhancement of long wavelength response suggests that, as the longer wavelengths have larger absorption depths than the shorter wavelengths, the charge carriers are separated more efficiently in the interior of the film in (d). In other words, the charge separation in the interior of the film is more pronounced than that at the front Cu_2O /electrolyte contact for the film in Fig. 1 (d). Also, it is very clear in curve (d) that the photoresponse of shorter wavelengths is much weaker as compared that with the curves (a), (b), (c) and (e). This may be attributed to the formation of a p-n junction inside the film which could result in more efficient charge carrier separation in side the film. For the shorter wavelengths absorbed closer to the surface of the film, photogenerated carriers are driven in opposite directions due to the presence of the p-n junction in addition to the n- Cu_2O /electrolyte junction. Therefore the net result will be the reduction of the photosignal for shorter wavelengths. In other words, at the pH value of 6.9 (Fig. 1 curve (d)), where the transition from p-type to n-type is possible with a slight decrease in pH, a thin n-type layer could have grown on top of the p-type layer forming a p-n junction.

Fig. 2 shows the spectral response of Cu_2O films prepared in a bath of pH 6.0 containing 0.1 M sodium acetate and cupric acetate concentrations of (a) 0.0005 M, (b) 0.001 M (c) 0.002 M, (d) 0.005 M, (e) 0.008 M, and (f) 0.01 M. It is clearly seen in Fig. 2 that the films produced at lower concentrations of cupric ions , curves (a), (b) and (c), result in p-type films and at higher concentrations , curves (d), (e) and (f), result in n-type films. Most importantly, from the result given in Fig.1, the bath at pH 6.0 and cupric ion concentration of 0.01 M the film produced will be n-type. On the other hand, in Fig. 2, at

pH 6.0 and cupric ion concentrations of 0.0005 M, 0.001 M and 0.002 M deposited films are p-type. This result clearly suggests that the conduction type of the electrodeposited Cu_2O films depends not only on the pH but also on the cupric ion concentration of the bath. Further, in Fig.2 curve (c), the same tendency of long wavelength enhancement as in Fig.1 (d) is evident. The explanation given for Fig. 1 curve (d), formation of a p-n junction, will apply for Fig. 2 curve (c) too.

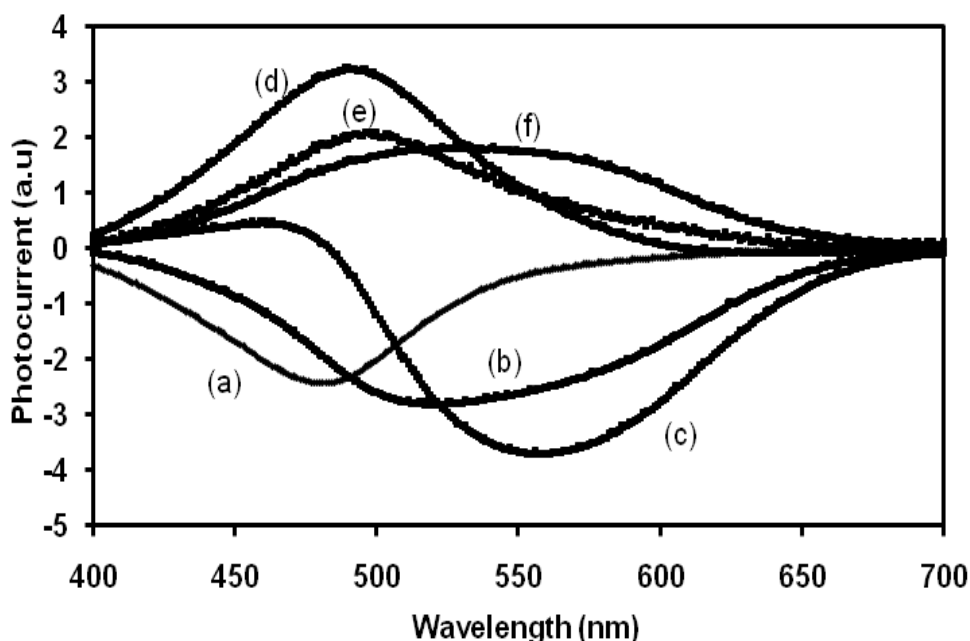


Fig. 2 Spectral photoresponse of Cu_2O films prepared in a bath containing 0.1 M sodium acetate and cupric acetate of concentration (a) 0.5 mM, (b) 0.001 M (c) 0.002M, (d) 0.005 M, (e) 0.008 M, and (f) 0.01 M. The pH value of the deposition baths is 6.0.

The conduction type of films was further verified by the capacitance-voltage measurements of the films using an electrochemical cell containing 0.1 M sodium acetate electrolyte. In general, the linear variation of $1/C^2$ vs. applied potential (Mott-Schottky plot), where C is the space charge layer capacitance of the film, gives a positive gradient for an n-type film and a negative gradient for a p-type film. The capacitance-voltage measurements on Cu_2O films prepared under different preparation conditions resulted Mott-Schottky plots giving the same n- and p- type results obtained from the spectral response measurements shown in Figures 1 and 2. As an example, Fig.3 shows the Mott-Schottky plots of the films prepared in baths containing 0.1 M sodium acetate and cupric ion concentration 0.01 M at pH (a) 6.6 and (b) 6.9 respectively.

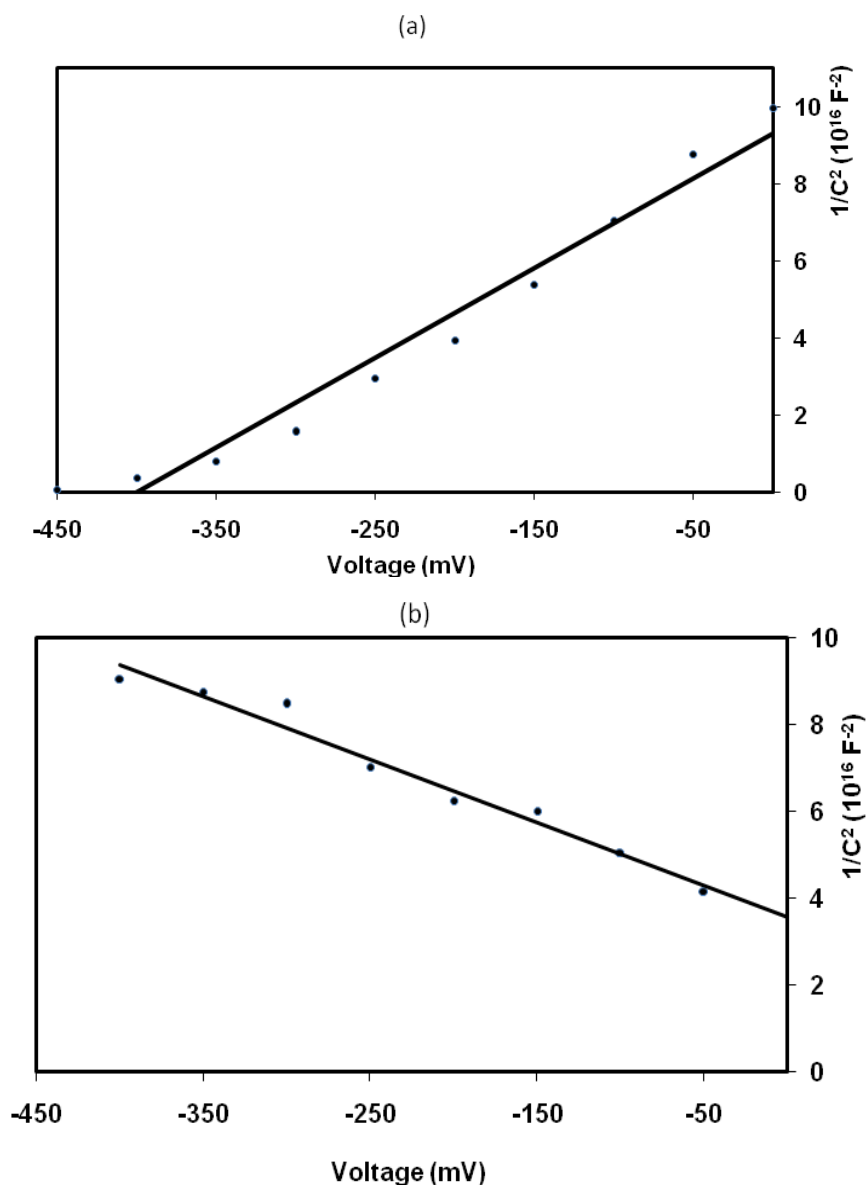


Fig. 3 Mott-Schottky plots of Cu_2O thin films deposited potentiostatically at -200 mV vs SCE at 60°C for 45 minutes duration in baths containing 0.01 M cupric acetate and 0.1 M sodium acetate of pH (a) 6.6 and (b) 6.9

In Fig.3, plot (a) shows the n-type and the plot (b) shows the p-type behaviors of the Cu_2O films. The conduction types obtained in Fig. 3 using capacitance-voltage measurements are in good agreement with the conduction types obtained in Fig.1 using photocurrent spectral response measurements.

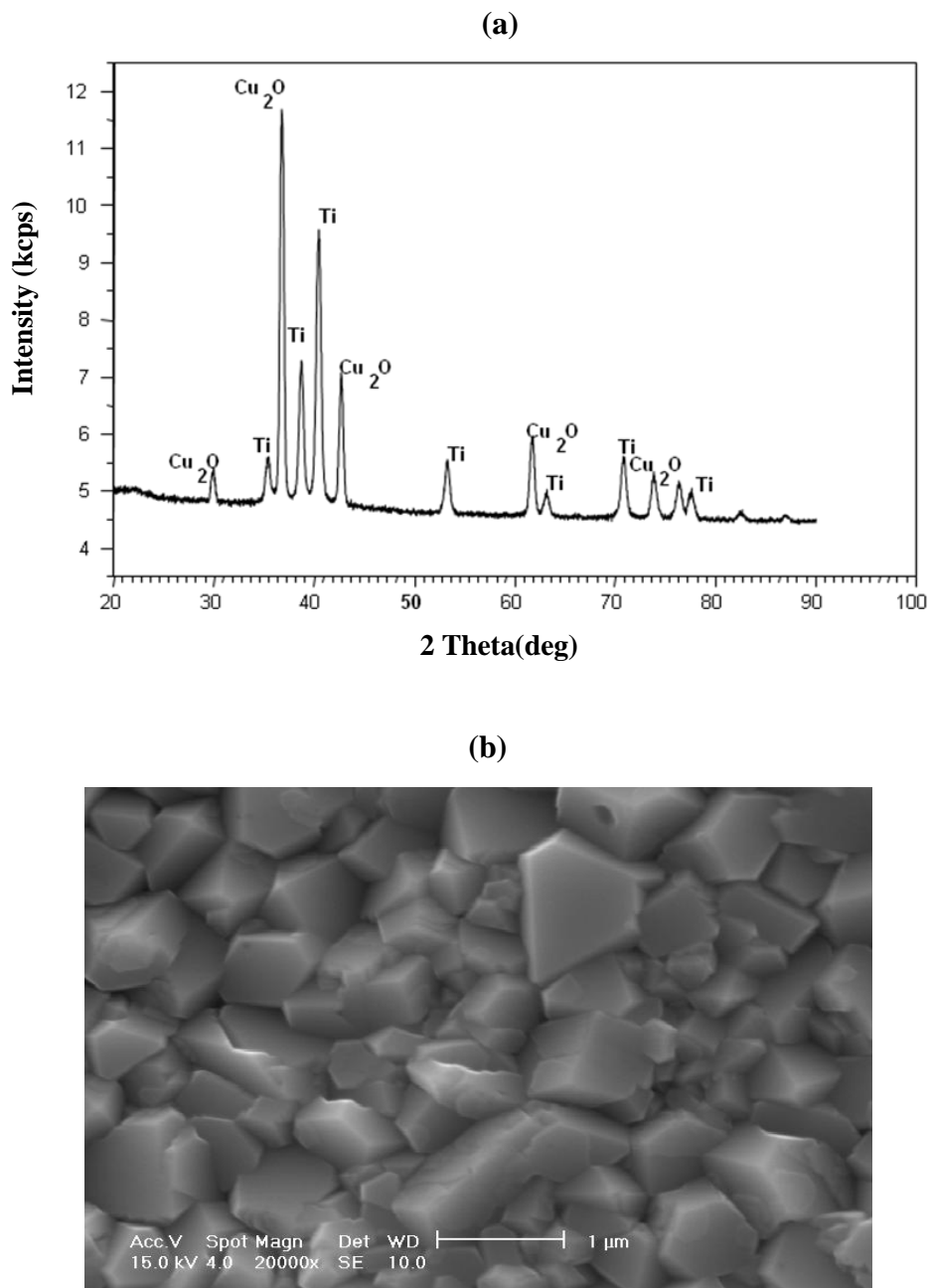


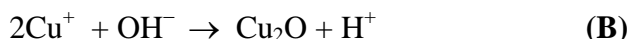
Fig. 4 (a) X-ray diffraction (XRD) spectrum and (b) scanning electron micrographs (SEM) of the Cu_2O film shown in Fig. 1(a)

Fig. 4(a) shows the X-ray diffraction (XRD) spectrum obtained for the film shown in Fig. 1(a). It is clear that the film is polycrystalline and there is no other phase except Cu_2O and Ti. Scanning electron micrographs (SEM) obtained for the same film is shown in Fig. 4(b). It shows that the film is polycrystalline and its grain sizes are in the order of 1-2 μm .

In an attempt to explain the above observations of the conduction type variation of the Cu₂O film with the pH and the cupric ion concentration of the deposition bath, we examined the reported growth mechanism of the Cu₂O films in the electrodeposition. The first step of the reaction in the electrodeposition will be the formation of Cu⁺ ions at the electrode surface due to the cathodic reaction **(A)** given below [11,18].



The second step will be the formation of Cu₂O by reacting Cu⁺ with OH⁻, as given by the reaction **(B)** below [11,18].



It is clearly seen that reaction **(B)** depends on the OH⁻ concentration (i.e. pH) of the bath. At low pH values presence of excess Cu⁺ ions may favor 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 may become n-type. This agrees well with the result shown in Fig. 1 where at low pH values and high cupric ion concentrations films grown are n-type. It has been shown earlier using photoluminescence measurements that n-type electrodeposited Cu₂O films have high density of oxygen vacancies [5]. However, when the pH of the electrolyte is higher, there will be a tendency to produce Cu₂O films with Cu vacancies. In other words, acceptor density will become significant and then the films become p-type. This agrees too with the result shown in Fig.1 where at higher pH values the resulted films are p-type. It is clear that the OH⁻ concentration value (pH) does not independently determine the conduction type but according to equation (B) it should depend on the concentration of the Cu⁺ as well. It is evident in Fig. 2 that the film produced at lower concentrations of Cu ions resulted in p-type films and higher concentrations resulted in n-type films at the pH value of 6.0. The tendency that the higher concentrations produces n-type films and the lower concentrations produces p-type films agrees well with the explanation given above that the Cu ion concentration and OH⁻ concentration of the film deposition bath determine the relative density of point defects of Cu and Oxygen vacancies in the Cu₂O films. At very low concentrations of Cu ions in the bath, according to equation (B), the tendency will be the formation of Cu vacancies in the films producing the p-type conductivity, irrespective of the pH. It is clear from the above results that the concentration of cupric ions and pH of the bath must be able to optimize to determine the values at which the n- to p-type transition occurs. In this investigation this aspect has not been studied and this will be a subject of our future investigation.

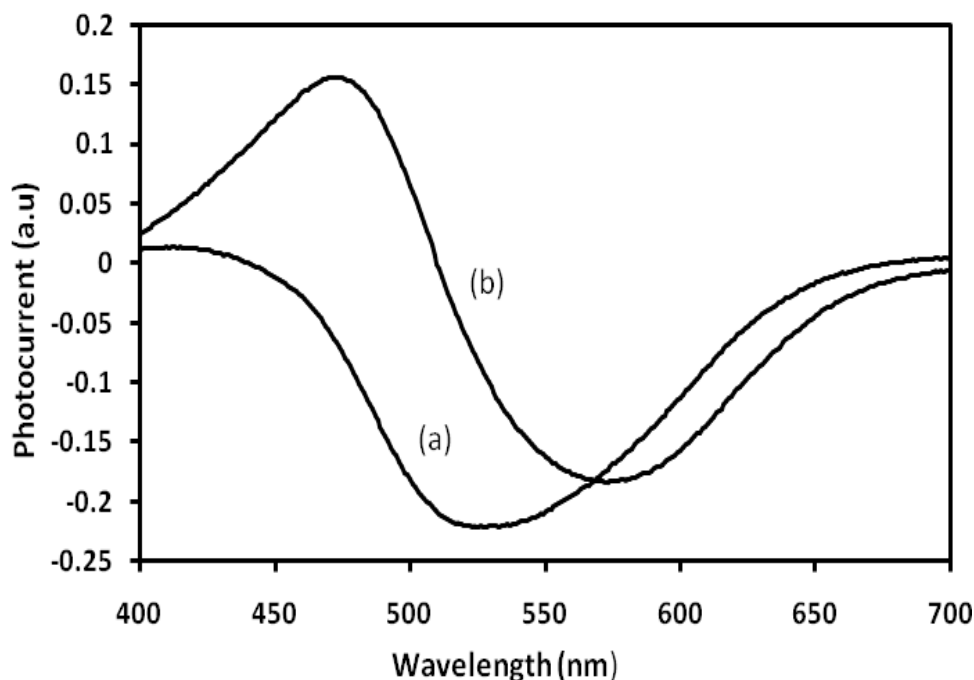


Fig. 5 Spectral photoresponse of (a) a p-type Cu_2O film deposited in the acetate bath of pH 7.9 (b) after depositing another Cu_2O film in a bath of pH 6.3 over the p-type film in (a).

The possibility of sequential deposition of the p-n homojunction is examined by depositing an n-type film on a p-type film. A similar method has been adopted by Wang and Tao in obtaining a p-n homojunction of Cu_2O using a lactate bath [12]. One of the results that we have obtained for p-n junction formation is shown in Fig. 5, where first a Cu_2O film was deposited on a Ti substrate in an acetate bath of pH =7.9 and cupric ion concentration of 0.01 M. The spectral response of the film shown in Fig. 5(a) clearly reveals that the film is p-type. When on the same film an n-type film was deposited in an acetate bath of pH= 6.3, the resulted film produced the spectral response shown in Fig. 5(b). It is evident from the photoresponse produced by the shorter wavelengths in Fig. 5(b) an n-type film is formed on top of the previously p-type film. But still in Fig. 5(b) the longer wavelengths produce the p-type signal. Since longer wavelengths have larger absorption depths, it is evident that the p-type layer still exists in the interior of the film and an n-type layer has grown over it. Change in the direction of the spectral response from n-type to p-type with the wavelength suggests that a p-n homojunction is established in addition to the Cu_2O /electrolyte junction and both junctions are photoactive. In general, by depositing a p-type layer first and then followed by the deposition of an n-type layer, p-n junctions of Cu_2O could be established using various concentrations and pH values of the deposition baths.

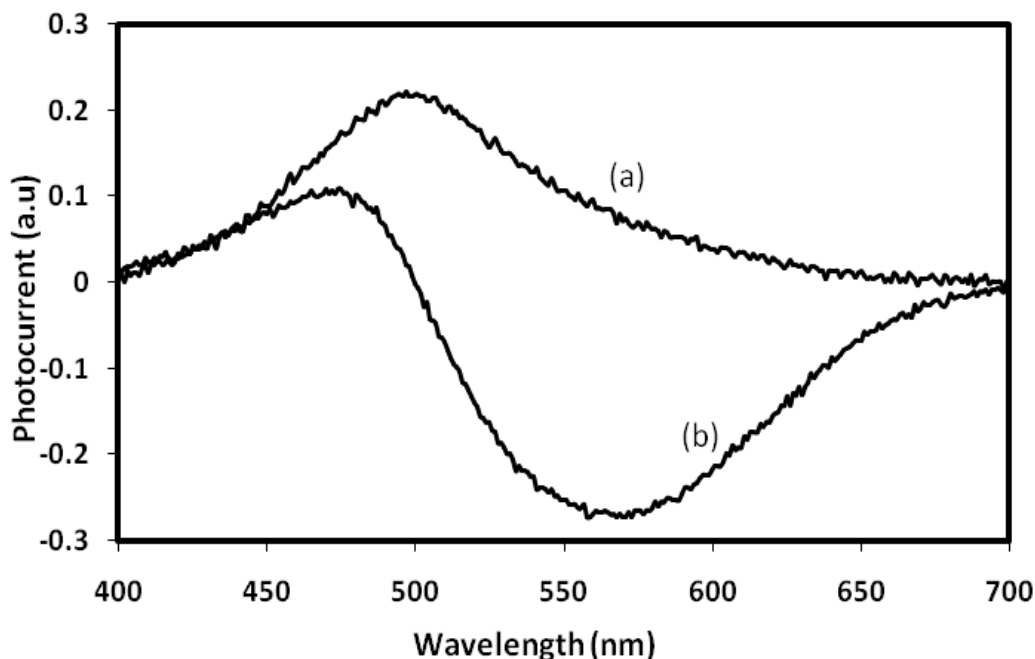


Fig. 6 Spectral photoresponse of a Cu_2O film (a) deposited in a bath of pH = 6.3 (b) after another Cu_2O film was grown in a bath of pH 7.9 over the n-type film in (a).

Fig. 6(a) shows the spectral response of a Cu_2O film deposited in a bath of pH=6.3, where the resulted film is n-type. Fig. 6(b) shows the spectral response of the film after a p-type film was attempted to grow over the n-type film. Here the electrode with the n-type film was used as the working electrode and the subsequent electrodeposition was carried out in a bath of pH=7.9 for 45 min. duration. As shown in Fig. 6(b), the long wavelength response becomes p-type and still the shorter wavelengths produce n-type photosignals. Therefore this result suggests that the interior of the film becomes p-type and outer film is still n-type. Further we have observed (not shown) that in longer duration of deposition in the bath of pH=7.9 the n-type films becomes completely p-type. As revealed by the result in Fig. 6 it is possible to grow n-type films on the p-type films of Cu_2O . However, when the electrodeposition is performed on an originally n-type film in a bath of high pH value, as shown in the results of Fig. 6, instead of growing a p-type film over the n-type film the interior of the n-type film becomes p-type. One possible explanation would be that the reaction (B) will proceed at a higher rate and Cu ions in the n-type films will also be used in the reaction creating Cu ion vacancies in the interior of the film. Then a p-type layer is gradually grown inside the film, starting from the substrate side. This explanation needs further evidences and currently we are investigating this in detail.

3. CONCLUSIONS

In conclusion we have shown, for the first time, that the conduction type, n-type or p-type, of electrodeposited cuprous oxide thin films is determined not only by the pH of the deposition bath but also by the cupric ion concentration. The general trend is that for high cupric ion concentrations, the films produced at low pH are n-type and high pH are p-type. However, at very low cupric ions concentrations p-type films could also be obtained at low pH values. Photocurrent spectral response measurements can be successfully employed to determine the conduction type variation of the films produced in the electrodeposition. Particularly the depth profile with respect to the conduction type of the film can be obtained with the spectral response measurements. Electrodeposition of p-n homojunction of Cu_2O can be obtained by sequential electrodeposition in two different acetate baths. Further, p-n homojunction of Cu_2O can also be formed in a single step electrodeposition for some pH and cupric ion concentration values of the deposition acetate bath.

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