ELSEVIER

Electrodeposition and characterization of nanocrystalline cuprous oxide thin films on TiO$_2$ films

Yiwen Tang*, Zhigang Chen, Zhijie Jia, Lisha Zhang, Jialin Li

Institute of Nano-science and technology, Central China Normal University, Wuhan 430079, China

Abstract

The grain size in cuprous oxide (Cu$_2$O) thin films is a key to improve the performance of solar application devices. In this paper, electrochemical deposition of nanocrystalline Cu$_2$O thin films on TiO$_2$ films coated on transparent conducting optically (TCO) glass substrates by cathodic reduction of cupric acetate has been investigated. The deposition kinetics of nanocrystalline Cu$_2$O thin films were studied and the parameters limiting the deposition of the films were determined. Pure Cu$_2$O deposited at bath temperature between 0 and 30 °C produced spherically shaped grains with 40~50 nm diameters which have not been reported previously. The effect of pH was studied and a solution with a pH between 5.5 and 6 was found to be best. The effect of annealing on bulk structure, electrical resistivity, and optical absorption of nanocrystalline Cu$_2$O thin films was also studied and the results were discussed.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Cuprous oxide films; Electrodeposition; Nanocrystalline; TiO$_2$ film

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 [1–4]. Among the various metal oxide materials for solar energy application, a promising material is cuprous oxide (Cu$_2$O), one of the oldest known semiconductors. It is low-cost and nontoxic and its component elements are readily available [5]. Hara et al. [6] reported Cu$_2$O as a photocatalyst for overall water splitting under visible light irradiation. Several authors also investigated Cu$_2$O thin films as photoelectrodes in

Sol. Cells [7–9]. However, Cu$_2$O has not been commonly used because of its low energy conversion efficiency ($\leq 1\%$), which results from the fact that the light-generated charge carriers in micron-sized Cu$_2$O grains are not efficiently transferred to the surface and lost due to recombination. For randomly generated charge carriers, the average diffusion time from the bulk to the surface is given by $\tau = r^2/\pi^2 D$, where r is the grain radius and D is the diffusion coefficient of the carrier [10]. If the grains radius is reduced from micron- to nano-size, the opportunities for recombination can be dramatically reduced. Therefore, the preparation of nanocrystalline Cu$_2$O thin films is a key to improve the performance of solar application devices. In addition, finding new combinations of materials to form heterojunctions with improved band matching at the interface to facilitate the carrier transfer may enhance energy conversion efficiency. For example, Siripala et al. [11] have also coupled the advantages of the chemical stability of TiO$_2$ and the photo absorbance spectrum of Cu$_2$O with their conveniently aligned inter-

---

* Corresponding author. Tel.: +86 27 67861185; fax: +86 27 67861185.

E-mail address: ywtang@phy.ccnu.edu.cn (Y. Tang).

face band structure to form n-TiO$_2$/p-Cu$_2$O heterostructure electrode to greatly improve separation of electron-hole pairs.

Based on the reasons mentioned above, photoelectrode of nanocrystalline cuprous oxide thin films on porous nano-TiO$_2$ films may tremendously improve the performances of solar application devices. This paper reports the electrodeposition of nanocrystalline Cu$_2$O thin films on nano-TiO$_2$ films. The parameters limiting the behavior of the electrodeposition of the films are discussed. Studies are focused on bulk structure, surface morphology, electrical resistivity, and optical absorption of these nanocrystalline Cu$_2$O thin films.

2. Experimental

The nanocrystalline TiO$_2$ films were prepared by the method described below [12]: TiO$_2$ powders (P25, Degussa AG of Germany) were ground in an attritor mill with ethanol containing acetylacetone for 1 h. Then, more ethanol and Triton X-100 were added and continuously ground for 3 h. The transparent conducting optically glass (TCO glass, fluorine-doped SnO$_2$-coated glass, 10 Ω/□, Asahi, Japan) was covered on two parallel edges with adhesive tape (about 40 μm thickness) to control the thickness of the TiO$_2$ film and to provide noncoated areas for electrical contact. The colloid was applied to one of the free edges of TCO glass and distributed with a glass rod sliding over the tape-covered glass. After air drying, TiO$_2$ films were annealed for 30 min at 450 °C.

A conventional three-electrode cell was used with a TiO$_2$/TCO substrate as the working electrode, platinum as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode to electrodeposit nanocrystalline Cu$_2$O films on TiO$_2$ films. The electrolyte consisted of 0.1 M sodium acetate and 0.02 M cupric acetate. The bath temperature was controlled by a DkB-501A high-precision water bath and the electrolyte was stirred continuously using a magnetic stirrer. Electrodeposition was carried out under potentiostatic mode using Princeton Applied Research Model 263A Potentiostat/Galvanostat.

The thickness of the electrodeposited nanocrystalline Cu$_2$O films was measured using Talysurf CCI 3000 surface profiler. The surface morphology of the films was studied using FEI Sirion FEG scanning electron microscope (SEM). X-ray diffraction (XRD) studies of the as prepared and annealed samples were carried out using a JEOL-JDX8030 X-ray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed using a XSAM800 system with Mg Kα radiation. Optical absorption studies were carried out employing a Shimadzu UV-2550 PC UV-VIS-NIR spectrophotometer.

3. Results and discussion

3.1. Electrochemical behavior of Cu2O films deposition on TiO2 films

The possible reactions during the cathodic reduction of cupric acetate solution are:

$$2Cu^{2+} + 2e^- + H_2O \rightarrow Cu_2O + 2H^+ \tag{1}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \tag{2}$$
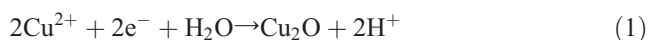
The linear sweep voltammogram of Cu$_2$O films deposition from cupric acetate solution at pH 5.8 is shown in Fig. 1. The sweep is scanned cathodically at 10 mV/s. It shows that the cathodic peak potentials are $-448(\pm2)$, $-395(\pm2)$, and $-385(\pm2)$ mV at bath temperatures of 0, 30, and 60 °C, respectively, which indicates that there are positive potential shifts with increasing temperature. Under potentiostatic conditions of lower potential, metallic Cu may form according to reaction (2), so most of the deposition of Cu$_2$O is conducted under -245 mV vs SCE.

3.2. Effect of bath temperature

The data in Fig. 2 reveal an increase in film thickness with deposition time at different bath temperatures of 0, 30, 45, and 60 °C for the electrolyte at pH 5.8. At the beginning of electrodeposition, the growth rates at different bath temperatures are high due to the porous nature and the high BET areas of the TiO$_2$ film substrate. However, after 3~5 min, the Cu$_2$O semiconductor material fills in the holes of the TiO$_2$ film and a Cu$_2$O thin film starts to appear, which results in rapidly decreasing BET areas. On the other hand, the polarizations of concentration and electrochemical reaction also increase rapidly, so the growth rates dramatically decrease. The growth rates also exhibit significant temperature dependence. When electro-
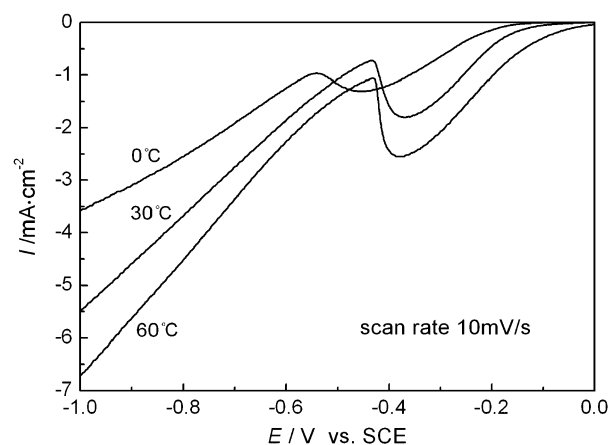

Fig. 1. Linear sweep voltammogram of Cu$_2$O deposition on TiO$_2$ film.
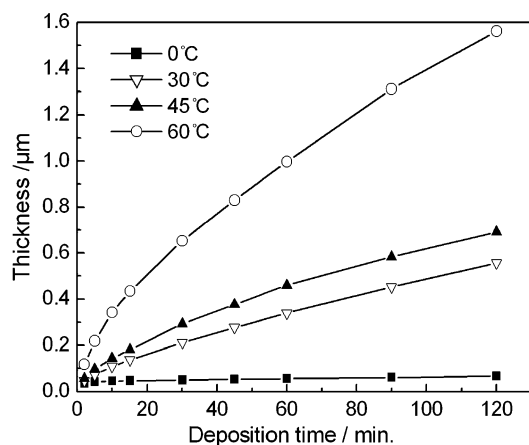
Fig. 2. Film thickness against deposited time at different bath temperatures.

deposition continues for 30 min at a bath temperature of 0 °C, the film thickness could hardly increase, remaining at about 60 nm, while the growth rates for deposition at 30, 45, and 60 °C are 3.5, 3.6 and 8.3 nm/min, respectively. Deposition kinetic studies reveal that the film thickness increases with increasing temperature for the same deposition time. Hence, deposition of Cu_2O thin films at higher temperatures is preferred.

The Cu $2p$ X-ray photoelectron spectra of the Cu_2O film electrodeposited at bath temperatures of 60 and 0 °C for 2 h are analyzed. The peaks having binding energies of 932.5 and 952.4 eV, which respectively correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu_2O, are observed. The stronger Cu $2p$ peak can be seen in the XPS spectrum of the films deposited at higher bath temperature. In particular, no small satellite peaks are accompanied, which is evidence indicating that neither Cu nor CuO coexist in the Cu_2O thin film electro-deposited at bath temperatures between 0 and 60 °C. Cu_2O thin films prepared by this method have higher purity and therefore are better than thin films electro-deposited using an electrolyte containing $CuSO_4$, lactic acid, and NaOH, in which the deposited films may have a Cu_2O/Cu composite at bath temperature <50 °C [13,14].

Scanning electron micrographs (SEM) obtained on Cu_2O thin film surfaces deposited at different bath temperatures for 2 h are shown in Fig. 3. In the case of 0 (Fig. 3A) and 30 °C (Fig. 3B), spherically shaped grains with a 40~50 nm diameter are observed. Similar grain structures have not been previously reported for the electrodeposited Cu_2O thin films. However, for bath temperatures above 38 °C, Cu_2O grain size rapidly goes up. Electrodepositing at 45 °C considerably changes the surface morphology, promotes the formation of highly branched dendrite, and enlarges the grain size from
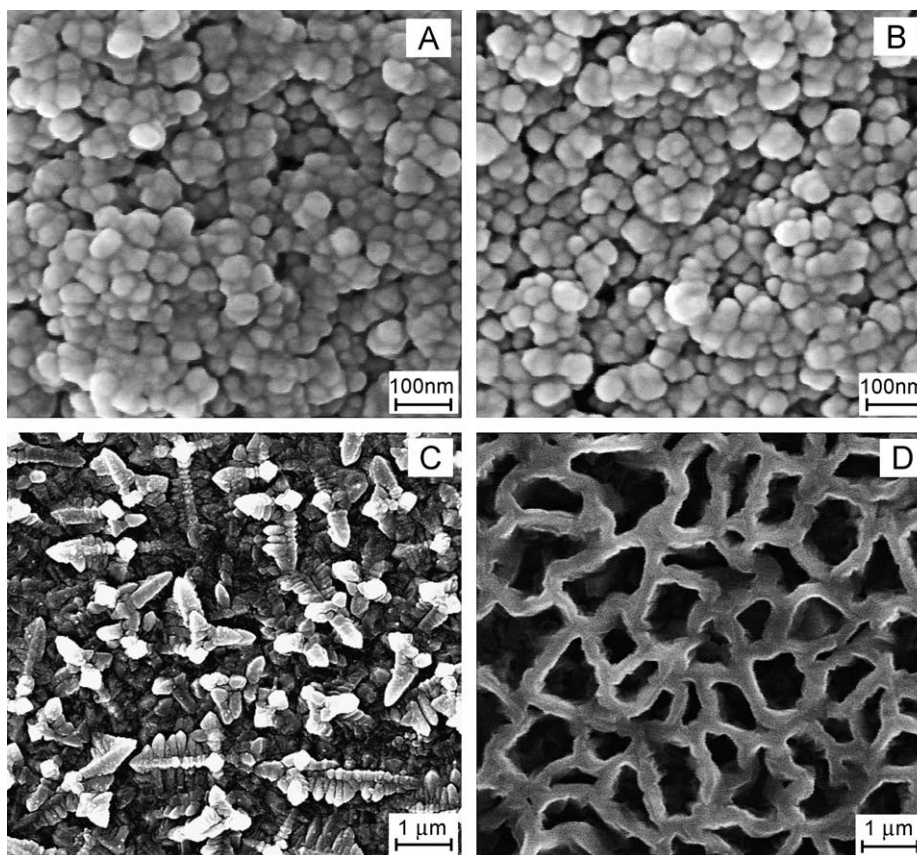

Fig. 3. SEM photographs of Cu_2O films deposited at various bath temperatures: (A) 0, (B) 30, (C) 45, and (D) 60 °C.
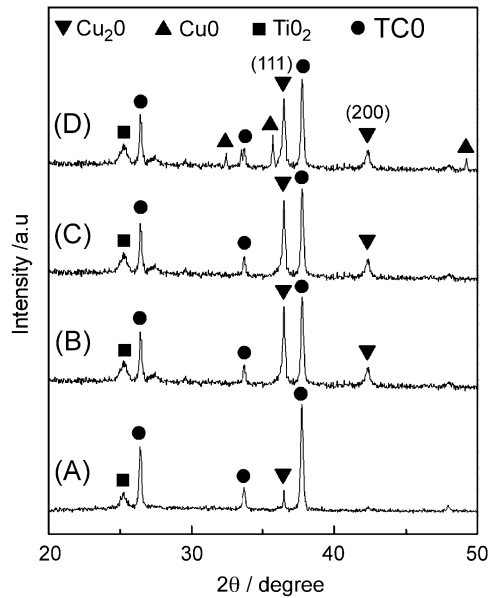
Fig. 4. X-ray diffraction patterns for the Cu_2O films as prepared at (A) 0 and (B) 30 °C and for the Cu_2O films annealed at (C) 300 and (D) 400 °C.

40~50 to 200~500 nm as demonstrated in Fig. 3(C). Furthermore, electrodepositing at 60 °C changes again the surface morphology by forming ring shaped structures introducing a more porous nature of the surface as showed in Fig. 3(D), which undoubtedly results from the fact that the branched dendrites of Cu_2O epitaxially grow and link together to form a ring. Therefore, the bath temperature must be controlled in the range of 0~30 °C to obtain nanocrystalline Cu_2O thin film.

Fig. 4(A) and (B) show the XRD spectrum of Cu_2O thin films electrodeposited at bath temperatures of 0 and 30 °C for 2 h. Both samples are crystalline as seen from the well-defined peaks in the pattern. Besides the characteristic peaks of the TCO glass and the TiO_2 film substrate, two characteristic diffraction peaks of the Cu_2O thin films (JCPDS 5-667) at 2θ values of 36.419° and 42.298° respectively corresponding to the reflections from the (111) and (200) planes are observed. With increase of bath temperature from 0 to 30 °C, the relative intensities of characteristic peaks of Cu_2O rapidly goes up, which result from increase of the thickness of the Cu_2O thin films. Furthermore, the characteristic peaks of Cu and CuO are not found, which also testifies to the superiority of this method with regard to film purity.

3.3. Effect of pH

The effect of bath pH on electrodeposition of Cu_2O thin film are investigated by selecting a bath temperature of 30 °C and an applied potential of −245 mV (vs. SCE). The pH is adjusted between 3 and 8 by the addition of sodium hydroxide or acetic acid. The films deposited at pH<4 are mostly metallic Cu and there is

little Cu_2O found (according to reaction (2) and the following reaction: $Cu_2O+2e^-+2H^+\rightarrow2Cu+H_2O$). In the region of 4<pH<5.5, the deposited films are a composite of Cu and Cu_2O according to the Cu $2p$ X-ray photoelectron spectra of the Cu_2O film, while the films deposited at pH between 5.5 and 6 are pure Cu_2O. With a further increase in pH, most cupric acetate in the electrolyte will hydrolyze to become the precipitate of $Cu(OH)_2$, which decreases the concentration of Cu^{2+}. Thus, electrodeposition carried out in the pH region 5.5~6 can yield good-quality Cu_2O thin films.

3.4. Annealing effect

The nanocrystalline Cu_2O films deposited at 30 °C for 2 h (film thickness of 0.56 μm) are annealed in air for 30 min at different annealing temperatures of 200, 300, and 400 °C. Fig. 4(C) and (D) show, respectively, the XRD spectrum of Cu_2O thin films annealed at 300 and 400 °C. There is no apparent change in the bulk structure after annealed at 300 °C. However, the new peaks corresponding to CuO have been observed in the spectrum of Cu_2O film annealed at 400 °C. The heat treatment in air at a temperature above 300 °C therefore causes the oxidation of Cu_2O.

The room temperature resistivity of the Cu_2O films as prepared and annealed at different temperature is measured. The resistivity of the Cu_2O films as prepared is 2×10^6 Ω cm, but that of the Cu_2O films annealed at 200, 300, and 400 °C is, respectively, 6×10^5, 2×10^5, 1×10^4 Ω cm. It is clear that annealing decreases the resistivity of Cu_2O thin films, which may be due to increase in hole conduction [13].

3.5. Optical properties

Fig. 5 shows the spectrophotometric transmittance of electrodeposited Cu_2O thin films annealed in air for 30 min at different temperatures, along with that of an as
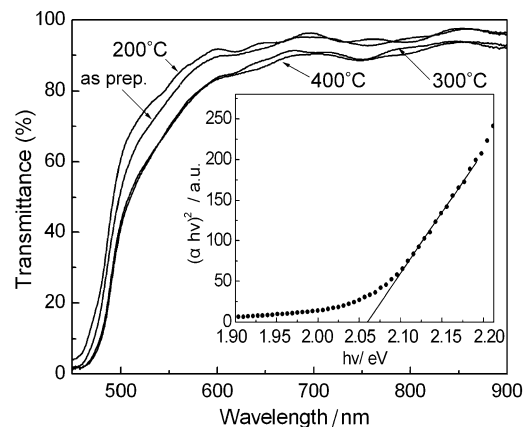

Fig. 5. Optical transmission spectrum of the Cu_2O films as prepared and annealed at different temperature. Inset shows the determination of the optical energy gap for as-deposited film.

prepared sample. With the decreasing wavelength of radiation, the transmittance of all samples tended to be lowered. In the case of an annealing temperature of 200 °C, the transmittance of the film is found to be better compared to that of the other films. Considering the fact that even at long wavelength, where the relative size of grain-to-wavelength is reduced, the transmittance of the films (as prepared, annealed at 300 and 400 °C) is not increased. It is possible that the transmittance of the films was influenced by scattering due to irregular grains or aggregates [7]. The absorption coefficient satisfies the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for a direct band gap material. The band gap (E_g) is obtained by extrapolation of the plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ and is found to be 2.06 eV for as-deposited film (see inset of Fig. 5). Results for annealed samples are very similar to that of as-deposited film. However, E_g of this nanocrystalline Cu_2O thin film is higher than the value of Refs. [15,16], which may be influenced by scattering [7].

4. Conclusions

In this work, we report the electrochemical deposition of nanocrystalline Cu_2O thin films on TiO_2 films coated on transparent conducting optically glass substrates by cathodic reduction of cupric acetate. The applied potential is conducted under -245 mV vs. SCE. The bath temperature and pH have strong effect on the composition and microstructure of the Cu_2O thin films, and the film thickness rapidly increases with bath temperature. Annealing in air at a temperature above 300 °C causes the oxidation of Cu_2O and annealing decreases the electrical resistivity of nanocrystalline Cu_2O thin films. Optical absorption measurements indicate that annealing at 200 °C can improve the transmittance of the nanocrystalline Cu_2O thin films and the band gap of nanocrystalline Cu_2O thin films is 2.06 eV.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] A.J. Nozik, Annu. Rev. Phys. Chem. 29 (1978) 189.
[3] M.S. Wrighton, Acc. Chem. Res. 12 (1979) 303.
[4] R. Memming, Electrochim. Acta 25 (1980) 77.
[5] P.E. de Jongh, D. Vanmaekelbergh, J.J. Kelly, J. Electrochem. Soc. 147 (2000) 486.
[6] M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanake, J.N. Kendo, K. Domen, Chem. Commun. (1998) 357.
[7] K.H. Yoon, W.J. Choi, D.H. Kang, Thin Solid Films 372 (2000) 250.
[8] V. Georgieva, M. Ristov, Solar energy mater, Sol. Cells 73 (2002) 67.
[9] T. Mahalingam, J.S.P. Chitra, G. Ravi, J.P. Chu, P.J. Sebastian, Surf. Coat. Technol. 168 (2003) 111.
[10] G. Rothenberger, J. Moser, M. Gratzel, J. Am. Chem. Soc. 107 (1985) 8054.
[11] W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S. Baeck, E.W. Mcfarland, Solar energy mater, Sol. Cells 77 (2003) 229.
[12] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382.
[13] T. Mahalingam, J.S.P. Chitra, S. Rajendran, M. Jayachandran, M.J. Chockalingam, J. Cryst. Growth 216 (2000) 304.
[14] Y.C. Zhou, S. Jay, Chin. J. Mater. Res. 10 (1996) 512.
[15] A. Aveline, I.R. Bonilla, Sol. Energy Mater. 5 (1981) 211.
[16] A.E. Rakhshani, Solid-State Electron. 29 (1986) 7.