Research Article

Potentiostatic Deposition and Characterization of Cuprous Oxide Thin Films

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Electrodeposition technique was employed to deposit cuprous oxide Cu_2O thin films. In this work, Cu_2O thin films have been grown on fluorine doped tin oxide (FTO) transparent conducting glass as a substrate by potentiostatic deposition of cupric acetate. The effect of deposition time on the morphologies, crystalline, and optical quality of Cu_2O thin films was investigated.

1. Introduction

Cuprous oxide is known as P-type semiconductor with a direct band gap that absorbs solar radiation up to 650 nm [1]. Cu_2O belongs to I–VI semiconductor compounds. Cu_2O has been researched as a potential material for photovoltaic applications for several reasons: source materials are abundant and nontoxic, band gap of 1.9–2.2 eV, which can be possibly adjusted by controlling the compositions [2], can be prepared with simple and cheap methods on large scale, and theoretical solar cell efficiency is approximately 20% [3–5]. All of these properties make Cu_2O a suitable material for many potential applications in solar energy conversion, electrode materials, sensors, and catalysis [6–9]. Various methods have been employed for the synthesis of Cu_2O such as thermal oxidation, thermal evaporation, sol-gel, spray pyrolysis, reactive magnetron sputtering, RF magnetron sputtering, and electrodeposition [10–16]. Among them electrodeposition has shown many advantages; it is a simple, economical method for preparation of large area films with good homogeneity, and it allows a good control for the growth parameters. Electrodeposition of Cu_2O involves two steps: the first step is reduction of Cu^{2+} ions to Cu^+ ions (1) and the second step is precipitation of Cu^+ ions to Cu_2O because of the solubility limitation of Cu^+ ions (2) [17]

In this study, the effect of deposition time on the morphologies, crystal and optical quality of electrodeposited thin films is investigated.

2. Experimental Details

Electrodeposition of Cu_2O was carried out in a three-electrode setup consisting of platinum wire counter electrode, Ag/AgCl reference electrode, and FTO-coated glass substrate as a working electrode. Before the electrodeposition, the FTO substrates were precleaned by sonication in acetone, isopropanol, and deionized water for 10 minutes, respectively, and then dried at 105°C for several hours. The electrolyte used was composed of 0.02 M cupric acetate and 0.1 M sodium acetate with pH 5.8. The electrodeposition was performed at fixed potential -0.50 V versus Ag/AgCl reference electrode using Bio-Logic SP-50 potentiostat at 60°C. A series of samples were deposited at 5, 10, 15, and 30 minutes.

The morphology of the deposited films at different experimental conditions was characterized by scanning electron

FIGURE 1: SEM photographs of Cu_2O thin films deposited at various deposition times: (a) 5, (b) 10, (c) 15, and (d) 30 min.

FIGURE 2: XRD pattern of deposited Cu_2O film in electrolyte containing 0.02 M copper acetate and 0.1 M sodium acetate at pH 5.8 for (a) 5, (b) 10, (c) 15, and (d) 30 min (* refers to FTO substrates).

FIGURE 3: The variation of $(\alpha h\nu)^2$ against photon energy E (eV) for deposited Cu_2O films at different deposition times: (a) 5, (b) 10, (c) 15, and (d) 30 min.

microscopy (SEM). Crystal structures and phase compositions of the films were measured by X-ray diffraction analysis using XRD-6000 Shimadzu diffractometer using Cu K_α radiation (40 Kv, 30 mA). Optical studies were carried out by recording the optical absorption spectra of the films using UV-VIS Shimadzu spectrophotometer.

3. Results and Discussion

Figure 1 shows SEM photographs of Cu_2O thin films electrodeposited on FTO substrate at -0.5 V versus Ag/AgCl reference electrode for 5, 10, 15, and 30 minutes. In the beginning of the deposition after 5 min, a small grains starts to nucleate on the substrate surface to form cubic islands as shown in Figure 1(a). As the deposition time increased to 10 min, the density of cube islands increased and they are interconnected with each other to change the surface morphology to be ring-shaped structures as shown in Figure 1(b) [18]. By continuing the deposition process to 15 min, spherical grain started to appear on the surface (Figure 1(c)). Finally after 30 min deposition time, it was found that the density of the spherical grains increased to cover most of the surface as it is clear in Figure 1(d) [19].

To identify the crystal structure of the deposited films XRD measurements were carried out. These measurements indicated that all samples are crystalline and the crystallographic phase of the films is cubic as it is clear from the well-defined peaks in Figure 2. At the deposition time of 5 min and 10 min, besides the characteristic peaks of the FTO glass substrate, three characteristic diffraction peaks of the Cu_2O thin film at 2θ values of 36.62° , 42.54° , and 62.14° , respectively, corresponding to the reflections from the (111), (200), and (220) planes are observed (Figures 2(a) and 2(b)). Except for the diffraction of Cu_2O and FTO substrate, there are no

other peaks observed, which means that pure Cu_2O can be obtained through electrodeposition and no impurity phase was observed.

As the deposition time increased to 15 min, in addition to XRD peaks of Cu_2O , the diffraction peak related to (111) plane of Cu metal appears as shown in Figure 2(c). With increasing the deposition time to 30 min, the intensity of the Cu metal peak increased (Figure 2(d)). These XRD results are in good agreement with the SEM results where some spherical grains started to appear at 15 min of growth. We observed before in SEM results that some spherical grains started to appear at 15 min which is the same time when Cu metallic characteristic peak appears in XRD chart. From both SEM and XRD one can explain that these spherical grains are metallic copper. Song et al. have proved this explanation with XPS (X-ray Photoelectron Spectra) measurements [19].

The optical absorption of electrodeposited Cu_2O films was recorded using a double-beam spectrophotometer in the wavelength region 200–800 nm.

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 $(\alpha h\nu)^2$ versus E where α is the absorption coefficient as shown in Figure 3 and was found to be 1.99 eV–2.16 eV for the deposited films, which agrees well with the values reported earlier [1].

4. Conclusion

In this work, we report the electrochemical deposition of Cu_2O thin films on FTO substrate by cathodic reduction of cupric acetate. The applied potential was -0.5 V versus Ag/AgCl reference electrode. We found that the deposition time has strong effect on the composition and crystal quality

of the Cu_2O thin films and 10 minutes is the preferable time for the deposition of high-quality Cu_2O thin films. Optical absorption measurements indicate that the band gap of Cu_2O thin films is 1.9–2.1 eV.

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