Photoassisted Electrodeposition of a Copper(I) Oxide Film

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Photoassisted electrodeposition of a cuprous oxide (Cu_2O) thin film was studied to find the optimum conditions lowering the deposition temperature. Cu_2O films were electrochemically deposited on FTO by cycling the electrode potential between 0.0 V and -0.8 V (Ag|AgCl), in an aqueous solution. A simple deposition cell was designed to allow simultaneous thermostating and polychromatic illumination. Under illumination, the Cu_2O film deposition occurred, even at a temperature lower than the temperature observed under dark conditions. X-ray diffraction (XRD) analysis confirmed that these films were indexed as cubic symmetric structured pure Cu_2O (JCPDS: 05-0667), and UV-visible absorption spectra show an optical band-gap energy of 2.5 eV. [doi:10.2320/matertrans.M2014391]

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1. Introduction

Electrodeposition (electrochemical deposition) of cuprous oxide (Cu_2O) has been widely studied for a rechargeable battery electrode,^{1,2)} a catalyst,^{3–7)} a sensor,^{8,9)} and as a sensitizer for solar cells.^{10–13)} The compound is especially attractive in photovoltaic devices because of its suitable band-gap energy. Additionally, its abundance and non-toxicity make Cu_2O an excellent candidate for large scale utilization in photovoltaic devices. Electrodeposition¹⁴⁾ has many advantages such as low cost, simple processes, and controllable thickness and structure of the films. Many studies have reported nanostructured Cu_2O deposition,^{2,15,16)} particle shape,^{3,11,12,17)} deposition temperature,^{18,19)} and film orientation control²⁰⁾ using electrodeposition methods. The electrodeposition of the Cu_2O film was usually achieved at temperatures^{5,10,20–23)} higher than room temperature to overcome the activation energy. We employed a photoassisted electrodeposition system, using a high-powered Xe-lamp as another energy source, which is expected to accelerate the rate of electrodeposition. Photoirradiation of the electrodeposition process^{13,24,25)} has additional advantages, such as the capability to grow both thin and thick high-quality films, with higher growth rate and less negative deposition potential. The photoassisted chemical deposition of p- Cu_2O /n-ZnO was reported for the construction of a heterostructure on a quartz glass.²⁶⁾

In this paper, we described a simple deposition cell, which was controlled by a thermostat and subjected to photo-irradiation at the same time. The deposition cell was constructed with a glass body, with the top and bottom sealed using Teflon[®] plates. At the bottom a transparent glass electrode, such as fluorine doped tin oxide (FTO), was fitted. Therefore, light could pass from the back side to the front active side of the FTO. We carried out the photoassisted electrodeposition of a Cu_2O film and determined the effect of the presence or absence of a polychromatic light source on the electrodeposited Cu_2O films.

2. Experimental Procedure

Photoassisted electrodeposition of Cu_2O was carried

out by cyclic voltammetry (CV), in an aqueous solution containing $0.10 \text{ mol}\cdot\text{L}^{-1}$ $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (99.0% Kanto Chemicals, Japan) and $1 \text{ mol}\cdot\text{L}^{-1}$ lactic acid (99% Kanto Chemicals, Japan). The pH of the solutions was adjusted to 12.7 with a concentrated NaOH solution (Dae-Jung Chemicals, Korea). A transparent conducting glass (fluorine doped tin oxide; FTO, TEC 8, Pilkington, USA) and a Pt mesh (99.99%, Sigma-Aldrich, USA) were used as the working electrode (deposition substrate) and the counter electrode, respectively. A reference electrode, Ag|AgCl (saturated KCl) was encased in a bridge tube, connected to the solution by a Vycor tip. All the potentials were measured against this reference electrode. For the CV, the potential scan was started at 0 V (Ag|AgCl), reversed at -0.8 V, and then terminated at 0 V, with 20 cycles of repetition, at a scan rate of 0.05 V s^{-1} . X-ray diffraction (XRD) patterns were measured with a Rigaku X-ray diffractometer (Tokyo, Japan) using $\text{Cu K}\alpha$ (40 kV, 30 mA) radiation. The 2θ range, from 20 to 70° , was scanned at 3°min^{-1} . The surface images of the films was observed using a scanning electron microscope (SEM; Philips XL-30 ESEM, USA). Optical studies were performed on the films deposited on the FTO substrates using an Agilent 8453 UV-Vis spectrophotometer (Palo Alto, CA, USA).

The photoassisted electrodeposition cell is shown in Fig. 1. A cylindrical water jacketed glass tube (Fig. 1-5) and three Teflon[®] plates (Fig. 1-4), one positioned at the top and two at the bottom of the glass tube, were clamped together using four sets of screw bolts and nuts. The working electrode, FTO-glass (Fig. 1-6), was positioned on the lowest Teflon[®] plate (Fig. 1-7) through which a bundle of optical fibers was inserted. The light source, 150 W Xe-lamp, used for photoassistance was irradiating at a wavelength above 230 nm (LS 150 Xe, Abet Technologies, Inc., USA).

3. Results and Discussions

The electrodeposition of the Cu_2O film was carried out using an electrode potential cycling between 0.0 V and -0.8 V (Ag|AgCl) in the lactic acid electrolyte solution (at pH 12.7), containing $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ as the precursor. As shown in Fig. 2, the well-defined cathodic peak arises from the reduction current of Cu^{2+} to Cu^0 at -0.6 V in the 1st cycle, and is followed by the current looping back when the direction of the potential change is reversed. This type of

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Fig. 1 Schematic diagrams and photographs of a photoassisted electro-deposition cell. 1. FTO working electrode and copper plate, for electrical contact; 2. Pt-mesh counter electrode; 3. Ag|AgCl reference electrode; 4. Teflon® plate; 5. Water-jacketed cylindrical body; 6. Front active surface of FTO; and 7. Insertion port for the fiber optic bundle (connected to the irradiation source).

hysteresis loop is a characteristic feature of a nucleation and growth-deposition process.^{27,28} The possible reaction during the cathodic reduction of Cu^{2+} in alkaline solution is:²⁹

The reduction current nearly vanished on the 2nd cycle, and the currents gradually increased later. This dramatic decrease in current is considered to be due to the change in conductivity between a bare FTO surface and the nucleated surface. Figure 2 shows the effects of temperature and light during the Cu_2O film deposition. Improvements in the film deposition were achieved by increasing the temperature, regardless of whether the experiment was conducted in darkness (Fig. 2(a)) or with illumination (Fig. 2(b)). (The improvements in the film deposition were confirmed by XRD analysis, shown in Fig. 4, as discussed below.) Under illumination, however, the Cu_2O deposition was enhanced, even at room temperature.

The cathodic process (C1) and anodic process (A1) in Fig. 3 are associated with the quasi-reversible Cu_2O -electrocatalysis as represented by the following reactions (eq. (2)). The formation of Cu_2O occurred in the C1-process and CuO is in the A1-process. The A1-process remained under the dark conditions, but the C1-process gradually disappeared under illumination and increasing temperature, shown in Fig. 2.

Under illumination, in Fig. 2(b) and Fig. 3(b), enhanced electrocatalytic processes are understood to be due to photoexcited electrons and photoinduced holes. At the lower temperature, 293 K and 303 K, the cathodic electrocatalytic currents (C1) increased more under illumination. The deposition of Cu_2O could be confirmed by the clear color change of the FTO surface, as shown in Fig. 2. Plain-view

Fig. 2 Cyclic voltammograms of Cu_2O film electrodeposition on FTO in aqueous $0.10 \text{ mol}\cdot\text{L}^{-1} \text{ CuSO}_4$ and $1 \text{ mol}\cdot\text{L}^{-1}$ lactic acid solution adjusted to pH 12.7 with NaOH, obtained in darkness (a) and with irradiation (b). Potential scan was started at 0 V (Ag|AgCl), reversed at -0.8 V , and then terminated at 0 V, with 20 cycles of repetition, at a scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$.

SEM images of electrodeposited films obtained at 293 K in Fig. 2(a) and (b) were shown in Fig. 3(a) and (b), respectively.

In Fig. 2 and Fig. 3, especially at the curved arrow in Fig. 3(b), the anodic reduction peak (near -0.4 V) featuring adsorption phenomena, is relevant to C2, which seems to be related to the adsorption of oxygen dissolved in the electrolyte solution; $\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{ads})$ following the reduction; $\text{O}_2(\text{ads}) + \text{e}^- \rightarrow \text{O}_2^-(\text{ads})$. The reduced and adsorbed oxygen ion, $\text{O}_2^-(\text{ads})$, is likely to be desorbed and reduced to the more stable oxygen anion, $\text{O}^{2-}(\text{aq})$ during the reversal of the anodic scan.³⁰ As the temperature was elevated, the reduction process (C2) and the anodic reduction peak could not be observed because of the decrease in solubility of the dissolved oxygen, regardless of whether the experiment was conducted with or without light. More detailed studies are necessary for the anodic reduction peaks:

The electrodeposited Cu_2O films in this study are photo-responsive semiconductor materials. The desorbed oxygen anion, $\text{O}^{2-}(\text{aq})$, seems to have been oxidized by the photoinduced hole (h^+_{ph}) in the anodic process (A1). The

Fig. 3 Cyclic voltammograms, at 293 K, showing the 1st cycle (dotted line) and the 20th cycle (solid line), obtained in darkness (a) and with irradiation (b), under the same conditions as Fig. 2.

oxidized oxygen was reduced by the photoexcited electron (e^-_{ph}) in the cathodic process (C1). In Fig. 2, when the dissolved oxygen concentration was high at low temperatures, these processes (A1 and C1 in Fig. 3) were clearly observed:

A1; photoinduced hole:

C1; photoexcited electron:

To identify the electrodeposited films, XRD analysis was carried out, as shown in Fig. 4. The three peaks appearing at 36.4° , 42.3° , and 61.3° were indexed, respectively, to the 111, 200, and 220 crystal planes of Cu_2O with cubic symmetry (JCPDS 05-0667). The 61.3° peak (220) was unfortunately superimposed on the 61.7° peak for FTO. Cu_2O films exhibited moderately weaker peaks than the underlying FTO thin films. With increasing temperature, the full width at half maximum (FWHM) of the (111) peak decreased. At 323 K and 333 K, FWHMs of the more intense peak (111) were obtained, by Lorentzian fitting, as 0.54° and 0.49° , respectively, under the dark condition, but at 293 K, 303 K, and 313 K, the FWHM could not be calculated. While under illumination, FWHMs at 323 K and 333 K were simulated as 0.44° and 0.45° , respectively, and at 293 K, 303 K, and 313 K as 0.82° , 0.56° , and 0.44° , respectively. The differ-

Fig. 4 XRD spectra of the electrodeposited Cu_2O films, obtained in darkness (a) and with irradiation (b), under the same conditions as Fig. 2.

Fig. 5 Plots of $(\alpha h\nu)^2$ vs. photon energy for determination of the band-gap energies for Cu_2O films by cyclic voltammetry, at 293 K, for electrodeposition in darkness (a) and with irradiation (b).

ence in area and height of the (111) peak at 333 K, between the dark and light experiments, was 2.38 times and 2.56, respectively. These values led us to assume that the Cu_2O electrodeposition was effected by increasing temperature, which increases the diffusion rate of precursors in the electrolyte solution and lowers the activation energy. Furthermore, light exposure during the electrodeposition accelerates the growth of Cu_2O films because the Cu_2O film possesses the characteristics of a semiconductor that is responsive to the light.

Color variations after the 5th cycle of CV were observed on the FTO-surface, owing to the buildup of a film with a characteristic yellow or green color, in the dark or in the light, respectively, as can be seen in the images in Fig. 5. Optical absorption studies of the Cu_2O films were carried out in the wavelength range 280–1100 nm. To estimate the band-gap energy (E_g) of the Cu_2O , the values of $(\alpha h\nu)^2$ versus $h\nu$ were plotted in Fig. 5. The optical band-gap was calculated using the Tauc relation:³¹⁾

$$\alpha h\nu = A(h\nu - E_g)^m \quad (7)$$

Fig. 6 Schematic electrodepositions of Cu_2O for FTO|Solution (a) and FTO| Cu_2O |Solution (b) systems.

$$\alpha = \ln \left(\frac{1}{T} \right) / d \quad (8)$$

where A is a constant, $h\nu$ is the incident photon energy, α is absorption coefficient, E_g is the band-gap energy of the film, $m = 2$ for the allowed direct transition, T is transmittance and d is the film thickness. The direct band-gap of Cu_2O films electrodeposited in the dark (Fig. 5(a)) and under illumination (Fig. 5(b)) was determined by extrapolating the straight line to the energy axis and were found to be around 2.5 to 2.6 eV. These measured values of E_g were larger than typical values (2.1 eV) accepted for polycrystalline Cu_2O films suitable for hetero junction solar cells used to mate with the Cu_2O , such as ZnO ,³²⁾ TiO_2 ,³³⁾ In_2S_3 ,³⁴⁾ and CdO .³⁵⁾ The expansion of band-gap energy could be explained by the change of lattice parameter due to trace amounts of impurities incorporated in the electrodeposition of Cu_2O .^{36,37)}

The photoassisted electrodeposition enhancement is schematically discussed in Fig. 6. In first cathodic sweep Cu^{2+} ions were reduced by electrochemical processes to Cu_2O on the optically transparent conducting glass (FTO) such as in Fig. 6(a). The semiconductor Cu_2O deposited on FTO was excited by absorption of photons so photoexcited electrons (e^-_{ph}) diffused toward the interface of the solution were participated in the electrochemical deposition of Cu_2O as in Fig. 6(b).

4. Conclusion

In this work, Cu_2O films were electrochemically deposited on FTO in the dark and in the light, from an aqueous CuSO_4 and lactic acid solution adjusted to pH 12 with NaOH. Both deposited films were identified as having cubic symmetry structured Cu_2O . The deposition rate was found to be higher under illumination than in the dark, at the same temperature. The driving force under illumination was considered to be a photoinduced hole produced from a valence band of the Cu_2O semiconductor film. We conclude that the photo-assisted electrodeposition of Cu_2O could be a useful method for lowering the temperature and shortening the deposition time. Further study is taking place to examine the mechanism closely and to ascertain whether other compounds may be used.

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