

Control of native acceptor density in epitaxial Cu₂O thin films grown by electrochemical deposition

Atsushi Ashida*, Shunsuke Sato, Takeshi Yoshimura, Norifumi Fujimura

Graduate School of Engineering, Osaka Prefecture Univ., Naka-ku, Sakai, Japan

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ABSTRACT

Controlling the native carrier is essential for using Cu₂O in devices such as solar cells. The origin of the native p-type carrier in Cu₂O is thought to be copper vacancies (V_{Cu}). In this work, epitaxially grown Cu₂O thin films were prepared by electrochemical deposition at a low temperature of 45 °C on a Pt (111) cathodic electrode. The sources of Cu and O for Cu₂O were Cu²⁺ and OH⁻ in the electrolyte and the ion concentrations were changed to control the stoichiometry of deposition and the density of V_{Cu} . The density of ionized acceptors (N_A^+) in the Cu₂O films was evaluated by the C-V properties measured with Schottky electrodes. N_A^+ did not depend on [Cu²⁺], whereas N_A^+ increased with increasing [OH⁻] when [OH⁻] was larger than 10⁻³ mol/L (electrolyte pH >11) with [Cu²⁺] fixed at 10⁻¹ mol/L. The ion concentration dependence of N_A^+ and the dependence of the total cathodic current density revealed that the generation of V_{Cu} was affected by a complex combination of the ion concentrations and film growth rate.

1. Introduction

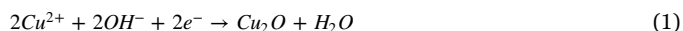
Copper(I) oxide (Cu₂O) is a cubic traditional semiconductor that displays native p-type conduction and a band gap of 2.1–2.4 eV [1–3], and is used in rectifiers [4] and ship bottom paint [5]. Cu₂O is also promising for solar cells [6] because of its relatively large optical absorption coefficient [3], its low toxicity, and abundant, cheap constituent elements. Various types of Cu₂O-based solar cells have been reported, including ZnO/Cu₂O [7], TiO₂/Cu₂O [8], NiO_x/Cu₂O [9], and Cu₂O electrodes in perovskite solar cells [10].

The Cu₂O photoabsorption layer has been prepared by several methods such as sputtering [11,12], chemical vapor deposition [13,14], pulsed laser deposition [15,16], thermal oxidation [17,18], spray pyrolysis [19], and mist chemical vapor deposition [20]. Electrochemical deposition (ECD) with an aqueous solution as the electrolyte is suitable for large area deposition with high raw material efficiency. In addition, ECD is a low-cost, low-temperature (below 100 °C), environmentally friendly process. Several oxides, including Cu₂O [21–24], ZnO [25–27], and Ga₂O₃ [28], have been prepared by ECD.

The highest energy conversion efficiency of a Cu₂O-based solar cell reported so far is 7.94% [29], although the theoretical maximum value under air mass 1.0 irradiation is 20% [30]. The conversion efficiency is partly limited by the difficulty in controlling the carrier concentration. The carrier density has been increased by doping [31–33], though

controlling the native carrier is also important for improving the device properties. The origin of the native p-type carrier is expected to be copper vacancies (V_{Cu}) [34–36], and their density is expected to be related to the slightly off-stoichiometry of Cu₂O.

During ECD, Cu₂O grows according to the electrochemical reaction



Although Cu₂O should have Cu:O stoichiometry of 2:1, native carriers are observed in the films, which means that V_{Cu} is generated during film growth. In vacuum processes, the difference in the vapor pressures of the constituent elements affecting the re-evaporation rate must be considered, whereas this is not the case for ECD. The main factor expected to affect to the stoichiometry during ECD is the difference in the supply rate of the elements. Fig. 1 shows a schematic illustration of the ECD setup and a cross section of the substrate. The electrical double layer is located immediately above the surface of substrate. Cu²⁺ and OH⁻, which are the sources of Cu and O in the Cu₂O film, are consumed by the electrochemical reaction (Eq. (1)) and converted to Cu₂O. The ions are supplied from the bulk electrolyte to the growth surface by the diffusion force generated by the difference between the concentrations of the ion in bulk and the growth surface. The cathodic potential is applied by an external source to supply electrons consumed by the electrochemical reaction (Eq. (1)) of Cu²⁺ and OH⁻.

The total cathodic current density (j (A/m²)) corresponds to the

* Corresponding author.

E-mail address: ashida@pe.osakafu-u.ac.jp (A. Ashida).

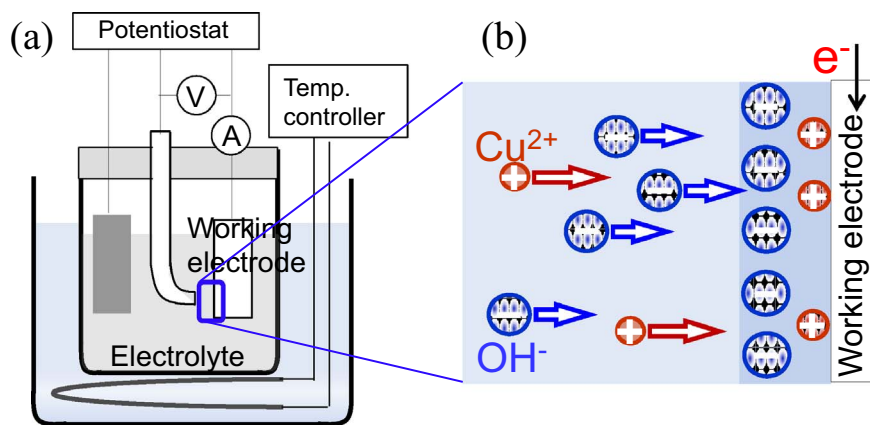


Fig. 1. Schematic illustration of the ECD setup (a) and a cross-section of the substrate (b).

reaction rate of Eq. (1) and to the growth rate of the film, and j is expressed by the Butler-Volmer equation [37,38],

$$j = j_0 \left[\exp \left\{ \frac{-\alpha z F \eta}{RT} \right\} - \exp \left\{ \frac{(1 - \alpha) z F \eta}{RT} \right\} \right], \quad (2)$$

$$j_0 = z F k^o C_o^{(1-\alpha)} C_R^\alpha, \quad (3)$$

where j_0 is the exchange current density, α is the ion activity coefficient, z is the number of electrons involved in the reaction, F is the Faraday constant, η is the activation overpotential, R is the gas constant, T is the absolute temperature, k^o is the ion diffusion coefficient, C_o is the oxidant concentration, and C_R is the reductant concentration. During the general electrochemical process, j is determined by η , C_o , and C_R . If η is too low to consume the ions supplied from the bulk electrolyte, j is determined only by η . However, the contribution of j_0 is dominant in determining j , when η is large, and thus j is controlled by j_0 , which is determined by C_o and C_R . Therefore, the rate-limiting factor of an electrochemical reaction should be controlled by the ion concentration in the electrolyte. Therefore, the reaction for generating Cu₂O in Eq. (1) should be controlled by the concentrations of Cu²⁺ ([Cu²⁺]) and OH⁻ ([OH⁻]). Hence, the generation of V_{Cu}, a non-stoichiometric defect, and the concentration of the native carrier was expected to be controlled by [Cu²⁺] and [OH⁻].

A nearly single-crystal Cu₂O film is desirable for evaluating the native defects generated by changes in ion concentrations. Therefore, we grew epitaxial Cu₂O thin films by ECD. We varied [Cu²⁺] and [OH⁻], that is, the electrolyte pH, without a precipitate forming. The factors that affect the density of the ionized acceptor (N_A^+) were determined by analyzing the dependence of N_A^+ on the ion concentration and the total cathodic current density, j (film growth rate).

2. Experimental

A conventional three-electrode electrochemical system was used to prepare Cu₂O thin films. The working electrode, which was the deposition substrate, was Pt (111) prepared on sapphire (0001) by rf magnetron sputtering. The reason why we chose Pt is resistance to acids and alkalis which is very important for deposition in electrolytes with various pH. The counter electrode and the reference electrode were Pt sheet and Ag/AgCl, respectively. The electrolyte consisted of 3×10^{-3} – 3×10^{-1} mol/L CuSO₄ and 3 mol/L lactic acid. The pH was adjusted to values between 7.0 and 12.5 by titration with aqueous NaOH and H₂SO₄ solutions. The water used to prepare the electrolyte was semiconductor grade with resistivity higher than 5 M Ω cm. The electrolyte was kept at 45 °C during ECD by using a water bath. A constant potential was applied to the working electrode vs. the reference electrode by a potentiostat (SP-150, Bio-Logic Science Instruments SAS). Fig. 2 shows the potential-pH diagram of the Cu-

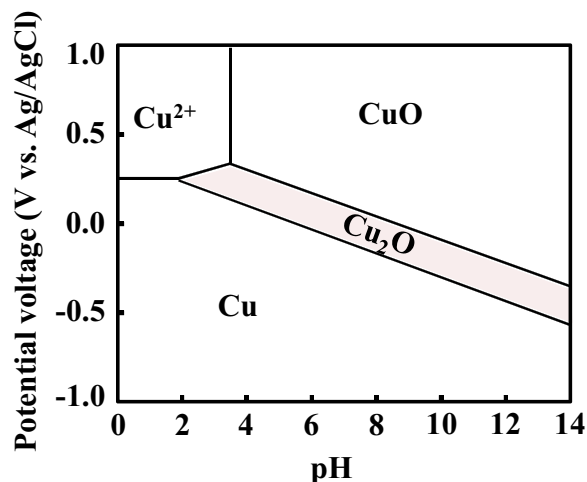


Fig. 2. Potential-pH diagram of the water-Cu system. The potential for stable Cu₂O depends on the pH (i.e., [OH⁻]).

water system, we calculated in accordance with the method reported by Linkson et al. [39] using the standard Gibbs energy of formation of Cu, Cu²⁺, CuO and Cu₂O [40]. The Cu₂O stable region in the diagram was narrow and the potential decreased with increasing pH. Therefore, the potential applied to the working electrode was changed from -0.2 to -0.4 V vs. Ag/AgCl by increasing the pH from 7.0 to 12.5. The total charge density supplied to the working electrode was 1.0 C/cm².

The surface morphology and thickness of the films were evaluated by scanning electron microscopy (SEM; S-4500, Hitachi). The crystallinity and in-plane and out-of-plane crystal direction relationships between Pt and Cu₂O were evaluated by X-ray diffraction (XRD; X'pert, PANalytical). N_A^+ was obtained from the C-V properties measured with Au/Ti Schottky electrodes deposited on the surface of the Cu₂O thin films.

3. Results and Discussion

Fig. 3(a) shows a typical SEM image of a Cu₂O film. The film was dense with no voids or cracks and had a thickness of about 1.1 μm. The XRD patterns of 2θ - ω scanning (not shown) indicate that all the films were <111> single-orientated Cu₂O with no other phases, such as CuO and Cu, on a Pt (111) substrate. As shown in Fig. 2, the potential for Cu₂O deposition should be changed by changing the pH. The diffraction peaks in 2θ - ω scanning XRD patterns of Cu₂O deposited at various pH and the applied potentials have almost same intensities and shapes. Therefore, it can be said that the effect of change of applied potential for the crystallinity is not significant. The 220 diffractions of Cu₂O and Pt were observed by ϕ -scanning XRD and the diffraction

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