Orientation of Copper(I) Oxide Electrodeposited From Aqueous Solutions
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Copper(I) oxide (Cu$_2$O) with cubic cuprite structure is known as an intrinsic p-type semiconductor. Cu$_2$O is used as a solar cells material because it has 2.1 eV band gap and high optical-absorption coefficient (~10$^4$ cm$^{-1}$). Cu$_2$O is often used in connection with n-type ZnO to fabricate p-n junction solar cells. In this case, <111>-oriented Cu$_2$O is favorable considering the lattice match with {0001} plane of wurtzite ZnO, giving high permeability of light in the crystal.

Potentiostatic electrodeposition of Cu$_2$O from aqueous solutions containing lactic acid and hydrated cupric salt has been reported [1], where orientation of the electrodeposited Cu$_2$O seemed to depend on the pH. For instance, <100>-oriented Cu$_2$O was electrodeposited at −0.344 V vs. SHE from a weak base (pH 9.5), while <111>-oriented Cu$_2$O was electrodeposited at −0.344 V and −0.644 V from a strong base (pH 12.5). In addition, galvanostatic electrodeposition of Cu$_2$O from an aqueous solution containing lactic acid also suggested pH dependence on Cu$_2$O orientation together with current-density dependence [2]. However, as far as we know, the pH dependence of the orientation of electrodeposited Cu$_2$O has not been studied in detail.

In this study, we electrodeposited Cu$_2$O from aqueous solutions containing lactic acid and hydrated copper(II) acetate. pH and/or cathode potential dependence of the preferred orientation was examined. pH was ranged from 9.5 to 12.5, while the cathode potential was controlled between −0.167 V and −0.644 V. The orientation of the obtained Cu$_2$O was evaluated using X-ray diffraction (XRD, Rigaku RINT2000) and scanning electron microscopy (SEM, Keyence VE-7800).

At −0.344 V, electrodeposited Cu$_2$O from pH 9.5 and 10.0 solution oriented <100> and those from pH 10.5, 11.5 and 12.5 solution oriented <111> (see Fig. 1). Notably, even from pH 9.5 and 10.0 solution, we obtained <111>-oriented Cu$_2$O below −0.492V. Previous study has suggested that preferred orientation of Cu$_2$O can be explained qualitatively by considering the elementary formation rate CuOH ($v_{CuOH} = k[\text{Cu}][\text{OH}]$) proportional to current density, where lower $v_{CuOH}$ gives <100> orientation, while higher $v_{CuOH}$ gives <111> [2]. Therefore, the <111> orientation obtained below −0.492 V from pH 9.5 and 10.0 solution should result from increased current density due to lowered cathode potential (about 2.0 mA cm$^{-2}$ for −0.492 V and about 0.11 mA cm$^{-2}$ for −0.314 V). The SEM images of <100>-oriented and <111>-oriented Cu$_2$O are shown in Fig. 2. The grains of <100>-oriented Cu$_2$O were square pyramidal in shape, while those of <111>-oriented Cu$_2$O were tetrahedral.

Based on given thermodynamic data [3], we drew $E$-$pH$ diagram of water-Cu-lactic acid (see Fig. 3(a)). According to the $E$-$pH$ diagram, when pH > 8, Cu$^{2+}$ ion hydrolyzes and precipitates as hydroxide (Cu(OH)$_2$). However, in our experiment, Cu$_2$O was electrodeposited without any precipitation such as Cu(OH)$_2$. This implies that the stability regions for cupric lactate complexes of some kind are larger. The XRD results are indicated in Fig. 3(b), which exhibit that <111>-oriented Cu$_2$O can be electrodeposited even from pH 9.5 solution by lowering the cathode potential.


Figure 1. XRD patterns of Cu$_2$O electrodeposited at −0.344 V on FTO substrate from pH 9.5, 10.0, 10.5, 11.5 and 12.5 solution.

Figure 2. SEM images of (a) <100>- and (b) <111>- oriented Cu$_2$O prepared at −0.344 V from pH 10.0 and 10.5 solution, respectively.

Figure 3. (a) $E$-$pH$ diagram of water-Cu-lactic acid and (b) its enlarged one where experimental results are mapped with open circles (Cu$_2$O<100>), closed circles (Cu$_2$O<111>) and an open diamond (Cu$_2$O<111>+Cu).