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Orientation of Copper(I) Oxide Electrodeposited From Aqueous Solutions

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Copper(I) oxide (Cu_2O) with cubic cuprite structure is known as an intrinsic p-type semiconductor. Cu_2O 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_2O is often used in connection with n-type ZnO to fabricate p-n junction solar cells. In this case, <111>-oriented Cu_2O is favorable considering the lattice match with {0001} plane of wurtzite ZnO, giving high permeability of light in the crystal.

Potentiostatic electrodeposition of Cu_2O from aqueous solutions containing lactic acid and hydrated cupric salt has been reported [1], where orientation of the electrodeposited Cu_2O seemed to depend on the pH. For instance, <100>-oriented Cu_2O was electrodeposited at −0.344 V vs. SHE from a weak base (pH 9.5), while <111>-oriented Cu_2O was electrodeposited at −0.344 V and −0.644 V from a strong base (pH 12.5). In addition, galvanostatic electrodeposition of Cu_2O from an aqueous solution containing lactic acid also suggested pH dependence on Cu_2O orientation together with current-density dependence [2]. However, as far as we know, the pH dependence of the orientation of electrodeposited Cu_2O has not been studied in detail.

In this study, we electrodeposited Cu_2O 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_2O was evaluated using X-ray diffraction (XRD, Rigaku RINT2000) and scanning electron microscopy (SEM, Keyence VE-7800).

At −0.344 V, electrodeposited Cu_2O 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_2O below −0.492V. Previous study has suggested that preferred orientation of Cu_2O can be explained qualitatively by considering the elementary formation rate CuOH ($v_{(CuOH)}$ = $k[Cu^+][OH^-]$) 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_2O are shown in Fig. 2. The grains of <100>-oriented Cu_2O were square pyramidal in shape, while those of <111>-oriented Cu_2O 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_2O 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_2O can be electrodeposited even from pH 9.5 solution by lowering the cathode potential.

[1] K. Mizuno *et al.*, *J. Electrochem. Soc.*, **152**, C179 (2005).
[2] T. Shinagawa *et al.*, *Cryst. Growth Des.*, **13**(1), 52 (2013).
[3] R. M. Smith *et al.*, *Critical Stability Constants, Vol. 5, First Supplement*, (Plenum Press, NewYork, 1982), p.291.

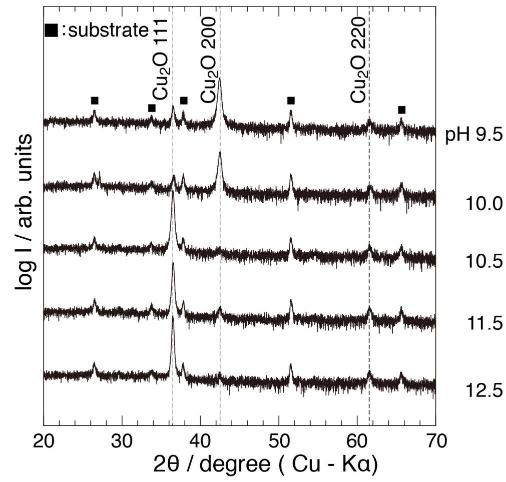

Figure 1. XRD patterns of Cu_2O electrodeposited at −0.344 V on FTO substrate from pH 9.5, 10.0, 10.5, 11.5 and 12.5 solution.

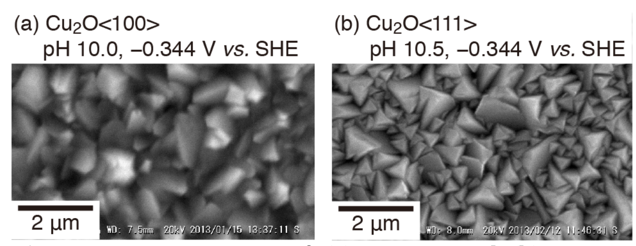

Figure 2. SEM images of (a) <100>- and (b) <111>-oriented Cu_2O prepared at −0.344 V from pH 10.0 and 10.5 solution, respectively.

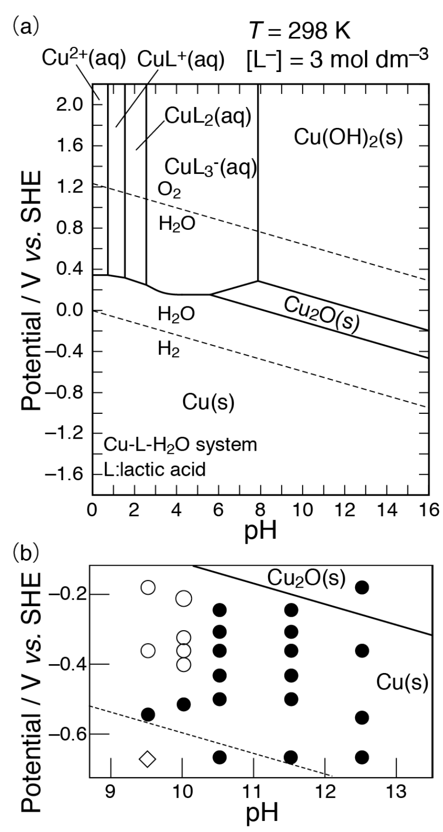

Figure 3. (a) *E*-pH diagram of water-Cu-lactic acid and (b) its enlarged one where experimental results are mapped with open circles (Cu_2O<100>), closed circles (Cu_2O<111>) and an open diamond (Cu_2O<111>+Cu).