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Electrical Characterization of Electrodeposited *p*-type Semiconducting Cu_2O Films

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Cu_2O films with a cuprite cubic structure have been prepared by cathodic electrodeposition at 318 K from an aqueous solution containing a lactic acid and copper sulfate hydrate. The electrical characterizations were carried out on the free-standing films prepared by splitting from the substrate at room temperature with a van der Pauw technique using a hall measuring system. The Cu_2O film showed *p*-type conduction irrespective of solution pH value. The resistivity, carrier concentration, and mobility strongly related to the solution pH value. And the Cu_2O film prepared at pH 12.5 showed resistivity of 2.7×10^4 Ωcm with carrier concentration of 1.9×10^{14} cm^{-3} and mobility of 1.2 $cm^2V^{-1}s^{-1}$.

Key words: cuprous oxide, cuprite structure, electrodeposition, *p*-type conduction, electrical property

1. INTRODUCTION

Cu_2O is a *p*-type semiconductor with band gap energy of 2.1 eV and has attracted increasing attention as a component in devices such as solar cell and photo diode. The Cu_2O films have been prepared by gas-phase deposition techniques such as radio-frequency magnetron sputtering, molecular beam epitaxy, and laser ablation techniques.

Electrodeposition of oxide films from aqueous solutions has several advantages over gas-phase deposition processes, is less hazardous and environmentally friendly, and is low temperature process. Semiconductors of ZnO,[1,2] CeO_2,[3] and a-Bi_2O_3,[4] and ferromagnetic material of Fe_3O_4[5] were prepared directly by electrodeposition and chemical deposition from aqueous solutions. Also, elestrodeposition of Cu_2O film from an aqueous solution has been demonstrated by Switzer's group, and the Cu_2O film showed optical band gap energy of 2.1 eV.[6] the evaluation of electrical characteristics for electrodeposited Cu_2O films is difficult, because of the existence of conductive substrate. However, the electrical characteristic is so important for the applications of electrical devices. Recently, it was reported that electrodeposited CdTe films could be evaluated on the free-standing films prepared by splitting from the conductive substrate with an epoxy-type adhesive.[7]

In this paper, we prepared *p*-type semiconducting Cu_2O films by cathodic deposition from an aqueous solution Switzer's group reported, and the electrical characterizations were carried out by using a hall-measuring system.

2. EXPERIMENTAL

Cu_2O films were prepared by cathodic deposition at 318 K on a conductive glass substrate (NESA glass, 20 Ω) from an aqueous solution containing a 0.4 mol/L copper sulfate hydrate and 3 mol/L lactic acid. The solution was prepared by reagent grade chemicals and distilled water. The solution pH was adjusted at 9.5 and 12.5 with an 1 mol/L NaOH aqueous solution. The electrodeposition was carried out potentiostatically at a chathodic potential of −0.55 V referenced to Ag/AgCl electrode by using a potentiostat connecting to a coulomb meter.

X-ray diffraction measurements were performed by a conventional $\theta/2\theta$ scanning technique using a MAC Science MXP18 system with a monochromated Cu Kα radiation source. Electron spectra were recorded with an ESCA (ULVAC-PHI5700MC) with a monochromated Al Kα radiation source. Electrical characterization was carried out on samples at ambient temperature using a hall-measuring system (Toyo Technika, Resitest 8320). The samples were prepared by splitting from the substrate by using a technique reported by Miyake.[7] Optical absorption spectrum was recorded with a spectrophotometer (Shimadzu, UV-3150).

3. RESULTS AND DISCUSSION

Cu_2O film with a cuprite structure was obtained irrespective of pH value. And the lattice constant calculated from the X-ray diffraction peaks was 0.4270 nm, which agreed with the standard value. The Cu_2O films had excellent preferred orientations of (111) and (200) depending on the pH value, as already reported by Switzer's group. It was confirmed from the electron spectra recorded with an XPS that the film was Cu_2O and did not contain Cu and CuO. The molar ratio of Cu to O (Cu/O), which was evaluated from the intensity of Cu2p and O1s spectra and relative sensitivity factors, was estimated to be 1.8 and 1.6 for pH values of 9.5 and 12.5, indicating that the ratio changed depending on the

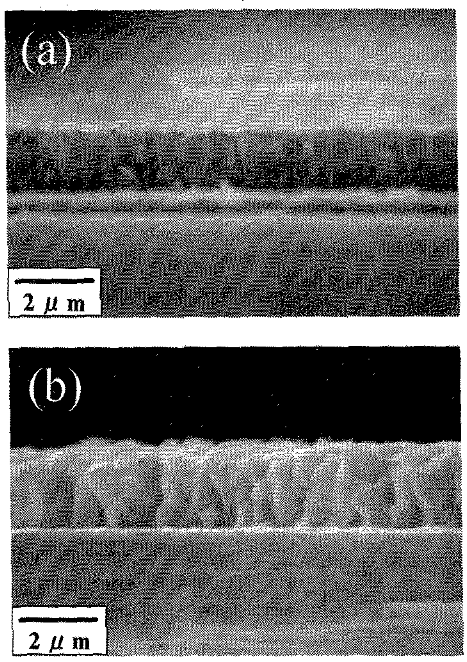

Figure 1 Scanning electron micrographs of cross-sectioned structure for Cu_2O films prepared at pH value of 9.5 and 12.5.

pH value, even if experimental and calculating errors were involved. Figure 1 shows cross-sectioned structure of Cu_2O films prepared at pH values of 9.5 and 12.5. The Cu_2O films were composed of columnar grains grown from the substrate surface. The grain sizes evaluated from the SEM micrographs were of around 0.25 and 0.6 μm for the pH value of 9.5 and 12.5. Any defects such as pored could not locate on the images.

The Cu_2O film formation proceeds by a tri-dimensional growth mechanism, because of the columnar structure. The preferred orientation of resultant Cu_2O films is determined by the nucleation stages, which closely related to the interfacial energy. The change in preferred orientation with pH value is evidence of the importance of the interfacial energy, and indicates that the interfacial energy changes depending on the solution pH value.

Figure 2 shows electrical properties for Cu_2O films prepared at pH values of 9.5, 10.5 and 12.5. The Cu_2O films showed *p*-type conduction irrespective of pH value. The resistivity was 6.9×10^5 Ωcm at pH 9.5 and decreased to 2.7×10^4 Ωcm with the raise in pH value to 12.5. The carrier concentration and mobility were 9.5×10^{12} cm^{-3} and 0.95 $cm^2V^{-1}s^{-1}$ at pH 9.5 and increased to 1.9×10^{14} cm^{-3} and 1.2 $cm^2V^{-1}s^{-1}$ with the raise in pH value to 12.5. The resistivity, carrier concentration, and mobility corresponded to those prepared at ambient temperature by a magnetron sputtering technique. The decrease in resistivity with pH value was caused by the increase in carrier concentration and mobility. Figure 3 shows the relation between molar ratio of Cu to O and the carrier concentration for the Cu_2O films deposited under various conditions. The carrier concentration increased with the decrease in Cu/O molar ratio. It is generally accepted that *p*-type conduction for undoped Cu_2O film is originated from a copper vacancy.[8] This

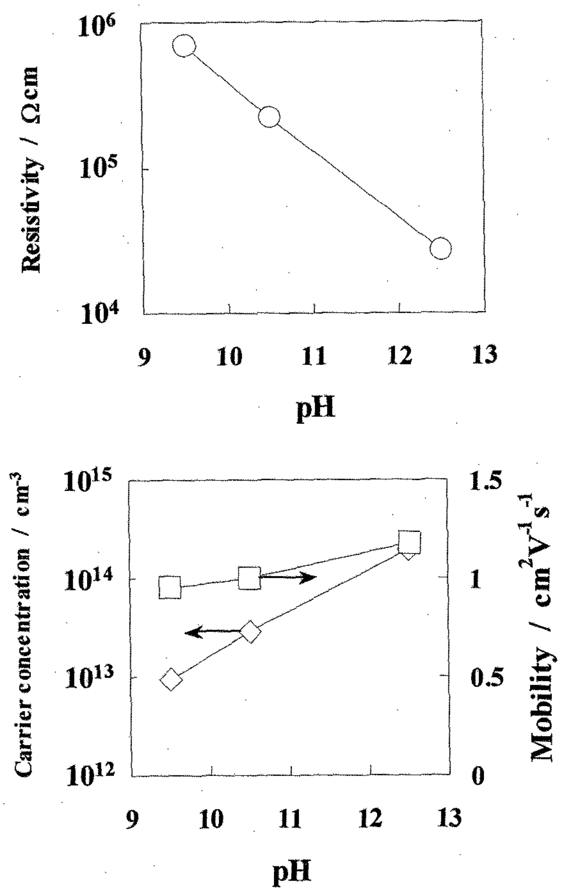

Figure 2 Electrical characteristics for Cu_2O films prepared at pH values of 9.5, 10.5, and 12.5.

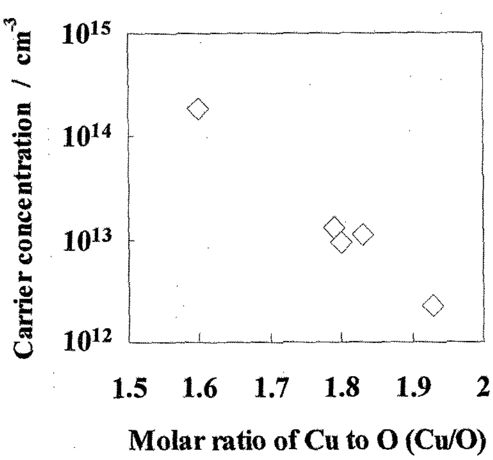

Figure 3 The relation between molar ratio of Cu to O (Cu/O) and carrier concentration.

will be the reason for the change.

The mobility in polycrystalline film should be generally limited by scattering from grain boundary, pore, and ionized impurity. Since the mobility is independent on the change in carrier concentration, the effectiveness of scattering from the ionized impurity including copper vacancies could not be seen. Because that the grain size increased with the raise in pH value, the increase in mobility was attributed to the change in grain size.

The optical band gap energy was calculated from the absorption edge evaluated on the absorption spectrum with an assumption of direct transition and was estimated to be 2.1 eV characteristic of Cu_2O.

4. CONCLUSION

Cu_2O films with a cuprite cubic structure have been prepared by cathodic electrodeposition at 318 K from an aqueous solution containing lactic acid and copper sulfate hydrate. The Cu_2O film showed *p*-type conduction irrespective of solution pH value. The resistivity, carrier concentration, and mobility strongly related to the solution pH value. And the Cu_2O film prepared at pH 12.5 showed resistivity of 2.7×10^4 Ωcm with carrier concentration of 1.9×10^{14} cm^{-3} and mobility of 1.2 $cm^2V^{-1}s^{-1}$.

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