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Fabrication of compositions of Cu-Cu_2O crystal films by electrochemical deposition with potential pulse settings

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ABSTRACT

Compositions of Cu-Cu_2O crystal films were fabricated using electrochemical deposition (ECD) with a strategy of potential pulse settings. The Cu-Cu_2O films were prepared by controlling the potentials and deposition periods of ECD processes. Intensities of Cu and Cu_2O crystals were revealed by X-ray diffraction (XRD) spectral data. Results demonstrated that the Cu and Cu_2O crystal compositions were significantly influenced by the potential and deposition period settings. Polycrystalline Cu_2O films were formed by the ECD at all tested potential settings. However, Cu-Cu_2O crystals were formed at potential more negative than −0.4 V and with long deposition times. The grain sizes of Cu_2O and Cu crystals fabricated by ECD were estimated to be 50 and 51 nm, respectively. We verified that the reaction mechanism of Cu_2O occurred in the solution phase, and Cu_2O transformed into Cu in the solid phase inside the deposition films. The compositions of Cu-Cu_2O crystal films can be controlled by a potential pulse strategy with adjusted potential range and pulse period settings. The formation of Cu-Cu_2O crystal films during ECD was also discussed.

1. Introduction

Copper-cuprous oxide (Cu-Cu_2O) has been used for many applications, such as capacitors [1], Li-ion batteries [2], sensors [3], and photoelectrochemical devices [4–6], because of its unique properties. The properties of Cu-Cu_2O, which are one of the critical factors for the application of these devices, are greatly influenced by preparation methods. The Cu-Cu_2O-based device performance i.e. the stability and efficiency, required to be improved by the preparation of the specific Cu-Cu_2O property for the device. Therefore, the characteristics of prepared Cu-Cu_2O should be analyzed before device implementation.

A popular method for fabricating Cu-Cu_2O was utilized to deposit Cu_2O deposition on a Cu surface, and the properties of the prepared Cu_2O were identified for further application [1–8]. Various approaches were employed to conduct Cu_2O film deposition, such as thermal oxidation [9], hydrothermal [10], sputtering [11], spray pyrolysis [12], and electrochemical deposition (ECD) methods [13–20], and the properties of the prepared Cu_2O film were investigated. ECD is one of the popular methods for fabricating Cu_2O and has been studied by many researchers. The growth of Cu_2O on Cu was influenced by the ECD variables, such as the ECD solution composition and the current and potential of the ECD system. The properties of the Cu_2O films were analyzed and found to be significantly influenced by the ECD variables. The solution composition characteristics, including precursors, surfactant additives, pH values, and ion additives, were examined to alter the properties of the prepared Cu_2O films [21,22]. The optoelectronic properties of the Cu_2O crystals were reported and varied by adjusting the ECD solution composition. Various properties of the Cu_2O particles were characterized and used for optoelectronic devices. For example, p-type Cu_2O and n-type Cu_2O films were fabricated to construct p-n junction diodes, which were used for the design and fabrication of solar cells [23–28].

The other major factor that influenced the Cu_2O properties was the set of process variables, i.e. current and potential, which affected Cu_2O formation and deposition. Various current and potential system configurations were investigated to prepare desired Cu_2O particles during the ECD [16,19,20,29,30]. Cyclic voltammetry parameters for the Cu_2O preparation were studied to obtain the particles with desirable properties [16,29]. A current pulse approach was adopted in an electrophoretic deposition system to control the morphology during deposition [16]. Different current and potential settings were used to fabricate Cu_2O particles and an

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optimal particle preparation was obtained to improve the performance of Cu_2O/Ag cube-shaped composites. Cu_2O particles with desirable properties were obtained by controlling the process parameters to vary the morphologies of the Cu_2O particles in their studies.

An alternative approach to produce Cu-Cu_2O films was to fabricate Cu and Cu_2O simultaneously in one processing step using a wet-chemistry method. The deposition processes of Cu and Cu_2O layers through potential oscillations in alkaline solutions with Cu(II) and citrate species was studied [30]. The mechanisms of the Cu and Cu_2O formation was explained and discussed in their work. Synthesized mesoporous Cu-Cu_2O films using an ECD method were studied [31]. However, the mechanism of Cu-Cu_2O during ECD processing was not described in the study.

Few studies have focused on studying the formation of Cu and Cu_2O during ECD. In this study, the compositions of Cu-Cu_2O crystals during ECD were fabricated by the adjustments of the process parameter settings. The effects of the ECD potential and period settings on the growth of Cu and Cu_2O crystals were studied. The properties of the ECD crystals were analyzed to evaluate the influence of the potential settings. The evolution and morphologies of the ECD crystals were analyzed to reveal the steps of Cu-Cu_2O film formation. The formation of Cu and Cu_2O within Cu-Cu_2O films were proposed on the basis of the analytical results. A potential pulse setting strategy for ECD was proposed to fabricate Cu-Cu_2O films. The composition of Cu and Cu_2O within the film can be controlled by adjusting the potential pulse range and deposition period.

2. Experimental method

2.1. ECD of Cu-Cu_2O crystal films

The ECD films was prepared by the ECD system using a solution, mixed of Copper (II) acetate ($Cu(OOCCH_3)_2 \cdot H_2O$). The concentration of $Cu(OOCCH3)_2$ is 0.02 M for all the fabrication processes in the work. Copper (II) acetate mixed with acetic acid under the control of pH = 5.0 and maintained at 60 °C was prepared for the ECD solution. All the chemicals were obtained from J. T. Baker Corp. The deposition of Cu-Cu_2O crystal films used an electrochemical analyzer type 6081 C with a three-electrode cell provided by CH Instruments in the ECD system. The deposited films were carried out using indium doped tin oxide (ITO) as the working electrodes. ITO glass is a commercial product and was purchased from AimCore Technology Co., Taiwan. The composition of the ITO film is 90% indium oxide and 10% tin oxide and the sheet resistance is 7 Ω/square. The counter electrode consisted of platinum and the reference electrode was an Ag/AgCl electrode in 3 M KCl solution. The potential value of the reference Ag/AgCl vs NHE is 0.198 V. The films fabricated by ECD processes were carried out using potential settings between −0.01 V and −1.0 V or potential pulse settings. The potential pulse strategy was conducted by setting the potential range between −0.01 V and −0.8 V with pulse period at 10 s for the whole deposition periods to fabricate the Cu-Cu_2O crystal films, as shown in Fig. 1. The potential values were expressed as absolute vales discussed in this study. After the deposition processing was completed, the properties of the fabricated Cu-Cu_2O crystal films were further evaluated.

2.2. Characterization of Cu-Cu_2O crystal films

The produced films were then analyzed using several analytical instruments to determine the properties of the deposited films. The crystal structure of the produced Cu_2O samples was measured by X-ray Diffraction (XRD, BRUKER D2 Phaser XRD), which emits Ni-filtered Cu Kα radiation that scans diffraction angles between 20° and 80° at intervals of 0.01° and at a rate of 1°/min. The morphologies of the Cu_2O samples were illustrated by an orthographic microscope. The electrical characteristics of the prepared ECD films were analyzed by current–voltage (I–V) measurements. The back contact area of ECD film deposited on ITO is designed as 1 cm × 1 cm for the device. Indium balls (0.2 cm × 0.2 cm) used for the metal contact with the device were set on top of the film layer for the film characterizations. Two probes are set to ITO and the film surface for the I-V measurement using a SourceMeter (Keithley model 2400). The resistance of the film was determined using the I-V data analysis.

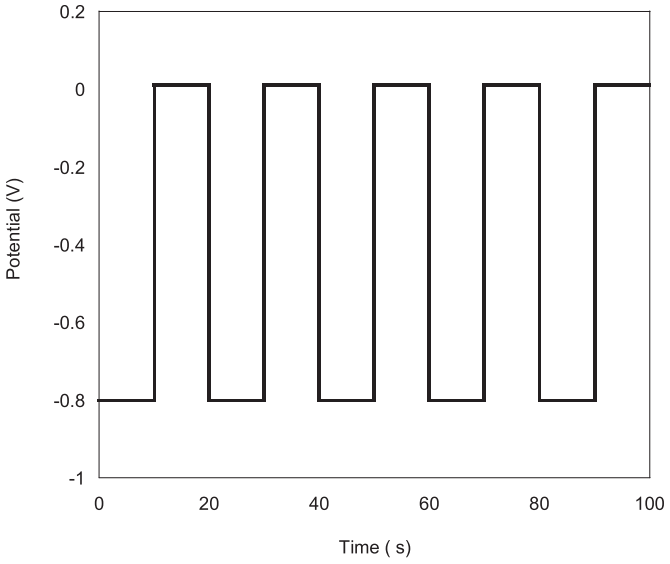

Fig. 1. Schematic plot of potential pulse setting applied in the ECD system.

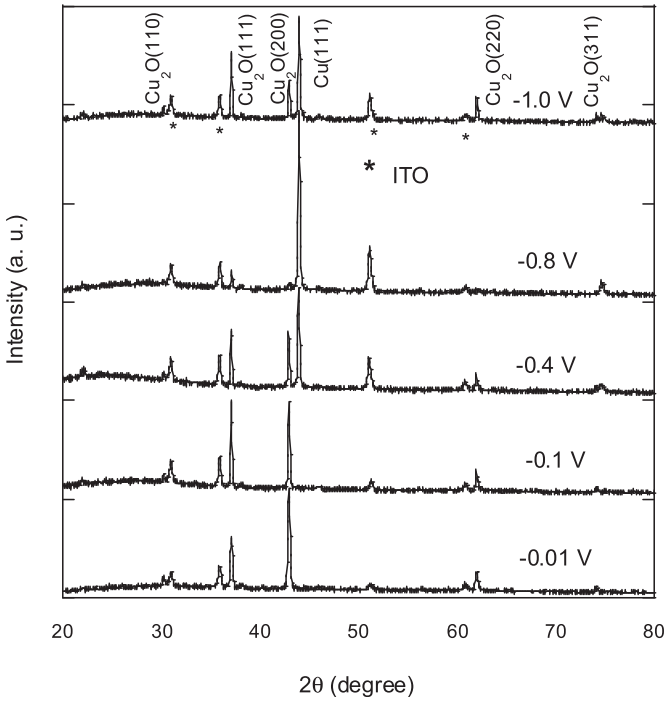

Fig. 2. XRD spectra of the sample films fabricated by ECD at various potential settings.