Electrodeposition of submicron/nanoscale Cu$_2$O/Cu junctions in an ultrathin CuSO$_4$ solution layer

Guangwei Yu *, Xiaobo Hu, Duo Liu, Daliang Sun, Jing Li, Huaijin Zhang, Hong Liu, Jiyang Wang

State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

ARTICLE INFO

ABSTRACT

The electrodeposition experiments were carried out in an ultrathin CuSO$_4$ solution layer under lower growth driving forces and the structure of electrodeposits were characterized by FESEM, chemical etching, EDS and DC conducting measurement. It was found that the Cu$_2$O crystallites distributed over the entire sample surface and formed submicron/nanoscale Cu$_2$O/Cu junctions. Meanwhile, the abnormal growth of Cu$_2$O crystallites in the electrodeposit front area was found for the first time. In the study, we present the obvious evidences for clarifying the relationship between the morphology and the compositional distribution of electrodeposits at grain size level. This result may be helpful for us to prepare the electrodeposits with controlled surface morphology at micro–nanoscale.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cu$_2$O is a p-type semiconductor with a direct forbidden band gap of approximately 2.1 eV. It was well known in the history of semiconductor physics and used as the early crystal rectifiers [1]. From the consideration of energy level, it could be excited to a weakly bound exciton state, which is very suitable for the investigation of the excitonic Bose–Einstein condensation [2–4]. Recently, much attention has been paid to the photo-physicochemical properties of Cu$_2$O materials since it could be used as light absorbing layer for photovoltaic cells and photocatalyst for overall water splitting under visible light irradiation [5–13].

The electrodeposition method for preparing Cu$_2$O is very attractive due to its advantages such as low synthesis temperature, low cost, shape controllability, and high purity [14–25]. To understand pattern formation mechanism of electrodeposits in two dimensional space, Wang and co-workers designed a unique electrolytic cell which could provide an ultrathin CuSO$_4$ solution layer with the controlled submicron thickness obtained by adjusting the experimental temperature [26–28]. Inside the ultrathin electrolyte layer, electrodeposited products often attach robustly to a substrate and their patterns can be taken by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

However, the growth process of an electrodeposit in the ultrathin electrolyte layer is very complex, the influence of experimental conditions on pattern of electrodeposit has not yet been fully understood. As the deposition occurs at a voltage of 3–5 V in the potentiostatic mode or a deposition current of several tens of microamperes in the galvanostatic mode, the finger-like branches of electrodeposit consist of a lot filaments which have the micron/nanoscale sections and are covered by periodic corrugated nanostructures [26,27,29]. The transmission electron microscopy (TEM) investigation revealed that these filaments are aggregated in the form of Cu and Cu$_2$O crystallites [26,29]. Such filaments have considerably low branching rate which may result from the convection suppression effect in the ultrathin electrolyte layer. In addition, the periodic corrugated structures covering the filament surface may result from the periodic variation of chemical environment at the deposit front region during growing process. The electrodeposits with film-like pattern were prepared under different experimental conditions [30], which showed that the lower deposition current is necessary when the thinner CuSO$_4$ electrolyte layer was employed. Moreover, the finer grains of electrodeposit can be easily obtained at a large deposition current, a high pH and a low electrolyte concentration [31]. The electric properties of electrodeposited filaments were characterized by conducting atomic force microscopy (CAFM). The result indicated that the Cu$_2$O crystallites may be more concentrated in the concave region of the periodic corrugated nanostructures and the filament has a metallic core formed by copper crystallites [32]. Pattern selection of electrodeposits at micron and submicron scale has been studied under different growth driving forces [33]. It was found that the probability of the electrodeposit taking the film-like pattern or the finger-like pattern becomes great when the lower deposition current was chosen. In contrast, the branches of electrodeposits

* Corresponding author. Tel.: +86 531 8836 4864; fax: +86 531 8857 4135.
 E-mail address: gwyu@sdu.edu.cn (G. Yu).

may turn to be tenuous and the morphology of filament was formed under high deposition current since the growth competition between the adjacent branches becomes intense.

Moreover, Zhang et al. fabricated the silicon substrates with the coating of a monolayer octadecyl–trichlorosilane film or an amino-silane film. It was found that the electrodeposits prepared in an ultrathin $CuSO_4$ solution layer took the morphology of regular filaments on such substrates [34,35]. In addition, both the width of a filament and the spacing between filaments can be controlled by adjusting the concentration of $CuSO_4$ solution or by tuning the patterned coating, across a range of 100 nm to more than 1 μm.

The investigations described above provided the probability for preparing patterned electrodeposits composed of metallic/semiconducting materials in the two dimensional scale. In order to explore the rules of the pattern selection and the compositional distribution of an electrodeposit at grain size level, we prepared the electrodeposits under lower growth driving force in an ultrathin $CuSO_4$ solution layer. It was expected that a detailed growth mechanism of electrodeposit in an ultrathin electrolyte layer can be revealed.

2. Experimental methods

The electrodeposition was carried out in a cell which is mainly composed of substrate and electrodes and put in a thermostat chamber horizontally. A glass plate or a silicon wafer was used as the substrate. Two parallel Cu foils with purity of 99.9% were fixed on the substrate surface with a spacing of 10 mm. They are used as the cathode and the anode respectively. A drop of $CuSO_4$ aqueous solution (0.05 mol/l, pH 4.5) was dropped to the gap between electrodes on the substrate. Then a cover glass slice covered upon the electrodes and an initial solution layer was formed. By cooling the thermostat chamber, an ultrathin $CuSO_4$ solution layer could be obtained, which distributed between the substrate and an ice layer of frozen $CuSO_4$ electrolyte. The details of the experimental setup and the operating steps were reported elsewhere [27,33]. Moreover, the temperature of thermostat chamber was set at −3.5 °C. The resistance of the ultrathin $CuSO_4$ solution layer was about 100 kΩ.

Under applied growth driving forces, electrodeposits will grow from the cathode toward the anode. In the study, the deposition current was less than or equal to 15 μA in the galvanostatic mode, and the deposition voltage was less than or equal to 1.2 V in the potentiostatic mode. Then, the ex situ observation of the morphology of electrodeposits was carried out by a field emission scanning electron microscopy (FESEM, LEO 1530VP, LEO Inc.). The chemical etching and energy dispersive spectroscopy (EDS) (GENESIS, EDAX Inc.) were used to analyze the compositional distribution of electrodeposits. Moreover, the DC conducting property of electrodeposit was assessed by CAFM (SPI 3800N, Seiko Instruments Inc.).

3. Results and discussion

To explore the compositional distribution of electrodeposits aggregated in the form of Cu and Cu_2O crystallites, we prepare the sample at the lower growth driving force since the larger grain size can be obtained easily in this case [31]. As shown in Fig. 1, electrodeposits have the flat branches in micron scale. In addition, numerous submicron/nanoscale crystallites distribute on the branch surface homogeneously.

Fig. 2 shows the morphologies of electrodeposits in growth front area. Such areas start from the deposit front and span several microns or more than 10 μm along the directions of blue arrows which point to the cathode. In addition, the crystallites distributed on the deposits surface near the front area become abnormal. To
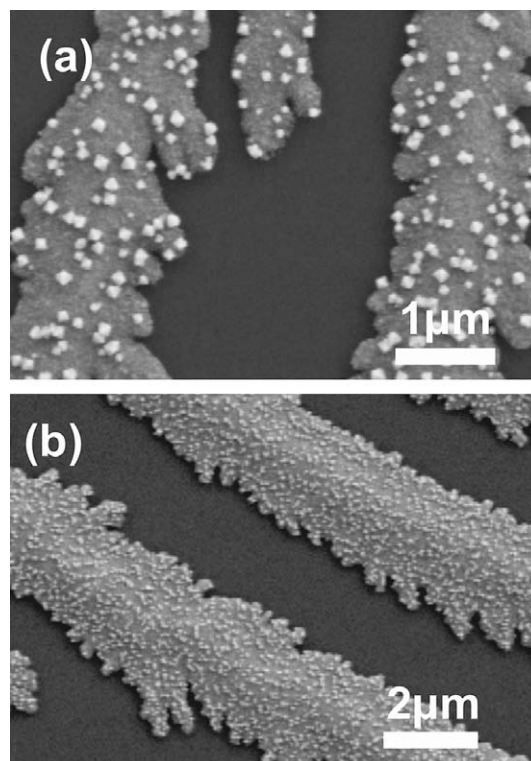

Fig. 1. FESEM images of the electrodeposits: (a) 8 μA, glass substrate; (b) 1.2 V, silicon substrate.

simplify the description, we name such abnormal grown crystallites as ACs. In contrast, crystallites distributed on the sample surface far away from the front area are named as the normal grown crystallites (NCs). As shown in Fig. 2a, the distribution of ACs upon the film-like electrodeposit presents some regularity. Close to the electrodeposit front, ACs with the small size covered densely the sample. Along the direction of blue arrow, the size of ACs increases and the density of ACs decreases gradually until the size reached the largest level. However, such regularity was not clearly presented when electrodeposits without the film-like morphology as shown in Fig. 2b and c though the ACs have the different size with the NCs' distinctly. Insets of Fig. 2 show that the ACs usually exhibit a faceted truncated octahedron shape when their size reached the submicron level. Moreover, inset of Fig. 2c presented clearly the boundary between the NCs region and the ACs region.

To differentiate the composition of deposited crystallites, we etched the electrodeposits by diluted sulfuric acid (pH 3). The morphologies of etched electrodeposits were investigated by FESEM. Corresponding to the original morphology as shown in Figs. 1a, 2a and b, the morphology of etched sample was shown in Fig. 3a, b, and c respectively. The images indicate that ACs and NCs almost disappeared from the etched sample surface. Since the Cu_2O can be etched by diluted acids while the Cu can not, we can deduce that both the ACs and the NCs are Cu_2O grains. In addition, the remainder of etched samples should be the aggregated Cu crystallites. The result of EDS analysis as shown in Fig. 4 also confirms the above judgment.

We have assessed the DC electric characteristics of electrodeposits by CAFM. Fig. 5a shows the AFM image of sample and all the measuring points located at the ACs or the NCs. In this measurement, the CAFM's probe with the coating of Pt–Ir alloy contacted to the Cu_2O grains, thus the measuring circuit is mainly formed by the metallic CAFM's probe, the semiconducting Cu_2O grain and the main body of electrodeposit in which the Cu