Phase transformations in copper oxide nanowires*

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Cu nanowires were electrodedeposited into the nanopores of self-ordered aluminum oxide films. CuO and Cu$_2$O nanowires were fabricated by oxidizing Cu nanowires in air. Cu nanowires oxidized at 250 °C transform only to Cu$_2$O (grain size ~21 nm), they transform to a mixture of CuO and Cu$_2$O above 350 °C and finally to CuO with a preferred orientation of CuO (111) at 900 °C. © 2005 American Vacuum Society. [DOI: 10.1116/1.2126672]

I. INTRODUCTION

Copper oxide nanowires, of both cupric oxide (CuO) and cuprous oxide (Cu$_2$O), are known for being useful in optical switch, high-temperature superconductors, solar cell, and other devices. A very significant characteristic of Cu$_2$O is that it can be prepared simply and cheaply by controlling the heating temperature and the oxygen partial pressure. One-dimensional nanostructures have attracted considerable attention in recent years. Preparation of metal and metal oxide nanowires is also of interest because of their electrical and magnetic characteristics, which have potential applications in the future generation of nanodevices. Recently, some studies have utilized chemical-vapor deposition, electrodeposition (ECD) and the sol-gel method with porous membranes as templates to prepare well-defined metal and metal-oxide nanowires. An ECD in conjunction with the template is an economic and controllable technique for producing nanowires extensively in the nanofabrication. Moreover, the size effects have shown that the reduction of nanoparticle size results in an increase in the ionicity and the stabilization of a more symmetric structure. Cu$_2$O could be converted to CuO through the size effect via simply oxidizing the Cu nanowire in air at a relatively low temperature of ~250 °C. This has rarely been reported. This work focused mainly on the fabrication of CuO and Cu$_2$O nanowires by the oxidation of the copper nanowire in air.

II. EXPERIMENT

In this work, Cu nanowires were formed by ECD in the nanopores of self-ordered anodic aluminum-oxide (AAO) films. The patterned structure of the AAO template has pores of ~80 nm diameter. A gold layer (~50 nm) was sputter deposited on one side of the through-hole AAO template as a working electrode in a conventional three-electrode cell. An aqueous bath that contains a 0.2 M aqueous solution of CuSO$_4$·5H$_2$O, and 0.1 M H$_3$BO$_3$ was used to prepare Cu nanowires, with a potentiostat as a power supply for the ECD. The solution pH was controlled in the range 4.5–5.0, adjusted by a 0.1 M H$_2$SO$_4$ solution. A glassy carbon plate and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. The ECD experiment was carried out at 0.193 VSHE for 2–3 h at room temperature, to yield Cu nanowire arrays. The arrays were then thermally oxidized at various temperatures in air for 12 h. Pieces of the AAO template with embedded Cu or Cu-oxide nanowires were etched in a 3% NaOH solution at room temperature for 15 min to completely remove the AAO template.

III. RESULTS AND DISCUSSION

Figure 1 presents scanning electron microscopy (SEM) micrographs of Cu nanowires with lengths of ~2 μm, corresponding to the thickness of AAOs. The diameter of the Cu nanowire is approximately that of the pore (~80 nm) of the AAO. Figure 2(a) shows the x-ray diffraction (XRD) patterns of the as-deposited Cu nanowires and the nanowires annealed at various temperatures in air. Cu (111) and (200) are the only two peaks from the as-deposited sample, as determined by comparison with the Joint Committee of Powder Diffraction Standards (JCPDS) card.19 The existence of the CuO and Cu$_2$O phases is consistent with the JCPDS cards.20,21 The Cu$_2$O phase is formed by the oxidation of the Cu nanowires that are first discernible at 250 °C. The diffraction-peak intensity decreases continuously as the oxidizing temperature increases. The CuO phase does not appear until the temperature reaches 350 °C. The intensity of diffraction peaks increases with the temperature. At 900 °C, the CuO (111) preferred orientation was evident. The full width at half maximum (FWHM) of the Cu (111) was mea-

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sured to calculate the grain sizes of the (111) cubic Cu$_2$O and that of the (111) monoclinic CuO based on Scherrer’s equation,$^{22}$ as displayed in Fig. 2(b). The grain sizes for Cu$_2$O at 250 °C and for CuO at 350 °C are around 16 and 30 nm, respectively. Clearly, the oxidation process promotes not only the phase transformation but also subsequent grain growth. Cu nanowires oxidized at 250 °C transform only to Cu$_2$O (grain size ~16 nm); those oxidized above 350 °C transform to a mixture of CuO and Cu$_2$O, and finally those oxidized at 900 °C transform to CuO with a preferred orientation of CuO (111). The thermodynamic data on bulk copper oxide$^{23}$ demonstrate that the corresponding temperature at which Cu$_2$O is in equilibrium with CuO is 1104 °C. However, the transformation temperature for Cu oxide nanowires is much lower than that of bulk Cu oxides. The more symmetric cubic Cu$_2$O phase should be more stable because it is smaller than the less symmetric monoclinic CuO phase. The formation of the CuO surface layer enables the stabilization of the symmetric cubic Cu$_2$O phase with large nanoparticles.$^{17}$ Additionally, Ayyub et al.$^{24}$ used rapid liquid dehydration and precipitation to synthesize copper oxide nanowires. They studied the effect of reducing the size of the particles on the crystal structure of Cu$_2$O and CuO over a nanometer scale. Below 25 nm, the face centered cubic structure of Cu$_2$O was found to be more stable than the monoclinic CuO since Cu$_2$O is more symmetric and more ionic than CuO. The reduction in the particle size increases the ionic nature of these materials and makes the lattice less directional so the more symmetric phase becomes more stable.$^{17,24}$ In this work, the CuO and Cu$_2$O nanowires were fabricated only through the oxidation of copper nanowire in air. The order of the size order of the fabricated Cu$_2$O is consistent with that obtained by Ayyub et al.$^{24}$ Figure 2(c) depicts the oxidation mechanism. The as-deposited nanowire Cu (denotes as stage I) diffuses to the outside of the grain, nucleates, and is oxidized to Cu$_2$O (stage II). The size effect induces transformation from Cu$_2$O to CuO above 250 °C (stage III). Diffused Cu is probably depleted at this time and a mixture of Cu$_2$O and CuO coexisted as a mixture (stage III) or the void may be existed in the center of the nanowire (stage IV). In spite of the different fabrication methods, the
CuO during oxidation. A single nanofiber has an average diameter of \(80\) nm and a length of \(2\) \(\mu\)m, which is the thickness of the AAO template. The retained AAO is responsible for the image contrast along the nanowire. The relevant selected area diffraction (SAD) pattern includes several sharp diffraction spots as shown in Fig. 3(b). These can be indexed as (110), (111), (200), (220), and (311) reflections from Cu\(_2\)O. Additively, some of the obtained broken-ring patterns reveal that the diffraction originates from randomly oriented grains along the nanofiber. The result elucidates that the nanofiber is polycrystalline, with a size that is similar to the diameter of the nanowire.

**IV. CONCLUSIONS**

In summary, both CuO and Cu\(_2\)O nanofibers were fabricated by the present approach of combining ECD and AAO templates to form the Cu nanowires and subsequently oxidize the Cu nanowire in air to yield copper oxides. Cu\(_2\)O was formed at \(250\) °C; it was converted to CuO by the size effect at \(350\) °C. CuO (111) was the dominant phase at \(900\) °C. The conclusion can thus be drawn that the ECD of the metal nanowire embedded in AAO subject to a simple thermal oxidation can be used to yield all other metal-oxide nanofiber and/or nanotube arrays. Further analyses, such as by varying the oxidizing atmosphere or the temperature, are still in progress. The authors suggest that the uniform copper-oxide nanowires may be employed to study the collective electronic and/or magnetic behavior in future applications, including field-emission displays, miniature gas sensors and photovoltaic cells.

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