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Abstract

Large-scale copper nanowires have been fabricated by potentiostatic electrochemical deposition (ECD) of copper sulphate solution within the nanochannels of porous anodic alumina templates. Scanning electron microscopy, transmission electron microscopy, selected-area electron diffraction and x-ray diffraction techniques were used to characterize the copper nanowires obtained. It is found that the individual copper nanowires are dense and continuous, with uniform diameters (60 nm) along the entire lengths of the wires (30 μm). The single-crystal and polycrystal copper nanowires can be prepared by choosing suitable applied potentials in the copper ECD processes. Moreover, the formation of copper oxides in nanochannels is also discussed in detail. The investigation results reveal that a lower overpotential is necessary to fabricate copper nanowires with fine crystalline structures by the potentiostatic ECD technique.

1. Introduction

Recently, one-dimensional (1D) nanostructures have attracted considerable attention owing to their novel physical and chemical properties, and the potential applications in a new generation of nanodevices [1–3]. Synthesis of 1D nanostructures with controllable composition and structures is very important for the studies of these materials. It is generally accepted that physical and/or chemical properties of materials are dominated mainly by their structures, which is one of the most important motivations for the studies on nanostructures [4]. Hence, identifying and understanding the relationship between preparation parameters and structures of the materials to be obtained are very important.

Template synthesis has been proved to be a versatile and simple approach for the preparation of 1D nanostructures since the pioneering work of Martin's group [5, 6]. An attractive synthesis method, electrochemical deposition (ECD) is controllable and inexpensive, and provides great opportunities for the preparation of new materials and nanostructures [7–10].

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In particular, by ECD of materials within the nanochannels of a template [5, 11], such as track-etched polymeric membrane or porous anodic alumina (PAA), various 1D nanostructures such as metals [12–16], semiconductors [17–19], and metal multilayers [20, 21] have been prepared.

Although great efforts have been made to fabricate long, free-standing metal nanowires with uniform diameters, the precisely controlled fabrication of crystalline metal nanowires is extremely challenging [14] and the details of metal ECD processes in the nanochannels of templates are still unclear [22]. We have investigated herein the template synthesis of single-crystal and polycrystal copper nanowires by the potentiostatic ECD approach and, moreover, the relationship between the applied potentials and the cathode processes in nanochannels is discussed in detail. Since electrochemical synthesis has been used widely, the investigation results presented in this work should be helpful not only as regards the template synthesis of metal nanowires, but also for the utilization of the ECD technique in nanofabrication and/or the electrochemical micromachining field [23, 24].

2. Experimental procedure

The PAA templates used in this work were prepared via a two-step aluminium anodic oxidation process in 0.3 M oxalic acid solution, which was similar to that described previously [25, 26]. The channel diameters and lengths of the through-hole PAA template used were about 60 nm and 30 μm, respectively. A thin gold layer (about 200 nm) was evaporated onto one side of the PAA template by using a JEE-4X vacuum evaporator in a vacuum of 2×10^{-5} Torr, which served as the working electrode in the subsequent ECD process.

The potentiostatic ECD of the copper nanowires was performed in a conventional three-electrode bath containing a mixture of 0.2 M $CuSO_4 \cdot 5H_2O$ and 0.1 M H_3BO_3 aqueous solutions. The pH of the solution was controlled in the range 4.5–5.0 by adding 0.1 M H_2SO_4 solution. A glassy carbon plate and a saturated calomel electrode (SCE) were used as counter-electrode and reference electrode, respectively. The copper ECD was carried out at different applied potentials (−0.15, −0.30, and −0.45 V, SCE) for 20–30 min at room temperature to prepare the copper nanowires. After the ECD, the upper parts of the samples were polished by using a 50 nm SiC polishing sandpaper in order to remove the copper particles that had grown excessively and stuck on the sample surface. Then the PAA template with copper nanowires was washed with ethanol and de-ionized water in turn, and dried in air before characterization.

A rotating-anode x-ray diffractometer (D/MaxrA, Cu Kα, $\lambda = 0.1542$ nm) was used to investigate the phase structures of copper nanowires. Before x-ray diffraction (XRD) characterization, the gold conductor layer on one surface of the PAA template was also polished by using the 50 nm SiC polishing sandpaper. Specimens for scanning electron microscopy (SEM, JEOL JSM-6300) were prepared by fixing a piece of copper nanowire/PAA template to a copper tape and soaking in a 5% H_3PO_4 solution to dissolve the upper part of the PAA template. After careful rinsing with de-ionized water and drying in air, the tape was attached to a SEM stub and a thin Pt layer was evaporated using a current of 7 mA for 10 min to form a conducting film for observation. For transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) characterizations, the samples were prepared by placing a small piece of the PAA template containing the copper nanowires in a 5% H_3PO_4 solution to dissolve the PAA template totally. The solution was removed via syringe and was replaced with de-ionized water to rinse the copper nanowires. After the remaining black solid was collected and triturated in a mortar with ethanol, small drops of the suspended solution were placed on a TEM grid for observation. Images were obtained in the JEM-200CX TEM working at an accelerating voltage of 200 kV. The SAED patterns were collected using this instrument at a camera length of 80 cm.
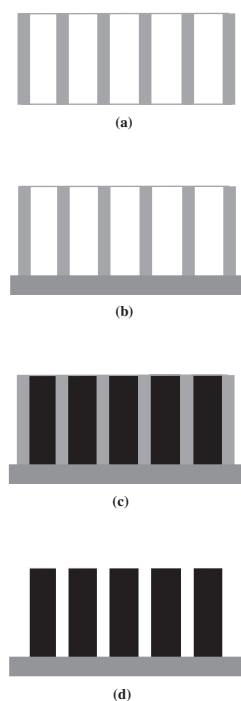
Figure 1. A schematic diagram of the template synthesis process. (a) The PAA template, (b) evaporation of conductor layers on one side of the PAA template, (c) the metal ECD process, and (d) metal nanowires after removing the PAA template.

3. Results

Template synthesis of metal nanowires is mainly performed by replicating the channel arrays of a PAA template (figure 1). It should be pointed out that PAA membrane has many advantages over track-etched polycarbonate membranes [27]; for example, the nanochannel diameters and lengths can be controlled by changing the anodization parameters [25, 26]. Hence, the PAA membrane can be used as an ideal template for preparing 1D nanostructures with different structural and geometrical characteristics, which is important for both theoretical studies and applications [28]. After removal of the PAA template, typical SEM images of the copper nanowires produced were taken, as shown in figure 2, revealing that large-scale copper nanowires have been fabricated by potentiostatic ECD of copper sulphate solution. The lengths of the copper nanowires are about 30 μm, which is in good agreement with that for the PAA template used.

The TEM technique was employed to get more details of the copper nanowire morphology and structures. Highly magnified TEM images (figure 3) show that the individual copper nanowires are dense, continuous, and uniform in diameter along their entire length. Additionally, it should be pointed out that there were no obvious differences between the morphologies of the individual copper nanowires formed at different applied potentials (-0.15, -0.30, and -0.45 V, SCE) because PAA templates with the same geometrical characteristics were used in every case. The diameter distribution of the wires was obtained from statistical results for twenty wire diameters through the TEM images; it revealed that the diameters of the copper nanowires varied from 58 to 62 nm with an average of 60 nm, in good agreement with the channel diameters of the PAA template used. However, the diameters of the single-
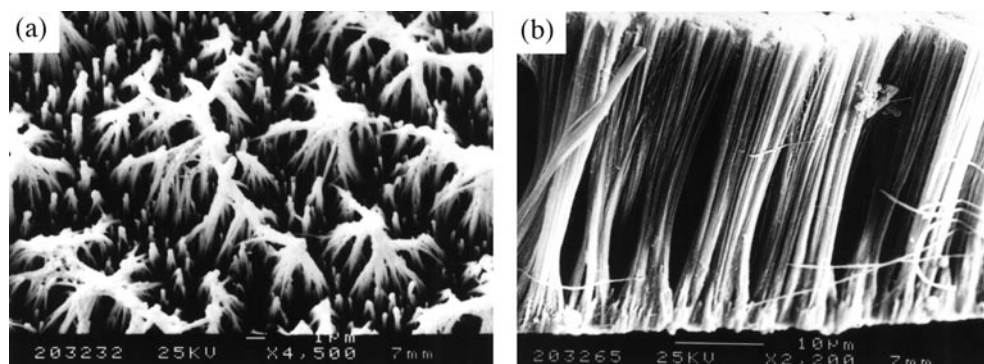
Figure 2. SEM images of copper nanowires formed at −0.15 V (SCE). (a) Top view and (b) cross-section view.
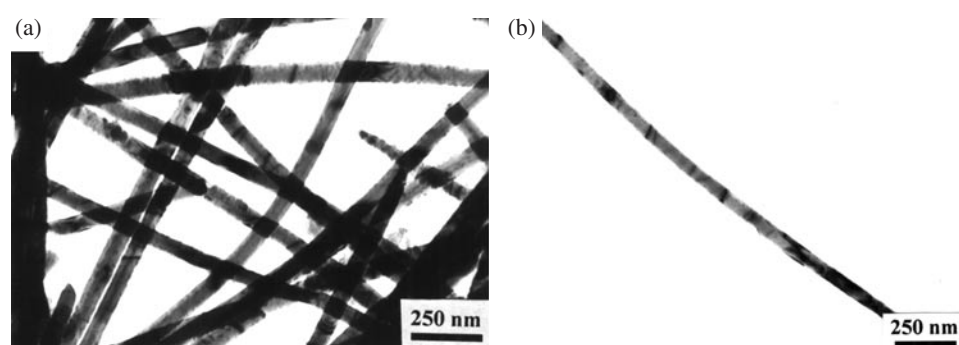
Figure 3. TEM images of copper nanowires formed at −0.15 V (SCE). (a) Copper nanowires and (b) an individual copper nanowire.

crystal copper nanowires presented by Molares *et al* [15] were always of micrometre scale and, moreover, Yi and Schwarzacher [13] have shown that the diameters of their single-crystal Pb nanowires changed by more than 20% along the wire length. Since they used track-etched polymeric membrane for the templates, this indicates the advantages of the PAA membrane in template synthesis of ultrafine 1D nanostructures.

The crystalline structures of the copper nanowires fabricated at different applied potentials were investigated by the SAED technique, and individual copper nanowires were used for characterization. Figure 4(a) shows the SAED patterns of the copper nanowires generated at −0.15 V (SCE). Many individual nanowires were characterized, and a single set of diffraction spots was always observed, indicating the single-crystal character of the copper nanowires formed at this potential [15, 22]. As the applied potentials become more negative (−0.30 V, SCE), copper nanowires with two sets of diffraction spots are observed (figure 4(b)). However, the copper nanowires formed at the most negative applied potentials used in this work (−0.45 V, SCE) show SAED patterns that are even more different than those formed at −0.15 and −0.30 V (SCE). Figure 4(c) shows several diffraction spots and an innermost ring from the copper (200) crystal plane, revealing that copper nanowires with polycrystal structures have been prepared. These results reveal that copper nanowires can be predictably synthesized as either single crystal or polycrystal by choosing suitable applied potentials in the potentiostatic ECD processes.
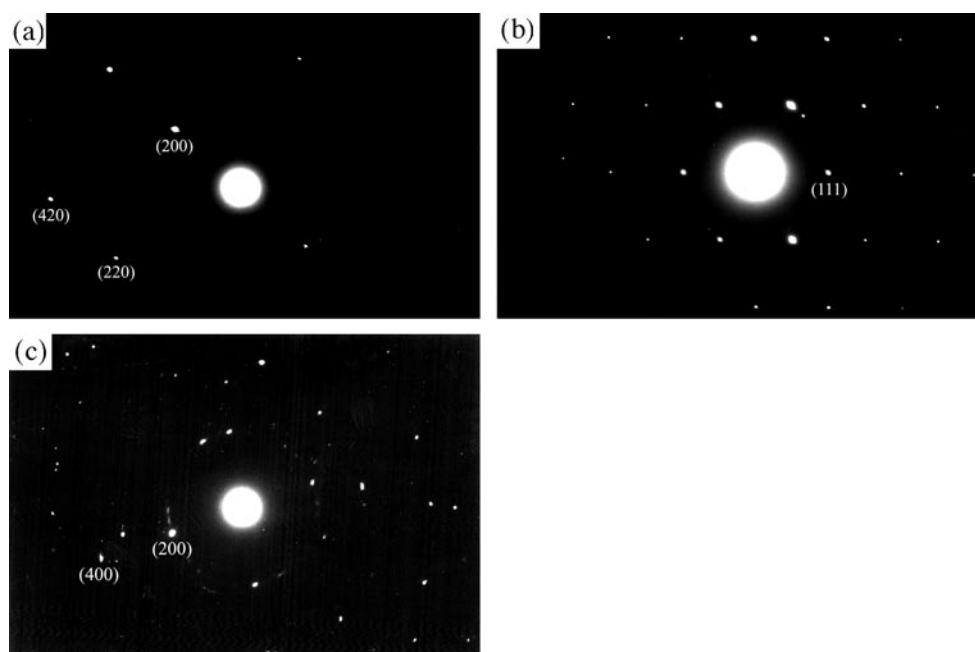
Figure 4. SAED patterns of the copper nanowires formed at applied potentials of (a) −0.15 V, (b) −0.30 V, and (c) −0.45 V (SCE). The instrument constant is 20.08 and the camera length is 80 cm.

It should also be pointed out that there exist some copper oxides in the polycrystal copper nanowires formed at −0.45 V (SCE), as is confirmed by our XRD experiments. The XRD spectra of the as-prepared copper nanowires within the PAA templates are shown in figure 5. It can be demonstrated that all the copper nanowires fabricated at different applied potentials show three intense peaks, with the highest for the (111) crystal plane and the other two lower peaks at (200) and (220). All the intense XRD peaks were at the same positions as for the polycrystalline copper standard (JCPDS, 4-386), indicating that copper nanowires with face-centred cubic crystal structures had been fabricated. It can also be seen that at more negative applied potentials (−0.30 and −0.45 V, SCE), the relative intensity of the copper (200) and (220) peaks becomes increased. Moreover, some copper oxide peaks appear (see CuO(111), CuO(310), Cu_2O(111), and Cu_2O(400) in figures 5(b) and (c)). Since the XRD characterizations of single-crystal and polycrystal copper nanowires were for the same conditions, the formation of copper oxides would be an interesting result of the XRD analysis. We characterized all the XRD samples repeatedly after they had been exposed to air at room temperature for two more weeks. It was found that there were no obvious changes in the relative intensities of the copper and copper oxide peaks. Hence, we suggest that the copper oxides were formed simultaneously with the copper potentiostatic ECD processes proceeding in the nanochannels. A more detailed discussion is presented in the following section of this paper.

4. Discussion

4.1. Relationship between applied potentials and crystalline structures of copper nanowires

During the copper deposition process, the Cu^{2+} ions deposit onto the cathode surfaces from the solutions to generate copper grains, and grow in the form of wires owing to the confinement
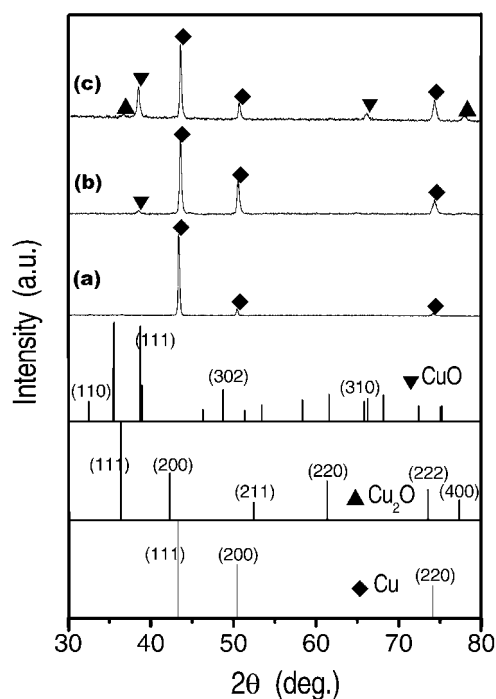
Figure 5. XRD spectra of the as-prepared copper nanowires formed at applied potentials of (a) −0.15 V, (b) −0.30 V, and (c) −0.45 V (SCE). Inset: the standard powder XRD data for Cu (JCPDS, 4-386), Cu_2O (JCPDS, 5-667), and CuO (JCPDS, 5-661).

effect of the nanochannels [11]. There would be two growth mechanisms of copper nanowires occurring simultaneously, i.e. the growth of existing nuclei and nucleation followed by the formation of new copper grains [15]. The deposition of copper takes place only when the potential of the cathode is lower than the equilibrium electrode potential of the Cu/Cu^{2+}; hence, a certain magnitude of cathode overpotential is necessary. The relationship between the overpotentials and the nucleation rates has been given as follows [29]:

$$N = a \exp\left(-\frac{b}{\eta_k^2}\right) \tag{1}$$

where N is the nucleation rate; η_k is the cathode overpotential; a and b are constants. It can be seen that the higher the overpotential, the higher the nucleation rates and the larger the nucleation sites in the electrocrystalline process [29, 30], which will lead to deposited copper nanowires with a polycrystal nature. For the creation of single-crystal copper nanowires, the growth of existing nuclei should be the dominant process and lower overpotentials were necessary [15, 22]. When a higher overpotential is used, for example −0.45 V (SCE) in this work, copper nanowires with polycrystal character would be obtained. These analysis results agreed well with our SAED and XRD investigation results. We have therefore suggested that the applied potentials used in the potentiostatic ECD processes have great influence on the crystalline structures of the copper nanowires obtained. Moreover, single-crystal and polycrystal copper nanowires can be fabricated by choosing the appropriate applied potentials in the potentiostatic ECD process. This will open up possibilities for investigating the relationship between structures and transport properties of metal nanowires.

4.2. Formation of copper oxides in nanochannels

It is true that the formation of metal oxides such as Cu_2O in direct-current ECD processes has been investigated before [31–34]. However, the results shown here are different from the previous ones in many ways. First, the amount of Cu_2O (about 2%) in our polycrystal copper nanowires is less than that of CuO (more than 16%; see figure 5(c)). Second, the periodic corrugated structures reported by Wang *et al* [34] are not observed along the copper nanowires in our TEM experiment. Hence, a more complex ECD process has been encountered, which is mainly caused by the reduced geometrical dimensions of the nanochannels (60 nm in diameter and 30 μm in length).

It is generally accepted that copper oxides deposited from aqueous environments are mainly governed by the applied potentials or current densities, the pH of the electrolyte, the temperature, etc [32]. As 'first-hand' information, the conditions for cathode deposition of copper oxides from aqueous solutions can be interpreted from the potential–pH equilibrium diagram for the copper–water system, in which solid Cu, Cu_2O, and CuO are considered [35]. It can be stated that the pH value of the ECD bath plays the important role of controlling the formation processes of the copper oxides [31–33]. With the above discussion in mind, the formation of Cu_2O and CuO in our polycrystal copper nanowires is expected to proceed as follows. In the potentiostatic ECD processes for copper, OH^- ions would be produced when the electrochemical conditions in the nanochannels were suitable. For example, the applied potentials were negative enough to induce hydrogen evolution:

$$2H^+ + 2e \rightarrow H_2 \tag{2}$$

or water decomposition:

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-. \tag{3}$$
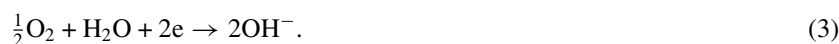
The hydrogen evolution that occurred in the template synthesis of metal nanowires by the potentiostatic ECD technique has been interpreted previously [16]. We only observed hydrogen bubbling from the PAA template surface when the most negative applied potential, -0.45 V (SCE), was used. With the evolution of hydrogen, the H^+ ions were exhausted and, consequently, the concentration of OH^- ions became high and the OH^- ions produced reacted with the Cu^{2+} ions to give copper hydroxide, which, however, is dehydrated to generate the more stable copper oxide:

$$
\begin{aligned}
& Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \\
& Cu(OH)_2 \xrightarrow{-H_2O} CuO + H_2O.
\end{aligned}
\tag{4}
$$

This process is similar to that of zinc oxide formation reported previously [36], and consistent with our XRD experiments (see figures 5(b) and (c)).

In addition, the formation of Cu_2O is also understandable on the basis of previous work focused on the ECD of cuprous oxide [31–34]. Cu_2O is usually generated in an alkaline electrolyte, in which certain magnitudes of the pH and current densities are necessary [32]. In our work, when the most negative applied potential, -0.45 V (SCE), was used for preparing polycrystal copper nanowires, the rates of production of OH^- ions and the current densities across the electrodes were higher than those for the other potentials used. Hence, Cu_2O can be generated at the cathode surface as in the following reactions reported by Mahalingam and Sanjeeviraja [31]:

$$
\begin{aligned}
& Cu^{2+} + OH^- + e \rightarrow Cu(OH) \\
& 2Cu(OH) \xrightarrow{-H_2O} Cu_2O + H_2O.
\end{aligned}
\tag{5}
$$

By comparing equation (4) to (5), it can be seen that the nucleation sites of CuO and Cu_2O in nanochannels of PAA template are very different from each other. Cu_2O can be formed only on the cathode surfaces, which is why it was possible to prepare periodic corrugated structures previously [34]. It should be pointed out that Cu_2O is thermodynamically unstable outside the pH range 6–14 in aqueous environments [32]. Therefore, the Cu_2O formed would decompose when the pH of the solutions inside the nanochannels was suitable, and this would decrease the amount of Cu_2O present in the polycrystal copper nanowires.

From the discussion presented above, we can predict that the formation of copper oxides in nanochannels should be avoided when the potentiostatic ECD technique is being used to produce fine crystalline copper nanowires. This can be accomplished by using lower overpotentials for the single-crystal copper nanowires. However, owing to the reduced geometrical dimensions of the nanochannels, it is difficult to give definite values, experimental or theoretical [24], for the extent of the hydrogen evolution and the water decomposition potentials within our systems. Indeed, the electrochemical conditions and copper ECD processes in nanochannels would be more complex than our analyses allow for. Therefore, further investigation focused on the details of electrochemical issues relating to nanochannels— for example, the mass transfer and metal electrocrystalline processes—should be given more attention.

5. Conclusions

In this paper, we have investigated in detail the electrochemical synthesis of copper nanowires with single-crystal or polycrystal structures by using PAA template, and the following conclusions were reached.

(a) The applied potentials used in the potentiostatic ECD processes for the fabrication of copper nanowires have great influence on the crystalline structures of the products.
(b) Single-crystal or polycrystal copper nanowires can be prepared by choosing suitable applied potentials in the potentiostatic ECD processes.
(c) Lower overpotentials are necessary not only for preparing single-crystal copper nanowires, but also to avoid the formation of copper oxides in the copper potentiostatic ECD process in nanochannels.

The investigation results presented herein should be helpful not only as regards template synthesis of other metal or semiconductor nanowires by ECD techniques, but also in the investigation of ECD processes on the nanometre scale.

Acknowledgments

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