Preparation and characterization of CuO nanowire arrays*

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Abstract: CuO nanowire arrays were prepared by oxidation of copper nanowires embedded in anodic aluminum oxide (AAO) membranes. The AAO was fabricated in an oxalic acid at a constant voltage. Copper nanowires were formed in the nanopores of the AAO membranes in an electrochemical deposition process. The oxidized copper nanowires at different temperatures were studied. X-ray diffraction patterns confirmed the formation of a CuO phase after calcining at 500 °C in air for 30 h. A transmission electron microscopy was used to characterize the nanowire morphologies. Raman spectra were performed to study the CuO nanowire arrays. After measuring, we found that the current–voltage curve of the CuO nanowires is nonlinear.

Key words: nanowires；CuO；semiconductors；current–voltage characteristic

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1. Introduction

Nanowires of low dimensional structure materials have been intensely researched in recent years. Many peculiar new properties have been observed in nanowire systems. For example, metal nanowire arrays behave as modulators of light[1], semiconductor nanowires show a wide band gap character[2], and magnetic nanowire arrays manifest anisotropic magnetic properties[3]. Based on the properties of the nanowires, some nanowire devices have been designed and fabricated[4]. Due to the wide range of potential applications of the nanowires, a lot of effort has been made on the preparation of well-defined nanowires, such as self-assembly of ZnO nanowires[5] and thermal evaporation preparation of Si nanowires[6].

CuO is a kind of narrow band-gap semiconducting oxide, which has been widely studied as a catalyst, electrochemical cells, dye-sensitized solar cells, photothermal and photoconductive materials[7−11]. Nanoscale CuO has attracted much interest in recent years since some new characteristics different from the bulk materials have been found. For example, UV–visible absorption spectrum studies show that the band gap in CuO nanoparticles (E_g = 2.18 eV) is much larger than that in bulk CuO (E_g = 1.85 eV)[12]. Different approaches have been used in the preparation of CuO nanostructures. CuO nanorods have been fabricated by thermal decomposition of the precursor of $Cu_2C_2O_4$[13], Large-scale CuO nanowires have been prepared by an evaporation method[14], CuO well-ordered nanofibers have been synthesized using a polycarbonate membrane as a template[15]. In this paper, the oxidation of Cu nanowires is studied and CuO nanowires with different diameters are prepared by using AAO membranes. Nonlinear *I–V* characteristics were observed in CuO nanowire arrays.

2. Experiments

The AAO membranes were prepared by anodizing aluminum foil in 0.3 mol/L oxalic acid with an anodic voltage of 48 V. The electrochemical cell was controlled at a constant temperature of 17 °C. After anodizing for 10 h, the AAO was formed with a nanopore length of about 30 μm. Afterwards, the AAO membranes were put into a 6 wt% phosphoric acid solution to widen the nanopores. After 20, 60, and 100 min widening, three kinds of AAO with different pore diameters were prepared. These AAO's were used as the templates for the electrodeposition of copper nanowires. In the deposition, a mixture of $CuSO_4$ and H_2SO_4 was used as the electrodeposition solution and a constant DC voltage of 0.5 V was employed. After depositing, about 25 μm copper nanowires were formed in the AAO nanopores. The copper nanowire arrays were calcined at 350, 400, 450, and 500 °C in ambient atmosphere for the oxidation study. After calcining at 500 °C for about 30 h, CuO nanowire arrays were formed.

A scanning electron microscopy (SEM, JSM-5900) was employed in the observation of the AAO morphologies. The crystal structure and the phase composition of the nanowires were analyzed by powder X-ray diffraction (XRD, Rigaku D/Max-RA) with CuKα radiation. After the template dissolved in a NaOH solution, the CuO nanowires were dispersed into ethanol by using an ultrasonic method for the transmission electron microscopy (TEM, JEM-200CX) studies. With 488 nm laser excitation, Raman scattering was measured at room temperature (RT) by a confocal laser microRaman

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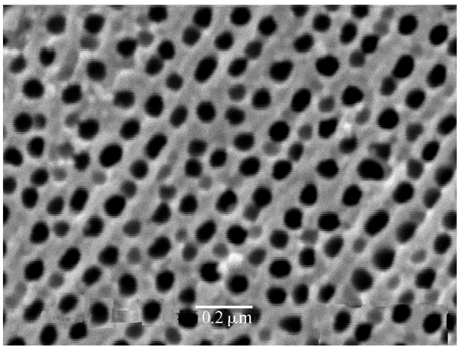

Fig. 1. SEM top view of the AAO membrane widened for about 100 min.

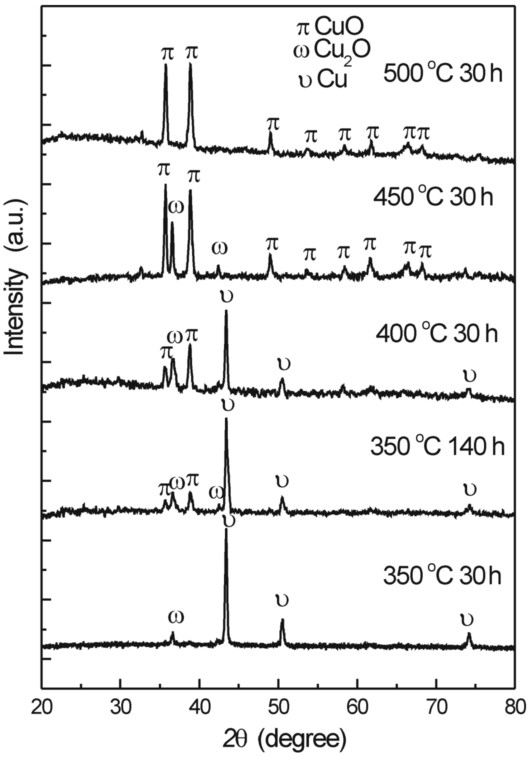

Fig. 2. XRD patterns of the samples oxidized under different conditions.

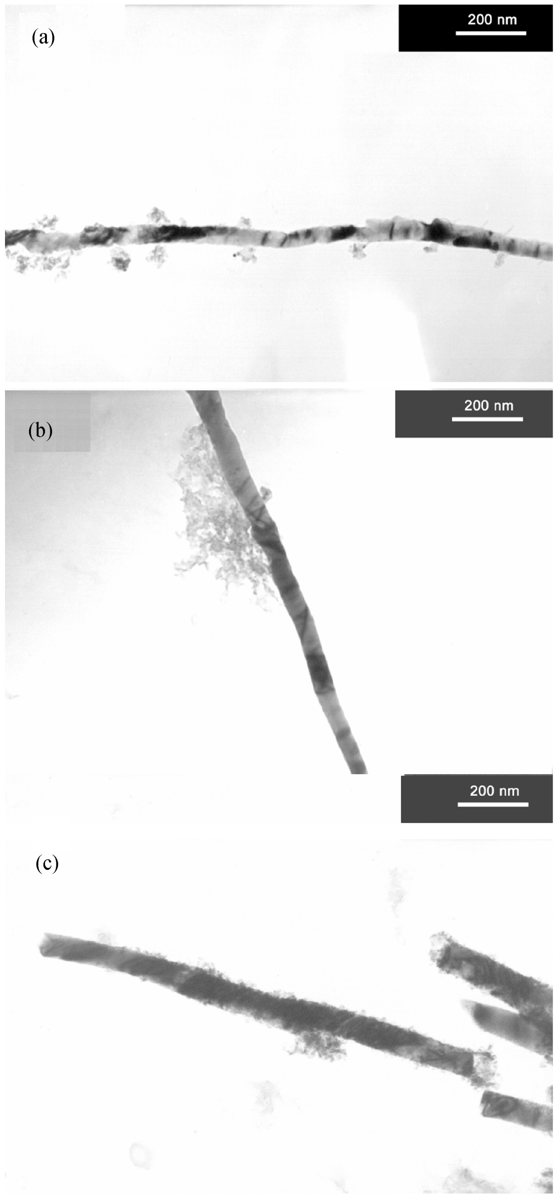

Fig. 3. TEM images of the nanowires prepared in the AAO membranes after widening of (a) 20 min, (b) 60 min, and (c) 100 min.

spectrometer (Raman, LABRAM-HR). The electrical properties of the CuO nanowire arrays and bulk material were measured by using a 2400 sourcemeter (Keithley) and a 2182 nanovoltmeter (Keithley).

3. Results and discussion

The SEM observation revealed the morphologies of the AAO membranes. Figure 1 shows the top view of the AAO widened for 100 min. In this figure, the diameters of the nanopores are almost the same. The nanowires were confined in the nanopores, which makes it possible to prepare the nanowires with the same diameter. The diameters of the AAO nanopores can be controlled by the widening time.

In order to find the best conditions for the preparation of CuO nanowires by oxidation, a series of calcining temperatures and times were selected. The XRD patterns of the oxidized samples are displayed in Fig. 2. A copper phase and a weak Cu_2O phase are observed in the 350 °C 30 h-calcined sample. As the annealing time extended to 140 h, both CuO and Cu_2O appeared while the copper phase is still a major part of the sample. So 350 °C is still not high enough for the oxidation of copper. When the calcining temperature increased to 400 °C and kept for 30 h, the copper oxide phases increased notably. When the annealing temperature reached 450 °C, the copper nanowires were completely oxidized, resulting in the coexistence of CuO and Cu_2O. A pure CuO phase was observed until the samples calcined at 500 °C for 30 h. Three CuO nanowire samples with different diameters embedded in AAO templates were prepared by calcining the copper nanowires at 500 °C for 30 h.

After the AAO was dissolved in NaOH solution, CuO nanowires were dropped onto a TEM grid with a carbon film for the TEM observation. Figure 3 shows the TEM images of the CuO nanowires of the three samples correspondingly.

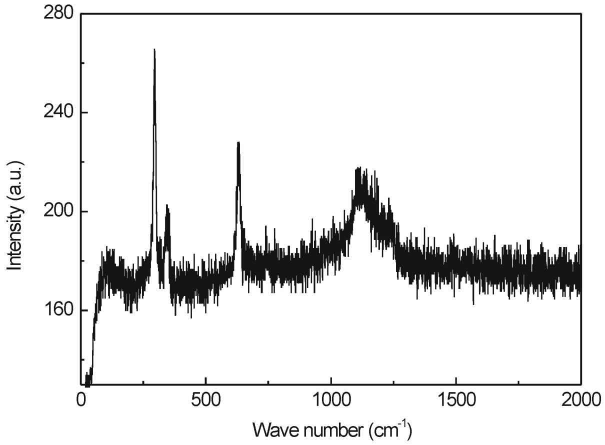

Fig. 4. Raman spectra of the CuO nanowires with a diameter of about 80 nm.

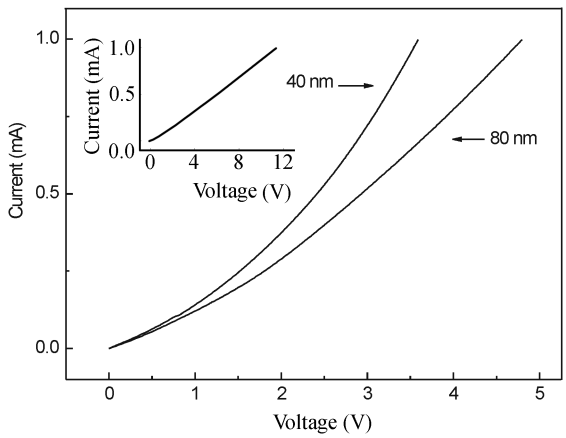

Fig. 5. Conductivity of the CuO nanowire with diameters of 40 and 80 nm.

From the TEM images, it is observed that the diameters are about 40, 60, and 80 nm, which matched the diameters of the AAO nanopores very well. It can be concluded that the diameter of the CuO nanowire could be controlled by the diameter of the nanopores.

Raman spectra measurements were performed during the characterization of the CuO nanowires embedded in the AAO membranes. Figure 4 shows the Raman spectrum of a sample. As no peak was observed in the Raman spectrum of the AAO membrane, the obtained peaks should belong to CuO nanowires. The peak at 297 cm^{-1} can be identified as the Ag mode and the peaks at 344 and 631 cm^{-1} as Bg modes in monoclinic CuO[16]. The broad feature centering at 1100 cm^{-1} might be assigned to multi-phonon scattering[16]. No difference in the peak position was observed in the three samples. The only difference in the Raman spectra is the intensity of the peaks. The smaller diameter of the nanowire, the lower Raman spectrum peaks that were observed, which may indicate a decrease in the ratio of CuO to Al_2O_3 in the samples.

The electrical properties of the CuO nanowire arrays were characterized at room temperature by a two-electrode method. The nonlinear *I*–*V* characteristics were observed for all three samples. *I*–*V* curves for the 40 and 80 nm diameter samples are shown in Fig. 5. The inset shows the *I*–*V* curve of a bulk CuO sample that is basically linear. The resistivity of an AAO template is correspondingly higher[17]. The nonlinear feature of the sample is similar to that obtained from the bare CuO nanowires. The conductivity of CuO is composed of volume conductivity and surface conductivity. However, for bulk CuO, the ratio of the surface to the volume is very small. So the conductivity of bulk CuO mostly comes from the volume conductivity, and the *I*–*V* curve is linear. For a CuO nanowire, the ratio of the surface to the volume is much larger, so the surface conductivity is dominance. At the same time, the surface conductivity of the CuO nanowires becomes larger with the reduction of the CuO nanowires diameter. The state of the surface decides the surface property. In most cases, there are some small impurities and imperfections in the CuO nanowires in the AAO templates, and the CuO nanowires are prepared and measured in air. So the surface conductivity of CuO nanowires shows a nonlinear property, but the relationship between the surface state and the surface conductivity will be researched in the future work.

4. Summary

In conclusion, CuO nanowire arrays were prepared by oxidized copper nanowires embedded in AAO membranes. A XRD study reveals the formation of a pure CuO phase by oxidation at 500 °C for 30 h. Raman spectra show typical CuO peaks for the nanowire arrays. The *I*–*V* curves of the sample are nonlinear. A TEM observation shows that the diameter of the CuO nanowire can be controlled by adjusting the diameter of the nanopore of the AAO membrane.

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