

Fabrication and characterization of highly ordered Au nanowire arrays

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In this paper, we report the electrochemical fabrication of highly ordered Au nanowire arrays within hexagonal close-packed nanochannel alumina (NCA) templates with pore diameters ranging from 35 nm to 100 nm. The observations of TEM, SAED, and HRTEM show that single crystal Au nanowires have been obtained within the templates with 45 nm diameters. The growth mechanism of the single crystal Au nanowires is also discussed.

Introduction

In recent years, there has been increasing interest in the fabrication of one-dimensional nanostructures because of their potential utilization in electronic, magnetic, optical, and micromechanical devices.^{1–6} Metallic nanowires are of great interest from a fundamental point of view as well as for future applications.^{7,8} Highly ordered metallic nanowire arrays are particularly important for obtaining scaled-up functional devices for use as microelectrodes, probes, and data storage devices.^{9–10} The ability to precisely prepare such structures on a large scale is an important goal of materials science. One strategy is to use a porous nanochannel alumina (NCA) template to fabricate such structures.^{10–13} An important advantage of the template method is that the nanowires prepared in this way can be diameter-controllable and well defined. Here, we report the electrochemical fabrication of highly ordered Au nanowire arrays within hexagonal close-packed nanochannel alumina (NCA) templates with pore diameters ranging from 35 nm to 100 nm. The influence of the preparation conditions on the structure of the Au nanowires is also discussed.

Experimental

NCA templates were prepared by means of anodization.^{14–16} Briefly, high purity (99.999%) aluminium foils were used as the starting material. Prior to anodizing, the aluminium was annealed at 500 °C in order to obtain homogeneous conditions for pore growth over large areas. Subsequently, the foils were electropolished in a 1:9 by volume mixture of HClO₄ and C₂H₅OH. Anodization was carried under a constant cell voltage in an oxalic acid solution. After the anodization, the remaining aluminium was removed in a saturated HgCl₂ solution. Subsequently, the pore bottoms were opened and widened by chemical etching in aqueous phosphoric acid. In order to fabricate the nanowire arrays, a layer of Au thin film was deposited as an electrode on one side of the anodic porous alumina membrane using a vacuum evaporation apparatus. Au nanowires were electrodeposited from the following solution: 12 g l⁻¹ HAuCl₄, 160 g l⁻¹ Na₂SO₃, 5 g l⁻¹ EDTA, 30 g l⁻¹ K₂HPO₄, 0.5 g l⁻¹ CoSO₄; pH 9.0. The cell voltages were kept at 0.8 V. The structure and morphology of the nanowire arrays were investigated using a scanning electron microscope (SEM

JEOL JSM-6300), a transmission electron microscope (TEM JEM-200CX), and a high-resolution transmission electron microscope (HRTEM, JEOL-2010). The SEM and TEM samples of Au nanowires were obtained by dissolving the alumina using a mixture of 6 wt% phosphoric acid and 1.8 wt% chromic acid.

Results and discussion

NCA templates

Hexagonal close-packed arrays of porous alumina with selectable diameters ranging from approximately 35 nm to 100 nm can be formed in oxalic acid solutions by varying the anodizing conditions and the time of the pore widening treatment. Fig. 1 shows the SEM images of hexagonal close-packed arrays of porous alumina. Fig. 1a shows the SEM image of porous alumina which was anodized in 0.3 M oxalic acid at 17 °C at 35 V; the average pore diameter and interpore

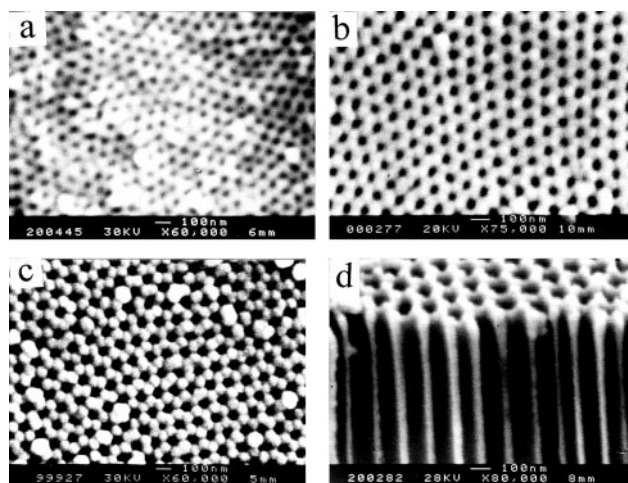


Fig. 1 Nanochannel alumina templates: (a) SEM image of the surface view of porous alumina anodized in 0.3 M oxalic acid at 17 °C at 35 V. (b) SEM image of the surface view of porous alumina anodized in 0.3 M oxalic acid at 12 °C at 40 V. (c) SEM image of the surface view of porous alumina anodized in 0.25 M oxalic acid at 5 °C at 60 V. (d) Oblique cross-section views of porous alumina anodized in 0.25 M oxalic acid at 3 °C at 70 V.

distance are 35 nm and 100 nm, respectively. Fig. 1b shows the SEM image of porous alumina which was anodized in 0.3 M oxalic acid at 12 °C at 40 V; the average pore diameter and interpore distance are 45 nm and 105 nm, respectively. Fig. 1c shows the SEM image of porous alumina which was anodized in 0.25 M oxalic acid at 5 °C at 60 V; the average pore diameter and interpore distance are 70 nm and 130 nm, respectively. Fig. 1d shows an oblique cross-section view of porous alumina which was anodized in 0.25 M oxalic acid at 3 °C at 70 V, in which the cross sections of the parallel cylindrical pores can be clearly seen; the average pore diameter and interpore distance are 95 nm and 135 nm, respectively.

Au nanowires

Fig. 2 show SEM images of highly ordered Au nanowire arrays prepared in the NCA templates with 95 and 70 nm diameter pores. It can be clearly seen that the Au nanowires are of an equal height and have a highly ordered tip array. The exposed Au nanowires retain the size and shape of the pores in the template. Fig. 3a shows a TEM image of one of the Au nanowires, which is prepared in the NCA template with 45 nm diameter pores. The Au nanowire is straight and has a uniform diameter about 45 nm and length about 5 μm. A selected-area electron diffraction (SAED) pattern [Fig. 3a, inset] of the nanowire could be indexed for the [110] zone axis of single crystal Au. The single-crystal structure was further confirmed by HRTEM images of the nanowires. The HRTEM image shown in Fig. 3b shows clearly the single-crystal structure of the nanowire and the (111) and (002) lattice fringes with interplanar spacings of around 0.24 nm and 0.20 nm, respectively. It can be seen that only the edge of the nanowire is visible because the central part of the nanowire is too thick to be transmitted by the electron beam. Fig. 3c shows a TEM image of an Au nanowire, which is prepared in the NCA template with 70 nm diameter pores. A selected-area electron diffraction (SAED) pattern [Fig. 3c, inset] of the nanowire shows that the nanowire presents a polycrystalline structure. The results indicate that the template with smaller pore diameter is favorable for the formation of single crystal nanowires, while the template with larger pore diameter is favorable for the formation of polycrystalline nanowires.

Template syntheses of single crystal metal and semiconductor nanowires have been reported by using electrodeposition^{17,18} and other methods.¹⁹ However, there are few reports

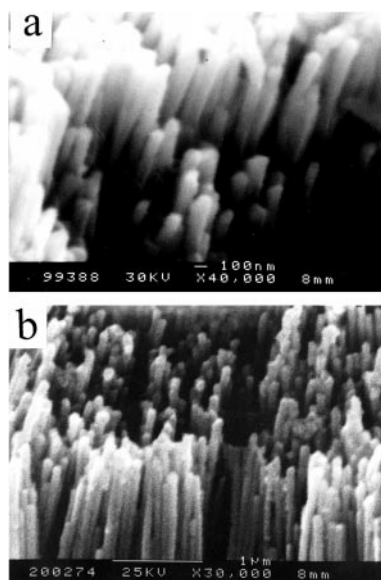


Fig. 2 SEM images of the highly ordered array of Au nanowires prepared in the NCA templates with pore diameters about 95 nm (a) and 70 nm (b).

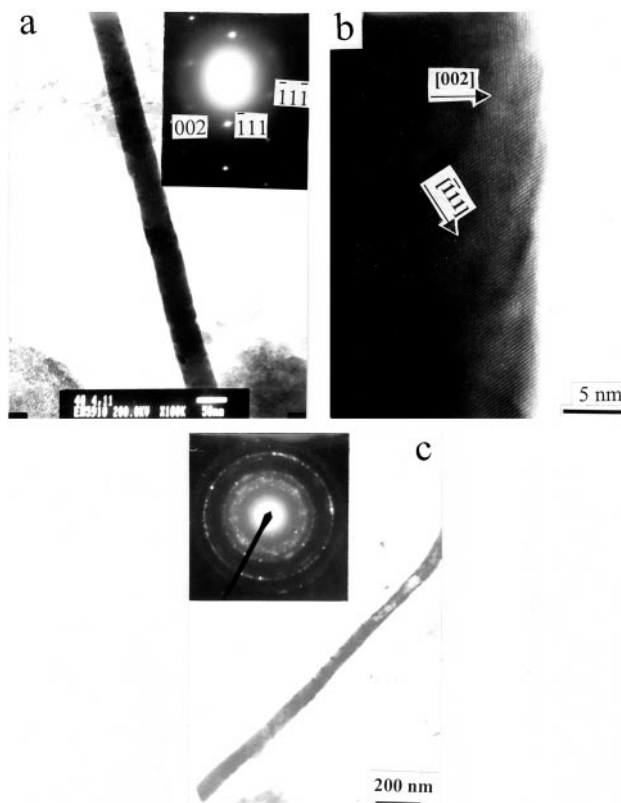


Fig. 3 (a) TEM image of an Au nanowire with a diameter about 45 nm, the inset shows the SAED of the nanowire, which is consistent with Au single crystal indexed as Au [110]. (b) HRTEM image of the single crystalline Au nanowire. (c) TEM image of an Au nanowire with a diameter about 70 nm, the inset shows the SAED of the nanowire, which is consistent with polycrystalline Au.

on the growth mechanism because the situation becomes more complex by the presence of the template. An explanation of the nanowire growth mechanism within the NCA template must remain speculative. Since the templates have parallel arrays of pores of uniform diameter, we assume that the pores are one-dimensional and the surface of the Au substrate is smooth. Therefore, the Au-coated NCA template can be considered as a porous electrode, which is a combination of single pores. It has also been proved that the electrochemical processes could be diffusion-limited within the porous electrodes.²⁰ Therefore, it can be inferred that the diffusion rate should have an effect on the electrodeposition of the nanowires. The diffusion rate of ions in the pores is slower than on the plane surface and the diffusion rate decreases with decreasing pore diameter. When the voltages are kept constant, the cathode current densities decrease with decreasing pore diameter, which has been confirmed by our experiments. The oriented growth of single crystals could only be obtained under low polarization (small current densities) conditions to avoid the formation of new nuclei. In other words, the deposition process is expected to approach an equilibrium process. Therefore, the slow diffusion rate and small cathode current density are essential to meet the requirement. Besides, the content of electrolyte also has an influence on the electrochemical process. Determining the exact nature of the deposition process will require further detailed study.

Conclusions

Highly ordered Au nanowire arrays have been electrochemically fabricated within hexagonal close-packed nanochannel alumina (NCA) templates with selectable channel diameters ranging from approximately 35 nm to 100 nm. Single crystal Au nanowires with 45 nm diameters have been prepared and

the growth mechanism has also been discussed. The gentle electrochemical fabrication method presented is fast and inexpensive. These highly ordered Au nanowire arrays would be useful for study of the material properties of nanowires and have potential utilization in the future.

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