

Ordered Ni nanowire tip arrays sticking out of the anodic aluminum oxide template

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We present a method for making highly ordered arrays of Ni nanowire (NW) tips fully exposed over the surface of anodic aluminum oxide (AAO) templates with uniform exposed lengths. Ni NWs are electrochemically deposited in the nanochannels of the AAO templates, and the templates surface is selectively etched to expose Ni NW tips of uniform lengths, which can be tuned by adjusting the etching time. The magnetic domain structure and magnetic hysteresis of the Ni NW tips were studied at room temperature, and the results indicate strong magnetic anisotropy for the NW arrays and magnetic coercivities significantly larger than that of bulk Ni. The ordered NW tips fully exposed over the surface of the AAO templates with uniform lengths could have various practical applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.1846942]

I. INTRODUCTION

Porous anodic aluminum oxide (AAO) is a self-ordered nanoporous membrane that consists of a hexagonal array of cells with uniform and parallel straight cylindrical nanopores perpendicular to the membrane surface.¹⁻⁵ The interpore distance and pore diameter can be tuned by adjusting anodic oxidation parameters, such as voltage and electrolyte solution composition.^{3,6,7} Furthermore, the pore diameter can also be widened homogeneously over the entire pore length by isotropic chemical etching in phosphoric acid solution after the anodic oxidation.^{6,8,9} These unique structural features with their thermal and chemical stability make the AAO membrane an ideal nanoporous template for the fabrication of ordered nanowires (NWs). Among the various methods used for the preparation of NWs within the nanochannels of the AAO templates, electrochemical deposition has been proven to be a low-cost and high-yield technique.¹ A variety of metal and semiconductor NWs,¹⁰⁻³⁰ as well as multilayered NWs,³¹⁻³⁹ have been produced by electrochemical deposition within the nanopores of the AAO templates.

One application of the template-synthesized NWs is as building blocks for the self-assembly of supramolecular architectures. For example, dithiol chemistry can be used to self-assemble colloidal Au nanoparticles onto the ends of the electrodeposited Au NWs within the pores of polycarbonate template.⁴⁰ Unfortunately, the efficiency of the self-assembly process was low because the ends of the Au NWs were recessed within the pores of the template.⁴⁰ The efficiency of the self-assembly process would be improved if the ends of the NWs could protrude from the template surface. Recently Martin's group has developed a method by etching a NW-containing polycarbonate template using O₂-plasma.⁴¹ The polymer at the template surface was selectively removed,

thus exposing the ends of the Au NWs. However, exposing NWs from AAO templates has not been reported yet, mainly due to the so-called "skyscraper" phenomenon,²¹ i.e., the as-electrodeposited NWs inside the AAO nanochannels usually have different lengths.¹⁷⁻²¹ Thus, it is difficult to expose all the NWs from the top surface of the template (facing electrolyte during electrodeposition) since the NW tips are not at the same height. Even if some tips can be exposed, the number of tips per unit area will be greatly reduced, and the exposed long NW tips aggregate into clumps due to the advent of capillary forces⁴² between the NWs upon dissolution of the template.

Here, we describe an alternative method for making highly ordered NW tip arrays with uniform sticking-out lengths from the AAO template surface by selectively etching the surface layer of the template bottom side (which is covered by an Au layer during electrodeposition) instead of from the top surface. We show this for electrodeposited metal (Ni) NW-containing AAO template. We demonstrate that the Au layer, on the bottom side of the electrodeposited Ni NW-containing AAO template, can be removed by Ar⁺ ion milling. By etching this bottom side in a 2 wt % aqueous sodium hydroxide (NaOH) solution, the surface layer of the AAO template is selectively removed, and the ends of the metal NWs are exposed, as illustrated schematically in Fig. 1. The exposed NW ends have the same length, since all the NW ends (the first deposited parts of the NWs) are at the same depth and hence at the same level near the bottom part of the template. In addition, the lengths of the protruding NW tips can be controlled by the wet chemical etching time in the 2 wt % NaOH solution.

II. EXPERIMENT

The nanoporous AAO templates were prepared by using a modified two-step anodizing process reported elsewhere.⁹ Al foils (99.9995%, 0.25 mm thick, Alfa Aesar) were cleaned with ethanol and acetone in sequence, followed by annealing at 450 °C for 5 h in a vacuum of about 10⁻³ Pa.

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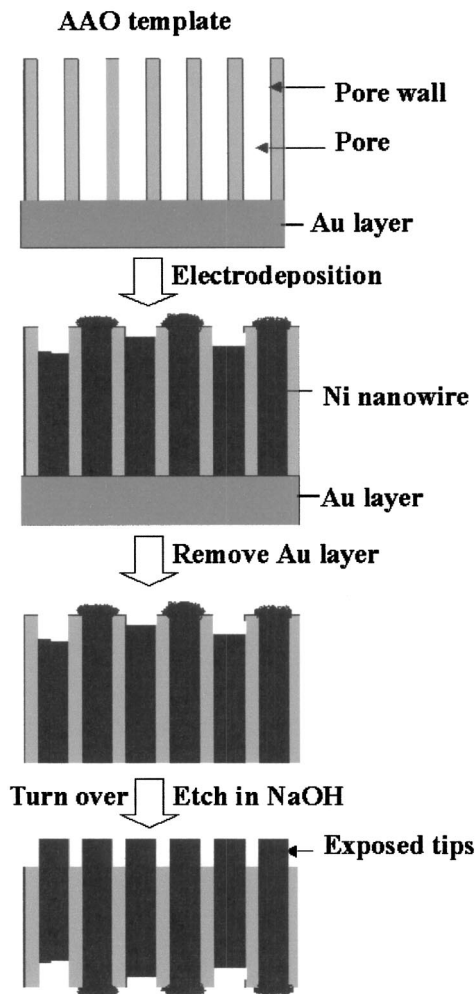


FIG. 1. Schematic cross-sectional illustration of making highly ordered metal NW tips sticking out of the surface of the AAO template.

The first anodizing process was conducted under a constant voltage of 40 V dc in a 0.3 M oxalic acid solution at 10 °C for 5 h. Then, the anodic oxide layer was removed in a mixed solution of phosphoric acid (6 wt %) and chromic acid (1.8 wt %) at 60 °C for 8 h. The second anodizing process was carried out for 8 h under identical conditions to those in the first anodizing. The remaining Al substrate was removed in a saturated stannic chloride (SnCl_4) solution at room temperature. Subsequently, the semimanufactured AAO template was immersed in a 5 wt % aqueous phosphoric acid solution at 30 °C for 90 min to remove the barrier layer on the bottom side, and simultaneously widen the pores. An adhesion layer of Ti (10 nm) and an Au film (600 nm) were coated onto one side of the through-hole AAO template by e-beam evaporation in order to cover the pores completely, and to serve as the working electrode during electrochemical deposition. For the electrochemical deposition of metal into the nanochannels of the AAO template, a specially constructed electrochemical cell was used. This cell consisted of a cylindrical copper base onto which the Au-coated AAO template was placed with the Au film facing the Cu base. This base was screwed into a polymethyl methacrylate cell, with a rubber O-ring in between to seal them up. The electrolyte was confined to the bare side of the

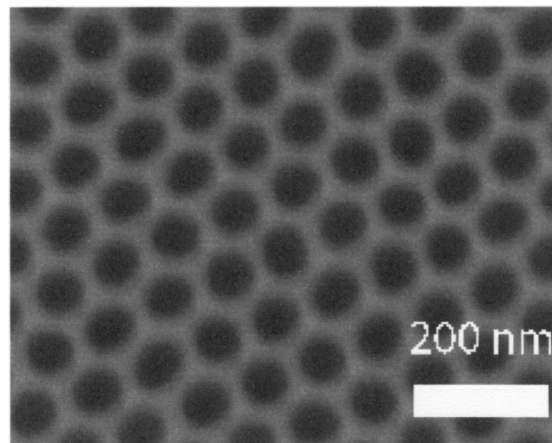


FIG. 2. A typical SEM plan view of the as-prepared nanoporous AAO template.

template so that the deposition of the NWs would initiate onto the Au layer at the template bottom and continue outward from the bottom of the pore to the pore opening. Ni NWs were electrodeposited from an aqueous solution of 0.2 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.1 M H_3BO_3 . The pH value of the electrolyte was adjusted to about 2.0 with 0.1 M H_2SO_4 solution. The electrochemical deposition was carried out at a constant voltage of 1.5 V dc with a graphite plate as the anode or counter electrode.

In order to expose the Ni NW tips out of the AAO template, the Ni NW-containing AAO templates were fixed onto copper rings (o.d. 3 mm, i.d. 1 mm) using epoxy with the Au layer on the topside, and then the Au layer was removed by Ar sputtering using an ion mill (Gatan Due Mill600). Subsequently the surface layer of the AAO template on the ion milled side was selectively etched by floating the Ni NW-containing AAO templates on the surface of a 2 wt % aqueous NaOH solution with the ion-milled side down.

III. RESULTS AND DISCUSSION

Figure 2 shows a typical scanning electron microscope (SEM) plan-view of the AAO template used in this work, the template exhibits hexagonally arranged nanopore arrays with pore diameter and interpore distance about 75 and 100 nm, respectively. To determine the crystal structure and the diameter of the Ni NWs by transmission electron microscope (TEM), the NWs were released by immersion of the Ni NW-containing AAO templates in a 10 wt % aqueous NaOH solution. Figure 3(a) is a TEM image of the individual Ni NWs liberated from the AAO template; the diameter of the NWs is about 75 nm, in agreement with that of the pores in the AAO template. Each NW is polycrystalline, and Fig. 3(b) shows the selected-area electron diffraction pattern of the NWs, revealing reflections corresponding to the face-centered-cubic (fcc) structure of nickel. Figure 3(c) is a high-resolution TEM image of a NW. The lattice spacing in the image is about 0.2 nm, indicating a (111) fcc plane of Ni.

Figure 4 is a representative SEM top view of the Ni NW tips sticking out of the AAO template after the ion milled side was etched in the 2 wt % NaOH solution for 30 min. The average diameter of the NWs is about 75 nm, in agree-

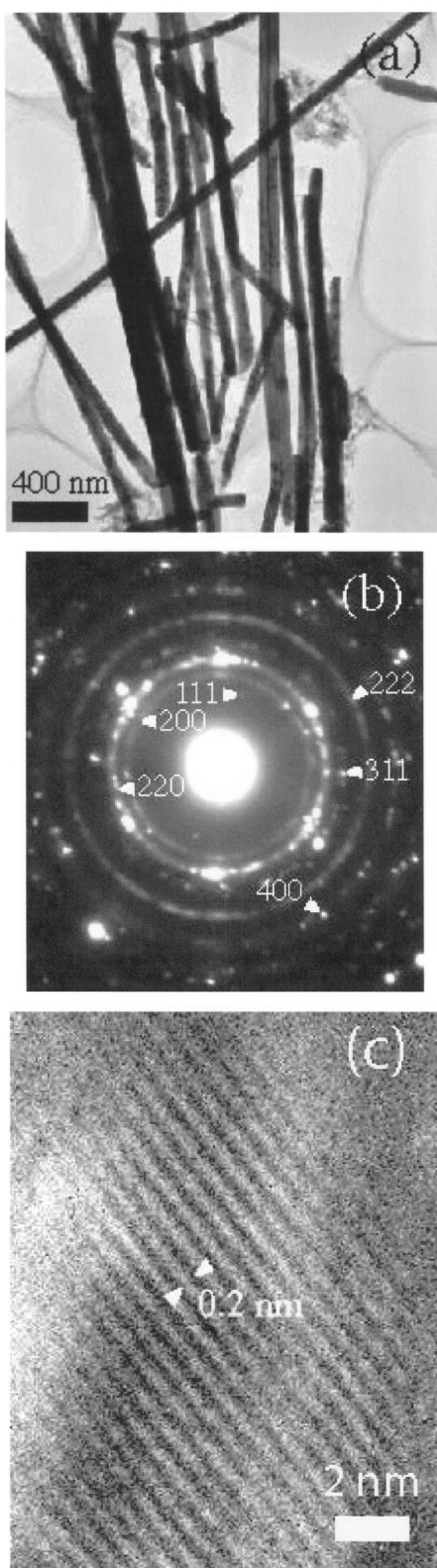


FIG. 3. (a) A typical TEM image of the individual Ni NWs liberated from the AAO template. (b) The selected-area electron diffraction pattern of the NWs; the rings can be indexed to the reflections of Ni. (c) A high-resolution TEM image of the Ni NW, revealing the (111) lattice fringes of Ni.

ment with that of the TEM observation. The lengths of the exposed NW tips can be identified by tilting the specimen stage with respect to the imaging electronic beam under SEM observation. Figures 5(a)–5(c) are typical oblique (with

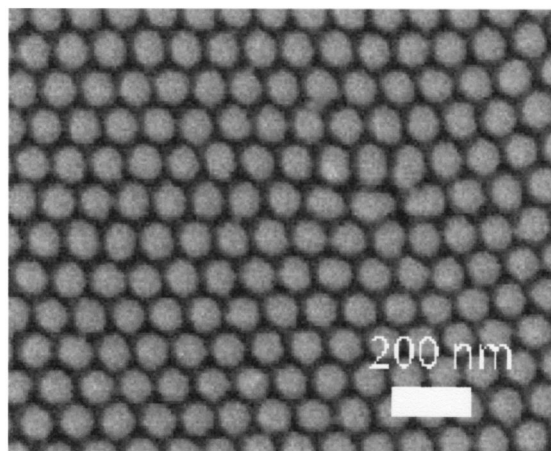


FIG. 4. A representative field emission SEM top view of the Ni NW tips sticking out of the AAO template after the ion-milled side being etched in the 2 wt % NaOH solution for 30 min.

specimen stage tilted at ~ 30 deg) SEM micrographs of the NW tip arrays after the ion-milled side was etched in the 2 wt % NaOH solution for 15, 30, and 45 min, respectively. These NW tips are well separated and uniform in length for a given etching time. It can be seen clearly that the lengths of the protruding NW tips increase with the etching time in the 2 wt % NaOH solution. The exposed NW tips in Figs. 5(a)–5(c) have a length of 20 ± 5 , 50 ± 5 , and 70 ± 5 nm, respectively.

It is well known that during the electrochemical deposition within the nanochannels of the AAO template, the growth of NWs starts at the pore tips, and continues from the bottom of the pore to the pore opening.¹⁸ Although the NWs exhibit the so-called “skyscraper” phenomenon associated with a lack of length uniformity and control,²¹ the NW tips on the pore bottom side are at the same level. So, when the Au layer is removed by ion milling, all the NW tips are observable (visible) and in the same plane, when viewed from the bottom side. Therefore, when the ion-milled surface is put onto the 2 wt % NaOH solution, a thin layer of the AAO template is selectively etched away. Thus, the ends of the metal NWs are exposed at uniform lengths.

Regular arrays of magnetic materials have potential applications in magnetic storage, where each magnetic pillar or particle could correspond to a bit, acting as a single domain nanomagnet. For the geometry of the NW arrays reported here, with the spacing of 100 nm between adjacent NWs, the data density on the order of 75 Gb/in^2 can be achieved, which is higher than the predicted paramagnetic limit of 70 Gb/in^2 for the conventional Co-alloy thin film media.⁴³ The exposed Ni NW tip arrays were also characterized using atomic force microscope (AFM) and magnetic force microscope (MFM). Figure 6(a) is a topographic AFM image of the Ni NW tip arrays after the ion-milled side was etched in the 2 wt % NaOH solution for 30 min. Figure 6(b) is a MFM image of the same Ni NW tips sample in the demagnetized state, showing the domain structure of the Ni NWs. Predominantly due to shape anisotropy, the vertical direction of the NW is the easy magnetization axis, and all the magnetic dipoles in the NWs have been shown to be oriented upward

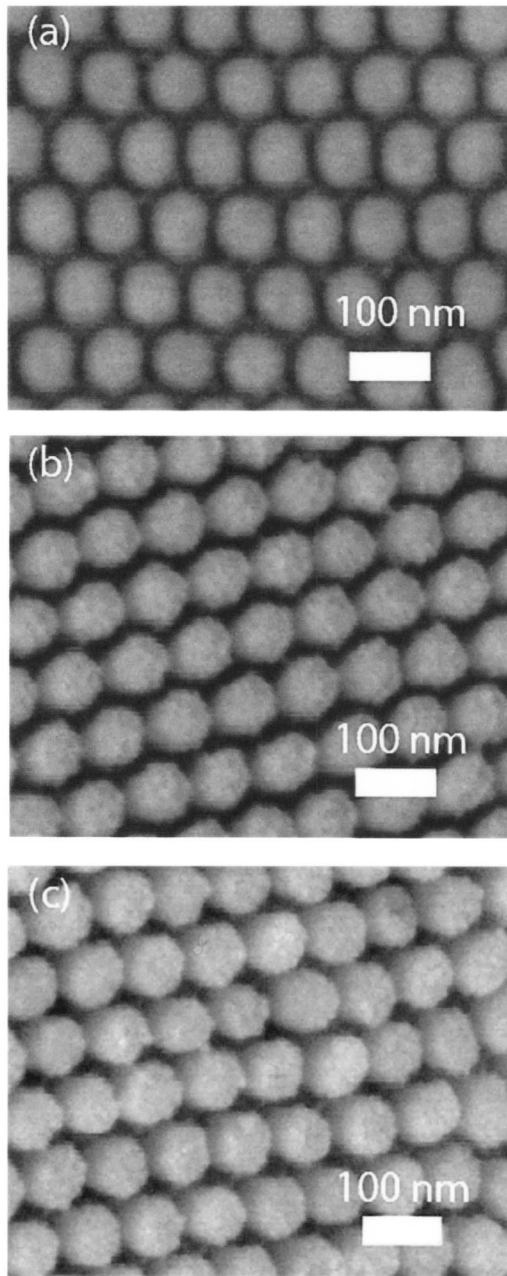


FIG. 5. (a), (b), and (c) are SEM oblique views of Ni NW tip arrays after the ion-milled side being etched in 2 wt % NaOH solution for 15, 30, and 45 min, respectively. The exposed NW tips have a length of 20 ± 5 , 50 ± 5 , and 70 ± 5 nm, respectively.

or downward along the vertical axis of the NWs.⁴⁴ The pattern observed in the demagnetized state is attributed to the weak magnetic interactions between adjacent magnetic NWs coupled with the axial orientation of the magnetization. The magnetic hysteresis loops of the Ni NW tips sticking out of the AAO template was measured with a vibrating sample magnetometer at room temperature. Figure 7 shows the magnetic hysteresis loops for the array of Ni NWs with the applied magnetic field perpendicular (“ \perp ”) and parallel (“ \parallel ”) to the surface of the Ni NW-containing AAO template, respectively. It is evident that the easy magnetization axis is perpendicular (“ \perp ”) to the surface of the NW-containing AAO template, i.e., along the axis of the NWs. The corresponding

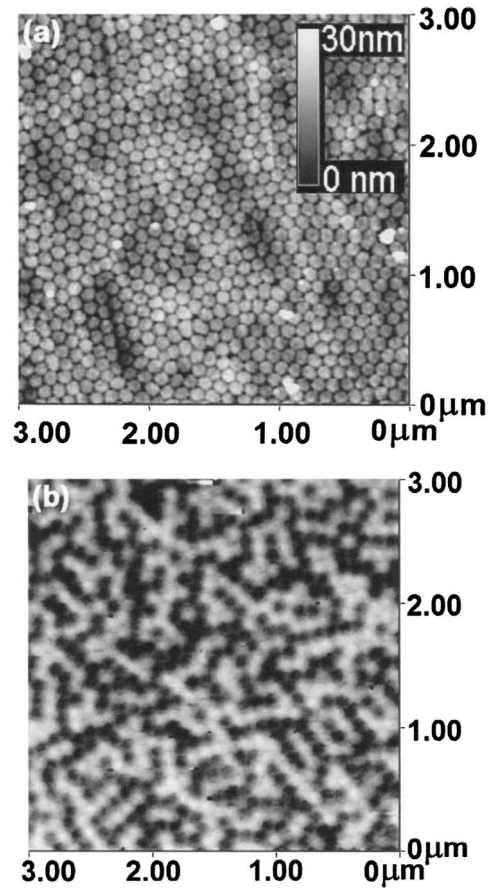


FIG. 6. (a) Topographic AFM image of the Ni NW tips sticking out of the AAO template after the ion-milled side being etched in the 2 wt % NaOH solution for 30 min. (b) MFM image of the corresponding Ni NW tip arrays in the demagnetized state, showing the NWs magnetized alternately “upward” (light) and “downward” (dark).

coercivities, $H_{C,\square}$, and $H_{C,\parallel}$, are 50.63 and 14.23 mT, while the squareness values R_{\square} and R_{\parallel} are 0.65 and 0.09, respectively, for the Ni NW array. Both $H_{C,\square}$ and $H_{C,\parallel}$ are significantly larger than those for the bulk nickel (~ 10 mT).

IV. CONCLUSION

In summary, we have demonstrated a method of making ordered Ni NW tips fully exposed over the surface of the AAO templates with uniform lengths by a combination of dc

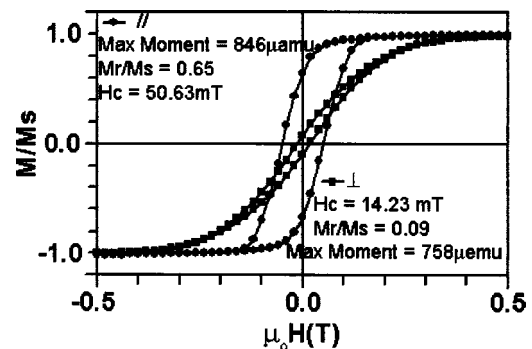


FIG. 7. Magnetic hysteresis loops for the array of Ni NWs with the applied magnetic field perpendicular (“ \perp ”) and parallel (“ \parallel ”) to the surface of the Ni NW-containing AAO template.

electrochemical deposition, ion milling the back Au layer (as a working electrode in electrodeposition) and selectively chemical etching a thin layer of the AAO template from the ion-milled side. The lengths of the exposed NW tips can be tuned by adjusting the etching time in the 2 wt % NaOH solution; the inter-NW tip distance and the diameter of the NW tip can also be controlled by adjusting the electrochemical parameters during the preparation of the AAO template.^{3,6-9} This method should be applicable to any materials that can be dc electrodeposited and etched at a slower rate than the AAO template in the 2 wt % NaOH solution. These highly ordered exposed NW tips could have various applications, as suggested in the literature, for example, self-assembly,^{40,41} high-density magnetic storage,⁴⁴ nano-electrode ensembles⁴⁵ or arrays,^{46,47} surface-enhanced Raman scattering active substrates,⁴⁷ and nanostamping.

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