Fabrication of highly ordered metallic nanowire arrays by electrodeposition

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(Received 2 March 2001; accepted for publication 4 June 2001)

Highly ordered hexagonal arrays of parallel metallic nanowires (Ni, Bi) with diameters of about 50 nm and lengths up to 50 μm were synthesized by electrodeposition. Hexagonal-close-packed nanochannel anodized aluminum oxide film was used as the deposition template. The deposition was performed in an organic bath of dimethylsulfoxide with metal chloride as the electrolyte. A high degree of ordering and uniformity in these arrays can be obtained with this technique by fine-tuning the electrodeposition parameters. Moreover, an unprecedentedly high level of uniformity and control of the wire length was achieved. The arrays are unique platforms for explorations of collective behavior in coupled mesoscopic systems, and are useful for applications in high-density data storage, field emission displays, and sensors. © 2001 American Institute of Physics.

Arrays of nanowires are attractive for their potential applications in high-density magnetic recording devices and sensors, as well as for fundamental scientific studies of nanomagnetics. The ability to produce highly ordered nanowire arrays cheaply and effectively is important for both purposes. Among the various methods used for fabrication of nanowires, template synthesis using electrodeposition has proved to be a low cost and high yield technique for producing large arrays of nanowires. It is particularly useful for producing nanowires from different materials, with diameters less than 100 nm. Possible templates include nuclear track-etched polycarbonate membranes, nanochannel array glasses, mesoporous channel hosts, and self-ordered anodized aluminum oxide (AAO) films. It has been found that AAO is stable at high temperature and in organic solvents, and that the pore channels in AAO films are uniform, parallel, and perpendicular to the membrane surface. This makes AAO films ideal templates for the electrodeposition of nanowire arrays. AAO films have previously been used as templates to synthesize a variety of metal and semiconductor nanowires through electrochemical processes. However, the nanowire arrays which resulted from most of the electrodeposition processes have exhibited the so-called “skyscraper” phenomenon associated with a lack of length uniformity and control. Common to these processes is the use of aqueous solutions, with the exception of a few that used organic solutions. Other drawbacks associated with electrodeposition in aqueous solution include the relatively limited number of elements that can be deposited from aqueous electrolytes, and the need for a conducting substrate. Additionally, the quality of the nanowire arrays may be affected by a number of side reactions, such as oxidation of the metal and water electrolysis. Eventually, stoppage of wire growth may occur due to the sealing of the pores.

The method we used is based on electrodeposition into the nanopores of AAO films using a dimethylsulfoxide (DMSO) solution containing metal chloride. Using this approach, the drawbacks associated with an aqueous bath can be overcome. Furthermore, with an appropriate choice of the electrodeposition parameters, it is possible to control the quality of the nanowire arrays with a remarkable degree of precision. The AAO template was generated by anodizing a high-purity Al foil in an acid solution using a two step process; the process was carried out at a constant voltage of 40 V in 0.3 M oxalic acid solution at 10°C. After the first anodization, which lasted several hours, the oxide film was removed and the newly patterned aluminum substrate was anodized again. The anodization time was determined by the required thickness of the AAO film. Figure 1 shows the patterned structure of the AAO template measured by atomic force microscopy (AFM) (Digital Instruments Nanoscope IIIa) and by scanning electron microscopy (SEM) (Hitachi, S-4500).

The electrodeposition was carried out in an organic bath—a DMSO solution with the desired metal chloride as the electrolyte. The AAO template was used as the cathode, and a graphite bar as the anode. Electrodeposition of metal into the porous alumina film directly following anodization can take place only under ac conditions. This restriction arises from the barrier layer of the AAO template and also due to diffusion in the nanopores. The concentration of metal chloride (NiCl₂ or BiCl₃) in DMSO was 0.05 M. The electrolytating was done in a sealed glass cell with a condensor. The solution was stirred and protected via ultrahigh-purity N₂ gas, and the temperature was maintained at 130±0.5°C.

FIG. 1. (a) AFM tapping mode image of the patterned surface after second anodization. (b) Cross-sectional image of the AAO film seen by SEM.

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by a temperature controller. We have studied the electrodeposition for several metals; in this letter we report deposition conditions for Ni and Bi, which represent two typical cases. The effects of electrochemical parameters on the quality and growth of the nanowires were studied in detail as follows.

The bath voltage has a considerable effect on the electrodeposition of Ni and Bi, but in a different way for each metal. For Ni nanowires, the electrodeposition can take place under ac voltage alone, while for Bi, the deposition can occur only when both ac and dc voltages are applied. The barrier-layer-thinning voltage has a significant effect on the bath voltage. For example, when the barrier-layer-thinning voltages are 8, 15, and 20 V, the optimal bath voltages for Ni electrodeposition are in the ranges of 3–6, 8–12, and 12–16 V, respectively. There will be nonuniform deposition or no deposition at all while the bath voltage is out of range. In Bi electrodeposition, for example, uniform deposition can be obtained under 6–8 V ac superimposed with 2–3 V dc for the template with barrier-layer-thinning voltage of 15 V. The difference between Ni and Bi likely arises because the Ni electrode is comparatively more irreversible than the Bi electrode. Hence, the deposited Bi tends to dissolve during the negative portion of the ac cycle if no dc offset is applied.

It was also found that the ac frequency ranges for uniform deposition were quite different for Ni and Bi. High quality deposition of Ni could be obtained with ac frequency from 10 to 750 Hz, while for Bi, the optimal frequency range was 10–100 Hz. For both metals, when the frequency was higher than the upper boundary of the optimal range, there was little or no deposition. This may be explained by the fact that the charging current of the solution double layer capacitor, which is proportional to the ac frequency, becomes much larger under high ac frequency, leading to a slower rate of electrochemical reaction.

SEM images in Fig. 2 show the effect of frequency on the filling percentage of the nanopores for Ni nanowire arrays. It is clear that the pore filling ratio increases with the ac frequency in the optimal frequency range, and near complete filling of the pores can be obtained at high frequencies. This likely occurs because, at higher frequency, more crystalline nuclei will be formed, resulting in easier deposition of the metals into the pores and promoting homogeneous growth of nanowires. This is similar to pulse electroplating, which is believed to have more “throwing” power and should therefore facilitate the filling of the high aspect ratio pores in the template with metals. The same results were obtained for Bi nanowires.

Figure 3 shows the current–time curves at different ac frequencies. One can see that the curves exhibit three stages for lower ac frequencies, which is similar to dc electrodeposition. It can also be found that the current and duration of the first stage increase and the current of the third stage decreases with increasing ac frequency, resulting in a diminished difference between the currents of the two stages. The second stage almost disappears at 750 Hz for Ni deposition. This occurs for two reasons: first, with rising ac frequency, the double-layer charging current represents an increasing part of the total current, leading to a decreasing deposition rate; second, the electrodeposition process is limited by mass transport in the solution double layer. From the experimental results, the average deposition rate can be estimated. This rate depends on the bath voltage, ac frequency, solution concentration, and temperature, as well as on geometrical features of the template such as the pore diameter and AAO film thickness. For example, when the ac frequencies were 0.1, 0.3, and 0.5 kHz (other conditions were as stated above), the average deposition rates along the pore axis for Ni nanowires were approximately 74, 40, and 32 nm/min, respectively.

The effects of different types of ac waves, including sine, square, triangle, and sawtooth waves, on the electrodeposition were also studied. From the experimental results, we determined that a high filling ratio can be obtained using a sawtooth wave, triangle wave, or sine wave, while poor results were obtained using a square wave.

The resultant nanowire arrays were characterized using SEM. Figure 4 shows SEM micrographs of Ni and Bi nanowire arrays. For ease of inspection, the wires in Figs. 4(a)–4(c) were partially exposed by etching back the alumina matrix. The nanowires are narrow and continuous, with lengths equal to the thickness of the membrane. Energy dispersive x-ray (EDX) spectra confirm the presence of pure nickel or bismuth with no correspondence to oxygen. They also revealed that pure Ni or Bi depositions can be obtained by using high quality chemicals (e.g., 99.99% NiCl₂ or BiCl₃), while a small quantity of Fe and S was shown in the spectrum of Ni nanowires since 99.8% NiCl₂ was used.

Further sample characterization was carried out using...
transmission electron microscopy (TEM) (H7000) and selected area electron diffraction (SAED). Samples were prepared for TEM by dissolving away the aluminum oxide film in a mixed solution of phosphoric and chromic acids, and placing a drop of the resulting free-standing nanowire suspension on a carbon-coated grid. Figures 5(a) and 5(b) show the morphology of Ni and Bi nanowires, respectively, indicating that nanowires with uniform diameter and length can be obtained. The SAED pattern for Ni nanowire [inset in Fig. 5(a)] presents several sharp diffraction spots, which can be indexed as (111), (222), (220), and (331) reflections from face-centered-cubic (fcc) nickel metal. The SAED pattern for Bi nanowire [inset in Fig. 5(b)] demonstrates some reflections from (111), (012), and (202) of the rhombohedral crystal structure of Bi. Additionally, some broken ring patterns were obtained and the diffraction patterns of different grains along the nanowire indicate different orientations. These results confirm the nanowires to be polycrystalline.

In summary, we have fabricated metallic nanowire arrays (Ni, Bi) by electrodeposition into self-ordered nanoporous AAO templates in a DMSO solution containing the desired amount of metal chloride. The nanowires form a highly ordered hexagonal array of uniform spacing and diameter, with an unprecedented level of uniformity and control in the length. The experimental results showed that bath voltages of the ac and/or dc biases and the frequency of the ac bias have a significant effect on the quality of the nanowire arrays. SEM/EDX and TEM/SAED results showed that these nanowires have a uniform length and diameter, and are pure in quality, demonstrating that this technique can be used to fabricate highly ordered arrays of uniform continuous metallic nanowires. Further measurements of magnetic and transport properties of the nanowire arrays are in progress. We believe that these extremely uniform metallic nanowire arrays could be used for studies of collective electronic and/or magnetic behavior of mesoscopic systems and in various future applications including high-density data storage, miniature sensors, or field emission displays.

This work was made possible through support from NSF (ECS-0070019), CIAR, Motorola, and DARPA (Bio-Info-Micro program).