

ELECTROCHEMICAL FABRICATION OF METALLIC NANOWIRES AND METAL OXIDE NANOPORES

Takeshi Ohgai¹, Masayuki Mizumoto¹, Shigeki Nomura²,
and Akio Kagawa¹

¹Department of Materials Science and Engineering, Faculty of Engineering,
Nagasaki University, JAPAN

²Department of Materials Science, Graduate School of Science & Technology,
Nagasaki University, JAPAN

1-14 Bunkyo-machi, Nagasaki 852-8521, JAPAN

Tel/Fax: +81-95-819-2638, e-mail: ohgai@nagasaki-u.ac.jp

Abstract: A nuclear track etched polycarbonate membrane filter with numerous cylindrical nanopores was applied as a nanoporous template for growing metallic nanowires. Nickel, cobalt and iron nanowires were electrodeposited into the cylindrical nanopores. Cathodic polarization curves were measured to determine an optimum condition for growing nanowires. The shape of nanowires was observed using SEM and the crystal structure was analyzed using TEM. Diameter and length of nanowires corresponded to those of nanopores and each nanowire was composed of a single crystal. Anodized aluminum oxide films were also fabricated as a novel nanoporous template. The pore length and diameter was controlled changing anodizing conditions. Ordering behavior of nanopores array in an anodized aluminum oxide film was also investigated to make a novel nanoporous template with a highly ordered honeycomb array of nanopores.

Keywords: nanopores, nanowires, anodization, electrodeposition, nickel, cobalt, iron, single-crystalline, polycarbonate, membrane, aluminum, aluminum oxide, magnetization, thin-film, TEM

INTRODUCTION

Metallic nanowires [1-5] have recently attracted much attention due to their novel physical properties, which can be applied to electric, magnetic and optical devices. Metallic nanowires can be fabricated by piling up metallic atoms using a STM-probe, and by stretching metallic bulk wires, while they can be also prepared by electrodeposition of metals into a nano-porous template with numerous cylindrical nano-pores [6,7]. In a fabrication technique using electrodeposition of nanowires, nano-porous templates such as anodized aluminum oxide films with random array of nano-pores have been used so far. If a template synthesis technique on the basis of fabrication of nano-pores and electrodeposition of nanowires [8,9] is applied to produce micro- and nano-scale devices, position of each nano-pore, inter-pore distance, pore diameter and pore shape should be controlled precisely. Novel nanowire devices can be

fabricated using polymer nanoporous templates fabricated by UV, X-ray, electron and ion beams [10] as well as anodized aluminum oxide templates with highly ordered array of nano-pores. In this study, ferro-magnetic metals such as Ni, Co and Fe were electrodeposited into ion track-etched polycarbonate membrane filters with numerous cylindrical nano-pores. Furthermore, the ordering behavior of nanopores array in an anodized aluminum oxide film was investigated to make a novel template with a highly ordered honeycomb array of nanopores.

EXPERIMENTAL

A nuclear track etched polycarbonate membrane filter was used as a starting material for making a nanoporous polymer template. The membrane filter has pore length of $6\mu\text{m}$, pore diameter of 100nm and pore density of $4 \times 10^8 \text{ pores/cm}^2$. A gold thin layer was sputter-deposited on one side of the membrane filter, which works as a cathode for the electrodeposition of metallic nanowires. First this membrane filter was soaked in ethanol for 10 min so that the aqueous solution containing metal ions infiltrated into the pores of the membrane. Then Nickel, cobalt and iron nanowires were electrodeposited potentiostatically into the cylindrical nanopores from aqueous solutions containing the metal ions. Ag/AgCl electrode was used as a reference electrode to control the deposition potential. After the electrodeposition of metallic nanowires, the membrane filter was removed by dissolving in dichloromethane and chloroform. The shape of metallic nanowires was observed by scanning electron microscope (SEM).

Pure aluminum (99.999%) sheets were used as a starting material to make a nanoporous aluminum oxide template. Electrolytic polishing was carried out for 5 min at 1 A in a solution of ethanol and perchloric acid. The ratio of ethanol to perchloric acid is 3 : 1. Then the anodization was performed in aqueous solution containing 0.3 mol/L oxalic acid. The pore widening treatment was carried out for 30 min in aqueous solution containing 5 wt% phosphoric acid. The surface of anodized aluminum oxide film was observed by SEM.

RESULTS AND DISCUSSIONS

Fabrication of metallic nanowires

Cathodic polarization curves were measured to determine an optimum deposition potential for electrodeposition of nanowires. Figure 1 shows the cathodic polarization curve of a polymer template in the solution containing Ni^{2+} ions. The cathodic current increases at around -0.8 V due to the beginning of electrodeposition of nickel. The charge transfer process would be rate-determining of reduction of Ni^{2+} ions at the potential range from -0.8 to -1.2 V . On the other hand, the mass transfer process would be the

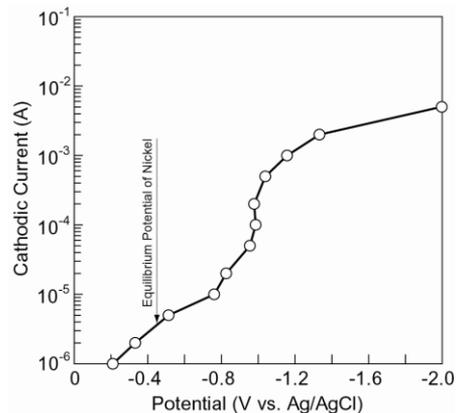


Fig.1 Cathodic polarization curve of nanoporous template in the solution containing nickel ions.

rate-determining at the potential less than -1.2 V. The cathodic polarization curves for cobalt and iron were also measured. Optimum deposition potential range for electrodeposition of nickel, cobalt and iron was determined to be around $-0.8 \sim -1.2$ V.

Electrodeposition of nanowires was performed at a potential determined from the cathodic polarization curve. Time-dependence of deposition current was monitored to investigate the growing process of nanowires. Figure 2 shows the time dependence of deposition current during growing nickel nanowires. As shown in this figure, the cathode current decreases at the beginning of electrolysis. Then, the current reached to a stable level due to depositing Ni nanowires at a constant growth rate in the pores of membrane filter. Finally, the current increases drastically due to depositing bulk Ni on the surface of membrane filter. Figure 3 shows the relationship between the growth rate of nanowires and the deposition potential. There are few differences among the growth rates of nickel, cobalt and iron nanowires. The growth rates of nanowires are increasing with the potential of electrodeposition. It was found that the growth rates of nanowires can be controlled by deposition potential at a wide range. Growth rate of nickel nanowires was around 10 nm/sec.

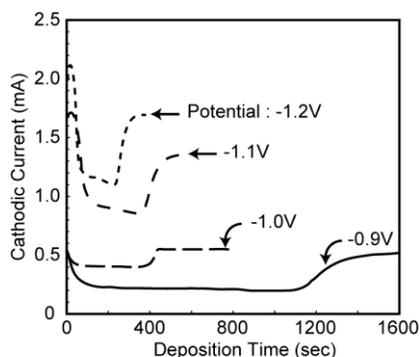


Fig.2 Time dependence of cathodic current during electrodeposition of nickel nanowires

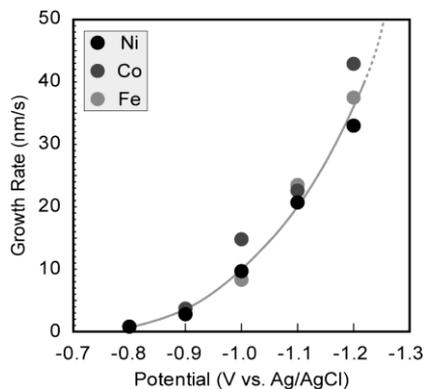


Fig.3 Relationship between growth rate of nanowires and deposition potential.

SEM images of the fabricated nickel, cobalt and iron nanowires are shown in Figure 4. As shown in these figures, the diameter and length of nanowires correspond well to those of nanopores in the template. It is suggested that the diameter and length of nanowires can be controlled using different size of nanopores. Figure 5 shows the TEM bright images and diffraction patterns of nickel, cobalt and iron nanowires. TEM bright images and the diffraction patterns show that the shape of nanowires are almost cylindrical and each nanowire is composed of a single crystal. Preferential growth direction of fcc-nickel nanowires is $\langle 111 \rangle$, and that of hcp-cobalt and bcc-iron nanowires are $\langle 001 \rangle$ and $\langle 210 \rangle$ respectively.

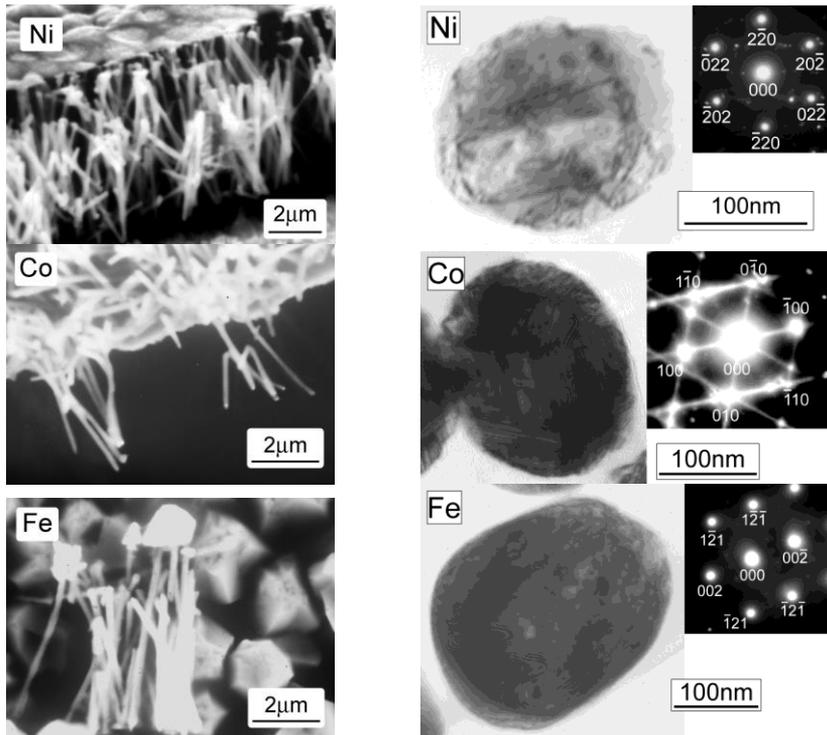


Fig.4 SEM images of nickel, cobalt and iron nanowires electrodeposited at -1.0V (left).
 Fig.5 TEM bright images and diffraction patterns of nickel, cobalt and iron nanowires (right).

Fabrication of anodized aluminum oxide films

SEM images of anodized aluminum oxide films fabricated at various anodizing voltage are shown in Figure6. As shown in these figures, the aluminum oxide films have numerous nanopores of around 10^{10} pores/cm². It is also found that the diameter of nanopores increases with increasing of anodizing voltage. Figure7 shows the relationship between the average diameter of nanopores and the anodizing voltage. The average diameter of nanopores lineally depends on the anodizing voltage ($d = 1.2 E$). Here, d (nm) is average diameter of nanopores and E (V) is anodizing voltage.

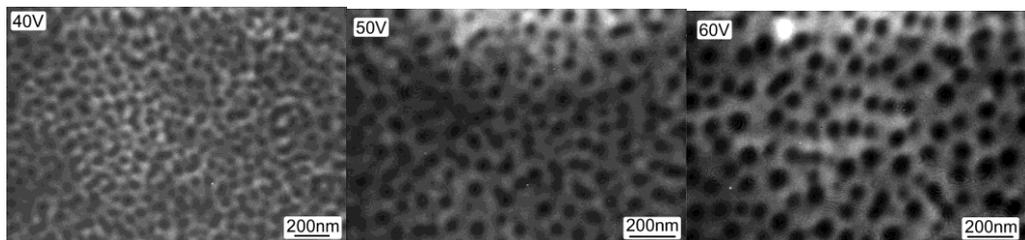


Fig.6 SEM images of anodized aluminum oxide films obtained at 40, 50 and 60V.

Figure8 shows the relationship between the aluminum oxide film thickness and the anodizing time. The thickness increases with increasing anodizing time. Growth rate of the aluminum oxide film fabricated at higher voltage is larger than that of the film fabricated at lower voltage. However, growth rate of the film is decreasing gradually with increasing anodizing time in each anodizing voltage. This phenomenon would be caused by the diffusion limit of oxygen ions in nanopores with increasing the film thickness.

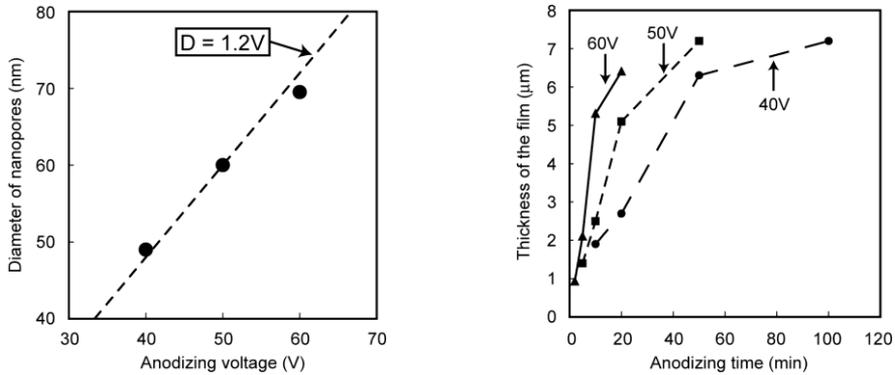


Fig.7 Relationship between the average pore diameter and anodizing voltage (left).
 Fig.8 Relationship between the thickness of aluminum oxide film and anodizing time (right)

Figure9(a) shows SEM image of aluminum oxide film that anodized at 50V for 10 min. Figure9(b) shows SEM image of aluminum oxide film with following treatment. First, aluminum sheet was anodized at 50V for 24 hours, then the surface aluminum oxide layer was partially removed using an aqueous solution containing phosphoric acid. Finally, the aluminum sheet was anodized again for 1 hour. As shown in Fig.9(a), the pore-size distribution is quite large and each pore arranges randomly. On the other hand, in case of sample as shown in Fig.9(b), the pore-size distribution is very small and each nanopore arranges in honeycomb order. Consequently, it is suggested that the formation sites of nanopores are gradually arranged in honeycomb order with increasing anodizing time. Therefore, by removing the initial aluminum oxide layer with random-array of nanopores, a novel aluminum oxide template with honeycomb ordered nanopores can be obtained.

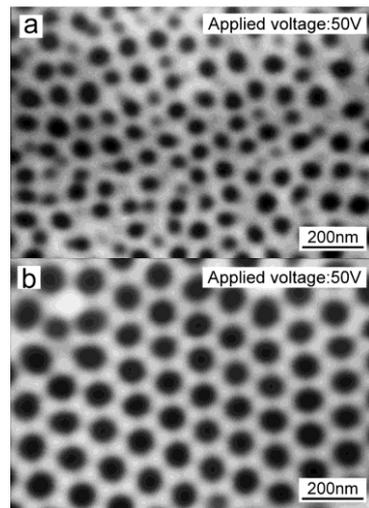


Fig.9 SEM images of aluminum oxide films with random array nanopores (a) and honeycomb array nanopores (b). The sample (a) was obtained by anodizing at 50 V for 10 min, while the sample (b) was obtained by anodizing for 24 hours and removing the surface oxide layer using phosphoric acid.

CONCLUSIONS

1. Optimum potential range for electrodeposition of nickel, cobalt and iron is determined to be around -0.8 ~ -1.2 V.
2. Growth rate of nanowires was controlled by deposition potential at a range between -0.8 and -1.2 V. At -1.0 V, growth rate of nickel nanowires was around 10 nm/sec.
3. Diameter and length of nanowires corresponded to those of nanopores in a template and each nanowire was composed of a single crystal.
4. The pore length and diameter of anodized aluminum oxide films was controlled changing anodization voltage and time.
5. Anodized aluminum oxide film with honeycomb array of nanopores was synthesized by long-time-anodization and the following optimum pore widening treatment.

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