Preparation of Ni Nanodot and Nanowire Arrays Using Porous Alumina on Silicon as a Template Without a Conductive Interlayer

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Recently, many nanostructures have been prepared successfully through electrodeposition of materials into anodic porous alumina coated with a conductive layer on the bottom. Here, the fabrication of Ni nanostructures using anodic porous alumina on Si as a template without a conductive interlayer is investigated. Morphologies of Ni nanostructures were dominated by the applied voltages and an excellent replication capability for this method was revealed. The novel electrodeposition behavior in this study is quite different from the "bottom-up" electrodeposition in conventional template-mediated growth of materials.

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Experimental

A high-purity Al film was deposited on a silicon substrate by E-beam evaporation. Anodization was first conducted in a bath of 0.3 M oxalic acid solution with cooling circulation under different voltages at 13°C. After removing the oxide in a mixture of 12 wt % H3PO4 and 6 wt % H2Cr2O7, the remaining Al was oxidized again until it was all converted into alumina. To prevent the underlying Si substrate from being oxidized, the anodization was stopped as the pore base reached the alumina/Si interface. The specimen was then immersed in a 5 wt % H3PO4 solution to remove the barrier layer at the alumina/Si interface. Cathodic dc electrodeposition was conducted in a conventional three-electrode cell. The aqueous solutions used for Ni deposition were composed of NiSO4 (2.13 M), NiCl2 (0.35 M), and H3BO3 (0.43 M). The working electrode was the alumina/Si substrate with an alumina template of different thicknesses and the electric contact was made from the back side of Si. The counter electrode was a platinum sheet and the reference electrode was silver/silver chloride. The solution was not stirred during the whole electrodeposition process. After electrodeposition, the PAA was removed through chemical etching in a 5 wt % NaOH solution, and a Ni layer containing nanostructures was obtained. The morphologies of porous alumina and Ni nanostructures were observed by scanning electron microscope (SEM, Hitachi S4100) and field-emission transmission electron microscope (FETEM, Hitachi FE-2000).

Results and Discussion

Figure 1 shows the dependence of the current on Ni electrodeposition time for an electrodeposition conducted at −1 and −3 V. Here, the PAA on the silicon substrate is denoted as PAA/Si substrate. The inset shows the current transient at a more negative voltage of −40 V on the PAA/Si substrate. Curve 1 shows the current transient for conventional Ni electrodeposition into the PAA obtained from the anodization of Al foil, where a conductivity-enhancing Au coating was first deposited on the PAA, and the coated side of PAA was attached to the Si substrate. The transition in region I indicates that Ni is continuously deposited in the pores. The increase in current within region II results from the increase in the deposition area when the pores are completely filled and the deposit begins to form hemispherical caps over the end of each nanowire. The current increases until the caps coalesce into a planar and continuous metallic top layer, as shown in region III. For the Ni electrodeposition on the PAA/Si substrate at −3 V (curve 2), a monotonically decrease of current was observed. A similar current transient was found when the electrodeposition was conducted at a more negative voltage of −40 V, as shown in curve 3. This indicates that Ni was probably deposited through different mechanisms for the different substrates.

Figure 2a shows the side view of the as-deposited PAA/Si template where the electrodeposition was conducted at −3 V. The thickness of PAA was 300 nm. A planar Ni layer was formed at the outer surface of PAA, accompanying the formation of extrusion into the pores. No deposit was observed either on the pore wall or the underlying Si substrate, quite different from deposits obtained for conventional template-mediated electrodeposition. Figure 2b shows an oblique view of Ni nanowire arrays embedded in a 600 nm thick PAA, which was electrodeposited at −40 V. The specimen for the SEM observation in Fig. 2a was prepared by directly peeling the template from the Si substrate to investigate the morphology at the PAA/Si interface. Most pores were filled completely during electrodeposition. Some dot-like structures were formed because some nanowires were torn with the template during preparation of the SEM specimen.

Figure 3a shows the morphologies of PAA obtained at 40 V. Ordered pore arrays were observed after the second anodization of the Al film. The diameter of the pores was somewhat larger (70 nm) than that of the as-anodized template (40 nm) because the pores were widened during the barrier-etching process. Each pore was maintained isolated by carefully controlling the duration of theetch-
The average pore distance is 105 nm, which is in good agreement with the proportionality of 2.2 nm/V reported in a previous study. After electrodeposition, the PAA was removed to observe the morphology of the Ni nanostructures. Figure 3b shows the Ni nanodots obtained at $-3 \text{ V}$. The distance of each dot is 105 nm, which is consistent with the characteristics of the PAA/Si template. Under a more negative electrodeposition voltage ($-40 \text{ V}$), Ni nanowires formed rather than Ni nanodots, as shown in Fig. 3c.

Figure 4 shows representative TEM images of the free Ni nanowires formed at $-40 \text{ V}$. Here a template with pores of even higher aspect ratio ($\geq 35 \text{ nm in diameter and } 800 \text{ nm in depth}$) was also used to investigate the reproducibility of this process. The diameter and the length of the nanowires replicate the characteristics of the templates, indicating that the growth of the Ni nanowires is defined by the pore wall. Some notches were formed adjacent to one side of each wire (indicated by arrows), coinciding with the shape of the pore base after chemical etching of the PAA. It was reported that some voids form directly under the pores when anodizing an Al film on a Si substrate. Although the formation of these voids is beneficial to the removal of the barrier layer, the etching duration must be carefully controlled to avoid the detachment of the template from the substrate. Therefore, parts of the barrier layer usually remained after chemical etching in this study, and the shape of the pore base was replicated during electrodeposition. This could be considered as more evidence that the pores were completely filled at a more negative voltage. The inset in Fig. 4 shows the typical electron diffraction pattern of the Ni nanowires. Several continuous rings were observed, meaning that the Ni nanowires are crystalline and have a polycrystalline structure.

Two phenomena were different from conventional template-mediated electrodeposition. First, no deposit was found either on the template or on the Si substrate at the oxide/Si interface unless the applied voltage reached $-2 \text{ V}$ or more negative voltages. As the applied voltage was more negative than $-2 \text{ V}$, the Ni began to deposit on the surface of PAA, accompanying the formation of the protrusions directing inward into the channels. This is quite different from the “bottom-up” growth in conventional template-mediated electrodeposition and the electric characteristics of the templates are considered to play an important role to account for this. For the pure anodic oxide, electrical breakdown usually occurred under the field of $10^6$ to $10^7 \text{ V cm}^{-1}$. However, for PAA, the pore wall is composed of the pure oxide at the inner part and the anion-contaminated oxide at the outer part. The anion-contaminated oxide is more conductive than the pure oxide. Owing to the limited thickness of the template, electron avalanches due to the electrical breakdown of the anion-contaminated oxide may occur under the applied electrodeposition voltage in this study, although the calculated field strength was only about $10^5 \text{ V cm}^{-1}$ for the electrodeposition voltage of $-3 \text{ V}$. The breakdown phenomenon also has been described for the
zinc oxide nanotubes by electrophoretic deposition at 60 V, using an alumina film 60 μm thick as a template. The template was negatively charged when the electrical breakdown occurred, therefore the total surface of the template may be considered as the cathode for the deposition of Ni. Because of the nanometer-sized channels, both migration and diffusion of ions play an important role in determining the electrodeposition behaviors. Under a lower applied voltage (~3 V), the migration of ions into the channels driven by the electrical field is low. At the same time, both the nucleation density and the growth rate of Ni on the surface of the template were low. Owing to the geometry factor of the pore mouth and the diffusion resistance within the channel, the plating rate is higher at the pore mouth than the rate in the channel, indicating that the extent of the consumption of Ni ions is higher at the pore mouth. Some nuclei of Ni may be formed on the pore walls in the beginning of the electrodeposition. However, the deposition of Ni into the channel is self-terminated when the pore mouth is closed as a result of a faster deposition rate at the pore mouth. Under a more negative voltages (~40 V), the nucleation density and the growth rate of Ni are much higher because the surface of the template is highly negatively charged. The migration of Ni ions into the channels is higher at more negative voltages. Therefore, a sufficient amount of Ni ions may run into the pores and fill the channels completely before the pore mouth is closed, coinciding with the formation of Ni nanowires. The effect of the double layer on growth behavior of Ni in this study is considered negligible because the diffusion part of the double layer is compressed when the salt concentration is high. A continuous Ni layer finally forms on the surface of PAA by prolonging the electrodeposition duration. After removing PAA by chemical etching, a Ni layer containing nanodot or nanowire arrays may be obtained for different applied voltages. Second, during the electrodeposition in this study, no obvious hydrogen evolution was observed even when the applied voltage was as negative as ~40 V. For electrodeposition on a conductive substrate, hydrogen evolution usually occurs as the applied voltage reaches ~1.0 V vs. Ag/AgCl, with obvious presence of hydrogen bubbles at the surface of the cathode. However, no obvious hydrogen bubbles were observed on the PAA/Si substrate, regardless of duration of the electrodeposition. This indicates that the extent of hydrogen evolution on the PAA/Si substrate is much less than that on the conductive substrate and most current is contributed to the deposition of Ni. Some details in the mechanism of Ni electrodeposition on the PAA/Si substrate are underway and will be published elsewhere in the future.

Conclusion

Ni nanodots and nanowires were produced by electrodeposition using PAA on the silicon substrate as a template. The negatively charged PAA was used as the cathode for the deposition of Ni, instead of the metal layer in conventional template-mediated electrodeposition. The type of nanostructure was determined by the applied voltage and the feature of the template, but not the electrodeposition duration. The formation of either nanodots or nanowires shows the good replication of the characteristics of PAA. This process is beneficial to the fabrication of metal- and semiconductor-based nanostructures because it is efficient, inexpensive, and relatively facile.

Acknowledgment

The authors acknowledge financial support from the National Science Council of Taiwan, Republic of China under contract no. NSC 91-2216-E-006-028.

National Cheng Kung University assisted in meeting the publication costs of this article.

References


![Figure 4. TEM images and diffraction pattern of the Ni nanowires. The pore diameter/depth is (a) 70 nm/600 nm and (b) 35 nm/600 nm.](image-url)

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