Journal of the Korean Physical Society, Vol. 45, No. 1, July 2004, pp. 141∼144

Size Control of Anodic Alumina Oxide Layer by an Anodic Oxidation Method for the Application of Magnetic Quantum Dots and Carbon Nanotubes

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(Received 28 November 2003)

Anodic aluminum oxide (AAO) templates were fabricated by means of a two-step anodic-oxidation method with a new current-'mode process. The experimental results for pore size are presented as a second anodic oxidation current function. The AAO pore size increases with current, constant potential and time. The pore size is controlled on a several-nanometer scale, and the template depth is regulated on a micrometer-order scale. In addition, a simple growth-dissolution model is discussed for the relation between the aluminum and aluminum oxide with increasing time. Finally, it was found that further pore adjustment depended on the time and temperature of pore widening in phosphoric acid. Structural properties of the AAO template were measured by using a scanning electron microscope (SEM).

PACS numbers: 82.81, 82.61, 82.63
Keywords: Anodic aluminum oxide, Scanning electron microscope, Current mode, Carbon nanotubes

I. INTRODUCTION

Following the surprising growth of various materials, great interest has been focused on low dimensional nanostructures, including nanotubes and nanowires, because of their unique structures and properties as well as applications in electronic devices [1]. Recently, synthesis of carbon nanotubes (CNTs) by using anodic aluminum oxide (AAO) templates has drawn much attention, because this method allows precise and reproducible control of the CNT dimensions [2–6]. In addition, the AAO template-based growth of CNTs is inexpensive and not limited to a small area. The AAO templates can be prepared by anodic oxidation of aluminum in various acid solutions. Various anodizing conditions, such as temperature, applied voltage, widening time and current are used to control the pores' diameter and length [7, 8]. In general, the ordering of the pore arrangement in the AAO template is known to depend on constant voltage and electropolishing degree [9–11], an anodizing process with a current mode has not yet been reported to control the pore diameter.

In this paper, we present experimental results for pore diameter control as a function of second anodic oxidation current in a two step anodizing method. The ordering of the pore arrangement in AAO templates is performed with a new current mode. In addition, a simple growing dissolution model is discussed, to explain the proportionality of the pores as between diameter and spacing. Structural properties of AAO templates are investigated by using a scanning electron microscope (SEM).

II. EXPERIMENTS

High-purity aluminum foil (99.999 %, 0.5 mm thick) was used as substrate material. The substrates were electrically polished in a solution mixture of perchloric acid and ethanol for do mirror treatment, and then they were anodized in a 0.3 M oxalic acid solution at 10 °C with a constant voltage of 40 V for 10 h. The aluminum samples were dipped into an aqueous mixture of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 65 °C. The aluminum samples were anodized again for 6 ∼ 8 h under the same conditions, and they were etched in 0.1 M phosphoric acid at 30 °C in order to enlarge the pore depth. The anodizing current was monitored by using a computer-interfaced galvanometer that could be controlled with circuit current by regulating resistance at constant potential. The anodizing process was performed in constant voltage mode and regulating-current mode. Our experiment was restricted to solution concentration, time, and temperature for the sake of simplicity.

III. RESULTS AND DISCUSSION

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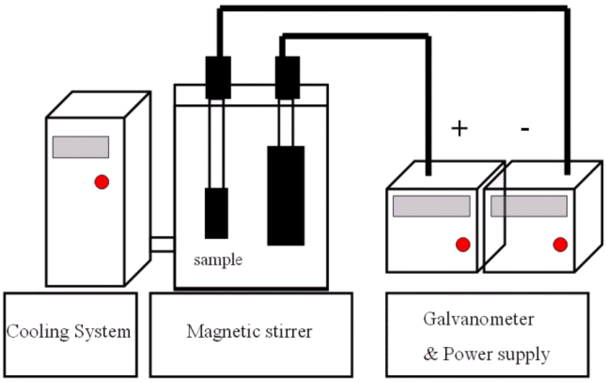

Fig. 1. Schematic diagram of AAO experiment equipment in current mode.

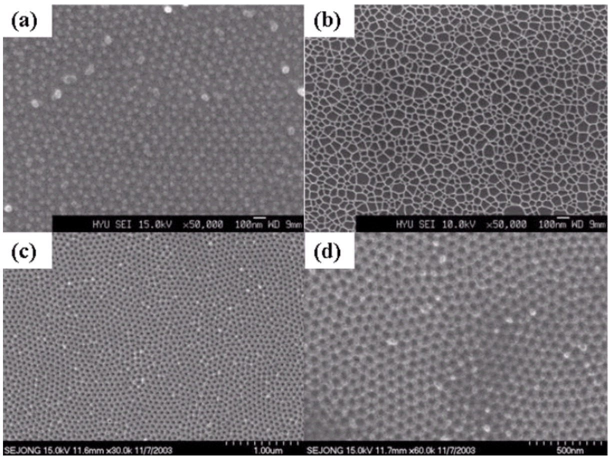

Fig. 2. SEM images of the AAO surfaces after first anodizing under different conditions: (a) 6.0 mA 10 h, and (b) 2.5 mA, 6 h. (c) and (d) show SEM images after second anodizing and widening in phosphoric acid at 30 °C, respectively.

Figure 1 represents a schematic diagram of the AAO experiment equipment. This equipment is designed for different current regulation with increasing time. The anodizing voltage has a range of 0 ∼ 250 V in constant current mode, and the anodizing current is recorded on the computer at all times.

Figure 2 shows typical SEM images of the AAO template surface after the anodization process. Figure 2(a) and (b) display the SEM images obtained under two different conditions : 60 mA for 10 h and 2.5 mA for 6h, respectively. Then, the second anodizing was carried out under the same conditions as the first anodizing process. As shown in this figure, the average diameter and interpore distance were 30 and 65 nm, respectively. The pore density was about $3.0 \times 10^{10}/\mathrm{cm}^2$. Figure 2(c) and (d) show the SEM images obtained after the second anodizing and widening processes in phosphoric acid at 30 °C. The pores were widened uniformly, and the average diameter of the pores was about 40 nm.

Figure 3 represents the SEM images of AAO templates formed at different currents. The current was varied, at a constant voltage of 40 V, from 4 mA to 8 mA. Figure 3(a), (b) and (c) indicate typical SEM images prepared at 8 mA, 6 mA, and 4 mA, respectively. As shown in this figure, the pore spacing and diameter were proportional to the increasing current. It was found that the current mode in anodizing process was much simpler than the voltage mode to control the diameter and spacing of nano-pores.

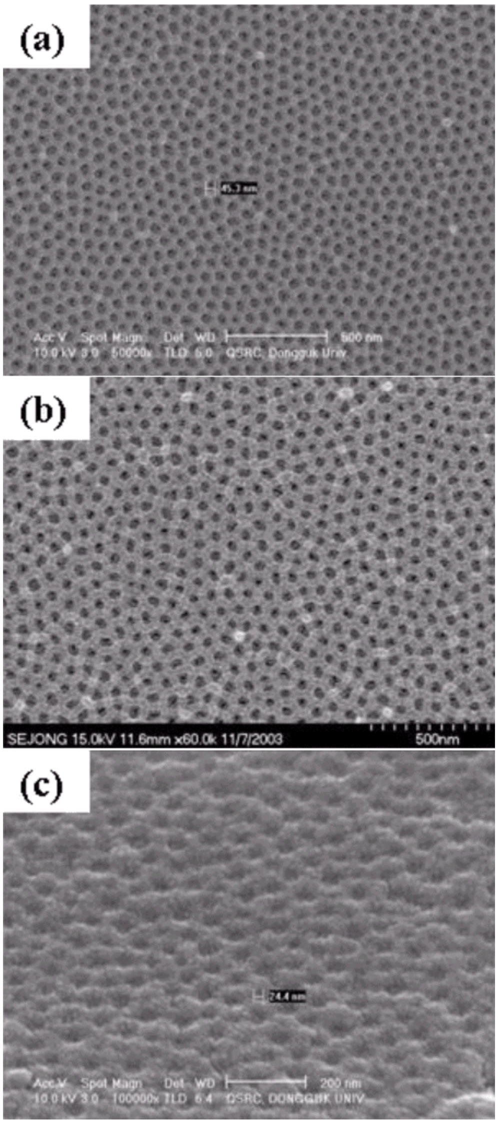

Fig. 3. SEM images of AAO templates prepared under different current conditions, with a constant bias voltage of 40 V and a time duration of 7 h: a) 40 V, 8 mA, 7 h ; (b) 40 V, 6 mA, 7 h; (c) 40 V, 4 mA, 7 h.

Figure 4 exhibits the AAO template current variation with time. As shown in this figure, in region a the anodizing current decreased exponentially to 3 mA/cm^2. This implies the growth of a resistant oxide on the top surface of the aluminum; that is an ultra-thin Al_2O_3 layer may be formed on the surface of the aluminum during the initial process time, resulting in an increase in the

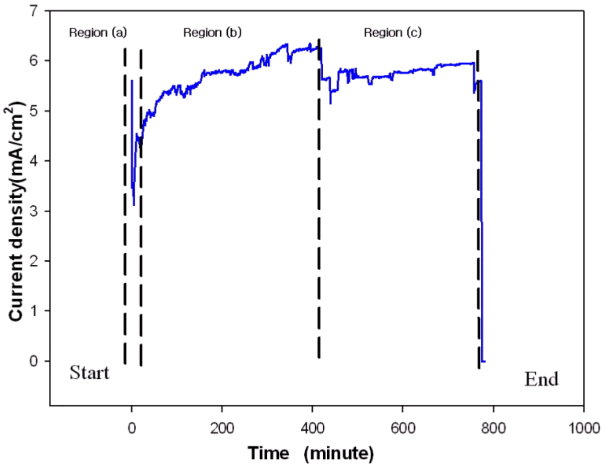

Fig. 4. Anodizing current density versus time, where the operation was done in current mode.

AAO's resistance. As the anodization proceeds, the array of pores develops on the surface of the aluminum, their diameter growing to reach a steady-state condition. It was found that a total time of 400 min was the saturation time for our process. At above 400 min, the anodizing current abruptly decreased to 1.2 mA/cm^2 and the aluminum sample showed full exchange with the Al_2O_3 insulating layer, not only at the surface but also in the pore-base of the sample. If the anodizing process was stopped immediately in region c, before observing the decrease in current, no further nanohole array was formed in our experiment.

If the experiment is preceded by changing the current density, solution concentration and time, various Al_2O_3 pore sizes are specified selectively in this region b. In region c, various depths of the AAO templates were also observed, except for the saturation region. In contrast to voltage mode, the current mode was found to regulate the pore size and depth at the scale nano easily, and regulating the current led to effective anion migration quantities in the anodizing process.

Figure 5(a) and (b) show tilted and cross-sectional SEM images of the AAO templates for the hole-depth measurement, respectively. As shown in this figure, the pore depth was approximately 200 nm (200 nm ± 15 %). The pores of the template were widened by immersion in aqueous phosphoric acid.

IV. CONCLUSION

AAO templates with a highly ordered pattern were successfully fabricated by using various anodizing conditions: voltage, current and time of pore widening in phosphoric acid. The relation between the pore ordering arrays and anodizing voltage was estimated by a simple growth-dissolution model in terms of current variation with time. The diameter and depth of the pores were controlled by regulating the current and changing the etching time, respectively. Experimental results indicate that further pore adjustment can be effected by exposure to phosphoric acid and regulating the circuit current, in a current mode rather than a voltage mode.

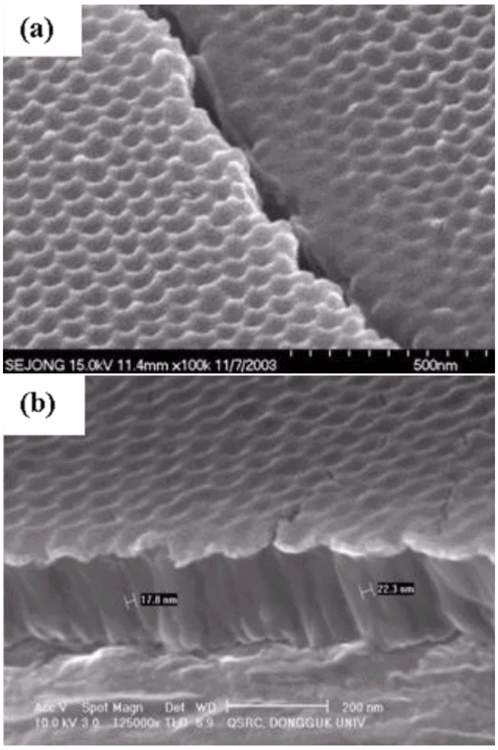

Fig. 5. (a) tilted and (b) cross-sectional SEM views of the AAO templates, to observe pore depth.

ACKNOWLEDGMENTS

This work was in part supported by q-Psi of KOSEF at Hanyang University, and in part by funds from 2004 Samsung Advanced Institute of Technology.

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