

# Fabrication of Alumina Nanotubes and Nanowires by Etching Porous Alumina Membranes

Z. L. Xiao,\* Catherine Y. Han, U. Welp, H. H. Wang, W. K. Kwok, G. A. Willing, J. M. Hiller, R. E. Cook, D. J. Miller, and G. W. Crabtree

*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

*Received August 18, 2002; Revised Manuscript Received October 9, 2002*

## ABSTRACT

Porous alumina membranes are commercially available and have been widely used in recent nanoscale research, for example, as templates in nanowire fabrication through electrodeposition. In this report, we present a new use for porous alumina membranes in the fabrication of alumina nanotubes/nanowires desired in electrochemical devices and catalytic applications. A high yield of alumina nanotubes/nanowires is obtained by etching porous alumina membranes in an aqueous sodium hydroxide solution. We studied the effects of etching time and solution concentration and characterized the alumina nanotubes/nanowires using a scanning electron microscope (SEM). A discussion of the possible mechanism for the formation of nanotubes/nanowires is given. Our results also imply that in nanowire fabrication through the template approach where alumina membranes are removed with sodium hydroxide solution to release the nanowires special attention is needed in characterizing the nanowires with the SEM because alumina nanotubes/nanowires can be easily mistaken for electrodeposited nanowires.

There has been a rapidly increasing interest in nanotubes and nanowires because of their unique properties as well as their wide variety of potential applications.<sup>1–6</sup> Special attention has been paid to the preparation of nanotubes/nanowires of metallic oxides because of their possible applications in electrochemical processes and catalysis.<sup>7–9</sup> Various methods have been reported with which to fabricate oxide nanotubes of silicon,<sup>10</sup> vanadium,<sup>8,11</sup> titanium,<sup>12</sup> molybdenum,<sup>13</sup> aluminum,<sup>13–15</sup> and others.<sup>16</sup> Alumina nanotubes and microtubes have recently been prepared by coating the carbon nanotubes with aluminum isopropoxide<sup>13</sup> and by adsorbing aluminum hydride solution in diethyl ether on a fibrous carbonaceous substrate,<sup>9</sup> followed by calcination at high temperatures (up to 1600 °C). Short (up to 400 nm) alumina nanotubes have also been fabricated by controlling the anodization process of aluminum in dilute sulfuric acid.<sup>14,15</sup> The catalytic synthesis of alumina nanowires by heating mixtures of Al, SiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> to temperatures of 1000–1200 °C has been reported.<sup>17</sup> Alumina nanowires with diameters on the order of 5 nm have also been observed during the etching of alumina membranes with highly ordered arrays of uniform pores.<sup>18</sup> In this letter, we report a convenient and inexpensive way to produce a high yield of both alumina nanotubes and nanowires by etching commercial porous alumina membranes in an aqueous sodium hydroxide (NaOH) solution at room temperature, with

emphasis on the role of both the disordered distribution of pores and the variance of the pore size.

Porous alumina membranes have been used as templates to fabricate nanowires<sup>16,19–22</sup> through electrodeposition. An easy way to characterize the grown nanowires is to image them in the scanning electron microscope (SEM) after removing the alumina matrix with aqueous NaOH solution. The results reported herein indicate that special attention is needed to characterize the electrodeposited nanowires, as alumina nanotubes/nanowires formed during the dissolution of the alumina membranes are similar in shape and size to the nanowires expected to be grown in the pores.

Porous alumina membranes with nominal pore diameters of 20, 100, and 200 nm were purchased from the Whatman Company.<sup>23</sup> Because the thickness of the membranes is about 60 μm, it is difficult to handle the membranes if they are immersed in aqueous solution without any support. Also, a gold layer is usually coated on one side of the membranes as an electrode for the electrodeposition of nanowires. In these experiments, we deposited gold films of ~400 nm on one side of the membrane and used silver epoxy to fix the membranes on a copper support (10 × 10 × 0.2 mm<sup>3</sup>) with the gold side down. The purpose of the gold layer is twofold: to hold the nanoscale species during the etching process and to aid in understanding the dissolving process of the membranes used in nanowire fabrication because a gold layer serving as an electrode is also coated on one surface of the membrane during electrodeposition. The gold film and

\* Corresponding author. E-mail: xiao@anl.gov.

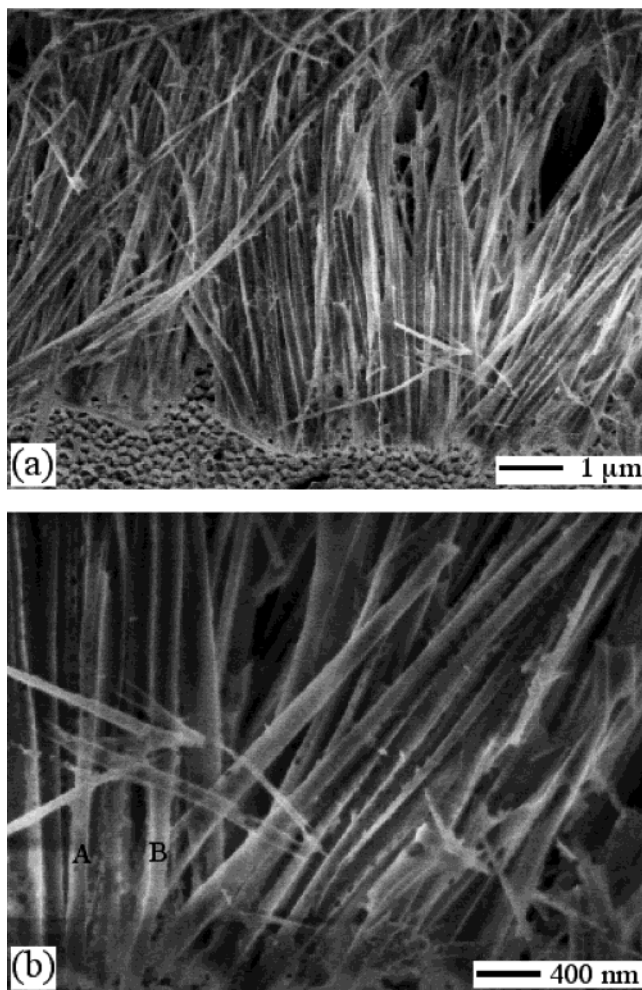
copper support can also minimize the charging effect during SEM imaging.

Samples ( $3 \times 3 \text{ mm}^2$ ) cut from the same porous alumina membrane were immersed in an aqueous NaOH solution for various periods of time. We tested NaOH concentrations of 0.1–1.2 M and found that the dissolving process slows down with decreasing NaOH concentration. Here we report the results obtained with 1 M NaOH(aq) solution because this concentration was most often applied in dissolving the porous alumina membranes containing nanowires.<sup>21,22</sup> To ensure that a consistent concentration of NaOH remained in the solution, we used about 10 times the calculated volume of solution needed to dissolve the corresponding amount of alumina samples completely.

The characterization of the possible nanoscale species was carried out with a high-resolution scanning electron microscope (SEM) (Hitachi S-4700 II). As discussed below, the sizes and shapes of the alumina nanotubes/nanowires are very similar for all three types of commercial membranes. Therefore, the results shown in this paper are from the membranes with a nominal pore size of 200 nm, except in Figure 4, where the results from membranes with nominal pore sizes of 20 and 100 nm are presented for comparison.

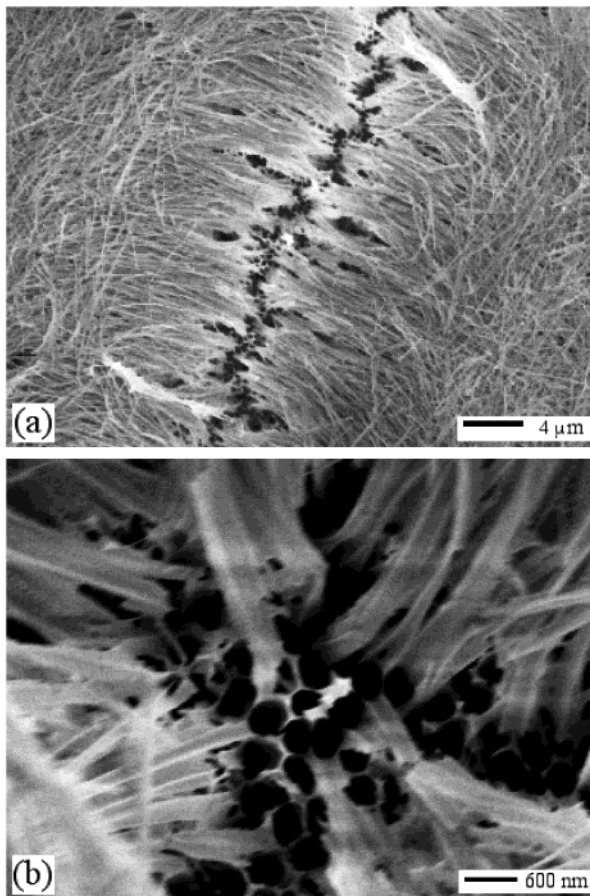
We found that in certain etching periods a high yield of nanoscale species can be observed. SEM images of a sample immersed in 1 M NaOH for 35 min are presented in Figure 1 a and b, where part b is an expanded view of the lower right corner of part a. Both images show a high density of tube- and wirelike alumina species. At places denoted by symbols A and B in b, tubes can be identified with the help of the broken top parts. But most of the tubes do appear to be broken. (The term “nanotubes” used below includes both the intact and broken tubes.) The typical sizes of the nanotubes and nanowires are in the range of 100–200 nm, though small species of tens of nanometers can also be seen. The presence of these species is probably due to the breakage of the tubes. In Figure 1a, a portion of the gold layer on which no alumina nanotubes/nanowires stand can be clearly seen at the bottom of the image. In fact, we found that at this etching condition the alumina nanotubes form islands of 10–20  $\mu\text{m}$  with gaps of 2–5  $\mu\text{m}$  between them. The appearance of the bare parts of the gold film is probably due to the inhomogeneous adhesion strength of the gold film to the membrane. The nanoscale species on the gold areas with weaker adhesion might fall into the solution. The observed shrinkage of the island size with increasing etching time supports this assumption.

Usually a solution can enter small pores through the capillary effect. If air exists in the pores, however, it could hinder the complete filling of the pores. This situation is likely the case in our geometry, as one side of the membrane is coated with gold, effectively closing off the pores on that side. Subsequently, this means that the solution could reach only a certain depth within the pore through its open end. This is verified by the results in Figure 2, which shows SEM images of porous alumina membranes immersed in 1 M NaOH for 15 min. Again, a high density of the nanotubes/nanowires can be seen. In the middle of Figure 2a where



**Figure 1.** SEM images of a porous alumina membrane (nominal pore size of 200 nm) etched in 1 M NaOH for 35 min. The lower right corner of image a is shown in b at higher magnification. Symbols A and B in image b denote places where nanotubes can be identified.

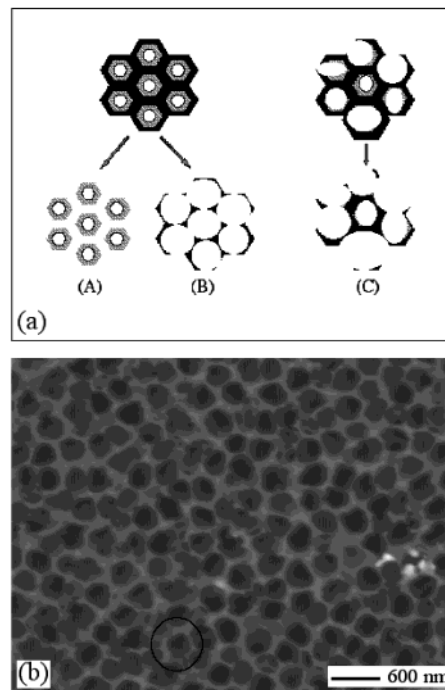
the nanotubes/nanowires part, pores with a diameter of about 200 nm can be seen. At higher magnification, as shown in Figure 2b, we identified that the pores are from the membrane itself. The observation of the pores instead of the gold film as shown in Figure 1a indicates that the part of the membrane beneath the nanotubes/nanowires was not reached by NaOH solution. Figure 2a shows that the length of the nanotubes/nanowires is on the order of 15–20  $\mu\text{m}$ , which should be longer than or equal to the penetration depth of the solution into the pores. These results, together with those in Figure 1, indicate that the etching of the alumina membrane starts at the top bare surface and gradually develops toward the bottom surface that is coated with gold. After an etching time of about 50 min, no nanoscale species can be found on the gold film, probably because of the complete detachment of the nanoscale species from the gold film. In fact, broken nanotubes/nanowires can still be found in the NaOH solution, though, even after etching times of 120 min. This was confirmed by SEM images of a drop of solution containing the etched alumina membranes placed on a gold-coated glass slide.



**Figure 2.** SEM images of a porous alumina membrane (nominal pore size of 200 nm) etched in 1 M NaOH for 15 min. The middle part of image a is shown in b at higher magnification.

As indicated on its website,<sup>23</sup> the Anopore porous alumina membranes are manufactured electrochemically (i.e., by anodizing aluminum in an acid solution). The ideal membranes could consist of a densely packed array of regular, hexagonal-shaped cells with columnar pores in the cell center. The cell wall was found experimentally to consist of two parts: (1) a pure alumina layer near the cell boundary and (2) contaminated alumina with incorporated acid anions adjacent to the pores.<sup>24</sup> On the basis of the microanalysis results and the steady-state film growth rate in various acids, Thompson and Wood<sup>25</sup> proposed a cell structure that is shown in the left upper part of Figure 3a. There, the membranes consist of ideally packed hexagonal cells. The black and gray dotted areas of the cell consist of pure and contaminated alumina, respectively. In this case, nanotubes could form if the etching rate of the pure alumina were much larger than that of the contaminated alumina using a NaOH solution, as shown in case A of Figure 3a. Small nanowires should form from the remains at the corners of the cells if the pores expand homogeneously, as indicated in case B of Figure 3a. Unfortunately, the distribution of cells in the Whatman membranes is totally disordered and contains a large variation of pore sizes as seen in the SEM image of Figure 3b.

A more realistic mechanism for nanotube formation is presented in Figure 3a as case C, where the variation of the

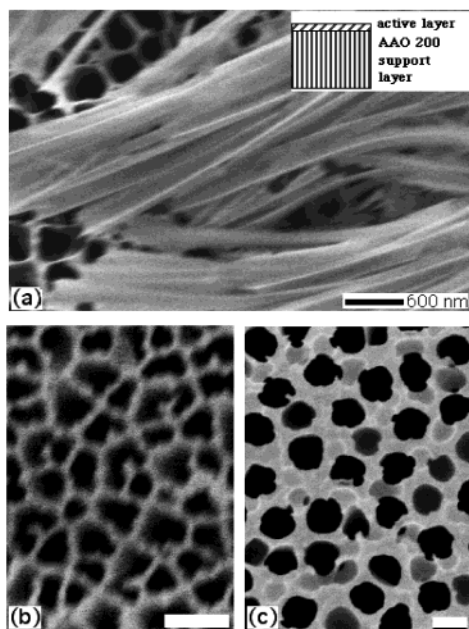


**Figure 3.** (a) Possible formation pathways for alumina nanotubes and nanowires during the etching of porous alumina membranes. The gray and black areas represent contaminated and pure alumina, respectively. Cases A and B correspond to an ordered array, whereas case C corresponds to the disordered array (see text for details). (b) Typical SEM image of unetched porous alumina membranes with a nominal diameter of 200 nm. The solid circle represents a place where a nanotube will most likely form.

pore size and the distance between the pores are considered. Nanotubes will form if the wall between a pore and its neighbors is thicker than any wall separating neighbors from each other. When all pores expand homogeneously, a nanotube can be observed at certain moments when all or most of the walls between its neighbors break. With increasing etching time, the nanotubes will break, as observed earlier. Figure 3b also shows that at some places the wall thickness is much larger than the average value. Large alumina nanowires are expected to form at these places.

Our proposed mechanism emphasizes the role of the nonuniform pore size and the disordered pore distribution for forming nanotubes and large nanowires. It can be further tested by etching alumina membranes containing highly ordered pore arrays with uniform pore sizes. Previous reports<sup>18,26,27</sup> have shown that it is possible to obtain such alumina membranes by strictly controlling the anodization conditions. In fact, alumina nanowires with diameters on the order of only 5 nm, as expected from case B of Figure 3a, have been observed during the etching of alumina membranes with highly ordered arrays of uniform pores.<sup>18</sup>

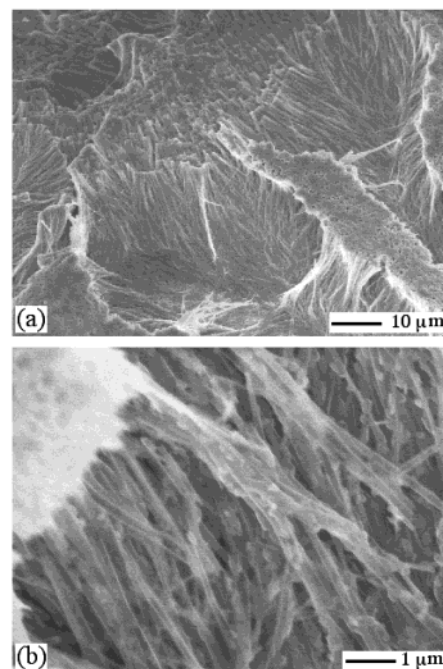
Figure 4a shows an SEM image of the nanoscale species obtained by etching alumina membranes with a nominal pore size of 20 nm. Surprisingly, the sizes and shapes of these nanoscale species are similar to those obtained by etching alumina membranes with a pore size of 200 nm, as shown in Figures 1 and 2, even though they are expected to be much smaller because of the smaller nominal pore size. To



**Figure 4.** (a) SEM image of a porous alumina membrane with a nominal pore size of 20 nm etched in 1 M NaOH for 12 min. (b) and (c) SEM images for the top and bottom surfaces, respectively, of a porous alumina membrane with a nominal pore size of 100 nm without etching. The white scale bars in b and c correspond to 200 nm. Inset of c gives a possible structure of the membranes consisting of an active layer and an alumina support layer with a pore diameter of 200 nm.

understand these results, we imaged the membranes from both the top and bottom surfaces as well the cross section. SEM images of the top and bottom surfaces of a membrane with a nominal pore size of 100 nm are shown in Figure 4b and c, respectively. The SEM image of the top surface does show a nominal “hole” size of 100 nm. It also shows that the holes seem to be formed by a thin network layer, beneath which are pores of 200 nm. The SEM image of the bottom surface shows a totally different pore size and shape from those in Figure 4b for the top surface. The nominal pore size in Figure 4c is very close to that in Figure 3b for the membrane with a nominal pore size of 200 nm. Cross-section images further show that the pore size inside the membranes is 200 nm, even for the membranes with a nominal pore size of 20 nm.

On the basis of these results, we propose the model that is shown in the inset of Figure 3a for a Whatman membrane: it consists of a porous alumina support layer and an active layer. The support layers have the same nominal pore size of 200 nm for all three types of membranes. The networklike active layers actually control the pore size claimed by the company (i.e., the nominal pore sizes of the membranes bought from company means the hole size of the active layer). Such a membrane structure is suitable for the typical application of the membranes as filters where the holes of the active layer control the sizes of the species that can go through. For applications in nanoscale research (e.g. metal nanowire growth through electrodeposition), however, the pores in the alumina support layer rather than the holes of active layer are useful. For example, the diameters of the



**Figure 5.** SEM images of a porous alumina membrane used to grow lead nanowires followed by etching in 1 M NaOH for 10 min. The magnification used for b is about 10 times larger than the magnification used for a.

nanowires grown into the pores of the membranes of all three types will have the same nominal size of 200 nm, making an investigation of the size effect of nanowires difficult.<sup>21</sup>

As mentioned above, the porous alumina membranes have been used in fabricating metal nanowires through electrodeposition. One way to characterize the nanowires is to dissolve the membranes in NaOH solution and then image the nanowires with SEM. The alumina nanotubes/nanowires formed by the etched porous alumina membrane itself can be easily mistaken as electrodeposited nanowires, even if nanowire growth was unsuccessful. Figure 5 shows an example that we encountered in fabricating superconducting lead nanowires with porous alumina membranes. There, the etching time and the NaOH concentration were 10 min and 1 M, respectively. SEM images showed the existence of nanoscale species with a size similar to that of the expected lead nanowires. Also, some of the membranes turned black. Magnetization measurements showed signals characteristic of superconductivity. All results suggested that the nanoscale species might be lead nanowires. Careful energy-dispersive X-ray spectrometry (EDXS), however, found no lead, and the lead nanowires were actually alumina nanotubes/nanowires. The shape of the nanoscale species seen in Figure 5b is clearly the same as that of broken alumina nanotubes. The superconducting signals are also different from that expected from lead nanowires. One possible reason for the inconsistency may be the pore size dependence of the growth rate for the lead nanowires. It is possible that the lead grew much faster in the few pores with much larger than average diameter or defects and quickly covered the surface once the growth reached the top of the large pores or defects. The black color of the membranes is due to the lead layer on the

top surface rather than the few large wires in the membrane. The superconducting signal can mainly be induced by the lead layer on the top surface. Therefore, our observations suggest that special attention should be paid to characterizing nanowires electrodeposited in alumina membranes. Different types of measurements should be carried out to double check the existence of desired nanowires. Although it is sometimes difficult to focus on small species due to charging effect, EDXS microanalysis should be useful.

In conclusion, we studied the dissolution process of porous alumina membranes in NaOH solution. We demonstrated that a high output of alumina nanotubes/nanowires can be achieved by controlling the etching time and the solution concentration. The similarity of the observed alumina nanotubes/nanowires with the nanowires grown in the pores by electrodeposition calls for special care in characterizing the nanowires with scanning electron microscopy.

**Acknowledgment.** This work was supported by the U.S. Department of Energy (DOE), BES-Materials Science, contract no. W-31-109-ENG-38. The SEM imaging was performed in the Electron Microscopy Center of Argonne National Laboratory.

## References

- (1) Iijima, S. *Nature (London)* **1991**, 353, 56. Iijima, S.; Ichihashi, T. *Nature (London)* **1993**, 363, 603.
- (2) Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, 68, 1579.
- (3) Tenne, R.; Margulius, L.; Genut, M.; Hodes, G. *Nature (London)* **1992**, 369, 444.
- (4) Chopra, N. G.; Luyken, R. J.; Cherry, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. *Science (Washington, D.C.)* **1995**, 269, 966.
- (5) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Goesele, U. *Science (Washington, D.C.)* **2002**, 296, 1997.

- (6) Gerhard, F. *Science (Washington, D.C.)* **1998**, 280, 545. Thiaville, A.; Miltat, J. *Science (Washington, D.C.)* **1999**, 284, 1939.
- (7) Nakamura, H.; Matsui, Y. *Adv. Mater.* **1995**, 7, 871.
- (8) Spahr, M. E.; Bitterli, P.; Nesper, R.; Mueller, M.; Krumeich, F.; Nissen, H. U. *Angew. Chem., Int. Ed.* **1998**, 37, 1263.
- (9) Comet, M.; Schreyeck-Reinert, L.; Louis, C.; Fuzellier, H. *J. Mater. Chem.* **2002**, 12, 754.
- (10) Nakamura, H.; Matsui, Y. *J. Am. Chem. Soc.* **1995**, 117, 2651.
- (11) Ajayan, P. M.; Stephan, D.; Redlich, Ph.; Colliex, C. *Nature (London)* **1995**, 375, 564.
- (12) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir* **1998**, 14, 3160.
- (13) Satishkumar, B. C.; Govindaraj, A.; Vogl, E. M.; Basumallick, L.; Rao, C. N. R. *J. Mater. Res.* **1997**, 12, 604.
- (14) Pu, L.; Bao, X. M.; Zou, J. P.; Feng, D. *Angew Chem., Int. Ed.* **2001**, 40, 1490.
- (15) Zou, J. P.; Pu, L.; Bao, X. M.; Feng, D. *Appl. Phys. Lett.* **2002**, 80, 1079.
- (16) Hulteen, J. C.; Martin, C. R. *J. Mater. Chem.* **1997**, 7, 1075.
- (17) Tang, C. C.; Fan, S. S.; Li, P.; Lamy de la Chapelle, M.; Dang, H. Y. *J. Cryst. Growth* **2001**, 224, 117.
- (18) Yuan, Z. H.; Huang, H.; Fan, S. S. *Adv. Mater.* **2001**, 14, 303.
- (19) Evans, U.; Colavita, P. E.; Doescher, M. S.; Schiza, M.; Myrick, M. L. *Nano Lett.* **2002**, 2, 641.
- (20) Shen, C. M.; Zhang, X. G.; Li, H. L. *Mater. Sci. Eng., A* **2000**, 303, 19.
- (21) Strijkers, G. J.; Dalderop, J. H. J.; Broeksteeg, M. A. A.; Swagten, H. J. M.; de Jonge, W. J. M. *J. Appl. Phys.* **1999**, 86, 5141.
- (22) Zhu, H.; Yang, S. G.; Ni, G.; Yu, D. L.; Du, Y. W. *Scr. Mater.* **2001**, 44, 2291.
- (23) <http://www.whatman.plc.uk/index2.html>.
- (24) Thompson, G. E.; Furneaux, R. C.; Wood, G. C.; Hutchings, R. J. *Electrochem. Soc.* **1978**, 125, 1480.
- (25) Thompson, G. E.; Wood, G. C. *Nature (London)* **1981**, 290, 230.
- (26) Masuda, H.; Fukuda K. *Science (Washington, D.C.)* **1995**, 268, 146. Masuda, H.; Satoh, M. *Jpn. J. Appl. Phys.* **1996**, 35, L120.
- (27) Xiao, Z. L.; Han, C. Y.; Welp, U.; Wang, H. H.; Vlasko-Vlasov, V. K.; Kwok, W. K.; Willing, G. A.; Hiller, J. M.; Cook, R. E.; Miller, D. J.; Crabtree, G. W. *Appl. Phys. Lett.* **2002**, 81, 2869.

NL025758Q