Hexagonally Arranged Monodisperse Silver Nanowires with Adjustable Diameter and High Aspect Ratio

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Monodisperse silver nanowires with high aspect ratio are prepared via electrochemical plating into monodomain porous alumina templates. The nanowires have a length of 30 μm or more, adjustable uniform diameters ranging between 180 and 400 nm, and a monodispersity of about 2%. The templates were fabricated by anodization of imprinted aluminum with an interpore distance of 500 nm. Nearly 100% pore filling was obtained due to a thinning process which guaranteed a barrier layer of homogeneous thickness of a few nanometers. Moreover, hierarchically ordered porous alumina with about 25-nm−40-nm pore diameter on one side and 180-nm pore diameter on the other side was successfully infiltrated by the same method, yielding branched silver nanowires.

Introduction

A combination of lithography and self-ordering phenomena allows preparation of very monodisperse, high aspect ratio templates.[1] For example, monodomain porous alumina structures with a maximum thickness of about 100 μm and pore diameters in the range of a few 10 nm to about 400 nm were fabricated by the anodization of imprinted aluminum.[2−4] These perfectly arranged structures have been shown to exhibit photonic crystal properties.[5,6] Moreover, they can serve as perfect templates for the growth of monodisperse nanowires.

Electrochemical silver infiltration into self-ordered porous alumina templates with pores in the sub-100-nm range has been studied recently by us.[7] These nanowires may be used in the area of plasmonics,[8] nanoelectronics,[9] or nanobiotechnology.[10] If the template is perfectly arranged, the ensemble of silver nanowires may act as a metallo-dielectric photonic crystal. Theoretical studies of metallo-dielectric photonic crystals suggested that complete silver infiltration in monodomain templates with appropriate length and pore diameter increases the photonic band gap in the porous alumina photonic crystal material due to an effective negative dielectric constant of silver near the plasmon resonance.[11] These photonic structures should exhibit typical interpore distances of 500 nm in a two-dimensional hexagonal lattice and pore radii of more than 200 nm with a 100% degree of pore filling. Whereas we were able to prepare monodomain porous alumina templates recently, the 100% filling of large alumina pores is still a challenge in materials science. The problem in obtaining a high degree of electrochemical pore filling with metals in large pores of 400 nm in contrast to sub-100-nm pores arises from the thick barrier layer formed at higher anodization potential.[12] This results in a large instability during pore growth and a very inhomogeneous filling.[7] Therefore, methods for homogeneous silver infiltration in high aspect ratio structures with large pore diameters have not yet been established.

Here, we report on a method for fast silver infiltration in the monodomain porous alumina with large pore diameter and high aspect ratio by dc electrodeposition. Furthermore, we were able to combine the filling of sub-100-nm pores with that of large pores to form branched silver nanowires which might be of interest for nanoelectronics.

Fabrication of Monodomain Porous Alumina

We have developed in the past year a unique imprint stamp consisting of Si_3N_4 pyramids which were wafer-bonded to a silicon wafer. The distance of the hexago-

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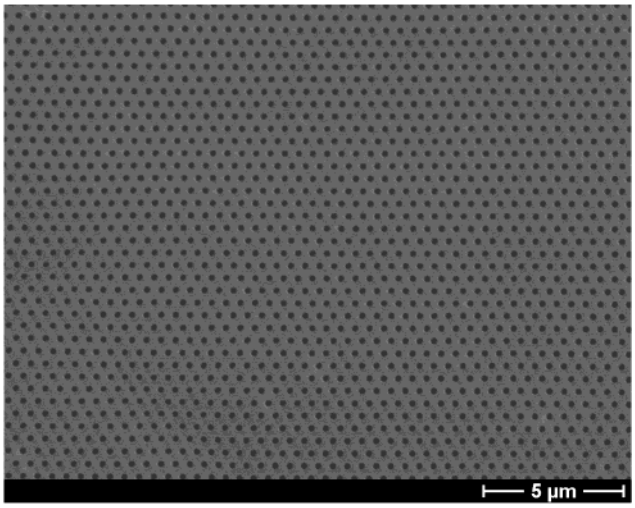

Figure 1. Scanning electron microscopy (SEM) micrograph of monodomain porous alumina with a pore diameter of 180 nm and interpore distance of 500 nm.

nally arranged pyramids was 500 nm and their height was 260 nm. After nanoindentation of the aluminum, monodomain porous alumina templates were fabricated via anodization (Figure 1).[3,6] The formed alumina templates have an initial pore diameter of 180 nm, a channel length of 100 μm, and an interpore distance of 500 nm. Note that in the case of monodomain porous alumina structures with straight long pore channels, the interpore distance is predetermined by the lattice constant of the master imprint stamp, whereas the length of the pore channel can be controlled by anodization time. The initial porosity of the imprint sample is about 10%, corresponding to a pore diameter of about 180 nm.[13] However, the diameter of the pores can be widened by isotropic chemical etching after the anodization. Typically, 1 M H_3PO_4 at 30 °C was used for pore widening. Under these conditions, the rate of pore widening is approximately 110 nm /h. For example, a 400-nm diameter can be obtained by immersing the template after the anodization for 2 h in H_3PO_4.

Thinning Process

Since the thickness of the barrier oxide (D_B) is proportional to the potential applied for aluminum anodization ($D_B = 1.2$ nm/V $\times$ applied potential),[14] the thick barrier film formed at high voltages is a big obstacle for a subsequent electrochemical deposition. Small fluctuations in the barrier oxide thickness lead to large current fluctuations and thus very inhomogeneous filling.[7] Therefore, a well-controlled process for homogeneously thinning the barrier is vital for achieving a degree of nearly 100% filling with metals by electrochemical deposition. For thinning the thick barrier layer by more than 100 nm, we developed a modified thinning process to that used by Nielsch et al.[15] It involves two different electrolytes: phosphoric acid is used for the thinning process from 195 V down to 80 V and oxalic acid from 80 V down to 1 V.[16] In this adopted thinning process, the applied potential is reduced stepwise as shown in Figure 2. In each step, a constant potential with 2 V lower than that of the former step is applied for 180 s in the range of phosphoric acid thinning. During the oxalic acid thinning, an exponentially decaying potential difference is applied for 30 s. For example, the potential difference in the last step is only 0.01 V, whereas that in the beginning step is 2 V. Note that if the thinning process is too fast, some pores lose their chance to be thinned. In contrast, if a thinning is too slow, the thickness of undesired dendritic structures becomes very thick.

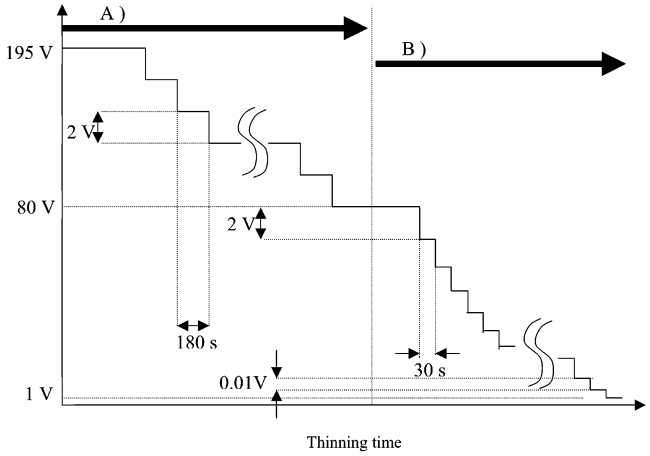

Figure 2. Schematic diagram of the thinning process, which is divided into two parts: (A) Constant potential 2 V lower than that in the former step is applied for 180 s in 0.1 M phosphoric acid during each step. (B) Potential step with exponentially decaying difference is applied for 30 s in 0.3 M oxalic acid.

Silver Infiltration

A commercial electrodeposition bath (Silver 1025, Technic Corp.) under dc plating conditions (10 mA/cm^2) was used for the infiltration of silver into porous alumina templates.[17] The cell potential during the electrodeposition of silver was about 2.5 V, thus significantly larger than the breakdown potential of the remaining barrier layer. Therefore, dc electrodeposition was possible. During the deposition, the temperature was kept at 25 °C. When the wires reach the top of the template, there is a significant potential drop and deposition was stopped. Scanning electron microscopy (SEM) observations were performed to characterize the silver nanowires. The overgrown silver layer was removed by Ar sputtering with an ion mill (Gatan Duo Mill 600) for the top view images. Free-standing silver rods were fabricated by dissolving the aluminum substrate in a Cu-containing solution for cross-section view images.

Results and Discussions

The results for silver infiltration achieved by dc deposition for 10 min are shown in Figure 3. The

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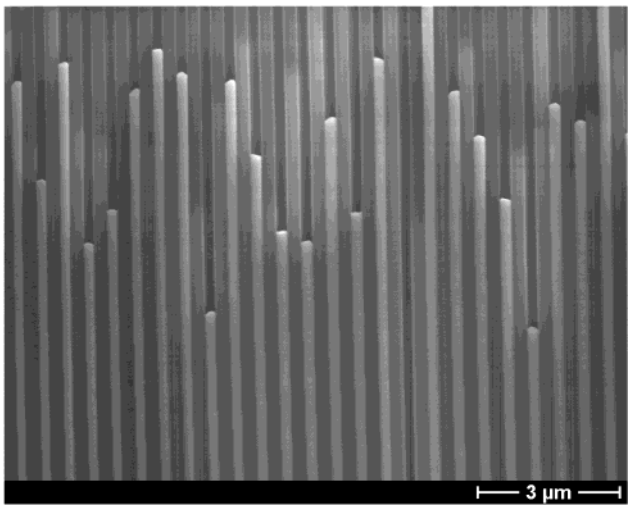

Figure 3. SEM image of a cross-section view of silver wires infiltrated in the monodomain porous alumina template with a pore diameter of 180 nm. The bright strips are silver wires.

average length of the silver rods is about 22 μm. The filling of silver in the monodomain porous alumina template with straight long channels is almost 100% on large areas, thus enabling their usage as metallodielectric photonic crystals. The growth rate of silver wires in the porous alumina channels is rather swift, compared with results obtained by pulsed or electroless deposition.[7,12] By comparing the height of silver rods determined by SEM observation with the theoretical value obtained by considering the charge flow during the deposition, we have determined the current efficiency for the silver infiltration to be about 75%. In other words, the current consumed by hydrogen evolution, which is regarded as the main side reactions, is low. This could be a result caused by the high concentration of Ag^+ in the bath ($\rho_e = 18$ Ωcm, AgCN: 2.5−10 wt % in the bath) as already pointed out in a previous report.[7] To verify the general applicability of this method, porous alumina templates with widened pores (≈300 and ≈400 nm diameter) were also infiltrated with silver. Subsequently, the alumina matrix was partly dissolved in a chromic acid containing solution for scanning electron microscopy (SEM) observation of free-standing silver wires. From the top view, it is observable that the silver wires embedded in the alumina structure are rods and not hollow tubes (Figure 4a,b). Furthermore, the filling degree is nearly 100% and a coefficient of variation of diameter distribution (C.V. value = 100 × standard deviation/actual diameter) is as low as 2.1% due to the high monodispersity of the template obtained via an imprint process. This is a significant improvement compared to disordered (21% dispersity) or even self-ordered pores (7.8% dispersity).[18−20] However, there are some fluctuations in the height of the silver rods. This might be caused by the electrostatic instability which is inherent to electrodeposition of metal in parallel.[7]

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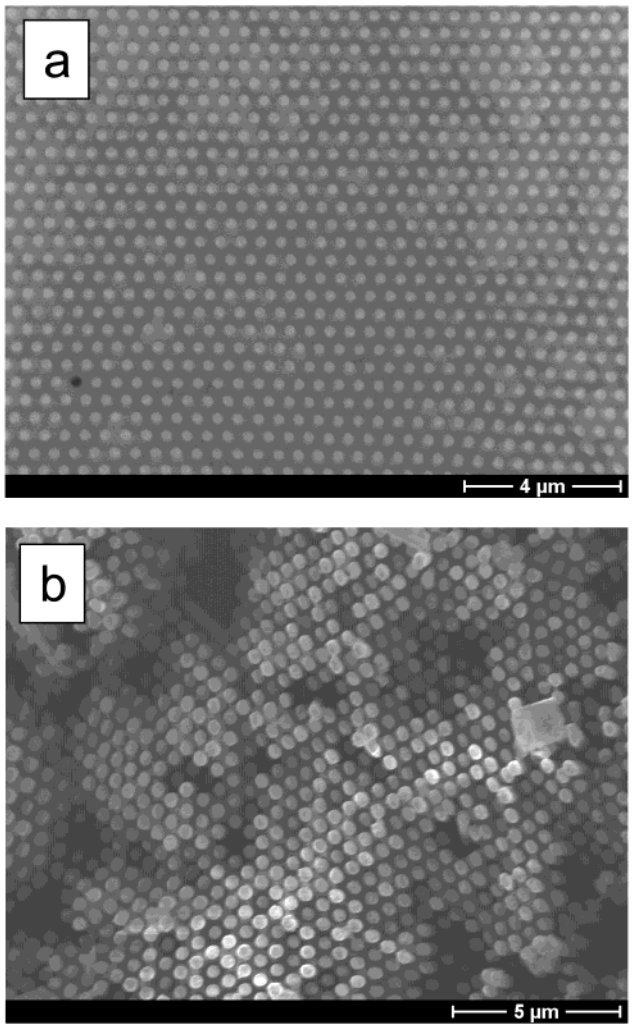

Figure 4. Top view SEM images of silver wires embedded in monodomain porous alumina with (a) 300-nm pore diameter (top view after removing overgrown wires) and (b) 400-nm pore diameter (top view after partly dissolving the alumina matrix in a chromic acid-containing solution). Note that the difference in the darkness of color in Figure 5b indicates fluctuations of the height of the silver rods. The higher the rods, the brighter they appear.

For comparison, we also performed silver electroplating on free-standing porous alumina membranes. However, the preparation of such membrane structures is rather complicated and uniform metal back contacts on the porous alumina membrane are difficult to achieve. These problems result in lower degrees of filling compared to the method described above and poor reproducibility of the filling.

Branched Nanowires

It is possible to prepare hierarchically ordered structures, for example, monodomain porous alumina having 500-nm periodic pores connected with polydomain porous alumina having either 65- or 100-nm interpore distance. For such self-ordered branches underneath monodomain pore channels, the thinning process was, for example, stopped at 40 V corresponding to the self-ordering regimes of oxalic acid,[13,21] instead of completely thinning down to 1 V. A self-arranged structure was

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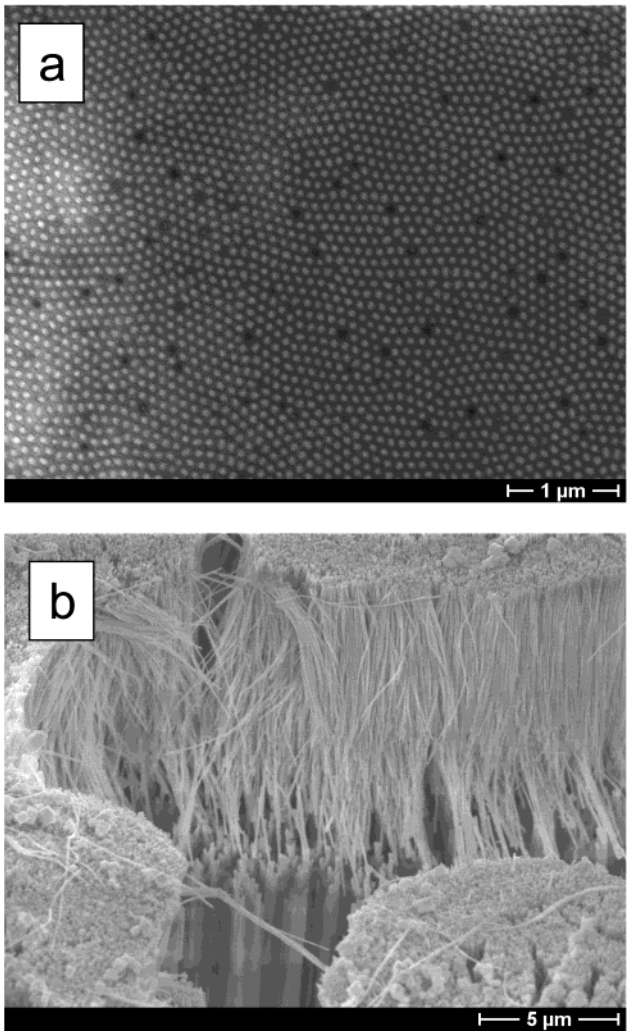

Figure 5. SEM images of branched silver nanowires. Monodisperse 180-nm-diameter silver wires are connected with 40-nm-diameter wires. Bottom view: (a) Silver wires infiltrated in a self-ordered branched alumina template with 100-nm interpore distance. Tilted side view: (b) Silver wires with several small branches. Typically, two to five nanowires start to grow initially from one large nanowire. For the view with 10° tilting, the alumina matrix was partly dissolved in a chromic acid-containing solution.

grown during subsequent anodization in 0.3 M oxalic acid. The degree of ordering of the bottom of the porous alumina structure formed during the self-ordering process is comparable with that formed by the known two-step self-ordering in 0.3 M oxalic acid.[21−22] Experimental details for fabricating self-ordered branched structures underneath monodomain porous alumina structure will be discussed in detail elsewhere.[16] Subsequently, the barrier layer was thinned down to 1 V for the electrochemical infiltration of silver similar to the method described in the previous section. Totally, there are typically a few tens of small pores (<25) branching from one large pore. A total length of 50 μm was infiltrated with silver by the procedure as described above (Figure 5a,b). This type of structure consists of four parts: monodomain channels formed during anodization of imprinted aluminum, a dendrite layer formed during the thinning, self-ordered branches evolved during the second anodization, and a dendrite layer formed during subsequent thinning from the self-ordering potential down to 1 V. Therefore, infiltration of silver into such a structure leads to monodisperse long silver wires with well-arranged branches. From a nanoscience perspective, our procedure could be a useful and easy technique for the fabrication of nanowires with several outlets for distributing current, for the study of electrical transport through nanowires, or for use as antennas for amplifying signals.

Conclusions

We demonstrated the preparation of monodisperse silver nanowires by dc electrochemical plating into monodomain porous alumina templates. The nanowires have a length of 30 μm or more, adjustable uniform diameters ranging between 180 and 400 nm, and a monodispersity of about 2%. The templates were fabricated by the anodization of imprinted aluminum with an interpore distance of 500 nm. Nearly 100% pore filling was obtained when using a thinning process which guaranteed a barrier layer of homogeneous thickness of a few nanometers. Due to the perfect hexagonal arrangement of the silver wires embedded in the template, this ensemble corresponds to a two-dimensional metallo-dielectric photonic crystal as predicted by van der Lem and Moroz.[11] Moreover, hierarchically ordered branched silver nanowires having on one side 40-nm wire diameter and on the other side 180 nm were fabricated.

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