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# High Density Silver Nanowire Arrays using Self-ordered Anodic Aluminum Oxide (AAO) Membrane

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**ABSTRACT**

Highly ordered silver nanowire with a diameter of 10 nm was arrayed by electroless deposition in a porous anodic aluminum oxide (AAO) membrane. The AAO membrane was fabricated electrochemically in an oxalic acid solution via a two-step anodization process, while growth of the silver nanowire was initiated by using electroless deposition at the long-range-ordered nanochannels of the AAO membrane followed by thermal reduction of a silver nitrate aqueous solution by increasing the temperature up to 350°C for an hour. An additional electro-chemical procedure was applied after the two-step anodization to control the pore size and channel density of AAO, which enabled us to fabricate highly-ordered silver nanowire on a large scale. Electroless deposition of silver nitrate aqueous solution into the AAO membrane and thermal reduction of silver nanowires was performed by increasing the temperature up to 350°C for 1 h. The morphologies of silver nanowires arrayed in the AAO membrane were investigated using SEM. The chemical composition and crystalline structure were confirmed by XRD and EDX. The electroless-deposited silver nanowires in AAO revealed a well-crystallized self-ordered array with a width of 10 nm.

***Key words*** **: *Silver nanowires, AAO (anodic aluminum oxide) membrane***

## 1. Introduction

The anodization process has been used for metallic surface treatments and surface decorations by forming a pore oxidation coating. Recently, this process has become widely popular for industrial applications. The most characteristic feature of these materials has been the extremely high aspect ratio of their channels, which is difficult to achieve with conventional lithographic techniques.

Anodic Aluminum Oxide (AAO) is a well-established nanotechnique for various research subjects, such as metallic nanowires, carbon nanotubes, quantum dots, and masks.[1-4] Extensive research on processing anodization continues to improve AAO templates.[5] The structure of self-ordered AAO membranes has been known to form during the transformation of aluminum into alumina by volume expansion and mechanical driving forces. When the volume expansion ratio peaks with the highest mechanical driving force, pores are unable to form under oxidation conditions. On the contrary, by lowering the ratio below a critical value, a non-ordered porous alumina structure forms due to a weak mechanical driving force. Self-ordered AAO membranes are influenced by the following: voltage in anodic oxidation, temperature, concentration of electrolytes, purity of aluminum, and electrochemical conditions.[6-8] Selfordered AAO templates are available with high porosity (having unit area $10^8$ to $10^{11}$ pores/cm$^2$) and the pore size can be controlled from 10 to 250 nm.[3,9] The template's pore size can also be adjusted from 20 to 100 nm by changing voltage and time.[10] Porous discrepancy using the template technique is optimized when under 8%, and it has more than a 500 to 1 ratio of pore length/pore size in a porous alumina oxidation coating. Current research techniques to manufacture silver nanowires and carbon nanotubes include a sol-gel process, electro-deposition, wetting, and CVD on the AAO template.[11-14] Electro-deposition is very unstable with DC to make the AAO template uniformly dense. This technique increases the pH on the cathode to partially etch the wall barrier of pore. Doing so leads to a lack of resistance at the wall barrier of the pores, making only a partial adsorption. However, AC makes it possible to create a stable adsorption on the AAO template.[6] Silver nanowires in photography processing are being widely studied. Photolithography and etching, which shed light on the silicon wafer, have been used to fabricate highdensity direct circuits housed with numerous transistors. However, using this technique, it is difficult to fabricate circuits less than 100 nm in size, a limitation that has prompted research on nanowire synthesis using an AAO template.[15] Ultra high-density direct circuits have more transistors housed on a high-density direct circuit Si wafer. The reduced volume promotes higher efficiency. Highly-conductive silver nanowires connected between micro transistors would contribute to a better and

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higher capacity.

In this paper, we demonstrate a procedure to prepare highly-oriented silver nanowires via electroless deposition in a nanoporous AAO membrane. Firstly, electroless deposition of silver nitrate aqueous solution into an AAO membrane was performed. Afterward, thermal reduction of the sample was performed by increasing the temperature up to 350°C for 1 h under atmosphere. Particularly, the silver nanowires possess a tremendously high aspect ratio of nanochannels, which is difficult to accomplish with conventional nanolithography. The developed method, even without using electrodepostion, enables the synthesis of uniform silver nanowires embedded in AAO membranes with a pore size of 10 nm, which could be directly applicable to connect transistors on a Si wafer.

## 2. Experimental Procedure

### *2.1. Fabrication of AAO membrane and preparation of silver nanowires*

The fabrication process involves three steps: (1) electrochemical preparation of an AAO membrane with ordered hexagonal arrays of nanochannels, (2) electroless deposition of silver ions in AAO, and (3) thermal reduction of silver nanowire by increasing the temperature. A high-purity aluminum membrane (99.99%) was cut into 1 cm × 3 cm sheets. The aluminum sheets were cleaned in ethanol/acetone and annealed at 550°C with a heating rate of 5°C/min under $N_2$ gas to increase the grain boundary. It was electropolished to remove the native surface aluminum oxide (passive oxidation layer) in a mixture solution of perchloric acid and ethanol ($HClO_4/CH_3CH_2OH = 1:4$ in v/o), and applied a constant voltage of 30 V for 1.5 min. The first step of the anodization process was done in a 0.3 M oxalic acid solution at 18°C for 7 h to form a porous alumina film and immersed in a mixture solution of 6 wt% phosphoric and 1.8 wt% chromic acid to remove the produced alumina film at 60°C for 1 h. The AAO membrane can be fabricated by repeating the anodization process under the same conditions of the first step anodization. Afterward, the transparent AAO membrane was immersed in a 0.1 M phosphoric acid solution to widen the nanochannels. The immersing times were controlled at 0, 1 h and 2 h. To form silver nanowires in AAO, a few droplets of 0.1 M $AgNO_3$ aqueous solution were dropped onto the surface of the AAO membrane and heated up to 350°C for an hour under atmosphere. The silver nanowire became denser in the alumina nanochannels.

### *2.2. Measurement of the AAO membrane and silver nanowires*

The pore size of the AAO membrane for each controlled widening time and the silver nanowires were examined using a Scanning Electron Microscope (SEM, Hitachi, S-3500N). Silver nanowires fabricated in the nanochannels of the AAO membrane were analyzed using an Energy Dispersive X-ray Spectrometer (EDX, Horiba, EMAX). The crystallographic structures of the samples were identified using an X-ray Diffractometer (XRD, PANalytical, X'pert-Pro) with CuKα radiation at a scanning step size of $2\theta = 0.02°$ in the $2\theta$ range from 10° to 80°.

## 3. Results and Discussion

Fig. 1 shows schematic diagrams of silver nanowire formation in the AAO membrane via the electroless and thermal reduction process. Fig. 1(a) shows an AAO membrane fabricated after a second anodization procedure, while Fig. 1(c) shows electroless deposition was performed by dropping

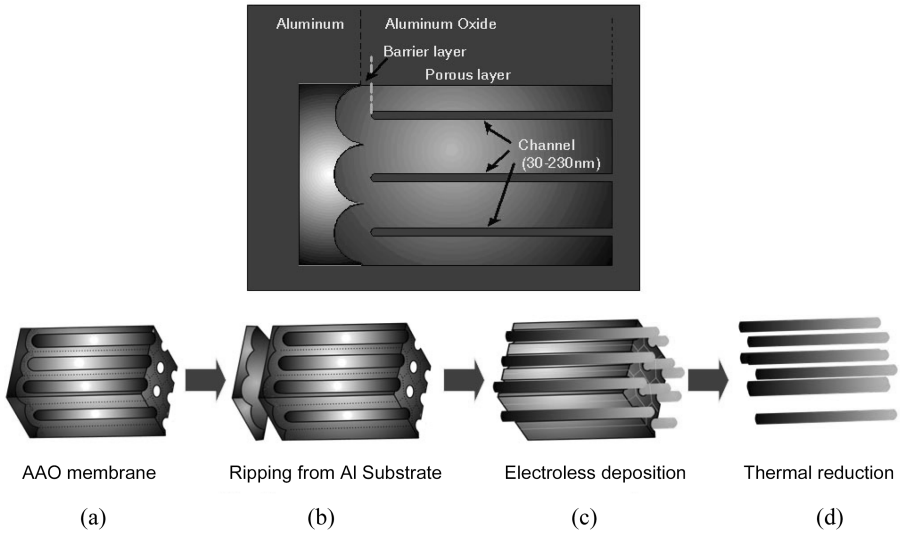


**Fig. 1.** Schematic diagrams of silver nanowires formation in AAO prepared by electroless deposition and thermal reduction. (a) The AAO membrane was fabricated by a two-step anodization process through pore widening. (b) Ripping the aluminum layer from AAO. (c) $AgNO_3$ was electroless deposited into the nanochannels of the AAO membrane. (d) The AAO membrane was dissolved by immersion in 0.2M NaOH for 1 h to separate the silver nanowires.

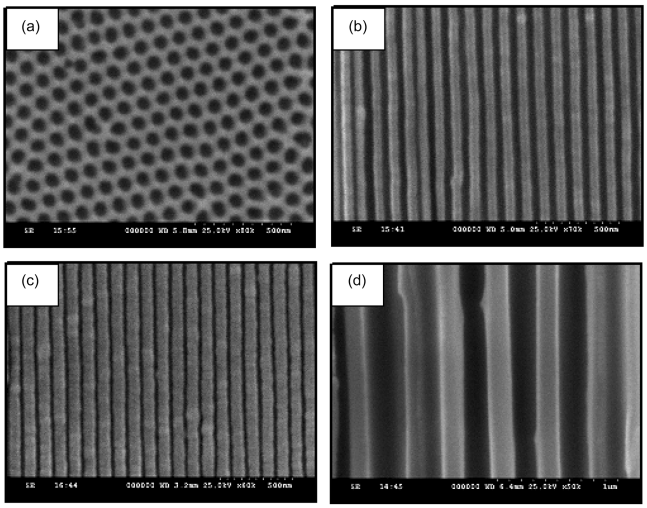


**Fig. 2.** (a) SEM image of the AAO membrane fabricated by a second anodization process using a pore widening process for 2 h (pore size about 50 nm). (b) A cross-sectional image of the AAO membranes (pore size about 50 nm). (c) A cross-sectional image of AAO membrane (pore size about 10 nm) without applying the pore widening process. (d) After four hours of the pore widening process (pore size about 100 nm).

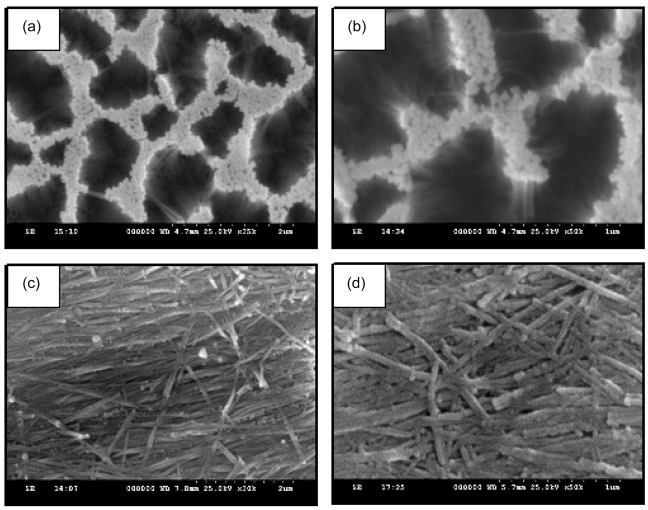


**Fig. 3.** SEM top image of silver nanowires array grown on the surface of AAO membrane: (a) low magnification image, (b) high magnification image, and (c) and (d) silver nanowires after eliminating the AAO membrane in a NaOH solution.

a 0.1M $AgNO_3$ aqueous solution into nanochannels and thermally reduced by increasing the temperature to 350°C, and silver nanowires were separated by immersing the sample in a NaOH solution.

Fig. 2 shows SEM images of the surface of the AAO membrane after the second anodization process. The thickness and pore size of the AAO can be controlled by changing the concentration of electrolytes, the time of anodic oxidation, time of pore widening, and other conditions.

The morphological structure of a self-ordered AAO membrane has around 50 nm pores as shown in Fig. 2(a). The nanopores exhibit almost perfect two-dimensional arrays with a hexagonal pattern. Especially, hexagonal patterns are more apparent when the pore size is larger than 80 nm. In this image, we could confirm that around 50 nm nanopores can be prepared by immersing the sample in a 0.1 M phosphoric acid solution at 60°C for 2 h. Fig. 2(b) shows that the formed nanochannels can be comparatively homogeneous without distorting the structures, resulting in them being highly oriented in one direction with a large aspect ratio. Fig. 2(c) shows a cross-sectional image of a sample prior to the pore widening process. In the sample, the distance among the pores is around 100 nm with a pore size of 10 nm. In Fig. 2(d), pore sizes are around 100 nm after implementing the widening process for 3 h. From the results, pore density of the AAO membranes are rather constant with a uniform range between $10^8$/cm$^2$ and $10^{11}$/cm$^2$ although pore diameter was controlled by changing the immersing time in phosphoric acid.

Fig. 3 shows SEM micrographs of silver nanowires on the AAO membrane. Electroless deposition 0.1 M $AgNO_3$ was directly dropped into the AAO membrane. The nanopores have a strong capillary force when the Ag solution is applied onto the surface resulting in spontaneous ion movement into the nanochannels by driving force. When Ag+ was dissolved in the aqueous solution, the surface tension is smaller than water droplets alone. Consequently, the Ag+ solution has a smaller wetting angle than water itself. Even though the nanochannels have a strong capillary force, the intermolecular interactions between the alumina surface and Ag+ solution are of an immiscible phase resulting in strong surface tensions. Generally, the oxide surfaces have hydrophobic properties and it repels water droplets minimizing the surface tension. To improve the final density of the silver nanowires, the AAO membrane was immersed in a 0.1 M $AgNO_3$ solution under ultrasonic agitation for 1 min to eradicate the air bubbles in the nanopores. This step is quite significant for the fabrication of high quality nanowires. Fig. 3 (a-b) shows the micrograph images of an AAO membrane surface after thermal reduction at 350°C for 1 h. It seems that silver nanowires were coalesced on the surface of AAO because the gravity of the metal silver is 10.5. The silver nanowires are sufficiently small after being thermally reduced and can be easily melted because their high surface area is sufficient to absorb the energy, even though the meting point of metal silver is 961°C. It is already well known that metal nanoparticles are quite reactive and explosive in certain conditions when their sizes are small enough. For this reason, the metal solution can be reaching out during the heat treatment as shown in Fig. 3 (a-b). These metal affluent surfaces of the AAO membrane can be straightforwardly removed using an ion milling process. Fig. 3 (c-d) shows micrograph images of silver nanowires after dissolving the AAO membrane in NaOH solutions. This figure shows that the diameter of Ag nanowires is about 10 nm, which is essentially equal to that of the pores of the AAO membranes used. Essentially, the smallest pore size of AAO

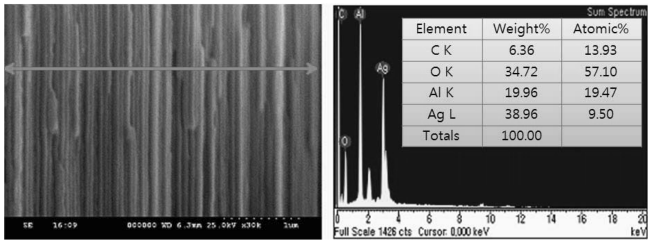


**Fig. 4.** (a) SEM image of a cross-sectional AAO membrane (pore size 50 nm) fabricated by electroless and thermal reduction of silver nanowires in AAO. (b) EDX spectrum of area marked by the arrow in (a).

was preferred for the growth of Ag nanowires. Length of the nanowires is in the range of hundreds of nanometers to several microns depending on the thickness of AAO membranes used. From the images, the diameter and surface of nanowires were quite uniform and homogeneous. However, some nanowires showed bent shapes, instead of straight wire, which could result from the induced mechanical forces during the dissolution and drying process.

Fig. 4(a) shows a dense cross-sectional SEM image of silver nanowires in AAO membranes thermally reduced at 350°C for 1 h. The chemical composition of the resulting silver nanowires in AAO membranes prepared by thermal reduction was analyzed by EDX elemental analysis as shown in Fig. 4(b). The electron beam for EDX analysis was focused on the cross-sectional area marked on Fig. 4(a), at the low magnifications. In this spectrum pattern, Ag, Al, and O peaks are noticeably shown, which indicates that the presence of silver ion is an indirect evidence of silver nanowire formation. By this technique, no differences were detected between the samples obtained at different temperatures or between areas of interest, such as the central and edge zones. From the figure, only one Ag peak indicates that there is only one Ag phase presented as a monocrystalline which is in good agreement with XRD results shown in Fig. 5.

Fig. 5 shows the XRD pattern of resulting silver nanowires prepared in AAO membranes. The figure confirms that the silver nanowires possessed a face-centered cubic (FCC) structure and were well crystallized. The diffraction peaks at $2\theta = 38.39°$, 44.51°, 64.45°, and 77.42° are assigned as the

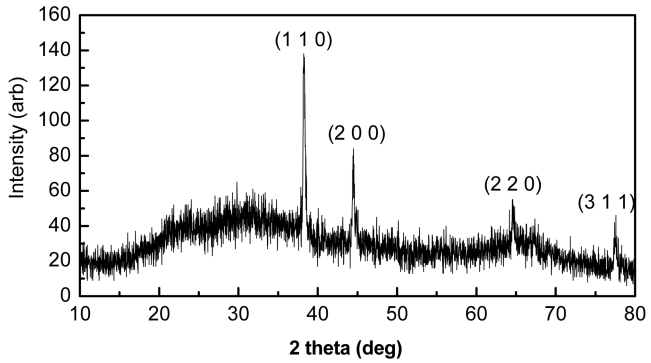


**Fig. 5.** XRD spectra of silver nanowires prepared in an AAO membrane. The measurement was performed without removing the AAO membranes.

(1 1 1), (2 0 0), (2 2 0), and (3 1 1) reflection lines, respectively, of the FCC phase of silver. The sharp peaks are good evidence of silver nanowires with high crystallinity. However, the broadening background curve results from the amorphous AAO membrane.

## 4. Conclusion

Large-scale uniform silver nanowires with a size of 10 nm have been fabricated in AAO membranes via an electroless deposition and thermal reduction process. This fabrication process can be broadened to synthesis of novel metal and metal oxide nanowires. It is expected that the Ag nanowires/AAO assembly system can be applicable in functional nanodevices, such as optical or electronic device. Moreover, it could be applicable in the biomedical field, because silver has a toxic effect on some bacteria, viruses, algae, and fungi. Moreover, as a nanowire form, it could be used as catalysis. To summarize, we prepared AAO membranes with pore sizes of 10 nm, 50 nm, and 100 nm by adjusting the immersing time. It was confirmed that the silver nanowires became denser in the AAO membrane after the heat treatment. The synthesized silver nanowires show high crystallinity with an average diameter of 10 nm and a FCC structure. The proposed procedure for preparing silver nanowires by electroless and thermal reduction is rather facile and cost effective, since electro disposition for the growth of nanowires is not accompanied.

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