Fabrication of Nanostructured Thin Films using Porous Alumina Templates

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ABSTRACT

We demonstrate a method for fabricating a variety of nanostructured metallic thin films by using one simple approach based on the use of anodic aluminum oxide (AAO) membrane as masking template. Highly-ordered large-area metallic nanopore- or nanotip-arrays (e.g., Ni, Ag, Au), with various sizes and shapes, were deposited onto AAO membranes through e-beam evaporation. Free standing nano-patterned metallic films were obtained after chemically removing the template and characterized using scanning electron microscopy and electrochemical methods. The nanostructured films will find use in a number of applications, such as plasmonics, electrochemical and biomedical analysis, and catalysis.

INTRODUCTION

Nanostructured thin films, with two-dimensional highly ordered nanopore or nanorods arrays, have attracted a lot of research interests because of their potential applications in optical, electronic, chemical and electrochemical fields, such as photonic and opto-electronic devices [1,2], gas- or bio-sensors [3, 4], catalysis [5], storage [6] or superconductive media [7], surface-enhanced Raman scattering (SERS) [8] and cell culture [9]. Several sophisticated approaches have been developed for the fabrication of nanostructured thin films including electron-beam lithography [10], X-ray lithography [11], focused ion beam patterning [12], micro-contact printing [13], self-assembling [14], and template-assisted methods [6-8, 15-25]. In the later case, template-assisted fabrication using anodic aluminum oxide (AAO) has been received much attention [6, 7, 16-25]. An AAO membrane can be obtained by anodizing pure Al foil. When prepared under certain conditions, highly ordered hexagonal pore arrays would form with controlled pore size and channel depth [16]. As compared to colloid crystals [8] or sphere particles [15] which have been used as templates for the fabrication of two-dimensional (2D) highly ordered porous materials, the smaller pore size and higher level of ordering make AAO an attractive template in nanofabrication for materials, such as semiconductors [17, 18], metals [6, 7, 19-23], and oxides [24, 25]. With such a template, many techniques can be applied, such as sputtering [6, 22], electron-beam or thermal evaporation [7, 19, 20], reactive ion etching (RIE) [17, 18], electrodeposition [22, 23], pulsed laser deposition [24], and sol-gel [25]. The properties and applications of the resultant films have been extensively studied as well. For example, magnetization properties of magnetic films containing ordered antidots (arrays of pores) sputtered on anodic alumina substrates have been studied [6], with potential applications in ultra-high-density recording media. Au nanotube membranes grown by electrodeposition using AAO template were used as shadow masks for generating extended 2-D arrays of metal nanodots via sputter deposition [22]. The crystal structure of metal films evaporated on AAO templates has been investigated and it has been found that Pb and Sn films spontaneously form an array of nanometer scale crystals in registry with the pores of the AAO substrates, while other materials,
like Au, Pd, and Ge, do not form grain arrays [20]. Fabrication of Au films with nanorod arrays has been reported [19], which was based on thermal evaporation of Au onto an AAO membrane used as template. Electrochemical behavior of electrodes generated from porous Au films was also studied and high electroactive surface area has been revealed [21].

Of these, e-beam evaporation using the AAO template seems to stand out as a simple, inexpensive, and versatile method for obtaining thin films of either nanopore or nanorod arrays, as we attempt to demonstrate in this work through the fabrication of ultra-thin metallic (Au, Ag, Ni, etc.) films with highly ordered nanopore- or nanotip-arrays. Free-standing films were obtained by selectively etching away the AAO templates and the underneath Al substrates and transferred onto other substrates, such as silicon or quartz, for optical measurements or serving as etching mask for pattern transfer on them via RIE. The physical characteristics of the fabricated films were assessed by scanning electron microscope and atomic force microscope, while the electrochemical properties of the surfaces were characterized by the cyclic voltammetry (CV) method. The detailed electronic properties modified or enabled by the nano-patterning (or ordered scaling of dimensionality) are interesting subject of investigation but beyond the scope of the present work.

EXPERIMENTAL DETAILS

The principle of the nanostructured thin film fabrication process is schematically shown in Figure 1. Anodization of pure aluminum foil (99.999%) was carried out at a constant voltage of 40 V in 0.3 M oxalic acid at 10 °C using a two-step approach (Figure 1 (a)-(d)) [16]. The AAO thickness, ranging from a few hundred nanometers to several tens of microns, is controlled through the second anodization time. Wet chemical etching or widening of the resultant AAO using 0.5 M phosphoric acid at room-temperature was applied to alter the pore diameter while keeping the same pore periodicity. The AAO pore diameter is readily adjustable by the wet-etching conditions, such as etching time and temperature as well as concentrations of the chemical solutions.

Metal films were deposited onto the AAO templates by electron-beam evaporation in high vacuum (10⁻⁷ torr) using a custom-designed evaporation system featured with a rotating and temperature-controlled sample holder for better film uniformity. The evaporation rate was in the range of 0.2 to 2 A/s and the film thickness varied from 30 to 200 nm, resulting in formation of different thin metal film structures, as shown in Figure 1 (e)-(g). To obtain free-standing nanostructured thin metallic films, the AAO templates and the Al substrates were selectively etched away by chemical solutions including 0.1 M sodium hydroxide, 0.5 M phosphoric acid and 1%(wt) mercury chloride. After extensively cleaning using deionized (DI) water, the free-standing porous metallic films would float in the water and could be easily transferred onto any substrates, such as semiconductors or quartz, in water media (Figure 1(h)). Using the porous thin metallic film as etching mask, porous semiconductors were produced via RIE, as shown in Figure 1 (i).

For electrochemical characterizations, electrodes with exposed nanotip arrays atop of one surface were fabricated from films with nanorod arrays (Figure 1 (g)) or with two consecutively deposited materials (e.g., a first layer of Al or silicon oxide and a second layer of Au, as shown in Figure 1(j)).

Before etching away the AAO film and Al substrate, a metal wire (e.g. Pt or Au) as electrode lead was attached to the metal film surface by silver paint and the whole surface of the
film was then covered with poly(methyl methacrylate) (PMMA) or chemically resistive insulating epoxy to serve both as a protection layer and a supporting substrate (Figure 1(k)). The morphology of the AAO and the resultant porous thin films were characterized using atomic force microscopy (AFM) scanning electron microscopy (SEM). Electrochemical properties of the electrodes made from the nanostructured thin films were revealed by cyclic voltammetry (CV) measurements in a solution of 1 M sodium sulfate and 5 mM potassium ferricyanide, with a Pt wire counter electrode and an Ag/AgCl reference electrode.

Figure 1. schematic for the fabrication of highly ordered metal nanopore/nanotip arrays: (a) pure Al substrate; (b) AAO formed on Al after first anodization; (c) textured Al substrate after removal of the AAO film formed during the first anodization; (d) AAO templates on Al after second anodization; (e)-(g) electron-beam evaporation of metal onto AAO templates, different evaporated thickness resulting in formation of different metal film structures; (h) porous metal films transferred onto semiconductor or quartz substrates; (i) pattern transfer into semiconductor substrates by RIE; (j) double layered thin film with nanotip arrays; (k) electrode using free standing double layered thin film.

RESULTS AND DISCUSSION

Morphological characterization of the AAO templates

Typical AFM and SEM images of the AAO templates are shown in Figure 2. Highly ordered AAO membranes with uniform pore size are clearly seen. The pore diameter and the interpore distance of the AAO fabricated under the conditions stated above were around 40 nm and 100 nm, respectively. Figure 2 (b) shows the cross-section view of the AAO template. It is
clear that the AAO pore channels are uniform, straight, parallel to each other, and perpendicular
to the AAO surface, which make AAO good candidate as templates or masks for
nanofabrication.

AAO templates with pore diameters of 60 nm and 80 nm were obtained by widening in
0.5 M phosphoric acid for 1 h and 2 h, respectively, while the periodicity of the pores remained
fixed, as shown in Figure 2 (d) and (e). In addition, AAO with smaller or bigger pore size and
varied center-to-center spacing (periodicity) can be generated through anodization of Al in other
electrolytes, such as sulfuric acid (for AAO with small pore and interpore distance) and
phosphoric acid (for AAO with large pore and interpore distance).

Figure 2. (a) AFM image shows highly ordered AAO pore structure; (b) SEM image of the
cross-section view of the AAO pore channel, scale bar 200 nm; (c)-(e) SEM images show AAO
pore size change after etched in 0.5 M H₃PO₄ solution for 0 h, 1 h, and 2 h respectively, scale bar
100 nm.

**Morphological characterization of the evaporated thin nano-patterned metal films**

Evaporation of metals was conducted in high vacuum (10⁻⁷ torr) and at a relatively low
evaporation rate (typically 0.5 Å/s) for good film uniformity. SEM images obtained after
evaporation of metals onto AAO template and before chemically removing the AAO membrane
are shown in Figure 3 (a)-(c). By controlling evaporation time, thereby the film thickness,
typically, four kinds of nanostructured films were obtained.

When the thickness of the evaporated film was less than 30nm, a porous thin film was
obtained, as shown in Figure 3(d), corresponding to the step illustrated in Figure 1 (e).

When evaporation continued beyond that point, films with extruded tips (or pipette
shaped) arrays were obtained in the medium film thickness range (50nm to 70nm), as illustrated
in Figure 1(f). These porous films can be then used as substrates for fabrication of double layered
films and the process is described below.

To obtain a double layered film, a second material (e.g., Au, for electrochemical
applications) was deposited on the top of the first porous layer (e.g., silicon oxide or metal which
could be oxidized afterwards), resulting in the formation of arrays of exposed nanotips, as shown in Figure 3(e) and as illustrated in Figure 1(j).

When evaporation was carried out with only one material and the evaporated films were thicker than 100 nm. Thin films with nanotip arrays formed, as shown in Figure 3(f) and as demonstrated in Figure 1(g).

Due to their intrinsic physical differences of the resultant nanofilms, various stacked or rolled forms were observed after transferring onto other substrates, as shown in Figure 3 (g)-(i), which could be interesting for catalysis and optical applications.

Figure 3. SEM images of the evaporated thin films of various nanostructures: (a)-(c) Porous Ni films before detached from AAO template, where the edge of the metal film on AAO and scratched metal film pieces on AAO were shown in (b) and (c), respectively; (d)-(i) nanostructured films after transferring onto silicon or quartz substrates: (d) a piece of flipped porous film, which shows both the top and the bottom pore morphology of the film; (e) film with nanopore and exposed nanotip array; (f) film with nanotip or nanorod array; (g) stacked or folded film; (h) wrinkle on spread film; and (i) micro film rolls.
Porous metal film as etching mask

Porous Ni film of 30 nm thick was formed on AAO at an evaporation rate of 0.5 Å/s. The AAO template was removed in 0.1 M NaOH solution and the Al substrate was peeled off during the etching. The porous Ni film was completely cleaned using DI-water and transferred onto silicon substrate. Figure 4 (a) and (b) show the morphology of the porous Ni film on the AAO template after evaporation and on the silicon substrate after membrane transfer, respectively.

Using the porous Ni film as etching mask, patterning of the silicon substrate was carried out via RIE in CF₄ and O₂ gases. Figure 4 (c) shows the SEM image of the patterned porous silicon surface. The porous Ni mask could be an alternative to AAO mask in case of the later is not sustainable in certain etching environment. However, the defects generated during both electrochemical anodization and evaporation processes will be passed on or copied to the etched substrates, such as irregular pore shapes or missed pores, as shown in Figure 4(c).

![Figure 4. SEM images of porous Ni films: (a) on AAO after evaporation; (b) on silicon substrate after film transfer; (c) porous silicon surface after RIE using the porous metal film as etching mask.](image)

Electrochemical characterization of nanostructured thin metal film electrode

Au films with nanotip array (Figure 1 (g)) and evaporated thickness of 200 nm were obtained at evaporation rate of 2 Å/s. To make an electrode using this nanostructured thin film, a thin Pt wire was attached to the top surface of the Au layer using silver paint. A protective and supporting layer, either PMMA or chemically resistive insulating epoxy, was applied after the silver paint dried. Then the AAO membrane was etched away using 1 M sodium hydroxide while the Al substrate was partially etched and peeled off. In order to investigate the electrochemical properties of the prepared nanostructured Au film electrode, CV measurement was carried out in a solution of 1 M sodium sulfate and 5 mM potassium ferricyanide at the scan rate of 10 mV/s. As shown in Figure 5, a pair of well-defined redox peaks of the ferricyanide was obtained at the nanostructured Au film electrode with anodic peak potential 0.29 V vs. Ag/AgCl and cathodic peak potential 0.23 V vs. Ag/AgCl. For comparison, similar measurement was also applied to a Au plate electrode with the same geometric area, as shown in Figure 5, dashed line. It was found that the redox peak potential of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ at the Au film was the same as that at the Au plate, which indicates the same kinetics of electron transfer of ferricyanide at both electrodes. In addition, it is clear that the redox peak currents at the Au film electrode is about 1.5 times of that of the Au plate electrode, suggesting the higher active surface area of the nanostructured film electrode.

A double-layered film was fabricated by first depositing a thin layer of silicon oxide (20-30 nm in thickness) and then deposited with Au (100 nm), resulting in the formation of exposed Au nanotip array. The electrochemical behavior of electrodes using these thin films might be interesting in this configuration and useful for biomolecule sensing. The advantage of using a
densely packed nanoelectrode array lies in the fact that a very high signal-to-noise (SNR) and Faradic-to-capacitive current ratios can be obtained, as compared to a conventional planar electrode with the same geometric area. This is because in a densely packed nanoelectrode array, the individual diffusion fields overlap to form an essentially linear diffusion layer. Therefore, the time dependent current that is observed will be equivalent to that of a macroelectrode with the same geometric area as the nanoarray, whilst the background and capacitive currents generated will be proportional to the active area alone, which is much smaller than the geometric area in the nanoarray case.

Figure 5. Cyclic voltammogram of nanostructured Au film electrode (solid line) and Au plate electrode (dashed line) in 5 mM potassium ferricyanide and 1.0 M sodium sulfate solution.

CONCLUSIONS

In summary, we have demonstrated that nanostructured metal/oxide free-standing or composite films with various ordered features, including nanopore array, nanotip array, and porous tip array, can be fabricated by e-beam evaporation of the desired materials onto an AAO template with highly ordered pore arrays. The detailed features of the structures of the evaporated films are found to vary with the deposited film thickness. Thinner films have porous structures and can be used as etching mask for pattern transfer onto other generic substrates, while thicker films are featured with nanopore or nanorod tip-arrays and have potential applications in electrochemical analysis, sensing and catalysis due to high surface area or intrinsic electrochemical behavior of the highly ordered nanotip arrays.
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REFERENCES