

Nanostructured Metal Surfaces Fabricated by a Nonlithographic Template Method

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We have developed a simple and completely nonlithographic preparation technique for free-standing nanostructured metallic films with a close-packed hexagonal array of metallic nanoembossments, by utilizing electrochemically prepared textured aluminum sheets as a replication master in conjunction with electrochemical deposition of metals. Microscopic analyses using field emission scanning electron microscopy and atomic force microscopy revealed that the present nanofabrication technique offers a highly facile and economical way for the production of periodic metallic nanostructures in a large area with high fidelity in pattern transfer as well as with a good degree of flexibility in materials.

Introduction

Recently, studies on the surface undulation in the nanometer length scale have been an area of considerable interest in materials sciences, since they could provide an opportunity for successful development of functional nanocomposites, miniaturized fluidic devices, biosensors, and various optical devices.^{1,2} A material's bulk properties such as mechanical friction, optical properties, and chemical and biological compatibility are substantially affected by the topography of a surface.^{3,4} And the development of structurally well-defined nanostructured surfaces, whose physical properties are easier to interpret and more amenable to theoretical treatment, is a prerequisite to thoroughly understand surface properties.⁵ On the other hand, heretofore, most studies have mainly been directed to the surfaces where topography is induced by electric fields, phase separation, or entropy-driven relaxation of polymeric materials and is generated by mechanical roughening, sol-gel deposition, or plasma deposition.^{6–9} However, these surfaces are often comprised of features with microscopic random orientation such as those in fractal surfaces. In addition, it is quite difficult to theoretically correlate the macroscopic properties of a surface with its detailed substructure because of statistical

treatment of the surface roughness.^{10,11} Recent advances in various lithographic techniques seem to solve these problems and provide routine access to nanometer-scale periodic arrays.^{12,13} However, current techniques are not cost-effective, requiring state-of-the-art facilities, and the whole area of nanopatterning is still a challenging job.

Here, we describe a simple and completely nonlithographic route for fabricating free-standing nanostructured metallic films with a well-defined, close-packed hexagonal array of nanoembossments, which could be the model surface nanostructures that are suitable for systematic studies on the relevance of surface topography on the macroscopic properties of materials. The method involves the utilization of electrochemically prepared textured aluminum sheets as a replication master and provides a convenient route to produce multiple copies of metallic nanostructures over an area of several square centimeters from a single textured aluminum master. In addition, the approach is very promising for the preparation of large-area, ordered nanostructures with a full-fill factor (i.e., no separation between features), which are difficult to obtain by conventional lithographic processes.

Experimental Section

Nanoporous Al₂O₃ films with different interpore distances of 61, 111, and 420 nm have been electrolytically prepared as described in the literature,^{14–16} via the electrochemical oxidation of Al using 0.3 M H₂SO₄ (10 °C), 0.3 M H₂C₂O₄ (17 °C), and 0.9 M H₃PO₄ (–3 °C), respectively. Briefly, surface-finished Al sheets were anodized under regulated cell voltages of 25 V for 0.3 M H₂SO₄, 40 V for 0.3 M H₂C₂O₄, and 160 V for 0.9 M H₃PO₄ for 15 h, using graphite cathodes. The bottom surface of as-anodized

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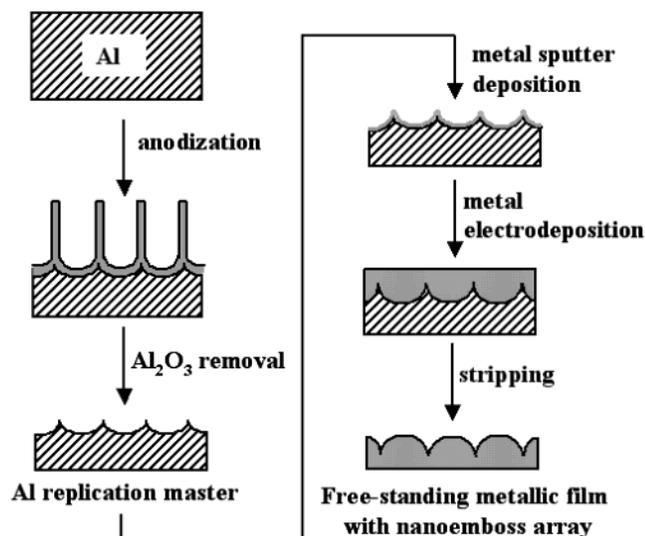


Figure 1. Schematic outline of the experimental procedure that was used to fabricate free-standing metallic films with a close-packed hexagonal nanoembossed array.

AAO film is characterized as a nonporous thin oxide layer (i.e., barrier layer) with approximately hemispherical geometry. At the same time, the surface of the aluminum substrate just underneath this thin oxide layer is textured with an array of hexagonally close-packed concaves due to the acid-catalyzed local dissolution of barrier oxide at the pore bottom, where significant Joule heating occurs due to the concentrated electric field.^{17,18} This preferential barrier oxide dissolution produces an approximately hemispherical barrier layer at the pore bottom while leaving an array of hexagonally organized concave patterns on the aluminum substrate. After the anodization, the porous oxide layer was completely removed by immersing the resultant films into the acid mixture (1.8 wt % chromic acid and 6 wt % H_3PO_4) at 65 °C for 24 h to obtain a textured aluminum master with an array of hexagonally close packed concaves on its surface. The resulting textured aluminum was thoroughly washed with a large amount of distilled water with intermittent sonication and kept in acetone prior to use.

Fabrication of self-supporting films of metal (for instance, Au) replicas of the textured aluminum master has been realized as schematically illustrated in Figure 1. Initially, thin metallic gold film was plasma sputtered onto the textured aluminum surface at the deposition rate of 1 nm/min for 10 min. And then, this thin gold layer was thickened to the desired thickness by electroplating gold using commercially available plating solution (Orosen 999) at the current density of 1 mA/cm² for 25 min. The thickness of nanostructured films could be easily controlled by changing the amount of total integrated charges involved in the electrochemical reaction. On the other hand, the direct metal deposition on a textured aluminum master could not give satisfactory results, producing aggregated deposits of metal on the surface of textured aluminum. This is probably due to an intrinsic insulating thin oxide layer existing at the surface of the textured aluminum master, which has been handled in the air. Free-standing Au films with nanoembossed arrays on their surfaces were obtained by stripping the film from the replication master.

Results and Discussion

Figure 2 shows some representative field emission scanning electron microscopy (FE-SEM) images of replicated Au films (d–f) that have been fabricated using this procedure, together with the respective textured aluminum masters (a–c). It is clear from the present micrographs (Figure 2a–c) that the surface of the textured aluminum is characterized as a close-packed hexagonal

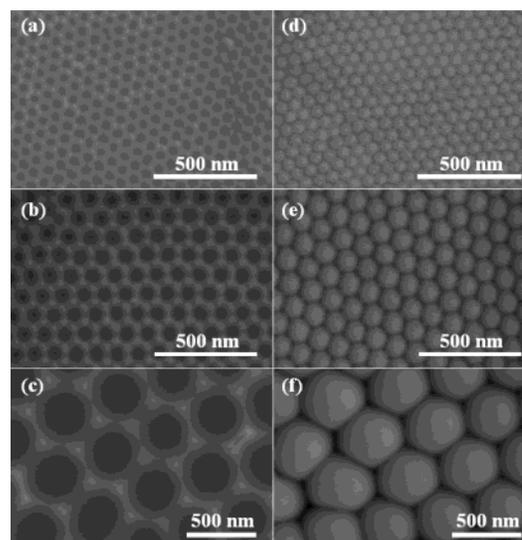


Figure 2. Representative FE-SEM images of the textured aluminum masters that were prepared by long-term, second anodizations of Al in (a) sulfuric acid, (b) oxalic acid, and (c) phosphoric acid, followed by stripping of porous oxide. FE-SEM images of nanostructured Au films that were replicated from the textured aluminum masters are presented in panels d–f.

array of approximately hemispherical concaves. The radius of each concave, which corresponds to the cell radius, varies as a function of the anodization voltage (2.6 nm/V); the average radii of concaves in the textured aluminum prepared from 0.3 M H_2SO_4 (25 V), 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ (40 V), and 0.9 M H_3PO_4 (160 V) are 30.5, 55.5, and 210.0 nm, respectively. Figure 2d–f shows FE-SEM micrographs of free-standing Au films which were fabricated from textured aluminum masters. The surface structure of replicated Au films is also mainly characterized as a 2D hexagonal arrangement of nanoembossments with no separation between features (i.e., full-fill factor), where the dimension of each embossment is predefined by the size of concaves on the textured aluminum masters. The density of the nanoembossments for sulfuric acid (H_2SO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), and phosphoric acid (H_3PO_4) produced aluminum masters was determined to be 3.1×10^{10} , 1.1×10^{10} , and 7.0×10^8 cm⁻², respectively.

Figure 3a shows representative atomic force microscopy (AFM) images of a two-dimensional (2D) array of Au nanoembossments that was replicated from oxalic acid produced aluminum. To amplify our knowledge of the surface morphology of the sample, a topographic AFM image is presented in Figure 3b showing clearly a close-packed 2D hexagonal arrangement of nanoembossments. The surfaces of the replicated Au films have exactly complementary structures of the replication Al masters, manifesting the high fidelity of the technique for producing a close-packed hexagonal arrangement of metallic nanostructures over a large area. According to sectional analyses on the AFM image, the height profiles along the two zone axes (i.e., [100] and [210] in the 2D hexagonal lattice) turned out to be not equivalent. Nanoembossments are attached to each other along the [210] direction, as clearly seen by the topographic AFM image in Figure 3b. Such a lack of circular symmetry of the nanoembossments is a natural consequence of the geometric structure of the replication master (i.e., textured aluminum): in the textured aluminum master each concave is surrounded by six bumps and each bump is surrounded by three concaves.

Preliminary investigations into the topography-induced surface properties of the present nanostructured surfaces

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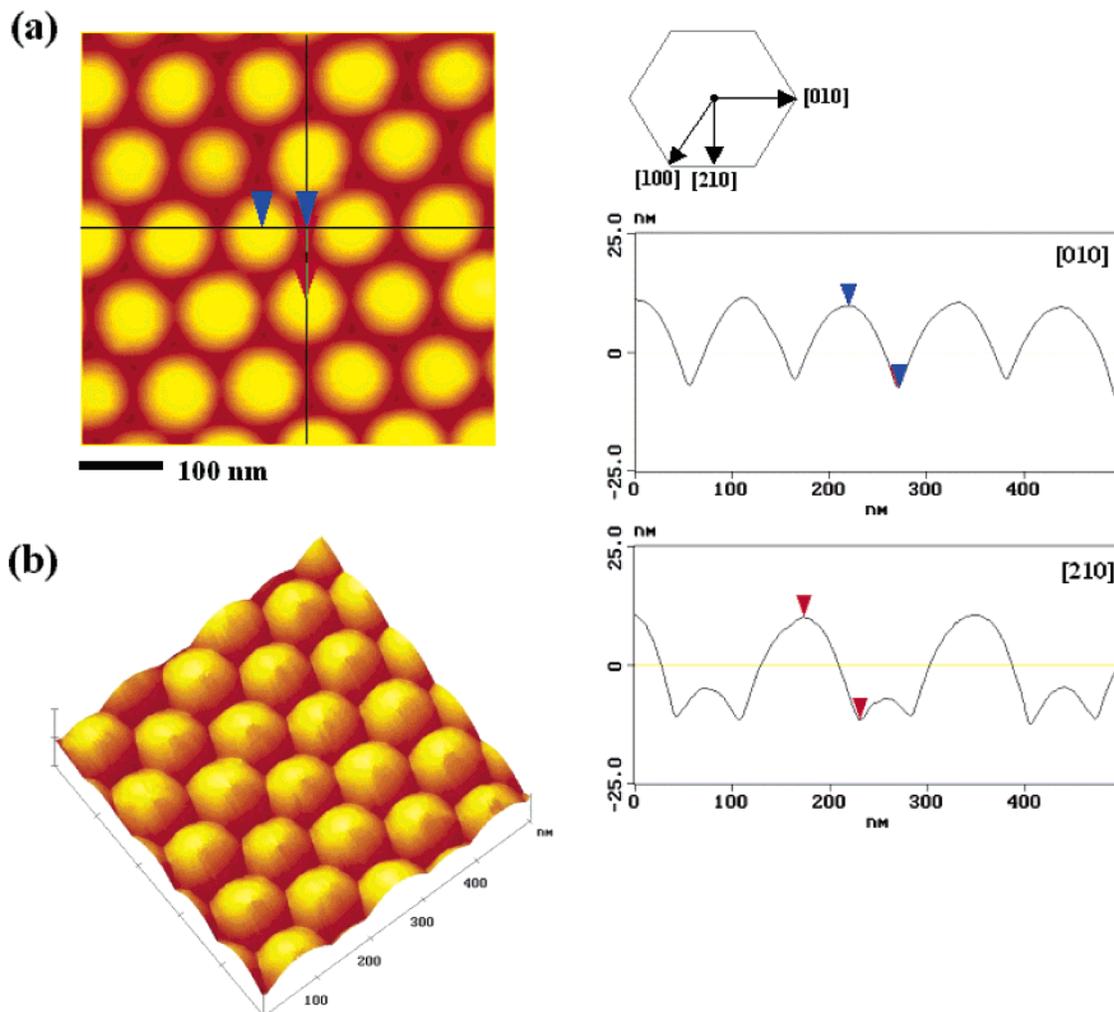


Figure 3. (a) A representative AFM image of a nanoembossed array that was replicated from the oxalic acid produced textured aluminum. A topographic AFM image is presented in panel b. The average height and width of each embossment estimated from the height profile along the [100] direction are about 20 and 100 nm, respectively.

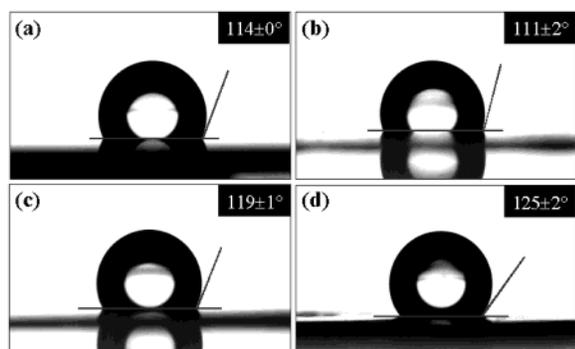


Figure 4. Shapes of water droplets placed on HDT self-assembled nanostructured Au surfaces that were replicated from (b) sulfuric, (c) oxalic, and (d) phosphoric acid produced textured aluminum masters. The shape of a water droplet placed on a HDT self-assembled smooth Au surface is presented in panel a, as a comparison. The water contact angles of the respective surfaces are presented in the upper-right insert.

were conducted by monitoring the evolution of contact angle for the hexadecane thiol (HDT) self-assembled nanostructured Au surfaces. It was observed that the water contact angle varies from 111.7° to 126.6° depending on the size of the nanoembossment as shown in Figure 4. In surfaces with close-packed arrays of hemispheres, the Wenzel's roughness factor (r), which is defined as the ratio

of the actual surface area to the geometrically projected area, is independent of the radii of the hemispheres and constant at 1.91. Accordingly, the observed contact angle variation of the present nanostructured surfaces cannot be adequately explained by Wenzel's equation describing the contact angle (θ') on a rough surface with $\cos \theta' = r \cos \theta$, where θ is the contact angle on a flat surface.¹⁹

For a surface with a 2D close-packed array of micro-hemispheres, previously Nakae et al. have formulated a parabolic relation between the height roughness (h) and the water contact angle by modifying Cassie's equation, in which the height roughness influences the curvature radius of the liquid in trapped air pockets at the solid-liquid interface.^{20,21} They suggested that when the height roughness is larger than a certain value (ca. $125 \mu\text{m}$), the contact angle decreases with an increase in height roughness. On the other hand, if the height roughness is less than this value, the curvature radius varies as a function of the height roughness and the free energy of the solid-liquid interface, and the contact angle decreases with a decrease in height roughness. Therefore, the observed wetting behaviors of the present Au nanostructured surfaces could be understood in terms of the variation of the height roughness (or the curvature radius)

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in the submicrometer scale range. However, there remains much room for further discussions of contact angle in the nanometer scale region and more systematic study should be carried out to thoroughly understand the wetting behavior of the present nanostructured surfaces.

Conclusions

We have shown that the electrochemically prepared textured aluminum sheet could be successfully used as a replication master for generating large-area nanostructured metallic films. It is clear, from our experiences, that the present method can be readily extended to make novel surface nanostructures from a wide range of different metals (e.g., Ag, Ni, Pt, Pd) that can be electrochemically deposited from aqueous solutions. Accordingly, it is expected that the present nanofabrication technique offers a highly facile and economic way for the production of large-area, periodic arrays of metallic nanostructures with potentially useful catalytic, magnetic, or other interesting

properties due to their increased surface area compared to their plain counterparts and dimensional periodicity. In addition, considering the high degree of flexibility in metal selection in the fabrication process and the tailoring capability of the resulting surfaces with suitable organic molecules, it is also expected that our fabrication method can provide a model surface for investigating the topological control of cell adhesion and activity.

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Supporting Information Available: Additional AFM data for the textured aluminum master. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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