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High speed fabrication of aluminum nanostructures with 10 nm spatial resolution by electrochemical replication

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Abstract
A high fidelity electrochemical replication technique for the rapid fabrication of Al nanostructures with 10 nm lateral resolution has been successfully demonstrated. Aluminum is electrodeposited onto a lithographically patterned Si master using a non-aqueous organic hydride bath of aluminum chloride and lithium aluminum hydride at room temperature. Chemical pretreatment of the Si surface allows a clean detachment of the replicated Al foil from the master, permitting its repetitive use for mass replication. This high throughput technique opens up new possibilities in the fabrication of Al-related nanostructures, including the growth of long range ordered anodic alumina nanochannel arrays.

1. Introduction

Micro- or nanostructures made of aluminum (Al) are expected to have interesting properties because Al exhibits excellent electrical conductivity, high tensile yield strength, and high reflectivity in the visible, ultraviolet, and infrared region. It can be easily transformed into dielectric oxide by anodization. Nanostructured Al has been used as mirrors, optical gratings, and microlens arrays in micro-optics [1]. Nanostructured Al substrates with different fluorophores can be used in surface-localized bioassays for potential medical and biotechnological applications [2]. One of the important applications of nanostructured Al is its use as a patterned substrate to grow highly ordered arrays of anodic aluminum oxide (AAO) nanochannels [3–5], which can be utilized as templates to grow various nanomaterials and nanodevices. For example, AAO has been used as a substrate for terabit magnetic storage devices [6] as well as chemical/biological sensors [7]. Therefore, it is desirable to develop an effective method for the rapid and large scale fabrication of various Al nanostructures with high precision.

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Herein, we introduce a high fidelity electrochemical replication technique for the rapid fabrication of aluminum nanostructures with 10 nm spatial resolution. In this technique, Al is electrochemically deposited onto a nanopatterned silicon (Si) master fabricated by electron beam (EB) or focused ion beam (FIB) lithography. The Al film with the replicated nanostructures is attached to a substrate with adhesives and then mechanically peeled off from the Si master. The integrated Al/substrate sheet can be flexible or rigid depending on the materials used as the substrates, for example plastics or bio-materials, because Al has high tensile yield strength. This room temperature replication technique is scalable for industrial production due to its compatibility with the existing Si technology. We have utilized the replicated freestanding Al films as patterned substrates to grow highly ordered AAO nanochannel arrays.

2. Experimental procedure

An n-type highly doped atomically flat silicon (100) wafer (resistivity $= 1.5 \times 10^{-3}$ Ω cm) was used as the substrate (cathode) for the electrochemical deposition of aluminum

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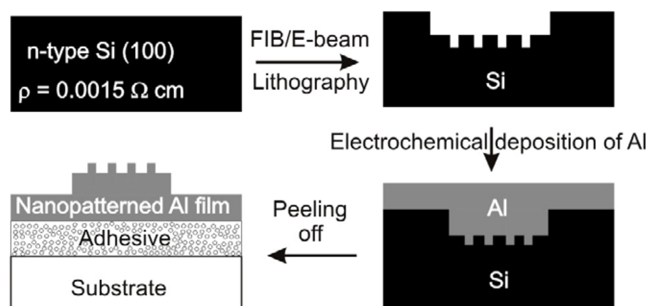

Figure 1. Schematic diagram illustrating the electrochemical replication process for the fabrication of nanostructured Al film.

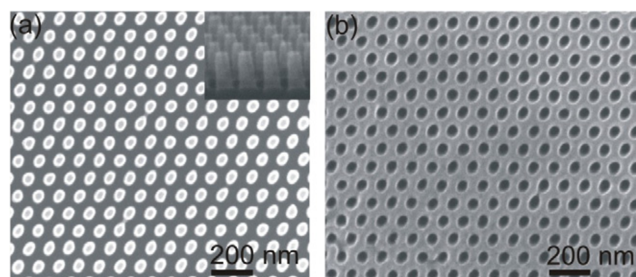

Figure 2. (a) Top view SEM image of the silicon master showing a hexagonal array of nanopillars fabricated by EB lithography. The inset shows the cross sectional view. (b) Top view SEM image of the replicated aluminum film showing a hexagonal array of nano-concaves.

inside a sealed glove box. The silicon wafers were cleaned by sonication consecutively in acetone and methanol for 3 min, followed by rinsing in deionized water (resistivity > 18 MΩ cm). Finally, the silicon wafers were dipped in pure hydrofluoric acid (HF, 49%) for 10 s to remove the native oxide layer, rinsed in deionized water for 45 s and dried completely before transferring into the glove box. Highly pure aluminum foil was used as the anode material. We have used the DC electrochemical deposition method to grow aluminum film using a current density of 15 mA cm^{-2}. The electrodeposition bath consists of aluminum chloride (3.0 M) and lithium aluminum hydride (0.4 M) in diethyl ether solution. Aluminum chloride was slowly mixed with the diethyl ether to avoid the evaporation of diethyl ether solution. The solution was cooled in a thermo-electric cooler during the addition of aluminum chloride which reduces the loss of diethyl ether and also facilitates the rapid addition of aluminum chloride. After the addition of the aluminum chloride, the lithium aluminum hydride in diethyl ether solution was added dropwise into the aluminum chloride solution and was stirred for good mixing. The aluminum electrodeposition bath was extremely stable and could be used over four weeks with no change in aluminum electrodeposition quality.

3. Results and discussion

Electrochemical deposition of Al using an aqueous bath is not possible because the reduction of hydrogen ions in water suppresses the cathodic Al deposition. This problem has been overcome by using a non-aqueous organic hydride bath containing aluminum chloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$) in a diethyl ether solution [8–10]. Since the chemicals are sensitive to oxygen, carbon dioxide, and water, the electrodeposition is carried out at room temperature in nitrogen atmosphere inside a sealed glove box.

The schematic diagram presented in figure 1 illustrates the electrochemical replication process for the fabrication of nanopatterned Al film. Nanopatterns on an n-type highly doped Si(100) wafer (resistivity $= 1.5 \times 10^{-3}$ Ω cm) were designed with the help of both EB and FIB lithography. The highly doped nanopatterned Si acts as a cathode, while highly pure Al foil was used as the anode in the electrochemical deposition step. However, p-type or low-doped nanopatterned Si cannot be used for this purpose.

In the subsequent step, almost 100 μm thick Al film was electrodeposited onto the nanopatterned Si master with a typical growth rate of 700 nm min^{-1} (using a current density of 15 mA cm^{-2}), which is much faster than that of most commonly used vapor deposition techniques. Finally, the replicated Al nanostructure was attached to a substrate using adhesive and peeled off from the master mechanically without any damage to the Al nanostructure or the nanopatterned Si master, thus preserving the nanometer-scaled surface features. The tunable adhesion of electrochemically deposited Al on Si can be controlled by adjusting the water rinsing time of the HF treated Si wafer, which facilitates the success of the peeling off procedure and the entire replication technique [11]. The replicated nanostructured Al film is of high quality, free from voids and cracks, as revealed by cross sectional SEM studies [11].

Figure 2(a) shows the top view scanning electron microscope (SEM) image of the nanopatterned Si master fabricated by EB lithography displaying a hexagonal array of nanopillars with diameter of 50 nm, height 140 nm, and periodicity of 100 nm. The inset shows the cross sectional SEM image of the silicon nanopillars. The corresponding SEM image of the Al film in figure 2(b) shows a hexagonal array of nano-concaves obtained by electrochemical replication. The general features shown in figure 2(b) qualitatively demonstrate the high quality of the top surface of the replicated Al film without the presence of defects. The SEM image in figure 2(b) shows that the diameter and periodicity of the nano-concaves on the replicated Al are 50 nm and 100 nm respectively, which quantitatively points out the high fidelity of the process.

To demonstrate the resolution of the technique, a nanopatterned Si master was fabricated using 30 keV Ga^{+} FIB with 10 pA beam current. A square array of nanotrenches with lateral dimension of 50 nm is delineated by FIB lithography while the gap between the trenches is only 10 nm, reaching the limit of FIB fabrication. Figure 3 shows the top view SEM image of the Al film replicated from the said Si master. A part of the SEM image in figure 3 marked with the rectangular box has been magnified and is shown here along with a line profile. As a consequence of the replication, the gap between the trenches is transformed into a deep line between raised platforms on the replicated Al surface. The width of the line

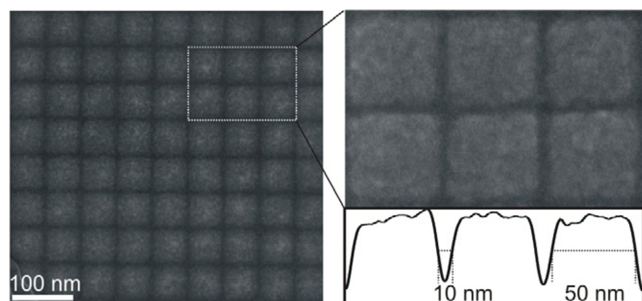

Figure 3. Top view SEM image of the aluminum film replicated from a square array of nanotrenches fabricated by FIB lithography. The inset shows the magnified view of the same image along with the line profile to demonstrate the spatial resolution of the method.

revealed by the line profile in figure 3 is 10 nm which is the same as the dimension of the gap between the nanotrenches patterned on the master. Thus, geometric features with lateral dimension up to 10 nm can be faithfully replicated by this process.

As an application of the replicated nanostructured Al film obtained by our technique, a freestanding Al foil with arrays of hexagonally close-packed guiding nano-concaves (shown in figure 2(b)) was used to grow long range ordered AAO nanochannel arrays. Figure 4(a) shows the top view SEM image of the long range ordered arrays of AAO nanochannels grown by a single step anodization of the nanopatterned Al foil in 0.3 M oxalic acid at 3 °C using a constant anodization voltage of 40 V for 3 h. The SEM image was taken after the pore widening of the nanochannels using 5% phosphoric acid (by weight) solution at room temperature for 30 min. The SEM image illustrates that the average pore diameter and inter-pore distance of the nanochannels are respectively 50 nm and 100 nm, comparable to the reported values [12]. The right-hand side in figure 4(b) and its corresponding inset show that the AAO nanochannels grown outside the nanopatterned area on the replicated Al foil have a large size variation without any orientational order. However, the left-hand side in figure 4(b) and its corresponding inset clearly demonstrate the growth of long range ordered arrays of AAO nanochannels. This result confirms that the pattern formation during the replication process can act as initiation points and subsequently guide the growth of ordered nanochannels arranged in a two-dimensional hexagonal configuration in the oxide film. It is important to mention here that generally nanoimprint lithography is employed to fabricate the patterned Al substrates, which can be subsequently anodized for the mass production of long range ordered AAO nanochannel arrays [5, 13]. However, the use of nanoimprint lithography for patterning onto metal substrates like Al requires higher pressures and damage to the imprint stamp often takes place after several uses due to high mechanical stresses. Unlike the nanoimprint techniques, our technique does not require high pressure to fabricate a patterned Al substrate. Therefore, it is expected that our technique can be an alternative to the nanoimprint lithography based guiding technique for the mass production of highly ordered AAO nanochannel arrays. The technique can be further applied for the growth of highly

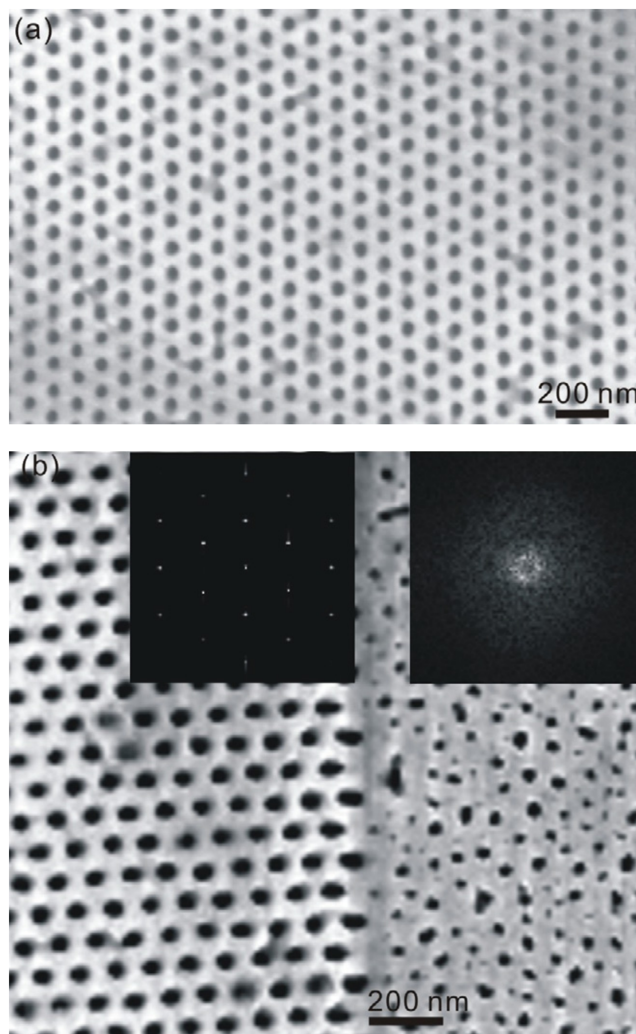

Figure 4. (a) Top view SEM image of long range ordered AAO nanochannel arrays grown on the electrochemically replicated freestanding Al foil. (b) Top view SEM image of the disordered (right) and long range ordered (left) AAO nanochannel arrays grown on an electrochemically replicated nanopatterned Al foil. The insets show Fourier transformations of the corresponding areas of the image.

ordered AAO nanochannels over larger areas, as the size of the nanopatterned Si master can be readily scaled up using the existing Si lithographic technology. It is important to mention here that fabrication of patterned Al substrates to grow highly ordered AAO nanochannel arrays has been carried out recently by some other replication techniques based on physical methods such as vapor deposition and sputtering of Al onto molds [14, 15].

4. Conclusions

In conclusion, we have demonstrated a high fidelity electrochemical replication technique to fabricate Al nanostructures with 10 nm spatial resolution. The high electrodeposition rate ($\sim$1 μm min^{-1}) makes this technique highly competitive as a stand-alone process or complement of other nanofabrication techniques. Tunable adhesion of the Al/Si interface

facilitates a clean detachment of Al from the master, permitting its repetitive use for mass replication. This high throughput technique can be easily scaled up for mass production. Due to the high tensile yield strength of Al, the nanostructured Al film can be attached to flexible or rigid substrates such as plastics or bio-materials. Such nanostructured Al film on versatile substrates is expected to find broad applications in micro- and nano-optics. We have successfully grown long range ordered AAO films, anodizing the freestanding nanopatterned aluminum foils obtained by this technique.

Acknowledgments

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