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Electrochemically replicated smooth aluminum foils for anodic alumina nanochannel arrays

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Abstract
A fast electrochemical replication technique has been developed to fabricate large-scale ultra-smooth aluminum foils by exploiting readily available large-scale smooth silicon wafers as the masters. Since the adhesion of aluminum on silicon depends on the time of surface pretreatment in water, it is possible to either detach the replicated aluminum from the silicon master without damaging the replicated aluminum and master or integrate the aluminum film to the silicon substrate. Replicated ultra-smooth aluminum foils are used for the growth of both self-organized and lithographically guided long-range ordered arrays of anodic alumina nanochannels without any polishing pretreatment.

1. Introduction

Many modern industries rely heavily on the technology for fabricating smooth semiconductor substrate surfaces. The rapid progress in nanotechnology has further elevated the importance of this technology because of the reduction in the dimensions of the structures and devices. Fabrication of metallic and semiconductor nanostructures in the sub-100 nm range is essential for nanotechnological applications. Surface roughness of the substrate surface plays an important role in the fabrication of structures and devices of nanometer dimension. For example, to prepare nanodevices based on self-assembled monolayers of molecules, the surface of the substrate has to be smooth enough to ensure the uniformity of the atomic structure and therefore the properties of the devices; to grow long-range ordered arrays of anodic aluminum oxide (AAO) nanochannels by lithographic guiding techniques, the surface of the aluminum (Al) need to be polished to an rms roughness of less than a few nanometers [1, 2].

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Different methods [3–6] have been employed to fabricate smooth metal surfaces with varying degree of success. Here, we introduce a fast electrochemical replication (ER) technique to fabricate an ultra-smooth aluminum (Al) surface by taking advantage of the smoothness of readily available silicon (Si) substrates as a master for replication. Due to our ability to vary the adhesion of the electrochemically deposited Al on Si, the replicated Al foil can be easily detached from the master substrate without damaging either the replicated Al surface or the Si master. This non-destructive ER technique can be scaled up for the mass production of smooth Al foils with large areas because smooth Si masters are readily available from the semiconductor industry and can be used repeatedly. We have utilized these smooth aluminum foils to grow self-organized and lithographically guided ordered arrays of AAO nanochannels. We have also integrated thick AAO films on Si substrates utilizing this technique.

2. Experimental procedure

An n-type highly doped atomically flat silicon (100) wafer (resistivity $= 1.5 \times 10^{-3}\ \Omega$ cm) was used as the substrate

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(cathode) for the electrochemical deposition of aluminum inside a sealed glove box. The silicon wafers were cleaned by sonication successively 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 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.

All the chemicals used for the preparation of the electrodeposition bath were extremely pure and obtained from Aldrich. The electrochemical deposition was carried out at room temperature in a sealed glove box with dry nitrogen as the working gas due to the presence of strong reducing agents like lithium aluminum hydride (air and moisture sensitive) and highly flammable solvents like diethyl ether. To prepare the bath, aluminum chloride ($AlCl_3$) was slowly added to diethyl ether in order to avoid the evaporation of diethyl ether solution since the reaction is exothermic. The solution was cooled in a thermo-electric cooler during the addition of $AlCl_3$ which reduces the loss of diethyl ether and also facilitates the rapid addition of $AlCl_3$. After the addition of the aluminum chloride, the lithium aluminum hydride in diethyl ether solution was added dropwise into the $AlCl_3$ solution and was stirred for good mixing. The aluminum electrodeposition bath was extremely stable and could be utilized over four weeks with no change in aluminum electrodeposition quality. The silicon wafer was kept inside a Teflon sample holder with an open circle of 1 cm^2 so that only this open circle region can be electrodeposited with aluminum. During the electrodeposition, the moisture and oxygen concentration were less than 0.1 and 1 ppm respectively, as shown by the sensors attached to the glove box. The rms roughness of the aluminum substrate was measured by a contact mode atomic force microscope (AFM) in air.

The aluminum foil replicated by the ER technique was anodized for 5 h in 0.3 M oxalic acid at 3 °C using a constant anodization voltage of 40 V. After the first anodization, AAO was dissolved in 3% (by weight) CrO_3 solution. The second anodization was continued to grow almost 20 μm long self-organized nanochannels. A scanning electron microscope (SEM) image was taken after the pore widening of the nanochannels using 5% phosphoric acid (by weight) solution. A commercial 30 keV Ga focused ion beam (FIB) with a beam current of 10 pA was employed to create arrays of hexagonally close-packed concaves on the ultra-smooth Al foil obtained by the ER process. The prepatterned Al foil was later anodized for 3 h in 0.3 M oxalic acid at 3 °C using a constant anodization voltage of 40 V.

3. Results and discussion

The most essential step in the ER technique is the process to replicate the surface topography of the master substrate

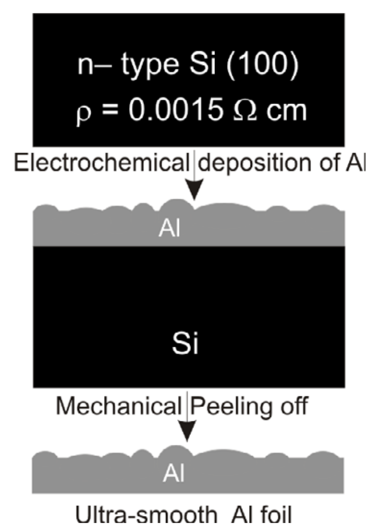

Figure 1. Schematic diagram showing the electrochemical replication process for the fabrication of nanometric smooth Al foil.

by depositing Al electrochemically. This is followed by the mechanical peeling off to detach the electrodeposited Al foil from the master. Electrochemical deposition of Al in an aqueous bath is not possible. Reduction of the hydrogen ions (H^+) in the water completely suppresses the reduction of Al ions (Al^{3+}) [7]. Among the various attempts to tackle the challenge of depositing Al at room temperature [8, 9], only the employment of a non-aqueous organic hydride bath, which contains aluminum chloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$) in a diethyl ether solution, has found its success [10]. Since the chemicals used in this approach are highly sensitive to oxygen, carbon dioxide and water, the electrochemical deposition cannot be carried out in ambient atmosphere [9]. A sealed glove box with nitrogen as the working gas was used in our experiment.

Figure 1 shows the complete scheme of the electrochemical replication process for the fabrication of ultra-smooth Al foils. As shown schematically in figure 1, an n-type highly doped atomically flat silicon (100) wafer (resistivity = 1.5×10^{-3} Ω cm) was used as the substrate (cathode) for the electrochemical deposition of aluminum. For the fabrication of an ultra-smooth foil, ~50 μm thick Al film is electrodeposited onto the Si substrate with a typical growth rate of 700 nm min^{-1}, which is much faster than that of most commonly used vapor deposition techniques. We have grown ultra-smooth Al foils with areas of 1 cm^2. The atomic force microscope (AFM) image of the top surface (electrolyte facing surface) in figure 2(a) shows a very rough surface with large grains. The rms roughness of a 15 μm × 15 μm surface area is ~0.6 μm. Similar surface roughness has been observed by other research groups [11] and is typical of most of the metal surfaces prepared by electrodeposition. The energy dispersive x-ray (EDX) spectrum in figure 2(b) indicates that the composition of the top surface is mainly aluminum with some amount of oxygen (34 at.%) and chlorine (9 at.%). The oxygen comes from the native oxide layer, which is expected to form on the surface after the Al is exposed to air, whereas the chlorine comes most likely from the electrolyte consisting of $AlCl_3$

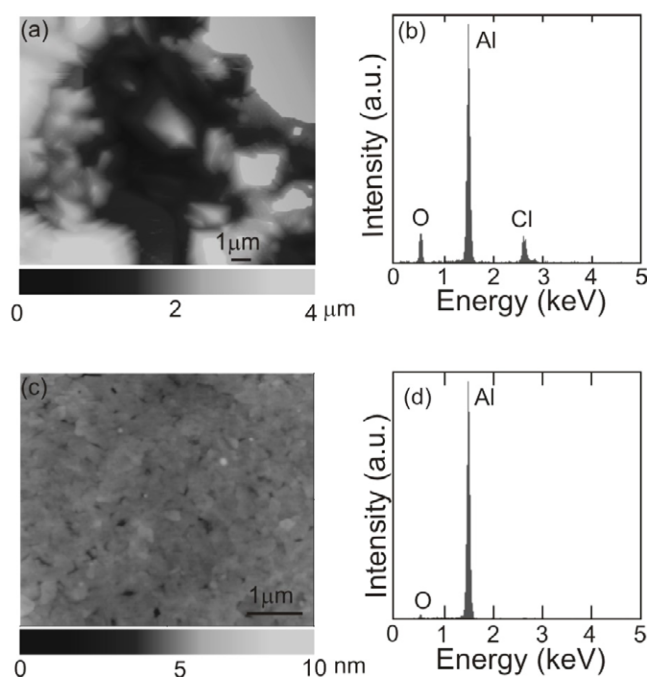

Figure 2. (a) AFM image of the top surface (electrolyte facing side) of the electrochemically deposited aluminum foil. (b) EDX spectrum of sample shown in (a). (c) AFM image of the bottom surface (Al/Si interface). (d) EDX spectrum of the sample shown in (c).

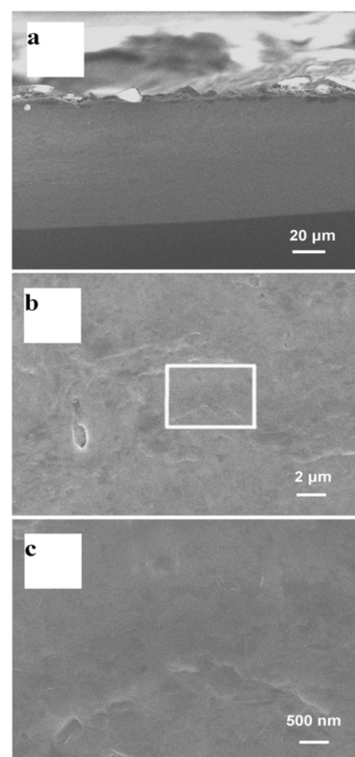

Figure 3. Cross-sectional SEM image of the aluminum foil obtained by ER process. Scale bars: (a) 20 μm, (b) 2 μm. (c) Magnified view of the marked area shown in (b) of the same sample.

and $LiAlH_4$ as well as the chloride components in the diethyl ether solution. The AFM image in figure 2(c) shows the surface topography of the replicated Al with an rms roughness of $\sim$1 nm (10 μm $\times$ 10 μm area), which is almost as smooth as the Si master. The results indicate the formation of a continuous layer of Al on the Si surface in the initial stage of the electrodeposition; and the subsequent detachment of the Al from the master is adequately controlled such that surface morphology of both the Al and Si is preserved with nanometer-scale precision. The EDX spectrum shown in figure 2(d) exhibits no detectable amount of chlorine and only a small amount of oxygen (7 at.%), indicating the high purity of the bottom surface of the replicated Al foil. It is worth noting that the oxygen signal from the bottom surface is only 1/5 of that from the top. Since the signal is proportional to the amount of native oxide per unit area spontaneously formed on the surfaces when the foil is exposed to air, the large difference is qualitatively consistent with the expectation that the rough top surface has a larger surface area per unit area and oxygen can penetrate deeper into the bulk through its cracks and defects to form thicker aluminum oxide locally. In other words, the smaller average thickness of the native oxide layer formed on the bottom surface is also an indication of its much better smoothness.

Figure 3 shows a cross-sectional scanning electron microscope (SEM) image of the Al foil fabricated by the ER technique. The figure clearly reveals the inner structure of the electrochemically deposited Al foil, which is free from voids and cracks, with uniform thickness. This proves the high quality of our sample obtained by the ER technique.

The success of the ER technique hinges on the high fidelity of the fast electrochemical deposition and the moderate adhesion of Al on Si master which facilitates the detachment of the foil. Since void formation is commonly observed in electrochemical deposition due to its relatively high growth rate, it is quite remarkable to achieve the high fidelity replication with formation of only a few shallow ($\sim$5 nm) voids in samples shown in figure 2(c). Because electrochemical deposition is a three-dimensional growth process after the initial nucleation stage, the observed low density of shallow voids indicates the presence of a high density of nuclei ($>10^{12}$ cm^{-2}) on the Si master. The small average spacing between the nuclei prevents the formation of large islands before the coalescence of islands takes place, reducing the possibility of large void formation. On the other hand, the adhesion of the Al on Si surface depends on the chemistry of the Si/Al interface, which dictates the interfacial energy as well as the morphology of the replicated surface discussed above. Although the Al/Si interface has been studied extensively [12, 13], the interfacial chemistry of this material system in the presence of the electrolyte consisting of $AlCl_3$ and $LiAlH_4$ in the diethyl ether solution is yet to be clarified.

The adhesion of electrodeposited Al on Si depends strongly on the pretreatment of Si surface. HF treatment of a Si substrate results in a hydrophobic surface whereas exposure of an HF-treated surface to water decreases its hydrophobicity, as evidenced by the water contact angle measurement shown in the inset of figure 4. The decrease in hydrophobicity is accompanied by a dramatic decrease in the adhesion of electrodeposited Al on Si, as shown by the break-off force versus water rinsing time plotted in figure 4. (The data are

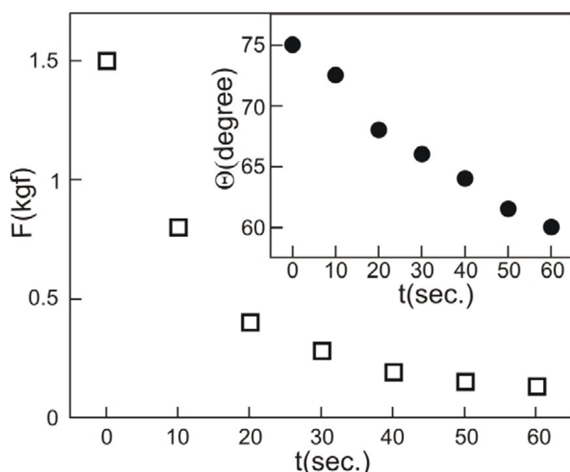

Figure 4. Plot for break-off force (F) of Al/Si interface versus water rinsing time (t). The inset shows the variation of water contact angle (Θ) of the HF-treated Si substrate as a function of water rinsing time (t).

acquired by measuring the force needed to peel off the Al foil from the Si wafer using a mechanical peeling off machine.) The exponential decay of adhesion is most likely the result of the logarithmic increase in the concentration of surface Si–OH bonds, which replace the Si–F and Si–H bonds formed in the HF treatment. The reaction of water with an HF-treated Si surface proceeds through the following steps: [14]

$$\text{Si–F} + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \text{HF}$$

$$\text{Si–H} + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \text{H}_2.$$

The empirical result implies that the adhesion of Al on Si can be tuned by simply adjusting the water rinsing time of the HF-treated Si substrate. The tunable adhesion of electrodeposited Al on Si can be utilized to grow integrated AAO film on Si by exploiting the region of strong adhesion and replication of patterns onto the surface of Al by exploiting the region of moderate adhesion. Further studies, preferably *in situ* monitoring of the species on the Si under the electrochemical environment using techniques such as sum frequency generation [15], are necessary to improve our understanding of this interesting phenomena with important technological implications.

Although the surface of the electrodeposited Al film integrated on Si substrate (strong adhesion of the Al/Si interface) is rough, it still can be electrochemically polished to nanometric smoothness before anodization. Thus, we have successfully integrated an AAO film of thickness around $\sim$20 μm on a Si substrate by this approach, and the detailed results will be communicated later. Our method of integration of AAO film is more convenient compared to the other methods involving different vapor deposition techniques like evaporation or sputtering [16]. The integration of AAO film on Si based on vapor deposition techniques is carried out at very high temperatures in vacuum environment, yielding much thinner AAO films of thickness typically from tens of nanometers to a few micrometers.

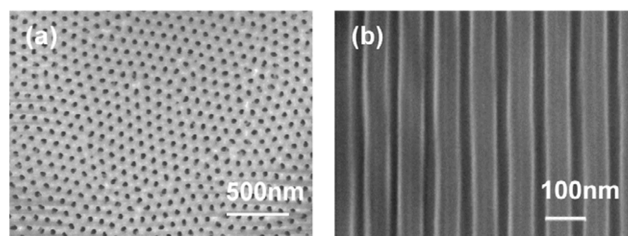

Figure 5. SEM image showing an array of self-organized alumina nanochannels grown by anodizing an electrochemically replicated nanometric smooth Al foil. (a) top view, (b) cross-sectional view.

As an application of the ultra-smooth Al foil prepared by the ER technique, a sample is used as a substrate for fabricating self-organized arrays of AAO nanochannels. Figure 5(a) shows the top-view SEM image of the nanochannel array obtained by a two-step anodization process [17] in oxalic acid (0.3 M) at a constant anodization voltage (40 V). To be noted is that, conventionally, electrochemical polishing of the Al sample to nanometric smoothness is needed before anodization in order to grow such self-organized arrays of AAO nanochannels. The invention of the ER method for the preparation of ultra-smooth Al foil allows us to skip the potentially explosive electrochemical polishing step, and therefore should be considered a significant step towards the development of AAO technology. The average pore diameter and inter-pore distance of the nanochannels grown on the as-deposited Al foil are respectively 50 and 100 nm, comparable to the reported values [18]. The nanochannels laterally self-organize into hexagonally close-packed domains with a range of order comparable to that of the self-organized nanochannel arrays fabricated by anodizing a finely electropolished Al foil [19]. The maximum domain size of these self-organized nanochannel arrays is restricted to a few micrometers. Figure 5(b) is a cross-sectional SEM image of the film, showing the straightness and uniformity of the nanochannels.

These ultra-smooth Al foils can also be utilized to grow arrays of long-range ordered AAO nanochannels by the lithographic guiding technique. We have used a commercial 30 keV Ga focused ion beam (FIB) with a beam current of 10 pA to create arrays of hexagonally close-packed concaves on the smooth Al surface obtained by ER. This is followed by an one-step anodization in 0.3 M oxalic acid at 3 °C, using a constant anodization voltage of 40 V. Figure 6 shows the top-view SEM image of the long-range ordered arrays of AAO nanochannels grown by a single step anodization of an FIB-prepatterned Al foil. The SEM image shows that the average pore diameter and inter-pore distance of the nanochannels are respectively 50 and 100 nm, comparable to the reported values [1, 2]. The left-hand side of the image in figure 6 and its corresponding inset also show that the AAO nanochannels outside the FIB-prepatterned area have large size variation and almost no orientational order. The right-hand side of the image in figure 6 and its corresponding inset clearly demonstrate that the FIB-patterned area can guide the growth of long-range-ordered arrays of AAO nanochannels on an Al foil prepared

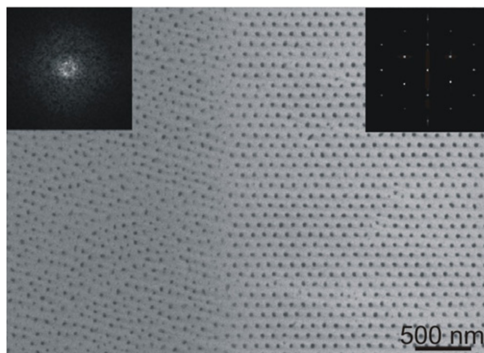

Figure 6. Top view SEM image of disordered (left) and long-range-ordered (right) AAO nanochannel arrays grown on an electrochemically replicated Al foil. The insets show Fourier transformations of the corresponding areas of the image.

by ER. The results shown in figure 6 confirm that the patterns fabricated by FIB lithography can act as an initiation point and guide the growth of nanochannels arranged in two-dimensional hexagonal configurations. It is important to mention here that patterns on aluminum surfaces can also be obtained by nanoimprint lithography, which is less expensive than FIB lithography [1]. The results shown in figures 5 and 6 indicate that the structure of the porous AAO nanochannel is very similar in both cases, with a difference only in the surface pore arrangement. The successful fabrication of self-organized and long-range-ordered AAO nanochannel arrays using smooth Al foils prepared by ER demonstrates its potential applications in the AAO technology as well as future nanotechnology that requires a smooth Al surface. The freestanding porous AAO films grown by this technique can be used as filters in gas filtrations and biological separations [20–22] and as chemical/biological sensors [23].

4. Conclusions

In conclusion, we have successfully fabricated Al foils by a fast electrochemical replication process using Si wafers as master substrates. When detached from the Si, the bottom surface of such a freestanding Al foil has an rms roughness of ∼1 nm, comparable to that of the Si master. The size of the foil can be readily scaled up because large Si wafers are commercially available. Applications of the foil have been exemplified by the growth of AAO nanochannel arrays with either short-range self-organized order or long-range lithographically guided order. Since the process can be tuned to make the Al adhere strongly to the Si, it also lays down a foundation for the integration of AAO technology with Si technology.

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