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FULL PAPER

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Soft Imprinting: Creating Highly Ordered Porous Anodic Alumina Templates on Substrates for Nanofabrication**

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We demonstrate a "soft-imprinting" method for the fabrication of highly ordered porous anodic alumina (HOPAA) templates on different substrates (such as Si, glass slides, and flexible polyimide films) over large areas (> 1.5 cm^2). In this process, Ar plasma etching is employed to soft imprint an evaporated Al film on the substrates using a free-standing HOPAA template as a mask, thus creating ordered nanoindentations on the Al surface. The ordered nanoindentations in turn guide the subsequent anodization of Al to generate HOPAA templates on the substrates (HOPAA–substrates), which inherit the pattern of the free-standing HOPAA mask. This soft-imprinting technique is also applicable to the fabrication of HOPAA on flexible polymer films. To demonstrate the potential uses of the HOPAA–substrates in nanofabrication, highly ordered Au nanowire arrays are fabricated on a Si substrate and TiO_2 nanotube arrays are prepared on a glass substrate via solution- and vapor-based fabrication processes, respectively.

1. Introduction

Nanostructured arrays fabricated on surfaces have a wide range of potential applications in areas such as micro- and nanoelectronics, photoelectronics, information storage, and sensing. From the viewpoint of practical applications, nanostructured arrays with uniform size, tunable dimensions, and long-range order are highly desired. For example, highly ordered TiO_2 nanotube arrays serving as electrodes in solar cells have been reported to exhibit enhanced charge separation efficiency and also offer excellent pathways for charge transport.[1] Over the past two decades, porous anodic alumina (PAA) has been widely used as a template to prepare various nanowire and nanotube arrays, including those of metals, semiconductors, carbon, and polymers.[2–7] The PAA-assisted approach provides many advantages over conventional lithographic techniques for the fabrication of simple sub-100 nm nanostructured arrays.[8,9] For example, its parallel nature allows for the simultaneous preparation of nanostructured arrays over very large areas at low cost. No complicated equipment is required in this process because hexagonally packed sub-100 nm pores are formed naturally during Al anodization. The pore diameter and length, as well as the interpore distance, can be easily tuned by varying the applied potential and choosing an appropriate acidic electrolyte.[10–14] To achieve long-range-order pores, highly ordered PAA (HOPAA) templates have been successfully prepared by two-step anodization,[11] pretexturing Al surfaces using imprinting-based methods,[15–19] as well as by directly writing the patterns on Al surfaces using a focused ion beam.[20]

For practical applications, it is highly desirable to directly grow the nanostructures on various substrates using PAA templates. Several methods, including the use of ultrathin free-standing PAA templates,[21] flexible and robust gold membranes replicated from PAA,[22] and PAA templates directly bonded to the substrates,[23] have been employed to transfer PAA patterns onto the substrates. In particular, we and others have recently demonstrated that the direct integration of PAA templates with substrates (PAA–substrates) provides a versatile and simple method for fabricating nanostructured arrays on substrates over large areas.[8,9,15,18,24–29] By anodizing an Al film evenly deposited on a substrate, ultrathin, large-area (4 in. wafer experimented in our laboratories) PAA templates with a thickness of ca. 100 nm can be easily fabricated with the support of the substrate. The intimate contact between the template and the substrate enables both solution- and vapor-based fabrication of a variety of nanostructured materials. In addition, the PAA–substrates are thermally and chemically stable in most fabrication processes and can also be easily removed by selective wet etching. By utilizing this method, a variety of nanostructured materials, including metal and metal oxide nanowires/nanotubes,[9,24,30] semiconductor nanoparticles and holes,[31,32] as well as patterned self-assembled monolayers,[25] have been successfully fabricated on various substrates.

Even though the PAA–substrates show great potential for the fabrication of nanostructured arrays on substrates, one challenge that still remains is the preparation of HOPAA templates on substrates (HOPAA–substrates). HOPAA can be fabricated by the anodization of Al with well-patterned nanoindentations, which guide the development of the pores during

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the anodization process under appropriate conditions.[17] Several methods have been reported to prepare HOPAA on Al foils, but the fabrication of HOPAA substrates is not very well developed yet. Ideally, the preparation of HOPAA–substrates should be simple, cost-effective, and compatible with high-throughput methods to create patterned nanoindentations on the Al surface. It should also be substrate-friendly to avoid undermining the substrate underneath the very thin Al films (usually < 1 μm). Methods used for creating ordered nanoindentations such as energetic-particle-beam writing[20] or anodization for long periods of time (known as two-step anodization)[11] are substrate-friendly. However, the direct-writing method is generally serial in nature and is not cost-effective. The two-step method frequently used to prepare free-standing HOPAA relies on anodization for a long period of time in the first step, which creates highly ordered nanoindentations to guide the second anodization. To obtain PAA with large ordered domains (e.g., > 1 μm^2), this method requires the use of a thick Al film (usually requiring anodization for 4 h at room temperature with an Al thickness > 40 μm) for long-time anodization.[11,13] Deposition of such a thick Al film on a substrate is neither easy nor cost-effective by electron-beam evaporation, especially when considering the quality of the evaporated Al. The electron-beam evaporation of Al films with a thickness of about 9 μm has recently been demonstrated by Tian et al;[29] however, the use of such Al films for two-step anodization has not yet been reported. Imprinting-based methods have been used by several groups to prepare HOPAA,[15–19,30] wherein nanoindentations are created by transferring patterns from a hard master stamp onto the Al surface under high pressure (such as by an oil press) prior to anodization. Despite the ideally ordered patterns obtained, this method is limited by the pattern transfer protocol. The applied pressure for pattern transfer tends to crack substrates with low mechanical strength, such as silicon and glass, and leads to substrate deformation and Al separation from soft substrates.

In this work, we report a "soft imprinting" approach to prepare HOPAA on various substrates, including Si, glass slides, and flexible polyimide films. In this approach, the nanoindentations on the Al surface are soft imprinted via Ar plasma etching through a free-standing HOPAA mask. This approach provides a gentle method for creating nanoindentations without undermining the substrate, because almost no mechanical force is applied on the substrate. The mask used for Ar plasma etching is prepared by a simple two-step anodization process. For effective pattern transfer using Ar plasma etching, we have employed several improved techniques to fabricate through-pore, large-area (> 1.5 cm^2), and ultrathin free-standing HOPAA masks (with thickness ranging from ca. 200–400 nm). Finally, we demonstrate that the HOPAA–substrates are versatile and can be used to fabricate highly ordered nanostructures directly on substrates. Au nanowire arrays are created on Si substrates via electrodeposition (solution-based fabrication), and TiO_2 nanotube arrays are fabricated on glass substrates by atomic layer deposition (ALD, vapor-based fabrication).

2. Results and Discussion

The method used to prepare HOPAA–substrates is schematically depicted in Figure 1. Firstly, a free-standing PAA mask with a protective poly(methyl methacrylate) (PMMA) layer (Fig. 1a) is fabricated by the two-step anodization of Al foils. Next, the mask is attached to the substrate (Fig. 1b). After removal of the protective layer, through-pore HOPAA is formed, which acts as a mask for soft imprinting such that the Al surface is selectively etched by the Ar plasma (Fig. 1c), thereby creating arrays of nanoindentations on the Al substrate (Fig. 1d). The nanoindentations then direct the anodization of Al into the HOPAA template on the substrate (Fig. 1e).

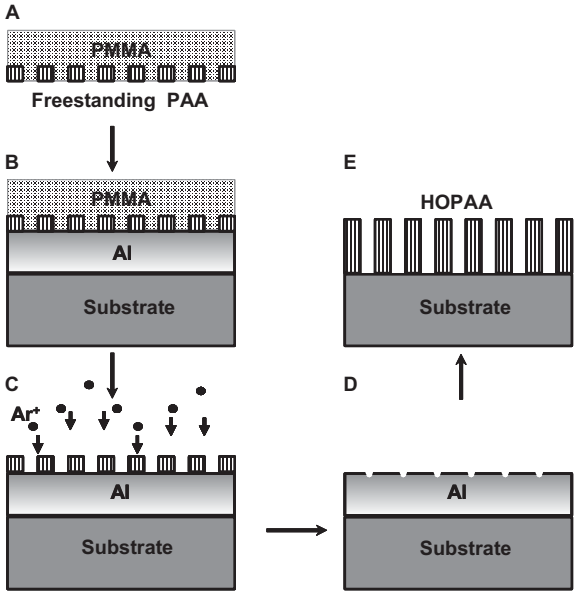

Figure 1. Schematic depiction of the soft-imprinting method for preparing HOPAA–substrates. Poly(methyl methacrylate) is used as a protective layer for the free-standing PAA.

By using soft imprinting, we have successfully fabricated HOPAA on various substrates. Figure 2 shows top-view scanning electron microscopy (SEM) images of the sample during three key stages of the process (a Si substrate is used for SEM observations). The pattern transfer from the HOPAA mask (Fig. 2a, ca. 60 and 105 nm pore diameter and interpore distance, respectively) to the Al surface is clearly discernible after soft imprinting. The nanoindentations replicated from the HOPAA mask have smaller diameters and similar pore distances and shapes, as shown in Figure 2b. The Ar plasma etching process is good enough to create nanoindentations with sufficient depth to guide the subsequent anodization. Figure 2c shows that the top of the HOPAA–substrate has the same pore structure and pore arrangement as the HOPAA mask. The inset of Figure 2c indicates that the pores are straight through to the substrate. The ability of the soft-imprinting method to create nanoindentations with sufficient depth for guiding the anodization process is further confirmed by the SEM image

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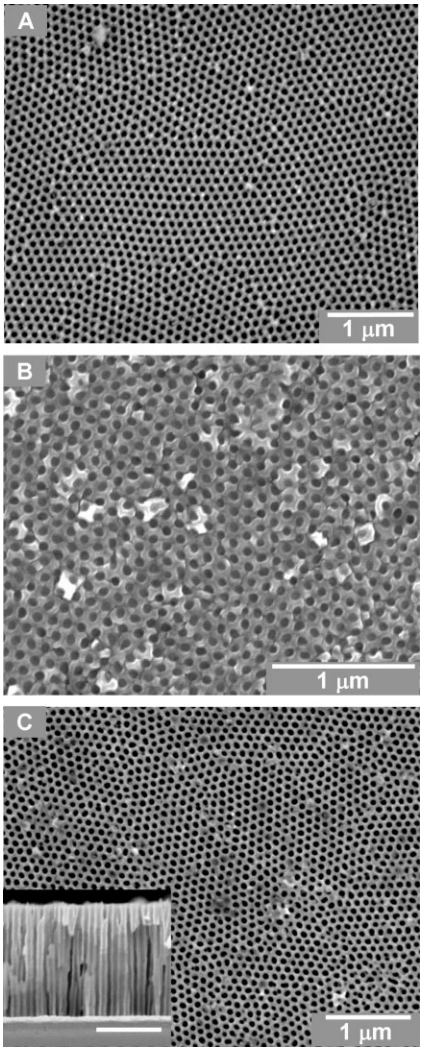

Figure 2. Scanning electron microscopy images of the sample at three crucial stages of the soft-imprinting process: A) the free-standing HOPAA mask, B) nanoindentation arrays on the Al surface after Ar plasma etching through the HOPAA mask, and C) the HOPAA template on the substrate after anodization of the soft-imprinted Al. The inset shows a cross-sectional view of the HOPAA on the substrate (the scale bar represents 200 nm in the inset).

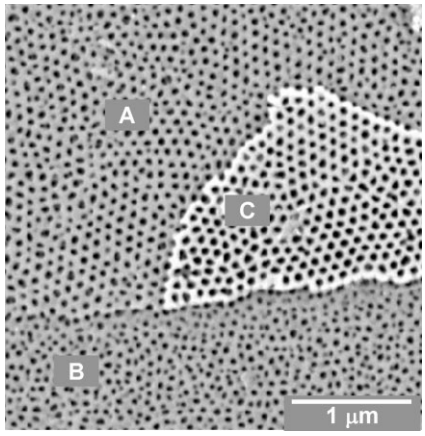

Figure 3. Top-view SEM image of a PAA surface with three different regions: the highly ordered pores in Region A are anodized from the soft-imprinted Al surface through the free-standing HOPAA mask, whereas Region B is characterized by random pores (fabricated without a HOPAA mask during the soft-imprinting step). The HOPAA in Region a follows the pattern of the free-standing HOPAA mask (Region C).

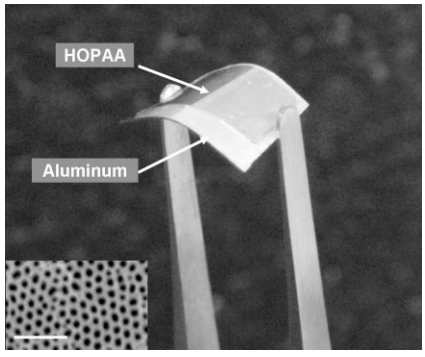

Figure 4. Photograph of a HOPAA template created on a flexible substrate (a polyimide film). The image shows that the sample can be bent by a pair of tweezers. The inner rectangular section with a darker color is the anodized region. The inset shows a SEM image of the HOPAA template on the flexible substrate (the scale bar represents 500 nm).

shown in Figure 3. It can be clearly seen that there are three distinct regions on the soft-imprinted and anodized Al surface: Region A is the HOPAA-mask-covered area during the soft imprinting process, whereas Region B is the area not covered by the mask, and Region C contains residues of the HOPAA mask. It can also be clearly seen that the anodized surface in Region A has pores with a hexagonal arrangement, which extend the pattern of the HOPAA mask (Region C). In contrast, Region B shows random pores.

To further demonstrate the substrate-friendly features of the soft-imprinting method, apart from fabricating HOPAA on Si substrates, we have also extended this method to the other mechanically weak substrates, such as glass slides and flexible polyimide films (Fig. 4). The HOPAA–glass may be useful for applications in photovoltaic devices, whereas HOPAA–flexible-substrates may be useful for fabricating flexible displays. Notably, the use of conventional imprinting methods on these substrates leads to the formation of cracks or deformations upon the application of a mechanical force for pattern transfer. Figure 4 shows a photograph of a bent HOPAA–flexible-polyimide-substrate held by a pair of tweezers. The inset shows the SEM image of the HOPAA layer on the flexible polyimide film. Although we have demonstrated here that soft imprinting can be used on flexible polyimide films, further improvements are necessary to ensure firm adhesion between the template and the flexible substrate.

In the soft-imprinting process, the main challenges are efficient pattern transfer from the HOPAA mask to the Al surface through Ar plasma etching, and the large-area fabrication of an intact free-standing HOPAA mask. For efficient pattern transfer, the HOPAA mask should be as thin as possible, and the pore openings need to be large in size. Utilizing the same pore opening size, we have determined that the time required

for effective Ar plasma etching ("effective" implies that the nanoindentations can be clearly observed under SEM) increases from 5 to 15 min when the thickness of the HOPAA mask is increased from ca. 200 to 400 nm. Larger pore openings are as effective at facilitating the Ar plasma etching process. In order to prepare the mask with large pores, we have carried out wet chemical etching of the PMMA/HOPAA mask for 2 h to firstly remove the barrier layer at the base of the template, and then to enlarge the pores after the removal of the barrier layer. Since the etching rate is estimated to be ca. 0.5 nm min^{-1} at room temperature, we originally believed that chemical etching for 2 h would be sufficient to remove the barrier layer (ca. 40 nm thick), and subsequently enlarge the pores. Unfortunately, we have determined that this treatment does not improve the pattern transfer even upon using a 200 nm thick PAA mask. Further prolonging the chemical etching time is supposed to enlarge the pores but it also does not improve the pattern transfer. SEM observations of the back surface of the PMMA/HOPAA mask after removal of the barrier layer indicate the presence of PMMA nanowire bundles (Fig. 5), suggesting that PMMA infiltrates into the pores.[33] The presence of PMMA within the pores may prevent H_3PO_4 from uniformly etching along the pores, resulting in conical morphologies of the etched pores, as schematically shown in Figure 6A.

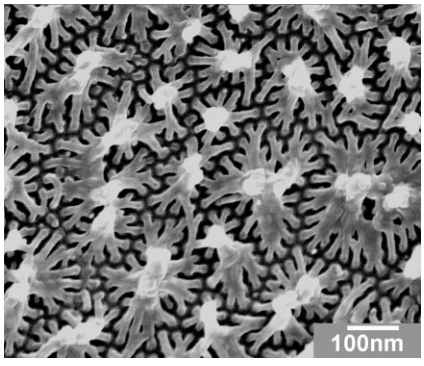

Figure 5. SEM image of the back surface of a PMMA-covered free-standing HOPAA mask after partial removal of the template. The nanowire bundles observed are likely to arise from the infiltration of PMMA into the pores of the template. These structures prevent the etchant from penetrating into the pores and hinder the widening of the pores, especially close to the pore openings.

It has previously been reported that upon heating PMMA to temperatures above its glass transition temperature (120 °C), its viscosity is greatly reduced, enabling it to easily infiltrate into the PAA pores.[33] We prefer to maintain the PMMA drying temperature at 120 °C because we believe that the infiltration of PMMA into the PAA pores produces a more robust supported mask for handling. Meanwhile, to obtain large pores for efficient pattern transfer, we have enlarged the pores by etching the mask in 5 wt % H_3PO_4 for 50 min before PMMA coating, followed by an additional etching step in the same solution for 30 min after separation of the PMMA/HOPAA mask from the Al foil, to remove the barrier layer. We have found that the combination of the two chemical etching processes (50 min pore widening prior to PMMA coating plus 30 min barrier layer removal) is optimal for the fabrication of a HOPAA mask with pores large enough for pattern transfer and strong enough for handling (pore-enlargement weakens the mechanical strength of the free-standing HOPAA). Since the pore-widening process is conducted before removal of the barrier layer, we have been able to obtain a HOPAA mask with large and straight pores, as shown in Figure 6B.

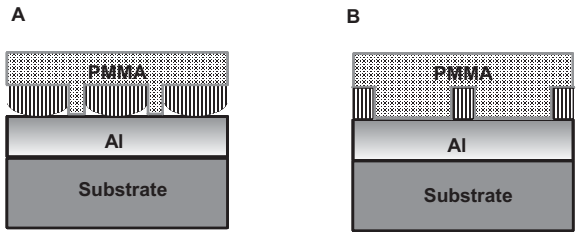

Figure 6. The pore openings of the mask are critical for efficient pattern transfer in soft imprinting. A) The one-step widening of the pores results in the formation of conical pores. After removal of the barrier layer at the bottom of the PMMA/HOPAA mask, the etchant might not be able to attack the pore openings since the pores are blocked by PMMA nanowires. B) Two-step pore widening increases the pore openings to a size that ensures efficient pattern transfer prior to coating with PMMA. This is followed by the removal of the barrier layer by chemical etching for a brief period. The two-step pore widening process generates large and straight pores.

The ultrathin free-standing HOPAA mask is extremely fragile and difficult to handle without the protective PMMA layer.[22] Even with the protective layer, the possibility of damaging the mask during the removal of PMMA by conventional methods such as dripping with acetone or chloroform cannot be ruled out.[21] To thoroughly remove the PMMA without damaging the HOPAA, we used a UV-ozone dry stripping method. This method enables us to easily obtain a large-area intact free-standing HOPAA mask (>1.5 cm^2), as shown in Figure 7 (for clearer contrast, we attached the large-area PAA mask to a darker SiO_2/Si substrate, instead of the silvery Al surface).

The direct integration of HOPAA with substrates allows for the template-assisted fabrication of nanostructured arrays on various substrates via vapor- or solution-based processes. Highly ordered templates offer good control over the fabrica-

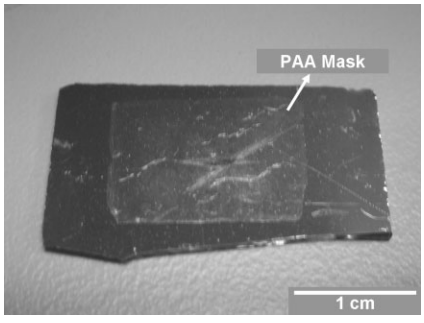

Figure 7. Photograph of a large-area intact PAA mask on a SiO_2/Si substrate after the removal of PMMA by UV-ozone dry stripping.

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tion of nanostructures (parameters such as size, height, and interpore distance). To exploit the HOPAA–substrates for nanofabrication, we have first demonstrated the preparation of highly ordered Au nanowire arrays on Si substrates via electrodeposition (solution-based fabrication). We have also carried out the ALD (vapor-based fabrication) of TiO_2 nanotube arrays on glass substrates. Although only two nanostructured materials are demonstrated here, this template-assisted approach should be generally applicable to other materials.

A thin Au layer (ca. 50 nm) sandwiched between the PAA and Si substrates serves as an electrode for the electrodeposition of Au nanowire arrays. Figure 8A shows the top view of a highly ordered Au nanowire array deposited on a Si substrate after removal of the HOPAA template. The Au nanowire arrays are hexagonally ordered, well-aligned, and stand upright on the silicon substrate. The length of the nanowires can be adjusted by varying the electrodeposition time. Figure 8B shows the side view of the well-aligned Au nanowires perpendicular to the substrate, and Figure 8C is a magnified top-view image of the array. The length of the Au nanowires synthesized in this work is around 200 nm; nanowires ranging up to ca. 1 μm in length can still align vertically and independently on the substrate without collapsing. Figure 8D shows a SEM image of a Au nanowire array fabricated on a random PAA–substrate, in which no apparent order is observed. The Au nanowires fabricated on the HOPAA–substrate are much more uniform in size than the nanowires formed on the random PAA–substrate. As shown in Figure 8E and F, the highly ordered Au nanowire arrays show a much narrower size distribution than those grown on random PAA. In this work, we have employed a free-standing HOPAA mask with 6 h anodization in the first step. To obtain larger ordered domains, further prolongation of the first anodization of the mask is needed (e.g., 24 h anodization). Dense ($>10^{10}$ cm^{-2}), uniform, and well-aligned Au nanowire arrays with tunable interpore distances grown on Si substrates may have a number of applications in biosensors, nanoelectrode arrays, surface plasmon resonance, and surface enhanced Raman microscopy.[34]

To demonstrate the potential applications of our HOPAA–substrate templates in preparing functional devices,[1] we have fabricated TiO_2 nanotube arrays on transparent glass substrates. We have used HOPAA, prepared by the soft-imprinting method, as a template for the ALD of TiO_2. ALD allows for uniform and conformal coating with precise control of the wall thickness of the tubes since the deposition occurs by a self-limiting layer-by-layer reaction on the surfaces.[30] Figure 9A shows a photograph of a typical anodized PAA film on a glass slide, indicating the HOPAA-mask-covered region (HOPAA–substrate) and the uncovered region (random-PAA–substrate). Upon completion of the anodization process, the Al-coated glass slide became transparent in both the mask-covered and uncovered regions. However, the two regions can be differentiated by a slight variation in color. Highly ordered patterns of the TiO_2 nanotube arrays after removal of the HOPAA template are shown in Figure 9B and its inset (magnified top view). The outer diameter of the nanotubes is about 80 nm, and the thickness of the tube walls is ca. 7 nm (the rate of TiO_2 ALD is ca. 1.0 Å $cycle^{-1}$). The length of the nanotube arrays can be tuned up to several micrometers by appropriately adjusting the thickness of the HOPAA template; however, long nanotubes exhibit a tendency to collapse. We have also studied the effects of the wall thickness of the tubes on the optical properties of the arrays by varying the number of ALD cycles. We have carried out UV-vis absorption spectroscopy measurements directly on the as-deposited samples. The transparent glass substrates used here greatly facilitate these measurements. As shown in Figure 9C, a red-shift in the adsorption edge is observed upon increasing the number of ALD cycles from 10 to 50. However, the adsorption edge starts to overlap for more than 50 ALD cycles. This result is similar to the phenomena observed in a previous report.[30] Though the mechanism for the shift in absorption is controversial, our results confirm that the optical properties of the TiO_2 nanotubes can be tuned by the ALD technique. The TiO_2 nanotube arrays on the transparent substrates have controllable dimensions and tunable optical properties, and are arranged in highly ordered patterns, which may facilitate their use in photovoltaic devices.

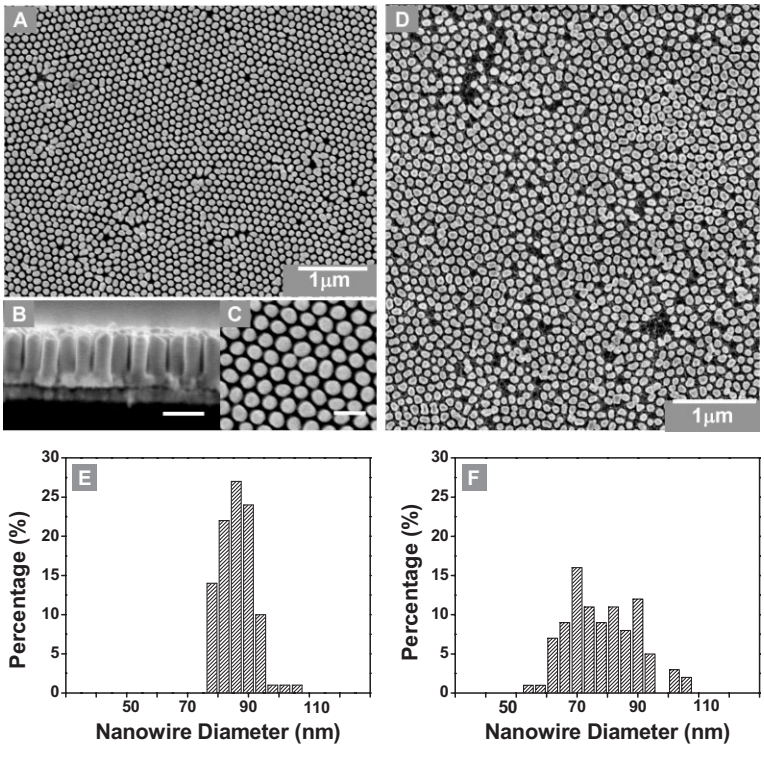

Figure 8. SEM images of Au nanowire arrays on a Si substrate obtained using A) HOPAA and D) random PAA templates. The cross section and magnified top view of the highly ordered Au nanowire arrays grown vertically on the substrates are shown in (B) and (C), respectively (the scale bars in these images represent 200 nm). The size distribution of Au nanowires fabricated from E) HOPAA is much narrower than that prepared from F) random PAA.

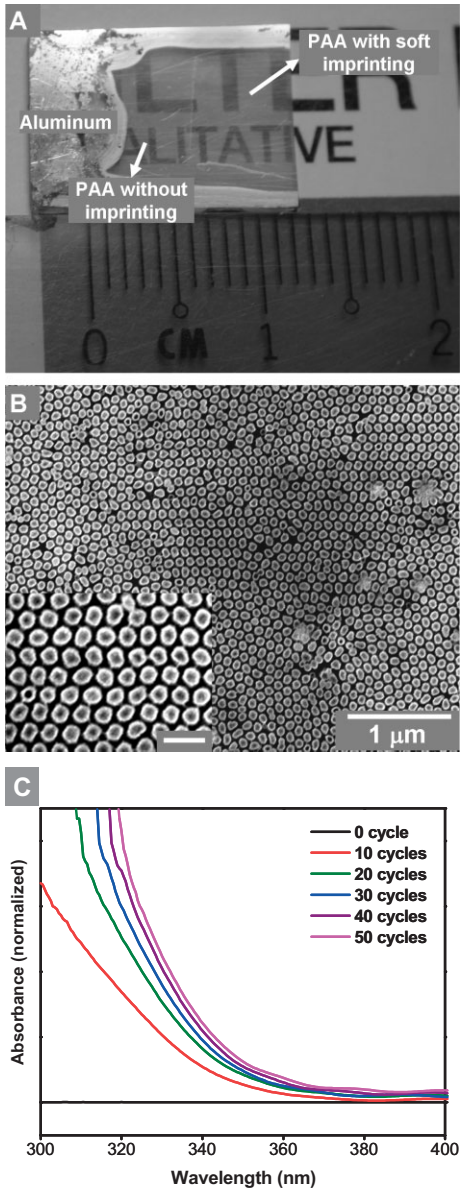

Figure 9. Highly ordered TiO_2 nanotube arrays on a glass substrate fabricated using HOPAA–glass. A) Photograph of the as-prepared PAA template on a glass substrate. The sample is transparent after anodization. B) Top-view SEM image of highly ordered TiO_2 nanotube arrays on the substrate. The inset shows a magnified image, clearly showing the hexagonal array of nanotubes (the scale bar in the inset represents 200 nm). C) UV-vis spectra of TiO_2 nanotubes with different wall thicknesses. The adsorption edge shifts to lower energies with increasing wall thickness. The wall thicknesses are adjusted by varying the number of ALD cycles from 10 to 50.

3. Conclusions

We have demonstrated the soft-imprinting method by using Ar plasma etching to fabricate HOPAA templates on substrates. In comparison with conventional techniques for the fabrication of HOPAA, our method can be used for the preparation of large-area HOPAA templates in good contact with various types of substrates (Si, glass slides, and flexible polyimide films are demonstrated here). In particular, we have also demonstrated the use of soft-imprinting methods to fabricate HOPAA templates on flexible substrates. By using HOPAA templates, highly ordered Au nanowire arrays have been fabricated on Si substrates, and TiO_2 nanotube arrays have been fabricated on glass substrates via solution- and vapor-based methods, respectively. Our method can also be used to prepare perfectly ordered PAA templates on substrates by using free-standing PAA masks fabricated by lithographic techniques.[17]

4. Experimental

Preparation of HOPAA Masks for Soft Imprinting: The free-standing HOPAA masks were prepared by the two-step anodization of Al foils, as reported previously [2]. Briefly, high purity (99.999 %) Al foil (Goodfellow Cambridge) was annealed under a flow of nitrogen at 550 °C for about 1 h, and then electropolished in a mixture of 1:4 (v/v) perchloric-acid/ethanol in an ice bath. The electropolished Al foil was first anodized at room temperature for 6–10 h in 0.3 M oxalic acid using 40 V, followed by removal of the prepared PAA film by etching with a solution of 3.5 vol % H_3PO_4 and 45 g L^{-1} CrO_3 at ca. 60 °C until the PAA was totally etched and a shiny Al surface was revealed. Subsequently, a second anodization process was performed at 2 °C for 10 min under the same conditions as the first anodization. The second anodization step generated a very thin and highly ordered layer of PAA (ca. 400 nm after 10 min of the second anodization step). The thickness of the HOPAA films was controlled by the anodization time. The pores of the as-prepared HOPAA on the Al foil were widened in 5 wt % H_3PO_4 for 50 min. This widening step, performed before coating a protective PMMA layer, enabled a free-standing HOPAA mask to be obtained with large pores, which helped to increase the efficiency of the subsequent Ar plasma etching step. A layer of 5 wt % PMMA in anisole was applied onto the free-standing HOPAA mask with widened pores, and was allowed to dry at 120 °C for ca. 30 min. The separation of the PMMA/HOPAA (PMMA layer on top of the HOPAA mask) film from the Al foil was achieved by selective wet chemical etching with a mixture of 0.1 M $CuSO_4$ and 10 wt % HCl (1:1 by volume). A thin transparent membrane of PMMA/HOPAA floated to the surface of the solution after the separation step. This membrane was rinsed several times with deionized water. The PMMA/HOPAA film was floated in a 5 wt % H_3PO_4 solution for ca. 30 min to remove the barrier layer at its base, as shown in Figure 1a.

Preparation of HOPAA–Substrates by Soft Imprinting: Three types of substrates were used in our work: p-type Si (100) with a native oxide layer and a ca. 50 nm gold coating (with ca. 5 nm Ti as an adhesion layer), glass slides, and flexible polyimide (Dupont-Kapton). An Al film with a thickness of 0.5–1 μm was deposited by electron-beam evaporation (Edwards Auto360).

The PMMA/HOPAA film after removal of the barrier layer was then attached to the Al–substrate system (Fig. 1b). The PMMA protection layer was removed by treatment with UV-ozone in a dry stripper (Samco UV-1) at 200 °C for ca. 30 min. Prior to the Ar plasma etching step, the surface was cleaned by O_2 plasma to remove any contaminants or PMMA residue (in case any residue is present after the UV-ozone step) remaining on the free-standing HOPAA-masked substrate. The Ar plasma etching process was carried out in an Oxford RIE II Etcher for 15 min with five intercooling cycles (Fig. 1c). After soft imprinting, the free-standing HOPAA mask was removed using adhesive tape, followed by ultrasonication in acetone for ca. 2 min before anodizing the pretextured-Al–substrate system (Fig. 1d).

Methods for anodizing Al on various substrates have been reported previously in the literature [9]. Anodization of the soft-imprinted substrates with ca. 1 μm Al at 2 °C required roughly 40 min for an observable color change (from shiny silver to dark purple), indicating the complete anodization of the substrate (Fig. 1e). The anodization condi-

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tions were the same as those for the second anodization step of the HOPAA mask. The anodized substrate was immersed in a 5 wt % H_3PO_4 solution at room temperature for 1 h to remove the barrier layer in order to deposit nanostructures via electrochemical deposition or ALD.

Preparation of Highly Ordered Nanostructured Arrays on Substrates: Au nanowire arrays were fabricated via electrochemical deposition at –0.75 V (vs. saturated calomel electrode (SCE)) in a commercial solution (Orotemp 24 , Technic) at 40 °C [6].

The ALD of TiO_2 nanotubes on glass substrates was performed in a home-built ALD setup at room temperature. The glass slides with the HOPAA template were placed inside a vacuum chamber with a base pressure of 1×10^{-3} torr (1 torr = 133 Pa). The sample inside the chamber was repeatedly exposed to two sequentially introduced vapor precursors, $TiCl_4$ (Merck, ≥ 99 %) and water. The exposure time for the both precursors was 2 s, and the interval between the two exposures was 30 s. The samples were immersed in 1 M KOH solution for at least 15 min to remove the HOPAA template, and were subsequently rinsed with isopropyl alcohol and deionized water.

Characterization Methods: Field emission scanning electron microscopy (FESEM, JEOL-6700F) was employed for the structural characterization of the HOPAA template, the Al surface, and the Au and TiO_2 nanostructures. PAA templates were coated with carbon to avoid charging effects. UV-vis absorption measurements of the TiO_2 nanotube arrays were carried out on the as-prepared samples using a Shimadzu UV-3101PC instrument.

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