3D Nanoarchitecture from Ultrathin Titania Film via Surface Sol–Gel Process and Photolithography

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(Received August 2, 2005; CL-051001)

We demonstrated the fabrication of 3D nano-architectures composed of ultrathin TiO_2-gel (titania) layers. Titania films with a thickness of a few tens nanometers are prepared on lithographically-fabricated line and hole patterns by the surface sol–gel process. Oxygen plasma treatment is employed to remove the template moiety, and gives positive replicas of the template structures.

A general fabrication method for three dimensional architectures in the nanometer scale may be regarded as one of the most ambitious targets in nanotechnology due to its far-reaching effects.

Stereolithography[1,2] and soft lithography[3] are the representative method as top-down fabrication approaches. However, their resolution largely remains in the micrometer regime. Although supramolecular assembly as the bottom-up approach gives unique higher-order structures, it is not an easy task to establish a general method to design supramolecular systems which are effective as parts of larger, more sophisticated devices. Template-directed fabrication may provide an alternative approach. Unfortunately, templates were limited in the past to readily available objects such as nanospheres,[4–10] porous materials,[11,12] virus,[4,13] and simple molecular assemblies.[14,15] More flexible design of the template morphology is strongly desired.

In this study, we employed photolithographic patterns as a template. Photolithography can provide highly varied patterns on solid substrates with nanometer precision. Our approach consists of three parts: first, fabrication of resist patterns by photolithography, second, surface covering of the patterns with ultrathin layers of metal oxides, and third, removal of the patterned template. The surface sol–gel process we employed for surface covering can provide ultrathin films of metal oxides in the stepwise manner with the precision of film thickness as small as approximately 1 nm. An additional feature is flexible shape adaptability of the titania layer with nanometer precision.

A solution of resist polymer (Tokyo Ohka Kogyo, TDUR-P015 PM) was spin-coated on a silicon wafer with thickness of 390 to 400 nm. The polymer is based on poly(vinyl phenol) structures, and contains unprotected phenol-hydroxyl groups (the detailed molecular structure is undocumented). After baking the polymer-coated silicon wafer at 90 °C for 90 s, the resist polymer was exposed to KrF excimer laser (Canon: FPA-3000EX3, wavelength: 248 nm) through a mask, and was then developed by aqueous tetramethyl ammonium hydroxide (1%) to obtain line and hole pattern on the silicon wafer. The titania precursor preferably reacts with hydroxyl and carboxyl groups that are generated by mild oxygen plasma treatment before the surface sol–gel reaction. Prior to surface coating, the photolithographic pattern was treated with oxygen plasma (South Bay Technology: PE-2000 Plasma Etcher, radio frequency: 13.56 MHz, Power: 10 W, Oxygen pressure: about 180 mTorr) for 10 min at room temperature, in order to produce an active surface. The surface sol–gel process was then conducted by dipping the substrate into 100 mM of titanium(IV) *n*-butoxide (Azmax) in heptane for 2 min, and rinsed by heptane and ion-exchanged water for 1 min each, dried by flushing nitrogen gas. This process was repeated several times. Finally, the oxygen plasma treatment (30 W for 2 h) was carried out to completely remove the inner template pattern. The surface and cross sectional morphologies were observed by scanning electron microscopy (SEM, Hitachi S-5200, acceleration voltage of 1 kV, without coating).

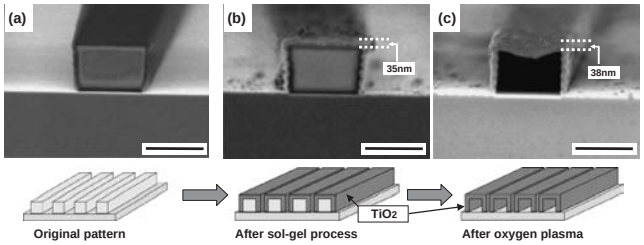

Figure 1. Scanning electron micrographs of cross section of the line pattern-templated titania and their schematic illustrations. (a) Original line pattern, (b) after 20 cycles of the surface sol–gel process, (c) after 2 h exposure to oxygen plasma. The scale bar in SEM images corresponds to 500 nm.

The width and height of the original line pattern are 620 and 390 nm, respectively, as estimated from Figure 1a, and the pattern size did not change much after mild oxidation (data not shown). After 20 cycles of sol–gel reaction, the thickness of the titania shell was estimated to be about 35 nm from the cross sectional SEM observation (Figure 1b). The surface morphology became rugged after the sol–gel reaction. This is probably caused from insufficient removal of the physically-adsorbed titania species. It is important to note that the template surface was fully covered with the titania layer and that the overall shape of the titania-coated template was essentially identical with that of the original template. Subsequently, the whole organic moiety was removed from the titania-coated line pattern by oxygen plasma treatment for 2 h. As can be seen from SEM observation (Figure 1c), the inner organic component was totally decomposed at this stage, leaving only rectangular titania tubes on the substrate. The thickness of the titania shell was measured to be ca. 38 nm. This figure is sufficiently close to the thickness of the titania wall (approximately 35 nm) before template removal. At the resolution of these SEM images, the thickness difference of the TiO_2 layer before and after plasma treatment is negligible, and the thickness of the TiO_2 layer was not changed much after plasma treatment. The width of the as-prepared tube was only slightly reduced upon template removal (less than 5%), and the titania shell kept the original shape of the titania-coated

pattern without any inner support. These titania walls of a few tens of nanometer have mechanical strength sufficient to maintain the three dimensional structures. The TiO_2 layer has been proved to be amorphous.[16] The oxygen plasma treatment is performed at room temperature which is much lower than the phase transition temperature of TiO_2 from amorphous to anatase state (higher than 350 °C).

The thickness of the titania wall will affect the stability of the resulting tubular structure, since thinner shells could cause wall collapse after removal of the inner organic moiety. In the case of the titania shell with about 10 nm thickness (5 cycles of the surface sol–gel process), the original shape was not preserved, and the roof and side walls were pulled closer to each other (data not shown).

The template removal process is particularly important in maintaining the original morphology. We examined dissolution and calcination of the template, in addition to the oxygen plasma treatment. The photoresist polymer which we employed here is readily dissolved in ethanol. After the specimen with 20 cycles of titania coating was immersed in ethanol overnight, the inner polymer was not removed, as confirmed by SEM. On the other hand, the calcination process produced shrunk tubes which possessed T-shaped cross section, instead of the rectangular tube structure, even with the same wall thickness of the titania layer (data not shown). The current results are consistent with the previous observation on latex particle,[4] and gradual template removal by oxygen plasma is essential for maintaining the original 3D-structure.

The effectiveness of the current approach was further examined by using a hole pattern. A layer of the photoresist polymer with a thickness of 400 nm was formed on a silicon wafer, and square holes with a side of the square of 900 nm are periodically aligned in this layer (Figure 2a). The hole pattern was not affected at all after mild oxidation (data not shown). After 20 cycles of the surface sol–gel process, the substrate surface became rough (Figure 2b), as we have also observed for the line pattern. The height of the titania/polymer double layer is estimated to be about 430 nm (Figure 2b), and, therefore, the thickness of the titania layer is calculated to be 30 nm. After the oxygen plasma treatment (30 W, 2 h), no polymer was left in the interior (black arrow in Figure 2c), leaving the titania shell alone. The pattern shape of the titania shell is identical with that of the original hole template, and the original hole was converted to a tubular pillar.

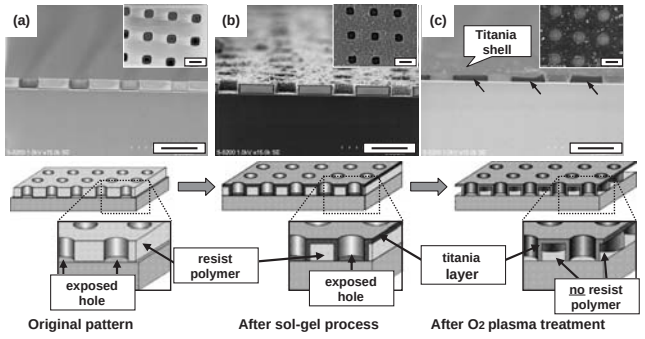

Figure 2. Scanning electron micrographs of cross sections of hole pattern-templated titania and its schematic illustrations corresponding to each SEM image. (a) Original hole template, (b) After 20 cycles of the surface sol–gel process, (c) After 2 h of exposure to oxygen plasma. The inset in each SEM image is the top view of the sample. The scale bar in SEM images and its inset corresponds to 1.5 μm.

We can conclude that the 3D nano architectures are fabricated from ultrathin titania overlayers, and that their shapes are controlled by film thickness and template morphology. In this report, tubes and tubular pillars were successfully fabricated, and these basic structures can be applied to microdevices including microreactors. In our previous reports, we employed structurally single template such as sphere (polystyrene particle[4]), tube (tubular virus[4]), strand (DNA),[17] and natural cellulosic substances.[18] Unfortunately, these templates cannot provide flexibility in morphology design. The current results demonstrated that our approach was applicable to more complex morphologies and patterns. Moreover, the template size can vary from the molecular size to the centimeter scale. Wide size adaptability and self-supporting property of metal oxide thin layers is noteworthy.

"Nano-copy" concept which we proposed recently is defined as "copying of nanometer-sized objects, such as molecules, supramolecular assemblies, nano particles and surface morphologies with nanometer precision."[19] The combination of the nano-copy technique with photolithographic patterning creates a remarkably rich methodology to fabricate 3D nano-architectures.

We are very grateful to Mr. T. Ogata, Mr. H. Hada and Mr. H. Komano in Tokyo Ohka Kogyo Inc. for providing silicon wafer with line and hole patterns on its surface.

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Published on the web (Advance View) September 17, 2005; DOI 10.1246/cl.2005.1414