Liquid-Phase Infiltration (LPI) Process for the Fabrication of Highly Nano-Ordered Materials

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A novel technique for the direct synthesis of two-dimensional metal oxide films with highly ordered periodic structure has been studied. The technique involves liquid-phase infiltration (LPI) in an aqueous solution. 2D TiO_2 structures with diameters ranging from 120 to 1065 nm are fabricated by filling the holes in a Si wafer using a solution of $(NH_4)_2TiF_6$ and H_3BO_3 at ambient temperature, and subsequently peeling off the template. Field emission scanning electron microscopy (FESEM) reveals that the resultant TiO_2 structures have highly nano-ordered architectures and represent negative and positive replicas of the template. The TiO_2 structures are transferred from the template with precision; no voids or seams are introduced during the transfer. The film thickness or filling rate of TiO_2 can be controlled by adjusting the reaction time. The LPI process is conducive to the preparation of advanced metal oxide films with highly ordered structures, and enables modification of optical properties of photonic crystals on a nanometer scale.

Introduction

Two- (2D) and three-dimensionally (3D) ordered nanomaterials have attracted much interest due to their potential applications, for example, in photonics, in electronics, and as nano-mechanics. Periodically nano-ordered structures should impart interesting photonic properties to films composed of photonic crystals, above and beyond the intrinsic luminescent and piezoelectric properties of the materials.[1,2] Extensive studies involving various chemical and physical techniques have recently led to the development of advanced materials having structures with periodicity on the nanometer scale.[3−14] Using these periodic structures as templates, well-ordered structures were prepared through templating techniques. Template methods using colloidal crystals such as silica or polystyrene provide a simple and effective route for fabricating 3D well-ordered materials.[15−22] Filling these templates with high-refractive-index materials such as TiO_2 and subsequently removing the template yields inverse opal structures.[14,16−18] 2D well-ordered materials are fabricated through infiltration of semiconductor or organic molds having evenly spaced holes.[23−25] However, in the fabrication of highly structured materials, infiltrating the templates sometimes results in incomplete filling because of the presence of voids and seam. Preparation of multicomponent oxides through conventional methods is also difficult. A simple technique is thus desirable for the preparation of highly ordered materials, enabling them to be transferred from the template with precision.

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We have recently proposed a liquid-phase deposition (LPD) method as a novel soft-solution process for preparing metal oxide thin films from aqueous solutions.[26,27] In this process, metal oxide thin films can be deposited onto various kinds of immersed substrates through the chemical equilibrium reaction between a metal fluoro-complex and metal oxide in aqueous solution. The formation of the metal oxides in solution is believed to proceed via the following ligand-exchange (hydrolysis) equilibrium reaction:

$$MF_x^{(x-2n)-} + nH_2O = MO_x + xF^- + 2nH^+ \quad (1)$$

This reaction can be shifted to the right by adding boric acid, which reacts with F^- ions to form more stable complex ions:[28]

$$H_3BO_3 + 4HF = BF_4^- + H_3O + 2H_2O \quad (2a)$$

$$Al + 6HF = H_3AlF_6 + {}^3/_2H_2 \quad (2b)$$

The addition of boric acid leads to the consumption of F^- ions and accelerates the ligand-exchange reaction. Thus, thin films are slowly deposited homogeneously on the substrates; the process requires no special equipment. Multicomponent and graded metal oxide films[29,30] can be formed by the addition of the target metal ions to the treatment solution, as LPD occurs via heterogeneous nucleation in an aqueous solution, which is a typical homogeneous mixture. Deposition of uniform metal oxide films at room temperature is simple, even on substrates with complex morphologies such as glass wool or porous materials.[31]

The present study reports the development of the liquid-phase infiltration (LPI) method for preparing metal oxide thin films with 2-dimensional periodicity by using a soft-solution process as an extended process of the LPD method. We describe a new approach for the preparation of TiO_2 with highly ordered periodic structure. The surface morphology and microstructure of the deposited films were identified by field emission scanning electron microscopy (FESEM) and cross-sectional transmission electron microscopy (TEM). FESEM observations confirmed that the TiO_2 films prepared by transferring from templates had a highly ordered structure.

Experimental Section

Materials. Ammonium hexafluorotitanate, $(NH_4)_2TiF_6$ (Morita Chemical Industries Co. Ltd.), and boric acid, H_3BO_3 (Nacalai Tesque Inc.), were separately dissolved in ion-exchanged water to give concentrations of 0.5 mol dm^{-3}. These two solutions were then mixed together and used as the treatment solution. TiO_2 with a highly ordered periodic structure was obtained by templating using a Si wafer with evenly spaced holes. The templates were prepared by electron-beam lithography, producing via holes with a diameter of 165−1065 nm and a depth of 1.5 μm.

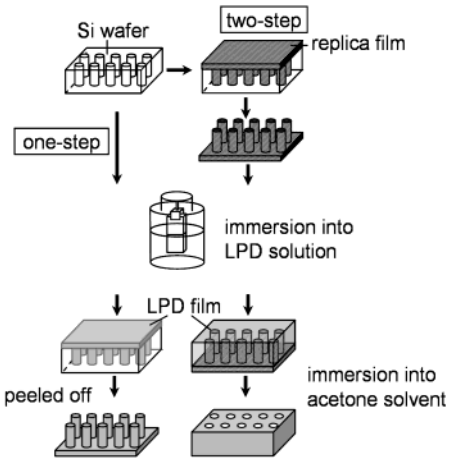

Figure 1. Schematic diagram of the reaction cell for preparation of graded thin films by the LPD method.

One-Step Templating Methods. This study employed one-step and two-step templating methods for the fabrication of TiO_2 with highly ordered periodic structure. The processing steps used are schematized in Figure 1. In the one-step templating method, the final products are negative replicas of the Si wafer templates. The substrates were immersed in a 5% aqueous solution of hydrofluoric acid (Stella Chemifa Co. Ltd) for 30 s prior to use. For the deposition of TiO_2 films with highly ordered architectures, the substrates were immersed vertically in the treatment solution, which was kept at 30 °C. The deposited films were prepared using 0.1 mol dm^{-3} $(NH_4)_2TiF_6$ and 0.2 mol dm^{-3} H_3BO_3, i.e., the concentration range that obtains transparent films.[27] The substrates were immersed immediately after mixing the treatment solution. After immersion for 2.5−50 h, the substrates with deposited TiO_2 films were removed from the solution, washed with distilled water, and dried at room temperature. A glass slide was attached to the top surface of the TiO_2 thin film using carbon adhesive tape (Scotch tape), and the TiO_2 films were peeled off the template. The resultant TiO_2 films on the glass substrate were negative replicas of the template.

Two-Step Templating Methods. Two-step templating methods based on the replica technique have also been applied to the fabrication of positive replicas of the Si wafer. The replica technique was effective in forming a negative replica to the finest detail.[32−39] Bioden acetate films (Okenshoji Co., Ltd) were used as templates in the alternate templating process. In this technique, a piece of acetate film was first softened in methyl acetate. The film was then pressed against the surface to be replicated (Si wafer). After 10 min, the acetate film was peeled off and used as substrate. The substrate was suspended in the treatment solution vertically. After several hours, the substrates were removed from the solution and washed with distilled water. The samples were dried at room temperature. A glass slide was then attached to the top surface of the TiO_2 film with an epoxy resin matrix. The acetate film was immersed in acetone for 2 min, revealing the TiO_2 film, a positive replica of the Si wafer.

Instruments. The surface morphology and the filling capability of deposited films were observed by FESEM (JEM-

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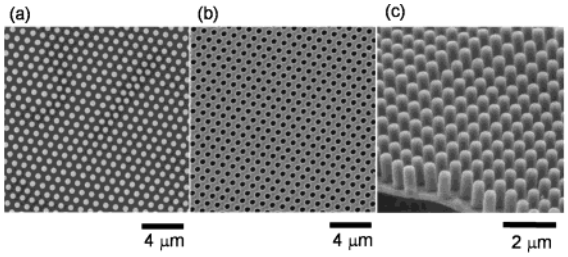

Figure 2. FESEM images of (a) TiO_2 arrays with a rod diameter of 440 nm, (b) the Si wafer used as a template, and (c) TiO_2 arrays with a different rod diameter (660 nm) (film deposited in 10 h).

6335F, JEOL). The samples were carbon-coated to avoid charging. The microstructures of the deposited films were observed with a cross-sectional TEM (JEOL JEM-2010). The TEM samples were prepared by conventional ion milling techniques.

Results and Discussion

Synthesis and Characterization of TiO_2 Arrays. Because the deposited films were not strongly adhered to the Si wafer substrate, the films could be readily peeled off using the Scotch tape without forming cracks. Typical FESEM images obtained after reaction of 10 h of the one-step LPI process are shown in Figure 2a and c. Arrays of 440-nm-diameter TiO_2 rods (length 1.5 μm) are shown in Figure 2a. This sample exhibits a hexagonal array of TiO_2 on long length scales, with the same periodicity as the holes on the Si wafer used as a template (Figure 2b). Although the highly ordered periodic structure was slightly deformed while being peeled off of the template, the TiO_2 structure clearly represents a negative replica of the template with a highly ordered architecture precisely transferred from the template. Figure 2c shows the FESEM image of a 2D-TiO_2 array with a different rod diameter. The diameter and length of rods in this case were 660 nm and 1.5 μm, respectively. It was clearly demonstrated that the aspect ratio and diameter of TiO_2 arrays could be controlled by changing the template diameter. The LPI process enabled the transcription of highly ordered architectures using templates of a variety of shapes. The process provides a direct fabrication route for metal oxide films with the highly ordered structures, making it possible for the optical properties of photonic crystals to be modified on the nanometer scale. High-resolution observation (Supporting Information, Figure S1) revealed that the lattice fringes due to the nanocrystalline TiO_2 phase (ca. 2 nm in size) appear.

Formation Process of the TiO_2 Arrays. To be able to fabricate a metal oxide thin film through transcription of a template having a highly ordered architecture with precision, it is important that the thin film cover the intricate surface of the substrate uniformly. Thus, FESEM was performed to investigate the growth of the deposited films. The plan view and the cross-sectional FESEM images of the original template and TiO_2 films deposited on an Si substrate with 320-nm holes are shown in Figure 3a. The surface morphology and internal microstructure of the TiO_2 films deposited into the holes at various reaction times is shown in Figure 3b−e. In the top-view SEM images, it is clear that the size of the hole decreased with increasing reaction time.

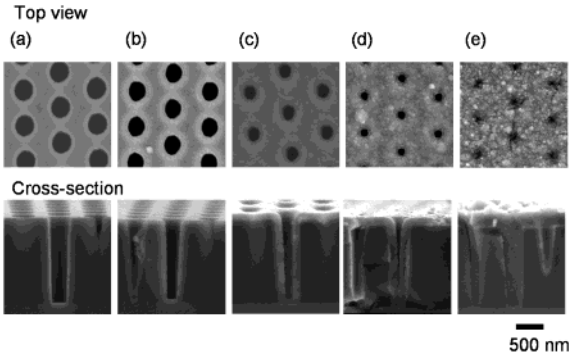

Figure 3. Plan view and cross-sectional FESEM images of (a) the original template and (b)−(e) films composed of 320-nm-diameter rods deposited over various reaction times: (b) 2.5, (c) 7.5, (d) 10, and (e) 20 h.

The TiO_2 grain size was ca. 20 nm in films obtained after 20 h.

The cross-sectional SEM images (Figure 3b) show that no film was deposited at a reaction time of 2.5 h. In the solution, $[TiF_6]^{2-}$ complex ions partially hydrolyze and release F^- ions. Thus, free F^- ions may exist in the solution at the initial stage. In a previous study, we have already reported that these free F^- ions react with H_3BO_3 in the initial stage of the deposition reaction (defined as "induction period") and then, F^- ions of the $[TiF_{6-n}(OH)_n]^{2-}$ complex ion react with H_3BO_3.[40] Therefore, no deposition was observed at the reaction time of 2.5 h. The films obtained after 7.5 and 10 h were deposited not only on the surface, but also on the sides and the bottom of the holes, as shown in Figure 4c and d. The TiO_2 film formed in a manner that precisely traced the contours of the periodic structures of the Si wafer. An important observation can be made in Figure 4c and d: the thickness of TiO_2 deposited on the sides and the bottom of the holes was about the same. As shown in Figure 3e, the holes were completely infiltrated with TiO_2 in the film obtained after 20 h. The roughly 200-nm-thick TiO_2 film that filled the hole was entirely free of the voids and seams which were observed by previous researchers using different infiltration methods such as the sol−gel method.[16−17,41−42] In the sol−gel method, the presence of voids or seams indicated that the precursor was insufficient for filling the template because the viscosity of gel is generally high. In our LPI process, however, the precursors are metal fluoro-complex solution (not sol) and viscosity of the treatment solution is very low. Therefore, the infiltration of the precursor was completed.

FESEM reveals that TiO_2 films were deposited on Si substrates with various via hole diameters (Supporting Information, Figure S2). It is easy to obtain uniform coverage of TiO_2 on the periodic structures of the template. FESEM results indicate that the deposition of TiO_2 films was unaffected by the diameter of the holes.

The time dependence of feature filling via TiO_2 deposited in different patterned holes is illustrated in Figure 4. The hole filling ratio increased with increasing

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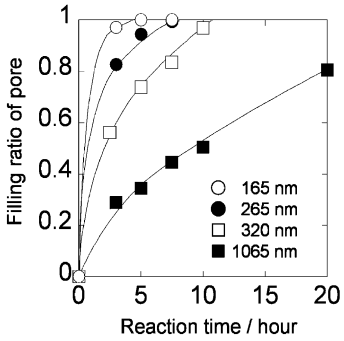

Figure 4. Relationship between TiO_2 filling ratio of via hole and reaction time: films deposited on templates with 165-, 265-, 320-, and 1065-nm-diameter via holes.

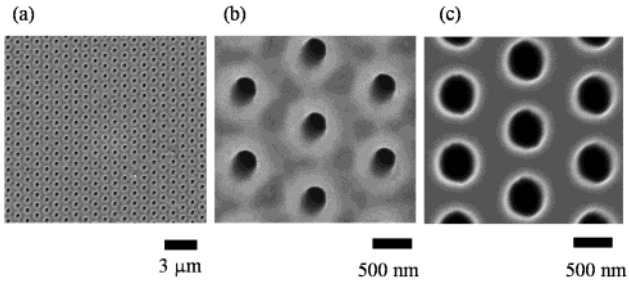

Figure 5. FESEM images of (a) and (b) TiO_2 arrays fabricated using the replica technique, and (c) the Si wafer used as a template with 440-nm-diameter via holes.

reaction time and decreasing hole diameter. The 165-nm-diameter holes were completely infiltrated after about 7.5 h. The 1065-nm-diameter holes, on the other hand, took 40 h to be completely filled. These results indicate that the final film thickness and filling ratio of TiO_2 could be controlled by simply varying the reaction time. Thus, the technique could be applied to the fabrication of TiO_2 nano-arrays.

Synthesis of TiO_2 Array with Nanoholes. TiO_2 films that were positive replicas of the Si wafer template were prepared using the replica technique. Figure 5a shows the FESEM image of a TiO_2 array with nanoholes deposited in 50 h. This 2D-TiO_2 sample exhibits a hexagonal array of holes on a long length scale. Figure 5b and c show an enlarged version of the FESEM image in Figure 5a and the template with 440-nm-diameter via holes used in fabricating that sample, respectively. The TiO_2 hole diameter was ca. 310 nm, which is about 30% smaller than the template diameter. This indicated that considerable shrinkage occurs during the second templating process. Thus, the shrinkage of the acetate films occurs during the drying process prior to use of the substrate. Therefore, the TiO_2 hole diameter got smaller than the original template diameter. However, the replica technique is simple and economical. If there is only one substrate with a periodic structure, metal oxide arrays can be mass-produced by the replica technique making use of the LPI process.

Conclusion

TiO_2 films with highly nano-ordered architectures were directly deposited on substrates at room temperature by the LPI process using a soft-solution approach. 2D arrays of TiO_2 rods with diameters between 120 and 1065 nm were fabricated by filling holes in Si wafers using a one-step templating method. The filling ratio of TiO_2 could be controlled over a wide range by varying the reaction time. Electron microscopy revealed that the 2D TiO_2 arrays fabricated contained no voids or seams and that the aspect ratio and diameter of the TiO_2 arrays could be controlled by changing the template diameter.

TiO_2 films that were positive replicas of the Si wafer template were also prepared by the replica technique using a two-step templating method that would allow mass production of metal oxide arrays. This method represents a simple route for the production of highly nano-ordered metal oxide films with potentially interesting and useful photonic, catalytic, and magnetic properties.

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Supporting Information Available: HRTEM image of TiO_2 arrays and cross-sectional FESEM images of TiO_2 films (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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