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Fabrication of two-dimensional arrays of graded oxide thin films by the LPI Method

Sachihiko Iizuka[1], Minoru Mizuhata[2], Akihiko Kajinami[2] and Shigehito Deki[1, 2]

[1] Department of Molecular Science, The Graduate School of Science and Technology, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan
[2] Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan

Nanoscale materials are of great interest scientifically and technologically because of their potential to exhibit novel properties which cannot be achieved by bulk materials. In particular, two- (2D) and three-dimensionally (3D) ordered nanomaterials have attracted much interest owing to their potential applications in photonic crystals, data storage, and biosensors. 2D well-ordered materials (e.g., nanohole arrays or nanopillar arrays) are fabricated through infiltration of semiconductor or organic molds with evenly spaced holes. However, in the fabrication of nanohole and nanopillar arrays, preparation of graded oxide or multicomponent oxides through conventional methods is difficult. Moreover, infiltrating the templates sometimes results in incomplete filling because of the presence of voids and seams. A simple technique is thus desirable for the preparation of both nanohole and nanopillar arrays, enabling them to be transferred from the template with precision.

We have recently developed and proposed a liquid phase deposition (LPD) method as a novel aqueous solution-based process to prepare metal oxide thin films using ligand-exchange hydrolysis of metal-fluoro complexes and the F^- consumption reaction with boric acid, aluminum metal and so on.[1,2] Since this method relies on the chemical equilibrium between the metal-fluoro complex and metal oxide in an aqueous solution, which is a typical homogeneously mixed system, homogeneous and/or composite thin films can be readily deposited on various kinds of substrates with large surface areas and complex morphologies. Here, we propose the development of the liquid-phase infiltration (LPI) [3] method for preparing graded oxide thin films with 2-dimensional periodicity by using a soft solution process as an extended process of the LPD method.

For the deposition of gradient-type films of Fe /Ti oxide, the substrates were first immersed into the solution of $FeOOH\text{-}NH_4F{\cdot}HF$ containing H_3BO_3. After immersion for several hours, $(NH_4)_2TiF_6$ solution containing H_3BO_3 was added into the treatment solution, respectively. The mixed solution was removed simultaneously to keep maintain the volume of the treatment solution. After several hours of adding solution B, the substrates with deposited graded oxide films were removed from the solution, washed with distilled water and dried at room temperature. To back up the deposited film with Ni film, a Ni film was obtained by immersing the activated substrate into an electroless plating bath. A glass slide was attached to the top surface of the Ni film using carbon adhesive tape, and the graded films were peeled off the template.

The oxide nanopillars obtained by the LPI process are shown in Fig. 1. Typical FE-SEM images of the top surface of periodic nanopillars fabricated by using a Si wafer as template are shown in Fig. 1(a). Figures 1(b) shows the template with 270-nm-diameter via-holes used in fabricating the sample in Fig. 1(a). This sample exhibits a hexagonal array of oxide film on long length scales. The array structure had the same periodicity as the holes on the template (Fig. 1(b)). The structure of the oxide films clearly represented a negative replica of the Si template; the films precisely traced the contours of the periodic structure of the Si wafer. This indicates that the present LPI process led to the formation of a negative replica of the Si wafer with a geometrical structure. SEM images (tilted 45º) of the graded film obtained by the LPI process are shown in Figs. 1(c) and 1(d). Nanopillar aspect ratios as high as 5:1 were achieved. The periodic nanopillar array extended over the entire surface of the sample. No macroscopic defects were observed in the Si template prepared, which indicates that the films could be readily peeled off using Scotch tape without forming cracks because the deposited films did not adhere to the Si wafer substrate strongly. TEM and X-ray microanalysis of the films revealed that the present technique enabled wide-range control of the composition and graded profile of the deposited films in the depth direction. Along with the change in composition, the microstructure of the films changes from microcrystalline β-FeOOH at the base to nanocrystalline anatase-TiO_2. Our results indicate that it is possible to control the size, shape, and height of nanopillar arrays using various templates. The present method represents a simple route for the production of highly nano-ordered metal oxide films with potentially interesting applications.

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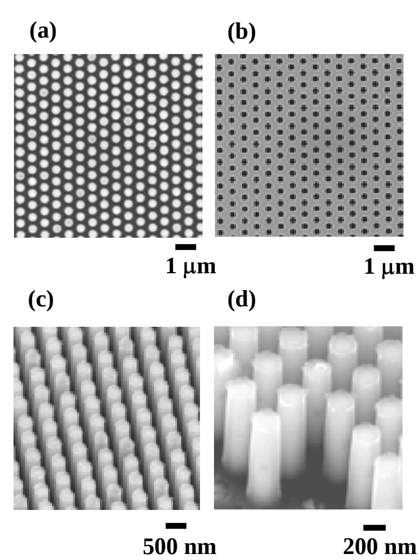

Figure 1 FE-SEM top-view images of (a) graded oxide nanopillar arrays, (b) the template Si wafer with a rod diameter of 270 nm, (c)-(d) SEM images (tilted 45º) of graded oxide arrays with a rod diameter of 270 nm.