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Fabrication of two-dimensional close-packed shell structure in ceramic thin films

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Abstract

TiO₂ thin films with a periodical two-dimensional close-packed hemispherical structure were prepared on Si substrates using pulsed laser deposition and close-packed monolayer polystyrene colloidal crystals as a template. Compared with conventional methods, which use a top-down approach, this route supports low-cost production of a periodic structure. Additionally, it is applicable to various ceramics for use in applications related to photonic crystals, surface self-cleaning materials, data storage media, bioassays, and so on.

Keywords: two-dimensional close-packed shell structure, ceramic thin film, monolayer colloidal crystal (MCC), pulsed laser deposition (PLD)

1. Introduction

Recently, highly ordered two-dimensional (2D) nanostructures have attracted much attention because of their wide variety of potential applications related to catalysis [1], gas sensors [2], biosensors [3], photonic crystals [4], optoelectronic devices [5], microlens array [6] and surface self-cleaning materials [7].

Although lithography has been widely used to fabricate 2D nanostructures, it requires expensive equipment. To overcome cost problems, other techniques such as nanoimprinting and soft lithography have been proposed [8, 9]. Another method of fabricating 2D nanostructures is called ‘nanosphere lithography’ (NSL); it uses monolayer colloidal crystals (MCCs) as the lithography mask. Monodispersed polystyrene and polymethyl methacrylate (PMMA) have been employed to fabricate MCCs [10–12]. The principle of NSL is as follows: first, polystyrene (PS) or PMMA MCCs are fabricated on the substrate by self-assembly or spin coating; then, a film is coated on the MCCs by solution casting [13, 14], spray pyrolysis [15], electrochemical deposition, or physical vapour deposition, which includes sputtering [16–19] and subsequent pulsed laser deposition (PLD) [7]. Finally, the MCCs are removed to form a 2D nanostructure. Most 2D nanostructures fabricated using NSL are ordered arrays of nanopyramids or pores, as shown in figures 1(a) and (b). During solution casting and spray pyrolysis, the solution infiltrates the interstitial voids. Therefore, it is feasible to realize pore arrays or nanopyramids at the interstitial voids among the MCCs. For electrochemical deposition and PLD [7, 16–19], the surfaces of PS and interstitial voids are covered with the target material. After deposition, the film is soaked in a solvent to remove the material deposited on the surface of PS and to create a 2D pore structure. Few reports describe the fabrication of arrayed 2D nanostructures formed using the surface of PS. Li et al prepared hierarchically ordered TiO₂ hemispherical particle arrays with hexagonal nonclose-packed (hncp) top layers [7]. They deposited TiO₂...
using PLD on the MCCs of PS (350 nm diameter) and subsequent annealing to burn out PS. Then, they fabricated ordered TiO\textsubscript{2} particle arrays with a top hncp arrangement.

The purpose of this work is fabrication of films with a 2D close-packed shell structure resembling that shown in figure 1(c). This film consists of a hemispherical shell that inherits the morphology of PS MCCs. This structure may find applications in perpendicular magnetic recording devices, bioassay media, microlens array, and micro-electro-mechanical systems. The effect of positional relation between the substrate and PLD target on the morphology of 2D close-packed shell structure film was also investigated in this work. TiO\textsubscript{2} was used as the model material for the 2D close-packed shell structure.

2. Experimental section

Si(100) substrates (1 × 1 cm\textsuperscript{2} size) covered with a natural oxide were cleaned ultrasonically in acetone for 5 min and rinsed in deionized water for 1 min. They were then soaked in a piranha solution (H\textsubscript{2}SO\textsubscript{4} : H\textsubscript{2}O\textsubscript{2} = 3 : 1) at 100°C for 1 h and rinsed with deionized water. Then, the substrates were sonicated for 1 h in an RCA solution (H\textsubscript{2}O : NH\textsubscript{4}OH : H\textsubscript{2}O\textsubscript{2} = 5 : 1 : 1), followed by thorough flushing with deionized water [20]. A PS colloidal solution was prepared by dispersing PS particles of 3.5 \(\mu\)m diameter (Sekisui Plastics Co. Ltd) in an 8 : 2 mixture of water and toluene. The MCCs were formed on the treated Si substrate by spin coating (1300 rpm, 30 s) of the prepared PS colloidal solution. The Si substrate with PS MCC was transferred into the PLD chamber and installed in a horizontal or vertical position with respect to the target as shown in figure 2. Thin film deposition was conducted at room temperature in a 10 Mtorr oxygen atmosphere by focusing a KrF excimer laser (248 nm wavelength, 7 Hz repetition rate, fluence \(\sim 2\) J cm\textsuperscript{-2}) on the surface of a TiO\textsubscript{2} ceramic target. The target was prepared by pressing reagent-grade TiO\textsubscript{2} powder in the rutile form (Kanto Chemical Co, Inc.) into 20 mm diameter pellets and sintering at 1200°C for 6 h in air; it contained rutile phase only. After the deposition, the sample was annealed at 800°C for 2 h in air. The crystal structure of the film was examined using an x-ray diffractometer (D8 Advance, Bruker AXS). Morphological observation and elemental analysis were conducted using a scanning electron microscope (SEM, JSM-5010LV, JEOL) equipped with an energy-dispersive spectrometer (EDS), a field emission scanning electron microscope (FE-SEM,
interstitial voids between spheroids are also covered with TiO\(_2\). However, owing to the low step coverage of PLD, the thickness of TiO\(_2\) at the interstitial voids is smaller than that on the top of the spheroid. These results indicate that annealing removed PS-derived carbon while maintaining the 2D close-packed morphology.

To clarify the morphological changes, cross-sectional SEM images were recorded and plotted in figures 4(a) and (b). The cross section of the as-deposited sample has a spherical morphology derived from the PS template. The lower half of the sphere disappears during the annealing and, eventually, the periodic arrangement of the upper halves of the spheres is observed. SEM images also suggest that the upper half of the sphere consists of a shell structure with occasional microcracks.

Figure 5 shows x-ray diffraction (XRD) patterns revealing that the film deposited on PS MCC is amorphous, but it becomes crystalline after annealing at 800 °C. Two peaks are observed at \(2\theta = 25.43°\) and \(37.93°\) after annealing. Although the XRD peak positions are similar for anatase and brookite, we believe that the resultant phase is anatase because of the absence of a doublet peak at approximately \(2\theta = 25°\) and of a singlet at \(2\theta = 31°\) characteristic of brookite.
3.2. TiO$_2$ film with 2D periodic hemisphere shell structure prepared by setting the substrate in a vertical position

To clarify the effect of substrate positioning in the PLD setup on the morphology of the resultant film, we have also deposited a TiO$_2$ film on the PS MCCs placing the substrate vertically, as depicted in figure 2(b). Other experimental conditions were unchanged. Figures 6(a) and (d), respectively, show SEM images of the surface of the as-deposited and annealed samples. Figures 6(b) and (e) show EDS maps of the C K$_\alpha$ signal, and figures 6(c) and (f) present the Ti K$_\alpha$ maps of the as-deposited and annealed samples, respectively. Figure 6(a) indicates that the as-prepared sample has a 2D periodic, but not a close-packed structure. A distinct gap is observed both in the SEM images and the Ti K$_\alpha$ map. Figures 6(d) and (e) reveal that the particles become elongated and the C K$_\alpha$ signal vanishes upon annealing owing to the burnout of PS.

To clarify the details of the morphological change, cross-sectional SEM images were obtained and shown in figures 7(a) and (b). Occasional microcracks are seen in figure 7(b).
Figure 8. FE-SEM images of semispheres cut with an FIB, prepared using (a) horizontal and (b) vertical positions of the substrate in the PLD chamber.

To summarize this section, a 2D periodic arrangement of isolated ellipsoidal particles can be produced by placing a substrate in the vertical position in the PLD chamber.

3.3. Investigation of the inside of the spheres

To examine the internal structure of the hemispheres, a cross-sectional image was observed after the semispheres were cut with an FIB. Figures 8(a) and (b) show cross-sectional FE-SEM images of the shells prepared by placing the substrate horizontally and vertically in the PLD chamber. These figures reveal that the inside of the sphere is hollow, and that the shell thickness is about 100 nm. Whereas the shell prepared using the horizontal positioning is smooth, the left part of the shell is rough in the case of vertical positioning. It is noteworthy that the gas flow direction during the deposition is from right to left and this might have affected the shell morphology.

3.4. Formation mechanism of the hemispherical shell structure

On the basis of the results described above, we propose the following mechanism of hemispherical shell formation. For the horizontal position of the substrate, the gas flow direction and the structure of the substrate with PS MCCs are presented schematically in figure 9(a). In this case, the PS MCC surface is covered uniformly with amorphous TiO$_2$ on the Si substrate. Therefore, a continuous film that follows the PS MCC surface contour is obtained as outlined in figure 10(a). The PS MCCs are burned out by annealing in air as shown in figure 10(b) to form the 2D close-packed hemispherical shell structure (figure 10(c)). For a vertical position of the substrate, the details of the substrate with PS MCCs are presented schematically in figure 9(b). In this case, amorphous TiO$_2$ is deposited preferentially at the lower half of the sphere, as shown in figure 10(d). Annealing in air burns PS as reflected in figure 10(e), and the formed hemispherical shells are isolated (figure 10(f)) because their upper parts were only partially covered with TiO$_2$.

4. Conclusions

TiO$_2$ thin films with a two-dimensional close-packed shell structure were prepared by combining a close-packed PS monolayer template and PLD. The films could be crystallized by annealing. The film morphology depends on the substrate positioning in the PLD chamber, and a 2D periodic array of isolated ellipsoidal hemispheres is obtained for the vertical orientation of the substrate. These results should be useful for fabricating new devices requiring 2D periodicity.
Figure 10. A diagram of the proposed film deposition mechanism.

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