Direct Sol–Gel Fabrication of Patterned Zirconia Thin Films Using Self-assembly in Phase-separated Mixed Langmuir–Blodgett Films

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We demonstrate a new method through sol–gel processes for the preparation of patterned zirconia thin films by using directed self-assembly into patterns reflecting the phase-separated structures of mixed Langmuir–Blodgett films. Atomic force microscopy and Kelvin probe force microscopy images confirmed the formation of patterned zirconia thin films.

A sol–gel method has been used to prepare ceramics and is suitable for controlling the shapes of ceramics to obtain particles,[1] thin films,[2] and fibers.[3] Metal oxide thin films have attracted much attention as promising materials for electrodes[4] and catalysts.[5,6] Thin films obtained through conventional sol–gel processes are uniformly formed on the substrates, which shows that one-step patterning is very hard.

The Langmuir–Blodgett (LB) technique is one of the bottom-up technologies and has been used to fabricate organic ultrathin films with well-defined structures.[7] In particular, phase separation often occurs in mixed LB films and leads to the two-dimensional confinement of one component on a micrometer or nanometer length scale, which will be useful for high-density recording and sensing with high sensitivity.[8]

We have recently succeeded in the preparation of templates, the patterns of which reflect the phase-separated structures of mixed LB films.[9] In addition, organic and inorganic material including gold colloidal particles and copper have been patterned on the templates.[10] When this technique is applied for sol–gel processes, various inorganic thin films will be patterned for use in memories, switches, electrodes, and sensors through one-step sol–gel systems.

Here, we report a new method for directed self-assembly of inorganic films, reflecting the phase-separated structures of mixed LB films, through a sol–gel route using metal ions as precursors. We have employed zirconia (zirconium dioxide) because of their possible applications to catalysts.[6]

Amphiphilic molecules used in this study are eicosanoic acid (H19A; Acros Organics), (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (F8H2SiCl; Gelest) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA-Si; Gelest). The numbers following “H” and “F” denote the chain length of hydrocarbon and perfluorocarbon, respectively. Hexane was purchased from Dojindo. Zirconium sulfate tetrahydrate (Kanto Chem. Co., Inc.) was used as a zirconia precursor.

A Lauda film balance was used for preparation of mixed LB films. A spreading solution at a concentration of 1.0×10^{-3} M was spread on an aqueous subphase. The mixing ratio of H19A to F8H2SiCl was 1 to 9. The subphase temperature was 293 K. Molecules were compressed at a speed of 1.2×10^{-2} nm^2/molecule·min after 30 min of evaporation time. The Langmuir film was transferred at 10 mN/m using the vertical dipping method at a withdrawal speed of 5 mm/min onto oxidized Si wafers. Templates were prepared according to the method described in a previous paper.[9] The surface of the templates has silanol groups confined in domains that are surrounded by the SAM of F8H2SiCl. The surface silanol groups were reacted with EDA–Si to functionalize the templates with amino groups. Zirconia/SAM composite films were prepared by immersing the functionalized templates in 360 mM aqueous zirconium sulfate ($Zr(SO_4)_2$) solution at room temperature for 6 h. The samples were calcined at 1073 K for 6 h to obtain zirconia thin films. Structural properties of the obtained films were investigated by atomic force microscopy (AFM) and Kelvin probe force microscopy (KFM) observations.

Figure 1 shows AFM and KFM images of a functionalized template and a zirconia/SAM composite film. The AFM and KFM images of the functionalized template show a structure similar to that of an as-deposited LB film with circular domains of the size of 1–5 µm. The domain region is lower than the rest. This is consistent with the film structure in which the domains consist of the SAM of EDA–Si and the other part is comprised of the SAM of F8H2SiCl. The surface potential of the domains is larger than that of the SAM of F8H2SiCl because the surface

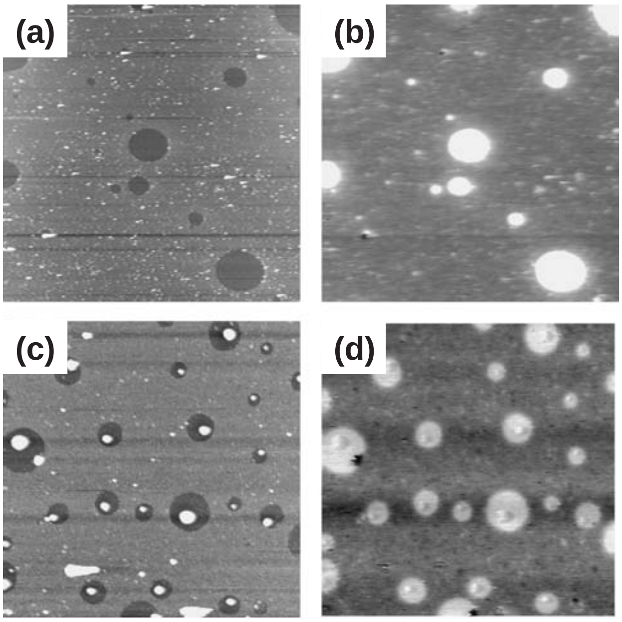

Figure 1. AFM ((a) and (c)) and KFM ((b) and (d)) images ($20 \times 20\,\mu m^2$) of functionalized templates before ((a) and (b)) and after ((c) and (d)) immersion in aqueous $Zr(SO_4)_2$ solution at room temperature for 6 h.

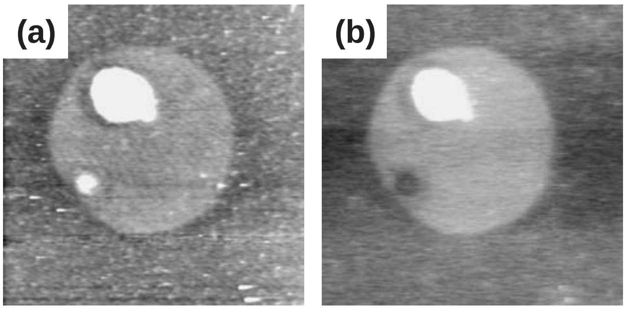

Figure 2. (a) AFM and (b) KFM images ($5 \times 5\,\mu m^2$) of a functionalized template immersed into a zirconia precursor, following by calcination at 1073 K for 6 h.

of the SAM of F8H2SiCl is covered with fluorine atoms with large electronegativity. After immersion in aqueous $Zr(SO_4)_2$ solution, the AFM image (Figure 1c) shows that the domains have locally higher points, indicating the confinement of material in the domains. The KFM image of this film suggests that these circular domains are covered with a single component because the observed domains have almost the same surface potential. These results suggest that a zirconia precursor is confined in the circular domains.

Figures 2a and 2b shows AFM and KFM images, respectively, of the film calcined at 1073 K for 6 h. The circular domains are higher than the rest in contrast to the structure of the zirconia/SAM composite film shown in Figure 1c. In addition, the chemical species in the domains and the other part are different because the KFM image shows that they have different surface potentials. A functionalized template calcined under the same condition showed smooth surface due to the burning off of the SAMs of EDA–Si and F8H2SiCl. These results indicate that the products confined in the domains remain even after the calcination, while the SAMs of EDA–Si and F8H2SiCl are removed from the substrate. Scanning electron microscopy (SEM) observation and the elemental analysis using energy dispersive X-ray (EDX) spectroscopy were carried out to determine the chemical species of the products in the domains. The SEM image showed a patterned surface similar to that of the phase-separated structure of an as-deposited LB film with circular domains shown in Figure 2, confirming the existence of products in the circular domains. A peak assigned to Zr[11] was clearly observed in the EDX spectra of the domain region. In contrast, the EDX spectra of the other part showed no peak assignable to Zr. These results confirmed that the patterned zirconia thin film was prepared on the templates fabricated from phase-separated LB films.

Finally, we succeeded in confining zirconia thin films on templates having patterns on a nanometer length scale. We fabricated mixed LB films of stearic acid (H17A), 10, 10, 11, 11, 12, 12, 13, 13, 14, 14, 15, 15, 16, 16, 17, 17, 17-heptadecafluoroheptadecanoic acid (F8H8A) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane (F8H2SiOEt) at mixing ratios of 2, 2 to 5. Mixed LB films of this type have phase-separated structures of nanowire patterns with nanowires consisting of H17A and F8H8A surrounded by F8H2SiOEt.[10] Templates were fabricated and functionalized as described above. Zirconia thin films were fabricated by immersing the functionalized templates in 360 mM aqueous zirconium sulfate solution at room temperature for 24 h, followed by calcination at 1073 K for 6 h. Figure 3 shows AFM and KFM images of a calcined zirconia thin film. Both images confirm the formation of a zirconia thin film confined in nanowires. These results show that the present method is available for patterning zirconia thin films.

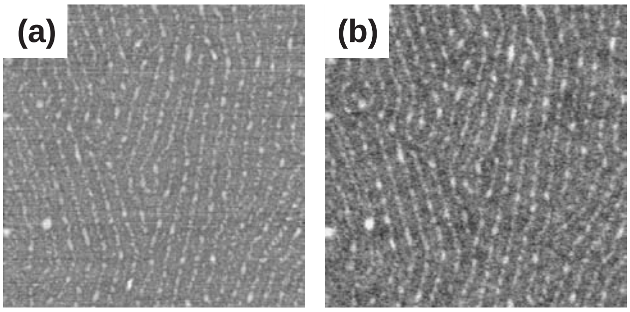

Figure 3. (a) AFM and (b) KFM images ($5 \times 5\,\mu m^2$) of a zirconia thin film. The template was fabricated from a mixed LB film of H17A, F8H8A, and F8H2SiOEt at mixing ratios of 2, 2 to 5.

This study demonstrates the patterning of zirconia thin films using templates fabricated by self-assembly in phase-separated mixed LB films. To the best of our knowledge, this is the first report on the directed self-assembly of inorganic thin films reflecting the phase-separated structures of mixed LB films through sol–gel processes. The structures of the zirconia films can be designed by controlling the original phase-separated structures of the mixed LB films. The present method will be important in the fabrication of patterned materials on the micrometer/nanometer length scale for applications to memories, switches, and sensors, because various metal ions can be used as precursors.

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