

Direct Sol-Gel Synthesis of Patterned Zirconia Thin Films Using Self-Assembly in Phase-Separated Mixed Langmuir-Blodgett Films

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We demonstrated a new method for directed self-assembly of zirconia thin films, reflecting the phase-separated structures of mixed Langmuir-Blodgett (LB) films, through a sol-gel route. Templates were fabricated by heat treatment of mixed LB films of fatty acid and silane-coupling agent, followed by selective removal of the fatty acid. Templates functionalized with amino groups were immersed into zirconia precursor solution. Atomic force microscopy and Kelvin probe force microscopy images showed that the films prepared under optimal conditions had products with the same surface potential within the ex-domain region. Energy dispersive X-ray (EDX) spectra of the products in the ex-domain region clearly showed a peak assigned to Zr. These results confirmed that the patterned zirconia films were prepared on the templates fabricated from phase-separated LB films.

Key words: Langmuir-Blodgett Films, Zirconia, Sol-Gel method, Self-Assembly

1. Introduction

The sol-gel method has gathered considerable attention because it is one of the most promising processes for preparing ceramics at low temperatures and controlling their shapes to obtain particles [1], films [2] and fibers [3]. Syntheses of ceramics thin films using sol-gel processes have been investigated in material science for catalysts [4] and electrodes [5], taking advantage of the availability of various precursors.

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. In particular, phase separation at a micrometer or nanometer length scale often occurs in mixed LB films, forming various structures such as circles, wires and spirals [6].

We have succeeded in immobilizing gold colloidal particles on functionalized templates followed by electroless deposition of copper [6]. It is important that the patterns reflect the phase-separated structures of mixed LB films. Recently this technique was applied to sol-gel processes for direct fabrication of patterned zirconia (zirconium dioxide) thin films through one-step sol-gel systems [7]. This novel technique is useful in the preparation of patterned inorganic thin films with the

structures controllable by adjusting the phase-separated structures of mixed LB films.

This study aims to prepare patterned zirconia thin films using templates fabricated from phase-separated mixed LB films and investigate the effect of reaction conditions on the structures of the formed zirconia films.

2. Experimental

Eicosanoic acid (H19A; Acros Organics), (Heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl)trichlorosilane (F8H2-SiCl; Gelest) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA-Si; Gelest) were used as film-forming material. Hexane and methanol were purchased from Dojindo. Zirconium sulfate tetrahydrate (Kanto Chem. Co., Inc.) was used as a zirconia precursor.

A Lauda film balance was used for the preparation of mixed LB films. A spreading solution at a total concentration of 1.0×10^{-3} M was spread on an aqueous subphase. The molar 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} nm²/molecule·min after 30 min for evaporation. The Langmuir films were transferred at 10 mN/m using the vertical dipping method at a withdrawal speed of 5 mm/min onto

oxidized Si wafers. Mixed LB films were heated at 383 K for 30 min and ultrasonicated in ethanol for 5 min to fabricate templates. The templates were dipped in 10 mM EDA-Si methanol solution at room temperature, followed by heat treatment at 383 K for 30 min to give functionalized templates (FT).

Zirconia/FT composite films were prepared by immersing the functionalized templates in zirconium sulfate ($Zr(SO_4)_2$) aqueous solution. Then 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), Kelvin probe force microscopy (KFM) and scanning electron microscopy (SEM) observations and energy dispersive X-ray (EDX) spectroscopic measurements.

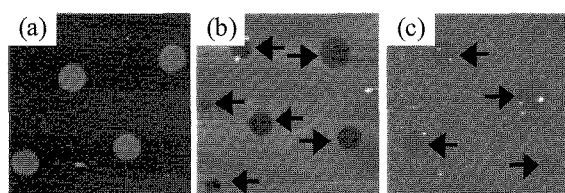


Fig. 1 AFM images ($20 \times 20 \mu m^2$) of (a) a mixed LB film, (b) a template and (c) a functionalized template. The arrows indicate the ex-domain regions.

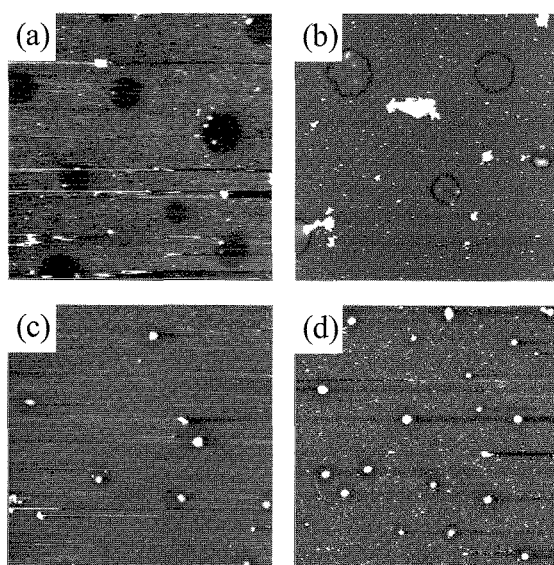


Fig. 2 AFM images ($20 \times 20 \mu m^2$) of zirconia/FT composite films fabricated by the reactions at room temperature for 24 h in (a) 36 mM, (b) 100 mM, (c) 360 mM, and (d) 720 mM $Zr(SO_4)_2$ aqueous solution.

3. Results and Discussion

3.1 Structure of functionalized template

Figure 1(a) shows an AFM image of a phase-separated mixed LB film. The AFM image shows a structure with circular domains of the size of 1-5 μm . Heat treatment of the film gives rise to the formation of covalent bond between F8H2SiCl and the substrate [8]. Ultrasonication selectively removes H19A. The AFM image in Fig. 1(b) shows that the ex-domain region is lower than the surrounding region. The surface of the template has silanol groups confined in the ex-domain region that are surrounded by the self-assembled monolayer (SAM) of F8H2SiCl. A SAM of EDA-Si forms in the ex-domain region of the functionalized template (Fig. 1(c)) [9].

3.2 Effect of precursor solution concentration on the zirconia film formation

Functionalized templates were reacted at room temperature with a reaction time of 24 h to investigate the effect of the concentration of precursor solution on the film formation. Figure 2 shows AFM images of zirconia/FT composite films prepared by immersing functionalized templates into zirconia precursor solutions at various concentrations. Immersion of a functionalized template into 36 mM zirconium sulfate aqueous solution yields no products on the template (Fig. 2(a)). Locally higher structures are formed in the ex-domain region at concentrations of 100 and 360 mM, indicating the confinement of products in the ex-domain region. When a functionalized template is immersed in 720 mM zirconia precursor solution, products form on both the ex-domain region and the surrounding region. This indicates that zirconia forms in the aqueous solution, resulting in the adsorption of zirconia randomly onto the substrate. In the cases of the precursor concentrations of 100 and 360 mM, zirconia formation in the solution and/or random adsorption should be retarded or suppressed. These results show that selective adsorption of zirconia precursor on the ex-domain region requires the precursor concentration of 100 to 360 mM. In the following, the precursor concentration is fixed at 360 mM.

3.3 Effect of reaction temperature on the zirconia film formation

Figure 3 shows the AFM images of zirconia/FT composite films prepared by immersing functionalized templates in precursor solutions at a concentration of 360 mM for 24 h at various reaction temperatures. Product formation is evident in the ex-domain region of all the films. However, the zirconia/FT composite film prepared at 317 K shows structures not only in the ex-domain region but also in the surrounding region. Functionalized templates were water repellent because a major portion of the surface was covered with fluorocarbon chains of silane-coupling agent. Although composite films prepared under room temperature remained water repellent, the films synthesized at 317 K were not. These phenomena suggest that the SAM of silane-coupling agent has been destroyed by the action of acid at 317 K.

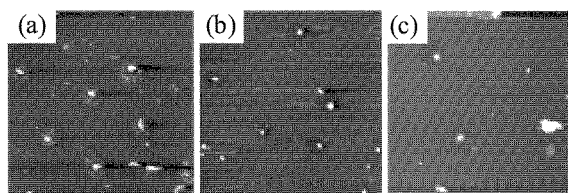


Fig. 3 AFM images ($20 \times 20 \mu\text{m}^2$) of zirconia/FT composite films fabricated by the reactions in 360 mM $\text{Zr}(\text{SO}_4)_2$ aqueous solution for 24 h at (a) 273 K, (b) room temperature and (c) 317 K.

3.4 Effect of reaction time on the zirconia film formation

The reaction time was changed from 1 to 24 h. The reaction temperature and the concentration of precursor solution were fixed at room temperature and 360 mM, respectively. AFM images of the zirconia/FT composite films prepared by the reaction for varying periods showed product formation in the ex-domain region in a manner similar to that shown in Fig. 3(b). Figure 4 shows the relationship between the reaction time and the average height of locally higher structures formed in the ex-domain regions. The average height of the products is almost constant. These results suggest that the reaction time affects only slightly the volume of products formed in the ex-domain region. The reaction time was fixed at 6 h in the following.

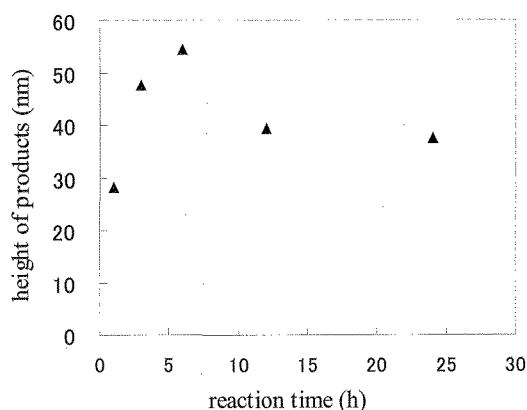


Fig. 4 Relationship between the reaction time and the average height of locally higher region in the ex-domain region.

3.5 Characterization of patterned zirconia thin films

Above results show optimal conditions for the patterned zirconia thin film formation: the concentration of precursor solution, reaction temperature and reaction time are 360 mM, room temperature and 6 h, respectively. Figure 5 shows AFM and KFM images of a patterned zirconia/FT composite film prepared under the optimal conditions. The AFM image shows the presence of higher structures in the ex-domain region. The KFM image reveals that the surface potential of the ex-domain region is almost constant. These results suggest that the ex-domain region is covered with a single component.

Figure 6 shows AFM and KFM images of a zirconia/FT film after calcination at 1073 K for 6 h. The ex-domain region is higher than the surrounding region in comparison with the zirconia/FT film before calcination shown in Fig. 5(a). The KFM image shows that the ex-domain region and the surrounding region have different surface potentials. The SAM of

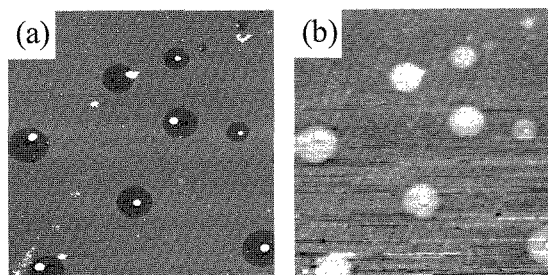


Fig. 5 (a) AFM and (b) KFM images ($20 \times 20 \mu\text{m}^2$) of a zirconia/FT composite film prepared under the optimal conditions.

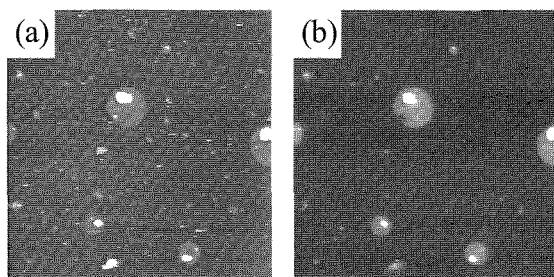


Fig. 6 (a) AFM and (b) KFM images ($20 \times 20 \mu\text{m}^2$) of a zirconia/FT film after calcination at 1073 K for 6 h.

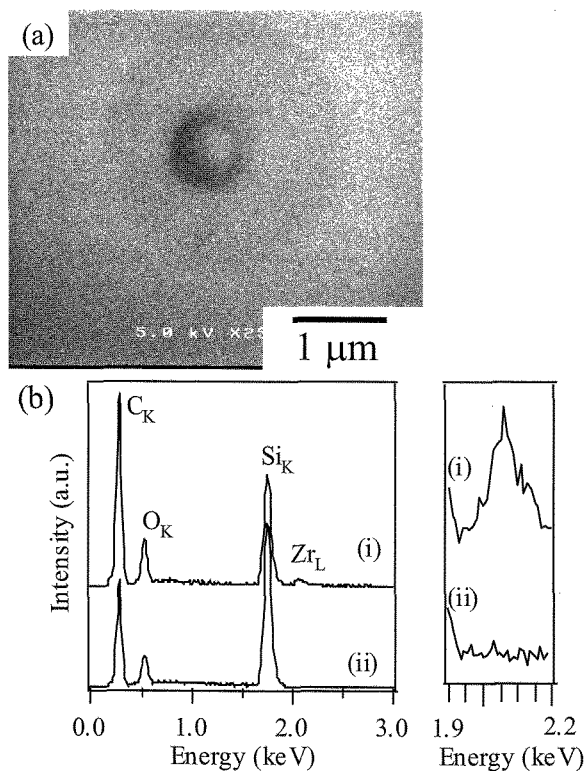


Fig. 7 (a) An SEM image and (b) EDX spectra of a zirconia/FT film after calcination at 1073 K for 6 h. Spectra (i) and (ii) in part (b) show EDX spectra of the ex-domain and the surrounding region, respectively.

$\text{F8H}_2\text{SiCl}$ should be removed from the substrate by calcination. These results indicate that the product formed in the ex-domain region remains even after calcination.

Figure 7 shows an SEM image and EDX spectra of a zirconia/FT film after calcination. The SEM image (Fig. 7(a)) shows a structure of the size of ca. $2 \mu\text{m}$ in the ex-domain region. The EDX spectrum of the higher structure in the ex-domain region shows a peak at 2.1 keV assignable to Zr [10]. This peak is absent in the spectrum of the surrounding region. Zirconia should be

formed in the whole ex-domain region since that region shows almost the same surface potential. These results show that under the optimal reaction conditions we can prepare patterned zirconia thin films.

4. Conclusion

In this study, we have prepared patterned zirconia thin films using templates fabricated from mixed LB films. The reaction conditions such as the reaction temperature and the precursor concentration strongly affect the zirconia self-assembly on the templates. Under the optimal reaction conditions we can fabricate patterned zirconia thin films, the patterns of which reflect the phase-separated structures of mixed LB films. The present methodology will be important in the applications to catalysts, electrodes and sensors using various metal ions as precursors.

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