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Oriented Growth of TS-1 Zeolite Ultrathin Films on Poly(ethylene oxide) Monolayer Templates

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Self-assembled monolayers of poly(ethylene oxide) (PEOM) were used as templates to direct the nucleation and subsequent oriented growth of TS-1 zeolite thin films. The resulting TS-1 zeolite thin films exhibited completely oriented crystalline domains with the (010) crystallographic direction parallel to the surface normal with a little deformation in the in-plane direction. Remarkably, the correlation length of the film is as extremely large as 1700 Å (1200 Å) in the out-of-plane (in-plane) direction. PEOM act as two-dimensional media for the nucleation and growth of highly oriented TS-1 zeolite thin films. This study demonstrates that the highly oriented TS-1 thin films can be achieved by using the inner parts of PEOM as templates.

Introduction

The development of new synthetic routes which can tailor properties, morphologies, and structures of both organic and inorganic materials is important to lead to the proper functions of microelectronic devices. In nature, numerous examples of materials with finely tuned sizes, shapes, polymorphs, crystallographic orientations, morphology, patterning, and so forth have been grown at interfaces through site-directed nucleation and self-controlled growth.¹ Recently, cost-effective and simple methods using new synthetic approaches have been developed by mimicking nature to tailor the materials.² By simply mimicking the role of interfaces in nature, self-assembled monolayers (SAMs) on the substrate are often used as templates to generate appropriate interfaces at which the geometric matching and interactions such as van der Waals interactions, ionic interactions, and hydrogen bonding would be generated to the nuclei in the medium and can transfer patterns, order, and symmetry from the monolayer surface to growing polymers,³ metals,⁴ organic crystals,⁵ and inorganic crystals.⁶ As an extension of the biomimetic way, nanopatterns of conducting poly-

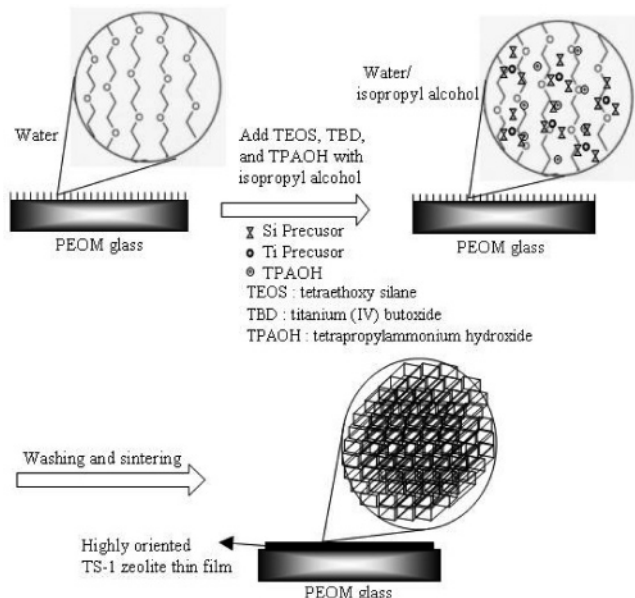
mers,⁷ gold,⁸ and silicon oxide⁹ have been easily grown by our group through regioselective nucleation; otherwise, those structures would not be simply attainable through simple methods. Furthermore, the growth direction of crystals was controlled using modified SAMs with designed chemical functionalities.^{5,6,10}

As an obvious extension of biomimetic processes, SAMs could be used to promote the growth of zeolite thin films for potential applications such as selective membranes, chemical sensors, and components in micro-optoelectronic devices.^{11–16} To be effective in these applications, oriented zeolite films with the surface normal direction and without intercrystal pores are indispensable because of their advantages in optimizing the efficiency of gas separation and catalytic processes.¹⁷ To attain the highly oriented zeolite thin films with surface normal direction, the growth of oriented zeolite films having MFI, LTA, and UTD-1 topologies has been investigated respectively by Jansen,¹⁸ Nishiyama et al.,¹⁹ Feng and Bein,²⁰ Yan et al.,²¹ Boudreau and Tsapatsis,²² and Balkus Jr.^{17,23} These authors used

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Scheme 1. Illustration for the Fabrication of Highly Oriented TS-1 Thin Films on PEOM Glass



either hydrothermal syntheses under high temperatures and pressures or chemical vapor deposition followed by secondary crystal growth to produce continuous and oriented zeolite thin films. Up to the present, the SAM has been utilized to generate proper nucleation sites for the precursors of zeolites through interactions between the exterior of the SAM and the precursors. However, the SAM method for the formation of oriented zeolite thin films had not been successful so far because the growth of zeolites was not homogeneous after the random nucleation on the surface of the SAM. However, if the precursors of zeolites could be condensed in the inner parts of the SAM and consequently be transformed into a solid phase, defect-free and oriented zeolite films could be easily obtained.

In this letter, we would like to report a new simple method for the preparation of the highly oriented TS-1 zeolite thin films using the inner parts of SAMs as templates. We chose poly(ethylene oxide) monolayers (PEOMs) as templates on a glass substrate because ethylene oxide units attract an inorganic precursor (e.g., silicic acid) from the aqueous phase²⁴ and stabilize tetrapropylammonium hydroxide (TPAOH) which acts as a structure-directing agent (Scheme 1). The orientation of the resulting crystalline TS-1 thin films was checked using conventional X-ray powder diffraction (XRD) and further investigated using synchrotron X-ray scattering measurements.

Experimental Section

Experimentally, PEOM with molecular weights (MWs) of 3400 and 500 can be simply attached on a glass plate ($1 \times 2 \text{ cm}^2$) using a simple procedure.²⁵ A contact angle meter (Ram-Hart contact angle goniometer), X-ray photoelectron spectroscopy (XPS; KRATOS XSAM800, Mg K α), and scanning probe microscopy (SPM; Parks Science, Autoprobe CP system) were used to investigate the PEOM on the glass plates. The fabrication of TS-1 zeolite films was carried out by dipping both bare and PEOM glass ($1 \times 2 \text{ cm}^2$) into the polypropylene reaction vessels containing tetraethoxy silane (TEOS)/titanium(IV) butoxide (TBD)/TPAOH/isopropyl alcohol/water with a molar ratio of

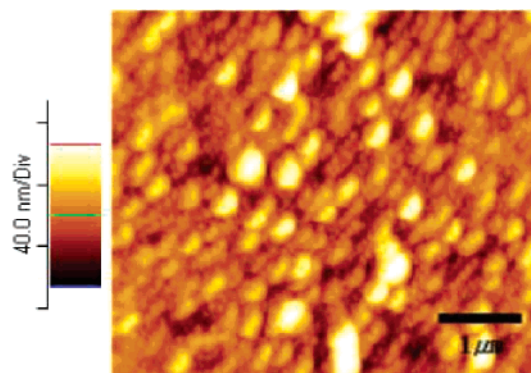


Figure 1. AFM image for PEOMs on a glass plate.

1:0.03:0.32:0.77:18.²⁴ The resulting vessels were kept in a thermostated bath at 80 °C over a period of 3–10 days. The substrates were positioned almost vertically in the reaction vessel to avoid having material deposited by precipitation from the gel. The resulting glass slides were rinsed in water that was being stirred for 5 min, dried at 100 °C for 5 h, and then heated at 450 °C for 3 h in air.

Scanning electron microscopy (SEM; JEOL JSM-6300) was used to study the morphology of the fabricated TS-1 zeolite thin films. The crystallinity of the resulting TS-1 thin films was checked using an XRD (Philips PW-1710, Cu K α) unit. To further examine the structural characteristics of the films, we performed synchrotron X-ray scattering measurements. The synchrotron X-ray scattering experiments were carried out at Pohang Light Source (PLS) in Korea. The incident X-rays were vertically and horizontally focused by a mirror and monochromatized to the wavelength of 1.479 Å by a double-bounced Si(111) monochromator. The momentum transfer resolution was set at 0.001 Å⁻¹ in the experiments. To achieve the exact scattering geometry, we employed a four-circle X-ray detector that enabled us to obtain an arbitrary momentum transfer in three-dimensional space.

Results and Discussion

The PEOM modified glass with MWs 3400 and 500 exhibited the contact angle of 30° while the bare glass was completely wetting. A SPM image for the PEOM on a glass plate showed aggregated small granules (Figure 1). The thickness of the PEOM on the glass plate was measured by cross-sectional analysis of the AFM image at the defect site and was about 27 nm. The observed thickness of the PEOM is slightly smaller than the calculated theoretical length²⁶ of 30 nm for the PEOM (MW 3400) because PEOMs may be aggregated themselves. The AFM image in Figure 1 directly supports the attained results. In XPS studies, the C(1s) spectrum exhibited binding energy of 288 eV originating from the PEOM on the glass. Those results clearly indicate that the surface of the glass was homogeneously covered by the PEOM. After the reaction with a molar ratio of TEOS (1) and TBD (0.03), TPAOH (0.32), isopropyl alcohol (0.77), and water (18), only the sample from 7 days of reaction on the PEOM exhibited the oriented TS-1 films from XRD study. Therefore, the samples reacted for 168 h at 80 °C with molar ratio of TEOS (1) and TBD (0.03), TPAOH (0.32), isopropyl alcohol (0.77), and water (18) were considered in this work. After the reaction of 168 h, both bare and PEOM modified glass plates were transparent after rinsing and drying. The grown films on bare and PEOM (MWs 3400 and 500, respectively) glass plates were checked by a conventional XRD. The films on the bare and PEOM (MW 500) glass plates appeared to be largely amorphous; on the other hand, the films on PEOM with

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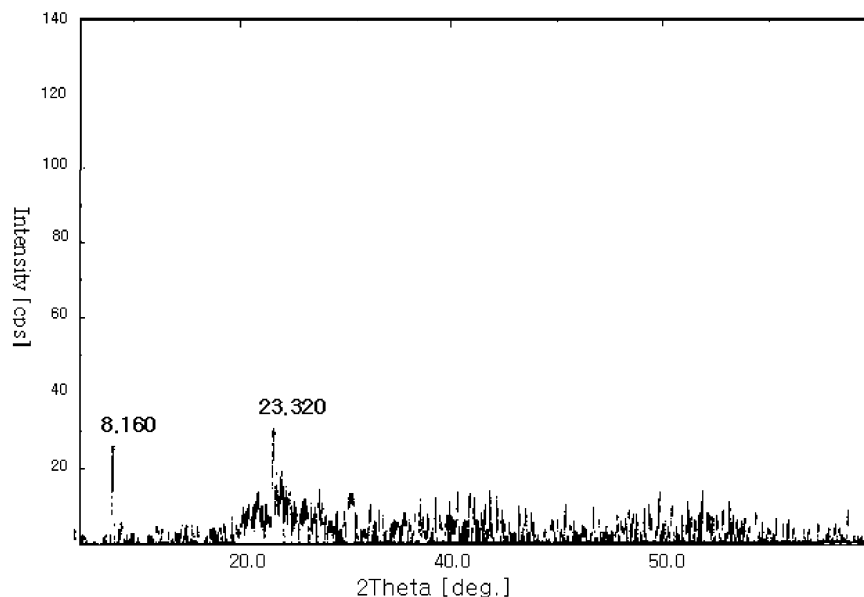


Figure 2. Conventional XRD patterns of the TS-1 zeolite thin films grown on a PEOM glass substrate.

MW of 3400 glass exhibited only orthorhombic ($0k0$) peaks in the XRD pattern (Figure 2), which differed dramatically from those of randomly ordered powders of as-synthesized TS-1 crystals.²⁷ Under the reaction condition, highly oriented TS-1 films are formed only on the PEOM (MW 3400) surface but not on the bare and PEOM (MW 500) glass. The featureless morphology of bare glass and the continuous film morphology of PEOM (MW 3400) glass were observed from SEM (Figure 3a,b). Because the film was very smooth (Figure 3b), it was hard to differentiate the morphology of the continuous film without a high-resolution SEM image at a defect site (Figure 3c). The thickness of the TS-1 film grown on the PEOM glass was about 170 nm from SEM cross-sectional image (Figure 3d). The TS-1 film may grow over the PEOM templates (thickness of 25 nm) by continuous feeding of inorganic precursors from the solution. In fact, mass transfer of monomer from the solution into the self-assembled bilayers in which the reaction was initiated has been reported.²⁸ Those results clearly show that only large lengths of PEOM play a key role in the formation of TS-1 thin films. We speculate that the PEOM with a MW of 3400 can only provide enough space to attract TBA and precursors of silica and titania for thin film formation.

To characterize the orientation of grown films in more detail, we carried out synchrotron X-ray scattering for the TS-1 films deposited on the PEOM glass in concentrations with a molar ratio of TEOS (1) and TBD (0.03), TPAOH (0.32), isopropyl alcohol (0.77), and water (18). First of all, the XRD (θ - 2θ scan) was performed by varying the momentum transfer q along the surface normal direction to elucidate the phase and the crystal structure of the film in the substrate normal direction, and the result is shown in Figure 4a. Only sharp regularly positioned TS-1 zeolite ($0k0$) Bragg reflections occur, indicating that the zeolite film was completely aligned with the (010) plane of the film parallel to the glass substrate surface normal. Because a blip around $2\theta = 35^\circ$ in Figure 4a is in the range of noise level of the instrument used, the blip cannot be accounted for as the (080) peak at this point. Although it is not clear to us why the (080) peak is not observed,

the regularity of the peaks demonstrates that a single crystal-like TS-1 zeolite film was formed on the PEOM (MW 3400) glass substrate. The broad hump at around $2\theta = 21.85^\circ$ with the full width at half-maximum of about 9.45° originated from a short-range ordering of the glass substrate.

To study the in-plane orientation of the film, a grazing incidence scattering was performed. The crystal structure in the in-plane direction of the films resulting from our studies is shown in Figure 4b. The pattern is same as that of TS-1 powders reported previously.^{27,29,30} This implies that the crystalline axis of the film is randomly distributed in the in-plane direction. It should be noted that intensities of the peaks in Figure 4b are much lower than those of the peaks obtained from the normal direction (Figure 4a). Those results indicate that the film has randomly oriented crystals in the in-plane direction. We cannot definitely assign the unlabeled peaks in Figure 4b, because the intensities of such peaks are in the range of background in the synchrotron measurement.

The lattice parameter of the film along the surface normal direction can be obtained simply from the peak position in Figure 4a. $q_{020} = 0.6315 \text{ \AA}^{-1}$ ($2\theta = 8.525^\circ$) yields $b = 19.899 \text{ \AA}$. The in-plane lattice parameters calculated from $q_{200} = 0.6248 \text{ \AA}^{-1}$ ($2\theta = 8.434^\circ$) and $q_{332} = 1.6309 \text{ \AA}^{-1}$ ($2\theta = 22.133^\circ$) in Figure 4b are $a = 20.113 \text{ \AA}$ and $c = 13.363 \text{ \AA}$, respectively. This result indicates that the crystal structure of the TS-1 zeolite film is orthorhombic. The correlation length in the surface normal direction, estimated from the broadening of the scattering profile in the l direction of reciprocal space (inset in Figure 4a), is as large as about 1700 \AA . That correlation length is the same order of magnitude as the film thickness measured by the cross-sectional SEM image. This result strongly suggests that the TS-1 zeolite film has a perfectly aligned nature along the surface normal direction for the whole film. The in-plane correlation length from the broadening of the TS-1 (332) peak (inset in Figure 4b) is about 1200 \AA . It is reasonable to assume that the TS-1 film on the PEOM (MW 3400) glass is composed of single-crystal domains whose sizes correspond to the correlation lengths.

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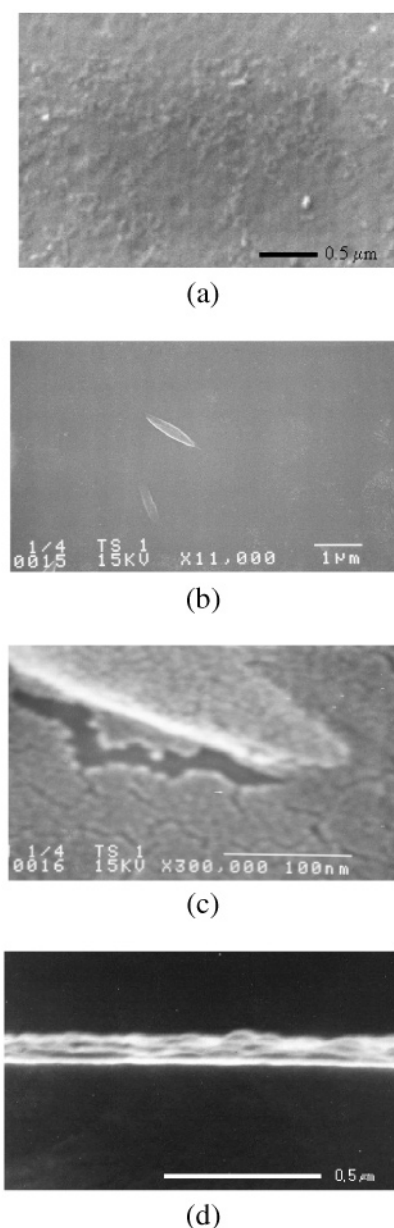


Figure 3. SEM micrographs after TS-1 deposition process on bare (a, top) and PEOM glasses (b and c; d, cross-sectional image).

The PEOM with MW of 3400 should be responsible for such large single-crystal domains. However, the PEOMs (MW 3400) themselves did not show any characteristic crystalline order from the synchrotron X-ray scattering study. Therefore, the reason for the growth of highly oriented TS-1 ultrathin films is that crystals can only form during slow growth, favored by very low concentrations of reactants in the reaction medium, which can nevertheless be partitioned into the PEOM (MW 3400) to favor crystal formation. The crystal growth on the substrate surface is probably controlled by a solid-phase transformation process³¹ in which the solid hydrogel is reorganized for the formation of zeolite crystal, and this process is mediated by the large MW (3400) of PEOM. In fact, it has been reported that an inorganic precursor (e.g., silicic acid) can be preferably transferred and condensed into the layers of poly(ethylene oxide) from the aqueous

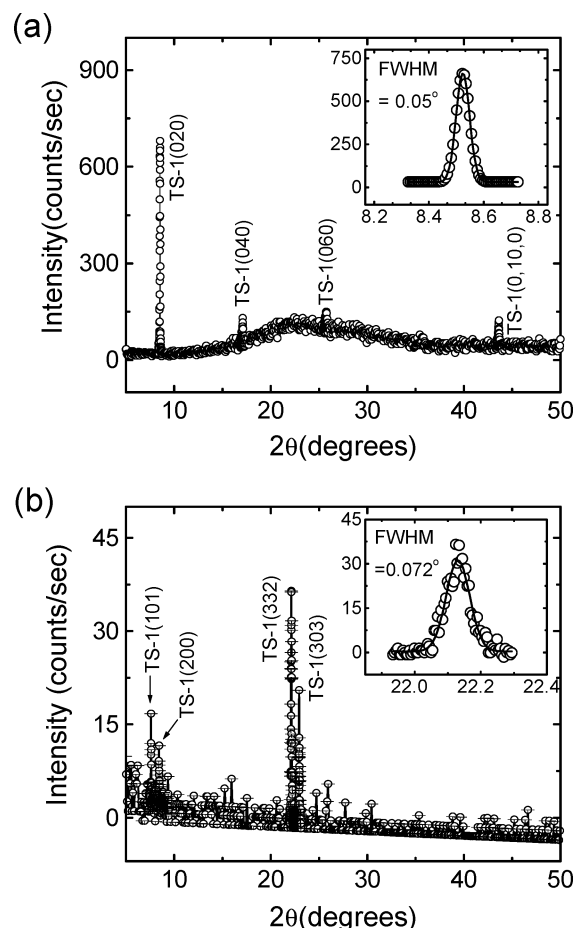


Figure 4. XRD from synchrotron X-ray scattering measurements (a) and grazing incidence XRD (b) patterns of the TS-1 zeolite thin film grown on a PEOM glass substrate. The insets represent respectively the diffraction profile of the fine scan for the TS-1 (020) and (332) peaks.

phase.³² However, on the bare glass surface and low MW (<500) of PEOM, only amorphous material is deposited because the surface concentrations of precursors are as low as in the aqueous phase. Therefore, the size of the PEOM should be large enough to accumulate TBAOH and precursors for the growth of highly oriented TS-1 zeolite ultrathin films.

Conclusion

In summary, we have prepared the first ultrathin films of highly oriented crystalline TS-1 zeolites through a biomimetic process. The presence of the PEOM on a surface where the direction of the channels may be mostly perpendicular to the substrate is responsible for the growth of the oriented crystalline TS-1 films. The mechanism of the single crystal growth in the PEOM templates is probably dependent on the nature of the inner parts of the template on the substrate, and this is the subject of a continuing investigation. It is hoped that these films can be fabricated on a variety of support materials, and different applications in advanced technology will be forthcoming.

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