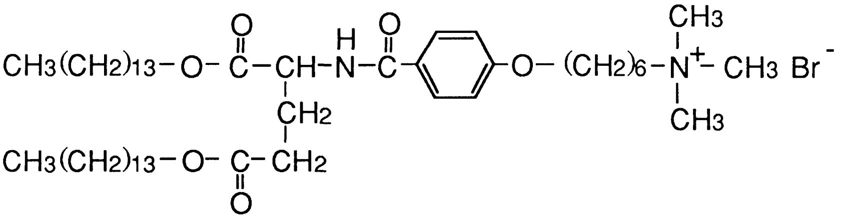
CHEMISTRY LETTERS, pp. 1465-1468, 1992.

Multi-Layered Thin Films of Ordered Alumina Particles

Nobuo TSUTSUMI, Kanji SAKATA, and Toyoki KUNITAKE[*,†]
Molecular Architecture Project, JRDC, Kurume Research Park, Kurume 830

Multi-layered alumina thin films with crystalline anisotropy and high surface area were prepared from ultra-fine particles of alumina using a multi-bilayer cast film of a double-chain ammonium amphiphile as a molecular template.

Cast films of synthetic bilayer membranes have been used as molecular templates for preparation of two dimensional molecular networks of polysiloxanes[1)] and vinyl polymers.[2,3)] The interbilayer space of the cast film is also suitable for orderly incorporation of myoglobin, a globular protein.[4-6)] This result suggests that other nanometer-size particles can be introduced into the cast film. Thus, we conducted incorporation of Al_2O_3 particles into a cast film and obtained multi-layered alumina films upon calcination.



1

Bilayer-forming ammonium amphiphile **1**[7)] was dispersed in water by sonication (Branson Ultrasonics Co., Sonifier II model 250) to give a clear 50 mM dispersion, and aqueous alumina sol (eight times by weight) (Nissan Chem. Ind., Alumina Sol-200 : 10-11% Al_2O_3 ; particle size, 10-100 nm ; surface charge, cation) was added and sonicated. The mixture was cast on a fluorocarbon membrane filter for 3 days at 25 °C and 60% relative humidity. The resultant cloudy composite film was then calcined in air at high temperature for 10 h.

Figure 1 is a photograph of a typical, self-supporting alumina film thus obtained. The amphiphile component was completely removed from the calcined alumina films, as comfirmed by IR spectroscopy. When casting was conducted without the amphiphile, only broken pieces of an alumina film (thickness, ca. 80 μm) were obtained. Therefore, the film forming property is derived from the presence of the molecular template.

[†] Permanent address: Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812.

The regular, multi-layer structure observed for a cast film of amphiphile **1** was transcribed in the alumina film. A scanning electron micrograph (Hitachi, S-900) of the

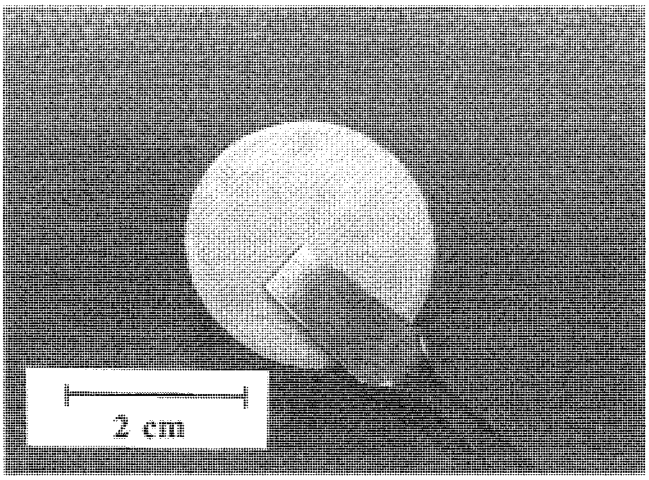


Fig.1. Photograph of an alumina thin film (thickness; ca. 20 μm) prepared by using a cast film of amphiphile **1** as template. (calcination; 500 °C, 10 h)

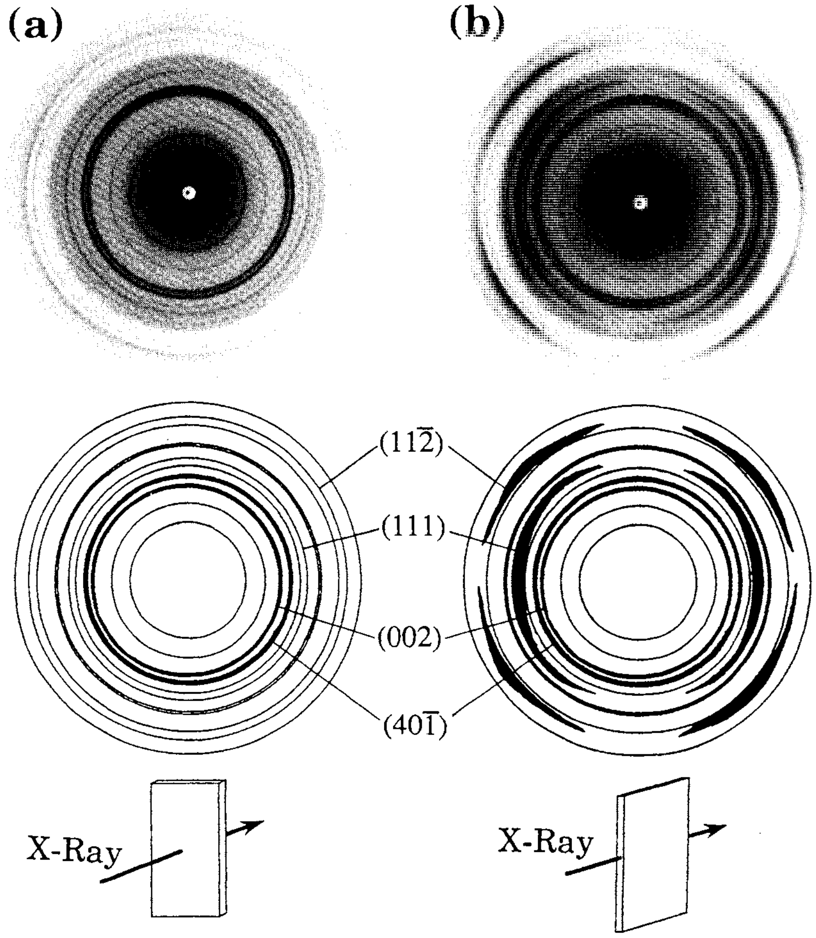


Fig.2. X-Ray diffraction patterns of θ-alumina thin films: X-Ray beam directed perpendicular (a) or parallel (b) to the film plane.

cross section of the film indicated the presence of a layered microstructure parallel to the film plane. The thickness of the individual layer, ca. 10 nm, was of the same size as that of the starting alumina sol. When the molecular template was not used, the cross section was composed of irregular coagulation of alumina particles. These alumina samples were amorphous without regard to the use of the template, as confirmed by X-ray diffraction analysis (Rigaku Denki Co., RAD R32, $\text{CuK}\alpha$, 50 kV, 200 mA).

When the alumina film was further calcined at 800 °C for 10 h in air, anisotropic formation of the $\theta\text{-Al}_2\text{O}_3$ structure was recognized in X-ray diffraction. As shown in Fig. 2a, the transmission diffraction displays a typical powder pattern of the $\theta\text{-Al}_2\text{O}_3$ crystals,[8,9] when X-ray beam is directed normal to the film plane. In contrast, anisotropic diffractions are seen at (111) and $(11\bar{2})$ planes when X-ray beam is parallel to the film plane (Fig. 2b). The alumina pieces formed without the template do not show the anisotropy.

The $\theta\text{-Al}_2\text{O}_3$ crystal structure was converted completely to that of $\alpha\text{-Al}_2\text{O}_3$ when calcined at 1000 °C for 10 h. It was particularly noticeable for the (104) diffraction parallel to the film plane. Scanning electron micrographs of these $\alpha\text{-Al}_2\text{O}_3$ films are shown in Fig. 3. A multi-layer structure resulting from the bilayer template is retained even upon calcination at 1000 °C. The crystal anisotropy similar to those of Fig. 2 was also observed in this case. The multi-layer morphology did not change by calcination at 1500 °C. Without the template, more extensive, isotropic sintering of alumina particles is observed, as shown in Fig. 3b.

The morphological characteristics are reflected in the surface area measured by the BET method (Carlo Erba, Sorptomatic-1800). The surface area of the template-synthesized film

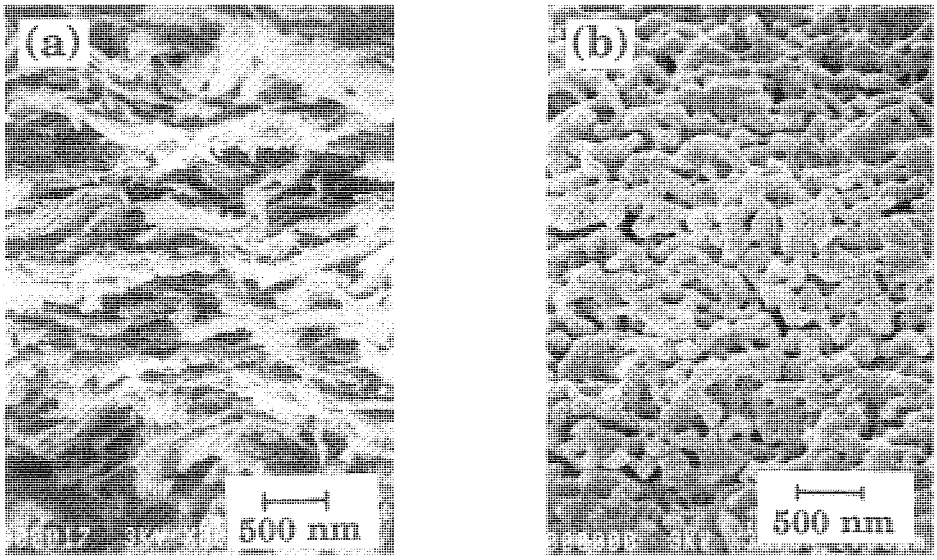


Fig.3. SEM photograph of α-alumina thin films calcined at 1000 °C (cross section). The films were prepared by using the template (a) or without a template (b). The specimens were coated with Pt in an ion sputter coater prior to SEM observation (Hitachi, S-900).

does not decrease drastically at calcination temperatures above 1000 °C; ca. 100 m^2/g at 1300-1500 °C. This value is much greater than that of the non-template alumina. A sharp decrease of surface area in the non-template alumina at calcination temperatures above 1000 °C has been explained by phase transition to α-Al_2O_3.[10-12] This dose not happen with our template-synthesized film.

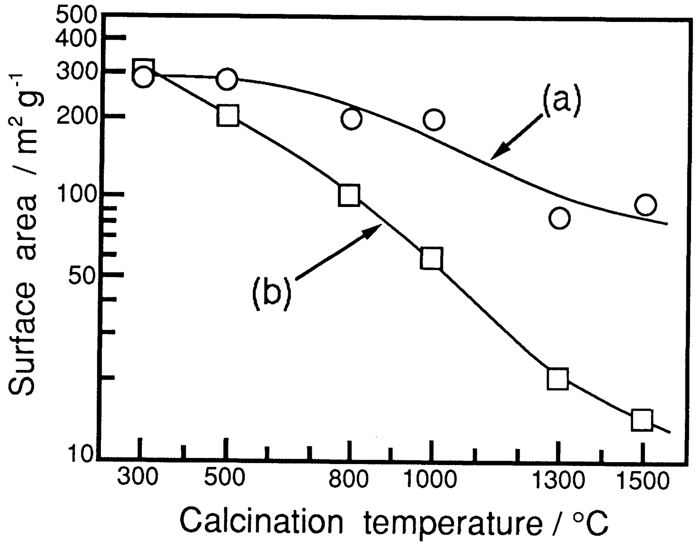


Fig.4. Temperature dependence of the BET surface area of alumina thin films. Sample: (a) template-synthesized film; (b) non-template pieces.

In conclusion, we prepared an anisotropic, crystalline alumina film with a multi-layer morphology by using a multi-bilayer template of a double-chain ammonium amphiphile. Its novel morphology and high surface area should find many interesting applications.

References

1) K.Sakata and T.Kunitake, J.Chem.Soc., Chem.Commun., **1990**, 504.
2) S.Asakuma and T.Kunitake, Chem.Lett., **1989**, 2059.
3) S.Asakuma, H.Okada, and T.Kunitake, J.Am.Chem.Soc., **113**, 1749 (1991).
4) I.Hamachi, S.Noda, and T.Kunitake, J.Am.Chem.Soc., **112**, 6744 (1990).
5) I.Hamachi, T.Honda, S.Noda, and T.Kunitake, Chem.Lett., **1991**, 1121.
6) I.Hamachi, H.Fujimura, and T.Kunitake, Chem.Lett., **1991**, 2227.
7) Y.Ishikawa and T.Kunitake, J.Am.Chem.Soc., **113**, 621 (1991).
8) H.C.Stumph, A.S.Russel, J.W.Newsome, and C.M.Tucker, Ind.Eng.Chem., **42**, 1398 (1950).
9) G.Yamaguchi, I.Yasui, and W.C.Chiu, Bull.Chem.Soc.Jpn., **43**, 2487 (1970).
10) H.Schaper, E.B.M.Doesburg, P.H.M.De Korte, and L.V.Reijen, Solid State Ionics, **16**, 261 (1985).
11) M.Machida, K.Eguchi, and H.Arai, J.Catal., **103**, 385 (1987).
12) M.Machida, K.Eguchi, and H.Arai, Bull.Chem.Soc.Jpn., **61**, 3659 (1988).

(Received May 12, 1992)