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Preparation of TiO_2 Ultrathin Film by Newly Developed Two-Dimensional Sol−Gel Process

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Currently, the sol−gel process is employed quite often for the synthesis of glasses and ceramics in the form of bulk bodies, fine particles, fibers, and films.[1,2] The sol−gel process is based on the hydrolysis and condensation of molecular precursors represented by metal alkoxides.[3,4] These reactions proceed in solutions in the conventional sol−gel process. By contrast, this communication reports, for the first time, a two-dimensional (2D) sol−gel process in which the hydrolysis and condensation reactions take place at the air/water interface in a two-dimensionally controlled manner.

The sol−gel derived thin films are generally prepared by the dip- or spin-coating of solutions of precursor molecules or sol solutions on substrates, followed by drying and heating processes.[5,6] In this preparation, the quality of the resulting thin films is largely dependent not only on the properties of the coating solution (density, viscosity, etc.) but also on the pull-up or spinning speed,[1,7] and the controllable thickness is usually on the order of submicrons at the thinnest.[8] On the other hand, the nanothick films could be prepared successfully by the present 2D sol−gel process, which is composed of the formation of the hydrolyzed polycondensate film at the air/water interface, the deposition of the film on a substrate by Langmuir−Blodgett (LB) techniques, and the densification (heating) process. In recent years, inorganic semiconductor materials have been drawing much attention with respect to quantum electronics, nonlinear optics, and photonics, and inorganic nanoparticles and nanoclusters have become synthesized easily by chemical methods.[9,10] The 2D sol−gel process is expected to be a potential chemical process for the synthesis of oxide semiconductor nanofilms. This communication reports the synthesis of the TiO_2 nanofilm showing the quantum size effect by the 2D sol−gel process.

A chloroform solution of tetrabutoxytitanium (TBT) tetramer (10 mg$\cdot$cm^{-3}) was spread on a surface of pure water, and the surface pressure−area (π−A) isotherm was measured by a computer-controlled film balance at 288 K (Figure 1a). Separately, the morphology of the TBT tetramer on the water surface at various surface pressures was observed by fluorescence microscopy by using 0.5 mol % rhodamine B octadecyl ester as a fluorescence probe[11] (Figure 2). Just after the TBT tetramer was spread at 0 surface pressure, a lot of floating laminar islands were observed (Figure 2, panel 1), and with progressive compression, they gathered (panel 2) and eventually formed a featureless, homogeneous film at a surface pressure of 10−20 mN$\cdot$m^{-1} (panel 3), which corresponds to the "solidus" region of the π−A isotherm. The observed apparent molecular area (0.4 nm$^2\cdot$molecule^{-1}), which is much smaller than the calculated area of the TBT tetramer (more than 2.0 mm$^2\cdot$molecule^{-1}),[12] suggests that the film formed on the water surface is not the molecular monolayer film of the TBT tetramer. The film deposited on a CaF_2 substrate showed IR absorption bands of

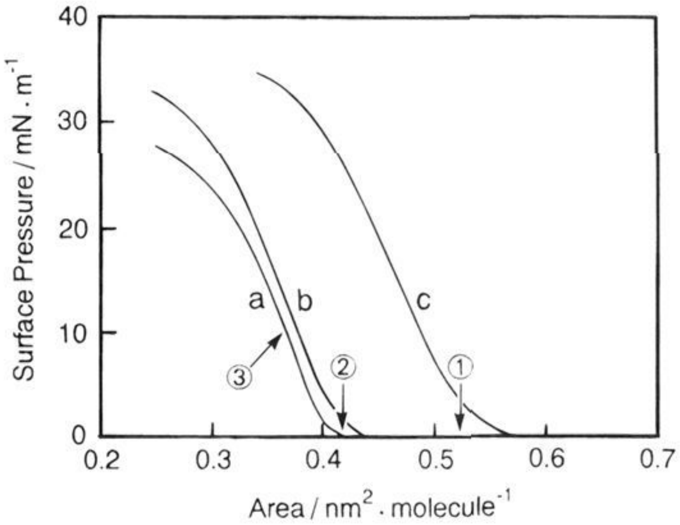

Figure 1. Surface pressure−area (π−A) isotherms of the tetrabutoxytitanium tetramer at 288 K on pure water (a), 0.01 M aqueous acetic acid (b), and 0.01 M aqueous acetylacetone (c).

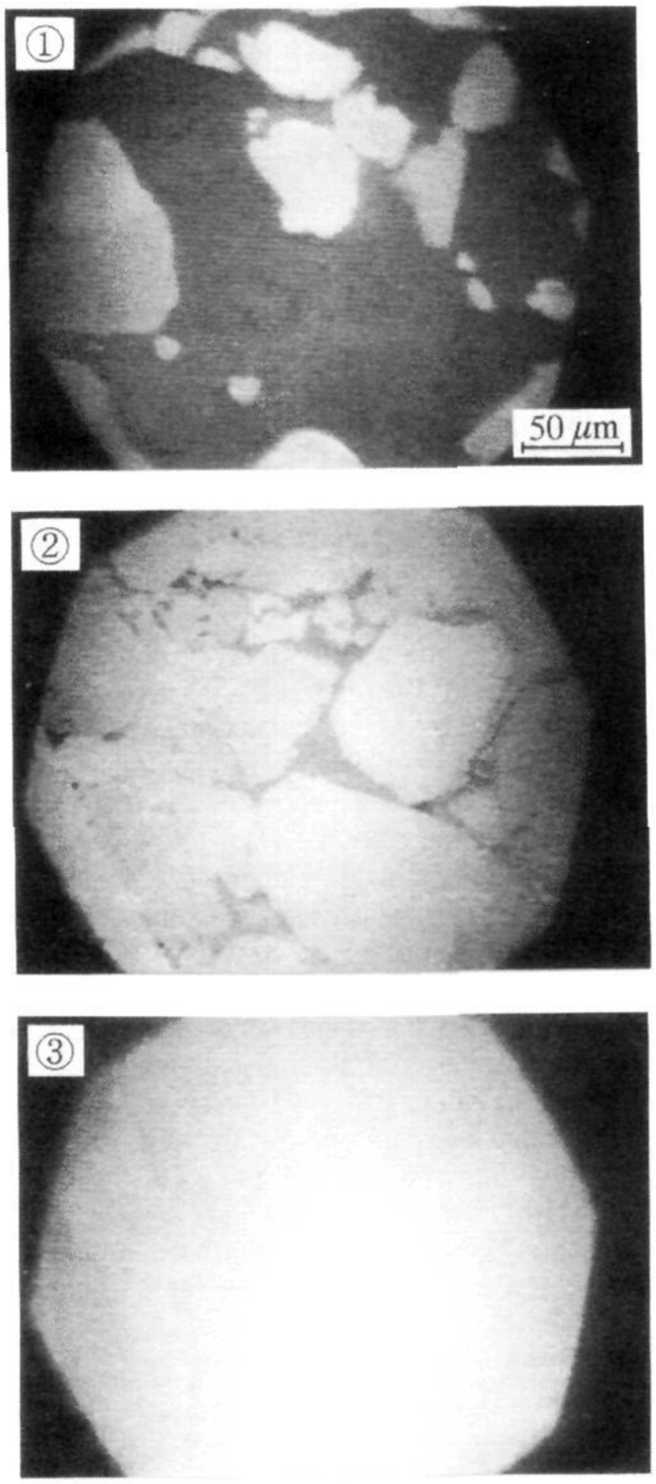

Figure 2. Fluorescence images of the tetrabutoxytitanium tetramer on pure water: panels 1−3 were taken at the compression stages indicated in Figure 1. The octagonal area represents a microscope field.

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C−H stretching vibrations at 2964, 2924, and 2851 cm^{-1} and a Ti−O−C stretching vibration around 1100 cm^{-1}.[3] The elemental analysis of the vacuum-dried film revealed that the contents of C and H were much less than those expected for the TBT tetramer.[13] These results clearly show that the TBT tetramer is hydrolyzed and condensed on the water surface to form the floating film (island) of TiO_2 gel with some residual butoxy groups and that the increase in surface pressure is due to the two-dimensional aggregation of the floating hydrolyzed condensates. The monomer of TBT also gave the $\pi-A$ isotherm with the observed area per Ti atom equal to that of the tetramer, indicating that the monomer and the tetramer give almost the same hydrolyzed condensates. On the other hand, no increase in surface pressure was observed with the tetraethoxytitanium monomer, which is more reactive toward hydrolysis and less hydrophobic than the butoxide.[3,4] Accordingly, it is speculated that the hydrophobicity of the butoxy groups remaining in the condensates and probably the moderate reactivity of the butoxide are indispensable to form floating hydrolyzed condensates. The good reproducibility of the $\pi-A$ isotherm indicates that the hydrolysis and condensation reactions on the water surface are well controlled under the present experimental conditions.

It is well-known that acetic acid and acetylacetone can suppress the hydrolysis and condensation of metal alkoxides in solutions due to chelation to metal atoms.[3,4,14] Such a suppression effect was also observed in the present 2D sol−gel process as demonstrated by the increased apparent molecular area on aqueous subphases (0.01 M) of acetic acid and acetylacetone (Figure 1b,c).[15] Also observed on these subphases were an increase in the collapse pressure and therefore the expansion of the "solidus" region; fluorescence images revealed the same morphology of the floating condensate films on both pure water and aqueous acetic acid subphases. These chelating effects resulted not only in the enhanced stability of the floating condensate film but also in stable and reproducible transfer onto substrates.

The results shown above prove that the homogeneous and densely packed film of TiO_2-based condensates can be formed by 2D hydrolysis/condensation reactions and subsequent compression in the LB trough. It is expected that the floating condensate film should be a favorable precursor of ultrathin TiO_2 film if it can be transferred on substrates as it has been on the water surface. The transfer of a hydrolyzed condensate film of TiO_2-based gel onto substrates was investigated on the aqueous acetic acid subphase at a constant surface pressure of 15 mN·m^{-1}. The floating film was successfully deposited on substrates only at every upstroke with a transfer ratio of unity. The fluorescence spectroscopic study showed that the homogeneous state of the floating film was preserved in the deposited film. The film deposited on quartz substrates showed a UV−vis absorption with the edge at 328 nm. This absorption edge is considerably blue-shifted from that of bulk TiO_2 (anatase, 387 nm; rutile, 413 nm)[16] as well as the quantum-size TiO_2 (370 nm for 24-Å anatase,[17] 375.1 nm for 38-Å anatase, and 398 nm for 55-Å rutile[18]), indicating that the film is composed of very fine condensates of TiO_2-based gel. The absorbance at 250 nm increased linearly with increasing the number of deposition, while keeping the absorption edge constant. This result confirms that the condensate film can be quantitatively transferred onto the substrate. The fact that the film deposited at 2 mN·m^{-1} absorbed considerably less UV light than that deposited at 15 mN·m^{-1} implies that the density of the deposited film can be controlled by the surface pressure of the LB deposition.

The thermogravimetric measurement on the powder of condensates scraped up from the subphase surface showed that the conversion of the condensates into TiO_2 by the elimination of butoxy groups and dehydration was completed at about 723 K; the IR peaks due to butoxy groups completely disappeared by heat treatment at 573 K for 30 min. Accordingly, heat treatment at 773 K for 30 min was employed to convert the 15-layer TiO_2-based condensate film, which was deposited from the aqueous acetic acid subphase, into the ultrathin TiO_2 film. The resulting TiO_2 film was characterized by XRD, SEM, XPS, and UV−vis spectroscopy, and the presence of TiO_2 was confirmed by XPS and UV−vis measurements. The thickness of the TiO_2 film was estimated to be 43 Å by the depth-profiling XPS measurement.[19] The ultrathin TiO_2 film had a UV absorption edge at 337 nm, which is still considerably blue-shifted from those of the quantum-size TiO_2 reported.[17,18] Anpo et al.[20] reported the synthesis of highly dispersed TiO_2 on porous Vycor glass by the chemical anchoring of $TiCl_4$ by which the atomic layer growth is possible in principle. The absorption edge of the present TiO_2 film is close to that of one or two TiO_2 layers anchored on porous Vycor glass.[20] These results clearly indicate that the TiO_2 nanoparticle film can be prepared by the present 2D sol−gel process. Although XRD and SEM were found to be ineffective to characterize such a thin film at the present, more detailed investigation on the structural and physico-chemical characterization of the ultrathin TiO_2 films is now in progress.

To our best knowledge, this is the first example of sol−gel chemistry at the air/water interface as well as sol−gel synthesis of oxide nanofilms, and thus the 2D sol−gel process developed in this study is a potential and promising chemical process to synthesize metal oxide films in a nano-order thickness. The most essential step of the process is the hydrolysis and condensation reactions at the air/water interface. In principle, this process can be applied to the synthesis of various metal oxide nanofilms if the precursor materials and the chelating agents are adequately selected so as for the hydrolysis and condensation reactions to take place at the air/water interface in a two-dimensionally controlled fashion.

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(12) The determination of the exact molecular area of the TBT tetramer is quite difficult because its molecular structure at the air/water interface is unknown. At the first approximation, however, it should be larger than 2.0 nm^2·molecule^{-1}, which is 10 times the cross-sectional area of the alkyl chain.

(13) Found: C, 3.10; H, 2.52. Calcd for TBT tetramer: C, 49.48; H, 9.28. The rational formula of $TiO_{0.88}(OH)_{2.16}(OC_4H_9)_{0.08}$ was suggested from the elemental analysis.

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