Preparation of a TiO_2 Nanoparticulate Film Using a Two-Dimensional Sol−Gel Process

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The preparation of a TiO_2 thin film was investigated by a newly developed two-dimensional (2D) sol−gel process. When a chloroform solution of monomer or tetramer of tetrabutoxytitanium (TBT) was spread on the surface of an aqueous subphase, the TBT was hydrolyzed and polycondensed at the air/water interface to give floating gels. These gels were gathered by 2D compression to yield a uniform gel film on the water surface. The addition of chelating agents such as acetic acid and acetylacetone to the aqueous subphase or spreading solution was effective in suppressing the 2D hydrolysis/polycondensation reactions and in increasing the stability of the floating gel film. Up to 20 layers of the floating gel film prepared on aqueous acetic acid could be quantitatively transferred onto a suitable substrate using Langmuir−Blodgett techniques. The addition of *n*-octadecyl acetoacetate in the spreading solution of monomeric Ti butoxide and ethoxide resulted in quantitative transference of the gel films onto substrates without a limitation on the number of depositions. The deposited TiO_2-based gel films could be converted into nanothick TiO_2 films by calcination at 773 K for 30 min. It was suggested that the oxide films prepared from gel films of less than a few tens of layers were composed of quantum-size TiO_2 particulates. The thickness and the density of the nanoparticulate TiO_2 films could be controlled by the number of deposited gel film layers and the surface pressure of the gel film layer during deposition. The controllable thickness of the TiO_2 film by one deposited gel film layer was estimated to be 2−3 Å.

Introduction

The sol−gel process is a soft-chemical method permitting the synthesis of technologically important glasses and ceramics as bulk materials, fine particles, fibers, and films.[1,2] This process is based on hydrolysis and condensation reactions in a liquid phase of molecular precursors such as the metal alkoxides.[3,4] In conventional sol−gel synthesis, thin oxide films are generally prepared by dip- or spin-coating precursor molecules or sol solutions on a substrate, followed by drying and heating.[5,6] The quality of the resulting thin film is largely dependent not only on the properties of the coating solutions (density, viscosity, etc.) but also on the dip or spin rates.[1,7] The controllable film thickness is usually of the order of microns, so that conventional sol−gel processes are not suitable for the preparation of nanostructured oxide thin films.[8,9]

In a recent communication,[10] we described a novel two-dimensional (2D) sol-gel process. The unique features of the above 2D sol−gel process are that the hydrolysis and condensation reactions occur at the air/water interface and that Langmuir−Blodgett (LB) techniques are used to deposit the gel film on a substrate. The 2D sol−gel process is composed of four steps as shown in Figure 1. A metal alkoxide is hydrolyzed and polycondensed at an air/water interface to form floating gels (step 1). The gels are gathered by two-dimensional compression to give a uniform gel film (step 2), and then the gel film is transferred onto a substrate by LB technique (step 3). Finally, the deposited gel film is converted into the corresponding metal oxide film by heating (step 4).

In addition to the novelty of the 2D sol−gel process from a chemical point of view,[9] the process is promising with respect to the synthesis of nanostructured oxide films. That is, a nanometer thick TiO_2 film composed of quantum-sized particles may be prepared adopting this approach.[10] Recently, the preparation of nanostructured semiconductor materials has been attracting great attention as an important branch of advanced materials.[11,12] Nanosized semiconductors possess chemical and physical properties different from the corresponding bulk material due to the quantum size effect which is characterized by the blue-shifted energy gap and discrete electronic levels[13−16] and exhibit some novel functions for quantum electronics, nonlinear optics, and

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(1) Sakka, S. *Science of Sol-Gel Technique*; Agune-Shofu: Tokyo, 1988.

(2) Lee, G. R.; Grayston, J. A. *Adv. Mater.* **1993**, *5*, 434.

(3) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

(4) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

(5) Dishlich, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 363.

(6) Rao, C. N. R. *Mater. Sci. Eng.* **1993**, *B18*, 1.

(7) Dislich, H.; Hussmann, E. *Thin Solid Films* **1981**, *77*, 129.

(8) Takahashi, Y.; Matsuoka, Y. *J. Mater. Sci.* **1988**, *23*, 2259.

(9) Reuter, H.; Brandherm, M. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1578.

(10) Moriguchi, I.; Maeda, H.; Teraoka, Y.; Kagawa, S. *J. Am. Chem. Soc.* **1995**, *117*, 1139.

(11) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

(12) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, *7*, 607.

(13) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.

(14) Lippens, P. E.; Lanno, M. *Phys. Rev.* **1989**, *B39*, 10935.

(15) Liu, C.; Bard, A. J. *J. Phys. Chem.* **1989**, *93*, 7749.

(16) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.

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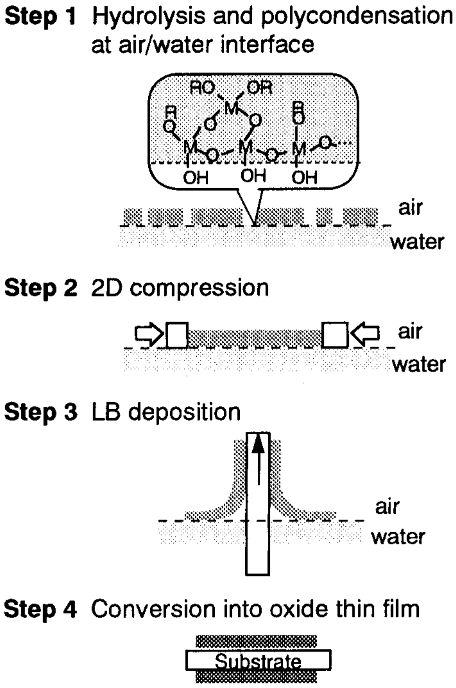

Figure 1. Schematic illustration of two-dimensional (2D) sol–gel process.

photonics.[17–23] Therefore the development of techniques for the synthesis of semiconductor nanocrystallites and their integration is expected to lead to a new generation of functional materials. Gas-phase dry processes such as physical and chemical vapor deposition, molecular beam epitaxy, and atomic layer epitaxy have been successfully used to prepare nanostructured devices possessing ultrathin layers, superlattices, or quantum wells.[24] They require, however, costly equipment usually operated under ultrahigh-vacuum conditions. In contrast, the 2D sol–gel process[10] and assembling surfactant-coated nanocrystallites by the use of LB techniques[25,26] are expected to be chemical wet processes which will enable the synthesis of nanostructured semiconductor oxide films without heavy equipment and technologically difficulties.

This paper describes a detailed investigation on each step of the 2D sol–gel process shown in Figure 1 for the preparation of ultrathin TiO_2 films. The characterization of the resultant TiO_2 films is also described.

Experimental Section

Materials. The monomer and tetramer of tetrabutoxytitanium (TBT, Wako Pure Chemical Ind., Ltd., extra-pure grade), tetraethoxytitanium (TET) monomer (Merck, extra-pure grade), acetic acid, acetylacetone, and chloroform (Kishida Chemical Co. Ltd., guaranteed reagent) were used as received.

n-Octadecyl acetoacetate ($C_{18}AA$) was synthesized from *n*-octadecanol and diketene (Tokyo Kasei Ind. Ltd., extra-pure grade) according to the procedure previously reported[27] and was identified by IR, NMR, and elementary analysis. The water used to prepare the subphase solutions was purified by using the Milli Q system (Millipore Corp., resistivity > 14 MΩ cm). CaF_2 plates (20 mm diameter × 2 mm, Japan Spectroscopic Co. Ltd.), quartz plates (10 mm × 45 mm × 1.25 mm, Fujiwara Co. Ltd.), borosilicate glass plates (76 mm × 26 mm × 1.5 mm, Matsunami Glass Ind., Ltd.), and Si wafers (kindly supplied by Sumitomo Sitix Corp.) were used as substrates on which gel films were deposited. These substrates were chosen properly to meet the requirements of a given instrumental analysis. Surfaces of substrates were cleaned by the O_3 treatment for 2 h using a UV/O_3 cleaner (Nihon Lazer & Electronics Lab., NL-UV253), followed by washing with pure water and methanol (Kishida Chemical Co. Ltd., guaranteed reagent).

Preparation of Titanium Oxide-Based Gel Films at an Air/Water Interface. A 100 μL portion of a chloroform solution of titanium alkoxide (10 mg cm^{-3}) was spread at 288 K on the surface of pure water, 0.01 M (1 M = 1 mol dm^{-3}) aqueous acetic acid or 0.01 M aqueous acetylacetone in LB trough by using a Hamilton syringe. A chloroform solution of a mixture of TBT monomer and $C_{18}AA$ with 1:1 molar ratio, which was kept for more than 2 h at room temperature to allow complexation, was also spread at 288 K on the surface of pure water. The spreading solvent was allowed to evaporate for 15 min prior to the two-dimensional compression. The two-dimensional compression was performed on an LB trough by using a computer-controlled film balance (USI system Co. Ltd., FSD 110) and monitored by measurement of surface pressure–area (π–A) isotherm.

LB Deposition. The LB deposition of gel films prepared from TBT monomer and tetramer was performed at a surface pressure of 3–15 mN m^{-1} by a vertical dipping of a substrate at 10 mm min^{-1} with the film balance and a lifter (USI System Co. Ltd., FSD23). The gel film of mixture of TBT monomer and $C_{18}AA$ was transferred onto substrate at 20 mN m^{-1}. The progress of the LB deposition was monitored by the measurement of time course of area (A–t curve).

Conversion of Titanium Oxide-Based Gel into TiO_2. The conversion of titanium oxide-based gel films into TiO_2 films was carried out by a heat treatment at 773 K for 30 min in air. The condition of the heat treatment was determined by thermogravimetric (TG) measurememts (Seiko Instruments Inc. TG-DTA 200, programmed heating rate 10 °C min^{-1}) of titanium oxide-based gel scooped up from the water surface. Infrared (IR) spectroscopy was also used to check the elimination of organic moieties from gel films by the conversion process.

Instrumental Analysis. The morphology of the TBT tetramer on the water surface at various surface pressures and deposited gel films on borosilicate substrates was observed by fluorescence microscopy (Olympus, BHS-RFK) by using 0.5 mol % rhodamine B octadecyl ester perchlorate salt (Wako Pure Chemical Inc., Ltd.) as a fluorescence probe.[28] UV–vis spectra of quartz-supported films were recorded on a Shimadzu UV-3100 spectrometer in the transmission mode. The absorption edge energy (E_g) was determined by using the relation between the absorption coefficient (α) and the photon energy ($h\nu$) for an indirect transition, $\alpha \propto (h\nu - E_g)^2/h\nu$.[29] Since the absorbance (*Abs*) is proportional to α, the E_g value was obtained by extrapolating a linear portion of a plot of $(Abs \cdot h\nu)^{1/2}$ vs $h\nu$ to the $h\nu$ axis. IR spectra of CaF_2-supported films were measured using a Perkin-Elmer 1650 spectrometer in a transmission mode. X-ray photoelectron spectra (XPS) of quartz-supported films were recorded on a Shimadzu ESCA-850 instrument with a Mg Kα source (1253.6 eV). The binding energies were calibrated in reference to C 1s line of carbon (285.0 eV) or Si 2p line of SiO_2 (103.5 eV). The depth-profiling

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(17) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. *J. Phys. Chem.* **1985**, *89*, 5017.

(18) Nedeljkovic, J. M.; Nenadovic, M. T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1986**, *90*, 12.

(19) Nosaka, Y.; Fox, M. A. *J. Phys. Chem.* **1988**, *92*, 1893.

(20) Wang, Y. *Acc. Chem. Res.* **1991**, *24*, 133.

(21) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 263.

(22) Moriguchi, I.; Hanai, K.; Teraoka, Y.; Kagawa, S.; Yamada, S.; Matsuo, T. *Jpn. J. Appl. Phys.* **1995**, *34*, L323.

(23) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41.

(24) For example, Japan Society for the promotion of science 131 Committee; *Thin Film Handbook*; Ohmsha: Tokyo, 1983.

(25) Kotov, N. A.; Melrum, F. C.; Fendler, J. H. *J. Phys. Chem.* **1994**, *98*, 8827.

(26) Doherty, S.; Fitzmaurice, D. *J. Phys. Chem.* **1996**, *100*, 10732.

(27) Lawesson, S. O.; Gronwall, S.; Sandberg, R. *Org. Synth.* **1962**, *42*, 28.

(28) Moriguchi, I.; Teraoka, Y.; Kagawa, S. *Langmuir* **1992**, *8*, 1431.

(29) Salvador, P. *Solar Energy Mater.* **1982**, *6*, 241.

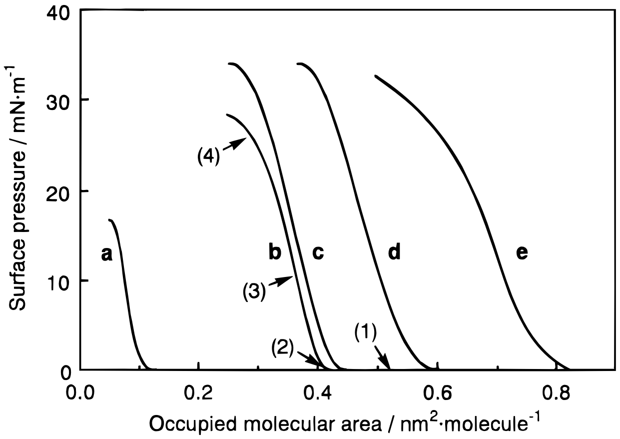

Figure 2. Surface pressure−area (π−A) isotherms of (a) tetrabutoxytitanium (TBT) monomer, (b−d) TBT tetramer, and (e) a 4:1 mixture of acetylacetone and TBT tetramer at 288 K on water subphases; (a, b, e) on pure water, (c) on 0.01 M aqueous acetic acid, (d) on 0.01 M aqueous acetylacetone. (1−4) compression stages at which fluorescence images shown in Figure 3 were taken.

XPS analysis was performed by alternative repeats of the spectra acquisition and the Ar$^+$ sputtering (2.0 kV, 25 mA). The depth profile was measured on sol−gel-derived TiO_2 films of known thickness, and the sputtering rate (30 ± 2 Å min^{-1}) was obtained from the thickness and time necessary for the 50% reduction of the XPS intensity. Note that the estimated film thickness was identical when using sputtering rates based on 50% and 90% reduction. X-ray diffraction (XRD) patterns of films deposited on borosilicate glass substrates were taken with a Rigaku LINT-2200 instrument using Cu Kα radiation.

Results and Discussion

Preparation of Titanium Oxide-Based Gel Films at an Air/Water Interface. Titanium oxide-based gel films were formed by a 2D hydrolysis/condensation reaction (step 1 in Figure 1) and subsequent 2D compression (step 2) on the subphase surface of the LB trough. These steps were investigated by the measurement of π−A isotherms (Figure 2) and fluorescence images of the gel film (Figure 3).

When a chloroform solution of TBT tetramer was spread on a surface of pure water, floating laminar islands were observed by fluorescence microscopy at zero surface pressure (Figure 3, panel 1). Upon compression they gathered (panel 2), forming a featureless homogeneous film at surface pressures between 10 and 20 mN m^{-1} (panel 3). This pressure range corresponds to the “solidus” region of the π−A isotherm (Figure 2b). Above 20 mN m^{-1}, the π−A isotherm leveled off and the film collapsed and overlapped to change into a striped heterogeneous film as shown in panel 4. The apparent molecular area was estimated to be 0.4 nm^2 molecule^{-1} by extrapolating the linear portion of the solidus line to the zero surface pressure. This value is much smaller than the molecular area of the TBT tetramer (more than 2.0 nm^2 molecule^{-1}),[10] suggesting that the film formed on the water surface is not a molecular monolayer of the TBT tetramer. The IR spectrum of the same film deposited on a CaF_2 substrate showed C−H stretching vibrations at 2964, 2924, and 2851 cm^{-1} and a Ti−O−C stretching vibration at about 1100 cm^{-1}.[3] An elemental analysis of a sample of the vacuum-dried gel revealed that the content of C and H (C 3.10, H 2.52) were much less than those expected for the TBT tetramer (C 49.48, H 9.28). Assuming the general formula of the gel as $TiO_x(OH)_y(OC_4H_9)_z$ ($2x + y + z = 4$), the rational formula of $TiO_{0.88}(OH)_{2.16}(OC_4H_9)_{0.08}$ was suggested. These findings clearly show that at adequate surface pressures (“solidus” region of the π−A isotherm) the TBT tetramer is hydrolyzed and polycondensed on the surface of pure water to give a homogeneous gel film with residual butoxy groups and that the observed increase in surface pressure is due to the two-dimensional aggregation of floating hydrolyzed condensates. The reproducibility of the π−A isotherm indicates that the hydrolysis and condensation reactions are well controlled under the present experimental conditions.

The monomer of TBT also gave a π−A isotherm on pure water, with the apparent area per molecule a quarter of, or per Ti atom equal to, that of the TBT tetramer (Figure 2a), suggesting that the monomer and the tetramer of TBT give almost the same hydrolyzed condensates. On the other hand, no increase in surface pressure with decreasing area was observed with the TET monomer, which is more reactive toward hydrolysis and less hydrophobic than TBT. Accordingly, it appears that the hydrophobicity of the residual butoxy groups in the condensate, and possibly also the lower reactivity of the butoxide, are necessary for formation of floating hydrolyzed condensates.

It is well-known that acetic acid and acetylacetone can suppress the hydrolysis and condensation reactions of metal alkoxides in solution.[3,4,30] Such a suppression effect was investigated in the above 2D sol−gel process. As can be seen from the π−A isotherms (Figure 2c,d), addition of acetic acid and acetylacetone to the subphase increases the apparent molecular area and the collapse pressure by comparison with pure water. Since these two parameters were scarcely affected when the pH of the subphase was adjusted by addition of HCl or NaOH, the effect of adding acetic acid or acetylacetone likely originates from their chelation to Ti atoms. The increased apparent molecular area suggests suppression of hydrolysis and condensation reactions at the air/water interface. In this latter sense, acetylacetone was more effective than acetic acid. The increased collapse pressure, on the other hand, indicates increased stability of the gel film. Fluorescence microscopy of the gel film formed on aqueous acetic acid showed a continuous and homogeneous film at surface pressures between 5 and 25 mN m^{-1} and gel film collapse above 30 mN m^{-1}. It should be noted that the range of surface pressures at which a homogeneous floating gel film is formed is extended to lower and higher values by the addition of acetic acid or acetylacetone to the subphase.

Incorporation of acetic acid and acetylacetone in the gel film was confirmed by the presence C−O stretching (1260 cm^{-1}) and C−H stretching (2800−3000 cm^{-1}) bands in the IR spectrum. Chelation of these molecules to Ti could not be confirmed because the C=O bands sensitive to chelation were entirely obscured by bands assigned to water molecules coexisting in the gel. To make the chelating effect more clear, acetylacetone was mixed into the chloroform solution of the TBT tetramer in which the chelation was evidenced by the presence of IR bands of C=C stretching (1524 cm^{-1}) and C=O

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(30) Baroux-Doeuff, S.; Sancez, C. *Mater. Res. Bull.* **1994**, *29*, 1.

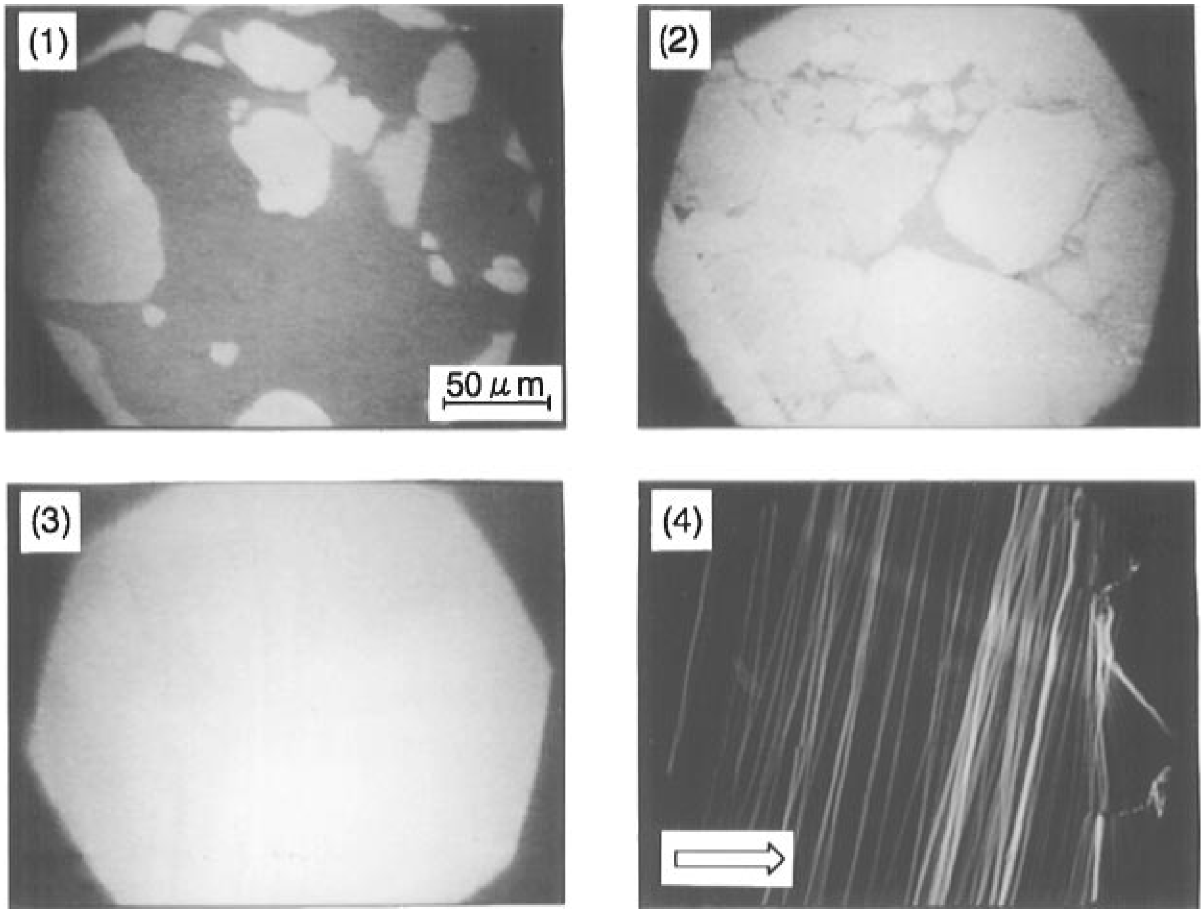

Figure 3. Fluorescence images of the tetrabutoxytitanium tetramer on pure water; panels (1−4) were taken at the compression stages indicated in Figure 2. The octagonal area represents a microscope field and the arrow in panel 4 indicates the direction of 2D compression.

stretching (1577 cm^{-1}) due to the β-enol group, and then the mixed solution was spread on the pure water surface. In this case, the $\pi-A$ isotherm (Figure 2e) shifted further to the large molecular area direction as compared with Figure 2d. This clearly indicates that chelation to Ti causes the apparent molecular area to increase in the $\pi-A$ isotherm. When the solution of the TBT tetramer was spread on the aqueous subphase of chelating agents, acetylacetone and acetic acid, chelation reactions on the subphase compete with hydrolysis/condensation of the TBT tetramer, and the observed increase in the apparent molecular area is smaller than observed above.

It can thus be concluded that the addition of chelating agents such as acetic acid and acetylacetone is effective in increasing the apparent molecular area and collapse pressure and therefore in increasing the stability of the floating gel films formed on the subphase. Such stabilizing effects were not observed for the TET monomer which did not form the gel film on chelating agent-free subphases.

Deposition of Gel Films onto Substrates. The homogeneous and densely packed floating film of TiO_2-based condensates, which are formed by the 2D hydrolysis/condensation reactions and subsequent compression at the air/water surface, should be a favorable precursor of ultrathin films of TiO_2 if it can be transferred onto substrates. The transfer of a floating gel films from the water subphase onto a given substrate (step 3 in Figure 1) was achieved using a vertical dipping method.

$A-t$ curves of the gel film of TBT tetramer were measured on subphases of pure water and aqueous acetic acid at surface pressures between 10 and 20 mN m^{-1}. After reaching the steady state within ca. 15 min, no change in the area was observed for a few hours, indicating that the floating gel films are stable on the aqueous subphase. However, the gel film of the TBT tetramer on pure water could not be transferred quantitatively onto substrates as shown in Figure 4a. The deposited gel film from the surface of pure water at 10 mN m^{-1} showed a heterogeneous fluorescence image like panel 4 of Figure 3. These results show that the gel film on pure water is unstable against the transfer process. By contrast, the gel film on aqueous acetic acid was successfully transferred onto substrates with a transfer ratio of unity only at every upstroke (Figure 4b), and the fluorescence image showed that the homogeneous state of the floating film was preserved in the deposited film on the substrate. The same deposition behavior was also observed on the aqueous acetylacetone subphase. The addition of chelating agents to the subphase was found to be effective in establishing a stable deposition of the gel film onto substrates as well as to yield a stable floating gel film as mentioned above. The quantitative deposition from aqueous subphases of acetic acid and acetylacetone was possible for up to 20 layers. Above 20 layers, however, the deposition behavior became irregular.

The TiO_2-based gel films, prepared from TBT tetramer on an aqueous acetic acid subphase and deposited on quartz, were characterized by UV−vis spectroscopy.

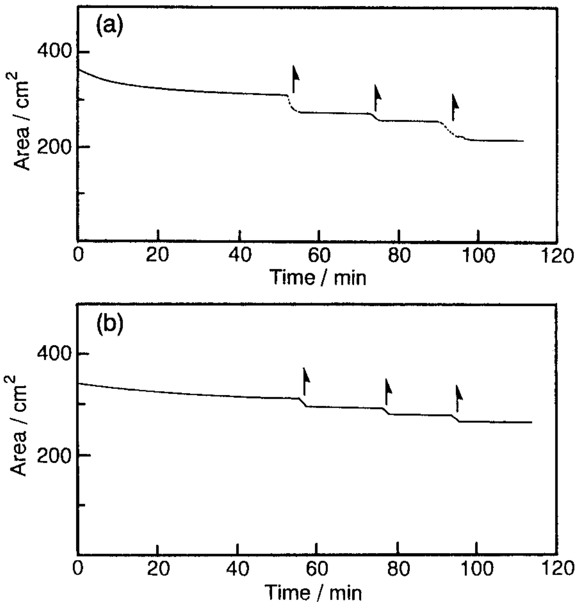

Figure 4. Time course of area at 10 mN m^{-1} of TiO_2-based gel films derived from tetrabutoxytitanium tetramer on (a) pure water and (b) 0.01 M aqueous acetic acid subphases.

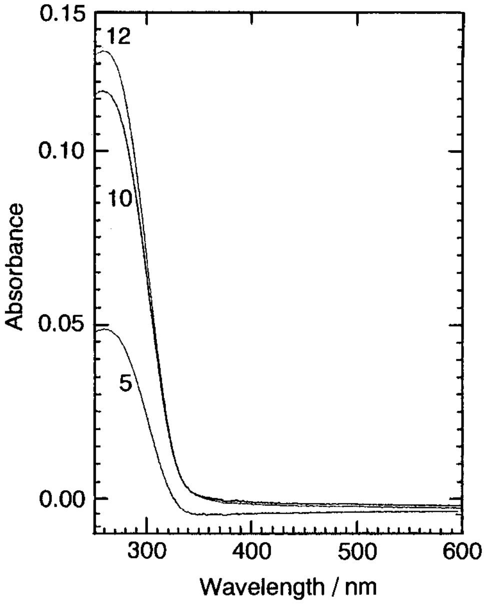

Figure 5. UV−vis spectra of TiO_2-based gel film deposited on quartz plates from 0.01 M aqueous acetic acid subphase at the surface pressure of 10 mN m^{-1}. Ti source: tetrabutoxytitanium tetramer. The number of deposited layer on each side of quartz plate are shown in the figure.

Figure 5 shows UV−vis spectra of gel films deposited at 10 mN·m^{-1}. The absorbance due to the titanium oxide-based gel increased linearly with increasing the number of deposited layers. It is noted, however, that the E_g value remained constant at 3.58 eV (Figure 6). This confirms the quantitative deposition of the titanium oxide-based gel film from the subphase surface of aqueous acetic acid. On the other hand, when the number of deposited layers was constant at 5 layers, the absorbance of deposited gel film increased with an increase in the surface pressure (Figure 7). This means that the density of the deposited gel film can be controlled by the surface pressure. Figure 7 also showed that the E_g value of TiO_2-based gel film decreased with increasing surface pressure. According to the size-quantization theory,[31,32] this indicates that the size, or the degree of polycondensation, of the TiO_2-based gel increases with an increase in the surface pressure. It has turned out that the two-dimensional compression is an important step in controlling the condition of the gel film, such as its density and the degree of polycondensation.

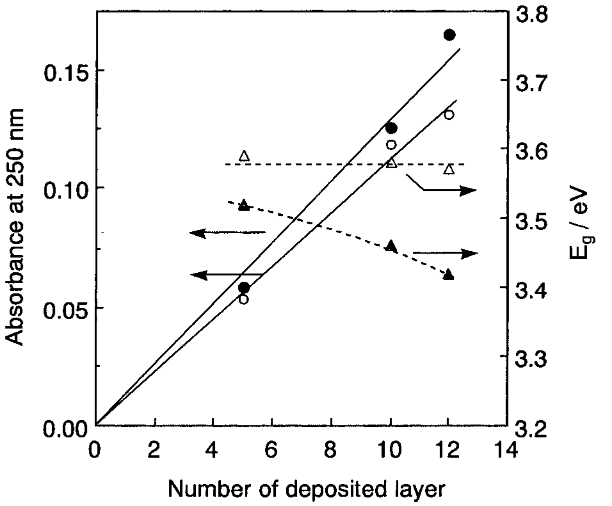

Figure 6. Dependence of UV−vis absorbance at 250 nm and absorption edge energy (E_g) on the number of deposited layers. Open and closed symbols correspond to the gel and heat-treated oxide TiO_2 films, respectively. Ti source: tetrabutoxytitanium tetramer. Deposition pressure 10 mN m^{-1} from 0.01 M aqueous acetic acid subphase.

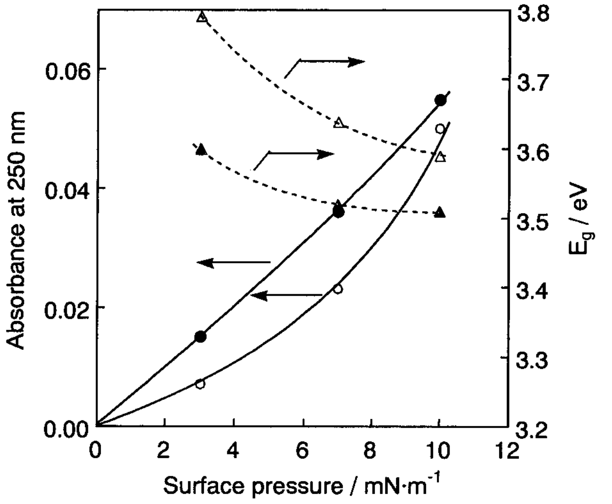

Figure 7. Dependence of UV−vis absorbance at 250 nm and absorption edge energy (E_g) on the surface pressure at LB deposition from 0.01 M aqueous acetic acid subphase. Open and closed symbols correspond to the 5-layer gel films and heat-treated TiO_2 films, respectively. Ti source: tetrabutoxytitanium tetramer.

Formation of TiO_2 Film by the Heat Treatment. The conversion of titanium oxide-based gel films into nanocrystalline TiO_2 films was carried out by heat-treatment in air. TG measurements, performed on the powder of condensates of the TBT tetramer lifted from the surface of pure water, indicated that weight loss was complete at about 773 K. The observed weight loss (22.6%) was in good agreement with that calculated

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[31] For example, Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471.

[32] Enright, B.; Fitzmaurice, D. *J. Phys. Chem.* **1996**, *100*, 1027.

(23.6%) based on the formation of TiO_2 from the rational formula mentioned above. IR measurements on CaF_2-supported gel films confirmed the disappearance of organic moieties (butoxy groups and optionally acetic acid) following the heat treatment at 573 K for 30 min. Therefore heat treatment at 773 K for 30 min was used to convert the titanium oxide-based gel film into a nanocrystalline TiO_2 film.

The absorbance and the E_g value of TiO_2 films prepared from the TBT tetramer/aqueous acetic acid system are plotted against the number of deposited layers in Figure 6. As in the gel film, a linear increase of absorbance was observed, indicating that the thickness can be controlled even in the heat-treated TiO_2 films by the number of gel layers deposited. The higher absorbance of the heat-treated film than the corresponding gel film might be due to the densification of the film. The E_g value of the heat-treated TiO_2 film decreased with increasing deposition number and was smaller than that of the corresponding gel film. The former suggests that the size of TiO_2 crystallites increases with increasing numbers of deposited layers (vide infra) and the latter corresponds to the growth of the TiO_2 crystallites by the gel-to-oxide conversion.[26,33] The effects of surface pressure during deposition are shown in Figure 7. Apart from the decrease in E_g and the increase in the absorbance by the gel-to-oxide conversion, the dependence of the absorbance and E_g on the surface pressure was essentially the same for the gel and heat-treated films. This indicates that the density of the heat-treated TiO_2 film can be controlled by the surface pressure at deposition.

Effect of Monolayer-Forming Amphiphile (C_{18}AA) on the Formation of TiO_2 Film. As stated above, the addition of chelating agents such as acetic acid and acetylacetone enhanced the stability of the gel film on the subphase and during the deposition. However, even from aqueous subphases of these chelating agents, quantitative deposition of more than 20 layers was never possible. Conventionally, the instability of a molecular film on a subphase is due to an imbalance between the hydrophobicity and hydrophilicity. In the present case, the hydrophobicity of the floating gel film is provided by the residual butoxy groups. Thus, increasing the hydrophobicity of the gel film is expected to increase its stability against deposition. *n*-Octadecylacetoacetate (C_{18}AA) was used for this purpose in this study. The C_{18}AA possesses hydrophobic C_{18} chain and a hydrophilic moiety with metal ion-binding ability, so as to form a monolayer at an air/water interface.[34]

When a 1:1 mixture of monomeric Ti alkoxide and C_{18}AA was spread on pure water, π−A isotherms were obtained with not only TBT but also TET (Figure 8c,b). The apparent molecular areas were larger than that of C_{18}AA (Figure 8a), suggesting that a gel film which was stabilized by the interaction between TET or TBT and C_{18}AA was formed on pure water. The interaction between C_{18}AA and TET was investigated by IR measurements. C_{18}AA showed two C=O stretching bands around 1750−1720 cm^{-1} which are assigned to the β-ketoester.[35] For the C_{18}AA-TET mixed gel film on a CaF_2 plate, antisymmetric C=O and perturbed C=C stretching vibrations assigned to β-enolester are observed at 1620 and 1530 cm^{-1} respectively,[36,37] although the C=O stretching IR bands due to the β-ketoester did not disappear completely. This indicates that some C_{18}AA molecules complex with Ti atoms to stabilize the floating gel film.

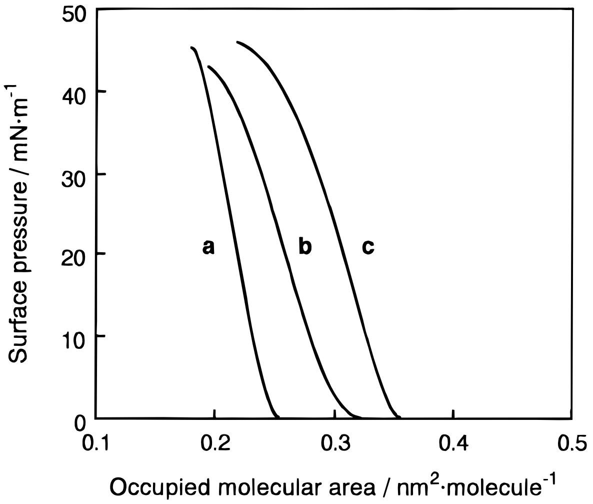

Figure 8. π−A isotherms of (a) *n*-octadecyl acetoacetate (C_{18}AA), (b) a 1:1 mixture of C_{18}AA and TET monomer, and (c) a 1:1 mixture of C_{18}AA and TBT monomer on pure water at 288 K.

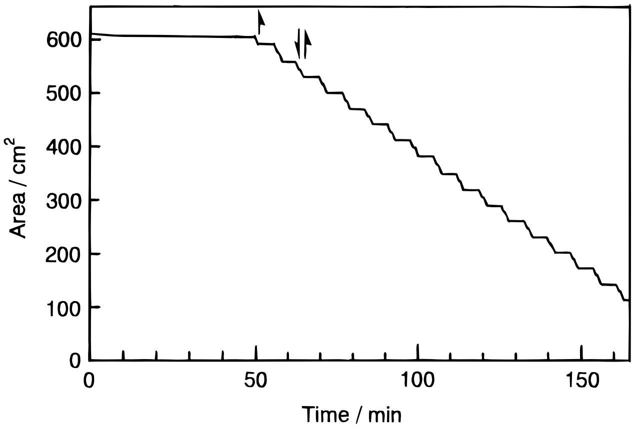

Figure 9. Time course of area (A−t curve) at 20 mN m^{-1} of a TBT monomer−C_{18}AA mixed gel film on pure water at 288 K. Arrows indicate the direction of dipping stroke of substrate.

Figure 9 shows an A−t curve of the TBT monomer−C_{18}AA mixed gel film on pure water during the deposition at 20 mN m^{-1}. The mixed gel films were transferred onto a borosilicate glass substrate quantitatively with a transfer ratio of unity and without any apparent limit on the number of layers that may be deposited. Similar deposition behavior was observed for all substrates used. In the first deposition, the film transfer was observed only on the upstroke due to the hydrophilic nature of the substrate surface. After the second dipping however, the film transfer was observed both on the down- and upstrokes, or as a Y-type (head-to-head and tail-to-tail) film. The deposition behavior of the system containing C_{18}AA suggests an improved

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(33) Kavan, L.; Stoto, T.; Gratzel, M.; Fitzmaurice, D.; Shklover, V. *J. Phys. Chem.* **1993**, *97*, 9493.

(34) Moriguchi, I.; Nii, H.; Hanai, K.; Nagaoka, H.; Teraoka, Y.; Kagawa, S. *Colloids Surf. A* **1995**, *103*, 173.

(35) Bellamy, L. J.; Beecher, L. *J. Chem. Soc.* **1954**, 4487.

(36) Bellamy, L. J.; Branch, R. F. *J. Chem. Soc.* **1954**, 4491.

(37) Yamamoto, A.; Kambara, S. *J. Am. Chem. Soc.* **1957**, *79*, 4344.

balance between the hydrophobicity and hydrophilicity of the floating gel film by incorporation of $C_{18}AA$ chemically binding to the Ti atom.

The UV–vis absorbance of the mixed gel film deposited onto a quartz plate increased linearly with the number of deposited layers, suggesting quantitative transference. The deposited TBT monomer–$C_{18}AA$ mixed gel film showed (00l) XRD peaks up to $l = 4$, from which the periodic long spacing (d) was calculated to be about 62 Å. The d spacing was as twice as the molecular length of $C_{18}AA$ which was roughly estimated on the basis of the molecular structure, being consistent with the Y-type configuration.

The conversion of the TBT monomer–$C_{18}AA$ mixed gel film into a TiO_2 film was also carried out by heat-treatment at 773 K for 30 min. It was confirmed that the IR peaks of $C_{18}AA$ in the mixed gel films disappeared completely after the heat-treatment. The UV absorbance and thus the thickness of the heat-treated TiO_2 film increased linearly with an increase in the number of depositions up to 100 layers. The E_g value of the heat-treated TiO_2 film decreased with the number of deposited gel film layers as 3.36 eV (20 layers), 3.23 eV (50 layers) and 3.20 eV (100 layers).

Characterization of TiO_2 Films. Depth-profiling XPS analysis was performed on TiO_2 films prepared from gel-films in TBT tetramer/aqueous acetic acid and TBT monomer–$C_{18}AA$ systems in order to evaluate the film thickness. In both the gel and oxide films, Ti $2p_{3/2}$ XPS signals were observed at around 458.5 eV, which is consistent with the reported value for TiO_2.[38] As can be seen from the depth-profile of the TiO_2 film prepared from a 100-layer TBT monomer–$C_{18}AA$ mixed gel film (Figure 10), the intensity of the Ti $2p_{3/2}$ signal decreased with an increase in the sputtering time, while the intensity of the Si 2p signal of the quartz plate at 103.5 eV increased. The thickness of TiO_2 films evaluated from the depth-profiling XPS analysis was summarized in Table 1.

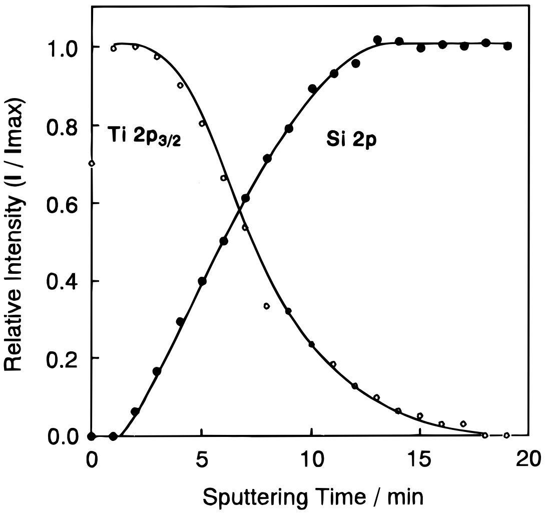

Figure 10. Depth profiling XPS analysis of quartz-supported TiO_2 film prepared from TBT monomer–$C_{18}AA$ mixed gel film (100-layer). I_{max} of Ti $2p_{3/2}$ and Si 2p are intensities at sputtering times of 1 and 19 min, respectively.

Table 1. Thickness (Å) of TiO_2 Films Prepared by the 2D Sol–Gel Method

precursor gel film	evaluation by XPS	evaluation by UV
10-layers from the TBT tetramer/ aqueous acetic acid system	30	27
15-layers from the TBT tetramer/ aqueous acetic acid system	43	
100-layers from the TBT monomer–$C_{18}AA$ system	200	224

The TiO_2 film thickness was also evaluated from the UV–vis absorbance (Abs) of TiO_2 by using the following general relation:[39,40]

$$\alpha = 2.303\rho Abs/lCM_w \qquad (1)$$

where α, ρ, C, and M_w are the absorption coefficient, the TiO_2 density (3.9 g cm^{-3}), the loading of the TiO_2 in g cm^{-3} and molecular weight of TiO_2 (=79.9 g mol^{-1}), respectively, and l the optical path length. Assuming that the TiO_2 film under discussion is a nonporous film with the average thickness of t and taking account of the fact that the film was formed on both sides of the substrate ($l = 2t$), eq 1 can be simplified as

$$t = 2.303Abs/2\alpha \qquad (2)$$

According to Kormann et al.,[39] the absorption coefficient of TiO_2 colloids was not affected by the size of the TiO_2 colloids in the photon energy range above ca. 4.5 eV. Thus, the film thickness was calculated by eq 2 by using the observed Abs value and reported α value[39] of 1.6×10^{13} cm^{-1} at 250 nm (4.96 eV). As can be seen from Table 1, the calculated thicknesses are in good agreement with those evaluated by the XPS depth-profiling.

Since the UV–vis absorbance of the TiO_2 film increased linearly with the number of deposited gel film layers, these results strongly suggest that in the present 2D sol–gel process the film thickness could be controlled, in principle down to levels as thin as 2–3 Å. Desu reported the preparation of ultra-thin TiO_2 films on silica and silicon substrates by gas-phase, layerwise, chemisorption which was consisted of two gas-phase steps of the reaction of $TiCl_4$ with the surface silanols and subsequent hydrolysis.[41] He stated that the film thickness of the TiO_2 films could be controlled to 2.7 Å/cycle, close to the size of the Ti–O octahedron (2.8 Å). The thickness controllable by one deposited gel layer in the 2D sol–gel process is comparable to that of one cycle of layerwise chemisorption.

Figure 11 shows the relation between the number of deposited gel-layers and the E_g value of calcined TiO_2 films prepared from the TBT tetramer/aqueous acetic acid and TBT monomer–$C_{18}AA$ systems. Irrespective of the precursor gel film layers, the E_g value decreased with an increase in the number of deposited layers, indicating that the size of TiO_2 particles in the films increases as the number of deposited gel films increases. At 50 (3.23 eV) and 100 (3.20 eV) gel layers, E_g values were consistent with that of bulk anatase-type TiO_2 (3.20 eV).[42] Below 20 gel layers, E_g values were greater

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(38) Andersson, S. L. T. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1356.

(39) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *J. Phys. Chem.* **1988**, *92*, 5196.

(40) Bahnemann, D. W. *Isr. J. Chem.* **1993**, *33*, 115.

(41) Desu, S. B. *Mater. Sci. Eng.* **1992**, *B13*, 299.

(42) Cox, P. A. *Transition Metal Oxides*; Oxford Science Publications: New York, 1992.

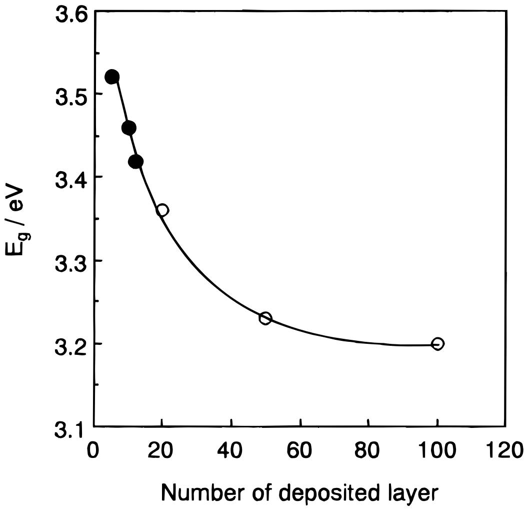

Figure 11. Relation between the absorption edge energy (E_g) and the number of deposited gel layers of TiO_2 films prepared from TBT tetramer/aqueous acetic acid (closed symbols) and TBT monomer−$C_{18}AA$ (open symbols) systems.

than reported values of TiO_2 fine particles (3.35 eV for 24-Å anatase,[39] 3.31 eV for 38-Å anatase, and 3.12 eV for 55-Å rutile[43]). Accordingly, it has been suggested that the TiO_2 films, which are prepared from deposited gel films of less than 50 layers by the 2D sol−gel process, are composed of size-quantized TiO_2 particulates. Investigations are now in progress concerning the size-quantization effect in this system, including direct observations of film surface and TiO_2 particles by microscopy, etc.

Conclusions

The present study disclosed that the 2D sol−gel process is an entirely new version of sol−gel chemistry. As compared with the conventional solution sol−gel process, the 2D sol−gel process is characterized by the two-dimensionally controlled reactions of hydrolysis and condensation at the air/water interface. The uniform floating gel films formed on the water surface are successfully transferred onto substrates by Langmuir−Blodgett (LB) technique. From the technological point of view, the process is a potential and promising chemical process to synthesize metal oxide films of a nanoscale thickness.

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 to allow the hydrolysis and condensation reactions to take place at the air/water interface in a two-dimensionally controlled fashion. In this sense, the effect of *n*-octadecyl acetoacetate ($C_{18}AA$) seems to be fascinating, since it improves the stability of gel films floating on the subphase surface to leading to successive and quantitative depositions of gel films onto substrates. Moreover, this process has some potential for the construction of mixed oxide nanofilms and hetero-multilayers since the technique is based on the molecular reactions of precursor molecules and the layer-by-layer deposition of the LB technique.

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(43) Anpo, M.; Shima, T.; Kodama, S.; Kubokawa, Y. *J. Phys. Chem.* **1987**, *91*, 4305.