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A Surface Sol−Gel Process of TiO_2 and Other Metal Oxide Films with Molecular Precision

Izumi Ichinose, Hiroyuki Senzu, and
Toyoki Kunitake*

Department of Chemical Science & Technology
Faculty of Engineering, Kyushu University
Hakozaki, Fukuoka 812, Japan

Fabrication of metal oxide thin films with thickness control to nanometer precision is an important technology which leads to wide applications in future.[1] Several different techniques based on the layer-by-layer growth have been developed for this purpose in recent years. For example, regular growth of metal oxide films with atomic precision has been accomplished by sequential surface chemical reactions using chemical vapor deposition technique.[2] Chemisorbed surfaces of vapors of metal halides or metal alkoxides can be reactivated for the subsequent adsorption by treatment with hydrogen peroxide and water vapor or by light-induced and thermal decompositions. A similar chemisorption/reactivation approach has been applied to the preparation of one-atomic-layer metal oxides and thin-layer oxide catalysts.[3]

Preparative techniques for oxide thin films via wet procedures are even more abundant. Langmuir−Blodgett multilayers of poly(dimethylsiloxane) or titanium alkoxide derivatives built up from the air/water interface have been converted to oxide nanofilms by low-temperature plasma treatment, UV ozone exposure or heating.[4] Alternate adsorption of oppositely charged colloidal particles[5] has been extended to assembling of two-dimensional, charged inorganic sheets or polyoxometallate ions.[6] Stepwise adsorption of self-assembled monolayers, as pioneered by Sagiv, Ulman, and their co-workers,[7] was recently used as a preparative technique of ultrathin oxide films by Brunner et al.,[8] where assembly of alkylsiloxane monolayers from solution and the subsequent UV ozone oxidation resulted in layer-by-layer growth of SiO_x thin films with atomic precison.

We recently reported the preparation of ultrathin films of metal oxides by means of stepwise adsorption of alkoxides.[9] This "surface sol−gel process" is composed of four steps: chemisorption of alkoxide, rinsing, hydrolysis of the chemisorbed alkoxide, and drying (Figure 1a), and is applicable to a wide range of alkoxides. We describe herein a plausible mechanism for the film growth as well as the structural characterization by scanning electron microscopy, quartz crystal microbalance (QCM), and X-ray photoelectron spectroscopy.

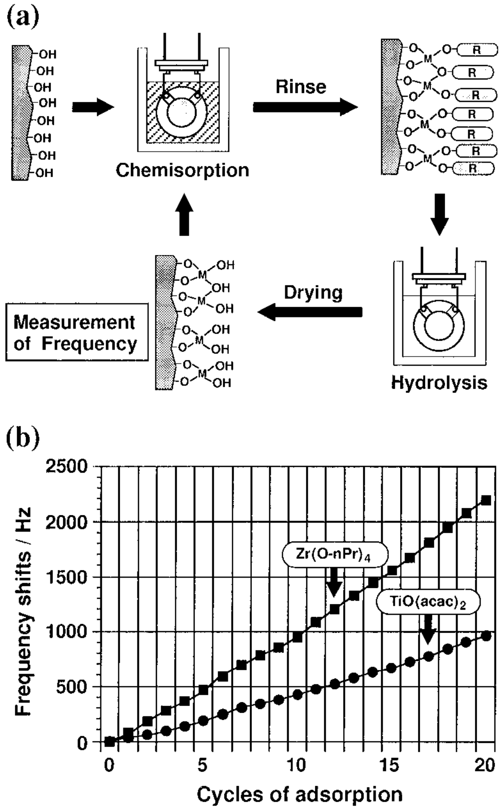

Figure 1. Sequence of the surface sol−gel process (a) and QCM frequency shifts ($-\Delta F$) (b). (■) $Zr(O^nPr)_4$ (100 mM in toluene/propanol = 1/1, 10 °C), (●) $TiO(acac)_2$ (20 mM in methanol containing 300 mM of acetic acid, 60 °C).

A gold-coated QCM resonator (9 MHz) modified with mercaptoethanol[10] was immersed in metal alkoxide solutions for 3−10 min and rinsed in appropriate solvents. The resonator was then, in most cases, immersed in pure water for 1 min, dried with nitrogen gas, and used for the next adsorption cycle. Figure 1b shows frequency changes of the QCM at each adsorption cycle. The frequency shift of QCM is proportional to the mass of the oxide thin film adsorbed on the electrode,[11] and the decrement of 1 Hz corresponds to the thickness increase of 0.011−0.018 nm in the range of the film density (=ρ) of 1.5−2.5 g/cm^3, as given by

$$2d\ (\text{Å}) = -\Delta F\ (\text{Hz})/1.83\rho\ (\text{g/cm}^3) \qquad (1)$$

The linear frequency decrements in Figure 1b indicate regular film growth at nanometer scale during consecutive adsorption cycles.

Conditions and results of the stepwise adsorption of various compounds are summarized in Table 1. The adsorption of these compounds was uniform for at least

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(10) QCM resonator was immersed in mercaptoethanol solution (10 mM in ethanol) for 12 h, rinsed with ethanol, and dried with nitrogen gas. This surface modification is required for the reproducible adsorption of alkoxides.

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Table 1. Conditions of Stepwise Adsorption and QCM Frequency Changes

	adsorption		hydrolysis		
compd	concn/solvent[a]	immersion time/temp	solvent	immersion time/temp	frequency change
$Zr(O^nPr)_4$	100 mM/T−P	3 min/10 °C	water	1 min/10 °C	109 ± 57 Hz
$Ti(O^nBu)_4$	100 mM/T−E	10 min/18 °C	water	1 min/18 °C	61 ± 37 Hz
$Al(O^nBu)_3$	88 mM/E−C	10 min/45 °C	water	1 min/45 °C	272 ± 90 Hz
$B(OEt)_3$	300 mM/benzene	5 min/20 °C			517 Hz[c]
$TiO(acac)_2$	20 mM/methanol[b]	5 min/60 °C	aq. NaOH (pH = 12)	1 min/20 °C	48 ± 35 Hz

[a] T−P, toluene/propanol = 1/1; T−E, toluene/ethanol = 1/1; E−C, ethanol/carbon tetrachloride = $^2/_3$. [b] Methanol containing 300 mM of acetic acid. [c] Average frequency change for 20 cycles.

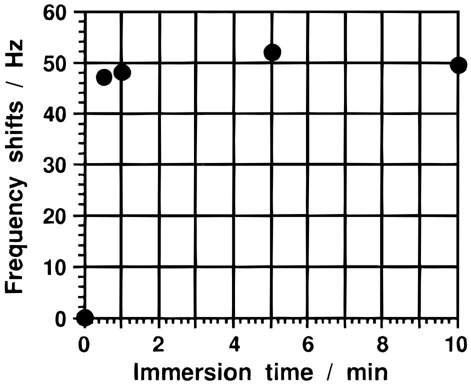

Figure 2. Immersion time dependence of QCM frequency shift for $Ti(O^nBu)_4$ adsorption[13] (100 mM in toluene/ethanol = 1/1, 16 °C).

20 cycles. In the case of $Zr(O^nPr)_4$, regular film growth was observed only at low temperature with a frequency change of 109 ± 57 Hz in each cycle (Figure 1b). Adsorption of $Ti(O^nBu)_4$ is similar to that of $Zr(O^nPr)_4$, and the frequency change is 61 ± 37 Hz at 18 °C. On the other hand, $Al(O^nBu)_3$ does not adsorb at room temperature due to its lower reactivity. Reproducible adsorption was, however, achieved when the chemisorption and hydrolysis procedures were performed at 45 °C. The large frequency change of 272 ± 90 Hz indicates that the $Al(O^nBu)_3$ formed oligomers in stock solutions, and they were adsorbed on the hydrolyzed surface without disaggregation.[12] $B(OMe)_3$ chemisorbed on a surface is readily desorbed upon hydrolysis in water. Instead, the chemisorbed surface can be hydrolyzed with humidity in air, and the stepwise adsorption is achieved by repeating the chemisorption and rinsing alone. Chemicals useful in the surface sol−gel process is not restricted to alkoxides. Their requirements are chemisorption on surface hydroxyl groups and regeneration of the hydrodxyl groups after the hydrolysis. For example, $TiO(acac)_2$ is repeatedly adsorbed, when acetic acid and NaOH are added to the adsorption and hydrolysis media, respectively (Figure 1b).

Figure 2 shows an influence of immersion time on frequency shift in $Ti(O^nBu)_4$ adsorption.[13] The adsorption is saturated in 1 min and gives a constant frequency shift of ca. 50 Hz. The elemental composition of this film was estimated by XPS measurement as Ti:C:O = 1.0:5.1:4.2 and indicates that the film is made of a TiO_2-based gel including unhydrolyzed alkoxyl groups. Assuming the titanium content of 27 wt % so as to satisfy the XPS data,[14] the shift of 50 Hz corresponds to surface titanium density of 4.8 atoms/nm^2. Using the bulk density (1.7 g/cm^3) of TiO_2-based gel,[15] the frequency shift also corresponds to a thickness increase of 8 Å from eq 1. These results indicate either that adsorption of $Ti(O^nBu)_4$ is terminated upon monolayer formation or that the amount of adsorbed alkoxide is restricted by the number of surface hydroxyl groups. In any case, a uniform hydroxyl surface is reproduced after each hydrolysis procedure. Compositions of ultrathin films prepared from $Zr(O^nPr)_4$ and $Al(O^nBu)_3$ are Zr:C:O = 1.0:3.7:4.0 and Al:C:O = 1.0:2.0:1.9, respectively. The former film seems to have an unhydrolyzed alkoxyl group similarly with TiO_2-based film. In the latter film, hydrolysis and condensation reactions have proceeded more than the other two films, as judged from the aluminum/carbon ratio.

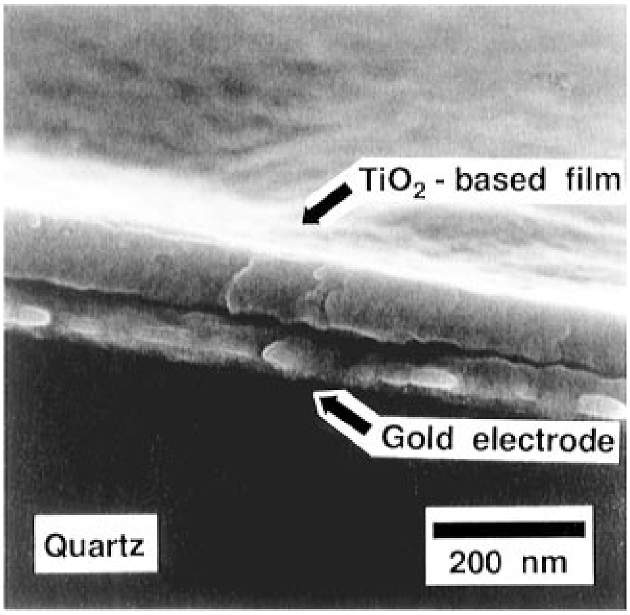

Figure 3. Scanning electron micrograph of TiO_2-based film on Au-coated resonator (×53 000). Total frequency shift 5221 Hz.

Figure 3 shows a scanning electron micrograph of the cross section of a TiO_2-based film deposited onto a gold-coated QCM resonator.[16] The film has a constant thickness of 900 ± 100 Å, and the surface is smooth over a large area. The film density is estimated as 1.6 g/cm^3

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[12] Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.

[13] Average frequency changes of the first five cycles were plotted for each immersion time.

[14] Formula of $TiO_2(BuOH)(H_2O)$ (MW 172) was supposed as the composition of TiO_2-based gel.

[15] We prepared a TiO_2-based gel by hydrolysis of $Ti(O^nBu)_4$ in ethanol. The precipitates were separated, dried in vacuo, and finely ground. The bulk density (1.7 g/cm^3) of the dried gel was directly measured in toluene.

[16] TiO_2-based film was prepared from $Ti(O^nBu)_4$ including 0.67 equiv of water by the procedure descrived in ref 9.

from the thickness and the total frequency shift (5221 Hz). This value is close to the bulk density of TiO_2-based gel prepared by conventional methods.[15]

The present study demonstrates that the surface sol–gel process is a superior technique for the preparation of ultrathin films of metal oxide-based gels with molecular precision. The regular film growth is achieved by repetition of saturated adsorption of alkoxides and subsequent regeneration of a uniform hydroxyl surface. This process can be, in principle, applied to the surface of complicated morphologies including the inner surface of porous materials. The simplicity of this process is a great advantage in commercial production of nanosized oxide films.

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