Stepwise Adsorption of Metal Alkoxides on Hydrolyzed Surfaces : A Surface Sol-Gel Process

Izumi Ichinose, Hiroyuki Senzu, and Toyoki Kunitake*
Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812

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Ultrathin films of TiO_2-based gel were prepared by repeating adsorption of titanium(IV) butoxide ($Ti(O\text{-}nBu)_4$) and subsequent hydrolysis of the surface. Linear film growth was observed for at least 20 cycles, as monitored by quartz crystal microbalance (QCM). Similar thin films were prepared from aluminum(III) butoxide ($Al(O\text{-}nBu)_3$), zirconium (IV) propoxide ($Zr(O\text{-}nPr)_4$), niobium(V) butoxide ($Nb(O\text{-}nBu)_5$), tetramethyl orthosilicate ($Si(O\text{-}Me)_4$), and their combinations.

Preparative techniques of metal-oxide thin films of nanoscale thickness are rapidly developing in recent years. Alternate adsorption of oppositely-charged polymers[1] has been extended to assembling of two-dimensionally charged inorganic sheets or polyoxometallate ions.[2] Moriguchi et al. prepared TiO_2 thin films by build-up of monolayers of TiO_2-based gel formed at the air / water interface, and subsequent heating.[3] Similar thin films were prepared by oxygen plasma or UV-ozone treatment of LB multilayers of poly(dimethylsiloxane) derivatives.[4]

Controlled growth of metal-oxide thin films with atomic precision has been accomplished by sequential surface chemical reactions using the CVD technique.[5] Chemisorbed surfaces of metal halide or metal alkoxide vapors can be reactivated for the subsequent adsorption by hydrogen peroxide, water vapor, light, or thermal decomposition. One-atomic-layer metal-oxides and thin-layer oxide catalysts have also been prepared by stepwise adsorption process composed of the impregnation of alkoxide, thermal decomposition, and hydration of the surface.[6] In the latter case, regular film growth is, however, not explicitly discussed.

We describe herein a new method for the preparation of ultrathin films of metal oxides by means of stepwise adsorption of alkoxides. This process is composed of chemisorption of alkoxides, rinse, hydrolysis of the chemisorbed alkoxides, and drying (Figure 1a), and gives the first example of highly controlled film growth by totally wet procedures. QCM measurement was used for monitoring of the film growth upon repetition of these procedures.

A gold-coated QCM resonator (9 MHz) modified with mercaptoethanol[7] was immersed in metal alkoxide solution for 3 - 10 min and rinsed in appropriate solvents. The resonator was then immersed in pure water for 1 min, dried with nitrogen gas, and used for the next adsorption cycle. Figure 1b shows

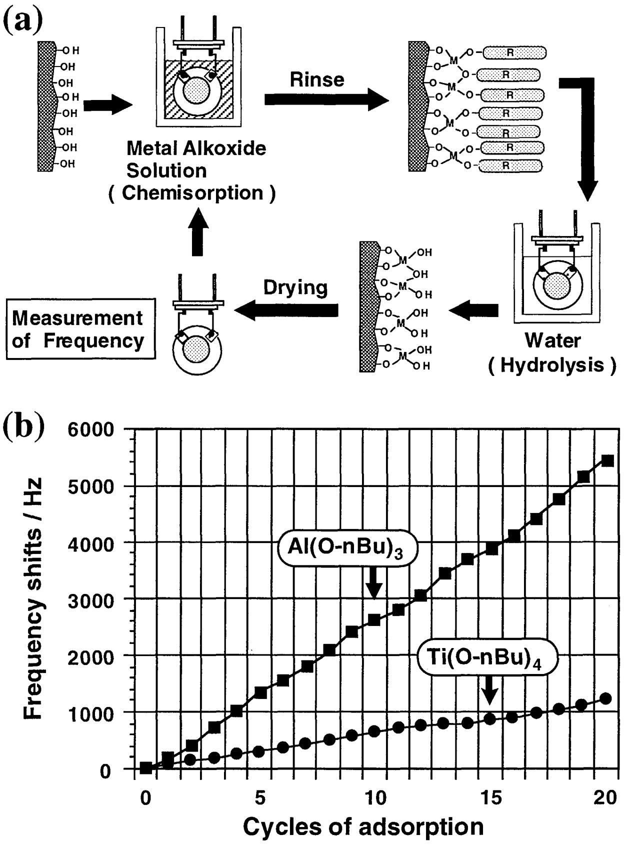

Figure 1. Schematic representation of the surface sol-gel process (a), and QCM frequency shifts (-ΔF) (b). (●) $Ti(O\text{-}nBu)_4$ (100 mM in toluene / ethanol = 1 / 1, 18 ℃), (■) $Al(O\text{-}nBu)_3$ (88 mM in ethanol / carbon tetrachloride = 2 / 3, 45 ℃).

Table 1. Stepwise adsorption of metal alkoxides

Metal Alkoxide	Concentration / Solvent[a]	Immersion Time / Temperature[b]	Frequency Change	Metal Alkoxide	Concentration / Solvent[a]	Immersion Time / Temperature[b]	Frequency Change
$Ti(O\text{-}nBu)_4$	100 mM / T-E	10 min / 18 ℃	61±37 Hz	$Ti(O\text{-}nBu)_4$ + $2/3H_2O$	100 mM / T-E	10 min / 20 ℃	278 Hz[c,e]
$Al(O\text{-}nBu)_3$	88 mM / E-C	10 min / 45 ℃	272±90 Hz				
$Zr(O\text{-}nPr)_4$	100 mM / T-P	3 min / 10 ℃	109±57 Hz	$Ti(O\text{-}nBu)_4$ + $1H_2O$	100 mM / T-E	10 min / 20 ℃	440 Hz[c,e]
$Nb(O\text{-}nBu)_5$	10 mM / T-E	5 min / 20 ℃	35 - 397 Hz[c]	$Ti(O\text{-}nBu)_4$ + $2H_2O$	100 mM / T-E	10 min / 20 ℃	1812 Hz[d,e]
$Si(O\text{-}Me)_4$	50 vol% / M	10 min / 50 ℃	230 Hz[e]				

[a] T-E; toluene / ethanol = 1 / 1, E-C; ethanol / carbon tetrachloride = 2 / 3, T-P; toluene / propanol = 1 / 1, M; methanol. [b] Adsorption, rinse and hydrolysis procedures were carried out at the same temperature. [c] Alkoxide solution was renewed once. [d] Alkoxide solution was renewed four times. [e] Average frequency change for 20 cycles.

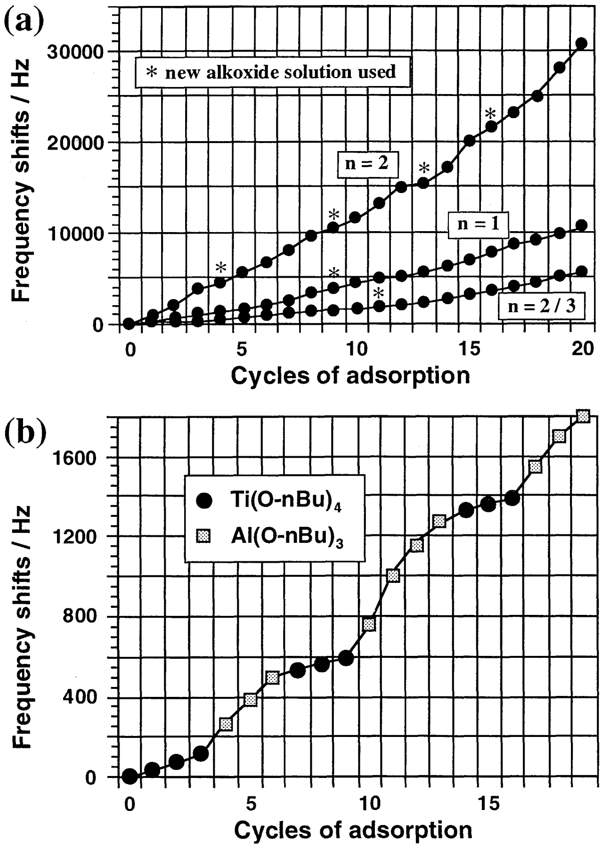

Figure 2. QCM frequency shifts. (a) $Ti(O\text{-}nBu)_4$ adsorption in the presence of water; $\mathbf{n}$ = H_2O / $Ti(O\text{-}nBu)_4$, (b) alternate adsorption of $Ti(O\text{-}nBu)_4$ and $Al(O\text{-}nBu)_3$. The adsorption conditions are given in Table 1.

frequency decrements of the QCM at each adsorption cycle. The linear frequency shifts indicate regular film growth on the electrode during consecutive adsorption cycles. The frequency change for $Ti(O\text{-}nBu)_4$ adsorption is 61±37 Hz in each cycle. Using the bulk density (1.7 g/cm^3) of TiO_2-based gel for the adsorbed film,[8] the ΔF value of 61±37 Hz corresponds to a thickness increase of 10±6 Å from eq. (1).[9] The film prepared

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

by repeated adsorption has a uniform thickness, as confirmed by SEM observation. The measured thickness agrees with the thickness estimated from the total frequency shift and the bulk density. $Al(O\text{-}nBu)_3$ can not adsorb at room temperature due to the lower reactivity. The reproducible adsorption was, however, achieved when the chemisorption and hydrolysis procedures were performed at 45 ℃. The large frequency change of 272±90 Hz indicates that the $Al(O\text{-}nBu)_3$ formed oligomers in stock solutions and they were adsorbed on the hydrolyzed surface without disaggregation.[10]

Adsorption results of other metal alkoxides are summarized in Table 1. In the case of $Zr(O\text{-}nPr)_4$, regular film growth was observed even at 10 ℃, with a frequency change of 109±57 Hz. The adsorption was uniform for at least 20 cycles. On the other hand, the frequency change in each cycle gradually increased for $Nb(O\text{-}nBu)_5$. This increase seems to arise from hydrolysis of $Nb(O\text{-}nBu)_5$ solution by humidity, as the ΔF value again decreases after renewal of the solution. $Si(O\text{-}Me)_4$ adsorption requires a stronger condition, and is less reproducible than the adsorption of $Al(O\text{-}nBu)_3$.

Figure 2a shows frequency shifts of $Ti(O\text{-}nBu)_4$ adsorption in the presence of water. The adsorption tends to be excessive after several cycles, but, by renewal of the alkoxide solution at the cycle marked with an asterisk, the original adsorption is recovered. The average ΔF values increased with the molar ratio (**n**) of water against $Ti(O\text{-}nBu)_4$, as listed in Table 1. The thicknesses estimated from these ΔF values were 46 Å (**n** = 2/3), 72 Å (**n** = 1) and ca. 300 Å (**n** = 2). These results suggest that partial condensation of alkoxides is effective for thickness control in each cycle.

Multilayered metal oxide films are readily prepared by the selection of adsorption sequence. As shown in Figure 2b, $Ti(O\text{-}nBu)_4$ and $Al(O\text{-}nBu)_3$ can be adsorbed on the other metal oxide layer. The multiple film growth is confirmed by XPS measurements at each cycle.[11]

The present study demonstrates that the surface sol-gel process is a simple and general technique for the preparation of metal oxide thin films with molecular precision. The process not only lowers the thickness limit (~1 μm) of the conventional sol-gel method but enables us to design the internal layer structure.[12] Furthermore, this process, in principle, can be applied to various material surfaces irrespective of their shape and size, if the surface is modified with hydroxyl group. Chemical versatility of the available alkoxides is also important. For these reasons, this technique shows advantages that are not achieved with previous approaches.[3-6] The investigation on the precise mechanism of the stepwise adsorption is now in progress in this laboratory.

References and Notes

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

8 TiO_2-based gel was prepared by hydrolysis of $Ti(O\text{-}nBu)_4$ in ethanol. The precipitates were separated, dried in vacuo, and finely ground. The bulk density of the dried gel was directly measured in toluene.

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11 When $Ti(O\text{-}nBu)_4$ was adsorbed on an Al_2O_3-based film, the titanium content (Ti / Al+Ti) estimated from the XPS spectra increased in proportion to the adsorption cycle of $Ti(O\text{-}nBu)_4$.

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