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Stabilization of Self-Assembled Monolayers of Carboxylic Acids on Native Oxides of Metals

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Abstract: Alkanoic acids adsorb weakly to the native oxide surface of aluminum. Treating the oxide surface first with an alkoxide of zirconium provides for strong subsequent adsorption of the alkanolic acid. The formation of an interfacial zirconium carboxylate gives rise to this strong adhesion. A combination of quartz crystal microbalance and ultrahigh-vacuum IR spectroscopic techniques were used to establish the stoichiometry and structural features of the interfacial zirconium carboxylate film.

Strong interactions between the surface of a metallic layer in a device and an organic "packaging" film can help enhance the integrity of the device and enable it to withstand failure by chemical attack or mechanical stress. In a gold-plated world, such surface "packaging" could be accomplished using alkanethiols;¹ however, alkanethiols do not adsorb to the surface of many metals important in electronics or structural applications in part because such metals are covered with a hydrophilic, native oxide film.² Adsorption of organics has been studied on native oxide surfaces using carboxylic³ and hydroxamic acids⁴ and alkyltrichloro- or alkyltrialkoxysilanes.⁵ Adsorption of the acids could occur by hydrogen bonding or proton transfer processes,⁴ but such interactions can be weak or reversible; furthermore, synthesis considerations limit the availability of alkyltrichloro- or alkyltrialkoxysilanes. Carboxylic acids are

appealing candidates for studies aimed at enhancing adsorption of organics to native oxides of metals, given their accessibility, range of chain length and steric factors, and potential for incorporation of reactive functionality. We now report a simple methodology which enables alkanecarboxylates to bind strongly to a prototypical native oxide layer of an oxyphilic metal through covalent interactions involving an easily constructed interface.

The deposition reaction of tetra-*tert*-butoxyzirconium ((*t*-BuO)₄Zr) onto the hydroxylated aluminum surface^{6,7} proceeds, on average, by protolytic loss of 2 equiv of *tert*-butyl alcohol.⁶ We have characterized this reaction in terms of its deposition kinetics and stoichiometry using quartz crystal microbalance (QCM) techniques⁸ and by electronic and electron energy loss spectroscopies in ultrahigh vacuum.⁷ An interesting aspect of this deposition sequence is that it replaces one type of reactive functionality on the surface of the oxide (-OH) by another: The surface Zr-OR units are available for ligand metathetical reactions with a second surface-derivatizing reagent. We now note that QCM techniques and IR analysis are useful to characterize the reaction between an alkanolic acid and either

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(1) For example, see: Porter, D.; Bright, T. B.; Allara, D. L.; Chidsey, E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(2) Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science* **1989**, *245*, 845.

(3) For example, see: (a) Kumar, A.; Biebuyck, H.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498. (b) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45.

(4) Folkers, J. P.; Gorman, C. B.; Laibinis, P. E.; Buchholz, S.; Whitesides, G. M.; Nuzzo, R. G. *Langmuir* **1995**, *11*, 813.

(5) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576.

(6) Miller, J. B.; Schwartz, J.; Bernasek, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 8239.

(7) Miller, J. B.; Bernasek, S. L.; Schwartz, J. *J. Am. Chem. Soc.* **1995**, *117*, 4037.

(8) Miller, J. B.; Schwartz, J. *Inorg. Chem.* **1990**, *29*, 4579.

the native oxide surface or the zirconium alkoxide-derivatized oxide surface of aluminum in terms of stoichiometry and thermal stability of the films thus formed.

Experimental Section

Preparation of the QCM Electrodes.⁸ Quartz crystals (5.5 MHz, AT-cut, fundamental mode, 3 μ polish) were obtained from Valpey-Fisher and were cleaned before use by soaking first in concentrated, aqueous NaOH, then concentrated H₂SO₄, followed by copious rinsing with distilled water. The crystals were then oven-dried. Electrodes were vapor-deposited onto the crystals using an Edwards Coating System E306A operating at <10⁻⁶ Torr. Electrodes were prepared as 200 nm aluminum layers deposited directly onto the quartz crystal; the geometrical electrode overlap area, on the basis of planar measurement, was 0.27 cm². Air was admitted into the chamber after Al deposition, and the QCM electrodes were further hydroxylated by being exposed to water vapor at 80 °C for 4 h. Hydroxylated QCM ensembles were evacuated for approximately 15 h and were stored in a drybox prior to use. Profilometry, SEM imaging, and an optical micrograph of the oxidized QCM Al electrodes all showed qualitatively rough surfaces.

Vapor Phase Reaction between the QCM Surface and (*t*-BuO)₄Zr. An evacuable reaction chamber equipped with two separate inlet ports was used. The QCM ensemble was attached to this apparatus as previously described for a single port system.⁸ Distilled (*t*-BuO)₄Zr (ca. 300 mg) was placed in a small vial attached to one port *via* a high-vacuum stopcock, and octanoic acid (ca. 300 mg) was placed in a second small vial attached to the other inlet port *via* a high-vacuum stopcock. Both were degassed by three freeze-pump-thaw cycles. The assembly was isolated from the two organic reagents and was evacuated for 2 h at ca. 10⁻⁵ Torr. With the vessel opened to the vacuum system, the QCM was exposed to (*t*-BuO)₄Zr by opening the appropriate stopcock. After reaction with the electrode surface was complete as measured by the QCM, the (*t*-BuO)₄Zr-containing vial stopcock was closed, and the QCM-containing vessel was evacuated at ca. 10⁻⁵ Torr for approximately 1 h.

Vapor Phase Reaction between the QCM Surface and Octanoic Acid. A procedure similar to that described above was performed using octanoic acid in place of (*t*-BuO)₄Zr. The QCM frequency was monitored throughout the entire sequence.

Vapor Phase Reaction between the (*t*-BuO)₄Zr-Treated QCM Surface and Octanoic Acid. Following reaction of the QCM surface with (*t*-BuO)₄Zr as described above, the octanoic acid-containing vial stopcock was opened and the treated QCM surface was exposed to octanoic acid vapor. After reaction with the electrode surface was complete as measured by the QCM, the ensemble was evacuated for ca. 3 h.

Reflectance FT-IR Studies Done on Treated Glass Slides. Pre-cleaned glass slides (VWR Scientific) were treated as were QCM crystals. Aluminum (ca. 200 nm) was deposited as described above. FT-IR investigations of surface-bound materials were performed in parallel with QCM studies on hydroxylated aluminum-coated glass slides. Spectra were recorded immediately after reactions were complete; a freshly Al-coated slide was used as reference. Spectral data were collected for 2000 scans at 4 cm⁻¹ resolution.

General UHV Information. Ultrahigh-vacuum (UHV) chamber equipment and procedures used are fully described elsewhere.⁷ Here, a UHV system with a base pressure of 2 × 10⁻¹⁰ Torr was used which was fitted with a Mattson Research Series FT-IR spectrometer, low-energy electron diffraction (LEED) optics, a quadrupole mass spectrometer (QMS), Auger electron (AES), X-ray photoelectron (XPS), and ultraviolet photoelectron (UPS) spectroscopic capabilities. The sample, a (110)-oriented Al single crystal, was cleaned and characterized *in situ* using these probes. Water (HPLC grade) was degassed by several freeze-pump-thaw cycles prior to use. Exposures are reported using uncorrected ion gauge background pressure readings.

Hydroxylation of the Al(110) Surface in UHV.⁹ Hydroxylation was accomplished by dosing water onto the clean Al(110) surface at 105 K followed by heating to >200 K. Redosing was used as part of the hydroxylation process.

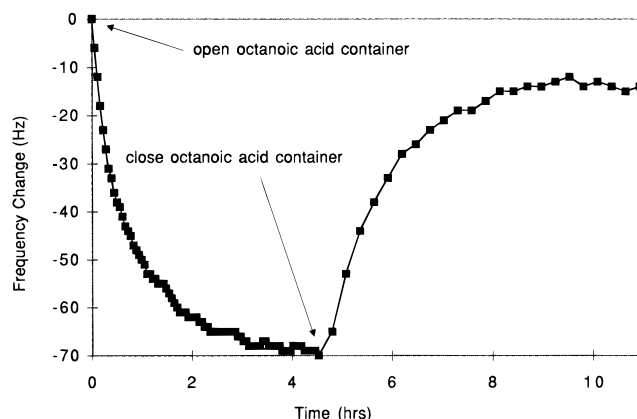


Figure 1. Deposition of *n*-octanoic acid onto hydroxylated Al and subsequent evacuation.

Deposition of (*t*-BuO)₄Zr onto Al(110)-OH in UHV with AES Monitoring.⁷ Distilled (*t*-BuO)₄Zr (74 °C, 0.1 Torr) was dosed onto the Al(110)-OH surface through a leak valve separate from that used for water dosing, with the crystal located directly in front of the outlet of the effusive doser at a distance *ca.* 1.5 cm from the opening.

Reflection Absorption Infrared Spectroscopy (RAIRS). The FT-IR spectrometer, optical benches, and the detector-containing compartment were sealed and constantly purged with dry nitrogen. External RAIRS was accomplished in an arrangement utilizing two differentially pumped CaF₂ windows mounted on the UHV chamber. Reflected light was detected using a liquid-nitrogen-cooled MCT detector located on the opposite side of the chamber from the incident beam. Because of absorption by the windows, the low-frequency cutoff is at 1000 cm⁻¹. A polarizer was placed between the front focusing mirror and the first CaF₂ window, and p-polarization was used in all RAIRS measurements. Spectral resolution was 16 cm⁻¹. Each RAIRS spectrum comprised *ca.* 2000 scans (about 5 min data collection time for each).

Results and Discussion

When a hydroxylated aluminum QCM ensemble⁸ was exposed to vapor of *n*-octanoic acid in a closed system (25 °C, initial pressure 10⁻⁵ Torr), rapid adsorption of the acid was noted gravimetrically. An initial frequency change of *ca.* 70 Hz was recorded (to give "film 1"), but rapid desorption of most of the alkanecarboxylic acid was noted when the QCM ensemble was evacuated, as monitored by a return of the QCM frequency close to its original value (net change 10 Hz; Figure 1);¹⁰ p-polarized reflection absorption FT-IR analysis showed no detectable surface alkanecarboxylate.

When a hydroxylated aluminum QCM ensemble⁸ was exposed to vapor of (*t*-BuO)₄Zr (25 °C, initial pressure 10⁻⁵ Torr; step 1, Scheme 1), a net frequency change of 640 Hz was observed (Figure 2a).¹¹ Deposition occurs with protolytic loss of two alkoxy groups,^{6,7} so this frequency change¹² would correspond to a nominal areal coverage (assuming the electrode were smooth) of 67 nmol/cm² (1.59 × 10⁴ ng/cm²) of di-*tert*-butoxyzirconium. Exposure of this alkoxyzirconium-treated QCM to vapor of *n*-octanoic acid (25 °C; initial pressure 10⁻⁵ Torr; step 2, Scheme 1) gave rise to a second net QCM

(10) Initial exposure could yield a multilayer of alkanecarboxylic acid on the surface adsorbed carboxylate. Apparently, both the multilayer and the alkanecarboxylate overlayer (film 1) are unstable, even at room temperature, with regard to desorption *in vacuo*.

(11) We note a small frequency change following step 1 (Figure 2a), consistent with physisorption of (*t*-BuO)₄Zr onto (AlO_x)Zr(*t*-BuO)₂, when the treated QCM surface is exposed to that vapor; this multilayer desorbs on subsequent evacuation.

(12) Replacement on average of two H by Zr(*t*-BuO)₂ corresponds to a net molecular weight change of 237.5 Da. Since the stoichiometry of deposition is determined titrimetrically, it is possible that some -Zr(*t*-BuO)₃ and -Zr(*t*-BuO)₁ species are present, formed by protolytic loss of one or three alkoxydes, respectively.

(9) Miller, J. B.; Bernasek, S. L.; Schwartz, J. *Langmuir* **1994**, *10*, 2629.

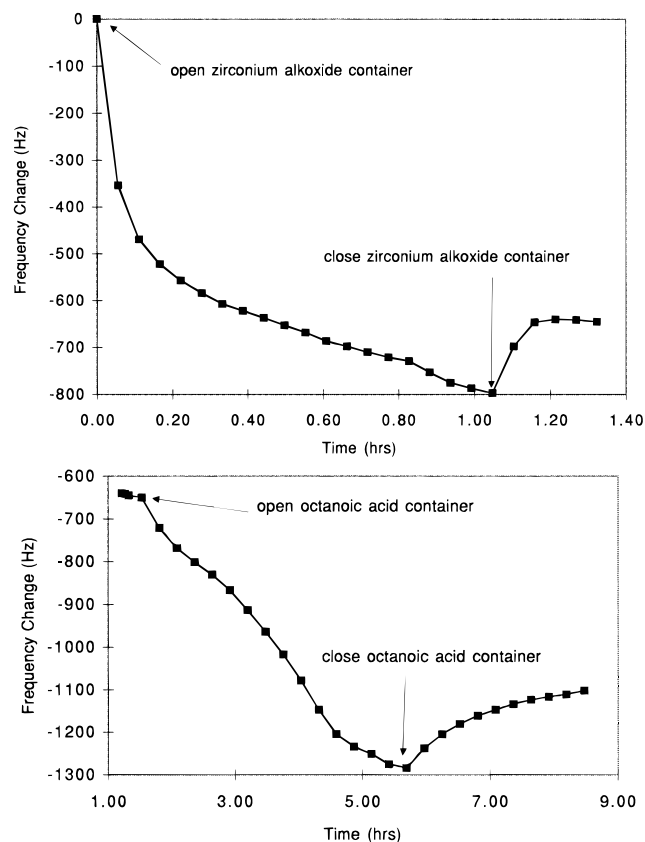
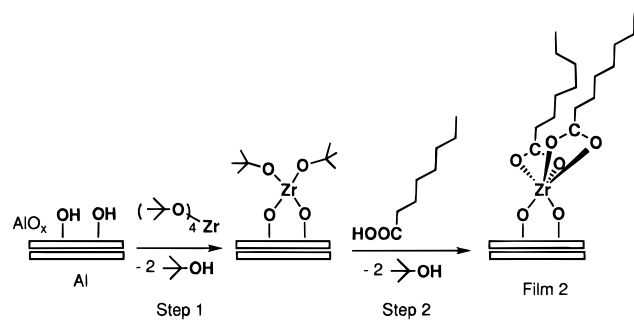


Figure 2. QCM frequency changes for (a) reaction of hydroxylated Al and $(t\text{-BuO})_4\text{Zr}$; (b) subsequent reaction with n -octanoic acid.

Scheme 1. Irreversible Adsorption of n -Octanoic Acid onto the Zr Alkoxide-Treated Hydroxylated Al Surface by Formation of a Zr η^2 -Carboxylate



frequency change of *ca.* 400 Hz.¹³ For the stoichiometry shown, preparation of film 2 entails a net molecular weight change of 140.2 Da:¹⁴ the predicted QCM frequency change for step 2 should be 59% of that recorded for step 1; the measured change was 62%.¹⁵ In marked contrast to results obtained for film 1, film 2 is stable at room temperature *in vacuo*: isolation from

(13) In a typical experiment, the frequency change initially measured on exposure to the acid was 644 Hz, which was reduced to 462 Hz after isolation of the acid source and exposure to vacuum. Re-exposure of the QCM to vapors of the acid gave an additional frequency change of 838 Hz. When the acid source was closed off and the QCM was exposed to vacuum, the net total frequency change (based on the clean oxide surface) returned to *ca.* 400 Hz and was stable for at least 10 h (Figure 5). Apparently, acid can physisorb onto the surface of film 2 (Figure 2b), likely through weak Van der Waals interactions.

(14) Calculated for replacement of, on average, $(t\text{-BuO})_2$ by $(\text{C}_7\text{H}_{16}\text{COO})_2$.

(15) In other runs, ratios of 76, 62, 61, 49% were noted (five run average 62%). In one case a very high change in frequency was noted on initial deposition (1513 Hz), and a low ratio (29%) for acid/Zr deposition was recorded. We believe this last result could derive from residual water on the QCM electrode surface.

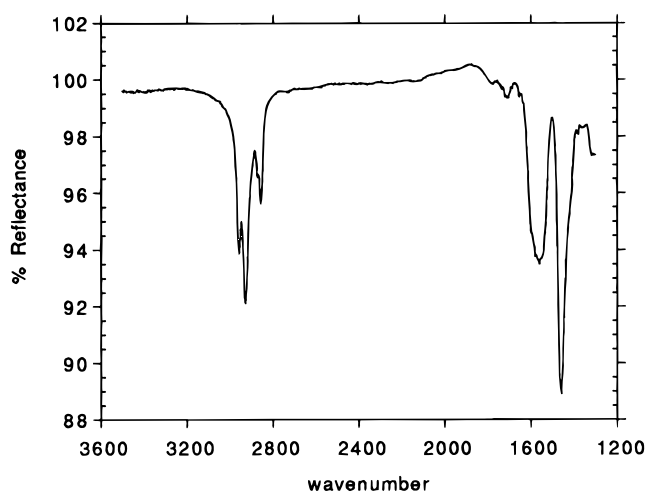


Figure 3. p-Polarized reflection-absorbance FT-IR of film 2.

the alkanolic acid reservoir and evacuation resulted in no significant negative frequency change associated with surface alkanolic acid loss (Figure 2b).

Reflectance IR analysis of film 2 showed peak maxima at 2959 (asym str CH₃), 2928 (asym str CH₂), 2872 (sym str CH₃), and 2857 cm⁻¹ (sym str CH₂), assigned by comparison with octanoic acid films formed by deposition of the acid onto oxidized aluminum from solution,^{3b,4} and indicates disordered alkyl chains in film 2.¹⁶ No carboxylic acid carbonyl group was detected; only the strong bands of the η^2 -carboxylate were observed (at 1557 and 1455 cm⁻¹; Figure 3).¹⁷ Infrared analysis of the zirconium octanoate film showed no significant changes after 2 months of exposure to ambient conditions. Nor was any significant change noted in the IR spectrum of a film washed in neat diethyl ether or 10⁻³ M octanoic acid in diethyl ether for 10 min. The film was approximately 80% destroyed after 15 h in water as measured by the reduction in intensity of C-H stretching peaks.

The interface synthesis reaction between the hydroxylated Al(110) surface and $(t\text{-BuO})_4\text{Zr}$ was followed by both AES and RAIRS in UHV. Analysis^{7,18} of Zr(143 eV)/C(272 eV), C(272 eV)/O(512 eV), and Zr(143 eV)/O(512 eV) AES peak height ratios provides details of the deposition process which are consistent with the two deposition stages noted by QCM analysis (Figure 2a): in the first, the metal complex reacts with surface hydroxyl groups, losing 2 equiv of *tert*-butoxy ligands as *tert*-butyl alcohol, which apparently desorbs immediately,⁷ to give surface bound di-*tert*-butoxyzirconium, ZrC₈H₁₈O₂; in the second, the intact tetra-*tert*-butoxyzirconium, ZrC₁₆H₃₆O₄, adsorbs as a multilayer.

The reaction between the hydroxylated Al(110) surface and $(t\text{-BuO})_4\text{Zr}$ at 170 K was also monitored by RAIRS in UHV. While it is not possible to draw quantitative IR intensity correlations between species formed in UHV on a single-crystal substrate and those prepared on a coated slide in the absence of detailed structural and orientational information for the chemisorbed monolayer, qualitative correlations are of interest.¹⁹ The C-H peak at 2977 cm⁻¹ was observed at an exposure of 0.27 L. This peak was more apparent at 1.0 L, and the C-O

(16) The octanoate chains are apparently not in an *all-trans*, crystalline arrangement (Sondag, A. H. M.; Raas, M. C. *Chem. Phys.* **1989**, *91*, 4926), but this is not unexpected for a rough surface.

(17) Compare with zirconium tetraacetate. For the η^2 -carboxylate: 1540 (ν_{antisym}); 1455 (ν_{sym}) cm⁻¹. See: Tackett, J. E. *Appl. Spectrosc.* **1989**, *43*, 483.

(18) Determination of Zr is less sensitive than C by either AES or XPS. However, it is the most useful, since it is the central atom of the complex and is present in both the intact complex and the deposited fragment.

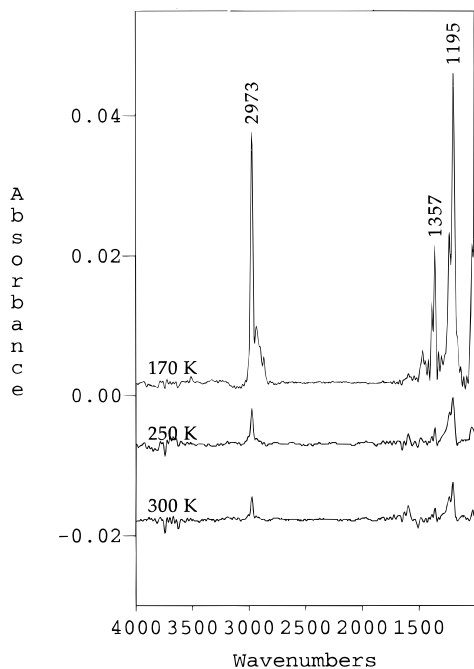


Figure 4. RAIR spectra of the reaction of hydroxylated Al and (*t*-BuO)₄Zr at 170 K, followed by heating at 205 and 275 K.

peak at 1203 cm⁻¹ could also be observed at this exposure. Upon further exposure (6.0 L), the C–H peak shifted 4 cm⁻¹ to lower energy and several other, lower frequency bands could be observed; the C–O peak also shifted to lower energy by about 12 cm⁻¹. At an exposure of 36 L, substrate attenuation of the Al(2p) XPS peak was consistent with a multilayer. Under these conditions, strong IR bands at 2973 and 1191 cm⁻¹ were observed, as were less intense ones at 2931, 2866, 1385, 1357, and 1230 cm⁻¹. Thermal desorption of surface (*t*-BuO)Zr species was then monitored by RAIRS. The sample was heated to progressively higher temperatures from 170 K, followed by cooling back to 170 K for RAIRS analysis. The intensity of the 2973 cm⁻¹ peak was constant when the sample was heated in the temperature range 170–210 K, but this intensity decreased to a constant value of about 10% of the initial level in the

(19) Reflectance IR analysis of (AlO_x)Zr(*t*-BuO)₂ showed strong peaks at 2975, 1196, and 1011 cm⁻¹ and weaker ones at 2930, 2872, 1358, 1227, 1196, 983, 905, and 774 cm⁻¹. For (*t*-BuO)₄Zr (neat, transmission), 2969, 2927, 2900, 2867, 1359, 1230, 1188, 1009, 786 cm⁻¹.

(20) Thermal desorption (by mass spectroscopy) and XPS experiments following deposition of (*t*-BuO)₄Zr onto Al(110) were consistent with these assignments (Bernasek, S. L.; Lu, G.; Schwartz, J. Unpublished results).

(21) It is useful to consider the expected coverage of (*t*-BuO)₄Zr on the hydroxylated QCM electrode under the conditions of the QCM experiment. Assuming an interaction energy for the physisorption of (*t*-BuO)₄Zr to be 5–10 kcal/mol based on TPD data (peak desorption temperature 240 K), the equilibrium coverage of (*t*-BuO)₄Zr on the QCM electrode surface can be calculated for relevant conditions, using the assumption that the coverage is given by the product of the (*t*-BuO)₄Zr flux to the surface and the surface residence time of the molecule. These calculations indicate a physisorption coverage of <10¹⁰ molecules/cm²; thus, multilayer coverage of the physisorbed species is not expected for the QCM surfaces at room temperature at the pressure indicated.

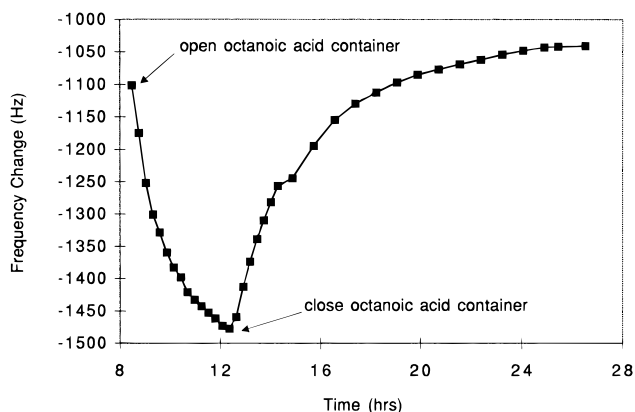


Figure 5. Deposition of *n*-octanoic acid onto “film 2” and subsequent evacuation.

temperature range 250–300 K (see Figure 4); above this range, further intensity reduction was noted. Peak intensity changes for the other bands were noted commensurately. The two intensity “plateaus”, between 170–210 K and 250–300 K, likely indicate the thermal stability ranges of the multilayer and monolayer, respectively; the latter range overlaps the temperature regimes used in QCM studies.^{20,21} Significantly, deposition at room temperature gave no evidence for multilayer formation: saturation coverage was observed at 10 L exposure, beyond which no intensity increase for the peak at 2973 cm⁻¹ was noted.

Conclusions

By reaction with a metal alkoxide, the native oxide surface of aluminum undergoes a change in its surface functionality that enables strong, subsequent interaction with an alkanecarboxylic acid. We believe results obtained using zirconium alkoxides as pretreatment reagents for the preparation of stabilized carboxylate films on this oxide surface indicate a general method for adsorption enhancement of carboxylates or similar reagents onto any hydroxylated native oxide metal film capable of reaction with a metal alkoxide. Studies to expand the scope and structural characterization of such enhanced adsorptive films are now in progress.

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Supporting Information Available: Figures showing QCM data for the complete sequence of deposition of (*t*-BuO)₄Zr and then *n*-octanoic acid onto hydroxylated Al, two IR spectra of film 2 in air, profilometry for the oxidized QCM Al electrode, an SEM image of the oxidized QCM Al electrode, and an optical micrograph of the Al electrode deposited on a 3μ polished QCM electrode (6 pages). See any current masthead page for ordering and Internet access instructions.

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