

Reaction between Tetra-*tert*-butoxyzirconium and Al(110)–OH in UHV

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Received August 8, 1994[Ⓢ]

Abstract: Single crystal Al(110) was hydroxylated in UHV to give a disordered overlayer. Protolytically labile tetraepentylzirconium did not react with hydroxylated Al(110) in UHV, which was interpreted through a mechanistic proposal for proton-transfer-based surface chemical modification. According to this proposal, a zirconium alkoxide, although less thermodynamically basic than a zirconium alkyl, could be a kinetically viable substrate for proton-transfer-based organometallic chemical vapor deposition (MOCVD) in UHV, and tetra-*tert*-butoxyzirconium did react with hydroxylated Al(110) to give a surface bound di-*tert*-butoxyzirconium species. The deposition reaction was readily studied by HREELS, XPS, and AES.

The irreversible deposition of a metallic species onto an activated surface by metal–organic chemical vapor deposition (MOCVD) is an established method for surface modification in contexts as diverse as epitaxial crystal growth¹ and the preparation of heterogeneous catalysts.² Despite the range of applications of MOCVD, little has been described concerning the actual, first steps in such surface modification by complex organometallic substrates. Because of their importance as olefin polymerization catalysts,³ we have studied aspects of surface complex formation using group 4 organometallics and both bulk metal oxides⁴ and oxide-overlaid metals.⁵ Our first ultrahigh-vacuum (UHV) investigations focused on protolytic deposition reactions of tetraepentylzirconium onto hydroxylated surfaces: this species is known to react easily with metal oxide surface hydroxyl groups by protolytic loss of 2 equiv of neopentane under “normal” laboratory conditions.⁴ Given this known protolytic lability, we were surprised to note the failure of tetraepentylzirconium to react irreversibly with either TiO₂(001)–OH⁶ or Al(110)–OH in UHV.⁷ When single crystal Al(110) was hydroxylated by water and then exposed to as much as 3000 L of tetraepentylzirconium, only a small increase in surface carbon could be measured by Auger electron spectroscopy (AES), and no zirconium was observed by either AES or X-ray photoelectron spectroscopy (XPS).

We had studied the mechanism of MOCVD of zirconium alkyls onto hydroxylated Al using quartz crystal microbalance (QCM)-derived kinetics.^{5,8} These studies suggested that the first step of the MOCVD sequence was the *reversible* formation of

an hydroxyl group–metal complex adduct (see Scheme 1). Irreversible surface attachment was accomplished by rate-limiting proton transfer from the OH of this adduct to the thermodynamically, *but not kinetically*, basic Zr–C σ -bond. Because of slow proton transfer from OH to the Zr–C σ -bond, surface complex desorption could be kinetically favored under UHV reaction conditions, and thus no irreversible adsorption would result. Tetra-*tert*-butoxyzirconium is structurally similar to but less thermodynamically basic than tetraepentylzirconium. However, lone electron pairs on the oxygen atoms or the Zr–O π -bonds could provide alternate, perhaps kinetically more favorable sites for proton transfer to the metal complex than is the σ -bond of the tetraalkyl. In fact, QCM studies⁵ indicated relatively fast proton transfer from surface hydroxyl groups to coordinated tetra-*tert*-butoxyzirconium, suggesting, counterintuitively from a thermodynamics perspective, that the alkoxide should be a better substrate for MOCVD in UHV than the alkyl. Indeed, when we reacted tetra-*tert*-butoxyzirconium vapor with Al(110)–OH in UHV, irreversible, protolytic deposition did occur, yielding a surface bound di-*tert*-butoxyzirconium species which could be characterized using the tools of surface science.

Experimental Section

General Procedure. The UHV chamber and procedures used are fully described elsewhere.⁹ Briefly, an ultrahigh-vacuum system with base pressure of 2×10^{-10} Torr was used in these studies. It was fitted with low-energy electron diffraction (LEED) optics, an Auger electron spectrometer, XPS, and ultraviolet photoelectron spectroscopic (UPS) capabilities, and a high-resolution electron energy loss spectrometer (HREELS). 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. Hydroxylation was accomplished⁹ by dosing water onto the clean Al(110) surface at 105 K, followed by heating to >200 K. High hydroxyl coverage was obtained by dosing sufficient water (up to 5 L) onto the clean Al(110) surface at 105 K to form a layer of ice. This surface was then flashed to >200 K to obtain the heavily hydroxylated surface, having a typical XPS peak area ratio, $R_{O/Al} = 3$, which is *ca.* 75% of saturation coverage. Redosing the surface with a second ice layer, followed by flashing the

[Ⓢ] Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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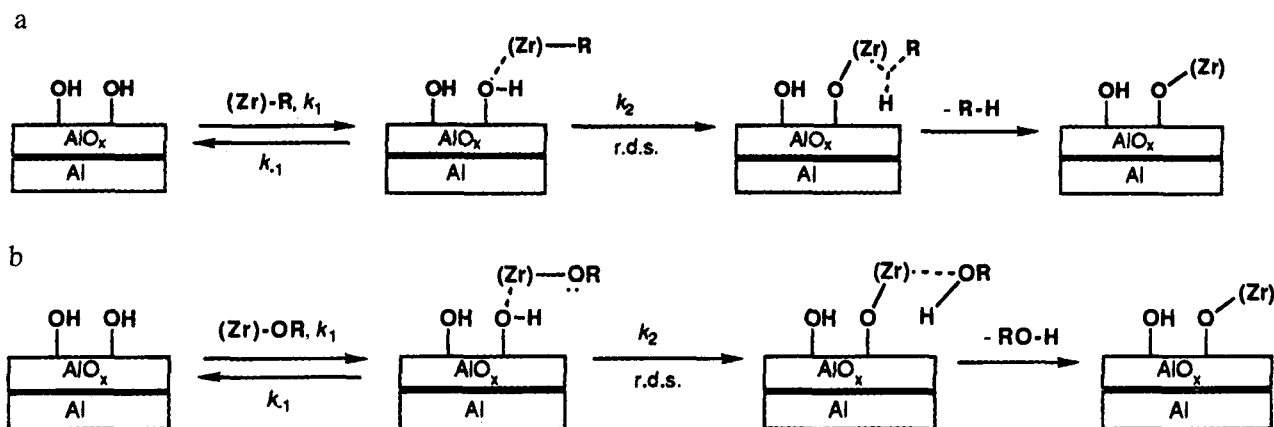
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Scheme 1. Deposition of Tetraeneopentylzirconium^a and Tetra-*tert*-butoxyzirconium^b onto the Hydroxylated Al Surface

^a Proton transfer from an oxygen lone pair to the C-Zr σ -bond ($k_2 \ll k_{-1}$). ^b Proton transfer from an oxygen lone pair to an oxygen lone pair ($k_2 \leq k_{-1}$).

surface to >200 K, enhanced the total hydroxyl coverage by about one-third but did not significantly change the relative proportion of hydroxyl and oxide oxygens, as determined by XPS.⁹ Redosing was only occasionally used as part of the hydroxylation process.

Deposition of Tetra-*tert*-butoxyzirconium onto Al(110)-OH in UHV. Distilled (74 °C, 0.1 Torr) tetra-*tert*-butoxyzirconium complex was dosed onto the Al(110)-OH surface with the crystal directly in front of the outlet of an effusive doser, about 1.5 cm from the opening. The effective pressure at the outlet of the dosing tube must be at least 22 times higher than the measured background pressure. This is based on the comparison of Auger peak-height ratios resulting from exposing the crystal, for equivalent times, to the complex (or another species, such as water) with the crystal turned away from, and turned toward, the inlet tube.

Attempted Deposition of Tetraeneopentylzirconium onto Al(110)-OH in UHV. A parallel series of experiments investigating the deposition of tetraeneopentylzirconium onto the Al(110) surface at several hydroxylation levels was attempted. However, even a 3000 L exposure (1.5×10^{-6} Torr, 2000 s) of the metal complex onto the 105 K surface led to only a small increase in the surface carbon as measured by Auger; no zirconium was observed by either Auger or XPS. Mass spectra (<100 amu) obtained during complex dosing were consistent with the pressure of the gas-phase tetraeneopentylzirconium.

Results and Discussion

Tetra-*tert*-butoxyzirconium reacts with surface-hydroxylated Al metal by protolytic loss of 2 equiv of *tert*-butyl alcohol to give a di-*tert*-butoxyzirconium surface species (Scheme 1) from ether solution at 21 °C and 1 atm, as well as from the gas phase at 10^{-2} Torr.⁵ When distilled (74 °C, 0.1 Torr) tetra-*tert*-butoxyzirconium was dosed onto the Al(110)-OH surface at 105 K under UHV conditions, AES analysis showed irreversible Zr complex binding, even at low exposure. For example, AES of the clean Al(110)-OH surface showed only Al and O, while at a tetra-*tert*-butoxyzirconium exposure of 0.3 L, the C_{KLL} (272 eV) signal appeared; at 0.8 L, the Zr_{LMM} (143 eV) became discernible. Both the C (272 eV) and Zr (143 eV) signals increased with exposure; the O_{KLL} (512 eV) signal was seen in all samples, but its intensity began to drop in the spectra of the two highest exposure surfaces. Uncorrected AES peak height ratios for C and Zr were also obtained as a function of exposure (Figure 1), using the Al_{KLL} (1397 eV) peak as a reference.

A comparison of Zr (143 eV)/C (272 eV), C (272 eV)/O (512 eV), and Zr (143 eV)/O (512 eV) peak-height ratios (Figure 2) provides details of the deposition process: at low exposures (<2 L), the Zr/C ratio was slightly more than double that seen at high exposures. Concomitant with the drop in the Zr/C ratio was a change in slope of both the C/O and Zr/O ratios with increasing exposure. After these slope changes, the Zr/C ratio remained fairly constant, while the Zr/O and C/O ratios

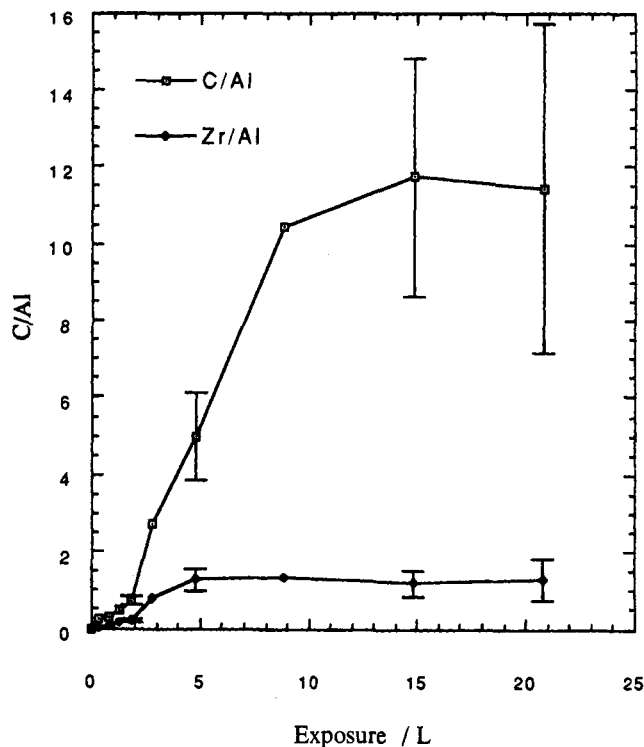


Figure 1. Comparison of the uncorrected C_{KLL}/Al_{KLL} and Zr_{LMM}/Al_{KLL} Auger peak-height ratios as a function of exposure to $Zr(O-t-Bu)_4$.

decreased slightly.¹⁰ These results (as well as those presented below) are consistent with two deposition stages. 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, to give surface bound di-*tert*-butoxyzirconium, $ZrC_8H_{18}O_2$; in a control experiment, no adsorption of *tert*-butyl alcohol was observed when the hydroxylated surface was exposed to that alcohol at 105 K. In the second, as surface hydroxyls are depleted, the intact tetra-*tert*-butoxyzirconium, $ZrC_{16}H_{36}O_4$, adsorbs in a multilayer.

The O (1s) XP spectrum of the hydroxylated surface prior to exposure to the organometallic can be fit with two components, with the hydroxyl group oxygen component as the high-energy tail and the main peak attributed to oxidic oxygens (Figure 3).⁹ On the basis of relative peak areas, the ratio of hydroxyl to oxide oxygens on this surface is 0.75:1. With increasing

(10) The Zr atom is the least sensitive measure of coverage by either AES or XPS (see Table 2). 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.

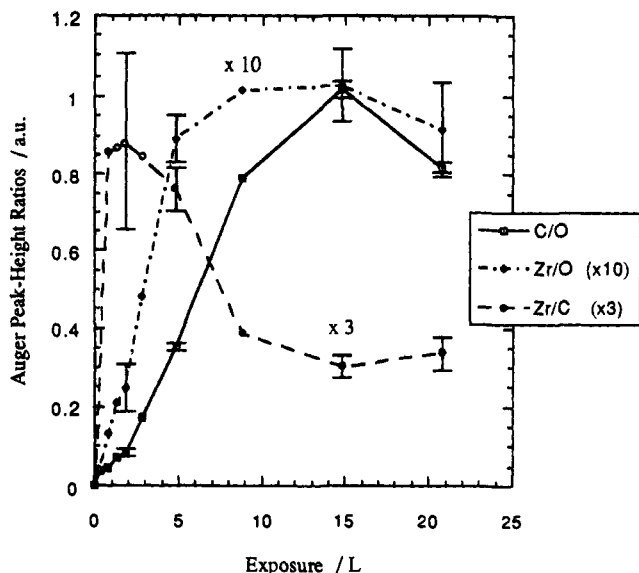


Figure 2. Uncorrected Auger peak-height ratios plotted as functions of tetra-*tert*-butoxyzirconium exposure. This shows an increase in the amount of deposited complex followed by formation of an overlayer of the intact complex.

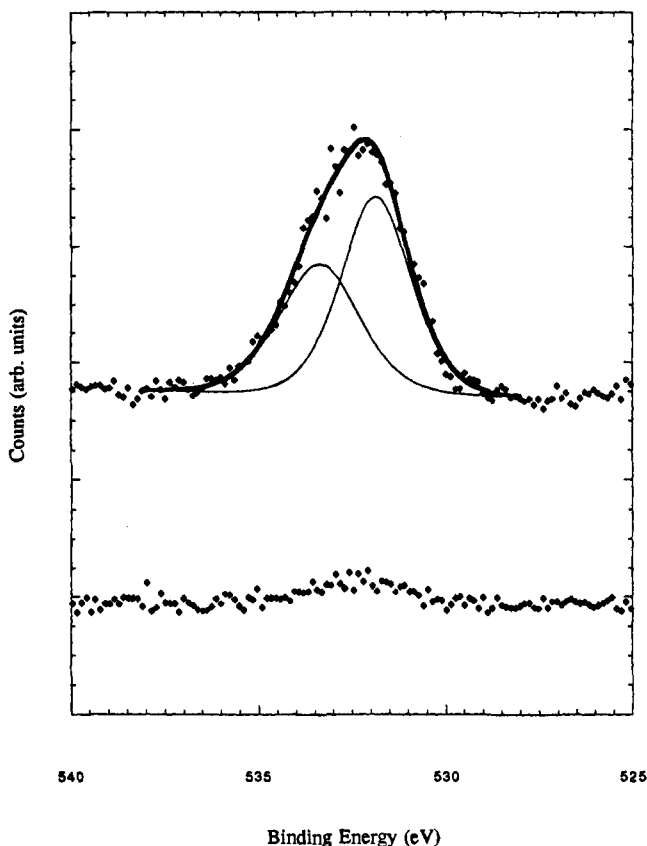


Figure 3. Deconvoluted O (1s) XP spectra for clean (lower) and hydroxylated Al(110) (upper): data points, filled squares; total fit, bold line; two components, narrow lines. The low binding energy component of the top spectrum is due to oxide oxygen; the high binding energy component is due to hydroxyl oxygen.

exposure to tetra-*tert*-butoxyzirconium, the peak maximum shifted first to lower energy, but at the highest exposure (71 L), the maximum had shifted 0.1 eV to higher binding energy, indicating a changing distribution of surface oxygens, while peak broadening with metal complex exposure suggested the presence of new oxygen-containing species.¹¹ It was not possible to adequately fit these spectra with either two or three components, but a four-component fit was more successful, assigned to the

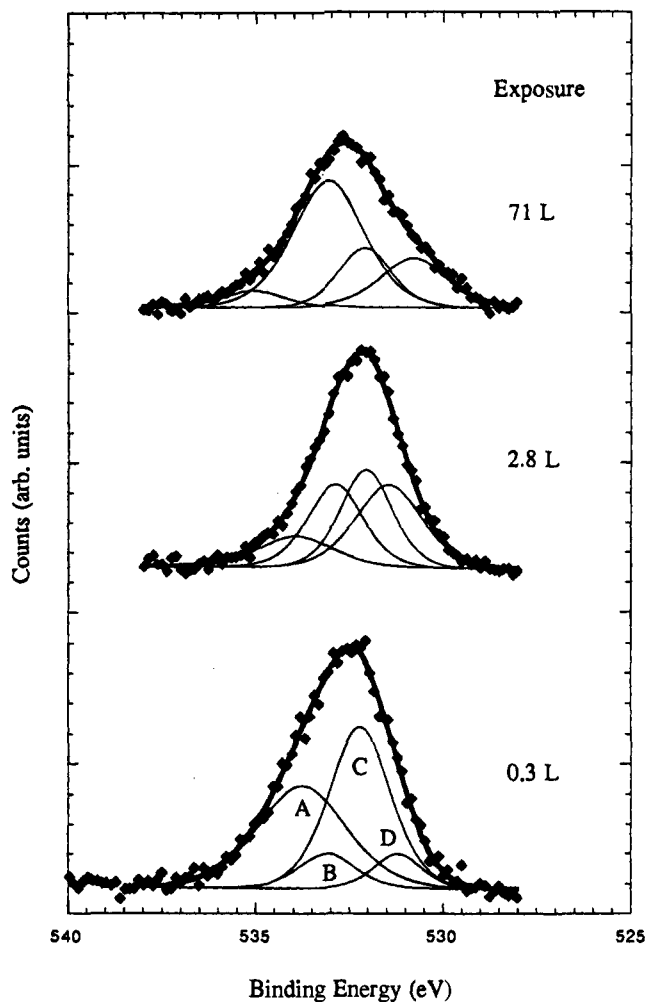


Figure 4. Sequential, deconvoluted O (1s) XP spectra for increasing exposures of tetra-*tert*-butoxyzirconium onto hydroxylated Al(110): data points, filled squares; total fit, bold line; four components, narrow lines. See Table 1 for peak assignments.

expected OH, Al-O-Al, Al-O-Zr, and Zr-O-C oxygens (Figure 4).⁷ While statistical measures of two-, three-, and four-component fits to the O (1s) data are similar ($R^2 = 0.98-0.99$ in each case), the two- and three-component fits gave peaks which varied with coverage unacceptably in binding energies and peak widths. Therefore, these fits, which might be statistically acceptable, are not physically valid. The four-peak fit summarized in Table 1 gave peaks with consistent widths and binding energy positions, which changed significantly only in relative intensities with coverage up to the multilayer spectrum. The four-peak fit is, therefore, physically as well as statistically valid. Peak binding energies (± 0.2 eV) and relative intensities resulting from this fit are given in Table 1.¹²

(11) Line shape analysis assumed a 50/50 Gaussian/Lorentzian shape and a linear background for each component of the O (1s) composite spectrum. See: Sherwood, P. M. A. *Data Analysis in X-ray Photoelectron Spectroscopy*. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; Wiley: New York, 1983.

(12) No component for *tert*-butyl alcohol is included in this fit. In a control experiment, *tert*-butyl alcohol did not adsorb when the hydroxylated Al(110) surface held at 105 K was exposed to that alcohol. This was monitored by noting no increase in carbon or oxygen Auger signal as a function of *tert*-butyl alcohol exposure, as well as by the observation of no *tert*-butyl alcohol-derived desorption peaks in TDS measurements following exposure. Perhaps failure to adsorb is due to the steric bulk of this alcohol and its consequent, relative hydrophobicity. Under identical conditions, exposure of the hydroxylated Al(110) surface to sterically less bulky *n*-butanol did give rise to an increase in the carbon Auger signal, and TDS experiments showed *n*-butyl alcohol-derived peaks following exposure of that alcohol to the hydroxylated surface.

Table 1. Peak Assignments and Relative Areas of the O (1s) XP Spectra of Reaction Products of Exposure of Hydroxylated Al(110) to Zr(O-*t*-Bu)₄

exposure (rel. areas)	(A) Al-O-H (533.7 eV)	(B) Zr-O-C (533.0 eV)	(C) Al-O-Al (532.1 eV)	(D) Zr-O-Al (531.3 eV)
0 L (Al-OH)	0.43		0.57	
0.3 L	0.40	0.088	0.44	0.074
0.8 L	0.31	0.21	0.28	0.20
2.8 L	0.13	0.26	0.29	0.31
4.8 L	0.13	0.32	0.20	0.35
11.0 L	0.084	0.41	0.19	0.32
71.0 L ^a	0.062	0.55	0.19	0.20

^a It is unremarkable that multilayer peak positions (at 71 L exposure (Figure 4)) are not the same as those for fractional monolayer coverages (peak positions are ± 0.2 eV); the oxygen bonding environment in the multilayer is that of the intact complex, not of the complex reacted with surface hydroxyl.

Table 2

atom	AES ^a	XPS ^b
C	0.2 (KLL)	0.21 (1s)
O	0.5 (KLL)	0.63 (1s)
Zr	0.22 (MNN)	0.87 (3d)
Al	0.05 (KLL)	0.11 (2p)

^a Relative to Cd_{MNN} = 1.00. See: Davis, L. E., McDonald, N. C.; Palmberg, P. W.; Riach, G. E.; Weber, R. E., *Handbook of Auger Electron Spectroscopy*; Perkin Elmer Corp.: Eden Prairie, MN, 1978.
^b Relative to F (1s) = 1.00. See: Muilenberg, G. E., Ed. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin Elmer Corp.: Eden Prairie, MN, 1979.

Interpreting the four-component fit, as exposure increased up to 2.8 L, two new peaks of about equal intensity grew, while the hydroxyl peak decreased. At 71 L, one of the two new peaks had increased greatly, while the other had not changed intensity relative to the oxidic peak, consistent with a multilayer of tetra-*tert*-butoxyzirconium. Even at this coverage, the initial surface oxide peak was detectable, consistent with the significantly high mean free path for O (1s) photoelectrons. When intensity ratios of each of these component peaks were determined against the total oxygen signal (Figure 4), it was found that the high-energy, hydroxyl peak smoothly and linearly decreased up to an exposure of about 3 L. At that point, the rate of decrease dropped; this transition occurred at about the same exposures as those found for AES ratio slope changes.

Zirconium (3d) XP spectra were recorded as a function of surface exposure to tetra-*tert*-butoxyzirconium, and the intensity of the Zr (3d) transitions increased accordingly. At low exposures, two overlapping peaks (Zr 3d_{3/2} and Zr 3d_{5/2} at 184.7 and 182.3 eV, respectively, spin-orbit splitting = 2.45 eV)^{10b} were noted and were of constant fitted full widths at half-maximum of 2.0 and 2.2 eV, consistent with the presence of a single zirconium species on the surface. At highest exposure (71 L) the spectrum had become noticeably broadened. A two-species (four-peak) fit (Figure 5) suggested that one pair (less oxidized Zr) was due to the species observed at low exposure and was assigned to surface bound di-*tert*-butoxyzirconium. The second pair of peaks was shifted by 0.6 eV to higher binding energy (more oxidized Zr), to 182.9 and 185.3 eV, and was assigned to tetra-*tert*-butoxyzirconium, consistent with the peak energies observed for multilayers of the intact complex.

A complementary series of Al (2p) XP spectra was recorded as a function of surface exposure to tetra-*tert*-butoxyzirconium (Figure 6). The hydroxylated surface showed a two-component peak corresponding to metallic Al (at 71.1 eV) and oxidized Al (at 73.4 eV binding energy).⁹ As this surface was exposed to increasing tetra-*tert*-butoxyzirconium, the intensity of the Al (2p) peak decreased, but no peak shift was observed. At the

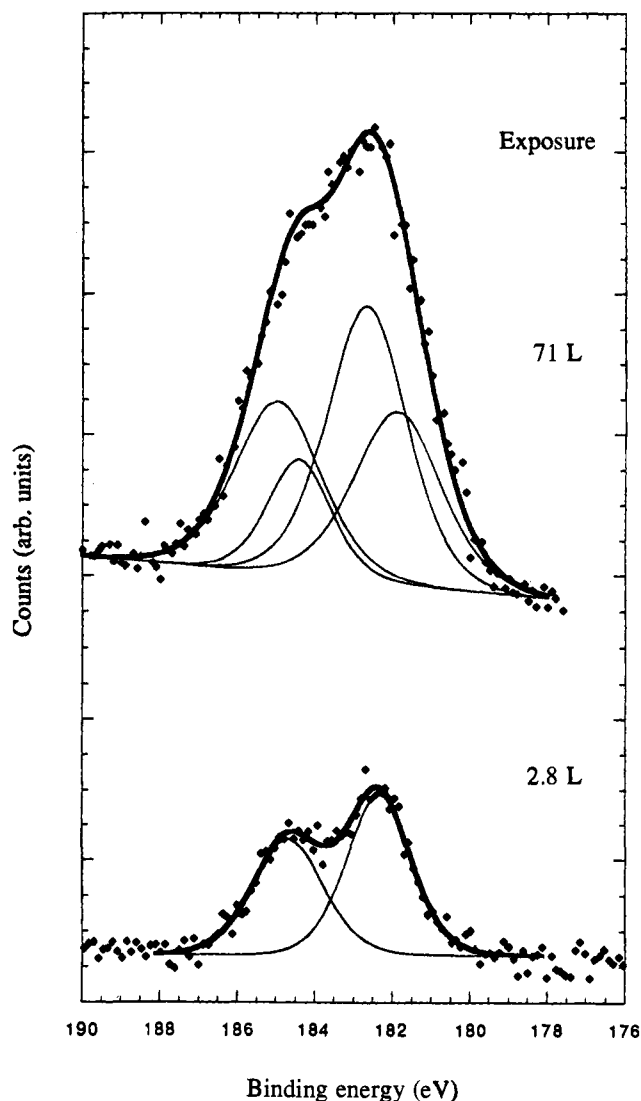


Figure 5. Sequential Zr (3d) XP spectra for increasing exposures of tetra-*tert*-butoxyzirconium onto hydroxylated Al(110): data points, filled squares; total fit, bold lines; components, narrow lines.

highest exposure to tetra-*tert*-butoxyzirconium (71 L), no Al (2p) signal was detected due to attenuation by the organometallic multilayer and consistent with the shorter mean free path of the lower energy Al (2p) photoelectrons.

HREEL spectra of the surface taken at various stages during the deposition process (Figure 7) support the above described AES and XPS interpretations. The hydroxylated surface showed strong vibrational losses at 3680 and 870 cm⁻¹, corresponding to ν_{OH} stretching and ν_{Al-OH} stretching modes, respectively. A small amount of residual water (1640 cm⁻¹) and hydrocarbon (2920 and 1420 cm⁻¹) contamination was seen on this surface, as well. At 0.8 L exposure to tetra-*tert*-butoxyzirconium, the loss peaks assigned to ν_{O-H} = 3680 cm⁻¹ and ν_{Al-OH} = 870 cm⁻¹ had disappeared due to chemical reaction with the Zr complex and four new loss peaks appeared which were similar to features noted⁵ by DRIFT for reaction of tetra-*tert*-butoxyzirconium with surface-hydroxylated bulk aluminum metal: ν_{CC} = 905 cm⁻¹, ν_{CO} = 1205 cm⁻¹, δ_{CH_3} = 1425 cm⁻¹, and ν_{CH} = 2945 cm⁻¹. Significantly, no losses in the 500–600 cm⁻¹ range (Zr–O) were noted (the transmission IR spectrum of the neat complex shows bands at 542 and 478 cm⁻¹). Even though all of the surface hydroxyls were not depleted at this coverage (by XPS analysis) neither the surface ν_{OH} = 3680 cm⁻¹ nor the strong ν_{Al-OH} = 870 cm⁻¹ loss peaks were seen: most of the intensity in these peaks is lost by chemical reaction of the OH with the Zr alkoxide species. The unreacted OH appears to be

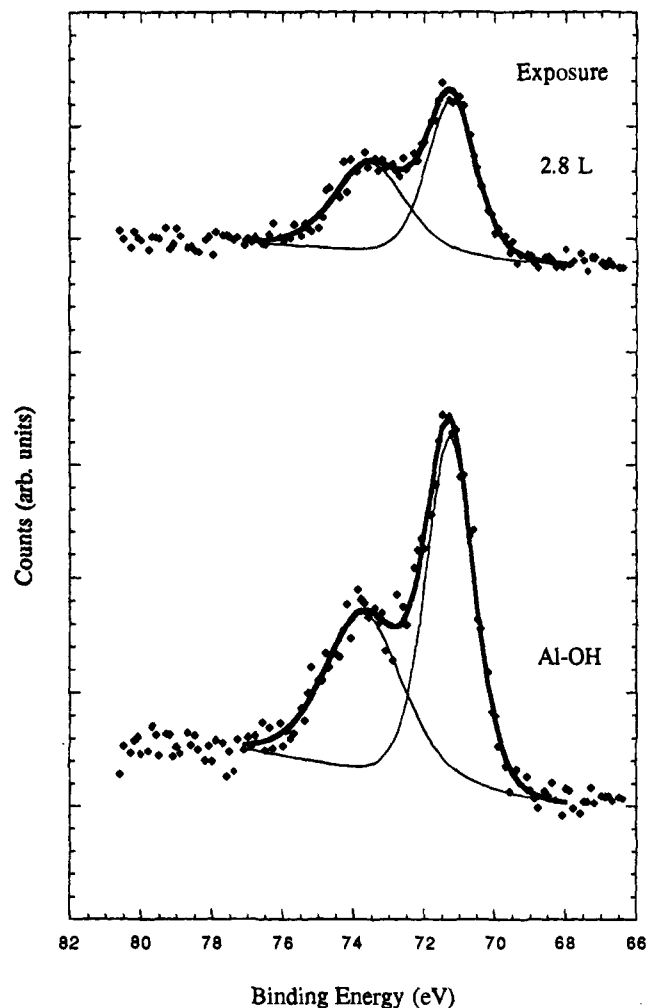


Figure 6. Al (2p) XPS spectra before and after exposure of hydroxylated Al(110) to 2.8 L of tetra-*tert*-butoxyzirconium: data points, filled squares; total fit, bold line; two components, narrow lines. The low binding energy component of each spectrum is due to Al metal; the high binding energy component is due to oxidized/hydroxylated aluminum.

effectively blocked for electron scattering by the rather bulky adsorbed alkoxide species. At intermediate exposure (11 L) some small changes were observed and a new loss peak appeared at 505 cm^{-1} , which may be $\nu_{\text{Zr-O}}$ of tetra-*tert*-butoxyzirconium, suggesting that this spectrum is of a mixture of surface bound di-*tert*-butoxyzirconium and tetra-*tert*-butoxyzirconium. At very high exposure (71 L), the low-energy losses at 270 and 505 cm^{-1} were more intense, consistent with a multilayer of the intact complex. The 930 cm^{-1} peak is assigned to $\nu_{\text{C-O}}$ of surface bound di-*tert*-butoxyzirconium, the low-energy shoulder noted may be due to residual Al-OH, and the 985 cm^{-1} peak recorded after 71 L is likely $\nu_{\text{C-O}}$ of tetra-*tert*-butoxyzirconium. The apparent shifting of the low-exposure 930 cm^{-1} peak to higher energies with increasing exposure is likely due to unresolved $\nu_{\text{C-O}}$ signals for a mixture of surface bound di-*tert*-butoxyzirconium and tetra-*tert*-butoxyzirconium.

Conclusions

The mechanism of deposition of tetraneopentylzirconium and tetra-*tert*-butoxyzirconium onto surface oxidized aluminum has been probed using mass-sensitive QCM techniques.⁸ Reactions between an hydroxylated metal surface and these organometallic

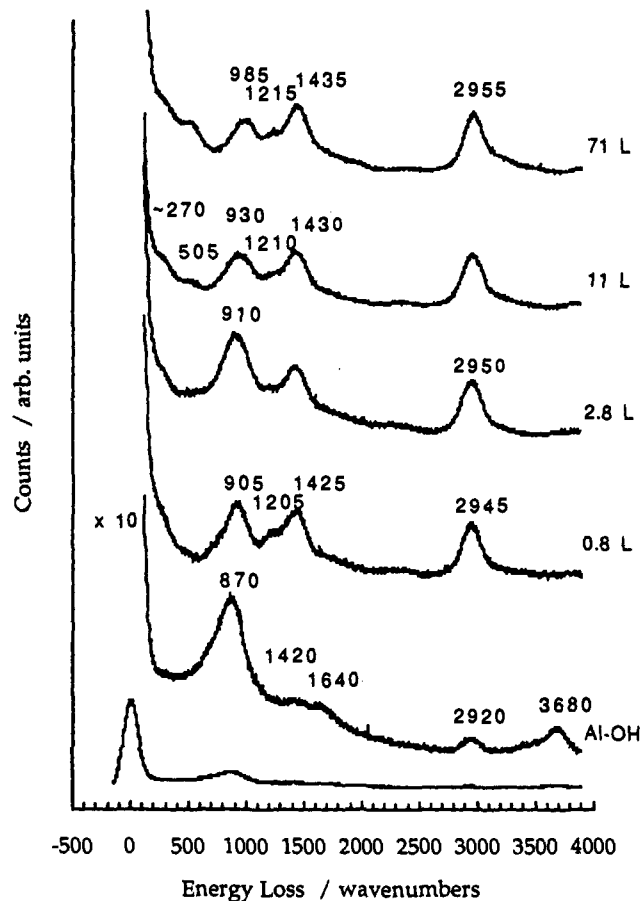


Figure 7. HREEL spectra of various metal complex exposures during the deposition of tetra-*tert*-butoxyzirconium onto the hydroxylated Al(110) surface. All spectra were obtained at 105 K.

complexes apparently proceed by *reversible* coordination of the metal complex to the hydroxylated surface, followed by rate-determining proton transfer and subsequent loss of the protonated ligand. Thus, the less thermodynamically basic tetraalkoxide was favored over the more basic tetraalkyl, ratewise, because lone pairs on oxygen or the Zr-O π -bond could provide kinetically favorable sites for proton transfer to a metal complex relative to the σ -bond of the alkyl. Successful protolytic deposition of tetra-*tert*-butoxyzirconium, but not of tetraneopentylzirconium, onto hydroxylated Al(110), despite thermodynamic intuition to the contrary, points out the importance of ligand *kinetic* basicity for designing reactive organometallics for MOCVD in high vacuum, where residence times on the surface might be short compared with proton-transfer lifetimes. Direct AES and XPS measurements for UHV deposition of tetra-*tert*-butoxyzirconium onto Al(110)-OH were consistent with bulk measurements of deposition stoichiometry. HREELS measurements for the UHV process also paralleled those made by IR for bulk materials. Thus, kinetics considerations can be used as a probe for choosing good MOCVD precursors and characterization techniques best adapted to UHV conditions can be used to elucidate surface-complex interfaces in systems which faithfully model those of interest in the "real world".

Acknowledgment. The authors acknowledge support for this work given by the National Science Foundation. They also thank Dr. J. M. Pan for *tert*-butyl alcohol 105 K adsorption experiments.