

Alternative Low Pressure Surface Chemistry of Titanium Tetraisopropoxide on  
Oxidized Molybdenum

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### **Elemental ratios and Surfaces Densities**

The elemental ratios and surface densities were calculated for all experiments at 573, 473 and 373 K and are summarized in Tables S1-S3 under the total precursor exposure. The results for the H<sub>2</sub>O doses are italicized. Elemental ratios were calculated with the appropriate sensitivity factors.<sup>1</sup> Surface densities were calculated from a calibration curve for O(1s):Mo(3d<sub>5/2</sub>) intensity ratios generated previously from known oxygen coverages spanning 0.3-2 monolayers and reported in Ref. 2. The plot of O surface densities versus O(1s):Mo(3d<sub>5/2</sub>) intensity ratio was linear, indicating that in this region the attenuation of the Mo(3d) signal is not significant. The peak intensity ratios is linear with the peak area ratios. A multiplication factor of 0.9 converts between intensity ratios to peak area ratios. A linear fit to the O surface density versus O(1s):Mo(3d) peak area ratio yielded the equation  $y = 92x$ . The x-axis intercept was constrained to 0, since the O(1s) signal should approach 0 as the O concentration approaches 0. Using sensitivity factors the equation relating O surface densities to peak areas can be used to derive corresponding equations for C and Ti surface densities with slopes of 243 and 34, respectively. These equations allowed us to calculate a Ti and C surface density for any measured Ti(2p):Mo(3d) and C(1s):Mo(3d) ratio. The Ti and total C surface density, including the contribution from the base substrate, are included in the tables below for each dose at each temperature.

### Elemental Ratios for TTIP Deposition onto 573 K MoO<sub>x</sub>

	Base	300 L	600 L	900 L
Mo:O <sub>tot</sub>	3:1	1.1:1	0.7:1	0.4:1
Mo:Ti	-	4:1	2:1	1.1:1
Ti:C	-	2.5:1	4.9:1	5:1
Ti:O	-	1:2.1	1:1.7	1:2
Ti surface density (atoms/nm <sup>2</sup> )	0.2	5.7	11.3	20.7
C <sub>tot</sub> surface density (atoms/nm <sup>2</sup> )	1.8	4.8	5.2	7.1

**Table S1.** TTIP was dosed on to a 573 K MoO<sub>x</sub> substrate in three 300 L intervals. O<sub>tot</sub> and C<sub>tot</sub> denote the total O(1s) and C(1s) signals, including the contribution from base substrate. O and C denote the O(1s) and C(1s) signals without the contribution from the base substrate.

### Elemental Ratios for TTIP and H<sub>2</sub>O Deposition onto 473 K MoO<sub>x</sub>

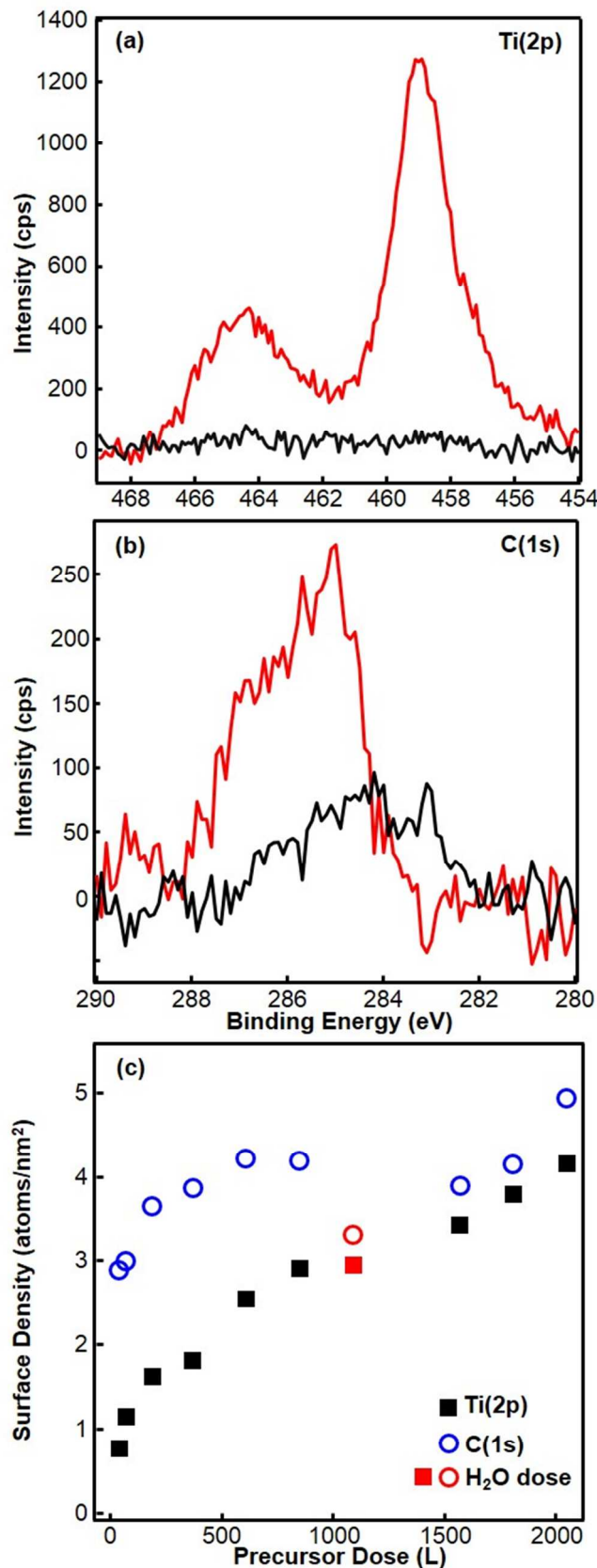
	Base	300 L	600 L	900 L	1200 L	300 L H <sub>2</sub> O	900 L H <sub>2</sub> O
Mo:O <sub>tot</sub>	1.8:1	1.4:1	1.3:1	1.2:1	1.2:1	1.1:1	1.2:1
Mo:Ti	-	12.8:1	9.3:1	7.4:1	6.4:1	6.1:1	6.4:1
Ti:C	-	1:1.3	1:1	1.4:1	1.3:1	2.2:1	2.3:1
Ti:O	-	1:1.8	1:1.8	1:1.6	1:1.5	1:1.6	1:1.7
Ti surface density (atoms/nm <sup>2</sup> )	0.4	2.1	2.8	3.4	3.9	4.1	3.8
C <sub>tot</sub> surface density (atoms/nm <sup>2</sup> )	2.0	4.4	4.6	4.4	4.7	3.9	3.7

**Table S2.** TTIP was dosed on to a significantly more oxidized 473 K MoO<sub>x</sub> surface in four 300 L intervals followed by a 300 and a 600 L H<sub>2</sub>O doses. O<sub>tot</sub> and C<sub>tot</sub> denote the total O(1s) and C(1s) signals, including the contribution from base substrate. O and C denote the O(1s) and C(1s) signals without the contribution from the base substrate.

### Elemental Ratios for TTIP Deposition onto 373 K MoO<sub>x</sub>

	Base	20 L	40 L	60 L	130 L	200 L	360 L H <sub>2</sub> O	220 L
Mo:O <sub>tot</sub>	1.6:1	1.5:1	1.5:1	1.5:1	1.4:1	1.4:1	1.4:1	1.3:1
Mo:Ti	-	67:1	37:1	26:1	20:1	18:1	16:1	14:1
Ti:C	-	1:5.8	1:2.8	1:2.9	1:2.8	1:2.8	1:1.3	1:1.6
Ti:O	-	1:-1.4	3.8:1	5.4:1	2.0:1	3.4:1	1.5:1	1.4:1
Ti surface density (atoms/nm <sup>2</sup> )	0.2	0.5	0.8	1.0	1.3	1.5	1.6	1.7
C surface density (atoms/nm <sup>2</sup> )	1.7	3.7	3.5	4.1	5.0	5.4	3.6	4.4

**Table S3.** TTIP was dosed on to a 373 K MoO<sub>x</sub> surface in increasingly larger intervals followed by a 360 L H<sub>2</sub>O dose. A final 20 L TTIP dose followed the H<sub>2</sub>O dose. O<sub>tot</sub> and C<sub>tot</sub> denote the total O(1s) and C(1s) signals, including the contribution from base substrate. O and C denote the O(1s) and C(1s) signals without the contribution from the base substrate. The first 20 L dose of TTIP resulted in a reduction in the O(1s) signal and is signified with the negative Ti:O ratio.



**Figure S1.** Displays the results for increasing doses of TTIP onto a less oxidized 473 K Mo substrate. (a) Ti(2p) spectra taken before (black) and after (red) a total of 2040 L of dosing time, (b) C(1s) spectra take of the base surface (black) and the total C(1s) signal (red) after a total of 2040 L of TTIP, (c) Ti (black squares) and C (open blue circles) surface densities for the base substrate and each precursor exposure.

### Effects of the Oxygen Coverage on the Base Substrate on TTIP Deposition

To investigate the influence of the degree of oxidation of the base MoO<sub>x</sub> substrate on the dehydration of TTIP, the deposition was repeated onto a 473 K MoO<sub>x</sub> substrate with a significantly lower O:Mo ratio. The doses into the UHV chamber were delivered with the Gemstar-6 rather than the dosing lines, however, the behavior remains the same. The elemental ratios are shown in Table S3. In this experiment the base substrate has ~0.5 monolayers of oxygen. This surface concentration of oxygen has been shown to have the chemical and physical properties of chemisorbed oxygen rather than a structured oxide. Figure S1a and b show the Ti(2p) and C(1s) spectra from the base substrate (black) and after 2040 L of TTIP exposure

(red). The binding energy for the Ti(2p<sub>3/2</sub>) is 459.0 eV, which is consistent with the results of the previous 473 K experiment. Similar to the results from the 573, 473 and 373 K depositions, the C(1s) spectrum after 2040 L of TTIP is bimodal with a shape resembling that of condensed isopropoxide ligands. The Ti(2p) and C(1s) surface densities as a function of precursor exposure are shown in Figure S1c. After the first TTIP dose the surface appears to be completely passivated with minor growth in the C(1s) signal until the water dose. Alternatively, the Ti(2p) signal is almost linear with exposure time after the first 60 L of TTIP. The linear dependence on TTIP exposure time along with the low C(1s):Ti(2p) suggests a CVD growth mechanism. The growth per L is not the same for each experiment performed on a 473 K substrate, but the observation of CVD instead of ALD is consistent. These results suggest that the degree of oxidation of our base MoO<sub>x</sub> substrate plays an insignificant role in the alternative reaction pathway of TTIP under our experimental conditions.

#### Elemental Ratios for TTIP Deposition onto a Less Oxidized 473 K MoO<sub>x</sub>

	Base	30 L	60 L	180 L	360 L	600 L	840 L
Mo:O <sub>tot</sub>	3.2:1	2.6:1	2.3:1	2.0:1	2.0:1	1.8:1	1.6:1
Mo:Ti	-	29:1	19:1	14:1	12:1	8.7:1	7.6:1
Ti:C	-	1:3.6	1:2.5	1:2.1	1:2.0	1:1.6	1:1.4
Ti:O	-	1:1.4	1:1.7	1:1.8	1:1.9	1:1.6	1:1.9
Ti surface density (atoms/nm <sup>2</sup> )	0.3	1.0	1.4	1.9	2.1	2.8	3.2
C <sub>tot</sub> surface density (atoms/nm <sup>2</sup> )	1.7	4.6	4.7	5.4	5.6	6.0	5.9

	1060 L	1560 L	1800 L	2040 L
Mo:O <sub>tot</sub>	1.6:1	1.4:1	1.4:1	1.3:1
Mo:Ti	7.5:1	6.5:1	5.8:1	5.4:1
Ti:C	1:1.0	1:1.1	1:1.0	1:1.1
Ti:O	1:1.8	1:2.2	1:2.1	1:1.9
Ti surface density (atoms/nm <sup>2</sup> )	3.2	3.7	4.1	4.4
C <sub>tot</sub> surface density (atoms/nm <sup>2</sup> )	5.0	5.6	5.9	6.7

**Table 4.** TTIP was dosed on to 473 K MoO<sub>x</sub> surface in increasingly larger intervals. After a total of 840 L of TTIP exposure, 1060 L of H<sub>2</sub>O was dosed on to the surface, followed by three more TTIP doses. O<sub>tot</sub> and C<sub>tot</sub> denote the

total O(1s) and C(1s) signals, including the contribution from base substrate. O and C denote the O(1s) and C(1s) signals without the contribution from the base substrate.

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2. Fryberger, T. B. Studies of Chemically Modified Mo(100) Surfaces using Photoelectron Spectroscopies and Physisorbed Xenon as a Probe. Northwestern, 1986.