Supplemental Data: Room Temperature Chemical Vapor Deposition of Aluminum and Aluminum Oxides on Alkanethiolate Self-Assembled Monolayers

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1. TOF SIMS Negative Ion Mass Spectra of -CH_3, -OH and -COOH Terminated SAMs after Exposure to TMA for 15 mins in a Reaction Chamber with a Base Pressure of 2.7 x 10^{-8} torr.

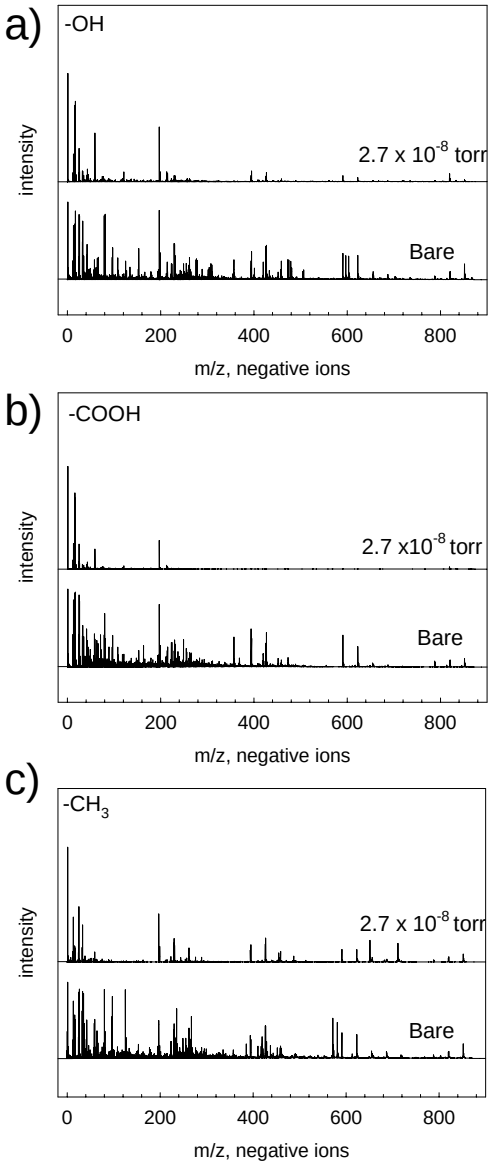

Figure S1. High resolution negative ion TOF SIMS mass spectra *m/z* = 0 - 900 of (a) -OH, (b) -COOH and (c) -CH_3 terminated SAMs exposed to TMA for 15 minutes in a reaction chamber with a base pressure of 2.7 x 10^{-8} torr.

2. TOF SIMS Positive Ion Mass Spectra of -COOH Terminated SAM after Exposure to 90 L TMA in a uhv Chamber.

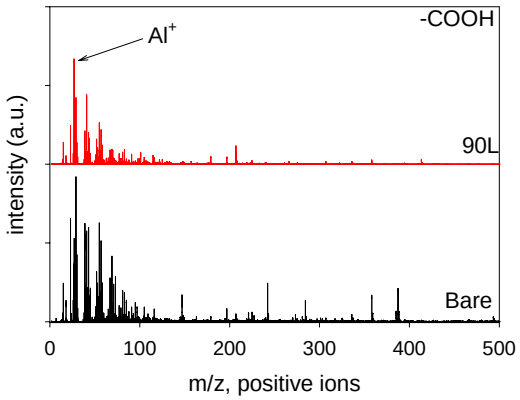

Figure S2. High resolution positive ion TOF SIMS mass spectra *m/z* = 0 - 500 of a -COOH terminated SAM exposed to 90 L TMA in uhv.

These data suggest that an Al overlayer is growing on the –COOH terminated SAM. The highest intensity ion in the mass spectrum is Al^+ (nominal mass *m/z* = 27) and the high mass ions (*m/z* > 200*)* have a very low intensity.

3. X-ray Photoelectron Spectroscopy (XPS)

3.1 Bare Monolayer

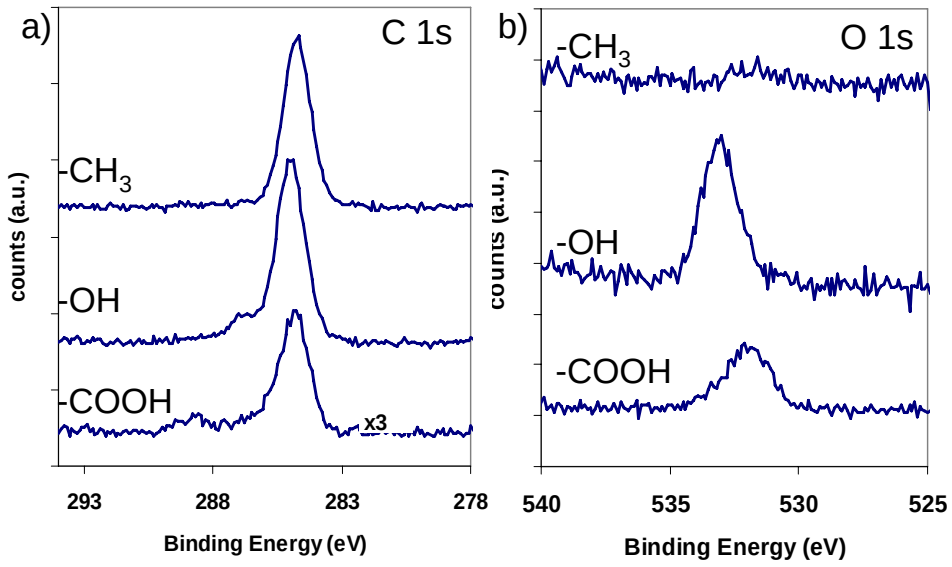

Figure S3. Core-level XPS spectra of the bare -CH_3, -OH and -COOH terminated self-assembled monolayers adsorbed on gold. (a) The C 1s core level spectrum. (b) The O 1s core level spectrum.

The core-level XPS spectra of the bare -CH_3, -OH and -COOH SAMs agree very well with previous studies.[1,2,3] For -CH_3 terminated SAMs there is a peak at 285 eV in the C1s spectrum. The C1s spectrum of the -OH terminated SAM displays two peaks, at 285.2 eV and 287.0 eV, which are assigned to -$\underline{C}H_2$- and -$\underline{C}H_2OH$, respectively. There is a single peak in the O1s spectrum at ~533 eV corresponding to the -$CH_2\underline{O}H$ functional group. For the -COOH terminated SAM the C 1s spectrum displays peaks at 285.2 eV and 289.2 eV which are assigned to -$\underline{C}H_2$- and -$\underline{C}OO$. In the O 1s spectrum there is a single broad peak at ~532 eV corresponding to the COOH oxygens.

3.2 Core-Level XPS Spectra of -CH_3, -OH and -COOH Terminated SAMs after Exposure to TMA

3.2.1 -CH_3 Terminated SAMs

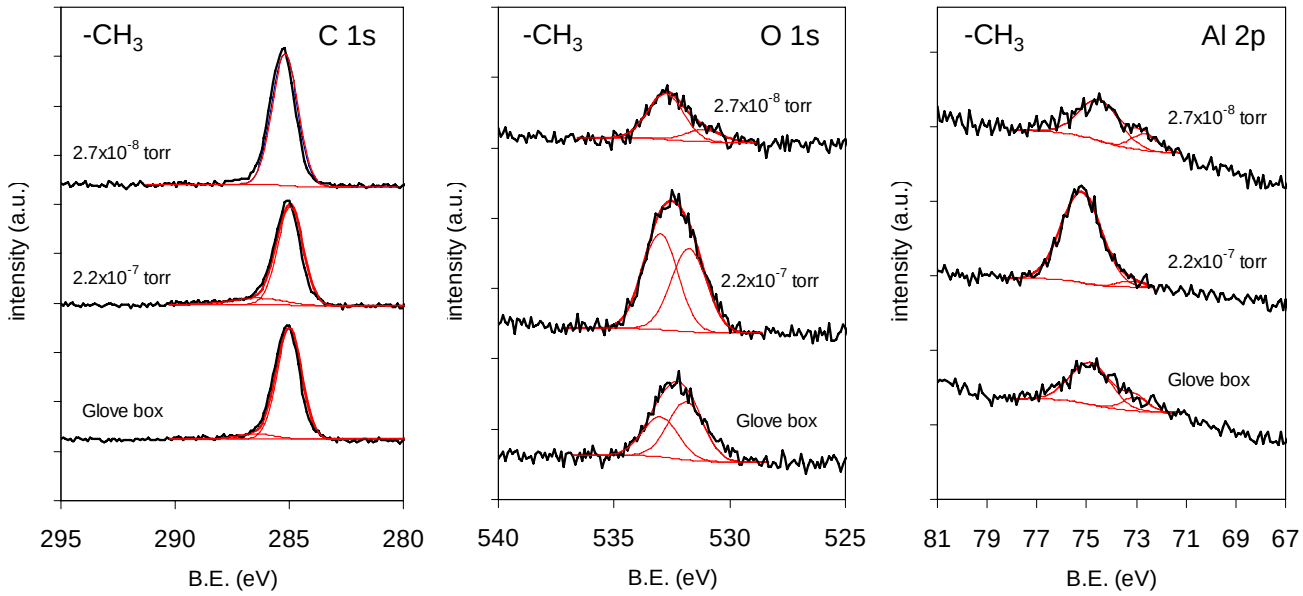

Figure S4. Core-level C 1s, O 1s and Al 2p XPS spectra of -CH_3 terminated SAMs after exposure to TMA vapor for 15 min in a nitrogen-purged glove box, a reaction chamber with a base pressure of 2.2 x 10^{-7} torr and a reaction chamber with a base pressure of 2.7 x 10^{-8} torr. The fits to the data are shown in red.

The C 1s core-level XPS spectra show that TMA does not react with -CH_3 terminated SAMs because no additional peaks are observed (for example at ~282 eV indicative of carbide formation) in the spectra. Two O 1s peaks of varying relative ratios are observed at ~531.5 eV and ~533 eV which we assign to oxygen in alumina, Al_2O_3 and AlO_x (or $Al(OH)_x$), respectively. The assignment of a non-stoichiometric aluminum oxide to the peak at ~533 eV seems reasonable since this peak increases in intensity as the base pressure of the deposition chamber decreases. The Al 2p data can be fit to two peaks at ~75 eV and ~73 eV which we assign to aluminum in Al_2O_3 and Al(0), respectively. We note that the ratio of the peaks at ~75 eV and ~73 eV is approximately constant for the three deposition conditions. This is surprising since one would expect that the relative intensity of the Al(0) peak would

increase as the base pressure of the deposition chamber decreases (as is the case for the -OH and -COOH terminated SAMs, see sections 3.2.2 and 3.2.3). In the fit procedure a FWHM of 1.9eV was assumed for the oxidized aluminum species. However, recent XPS experiments have observed a higher Al peakwidth (2.1 eV) for an amorphous aluminum oxide species due to the presence of a surface oxide.[4] This may account for the broad Al 2p peak observed here.

3.2.2 -OH Terminated SAMs

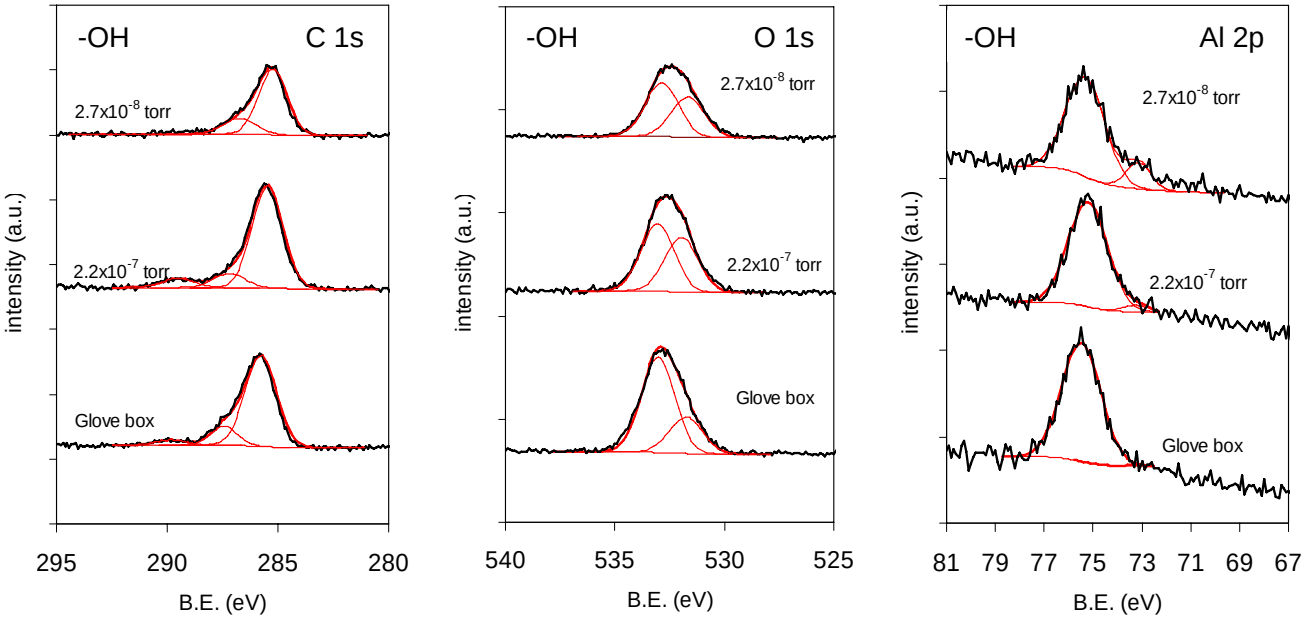

Figure S5. Core-level C 1s, O 1s and Al 2p XPS spectra of -OH terminated SAMs after exposure to TMA vapor for 15 min in a nitrogen-purged glove box, a reaction chamber with a base pressure of 2.2 x 10^{-7} torr and a reaction chamber with a base pressure of 2.7 x 10^{-8} torr. The fits to the data are shown in red.

TMA reacts with -OH terminated SAMs. The XPS C1s core-level spectra change noticeably upon exposure to TMA. The -$\underline{C}H_2$- 1s peak broadens considerably on the high binding energy side. A second peak also appears at a binding energy of ~290 eV, which indicates that TMA has reacted with the -OH terminated SAM. A peak associated with the formation of aluminum carbide, expected at 282.3 eV, is

not observed. The O 1s peak can be fit to two separate oxygen-containing species with binding energies of 531.8 eV and ~533 eV. We assign the peak at 531.8 eV to oxygen in alumina and the peak at 532.9 eV to oxygen in the hydroxyl group. The decrease in the binding energy indicates an increased electron density on the hydroxyl group atoms, which is consistent with TMA reacting with the -OH terminated SAM to form an aluminum-organic complex.[2] Two peaks are also present in the Al 2p spectra at 72.9 eV and 75.5 eV which we assign to Al (0) and Al_2O_3. We note that the intensity of the peak at 72.9 eV increases as the base pressure of the reaction decreases, suggesting that metallic aluminum is deposited, in agreement with the TOF SIMS data.

3.2.3 -COOH Terminated SAMs

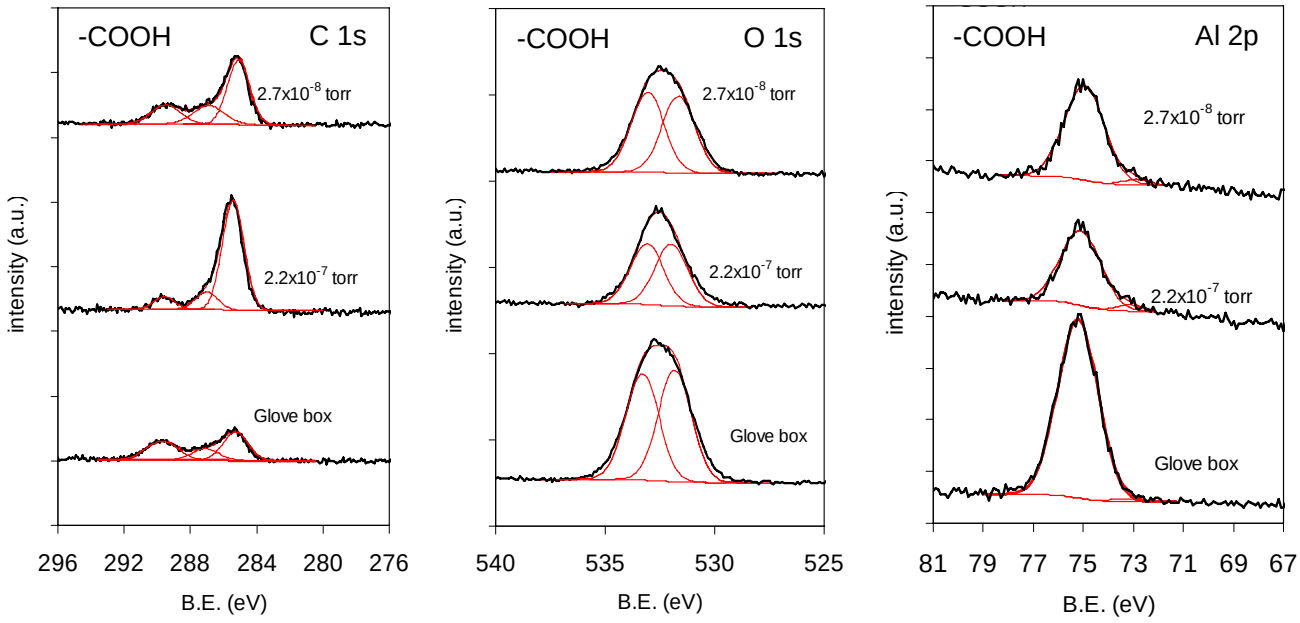

Figure S6. Core-level C 1s, O 1s and Al 2p XPS spectra of -COOH terminated SAMs after exposure to TMA vapor for 15 min in a nitrogen-purged glove box, a reaction chamber with a base pressure of 2.2 x 10^{-7} torr and a reaction chamber with a base pressure of 2.7 x 10^{-8} torr. The fits to the data are shown in red.

These data show that TMA also reacts with -COOH terminated SAMs and that the largest amount of Al deposition is observed on these surfaces. The XPS C 1s core-level spectra change considerably upon exposure to TMA. The -$\underline{C}H_2$- C 1s peak broadens on the high binding energy side. A second peak also appears at a binding energy of ~289 eV, which indicates that TMA has reacted with the -COOH terminated SAM. A similar peak is observed in the -OH terminated SAM spectra which suggests that the TMA reacts with -OH and -COOH to form similar metal-organic complexes. No peak is observed on the low binding energy side, indicating that aluminum carbide has not formed. The O 1s peak can be fit to two separate oxygen-containing species with binding energies of 531.9 eV and 533.0 eV. We assign the peak at 531.9 eV to oxygen in alumina and the peak at 533.0 eV to carboxyl oxygens which have reacted with TMA to form metal-organic complexes. In the Al 2p spectra, we also observe two peaks at 72.8 eV and 75 eV which we assign to Al (0) and alumina, Al_2O_3, respectively. The intensity of the peak at 72.9 eV increases as the base pressure of the reaction decreases, suggesting that metallic aluminum is deposited in agreement with the TOF SIMS data.

References

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2. Fisher, G. L.; Hooper, A. E.; Opila, R. L.; Allara, D. L.; Winograd, N., J. Phys. Chem. B 2000, 104, 3267-3273.

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