

**The reaction of tetrakis(dimethylamido)titanium with self-assembled
alkyltrichlorosilane monolayers possessing -OH, -NH₂ and -CH₃ terminal groups**

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Supporting Information (14 pages)

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Substrate Preparation. The substrates were scribed with a Florod LASER 1 MEL 40 laser system and subsequently cleaved into 16 samples, each a square of side 16.75 mm. After cleaving, these samples were sonicated in chloroform, washed with de-ionized (DI) water, dried with N₂, and then dipped in BOE for 1 min. A thin layer of silicon dioxide (so-called “chemical oxide”) was grown by placing the samples in Nanostrip solution (a stabilized formulation of sulphuric acid and hydrogen peroxide) for 15 min. at 75 °C. The samples were then subject to a BOE and Nanostrip treatment for a second time to yield “chemical oxide”, the starting surface for SAM formation.

SAM Formation. Deposition was carried out in a glove box (Unilab, M. Braun Inc.) equipped with a refrigeration unit (temperatures to -35 °C) and a nitrogen atmosphere with < 1 ppm O₂. All glassware was rinsed repeatedly with acetone, isopropanol and DI water and then baked overnight at 150 °C before use.

Formation of Terminal Groups. The vinyl terminated SAM ($\equiv\text{Si}-(\text{CH}_2)_9-\text{CH}=\text{CH}_2$) was converted to a -OH terminated SAM ($\equiv\text{Si}-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2\text{OH}$) by a 2 hour dip in 1.0 M BH₃-THF solution followed by a dry THF rinse, and a 2 min. dip in a 30% H₂O₂:0.1N NaOH solution. Samples were then washed with DI water, dried with N₂ and stored in precleaned fluoroware containers. The -CN terminated SAM ($\equiv\text{Si}-(\text{CH}_2)_{11}-\text{CN}$) was converted into an -NH₂ terminated SAM ($\equiv\text{Si}-(\text{CH}_2)_{11}-\text{CH}_2-\text{NH}_2$) by a 4 hour dip in 1.0 M BH₃-THF solution, followed by a 1 hour dip in methanol, and finally a 15 min. dip in 10% HCl to deprotonate the amine group. Samples were washed with DI water, dried with N₂ and stored in precleaned fluoroware containers.

Thermal Stability of Self-Assembled Monolayers. For a 11 carbon undecenyltrichlorosilane SAM, annealing to 125°C for 2 hours in a 10^{-2} - 10^{-3} Torr ambient was found to onset disordering as evidenced by water and hexadecane contact angle measurements. In addition, the 11 carbon SAM and 18 carbon OTS on SiO₂ have been reported to undergo disordering with a drastic increase in surface roughness from 0.4 nm to 1.5 nm and 2.0 nm respectively (from AFM) on annealing to 150°C in a 10^{-2} - 10^{-3} Torr ambient [1] for time periods of about 5 hours.

UHV Apparatus. The microcapillary array doser made of lead silicate glass, (0.3 mm thick, 18 mm dia. of capillary area, 5 μ m pore size, 6 μ m center to center spacing with solid border) was used to deliver a uniform flux of Ti[N(CH₃)₂]₄ to the surface of the sample, without producing a significant rise in the background partial pressure. The doser was 25.4 mm from the center of the sample during exposures. A ¼ in. silver plated 316 SS VCR gasket with an aperture 178.8 μ m in diameter and 125 ± 25 μ m long was placed upstream of the doser, and between the doser and the stainless steel vessel (“bubbler”) containing the Ti[N(CH₃)₂]₄. For most experiments, the flow was metered by controlling the temperature of the bubbler, and using the gasket as a flow-limiting orifice. Exposures were initiated by opening a bellows-sealed valve placed between the bubbler and the aperture. Exposures were shunted by condensing the Ti[N(CH₃)₂]₄ in a LN₂ cooled side arm placed up stream of the doser. The partial pressure vs. exposure time relationship was verified using mass spectrometry, and an initial transient caused by reversible adsorption of Ti[N(CH₃)₂]₄ on the inner surfaces of the feed line was quantified, and the exposures have been suitably adjusted. An estimate for the absolute

flux of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ reaching the sample surface was made using the following procedure. First, the resistance to flow was calculated for the section of (4.57 mm i.d.) tubing between the capacitance manometer (MKS) (placed between the bubbler and the flow-limiting orifice); the flow-limiting aperture, and the capillary array. For typical conditions (measured partial pressure of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ at the bubbler < 0.05 Torr), we found that the flow-limiting orifice provided $\sim 90\%$ of the resistance to flow. Coupled with the measured partial pressure this gave a total throughput of 4.171×10^{14} molecules- s^{-1} of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ entering the chamber.

X-ray photoelectron spectroscopy (XPS). The emission current for the source was 20 mA and the electron voltage was 12 kV.

Equations.

For emission from the C in the SAM, the intensity is given by:

$$I_{C(1s)}(\theta) = I_{0,SAM,C(1s)} \left(1 - \exp \left(- \frac{d_{SAM}}{\lambda_{SAM,C(1s)} \cos \theta} \right) \right) \quad (1)$$

whereas that for emission from the O in the chemical oxide is given by:

$$I_{O(1s)}(\theta) = I_{0,ox,O(1s)} \exp \left(- \frac{d_{SAM}}{\lambda_{SAM,O(1s)} \cos \theta} \right) \left(1 - \exp \left(- \frac{d_{ox}}{\lambda_{ox,O(1s)} \cos \theta} \right) \right) \quad (2)$$

where I_0 represents the emission from a semi-infinite thin film of either the SAM [for C(1s)] or the chemical oxide [for O(1s)].

Ti in the adlayer is arranged in a 2-D plane at a distance d from the surface.

Photoemission from such a layer is given by:

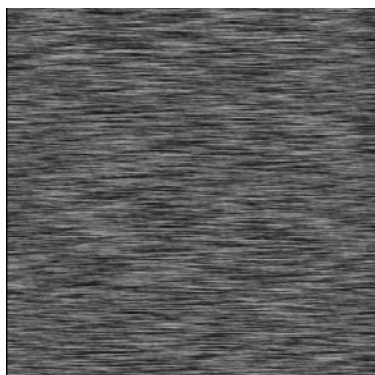
$$I(\theta) = \left(\frac{I_0}{\cos \theta} \right) \exp \left(\frac{-d}{\lambda \cos \theta} \right) \quad (3)$$

where I_0 represents the unattenuated emission one would achieve at a normal take-off angle and λ is the inelastic mean free path of the Ti(2p) photoelectrons.

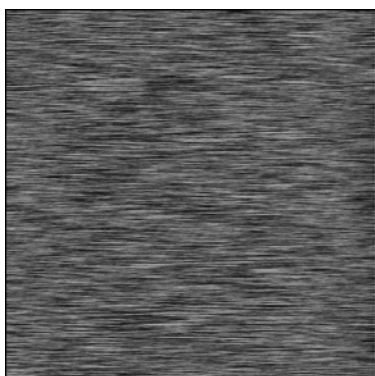
References

[1] Calistri-Yeh, M.; Kramer, E. J.; Sharma, R.; Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Brock, J. D. *Langmuir* **1996**, 12, 2747-2755.

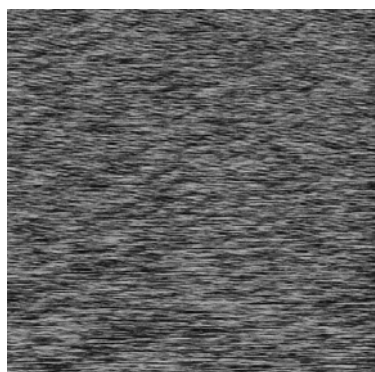
**Fig. S1 Killampalli,
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-OH



-NH₂



-CH₃ SAM

— 50 nm

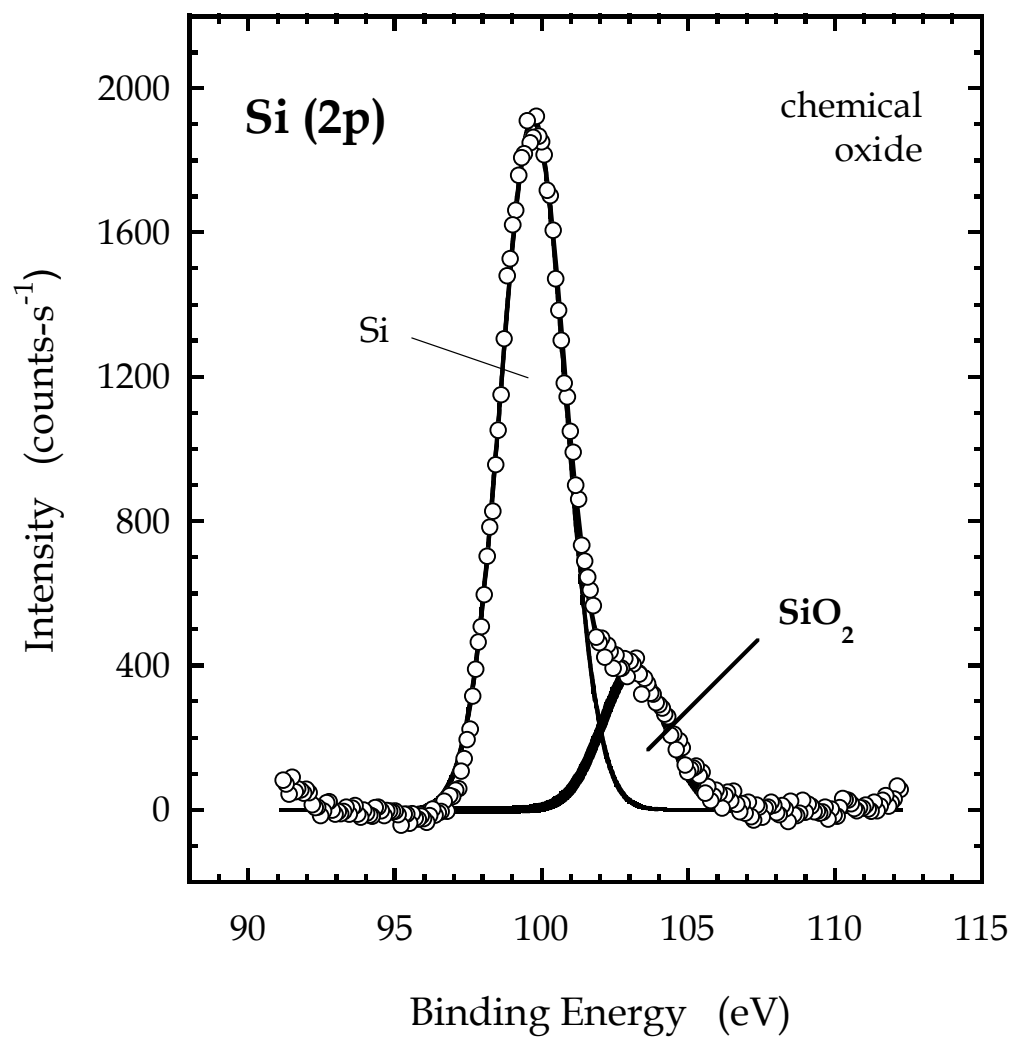


Fig. S2 Killampalli, Ma, Engstrom

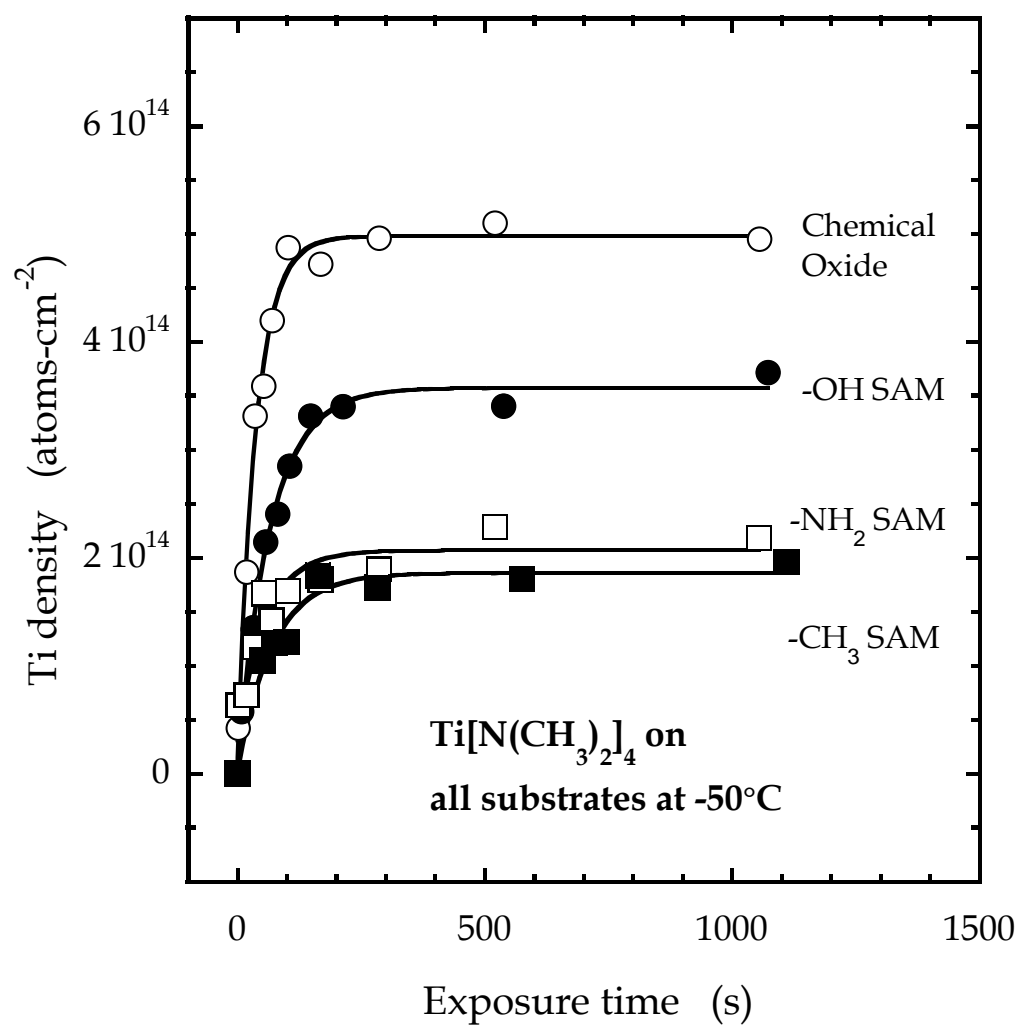


Fig. S3 Killampalli, Ma, Engstrom

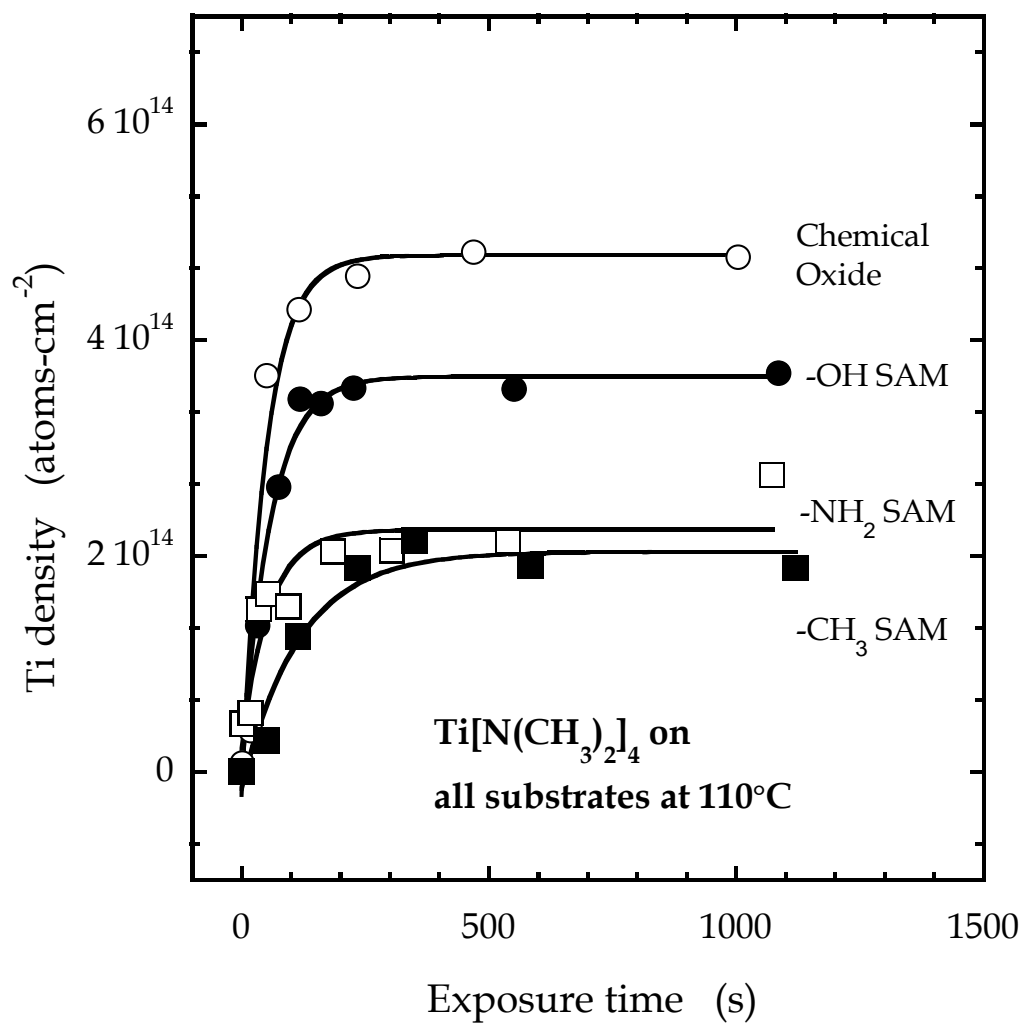


Fig. S4 Killampalli, Ma, Engstrom

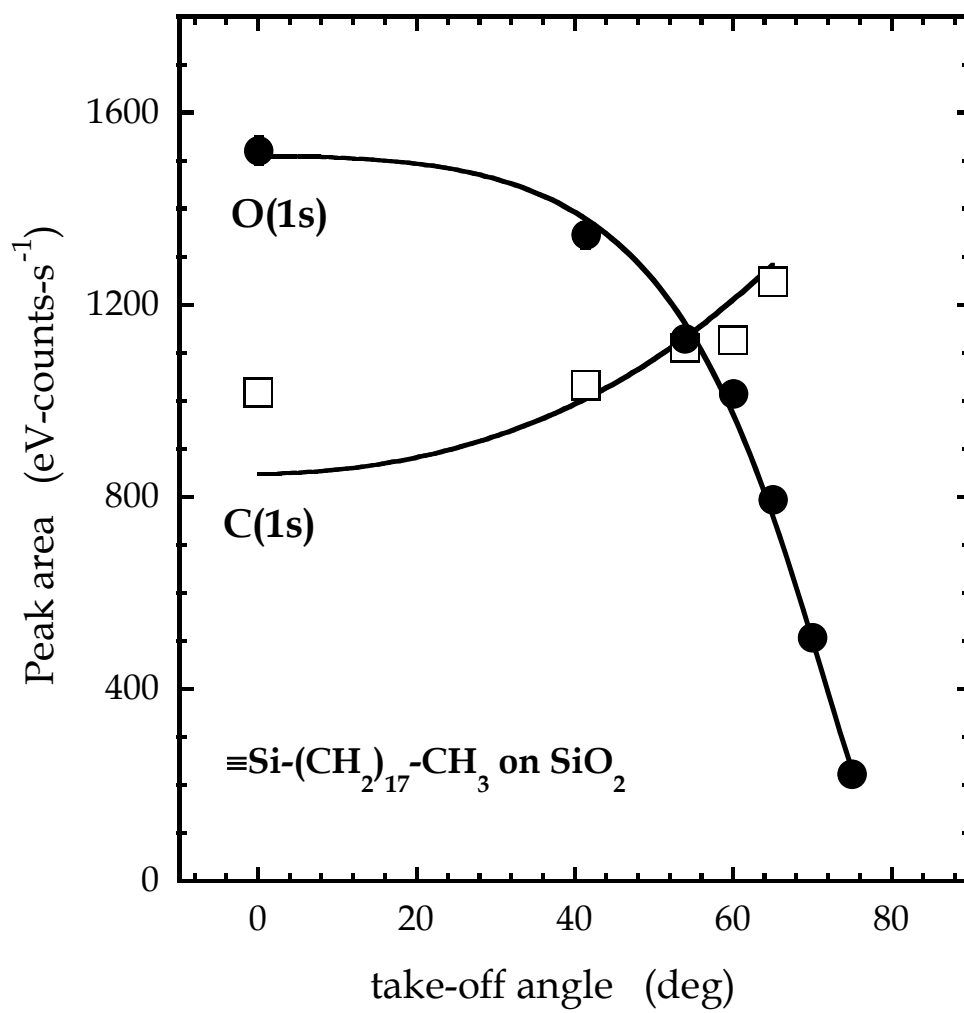


Fig. S5 Killampalli, Ma, Engstrom

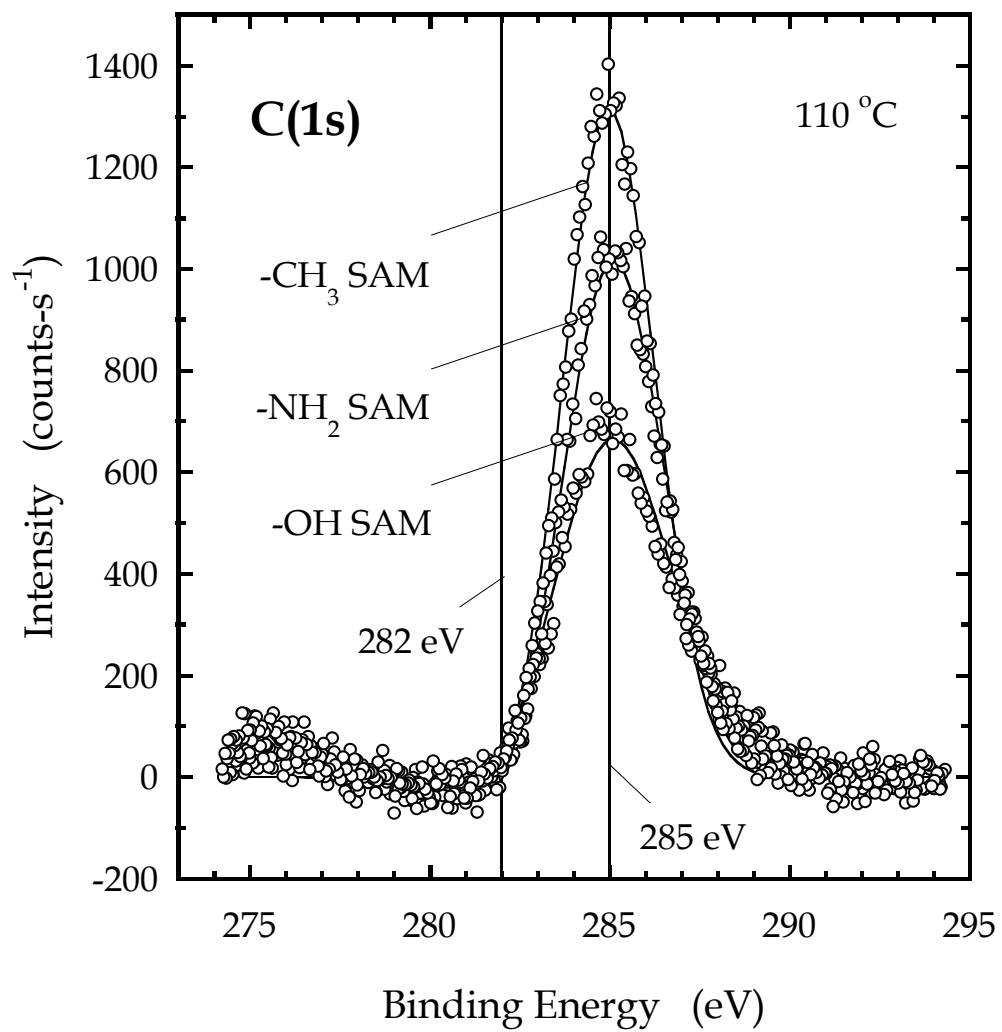


Fig. S6 Killampalli, Ma, Engstrom

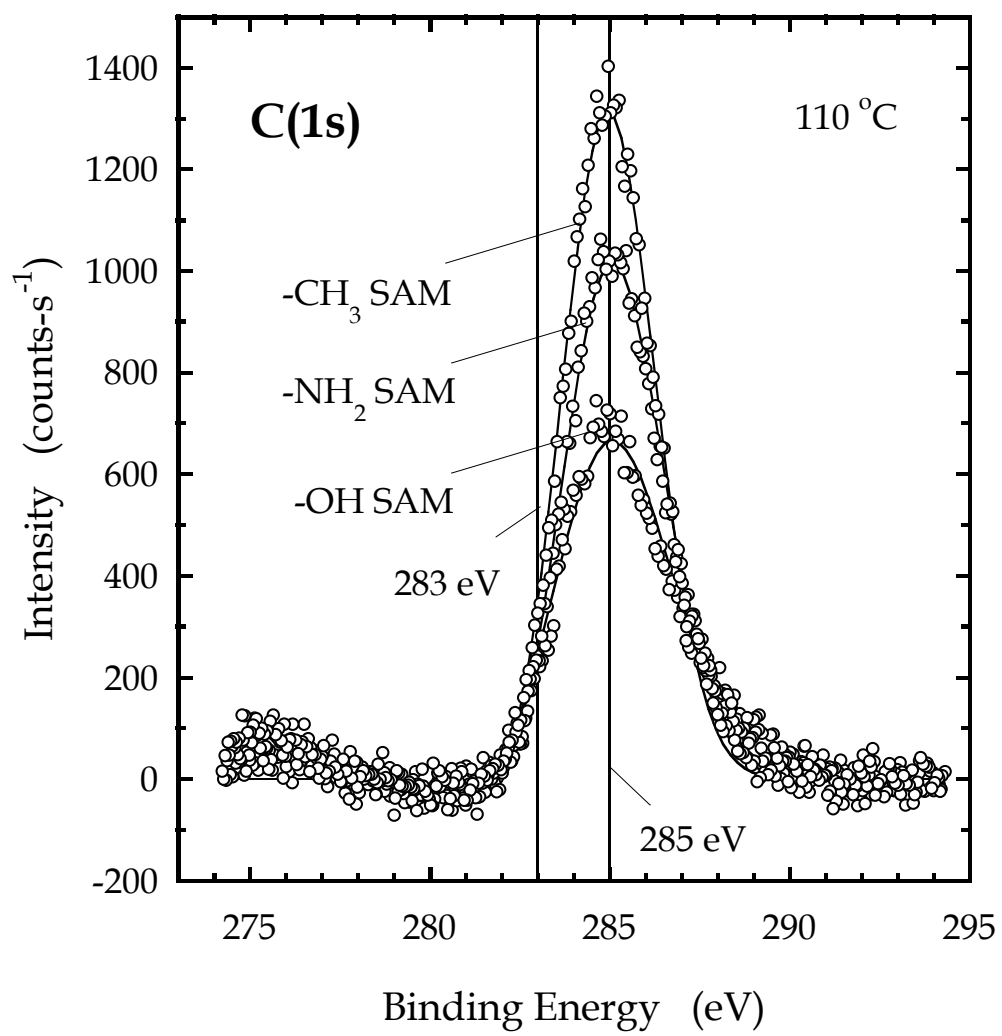


Fig. S7 Killampalli, Ma, Engstrom

- Fig. S1** Atomic force micrographs of the three SAM surfaces examined here: -OH, -NH₂ and -CH₃ terminated. These are representative micrographs, similar images were obtained at different spots on each sample. In each case the field of view is 250 nm × 250 nm. The RMS roughness was ~ 4 Å for all surfaces (see Table 1).
- Fig. S2** XP spectrum of the Si(2p) feature for silicon dioxide (“chemical oxide”) on silicon. The spectrum has been fit to two peaks (at 99.7 and 103.16 eV) as described in the text, and these are indicated by the smooth curves.
- Fig. S3** Coverage-exposure relationship, deduced from XPS, for the adsorption of Ti[N(CH₃)₂]₄ on chemical oxide, -OH terminated SAM, -NH₂ terminated SAM and -CH₃ terminated SAM at a substrate temperature of -50 °C. The fits to the data, shown as smooth curves, are for a first-order Langmuirian model of adsorption.
- Fig. S4** Coverage-exposure relationship, deduced from XPS, for the adsorption of Ti[N(CH₃)₂]₄ on chemical oxide, -OH terminated SAM, -NH₂ terminated SAM and -CH₃ terminated SAM at a substrate temperature of 110 °C. The fits to the data, shown as smooth curves, are for a first-order Langmuirian model of adsorption.
- Fig. S5** Peak areas of the O(1s) and C(1s) regions derived from XP spectra of a -CH₃ terminated SAM (≡Si-(CH₂)₁₇-CH₃) on chemical oxide as a function

of take-off angle. The smooth curves are fits to the data to Eqs. (1) and (2), which account for attenuation of the photoelectrons, and the finite thickness of both the SAM and the underlying chemical oxide.

Fig. S6 XP spectra of the C(1s) feature for the -OH, -NH₂ and -CH₃ terminated SAMs exposed to Ti[N(CH₃)₂]₄ at 110 °C. Spectra have been fit to two peaks using Gaussian-Lorentzian product functions. The first peak is forcibly centered at a binding energy of 282 eV corresponding to carbon bound to a titanium species.

Fig. S7 XP spectra of the C(1s) feature for the -OH, -NH₂ and -CH₃ terminated SAMs exposed to Ti[N(CH₃)₂]₄ at 110 °C. Spectra have been fit to two peaks using Gaussian-Lorentzian product functions. The first peak is forcibly centered at a binding energy of 283 eV corresponding to carbon bound to a titanium species.