Supporting Information for:

Use of Mixed CH_3–/$HC(O)CH_2CH_2$–Si(111) Functionality to Control Interfacial Chemical and Electronic Properties During the Atomic Layer Deposition of Ultrathin Oxides on Si(111)

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Calculation of Surface Coverage from X-ray Photoelectron Spectra

The average oxide thickness was measured using quantitative XPS and AFM was not used for thickness measurements. The oxide coverage on the Si surfaces was calculated according to published methods using the following equations:[1]

$$\Phi_A = Q_{AB}\frac{I_A/I_A^{\infty}}{I_B/I_B^{\infty}} \quad 5.61$$

$$Q_{AB}^{X} = \left[\frac{\lambda_A(E_A)\cos\theta}{a_A}\right] \quad 5.63$$

where Φ_A is the fractional coverage of monolayer A over the substrate B.

Q_{AB}^{X} is the monolayer matrix factor for XPS. $I_A^{\infty}/I_B^{\infty}$is an intensity ratio. λ_A is the inelastic mean free path in nm (IMFP). θ is the electron take-off angle from surface-normal. a_M is derived from $1000\ \rho N\ a_M^3 = A_M$ where, in turn, ρ is the density (in kilograms per cubic meter), N is Avogadro's Number and $A_M$is the mean atomic weight.

The full form of the equation is:

$$\Phi_A = \left[\frac{\lambda_A\ cos\ \theta}{\sqrt[3]{\frac{A_A}{1000\ \rho N}}}\right]\left(\frac{I_B^{\infty}}{I_A^{\infty}}\right)\left(\frac{I_A}{I_B}\right)$$

λ_A can theoretically be obtained from multiple-angle XPS experiments. Elastic scattering effects are presumed negligible, so this is taken to be equal to the inelastic mean-free path. We know that this expression is incomplete because λ_{SiO_2} and $\lambda_{Al_2O_3}$are not necessarily equal, however, we used λ = 2.1nm following a published procedure.[2]

On our Kratos spectrometer we measured $\left(\frac{I_{Si}^0}{I_{SiO_2}}\right) = 1.3$ and $\left(\frac{I_{Si}^0}{I_{Al_2O_3}}\right) = 2.0.$

For aluminum oxide:

$$\sqrt[3]{\frac{A_A}{1000\ \rho N}} = \frac{101.9\ g/mol}{\left(\frac{1000g}{1\ kg}\right) * \ 6.023 * \ 10^{23}\frac{1}{mol}3950\ \frac{kg}{m^3}\left(\frac{1\ m}{10^9 nm}\right)^3} = 3.5\ nm$$

On the Kratos $\theta = 0^o, \cos 90 = 1$.

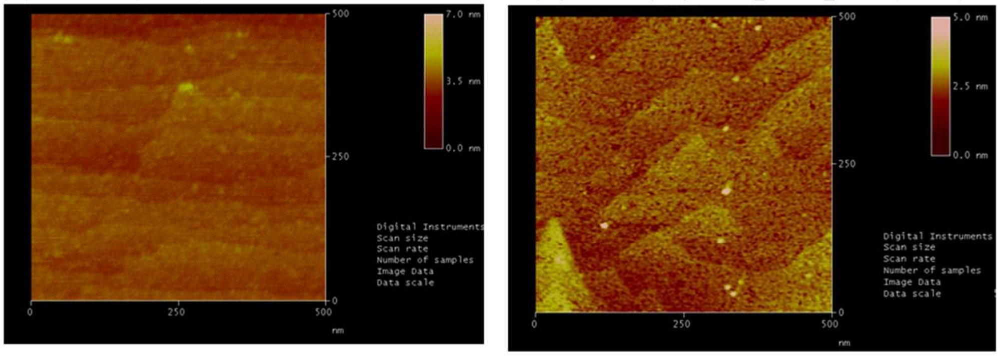
Using standard methods for propagation of errors, assumed errors on the relative sensitivity ratio to be 20%. For a_A and λ_A the assumed the relative error is 30%.

Microwave Conductivity Measurements

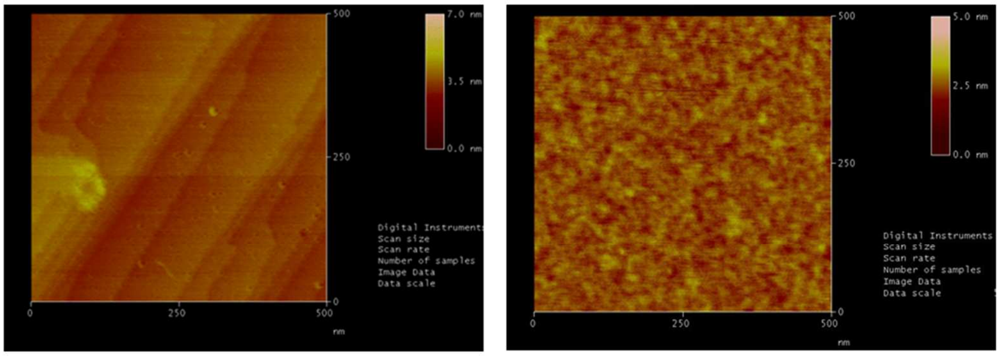
The SRV measurement was conducted in air, and the time taken to make the measurement prior to ALD deposition would have allowed for oxidation and a chemical change in the H-terminated Si(111) surface. A measurement of the recombination velocity for H-terminated Si surfaces prior to ALD is included in Table 1 (0-cycle column).

Supporting Figures

(a) H-Si(111) (b) $HC(O)CH_2CH_2$-Si(111)



(c) CH_3-Si(111) (d) Piranha-cleaned Si(111)



(e) Mixed $CH_3/HC(O)CH_2CH_2$-Si(111)

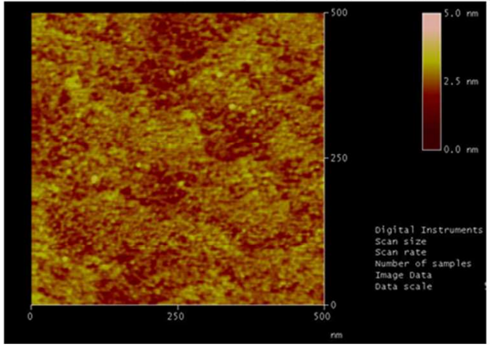


Figure S1. Atomic-force microscopy images of various surfaces after five cycles of atomic-layer deposition using TMA and H_2O. The starting surfaces were (a) H-Si(111), (b) aldehyde-functionalized Si(111), (c) methyl-functionalized Si(111), (d) piranha cleaned Si(111), and (e) Si(111) modified by a mixed monolayer containing aldehyde and methyl functional groups.

References

(1) Gleason-Rohrer, D. C.; Brunschwig, B. S.; Lewis, N. S. Measurement of the band bending and surface dipole at chemically functionalized Si(111)/vacuum interfaces. *J. Phys. Chem. C* **2013,** *117*, 18031-18042.

(2) Kim, K. J.; Jang, J. S.; Lee, J. H.; Jee, Y. J.; Jun, C. S. Determination of the Absolute Thickness of Ultrathin Al_2O_3 Overlayers on Si (100) Substrate. *Anal. Chem.* **2009,** *81*, 8519-8522.