Supplementary Information

**Quantum Chemical Calculations**

Computational Details
The program package TURBOMOLE[1] was used. All structural optimizations were performed at the BP86[2]/SV(P)[3] level of theory , involving full electrostatic screening (i.e. assuming a dielectric constant of infinity) via the solvation model COSMO[4]. As single-point energy method, BP86/TZVP[5] was employed. Gibbs free energies of reaction for a strongly dilute aqueous solution were computed as described by one of the authors[6], employing COSMO-RS theory[7] and statistic thermodynamics. As with certain larger model compounds (e.g. a methylated octasequisiloxane core) vibrational spectra will contain rather low frequencies that would give rise to artefacts in the vibrational molecular partition function, entropy contributions due to the vibrational partition function were omitted (as they should be small for the reactions under consideration, anyway), whereas zero point vibrational energetic contributions were computed at the BP86/SV(P) level.

Models for the Silicon Wafer Surface
Two models were chosen, a adamantine-like structure with one surface OH to represent the contact of intact silicon with the aqueous medium (a) and an octasesquisiloxane, reflecting surface oxidation to Si^{IV} (b). The latter species was terminated with methyl groups to avoid energetic artefacts from intramolecular H-bridge formation.

(a)   (b)
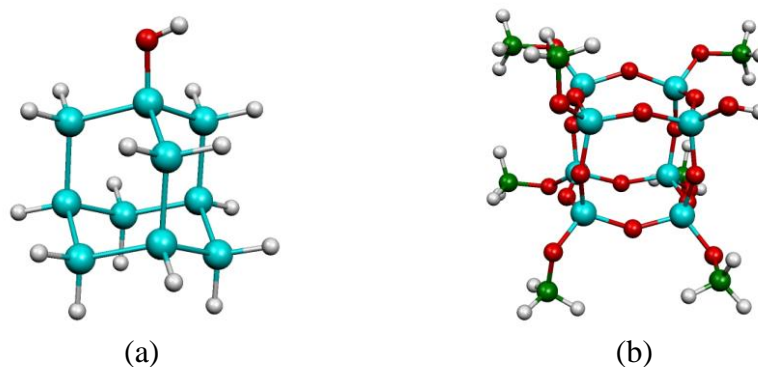
Computation of pK_a
For the acid-base couple isobutyric acid / isobutyrate as reference (pK_a=4.86[8]) which represents at the same time a model for polyacrylate, the following reaction was considered:
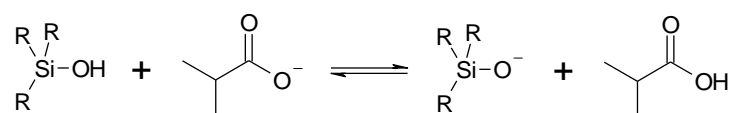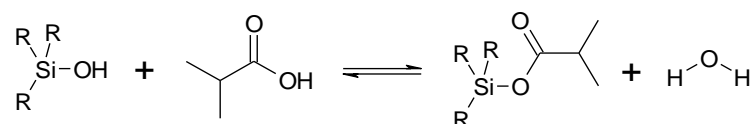

pK_a values were then computed from:

$$\Delta G = -RT \ln(K) = RT \ln(10) \cdot \{pK_a(R_3SiOH) - pK_a(iBA)\}$$

This yielded the following results:

	ΔG [kJ/mol]	pK$_a$
(a)	+42.23	12.43
(b)	+20.08	8.38

Computation of Wafer Surface Esterification
The following reaction was considered:

This yielded the following results:

	ΔG [kJ/mol]
(a)	+33.92
(b)	+52.99

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