Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Monte Carlo Model Fitting

Figure S1 shows the Monte Carlo fitting for the idealized structures of mono-, di-, and tri-functional silane SAMs with a high density of surface and in-plane linkages. We record an exponential decay for mono-functional silanes as expected. Variations from the model behavior are observed for di- and tri-functional silanes due to the in-plane connectivity.

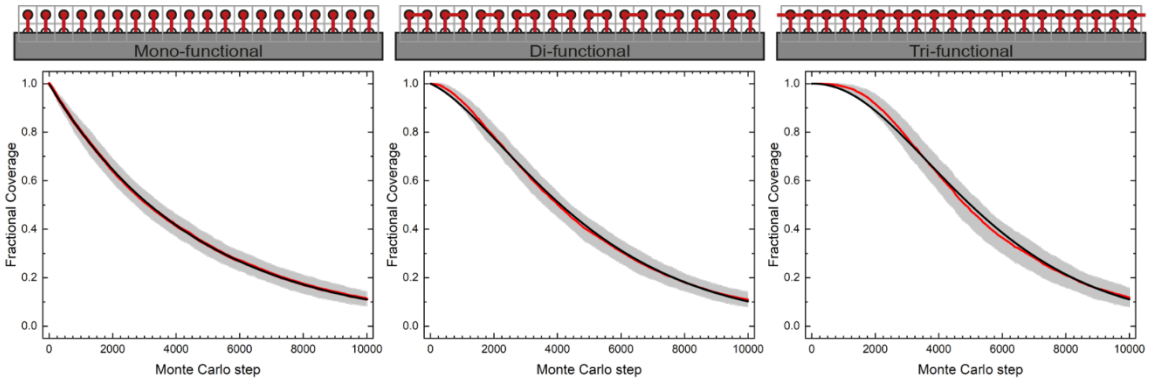

Figure S1. Fractional coverage of 100 molecules with a) mono-, b) di-, c) tri-functional molecules attached covalently to the surface as a function of the number of Monte Carlo (MC) steps. The red line and the grey shaded area denote the average and standard deviation from the MC simulation, respectively. The black lines are the best fits to Equations (1)-(3) in the main text.

Model Fitting of Experimental Data

Table S1. Summary of the rate constants (k in min^{-1}) for the various silane degrafting processes.

Silane	Degrafting temperature (°C)			
	40	**45**	**50**	**55**
OTMS	0.004	0.006	0.010	0.011
OTCS*	0.007	0.008	0.011	0.018
FTCS*	0.008	0.014	0.020	0.028
FDMCS*	0.044	0.077	0.102	0.134

APTES	0.004	0.004	0.006	0.017
eBMPUS	0.003	0.004	0.005	0.006

Table S1 lists the rate constants for the degrafting of the silanes studied resulting from the model fit. OTMS shows a nearly identical degrafting rate to what was previously observed for OTCS deposited from hexanes. OTCS deposited from the vapor phase shows a comparable rate to OTCS deposited from hexanes. The fluorinated silanes (FTCS and FDMCS) exhibit higher rate constants due to the lower density of silanes on the surface for a complete monolayer as a result of their bulkiness. eBMPUS has a lower reaction rate constant than the alkylsilanes most likely due to the longer backbone chain.

Table S2. Summary of the fitting parameters, activation energies (E_a), and Arrhenius pre-factors (A) for the various silane degrafting processes.

Silane	**α_0**	**β_0**	**γ_0**	**E_a (kJ/mol)**	**A (min^{-1})**	**R^2**
OTMS	0.542	0.000	0.373	54.76	$6.22x10^6$	0.936
OTCS*	0.644	0.000	0.261	54.74	$8.44x10^6$	0.938
FTCS*	0.235	0.743	0.001	68.36	$2.19x10^9$	0.994
FDMCS*	0.858	0.000	0.000	62.12	$1.09x10^9$	0.971
APTES	0.449	0.000	0.157	79.88	$6.47x10^{10}$	0.818
eBMPUS	0.527	0.000	0.415	45.80	$1.19x10^5$	0.991

The Arrhenius equation, $k = Ae^{-E_a/(RT)}$, was used to calculate the activation energy, E_a, and pre-exponential factor, A, for the degrafting process of each of the silanes studied.