

A Density Functional Theory with van der Waals Corrections Study of the Adsorption of Alkyl, Alkylthiol, Alkoxy and Amino-Alkyl chains on the H:Si(111) Surface

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Supporting Information

S.1 Clarifying the role of vdW interaction:

We did a few test calculations to find out more about van der Waals interactions of Chain-Chain vs Chain-Substrate. For this purpose, we created a 3×3 supercell (9 dangling bonds saturated with H), once functionalized with one hexane and next functionalized with two. We allowed the structure to relax and then removed the silicon slab and saturated the linker carbon with hydrogen and calculated total energy for each case. Chain-Chain interaction can be understood from here by calculating $\Delta E = [E_{\text{tot}}(2 \times C_6) - 2 \times E_{\text{tot}}(C_6)]$. We did it for both PBE and PBE+vdW cases. The result is presented in the below table:

	ΔE (eV)
PBE	0.04
PBE+ vdW	-0.19

We also calculated the adsorption energy of hexane chains as a result of 11% and 66% coverage. For 11% coverage, we can fairly consider the chain interacting only with substrate however for 66%, chain-chain interaction is also involved. The results are shown in the next table.

	E_{ads} (eV)	
	11%	66%
PBE	0.39	1.12
PBE+ vdW	-0.26	0.07

The results highlight some points:

(1) PBE approximation does not predict any chain-chain interaction however adding vdW term indicates that there is an attractive vdW force between chains that makes it more stable compared to single chain by -0.2 eV approximately.

(2) As discussed thoroughly in the paper, vdW correction does predict a lower adsorption energy compared to PBE. Also considering the difference between $E_{\text{ads}}(\text{PBE})$ and $E_{\text{ads}}(\text{PBE}+\text{vdW})$ for 11% and 66% which is 0.7 and 1 eV respectively we conclude that chain-chain interaction makes adsorption more favorable. This is also supported by the observation that for longer alkyl chain length, the adsorption energy decreases, that is, stability increases as shown in Figure S1 below. (The fact that 66% coverage seems less stable than 11%, is a separate issue which is related to optimum coverage of alkyl functionalization as discussed in the paper.)

S.2 Chain length dependence of stability ordering for (X)-Alkyl functionalization:

Figure S1 plots the adsorption energy against chain length for the Si surface modifiers, with the adsorption energies given in table 3 of the paper. It is clear that with the exception of the sulfur linker, convergence in the adsorption energies for chains with four or more carbon atoms is found. Finally, the difference between the adsorption energies of the chains with different linkers is not affected by changing the chain length. Oxygen is always the most stable linker and direct bonding of the alkyl chain the least stable, that is, $E_{\text{Alkoxy}}^{\text{ads}} < E_{\text{Thiol-Alkyl}}^{\text{ads}} < E_{\text{Amine-Alkyl}}^{\text{ads}} < E_{\text{Alkyl}}^{\text{ads}}$. The adsorption energies for chains with the sulfur linker do not appear to follow this convergence. We find three regimes for the adsorption energy versus number of carbons; one regime for $n \leq 2$, second for $2 < n < 8$ and the third regime for $n > 8$. This is the result of different structural properties as discussed in the paper.

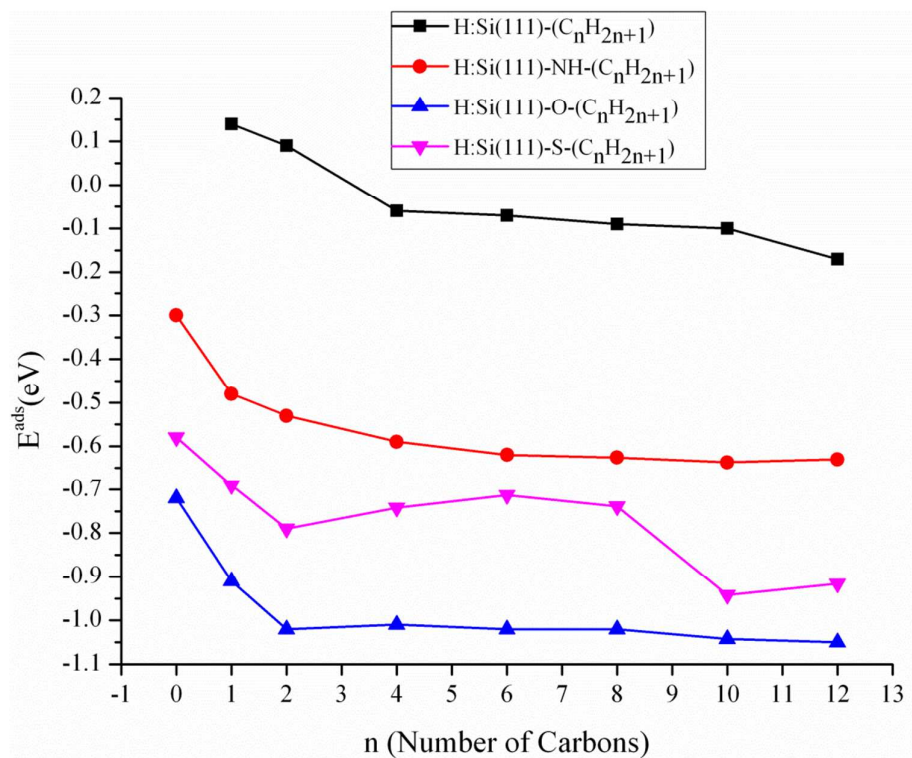


Figure S1. Adsorption energy for the alkyl chain ($n = 0, 1, 2, 4, 6, 8, 10, 12$) and linker combinations, O, N, S, studied in this work.

Now splitting the vdW effect into chain-chain and chain-interface interactions, the first term grows as the chain length grows, however the second term vanishes with distance from the surface with the factor of r^{-2} . Apparently for chains with almost 4 carbons and more the term that affects mostly the adsorption energy is the chain-chain interaction. Looking at the adsorption energy formula $[E(\text{H:Si-Molecule}) + E(\text{H}_2)] - [E(\text{Molecule}) + E(\text{H:Si})]$, the chain-chain interaction terms cancel with each other for long enough chains. However, it should be noted that the adsorption energy continues to decrease with increasing chain length if the vdW term is neglected in the $E(\text{Molecule})$.

Table S1. A comparison of energetic and structural parameters for dodecane chains with O and NH linkers. The original relaxed structures are presented in the columns headed NH-dodecane and O-dodecane. The column headed “Exchange O with NH and relax” signifies exchanging oxygen in the O-dodecane structure with NH and relaxing. The data show a structure very similar to the originally relaxed structure. A similar interpretation holds for the column headed “Exchange NH with O and relax”. vdW-DF2 correction has been included in the calculations.

	NH-Dodecane	Exchange O with NH and relax	OH-Dodecane	Exchange NH with O
E^{ads} (eV)	-0.63	-0.61	-1.05	-1.06
$(\alpha, \beta, \gamma)^\circ$	103.01, 111.51, 114.66	103.42, 111.40, 114.21	104.42, 109.74, 113.51	102.33, 111.73, 113.26
δ°	128.94	129.24	127.99	127.36
ω°	111.99	109.60	108.40	107.43
$d_{\text{Si-X}}$ (Å)	1.75	1.76	1.69	1.68
$d_{\text{X-C}}$ (Å)	1.48	1.48	1.46	1.47
$d_{\text{C-C}}$ (Å)	1.54	1.54	1.53	1.54

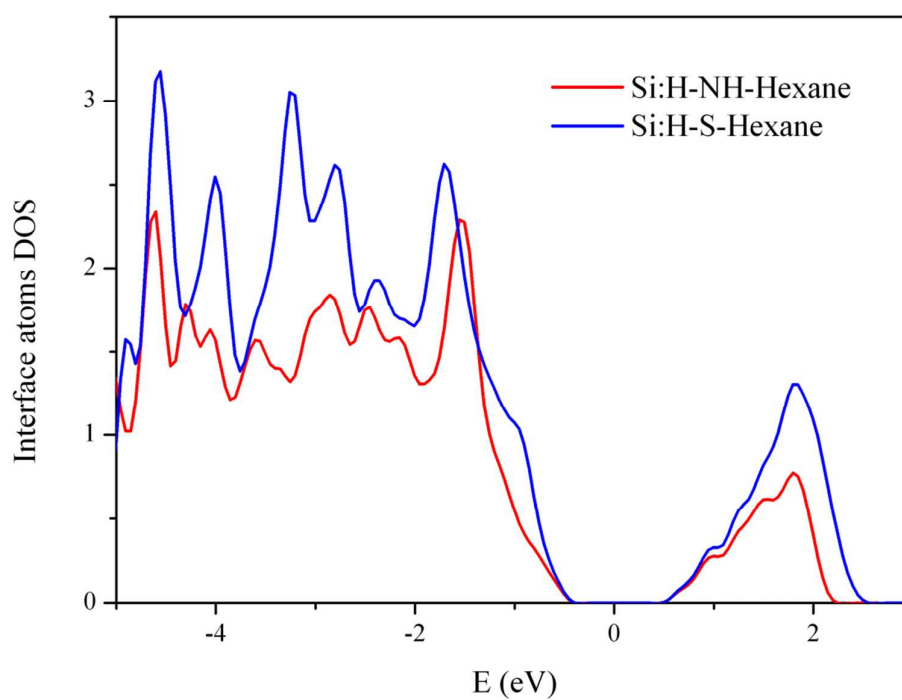


Figure S2: Interface DOS for N (red curve) and S (blue curve) linkers. Interface DOS is calculated as summation over Si(X), X, Si-nnn and C1 LDOSs.

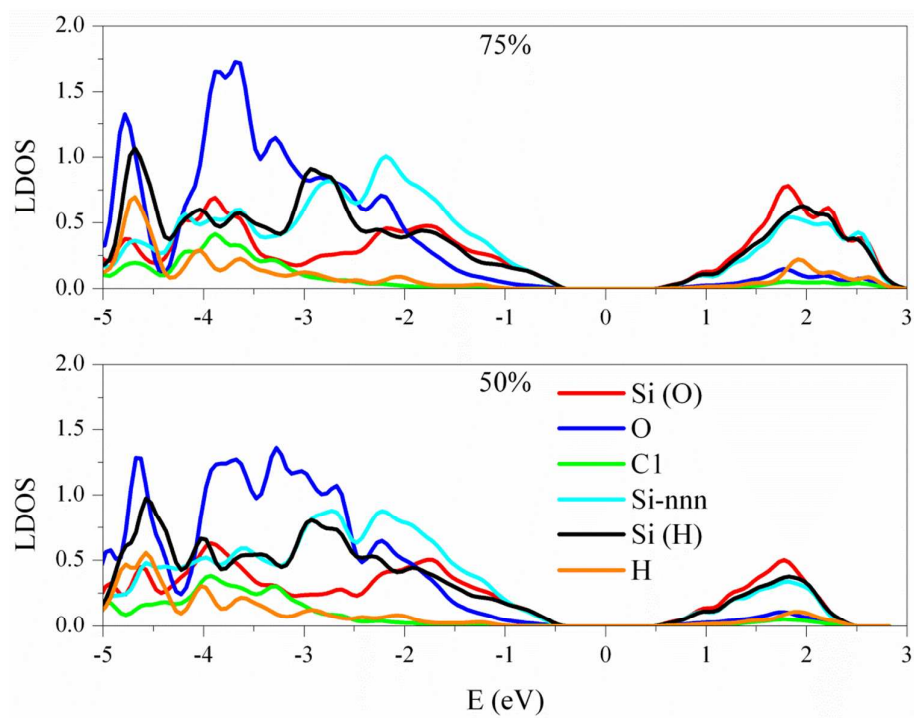


Figure S3: Local Density of States projected to the interface atoms (LDOS) for H:Si(111) functionalized with 50% (lower panel) and 75% (top panel) O-Hexane: surface silicon bonded to linker atom O, O linker itself, next nearest silicon neighbor to the O (Si-nnn) and the first carbon atom from the alkyl chain bonded to O (C1). The LDOSs for surface silicon (Si(H)) saturated with H, are also presented for comparison.