Supporting Information

Combined Theoretical and Experimental Study of Band-Edge Control of Si through Surface Functionalization

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1 Choice of GW parameters

To ensure the accuracy of our G_0W_0 calculations, we carefully tested the effect, on the final results, of all numerical parameters that entered the calculations, e.g. the number of bands $[n_{band}(\chi, \Sigma)]$ and the plane-wave cutoff $[E_{cut}(\chi, \Sigma)]$, used to evaluate the polarizability χ_0 (or equivalently the screened Coulomb interaction W) and the self-energy operator Σ. We performed extensive convergence tests for bulk silicon, and found that the parameter set in Table S1 yielded a good balance between accuracy and efficiency. The same set was then used for slab calculations. As the convergence over n_{band} is usually rather slow, we employed the approximation proposed by Bruneval *et al*[1] to improve the accuracy of the calculation of the sum over empty states. The optimal extrapolar energy (ΔE) for χ_0 was determined to be 1.2 Ha by allowing the sum rule[1] $\int_0^\infty d\omega \omega \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} \text{Im}[\chi_{0\mathbf{GG}}(\mathbf{q}, \omega)] = -\frac{\pi}{2}\omega_p^2$ to be best satisfied with 24 empty states. The optimal extrapolar energy for Σ was obtained by fixing ΔE at different values while monitoring the self-energy corrections with different $n_{band}(\Sigma)$. At $\Delta E = 1.5$ Ha, the self-energy corrections to the band edge positions only changed by a few meV when $n_{band}(\Sigma)$ was varied from 54 to 270.

Table S1: Parameters used for the calculations of the screened Coulomb interaction W and the self-energy Σ for bulk silicon. The lattice constant was fixed at a_0=5.43 Å, and a kinetic energy cutoff of 8 Hartree was used for LDA ground state calculations. ΔE is the extrapolar energy[1] chosen for the polarizability and the self energy. E_v is the valence-band edge.

	n_{band}	ΔE (Ha)	E_{cut} for $\phi(\mathbf{G})$(Ha)	E_{cut} for $W_{\mathbf{G},\mathbf{G}'}(\Sigma_{\mathbf{G},\mathbf{G}'})$ (Ha)
W	24 (32 eV above E_v)	1.2	6.0	6.0
Σ	54 (52 eV above E_v)	1.5	6.0	6.0

2 Finite size effects in slab calculations

Previous studies have found that the electronic properties of Si surfaces are sensitive to the choice of the slab model, and the convergence of the computed band gap is rather slow with respect to the slab thickness.[2] To examine whether the same is true for the energy-level positions of the band edges, we performed LDA and G_0W_0 calculations for H-, CH_3-, and C_2H_5-terminated Si(111)

Table S2: Computed valence- and conduction-band edge positions ($E_{v,c}$) and band gap (E_g) of functionalized Si(111) surfaces as a function of the number of layers in the slab (n_L). Both DFT/LDA results and G_0W_0 corrections to the LDA energy levels are listed. Results for bulk Si are listed for comparison. All energies are in eV.

		LDA			G_0W_0 corrections		
System	n_L	E_v	E_c	E_g	ΔE_v	ΔE_c	ΔE_g
H-Si(111)	6	-4.95	-3.94	1.01	-0.63	0.29	0.92
	12	-4.83	-4.10	0.73	-0.63	0.17	0.80
CH_3-Si(111)	6	-4.12	-3.23	0.90	-0.64	0.24	0.89
	12	-4.06	-3.36	0.70	-0.65	0.15	0.80
C_2H_5-Si(111)	6	-3.89	-2.92	0.97	-0.66	0.25	0.91
	12	-3.83	-3.11	0.72	-0.69	0.12	0.81
Bulk Si	–	$\Gamma \to X$		0.62	-0.57	0.12	0.69
	–	$\Gamma \to \Delta$		0.52	-0.57	0.10	0.67

slabs with 6 and 12 layers. The results are summarized in Table S2. Note that for Si(111) surfaces, the band gap was estimated between $\overline{\Gamma} = \{0,0,0\}$ and $\overline{M} = \{1/2,0,0\}$ due to the limited k-point sampling in our G_0W_0 calculations. To compare LDA and G_0W_0 results on Si(111) surfaces with those of bulk Si, we have listed E_c and E_g values that were computed for bulk Si at X (equivalent to $\overline{M}$ of the Si(111) surface), as well as at the actual conduction band minimum, Δ. From Table S2, one observes that G_0W_0 corrections to LDA electronic energies are similar for different functional groups, with differences within a few tens of meV. This results is consistent with both experimental[3] and theoretical findings,[2,4] showing that the electronic structure of the surfaces reported in the table are similar, except for the termination-specific surface states.

In addition to the finite slab thickness, several other factors may contribute to numerical errors in evaluating absolute ionization potential (IP) values: (1) within the GW approximation, the non-self-consistency treatment of the wave functions and orbital energies may lead to underestimated IP values. This was seen in the case of bulk Si, where the valence band edge was found to be systematically shifted *downward* as the level of self-consistency was systematically increased, from e.g. $G_0W_0 \to GW_0 \to GW \to$ QPscGW.[2] (2) The inclusion of vertex corrections (e.g. the use of the GWΓ approximations) may have the opposite effect, and was found to shift *upward* the valence band edge of bulk Si by 0.37 eV from the value obtained at the G_0W_0 level.[5]

3 Estimate of experimental surface coverage

A simple substrate-overlayer model[6–8] was used to calculate the thickness of the overlayer, d_{ov}:

$$d_{ov} = \ln\left[\left(\frac{I_{ov}}{I_{Si}}\right)\left(\frac{SF_{Si}}{SF_{ov}}\right)\left(\frac{\rho_{Si}}{\rho_{ov}}\right) + 1\right]\lambda\sin\theta, \tag{1}$$

where I_{ov}/I_{Si} is the intensity ratio of the overlayer element peak area to the Si $2p$ peak area, and SF is the modified sensitivity factor provided by Kratos:[9] Cl $2p = 0.891$, Br $3d = 1.055$, C $1s = 0.278$ and Si $2p = 0.328$. ρ_{ov} and ρ_{Si} are the atomic densities of the overlayer atoms and the substrate silicon atoms (0.083 mol cm^{-3}). λ is the escape depth through the overlayer for electrons originating in the Si $2p$ level. θ is the angle from the substrate plane to the detector ($90°$).

The fractional coverage Θ is obtained by dividing d_{ov} calculated using Eqn. (1) by a_{ov}, the atomic diameter of the overlayer atoms.[6] For halogens, the atomic densities were computed from the solid states molar volumes (Cl = 17.39 cm^3; Br = 19.78 cm^3) as $\rho_{Cl} = 0.058$ mol cm^{-3} and $\rho_{Br} = 0.051$ mol cm^{-3}. $a_{ov} = 0.35$ (0.37) nm, and $\lambda = 3.16$ (3.44) nm were obtained for the Cl (Br) overlayer[6] from the vdw radius of 0.175 (0.185) nm. a_{ov} for methyl and ethyl overlayer was estimated as the sum of the distance of top H atoms to the Si substrate (0.23 nm and 0.37 nm) and the vdW radius of H (0.12 nm). For these two hydrocarbon groups, $\rho_{ov} = 0.055$ mol cm^{-3} (based averaged density of solid and liquid hydrocarbons) and $\lambda = 3.5$ nm[6,10,11] were assumed.

The measured ratio of I_{ov}/I_{Si} and estimated coverage for CH$_3$-, C$_2$H$_5$-, Cl-, and Br-terminated Si(111) surfaces are summarized in Table S3. Given the approximations in the substrate-overlayer model and choice of parameters (ρ, a and λ), the calculated surface coverages should only be

Table S3: Measured I_{ov}/I_{Si} ratios and derived surface coverages of functionalized Si(111). I_{Si} was derived by multiplying measured Si $2p_{3/2}$ peak area by 1.5, assuming a peak area ratio of 1:2 for Si $2p_{1/2}$ and $2p_{3/2}$.[6]

Sample	I_{ov}/I_{Si}	$\Theta_{R-Si(111)}$
CH$_3$-	0.070	1.17
C$_2$H$_5$-	0.051	0.62
Cl-	0.200	0.91
Br-	0.226	1.01

considered as rough estimates. Nevertheless, the observed trends are consistent with previous experimental results, e.g. a nearly full coverage for methyl groups[12] and a partial coverage for ethyl groups (65-95%).[13]

4   IP shift of the C_2H_5-Si(111) surface

We note that the experimentally prepared C_2H_5-Si(111) surfaces are usually terminated by both H- and C_2H_5- groups, with an estimated C_2H_5-coverage between 60% and 95% of a monolayer.[13–15] To provide a comprehensive comparison with experiments, we also performed DFT calculations for the C_2H_5-Si(111) surface at partial coverages of 25%, 50% and 75%. The computed IP shifts as a function of the coverage have been plotted in Figure S1, and these shifts fell within the error bars of the experimental data.
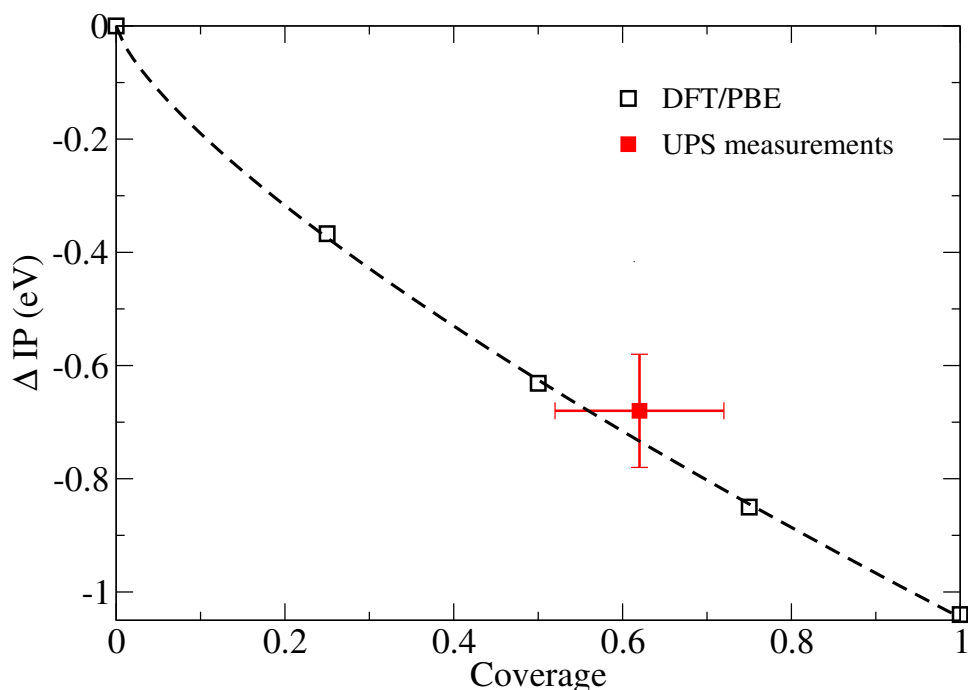

Figure S1: Computed IP shift (empty squares) of the C_2H_5-Si(111) surface as a function of the coverage, in comparison with experiment (filled square). The dashed line is a guide to the eye.

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