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

Doping of the hydrogen-passivated Si(100) electronic structure through carborane adsorption studied using density functional theory

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1 Geometry relaxations of silicon-molecule junctions

1.1 Generation of initial geometries for structure optimization

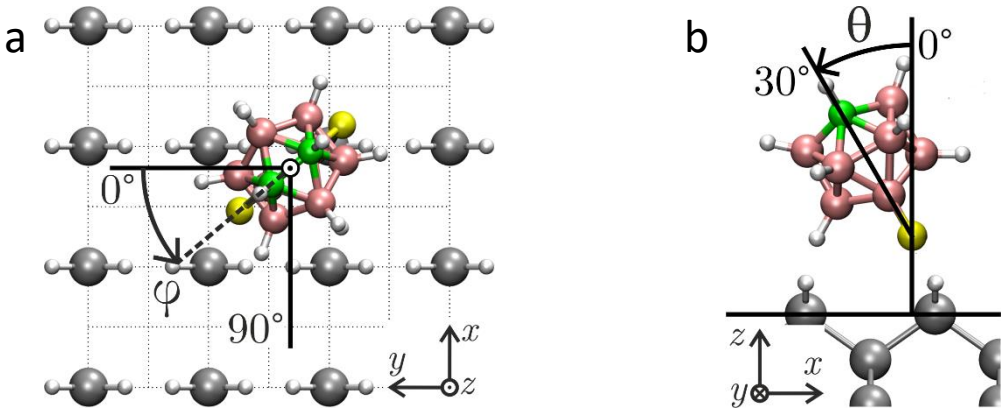

Fig. S1 *Position of the molecule above the Si substrate for structure optimization. a) Top view illustrating the sampling of the azimuthal angle ϕ from 0 to 90 degrees in steps of 10 degrees. b) Initial value of the polar angle θ (0 or 30 degrees).*

1.2 Total energy of final structures

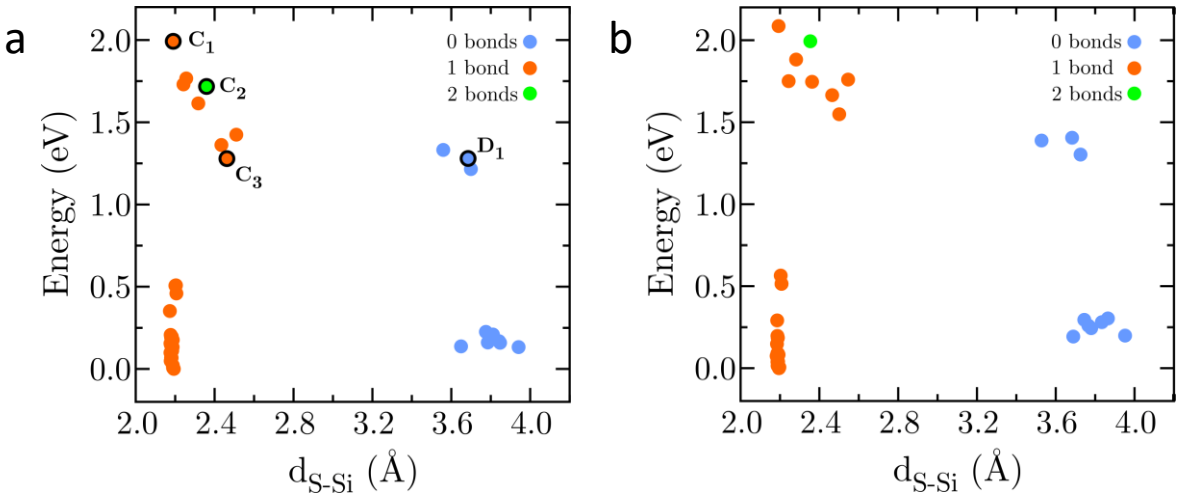

Fig. S2 *Total energy of relaxed geometries, relative to the most stable structure, as a function of the shortest S-Si distance calculated using a) PBE, b) vdW-DF.*

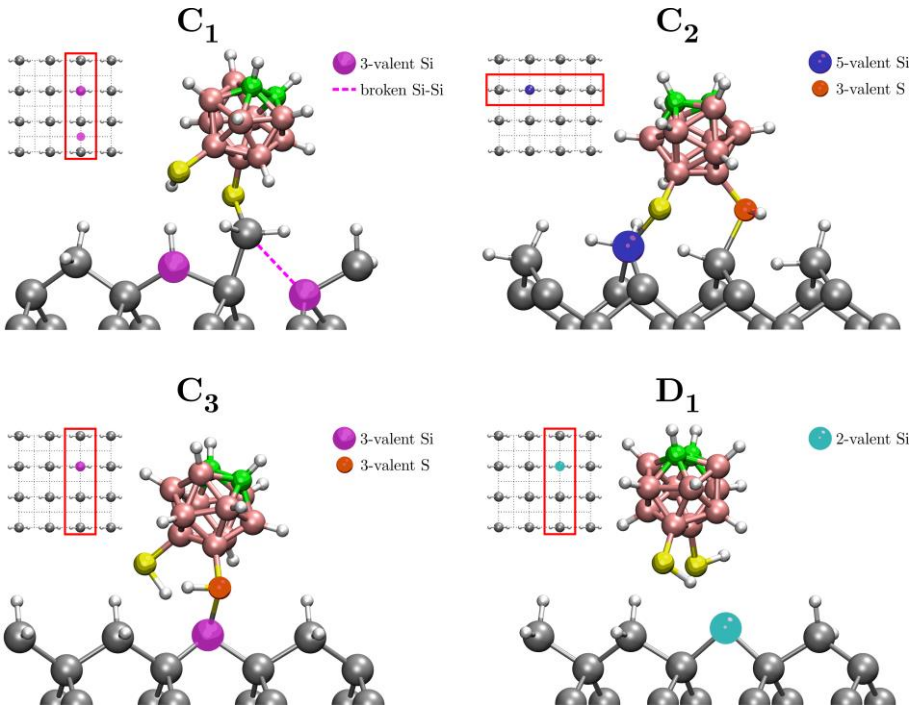

Fig. S3 *Side view of the high-energy structures labelled in Fig. S2. For each geometry, the inset depicts the position of the corresponding cut out structure in the unit cell. The legends show prominent elements with sub-optimal valence states, which lead to a higher total energy.*

2 Electrostatic properties of silicon and silicon-molecule junctions

We compute the plane-averaged electron density difference, $\rho_{diff}(z)$ upon adsorption. $\rho_{diff}(z)$ illustrates the reorganization in electron density by comparing the adsorbed structure with the sum of its individual constituents, whose geometry is kept fixed:

$$\rho_{diff}(z) = \rho_{jcn}(z) - [\rho_{mol}(z) + \rho_{Si}(z)] \quad \text{(S1)}$$

Fig. S4 shows the calculated profiles of electron density difference for the chemisorbed and physisorbed junctions A_{opt} and B_{opt}, respectively.

The change in the work function, given by the difference in the plane-averaged electrostatic potential profile in the vacuum regions beyond both surfaces of the slab, is related to the net dipole of the slab (A = 242 Å^2). Table S1 lists the different contributions in A_{opt} and B_{opt}. As expected, the sum of contributions of the isolated molecule, Si slab, and charge rearrangement match the value computed for the full junction.

Table S1 *Calculated electrostatic dipoles μ_z and work function changes $\Delta\phi_M$ of the adsorbed junctions, and of the different contributions.*

	μ_z (D)	$\Delta\phi_M$ (eV)
A_{opt}		
junction	+3.90	-0.61
Si substrate	-1.53	+0.24
molecule	+4.82	-0.75
charge redistribution	+0.61	-0.10
molecule + charge redistribution	+5.43	-0.85
B_{opt}		
junction	+5.04	-0.78
Si substrate	-2.48	+0.39
molecule	+5.67	-0.88
charge redistribution	+1.85	-0.29
molecule + charge redistribution	+7.52	-1.17

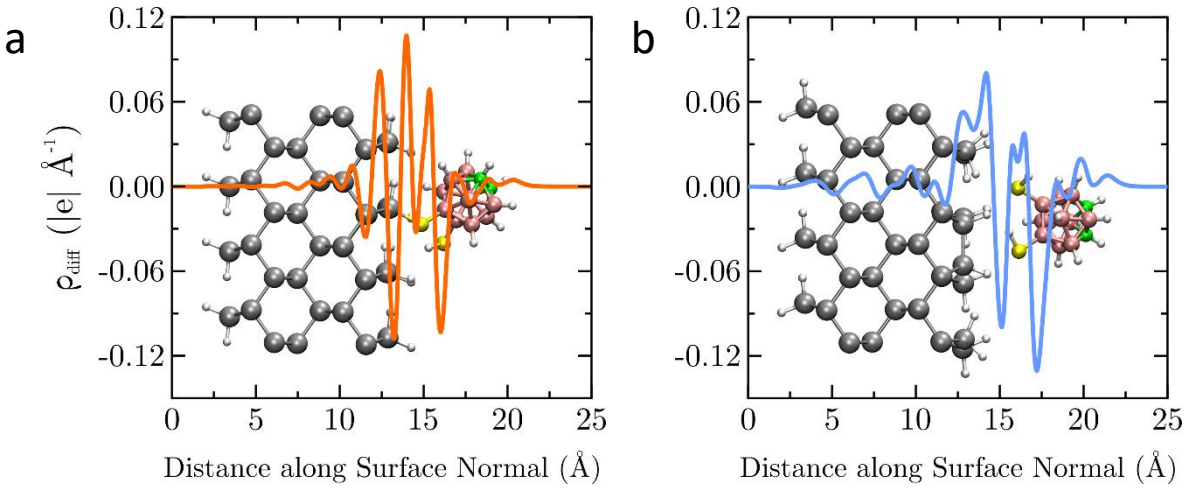

Fig. S4 *Calculated plane-averaged electron density difference of a) A_{opt}, b) B_{opt} structures.*

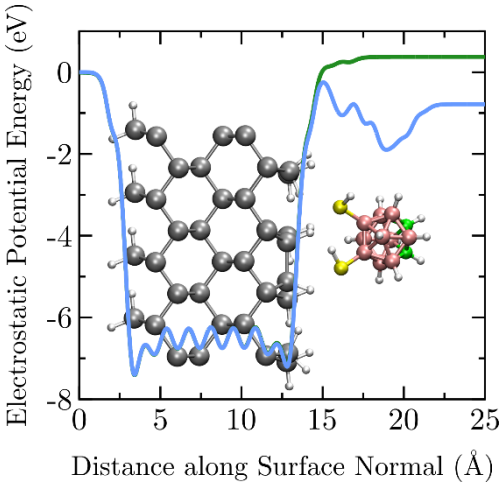

Fig. S5 *Plane-averaged electrostatic potential energy of the physisorbed B_{opt} structure (blue). The difference between the asymptotic values across the slab yields the work function change. Same for a Si slab with the geometry of B_{opt} but with the molecule removed (green).*

3 Calculated spectral properties of silicon and silicon-molecule junctions

3.1 Band structure of bulk Si and hydrogen-passivated Si(100) surface

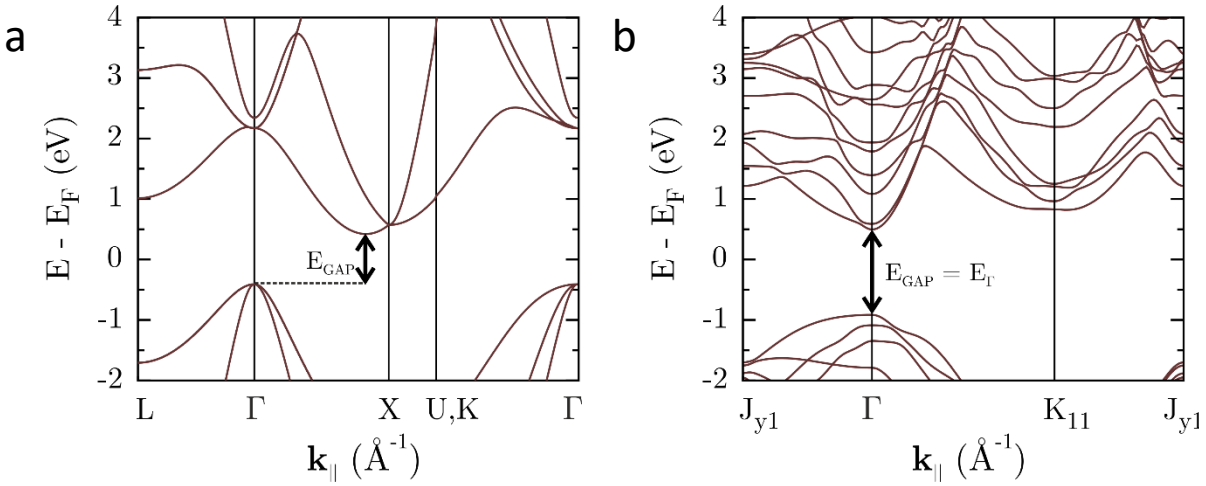

Fig. S6 Calculated (PBE) b*and structure diagrams. a) Bulk silicon [E_{GAP} = 0.83 eV, E_Γ = 2.58 eV, indirect band gap]; b) hydrogen-passivated 8-layer Si slab [E_{GAP} = E_Γ = 1.43 eV, direct band gap].*

3.2 Band structure of Si atoms and molecular density of states

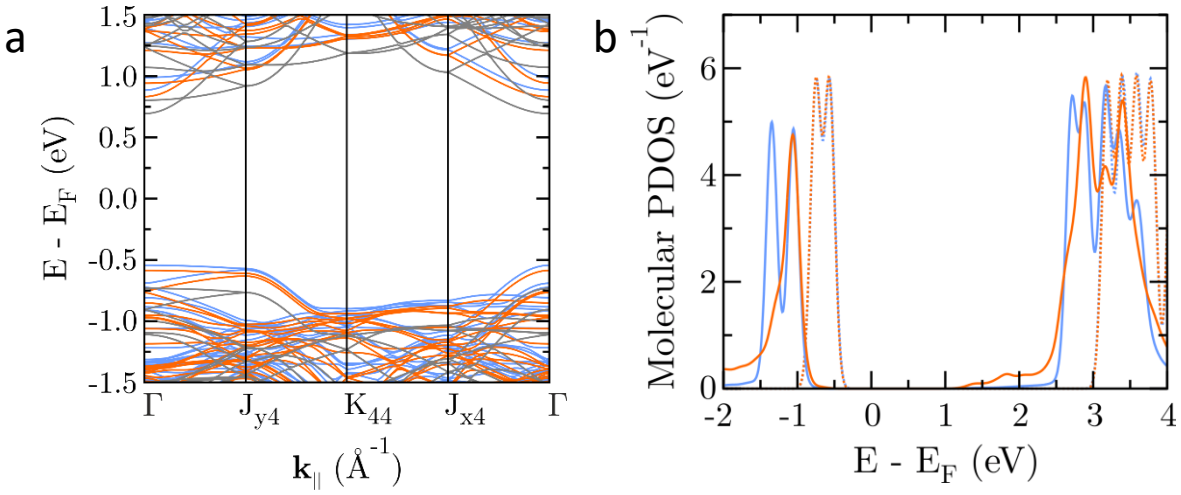

Fig. S7 *a) Band structure diagram of Si atoms in the clean Si slab (grey), in A_{opt} (orange), and in B_{opt} (blue). b) PDOS projected on molecular atoms in A_{opt} and B_{opt} junctions, as well as for isolated molecules in the same geometries (dashed lines).*

4 Mechanical properties upon junction stretching

4.1 Calculation of the stiffness of the S-Si bond in the A_{opt} junction

Fig. S8 shows the calculated force as a function of the S-Si bond length. The data in Fig. S8 are taken from Fig. 5 up to a vertical displacement of 2.5 Å. The stiffness of the S-Si bond is calculated from a linear fit of the first 10 data points in Fig. S8 (blue line) and gives 18.0 nN/Å.

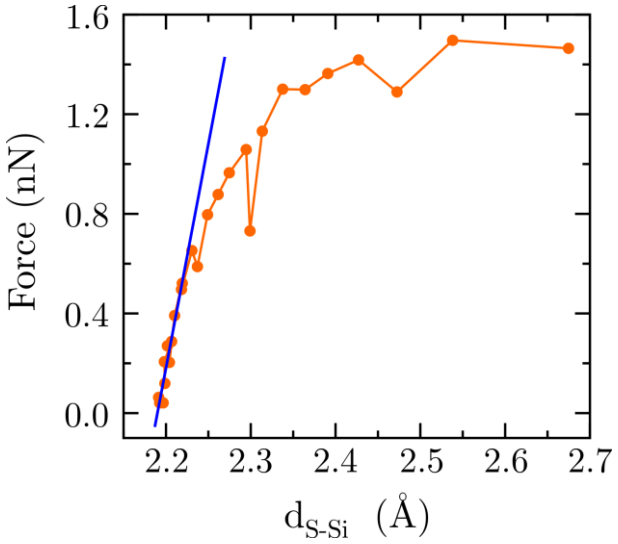

Fig. S8 *Calculated force in the stretched junction A_{opt} as a function of the S-Si bond length. The linear fitting of the slope of the force vs. S-Si bond length was computed from the first 10 data points.*

4.2 Mechanical properties of the B_{opt} junction

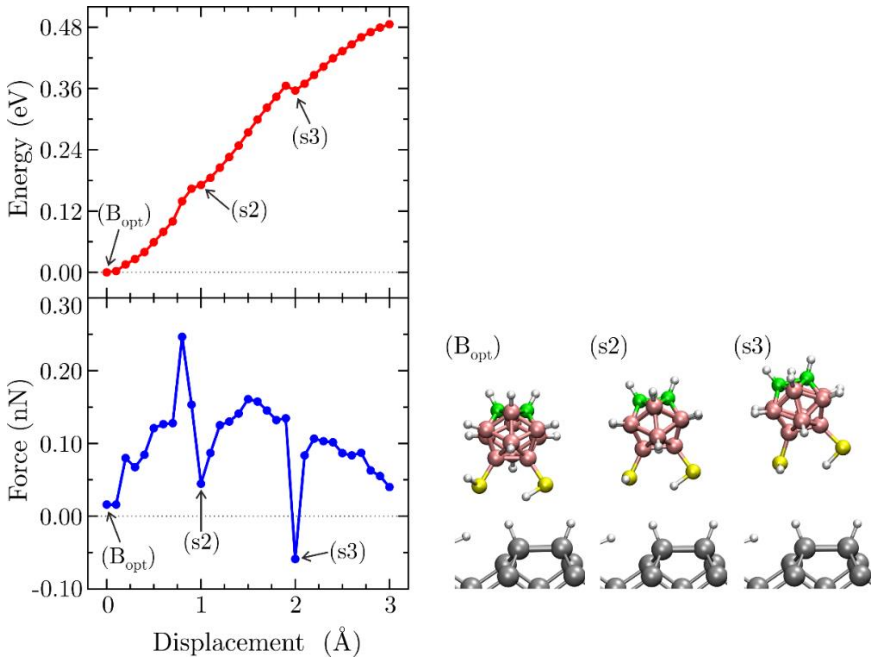

Fig. S9 *Same as Fig. 5 for the physisorbed junction B_{opt}.*

5 Geometry of carborane chemisorbed on the (2×1)-reconstructed Si(100) surface

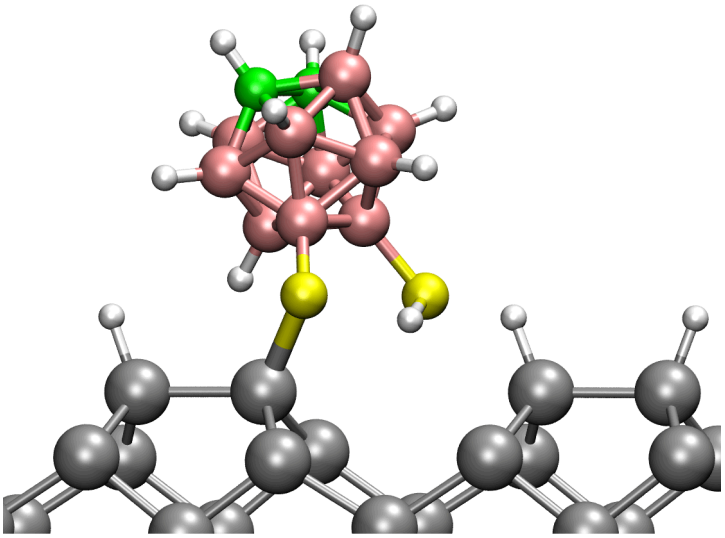

Fig. S10 *Optimized structure of carborane chemisorbed on the (2×1)-reconstructed Si(100) surface.*