Doping of the hydrogen-passivated Si(100) surface by carborane films studied using DFT

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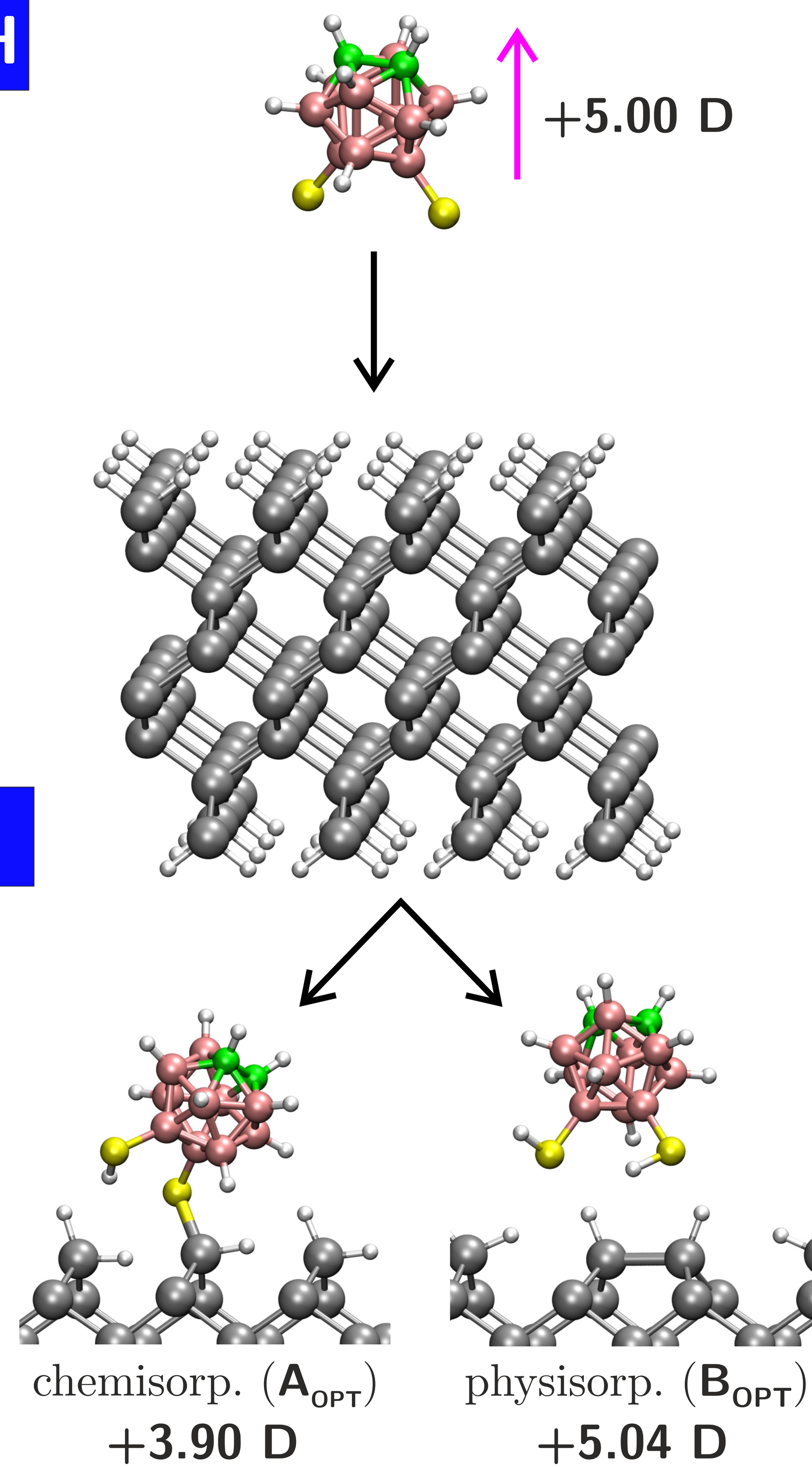
Carborane Molecules on Si(100)-H

Monocrystalline silicon wafer in (100) configuration is the mainstream of the current photovoltaic market.

Doping of the silicon base is commonly done by invasive methods (ion implementation, gas phase diffusion, laser doping, etc.) with destructive effects. As the alternative, there is a non-destructive method in the forem of MONOLAYER DOPING.

MONOLAYER DOPING: adsorption of the dopand-rich molecule with a large permanent dipole, such as dithiocarborane, capable of forming a stable monolayer on the silicon surface [1].

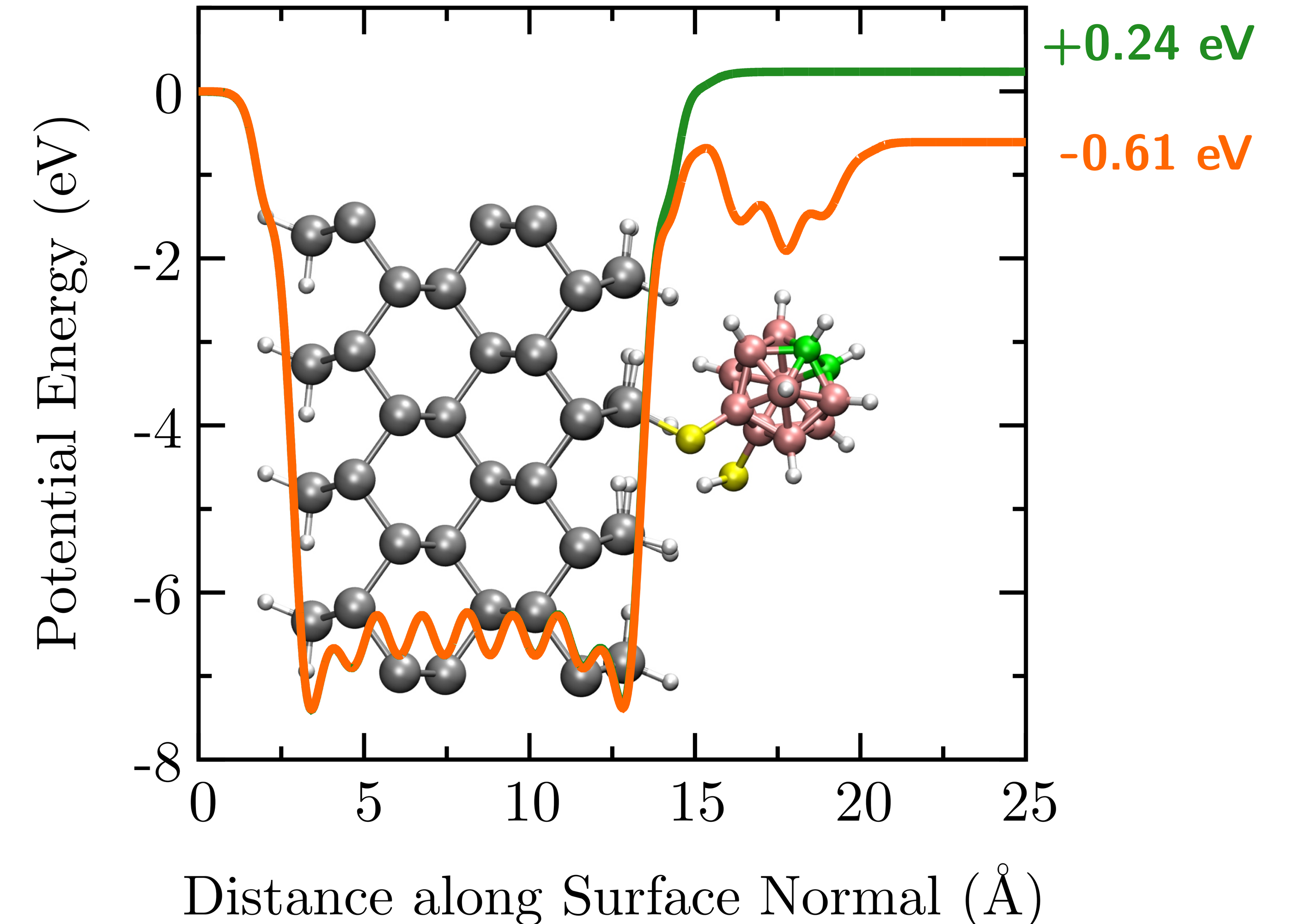


Methodology

General parameters: DFT-SIESTA method [2] with the GGA(PBE) functional for exchange-correaltion. SZP basis for Si; DZP basis for B,C,S,H.
Geometry optimization: coordinates of molecule and topmost 3 Si layers relaxed. *K*-point sampling in || direction with a 6x6 mesh. Force tolerance set to 0.02 eV/A.

Physical quantities calculation(total energy, potential energy, band structure, DOS): *k*-point sampling in || direction with a 6x6 mesh. Slab dipole correction included.

Electrostatic Potential Energy



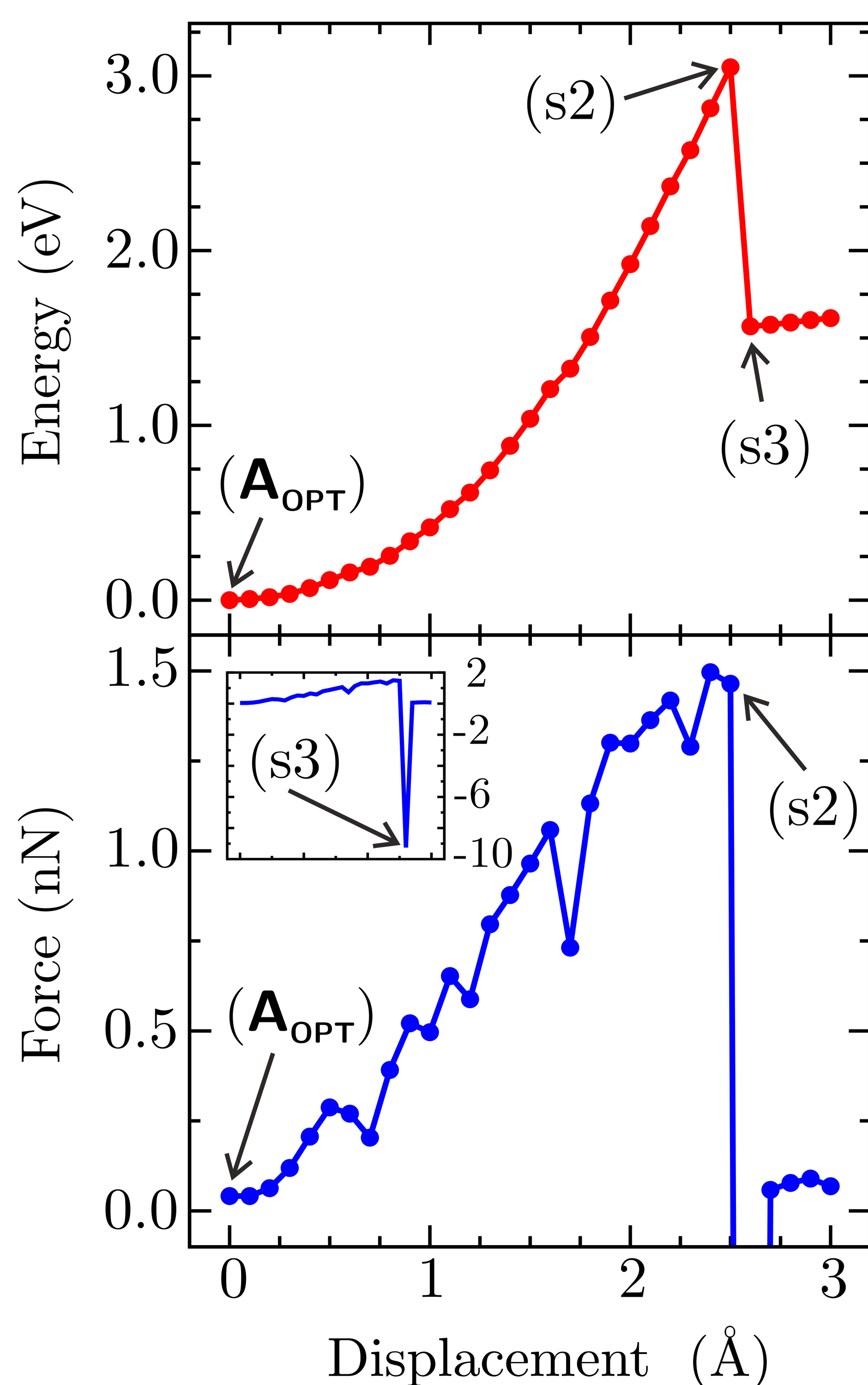
Helmholtz equation: $\Delta E_{POT} = \Delta\Phi_M = -(e.\Delta\mu_z)/(\varepsilon_0.A)$

The left side is a reference (0 D;0 eV), where the substrate is undistorted by the molecule adsorption.

A_{OPT}	$\Delta\mu_z$ (D)	$\Delta\Phi_M$ (eV)
junction	+3.90	-0.61
Si wafer	-1.53	+0.24
mol+interface	+5.43	-0.85

The **green curve** depict E_{POT} of the wafer in the chemisorption-induced geometric distortion. The **orange curve** depict E_{POT} of the final A_{OPT} junction. From **green** to **orange curve**: the molecule adsorption and molecule-silicon interface formation.

Mechanical Properties Upon Junction Stretching

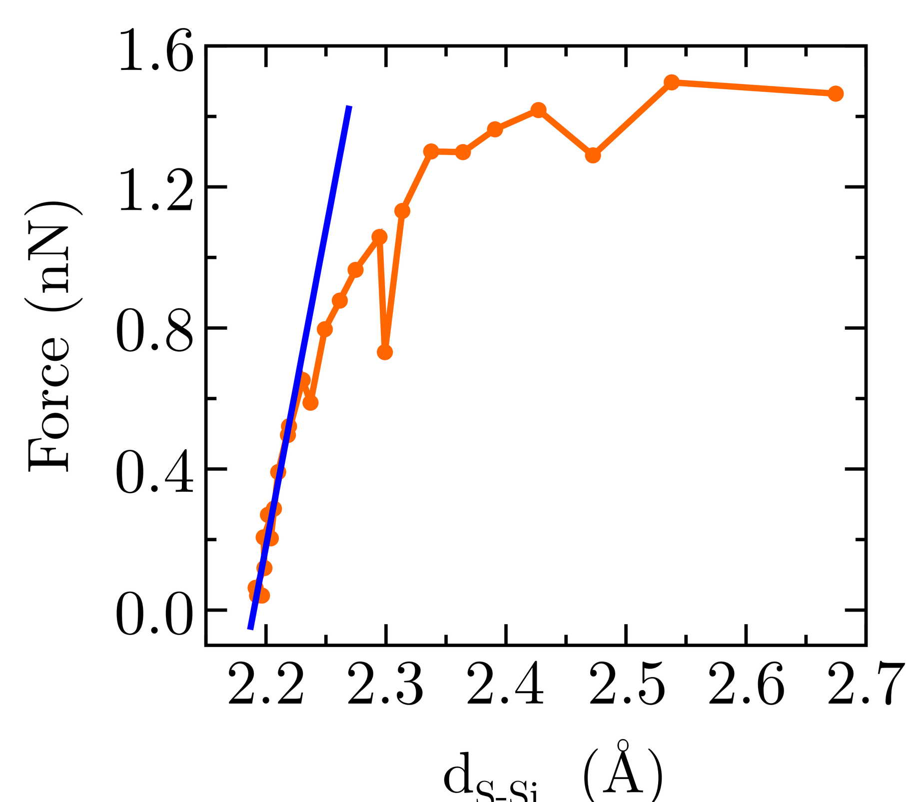


The molecule is incrementally pulled from the surface in the z-direction with steps of 0.1 Å. The upper C(z) is constrained and the junction geometry is relaxed.

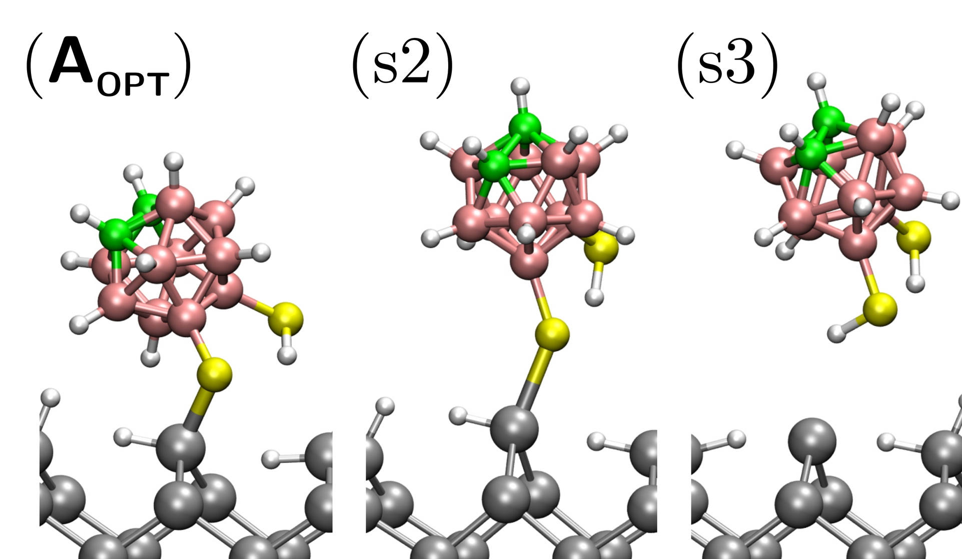
3 prominent junction geometries:
($\mathbf{A}_{OPT}$) the struct. before the first pulling
(s2) the struct. before the bond rupture at 2.5 Å
(s3) the struct. after the bond rupture at 2.6 Å

The bond stiffness calculation:

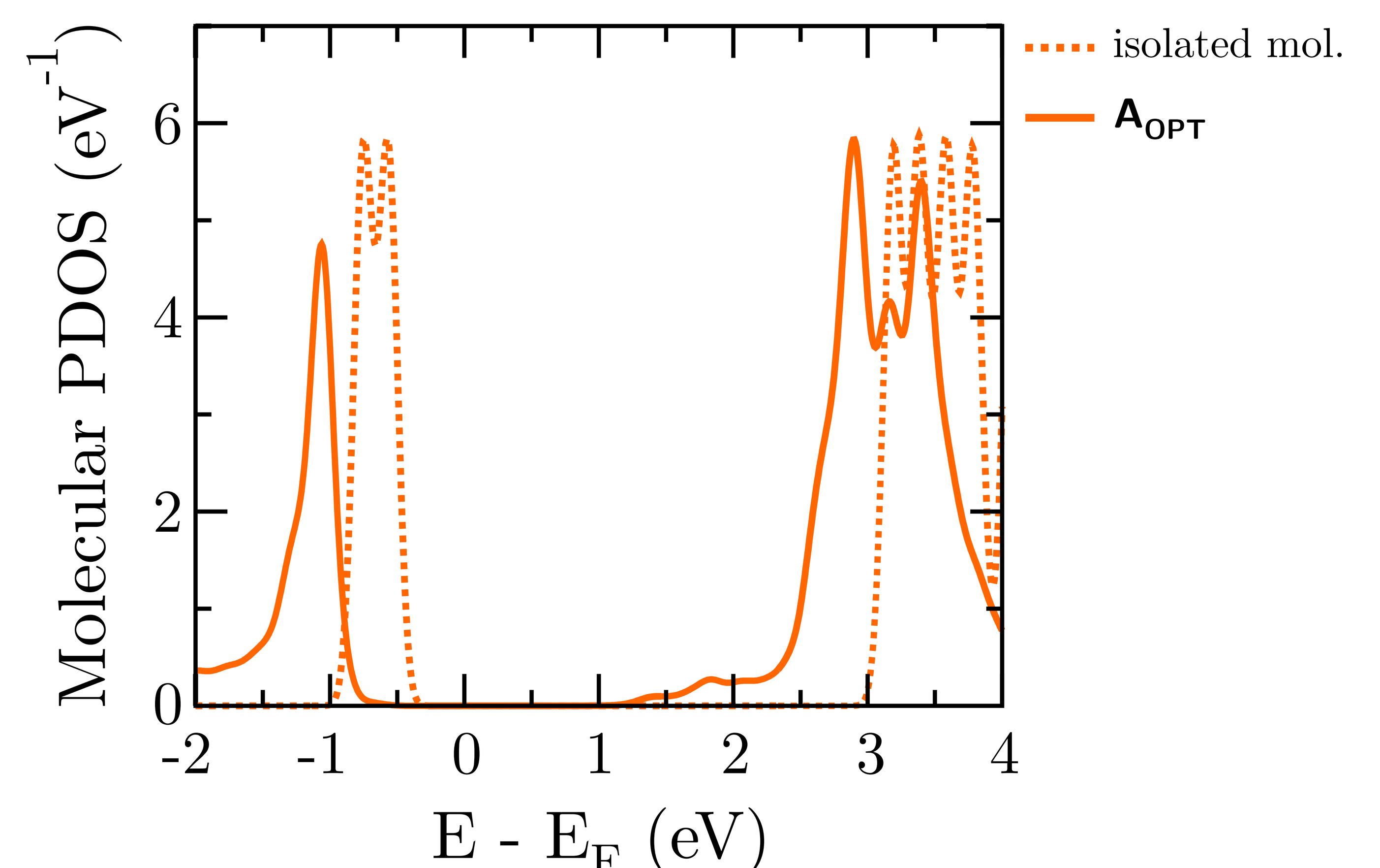
$$\text{STIFFNESS} = \{d(\text{Force})/d(d_{\text{S-Si}})\}_0$$



The calculated bond stiffness is **18.0 nN/Å**.
The reported bond stiffness is **22.0 nN/Å** [3].



Carrier Injection Barrier Change



Electron injection barrier height[4]: $\Phi_E = E_{LUMO} - E_F$

$\Delta\Phi_E = E_{LUMO}(\mathbf{A}_{OPT}) - E_{LUMO}(\mathbf{iso})$ **NEGATIVE** change

Hole injection barrier height[4]: $\Phi_H = E_F - E_{HOMO}$

$\Delta\Phi_H = E_{LUMO}(\mathbf{iso}) - E_{LUMO}(\mathbf{A}_{OPT})$ **POSITIVE** change

Conclusions

The carborane molecule behaves like the ***n*-type** doping agent for the monocrystalline silicon wafer. During the adsorption, the molecule **supplies electrons** to the Si substrate and thus **reduces** its work function. In addition, it **lowers** the electron injection barrier height.
In terms of mechanical properties, the simulation gives the stiffness of the S-Si bond of **18.0 nN/Å**, which is slightly smaller with respect to the previously reported of **22.0 nN/Å**.

References

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Computational Resources

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