Stability of finite single-walled carbon nanotubes adsorbed on Si(001)

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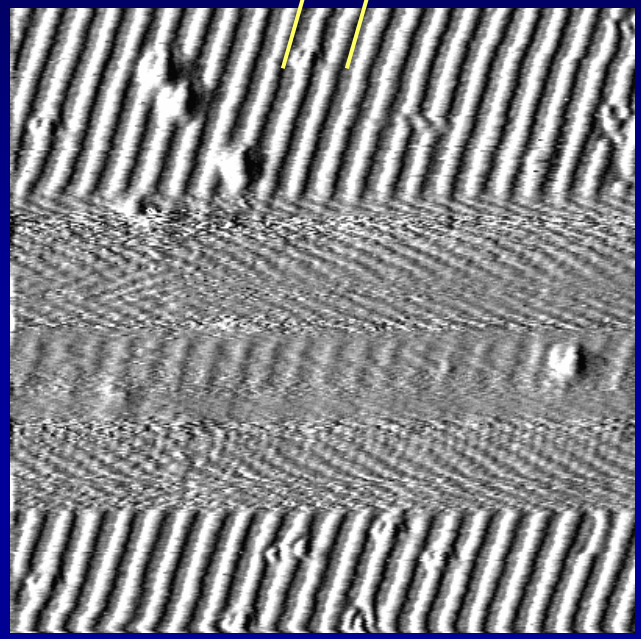
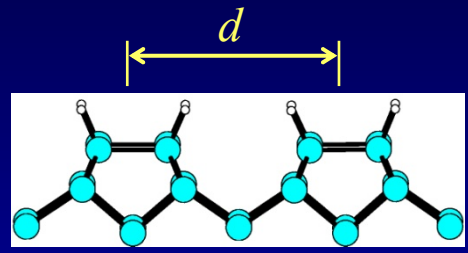
Motivation

- Investigate the incorporation of carbon nanotubes (CNTs) to the well-stablished silicon technology
- Find possible applications for CNTs as nanowires on Si(001)
- Determine the energetically favorable adsorption sites of CNTs on Si(001)
- Compare the stability between *zigzag* and *armchair* CNTs on Si(001)

Carbon nanotubes on H/Si(001)





16nm×16nm UHV-STM images of two single-walled CNTs
in situ deposited on UHV-prepared H/Si(001)-2×1 substrate

Room-temperature UHV-STM desorption of hydrogen at the CNT-H/Si(001) interface results in the local mechanical stabilization of the CNT

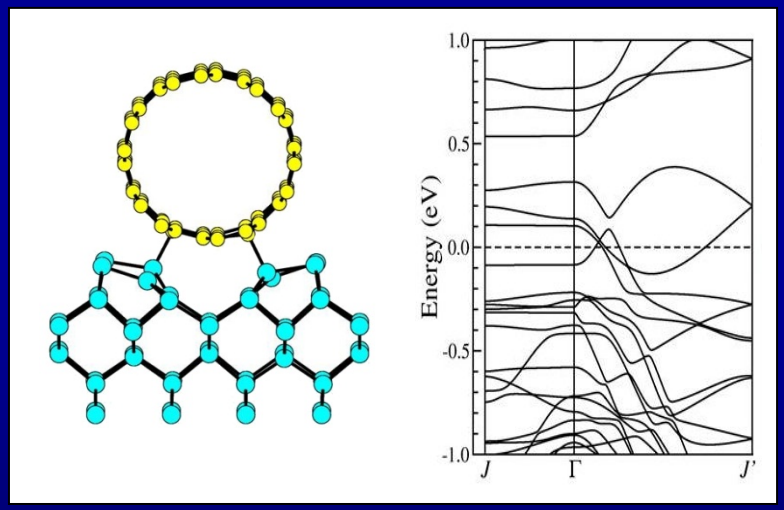
The atomically precise placement of a single molecule in proximity to the CNT would allows the bottom-up fabrication of molecular electronic devices

Albrecht & Lyding, Nanotechnology 18, 125307 (2007)

Infinte CNTs on Si(001)

Ab initio calculations of infinite CNTs on surfaces require that the lattices of the CNT and surface commensurate.

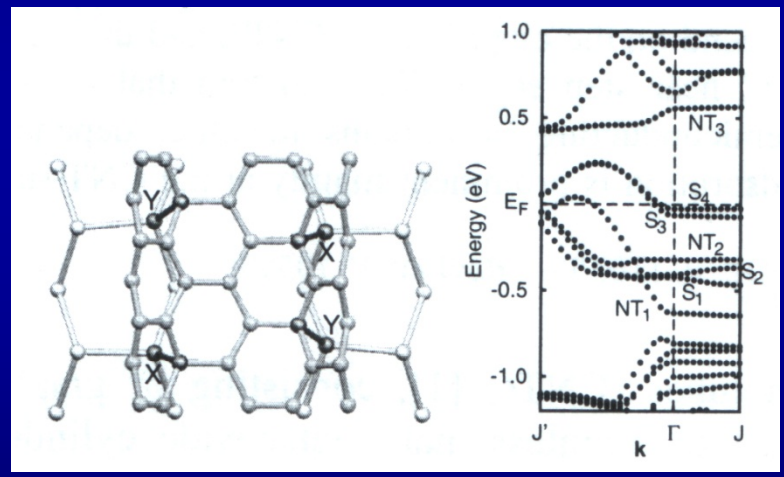
However, armchair- and zigzag-CNT lattices have a mismatch of 3% and 6%, respectively, with respect to the Si(001) lattice.



Side view of (6,6) CNT on the trench of Si(001)-(4x2)

- Two C-Si bonds are formed
- The system is metallic along the CNT

Orellana, Miwa & Fazzio, Phys. Rev. Lett. 91, 166802 (2003)



Top view (5,5) CNT on the trench of Si(001)-(4x2)

- Four C-Si bonds are formed
- The system is metallic along the CNT

Berber & Oshiyama, Phys. Rev. Lett. 96, 105505 (2006)

Theoretical Method

- Density functional theory calculations (DFT)
- Basis set of atomic orbitals (SIESTA ab initio package)
- Generalized gradient approximation (PBE) to the exchange correlation potential
- Norm-conserving pseudopotentials
- Armchair (5,5) and zigzag (9,0) capped nanotubes with diameter ~7 Å and length of ~24 Å
- 6 monolayers of Si(001) plus a vacuum region of 10 Å and surface periodicity 8x4

Checking the basis set

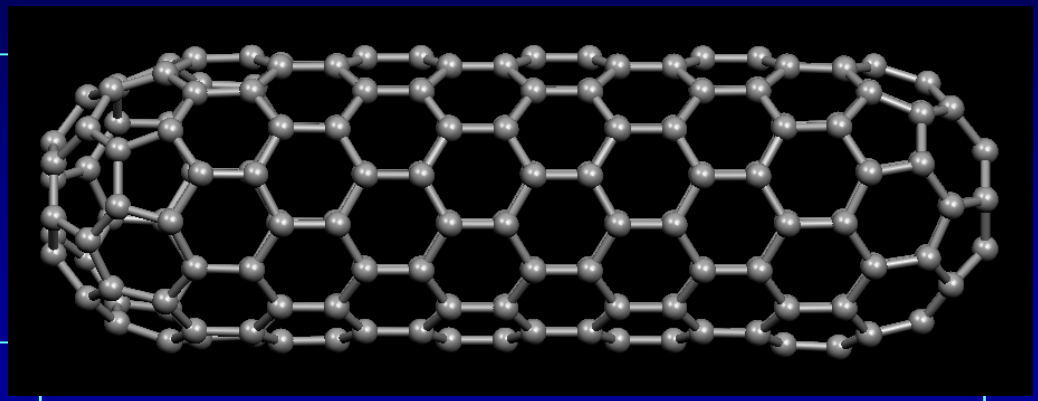
We use a combined bases: double-ζ + P (DZP) for silicon
double-ζ (DZ) for carbon
single-ζ (SZ) for hydrogen

H atoms do not need a good description because they are only used to passivate dangling bonds at the surface bottom

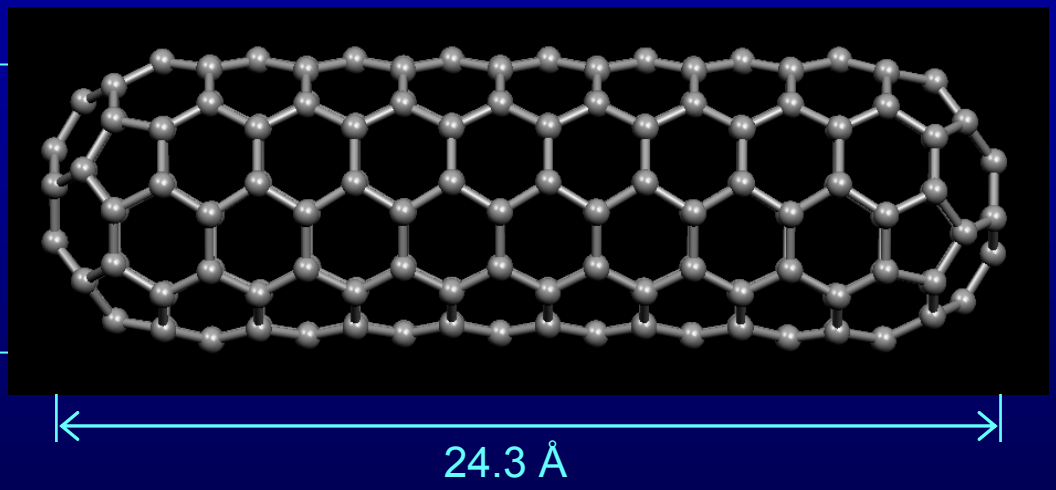
The bases were tested performing calculations for bulk structures:

System	Basis	$a_{theo.}$ (Å)	$a_{expt.}$ (Å)	Δa %
Diamond	DZ (C)	3.601	3.567	1
Graphite	DZ (C)	2.500	2.464	1.5
Si bulk	DZP (Si)	5.541	5.431	2
SiC bulk (3C)	DZP(Si) DZ (C)	4.404	4.359	1

Finite nanotubes: Macromolecules



zigzag (9,0)
204 atoms
HOMO-LUMO = 0.27 eV

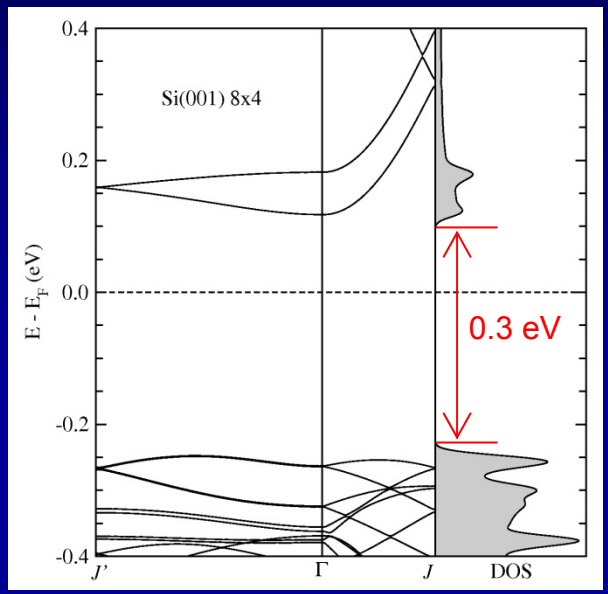


armchair (5,5)
200 atoms
HOMO-LUMO = 0.40 eV

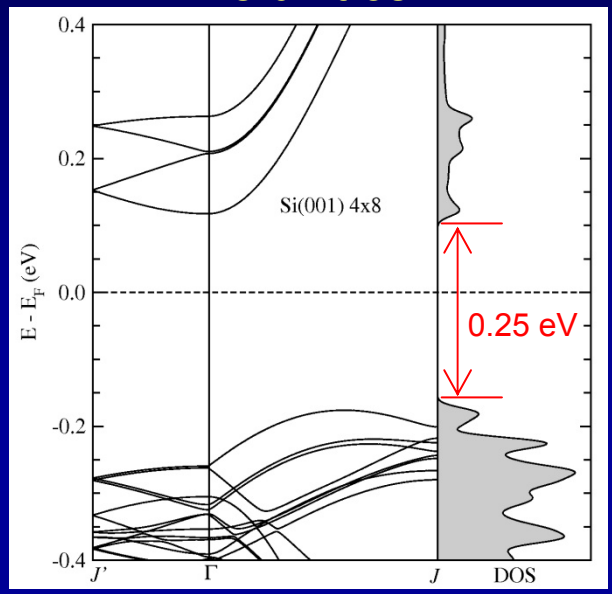
The similarity of the CNTs size allow us to compare their properties when adsorbed on Si(001)

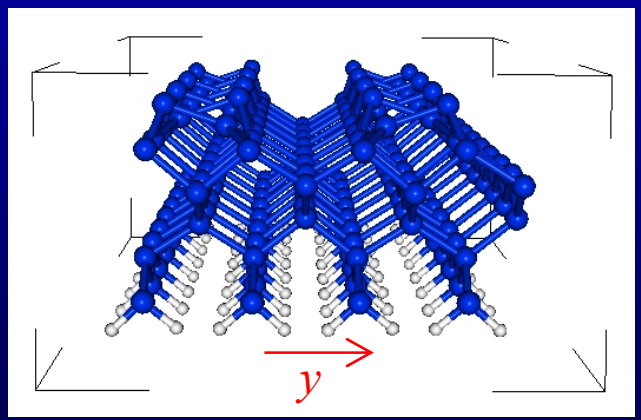
The Si(001) band structure

8x4 unit cell

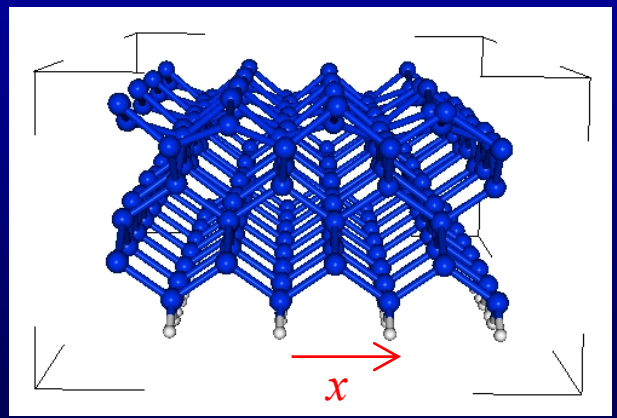


4x8 unit cell





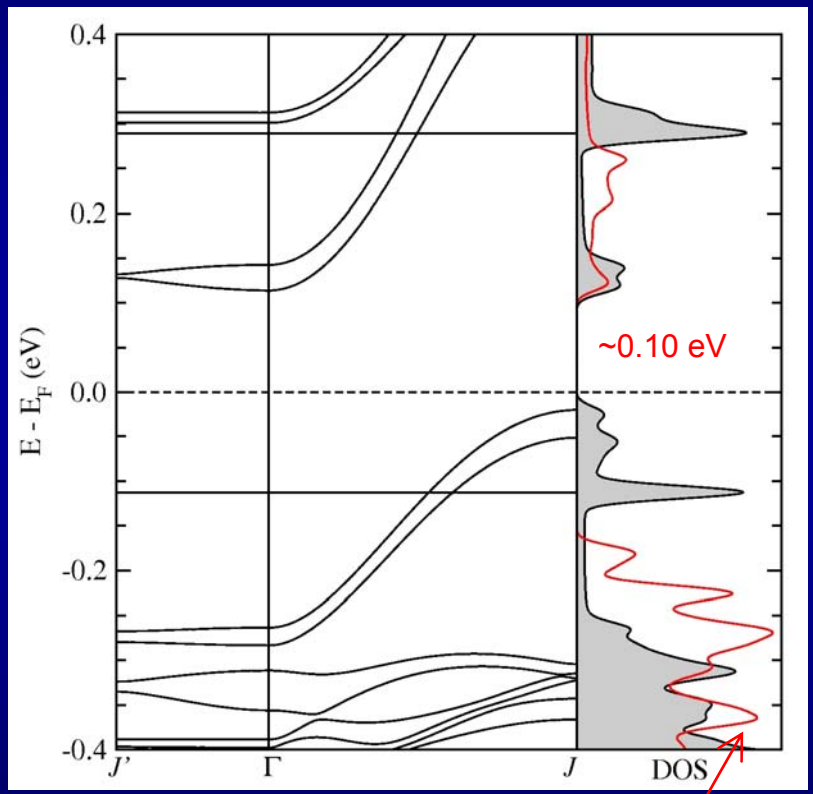
Si: 6 ML (192 atoms)
H: 1 ML (64 atoms)

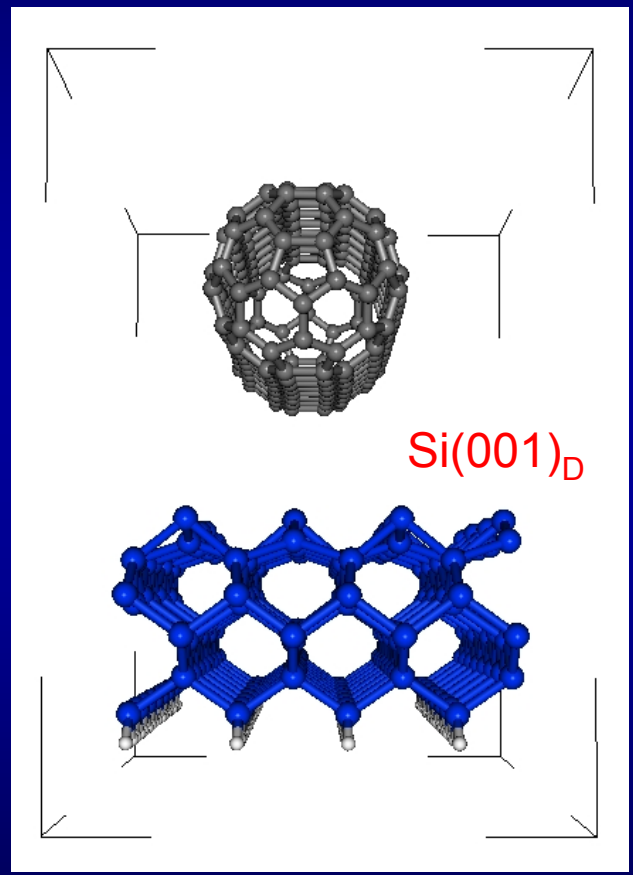


The topmost 5 ML are fully relaxed. The last Si ML and the hydrogens are fixed.

The CNT adsorption along the dimers

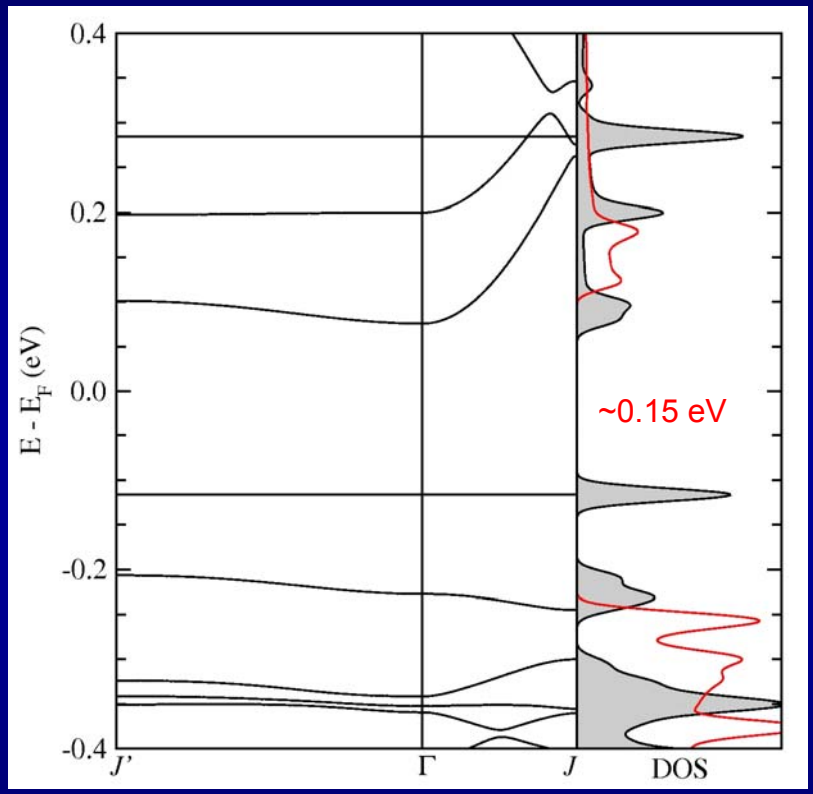
Band structure of the (5,5) CNT suspended 5 Å from the substrate

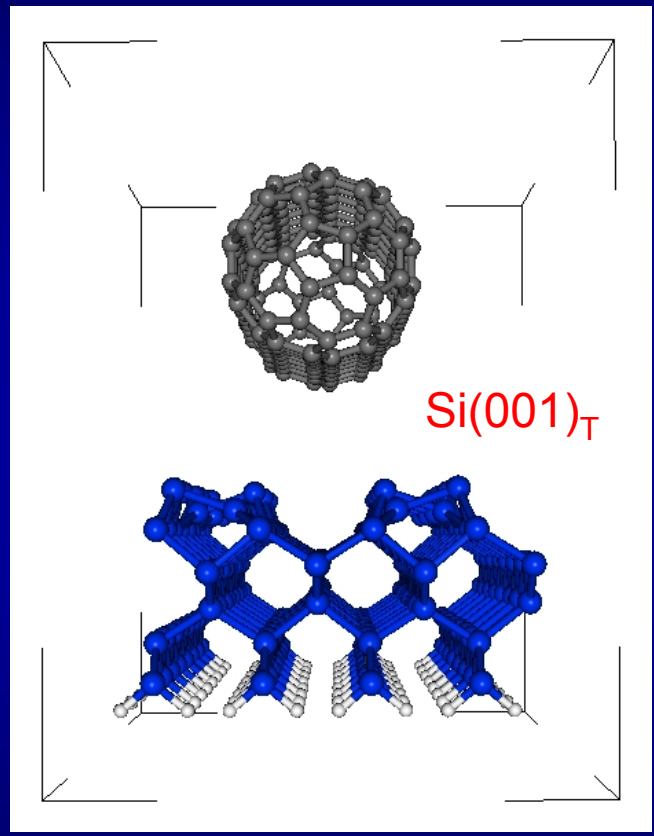




Efective vacuum region of 10 Å

The CNT adsorption along the trench



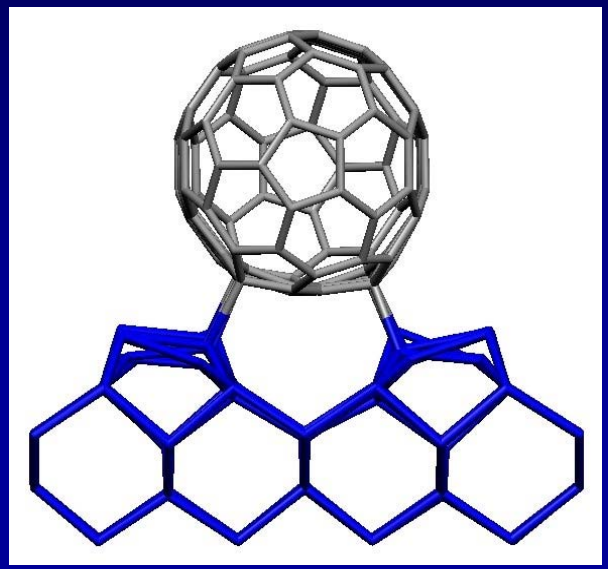


The proximity of the CNT splits the bands of the surface removing their symmetry degenerecency and reducing the band gap

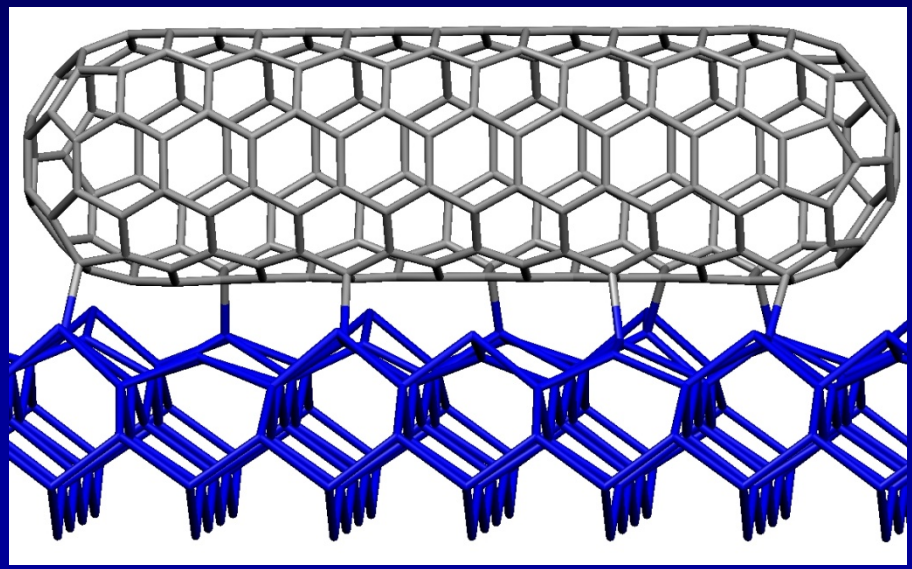
Results of the adsorbed CNTs

Armchair (5,5) on $Si(001)_T$

Front view



Side view

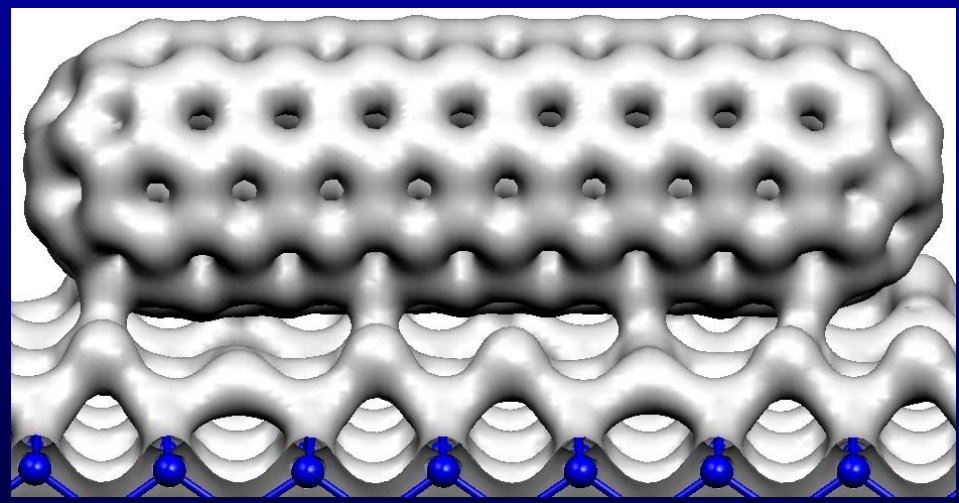


N_{bond} = 8

E_b = 3.73 eV

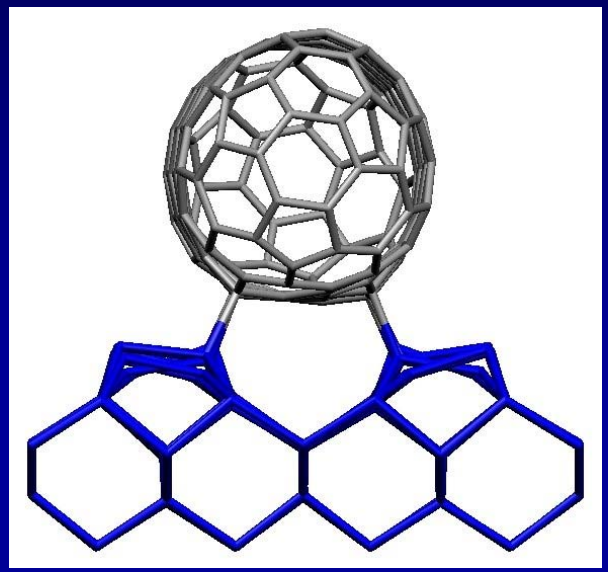
$\overline{d}_{C\text{-}Si}$ = 2.08 Å

Charge density isosurface [0.28 e/Å^3]

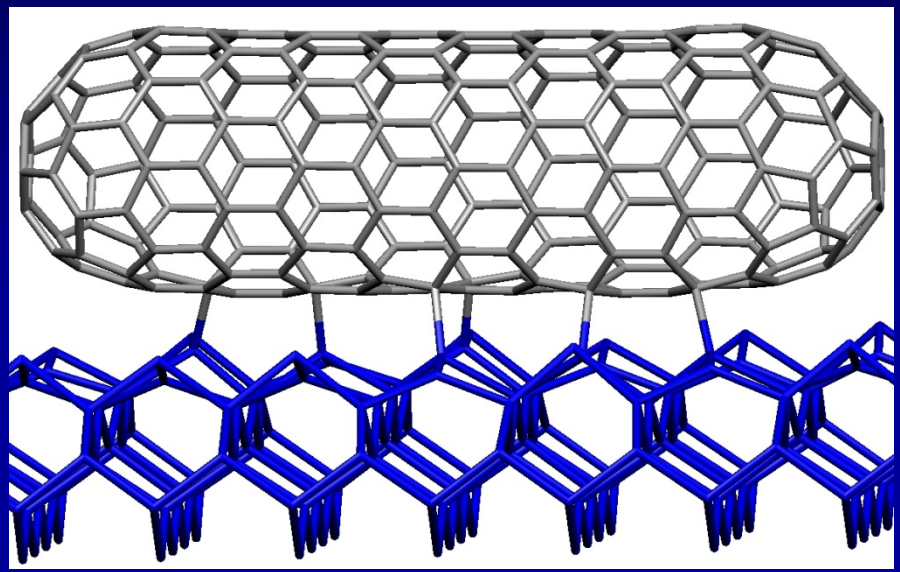


Zigzag (9,0) on $Si(001)_T$

Front view



Side view

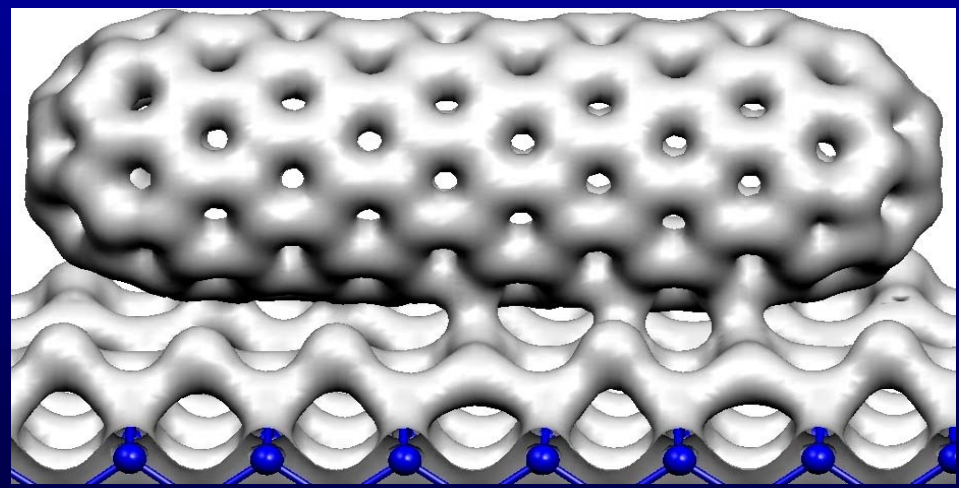


N_{bond} = 6

E_b = 3.40 eV

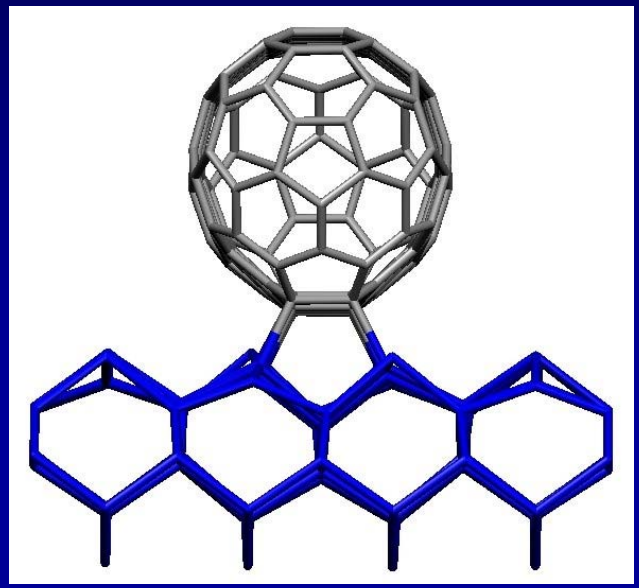
$\overline{d}_{C\text{-}Si}$ = 2.06 Å

Charge density isosurface [0.28 e/Å^3]

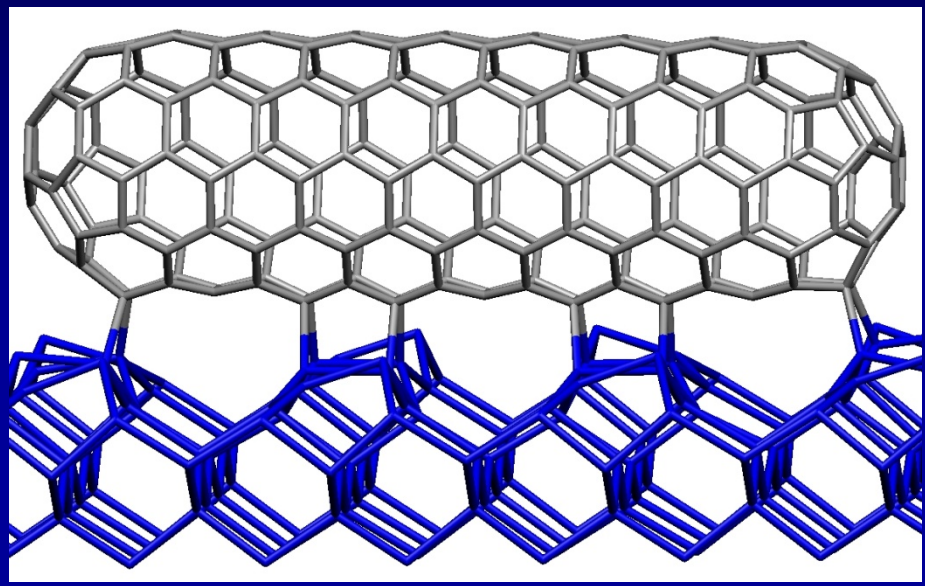


Armchair (5,5) on $Si(001)_D$

Front view



Side view

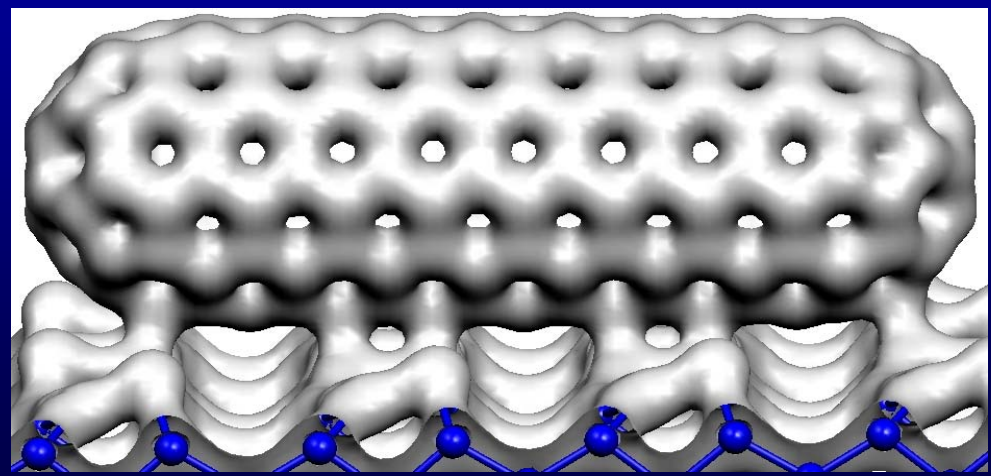


N_{bond} = 12

E_b = 4.77 eV

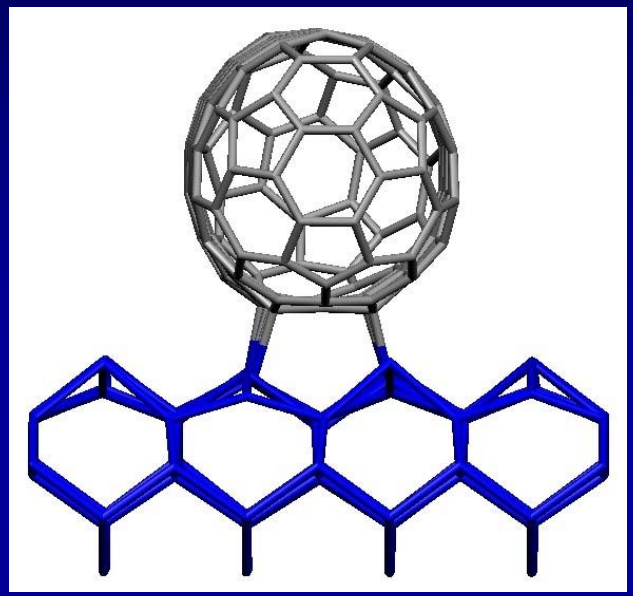
$\overline{d}_{C\text{-}Si}$ = 2.09 Å

Charge density isosurface [0.28 e/Å^3]

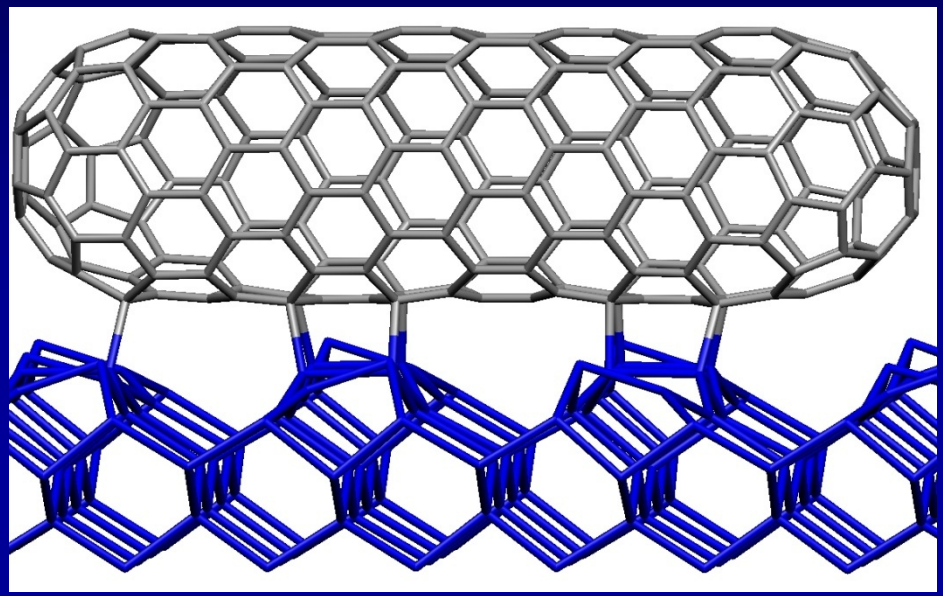


Zigzag (9,0) on $Si(001)_D$

Front view



Side view

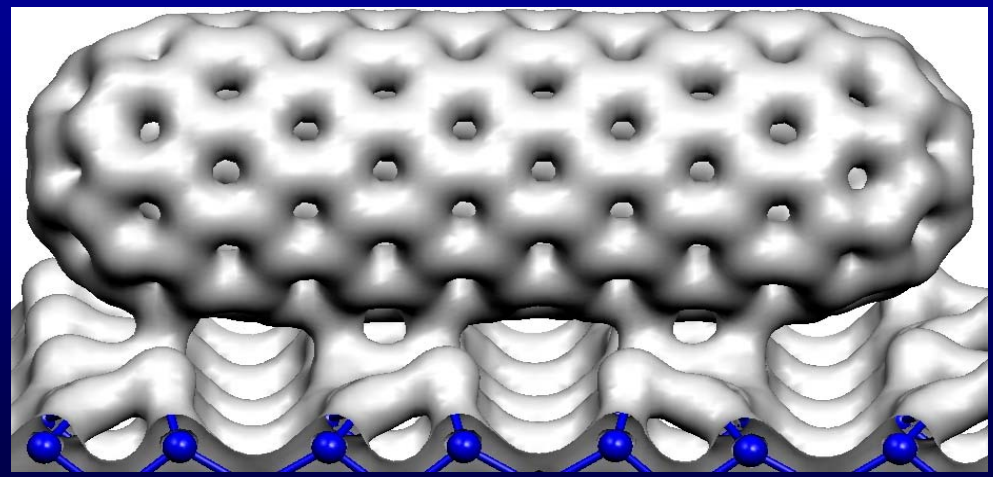


N_{bond} = 9

E_b = 5.54 eV

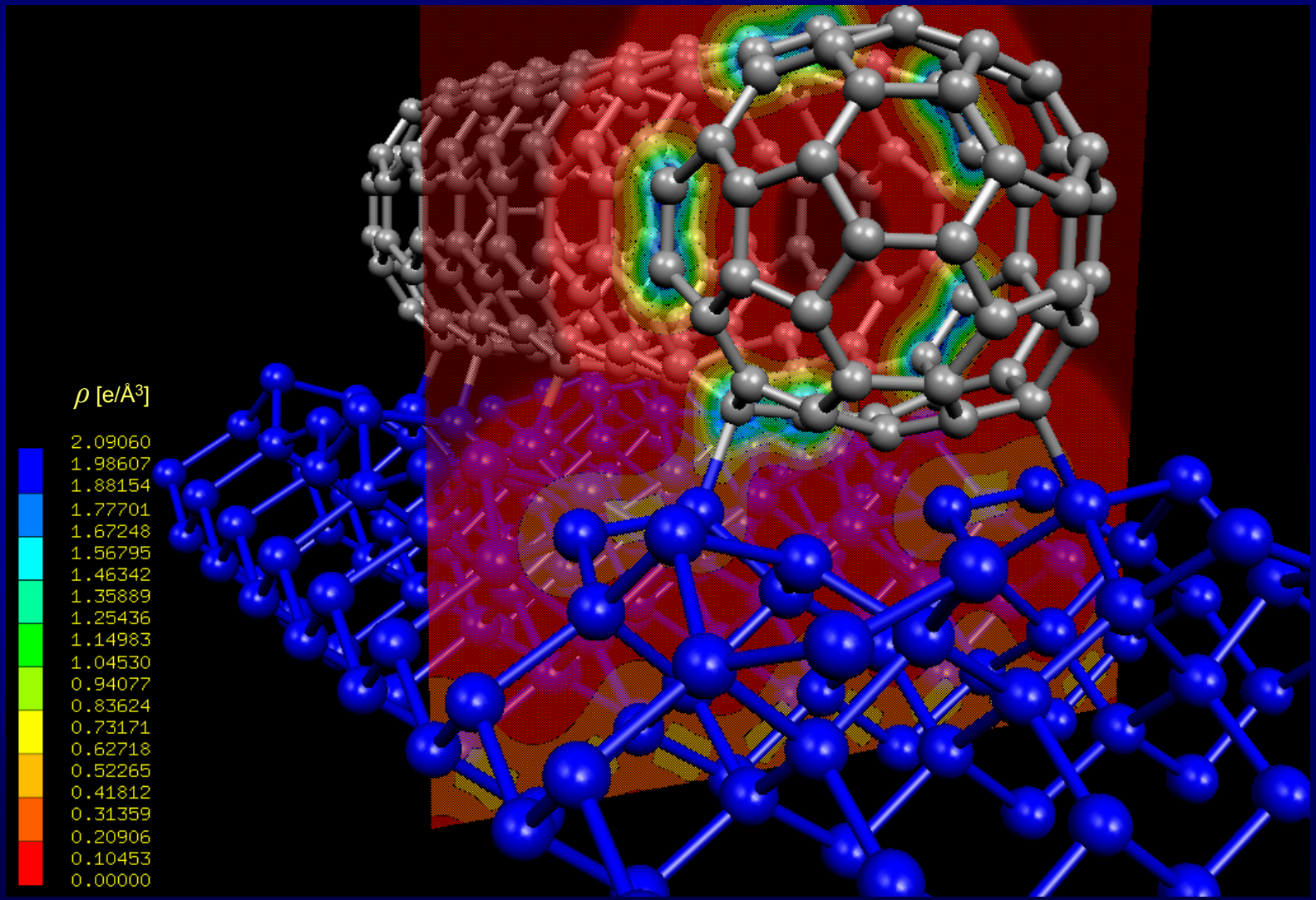
$\overline{d}_{C\text{-}Si}$ = 2.05 Å

Charge density isosurface [0.28 e/Å^3]

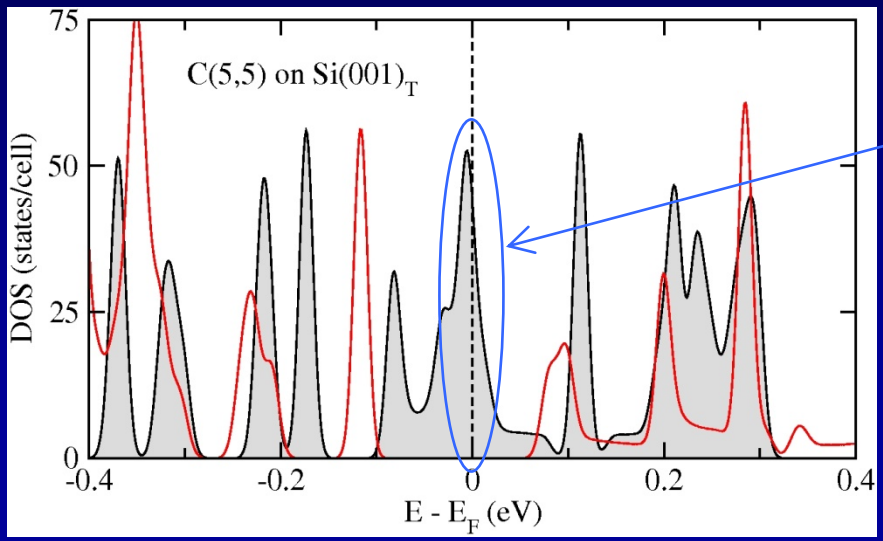


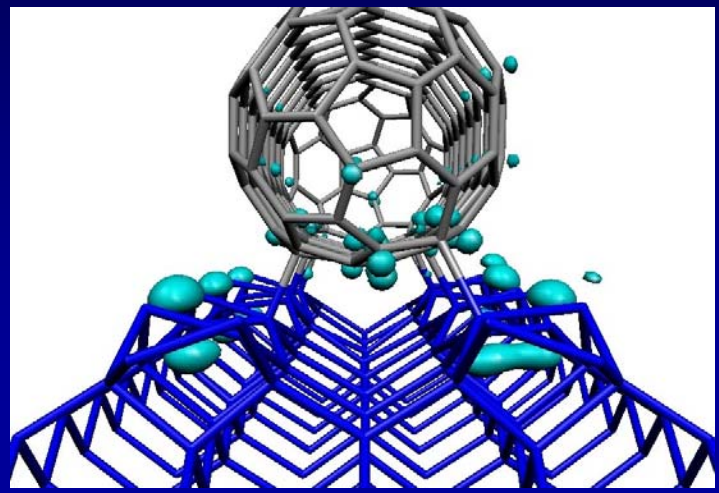
The bond properties

The Si-C bonds are weaker than C-C but stronger than Si-Si

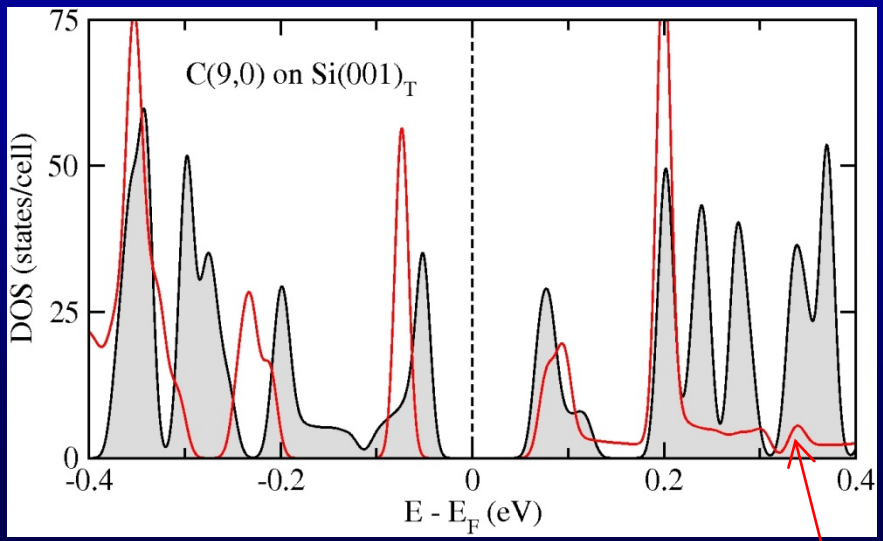


Density of states for CNTs on the trench





Charge density around de Fermi level for (5,5) on Si(001)$_T$.
Unit of 0.001 e/Å^3.

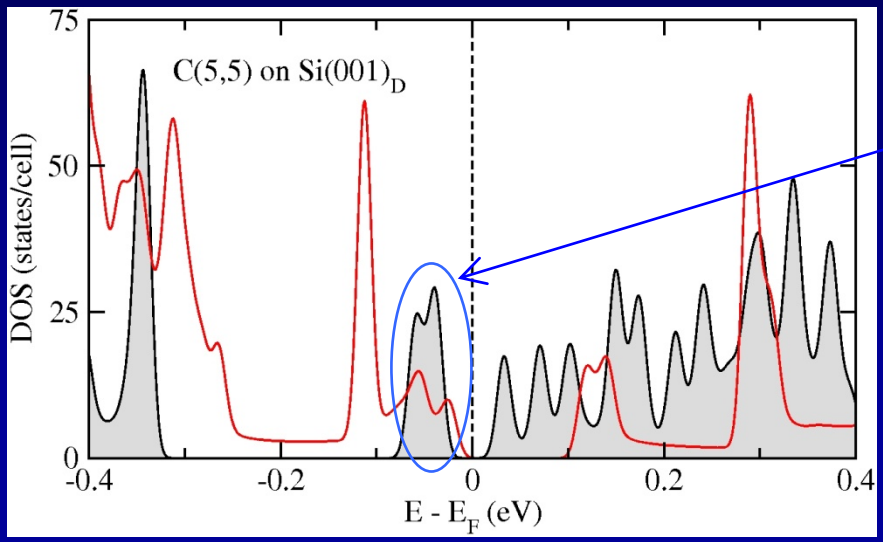


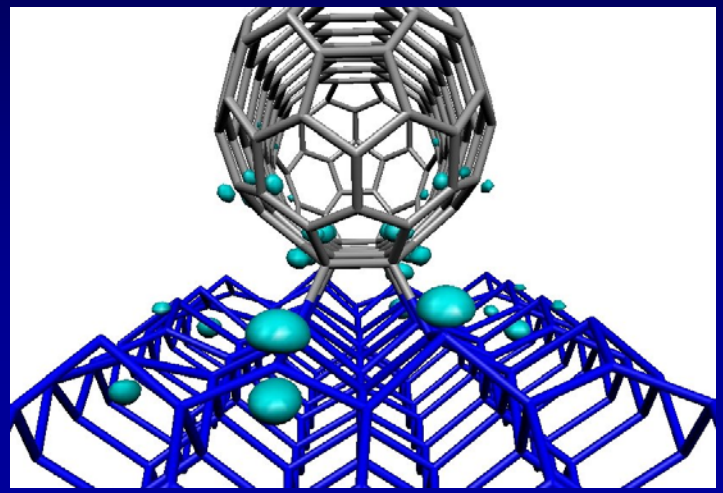
The (5,5) CNT adsorbed on the trench forms a metallic system in agreement with calculations on infinite systems

Whereas the (9,0) CNT adsorbed on the same region shows a semiconducting behavior

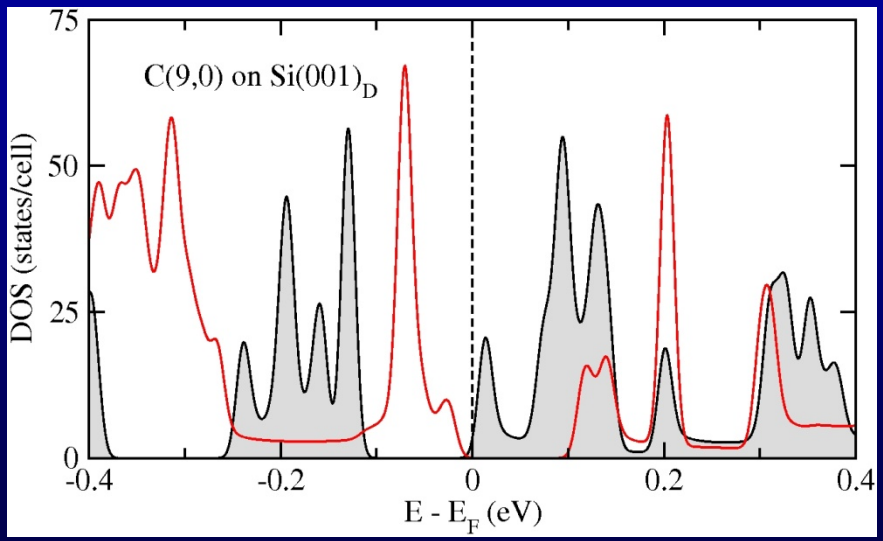
DOS of the suspended CNT on Si(001)

Density of states for CNTs on dimers





Charge density of the HOMO state for (5,5) on $Si(001)_D$.
Unit of 0.001 e/Å^3.



Both CNTs adsorbed along the dimers show a semiconducting behavior.

These results suggest that unsaturated dimers have a central role in the electronic character of the adsorbed CNTs.

Summary and Conclusions

System	E_b (eV)	E_b (eV/Å)	E_{gap}(eV)	$\bar{d}$ (Å)	N_{bond}
(9,0) on $Si(001)_D$	5.54	0.23	0.14	2.05	9
(5,5) on $Si(001)_D$	4.77	0.20	0.07	2.09	12
(5,5) on $Si(001)_T$	3.73	0.15	0.00	2.08	8
(9,0) on $Si(001)_T$	3.40	0.14	0.12	2.06	6

- The number of C-Si bonds is not directly related with the stability of CNTs on Si(001) the bonds formation occur when the distance between atoms is closer than 2.13 Å
- The preferential region for the CNT adsorption is along the dimers, where the zigzag CNT is found to be the most stable
- The electronic properties of the CNT-surface hybrid appear to be ruled by the CNT electronic character

W.O., Applied Physics Letters 92, 093109 (2008)