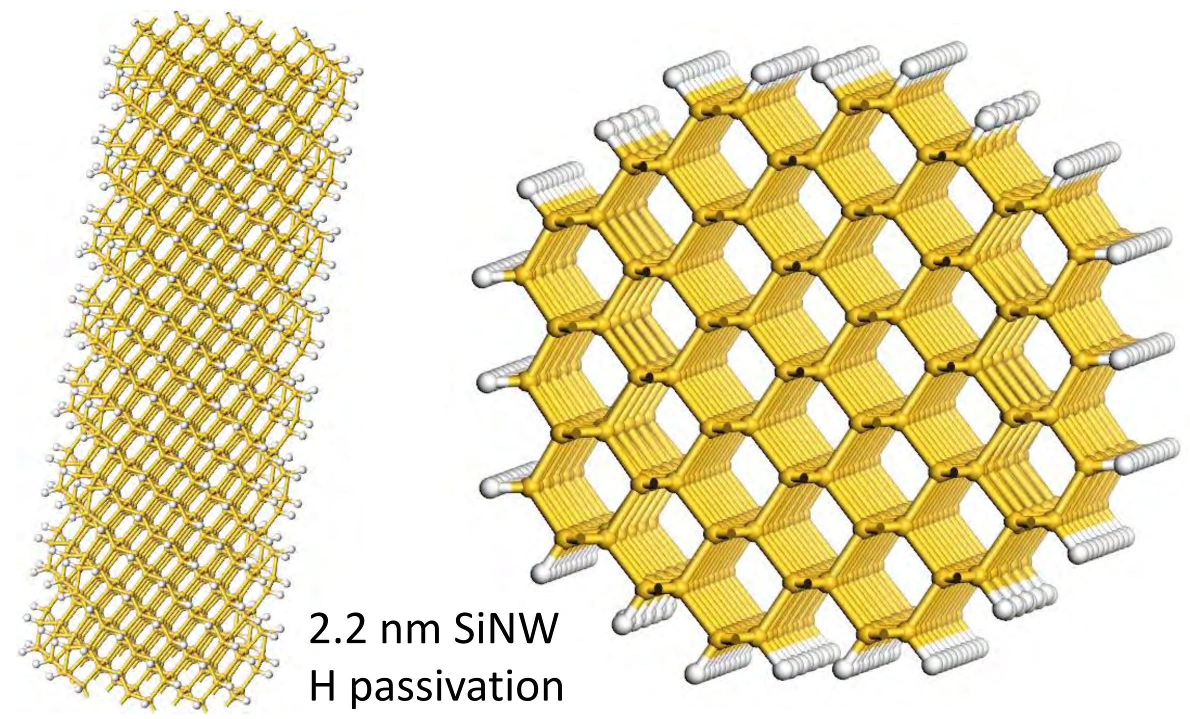
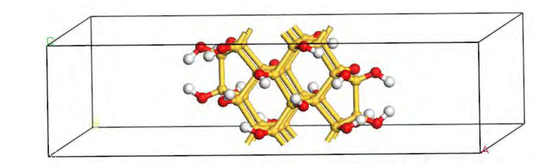


2.2 nm SiNW
H passivation

Functionalization of <110> Oriented Silicon Quantum Wires

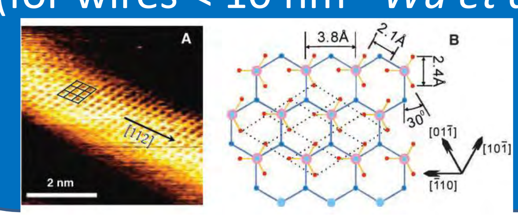


OH Passivation

R. Lochner, H. Li, Z. Wu, M. T. Lusk

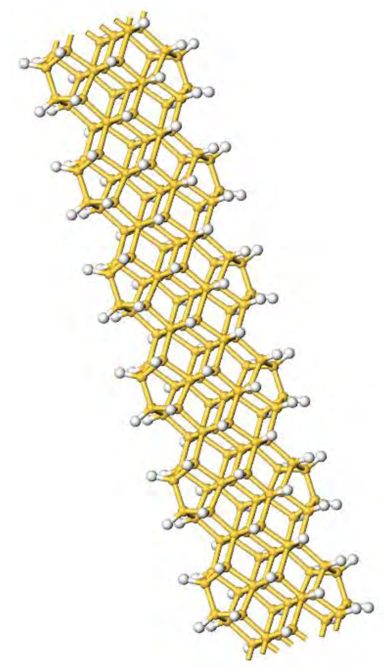
Silicon Nanowires (SiNW)

- Cylindrical crystals of diamond structured silicon
- Length >> Diameter
- ~1-100 nm in diameter
- <110> direction dominates (for wires < 10 nm –*Wu et al.)*

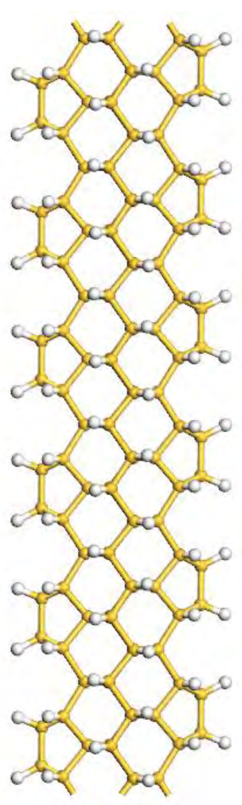


STM Image from *Wu et al.*

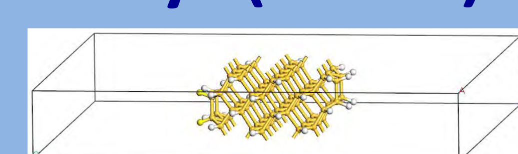
- Smallest wire: 1.3 nm diameter *(Ma et al.)*
- Electronic properties vary with
  - -- growth orientation
  - --surface restructuring
  - -- attached ligands
- Prospects good for use in future nanoelectronics and PV devices



H Passivation



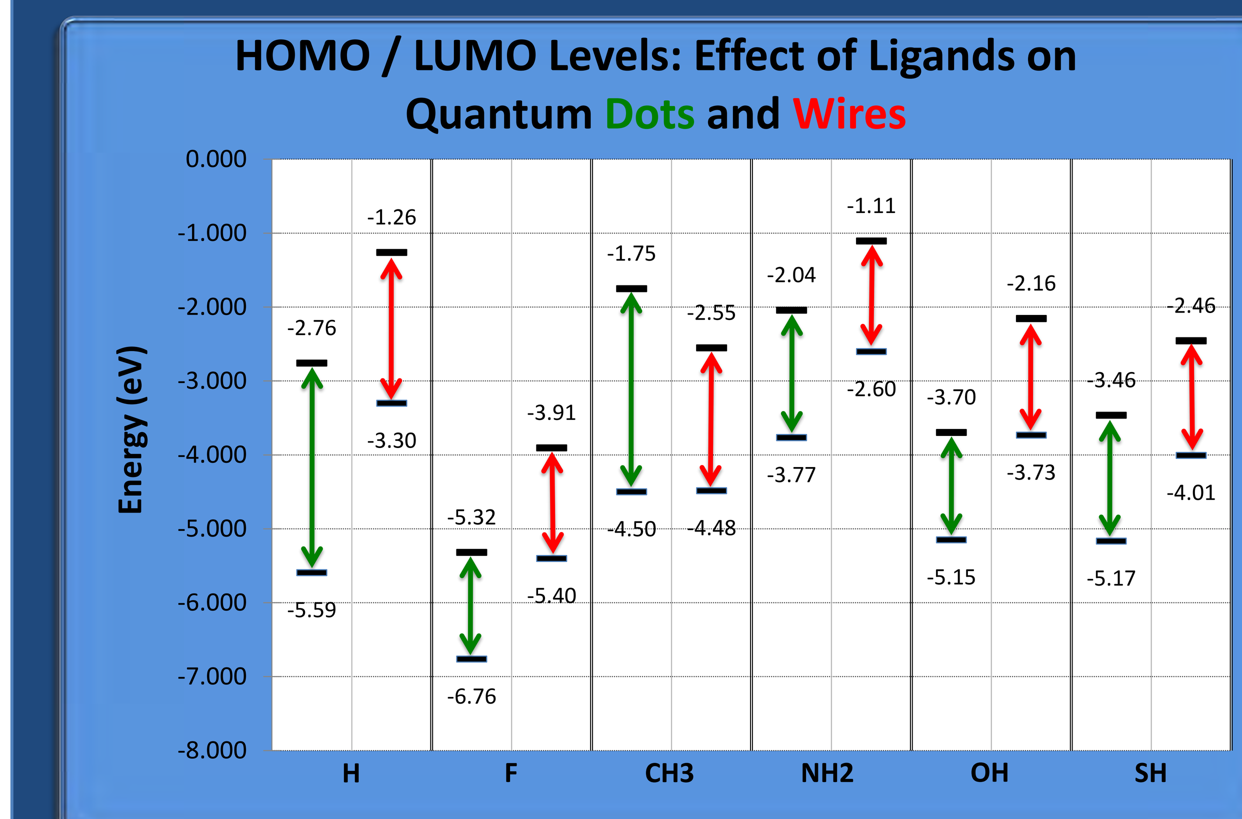
Density Functional Theory (DFT)

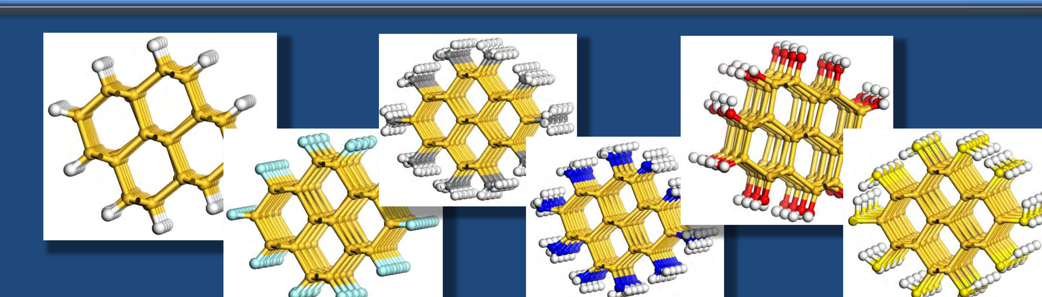


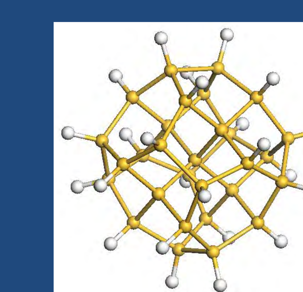
- Hamiltonian a functional of electron density
- Ground state properties all functionals of electron density
- Electron density obtained by solving N equations for N electrons instead of solving a single, high dimensional Schrodinger equation
- Initial guess for electron density seeds Hamiltonian and equations solved for improved electron density; repeat until self-consistent
- Provides qualitative excited state properties; Known to underestimate the band gap of Si
- More accurate methods needed for quantitative prediction of excited state properties

Effect of Ligands on Band Gap

- Ligands studied: H, NH2, CH3, SH, F, OH
- Same ligands investigated on Si quantum dots
- *How does geometry influence role of ligand?*





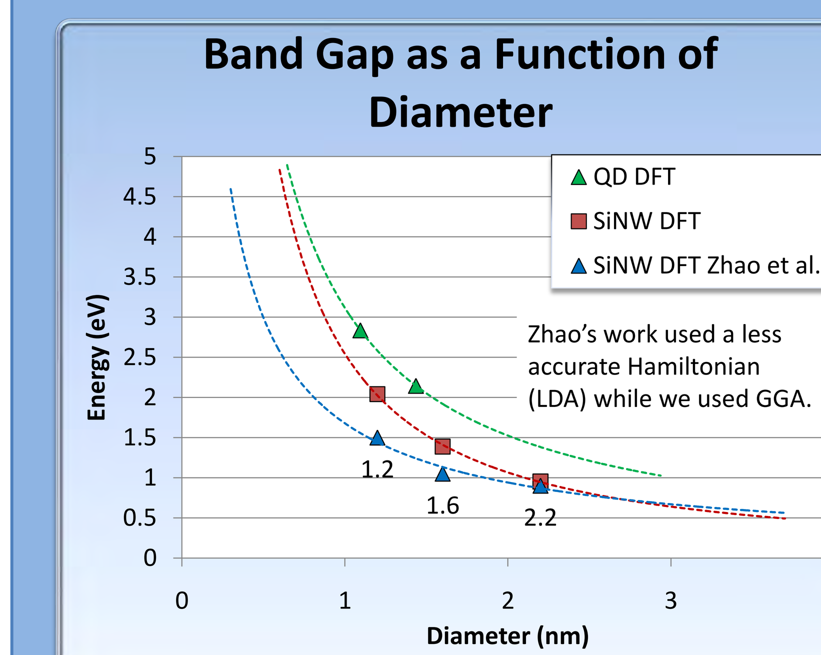


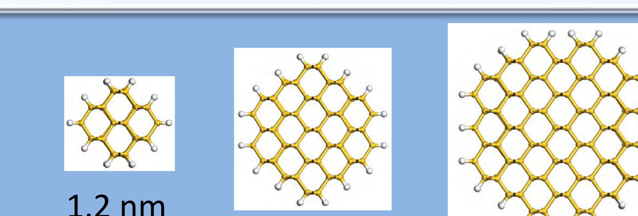
Si29H24 Quantum Dot

- Sizes:
  - -- dot: ~1.0 nm
  - -- wire ~1.2 nm
- 3-D v. 2-D quantum confinement
  - -- lower band gap for wire
  - -- HOMO/LUMO levels lower for wires
- Passivation trends same for dots and wires
  - -- steric effects, surface Si electronic structure, confinement cause differences

Quantum Confinement

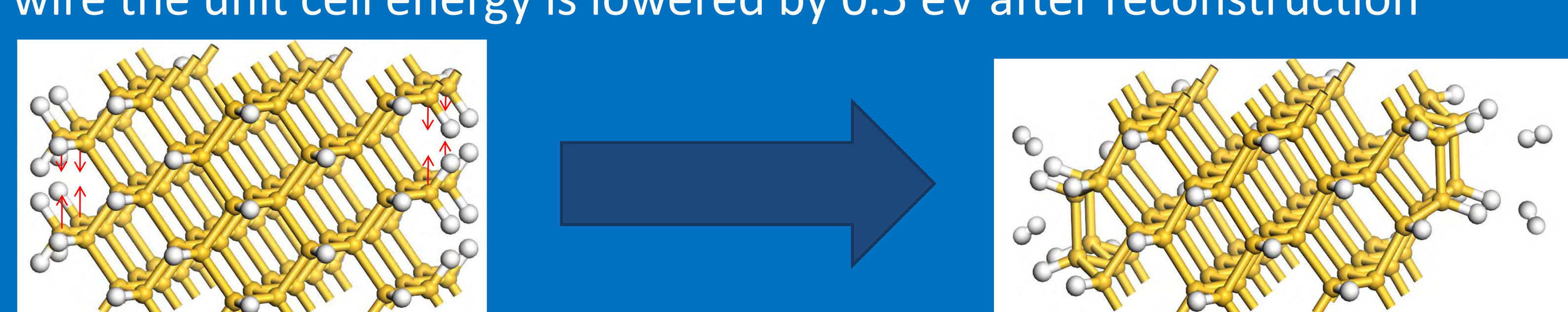
- Excitons (electron-hole pairs) are confined when structures approach exciton Bohr radius
  - -- 4.9 nm for Si
- Excited state energies therefore increase as size decreases
  - -- optical band gap increases
- Wires (2 small dims) are less confining than dots (3 small dims)
  - -- effect less severe for wires
- Band gap of larger wires should approach that of bulk Si
  - -- DFT predicts gap of bulk Si ~.7 eV
  - -- actual value 1.1 eV

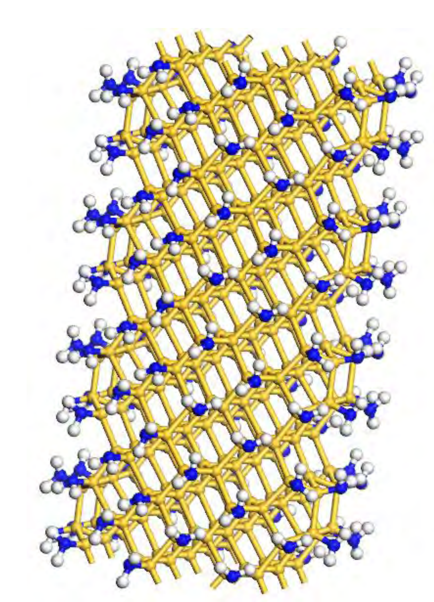




Surface Reconstruction

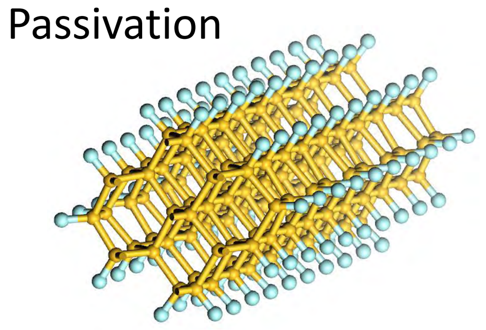
- Pristine wires, that is wires of pure Silicon, have many dangling bonds on the wire surface
- Surface may be *passivated* by adding ligands such as Hydrogen
- Most facets of <110> wires have only one ligand per surface Si atom
- Would have di-hydride passivation on {001} facets, but reconstruction of Si results in mono-hydride bonding
- Reconstruction occurs when adjacent surface Si atoms, each with 2 ligands, give up one ligand in order to bond to each other, forming a surface Si *dimer*
- Dimers form next to each other as opposed to an alternating pattern
- For the 1.2 nm wire the unit cell energy is lowered by 0.5 eV after reconstruction





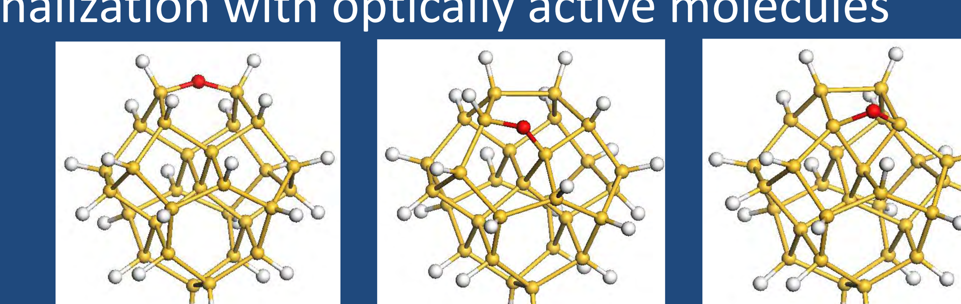
NH2 Passivation

F Passivation



Future Work

- Identify ligands which prevent oxidation of SiNW's
  - -- investigate <110> wires with di-hydride surfaces that cannot reconstruct and determine to what extent they can be passivated
- Use ligands to tune optical response of wires
- Use ligands to improve energy/charge transfer to/from wires
- Functionalization with optically active molecules



Oxygen atoms (red) bond to dot surfaces.
How does geometry influence this process for wires?

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Renewable Energy Materials Research Science and Engineering Center REMRSEC

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X. Y. Zhao, C. M. Wei, L. Yang, M. Y. Chou, Phys.Rev .L ett. 2004, 92, 236805. **Quantum Confinement and Electronic Properties of Silicon Nanowires**
D. D. D. Ma, C. S. Lee, F. C. K. Au, S. Y. Tong, S. T. Lee 3/21 /2003, SCIENCE 299 (5614), 1874