Predicting Structures and Properties of Nano-scale Materials

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Why do we need to predict the structures and properties of nano-scale materials ?

- Nanostructures have attracted an enormous amount of attention since they are expected to play a crucial role as building blocks for future molecular electronics applications.

- Many of the unusual and interesting properties of the nanostructures originate from quantum-size effects. These unique properties could not in general be predicted or explained by traditional models and theories.

- The study of the consequences of these effects must rely on a quantum mechanics-based theory which has the predictive power. Such a theory is necessary to complement the experimental investigation of structures and properties of nano-structures and to pave the way for understanding, designing, and controlling these properties for functional molecular assemblies.

- While the density functional theory (DFT)-based methods do possess the predictive power, their applications are limited by sizes of the systems of no more than a few hundreds of atoms.

- We need to develop a quantum mechanics-based approach which must have the predictive power to study structures and properties of nano-scale systems with sizes beyond the scope of DFT-based methods.

How do we predict the structures and the properties of nanostructures?

— Methodology —

- First Principles Simulations: Density functional theory (DFT)-based methods (small size/short time) (VASP, WIEN2K, etc.)
- Semi-empirical Simulations: Non-orthogonal tight-binding methods (larger size/longer time)
- Semi-empirical simulations: Self-consistent and environment-dependent (SCED) approach (larger size/longer time) (*Phys. Rev. B 74, 155408 (2006)*)

	Ab initio methods	Semi-empirical methods	Classical simulations
Major features	Have predictive power but have limitation on the size of the system	Address problems that are beyond the scope of *ab-initio;* may have transferability issues	Simulations of large systems possible- but poor predictive power
Major features	Electronic band structure Calculations required		Electronic band structure not required
Hamiltonian	Parameter free	Parameterized Functions used for the Hamiltonian	Parameterized inter-atomic Potential functions
Software	Gaussian, VASP, WIEN2K, SIESTA, ABINIT, CPMD, etc.	Gaussian, CHSSI-PET, Ames Lab, NRL Group	CHARMM, AMBER, DISCOVER

Methodology

Quantum Mechanical Simulations

accurate, reliable, and robust results, and therefore have the predictive power

- **Schrödinger equation for many-electron systems in the external ionic field:**

$$\hat{H}\psi = E\psi$$

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i,J} v(\vec{r}_i - \vec{R}_J) + \sum_{i,j} \frac{e^2}{4\pi\varepsilon_0 \left|\vec{r}_i - \vec{r}_j\right|} \quad ; \quad \psi = \psi(r_1, \ldots, r_n)$$

- **Schrödinger equation in the one-electron approximation (in an effective potential)**

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}\right)\psi_\lambda = \varepsilon_\lambda \psi_\lambda$$

First principles simulations

Density Functional Theory (DFT) — Kohn-Sham Equations:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}\right)\psi_\lambda = \varepsilon_\lambda \psi_\lambda \longrightarrow \rho(\boldsymbol{r}) = \sum_i |\psi_i|^2$$

DFT with Local Density Approximation (LDA):

$$V_{eff} = V_{eff}(\rho(\boldsymbol{r}))$$

or

DFT with Generalized Gradient Approximation (GGA):

$$V_{eff} = V_{eff}(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}))$$

$$E^{total} = 2\sum_i^{occ} \varepsilon_i - \frac{e^2}{2}\int d^3r d^3r' \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{xc}[\rho] - \int d^3r \upsilon_{xc}(\boldsymbol{r})\rho(\boldsymbol{r})$$

http://cms.mpi.univie.ac.at/vasp/vasp.html

- A complex package for performing *ab-initio* quantum-mechanical molecular dynamics (MD) simulations using a plane wave basis set.
- DFT-based method using either LDA or GGA for exchange-correlation energy.
- The interaction between ions and electrons is described by ultra-soft Vanderbilt pseudopotentials or by the projector-augmented wave method.

high reliability and reputation, and is considered to have the predictive power !

!! Limitations in DFT-based ab initio simulations

- The diagonalization and the calculation of the Hamiltonian matrix elements go as N^3.
- DFT-based simulations are applicable only for systems of no more than a few hundreds of atoms.
- The time scale available for the molecular dynamics study only reaches picoseconds.
- These limitations will prevent first-principles simulations from applications to complex chemical reactions, biological systems or nanostructures with low or no symmetry.

Semi-empirical simulations

Two-Center Non-Orthogonal Tight-Binding (NOTB) Eigenvalue Equation:

$$< \phi_n \mid \hat{H} \mid \phi_m > c^{\lambda}{}_m = \varepsilon_\lambda c^{\lambda}{}_m < \phi_n \mid \phi_m > \quad ; \ \psi_\lambda = \sum_n c_n^\lambda \phi_n$$

$$< \phi_n \mid \hat{H} \mid \phi_m >= H_{nm}$$

$$< \phi_n \mid \phi_m >= S_{nm}$$

Parameterized functions

- Two key advantages: (1) capturing the quantum nature of the problem; (2) increasing both the size and the time of simulation by about two orders of magnitude.

- A system-specific tool: the transferability of the NOTB Hamiltonian is crucially dependent on the parametric functions defining the Hamiltonian.

!! Disadvantage of the NOTB Hamiltonians: limitation of the transferability

- They include only two-center interactions and they have no framework to allow the self-consistent determination of the charge re-distribution and the environment-dependent multi-center interactions. These are two key ingredients for an appropriate description of bond-breaking and bond-forming processes.

- They are not equipped to determine the equilibrium configuration of systems such as nanostructures where these two processes are dominant. Thus they do not have the predictive power and can only be used, in the strictest sense, to provide explanation for system-specific experimental results.

Development of new semi-empirical Hamiltonian at CMT group of UofL

Self-Consistent and Environment-Dependent Hamiltonian in the framework of Linear Combination of Atomic Orbitals

SCED-LCAO

$$< \phi_{i\alpha} \mid \hat{H} \mid \phi_{j\beta} > c^{\lambda}{}_{i\alpha} = \varepsilon_{\lambda} c^{\lambda}{}_{i\alpha} < \phi_{i\alpha} \mid \phi_{j\beta} > \longrightarrow N_i = \sum_{\lambda}^{ooc} \sum_{\alpha} \sum_{j\beta} c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} f_{\lambda} S_{i\alpha,j\beta}$$

$$< \phi_{i\alpha} \mid \hat{H} \mid \phi_{j\beta} >= H_{i\alpha,j\beta}^{SCED-LCAO}(N_i, N_j, \{V_{ki}^{N}\}, \{V_{kj}^{N}\}, \{V_{ki}^{Z}\}, \{V_{kj}^{Z}\})$$

$$\psi_{\lambda}^{LCAO} = \sum_{i\alpha} c_{i\alpha}^{\lambda} \phi_{i\alpha}^{AO}$$

Phys. Rev. B 74, 155408 (2006)

Materials simulations based on the SCED-LCAO Hamiltonian are reliable, transferable, robust, and has the predictive power!

Construction of the SCED- LCAO Hamiltonian:

Hamiltonian matrix element:

$$H_{i\alpha,j\beta}^{SCED-LCAO} = \frac{1}{2}\{\underbrace{K(R_{ij})(\varepsilon'_{i\alpha}+\varepsilon'_{j\beta})}_{\text{Two-center interactions}} + \underbrace{[(N_i - Z_i)U_i + (N_j - Z_j)U_j]}_{\text{Treatment of charge re-distribution}}$$

$$+\underbrace{[\sum_{k\neq i}(N_k V_N(R_{ik}) - Z_k V_Z(R_{ik})) + \sum_{k\neq j}(N_k V_N(R_{jk}) - Z_k V_Z(R_{jk}))]}_{\text{Environment-dependent multi-center interactions}}\}S_{i\alpha,j\beta}(R_{ij})$$

Parametric functions:

$$K(R_{ij}) = e^{\alpha_K R_{ij}} \quad \text{(Scaling function)}$$

$$S_{ij,\tau} = (A_\tau + B_\tau R_{ij})\frac{[1+e^{-\alpha_\tau d_\tau}]}{[1+e^{-\alpha_\tau(d_\tau - R_{ij})}]} \quad \text{(Overlap matrix element)}$$

$$V_N(R_{ik}) = V_Z(R_{ik}) + \Delta V_N(R_{ik}) \quad \text{(Potential function of electron-electron interaction)}$$

$$V_Z(R_{ik}) = \frac{E_0}{R_{ik}}\{1-(1+B_Z R_{ik})e^{-\alpha_Z R_{ik}}\} \quad \text{(Potential function of electron-ion interaction)}$$

$$\Delta V_N = (A_N + B_N R_{ik})\frac{[1+e^{-\alpha_N d_N}]}{[1+e^{-\alpha_N(d_N - R_{ik})}]} \quad \text{(Short-range potential function)}$$

Framework of Establishing a Semi-Empirical Hamiltonian Possessing Predictive Power

$$\langle \phi_{i\alpha} | \hat{H} | \phi_{j\beta} \rangle c^{\lambda}{}_{i\alpha} = \varepsilon_{\lambda} c^{\lambda}{}_{i\alpha} \langle \phi_{i\alpha} | \phi_{j\beta} \rangle$$

$$\langle \phi_{i\alpha} | \hat{H} | \phi_{j\beta} \rangle = H^{SCED-LCAO}_{i\alpha,j\beta}$$

$$\langle \phi_{i\alpha} | \phi_{j\beta} \rangle = S_{i\alpha,j\beta}$$

} Parameterized functions

Transferability

Physical properties in small clusters, bulk phases, band-structures, etc.

Fitting

Corresponding *ab inito* calculations and/or experimental results

Robustness

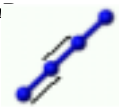
Physical properties in more complicated structures

Comparing

Corresponding *ab inito* calculations and/or experimental results

Transferability of the SCED-LCAO Hamiltonian

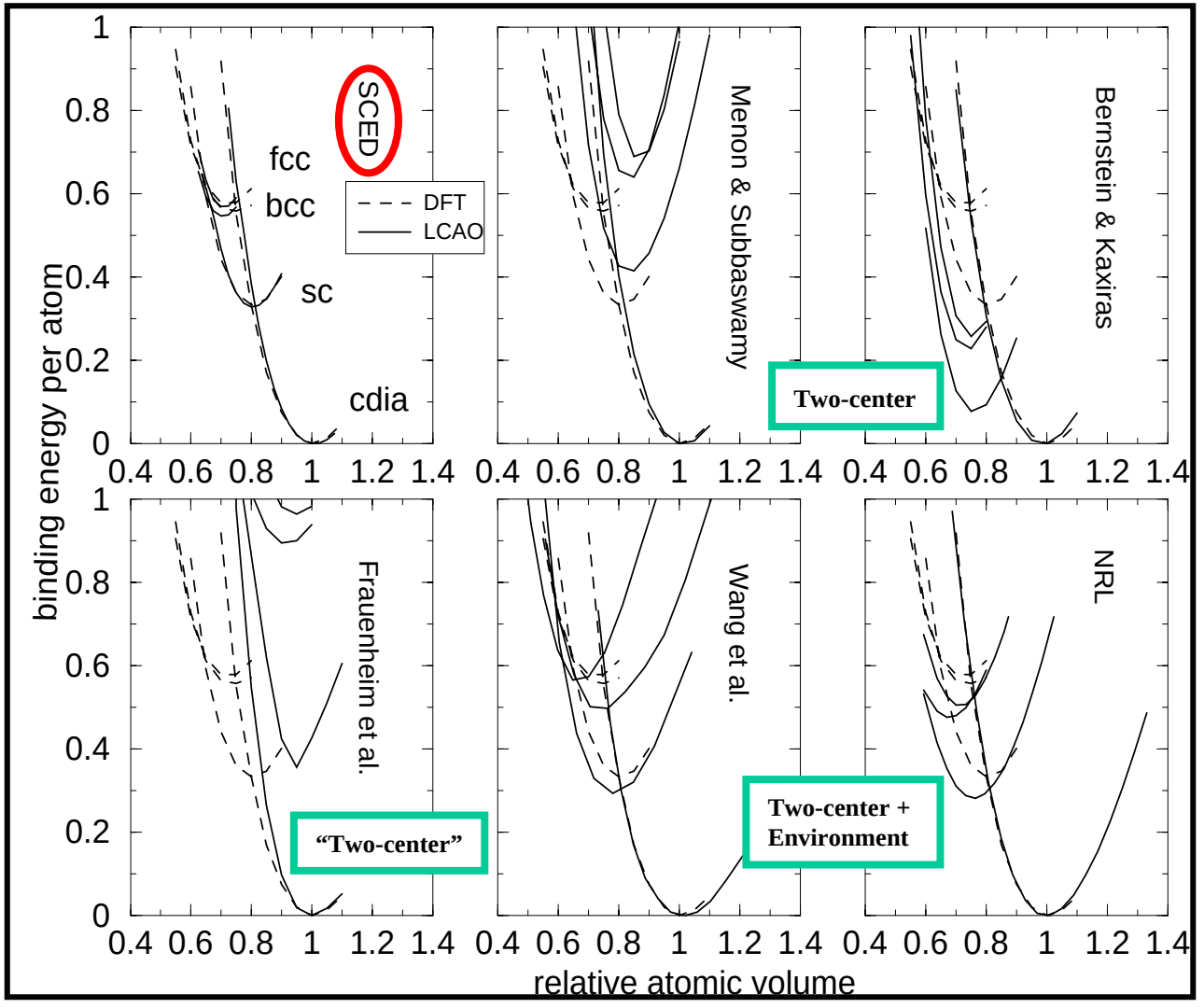
Fitting results on small Si clusters

Cluster	Symmetry	Present work	*ab initio* values[a]
SiB_{2B}	DB_{ihB} 	2.226 Å -2.435 eV	2.288 Å -2.499 eV
SiB_{3B}	CB_{2vB} 	2.284 Å 2.168 Å -3.413 eV	2.357 Å 2.158 Å -3.575 eV
SiB_{3B}	DB_{ihB} 	2.141 Å -3.427 eV	2.167 Å -3.404 eV
SiB_{4B}	DB_{2h} 	2.275 Å -4.101 eV	2.311 Å -4.242 eV
SiB_{4B}	TB_{dB} 	2.332 Å -3.773 eV	2.474 Å -3.659 eV
SiB_{4B}	DB_{ih} 	2.116 Å 2.164 Å -3.289 eV	2.156 Å 2.176 Å -3.364 eV
SiB_{5B}	DB_{3h} 	2.207 Å 3.141 Å -4.526 eV	2.306 Å 3.064 Å -4.453 eV

Cluster	Symmetry	Present work	*ab initio* values[a]
SiB_{5B}	CB_4 	2.209 Å 2.358 Å -4.327 eV	2.275 Å 2.513 Å -4.266 eV
SiB_{5B}	DB_i 	2.082 Å 2.128 Å -3.545 eV	2.133 Å 2.144 Å -3.534 eV
SiB_{5B}	TB_d 	2.127 Å 3.475 Å -3.334 eV	2.215 Å 3.617 Å -3.283 eV
SiB_{6B}	DB_{4hB} 	2.248 Å 2.639 Å -4.698 eV	2.363 Å 2.734 Å -4.664 eV
SiB_{6B}	DB_{3dB} 	2.261 Å 2.948 Å -3.896 eV	2.285 Å 3.208 Å -3.972 eV
SiB_{6B}	DB_{ihB} 	2.057 Å 2.072 Å 2.149 Å -3.446 eV	2.098 Å 2.134 Å 2.158 Å -3.446 eV

a. Gaussian 98 MPW1PW91/cc-pVTZ.

Fitting results on the phase diagram of bulk Si



The SCED-LCAO approach with the inclusion of explicit self-consistency and environment-dependence represents the most complete package to capture the environment-dependent screening effects under various local configurations.

Physical properties of bulk Si (diamond phase)

Properties	SCED-LCAO	Other TB	DFT	Expt.
Lattice constant (Å)	5.443	5.426[e]; 5.399[f]; 5.427[g]; 5.417[h]	5.451[a]; 5.399[f]	5.429[b]
Cohesive energy (eV/atom)	4.904	4.71[f]; 5.19[g]; 4.97[h]	4.67[a]; 4.70[f]	4.63[c]
Bulk Modulus (GPa)	96.6	108.3[e]; 104.8[f]; 153.5[g]; 115.1[h]	98[a]; 96.4[e]; 98[f]	99[d]
C_{11} (GPa)	166.3	179[e]; 145[f]; 218[g]; 185[h]	152[e]	166[d]
C_{12} (GPa)	61.7	73[e]; 84.5[f]; 121[g]; 80.1[h]	60[e]	64[d]
C_{44} (GPa)	93.7	95[e]	101[e]	80[d]

a: Phys. Rev. B**26**, 5668 (1982).
b: *The Structure of Elements* (Wiley, New York, 1974).
c: *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1949 (Circular No. 467, Vol. I)).
d: J. Appl. Phys. **24**, 988 (1953):**34**, 651 (1963): **35**, 2161 (1964).
e: Phys. Rev. B**62**, 4477 (2000).
f: Phys. Rev. B**56**, 10488 (1997).
g: Phys. Rev. B**55**, 9231 (1997): **47**, 12754 (1993): **50**, 11577 (1994).
h: Phys. Rev. B**52**, 11492 (1995).

Showing definitely the reliability of the SCED-LCAO Hamiltonian for Si

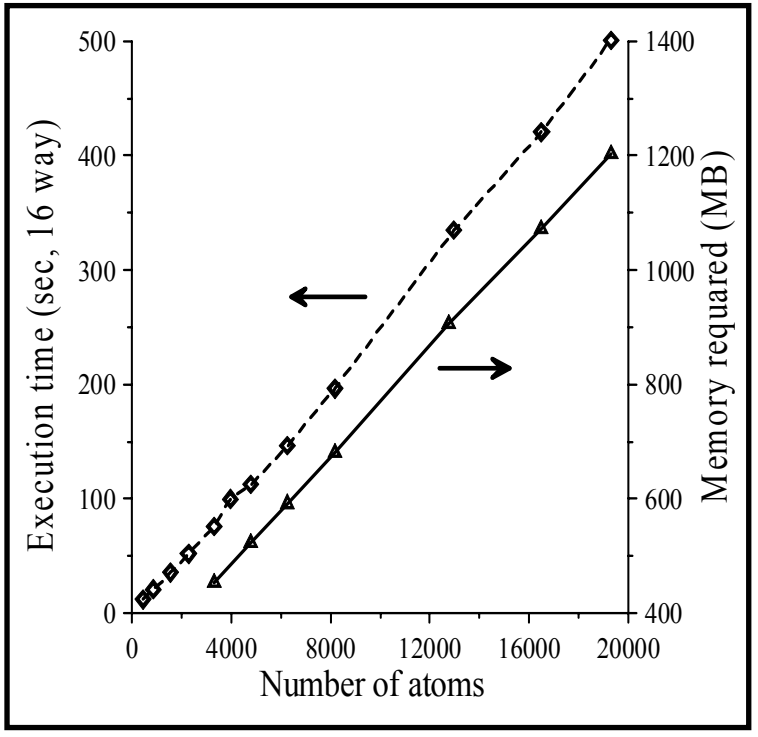
Efficiency of the SCED-LCAO approach

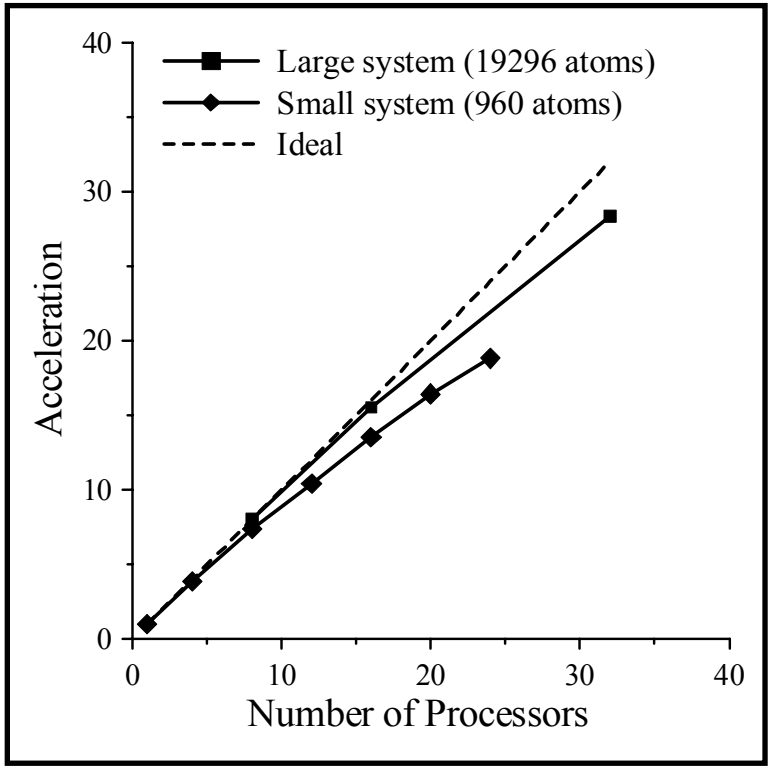
Computational speed and memory usage (testing on Si_{71} cluster)

Method	Execution time	Memory
VASP	~ 189 h 22 m 33 s	~ 300 MB
SCED-LCAO	~ 6 h 55 m	~ 63.4 MB

The SCED-LCAO approach is about 30 times faster than VASP, and requires about five times less memory for the relaxation of a Si_{71} cluster.

Implementation of the order-*N* scheme on top of the SCED-LCAO Hamiltonian for large-scale systems (testing on Si NWs)





The advantages of Order-*N* scheme (*C.S. Jayanthi, et al, PRB, 57, 3799 (1998)*):

(1) linear scaling with the size of the system;

(2) easy to develop its efficient parallelized version, which allows for the investigation of systems of up to tens of thousands of atoms and approaches two or three orders of magnitude speed up for those systems as compared to VASP.

The features of the SCED-LCAO Hamiltonian formulation

SCED-LCAO

$$< \phi_{i\alpha} \mid \hat{H} \mid \phi_{j\beta} > c^{\lambda}{}_{i\alpha} = \varepsilon_{\lambda} c^{\lambda}{}_{i\alpha} < \phi_{i\alpha} \mid \phi_{j\beta} > \longrightarrow N_i = \sum_{\lambda}^{ooc} \sum_{\alpha} \sum_{j\beta} c_{i\alpha}^{\lambda} c_{j\beta}^{\lambda} f_{\lambda} S_{i\alpha,j\beta}$$

$$< \phi_{i\alpha} \mid \hat{H} \mid \phi_{j\beta} >= H_{i\alpha,j\beta}^{SCED-LCAO}(N_i, N_j, \{V_{ki}^{N}\}, \{V_{kj}^{N}\}, \{V_{ki}^{Z}\}, \{V_{kj}^{Z}\})$$

$$\psi_{\lambda}^{LCAO} = \sum_{i\alpha} c_{i\alpha}^{\lambda} \phi_{i\alpha}^{AO}$$

- **Overcoming** the major drawback of other semi-empirical Hamiltonians in terms of the **transferability**.

- The physical content for terms in the parameterized functions also makes it possible to **track properties** of the system under consideration to their underlying physics.

- Based on the implementation of order-*N* scheme, the **SCED-LCAO** approach allows **quantum mechanics-based** simulations for **large-scale complex** nanostructures that are beyond the scope of DFT-based simulations.

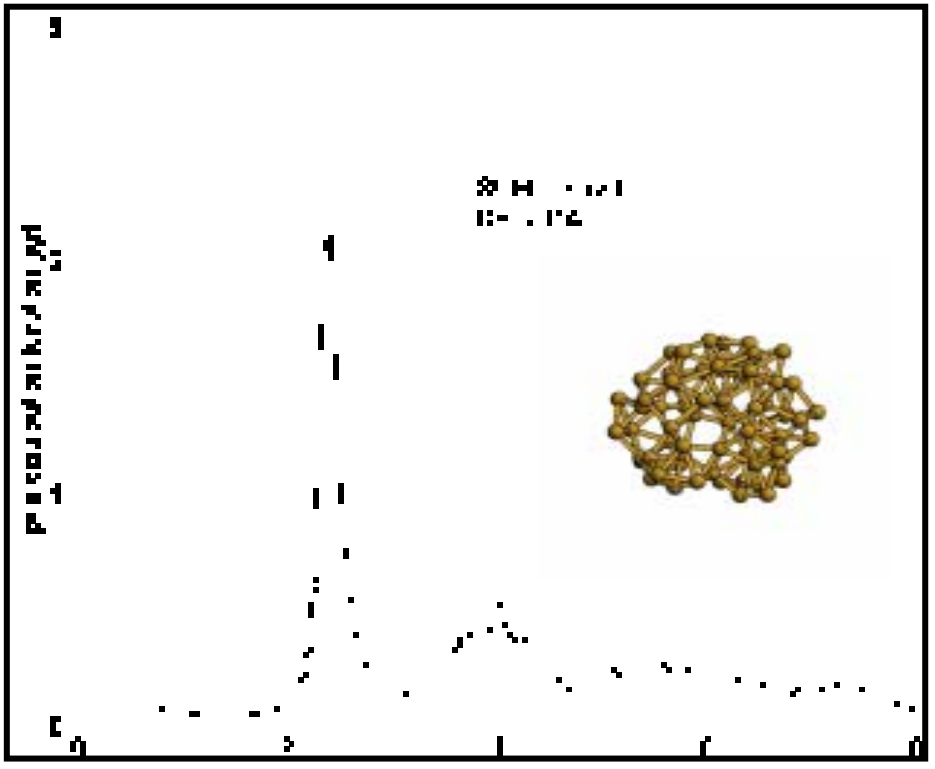
Demonstration of the robustness of the SCED-LCAO Hamiltonian

— Studies on Si-based systems —

- 0-dimensional system: The stable structure of Si_{71} cluster
- 1-dimensional system: The morphology of Si nanowires
- 2-Dimensional system: The reconstruction of Si (001) surface and the energy landscape of a Si monomer adsorbed on the reconstructed Si (111) -7x7 surface

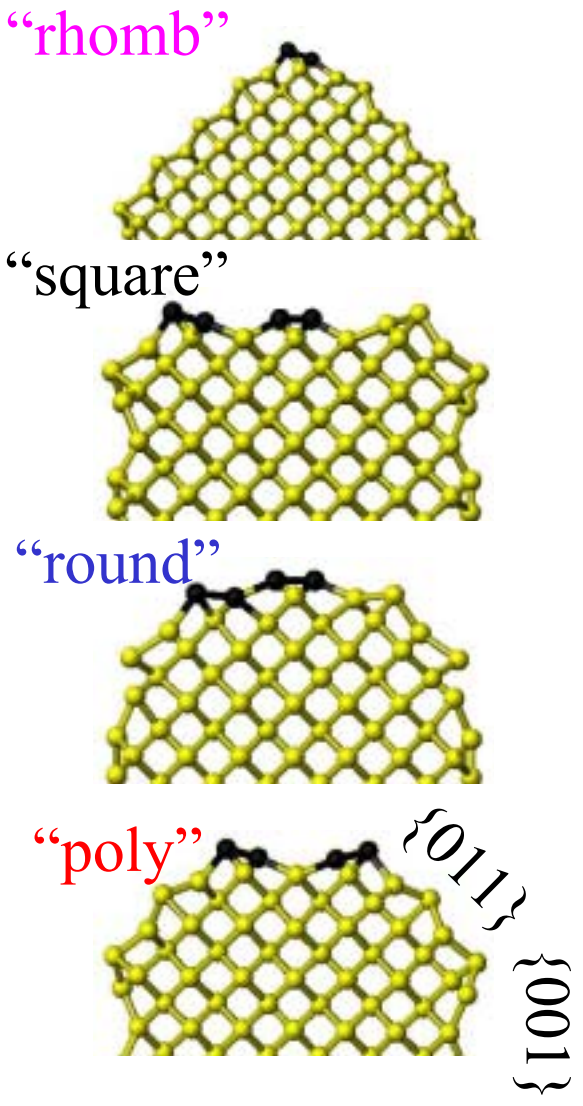
0-Dimensional Systems

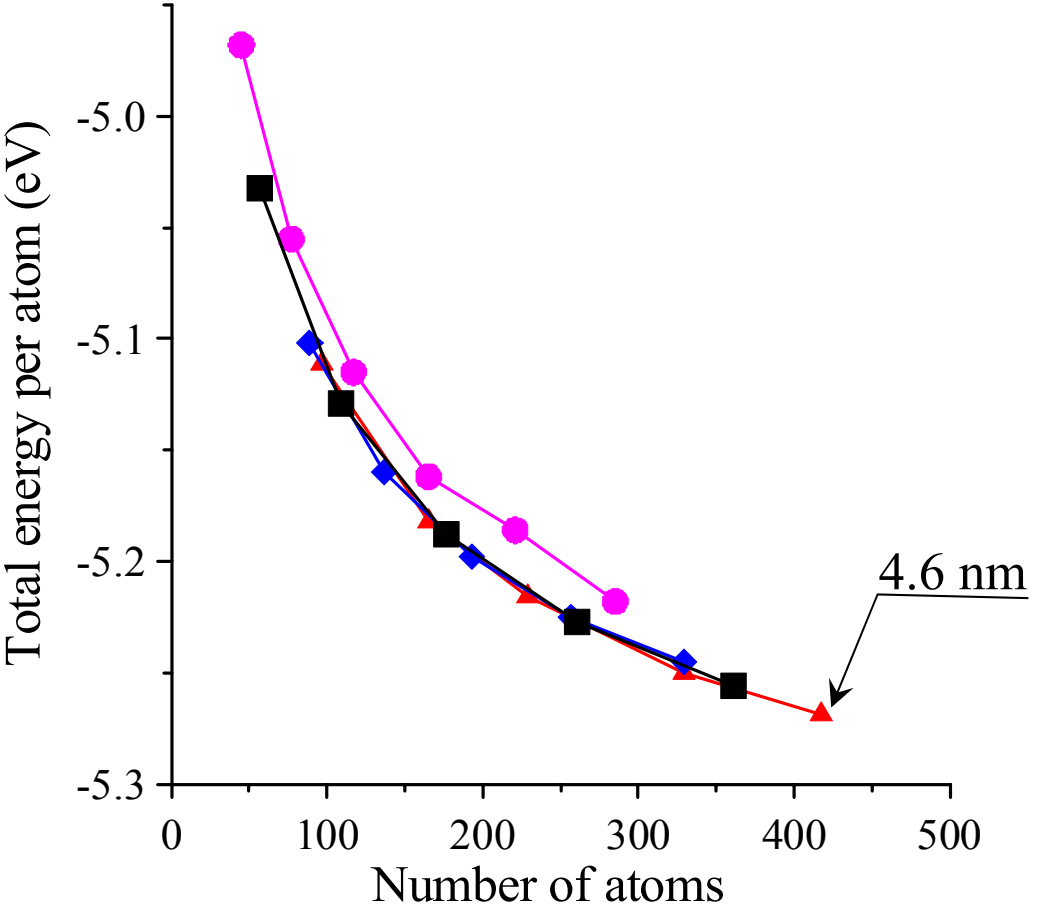
Relaxation of Si_{71} cluster (spherical truncated from bulk Si)



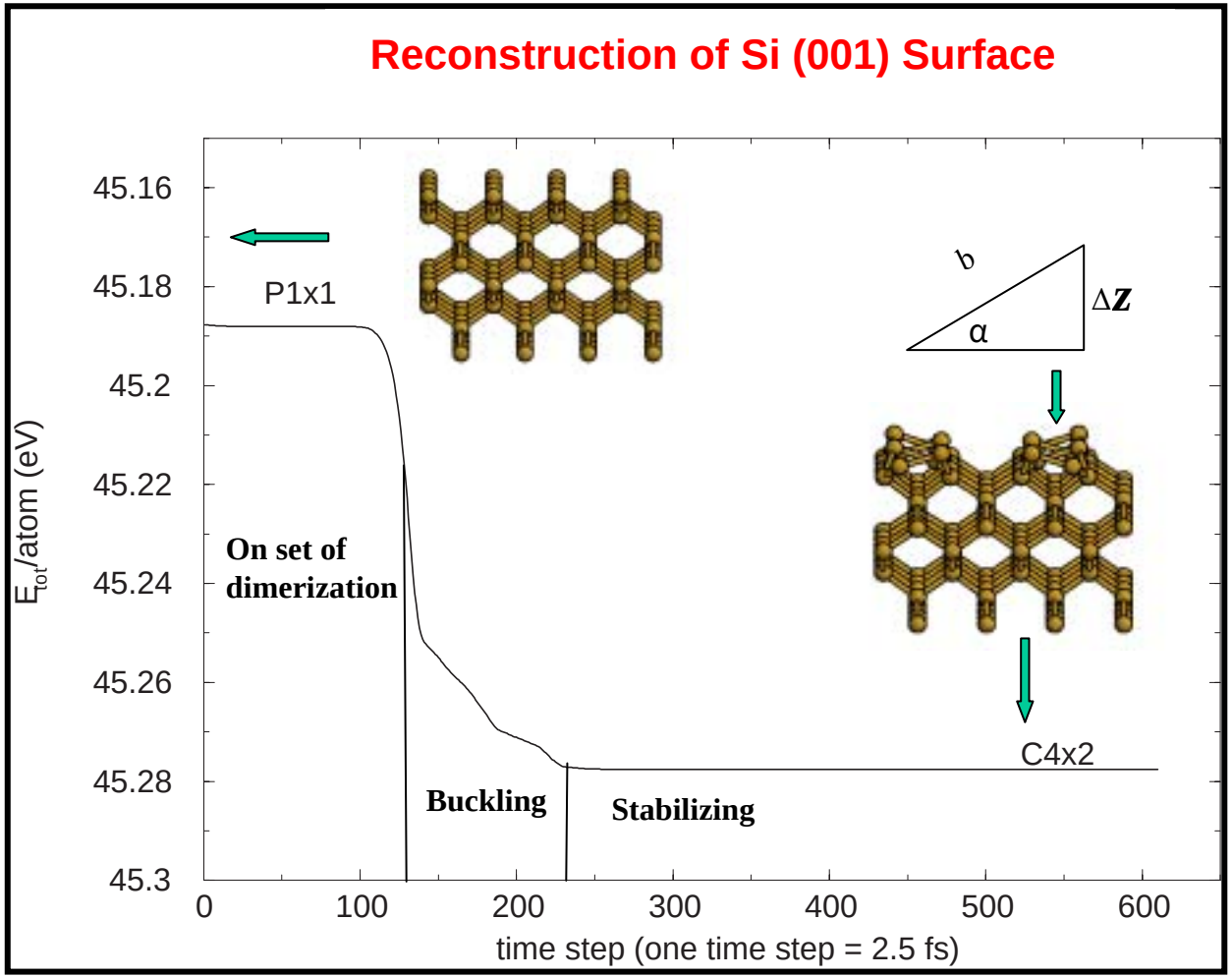
- Two factors that play key roles in determining a stable configuration of a Si cluster: 1) the saturation of the dangling bonds of surface atoms, and 2) the tendency to maintain the coordination number for Si atoms close to 4. The interplay of these factors will lead to a distorted surface for a stable Si cluster.
- The SCED-LCAO Hamiltonian drives the Si_{71} to a compact network in a more oblate structure.
- The pair-distribution function shows almost the same form as the one from DFT: a very sharp first peak followed by a broader second peak, a typical feature of distorted cluster structure, indicating that the SCED-LCAO-MD can simulate the complicate situation of the surface distortion.

Morphology of Silicon <001> nanowires





2-Dimensional System

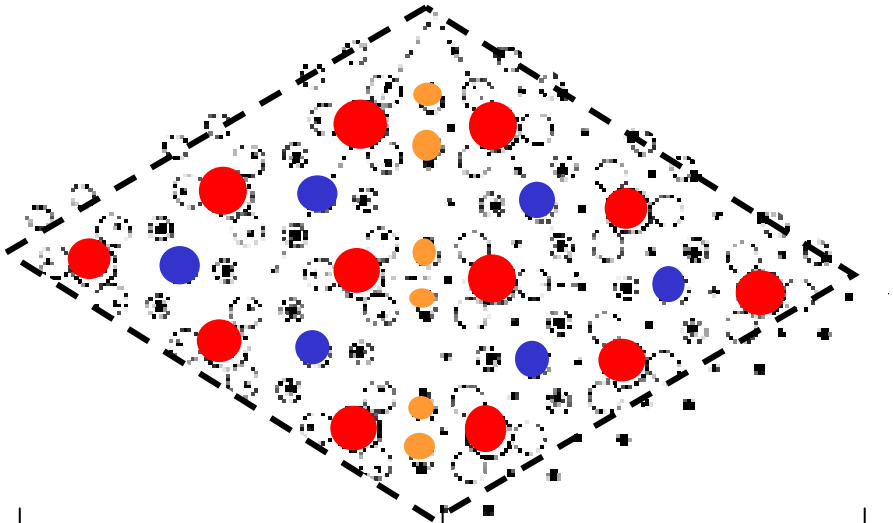


Properties	SCED-LCAO	DFT-LDA[a]	Experiment[b]
ΔE/dimer	1.18	1.39	
b	2.47	2.29	2.45 ± 0.1[b]
Δz	0.69	0.69	
α	16.19	17.5	

a. J.E. Northrup, Phys. Rev. B47, 10032 (1993).
b. Z. Zhu, N. Shima, and M. Tsukada, Phys. Rev B40, 11868 (1989).

Mapping the Energy Landscape of a Si monomer adsorbed on the reconstructed Si(111)-(7x7) Surface

Top view:



adatoms

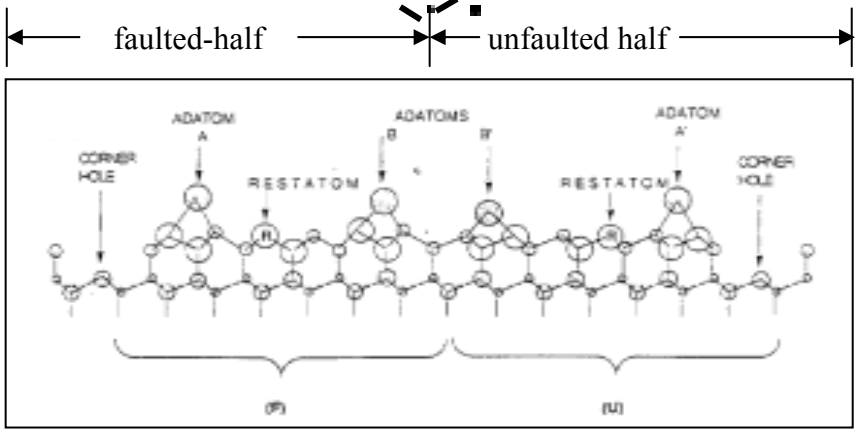
first layer atoms (rest atoms)

second layer atoms (dimers)

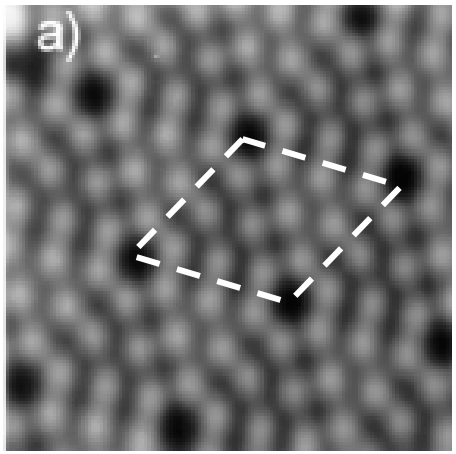
third layer atoms

fourth layer atoms

Side view:



STM image of the reconstructed Si(111)-7x7 surface



B. C. Stipe et al. Phys. Rev. Lett. 79, 4397 (1997)

Si(111)-(7x7) dimer-adatom-stacking-fault (DAS)-reconstructed surface: The (7x7) unit cell is indicated by the dashed lines, and the irreducible region is enclosed by the dotted lines.

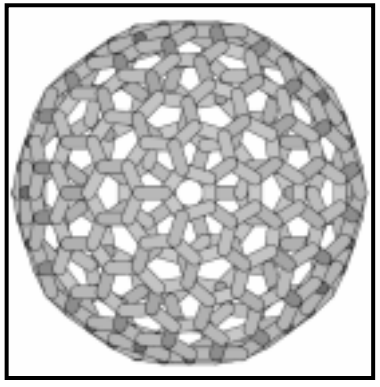
Applications of the SCED/LCAO Hamiltonian

— Predicting structures and properties of silicon/carbon-based nanostructures —

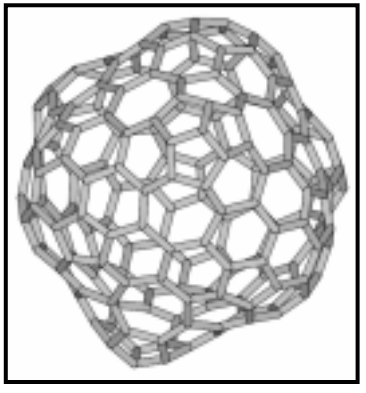
- The totality of carbon clusters
- Silicon Nanowires from a few to ~15 nm
- Silicon carbide clusters
- Silicon carbide nanowires
- Initial stage of growth of carbon single-wall nanotubes

Families of carbon clusters

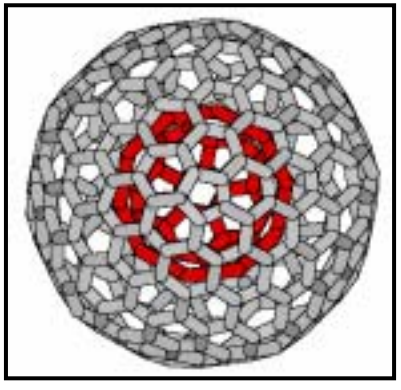
Fullerenes (sp^2)



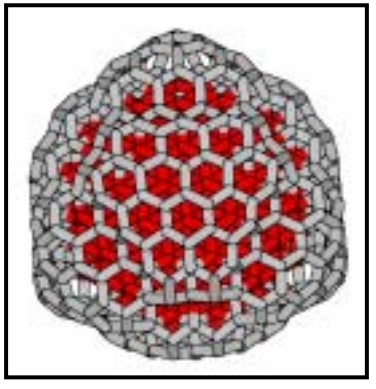
Cages (sp^2)



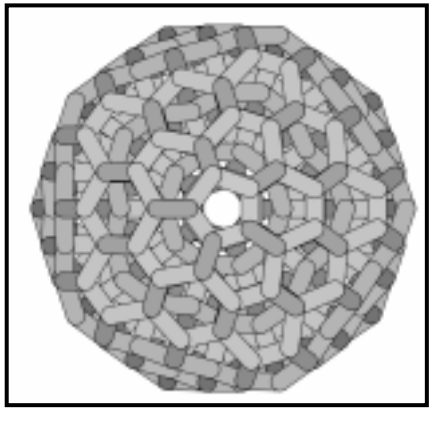
Onions (sp^2)

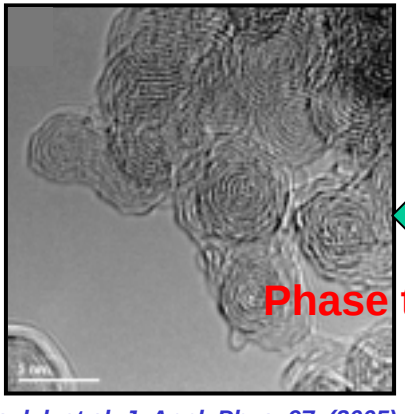


bucky-diamonds (sp^2/sp^3)

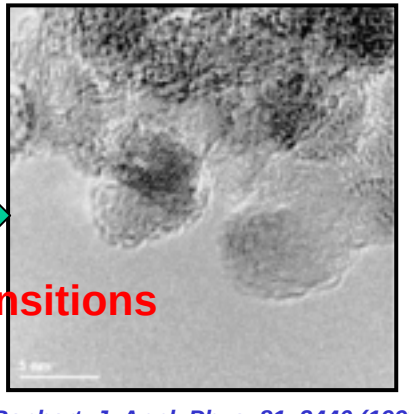


Icosahedrons (sp^2/sp^3)



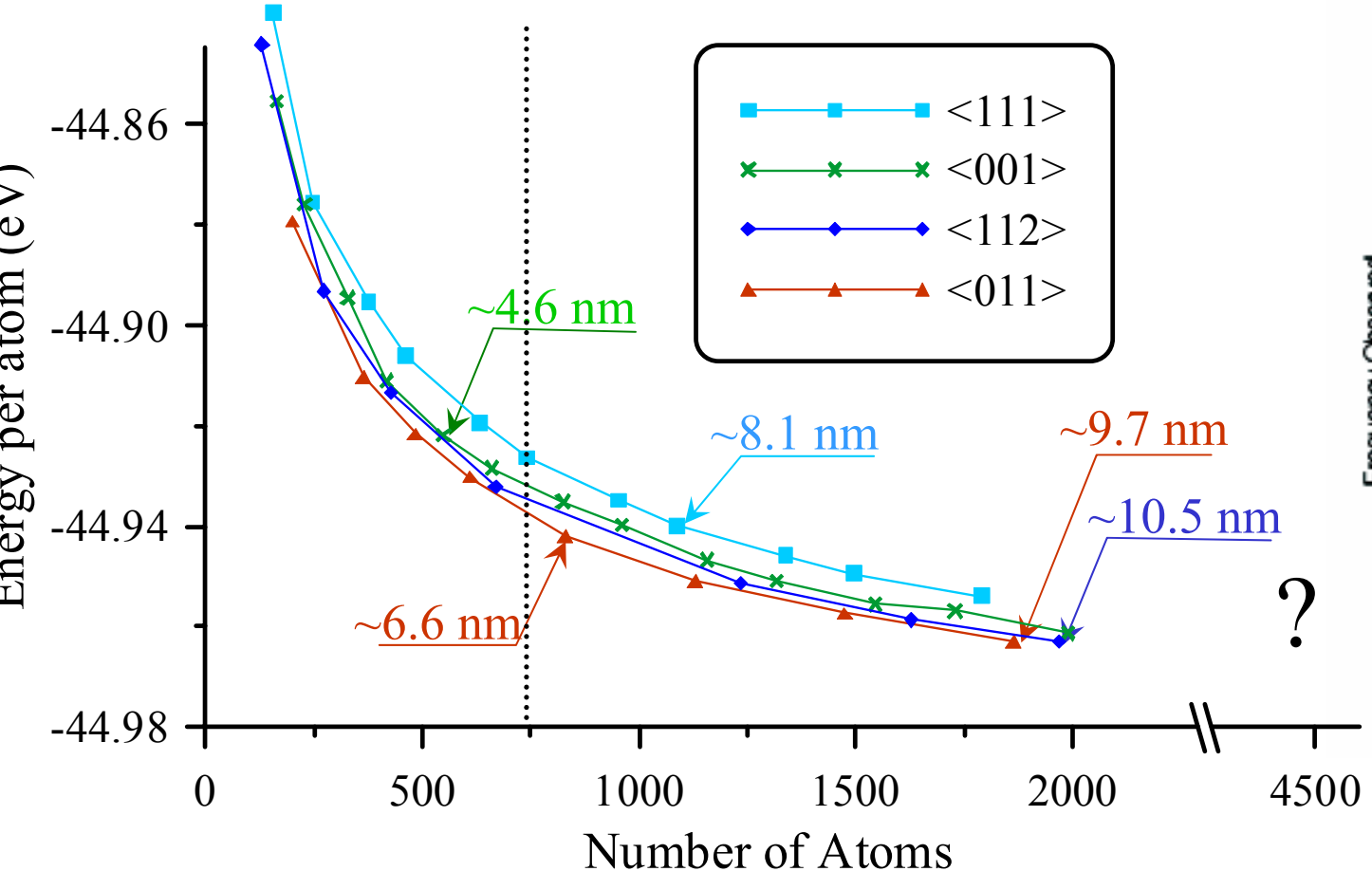


Phase transitions

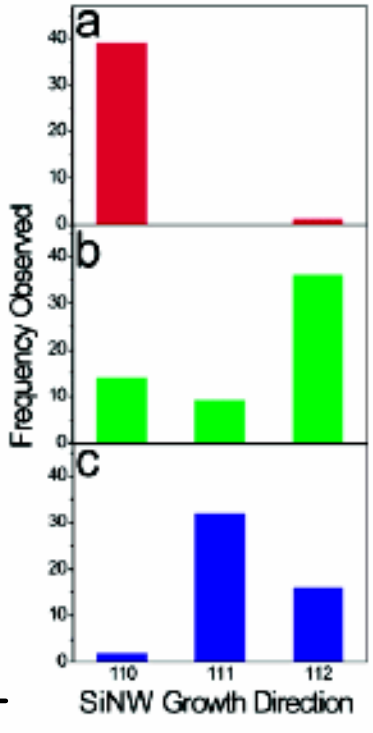


O. O. Myhaylyk et al. J. Appl. Phys. 97, (2005); F. Banhart, J. Appl. Phys. 81, 3440 (1997)

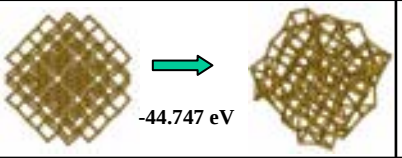
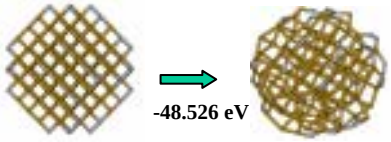
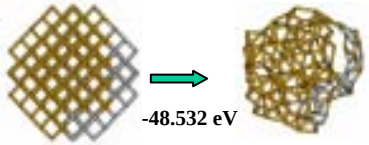
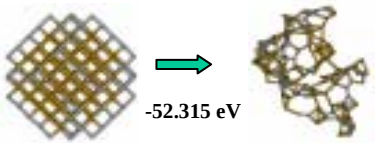
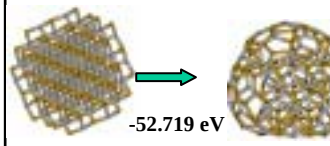
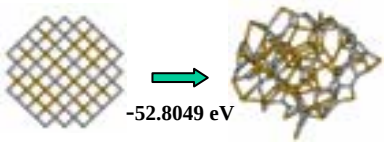
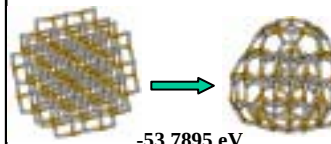
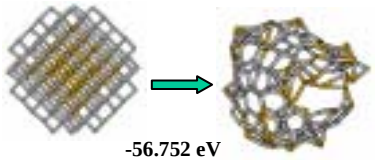
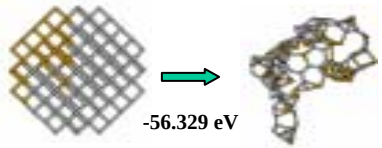
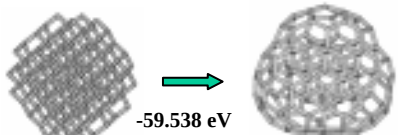
Stability of the nanowires



Wu et al, Nano Lett, **4**, 433, (2004)

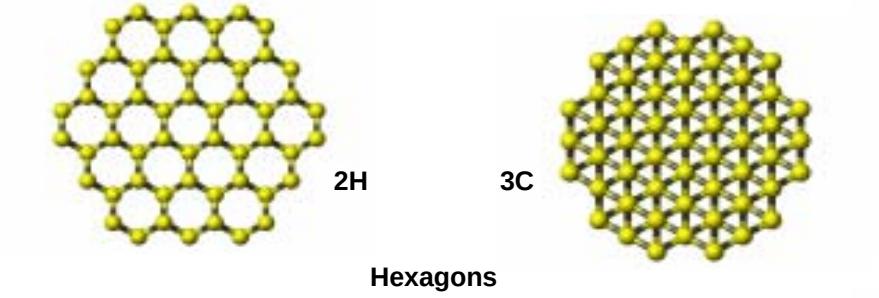


Stabilities of Si_nC_m clusters constructed from a tetrahedral network with various configurations (n+m=147)

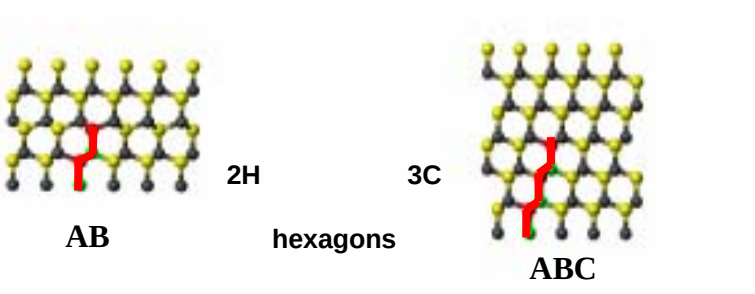
composition	Si_n-core/C_m-shell	C_m-core/Si_n-shell	Segregation	Cut from bulk SiC
Si_{147}				
$Si_{112}C_{35}$				
$Si_{79}C_{68}$				
$Si_{73}C_{74}$				
$Si_{68}C_{79}$				
$Si_{35}C_{112}$				
C_{147}				

Morphology and stability of SiC NWs

Initial configurations of hexagonal SiC NWs



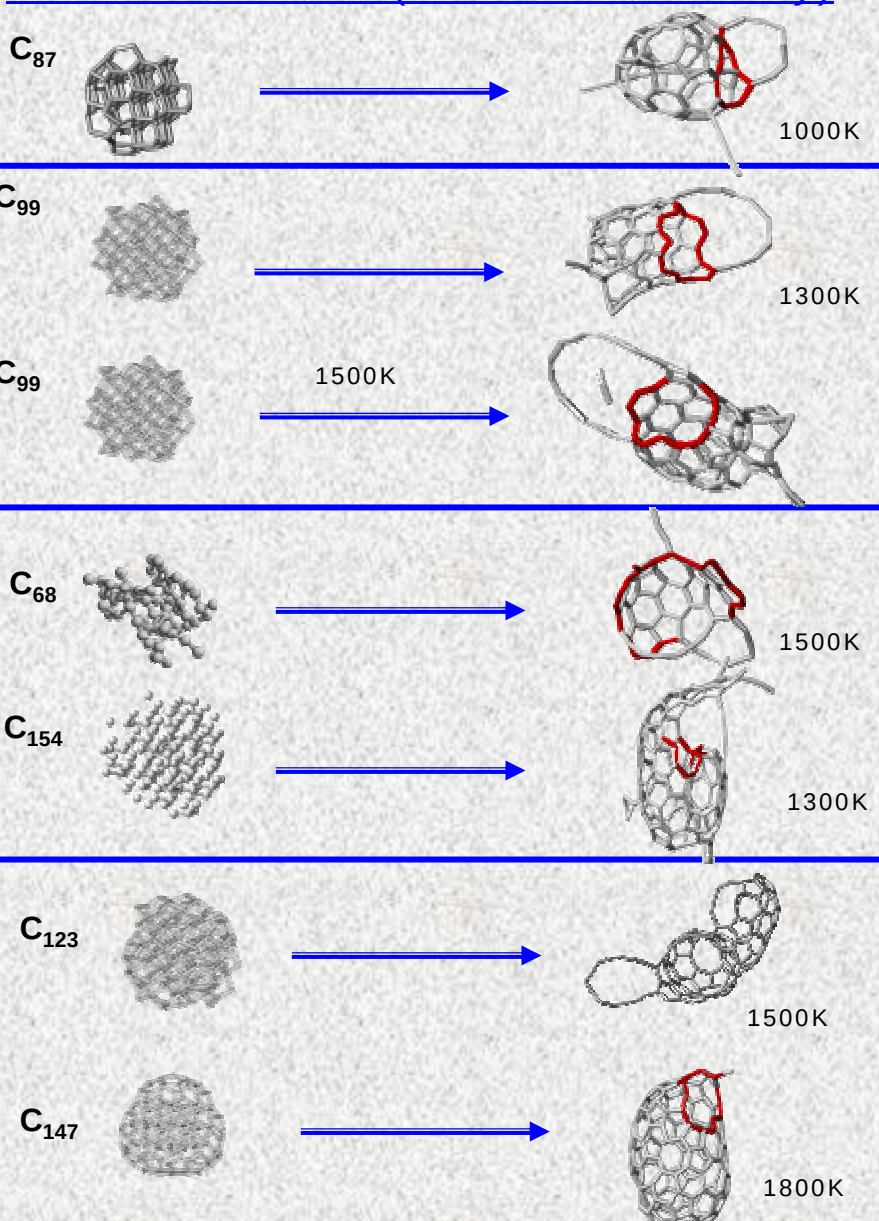
Cross-Sections of SiC NWs



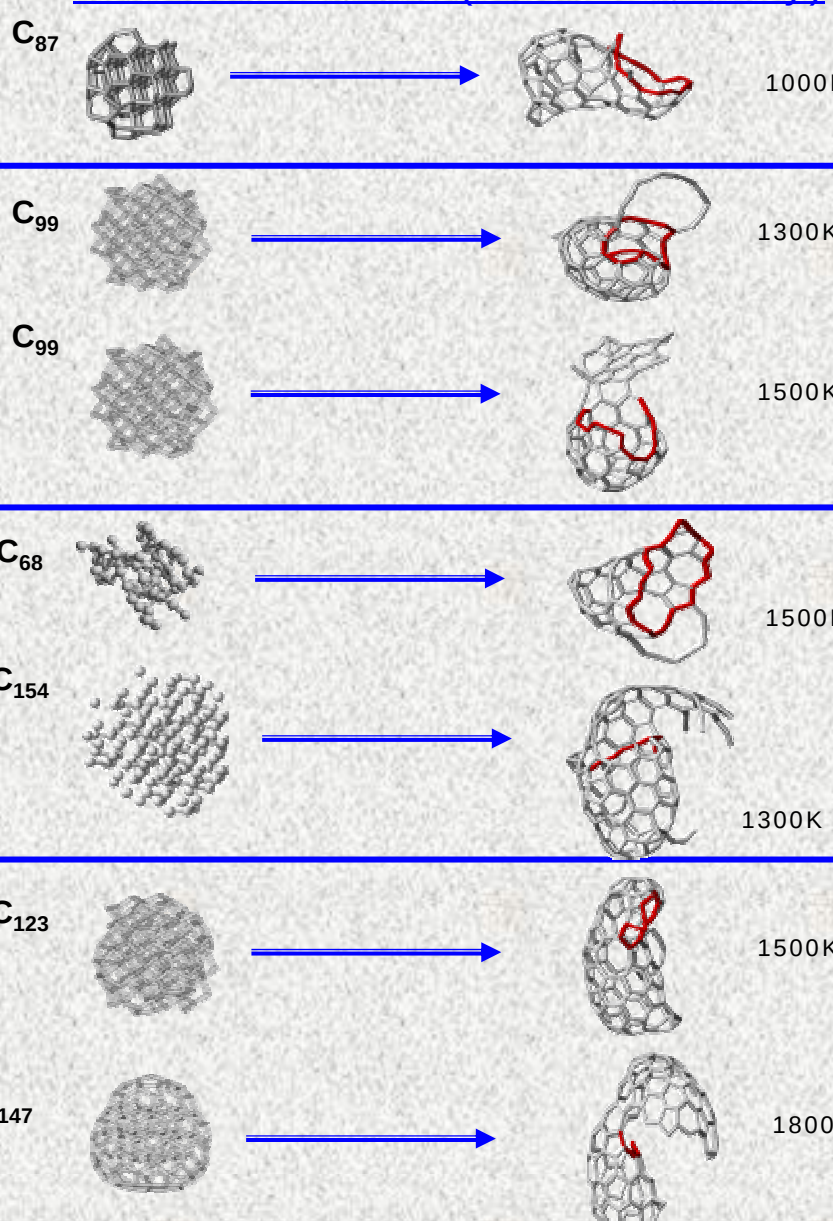
Side-Views of SiC NWs

Results

Jellium medium (Without boundary)



Jellium medium (With boundary)



Relative Stabilities of Silicon Nanowires of Different Orientations

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Motivation

➢ Si Nanowires (SiNW) are a promising material for future electronics applications. FET Transistors (Morales, Lieber, Science **279**, 208 (1998)) and sensors (Cui, et al, Science **293**, 1289 (2001)) have already been demonstrated.

	3-10 nm	10-20 nm	20-30 nm
Y.Wu, et al, Nanolett. **4**,433 (2004). Vapour-Liquid-Solid.	<011> - 95%, <112>	<112> - 61%, <011>, <111>	<111> - 34%, <112>
I.D.Holms, et al, Science **287**,1471 (2000). Solution-Phase Synthetic Method.	<011> <001>		
G.W.Zhou, et al, APL **73**, 677 (1998). Las. Abl.		<112>	
X. Lu et al, Nanolett. **3**, 93 (2003). Supercritical Fluid-Liquid-Solid.	<011>		
S. Ge et al, Adv. Mater. **17**, 56 (2005). VLS.			<111>

➢ There are theoretical works on the electronic structure of SiNWs (Zhao, et al, PRL, 92, 236805, (2004) and ref. therein). Structure and morphology – limited (PRB, **57**, 11923 and PRL, **94**, 026208).

➢ In this work we are presenting the results of a comprehensive study of the morphology and stability of SiNWs along directions reported in the experimental papers. Calculations are performed in *ab initio* (VASP) and tight-binding (SCED-LCAO) frameworks.

Computational procedure

- Determine the most favorable surface reconstructions and shape for small size SiNWs in the *<001>*, *<011>*, *<111>*, and *<112>* directions using *ab initio* calculations (we consider non-passivated SiNWs in order to be able to compare total energies).

- The only requirement for the reconstruction – no surface atoms with more then one dangling bond.

- Hydrogen or oxide passivation, kinetic effects (exp. T~500^{o} C), effects of gold-silicon interface (for the VLS growth) and such are not taken into account.

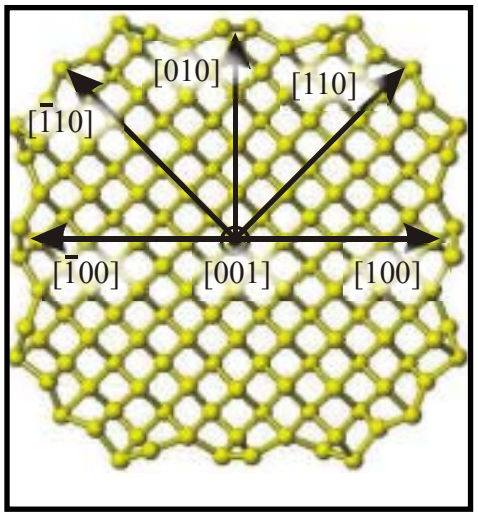
- VASP parameters: GGA (PW91), E_{cutoff}=200 eV, k-point mesh (1×1×10) for the smaller, and (1×1×6) for larger (>500 atoms in the system).

- Repeat these calculations in the SCED-LCAO framework, making sure that transferability of the parameters is not a problem.

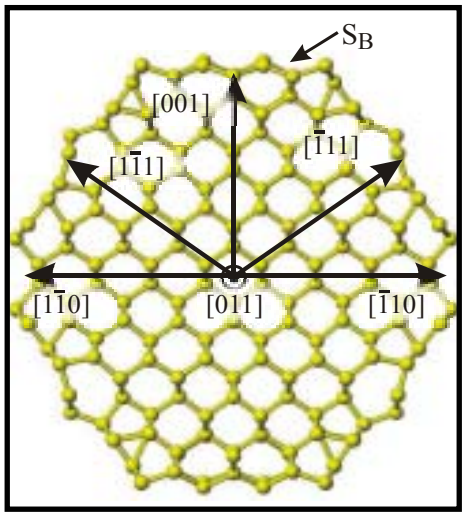
- Expand the size of the system to the 10 nm level and beyond utilizing 'Order-N' method on top of the SCED-LCAO semi-empirical Hamiltonian.

Relaxed Structures of SiNWs oriented along different directions

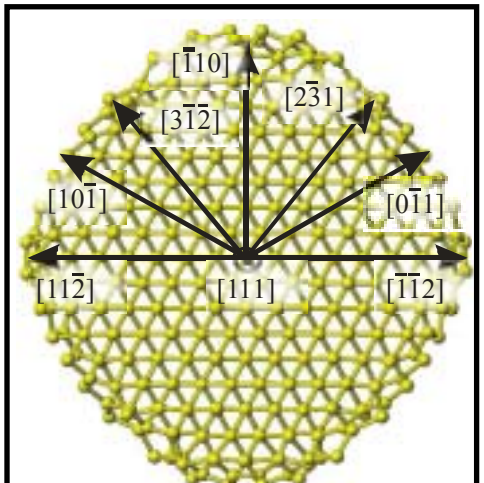
<001>



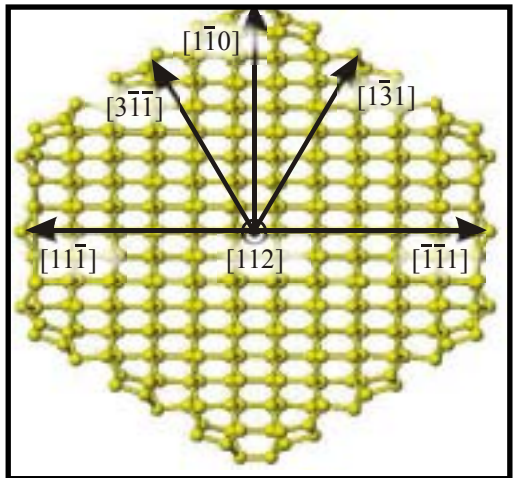
<011>

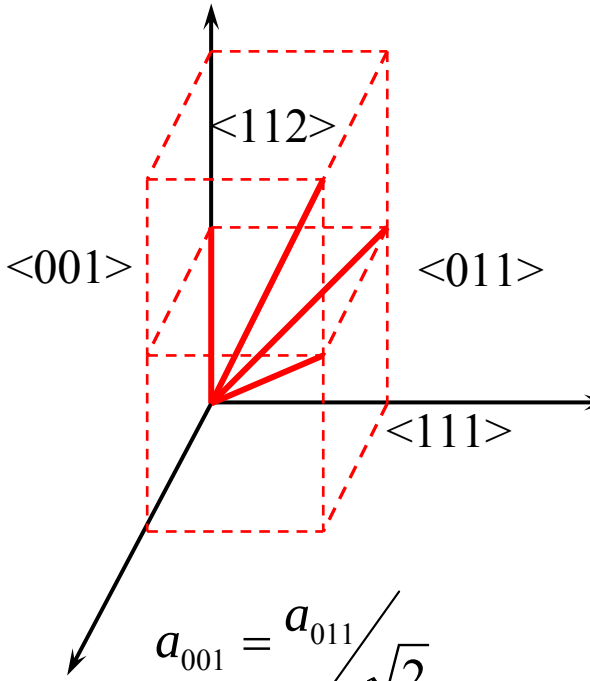


<111>



<112>





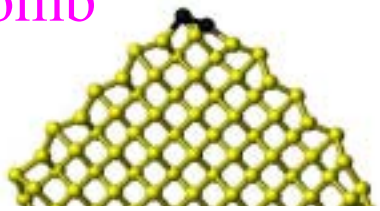
$$a_{001} = a_{011}/\sqrt{2}$$

$$a_{001} = a_{111}/\sqrt{3}$$

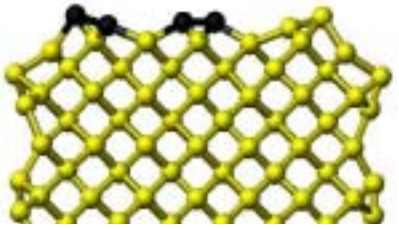
$$a_{001} = a_{112}/\sqrt{6}$$

Morphology of <001> nanowires

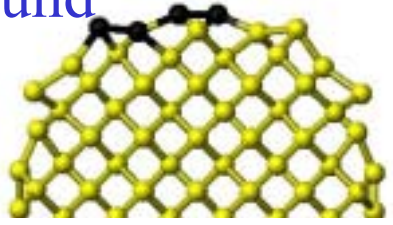
"rhomb"



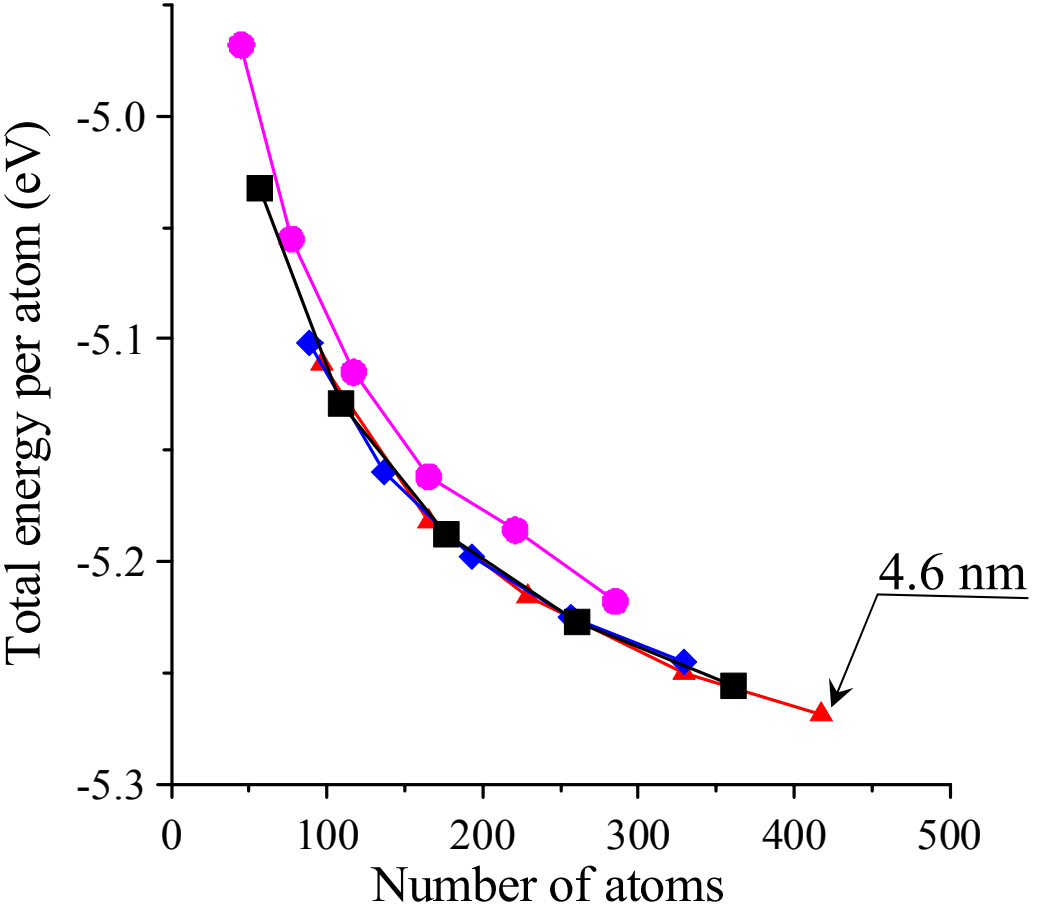
"square"



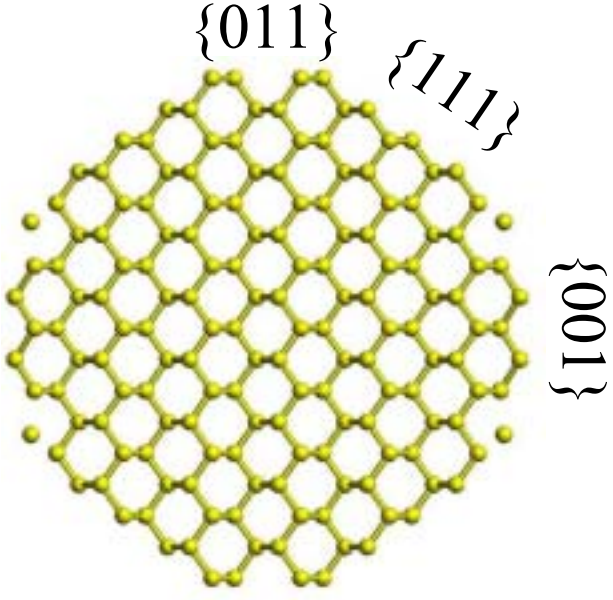
"round"



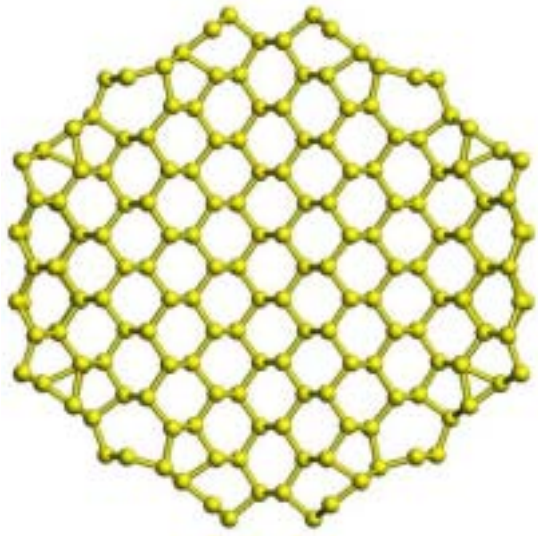
"poly"



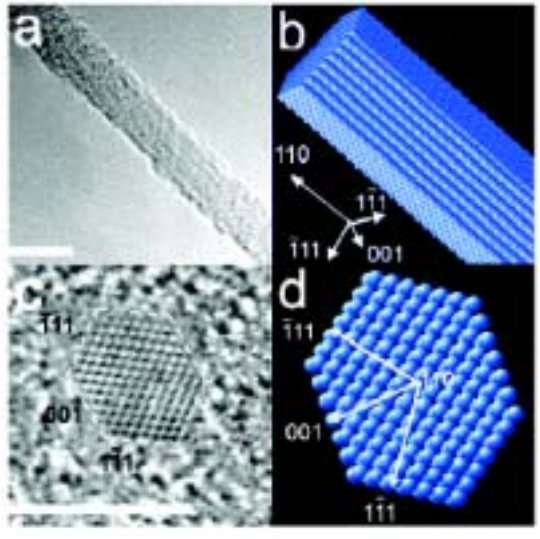
Morphology of <011> nanowires



As cut



Relaxed

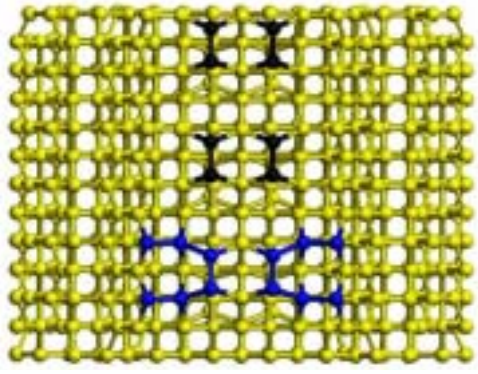


Experiment

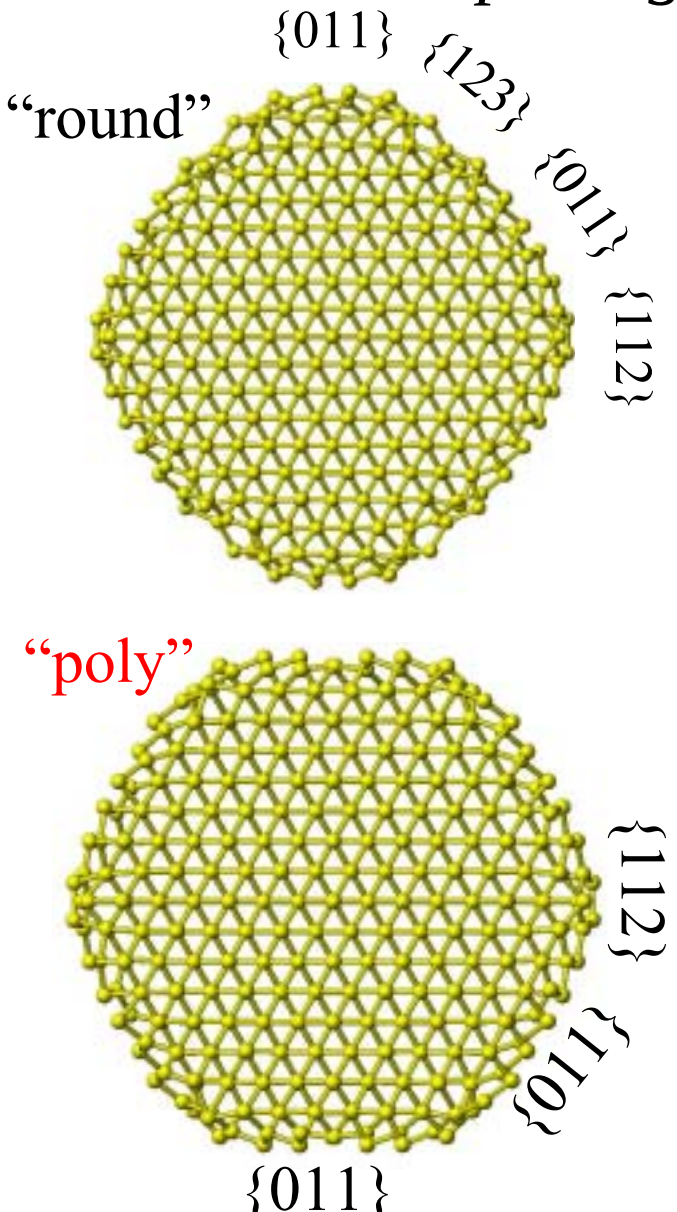
(Wu et al, Nano Lett, **4**, 433, 2004)

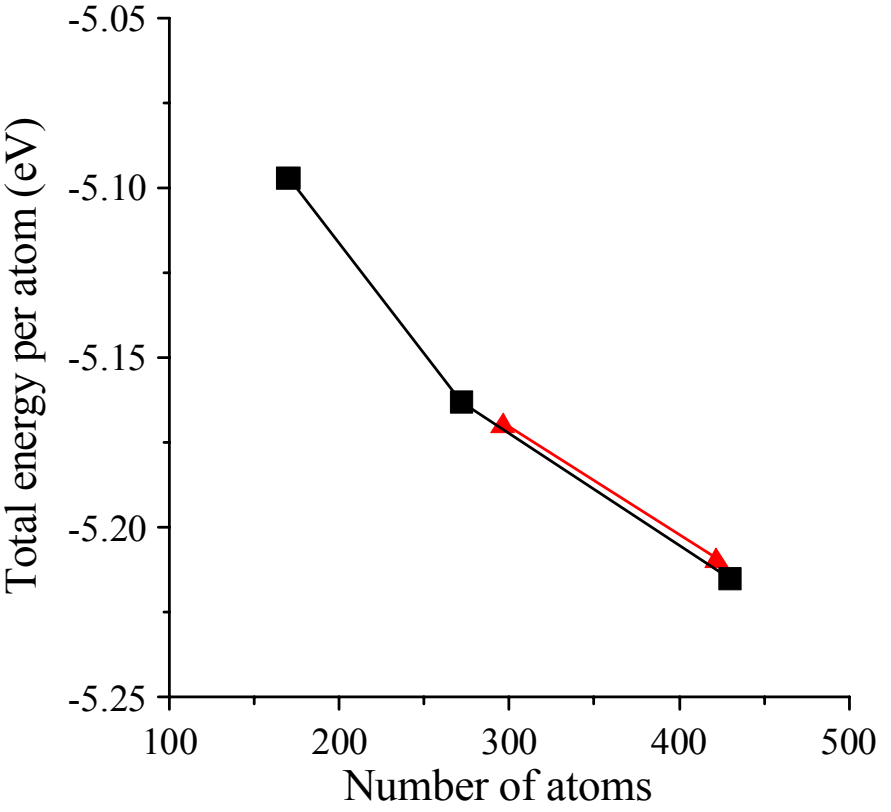
Latteral view:

Illustration of the S_B step

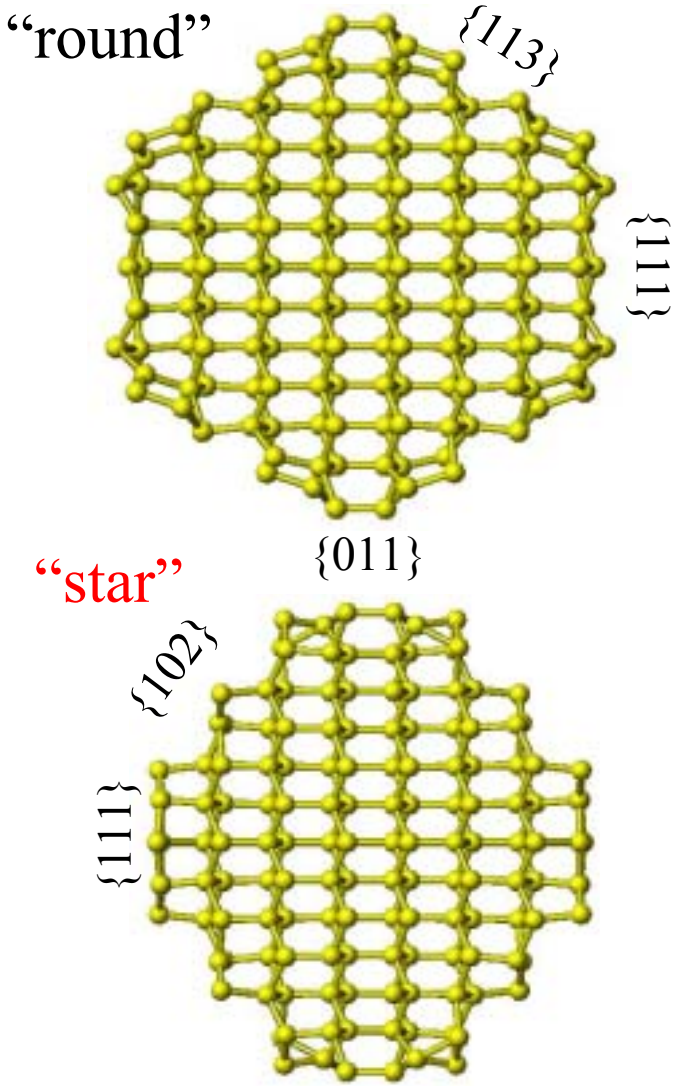


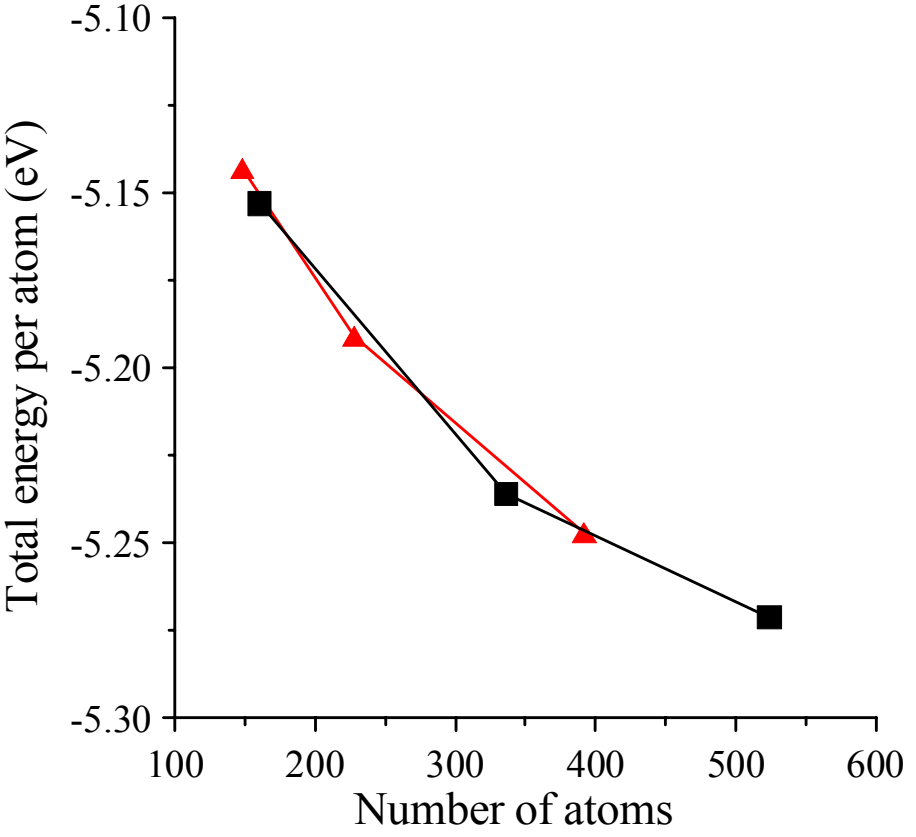
Morphology of <111> nanowires



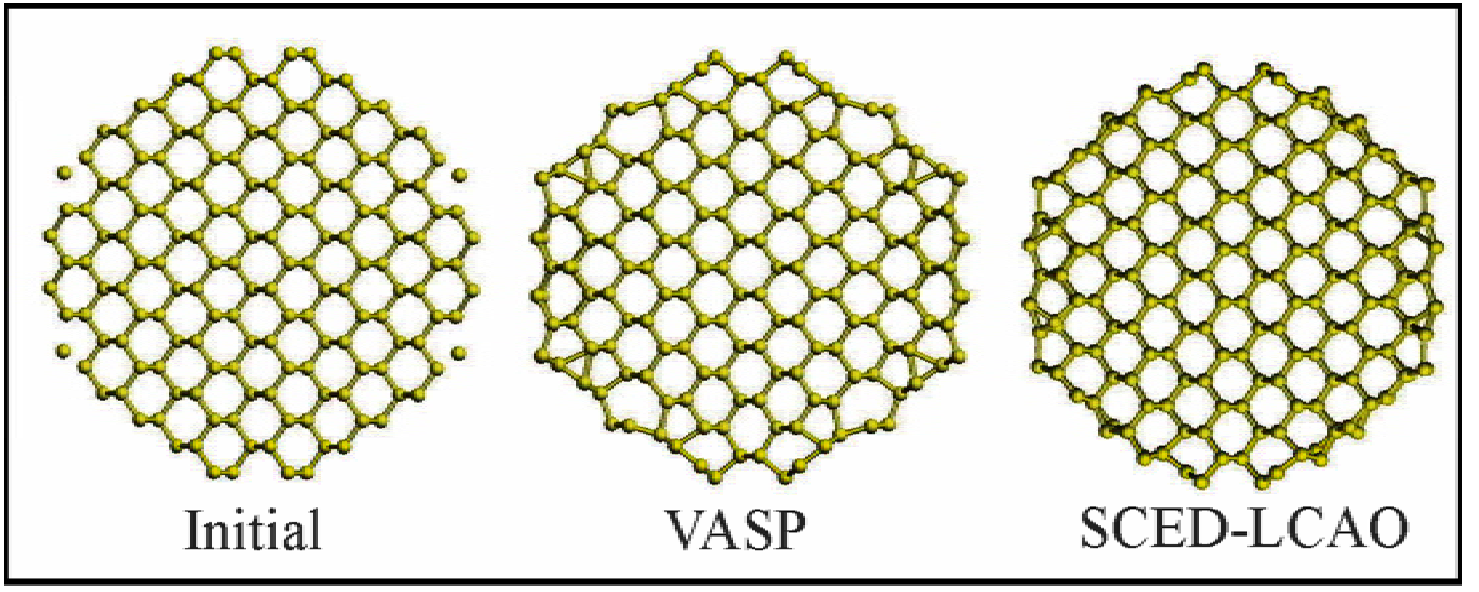


Morphology of <112> nanowires



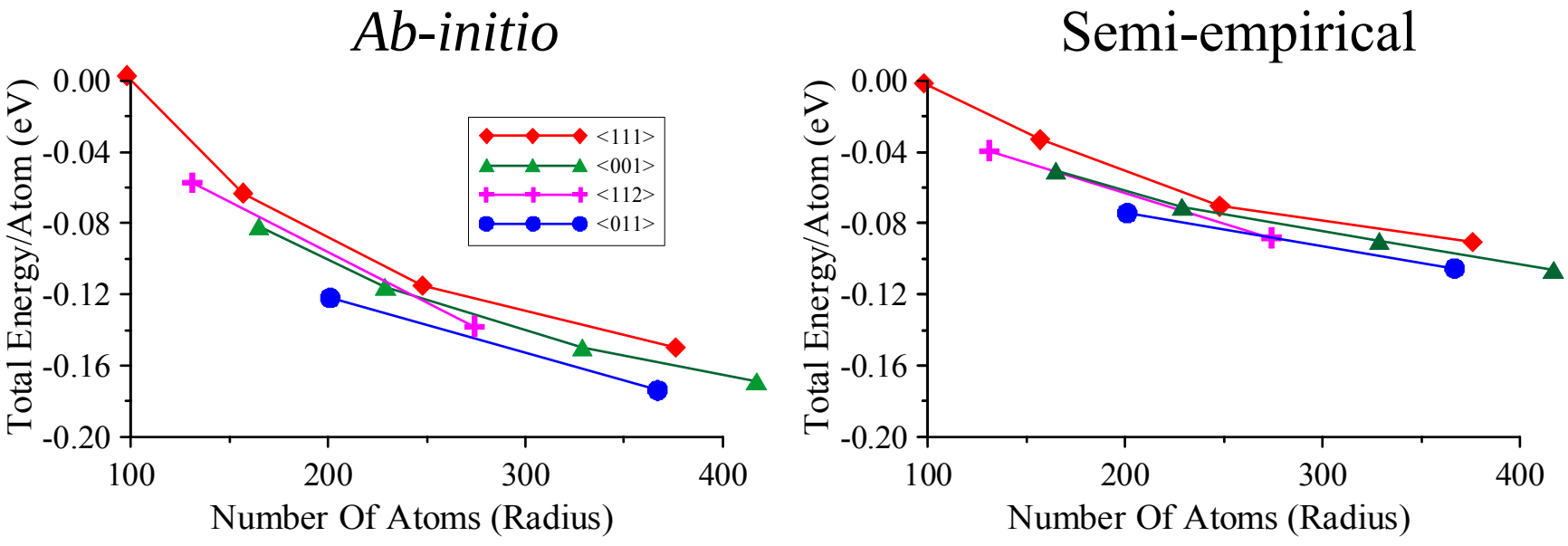


Surface Morphologies



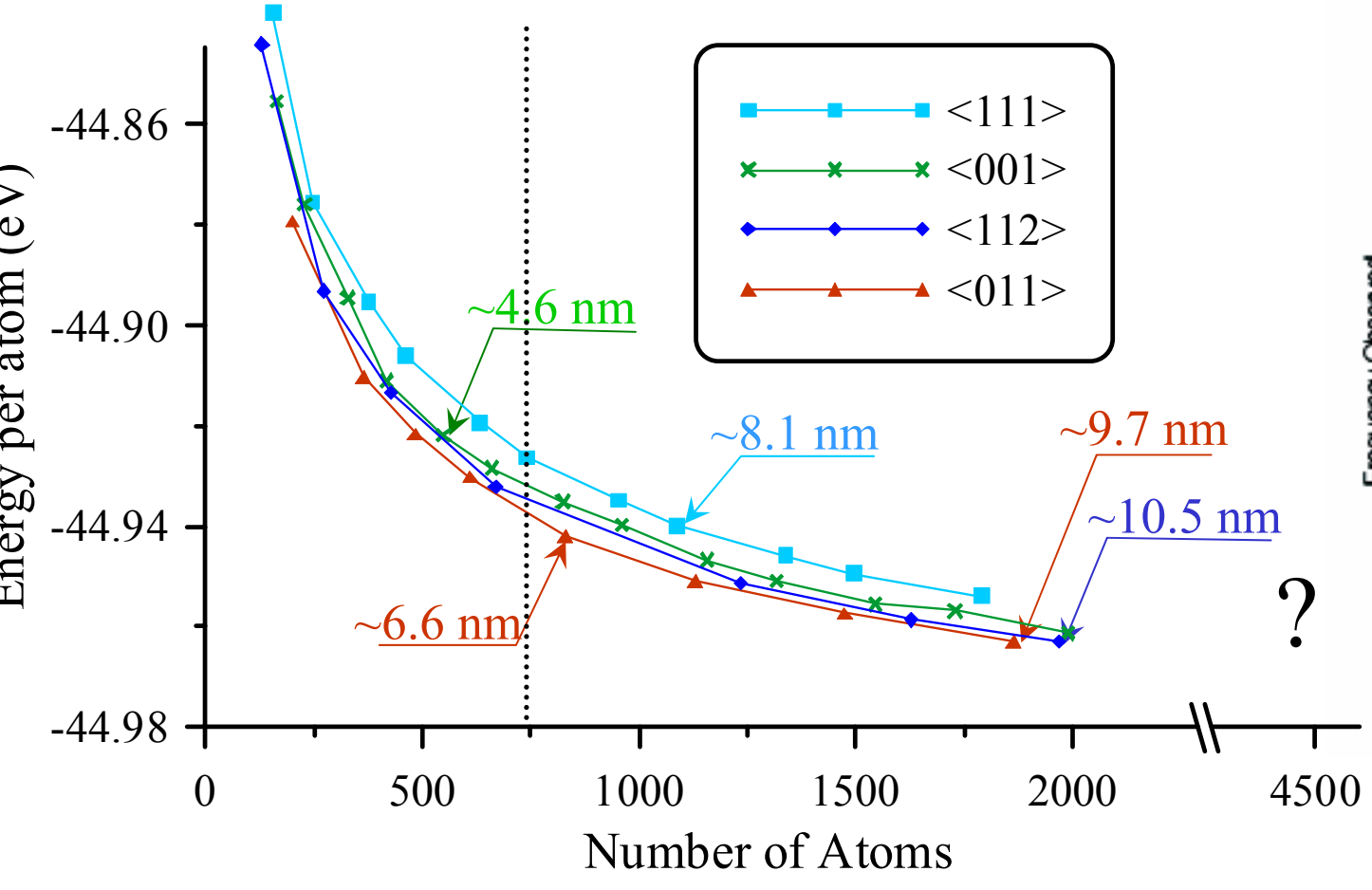
A comparison of the structures obtained by ab-initio and SCED-LCAO methods for SiNWs oriented in <011> direction (d ~ 4.7 nm)

Comparison of the USPP and SCED-LCAO results

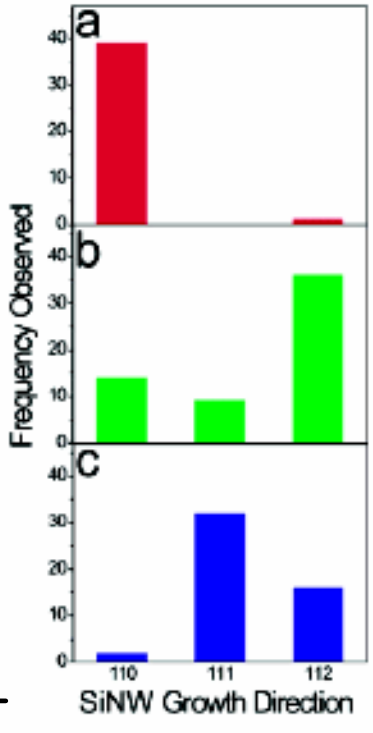


- Great qualitative agreement between two methods.
- The energetic ordering of the nanowires along the same direction but different morphologies is also correct in SCED-LCAO.
- Equilibrium lattice parameter for SCED-LCAO is always within *2%* of the *ab initio* calculations.

Stability of the nanowires



Wu et al, Nano Lett, **4**, 433, (2004)

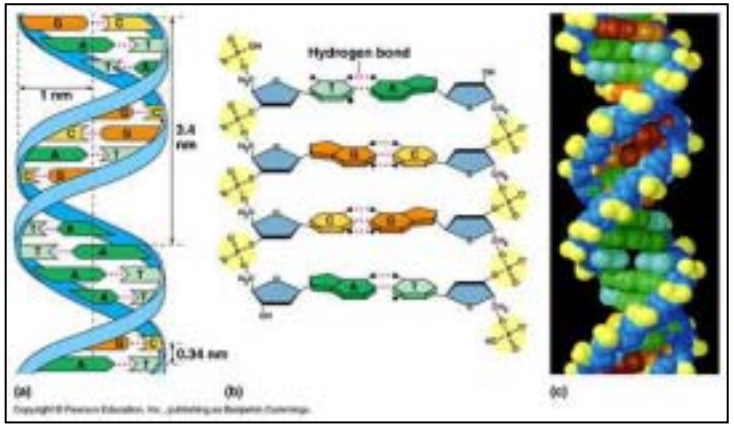


Conclusions

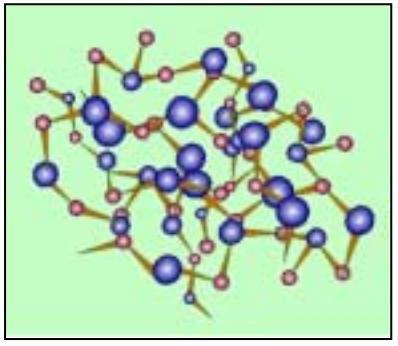
- Most energetically favored morphologies of the small (up to 3 nm) non-passivated SiNWs are determined through first-principles calculations for 4 different directions of growth.
- Very good agreement in the ordering of the energies of the different orientations and morphologies between first-principles and SCED-LCAO tight-binding approaches.
- In the < 10 nm range of the nanowire sizes we predict <011> direction of growth to be thermodynamically most favorable, in agreement with the experimental data.
- Future application: Extend the size of the nanowires into ~20 nm scale.
- In the SCED-LCAO framework include hydrogen passivation in order to obtain electronic structure information.

Applications for the study of biological and “soft mater” systems

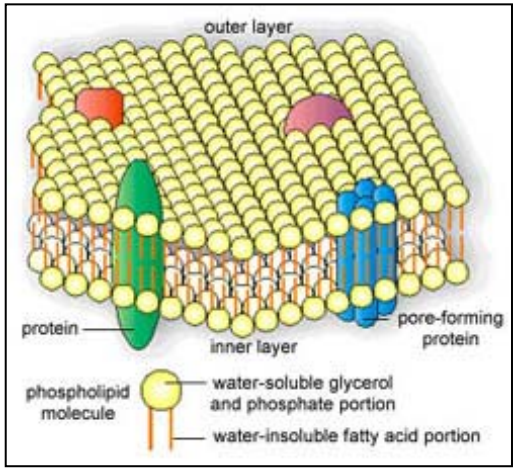
DNA



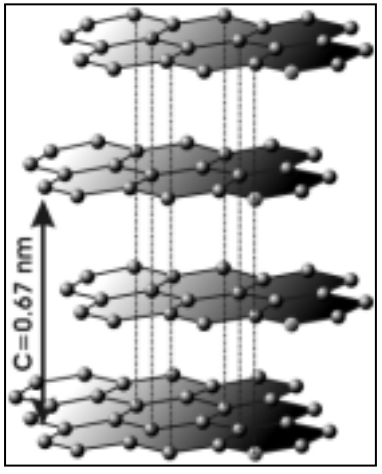
Polymer



Membrane



Graphite



Parallel Replica Dynamics (PRD) and SCED/LCAO-PRD:

A scheme to extend the accessible Simulation time for quantum mechanics-based molecular dynamics simulations

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