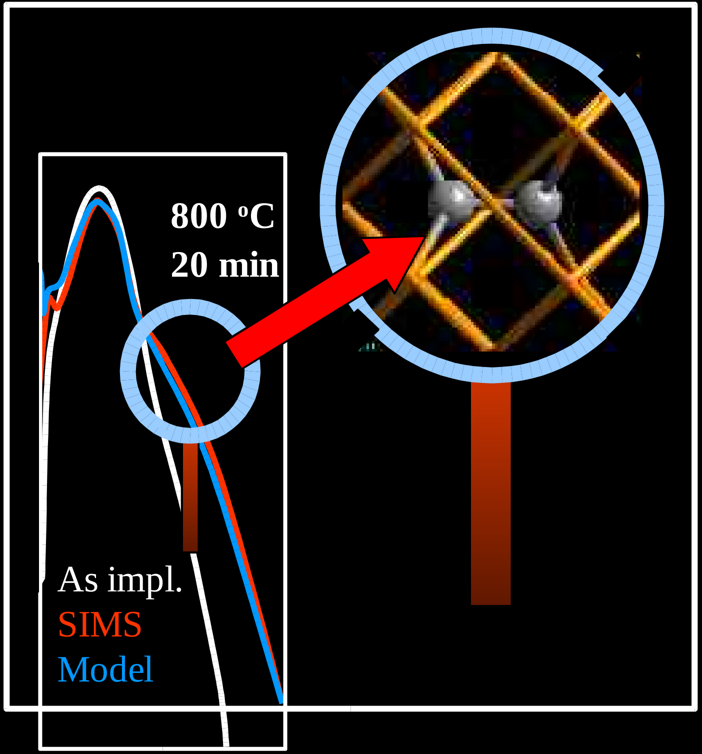
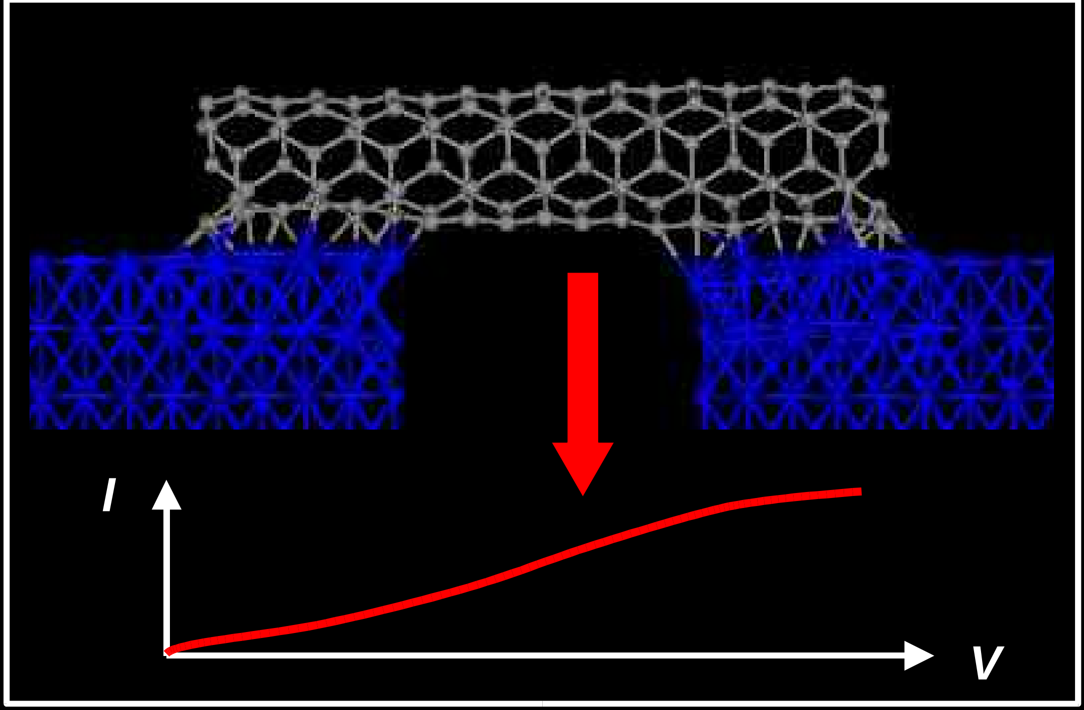
Ab-initio Assisted Process and Device Simulation for Nanoelectronic Devices





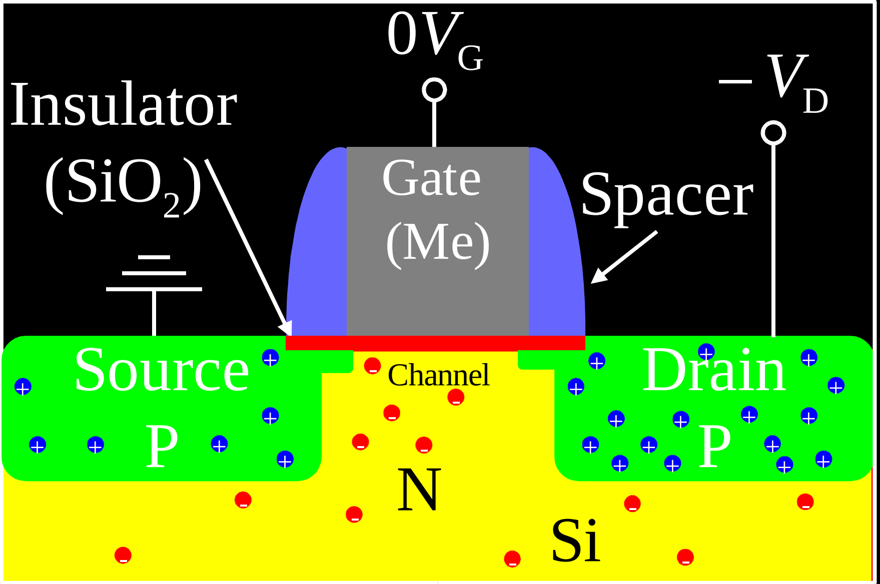
Wolfgang Windl

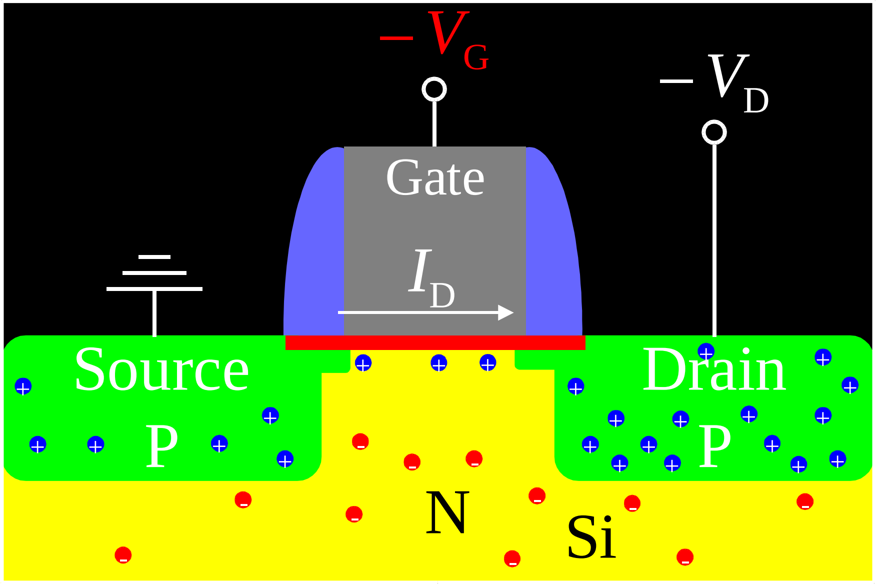
MSE, The Ohio State University, Columbus, OH, USA

Computational Materials Science and Engineering

Semiconductor Devices – MOSFET

Metal Oxide Semiconductor Field Effect Transistor

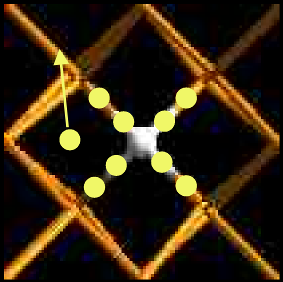


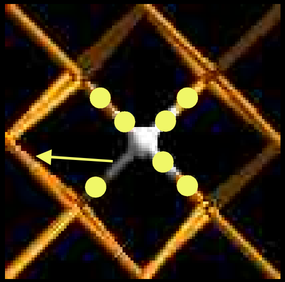


Doping:

N: e^-, e.g. As
(Donor)

P: holes, e.g. B
(Acceptor)

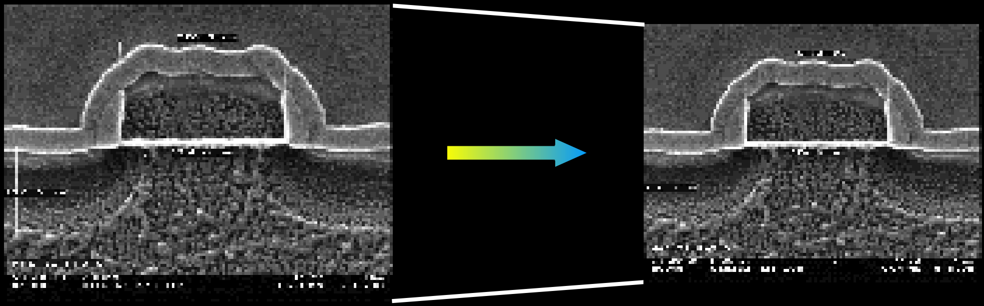




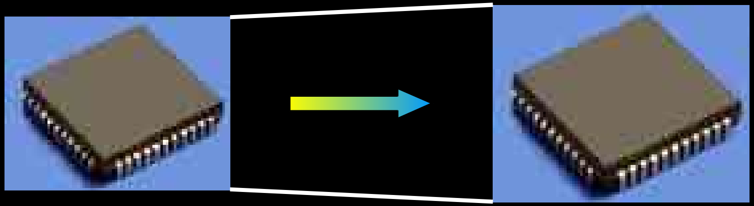
- Analog: Amplification
- Digital: Logic gates

1. Semiconductor Technology Scaling – Improving Traditional TCAD

- Feature size shrinks on average by 12% p.a.; speed ∝ size

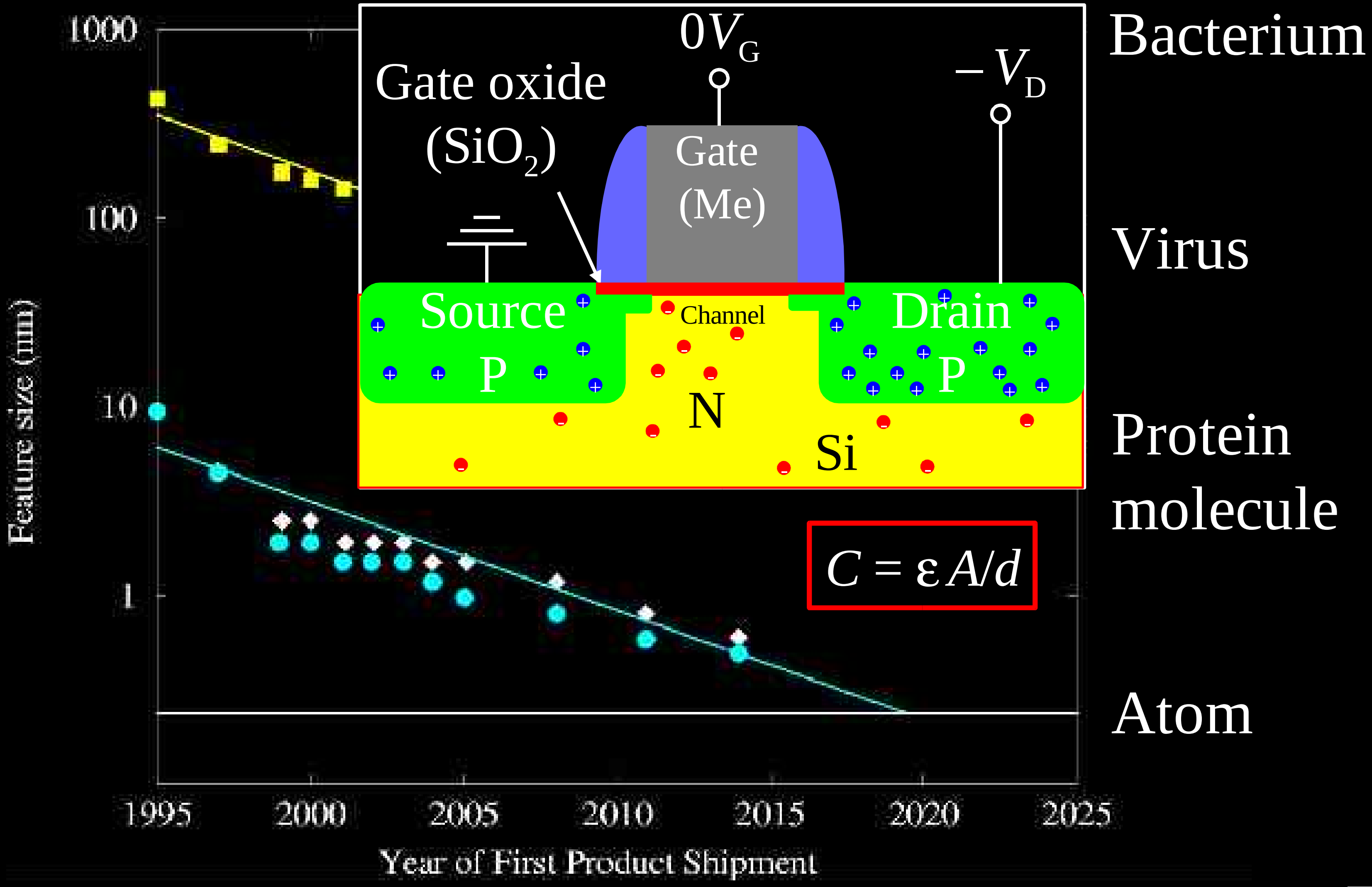


- Chip size increases on average by 2.3% p.a.



Overall performance: ↑ by ~55% p.a. or
~ doubling every 18 months ("Moore' s Law")

Semiconductor Technology Scaling – Gate Oxide



$$\boxed{C = \varepsilon A/d}$$

Role of Ab-Initio Methods on Nanoscale

1. Improving traditional (continuum) process modeling to include nanoscale effects
   - Identify relevant equations & parameters (“physics”)
   - Basis for atomistic process modeling (Monte Carlo, MD)

2. Nanoscale characterization

   = ***Combination*** of experiment & ab-initio calculations

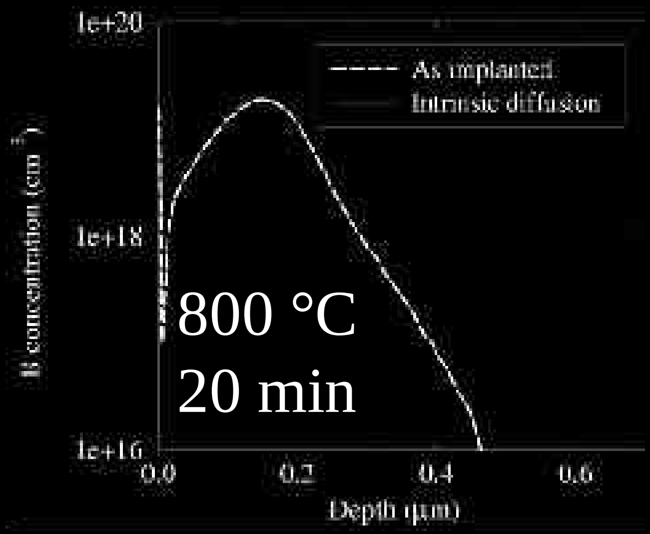
3. Atomic-level process + transport modeling

   = structure-property relationship (“ultimate goal”)

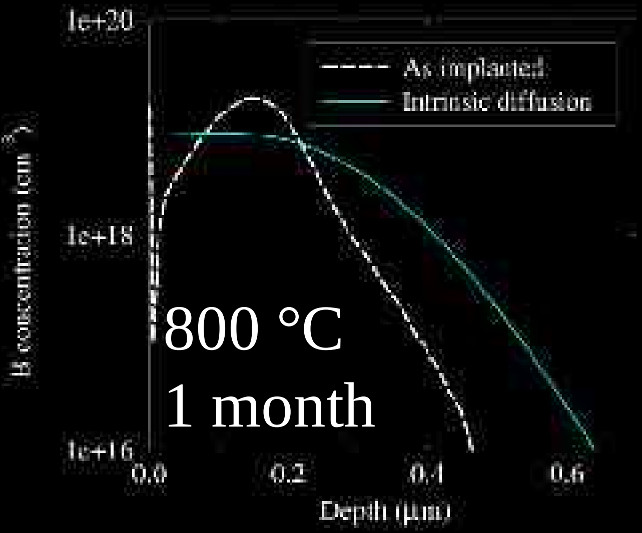
1. “Nanoscale” Problems – Traditional MOS

What you expect:

Intrinsic diffusion



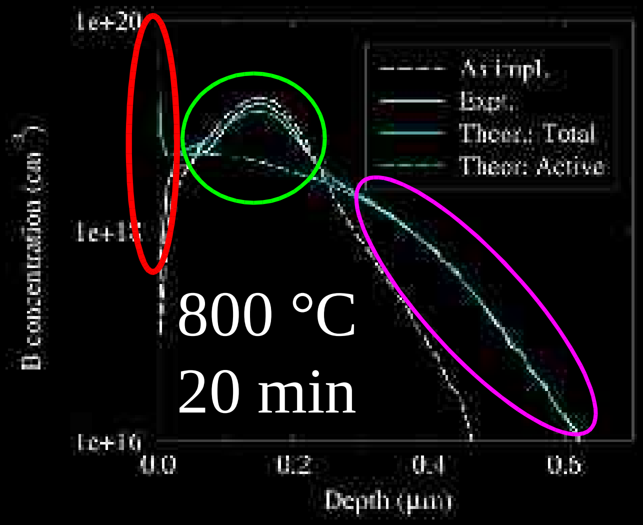
800 °C
20 min



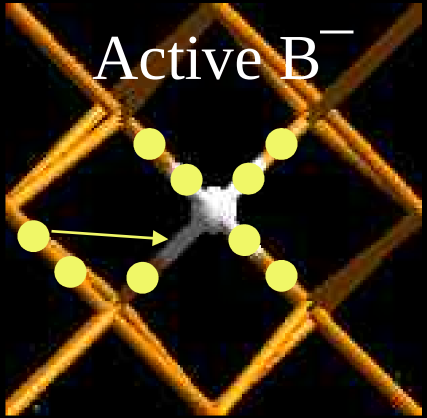
800 °C
1 month

What you get:

- fast diffusion (TED)
- immobile peak
- segregation

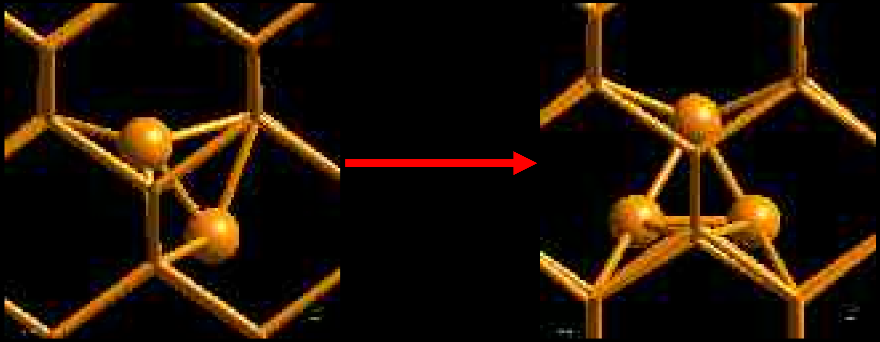


800 °C
20 min



Active B^-

Bridging the Length Scales: Ab-Initio to Continuum



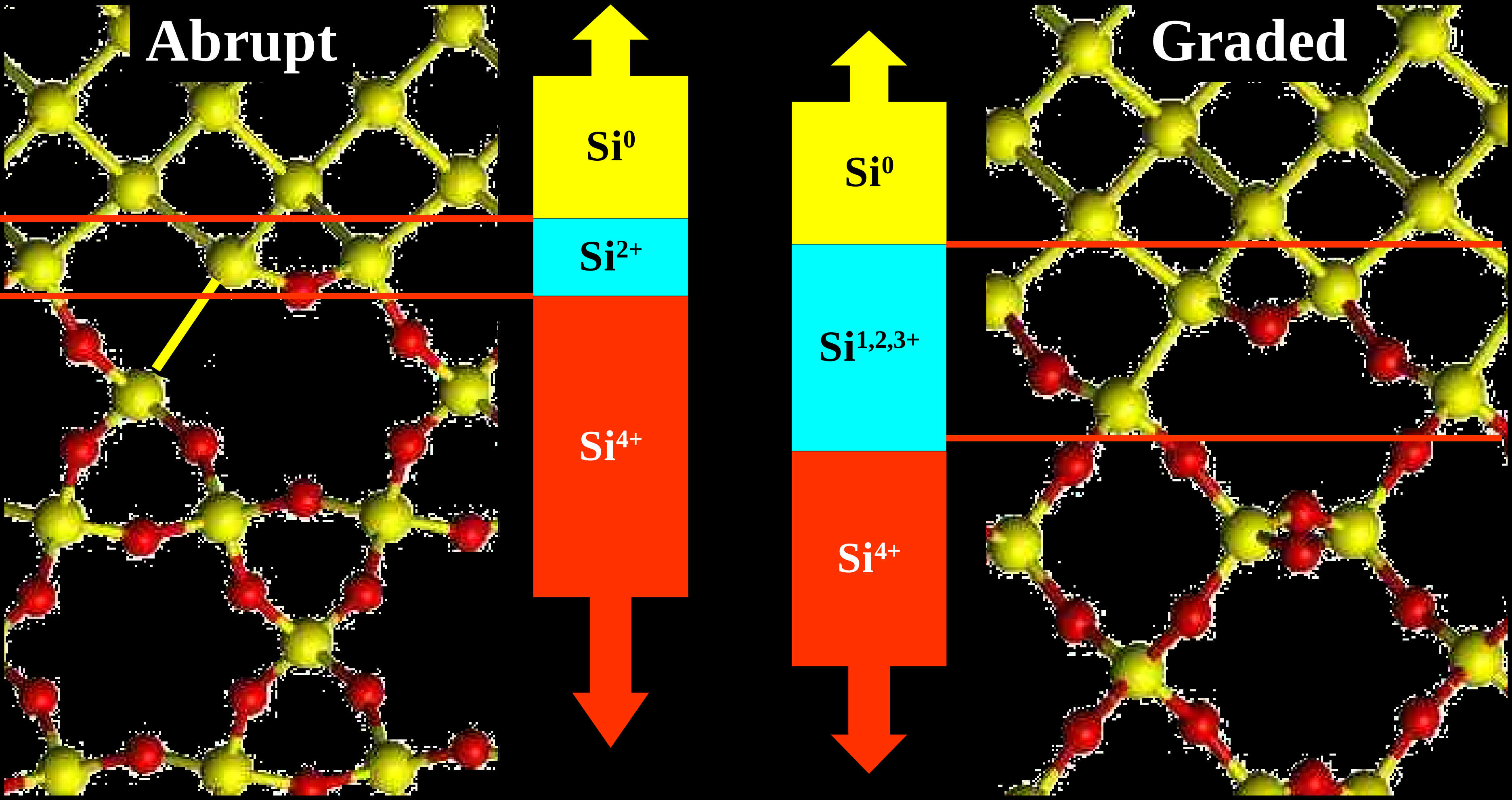
Need to calculate:

- ? Diffusion prefactors (Uberuaga *et al.*, phys. stat. sol. 02)
- ? Migration barriers (Windl *et al.*, PRL 99)
- ? Capture radii (Beardmore *et al.*, Proc. ICCN 02)
- ? Binding energies (Liu *et al.*, APL 00)

2. The Nanoscale Characterization Problem

- Traditional characterization techniques, e.g.:
  - SIMS (*average* dopant distribution)
  - TEM (interface quality; *atomic-column* information)
- Missing: “Single-atom” information
  - Exact interface (contact) structure (previous; next)
  - Atom-by-atom dopant distribution (strong V_T shifts)
- New approach: atomic-scale characterization (TEM) **plus** modeling

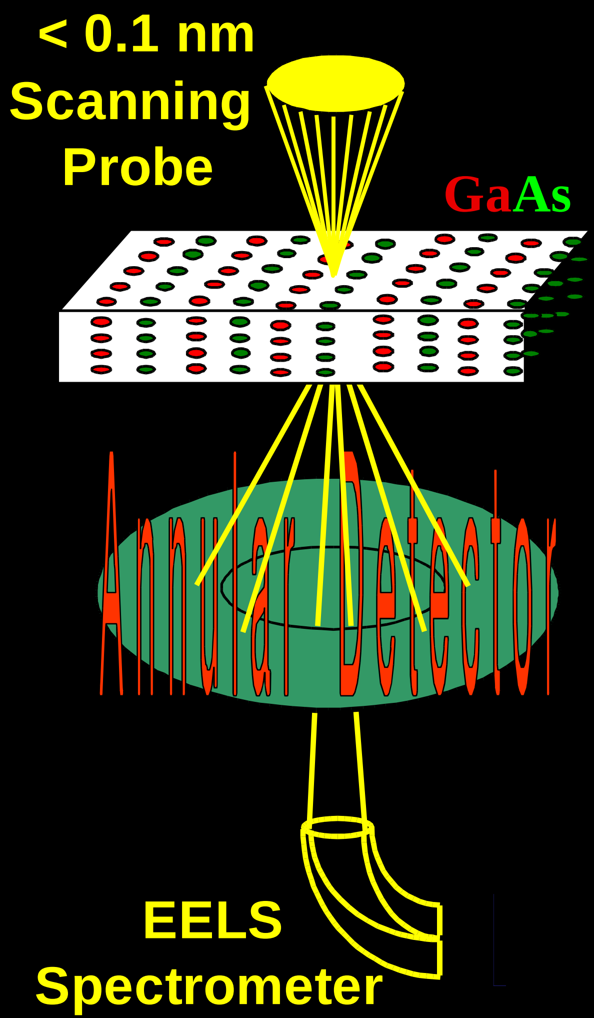
Abrupt vs. Diffuse Interface

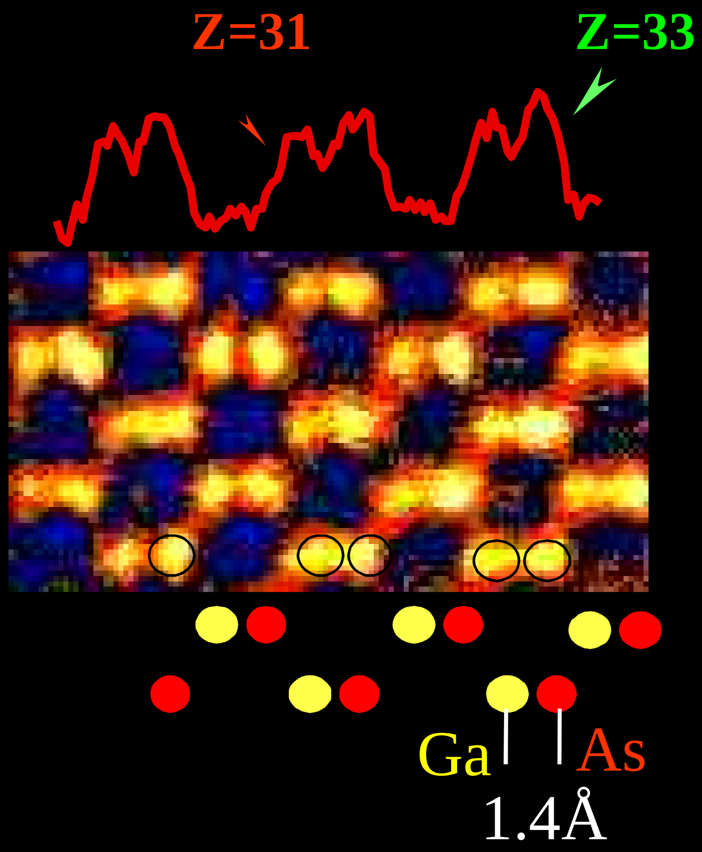


How do we know? What does it mean?

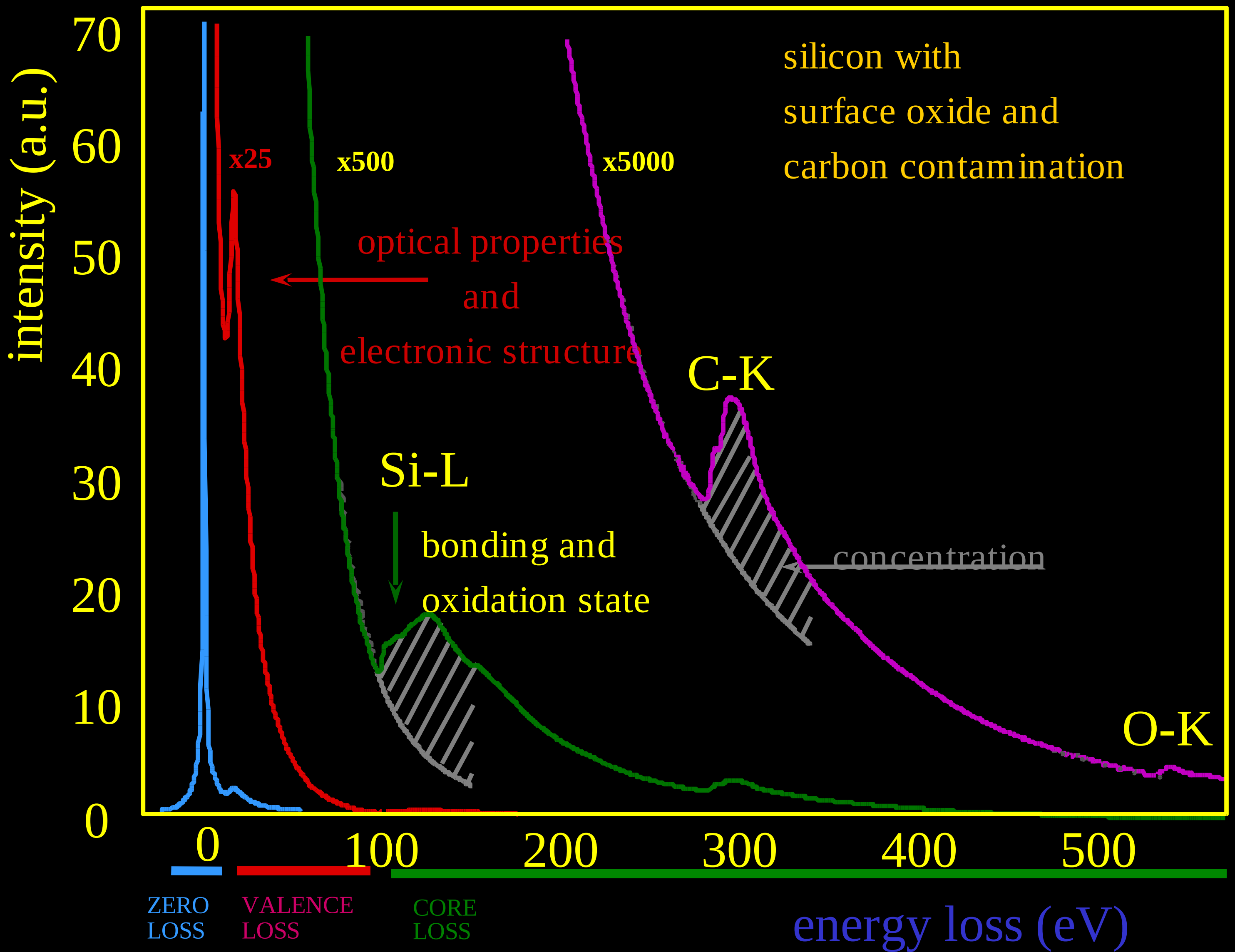
Buczko *et al.*

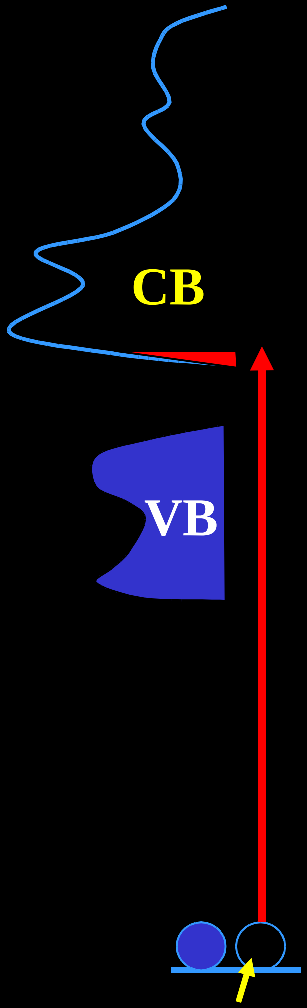
Atomic Resolution Z-Contrast Imaging





Electron Energy-Loss Spectrum





Core hole

⇒ *Z*+1

Theoretical Methods

ab initio Density Functional Theory
plus LDA or GGA

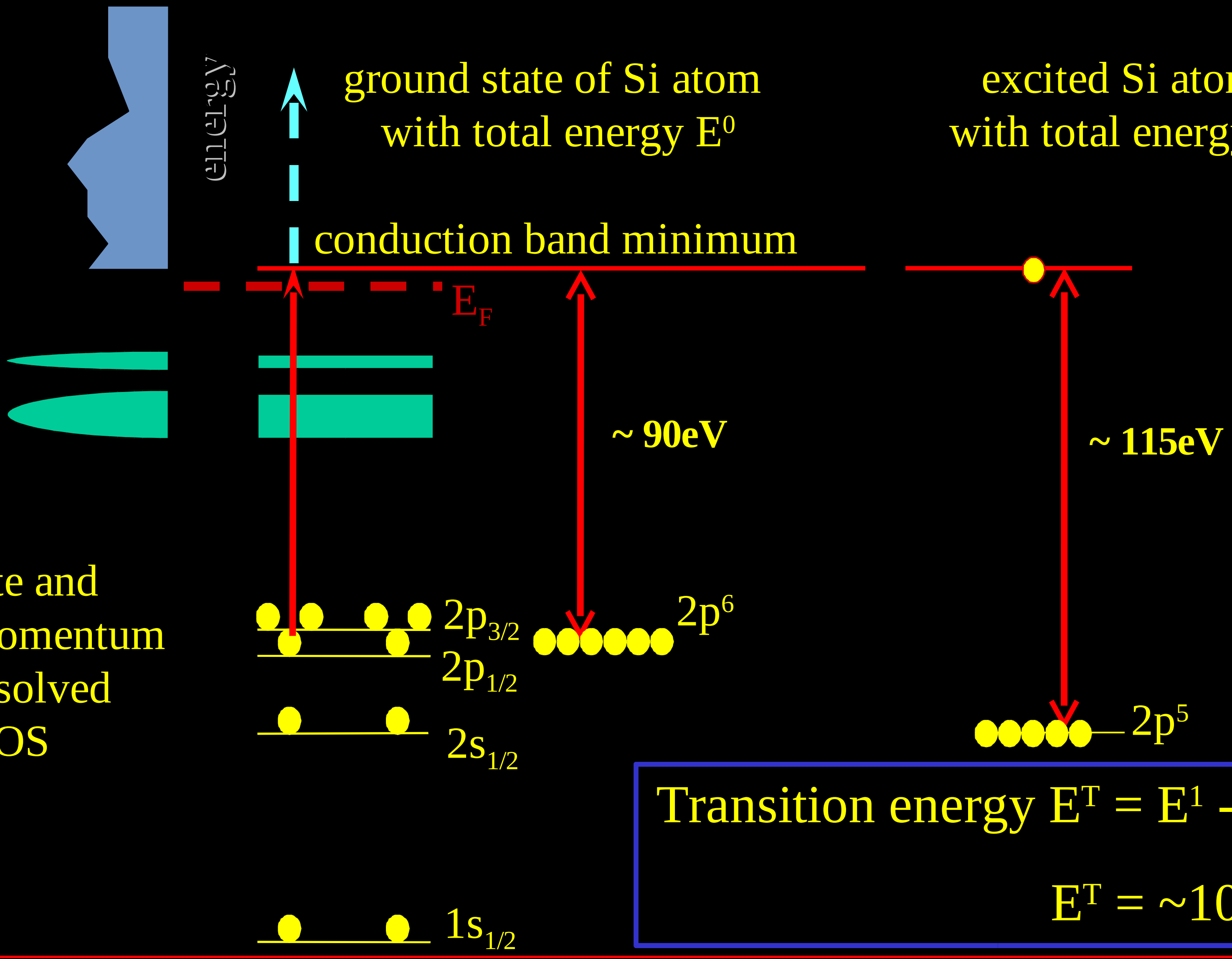
implemented within

pseudopotential

and

full-potential (all electron) methods

Si-$L_{2,3}$ Ionization Edge in EELS



energy

ground state of Si atom
with total energy E^0

excited Si atom
with total energy E^1

conduction band minimum

E_F

~ **90eV**

~ **115eV**

site and
momentum
resolved
DOS

$2p_{3/2}$

$2p_{1/2}$

$2s_{1/2}$

$1s_{1/2}$

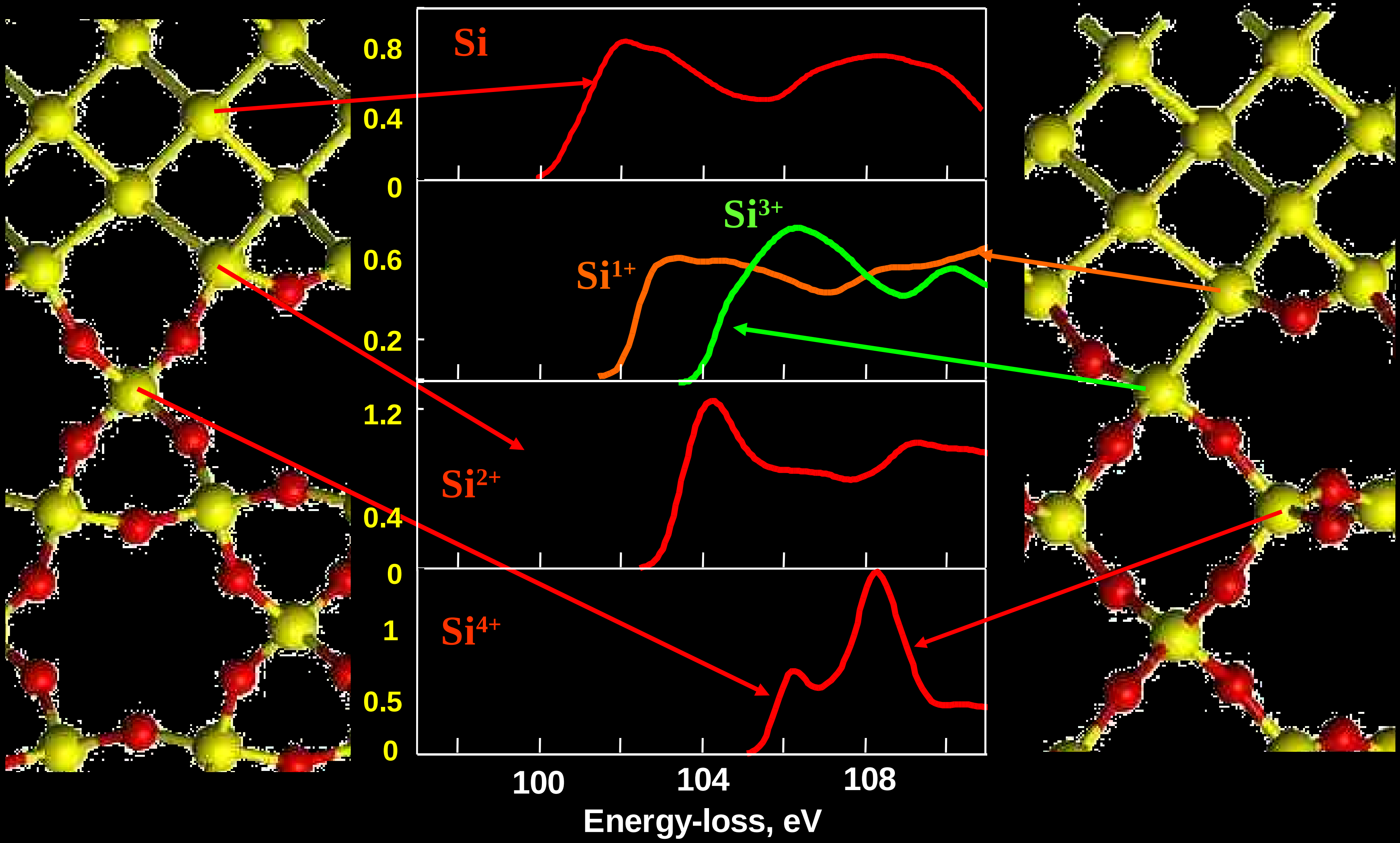
$2p^6$

$2p^5$

Transition energy $E^T = E^1 - E^0$

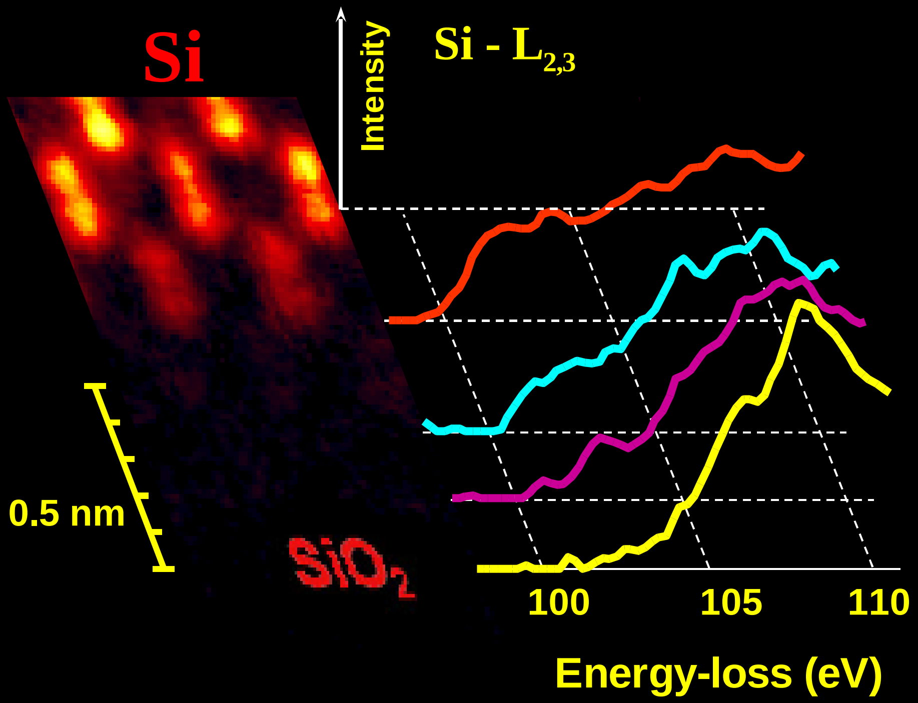
$E^T = \sim 100$ eV

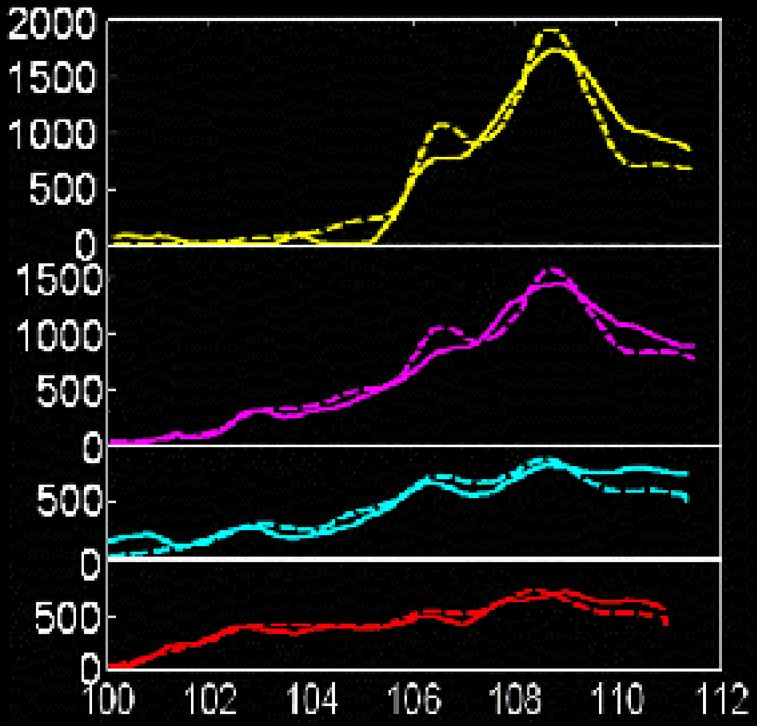
Calculated Si-$L_{2,3}$ Edges at Si/SiO_2



Combining Theory and Experiment

Calculation of EELS Spectra from Band Structure





Combining Theory and Experiment

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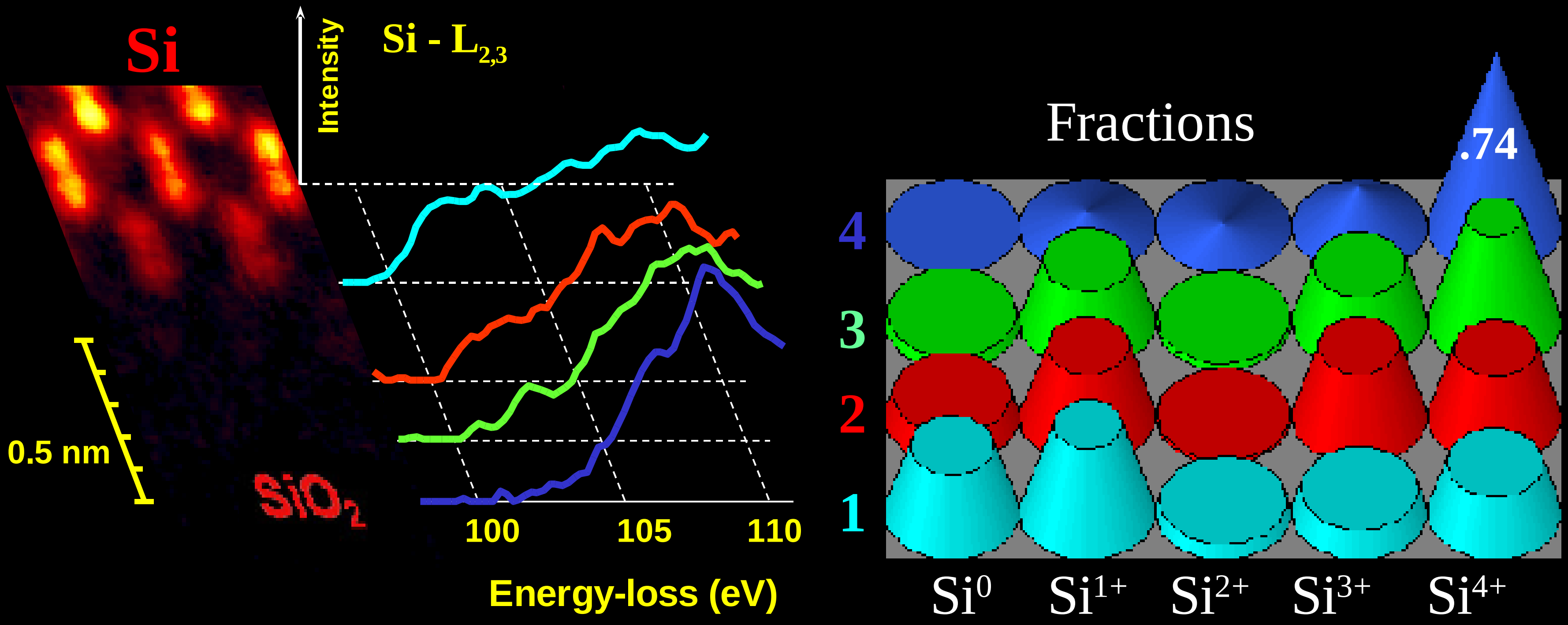
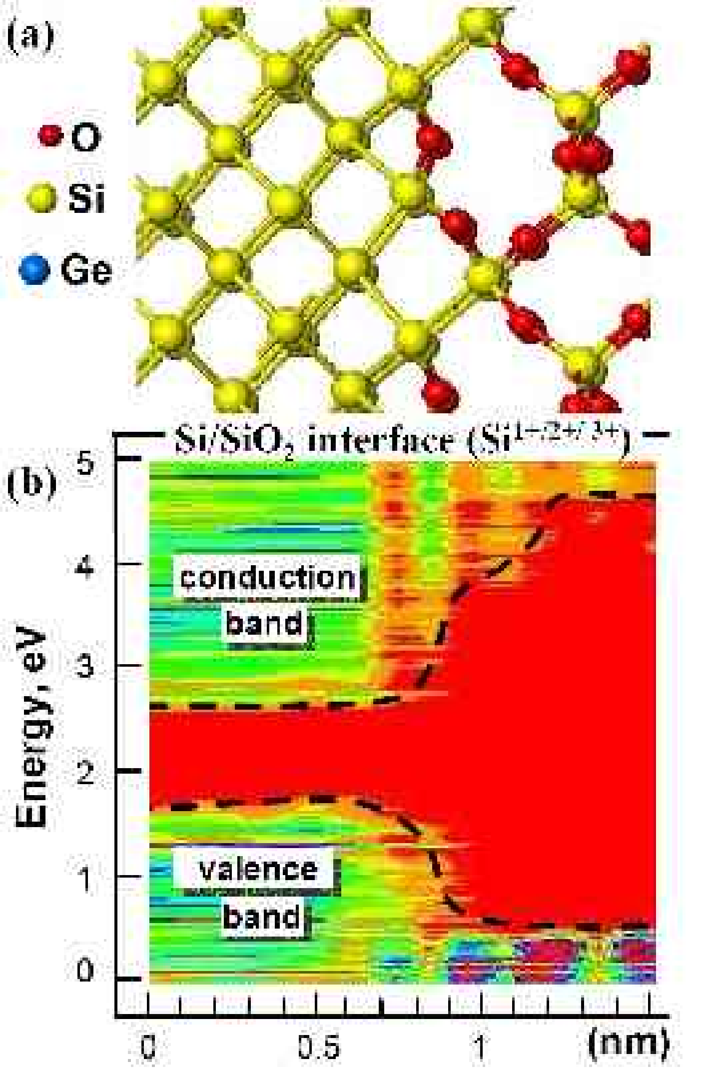


⇒ “Measure” atomic structure of amorphous materials.

Band Line-Up Si/SiO_2



Real-space band structure:

- Calculate electron DOS projected on atoms
- Average layers

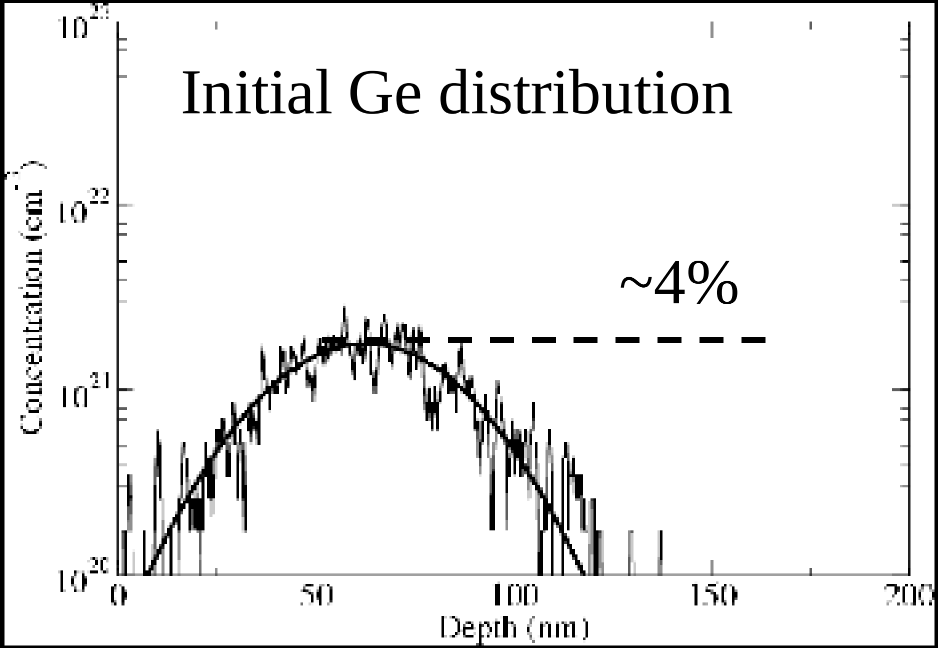
⇒ Abrupt would be better!

Is there an abrupt interface?

Lopatin *et al.*, submitted to PRL

Interfaces with Different Abruptness: Si/SiO_2 vs. $Si:Ge/SiO_2$

- Yes!
- Ge-implanted sample from ORNL (1989).
- Sample history:
  - Ge implanted into Si (10^{16} cm^{-2}, 100 keV)
  - ~ 800 °C oxidation

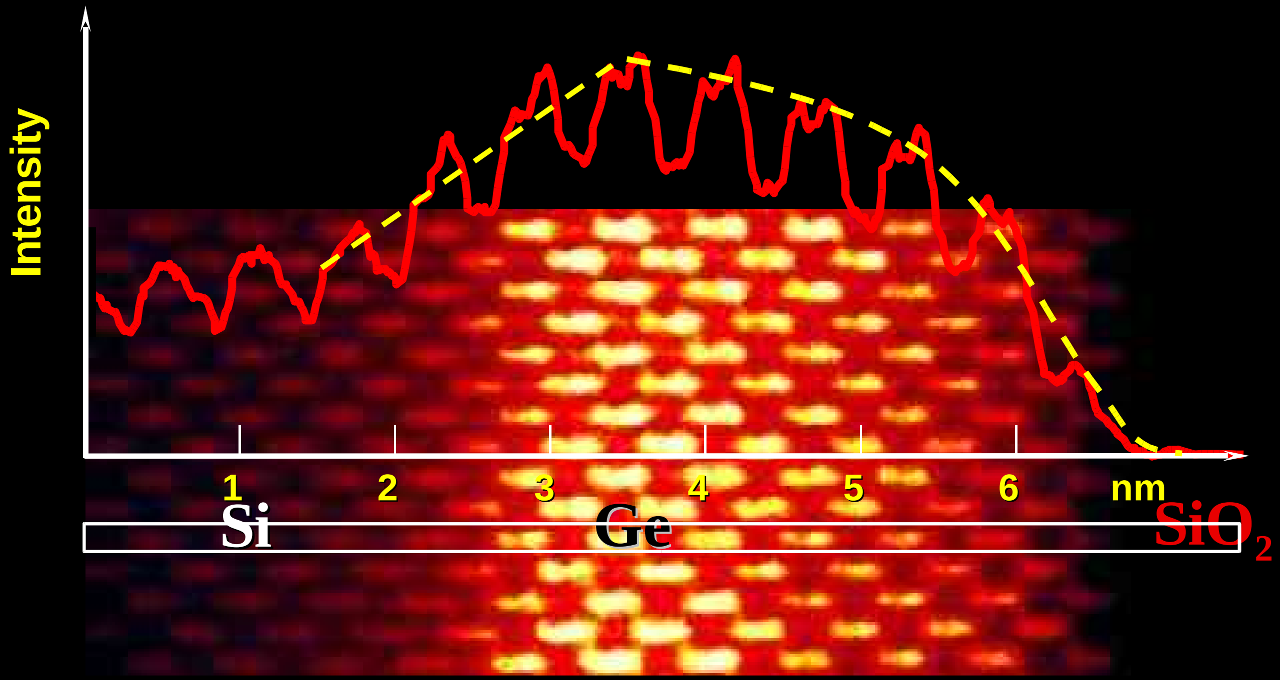


Initial Ge distribution

~4%

~120 nm

Z-Contrast Ge/SiO_2 Interface



- Ge after oxidation packed into compact layer, ~ 4-5 nm wide

- peak ~100% Ge

Kinetic Monte Carlo Ox. Modeling

Simulation Algorithm for oxidation of Si:Ge:

- Si lattice with O added between Si atoms
- Addition of O atoms and hopping of Ge positions by KMC*
- First-principles calculation of simplified energy expression as function of bonds:

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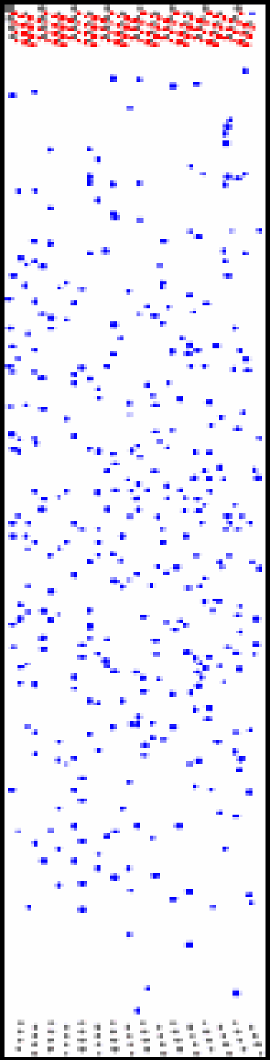
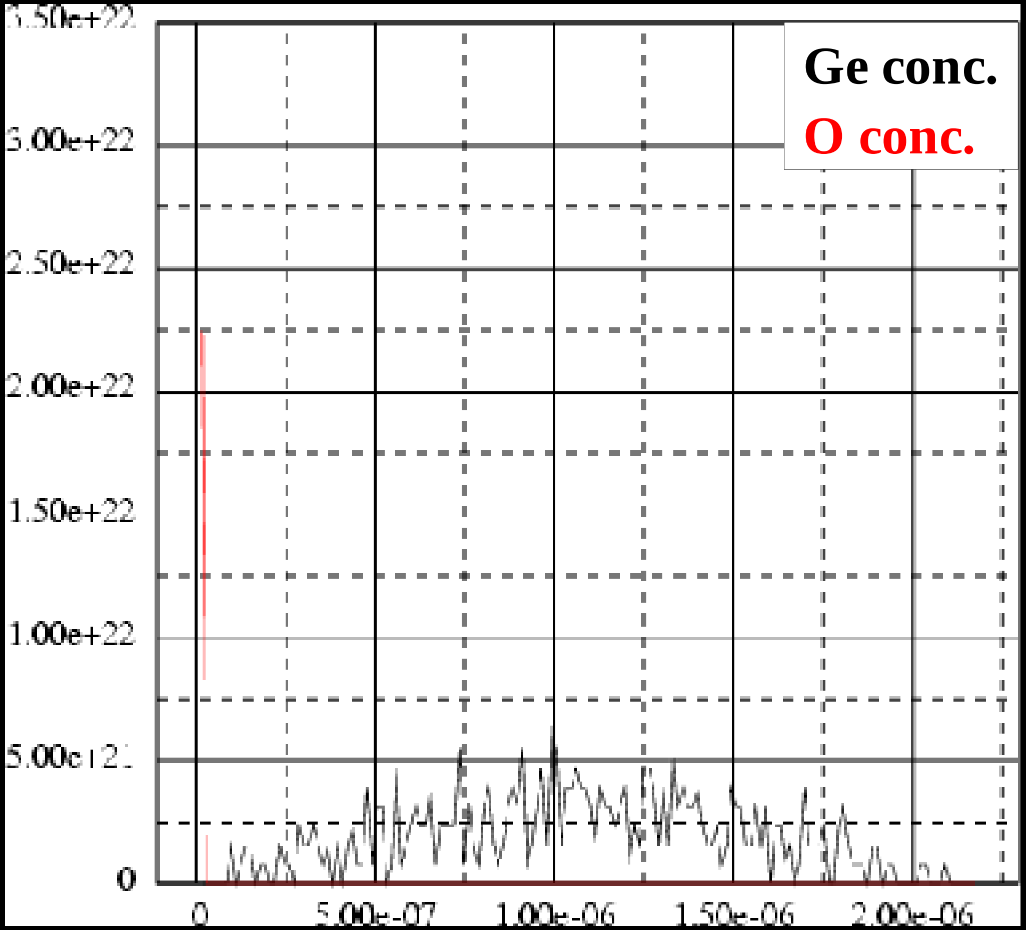
*Hopping rate Ge: McVay, PRB **9** (74); ox rate SiGe: Paine, JAP **70** (91).

Windl *et al.*, J. Comput. Theor. Nanosci.

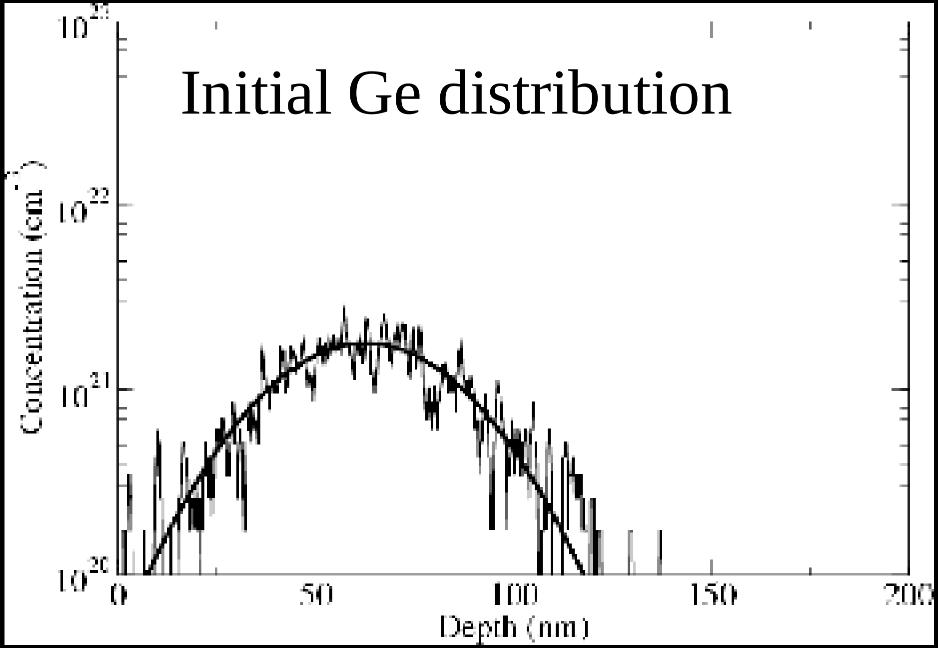
Monte Carlo Results - Animation

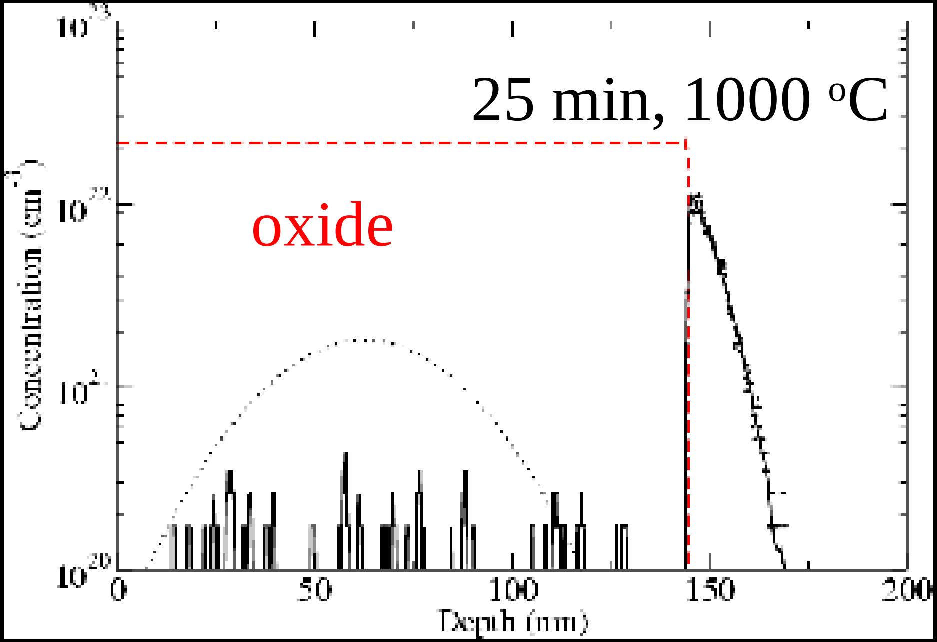


- ● **O**
- ● **Ge**



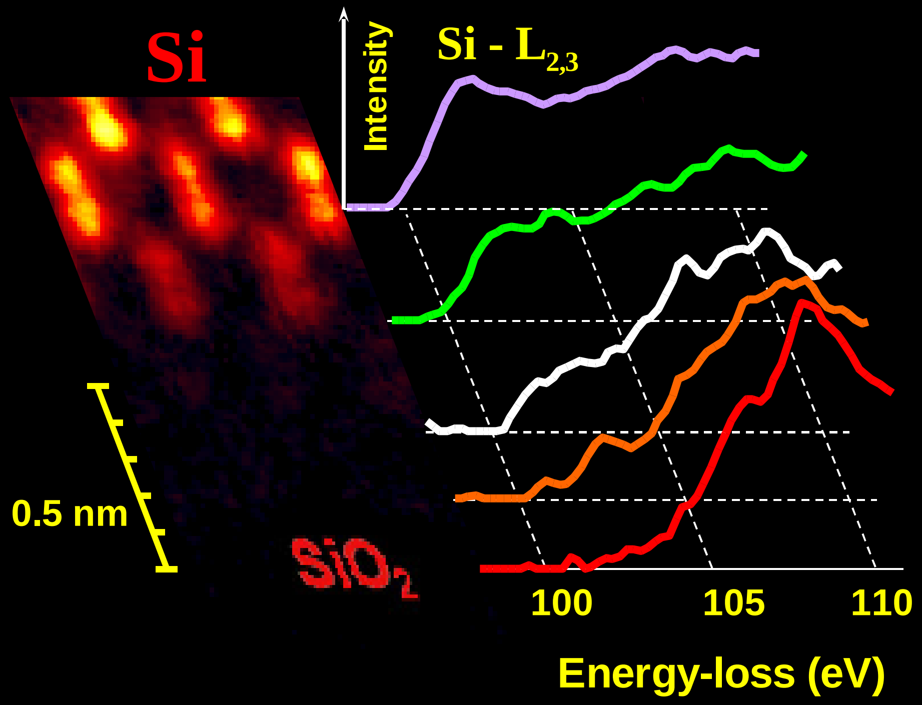
Monte Carlo Results - Profiles

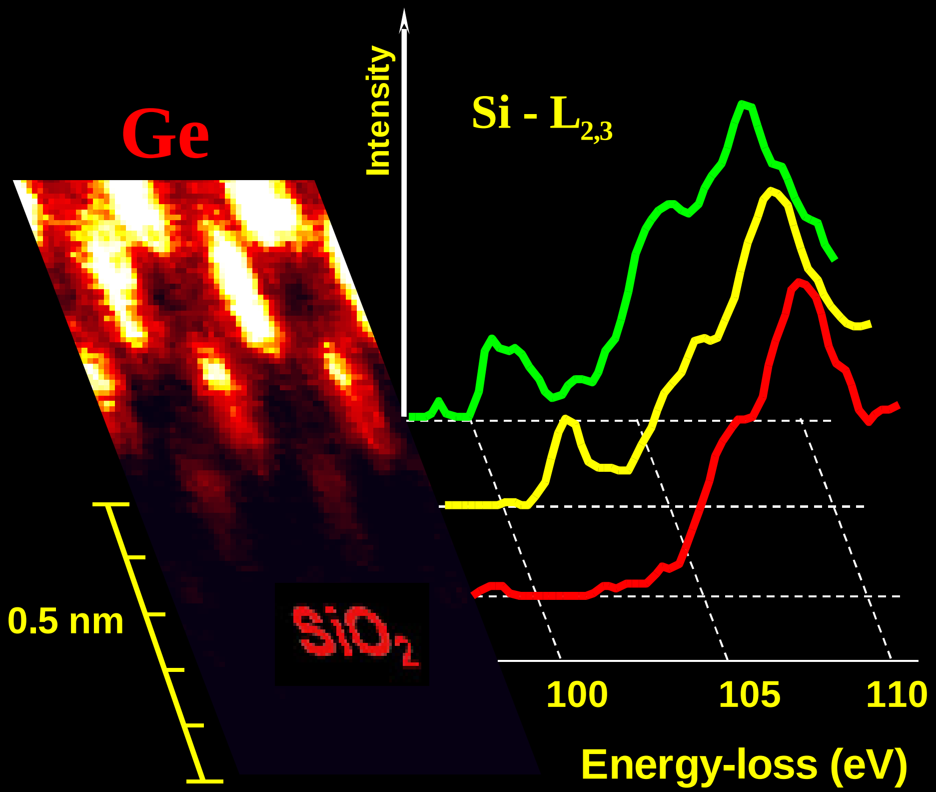

Initial Ge distribution

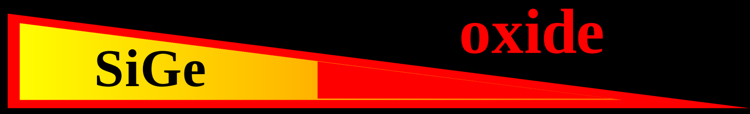

25 min, 1000 °C

Si/SiO$_2$ vs. Ge/SiO$_2$

Atomic Resolution EELS

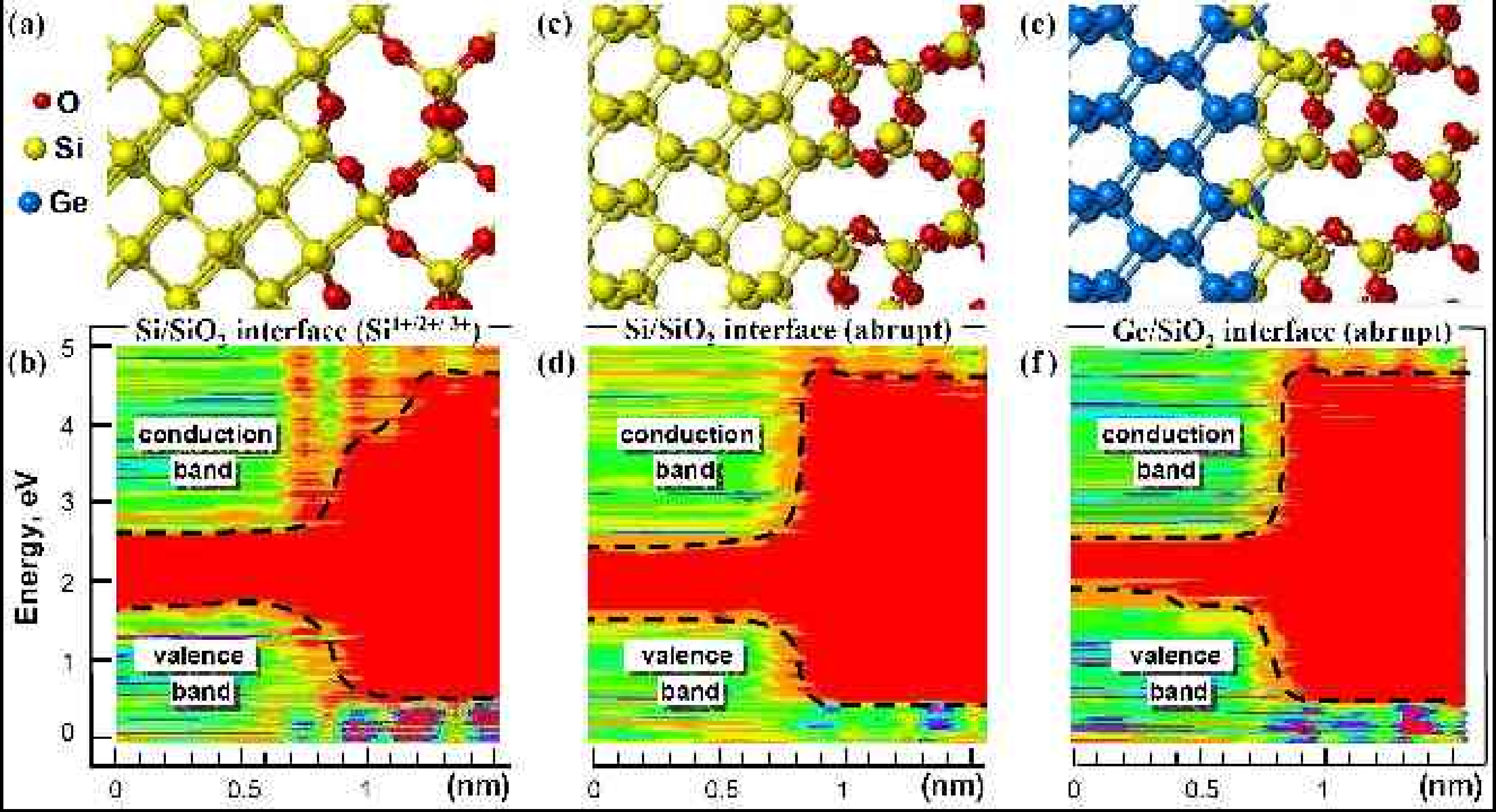






S. Lopatin et al., Microscopy and Microanalysis, San Antonio, 2003.

Band Line-Up Si/SiO_2 & Ge/SiO_2

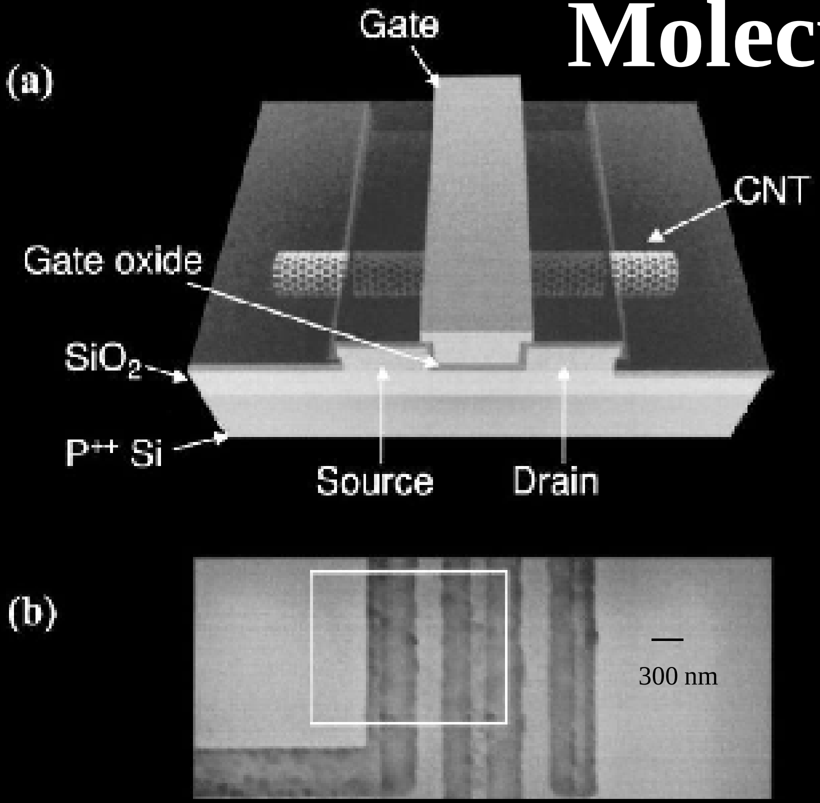


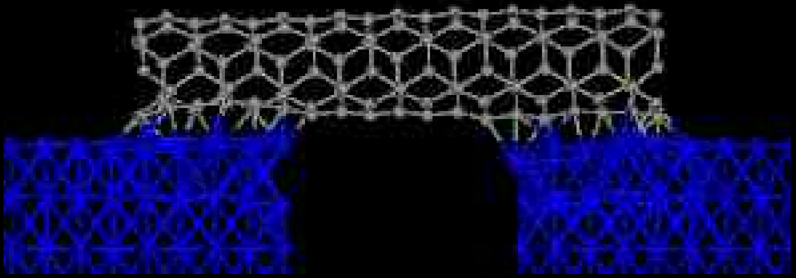
Lopatin *et al.*, submitted to PRL

Conclusions 2

- Atomic-scale characterization **is** possible:
  Ab-initio methods in conjunction with Z-contrast & EELS can resolve interface structure.
- Atomically sharp Ge/SiO_2 interface observed
- Reliable structure-property relationship for well characterized structure (band line-up)
- Abrupt is good
- Sharp interface from Ge-O repulsion (“snowplowing”)

3. Process and Device Simulation of Molecular Devices



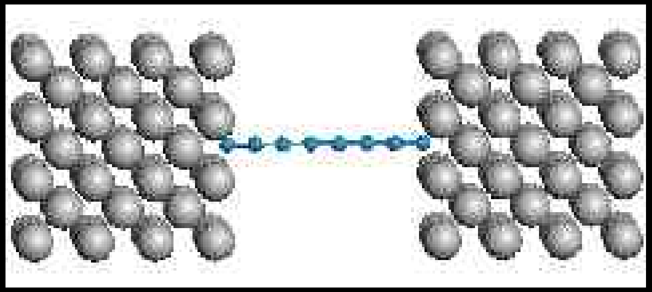


Possibilities:

- Carbon nanotubes (CNTs) as channels in field effect transistors
- Single molecules to function as devices
- Molecular wires to connect device molecules
- Single-molecule circuits where devices and interconnects are integrated into one large molecule

Wind *et al.*, JVST B, 2002.

Concept of Ab-Initio Device Simulation

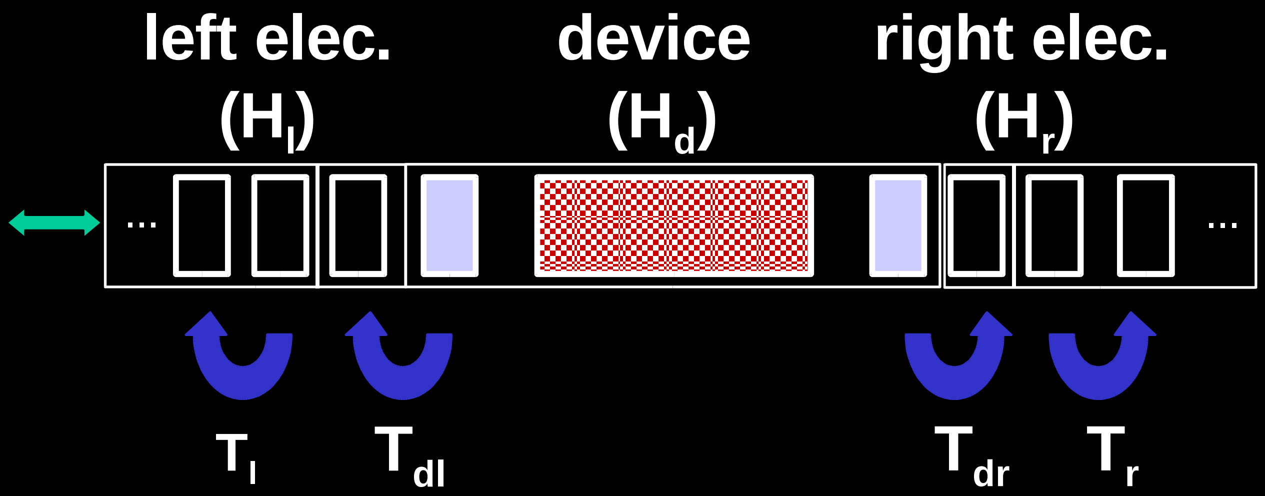


Using

- Landauer formula for $I_p(V)$
- Lippmann-Schwinger equation, $T_{lr}(E) = \langle\, l \,|\, V + VGV \,|\, r \,\rangle$
- Rigid-band approximation $T(E,V) = T(E + \eta V)$ with $\eta = 0.$

Zhang, Fonseca, Demkov, *Phys Stat Sol (b)*, 233, 70 (2002)

T_{lr} from Local-Orbital Hamiltonian



left elec. (H_l)

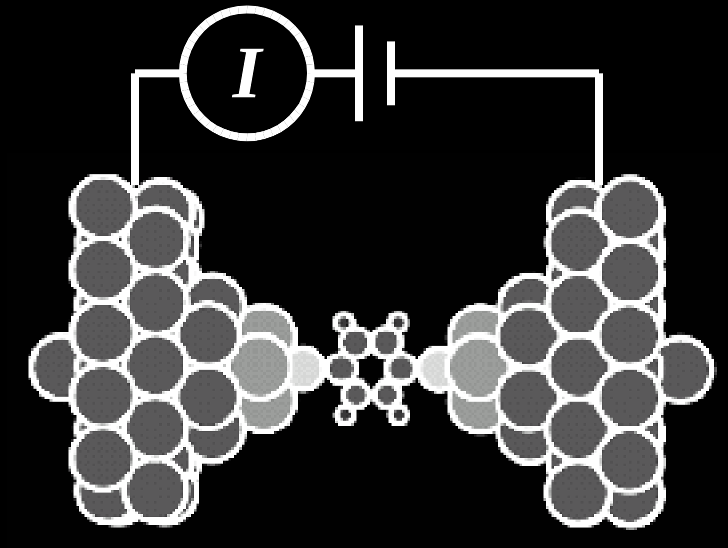
device (H_d)

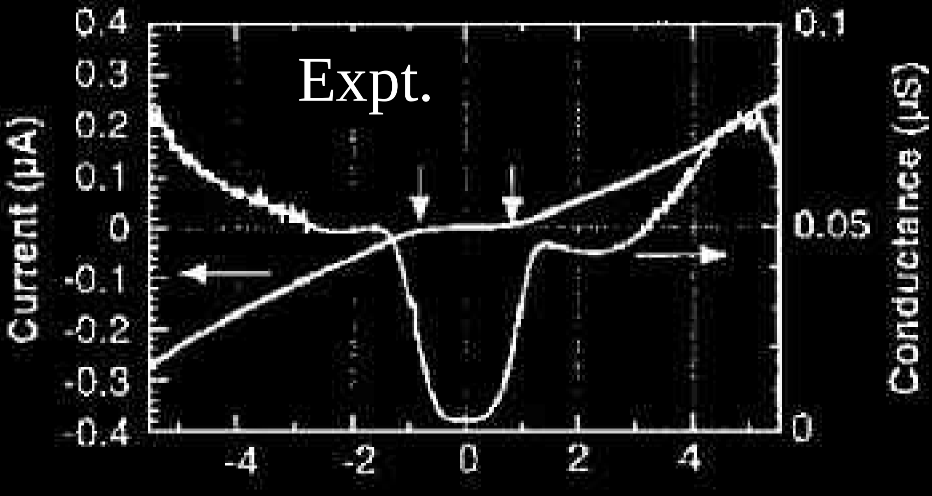
right elec. (H_r)

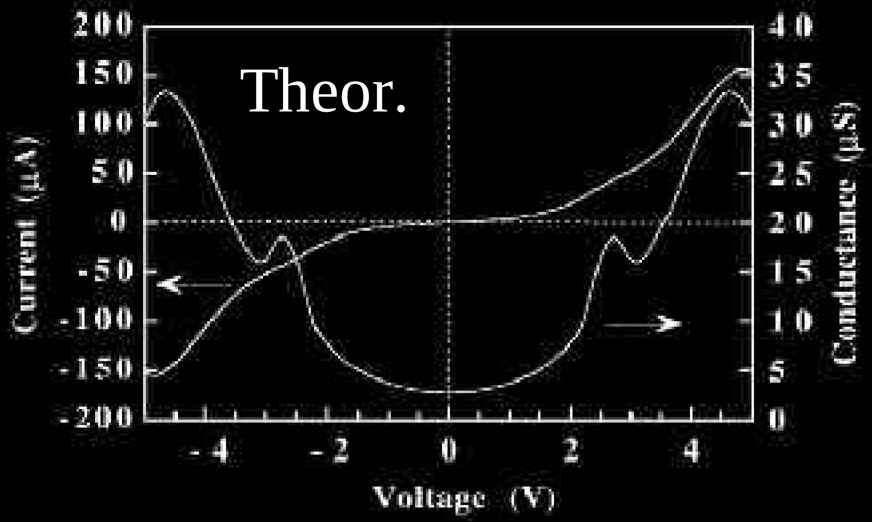
- $T_{lr}(E)$ can be constructed from matrix elements of DFT tight-binding Hamiltonian H. Pseudo atomic orbitals: $\psi(r > r_c)=0$.
- We use matrix-element output from SIESTA.

Zhang, Fonseca, Demkov, *Phys Stat Sol (b)*, 233, 70 (2002)

The Molecular Transport Problem







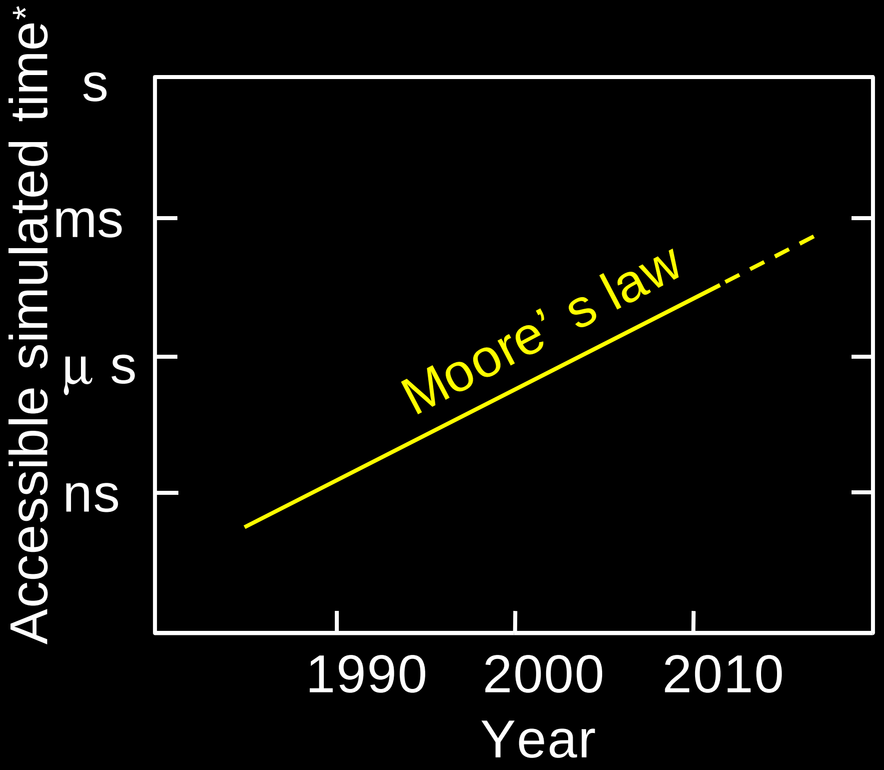
Strong discrepancy expt.-theory!

Suspected Problems:

- Contact formation molecule/lead not understood
- Influence of contact structure on electronic properties

What is “Process Modeling” for Molecular Devices?

- Contact formation: need to follow influence of temperature etc. on evolution of contact.
- Molecular level:
  atom by atom
  ⇒ Molecular Dynamics
- Problem:
  MD may *never* get to relevant time scales



* 1-week simulation of 1000-atom metal system, EAM potential

Accelerated Molecular Dynamics Methods

- Possible solution: accelerated dynamics methods.
- Principle: run for t_{run}. Simulated time: $t_{\mathrm{sim}} = n\, t_{\mathrm{run}}$, $n \gg 1$
- Possible methods:
  - Hyperdynamics (1997)
  - Parallel Replica Dynamics (1998)
  - Temperature Accelerated Dynamics (2000)

Voter *et al.*, Annu. Rev. Mater. Res. 32, 321 (2002).

Temperature Accelerated Dynamics (TAD)

Concept:

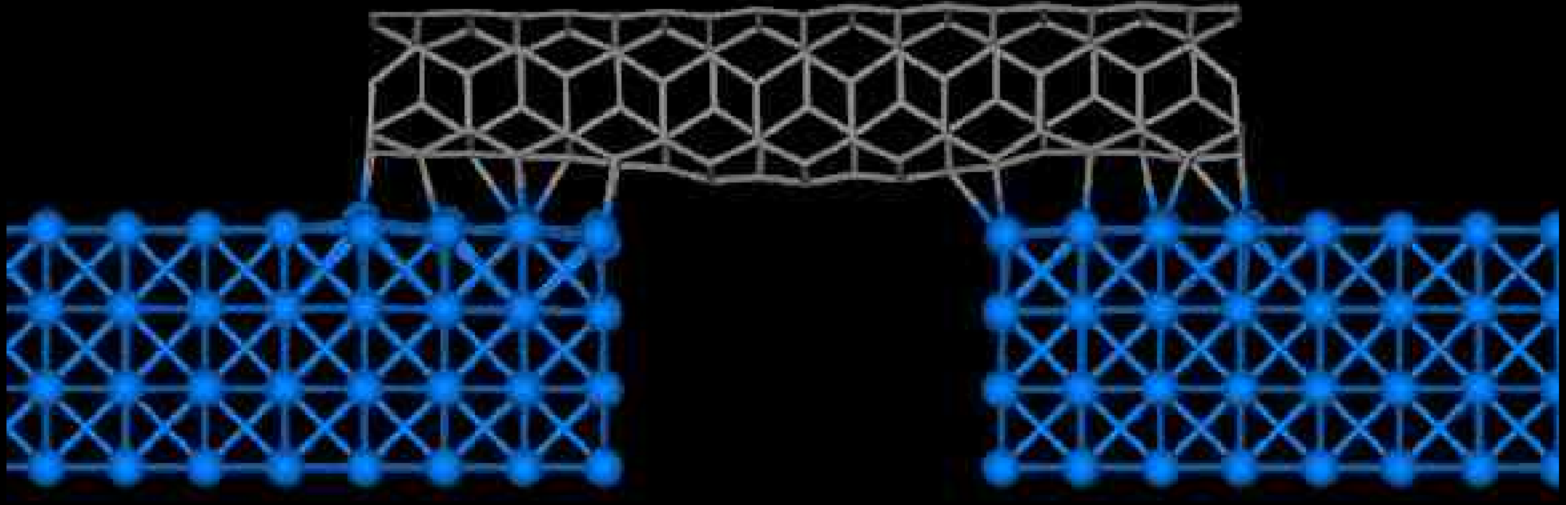
- Raise temperature of system to make events occur more frequently. Run several (many) times.
- Pick randomly event that should have occurred first at the lower temperature.

Basic assumption (among others):

- Harmonic transition state theory (Arrhenius behavior) w/ ΔE from Nudged Elastic Band Method (see above).

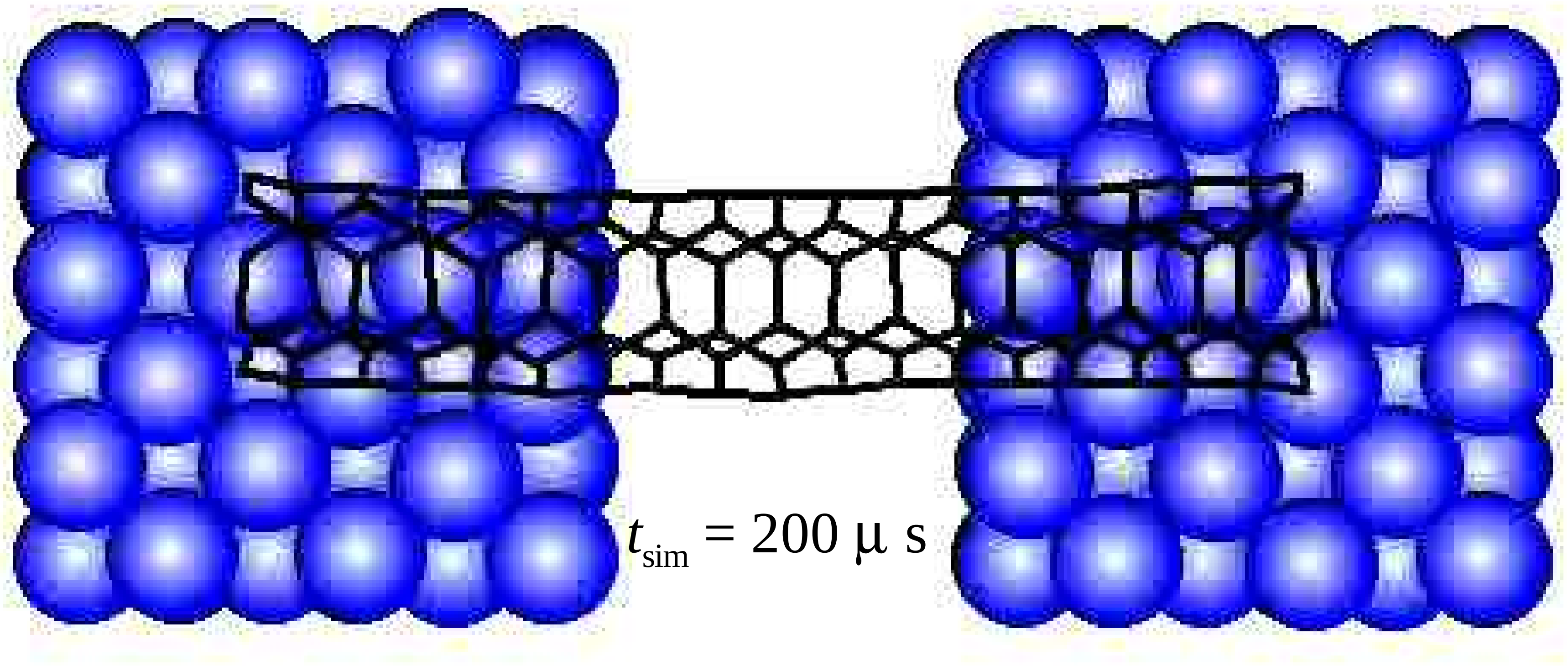
Voter *et al.*, Annu. Rev. Mater. Res. 32, 321 (2002).

Carbon Nanotube on Pt



- From work function, Pt possible lead candidate.
- Structure relaxed with VASP.
- Very small relaxations of Pt suggest little wetting between CNT and Pt (⇒ bad contact!?).

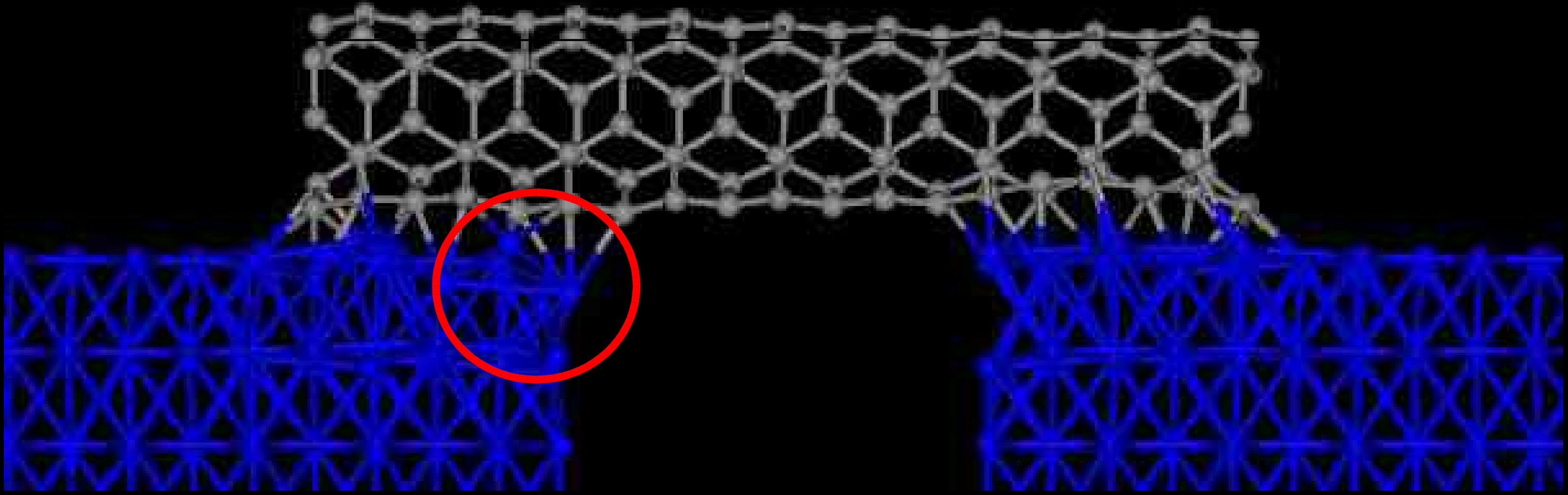
Movie: Carbon Nanotube on Pt
Temperature-Accelerated MD at 300 K



$t_{\text{sim}} = 200\ \mu\ \text{s}$

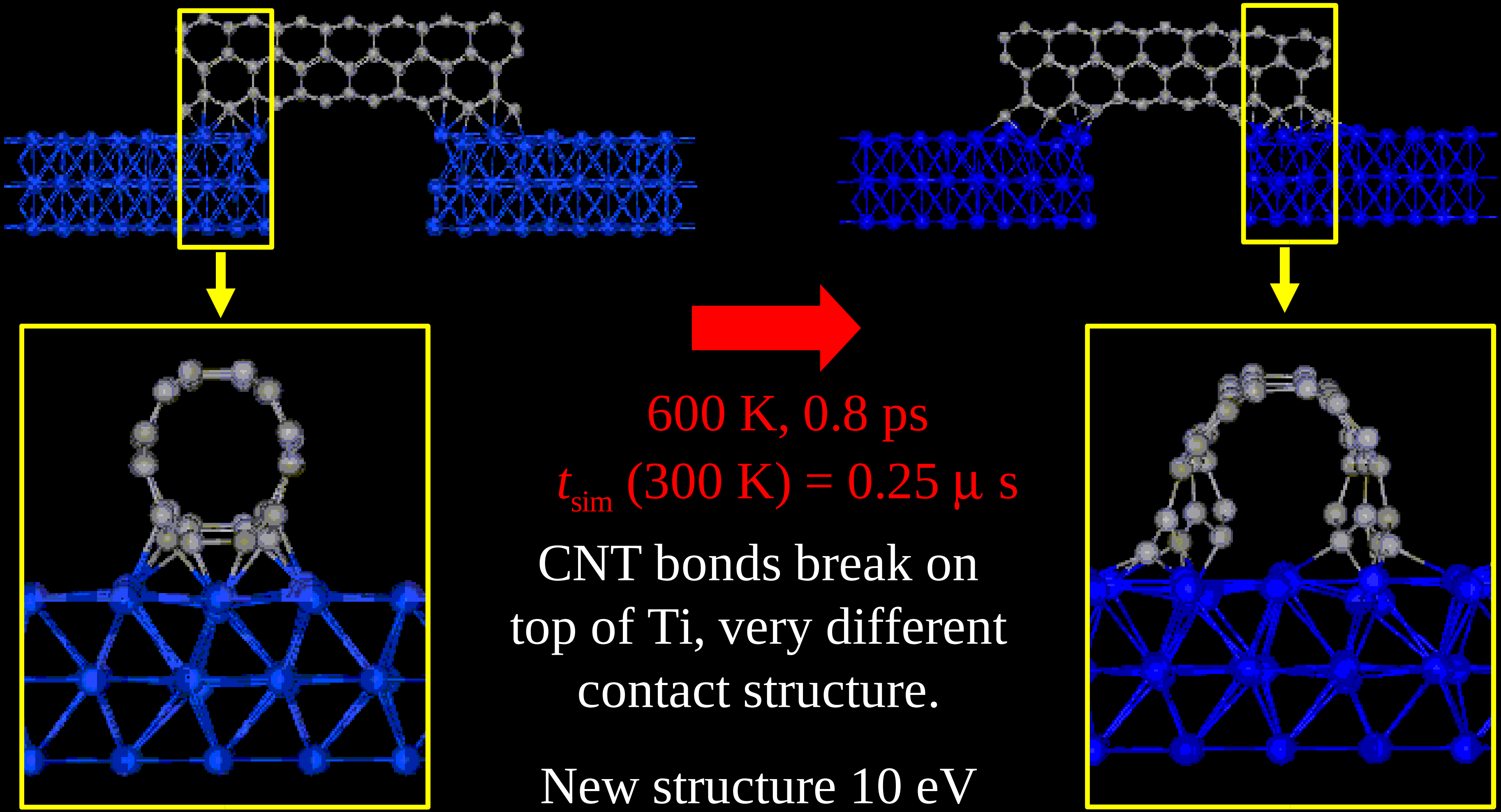
- Nordlund empirical potential
- Not much interaction observed $\Rightarrow$ study different system.

Carbon Nanotube on Ti



- Large relaxations of Ti suggest strong reaction (wetting) between CNT and Ti.
- Run ab-initio TAD for CNT on Ti (no empirical potential available).
- Very strong reconstruction of contacts observed.

TAD MD for CNT/Ti



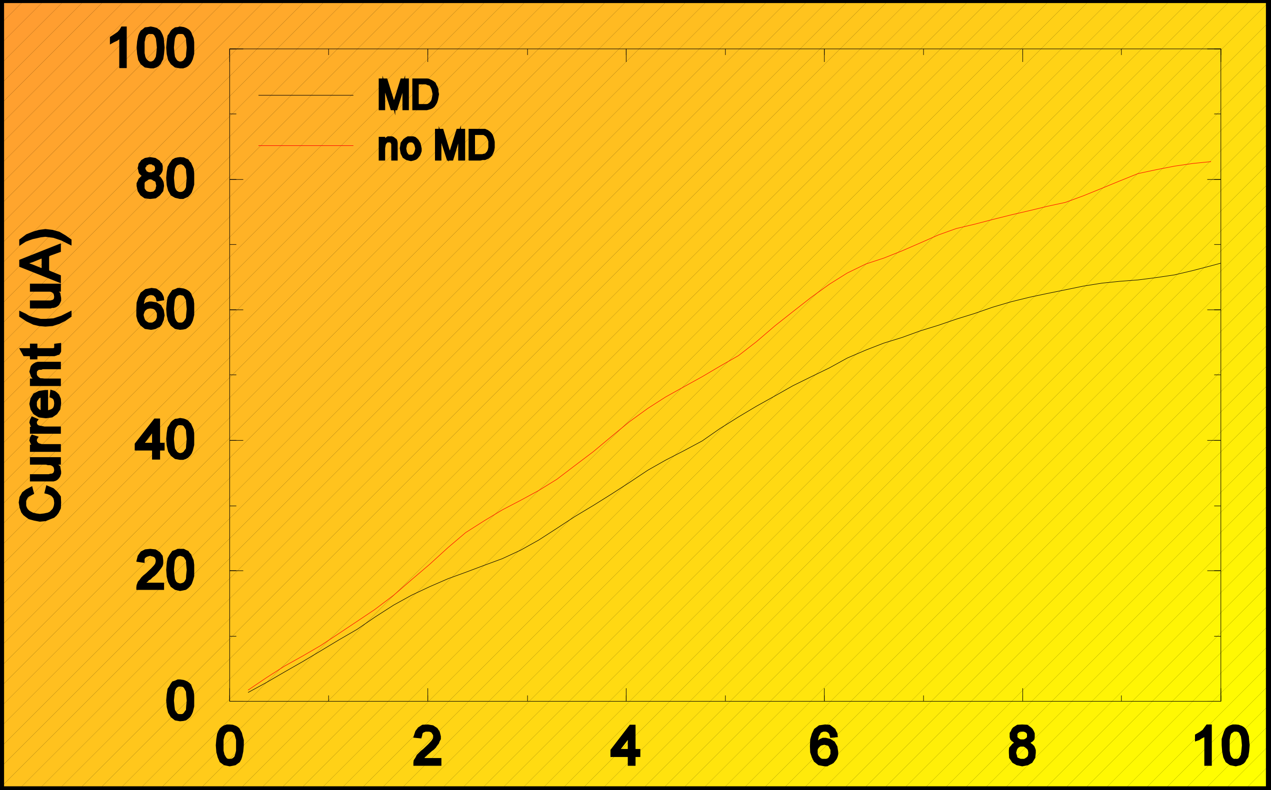
600 K, 0.8 ps

t_{sim} (300 K) = 0.25 μ s

CNT bonds break on top of Ti, very different contact structure.

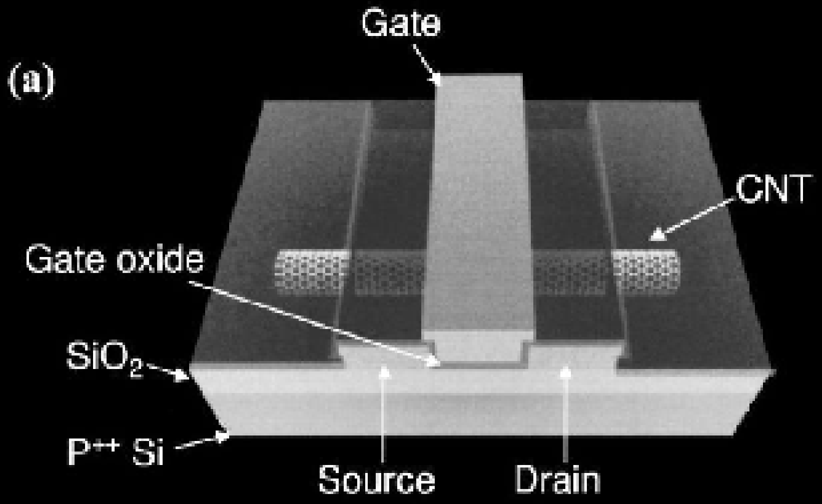
New structure 10 eV lower in energy.

Contact Dependence of I-V Curve for CNT on Ti

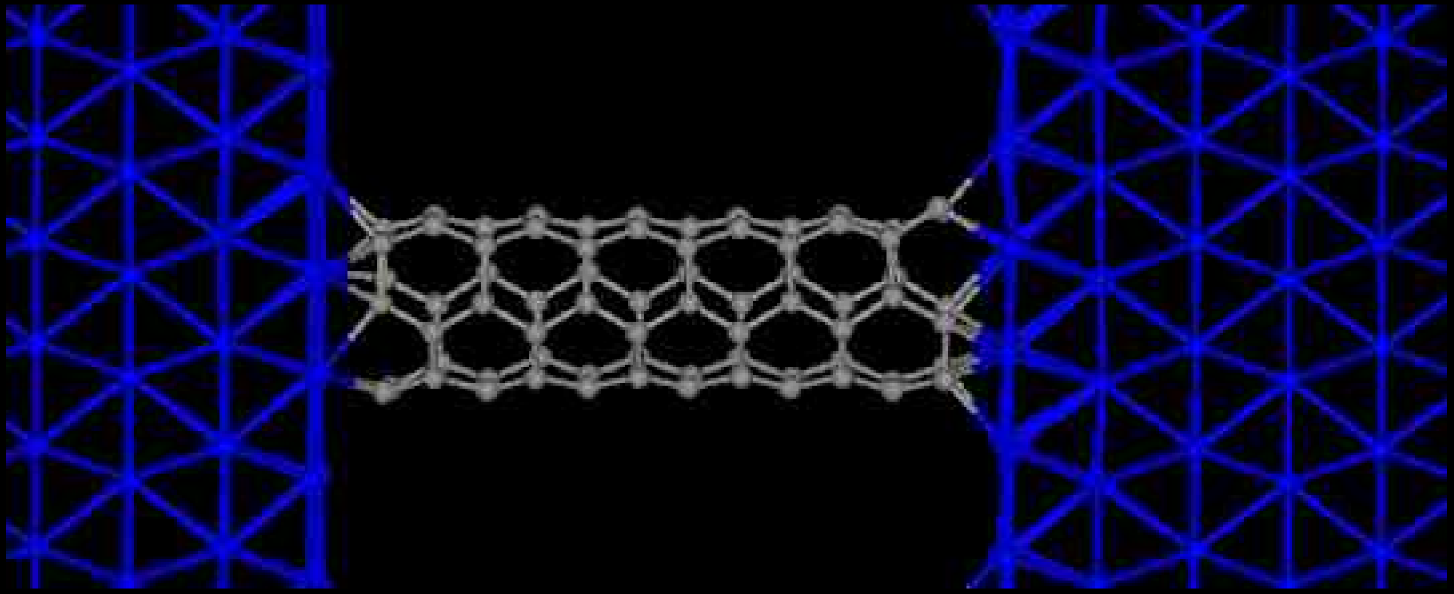


Difference 15-20%

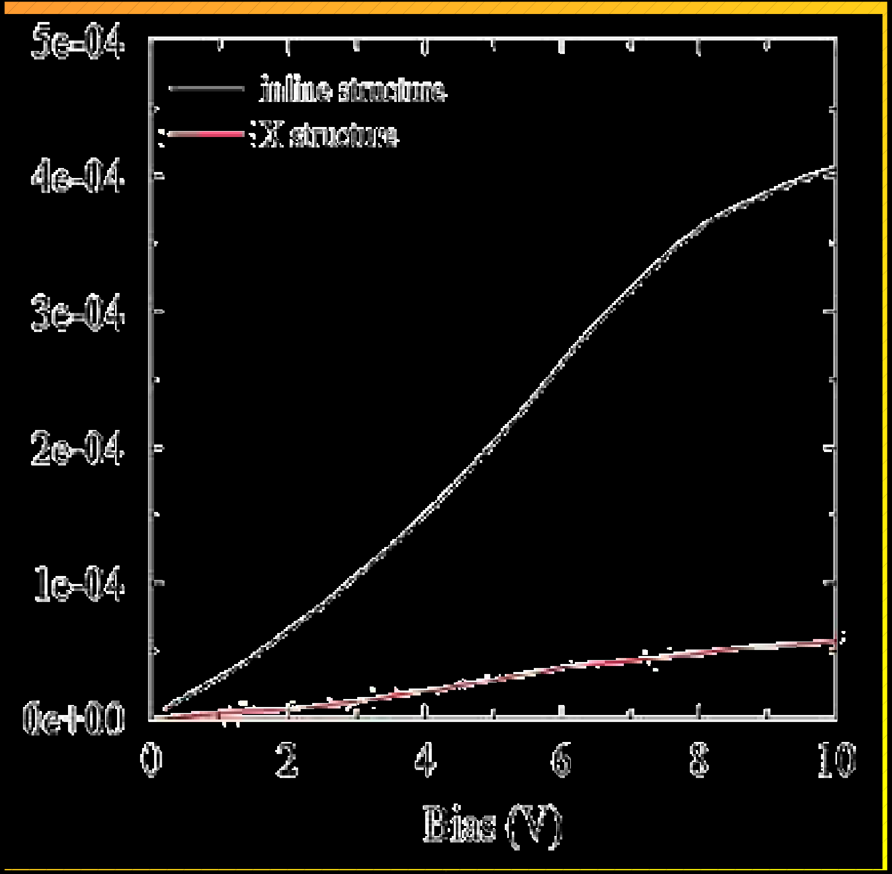
Relaxed CNT on Ti “Inline Structure”



- In real devices, CNT embedded into contact. Maybe major conduction through ends of CNT?



Contact Dependence of I-V Curve for CNT on Ti



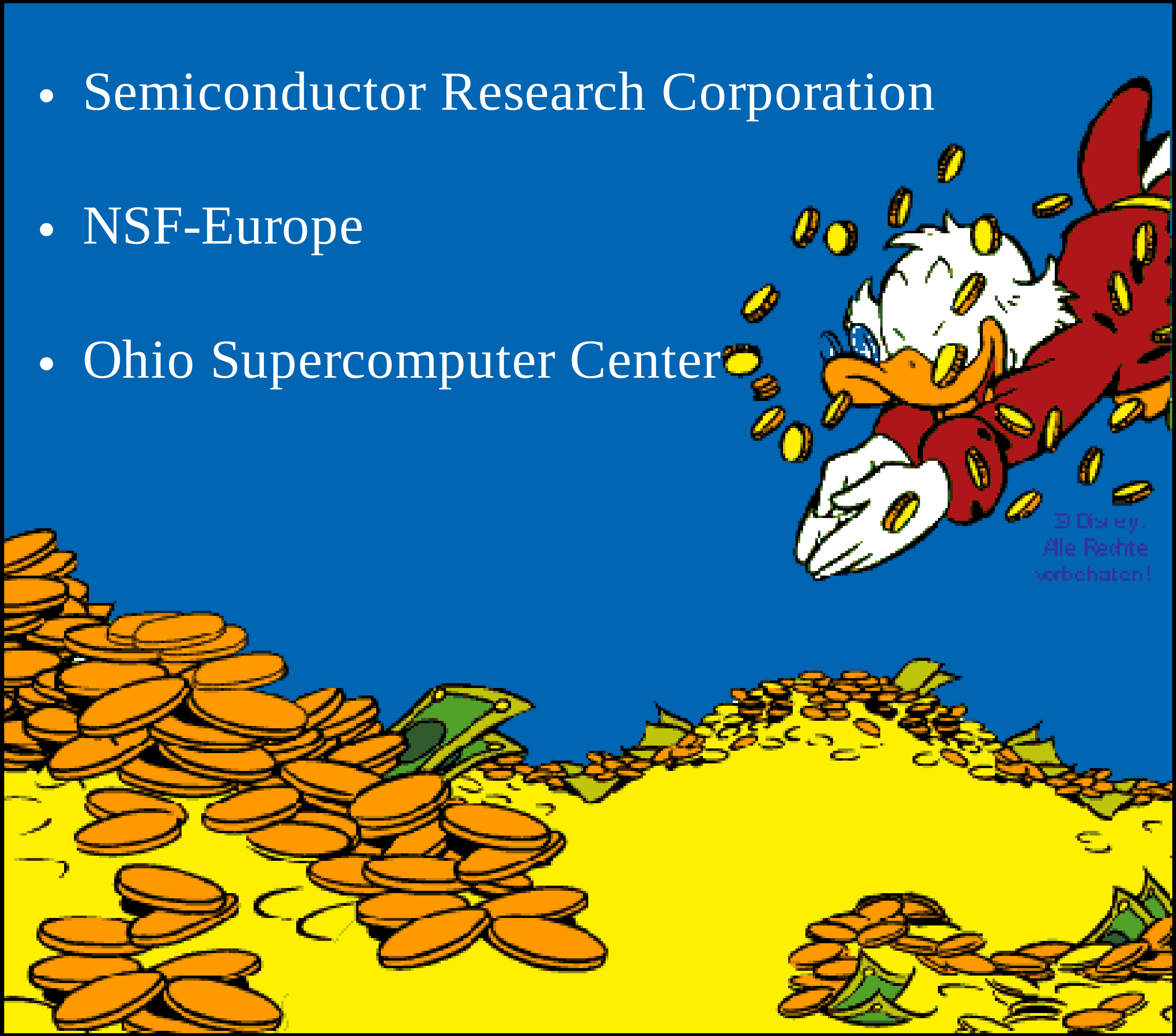
Inline structure has 10x conductivity of on-top structure

Conclusions

- Currently major challenge for molecular devices: contacts
- Contact formation: “Process” modeling on MD basis.
  - Accelerated MD
  - Empirical potentials instead of ab initio when possible
- Major pathways of current flow through ends of CNT

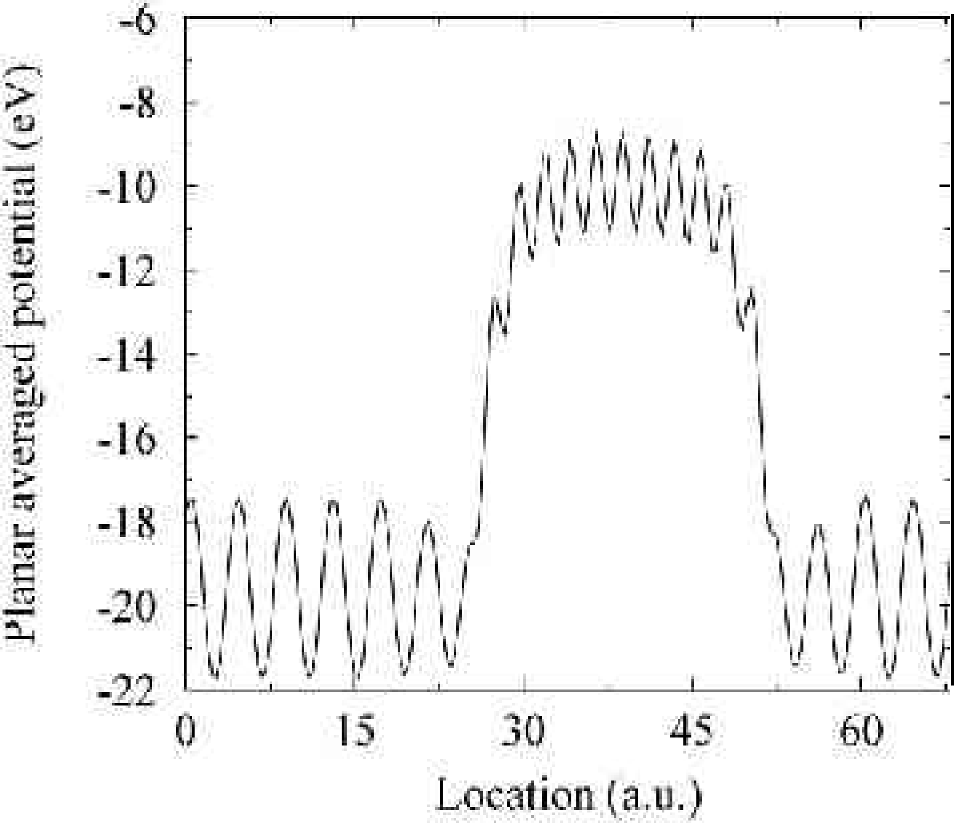
Funding

- Semiconductor Research Corporation
- NSF-Europe
- Ohio Supercomputer Center



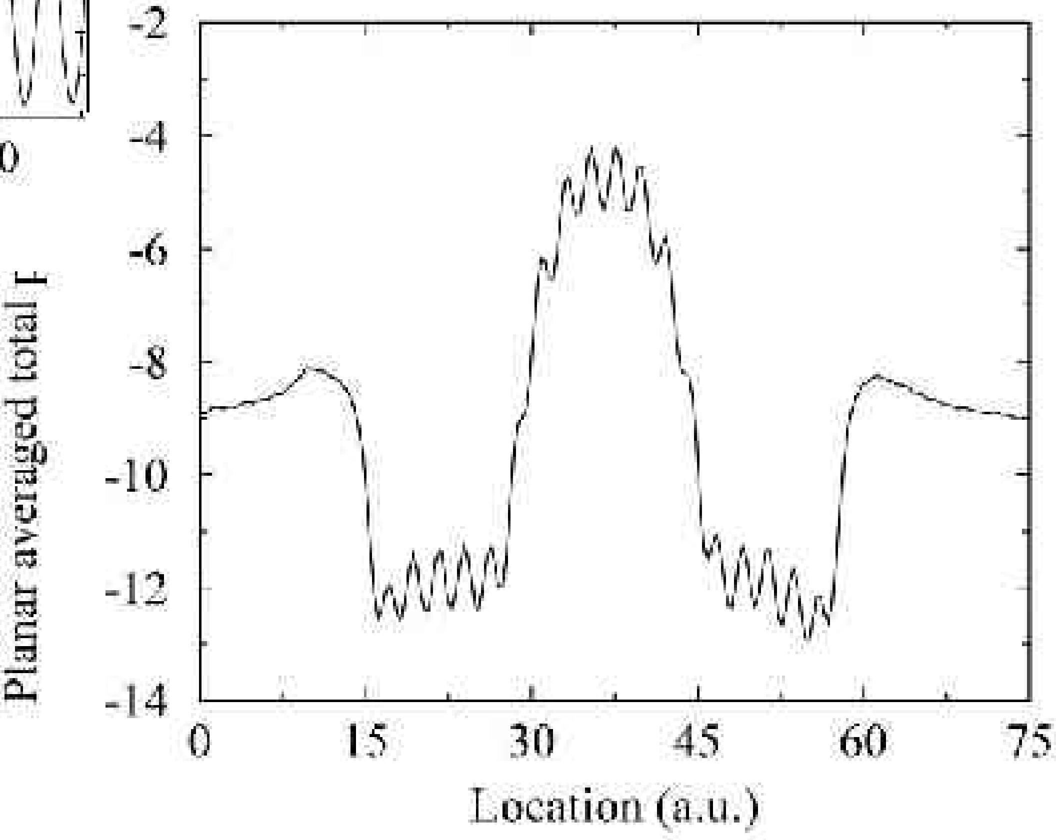
Acknowledgments (order of appearance)

- **Dr. Roland Stumpf** (SNL; B diffusion)
- **Dr. Marius Bunea and Prof. Scott Dunham** (B diffusion)
- **Dr. Xiang-Yang Liu** (Motorola/RPI; BICs)
- **Dr. Leonardo Fonseca** (Freescale; CNT transport)
- **Karthik Ravichandran** (OSU; CNT/Ti)
- **Dr. Blas Uberuaga** (LANL; CNT/Pt-TAD)
- **Prof. Gerd Duscher** (NCSU; TEM)
- **Tao Liang** (OSU; Ge/SiO$_2$)
- **Sergei Lopatin** (NCSU; TEM)



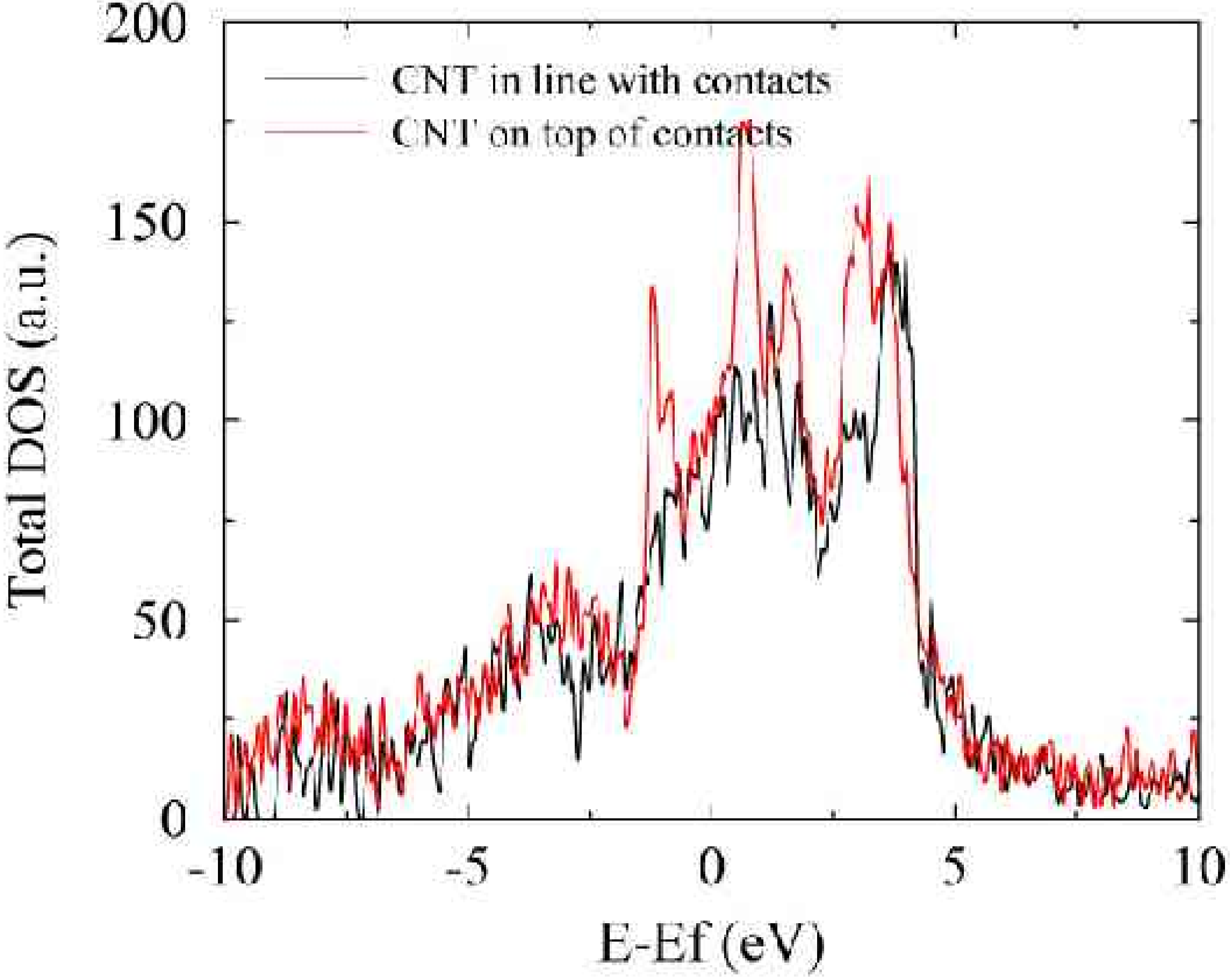
Left:

- Ti below 25 a.u. and above 55 a.u.
- CNT (armchair (3,3), 12 C planes) in the middle

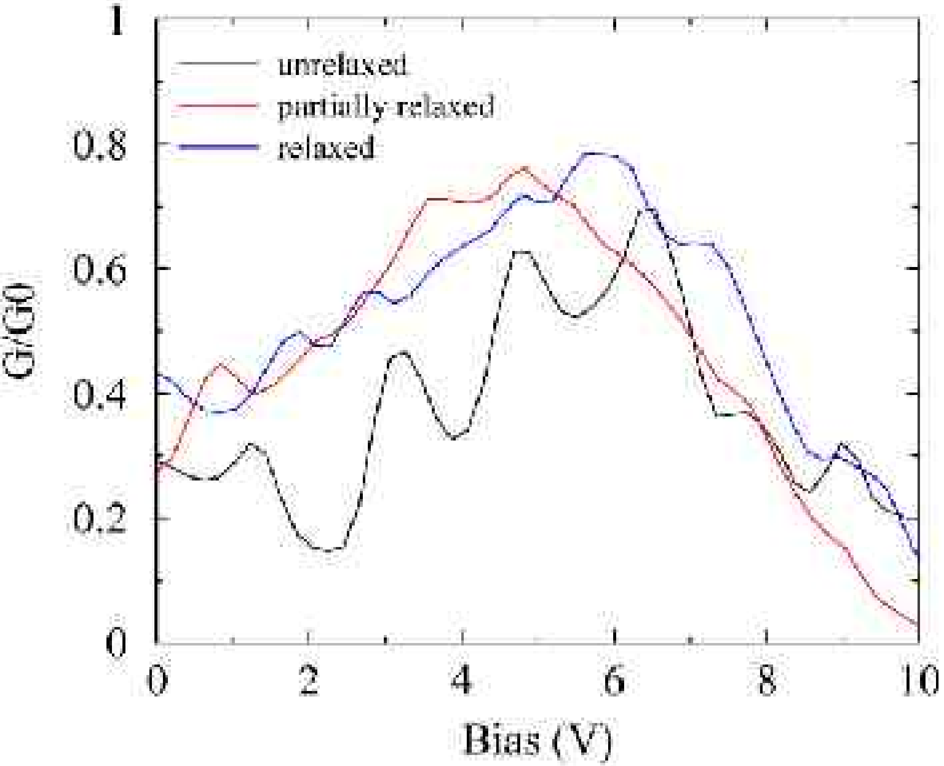


Right:

- Ti below 10 a.u. and above 60 a.u.
- CNT (3,3), 19 C planes, in contact with Ti between 15 a.u. anc 30 a.u. and between 45 a.u. and 60 a.u.
- CNT on vacuum between 30 a.u

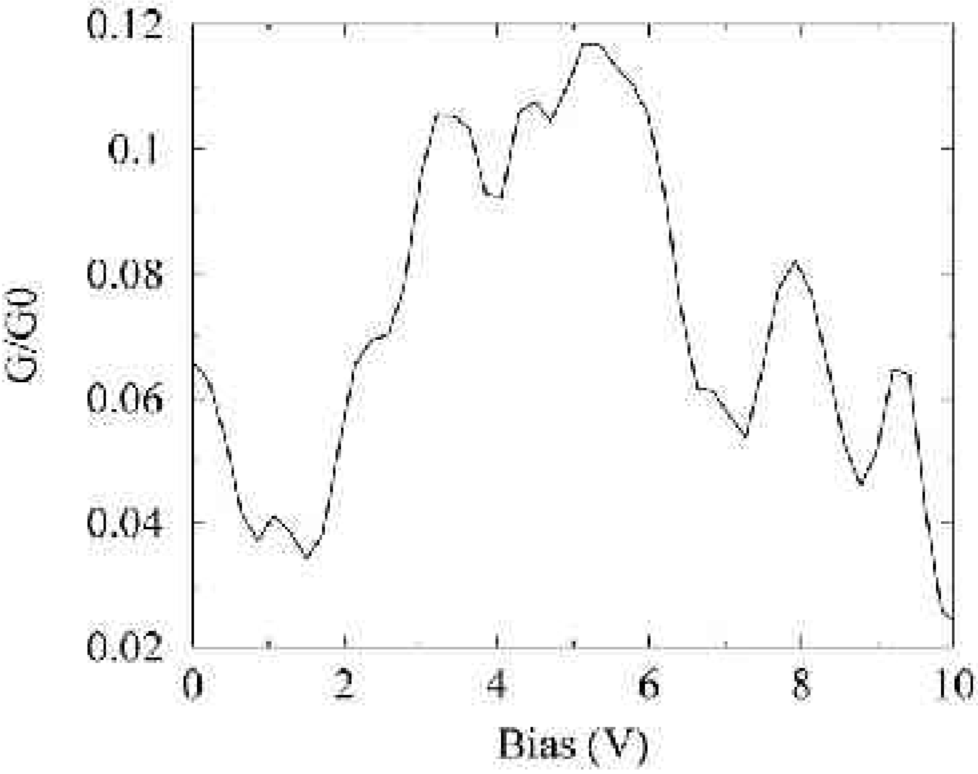


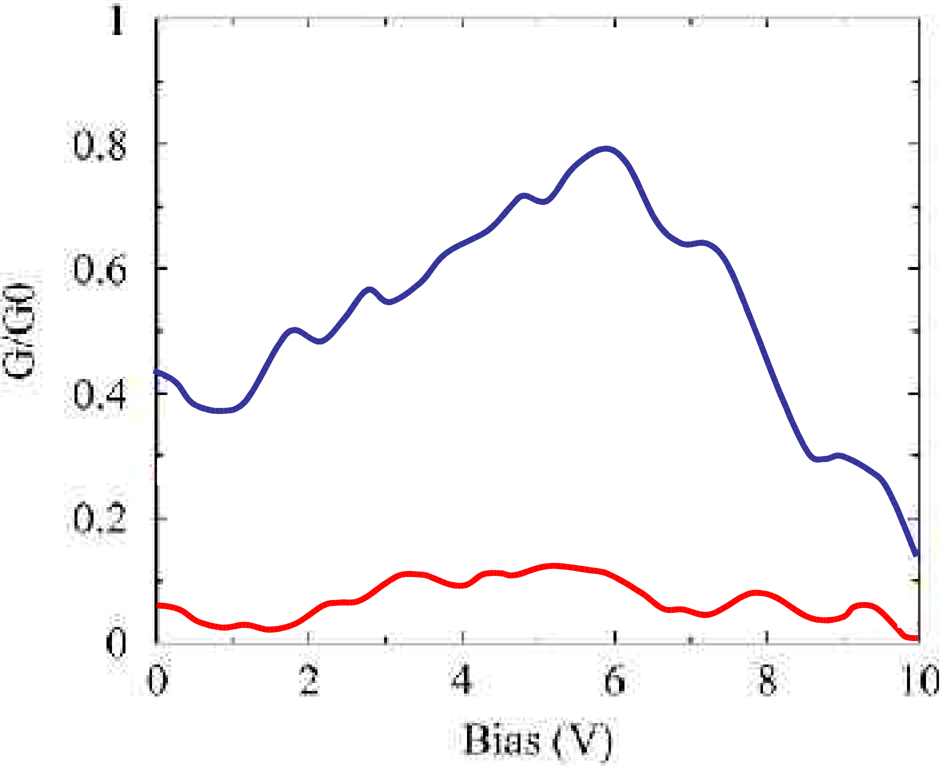
Minimal basis set used (SZ); I did a separate calculation for an isolated CNT (3,3) and obtained a band gap of 1.76 eV (SZ) and 1.49 eV (DZP). Armchair CNTs are metallic; to close the gap we need kpts in the z-direction.



Notice the difference in the y-axis. The X structure (below) carries a current which is about one order of magnitude smaller than the CNT inline with the contacts (left)

The main peak in the X structure is located at ~5 V, which is close to the value from the inline structure (~5.5 V). This indicates that the qualitative features in the conductance derive from the CNT while the magnitude of the conductance is set by the contacts. The extra peaks seen on the right may be due to incomplete





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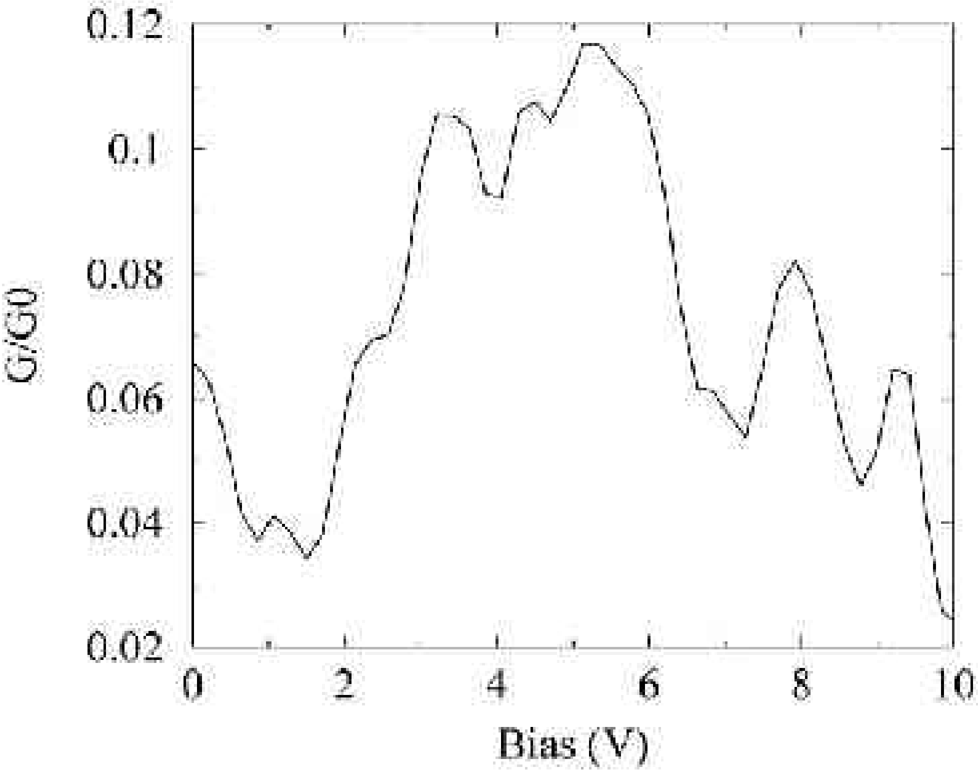
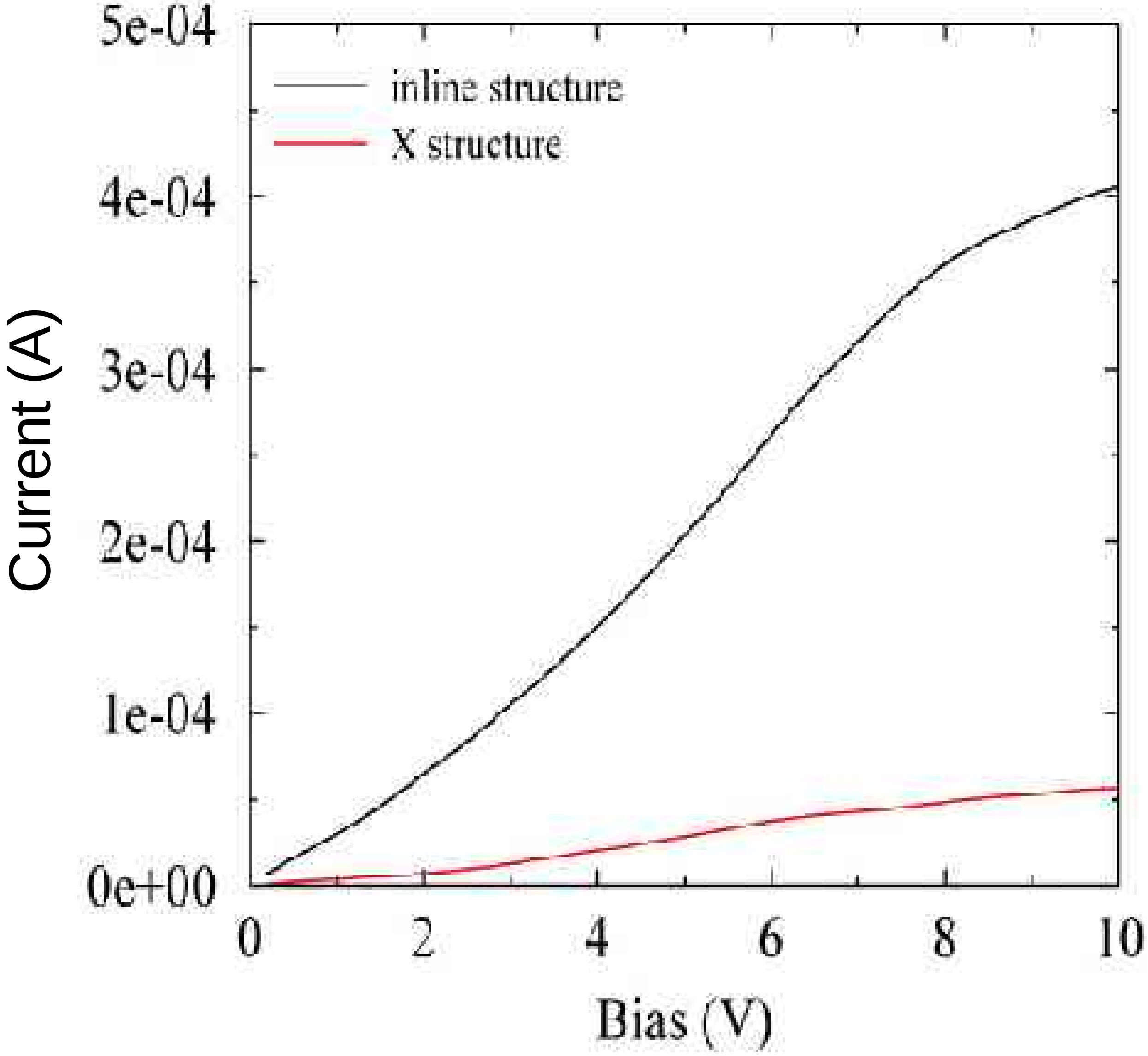
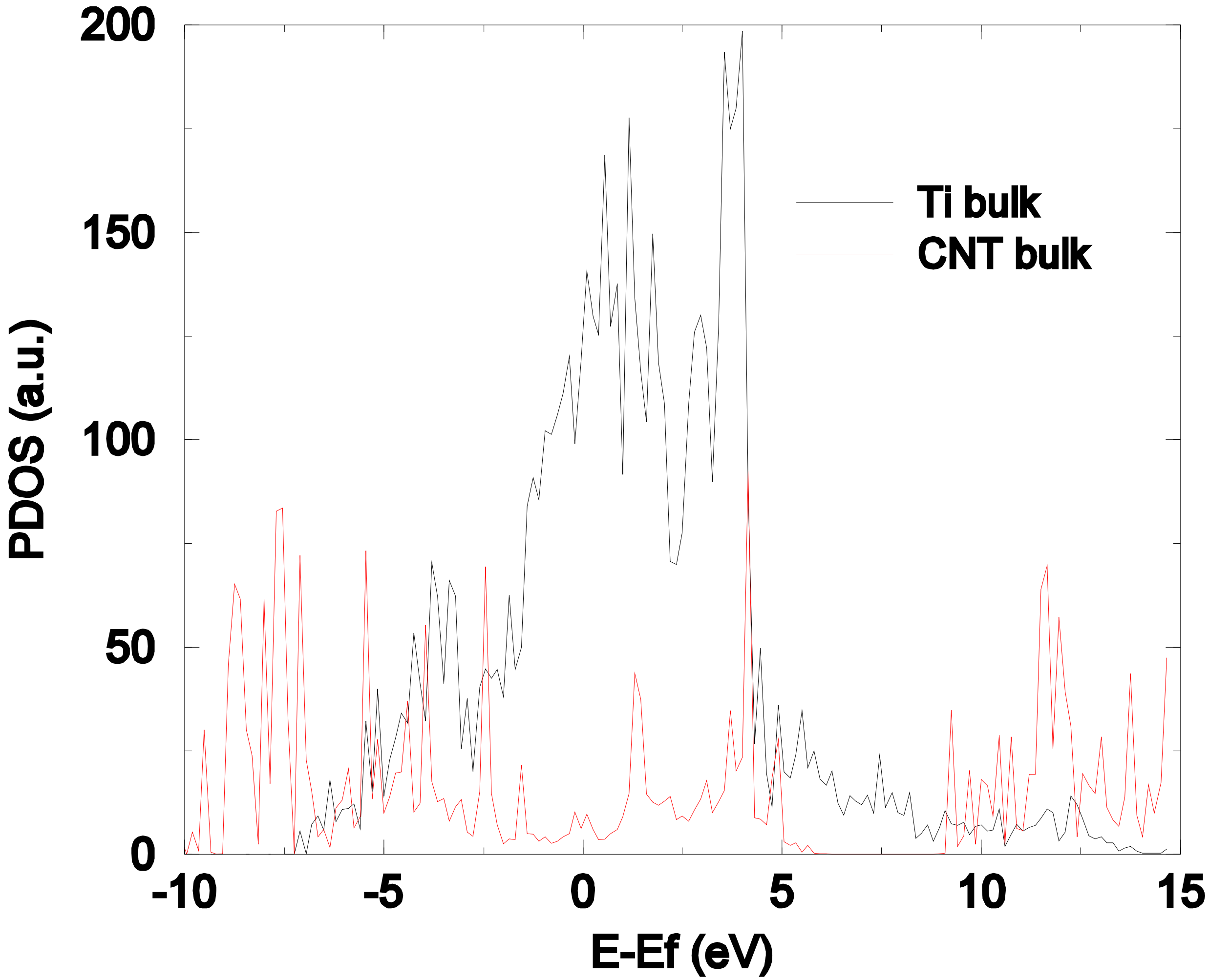
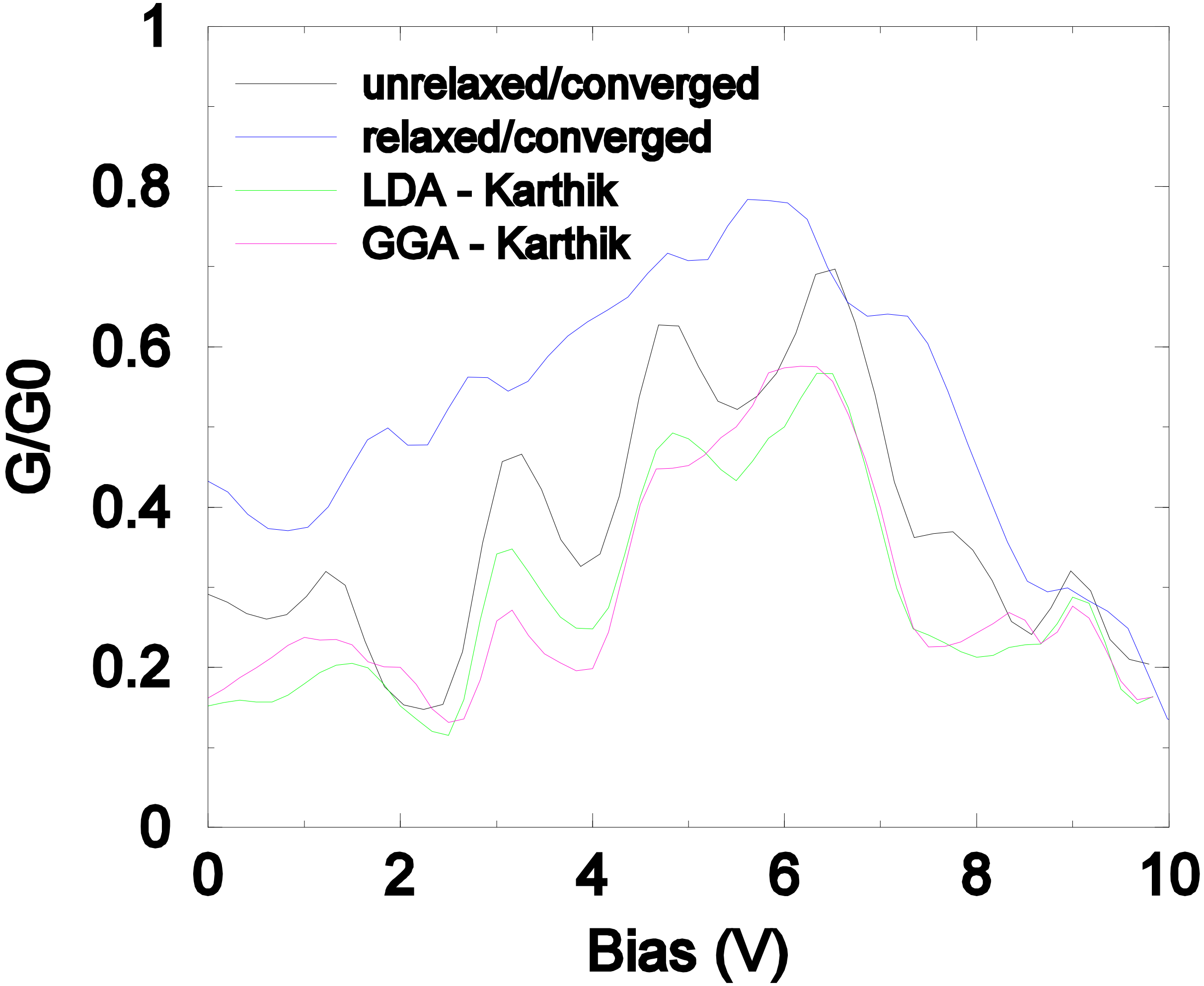


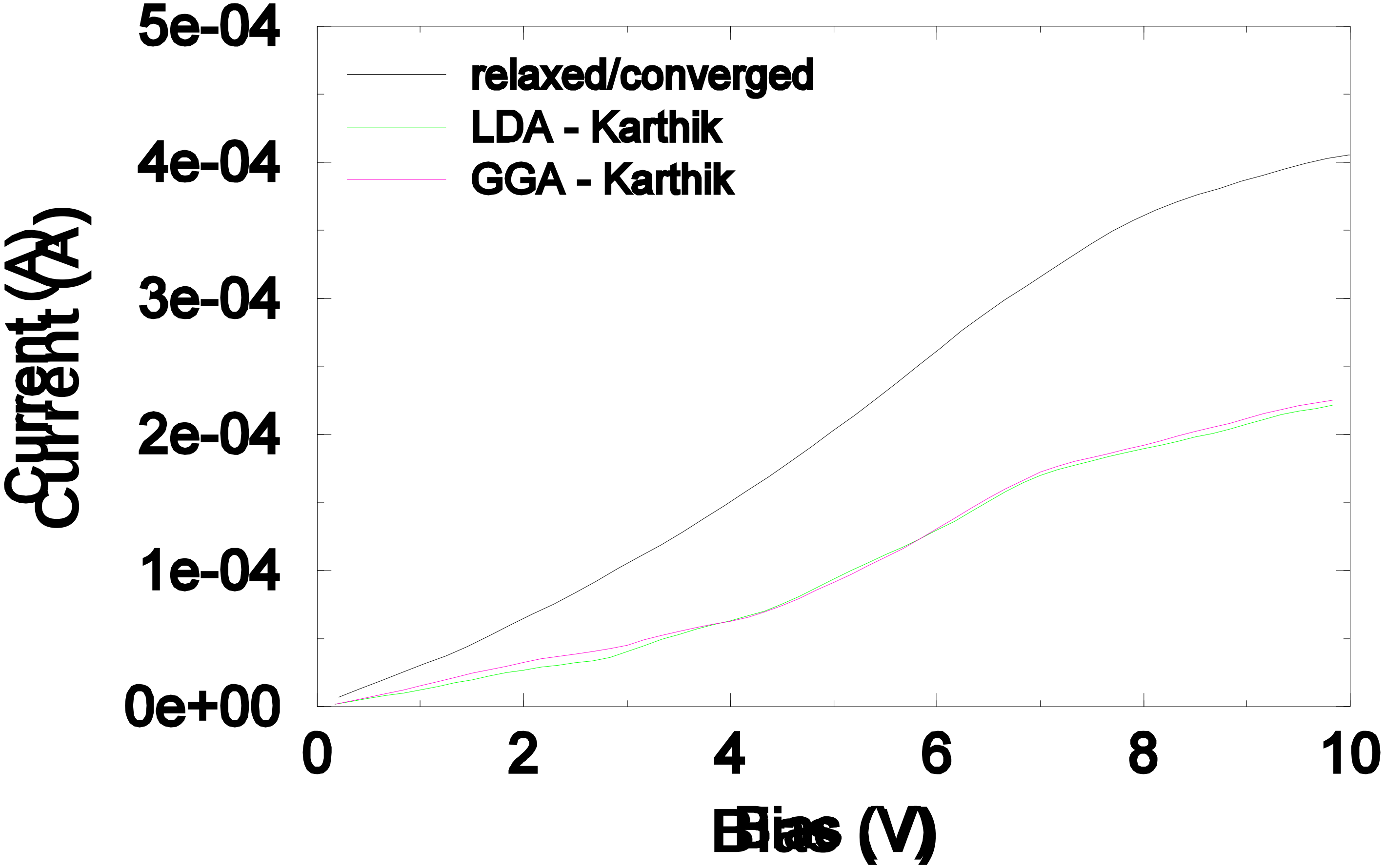

5e-04
4e-04
3e-04
2e-04
1e-04
0e+00
Current (A)
inline structure
X structure
0
2
4
6
8
10
Bias (V)



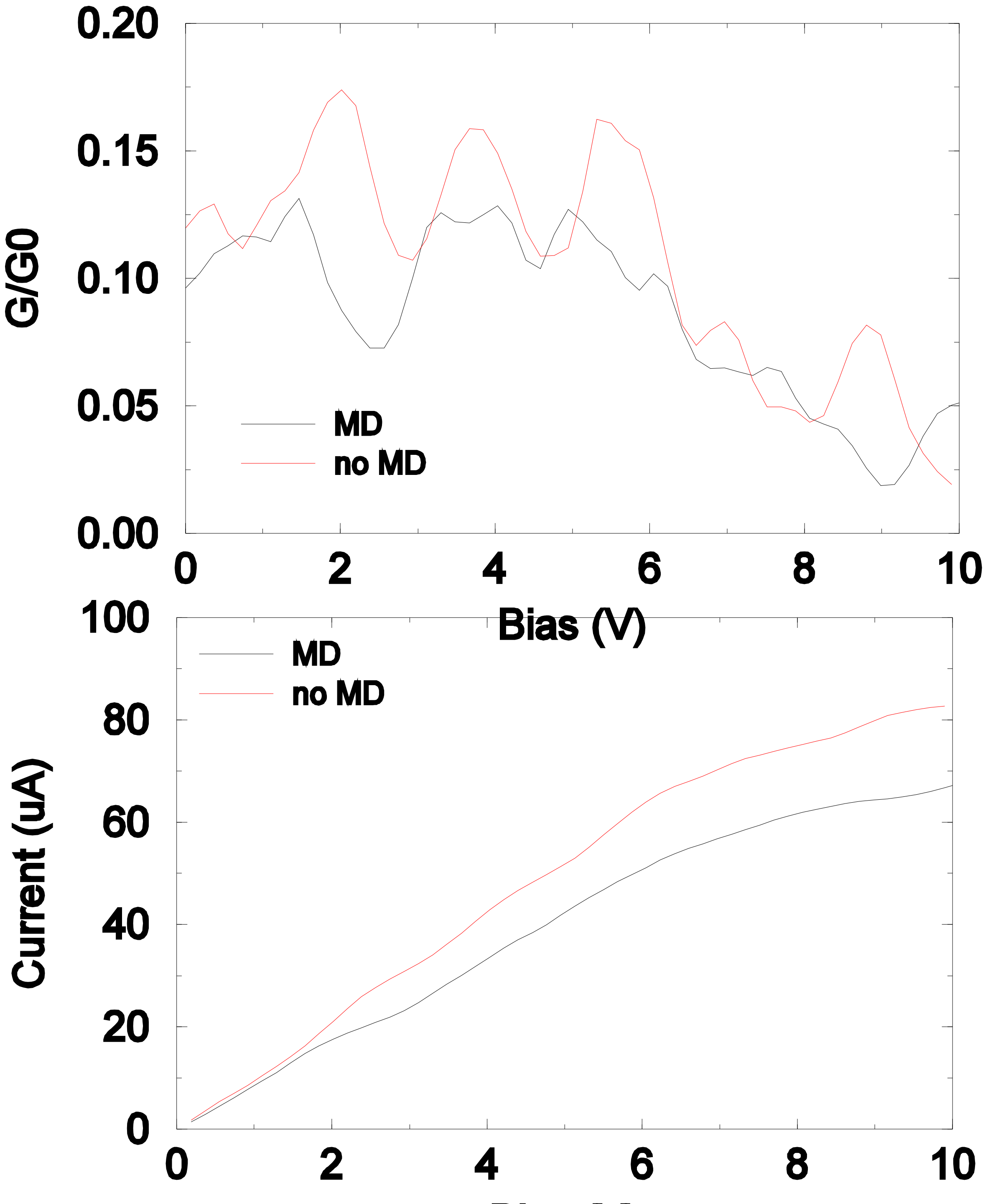
PDOS for the relaxed CNT in line with contacts. The two curves correspond to projections on atoms far away from the two interfaces. A (3,3) CNT is metallic, still there is a gap of about 4 eV. Does the gap above result from interactions with the slabs or from lack of kpts along z? This question is not so important since the Fermi level is deep into the CNT valence band.



Previous calculations and new ones. Black is unrelaxed but converged with Siesta while blue is relaxed with Vasp and converged with Siesta. From your results it looks like you started from an unrelaxed structure and is trying to converge it.



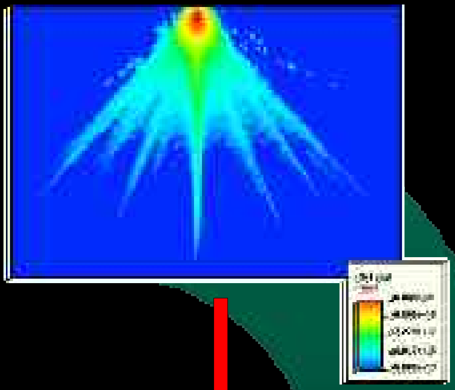
Previous calculations and new ones. Black is relaxed with Vasp and converged with Siesta.



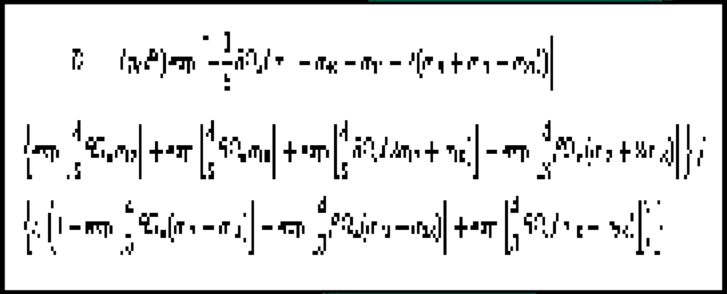
MD smoothes out most of the conductance peaks calculated without MD. However, the overall effect of MD does not seem to be very important. That is an important result because it tells us that the Schottky barrier is extremely important for the device characteristics but interface defects are not. Transport seems to average out the defects generated with MD. Notice in the lower plot that there is no exponential regime, indicating ohmic behavior. Slide 7 shows that for the aligned structure the tunneling regime is very clear up to ~6 V.

Physical Multiscale Process Modeling

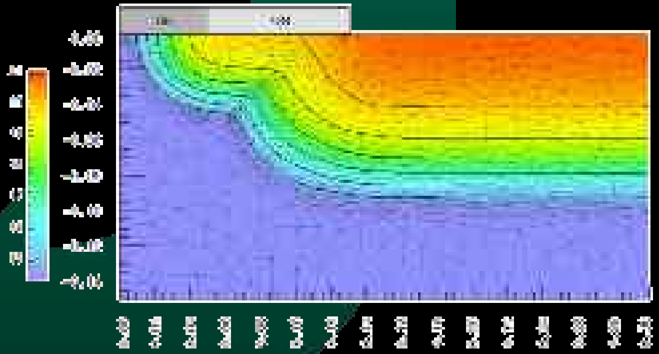
Ab Initio: Diffusion parameters, stress dependence, etc. ②

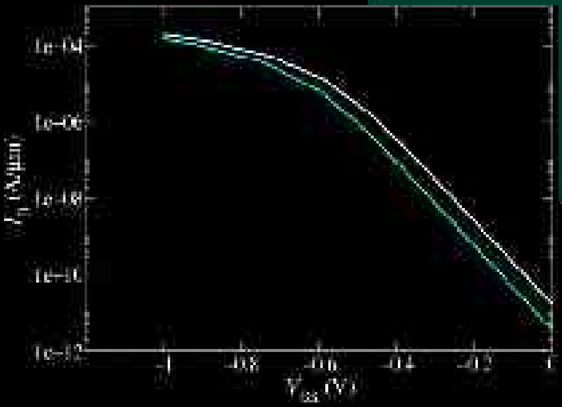


REED-MD Implant: “ab-initio” modeling (3D dopant distribution) ①



Relate atomistic calculations to macroscopic eqs. ③





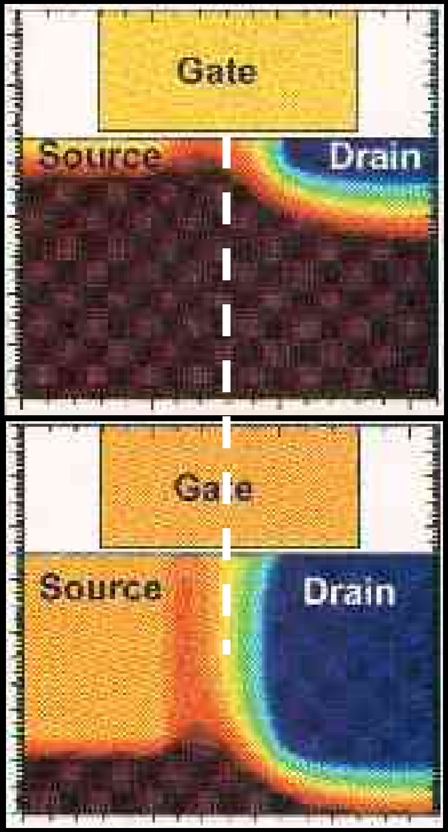
Device modeling compare modeled results to specs. Met ⇒ done, otherwise goto 1. ⑤

Diffusion Solver ④

- read in implant
- solve diffusion

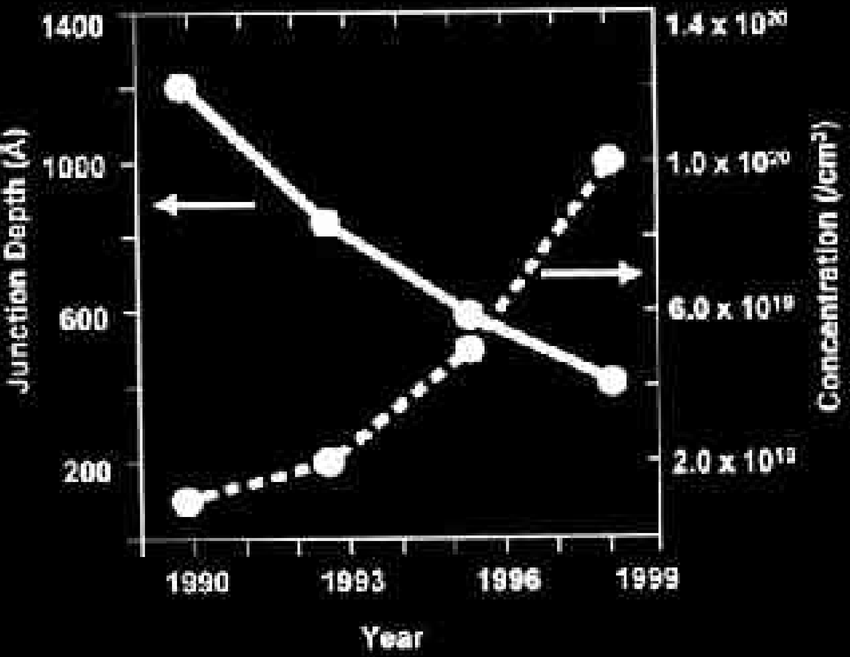
MOSFET Scaling: Ultrashallow Junctions

Shallower Implant



Better insulation (off)

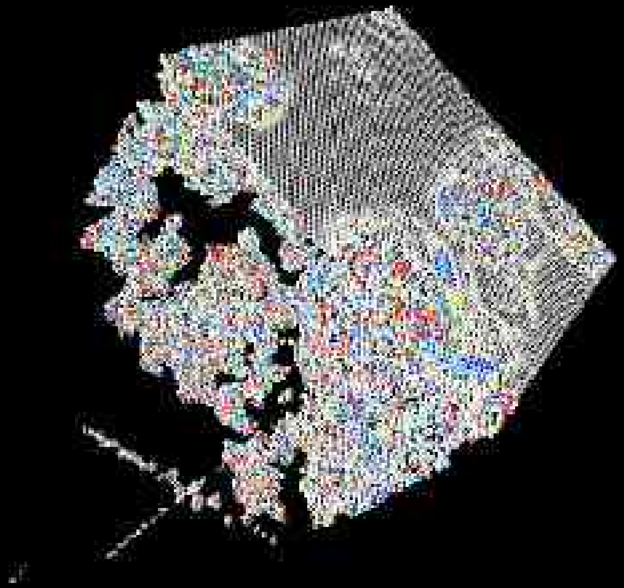
Higher Doping



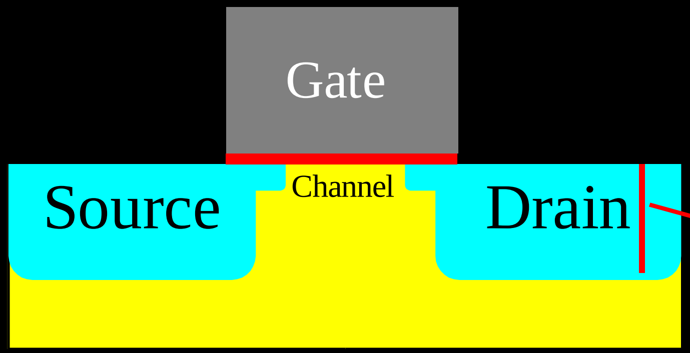
To get enough current with shallow source & drain

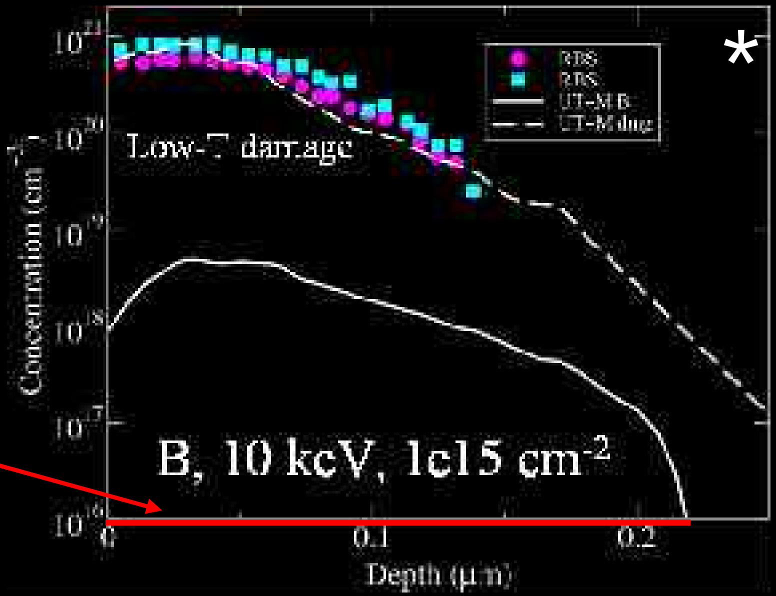
*P. Packan, MRS Bulletin

Implantation & Diffusion



- Dopants inserted by ion implantation
  ⇒ damage
- Damage healed by annealing
- During annealing, dopants diffuse fast (assisted by defects)
  ⇒ important to optimize anneal



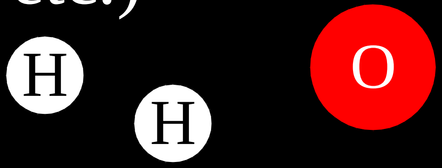


*Hoechbauer, Nastasi, Windl

Ab-Initio Calculations – Standard Codes

Input:

- Coordinates and types of group of atoms (molecule, crystal, crystal + defect, etc.)

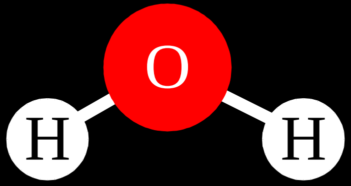


Output:

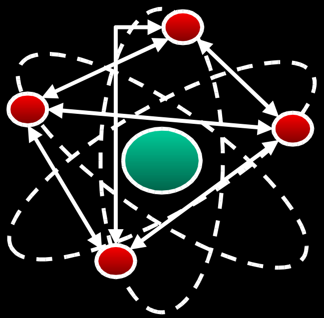
- Solve quantum mechanical Schrödinger equation, $H\psi = E\psi \Rightarrow$ **total energy of system**
- Calculate forces on atoms, update positions

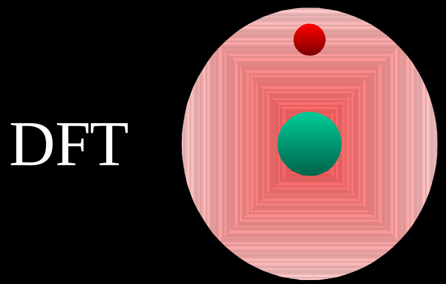
  $\Rightarrow$ **equilibrium configuration**

  $\Rightarrow$ **thermal motion (MD), vibrational properties**



Ab-Initio Calculations

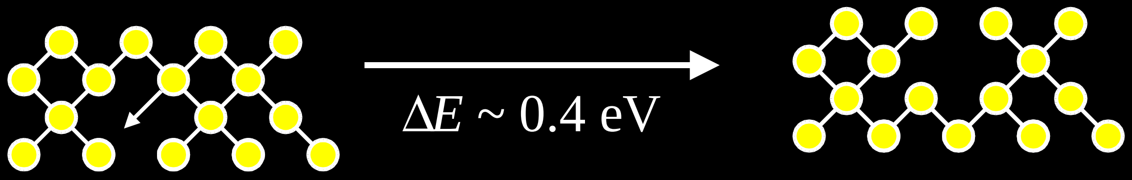


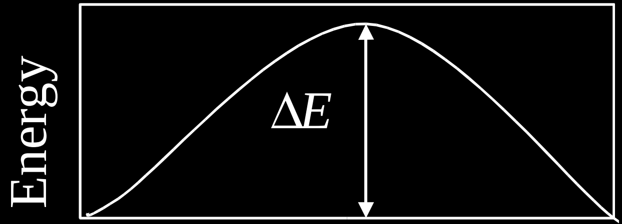


- Error from effective potential corrected by (exchange-)correlation term
  - Local Density Approximation (LDA)
  - Generalized-Gradient Approximations (GGAs)
  - Others ("Exact exchange", "hybrid functionals" etc.)
  - "Correct one!?"
- "Everybody' s" choice:
  Ab-initio code VASP (Technische Universität Wien), LDA and GGA

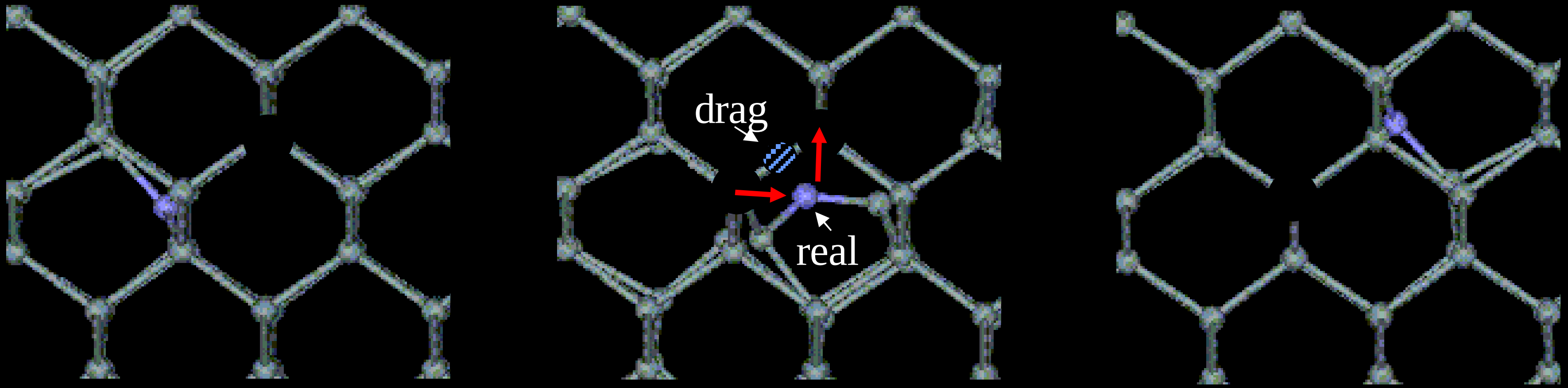
How To Find Migration Barriers I

Easy Can guess final state & diffusion path (e.g. vacancy diffusion)
"By hand", "drag" method. Extensive use in the past.





Fails even for exchange N-V in Si ("detour" lowers barrier by ~2 eV)

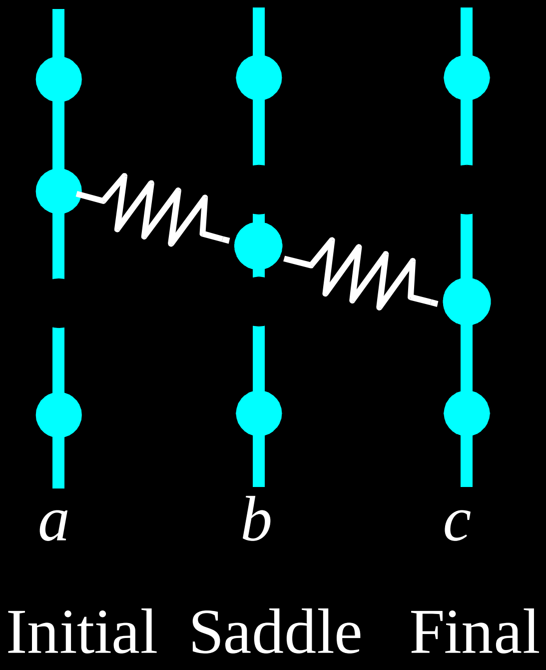


Unreliable!

How To Find Migration Barriers II

New ***reliable*** search methods for diffusion paths exist like:

- Nudged elastic band method (Jónsson *et al*.). Used in this work.
- Dimer method (Henkelman *et al*.)
- MD (usually too slow); but can do “accelerated” MD (Voter)
- All in VASP, easy to use.

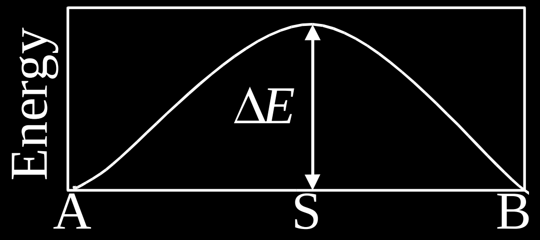


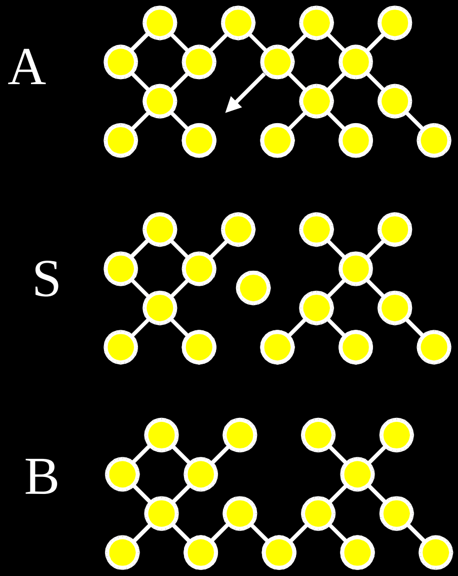
Elastic band method:

Minimize energy of all snapshots plus spring terms, E_{chain}:

Calculation of Diffusion Prefactors

- Vineyard theory
- From vibrational frequencies





- Phonon calculation in VASP
- Download our scripts from Johnsson group website (UW)

Reason for TED: Implant Damage

NEBM-DFT: Interstitial assisted two-step mechanism:

Intrinsic diffusion:

Create interstitial, B captures interstitial, diffuse together

$\Rightarrow$ Diffusion barrier: $E_{\mathrm{form}}(I) - E_{\mathrm{bind}}(\mathrm{B}I) + E_{\mathrm{mig}}(\mathrm{B}I)$

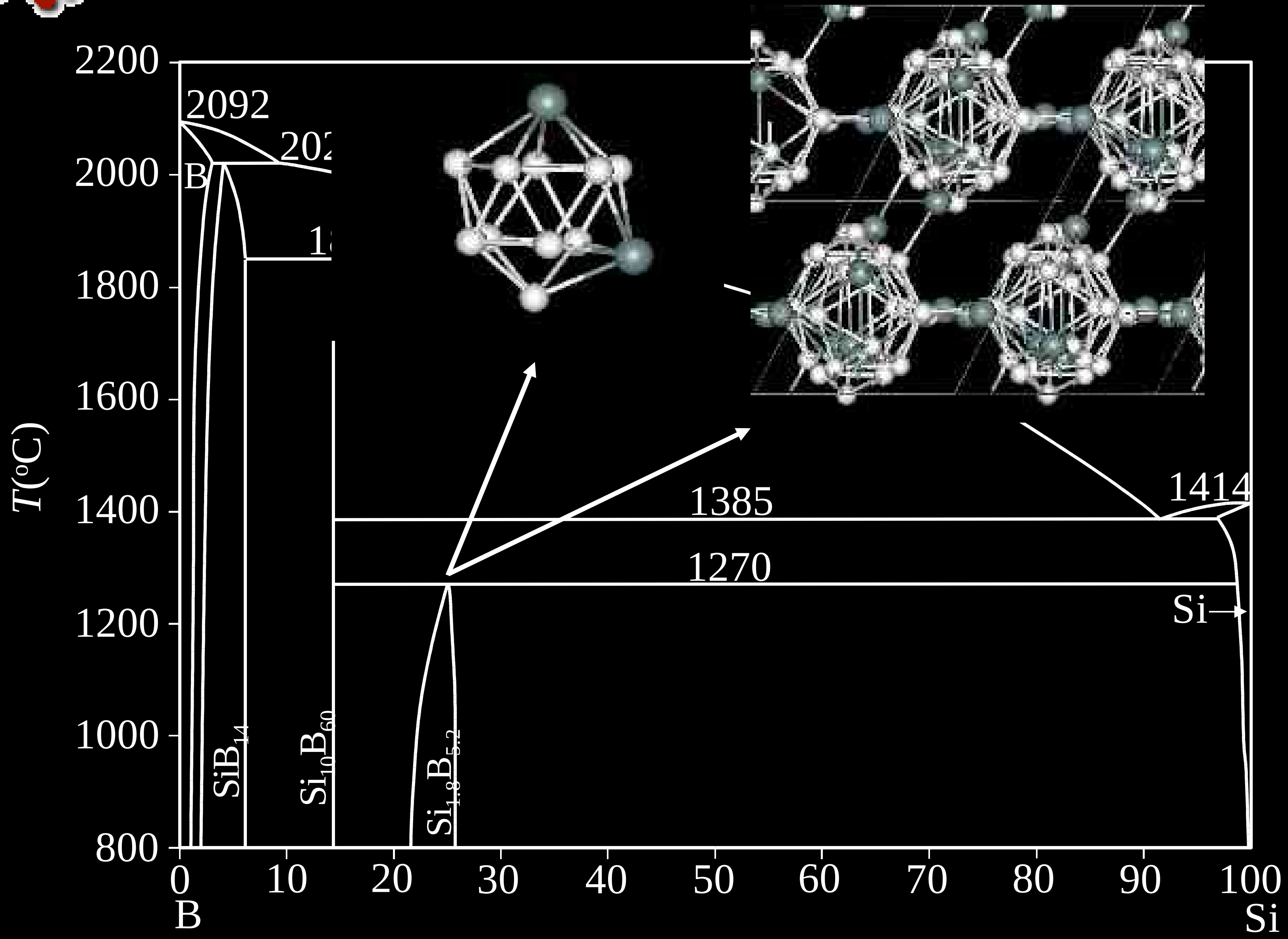
4 eV 1 eV 0.6 eV ~ 3.6 eV

After implant:

Interstitials for “free” $\Rightarrow$ transient enhanced diffusion

W. Windl, M.M. Bunea, R. Stumpf, S.T. Dunham, and M.P. Masquelier,
Proc. MSM99 (Cambridge, MA, 1999), p. 369; MRS Proc. **568**, 91 (1999); Phys. Rev. Lett. **83**, 4345 (1999).

Reason for Deactivation – Si-B Phase Diagram



Deactivation – Sub-Microscopic Clusters

Experimental findings:

- Structures too small to be seen in EM ⇒ only “few” atoms
  - New phase nucleates, but decays quickly
- Clustering dependent on B concentration and interstitial concentration

  ⇒ formation of $B_m I_n$ clusters postulated;

  experimental estimate: $m / n \sim 1.5$*

⇒ *Approach*:

- Calculate clustering energies from first principles up to “max.” m, n
- Build continuum or atomistic kinetic-Monte Carlo model

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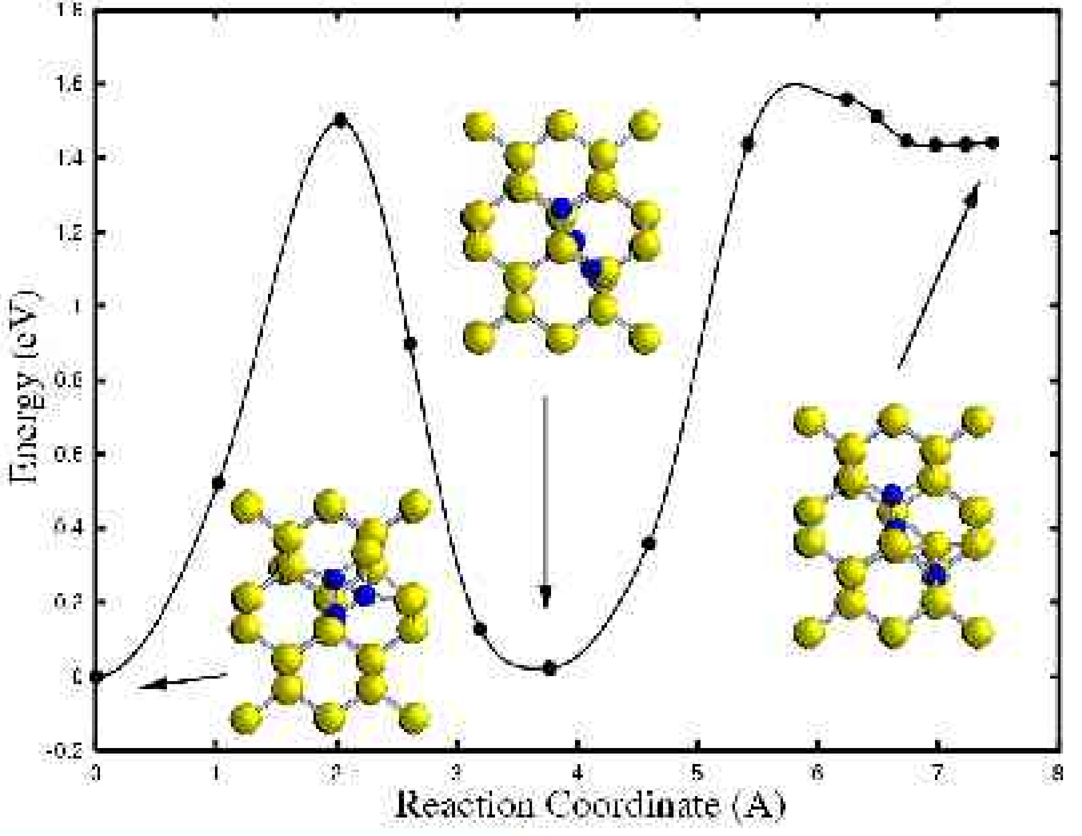
*S. Solmi *et al.*, JAP **88**, 4547 (2000).

Cluster Formation – Reaction Barriers



Dimer study of the breakup of B_3I_2 into B_2I and BI showed:*

- BIC reactions diffusion limited
- Reaction barrier can be well approximated by difference in formation energies plus migration energy of mobile species.

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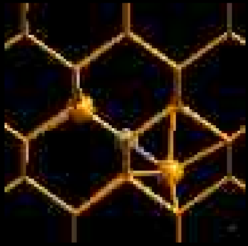
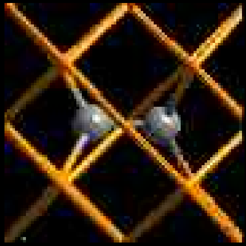
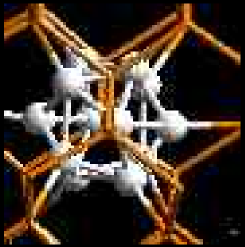
*Uberuaga, Windl *et al.*

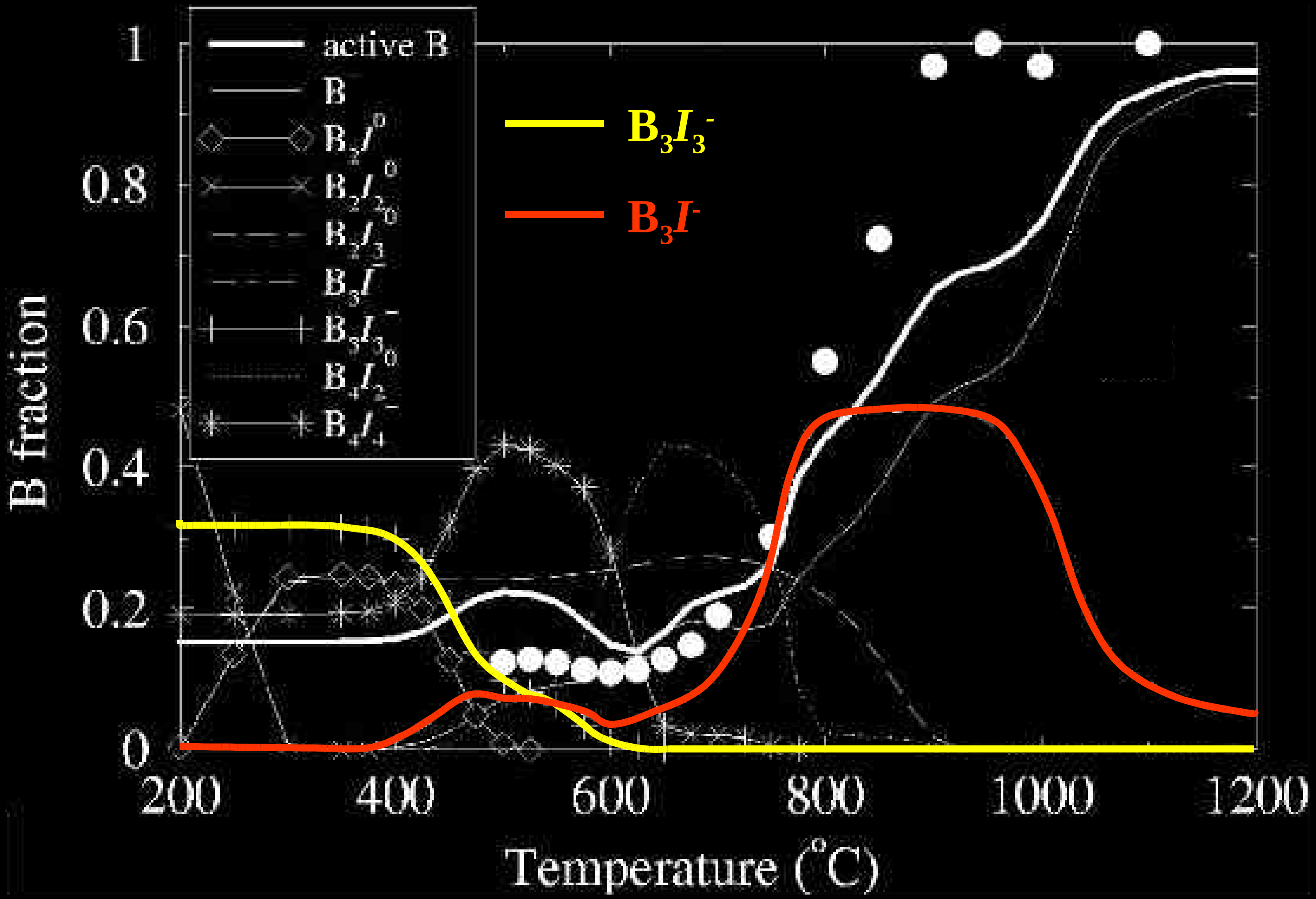
B-I Cluster Structures from *Ab Initio* Calculations

B_xI	BI^+	LDA –0.5	GGA –0.4	
	B_2I^0	–2.0	–1.2	
	B_3I^-	–3.0	–2.2	
	B_4I^{2-}	–5.5	–4.3	
B_xI_2	BI_2^0	–2.5	–2.3	
	$B_2I_2^0$	–3.0	–2.4	
	$B_3I_2^0$	–4.1	–2.6	
	$B_4I_2^0$	–5.5	–4.3	
B_xI_3	BI_3^+	–4.8	–4.5	
	$B_2I_3^0$	–6.0	–5.3	
	$B_3I_3^-$	–6.6	–5.6	
	$B_4I_3^-$	–7.0	–5.9	
I>3	$B_4I_4^-$	–9.2	–7.8	
	$B_{12}I_7^{2-}$	–24.4	N/A	

X.-Y. Liu, W. Windl, and M. P. Masquelier, APL **77**, 2018 (2000).

Activation and Clusters

30 min anneal, different *T* (equiv. constant *T*, varying times)

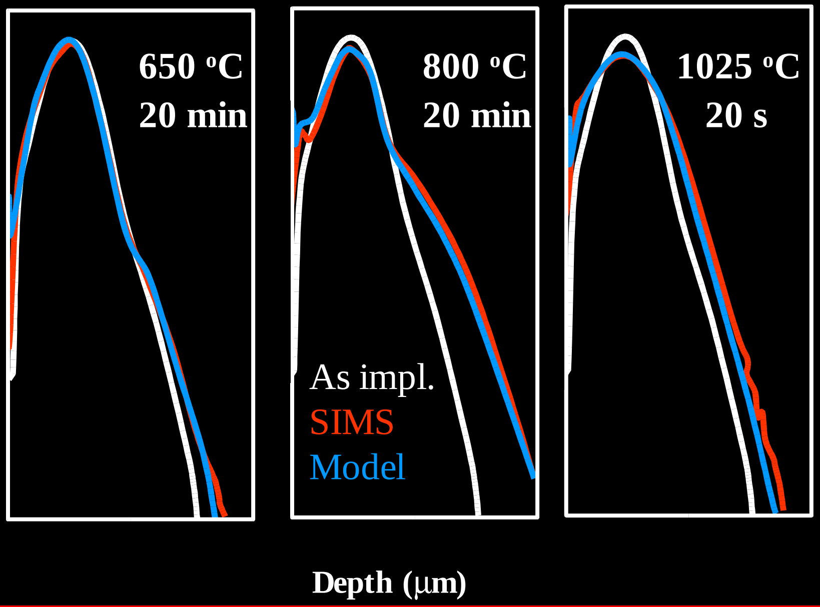


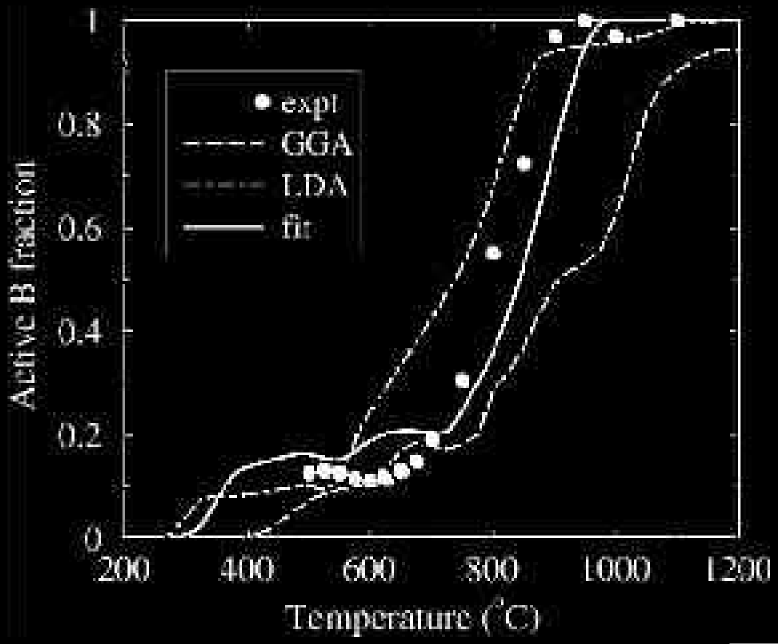
Calibration with SIMS Measurements

- Sum of small errors in ab-initio exponents has big effect on continuum model

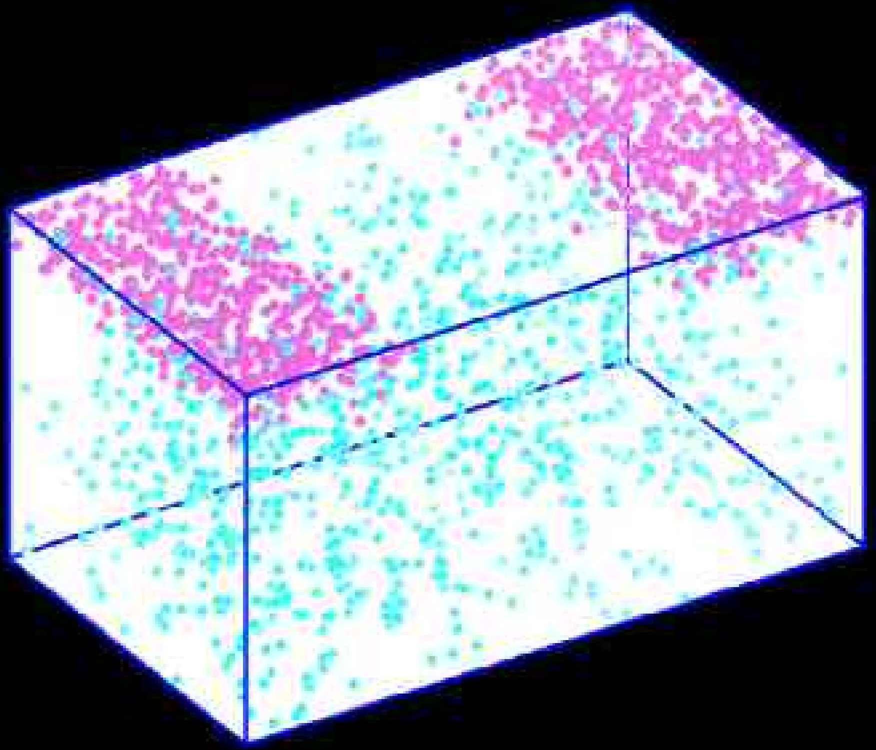
∀⇒ refining of ab-initio numbers necessary

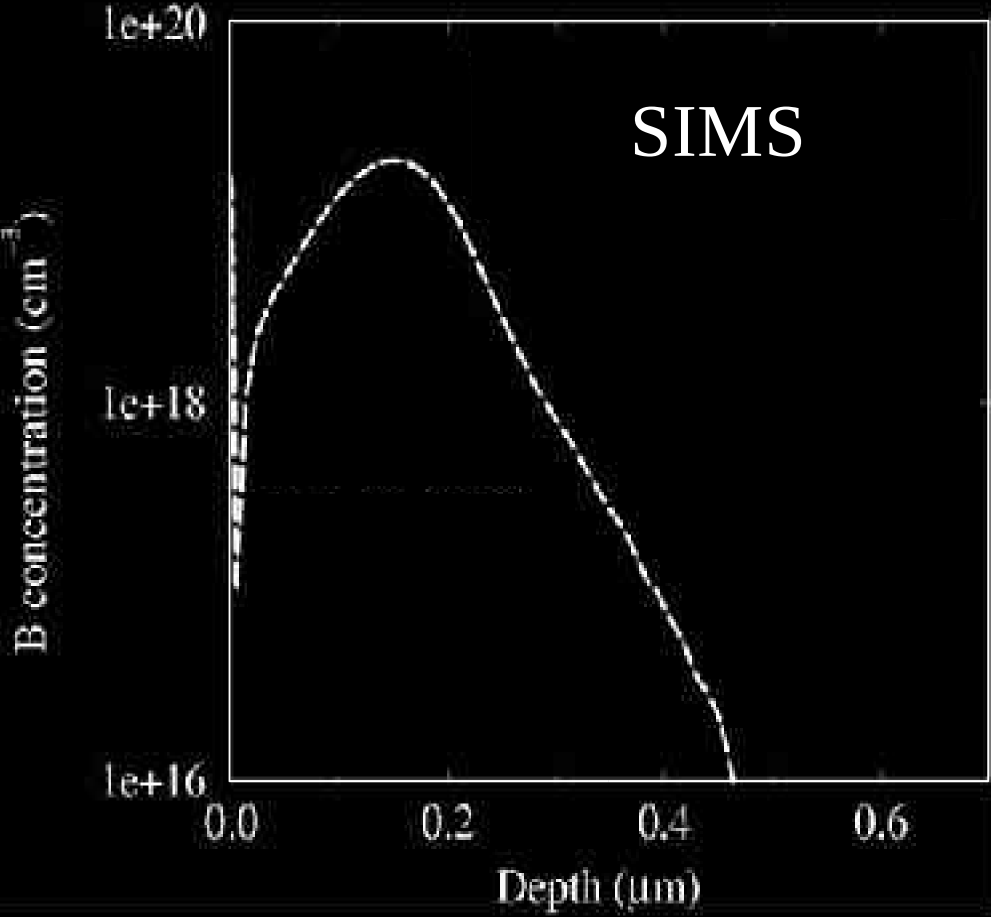
- Use Genetic Algorithm for recalibration





Statistical Effects in Nanoelectronics: Why KMC?





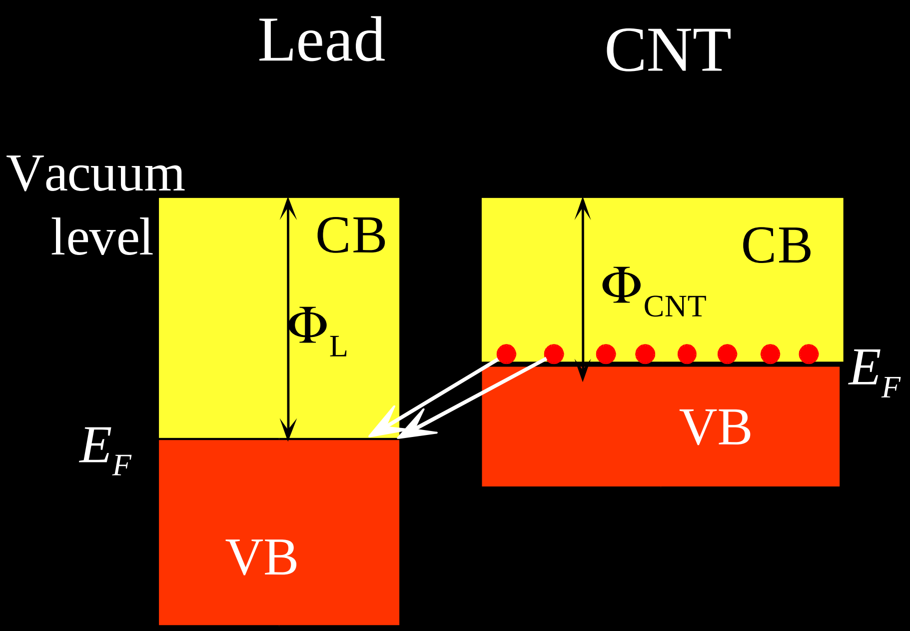
Need to think about exact distribution ⇒ atomic scale!

*A. Asenov

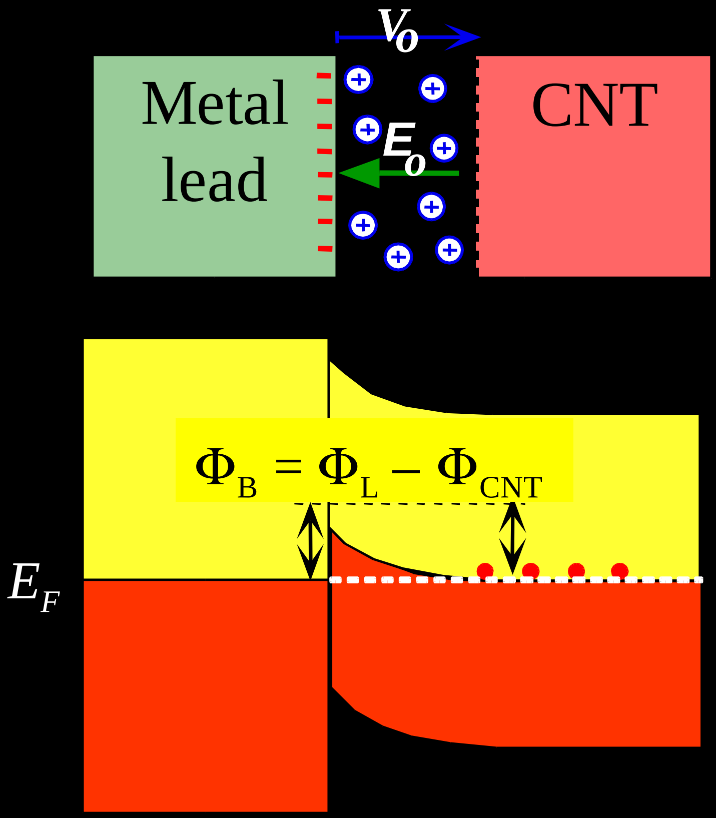
Conclusion 1

- Atomistic, especially ab-initio, calculations very useful to determine equation set and parameters for physical process modeling.
- First applications of this “virtual fab” in semiconductor field.
- In future, atomistic modeling needed (example: oxidation model later).

CNT-FET as Schottky Junction



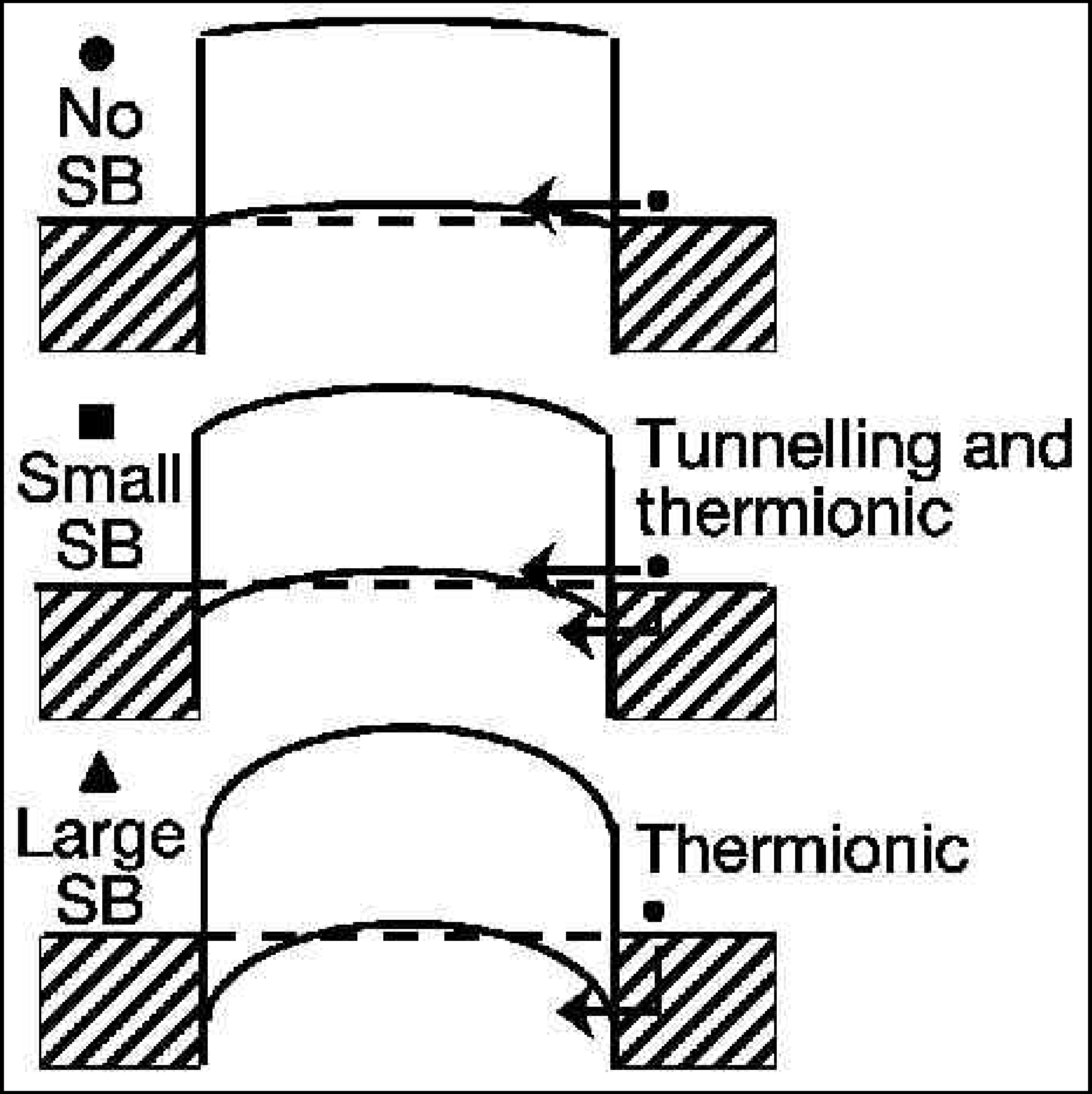
Before contact

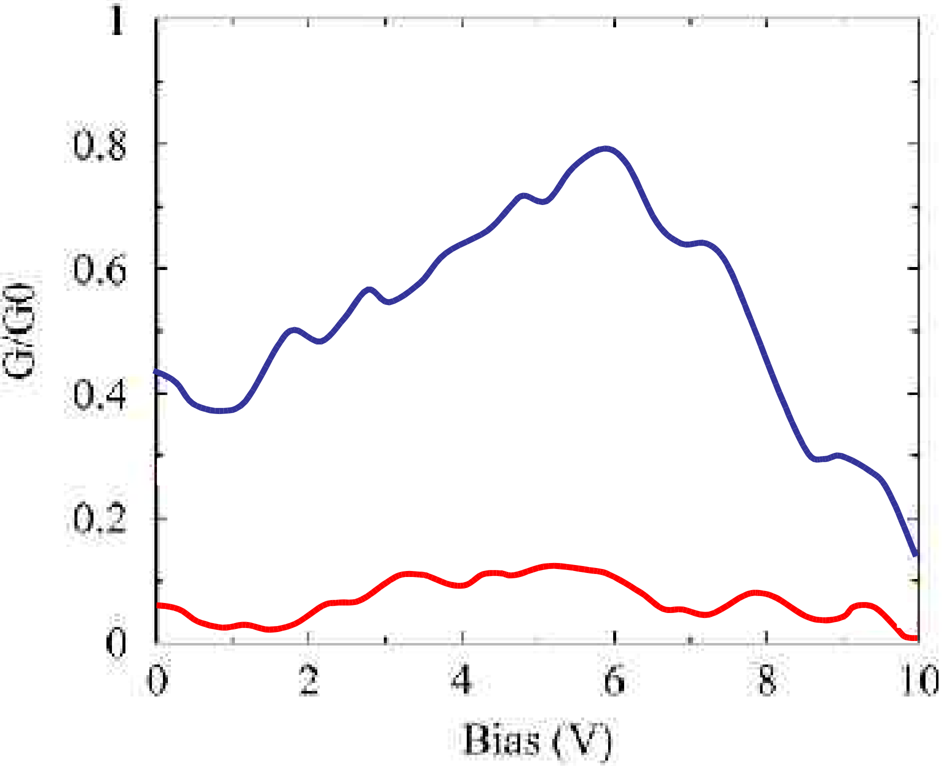


After contact

Desirable: $\Phi_B = 0$ to minimize contact resistance.

Metals with “right” Φ_B: Pt, Ti, Pd.


●
No SB
■
Small SB
Tunnelling and thermionic
▲
Large SB
Thermionic



Notice the difference in the y-axis. The X structure (below) carries a current which is about one order of magnitude smaller than the CNT inline with the contacts (left)

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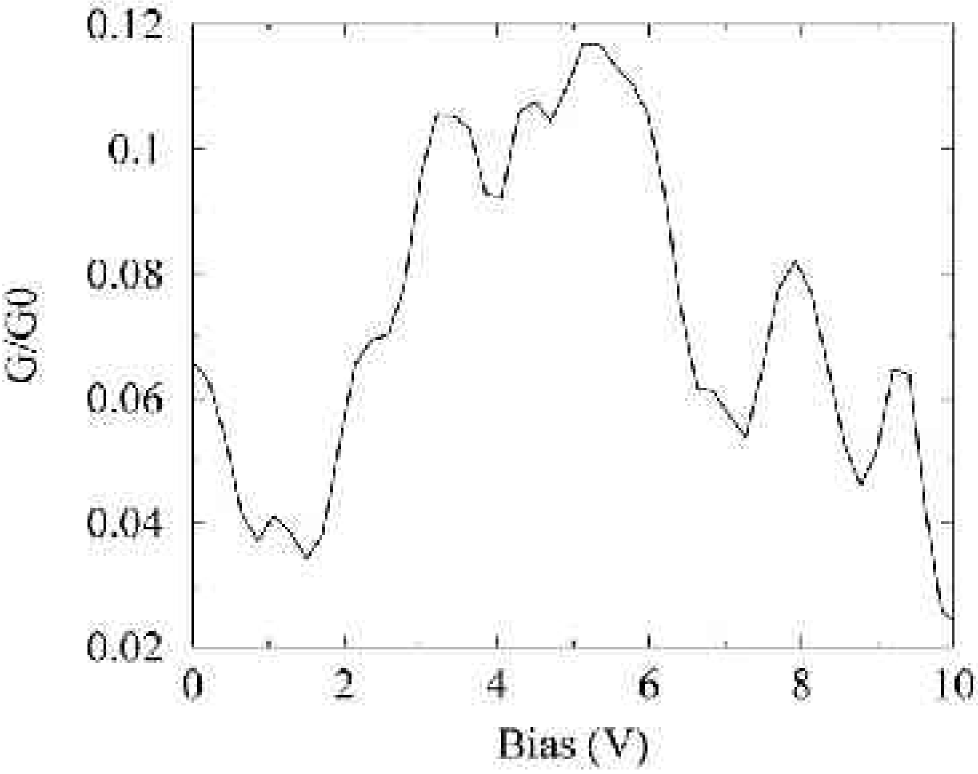
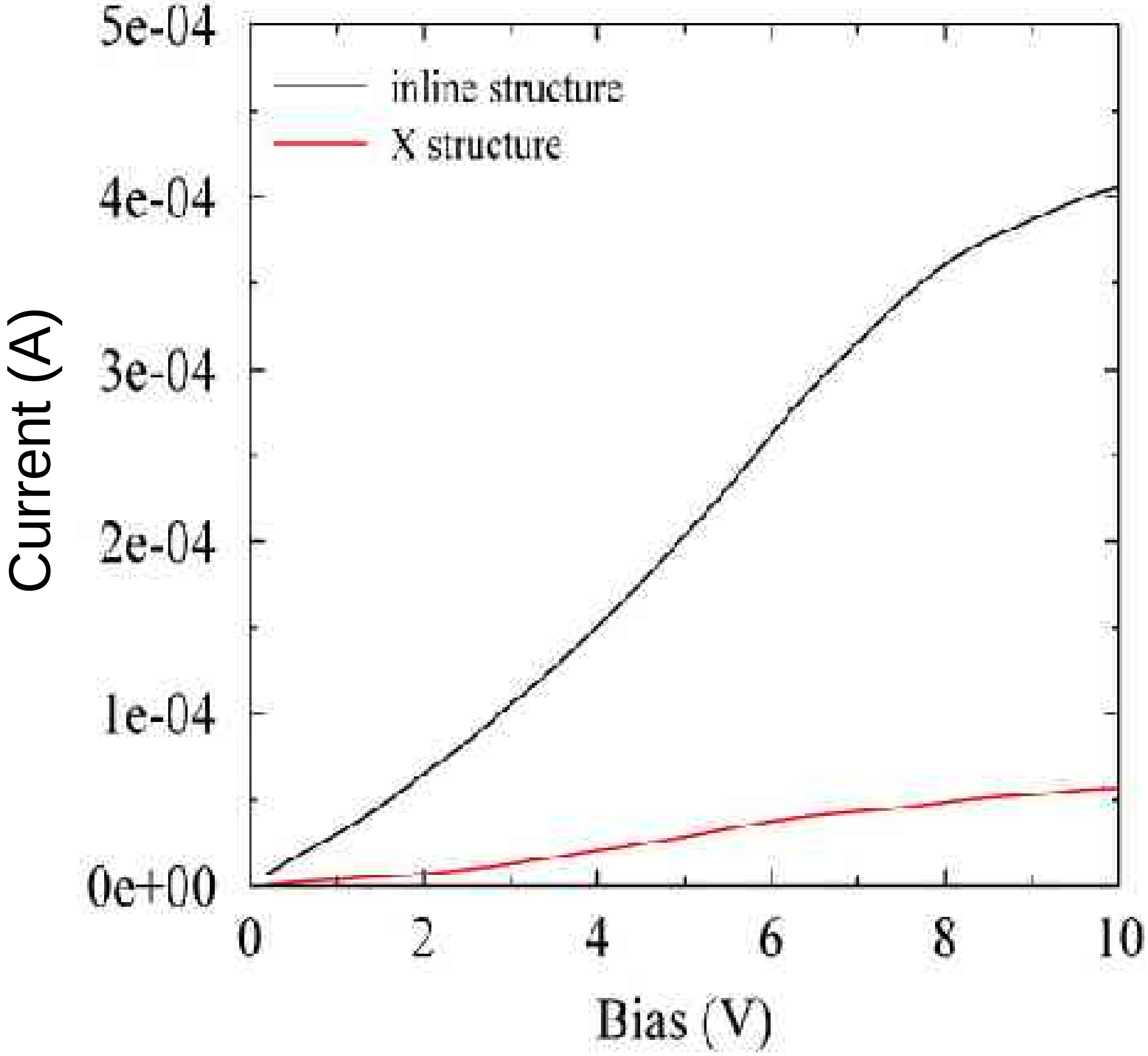
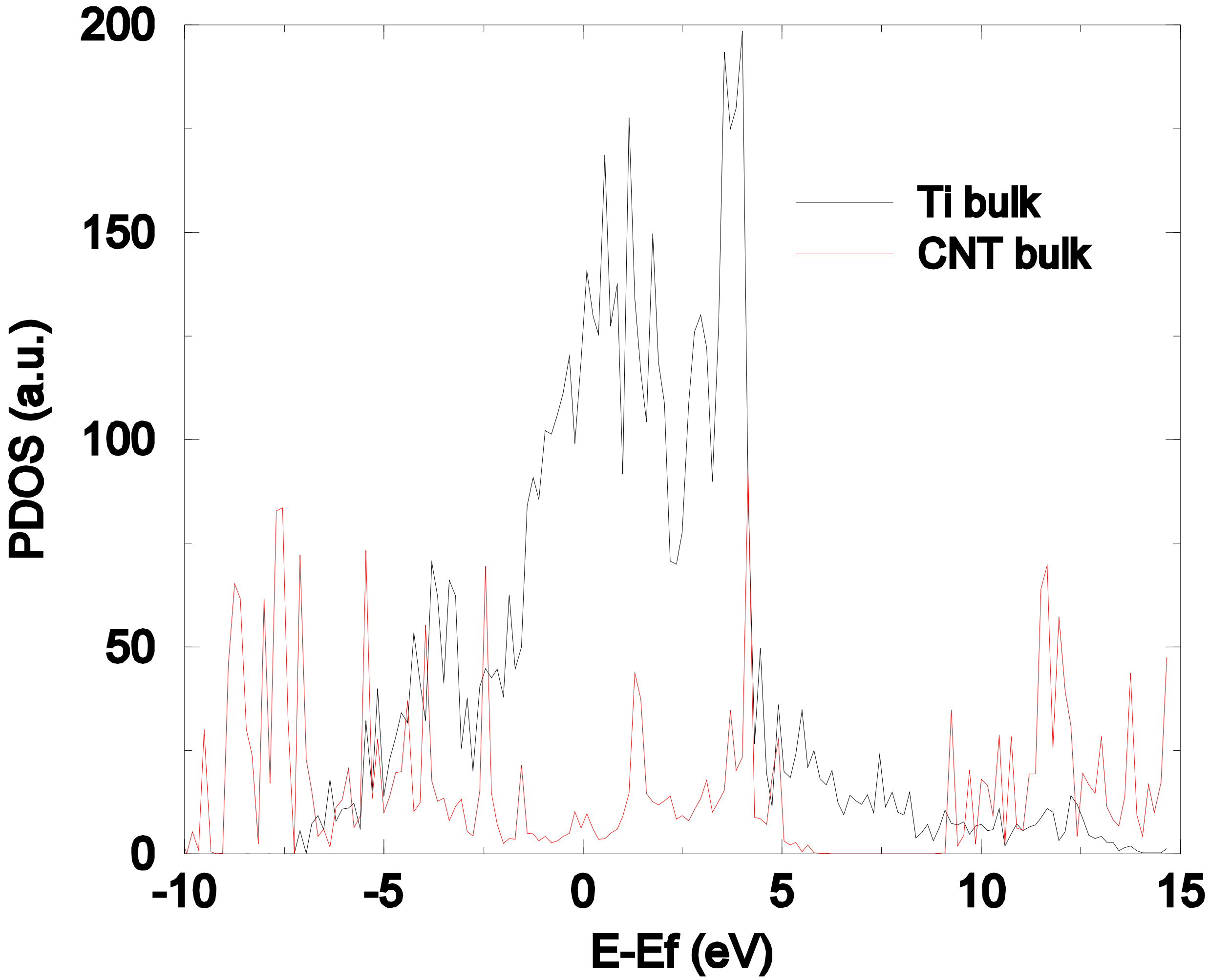




inline structure
X structure
Current (A)
5e-04
4e-04
3e-04
2e-04
1e-04
0e+00
0
2
4
6
8
10
Bias (V)



PDOS for the relaxed CNT in line with contacts. The two curves correspond to projections on atoms far away from the two interfaces. A (3,3) CNT is metallic, still there is a gap of about 4 eV. Does the gap above result from interactions with the slabs or from lack of kpts along z? This question is not so important since the Fermi level is deep into the CNT valence band.