Modeling interfaces and surfaces using density functional theory and Non-Equilibrium Green's Functions

Umberto Martinez Pozzoni, PhD

Quantum Wise

Ruđer Bošković Institute, 07/03/2017

QuantumWise – company background

- Founded in 2008 (but goes back to 2003)
- Specialists in simulation software for atomic-scale modeling
- 35 FTEs; majority has a PhD (+3-5/year)
- Headquarter in Copenhagen, Denmark
- Sales reps in USA, Singapore, Japan
- Resellers in India, China, Taiwan, Korea, …
- Profitable with 25% growth rate – no external capital

- Market leader in atomic-scale modeling software for the semiconductor industry

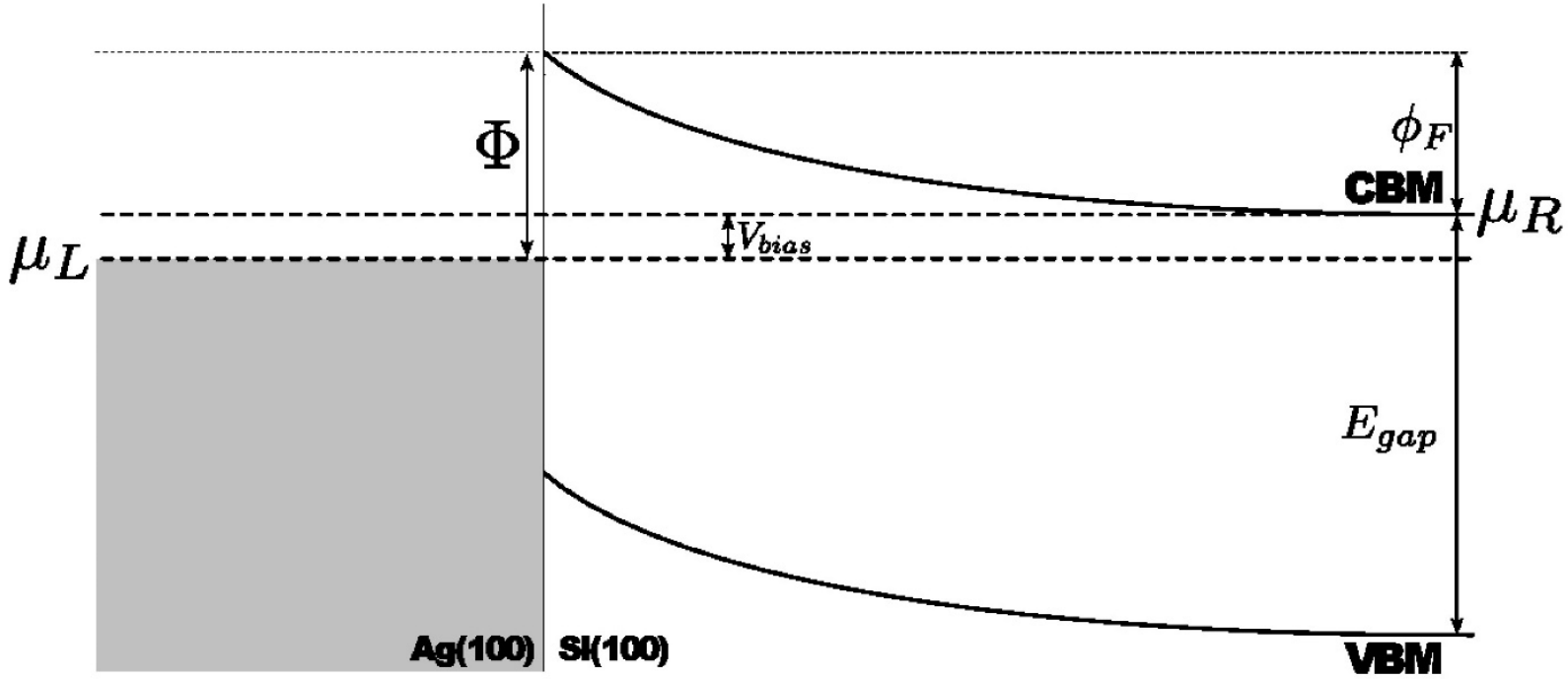
- Growing usage in the materials and chemical industry

- More than 300 users worldwide
- Rapidly expanding number of academic and industrial users

Outline

- **Modeling metal-semiconductor interfaces using Atomistix ToolKit (ATK)**
  1) Description of the interface using the DFT+NEGF method
  2) Semiconductor band-gap using MGGA xc-functional
  3) Semiconductor effective doping
- **Results: Ag(100)/Si(100) interface**
  1) Validation of the activation energy model
  2) I-V analysis based on the electronic properties of the interface
- **One-probe surface configuration**
  1) Si(100) surface
  2) Band alignment in semiconductor heterostructure, Si film on Ge(100)

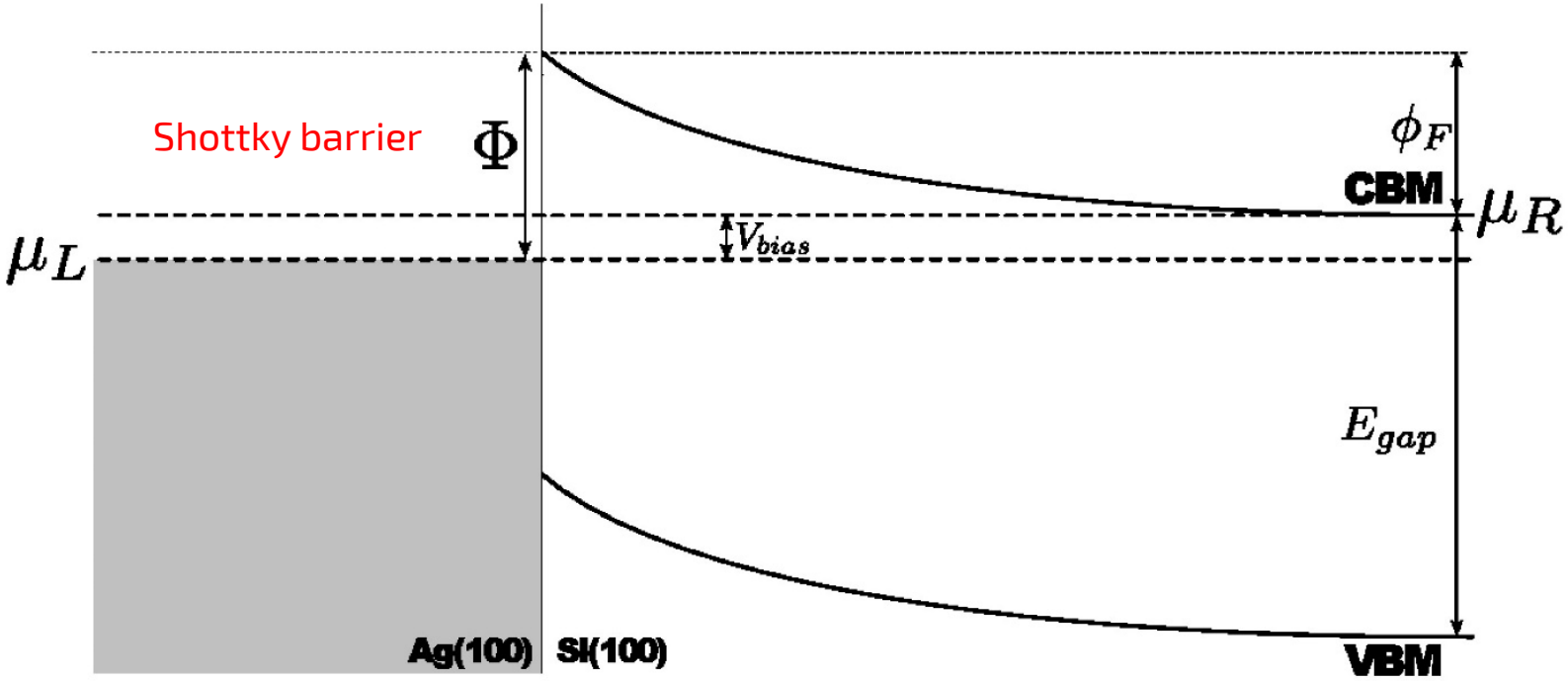
Metal-semiconductor interface



Sze, Ng *Physics of Semiconductor Interfaces 3rd ed.* Wiley 2007

Metal-semiconductor interface – Key aspects

Finite bias

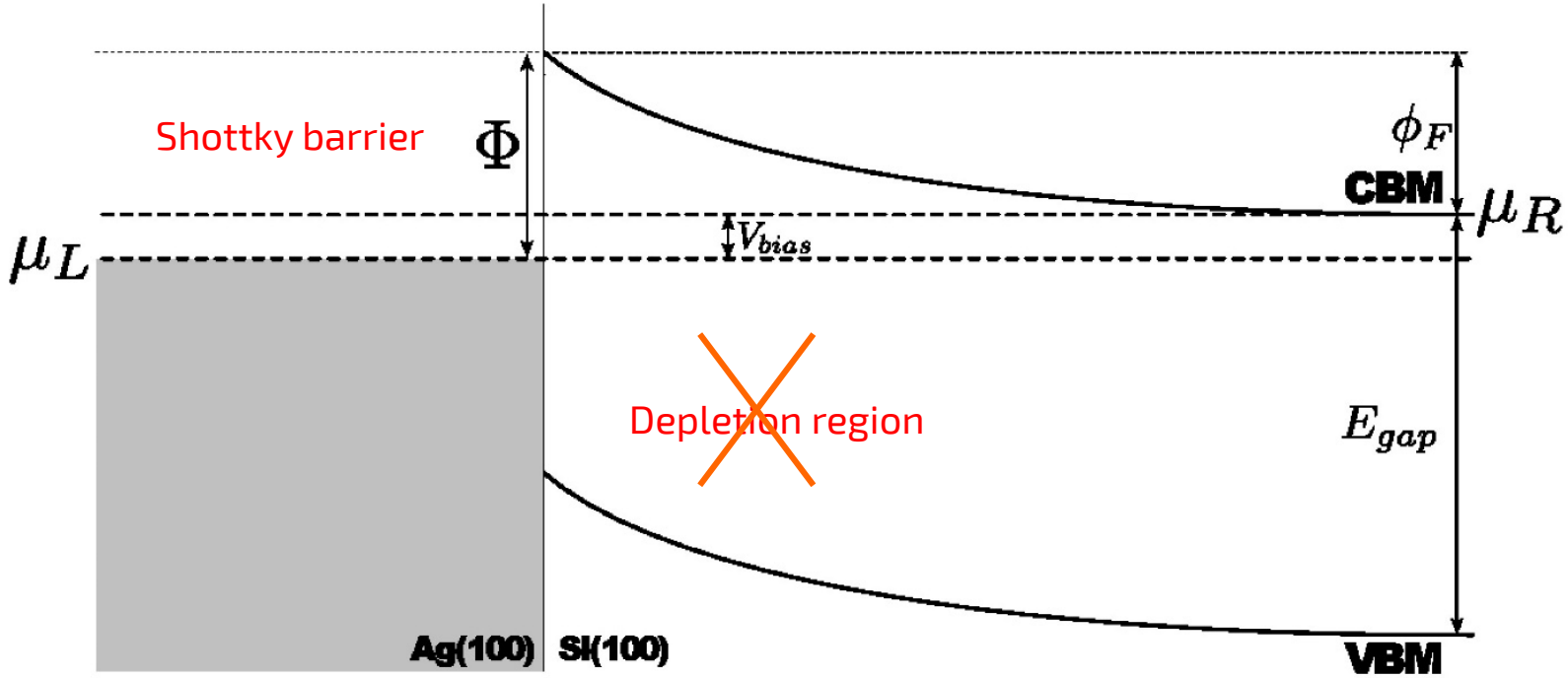


Doping

Depletion region

Metal-semiconductor interface

Traditional modeling – finite size slab



Finite bias

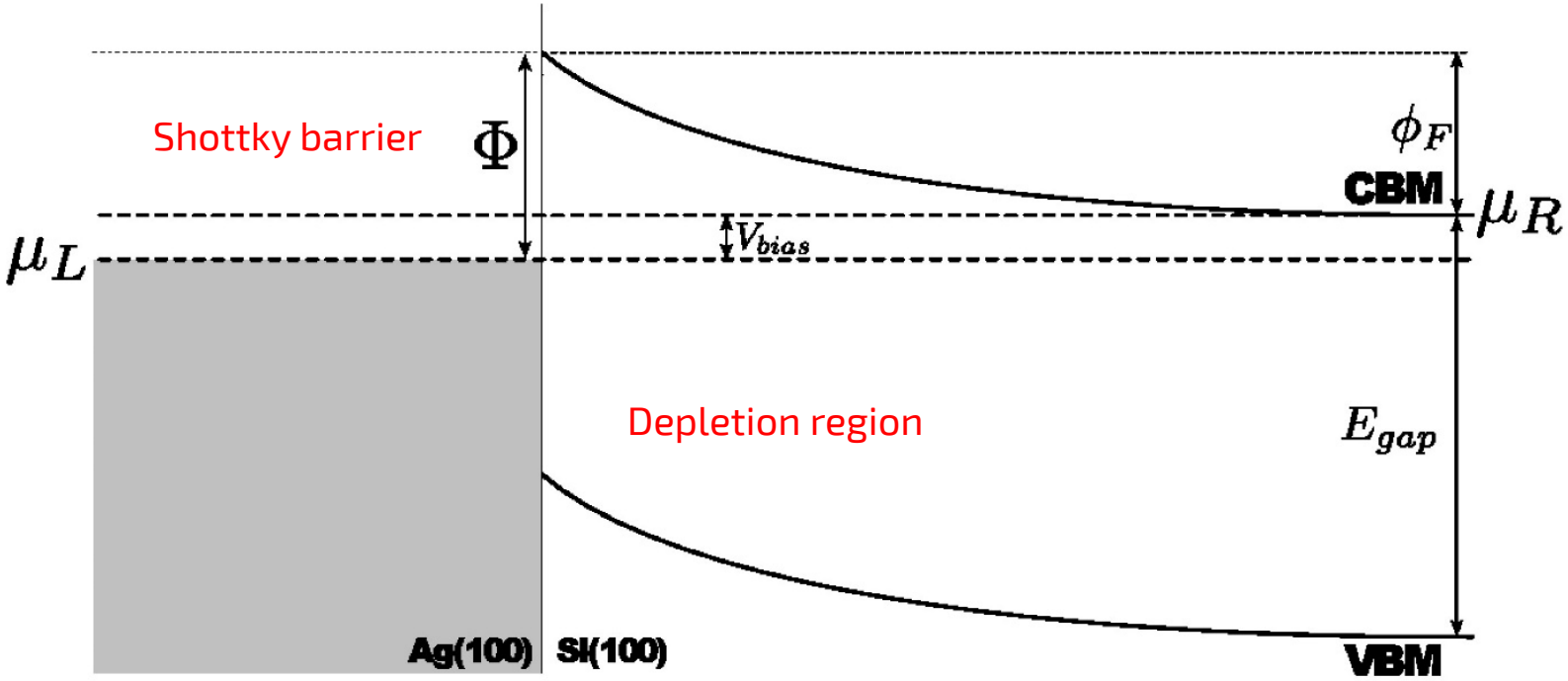
Doping

- Interface model is much smaller than the depletion region
- No doping
- No bias
- Very indirect comparison to experimental measurements

Metal-semiconductor interface

Two-probe configuration using Atomistix ToolKit (ATK)

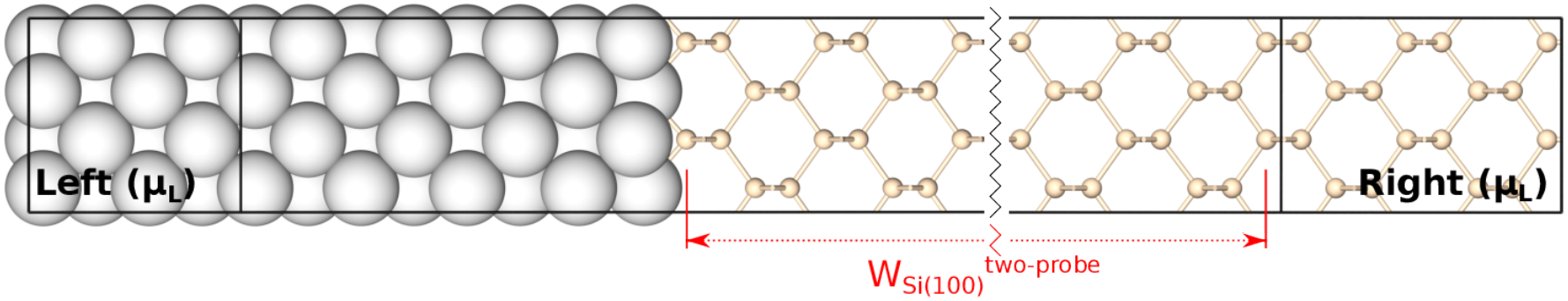
Finite bias



Doping

1) Description of the interface using the DFT+NEGF method
2) Semiconductor band-gap using MGGA xc-functional
3) Semiconductor effective doping

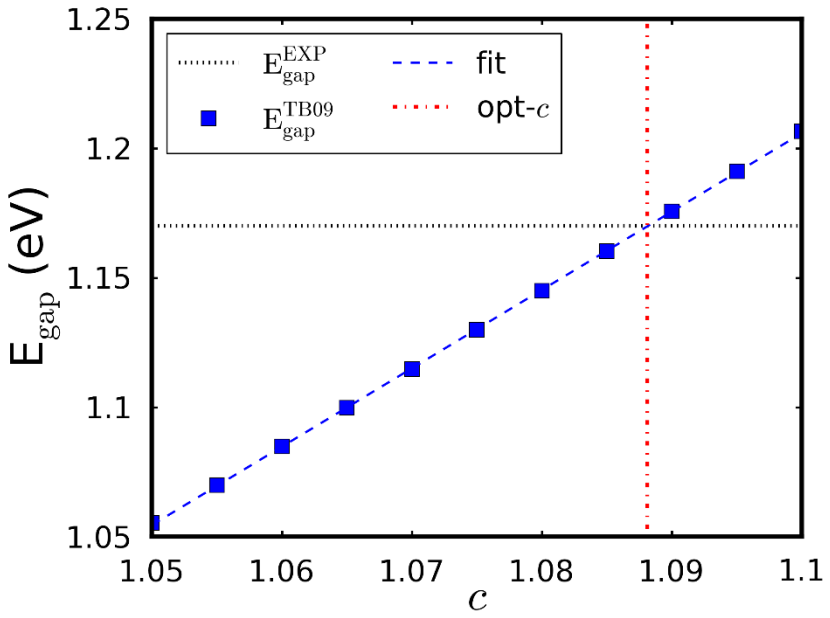
1) Description of the interface using the DFT+NEGF method

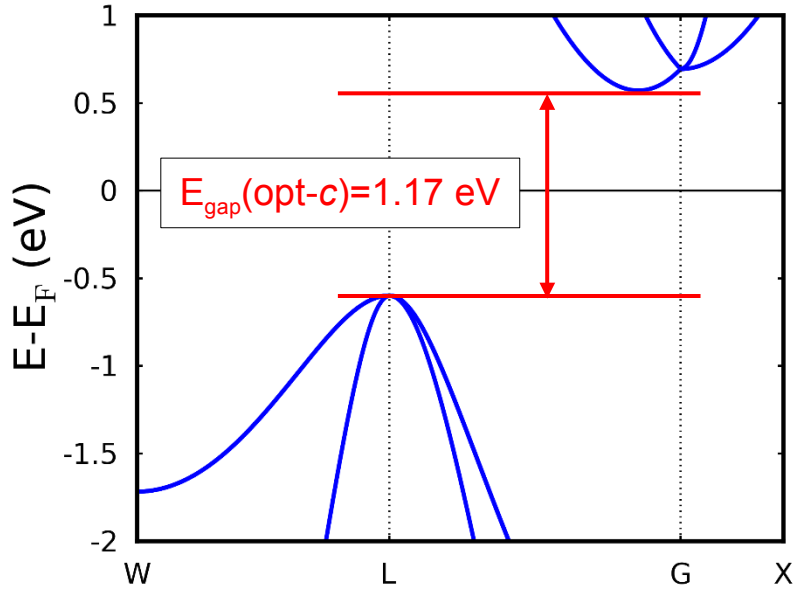


- Two-probe model → central region coupled to two electron reservoirs
- Exact representation of the non-periodic interface
- Setting $\mu_L \neq \mu_R$ allows to simulate the interface in the presence of a bias voltage

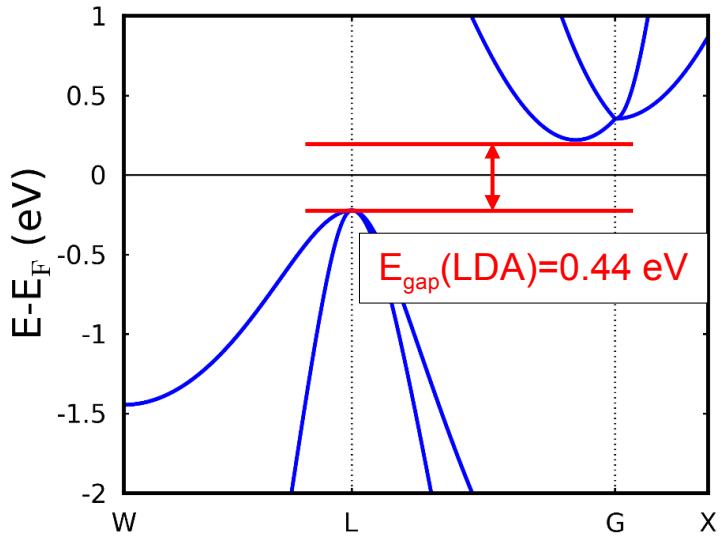
Brandbyge et al. *Phys. Rev. B* **65**, 165401 (2002)

2) Semiconductor band-gap using MGGA xc-functional





LDA

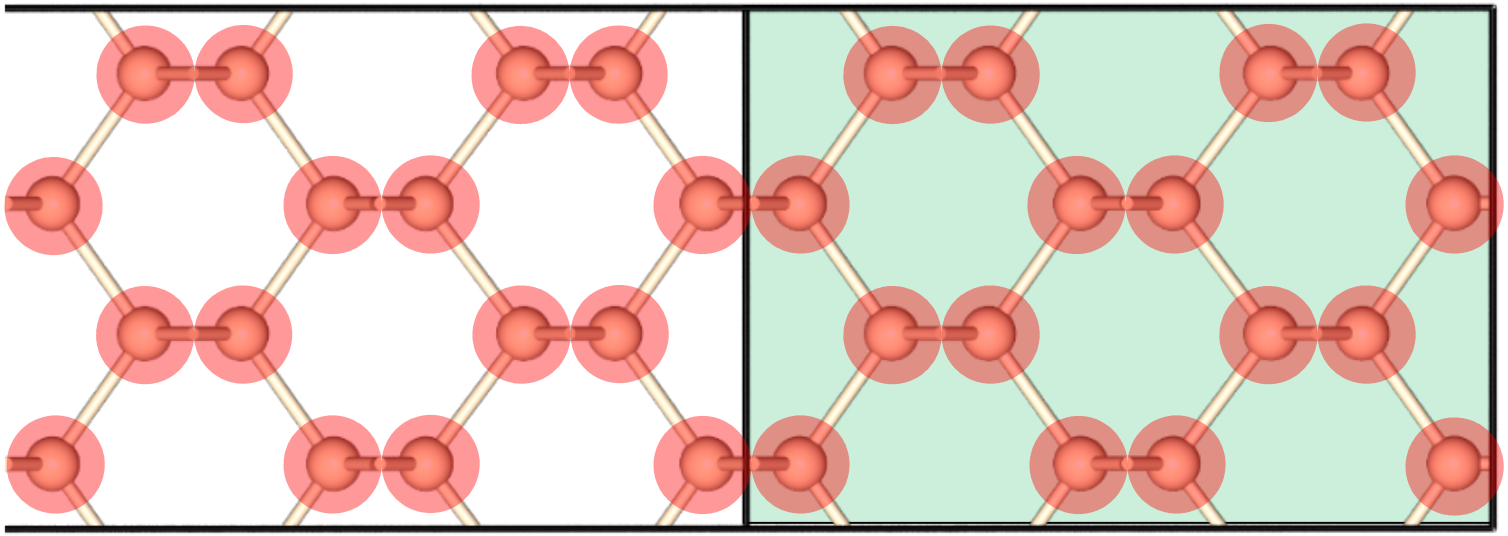


$$v_x^{\mathrm{TB09}}(\mathbf{r}) = c v_x^{\mathrm{BR}}(\mathbf{r}) + \frac{3c-2}{\pi}\sqrt{\frac{4\tau(\mathbf{r})}{6\rho(\mathbf{r})}}$$

c = adjustable enhancement parameter

Tran, Blaha *Phys. Rev. Lett.***102**, 226401 (2009)

3) Semiconductor effective doping



Unperturbed atomic densities

+ compensation charge bound the atomic cores ($+\Delta\rho_{compensation}$)

Advantages:

1- not depending on the precise atomistic details of the doping impurities

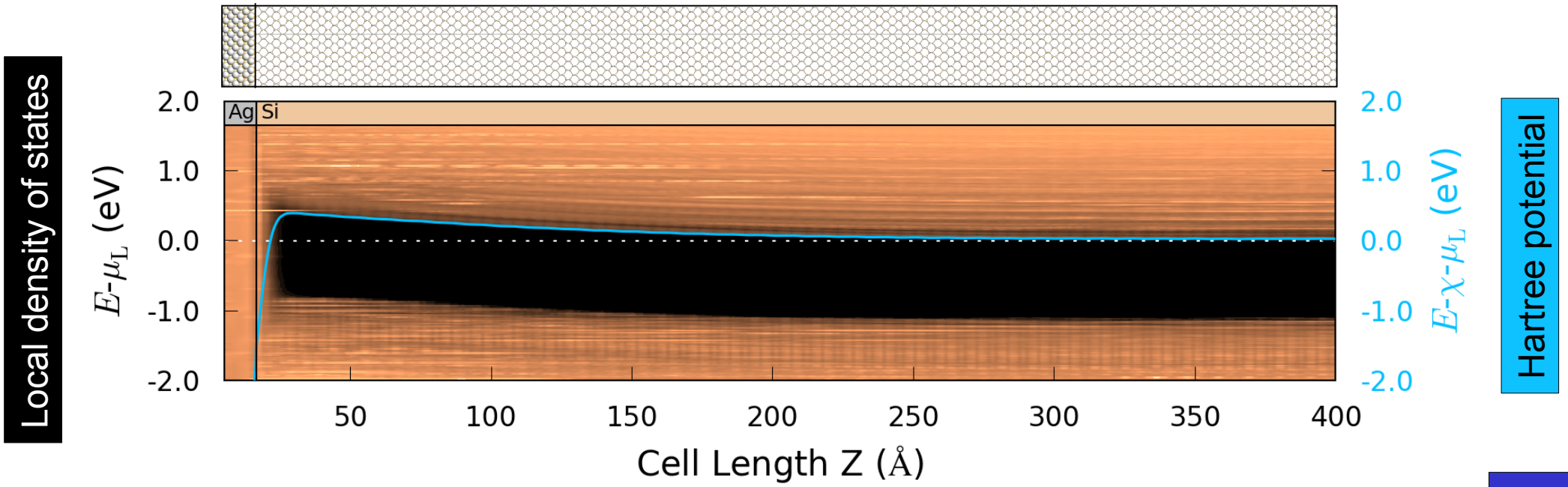
2- completely independent of the size and exact geometry of the system

Stradi et al. PRB **93**, 155302 (2016)

Results: Ag(100)/Si(100) interface

1) Validation of the activation energy model

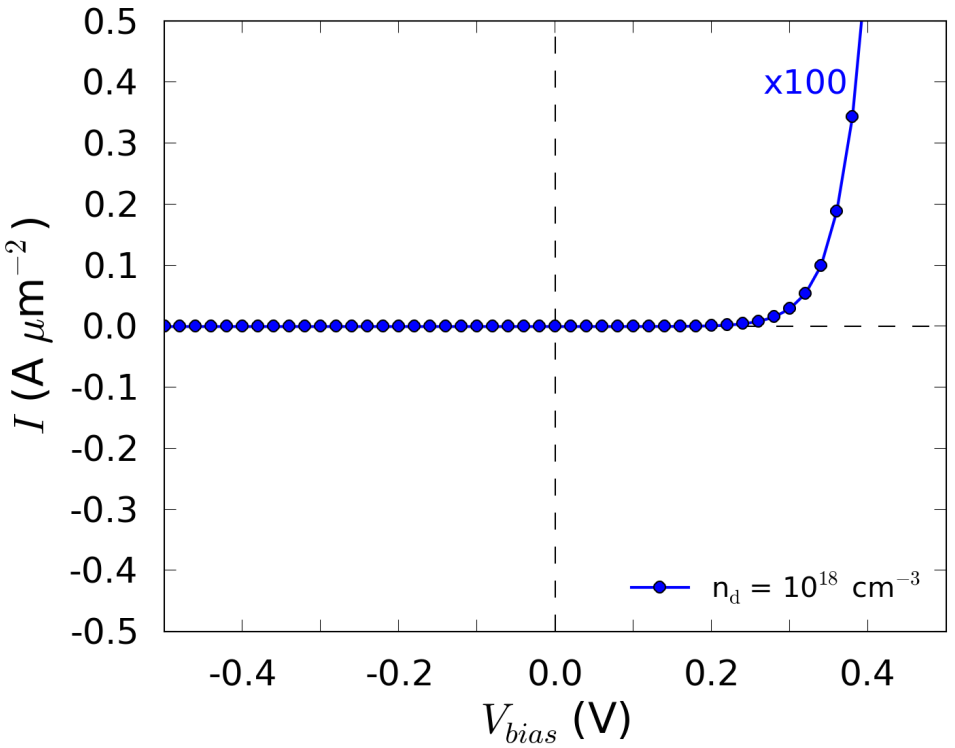
2) I-V analysis based on the electronic properties of the interface

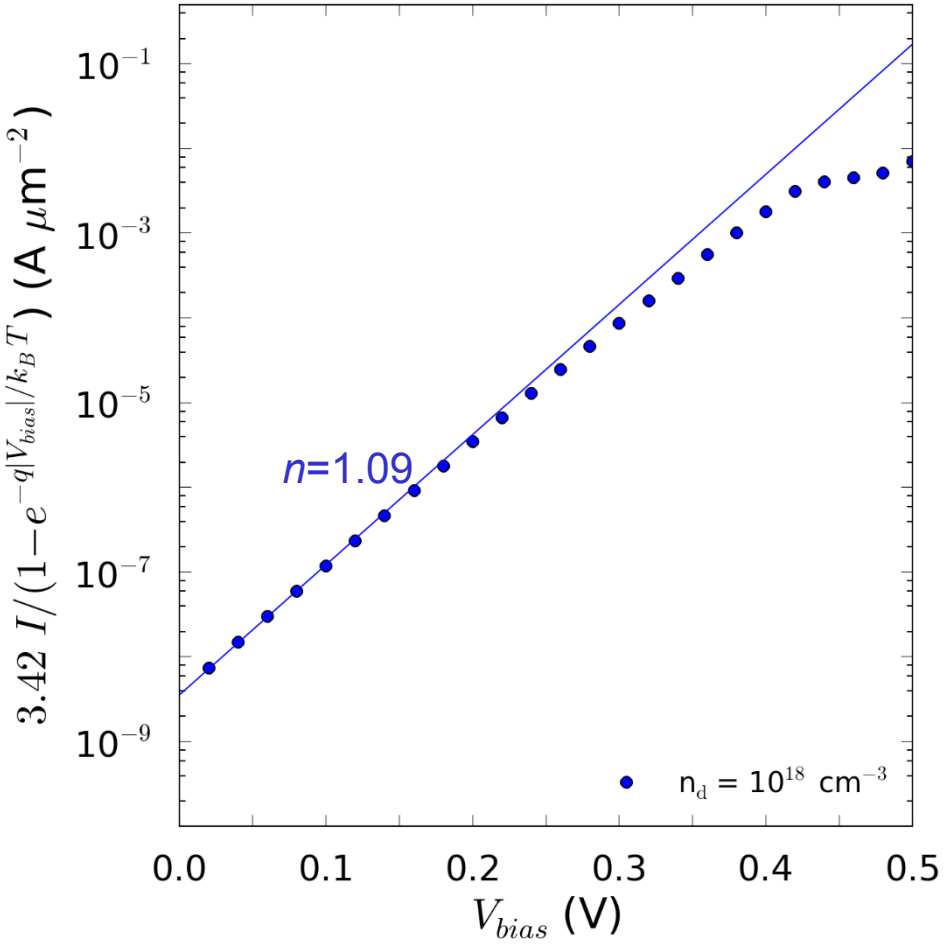


$n_d = 10^{18}$ cm^{-3}

Current-Voltage characteristics and ideality factor

According to thermionic emission theory $I = I_0 \left(e^{\frac{qV_{bias}}{nk_BT}} - 1 \right)$





n_d = 10^{18} cm^{-3} : Nearly ideal Schottky diode

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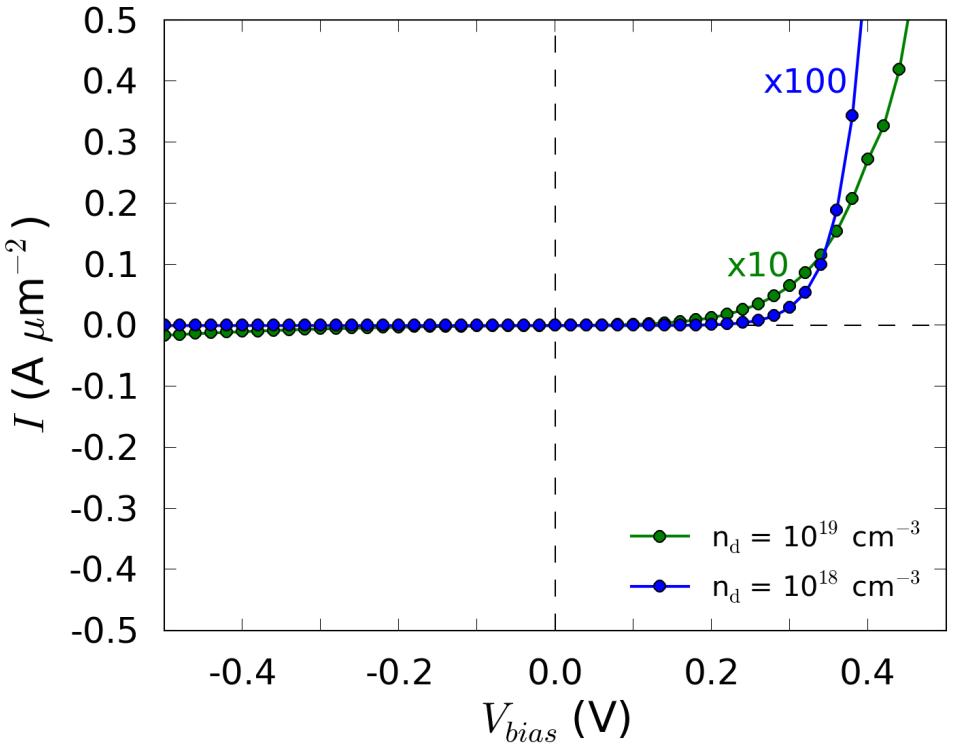
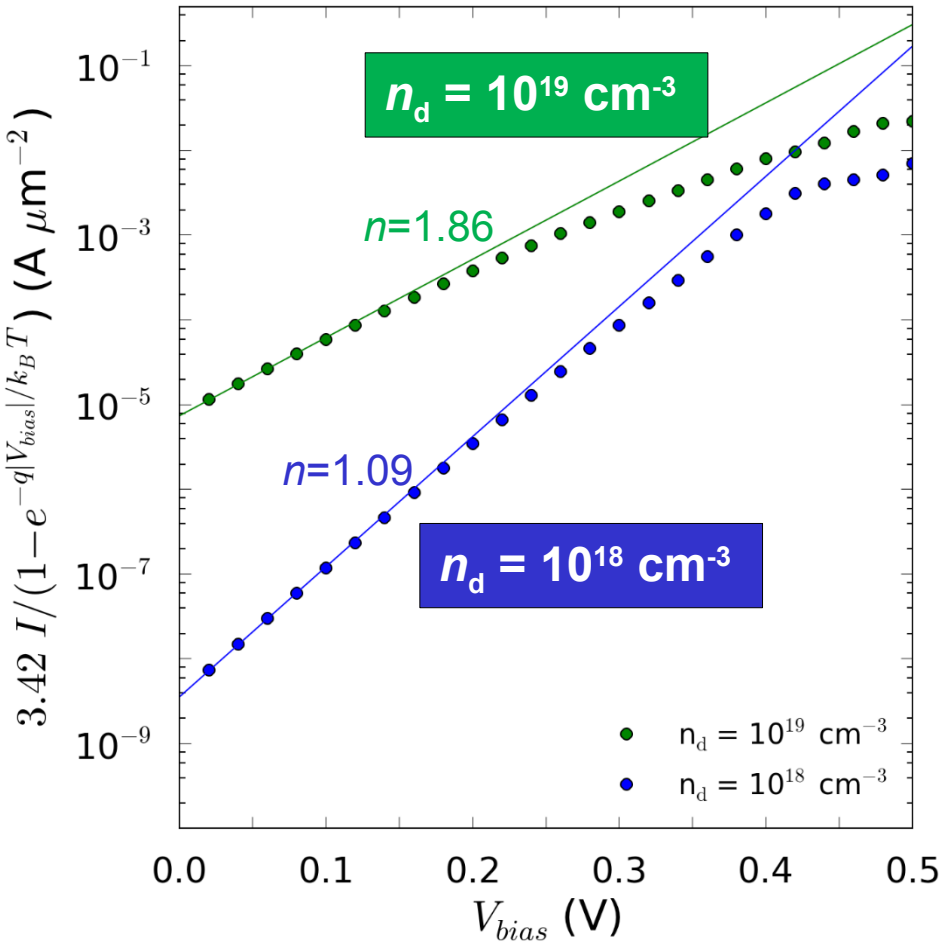




n_d = 10^{18} cm^{-3} : Nearly ideal Schottky diode

n_d = 10^{19} cm^{-3} : Not ideal Schottky diode

Activation Energy method

Experimental procedure to extract the Schottky barrier height from IV curves

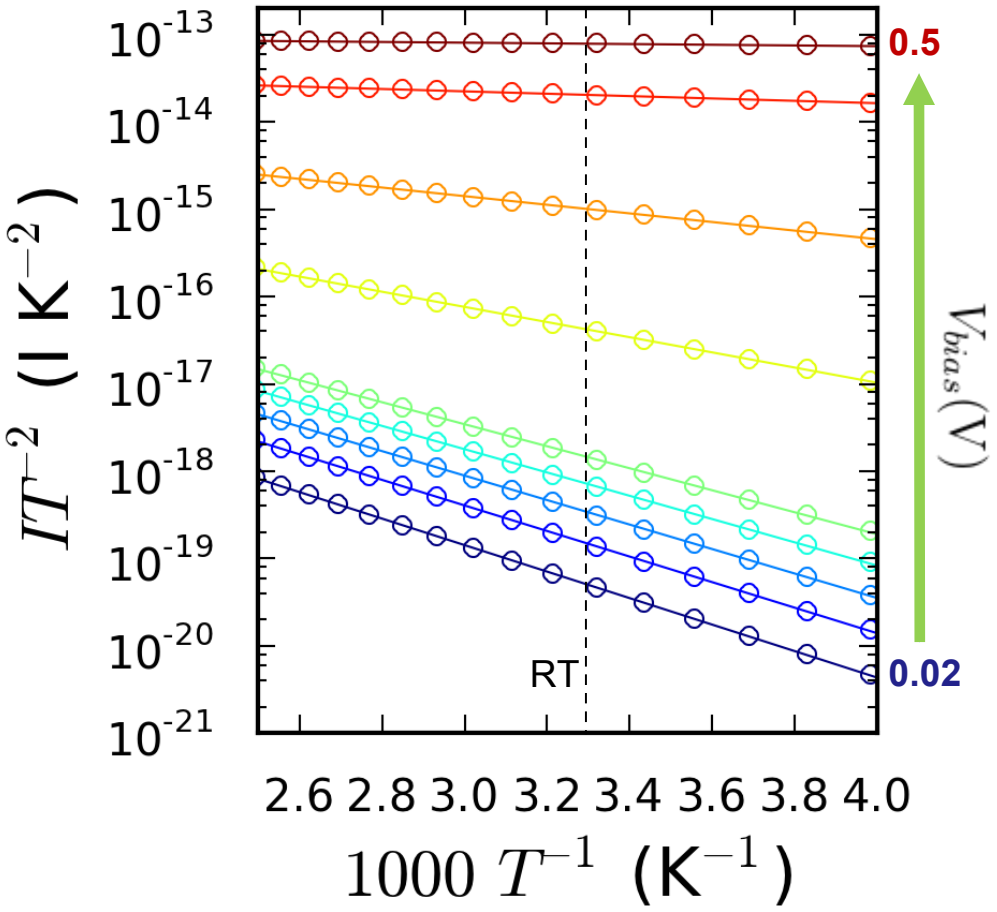
Small constant bias
T around room temperature
A* and ϕ^{AE} are constant

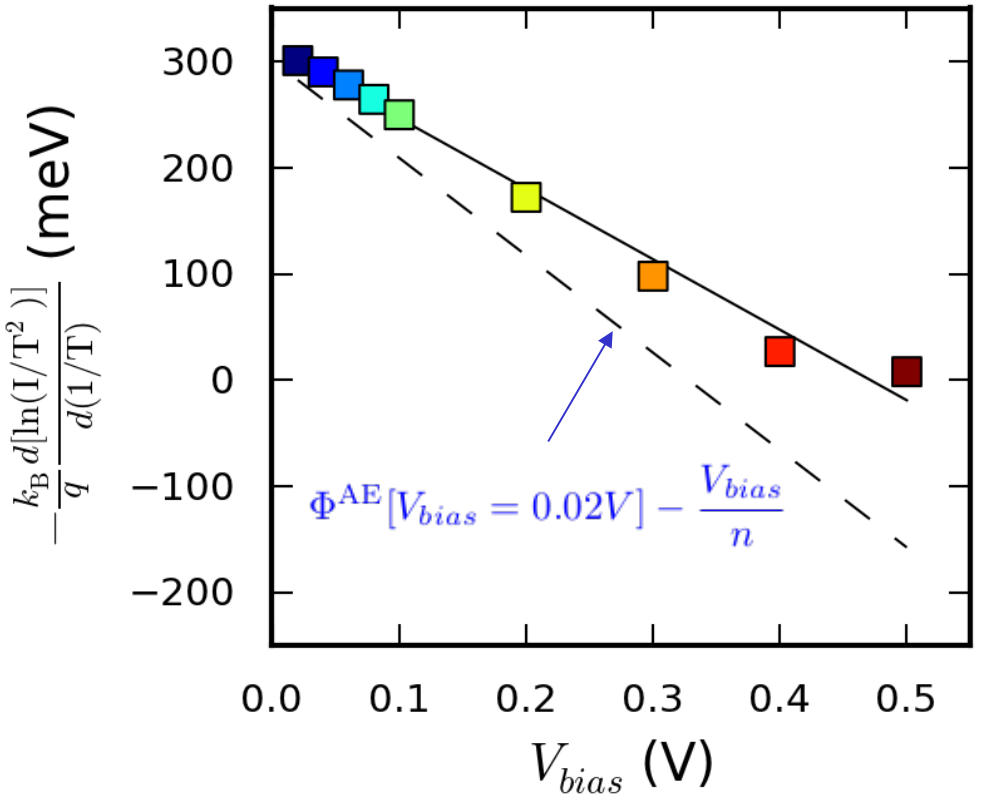
$$I T^{-2} = A A^{*} e^{-\frac{q\Phi^{AE}}{k_B T}} e^{\frac{q(V_{\text{bias}}/n)}{k_B T}}.$$

$$-\frac{k_B}{q}\frac{d[\ln(I/T^2)]}{d(1/T))} = \Phi^{\text{AE}} - \frac{V_{\text{bias}}}{n},$$

Activation Energy curves and Schottky barrier height

$$-\frac{k_B}{q}\frac{\ln[d(I/T^2)]}{d(1/T))} = \Phi^{\mathrm{AE}} - \frac{V_{bias}}{n}$$



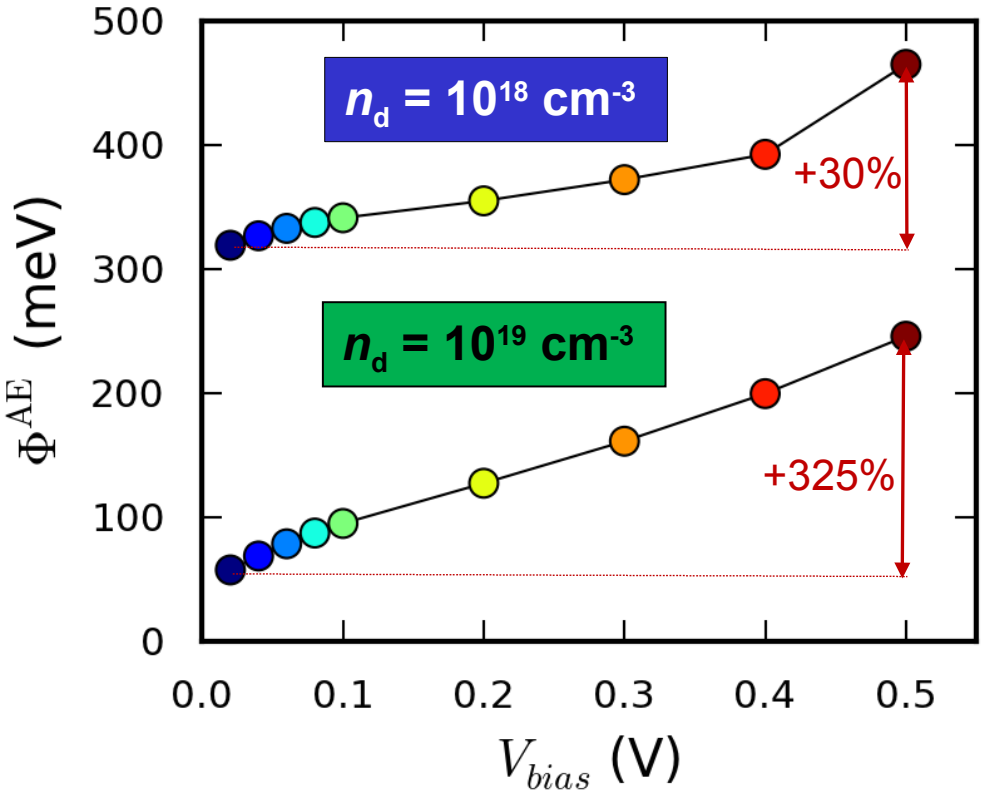


Activation Energy curves and Schottky barrier height

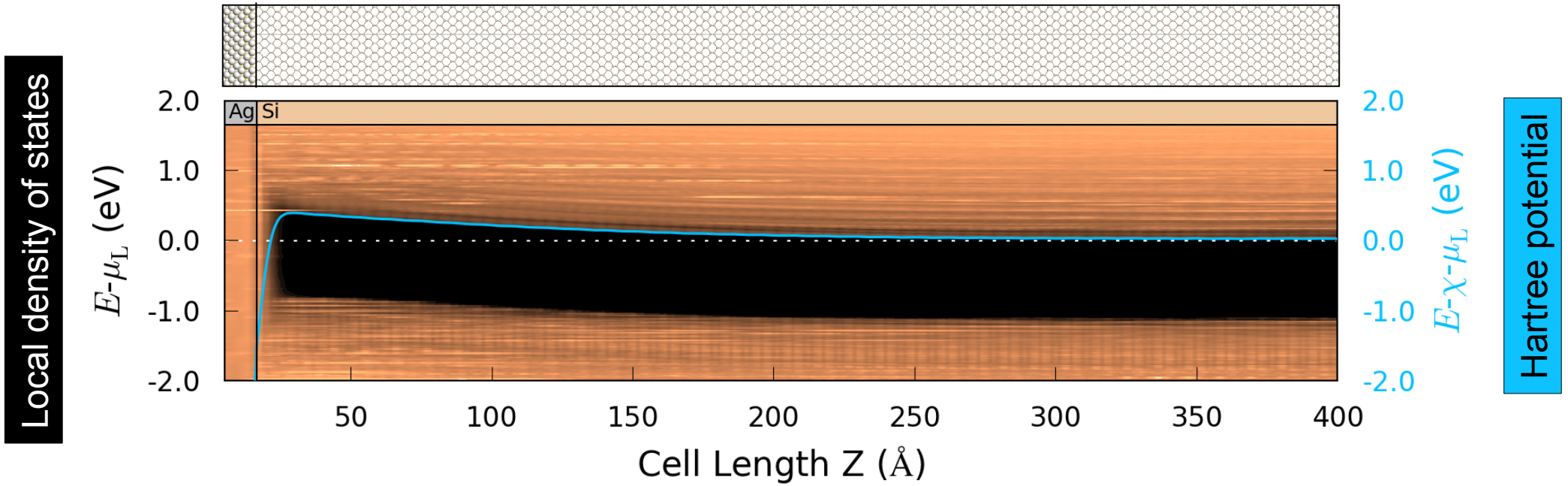
$$-\frac{k_B}{q}\frac{\ln[d(I/T^2)]}{d(1/T))} = \Phi^{\mathrm{AE}} - \frac{V_{bias}}{n}$$

The measured Schottky barrier depends on:

1) Applied source-drain bias
2) Semiconductor doping density



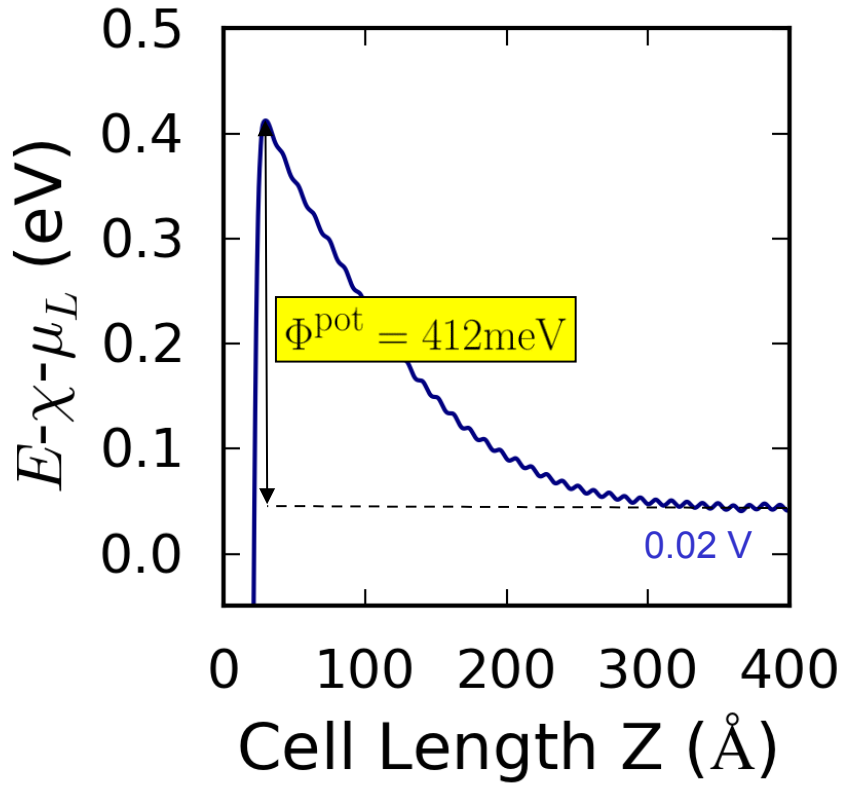
Electronic structure of the interface



$n_d = 10^{18}$ cm^{-3}

Analysis of the spectral current

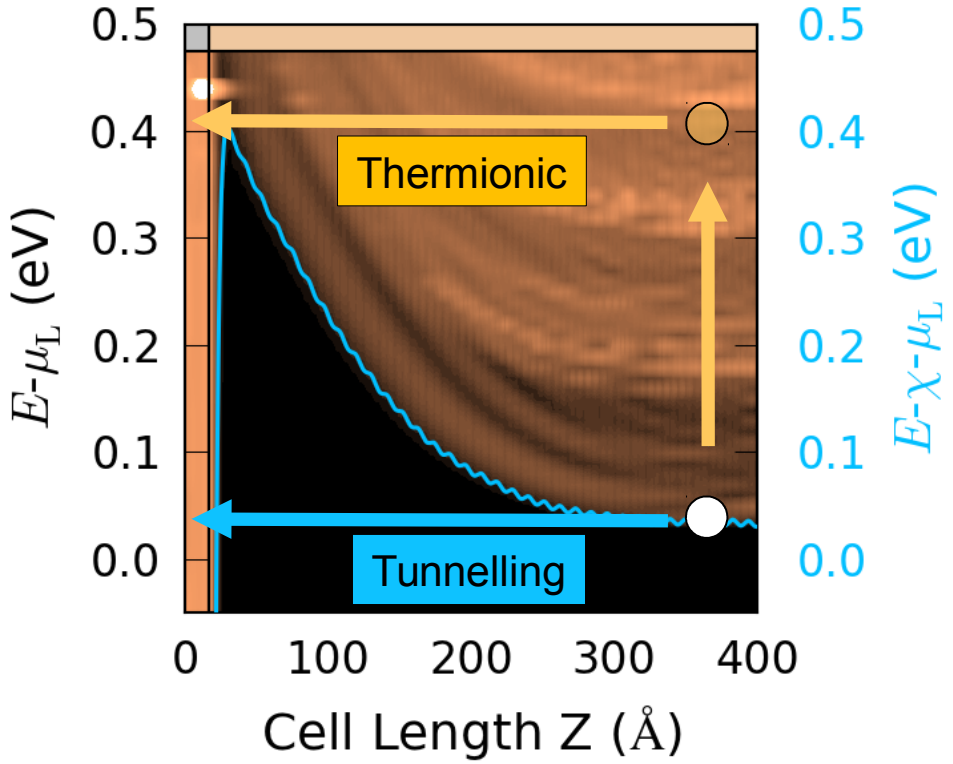
Hartree potential



Local density of states

+

Hartree potential

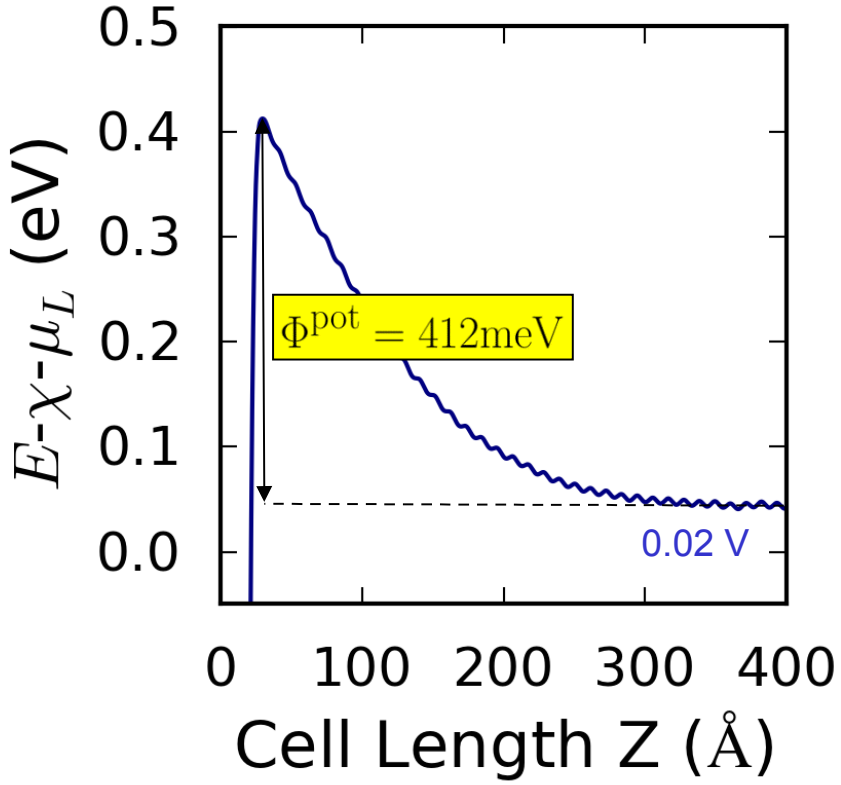


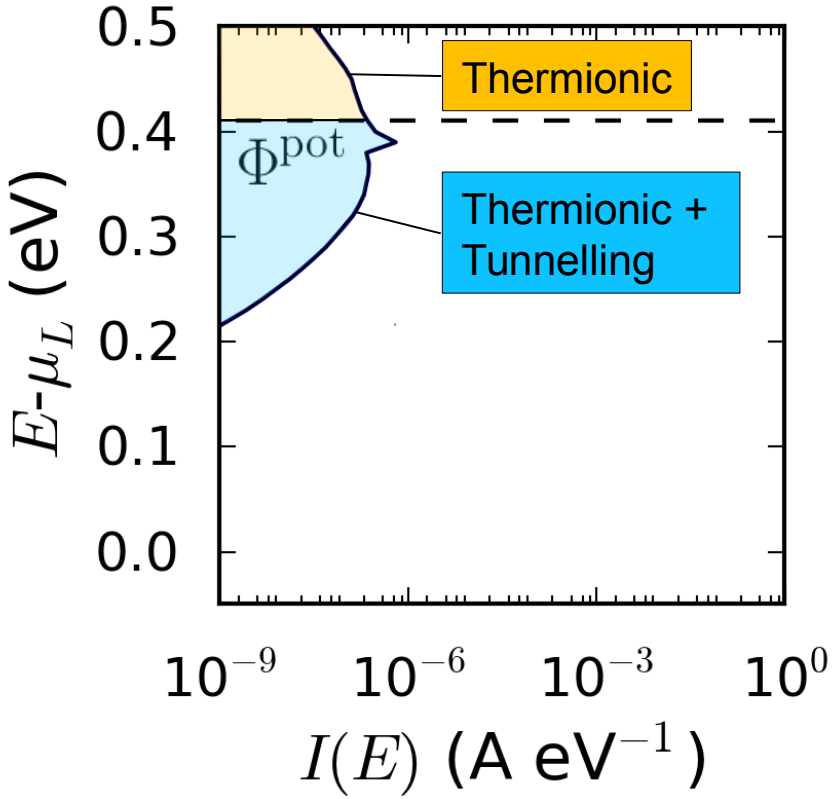
$n_d = 10^{18}$ cm^{-3}

Analysis of the spectral current

Spectral current

$$I(E) = \frac{2q}{h} T(E, \mu_L, \mu_R)[f(\frac{E-\mu_L}{k_B T}) - f(\frac{E-\mu_R}{k_B T})]$$





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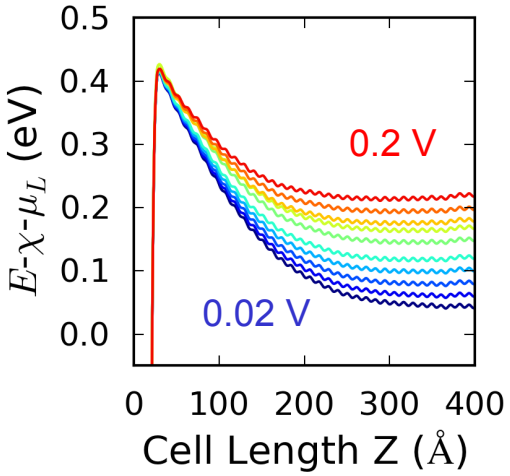
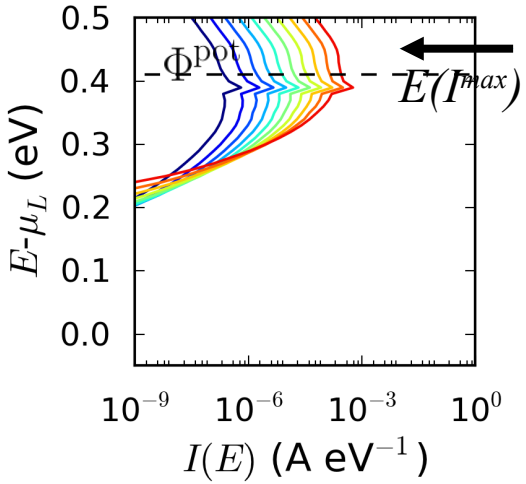


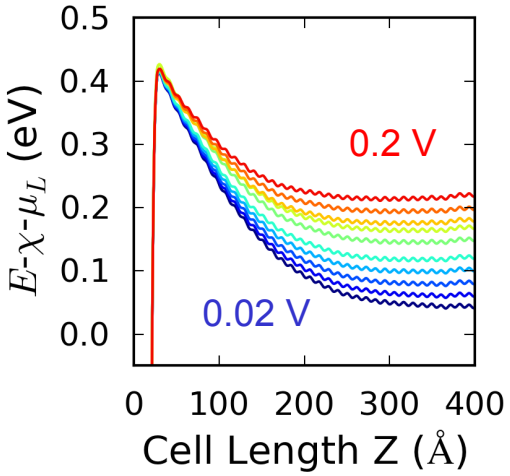


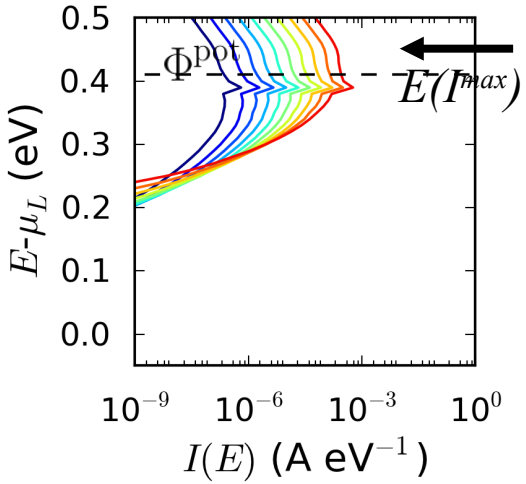
$n_d = 10^{18}$ cm^{-3}

Thermionic emission >> Tunnelling

Analysis of the spectral current

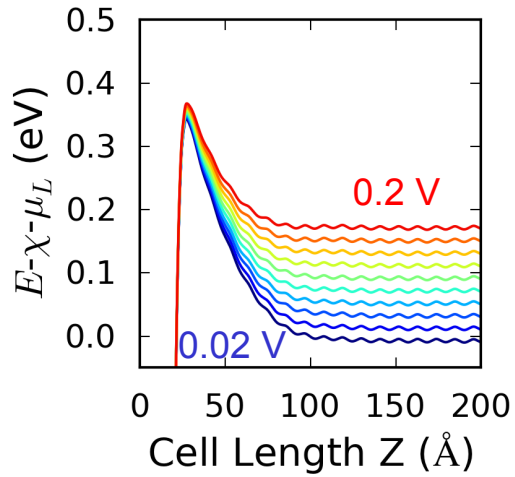
$n_d = 10^{18}$ cm^{-3}

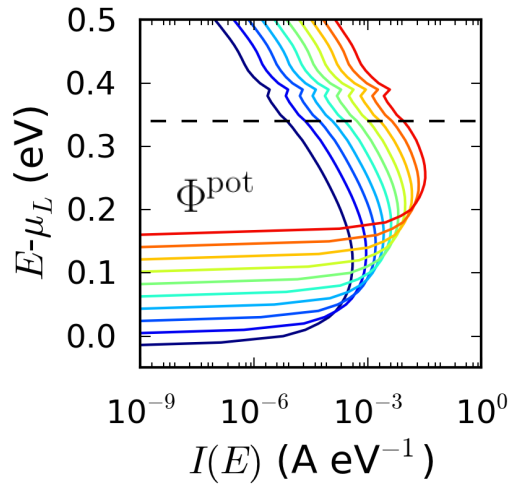




Thermionic emission >> Tunnelling

$n_d = 10^{19}$ cm^{-3}





Tunnelling >> Thermionic emission

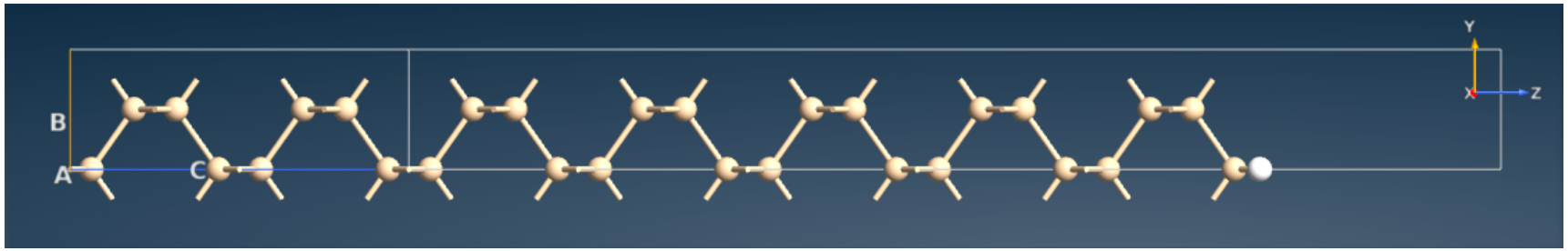
Conclusions

- We have implemented in ATK a general atomistic approach based on DFT+NEGF for simulating metal-semiconductor interfaces
- This approach:
  - includes all the necessary ingredients to describe realistic metal-semicondutor interfaces
  - allows for a direct comparison between theory and experiment as it can simulate I-V characteristics
  - provides an alternative to analytical methods to evaluate the properties of metal-semiconductor interfaces
  - is a better alternative to finite-size models to describe the interface between metals and doped semiconductors

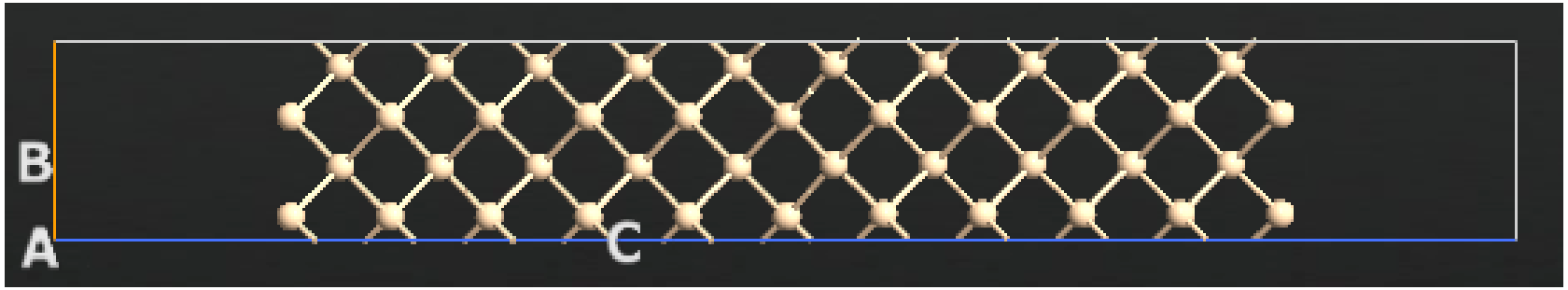
PHYSICAL REVIEW B 93, 155302 (2016)

One-probe surface configuration

- The ideal model for a surface is periodic in 2 directions, but semi-infinite in the third:

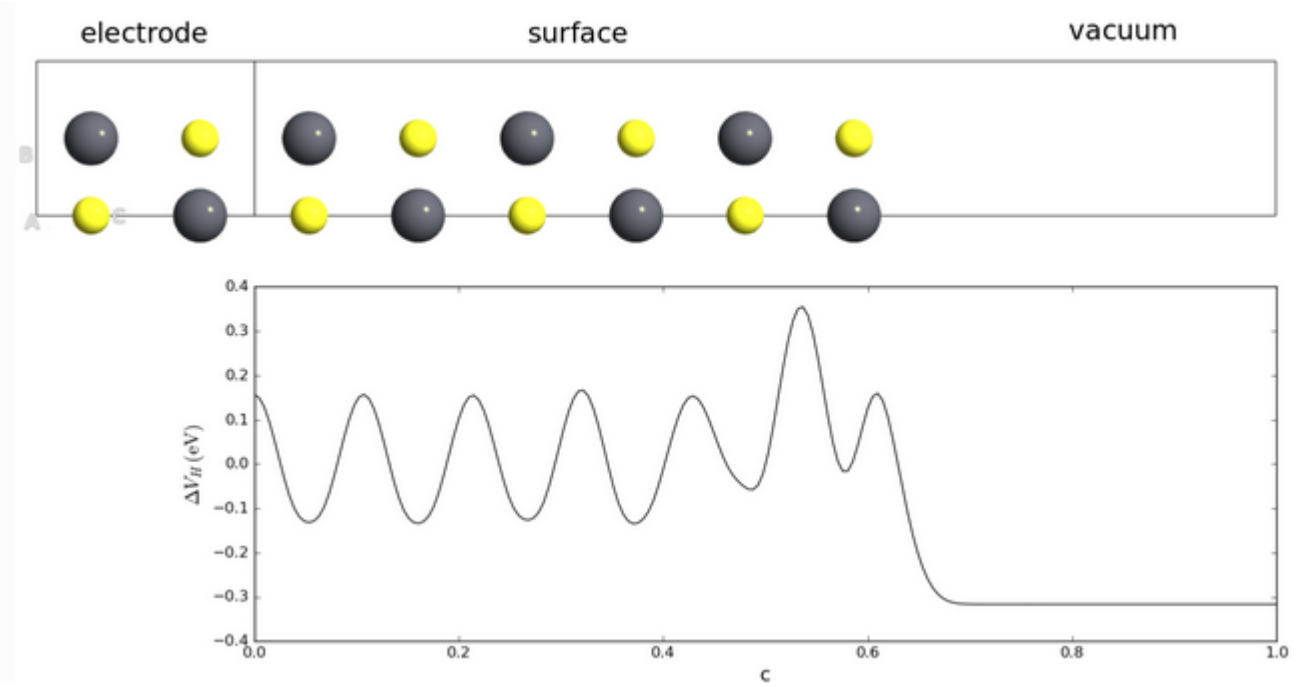


- Standard DFT software packages (VASP, QuantumEspresso, etc) provide only the following approximation, called the slab model:

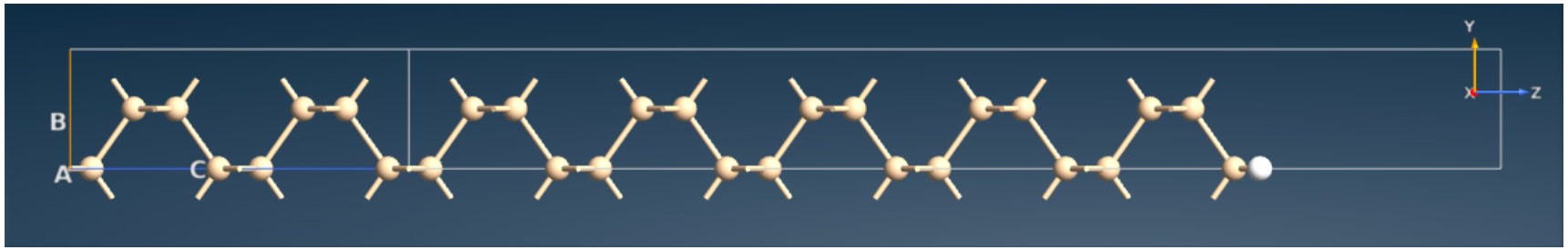


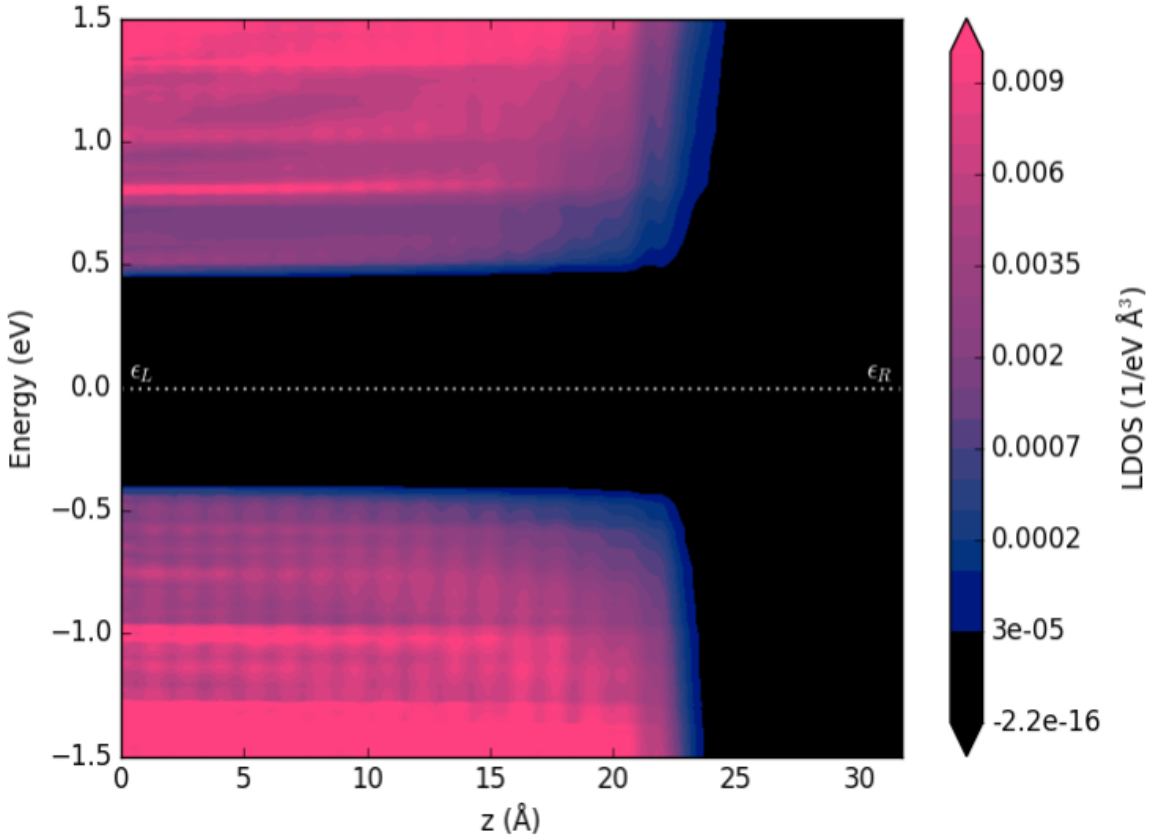
Surface configuration using Green's function methods (One probe)

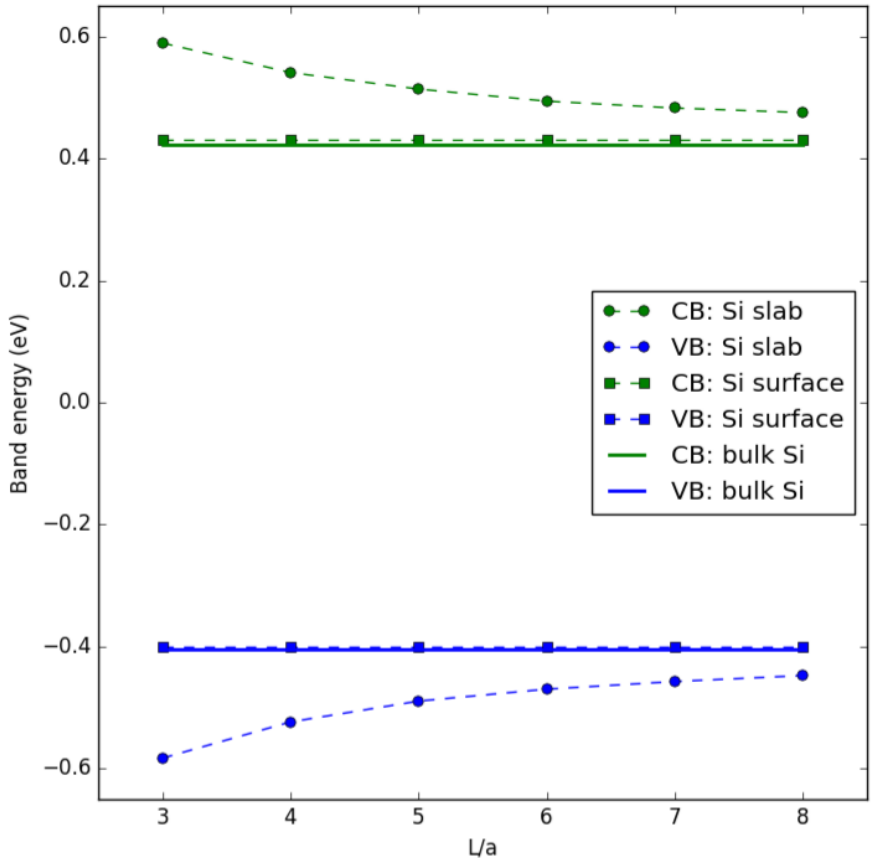
- **QuantumWise is introducing an alternative computational approach for properly describing surfaces**
- **Goal:** Calculate the surface properties of materials with more systematic convergence and effort (order of magnitude) than the slab approach
- **Methodology:** numerical contour integration of the surface Green's functions, coupled to DFT



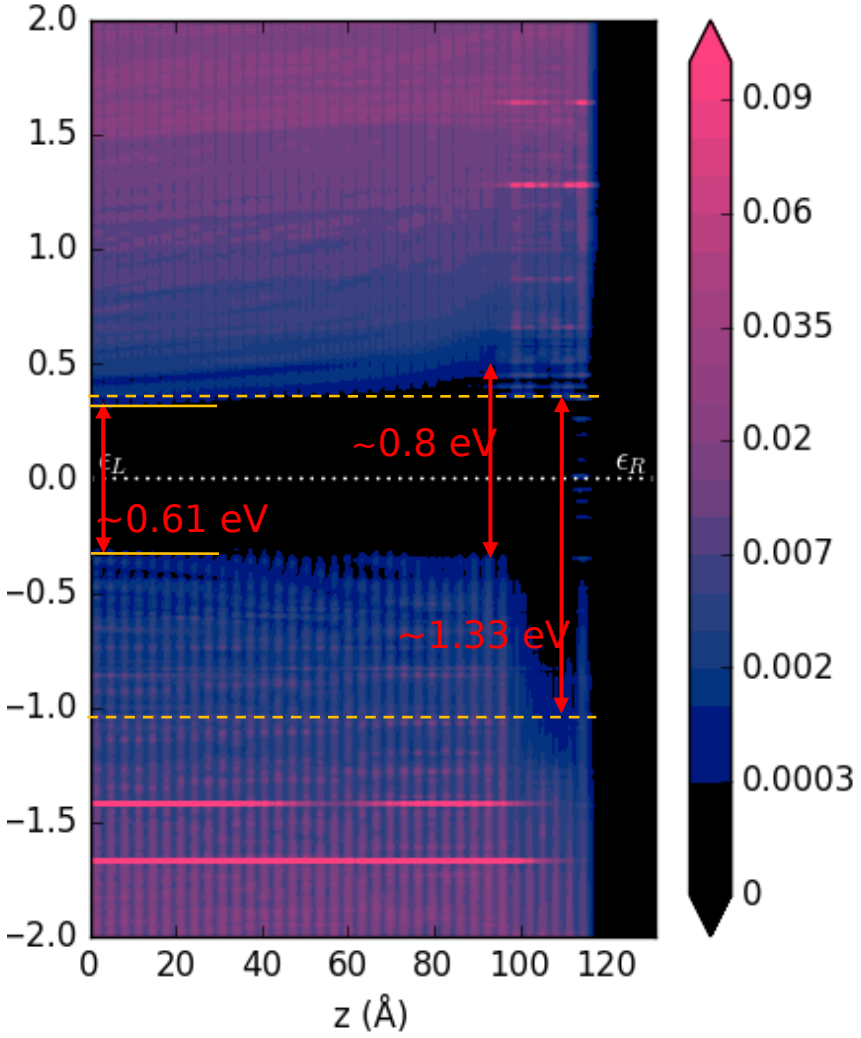
Silicon (100) electronic structure – preliminary results

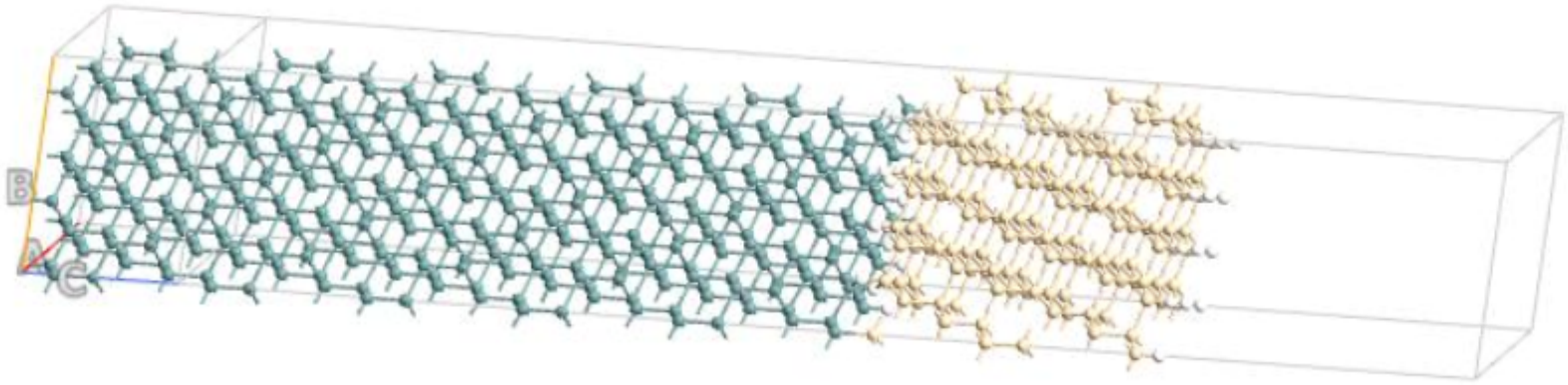


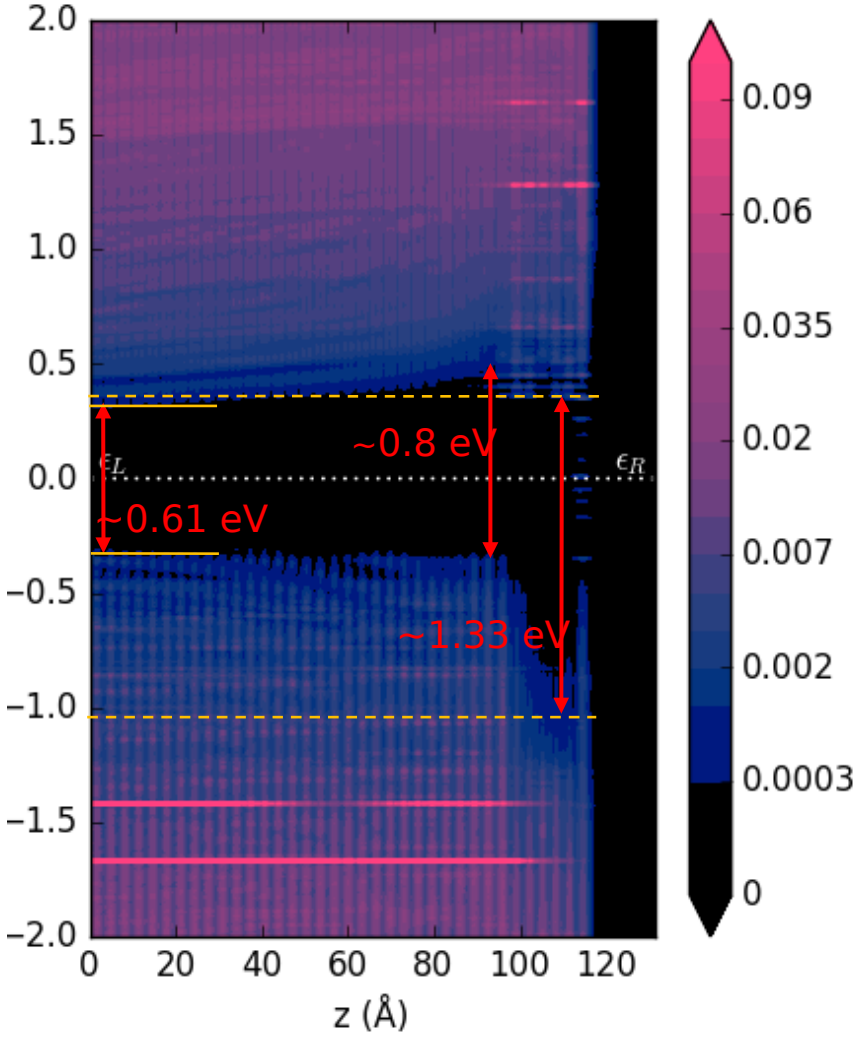


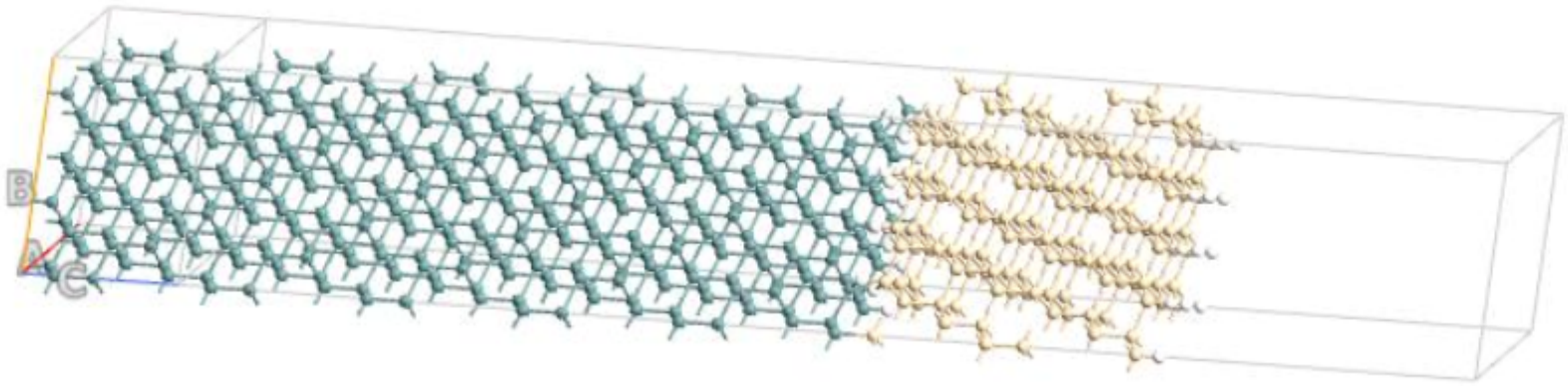


Band alignment in semiconductor heterostructure, Si film on Ge(111) – preliminary results









1) Band bending of Ge conduction band is clearly seen.

2) Band gap of Ge substrate increases near the interface.

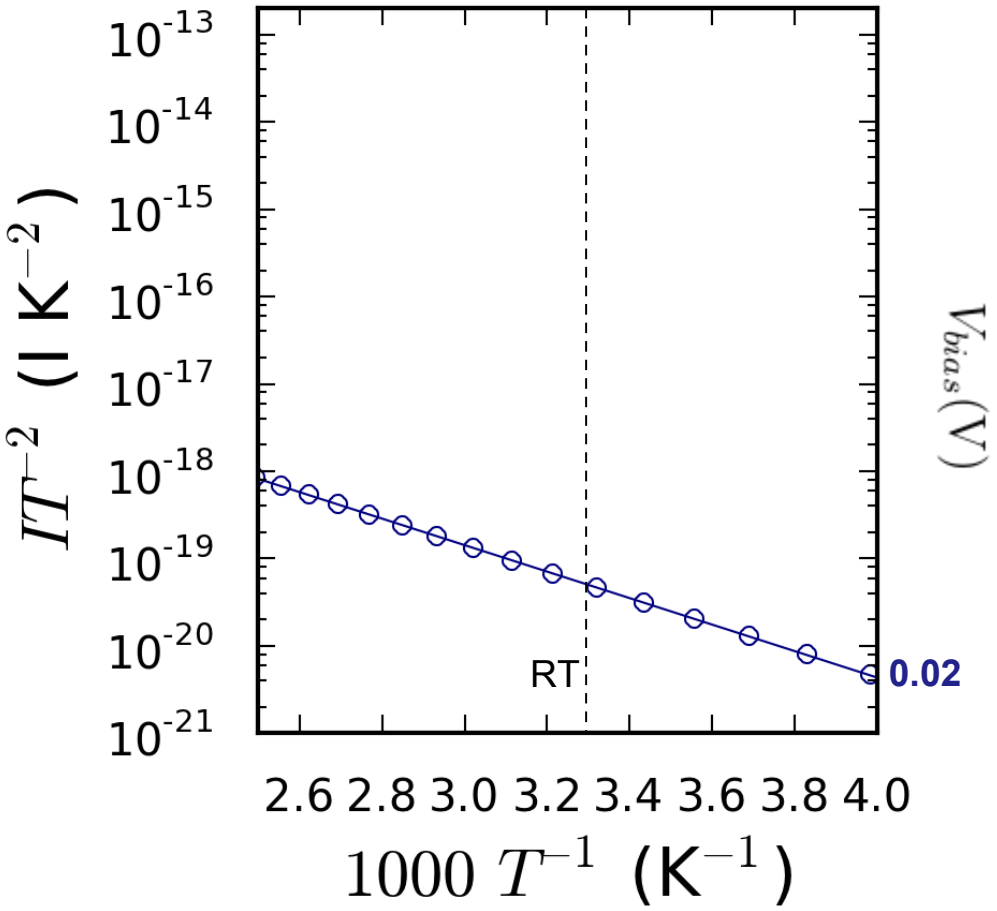
3) There exists a strong penetration of Ge valence states into the Si film within the Si film band gap.

One probe surface calculations combined with Projected LDOS analysis seems to be an insightful approach for studying the band alignment.

Thank You!

Activation Energy curves and Schottky barrier height

$$-\frac{k_B}{q}\frac{\ln[d(I/T^2)]}{d(1/T))} = \Phi^{\mathrm{AE}} - \frac{V_{bias}}{n}$$



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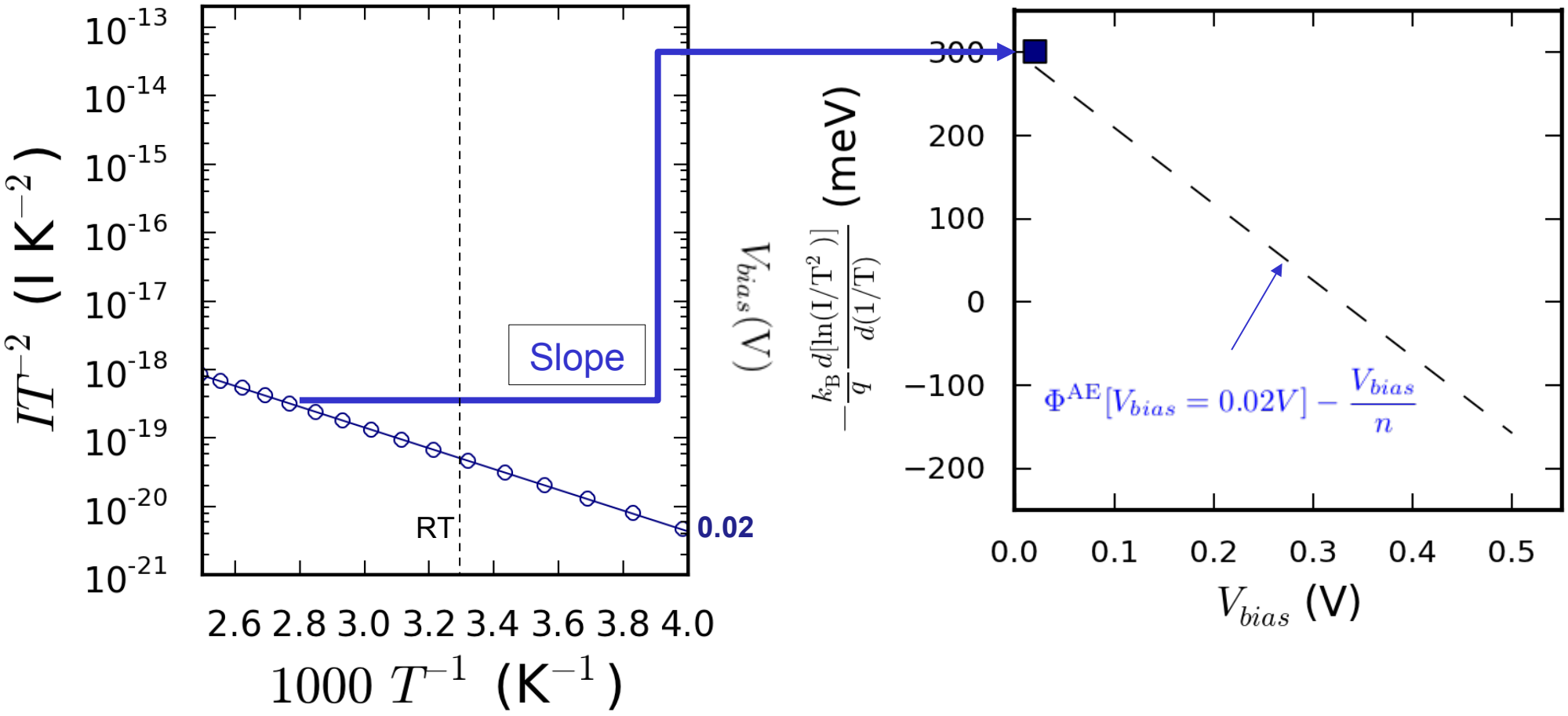

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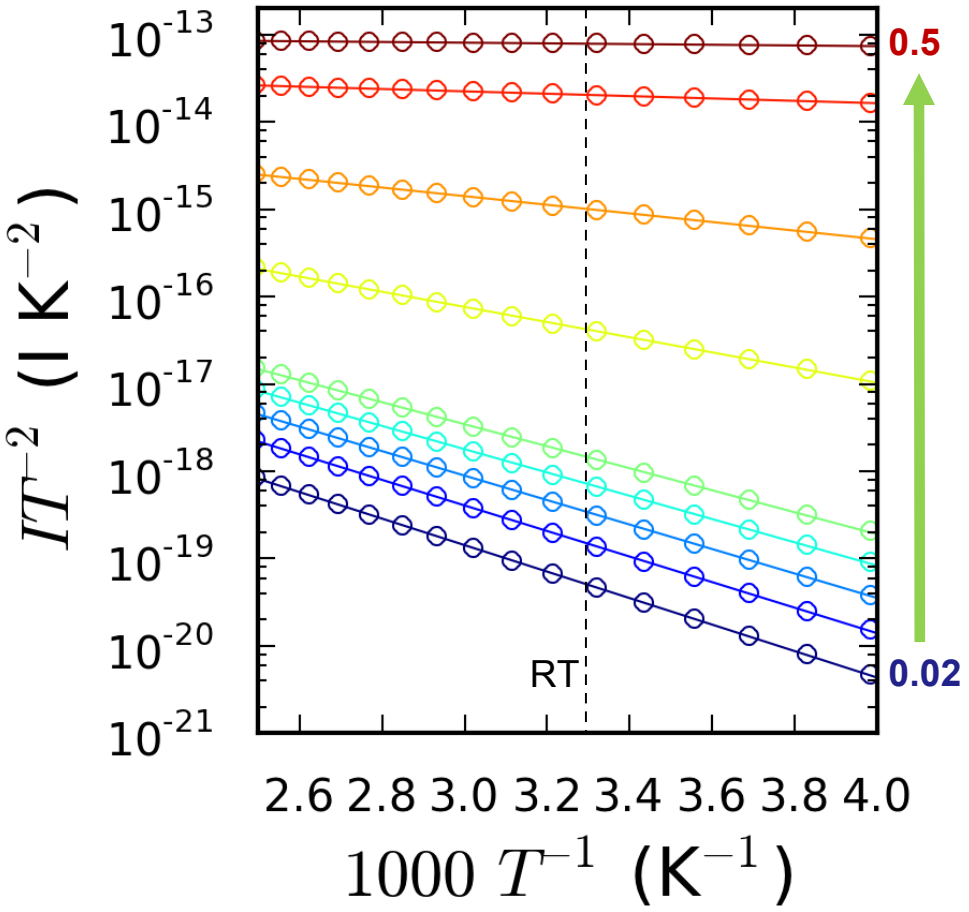
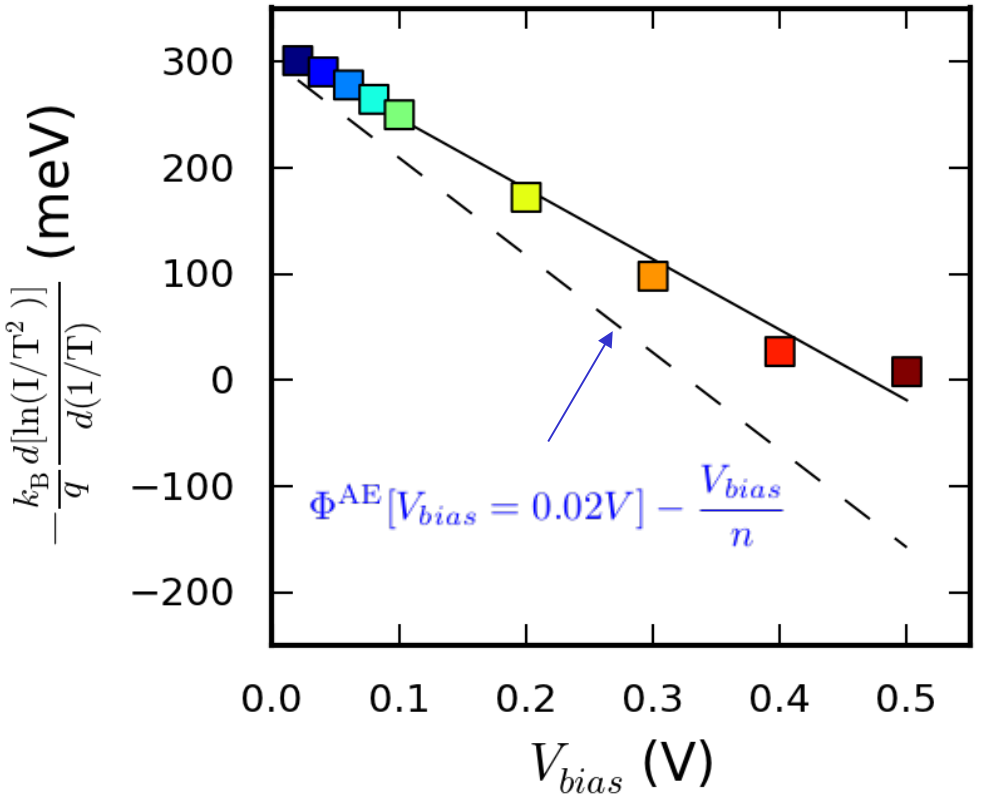
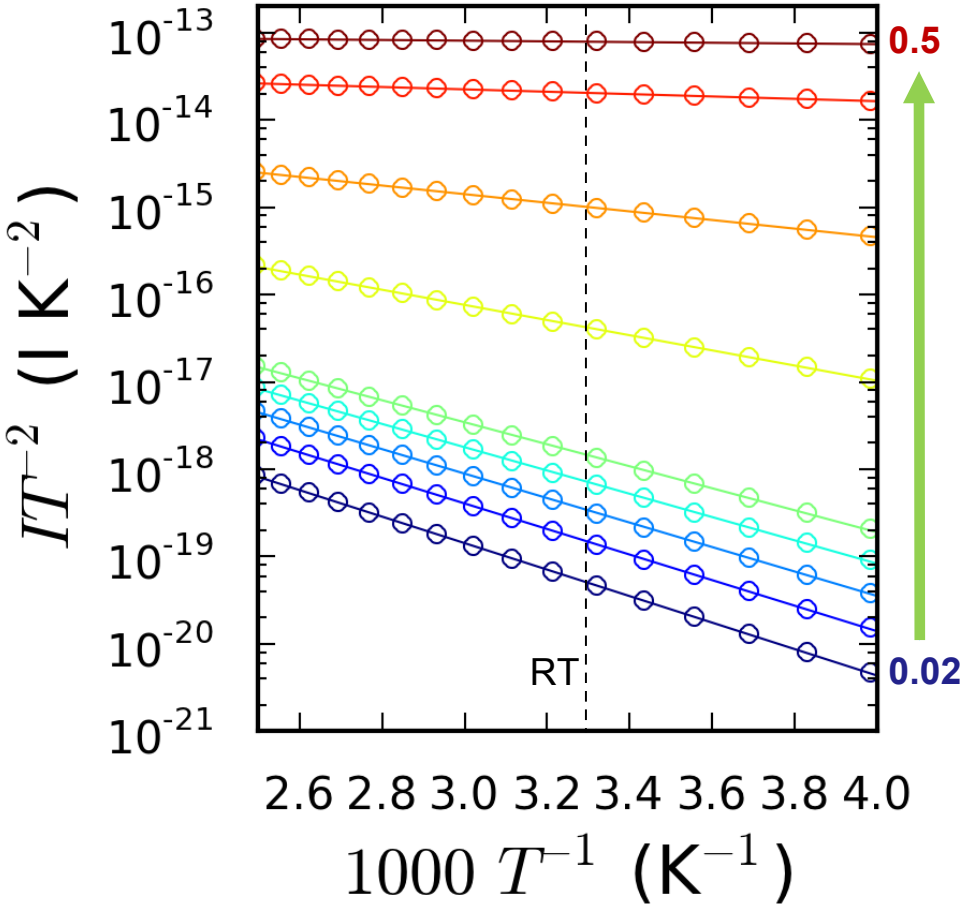
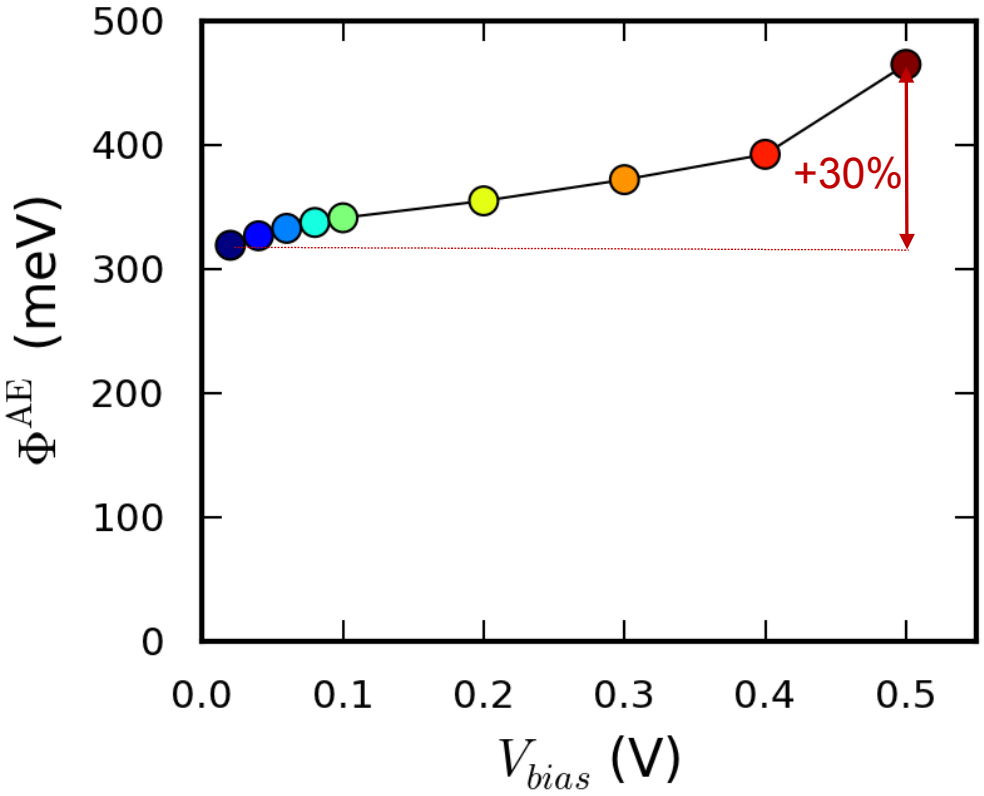




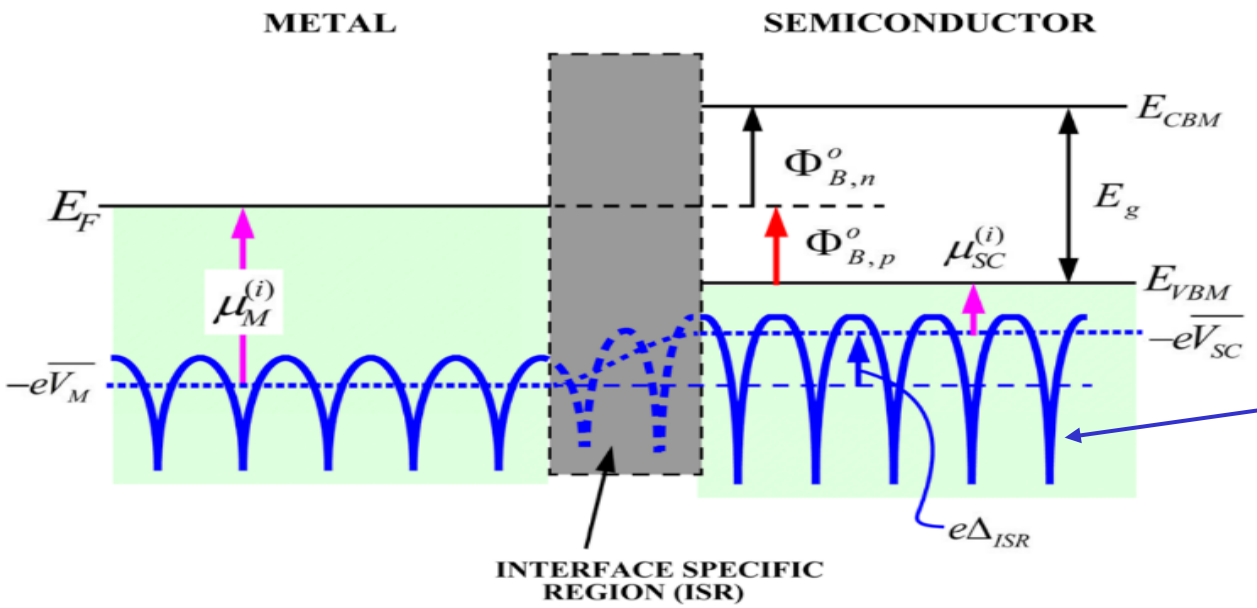
Activation Energy curves and Schottky barrier height

$$-\frac{k_B}{q}\frac{\ln[d(I/T^2)]}{d(1/T))} = \Phi^{\mathrm{AE}} - \frac{V_{bias}}{n}$$





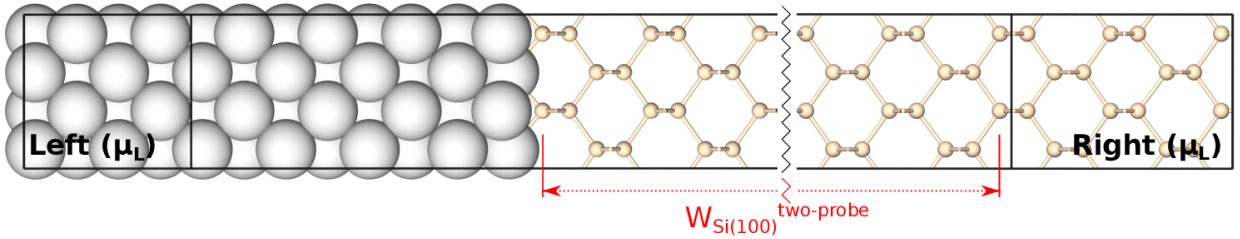
Comparison of the two-probe with the finite-size model



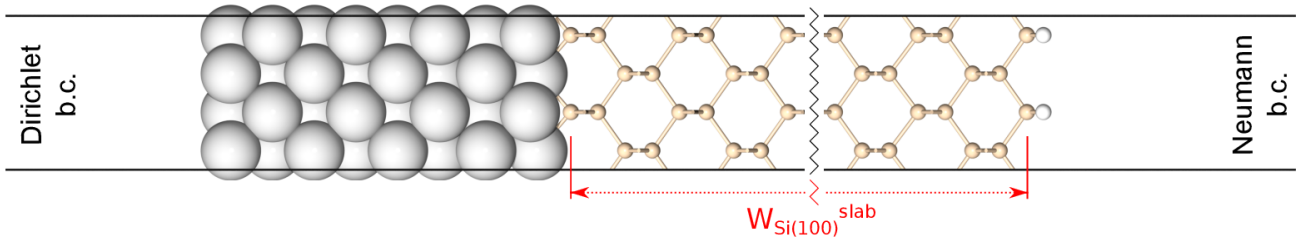
- Band diagrams using a finite-size model of the interface

Potential of the interface model used to align the electronic bands

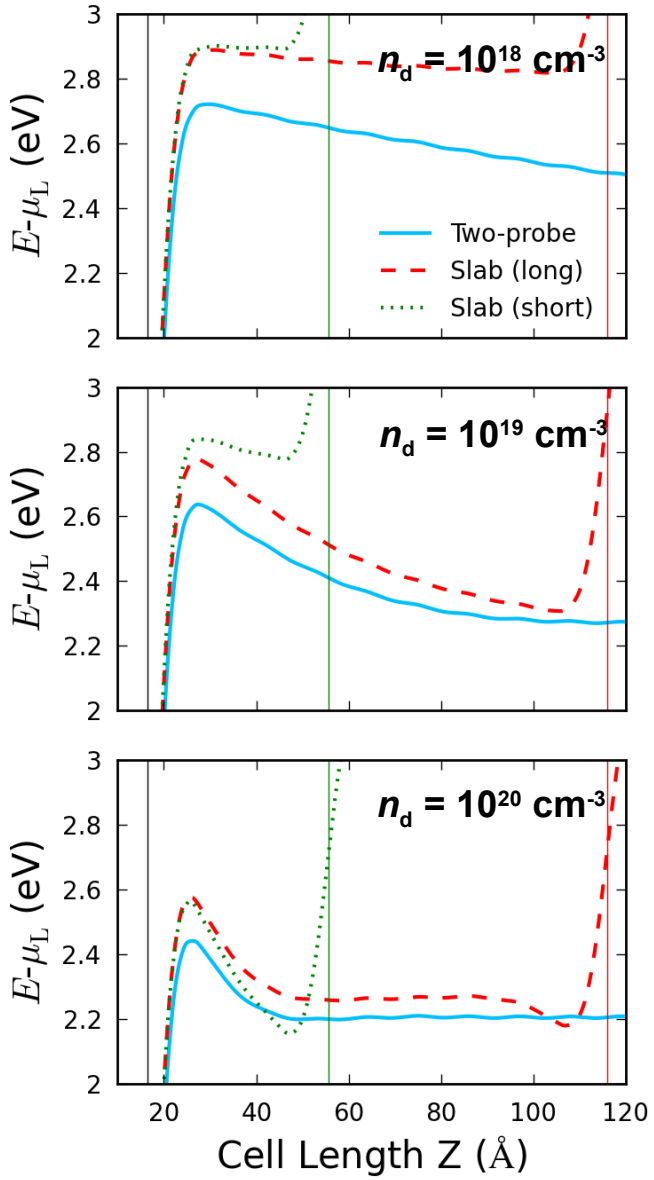
Two-probe model (DFT+NEGF)

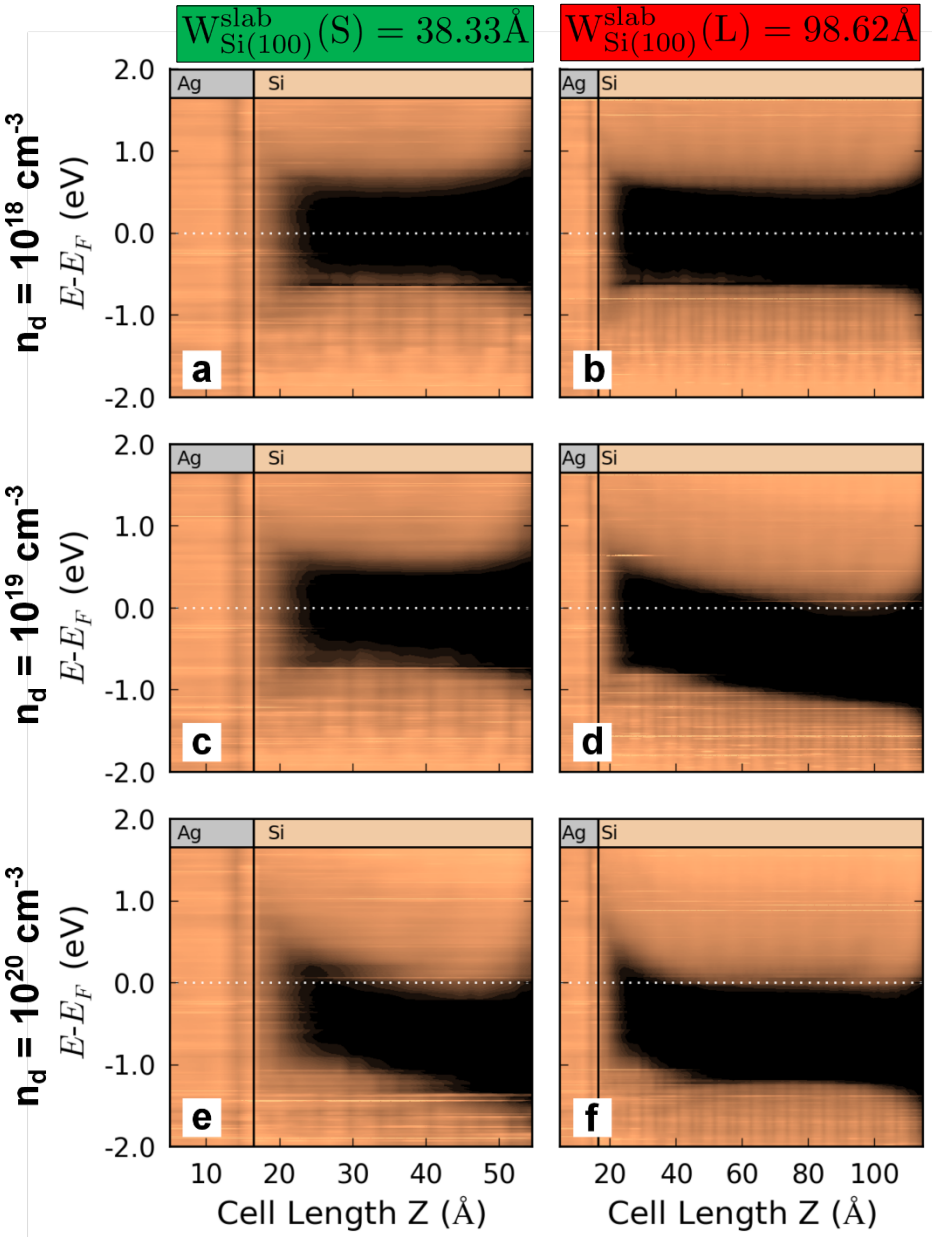


Finite-size model (DFT)

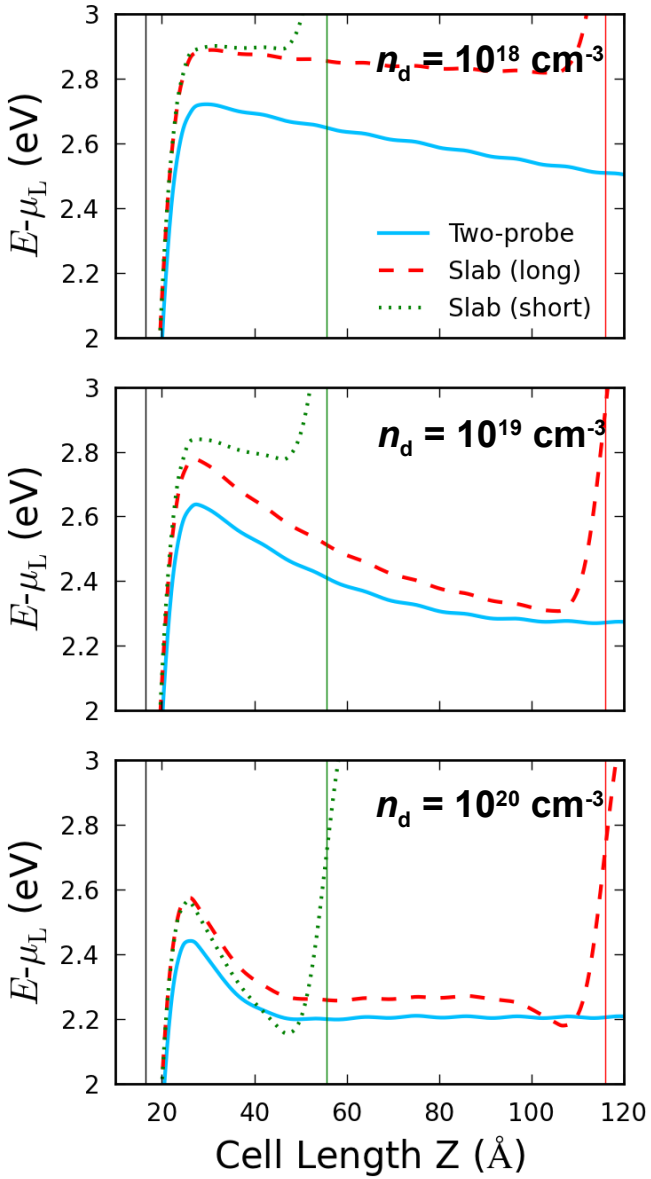


Comparison of the two-probe with the finite-size model





Comparison of the two-probe with the finite-size model



Model	Time/SCF step [s]
Two-probe	46.6
Slab (short)	47.1
Slab (long)	338.6