Ab initio theory and simulation of semiconductor nanostructures

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Outline

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- Introduction on nanoscience
- Ab initio simulations: Density Functional Theory (DFT)
- Quantum confinement in Si nanowires (Si NWs)
  - Electronic structure
  - Transport properties
  - Doping effects
- Crystal phase engineering in Si NWs
  - Crystal phase effects on bulk
  - Crystal phase effects on NWs
  - STEM-EELS experiments
- Conclusions

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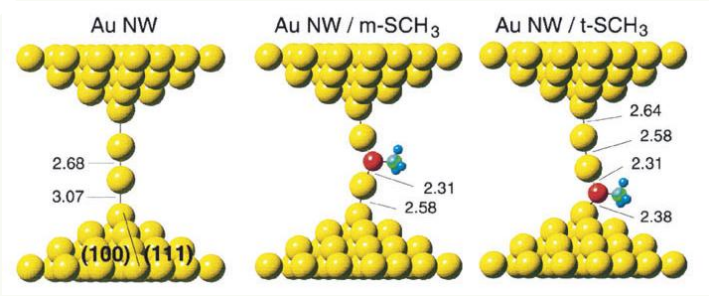
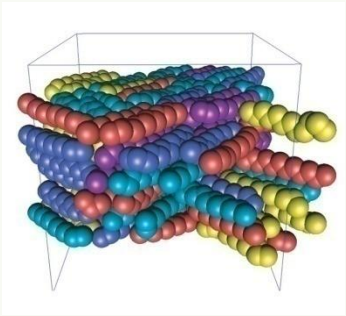
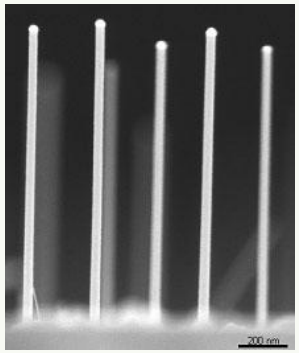
Nanoscience

Nanoscience

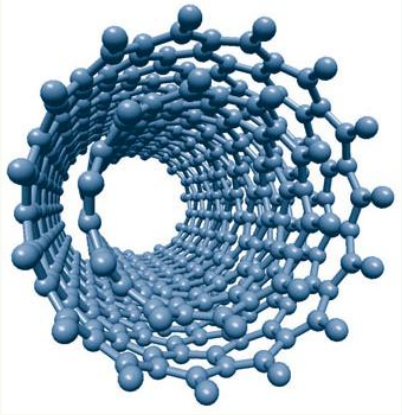


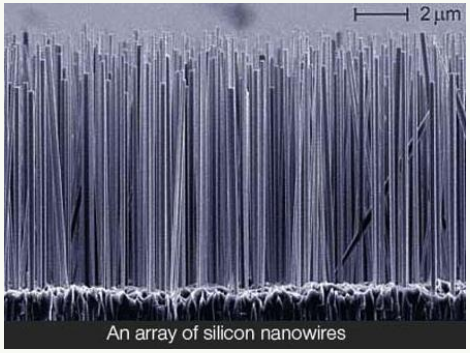


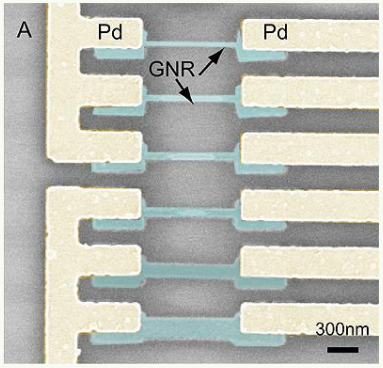


The study of structures, dynamics, and properties of systems
in which one or more of the spatial dimensions is nanoscopic (1-100 nm)
Dynamics and properties that are distinctly different (often in an extraordinary way)
from both small-molecule systems and systems macroscopic in all dimensions

U.S. National Nanotechnology Initiative, nano.gov







The importance of size

The importance of size

Gold bar

Gold coins

Gold flakes

Gold nanoparticles

As the size of the material is reduced, and the nanoscale regime is reached, it is possible that the same material will display totally different properties

Nano building blocks

Nano building blocks

What are the nano building blocks that would play an analogous role to macro building blocks ?

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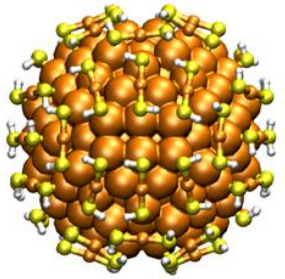
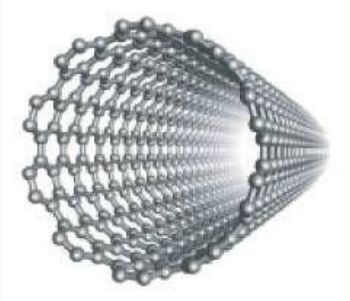
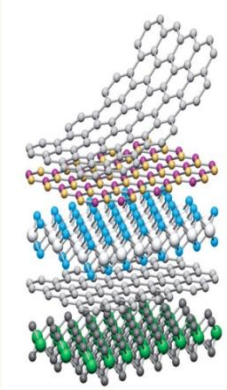
Clusters and molecular nanostructures





Nanotubes and related systems

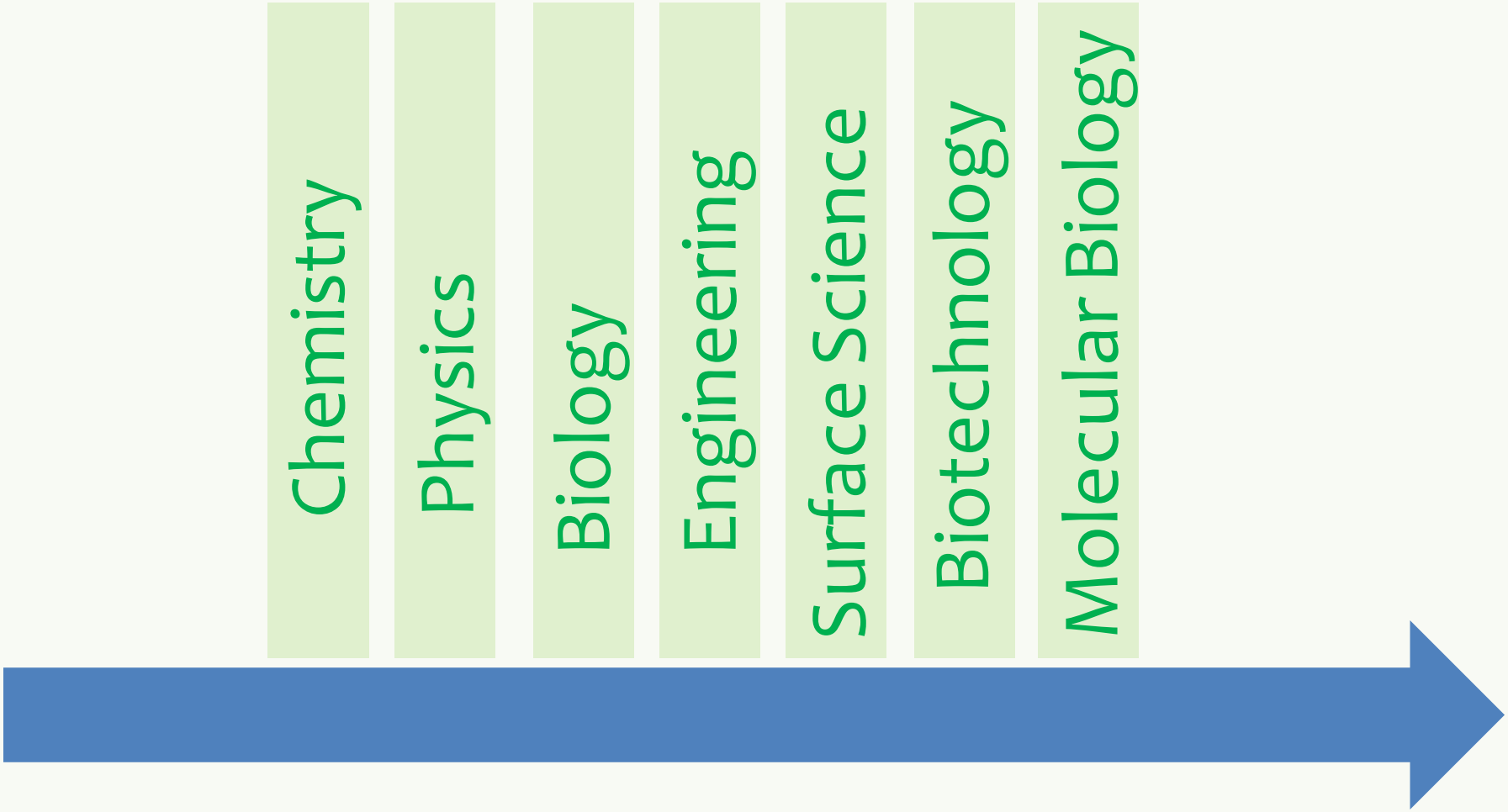
Quantum wells, wires, films and dots



2D materials

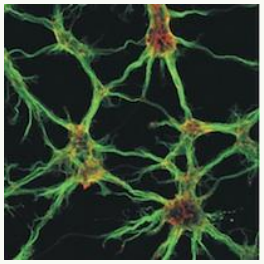
From nanoscience to …

From nanoscience to …

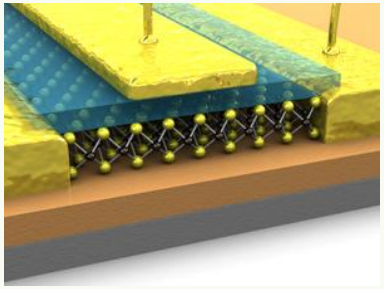


… nanotechnology

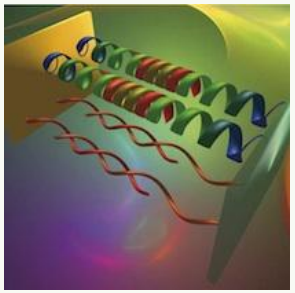
… nanotechnology



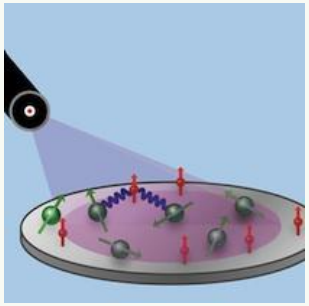
Biomedicine



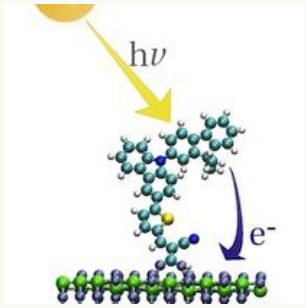
Nanoelectronics



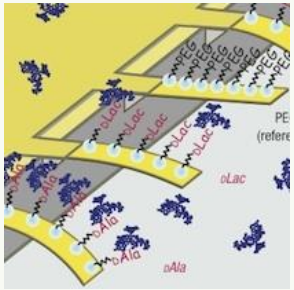
Biomaterials



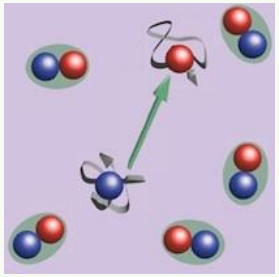
Quantum information



Optoelectronics



Sensors



Spintronics

The future of nanoscience

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- The application of new extraordinary experimental tools has created an urgent **need for a quantitative understanding** of matter at nanoscale

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- The application of new extraordinary experimental tools has created an urgent **need for a quantitative understanding** of matter at nanoscale
- The **absence of quantitative models** that describe newly observed phenomena increasingly limits progress in the field
- The absence of such tools would also **seriously inhibit wide-spread applications** ranging from molecular electronics to biomolecular materials

The case of thermal conductivity

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$$J = -k \nabla T$$

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Is the Fourier's law applicable to nanostructures?

How size effects can affect thermal conductivity?

Can present theories interpret satisfactorily experiments?

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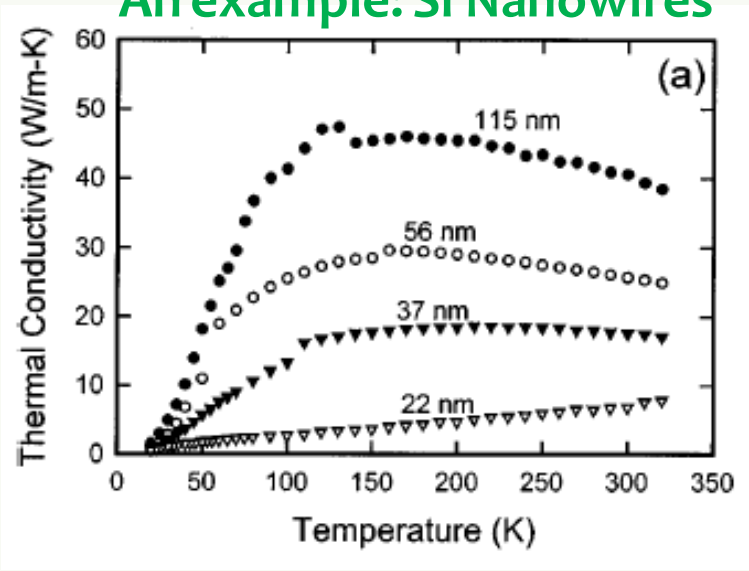
An example: Si Nanowires



Li et al. Appl. Phys. Lett. 83, 2934 (2003)

Measured thermal conductivity lower than bulk and diameter dependent

Quantum effects not negligible

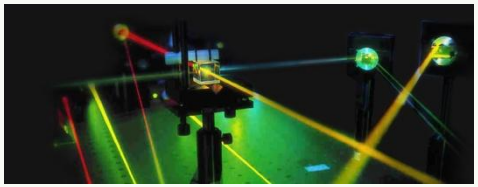
Breakdown of Fourier's law

Where do we need a theoretical effort?

Where do we need a theoretical effort?

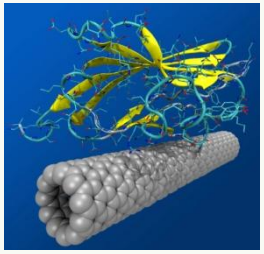
Transport in nanostructures

Electronic and optical properties



Coherence and decoherence tunneling

Soft/hard matter interfaces



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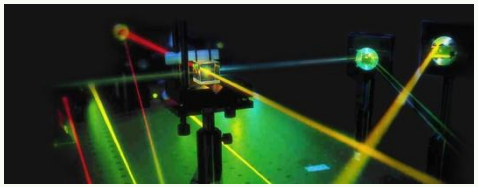

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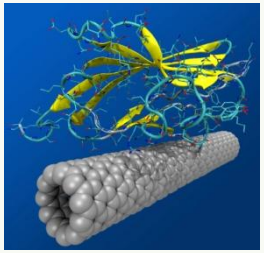

Spintronics

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Materials design

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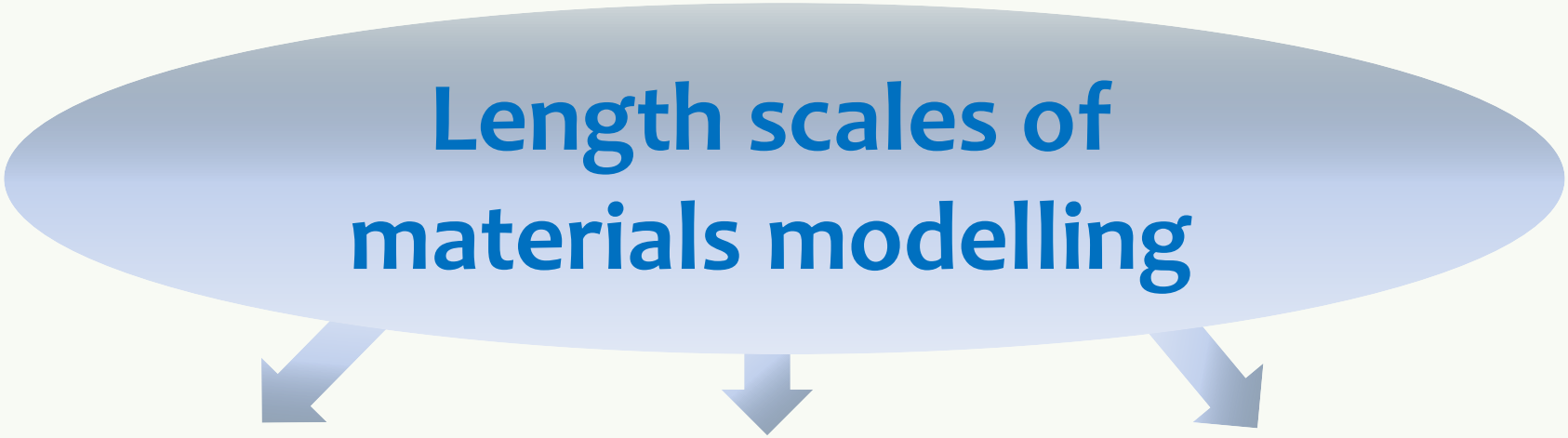
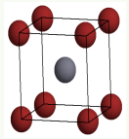
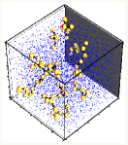
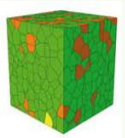


Materials design

Length scales of materials modelling







LENGTH [Å]

1 10^4 10^6 10^8

Ab initio (Density Functional Theory and post DFT methods)

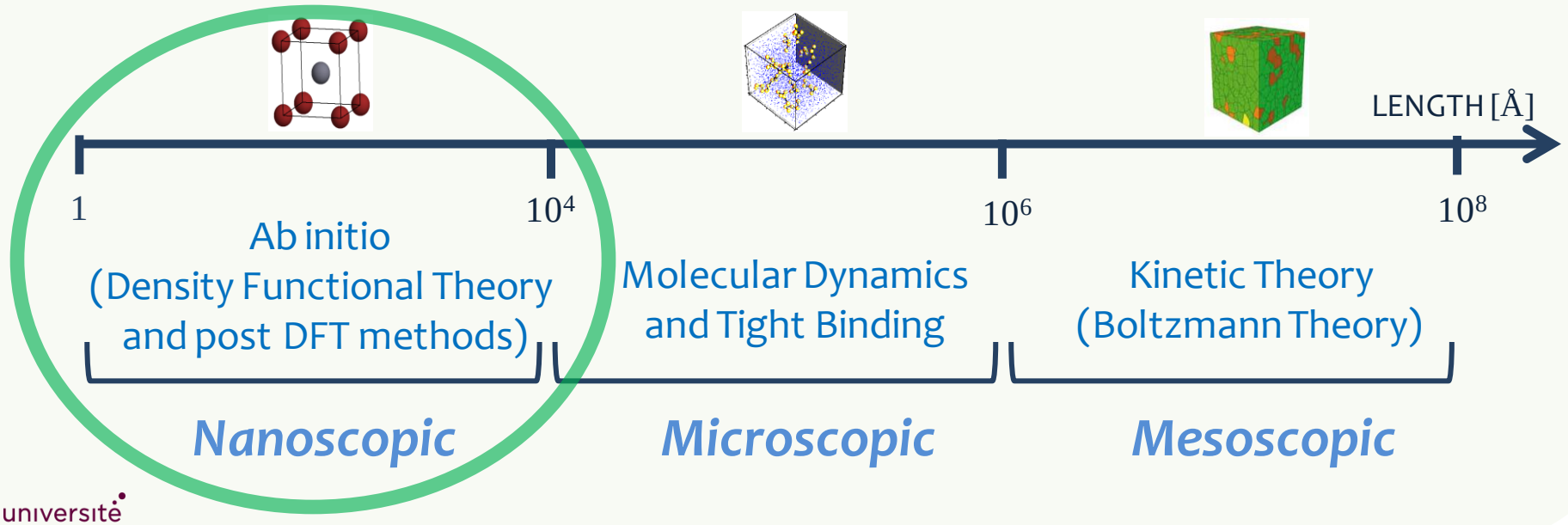
Molecular Dynamics and Tight Binding

Kinetic Theory (Boltzmann Theory)

Nanoscopic *Microscopic* *Mesoscopic*

Materials design

Length scales of materials modelling



Ab initio computational modelling

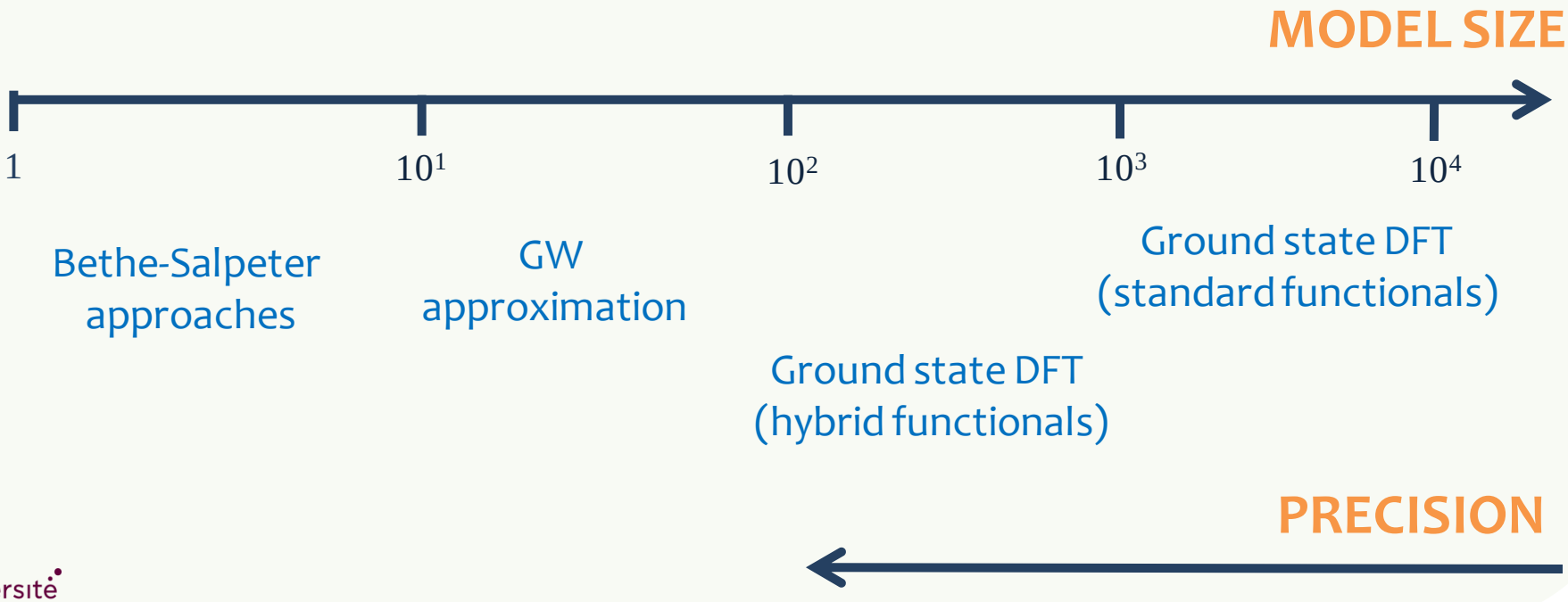
Ab initio computational modelling

- The developement and use of mathematical models for describing and predicting certain properties of materials at a **quantitative level**
- 'Ab initio' or 'from first principles' refers to a bottom-up modelling strategy in which we **do not use any empirical parameters**
- Such kind of calculations are completely based on **quantum mechanics**, that can be considered as an engineering tool
- The complexity of such problems requires the use of **supercomputers**
- This is a discipline at the boundary between **materials science, physics and chemistry** on the one side, and **applied mathematics and software engineering**

Materials design

Materials design

Precision of ab initio modelling



Density Functional Theory

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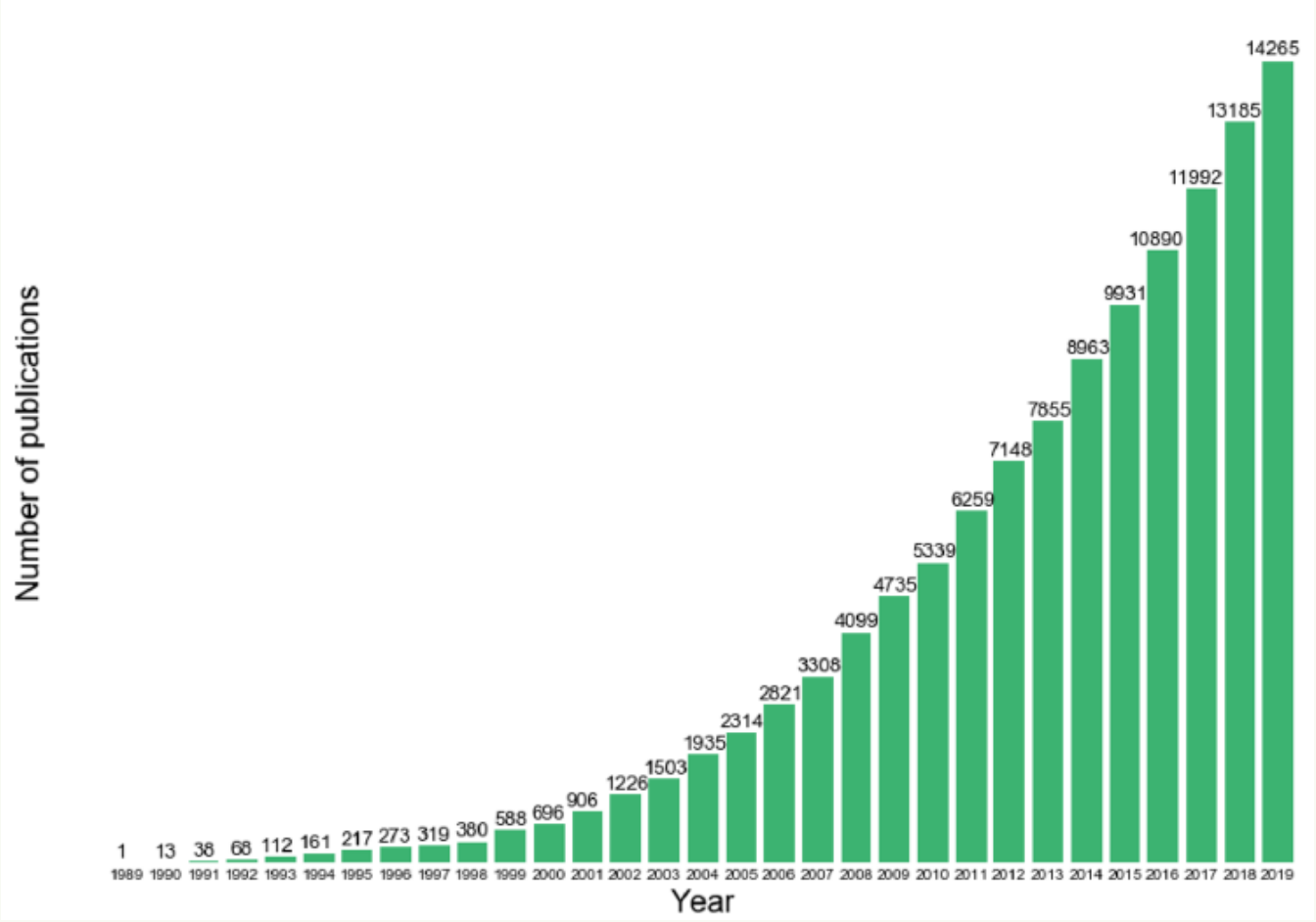
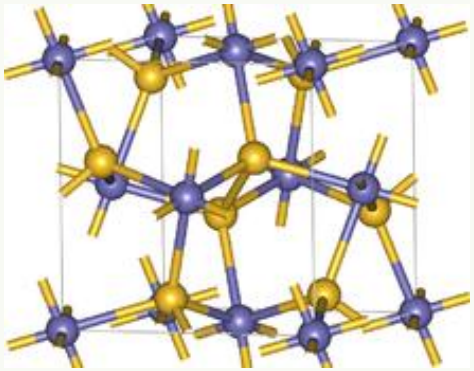


M. Dumaz et al. Scientometrics 126, 6681 (2021)

The many body electronic structure

The many body electronic structure



N_e electrons
N_n nuclei

Schrödinger equation for interacting particles

$$\hat{H}\Psi(\{R\},\{r\}) = E\Psi(\{R\},\{r\})$$

$$\hat{H} = \hat{T}_n(\{R\}) + \hat{V}_{nn}(\{R\}) + \hat{T}_e(\{r\}) + \\ + \hat{V}_{ee}(\{r\}) + \hat{U}_{en}(\{R\},\{r\})$$

The many body hamiltonian

The many body hamiltonian

$$\widehat{T}_n = \sum_{I=1}^{N_n} -\frac{\nabla_I^2}{2M_I}$$

Kinetic energy of nuclei

$$\widehat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m_e}$$

Kinetic energy of electrons

$$\widehat{V}_{nn} = \frac{1}{2} \sum_{I,J,I \neq J}^{N_n} \frac{Z_I Z_J}{|R_I - R_J|}$$

Ion-ion interactions

$$\widehat{V}_{ee} = \frac{1}{2} \sum_{i,j,i \neq j}^{N_e} \frac{1}{|r_i - r_j|}$$

Electron-electron interactions

$$\widehat{U}_{en} = -\sum_{j,J}^{N_e,N_n} \frac{Z_J}{|R_J - r_j|}$$

Electron-ion interactions

Exactly solvable for two particles (analytically) and very few particles (numerically)

How to deal with N ~ 10^{23} particles?

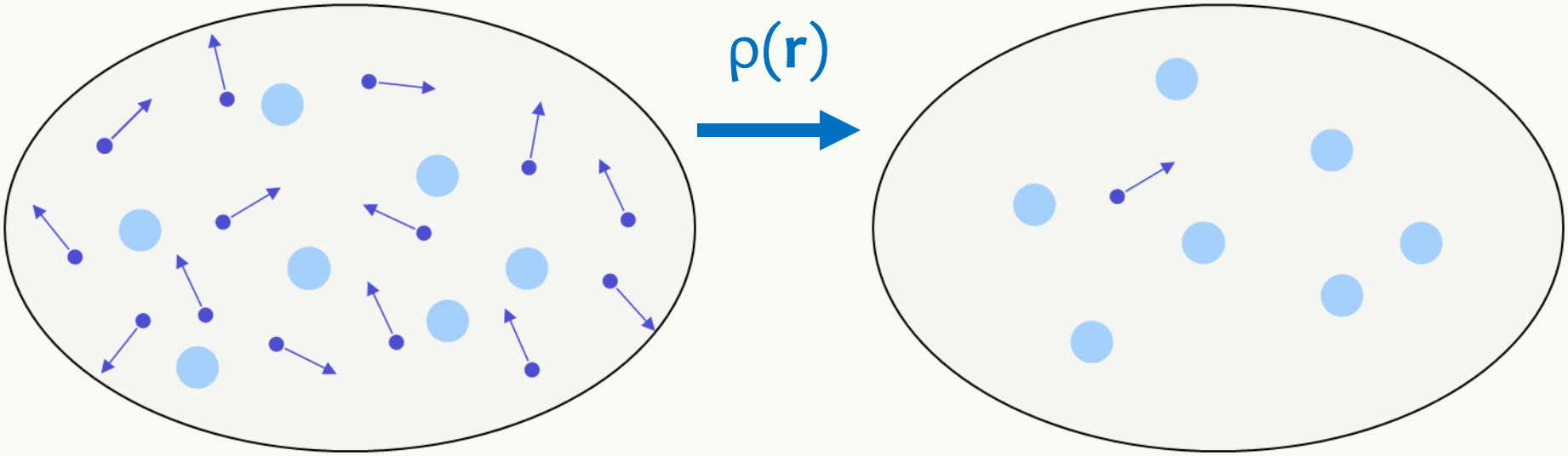
Density Functional Theory (DFT)

Density Functional Theory (DFT)

It can map, exactly, the **interacting** problem to a **non-interacting** one

Hohenberg and Kohn, Phys. Rev. B 136, 864 (1964)

W. Kohn
Nobel Prize in Chemistry in 1998



interacting particles in a real external potential

a set of non-interacting electrons (with the same density as the interacting system) in some effective potential

Popularity of DFT

Popularity of DFT

- **Transferability:** same technique for describing different classes of materials
- **Simplicity:** based on simply and intuitive equations
- **Realiability:** possibility of making direct and quantitative comparison with experiments
- **Software sharing:** online platforms and adoption of open-source software model
- **Reasonable starting point:** even when it fails in describing correctly a property, it represents an accurate starting point for more accurate theory (more computationally demanding)

Some specific comments

Some specific comments

- In principle DFT is exact and pure predictive, but in practice it needs some approximations (exchange-correlation functional)
- Good scaling of computational cost with system size
- Calculations on large and complex systems (surfaces, interfaces, nanostructures, defects)
- Accuracy of properties prediction is well known (i.e. 3% for bond length, 10% for bulk modulus and phonon frequencies)
- Good compromise between accuracy and computational time

Ab initio properties of materials

Ab initio properties of materials

STRUCTURAL PROPERTIES

Density Functional Theory,
Total energies, Forces, Stresses,
Atomic and cell geometries

SURFACE PROPERTIES

Nudge Elastic Bands
Activation barrier,
Surface and adsorption energies

ELECTRONIC STRUCTURE

Density Functional Theory,
Band structure, Density of states,
Wave function,

OPTICAL RESPONSE

Many Body Perturbation Theory,
Optical Absorption, Excitons,
GW approach, EELS

VIBRATIONAL PROPERTIES

Density Functional
Perturbation Theory (DFPT),
Raman spectra, phonons, phase diagrams

ELASTIC PROPERTIES

Density Functional Theory,
Elastic constants and
properties of solids

Ab initio properties of materials

STRUCTURAL PROPERTIES
Density Functional Theory,
Total energies, Forces, Stresses,
Atomic and cell geometries

SURFACE PROPERTIES
Nudge Elastic Bands
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Theoretical method and codes

Theoretical method and codes

SIESTA code http://icmab.es/siesta

Density Functional Theory (DFT)

- Exchange-correlation functional: LDA
- Optimized double-z polarized basis-set
- Troullier-Martins pseudopotentials

VASP code http://www.vasp.at

Hybrid - DFT

- Exchange-correlation functional: PBE-HSE06
- Plane-wave basis set
- PAW approach pseudopotentials

YAMBO code www.yambo-code.org

GW and optical properties calculations

- GW one short perturbative approach
- Plane-wave basis set
- RPA and BSE approaches

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Space for electrons in materials

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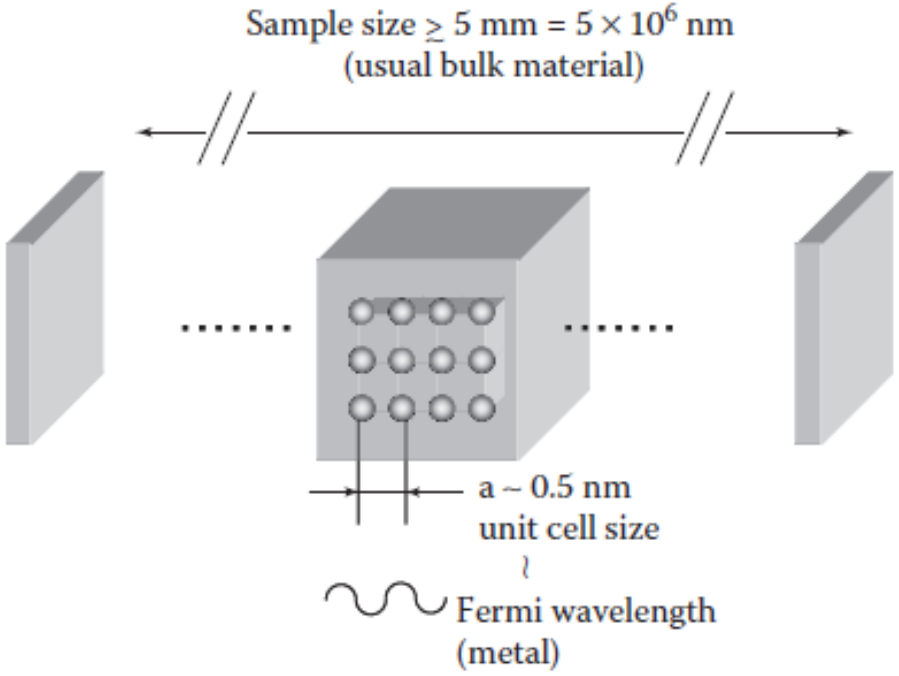
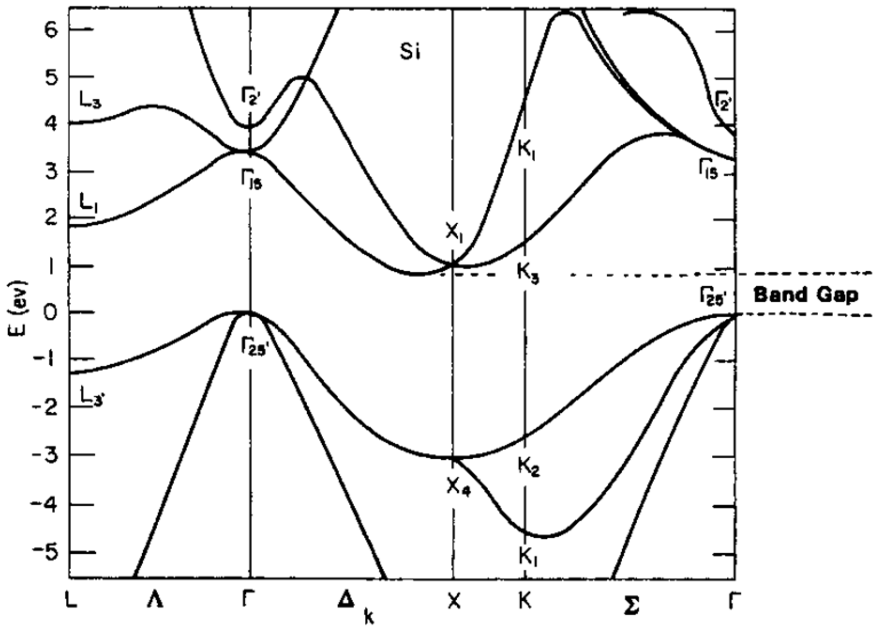




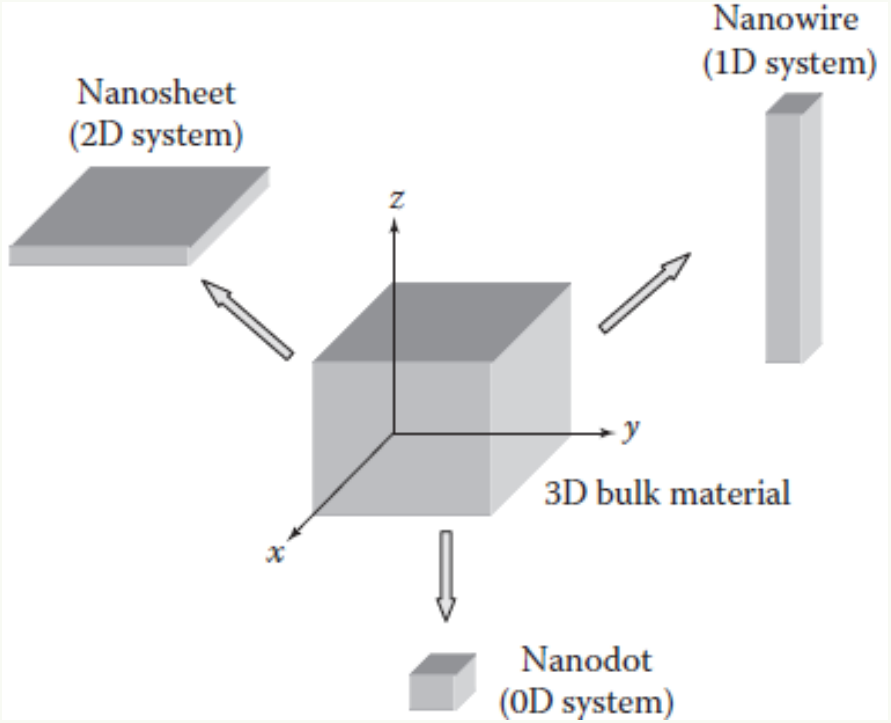
Si band structure

T. Tsurumi et al. *Nanoscale physics for materials science*, Taylor and Francis (2010)

- In macroscopic materials the Fermi wave length is of the same order as the unit cells
- Thus the inner space is too large for electrons to feel boundaries
- The possible energy levels for electrons $E(k)=(\hbar^2/2m^*)k^2$ are dense with very small energy spacing

Quantum confinement effect (QCE)

Quantum confinement effect (QCE)



T. Tsurumi et al. *Nanoscale physics for materials science*, Taylor and Francis (2010)

Quantum confinement effect (QCE) is defined as: a reduction in the degrees of freedom of the carrier particles, implying a reduction in the allowed phase space

E.G. Barbagiovanni et al. Appl. Phys. Rev. 1, 011302 (2014)

Consequences of QCE

Consequences of QCE

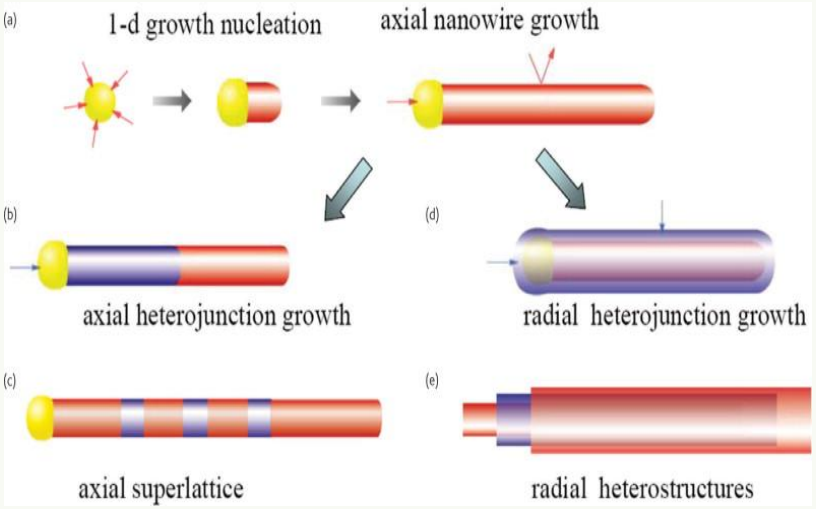
- Electrons traveling along the direction that has been reduced in size reach the boundaries and are confined
- This confinement causes the quantization of the electron wavelength and of the energy spectrum
- The contribution of edge-localized surface states can become relevant
- Size effects dominate the physics of nanostructures

The case of Si nanowires (Si NWs)

The case of Si nanowires (Si NWs)

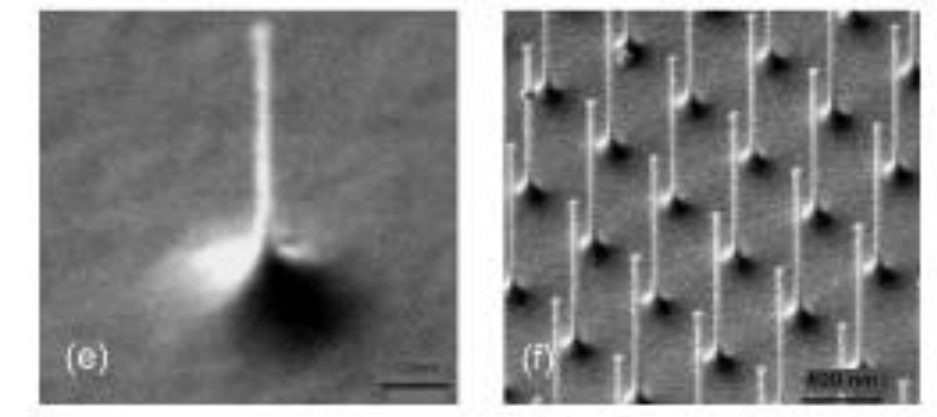
One-dimensional nanostructures with precise composition, morphology, interfaces and electrical properties (d=2-3 nm)

Vapor-Liquid-Solid (VLS) growth



O. Hayden et al., Nanotoday 3 5-6 (2008)

Lithography and etching processes

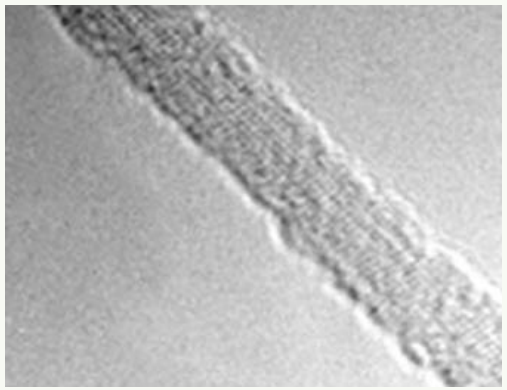


N. Singh et al., IEEE Trans. Electron Devices 55, 11 (2008)

QCE in Si NWs: electronic structure

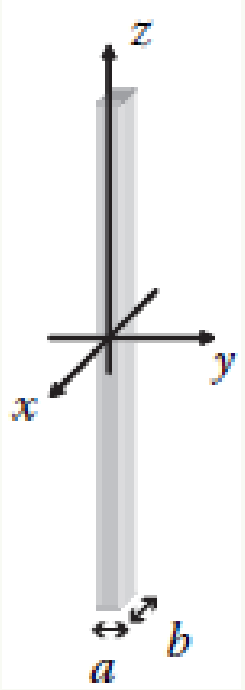
QCE in Si NWs: electronic structure

Real system



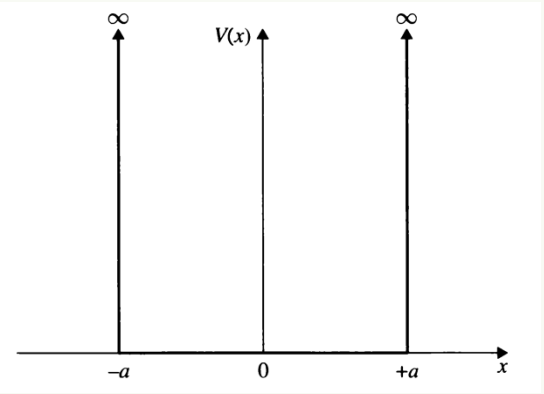
Wu et al., Nano Lett. 4, 433 (2004)

Geometrical model



T. Tsurumi et al., Taylor and Francis (2010)

Infinite potential well (particle-in-a-box model)



B.H. Brandsen and Joachin, *Quantum Mechanics* (2000)

QCE in Si NWs: electronic structure

QCE in Si NWs: electronic structure

The motion of electrons is restricted to be in the direction of confinement. Their kinetic energy increases and the eigenstates energies are given by:

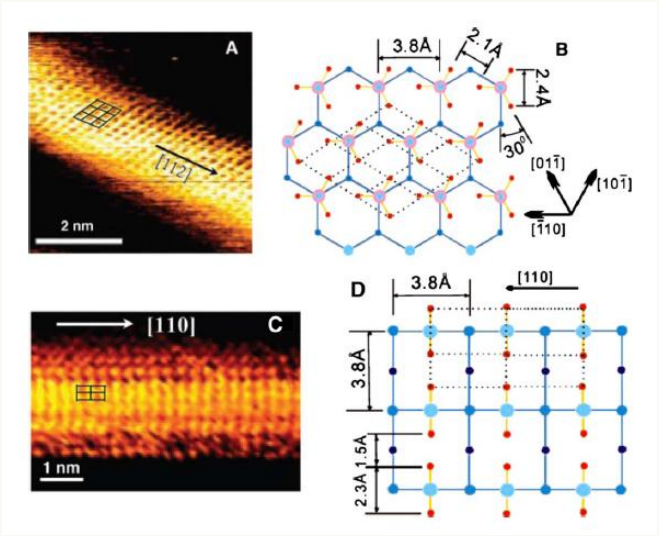
$$E_n = \frac{\hbar^2 n^2 \pi^2}{2m^* d^2}$$

m*=effective mass
d=width of the well

Not only the energy levels but even the spacing between them increase when the diameter is reduced (QCE increases)

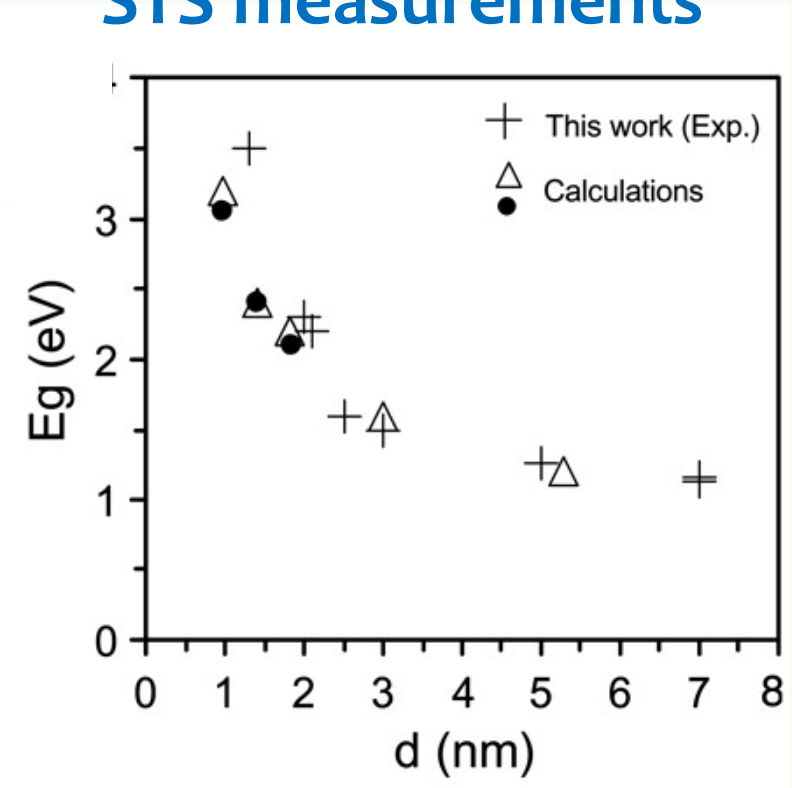
QCE has a dramatic effect on semiconductor NWs (like Si NWs) because it affects the **energy band gap**

QCE in Si NWs: electronic structure



Ma, D. D. D. et al., Science 299, 1874 (2003)

STS measurements



Ma, D. D. D. et al., Science 299, 1874 (2003)

$$E_{gap} = E_{bulk,\,gap} + C(1/d)^{\alpha}$$

with α=1.1 – 1.4

M. Bruno et al., Phys. Rev. Lett. 98, 036807 (2007)

QCE in Si NWs: DFT scaling of the gap

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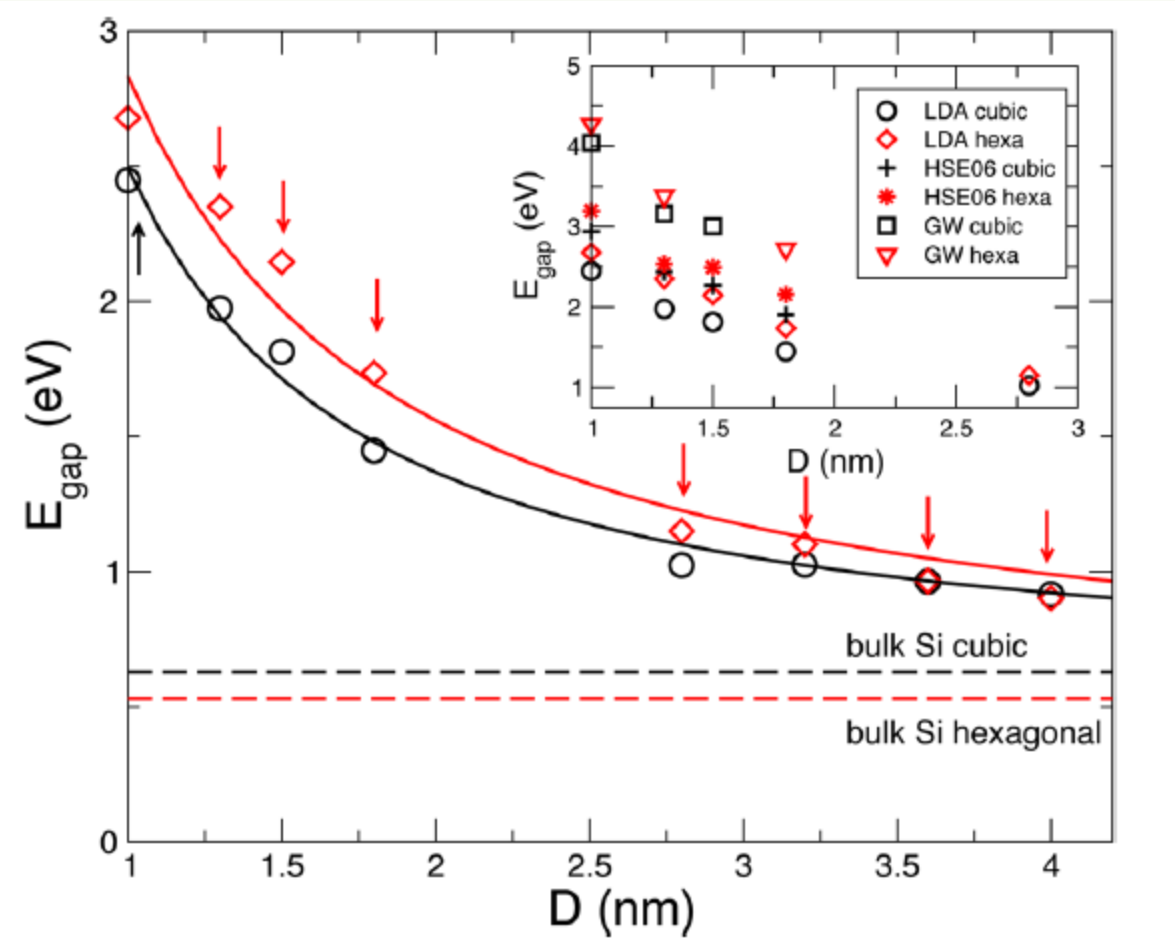

DFT – LDA

$\alpha_{hex} = 1.16$

$\alpha_{cub} = 1.34$

$$E_{gap} = E_{bulk,\,gap} + C(1/d)^{\alpha}$$

M. Amato et al., Nano Lett. 16, 5694 (2016)

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QCE in NWs: energy quantization

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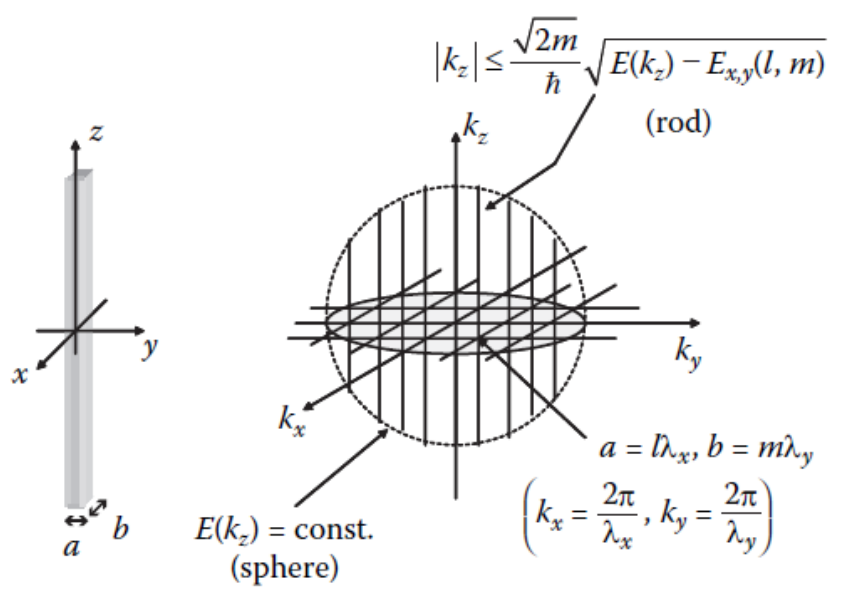


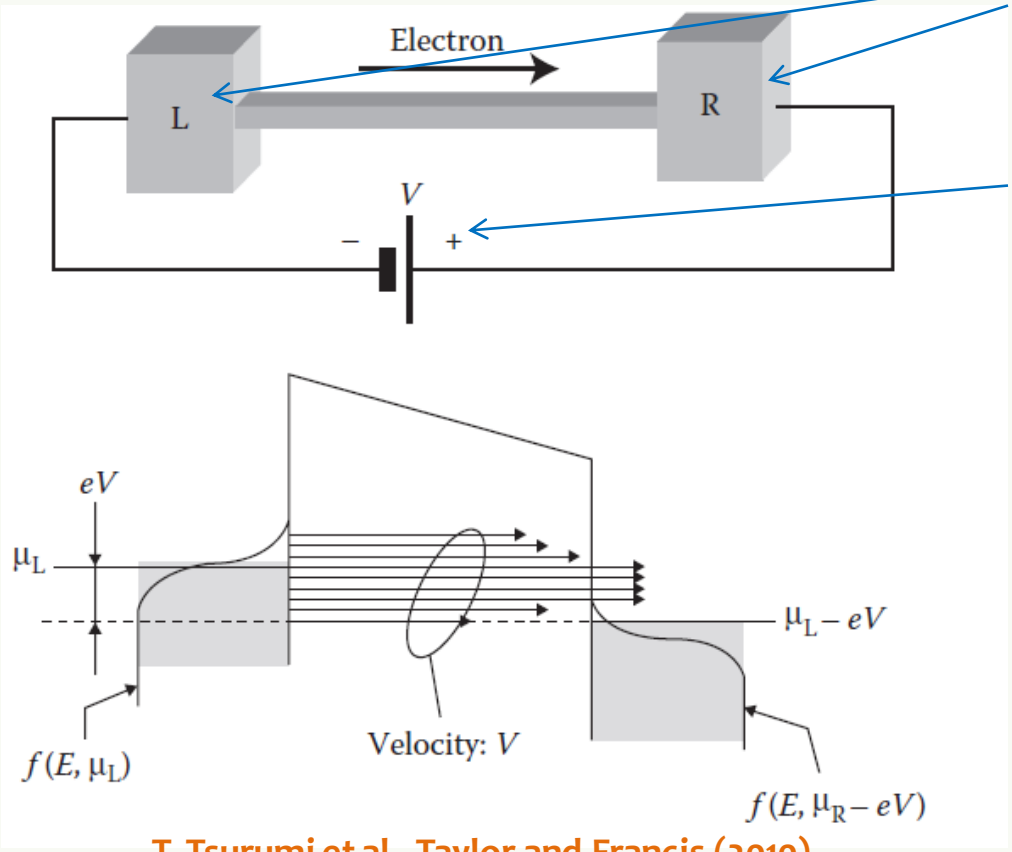
T. Tsurumi et al., Taylor and Francis (2010)

The total energy of electrons is given by the formula:

$$E\left(k_z\right) = \underbrace{\frac{\hbar^2}{2m^*}k_z^2}_{\text{Kinetic energy}} + \underbrace{E_{x,y}(l,m)}_{\text{Quantized energy in the plane}}$$

QCE in NWs: Landauer approach

QCE in NWs: Landauer approach



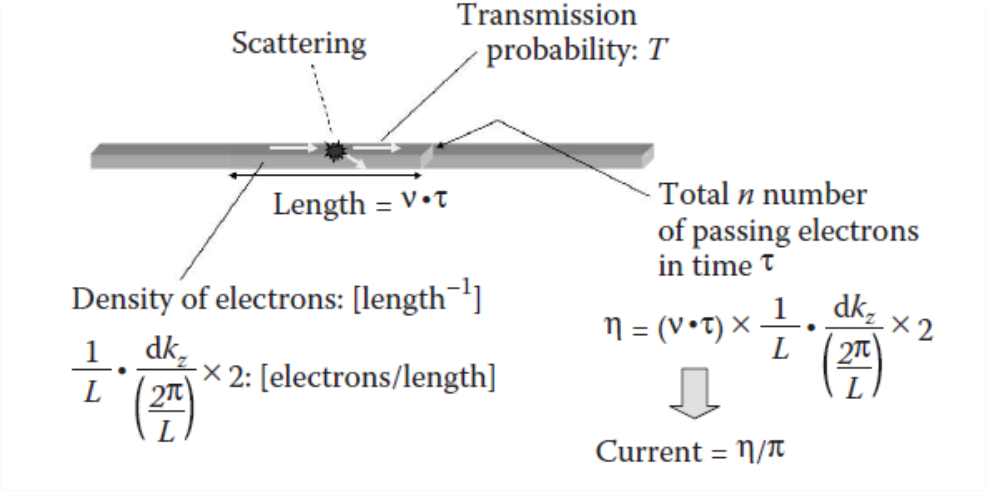
T. Tsurumi et al., Taylor and Francis (2010)

Electrons move with a group velocity v(k) and transmission probability T(k)

Can we calculate the current between electrodes?

QCE in NWs: quantized conductance

QCE in NWs: quantized conductance



T. Tsurumi et al., Taylor and Francis (2010)

Current

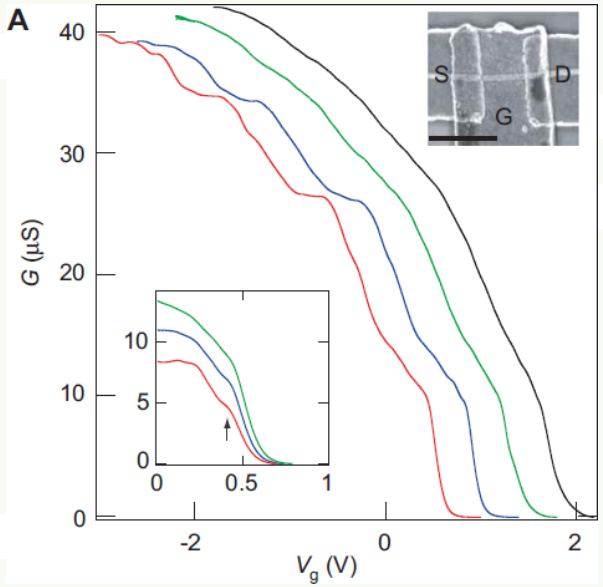
$$I = \frac{2e}{h} \int_0^\infty \{f(E,\mu) - f(E,\mu - eV)\} T(E) dE$$

Conductance (if the bias is small)

$$G = \frac{2e^2}{h} \int_0^\infty \left\{ -\frac{\partial f(E,\mu)}{\partial E} \right\} T(E) dE \equiv \frac{2e^2}{h} T_\mu$$

QCE in NWs: quantized conductance

- In 1D systems the conductance of electrons is quantized in units of $2e^2/h$
- Electrons states along the wire are associated with quantized states in the plane
- Each of the quantum states in the plane has equal unit of conductance $(2e^2/h)T_\mu$ along the wire axis (where T_μ is dimensionless)
- The conductance of NWs is hence the product of the number of quantum states and their quantized conductance $(2e^2/h)T_\mu$



Lu et al. PNAS 102, 29 (2005)

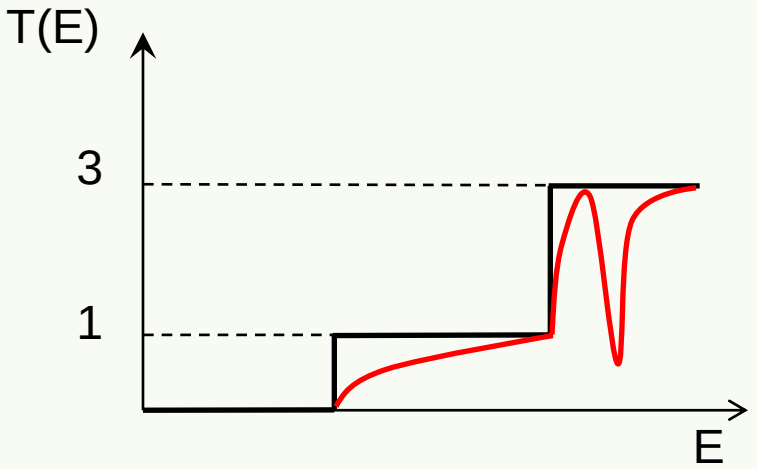
Experimental demonstration on SiGe core-shell NWs

QCE in Si NWs: DFT+Landauer approach

QCE in Si NWs: DFT+Landauer approach

Conductance is calculated in terms of transmission probability T(E) through the available transmitting channels

How many?
For an infinitely long NW: as many as electron states at that energy



M. Amato et al. Nano Lett. 12, 2717 (2012)

For a pristine Si NW: T(E) = 1
For a defected NW: T(E) < 1

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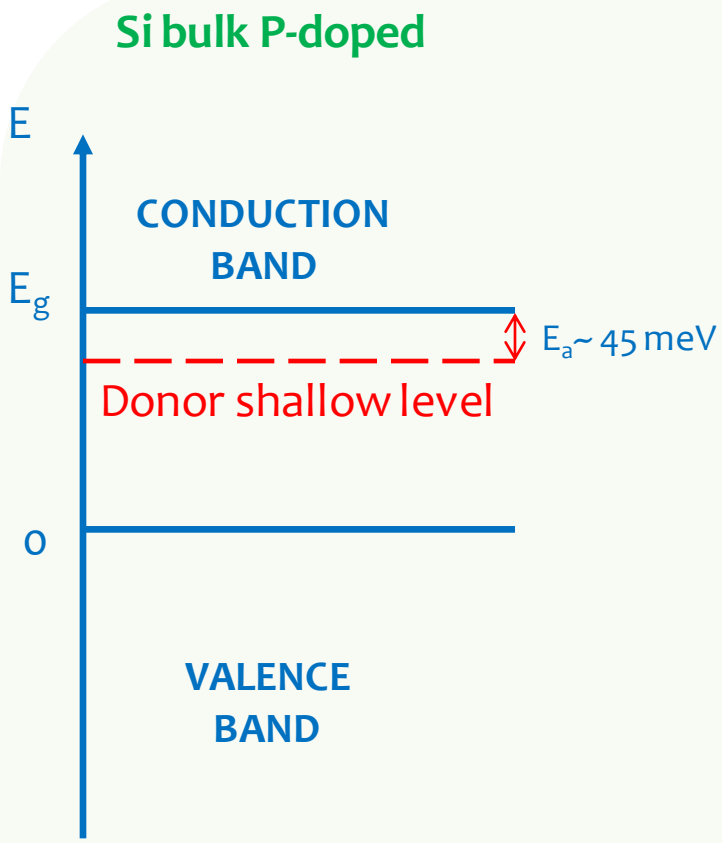

- Ionization energy ~ few hundredths of eV
- Ionized impurity at room temperature
- High doping efficiency

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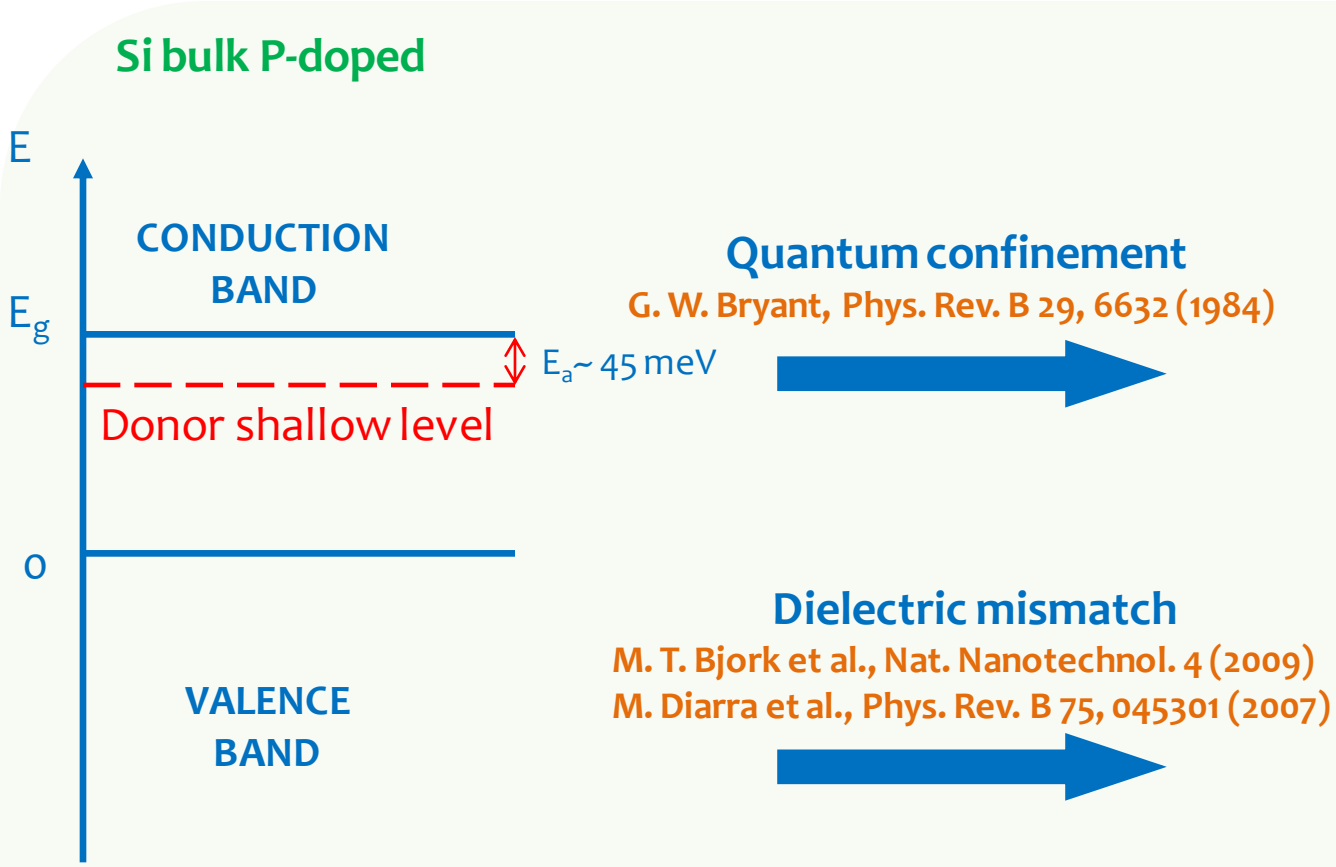

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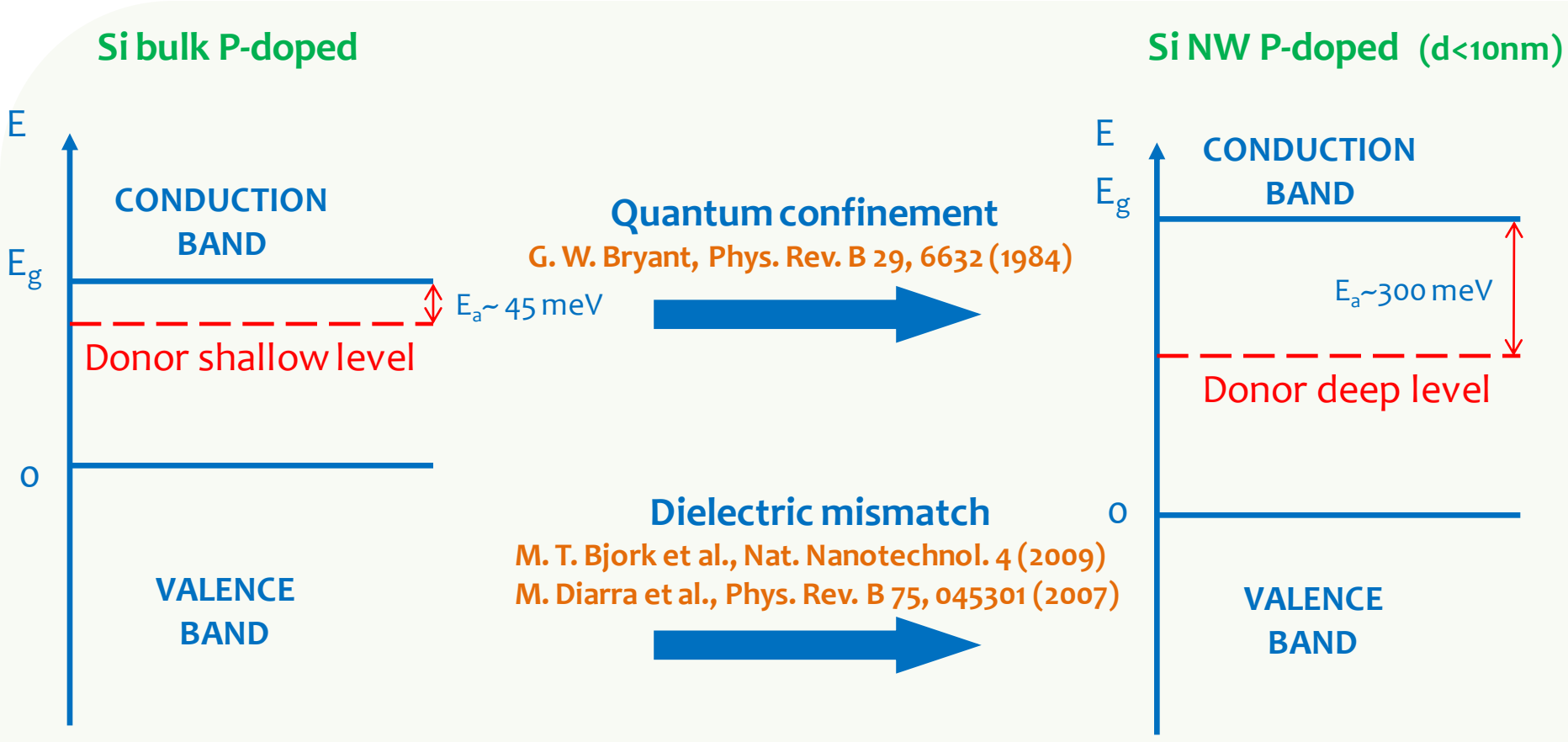

- Ionization energy ~ few hundredths of eV
- Ionized impurity at room temperature
- High doping efficiency

- Ionization energy increase
- Donor level deep into the band gap
- Doping deactivation with respect to bulk

QCE in Si NWs: P deactivation in DFT

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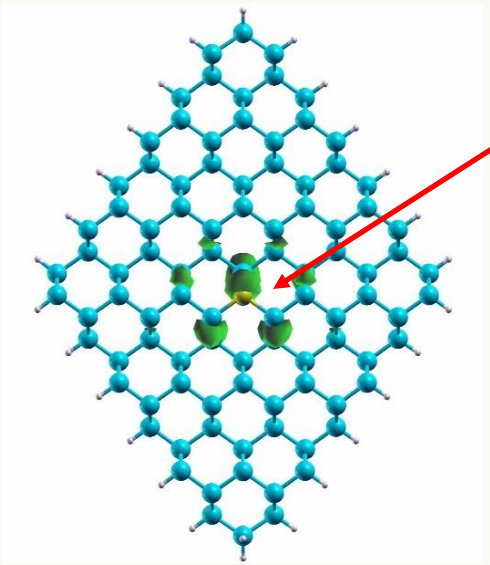

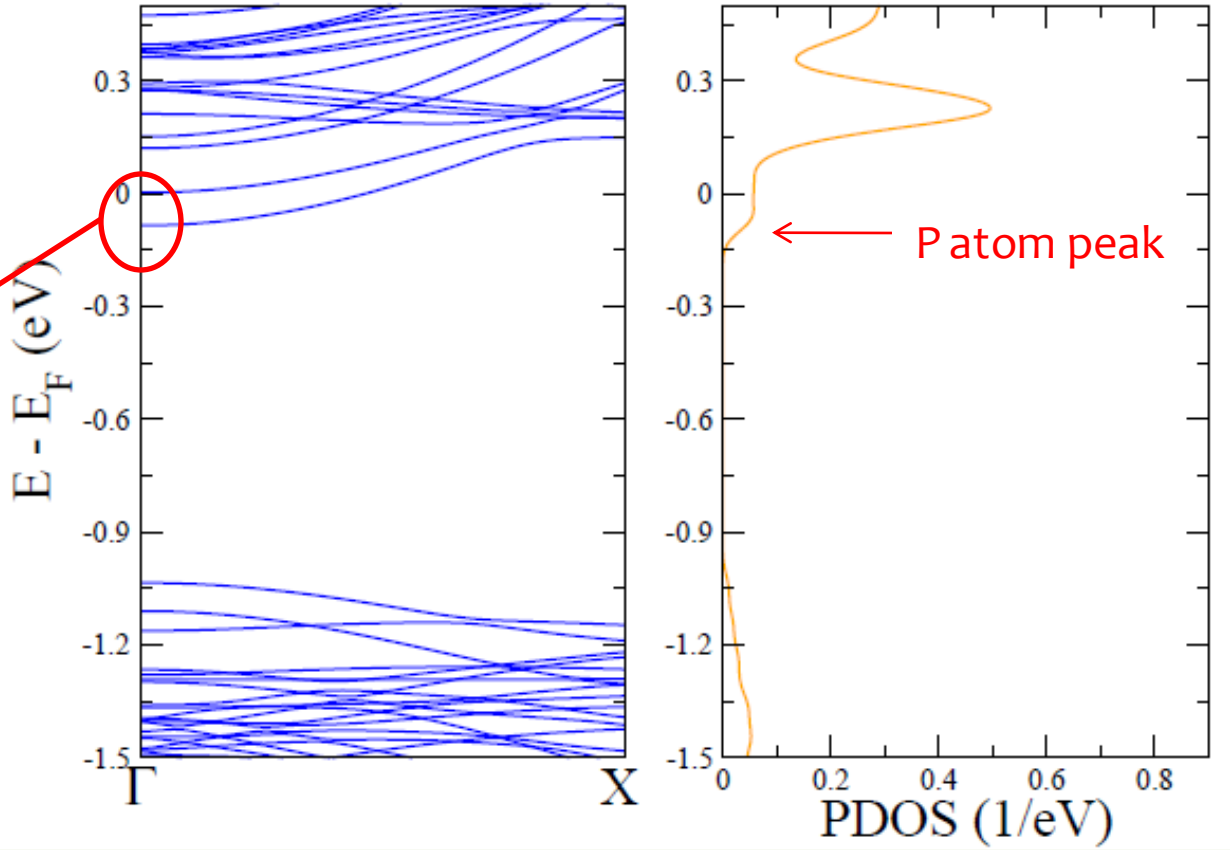

M. Amato et al., Nano Lett. 11, 594–598 (2011)

P-impurity state deep into the band gap
Activation energy is too high (~ 100 meV)

Some comments on QCE in Si NWs

Some comments on QCE in Si NWs

The diameter is a powerful tool to modulate physical properties

- **Electronic Structure.** Reducing the size can induce an opening of the bulk band gap that can cause a modulation of optical properties

- **Transport.** The quantization due to the confinement leads to a quantization of the electrical conductance. Si NWs are hence quantum confined ballistic conductors

- **Doping.** Intentional addition of impurities in Si NWs is not efficient as for bulk systems due to the impurity deactivation

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Is it possible to further modify the physical properties of Si NWs?

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The crystal phase of group IV NWs

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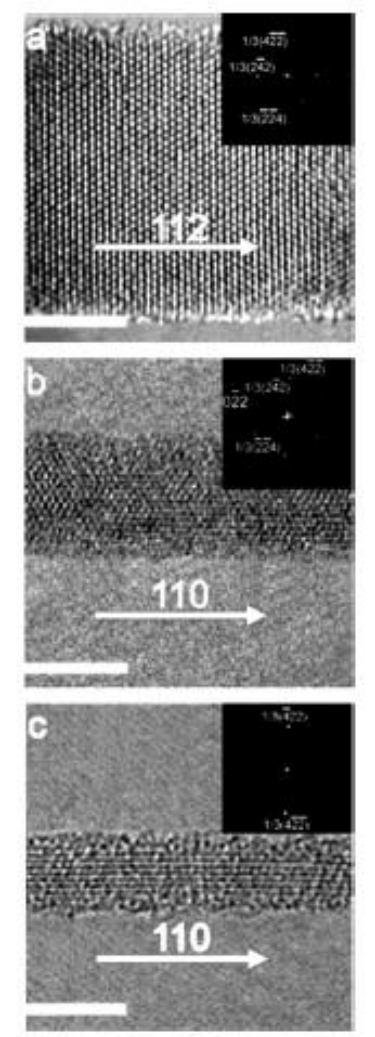

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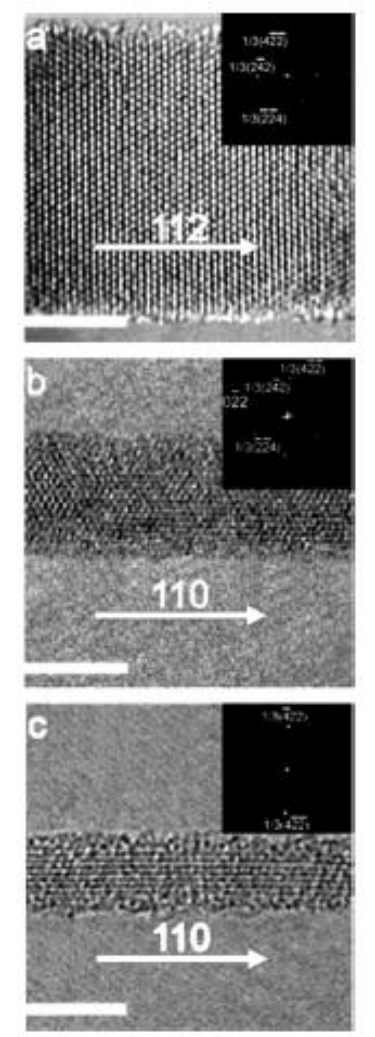
The crystal phase of group IV NWs



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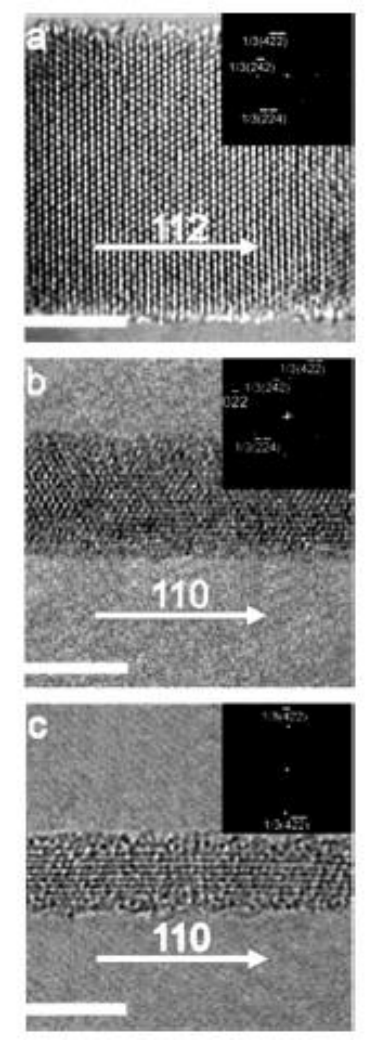

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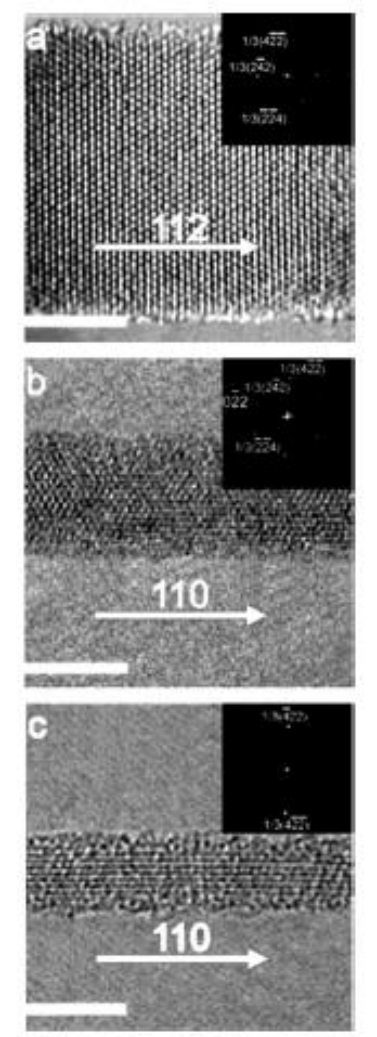

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- In particular it was found that they are rodlike structures constructed around a bulk Si single crystalline core
- This finding was mostly independent of the growth method, although it has been demonstrated that the quality of the crystal and the density of defects can depend on it
- All these experiments confirmed that, as can be intuitively expected, **Si NWs crystallize in the diamond-like cubic structure as in their bulk counterpart (3C phase)**

M. Amato and R. Rurali, Prog. Surf. Sci. 91, 1-28 (2016)

Properties of group IV NWs

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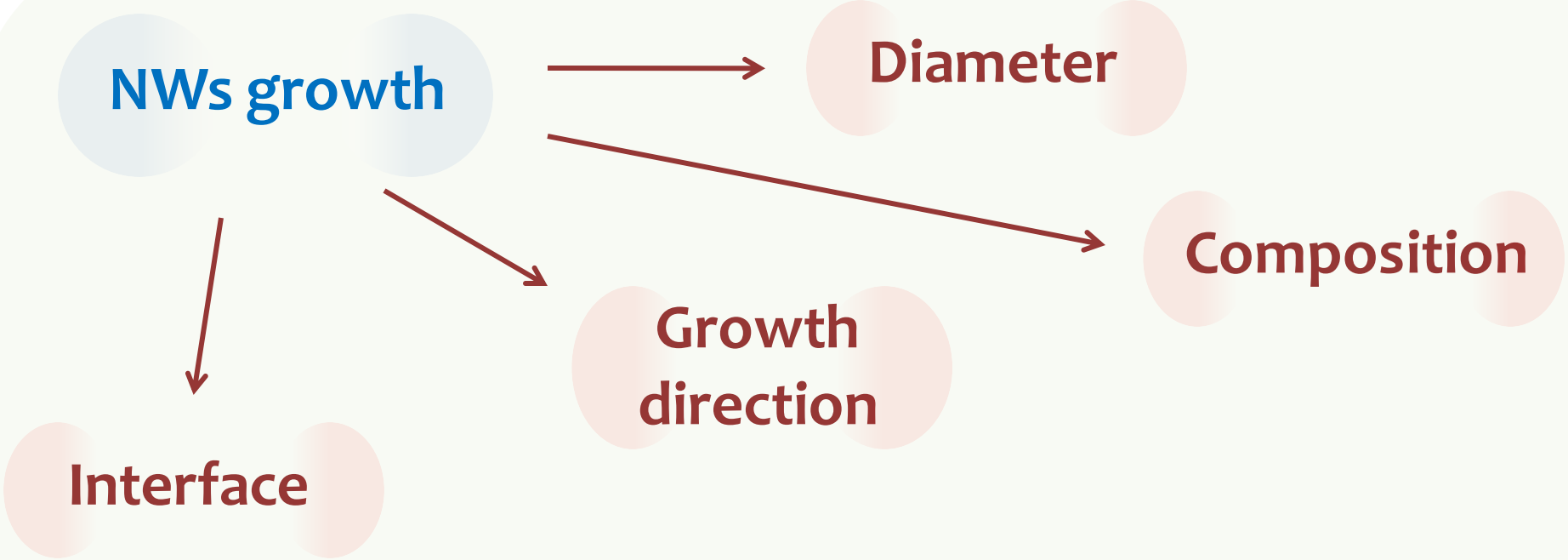
NWs growth

Properties of group IV NWs



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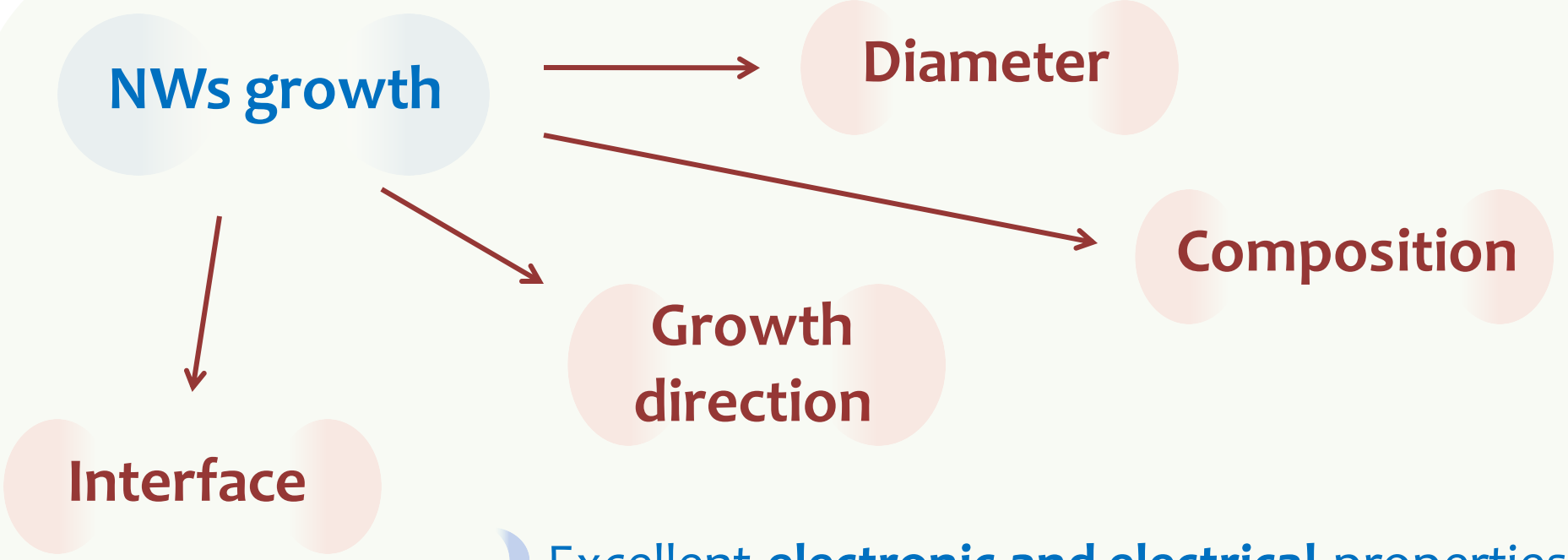
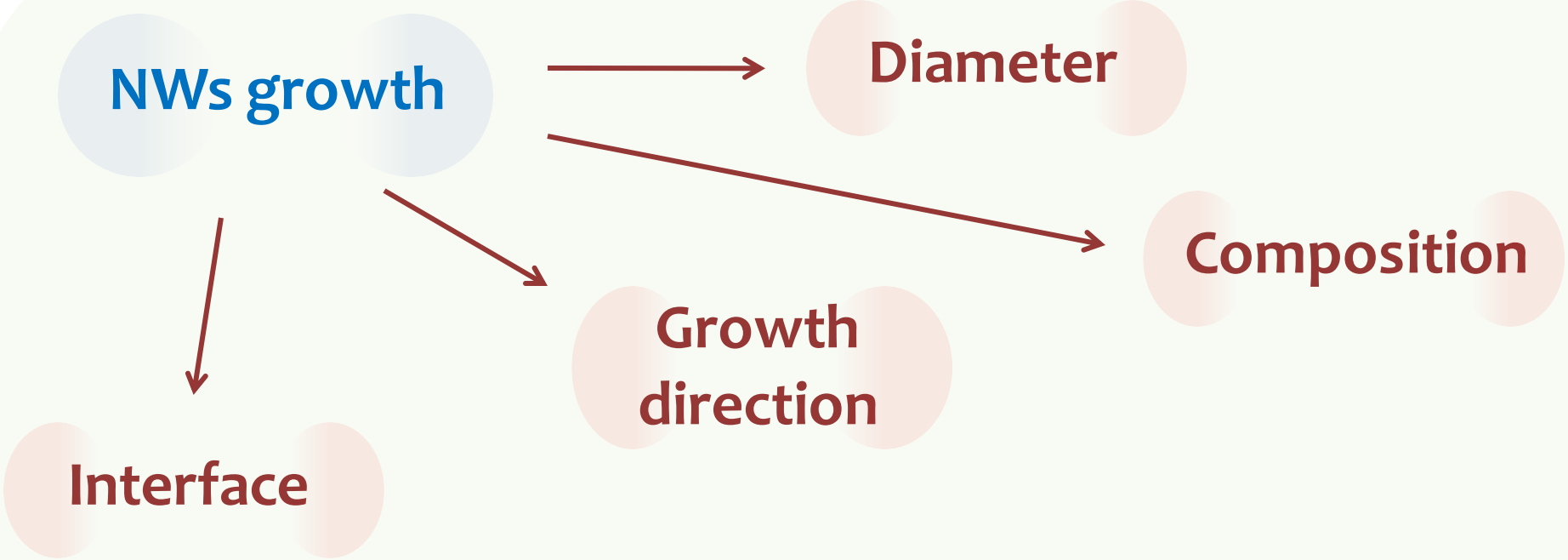


- Excellent **electronic and electrical** properties
- Novel sub-wavelength **optical phenomena**
- **High surface-to-volume ratio**
- The possibility to **functionalize** the surface
- The **decoupling of length scales**

M. Amato et al., Chem. Rev. 114, 1371 (2014)

Properties of group IV NWs



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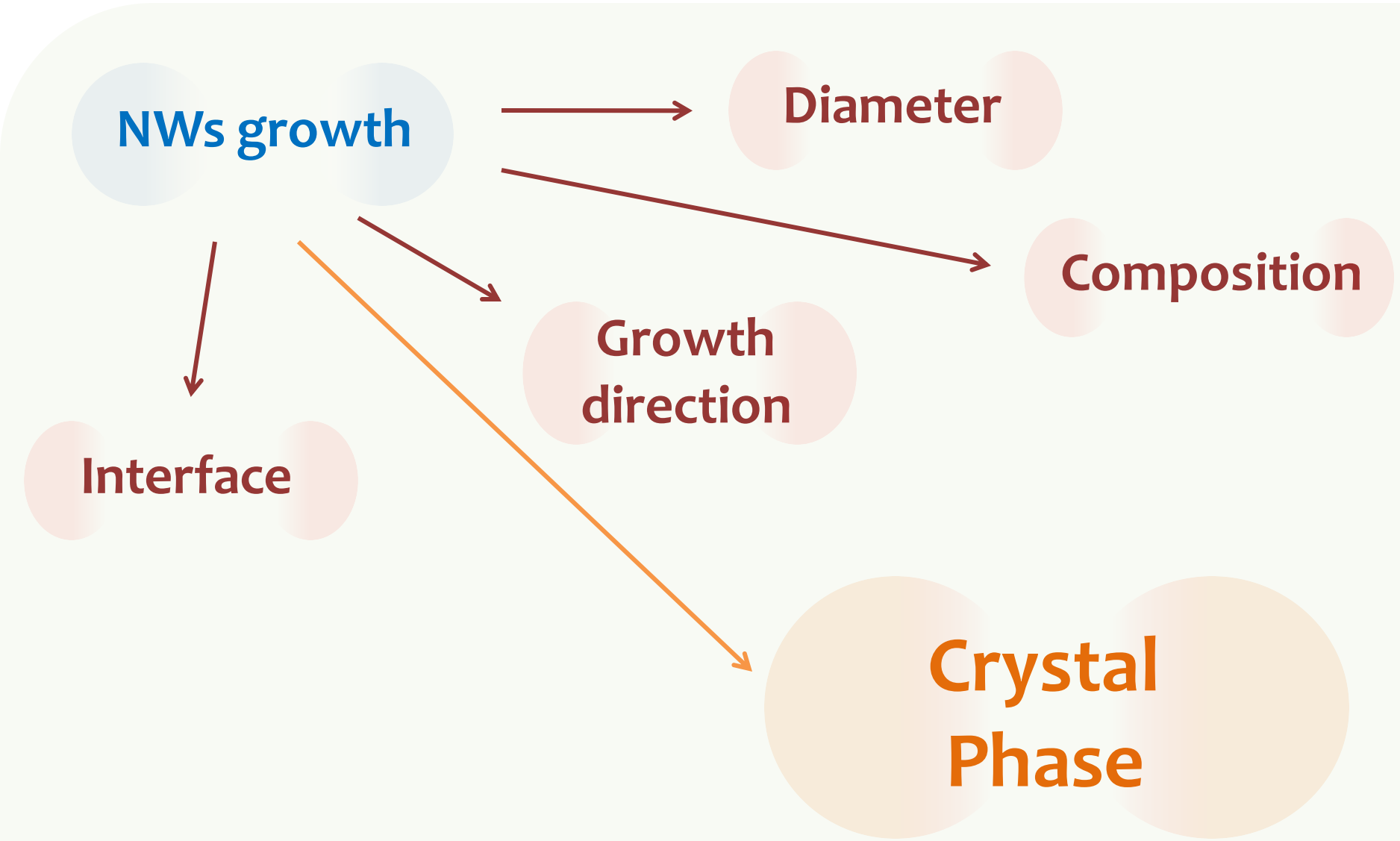

L. Tizei and M. Amato, Eur. Phys. J. B 93, 16 (2020)

Hexagonal-diamond (2H) NWs

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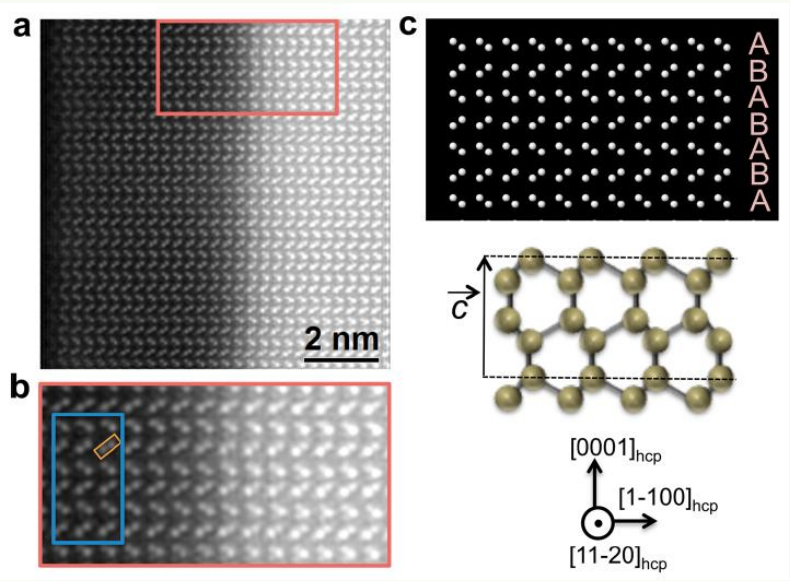
Hexagonal Si nanoshells on top of hexagonal GaP



H. T. Hauge et al., Nano Lett. 15, 5855 (2015)

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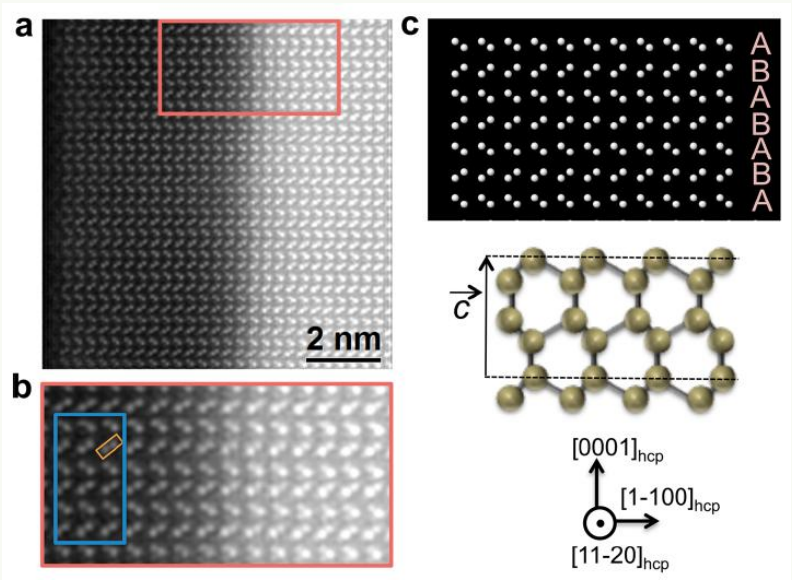

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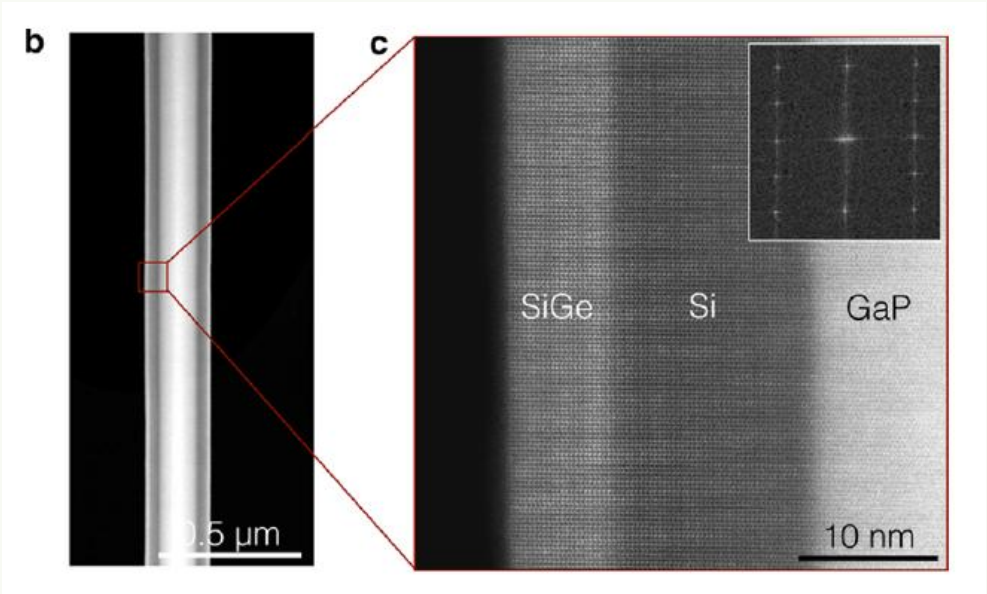

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Hexagonal-cubic junctions 2H/3C NWs

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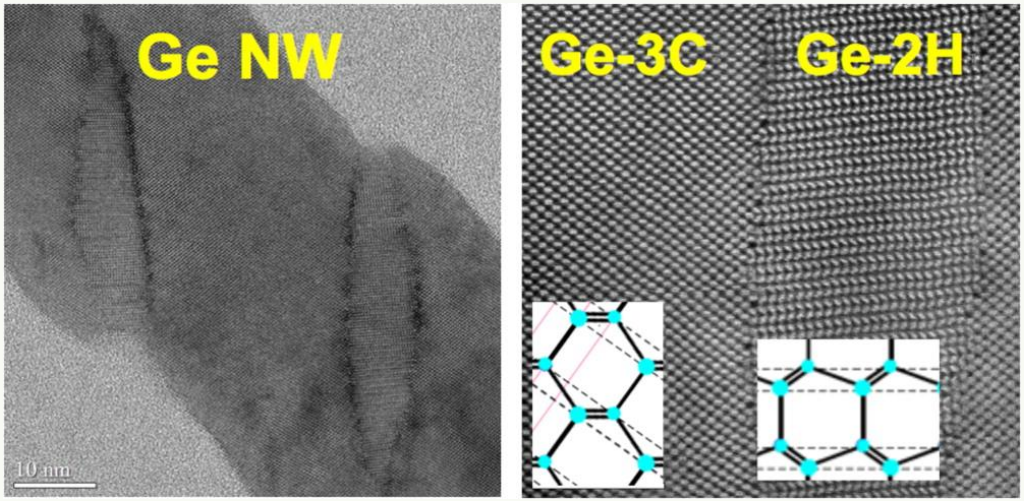
Hexagonal-cubic diamond Ge NWs homojunctions



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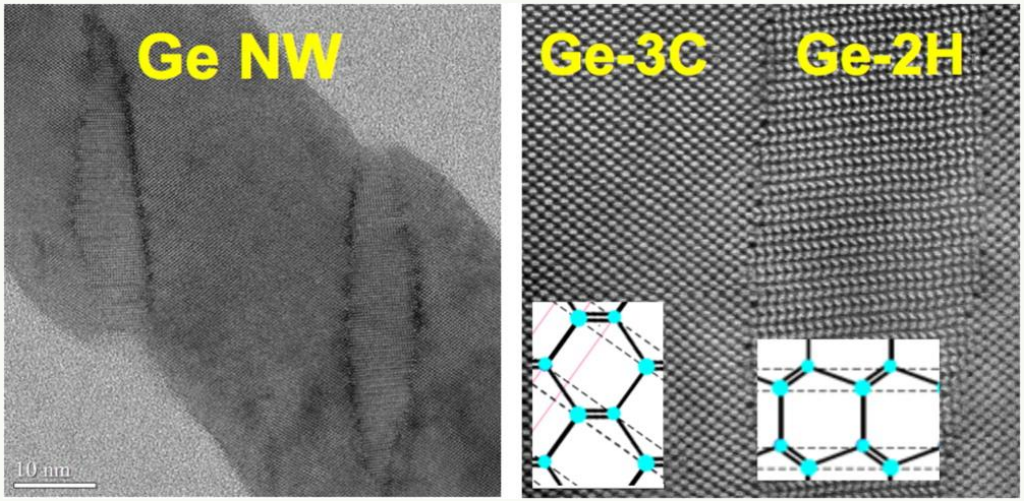

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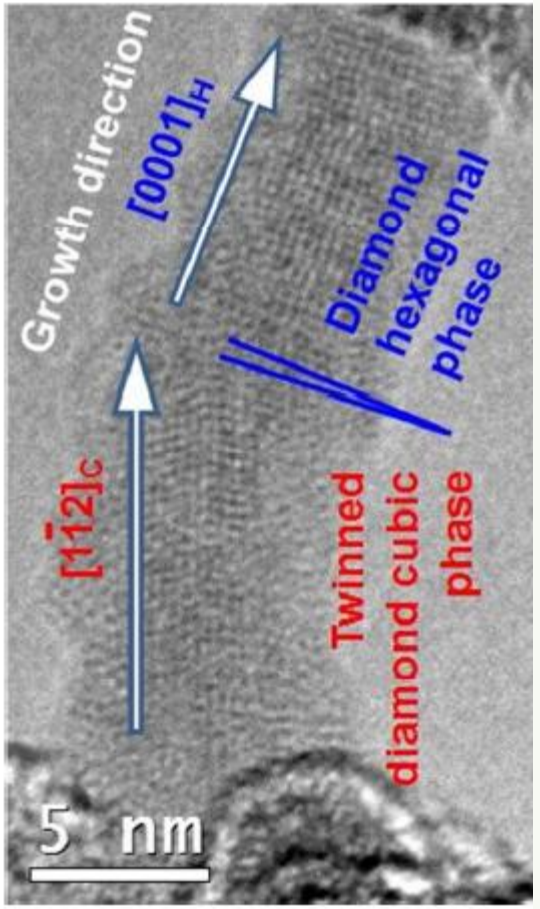

J. Tang et al., Nanoscale 9, 8113 (2017)

A not obvious result for bulk

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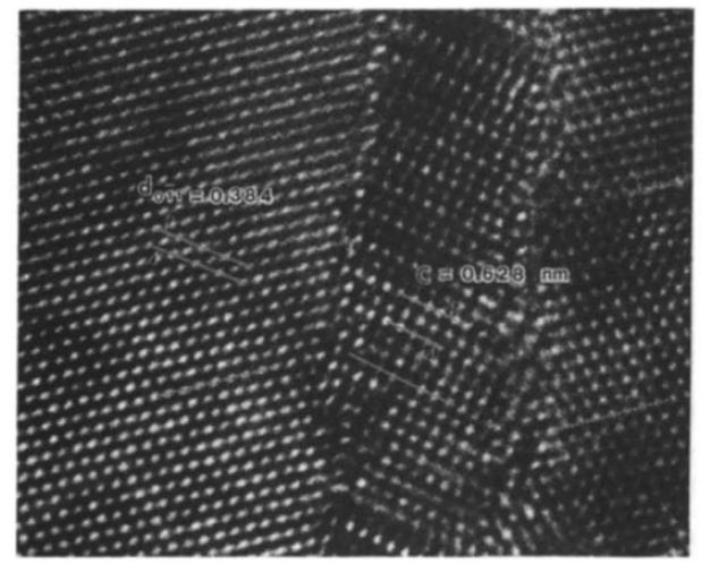
Bulk hexagonal diamond Si metastable and obtained only at high pressures



Pirouz et al., Acta Metall. Mater. 38, 313 (1990)

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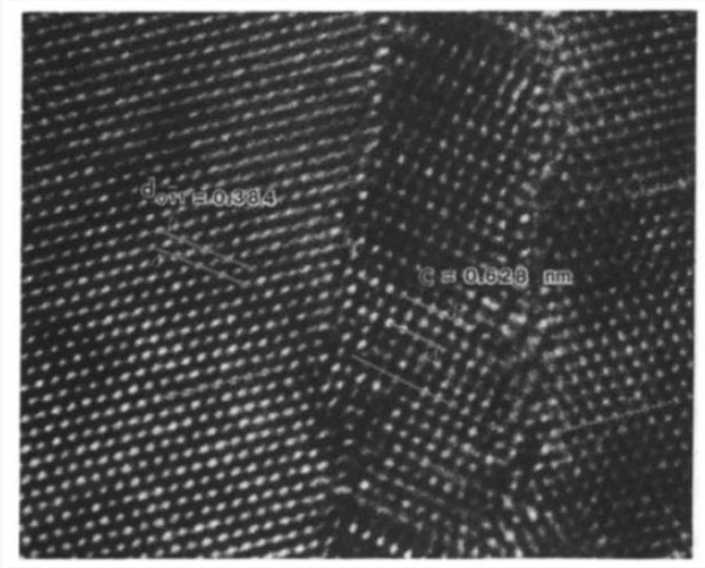

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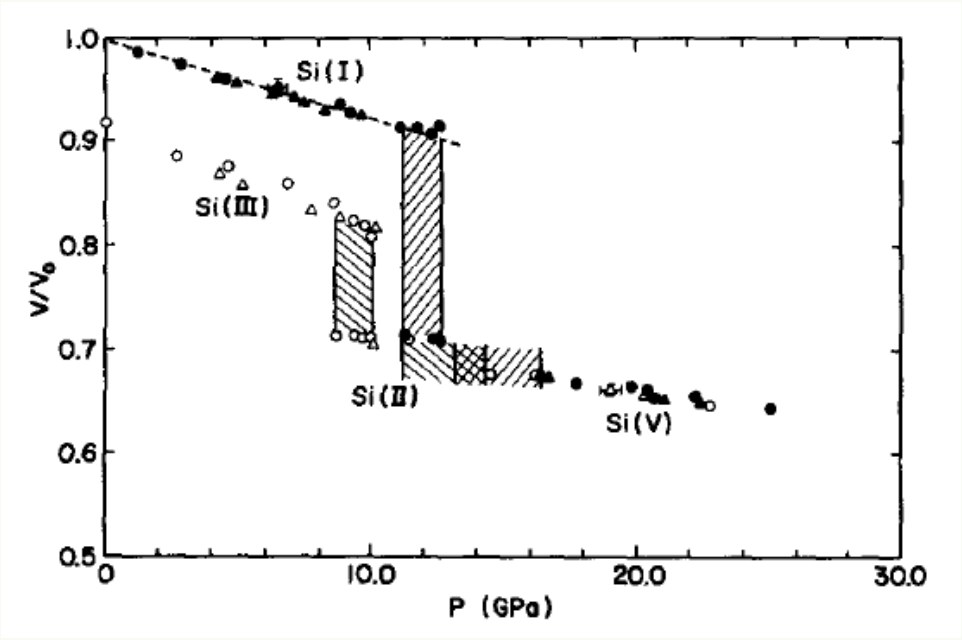

J. Z. Hu and I. L. Spain, Sol. State Comm. 51, 263 (1984)

Light emission from 2H-SiGe

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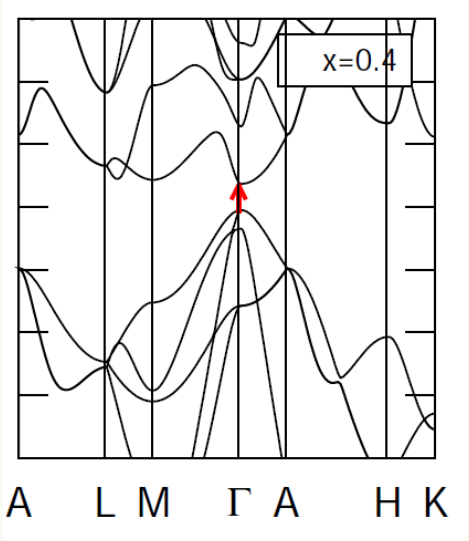
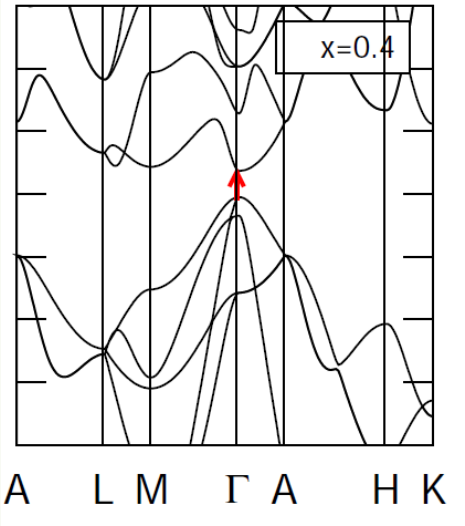
Ab initio Theory



X. Cartoixa et al. Nano Lett. 17, 4753 (2017)

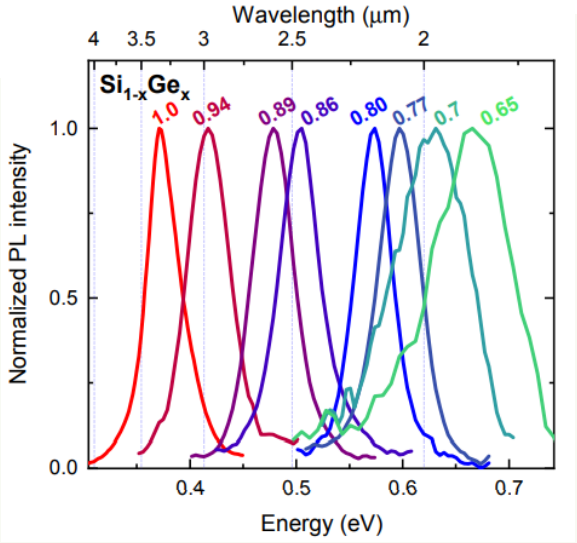
Light emission from 2H-SiGe

Ab initio Theory



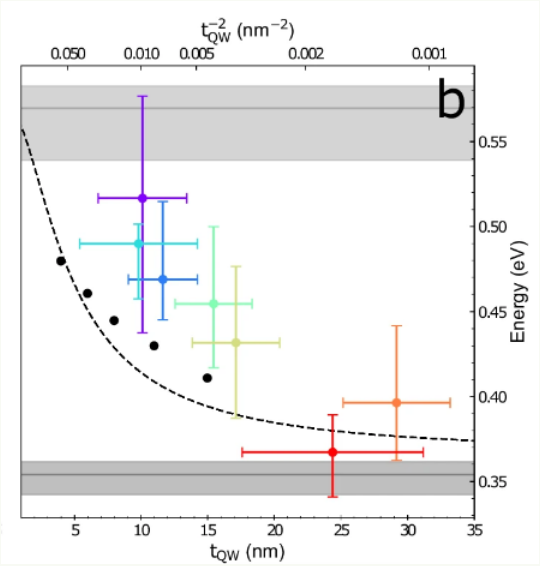
X. Cartoixa et al. Nano Lett. 17, 4753 (2017)

PL in 2H-SiGe nanowires



E. Fadaly et al., Nature 580, 205 (2019)

PL in 2H-SiGe quantum wells



W.H.J. Peeters et al. Nat. Commun. 15, 5252 (2024)

Outline

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Band structure of 2H and 3C bulk

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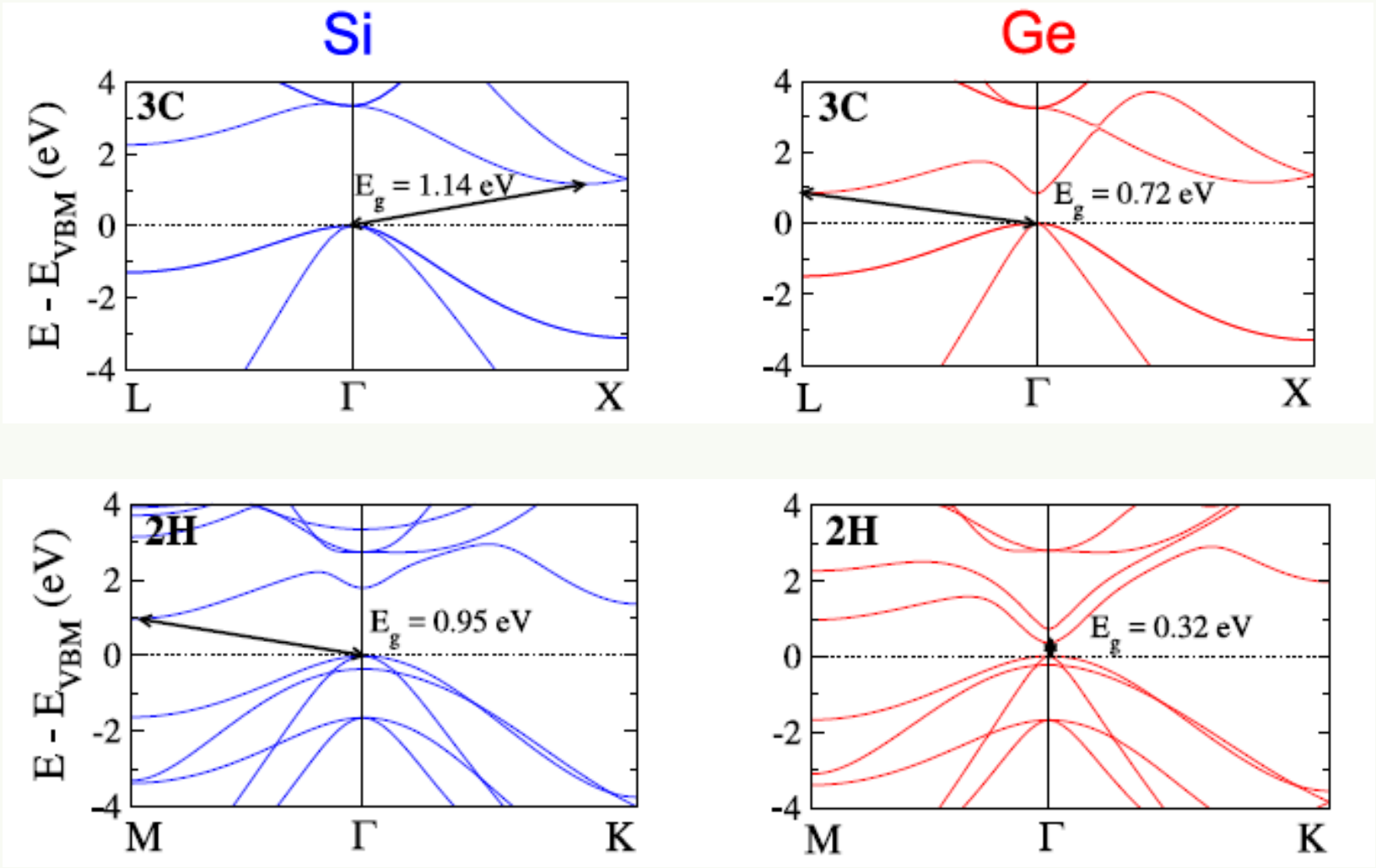
DFT – HSE06



T. Kaewmaraya et al., J. Phys. Chem. C 121, 5820 (2017)

Band gaps of 2H and 3C bulk

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Table 2: The calculated band gaps of Si and Ge.

Element	Crystal structure	E_g at Γ (eV)	E_g (eV)	E_g (SOC) (eV)	Band-edge	Notes
Si	Cubic-diamond (3C)	3.29	1.14		Γ – X	This work (HSE06)
		3.20	1.14		Γ – X	Cal. Ref.[16]
		3.33	1.15		Γ – X	Cal. Ref.[33]
		3.40	1.17		Γ – X	Exp. Ref.[61]
	Hexagonal-diamond (2H)	1.70	0.95		Γ – M	This work (HSE06)
		1.63	0.95		Γ – M	Cal. Ref.[16]
Ge	Cubic-diamond (3C)	0.84	0.72	0.61	Γ – L	This work (HSE06)
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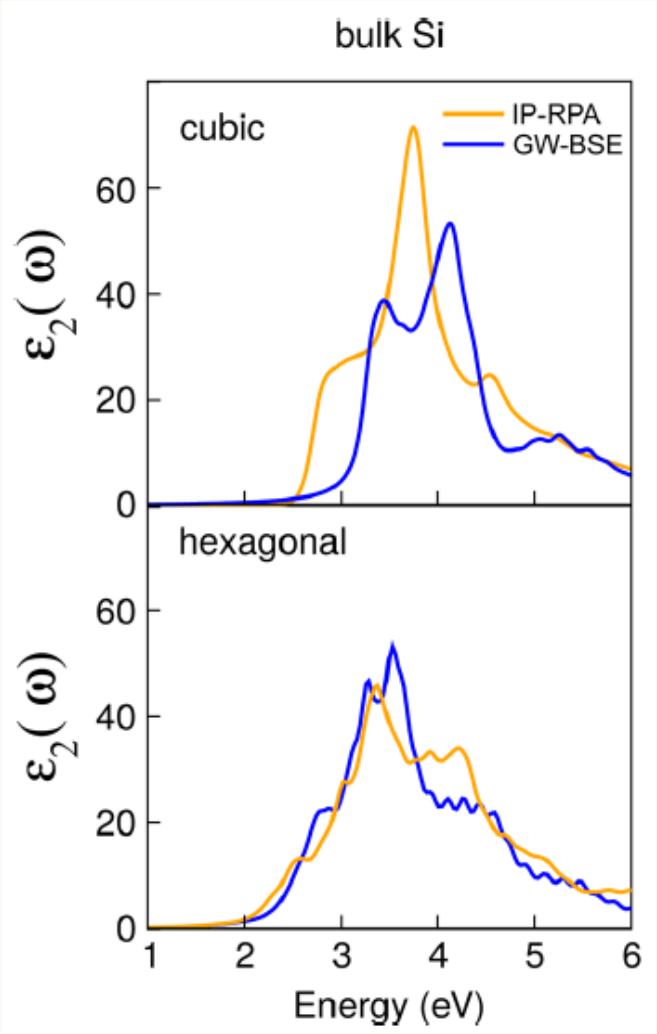

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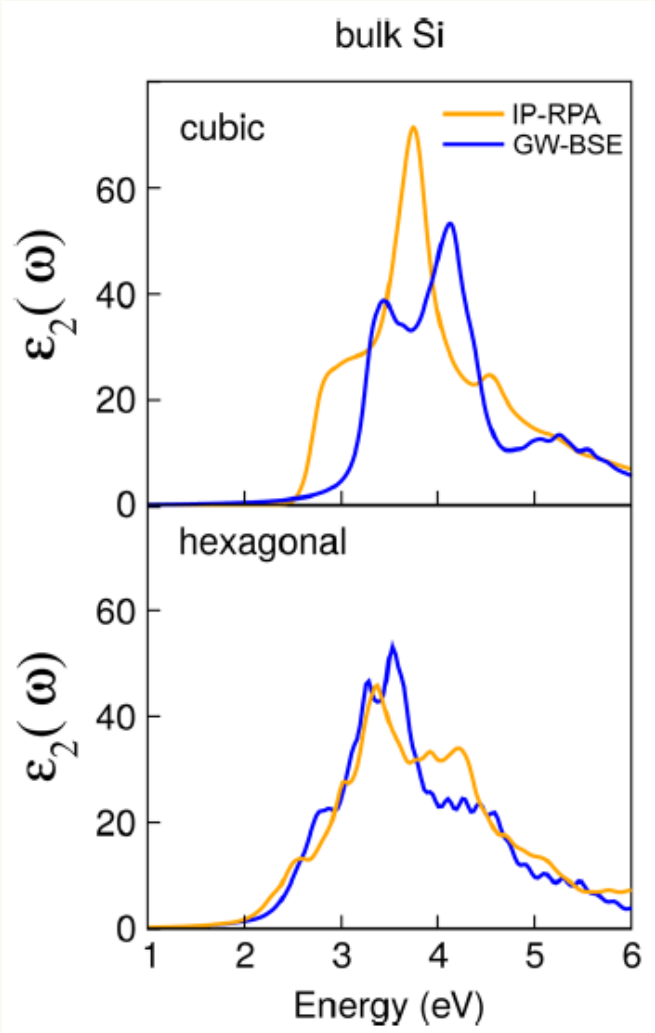

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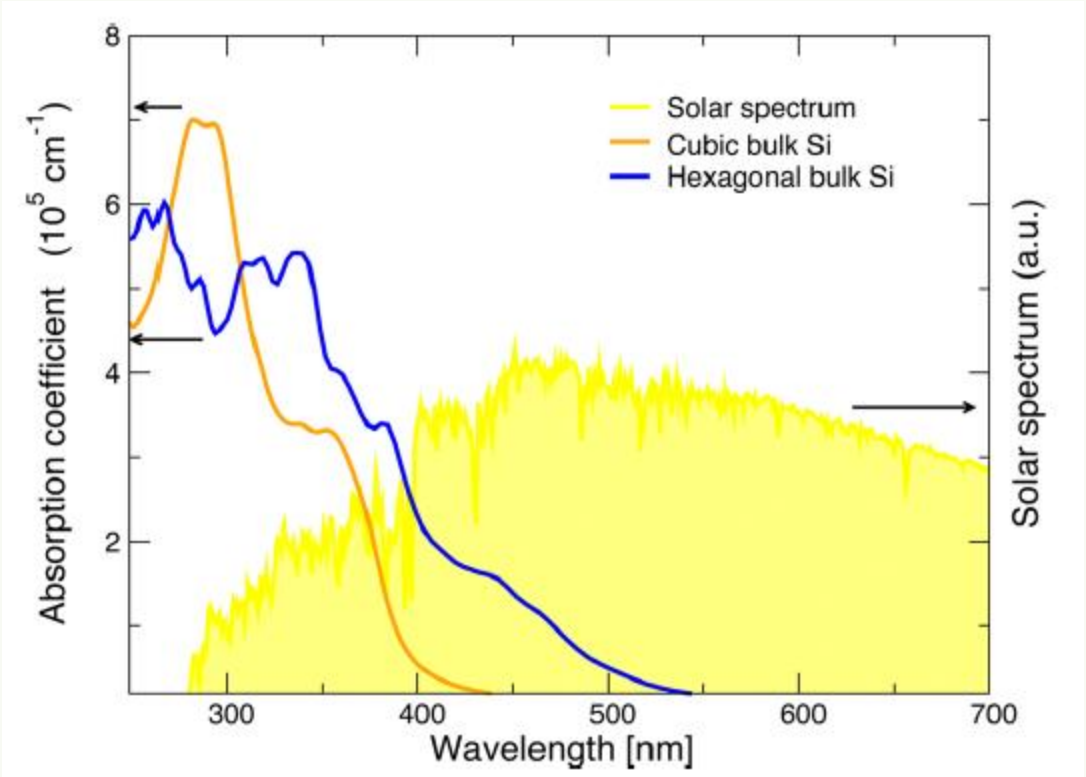

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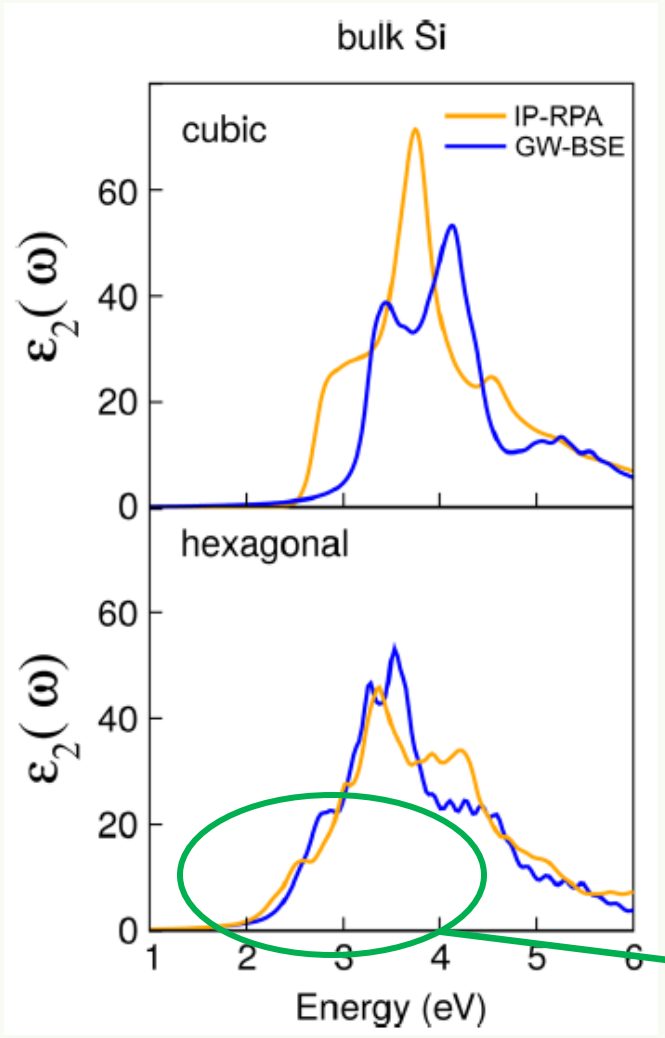

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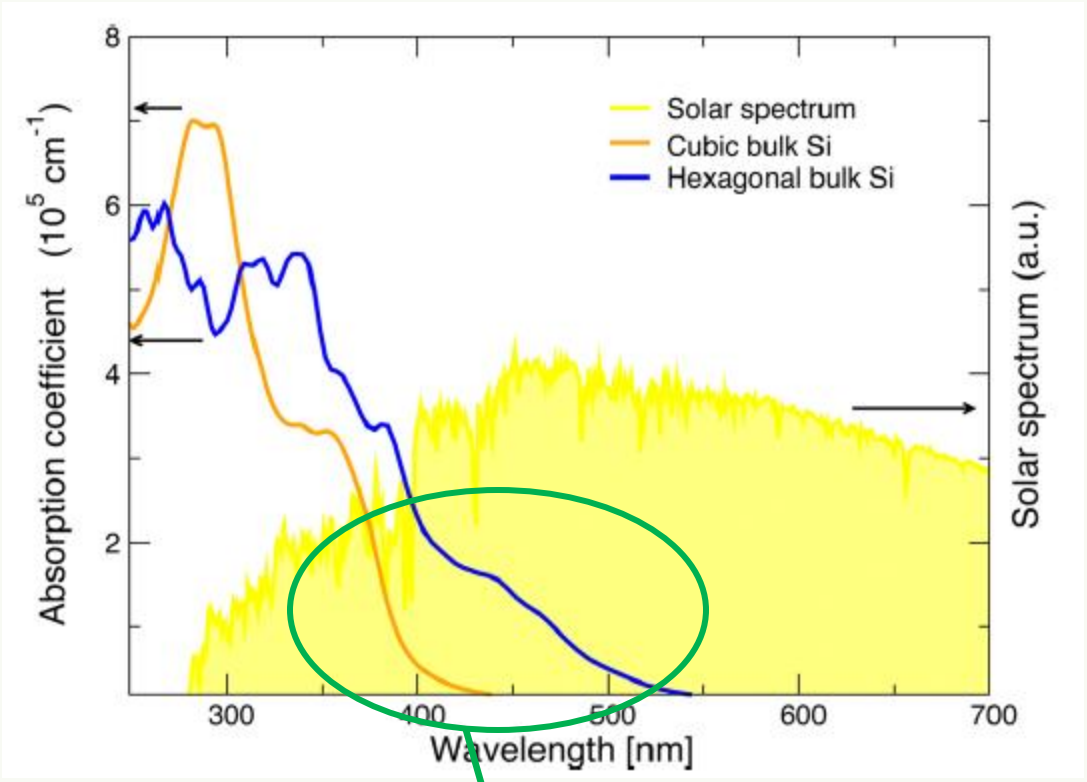

2H bulk phase

Larger absorption in the visible

Bigger overlap close to the max of solar spectrum

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What happens when we reduce the size?

Should we expect the same electronic and optical behaviour?

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Quantum confinement in 3C Si NWs

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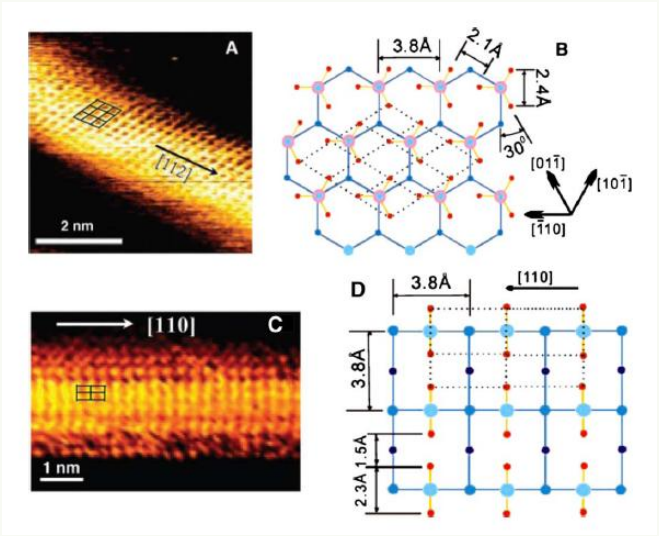
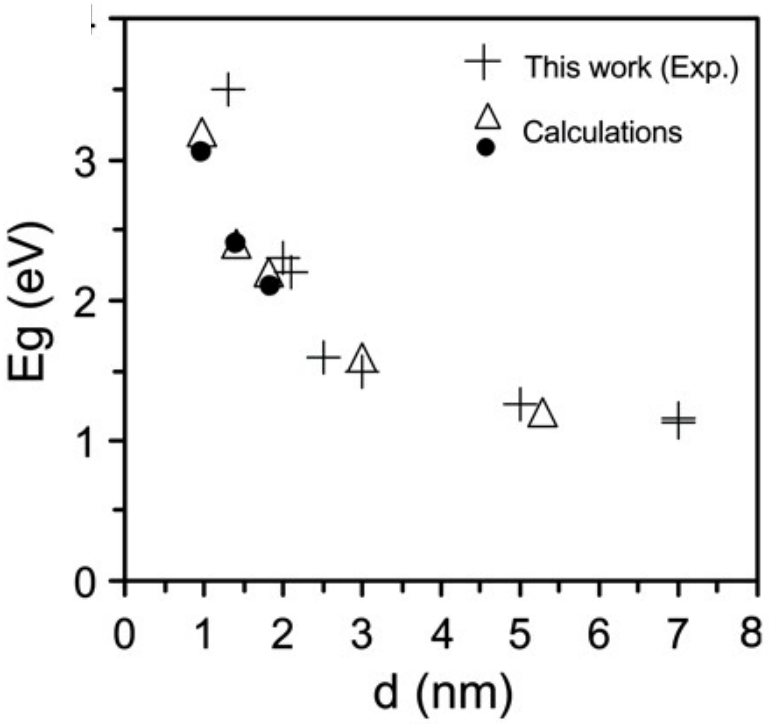


Ma, D. D. D. et al., Science 299, 1874 (2003)

STS measurements



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$$E_{gap} = E_{bulk,\,gap} + C(1/d)^{\alpha}$$

with α=1.1 – 1.4

M. Bruno et al., Phys. Rev. Lett. 98, 036807 (2007)

Band gap of 3C and 2H Si NWs

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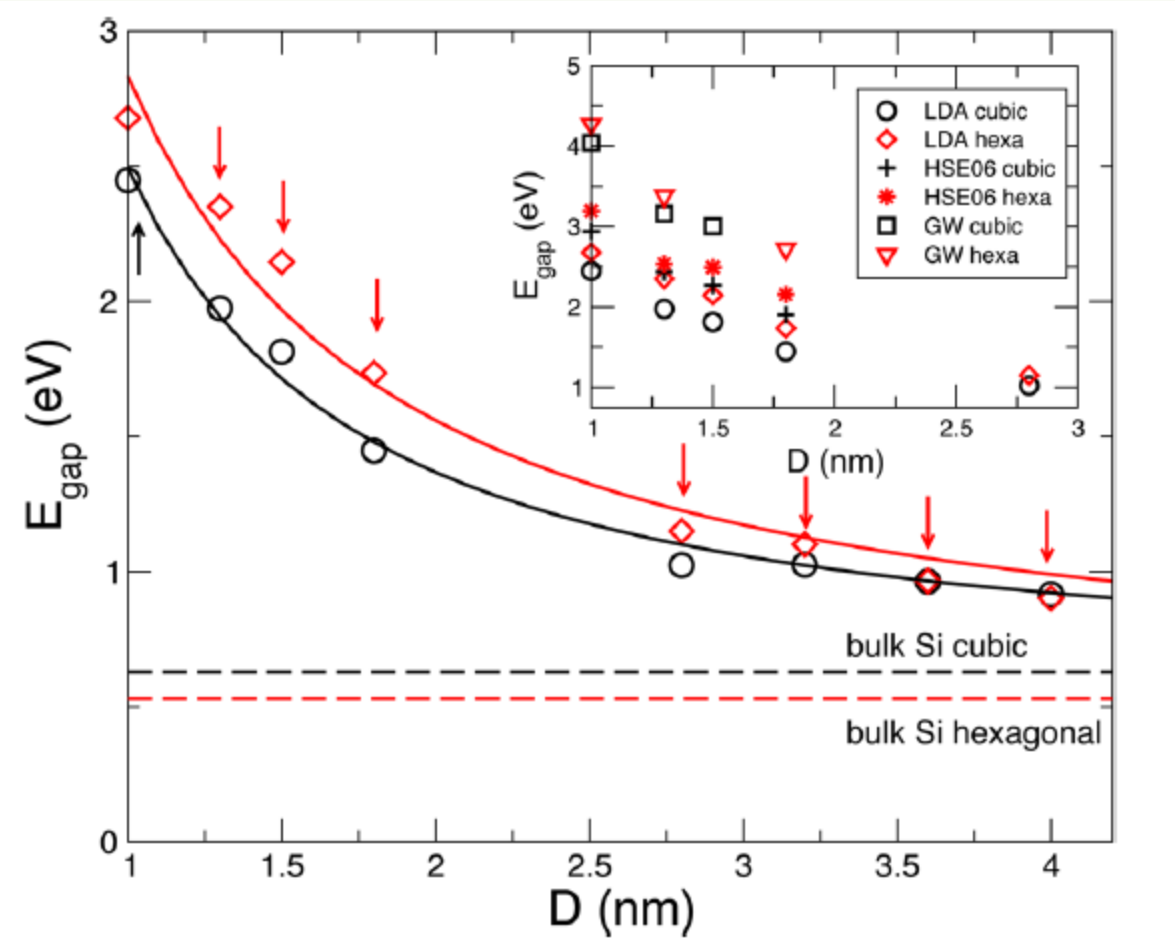

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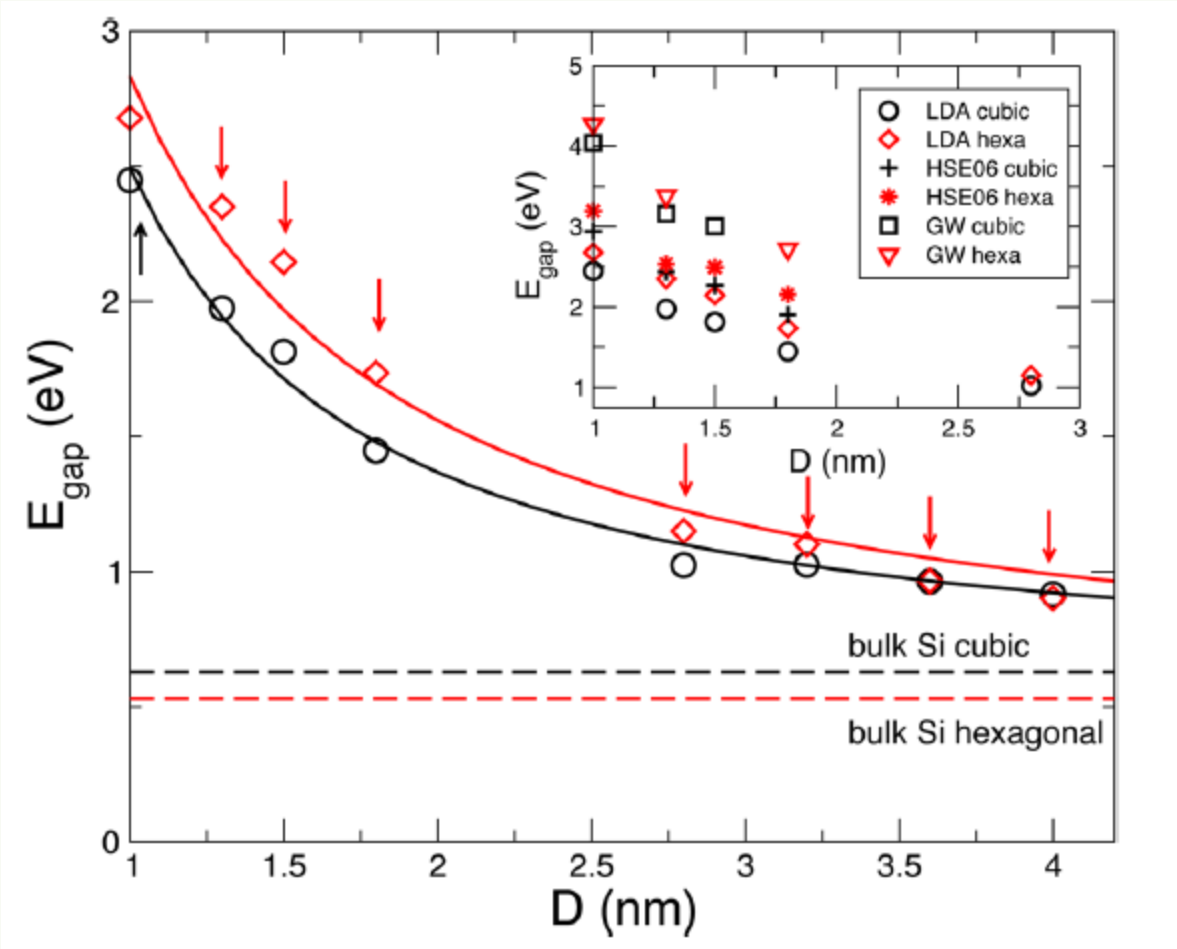

DFT – LDA

$\alpha_{hex} = 1.16$

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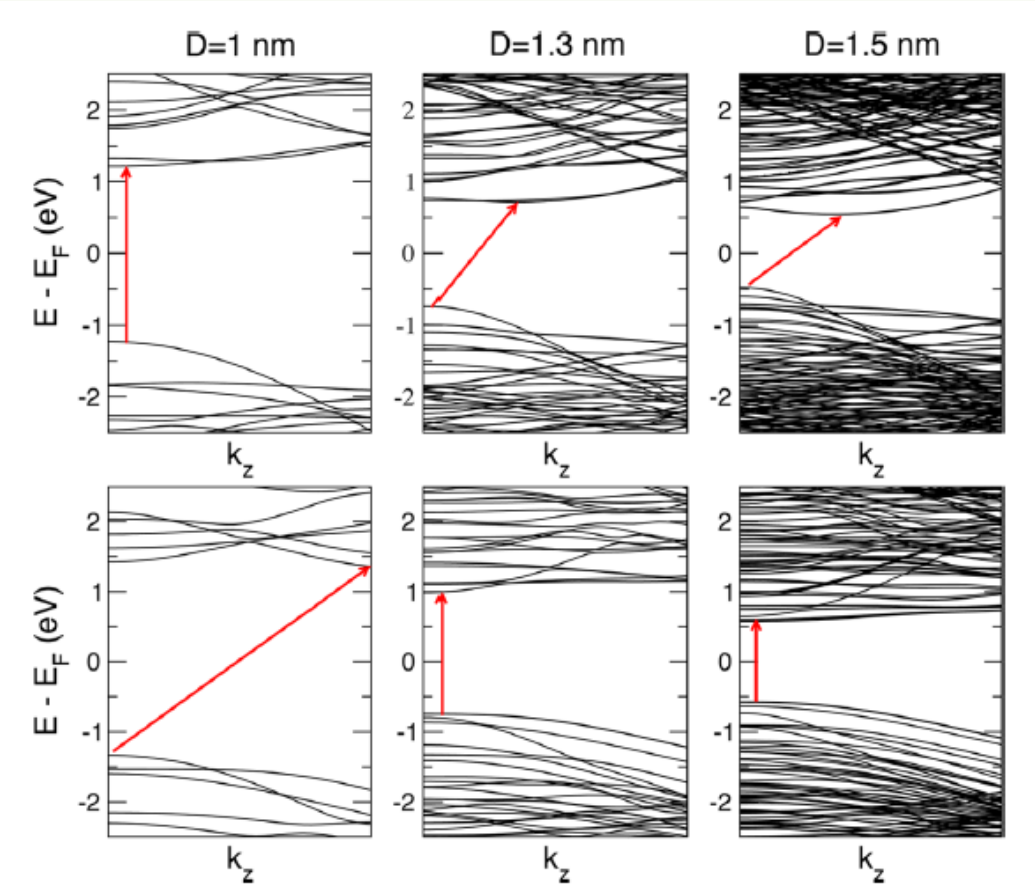
M. Amato et al., Nano Lett. 16, 5694 (2016)

Bands and optical absorption

DFT – LDA

3C

2H



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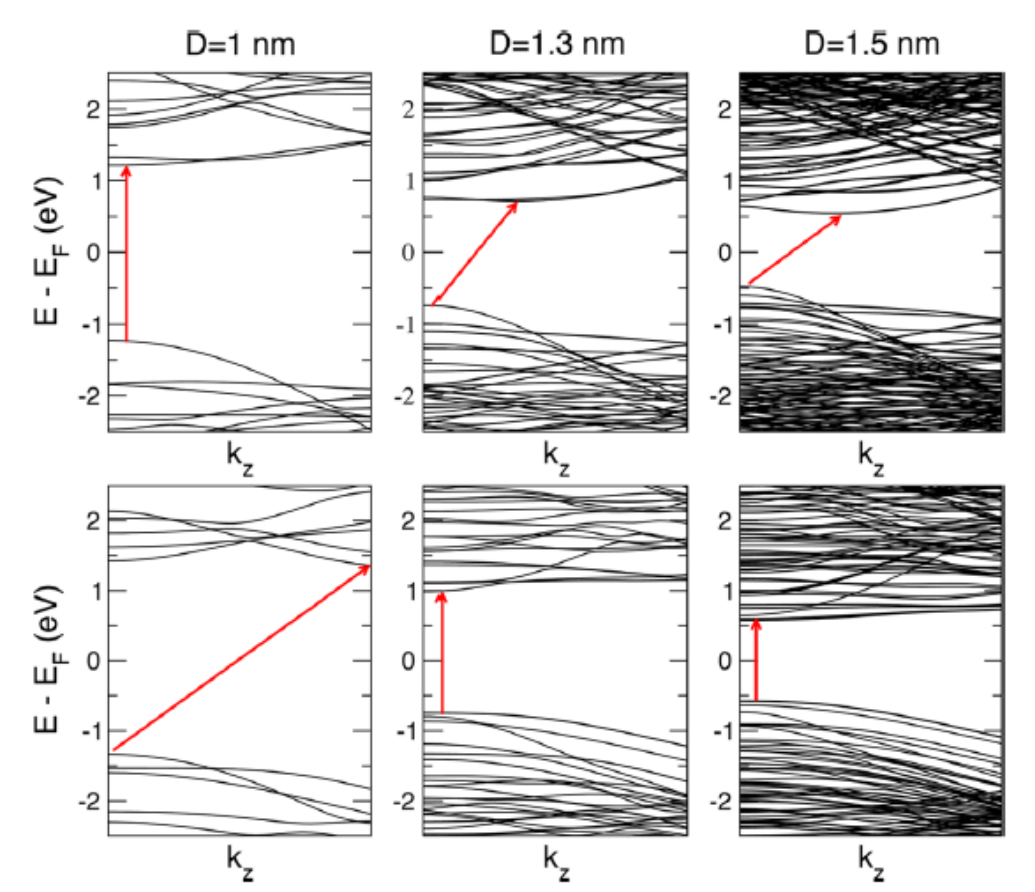
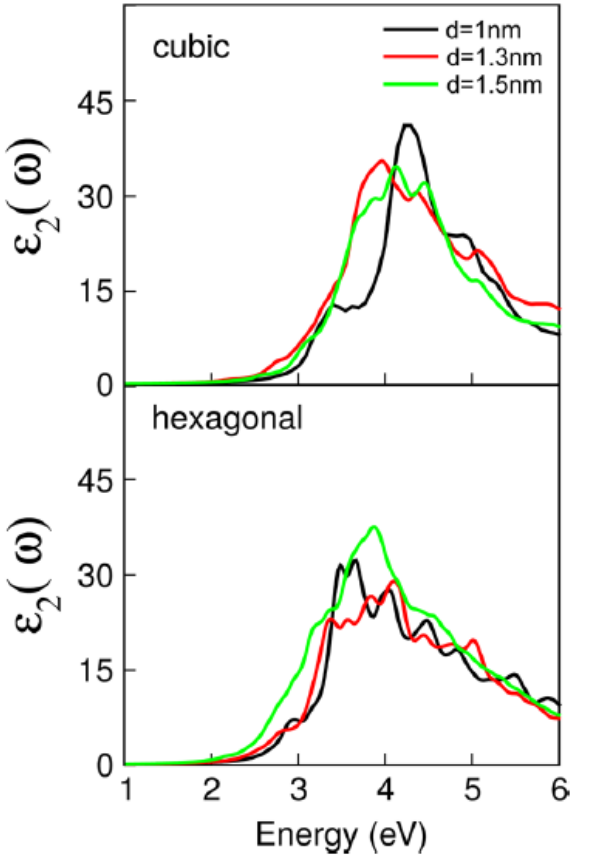


IP – RPA



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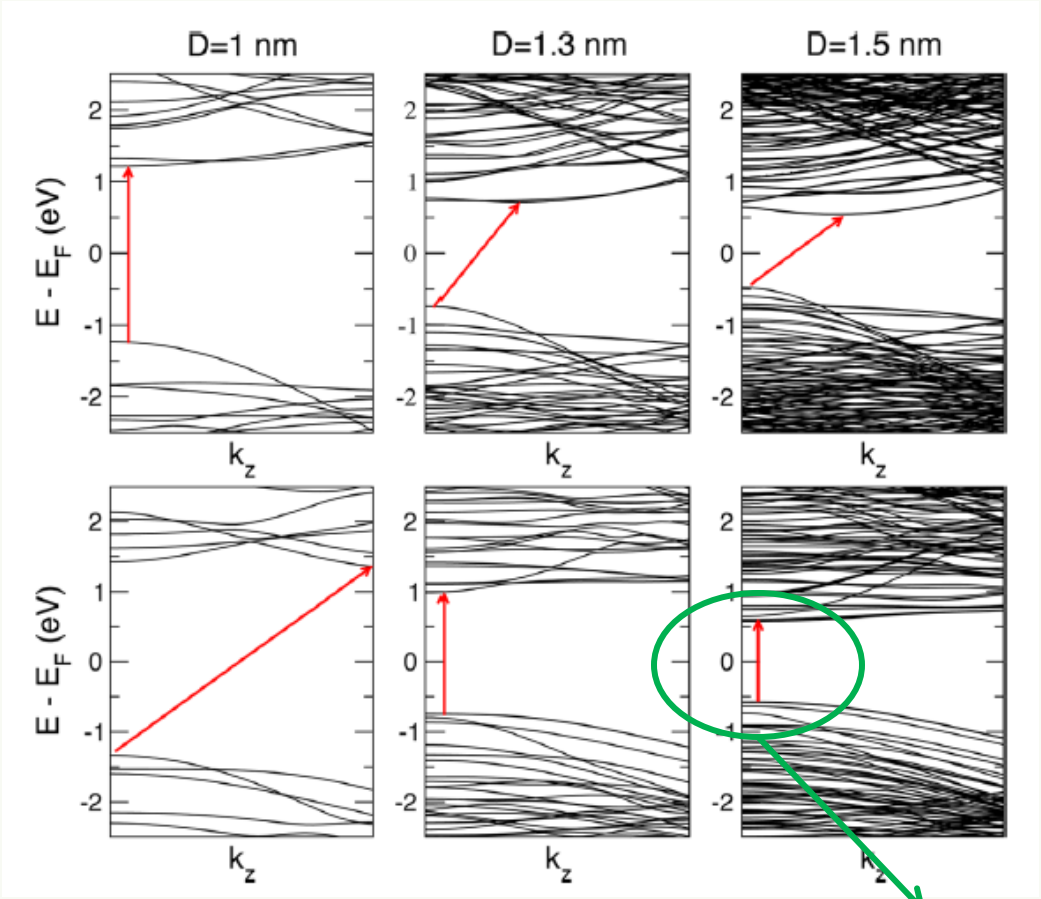

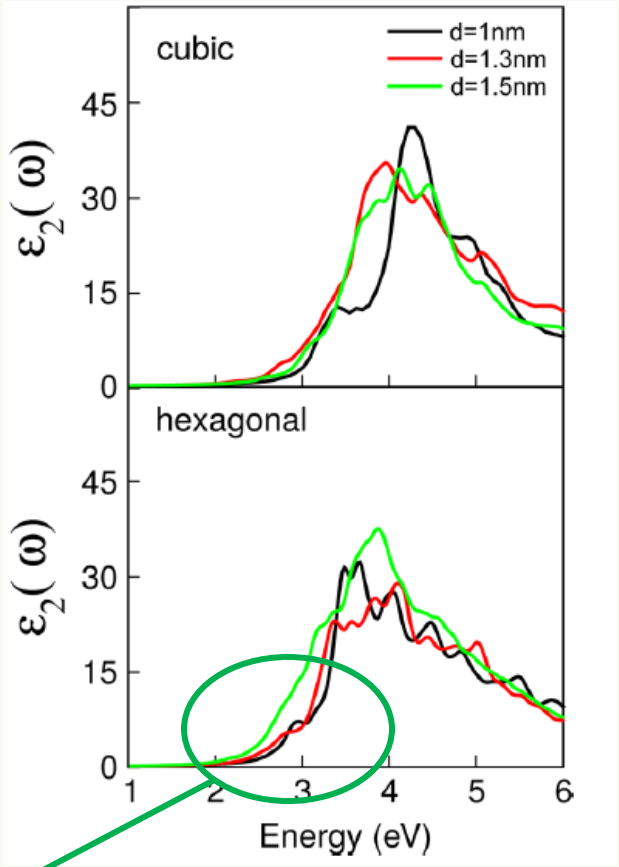

M. Amato et al., Nano Lett. 16, 5694 (2016)

2H <111> Si NWs

Larger absorption in the visible

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Y. W. Yeh et al. Phys. Rev. Appl. 16 054009 (2021)

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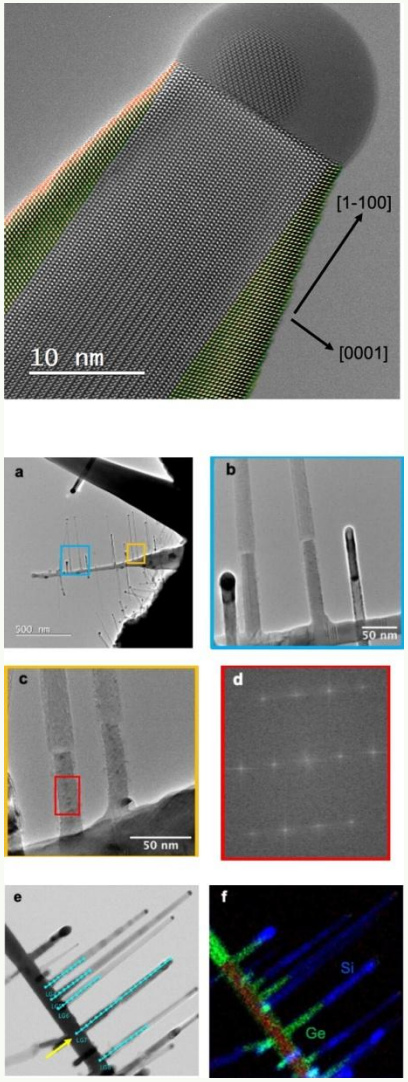

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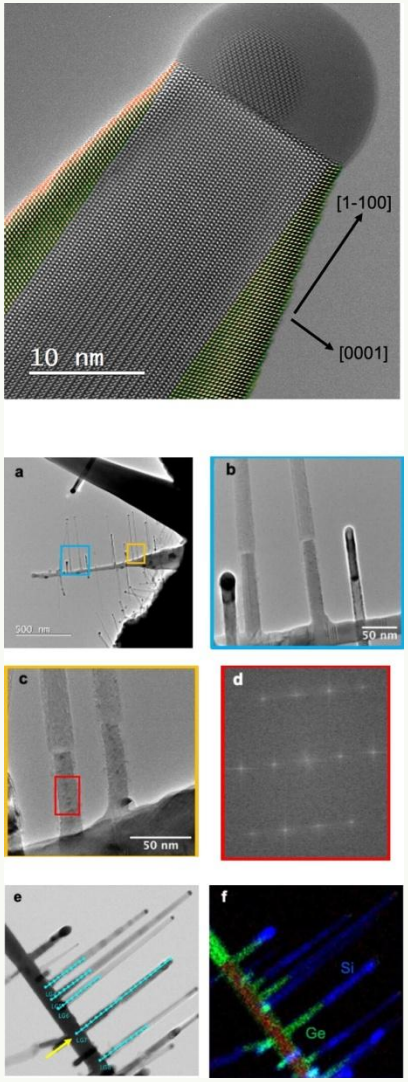

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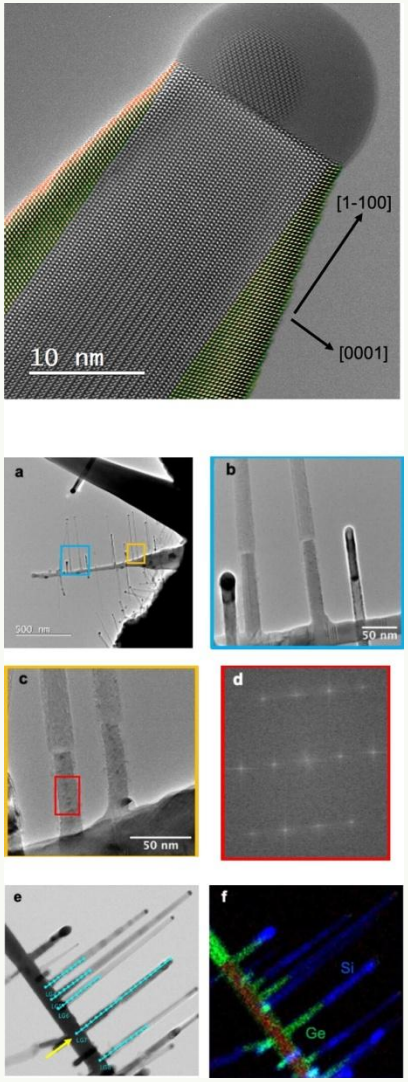

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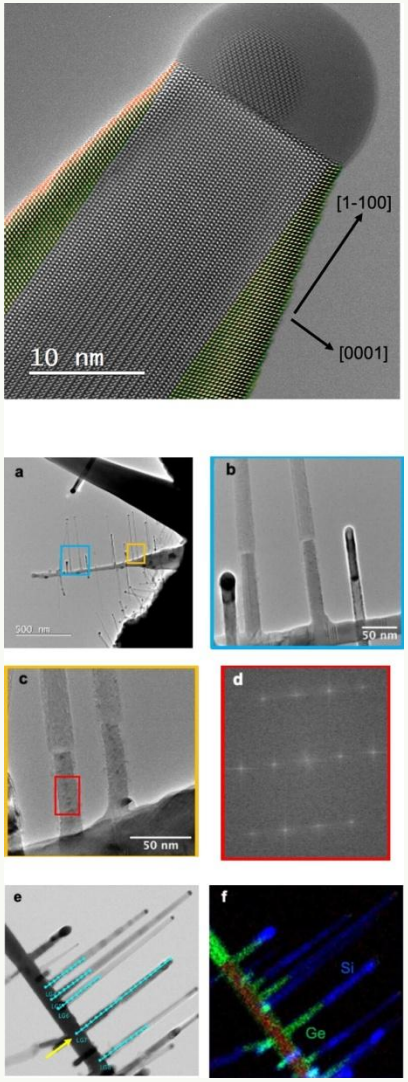

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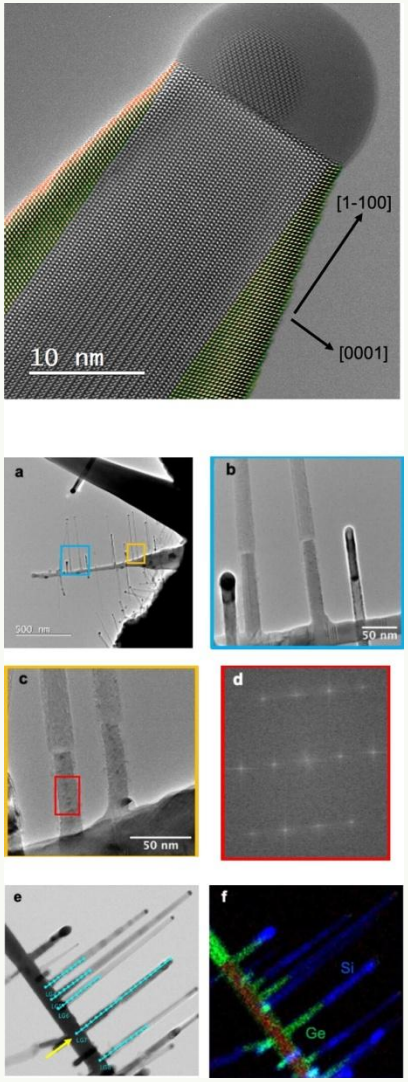

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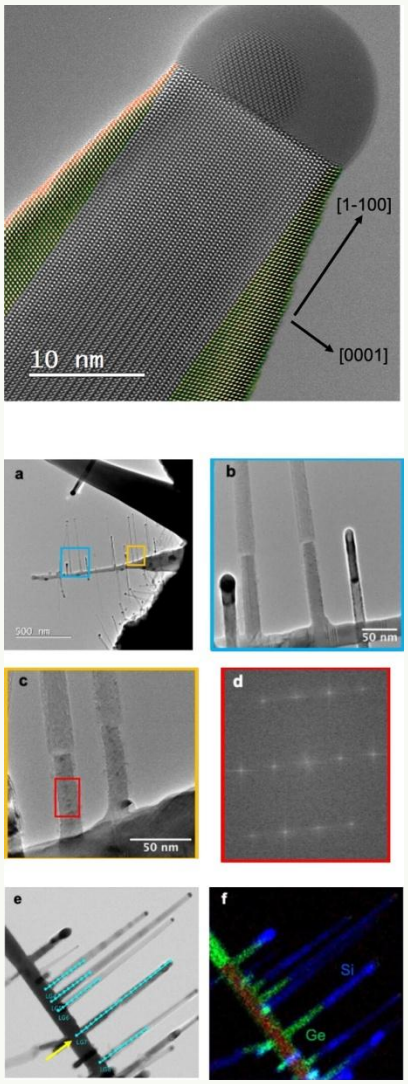

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Intersecting specimen EELS

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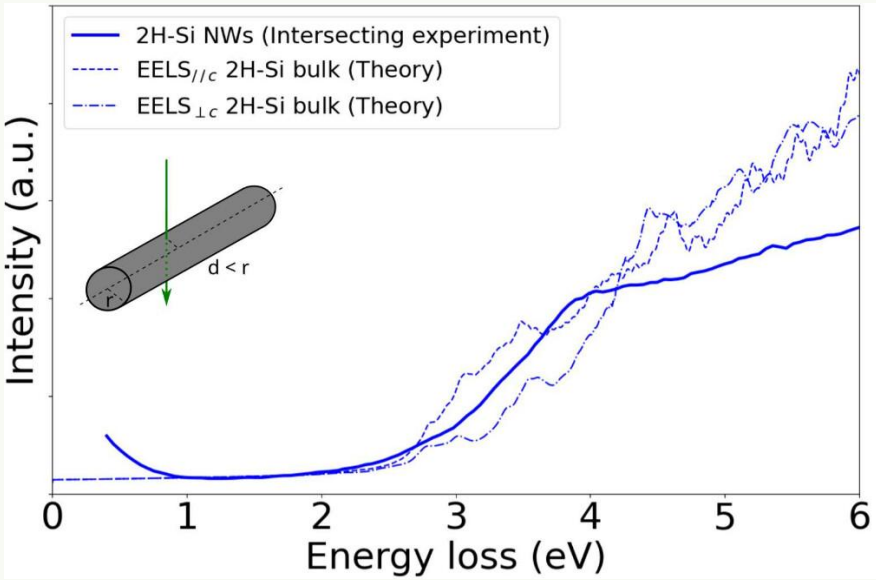

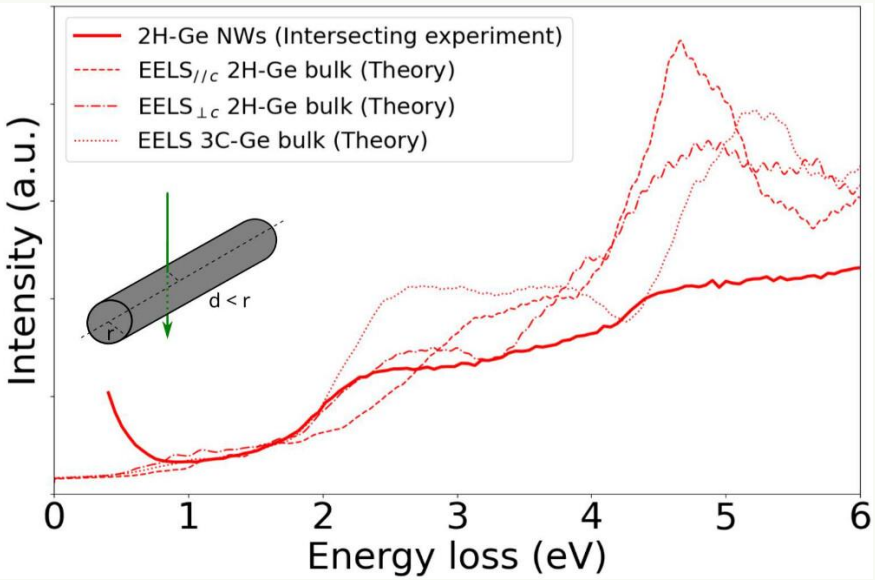

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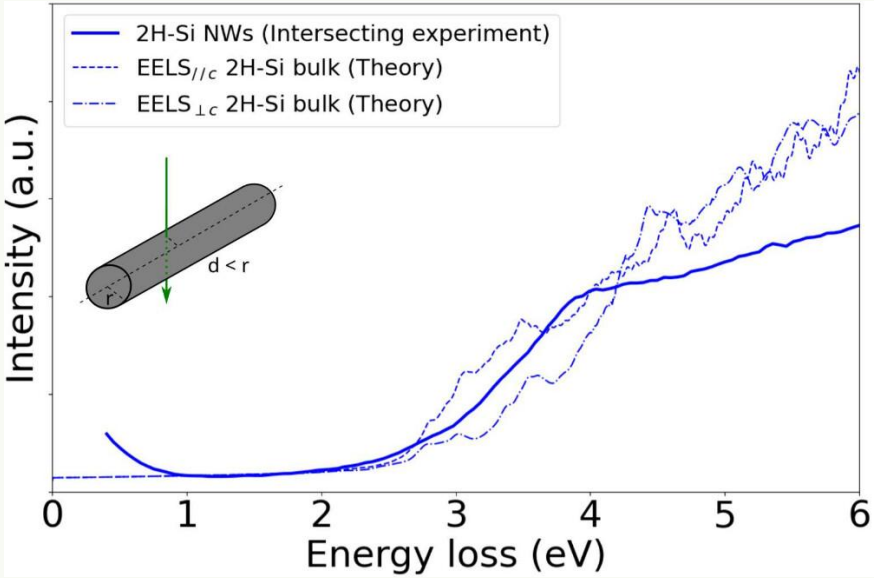

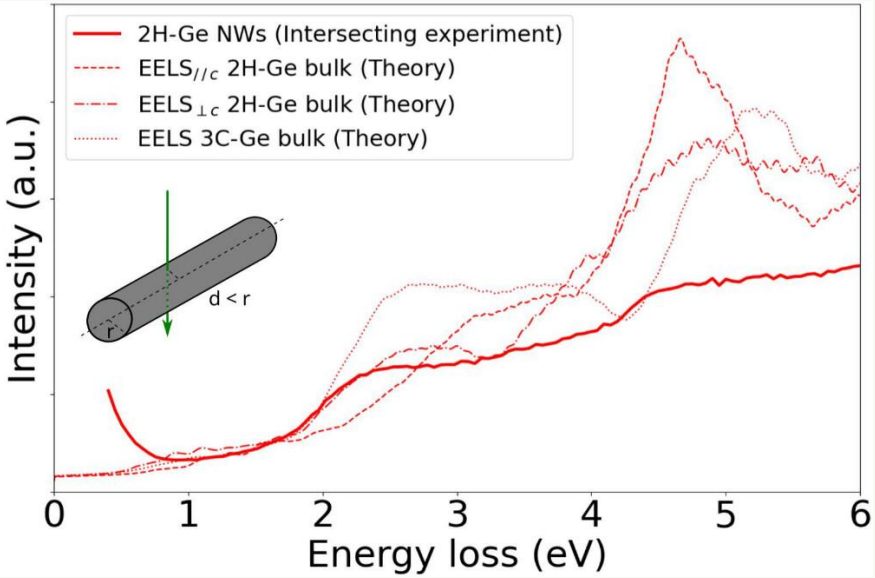

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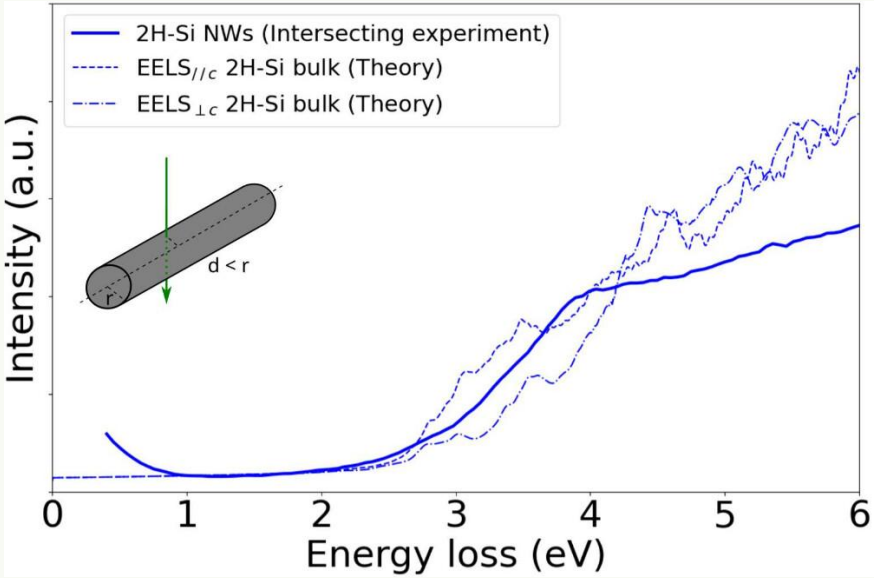

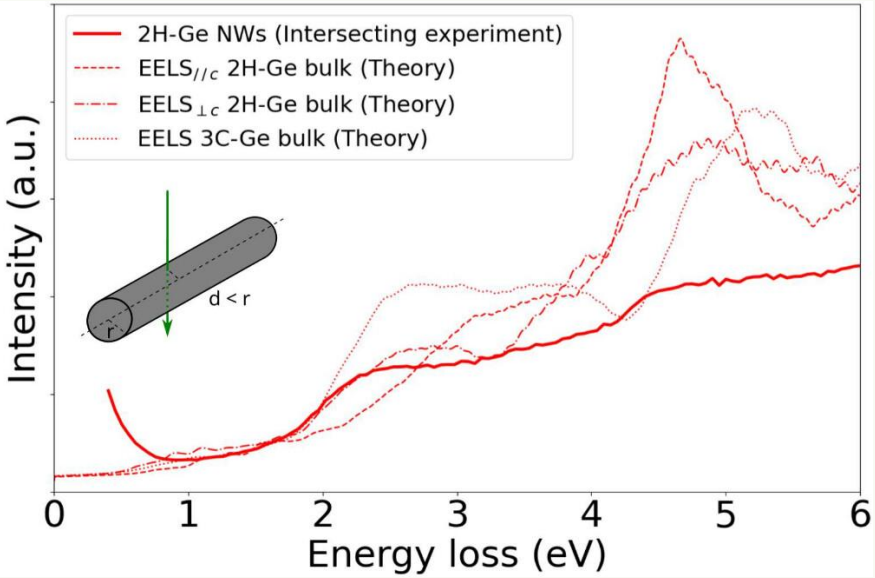

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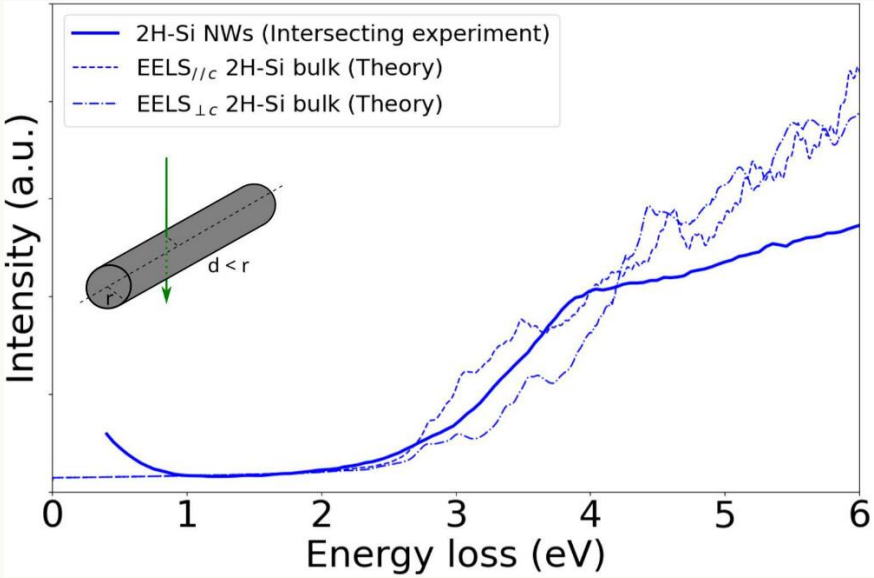
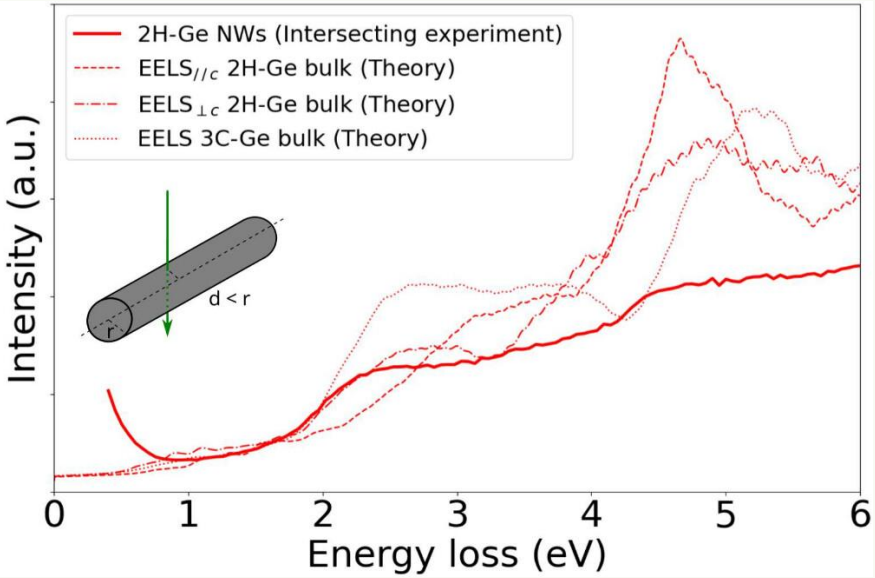
- This highlights the potential of 2H–Si NWs for photovoltaic applications, especially when combined with 3C–Si NWs in heterostructures

Intersecting specimen EELS



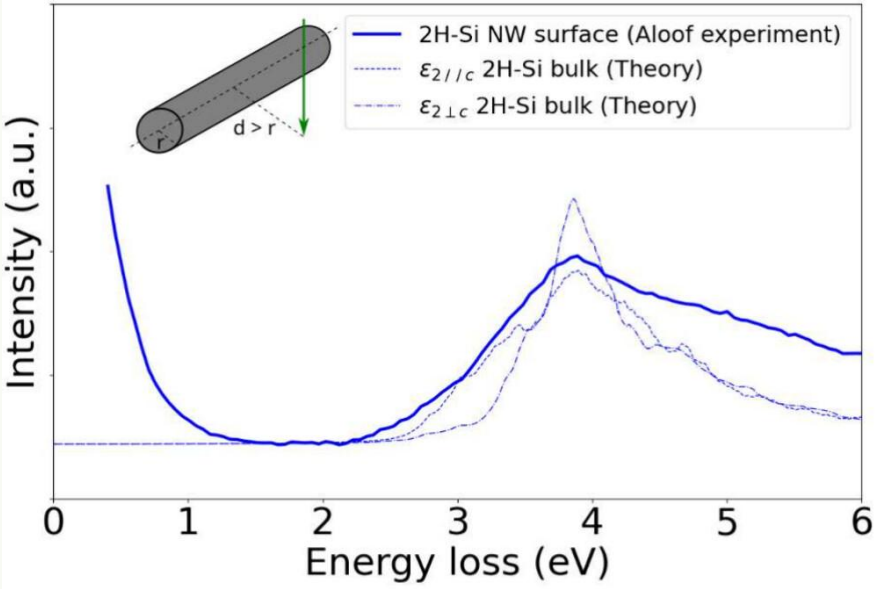


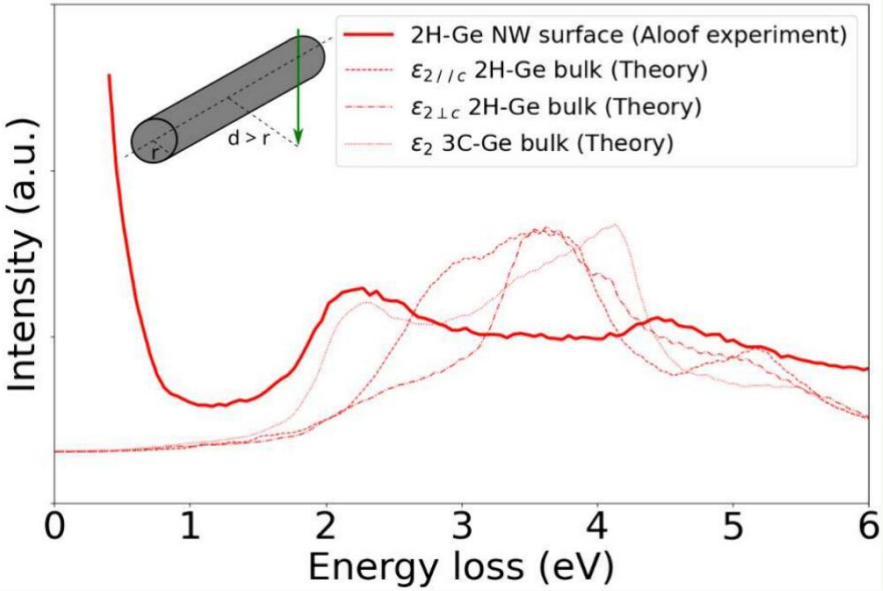
- 2H–Si NWs, with a reduced direct bandgap of 1.75 eV, exhibit stronger absorption in the visible range compared to 3C-Si, becoming significant only above 2.5 eV
- This highlights the potential of 2H–Si NWs for photovoltaic applications, especially when combined with 3C–Si NWs in heterostructures
- For 2H–Ge NWs, the intersecting-specimen EELS shows increased absorption near 0.9 eV, consistent with ab initio calculations (no absorption near the band gap)

L. Tizei et al., Nano Lett. 25, 8604-8611 (2025)

Aloof beam EELS

Aloof beam EELS





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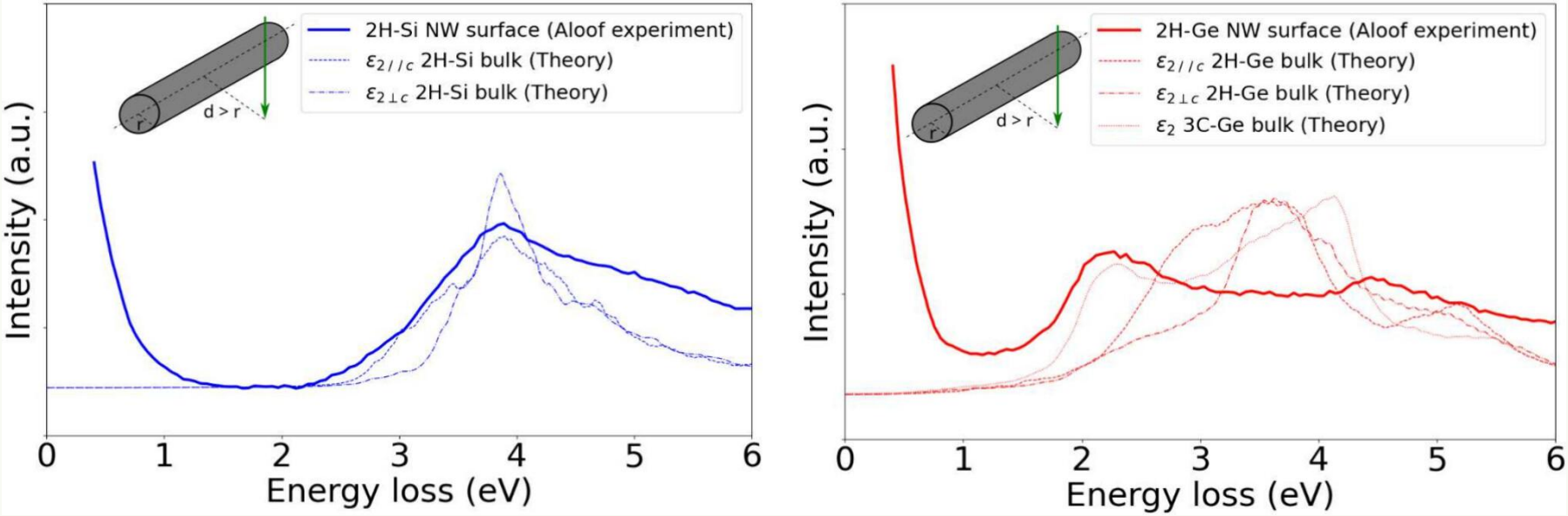

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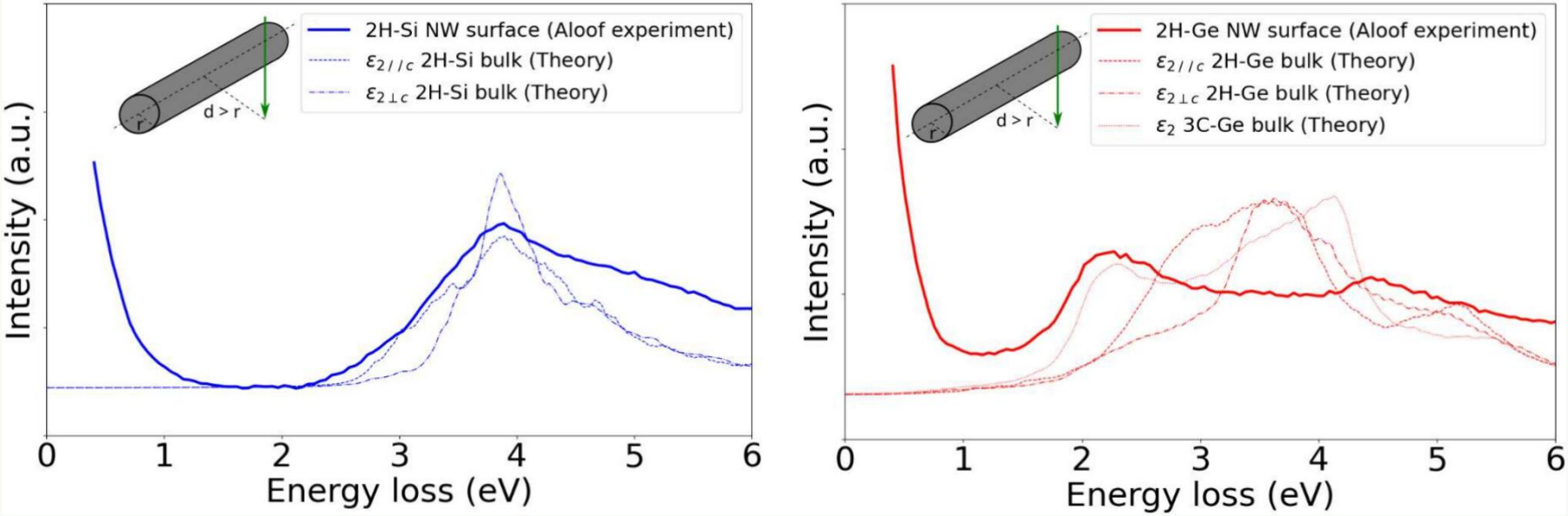

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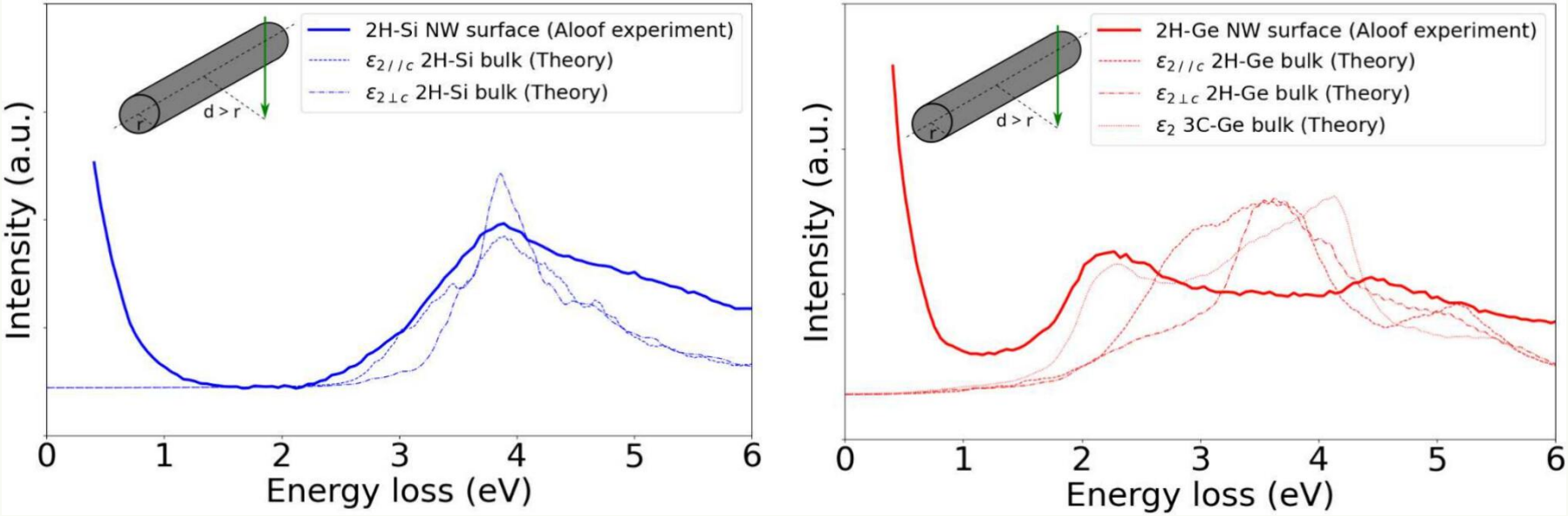

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- The observed light emission in 2H-Ge contradicts intrinsic optical transitions, similar to effects seen in other wurtzite nanowires
- An intense peak at 2 eV is observed in 2H-Ge, attributed to a thin 3C–Ge shell formed during growth

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Some comments

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- By matching simulated and experimental EELS data, local electronic transitions and plasmon modes in nanowires can be identified
- This coupling helps interpret complex EELS signals and guides the design of nanoscale optoelectronic devices

Outline

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- Ab initio simulations: Density Functional Theory (DFT)
- Quantum confinement in Si nanowires (Si NWs)
  - Electronic structure
  - Transport properties
  - Doping effects
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  - Crystal phase effects on bulk
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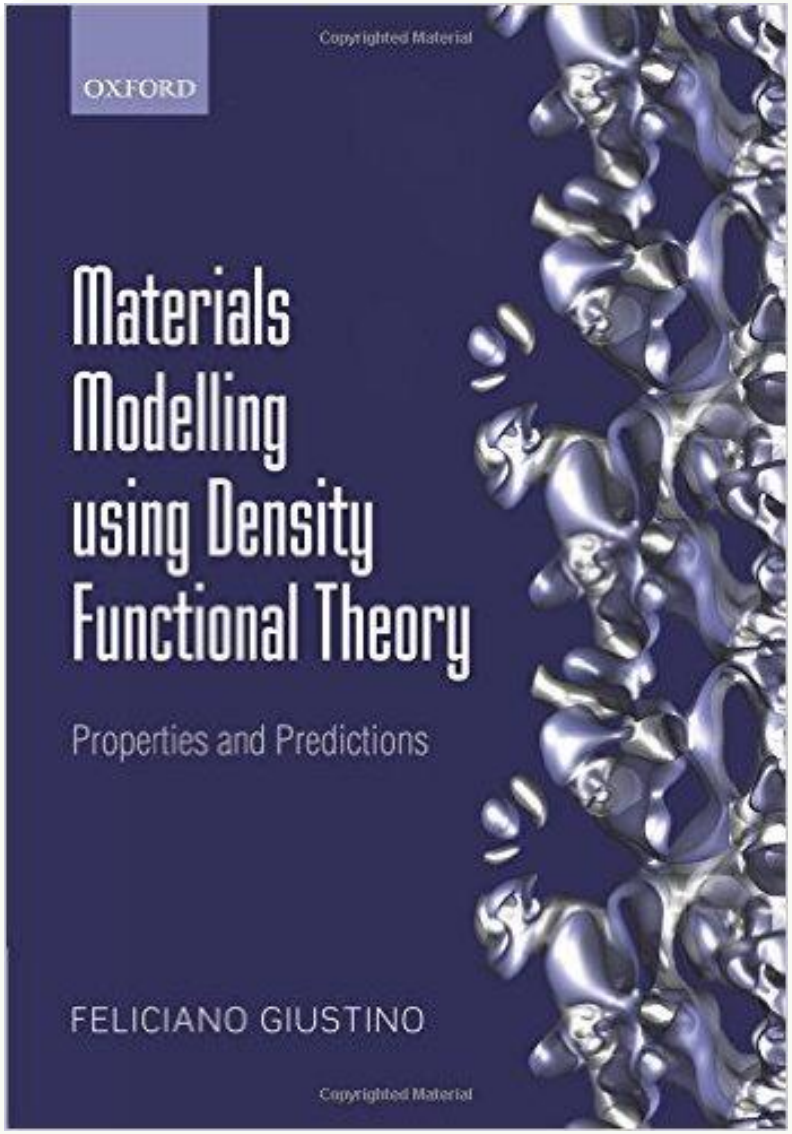

Materials modelling using Density Functional Theory
F. Giustino,
Oxford Univeristy Press 2014