# Electronic, optical and transport properties of semiconductor nanowires : Theory & Modelization

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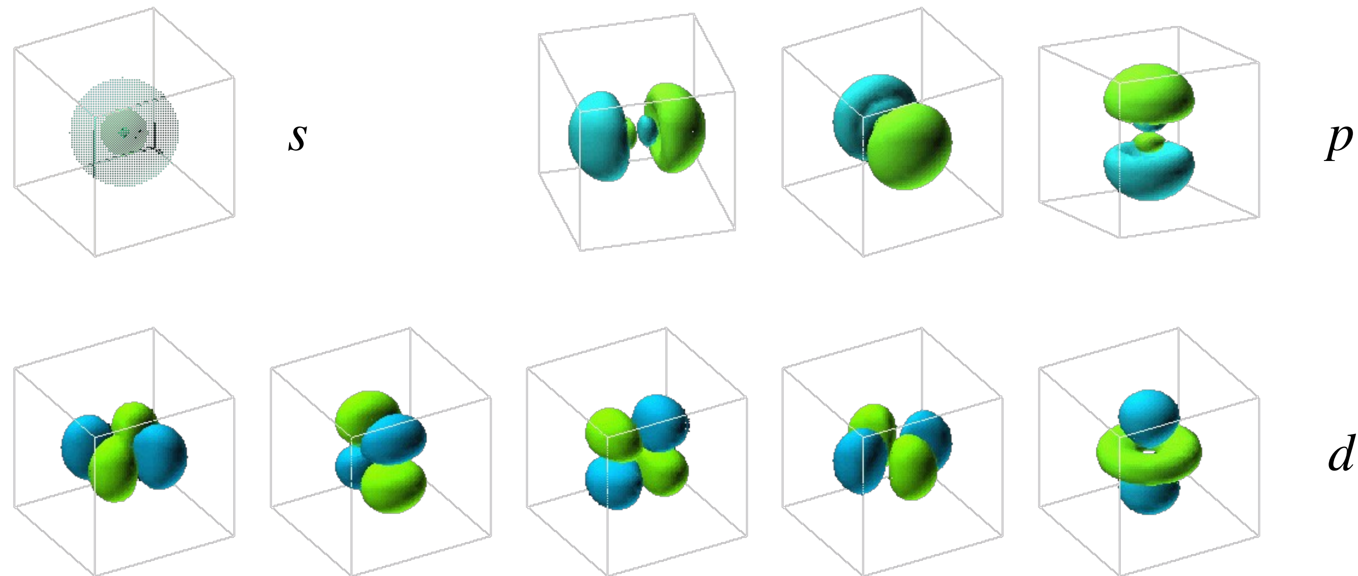
# Outline

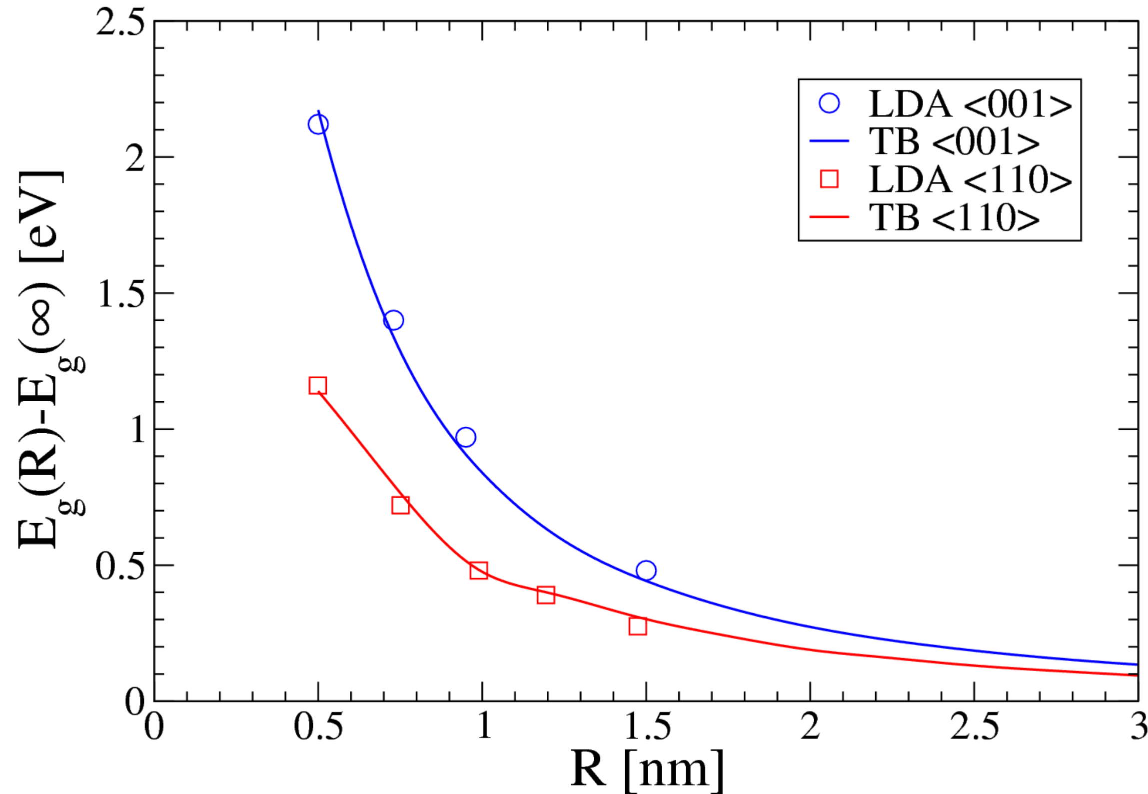
- **Doping the nanowires**...
  - Enhancement of the binding energies with decreasing radius.
  - Effects of the dielectric environment.
- **Nanowire heterostructures**.
  - Effects of strain relaxation on the electronic properties of nanowire heterostructures.
- **Transport properties of semiconductor nanowires**.
  - Surface roughness scattering.

# The tight-binding method




- Principle : Expand the wavefunctions as linear combination of atomic orbitals.
  - The **range** of the model is limited to 1$^{st}$, 2$^{nd}$ or 3$^{rd}$ nearest-neighbor atoms.
  - The matrix elements of the hamiltonian are considered as adjustable parameters usually fitted to the bulk band structures then **transferred** to the nanostructures.
  - **The computation time scales linearly with the number of atoms** (up to a few millions of atoms today).

# Application : Band gap energies of silicon nanowires




- **Very good agreement** between the tight-binding and the LDA down to the smallest nanowires.

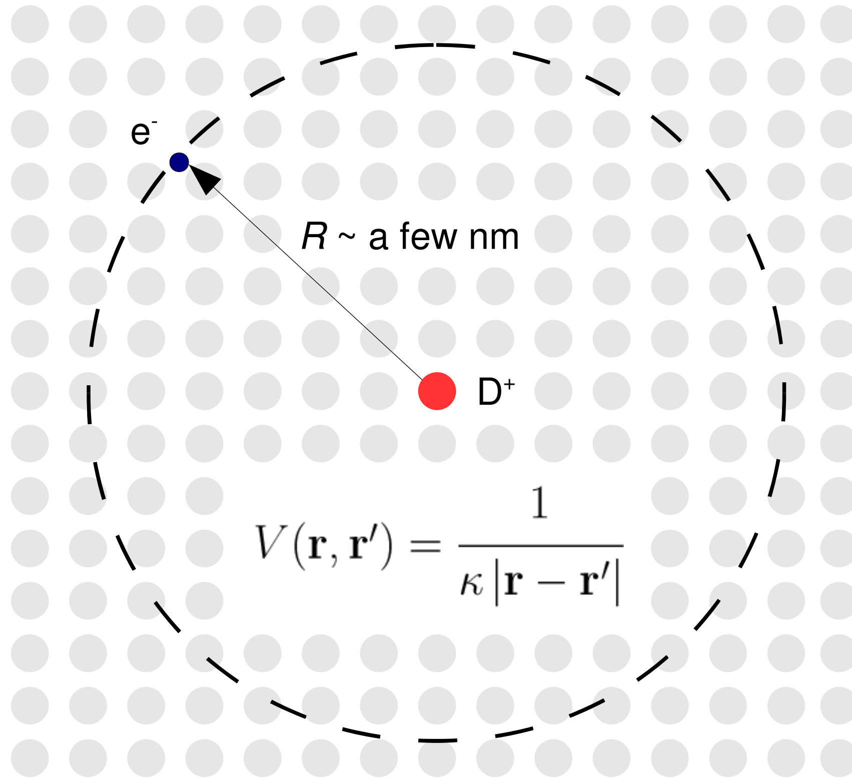
- The band gap energy of small silicon nanowires depends on their orientation.

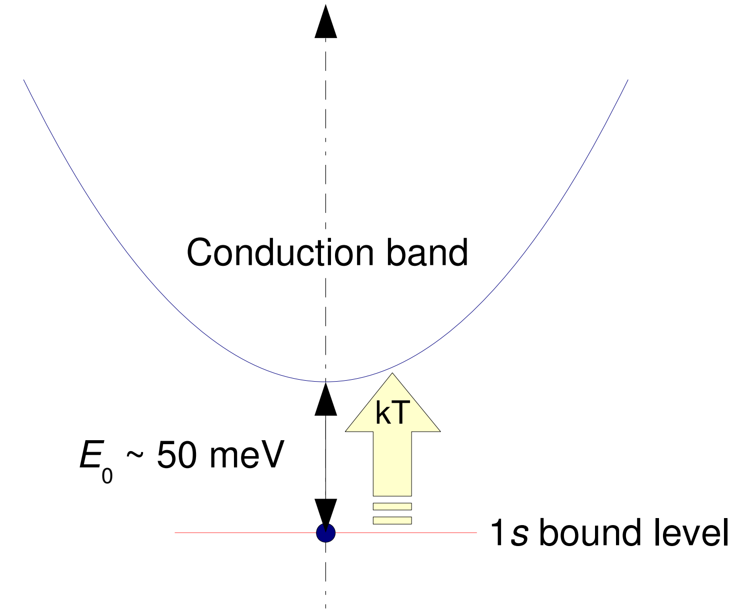
*Electronic structure of semiconductor nanowires*
Y. M. Niquet, A. Lherbier, N. H. Quang, M. V. Fernandez-Serra, X. Blase and C. Delerue, Phys. Rev. B **73**, 165319 (2006).

Part I :

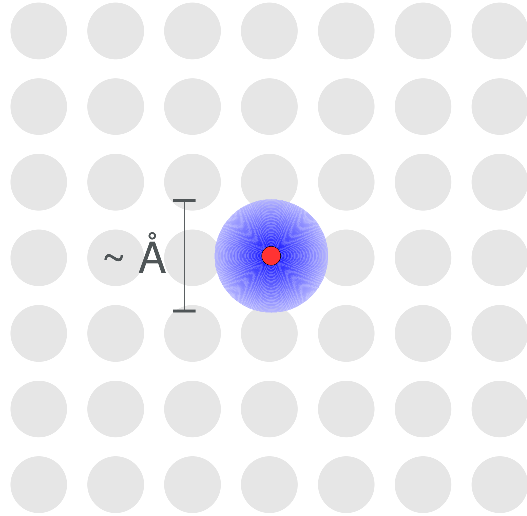
Doping the nanowires...

# The hydrogenoid impurity problem in bulk



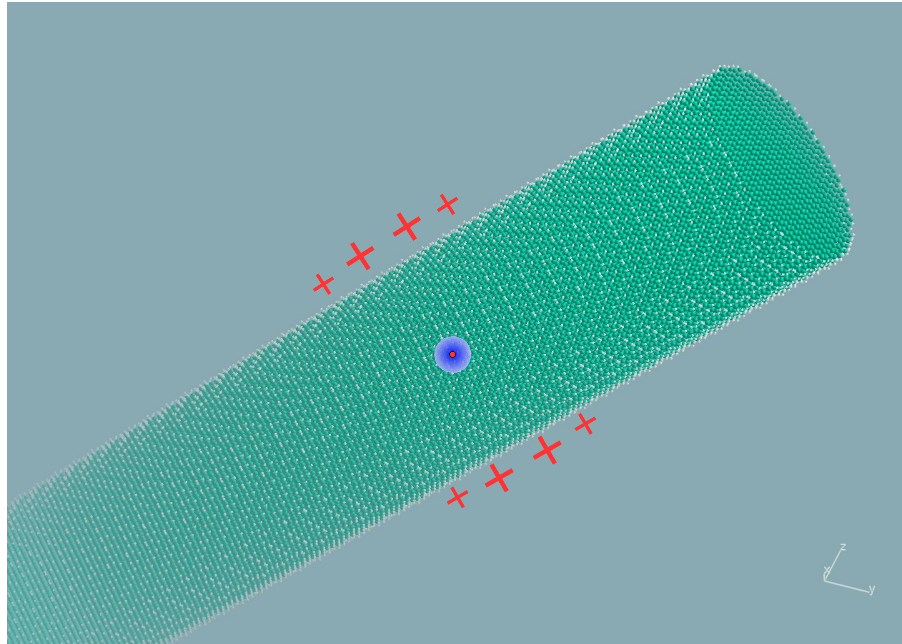

- The impurity potential :
  - is **isotropic**.
  - is **screened by the dielectric constant $\kappa$ at long distances**.




$$+1 \quad + \quad -\left(1-\frac{1}{\kappa}\right) \quad = \quad \frac{1}{\kappa}$$

- A ionized donor attracts nearby valence electrons and **gets screened by a short-range « cloud » of negative charges**.
- In bulk materials, the charge $-\left(1-\frac{1}{\kappa}\right)$ in this cloud comes « from infinity ».
- **The impurity and its cloud behave as a total charge $1/\kappa$** creating a potential $V(\mathbf{r}, \mathbf{r}') = 1/\kappa|\mathbf{r} - \mathbf{r}'|$ at long distances.

# The microscopic interpretation of classical electrostatics

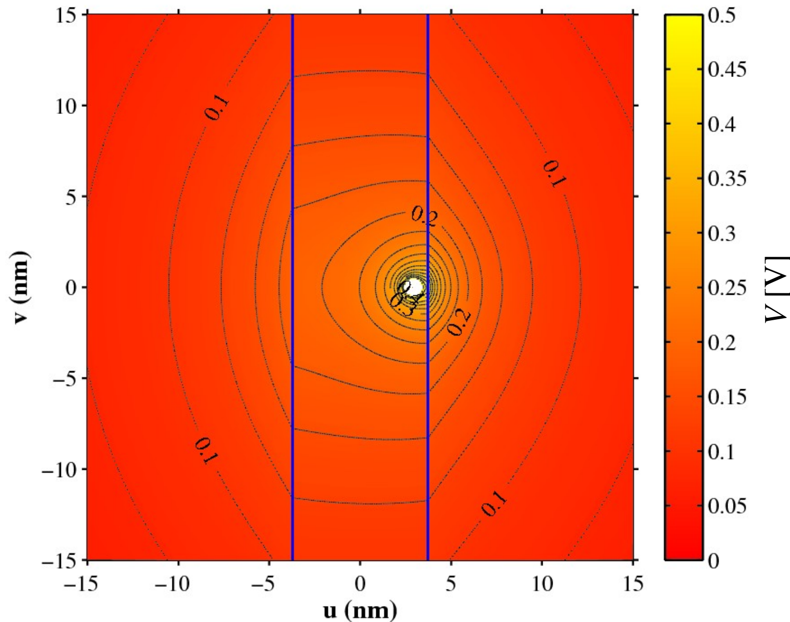


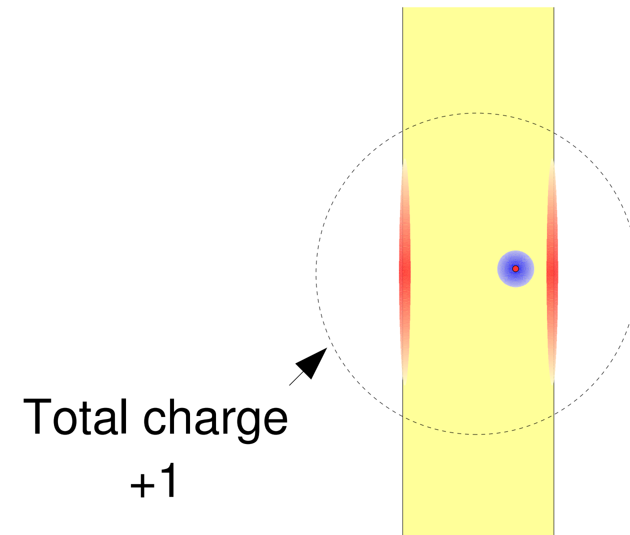
- In a nanowire, however, **the charge in the cloud comes from the surface** (« **image charges** » distribution).

- The solution of Poisson equation :

$$\nabla_{\mathbf{r}'} \left[ \kappa(\mathbf{r}') \nabla_{\mathbf{r}'} V(\mathbf{r}, \mathbf{r}') \right] = 4\pi\delta(\mathbf{r} - \mathbf{r}')$$

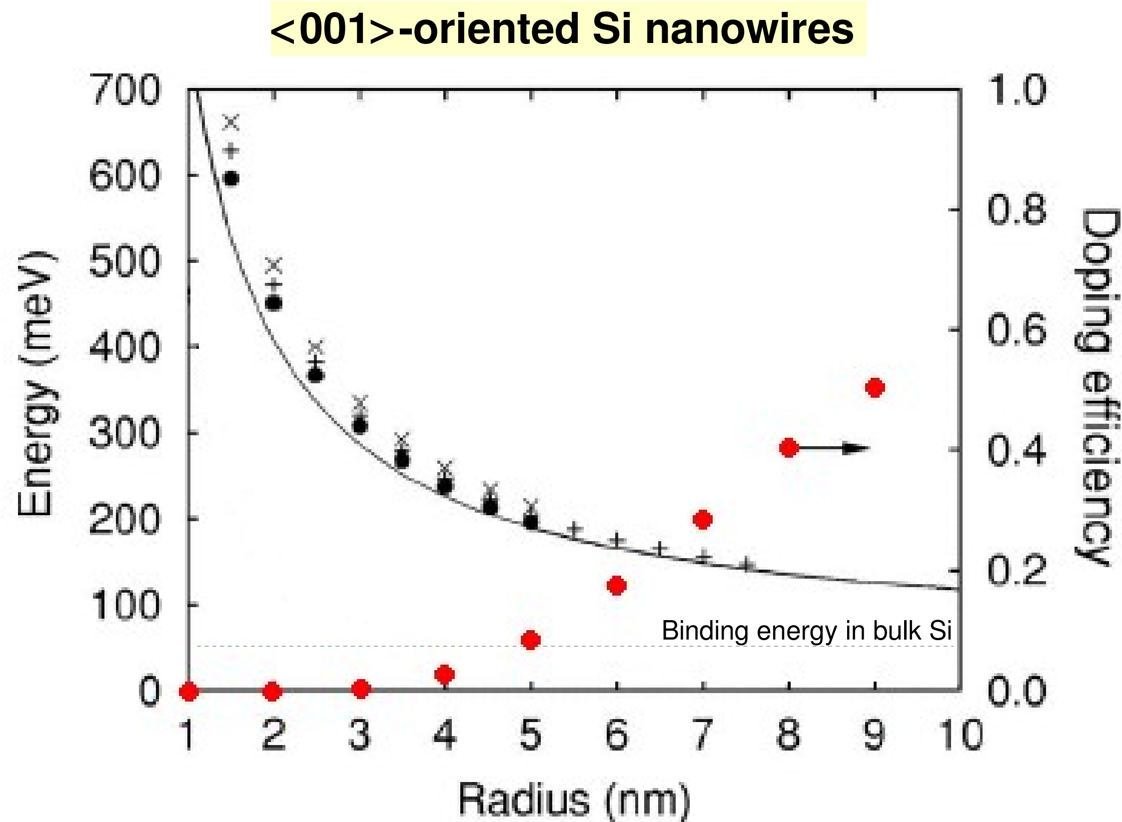
is actually the potential created in vacuum by the (unscreened) impurity, its cloud and its image charges.




- The potential is not isotropic due to the image charges.
- The total charge of the system (impurity + cloud + image charges) is +1 ; hence the potential decreases as $1/|\mathbf{r} - \mathbf{r}'|$ far enough (a few $R$'s) from the impurity.
- As a consequence, **the potential around the impurity is deeper than in bulk**.

# Doping the nanowires

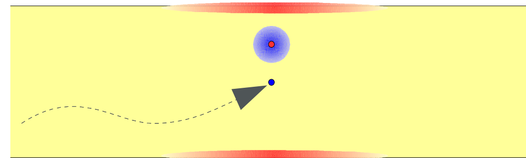



**Binding energy of a donor in a Si nanowire as a function of its radius.**

The donor is located along the nanowire axis.

+ P (45 meV in bulk)
× As (54 meV in bulk)
• Sb (39 meV in bulk)

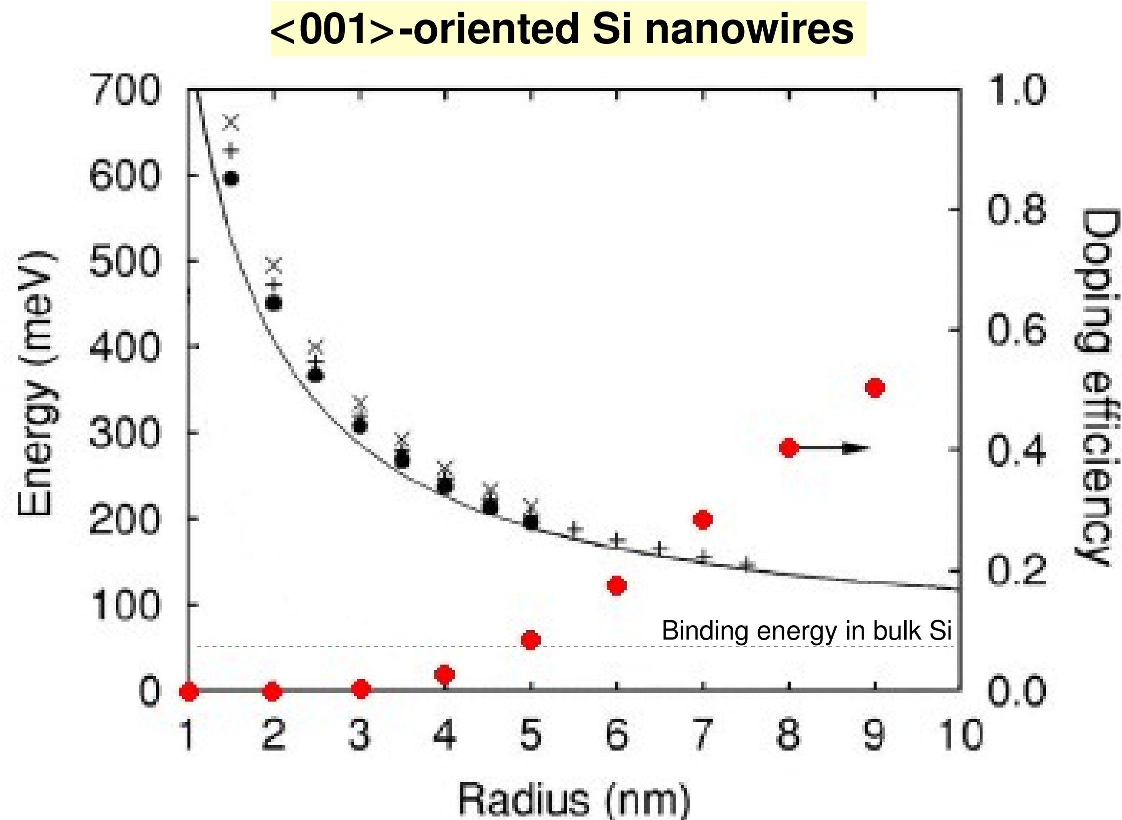
- The image charges **increase the binding energy of the donor up to a few hundreds of meV** in the smallest nanowires !!



The electron is trapped around the donor by the impurity and its image charges.

*Ionization energies of donor and acceptor impurities in semiconductor nanowires : importance of dielectric confinement*
M. Diarra, Y. M. Niquet, C. Delerue and G. Allan, Phys. Rev. B **75**, 045301 (2007).

# Doping the nanowires

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The donor is located along the nanowire axis.

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× As (54 meV in bulk)
• Sb (39 meV in bulk)

The binding energy of the impurities and the doping efficiency depend on the dielectric environment !

($E_0$ ↘ if $\kappa_{at}$ ↗)

**Electrostatic engineering of nanowire devices !!**

*Ionization energies of donor and acceptor impurities in semiconductor nanowires : importance of dielectric confinement*
M. Diarra, Y. M. Niquet, C. Delerue and G. Allan, Phys. Rev. B **75**, 045301 (2007).

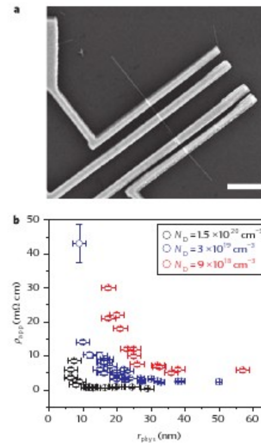
# Experimental evidences

nature nanotechnology | LETTERS
PUBLISHED ONLINE: 11 JANUARY 2009 | DOI: 10.1038/NNANO.2008.400

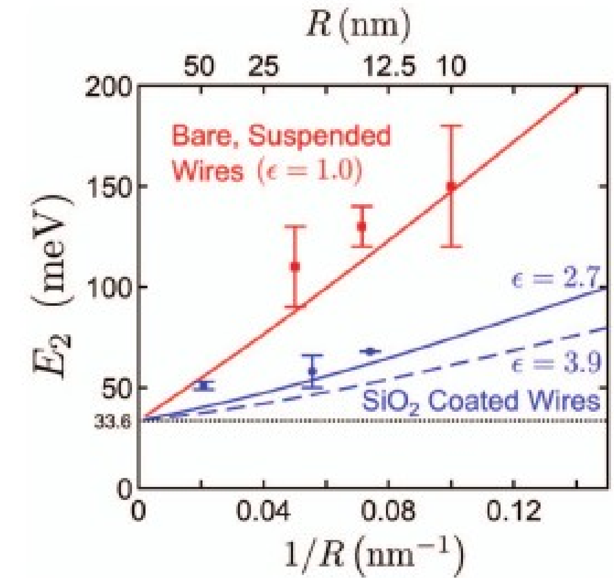
## Donor deactivation in silicon nanostructures

Mikael T. Björk*, Heinz Schmid, Joachim Knoch, Heike Riel and Walter Riess

**The operation of electronic devices relies on the density of free charge carriers available in the semiconductor; in most semiconductor devices this density is controlled by the addition of doping atoms. As dimensions are scaled down to achieve economic and performance benefits, the presence of interfaces and materials adjacent to the semiconductor will become more important and will eventually completely determine the electronic properties of the device. To sustain further improvements in performance, novel field-effect transistor architectures, such as FinFETs[1,2] and nanowire field-effect transistors[3-7], have been proposed as replacements for the planar devices used today, and also for applications in biosensing[8-10] and power generation[11]. The successful operation of such devices will depend on our ability to precisely control the location and number of active impurity atoms in the host semiconductor during the fabrication process. Here, we demonstrate that the free carrier density in semiconductor nanowires is dependent on the size of the nanowires. By measuring the electrical conduction of doped silicon nanowires as a function of nanowire radius, temperature and dielectric surrounding, we show that the donor ionization energy increases with decreasing nanowire radius, and that it profoundly modifies the attainable free carrier density at values of the radius much larger than those at which quantum[12,13] and dopant surface segregation[14] effects set in. At a nanowire radius of 15 nm the carrier density is already 50% lower than in bulk silicon due to the dielectric mismatch[15] between the conducting channel and its surroundings.**



Nature Nanotechnology **4**, 103 (2009)




APPLIED PHYSICS LETTERS **94**, 142102 (2009)

## Size-dependent impurity activation energy in GaN nanowires

J. Yoon,[1] A. M. Girgis,[2] I. Shalish,[1,a)] L. R. Ram-Mohan,[2] and V. Narayanamurti[1,b)]
[1]*School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA*
[2]*Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA*

(Received 23 February 2009; accepted 17 March 2009; published online 6 April 2009)

The effect of the surrounding dielectric on the conductivity of GaN nanowires is measured experimentally. The two following configurations are considered: bare suspended and $SiO_2$-coated nanowires. The measured conductivity is consistently fitted by two exponential terms with different activation energies, indicating multichannel conduction. The larger energy, attributed to activation of impurities into the conduction subband, shows essentially inverse dependence on nanowire radius, consistent with the dielectric confinement effect. This agrees with calculated values from finite element analysis. The smaller energy is independent of the nanowire radius, suggesting a surface conduction channel. © 2009 *American Institute of Physics*. [DOI: 10.1063/1.3115769]

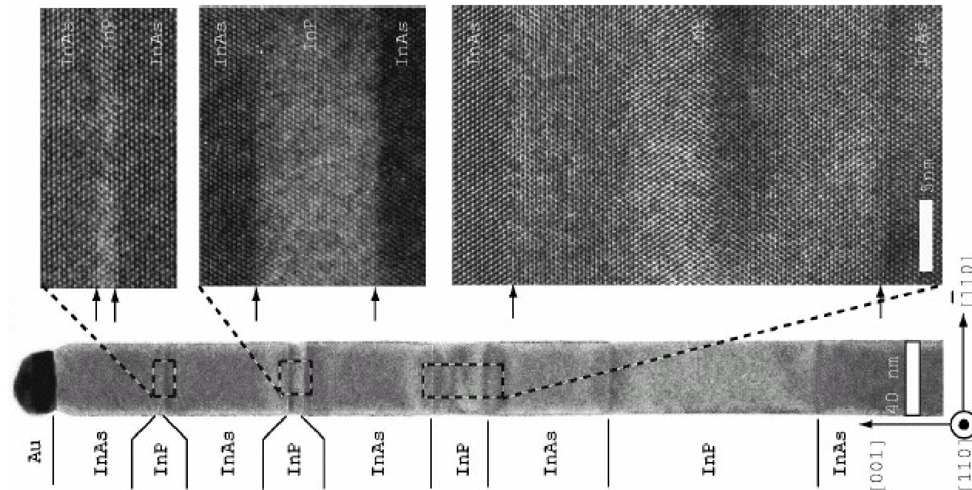
# Part II :

# Nanowire heterostructures

# Nanowire heterostructures

- Large interest in nanowire « heterostructures » for optics & transport :

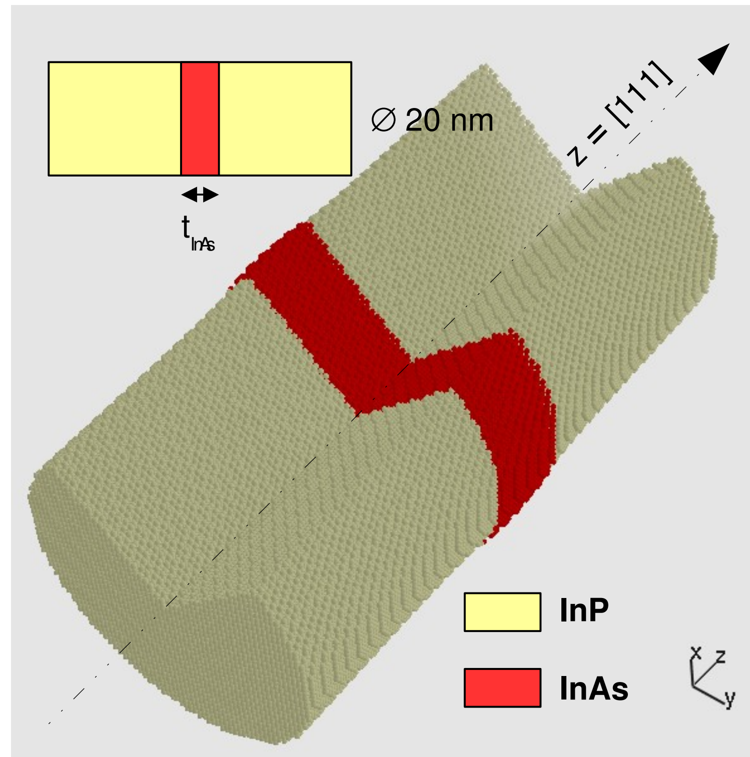
M. T. Björk *et al.*, Appl. Phys. Lett. **80**, 1058 (2002).




- Strain relaxation is believed to be efficient in these heterostructures, allowing the epitaxy of thick lattice mismatched layers.

- **What is the effect of residual strains on the electronic and optical properties of nanowire heterostructures ?**

# InAs/InP superlattices




- The bond length is 3.13% shorter in InP than in InAs. The InAs layer is thus **compressed** by the InP core, but can partly **relax** strains at the surface of the nanowire.

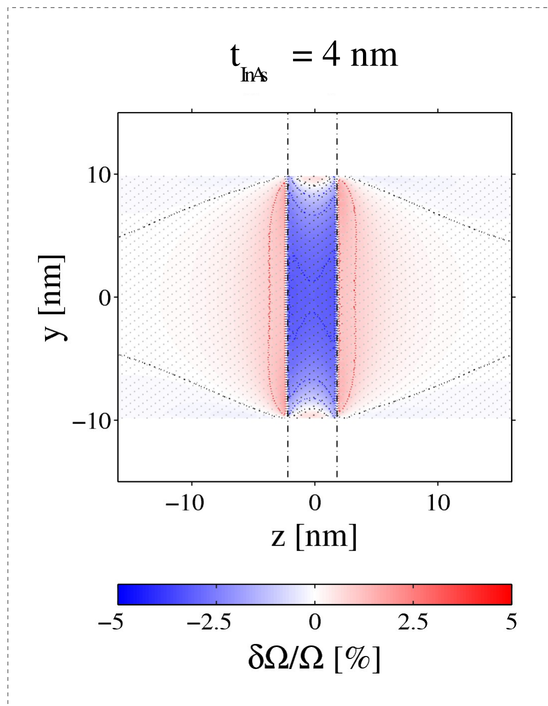
# Modeling nanowire heterostructures...

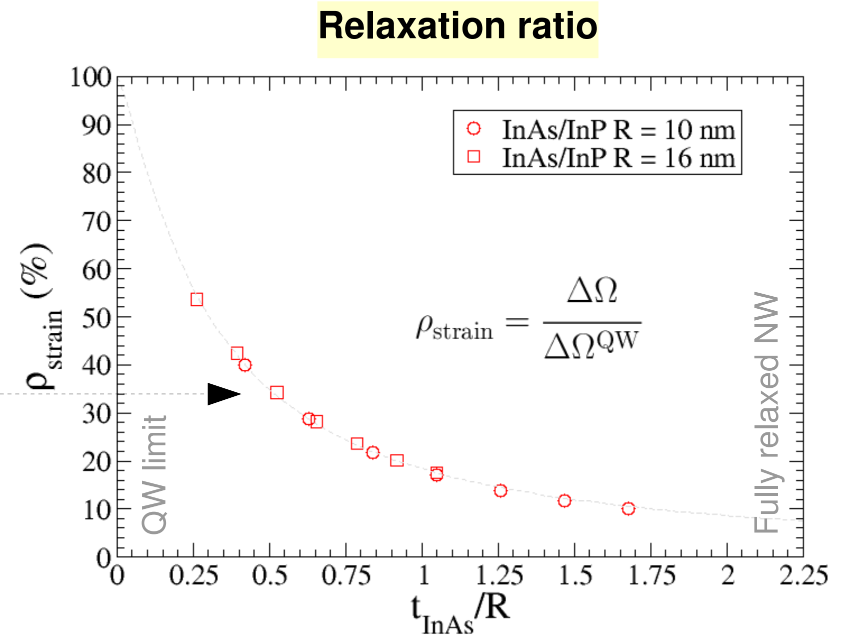
Strain relaxation (Keating) → Piezoelectric potential

Strain relaxation (Keating), Piezoelectric potential, Self-energy effects → One particle states (Tight-binding)

One particle states (Tight-binding) → Optical properties (Exciton)

# Strain relaxation

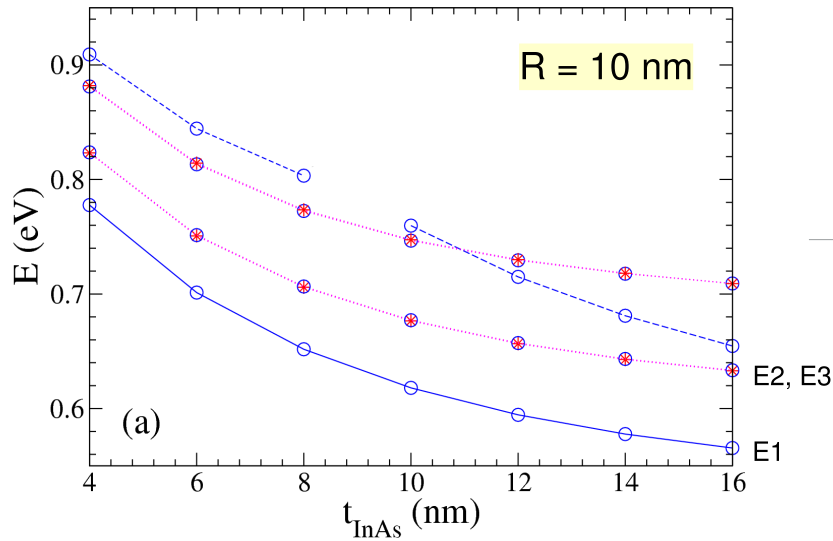


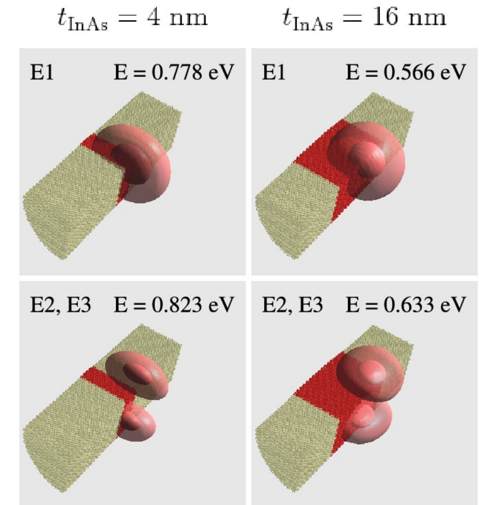



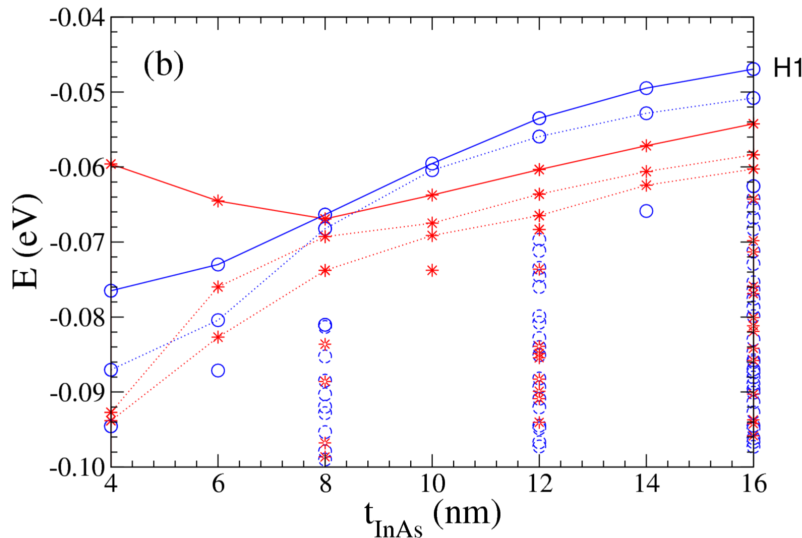

- Strain relaxation is very **efficient** in nanowire heterostructures. The InAs layer expands outwards and distorts the surface of the nanowire. The strain distribution is however very **inhomogeneous** in thin InAs layers : the surface is overrelaxed while the axis is still significantly compressed.

- The InAs layers are almost **completely relaxed** when $t_{InAs} > 2R$.

# Electronic structure

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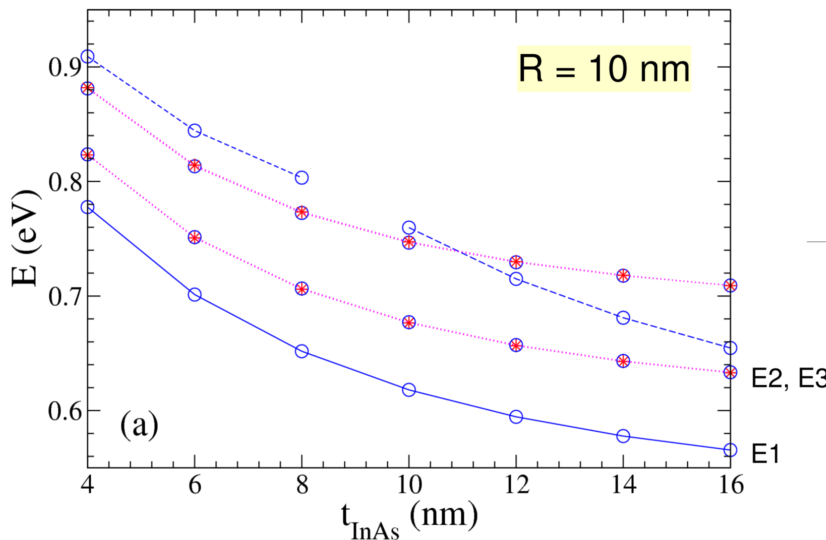
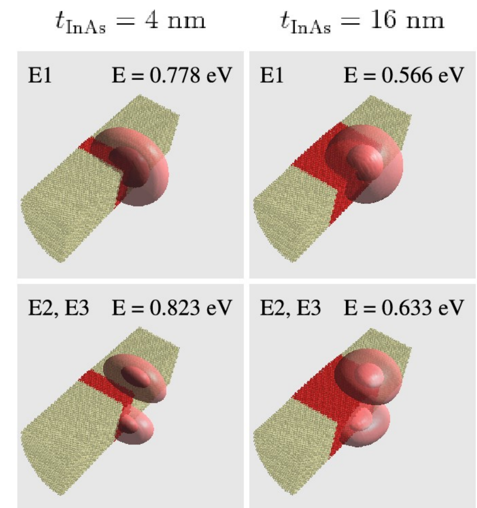
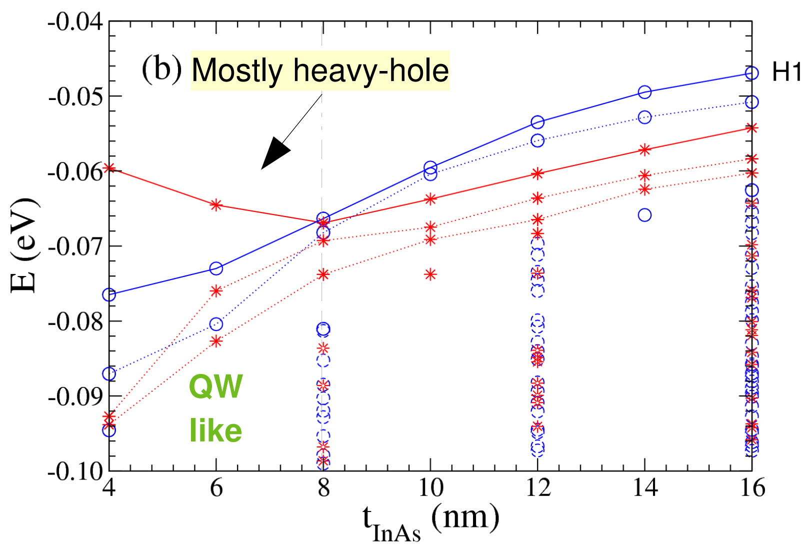
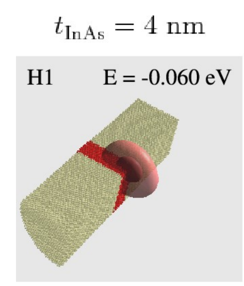
Y. M. Niquet and D. Camacho, Phys. Rev. B **77**, 115316 (2008).

# Electronic structure




- **Strains and longitudinal confinement** favor the **heavy-holes**...

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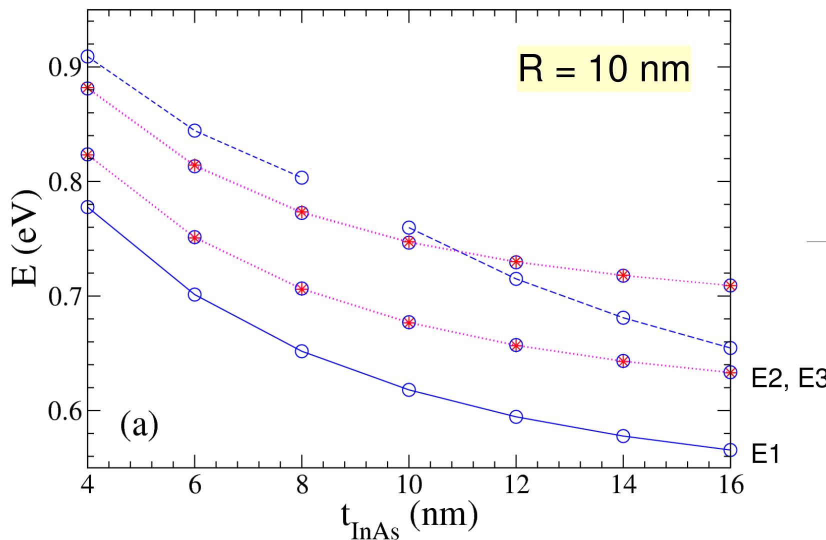
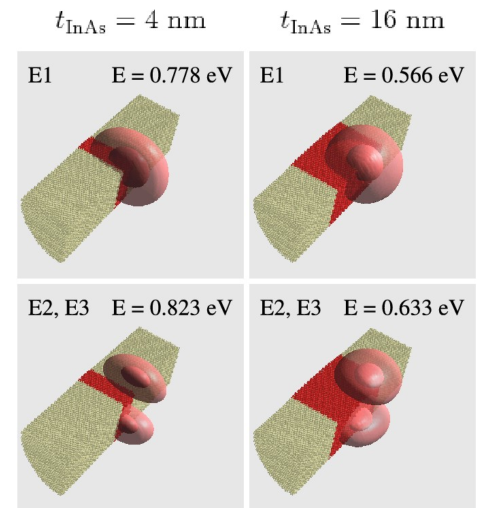
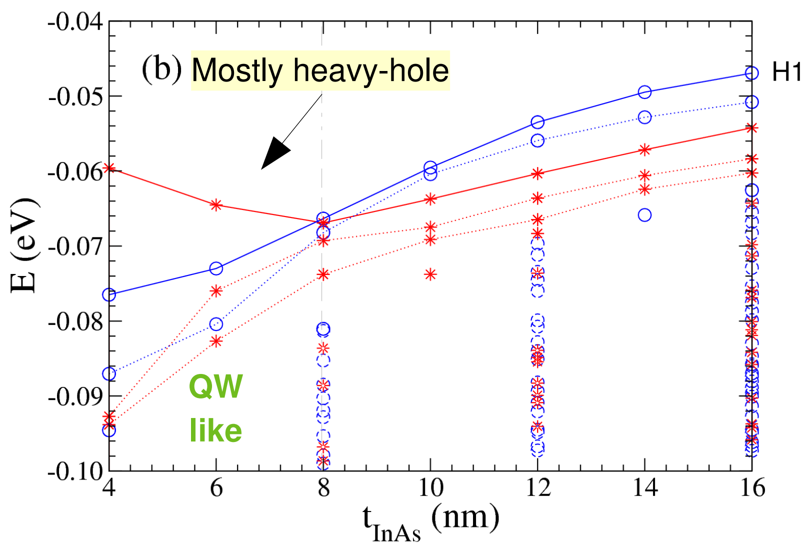
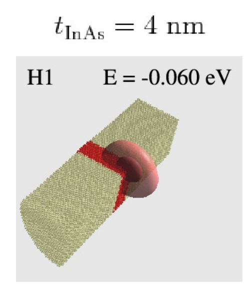
# Electronic structure




- **Strains and longitudinal confinement** favor the **heavy-holes**...
- ... while **lateral confinement** favors the **light-holes**.

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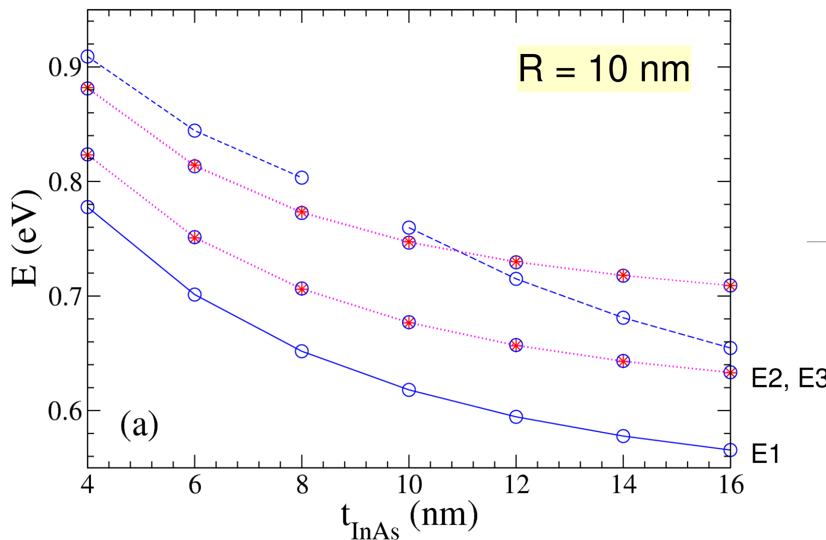
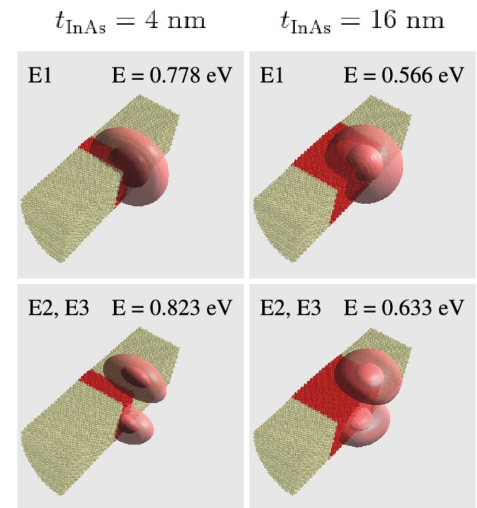
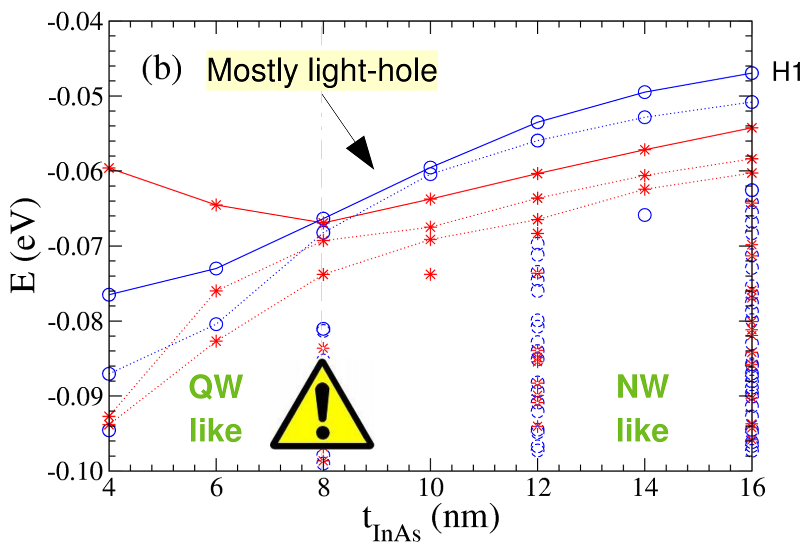
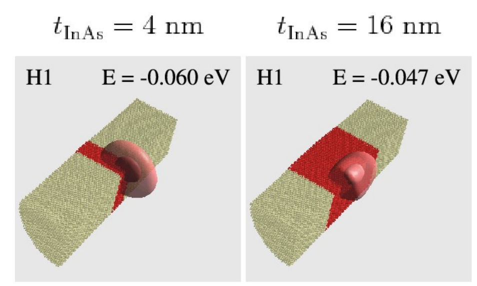
Y. M. Niquet and D. Camacho, Phys. Rev. B **77**, 115316 (2008).

# Electronic structure




- Transition from a mostly **heavy-hole** ground state (like in quantum wells) to a mostly **light-hole** ground state (like in homogeneous ⟨111⟩-oriented nanowires).

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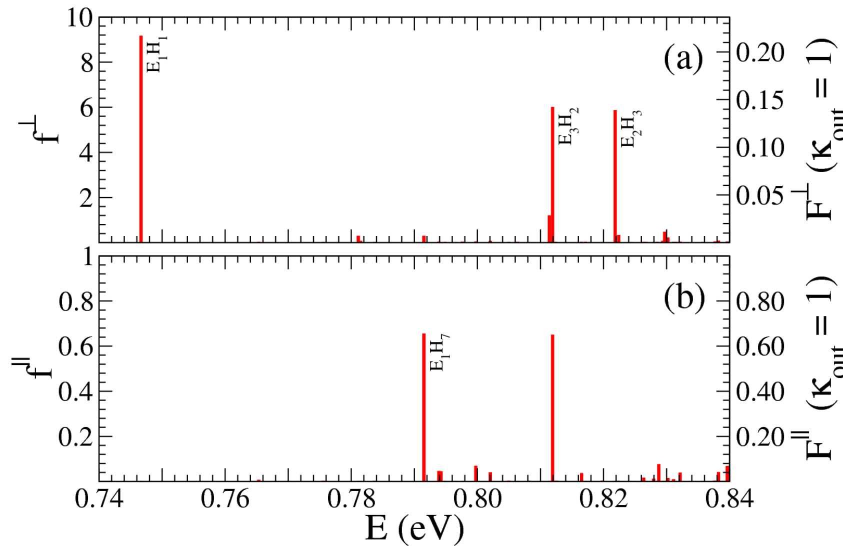
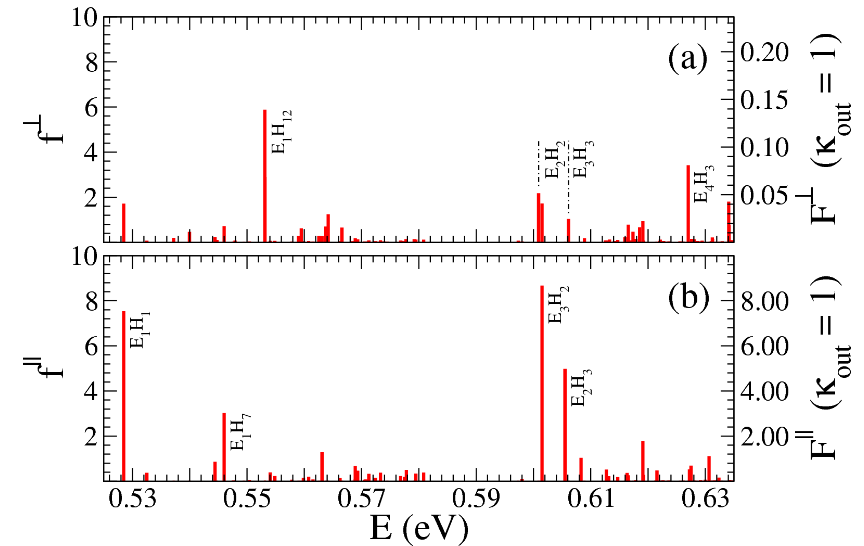
# Optical properties

**Absorption/luminescence**

R = 10 nm, $t_{InAs}$ = 4 nm

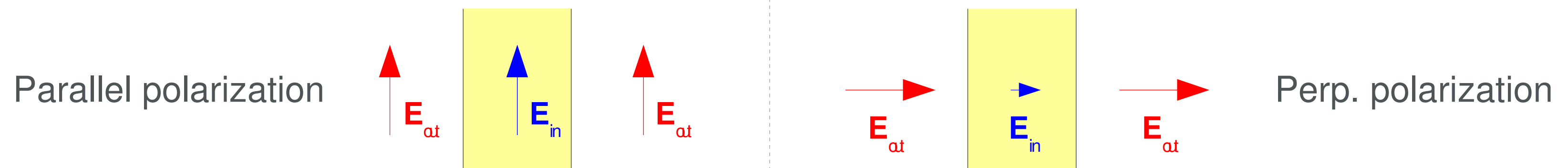



R = 10 nm, $t_{InAs}$ = 16 nm




- The light is polarized **perpendicular to the wire in thin, quantum-well like InAs layers**, **but perpendicular to the wire in thick ones** (like in homogeneous nanowires), as a result of the increasing light-hole character of the exciton.

- **Local field effects** might however reduce the perpendicular oscillator strength !!

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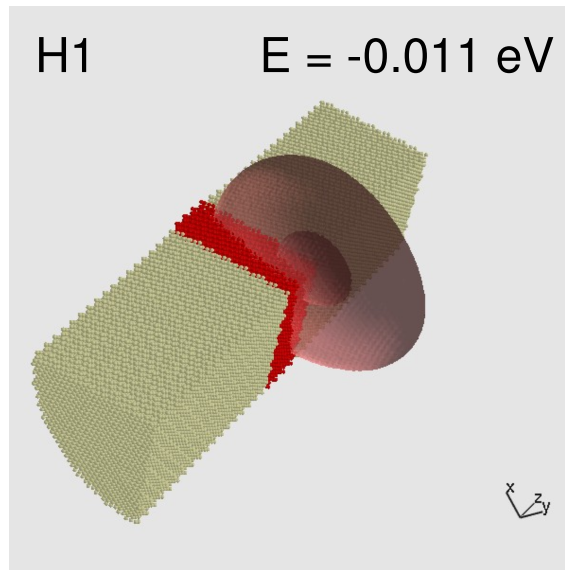
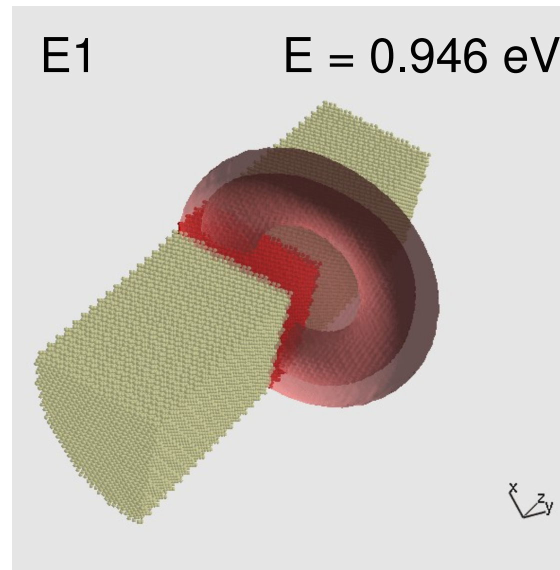
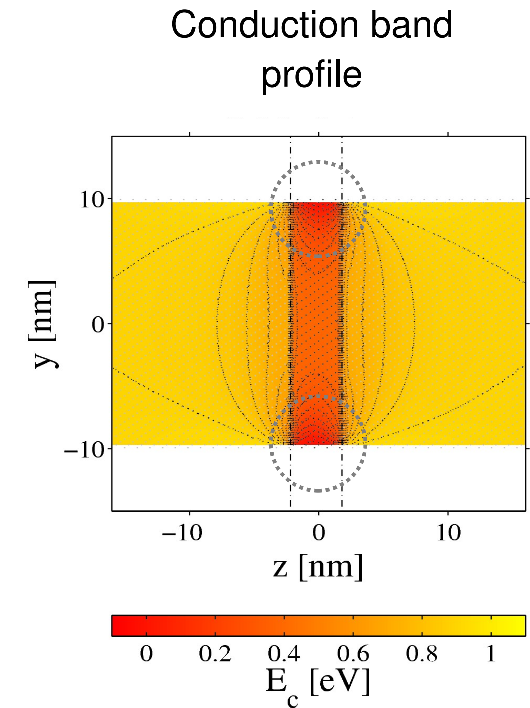
# Highly mismatched heterostructures

InAs/GaAs $t_{InAs}$ = 4 nm ($\varepsilon_{\parallel}$ = -6.69%)




Conduction band profile



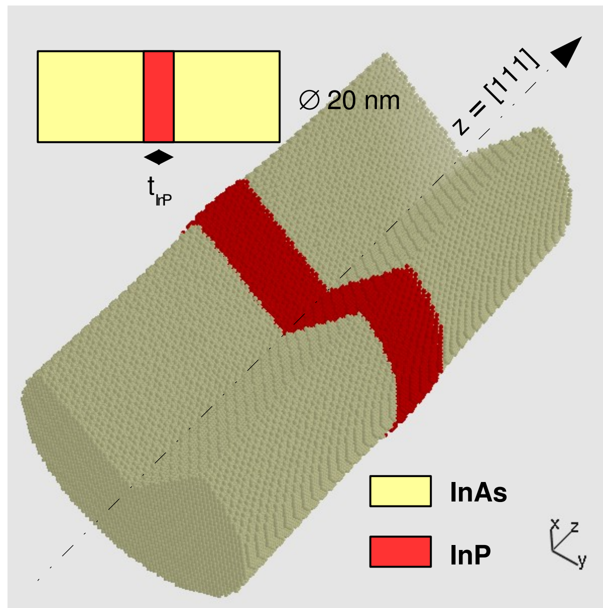

- The **electron**, **that prefers tensile strains**, **is trapped** near the surface of the nanowire by the inhomogeneous relaxation.

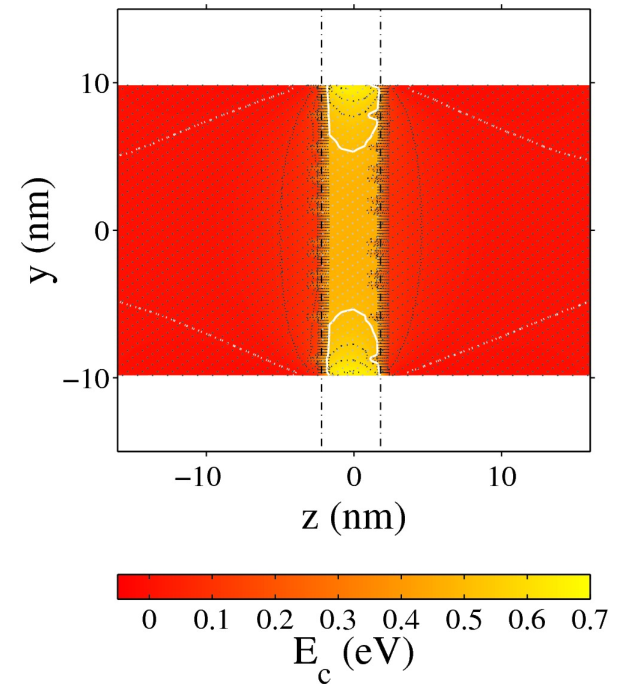
- **Solution** : **Grow a thin GaAs shell** around the nanowire !..

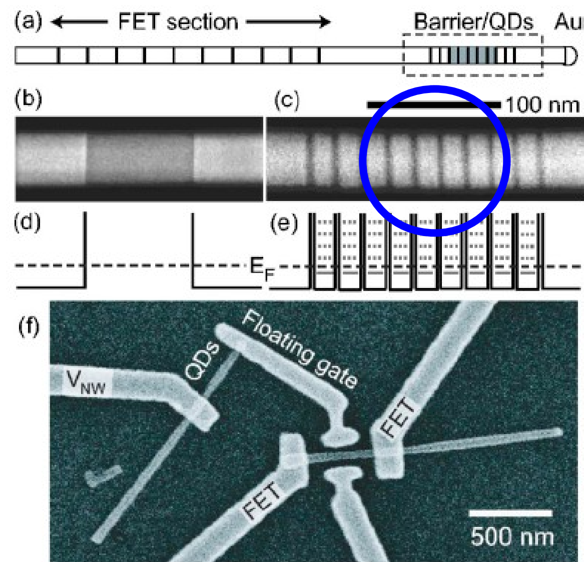
- Might happen even at moderate lattice mismatch in materials with larger electron effective mass than InAs ($m^* = 0.023\ m_0$) !

*Electronic and optical properties of InAs/GaAs nanowire superlattices*
Y. M. Niquet, Phys. Rev. B **74**, 155304 (2006) ; Nano Letters **7**, 1105 (2007).

# InP tunnel barriers in InAs nanowires



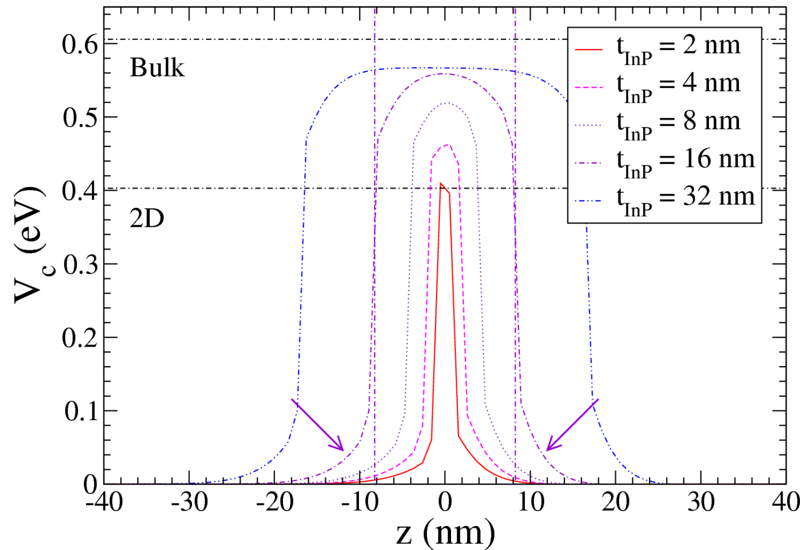




H. A. Nilsson *et al.*, Applied Phys. Lett. **89**, 163101 (2006).

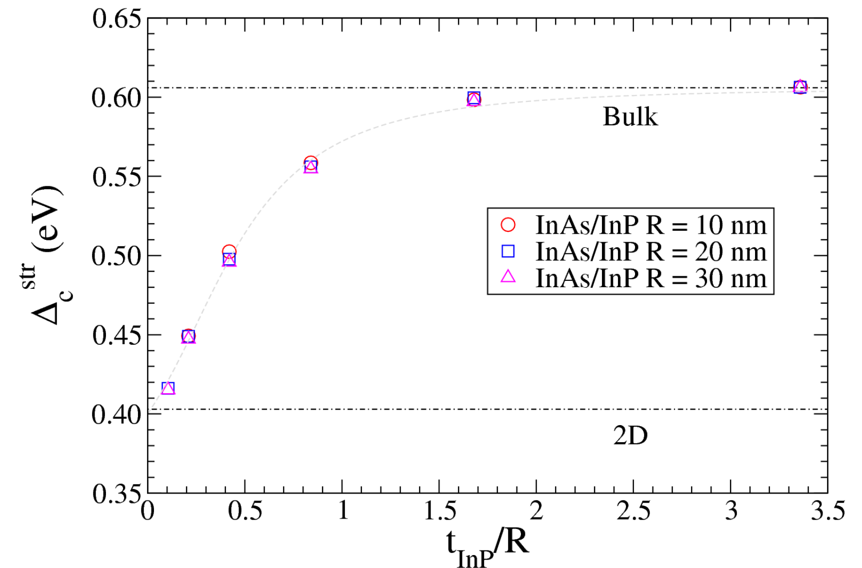
- The InP barrier is now dilated by the InAs core, which tends to **lower the conduction band energy**.

# Tunnel barrier heights in InAs/InP superlattices

**Conduction band profile (R = 10 nm)**




**Barrier height**




- The InP barrier is dilated by the InAs core, which decreases the barrier height for tunneling or thermionic emission.
- The barrier height is **close to the bulk value (0.6 eV)** in thick, almost strain-free InP layers ($t_{InP}$ > 1.5R), but tends to the **strained 2D limit (0.4 eV)** in thin ones. This must be taken into account in the design of nanowire tunneling devices.

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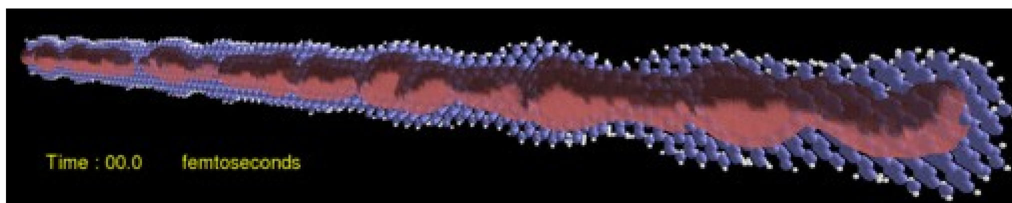
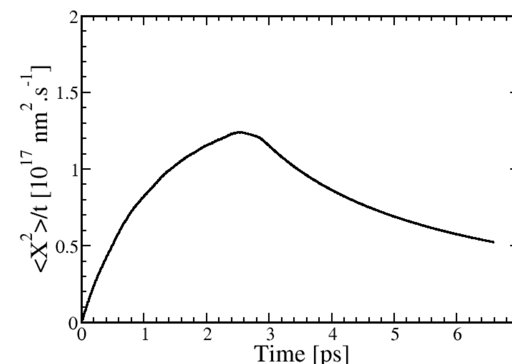
# Part III :

# Transport properties of semiconductor nanowires

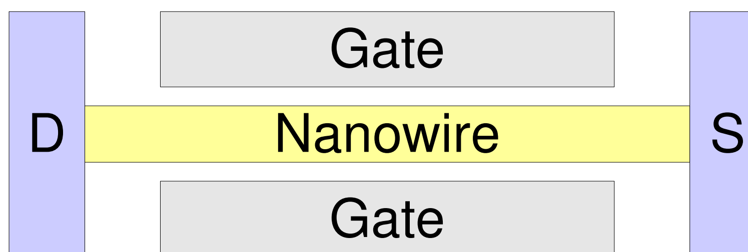
# The Kubo and Landauer-Büttiker methods

- **Kubo method** : progagate random wavepackets along the nanowires.
  - Yields the « **intrinsic** » transport properties of infinite, disordered nanowires (e.g., mean free paths and mobilities).




- **Landauer-Büttiker method** : Green function method.
  - Yields the transmission/conductance through a nanowire connected to drain and source **electrodes**.




- The two methods are complementary and well suited to localized basis sets.

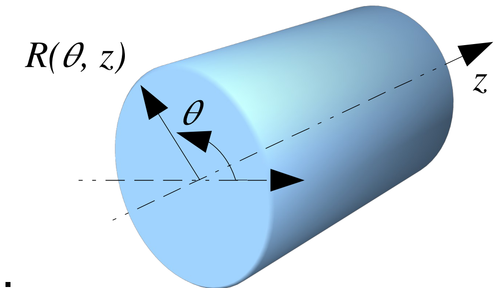
# Application : Surface roughness

- **Disorder** : **Random fluctuations of the radius** of the nanowire, characterized by the auto-correlation function :

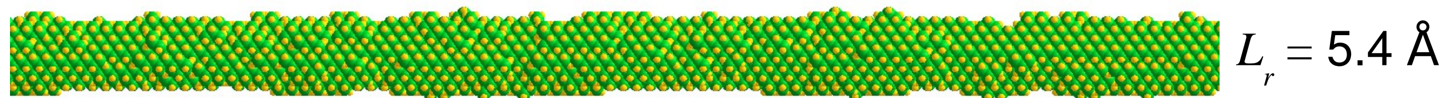
$$\langle \delta R(z,\theta)\delta R(z+\delta z,\theta+\delta\theta)\rangle \equiv \delta R_0^2 e^{-\sqrt{\delta z^2+R_0^2\delta\theta^2}/L_r}$$

Parameters :

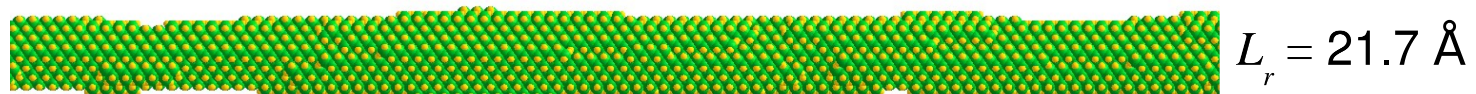
- $R_0$ : average radius.
- $\delta R_0$ : rms fluctuations of the radius.
- $L_r$ : correlation length (~ typical size) of the fluctuations.




**Si ⟨110⟩ nanowires $R_0$ = 1 nm, $\delta R_0$ = 1 Å**



$L_r$ = 5.4 Å



$L_r$ = 21.7 Å

- **How does the conductance decrease with the wire length $L$ ?**

*Quantum transport length scales in Silicon-based semiconducting nanowires: Surface roughness effects*
A. Lherbier, M. Persson, Y. M. Niquet, F. Triozon and S. Roche, Phys. Rev. B. **77**, 085301 (2008).

# Band structure of silicon nanowires

[100] [110] [111]

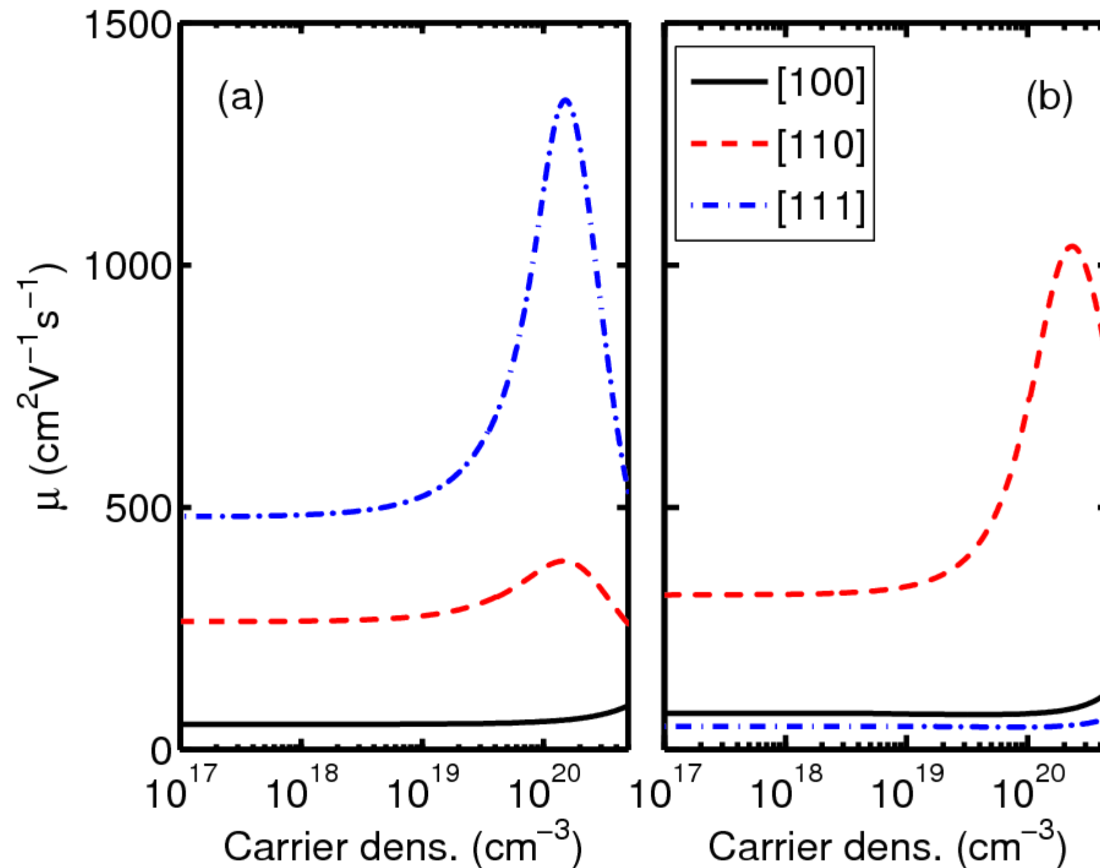
x 4 – m* = 0.30 (a)
x 2 – m* = 0.97 (b)
x 2 – m* = 0.13 (c)
x 1 – m* = 0.18 (d)
x 6 – m* = 0.96 (e)
x 1 – m* = 0.16 (f)

Energy (eV) · DOS · k (π/l)

- The band structure of thin Si NWs is strongly dependent on their orientation :
  - Conduction band **valley degeneracy** completely **lifted in [110] Si NWs**.
  - **Lightest hole mass** and largest valence subband splittings **in [111] Si NWs**.

*Orientational dependence of charge transport in disordered silicon nanowires*
M. Persson, A. Lherbier, Y. M. Niquet, F. Triozon and S. Roche, Nano Letters **8**, 4146 (2008).

# Mobility as a function of Si NW orientation




- In agreement with the trends evidenced on the band structures,
  - **[111]** is the best orientation for **hole** transport.
  - **[110]** is the best orientation for **electron** transport.

*Orientational dependence of charge transport in disordered silicon nanowires*
M. Persson, A. Lherbier, Y. M. Niquet, F. Triozon and S. Roche, Nano Letters **8**, 4146 (2008).

# Conclusions

- The **electrostatics of semiconductor nanowires is very peculiar** and affects their properties even in the > 20 nm range where quantum confinement becomes negligible.

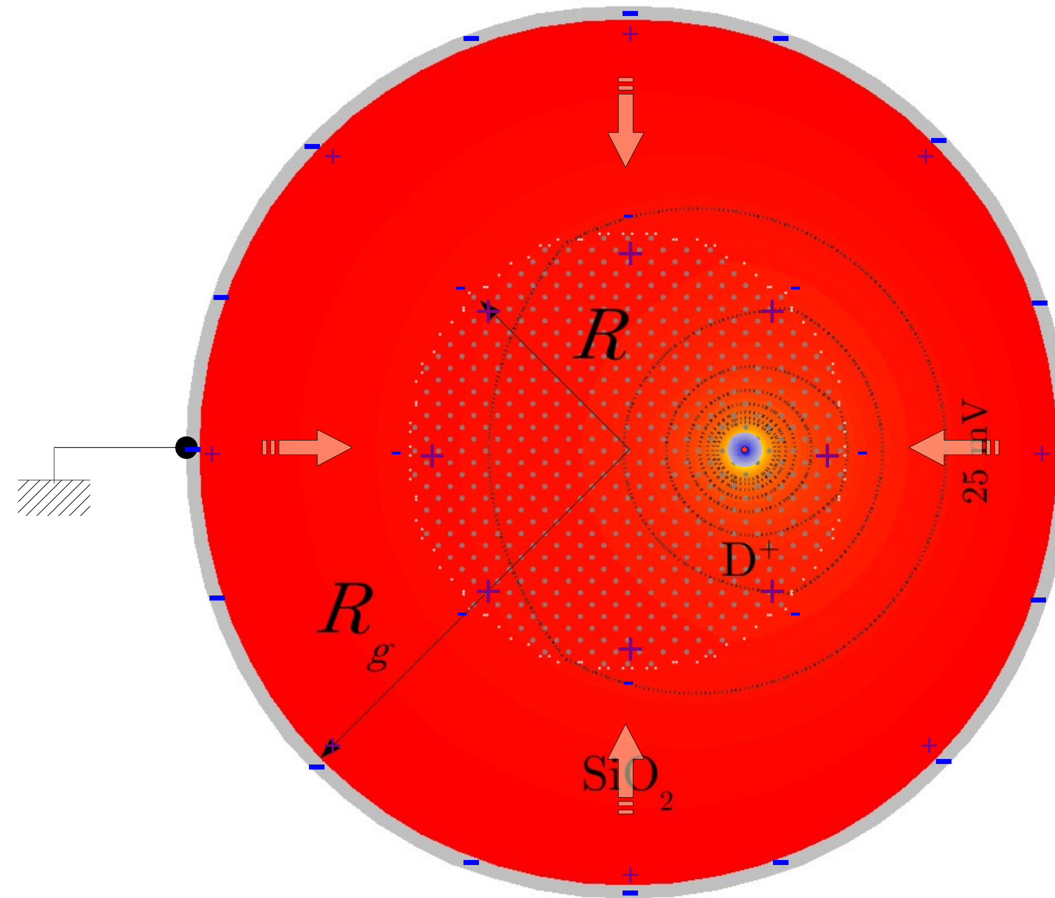
« **Electrostatic** » **engineering** of the environment of the NWs

(e.g. to decrease donor binding energies)

- **The strain relaxation is very efficient** (low cross-sectional area), which allows the growth of unprecedented heterostructures... but **residual strains might still affect their electronic properties** !

- The **[110]** direction is best for **electron** transport in ultimate Si nanowires, while the **[111]** direction is best for **hole** transport.

# Screening in a complex dielectric environment




- Oxydes and metallic gates screen the impurity potential...

⇒ **Decrease of the binding energy**

**... BUT ...**

- The dielectric response of the oxydes is slow...

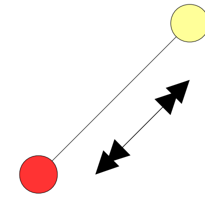
⇒ **Polaronic enhancement of the binding energy** !

# Keating's valence force field model

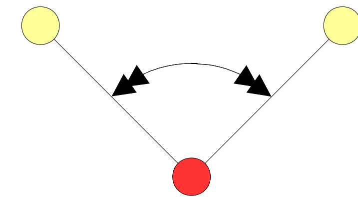
- We assume coherent growth. Strain relaxation is computed using Keating's Valence Force Field model :

$$E=\frac{1}{2}\sum_{i}\sum_{j}^{NN}\frac{3\alpha_{ij}}{8\left(d_{ij}^{0}\right)^{2}}\left[\left(\vec{R}_{j}-\vec{R}_{i}\right)^{2}-\left(d_{ij}^{0}\right)^{2}\right]^{2}$$

$$+\frac{1}{2}\sum_{i}\sum_{j,k>j}^{NN}\frac{3\beta_{ijk}}{8\left(d_{ij}^{0}\right)\left(d_{ik}^{0}\right)}\left[\left(\vec{R}_{j}-\vec{R}_{i}\right)\left(\vec{R}_{k}-\vec{R}_{i}\right)+\frac{1}{3}\left(d_{ij}^{0}\right)\left(d_{ik}^{0}\right)\right]^{2}$$



Bond stretching constant $\alpha$



Bond bending constant $\beta$

| | InAs | InP |
|---|---|---|
| $d^0$ | 2.623 Å | 2.541 Å |
| α | 32.650 N/m | 39.820 N/m |
| β | 7.350 N/m | 8.130 N/m |