Universitat Autònoma de Barcelona

ICMAB

Doping and sensing in Si nanowires

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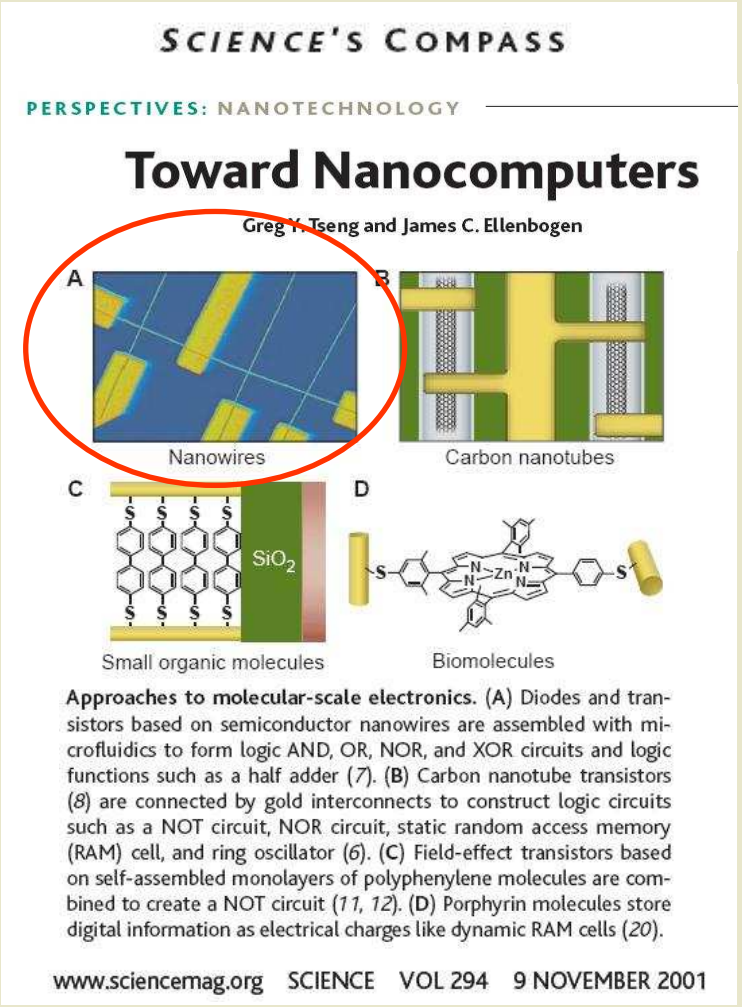
Summary

- Why nanowires?
- Substitutional dopants in NWs
- Molecular doping and gas sensing
- Conclusions

Beyond CMOS – Emerging devices



SCIENCE'S COMPASS

PERSPECTIVES: NANOTECHNOLOGY

Toward Nanocomputers

Greg Y. Tseng and James C. Ellenbogen

A

Nanowires

B

Carbon nanotubes

C

SiO_2

Small organic molecules

D

Biomolecules

Approaches to molecular-scale electronics. (A) Diodes and transistors based on semiconductor nanowires are assembled with microfluidics to form logic AND, OR, NOR, and XOR circuits and logic functions such as a half adder (*7*). (B) Carbon nanotube transistors (*8*) are connected by gold interconnects to construct logic circuits such as a NOT circuit, NOR circuit, static random access memory (RAM) cell, and ring oscillator (*6*). (C) Field-effect transistors based on self-assembled monolayers of polyphenylene molecules are combined to create a NOT circuit (*11*, *12*). (D) Porphyrin molecules store digital information as electrical charges like dynamic RAM cells (*20*).

www.sciencemag.org SCIENCE VOL 294 9 NOVEMBER 2001

Common paradigm

Complementing lithographic techniques with ***bottom-up*** **fabrication** and **molecular self-assembly**

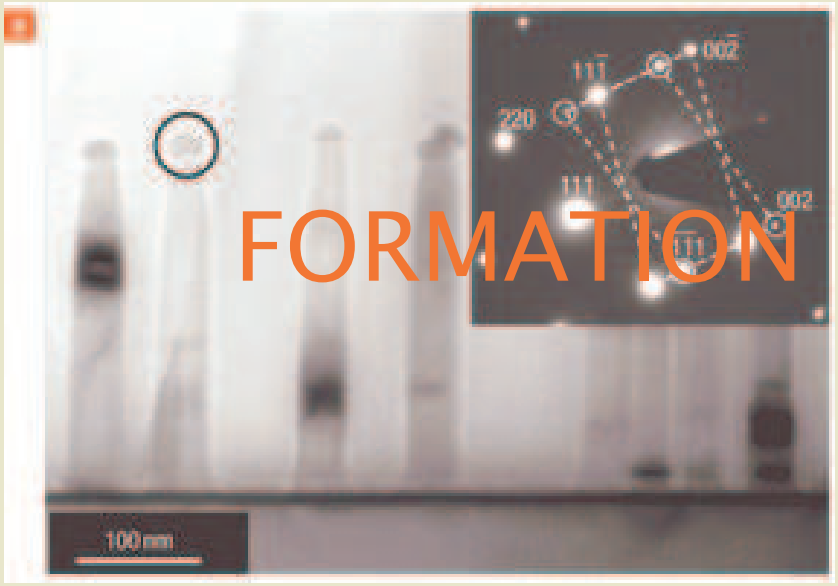
Advantages of Si nanowires

Good control of the electronic properties (always **semiconducting**)

Ideal **integration** with the existing Si technology

Why impurities?

- Can we dope nanowires effectively?
- Is any VLS/VSS catalyst cleaner than the others?
- Will dopants segregate towards the surface?
- How soluble is P in a SiNW?



Y. Wang et al., Nature Nanotech. 1, 186 (2006)

FORMATION ENERGIES!!!

S. Hofmann et al., Nature Mat. 7, 372 (2008)

Summary

- Why nanowires?
- Substitutional dopants in NWs
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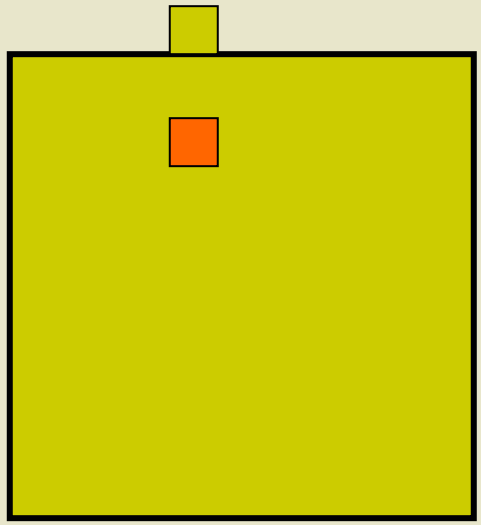
ZN formalism: Dopants

- Consider the "chemical reaction" for substitutional formation

$$Si_n + X_{ref} \rightleftarrows Si_{n-1}X + V_{Si} + Si_{bulk}$$



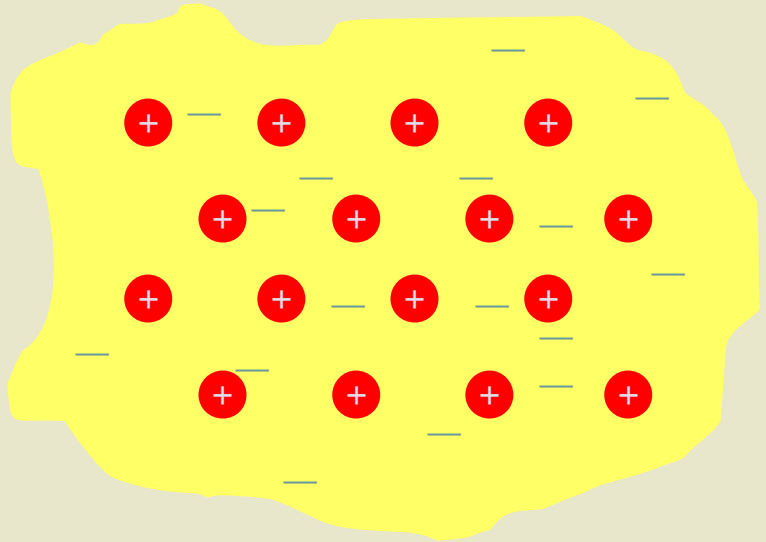
$$\Delta E_f = E_S + \mu_{Si} - E_{clean} - \mu_X = E_S - E_{clean} - \Sigma_i n_i \mu_i$$

S. B. Zhang and John E. Northrup, *Phys. Rev. Lett.* **67**, 2339 (1991)

n_i: Number of atoms *added* into the defect

Charged cells in PBCs

- The spurious contribution due to the interaction of charge with its images must be subtracted.
- A periodic array of charges has a divergent Coulomb energy…



- … but it can be embedded in a neutralizing jellium to make the sum convergent.
- We want the $L \to \infty$ limit.

Charged cells in PBCs: Ewald sum

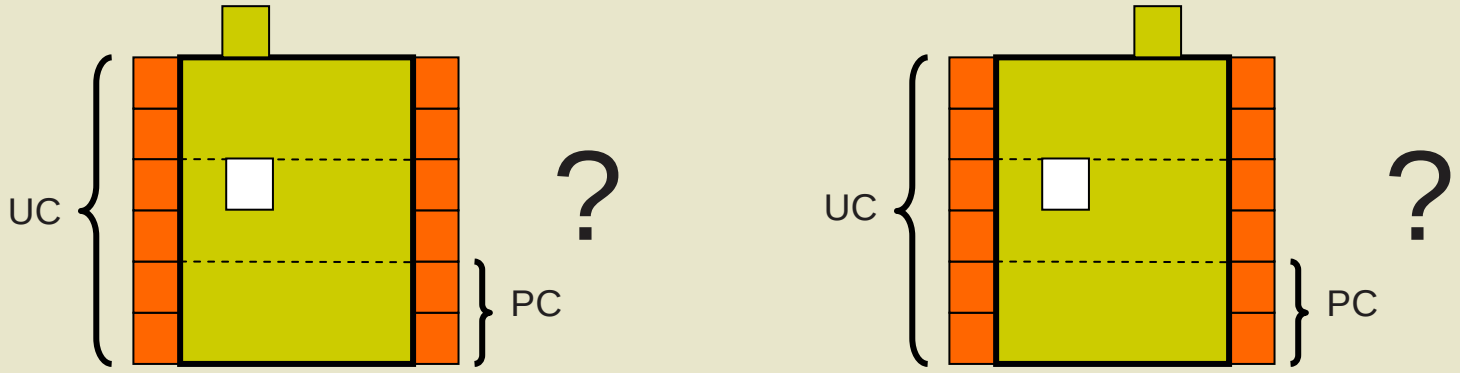
- The spurious energy is given by

$$\frac{E}{N} = \frac{1}{2}\sum_i \frac{q^2}{\varepsilon R_i} = \frac{1}{2}\alpha\frac{q^2}{\varepsilon L}$$

- α is the Madelung constant

$$\frac{\alpha}{L} = \sum_i \frac{erfc(\gamma R_i)}{R_i} + \sum_i \frac{4\pi}{V_c}\frac{\exp(-G_i^2/4\gamma^2)}{G_i^2} - \frac{2\gamma}{\sqrt{\pi}} - \frac{\pi}{V_c\gamma^2}$$

E_f in NWs: ZN formalism is hard

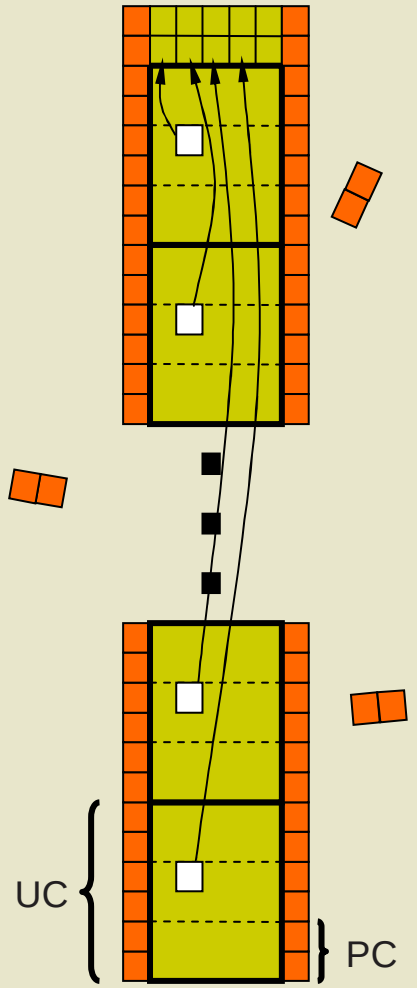


$$3(Si_nH_m) \rightleftarrows Si_{3n-1}H_{3m}+V_{Si}+Si_{NW}$$

- In a vacancy/substitutional, you want to add the displaced atom to the NW, but…
- … where does the displaced atom go?
- … what's the energy of that atom?
- … what about surface passivation?

E_f in NWs: Consider many instances!

- We consider the creation of as many defects as necessary to form a new primitive cell.
- Everything can be readily computed from first-principles.
- Reaction tells you how to deal with surface passivation.



$$3(Si_nH_m) \rightleftarrows Si_{3n-1}H_{3m}+V_{Si}+Si_{bulk}$$

$$n[3(Si_nH_m)]+m/2\ H_2 \rightleftarrows n[Si_{3n-1}H_{3m}+V_{Si}]+Si_nH_m$$

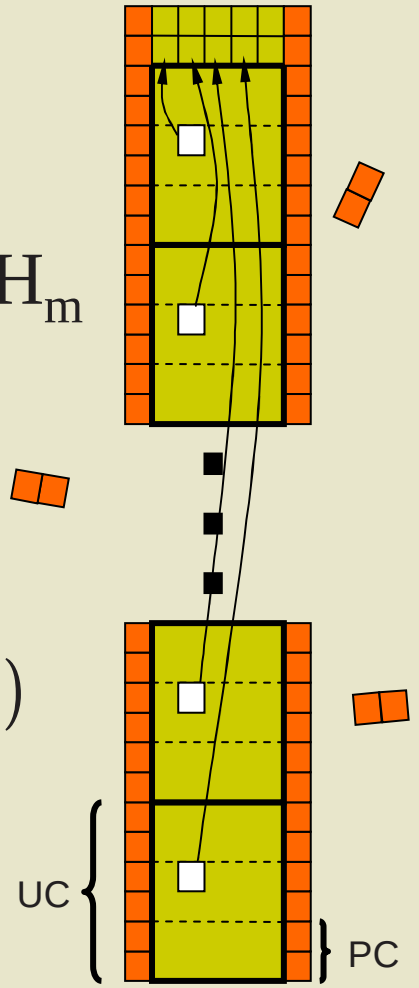
E_f in NWs: Modified expression

- The formation energy corresponding to the reaction

$$n[3(Si_nH_m)]+m/2\ H_2 \rightleftarrows n[Si_{3n-1}H_{3m}+V_{Si}]+Si_nH_m$$

is

$$\Delta E^f = E^D_{tot} - NE^{PC}_{NW} - \frac{n^{Si}}{n^{PC}_{Si}}\left(E^{PC}_{NW} - \frac{n^{PC}_H}{2}E_{H_2}\right) + q(\varepsilon_v + \mu_e)$$



Rurali and Cartoixà,
Nano Lett. **9** (3), 975-979 (2009)

E_f in NWs: Net charges

- The unit cell will no longer need to be cubic, but even if we choose it to be so…
- … ϵ is now a *tensor*

- Need to start from the potential due to a point charge embedded in an anisotropic medium:

$$V(r) = \frac{1}{\sqrt{\det(\varepsilon)}} \frac{1}{\sqrt{r \cdot \varepsilon^{-1} \cdot r}}$$

E_f in NWs: Ewald sum

- The general expression needed to compute the Madelung constant for the NWs is

$$\frac{\alpha}{L} = \sum_i \frac{1}{\sqrt{\det(\varepsilon)}} \frac{erfc(\gamma\sqrt{R_i \cdot \varepsilon^{-1} \cdot R_i})}{\sqrt{R_i \cdot \varepsilon^{-1} \cdot R_i}} +$$

$$\sum_i \frac{4\pi}{V_c} \frac{\exp(-G_i \cdot \varepsilon \cdot G_i / 4\gamma^2)}{G_i \cdot \varepsilon \cdot G_i} - \frac{2\gamma}{\sqrt{\pi \det(\varepsilon)}} - \frac{\pi}{V_c \gamma^2}$$

Rurali and Cartoixà,
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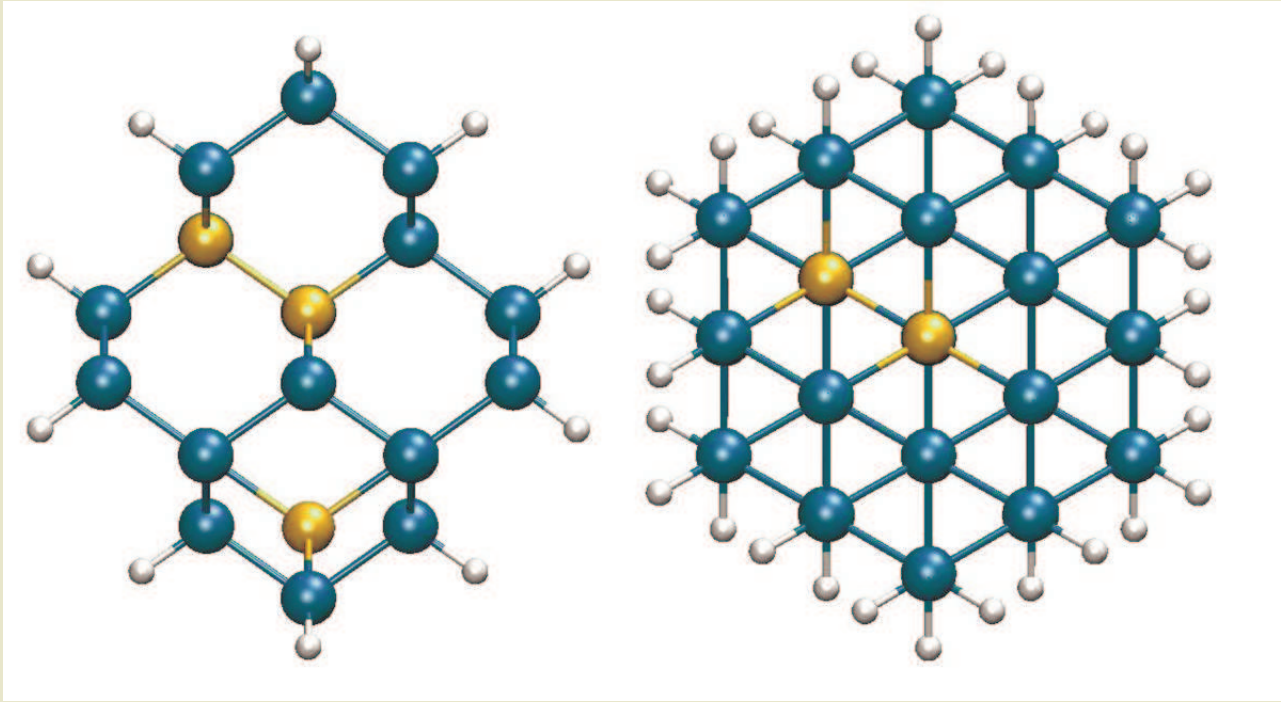
Al@SiNWs: Configurations

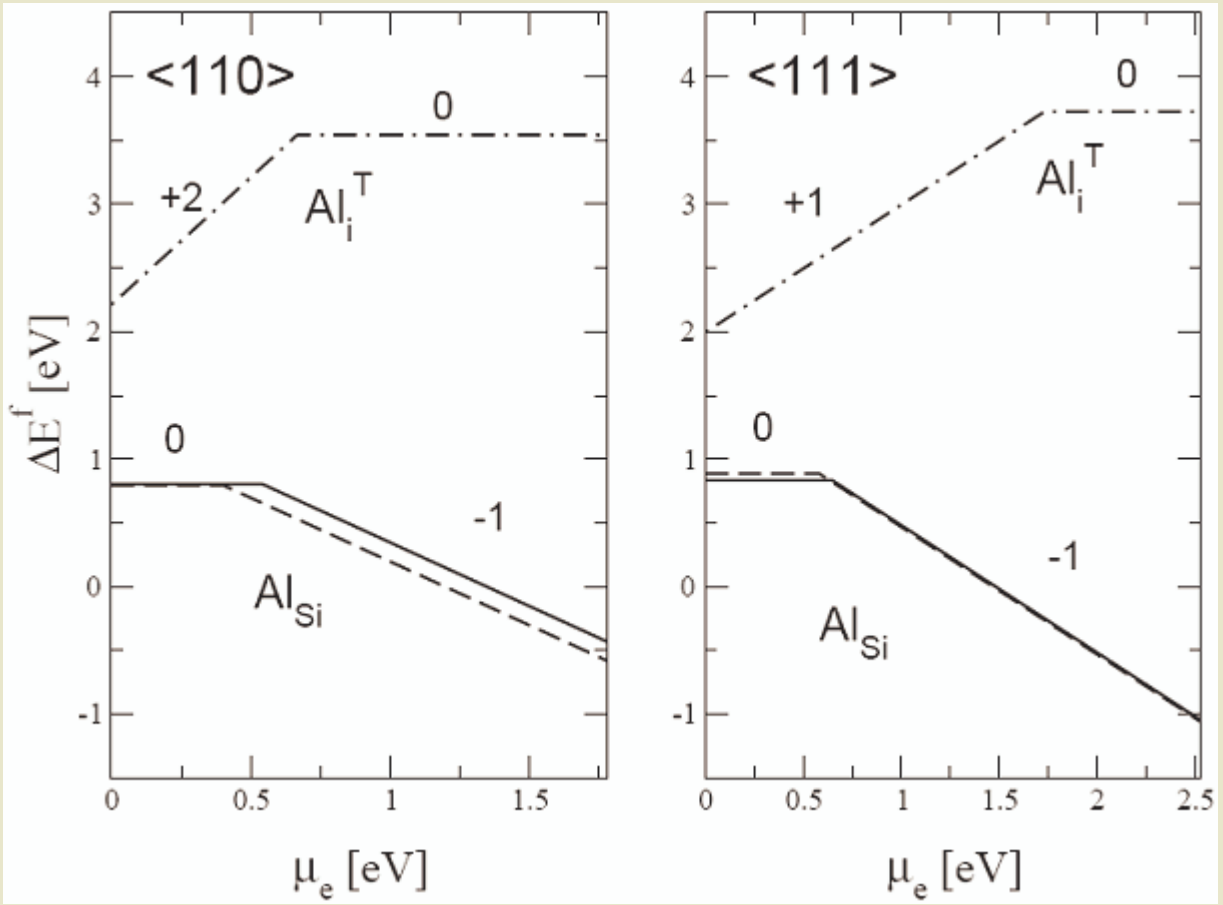
- We have studied substitutional and interstitial Al atoms in ∅=1.0 nm and 1.5 nm silicon NWs.



<110> <111>

Al@SiNWs: Configurations

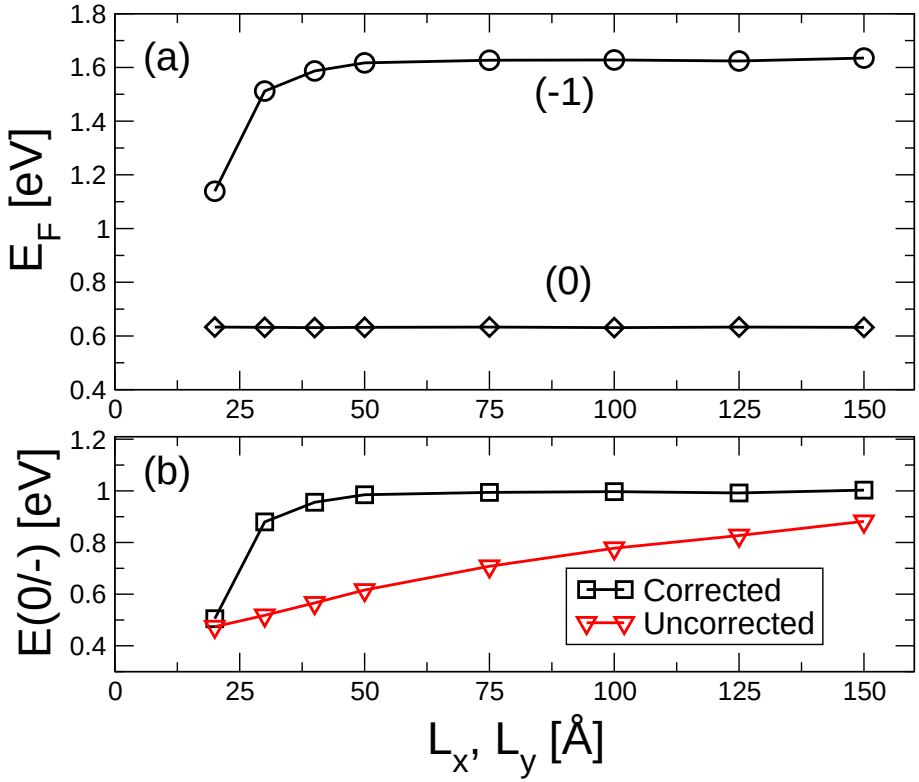
- Substitutional Al is preferred, Al is a acceptor.
- For heavily n-doped, Al dilution is eased.

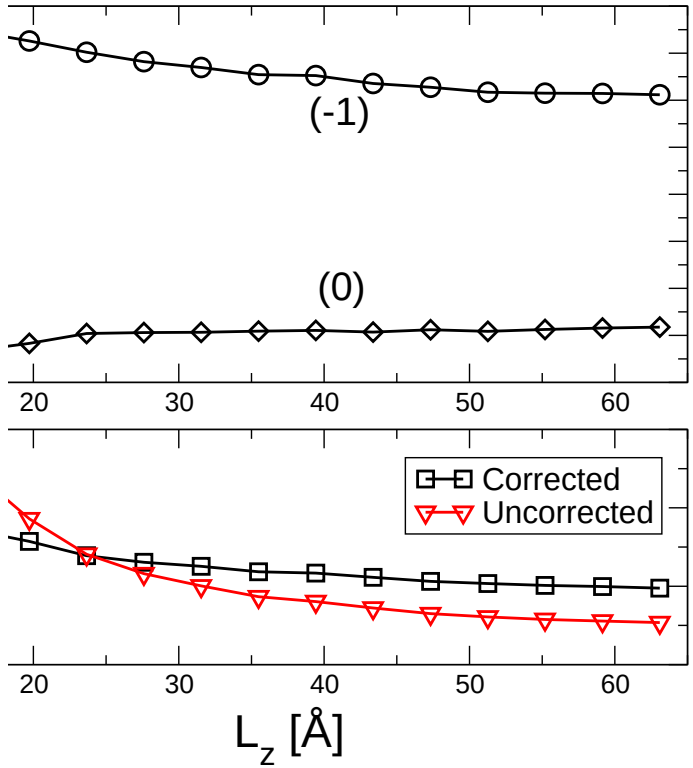


Rurali and Cartoixà,
Nano Lett. **9** (3), 975-979 (2009)

Al@SiNWs: Convergence study

- Need a 50x50x60 Å^3 supercell for a <110>





Rurali, Palummo and Cartoixà,
Phys. Rev. B **81**, 235304 (2010)

Summary

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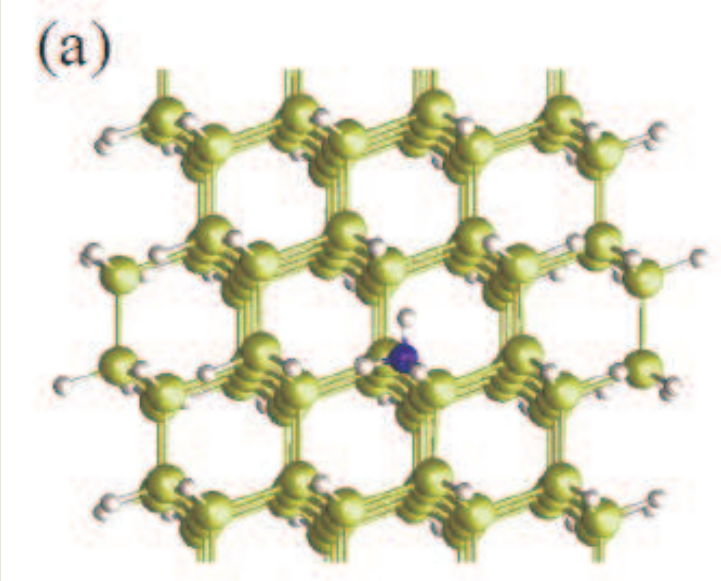
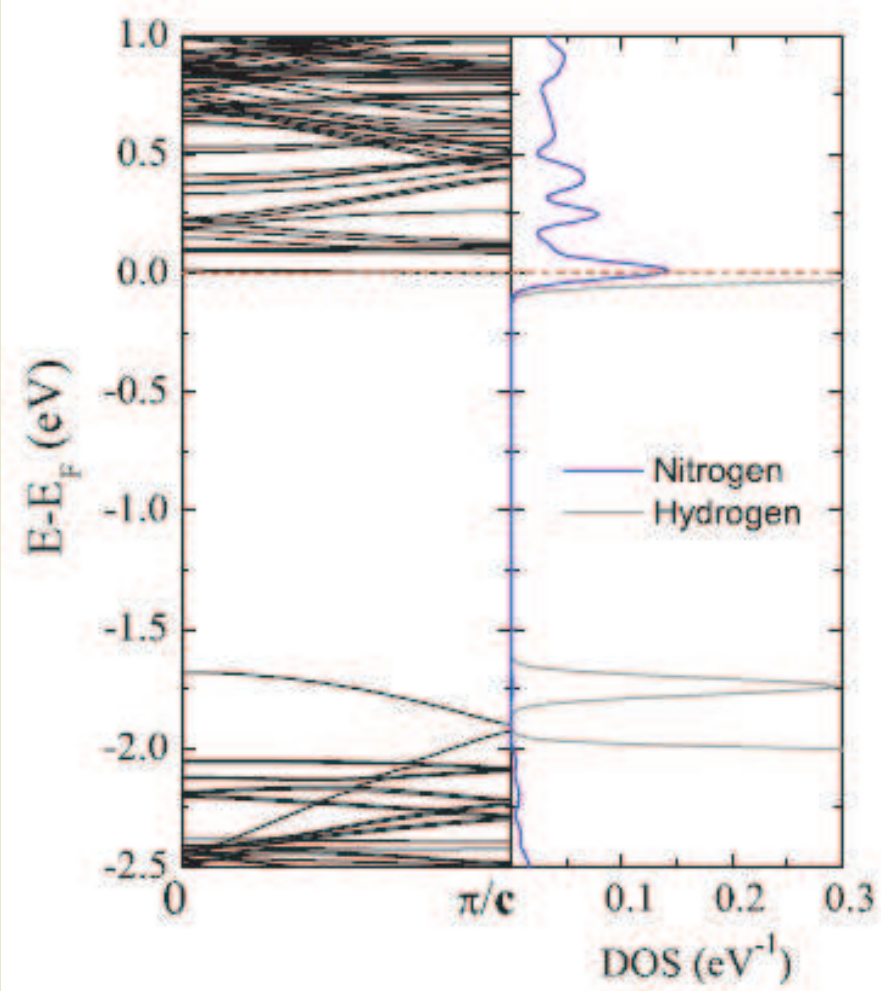
NH_3 on SiNWs

- NH_3@DB acts as a donor for SiNWs, surfaces



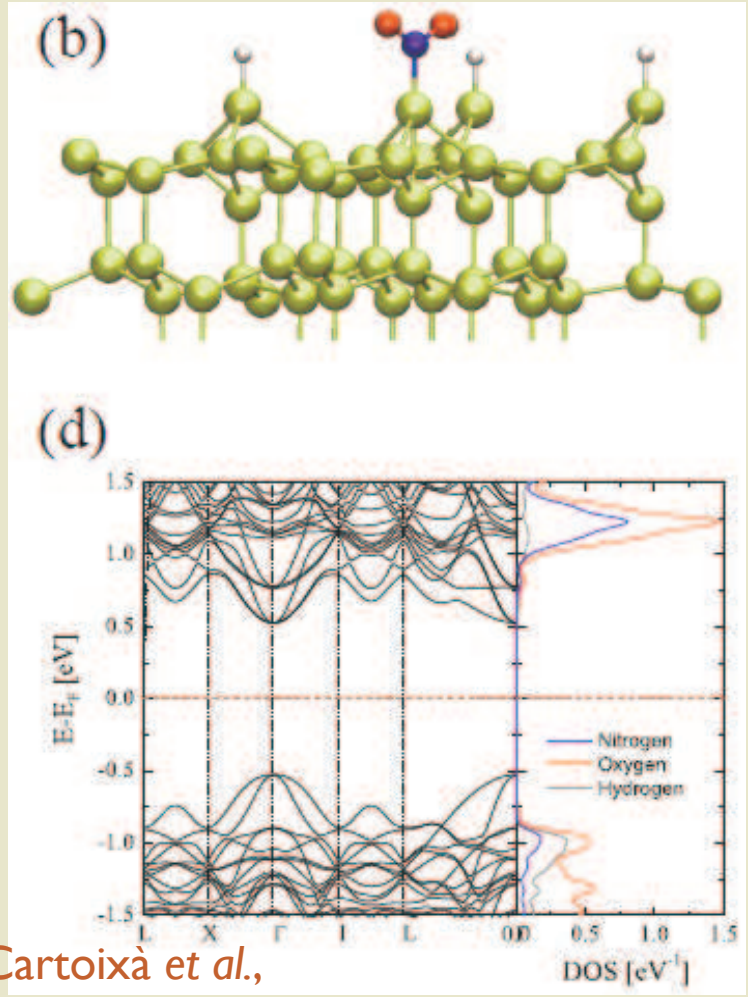


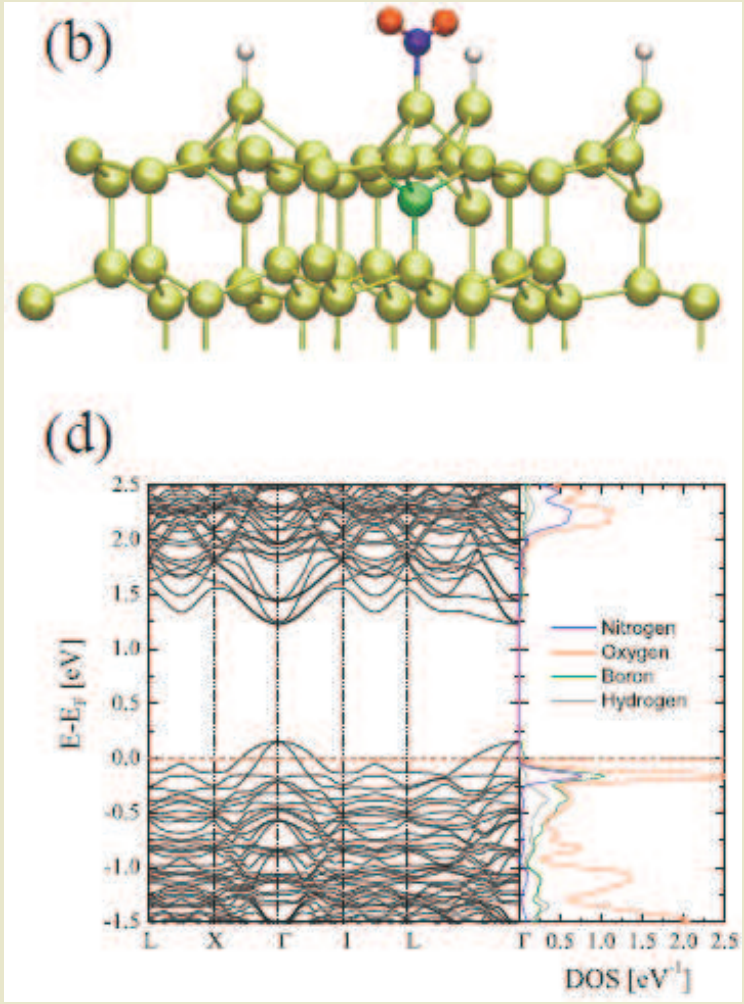
Miranda-Durán, Cartoixà *et al.*, *Nano Lett.* **10**, 3590 (2010)

Also see poster 89!!

NO_2 on SiNWs

- NO_2 can reactivate a B-DB complex.

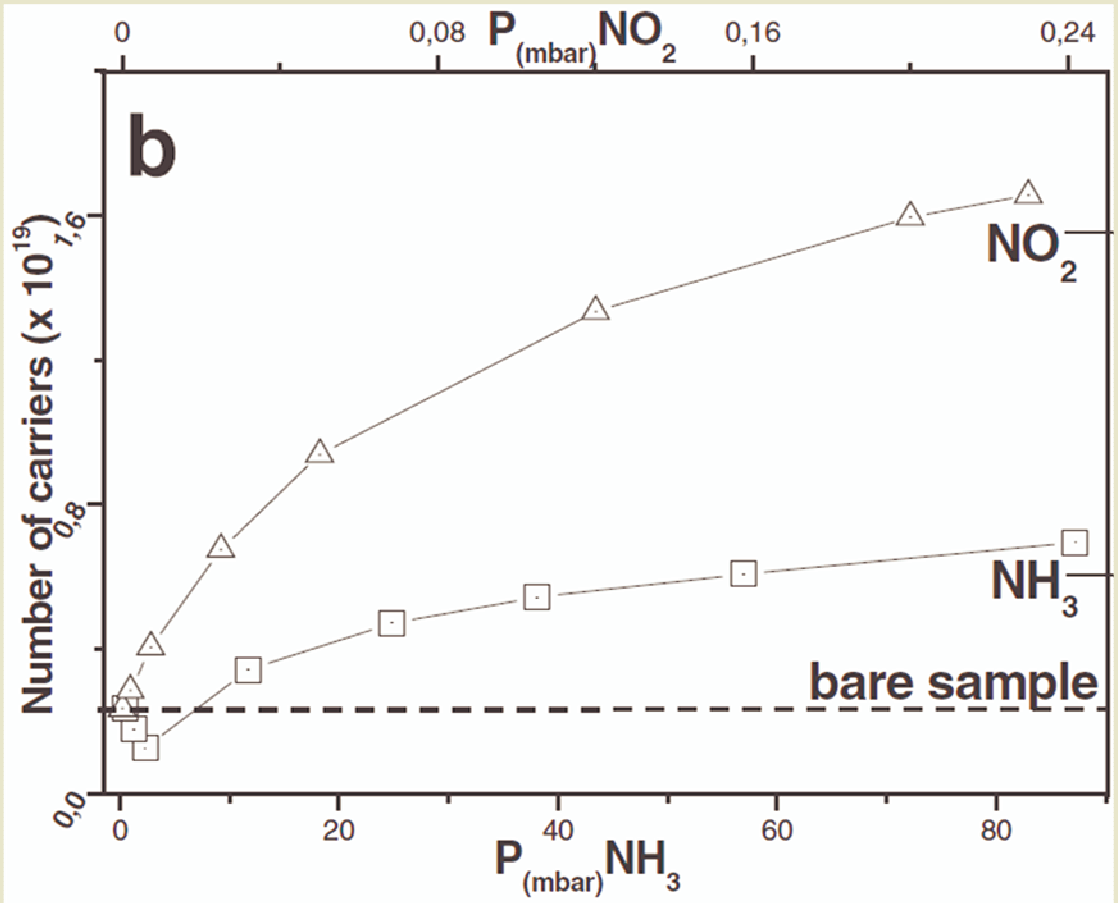


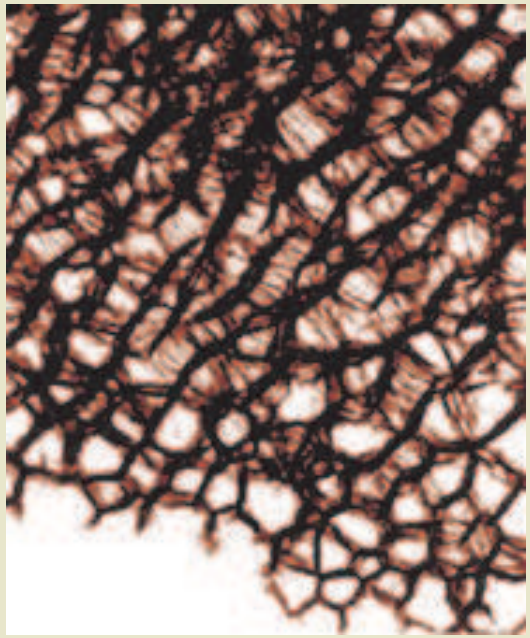


Miranda-Durán, Cartoixà *et al.*,
Nano Lett. **10**, 3590 (2010)

Experimental results in porous Si

- B stops etching
- Subsurface B are more frequent than inner B





Cullis and Canham, *Nature* **353**, 335 (1991)

Garrone *et al.*, *Adv. Mater.* **17** (5), 3590 (2005)

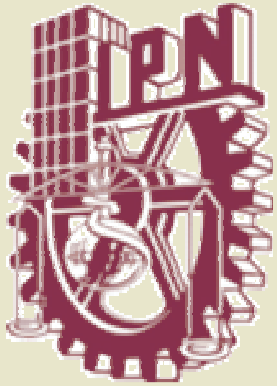
Conclusions

- Substitutional impurities traditionally used for semiconductor doping have too high activation energies to be effective for ultrathin nanowires.
- Molecular adsorption can be a viable alternative to substitutional doping in thin NWs.
- The conductivity behavior of mesoporous Si under the presence of NO_2 and NH_3 has been explained.

Collaborators

- ICMAB:
  - Dr. Enric Canadell

- Instituto Politécnico Nacional (México)
  - Prof. Miguel Cruz-Irisson



- Università di Roma "Tor Vergata"
  - Dr. Maurizia Palummo

- MICINN, TEC2009-06986

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THANK YOU FOR YOUR ATTENTION