# Polarization Doping of Silicon Nanowire Arrays by Molecular Grafting: Impact on Thermoelectric Properties

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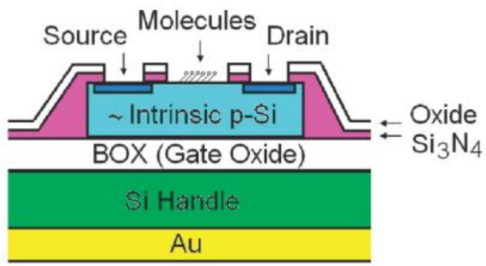
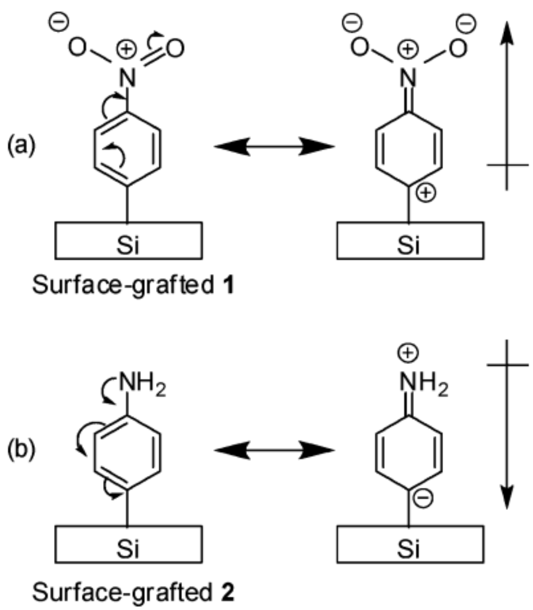
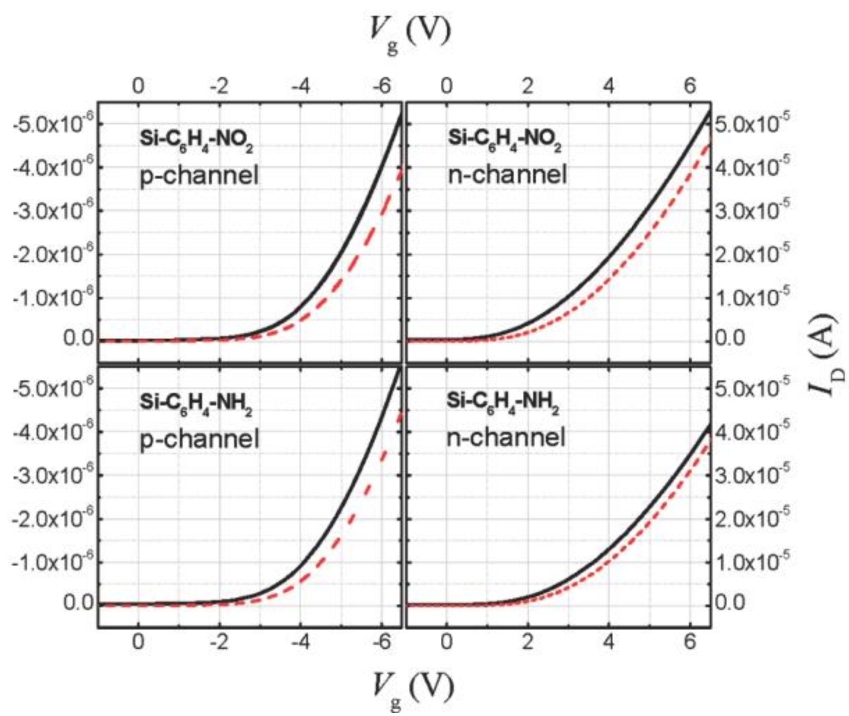
# Outline

- Polarization-induced doping and thermoelectric applications
- The experiment:
    - Redundant SiNW Arrays
    - Molecular Grafting onto SiNW
    - I-V characteristics: experimental
- I-V modeling
- Power factor enhancement

# Polarization-induced doping of thin films




al. et J.M. Tour, JACS, 131, 10023

# Prospects for thermoelectric applications

$$\mu_{\mathrm{BH}} = \frac{128\sqrt{2\pi / m^*}\,\epsilon^2 (k_B T)^{3/2}}{N Z^2 e^3} \times \left( \log \frac{24 m^* \epsilon (k_B T)^2}{n e^2 \hbar^2} \right)^{-1}$$

$$\alpha = \frac{8\pi^2 k_B{}^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3}$$

$$\frac{1}{\mu} = \frac{1}{\mu_{\mathrm{ii}}} + \frac{1}{\mu_{\mathrm{ni}}} + \frac{1}{\mu_{\mathrm{GB}}} + \frac{1}{\mu_{\text{e-ph}}}$$

→ $\mu \approx \mu_{\mathrm{ii}} \propto \frac{1}{N} \left[ = \frac{1}{n} \text{ at high doping levels} \right]$

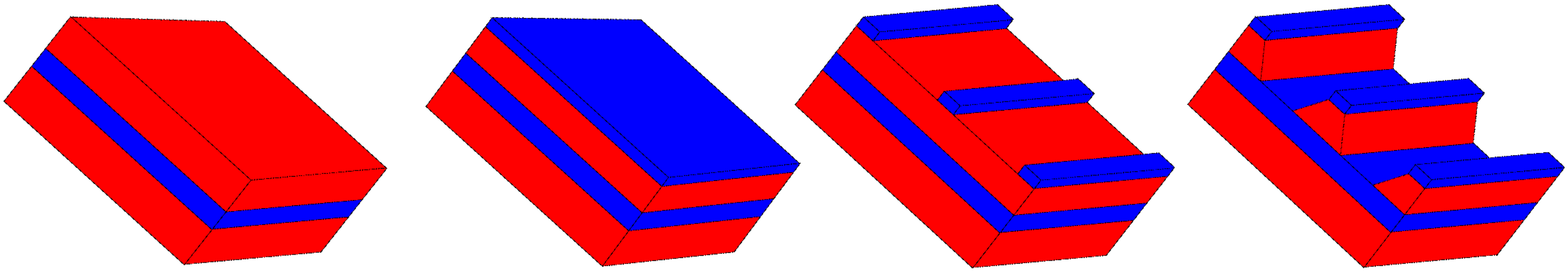
→ $\mu \approx \mu_{\text{e-ph}}$ at low doping levels

For i.i.-limited mobility $\sigma = e\mu n \approx$ const. so that PF=$\sigma\alpha^2 \propto n^{-4/3}$

For ph-limited mobility $\sigma = e\mu n \propto \mu_{\mathrm{L}} n$ so that PF=$\sigma\alpha^2 \propto n^{-1/3}$

Forcing high *n* by polarization-driven enhancement may lead to higher PF’s

# Top-down SiNW fabrication process



**Wafer SOI**
**110 nm, 260 nm or 340 nm**
**Si top layer**
**400 nm buried $SiO_2$ layer**

→

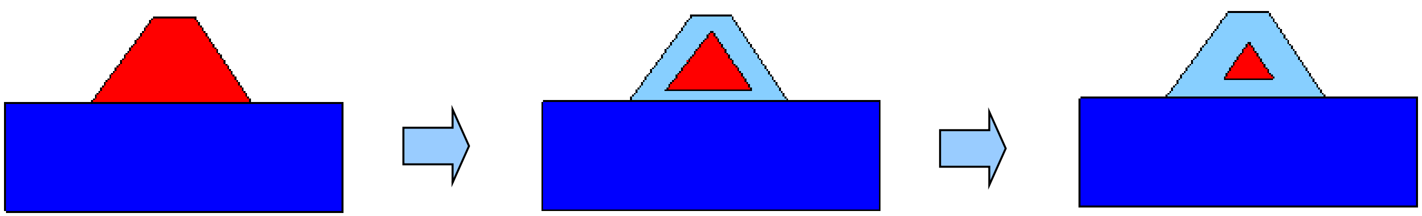
**Silicon dioxide layer**
**50 nm tick**
**dry thermal oxidation**

→

**E-beam lithography**
**standard PMMA resist**
**$SiO_2$ wet etch**

→

**Anisotropic (KOH)**
**etch: trapezoidal**
**cross section**

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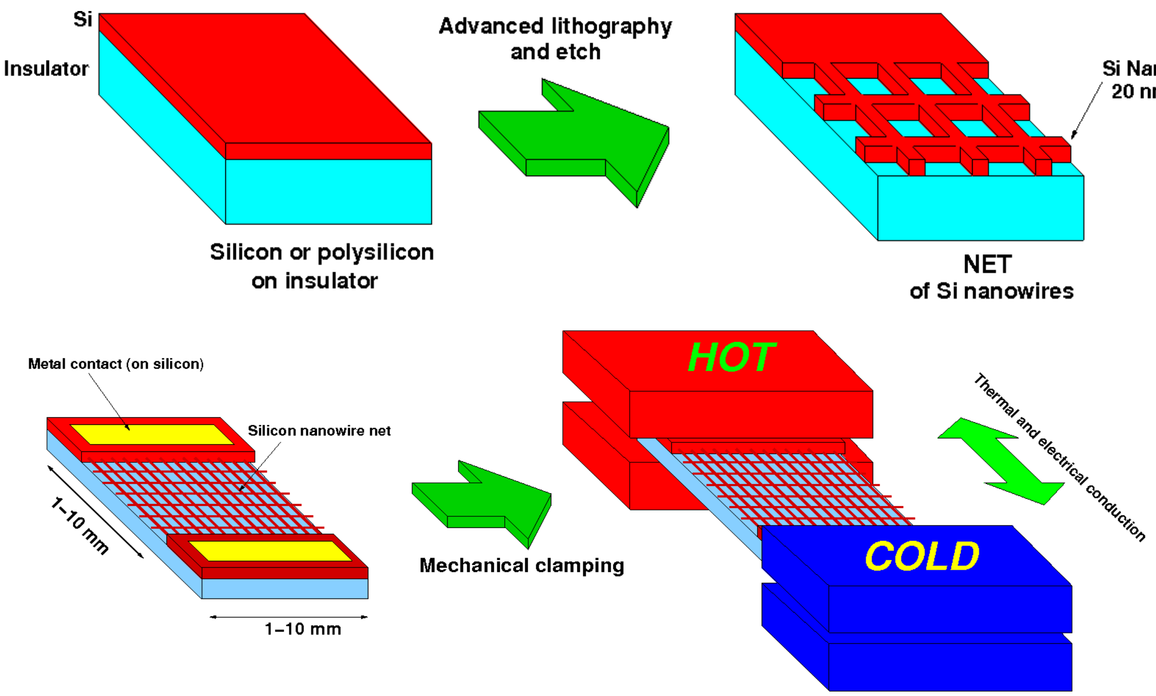
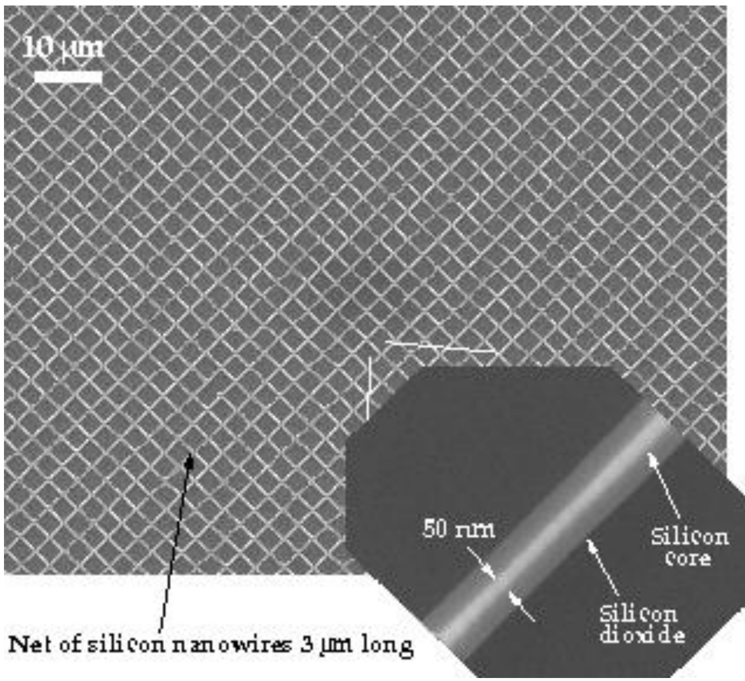
G. Pennelli, B. Pellegrini, JAP, 101, 104502 (2007)
G. Pennelli, Microel. Eng. 86, 2139 (2009)
G. Pennelli, et al,, Nano Letters, 13, 2592 (2013)
M. Ferri et al., Microelectron. Eng., 88(6), 877-881 (2011)
G F Cerofolini et al., Semicond. Sci. Techn., 25(9), 095011 (2010)
F. Suriano et al., MRS Proc., 1408, mrsf11-1408-bb11-04 (2012)

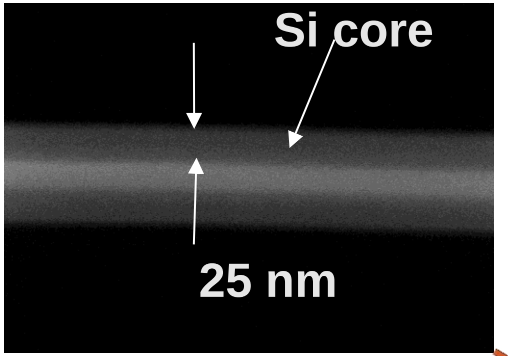
# Nanowire Arrays

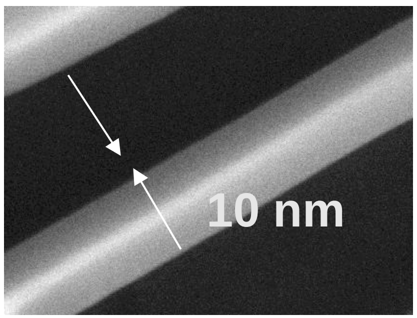


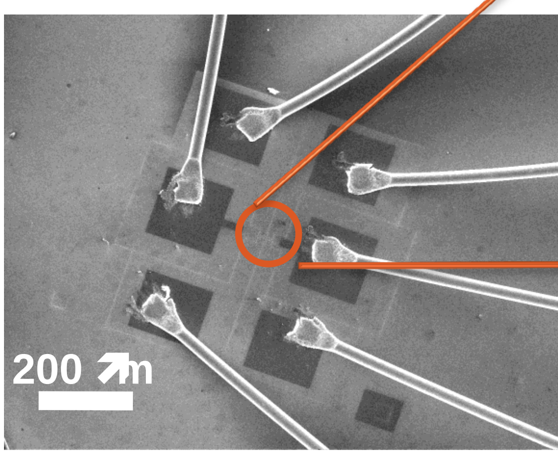



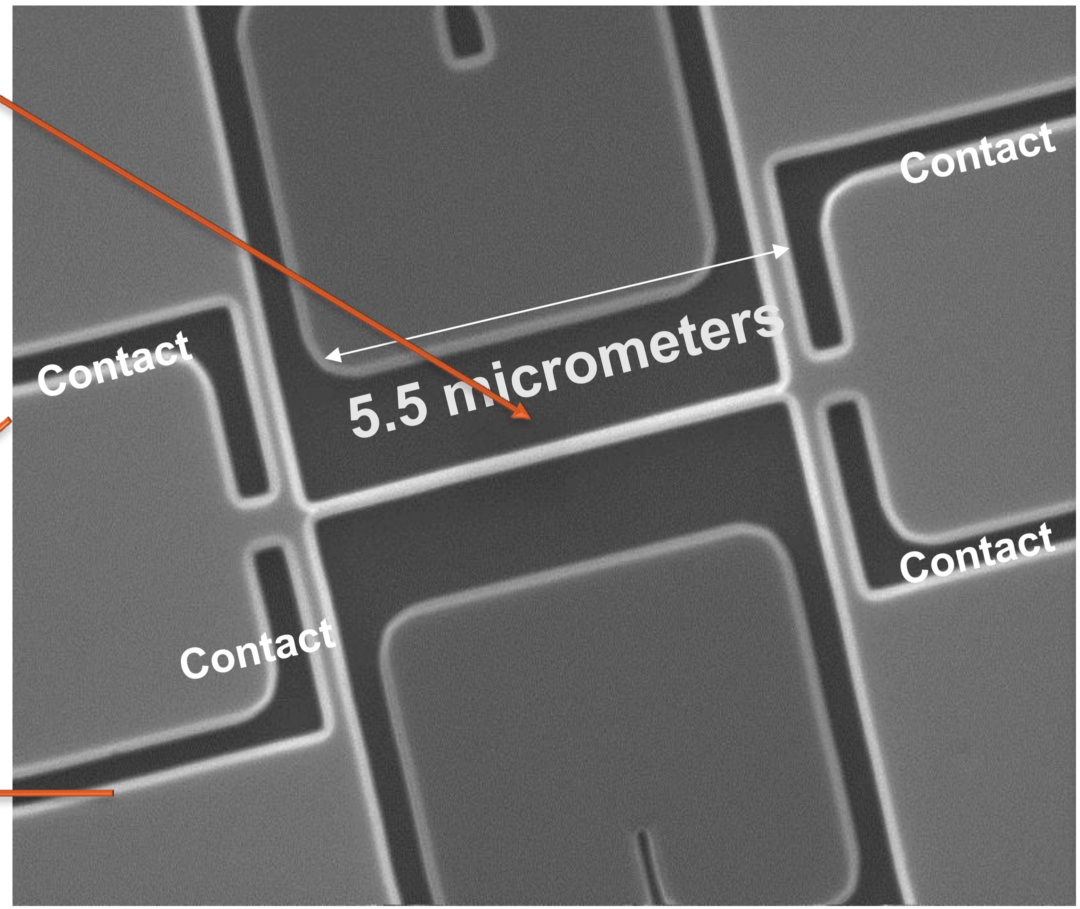

- 290×190 3-µm long SiNWs, 50 nm wide, electrically equivalent to 190 SiNWs in parallel, 1 mm long each.
- High redundancy ($10^5$ SiNW/$mm^2$)

# Nanowire Arrays



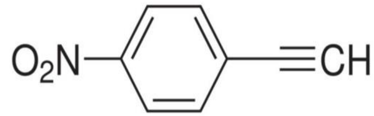



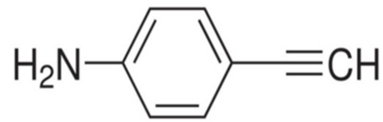



# Molecular Grafting

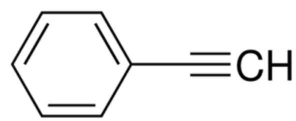
1-ethynyl-4-nitrobenzene (ENOB) ⇨ p-type doping




4-ethynylaniline (EA) ⇨ n-type doping



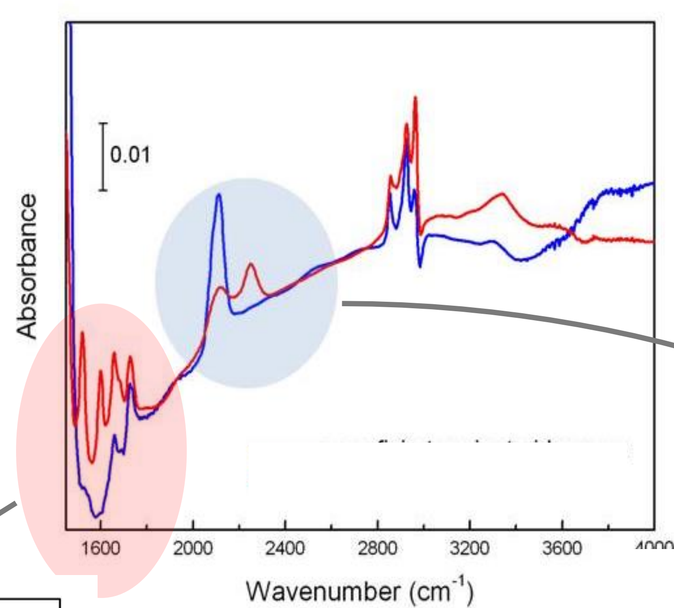

phenylacetylene (PA) ⇨ neutral



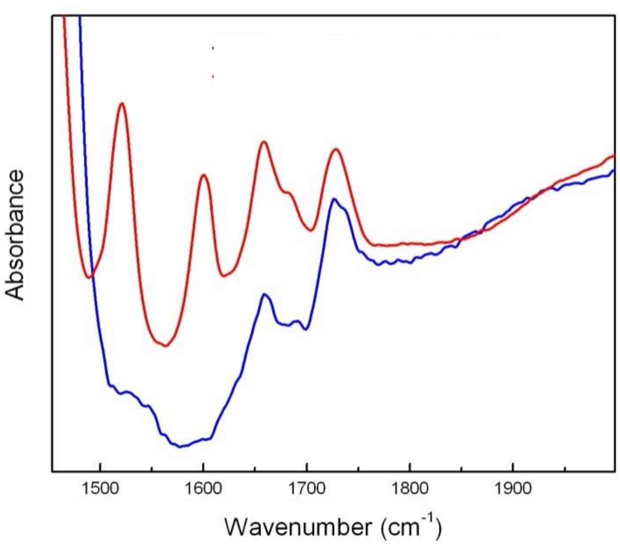

130 °C, 15 hours in mesitylene

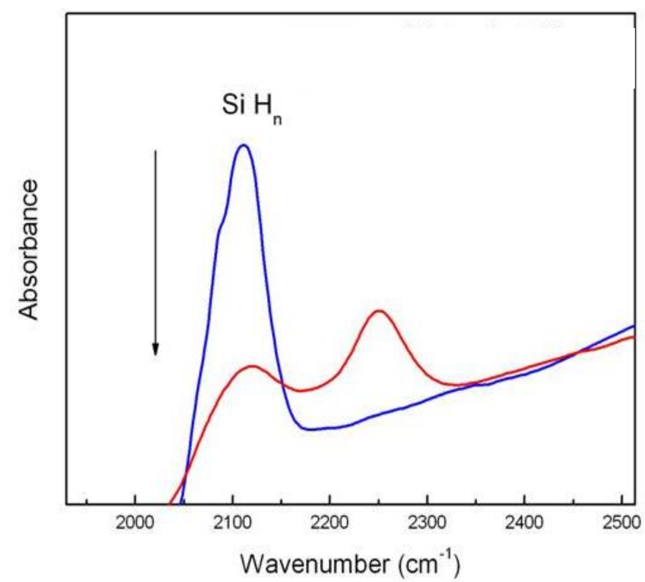
# ENOB Molecular Grafting

Benzene ring and $NO_2$ markers




Surface Si-H signal

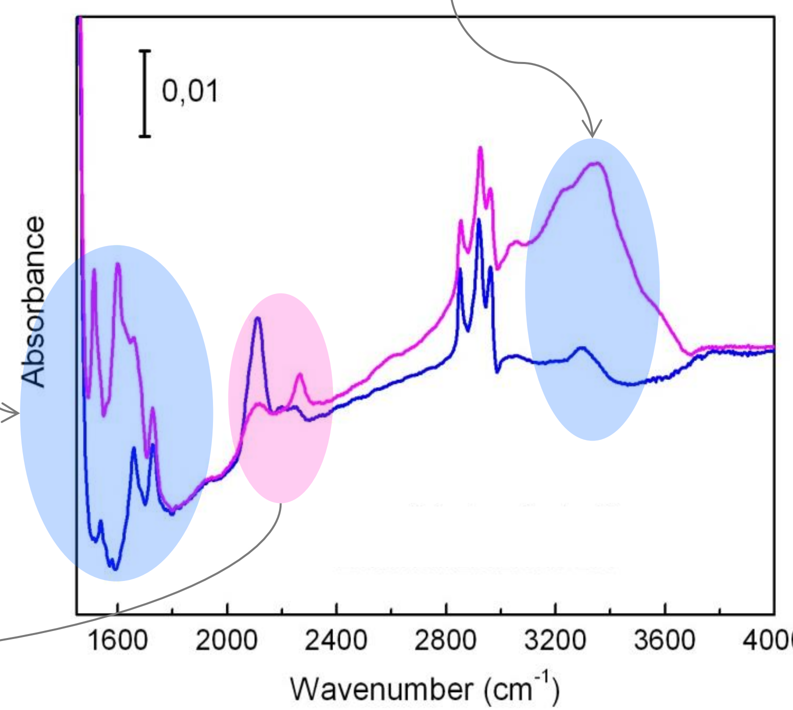


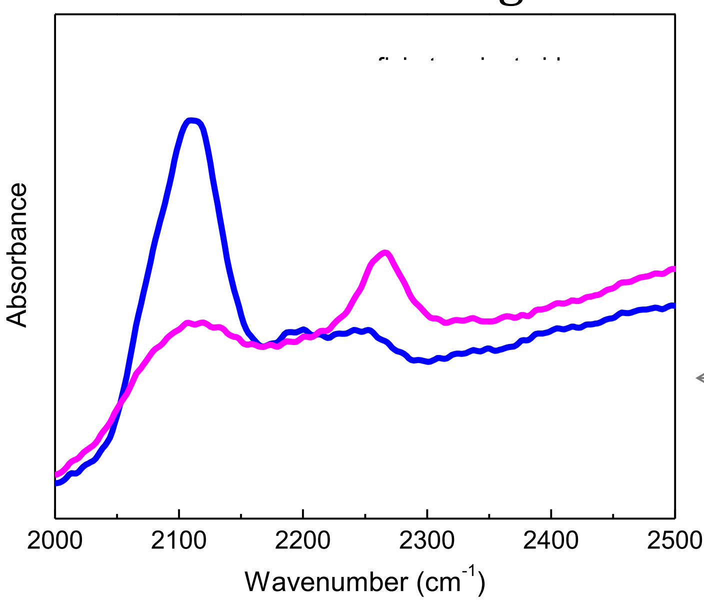
# EA Molecular Grafting

E. Romano et al., Surf. Interf. Anal. 2010, 42, 1321
G.F. Cerofolini et al. in Dekker Encyclopedia of Nanoscience & Nanotechnology, 1:1,4009, (2009)

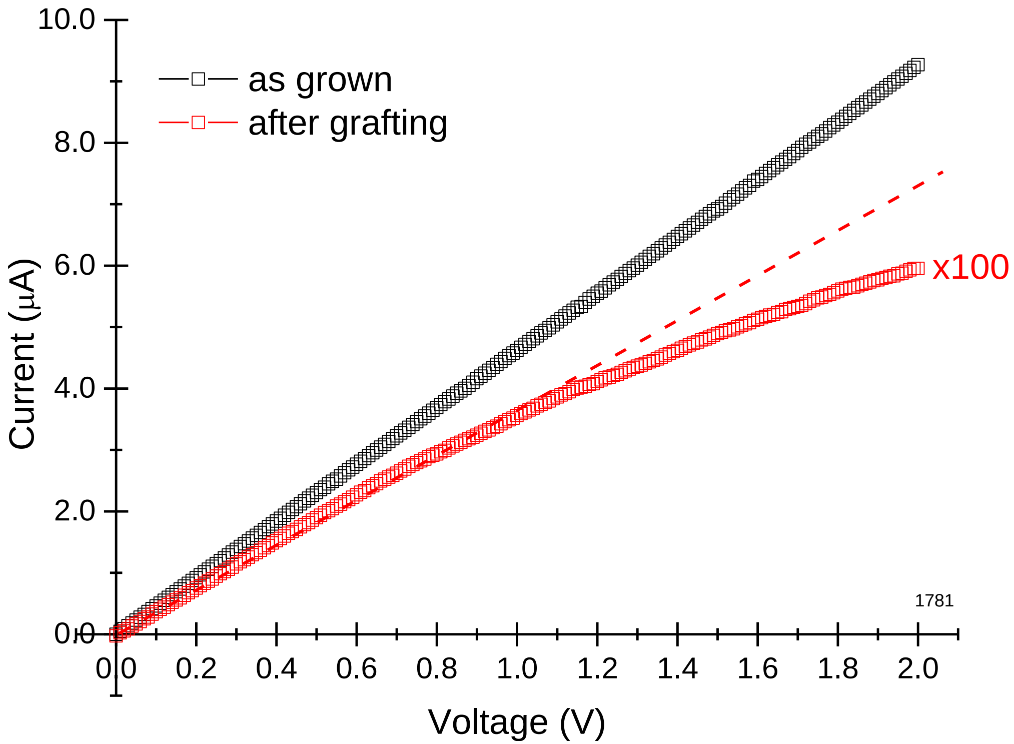
Markers of the aromatic ring and of the *p*-$NH_2$ group




Surface Si-H signal

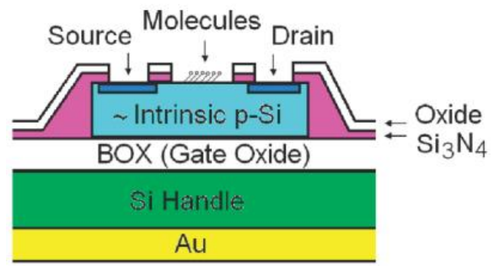


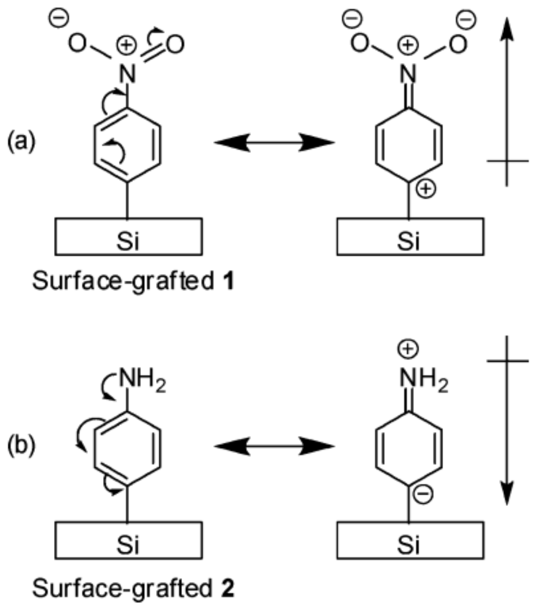
# Current-Voltage Characteristics

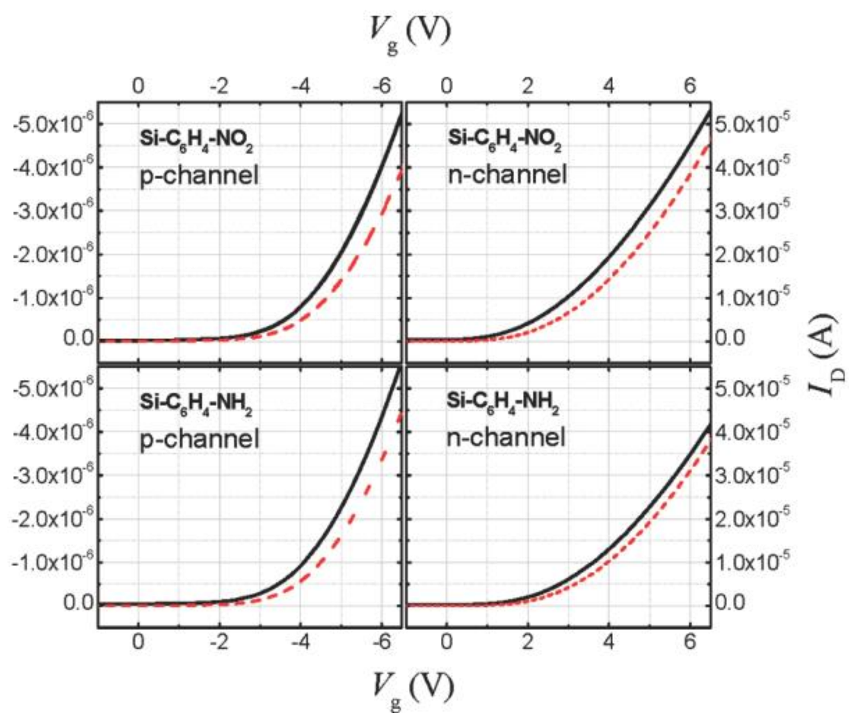



- Grafting causes a decrease of the NW conductance
- This happens independently of the type of grafted molecule/type of NW doping (cf. Tour)

# Polarization-induced doping in thin films

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# Modeling the electrical response

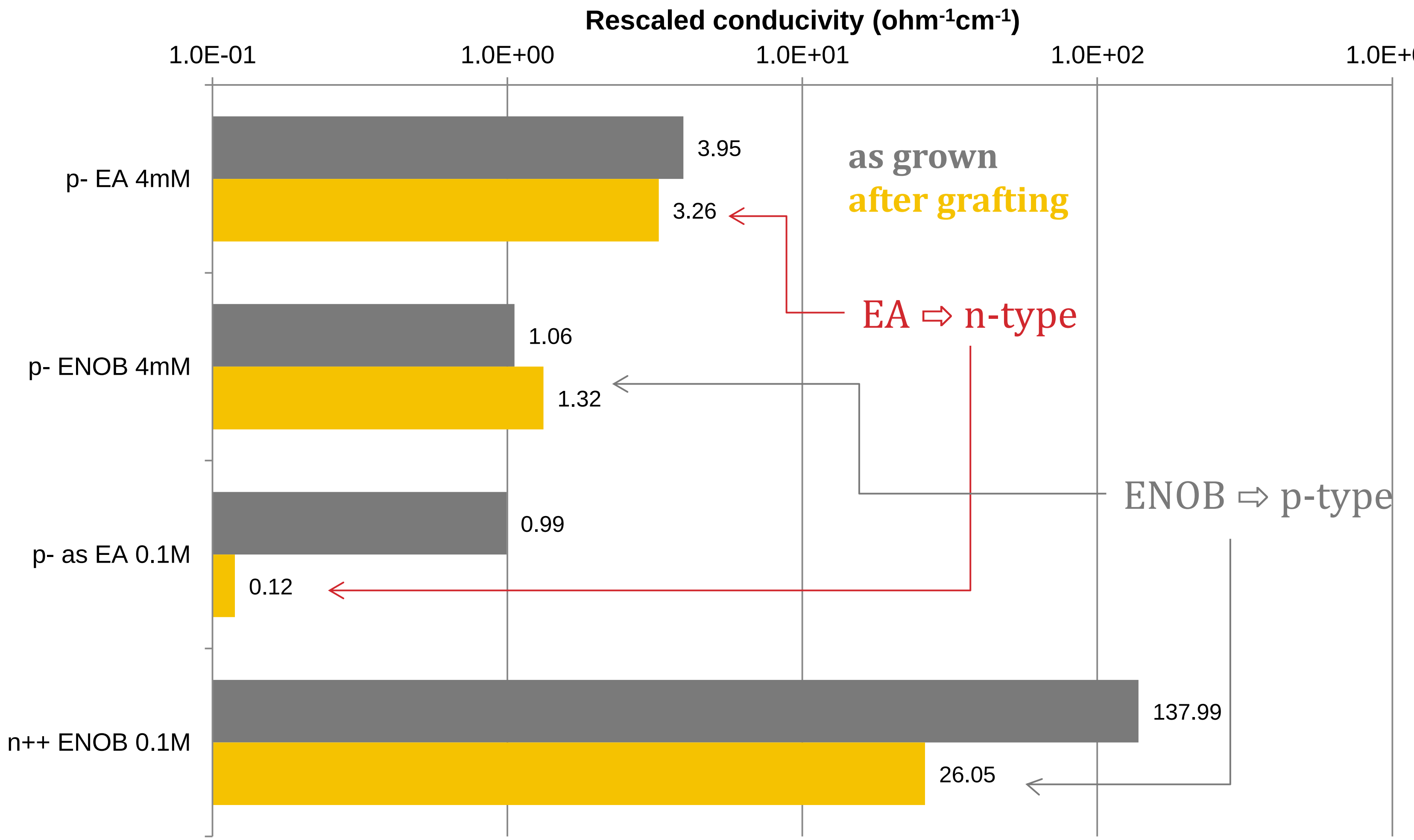
- Grafting shifts $E_f$ at the NW surface but also introduces surface trap states that decrease $\mu$
- Trap injection dominated by the coupling with the aromatic ring
- Their effect may be approximately accounted for by comparing conductivity changes in PA-grafted NWs:

$$\sigma_{\text{a-g}} = q\mu_{\text{a-g}} n_{\text{a-g}}$$

$$\sigma_{\text{PA}} = q\mu_{\text{t}} n_{\text{PA}} = q\mu_{\text{t}} n_{\text{a-g}}$$

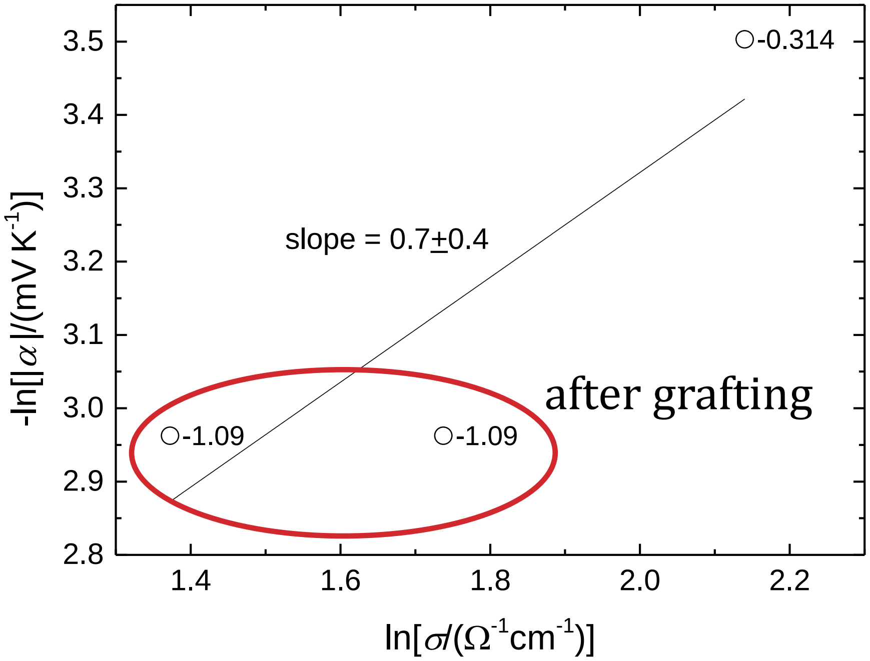
$$\sigma_{\text{EA/ENOB}} = q\mu_{\text{t}} n_{\text{EA/ENOB}}$$

# Rescaled conductivity



# Seebeck coefficients & Power factors

$$\alpha = \frac{8\pi^2 k_B{}^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3}$$




In spite of the mobility reduction, power factors are found to increase from 1.2 mW $m^{-1}K^{-2}$ (as grown) up to 6.5 mW $m^{-1}K^{-2}$(after grafting and BHF)

# Summary and conclusions

- Polarization-induced doping of NWs modulates both their conductivity and their Seebeck coefficient
- Grafting also introduces surface trap states that decrease the carrier mobility
- Rescaled conductivity reports the expected trend of $\sigma$ vs. molecular dipole orientation
- In highly doped NWs the conductivity modulation is smaller, still positively affecting the PF

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