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

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

\[ \alpha = \frac{8 \pi^2 k_B^2}{3 e h^2} m^* T \left( \frac{\pi}{3 n} \right)^{2/3} \]

\[ \frac{1}{\mu} = \frac{1}{\mu_{ii}} + \frac{1}{\mu_{ni}} + \frac{1}{\mu_{GB}} + \frac{1}{\mu_{e-ph}} \]

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

\[ \mu \approx \mu_{e-ph} \text{ at low doping levels} \]

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

For ph-limited mobility \( \sigma = e \mu n \propto \mu_L n \) 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, M. Piotto, JAP 100, 054507 (2006)
G. Pennelli, B. Pellegrini, JAP, 101, 104502 (2007)
G. Pennelli, Microel. Eng. 86, 2139 (2009)

• 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/mm²)
Nanowire Arrays

- Si core
- 25 nm
- 10 nm
- 5.5 micrometers
- 200 μm
Molecular Grafting

1-ethynyl-4-nitrobenzene (ENOB) $\Leftrightarrow$ p-type doping

\[ \text{O}_2\text{N}-\text{CH} = \text{CH} \]

4-ethynylaniline (EA) $\Leftrightarrow$ n-type doping

\[ \text{H}_2\text{N}-\text{CH} = \text{CH} \]

phenylacetylene (PA) $\Leftrightarrow$ neutral

\[ \text{CH} = \text{CH} \]

130 °C, 15 hours in mesitylene
ENOB Molecular Grafting

Benzene ring and NO$_2$ markers

Surface Si-H signal
EA Molecular Grafting

Markers of the aromatic ring and of the $p$-NH$_2$ group

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)
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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:

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

$$\sigma_{PA} = q\mu_t n_{PA} = q\mu_t n_{a-g}$$

$$\sigma_{EA/ENOB} = q\mu_t n_{EA/ENOB}$$
Rescaled conductivity

- p- EA 4mM: 3.95 as grown, 3.26 after grafting
- p- ENOB 4mM: 1.06
- p- as EA 0.1M: 0.99
- n++ ENOB 0.1M: 137.99

EA ⇨ n-type
ENOB ⇨ p-type

as grown after grafting
Seebeck coefficients & Power factors

\[ \alpha = \frac{8\pi^2 k_B^2}{3e\hbar^2} m^*T\left(\frac{\pi}{3n}\right)^{2/3} \]

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.
This work was supported by FP7-NMP-2013-SMALL-7, SiNERGY (Silicon Friendly Materials and Device Solutions for Microenergy Applications) Project, Contract n. 604169.