Программа Фонда Дмитрия Зимина «Династия»
„Краткосрочные визиты иностранных ученых в Россию“

Wet Chemically Etched Silicon Nanowires: A Key Component in New Generation of Energy Devices

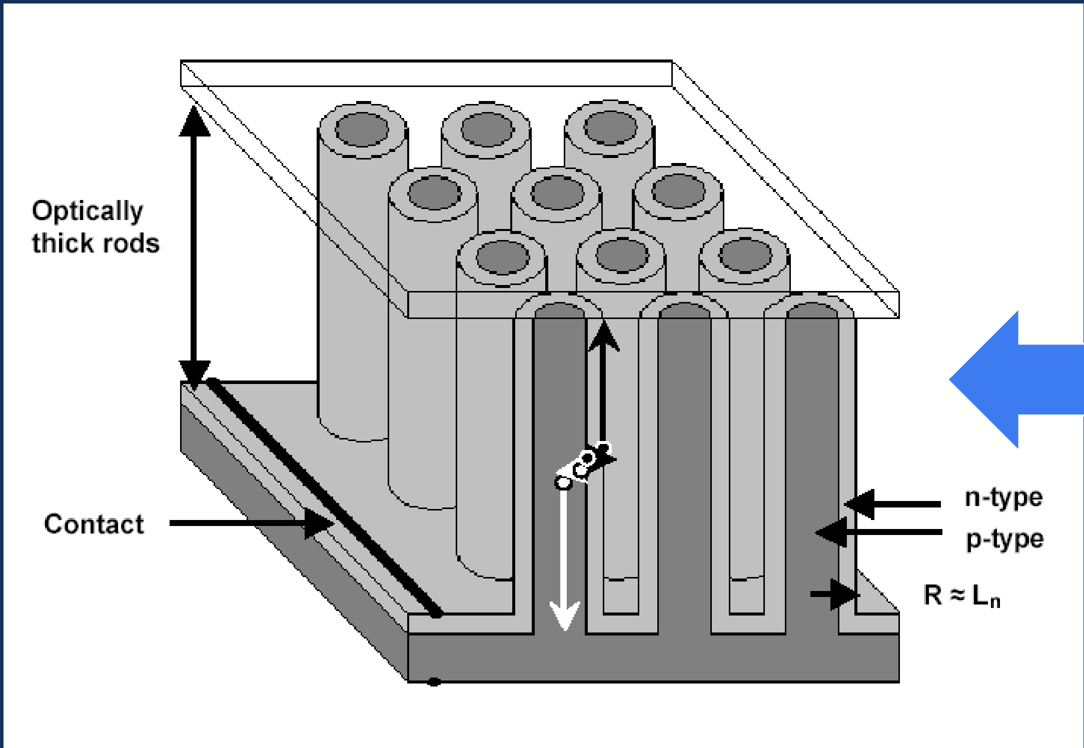
Vladimir Sivakov

Leibniz Institute of Photonic Technology, Jena/Germany

Outline

1. Top-down *vs* Bottom-up
2. 3 Keys for Novel Photovoltaic Devices
3. Photovoltaic Concepts Based on SiNWs
4. Solar Hydrogen

VISION

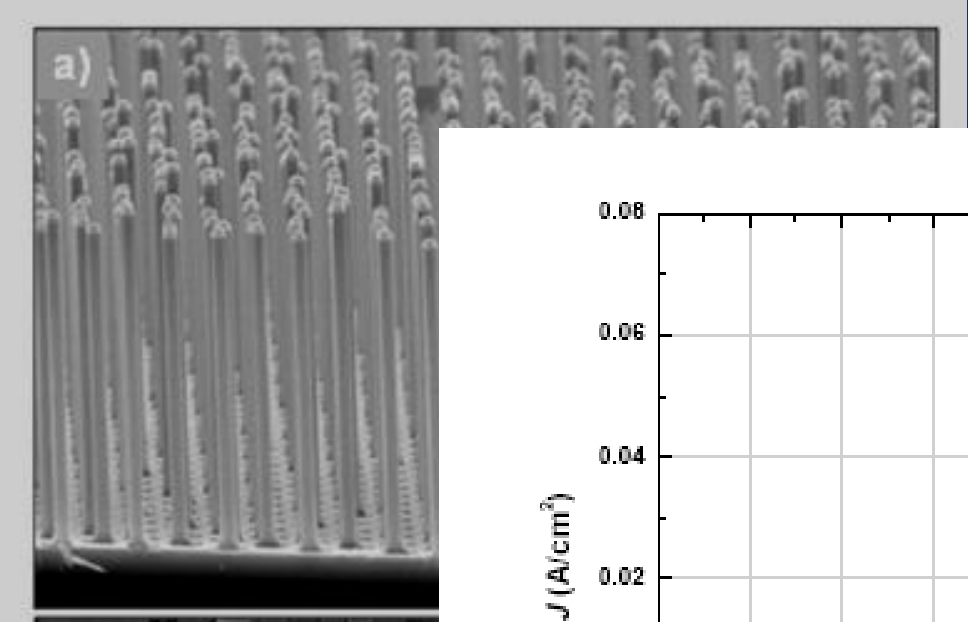


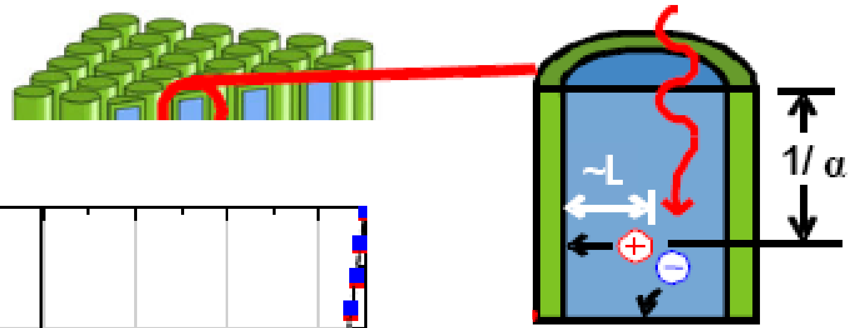
Si Nanowires: η=15-20%

mc-Si thin film: η=6-10%

B.M. Kayes, H.A. Atwater, N.S. Lewis, J. Appl. Phys. 97, 114302 (2005); B.M. Kayes, M.A. Filler,M.C. Putnam, M.D. Kelzenberg, N.S. Lewis, H.A. Atwater, Appl. Phys. Lett. 91, 103110 (2007); L. Tsakalakos, J. Balch, J. Fronheiser, B. A. Korevaar, O. Sulima, J. Rand, Appl. Phys. Lett. 91, 233117 (2007); M.D. Kelzenberg, D.B. Turner-Evans, B.M. Kayes, M.A. Filler, M.C. Putnam, N.S. Lewis, H.A. Atwater, Nano Lett. 8, 710 (2008)

Solar Cell Based on SiNWs





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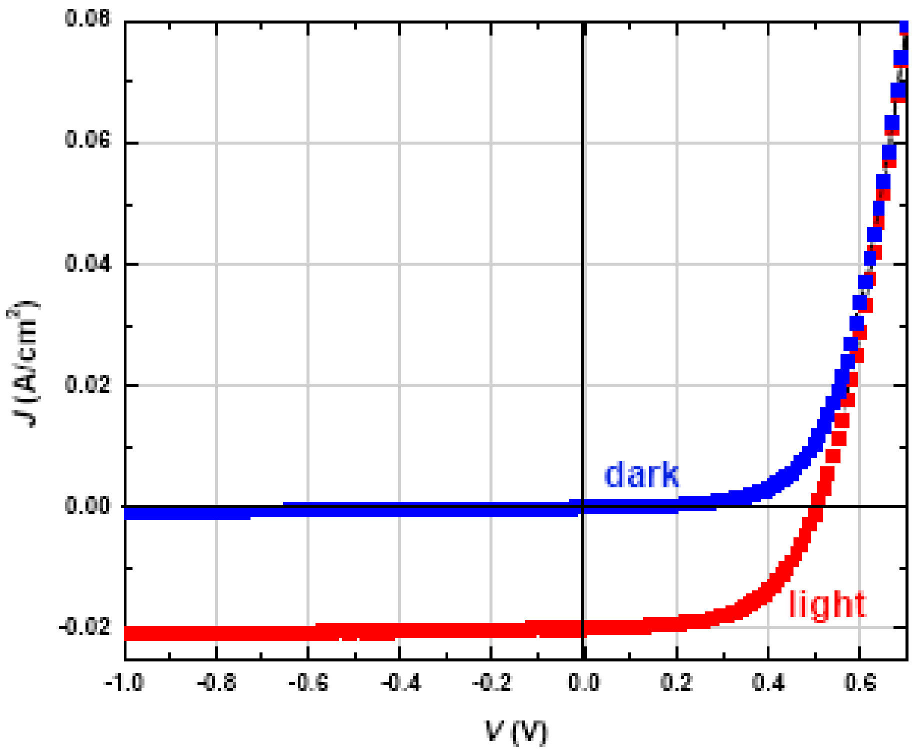
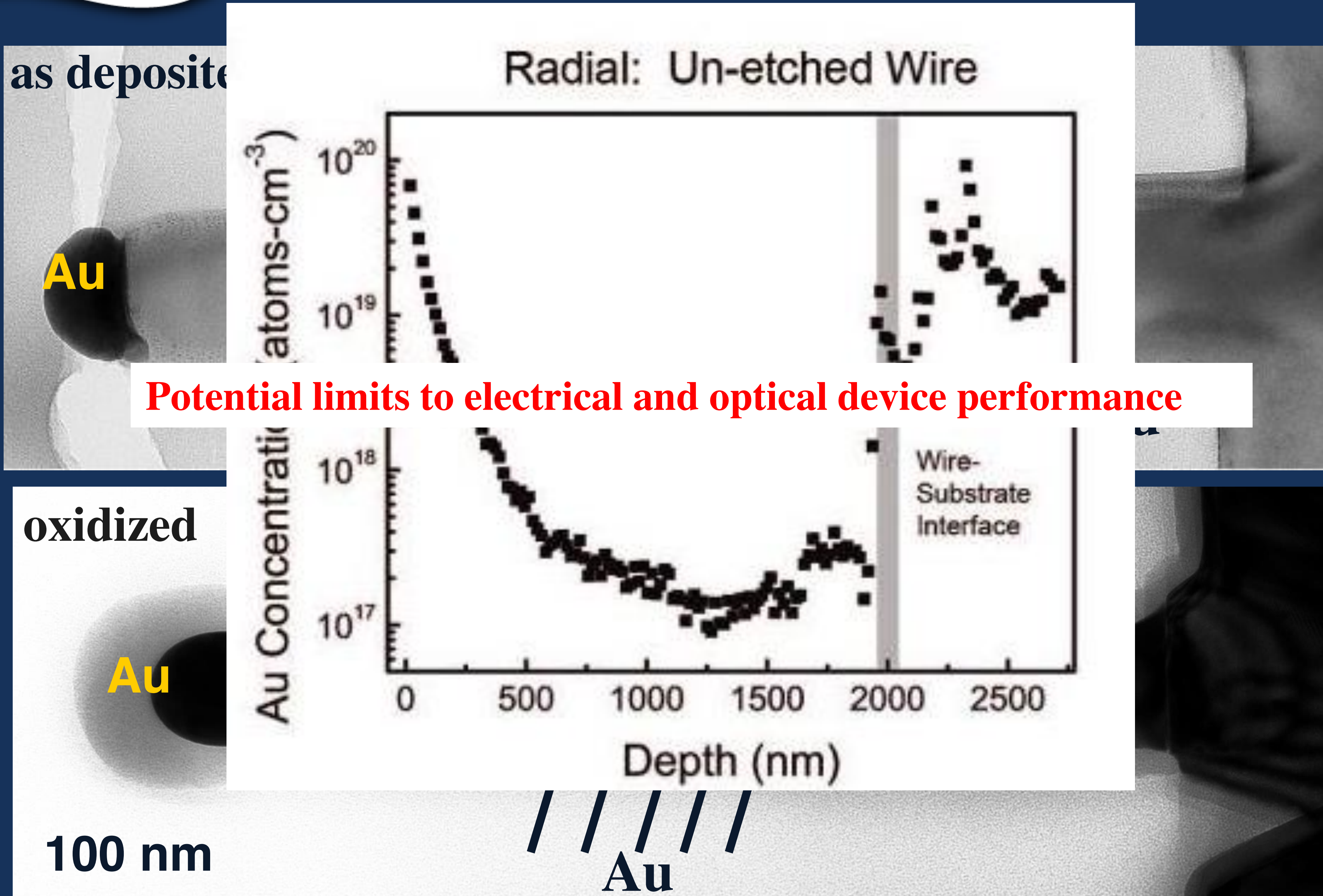


Fig. 4. *J-V* curve for measured 5 μm-diameter wire array. Efficiency = 5.7%, V_{oc} = 505 mV, J_{sc} = 19.7 mA/cm^2, *FF* = 57.7 %, total cell area 12.9 mm^2, wire array area 4 mm^2.

M.D. Kelzenberg et al. , Nano Lett. 8, 710 (2008)

Problematic: Gold Contamination



Potential limits to electrical and optical device performance

M.C. Putmann et al. Nano Letters 8(10), 3109 (2008)

Motivation

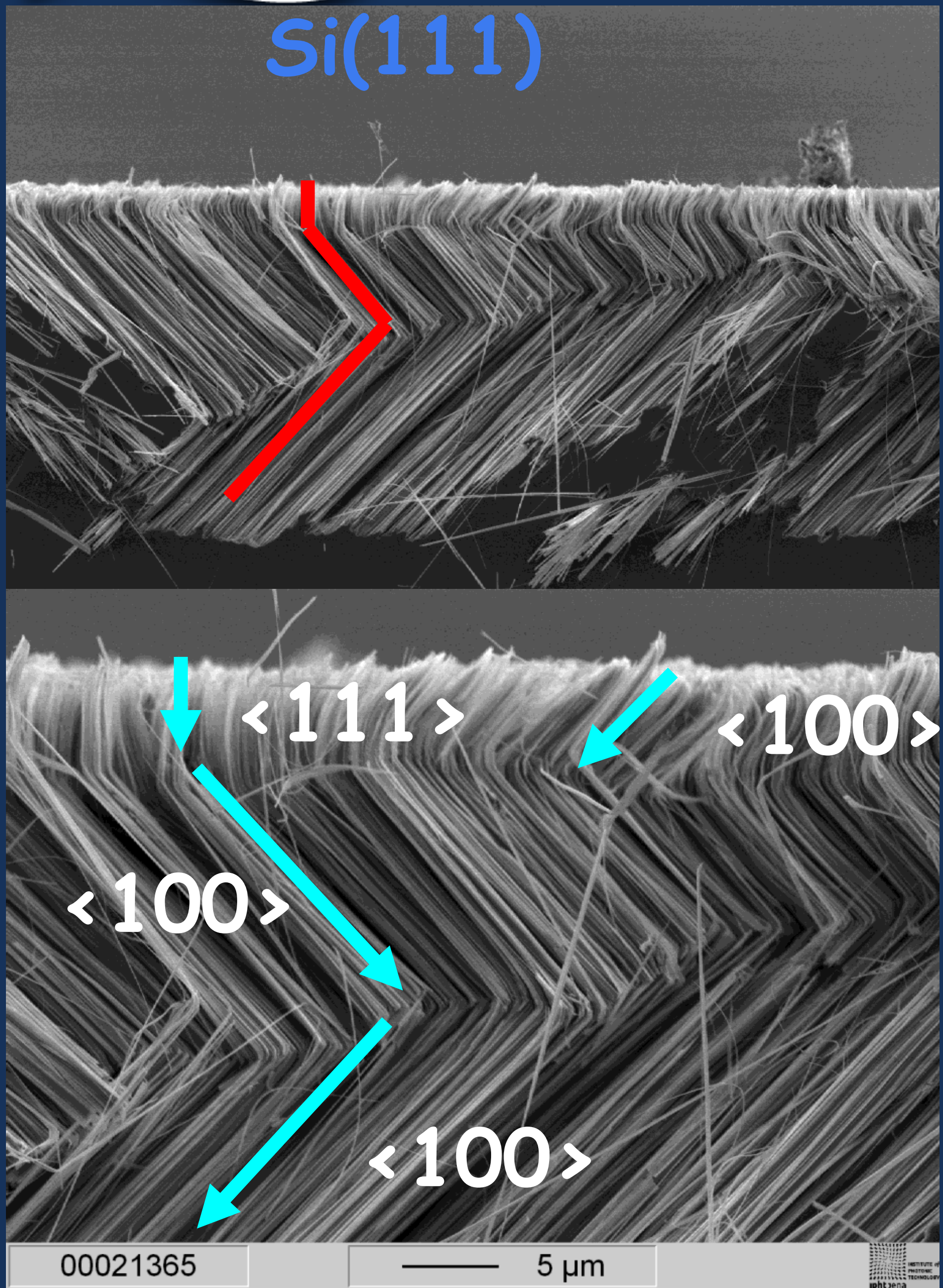
- ✓ Smart Material
- ✓ <u>Smart Technology</u>
- ▪ Smart Concept

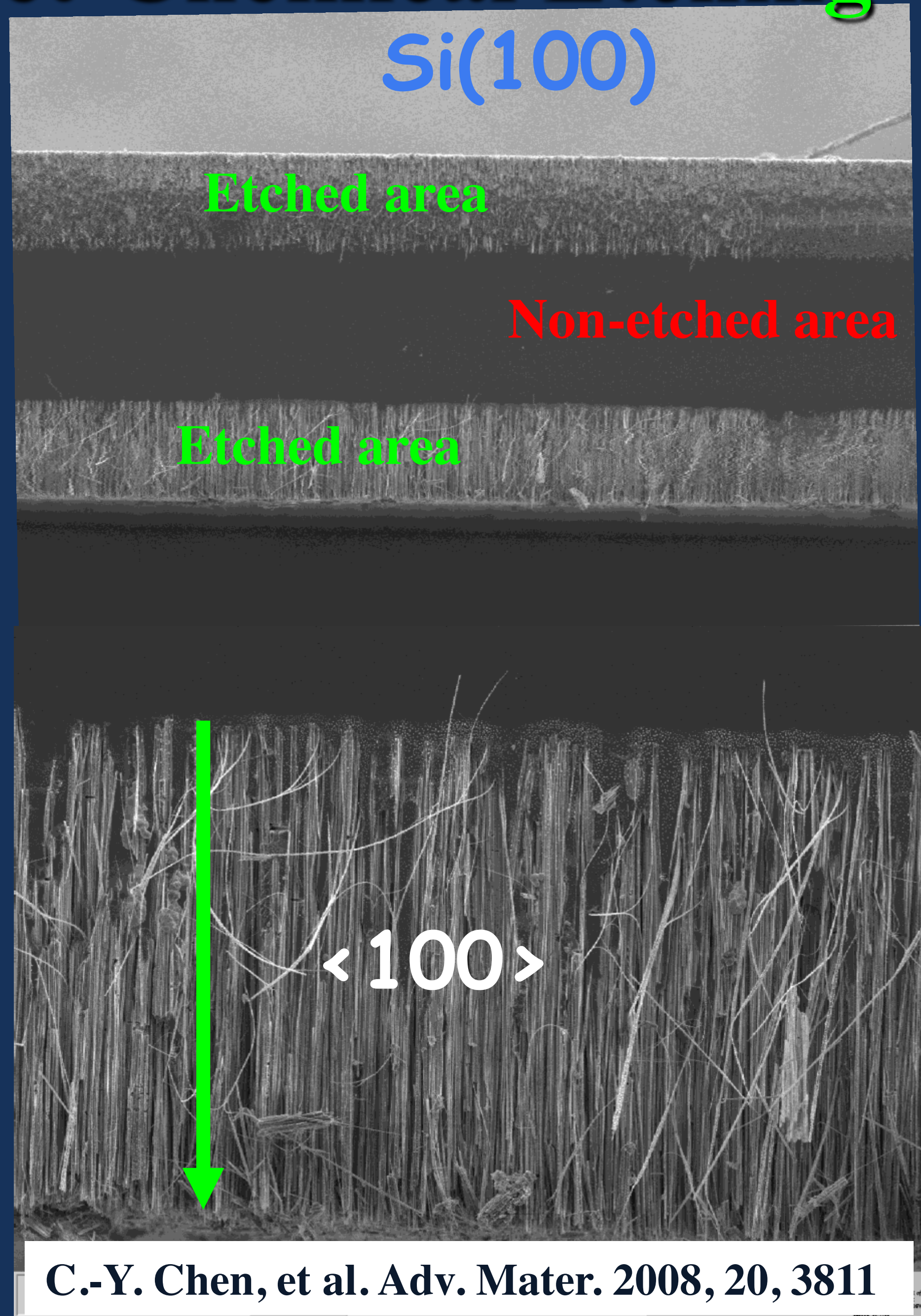
Top-down: Wet-Chemical Etching

V. A. Sivakov et al., J. Phys. Chem. C *114*, 3798–3803 (2010)

V. Sivakov et al., Intech "Nanowires - Fundamental Research", ISBN 978-953-307-327-9, p45 (2011)

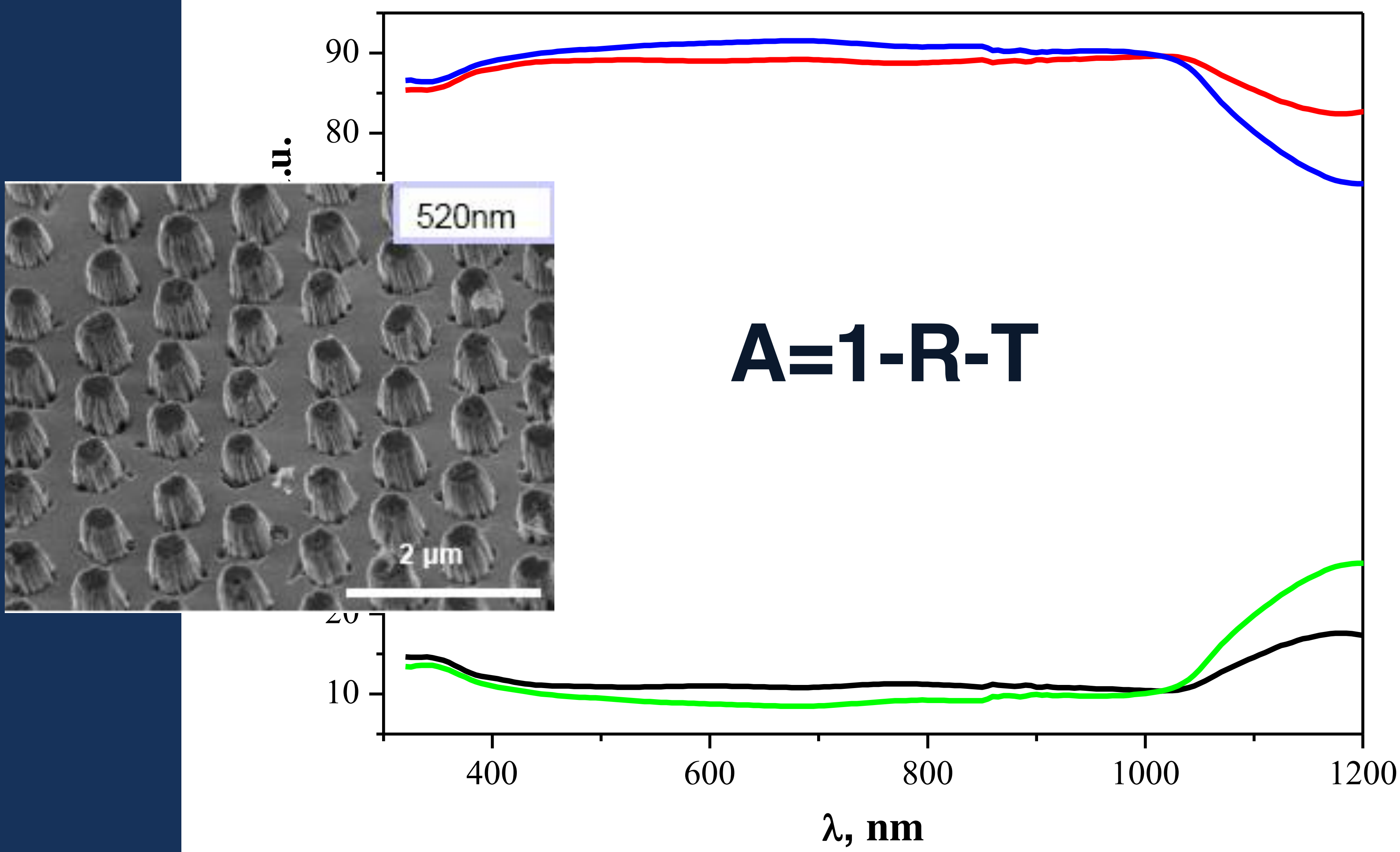
Top-down: Wet-Chemical Etching



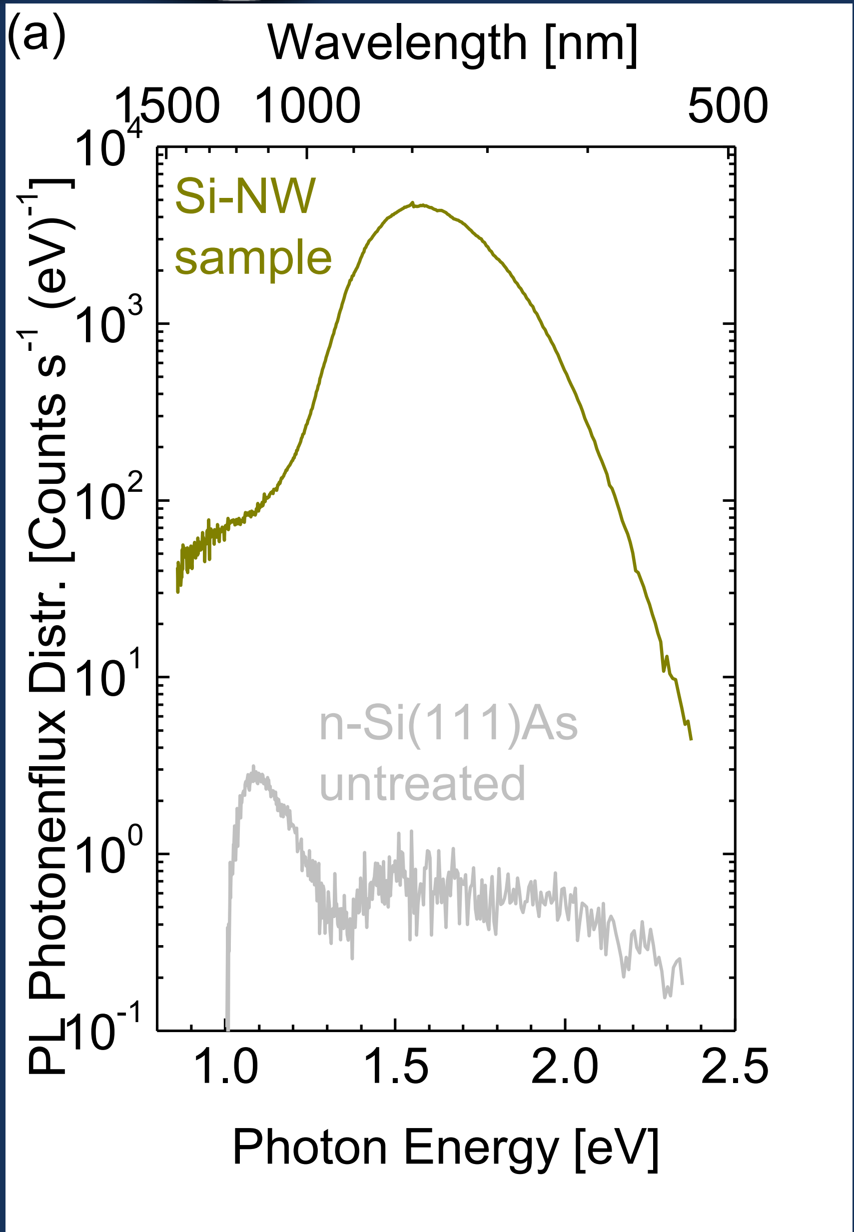


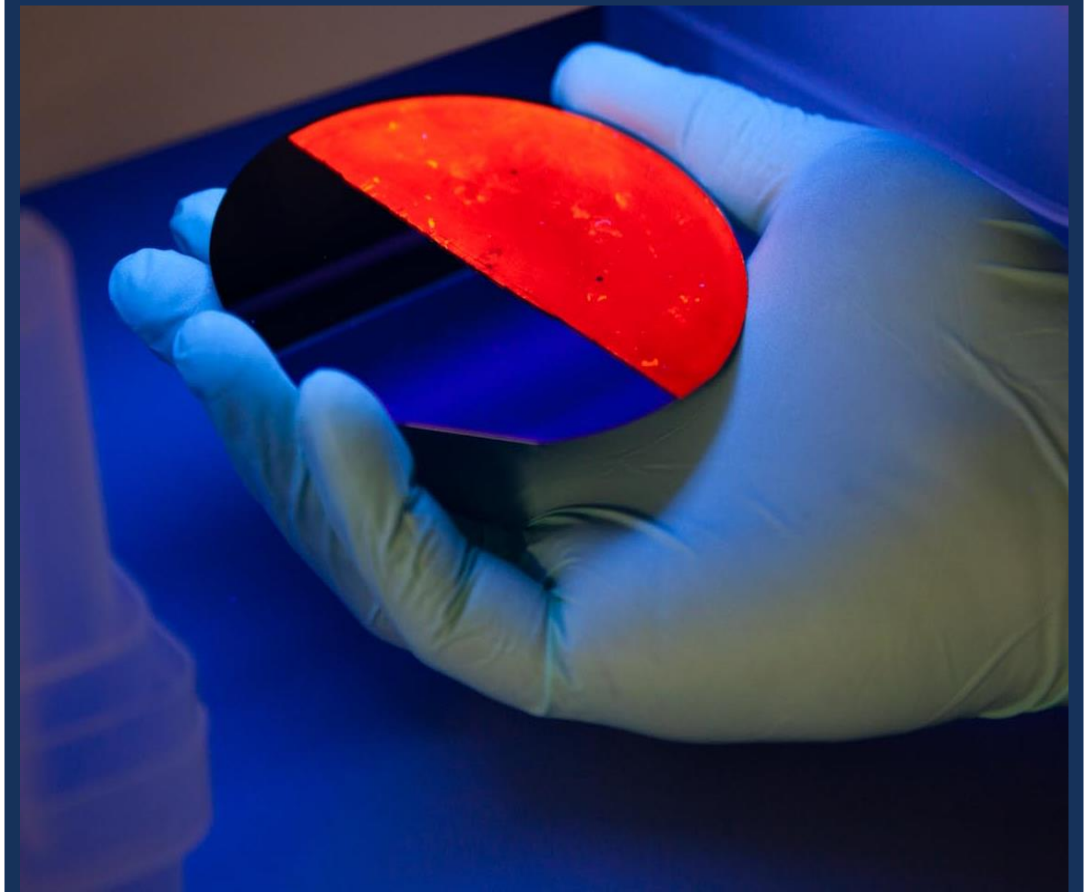
C.-Y. Chen, et al. Adv. Mater. 2008, 20, 3811

Top-down: Wet-Chemical Etching



Top-down: Wet-Chemical Etching





V. A. Sivakov et al. Phys. Rev. B 82, 125446(2010)

Motivation

- ✓ Smart Material
- ✓ Smart Technology
- ▪ Smart Concept

ALD Technology

Smart technology

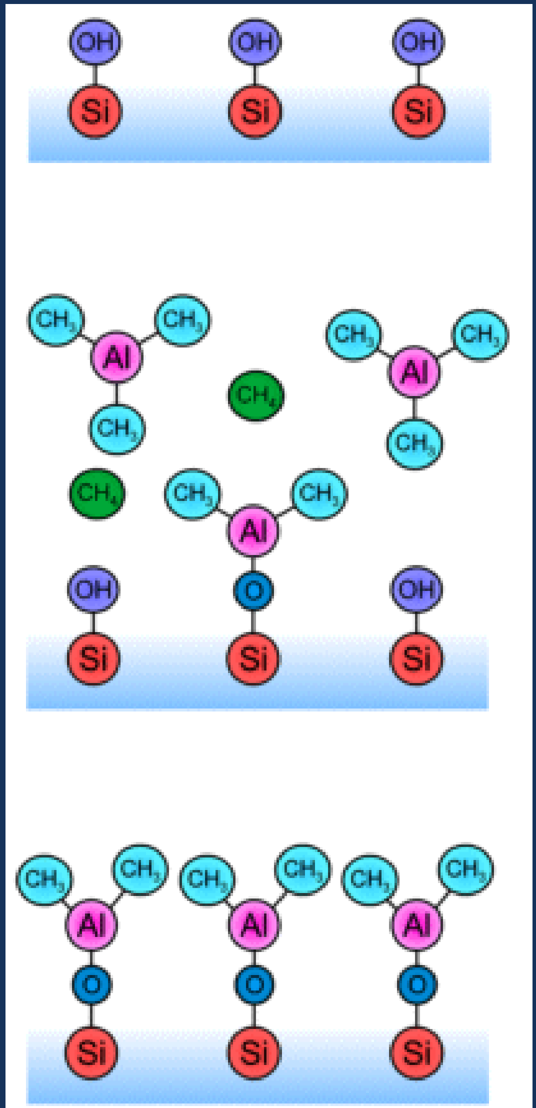
1. Component 1(TMA, $Al(CH_3)_3$)
2. Purge (Ar)
3. Oxidant: H_2O / Plasma: O_2
4. Purge (Ar)

Cycle

1)

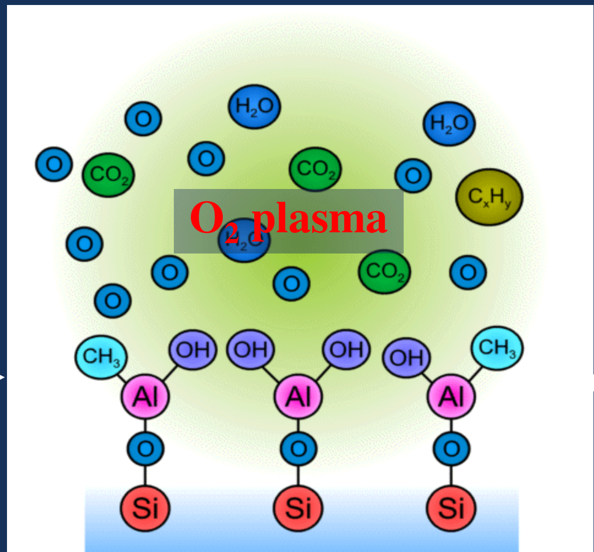
2)

3)



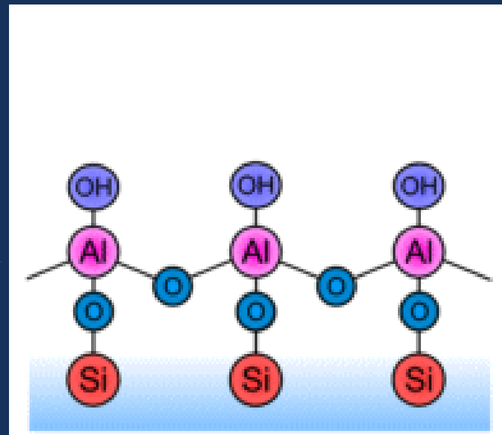
Purge

4)



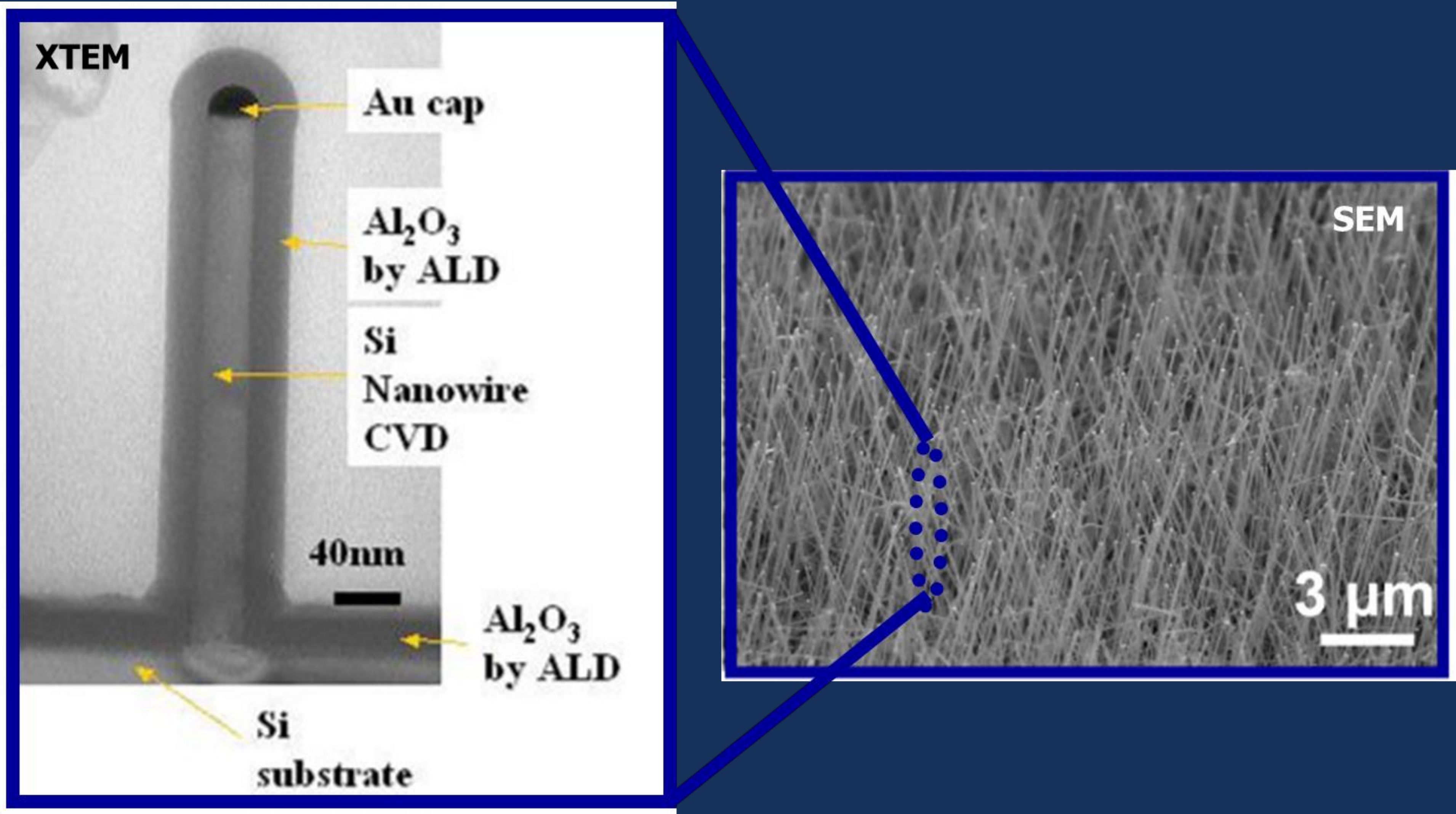
O_2 plasma exposure

5)



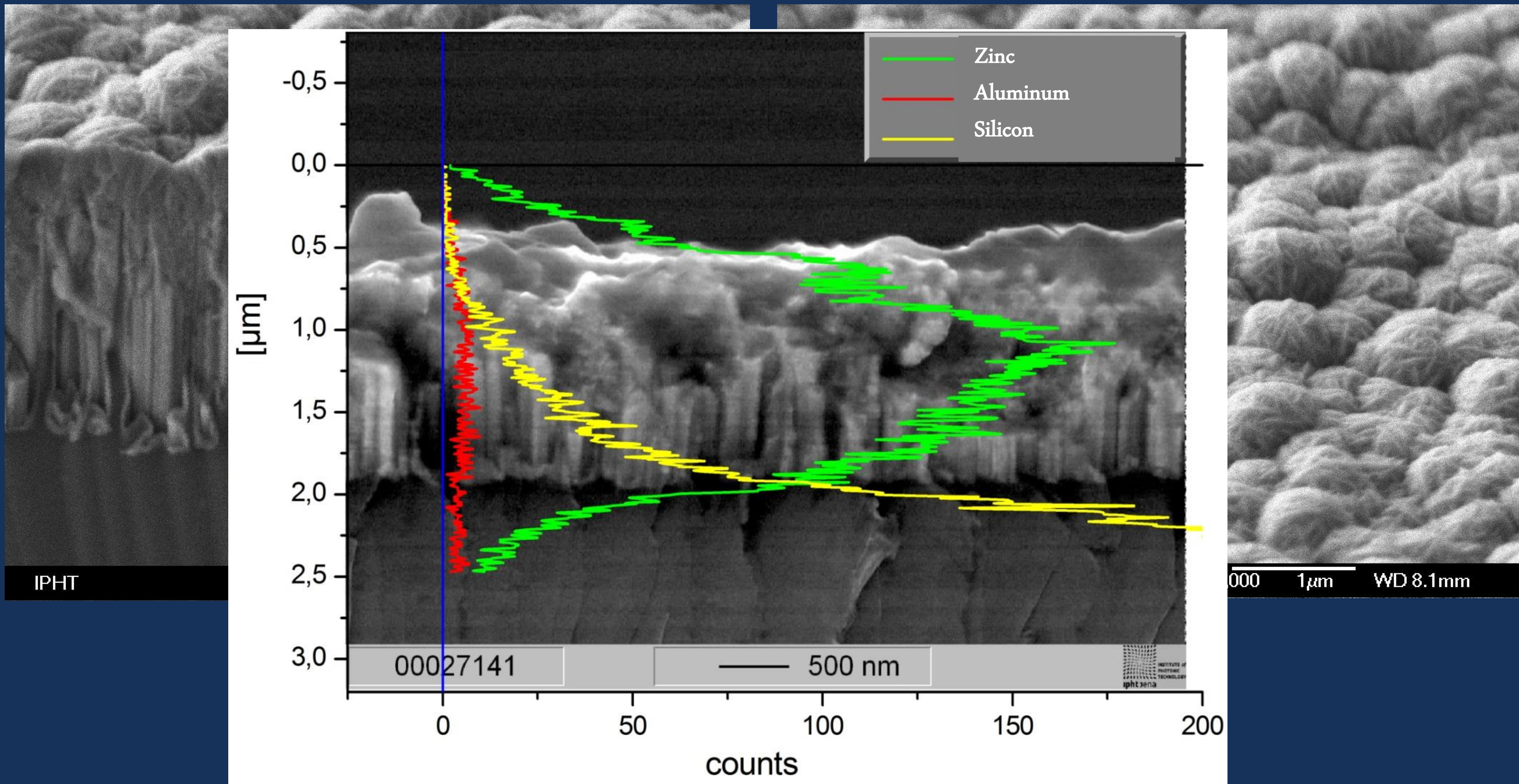
Purge

ALD Technology



ALD: Gao, Ley, Physik, Uni Erlangen

ALD Technology



Very homogeneous distribution of ZnO inside the nanowire carpet

Transparent Conductive Oxides (TCO)

Application examples:

- Organic light emitting diodes (OLED)
- Liquid crystal displays (LCD)
- Touch panels
- Thin film solar cells

Indium Tin Oxide

- **Low specific resistivity: ~ 10^{-5} Ωcm**
- **Poor raw material**

  → high cost

Aluminium Zinc Oxide

- **Present specific resistivity: ~ 10^{-4} Ωcm**
- **Better transmission in visible range**
- **Low cost**

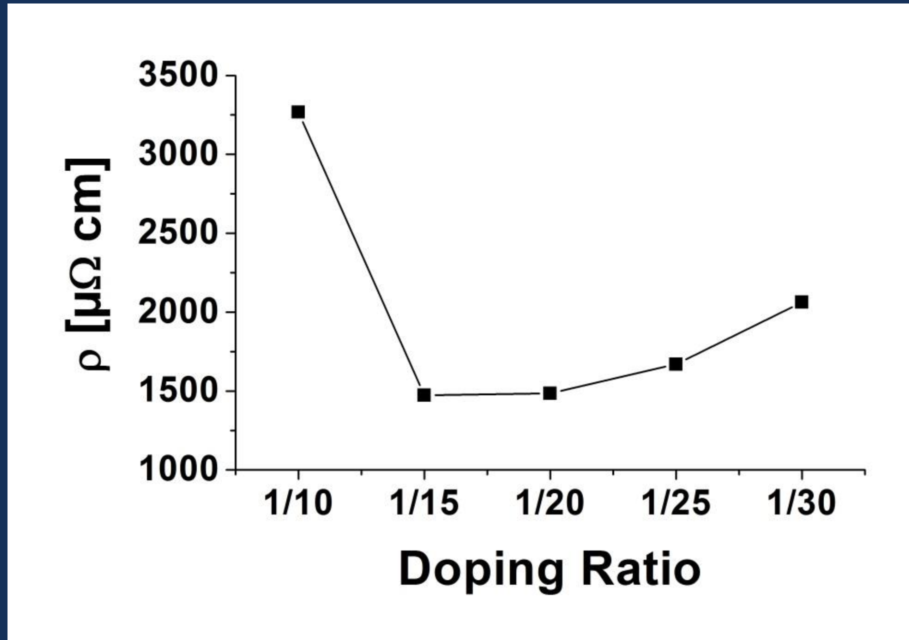
Transparent Conductive Oxides (TCO)

Farbication of Al doped ZnO using Atomic Layer Deposition

Precursors:

- Diethylzinc (DEZ)
- Trimethylaluminium (TMA)
- Water (H_2O)

Doping Sequence:
N cycles DEZ/H_2O + 1 cycle TMA/H_2O



Minimal specific resistivity:

$8x10^{-4}$ Ohm cm

Stoichiometry measurement (with RBS):

Doping Ratio	Zn [%]	O [%]	Al [%]
1/10	47.1	52.9	6.6
1/20	49.8	50.2	2.9
1/30	51.0	49.0	2.0

Best results:

- temperatures ≥ 200° C
- 1/15 ≥ best ratio ≥ 1/20

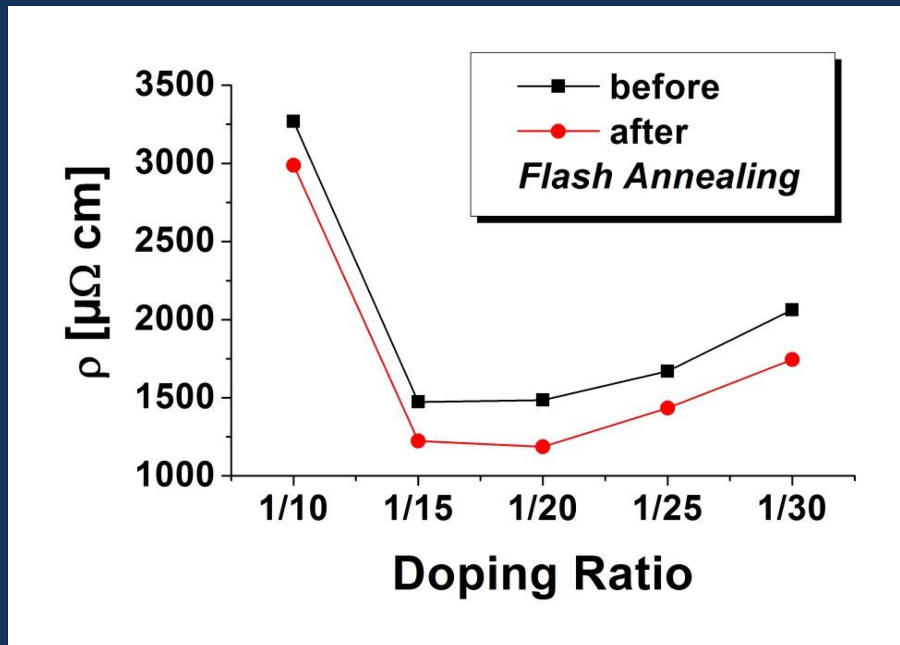
Transparent Conductive Oxides (TCO)

Flash Annealing

Flash Annealing System:

© by Dresden Thin Film Technology

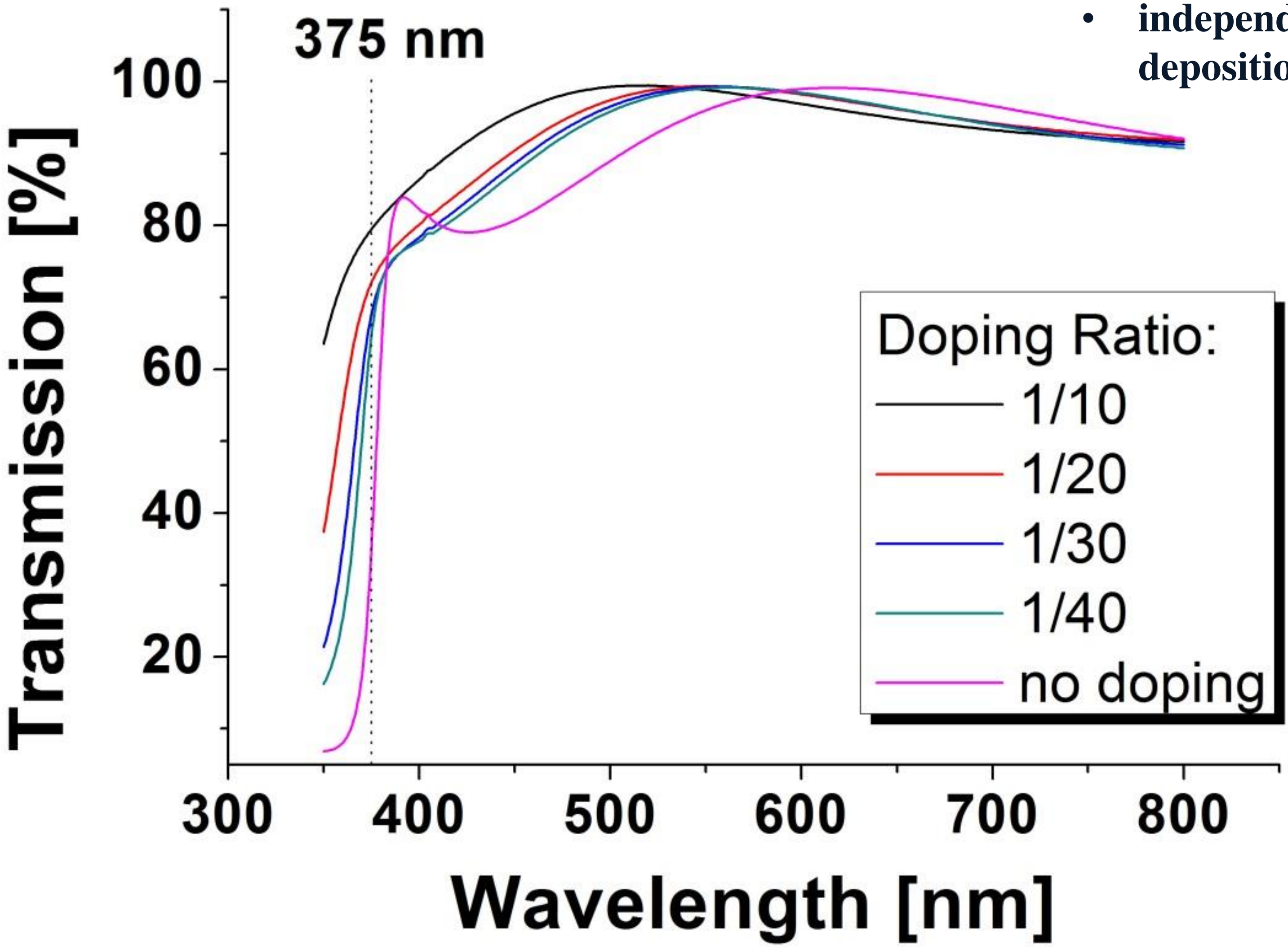
- Short impulslength of a few hundred microseconds
- High energy up to 120 J/cm²
- temperature sensitiv substrates possible



- Improvement of conductivity at all doping ratios
- Specific resistivity decrease up to 20%

Transparent Conductive Oxides (TCO)

- **Band gap: ~3.3 eV (375 nm)**
- **about 90% in visible range**
- **independent of doping and deposition temperature**

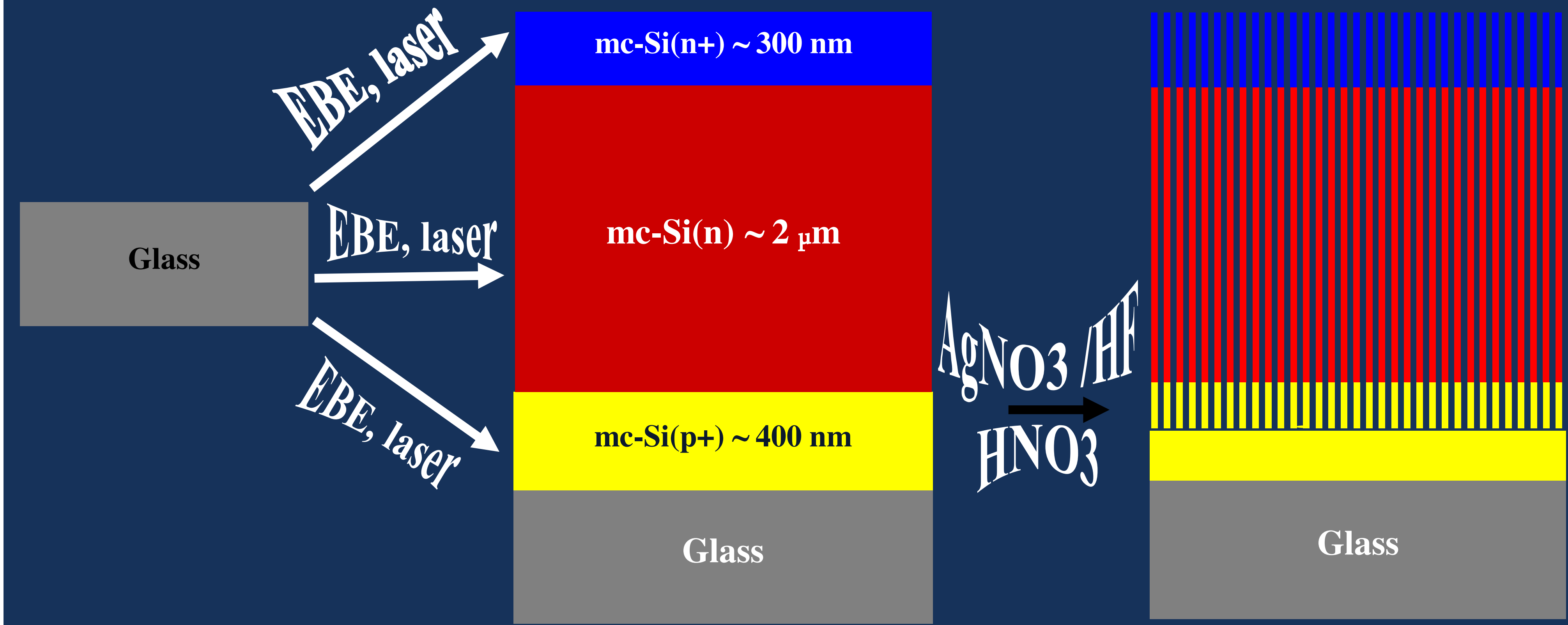


Motivation

- ✓ Smart Material
- ✓ Smart Technology
- ✓ Smart Concept

Photovoltaic Concept I

Solar Cell Based on VLS SiNWs

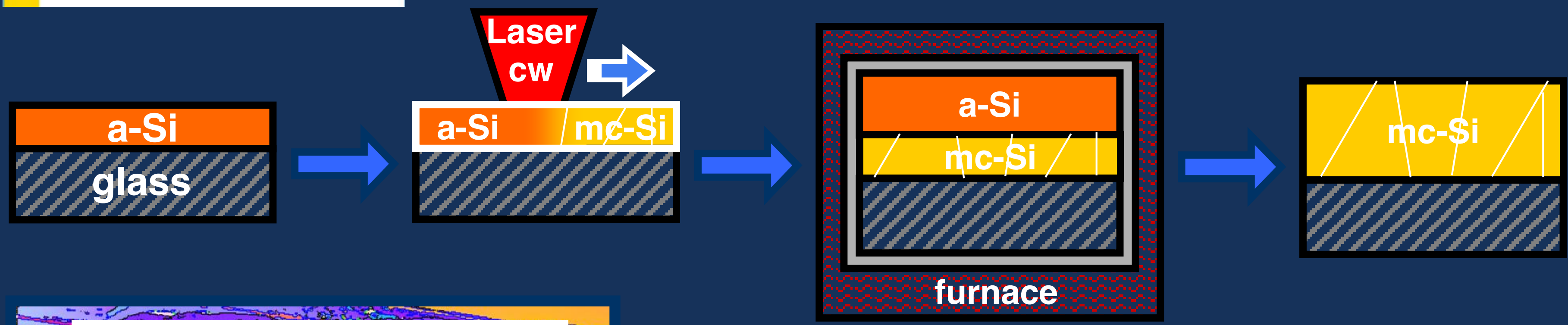


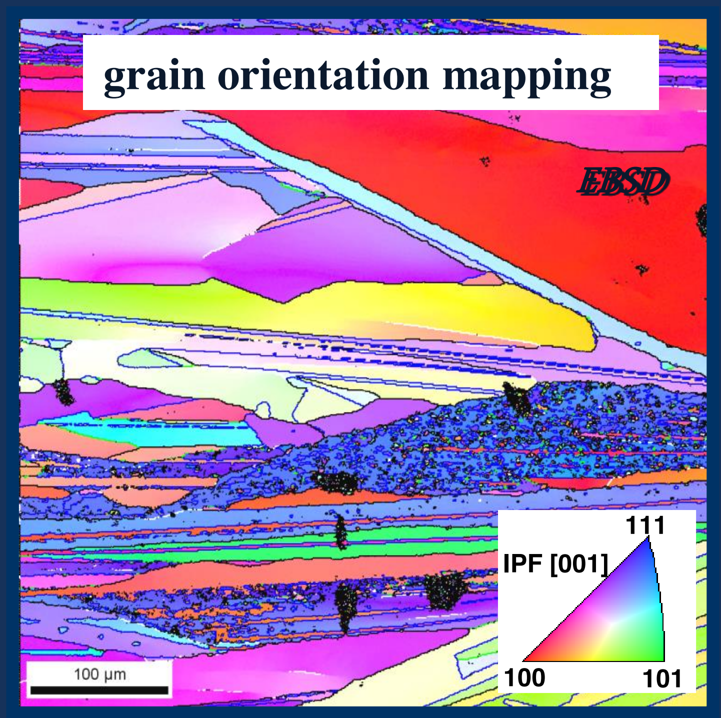
Schematic cross sectional view of the mc-Si p-n junction layer stack on a glass substrate before and after "Black Etch" treatment.

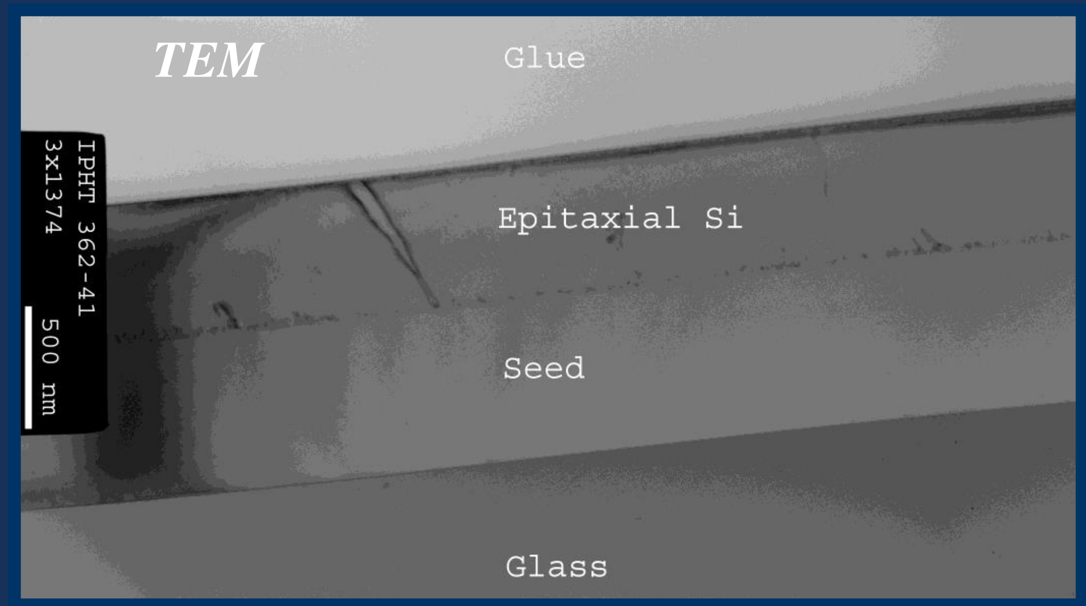
V. Sivakov et al. *Nano Lett.*, 9 (4),1549–1554(2009)

Growth and Analytical Stidies on mc-Si

Seeded Solid phase crystallization



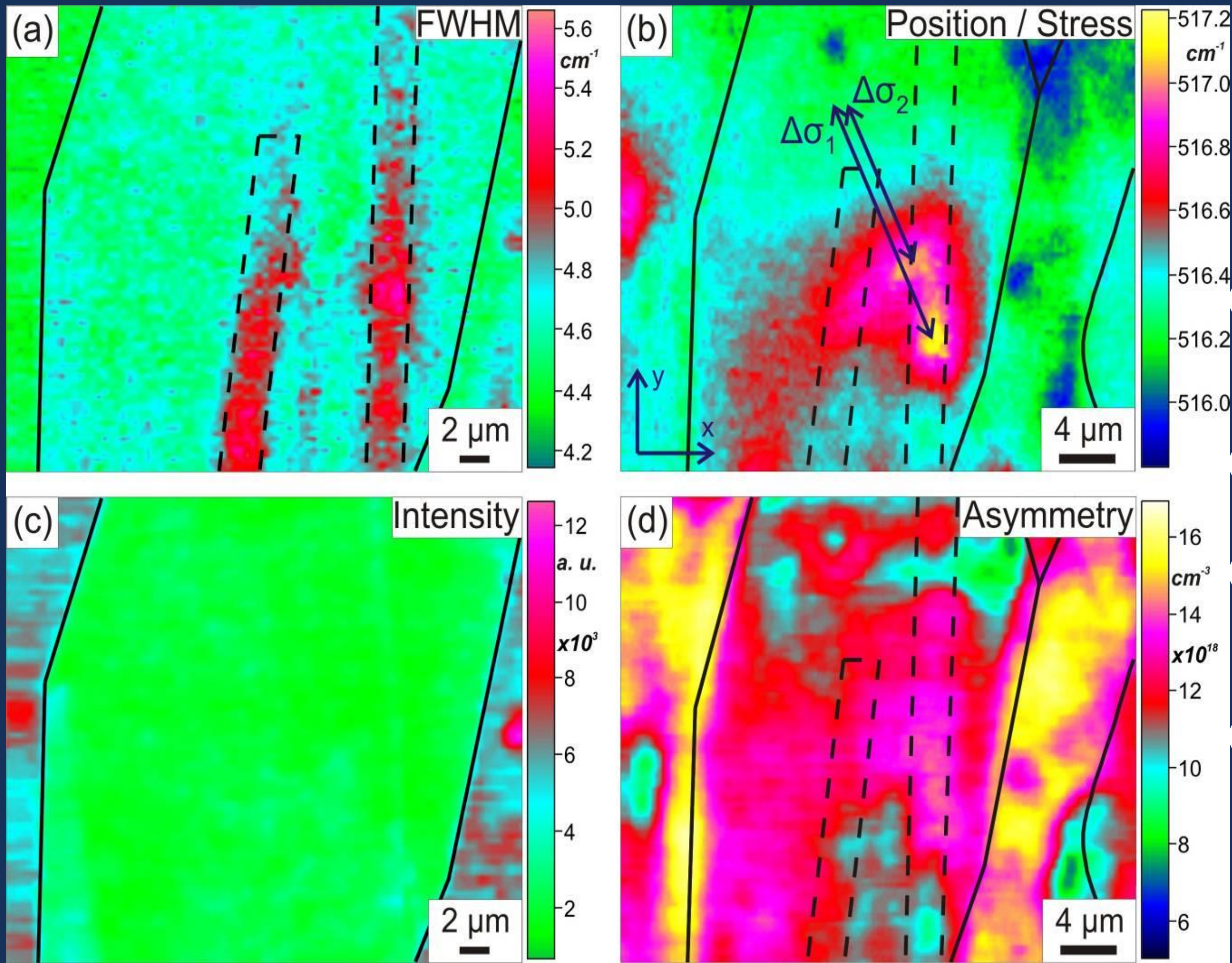




Dr. Vladimir Sivakov, IPHT

06.03.2014

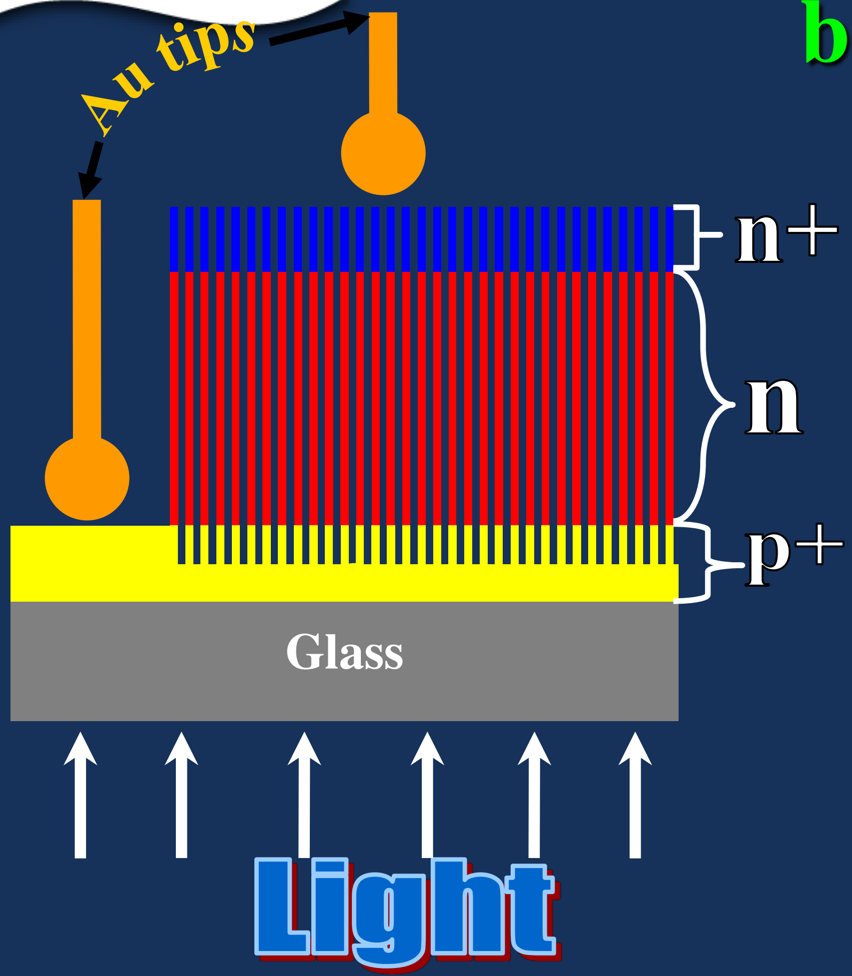
Growth and Analytical Stidies on mc-Si

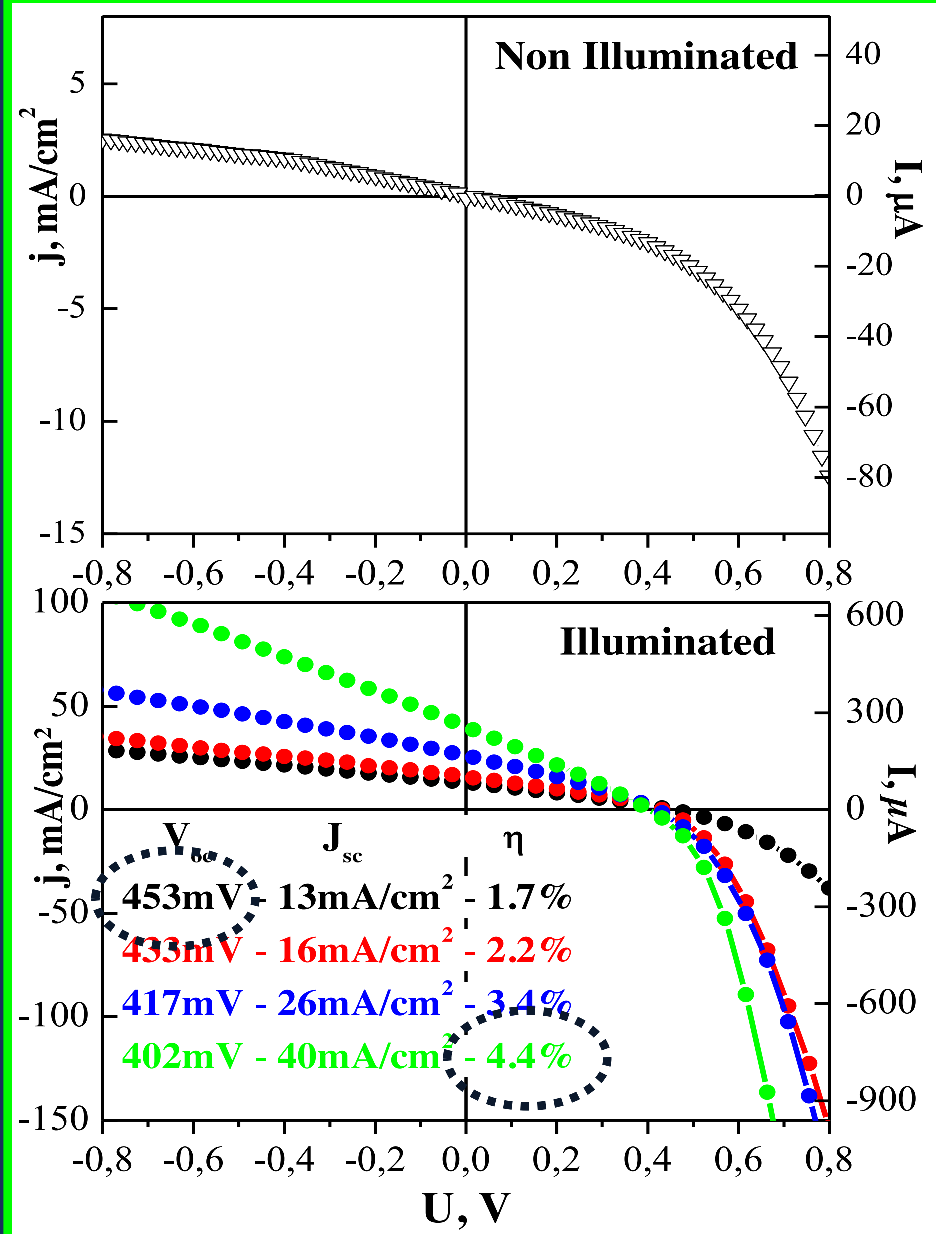


Raman Spectroscopy

(i) the distribution and qualitative comparison of defect densities;
(ii) amount and sign of internal stresses;
(iii) the grain orientation and the grain boundary pattern;
(iv) the distribution and amount of doping.

PV properties of solar cell based on SiNWs



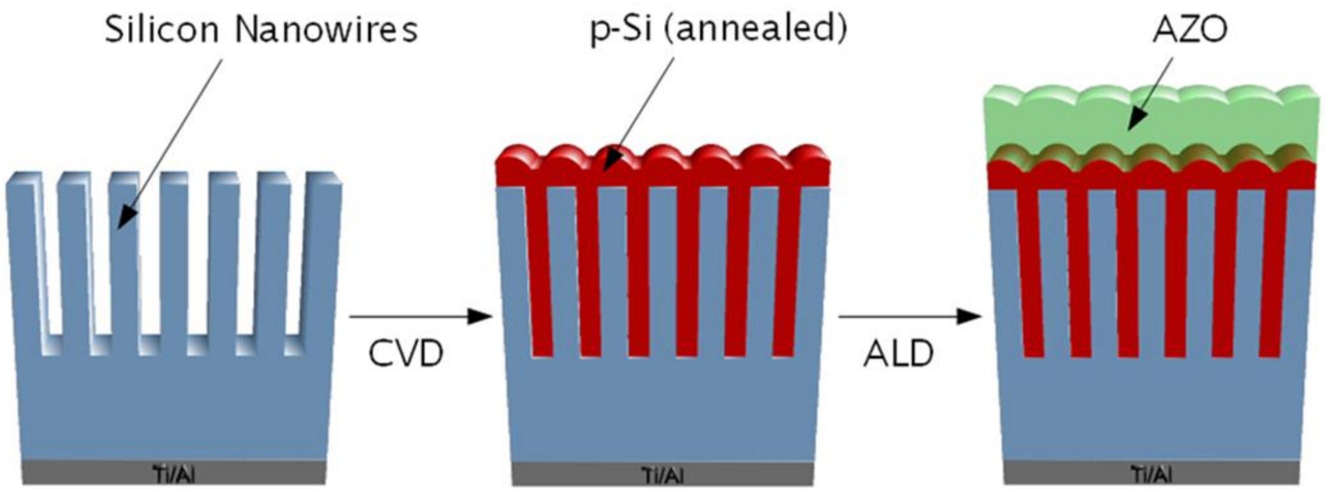


Non illuminated and illuminated (AM1.5) I-V curves of SiNWs etched into a mc-p+nn+-Si layer on glass. SiNW are irradiated through the glass substrate (super-state configuration) and contacted by metal tips at four different sample positions.

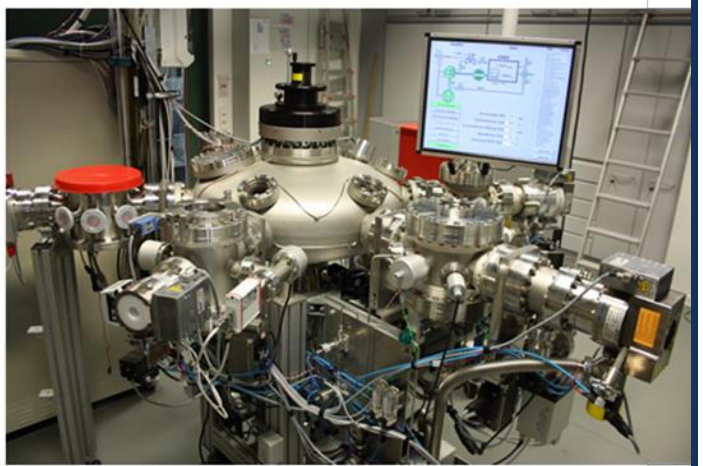
V. Sivakov et al. Nano Lett., 9 (4),1549–1554 (2009)

Photovoltaic Concept II

Realization of Radial p-n junction

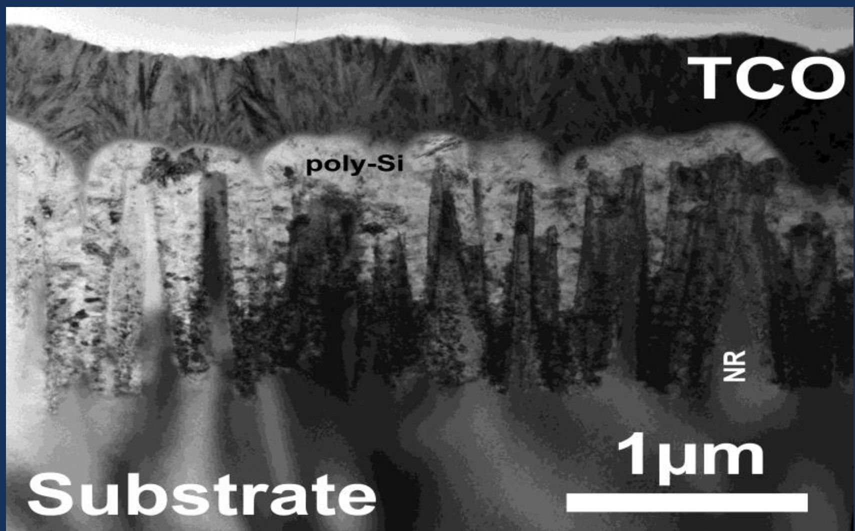


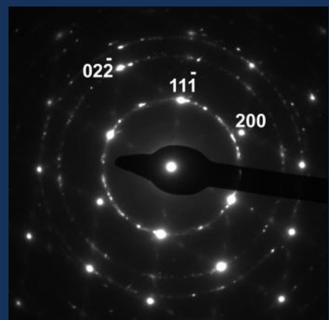
- Deposition of Boron-doped a-Si by CVD
- Annealing at 700° C in order to crystallize/activate the a-Si
- Deposition of AZO by ALD



Realization of Radial p-n junction

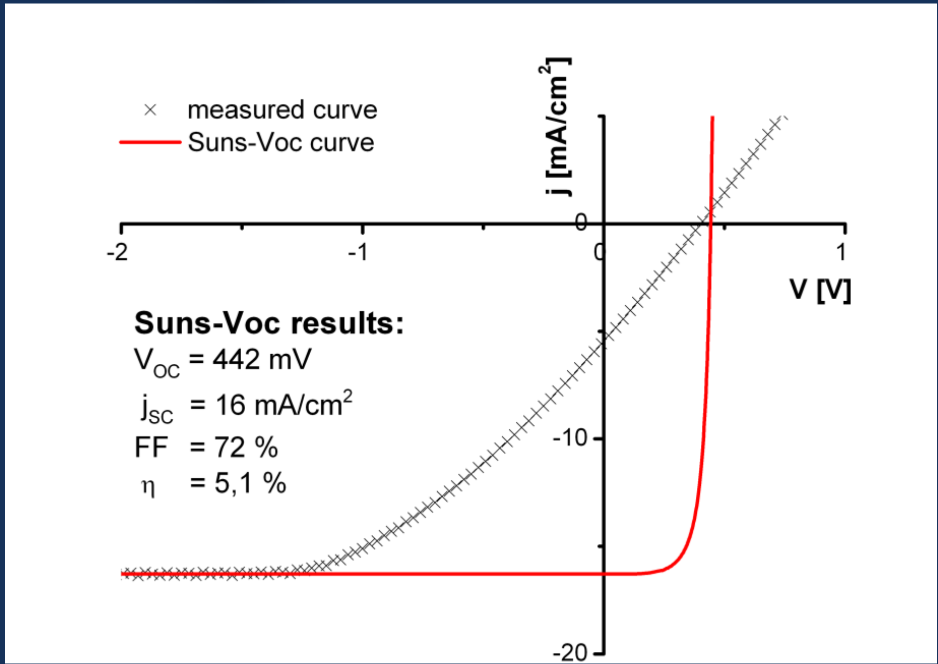
TEM Studies



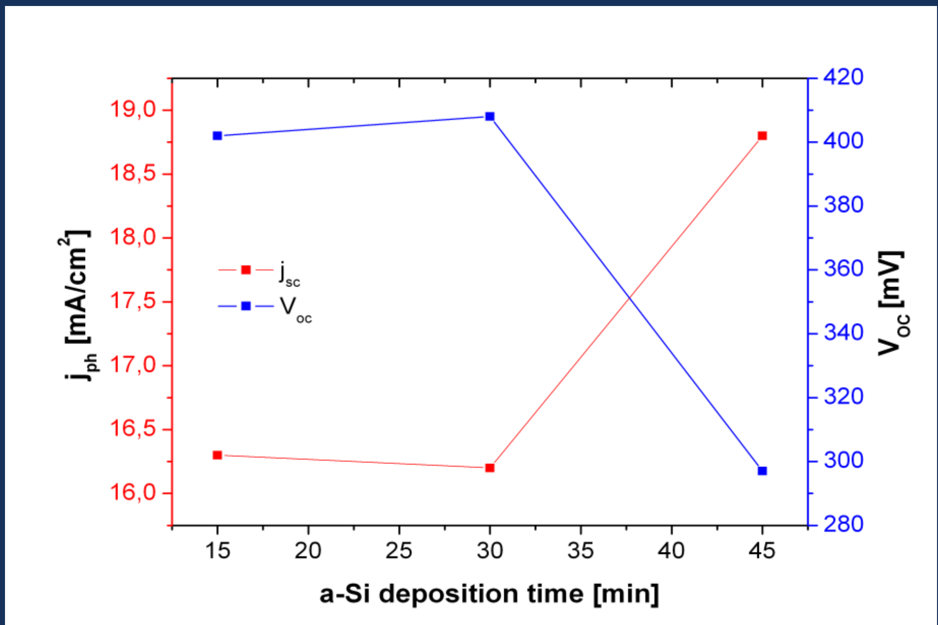


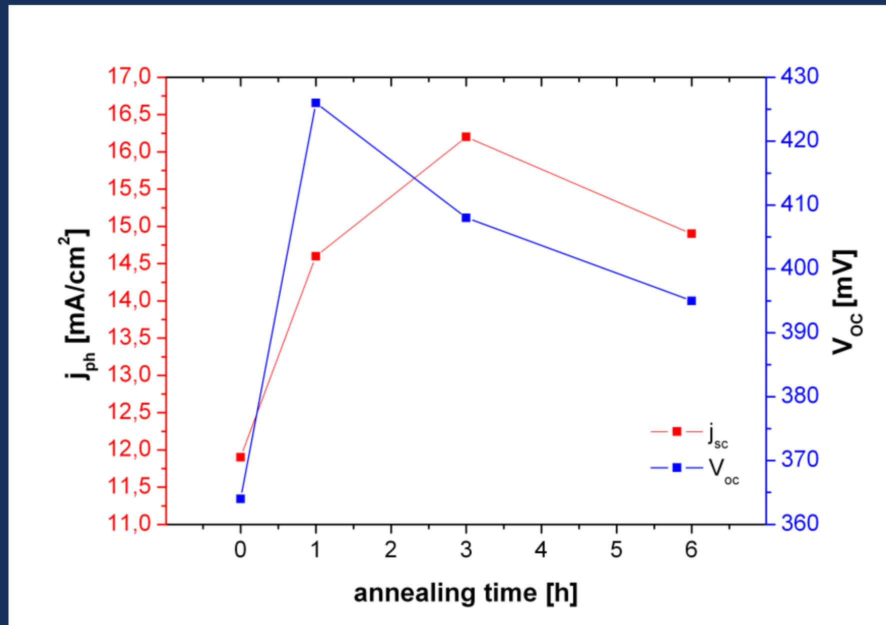
- SiNWs are cone-shaped
- a-Si homogeneously covers the SiNWs
- Annealing leads to partial crystallization of the a-Si
- Annealing times of more than three hours do not cause further structural changes

Realization of Radial p-n junction



- Characterization with I-V- and Suns-Voc-measurements
- Annealing times between one and three hours are optimal
- j_{sc} is relatively low (with respect to the high absorption)
- Efficiencies of 5% could be realized





Photovoltaic Concept III

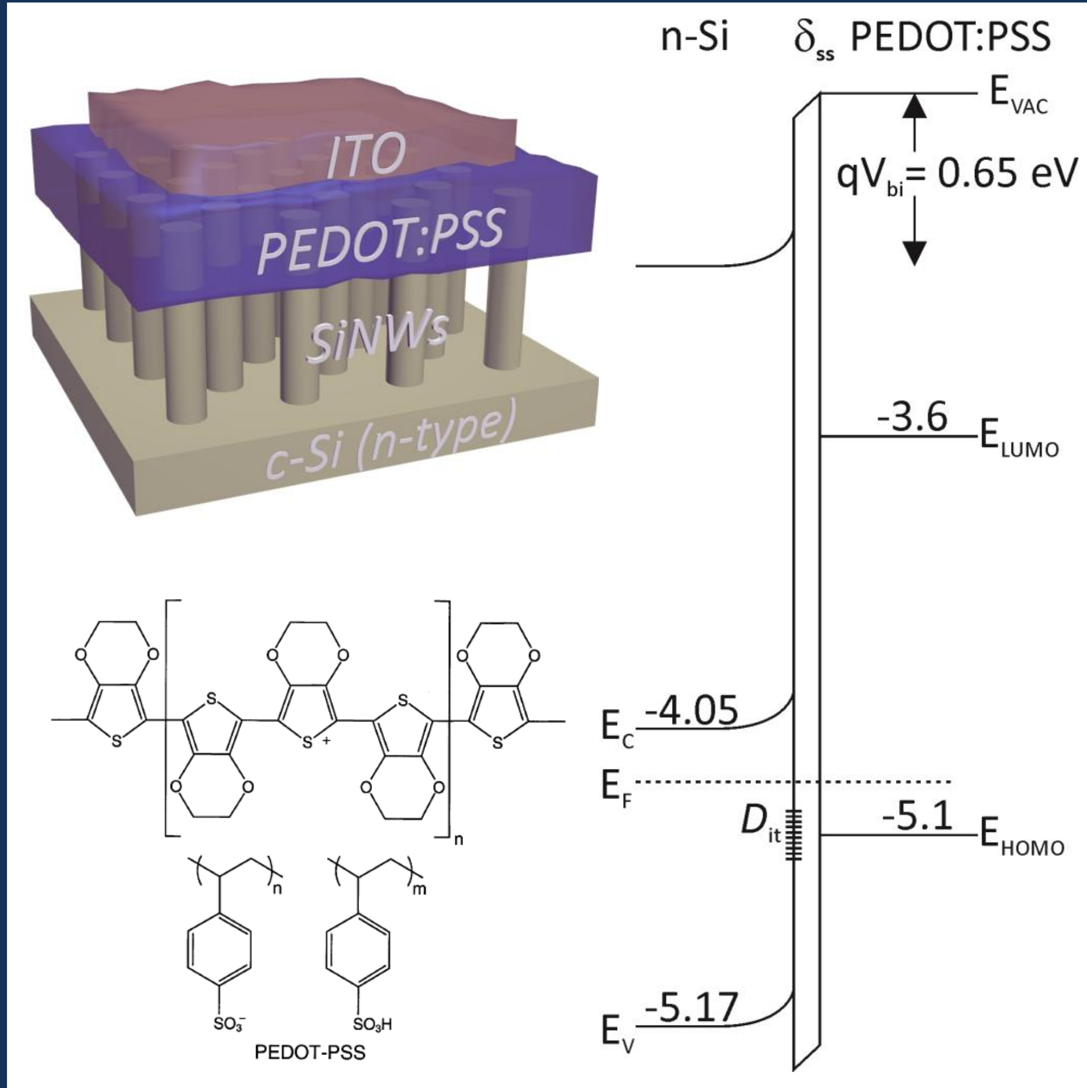
Hybrid Solar Cells

motivation

- combining high conduction of nanostructured ISC with the ease of processing of OSC
- Low cost processing for high efficient solar cells (aim 10%)
- charge carrier separation at organic/inorganic interface

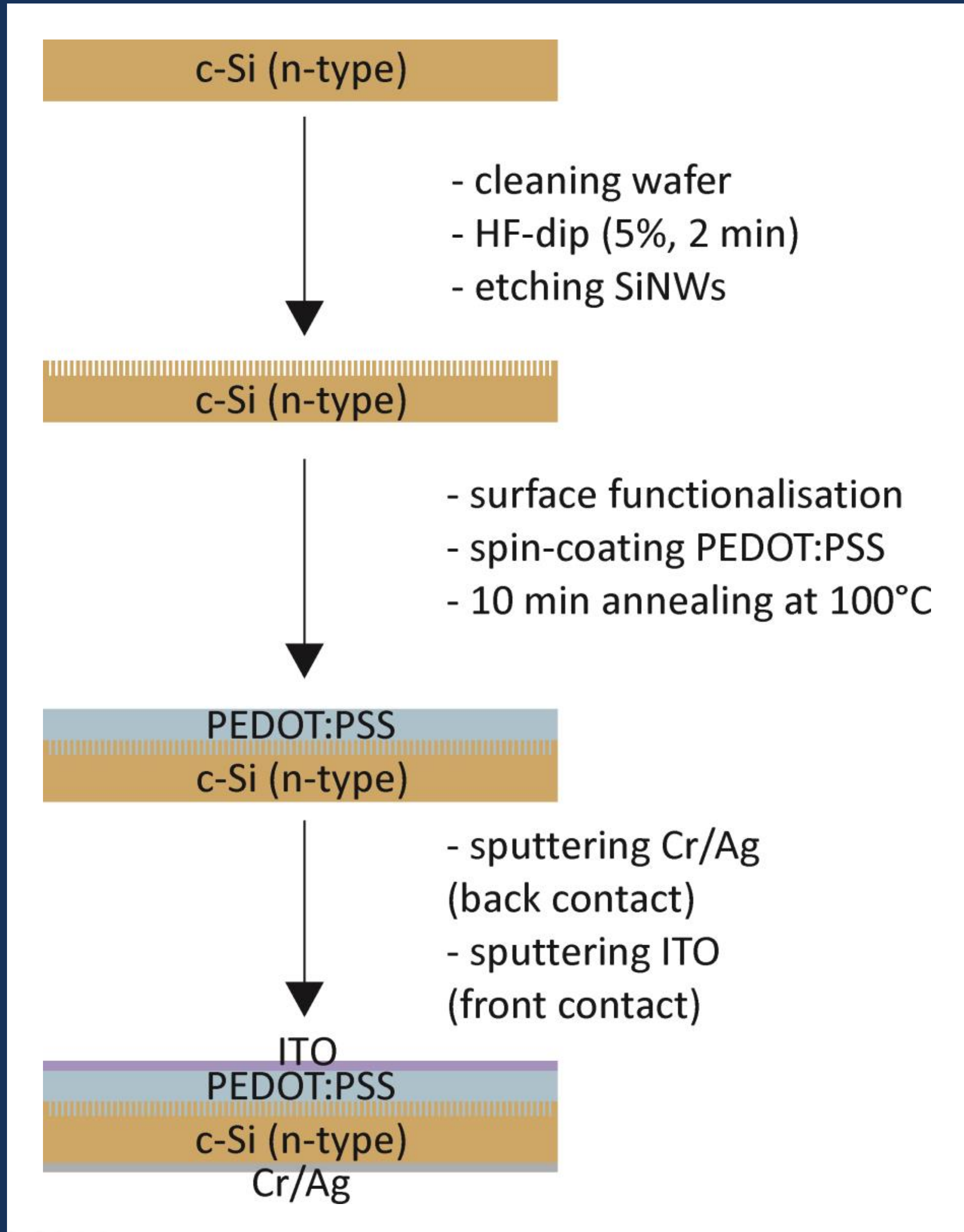
Features of PEDOT:PSS

- many approaches with different polymers
- Advantages of PEDOT:PSS:
  - most stable polymer (chemically and thermally)
  - Conduction is orders of magnitudes higher than for other conjugated polymers



Hybrid Solar Cell Processing

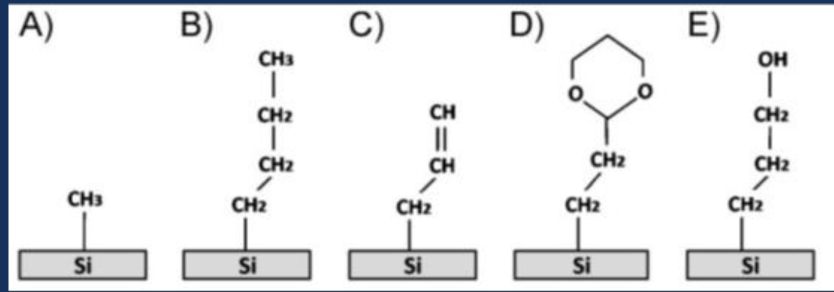
- Fuctionalisation of SiNW surfaces is necessary to obtain a hydrophilic surface
- other advantages of surface funtionalisation
  - → Passivation
  - → efficient charge injection
- Morphology of PEDOT:PSS on SiNWs depends strongly on spin-coating conditions/viscosity of PEDOT:PSS

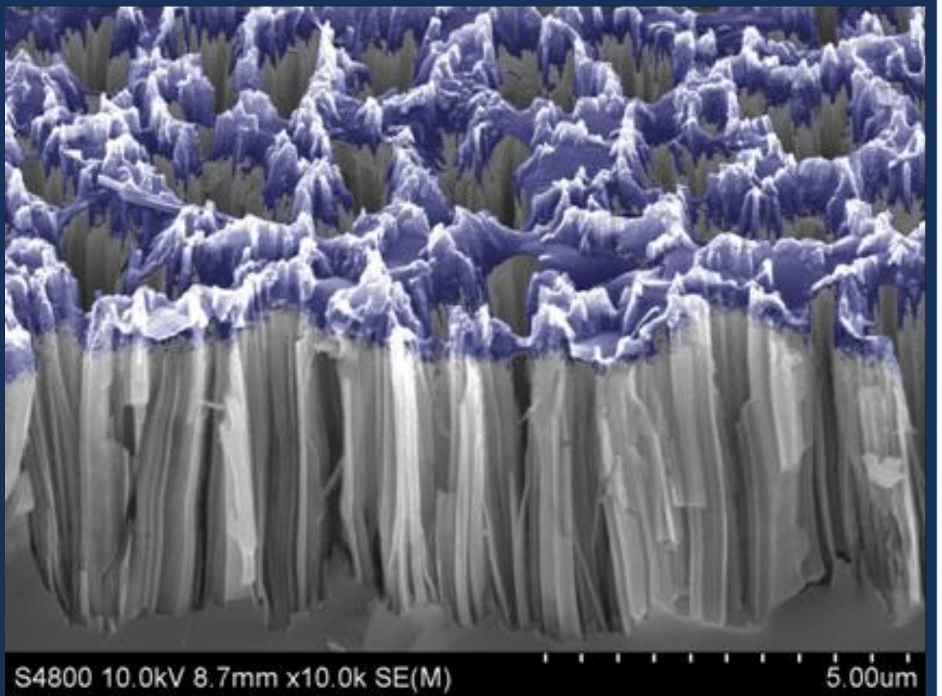


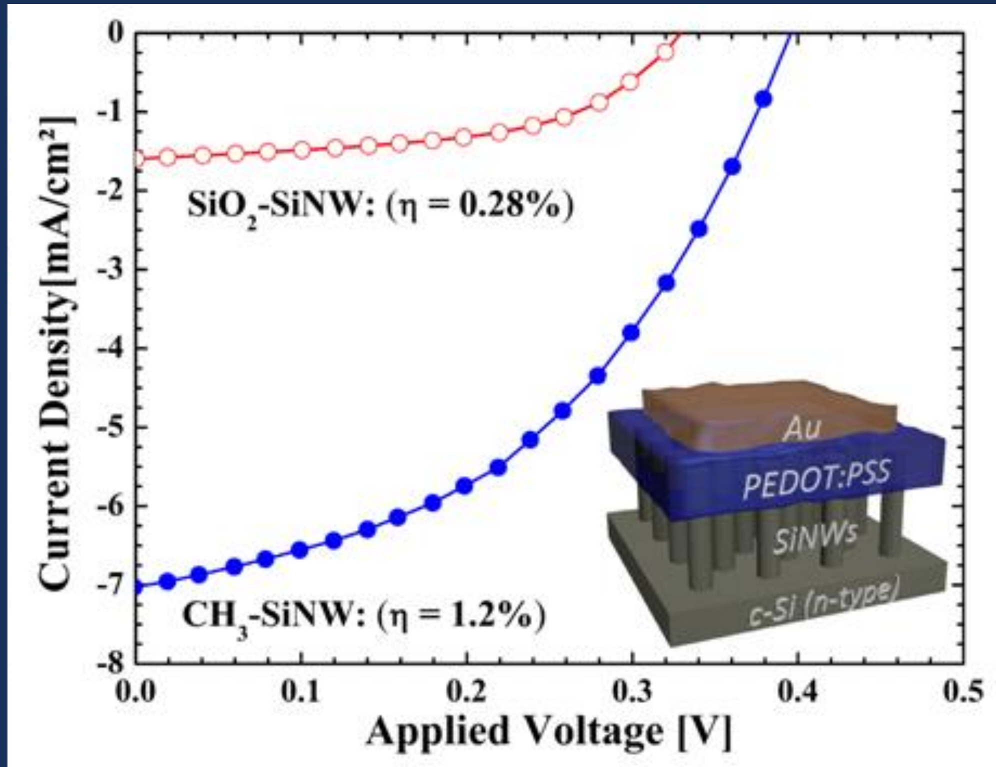
M. Y. Bashouti, et al., Nanowires - Recent Advances, ISBN: 978-953-51-0898-6, Chapter 9 (2012)

Funtionalization of SiNW surfaces

- Si surface is terminated by covalent bond between Si and C atoms
- different molecules change the surface dipole dramatically (over a range of 0.9 eV)
- Photoelectron Yield Spectroscopy (PYS) reveals higher yield for CH_3 –terminated SiNWs and reduced density of gap states

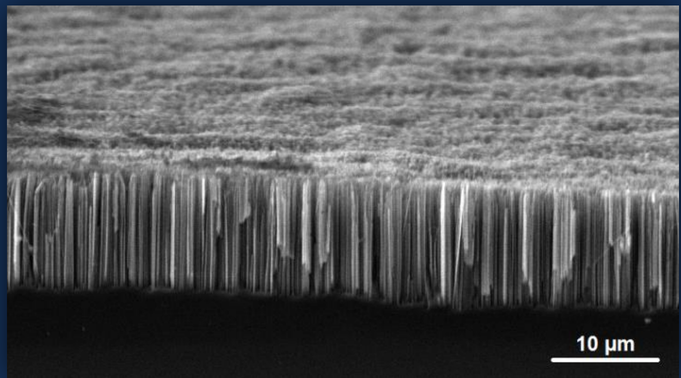


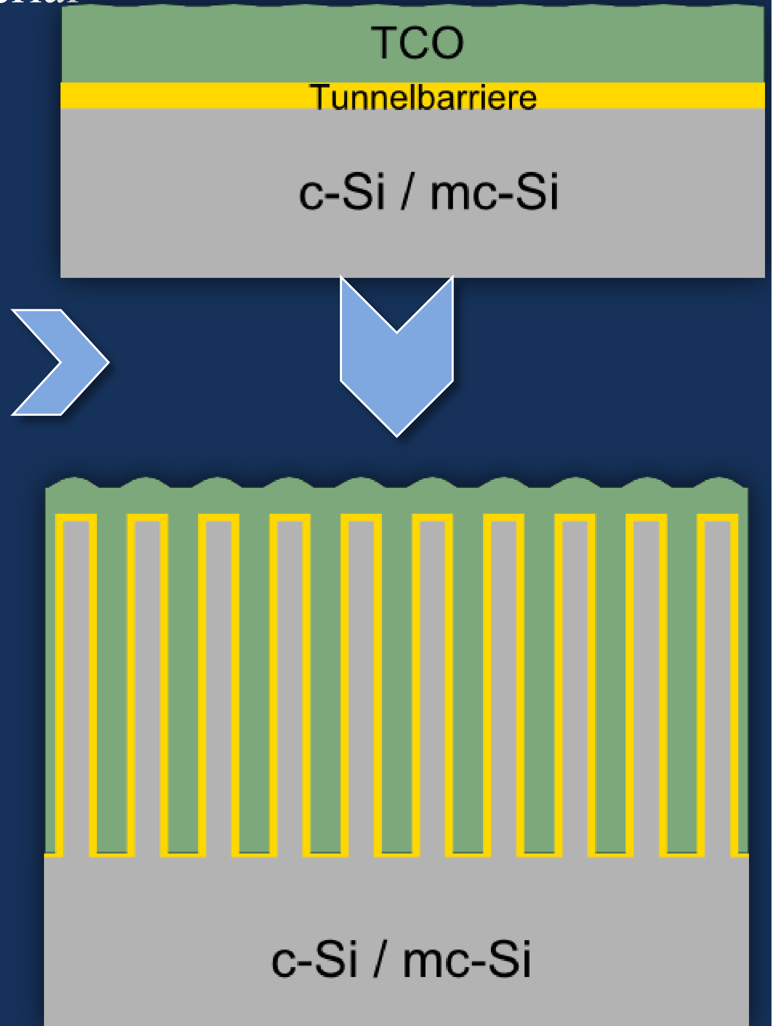




Photovoltaic Concept IV

- Semiconductor-Insulator-Semiconductor
- SiNWs as a light trapping and highly absorbative material



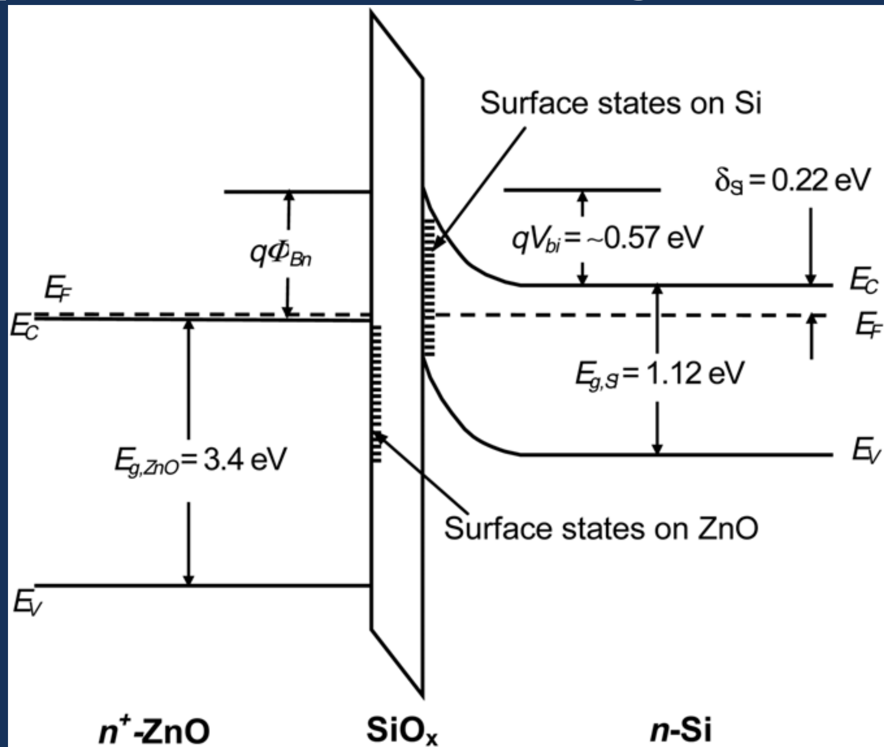


Smart concept

Schewchun et al., J. Appl. Phys. 49, S. 855 (1978)

Backgroung:SIS-Diode

- No pn-junction
- Insert tunnel barrier between both semiconductors → fermi level pinning
- → charge carrier separation is based on quantum mechanical tunneling of minority carriers through the barrier

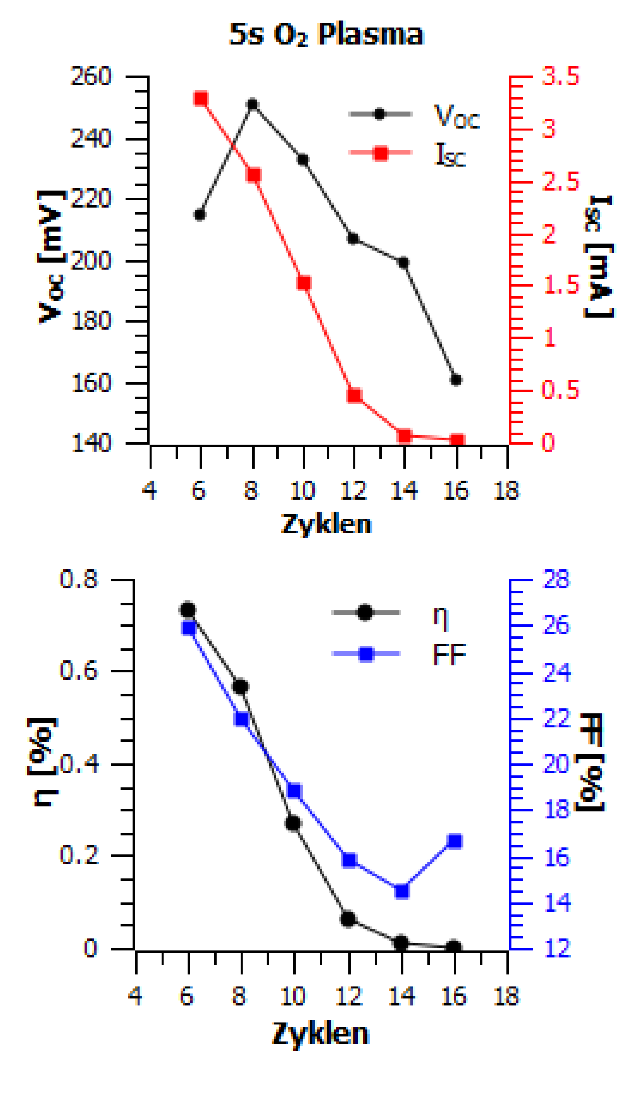


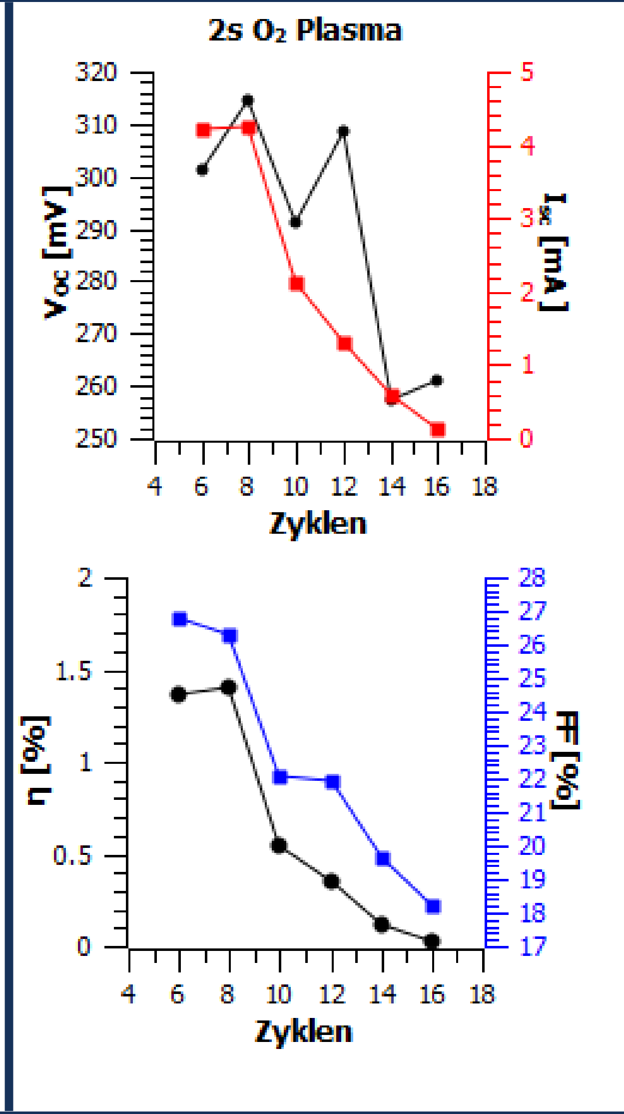
Challenge:

Transfer the planar wafer-based concept to a nanostructured substrate
→ Reach higher efficiencies because of better light absorption

Song, D. & Guo, B. Journal of Physics D: Applied Physics, 2009, *42*, 025103
V. Sivakov et al., Intech "Nanowires - Fundamental Research", ISBN 978-953-307-327-9, 45-80 (2011)
B. Hoffmann, V. Sivakov et al. INTECH “Nanowires - Recent Advances“, ISBN: 978-953-51-0898-6, Chapter10 (2012)

Planar SIS cells





Best Results

V_{OC} : 314.7 mV

J_{SC} : 17.04 mA/cm^2

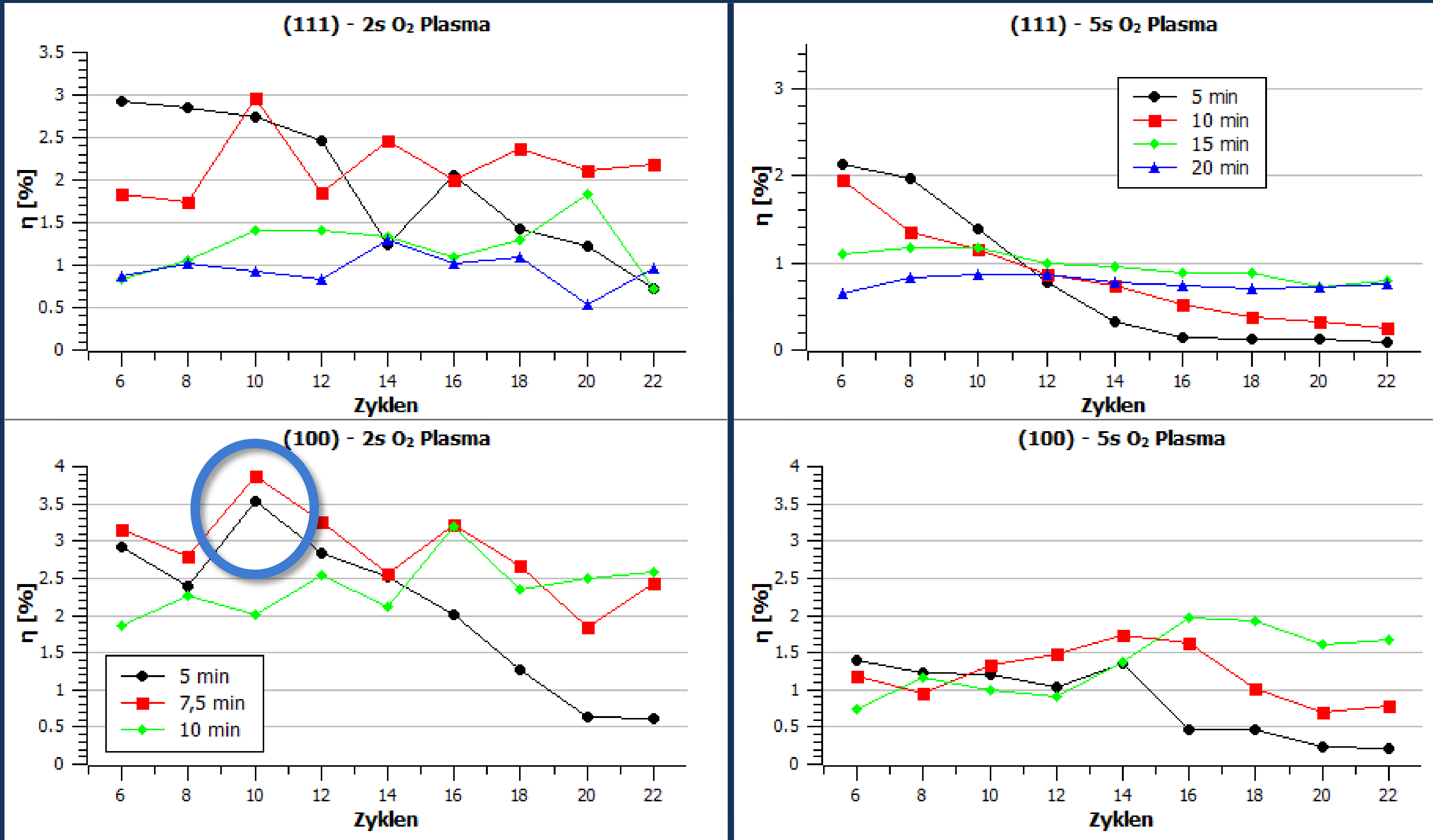
FF : 26.3 %

η : 1.4 %

8 Cycle TB ≙ 10 Å

@ GPC 1,25 Å/Cycle

Nanowire SIS Cells



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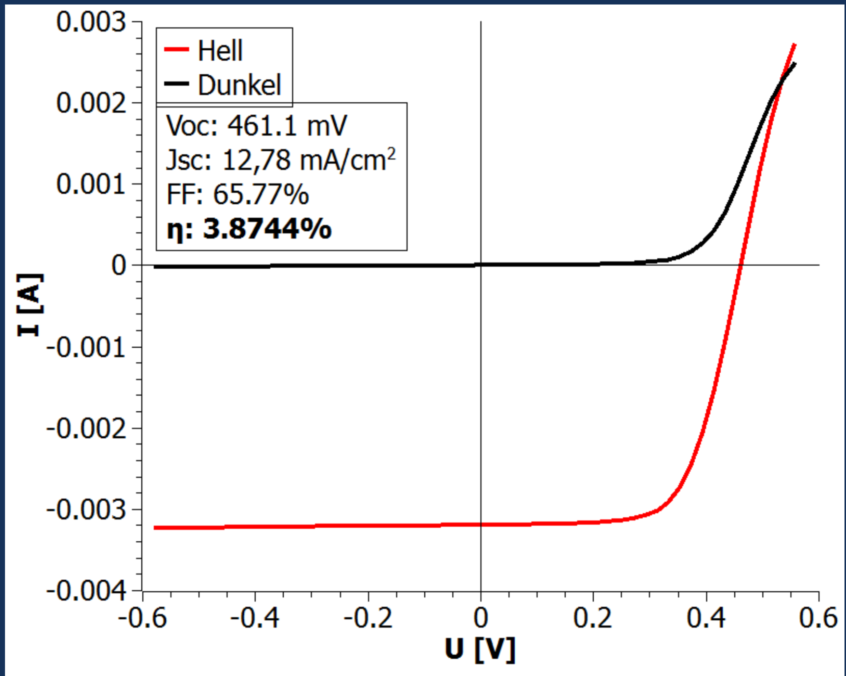
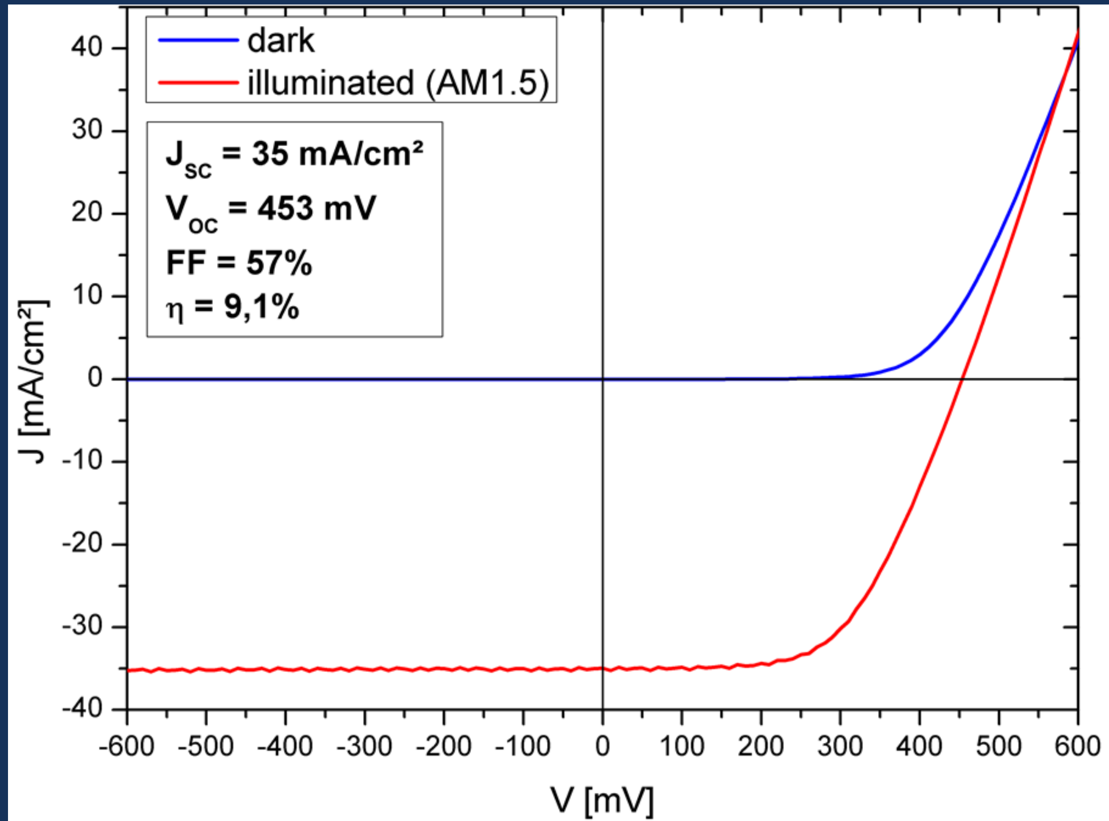
Best SIS Cells

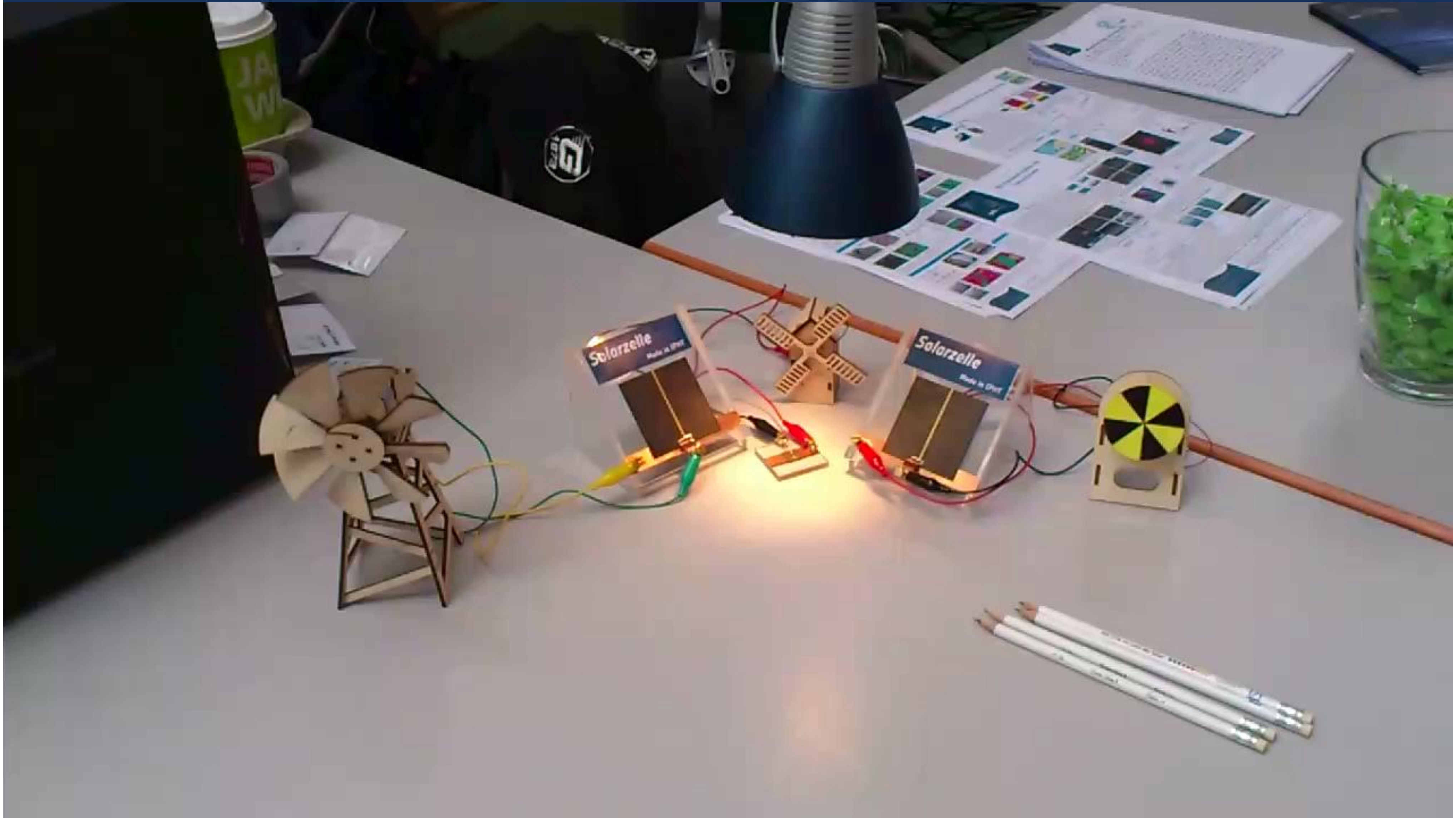


36 cm²



25 mm²

Solar Village



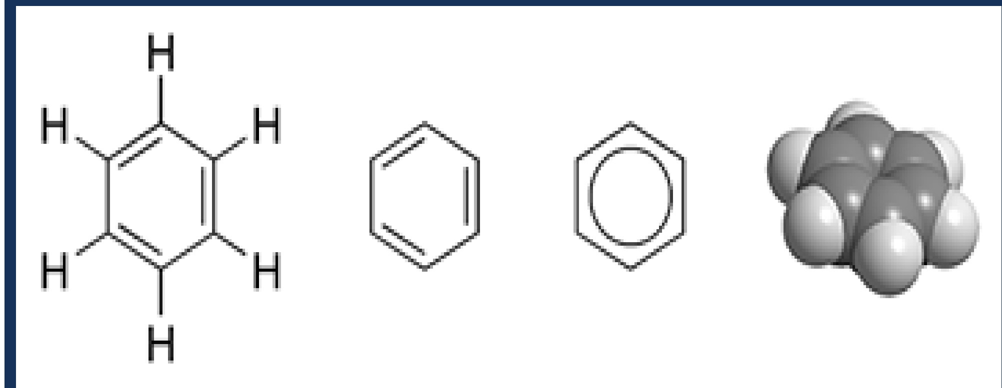
Nanowires based Solar Cell <u>WORKS</u>

Newton's Law of Gravity

$$F_g = G\frac{m_1 m_2}{r^2}$$

The Proverbial Apple

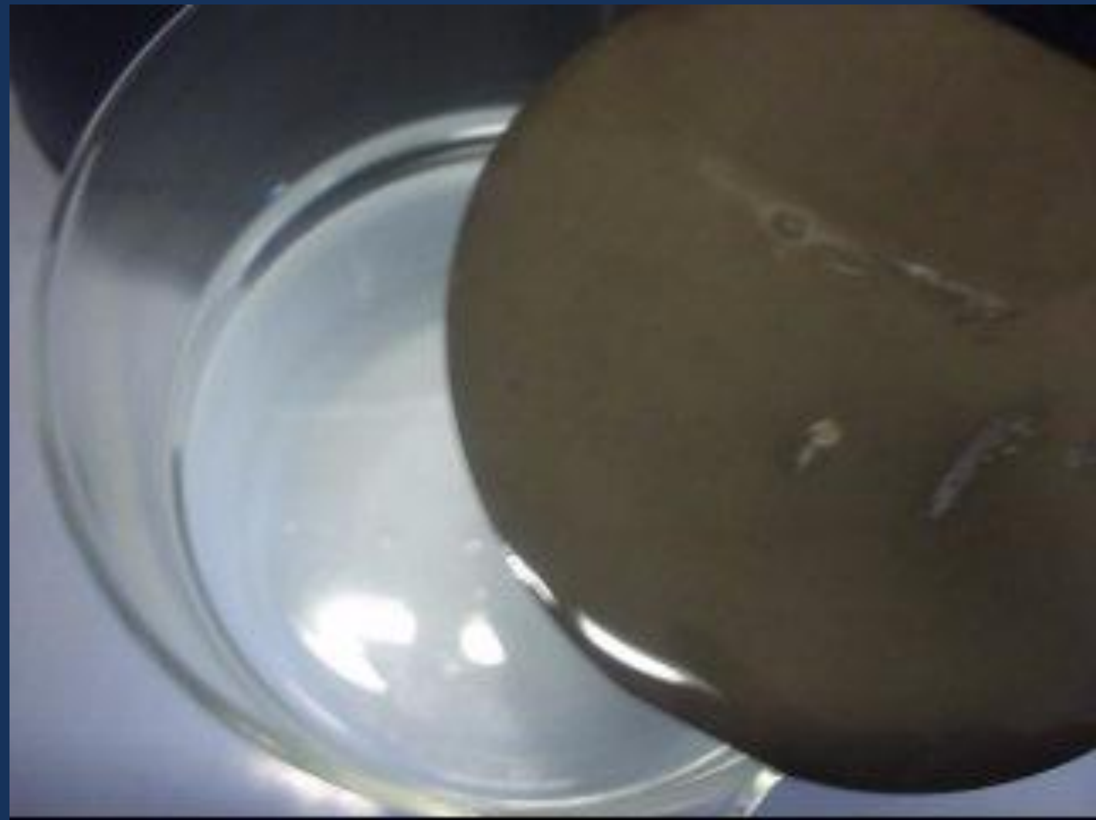
The famous story that Newton came up with the idea for the law of gravity by having an apple fall on his head is not true, although he did begin thinking about the issue on his mother's farm when he saw an apple fall from a tree.

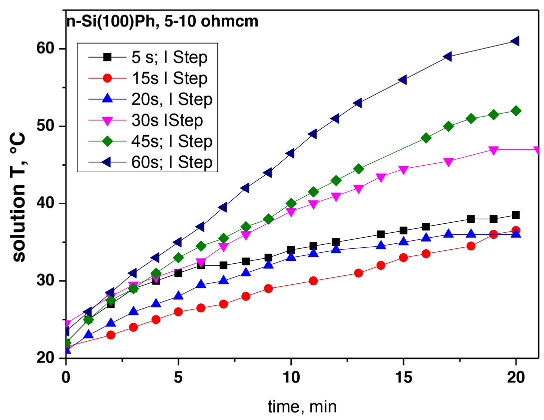


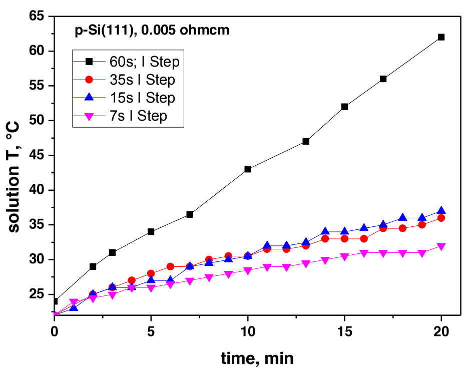
Friedrich August Kekulé **said that he had** ***discovered*** **the ring shape of the benzene molecule after having a reverie or day-dream of a snake seizing its own tail. This vision, he said, came to him** ***after years of studying the nature*** **of carbon-carbon bonds.**

Observation of NATURE!!!!!!

Energy detachment



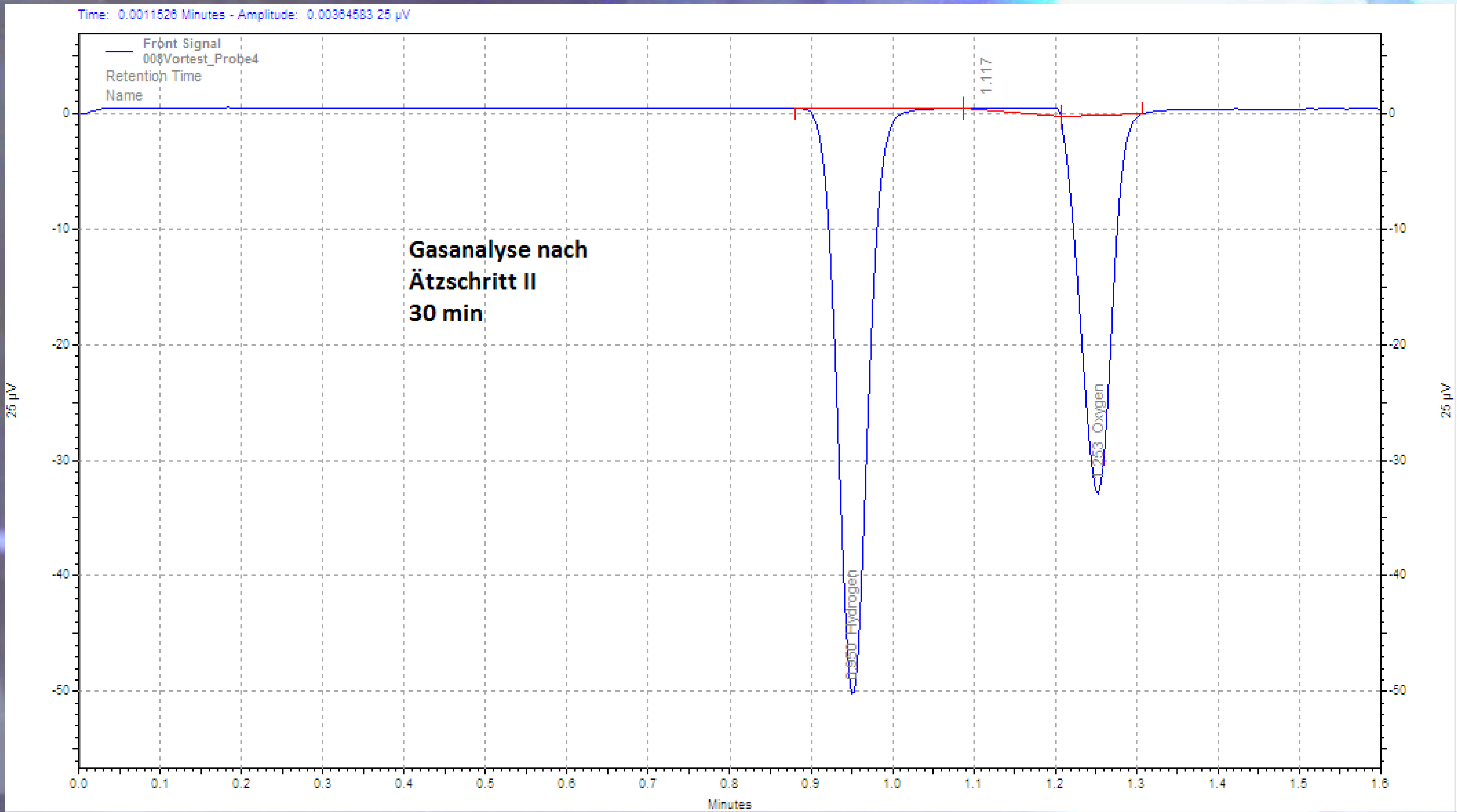




1l H_2O 1K 4.2 kJ/1.16 Wh

V. Sivakov et al., J. Phys. Chem. C114, 3798–3803 (2010)
V. Sivakov, Journal of Nanoelectronics and Optoelectronics, 7(6) 583 (2012)

Observation



>10% Hydrogen!!!

Hydrogen	141,9 MJ/kg
Oil	46,7 MJ/kg,
Methanol	23,3 MJ/kg,

Summary&Outlook

Yes, we can!

Chemical „Black Silicon“ has a big future for photovoltaic, solar fuel, optolectronic and life science applications.

But, a lot to do…….