Photonic Nanostructures

HZB Helmholtz Zentrum Berlin

Nano-architectures for solar energy conversion: synthesis, characterization & device integration

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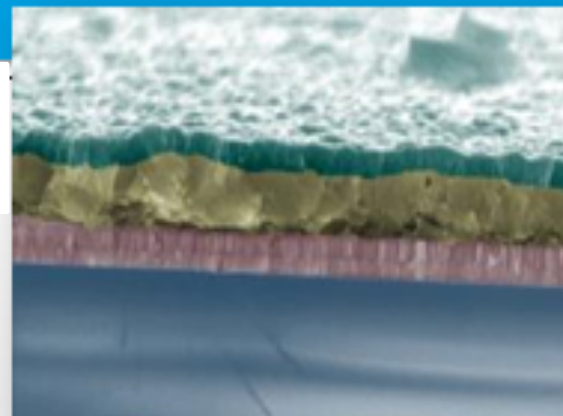
2 Helmholtz-Zentrum for Materials & Energy Berlin, Berlin, Germany

One Center – Two Sources



Science with Neutrons
Berlin-Wannsee

Energy Research

Science with Photons
Berlin-Adlershof

Key Numbers

Neutrons	Photons	User Service	Energy

Total Annual Budget: ~110 million EUR

- Neutrons, Photons, User Service: 75% ↘ 70% (2015)
- Energy: 25% ↗ 30% (2015)

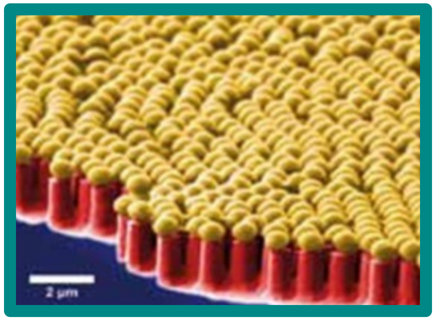
Total Staff: about 1,100

- Scientists: about 400

International Users: about 2,800 p.a.

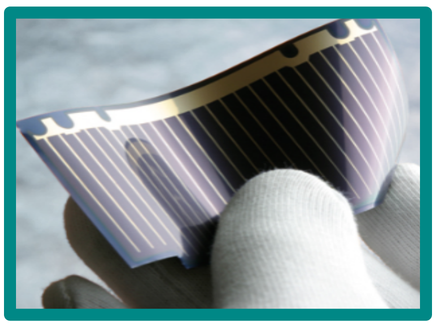
- Neutrons: 400
- Photons: 2,400

Si NW solar cells



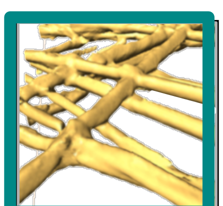
Si Nanowires (NWs) - Synthesis & Morphology

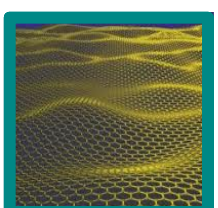
- top down NW etching



NWs in solar cell applications

- semiconductor NWs in different cell concepts
- surface functionalization of NWs to improve solar cell performance

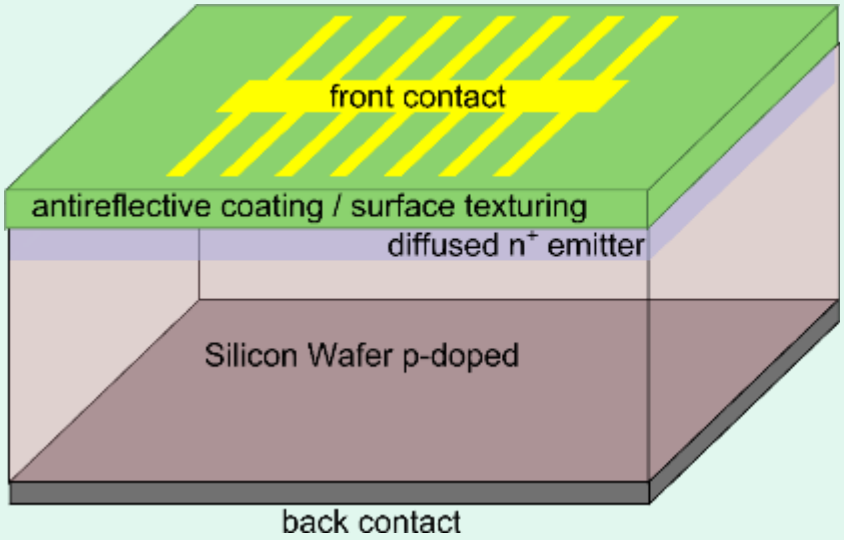




Novel contacts: graphene, Ag NW webs, TCOs

Setting the stage

Silicon is the dominating material for solar cells despite many other technologies!



Advantages:
Neither toxic nor rare on earth

State of the art for mono-crystalline silicon

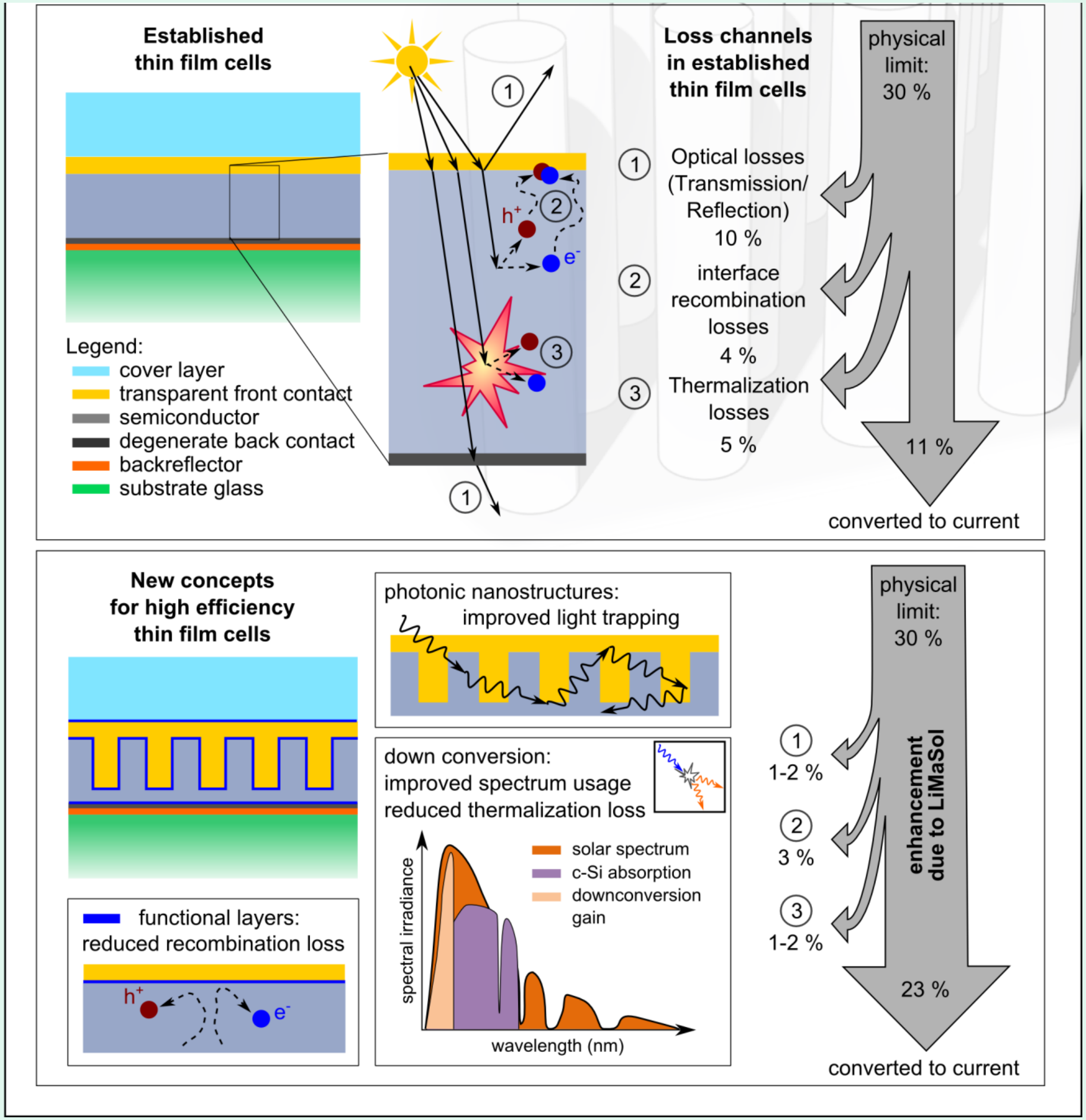
Lab-Cell 25%
(V_{OC}=706mV J_{SC}=42.7mA/cm² FF= 82,8%)

Module 22.9%

Solar cell efficiency tables (version 43)
Green et al. Prog. Photovolt: Res. Appl. 22 (2014)

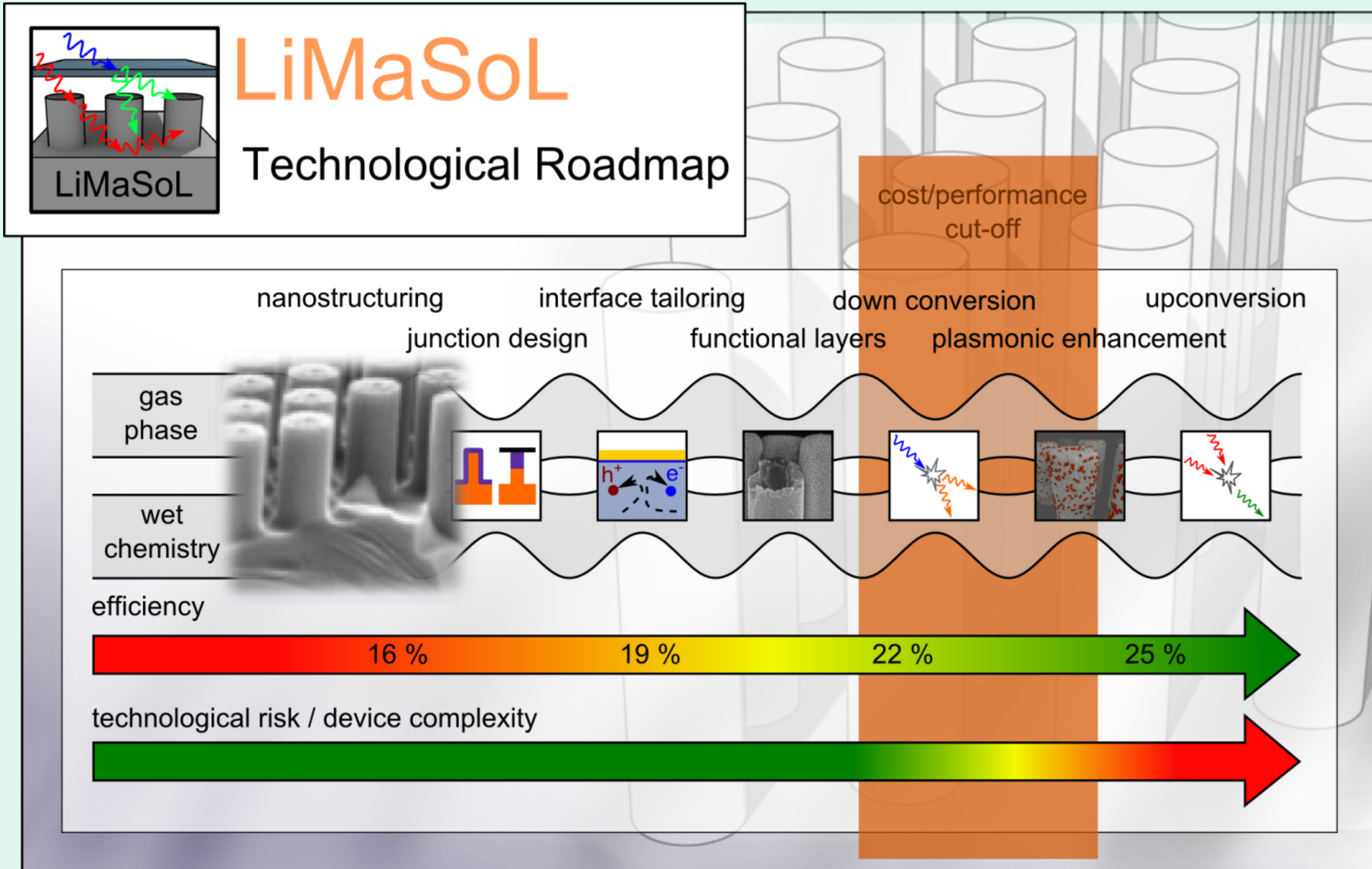
High quality material: silicon (mono-/micro-crystalline) thickness >100µm & high temperature processes needed

Nanostructured thin film solar cell



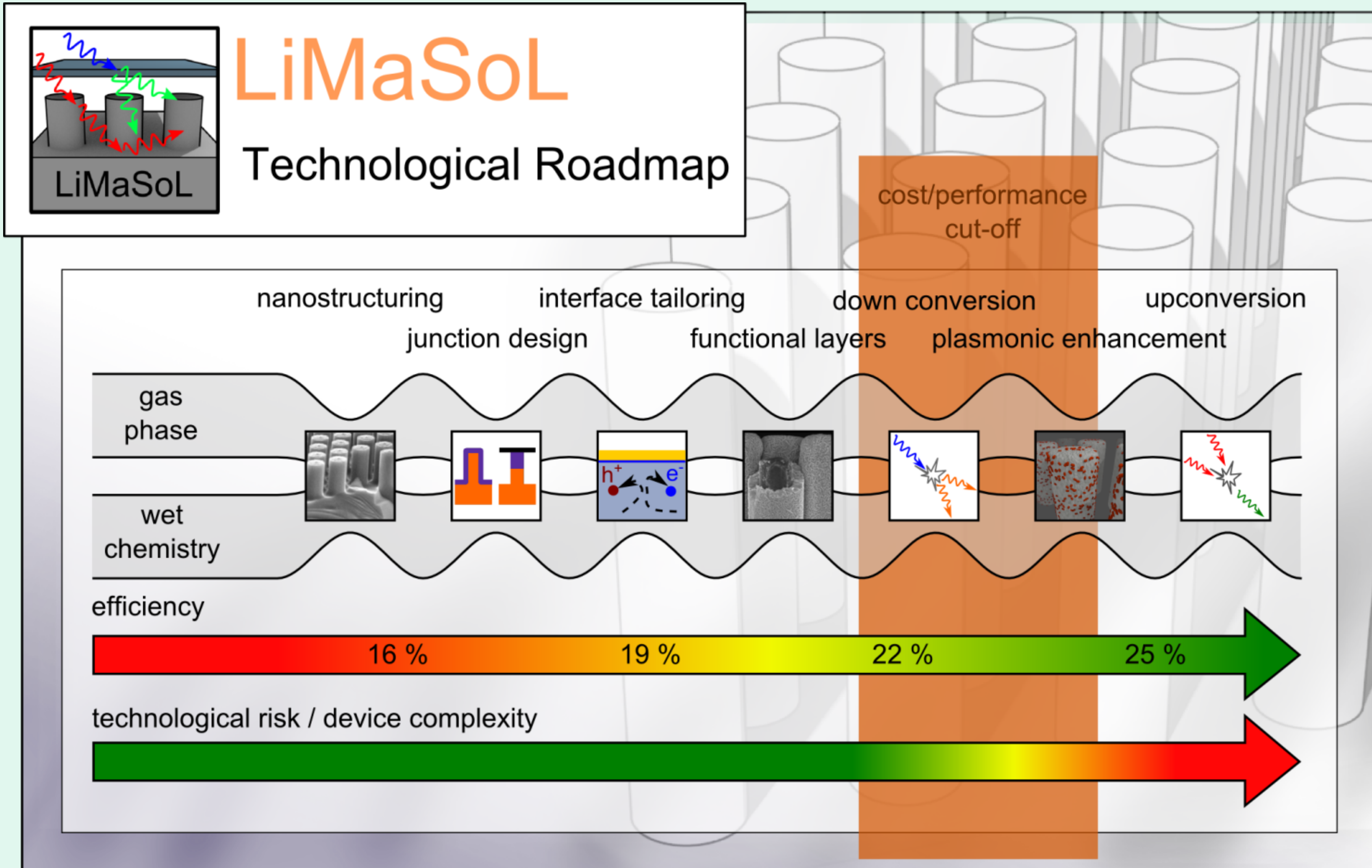
Nanostructured thin film solar cell

Where do we want to go?



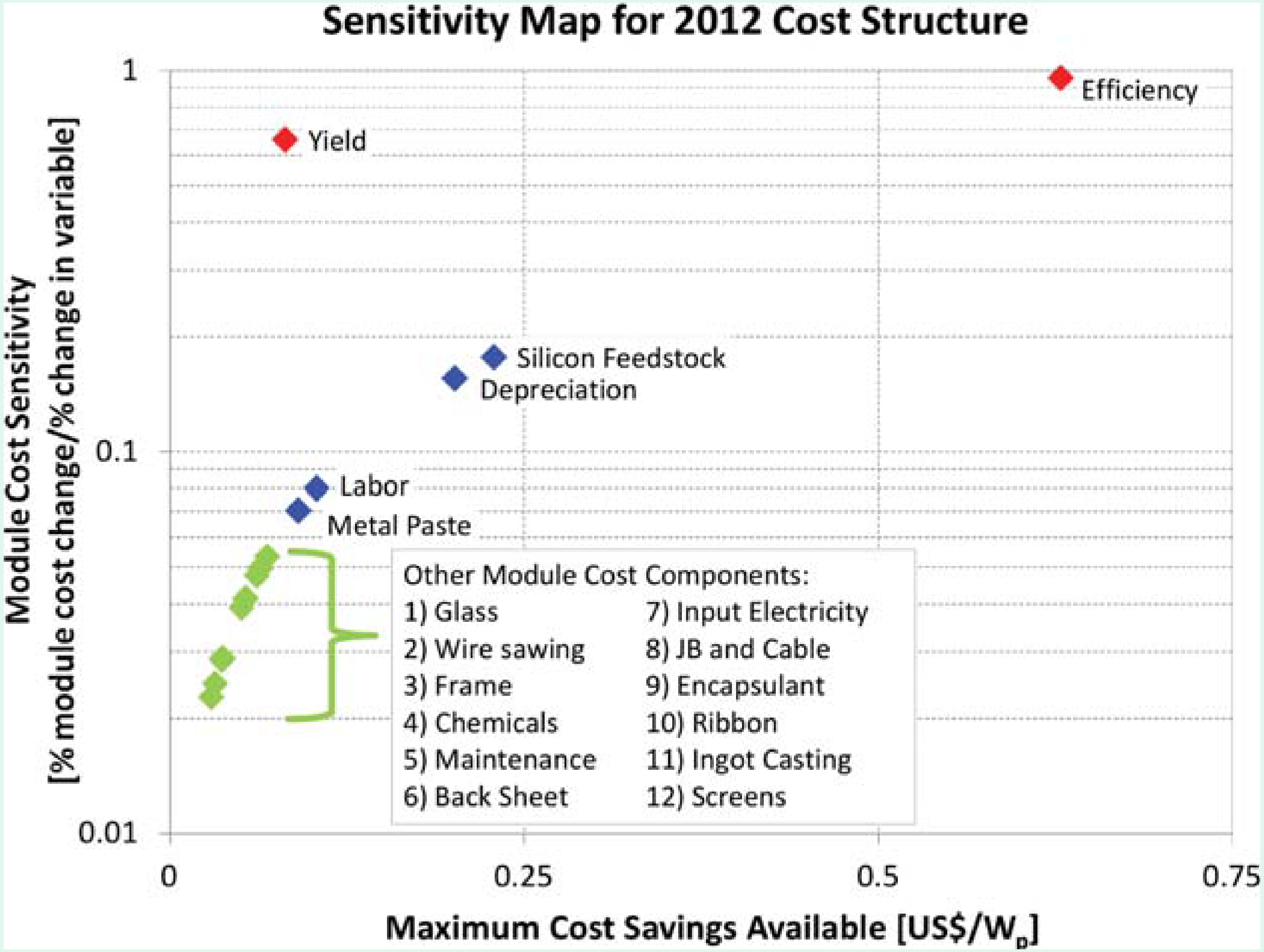
Nanostructured thin film solar cell

Where do we want to go?



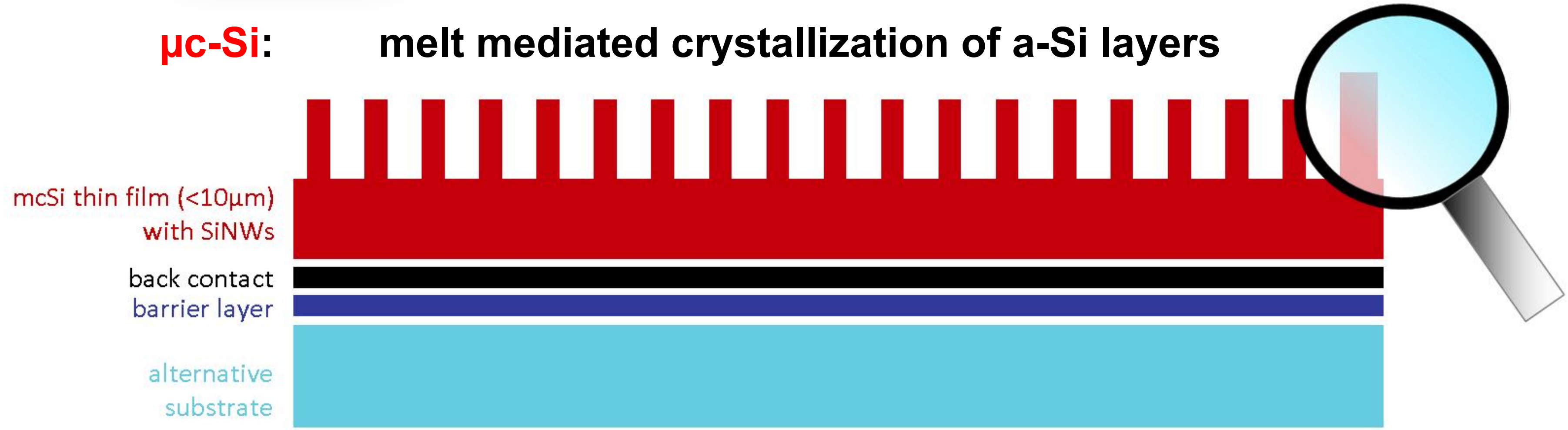
Nanostructured thin film solar cell

Where do we want to go?

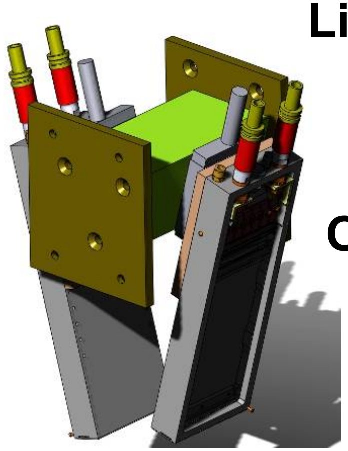


Powell, …, Buonassisi, Energy & Environm. Sci. 2012

μc-Si: melt mediated crystallization of a-Si layers



Line focus diode laser

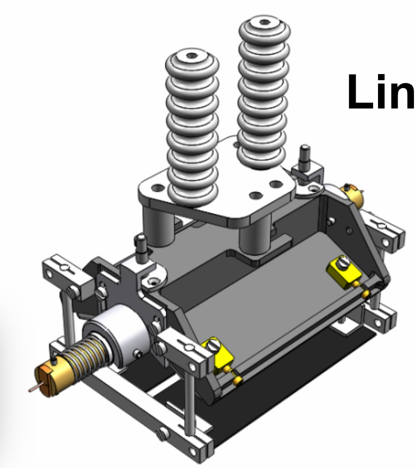


Oclaro, N. Lichtenstein et al.

FP7 high ef solar cell processing by diode lasers

J. Schneider et al., Proceedings of the EU-PVSEV_Valencia-2010, 3BV.3.12 (2010); www.high-ef.eu

Line focus e-beam



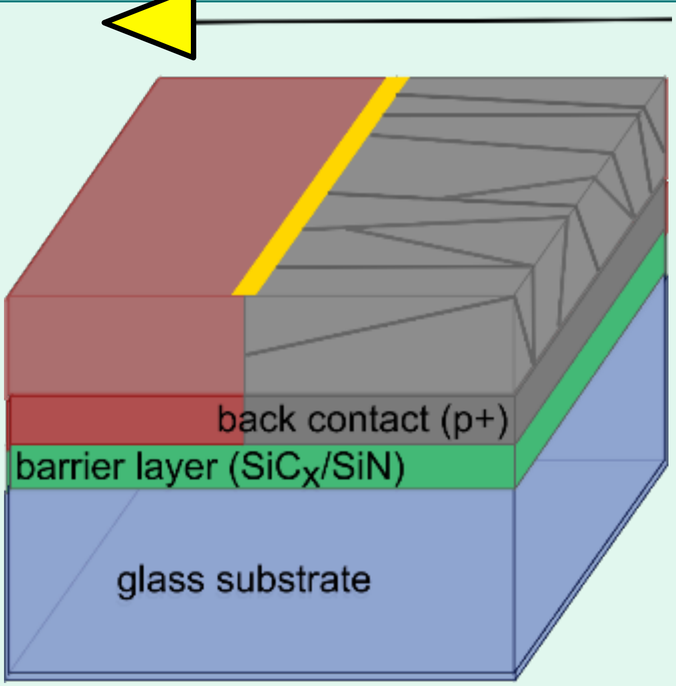
HZB, B. Rech et al.

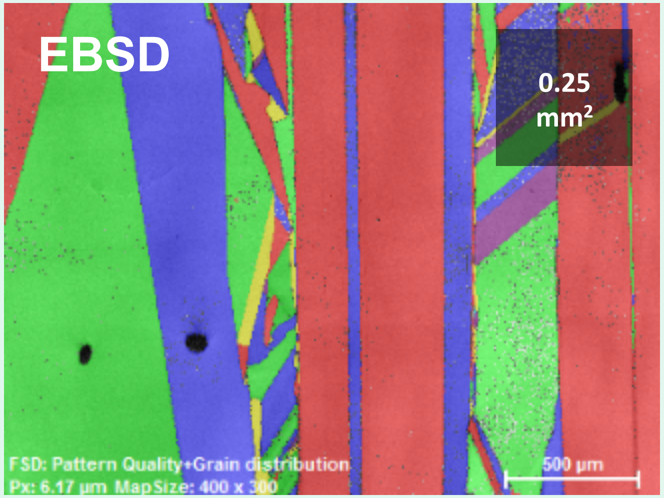
M. Pauli, et al., Rev. Sci. Instrum. 63 (1992) 2288
J.R. Pierce, J.Appl.Phys. 11 (1940) 548

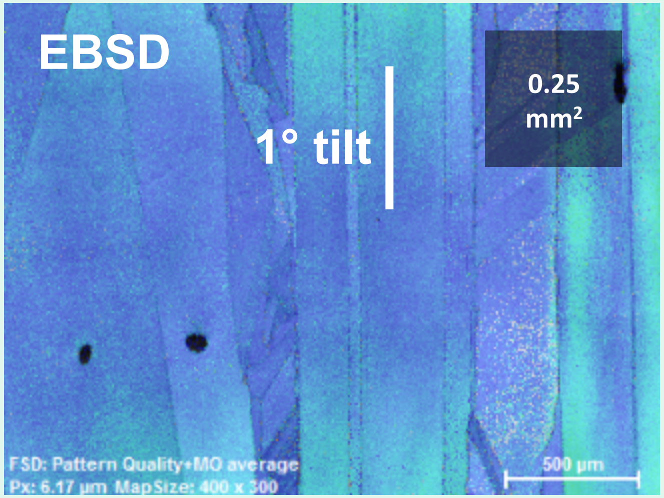
Multicrystalline thin film silicon

Deposition of amorphous silicon on glass
+ line focused e-beam / laser crystallization

Scanning e-beam / laser line: melting a-Si





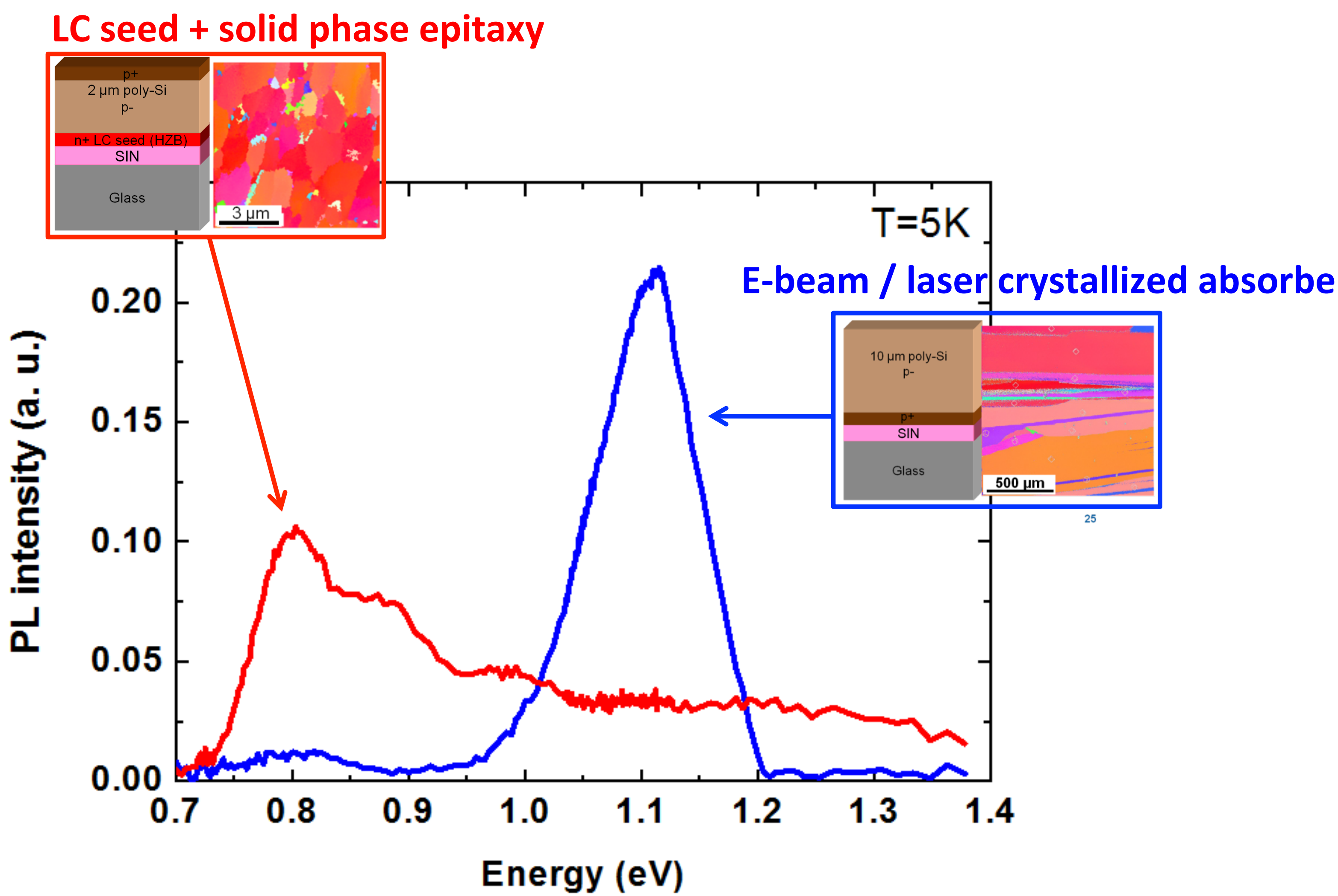


Large grains with small misorientation

B. Rech, et al. HZB

D. Amkreutz, et al. Prog. Photovolt. Res. Appl. 19, p. 937, 2011

Photoluminescence (PL)



D. Amkreutz, et al. Prog. Photovolt. Res. Appl. ***19****, p. 937, 2011*

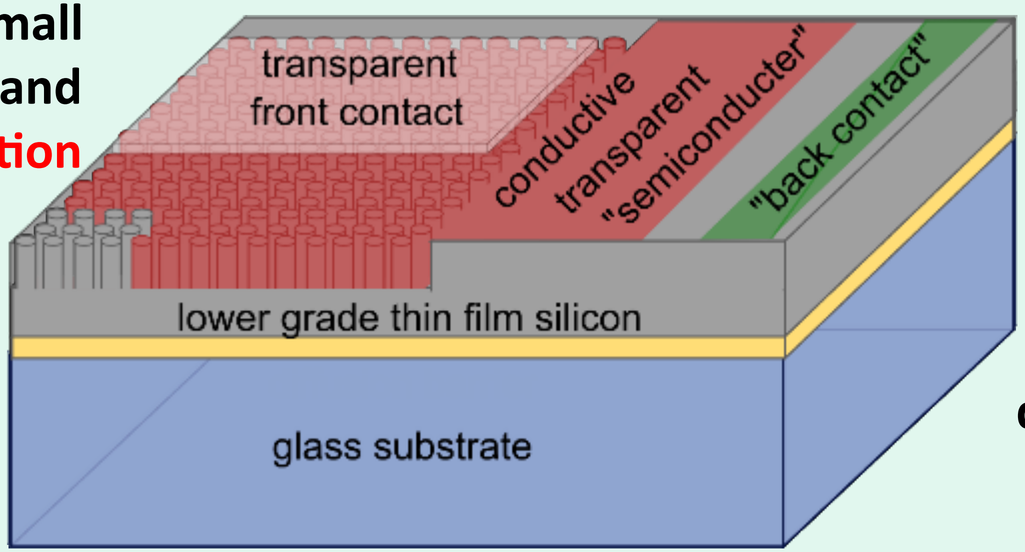
Nanostructured thin film solar cell

Where do we want to go?

cheap novel contact materials

Different cell concepts:
Hetero-junction with low T processing
Homo-junction by diffusion

nanostructures for small reflection and high absorption

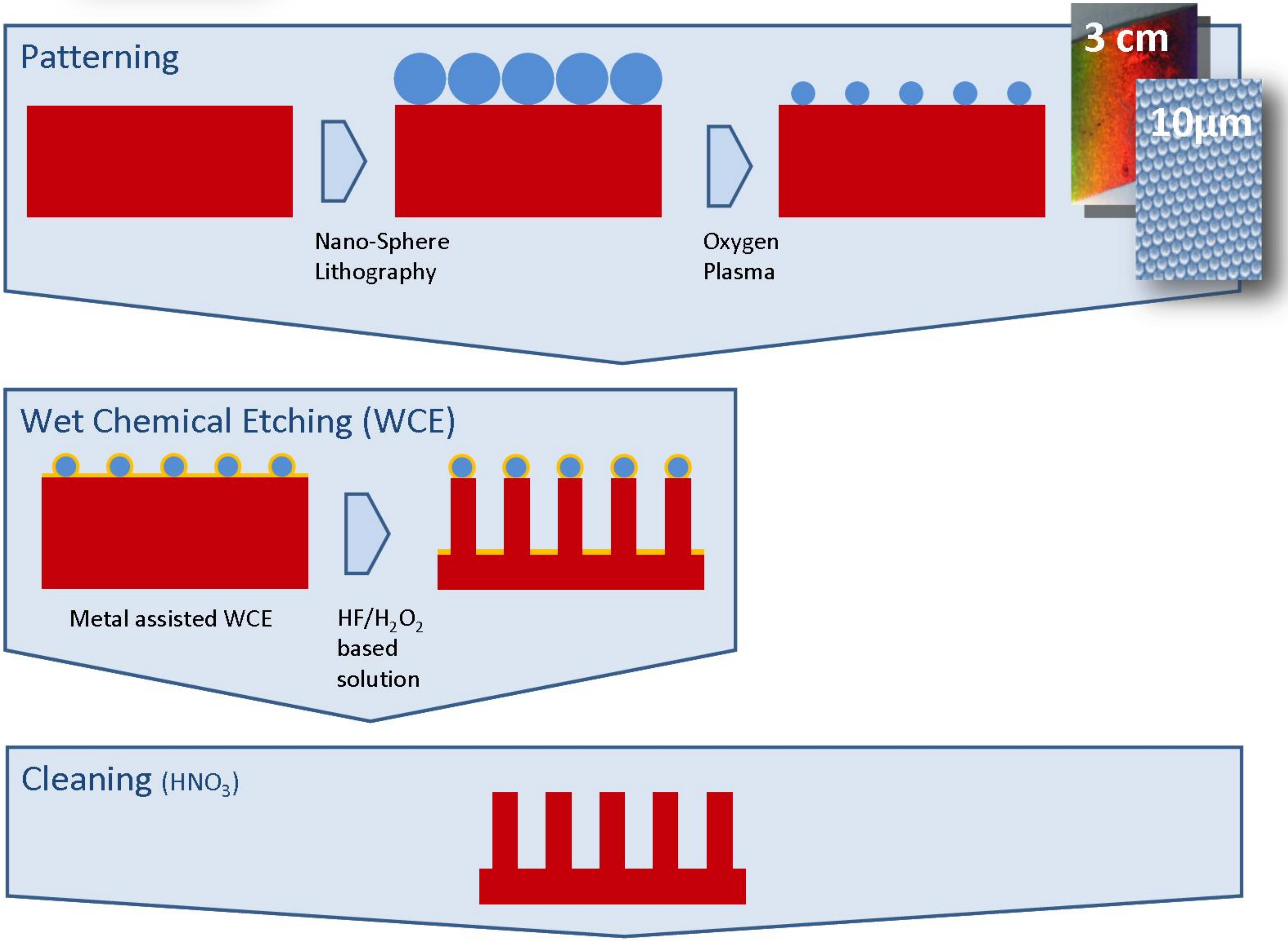


thin film using less material + low grade Si because of short diffusion distances

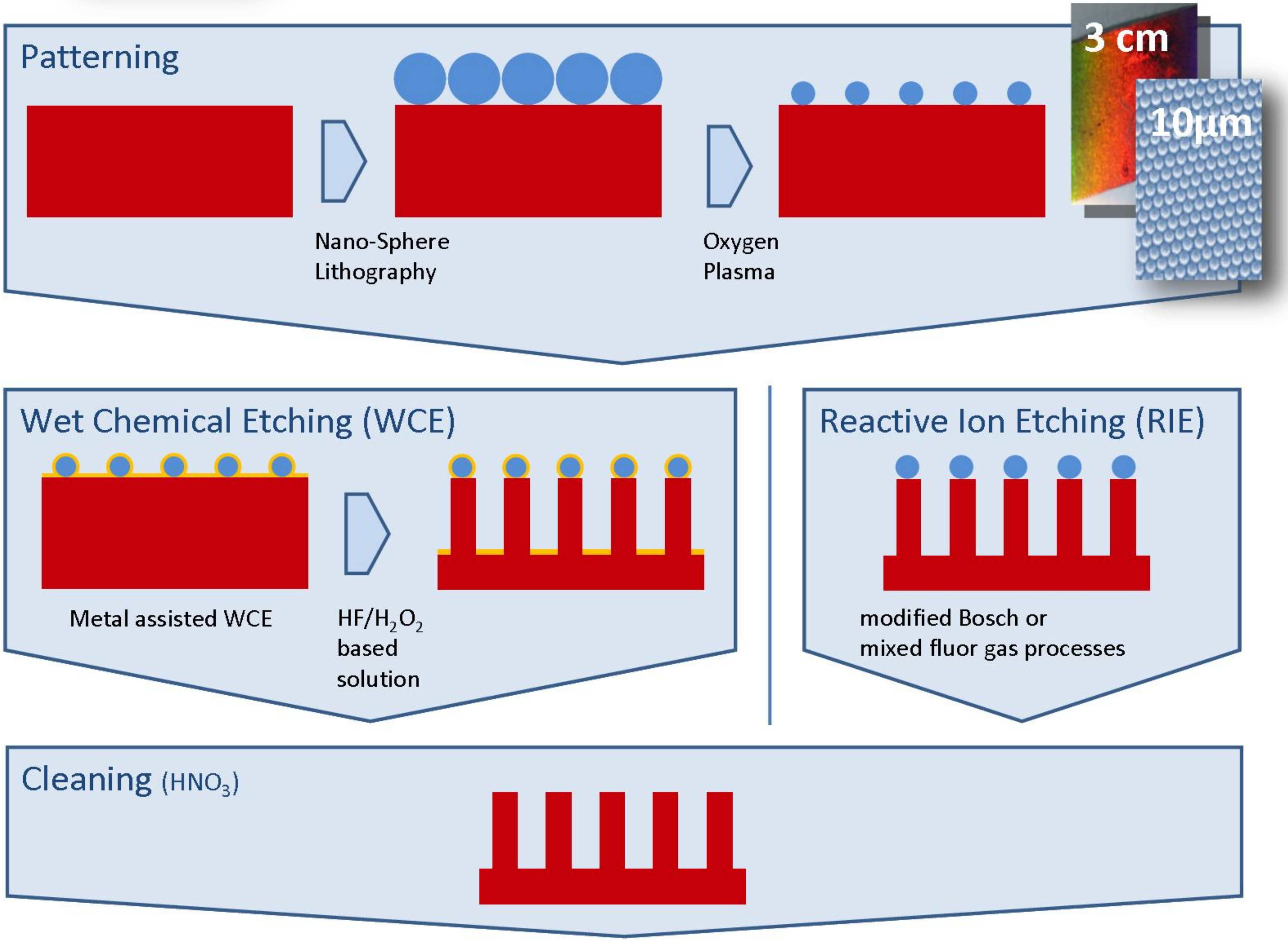
Goal:
nanostructured, silicon based, cheap & efficient (>15%) thin film solar cell concepts required

Sivakov et al. Nano Lett., 4 (2009)

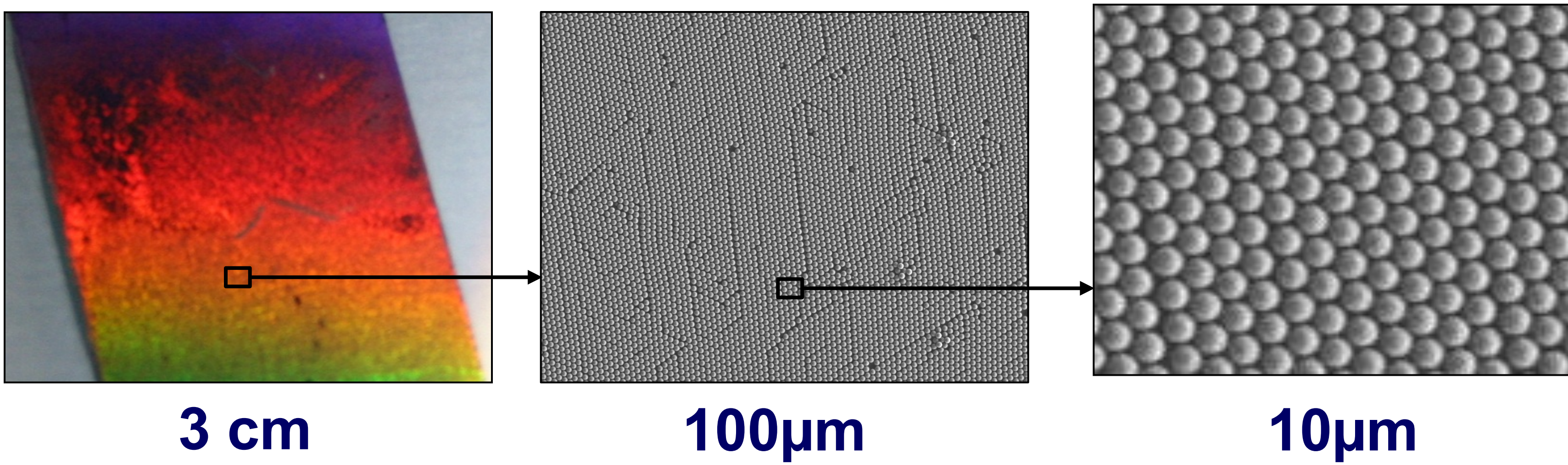
Large area nanosphere lithography



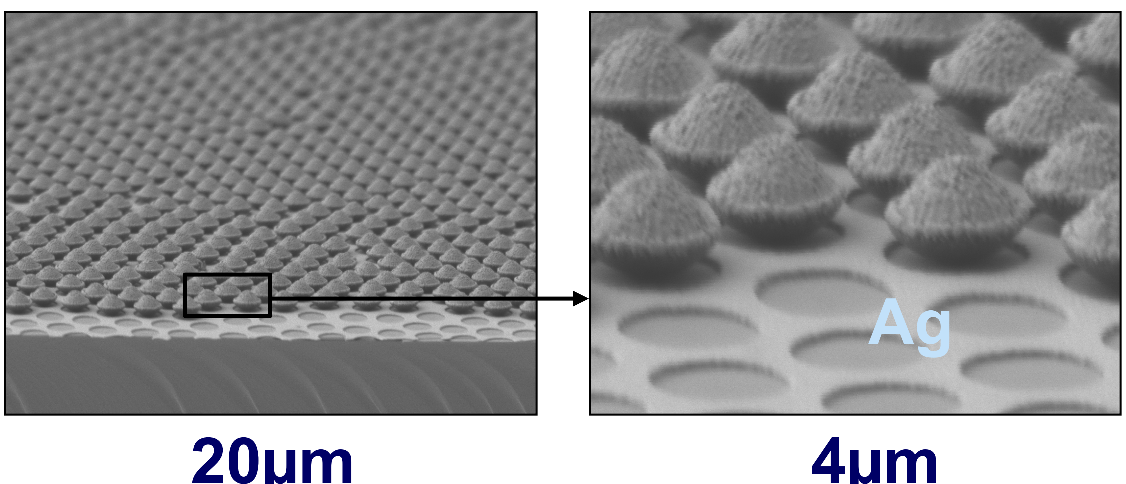
Large area nanosphere lithography



Ordered arrangement of PS-nanospheres in Langmuir trough over large areas



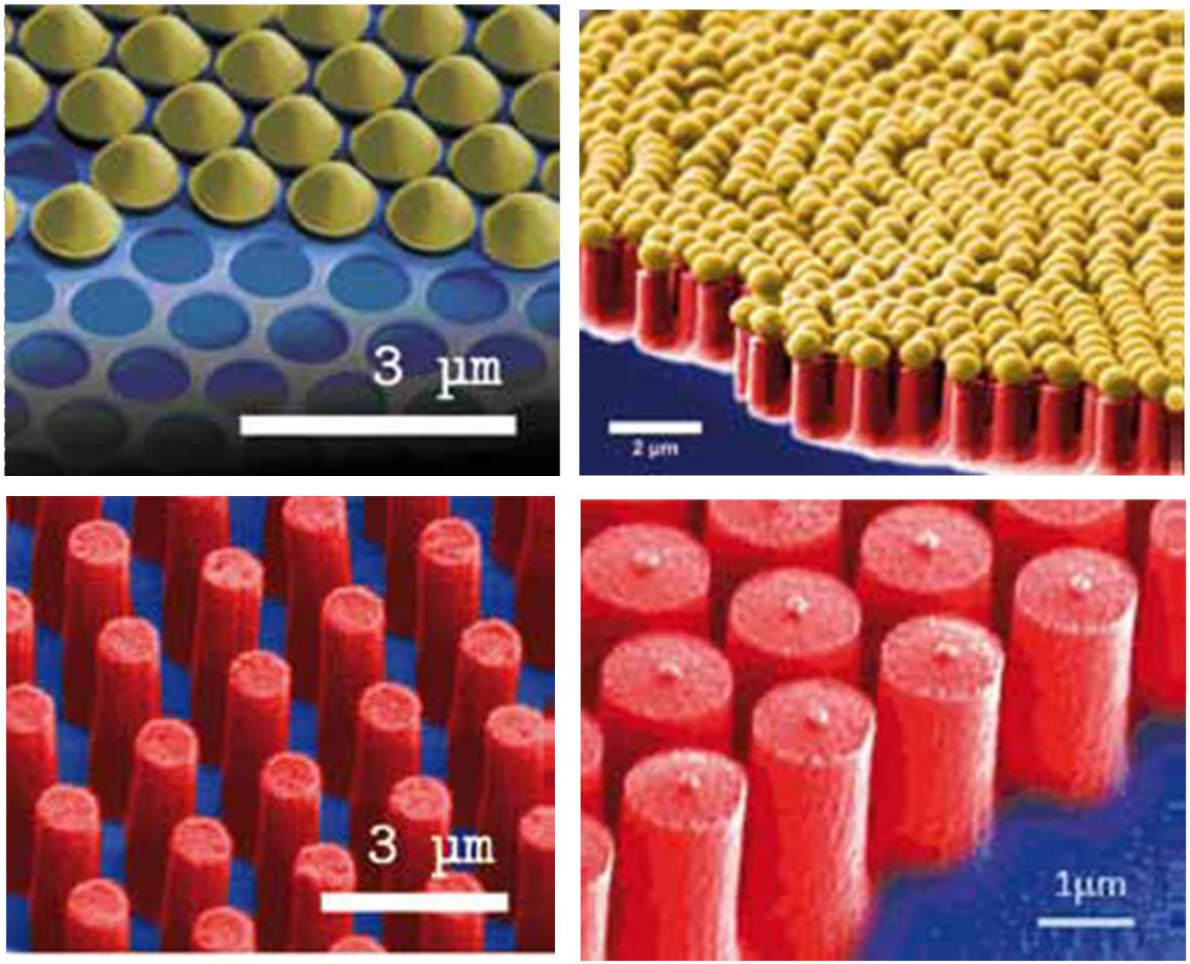
K.-Q. Peng, et al.
Adv. Mater. 14, 1164 (2002)



HF/H_2O_2 solution:
Metal (Ag) enhanced etching of Si

Langmuir Blodget densification of PS spheres

Wet chemical etching | dry etching



Si wafer | mcSi layer

Dry etching with combined Bosch / cryo process in Reactive ion etching (RIE) equipment:

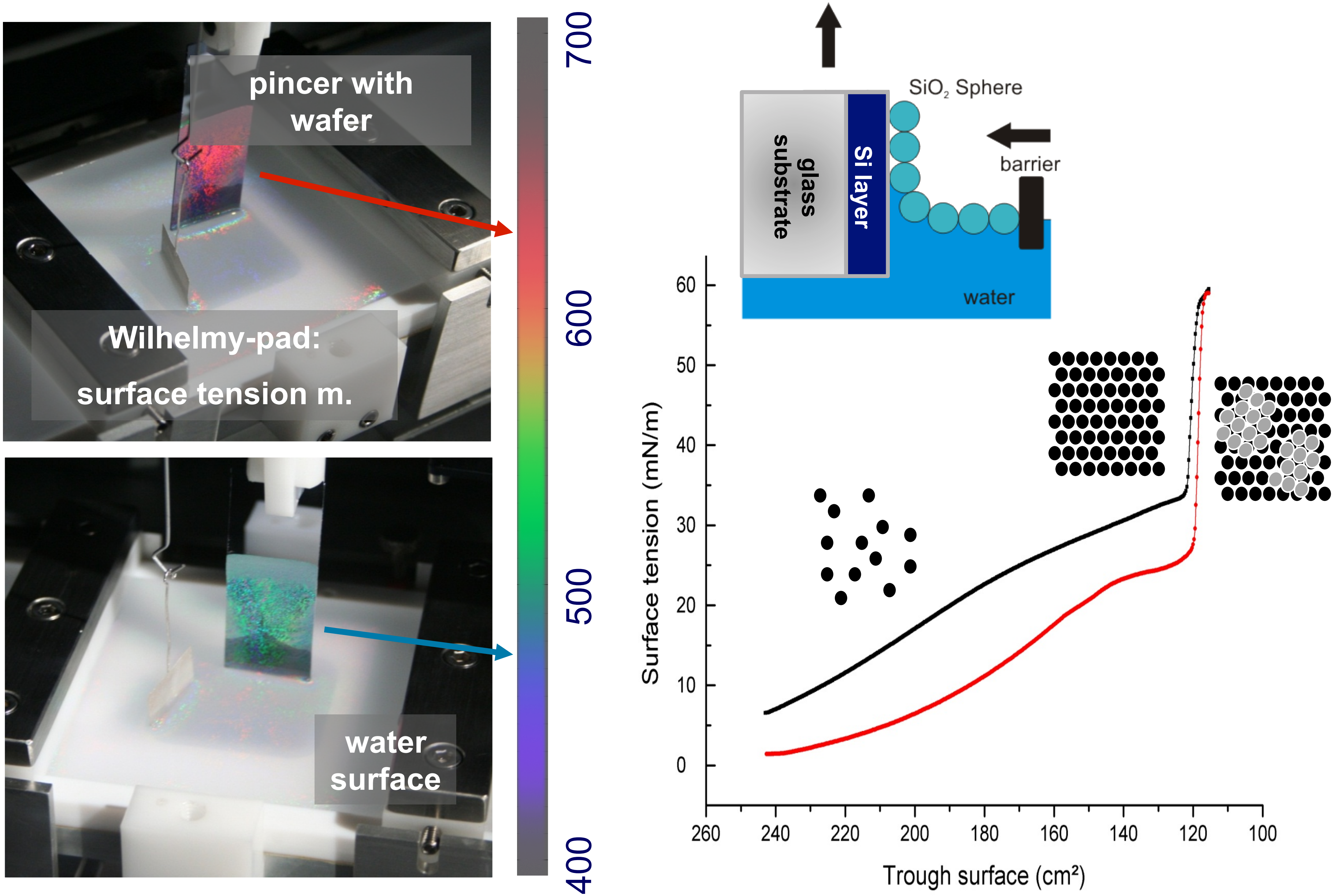
Etching of Si:

O_2:
- reacts with SiF
- form a passivation layer

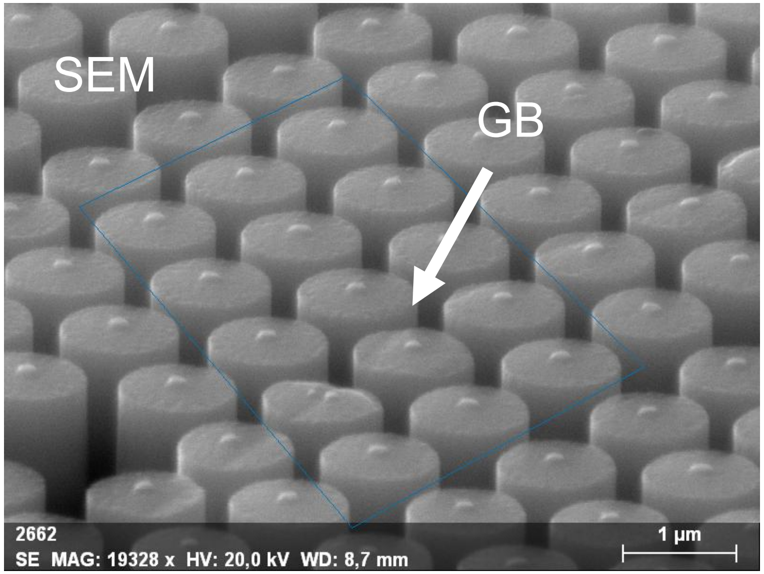
C_4F_8:
- physically etches Si
- in bombardment direction

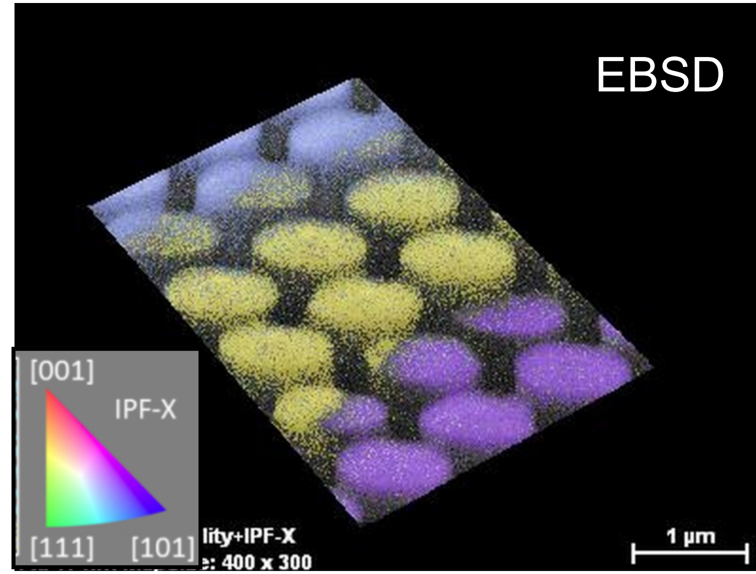
SF_6:
- physically & chemically etches Si
- reacts to form SiF_4 gas

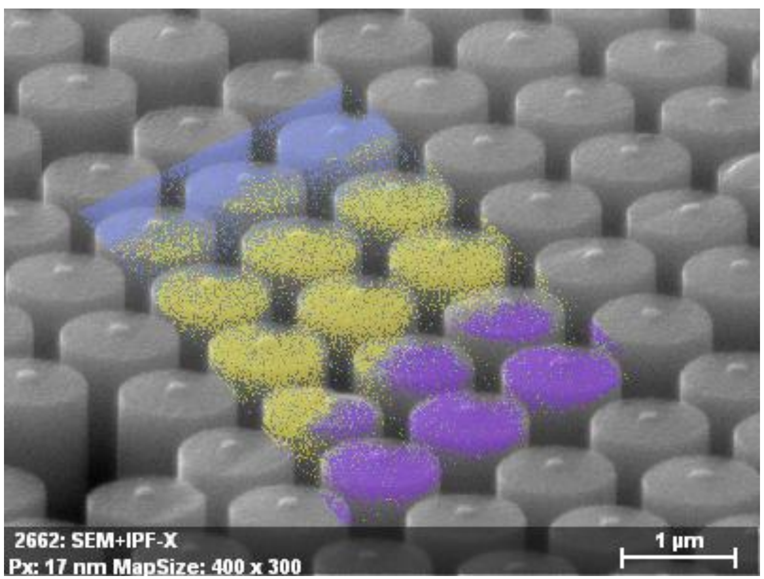
Langmuir Trough densification of PS spheres

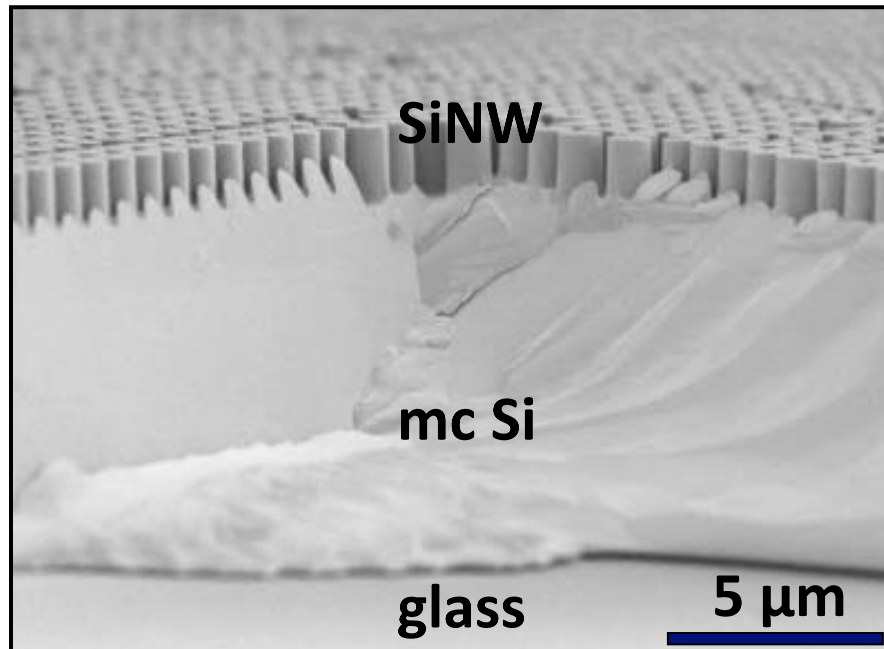


Electron Backscatter diffraction (EBSD)

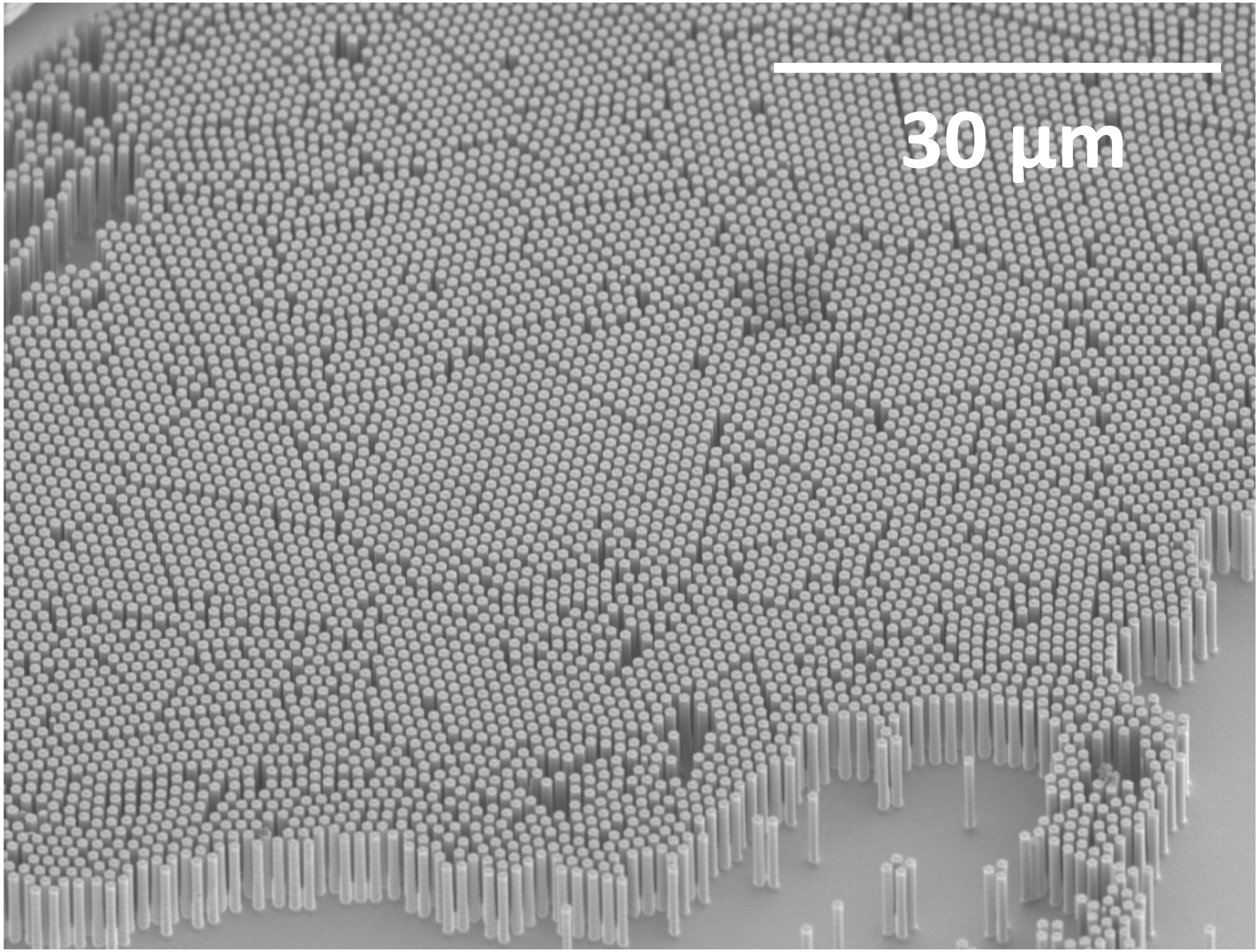




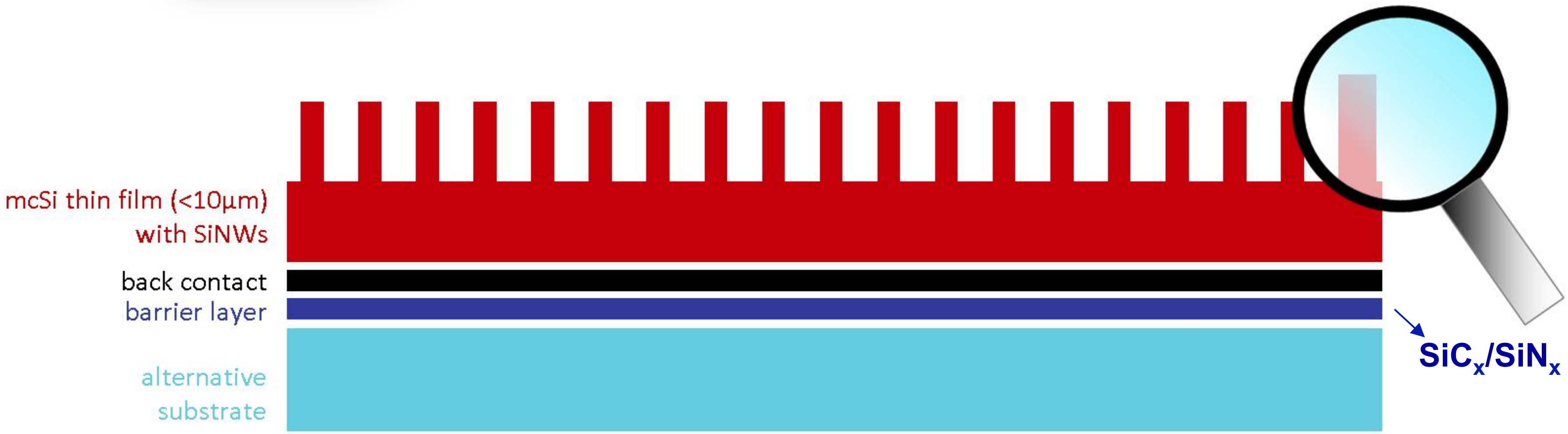




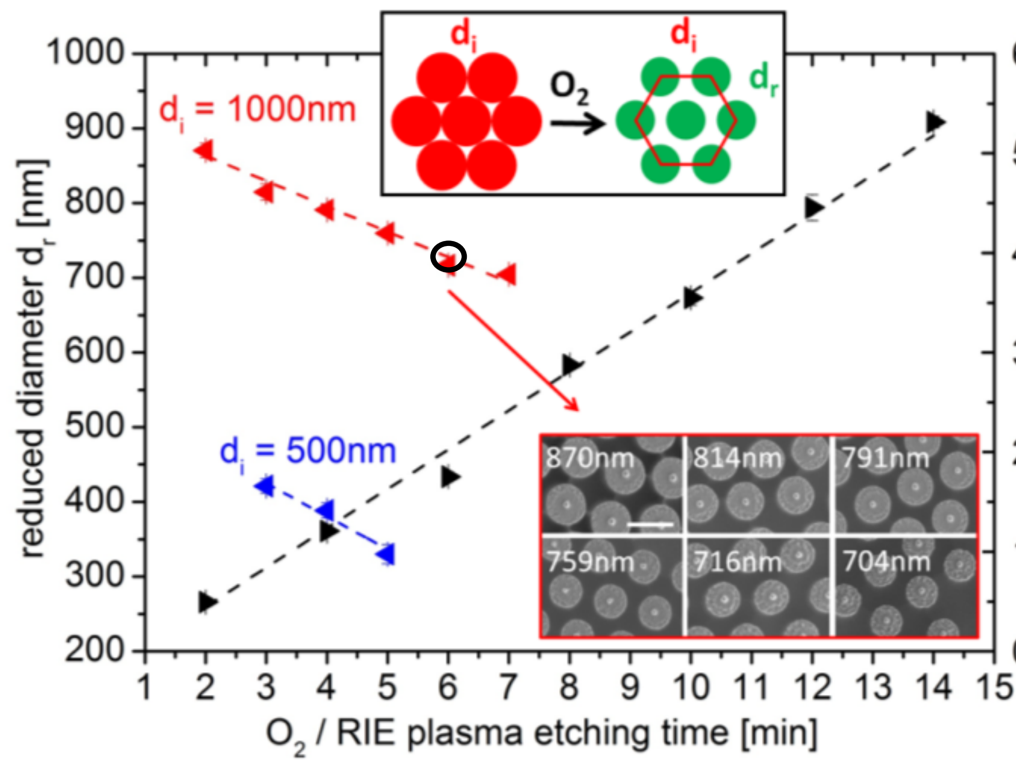
Controlled RIE etching of mc-SiNWs



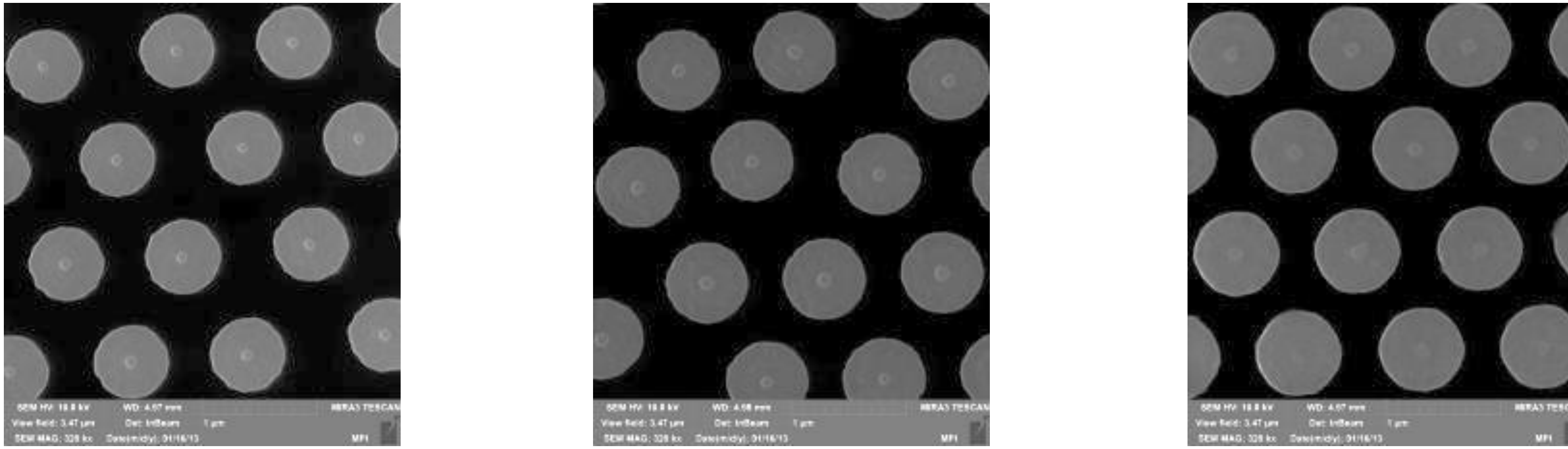
Nano-sphere lithography – controlled SiNWs



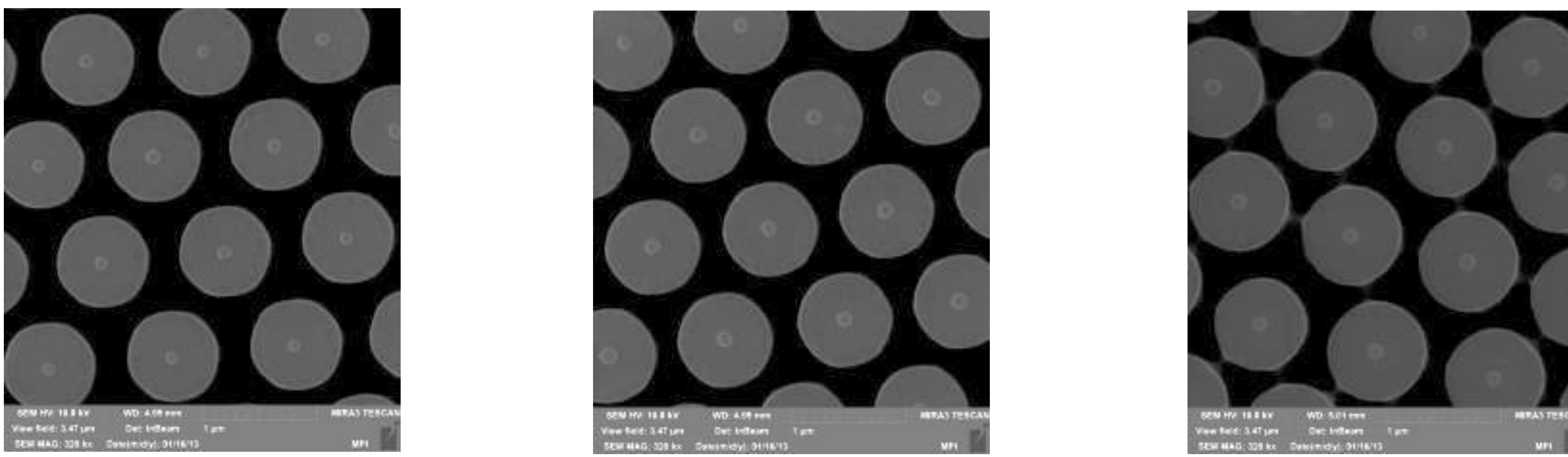
Length: 2.3 ± 0.1µm
Diameters: 737 ± 2nm



Controlled RIE etching of Si NWs/glass



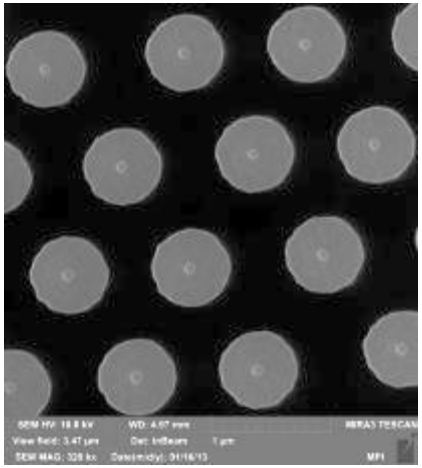
r = 310 350 365 nm



r = 395 405 425 nm

→ Controlling (dis)order
+/- 2nm diameter variations

Controlled RIE etching of Si NWs/glass

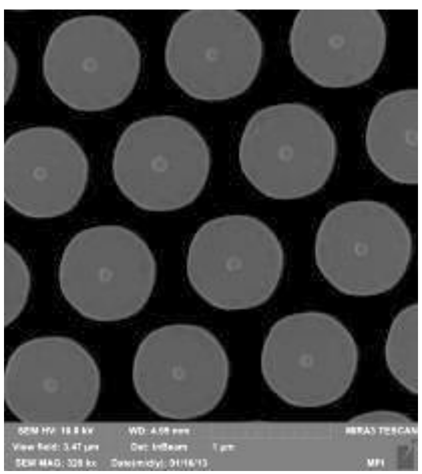


r = 310 350 365 nm

TAILORED DISORDER

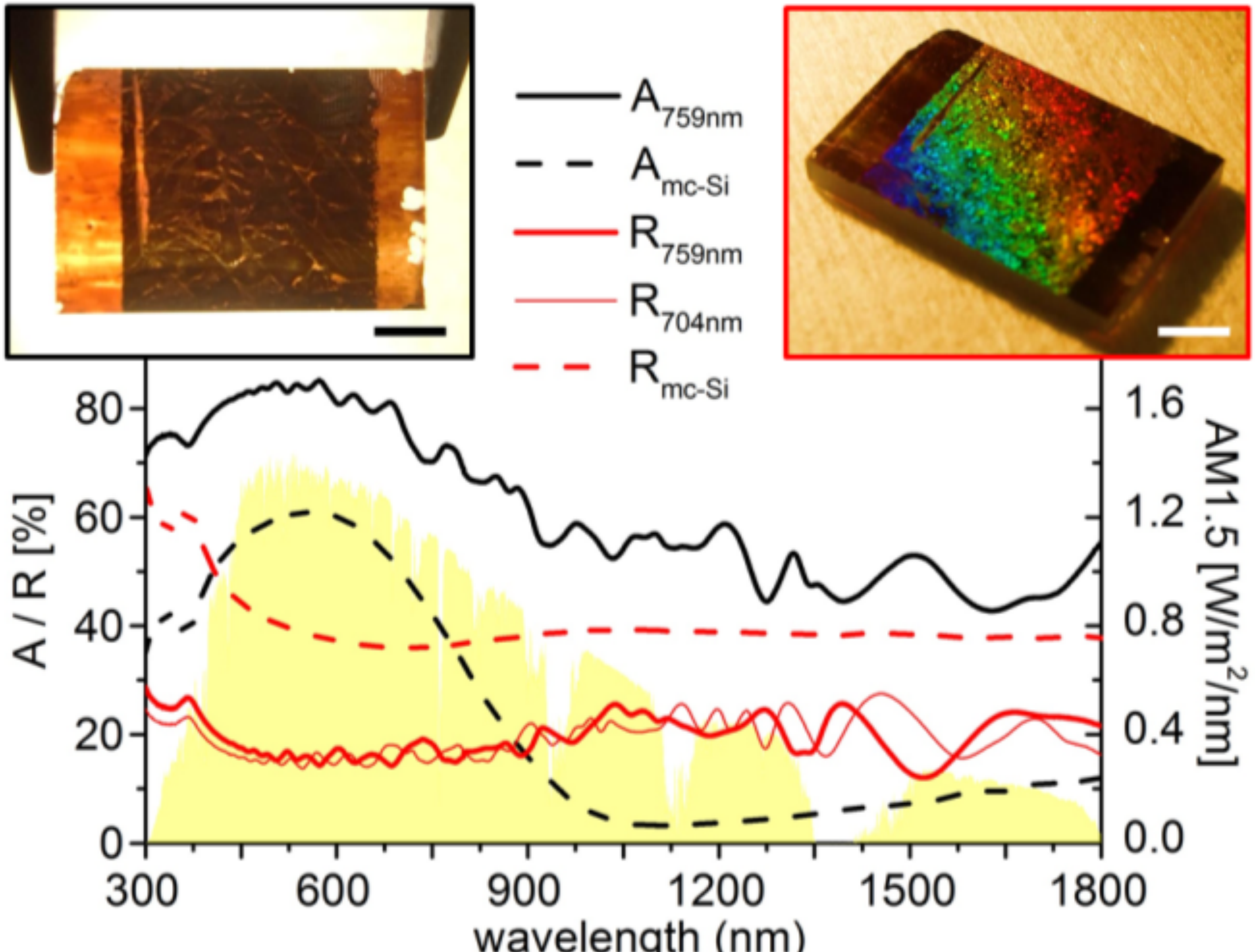
A science- and engineering-based aproach to materials design for advanced photonic applications | SPP 1839

DFG SPP Tailored Disorder:
Submissions of proposals 01/ 2015



r = 395 405 425 nm

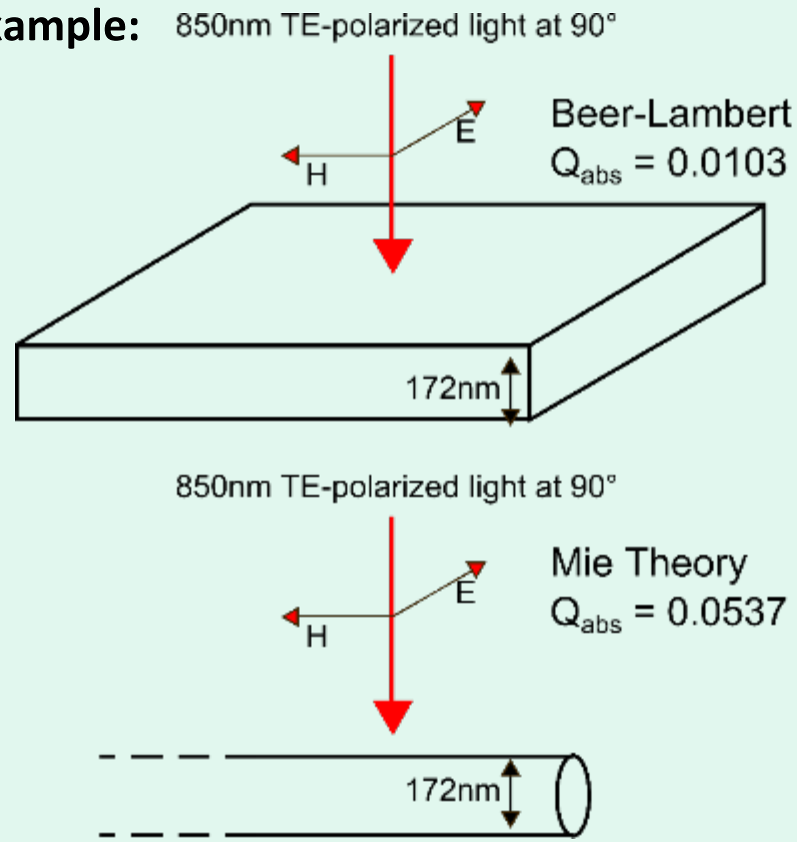
Integrating sphere measurements

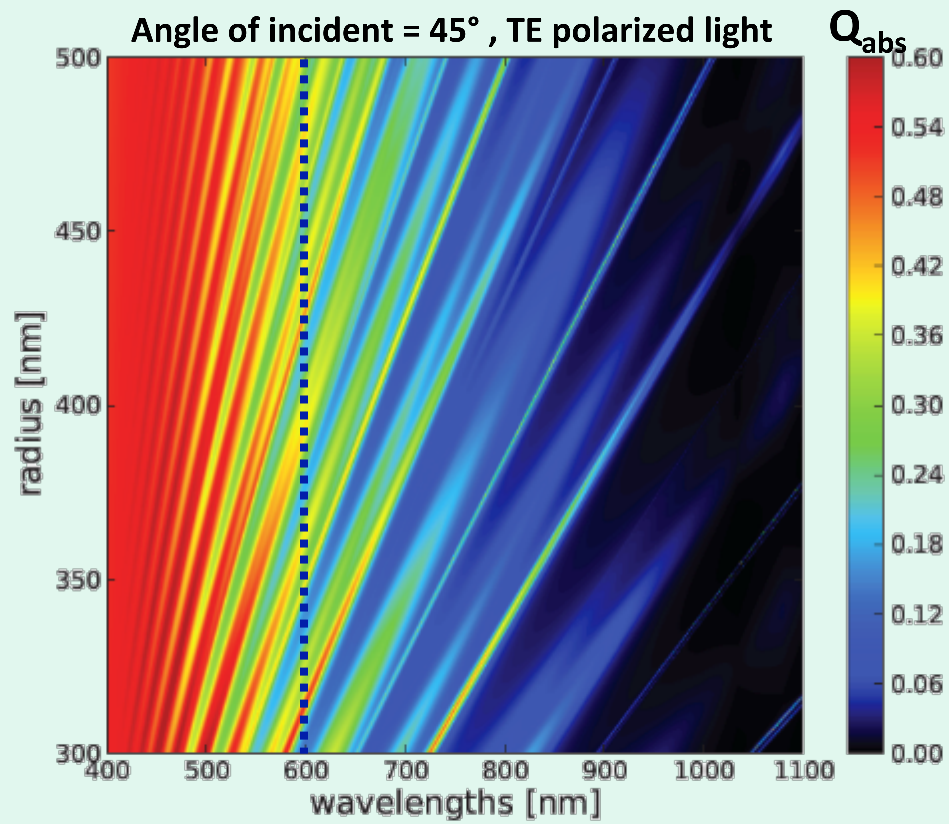


Resonances in Silicon Nanowires

Analytical calculation of scattering and absorption efficiencies with Mie theory for infinitely long single nanowires

Example:

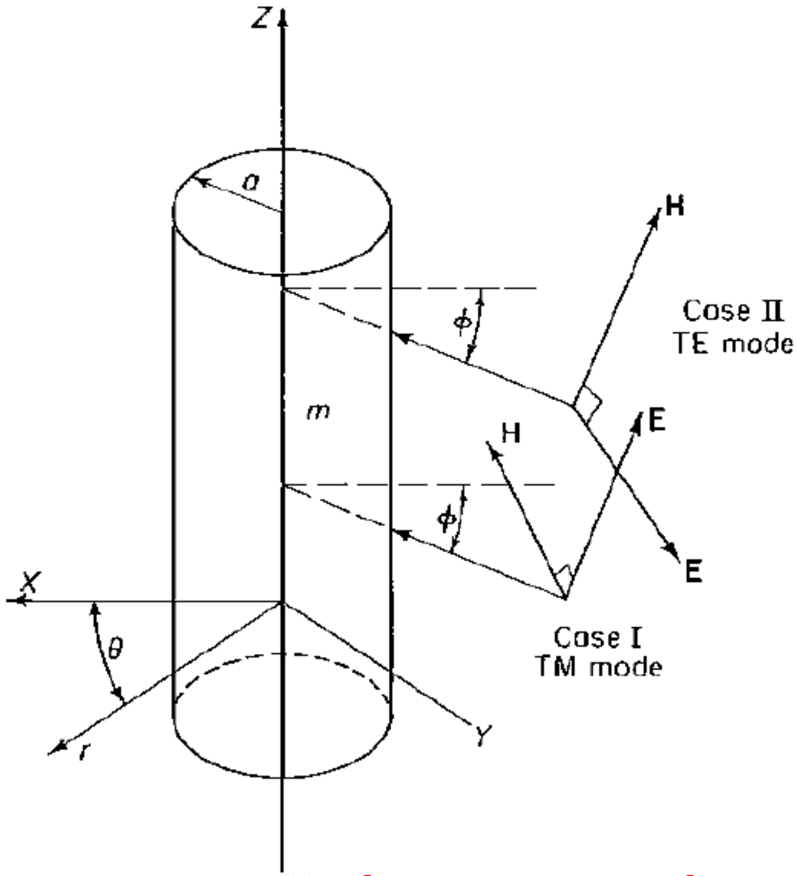




resonant absorption enhancement

G. Brönstrup, et al. ACS Nano 4, p. 7113-7122, 2010

Mie scattering of Si NWs



$$a_i = \frac{\tilde{n}J_i(\tilde{n}x)J_i'(x) - J_i'(\tilde{n}x)J_i(x)}{\tilde{n}J_i(\tilde{n}x)H_i^{(1)\prime}(x) - J'_i(\tilde{n}x)H_i^{(1)}(x)}$$

$$b_i = \frac{J_i(\tilde{n}x)J_i'(x) - \tilde{n}J_i'(\tilde{n}x)J_i(x)}{J_i(\tilde{n}x)H_i^{(1)\prime}(x) - \tilde{n}J'_i(\tilde{n}x)H_i^{(1)}(x)}$$

$$x = \frac{2\pi}{\lambda}\frac{d}{2}$$

$$\tilde{n} = n + ik$$

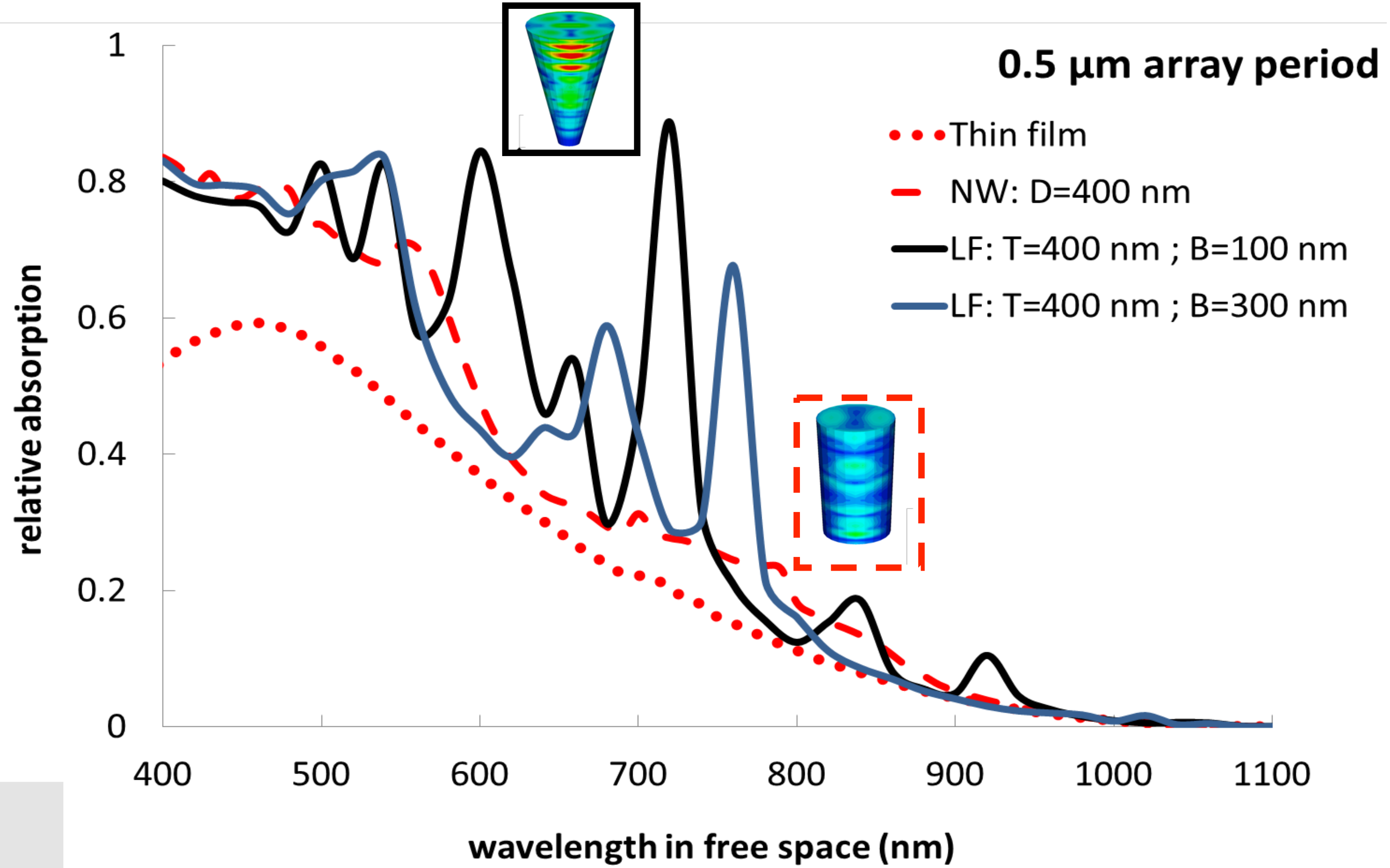
scattering cross sections

$$Q_{\text{sca,TM}} = \frac{2}{x}\left[|b_0|^2 + 2\sum_{i=1}^{\infty}|b_i|^2\right]$$

$$Q_{\text{sca,TE}} = \frac{2}{x}\left[|a_0|^2 + 2\sum_{i=1}^{\infty}|a_i|^2\right]$$

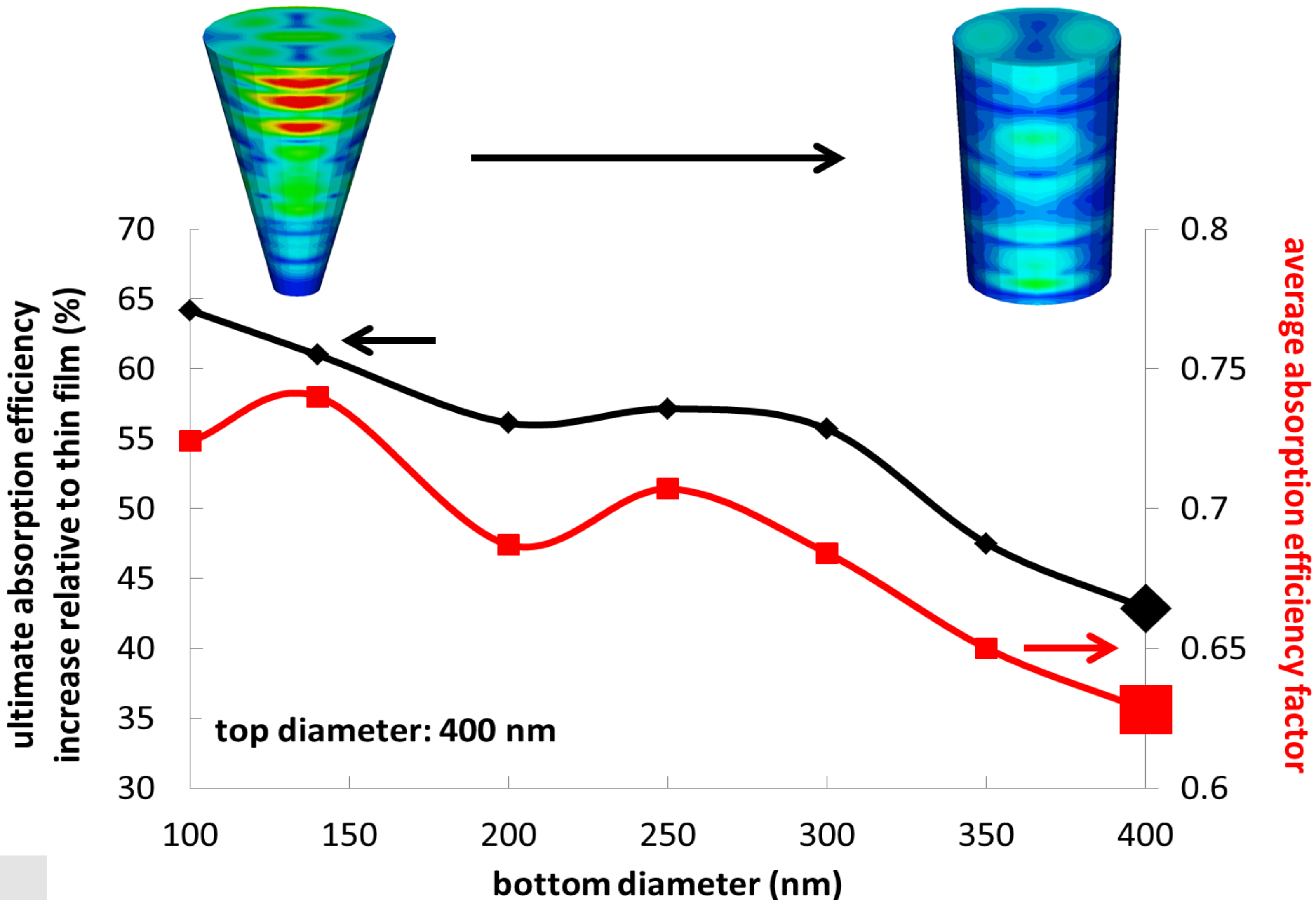
M. Kerker, The Scattering of Light. Academic Press Inc., New York, 1969

Absorption enhancement in optimized geometries



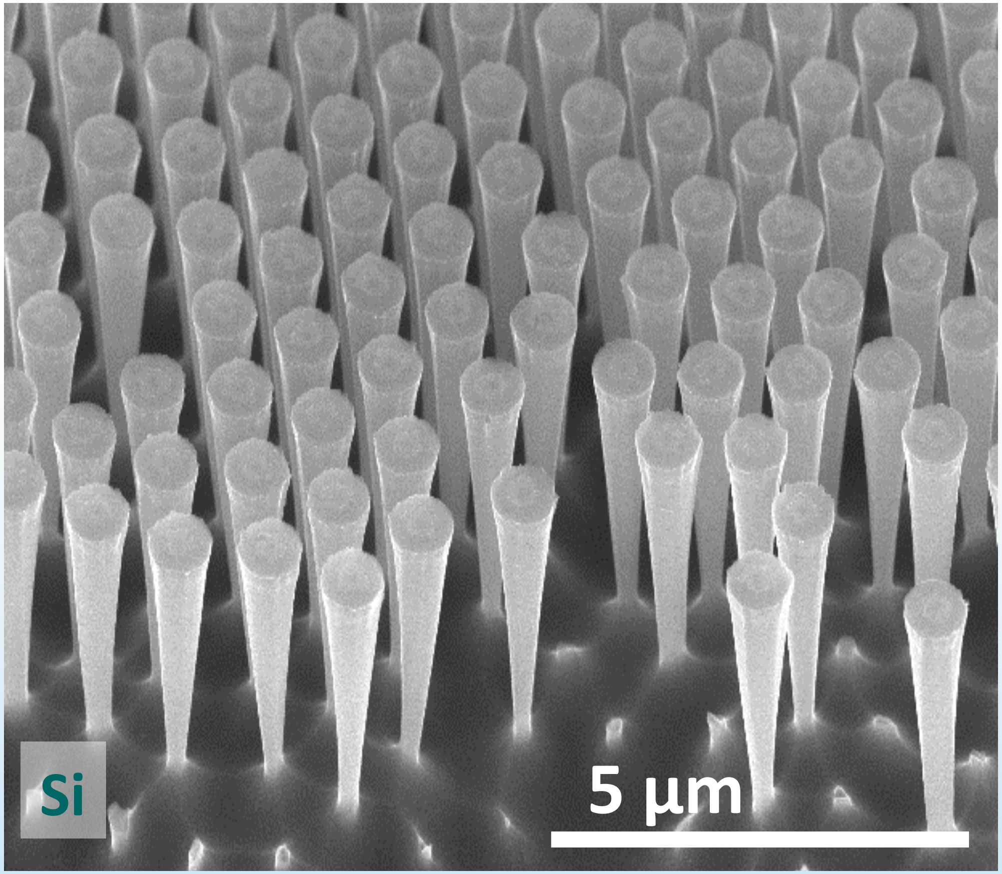
Shalev et al. Nature Scientific Reports in review (2014)

Absorption enhancement in optimized geometries



Shalev et al. Nature Scientific Reports in review (2014)

Si light funnels



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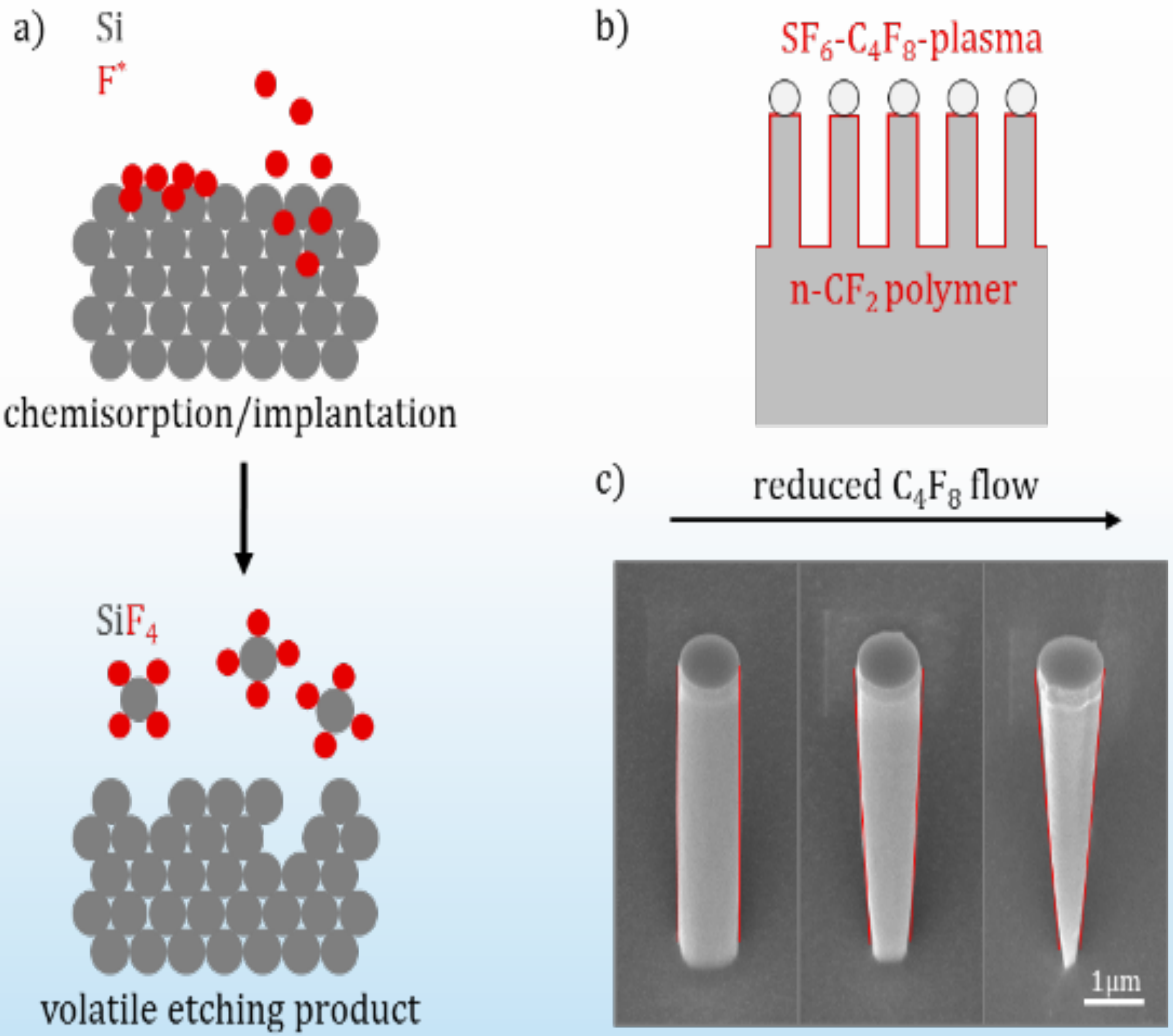
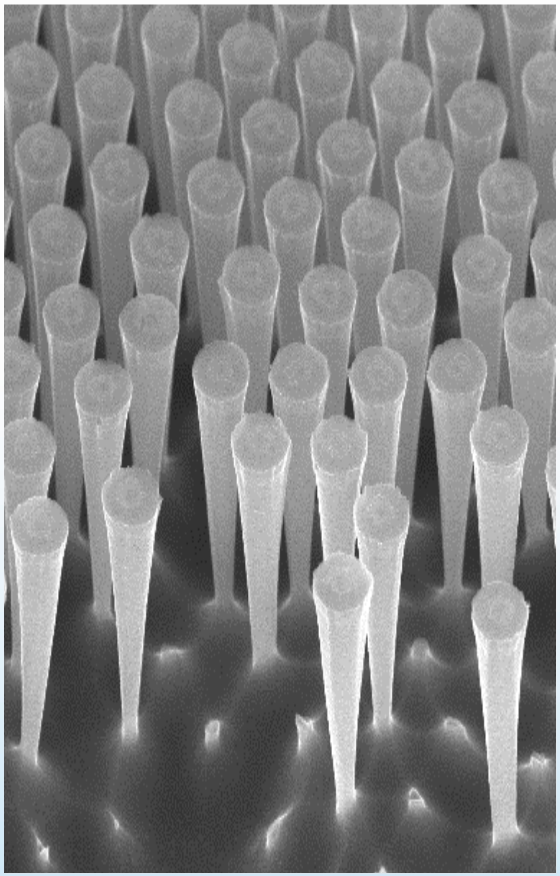
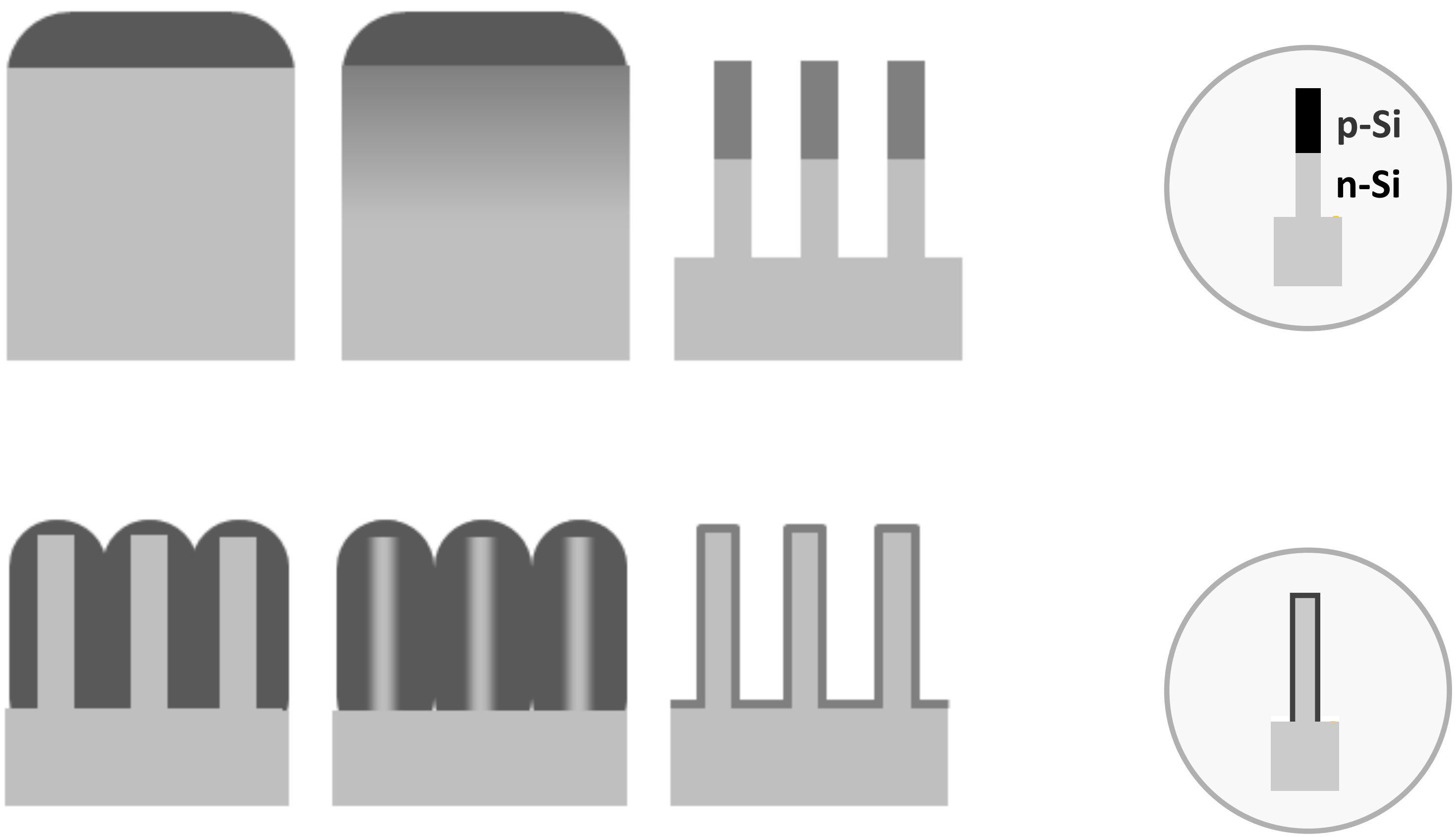


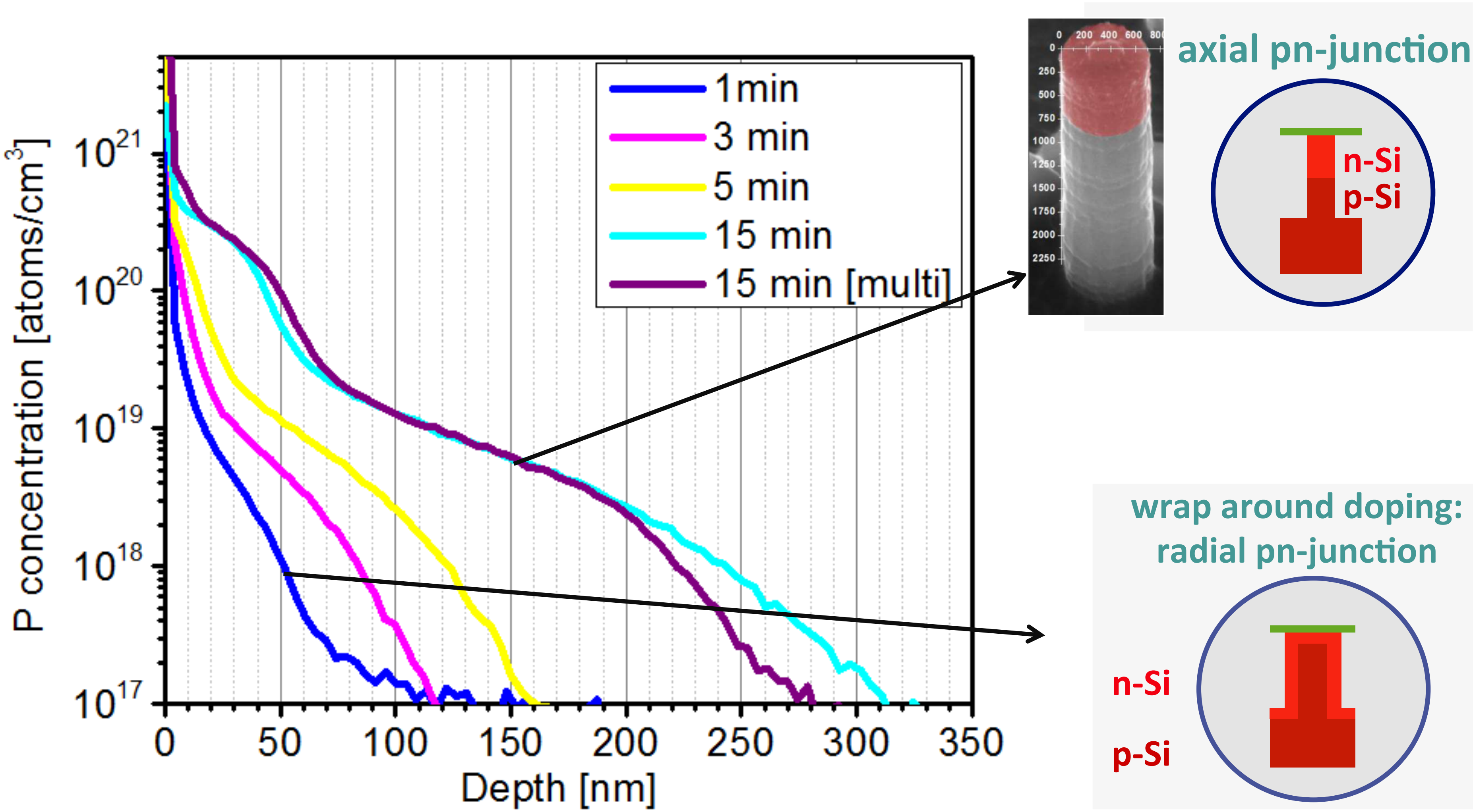


Si NW device concepts

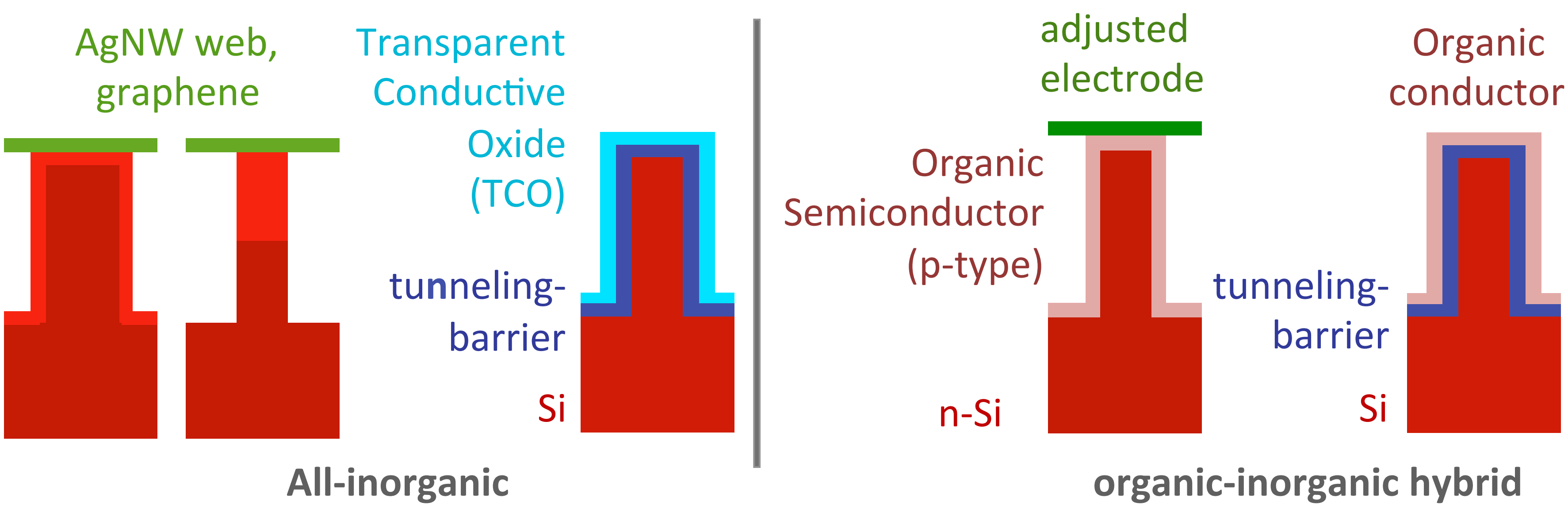
- formation of radial and axial p-n junctions in Si nanowires n / diffusion

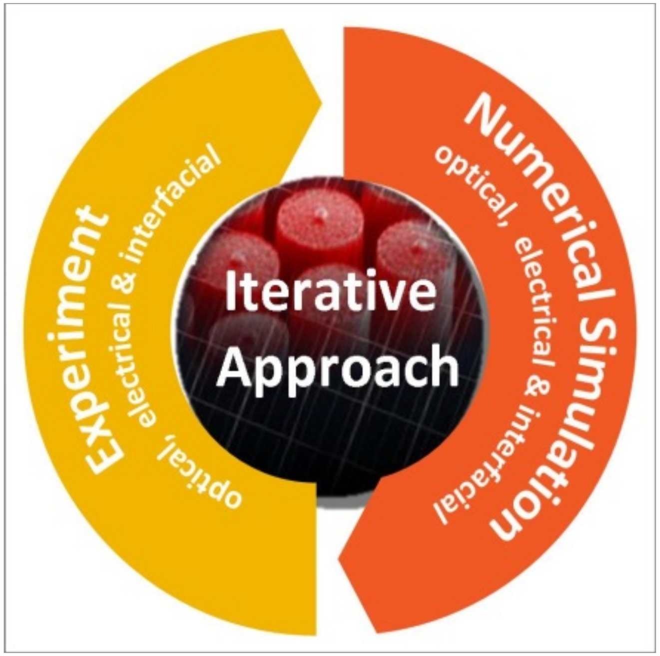


Spin on doping: SIMS



Si NW on glass platform





JCMsuite solves:

- **Maxwell's equations by advanced finite element technologies to obtain the electromagnetic near-field distribution in the illuminated 3D device**

Sentaurus TCAD solves e.g.

- **Poisson's equation**
- **carrier continuity equation**
- **the drift-diffusion transport model**
- **the energy balance transport model**

Materials parameters to be considered:
doping dependent

- **mobility**
- **bandgap narrowing**

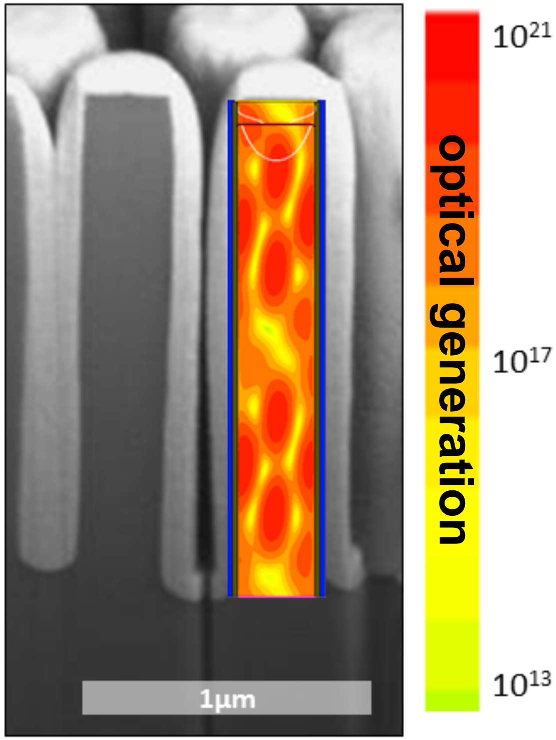
temperature dependent

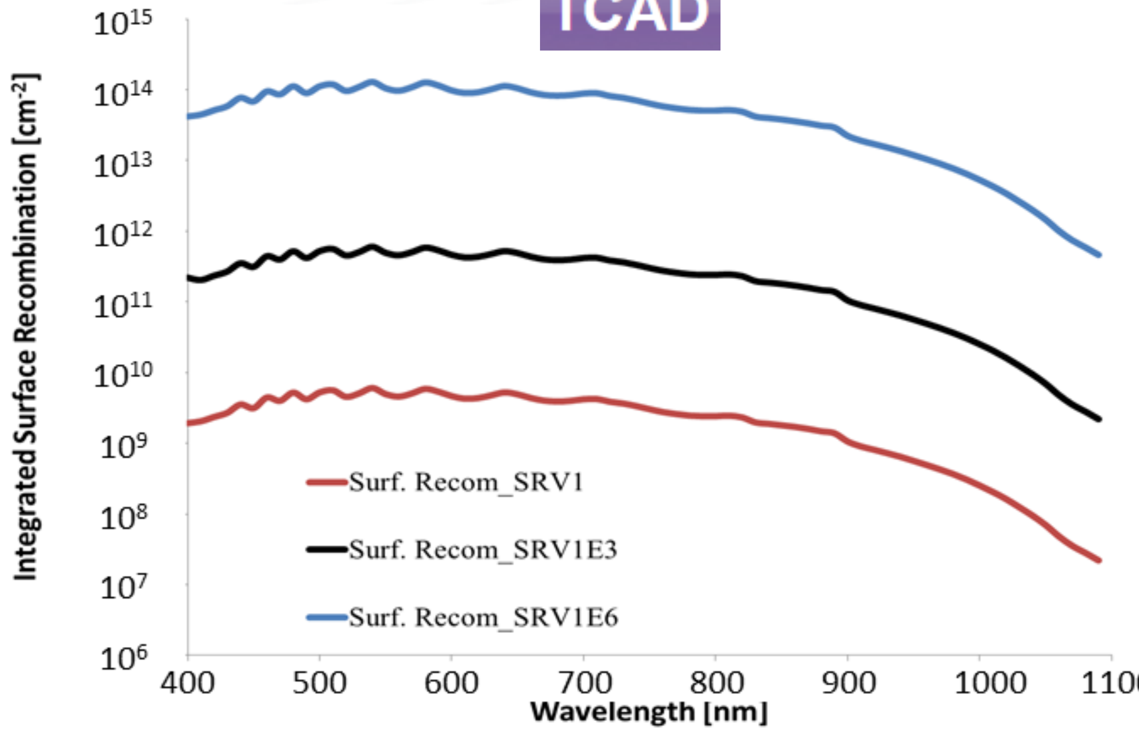
- **recombination rates**
- **optical coefficients**

→ Sentaurus TCAD appropriate for all-inorganic device simulations.

Optical properties of Si NWs on glass

SYNOPSYS® TCAD Optical Solutions



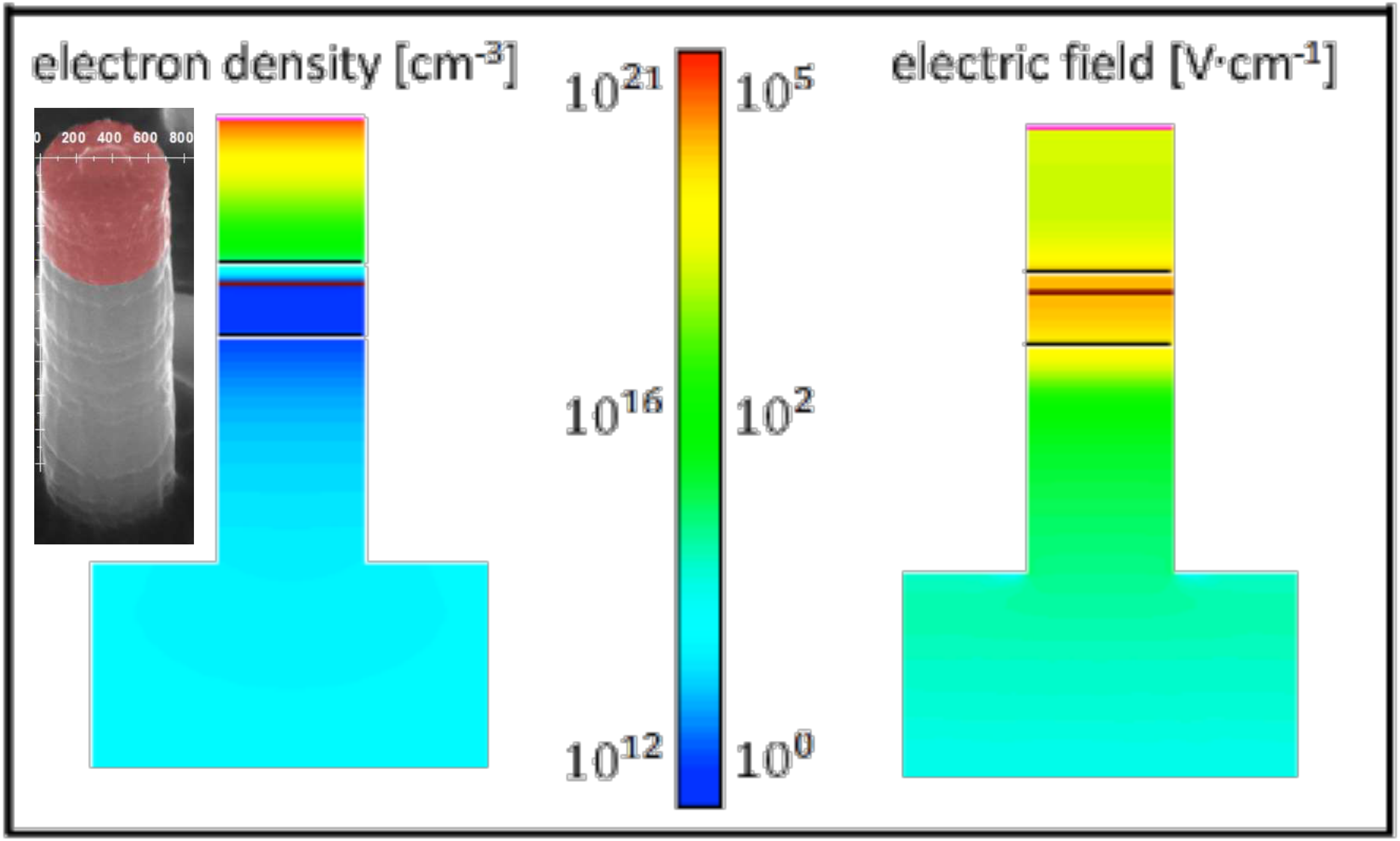


SiNW diameter: 300nm
SiNW height: 2 um
20 nm AZO
20 nm Al2O3
Wavelength: 900 nm

SiNW geometries for optimized ALD Al_2O_3 surface passivation by simulation of integrated surface recombination and optical generation

Kessels, W. M. M. et al. Silicon surface passivation by aluminium oxide studied with electron energy loss spectroscopy. Phys. status solidi - Rapid Res. Lett. 7, 937–941 (2013).

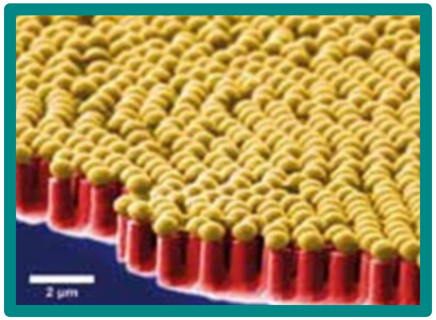
Device simulations to optimize SiNW cells



TCAD
Sentaurus Process

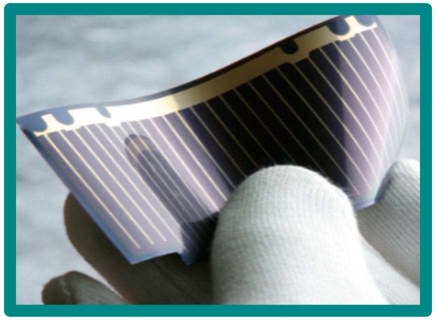
SYNOPSYS®
Accelerating Innovation

Si NW solar cells



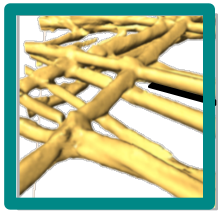
Si Nanowires (NWs) - Synthesis & Morphology

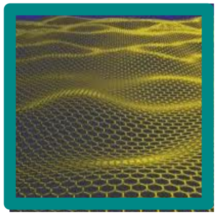
- top down NW etching



NWs in solar cell applications

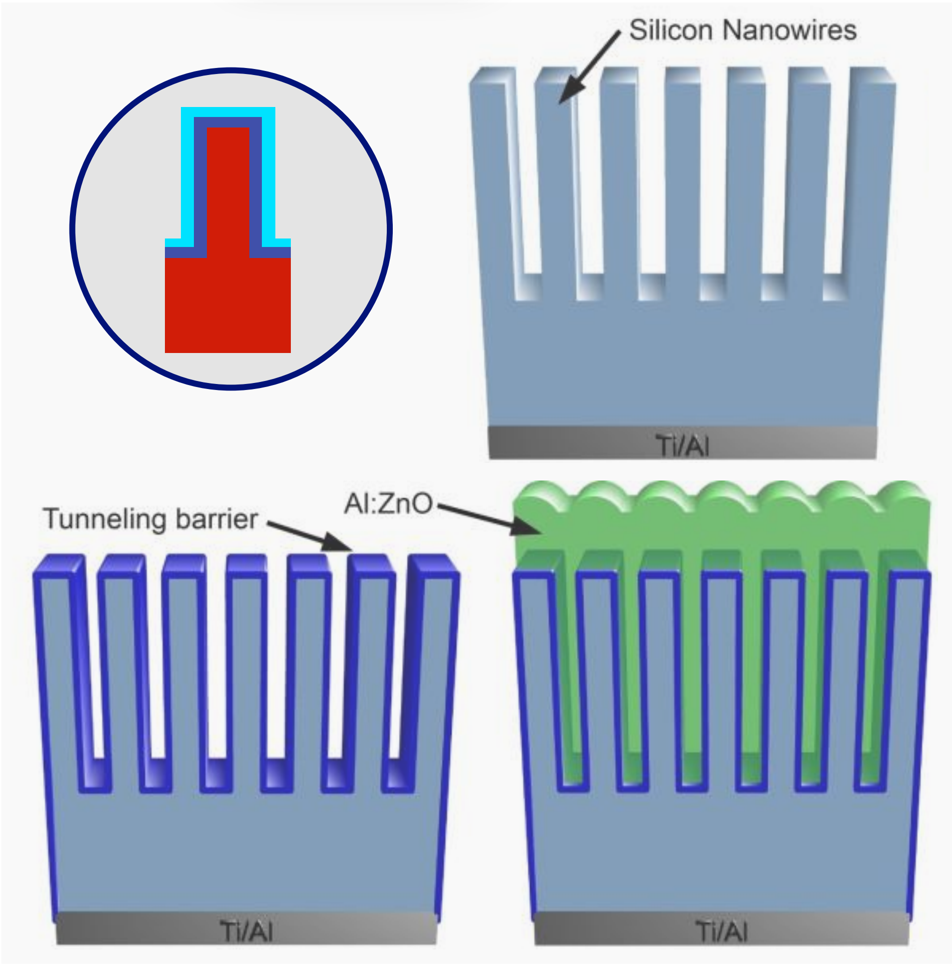
- semiconductor NWs in different cell concepts
- surface functionalization of NWs to improve solar cell performance

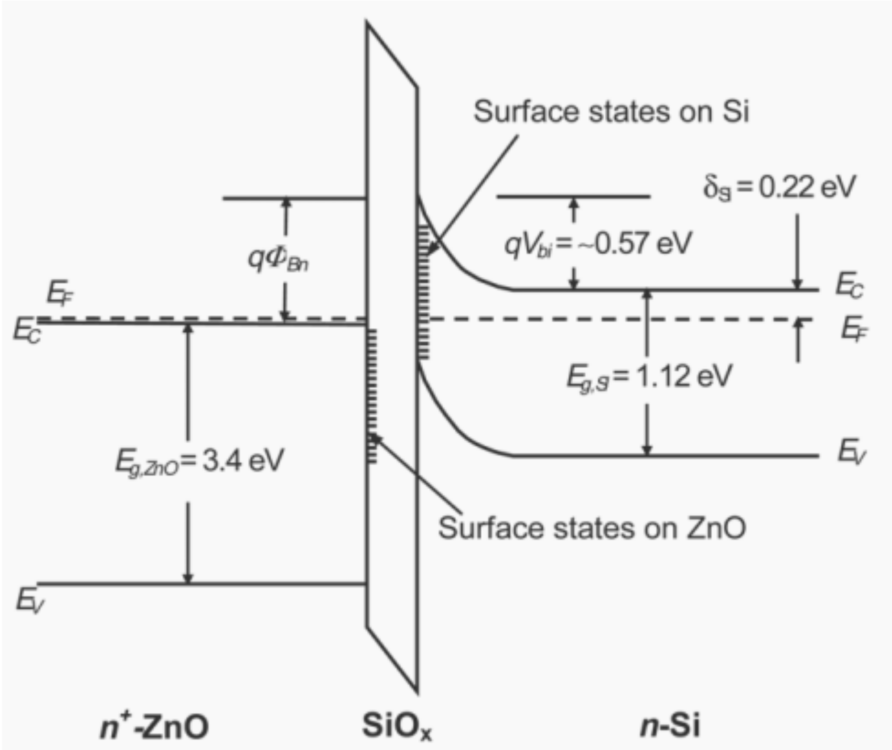




Novel contacts: graphene, Ag NW webs, TCOs

Nanowire-based SIS solar cell





Operation of the semic.-insulator-semic. (SIS) solar cell: Theory
J.Shewchun et al., J. Appl. Phys. 49(2), **(1978)**

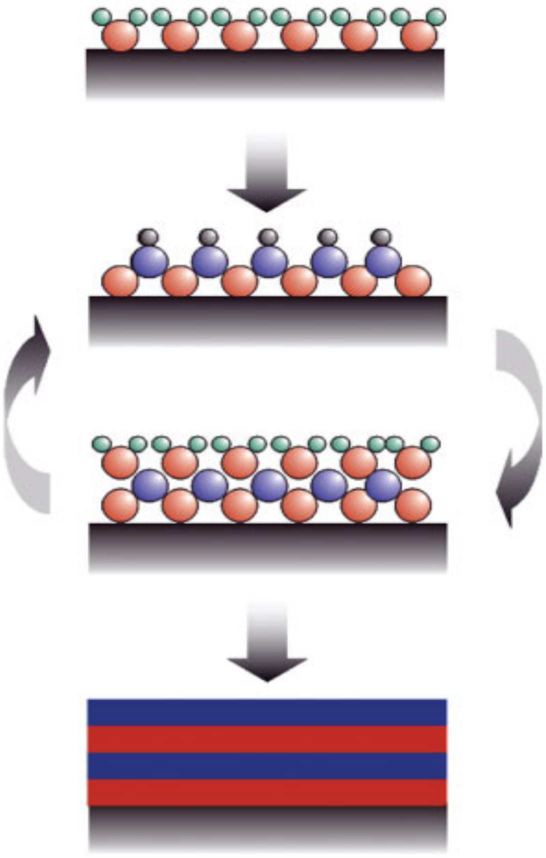
with atomic layer deposition (ALD): Angstrom level tunneling barrier thickness control possible

PA-Atomic layer deposition (ALD)

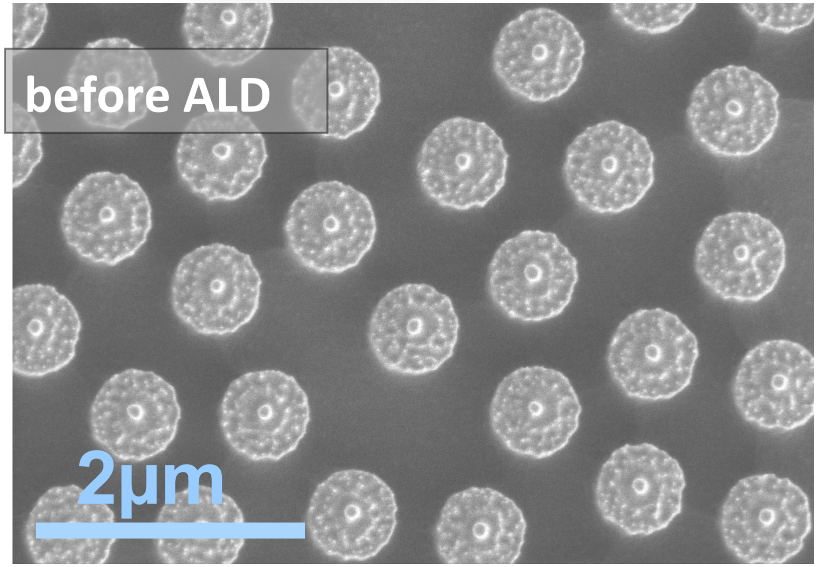
- Atomic layer deposition of Al_2O_3 and AZO
  - **AZO = Al_2O_3 / ZnO alloy material as TCO**
  - monolayers by sequential precursor exposition of a surface / self limited growth

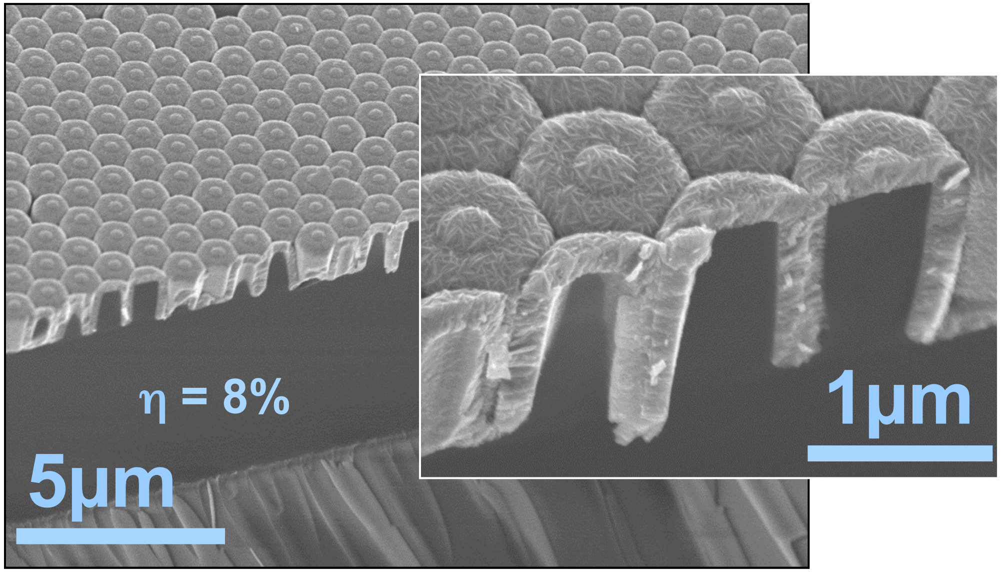
- Controlling Al_2O_3 / ZnO ratio → n-conductivity & refractive index tunable

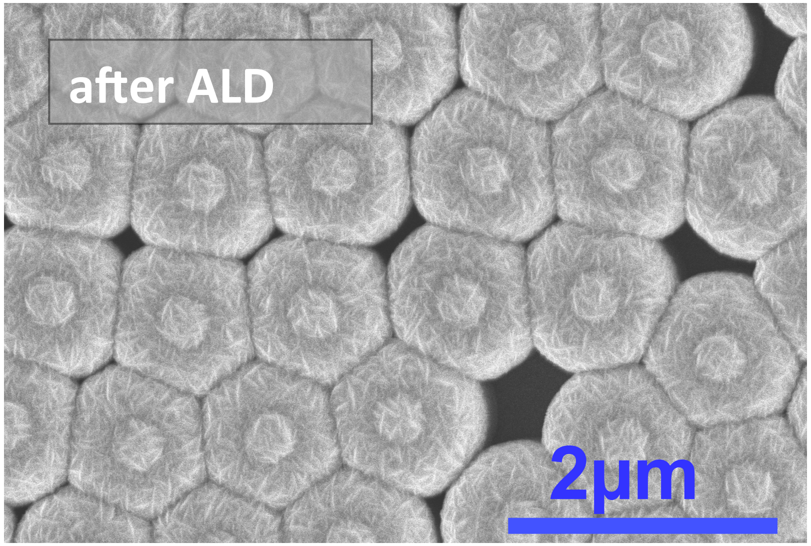
→ Flexible n-type semiconductor for (PV-)device development

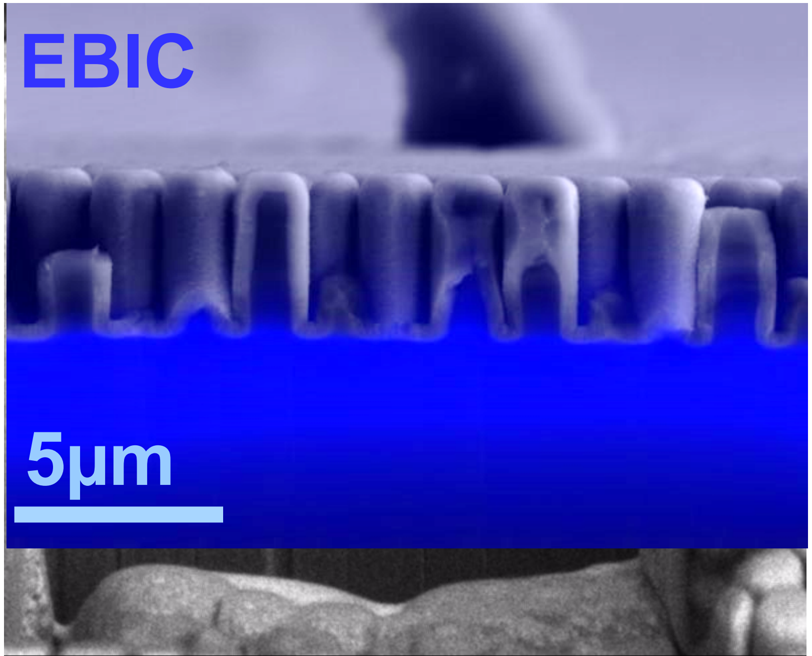


Si NW SIS solar cell on glass

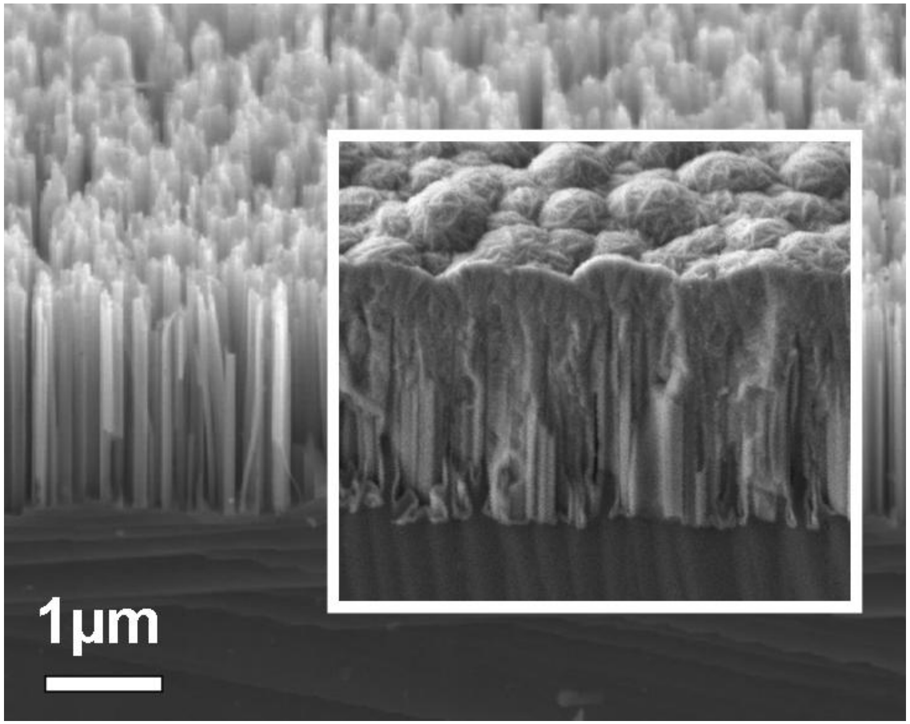


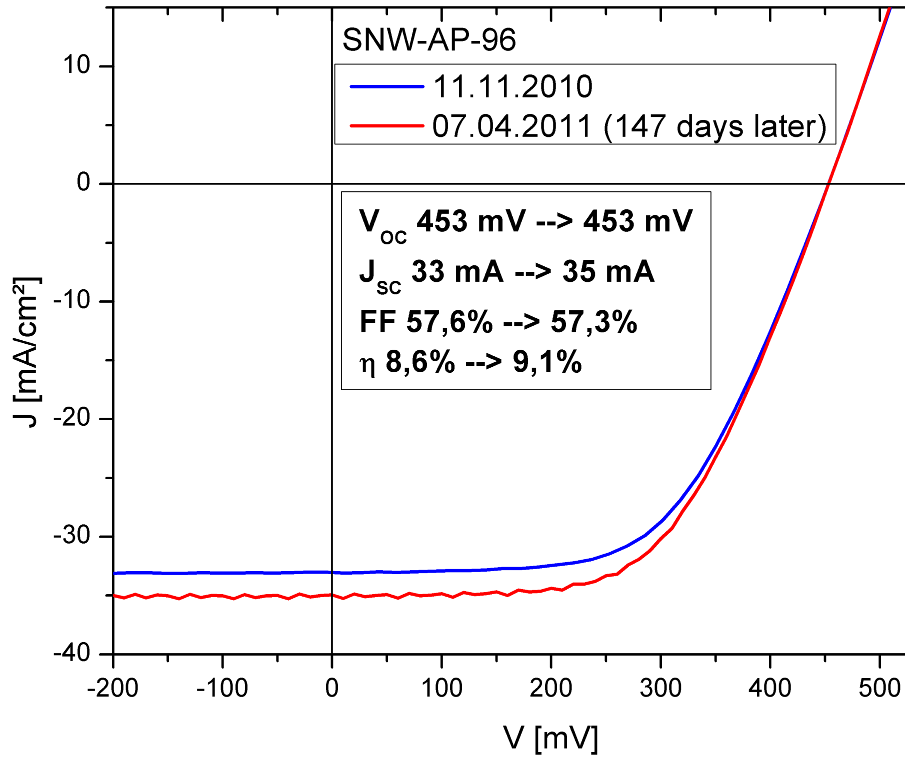


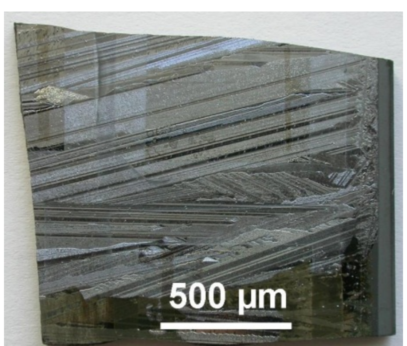


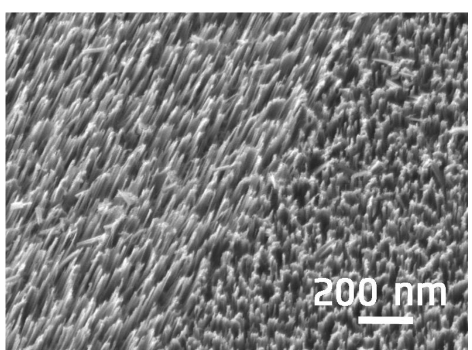


SIS nanowire solar cell







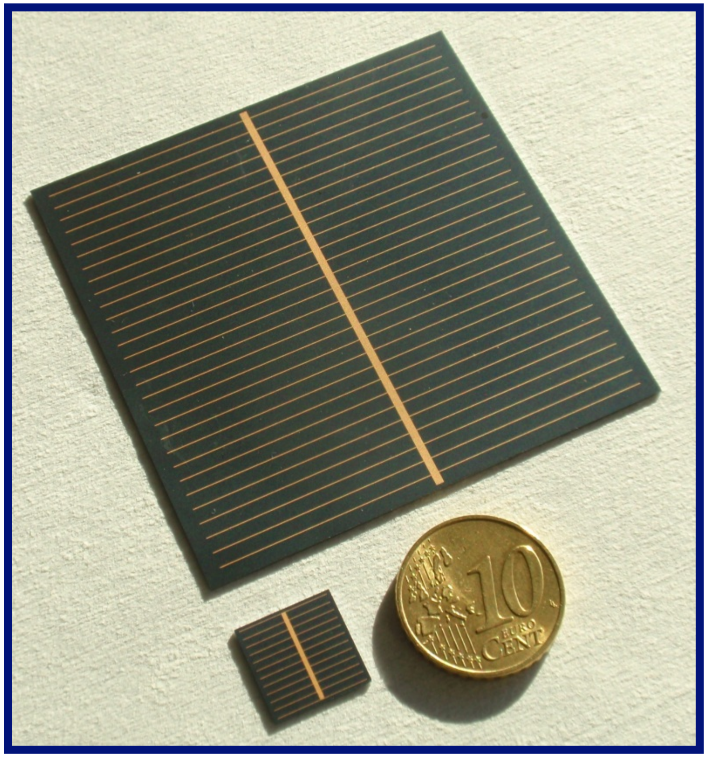


- **good short-current density**
- **Improvement of open-cirquit voltage**
- **Fill factor to be increased by better front- and backcontacts**

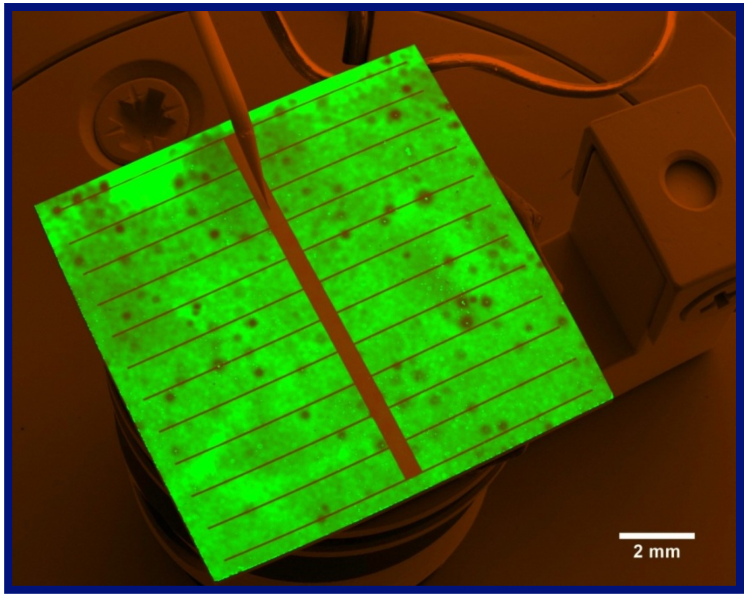
Demonstrator: Si NW SIS solar cell

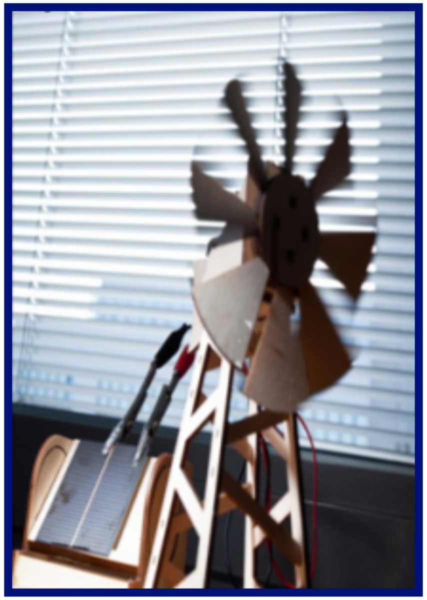
Large cell: size of 36 cm²
Gold grid: 1mm/100µm

Small cell: size of 1.44 cm²
Gold grid: 500µm/50µm



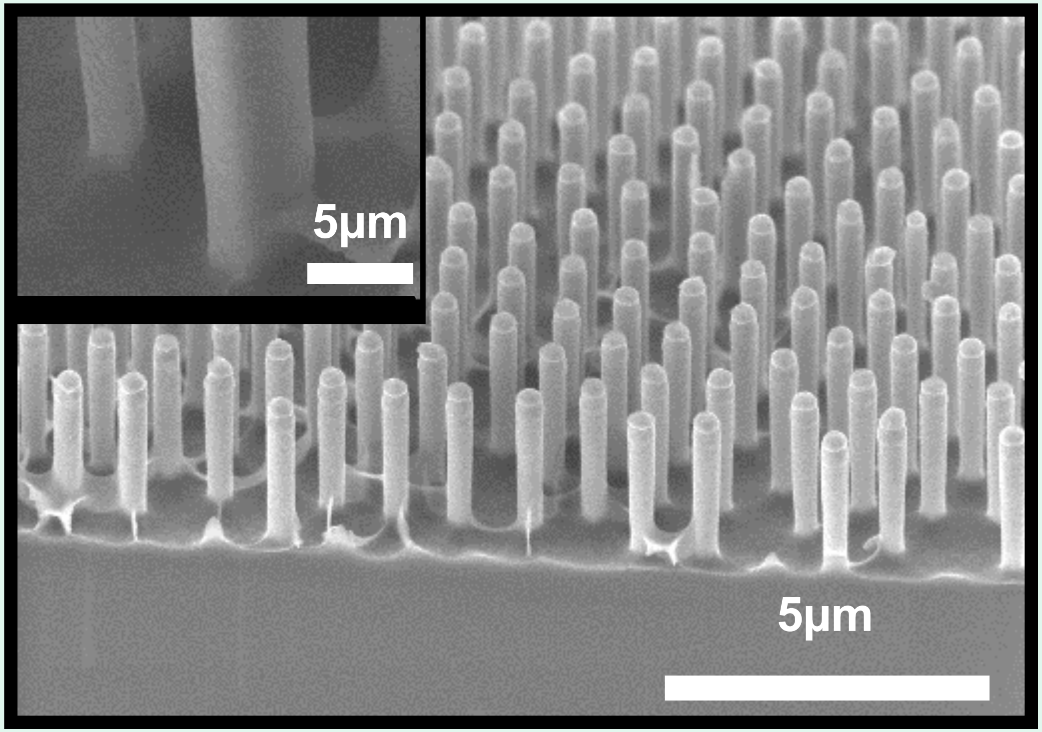
EBIC



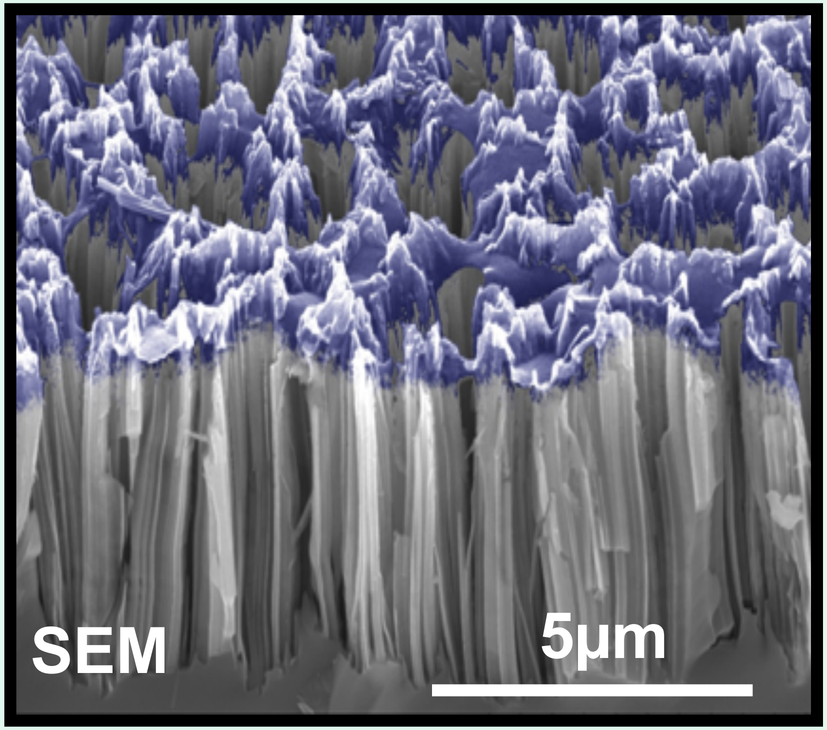


PEDOT:PSS on nanostructures

First results:
PEDOT:PSS penetrating the silicon nanostructure

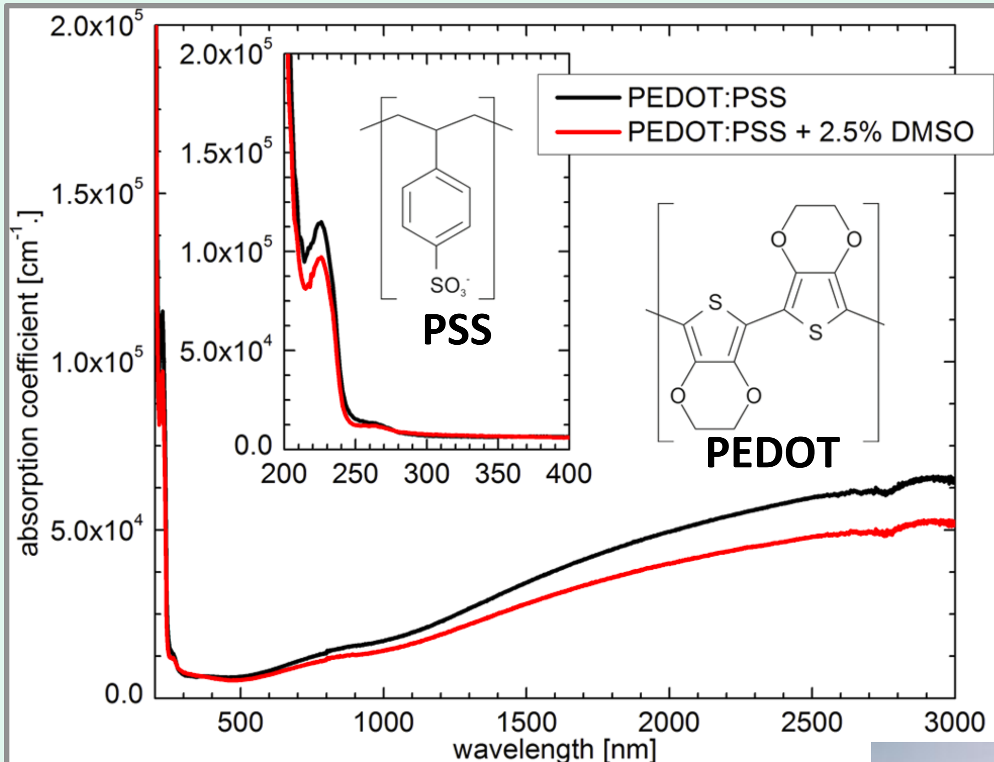


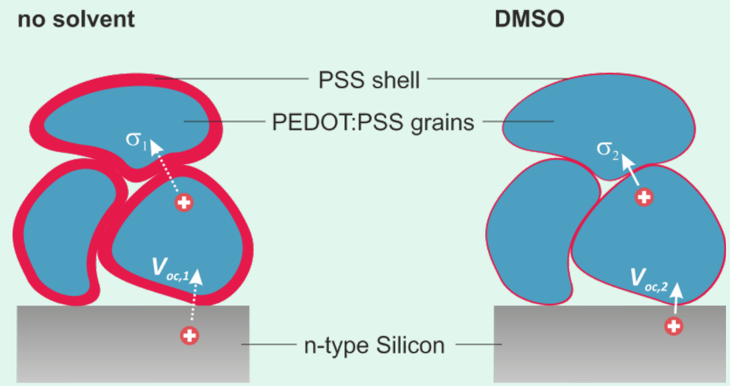
EBIC:
charge carrier seperation works

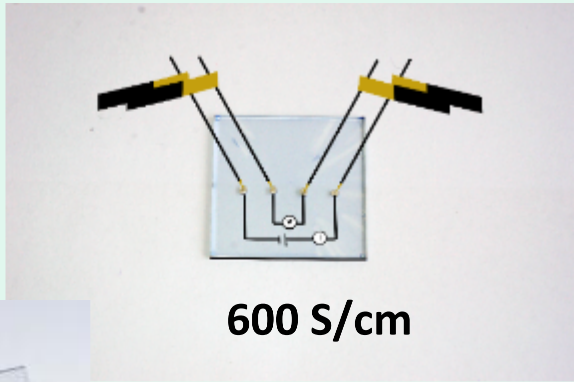


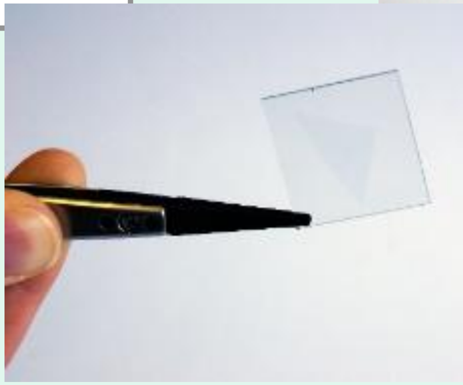
M.Y. Bashouti, M. Pietsch, G. Brönstrup, V. A. Sivakov, J. Ristein, S.H. Christiansen, Progr. Photovolt. Res. Appl. doi: 10.1002/pip.2315 (2013).

Hybrid solar cell – PEDOT:PSS/n-Si



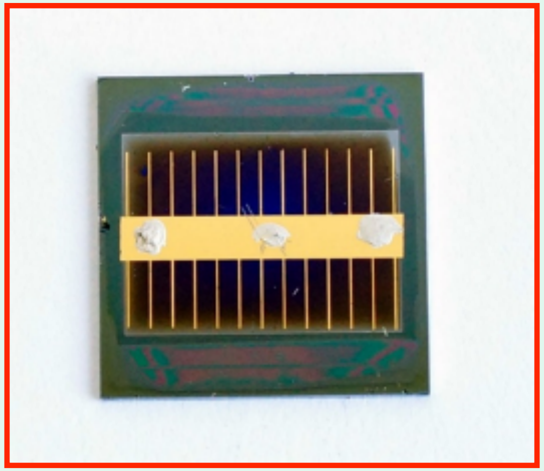


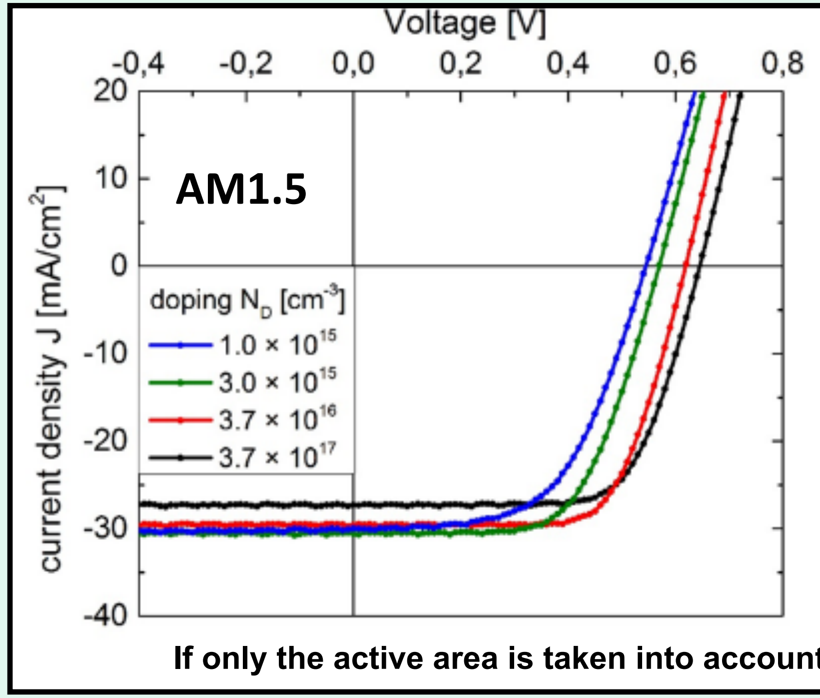




M. Pietsch, M. Bashouti, S.H. Christiansen, J. Phys. Chem. C 117(18), 9049 (2013).

PEDOT:PSS/nSi – solar cell

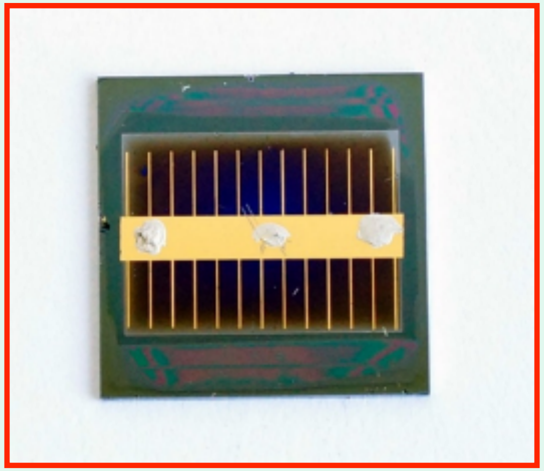


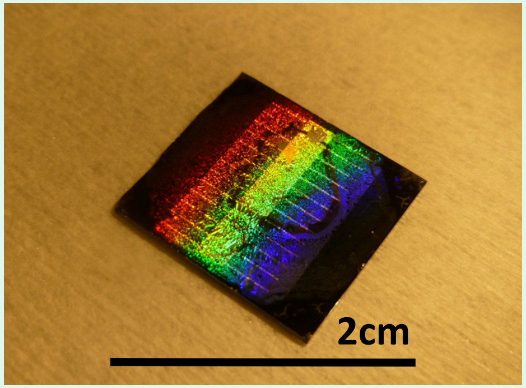


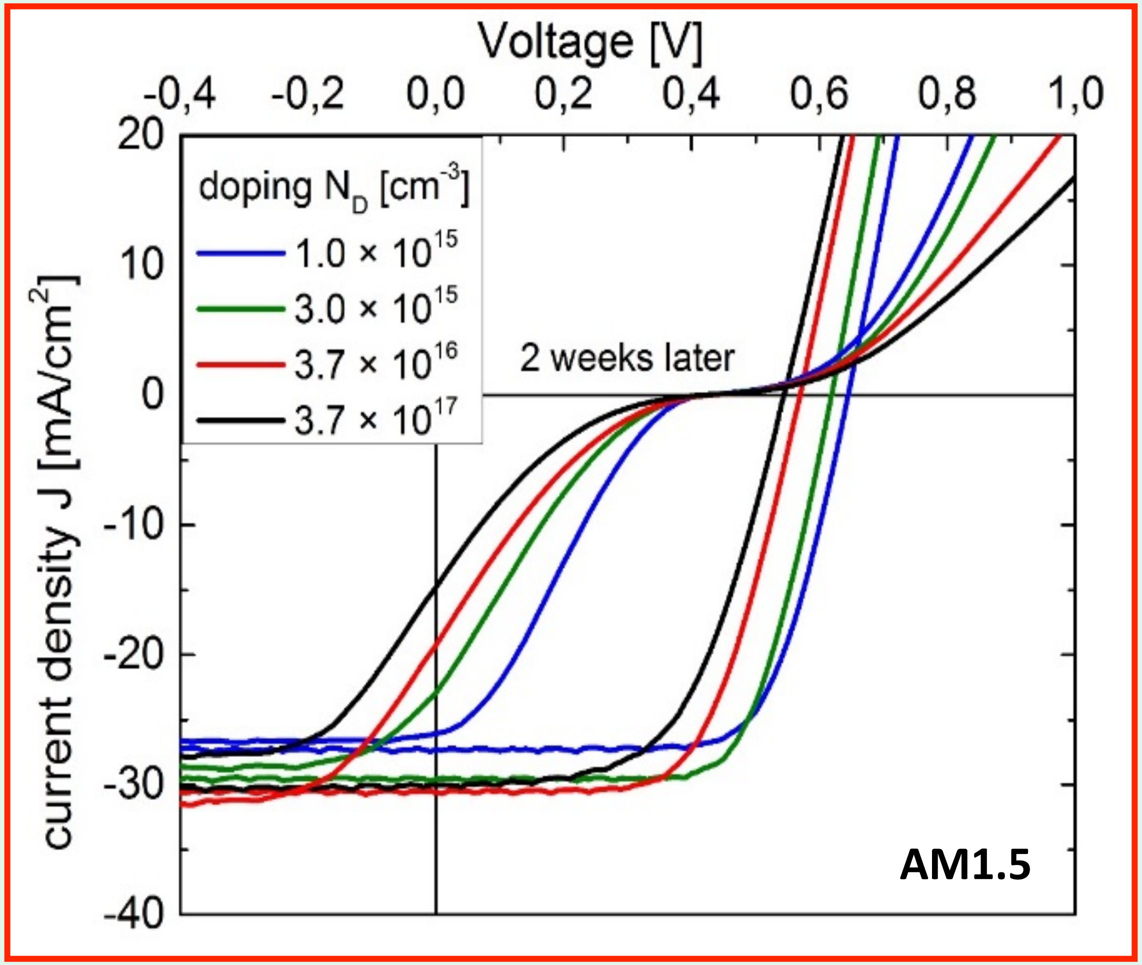
Si Doping N_D [cm^{-3}]	V_{OC} [meV]	J_{SC} [mA/cm²]	FF [%]	PCE [%]
1.0×10^{15}	550	30	0.57	9.4
3.0×10^{15}	570	30.6	0.63	10.9
3.7×10^{16}	620	29.6	0.69	12.6
3.7×10^{17}	640	27.3	0.69	12.2

M. Pietsch, S. Jäckle, S. Christiansen, Appl. Phys. A published online

PEDOT:PSS/nSi – solar cell

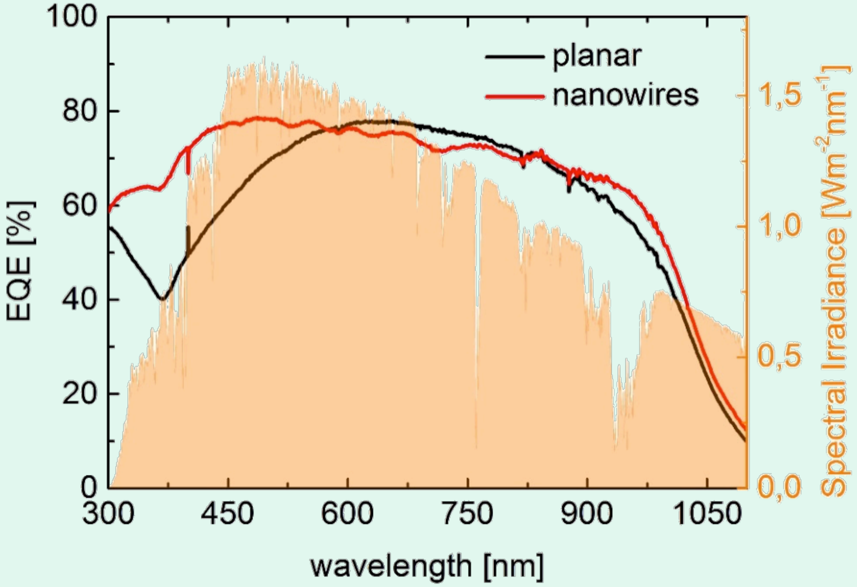


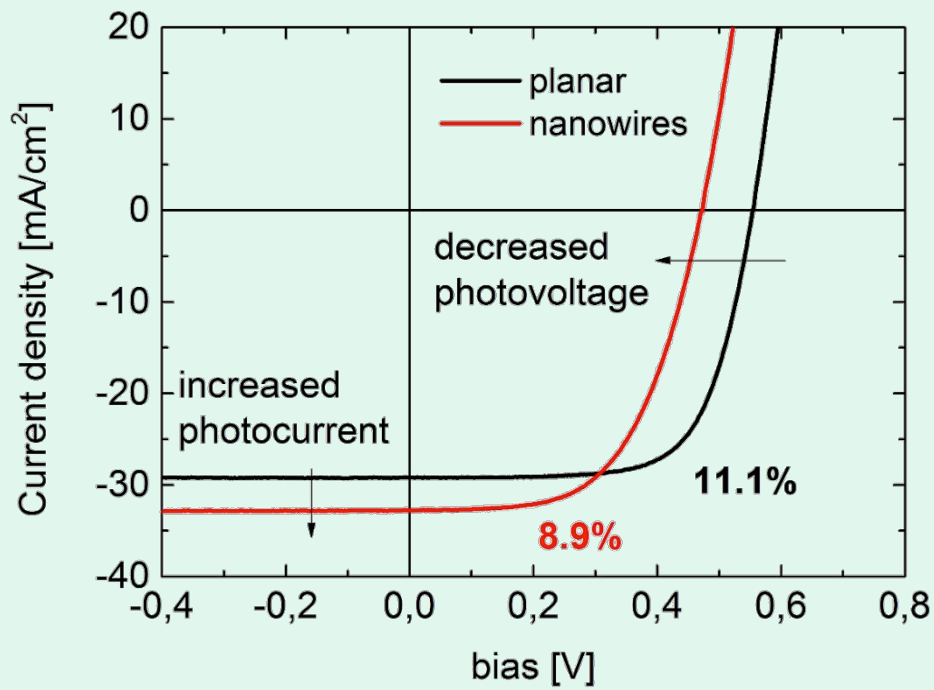




S. Jäckle, S. Christiansen, unpublished result

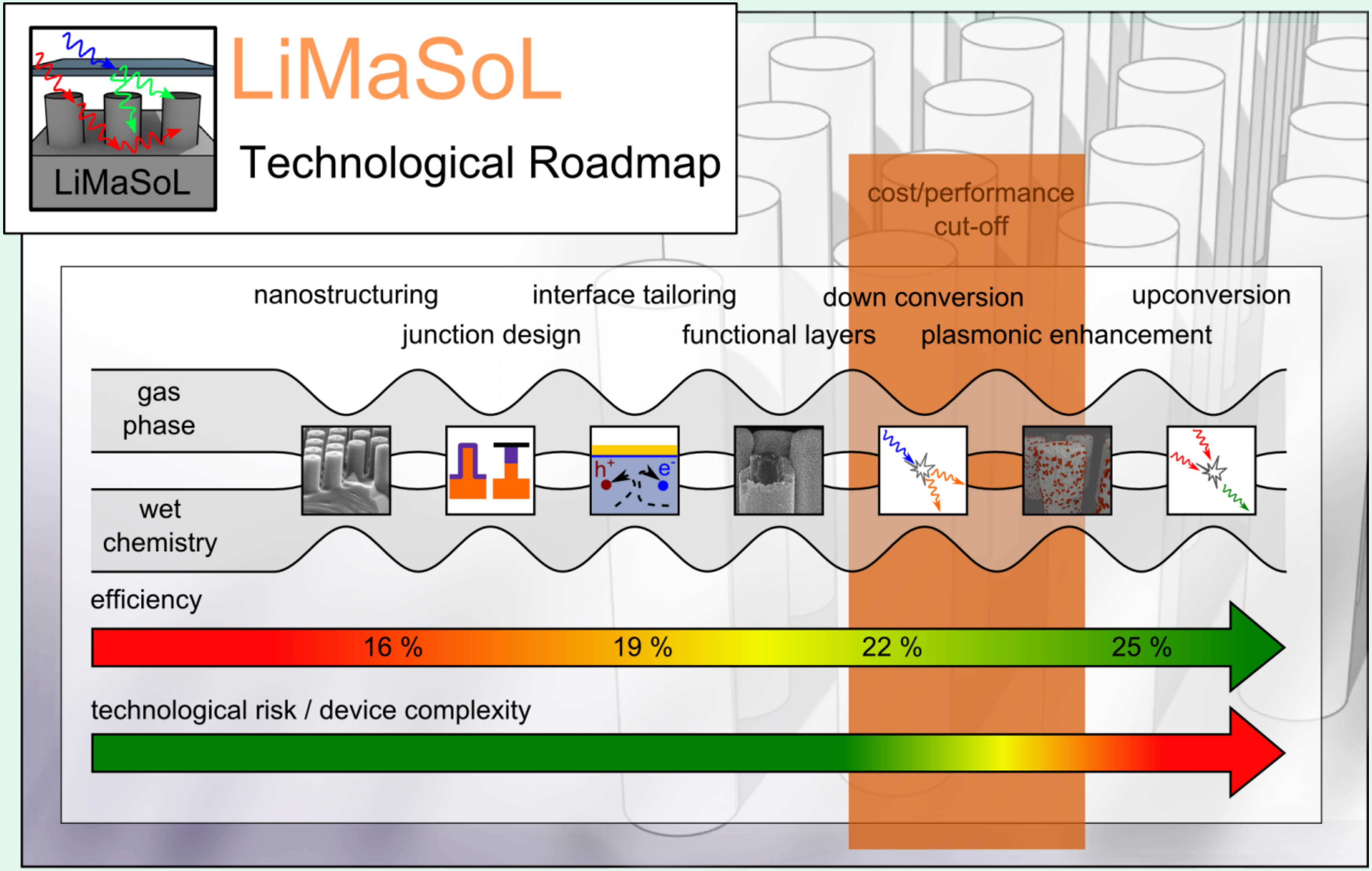
PEDOT:PSS/nSi – solar cell

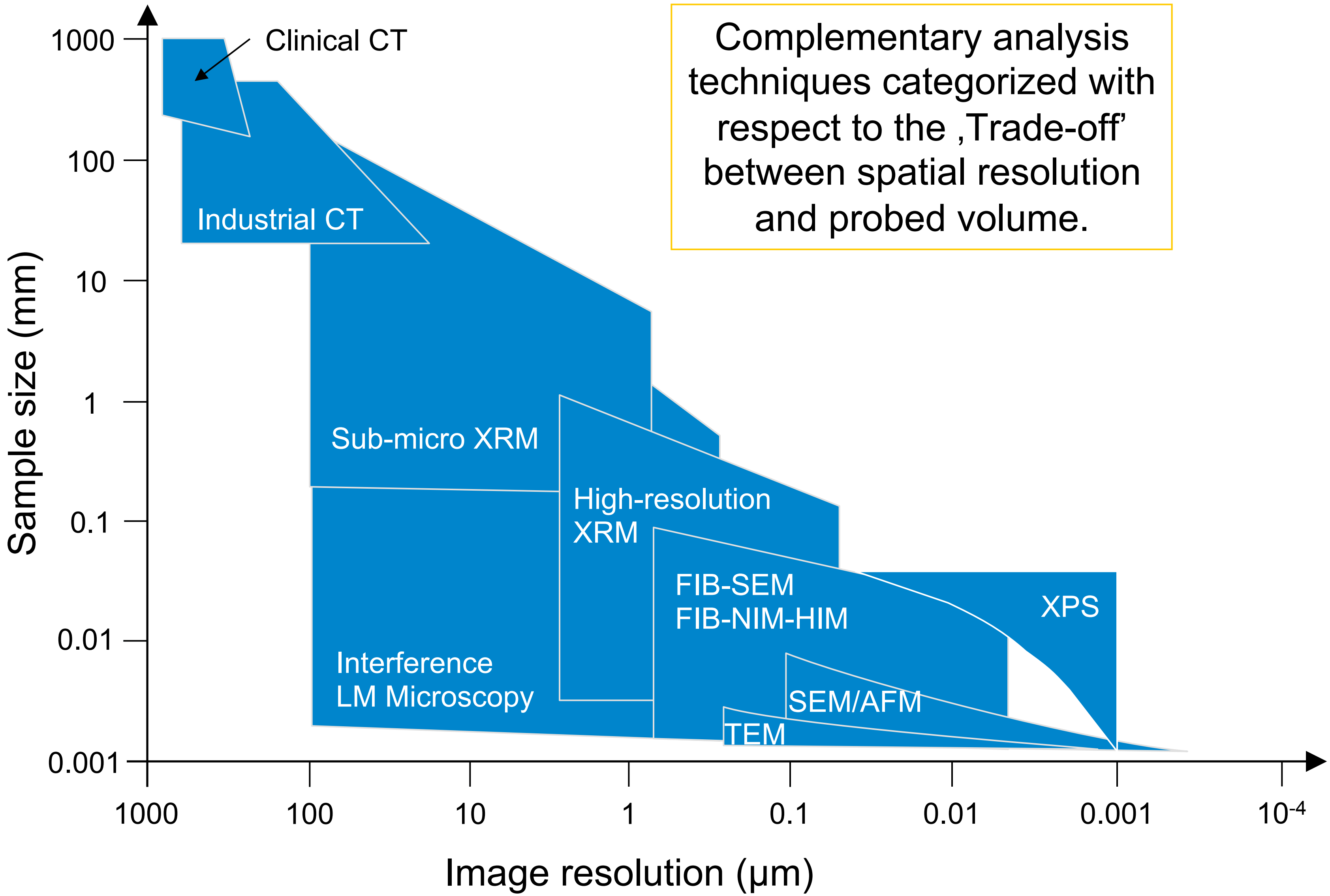




Nanostructured thin film solar cell

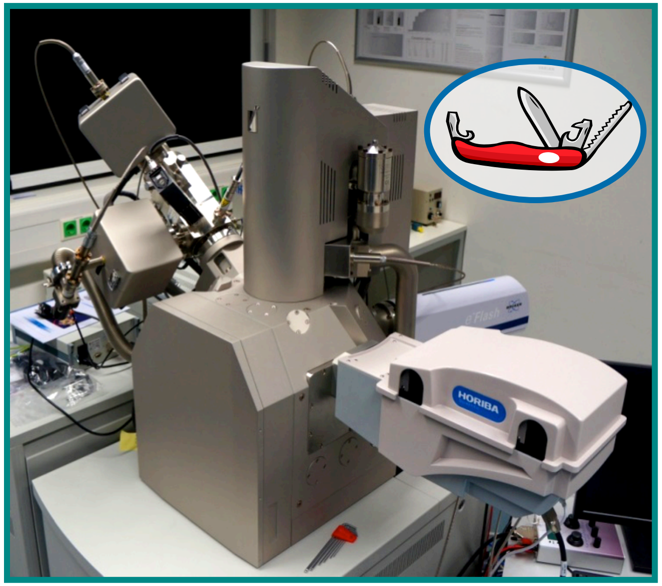
Where do we want to go?

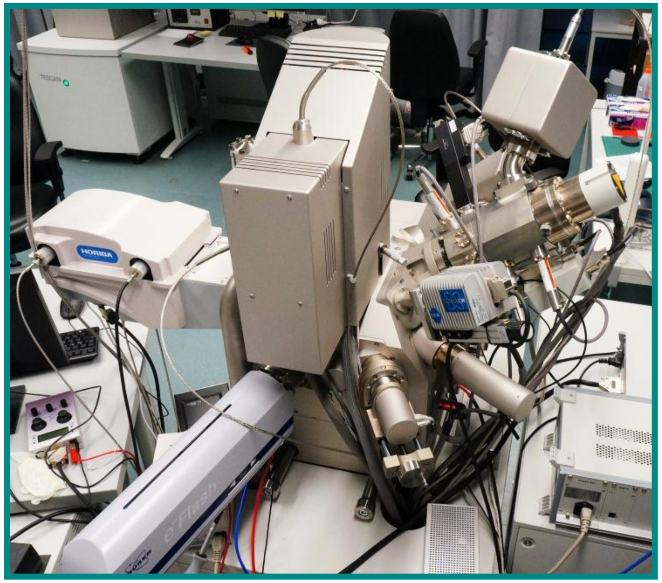


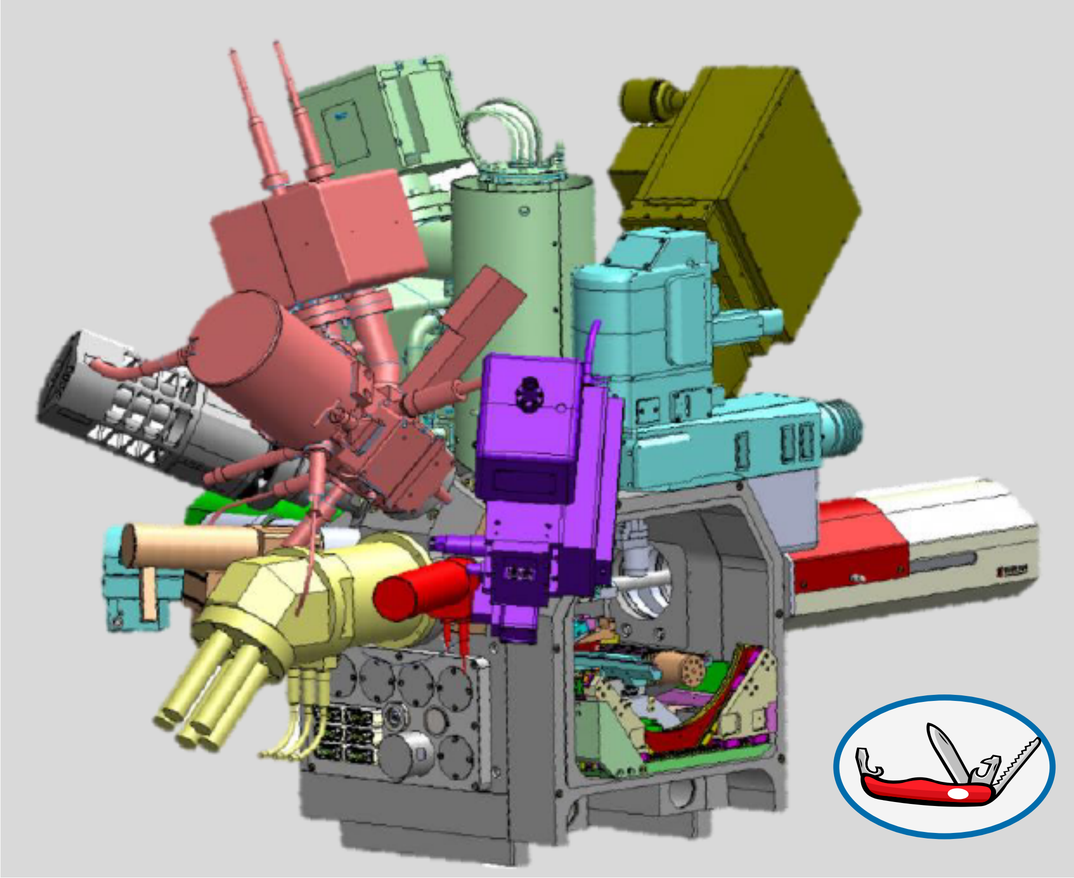


Complementary analysis techniques categorized with respect to the ‚Trade-off' between spatial resolution and probed volume.

EU projects FIBLYS & UnivSEM





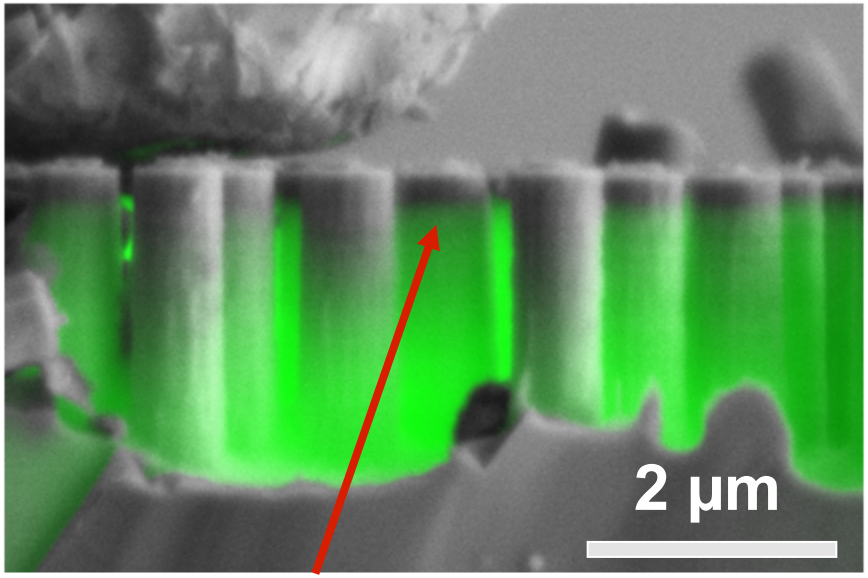


FIBLYS

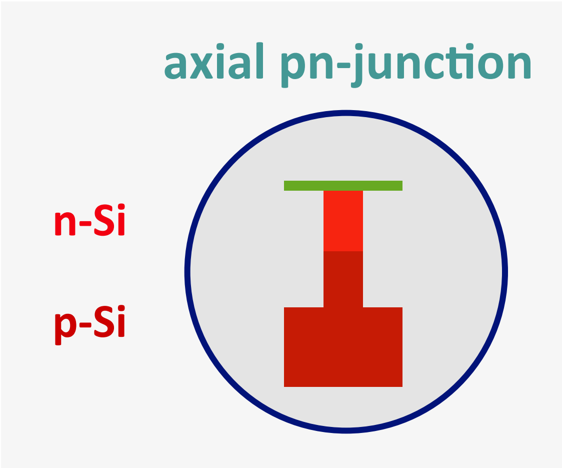
univ sem
universal scanning electron microscope

Electron beam induced current - EBIC

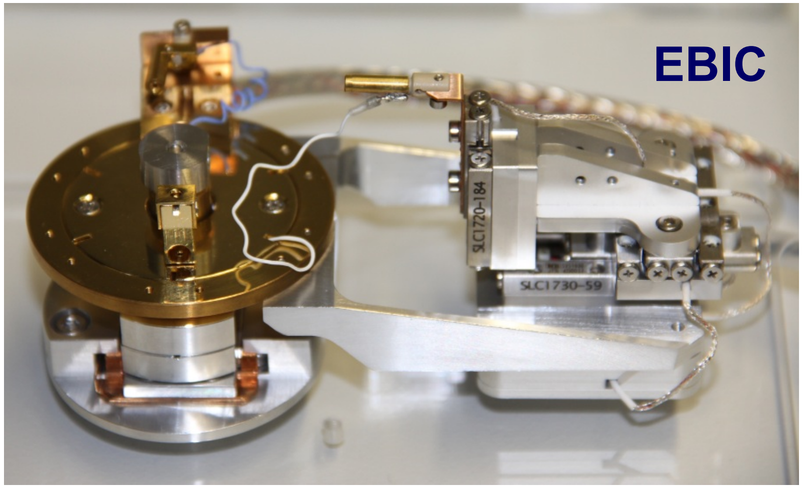
Axial p-n junctions in Si NWs (EBIC)



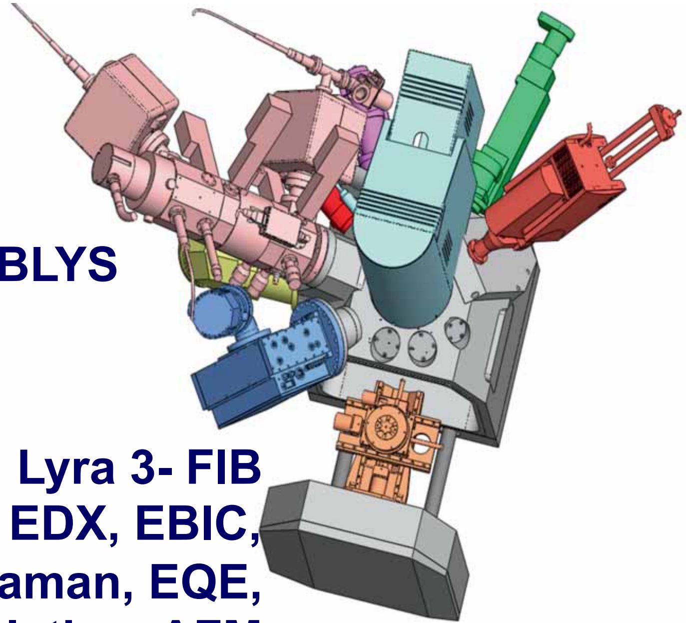
Dopant diffusion prior to etching



EBIC:
junctions in NW –
charge carrier separation



FP7 - FIBLYS



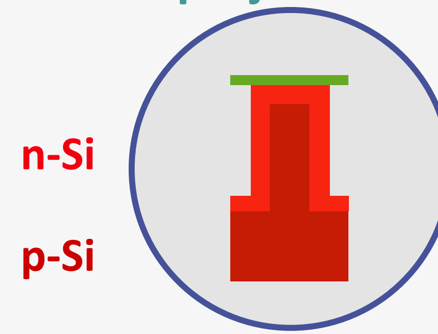
TESCAN Lyra 3- FIB
EBSD, EDX, EBIC,
CL, µ-Raman, EQE,
Nano-manipulation, AFM
TOF-MS

Si NWs doping

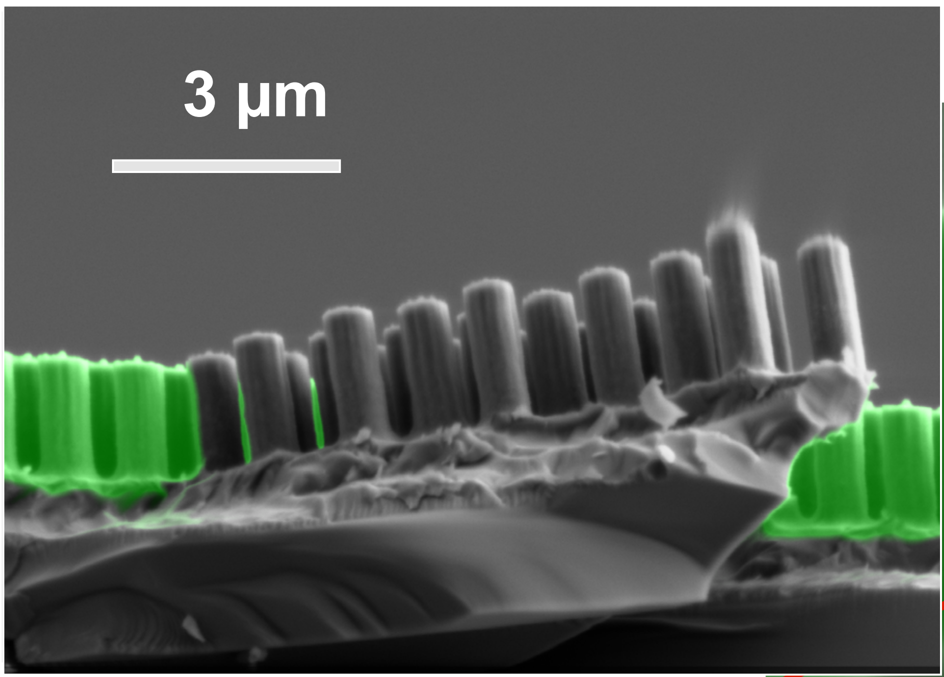
Spin-on-glass doping:

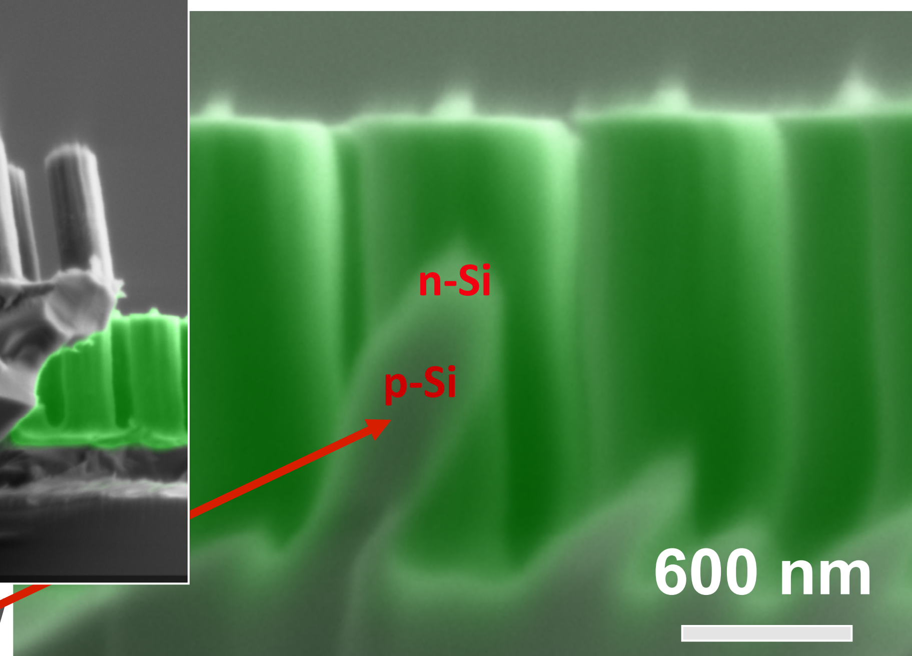
- p- and n-doping possible
- annealing to diffuse dopants
- removal of SOG in HF

wrap around doping: radial pn-junction



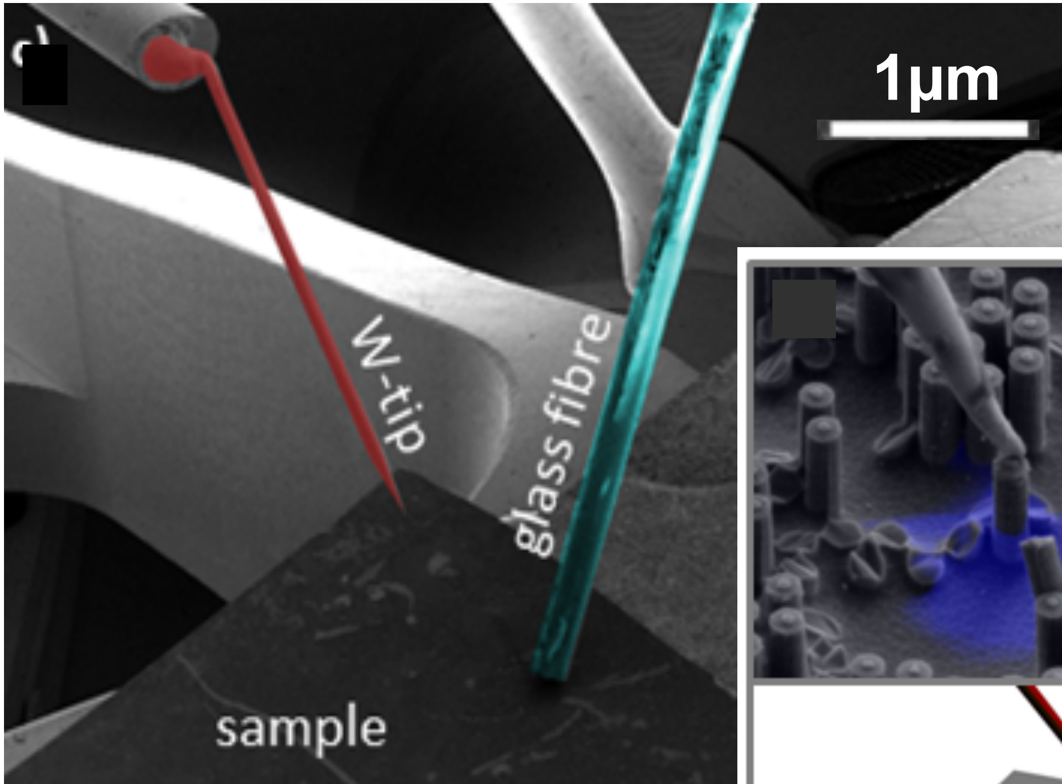
radial p-n junctions in Si NWs (EBIC)



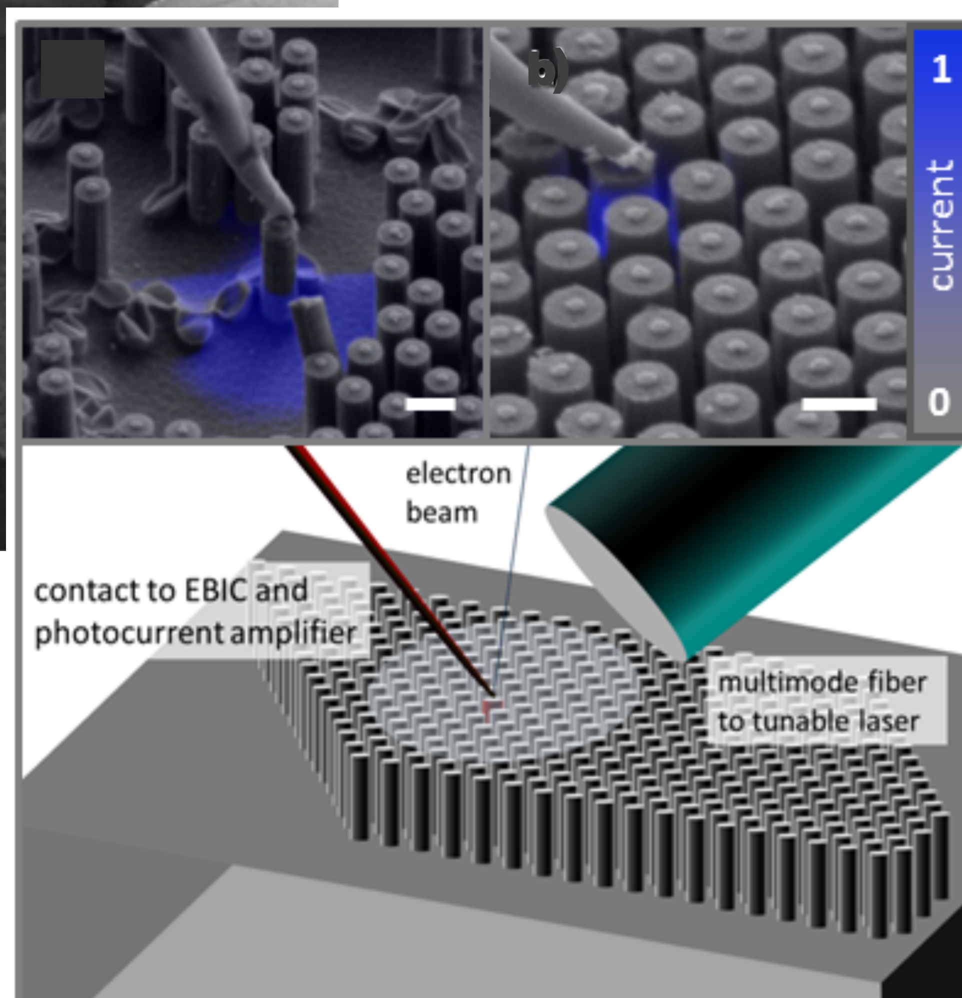


dopant diffusion after Si NW etching:
wrapped surface doping

I-V measurements (with/ w.o. light)

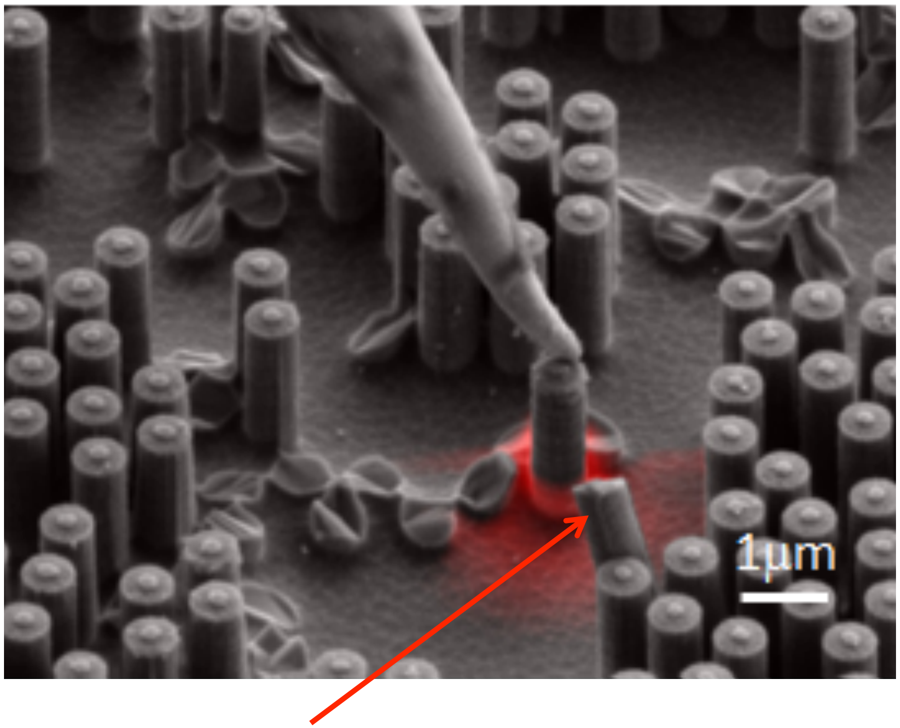


Multimode fiber:
500-800nm laser light
0-2000nW in steps of 50nW



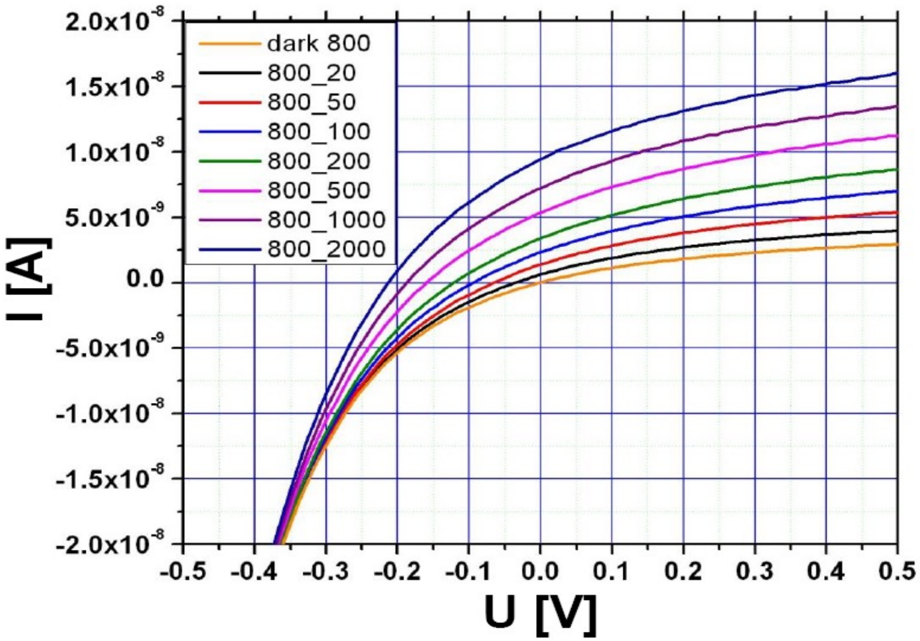
S. Schmitt, G. Brönstrup, G. Shalev, S. H. Christiansen, nanoscale published online (2014).

- EBIC



p-n junction axial in the wire /diffusion before etching

- LBIC: power dependent I-V characteristics

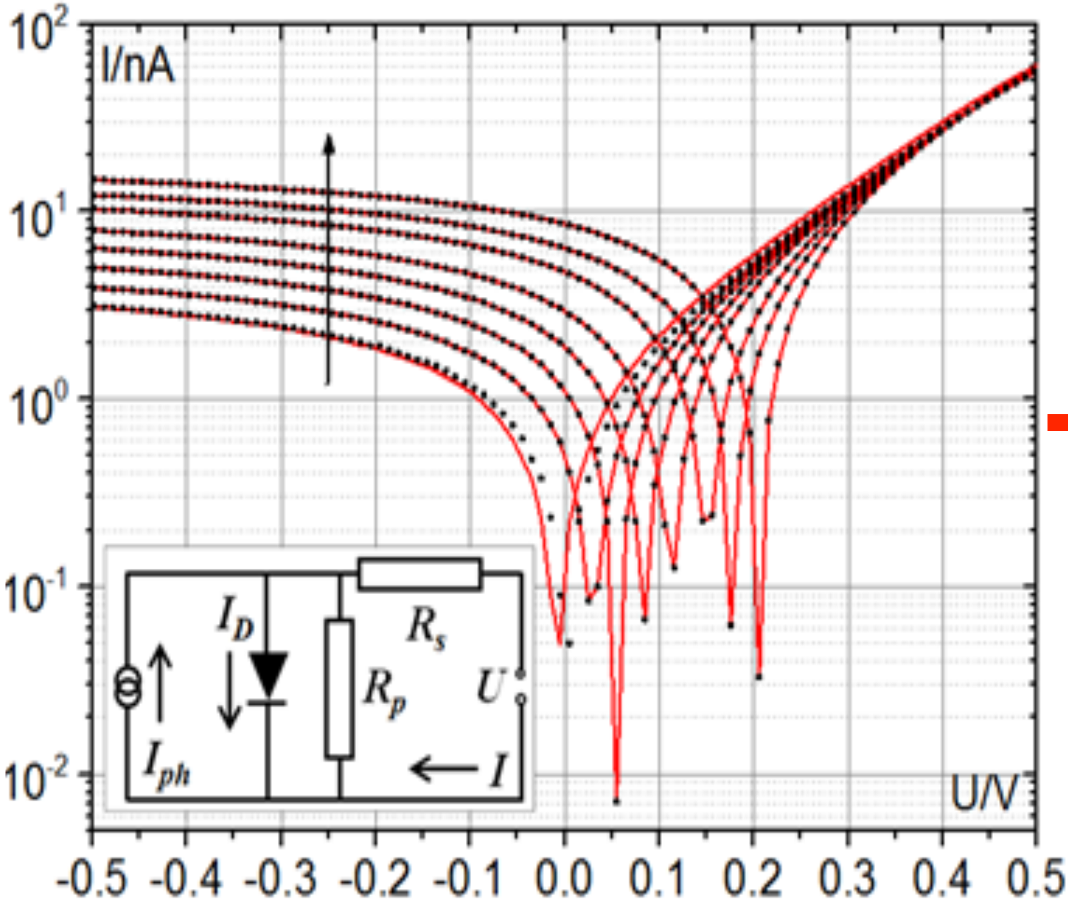


800nm laser illumination; 20-2000nW

S. Schmitt, G. Brönstrup, G. Shalev, S. H. Christiansen, nanoscale published online (2014).

P-n junction nanowire solar cells

single diode equivalent circuit model



free fit parameters
I_s, R_s, R_p, n and I_{ph}

●: measured I-V curves (semi-log. Scale; illumination with 700nm)

▬: fit of I-V curves with Eq. (1)

$$I_D = I_s \left(e^{\frac{U+IR_s}{nk_BT}} - 1\right)$$

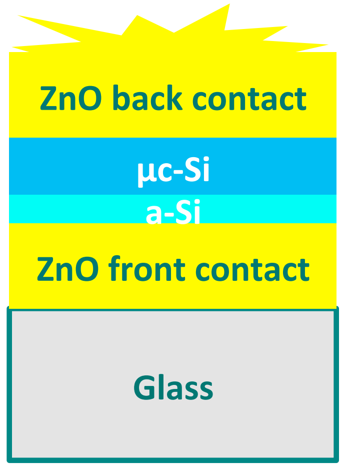
S. Schmitt, G. Brönstrup, G. Shalev, S. H. Christiansen, nanoscale published online (2014).

$$I = I_{ph} - I_s \left(e^{\frac{U+IR_s}{nk_BT}} - 1\right) - \frac{U + IR_s}{R_p}$$

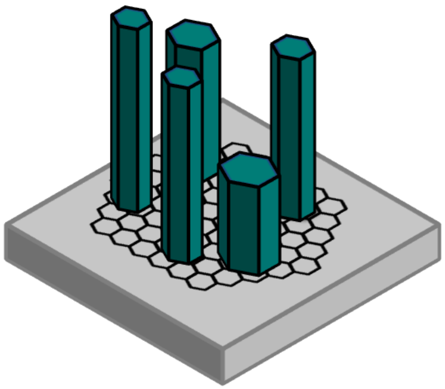
Eq. (1)

Applications

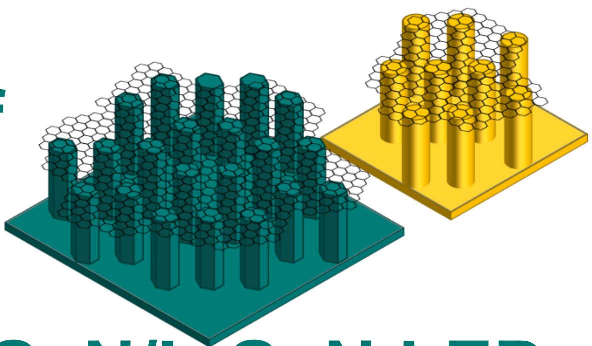
- **Thin film a-Si/µc-Si tandem solar cells**



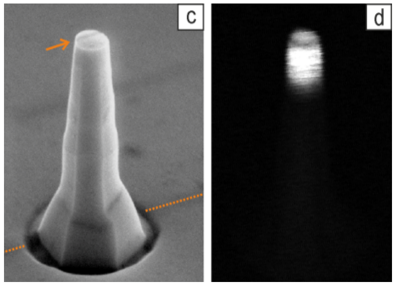
- **GaN nanowires grown on graphene**



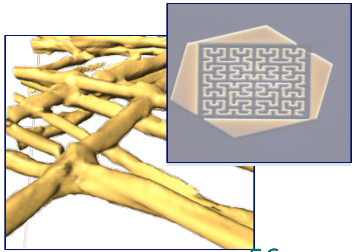
- **Graphene on top of GaN/Si nanorods**



- **Model & „real life“ GaN/InGaN LEDs**

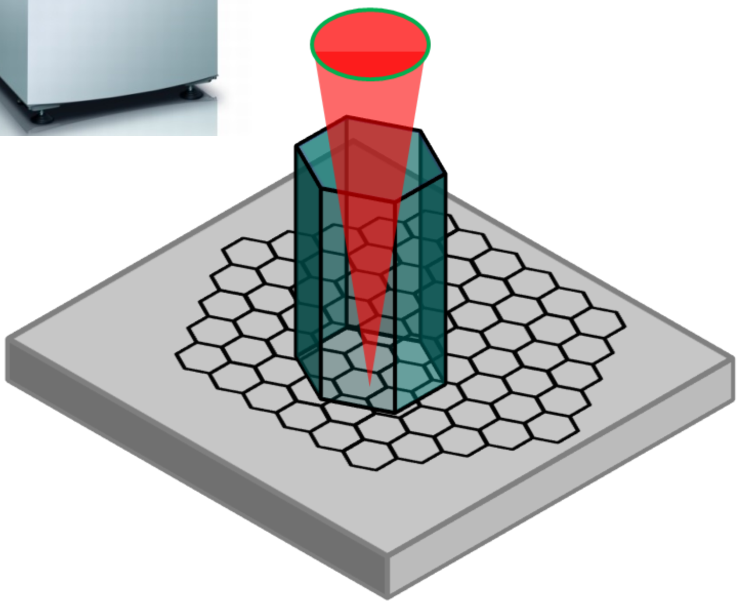


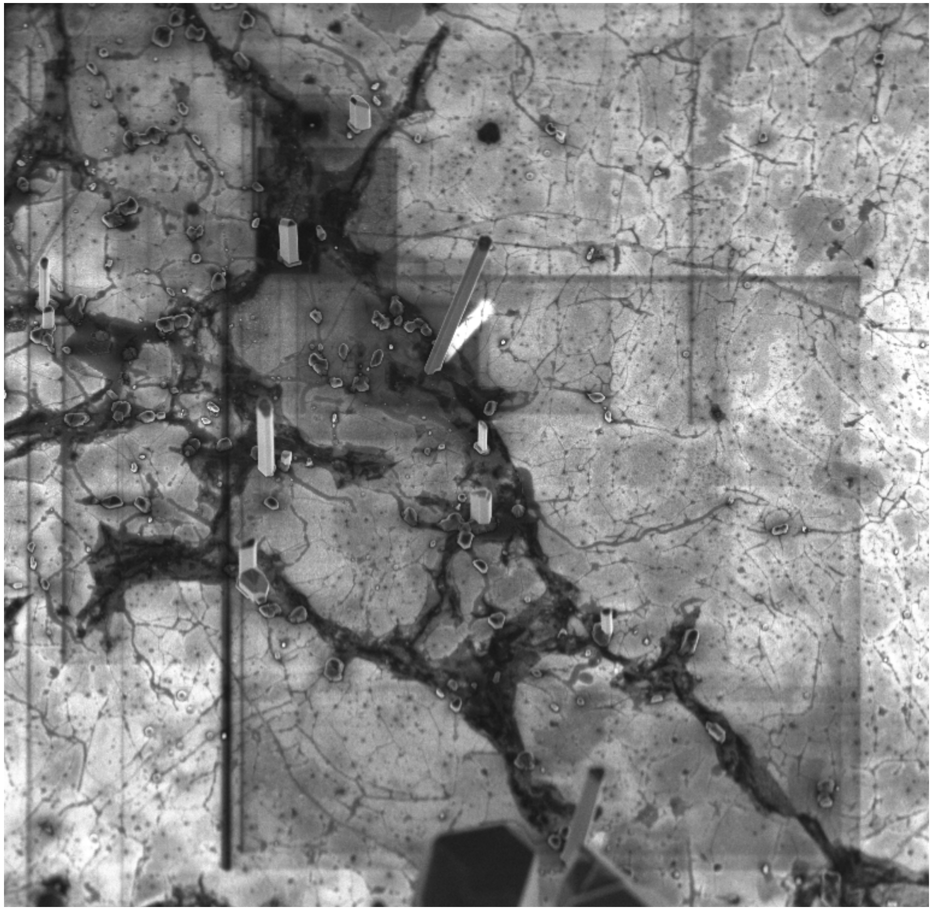
- **Ag-NW network electrodes + plasmonic antennas**



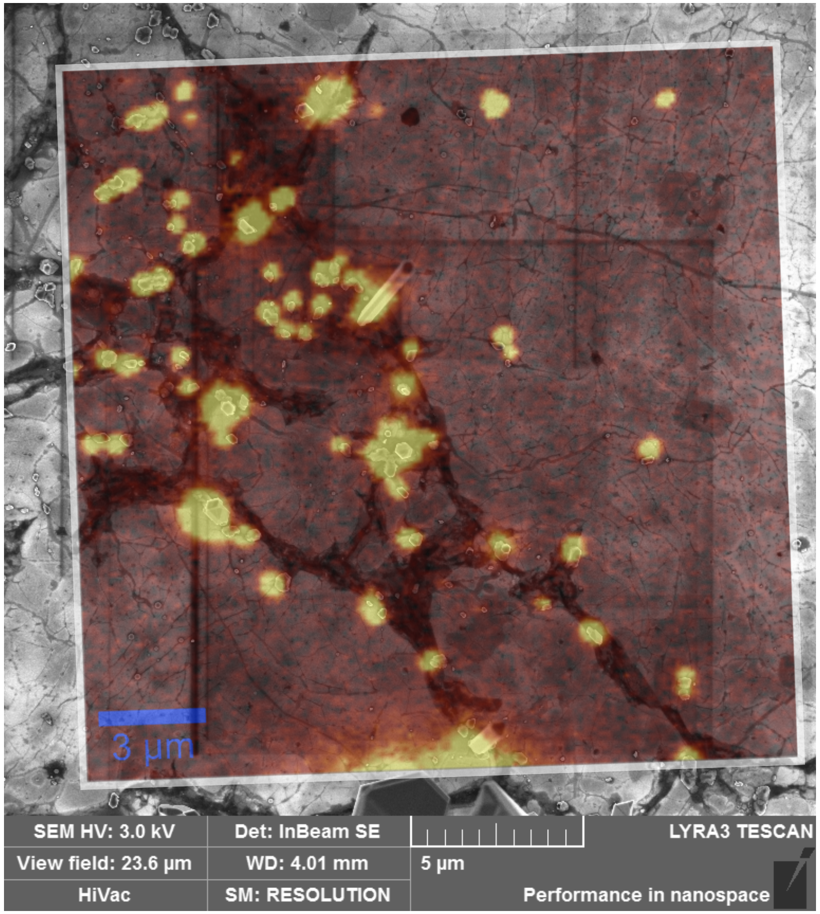
GaN nanowires grown on graphene

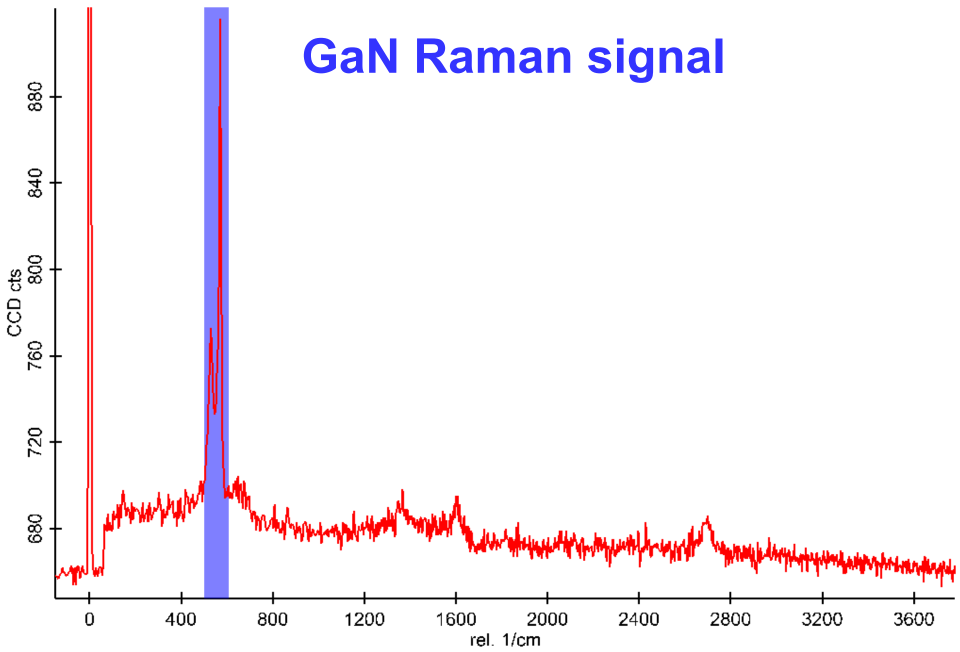
Another interesting sample for correlated meaasurements are GaN nanowires that are grown on graphene



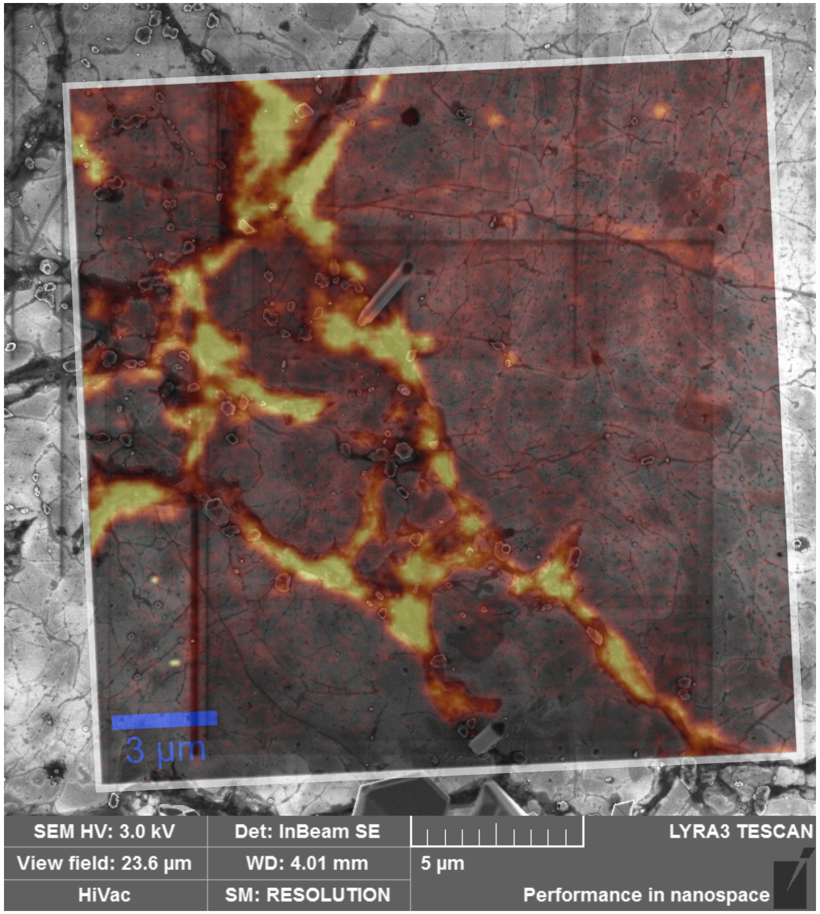


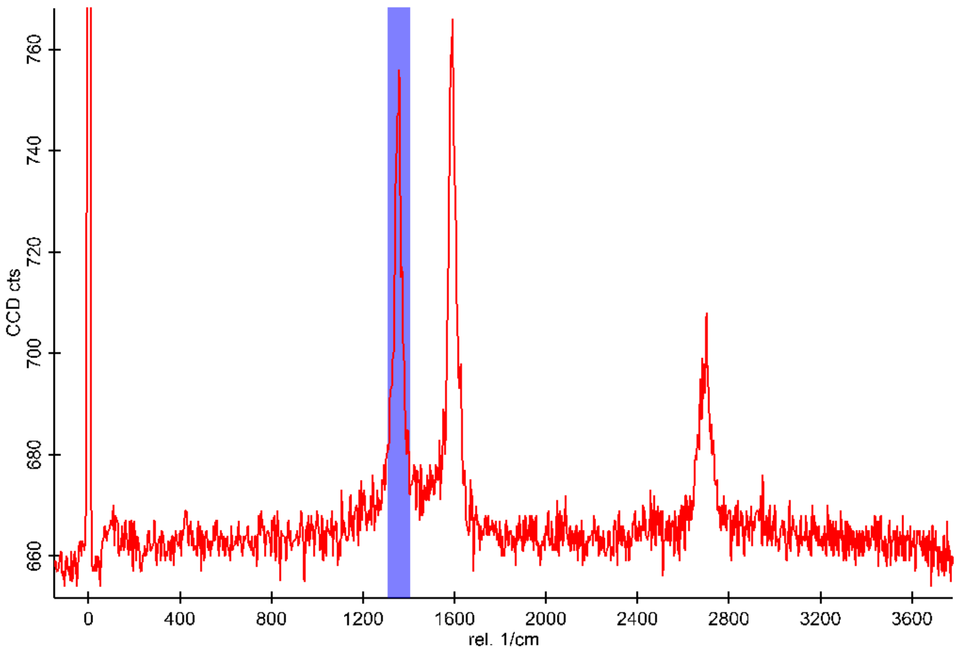
GaN nanowires grown on graphene





GaN nanowires grown on graphene

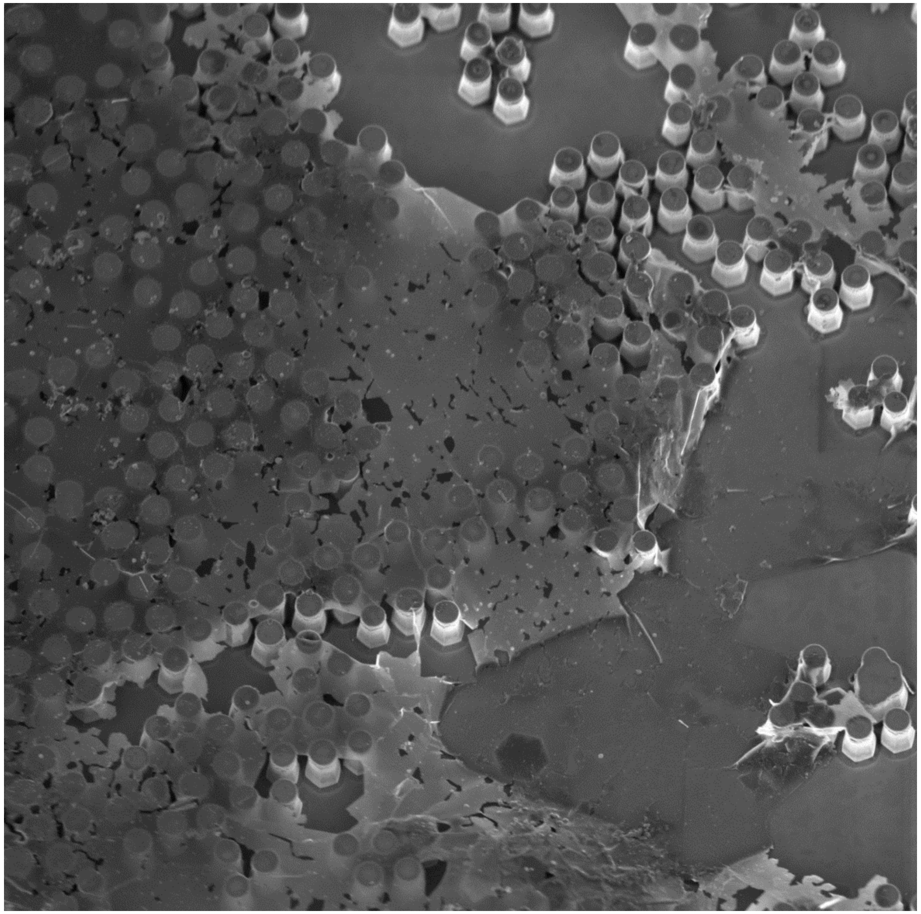


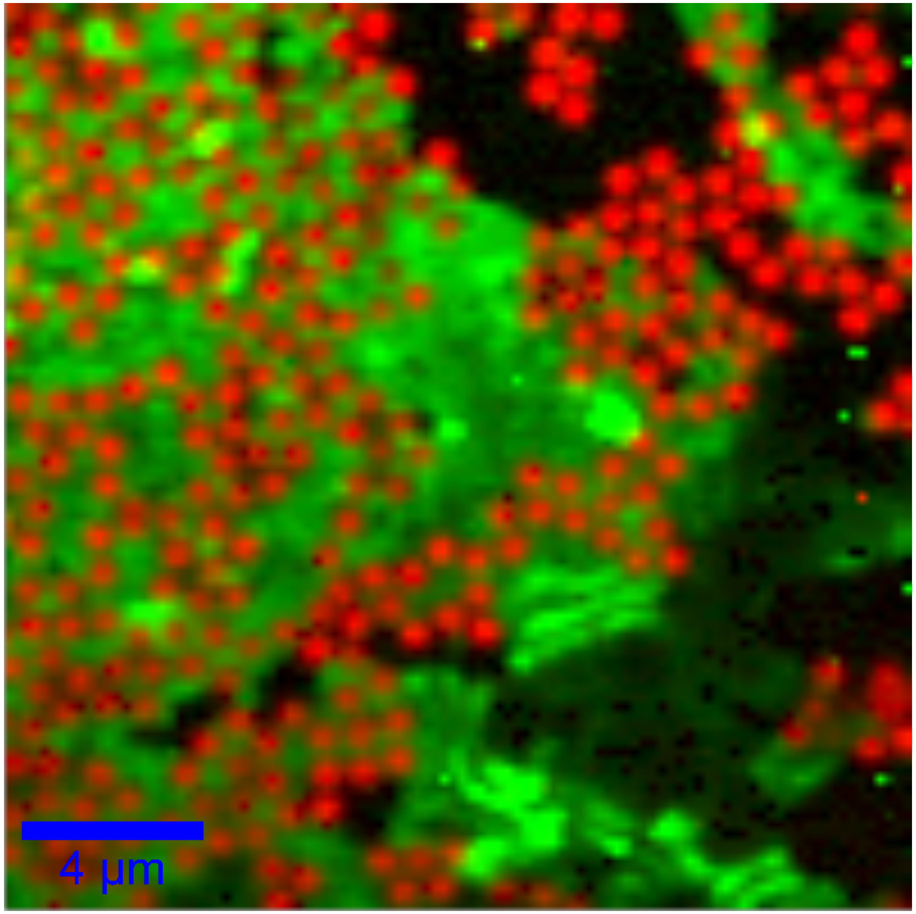


Disorder-induced D-band shows defects inside the graphene layer which act as nucleation points for GaN.

Graphene on top of GaN nanorods

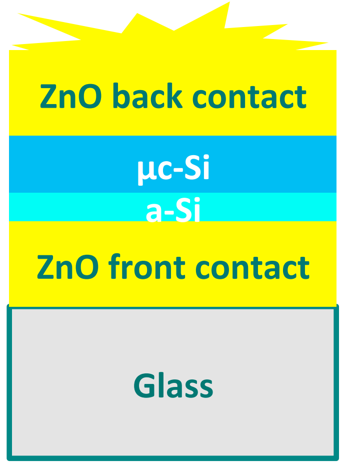
Freestanding graphene on top of GaN nanorods is an interesting system to test for resolution and nicely shows the signal increase compared to supported graphene.



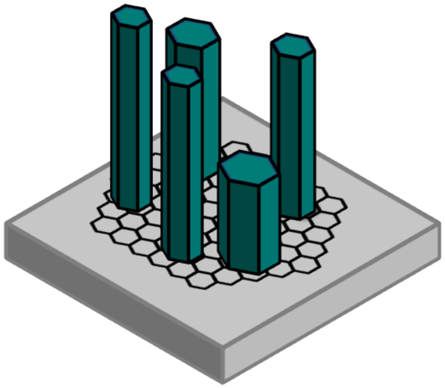


Applications

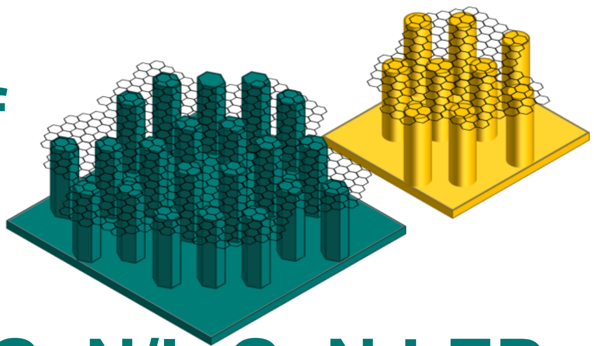
- **Thin film a-Si/µc-Si tandem solar cells**



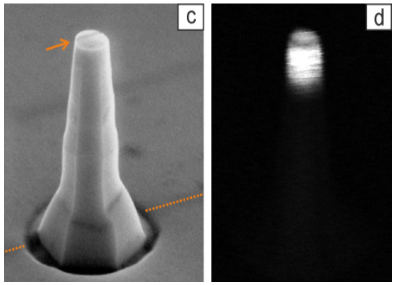
- **GaN nanowires grown on graphene**



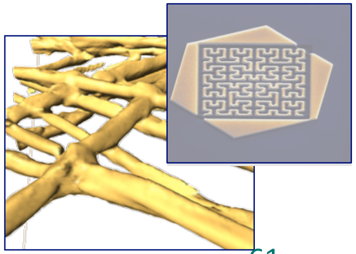
- **Graphene on top of GaN/Si nanorods**



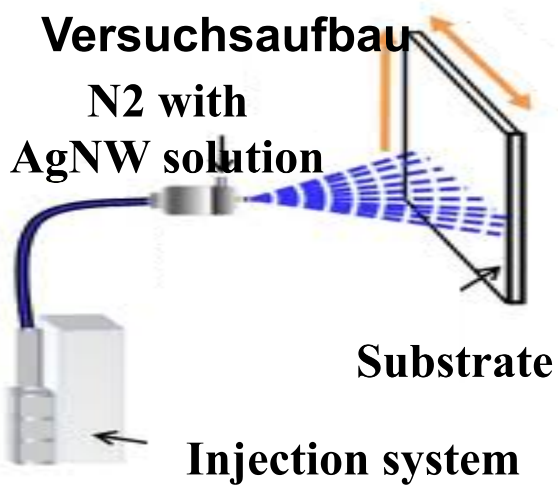
- **Model & „real life“ GaN/InGaN LEDs**

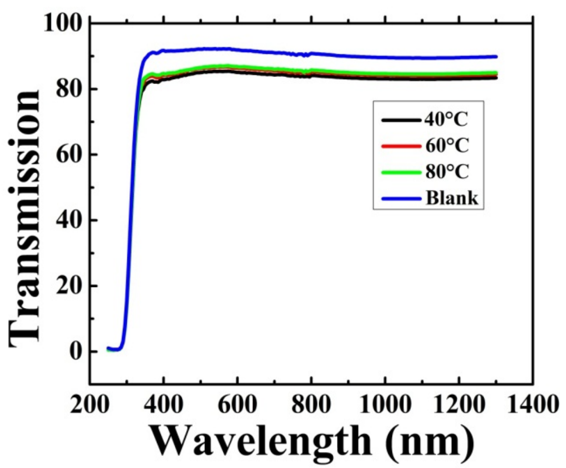


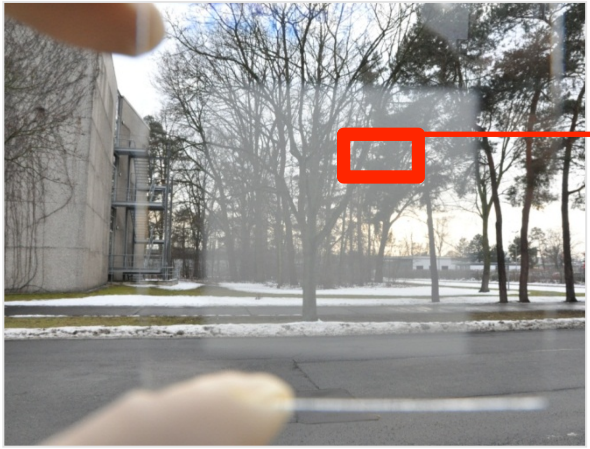
- **Ag-NW network electrodes + plasmonic antennas**

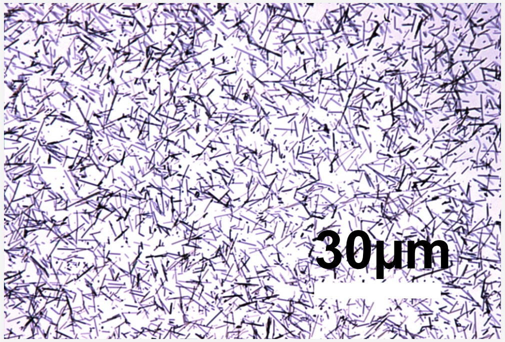


- **sprayed Ag-NW transparent electrode**

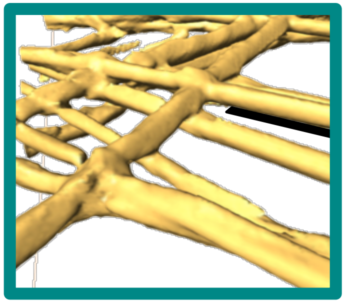




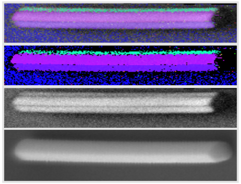




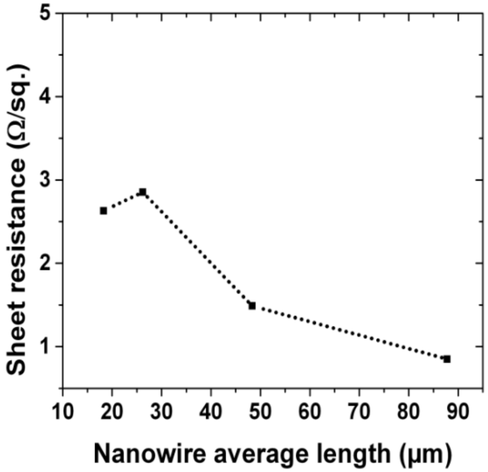
- **TEM tomography**



- **SEM - EBSD**

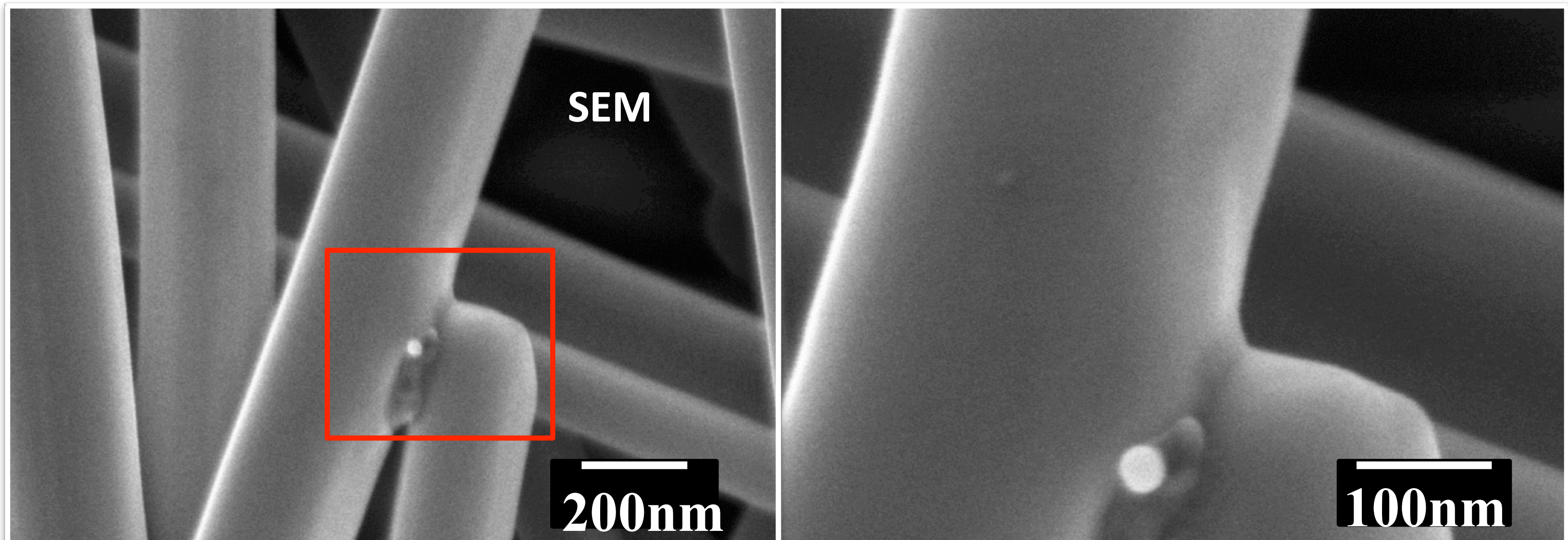


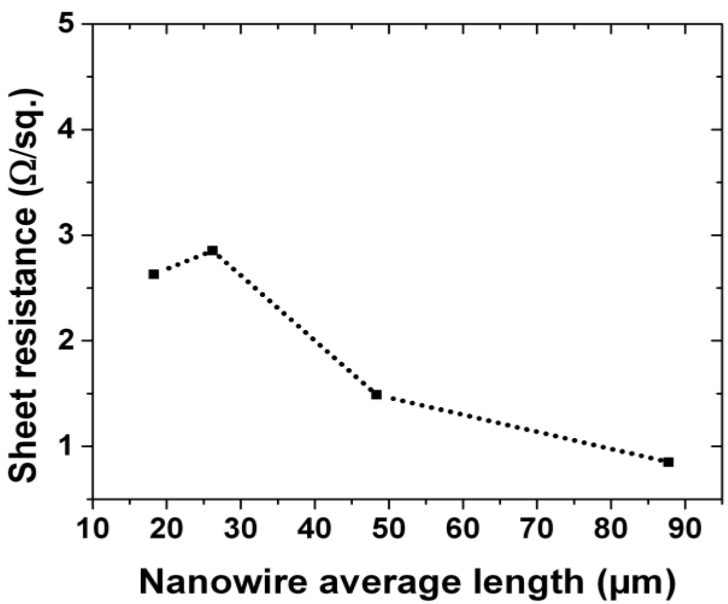
- **IV - probing**

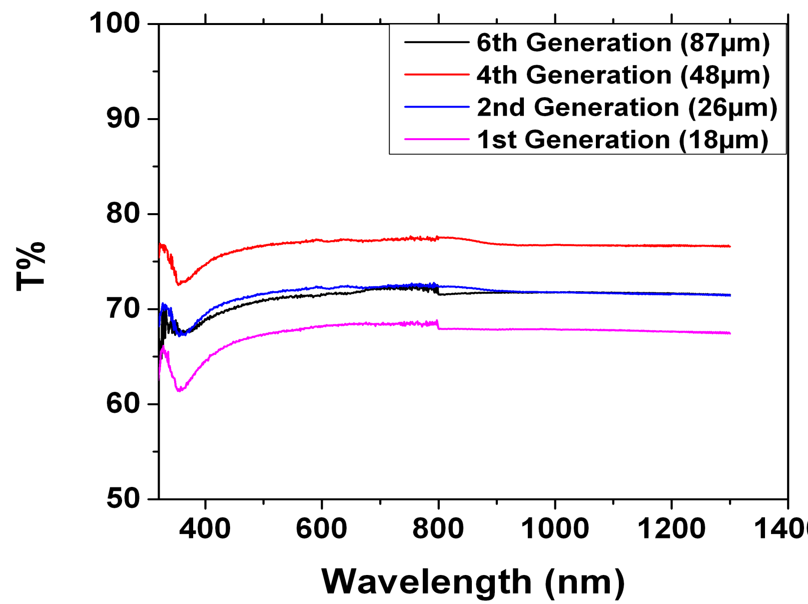


Novel contacts – Ag wires

Ag NW welding upon: heat treatment (300°C) or UV-illumination

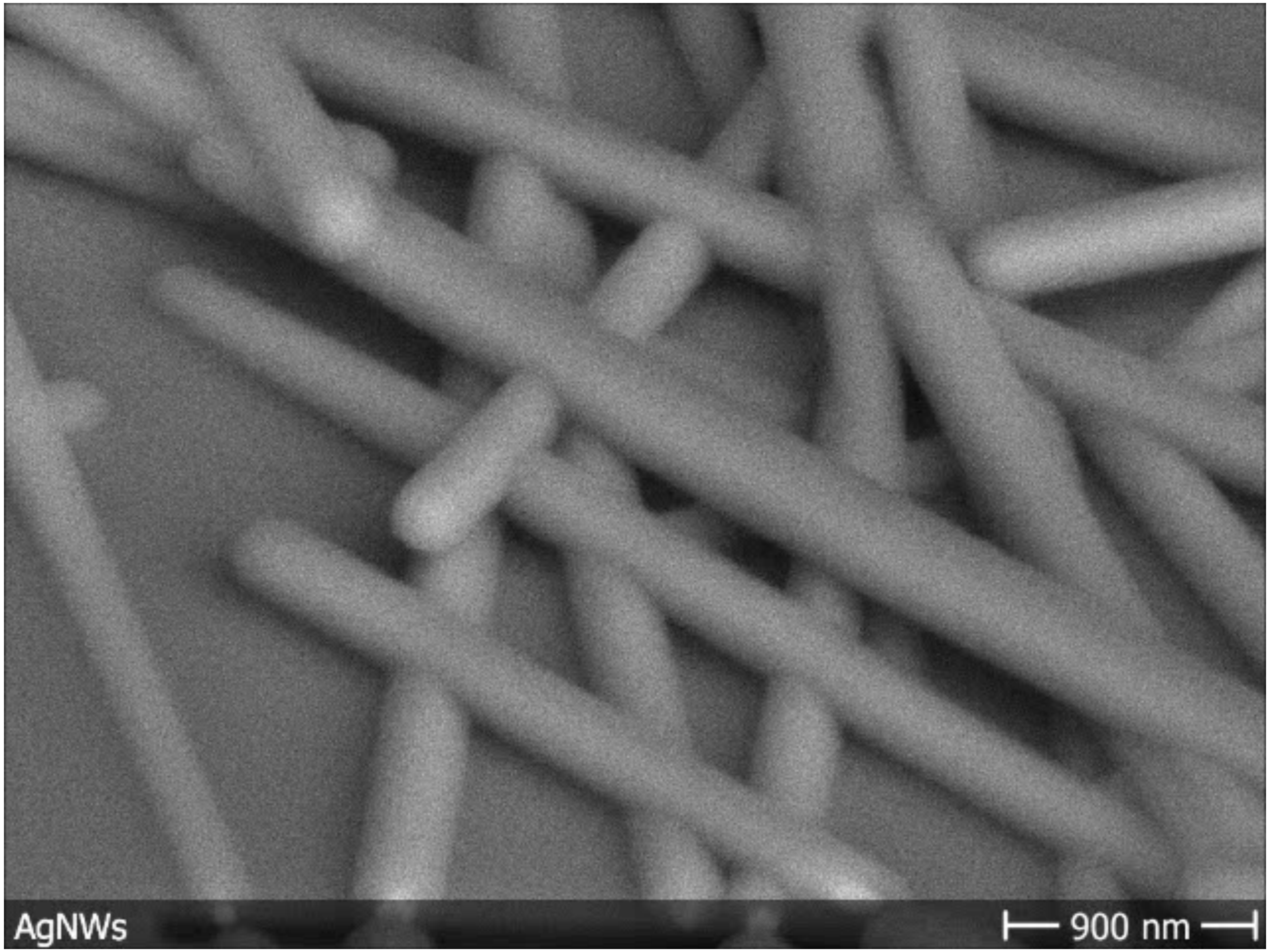






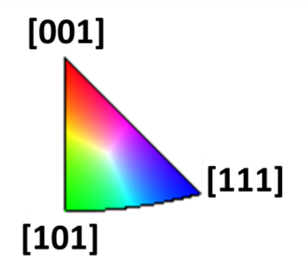
Novel contacts – Ag wires

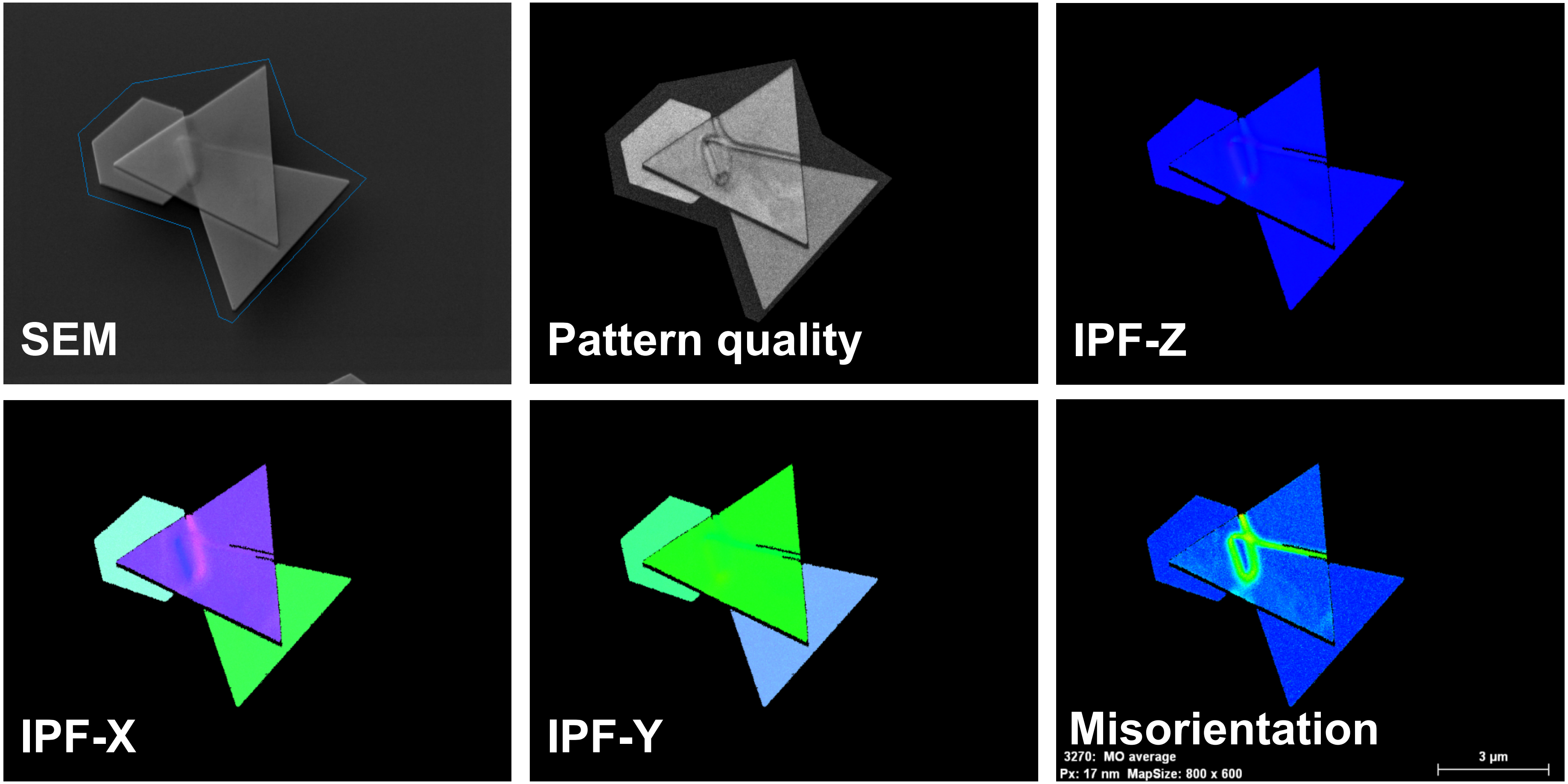
Ag NW electrode with AZO coating: stabilization & enhanced conductivity



Thinning and structuring of gold plates

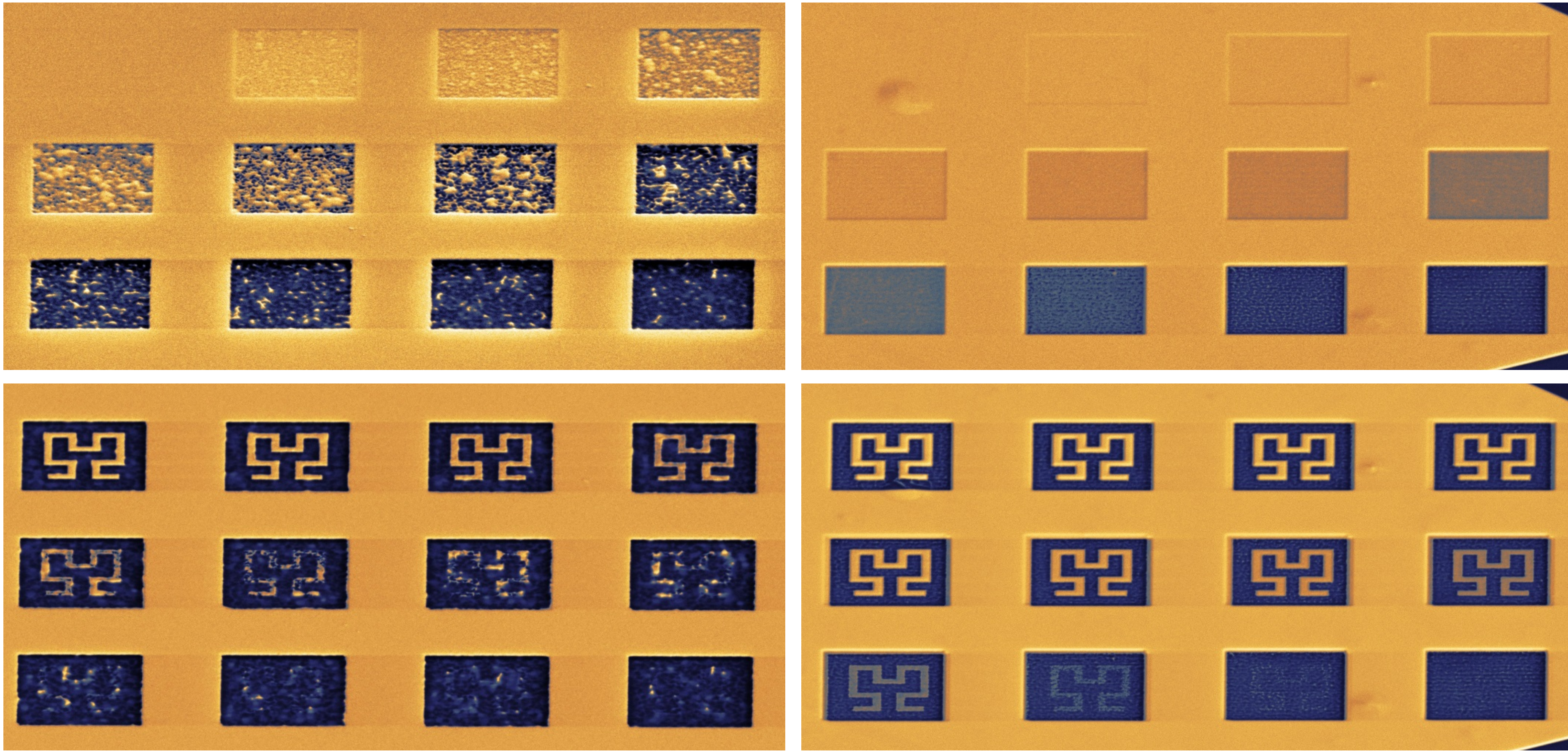
Wet-chemical grown, ultrathin, flat monocrystalline gold plates are an ideal substrate for plasmonic applications. We test an in-situ thinning process using the FIB.





Thinning and structuring of gold plates

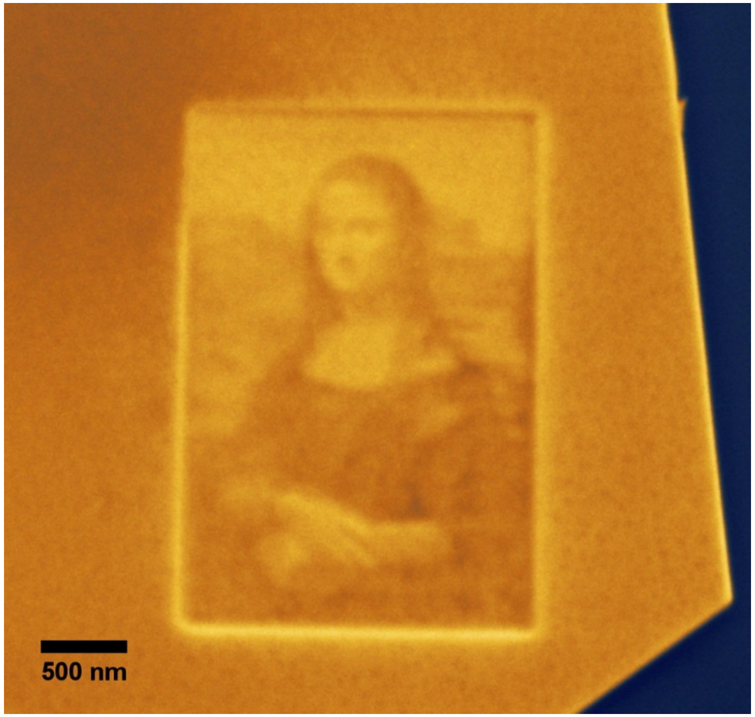
Sputtered Au layer | **Au flake**

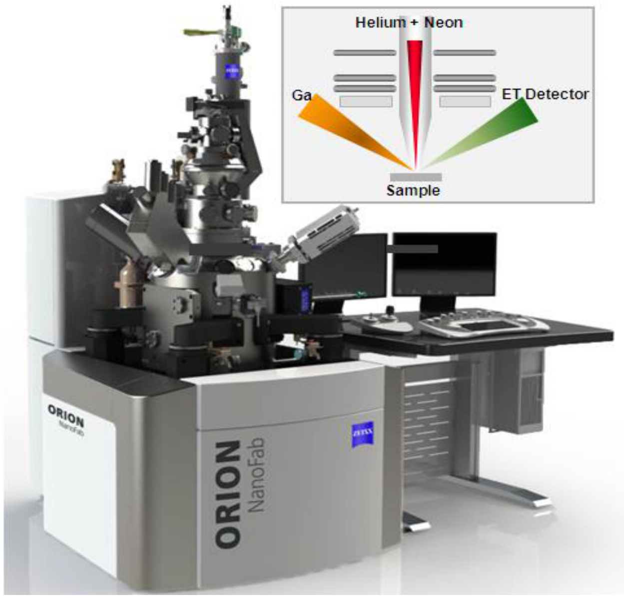


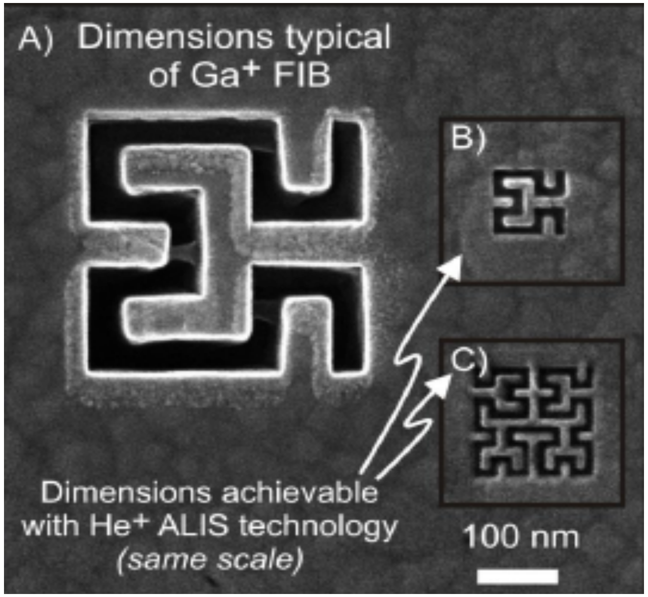
3*3 µm² small fields were milled into the layers with depth step sizes of ~5nm. Sputtered layers show an extreme anisotropic behaviour.

Hilbert curve antennas were milled into the thinned layers to generate ultrathin nanostructures. In the sputtered layers this is only possible for the first 4 steps.

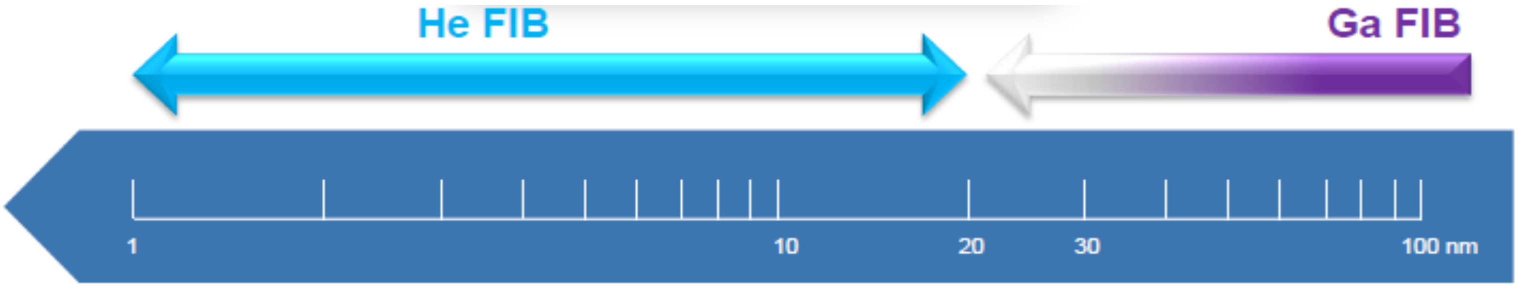
FIB patterning



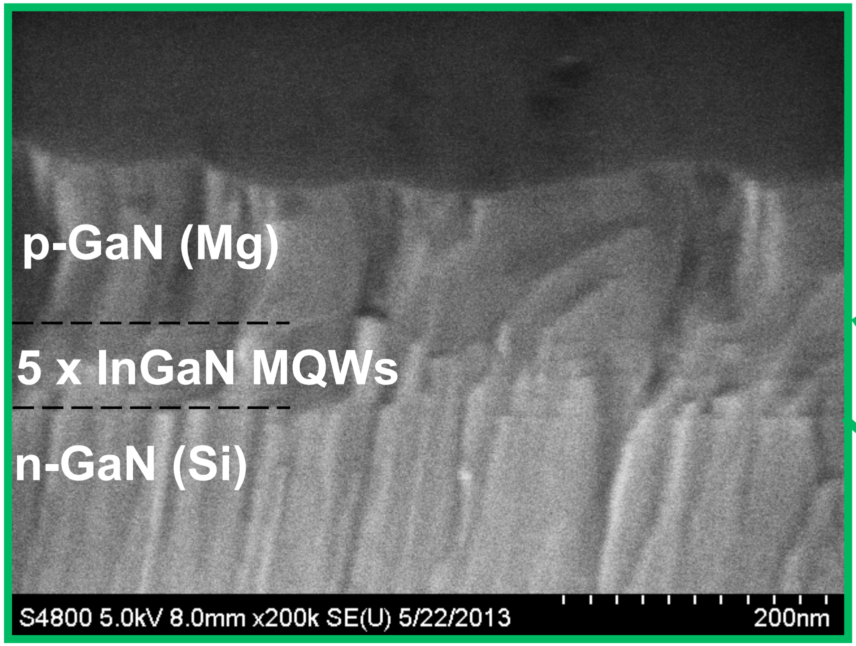




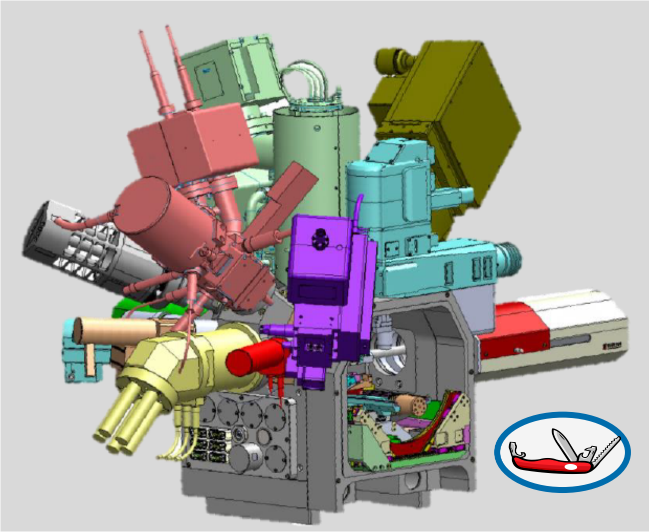
2D & 3D antenna structures possible



TOF-SIMS measurements on a GaN LED

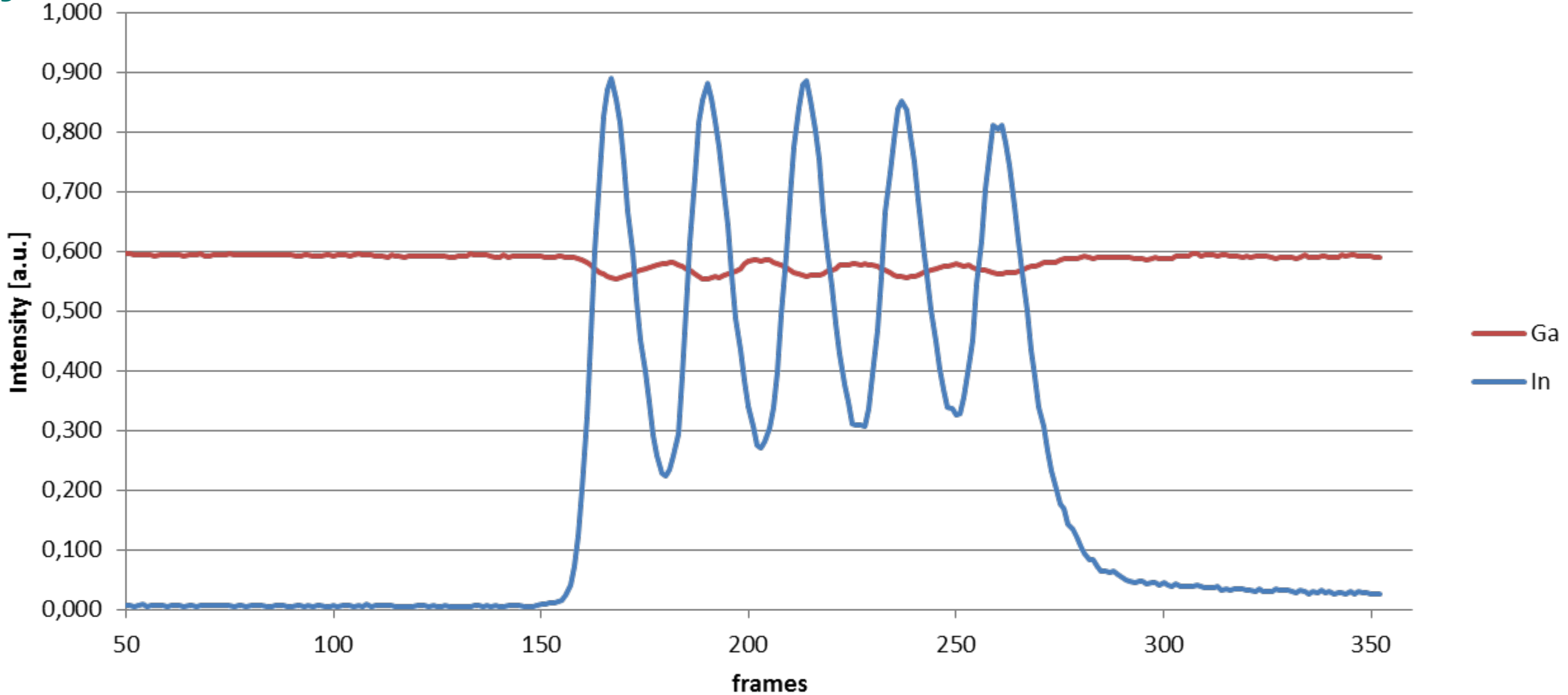


To analyze the model LED structure by TOF-SIMS inside the FIB/SEM, a typical Ga liquid metal ion source is unsuitable because it would inhibit the Ga identification from the GaN layers. Therefore we used a novel Xe plasma FIB.



TOF-SIMS measurements on a GaN LED

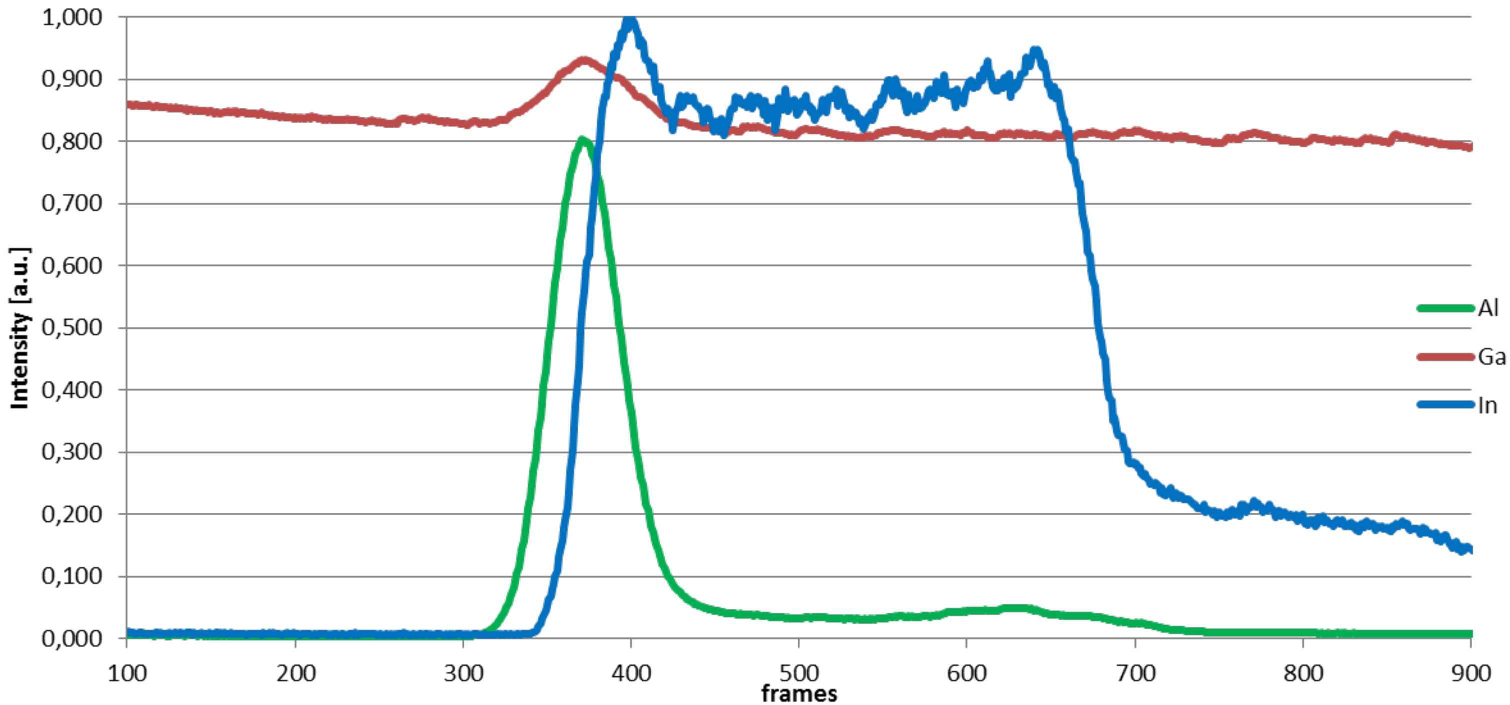
The ideal case: A model LED with smooth layers.



The Xe-FIB TOF-SIMS is capable of resolving ~2nm thin layers. Furthermore the use of Xenon enables the investigation of Ga-rich materials.

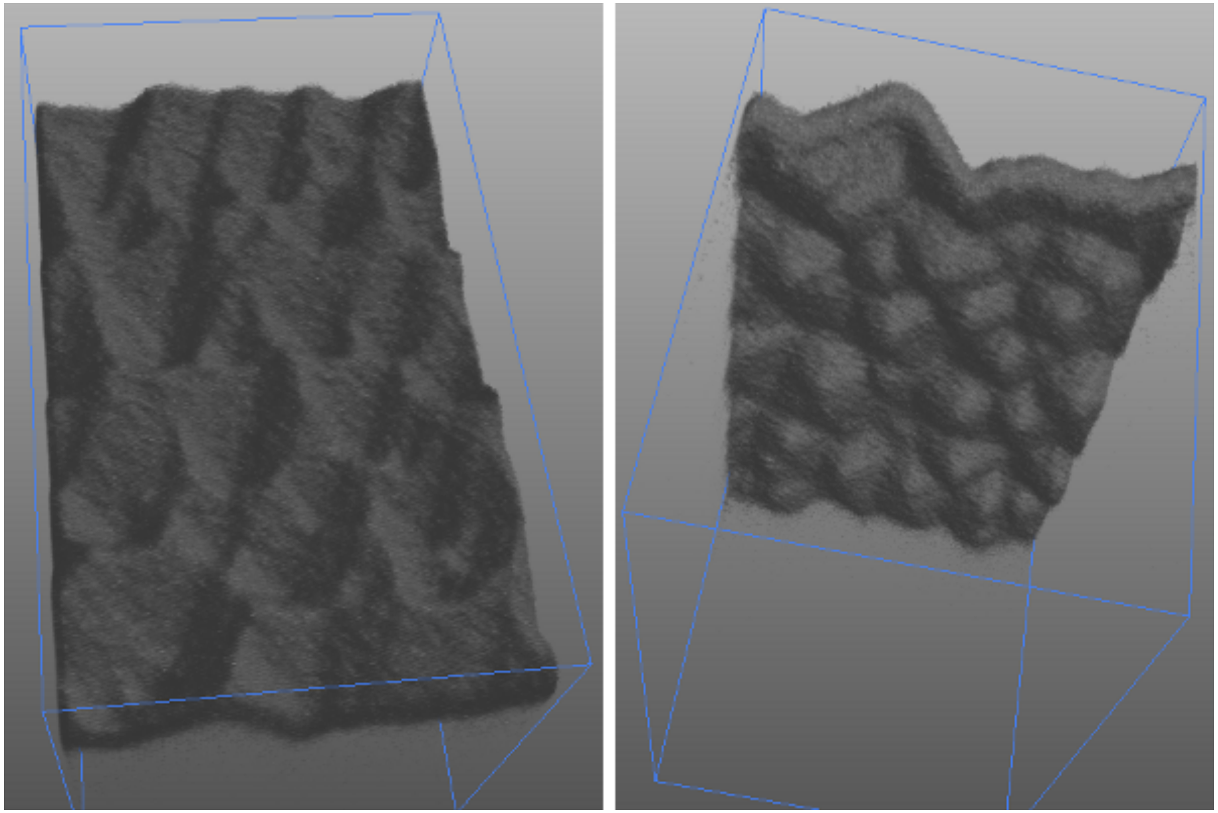
TOF-SIMS measurements on a GaN LED

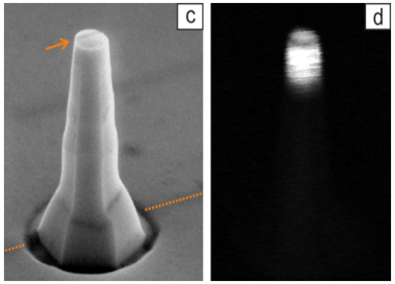
The non-ideal case: A industrial LED with rough QWs



Here, 10 QWs with a rough surface structure are preventing the resolution of single layers. A buffer layer of AlGaN on top enables a 3D visualization of the roughness.

TOF-SIMS measurements on a GaN LED



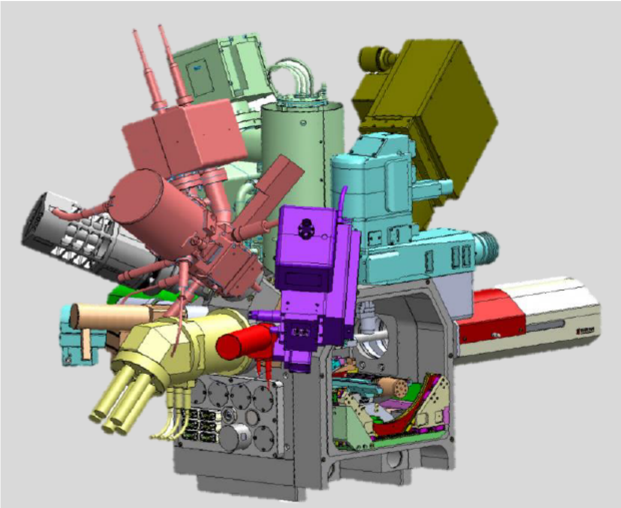


Cathodo-luminescence

3D reconstruction of TOF-SIMS $^{27}Al^{+}$ signal that shows an Al rich layer covering InGaN/GaN QWs in LED structures. The z-axis has been expanded 25 times to highlight the interfacial roughness. Field of view is 60 mm x 36 µm.

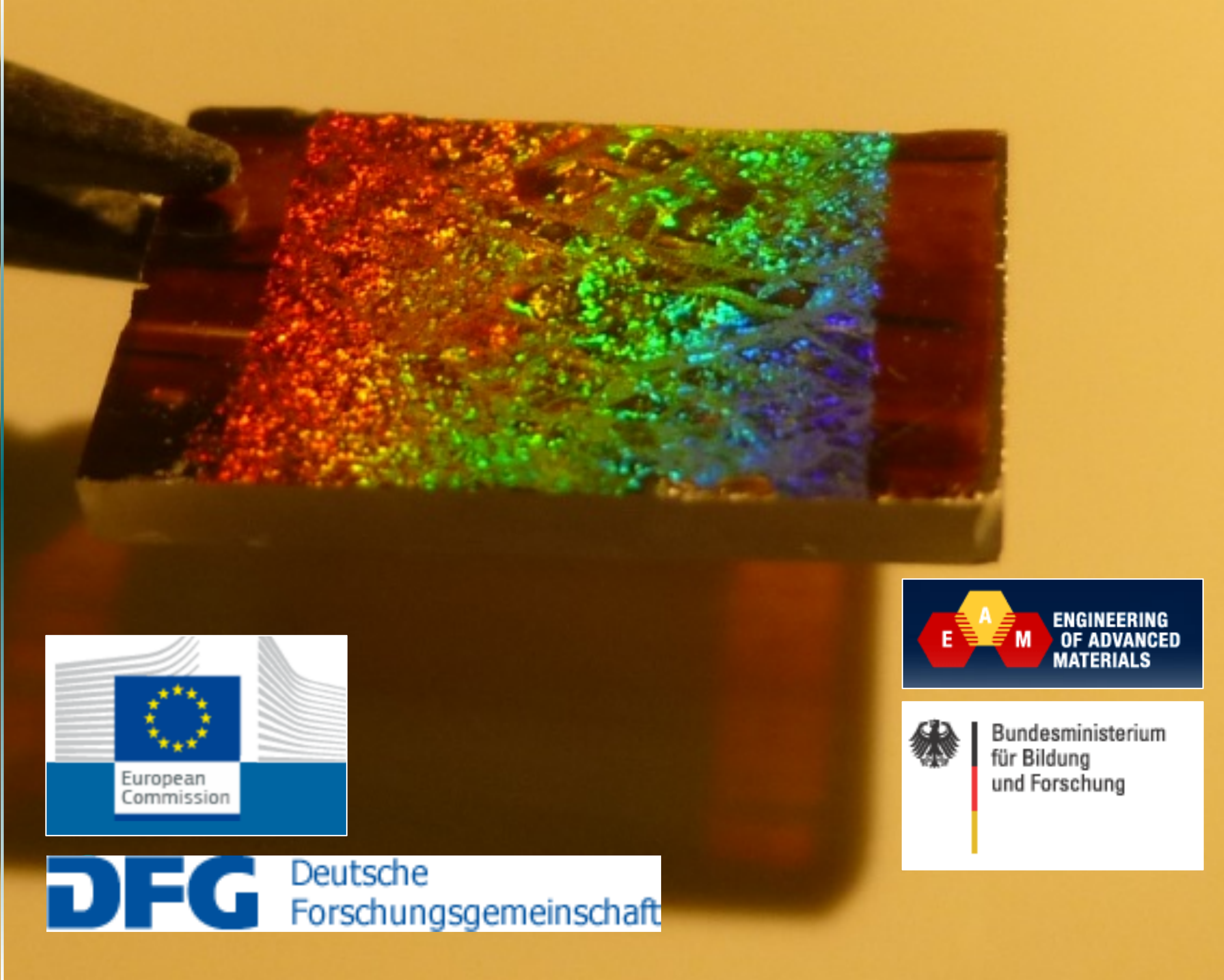
EU project UnivSEM

Innovations of UnivSEM:
- Plasma FIB (Xe), 50x faster than Ga
- Integrated AFM (Specs Curlew)
- TOF-SIMS (Tofwerk)
- Novel immersion optics
- Color-CL
- Integrated Raman microscope (WiTec)
- EQE
- Standards: EDX, EBSD, 5x multi-GIS, EBIC...

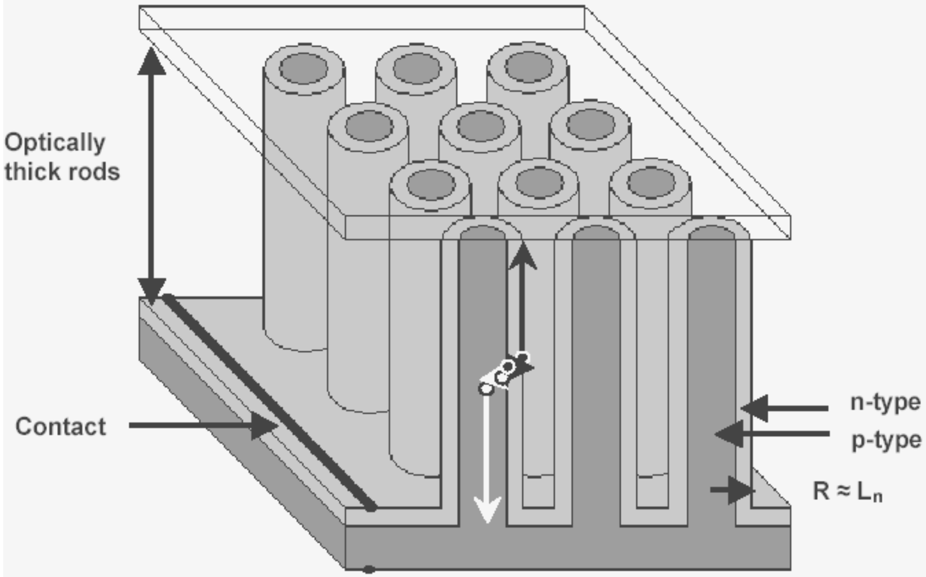


MPL tasks in UnivSEM:
- to compare the integrated Raman microscope with a standalone and a different integrated version
- To find, if necessary create, samples from different fields of research for benchmarking and public presentation of the prototype.

- Evaluating the Tescan/WiTec RISE microscope

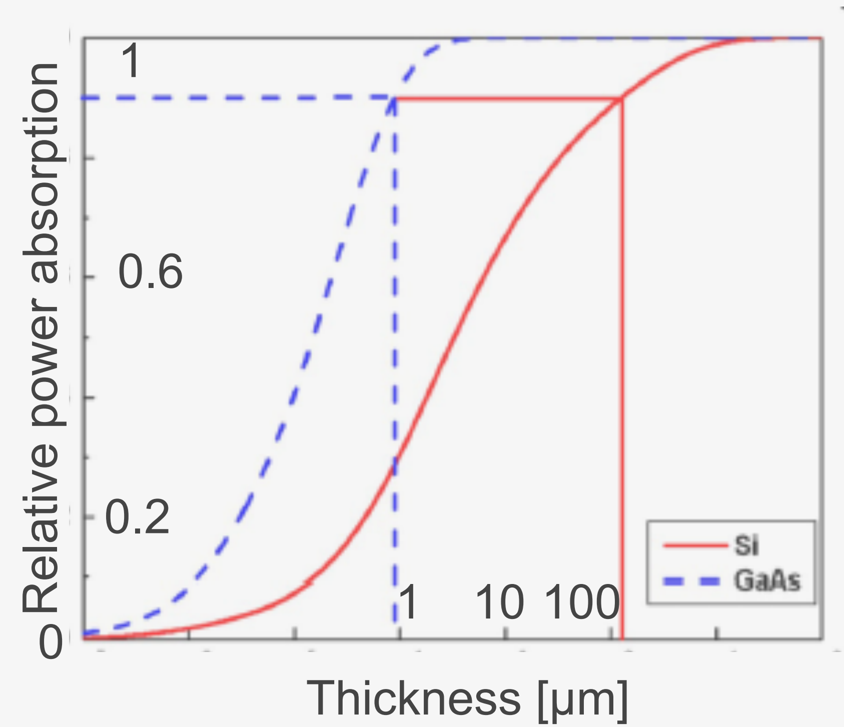

European Commission
ENGINEERING OF ADVANCED MATERIALS
E A M
Bundesministerium für Bildung und Forschung
DFG Deutsche Forschungsgemeinschaft

Si NW solar cells



Si NWs (5µm length): η ~ 15-20%

Si thin film: η ~ 6-10%



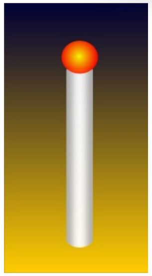
B.M. Kayes, H.A. Atwater, N.S. Lewis, J. Appl. Phys. 97, 114302 (2005)

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)

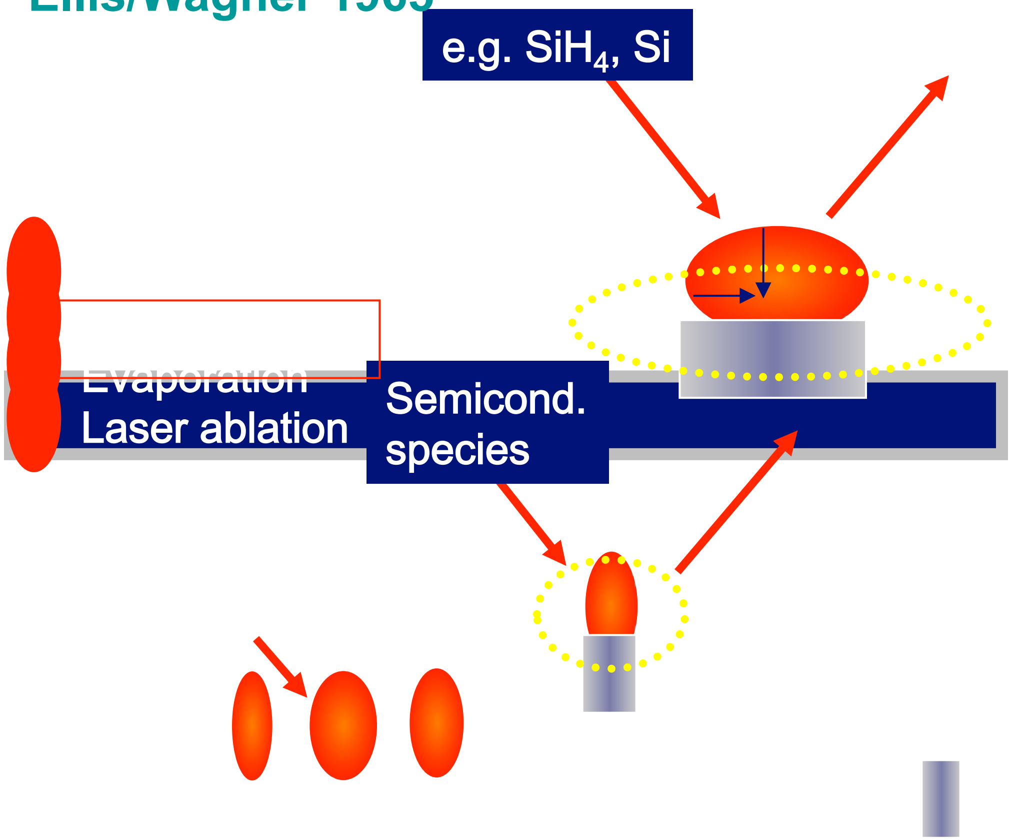
M.D. Kelzenberg, D.B. Turner-Evans, B.M. Kayes, M.A. Filler, M.C. Putnam, N.S. Lewis, H.A. Atwater, Nano Lett. 8, 710 (2008)

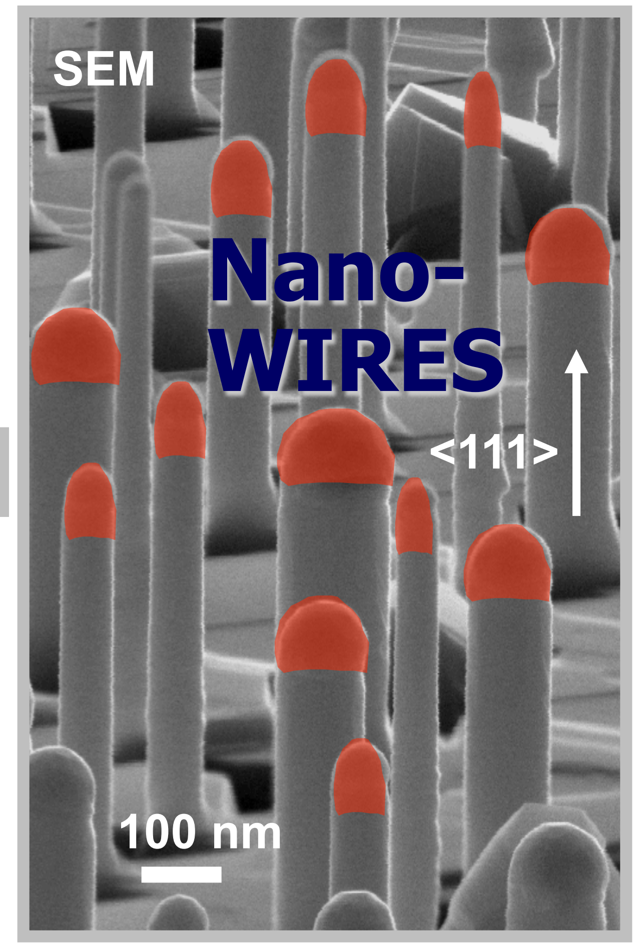
Si NW morphologies



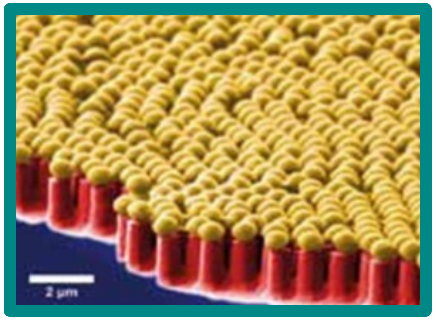
metal catalyzed Si NW growth
vs. wet chemical etching of Si

Ellis/Wagner 1965



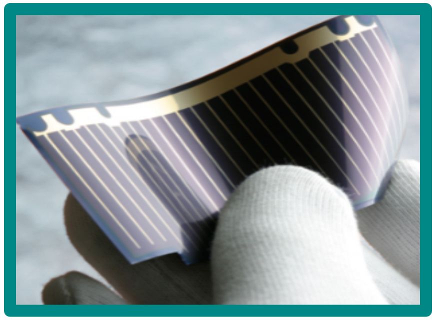


Outline



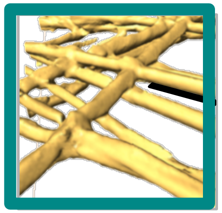
Si Nanowires (NWs) - Synthesis & Morphology

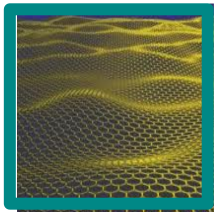
- top down NW etching



NWs in solar cell applications

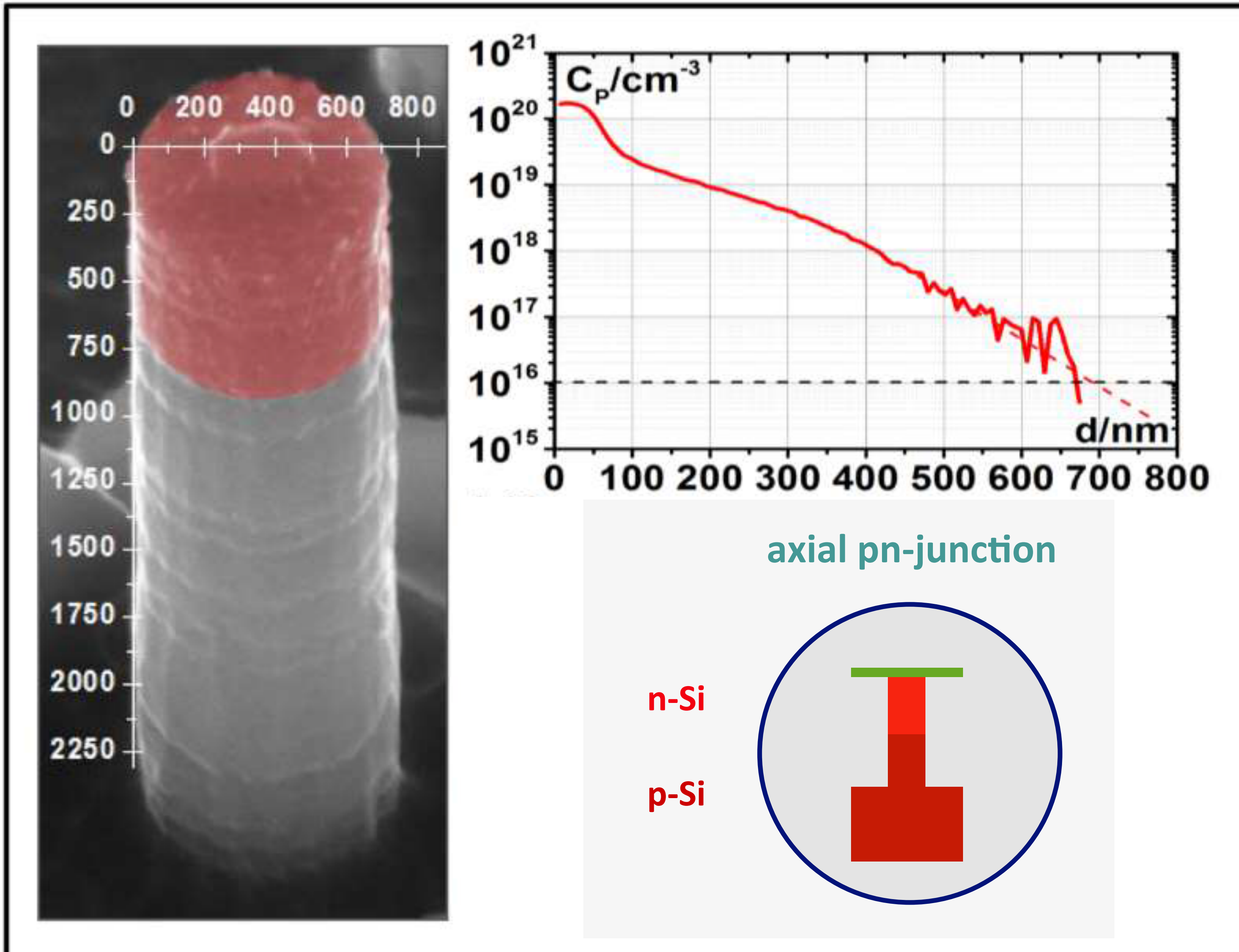
- **semiconductor NWs in different cell concepts**
- surface functionalization of NWs to improve solar cell performance





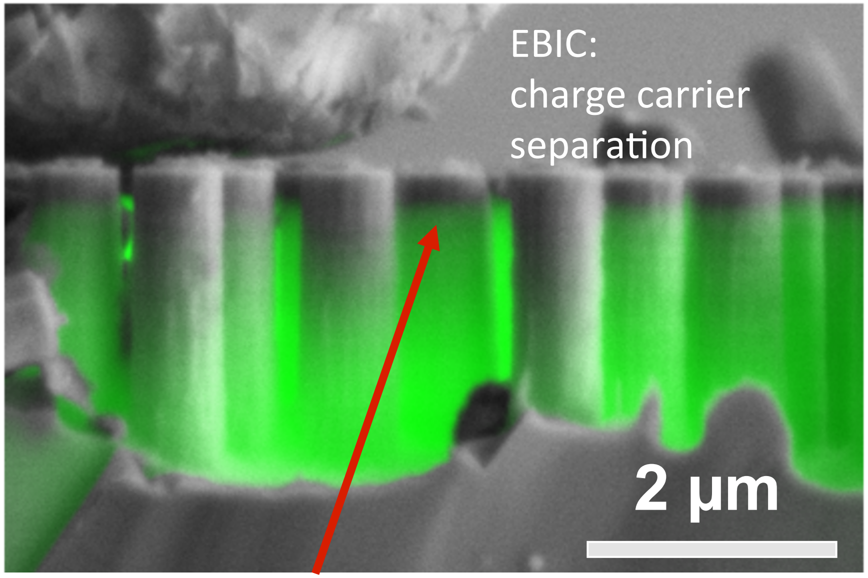
Novel contacts: graphene, Ag NW webs, TCOs

Spin on doping: SIMS



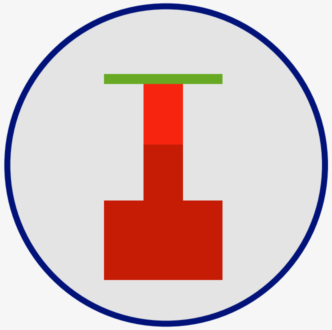
Electron beam induced current - EBIC

Axial p-n junctions in Si NWs (EBIC)



Dopant diffusion prior to etching

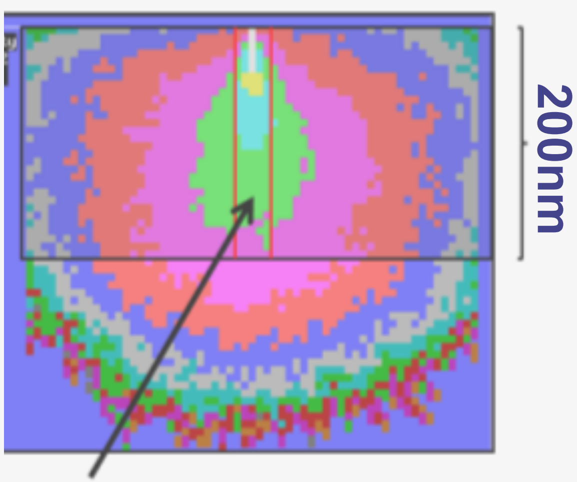
axial pn-junction



lateral EBIC resolution

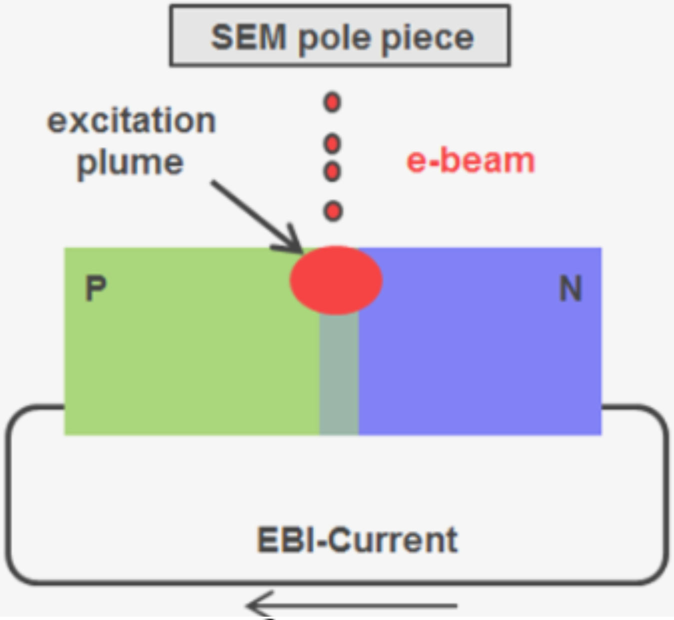
almost ~

resolution of SE image

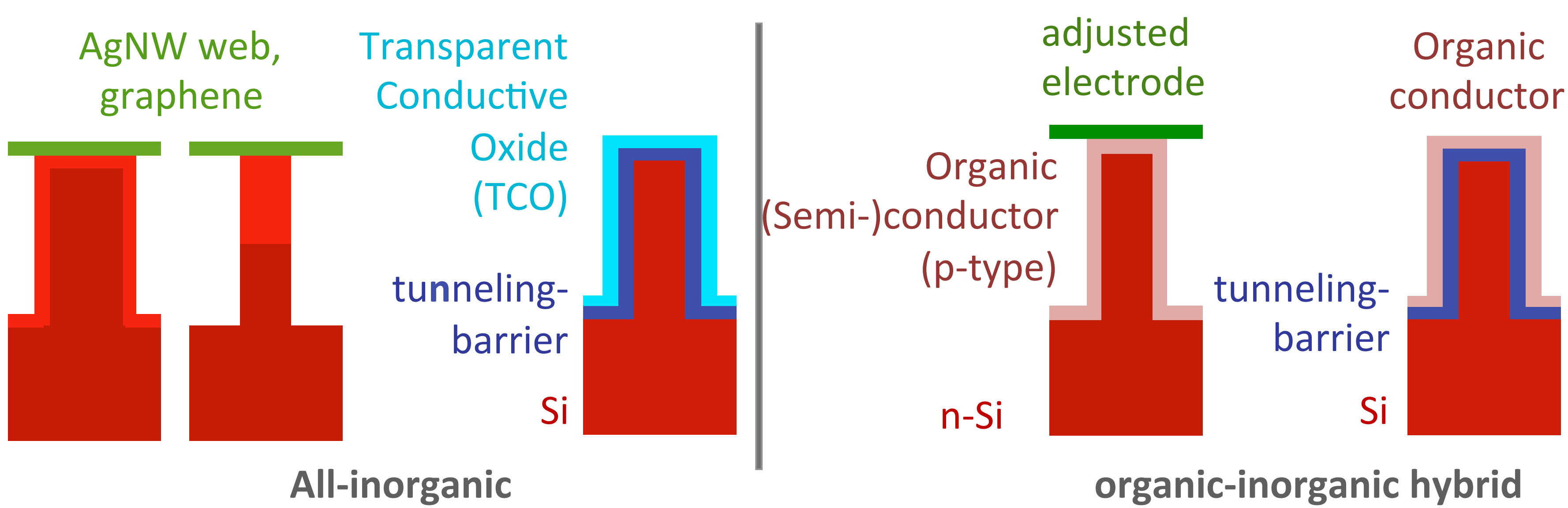


90% beam energy in 40nm channel

Electron Beam induced current (EBIC)



Si NW on glass platform



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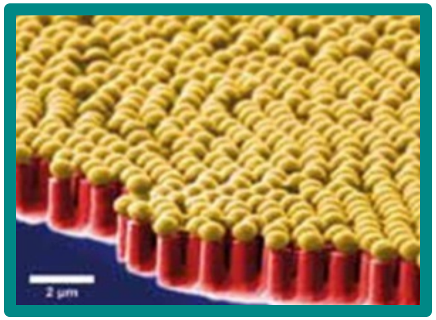
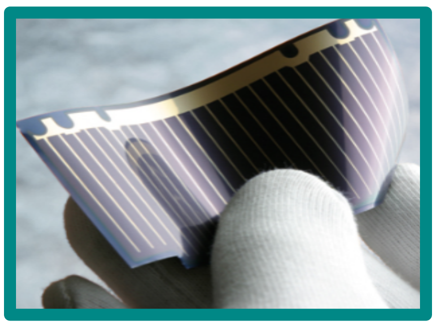


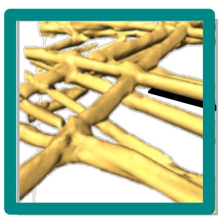
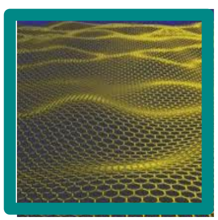
Si Nanowires (NWs) - Synthesis & Morphology

- top down NW etching



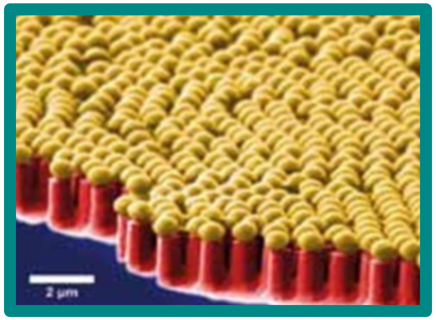
NWs in solar cell applications

- semiconductor NWs in different cell concepts
- **surface functionalization of NWs to improve solar cell performance**

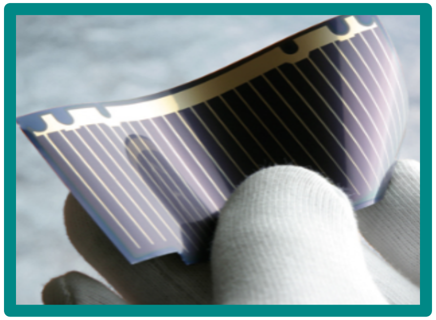
Novel contacts: graphene, Ag NW webs, TCOs

Outline



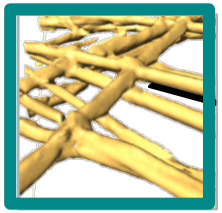
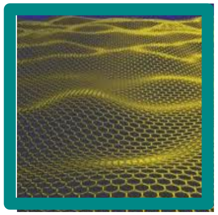
Si Nanowires (NWs) - Synthesis & Morphology

- top down NW etching



NWs in solar cell applications

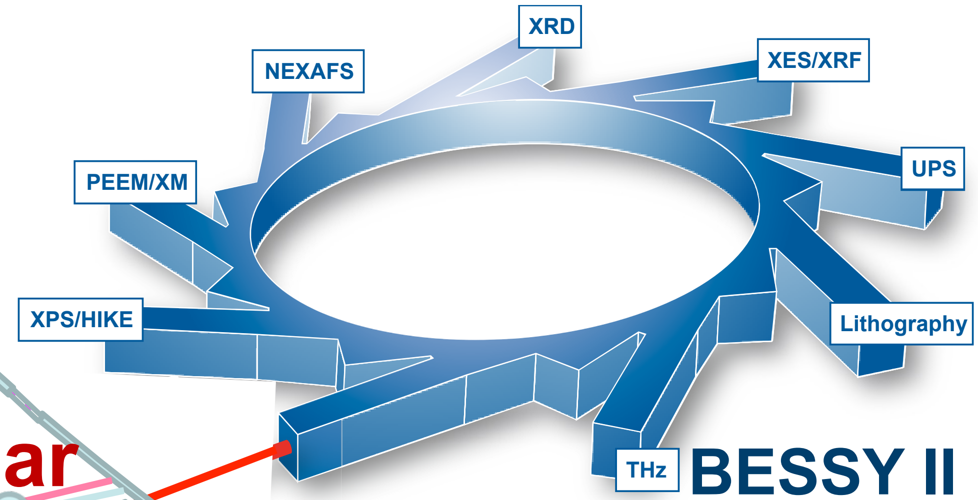
- semiconductor NWs in different cell concepts
- surface functionalization of NWs to improve solar cell performance

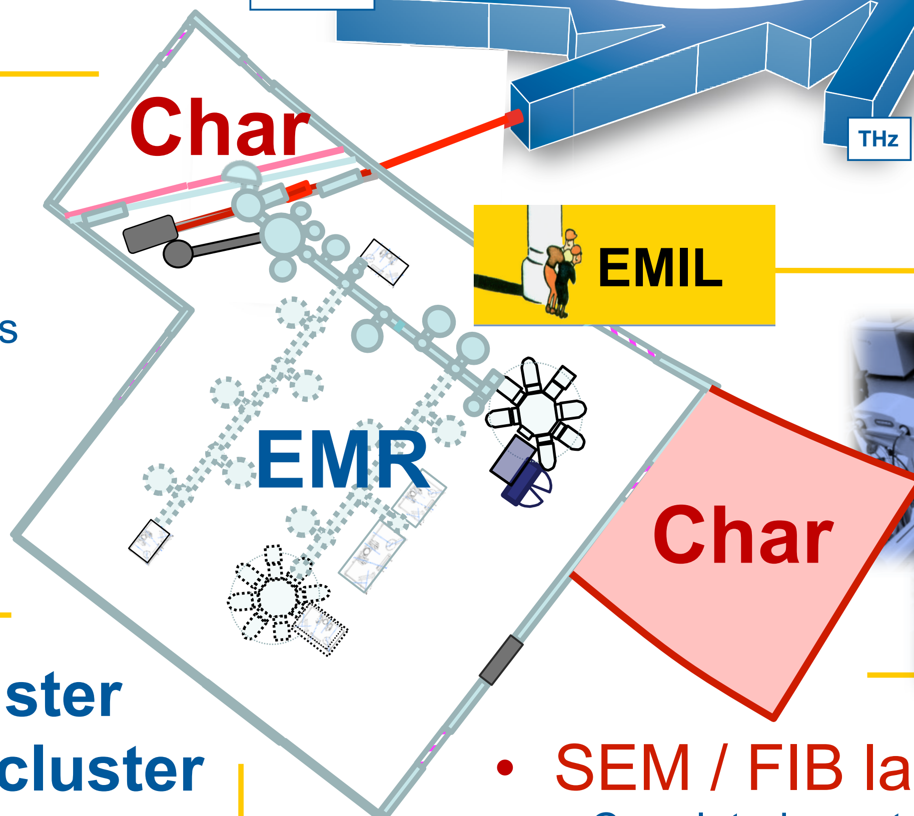



Novel contacts: graphene, Ag NW webs, TCOs

Materials – characterization – device integration

- X-ray analytics:
  - Spectroscopies & microscopies
  - Wide range of energies (80 eV - 10keV)

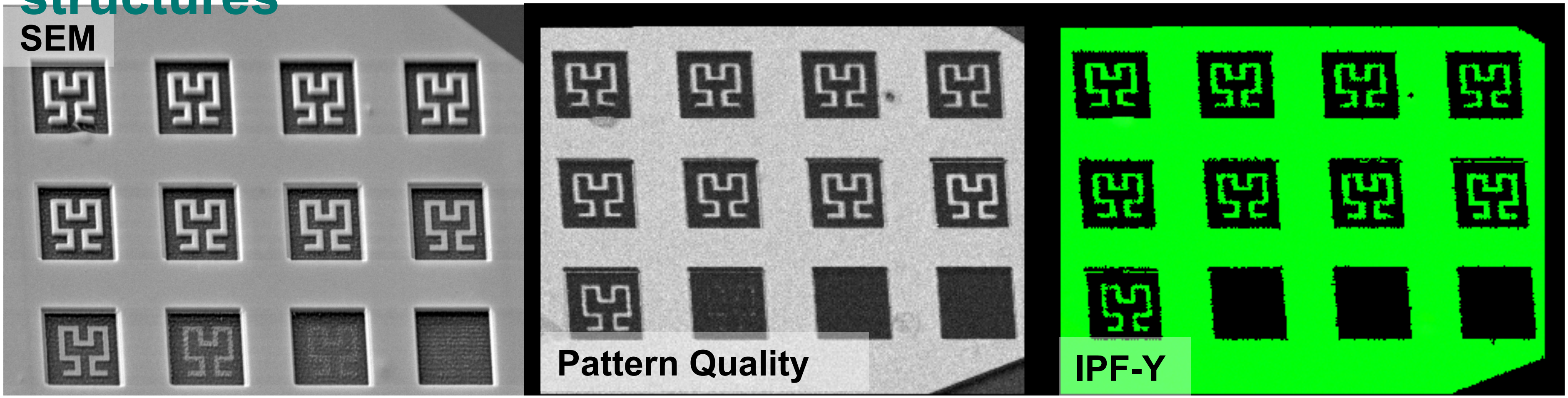


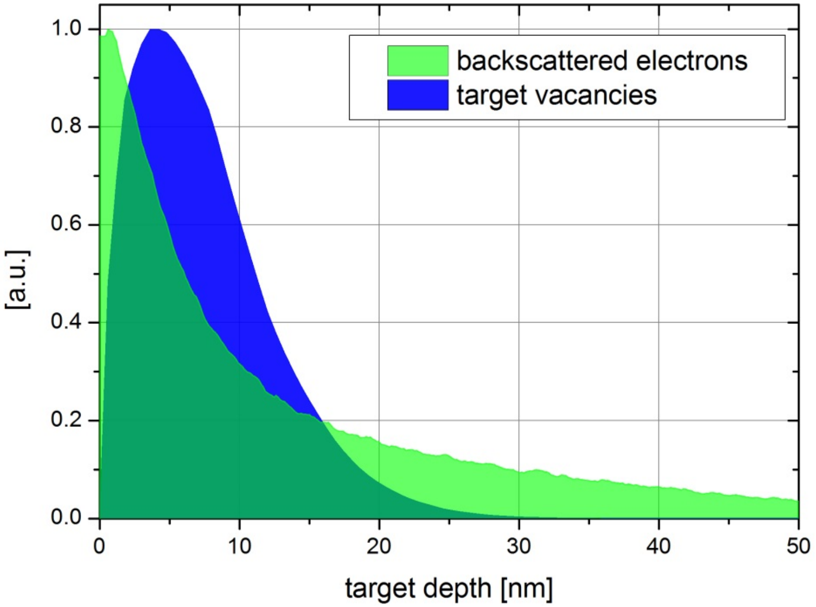


- **Si deposition cluster**
- **CIGS / Kesterite cluster**
- **Nano-/hybrid cluster**

- SEM / FIB lab:
  Correlated spectroscopies & microscopies

EBSD measurements on thinned antenna structures





SRIM and Casino simulations show that EBSD probing depth is similar to ion beam damaged layer thickness.

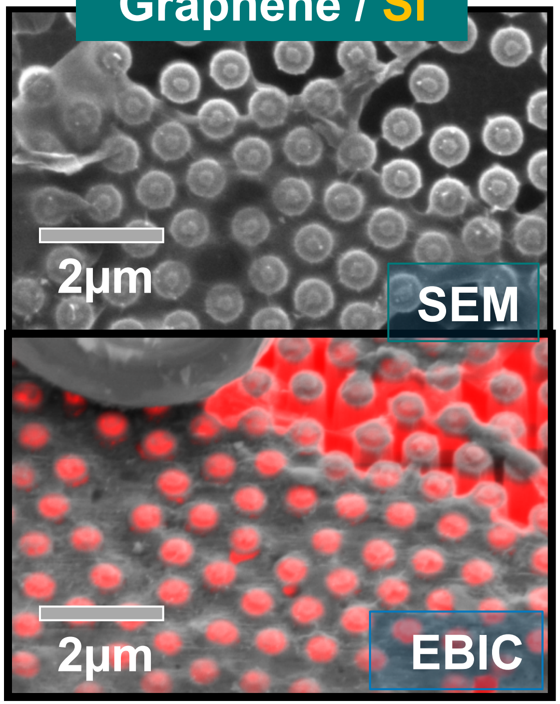
→ High energy Ga ions do not destroy the gold crystallinity!

→ Fabrication of 10nm thin monocrystalline structures possible!

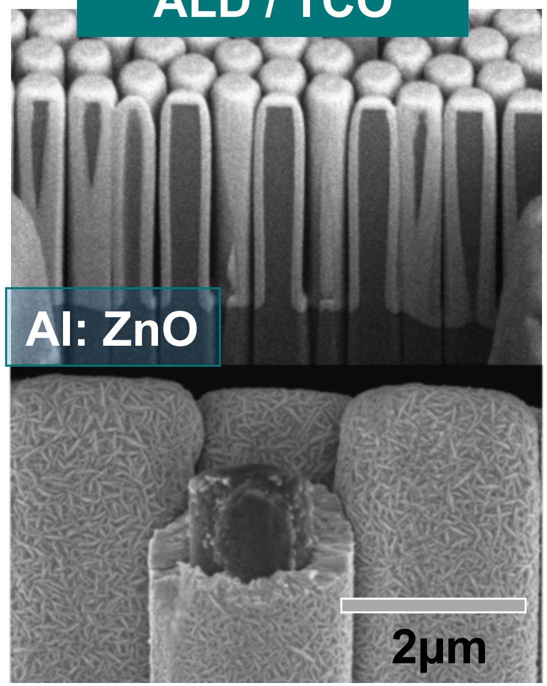
Novel transparent contacts

Goal: Higher transparency and conductance within reliable, fast and cheap processes despite complex 3D compostite materials

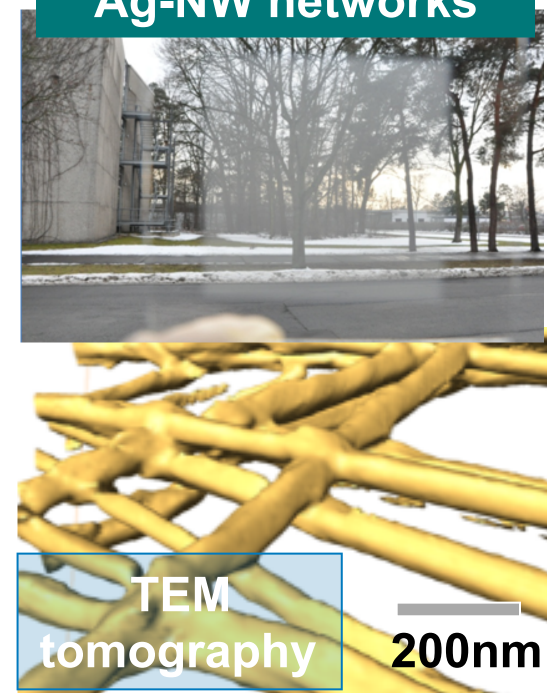
Graphene / Si



ALD / TCO



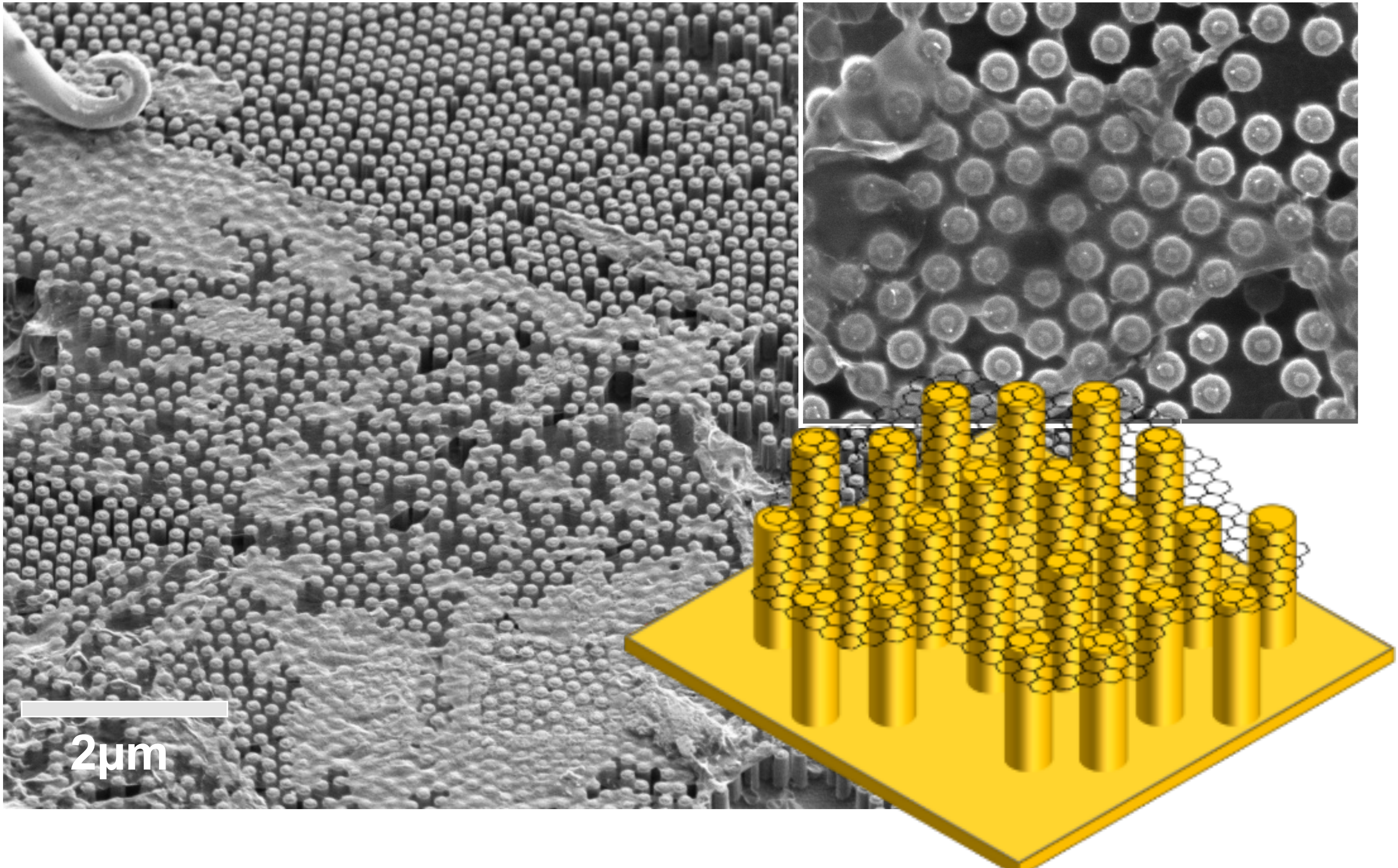
Ag-NW networks



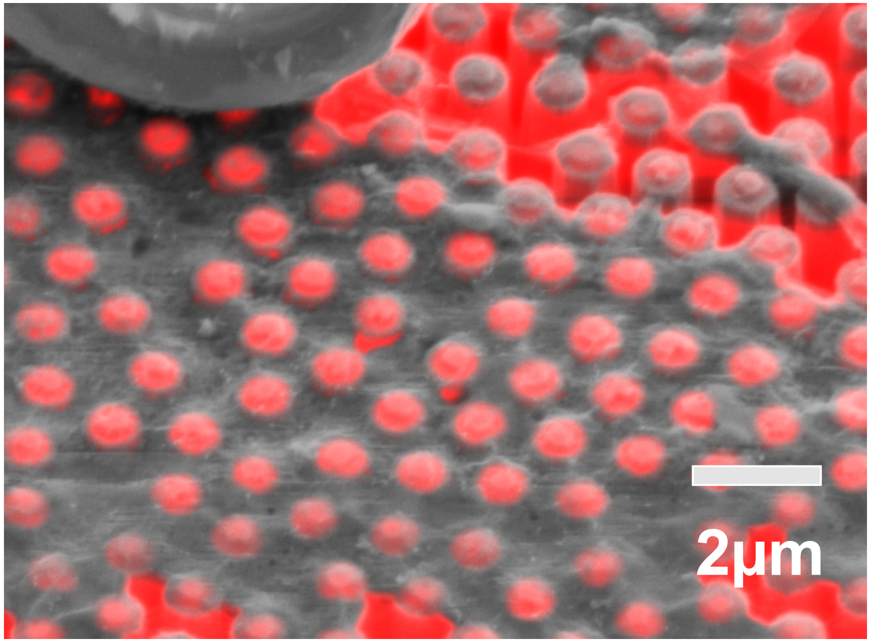
Publication: S. Schmitt et al.: Nano Letters 8, 8 (2012)
S. Schmitt et al.: submitted to Adv. Opt. Mat. (2014)
M. Bashouti et al.: unpublished

Novel contacts - graphene

Si NW solar cell with graphene contact

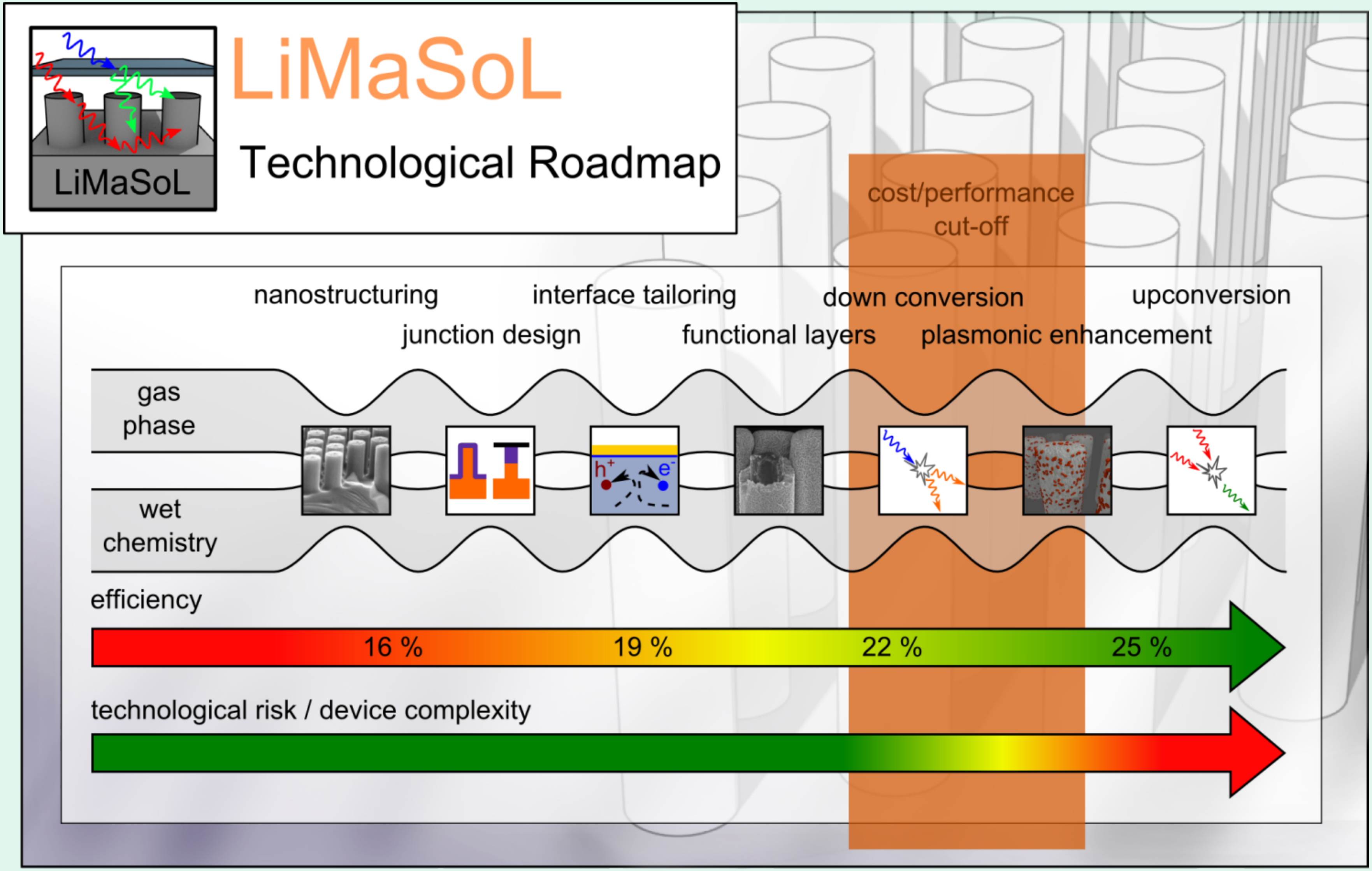


Si NW solar cell with graphene contact

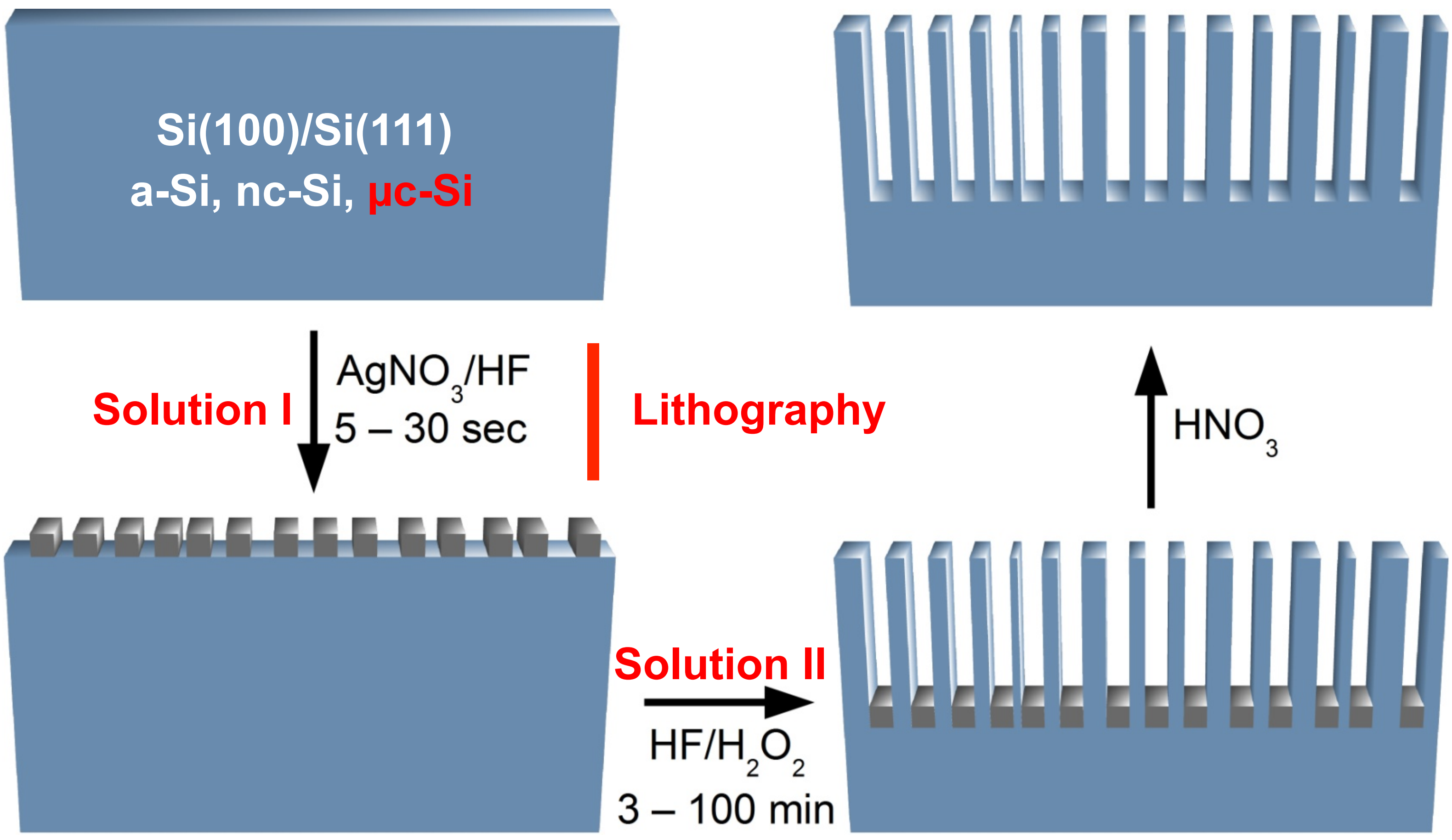


Nanostructured thin film solar cell

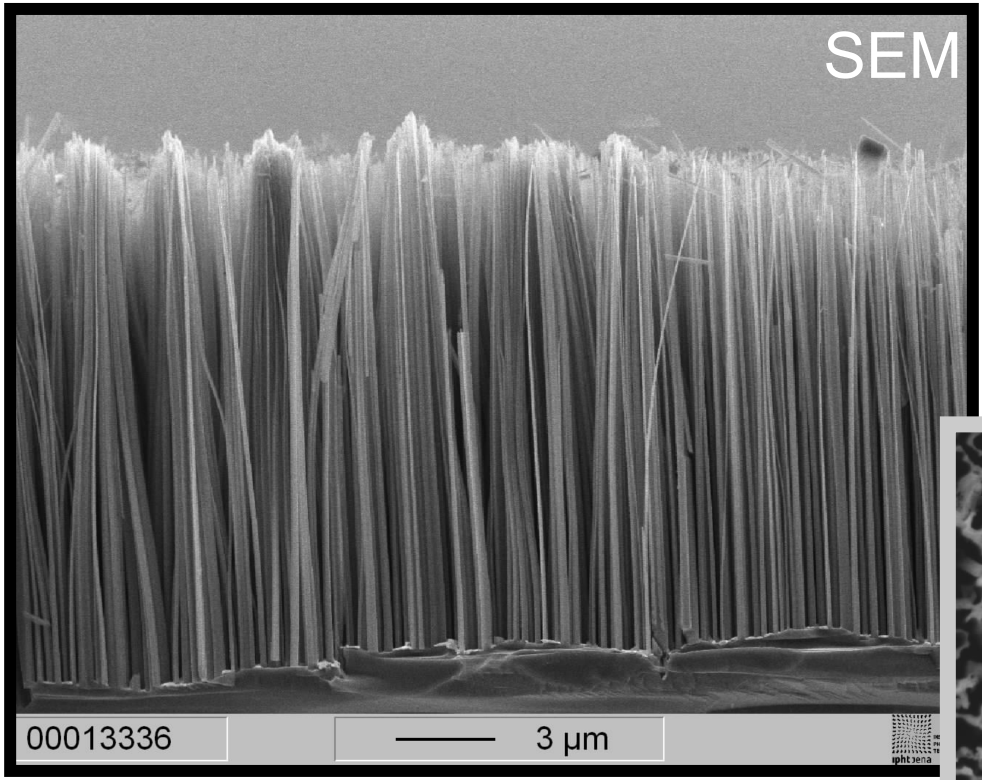
Where do we want to go?



Wet-chemically etched Si nanostructures

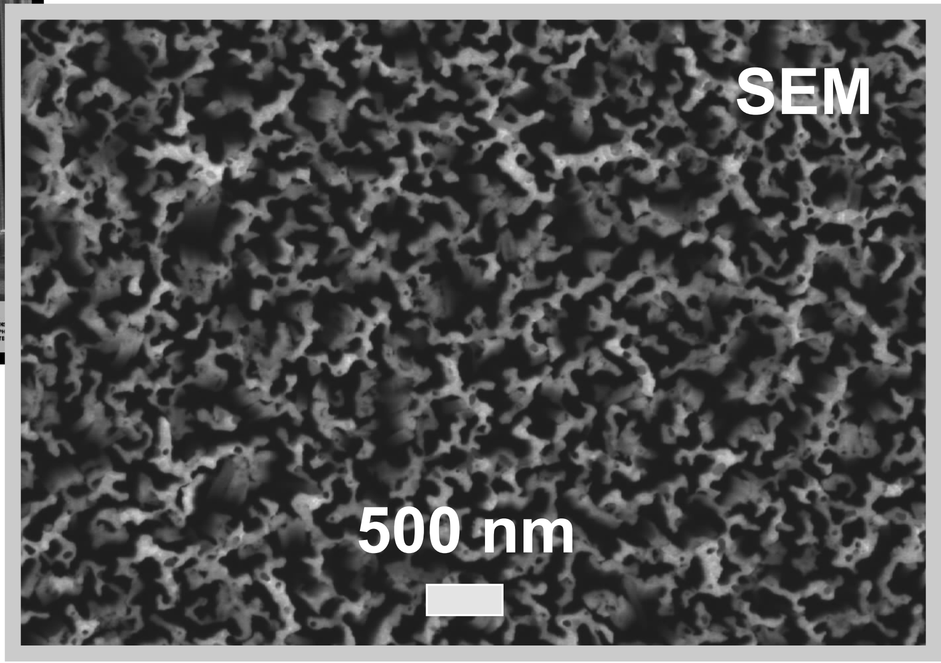


Wet-chemically etched Si nanostructures



Etching occurs in <100> directions

→ Vertical nanostructures on a Si(100) wafer

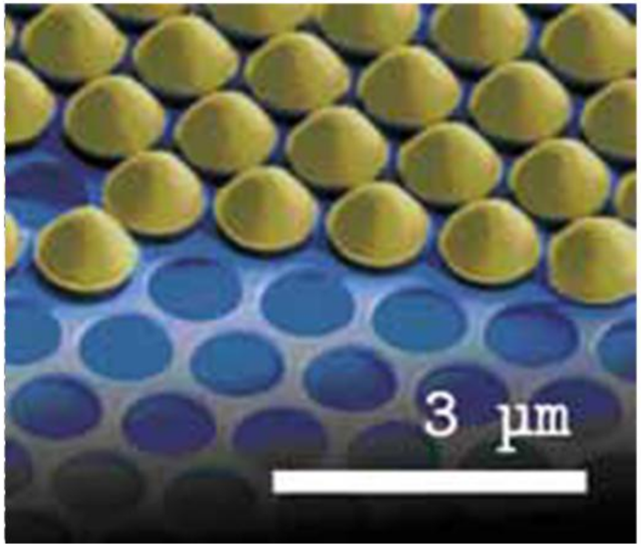


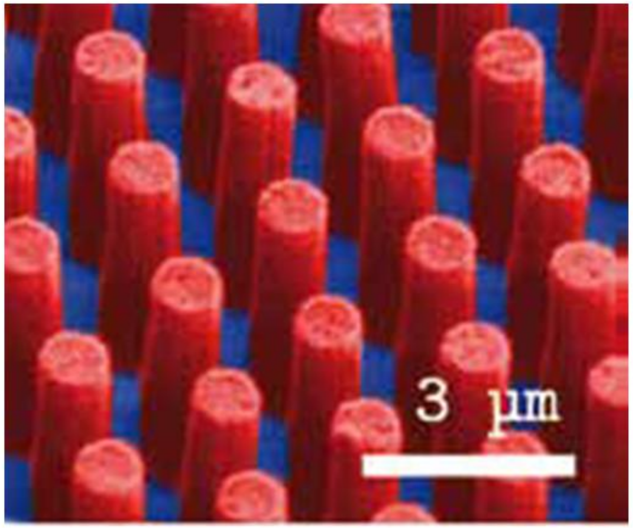
Etching depth depends on time in etching **solution II**

V. A. Sivakov, G. Brönstrup, B. Pecz, A. Berger, G. Z. Radnoczi, M. Krause, S. Christiansen, J.Chem.Phys.C 114, 3798 (2010)
V. A. Sivakov, F. Voigt, G. Brönstrup, G.H. Bauer, S. Christiansen, Phys. Rev. B 82, 125446 (2010).

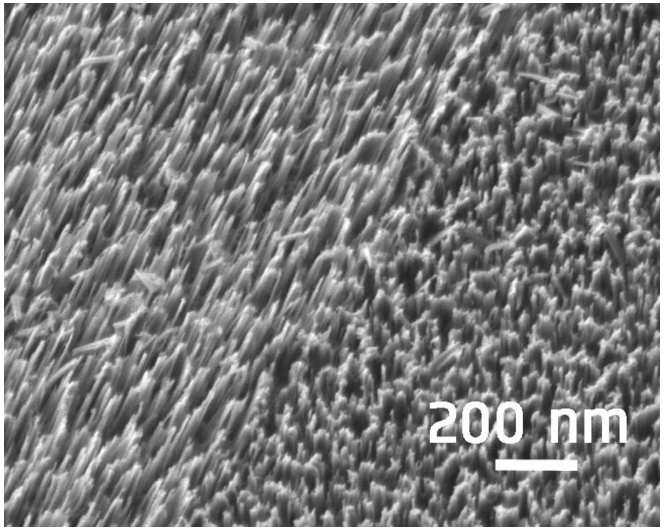
Langmuir Blodget densification of PS spheres

Wet chemical etching





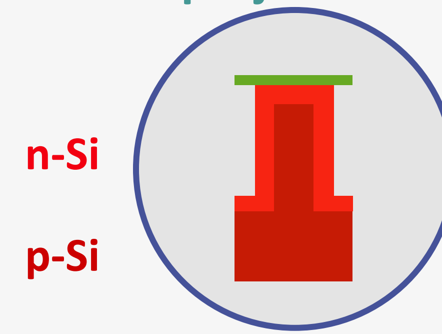
Si wafer



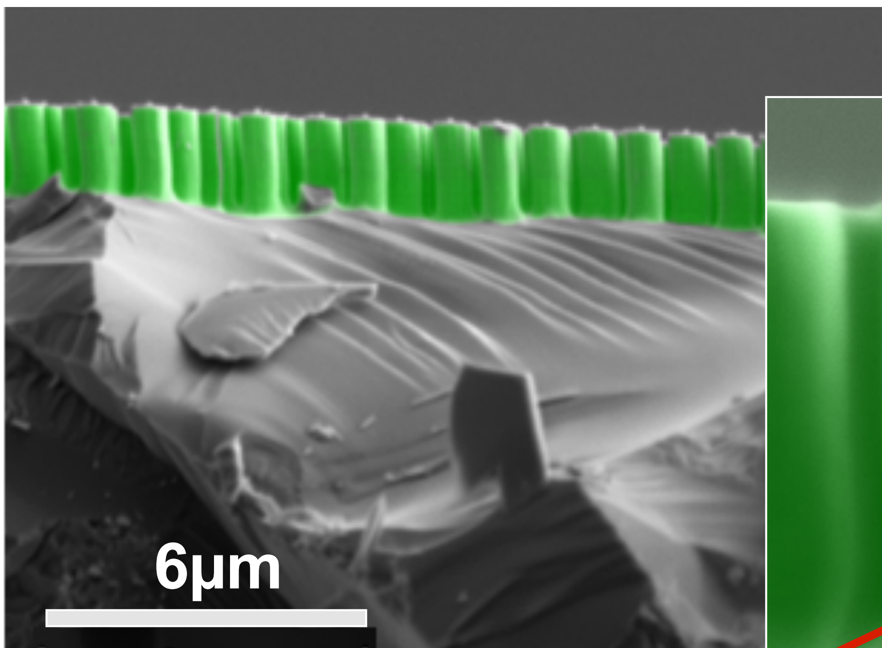
Si NWs doping

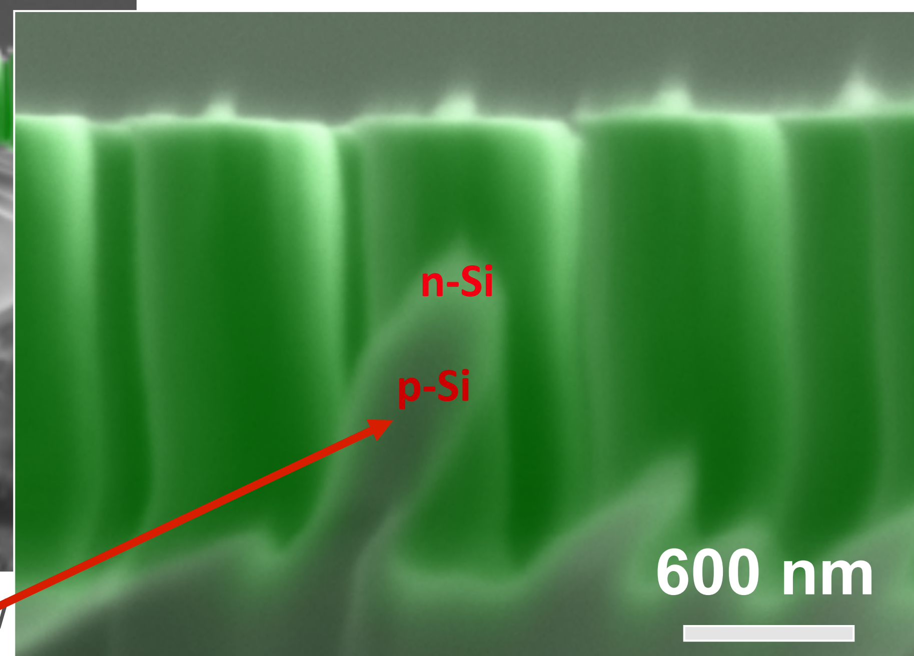
Spin-on-glass doping:
- p- and n-doping possible
- annealing to diffuse dopants
- removal of SOG in HF

wrap around doping: radial pn-junction



radial p-n junctions in Si NWs (EBIC)





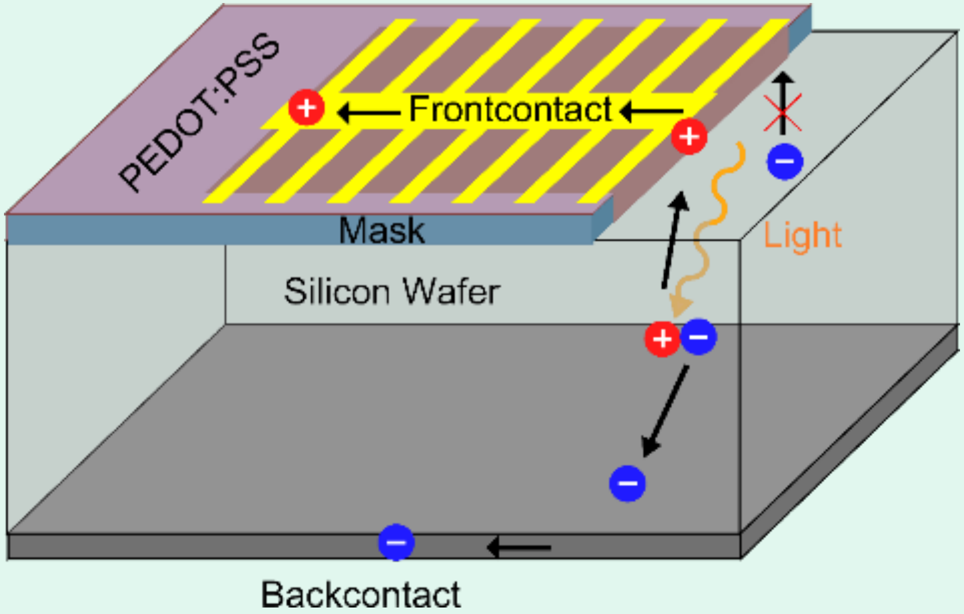
dopant diffusion after Si NW etching:
wrapped surface doping

Hybrid solar cell – PEDOT:PSS/n-Si

Taking the best of two worlds:

Easy processable, cheap and flexible organics
+ stable inorganic with superior electrical properties

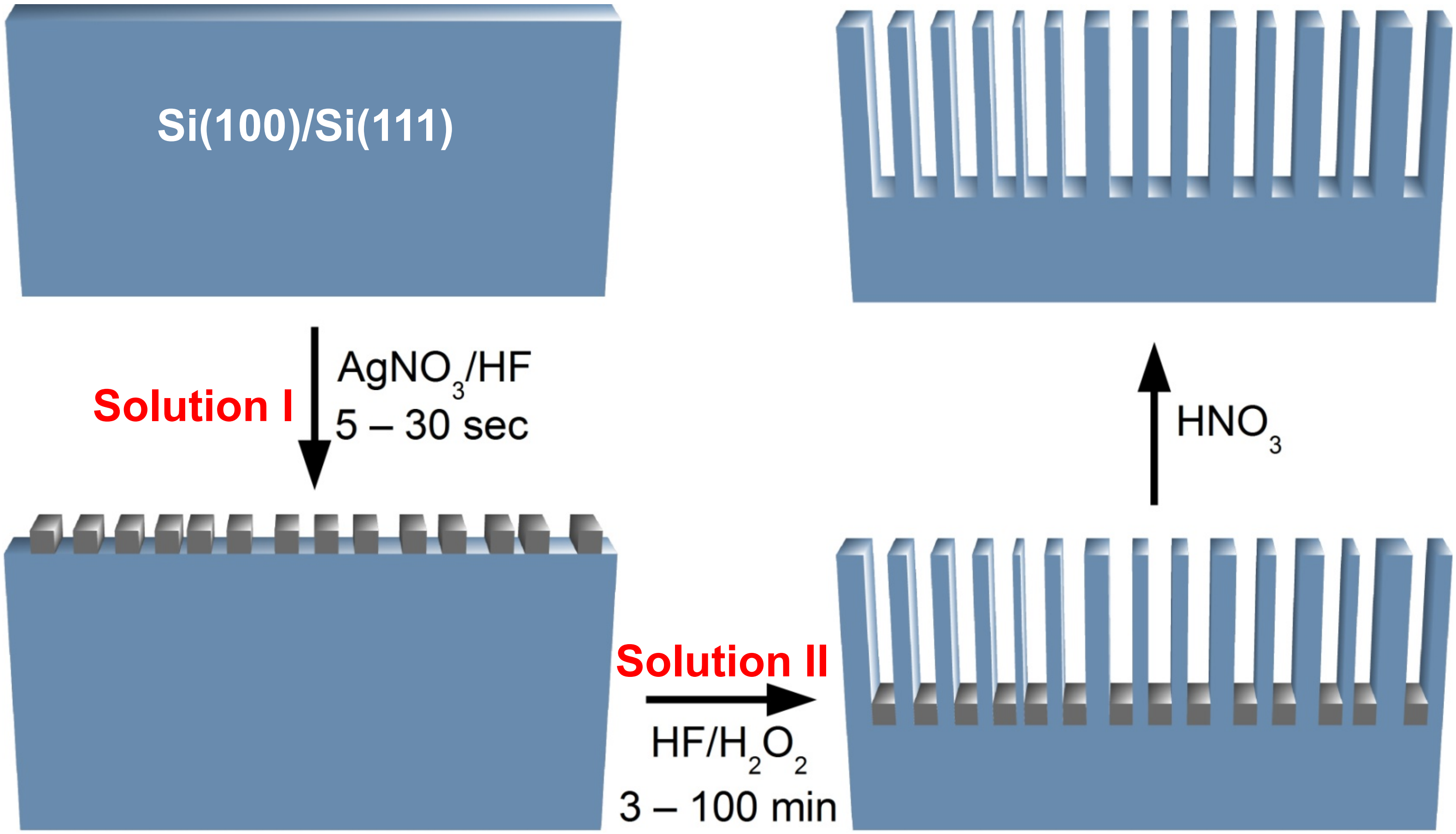
New Approach:
'quasi-metallic' transparent polymer
+ silicon as the absorber



Wet-chemically etched Si nanostructures

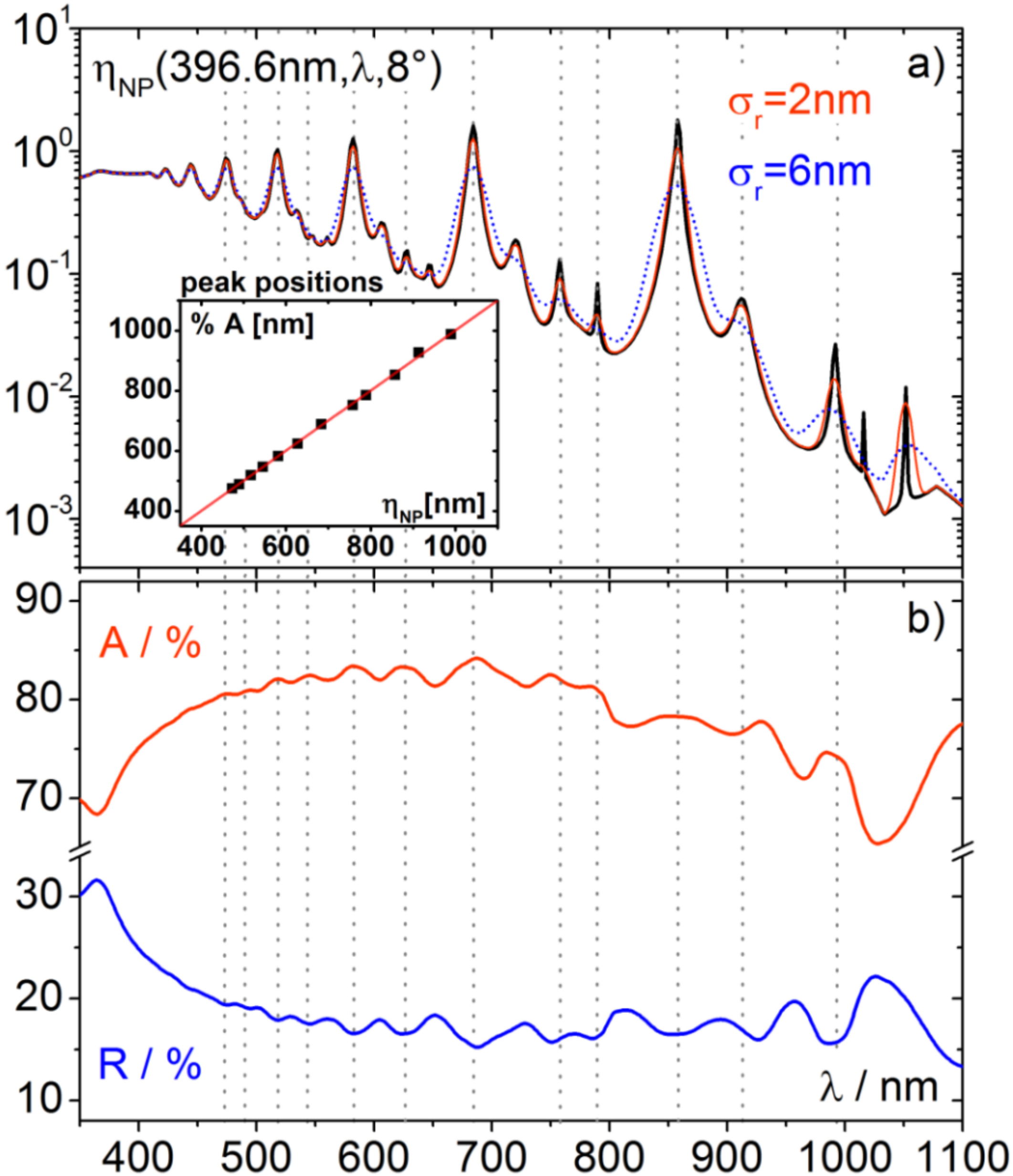
Top down etching has **advantages** over CVD-bottom up growth:

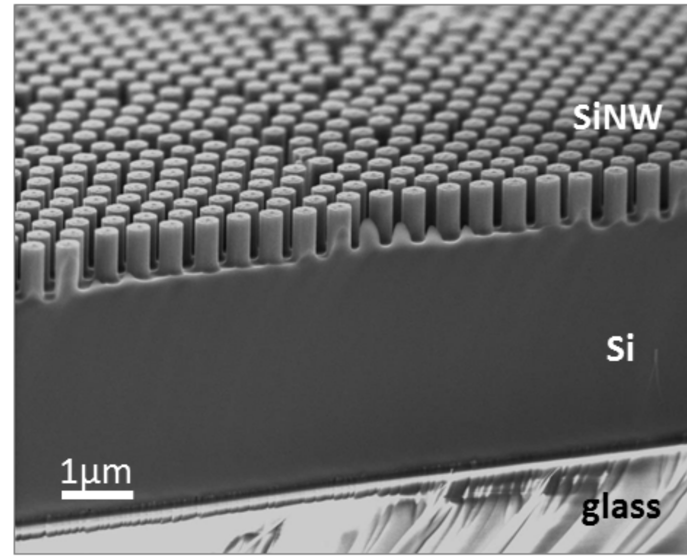
- No need of vacuum equipment
- No restrictions in substrate size → whole wafers are treated in a few minutes
- No contamination with gold (deep traps → carrier recombination)

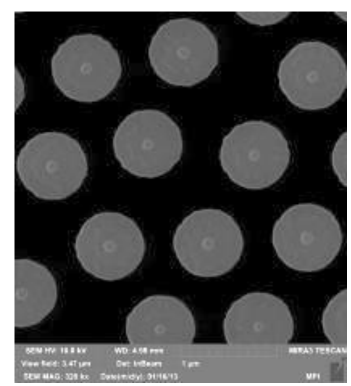


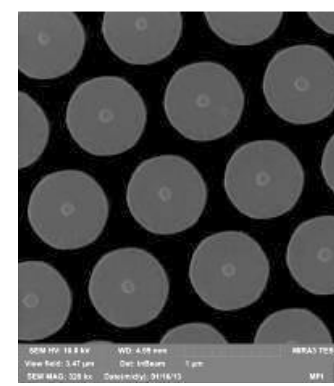
K.-Q. Peng, et al. Adv. Mater. 14, 1164 (2002)

Optical properties of Si NWs on glass

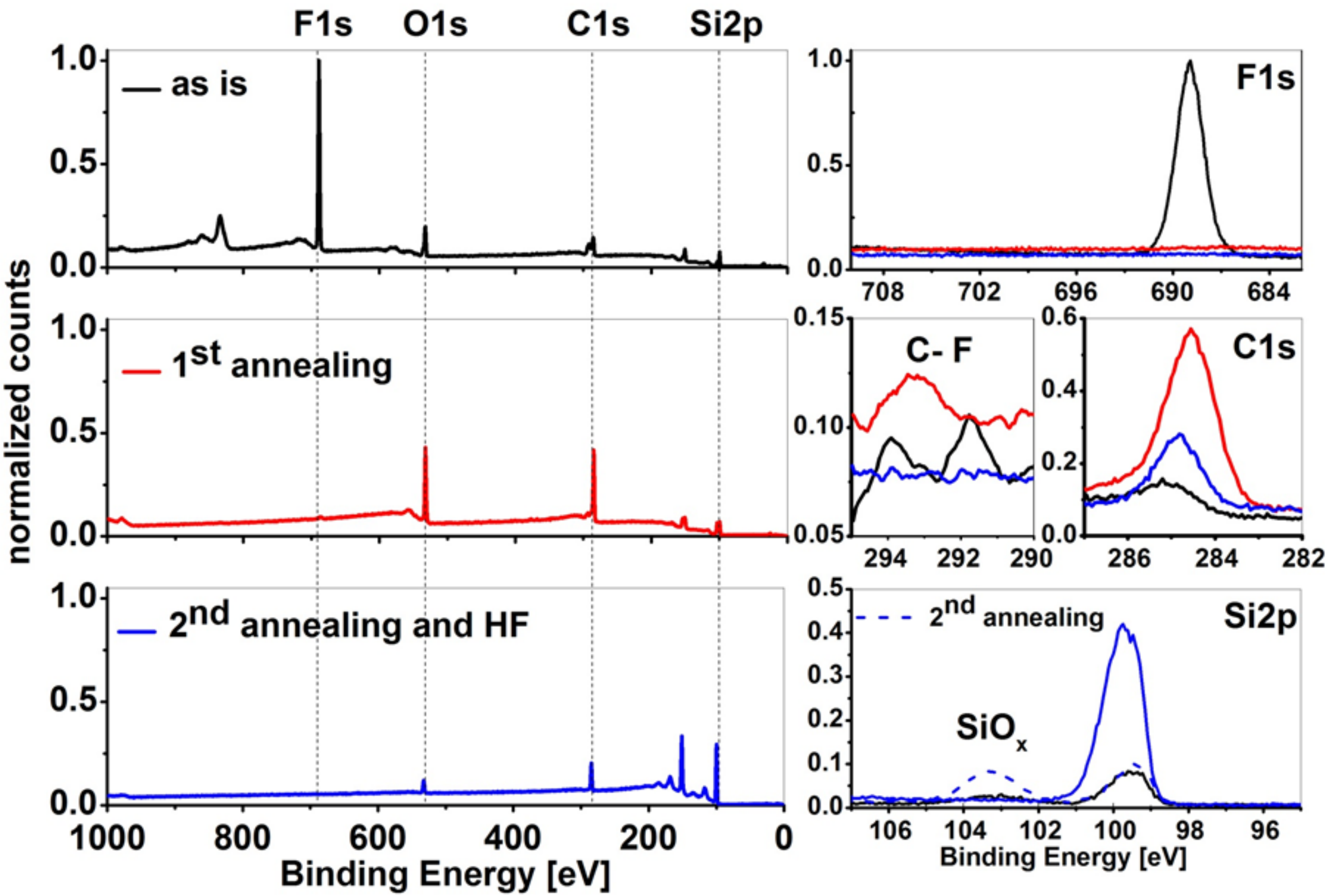








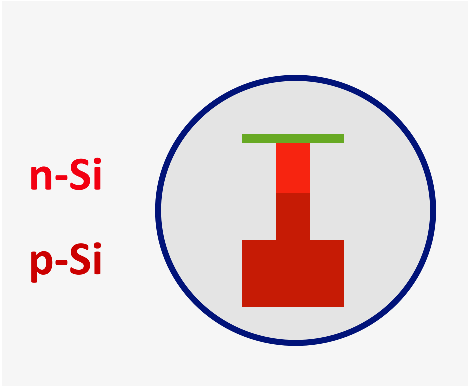
XPS: fluor incorporation in SiNWs during RIE

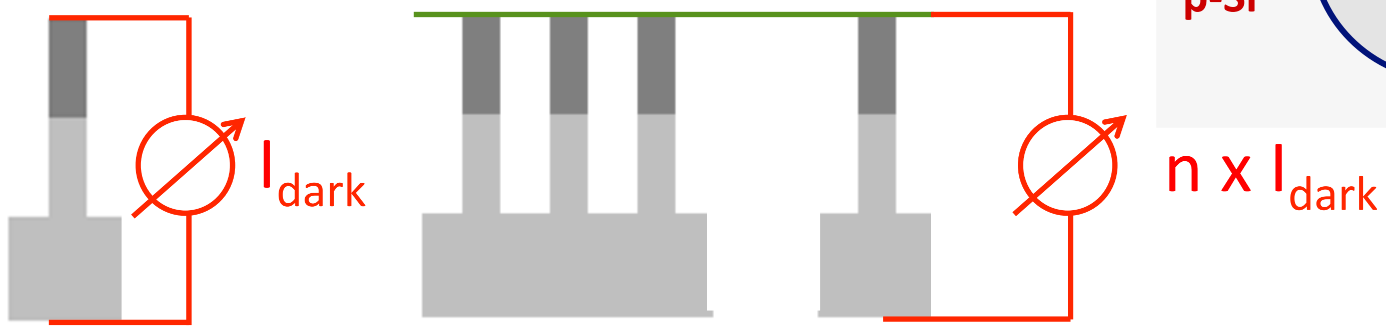


S. Schmitt, et al. nanolett. 12(8), 4050 (2012)

Novel contacts - graphene

- connection of several wires with graphene electrode / parallel resistances



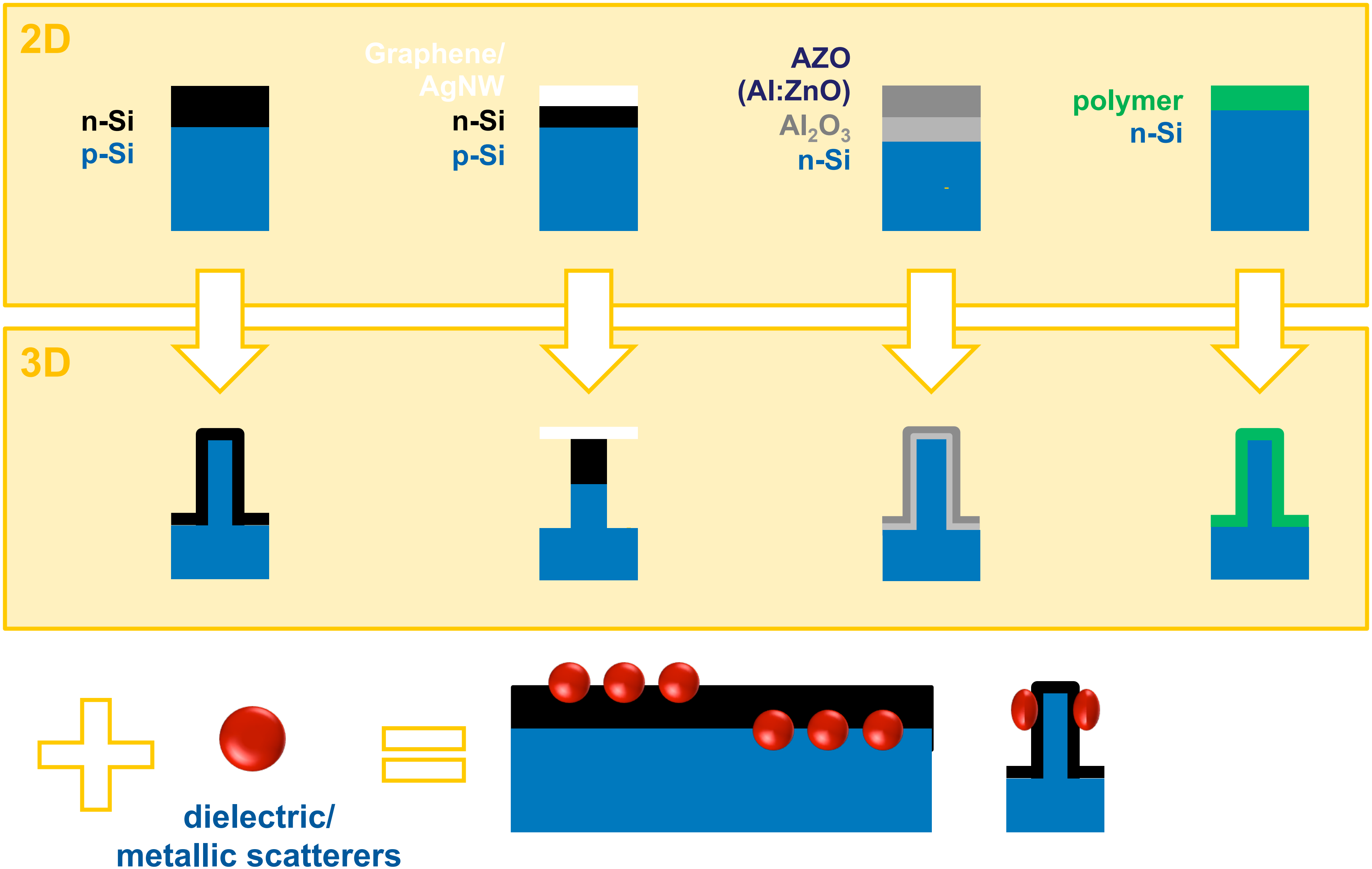


- dark current at 20mV

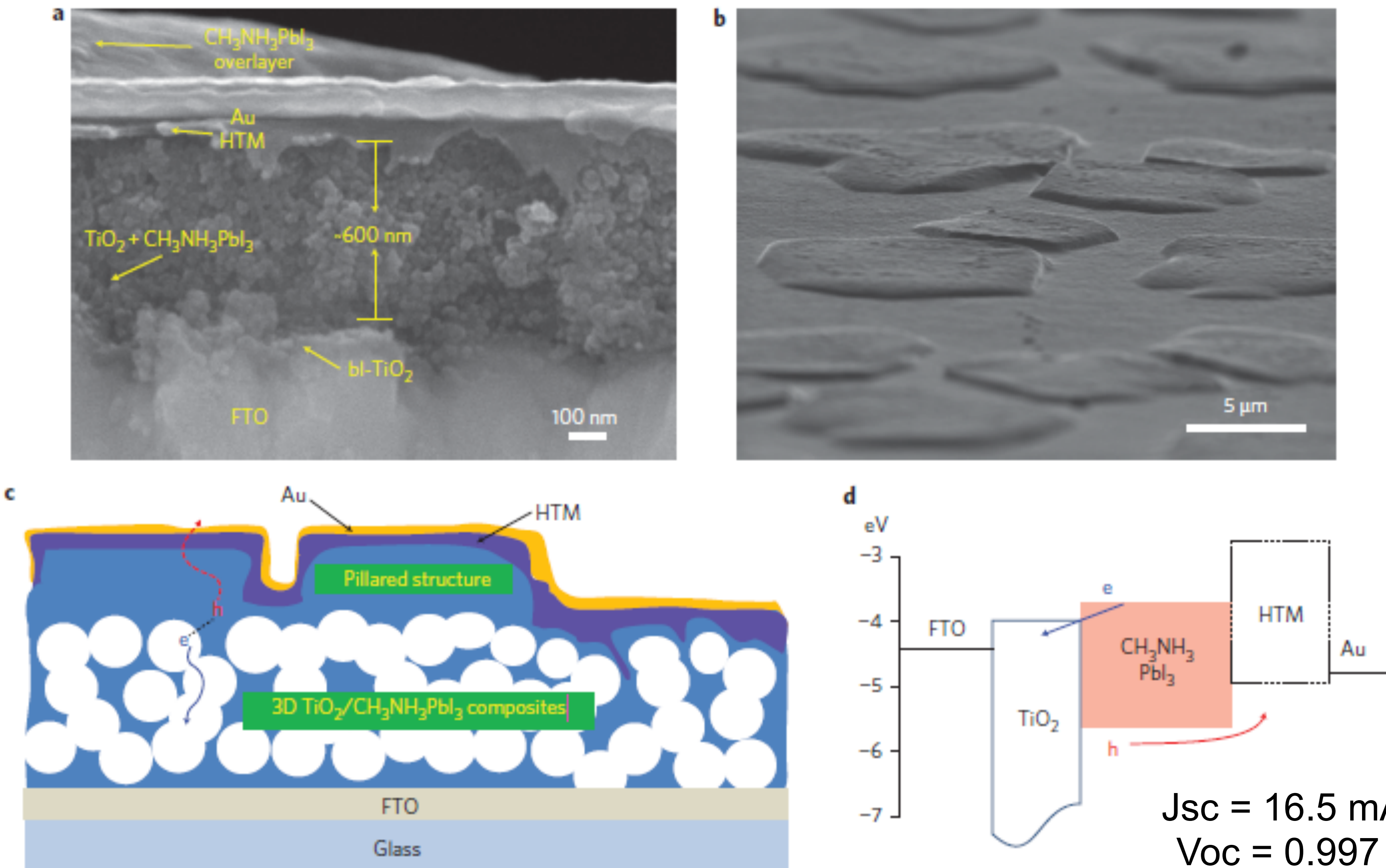
$$\frac{n\ x\ I_{dark}}{I_{dark}} = \frac{4.22\ x\ 10^{-9}A}{1.18\ x\ 10^{-10}A} \approx 36$$

- dark diode current scales with number of connected SiNW

3D nano-architectures



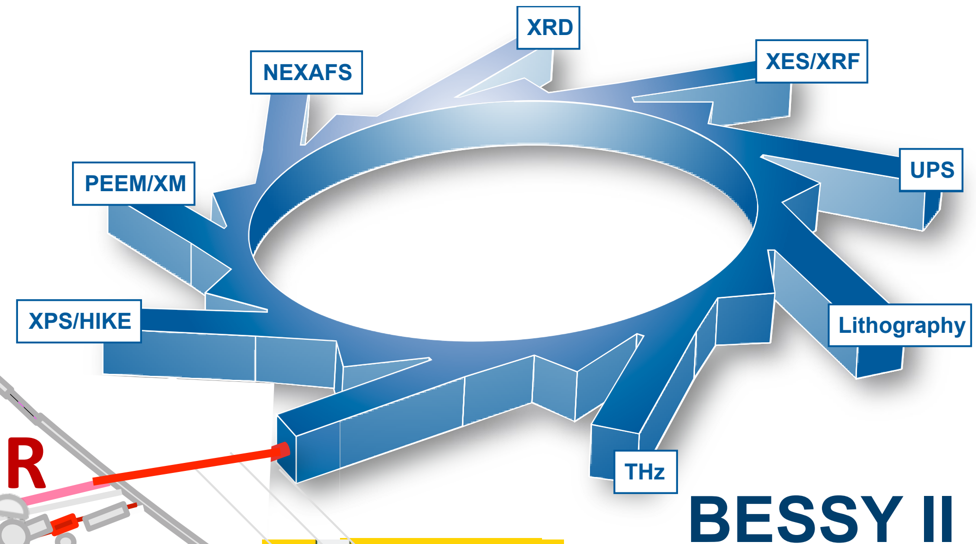
3D nano-architectured perovskite based solar cells



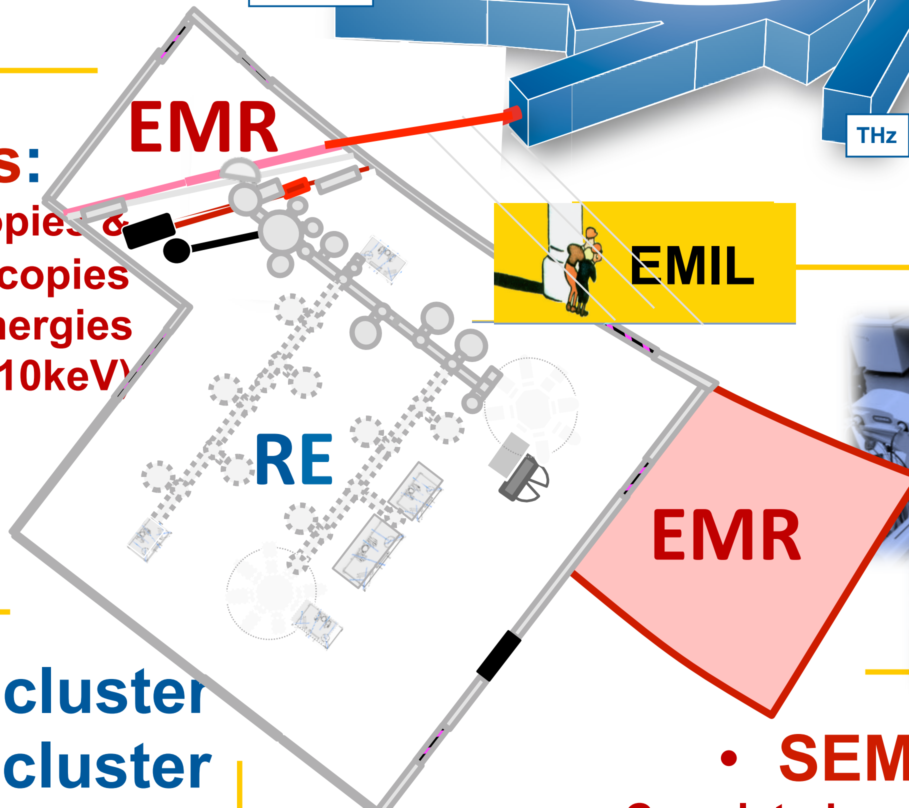
Jsc = 16.5 mA,
Voc = 0.997 V
FF = 0.727
PCE = 12.0% (AM 1.5)

Heo, Grätzel, et al. Nature Photonics, May 2013
Snaith et al. Science 2013

HZB Helmholtz Zentrum Berlin



- X-ray analytics:
  - Spectroscopies & microscopies
  - Wide range of energies (80 eV - 10keV)



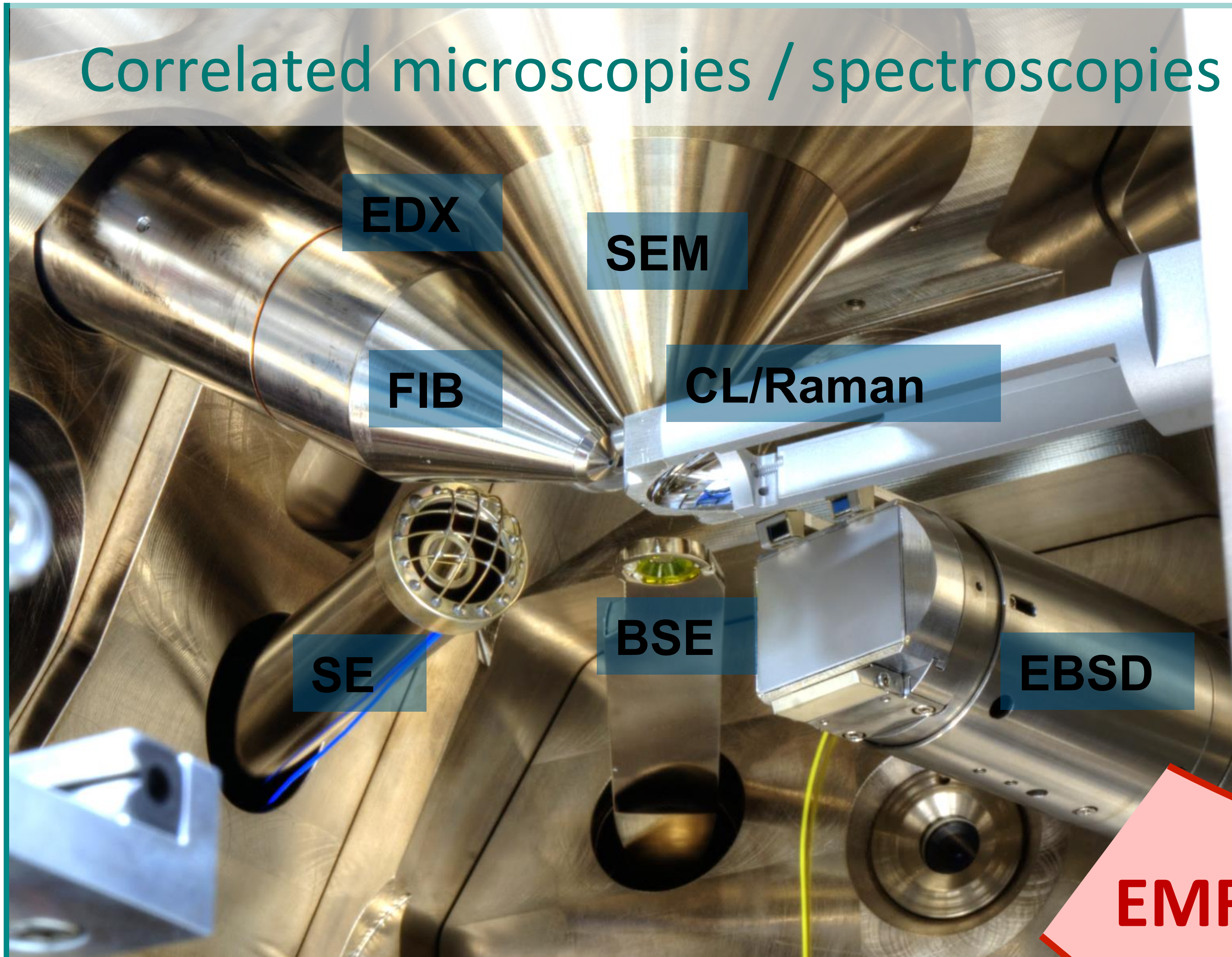
- Si deposition cluster
- CIGS / Kesterite cluster
- Nano-/hybrid cluster

- SEM / FIB lab:

Correlated spectroscopies & microscopies

Correlated microscopies / spectroscopies

HZB Helmholtz Zentrum Berlin

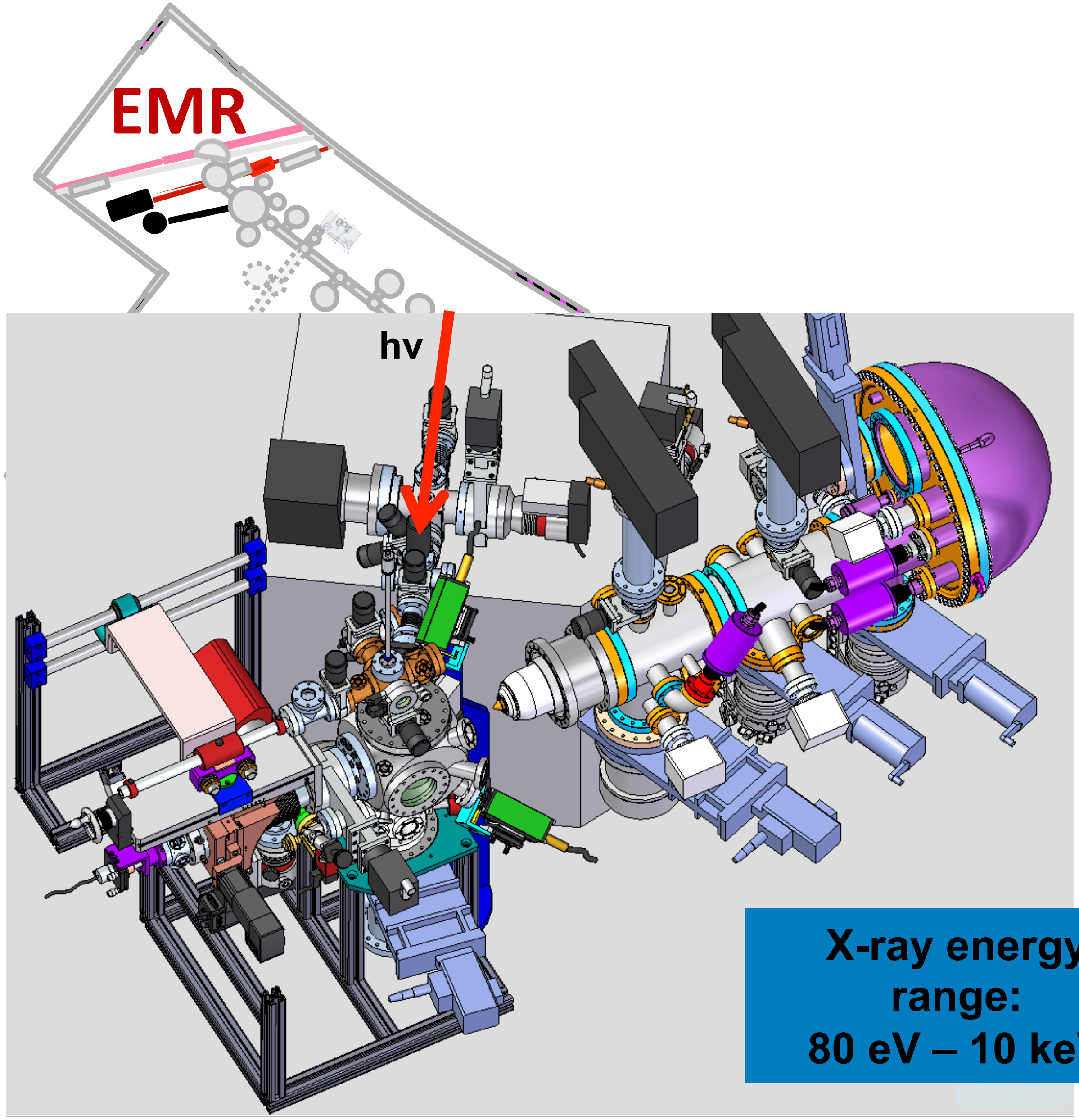


EMR

Interplay of electrical, optical, structural, mechanical properties to assess material - property relations

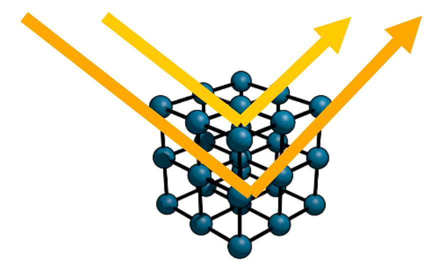
- **SEM / FIB lab:**
  Correlated spectroscopies & microscopies

In-situ / in-operando x-ray analytics

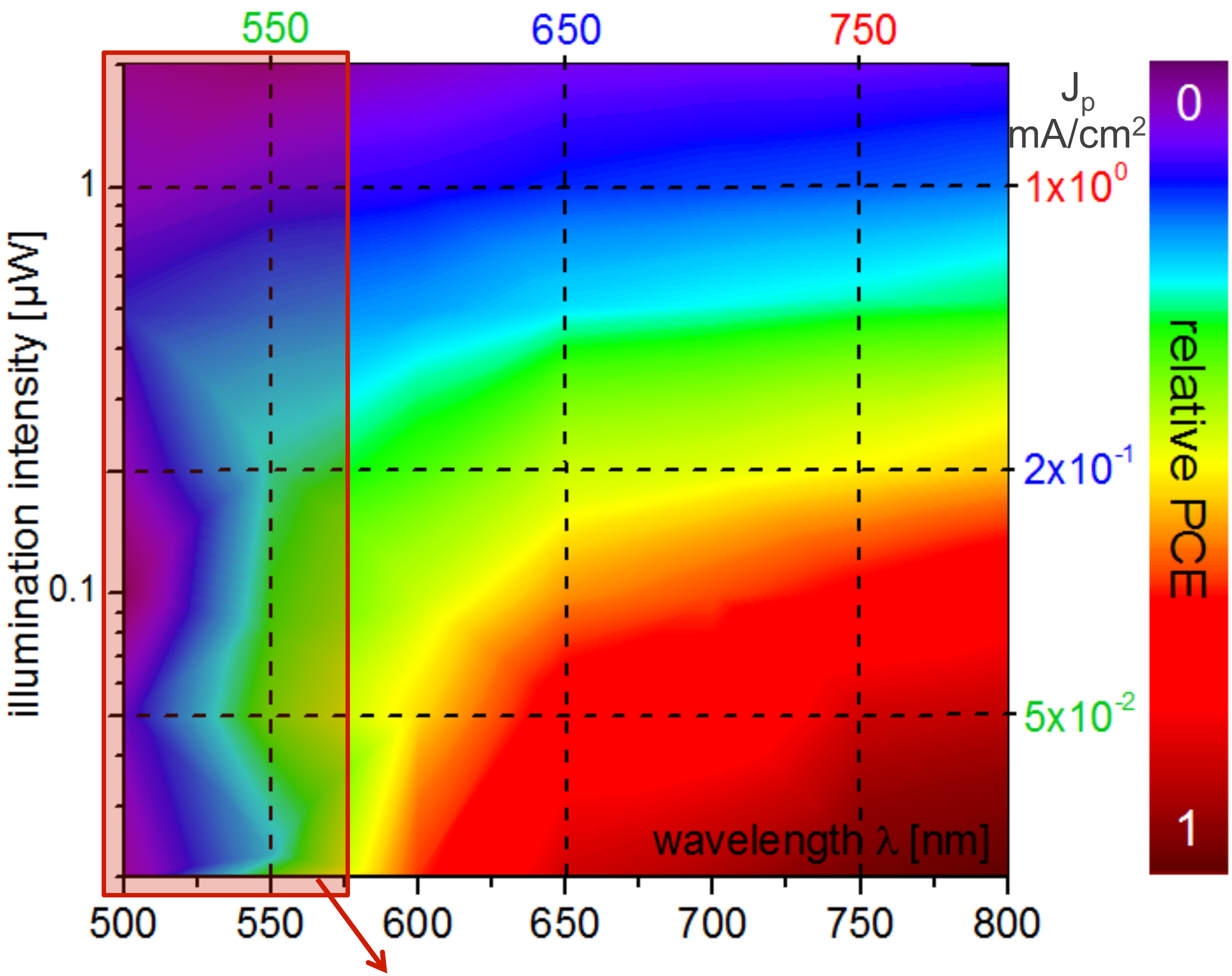


- Gas / solid interface
- Liquid / solid interface
- In-situ analysis of phase & surface formation of compound semiconductors
- Flexible sample environment

X-ray energy range:
80 eV – 10 keV



Design rules for SiNW cells from EBIC / LBIC



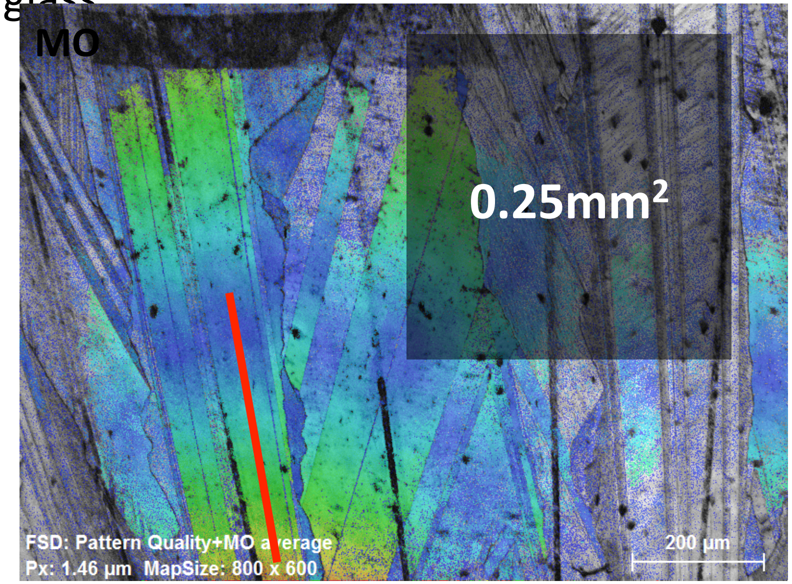
Assess surface passivation

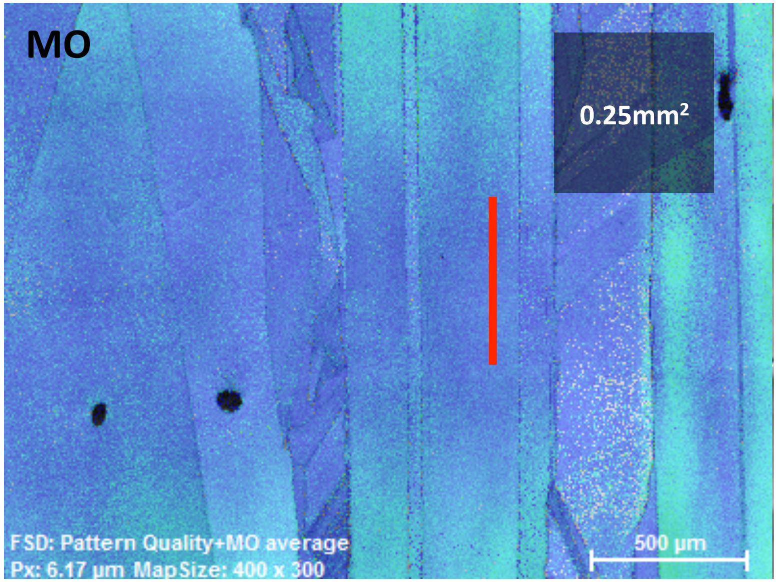
EBSD: multi-crystalline layer on glass

two ways of fabrication:

• deposition of an aSi film on glass or ceramics

1. **Solid phase recrystallisation** on mc-SiC
2. **e-beam / laser recrystallisation** on glass





- grain misorientation along a 500µm trajectory

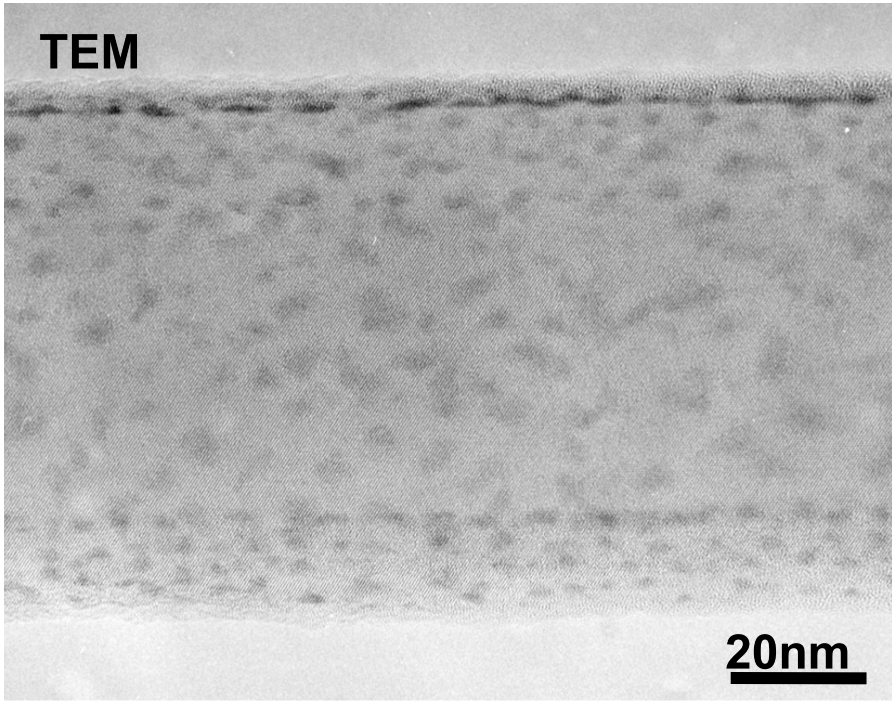
1: 15° tilt

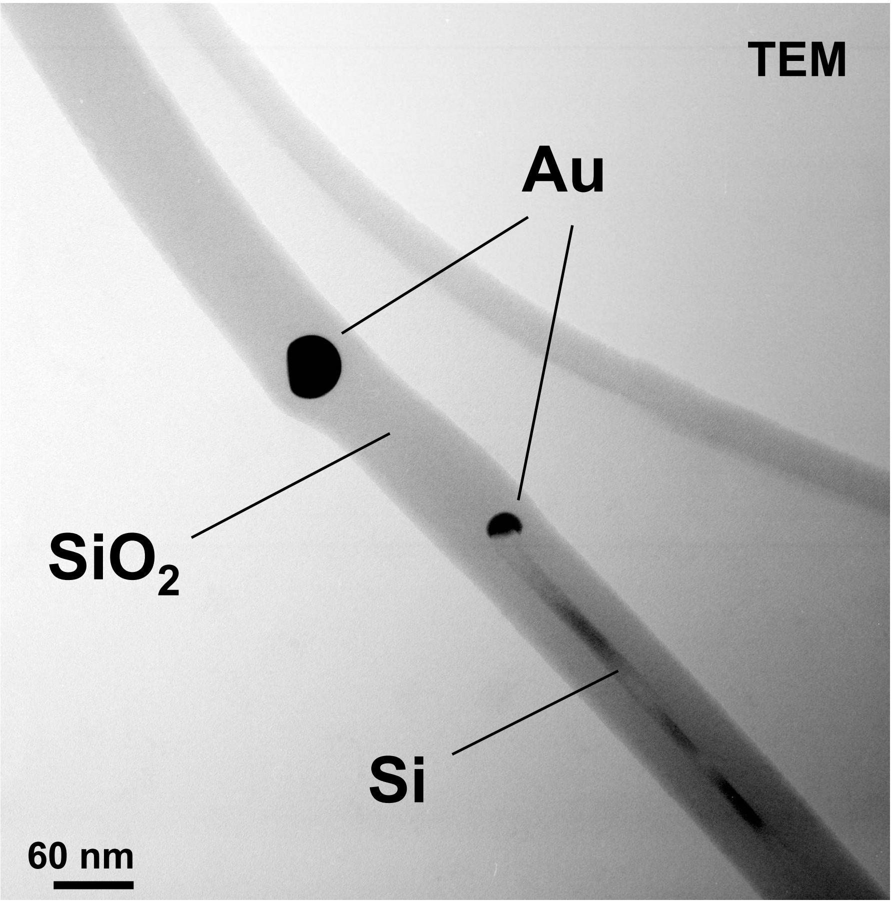
2: only about 1° tilt

Si NW passivation – Au is problematic

Problems:

- gold-enhanced oxidation
- complete removal of Au
  (caps, sidewalls, incorporated, …)





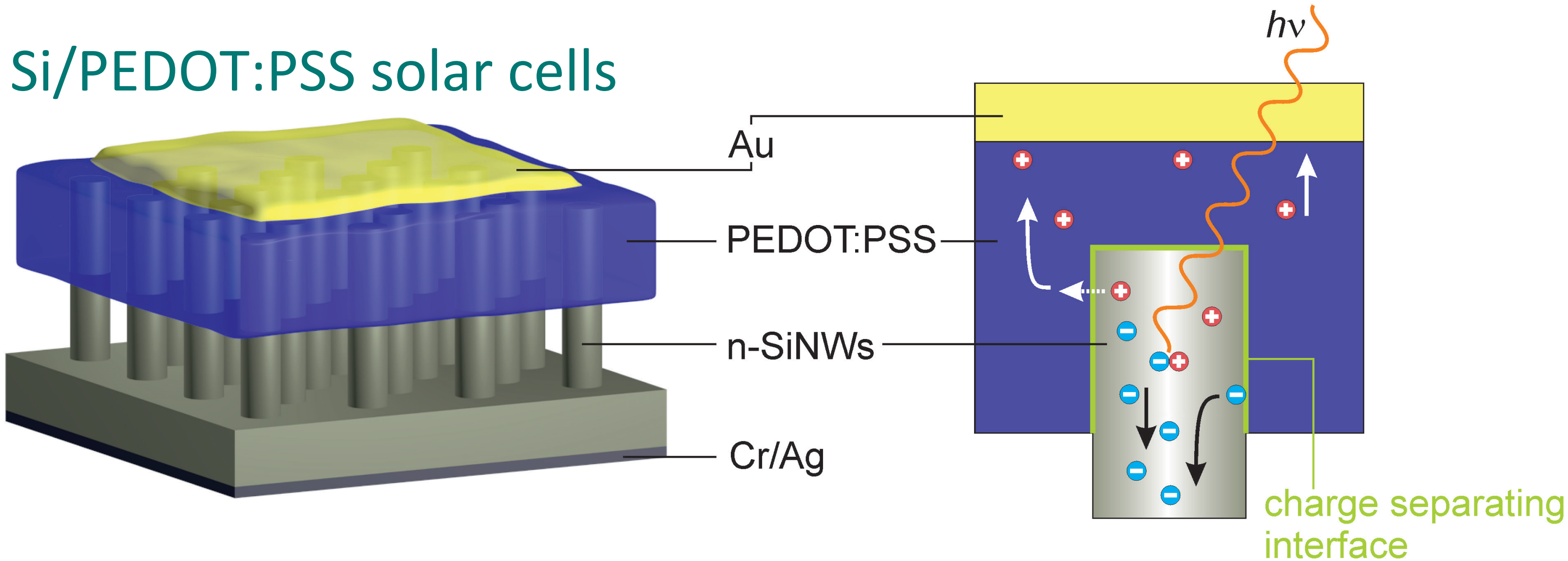
Si NW passivation

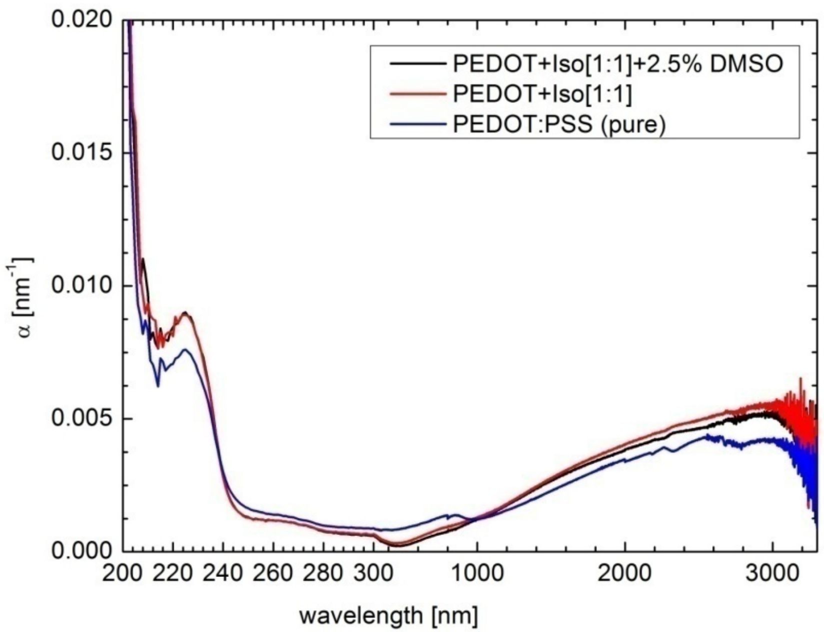
Carrier lifetime (at Δn = 10^{14} cm^{-3}) (µs)	Si wafer	Si wafer with SiNWs 30 nm AuNP	Si wafer with doped SiNWs 30 nm AuNP	Si wafer with SiNWs chem. etched
Native oxide	**1.0**	1.0	1.3	**1.3**
HF dip	**14.5**	1.5	2.1	**17**
50 nm intrinsic a-Si:H a) as deposited	**95**	1.5	1.4	**25**
			1.3	**36** **(4 min)**
b) 30 min anneal	**1041**	1.5		

- **Diffusion length (τ=1.5 µs): 72.5 µm**
- **Possible influence of Au as catalyst material**
- **Influence of surface passivation**

Si NW based hybrid solar cell

Si/PEDOT:PSS solar cells





- Efficiencies up to 13% on Si substrates
- V_{oc} up to 660 mV on $N_D=10^{17}$ cm^{-3} epi-Layer reported; others @ ≈550 mV
- J_{sc} up to 35 mA/cm²

Scattering solar cells

Original Problem:

Low interaction cross-section of light with thin film solar cells under (optimal) perpendicular illumination

Possible solutions for enhanced absorption in the active solar cell material - include scattering or localization via metallic [1] or dielectric particles or rough surfaces / interfaces

Scatterers or roughness on surface for (multiple) (resonant) scattering and/or reflection.

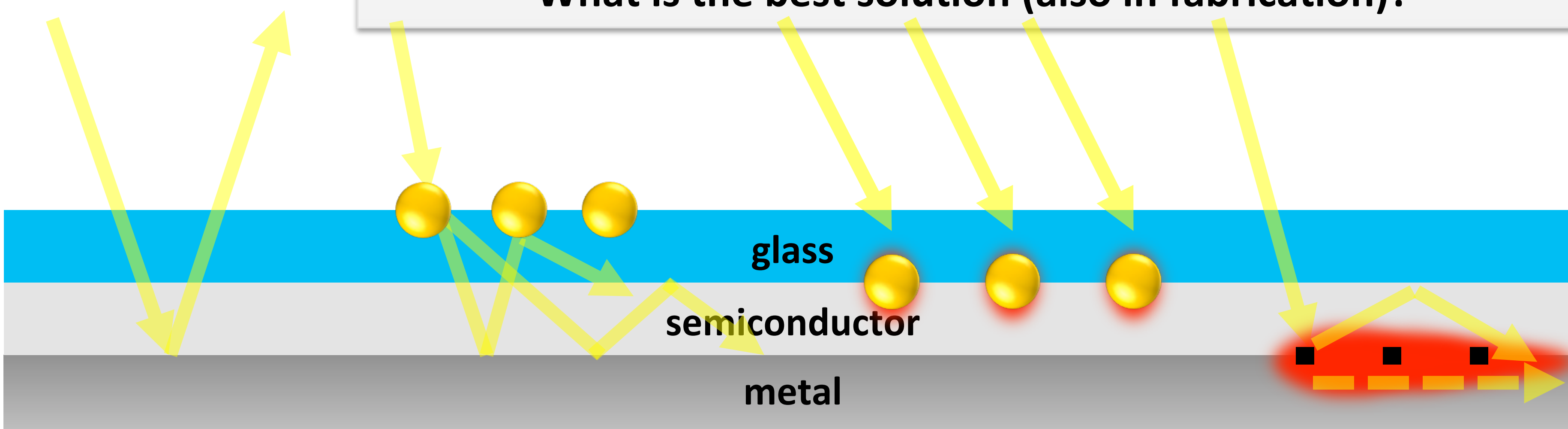
Localizers in active material for plasmonic resonances or (Anderson) localization

Grating at back contact for coupling into (plasmonic) waveguiding modes

Actual research: +45% efficiency for whole solar spectrum (June 2011)

But: Very many geometries with lots of parameters, materials, combinations are possible!

What is the best solution (also in fabrication)?

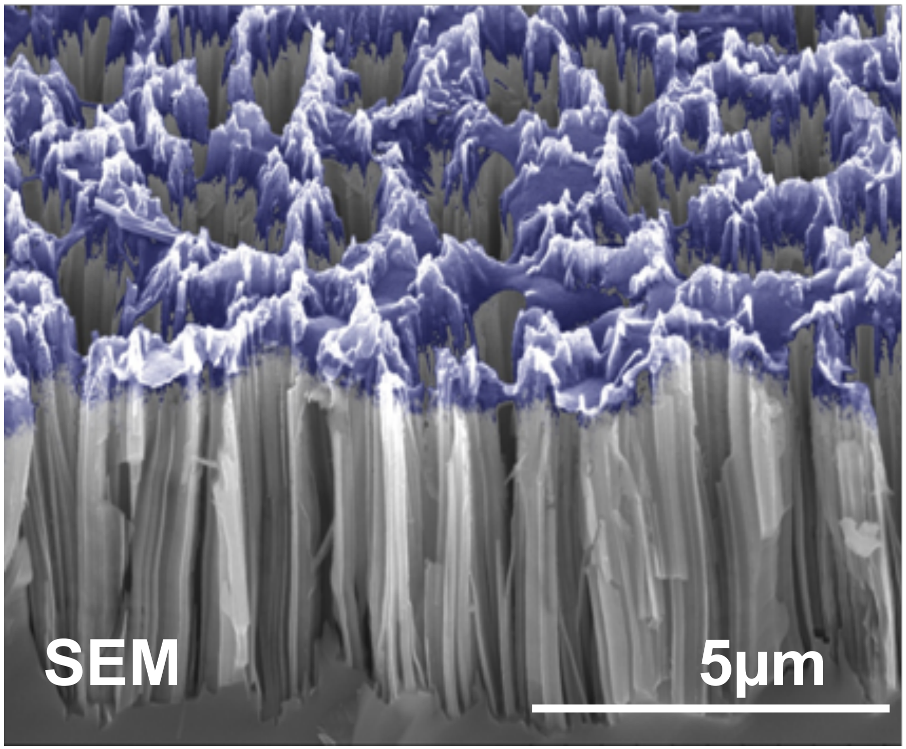


[1] Atwater, H. A. & Polman, A.; Plasmonics for improved photovoltaic devices; *Nat Mater, Nature Publishing Group,* 2010, *9*, 205-213

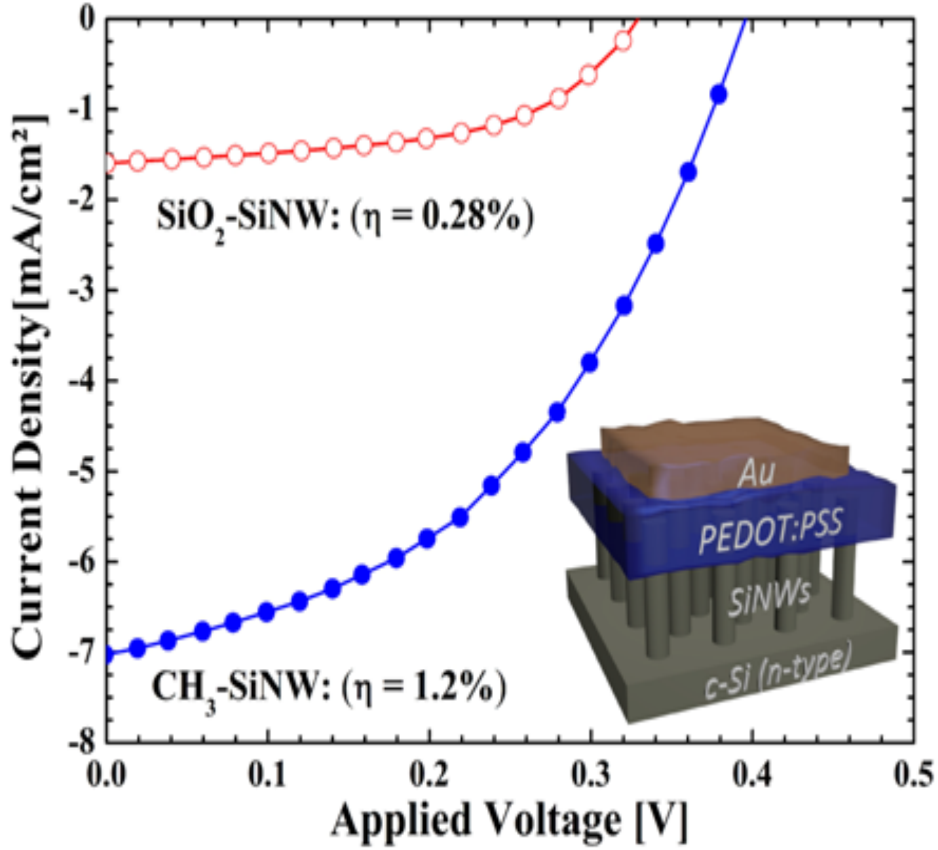
Our group

Si functionalization: preventing oxidation

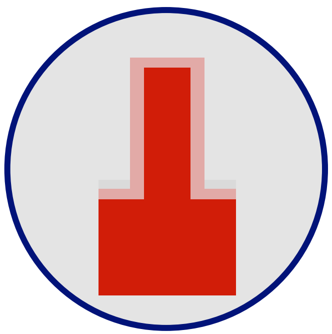
SiNW/PEDOT:PSS radial heterojunction

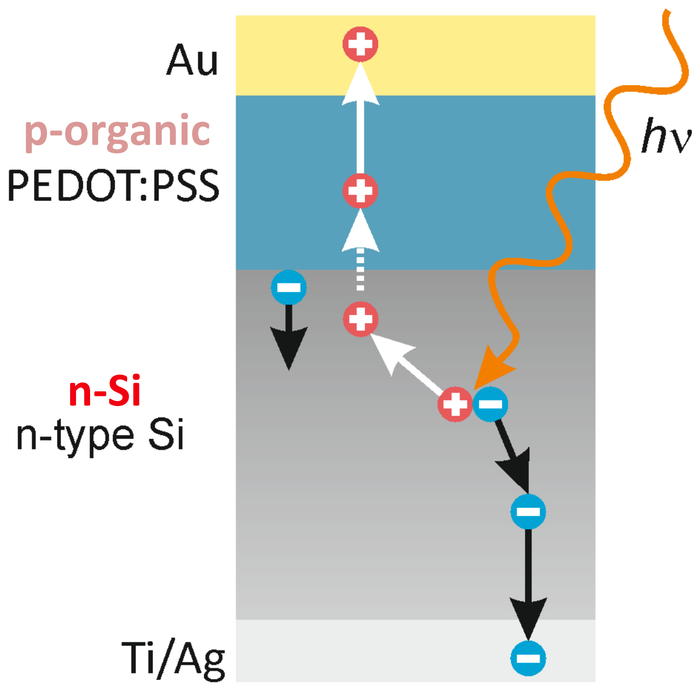


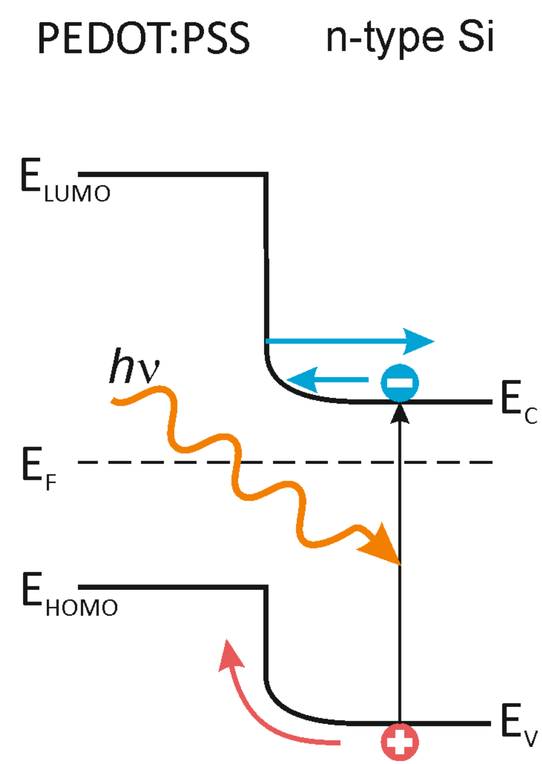
I-V curve (AM1.5 illumination): CH_3-SiNW and SiO_2-SiNW



Si NW based hybrid solar cell

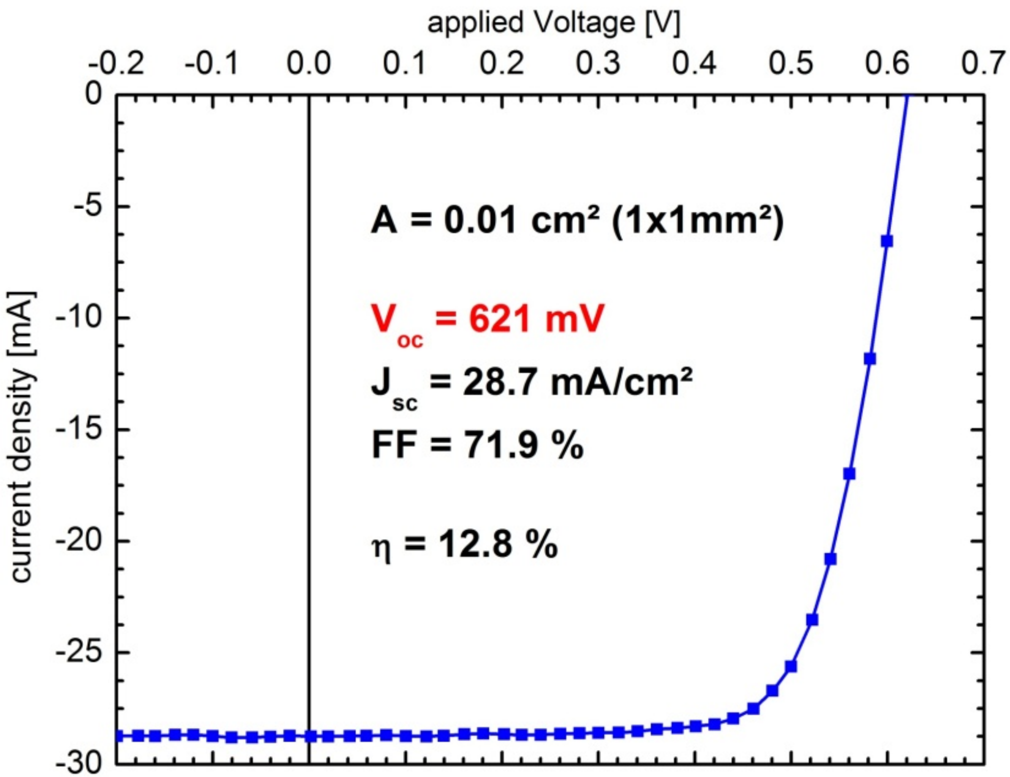






SUMMARY

- easy to fabricate
- High V_{oc}'s are attainable → 621 mV
- efficiencies of ~13 %
- MIS theory can be applied to hybrid solar cells

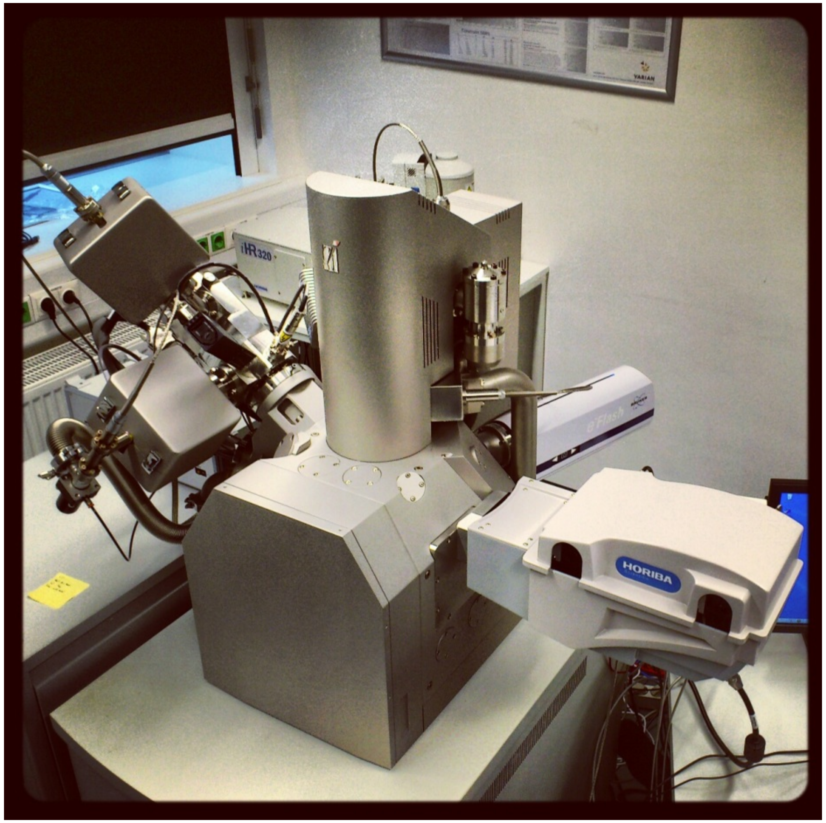


OUTLOOK

- AFORSHET simulation using literature values and measurements
- FET, XPS and FTIR measurements are prepared but not measured yet
- SiNW/PEDOT:PSS solar cells
- Thin film solar cells

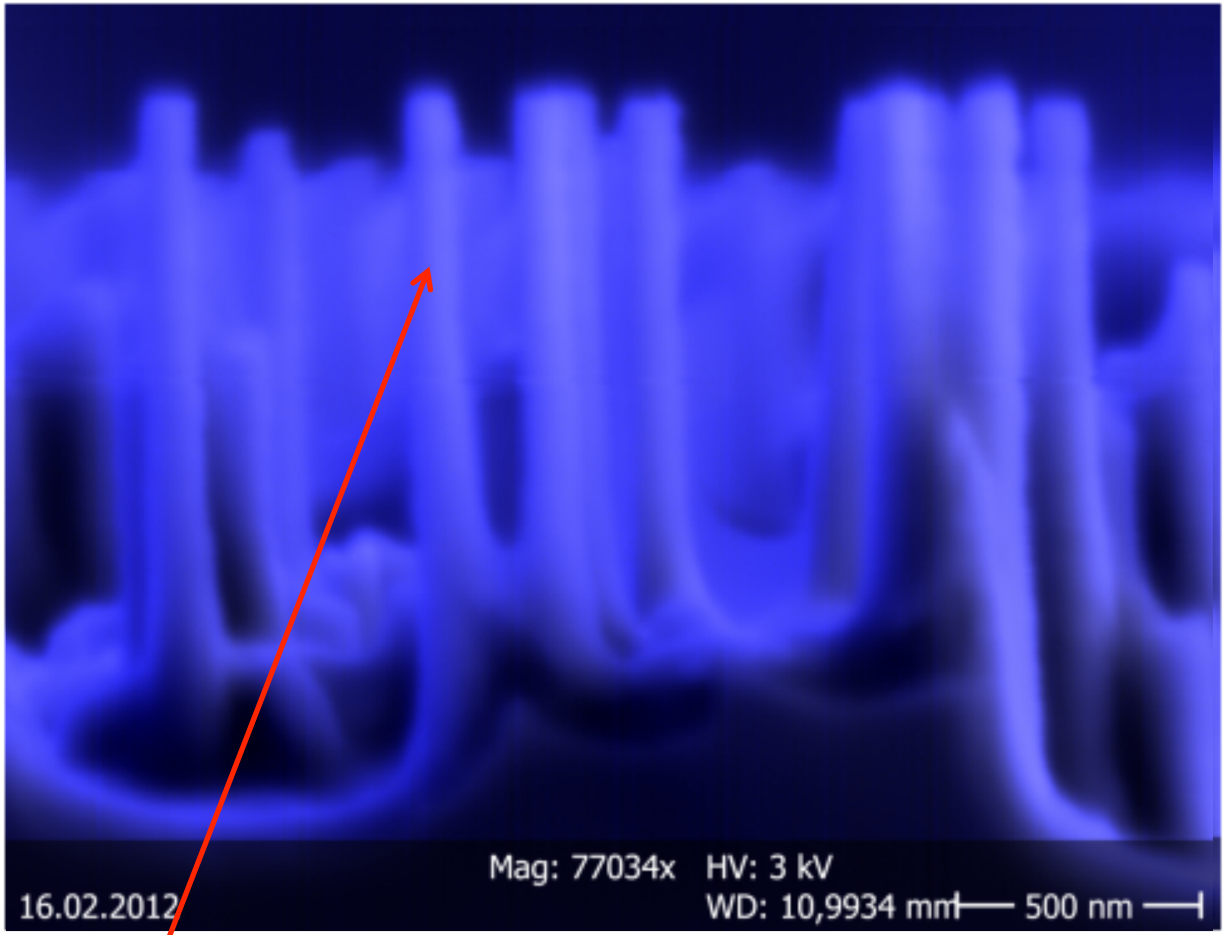
Dual beam FIB: a 'swiss knife' tool for nanotechnology

- **Tescan Lyra 3 prototype equipped with a Horiba „Clue“ for CL, EL, PL and Raman measurements.**
- **Together with EDX, EBSD, EBIC, FIB and a 4-point-prober it deserves the name „Swiss Knife of Nanoscience“!**
- **Correlated microscopies permit combined structural, electrical & optical characterizations on identical nanostructures.**



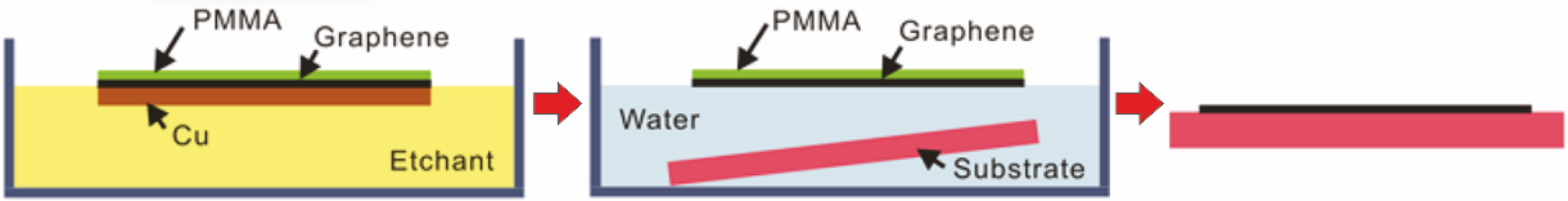
EBIC: hybrid organic-inorganic solar cell

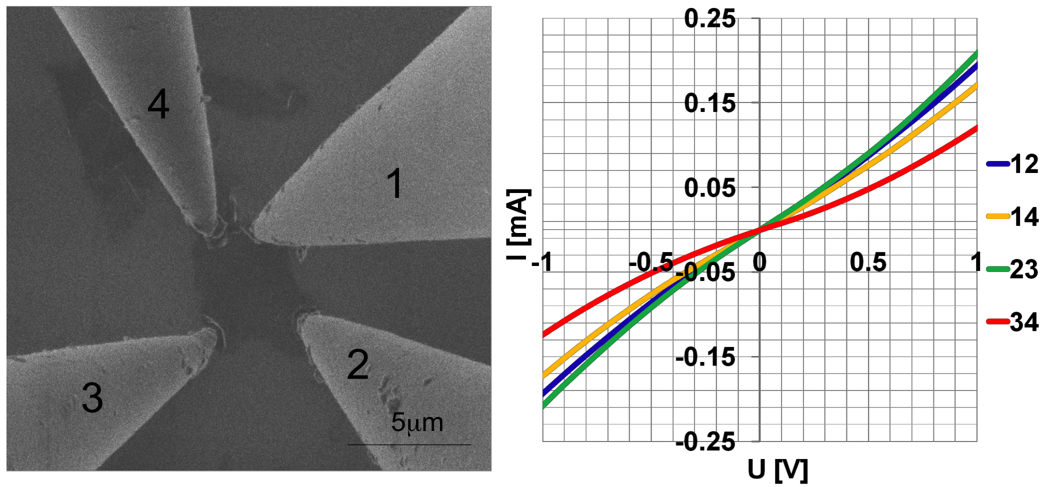
radial hybrid pn-junction



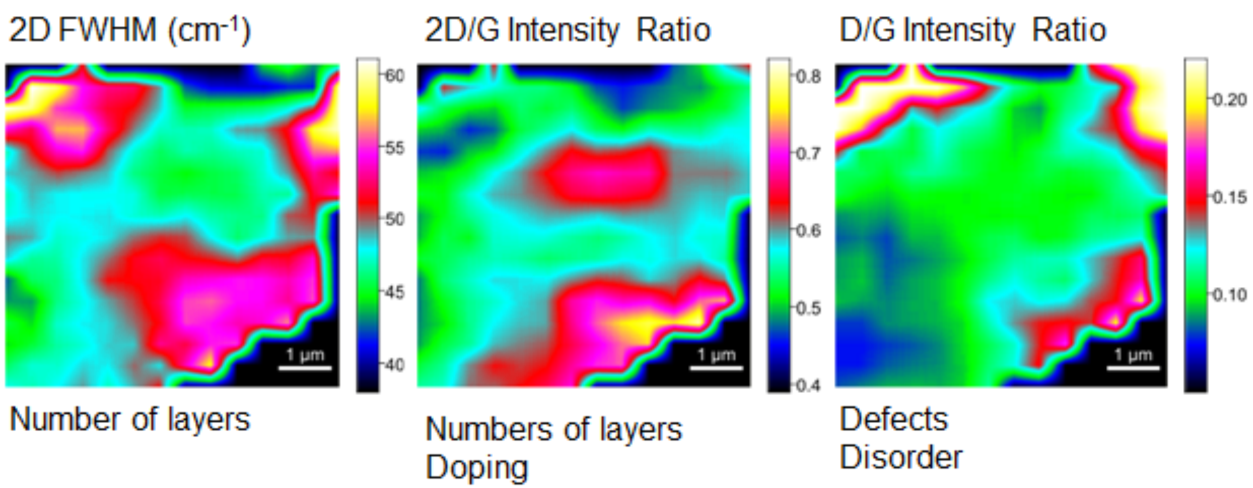
EBIC: charge carrier seperation works

Novel contacts - graphene





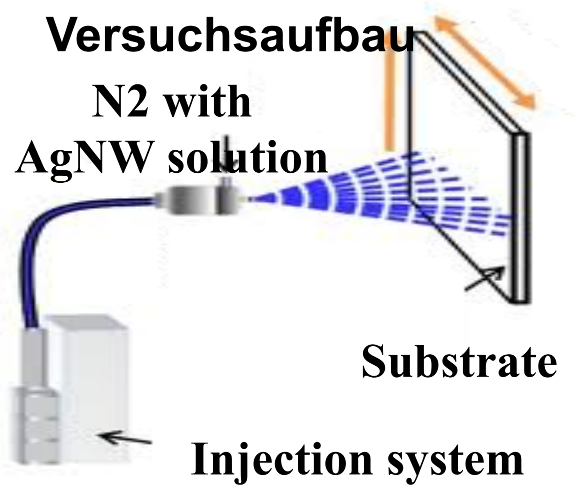
4 point nanoprober

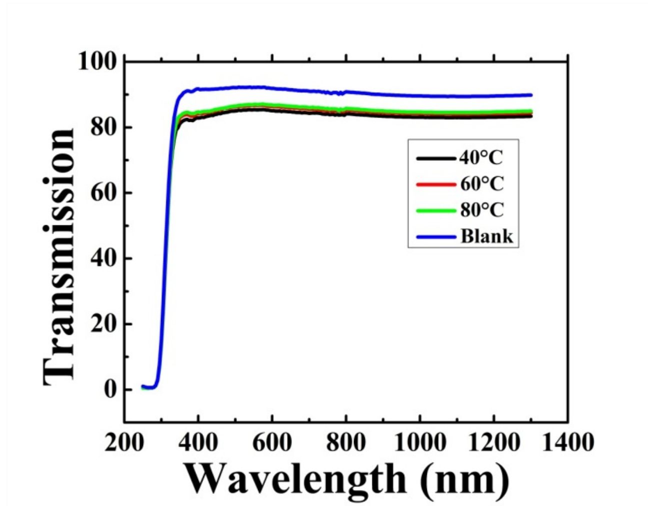


Raman spectroscopy

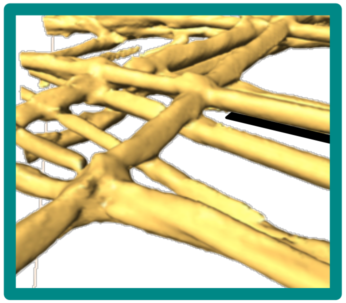
Ag NW web electrodes

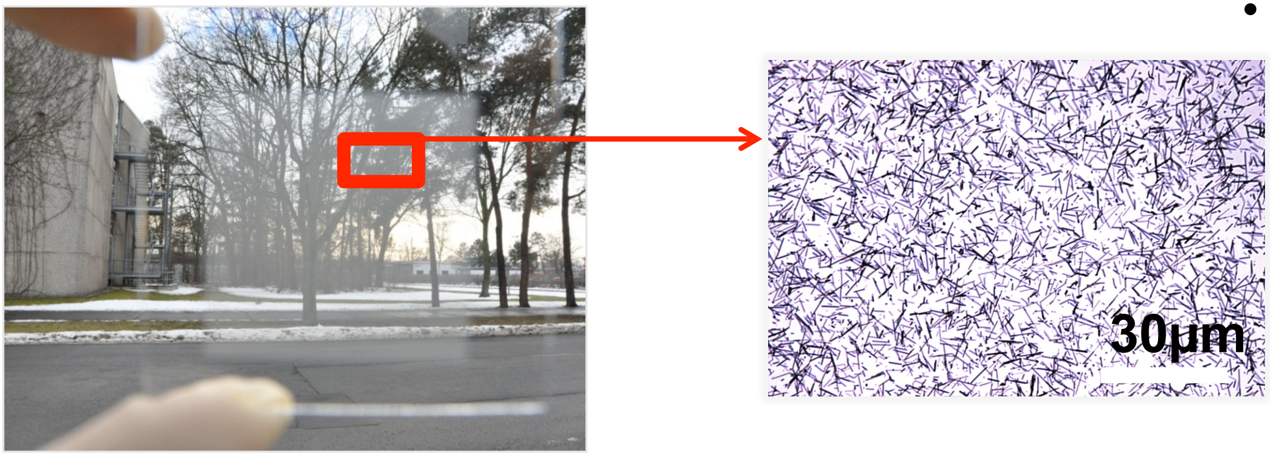
- **sprayed Ag-NW transparent electrode**



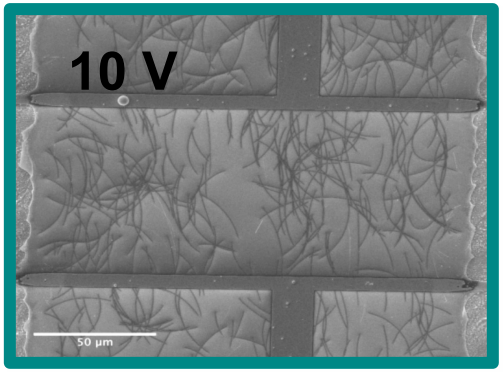


- **TEM tomography**





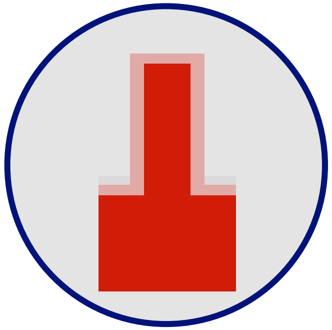
- **SEM: voltage contrast**

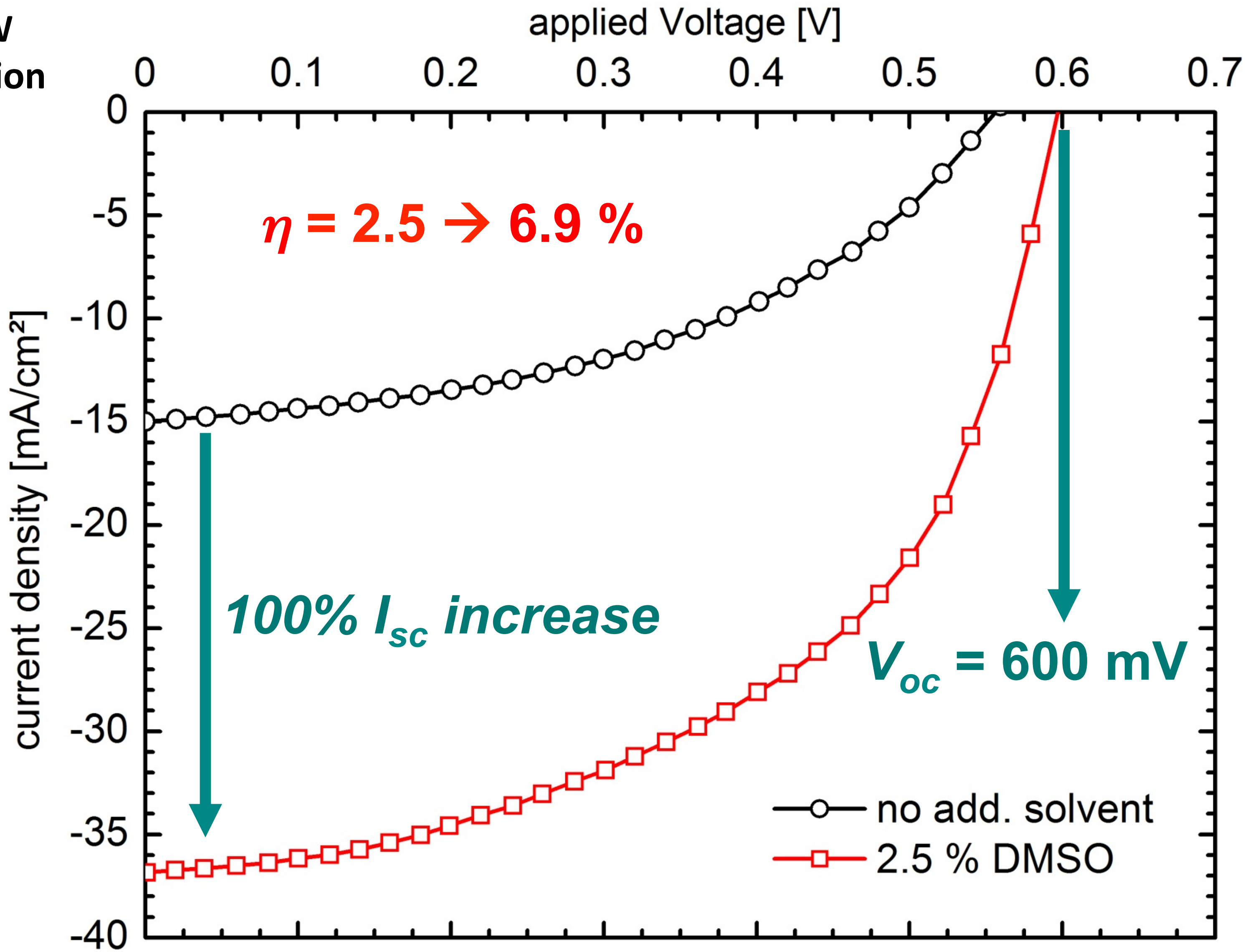


Voltage dependent SE-efficiency

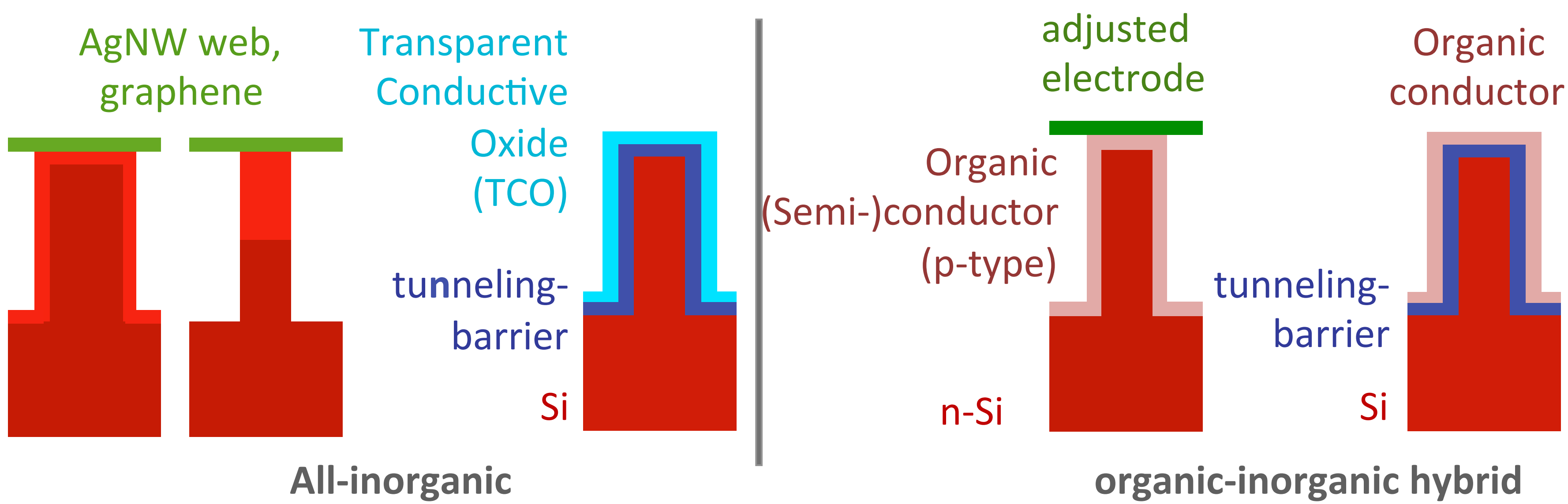
Si NW based hybrid solar cell

PEDOT:PSS / Si NW radial heterojunction

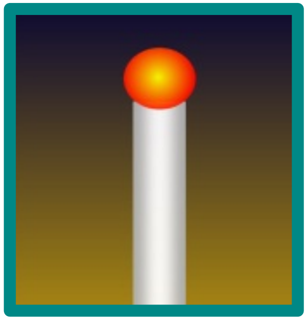




Si NW on glass platform



Outline

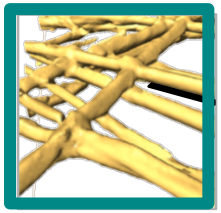


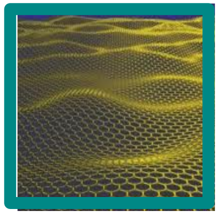
Si Nanowires (NWs) - Synthesis & Morphology

- top down NW etching

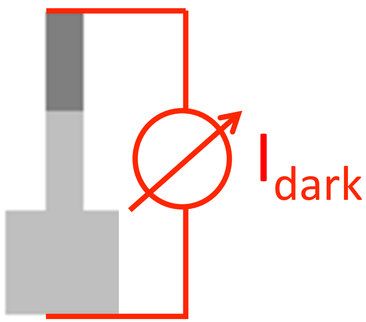
NWs in solar cell applications

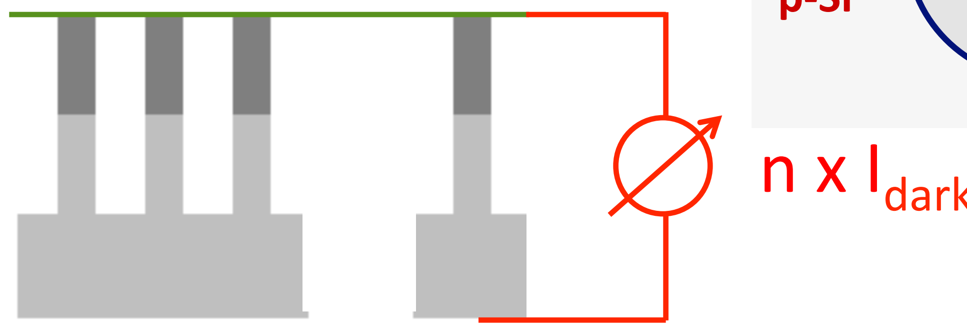
- semiconductor NWs in different cell concepts
- surface functionalization of NWs to improve solar cell performance
- **contacts & plasmonic add-ons etc.**





- connection of several wires with graphene electrode / parallel resistances



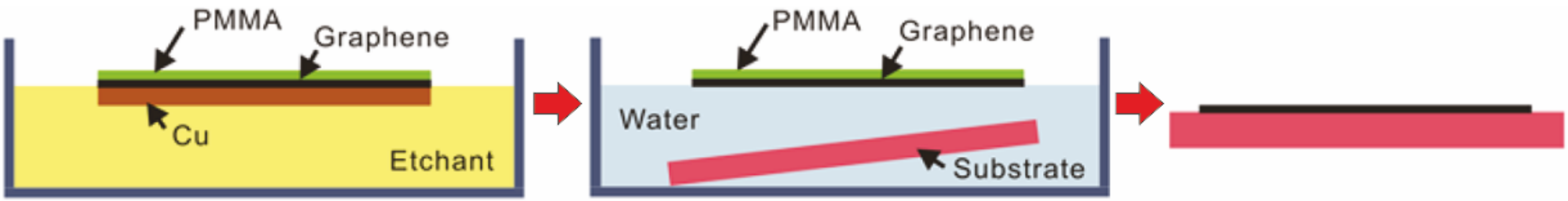


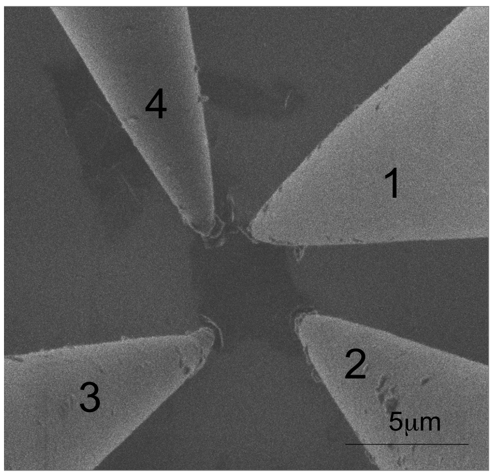
- dark current at 20mV

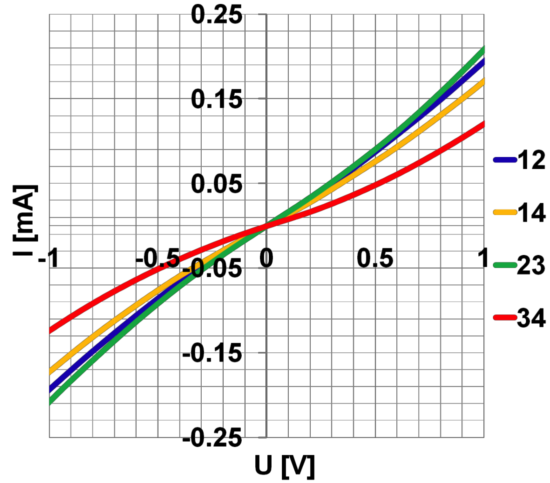
$$\frac{n \, x \, I_{dark}}{I_{dark}} = \frac{4.22 \, x \, 10^{-9} A}{1.18 \, x \, 10^{-10} A} \approx 36$$

- dark diode current scales with number of connected SiNW

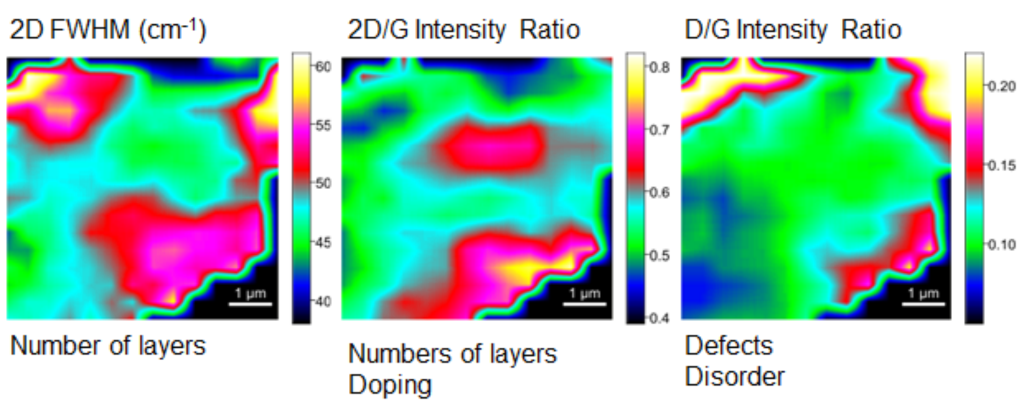
Graphene electrode







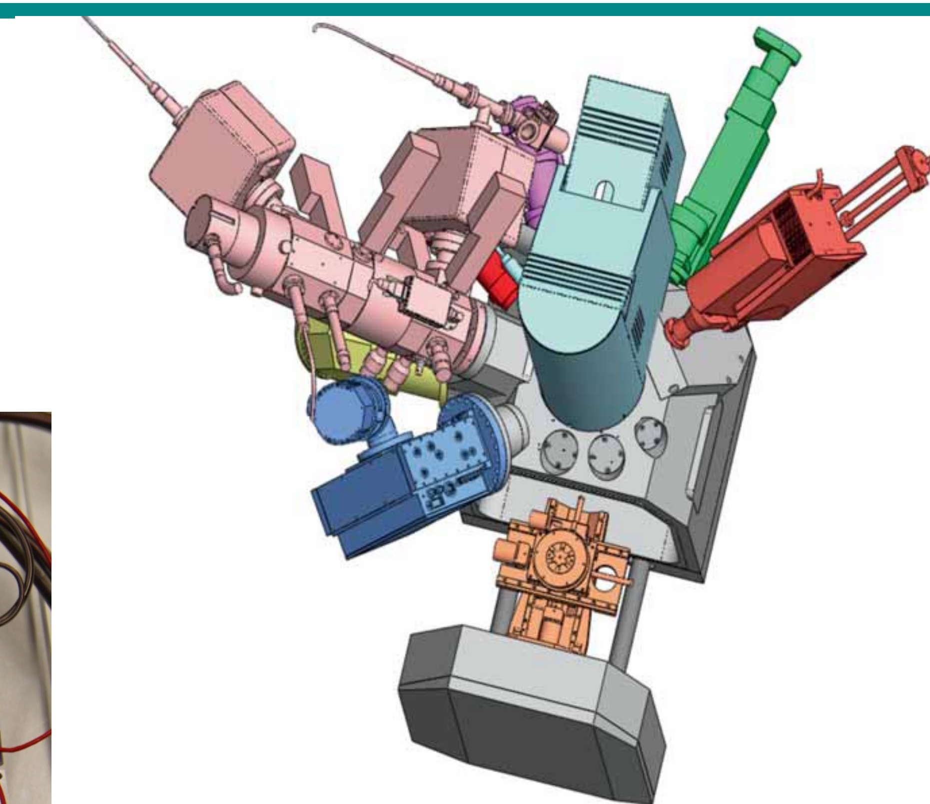
4 point nanoprober



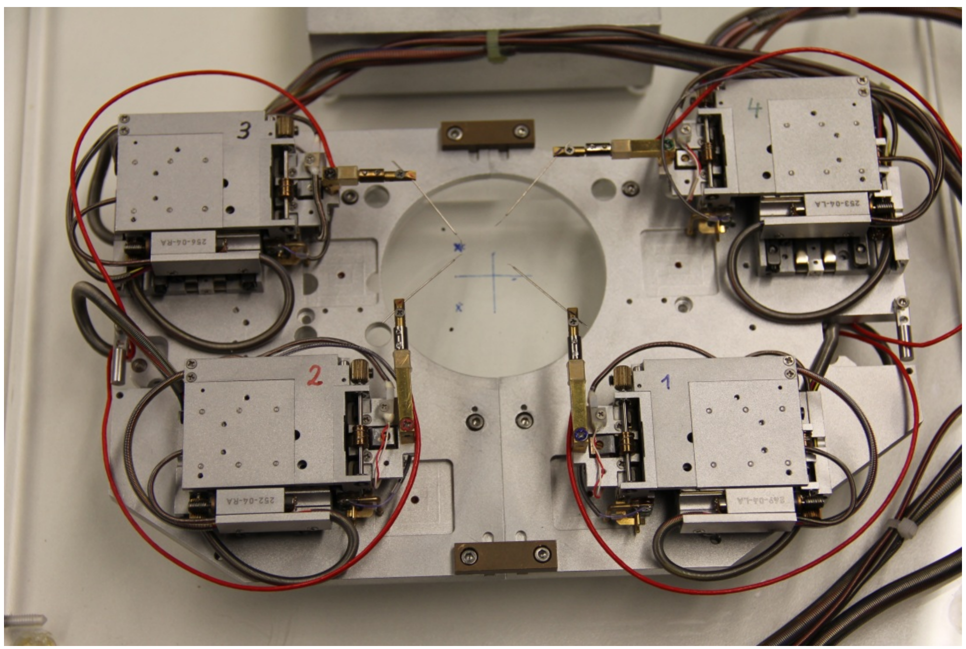
Raman spectroscopy

Nanomanipulation

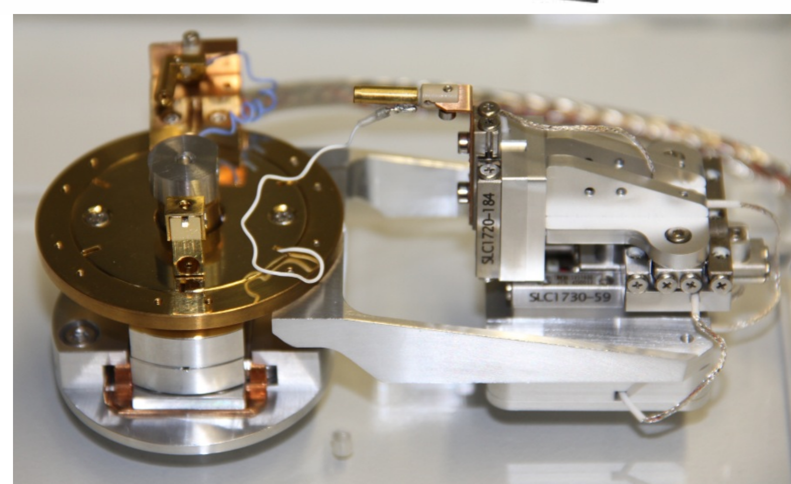
Dual Beam FIB
with various add-ons:
Incl. nano-manipulation, EBIC



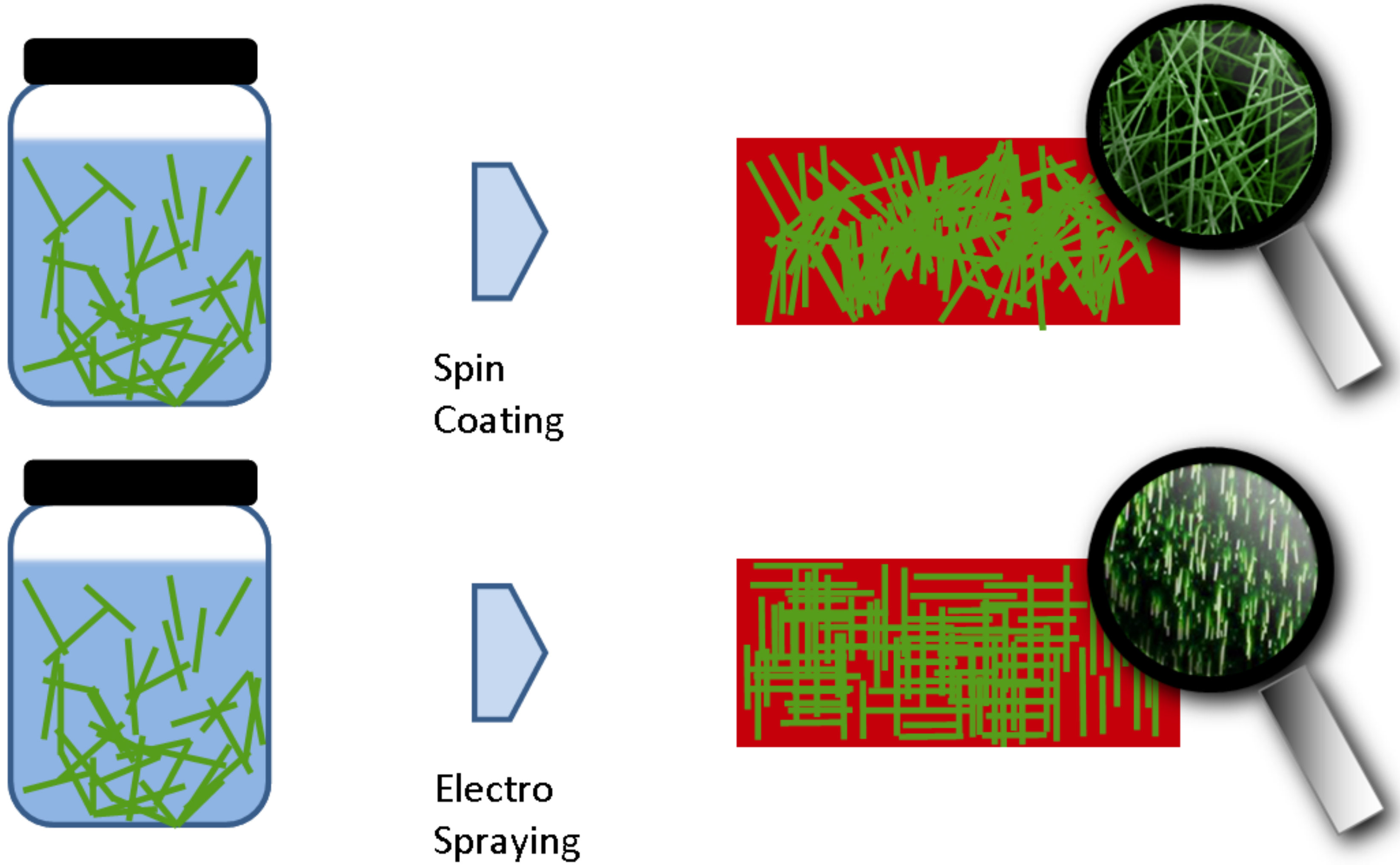
Nanoneedle setup
inside the SEM (Kammrath & Weiss)



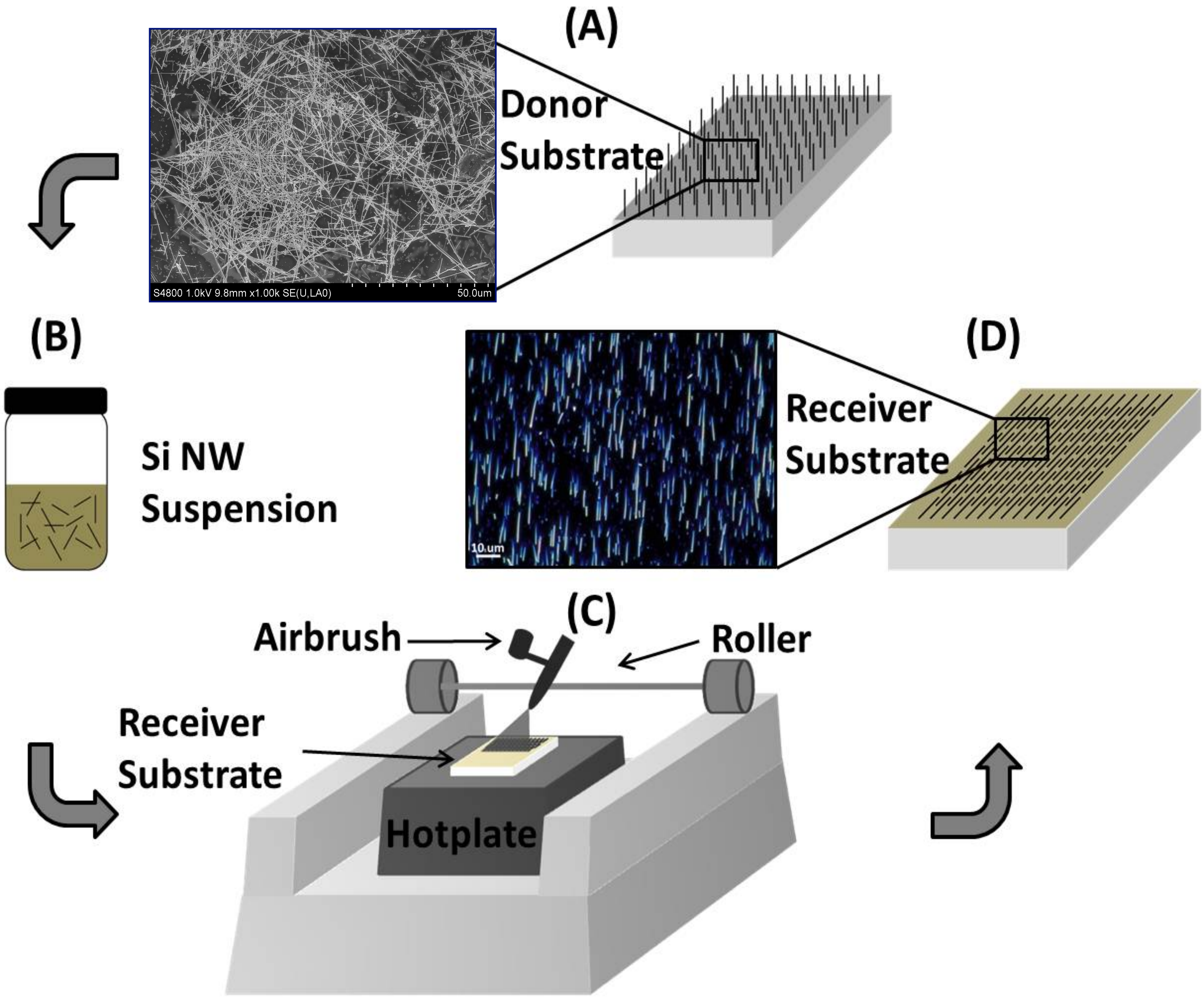
Electron Beam Induced Current setup
inside the SEM (Kammrath & Weiss)



Ag NW web electrodes

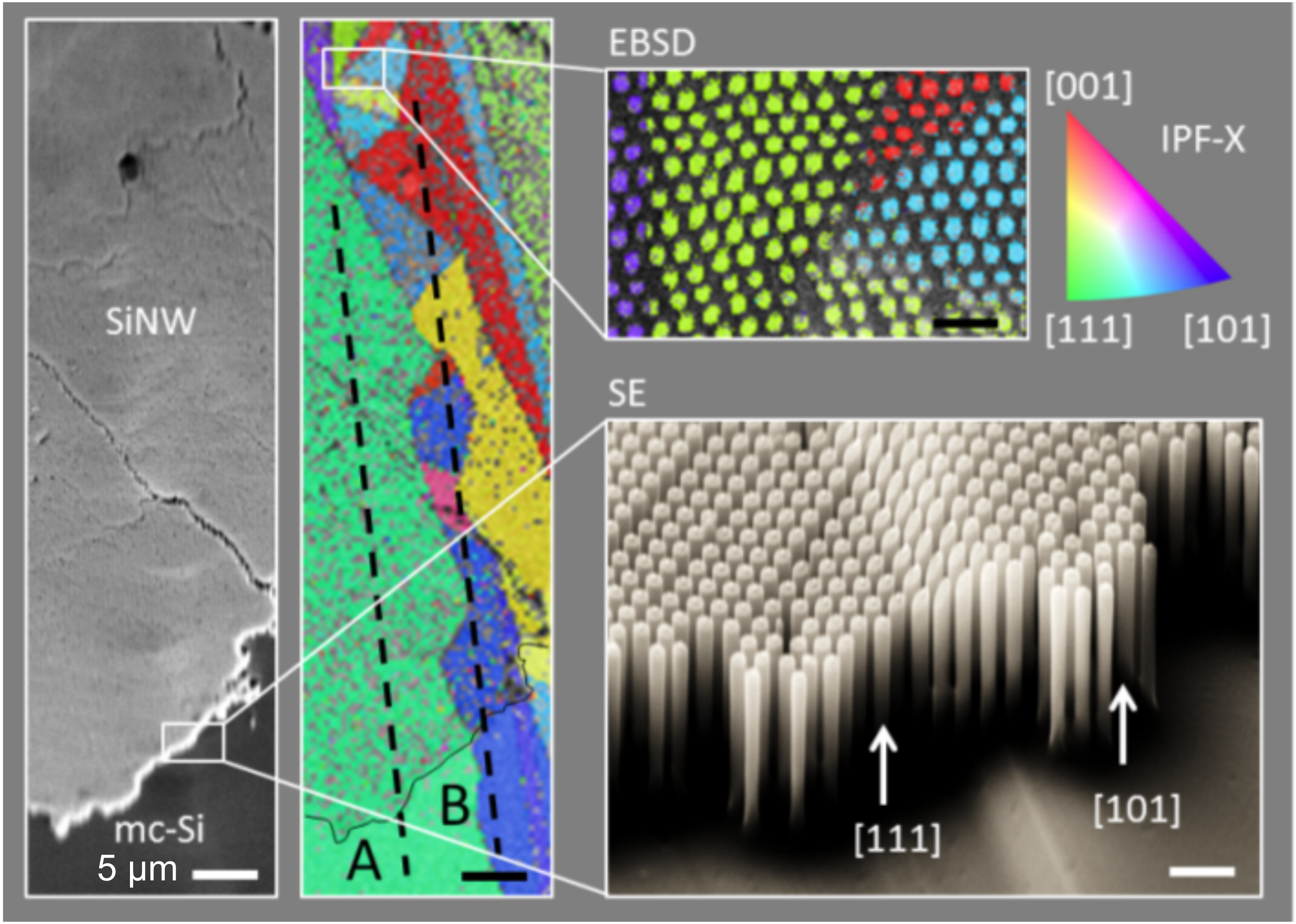


Garnett et al., Nature Mat. 11, 241 (2012)

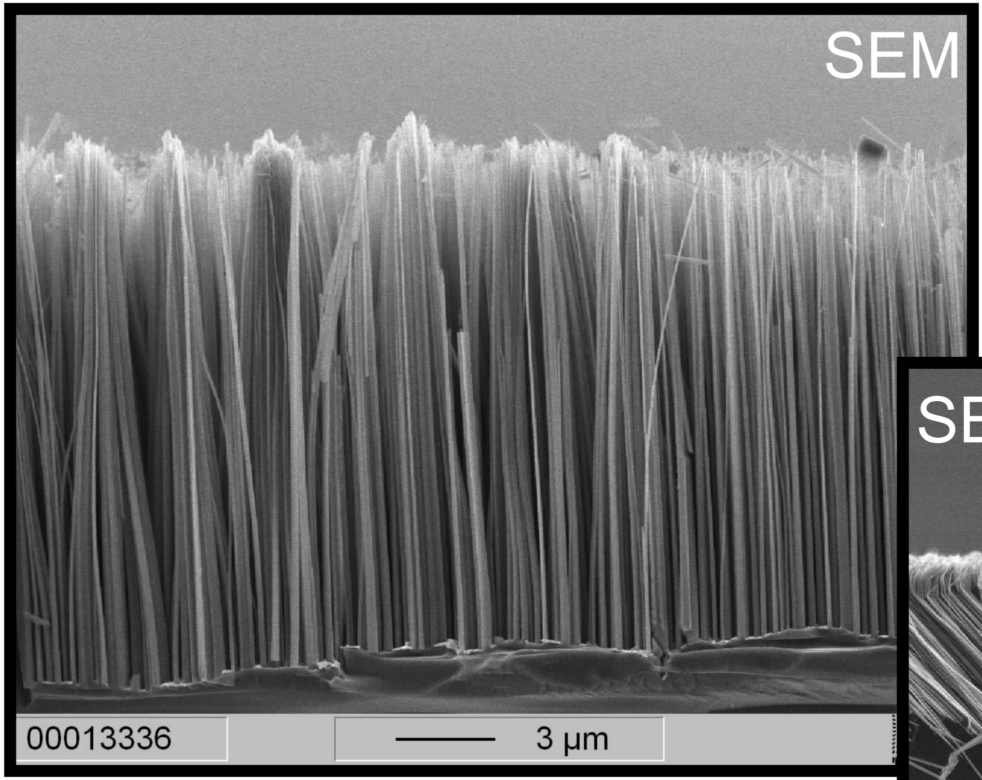


(A)
Donor
Substrate
S4800 1.0kV 9.8mm x1.00k SE(U,LA0)
50.0um
(B)
Si NW
Suspension
(D)
Receiver
Substrate
10 um
(C)
Airbrush
Roller
Receiver
Substrate
Hotplate

Electron Backscatter diffraction



Wet-chemically etched Si nanostructures

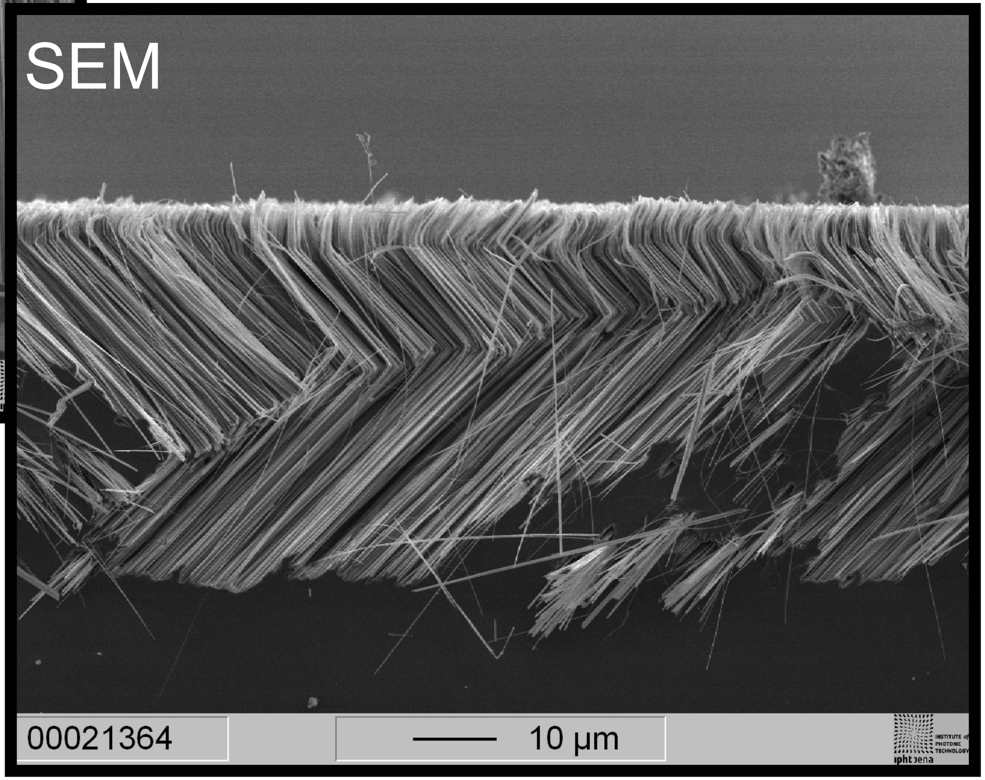


Etching occurs in <100> directions

→ Vertical nanostructures on a Si(100) wafer

Etching occurs in <111> directions

→ ZigZag nanostructures possible



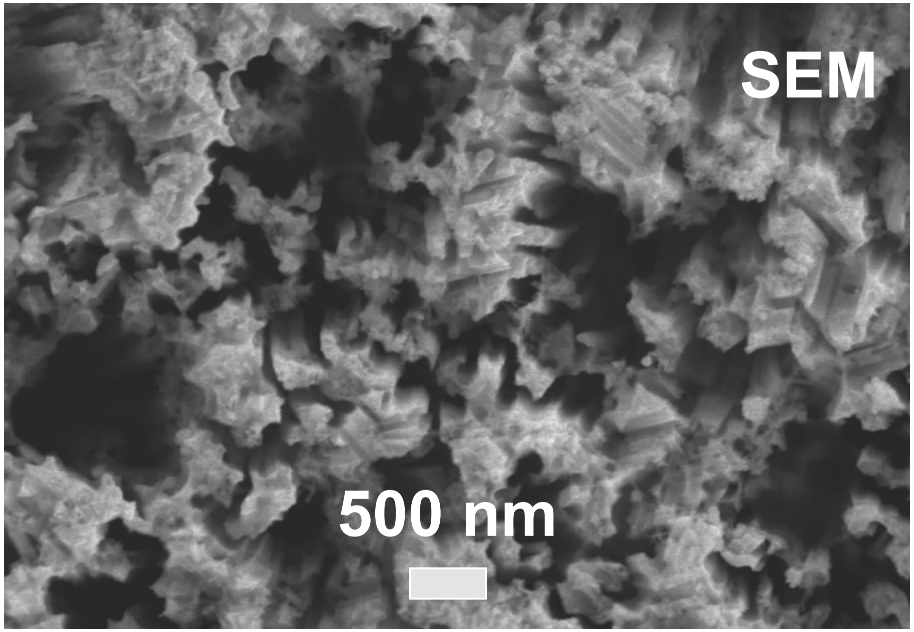
Etching depth depends on time in etching **solution II**

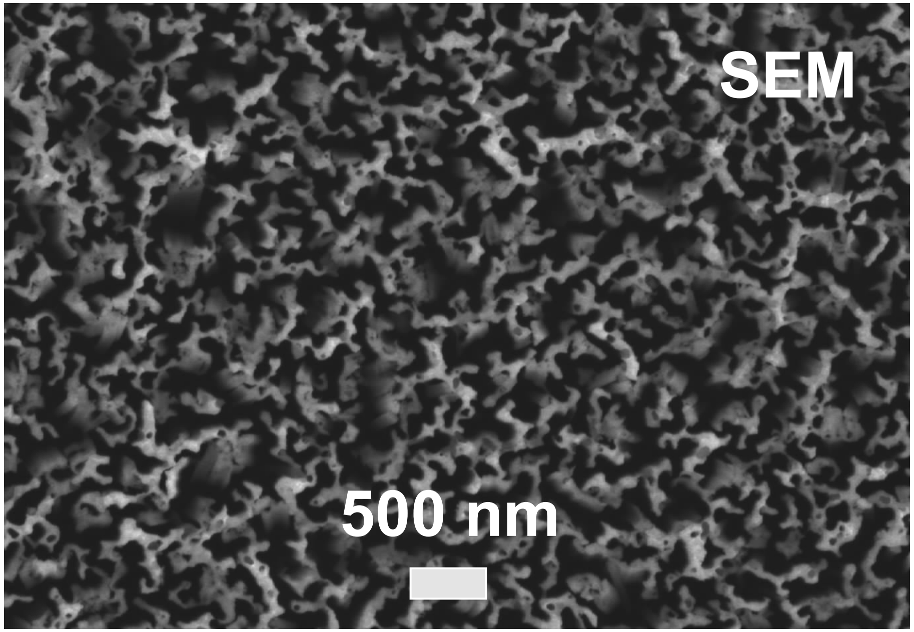
V. A. Sivakov, G. Brönstrup, B. Pecz, A. Berger, G. Z. Radnoczi, M. Krause, S. Christiansen, J.Chem.Phys.C 114, 3798 (2010)
V. A. Sivakov, F. Voigt, G. Brönstrup, G.H. Bauer, S. Christiansen, Phys. Rev. B 82, 125446 (2010).

Wet-chemically etched Si nanostructures

Porosity of SiNWs depends on

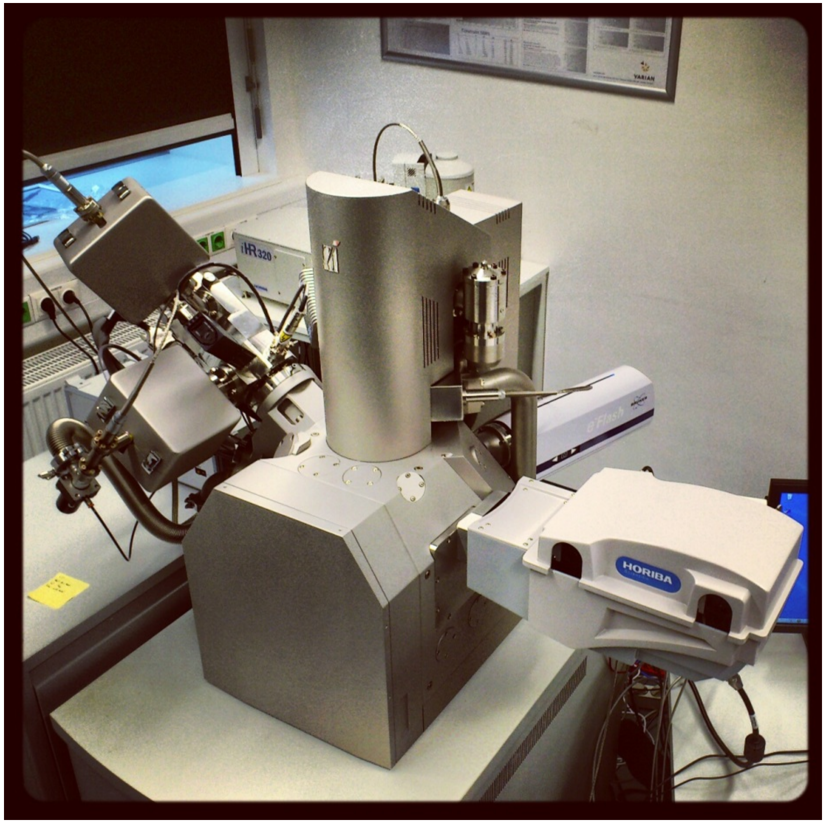
silver deposition time (**solution I**) controls massive (5s deposition) or fine (30s) structures.



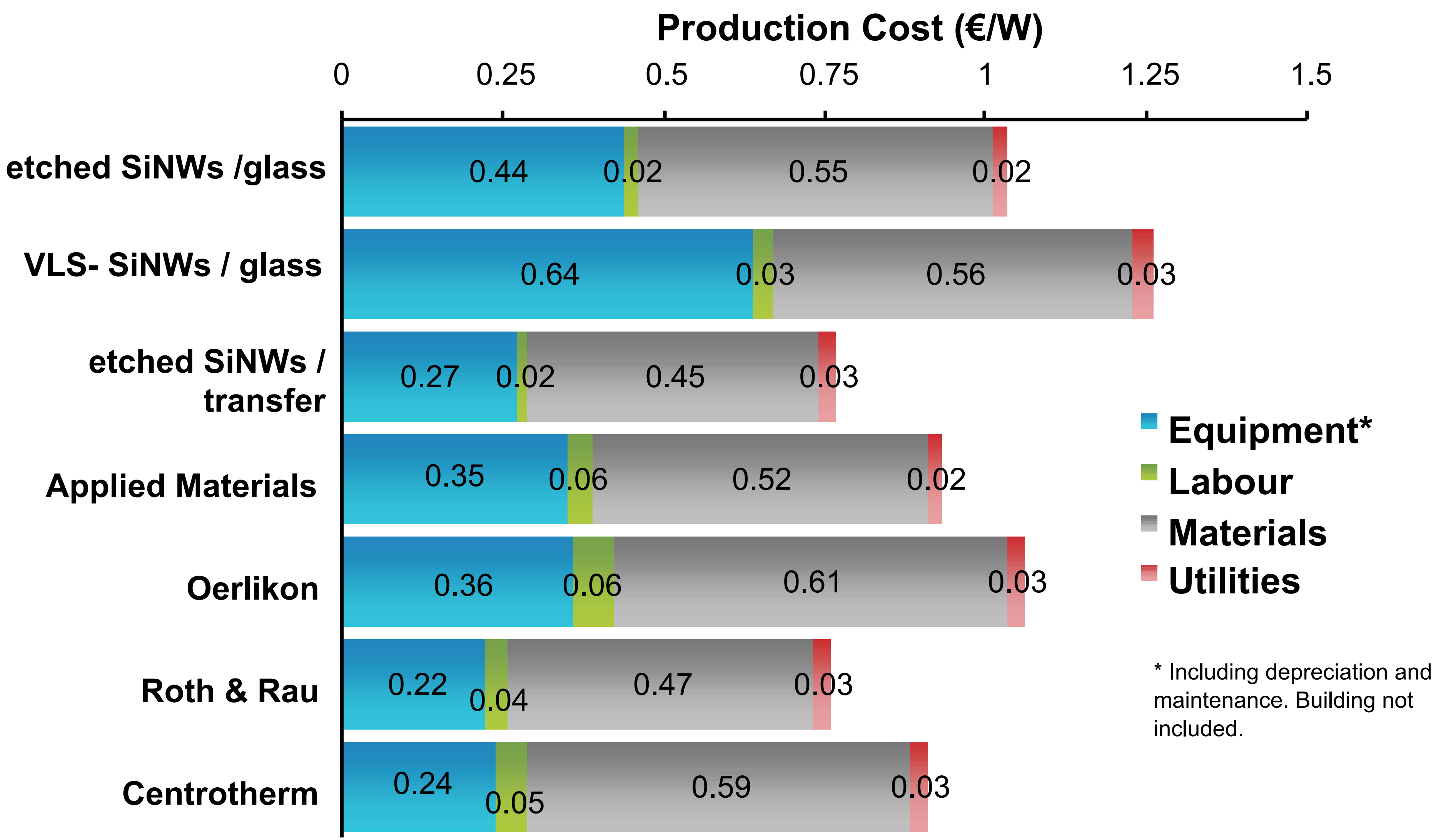


Dual beam FIB: a ‘swiss knife’ tool for nanotechnology

- **Recently our Tescan Lyra 3 „Fiblys“ prototype was equipped with a Horiba „Clue“ for CL, EL, PL and Raman measurements.**
- **Together with EDX, EBSD, EBIC, FIB and a 4-point-prober it deserves the nick name „Swiss Knife of Nanoscience“!**
- **Correlated microscopies permit combined structural, electrical & optical characterizations at identical nanostructures.**

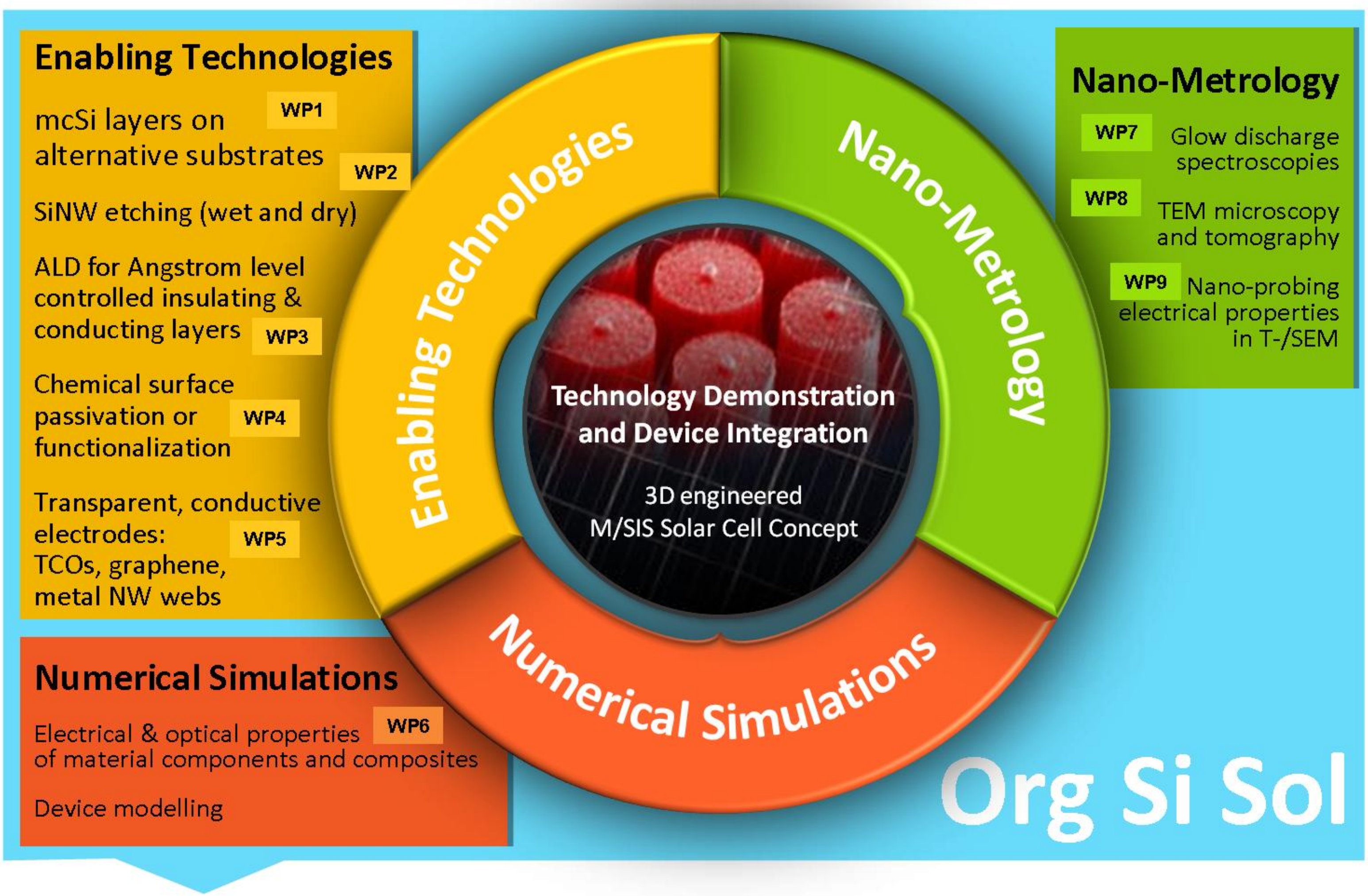


FP7 NMP ROD_SOL: cost models



IRS iSuppli 2010

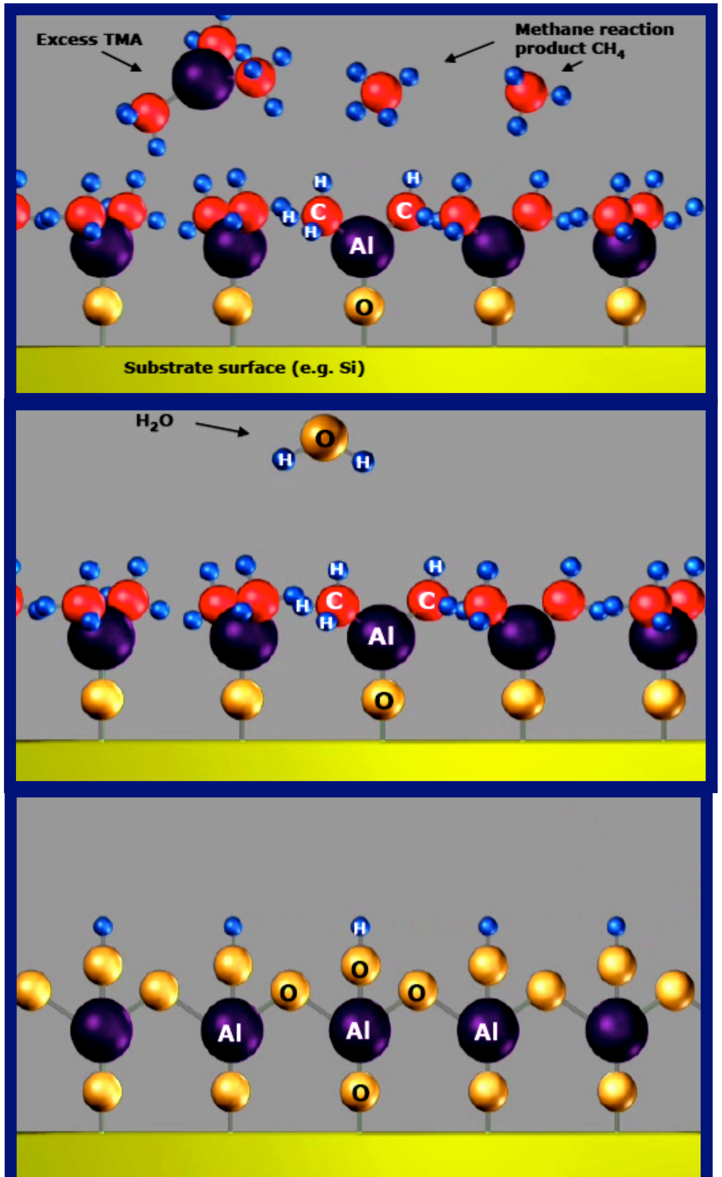
3D SiNW based thin film solar ell



Exploitable results:

- Novel cell concept based on novel nano-composite materials if efficiences permit.
- Atomic layer deposition of TCO's: processes and layout of high-throughput tooling.
- Glow discharge spectroscopies: tooling and procedures to assess nano-composite materials.

Atomic layer deposition (ALD)



hydroxyl groups await TMA (precursor I) pulse

Al-O bonds form

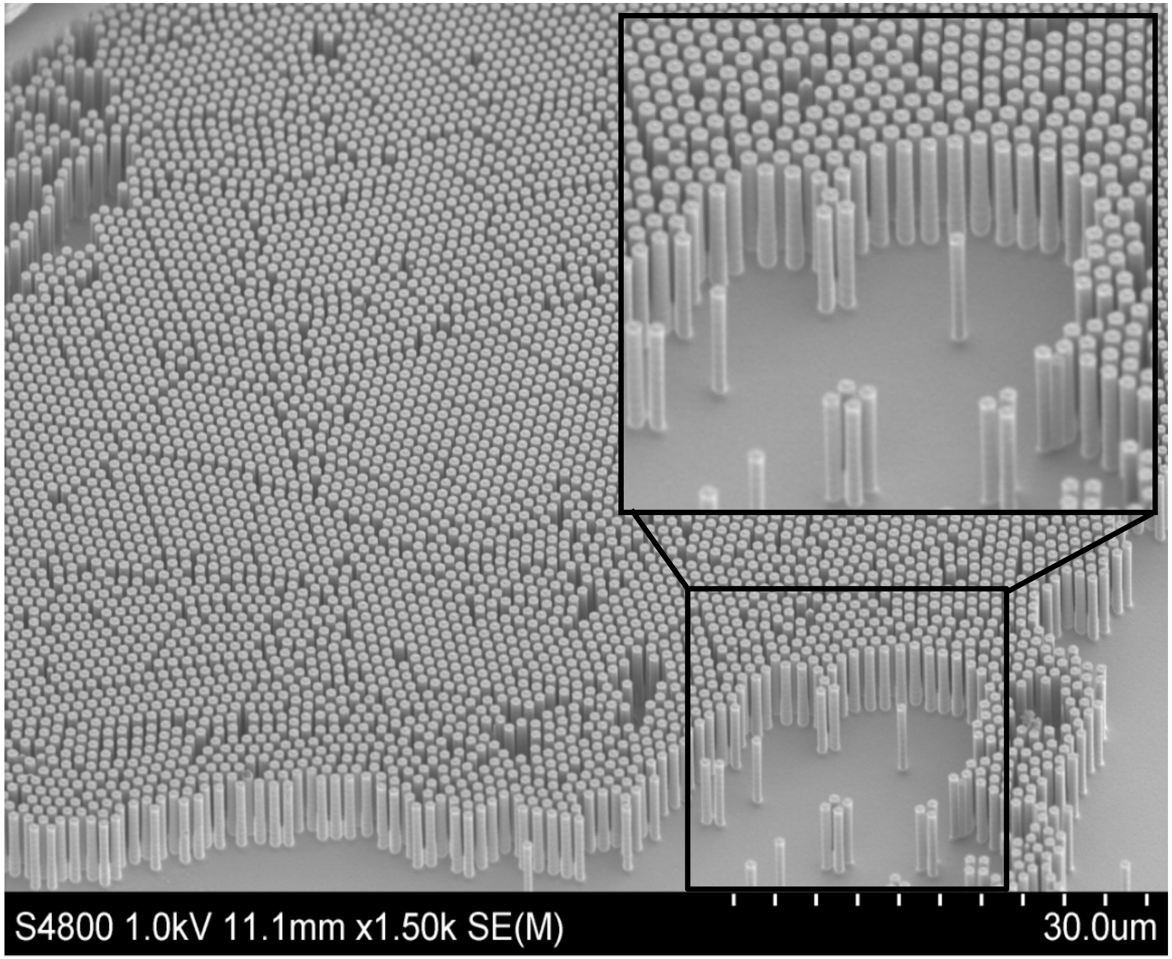
H_20 (precursor II) reacts with dangling methyl groups on newly formed Al-O bonds

Al-O bonds form;
OH-groups await new TMA pulse;
methyl groups are pumped out

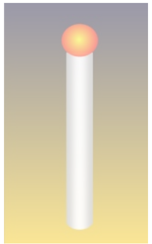
Al_2O_3 deposition

Dry etched Si NWs in µc-Si layers on glass

- morphology



Outline

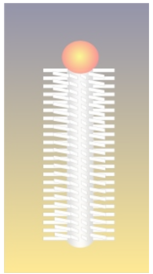


Nanowires (NWs) - Synthesis & Morphology

- top down NW etching

NWs in solar cell applications

- semiconductor NWs in different cell concepts
- surface functionalization of NWs to improve solar cell performance
- Si NW doping, contacts & plasmonic add-ons etc.

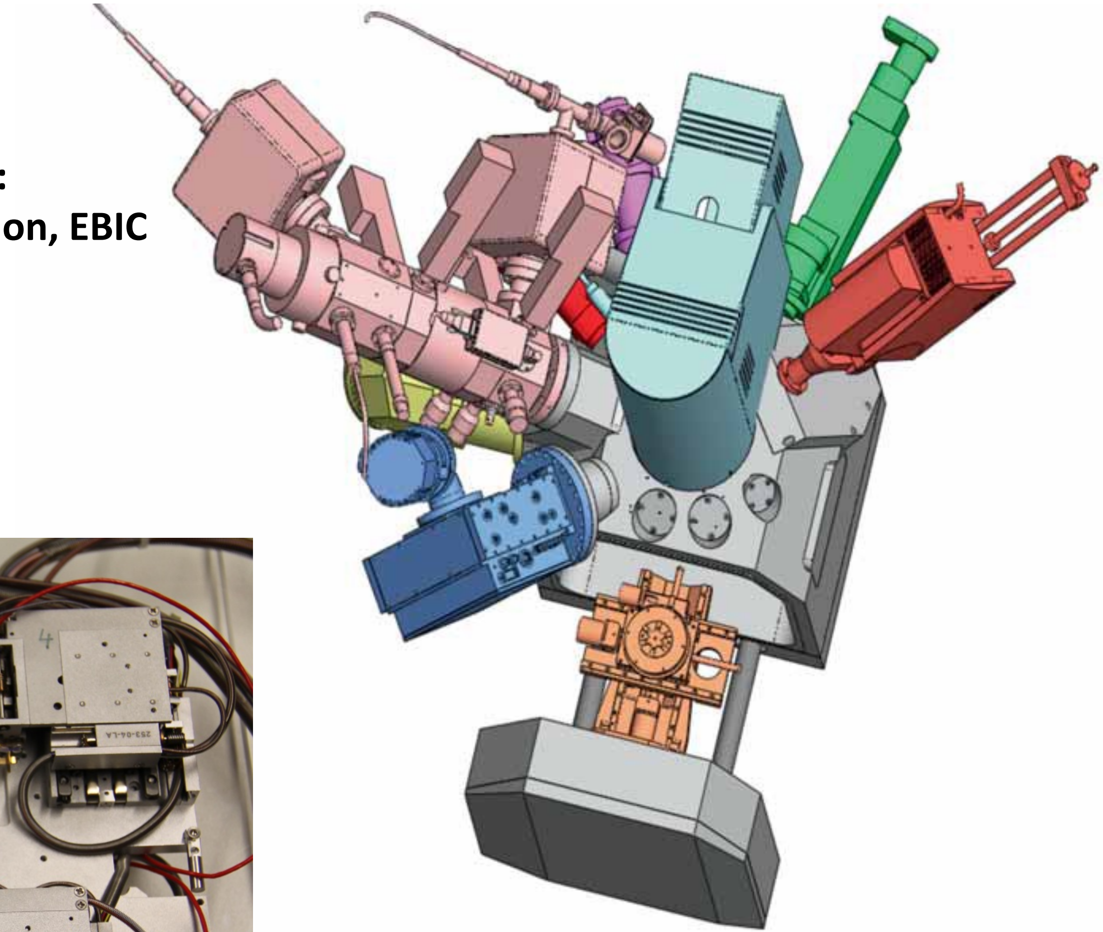


NWs in sensors

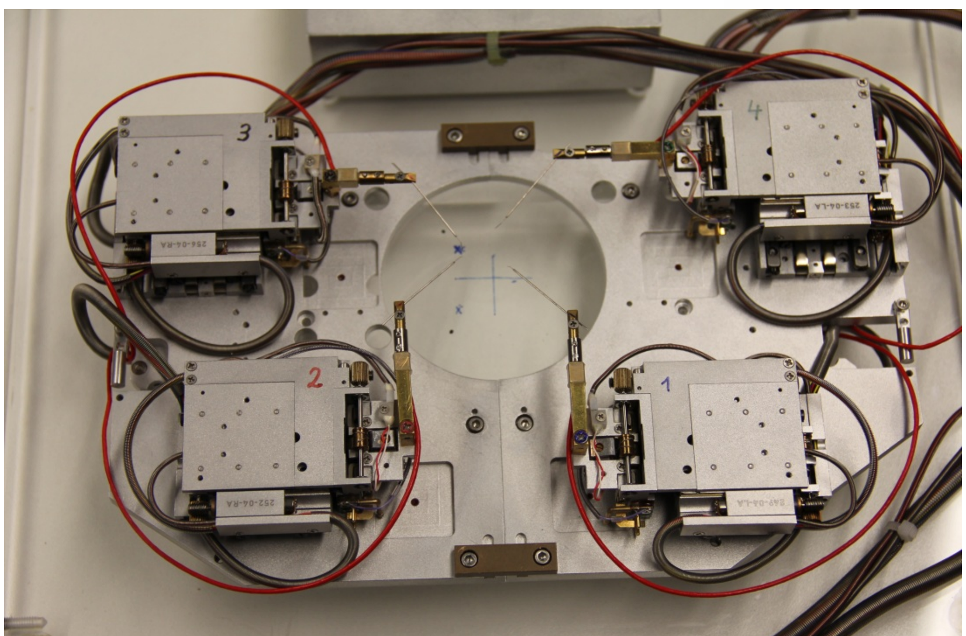
- spectroscopic finger prints
- functionalized NWs in field effect transisitors → highly sensitive & selective cancer sensing from breath

Nanomanipulation

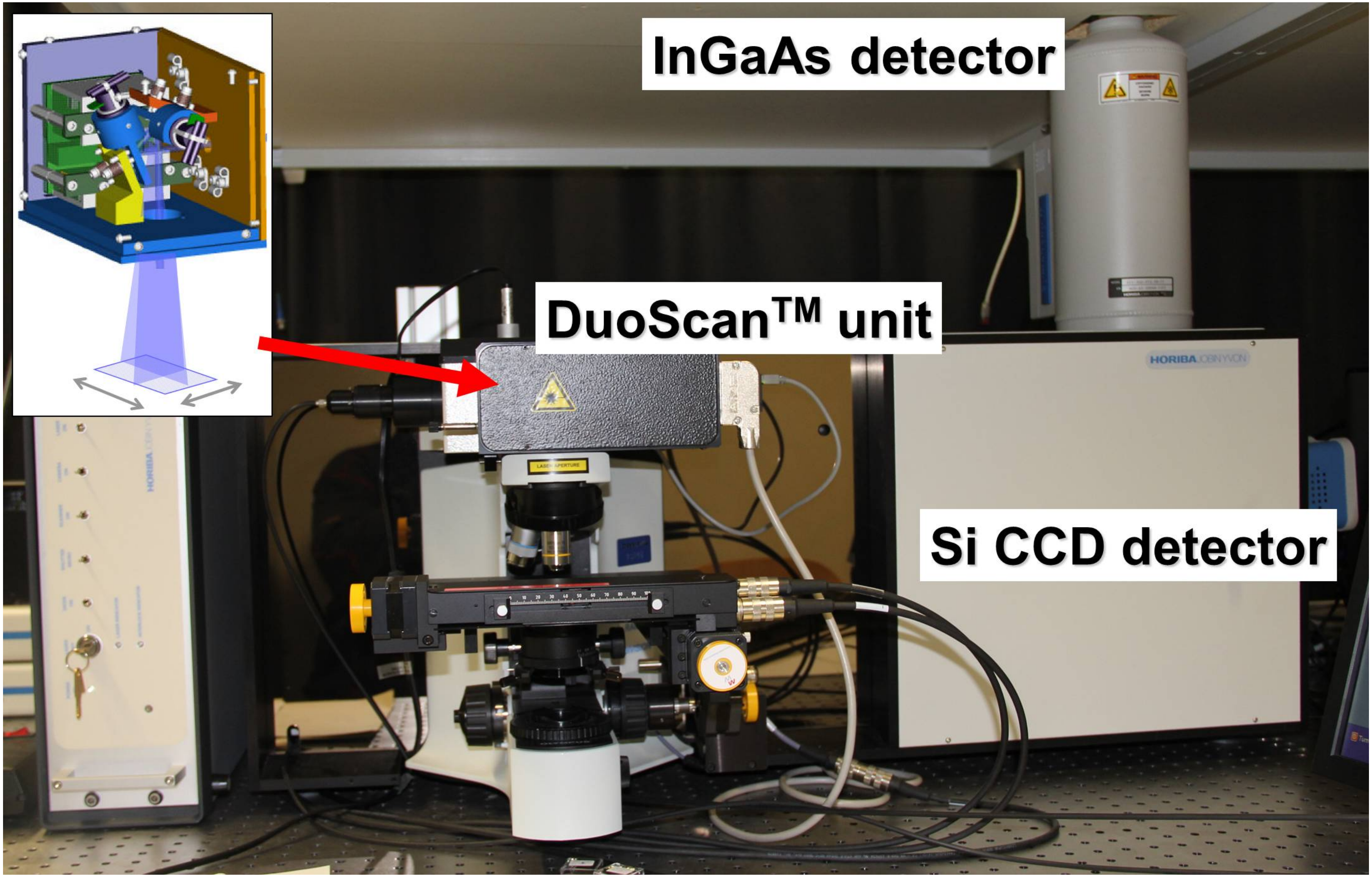
Dual Beam FIB
with various add-ons:
Incl. nano-manipulation, EBIC



Nanoneedle setup
inside the SEM (Kammrath & Weiss)

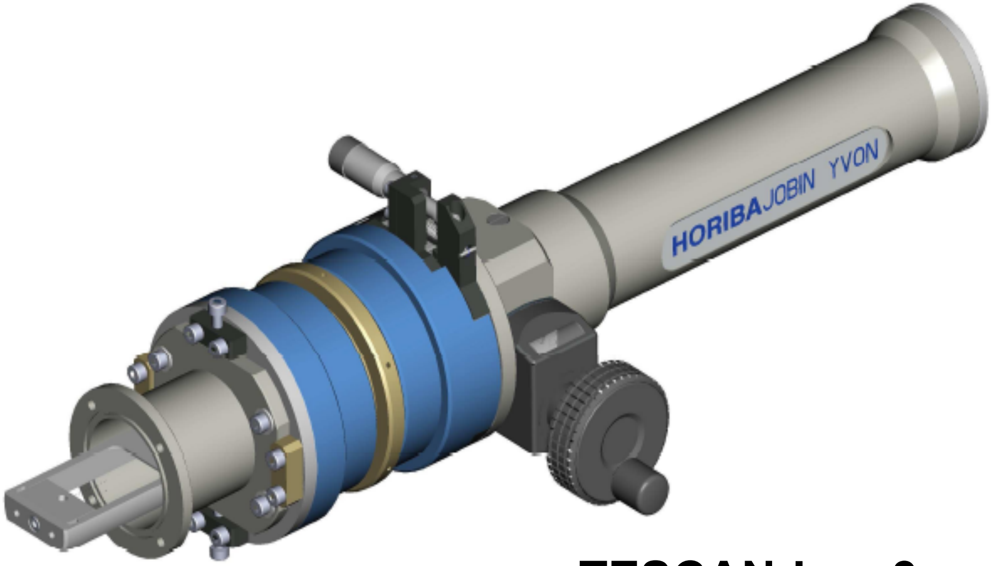


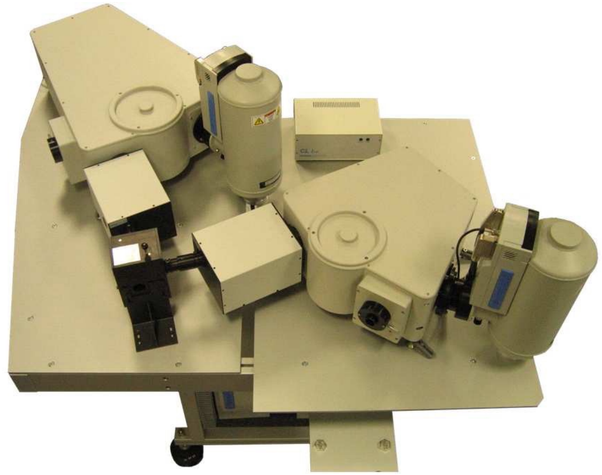
optical characterization: μ-Raman spectroscopy + PL

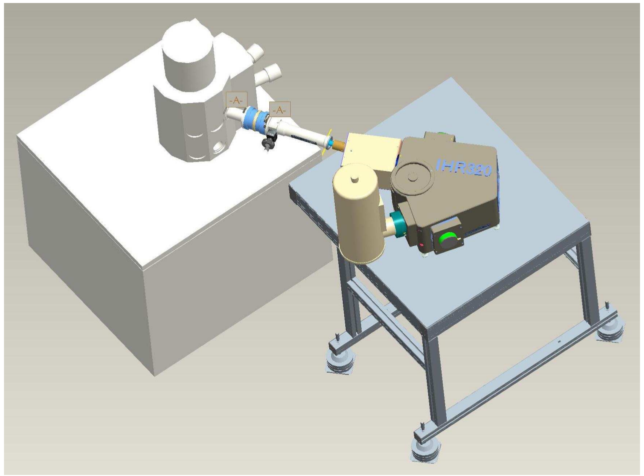


Raman

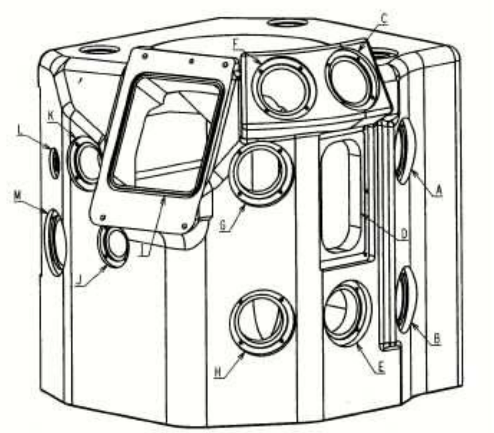
CL





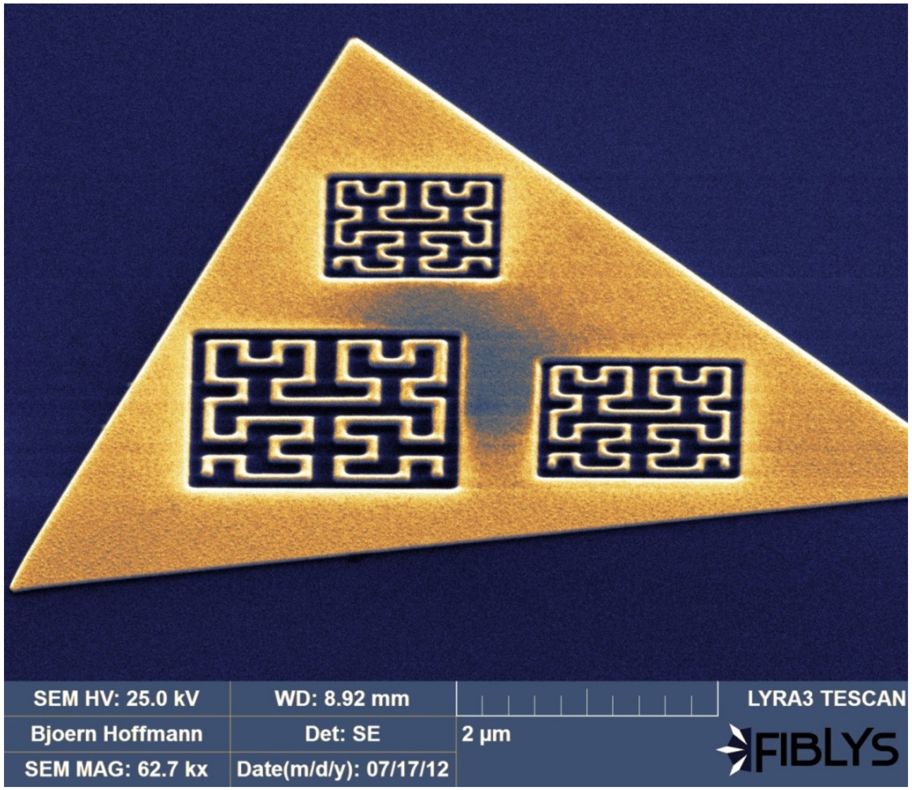


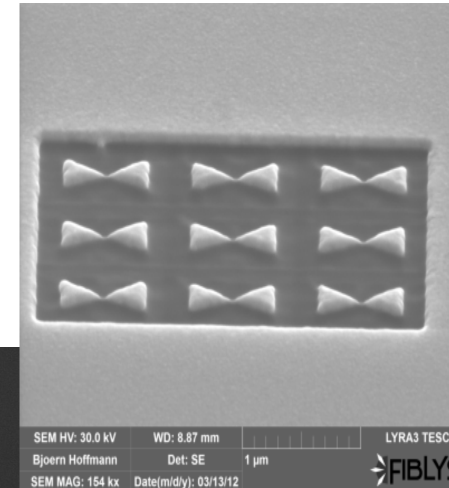
TESCAN-Lyra3

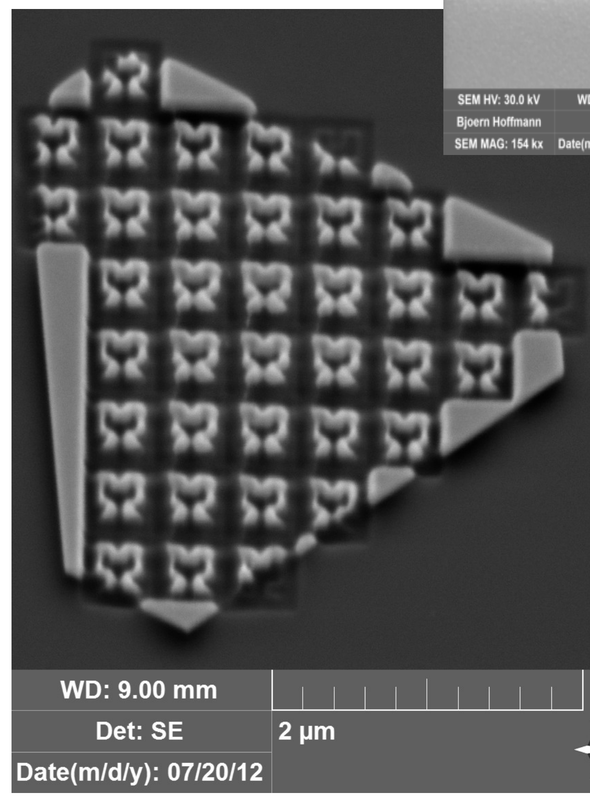


Plasmonic nanostructures

FIB patterning in single crystalline Au nanoflakes



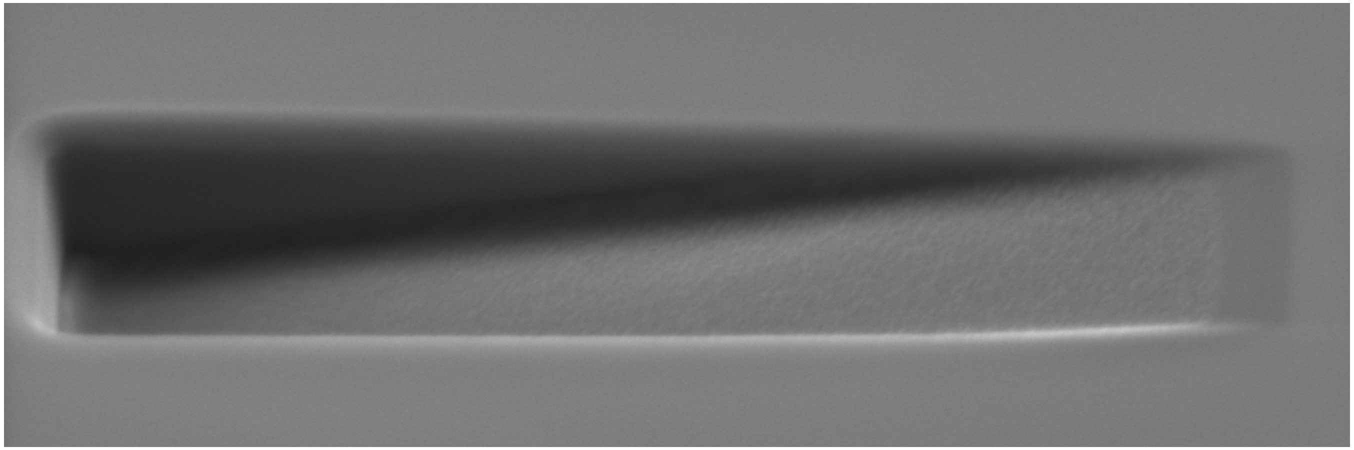




The problem of structures with a non-uniform depth-distribution is the design. Simple, object-based gradients are difficult to achieve.

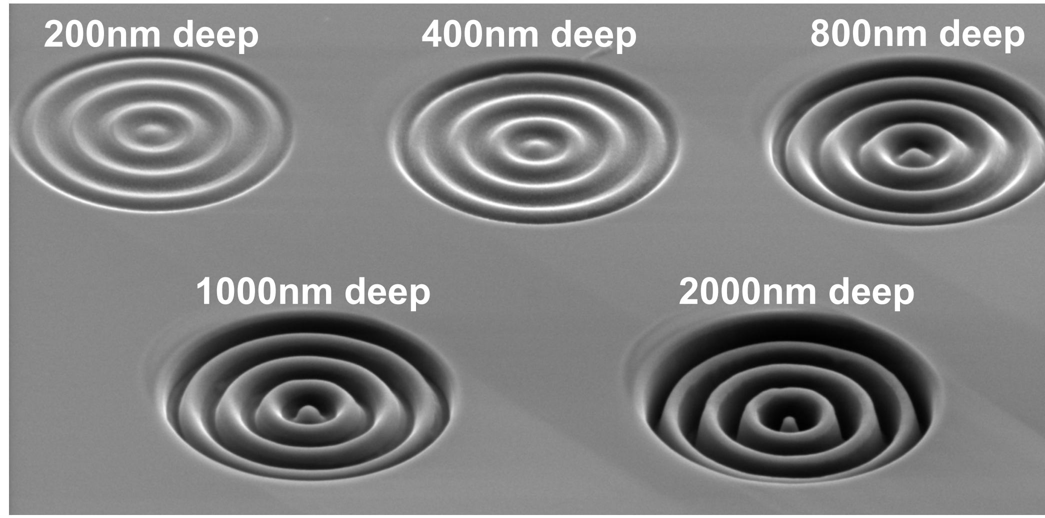
→ Greyscale bitmap etching can be used!

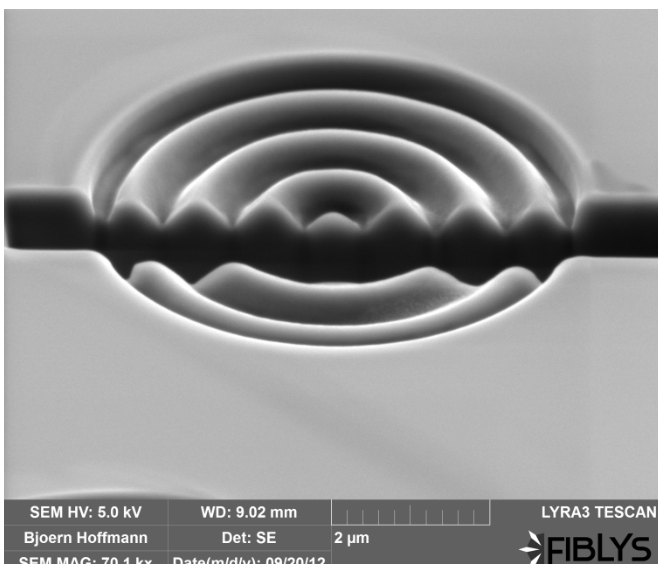
All you need is a greyscale bitmap where the depth is coded in the greyscale with black = no etching and white = full depth. RGB-value 0-255 (black – white)

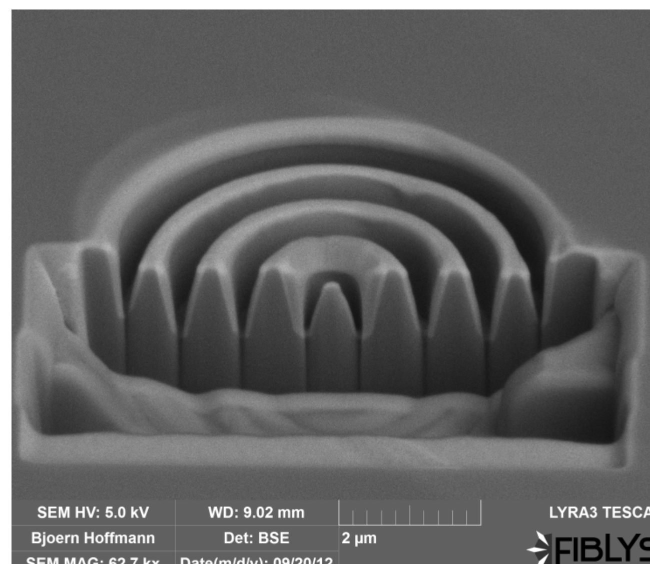


Concentric rings

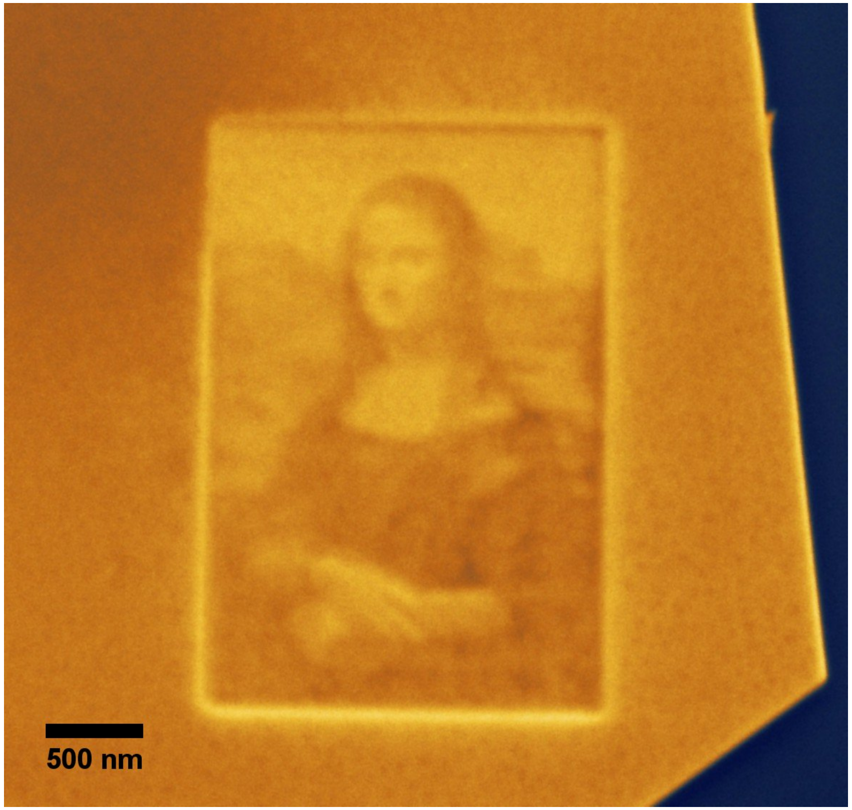
More complex structures are no problem and the depth scales linearly.



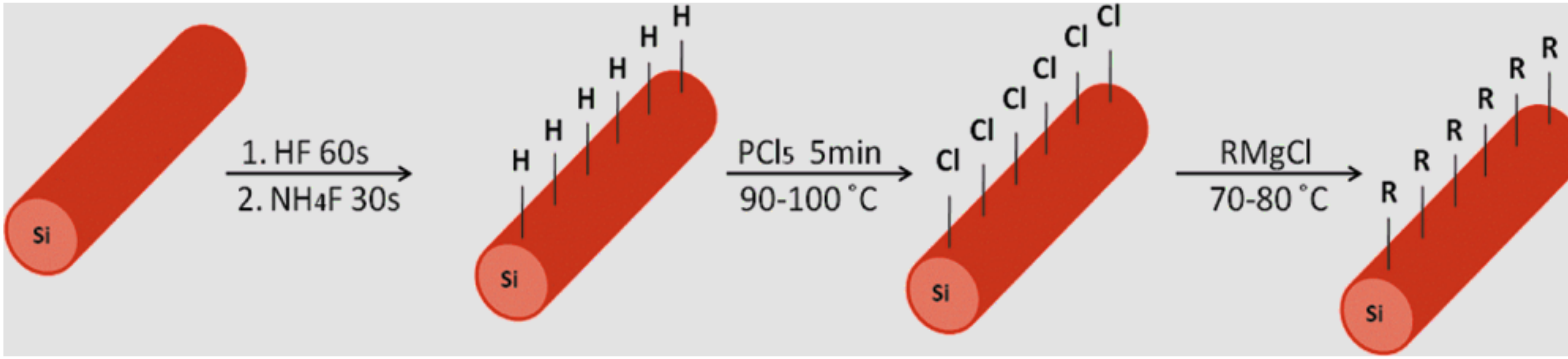




The (most likely) smallest Mona Lisa in the world, etched in a single crystalline gold flake!



Si functionalization: preventing oxidation



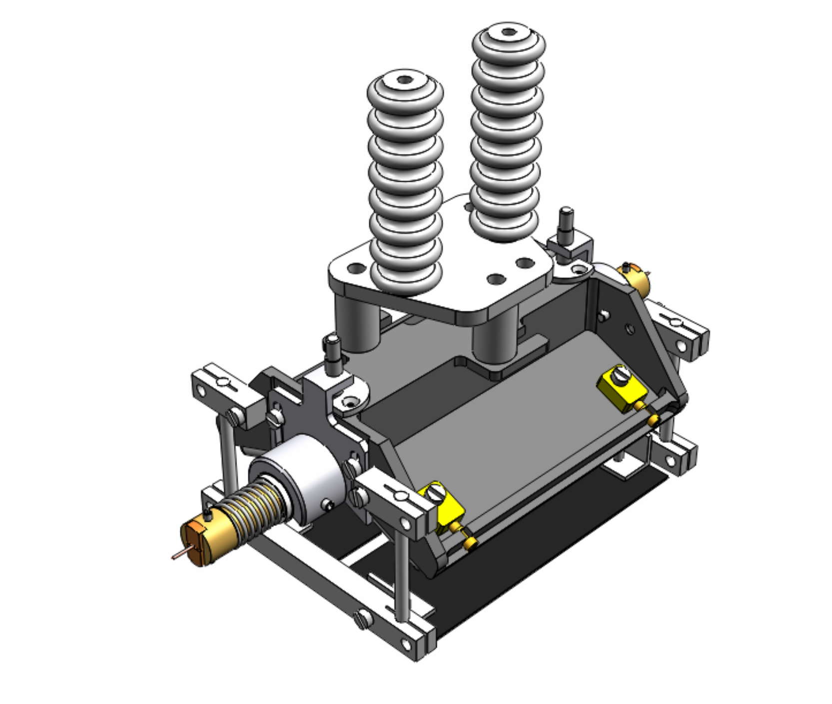
Grignard reaction: chlorination / alcylation process

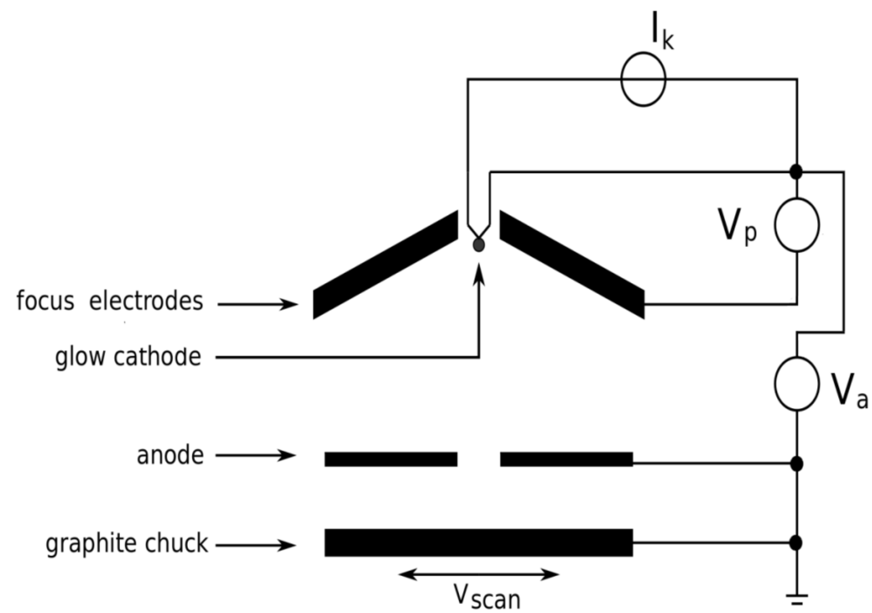
XPS studies	Optimal alkylation time for Si NWs	C_{Si}/Si_{2p} ratio for Si NW	Max. coverage on Si NW	Max. coverage[lit] on 2D Si (100)
CH_3	30 min	0.110±0.010	---	-----
CH_3CH_2	80 min	0.100±0.010	91±1%	60±20%
$CH_3(CH_2)_2$	130 min	0.090±0.010	82±1%	30±20%
$CH_3(CH_2)_3$	170 min	0.085±0.010	77±2%	30±20%

M. Y. Bashouti et al. PCCP 11, 3845 (2009) ; M. Bashouti et al. PCCP in press 2012

Electron beam crystallization

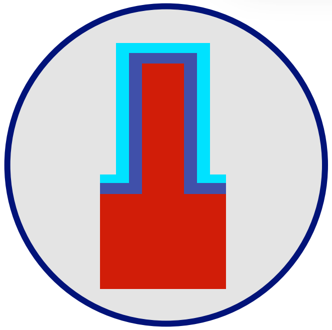
- developed at the Institute of Microsystems technology (TUHH) since 1990
- beam geometry: 90mm x 0,8mm (w x h)
- constant current heated tungsten wire
- pierce electrodes to focus the beam onto substrate



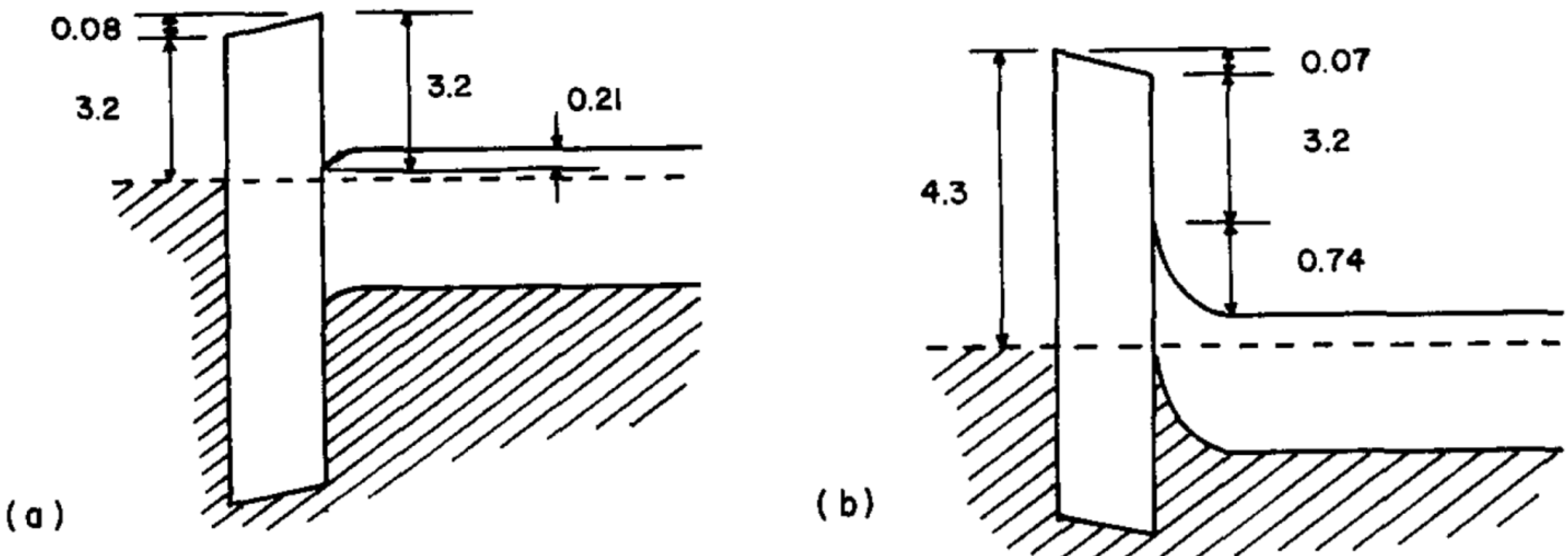


M. Pauli, et al., Rev. Sci. Instrum. 63 (1992) 2288
J.R. Pierce, J.Appl.Phys. 11 (1940) 548

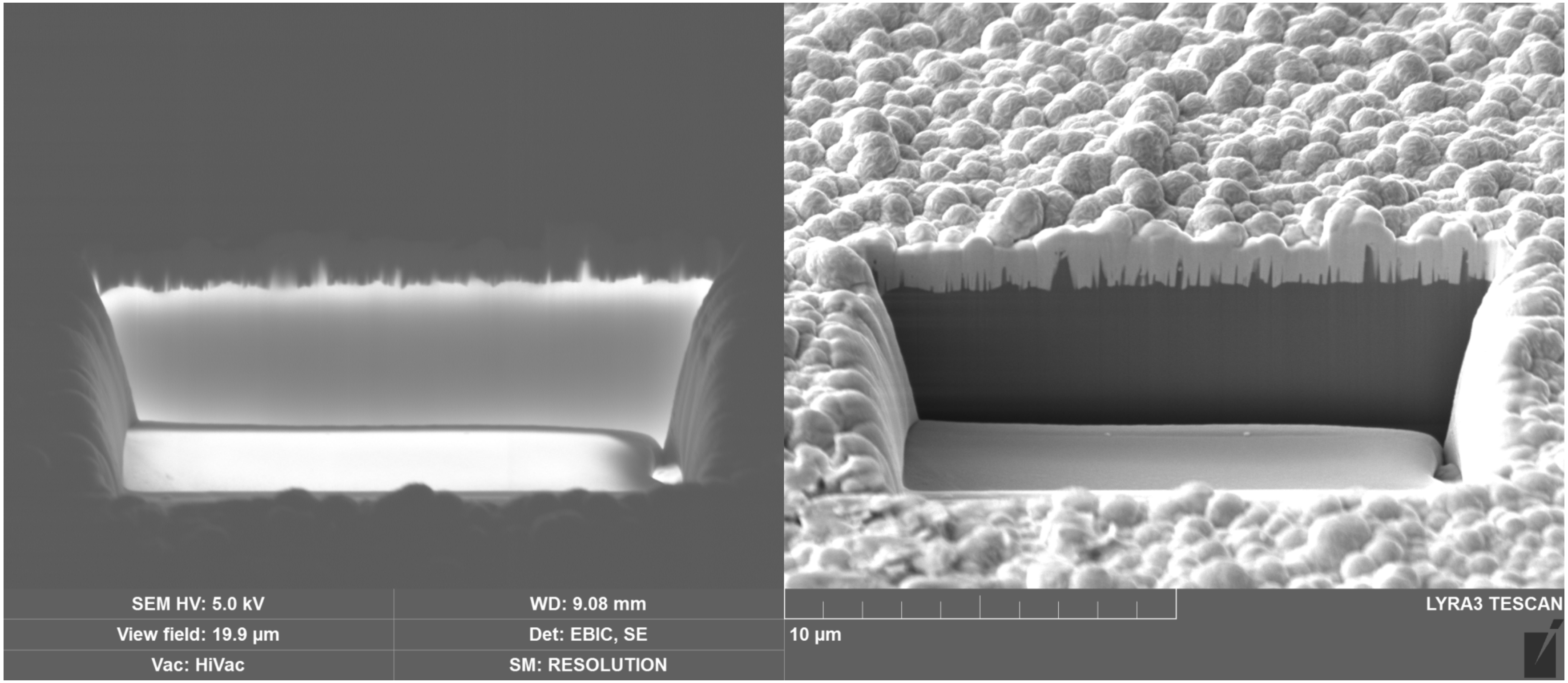
HZB, B. Rech et al.



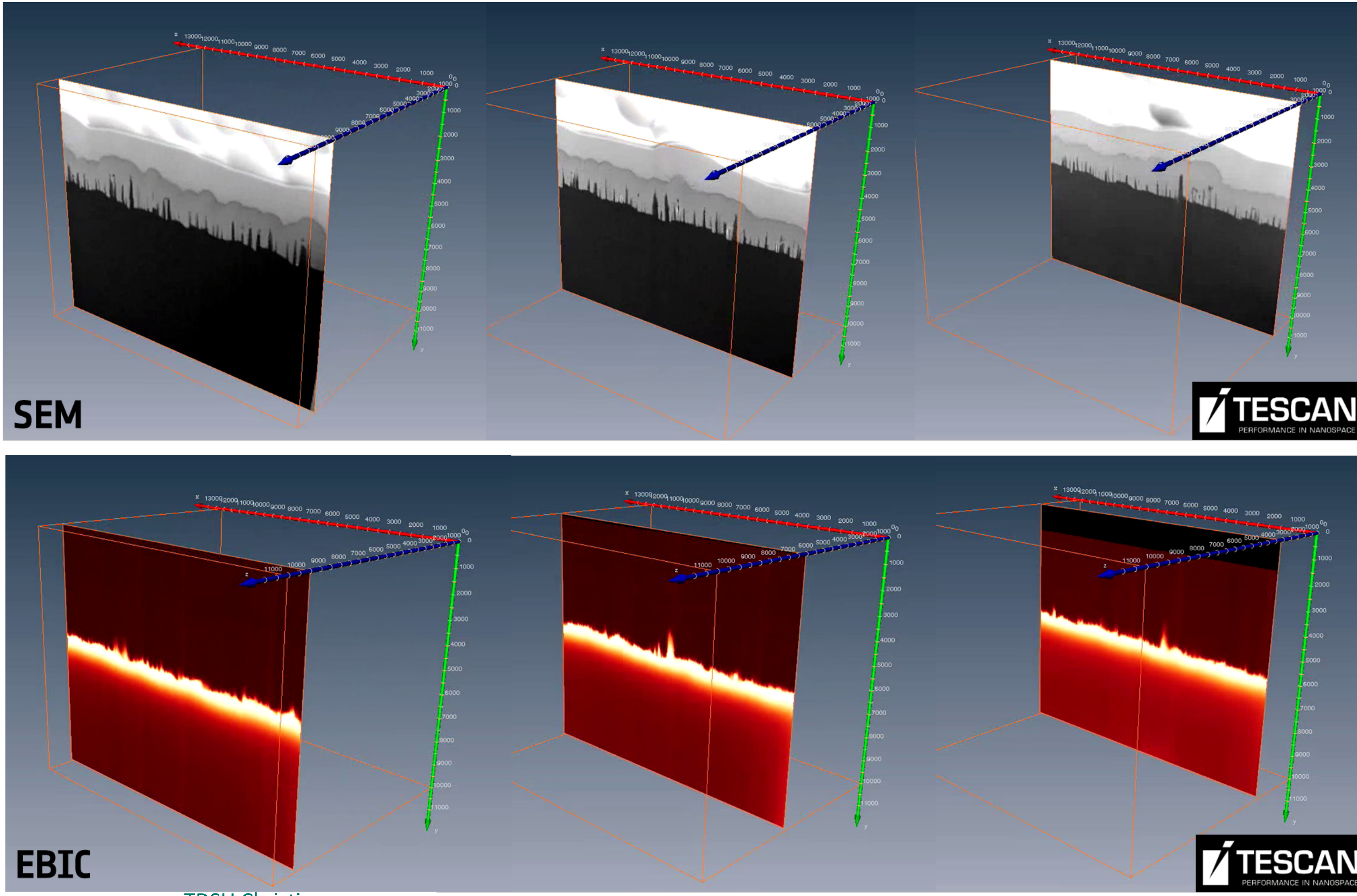
- Selection of proper metal (workfunction) drives the surface region in
  - accumulation (majority carrier solar cell) - a
  - or depletion/inversion (minority carrier solar cell) -b
- tunneling of electrons depends on thickness of insulator



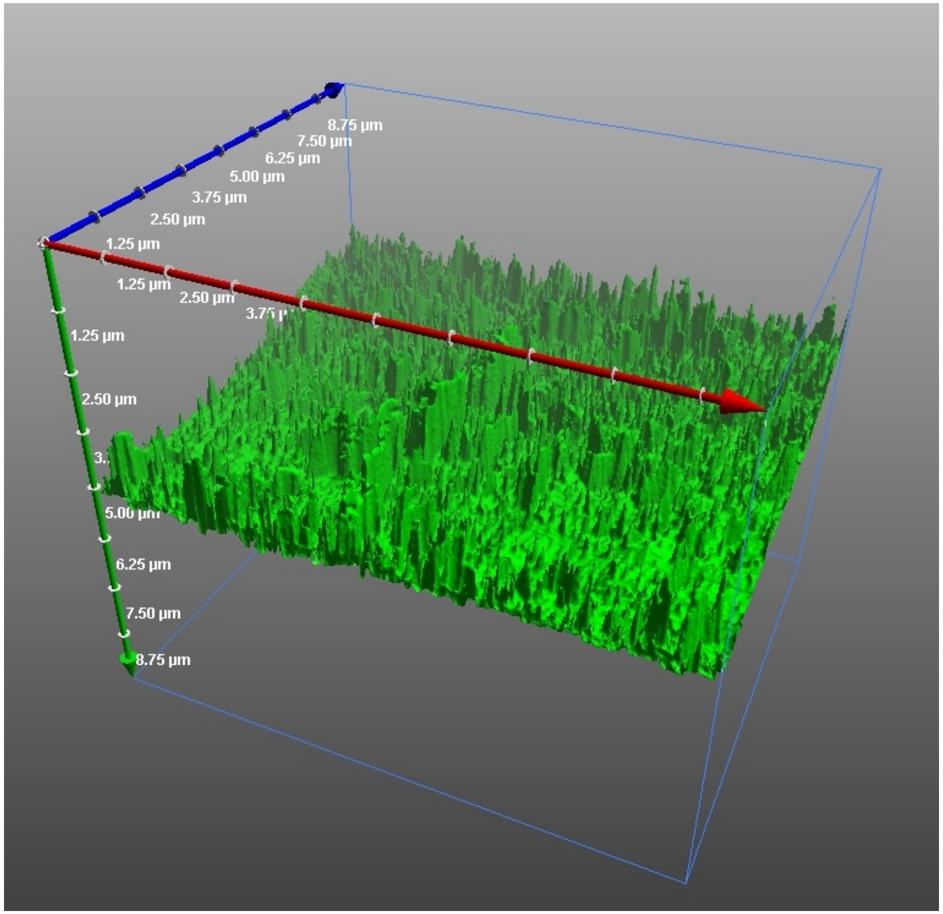
Cutting and slicing with a focused ion beam system enables a 3-dimensional reconstruction of the SiNWs as well as of the active region, determined by the EBIC-signal.



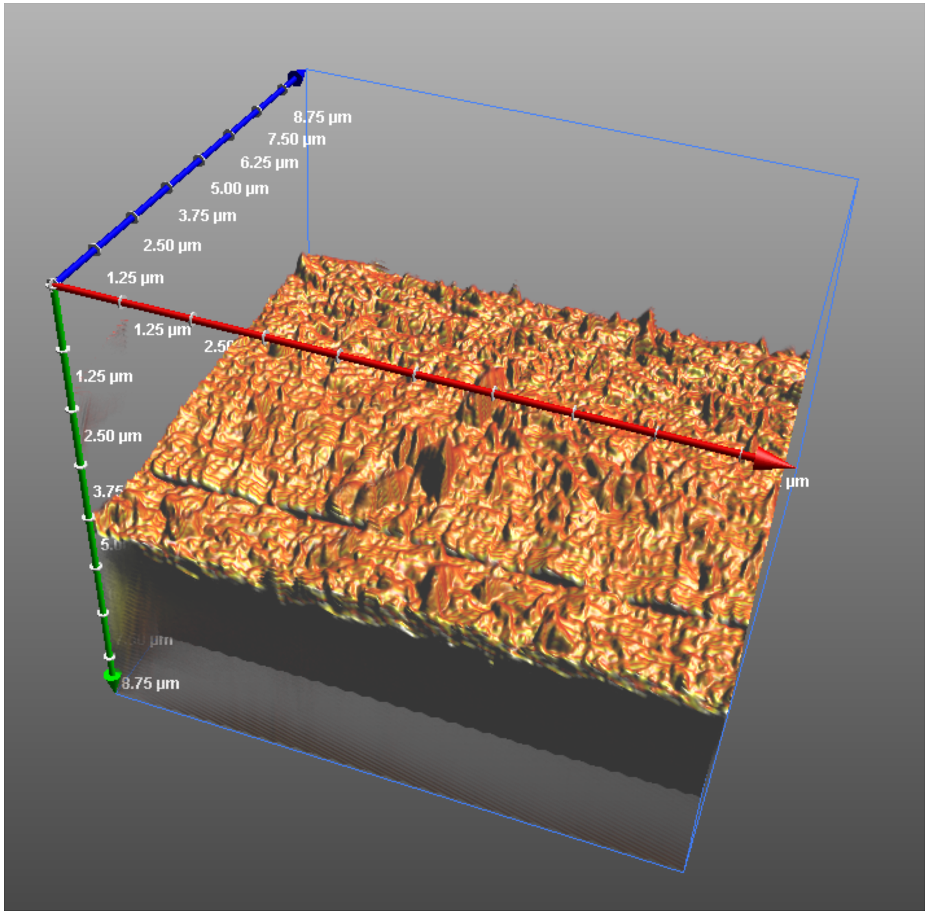
3-dimensional-EBIC



3-dimensional-EBIC



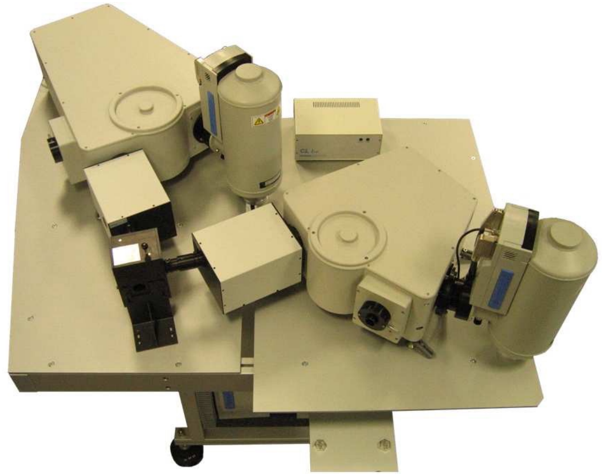
3D-Reconstruction of the SiNW carpet

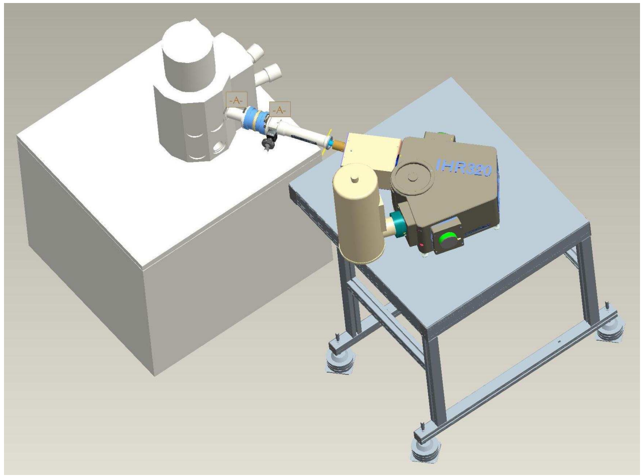


3D-Reconstruction of the EBIC signal

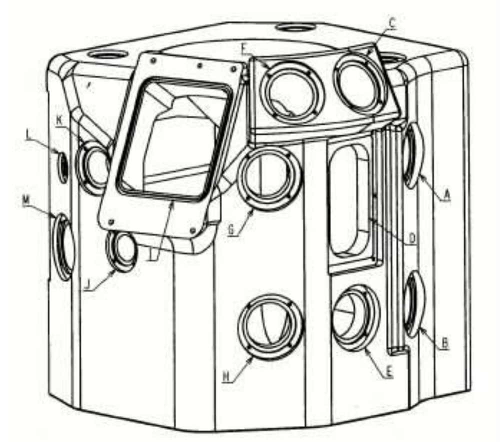
Raman

CL

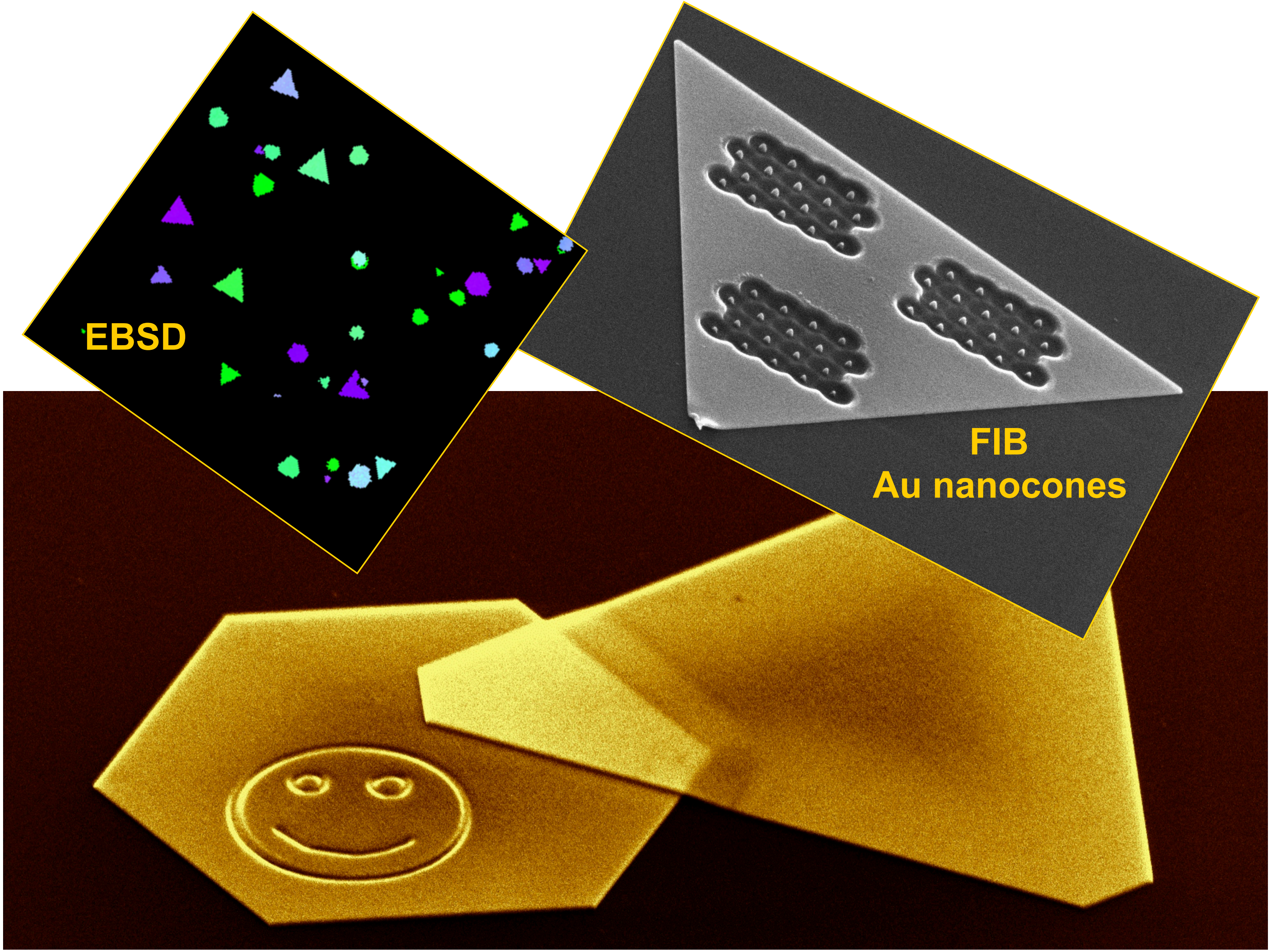




TESCAN-Lyra3

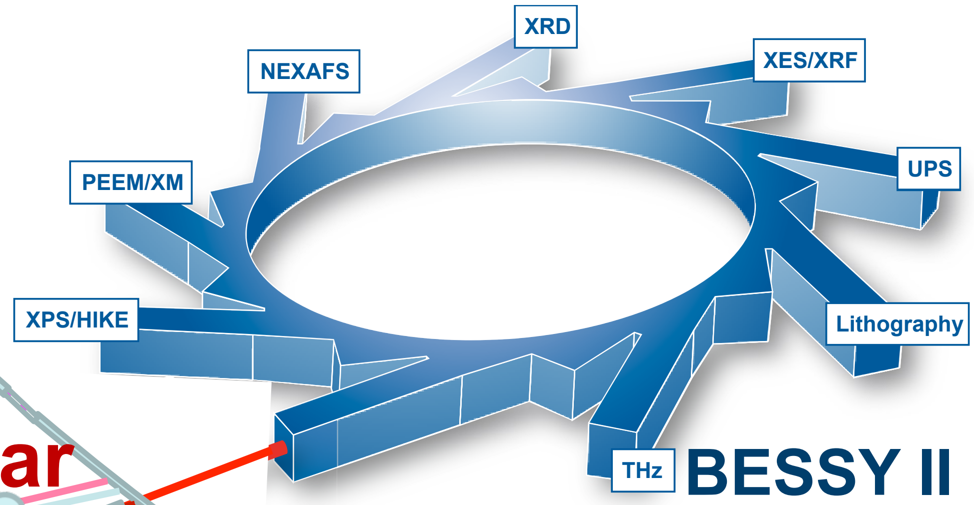


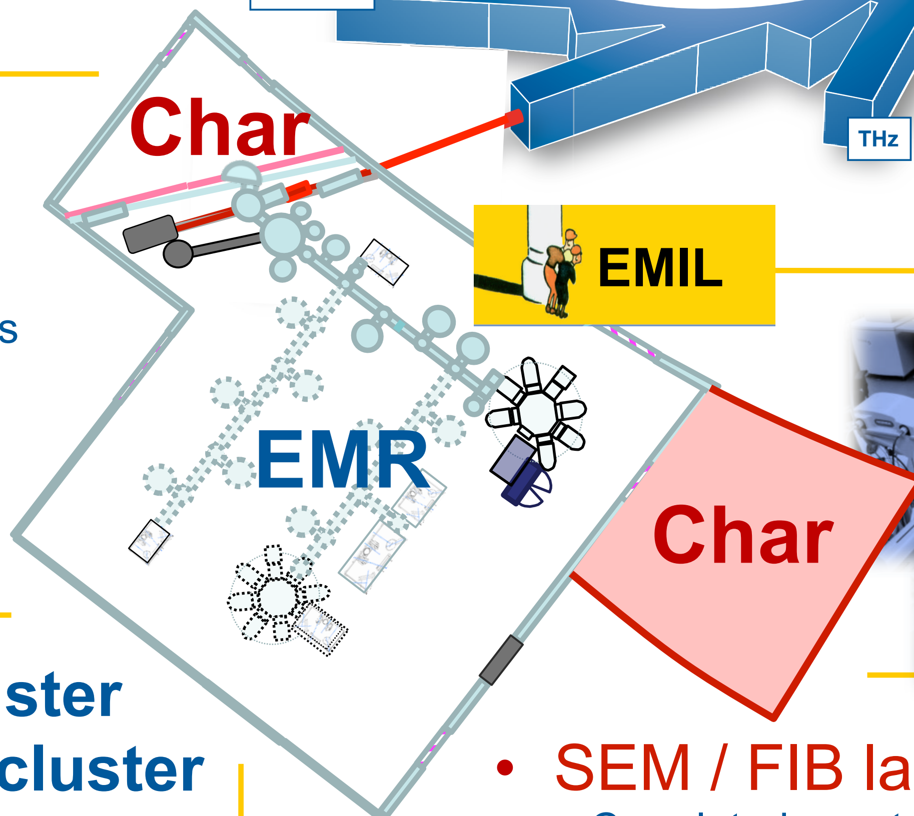
FIB structuring single crystalline Au flakes



P-n junction nanowire solar cells

Materials – characterization – device integration



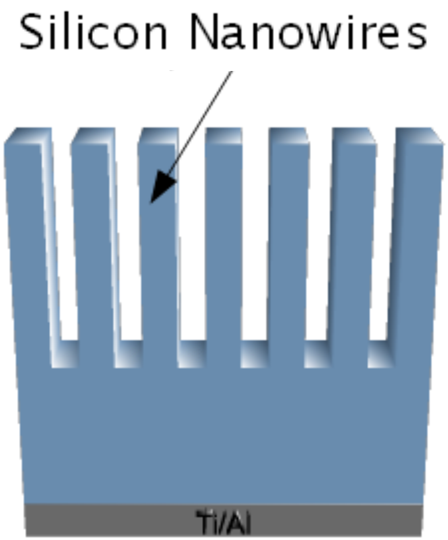


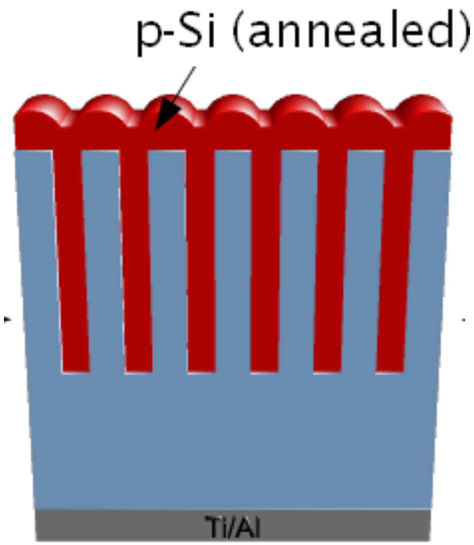
- X-ray analytics:
  - Spectroscopies & microscopies
  - Wide range of energies (80 eV - 10keV)

- **Si deposition cluster**
- **CIGS / Kesterite cluster**
- **Nano-/hybrid cluster**

- SEM / FIB lab:
  Correlated spectroscopies & microscopies

Si NW based radial pn-junction cell



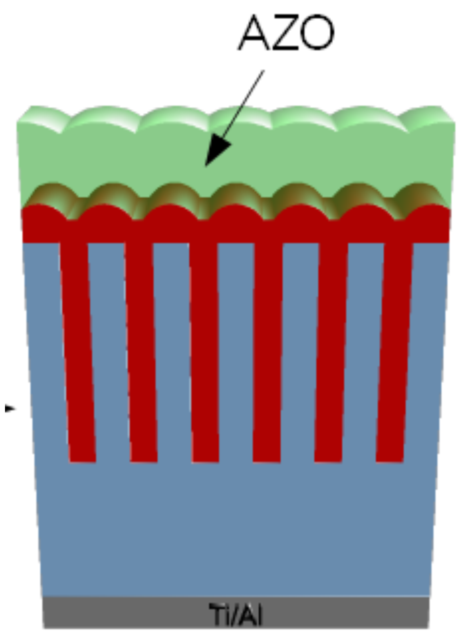


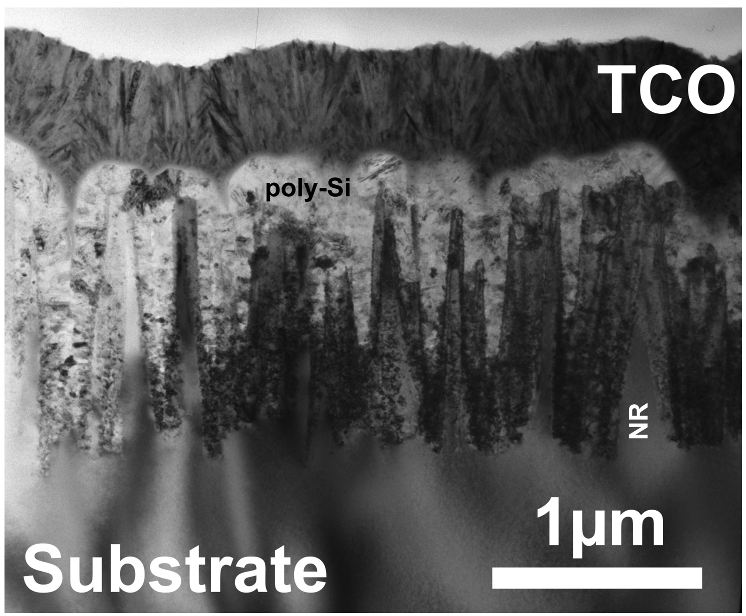
pn- iunction cell:
p,n (n,p) coating

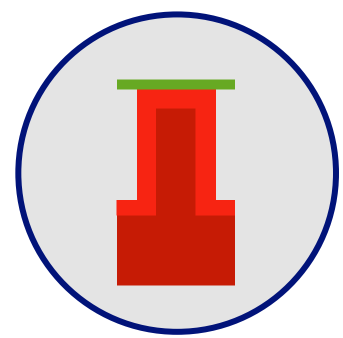
η ~ 6 %,

V_{oc} low:

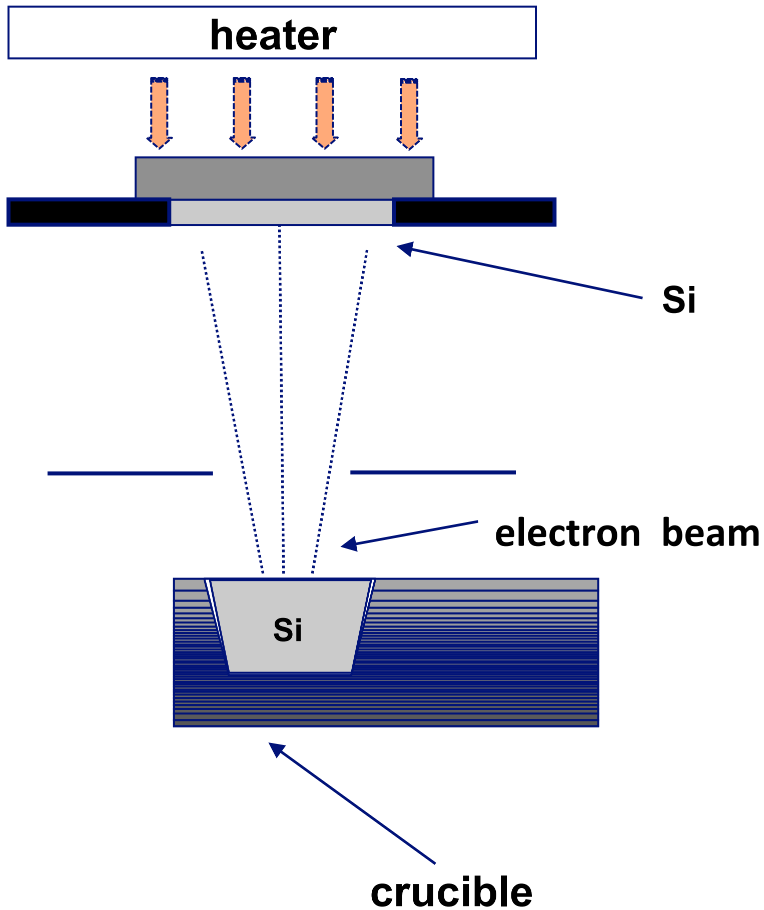
unpassivated surface states







Electron beam evaporation (e-beam)



- Deposition rates >1µm/min
- High Vacuum (not UHV)
  (10^{-7} to 10^{-6}mbar)
- No toxic gases

Question:

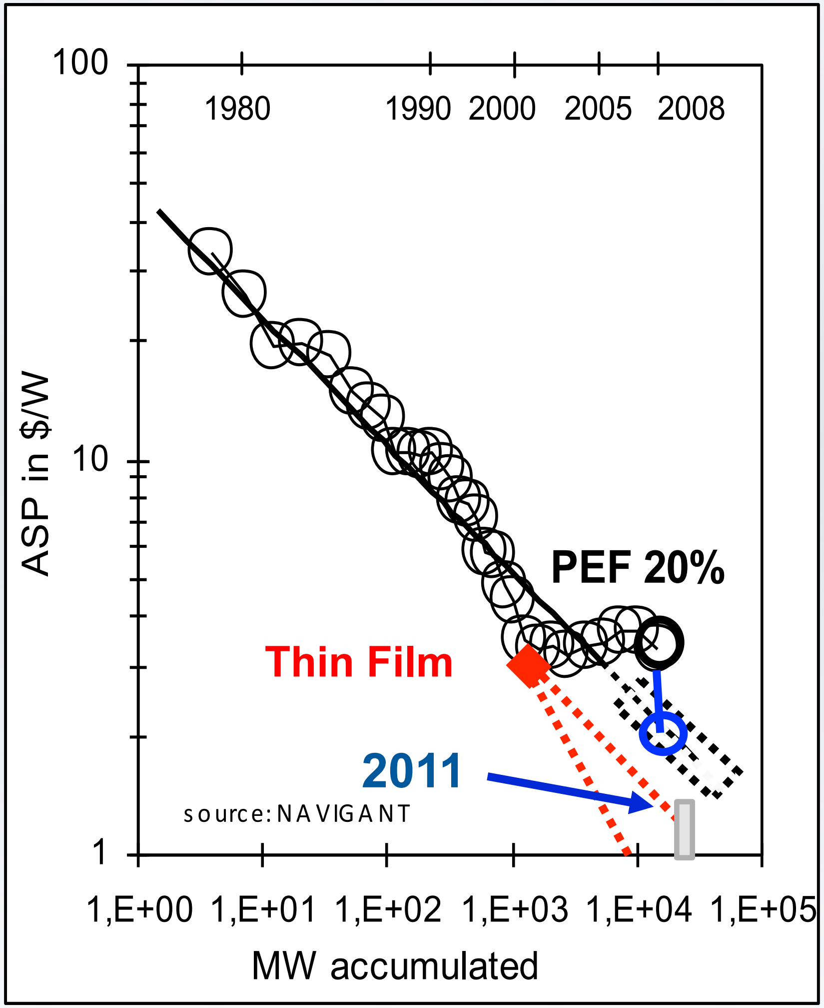
can we deposit PV grade silicon?

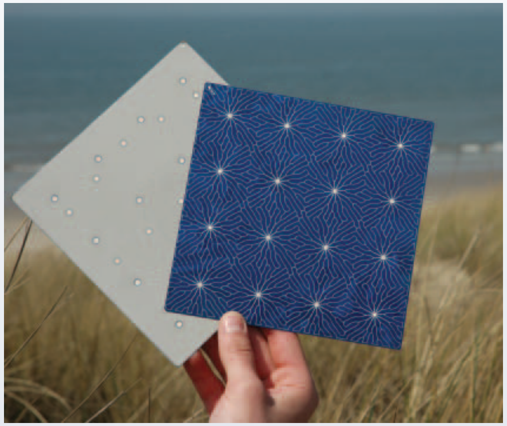
end of 2007: 2-3% reported *

end of 2010 10% in the lab

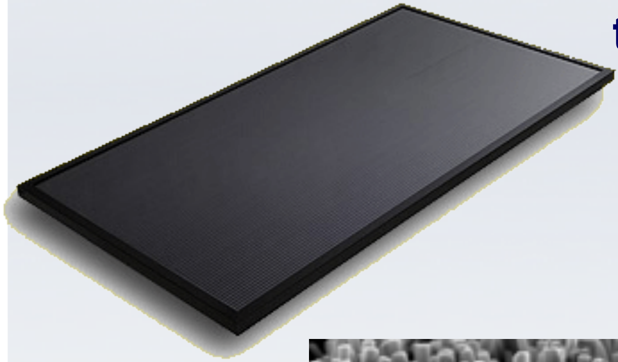
* A.G. Aberle et al. in Proc. of the 22nd European Photovoltaics Solar Energy Conference, Milan, Italy (2007), pp 1884

Learning curce in PV
(PEF: Price experience factor)



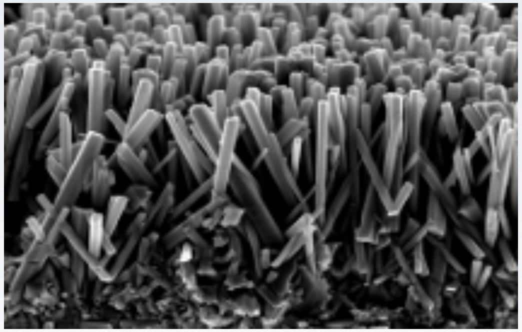


Si-Wafer



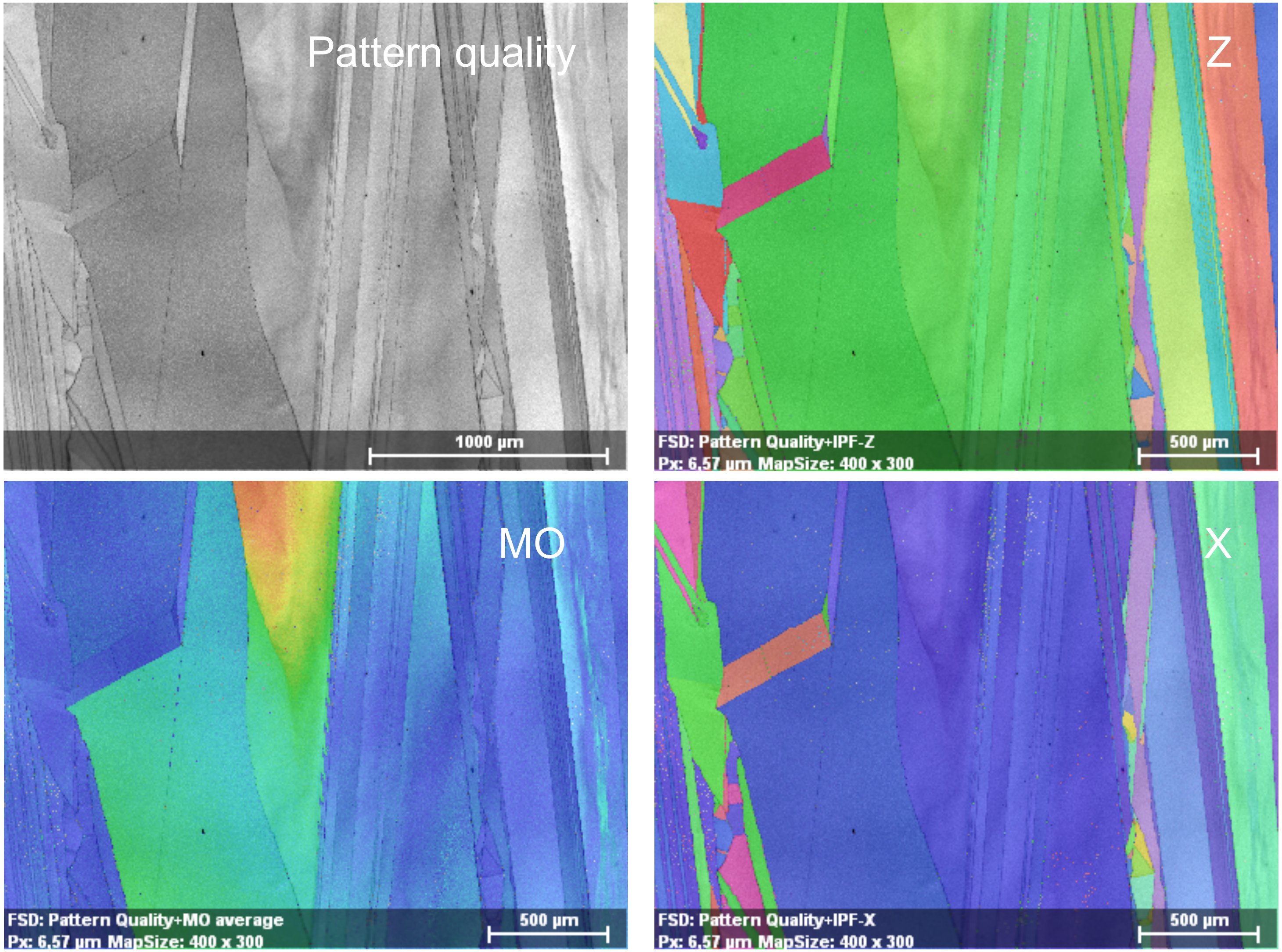
thin films

“Nano”



W. Hofmann et al., 25th EC-PVSEC, 2009

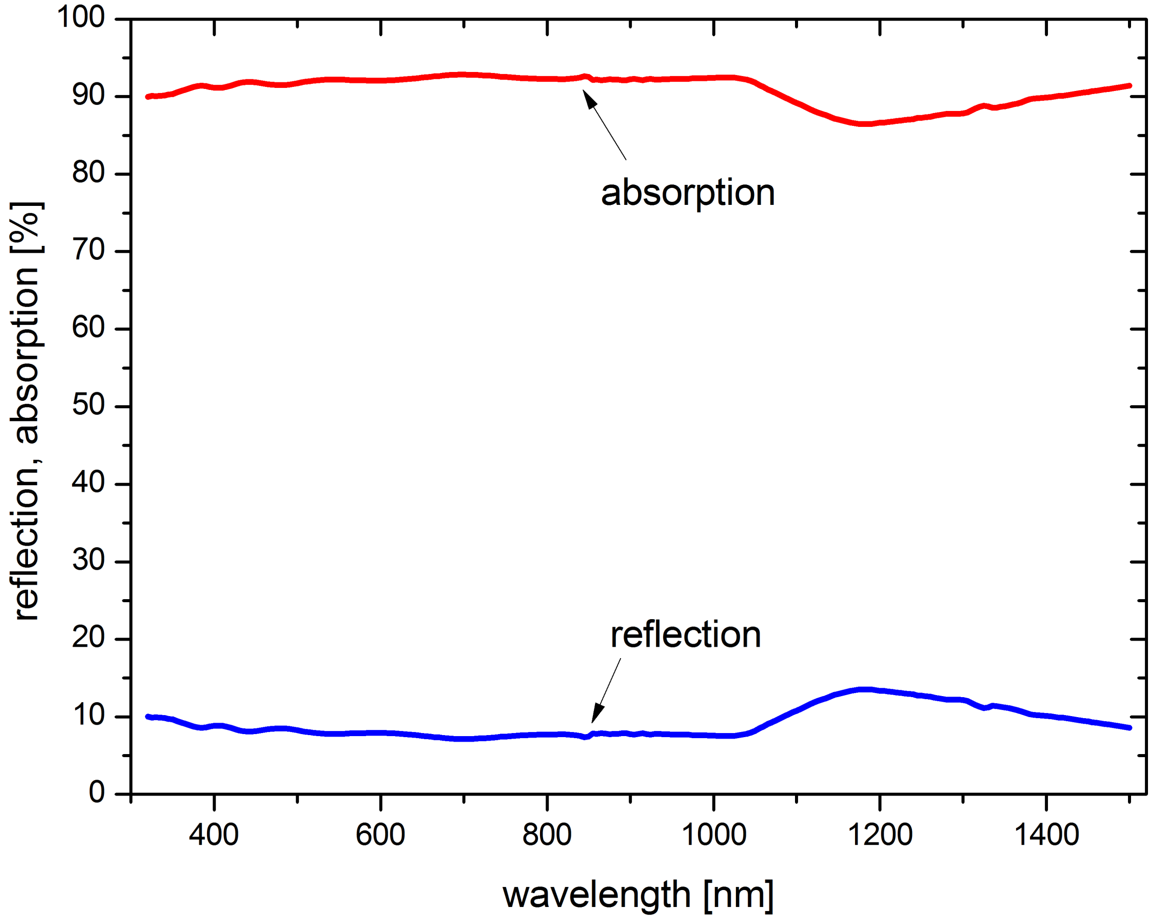
EBSD: multi-crystalline layer on glass

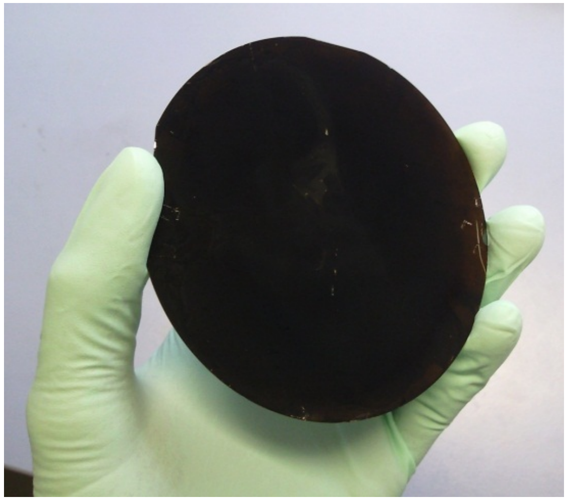


HZB material: Amkreutz/Rech

Integrating sphere measurements

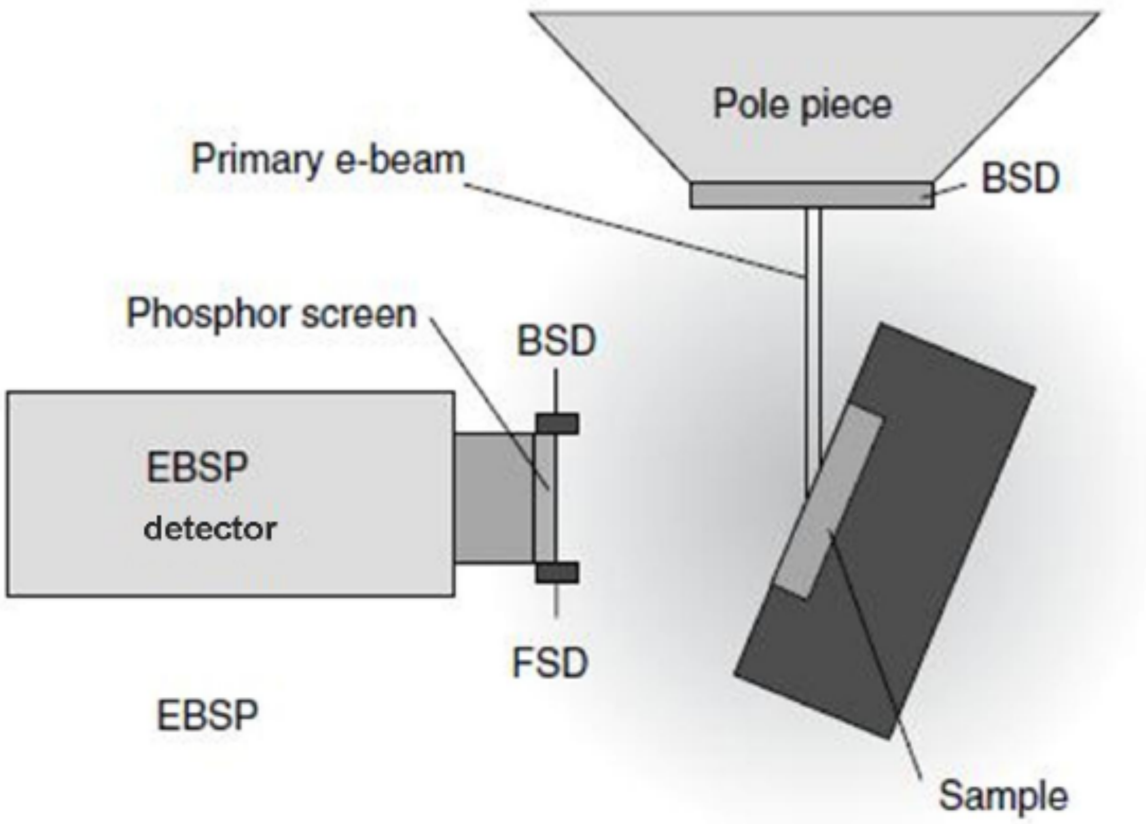
- Reflection measured in an integrating sphere
- Exceptional absorption of over 90% in the visible and near IR range





4 inch SIS solar cell wafer

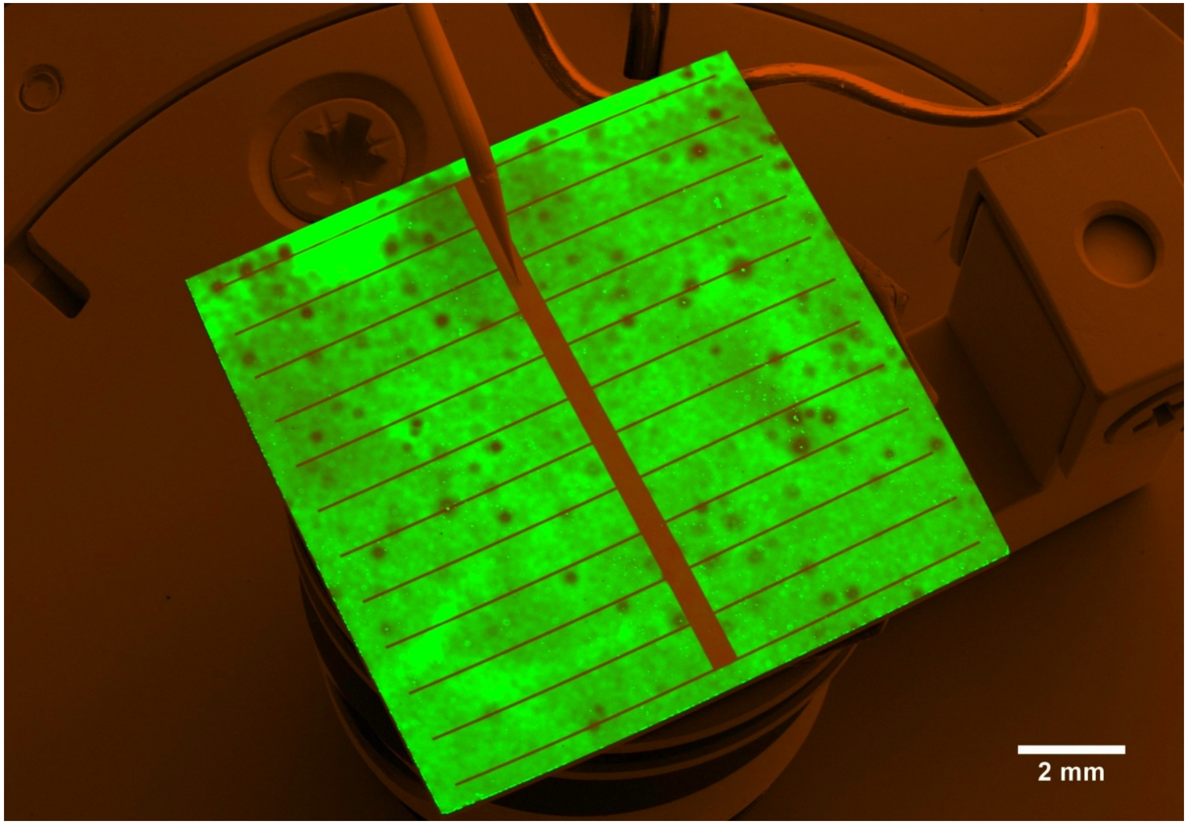
Electron Backscatter diffraction (EBSD)



Zhou, W.; Wang, Z. L. (ed.); Scanning Microscopy for Nanotechnology; Springer Science; 2007; New York; NY; USA.

Electron beam induced current analysis

EBIC measurements on a SIS demonstrator cell with a metallic front contact show good homogeneity in extracted current. Some areas show darker contrast due to local nanostructure variations but severe defects that completely annihilate the current are not visible.

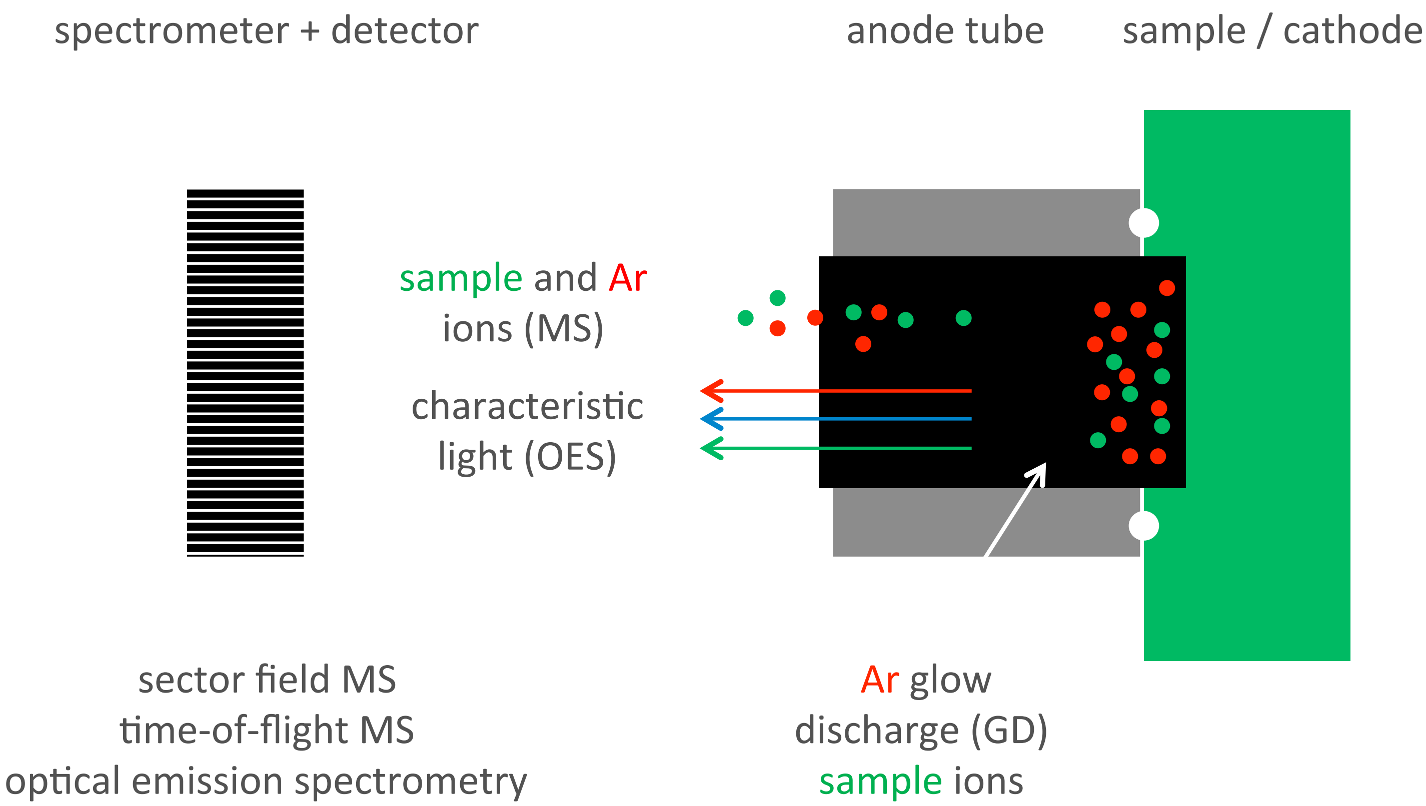


Electron beam crystallization

meets

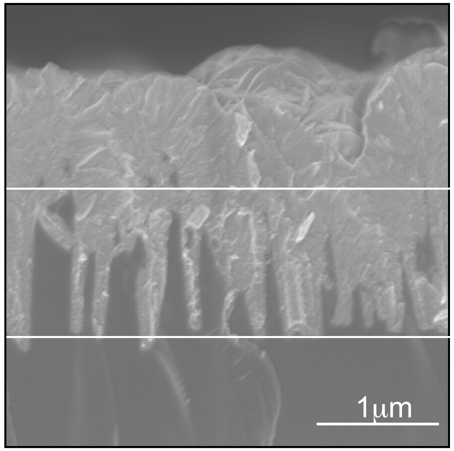
Nanowires

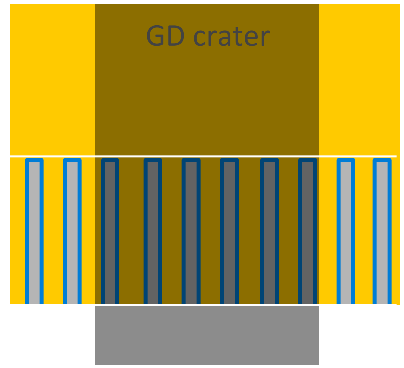
(uninstitutionalized collaboration since 05/2011
unpublished results - confidential)



spectrometer + detector
anode tube
sample / cathode
sample and Ar
ions (MS)
characteristic
light (OES)
sector field MS
time-of-flight MS
optical emission spectrometry
Ar glow
discharge (GD)
sample ions

estimation of nanowire surface area by GD-OES

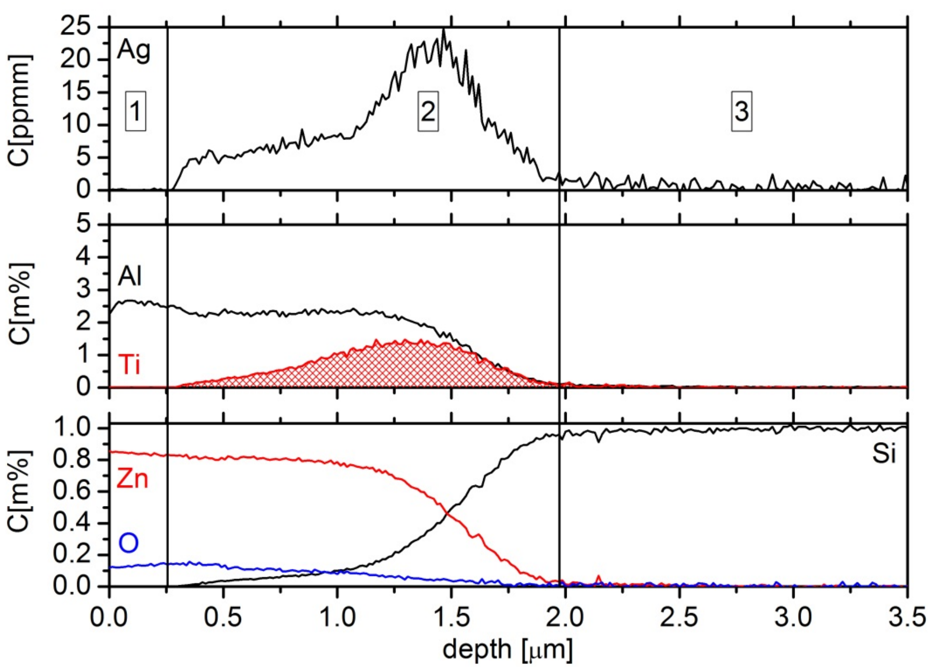




Al:ZnO (atomic layer depoition / ALD)

TiO_2 (atomic layer deposition / ALD)

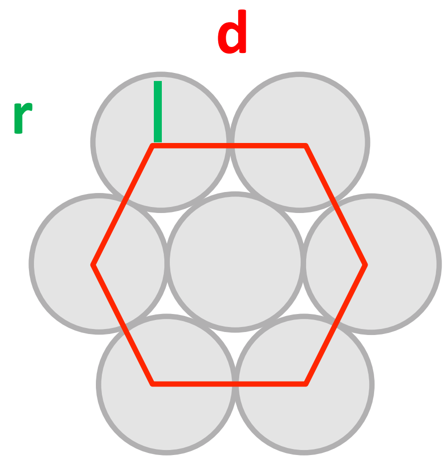
Si nanowires (n / 100)



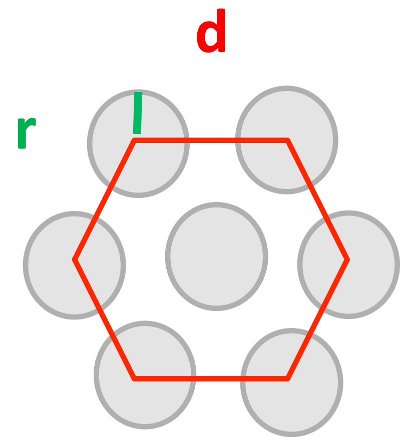
an effective surface multiplication factor f =6.2 caused by the nano structuring could be calculated according to:

$$f = \frac{V_{TiO_2}}{V_{crater}} = \frac{V_{TiO_2}}{A_{crater} \cdot d_{TiO_2}}$$

important quantity related to V_{oc} of the device



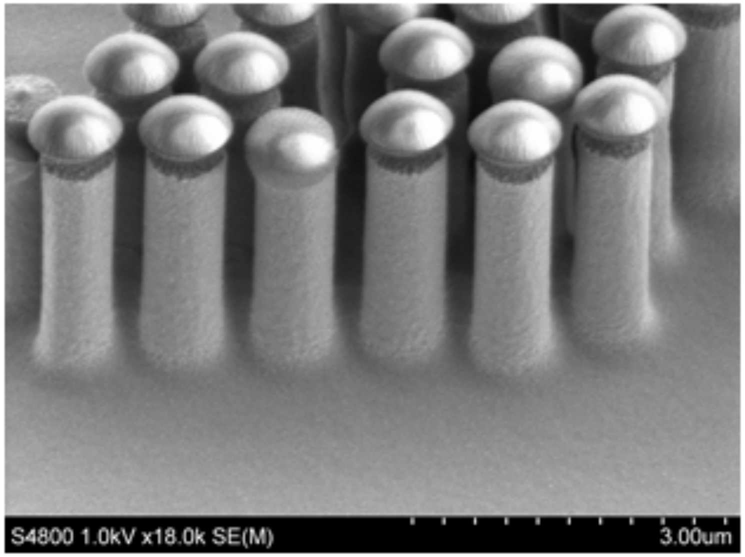
before size reduction

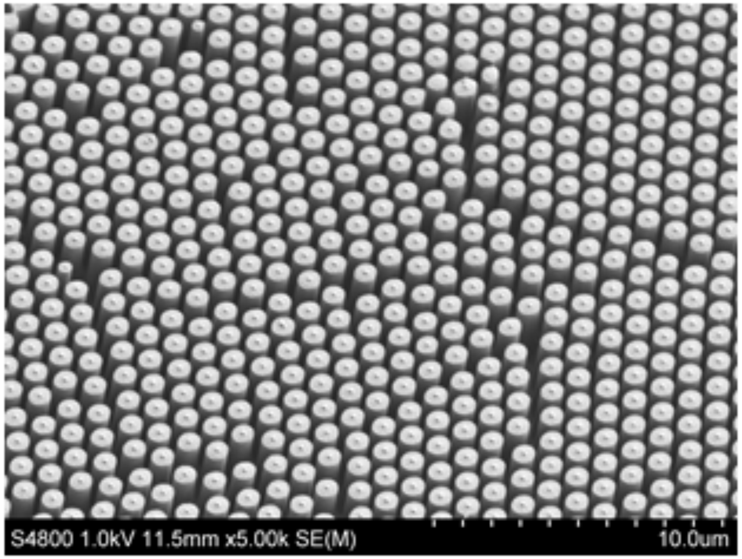


after size reduction

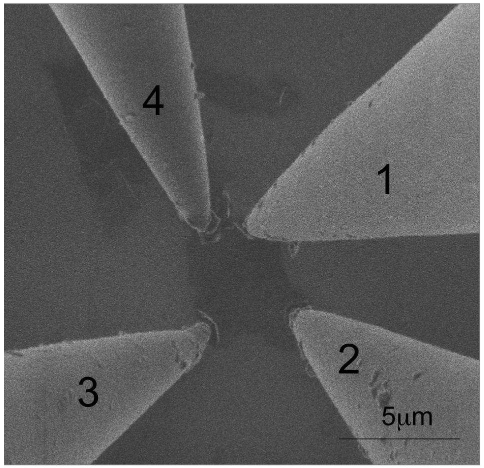
patterns are dependent on :

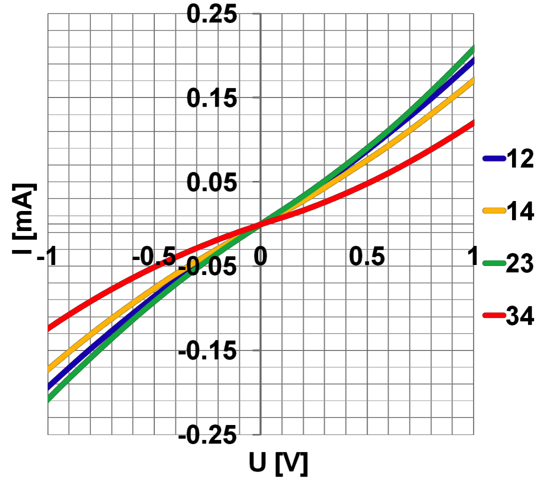
- initial sphere diameter (structure spacing)
- sphere diameter after plasma reduction (structure diameter)





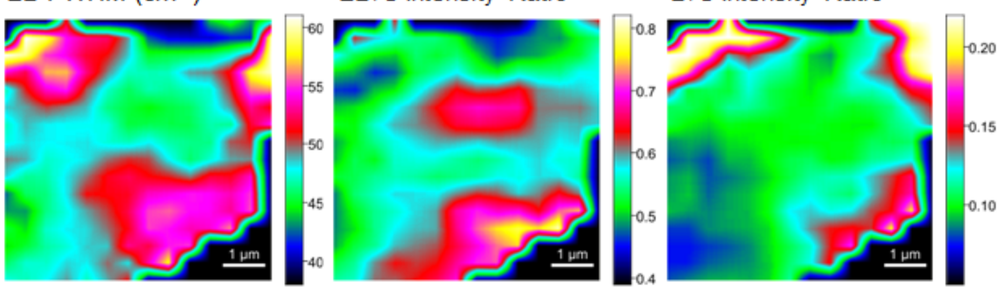
large scale nanostructured surfaces in silicon are accessible via nanosphere lithography and sucessive reactive ion eching





4 point nanoprober

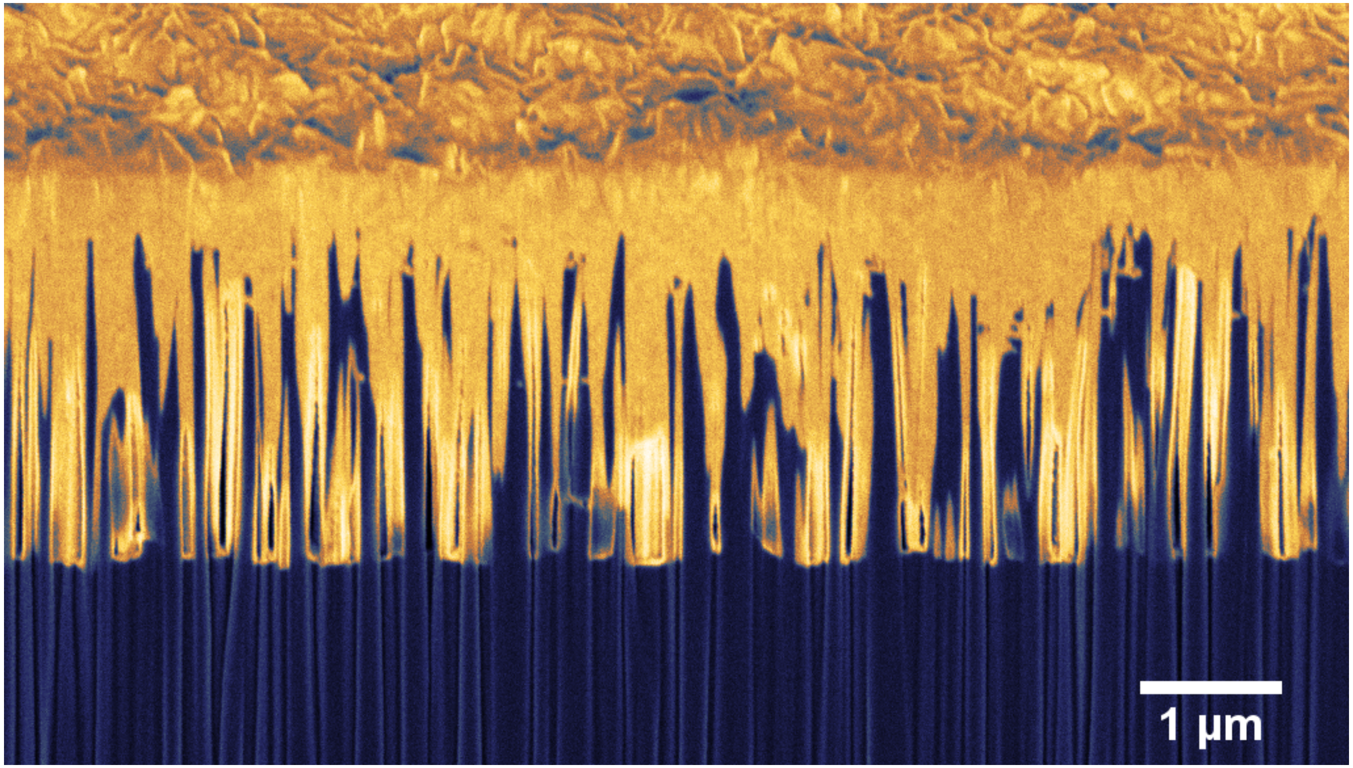
2D FWHM (cm^{-1}) | 2D/G Intensity Ratio | D/G Intensity Ratio



Number of layers | Numbers of layers Doping | Defects Disorder

Raman spectroscopy

Nanowire-based SIS solar cell



In rare cases the gaps between the wires are not filled completely, but usually the ALD process works fine.


Thank you for
your attention!

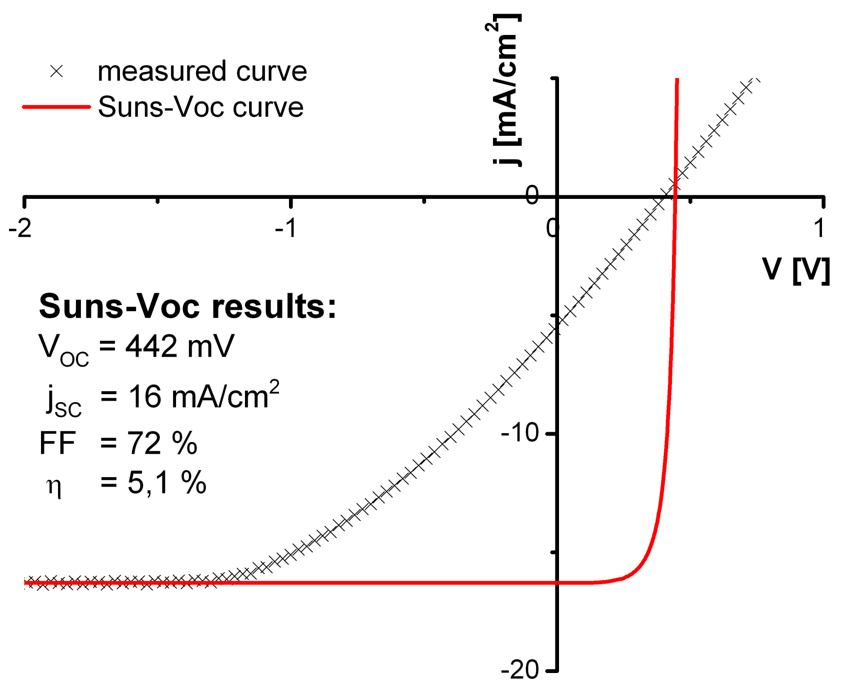
Nanowire-based SIS solar cell

Laser beam induced current analysis explanation

At 405nm, 544nm and 633nm the absorption of light occurs in the nanowires and thus the influence of their nanostructure is visible in the LBIC as well as in the EBIC. At 1064nm the absorption occurs inside the bulk wafer and the LBIC signal is homogeneous.

The bright area in the top left corner is already visible with the naked eye as an area of higher absorption. Therefore more charge carriers are generated and the current is also higher.

- Electrical characterization

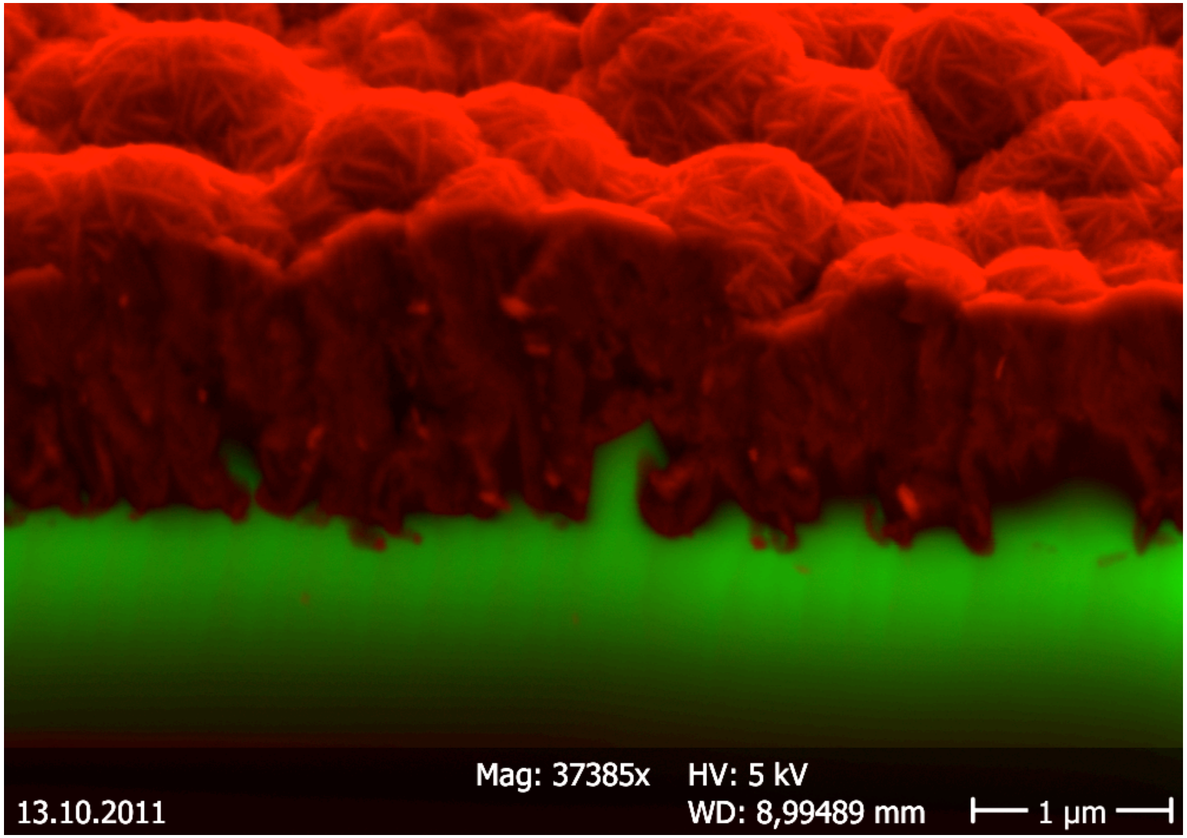


- Characterization with I-V- and Suns-Voc-measurements
- Annealing times between one and three hours are optimal
- j_{sc} is relatively low (with respect to the high absorption)
- Efficiencies of 5% could be realized

Conclusions & Outlook

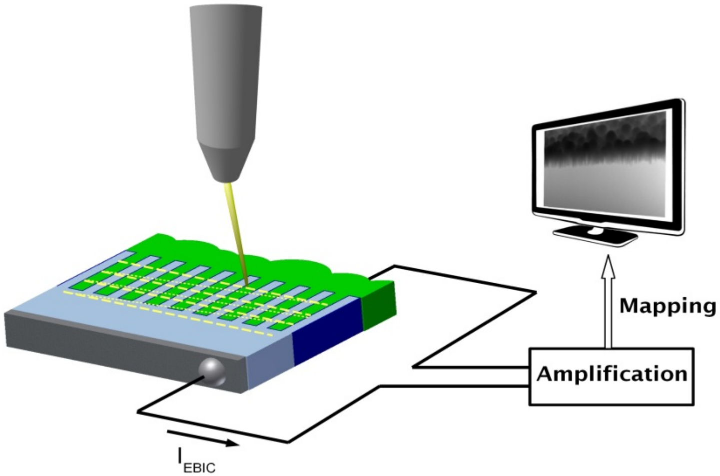
- SIS nanowire solar cells are easy to produce and offer high efficiencies
- All used materials are cheap, abundant and not toxic
- NWs are active photovoltaic components
- Transfer of concept to thin film substrates (mc-Si on glass/ flexible polymer foils) is no problem and is our next goal
- Combination of optimal patterned wires, advanced ALD process and improved contacts should easily reach 12-15%.

Nanowire-based SIS solar cell

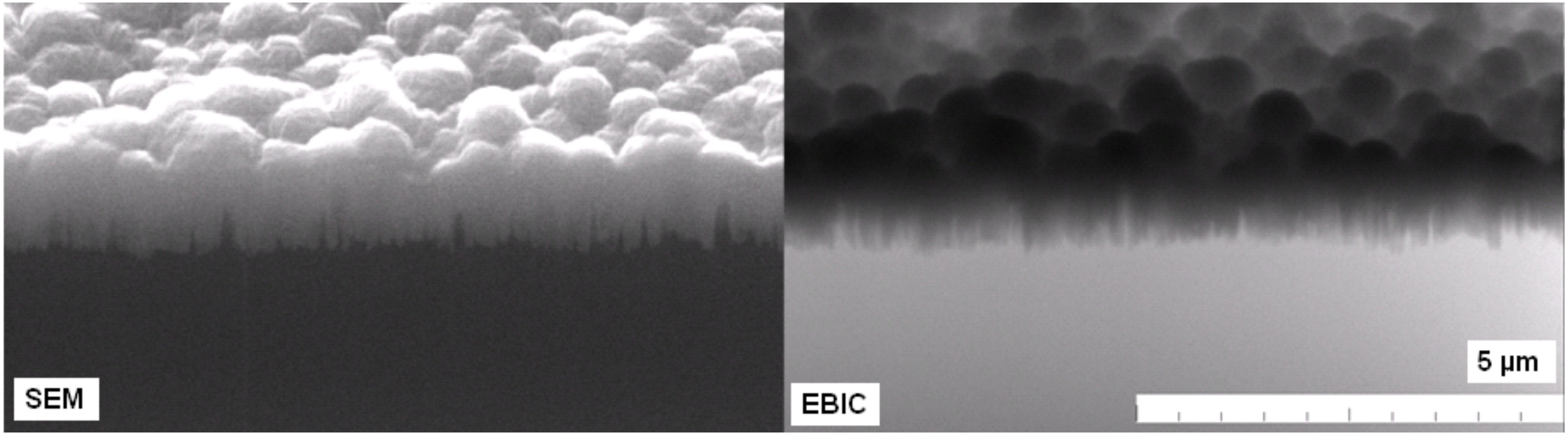


Combination of SE-signal (red) and EBIC-signal (green) clearly shows that charge carriers, once generated in a nanowire, can be separated.
→ Nanowires are active photovoltaic components and are not only acting as antireflective structures.

Electron beam induced current analysis



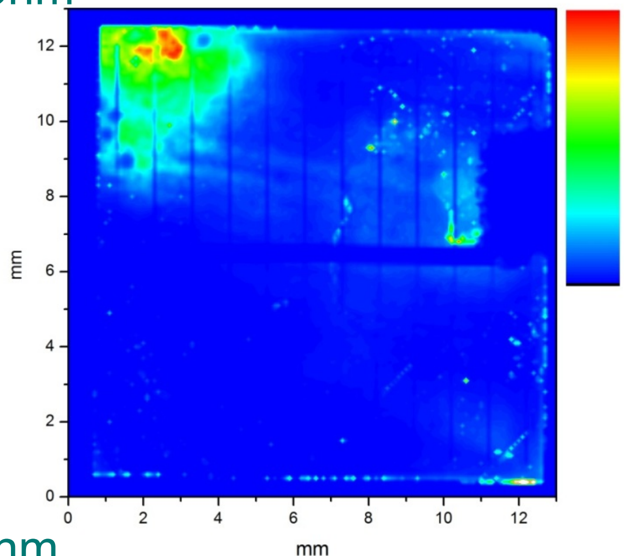
The structure of the nanowires is dissolved in the EBIC-image, which means, that free charge carriers, which are generated in the nanowires can effectively be separated.



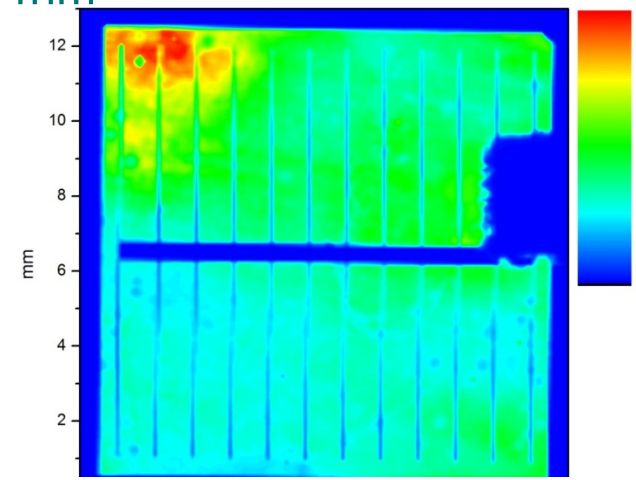
Nanowire-based SIS solar cell

Laser beam induced current analysis

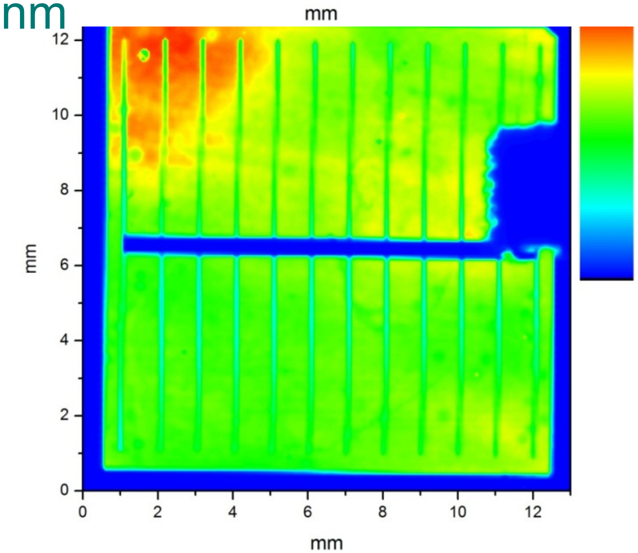
405nm



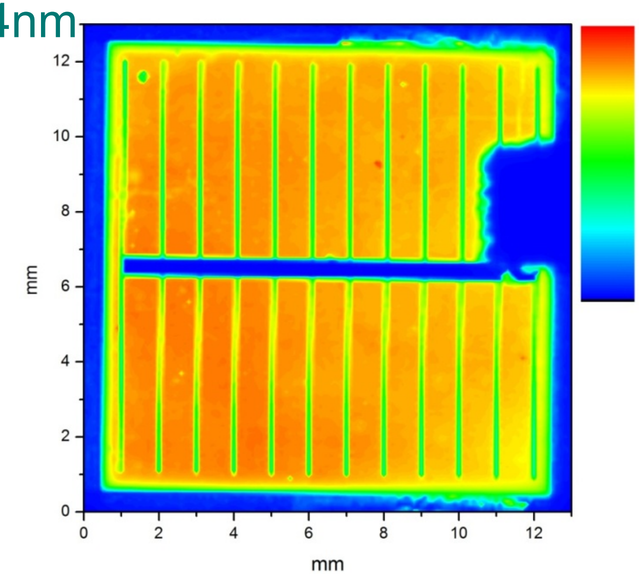
544nm



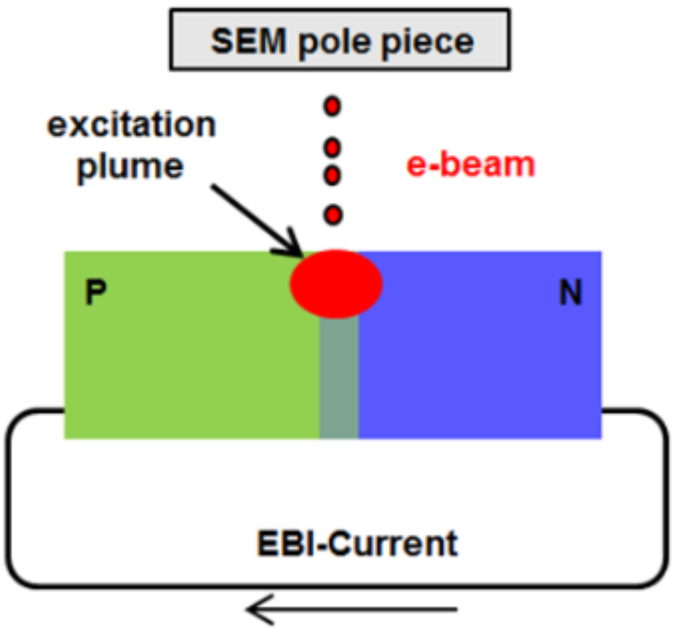
633nm

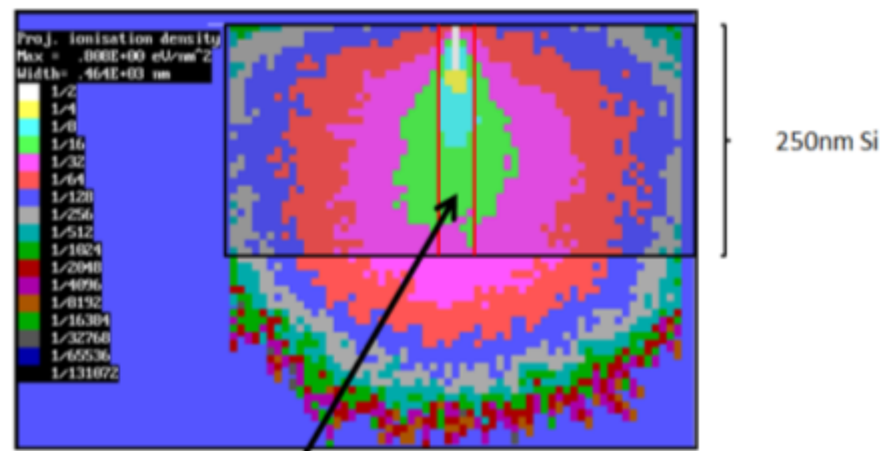


1064nm



- how to characterise the junction? → electron beam induced current (EBIC)





About 90% of the beam energy is deposited within 40nm ´channel´ lateral EBIC resolution in a pillar not significantly worse than the resolution of the SE image of a pillar (not considering edge effects)

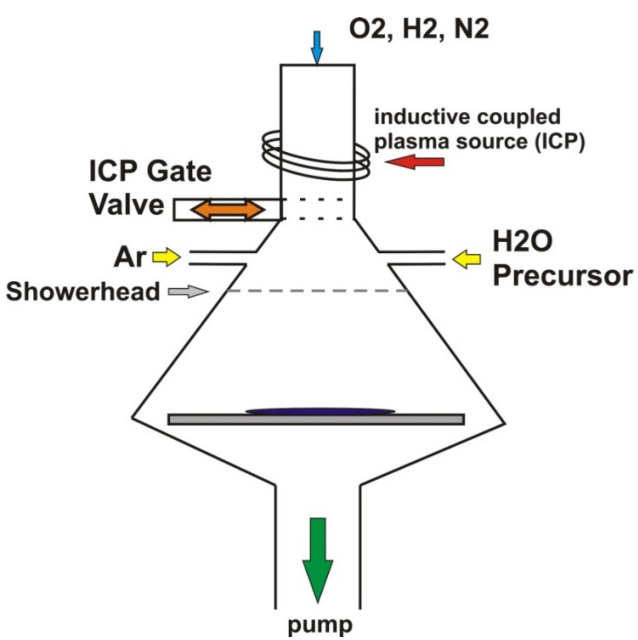
generation of excitons in the material → lock-in mapping of current distribution to localize the p-n junction

Nanowire-based SIS solar cell

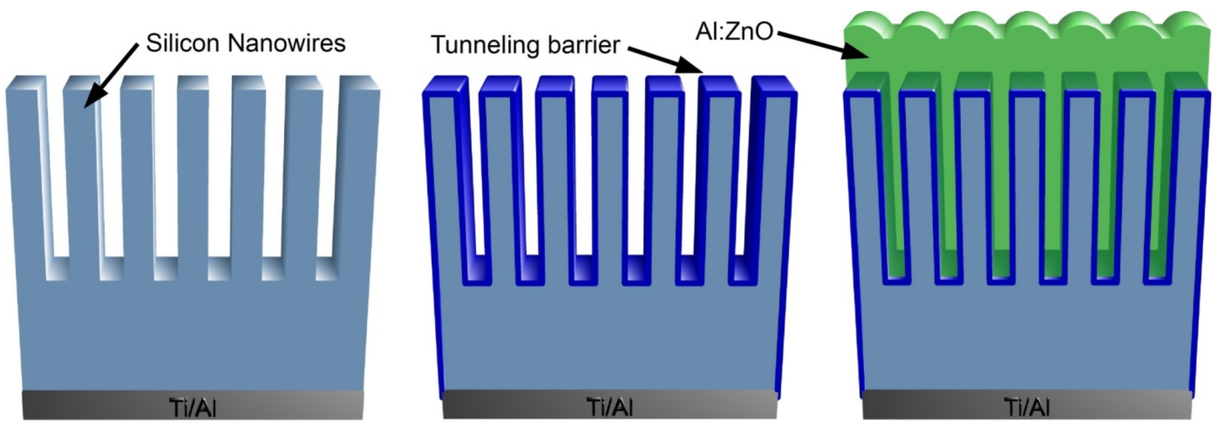
Preparation of cells:

- n-type Si-Wafer with Ti/Al back contact
- Wet chemically etching of nanowires
- HF-dip to remove native oxide
- Plasma assisted atomic layer deposition of 10-15 Å tunnel barrier material (Al_2O_3)
- Atomic layer deposition of 300-500 nm Al doped ZnO

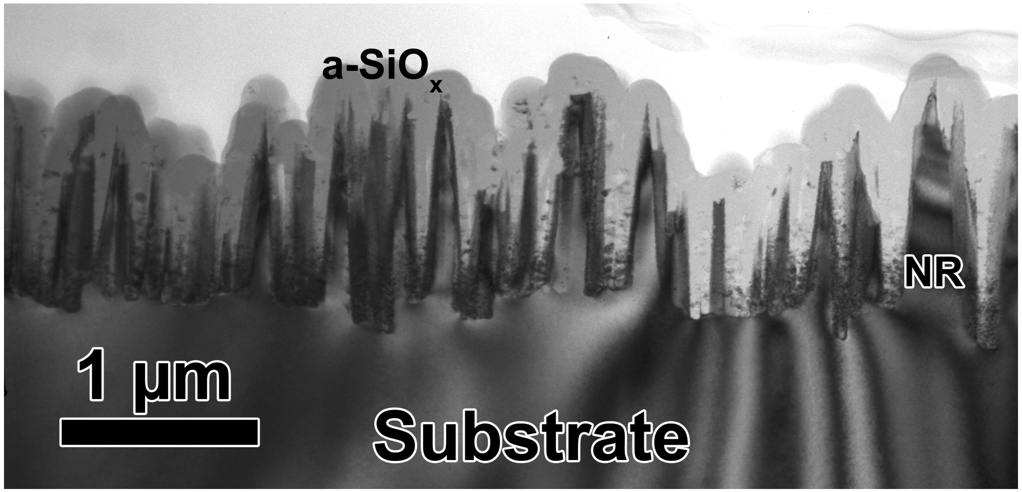
Oxford OpAL ALD reactor



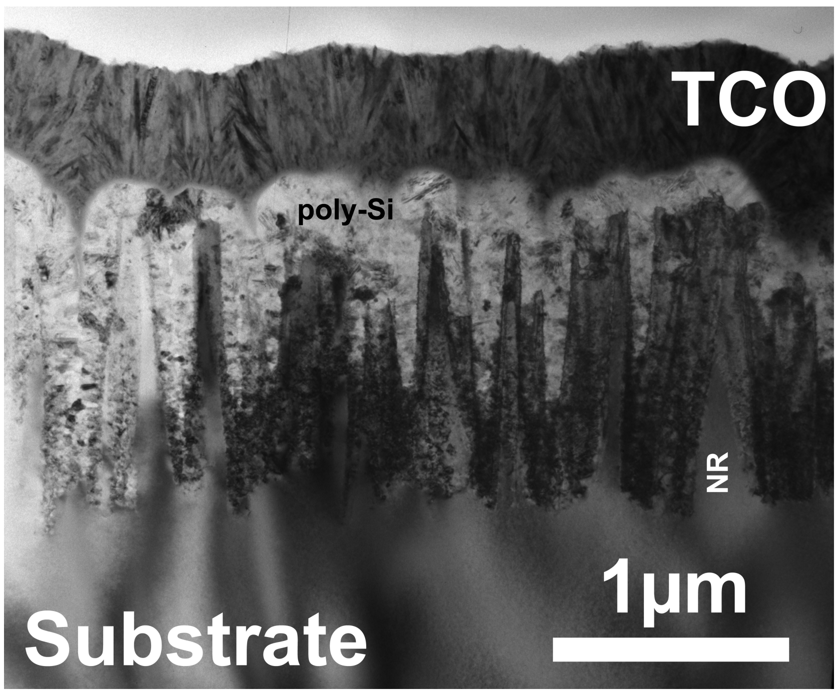
Schematic solar cell fabrication



TEM results

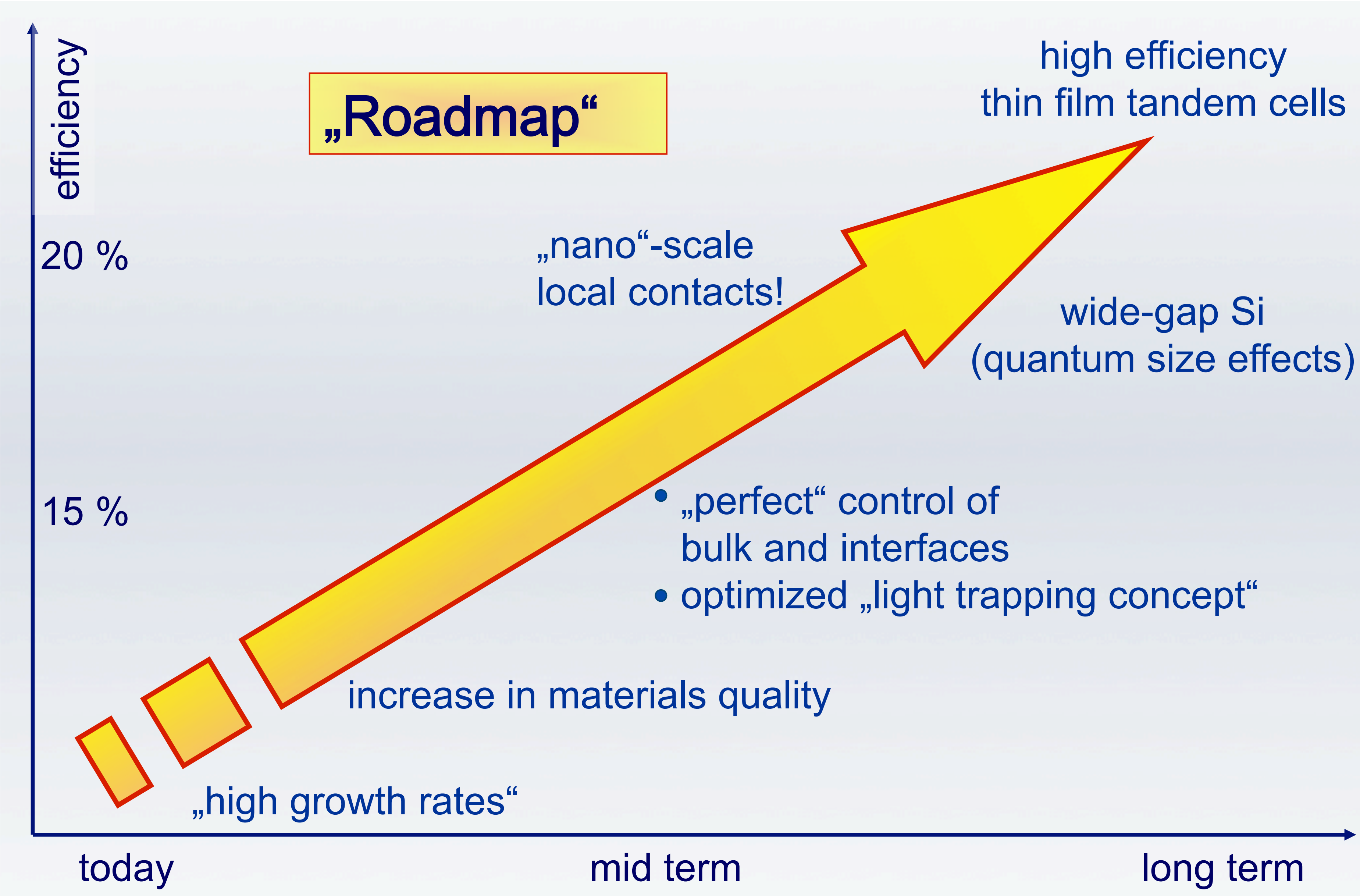


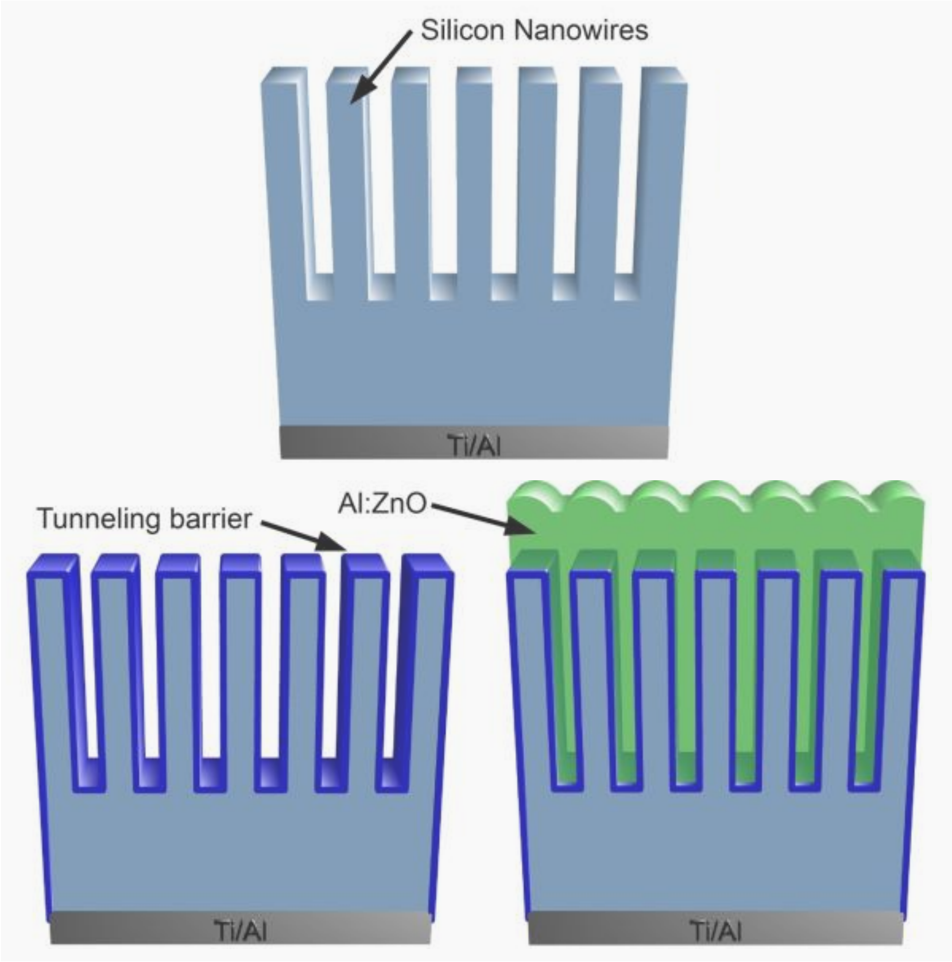
- SiNWs are cone-shaped
- a-Si homogeneously covers the SiNWs



- Annealing leads to partial crystallization of the a-Si
- Annealing times of more than three hours do not cause further structural changes

„Setting the stage‘

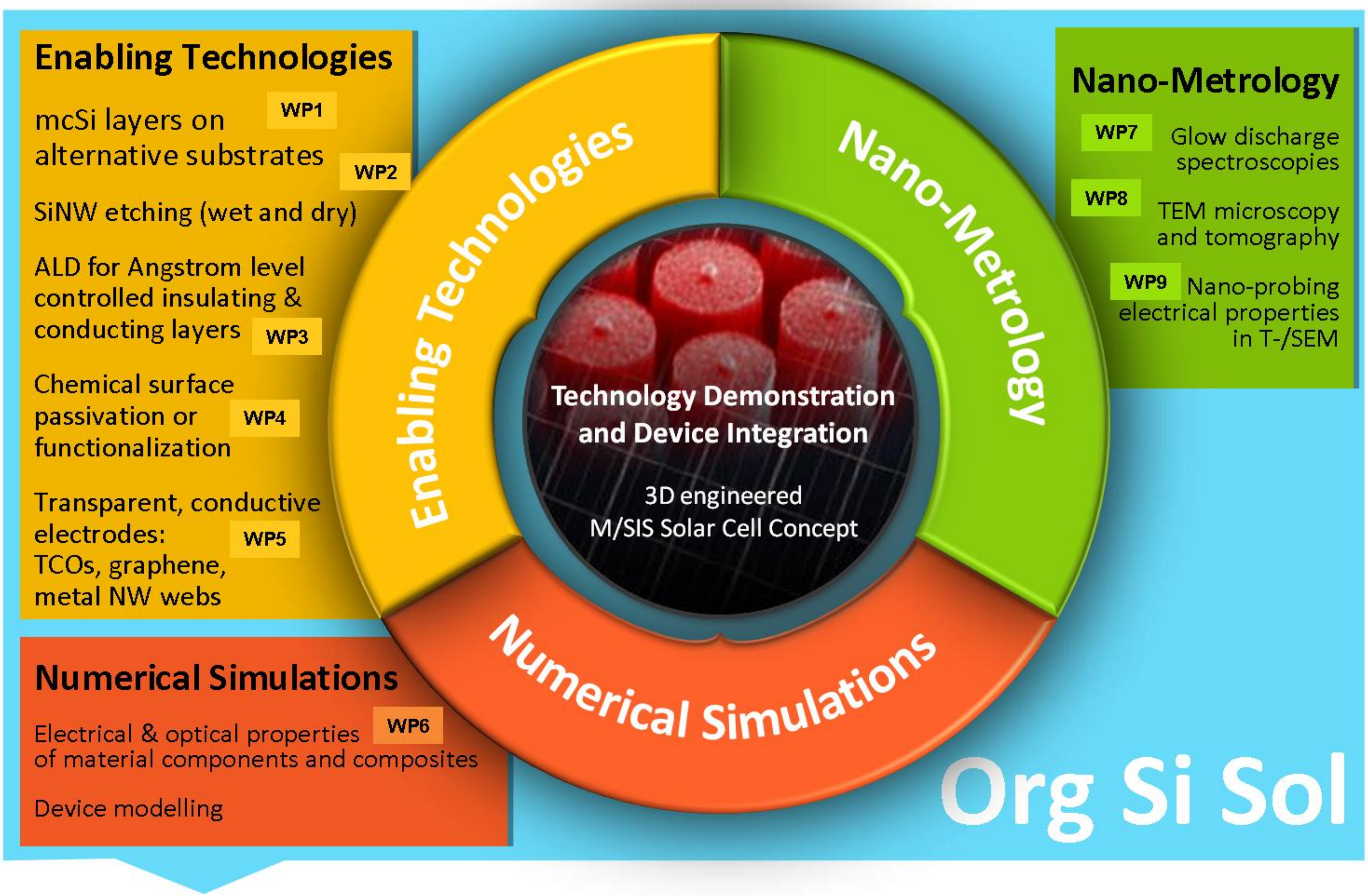




SIS solar cell principles:

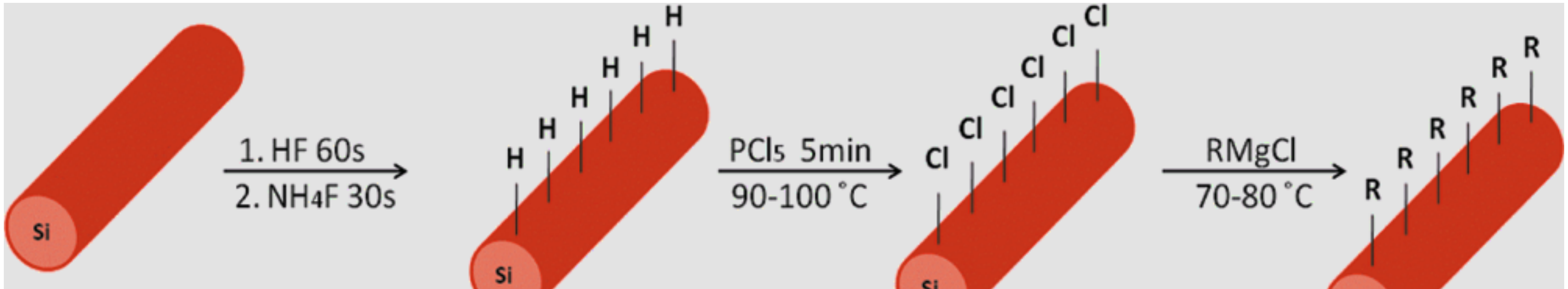
- Al doped ZnO (n-type) & n-type Si wafer → no pn-junction
- Insert tunnel barrier between both semiconductors → fermi level pinning
- charge carrier separation is based on quantum-mechanical tunneling of minority carriers through the barrier

3D SiNW based thin film solar
ell



Exploitable results:

- Novel cell concept based on novel nano-composite materials if efficiences permit.
- Atomic layer deposition of TCO's: processes and layout of high-throughput tooling.
- Glow discharge spectroscopies: tooling and procedures to assess nano-composite materials.



Grignard reaction

Carrier lifetime (at Δn = 10^{14} cm^{-3}) (μs)	Si wafer	Si wafer with SiNWs 30 nm AuNP	Si wafer with doped SiNWs 30 nm AuNP	Si wafer with SiNWs chem. etched
Native oxide	1.0	1.0	1.3	1.3
HF dip	14.5	1.5	2.1	17
50 nm intrinsic a-Si:H a) as deposited	95	1.5	1.4	25
			1.3	36 (4 min)
b) 30 min anneal	1041	1.5		

M. Bashouti, Th. Stelzner, A. Berger, S. Christiansen, H. Haick, J. Phys. Chem. C 112, 19168 (2008)

O. Assad, S. Puniredd, Th. Stelzner, S. Christiansen, H. Haik, JACS 130(52), 17670 (2009)

M. Bashouti, S. Puniredd, Y. Paska, Th. Stelzner, A. Berger, S. Christiansen, H. Haik, J. Am. Chem. Soc. 130, 17670 (2008)

M. Y. Bashouti, O. Assad, Y. Paska, S. Reddy Puniredd, Th. Stelzner, A. Berger, S. Christiansen, H. Haik, PCCP 11, 3845 (2009)

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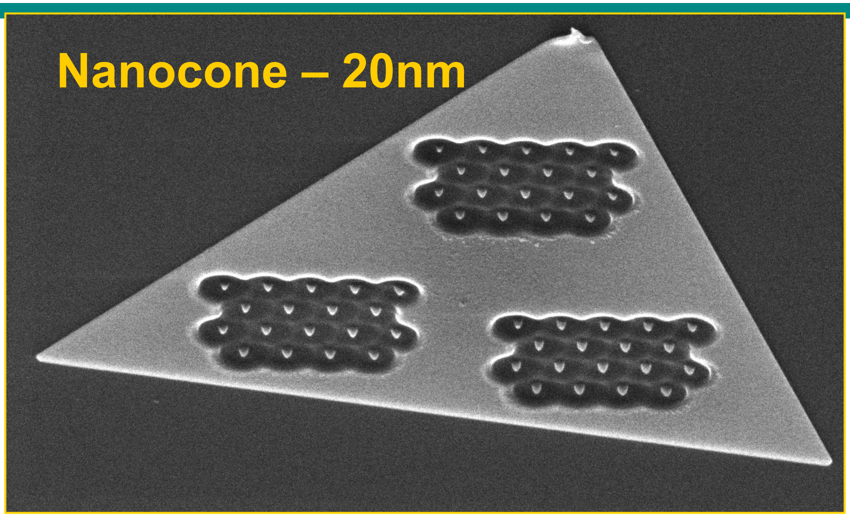
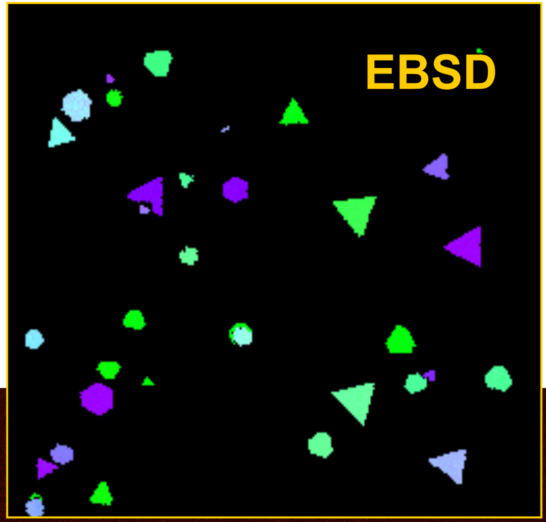
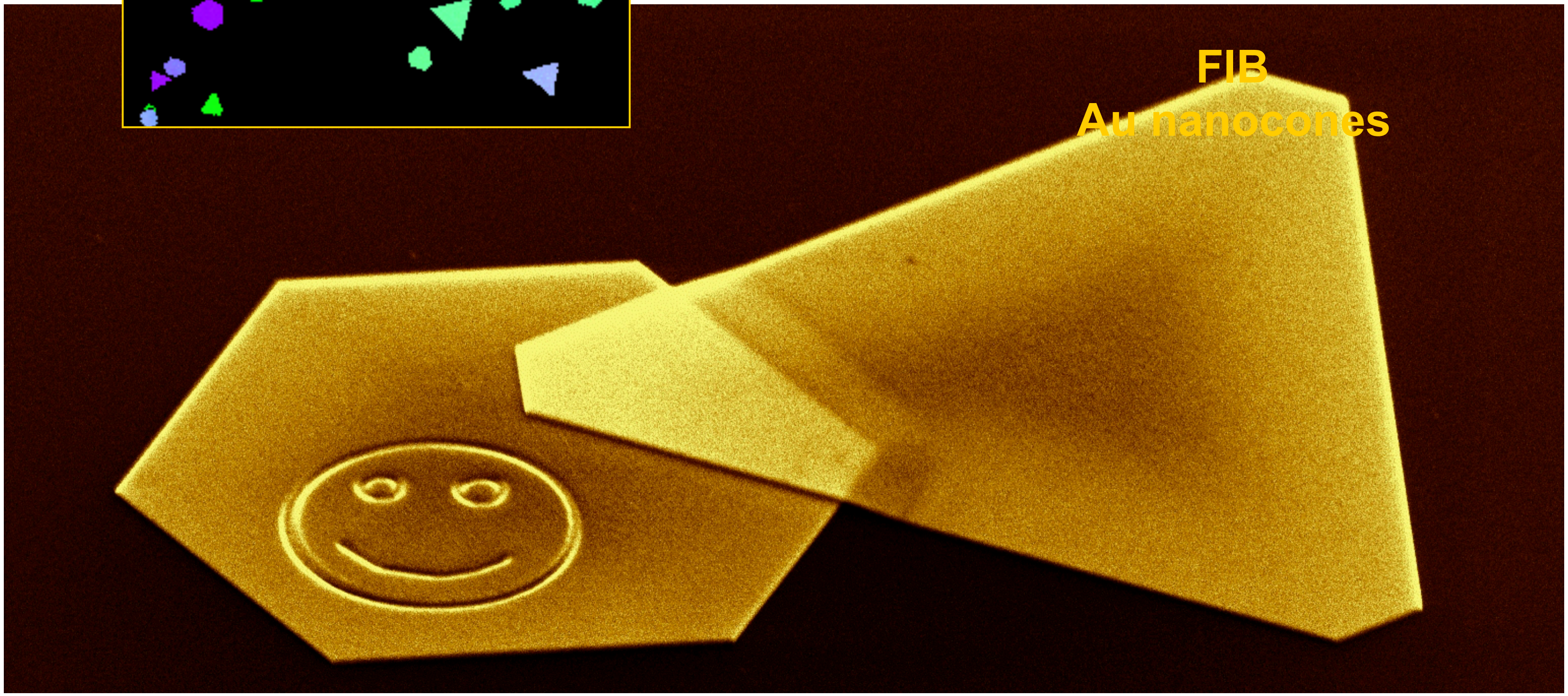
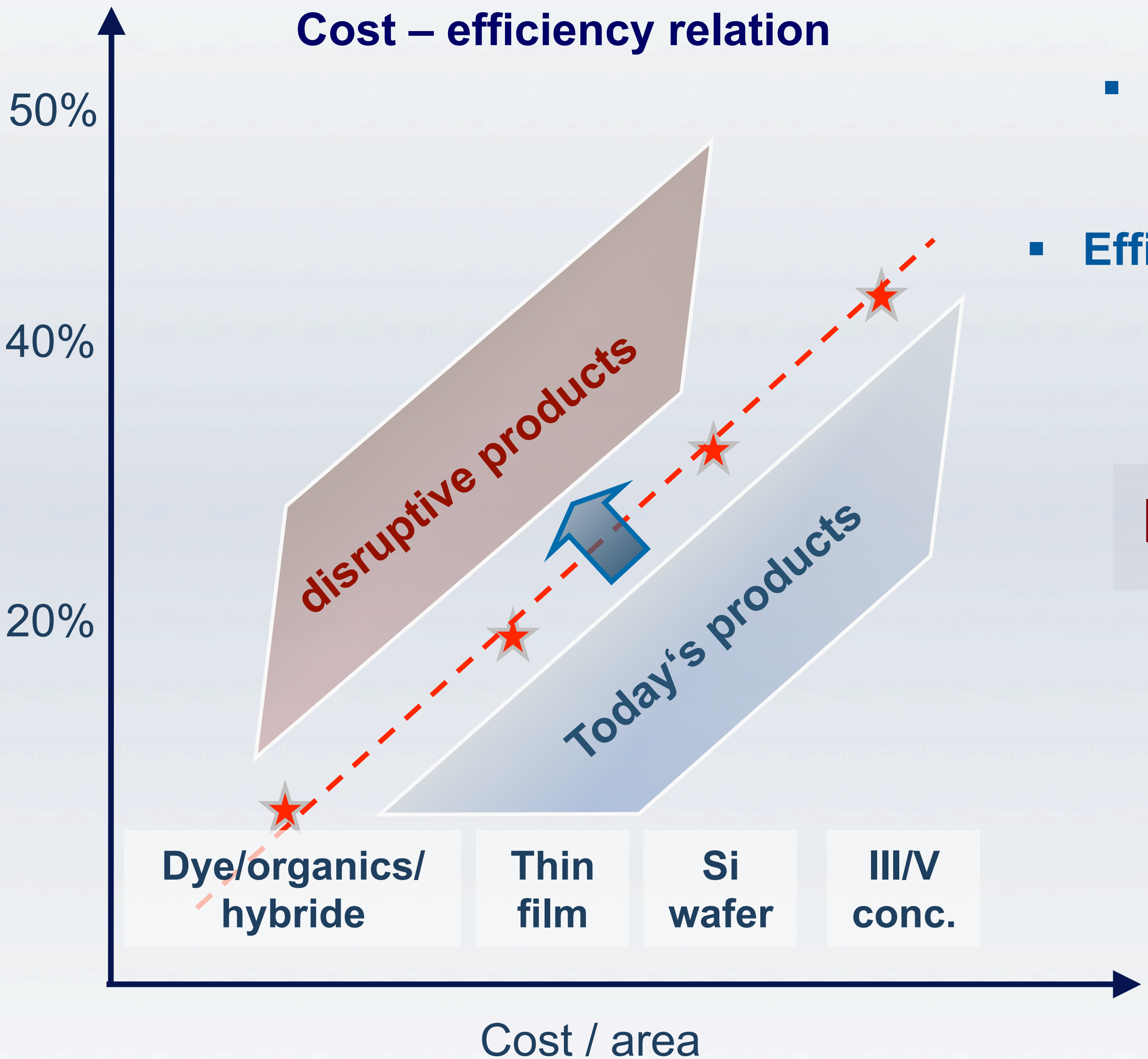
FIB structuring single crystalline Au flakes







‚Setting the stage'

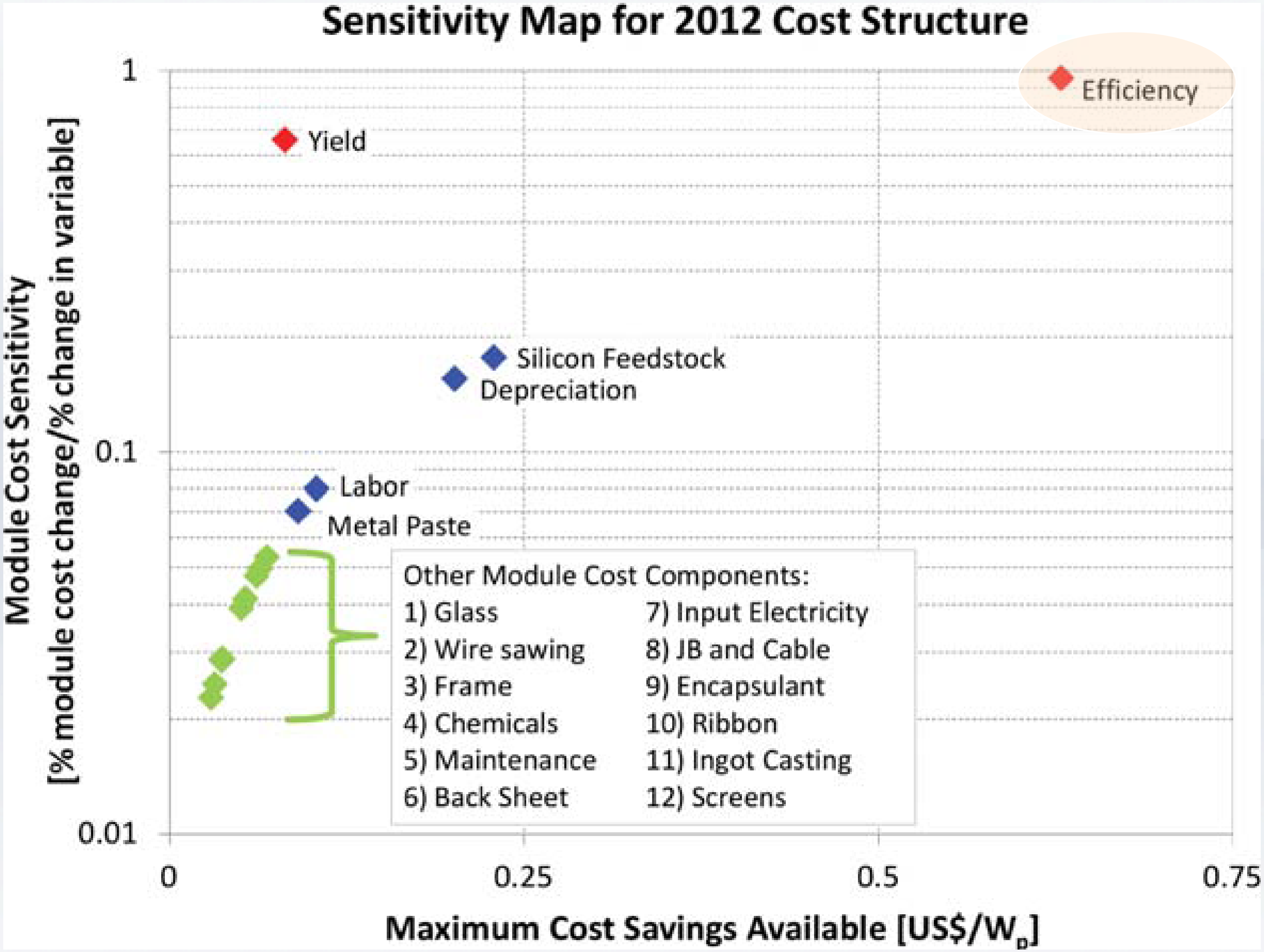


- Thin film technologies are key to future PV
- Efficiencies of Si wafers need to be addopted by cheap thin film technologies

Material challenges:

Materials
Interfaces
Processing technologies
Cell concept

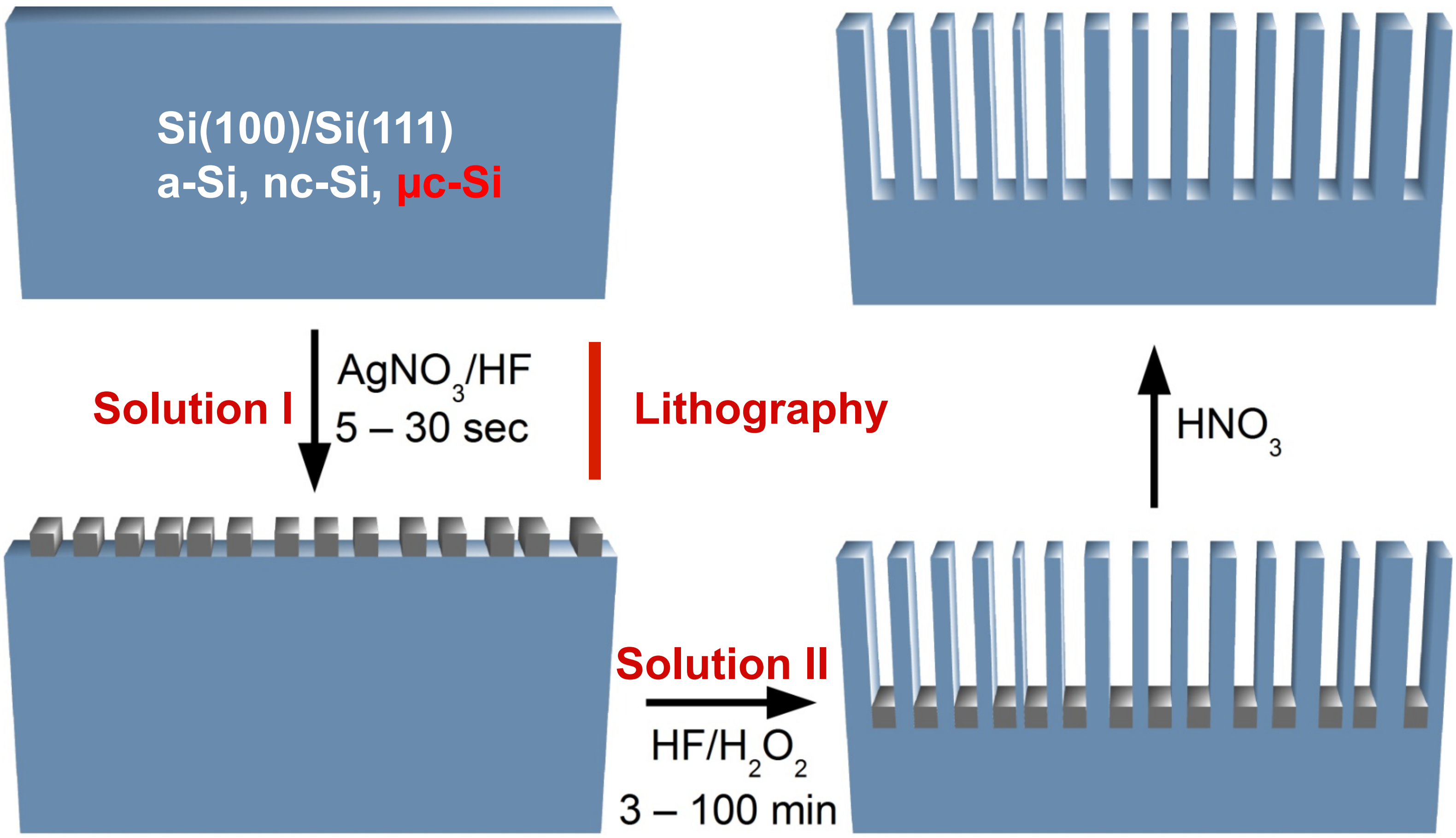
‚Setting the stage‘

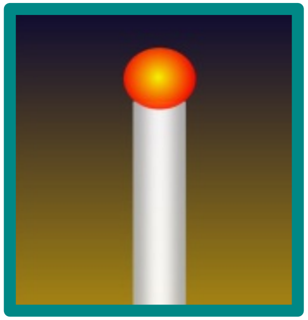


Powell, …, Buonassisi, Energy & Environm. Sci. 2012

Wet-chemically etched Si nanostructures

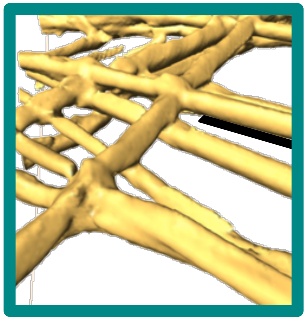
- Top down etching has advantages over CVD-bottom up growth:
  - No need of vacuum equipment
  - No restrictions in substrate size → whole wafers are treated in a few minutes
  - No contamination with gold (deep recombination center)
  - Better reproducibility





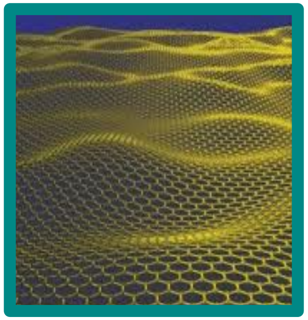
Si Nanowires (NWs) - Synthesis & Device integration

- top down NW etching & device concepts



Metal Nanowire webs - Synthesis & Properties

- Wet chemistries

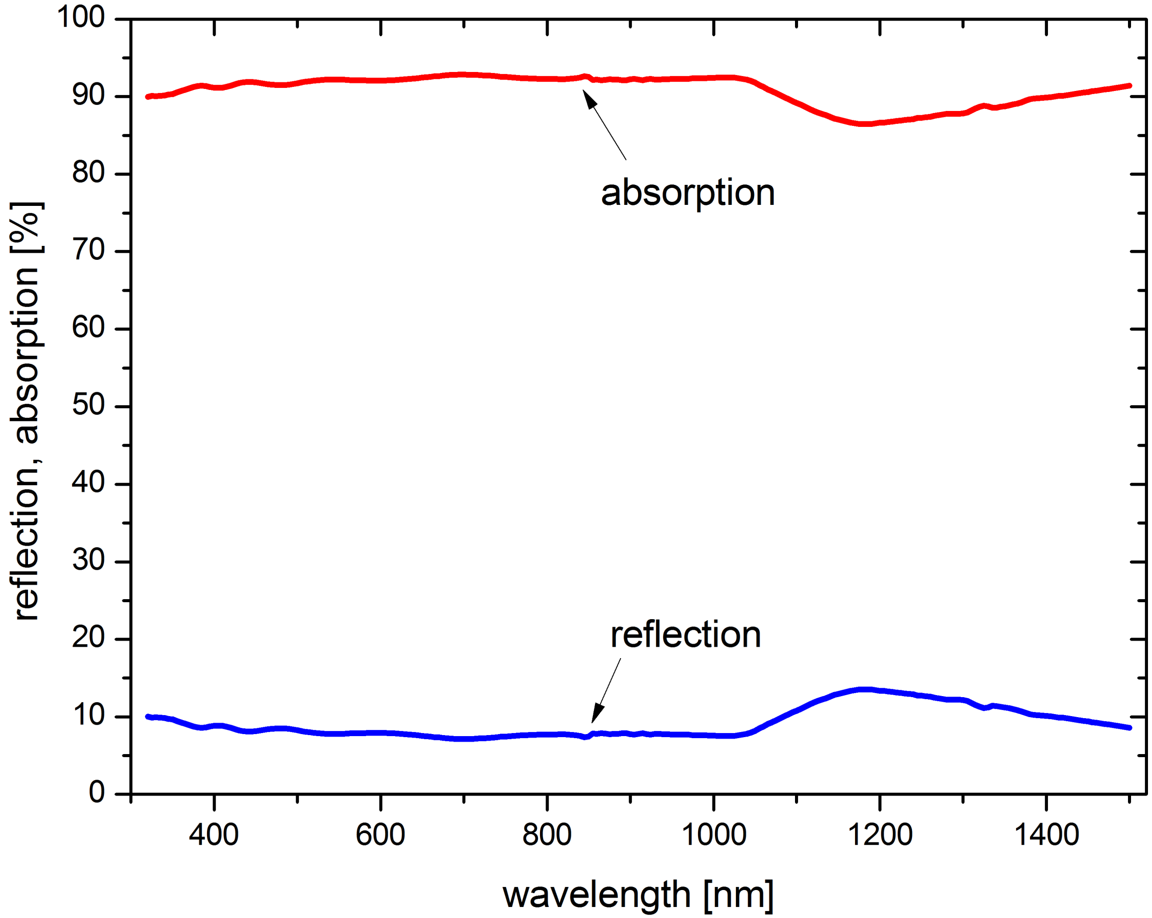


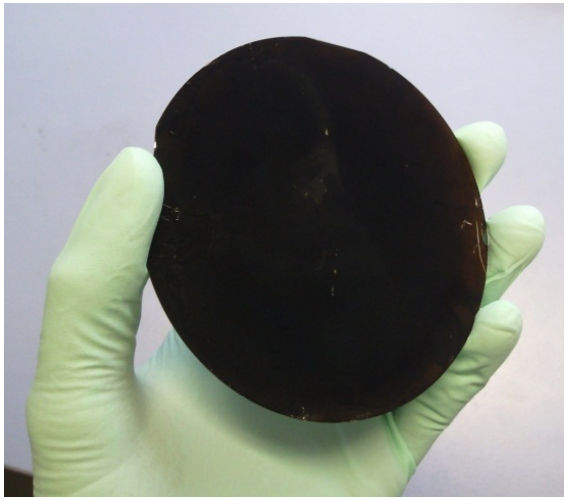
Graphene - Synthesis & Properties

- Chemical vapor deposition

Integrating sphere measurements

- Reflection measured in an integrating sphere
- Exceptional absorption of over 90% in the visible and near IR range



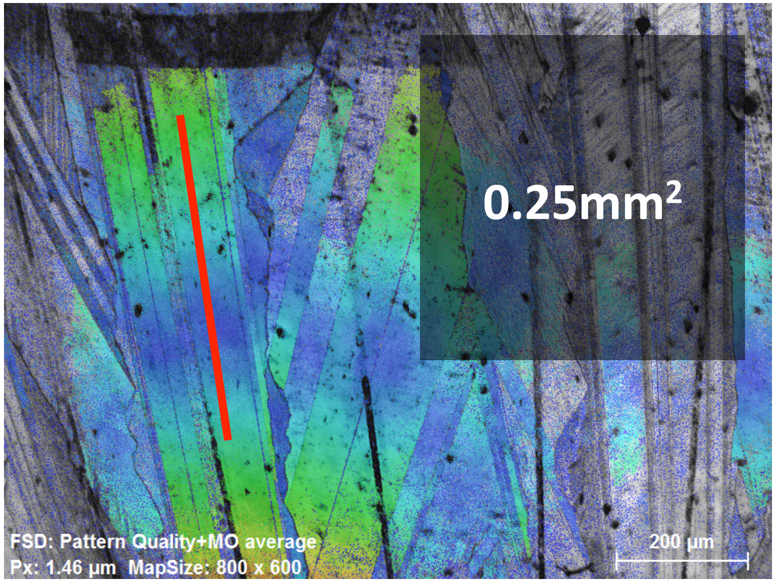


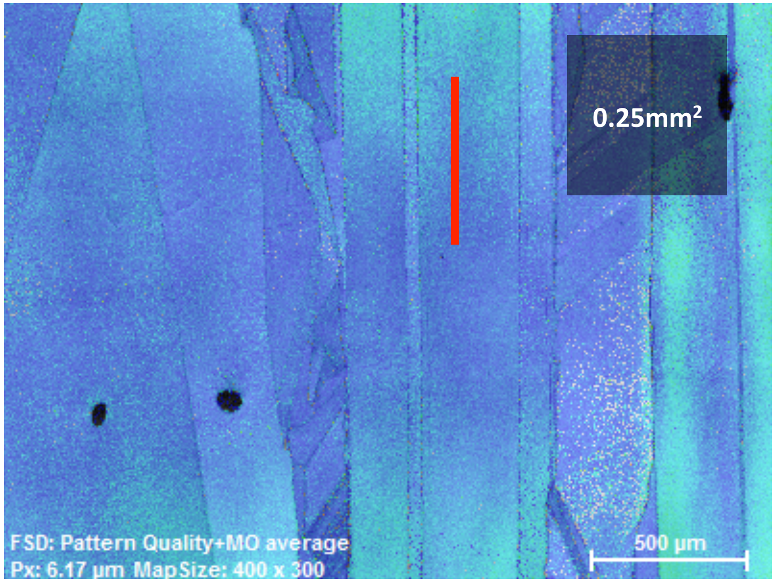
4 inch SIS solar cell wafer

EBSD: multi-crystalline layer on glass

1. laser recrystallisation on mc-Si

2. electron beam recrystallisation on glass





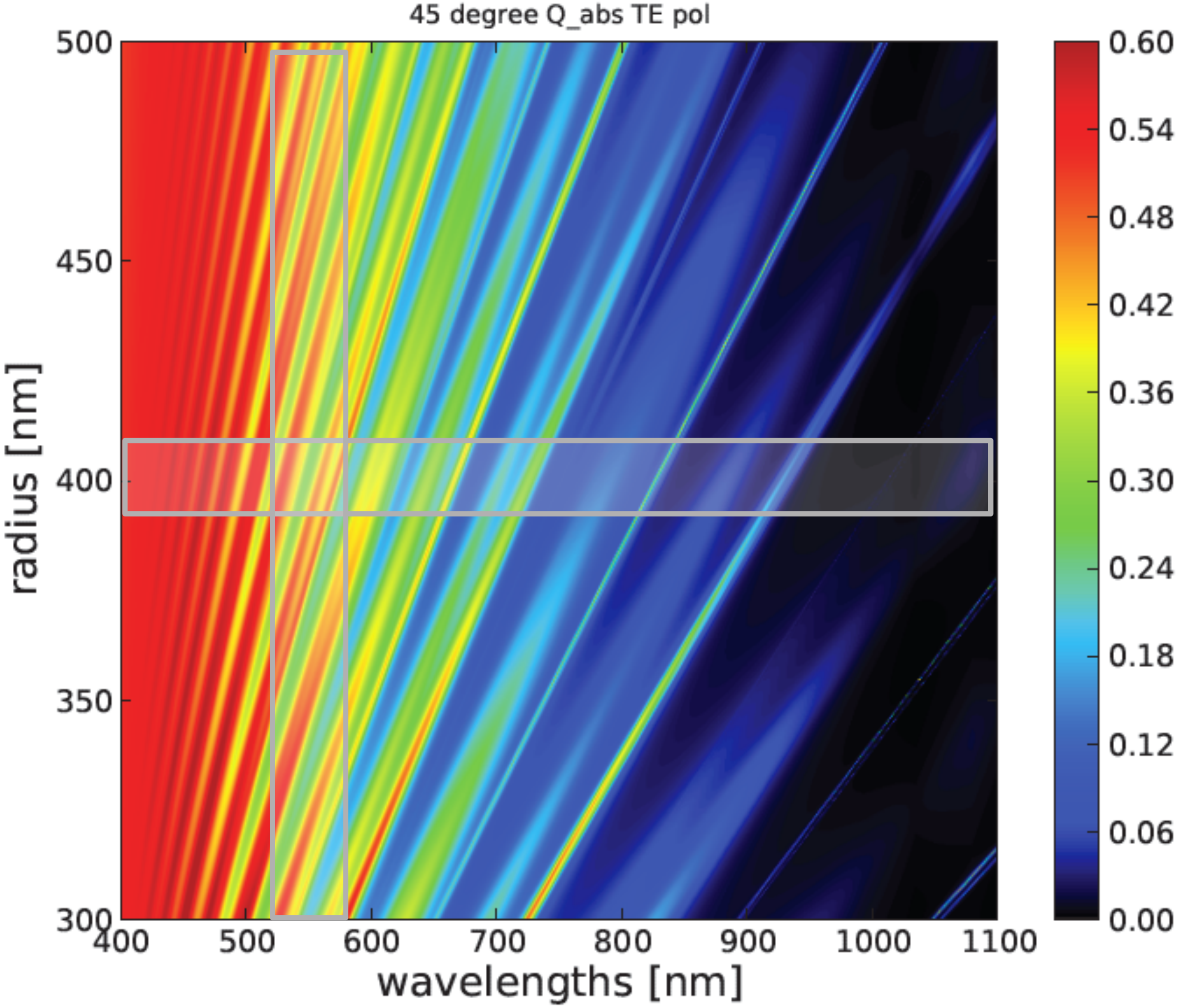
- grain misorientation along a 500µm trajectory

1: 15° tilt

2: only about 1° tilt

Optical properties of Si NWs on glass

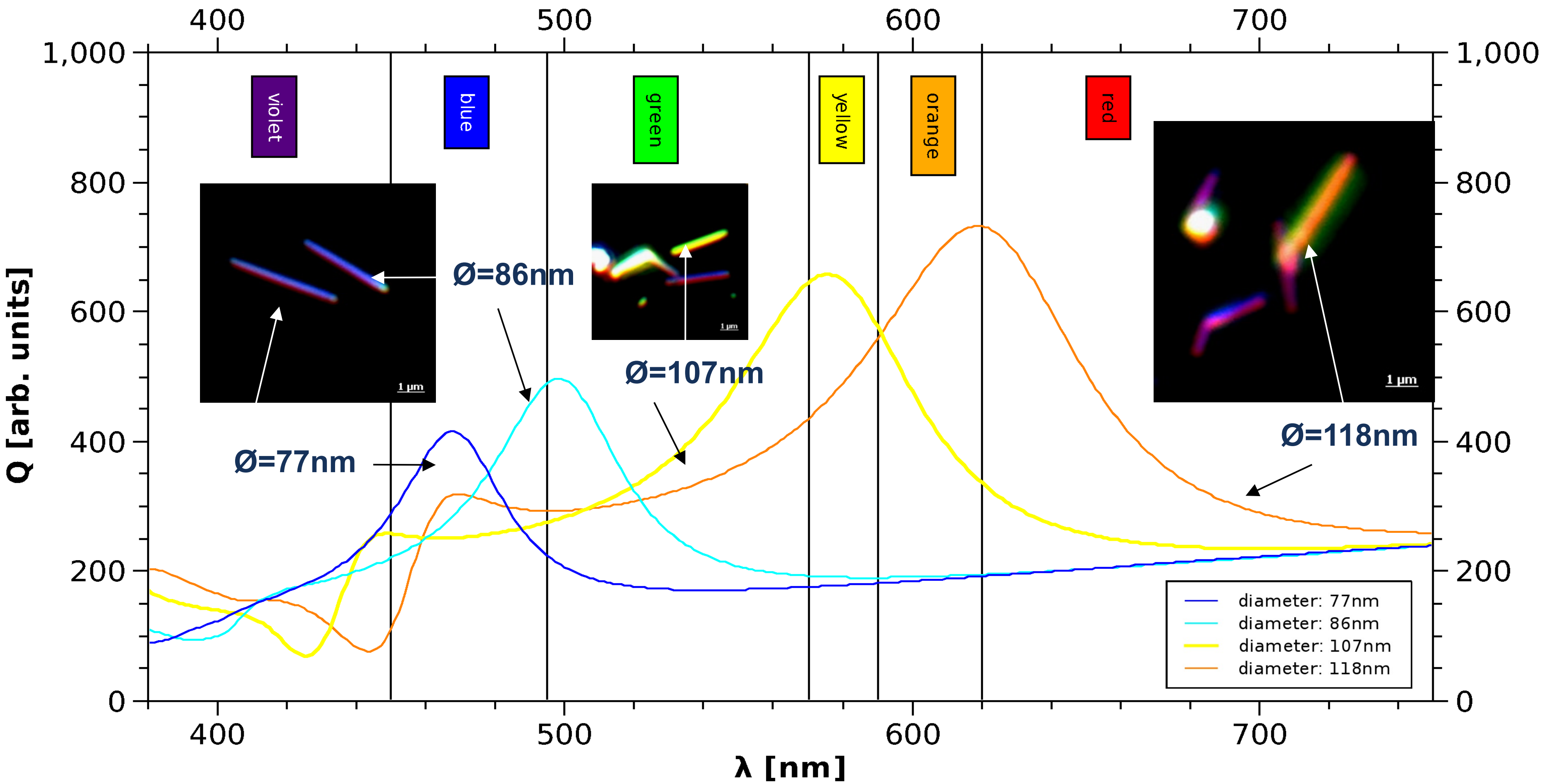
Mie scattering & absorption cross sections:



G. Brönstrup, et al. ACS Nano 4, p. 7113-7122, 2010

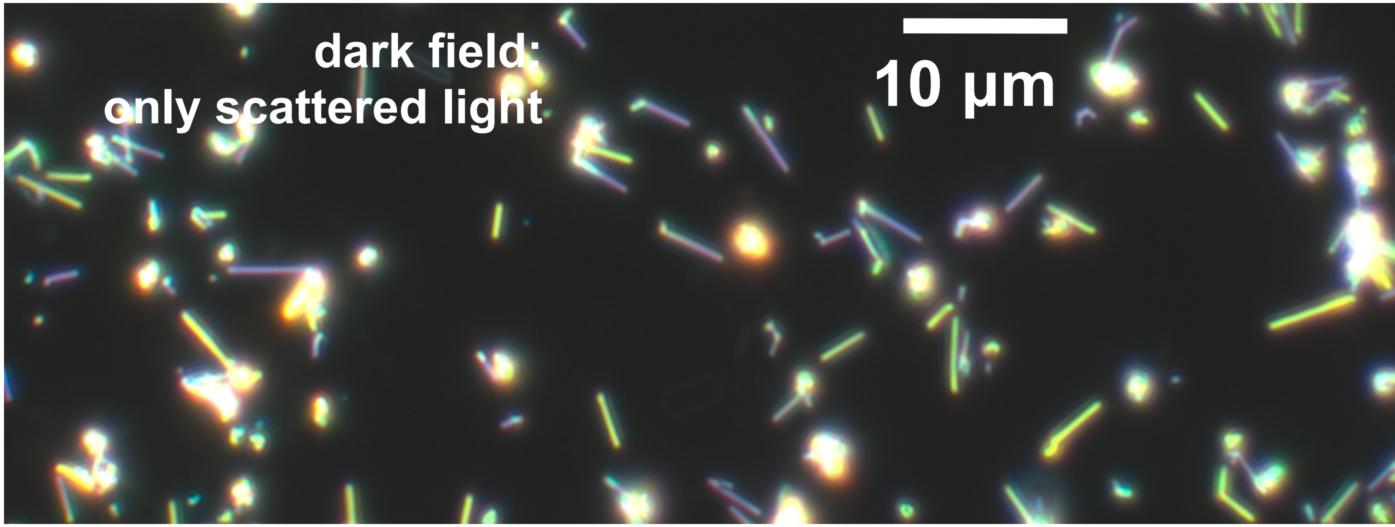
Mie scattering of Si NWs

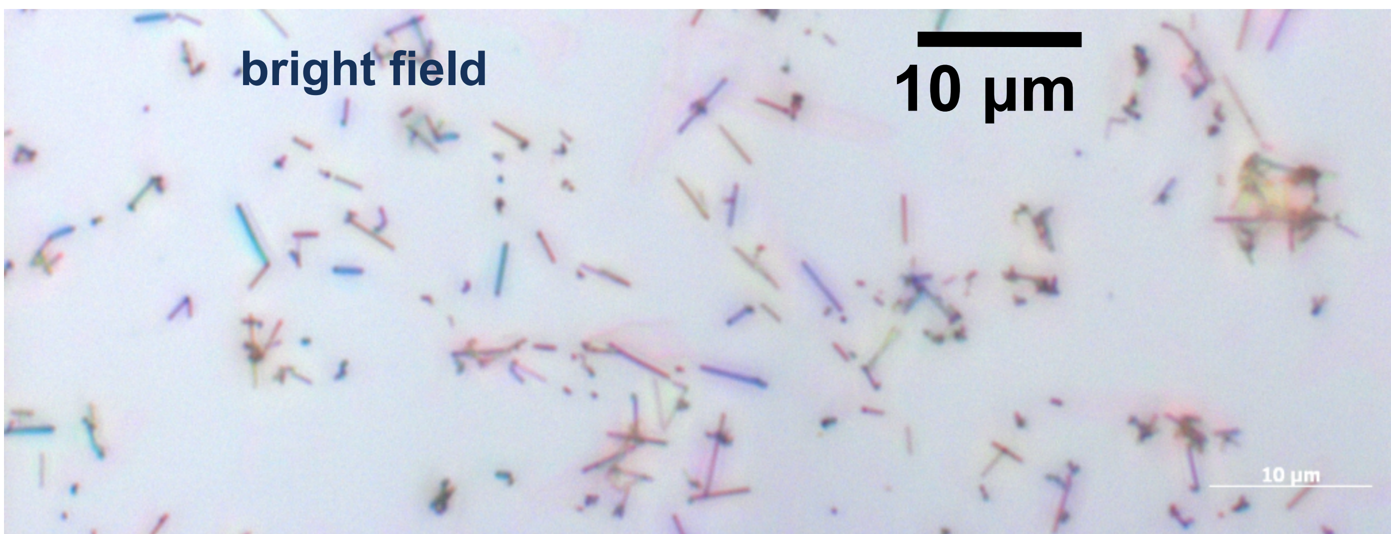
Scattering cross sections Q calculated using Mie-Theory for SiNW of different diameter in air (n=1) for incident unpolarized light; Insets: dark field pictures



G. Brönstrup, et al. ACS Nano 4, p. 7113-7122, 2010

Mie scattering of Si NWs

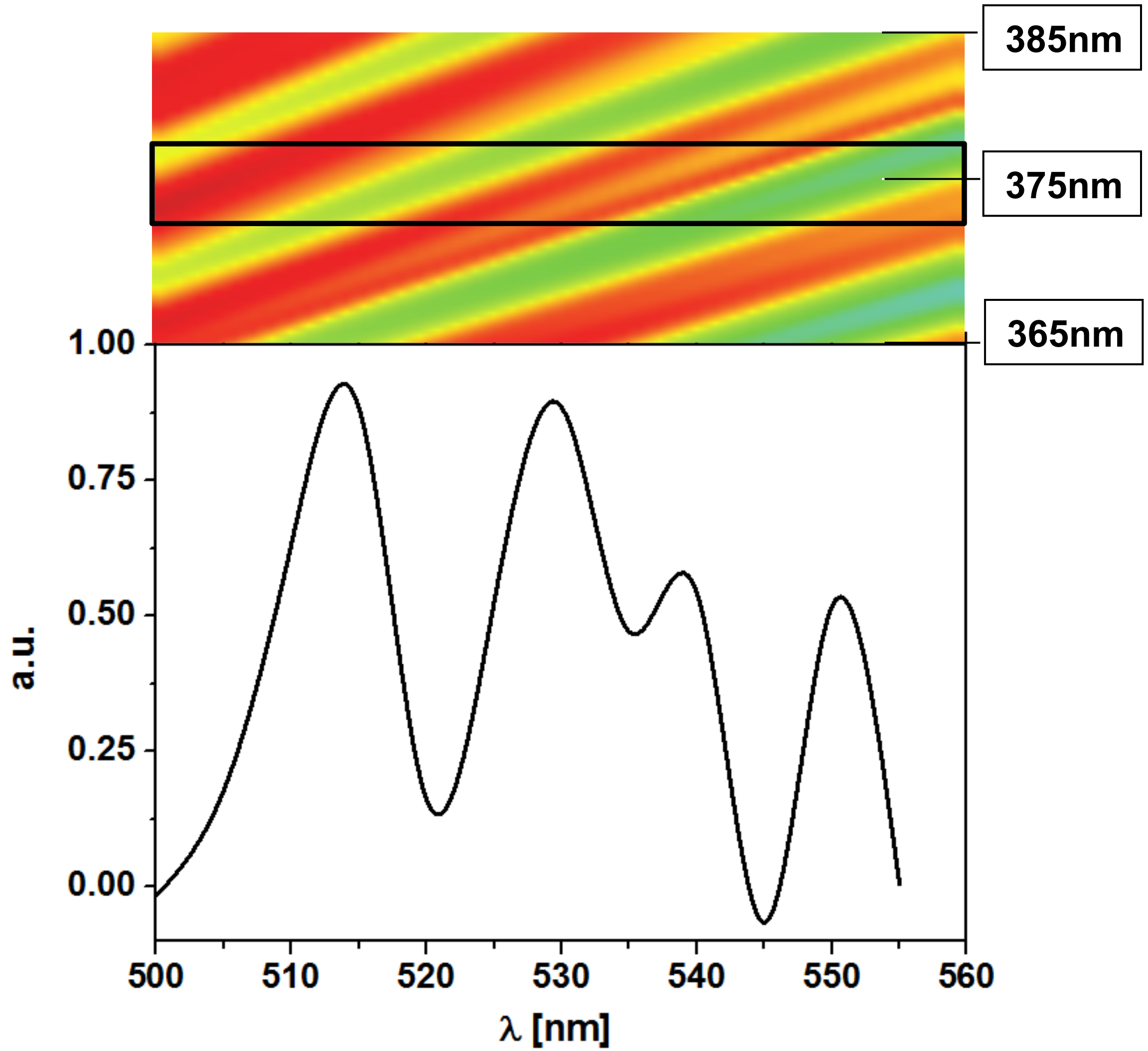




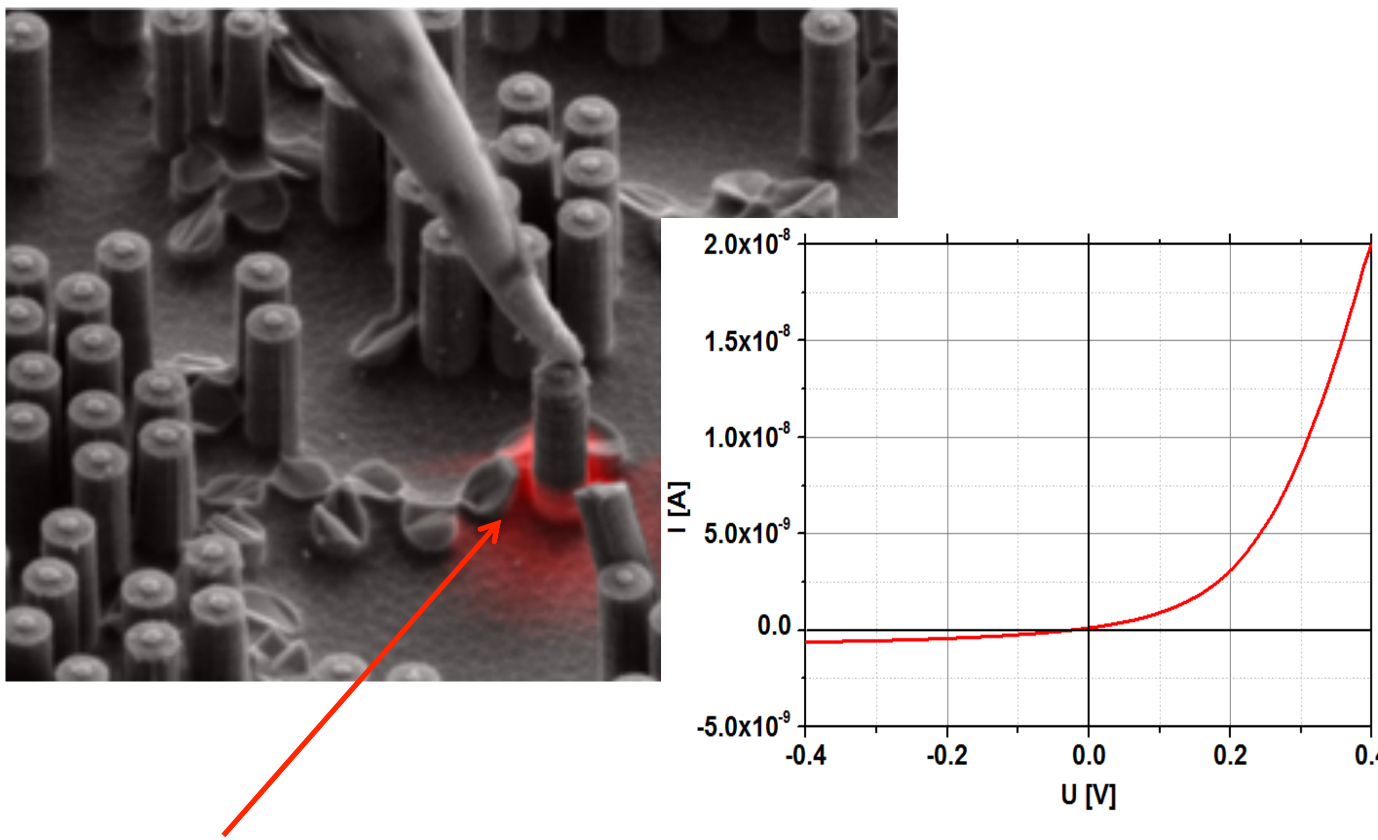
G. Brönstrup, et al. ACS Nano 4, p. 7113-7122, 2010

Optical properties of Si NWs on glass

- normalization of power to Si spectral response and incident light intensity and comparison to Mie scattering cross section (45°)
  - resonant scattering seems to trigger efficiency peaks

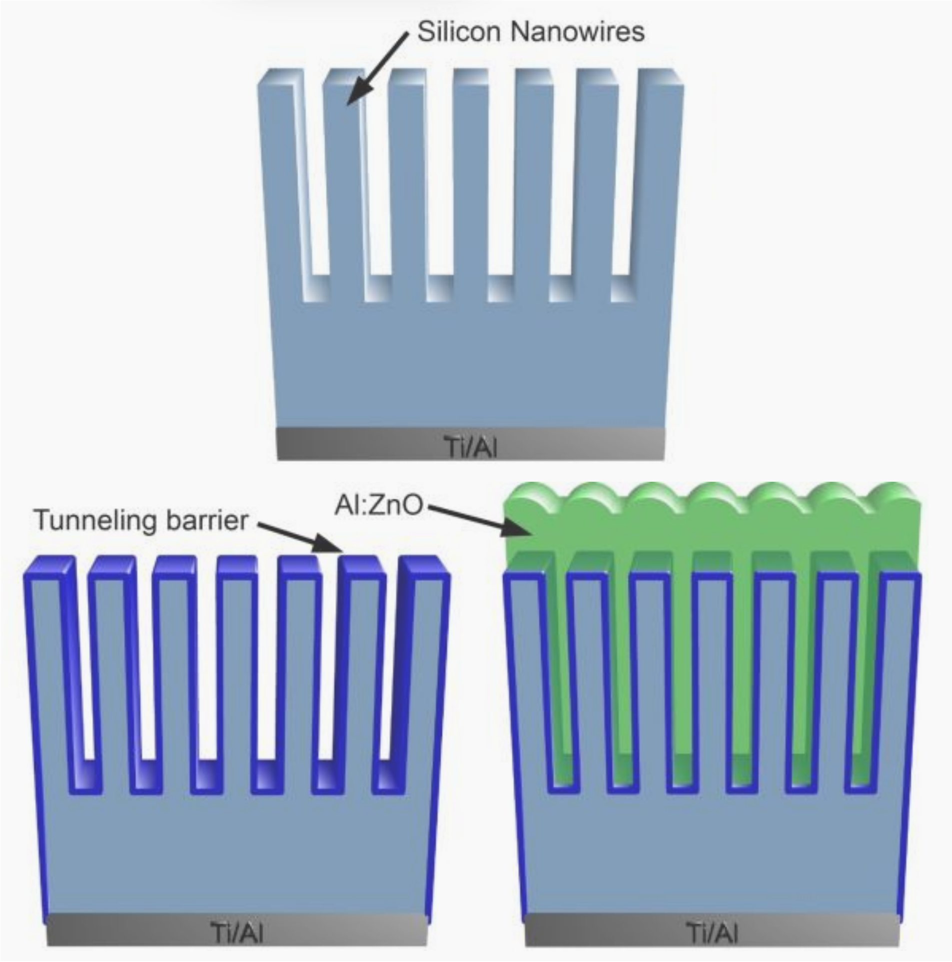


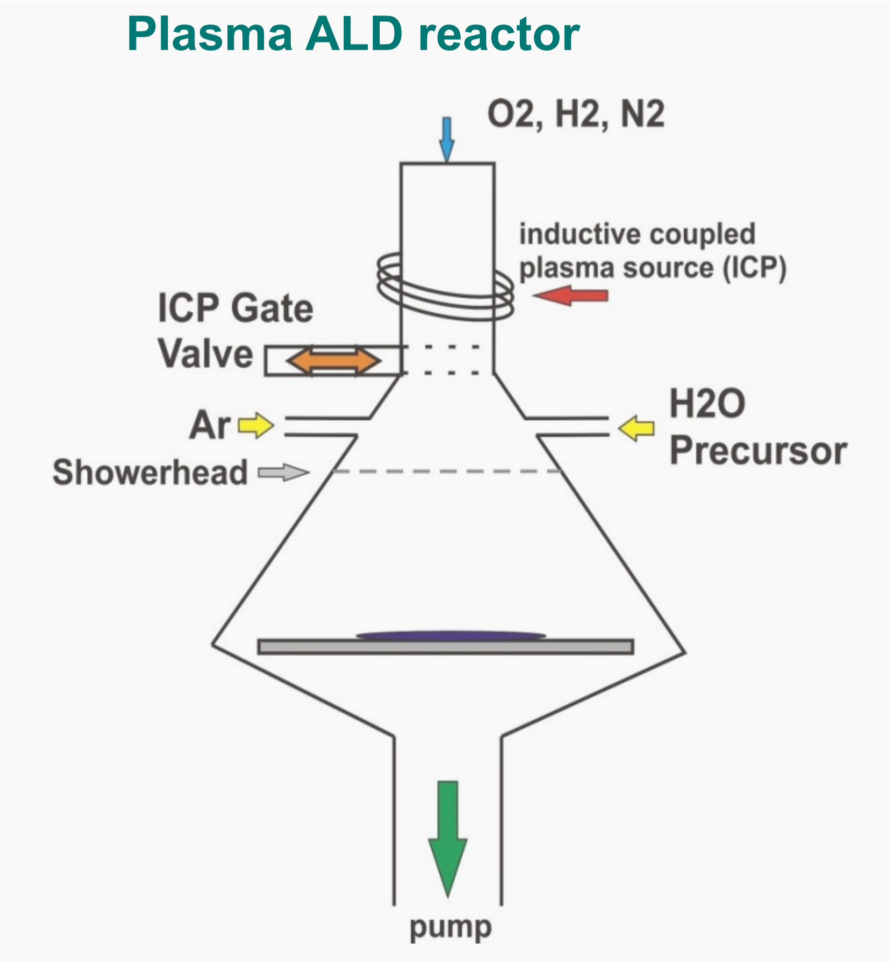
- axial p-n junctions in Si nanowires (EBIC)



Axial p-n junction in wire by diffusion before etching

Nanowire-based SIS solar cell





Two fundamental mechanisms in ALD:

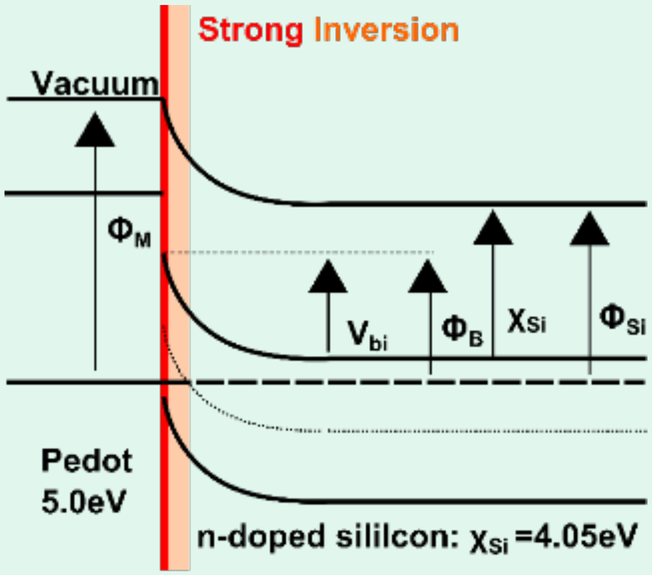
- **Chemisorption saturation process**
- **Sequential surface chemical reaction process**

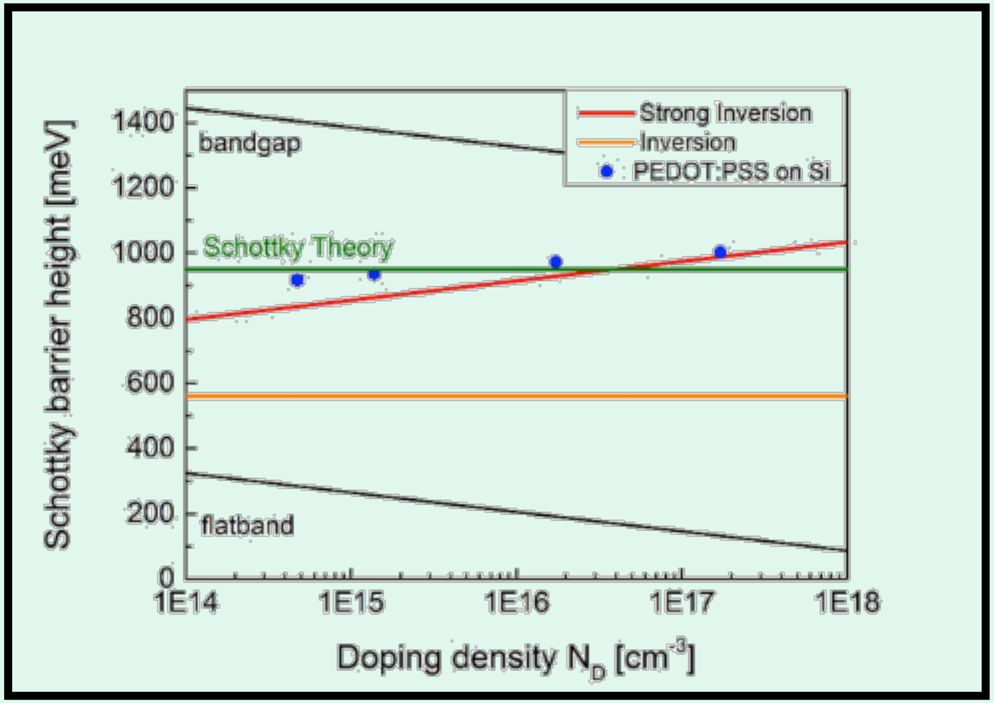
PEDOT:PSS/nSi – inversion layer

Work function of PEDOT:PSS ca. 5.0 eV

Theory Schottky Barrier Height

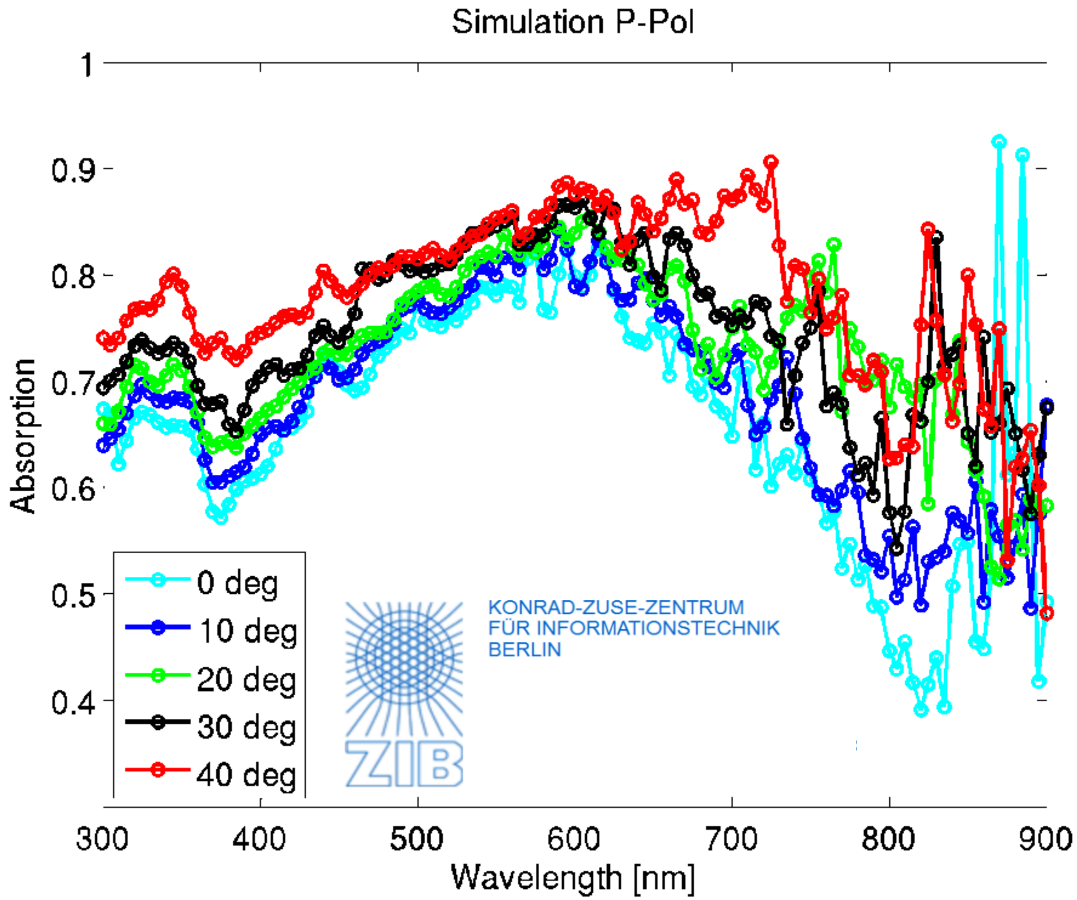
$$\Phi_B = V_{bi} + (\Phi_{Si} - \chi_{Si}) = \Phi_{PEDOT:PSS} - \chi_{Si} = 0.95\ \text{eV}$$



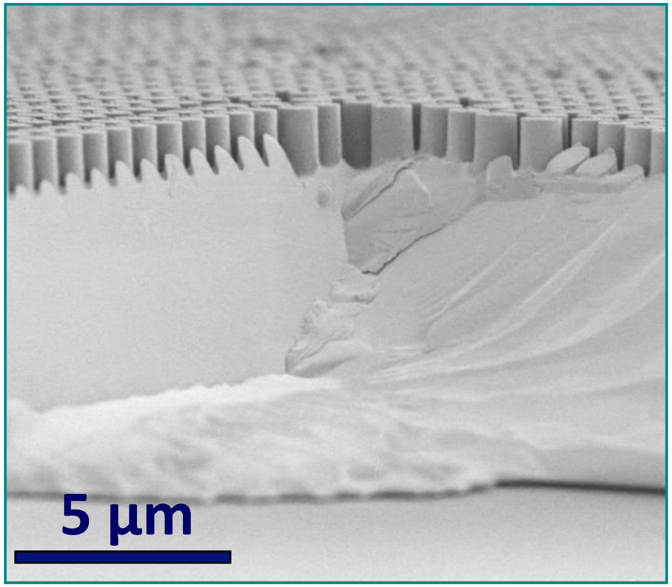


PEDOT:PSS inverts silicon at surface

Optical properties of Si NWs on glass



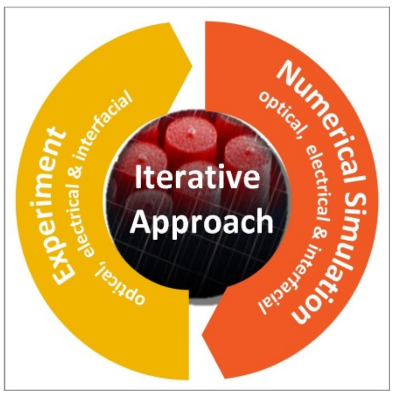
simulated absorption spectra
Hammerschmidt, Burger, Schmidt, ZIB

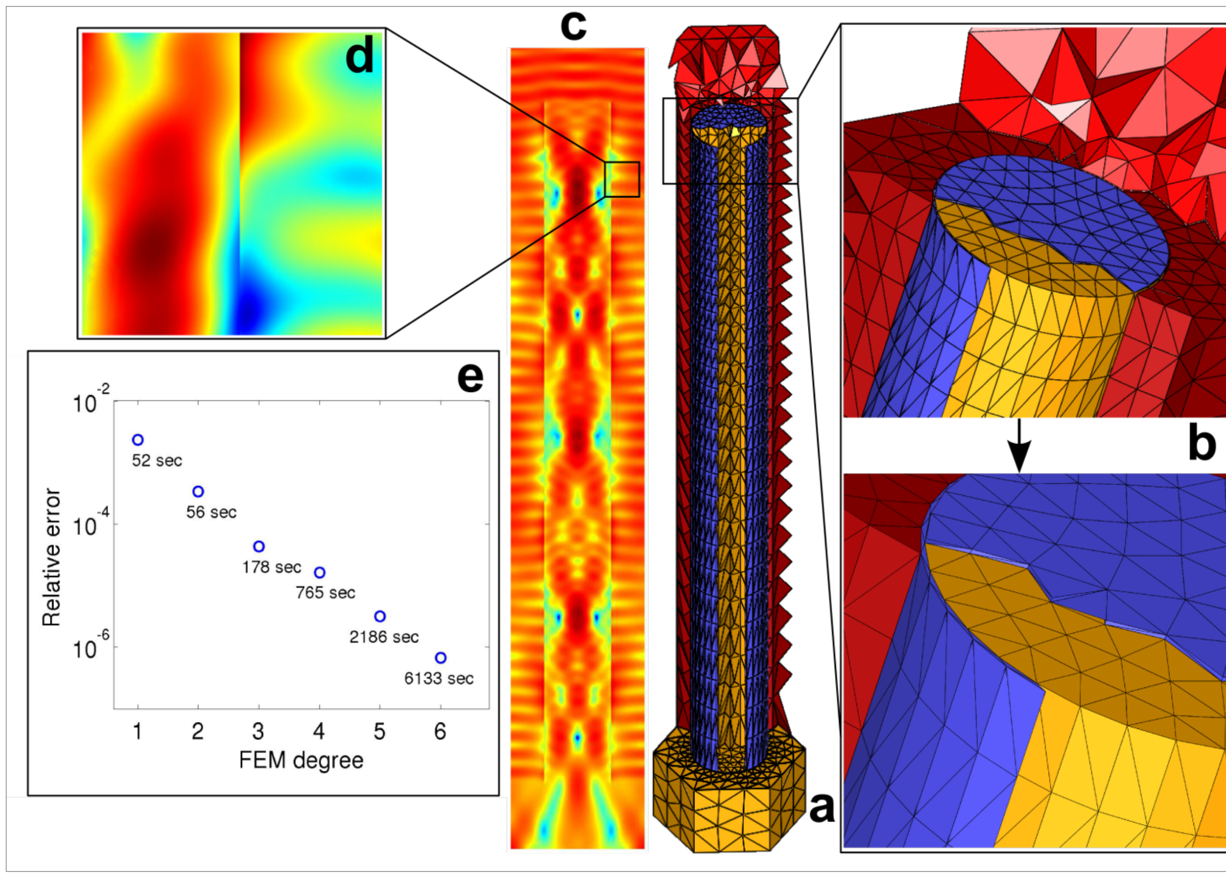


SEM of SiNW on glass

Optical properties of Si NWs on glass

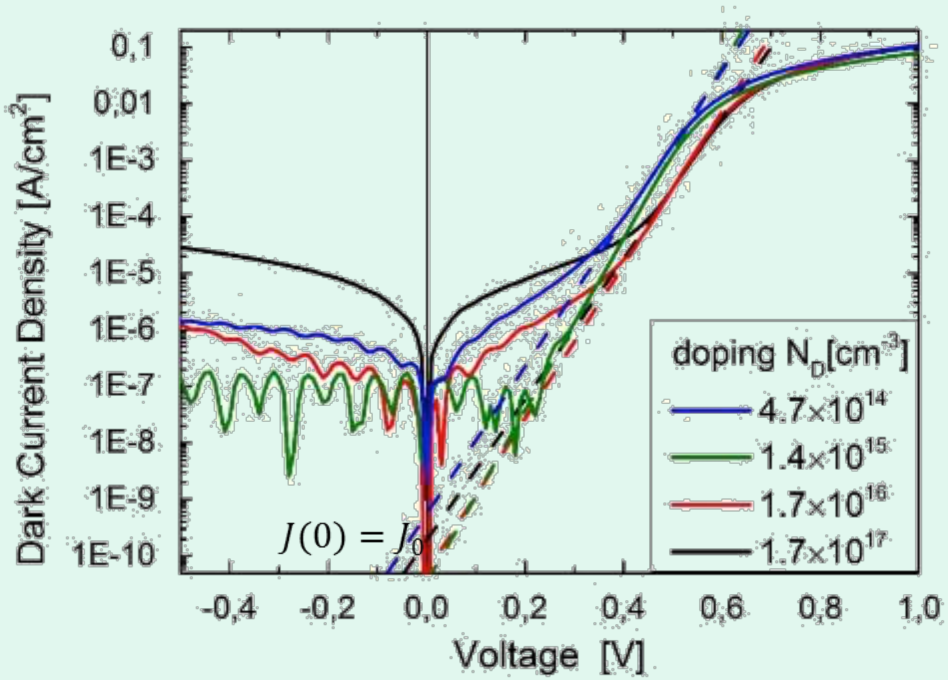
KONRAD-ZUSE-ZENTRUM
FÜR INFORMATIONSTECHNIK
BERLIN





Hammerschmidt, Burger, Schmidt, ZIB

PEDOT:PSS/nSi – solar cell



Minority carrier diffusion dominating

➡ **Small saturation currents**

$$J = J_0\left(e^{\frac{qV}{kT}} - 1\right)$$

➡ **dependents on doping**

$$J_0 \propto N_D$$

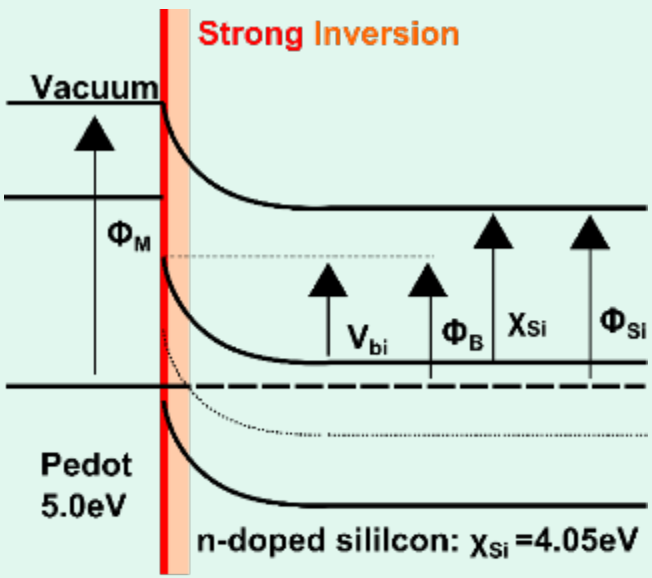
$$V_{OC} \propto \ln(1/J_0)$$

PEDOT:PSS/nSi – inversion layer

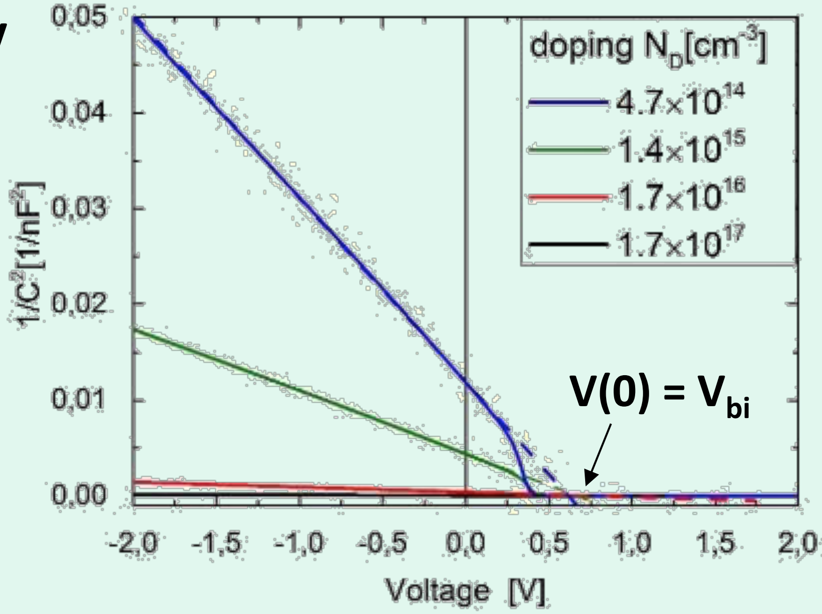
Work function of PEDOT:PSS ca. 5.0 eV

Theory Schottky Barrier Height

$\Phi_B = V_{bi} + (\Phi_{Si} - \chi_{Si}) = \Phi_{PEDOT:PSS} - \chi_{Si} = 0.95\ eV$



From capacity measurments at 10kHz



$\Phi_B \approx 0.92 - 1\ eV$

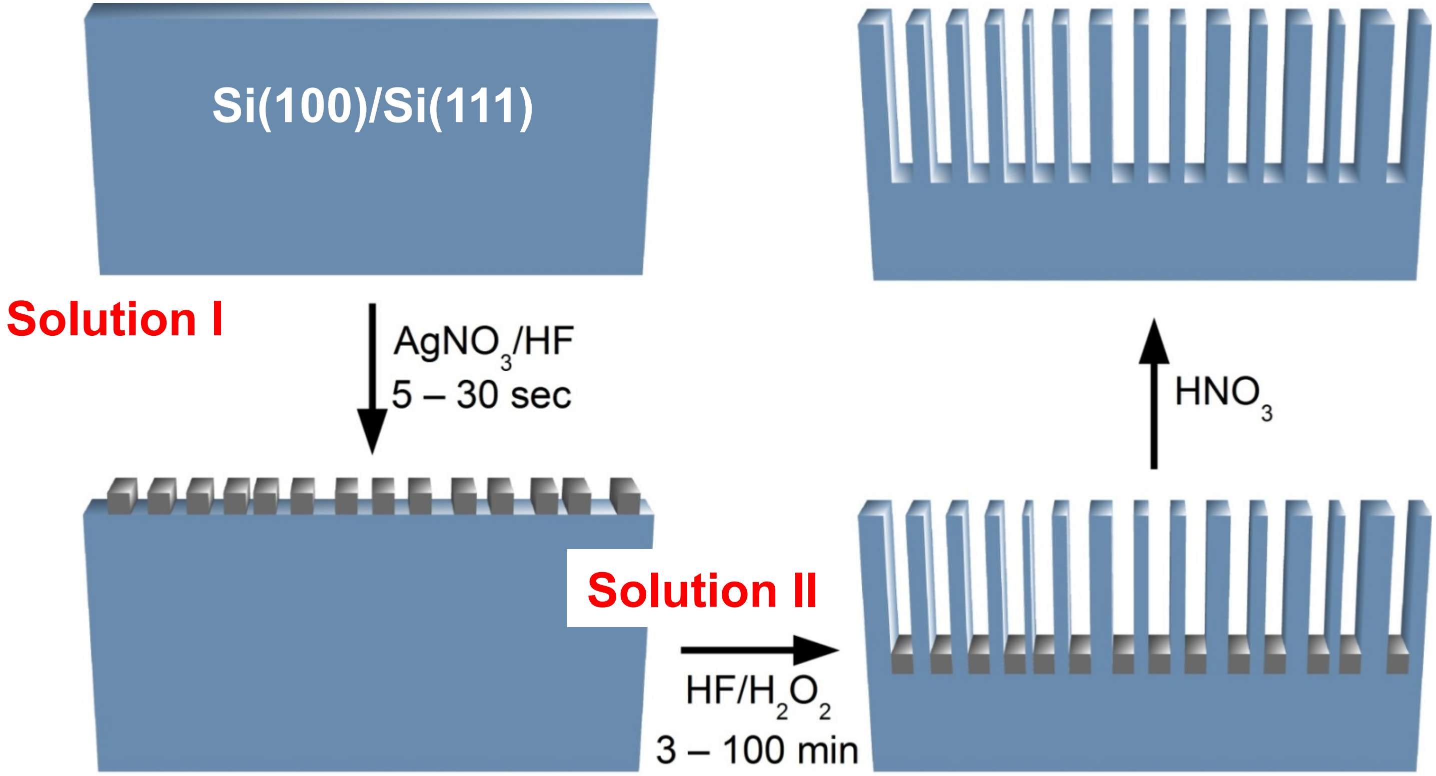
M. Pietsch, S. Jäckle, S. H. Christiansen, Appl. Phys. A, published online (2014).

acts like a metal but no Fermi-level pinning

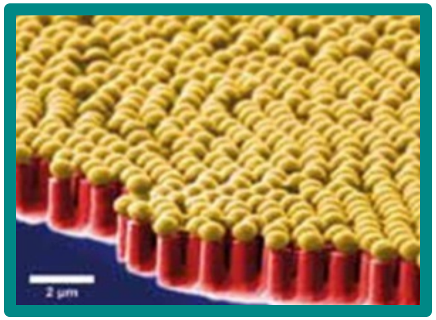
Wet-chemically etched Si nanostructures

K.-Q. Peng, et al. Adv. Mater. 14, 1164 (2002)
K.-Q. Peng, et al. Appl. Phys. Lett. 90, 163123 (2007)

V. A. Sivakov, et al. nanolett. 8(4), 1549 (2009)
V. A. Sivakov, et al. Phys. Rev. B 82, 125446 (2010)
V.A. Sivakov, et al. Wet- Chemically Etched Silicon Nanowire Architectures, in Intech: "Nanowires - Fundamental Research", ISBN 978-953-307-327-9; ed. Abbass Hashim; Chapter 3; p45-80 (2011).
S. Schmitt, et al. nanolett. 12(8), 4050 (2012)

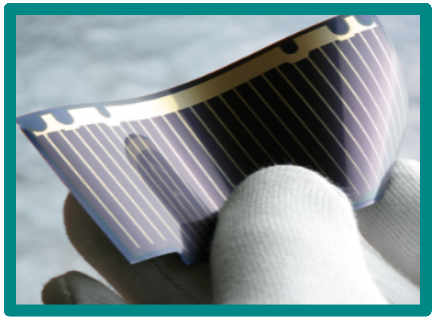


Outline



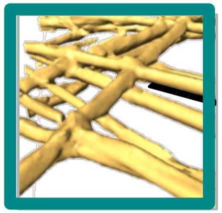
Si Nanowires (NWs) - Synthesis & Morphology

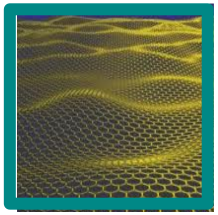
- top down NW etching



NWs in solar cell applications

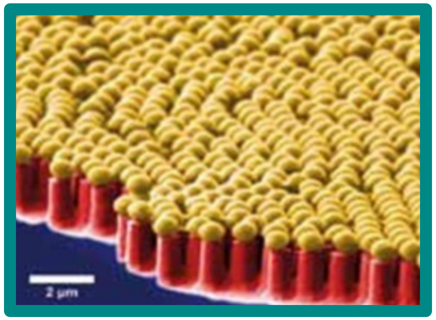
- **semiconductor NWs in different cell concepts**
- surface functionalization of NWs to improve solar cell performance





Novel contacts: graphene, Ag NW webs, TCOs

Outline



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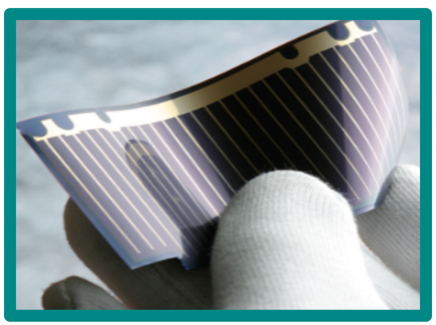

NWs in solar cell applications

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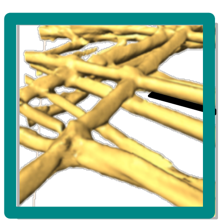
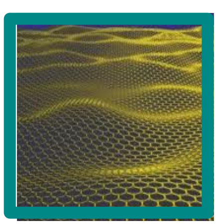
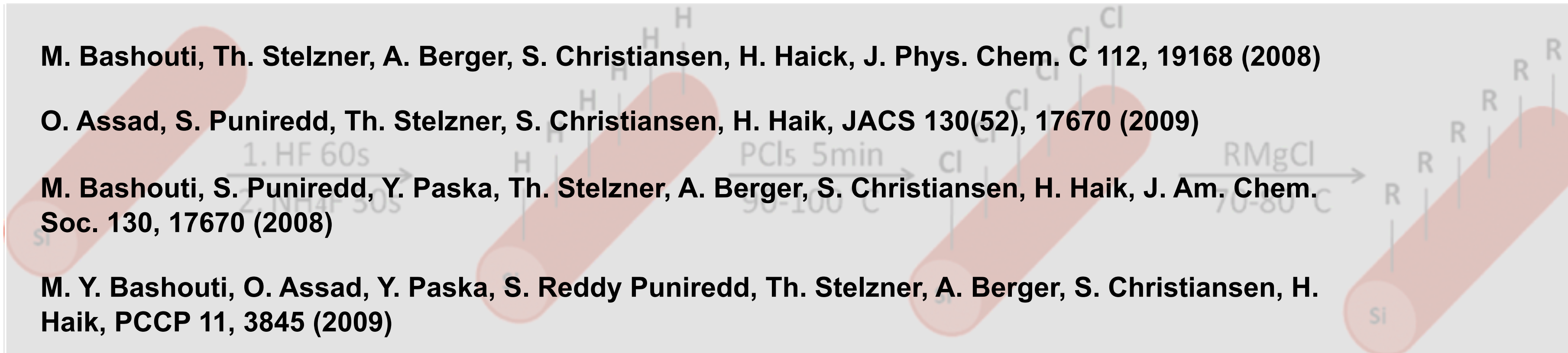




Novel contacts: graphene, Ag NW webs, TCOs

Si functionalization: preventing oxidation



M. Bashouti, Th. Stelzner, A. Berger, S. Christiansen, H. Haick, J. Phys. Chem. C 112, 19168 (2008)

O. Assad, S. Puniredd, Th. Stelzner, S. Christiansen, H. Haik, JACS 130(52), 17670 (2009)

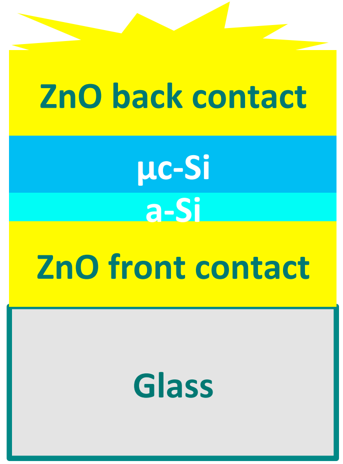
M. Bashouti, S. Puniredd, Y. Paska, Th. Stelzner, A. Berger, S. Christiansen, H. Haik, J. Am. Chem. Soc. 130, 17670 (2008)

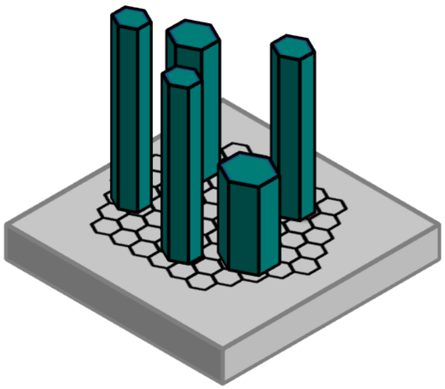
M. Y. Bashouti, O. Assad, Y. Paska, S. Reddy Puniredd, Th. Stelzner, A. Berger, S. Christiansen, H. Haik, PCCP 11, 3845 (2009)

Grignard reaction: chlorination / alcylation process

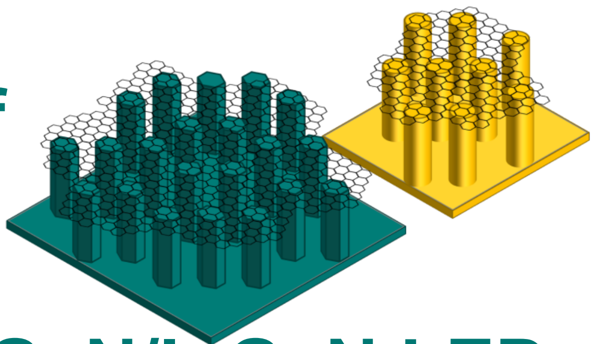
XPS studies	Optimal alkylation time for Si NWs	C_{Si}/Si_{2p} ratio for Si NW	Max. coverage on Si NW	Max. coverage(lit) on 2D Si (100)
CH_3	30 min	0.110±0.010	---	-----
CH_3CH_2	80 min	0.100±0.010	91±1%	60±20%
$CH_3(CH_2)_2$	130 min	0.090±0.010	82±1%	30±20%
$CH_3(CH_2)_3$	170 min	0.085±0.010	77±2%	30±20%

- **Thin film a-Si/µc-Si tandem solar cells**

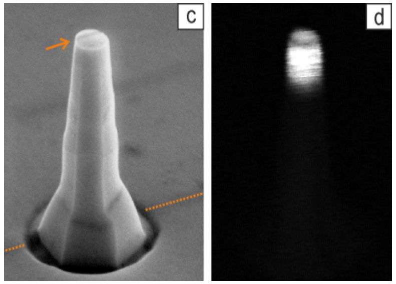




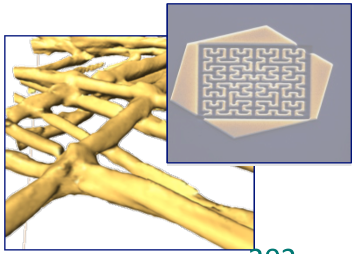
- **GaN nanowires grown on graphene**
- **Graphene on top of GaN/Si nanorods**



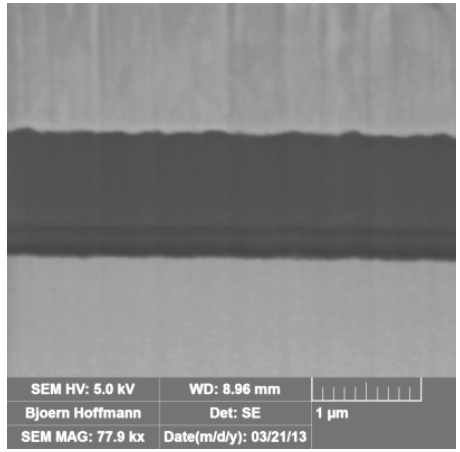
- **Model & „real life“ GaN/InGaN LEDs**

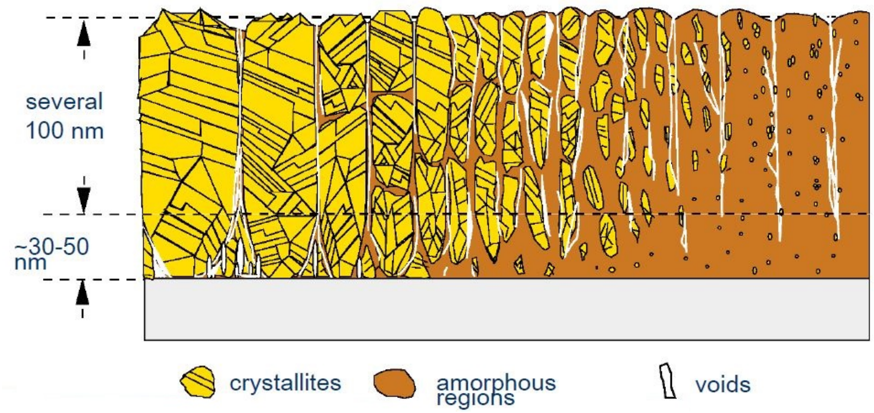


- **Ag-NW network electrodes + plasmonic antennas**



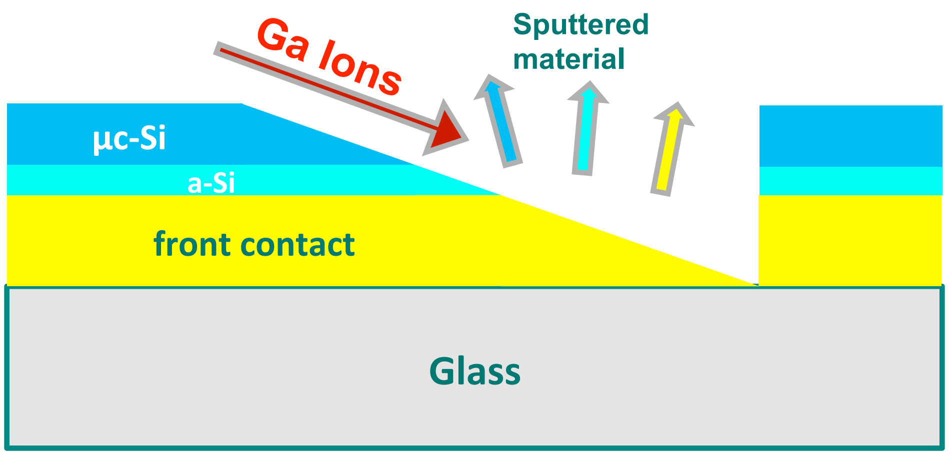
Thin film a-Si/µc-Si tandem solar cell

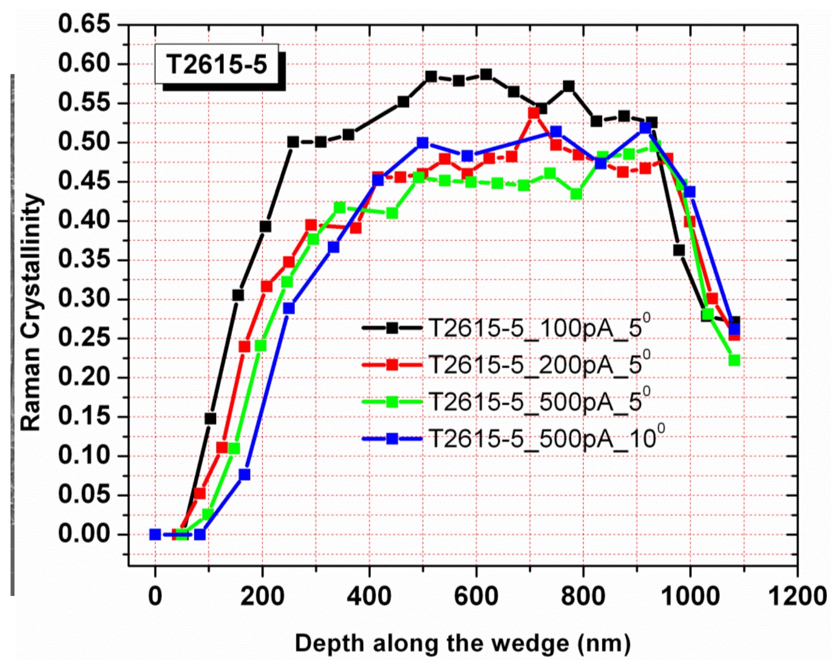




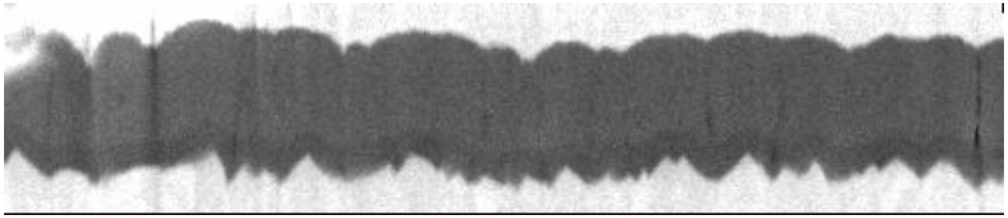
From Applied Materials

To measure crystallinity → Raman spectroscopy!

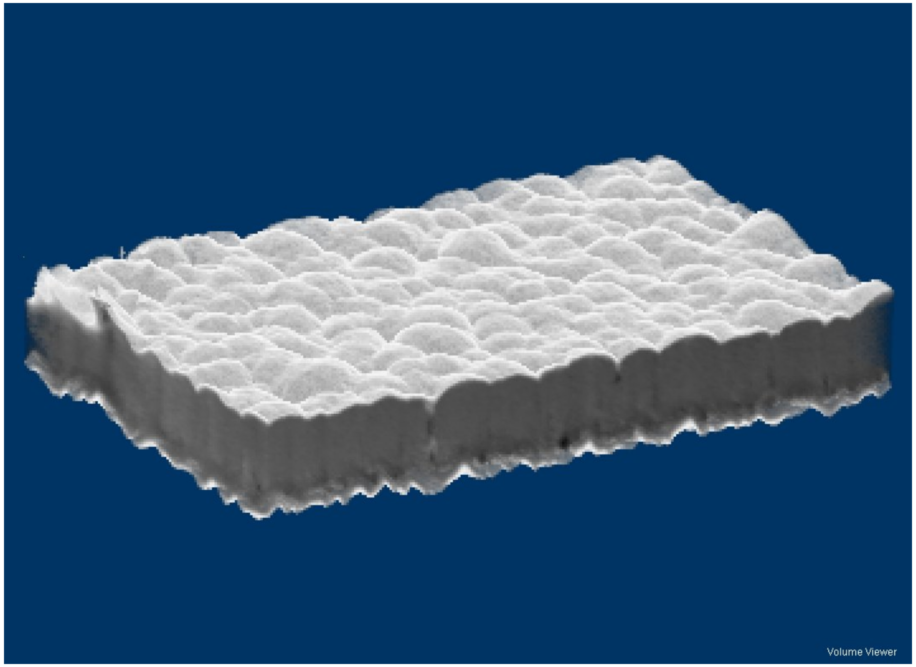


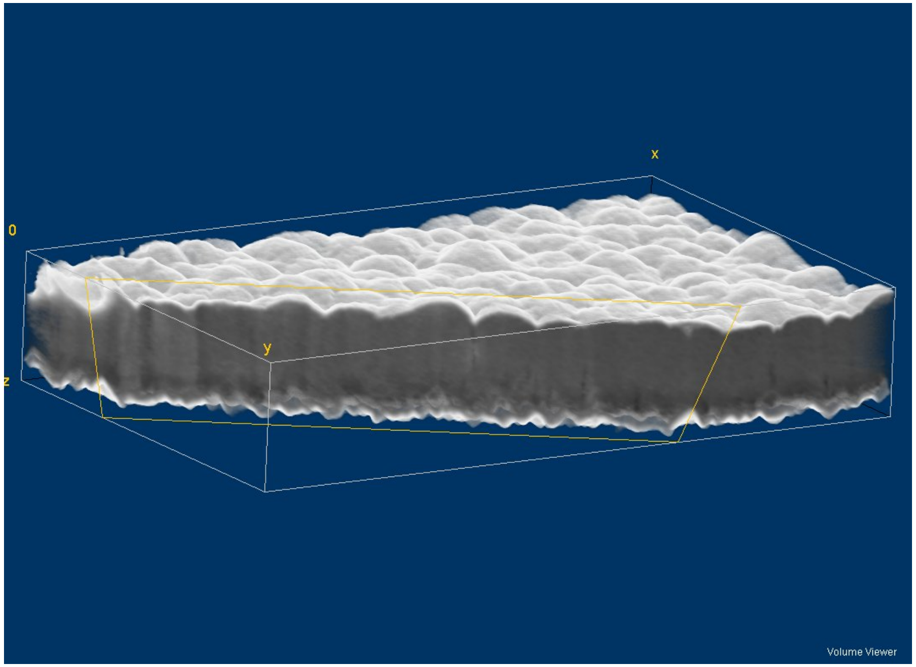


Crack distribution in thin film a-Si/µc-Si tandem solar cell



FIB-cut: crack distribution

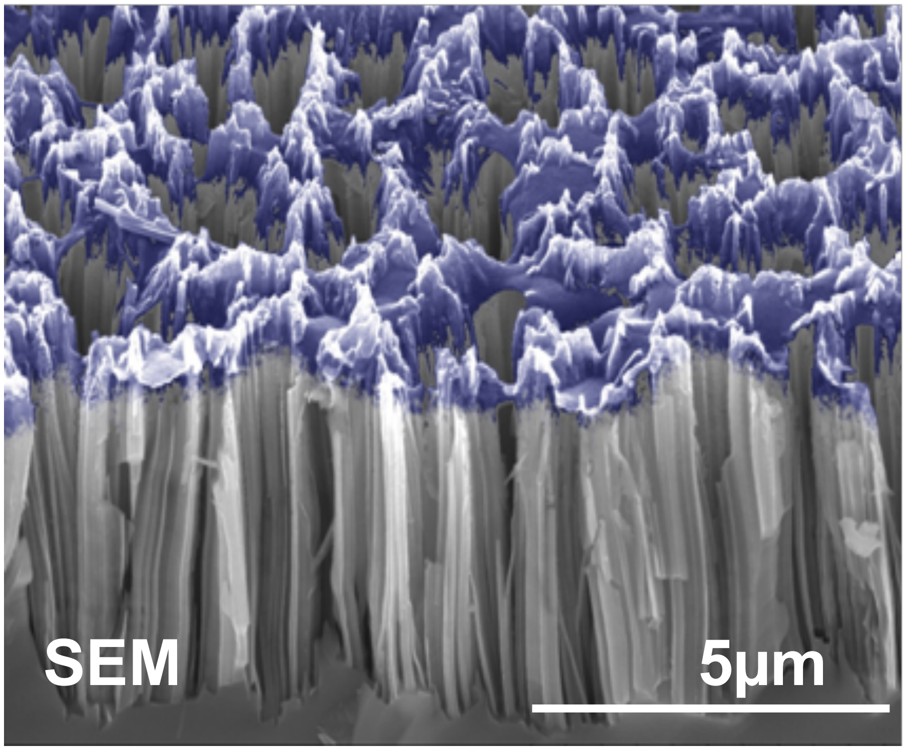


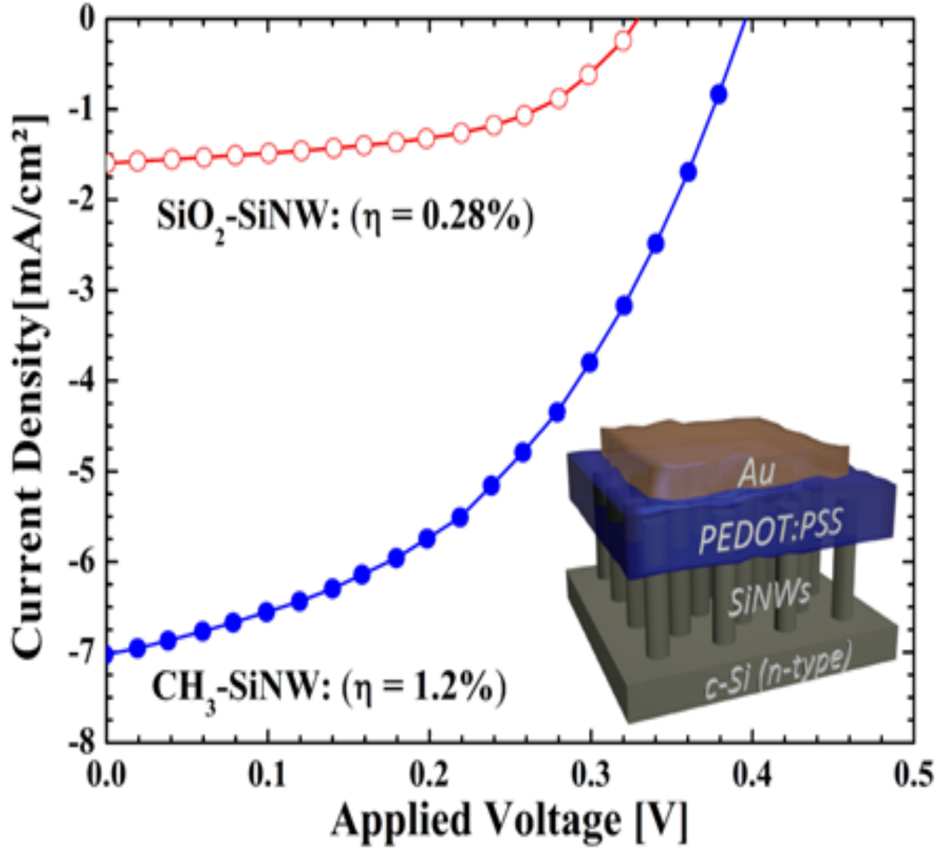


Si functionalization: preventing oxidation

SiNW/PEDOT:PSS radial heterojunction

I-V curve (AM1.5 illumination): CH_3-SiNW and SiO_2-SiNW





M. Bashouti, K. Sardashti, S. Schmitt, M. Pietsch, J. Riestein, H. Haick, S.H. Christiansen, *Oxide-free Hybrid Silicon Nanowires: From Fundamentals to Applied Nanotechnology*, Progr. in Surface Science 88(1), 39 (2013).