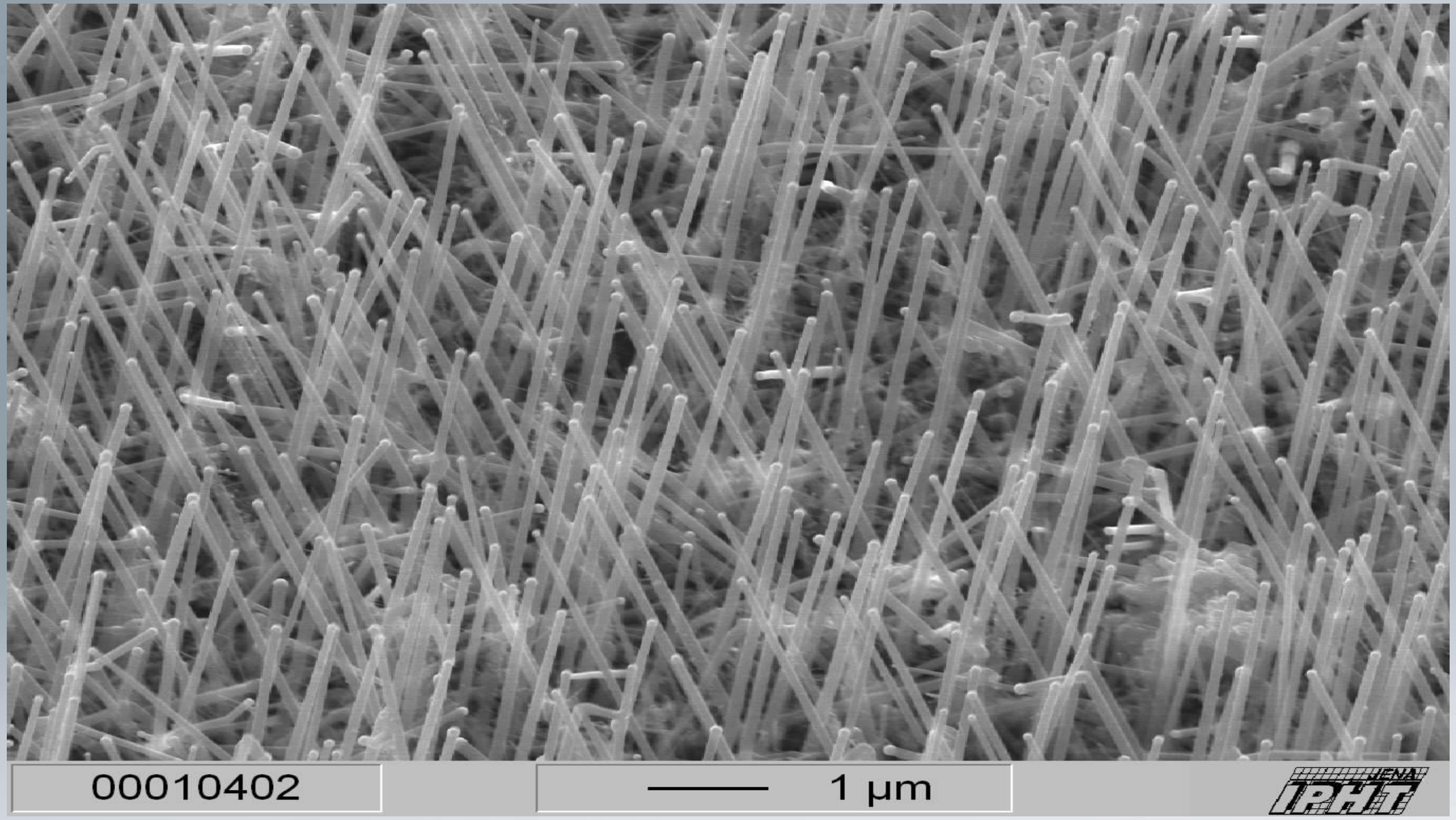
# 4. Energy Applications

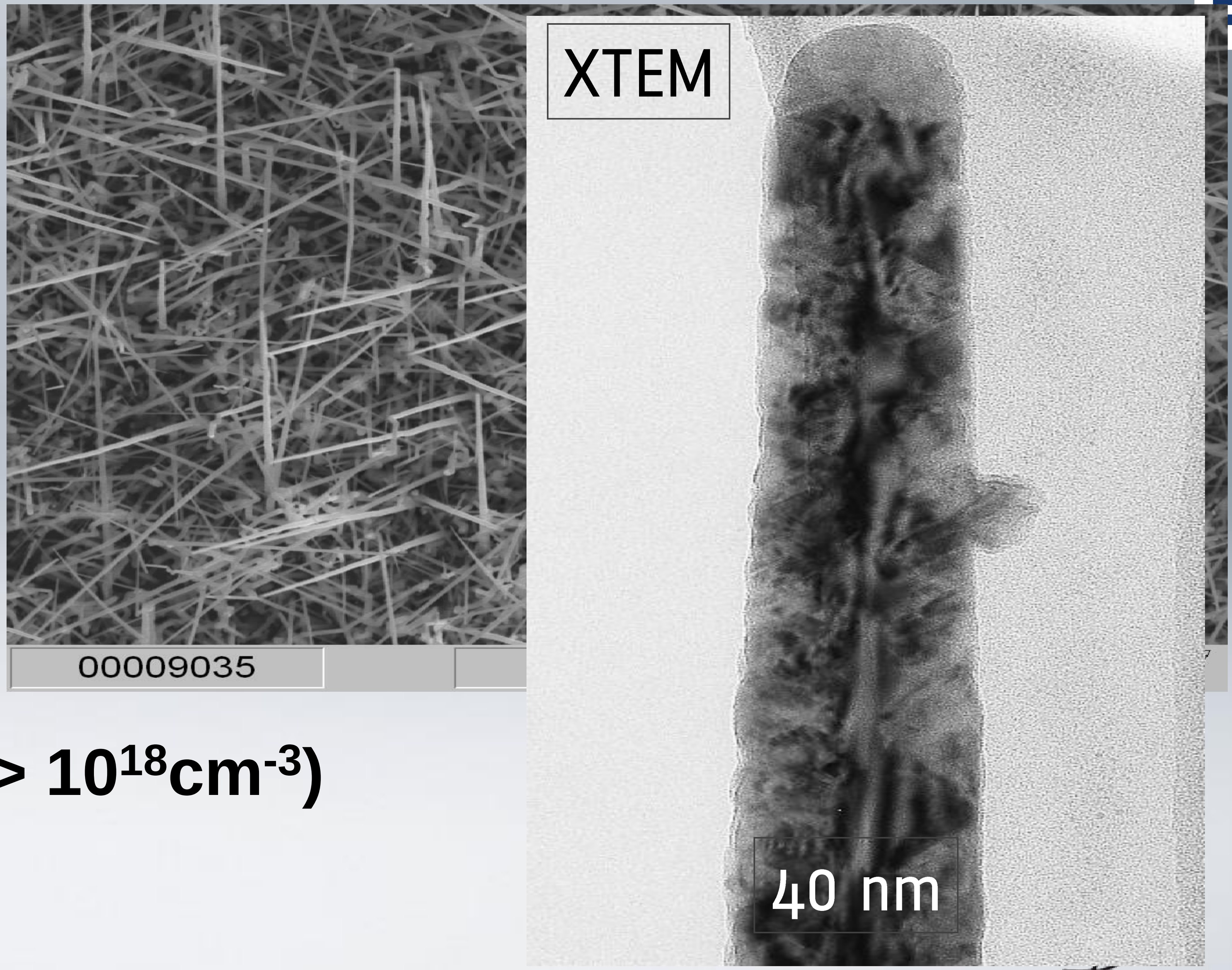
# Doping of Nanowires

- Doping during CVD growth
  - Co-doping in growth chamber ($B_2H_6$, $B(CH_3)_3$, $PH_3$ besides $SiH_4$)
- Post-growth doping
  - Spin on doping
  - Gaseous environment
  - Ion implantation (B, P)

# Doping during CVD growth

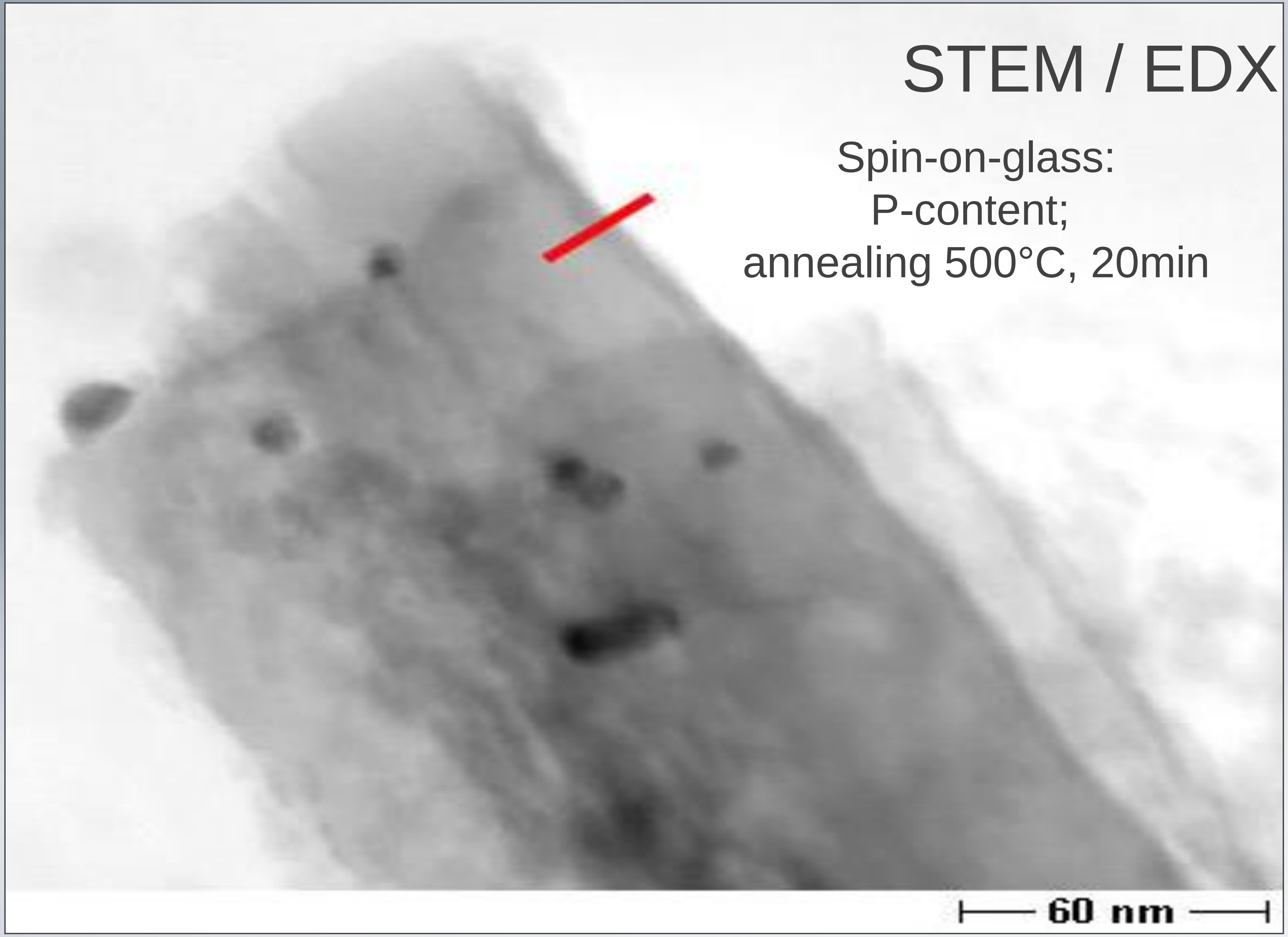
Preparation: CVD from $SiH_4$ with $B_2H_6$ bzw. $PH_3$

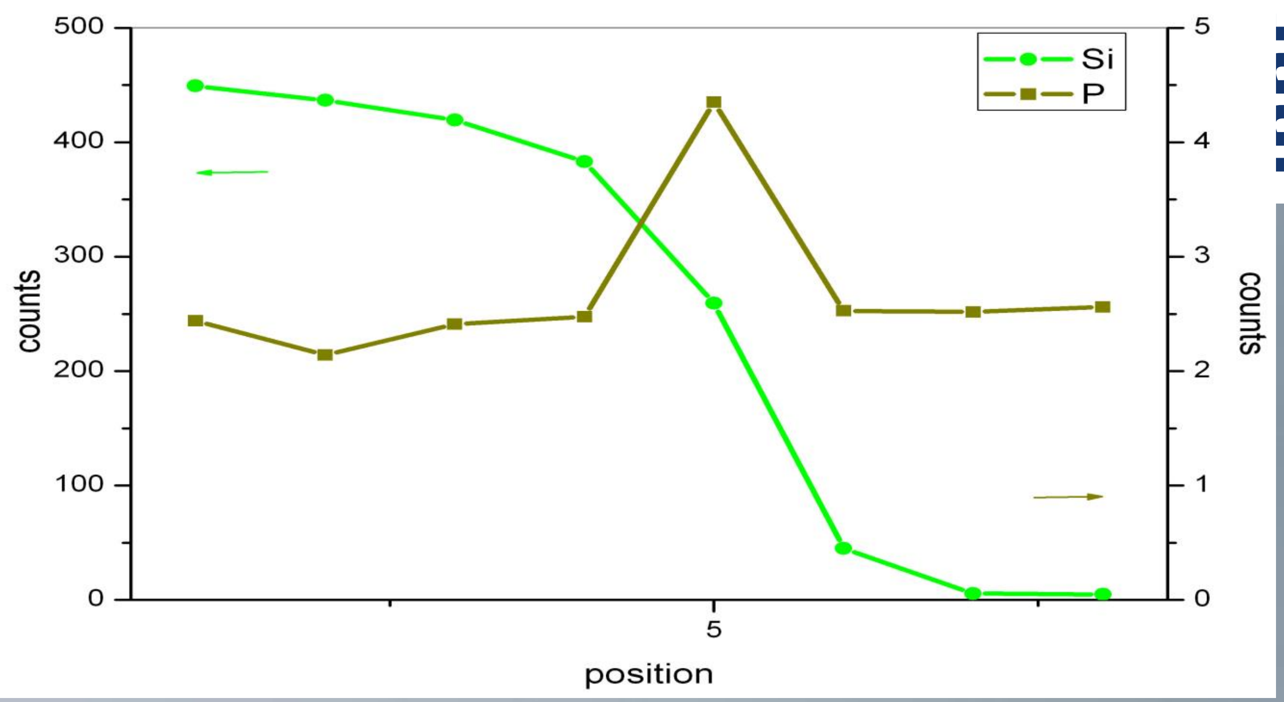


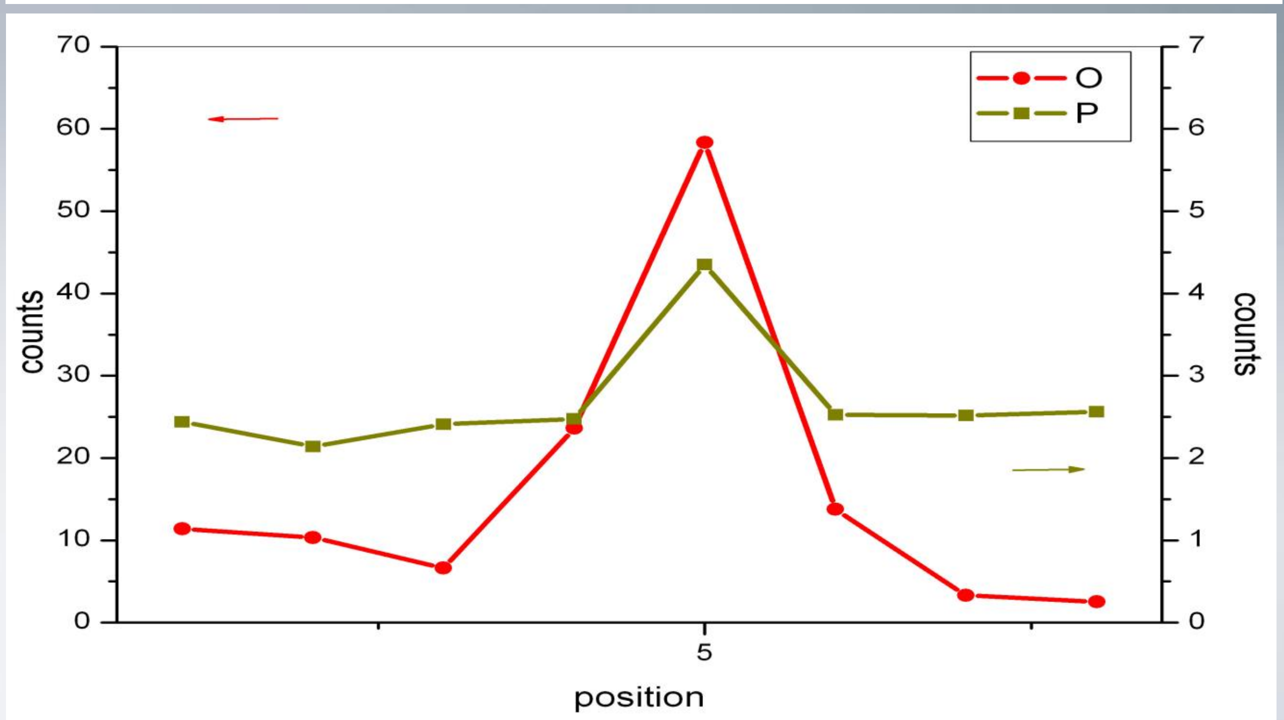




- **boron doping of NWs during growth (> $10^{18}$cm$^{-3}$)**
- **tapering of NWs**
- **different NW density and orientation**
- **easily nano-crystalline wires @ high doping levels**

# Post-growth Spin-on-Doping




Etched Si nanowires

# Doping of nanowires

- **Doping during CVD growth**
  - **Co-doping in growth chamber ($B_2H_6$, $B(CH_3)_3$, $PH_3$ besides $SiH_4$)**

- **Trade off between high doping levels & good materials quality;**
- **dopant gradients within NWs**

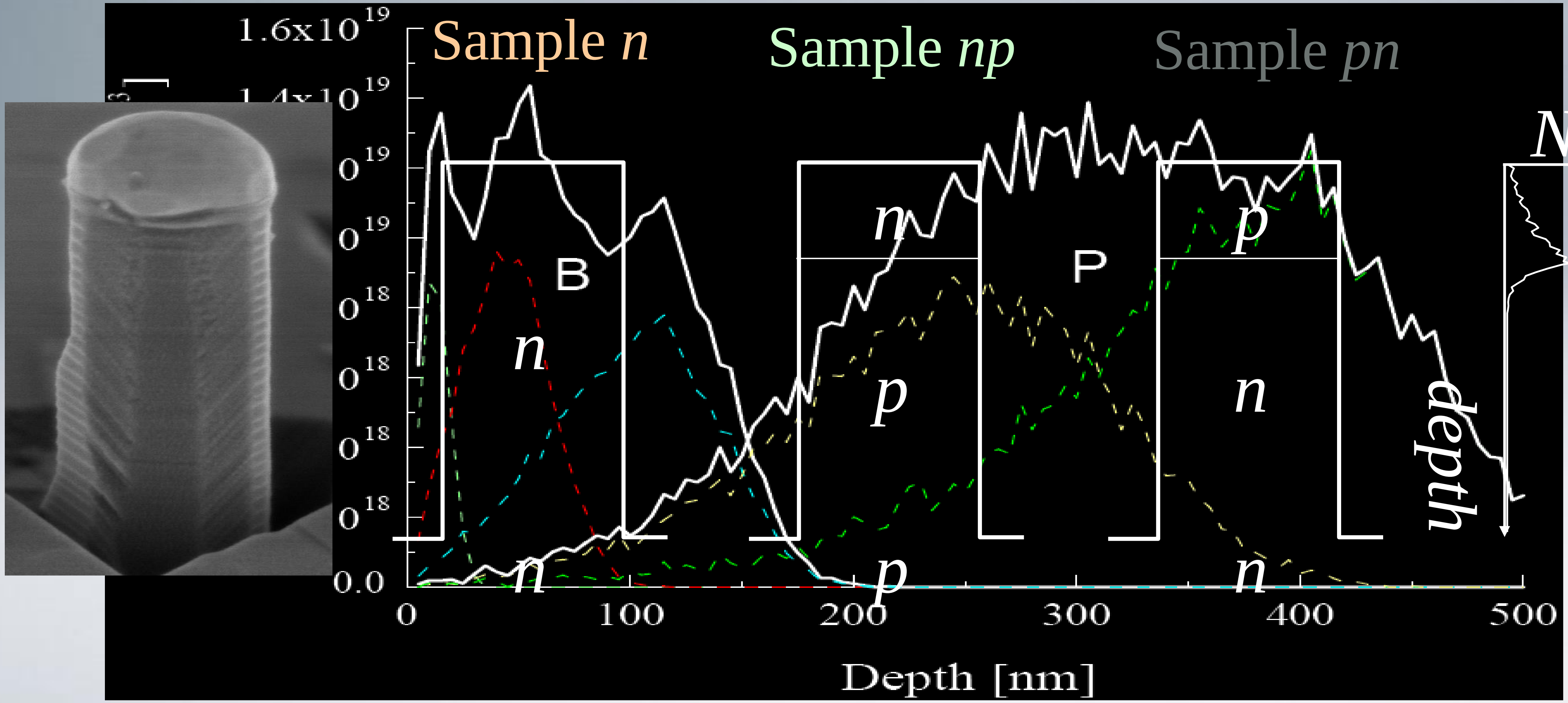
- **Post-growth doping**
  - **Spin on doping**
  - **Gaseous environment**

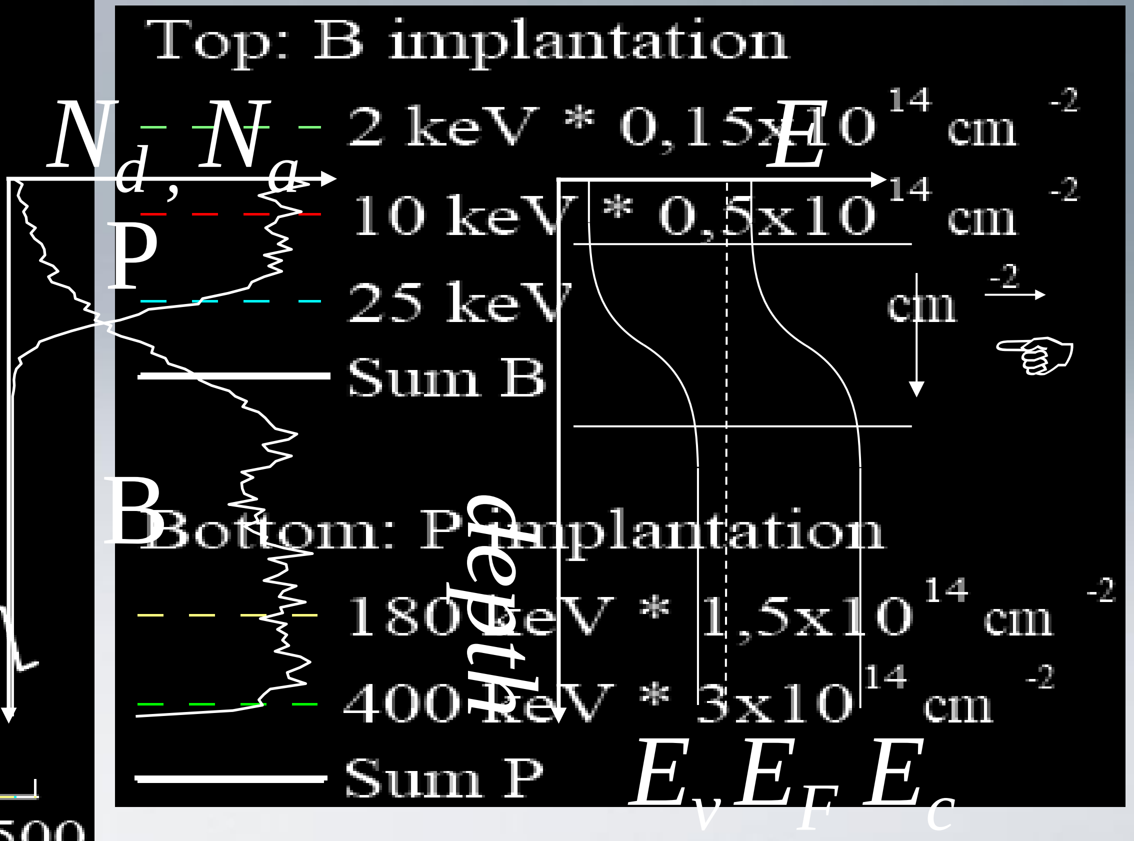
- optimized t/T schemes for annealing to be determined;
- homogeneous dopant distribution possible?
- full NW doping possible?

Mitglied der Leibniz-Gemeinschaft

# Doping of nanowires by Ion implantation

- Advantage: Control over doping profile
- Disadvantage: additional processing steps
- Novelty in nanowires: diodes realized (working device)





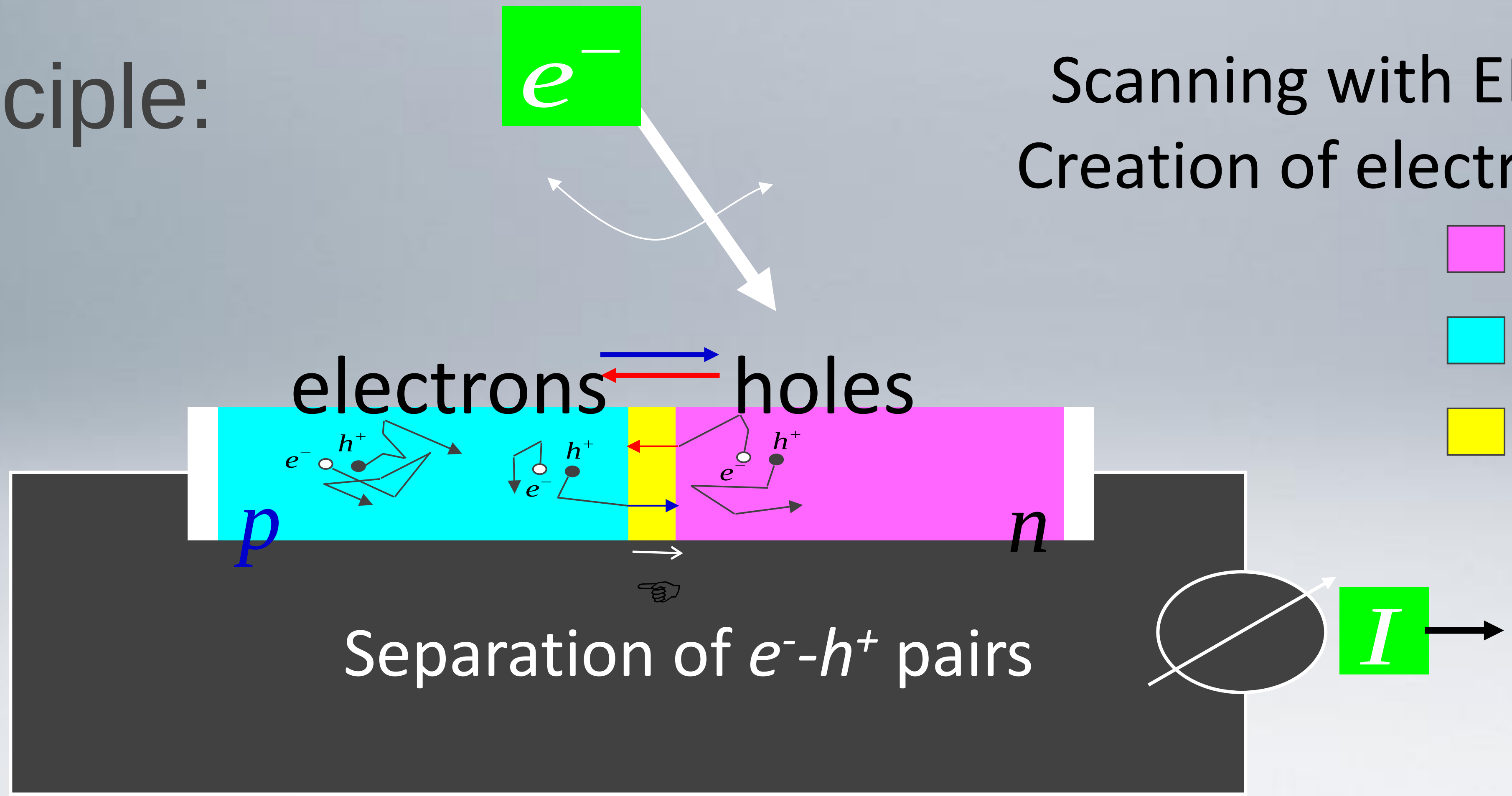

S. Hoffmann, VAS et al., Nano Letters 9 (4), 1341–1344 (2009)

# Electron Beam Induced Current (EBIC)

- EBIC to locate *p*-*n* junctions

  - EBIC = Electron Beam Induced Current

  - Principle:




Scanning with EBeam of SEM:
Creation of electron – hole pairs

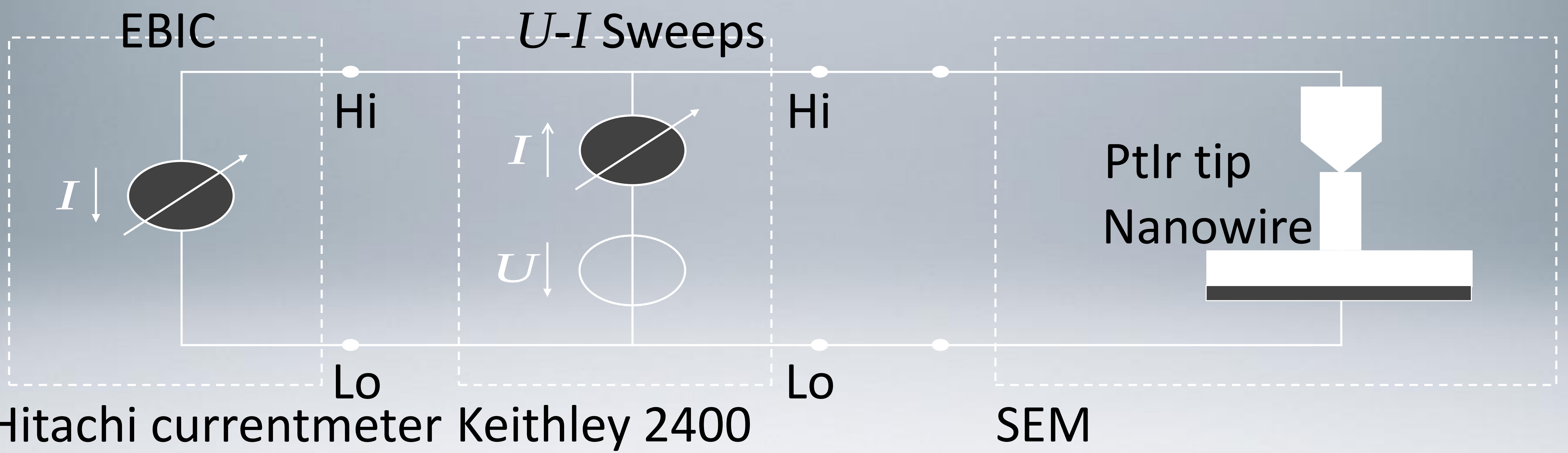
- *n* doped
- *p* doped
- Depleted region

Image based on current flowing at each pixel

S. Hoffmann, VAS et al., Nano Letters 9 (4), 1341–1344 (2009)

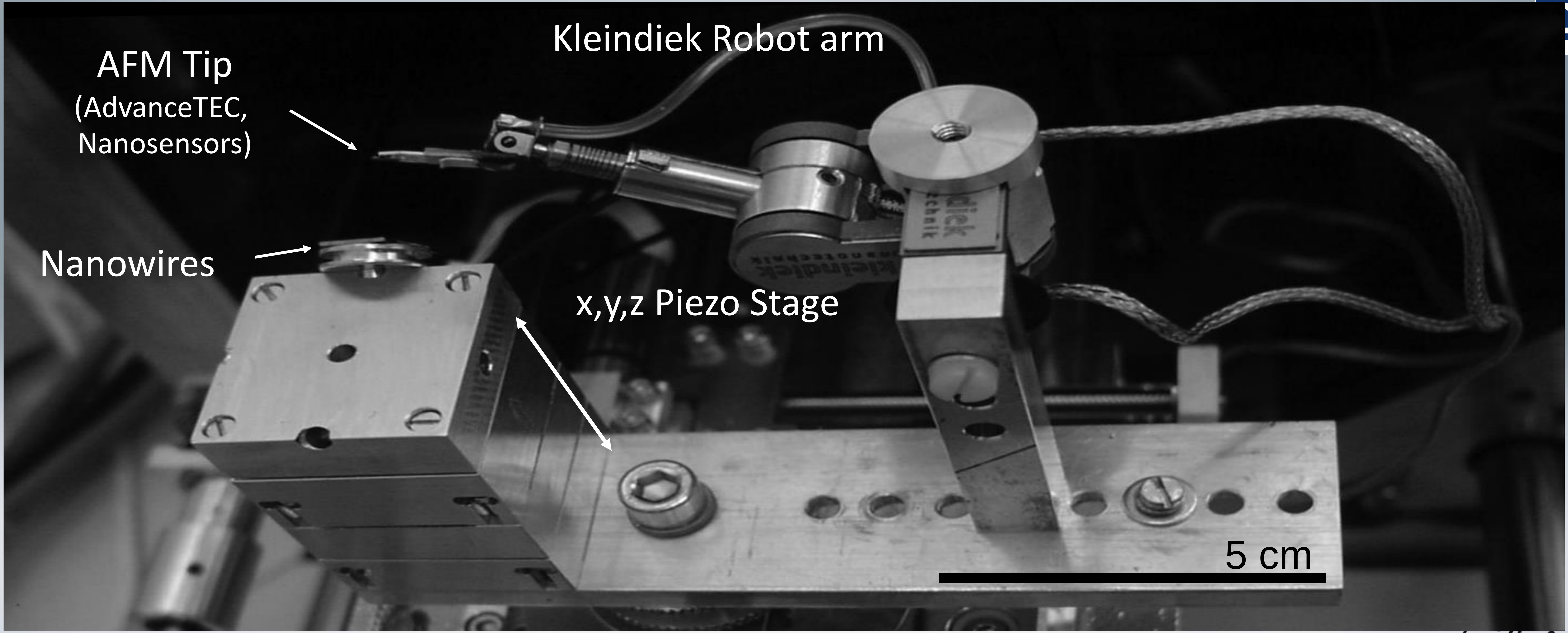
# Junctions in ion implanted nanowires

- Nanomanipulator equiped with PtIr tips




**S. Hoffmann, VAS et al., Nano Letters 9 (4), 1341–1344 (2009)**

# Nanomanipulator Setup



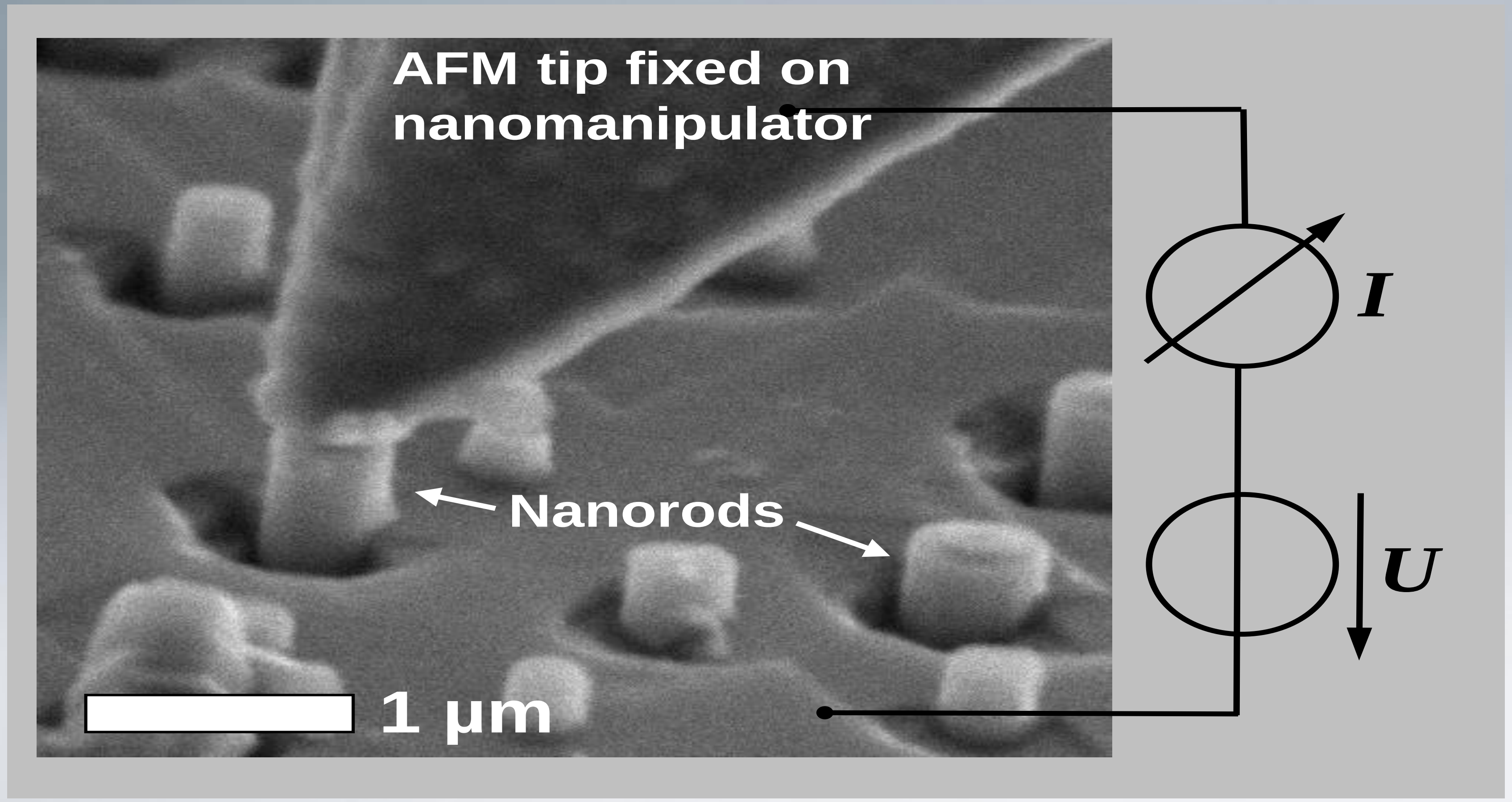
# Junctions in ion implanted nanowires

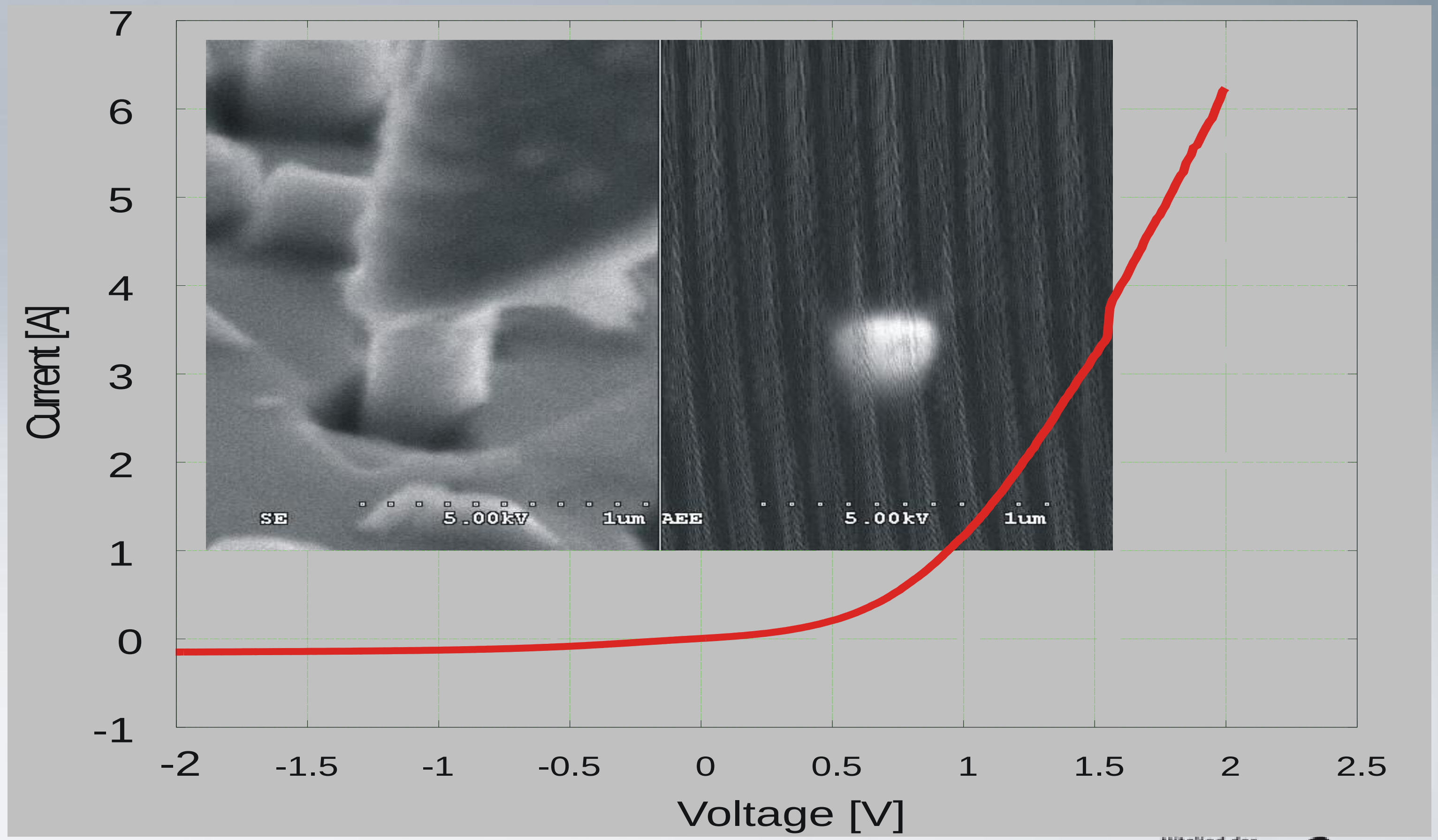
Pt(90)/Ir(10)-tip: Schottky contact for *n* doped (P, 1.2 × $10^{19}$cm$^{-3}$; resistivity in Si~$10^{-2}$Wcm;
NW: d=200nm x l=400nm → resistance ~100kW) SiNWs

$R^{up}$ tells that the NWs have successfully been doped by implantation & annealing

$R^{up}$ undoped Si NWs: 4 orders of magnitude higher resistivity

EBIC signal at contact interface



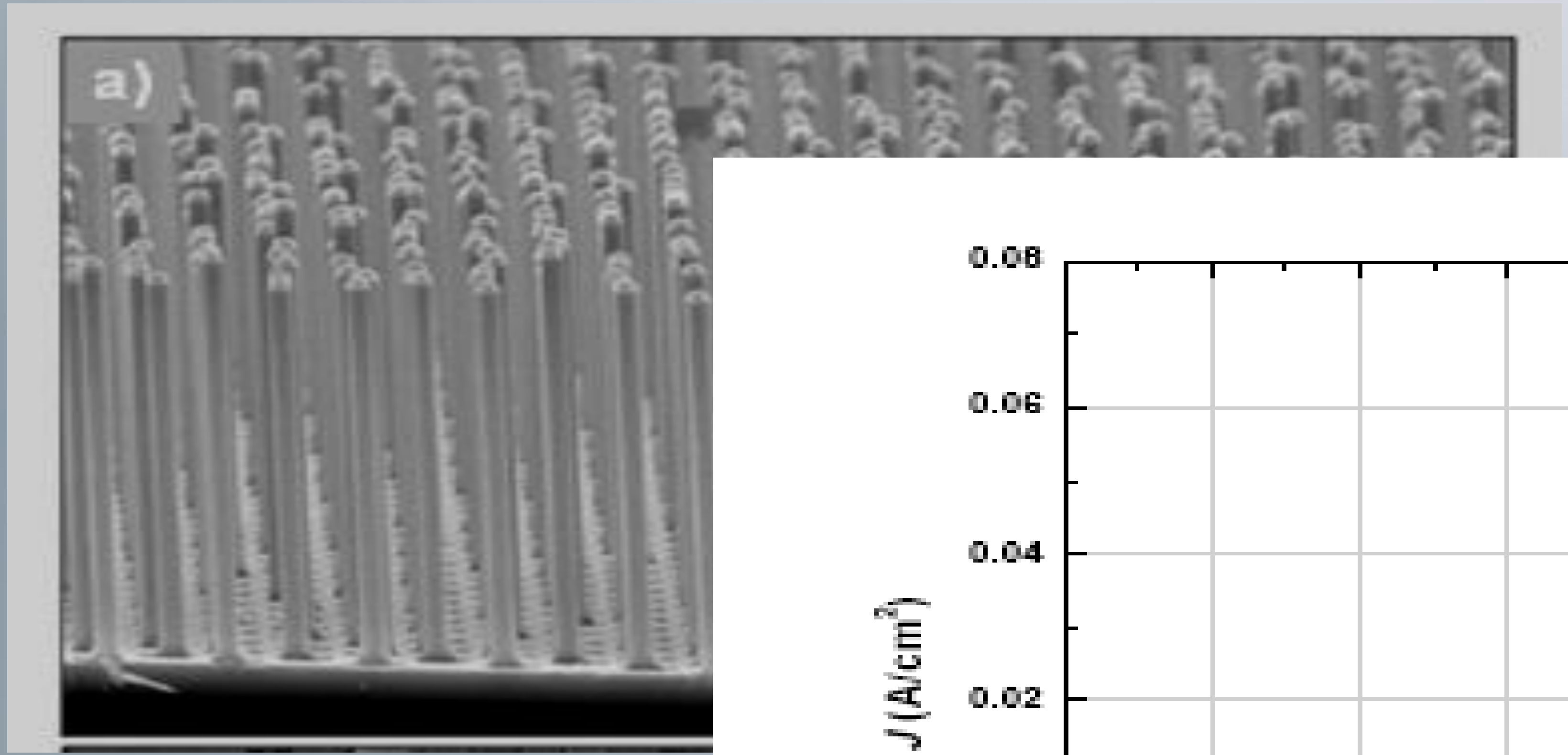



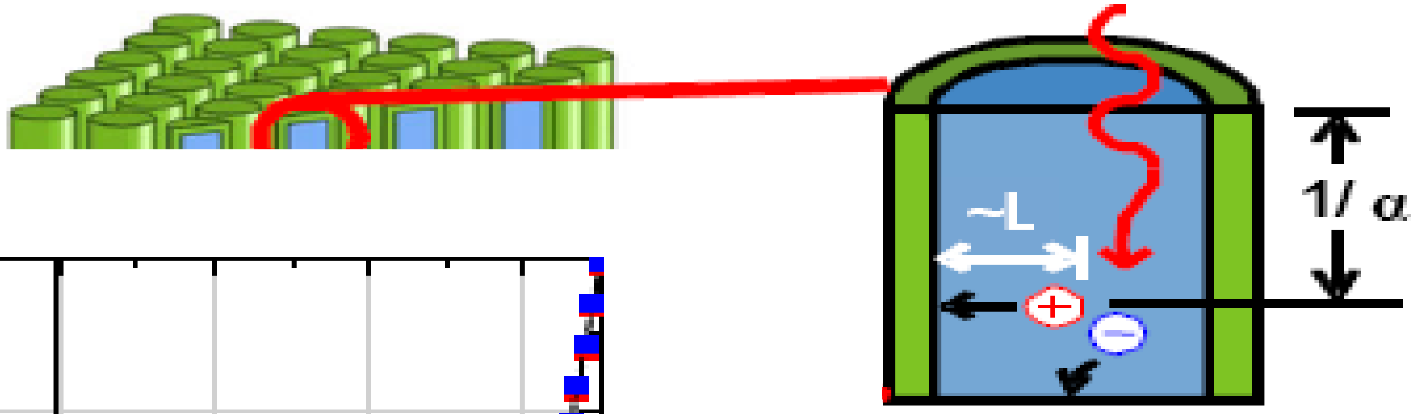

S. Hofmann, et al., Nanolett., in press

# Conclusions

- pn-junctions in NWs by respective doping
  - Successful realization of pn-junctions in working diodes by ion implantation
  - High doping levels realized ($10^{19}cm^{-3}$)
  - Good flexibility in choice of doping levels
  - Suitable junction abruptness by portion wise doping (various implantation energies used to dope at different depths from the surface; dopant concentrations add up to a net doping profile)
- Electrical characterization of nanowires
  - EBIC is used to identify the pn-junction area
  - In situ IV-measurements (nanomanipulation setup in an SEM) used to identify doping level and NW resistivity

# Solar Cell Based on SiNWs




ı of the radial pn junc-
ıt on the top surface.
ırs of the high-aspect
s optically thick (thick-
ption coefficient of the
ıority carriers are less
ınction.

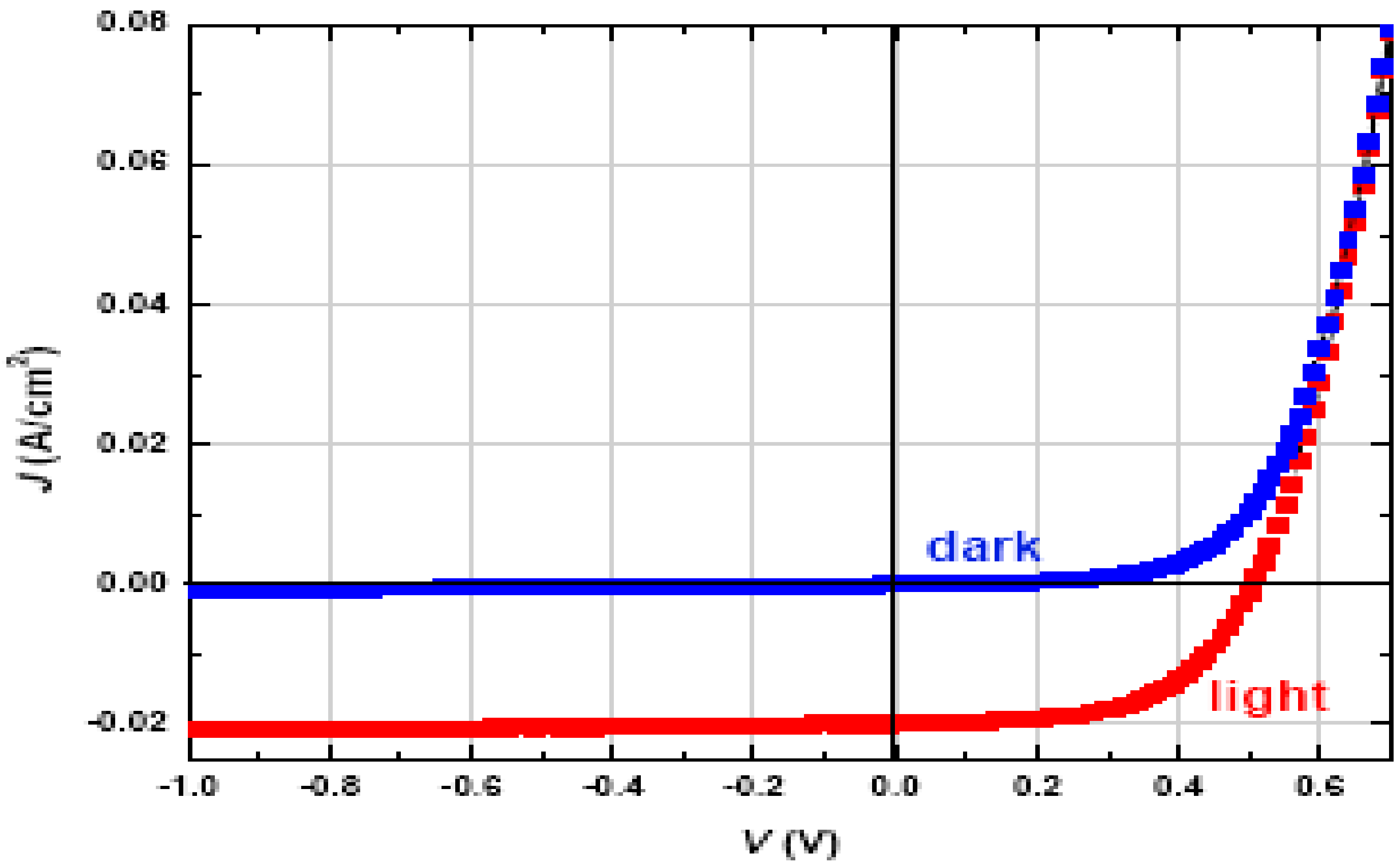
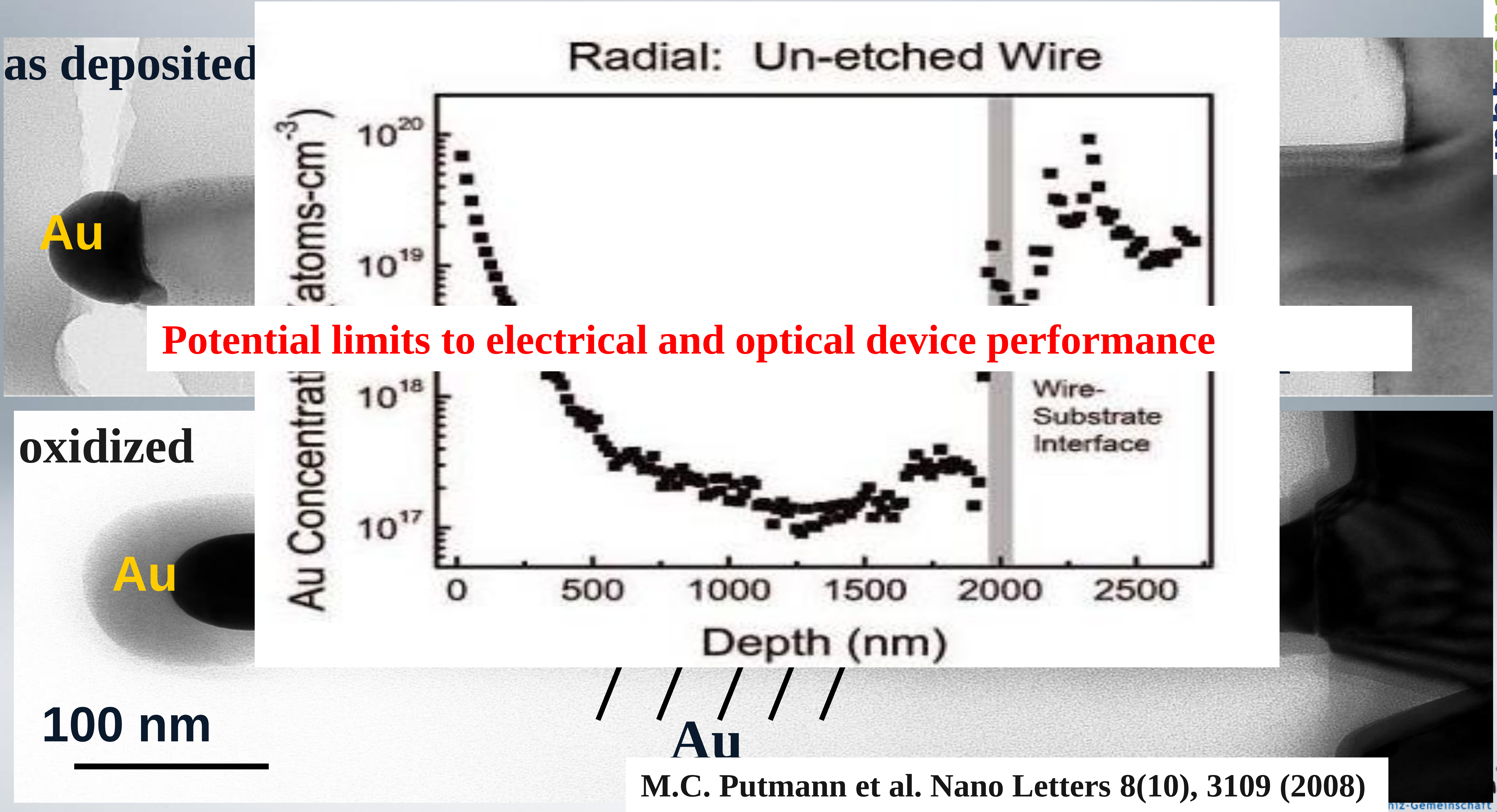



**Fig. 4.** *J*-*V* curve for measured 5 μm-diameter wire array. Efficiency = 5.7%, $V_{oc}$ = 505 mV, $J_{ss}$ = 19.7 mA/cm$^2$, *FF* = 57.7 %, total cell area 12.9 mm$^2$, wire array area 4 mm$^2$.

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

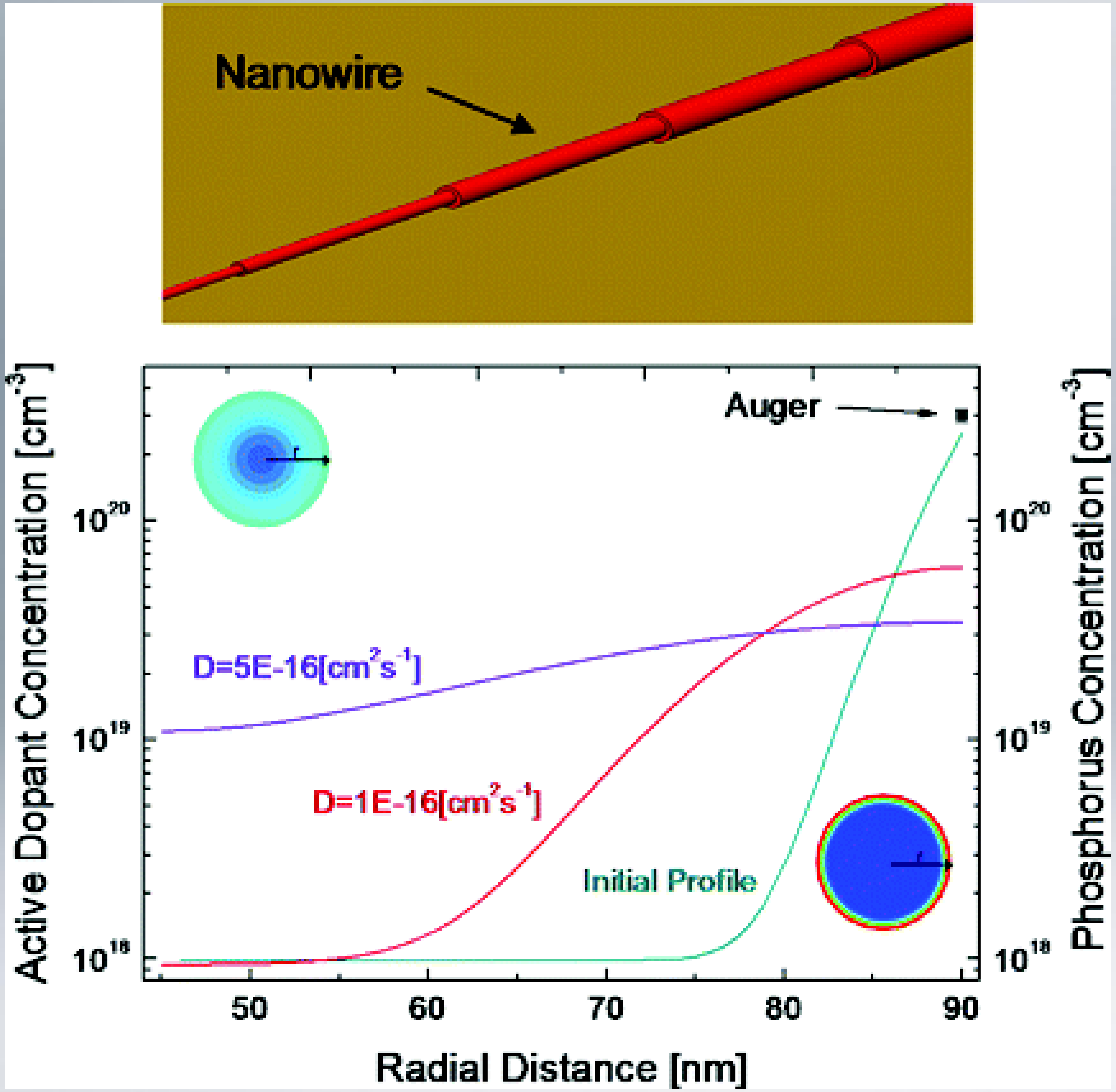
Mitglied der Leibniz-Gemeinschaft

# Problematic: Gold Contamination




**Potential limits to electrical and optical device performance**

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

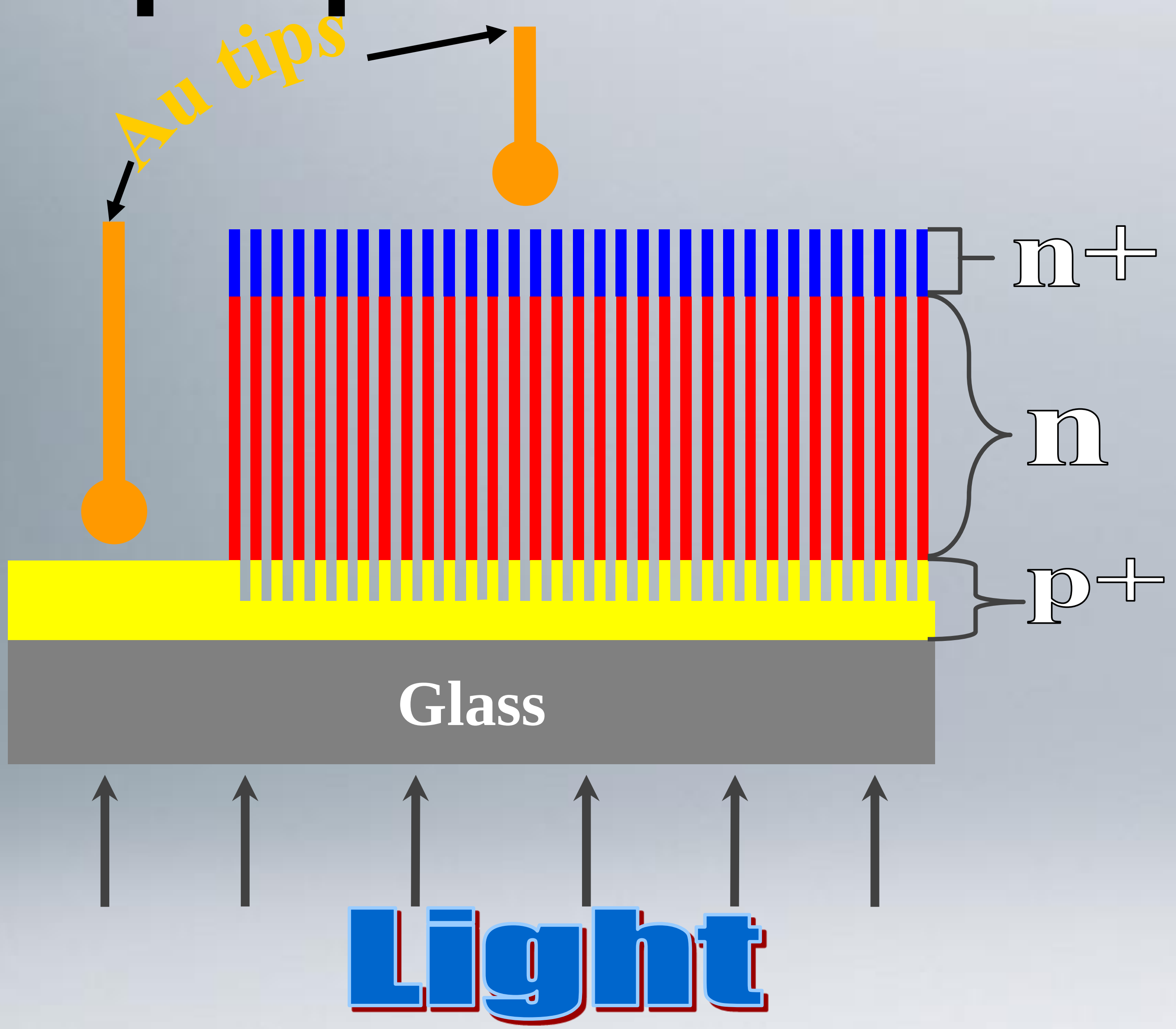


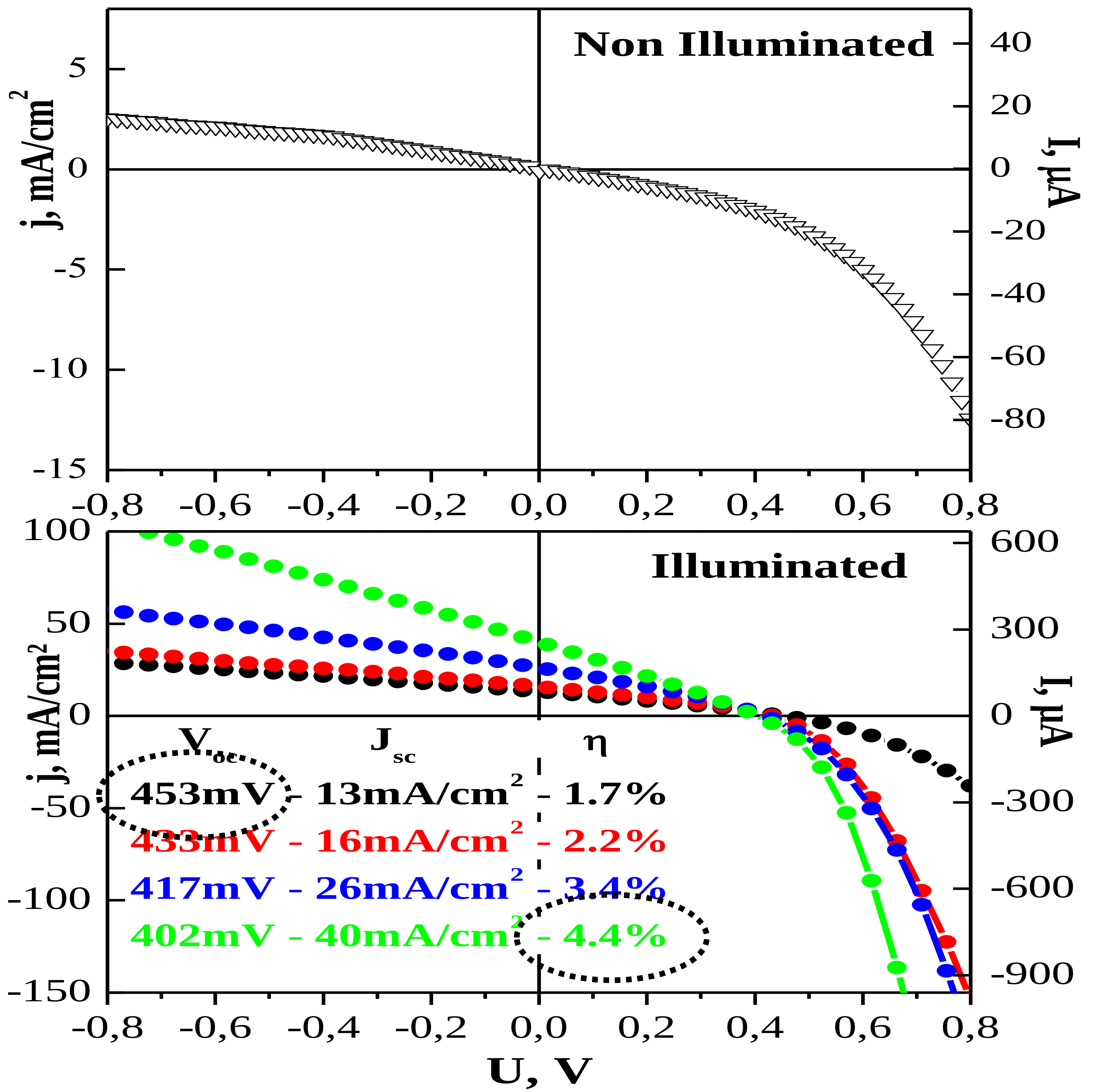

Koren et al., Nano Lett., 2011, 11 (1), pp 183–187

Semiconducting nanowires grown by the vapor−liquid−solid method commonly develop nonuniform doping profiles both along the growth axis and radially due to unintentional surface doping and diffusion of the dopants from the nanowire surface to core during synthesis. We demonstrate two approaches to mitigate nonuniform doping in phosphorus-doped Si nanowires grown by the vapor−liquid−solid process. First, the growth conditions can be modified to suppress active surface doping. Second, thermal annealing following growth can be used to produce more uniform doping profiles. Kelvin probe force microscopy and scanning photocurrent microscopy were used to measure the radial and the longitudinal active dopant distribution, respectively. Doping concentration variations were reduced by 2 orders of magnitude in both annealed nanowires and those for which surface doping was suppressed.

Leibniz-Gemeinschaft

# PV properties of solar cell based on SiNWs



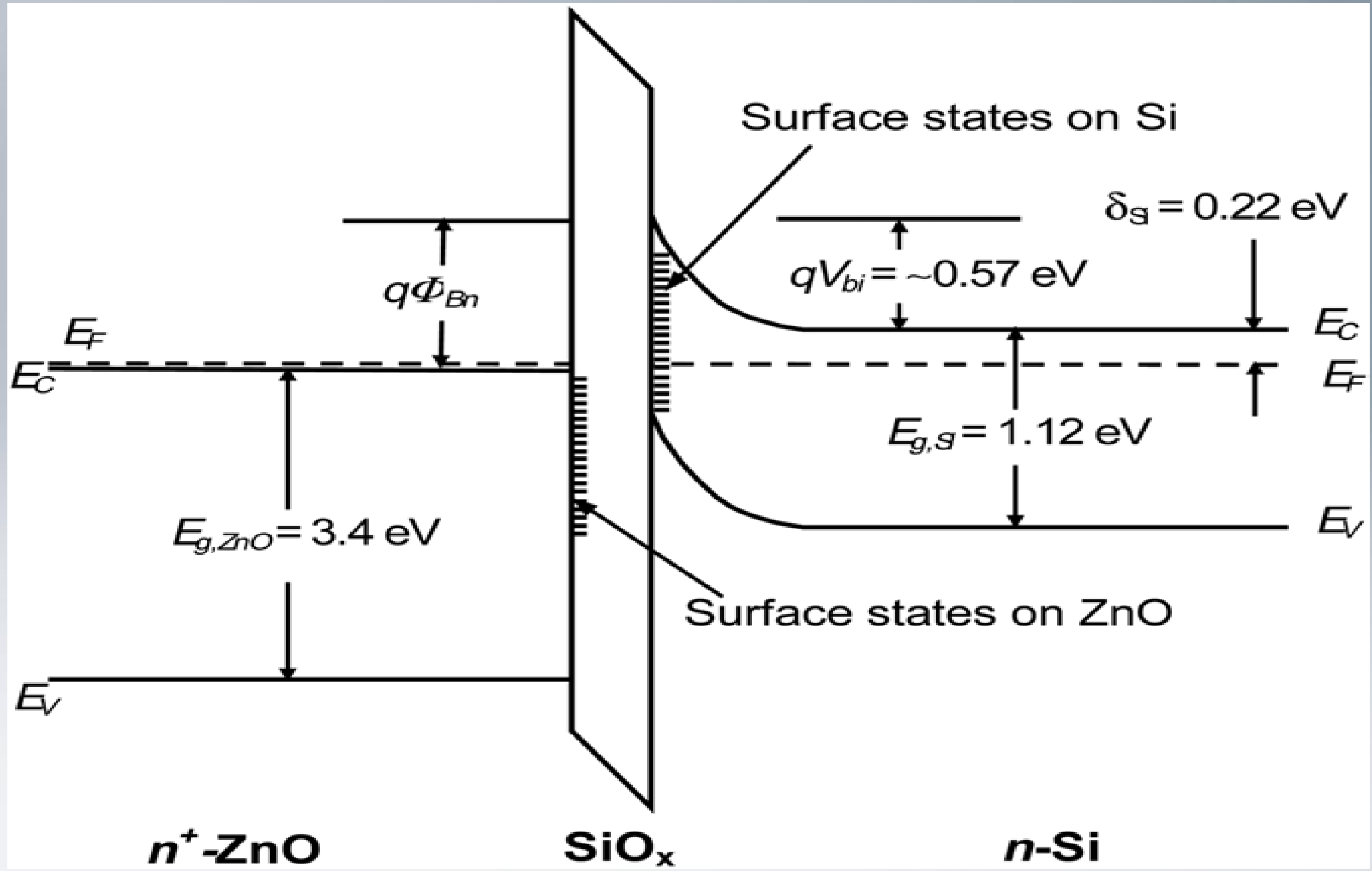




Non illuminated and illuminated (AM1.5) I-V curves of SiNWs etched into a mc-p+nn+-Si layer on glass. SiNW are irradiated through the glass substrate (super-state configuration) and contacted by metal tips at four different sample positions.

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

# Backgroung:SIS-Diode

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




## Challenge:

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


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

# Conclusions

SIS_Cell.mp4

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

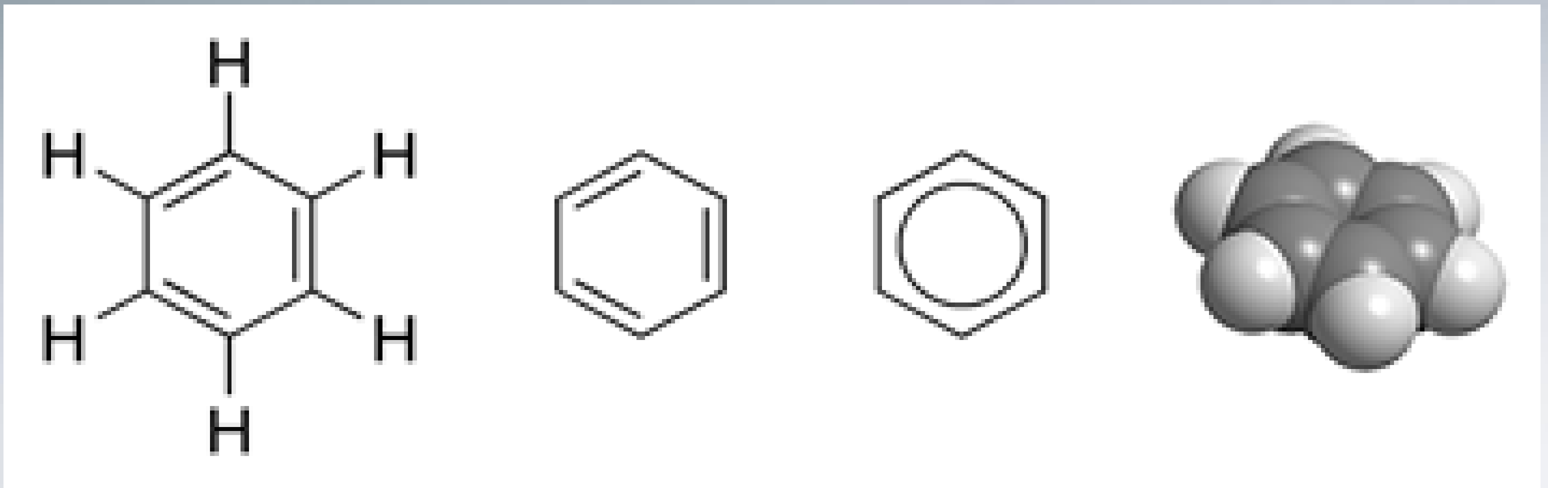
## Newton's Law of Gravity

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


**The Proverbial Apple**

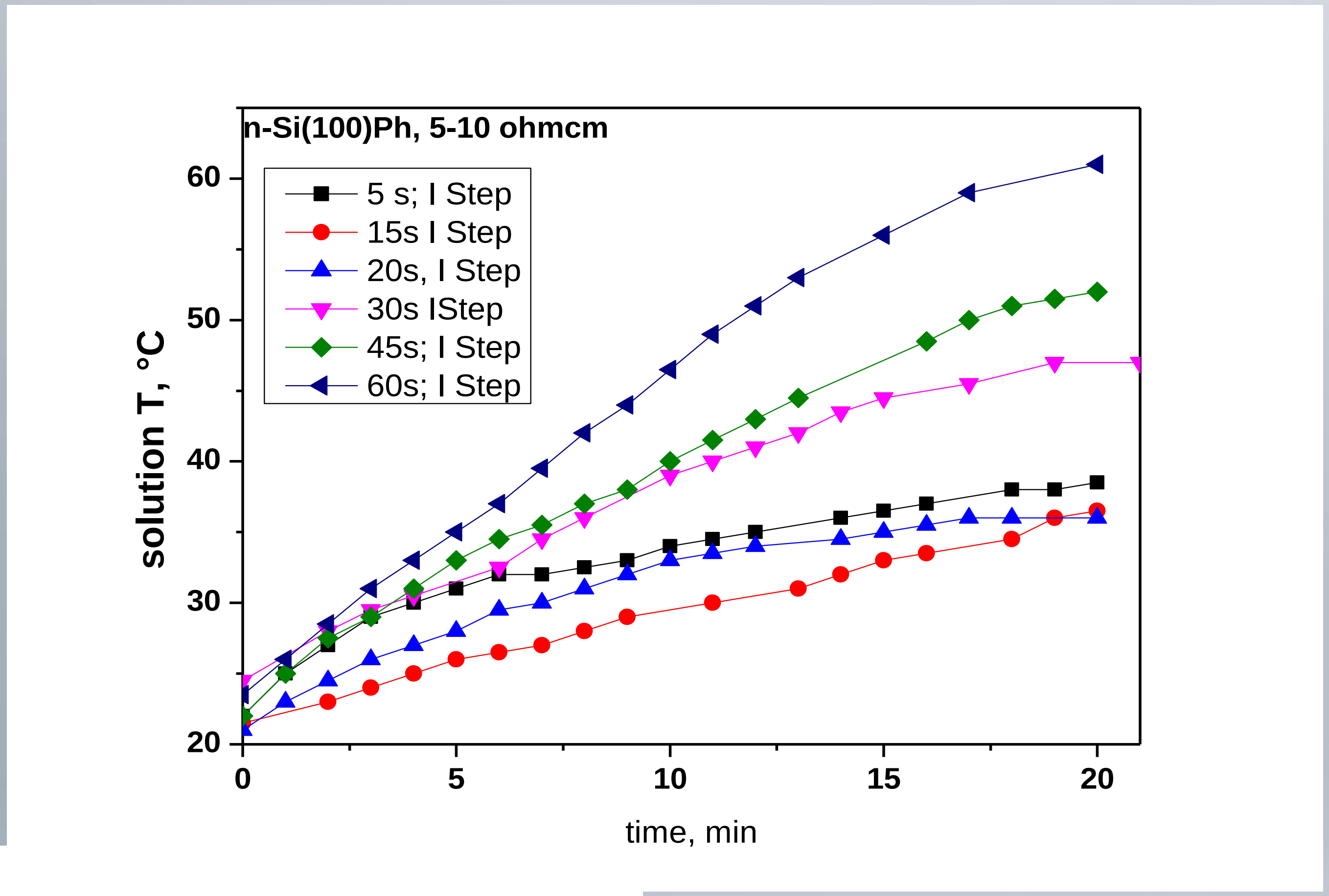
**The famous story that Newton came up with the idea for the law of gravity by having an apple fall on his head is not true, although he did begin thinking about the issue on his mother's farm when he saw an apple fall from a tree.**

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

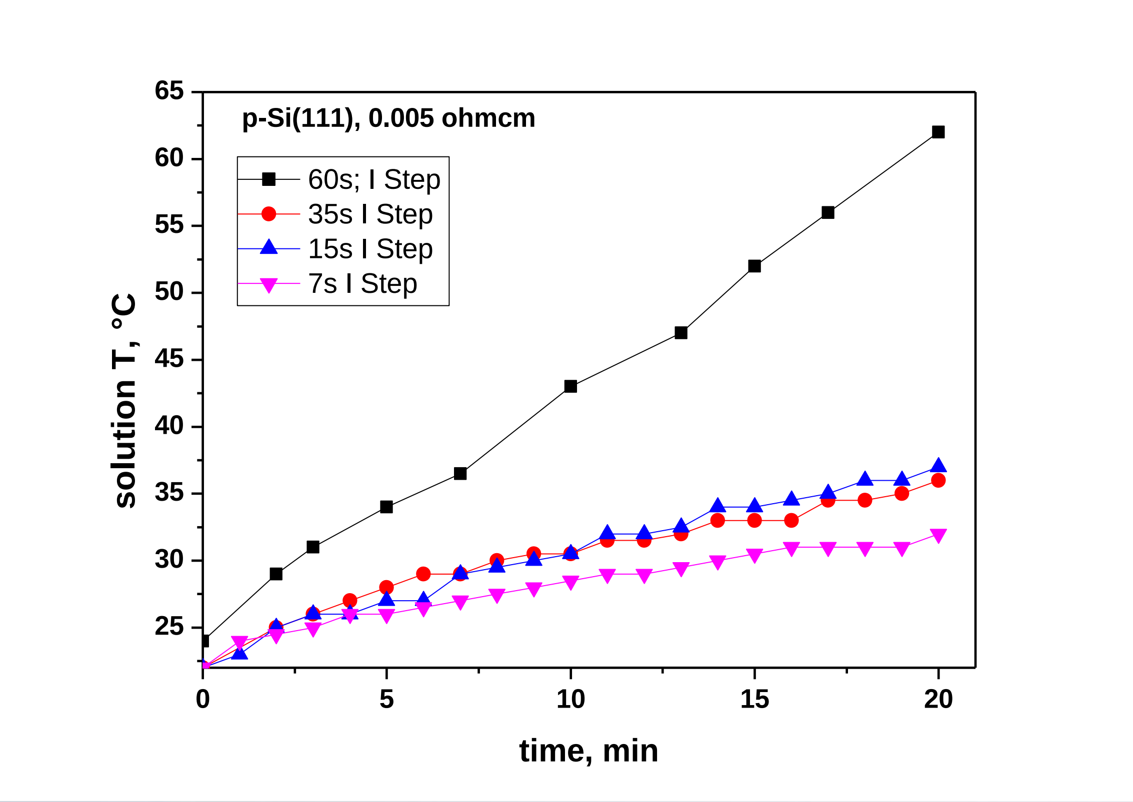


**Observation of <u>NATURE!!!!!!</u>**

# Energy Detachment




energy_detachment.AVI




**1l $H_2O$ 1K 4.2 kJ/1.16 Wh**

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

Mitglied der Leibniz-Gemeinschaft

iphtjena

# Solar Hydrogen

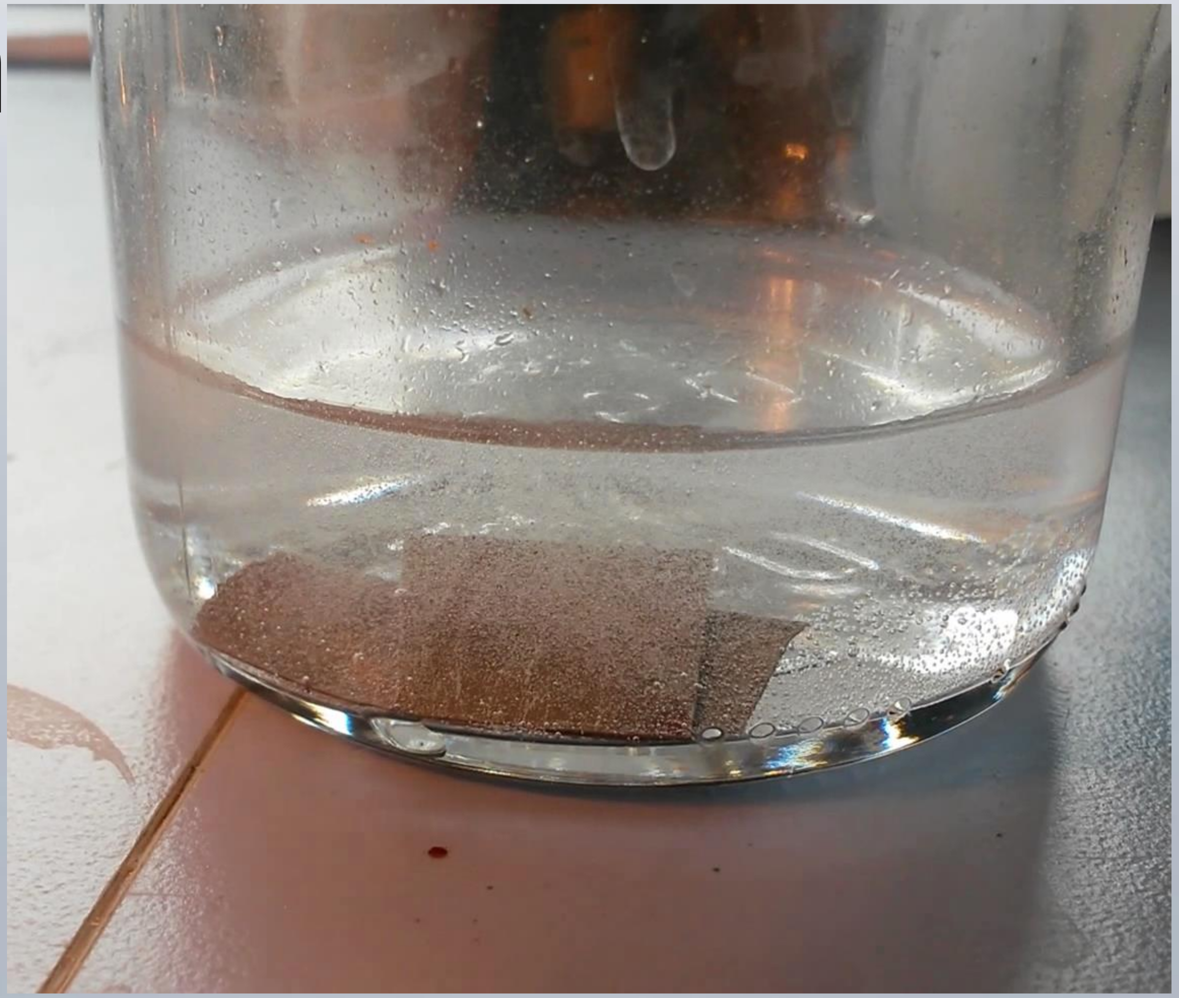
## Oxidation of Silicon

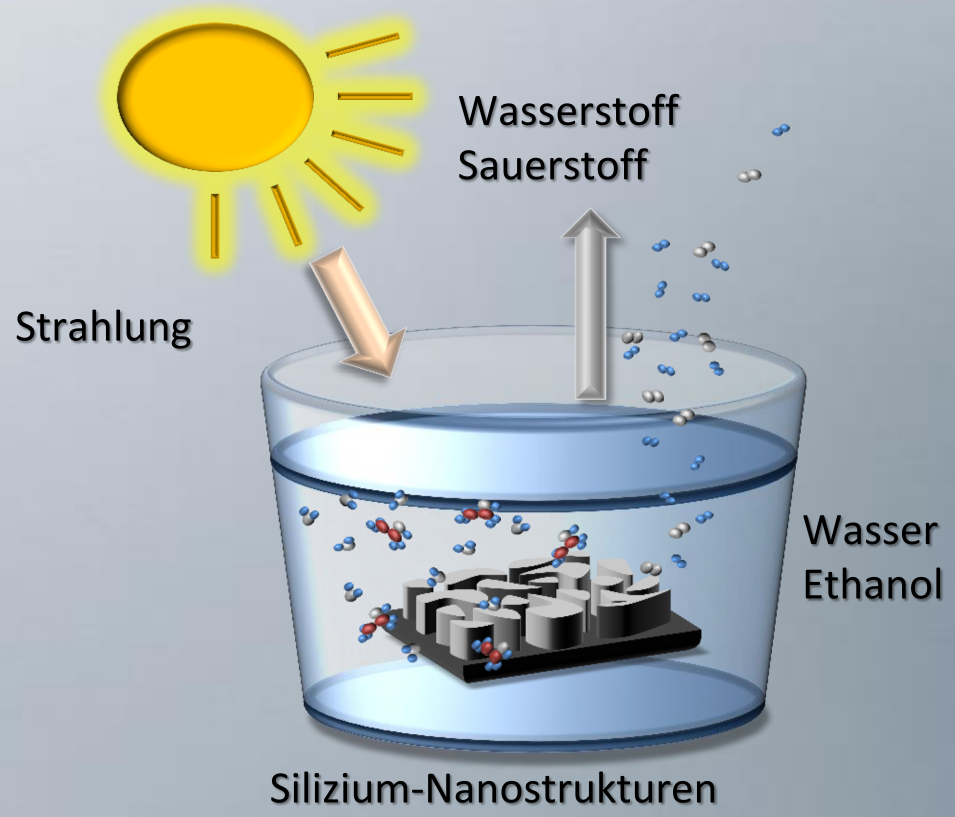
$$Si + h\nu \rightarrow e^- + h^+$$

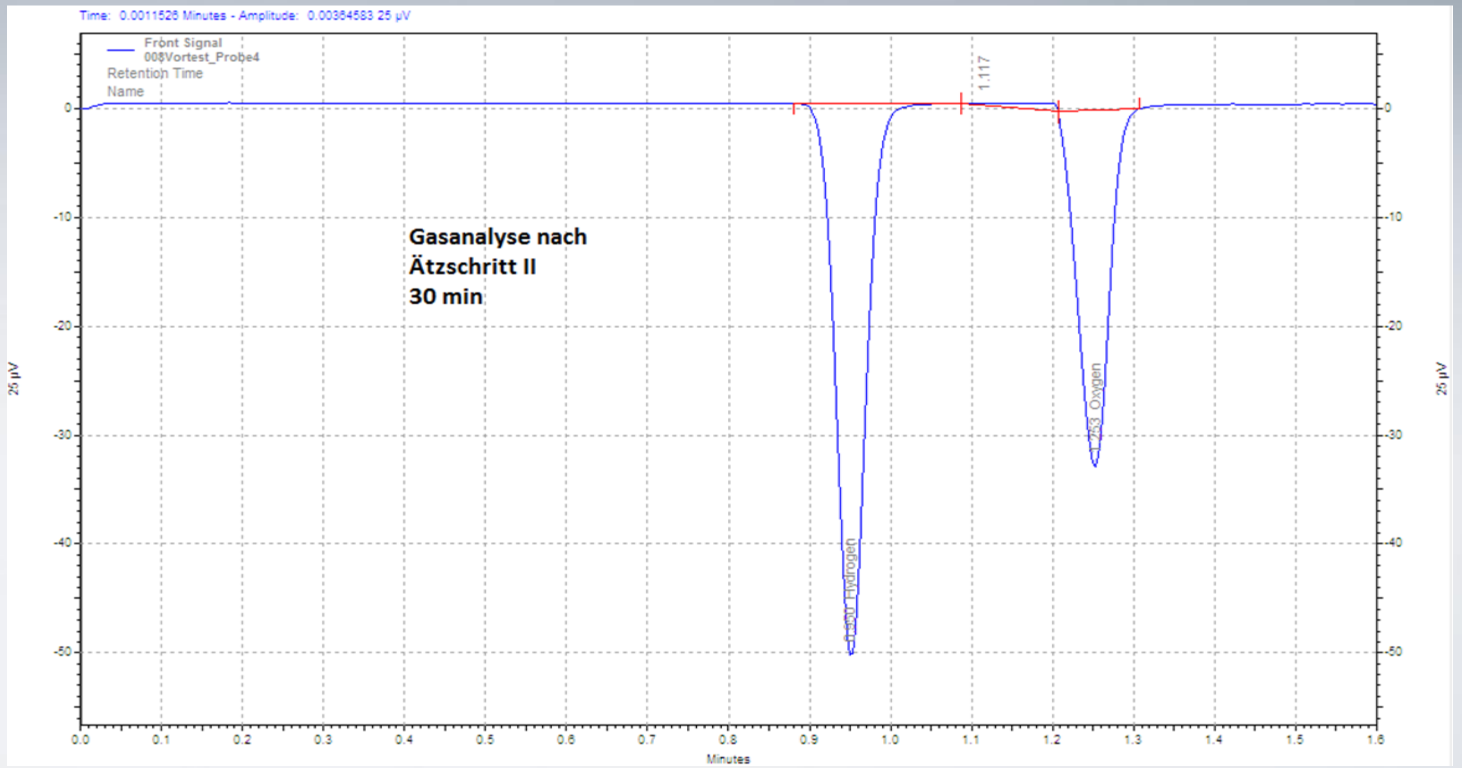
$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$

$$4H^+ + 4e^- \rightarrow 2H_2$$

$$\mathrm{Si} + 2H_2O \rightarrow SiO_2 + 2H_2$$





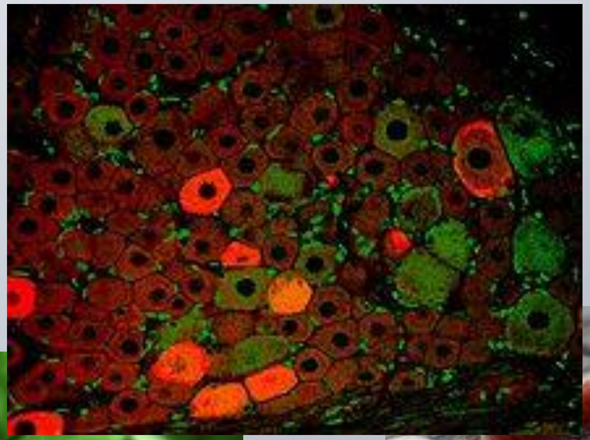
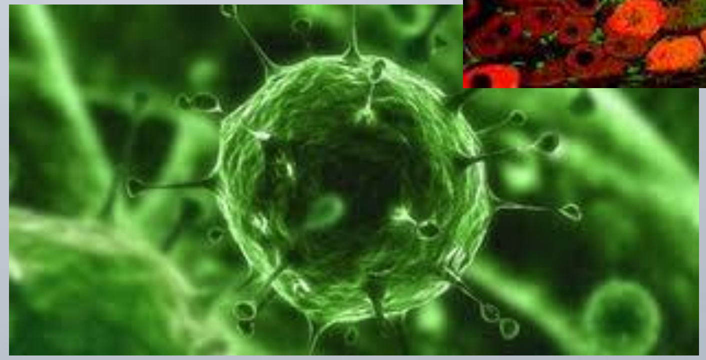
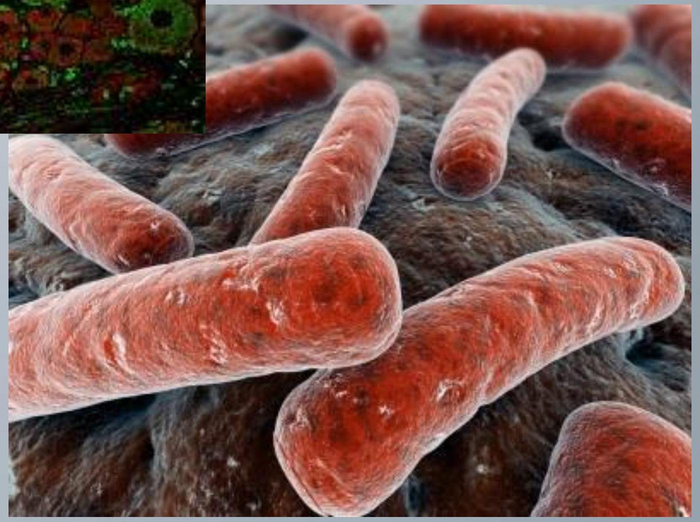




**1g 17.5 l $H_2$**

# 5. Silicon Nanoparticles in Biomedicine

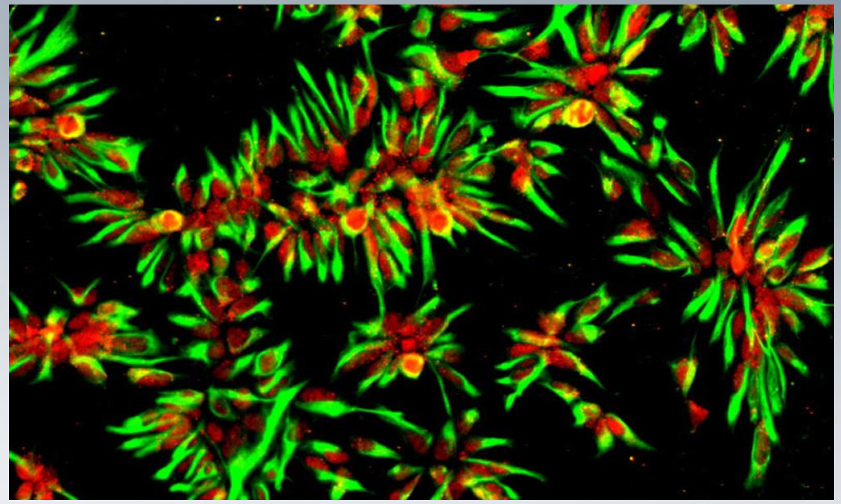
Mitglied der
Leibniz-Gemeinschaft

# Motivation

**Advanteges:** - high porosity
- low Cytoxicity
- Metabolism in der Lever
- Photoluminescence
- formation simplicity

Application in Theranostics: **Thera**py + Diag**nostic**



→ Cancer markers and treatment (Drug-Delivery-Agent) [1]

→ Antibacterial/Antiviral Effects [2][3]

→ non toxic, fluoreszierende Farbstoffe für Multi-Photonenmikroskopie [1][3]

[1] Norah O'F. et al: „Silicon nanoparticles: applications in cell biology and medicine"
[2] Elena P. et al: „Bactericidal activity of black silicon"
[3] Wendelin S.: „Nanopartikel in biologischen Systemen"

# Existing Biomaterials for DDS

**Carbon nanotubes**

- „-“: are not metabolized → must be eliminated after administration

**Bio-Glass**

- one of the first completely synthetic materials that seamlessly bonds to bone; developed by Prof. L.Hench in 1967
- „-“: containes at least four components ($SiO_2$, $Na_2O$, CaO, $P_2O_5$) that may influence negatively under certain conditions

(! Microporous Si showed much less level of Ca and Na)

**Q-Dots**

- used as dyes (20 times brighter and 100 times more stable than commonly used fluorescent dyes)
- „-“: in vivo toxicity! → Inhibition of the cell growth and viability, especially cadnium (CdSe) or lead-containing QDs

Mitglied der Leibniz-Gemeinschaft

# Biomedical Application of Silicon

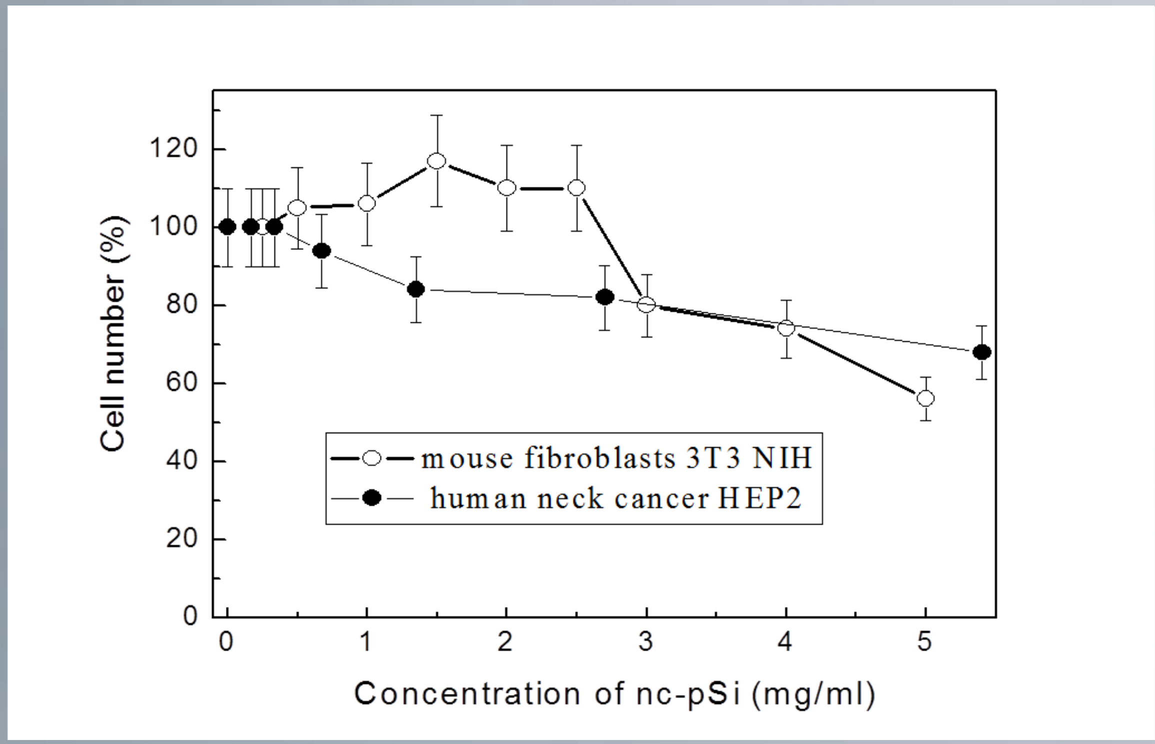
1990 **Prof. Leigh Canham →  PL properties of SiNPs** (new approach of manufactory by electrochemical and chemical dissolution steps → two-dimensional quantum size effects → emission far above the band gap of bulk crystalline Si)

1995 → **in vitro studies** of microporous Si films in simulated body fluids

→ Induced hydroxyapatite growth on Si that is absent in isolation
→ Bioactivity of porous Si: bonding with living soft tissue and bone
→ Resorbability of porous Si
→ Biocompatibility of porous Si
→ Low toxicity
→ Biodegradable
→ Luminescent → Bioimaging
→ Drug delivery


- **L. T. Canham, „Bioactive silicon structure fabrication through nanoetching techniques", *Adv. Mater.*, 7, 1995**
- **L. T. Canham, „Bioactive polycrystalline silicon", *Adv. Mater.*, 8, 1996**
- **L. T. Canham, „The effects of DC electric currents on the in-vitro calcification of bioactive silicon wafers", *Adv. Mater.*, 8, 1996**

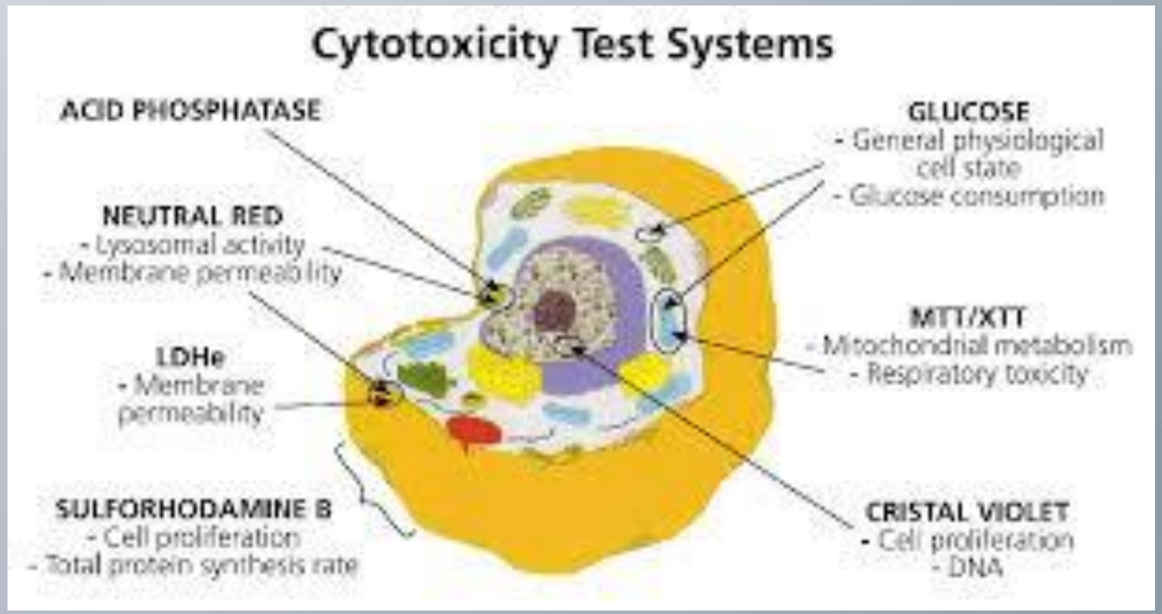
# Requirements for delivering materials

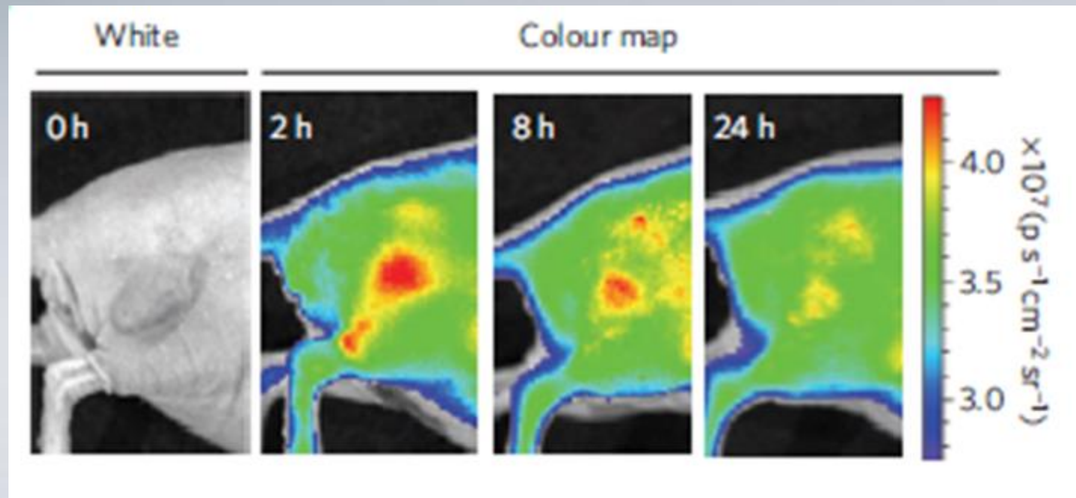



**Toxicity**

**Biocompability**

**Biodegradation**



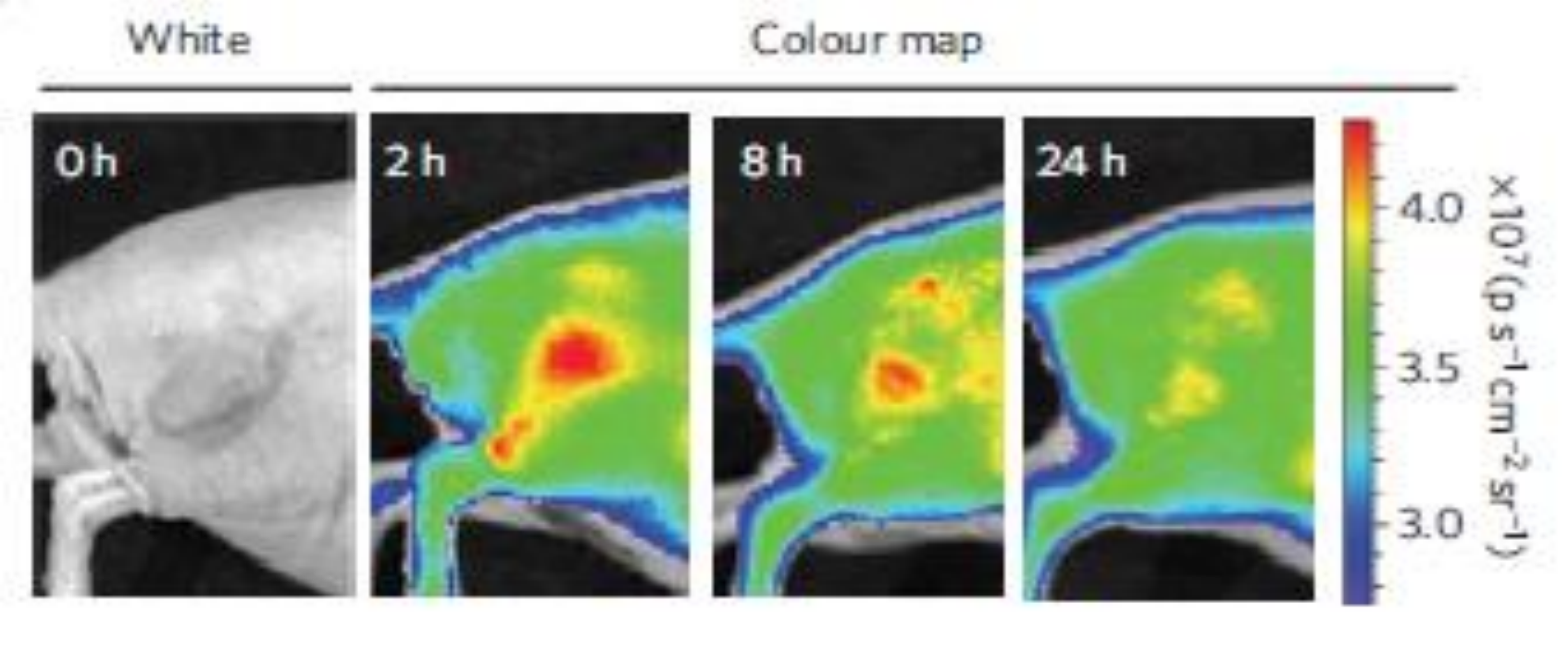

M. Sailor et al., Nature Materials 8, 332 (2009);Biomaterials 24, 1959 (2003)

# In vivo monitoring of Silicon

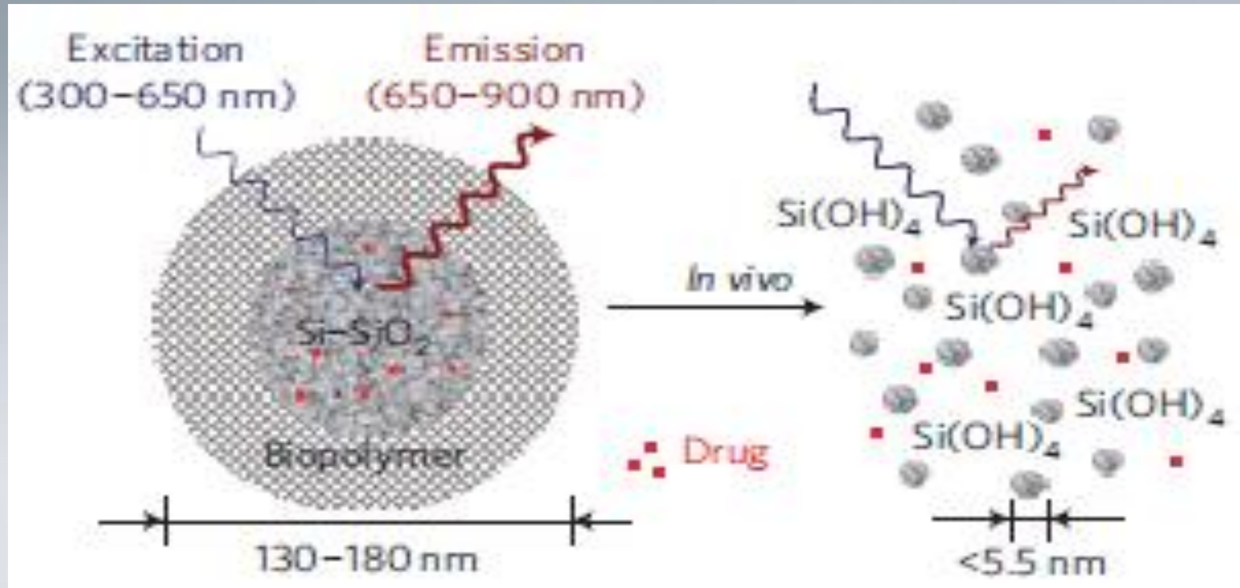
nature materials LETTERS
PUBLISHED ONLINE: 22 FEBRUARY 2009 | DOI: 10.1038/NMAT2398

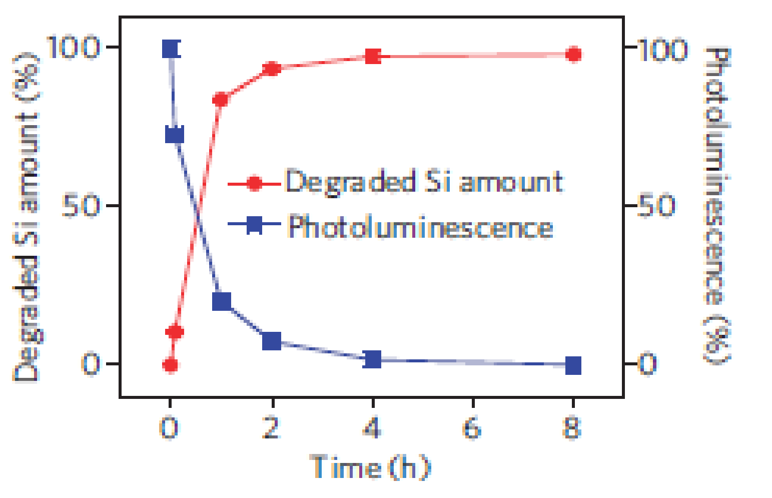
## Biodegradable luminescent porous silicon nanoparticles for *in vivo* applications

Ji-Ho Park[1,2], Luo Gu[1], Geoffrey von Maltzahn[3], Erkki Ruoslahti[4], Sangeeta N. Bhatia[3,5,6] and Michael J. Sailor[1,2,7]*



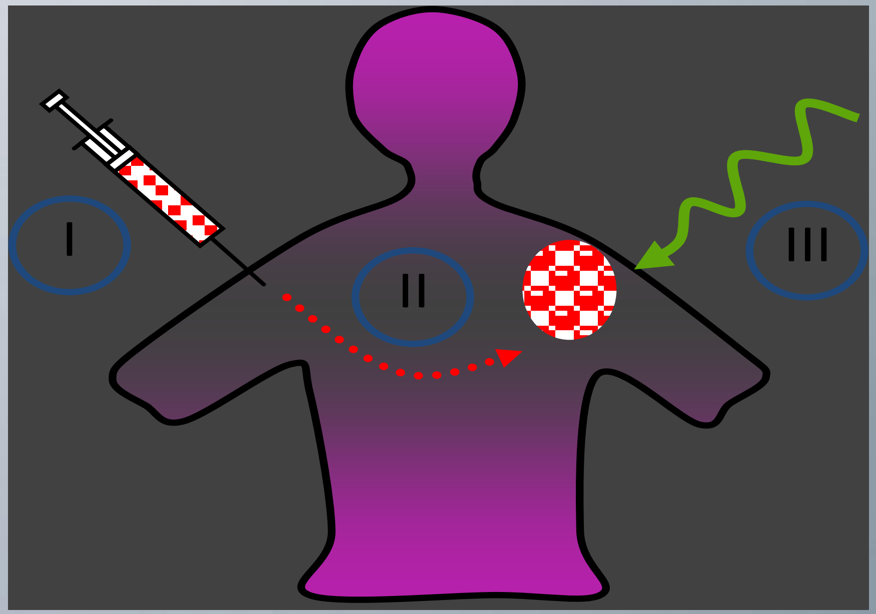

## Nanocontainers from Porous Si NPs




→ Injected PSi particles are fully degraded into silicic acid and cleared by excretion via the kidneys

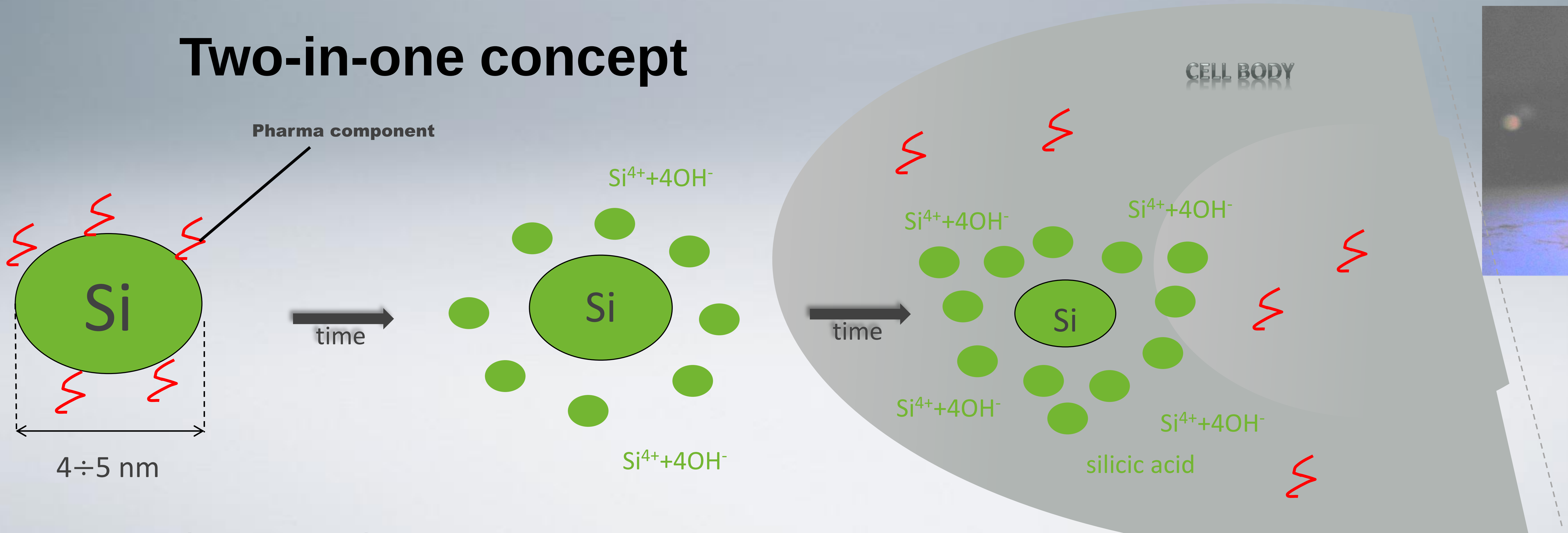
# THERANOSTICS THERAPY and DIAGNOSTICS.

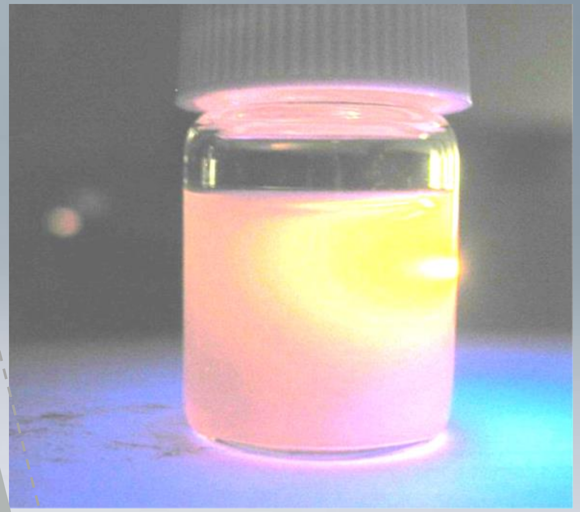



## Porous Si: non-toxic and biodegradable (bio-friendly)

- drug delivery carrier
- flexible therapy modalities (photo-, thermo-, ultrasound, em-rf, etc.)

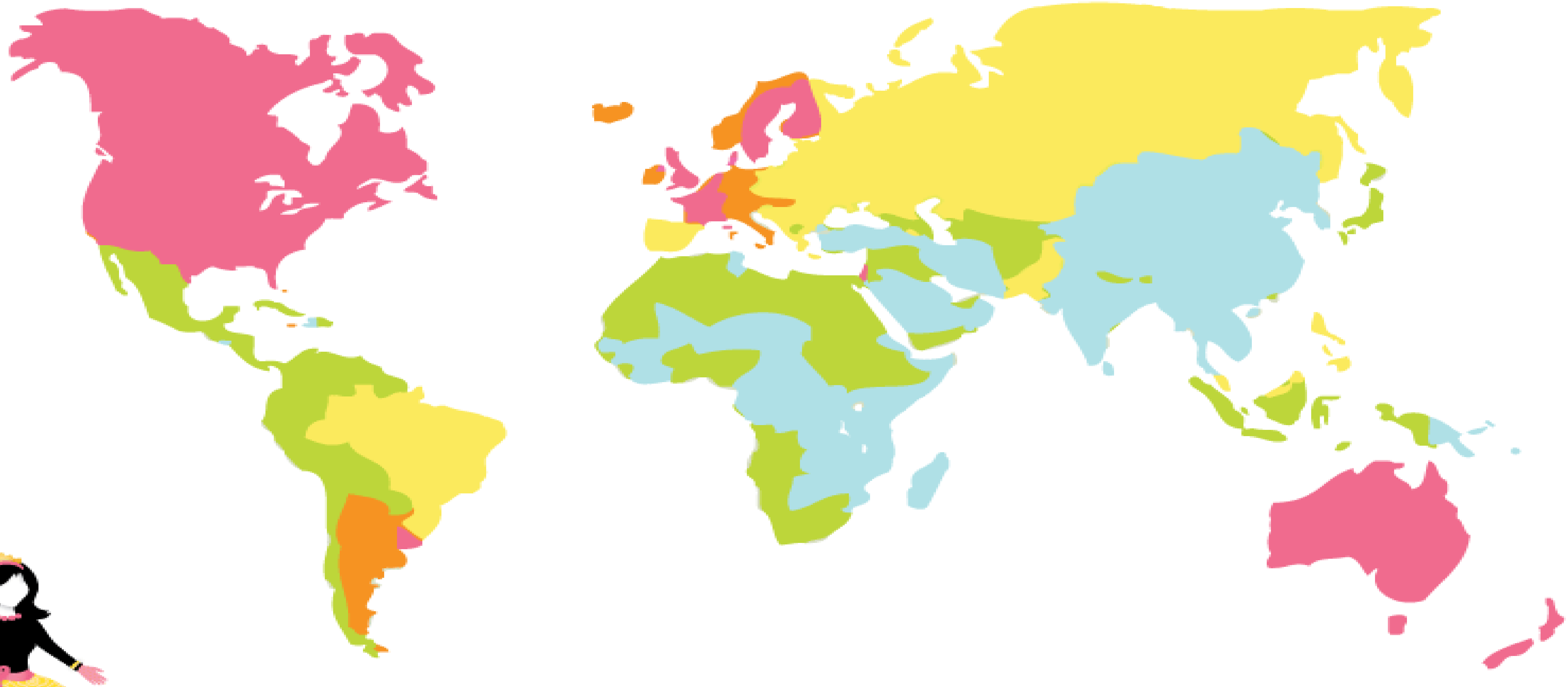
## Two-in-one concept



Adv. Drug Deliv. Rev., 60, 2008

# Breast Cancer



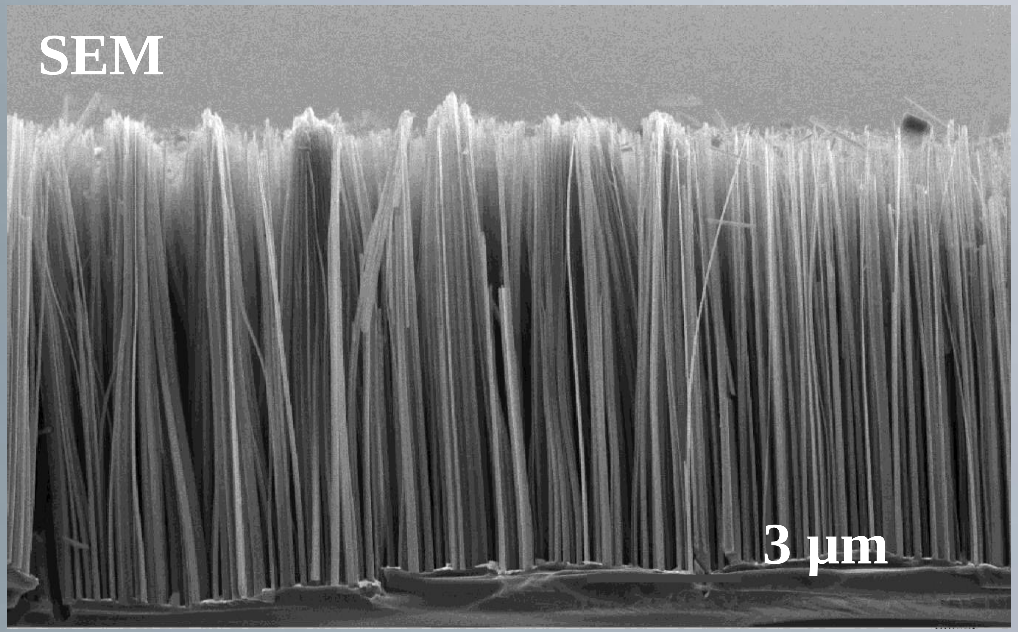

The number of new breast cancer cases occurring worldwide, per 100,000 persons, year 2000 estimate.

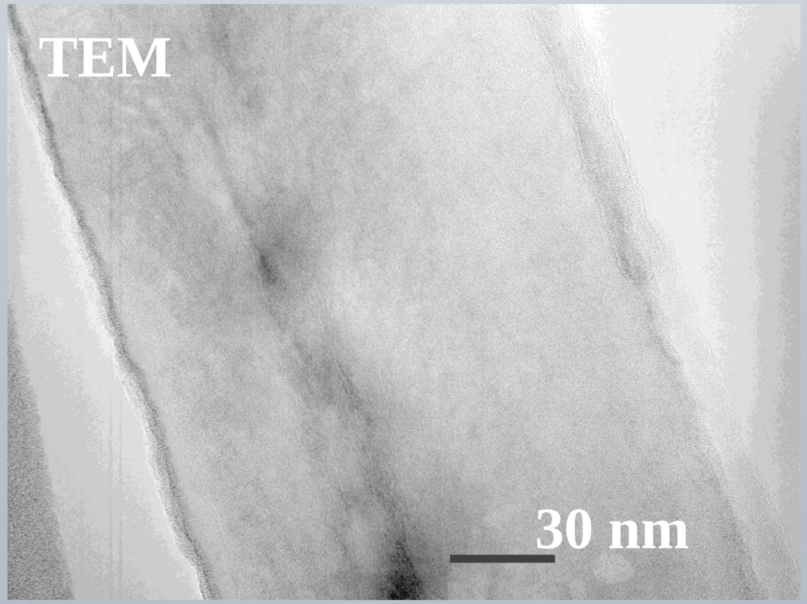
**World Health Organization, Breast Cancer Facts & Figures 2011-2012, http://www.cancer.org/acs/groups/content/@epidemiologysurveilance/documents/document/acspc-030975.pdf**

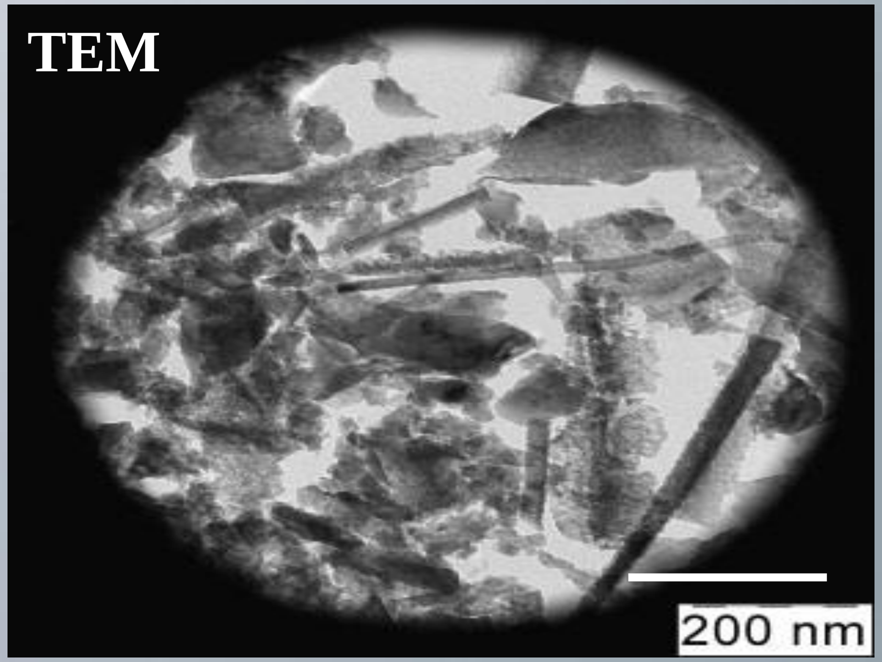
# How to visualize Si nanoparticles?

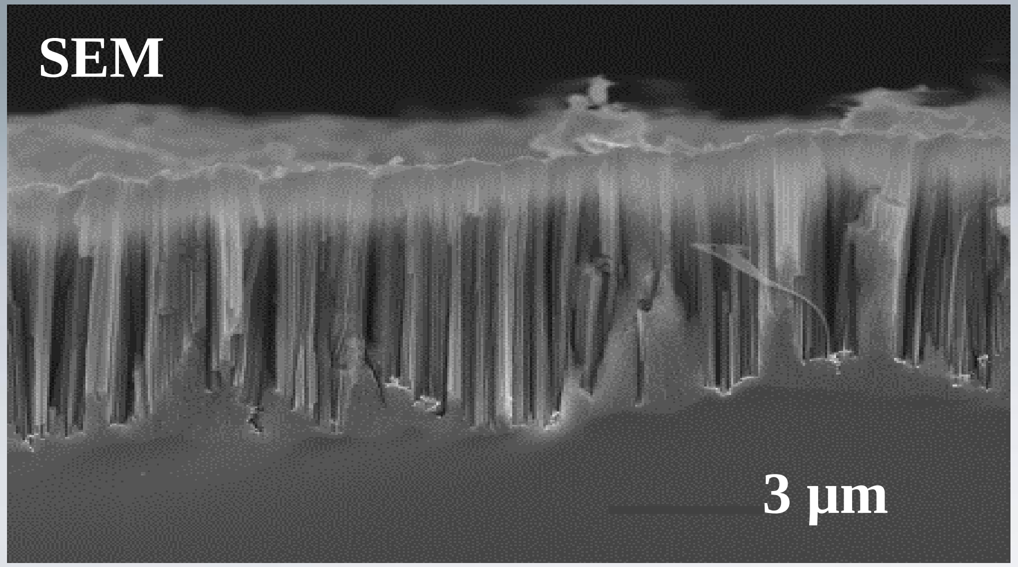
# Top-Down Silicon Nanostructures

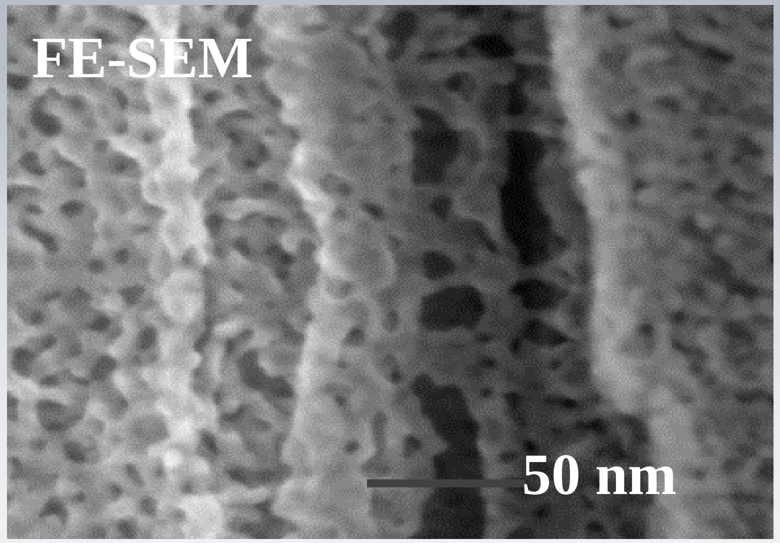
SEM LD-SiNWs

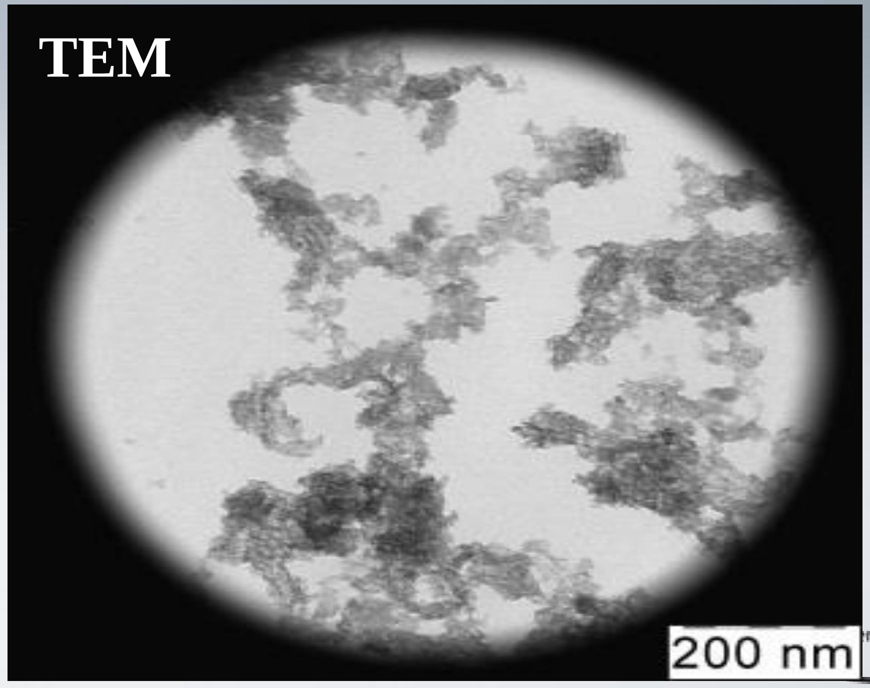


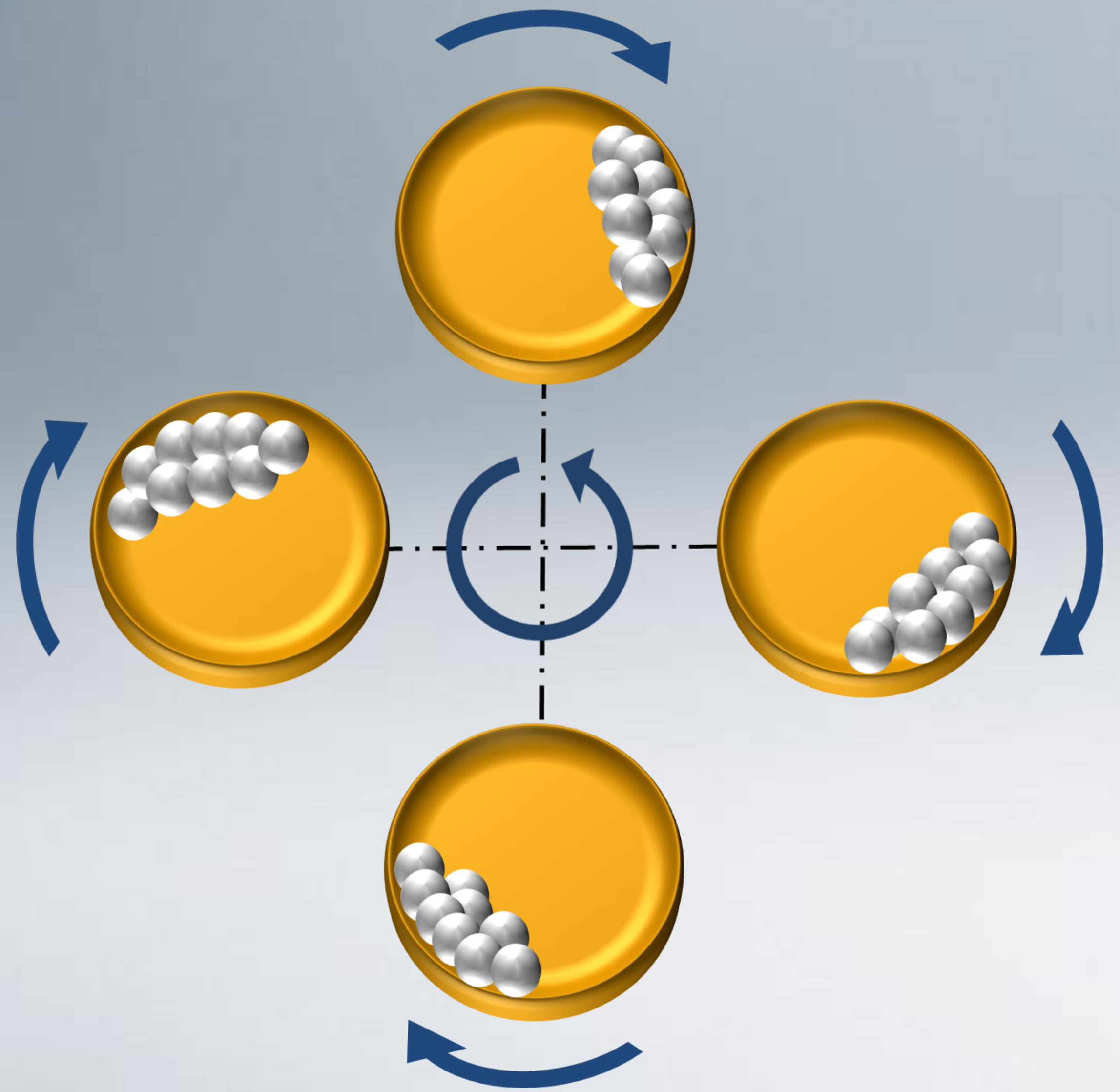




Leibniz-Gemeinschaft

# SiNPs Formation

wet chemical etching

electrochemical etching

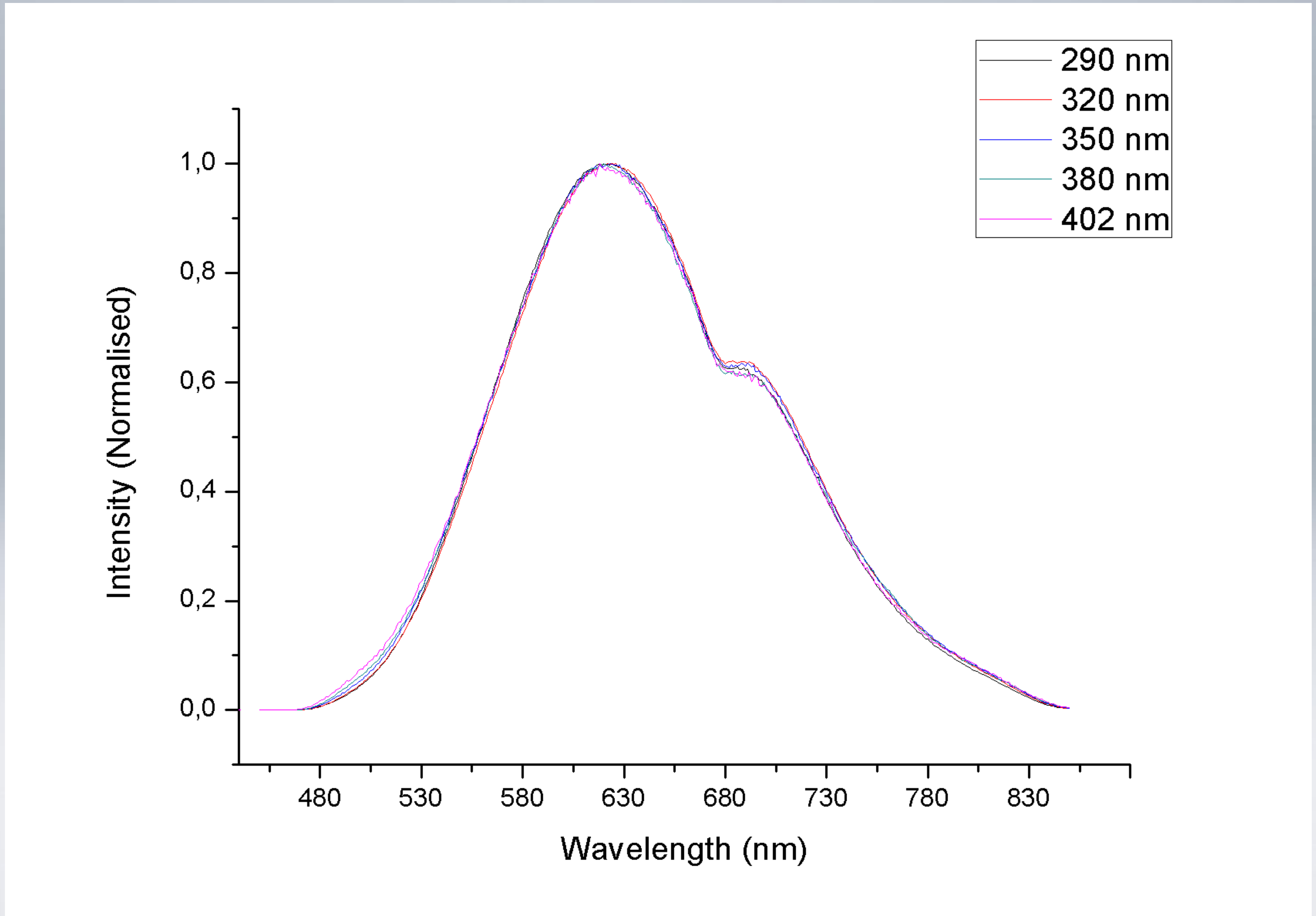


- ultrasound depletion from the surface

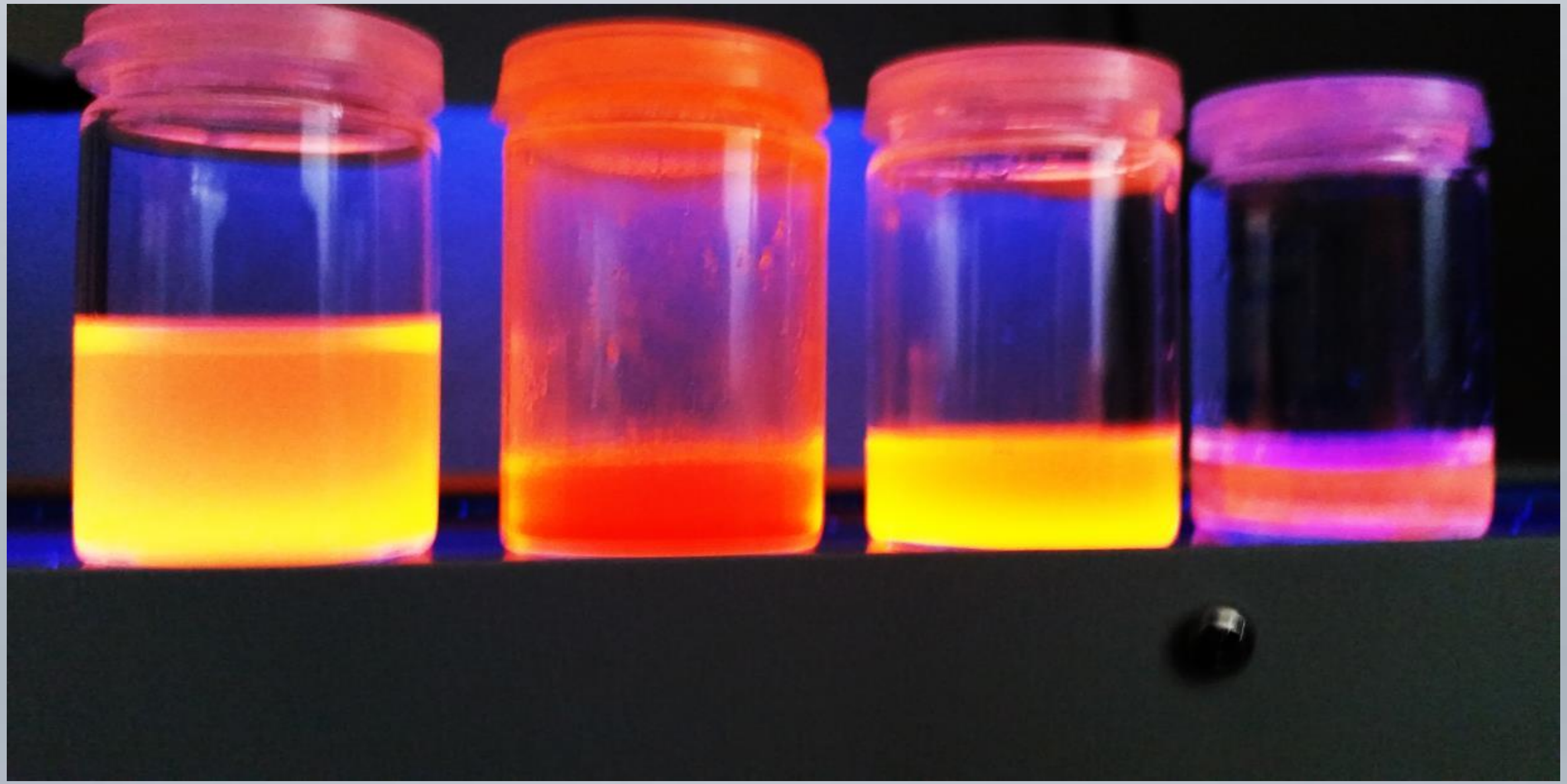
Mechnianical milling

- Forces upto 30 g possible

# PoSiNP emission graphs with different excitation wavelengths (normalised)



# Silicon Nanoparticles Applications in Nanomedicine

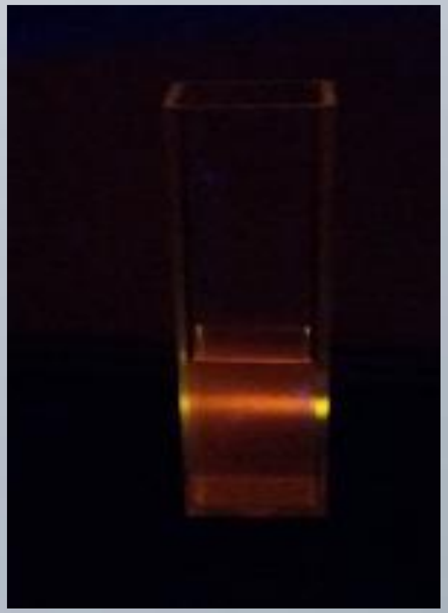


Digital micrograph of the silicon nanoparticles suspension irradiated by a UV lamp  at a wavelength of 366 nm. Visible red-orange emission is coming from the porous SiNPs prepared by top-down approach.

- Novel drug delivery agent based on biocompatible and biodegradable silicon nanoparticles
- Silicon nanoparticles application in nanomedicine (cancer, antivirulicid and antiseptic)

Mitglied der Leibniz-Gemeinschaft

# Silicon Nanoparticles Applications in Nanomedicine



UV-Lampe

254 nm + 366 nm

N2-Laser

Digital micrograph of the silicon nanoparticles suspension irradiated by a UV lamp and nitrogen laser. Visible red-orange emission is coming from the porous SiNPs prepared by top-down approach.

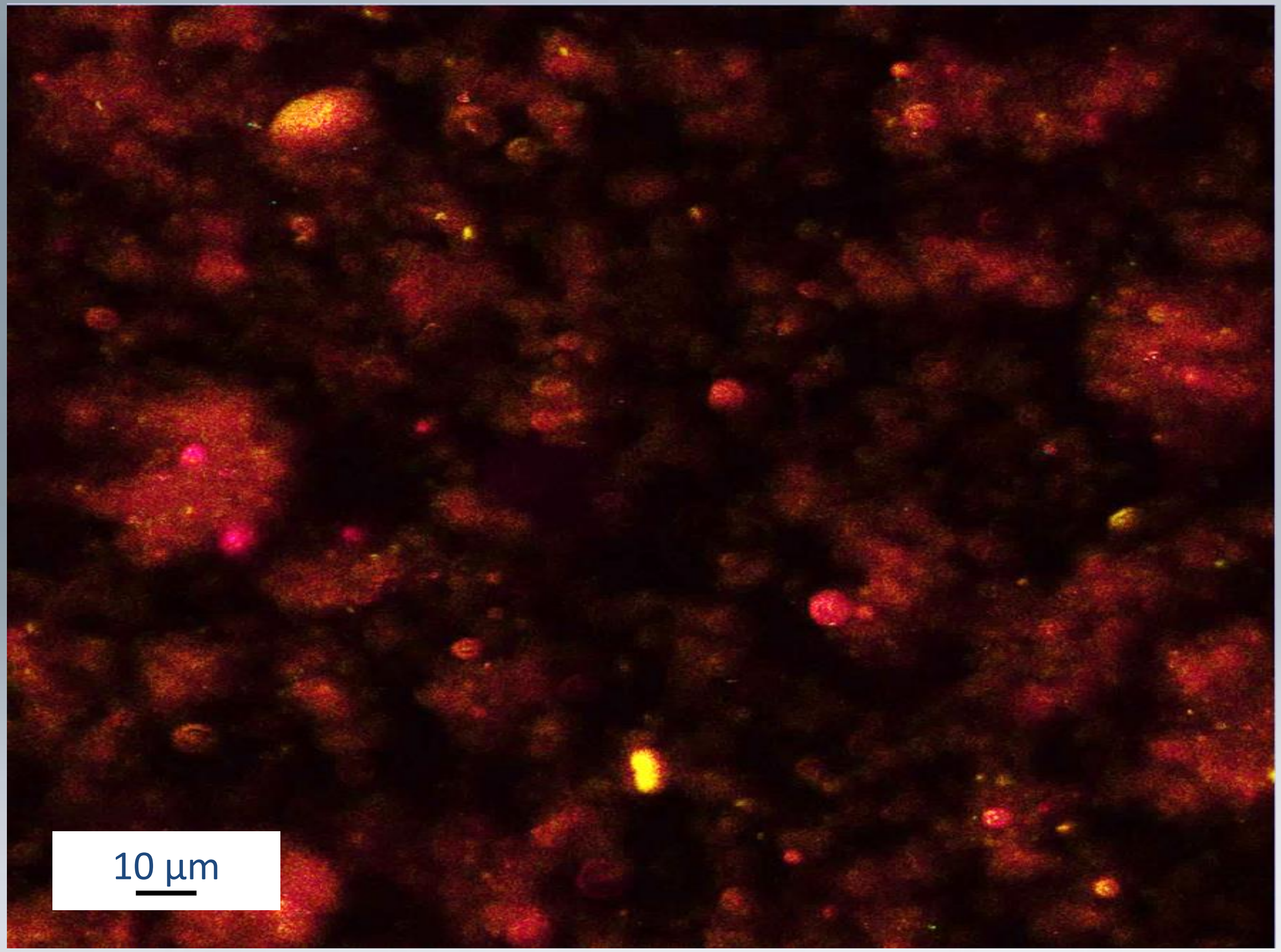
Mitglied der Leibniz-Gemeinschaft

# Silicon Nanoparticles Applications in Nanomedicine

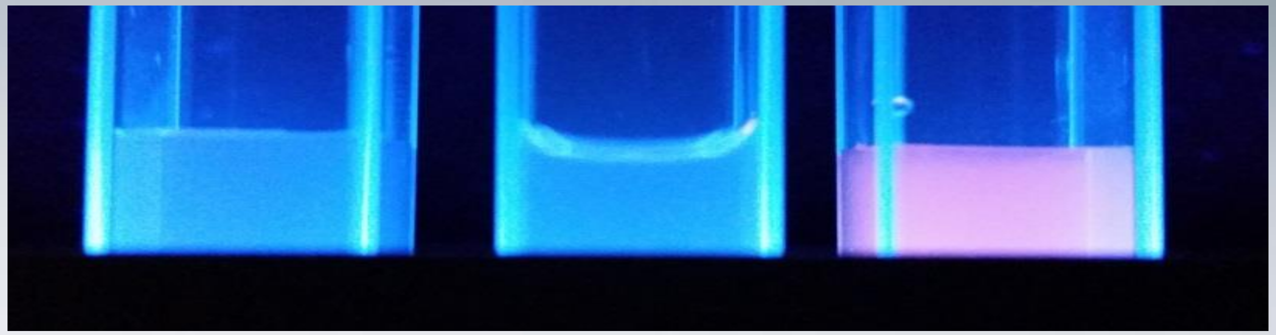
Problem: Photoluminescence of Silicon nanopartices der Partikellösung not stable for the longer time in water-containing solutions

→ Functionalization
→ Dextrane as cover (Bloodplasma-alternative)

- Incapsulation and formation of agglomerates
- Photoluminescence long-tim stability (>6 Wochen)




Multi-photons microscopy image of E-Coli culture labelled with Silicon NPs (red-orange emission).



Water Ethanol Dextrane

Digital photos of silicon nanoparticles in different media after 6 weeks of storage.

Mitglied der Leibniz-Gemeinschaft

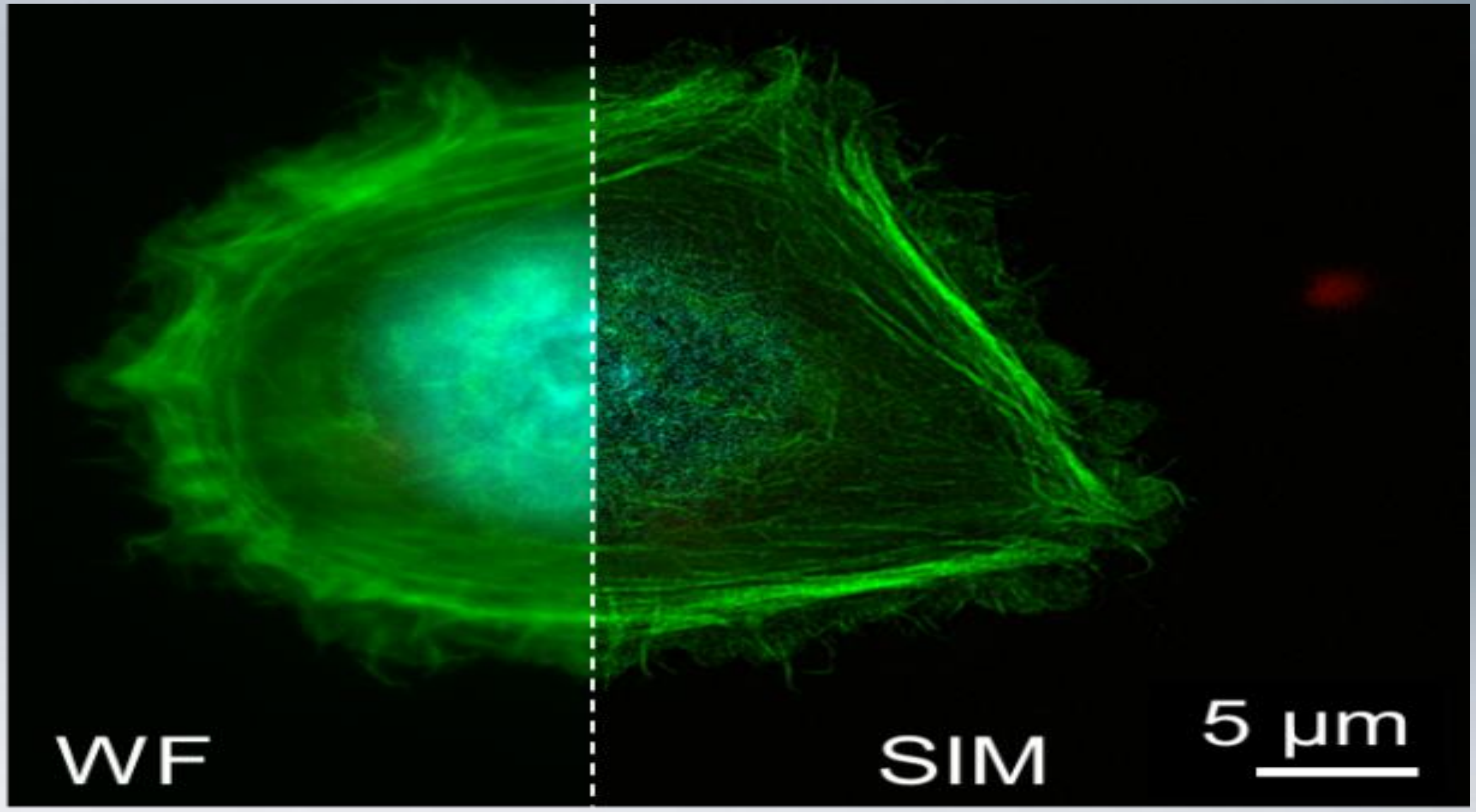
# Bioimaging with SiNWs

- **Cell line: MCF-7 (*Michigan Cancer Foundation - 7*)**
  **a breast cancer cell line**

- **Labeling:**

**405nm – cell nucleus: DAPI**
**488nm – cell body: Calcein AM**

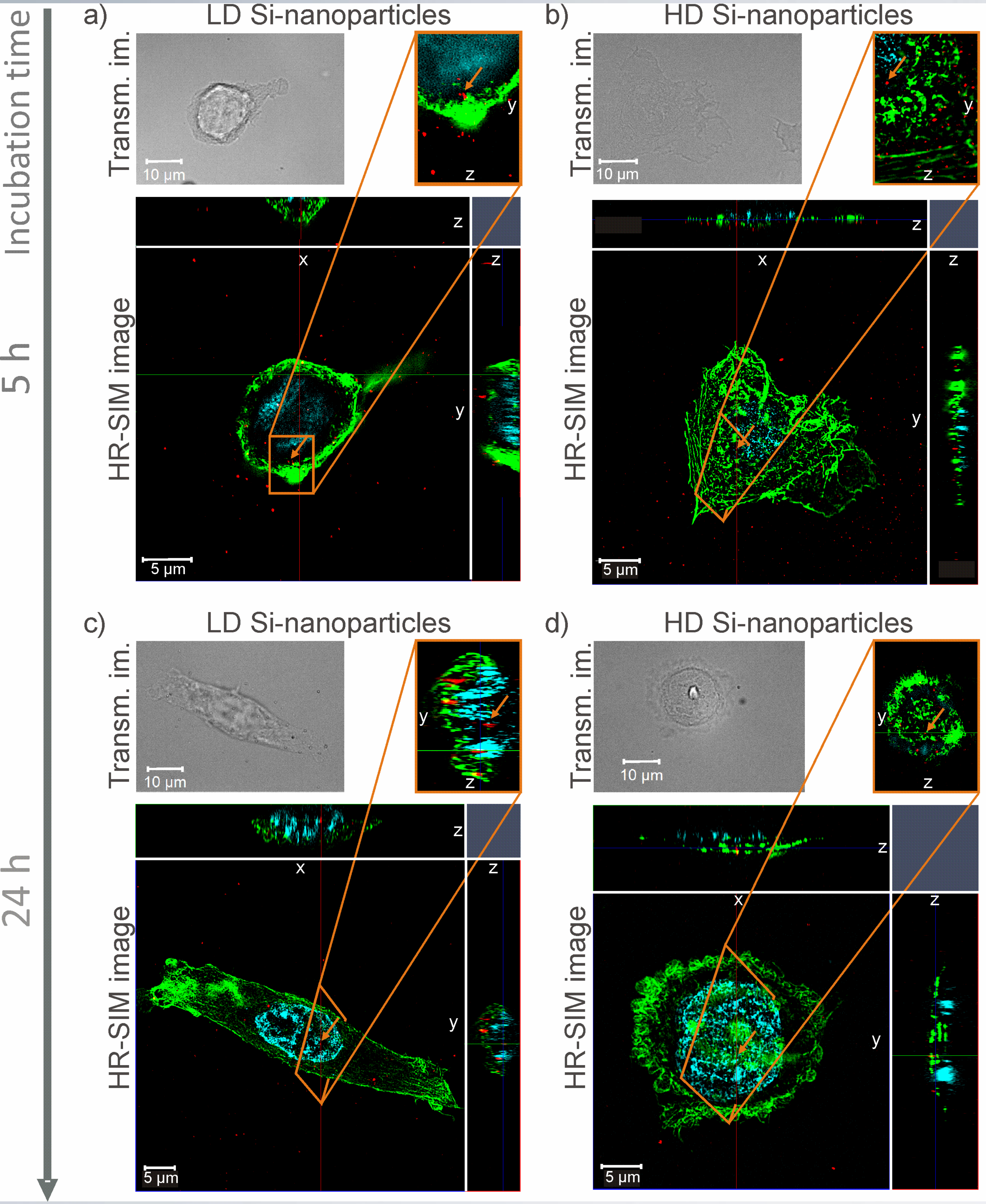
**561 nm / 642nm – Si**




**Wide-field (WF, left) and SIM (right) imaging of MCF-7 cells transfected with Cy5-coupled siRNA-peptide complexes**


A. Jost und R. Heintzmann, *Annu. Rev. Mater. Res.*, Bd. 43(1), 261, 2013.
L. Schermelleh, R. Heintzmann, und H. Leonhardt, *J. Cell Biol.*, 190( 2), 165, 2010.

# Bioimaging with SiNWs

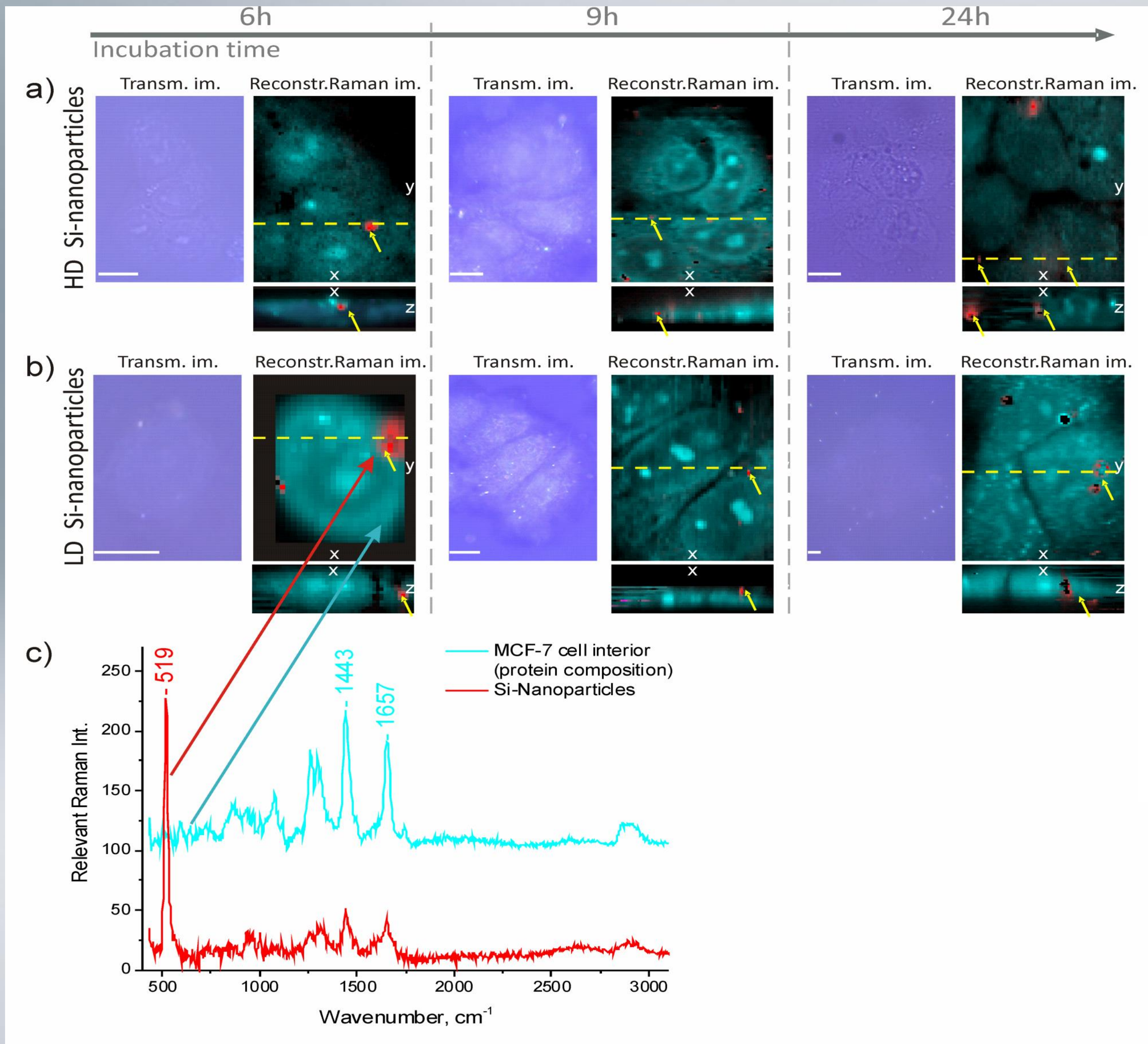



Transmission images and fluorescence microscopy images (HR-SIM image) of MCF-7 cells transfected with lowly doped ((a) and (c)) and heavily doped ((b) and (d)) filtered SiNPs generated by the transmitted light and HR-SIM (top view (xy) and yz and xz cross-sections); nucleus staining Hoechst 34580 (blue, 405 nm), actin staining Alexa Fluor® 488 Phalloidin (green, 488 nm); SiNPs photoluminescence autofluorescence is measured at 642 nm (red). The incubation time is 5 h for (a) and (b) and 24 h for (c) and (d).

E. Tolstik, VAS, et al., ACS Nano, in press (2015).

Leibniz-Gemeinschaft

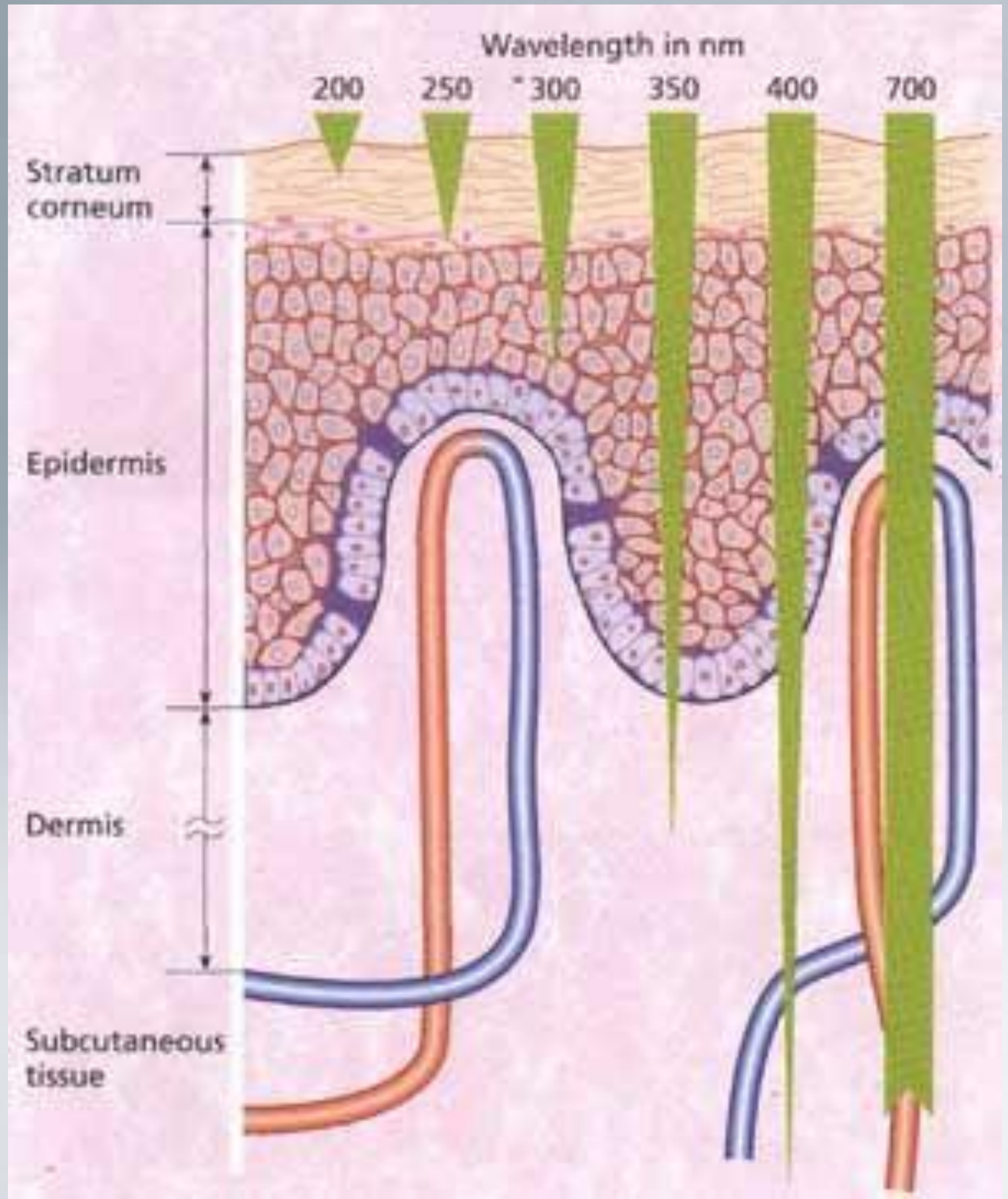
# Non-invasive Raman Imgaing

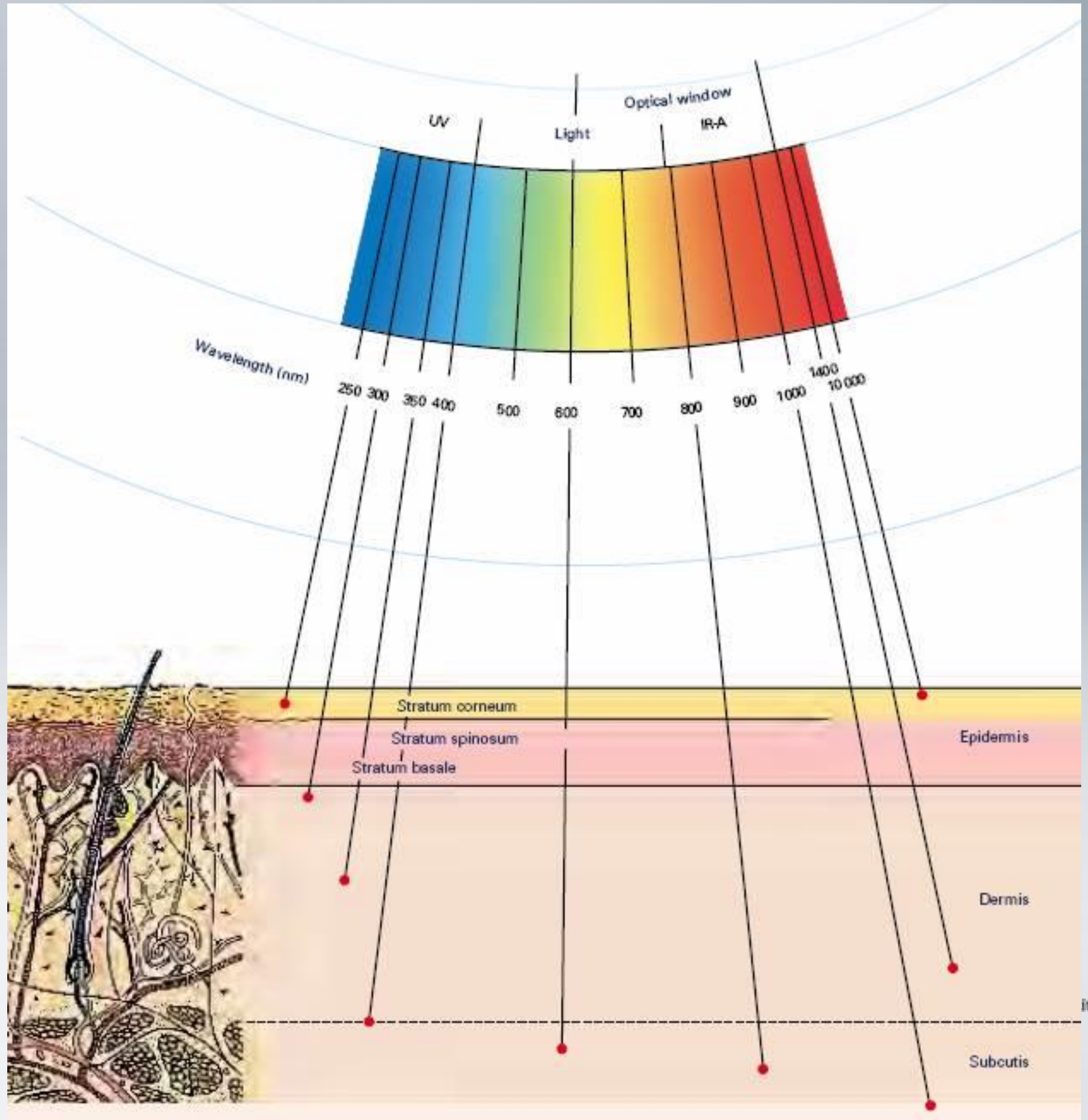



Raman microscopy images of MCF-7 cells transfected (a) with heavily doped and (b) with lowly doped (below) filtered SiNPs generated by the transmitted light and by Raman imaging (xy- and xz- cross-sections of the reconstructed Raman image with SiNPs depicted in red within the cell interior depicted in blue). (c) Corresponding to them SiNPs spectrum (depicted in red) and MCF-7 cell interior spectrum based on the protein composition (depicted in blue). Incubation time is 6 h, 9 h and 24 h; the scale bar is 10 µm

# Photo-Acoustic Imaging

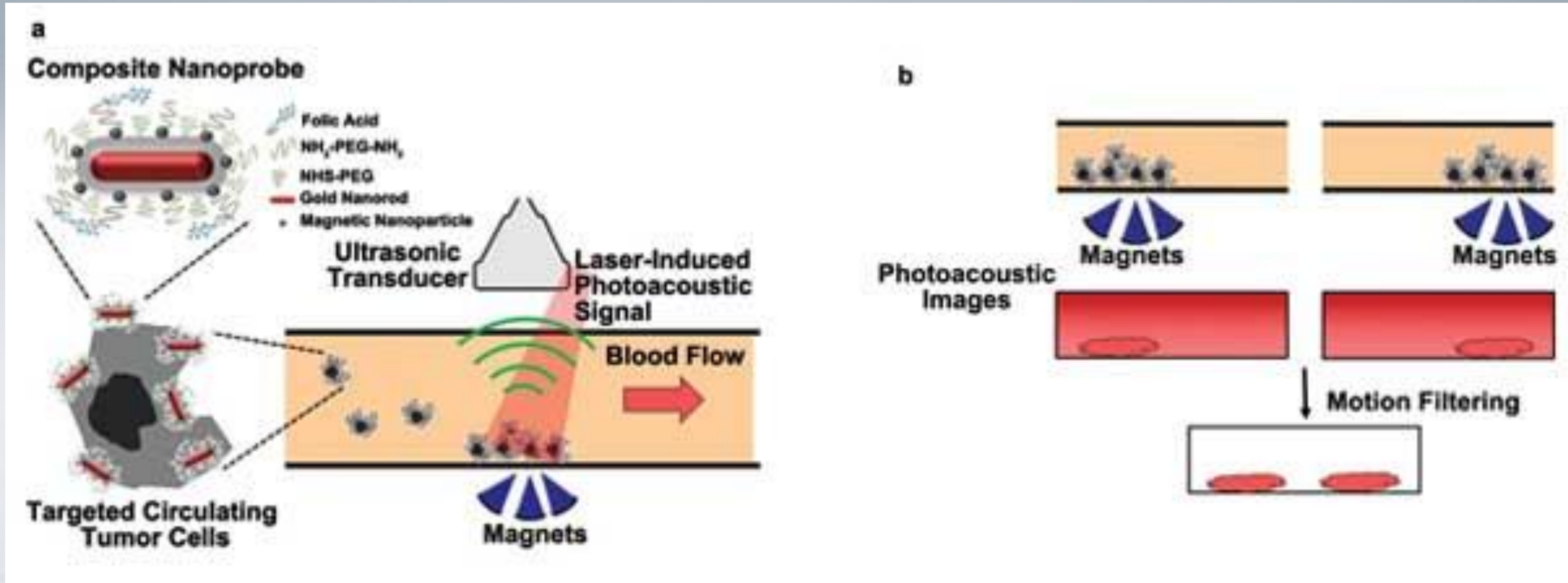
## Light Penetration



# Photo-Acoustic Imaging

The photoacoustic (PA), also referred as optoacoustic, eect was rst introduced by Alexander Graham Bell in 1880. He found that absorption of electromagnetic waves by a medium generated sound waves. Even though the PA efect was known for a long time, it was not until 1994 that Kruger demonstrated application of this phenomenon in highly scattering media. It was applied a few years later to biomedical imaging.



# Photo-Acoustic Imaging

Optical modalities benefit from high contrast due to electromagnetic interaction with materials, particularly absorption. Absorption in a biological tissue can be modeled with the well-known Beer-Lambert law:

$$I = I_0 x \exp(-\mu_a L) \quad (1)$$

where I is the intensity after light has traveled L meters, $I_0$ is the initial intensity and $\mu_a$ is the absorption coefficient.

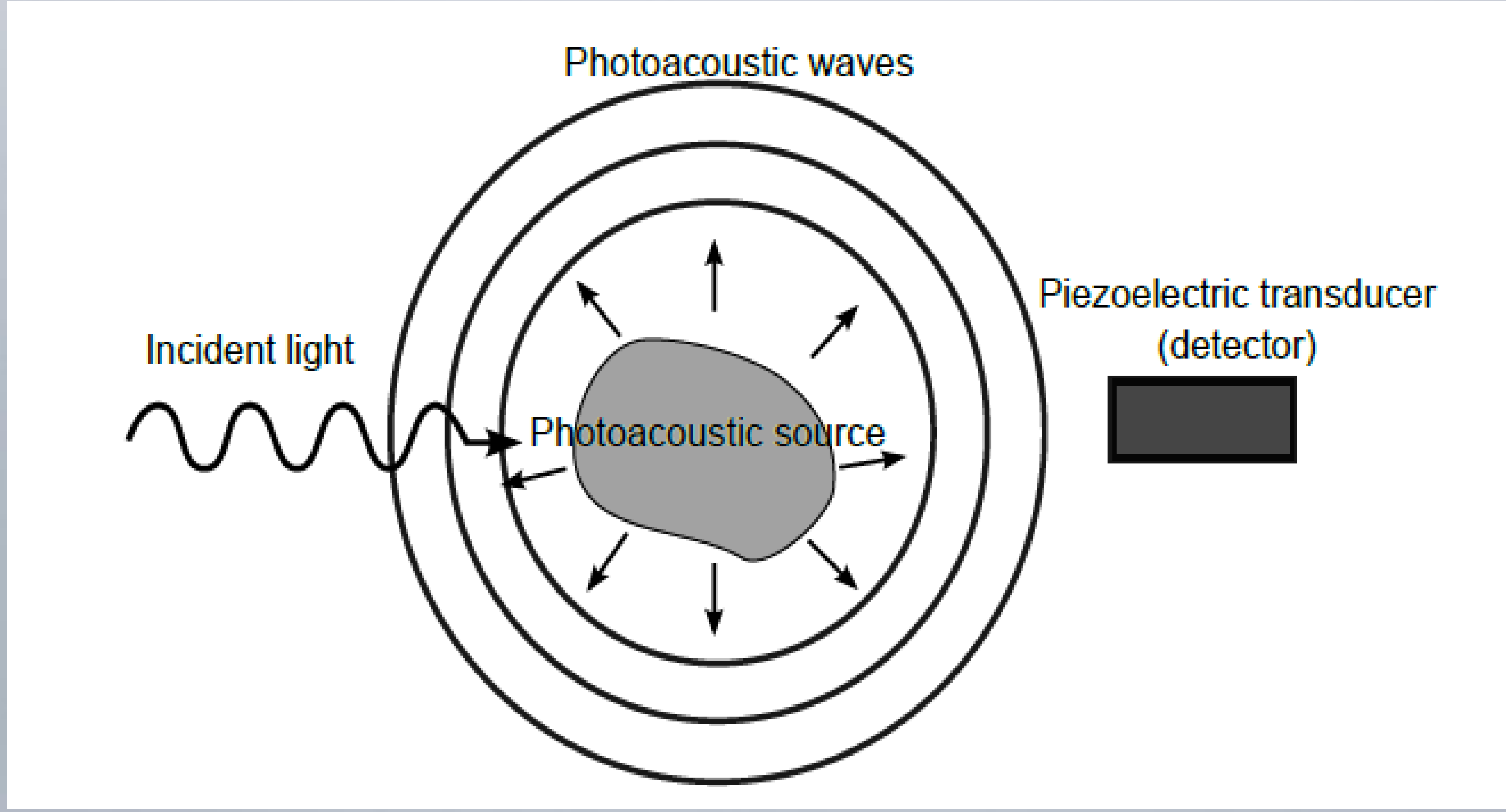
High resolution (1-10µm) can be obtained in optical imaging because of the short wavelengths used, typically between 650 and 1350 nm. The major problem in optical imaging is the penetration depth. Biological tissue scatters light a lot. By replacing $\mu_a$ by $\mu_s$, the Beer-Lambert law presented in Eq.1 can also be used to model scattering. This coefficient ($\mu_s$) is around 1-10 $mm^{-1}$ in biological tissue. This means that the major part of the incident light has scattered after one millimeter. Scattering increases with shorter wavelengths, this is why near infrared (NIR) light is mostly used in optical biomedical imaging. Since photons that have not scattered form the signal of interest, maximal imaging depth rarely exceeds 3 mm. Diffuse optical tomography extends the penetration depth by detecting diffuse photons. This requires complex algorithms and suffers from poor spatial resolution.

# Photo-Acoustic Imaging

On the other hand, ultrasound imaging, also known as echography, relies on acoustic waves to study a tissue. High resolution (100µm) can also be obtained with short wavelengths, because they can resolve smaller details. In addition, penetration depth is in the order of centimeters to a few tens of centimeters. The down side is that the signal of interest is reflected waves due to changes in the speed of sound and these changes are relatively small. Therefore, contrast is poor in ultrasound imaging. Functional information is provided by Doppler imaging, where the velocity of fluids such as blood is imaged.

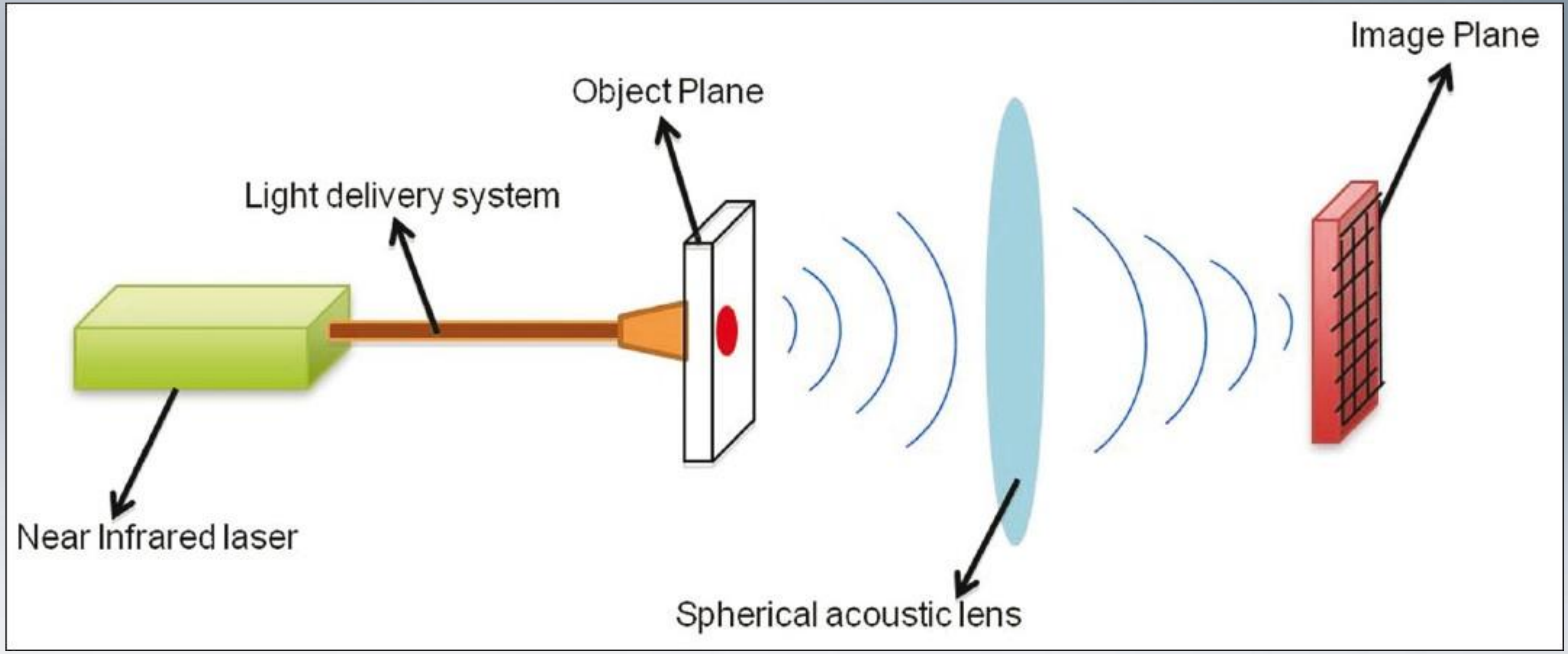
Photoacoustic tomography (PAT) aims to use the advantages of both optical and ultrasound imaging, without the disadvantages. This is done by illuminating the sample with diffuse, short pulses and collecting the ultrasound waves generated by the PA effect.

# Photo-Acoustic Imaging



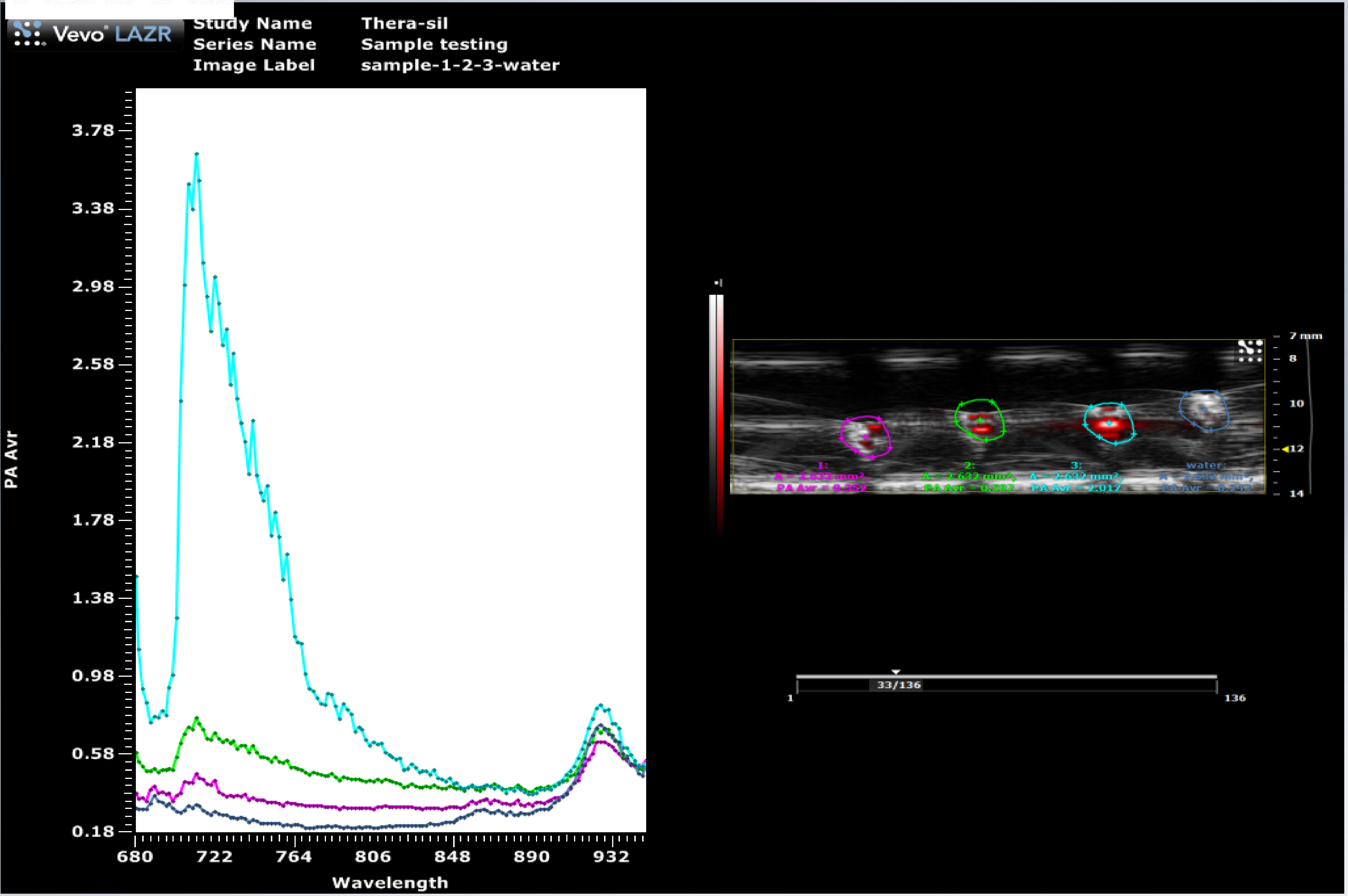

The basic idea of the photoacoustic effect is simple. Light is shone on a sample which absorbs a fraction of the incident energy. This energy is converted into heat. The temperature rise leads to thermoelastic expansion of the object. This sudden pressure rise propagates as a sound wave, which can be detected. By detecting the pressure waves, we can localize their source (i.e., where light was absorbed) and obtain important information about the studied sample.

# Photo-Acoustic Imaging


Mitglied der Leibniz-Gemeinschaft

# Photo-acoustic detection of Silicon




Dr. Jithin Jose

**Vevo LAZR Photoacoustic Imaging System**

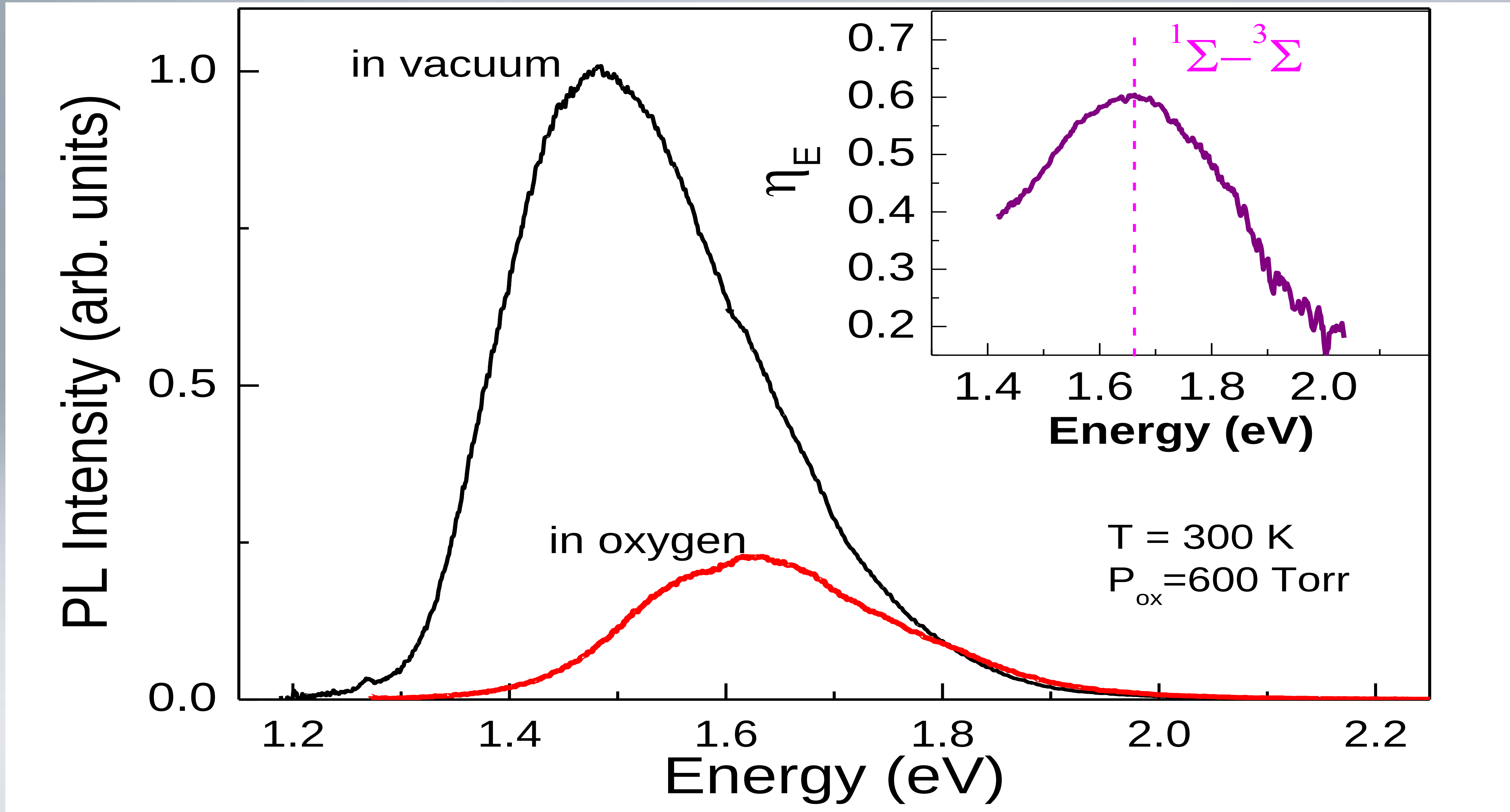
Mitglied der Leibniz-Gemeinschaft

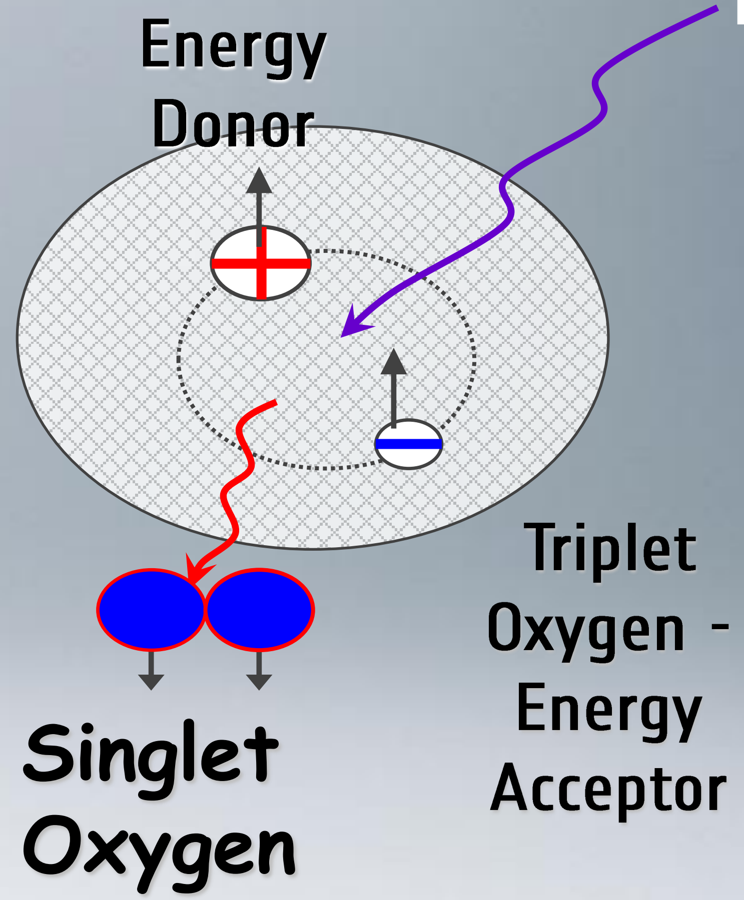
# SiNPs based theraphy?

Mitglied der
Leibniz-Gemeinschaft

# Singlet Oxygen Photosensitization by microporous Si at Room Temperature

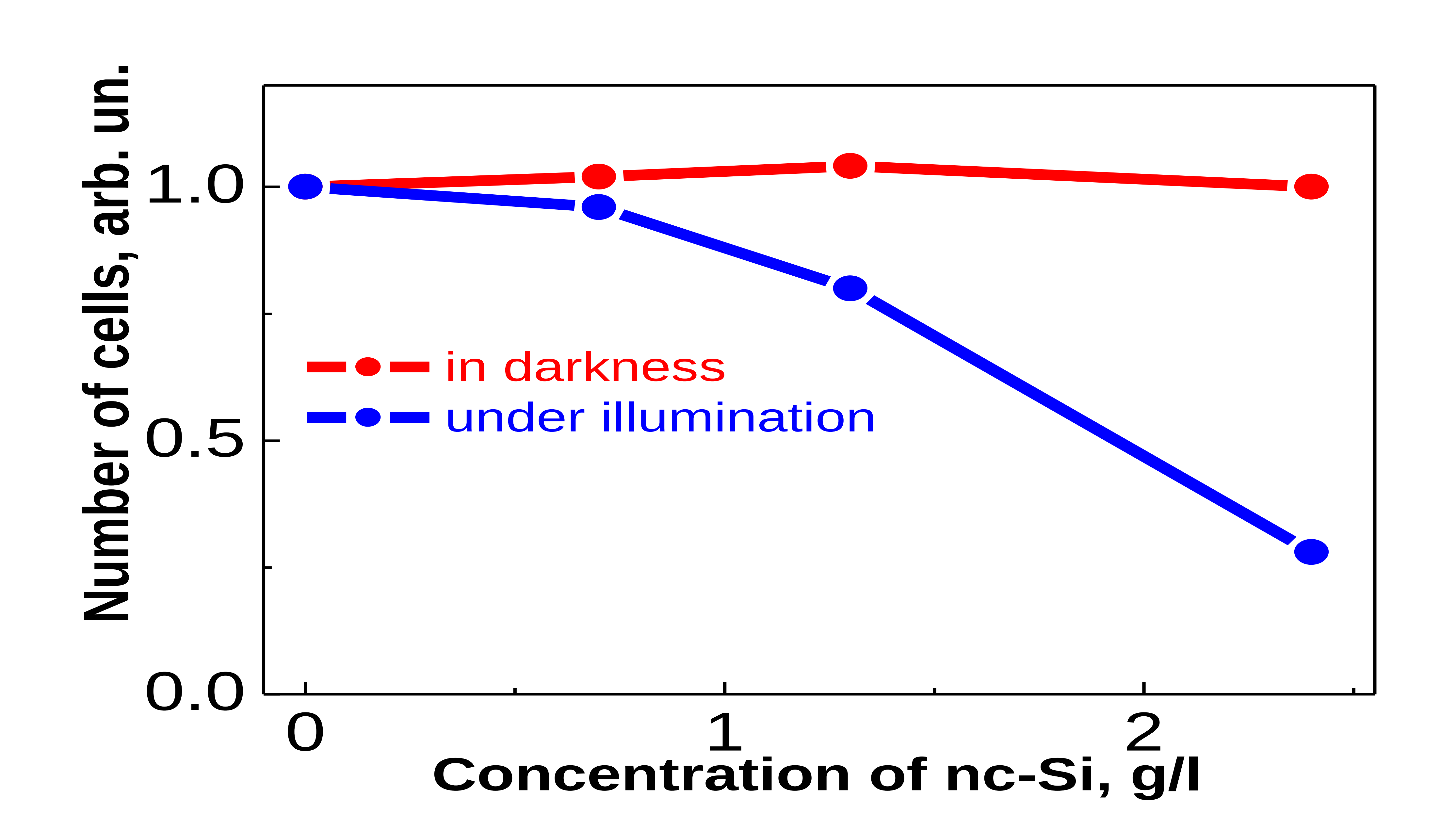
$$\eta_E = 1 - I_{PL}^{oxyg} / I_{PL}^{vac}$$




- Quantum efficiency of the SO generation: $h_{SO} = \eta_{PL} h_E \sim 5$ %

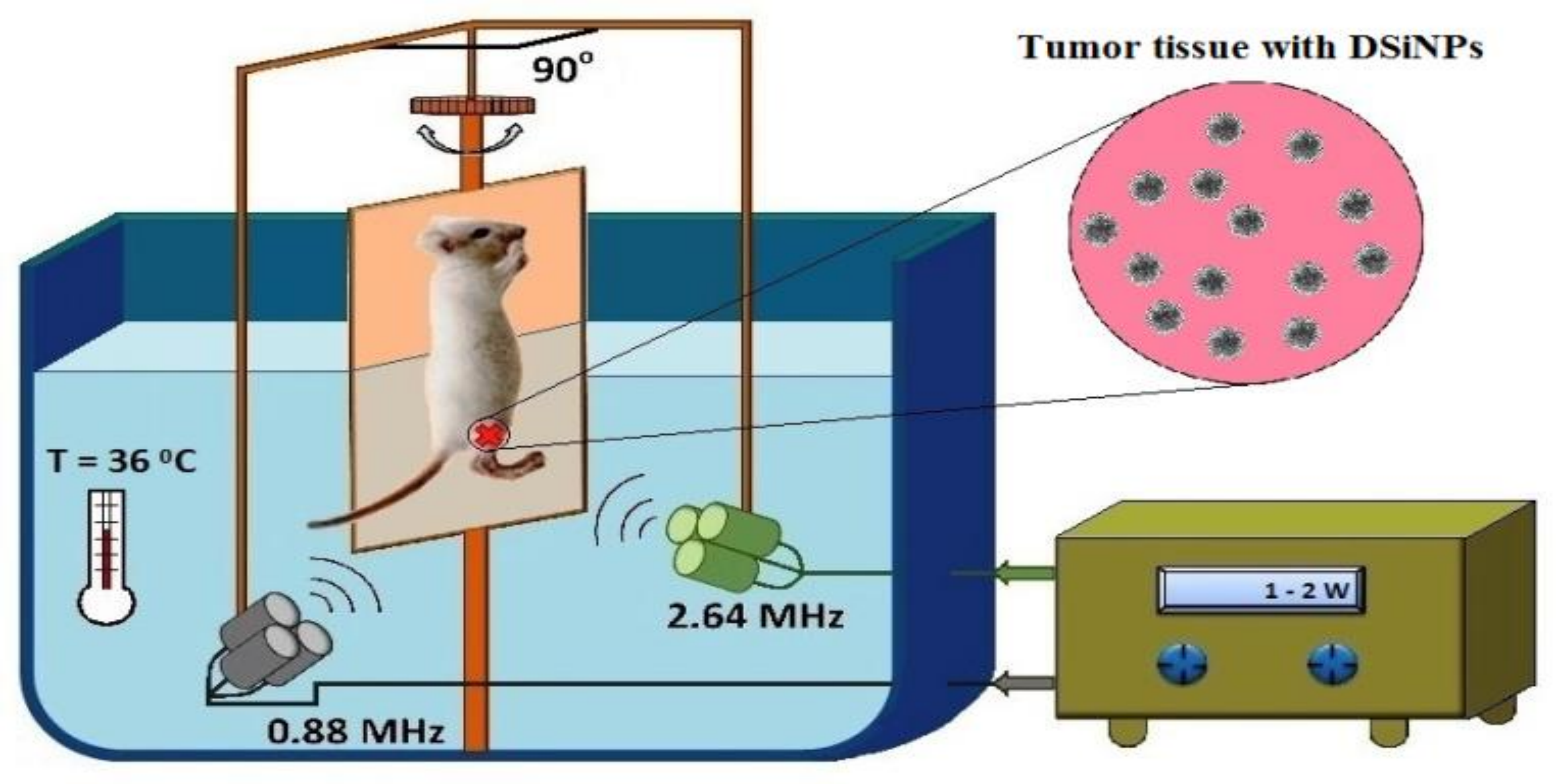
# Suppression of the cancer cell proliferation by photo-excited nc-Si




*V.Yu. Timoshenko et all.,*
**JETP Lett. 83 (9), 423 (2006).**

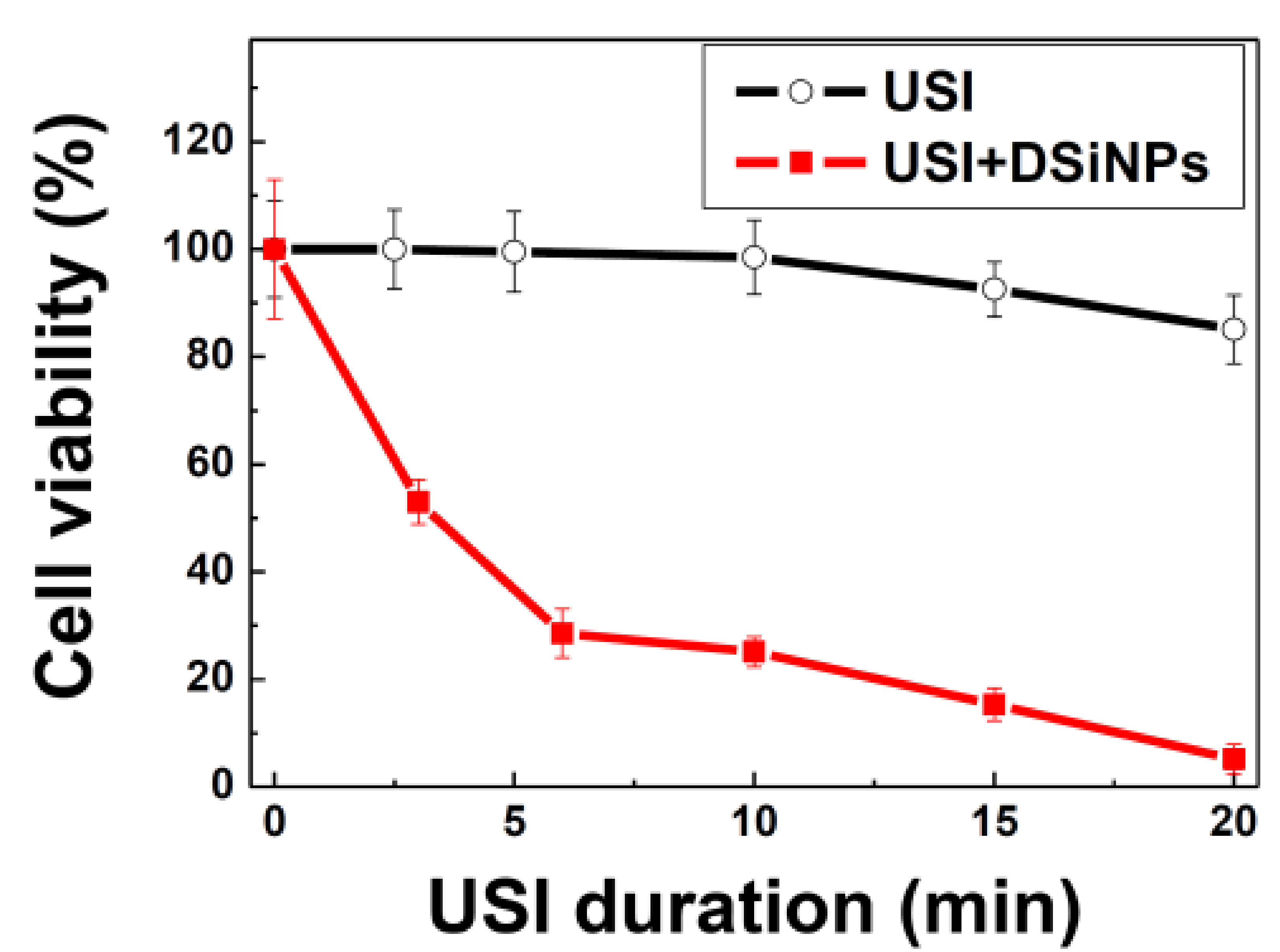
**The decrease of cancer cells (mouse fibroblasts) number was observed in suspensions of silicon nanocrystals under illumination. This decrease is explained by the effect of singlet oxygen photosensitized by nc-Si.**

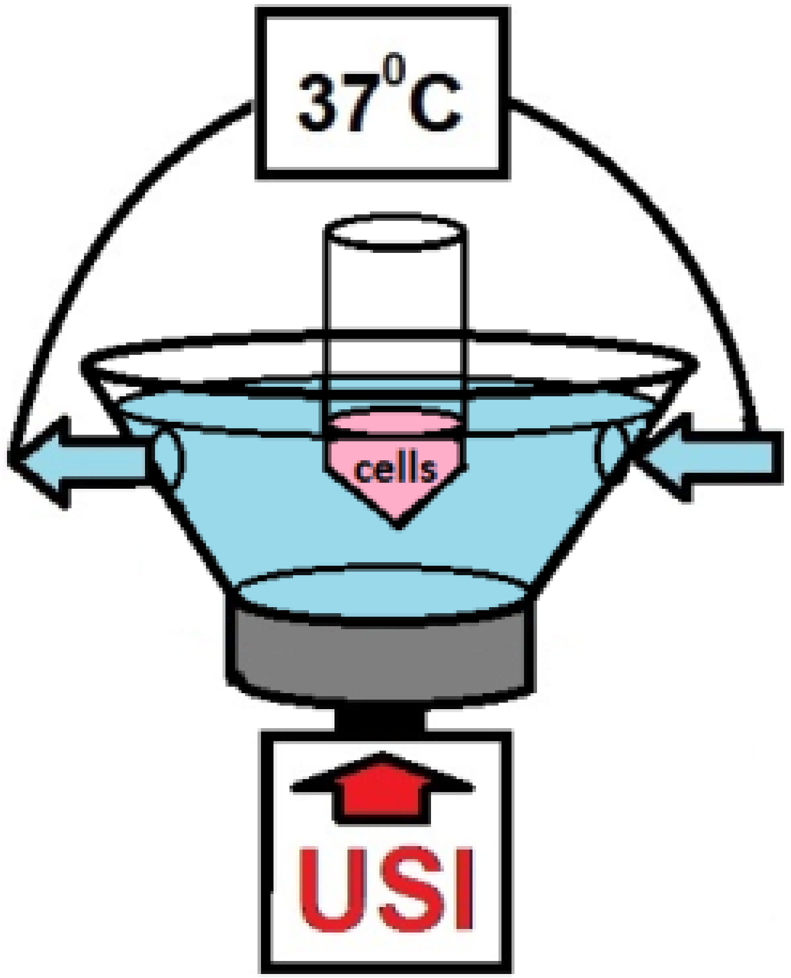
# Set up of in vivo experiments




L.Osminkina, VAS, et al., Nano Research Letters (2014)

# In Vitro Effect of Low Intensity MHz-ultrasound + Dextran-coated PSi NPs



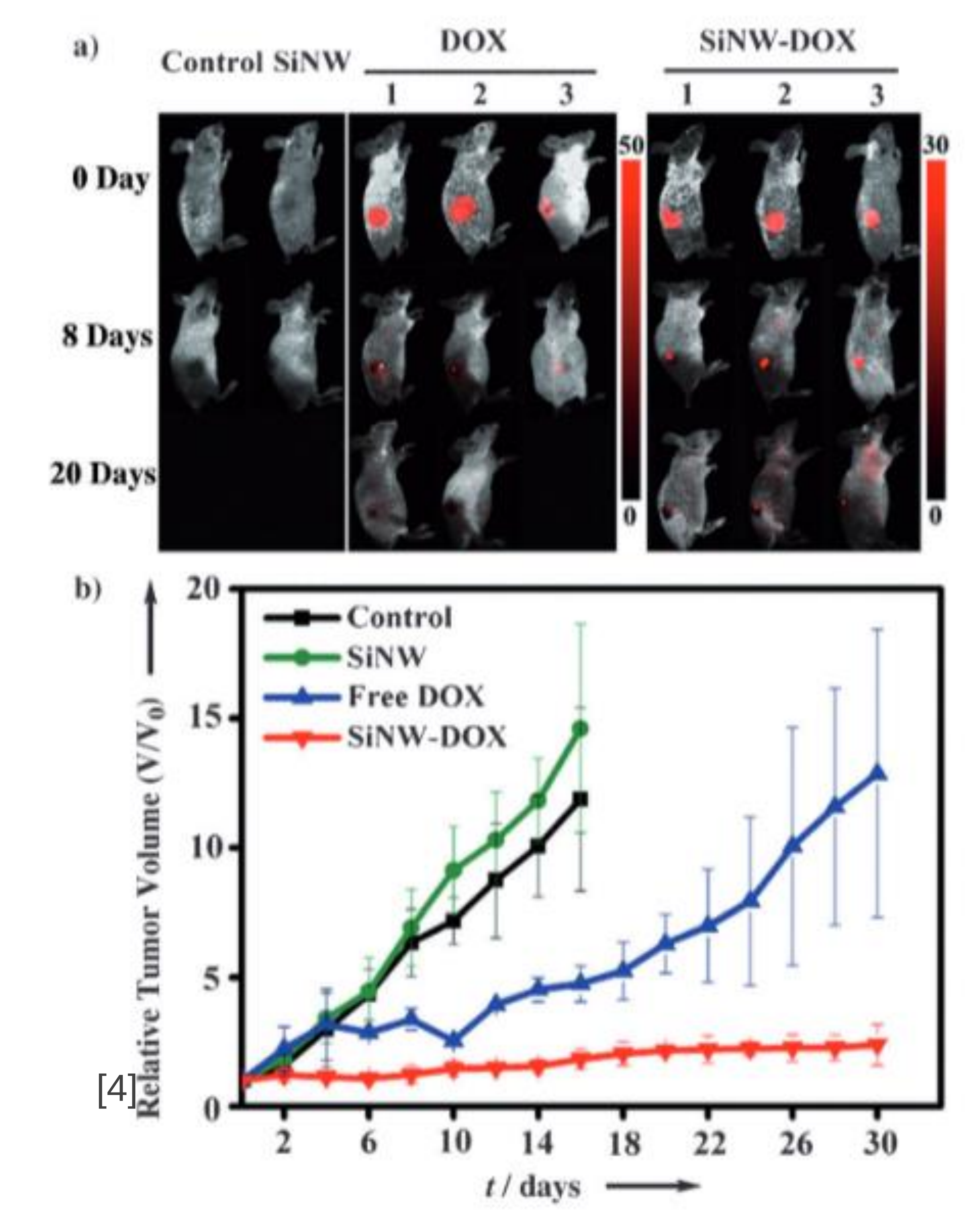




- Heating
- Cavitation
- Nano-scalpels

2 MHz, 1 W/cm$^2$

Hep2 cells with  dextran (DPSi) NPs at 0.25 mg/mL.

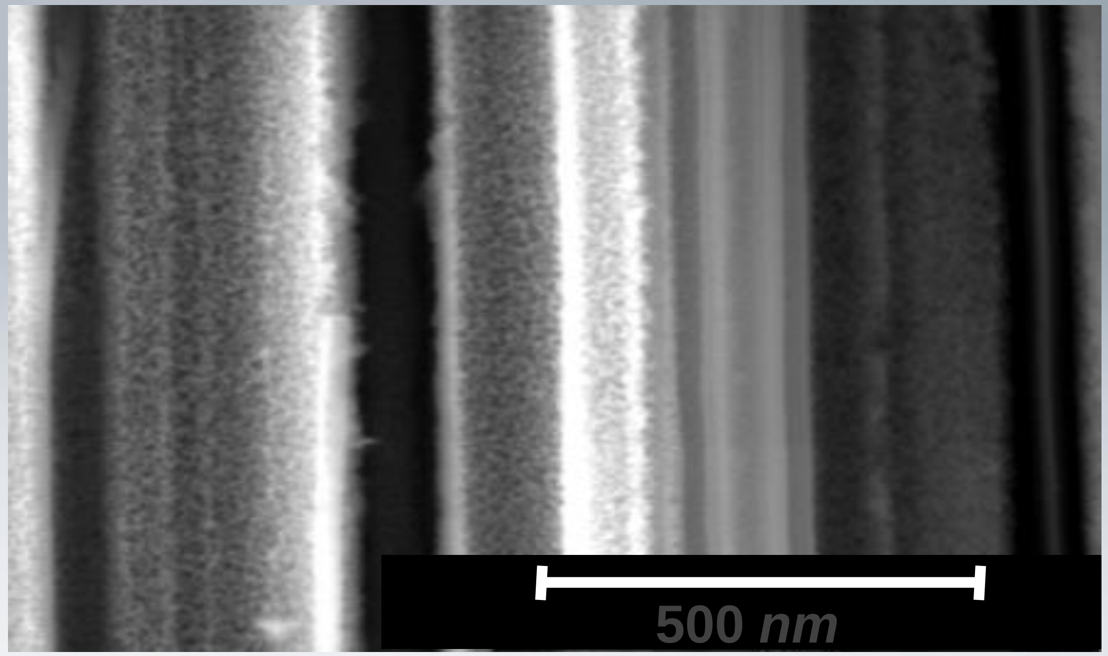
# Cancer Theranostics




[4]

- Container with Doxirubicin upto 20800 mg/g

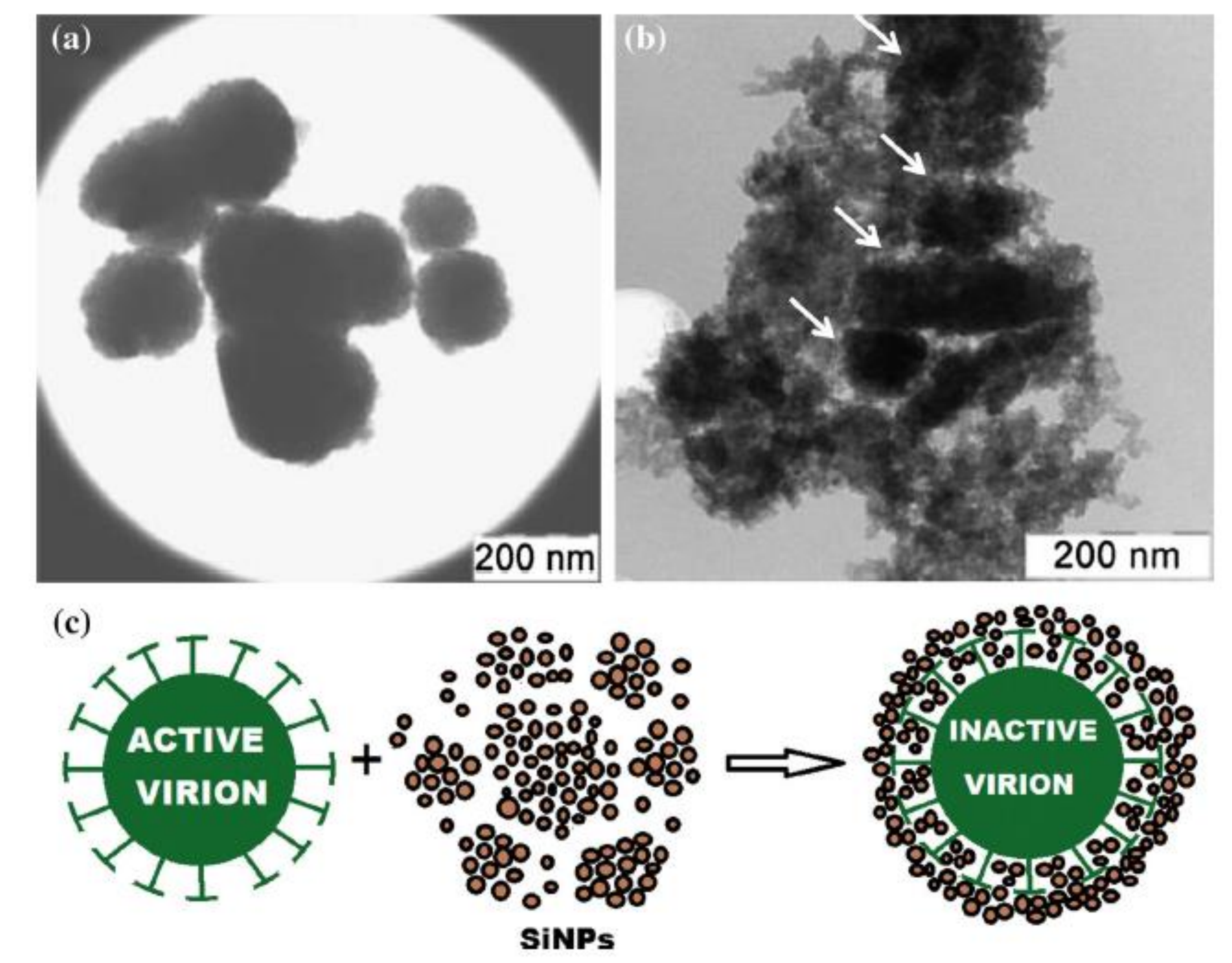
0,1-0,5 Ωcm; 0,1M $AgNO_3$ 60 s

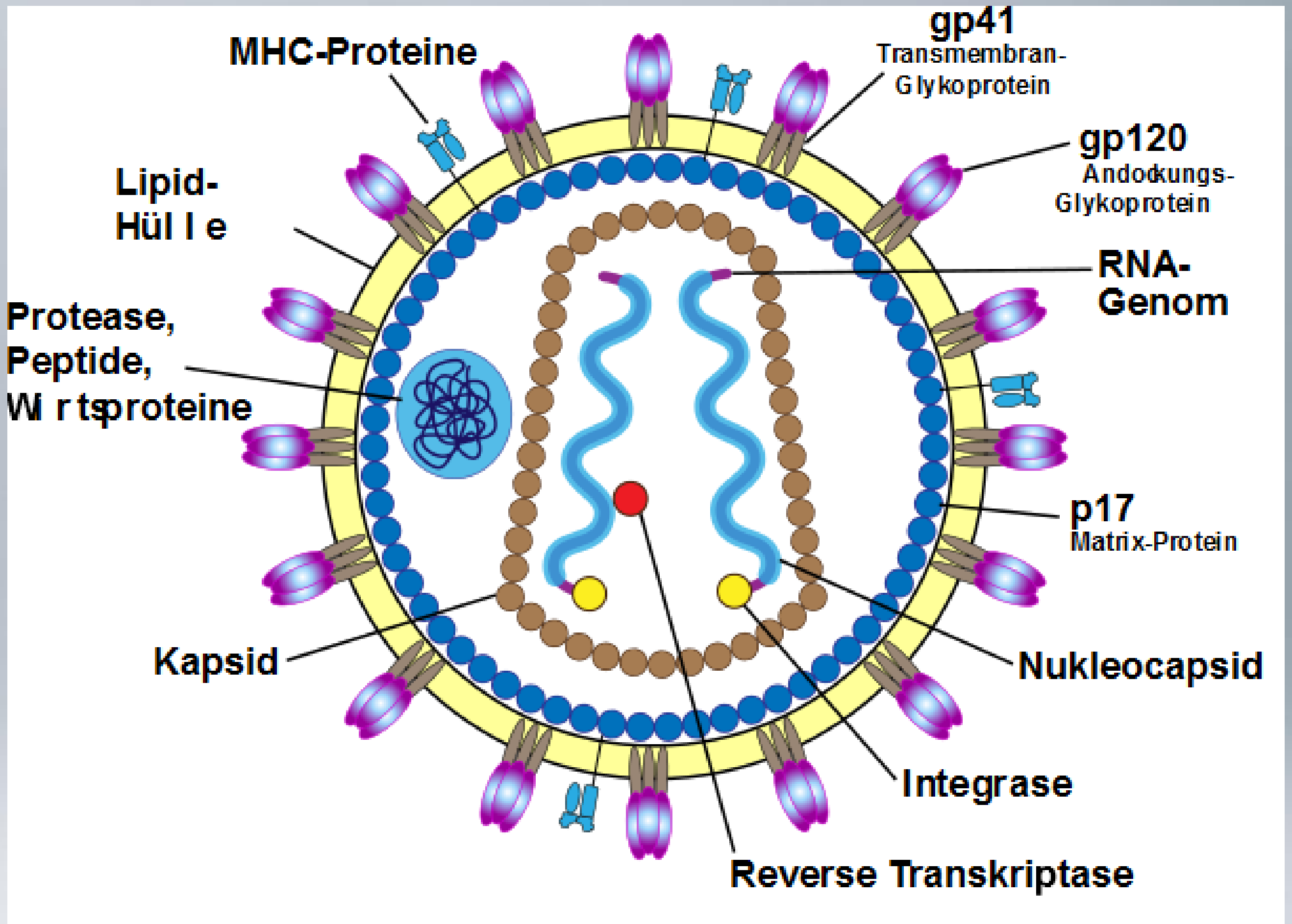



Fei P. et al: „Silicon-Nanowire-Based Nanocarriers with Ultrahigh Drug-Loading Capacity for In Vitro and In Vivo Cancer Therapy", *Angewandte Chemie International Edition* .

# Bacteria@Viruses

## Inhibition of Virusies



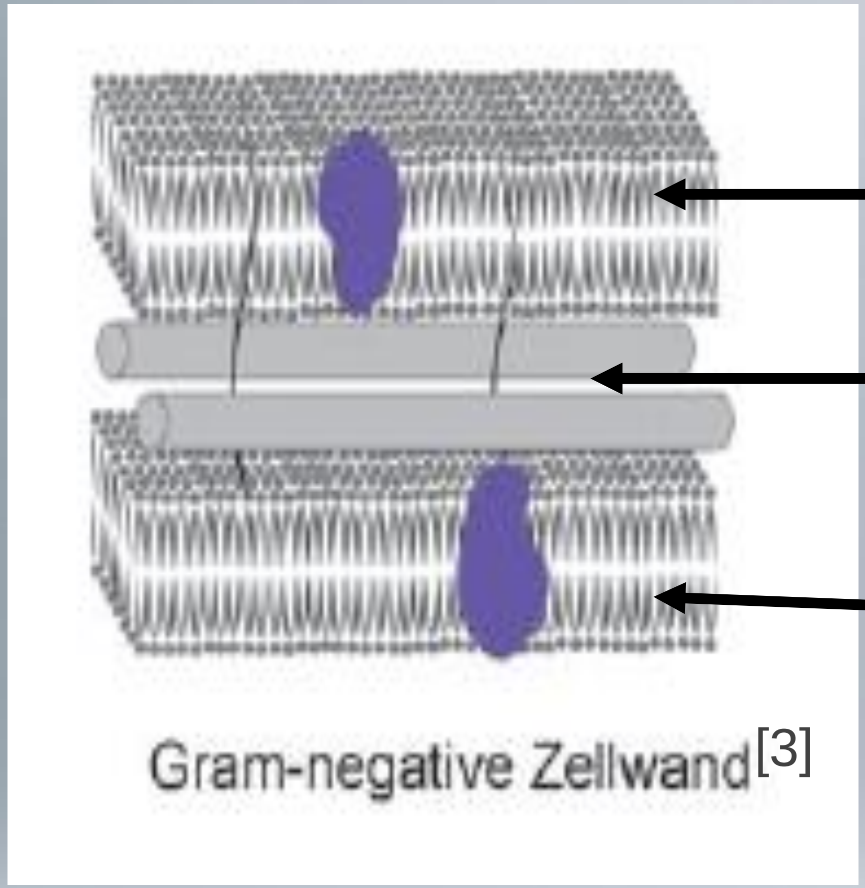




- Inhibition of viruses glycoproteins
- Sedimintation of Viruses
- Derease of viruses in patient



Mitglied der Leibniz-Gemeinschaft

# Antibactericidic Effect of SiNPs

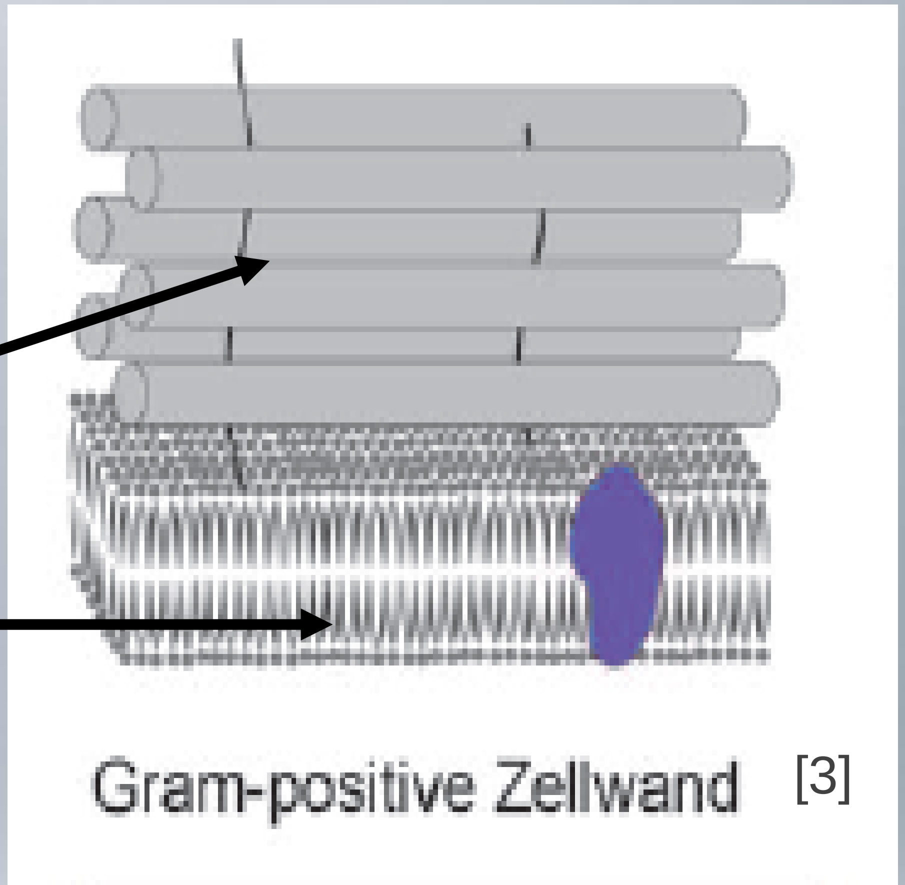



Escherichia coli

Lipide-doublelayer

Peptidoglycane

Lipide-Doublelayer

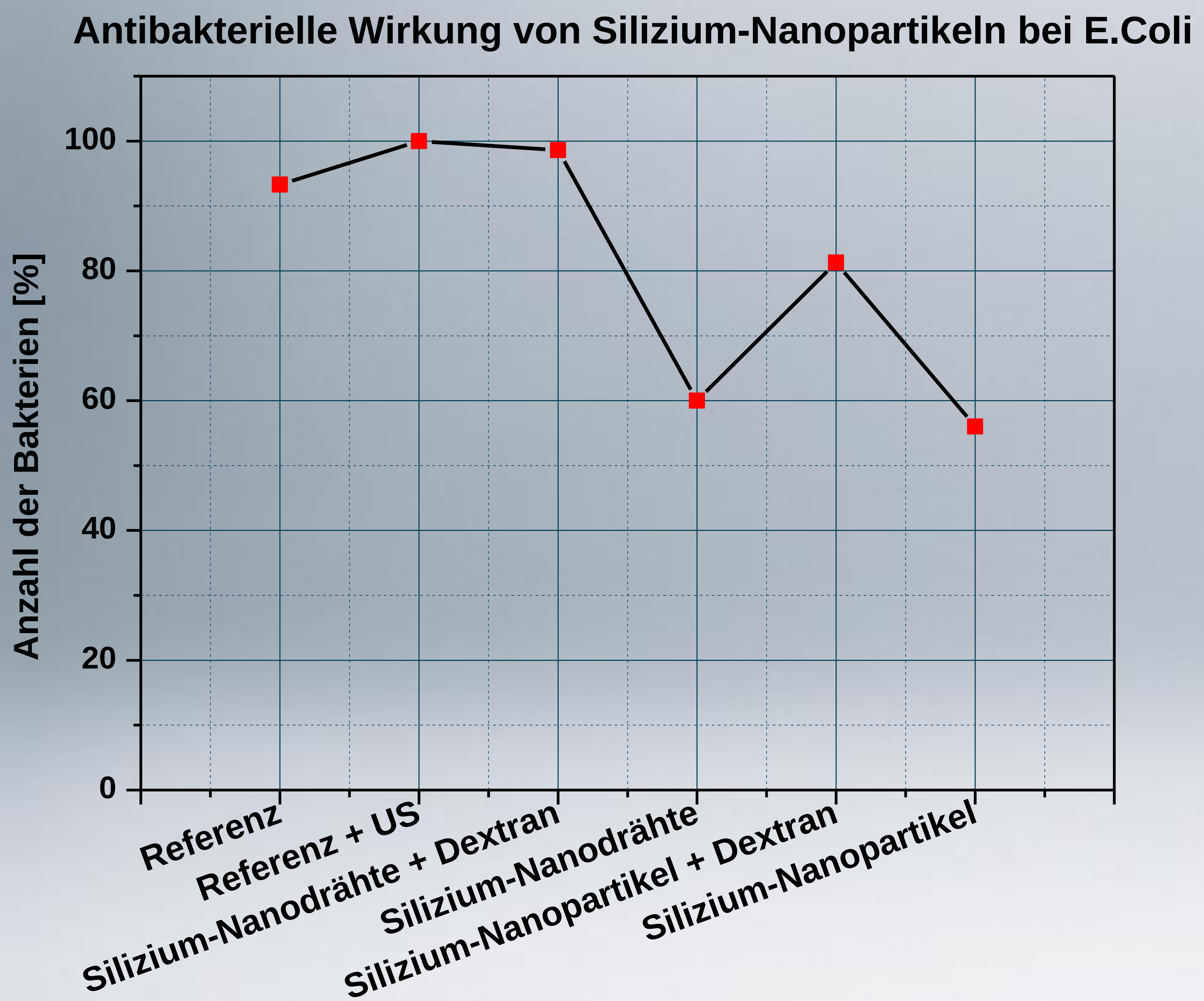


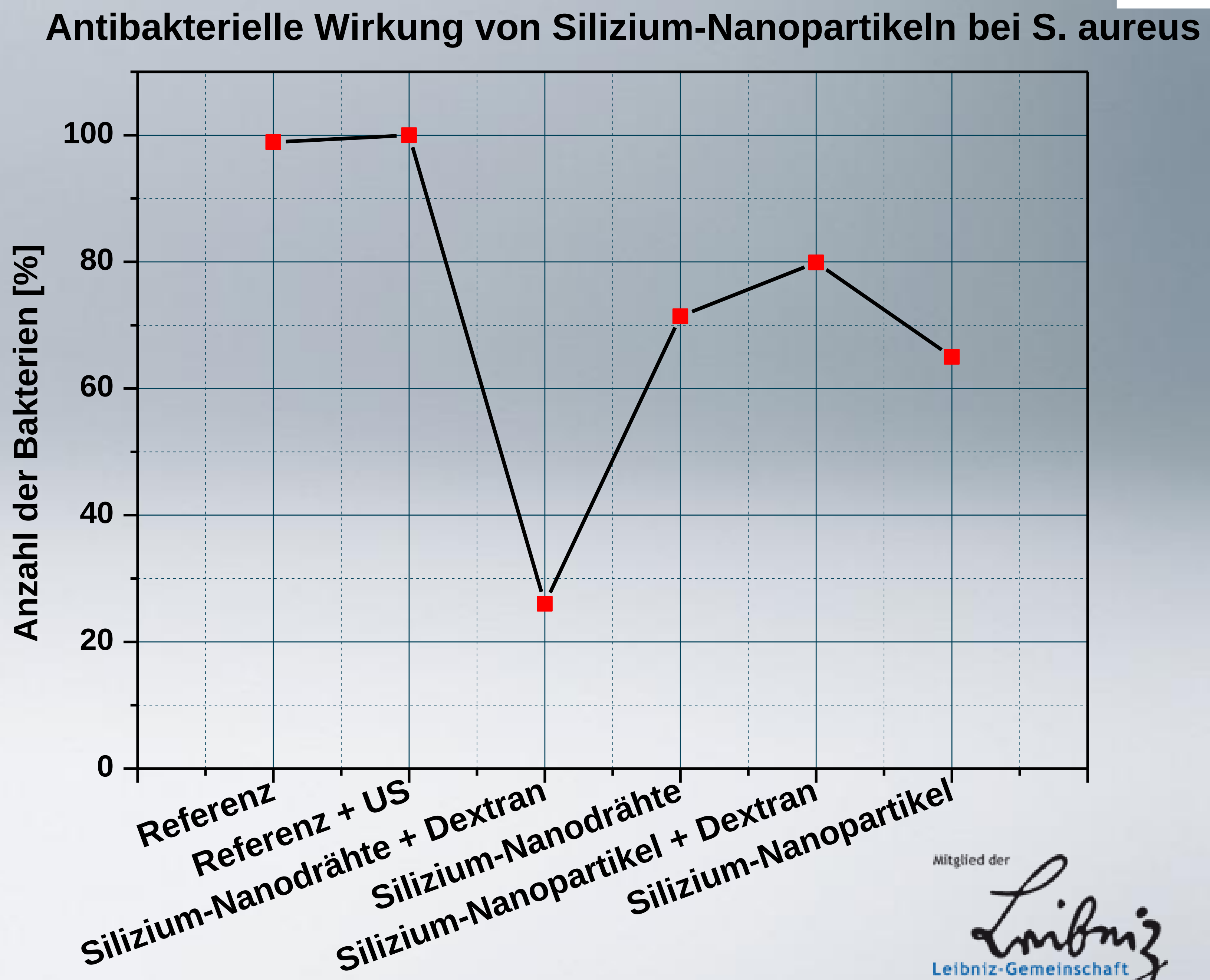

Staphylococcus aureus

- **Destruction of cell wall**
- **therapeutic ultrasound ( $1W/cm^2$; 1,5 MHz, 15 min)**

[3] Wendelin S.: „Nanopartikel in biologischen Systemen“

# Antibactericidic Effect of SiNPs




Mitglied der Leibniz-Gemeinschaft

# Conclusions

Silicon nanopartices can be succefully applied in nanomedicine as effective anti-cancer agent, as drug delivery agent and as possible therapeutica and disinfection agent. Quantum yiled (PL) was observed over 4%.

To do: photostability, surface modification and functionalization. Optimization of NPs particles for imiging technology

Mitglied der

Leibniz-Gemeinschaft

# Thanks for your attention!

vladimir.sivakov@ipht-jena.de

**Prof. Ulrich Gösele†**
**Prof. Victor Timoshenko**
**Dr. Liubov Osminkina**
**Prof. Jürgen Popp**
**Prof. Benjamin Dietzek**
**Dr. Martin Schultz**
**Prof. Rainer Heinzmann**
**Prof. Steffen Teichert**
**Dr. Silke Christiansen**
**Dr. Christian Matthäus**
**Dr. Elena Tolstik**
**Dr. Bela Pecz**
**Dr. György Radnoczi**
**Dr. Felix Voigt…..**
**Dipl. Ing. Alexander Schleusener**
**Dipl. Phys. Johannes Mühlenstädt**
**Dipl. Phys. Florian Talkenberg**
**Dipl. Phys. Arne Bochmann………**

iphtjena

Deutsche Forschungsgemeinschaft

Bundesministerium für Bildung und Forschung

Mitglied der Leibniz-Gemeinschaft

# Thanks for your attention!

vladimir.sivakov@ipht-jena.de

# Motivation

- Smart Material
- Smart Technology
- Smart Concept


iphtjena

Mitglied der Leibniz-Gemeinschaft

# Atomic Layer Deposition

- Part of Chemical-Vapour-Deposition (CVD) technique
- Temperature range from room temperature to several hundred degree Celsius
- Atmospheric to ultra high vacuum pressure
- Cyclic layer by layer deposition process
- Self-limited process

  →Maximal one atomic layer per cycle

  →High uniform film growth

# Atomic Layer Deposition

Example: thermal $Al_2O_3$-Process

a) Dosis-Step (TMA)

One Monolayer TMA absorption on surface

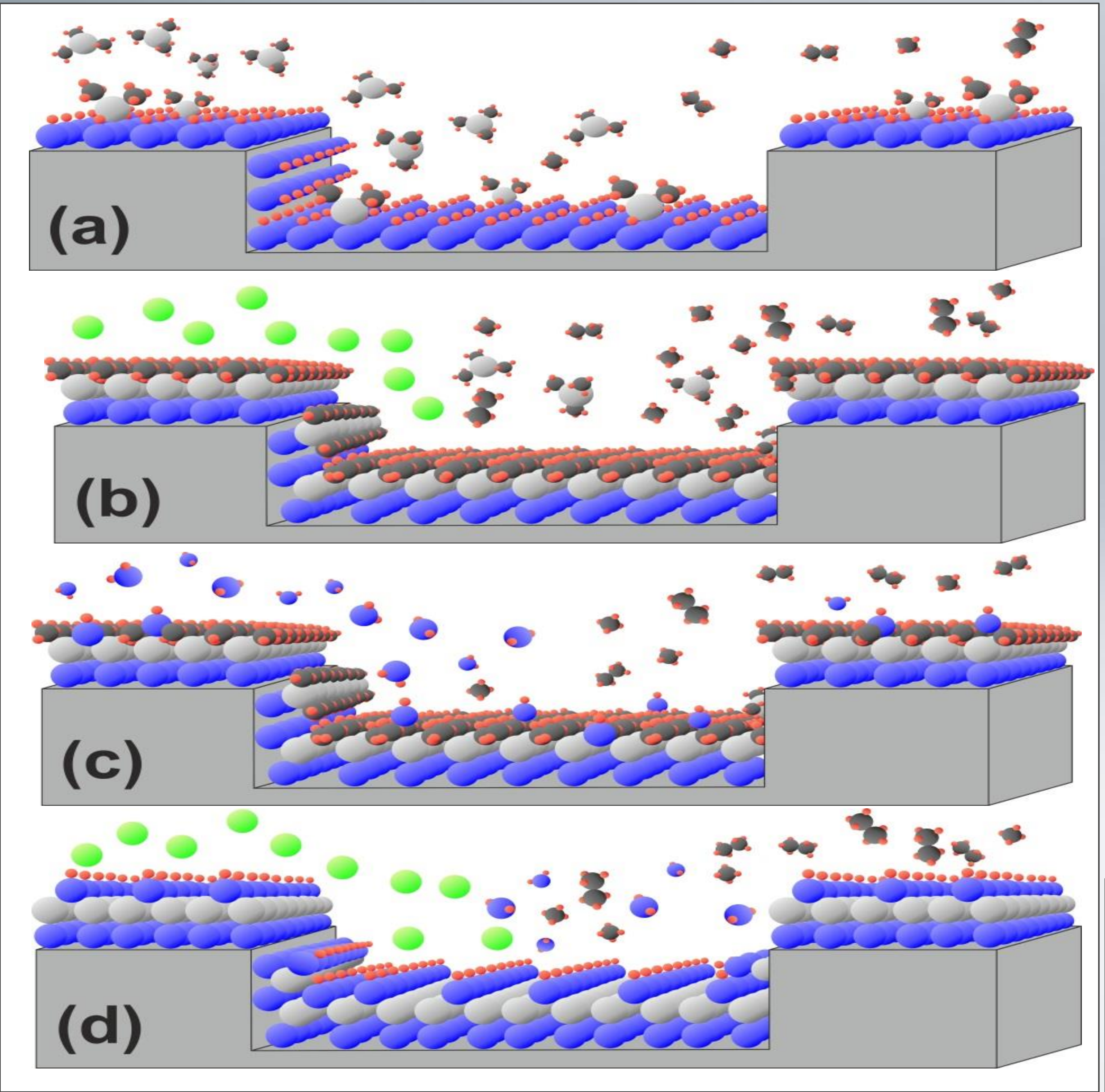
b) Purge Chamber by inertgas

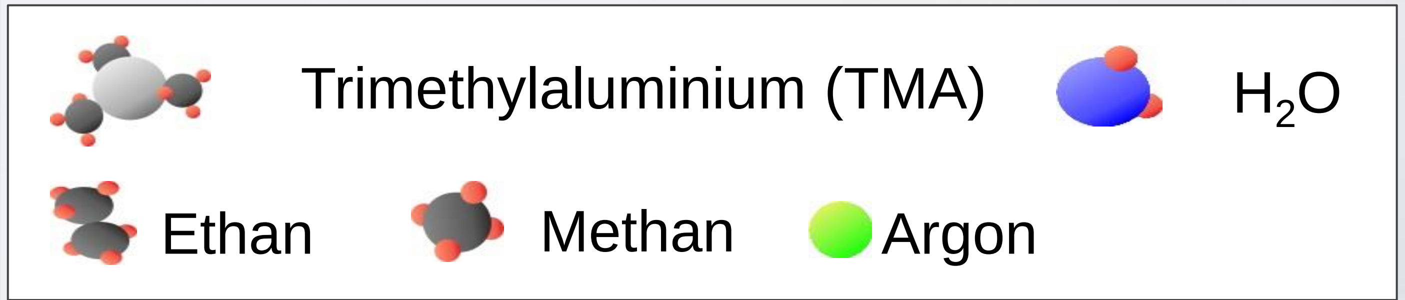
c) Dosis-Step ($H_2O$)

adsorpted TMA react with $H_2O$ to $Al_2O_3$

d) Purge Chamber by inertgas

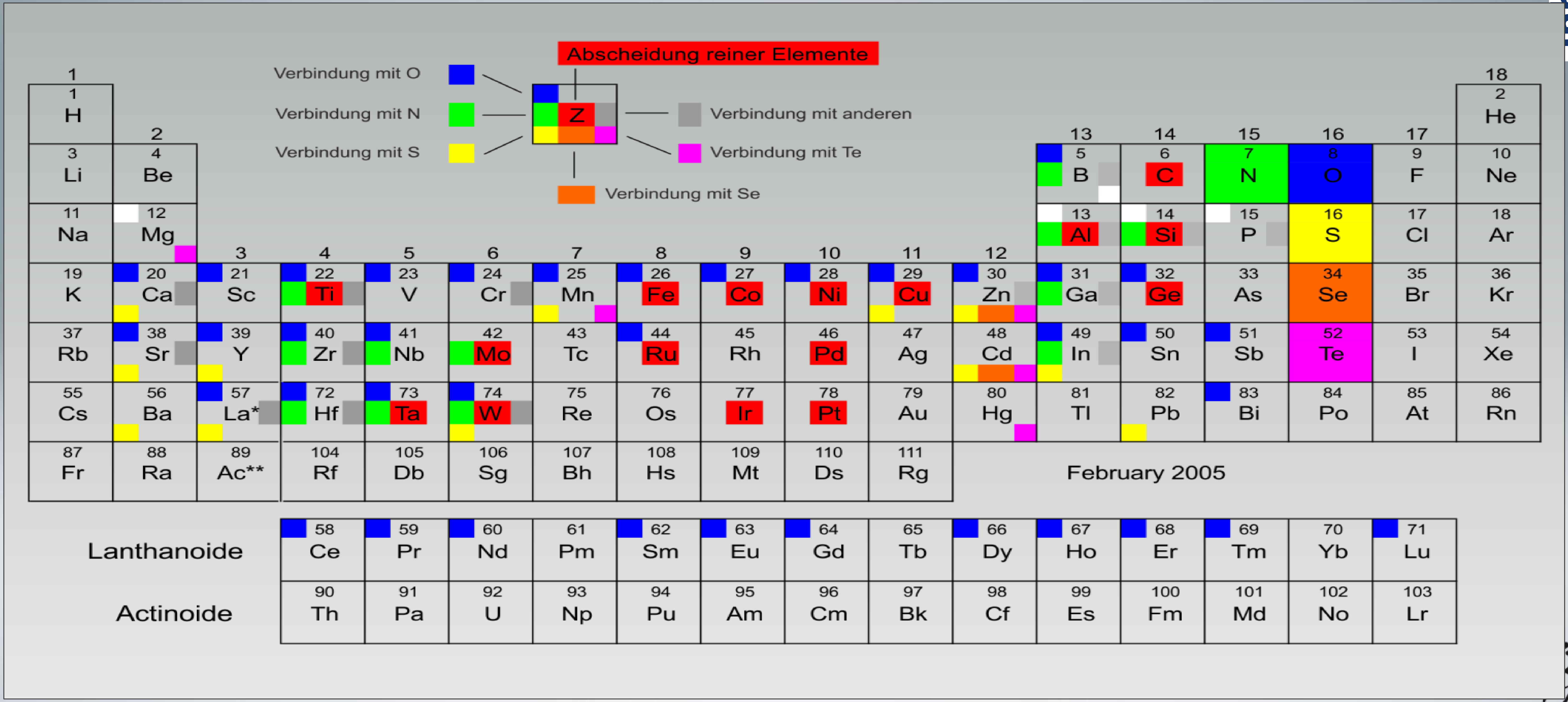
- ***Surface should be saturated by precursor***
- ***Long enough purge time to remove precursor and reaction products***
- ***Next to only thermal processing, possibility to activate precursor by plasma***



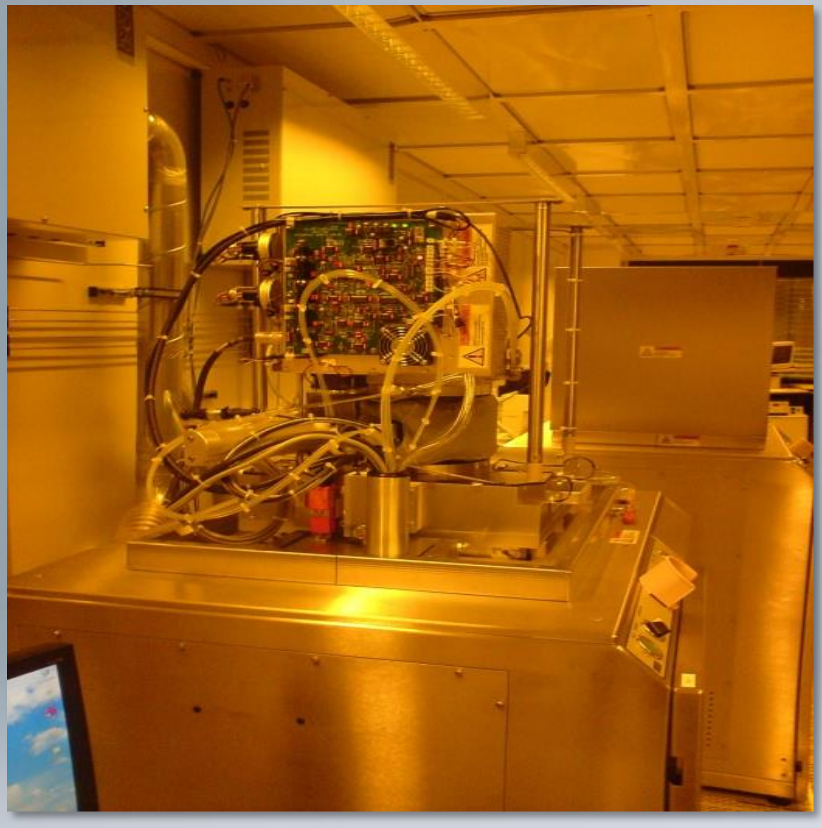




Mitglied der Leibniz-Gemeinschaft

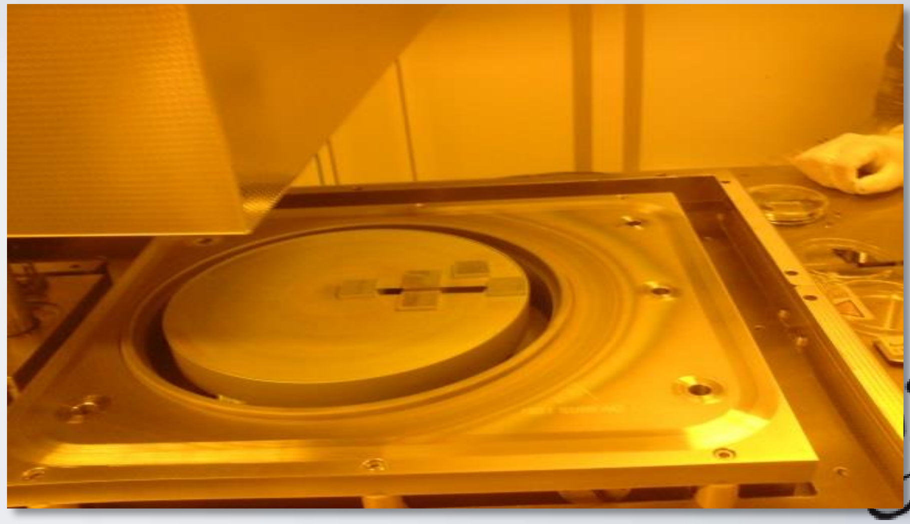
# Overview possible Deposition Compounds



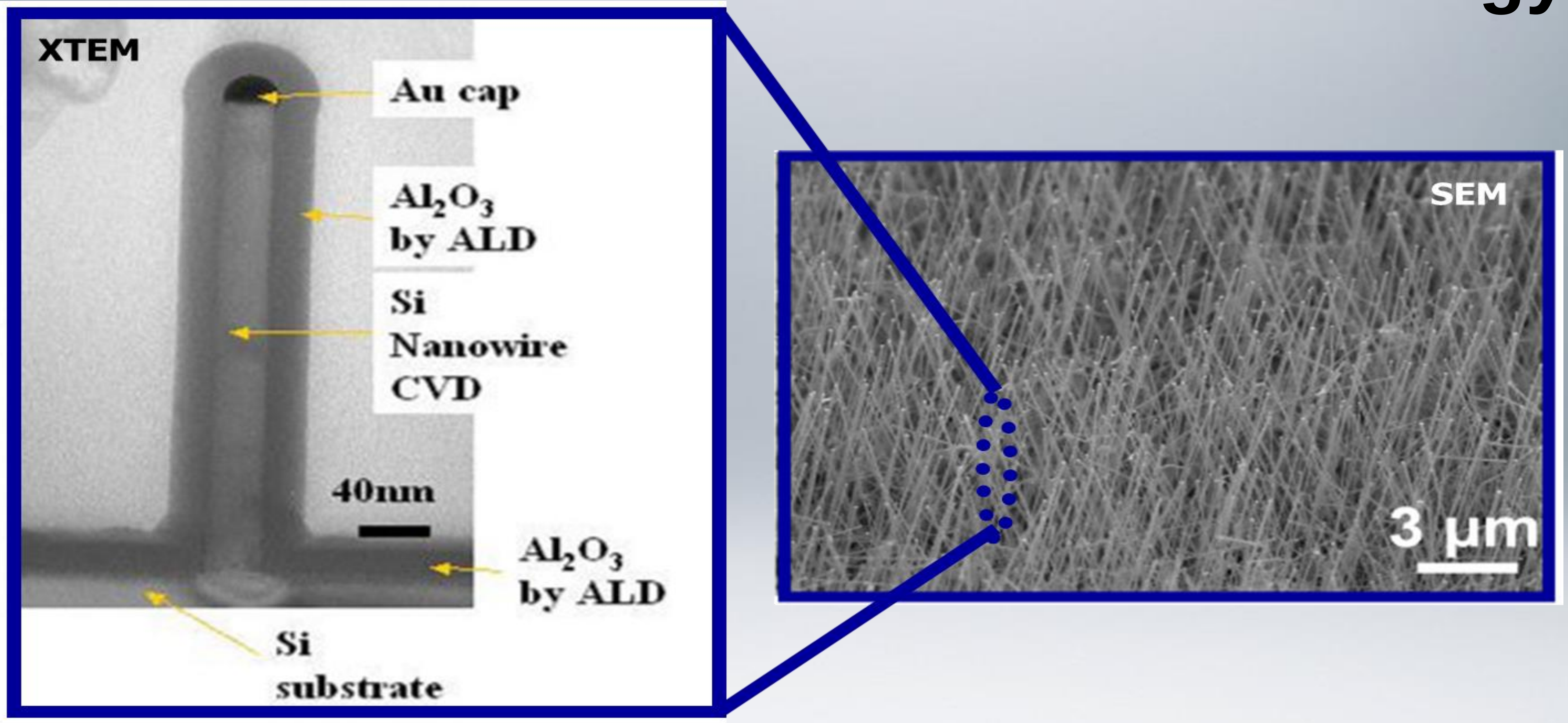
# Oxford OpAL – Atomic Layer Deposition Engine





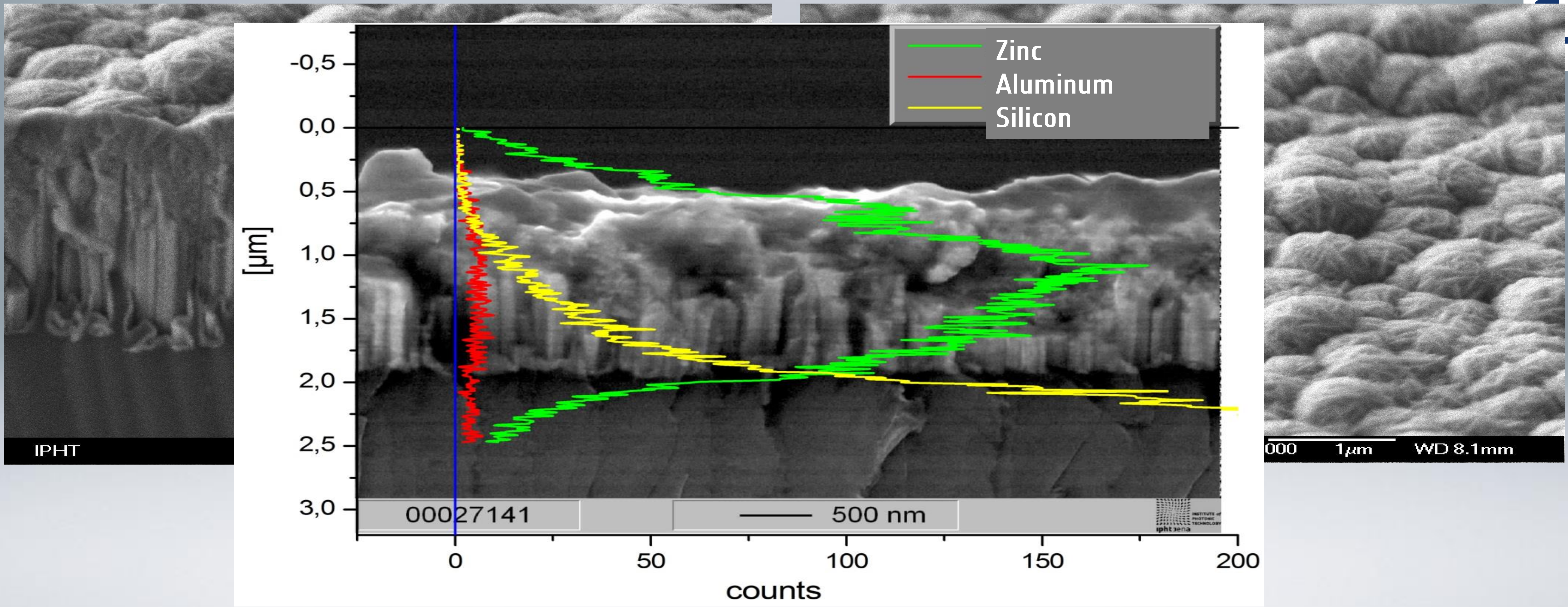


# ALD Technology




ALD: Gao, Ley, Physik, Uni Erlangen

# ALD Technology




**Very homogeneous distribution of ZnO inside the nanowire carpet**

# Transparent Conductive Oxides (TCO)

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

## Indium Tin Oxide

- Low specific resistivity: ~ $10^{-5}$ $\Omega$cm
- Poor raw material
  → high cost

## Aluminium Zinc Oxide

- Present specific resistivity: ~ $10^{-4}$ $\Omega$cm
- Better transmission in visible range
- Low cost

Mitglied der Leibniz-Gemeinschaft

# Transparent Conductive Oxides (TCO)

## Farbication of Al doped ZnO using Atomic Layer Deposition

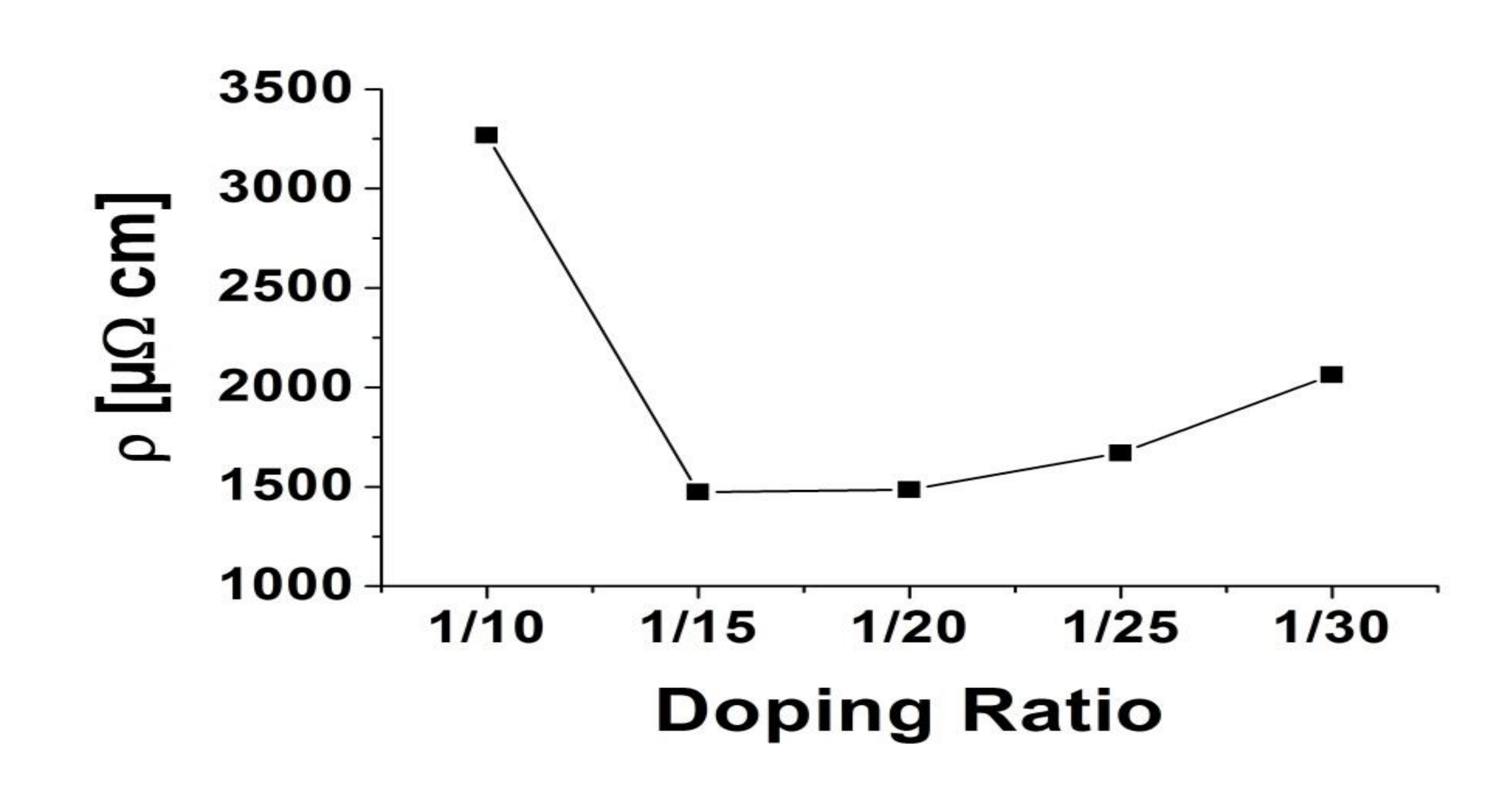
**Precursors:**

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

**Doping Sequence:**

**N cycles DEZ/$H_2O$ + 1 cycle TMA/$H_2O$**

→ ***Doping Ratio 1/N***




**Minimal specific resistivity:**

***1/15 ≥ best ratio ≥ 1/20***

**Stoichiometry measurement (with RBS):**

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

# Transparent Conductive Oxides (TCO)

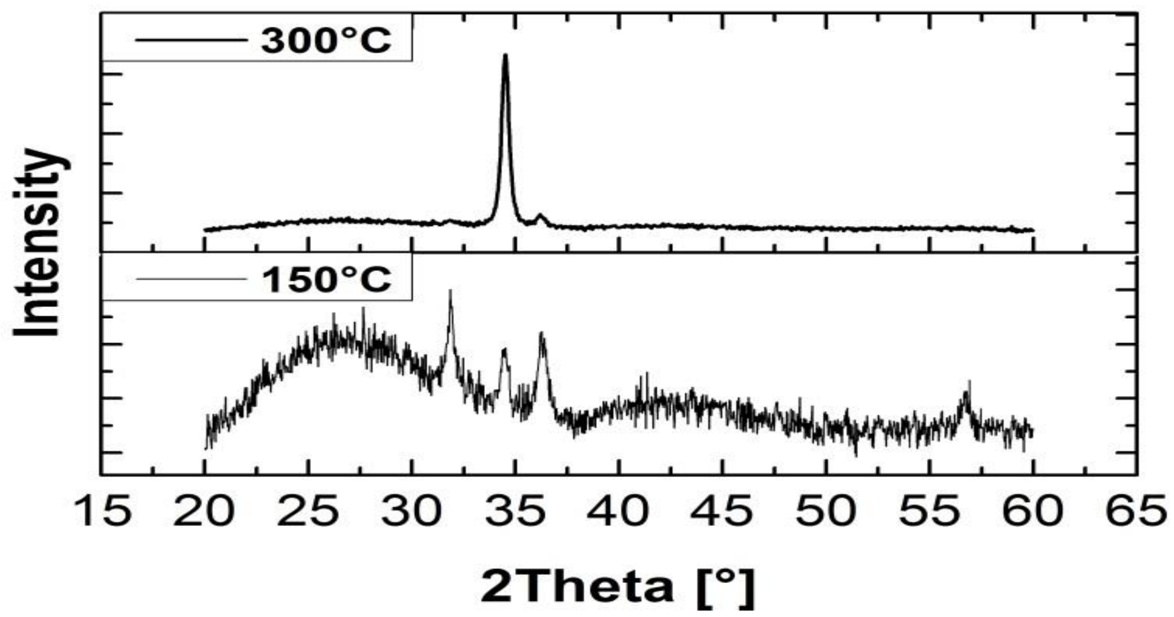
## Influence of Deposition Temperature

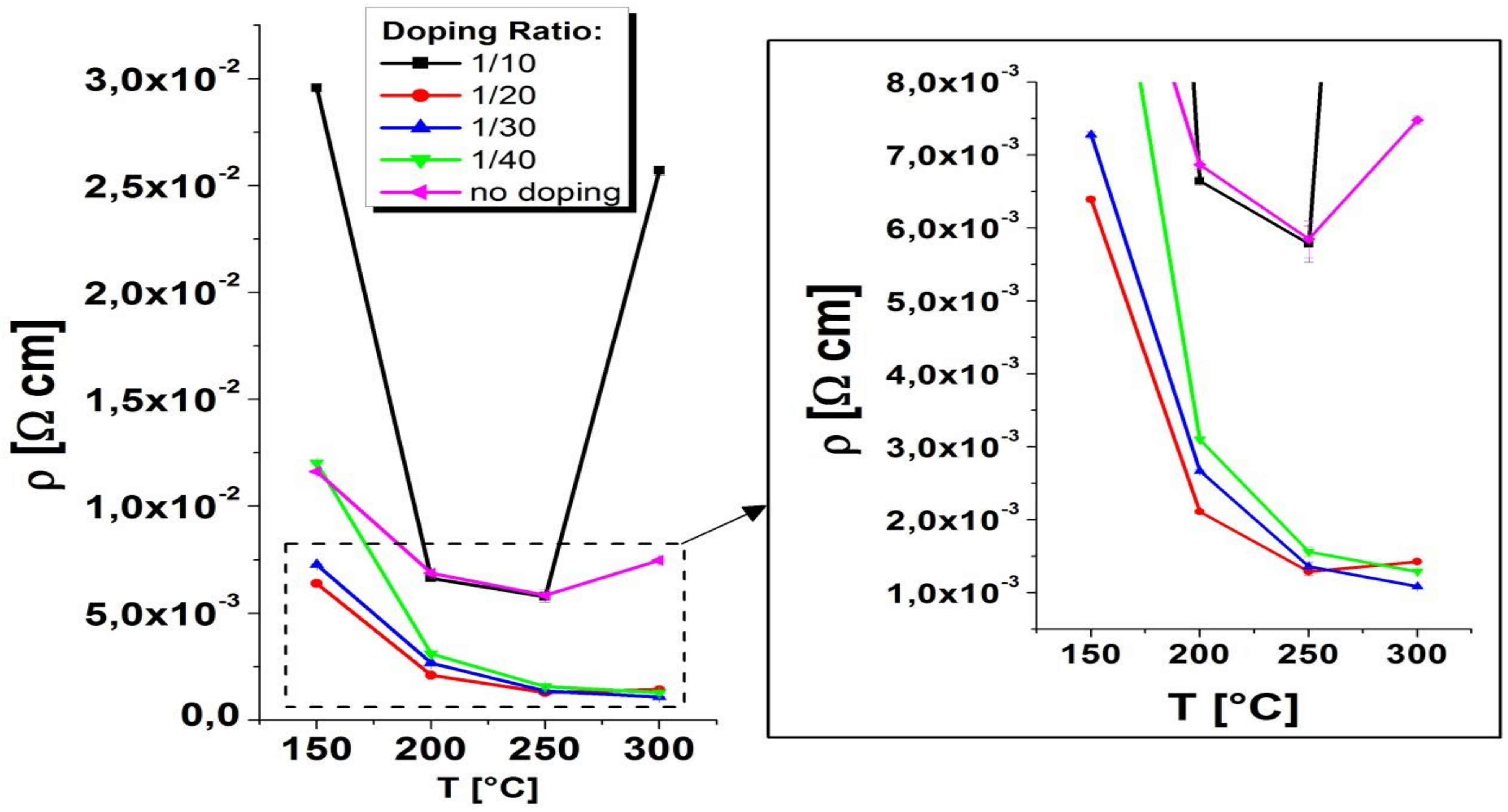
Influence on:

- Impurity doping of ZnO
- Cristallinity
- Dopant activation

→ specific resisitivity

**XRD pattern of ZnO:**



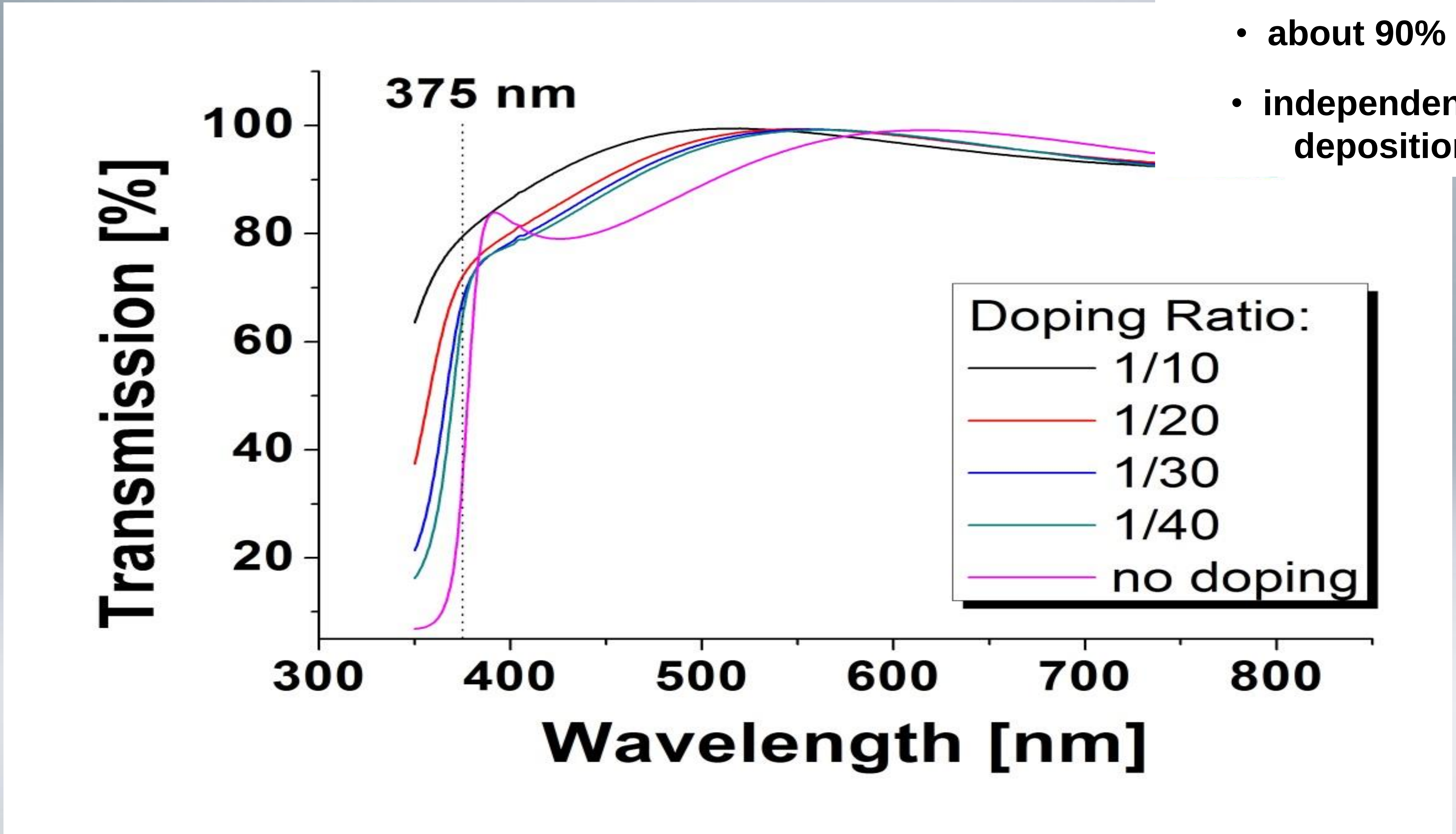

**Best results:**

- **temperatures ≥ 200°C**
- **doping ratio > 1/10**

Mitglied der Leibniz-Gemeinschaft

# Transparent Conductive Oxides (TCO)

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



# Transparent Conductive Oxides (TCO)

## Flash Annealing

**Flash Annealing System:**

*© by Dresden Thin Film Technology*

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

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