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PHOTONICS FOR LIFE

Interfaces and Me


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BUNDESREPUBLIK DEUTSCHLAND
Politische Gliederung · Stand: 01. 01. 2007
0 50 100
Kilometer
Ballungsraum Rhein-Ruhr
Bottrop
G.
Rh.
Herne
Moers
O.
E.
Bochum
Do.
Du.
Mülheim
Witten
Krefeld
Hagen
Düsseldorf
Wuppertal
Neuss
So.
Remscheid
DÄNEMARK
Flensburg
Schleswig-Holstein
Kiel
Neumünster
Itzehoe
Lübeck
Ostsee
Nordsee
Stralsund
Greifswald
Rostock
Wismar
Mecklenburg-Vorpommern
Schwerin
Neubrandenburg
Norderstedt
Hamburg
St. Hamburg
Wilhelmshaven
Bremerhaven
(zu Bremen)
Emden
Oldenburg
Bremen
Bremen
Delmenhorst
Lüneburg
Elbe
Oder
POLEN
NIEDERLANDE
Niedersachsen
Celle
Stendal
Oranienburg
Eberswalde
Berlin
Berlin
Brandenburg
Frankfurt
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Hannover
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Weser
Dessau
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Sachsen-Anhalt
Hamm
Paderborn
Göttingen
Essen
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Siegen
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Chemnitz
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Thüringen
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Zwickau
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Suhl
Plauen
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Wiesbaden
Frankfurt
Unterfranken
Coburg
Hof
Schweinfurt
Oberfranken
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Mainz
Offenbach
Aschaffenburg
Bamberg
Darmstadt
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Bayreuth
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Worms
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Amberg
Saarland
Saarbrücken
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Lu.
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Fürth
Nürnberg
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N.
Sp.
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P.
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Mittelfranken
Regensburg
Donau
Pforzheim
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Baden-Baden
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Ingolstadt
Passau
Niederbayern
Reutlingen
Schwaben
Tübingen
Bayern
Landshut
Ulm
Augsburg
Baden-Württemberg
ÖSTERREICH
Freiburg
Oberbayern
Memmingen
Villingen
München
Kaufbeuren
Rosenheim
Schwenningen
Friedrichshafen
Konstanz
Garmisch-Partenkirchen
Kempten
Bodensee
SCHWEIZ
B.G. = Bergisch Gladbach
F. = Frankenthal
G. = Gelsenkirchen
Lu. = Ludwigshafen
M. = Mönchengladbach
N. = Neustadt
O. = Oberhausen
P. = Pirmasens
Re. = Remscheid
Rh. = Recklinghausen
So. = Solingen
Sp. = Speyer
St. = Stade
Z. = Zweibrücken
Verwaltung
Staatsgrenze
Ländergrenze
Bezirksgrenze
Bundeshauptstadt
Landeshauptstadt
Hauptstadt eines Regierungsbezirks
Die Regierungsbezirke sind außer in Bayern nach ihrem Hauptort benannt.
Einwohnerzahlen
< 100 Tsd.
100–250 Tsd.
250–500 Tsd.
500 Tsd.–1 Mio.
> 1 Million


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Department

„Functional Interfaces“

“Semiconductor Nanostructures” Group at Leibniz IPHT

- Vladimir Sivakov
- vladimir.sivakov@ipht-jena.de

Mitglied der Leibniz-Gemeinschaft

Group Facilities

Chemical Vapor Deposition: 2D a-Si:H; 2D mc-Si; 1D Si; 1D Ge; 1D SnO_2; 1D VO_x; 1D Fe_3O_4; Au, Ag

Atomic Layer Deposition: ZnO, Al_2O_3; Al:ZnO; TiO_2; SiO_2; HfO2; ZrO2

Physical Vapor Deposition: a-Si, mc-Si, Ti, Al, Au, Ag, Pd, Cr

Wet @Dry Etching and Surface Modification@Functionalization: RIE

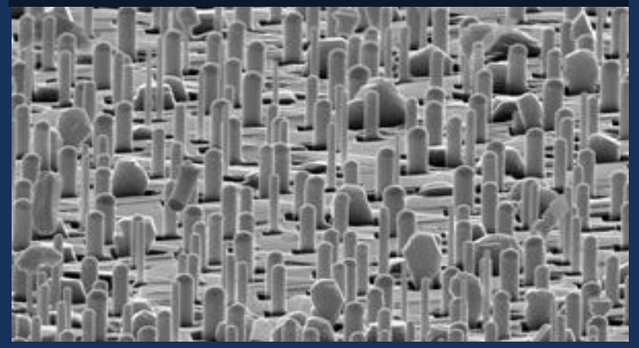
Focused Electron Beam Technology: FEI Helios; Tescan Lyra

Surface Structuring: Photolithography, EB Lithography, PS

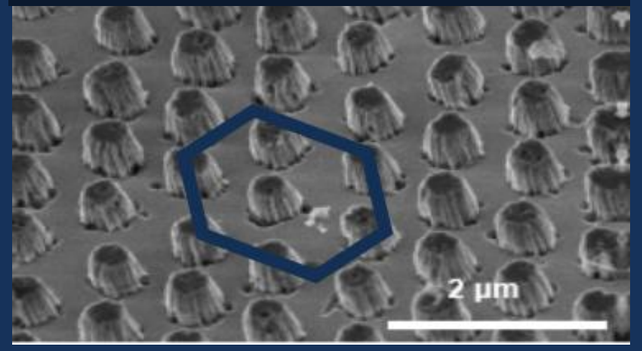
Characterization: SEM, AFM, PL, CL, µ-PL, XRD, Ellipsometry, EBSD, EBIC, I-V, C-V, Raman, CARS SER(S)S, µ-Raman

Material Facilities

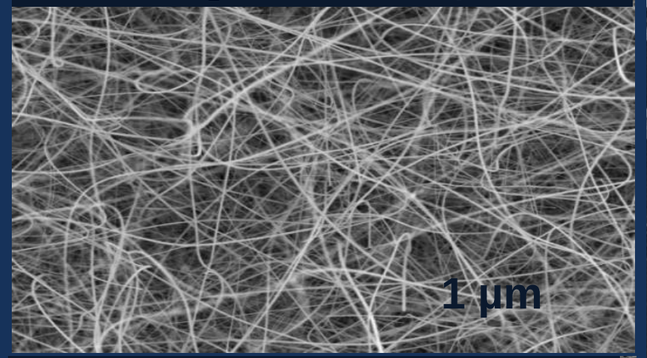
Bottom-up SiNWs



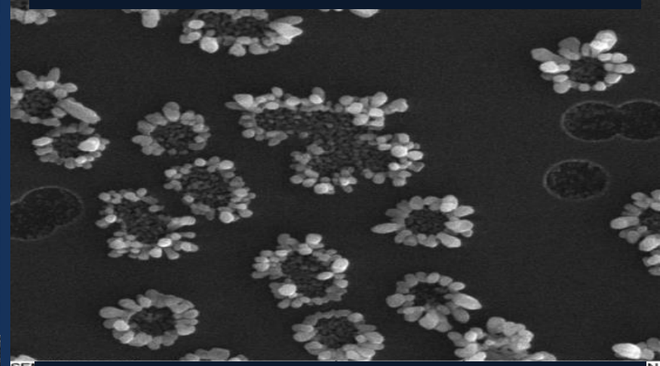
Top-down SiNWs Array



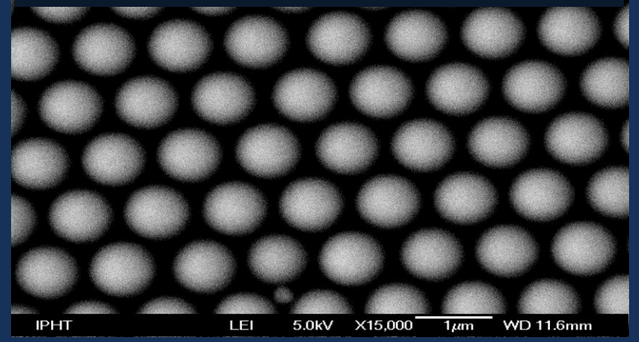
SnO_2 Nanowires Carpet



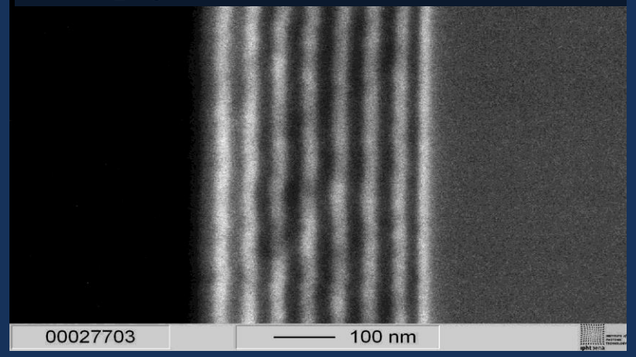
Silver „Sun-Flowers“



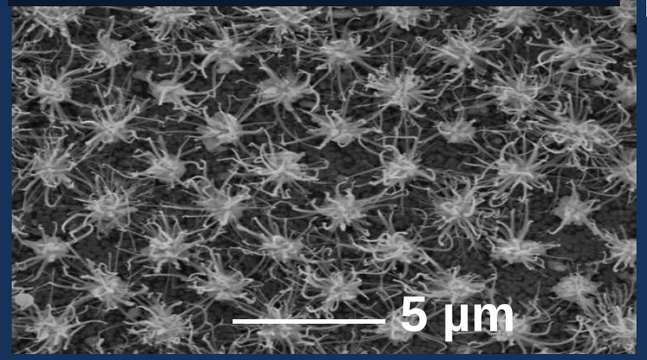
Au Array



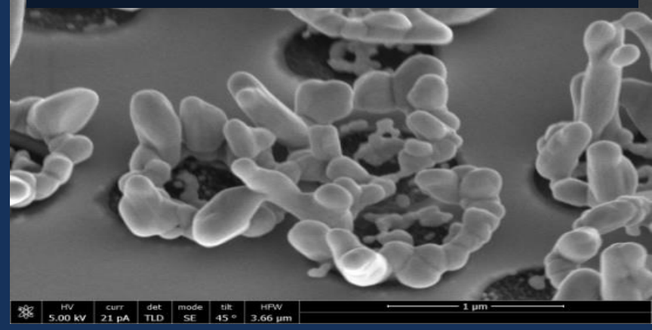
Al_2O_3-ZnO ALD heterostructure



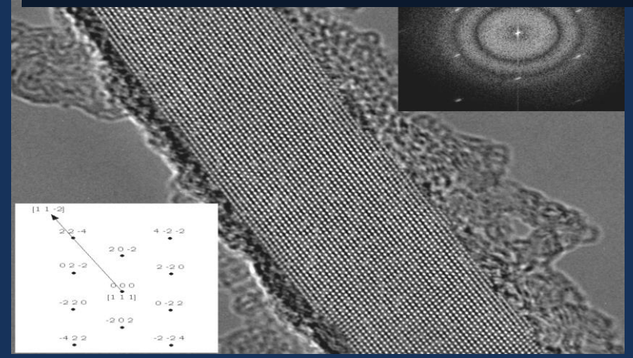
Bottom-up GeNWs



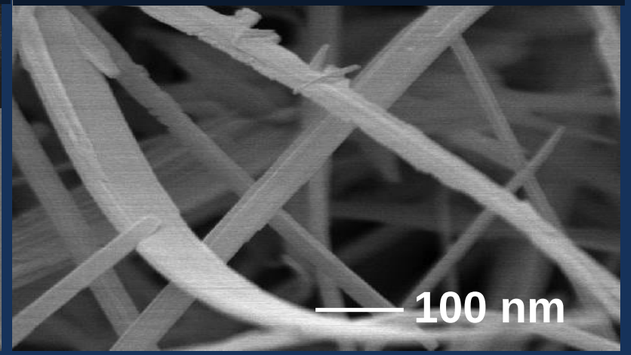
Silver for SERS



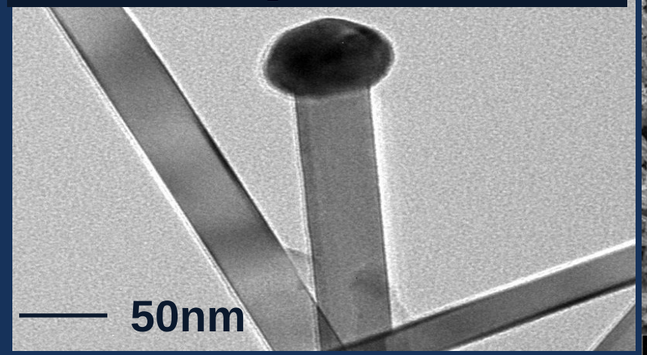
Single Ge Nanowire



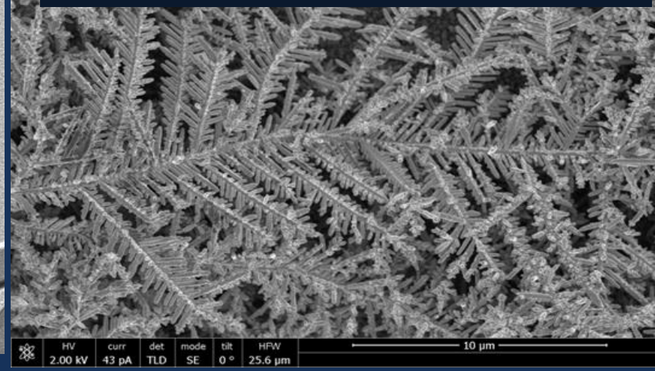
VO_x Nanobelts



SnO_2 Nanowire



Silver Dendrites

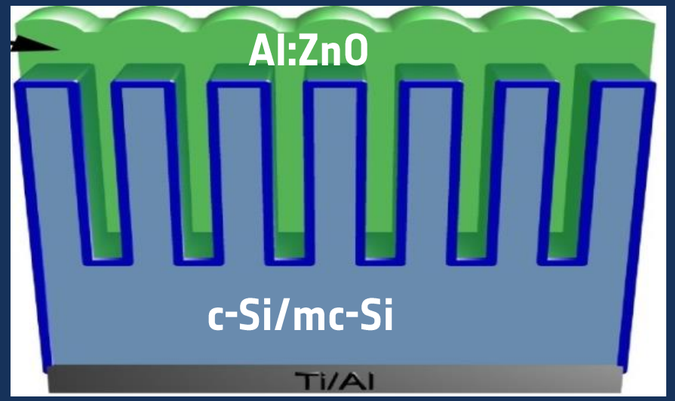


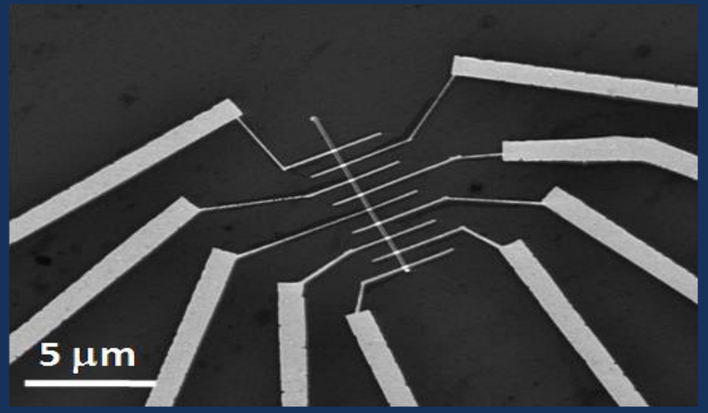
Applications

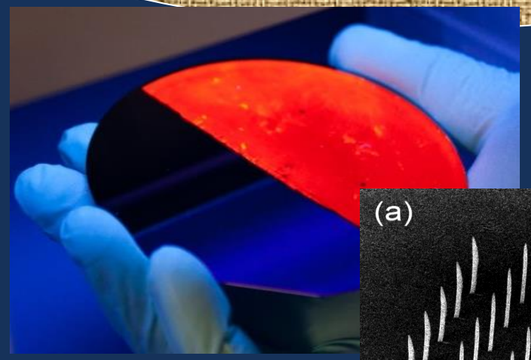
Energy
Third generation photovoltaic and fuel cell

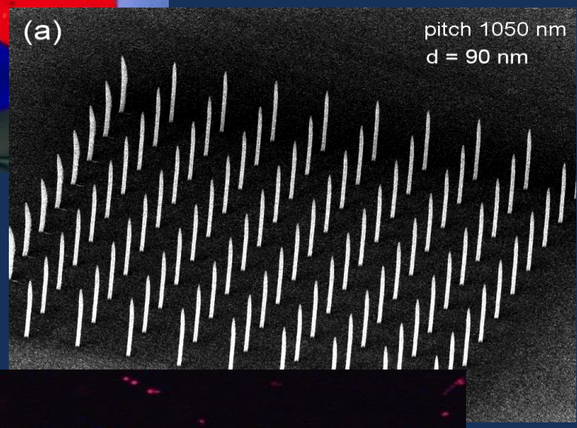
Sensoric
Life Science, Gas, Civil Security

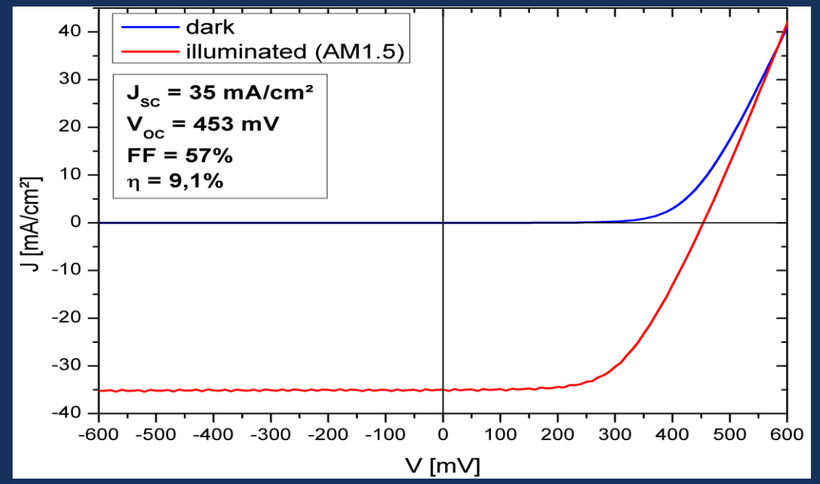
(Bio)-Plasmonic, (Bio)-Photonic
SERS/TERS, Theranostics

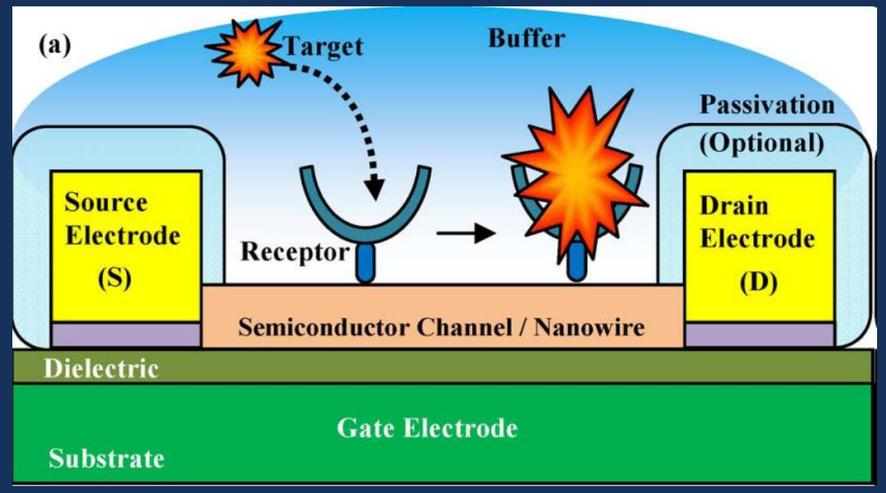


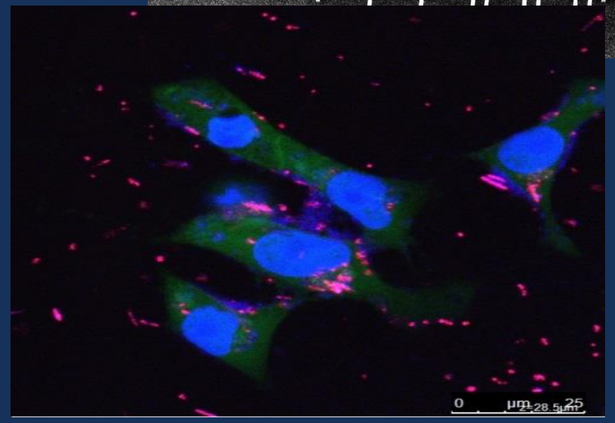












Silicon Nanostructures: Novel aspects and application perspectives

Vladimir Sivakov

Leibniz Institute of Photonic Technology,

Jena/Germany

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

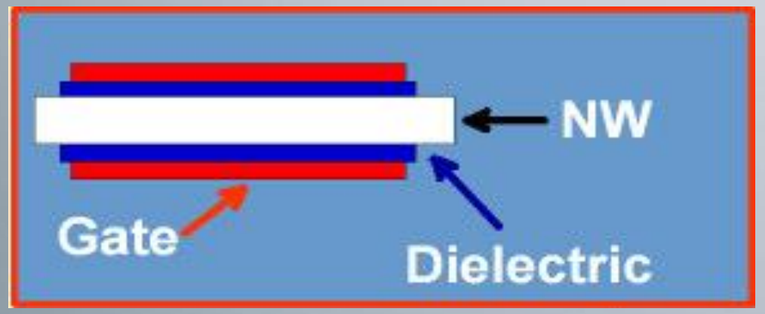
May 6th, 2015 Moscow Russian Federation

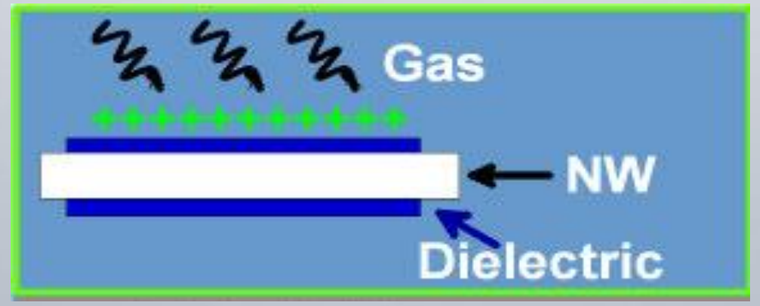
Outline

1. Silicon Nanowires Formation
2. Surface Enhanced Raman Spectroscopy
3. Silicon for Sensing Applications
4. Silicon Nostructures in Energy Applications
5. Silicon Nanoparticles in Biomedicine

Why Semiconductor Nanowires?

Applications of Nanowires

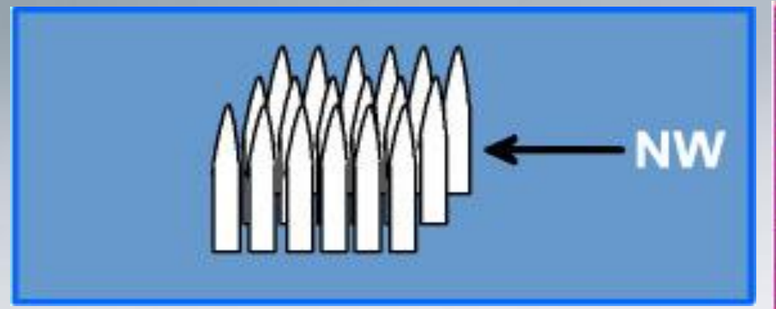


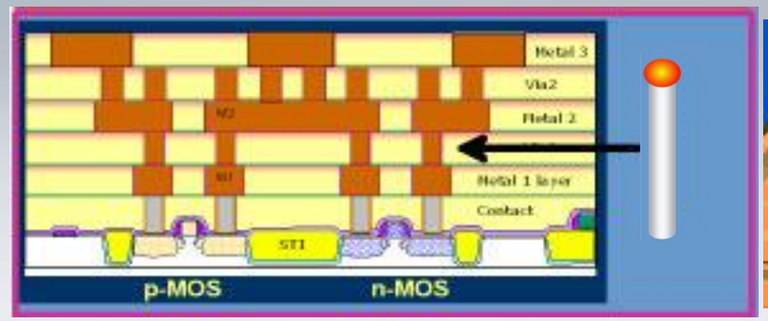


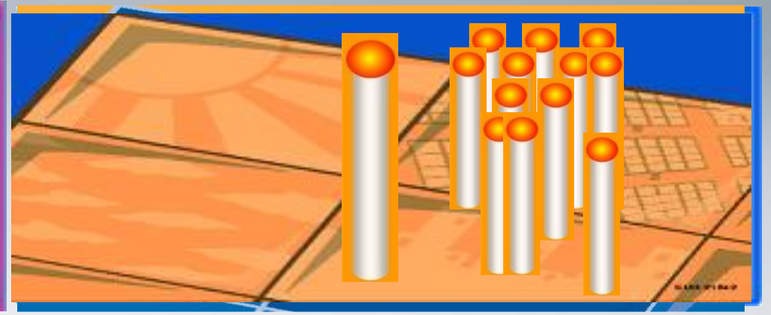
Micro-/Nanoelectronics (‚Next-generation‘ CMOS)

Sensors (Life sciences, Gas, Bio-Med.)

Optoelectronic/Photonic (LED, Laser)







Fieldemitter

Interconnects

Photovoltaic/Energy

Publication Activity on NWs

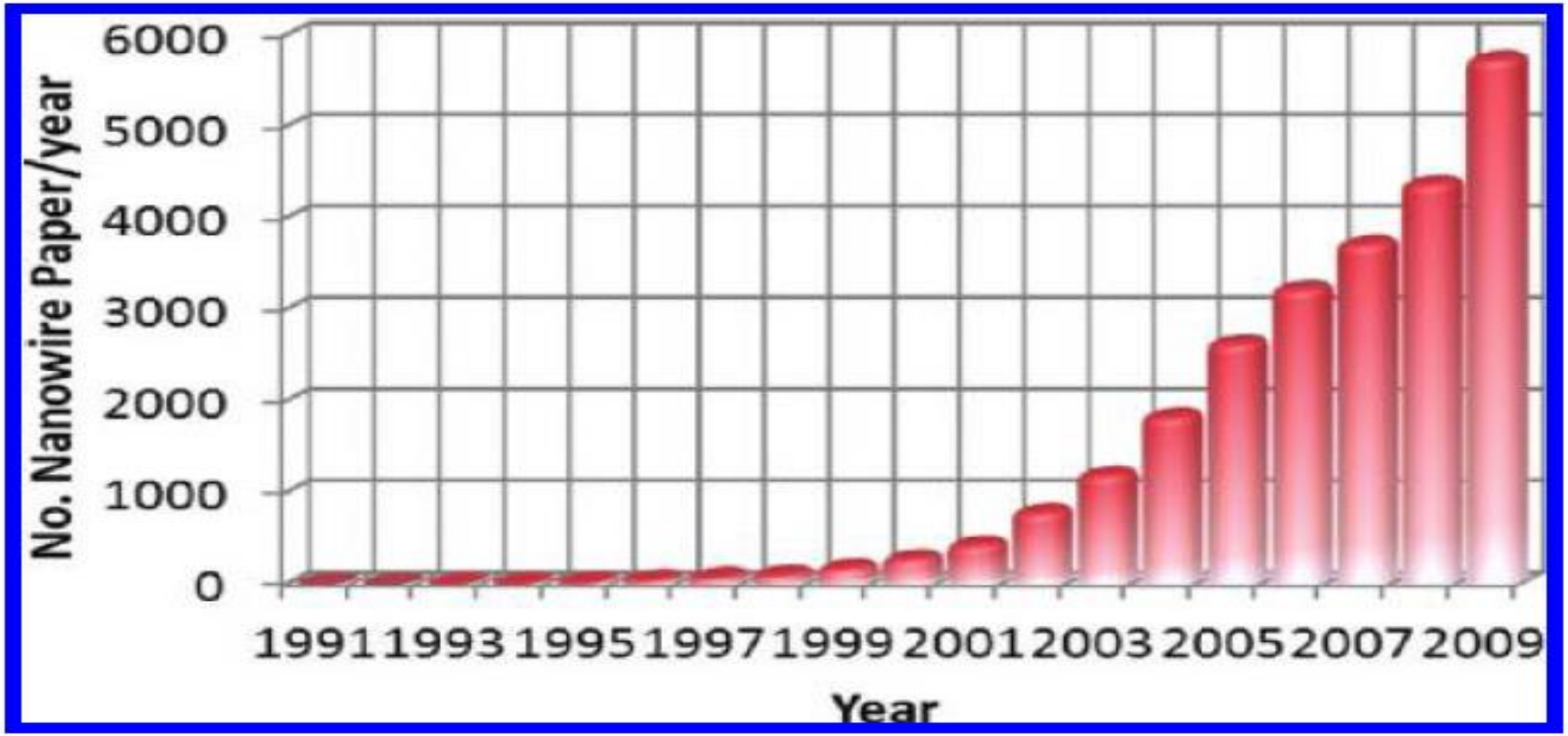
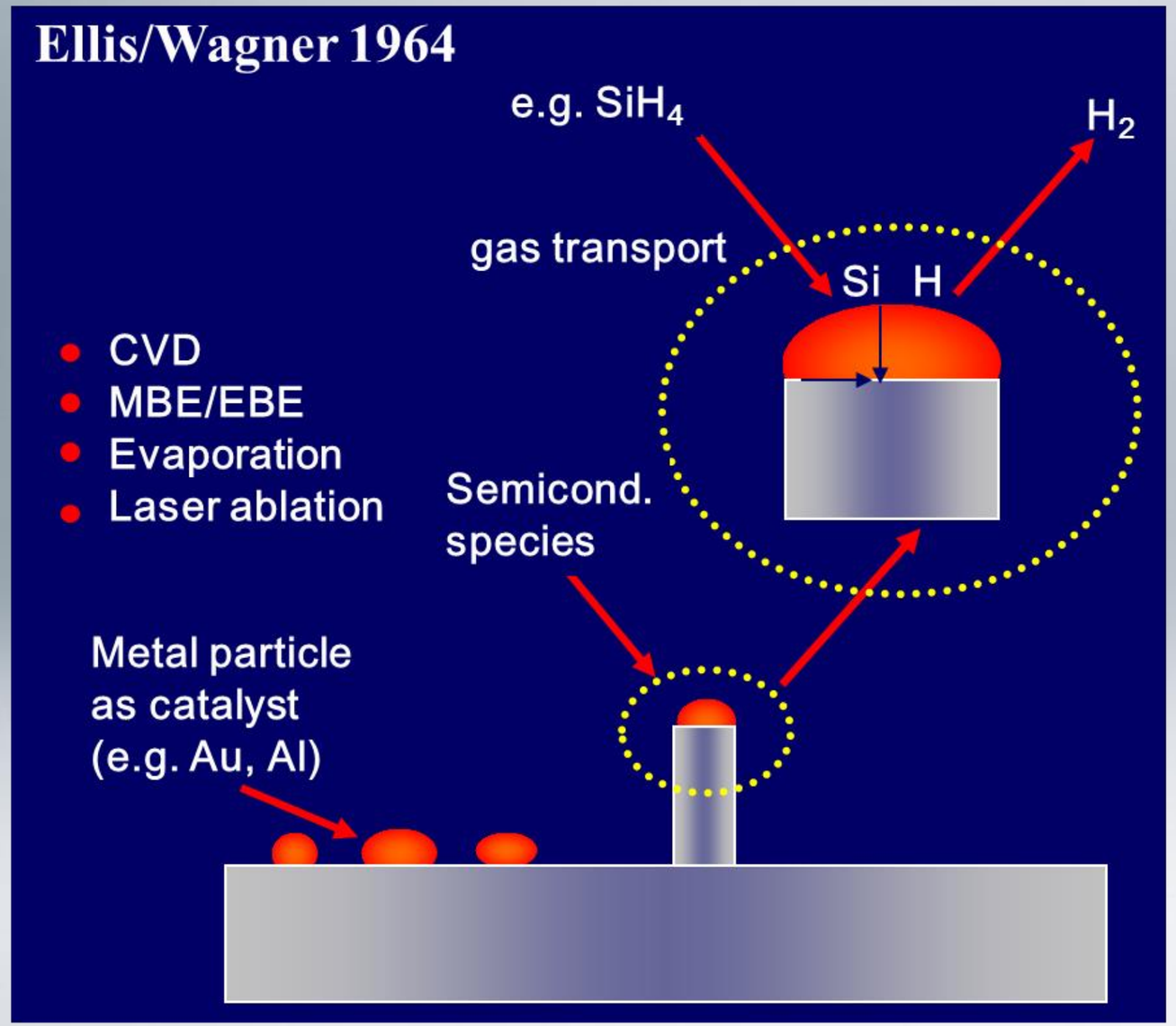


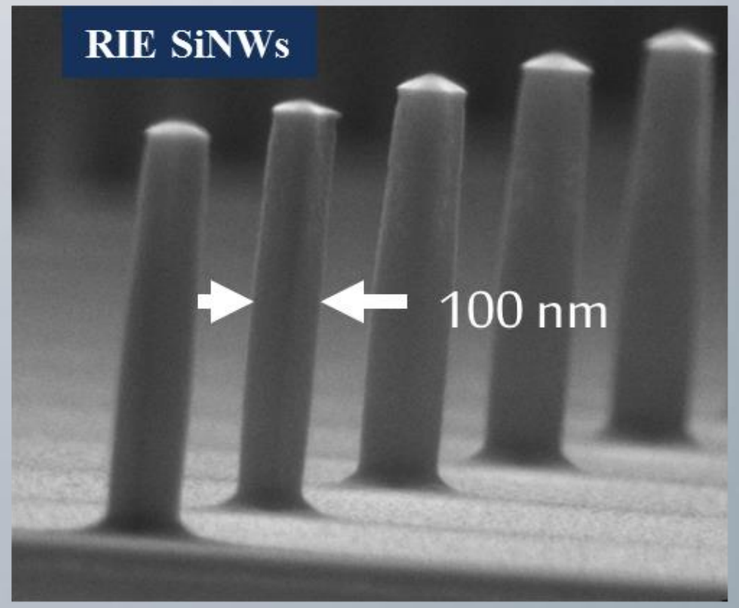
FIGURE 1. Increase in the number of publications on nanowire-related topics from year 1991–2009 (Source, ISI; keyword, nanowires).

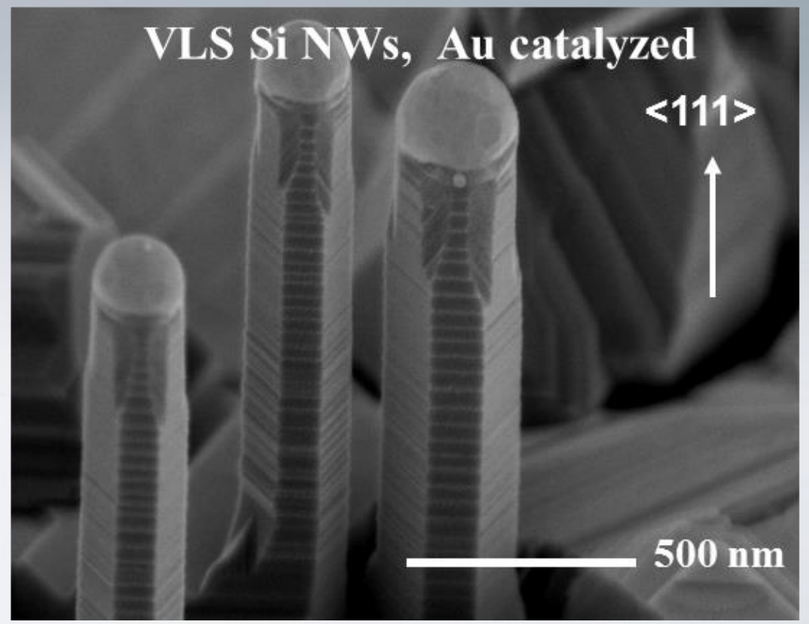
Peidong Yang, et al. Nano Lett. 10, 1529 (2010)

Silicon Nanowires Formation

1D Nanostructures *via* Bottom-up

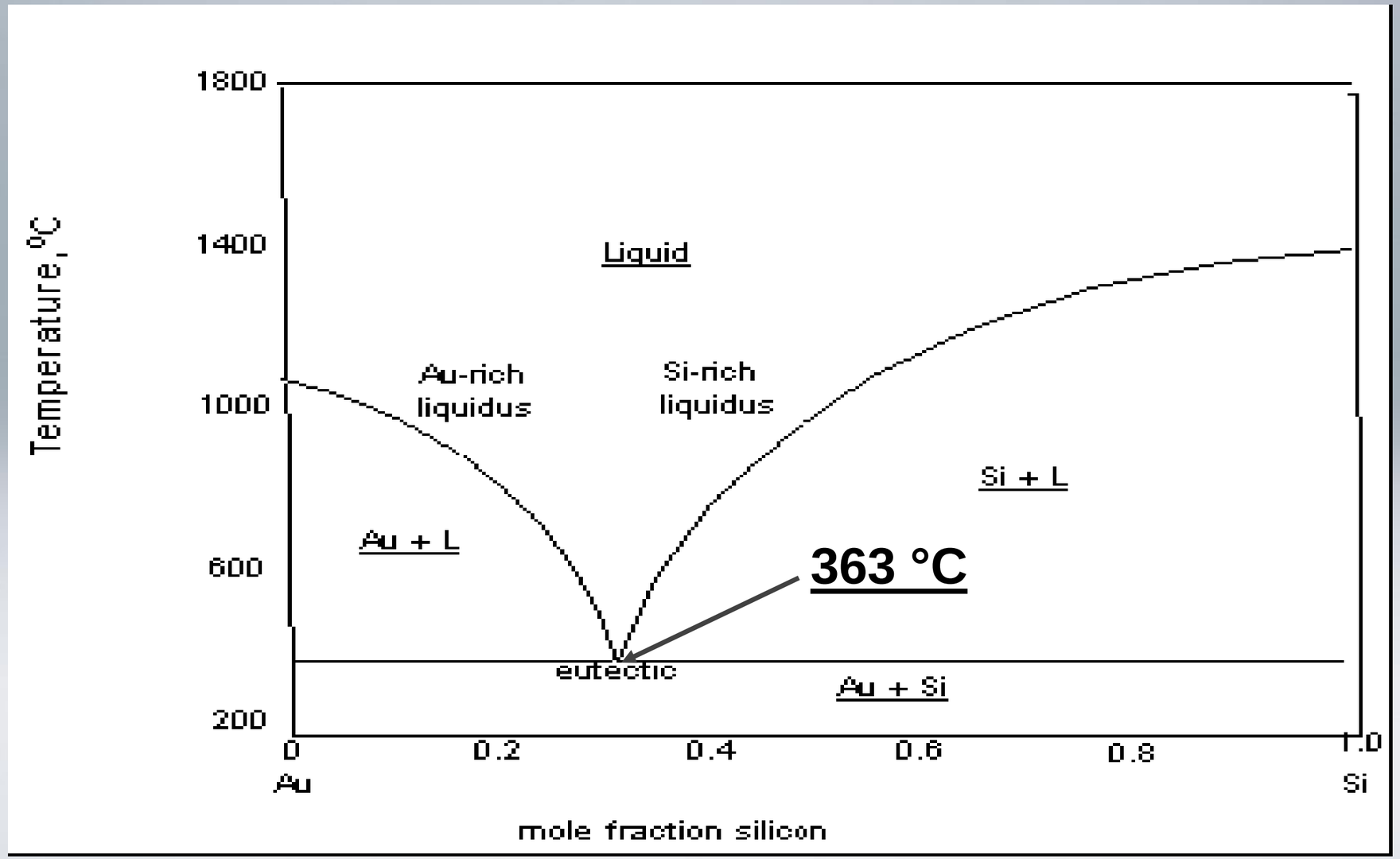






1D Nanostructures *via* Bottom-up

Gold-Silicon Phase Diagram



Experimental Equipment

Thermal CVD

Pressure: 0.5-5 mbar

Temperature: 580 / 500°C

Growth time: 1 min +

Gases: 20 sccm Ar

4 sccm SiH_4

Doping: B_2H_6,

PH_3

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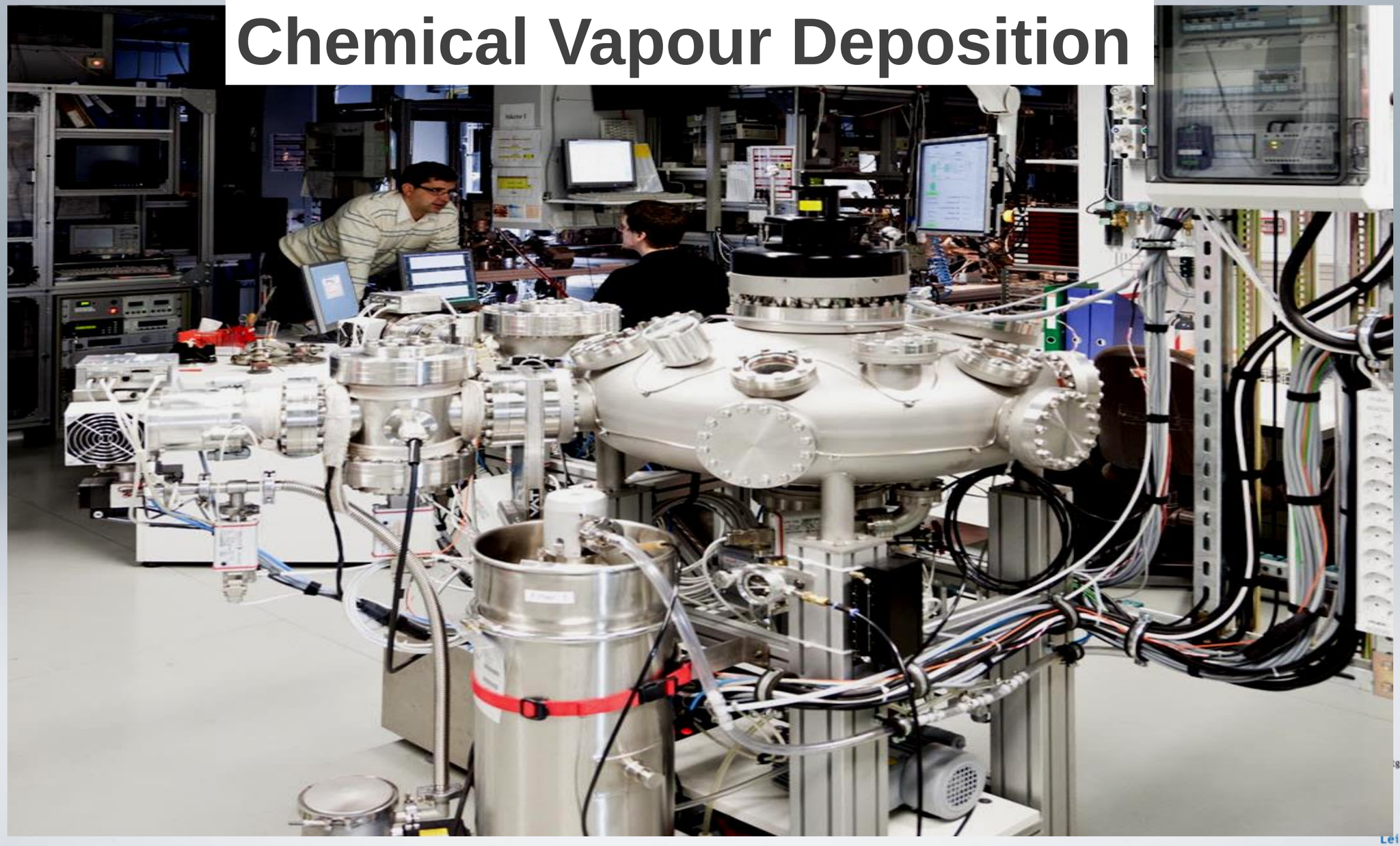
Experimental Equipment

Chemical Vapour Deposition



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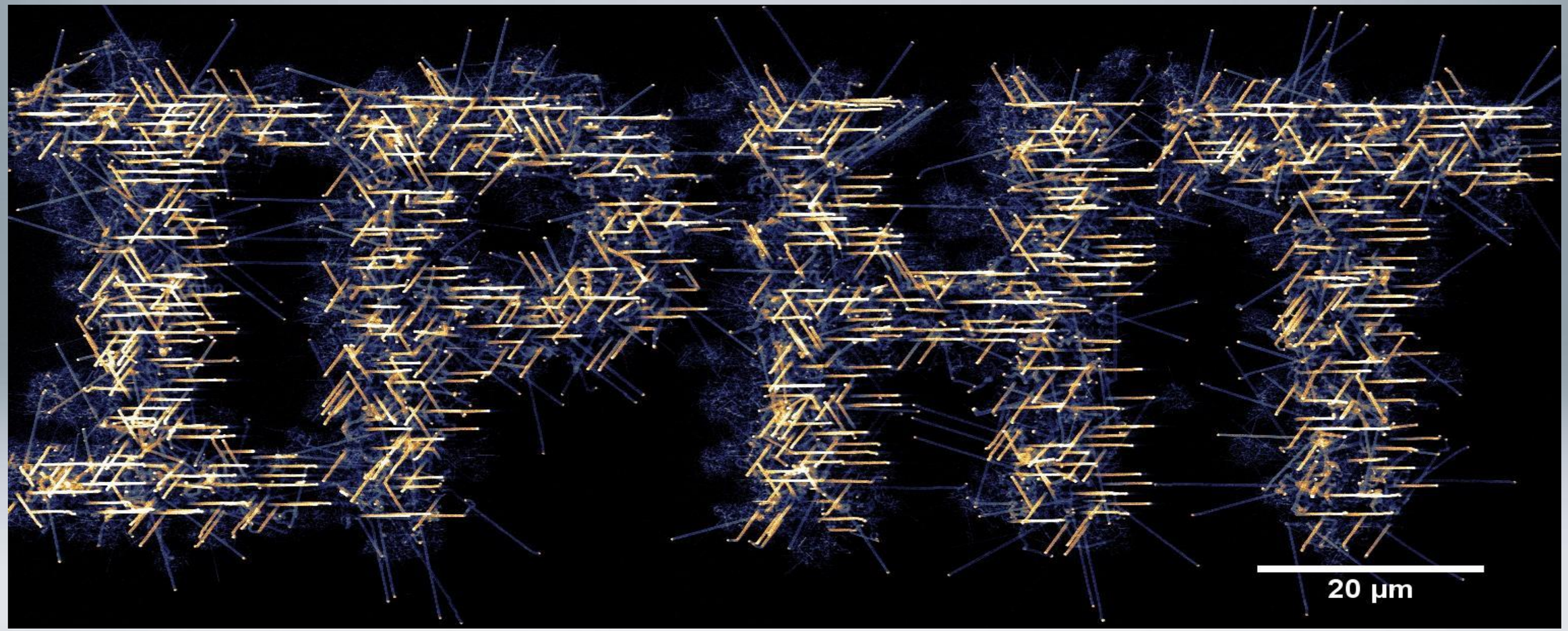
1D Nanostructures *via* Bottom-up

SEM micrograph of 50 nm gold array produced by Electron Beam Lithography

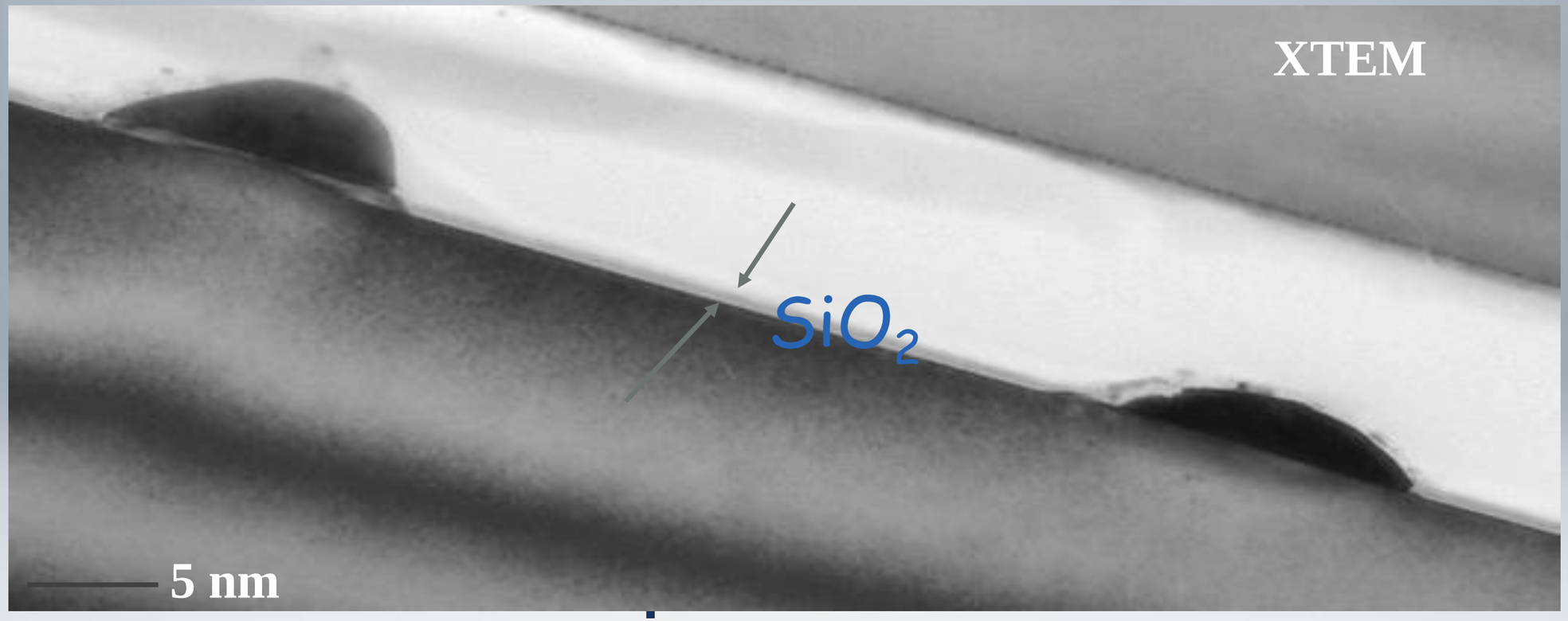
1D Nanostructures *via* Bottom-up

SEM micrograph of typically CVD grown SiNWs on Au pattered surfaces

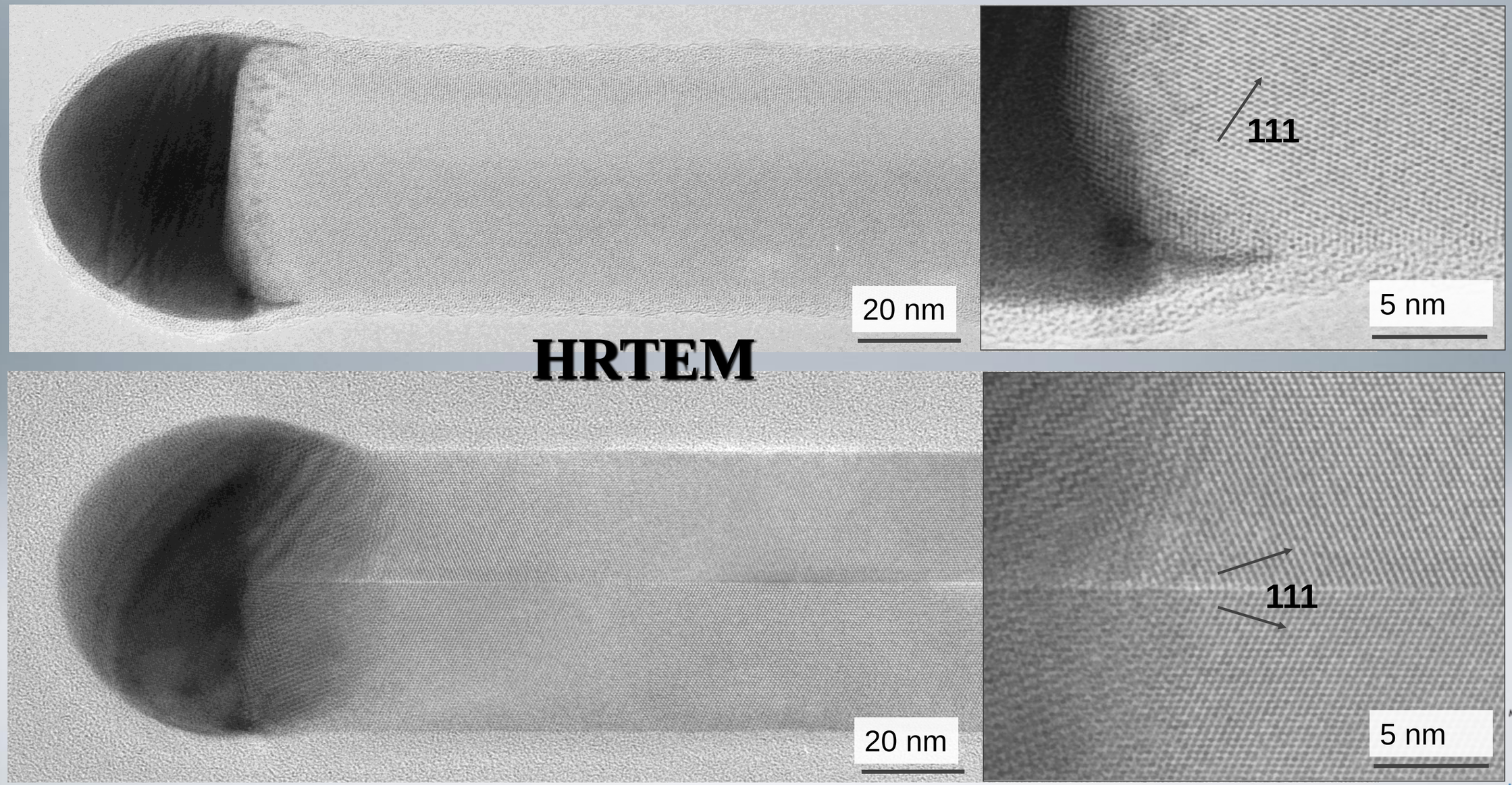


1D Nanostructures *via* Bottom-up

Cross sectional TEM view of Au//Si interface



1D Nanostructures *via* Bottom-up



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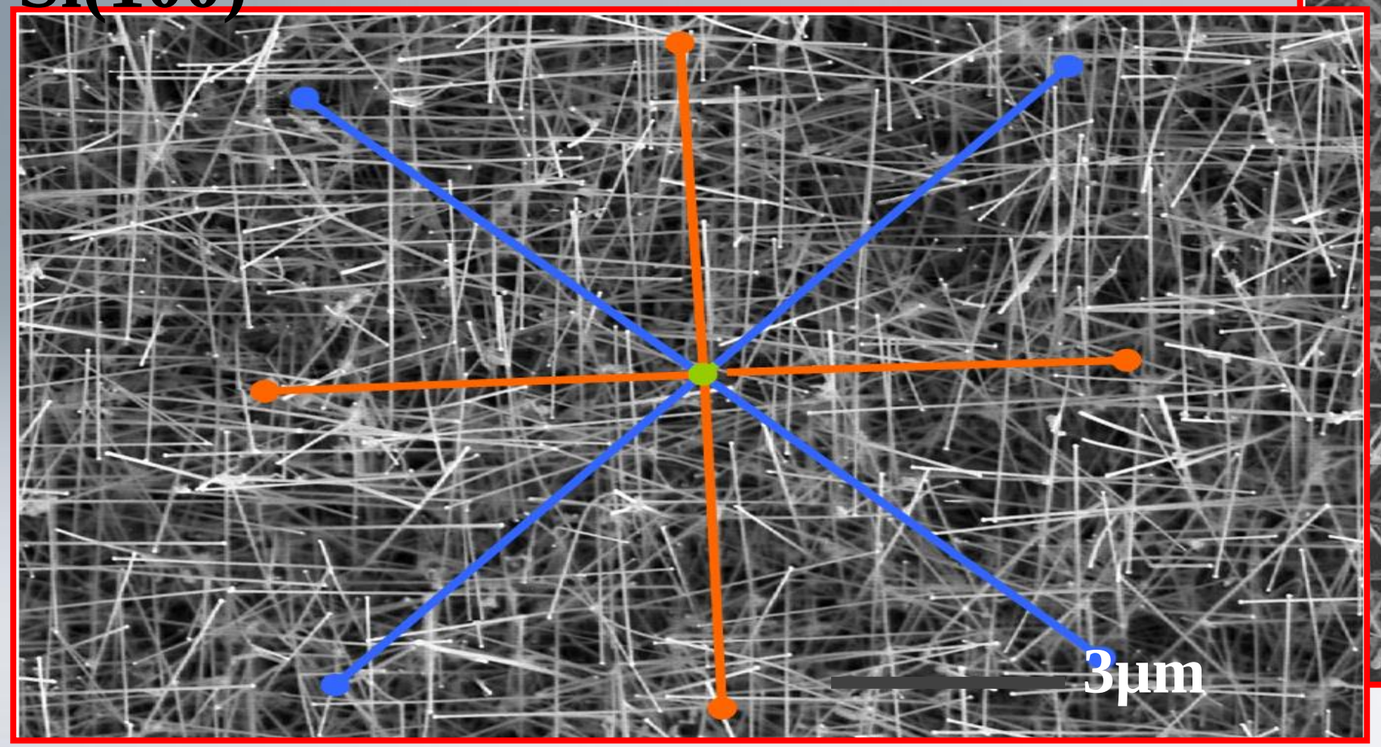
Bottom-up: Au Implantation

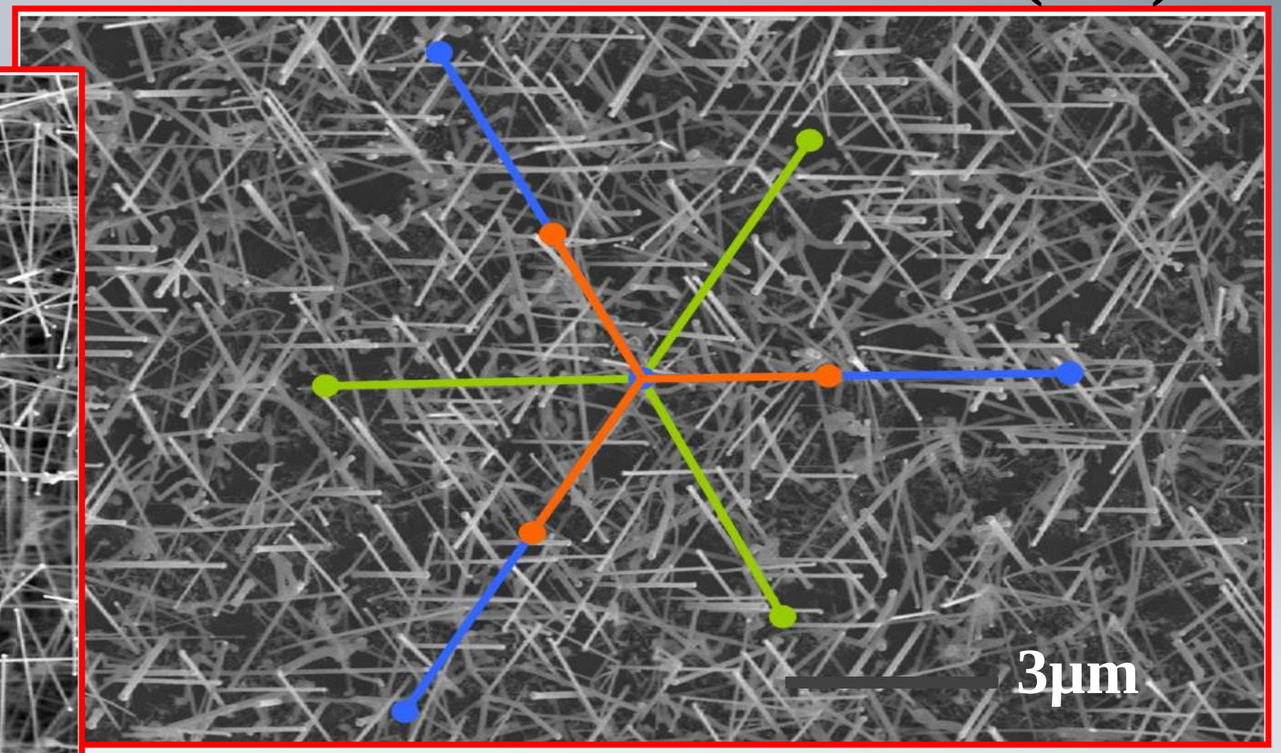
SiNWs CVD growth from implanted Au catalyst

SEM micrographs

Si(100)

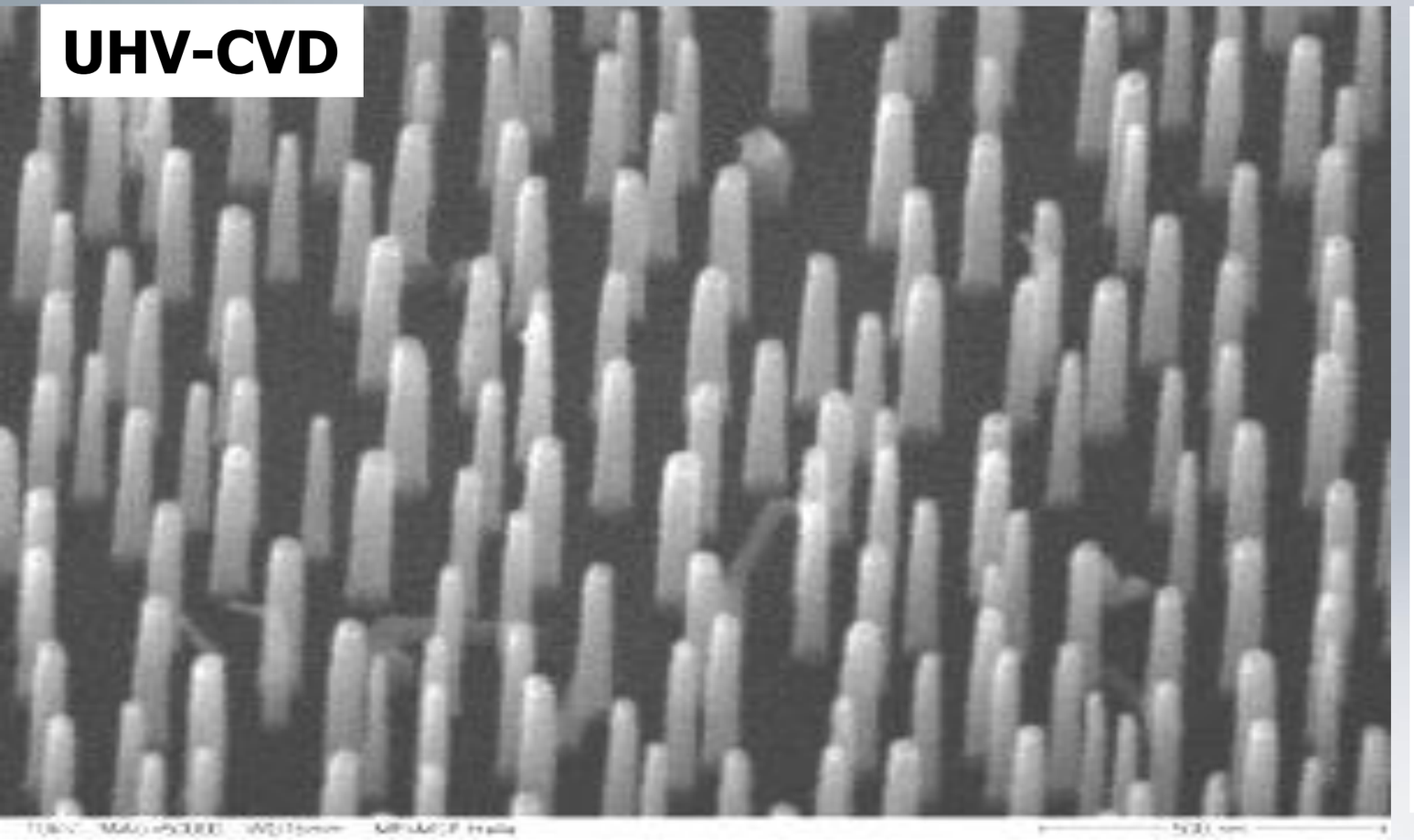


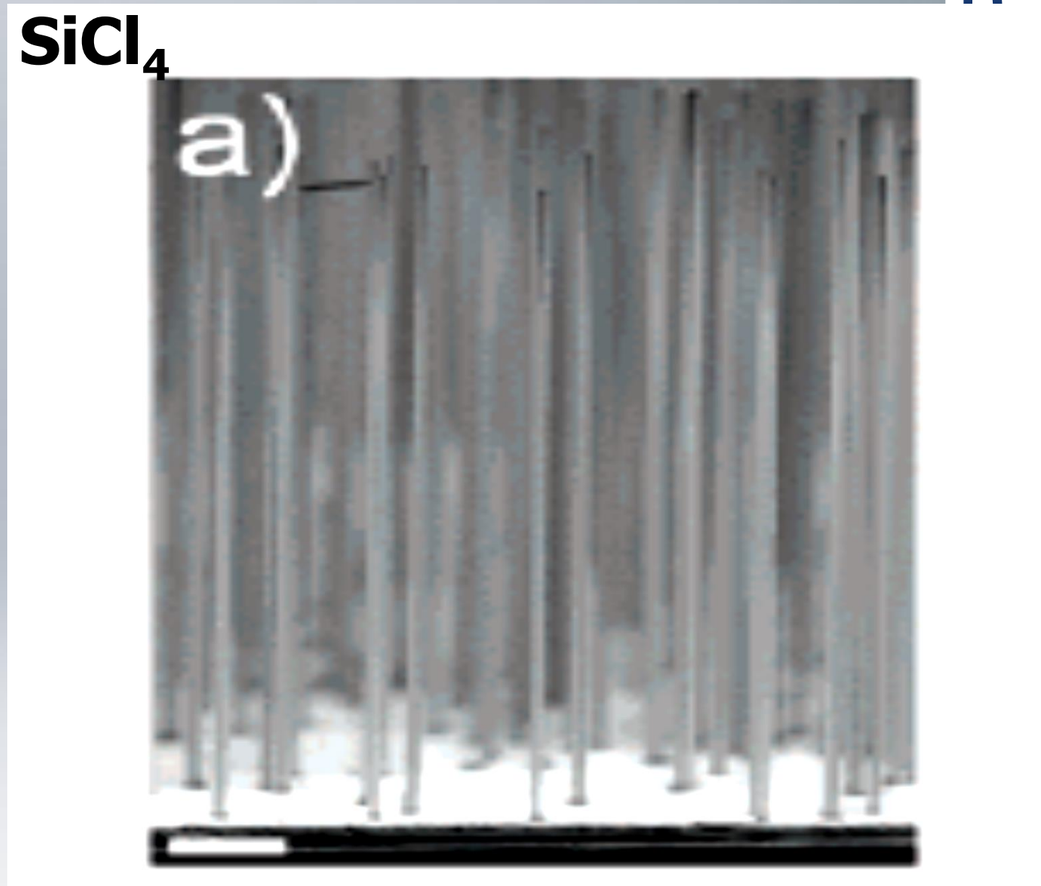
Si(111)



Mitglied der Leibniz-Gemeinschaft

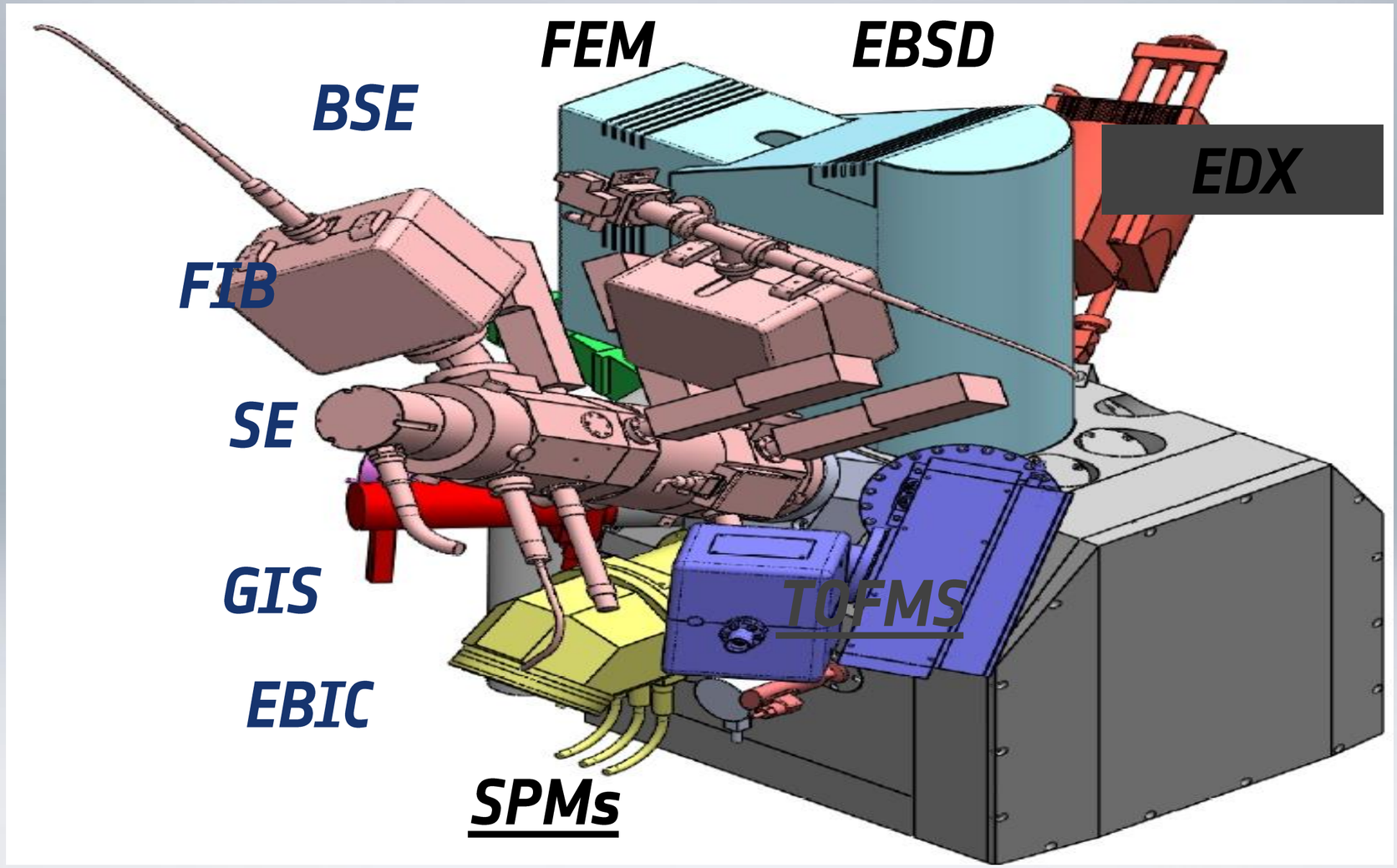
Silicon nanowires from Al catalyst



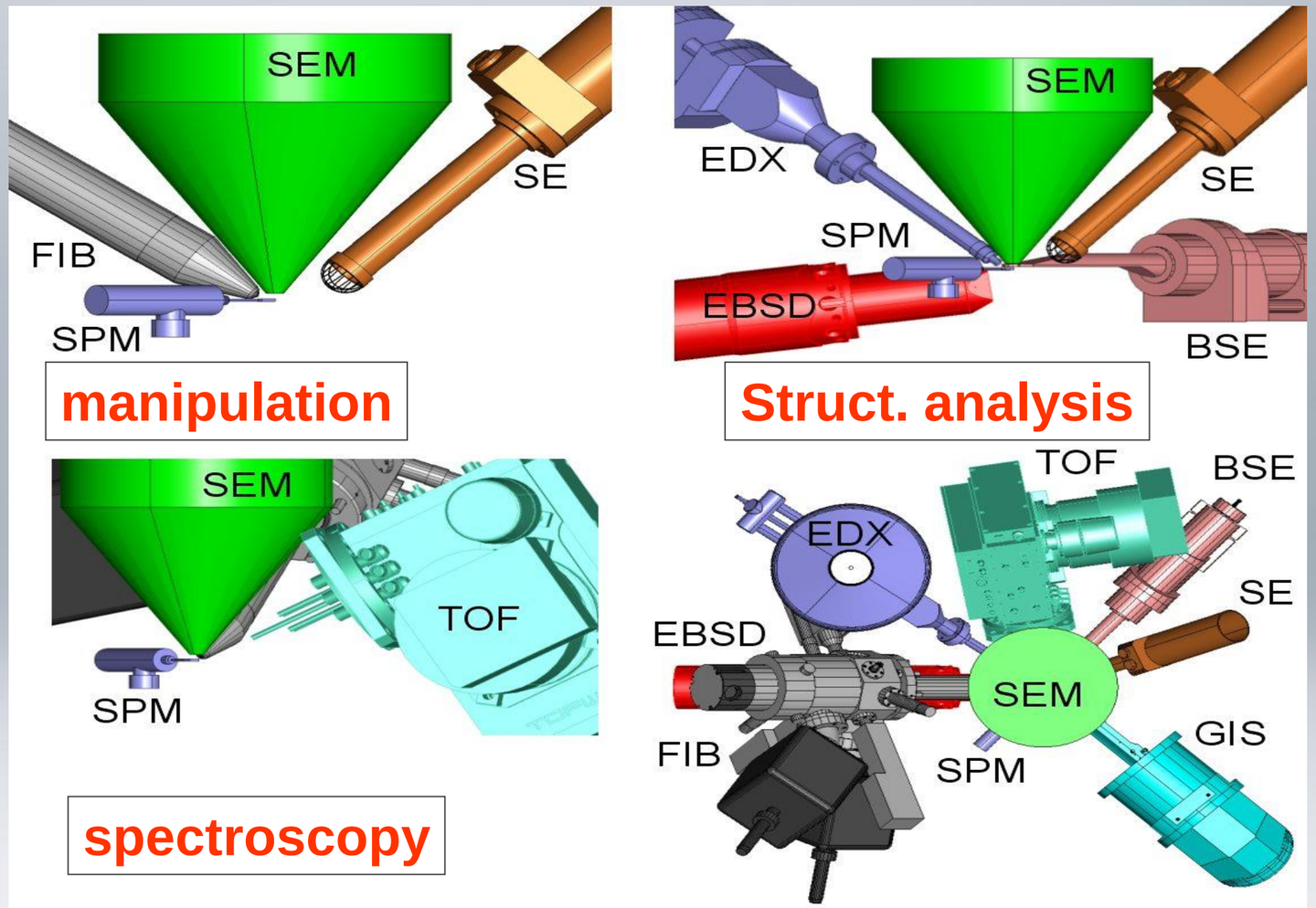


1. Wang, Y. , V. Schmidt , S. Senz , and U. Gösele, Nature Nanotechnology 1 (3) , p 186-189 (2006)
2. Allon I. Hochbaum, Rong Fan, Rongrui He, and Peidong Yang, Nano Lett., 5(3), 457(2005)

Dual Beam Systems



Dual Beam Systems

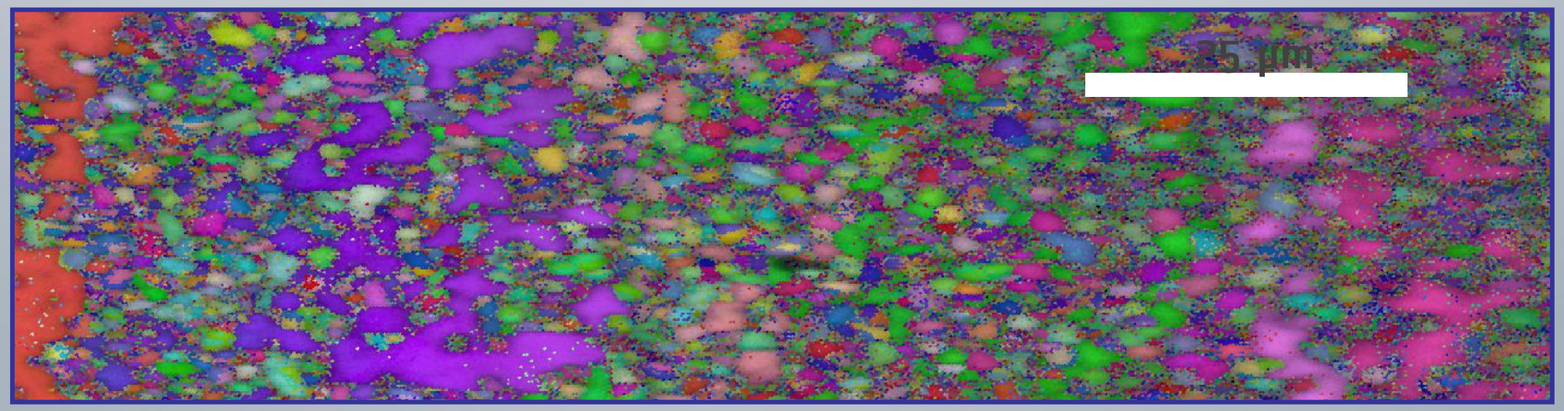


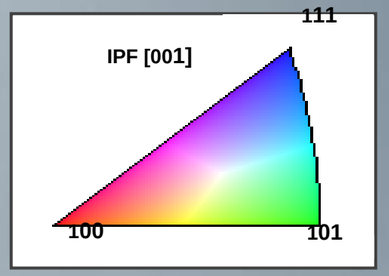
Project FP7-NMP: FIBLYS, Multi-functional FIB for Nanotechnology (Start: 04/2008)

Dual Beam Systems

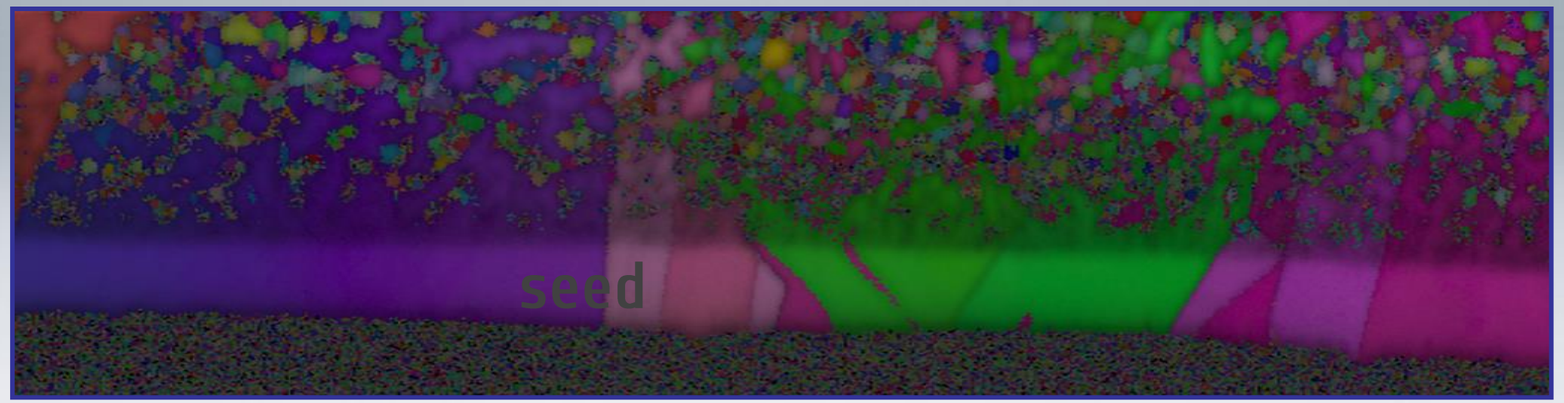
EBSD:
IPF + IQ

before





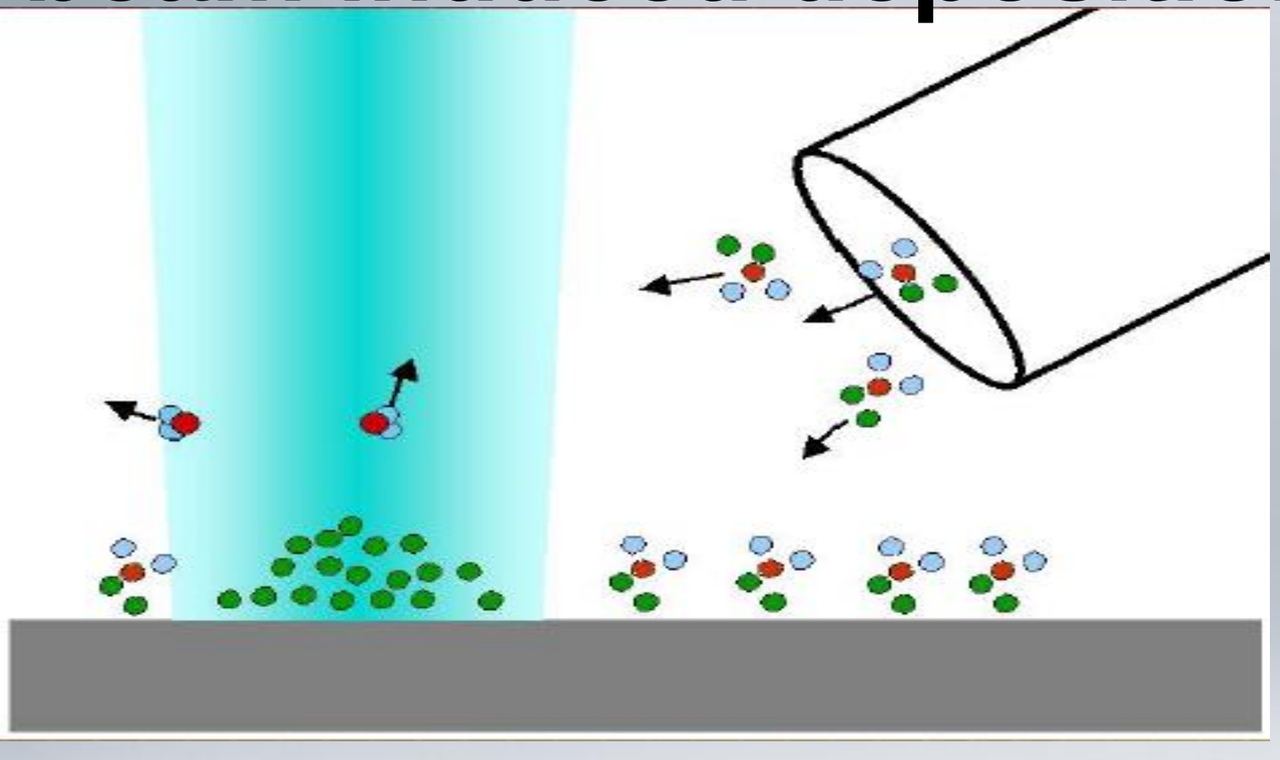
after



SPE sample: glass, seed 400nm, absorber 2000nm

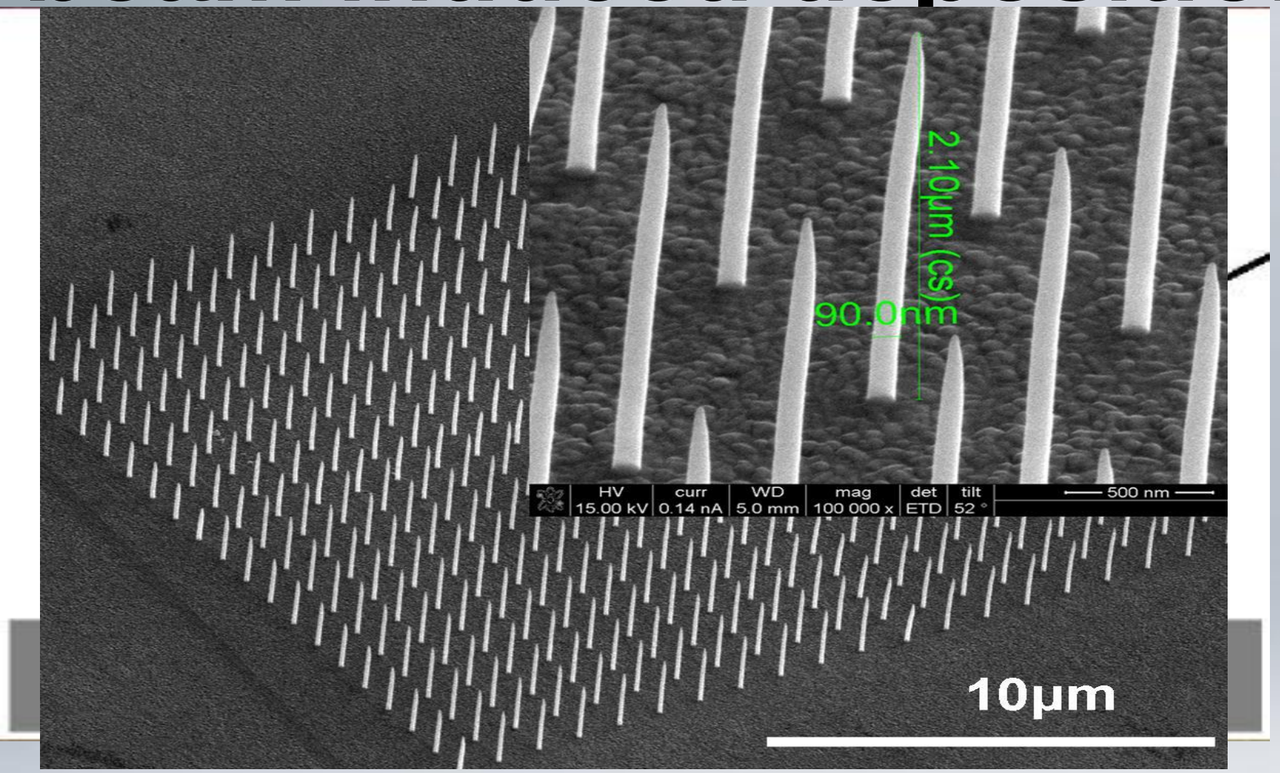
normally buried seed is clearly visible

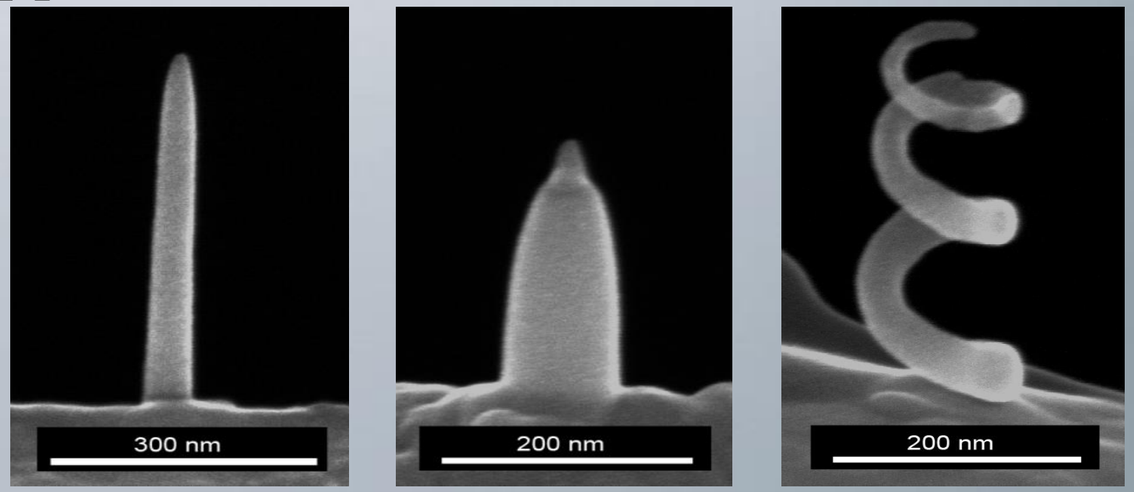
Nanostructures directly written by electron beam induced deposition

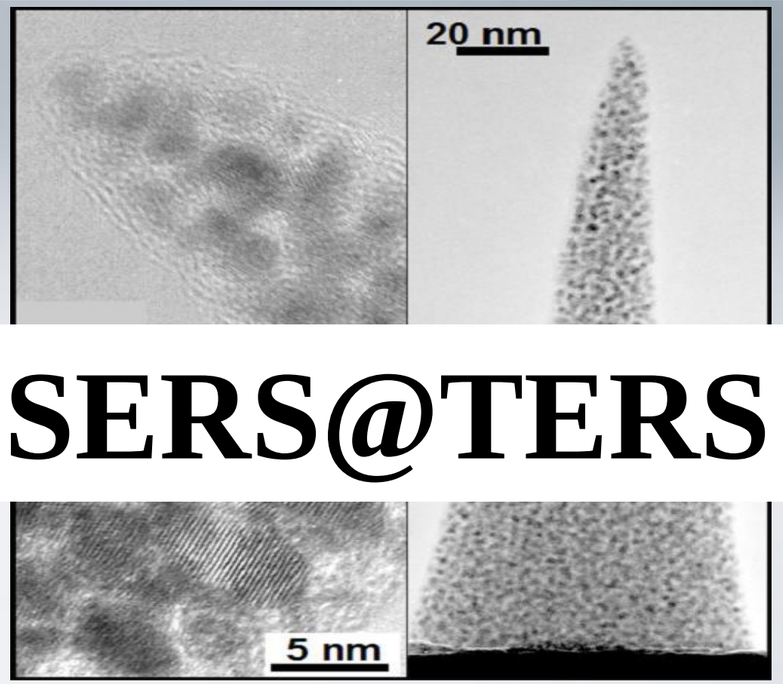


SE micrograph in tilted view (45°) of gold containing EBID needles on ITO-coated glass arranged in a 20 x 20 µm2 two dimensional square lattice with 1 µm pitch for optical investigations

Nanostructures directly written by electron beam induced deposition







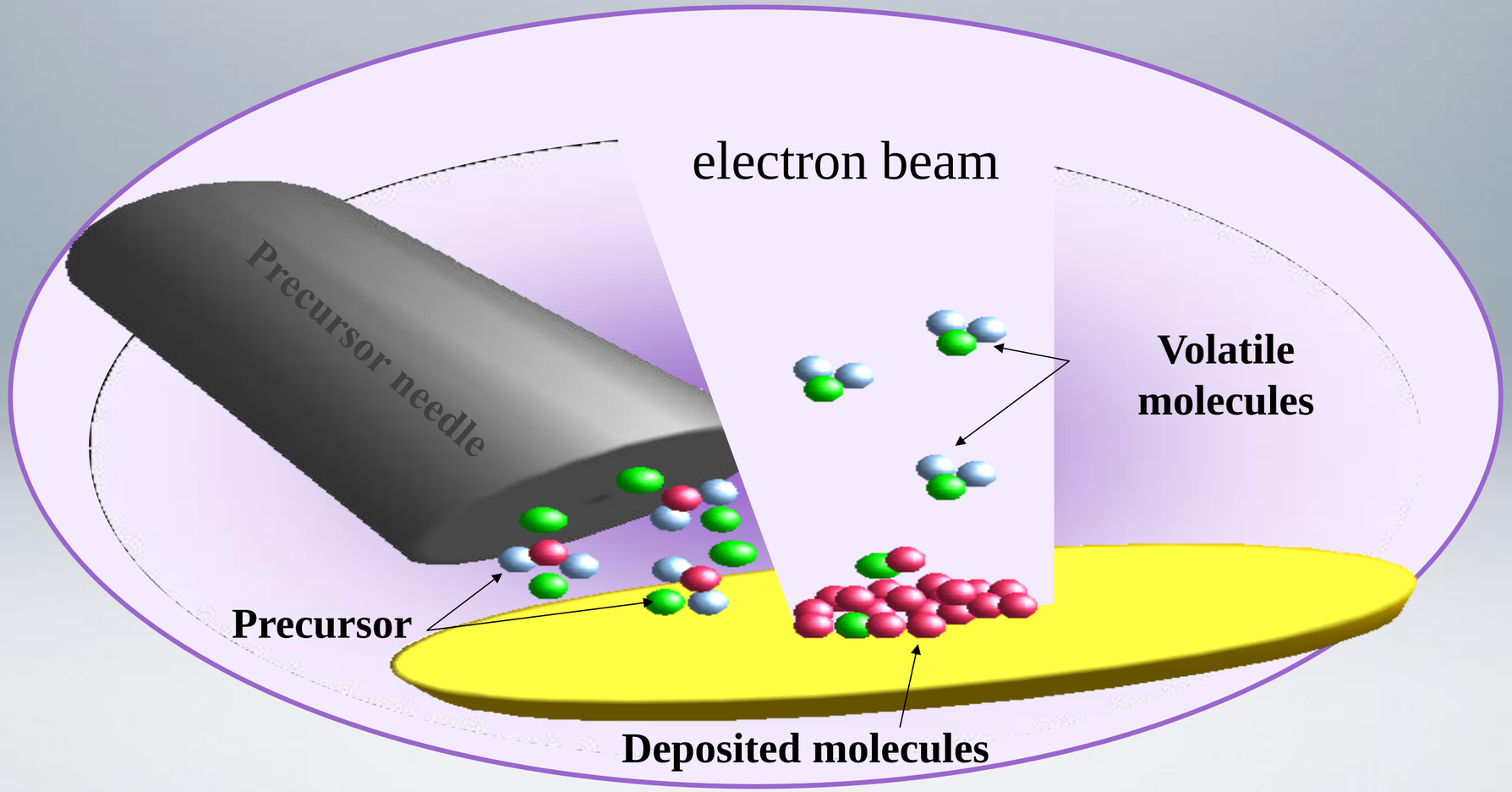
SE micrograph in tilted view (45°) of gold containing EBID needles on ITO-coated glass arranged in a 20 x 20 µm2 two dimensional square lattice with 1 µm pitch for optical investigations

SERS@TERS

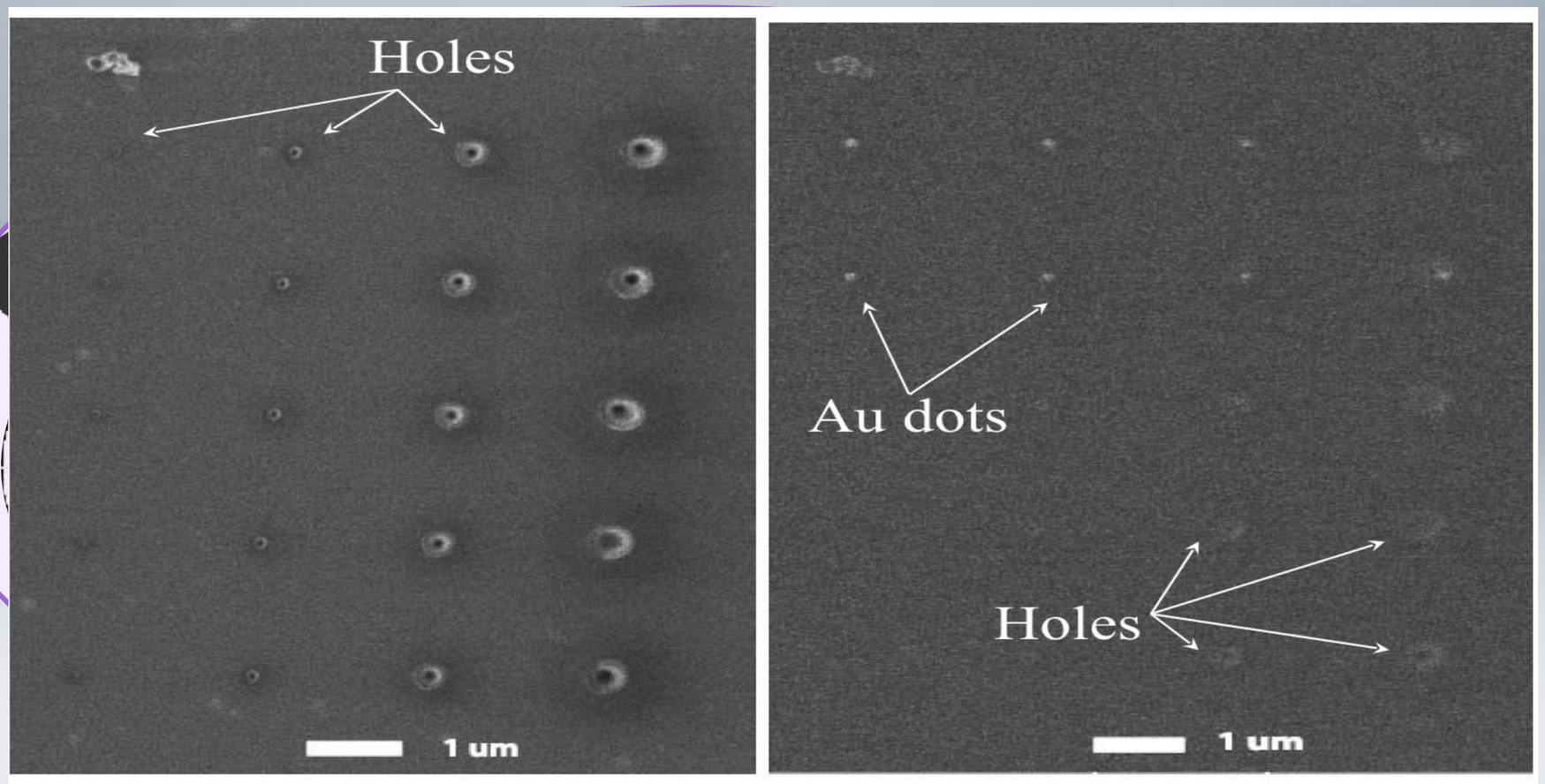
iphtjena

Mitglied der Leibniz-Gemeinschaft

Nanostructures directly written by electron beam induced deposition

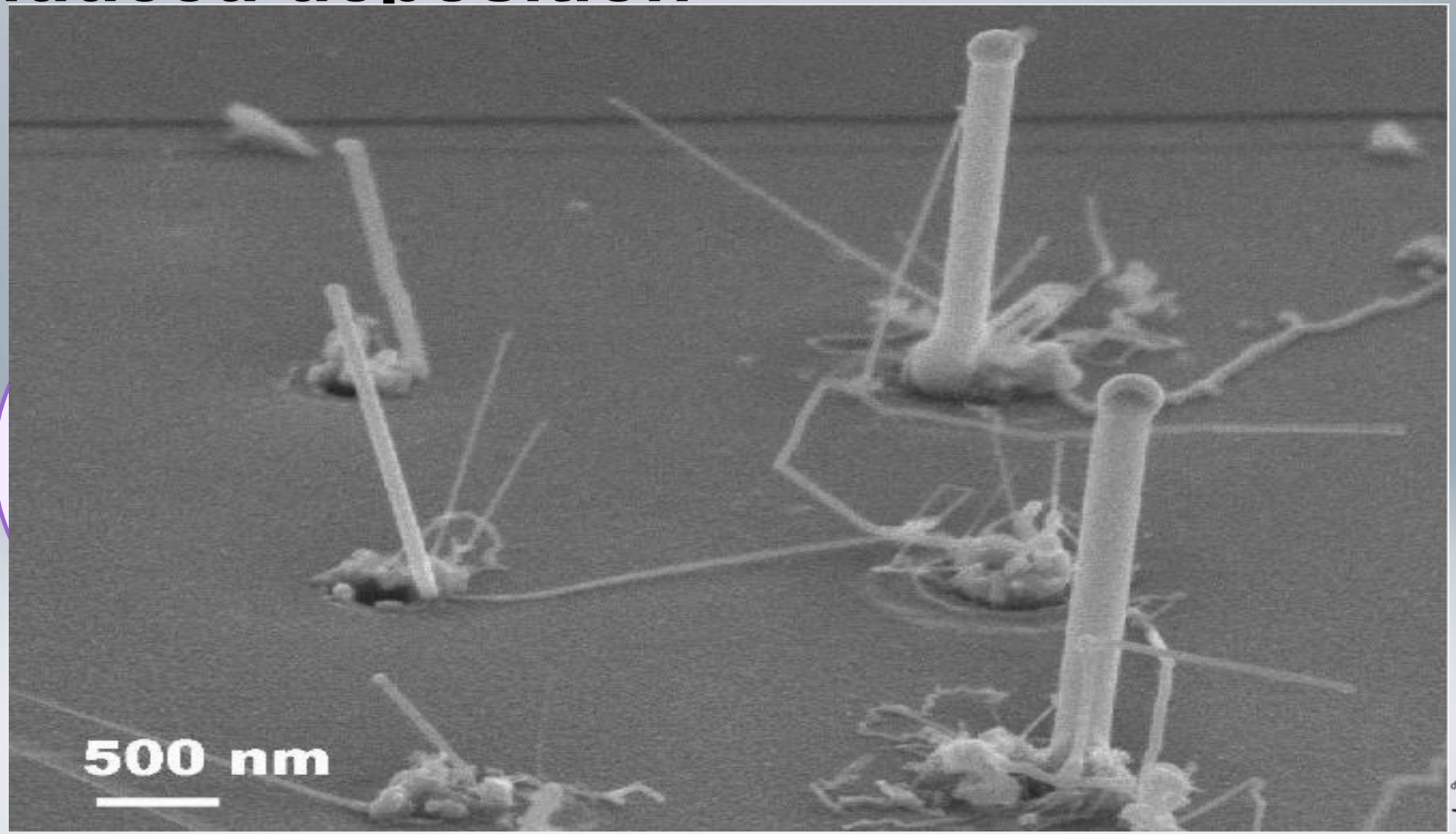


Nanostructures directly written by electron beam induced deposition

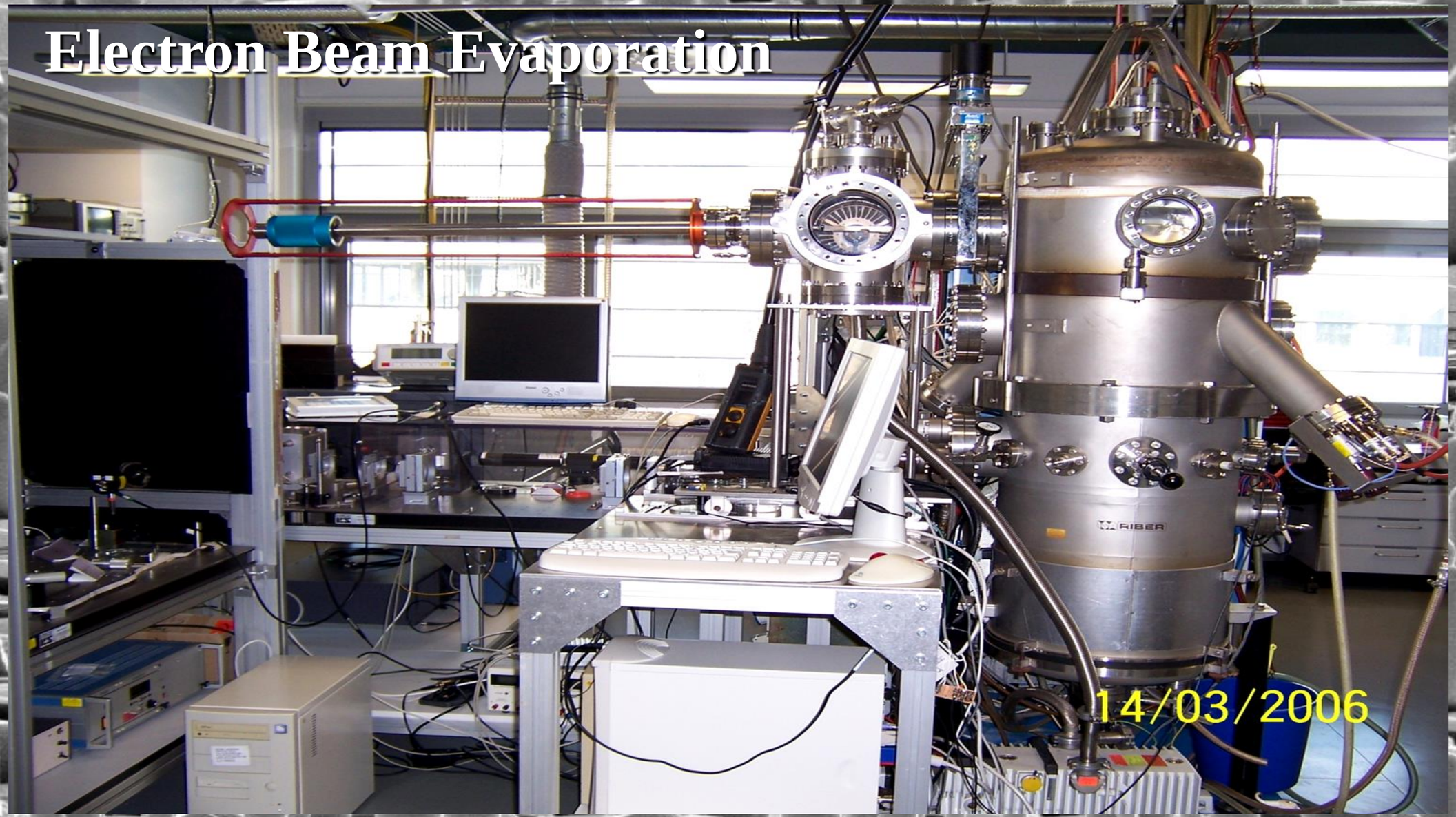


Deposited molecules

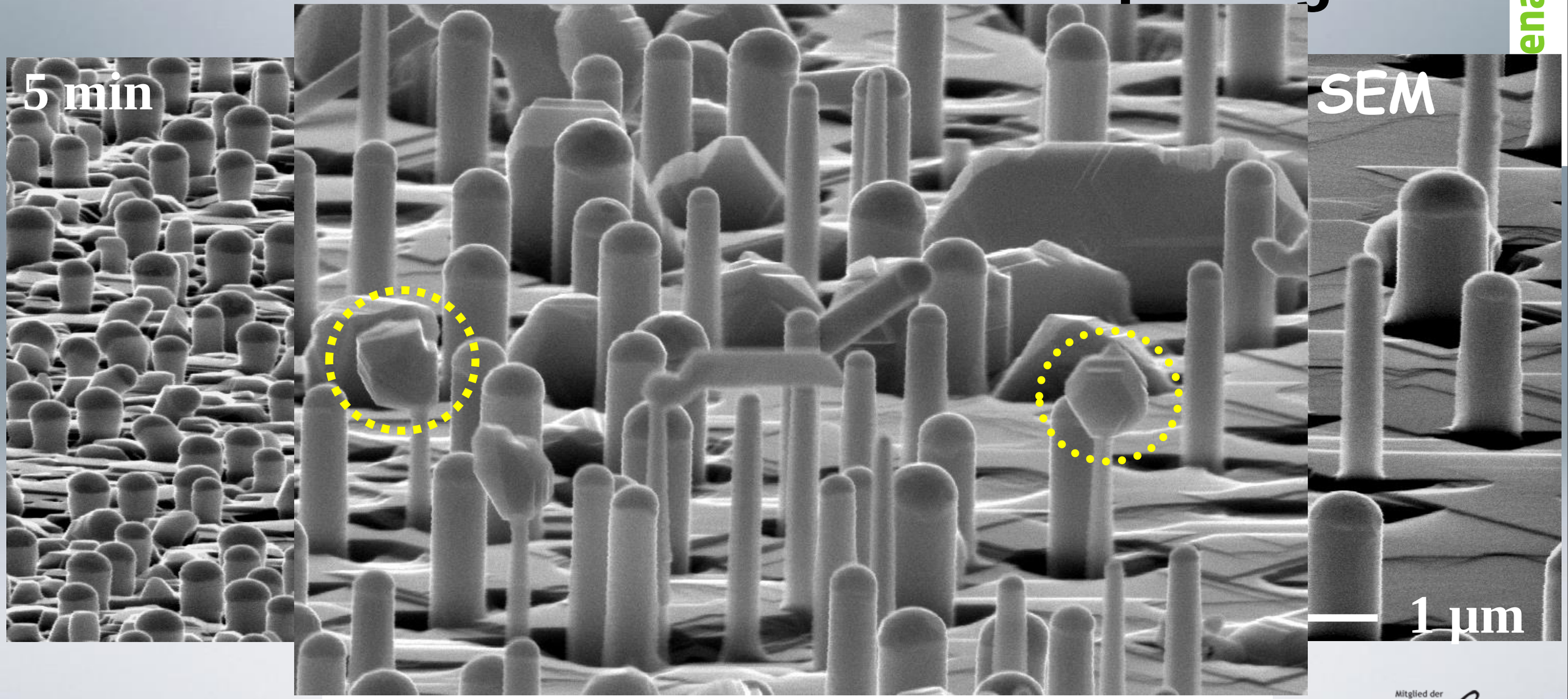
Nanostructures directly written by electron beam induced deposition



1D Nanostructures *via* Bottom-up: EBE

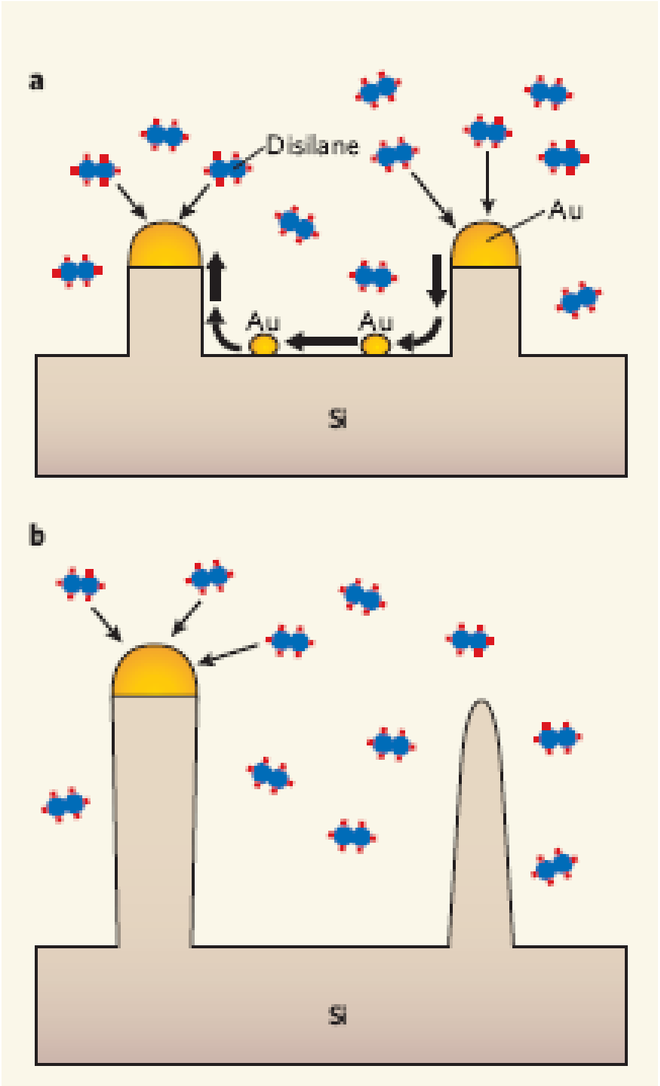


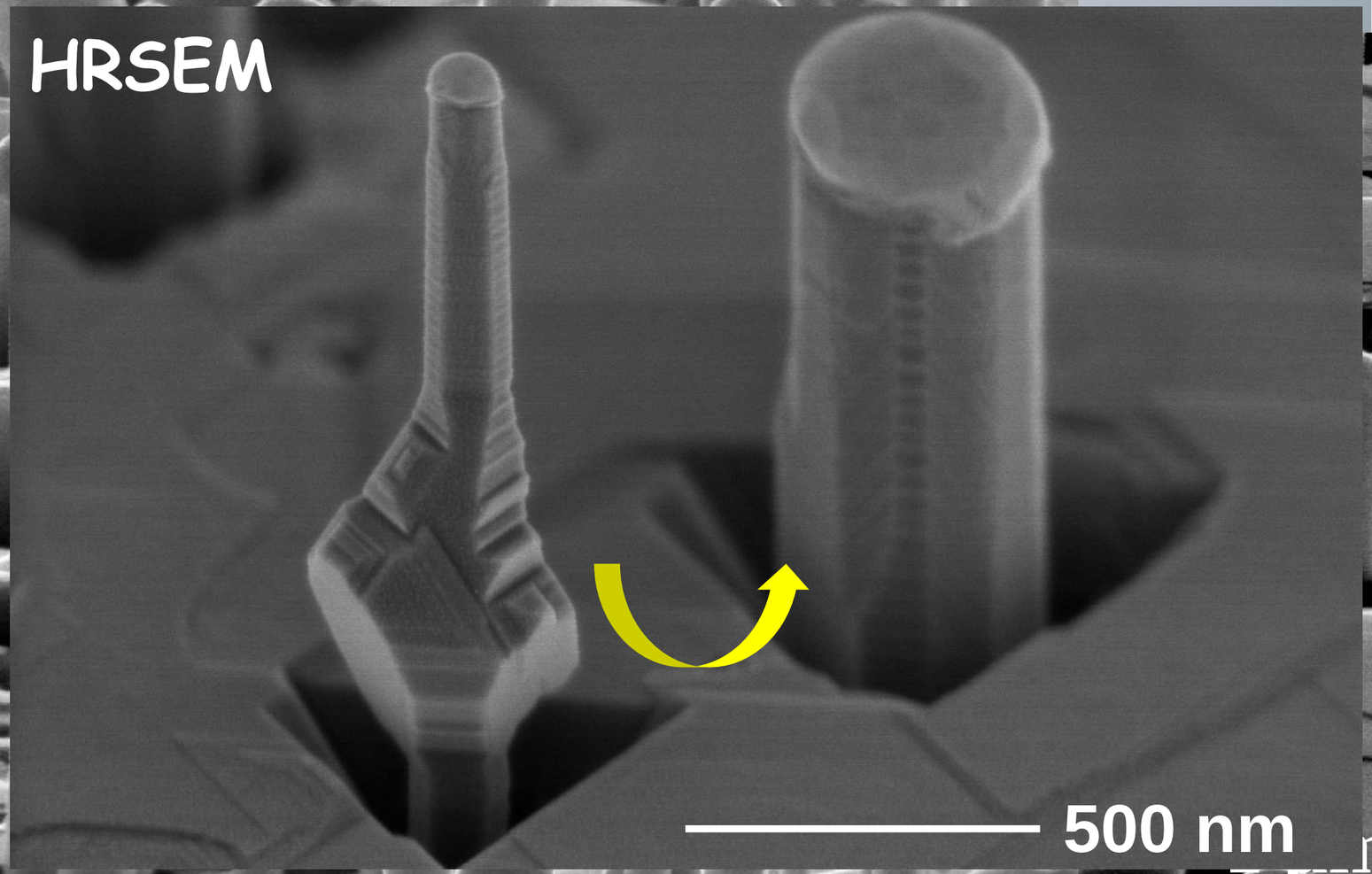
Growth Kinetic: Ostwald Ripening



J. B. Hannon, S. Kodambaka, F. M. Ross, and R. M. Tromp, *Nature*, doi: 10.1038/nature04574 (2006)
U. Gösele, *Nature*, DOI: 10.1038/nature04609 (2006)

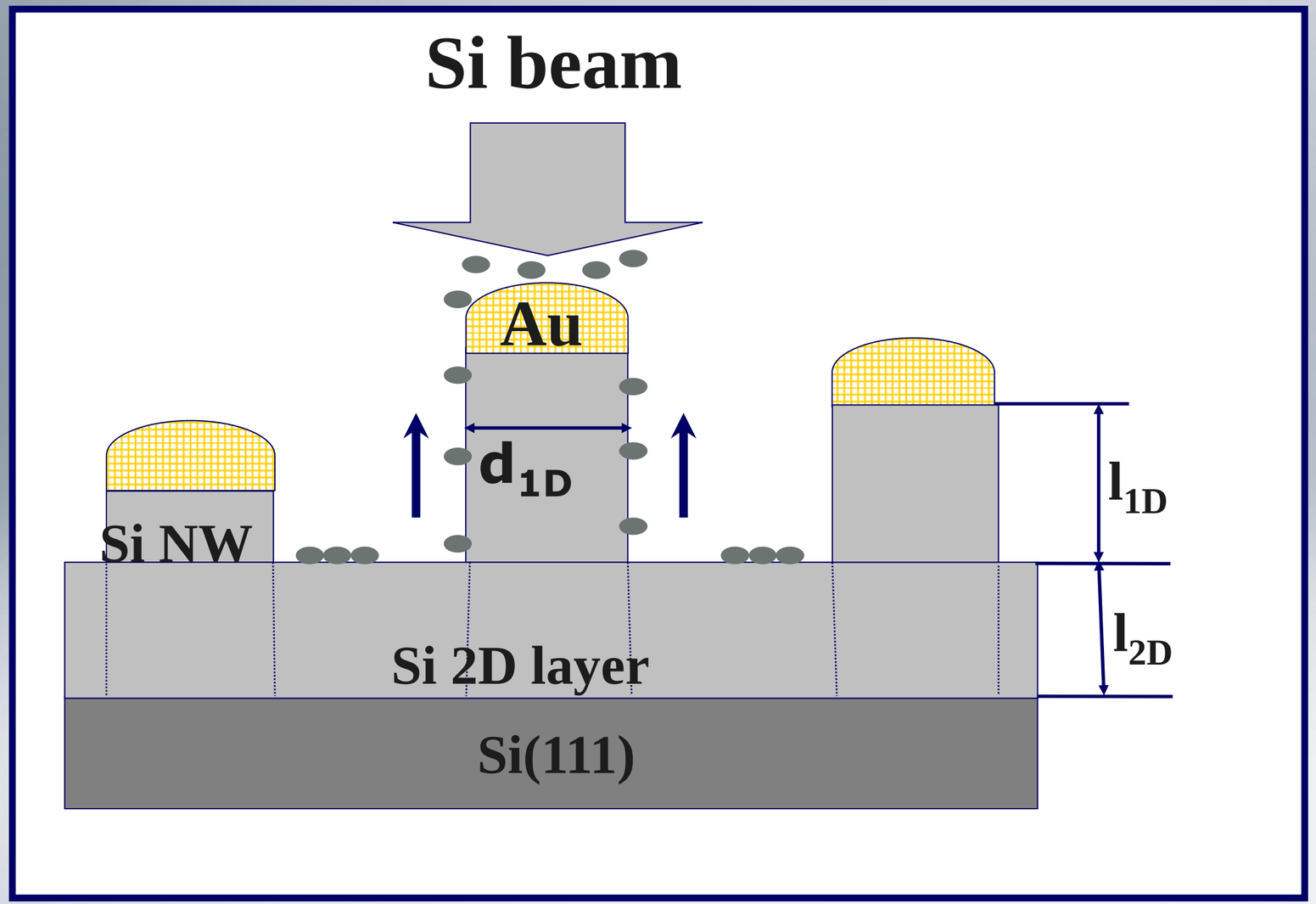
Growth Kinetic: Ostwald Ripening

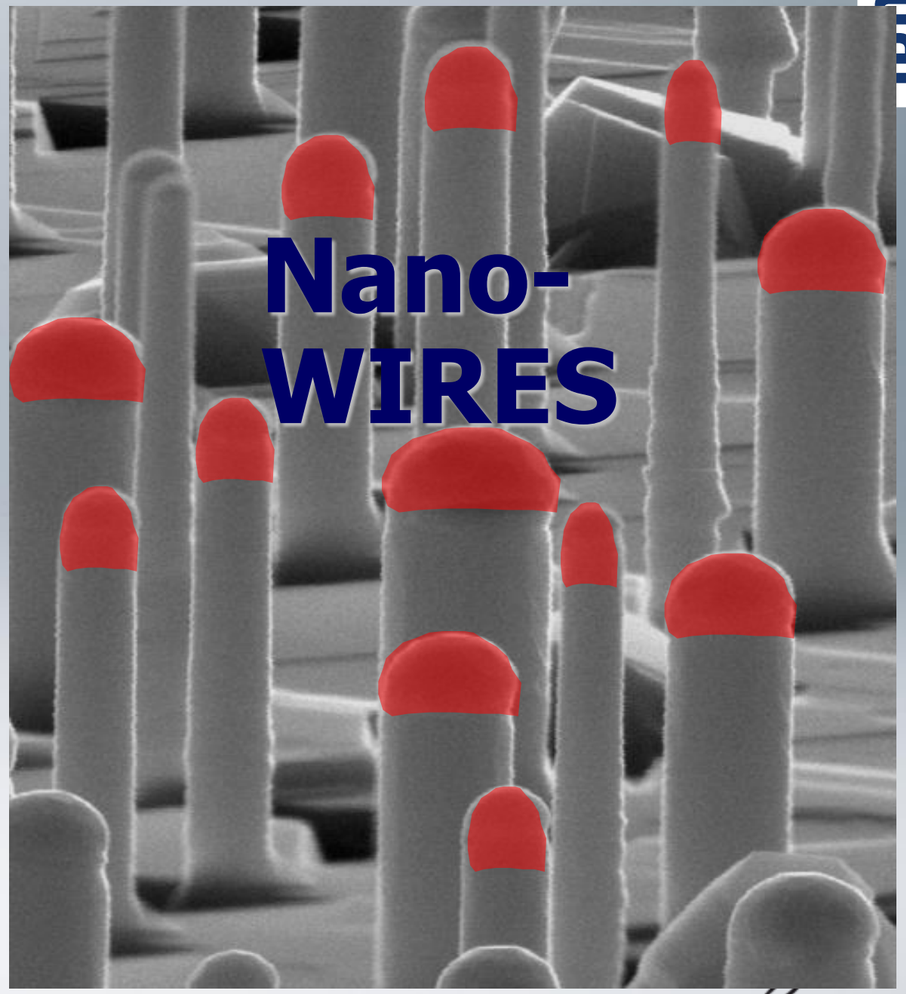




J. B. Hannon, S. Kodambaka, F. M. Ross, and R. M. Tromp, *Nature*, doi: 10.1038/nature04574 (2006)
U. Gösele, *Nature*, DOI: 10.1038/nature04609 (2006)

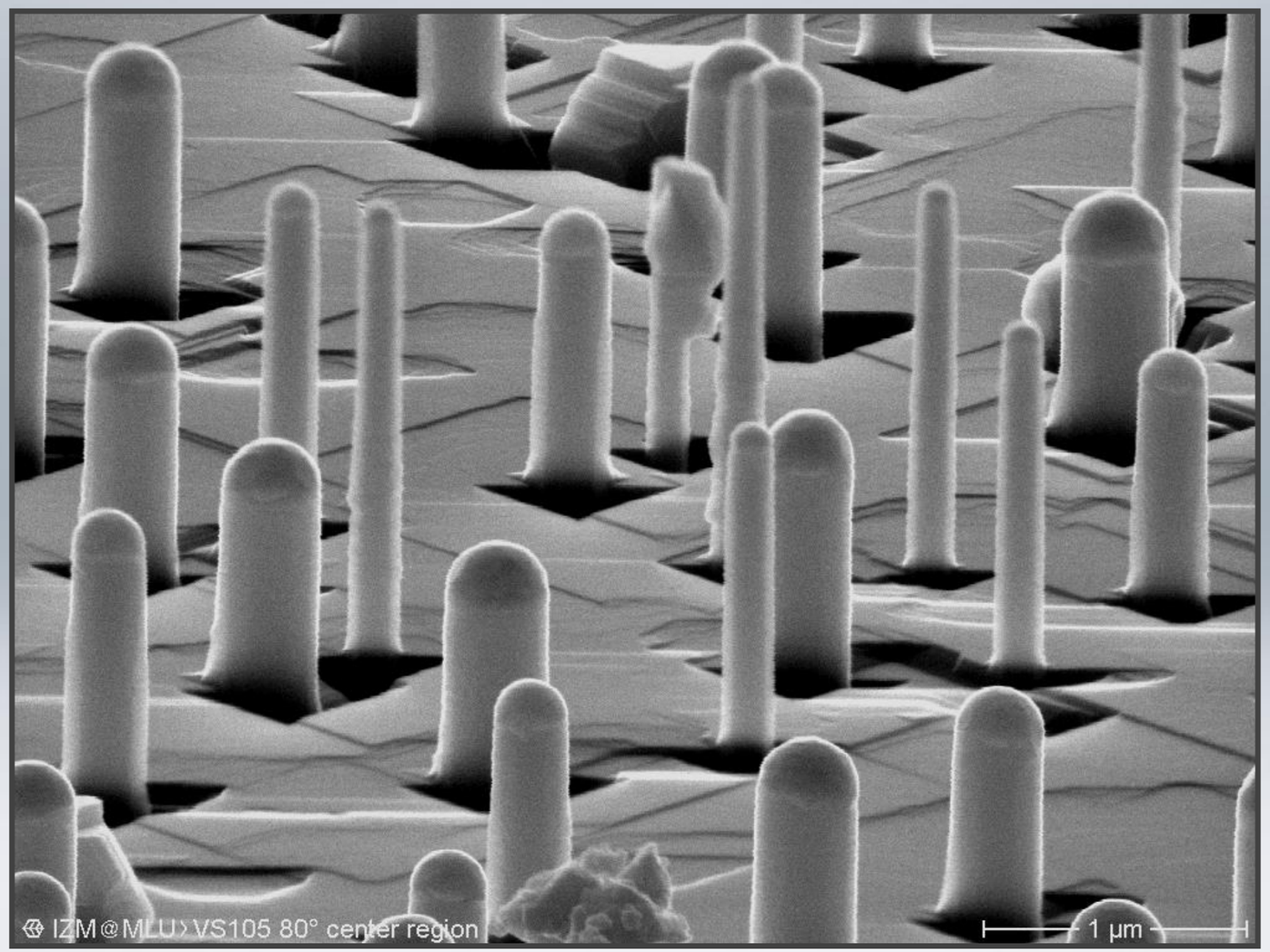
1D Nanostructures *via* Bottom-up





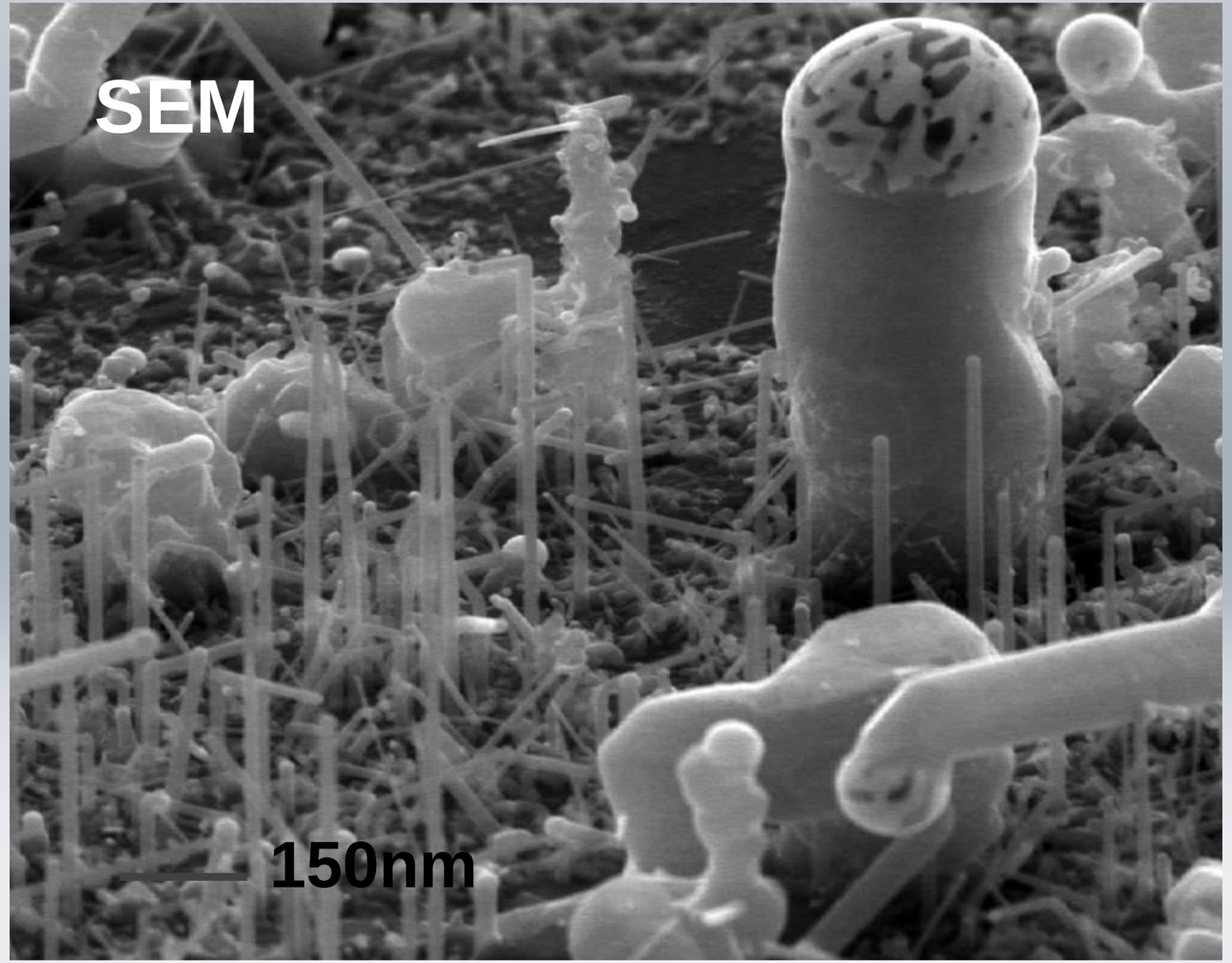
L. Schubert et al. APL 84, 4968 (2004)

Oxidation of Si NWs



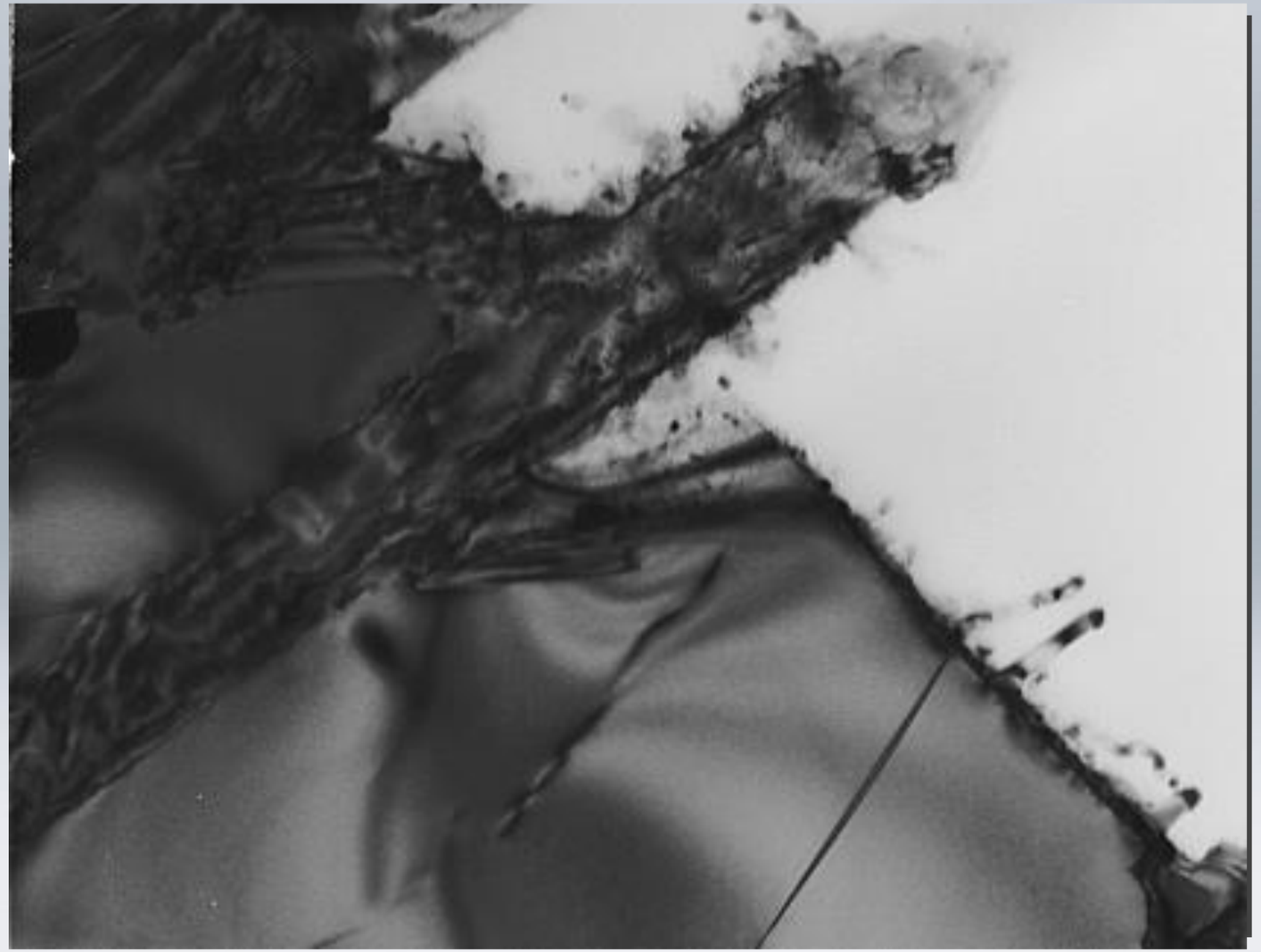
CVD on EBE SiNWs

Oxidation of Si NWs



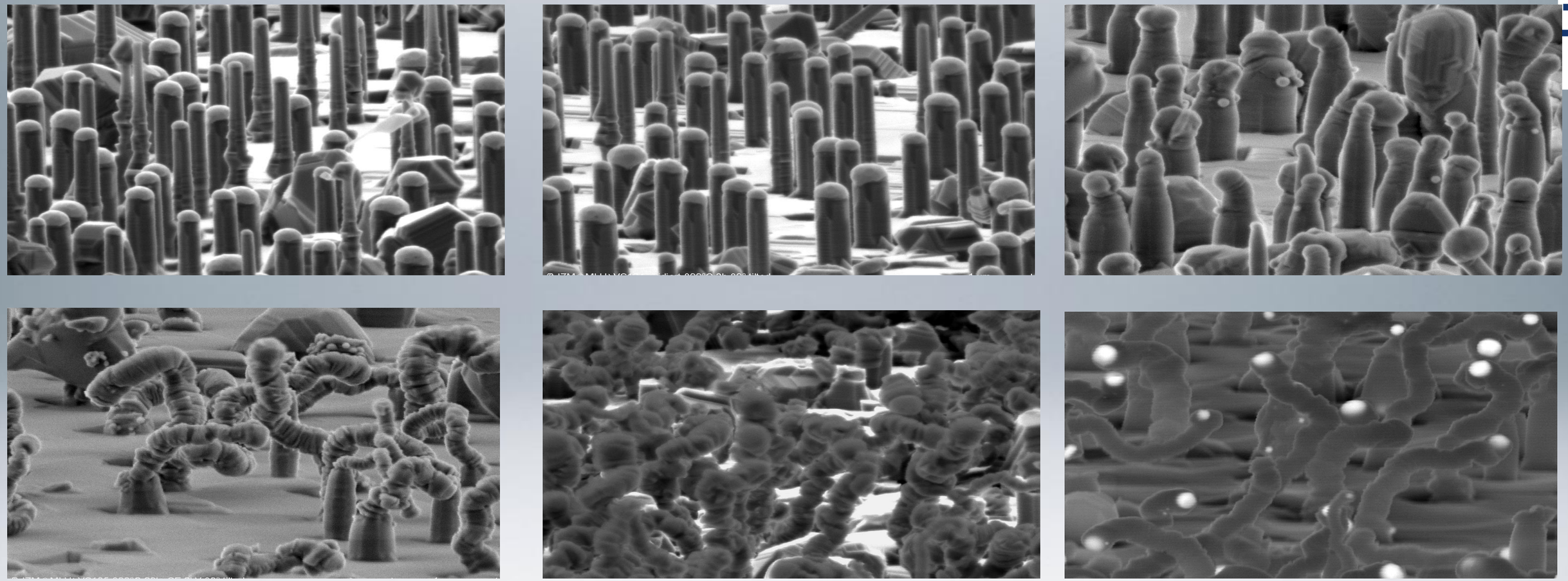
CVD on EBE SiNWs

Oxidation of Si NWs



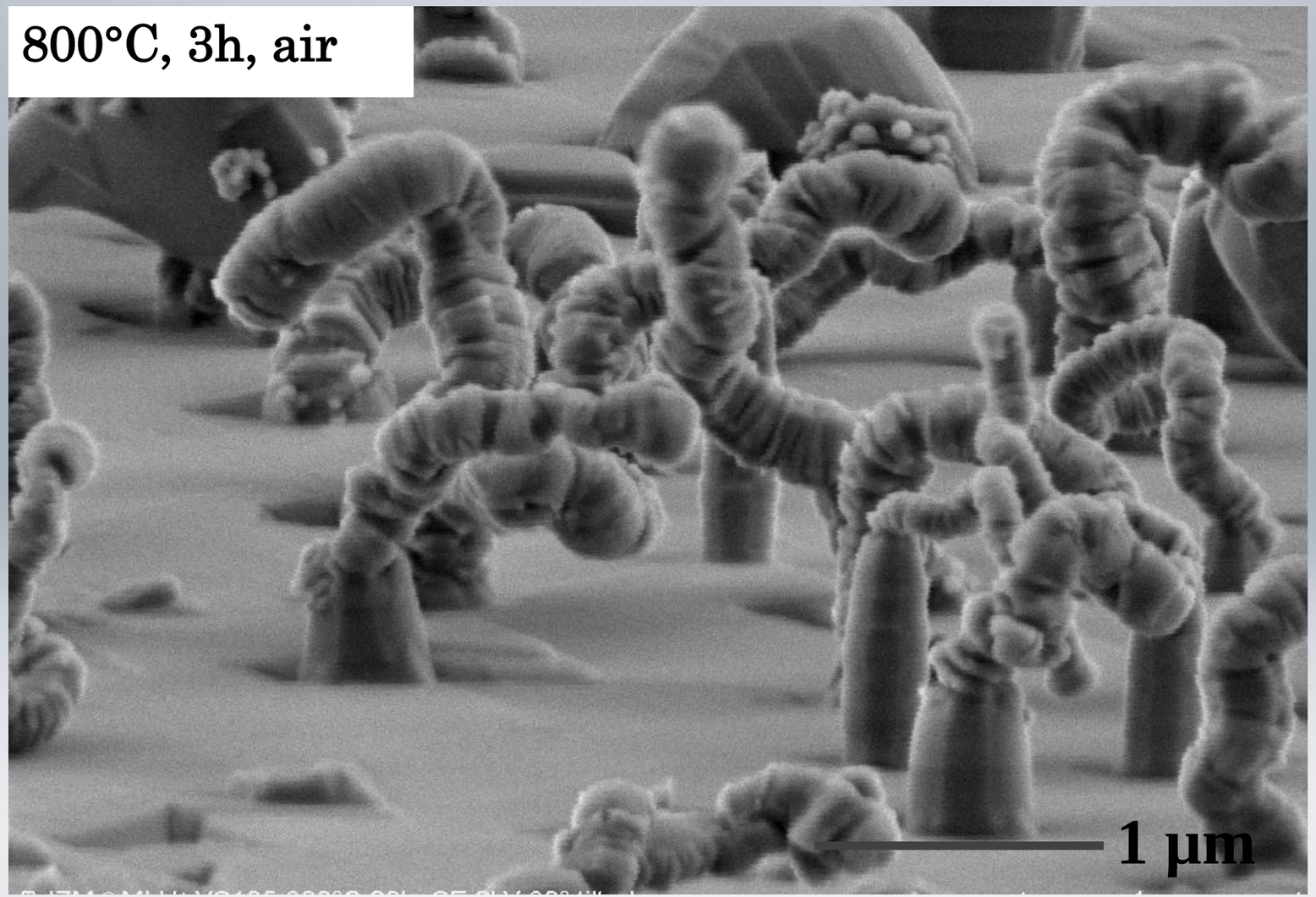
CVD on EBE SiNWs

Oxidation of Si NWs



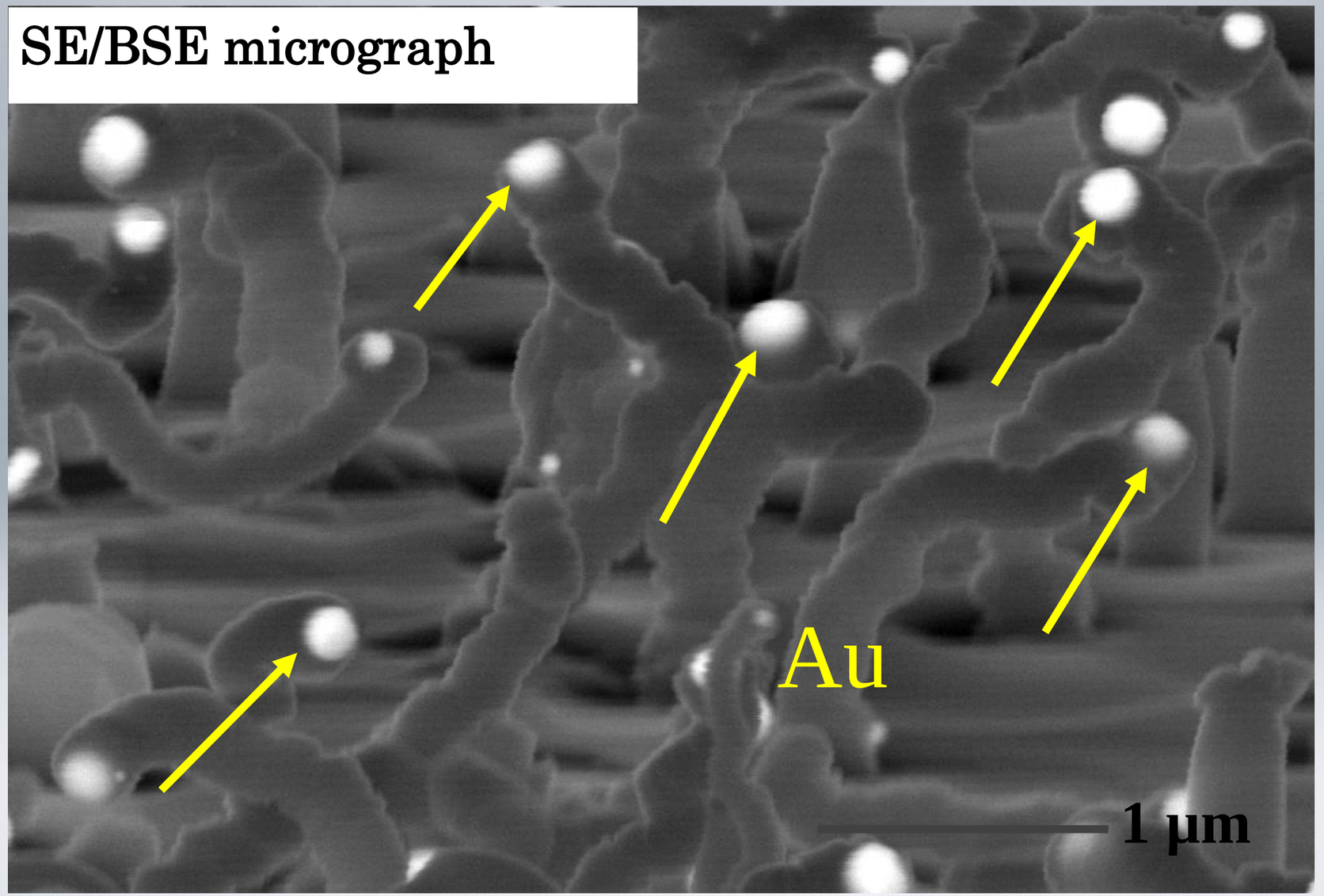
SEM cross section micrographs of the silicon nanowires heat treated at oxidative atmosphere for: (a) 0h, as deposited; (b) 300 °C, 3 h; (c) 500 °C, 3h; (d) 800 °C, 3h; (e) 900 °C, 3h; (f) Au EDX mapping of the sample heat treated at 900 °C.

Oxidation of Si NWs



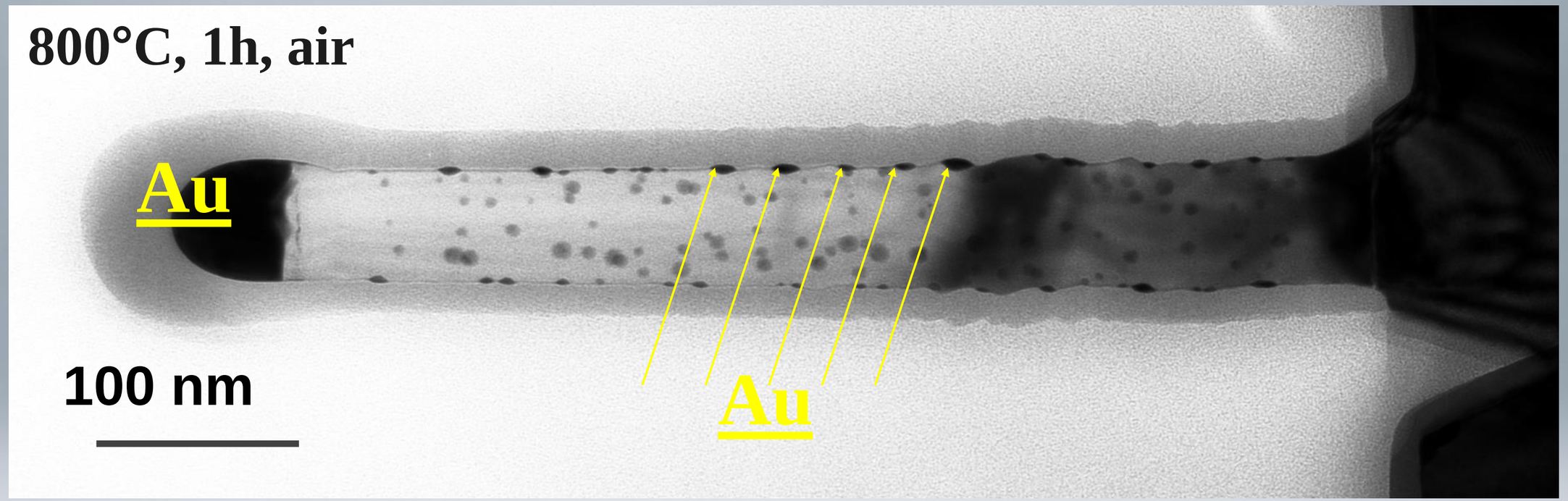
SEM micrograph of SiNWs grown by EBE

Oxidation of Si NWs



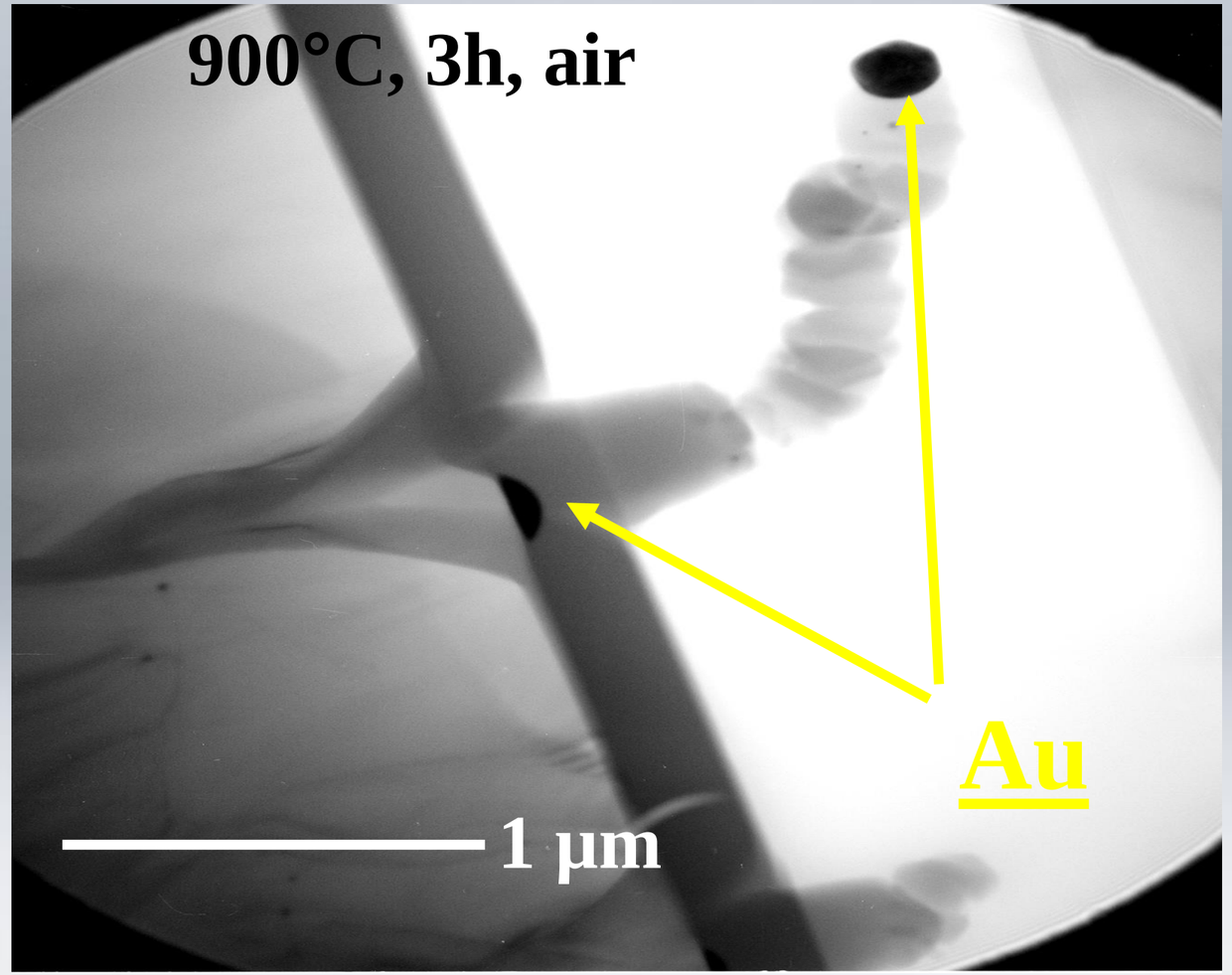
BSE micrograph of SiNWs grown by EBE

Oxidation of Si NWs



TEM micrograph of SiNWs grown by EBE

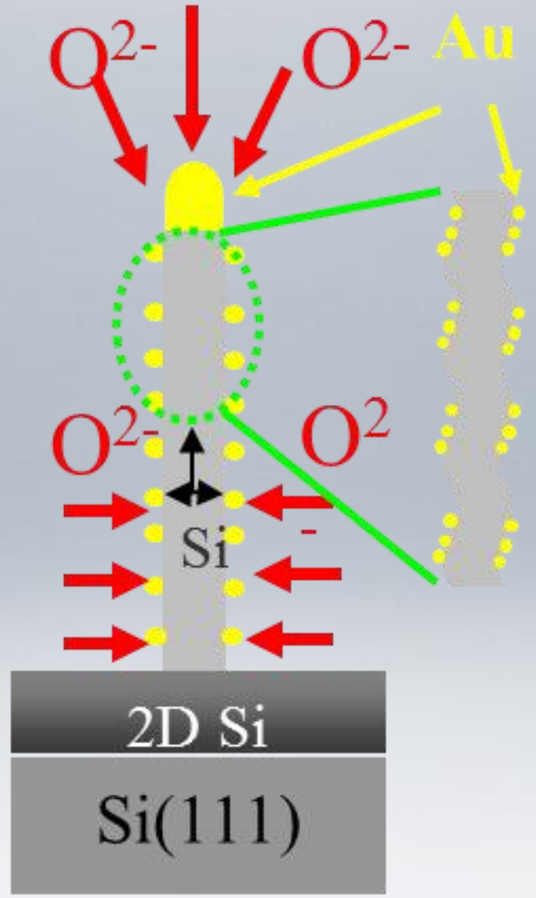
Oxidation of Si NWs

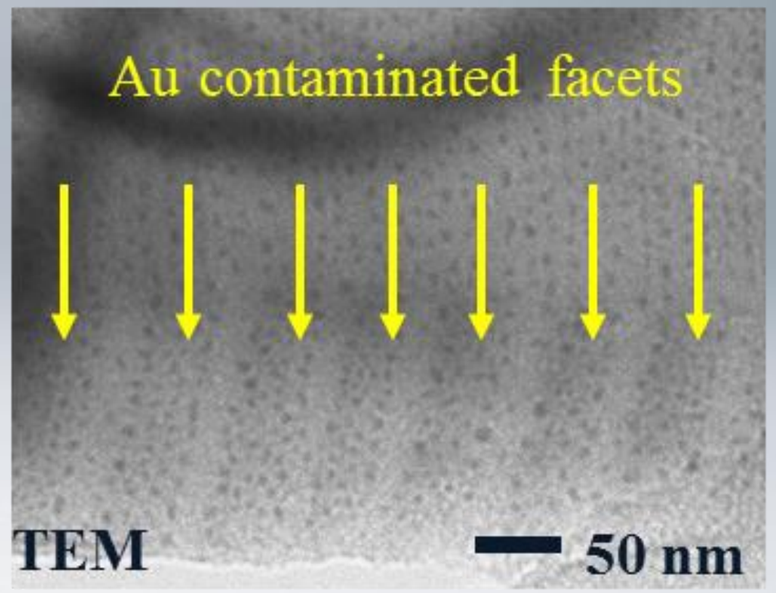


TEM micrograph of SiNWs grown by EBE

Oxidation of Si NWs

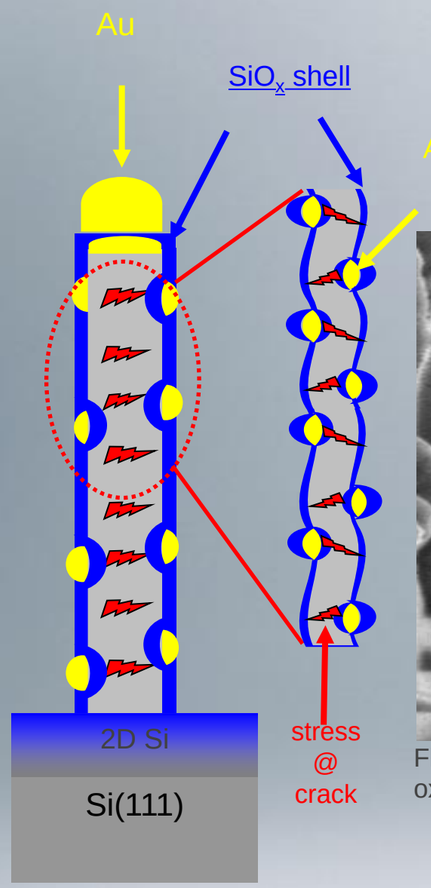
The mechanism of stress formation during oxidation is highly dependent upon the relative degree to which volume expansion occur normal to and in the plane of the oxidation front. In places where Au particles reside the oxidation velocity is supposed to be higher than in places without Au particles. The oxidation process leads to a large volume expansion (the volume of a molecule of SiO_2 is approx. 2.3 times larger than that of a silicon atom) that however is affected by large mechanical stresses on the order of hundreds of MPa.



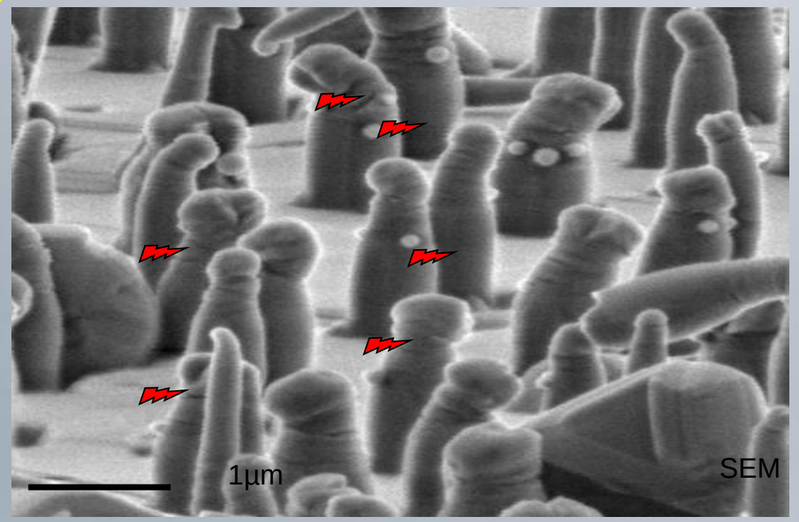


VAS et al., Nanotechnology, 20, 405607 (2009).

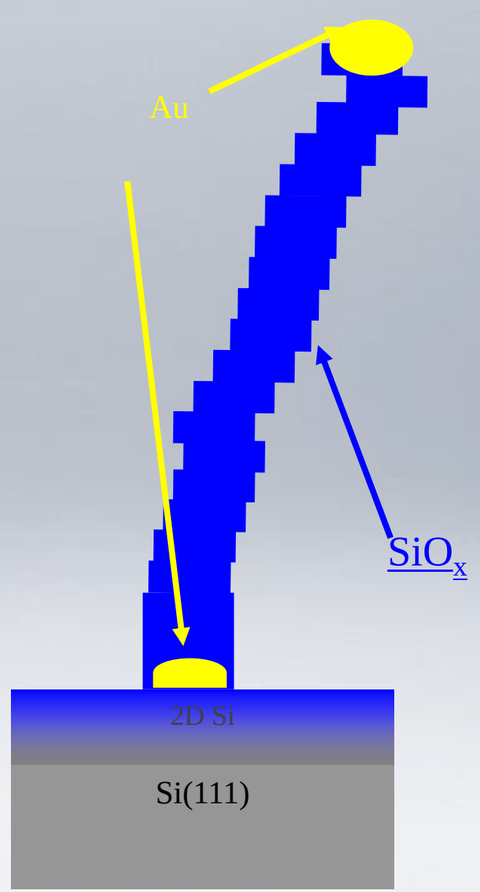
Oxidation of Si NWs



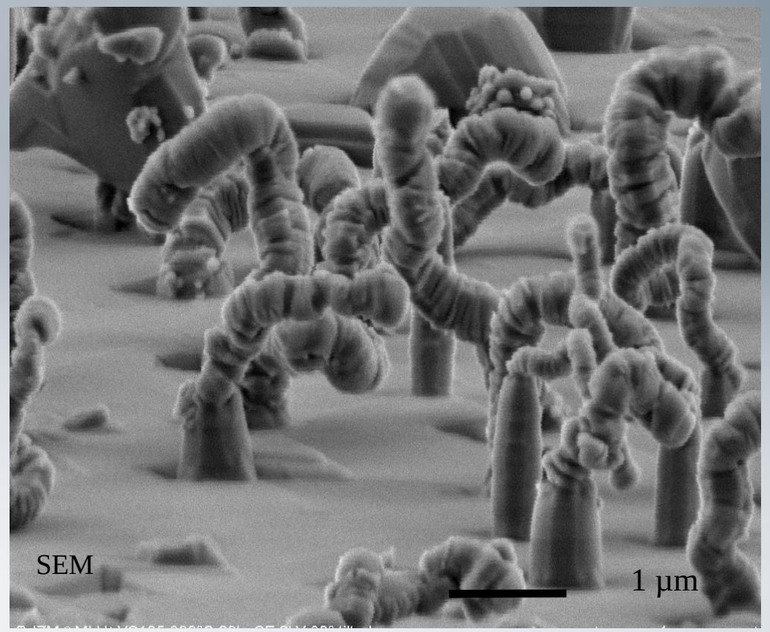
II STEP



Flash pointed places in the SEM image delineate places where oxidized SiNW are stressed and cracked oxide shells form.



III STEP



VAS et al., Nanotechnology, 20, 405607 (2009).

Conclusions

- Expensive, Many Steps Process
- Contamination by Catalyst
- Difficulties by Epitaxy Realization
- Defects in Single Crystal (twins)
- Arrays Realization Difficulties

AGENDA

Cheap NWs Growth Technology

NW Yield@Geometry Control

High Crystal Quality (single crystalline, defect free)

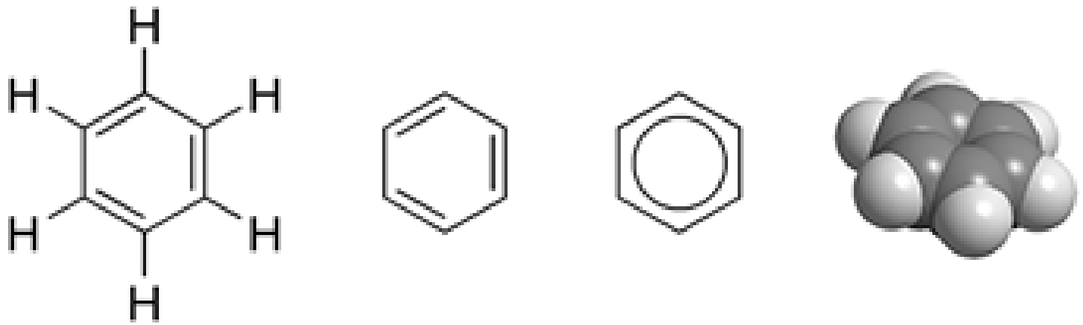
Without catalyzing atom contaminants

iphtjena

Mitglied der Leibniz-Gemeinschaft

Newton's Law of Gravity

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



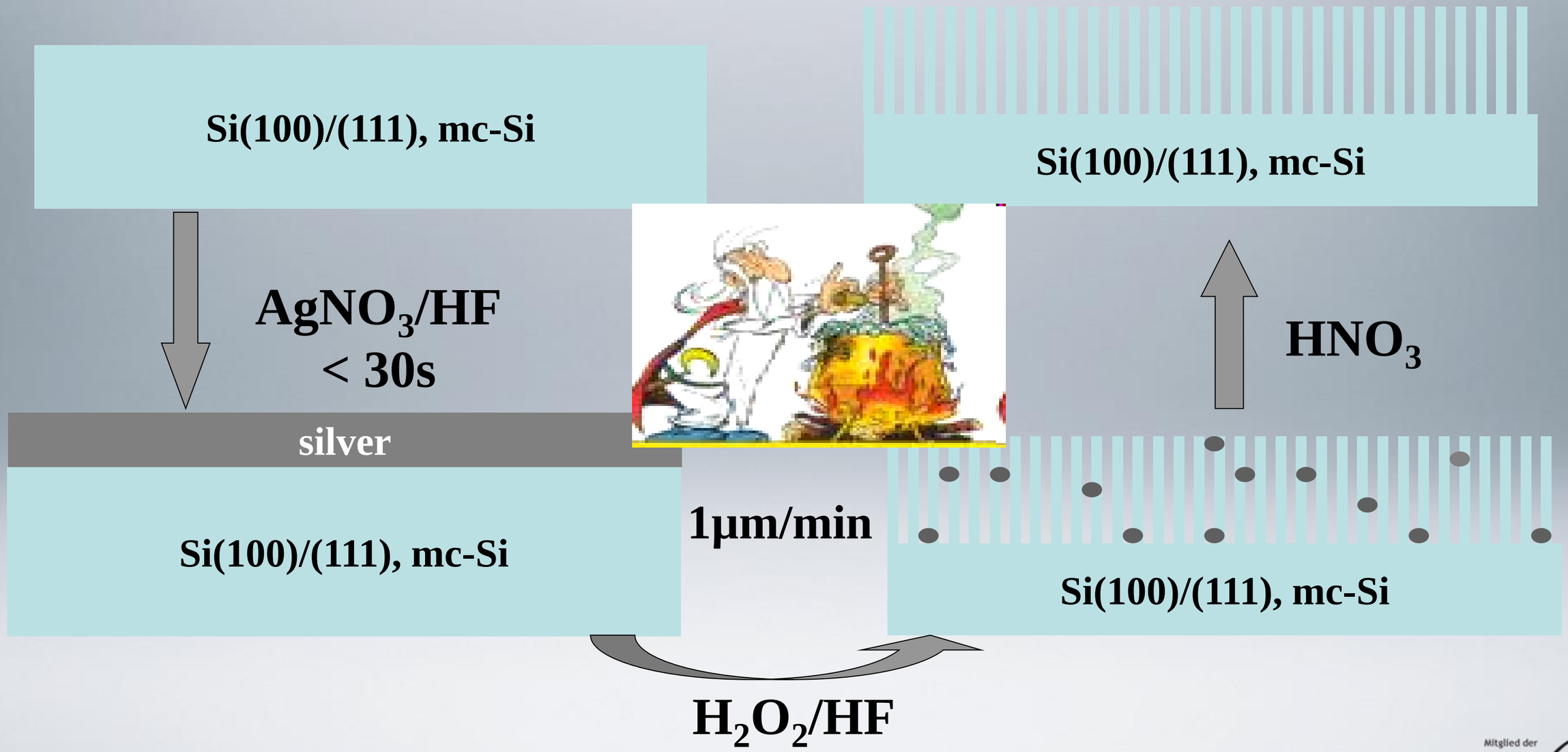
Observation of NATURE

The Proverbial Apple

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

Friedrich August Kekulé said that he had discovered the ring shape of the benzene molecule after having a reverie or day-dream of a snake seizing its own tail (this is a common symbol in many ancient cultures known as the Ouroboros). This vision, he said, came to him after years of studying the nature of carbon-carbon bonds.

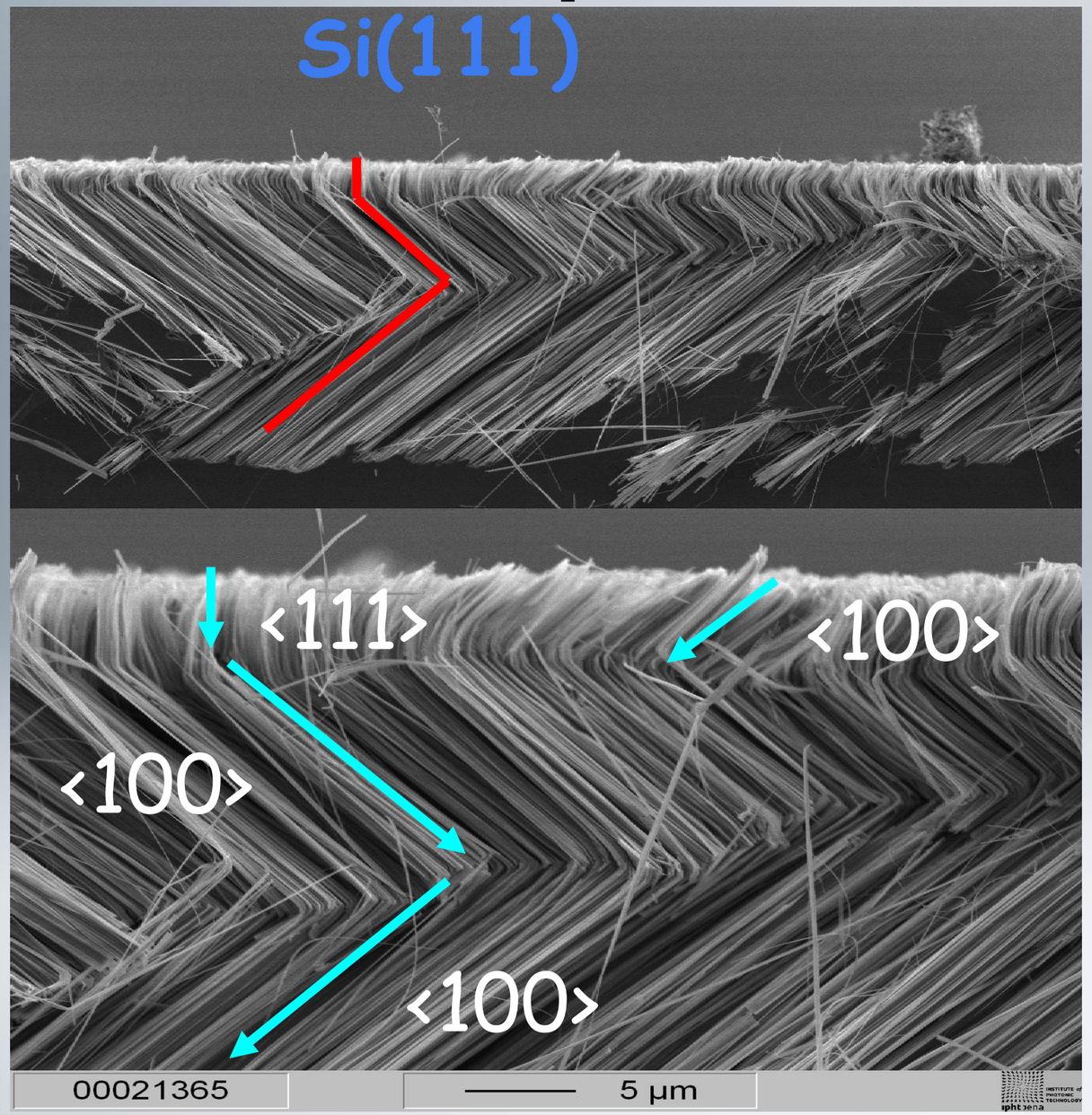
Top-down: Wet-Chemical Etching

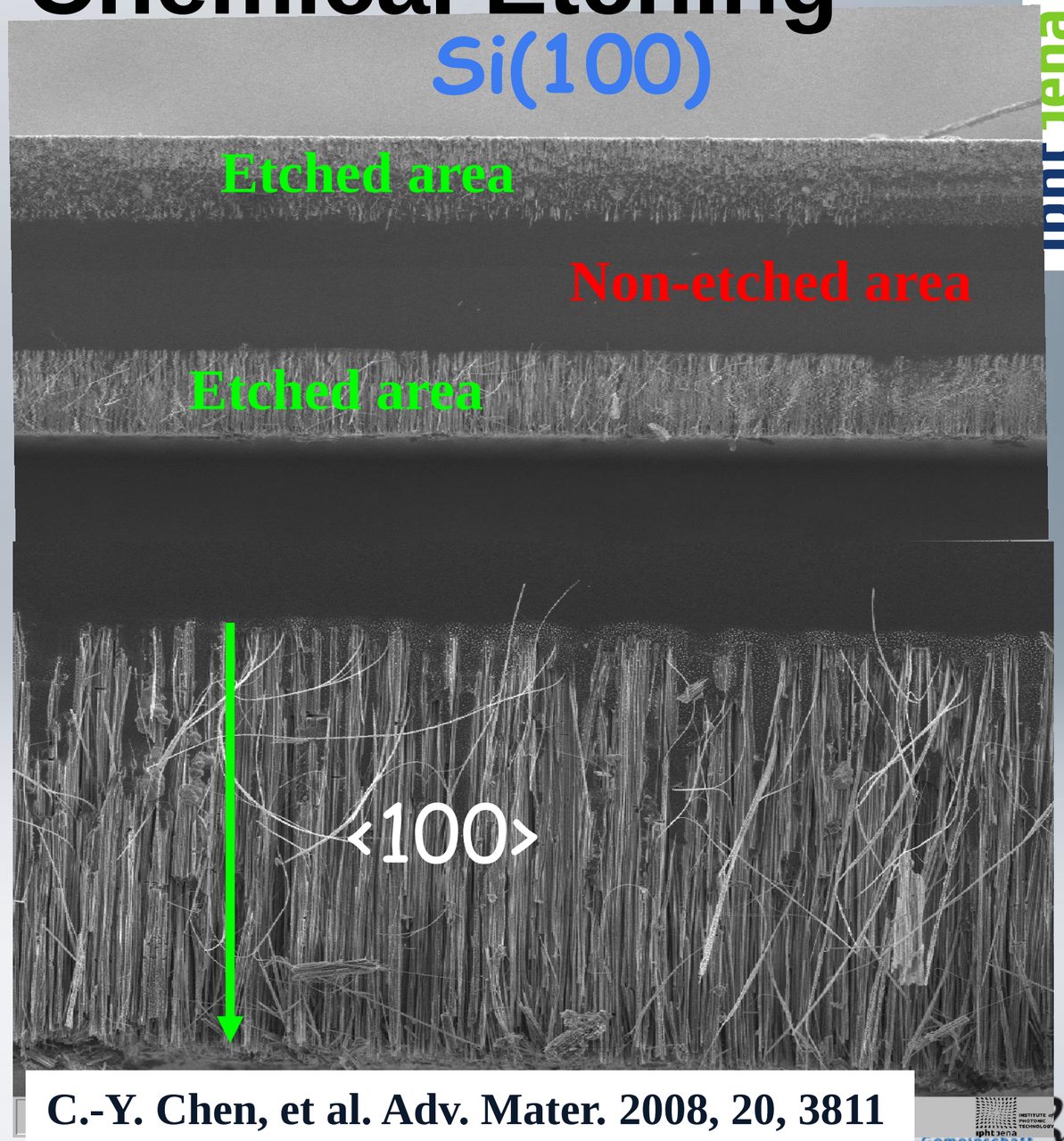


VAS et al., J. Phys. Chem. C*114*, 3798–3803 (2010)

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

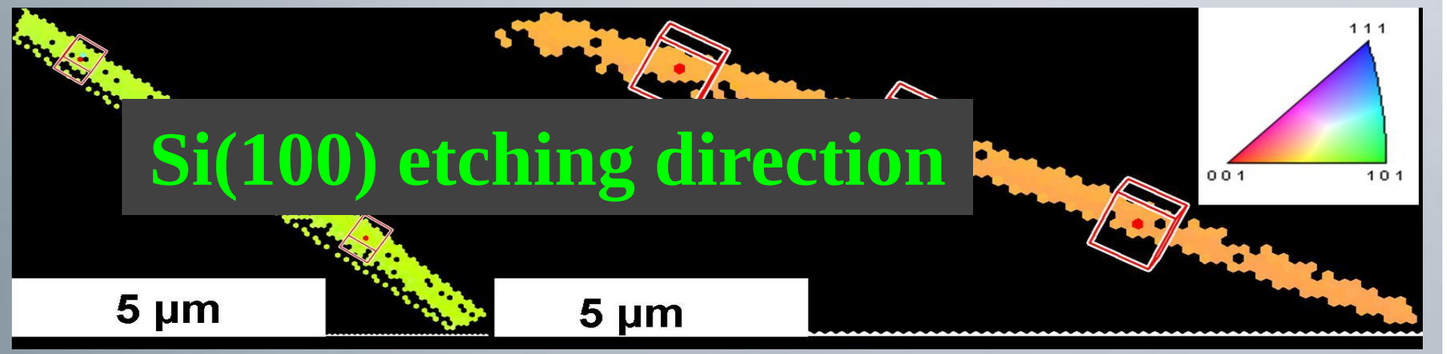
Top-down: Wet-Chemical Etching

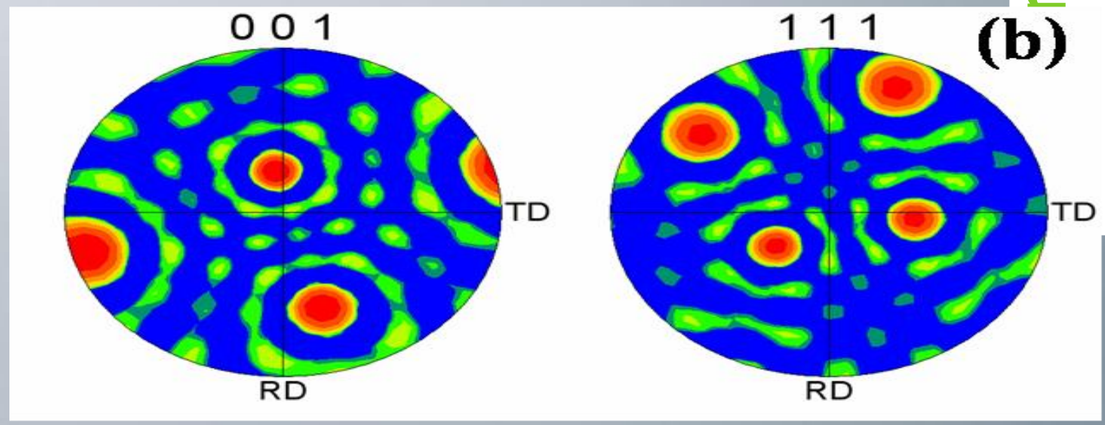


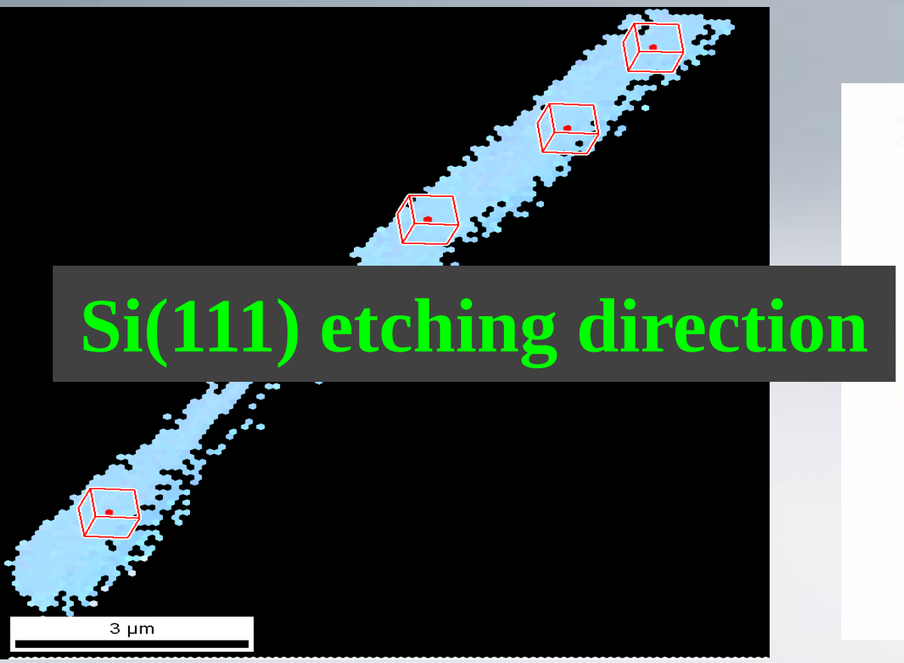


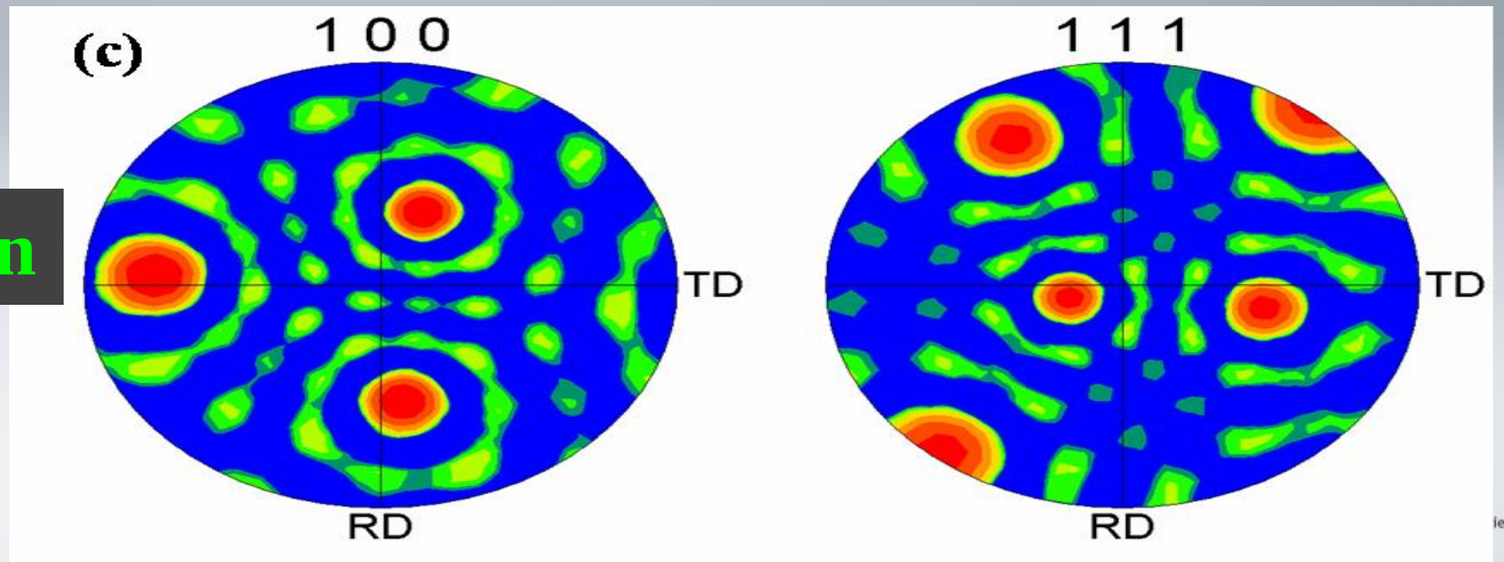
C.-Y. Chen, et al. Adv. Mater. 2008, 20, 3811

Top-down: Wet-Chemical Etching

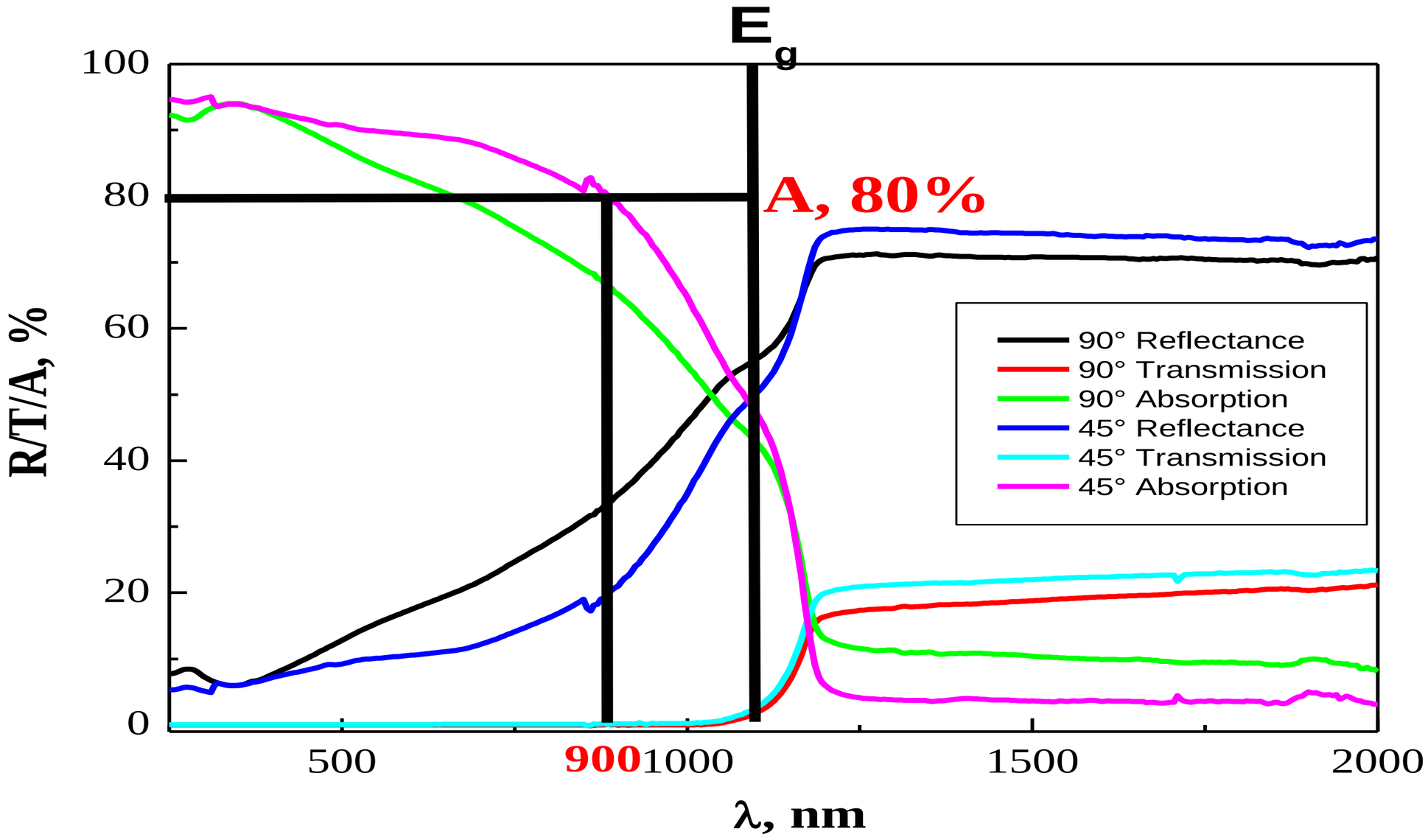




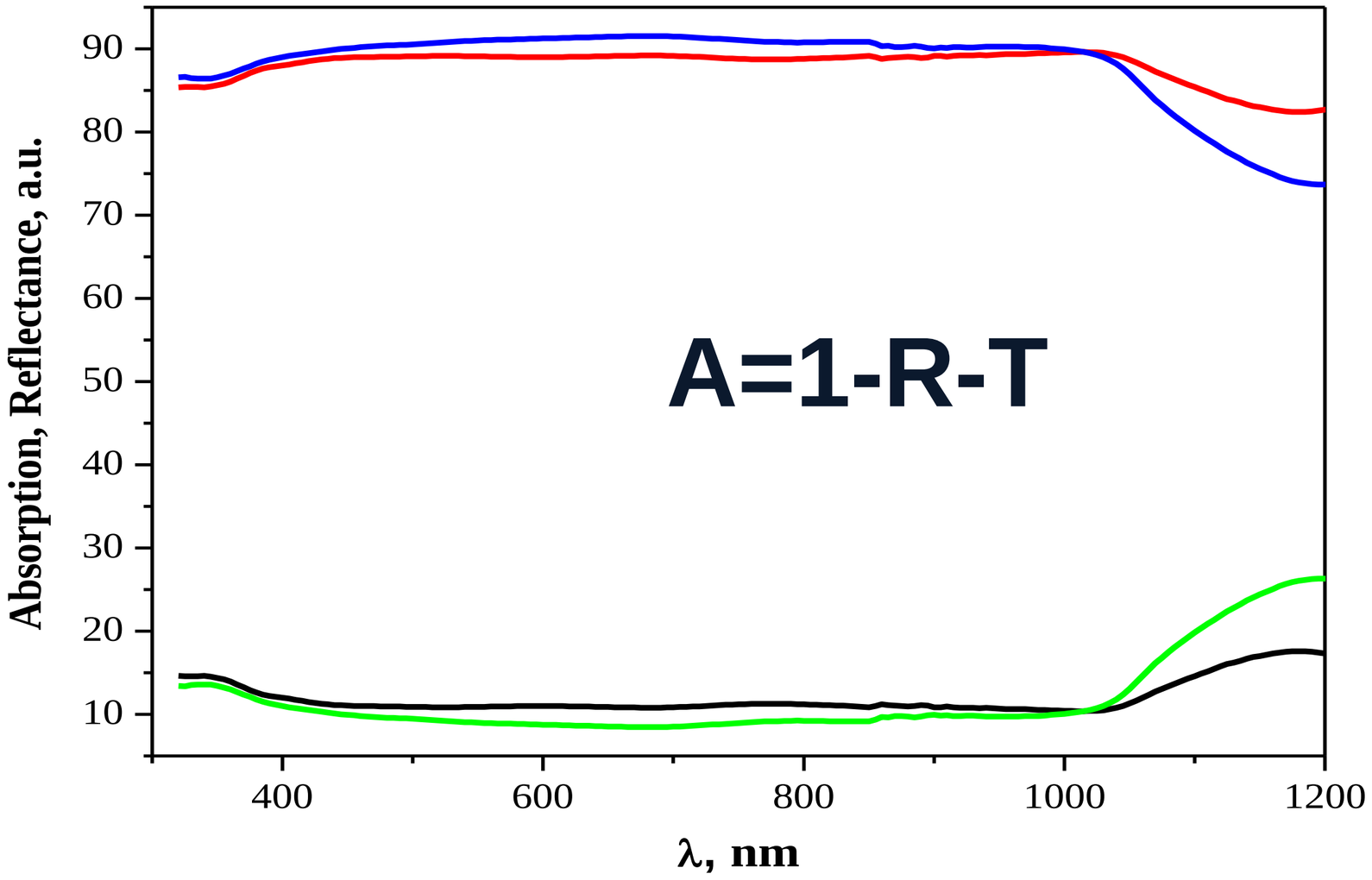




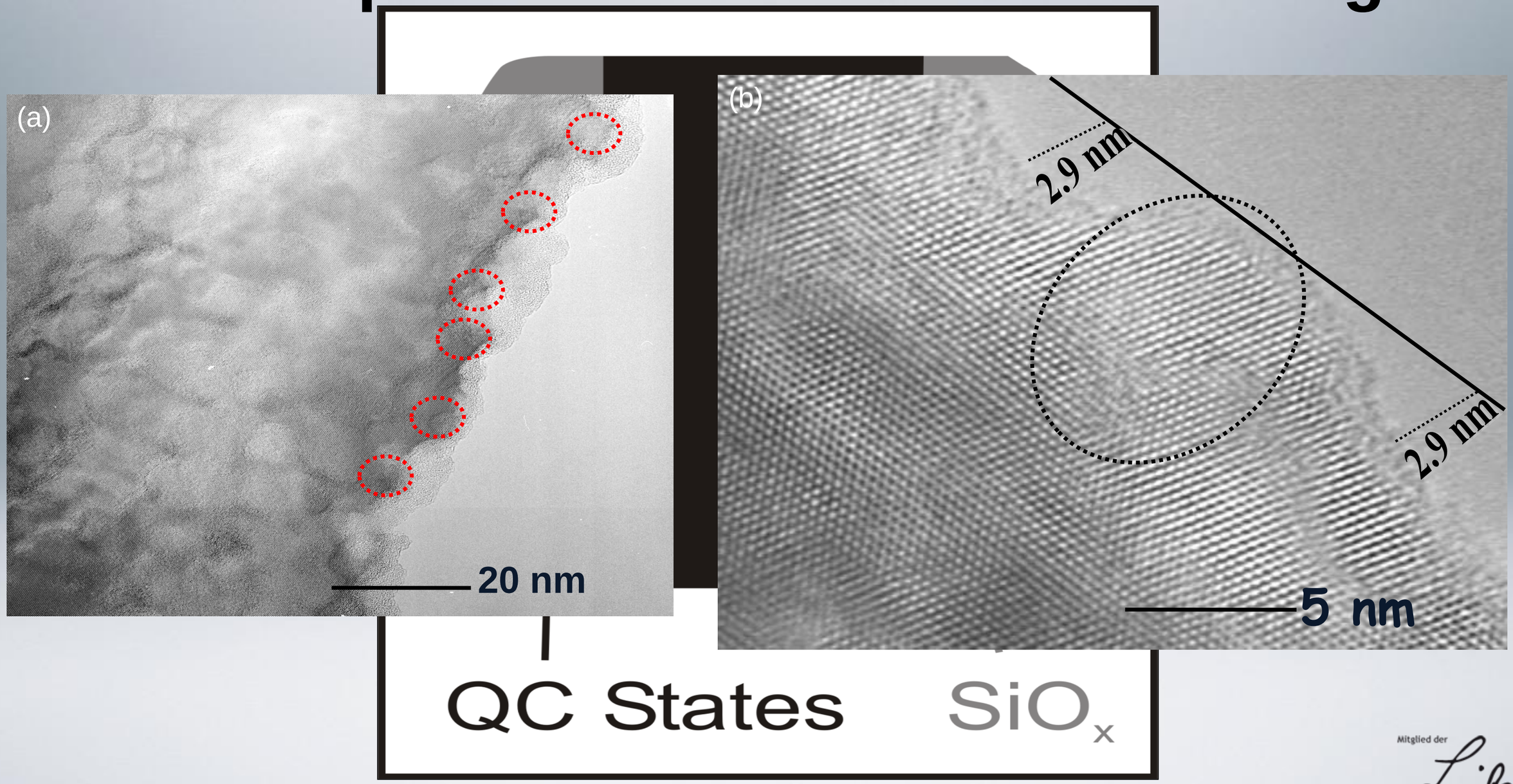
Top-down: Wet-Chemical Etching



Top-down: Wet-Chemical Etching

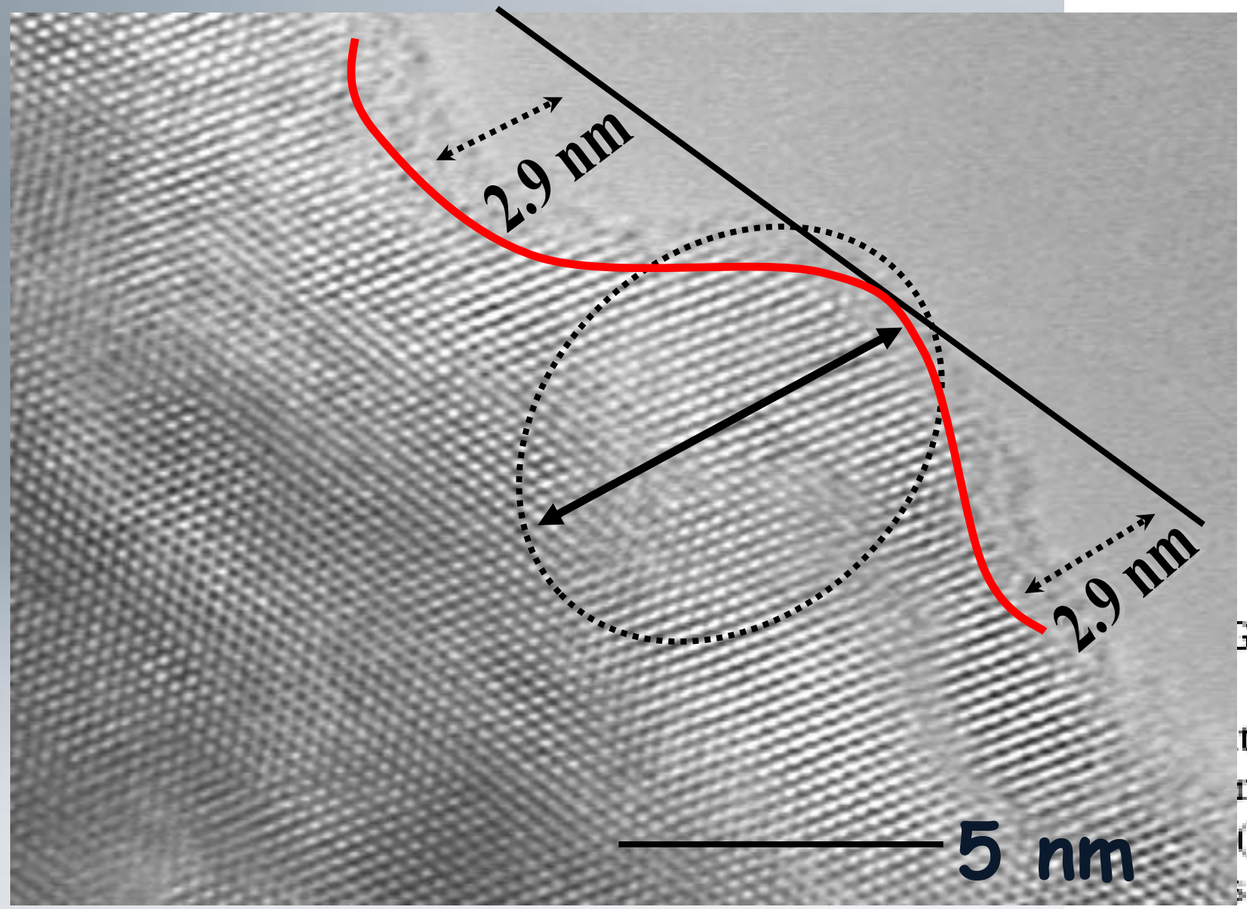


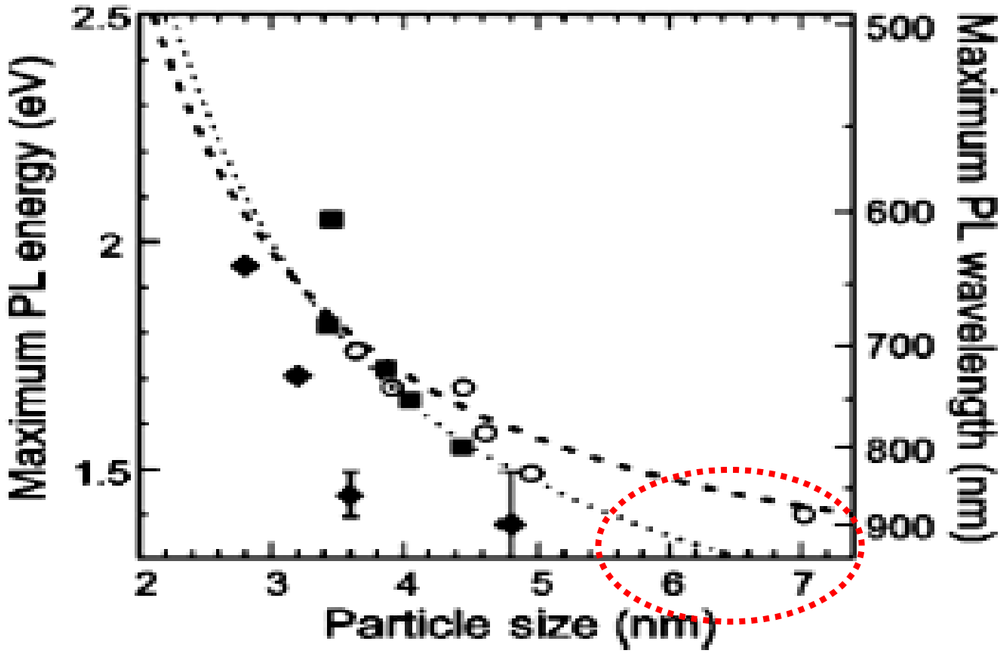
Top-down: Wet-Chemical Etching



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

Top-down: Wet-Chemical Etching





G. 7. Position of the PL maximum as a function of the size of nanoclusters determined by TOFMS. For the data of the t work we have used filled symbols (squares for the first and nds for the second series) whereas the results of an earlier PL (Ref. 17) are plotted as open circles. The dashed curve rep- s the theoretical results of Delerue, Allan, and Lannoo (Ref. 37), whereas the dotted curve includes the correction due to the lattice variation according to Eq. (4).

Ledoux, G., et al., V. Phys. Rev. B 62, 15942 (2000)

Conclusions

☺ Cheap Formation
☺ Catalyst Free
☺ High Absorption
☺ Room PL (E_g=1.6-1.8 eV)
☺ Low Reflection

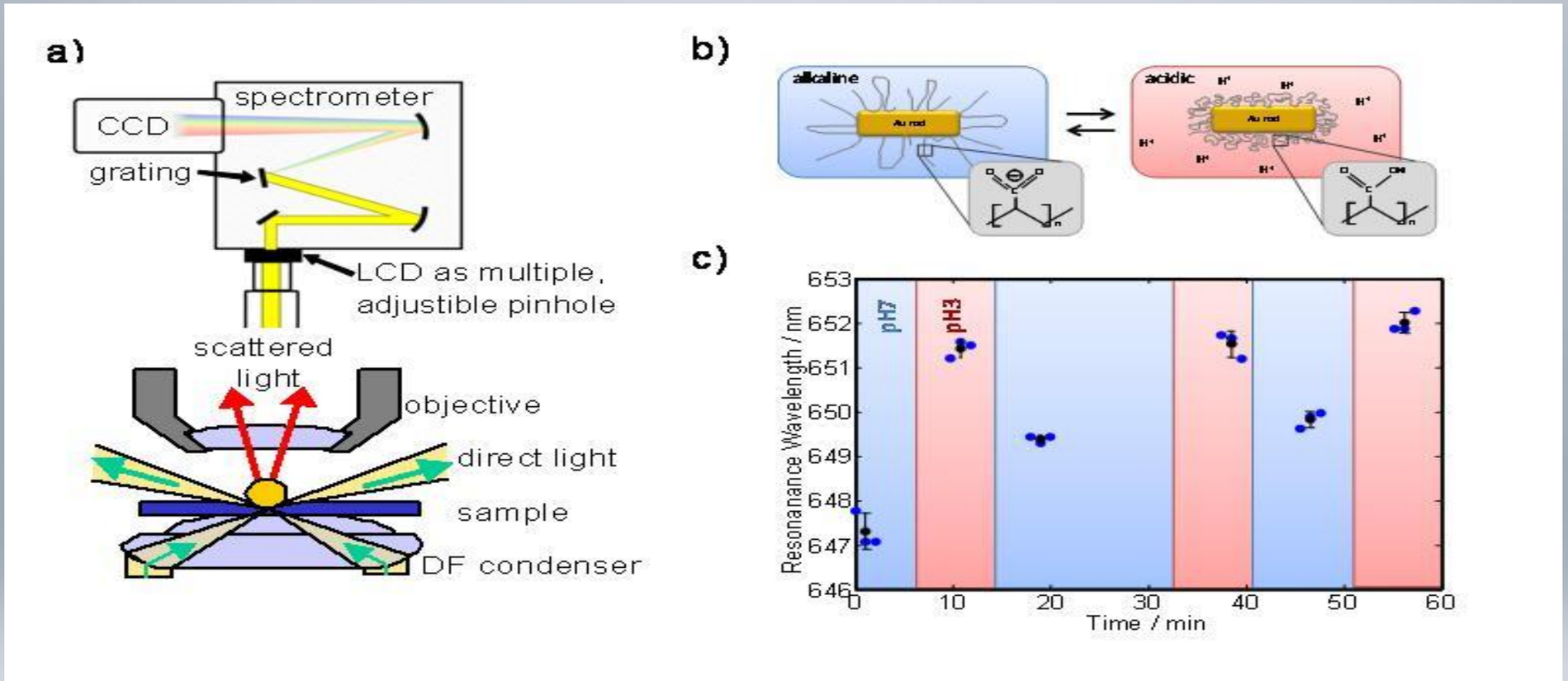
↓

Photonic, Optoelectronic, PV, Sensoric

VAS et al. Intech . Nanowires / Book 1, p45-80 (2011)

2. Raman Spectroscopy

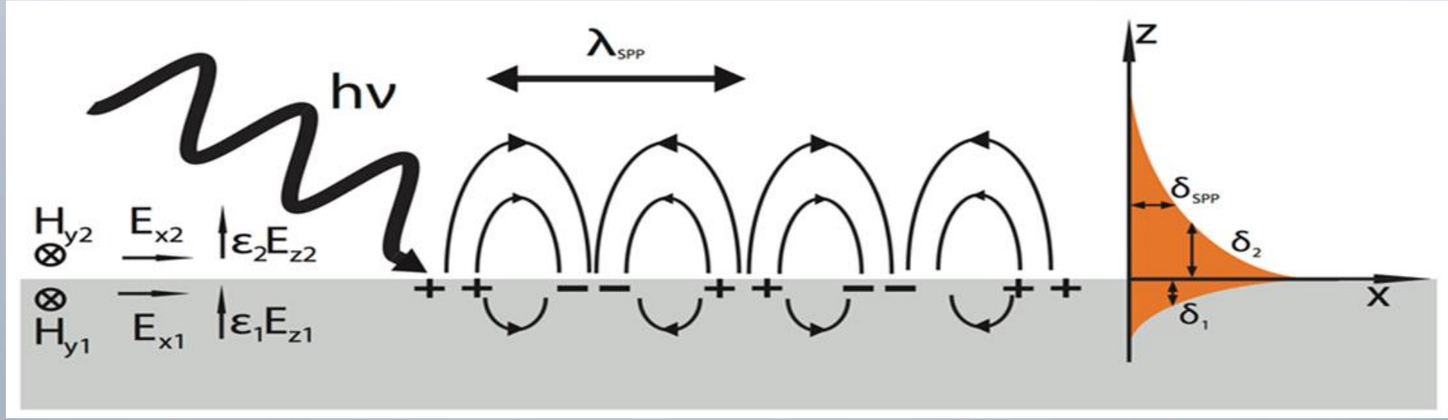
Surface Enhanced Raman Spectroscopy



Surface Enhanced Raman Spectroscopy (SERS) is a technique that was developed to detect extremely small quantities of molecules by determining their characteristic Raman signal, i.e. their characteristic vibrational modes.

To make use of the Raman signal enhancement nanoscopic noble metal particles in colloidal solutions or on substrates are usually used.

Surface Enhanced Raman Spectroscopy

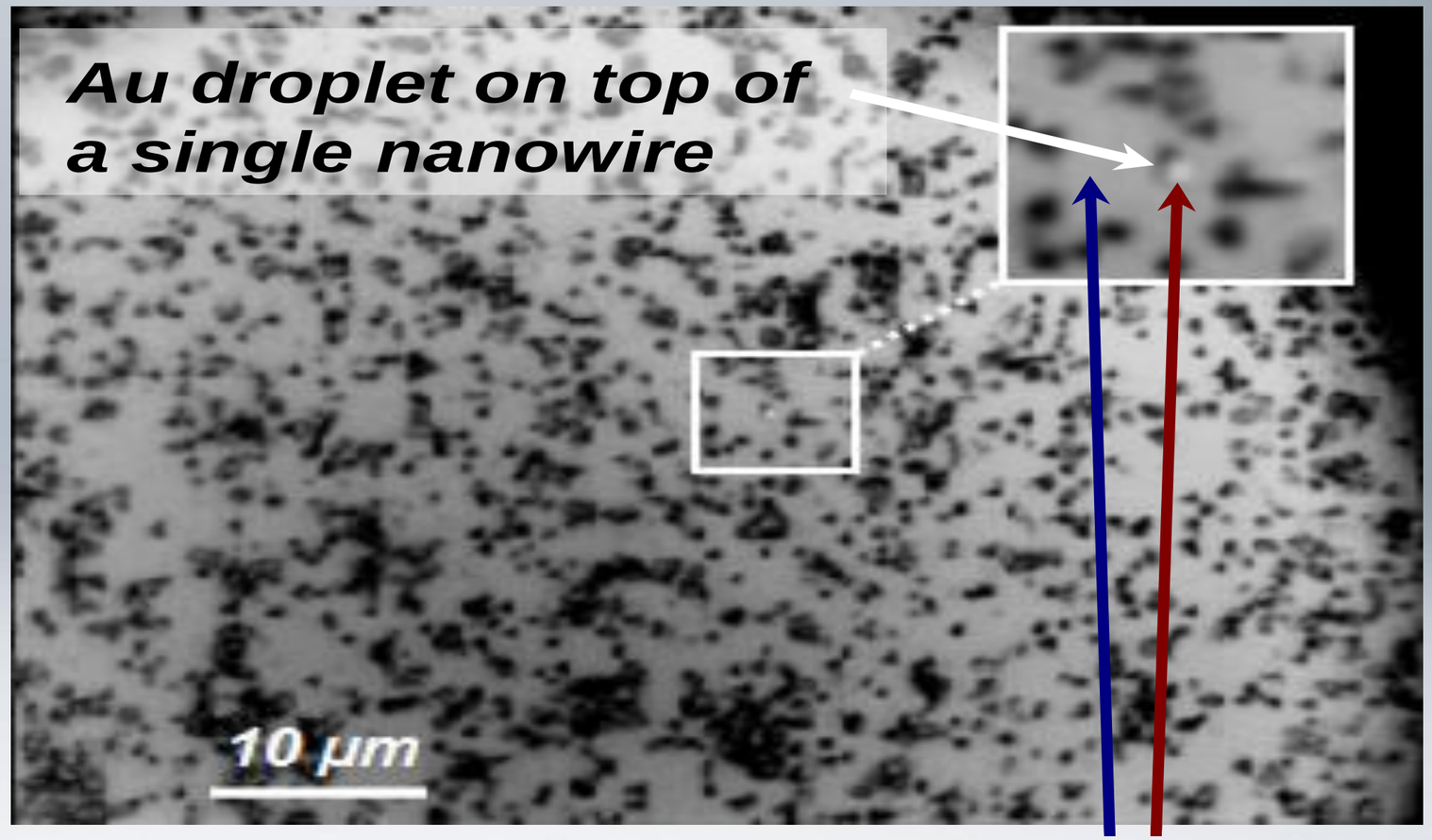


These metallic nanoparticles exhibit collective oscillations of the free-electron gas on the particle surface, so-called localized surface plasmons (LSP), excitable by the direct coupling to the incident light.

Due to the strong confinement of the evanescent fields onto the nanoscale, plasmons are accompanied by large electric field enhancements in the direct vicinity of the particle surfaces.

Particular strong intensity enhancements are expected at positions where adsorbed molecules (adsorbents) stay in close vicinity (a few nanometers apart, at most) to the so-called hot spots, points of strong field enhancement in-between the gap region of noble metal nanoparticle dimers.

Surface Enhanced Raman Spectroscopy

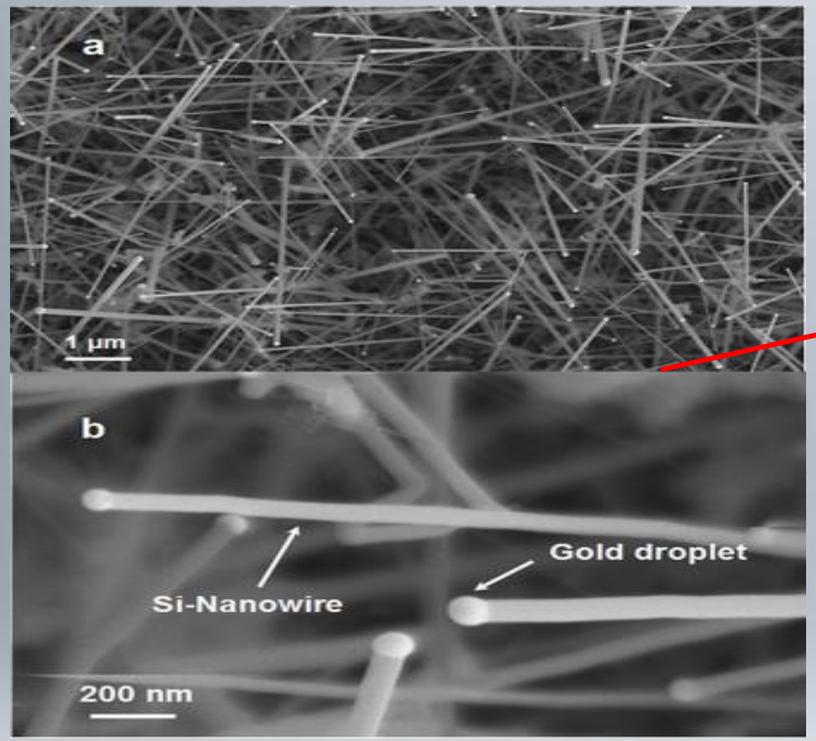


Optical micrograph

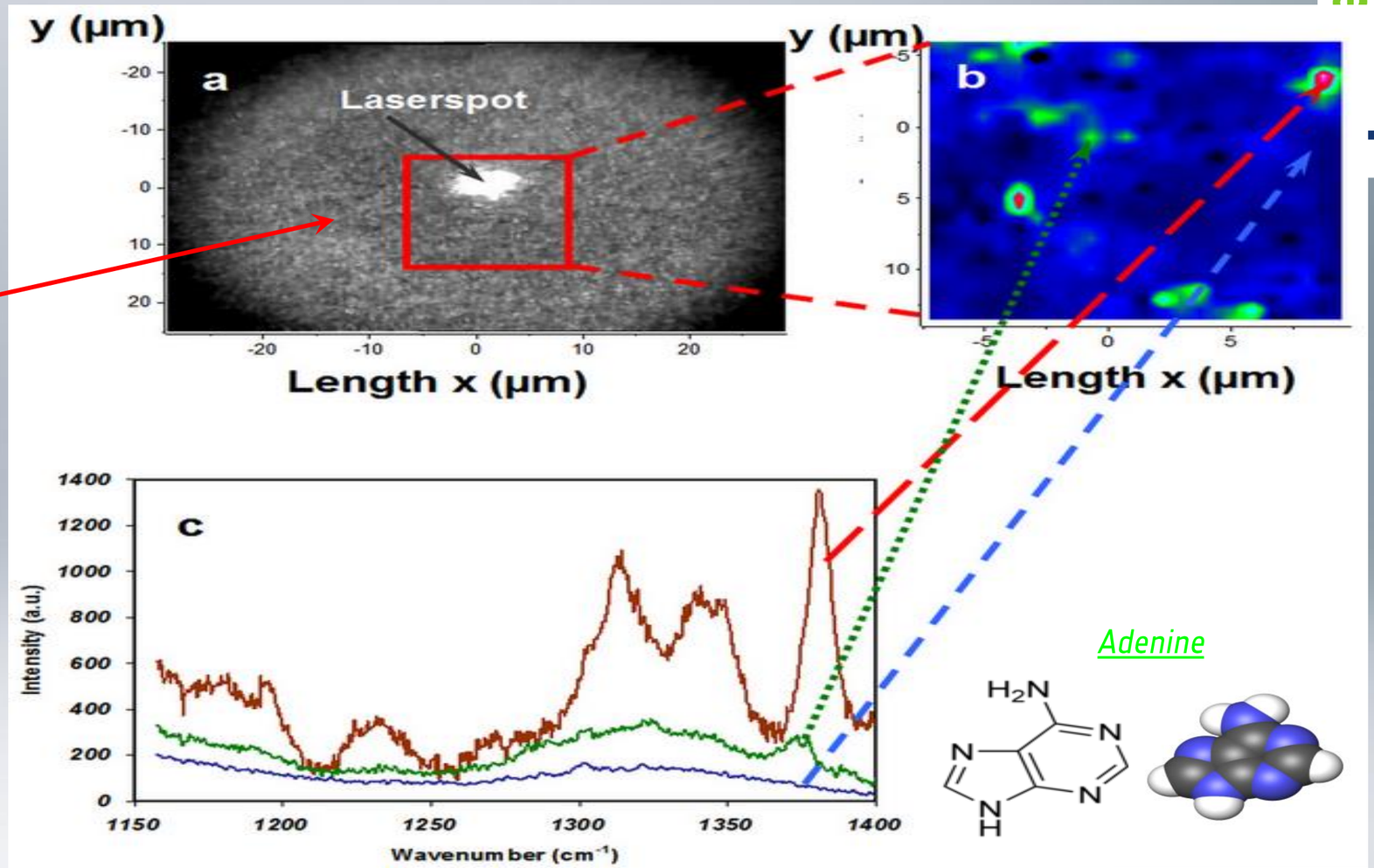
V. Sivakov et al. Nanotechnology 18 (3) , 035503/1-6 (2007)

Surface Enhanced Raman Spectroscopy

CVD-grown Nanowires



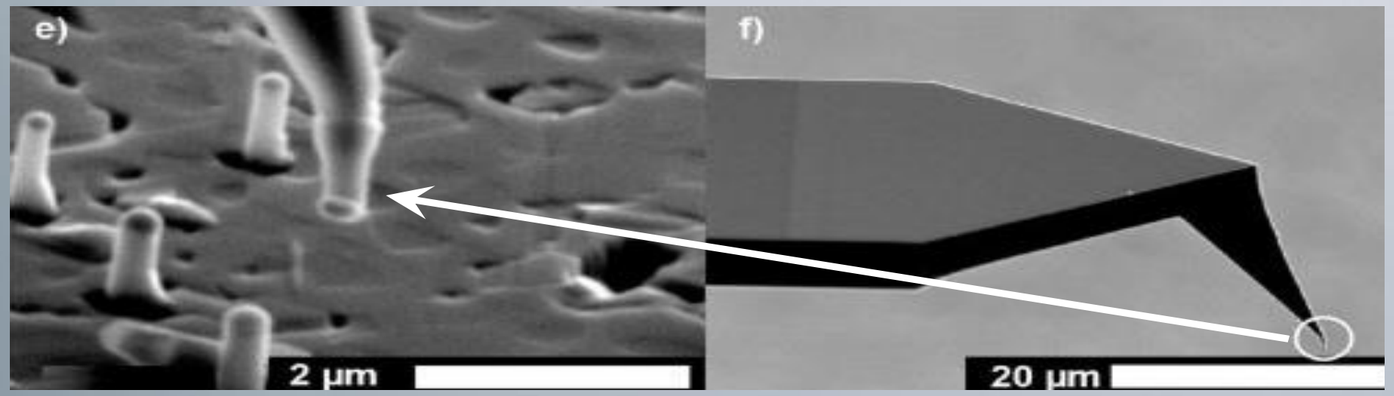
SERS-Mapping of Adenine

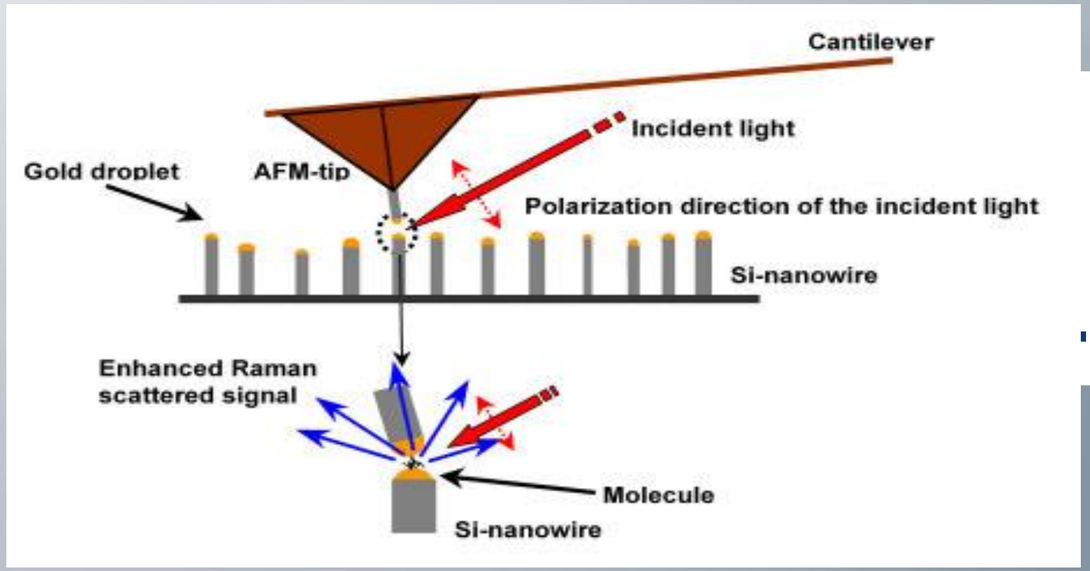


The lateral resolution of conventional micro-Raman spectroscopy is limited by the diameter of the focused laser spot on or in the probed sample and is usually at best in the range of ~1 μm. The SERS effect giving Raman spectroscopy a spatial resolution on the nanometer scale.

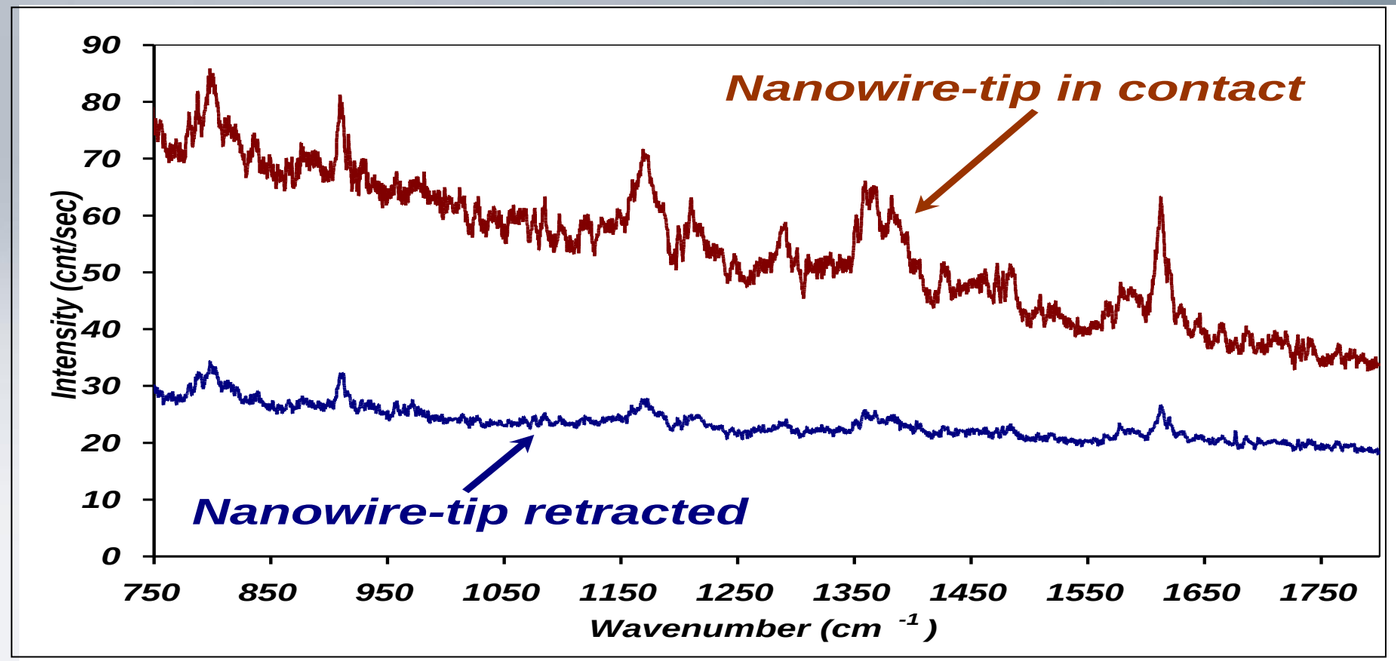
VAS, et al., Nanotechnology, 18, 035503(2007); VAS et al. Nano Lett., Vol. 7(1), 75(2007); VAS et al. Small, Vol. 4(4), 398(2008)

Tip Enchanced Raman Spectroscopy





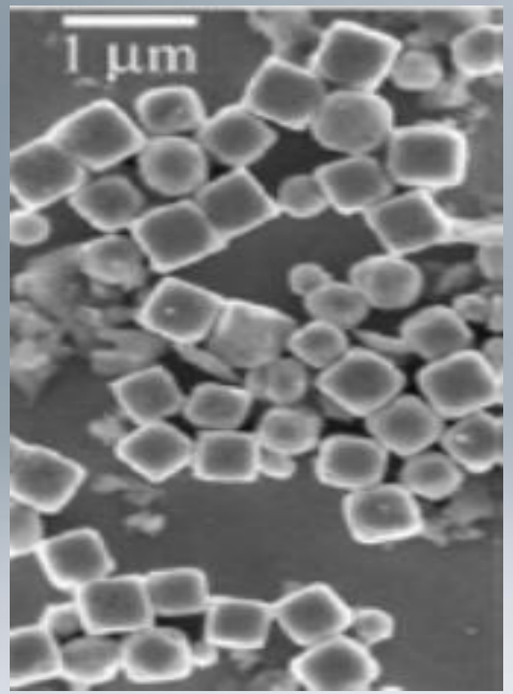
Tip-Enhanced Raman Spectroscopy (TERS) measurements was fabricated by welding a silicon nanowire with a gold droplet atop onto an AFM tip. Hemispherical gold droplets atop generate the SERS effect and that they are in addition well suited for TERS measurements, thereby giving Raman spectroscopy a spatial resolution on the nanometer scale.

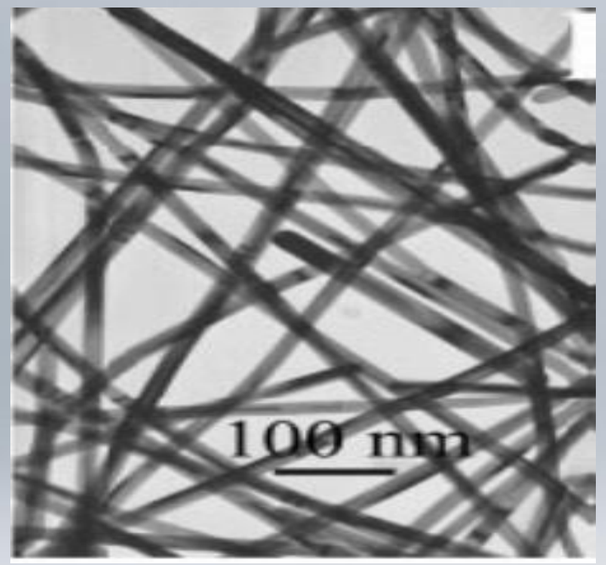


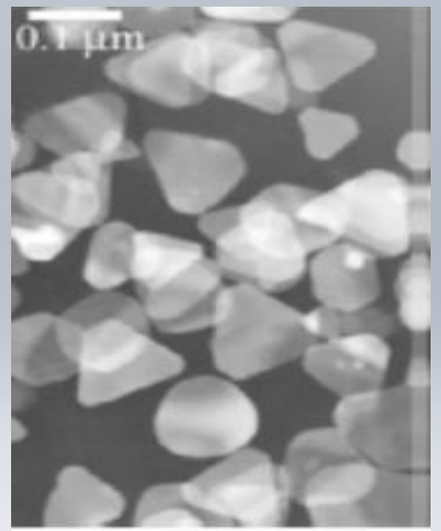
Nano Lett., Vol. 7(1), 75(2007); Small, Vol. 4(4), 398(2008)

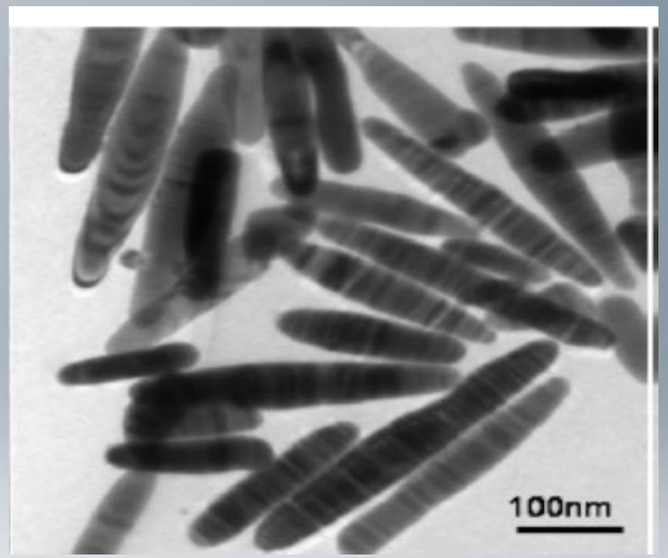
Leibniz-Gemeinschaft

Silver Nanostructures



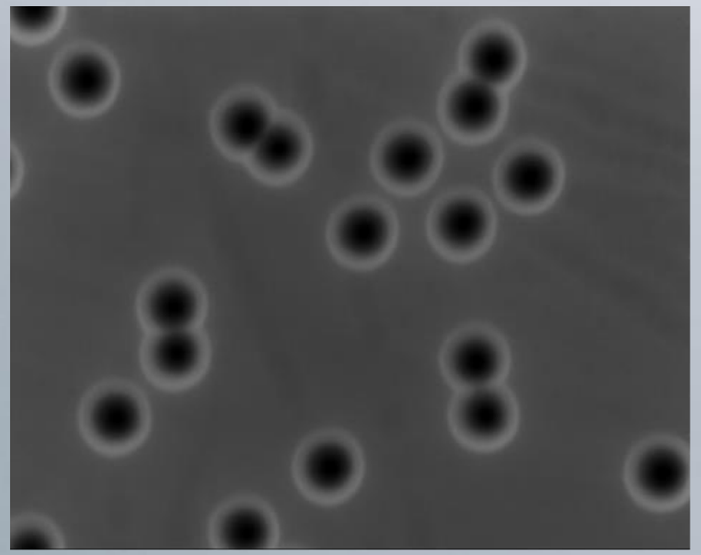


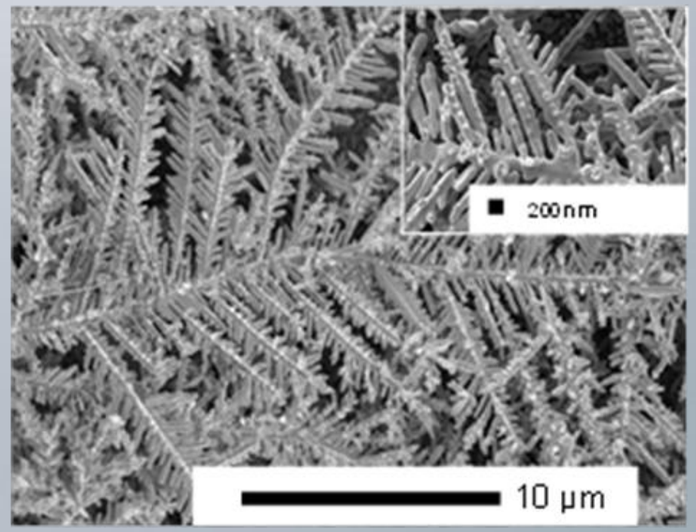


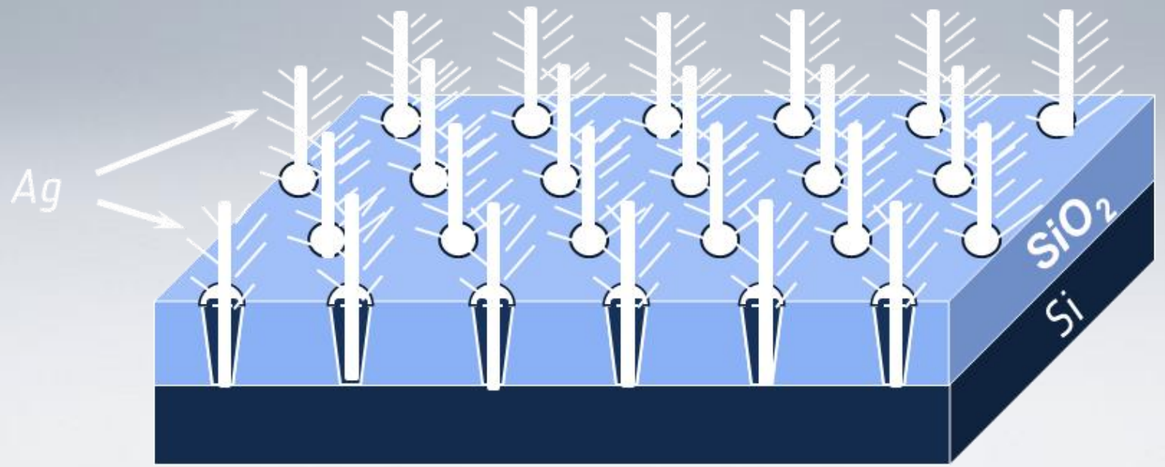


X. Sun, Y. Li, *Adv. Mater*. 17, 2626 (2005); H. Liang, H. Yang, W. Wang, J. Li, H. Xu, *J. Am. Chem. Soc.* 131, 6068 (2009); C. Marchal-Roch, C.M. Mayer, et al., *Chem. Commun*. 36, 3750 (2007); J. Zhang, H. Liu, P. Zhan, Z. Wang, N. Ming, *Adv. Funct. Mater.* 17, 1558 (2007); S.E. Skrabalak, L. Au, X. Li, Y. Xia, *Nature Protocols* 2, 2182 (2007); B.K. Jena, B.K. Mishra, S. Bohidar, *J. Phys. Chem.* C 113, 14753 (2009)

Surface Enhanced Raman Spectroscopy







Porous SiO_2 template on Si substrates with Ag-dendrites

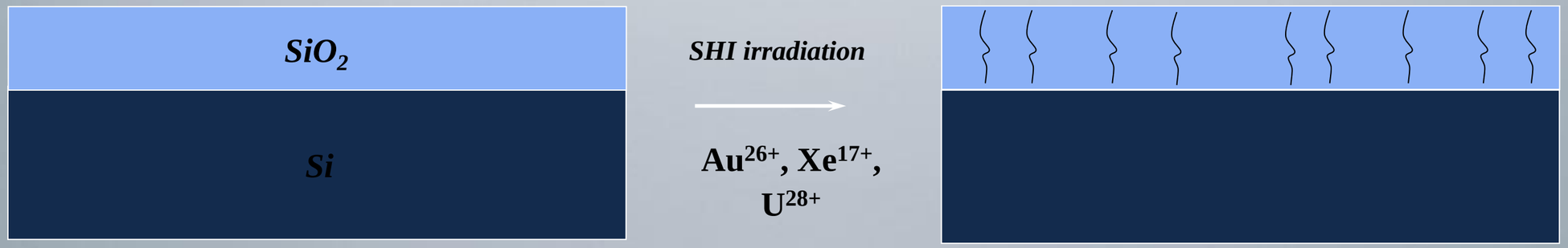
VAS et al., J. Cryst. Growth 300, 21-26 (2014)

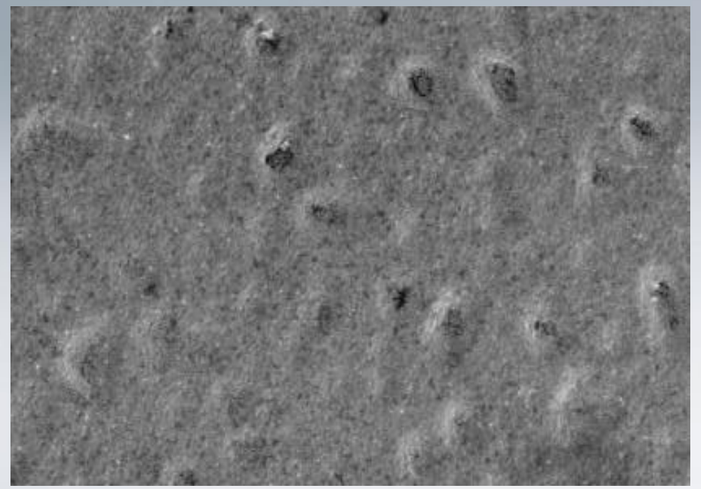
Mitglied der Leibniz-Gemeinschaft

Swift Heavy Ion Track Technology

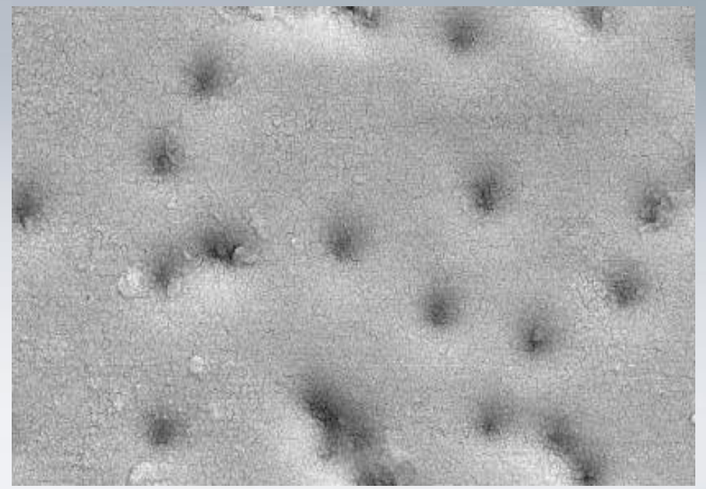
Si/SiO_2 substrate

Latent SHI tracks



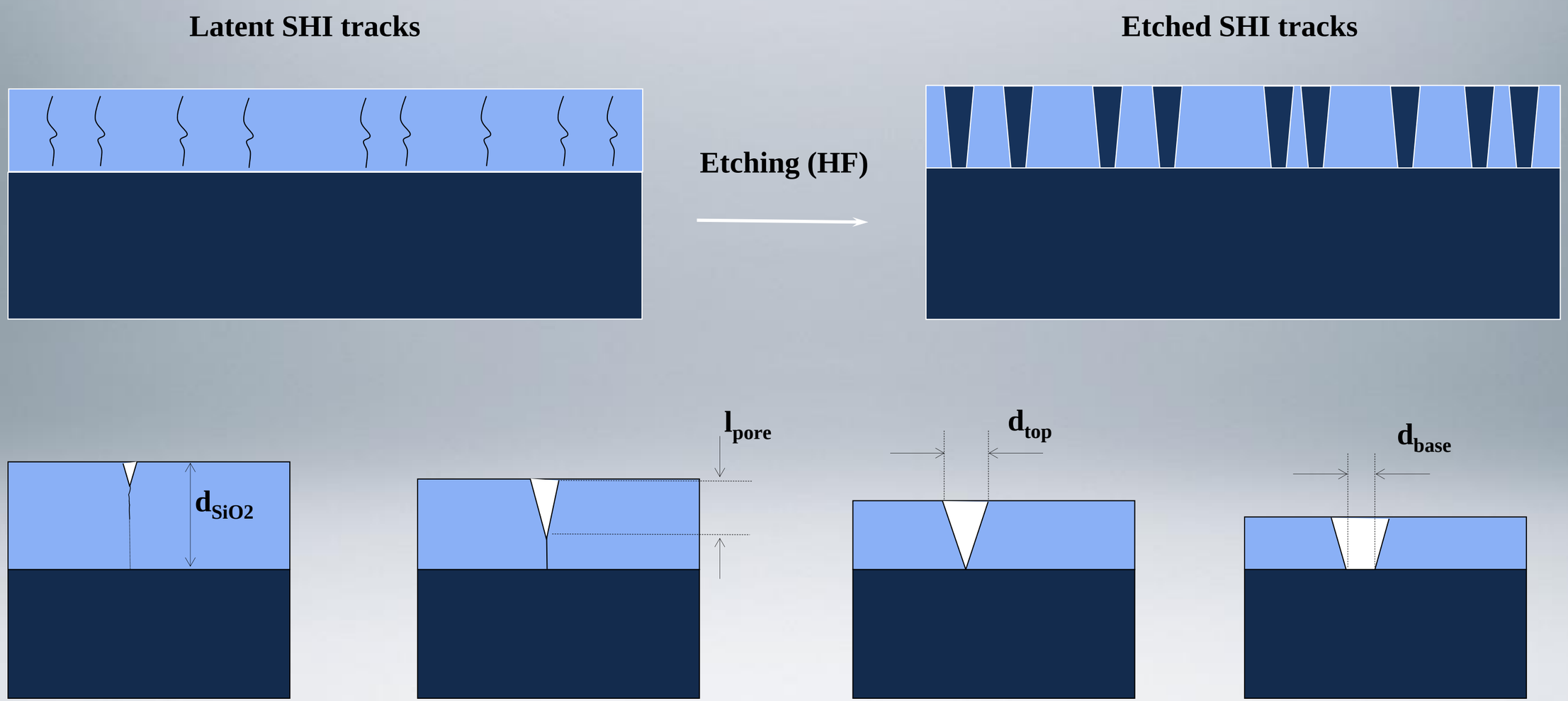


Au^{26+}, Xe^{17+}
Energy 350 MeV,
Fluence 5×10^8 cm^{-2}



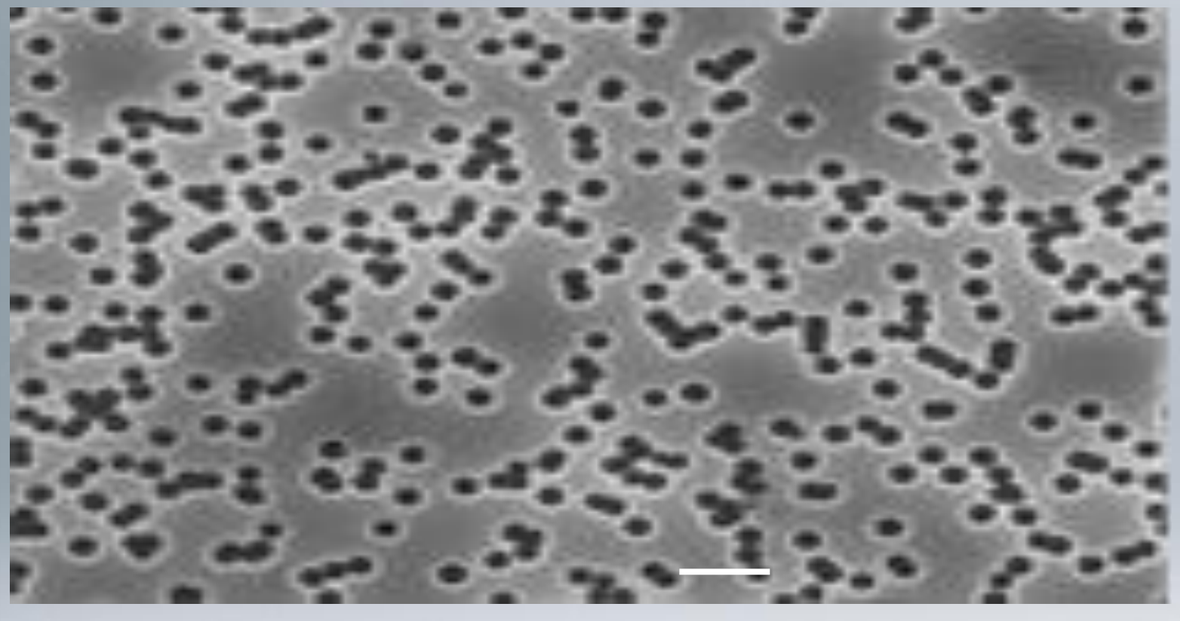
Ch. Trautmann, in *Ion Beams in Nanoscience and Technology*, R. Hellborg et al. (eds.), 2009, Springer, *369*.
VAS et al., The Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques 8(4), 805-813 (2014).

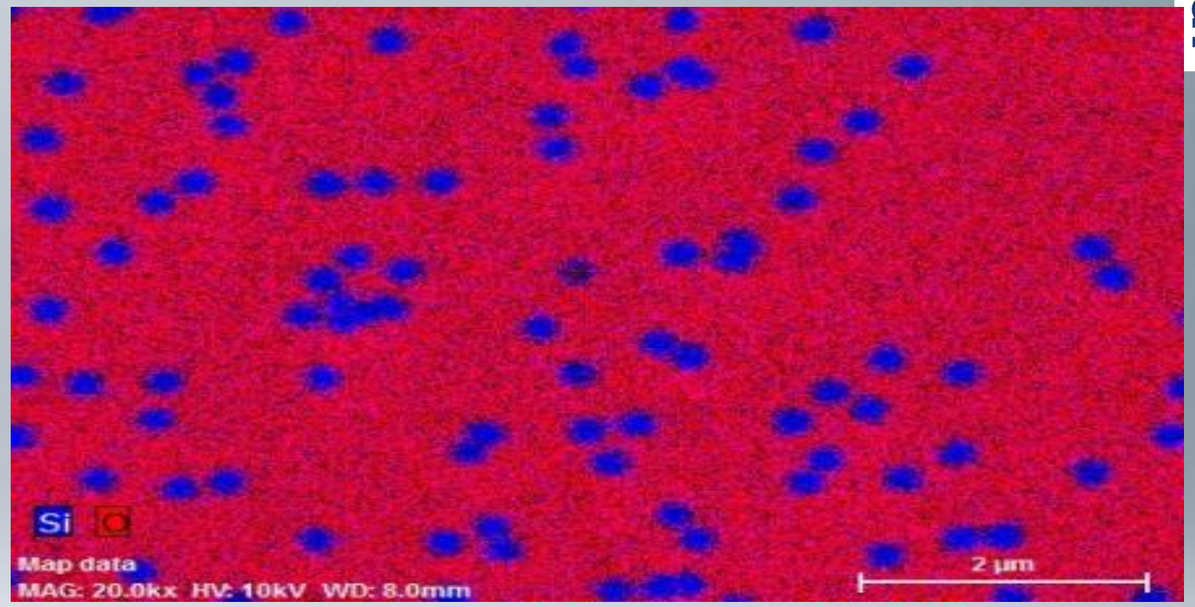
Swift Heavy Ion Track Technology



D. Fink, Fundamentals of Ion-Irradiated Polymers Springer Series in Materials Science 2004, 63, Springer, 391.
VAS et al. Sensors and Actuators A 400, 21-26 (2014).

Swift Heavy Ion Track Technology



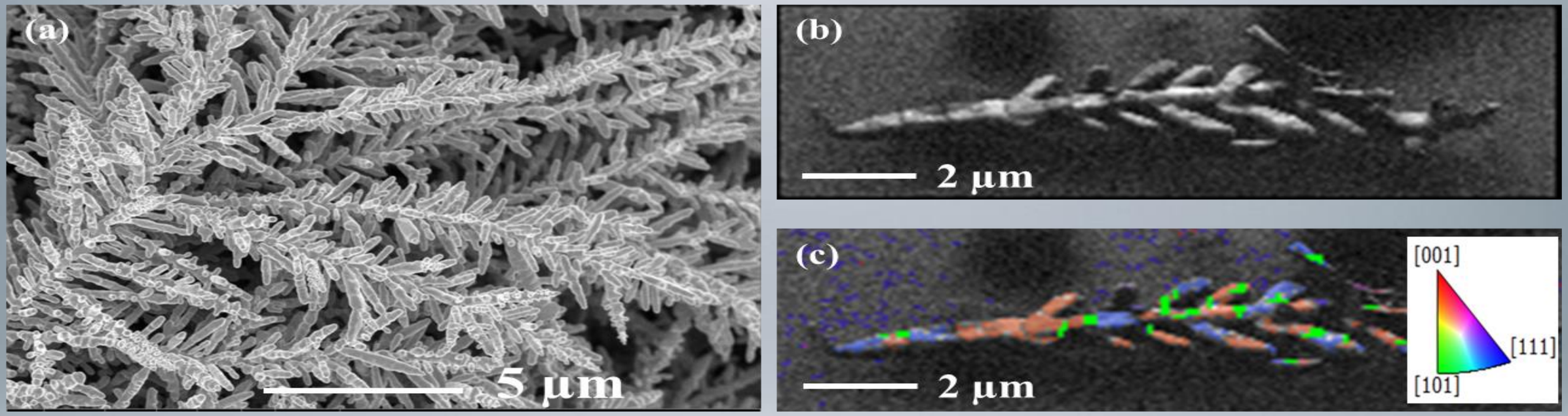


planar scanning electron microscopy micrograph and (b) element map (blue: silicon; red: oxygen) from energy dispersive X-ray analysis of a Si/SiO_2 sample irradiated with 350 MeV gold ions and exposed to chemical track etching

VAS et al., The Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques 8(4), 805-813 (2014).

Mitglied der Leibniz-Gemeinschaft

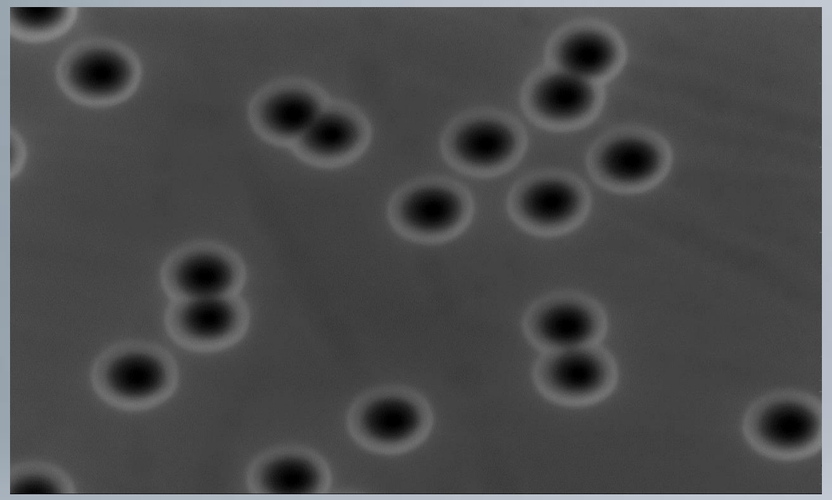
Swift Heavy Ion Track Technology

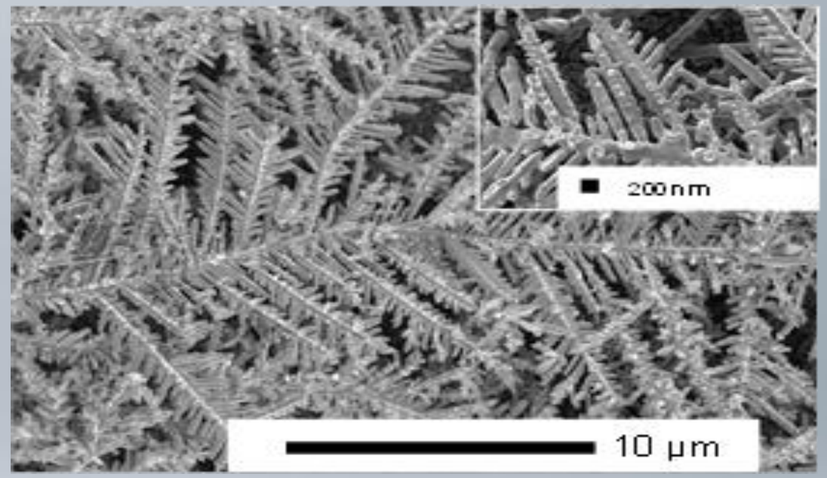


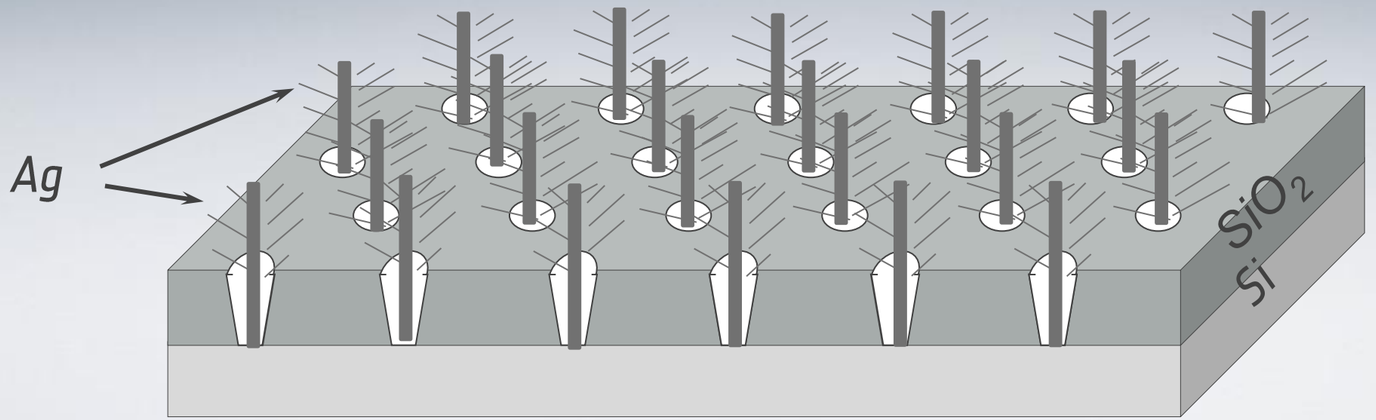
(a) SEM micrographs of silver dendrite nanostructure on n-Si (100) grown for 30 s at atmospheric conditions; (c) EBSD analysis of single silver dendrite; colour coded inverse pole figure representation.

VAS et al., J. Cryst. Growth 300,21-26 (2014)

Swift Heavy Ion Track Technology



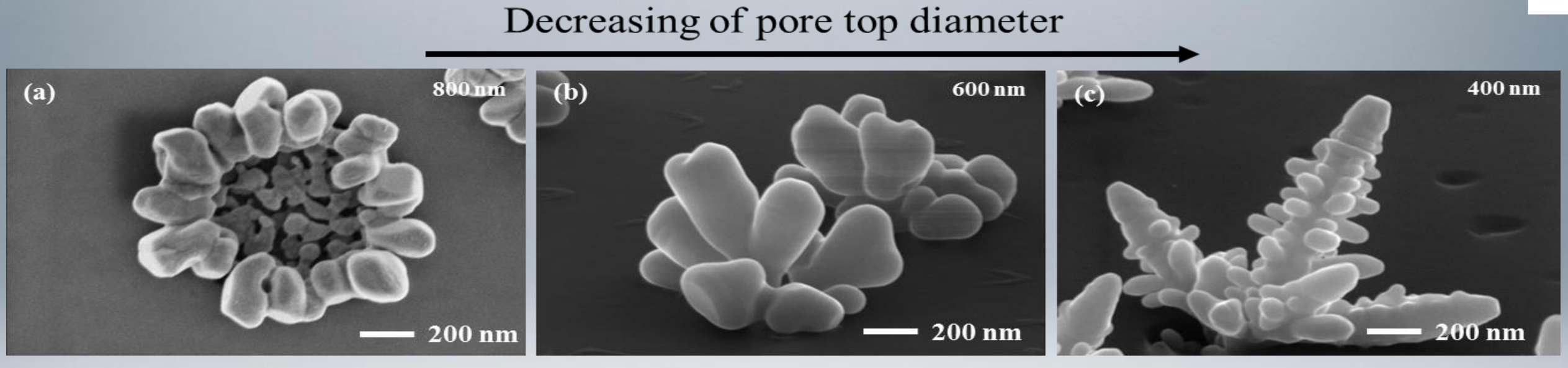




Porous SiO_2 template on Si substrates with Ag-dendrites

Mitglied der Leibniz-Gemeinschaft

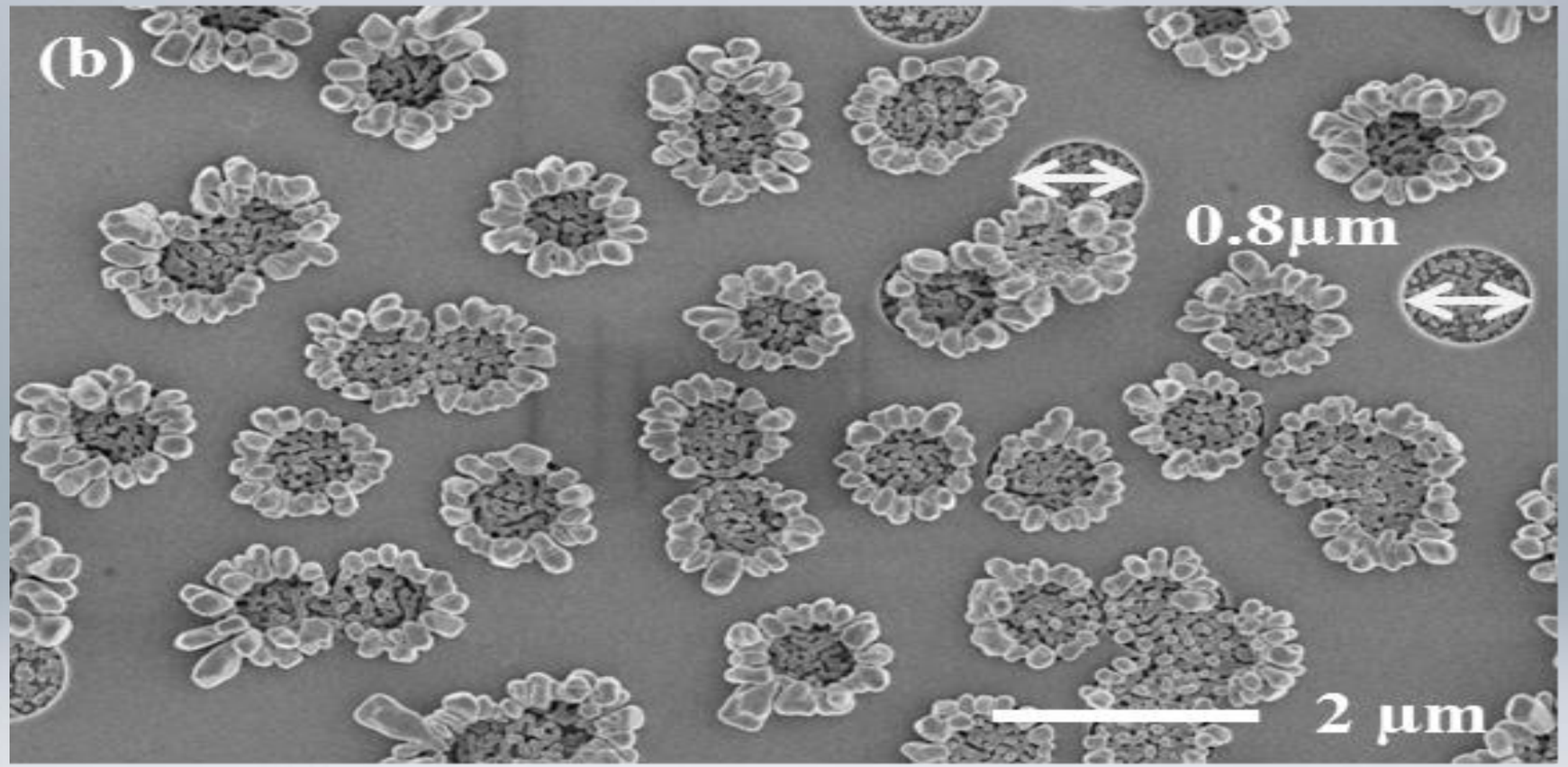
Swift Heavy Ion Track Technology



SEM micrographs of silver nanostructures with (a) “sunflower”, (b) “azalea” and (c) “corn”-like shapes.

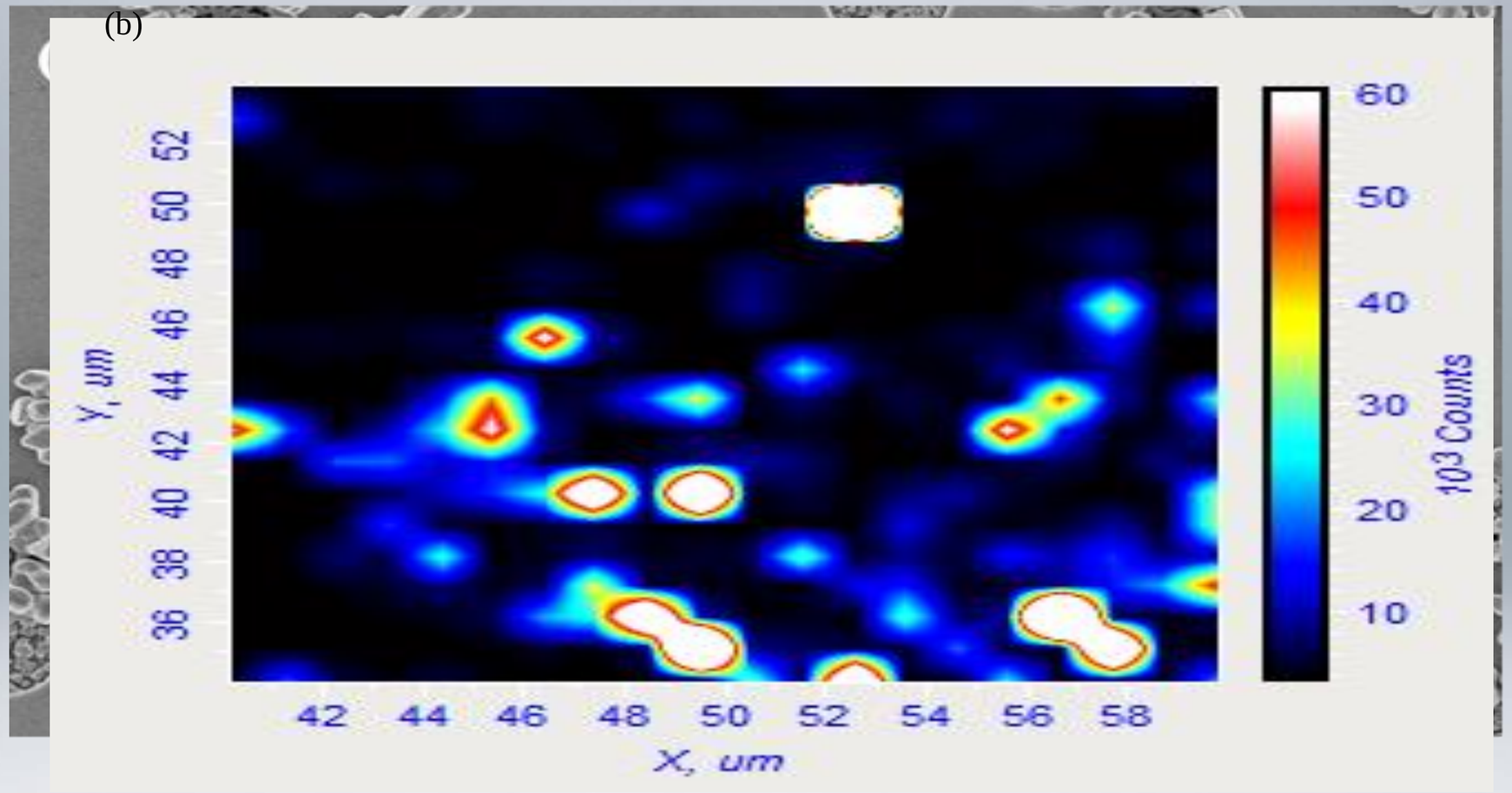
VAS et al., J. Cryst. Growth 300, 21-26 (2014)

Surface Enhanced Raman Spectroscopy



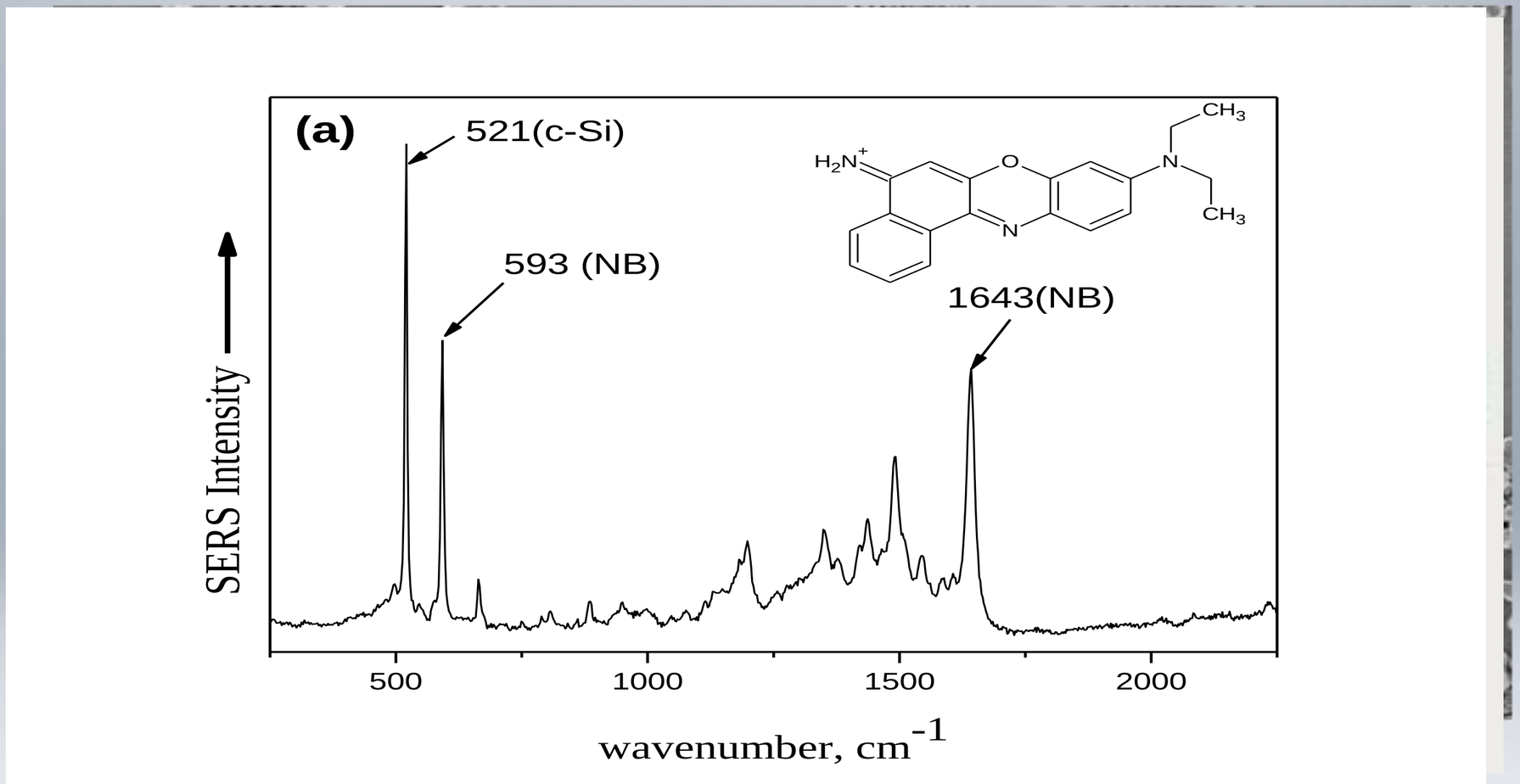
VAS et al., J. Cryst. Growth 300,21-26 (2014)

Surface Enhanced Raman Spectroscopy



VAS et al., J. Cryst. Growth 300,21-26 (2014)

Surface Enhanced Raman Spectroscopy



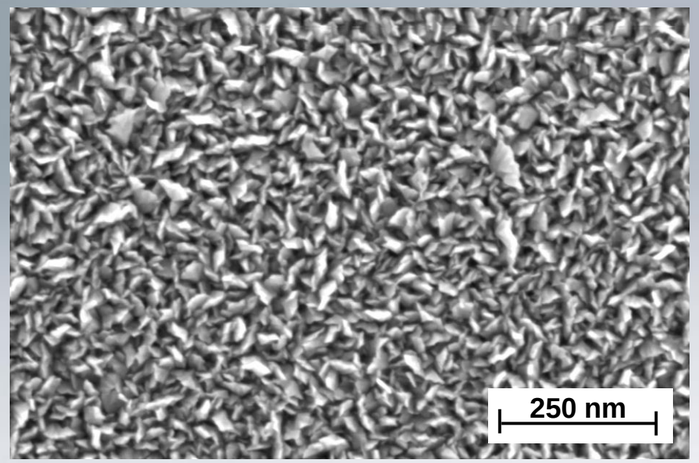
VAS et al., J. Cryst. Growth 300,21-26 (2014)

3. Nanostructured Silicon Surface for Sensing

In situ Disproportionation of Tin Oxide in porous Silicon Matrix

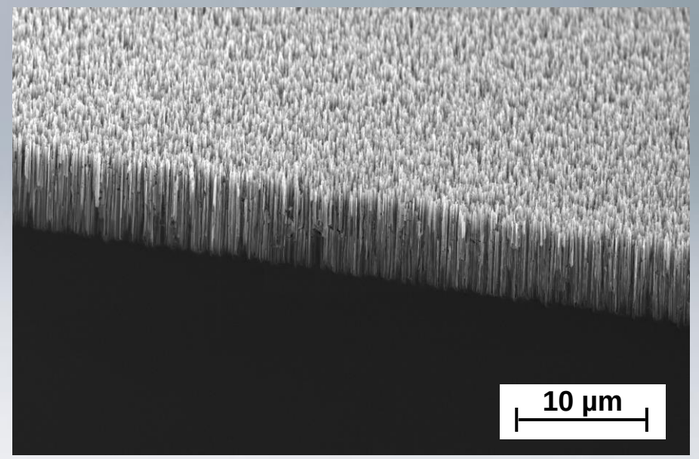
Functional Oxide

SnO_2



CVD

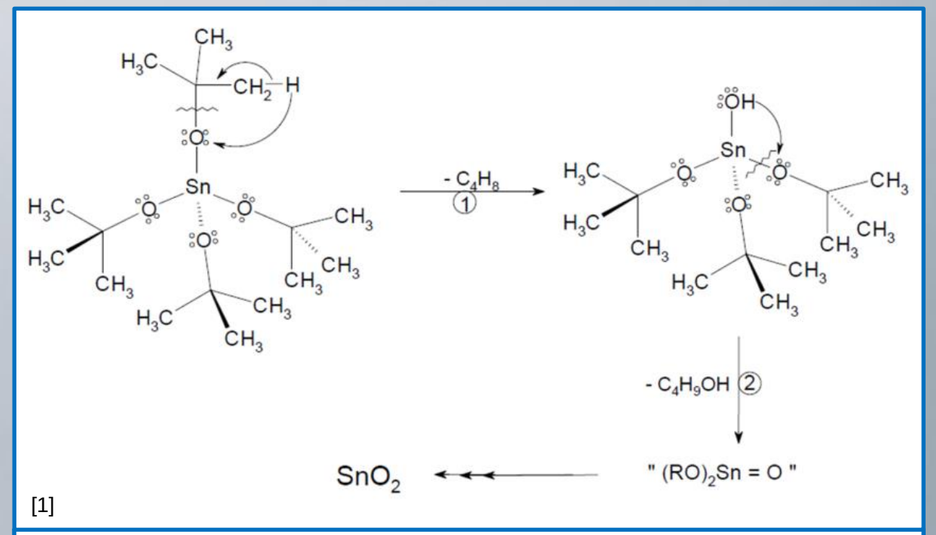
Silicon Nanostructures



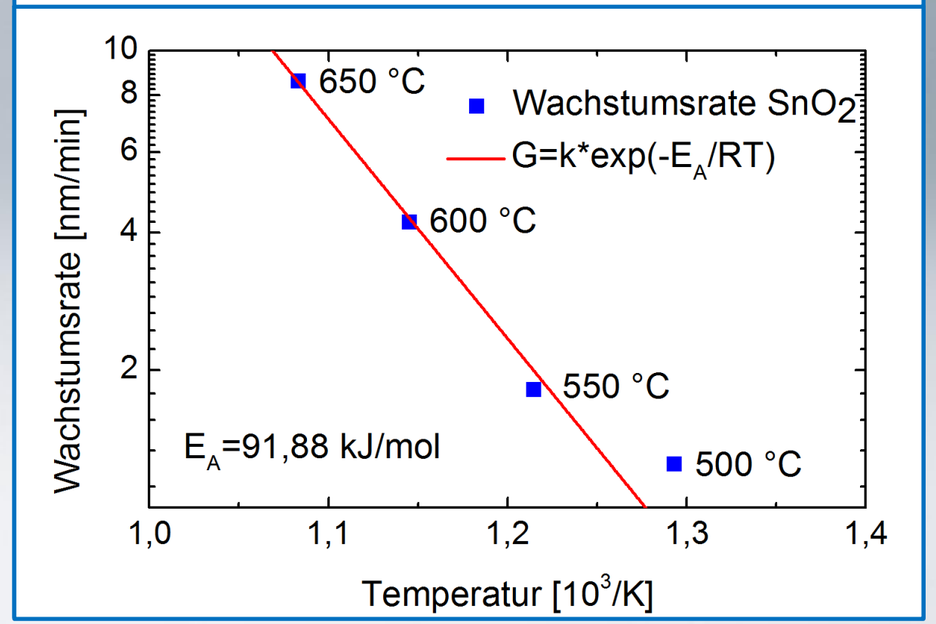
MAWCE

Growth Rate Determintaion

- $Sn(O^tBu)_4$ SSP for SnO_2 deposition
- β-Hydrid elimination → formation of intermediate Hydroxo-compundsg → decomposition of *tert.*-Butanol
- butene und BuOH as by-products
- exponential growth rate of layers in temperature region between 500 °C upto 650 °C



[1]

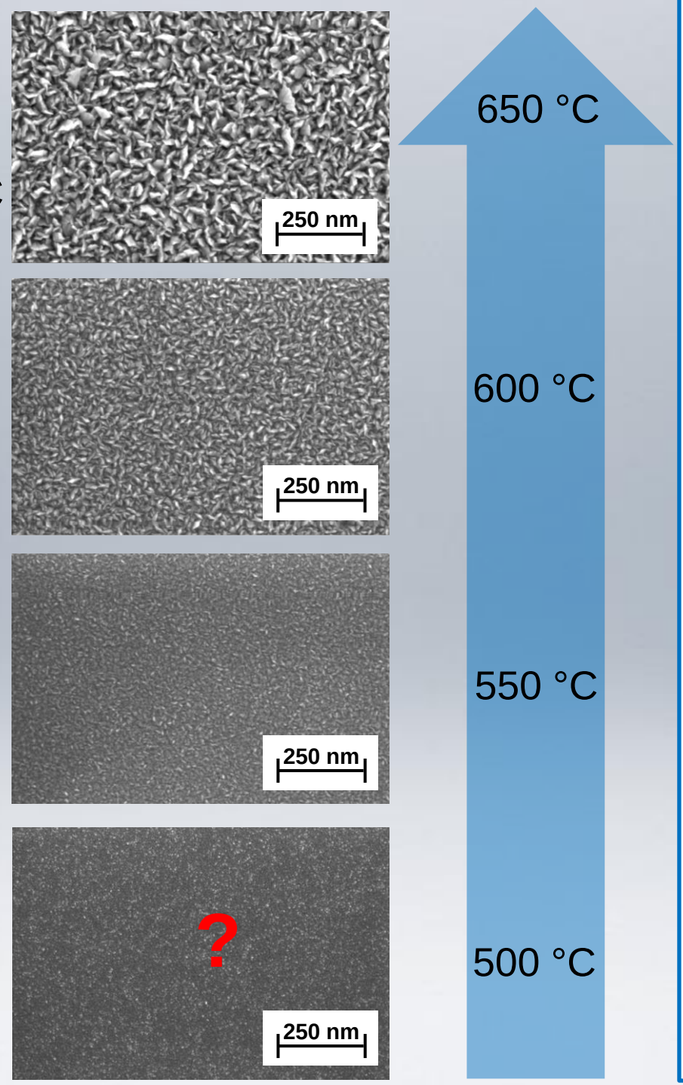


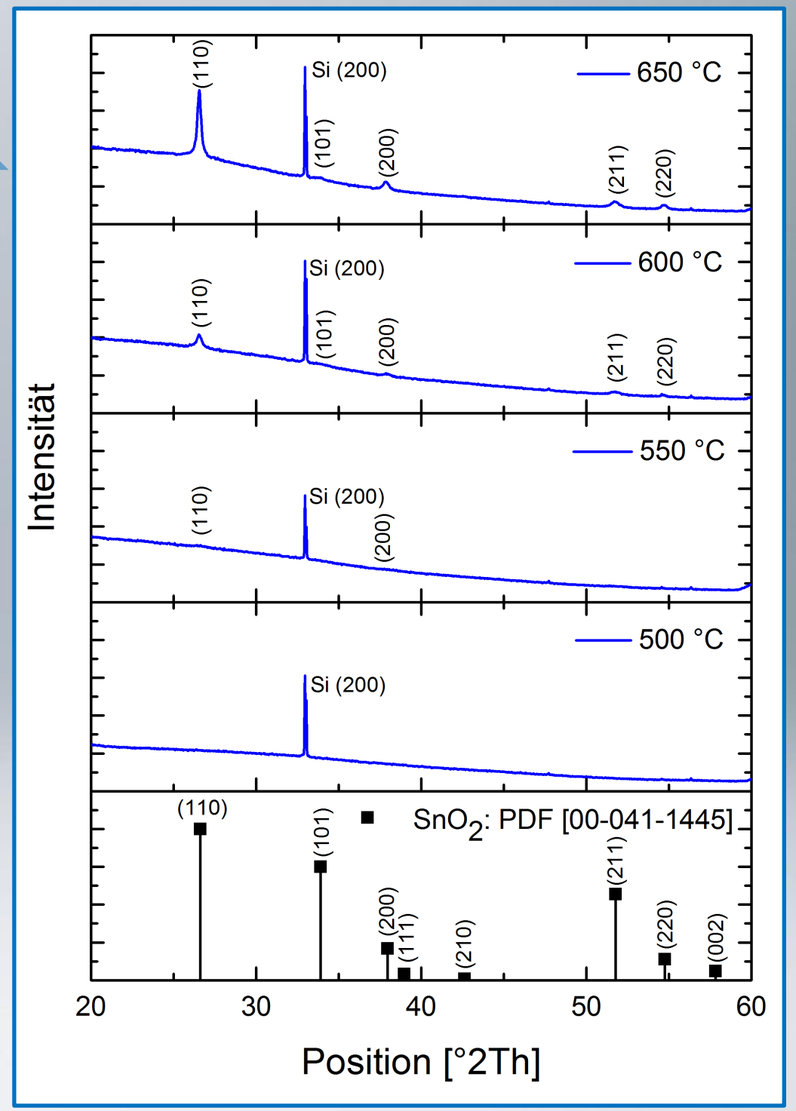
strongly controlled deposition of SnO_2 layers in region between 500 °C and 650 °C

[1] Sivakov, „Iron, Germanium and Tin *tert*-Butoxides in the CVD Process: Thin Film Deposition and Characterization“, 2004

Growth Rate Determintaion

- crystalline SnO_2 layers formation 550-650°C
- single pure rutile phase
- dominated growth direction [110]





Mitglied der Leibniz-Gemeinschaft

Formation of Silicon Nanostructures

Ag-Deponierung

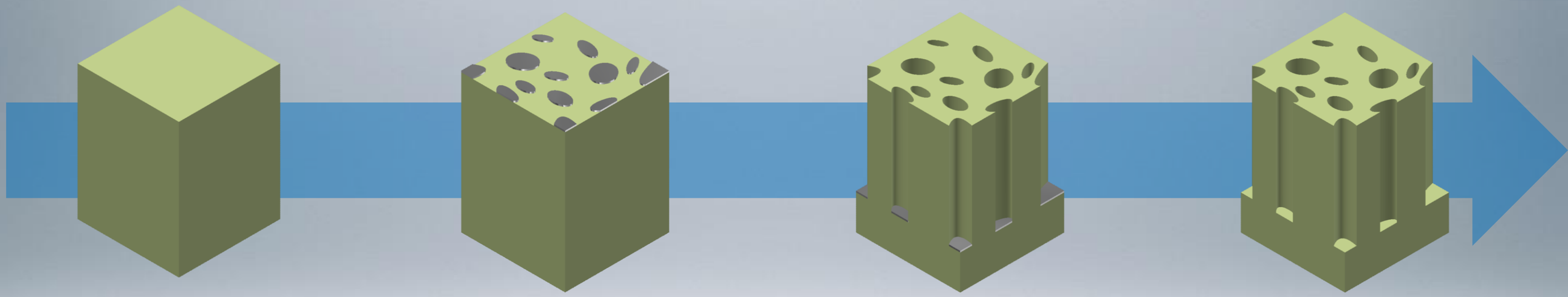
0,01 M $AgNO_3$+5 M HF (1:1)

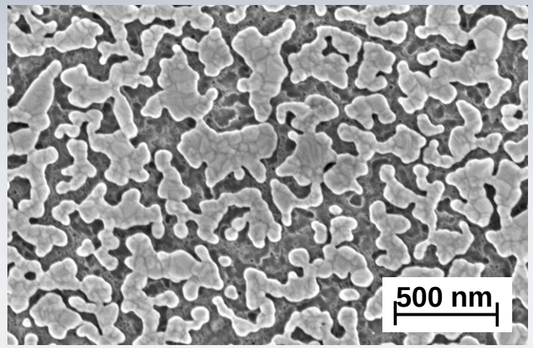
Ätzen

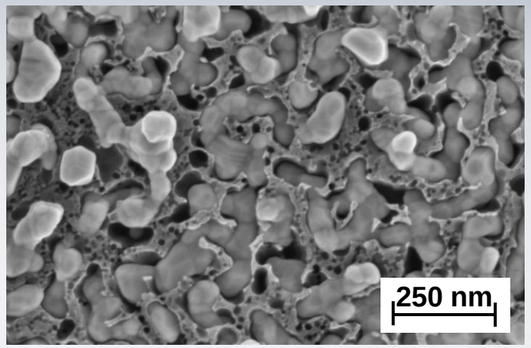
5 M HF+30% H_2O_2 (10:1)

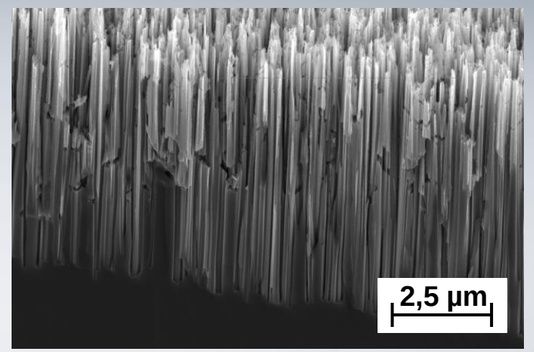
Ag entfernen

65 % HNO_3









$$Ag^+ + e^- \rightarrow Ag$$

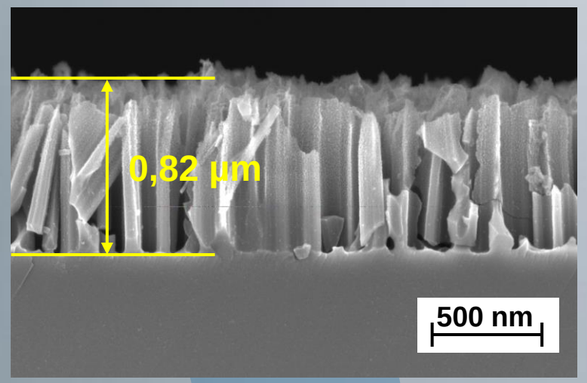
$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$$

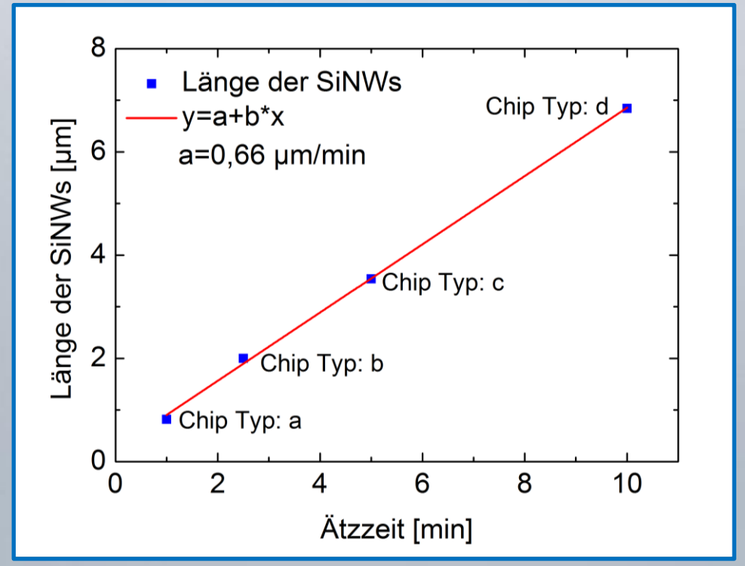
$$Si + 6HF + 4h^+ \rightarrow H_2SiF_6 + 2H^+ + H_2$$

Mitglied der Leibniz-Gemeinschaft

Etching Rate Determination

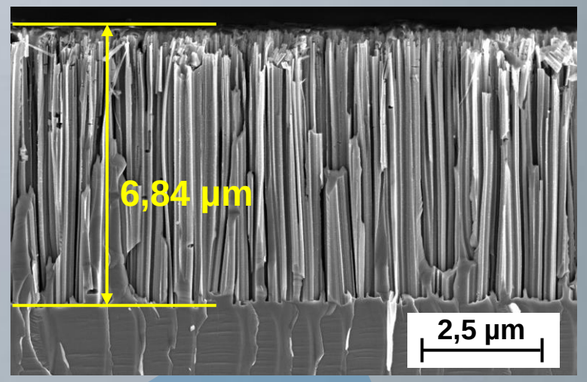
1 min



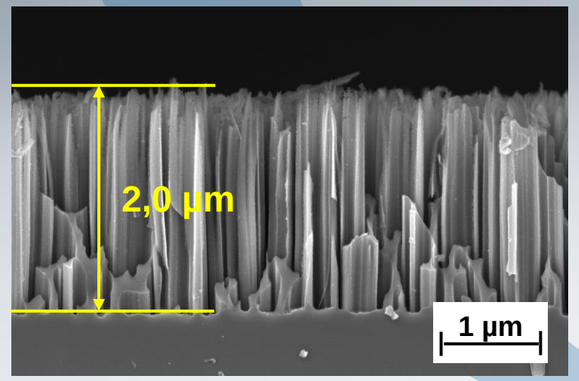


linear NWs length dependence on etching time

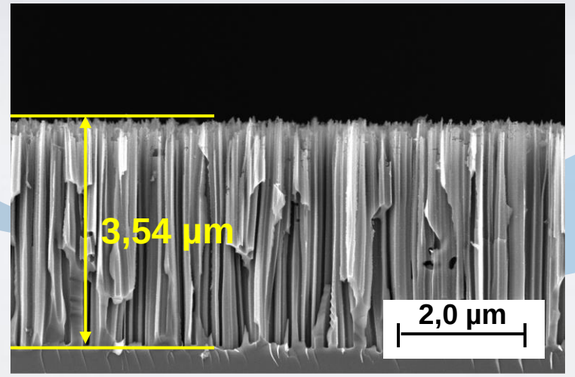
10 min



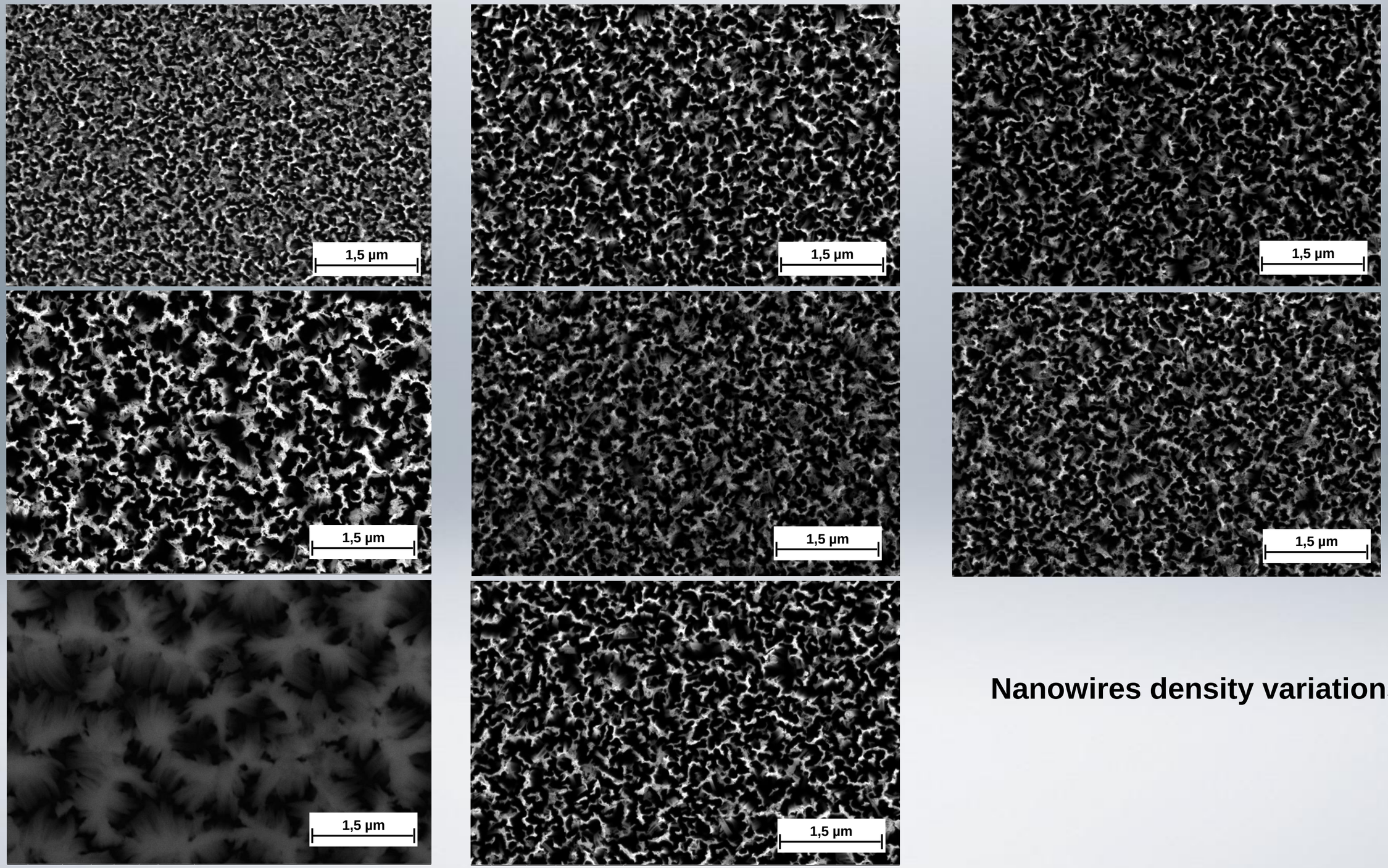
2,5 min



5 min



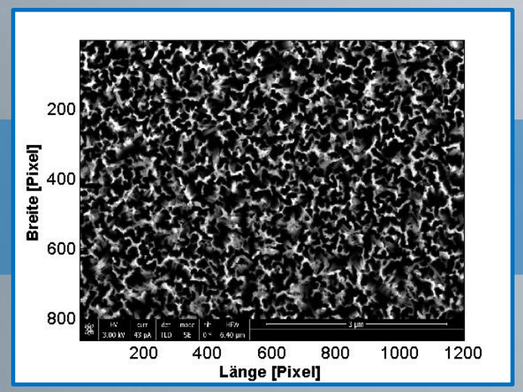
Mitglied der Leibniz-Gemeinschaft



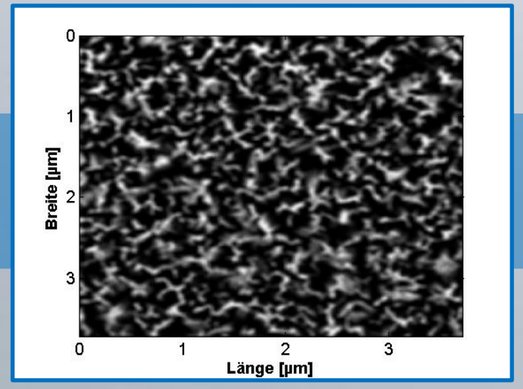
Nanowires density variations

Lateral Frequency Determination

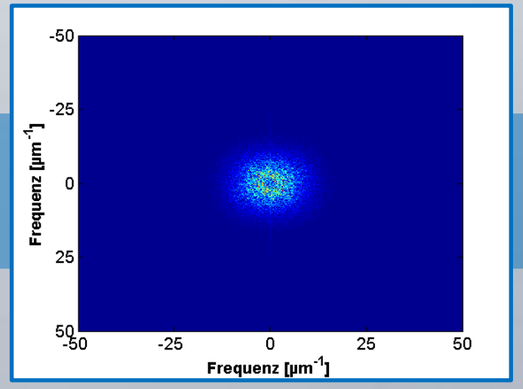
Original



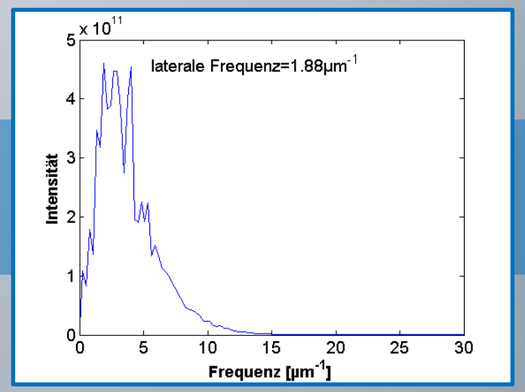
Cut



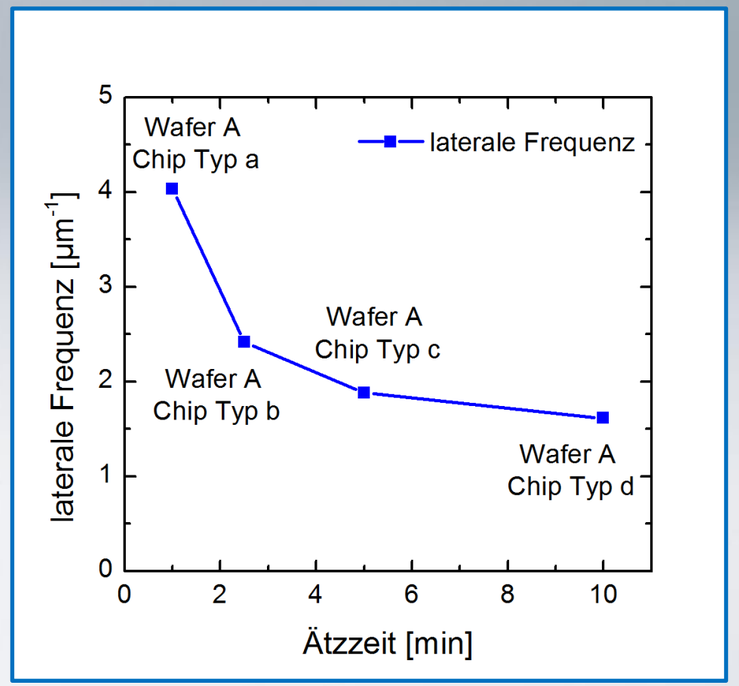
2D-FFT



Spectrum



- **Part of Image filtering**
- **Image transformation to the frequency → 2D-FFT**
- **Image as a diffusive ring**
- **Average of 2D-FFT → spectrum**

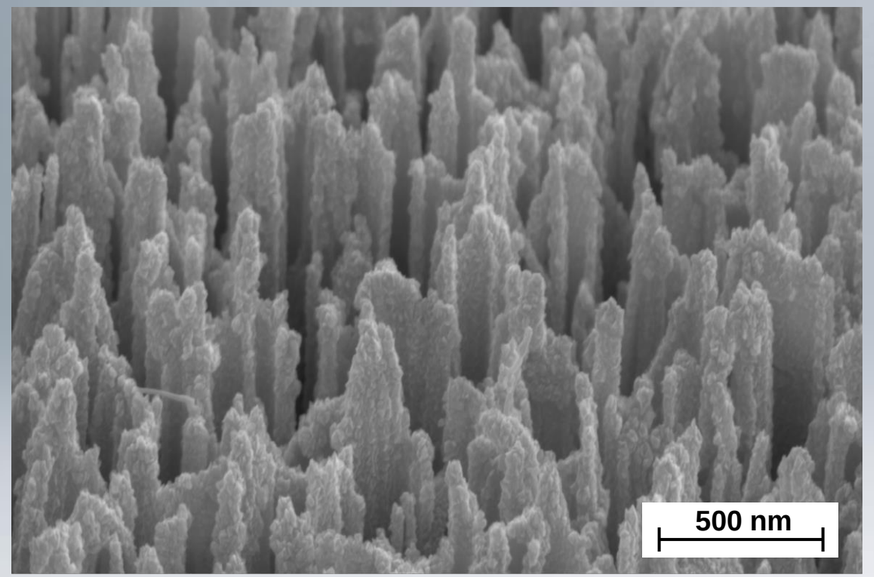


Decrease of lateral frequency with the etching time

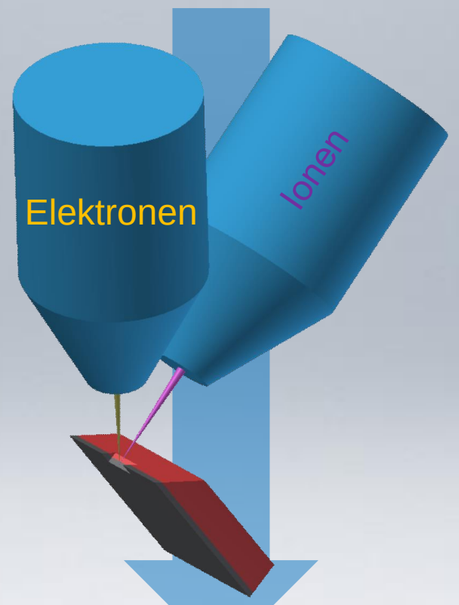
Mitglied der Leibniz-Gemeinschaft

Nanowires Cover with SnO_2

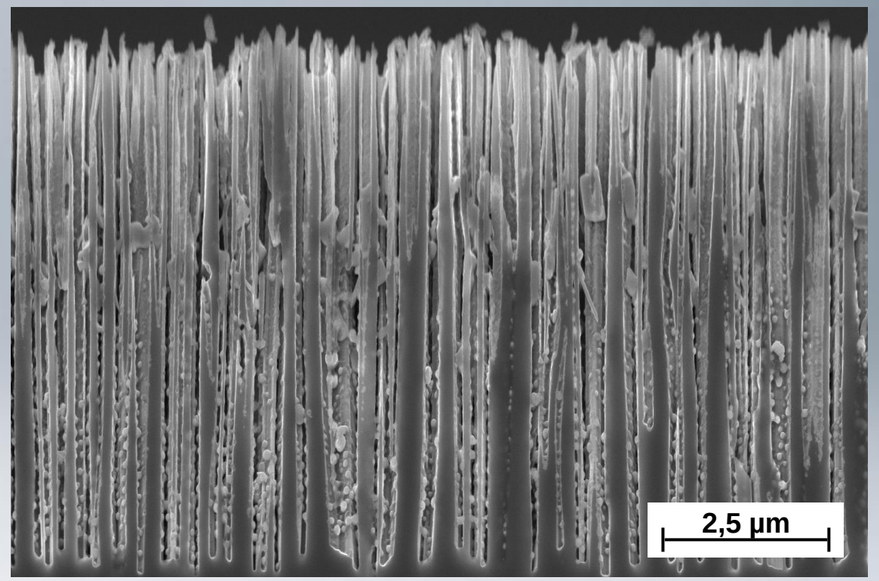
FIB



- SnO_2 layer at 600 °C on SiNWs



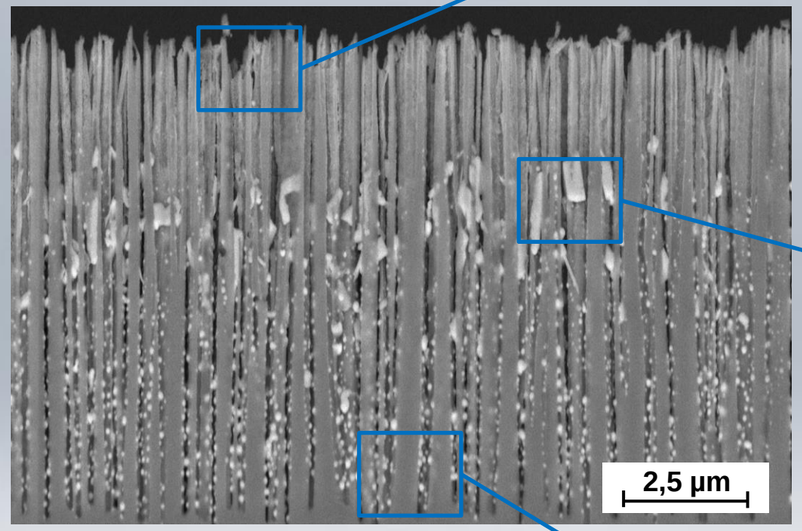
- prepared cross section

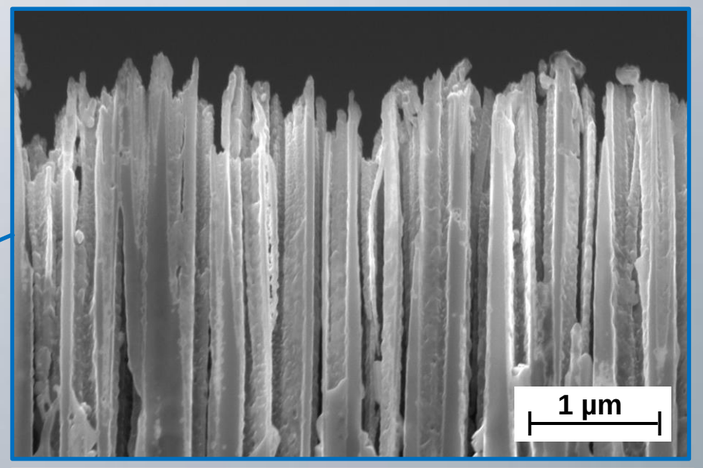


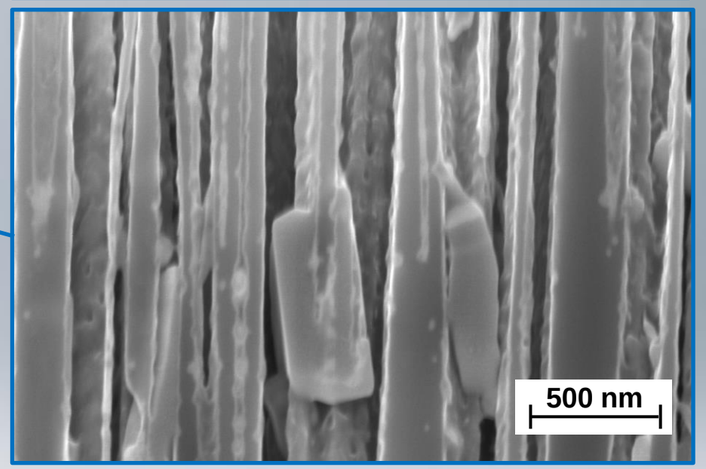
Studies of Cross-Section

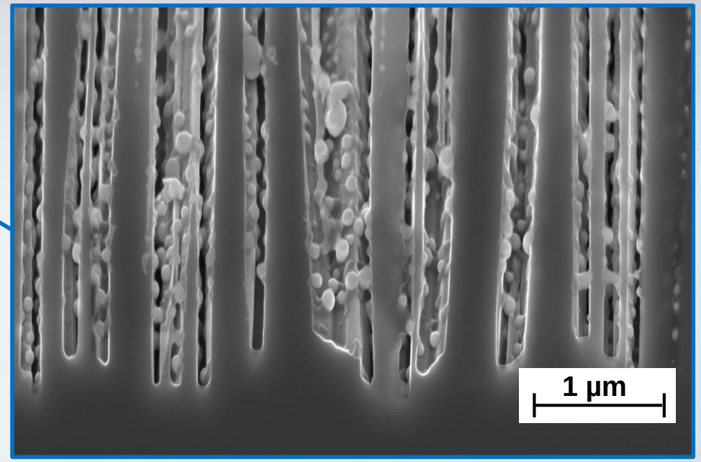
Three region was indentified from SEM studies:

- First region smooth
- Second region with big crystallites
- Third region with round NPs
- Material contract shows presence of different elements









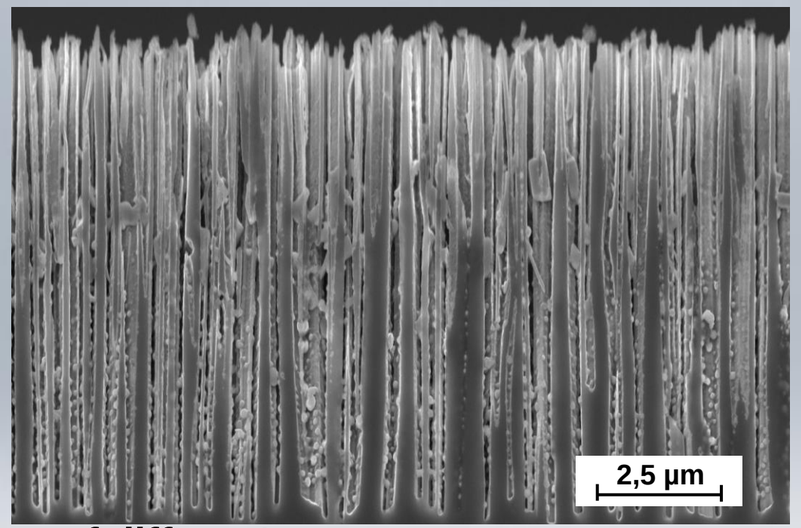
iphtjena

Mitglied der Leibniz-Gemeinschaft

Studies of Cross-Section

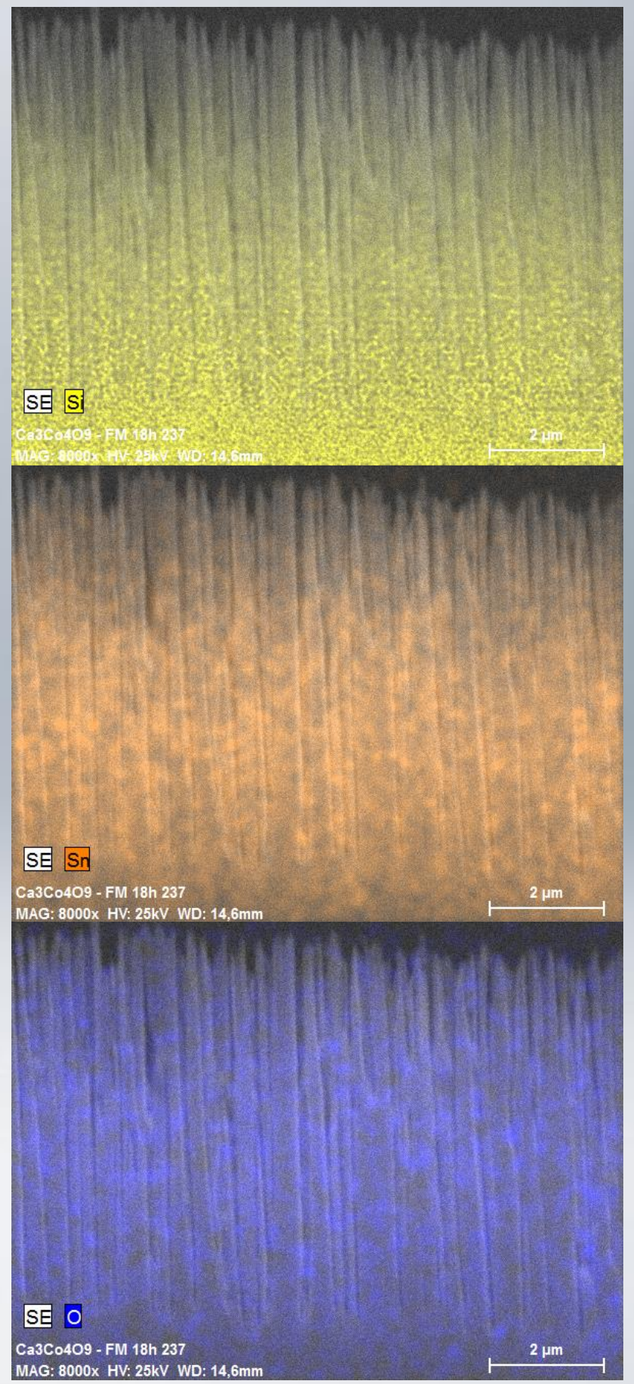
Three region was indentified from SEM studies:

- **First region smooth**
- **Second region with big crystallites**
- **Third region with round NPs**



- **Material contract shows presence of different elements**

- **Tin, Silicon and Oxygen were detected**
- **Strong Sn–signal in the second and third region**



Silicon

Tin

Oxygen

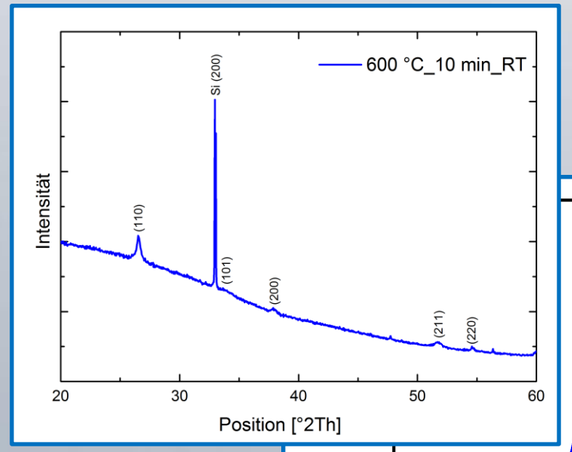
Mitglied der Leibniz-Gemeinschaft

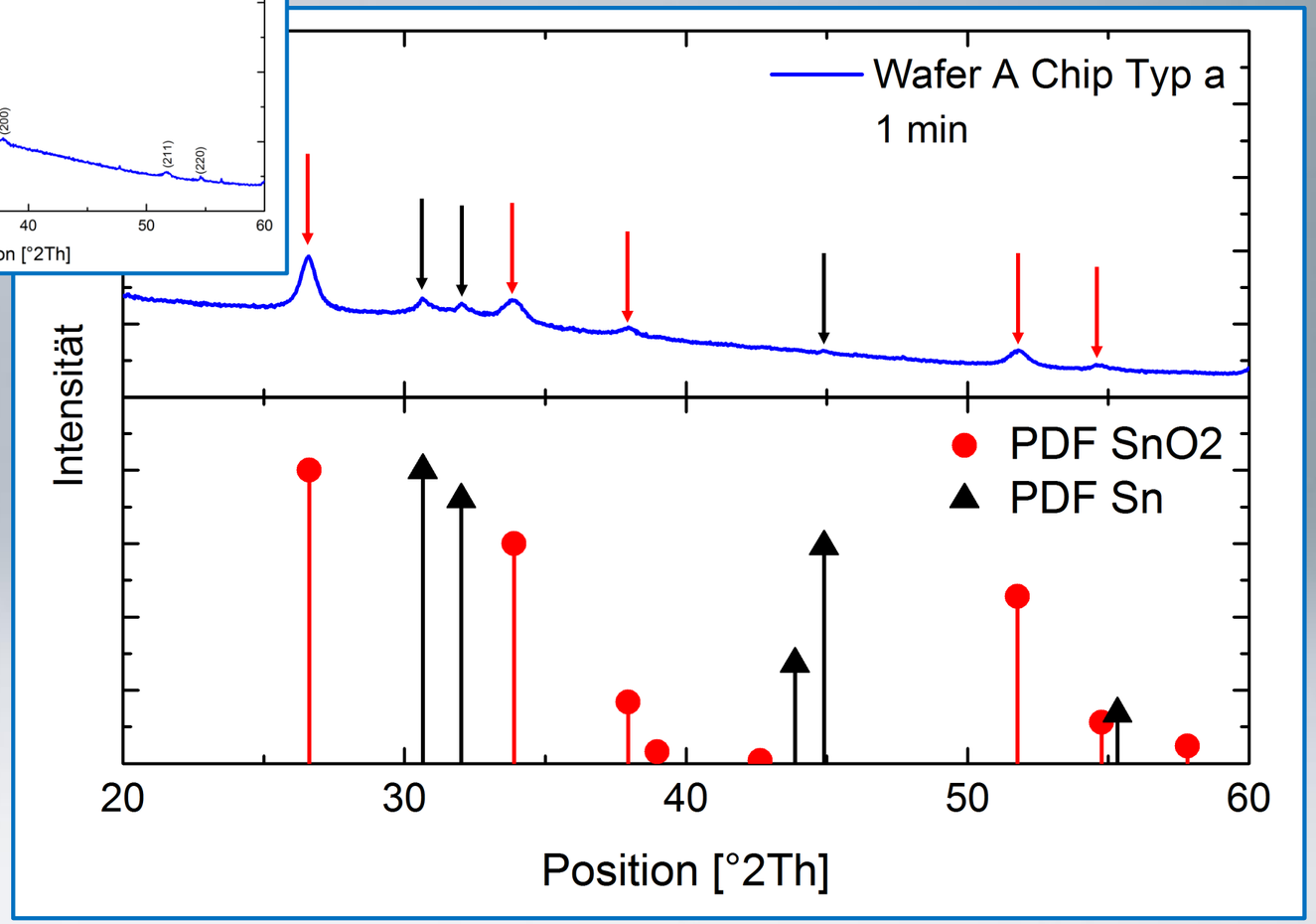
XRD-Studies

- **XRD pattern to 1min etched SiNWs**
- **similar to planar SnO_2 Reflexe**
- **additional reflexes are presented**
- **additional reflexes belong to metallic Sn**

transformation from Sn(IV) to Sn(0)

planar





Mitglied der Leibniz-Gemeinschaft

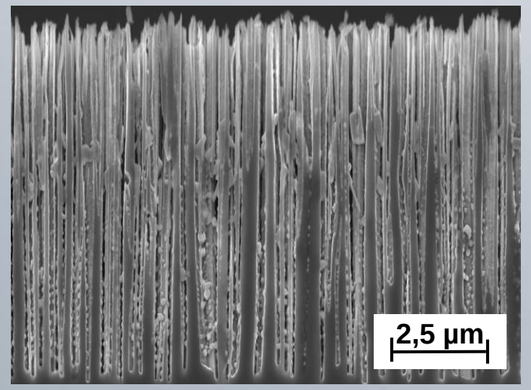
XRD Studies

- etching time influence
- SnO_2 und Sn Reflexe
- additional Reflexe presented
- SnO und Sn_2O_3 Reflexe

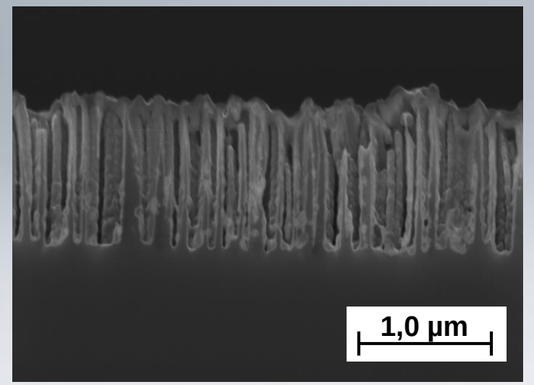
composition strongly depends on SiNWs profile

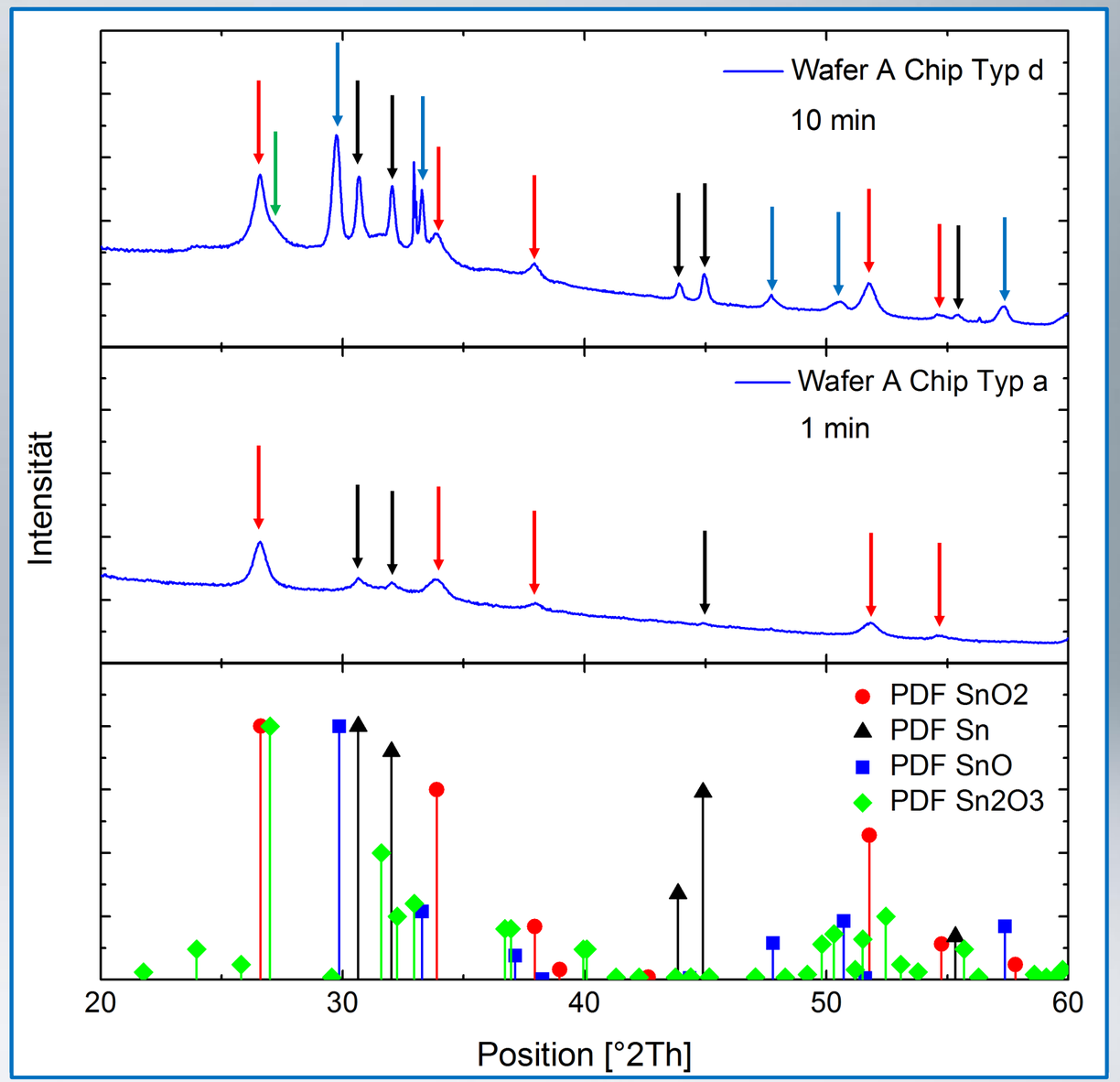
transformation from Sn(IV) to Sn(0), Sn(II) und Sn(II/IV)

10 min



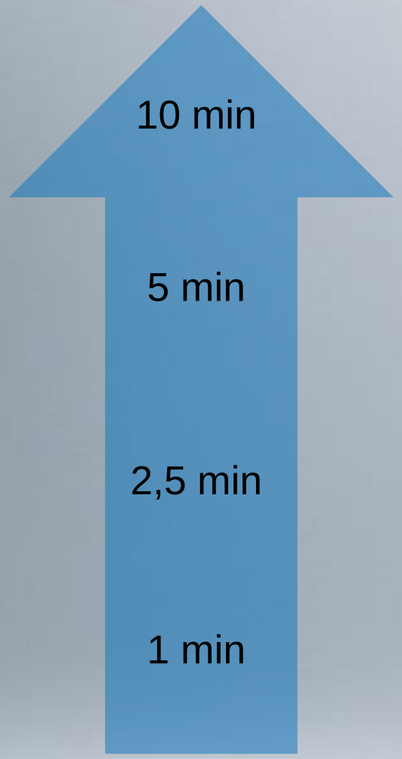
1 min

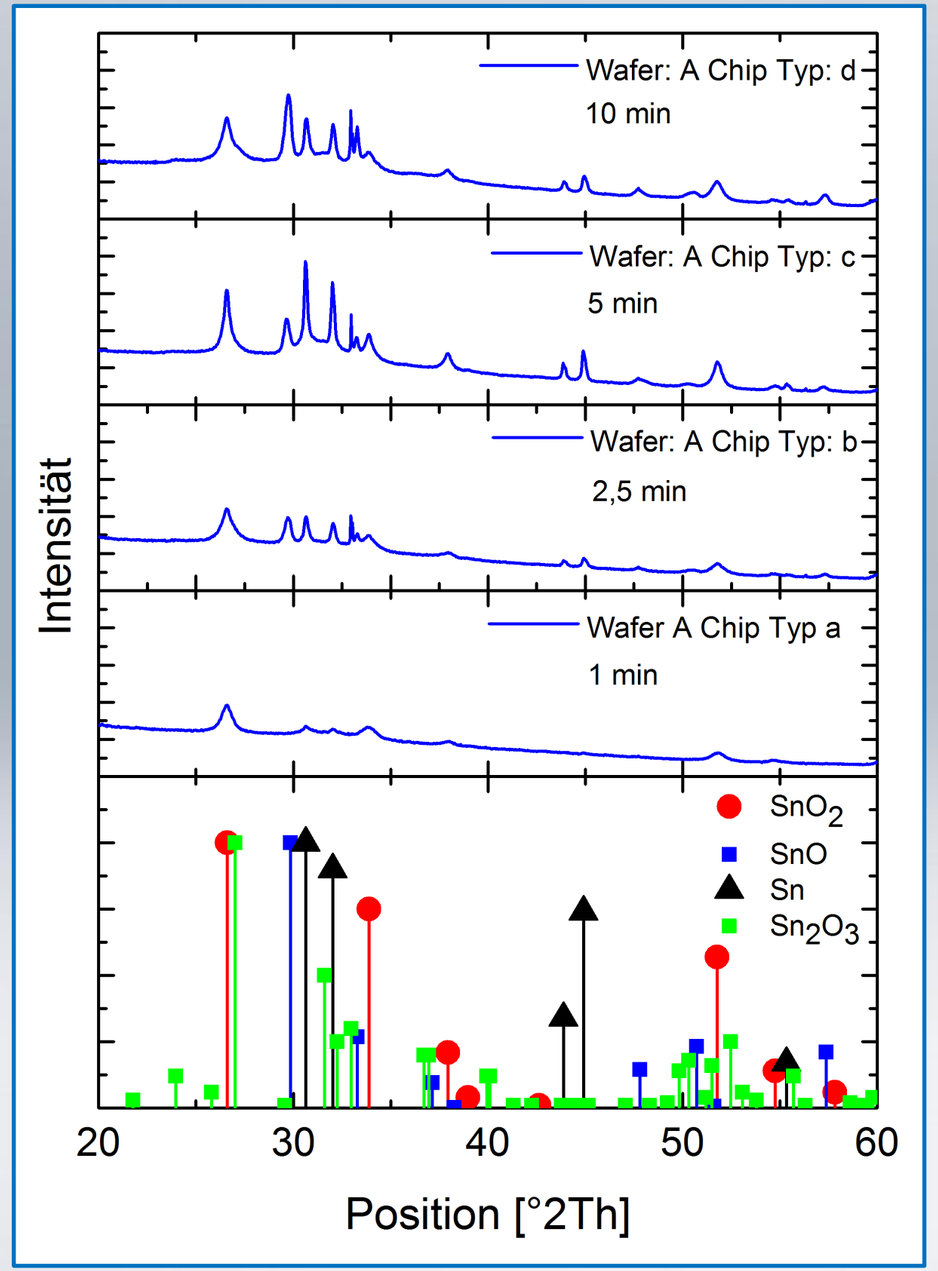




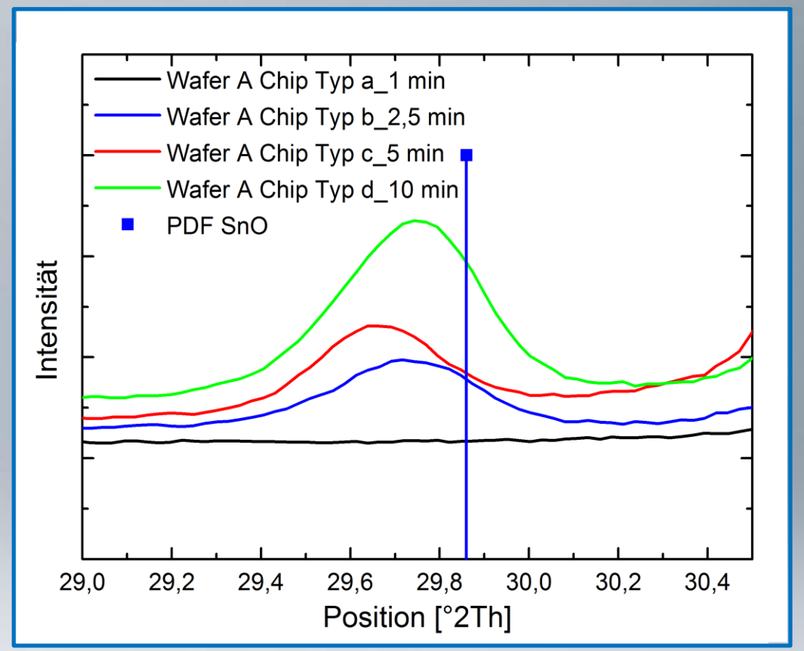
Mitglied der Leibniz-Gemeinschaft

XRD Studies





Shift of SnO Reflexes to smaller θ values



$$n\lambda = 2d_{hkl}\sin(\theta)$$

SnO → **SnO_{1+x}**

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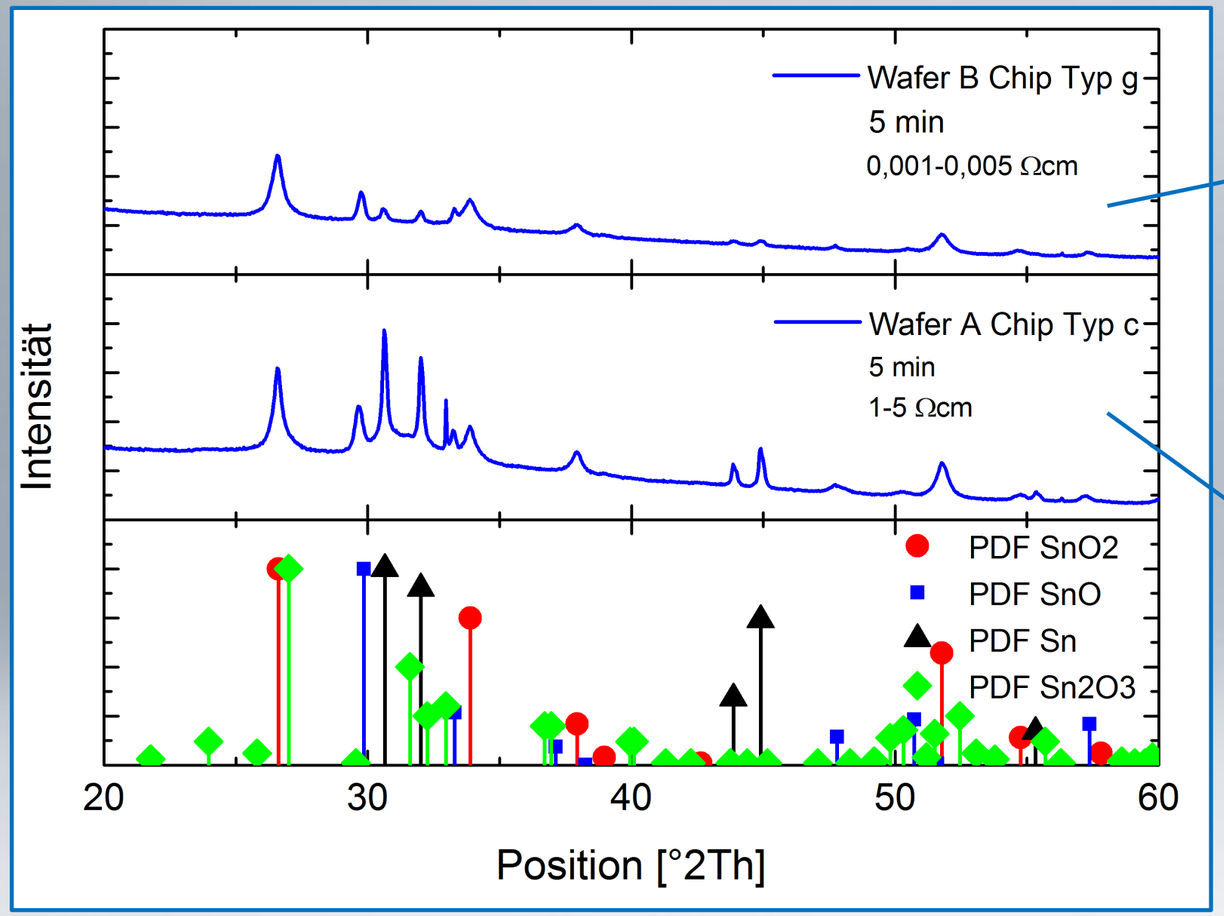
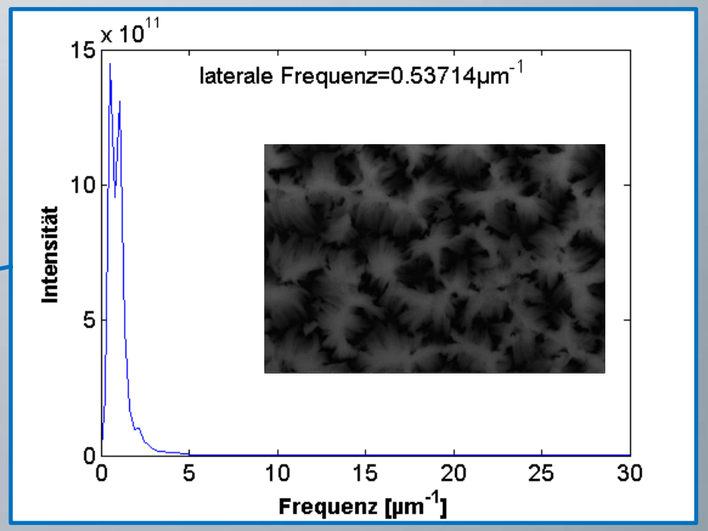
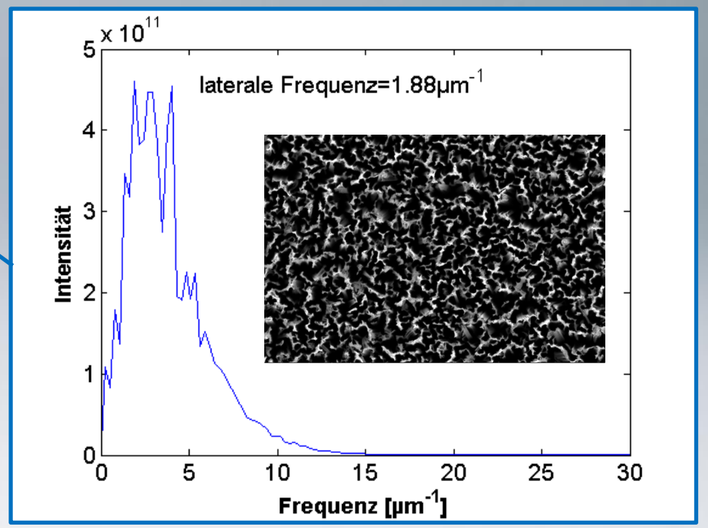
XRD Studies





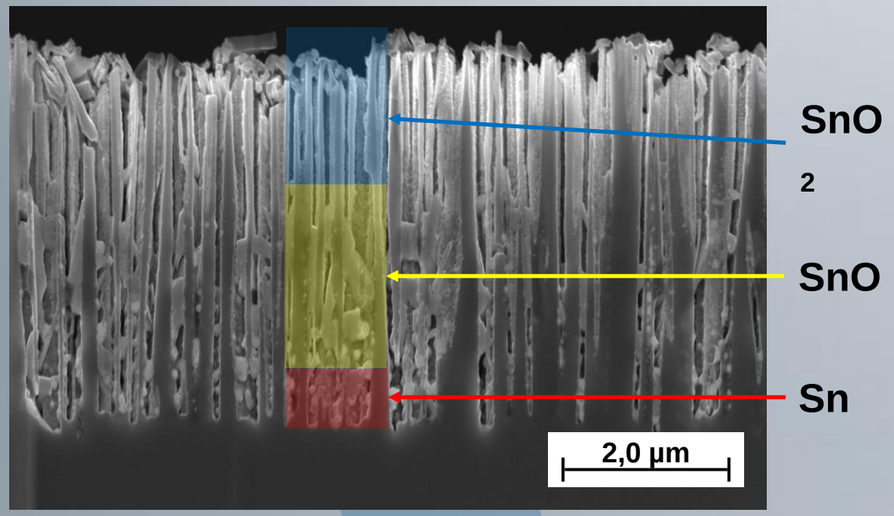


- same SiNWs formation conditions
- different wafer doping level

relevant morphology differences

Mitglied der Leibniz-Gemeinschaft

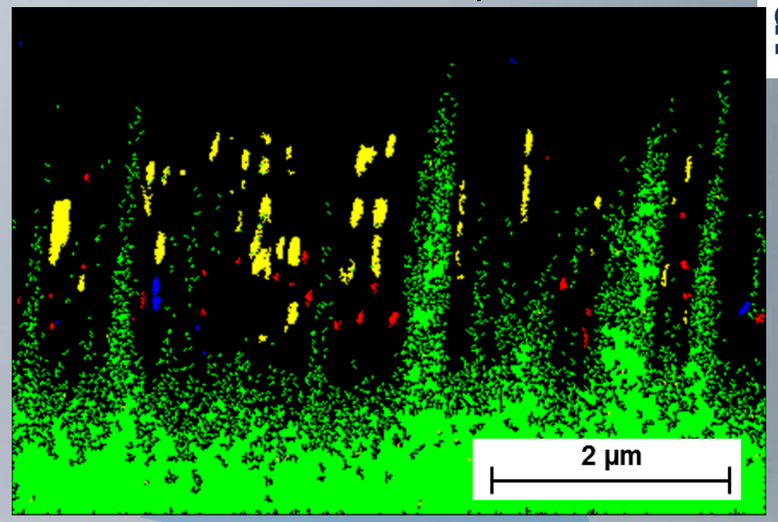
EBSD Studies



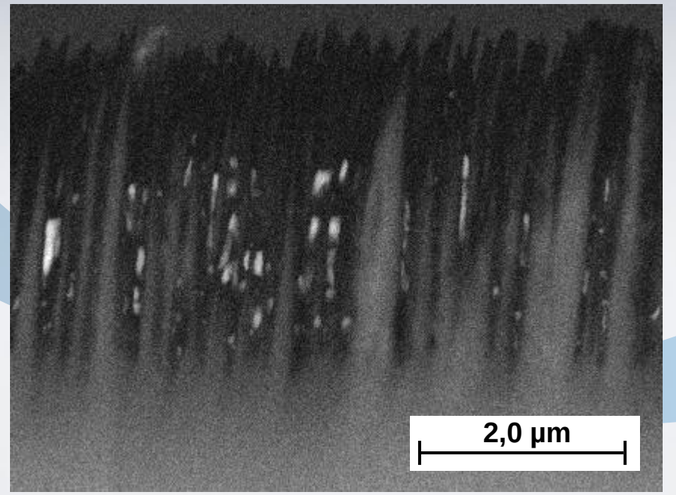
- bigger crytsallites correspond to SnO
- droplets to metallic Sn
- thin film in upper region to SnO_2

Si
SnO
SnO_2
Sn

Phasenmap



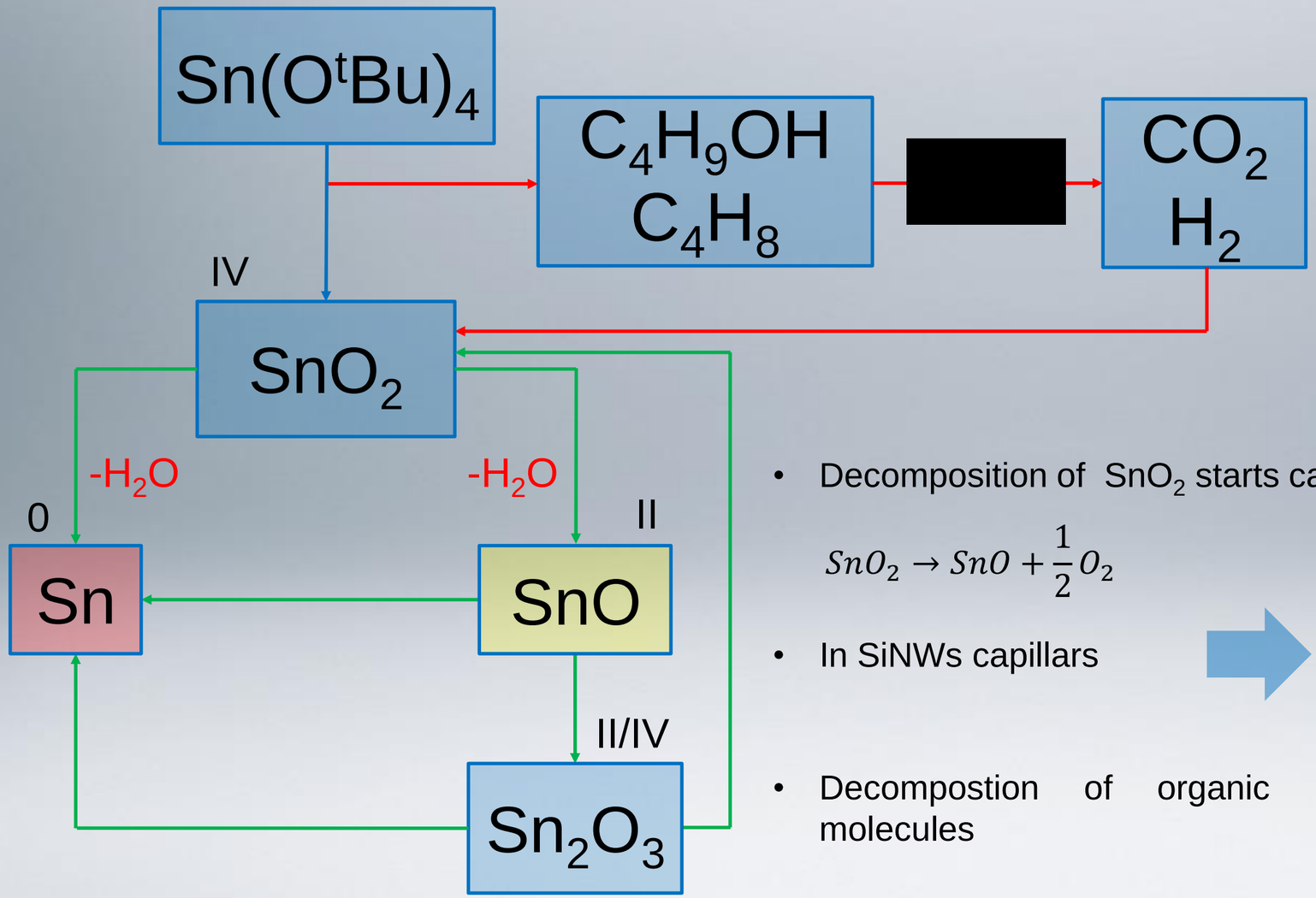
Qualitätsmap

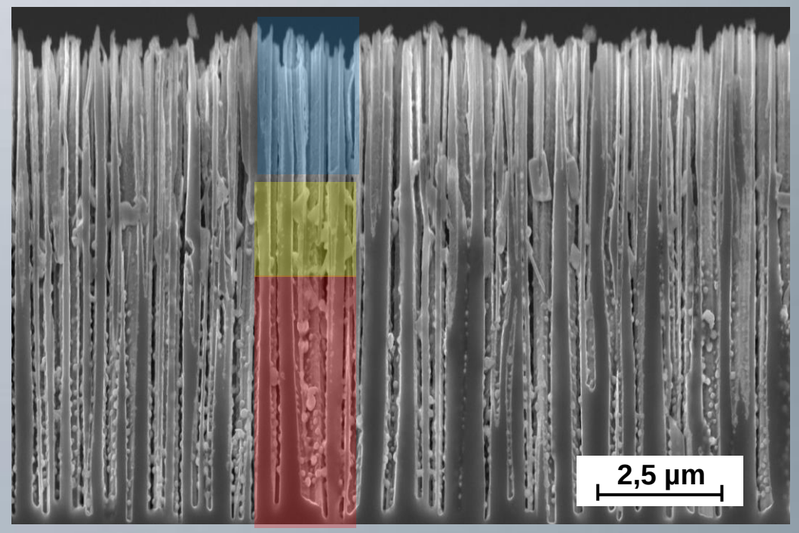


- EBSD qualitymap shows shaddow-effect
- upper part not detected

Mitglied der Leibniz-Gemeinschaft

Disproportionation mechanismus of SnO_2





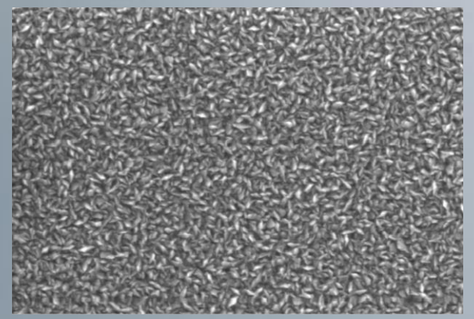
- Decomposition of SnO_2 starts ca. at 1500 °C

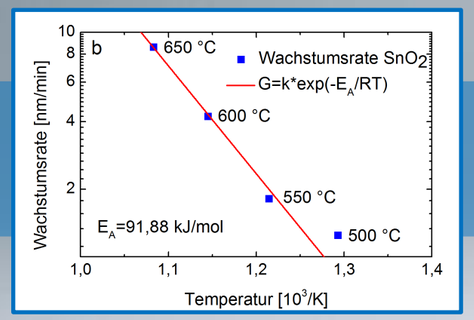
$$SnO_2 \rightarrow SnO + \frac{1}{2}O_2$$

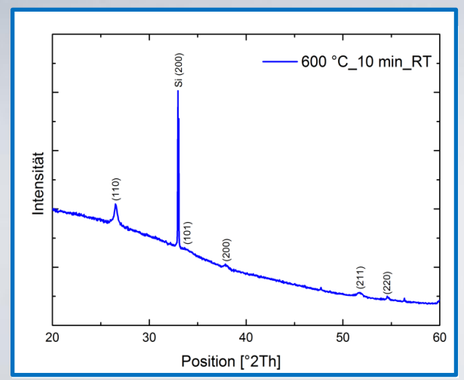
- In SiNWs capillars → „Supercritical Conditions “
- Decompostion of organic molecules → Reduction of SnO_2

Conclusions

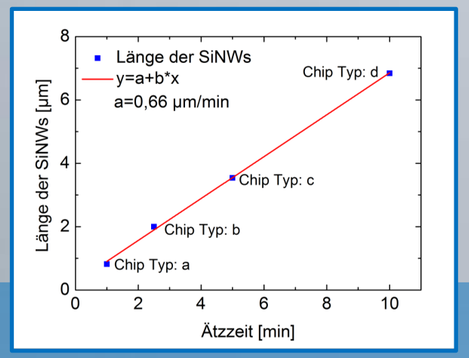
I

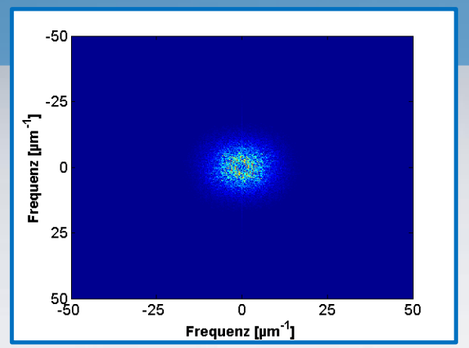






II





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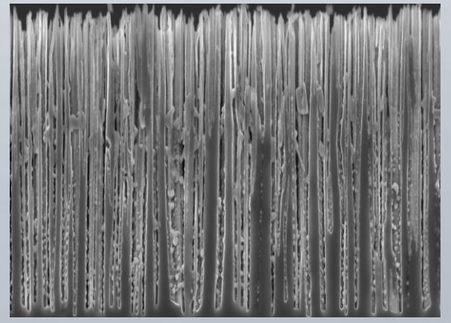
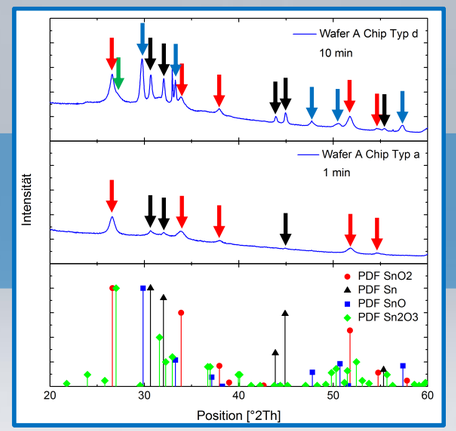
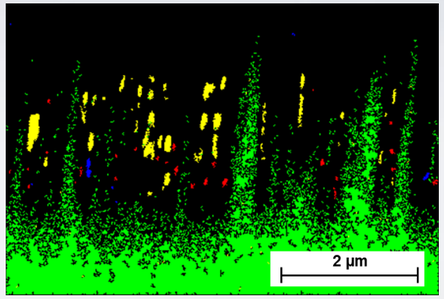
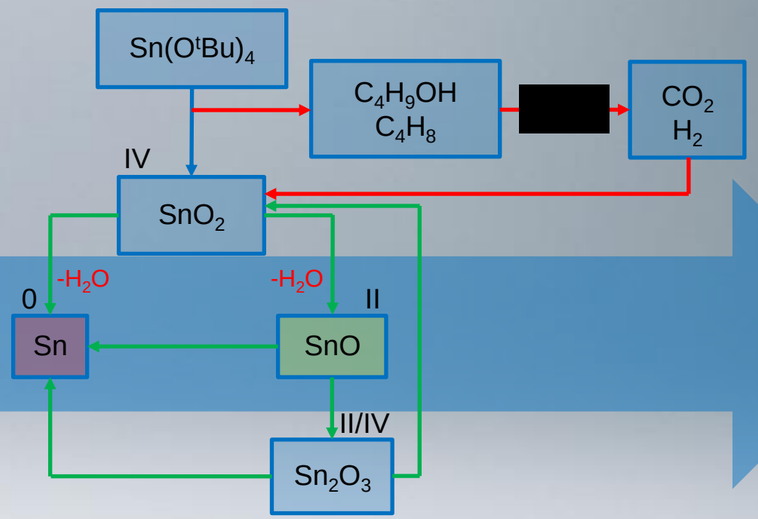






IV



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