Opto-Electronic Devices and Sensors Based on Nanostructured Silicon

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Outline

- Introduction
- Hierarchical structures by chemical etching
- Examples of applications of silicon nanostructures
- SERS on porous silicon with metalic nanoparticles
- Application to food analysis
- Silicon/organic hybrid IR detectors
- Conclusion

CENTER OF EXCELLENCE FOR ADVANCED MATERIALS AND SENSORS, CEMS

Mile Ivanda — NEW FUNCTIONAL MATERIALS

Marko Kralj — SCIENCE ON GRAPHENE AND RELATED 2D STRUCTURES

Mario Stipčević — PHOTONICS AND QUANTUM OPTICS

Milko Jakšić — PHYSICS AND TECHNOLOGY OF ION BEAMS

P1. Silicon nanostructures for advanced applications (M. Ivanda)

P2. Sol-gel technology for new functional materials (M. Ristić)

P3. Nanostructural materials for energetic (N. Radić)

P1. Silicon nanostructures for advanced applications

T1. Nanostructural silicon for gas sensing

T2. Novel silicon based materials for photonics

T3. Development and application of new Raman scattering techniques

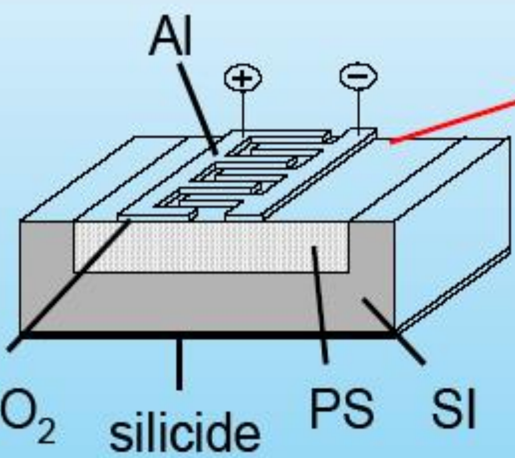
T4. Silicon hybrid light sensing devices

T1. Nanostructural silicon for gas sensing

Design similar for all types of sensors

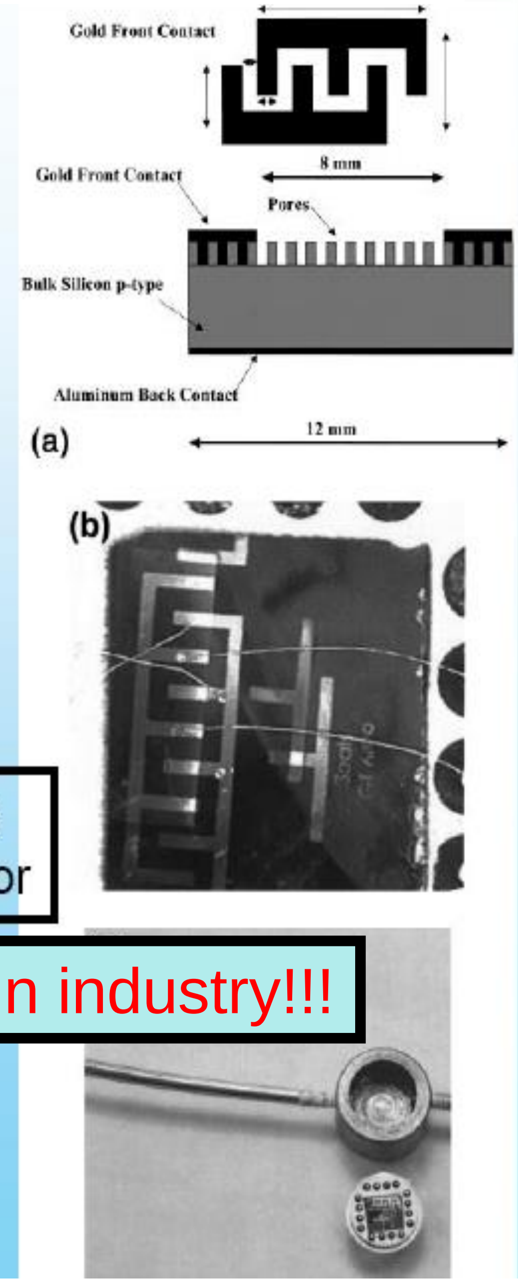
Differences in

- surface treatment
- electrode assembly
- measurement of conductivity/capacitance



special treatments for good ohmic contact

allows for high temperature treatments



gas sensor

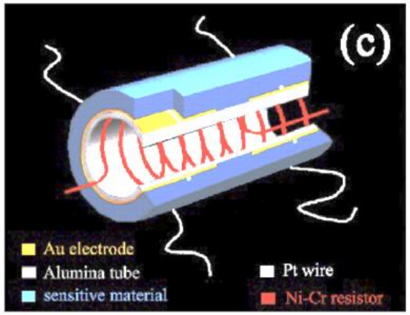
Interesting in industry!!!

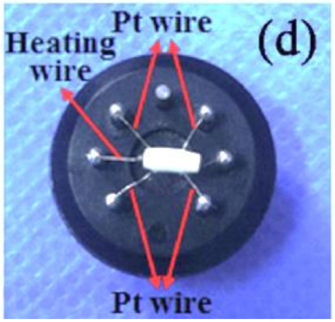
Seals et al.
J. Appl. Phys. 91, 2519 (2002)

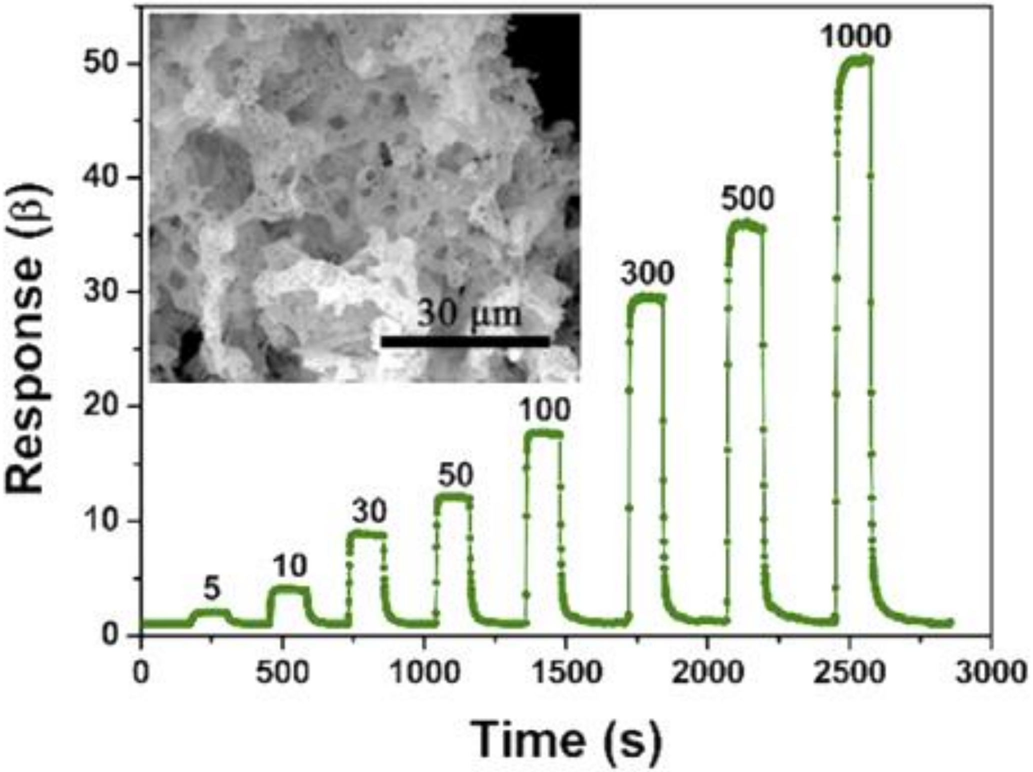
Hierarchically structures in sensing

- Hierarchically porous WO3 synthesized by combustion process.
- Hierarchically porous WO3 exhibits high gas response and excellent selectivity for acetone.
- The excellent sensing property was plausibly attributed to the porous morphology.

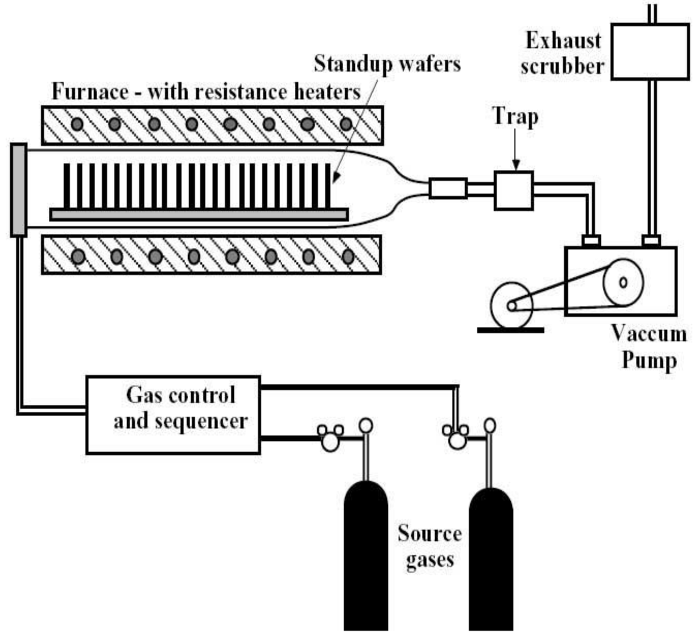
I. Djerdj et al., Materials Chemistry and Physics, 2016.

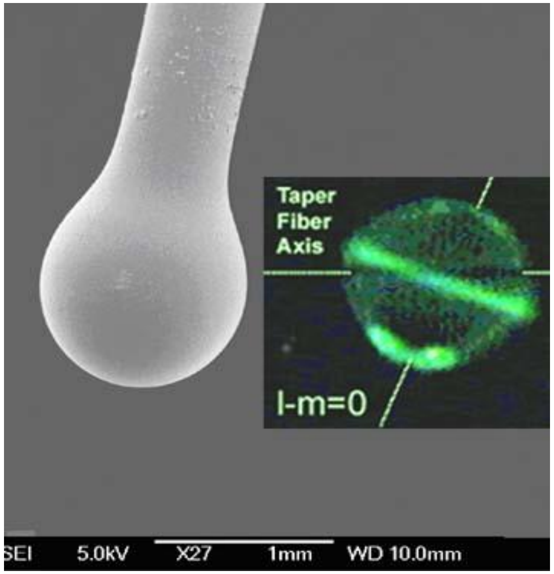




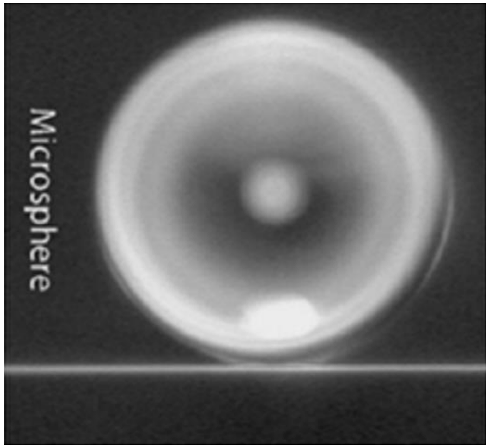


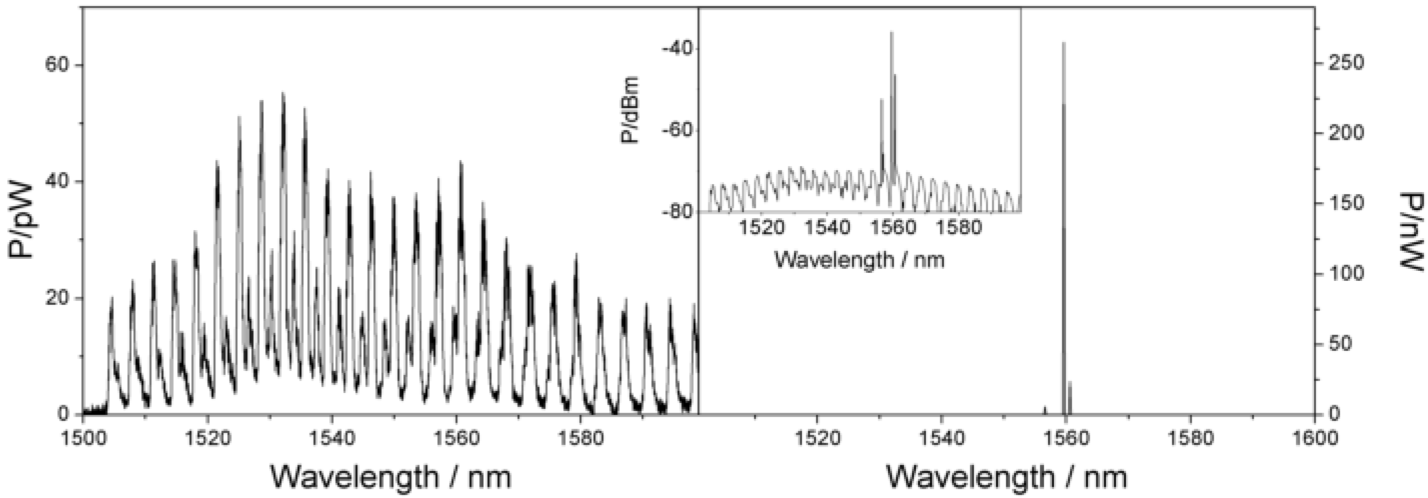
T2. Novel silicon based materials for photonics



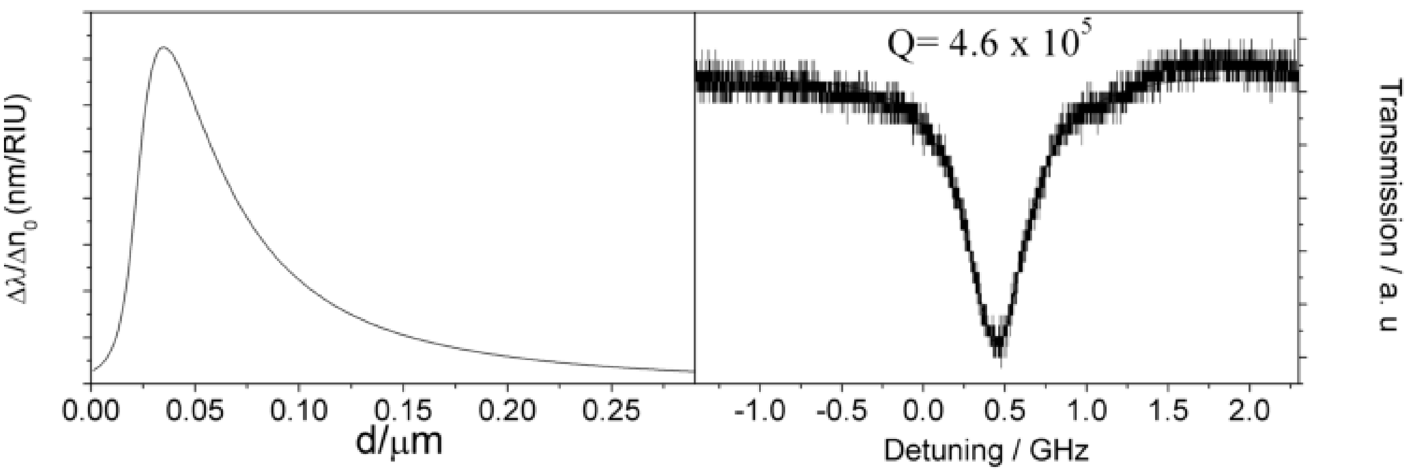


Silica microspheres are coated with silicon nanocrystals in silica doped with europium and erbium in order to investigate the stimulated Raman scattering as well as stimulated emission form the rear earth dopant.





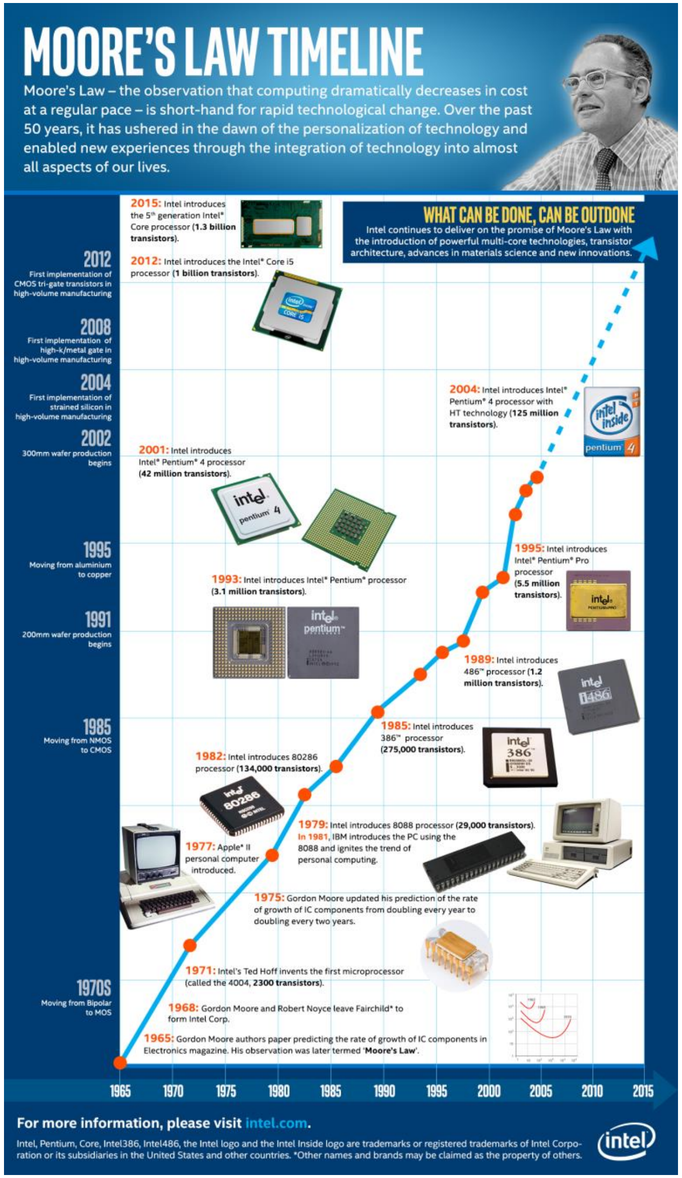
The luminescence and the lasing spectrum of an erbium doped microsphere. Lasing spectrum in log scale (inset).

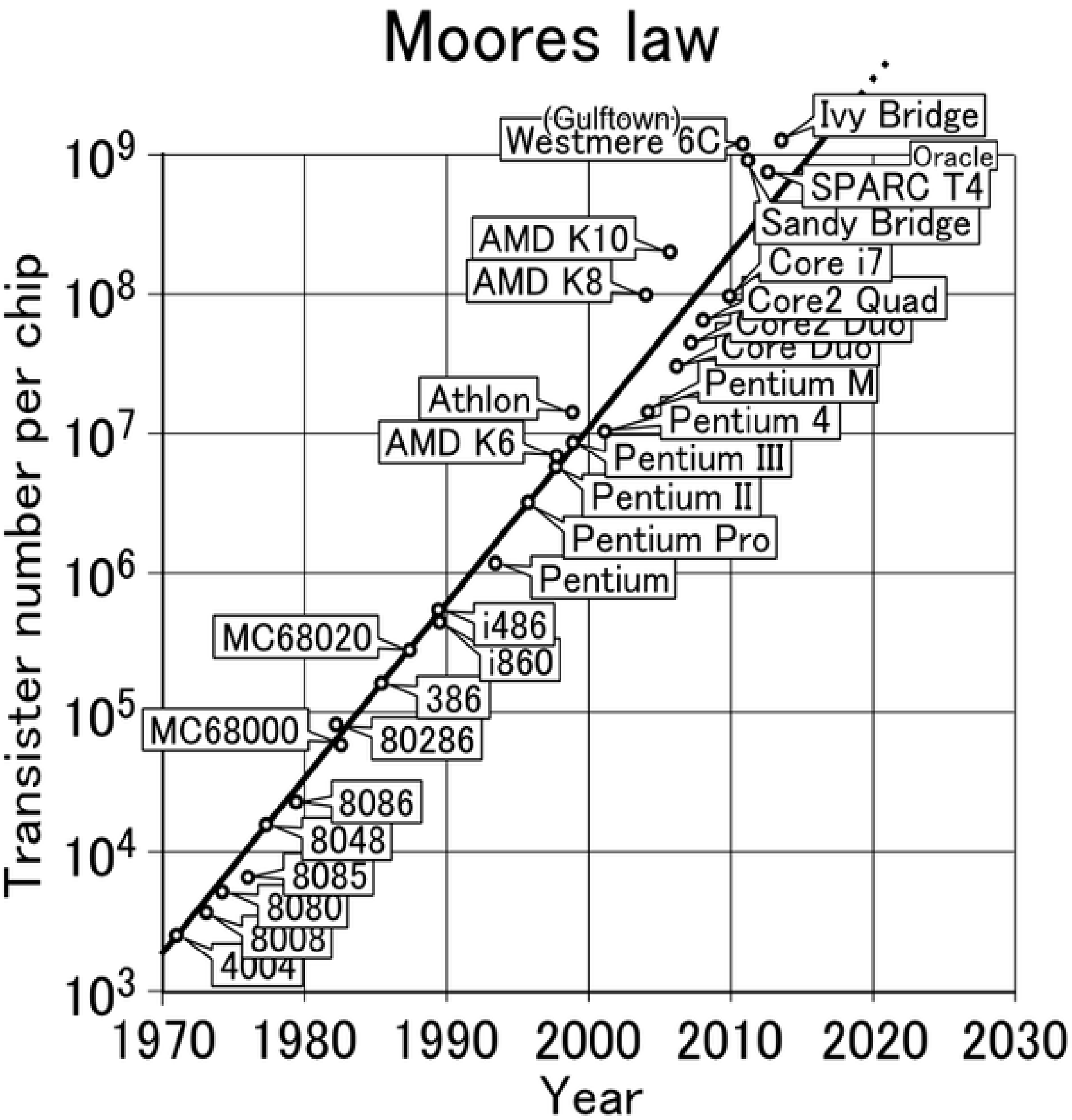


The sensing sensitivity vs. the coating thickness for an a:Si coated microsphere (left) and the measured Q factor for a LPCVD a:Si coated microresonator

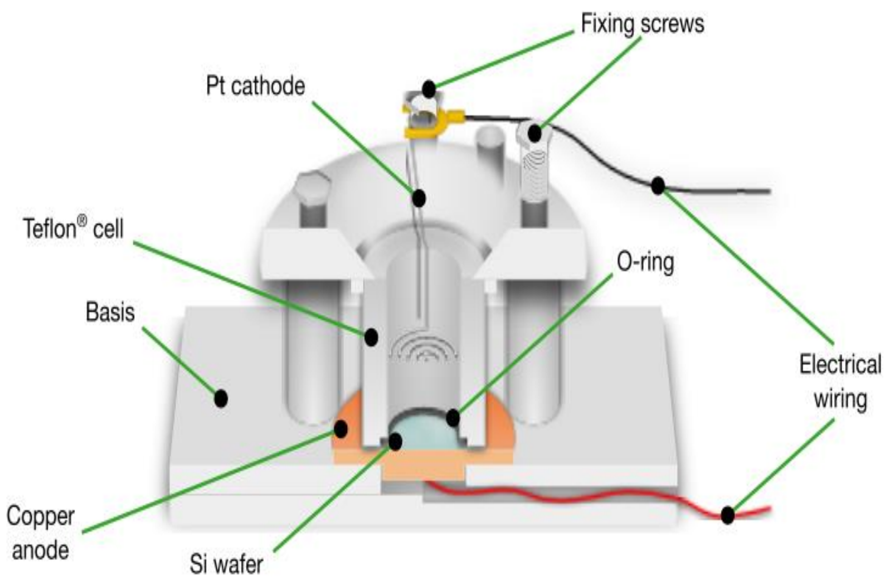
Davor Ristic, et al: *Whispering gallery mode profiles in a coated microsphere*. The European Physical Journal Special Topics 09/2014; 223(10):1959-1969.

Silicon nanostructuring in microelectronic industry





Porous silicon by anodic etching



Anodization of (bulk) silicon wafers:

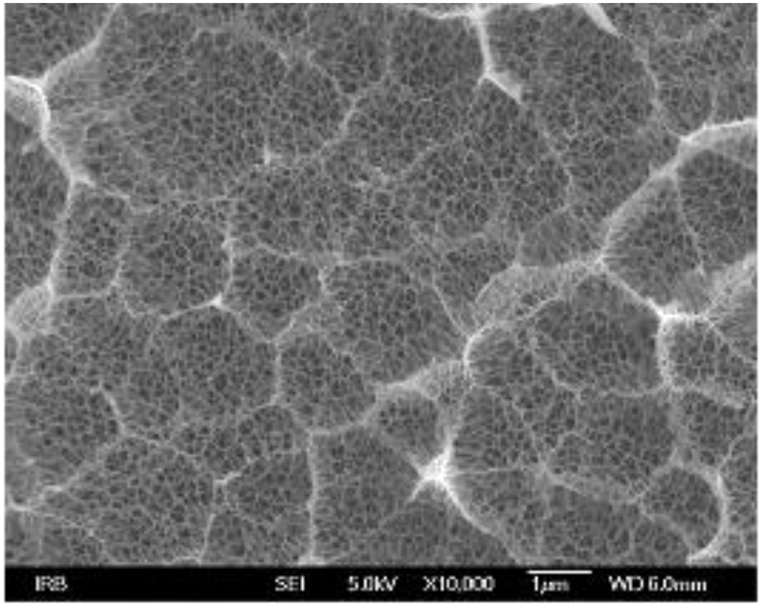
1. Porous Si formation ($J < J_{ps}$):

$$Si + 4HF_2^- + h^+ \rightarrow SiF_6^{2-} + 2HF + H_2 + e^-$$

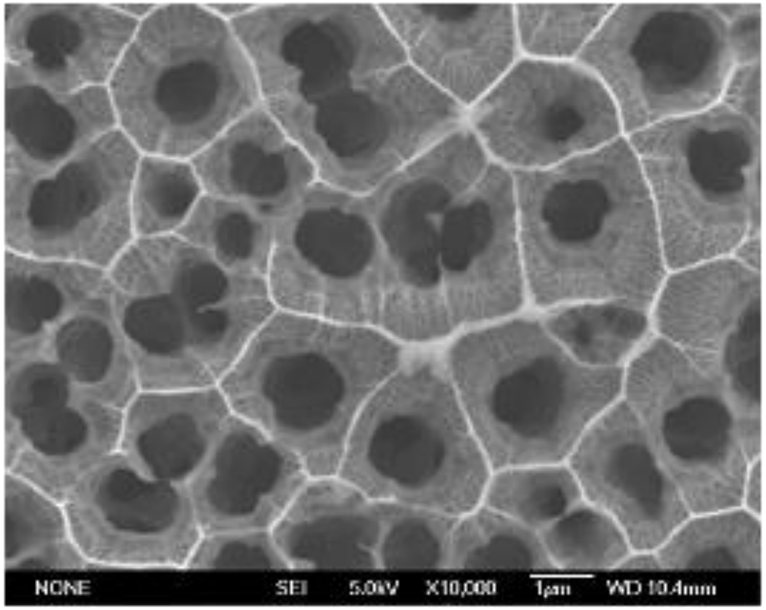
2. Electropolishing ($J > J_{ps}$):

$$Si + 2H_2O + 4h^+ \rightarrow SiO_2 + 4H^+$$

$$SiO_2 + 2HF_2^- + 2HF \rightarrow SiF_6^{2-} + 2H2O$$



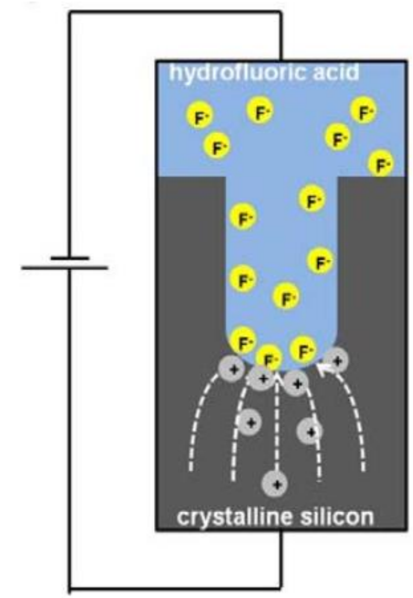
(a)

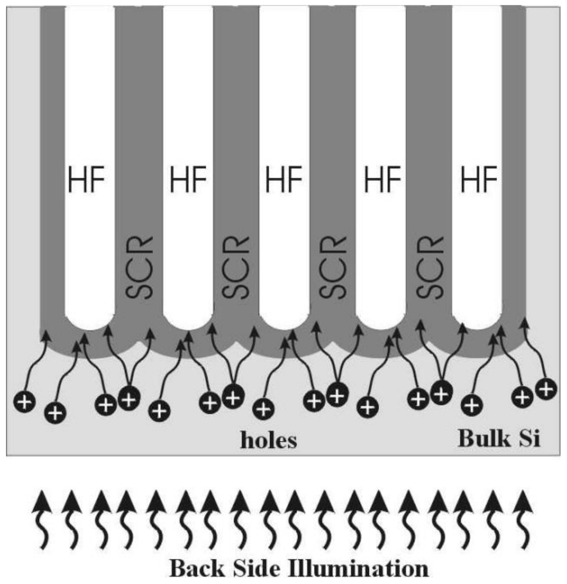


(b)

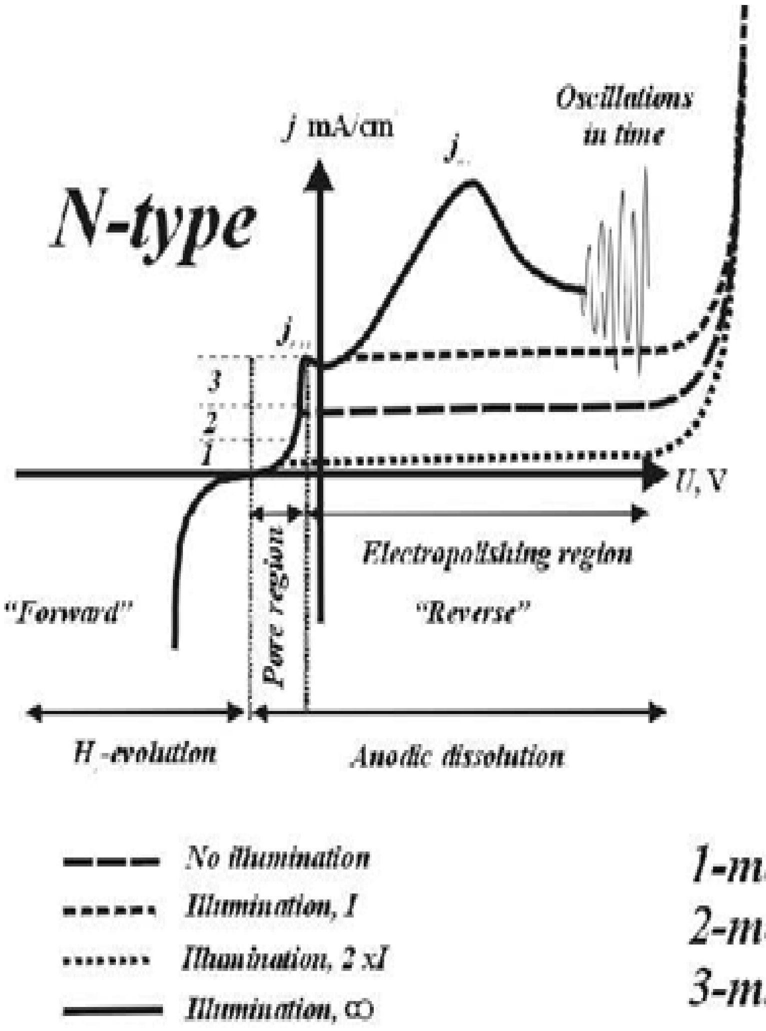
The surface chemistry of porous silicon

- governed by the reactivity of silicon-silicon and silicon-hydrogen bonds which are formed upon electrochemical etching
- both species can react with atmospheric oxygen and water at ambient conditions leading to the oxidation of the porous silicon structure
- the porous silicon surface has to be stabilized for (bio)sensing applications
- for this purpose two strategies have been developed resulting in the formation of either silicon-oxygen of silicon-carbon bonds
- the oxidized silicon surface presents silanol groups which can be utilized for further functionalization reactions including the introduction of amines and subsequent coupling of biomolecules to the porous silicon surface via the formation of amide bonds
- more stable surface functionalization was achieved by the formation of silicon carbon bonds
- silicon-carbon bonds are formed by hydrosilylation, chemical or electrochemical grafting techniques as well as carbonization reactions

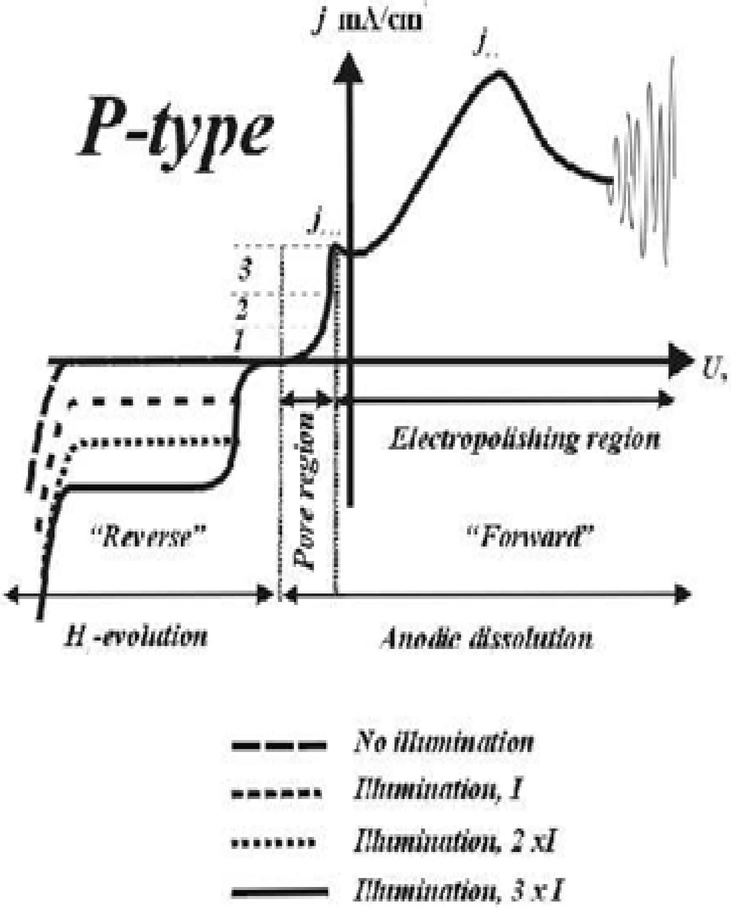




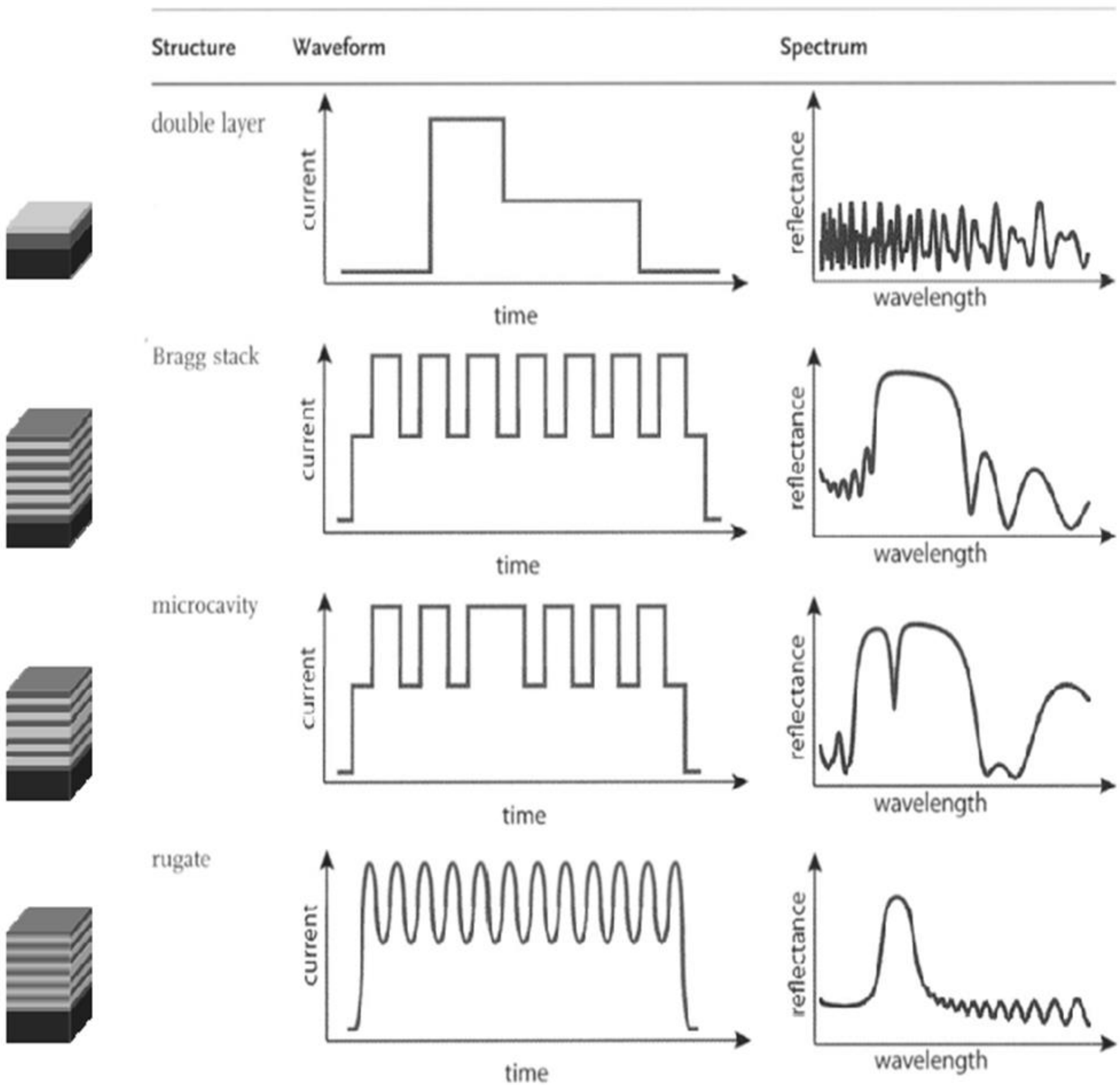
J/U curves of anodisation process of N- and P-type silicon

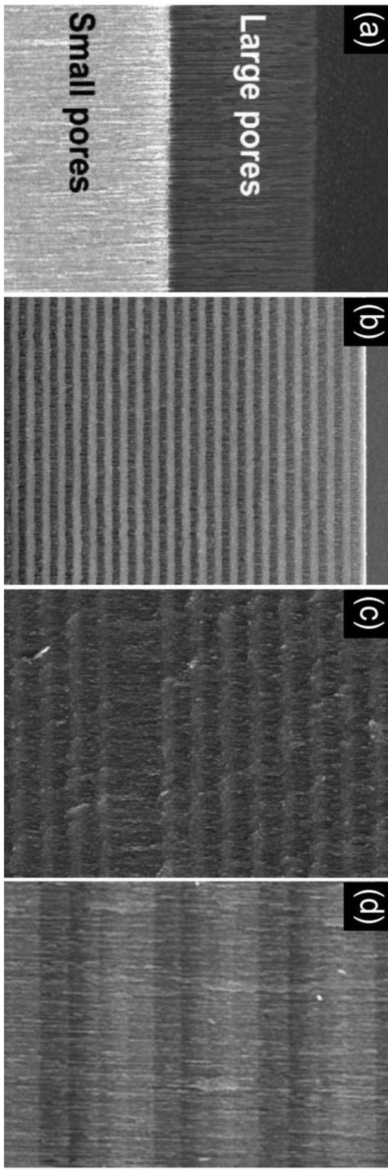


1-macropore
2-mesopores
3-micropores



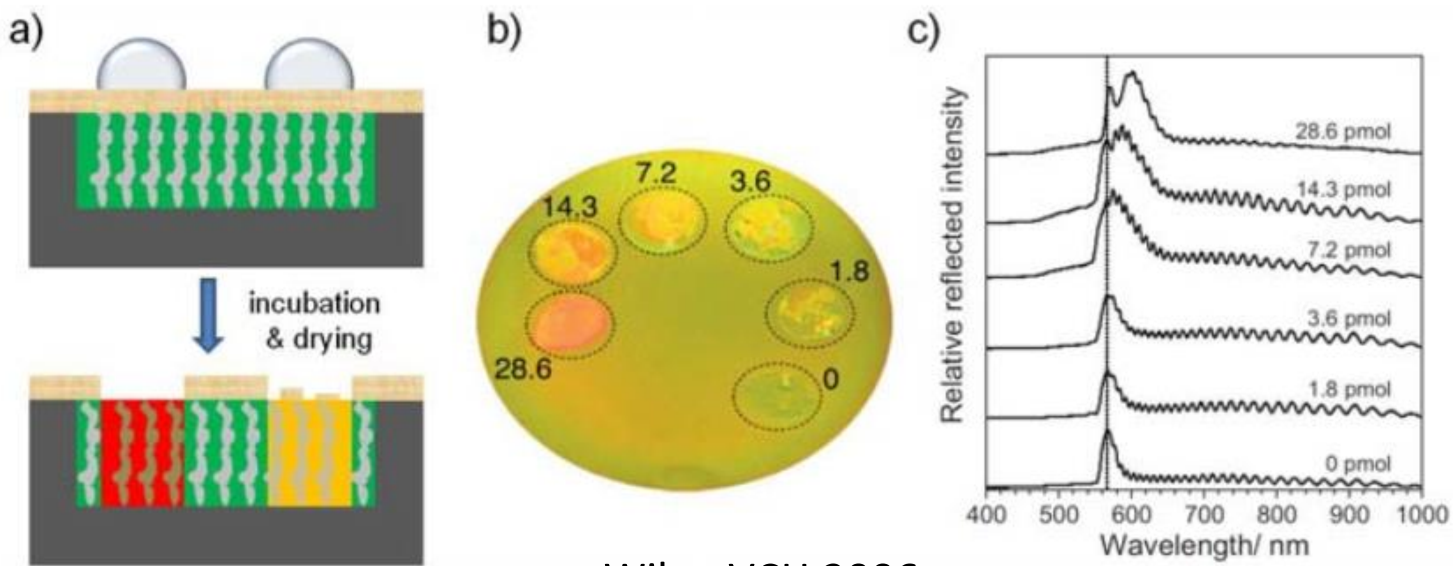
Porous silicon based 1D photonic crystals





Wiley-VCH 2012

Optical detection of protease activity using a protein-coated porous silicon sensor.



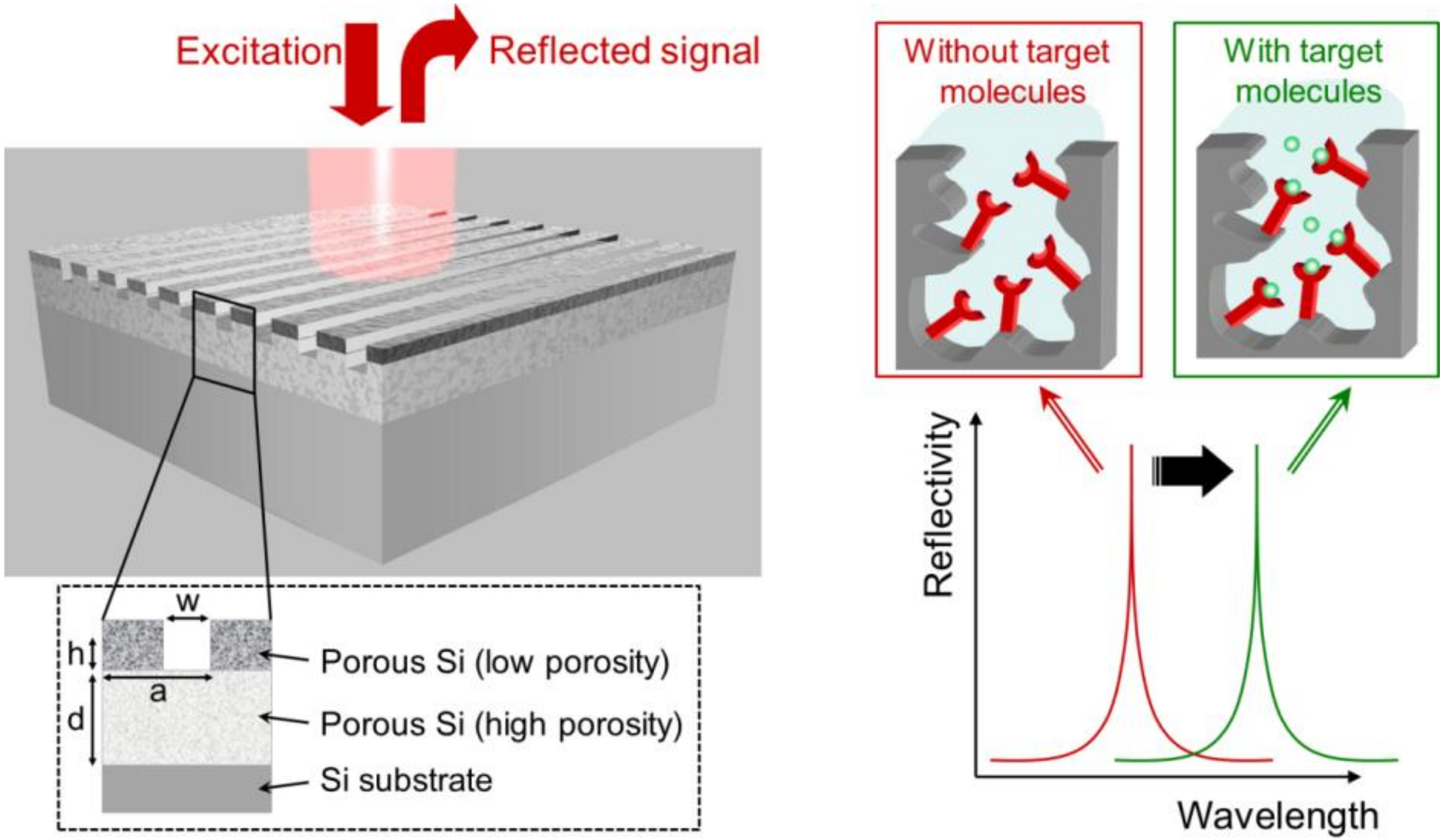
Wiley-VCH 2006.

(a) Schematic of the sensor principle. A hydrophobic porous silicon rugate structure is coated with a hydrophobic protein. Addition of small amounts of proteases leads to digestion of the protein layer. The proteolytic cleavage products infiltrate into the porous structure resulting in a visible color change.

(b) Photo of a protein-coated 1D photonic crystal which has been treated with different amounts of proteases (in picomoles).

(c) Reflectivity spectra taken from the spots on the protein-coated porous silicon sensor shown in (b).

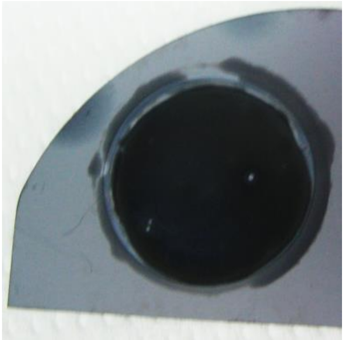
Integrated Photonic Biosensors Based on Porous Silicon



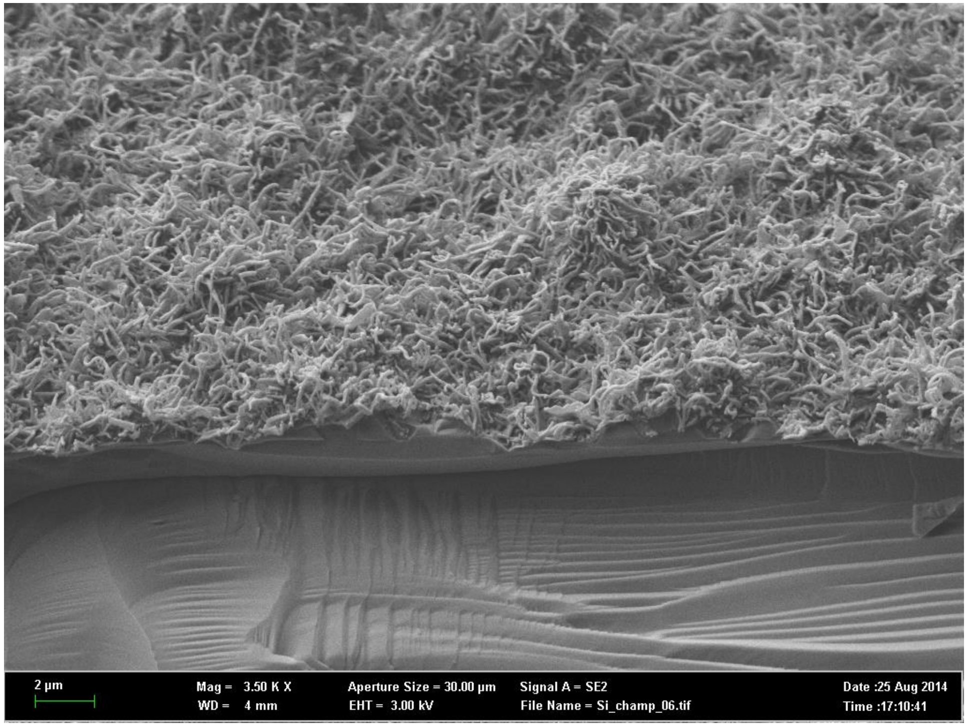
By specific binding of appropriate antibodies to the analyte the change in the refractive index is considerably increased resulting in a sensitive and reproducible optical response of the sensor to the analyte.

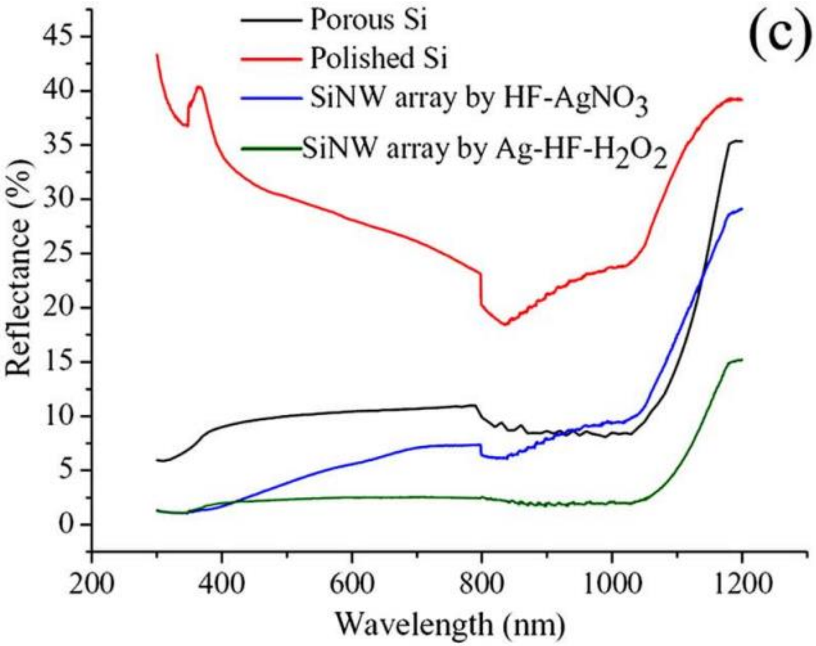
Metal assisted chemical etching of silicon

- Metal-catalyzed silicon electroless etching (Ag, Au nanoparticles + HF + H_2O_2)
- Light capture for solar cells and photosensing, chemical sensing



Si nanowires – „black silicon"



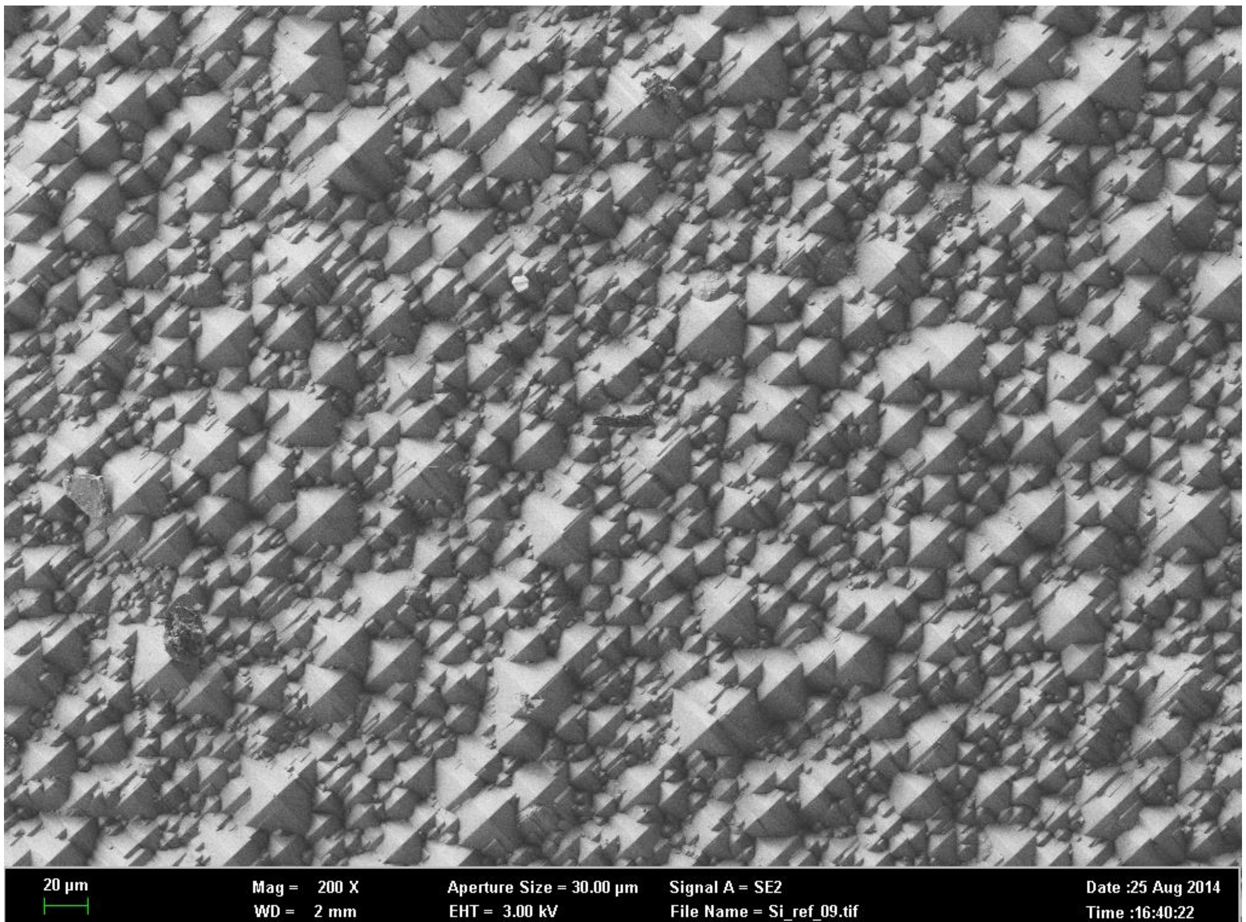


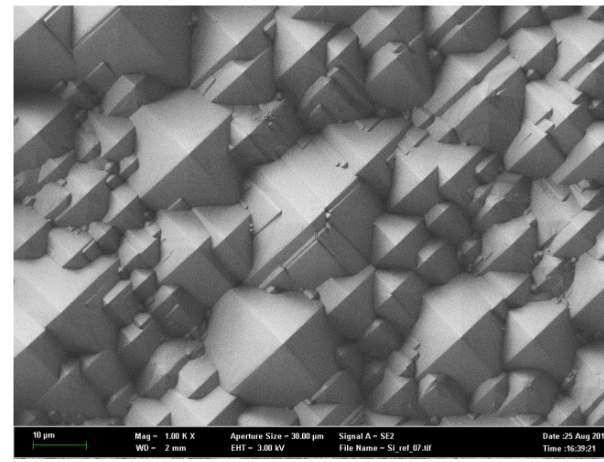
* Kuiqing Peng, Xin Wang, and Shuit-Tong Lee, Appl. Phys. Lett. 92, 163103 (2008)

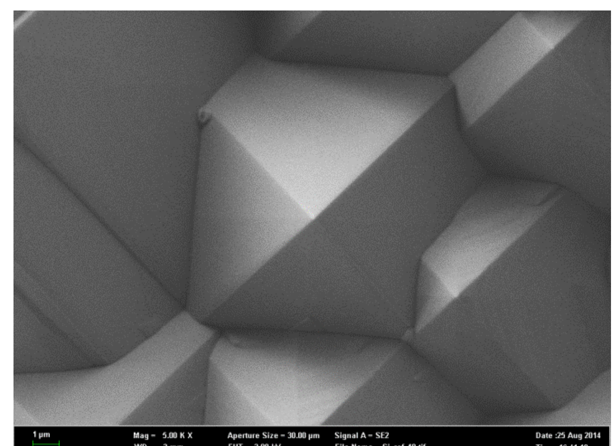
Silicon micropyramids

- Wet chemistry processing of silicon
- Random micropyramids by anisotropic silicon etch:

KOH (5%) + IPA (7%) + H_2O, 90°C
potassium hydroxide and isopropyl alcohol

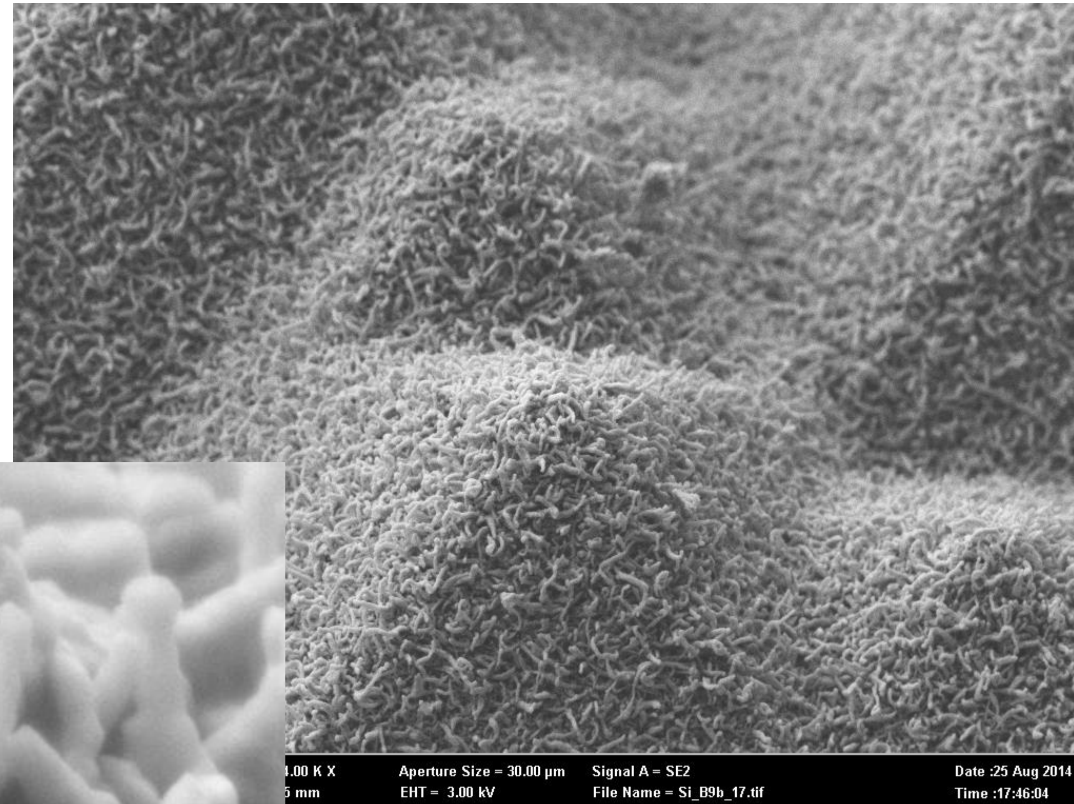


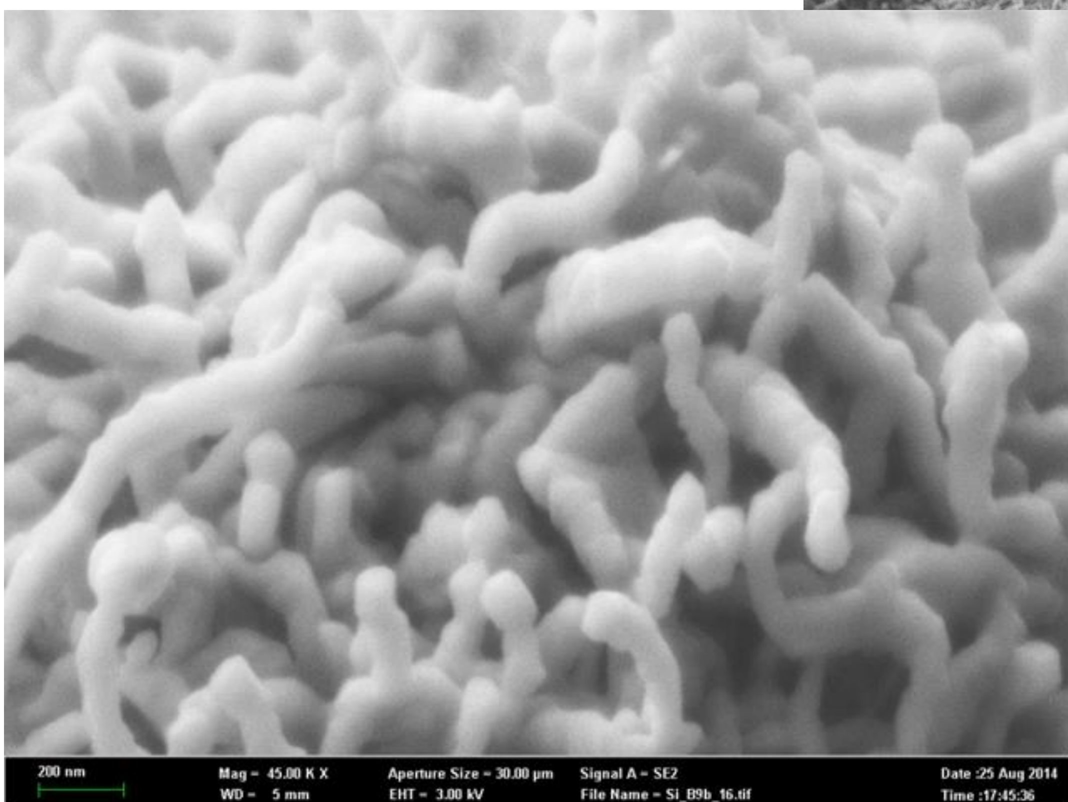




Hierarchically structured piramids with wires

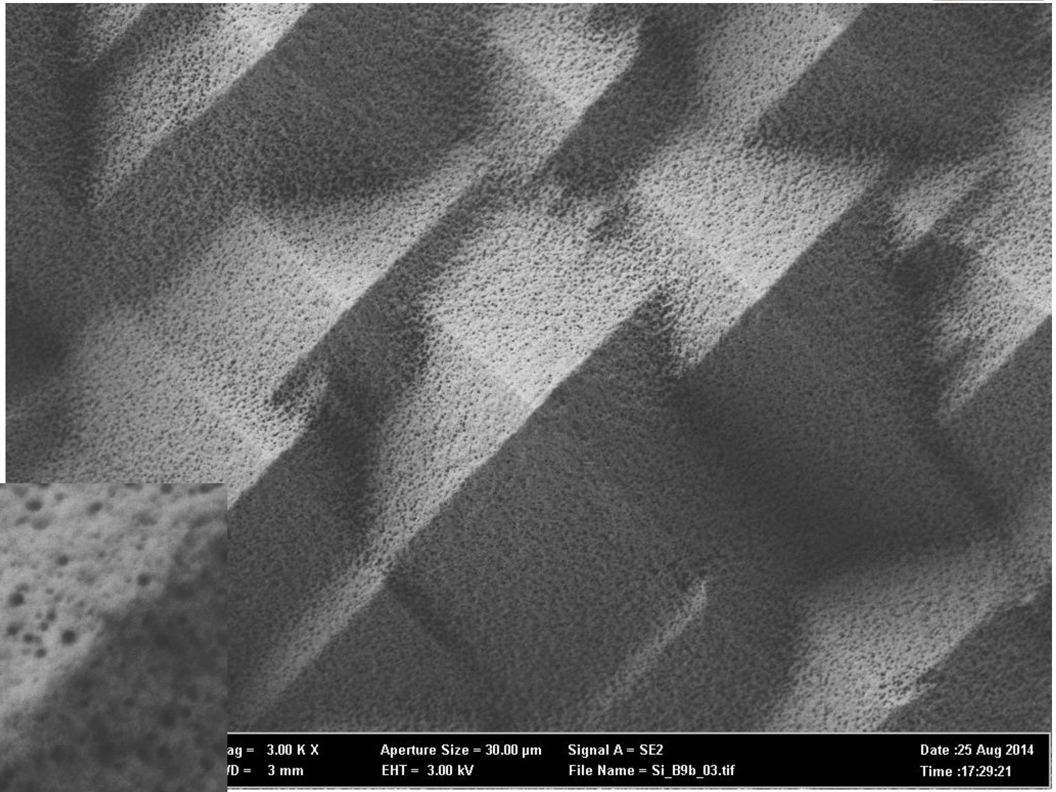
Micro-pyramids by KOH/IPA
+
Si nanowires by elektoless etching

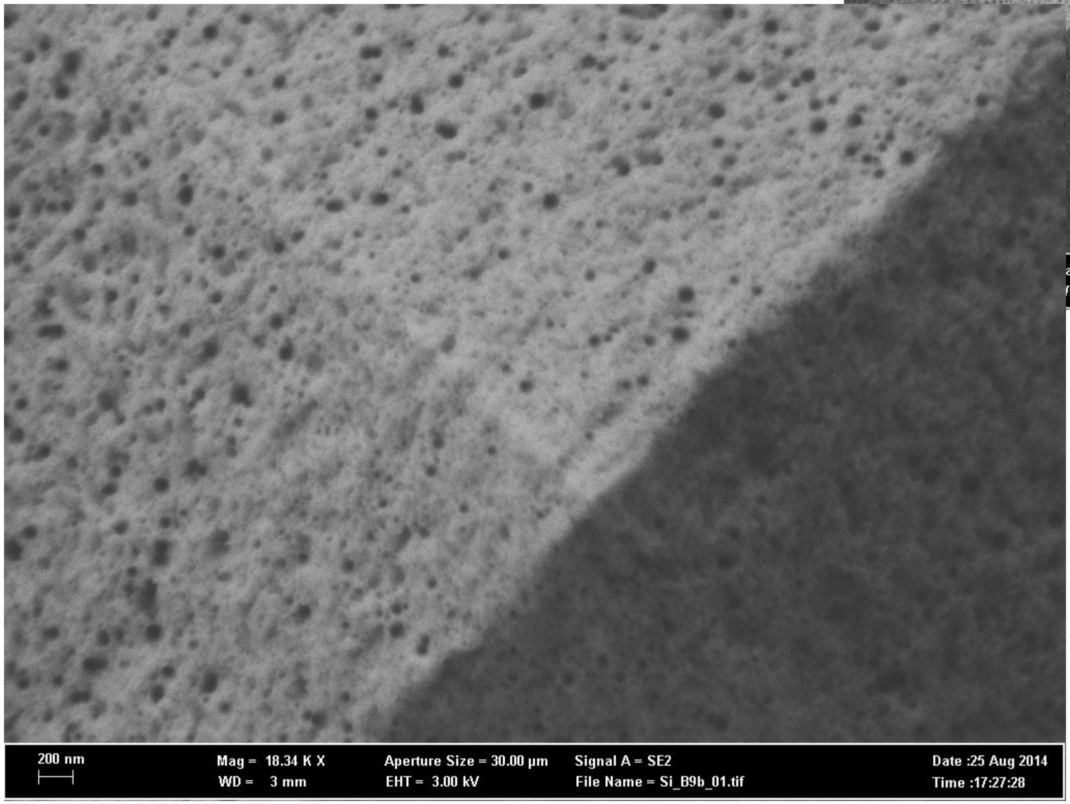




Hierarchically structured piramids with holes

Micro-pyramids by KOH/IPA
+
Anodisation etching





Nanostructured silicon as a highly promising anode for next-generation lithium-ion batteries (LIBs).

- Silicon has a large theoretical capacity of 4,200 mAhg-1
- The key challenge for Si anodes is large volume change during the lithiation/delithiation cycle that results in chemomechanical degradation and subsequent rapid capacity fading.

Comparison of various anode materials.

Anode Materials	C	Li	Si	Sn	Sb	Al	Mg	$Li_4Ti_5O_{12}$	Bi
Lithiated phase	LiC_6	Li	$Li_{4.4}Si$	$Li_{4.4}Sn$	Li3Sb	LiAl	Li_3Mg	$Li_{12}Ti_5O_{12}$	Li_3Bi
Theoretical specific capacity (mAh g_{-1})	372	3,862	4,200	994	660	993	3,350	175	385
Theoretical volume capacity (mAh cm^{-3})	837	2,047	9,786	7,246	4,422	2,681	4,355	613	3,765
Volume change (%)	12	100	320	260	200	96	100	1	215

nature COMMUNICATIONS

ARTICLE

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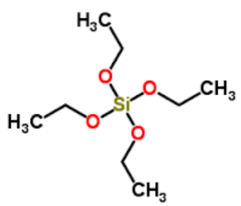
Inward lithium-ion breathing of hierarchically porous silicon anodes

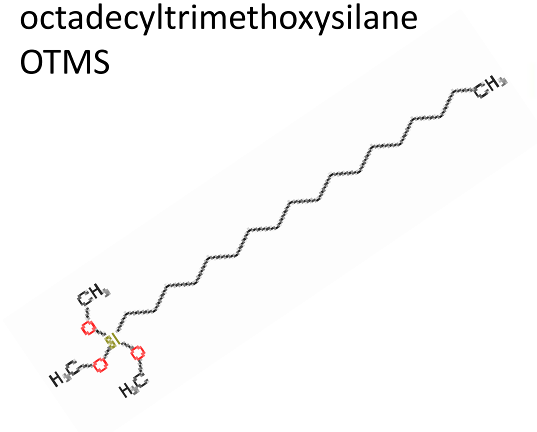
Qiangfeng Xiao[1,*], Meng Gu[2,*], Hui Yang[3,*], Bing Li[4], Cunman Zhang[4], Yang Liu[5], Fang Liu[5], Fang Dai[1], Li Yang[1], Zhongyi Liu[1], Xingcheng Xiao[1], Gao Liu[6], Peng Zhao[3], Sulin Zhang[3], Chongmin Wang[2], Yunfeng Lu[5] & Mei Cai[1]

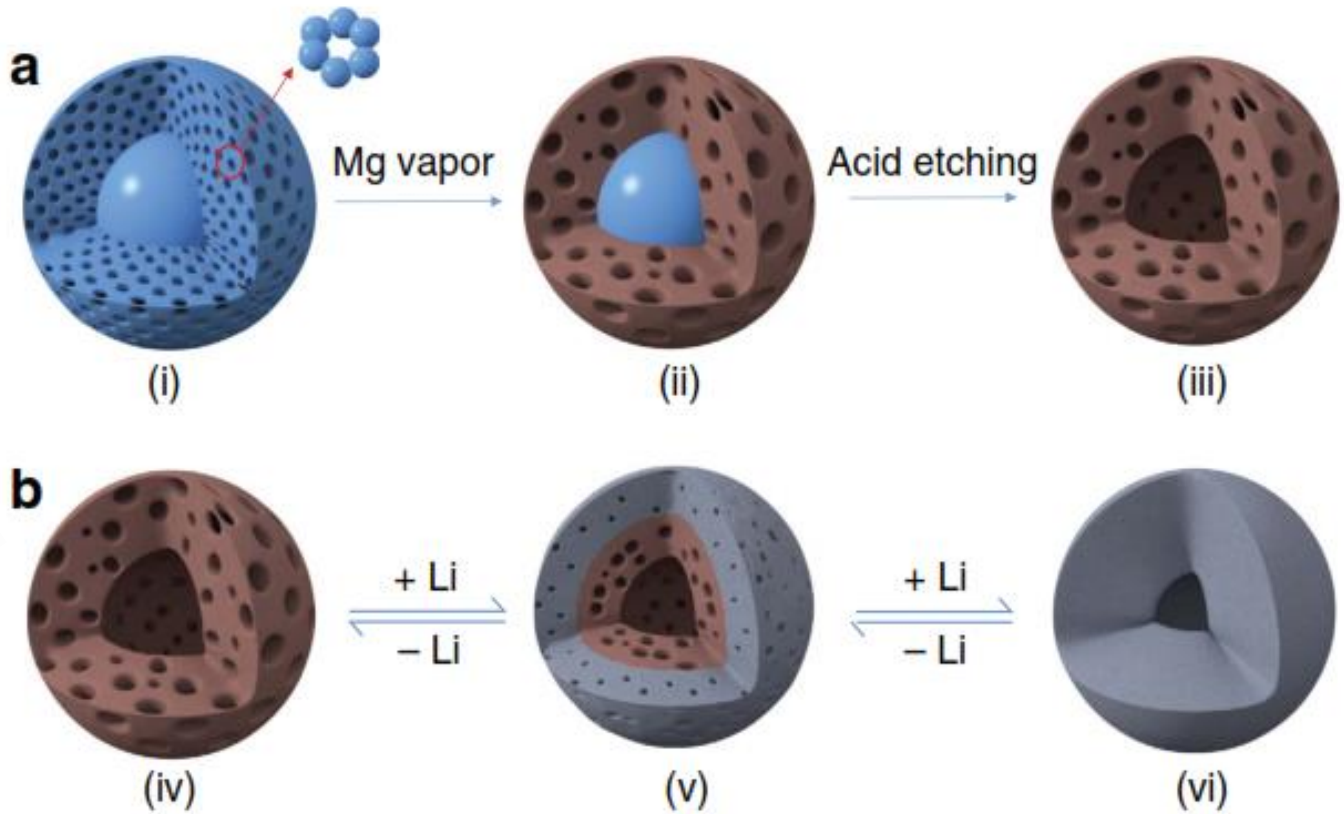
Hierarchically porous Si nanospheres which uniquely accommodate the volume change

SiO2 microspheres by hydrolisis of tetraethoxysilane TEOS:



and octadecyltrimethoxysilane OTMS

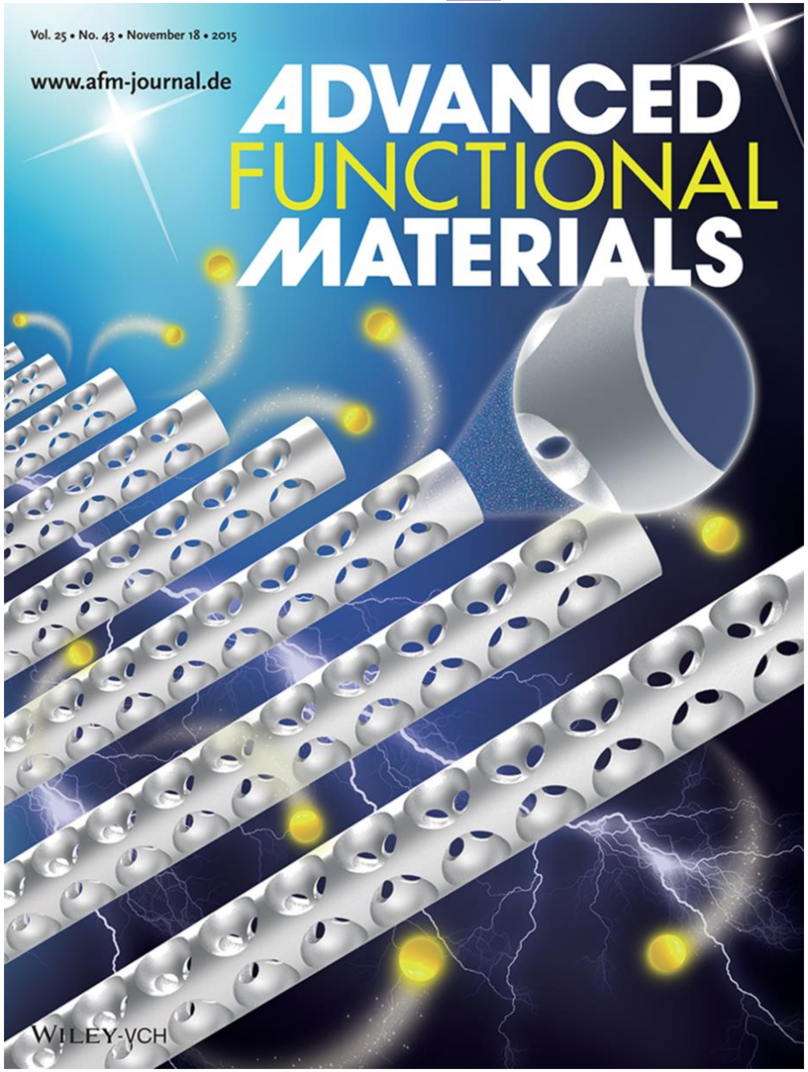




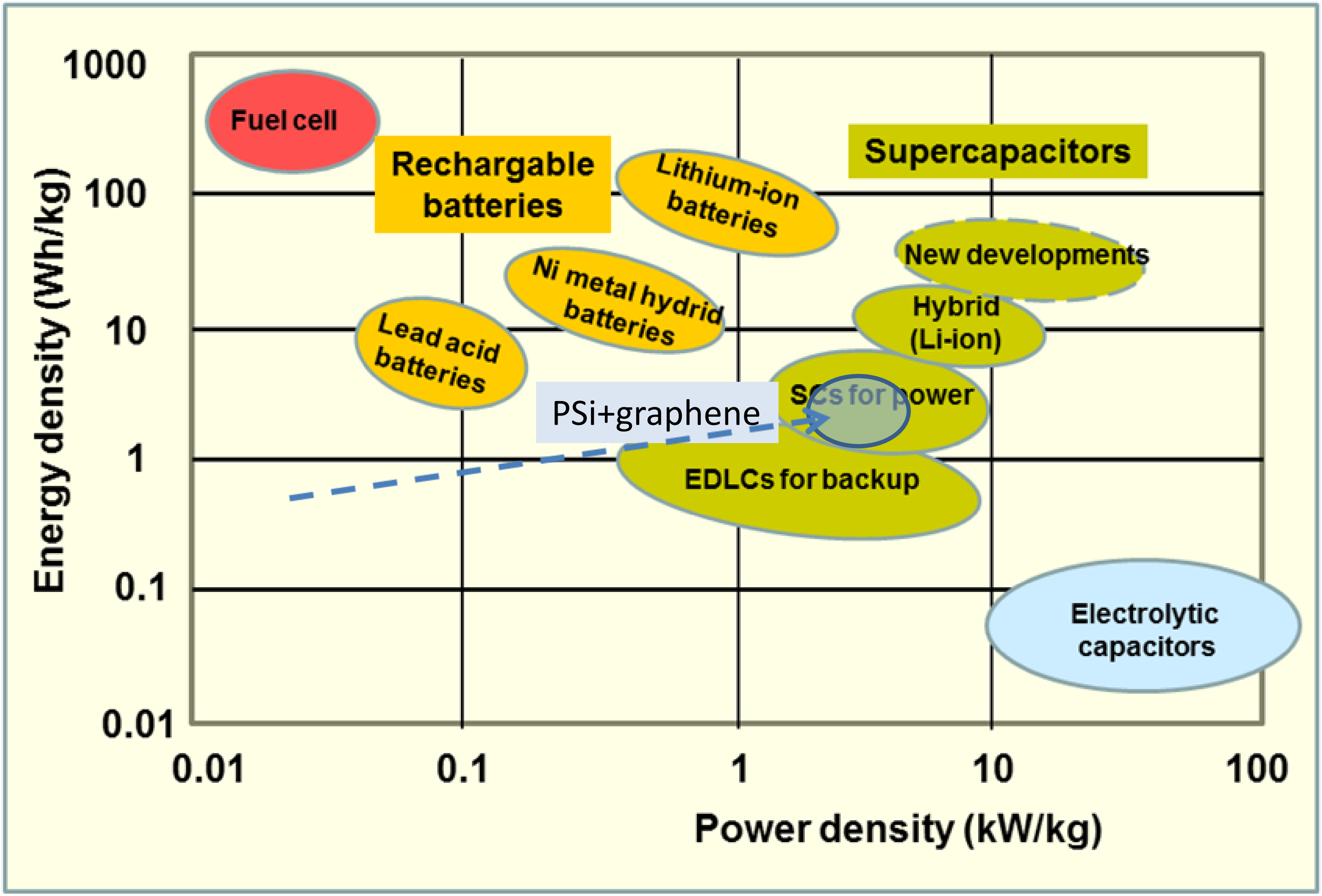
Lithium Ion Batteries: Porous Si Nanowires from Cheap Metallurgical Silicon Stabilized by a Surface Oxide Layer for Lithium Ion Batteries

Adv. Funct. Mater. 43, p. 6693, 2015

- sustainable route from cheap metallurgical silicon to porous Si/SiOx nanowires is demonstrated by J. Xiong, C. Yan, and co-workers
- with a surface oxide layer of suitable thickness, the huge volume expansion of Si during charge/discharge processes is greatly accommodated, resulting in superior cycling performance and high reversible capacity



Energy storage devices



SERS

by silver-coated self-assembled polystyrene spheres for surface enhanced raman spectroscopy

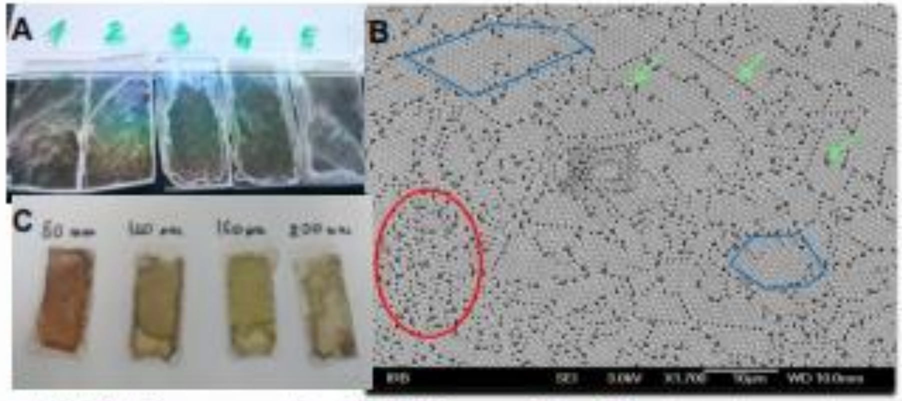


Figure 1. A) PS before evaporation, B) SEM image of 1 µm PS: red - spheres not organized in hexagonal close packing, blue - monolayer subdomains, green arrows – defects and C) spheres after evaporation of Ag

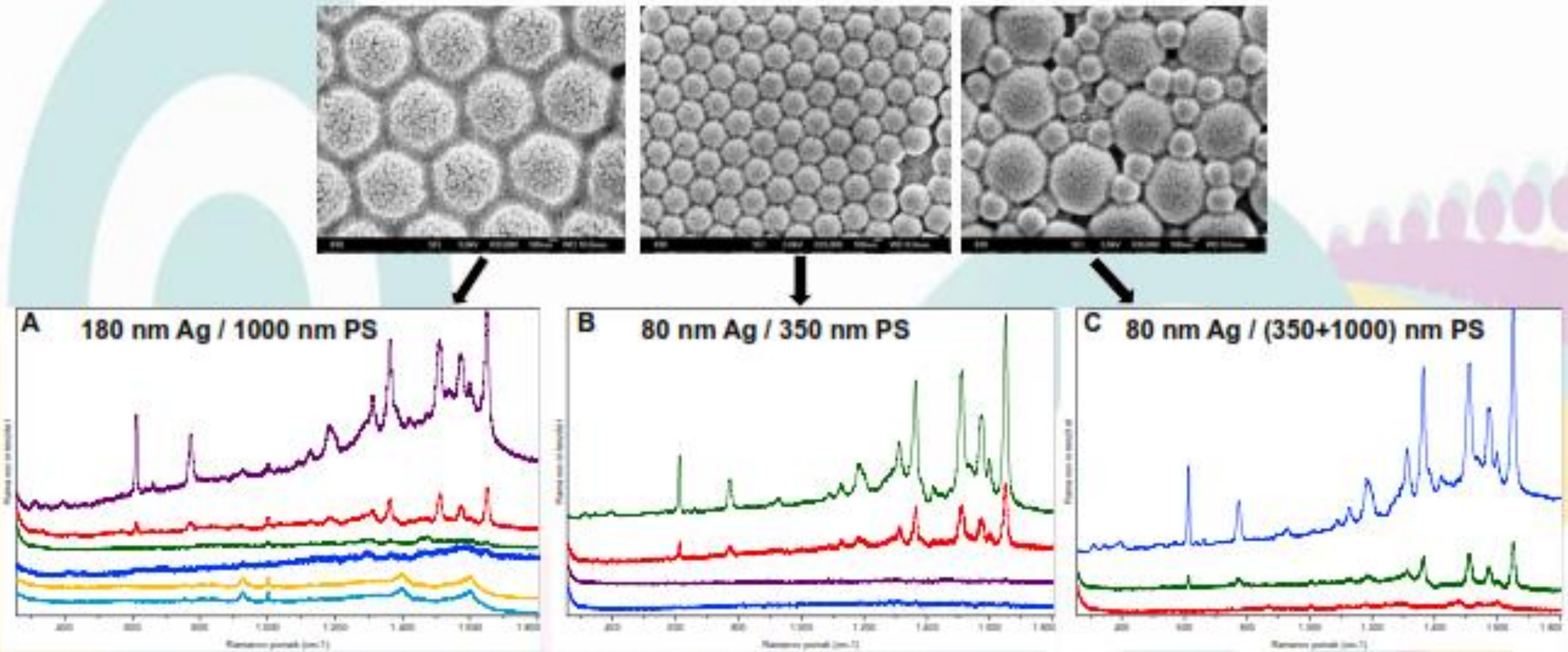
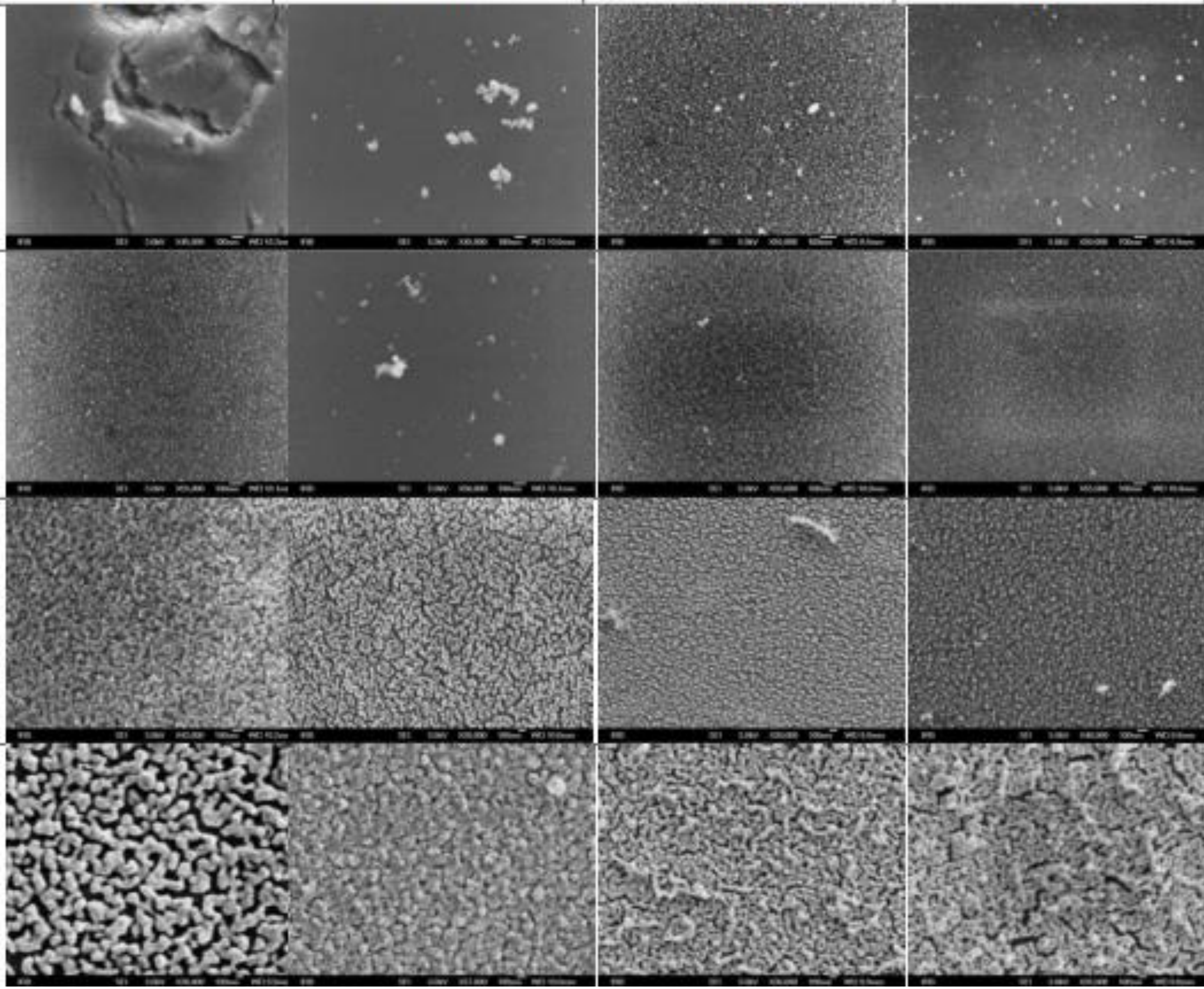


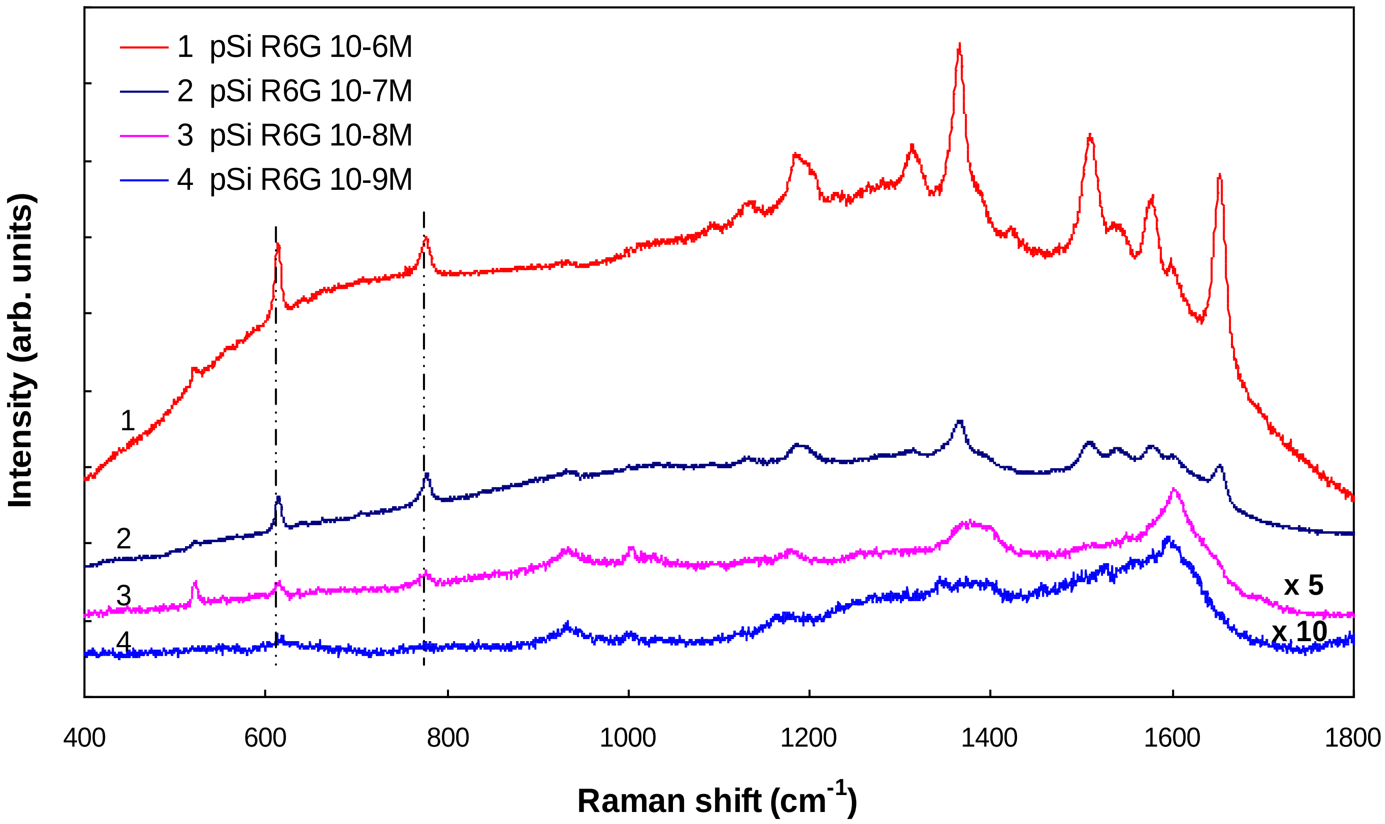
Figure 2. R6G SERS spectra. From top to bottom: A) 10^{-6} M, 10^{-8} M, 10^{-9} M, 10^{-6} M R6G on Ag without PS, Raman spectra of PS (yellow) and 180 nm of Ag on 1000 nm PS, B) 10^{-6} M, 10^{-8} M, 10^{-9} M and 10^{-5} M R6G on Ag without PS and C) 10^{-6} M, 10^{-8} M and 10^{-9} M R6G (514.5 nm, 0.5 mW, accumulation 30 s, 100x).

SERS by silver particles on nanoporous silicon by anodisation

	35 mA	25 mA	15 mA	5 mA
$AgNO_3$ 10^{-5} M 1 min				
$AgNO_3$ 10^{-4} M 1 min				
$AgNO_3$ 10^{-3} M 1 min				
$AgNO_3$ 10^{-2} M 1 min				



Raman spectra of rhodamine 6G with silver obtained by immersion plating



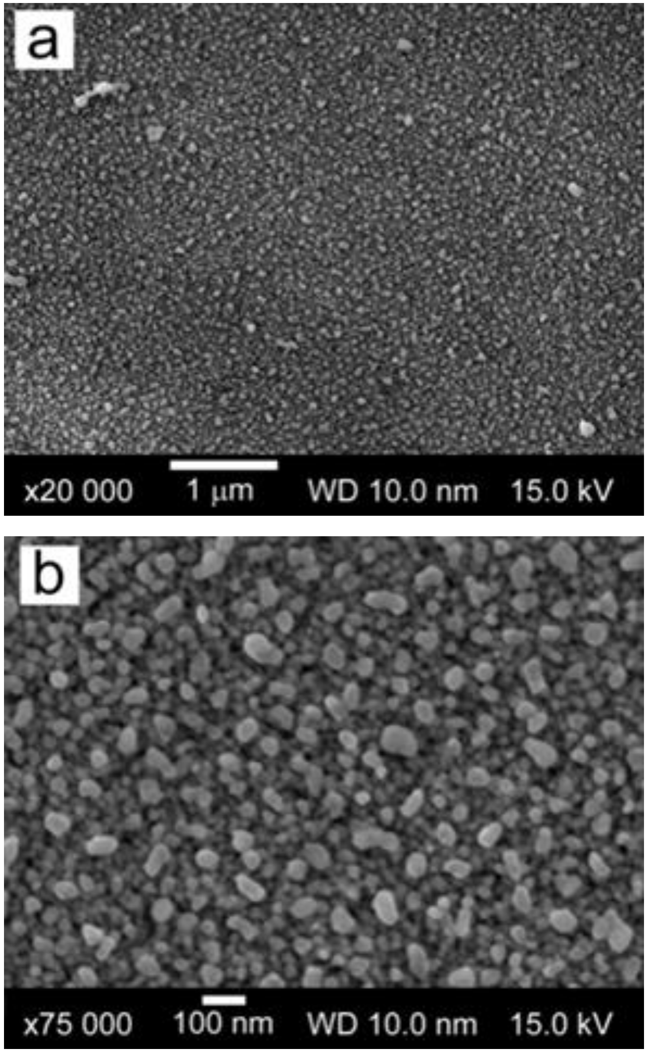
L. Mikac et al., Influence of mesoporous silicon preparation condition on silver clustering and SERS enhancement, J. Raman Spectrosc. 2016.

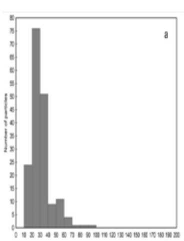
Preparation conditions for SERS substrates S1 and S2.

	HF wt.%	J mA/cm^2	Etching time/min	Immersion time/min
S1	24	9	10	6
S2	12	3	30	3

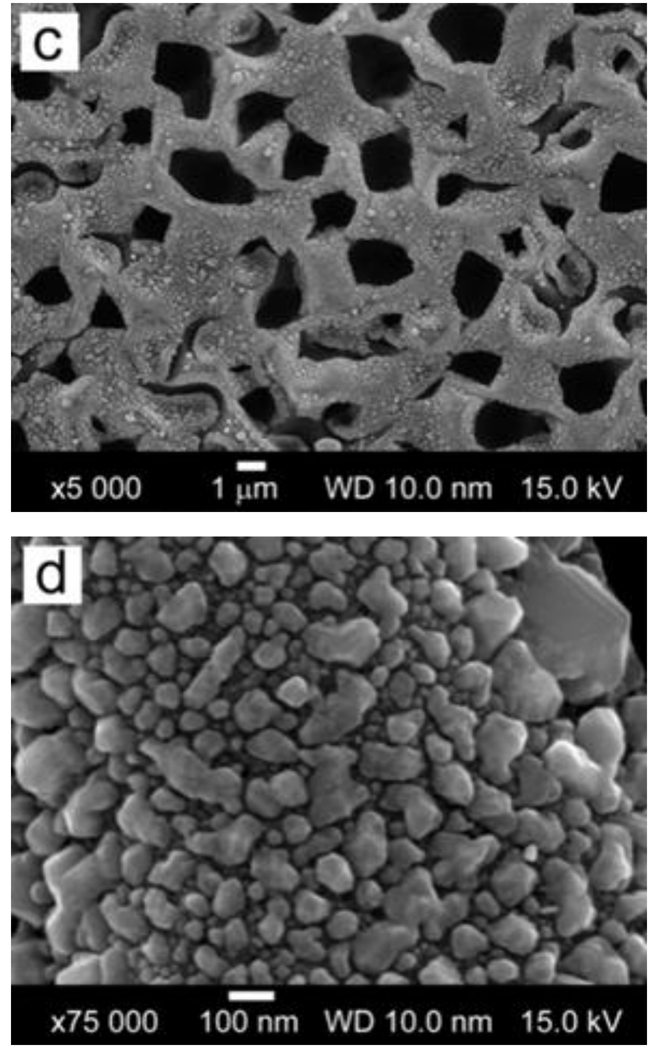
SEM comparison of S1 and S2

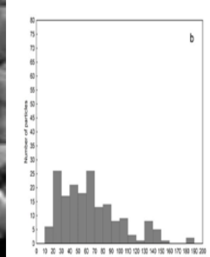
S1



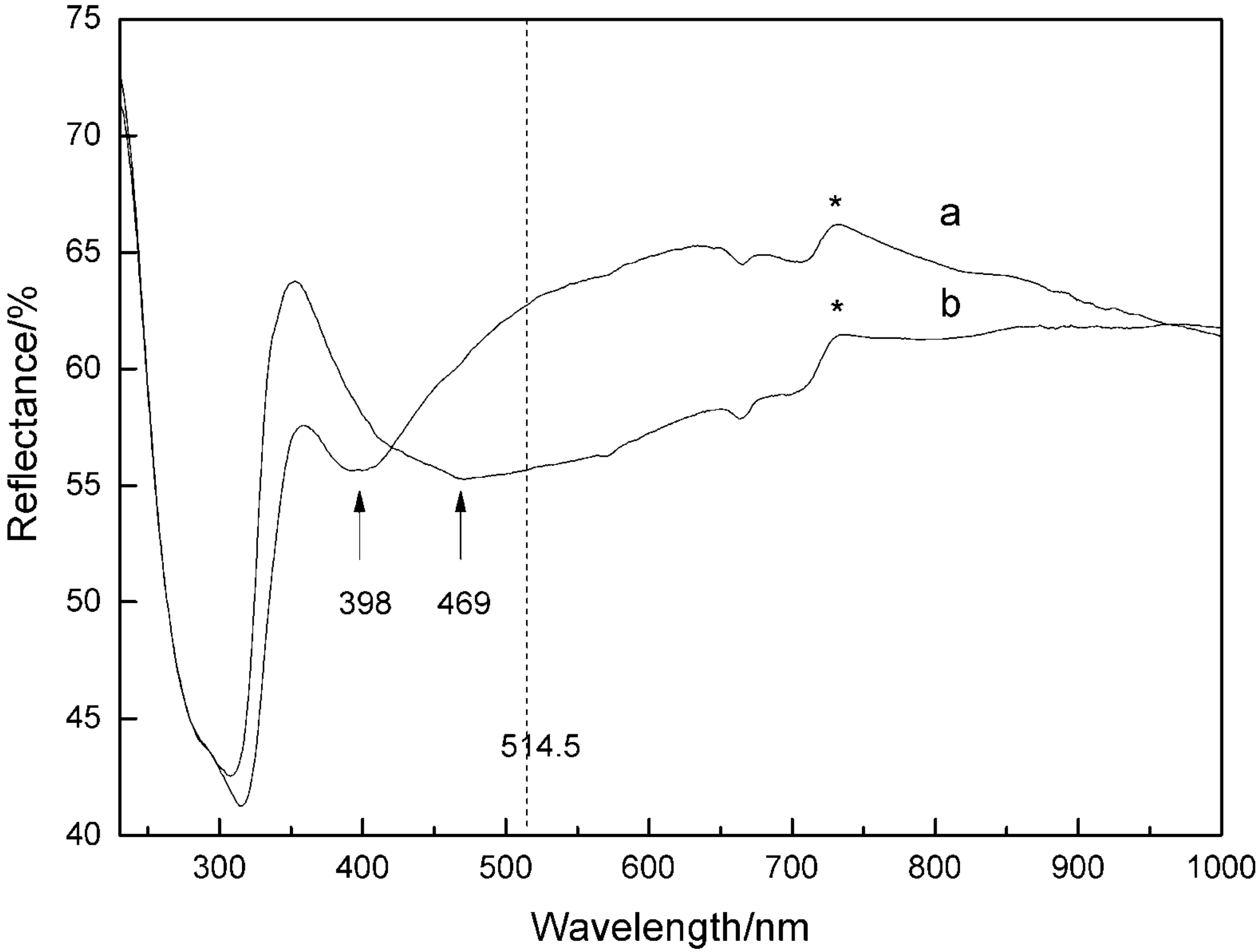


S2



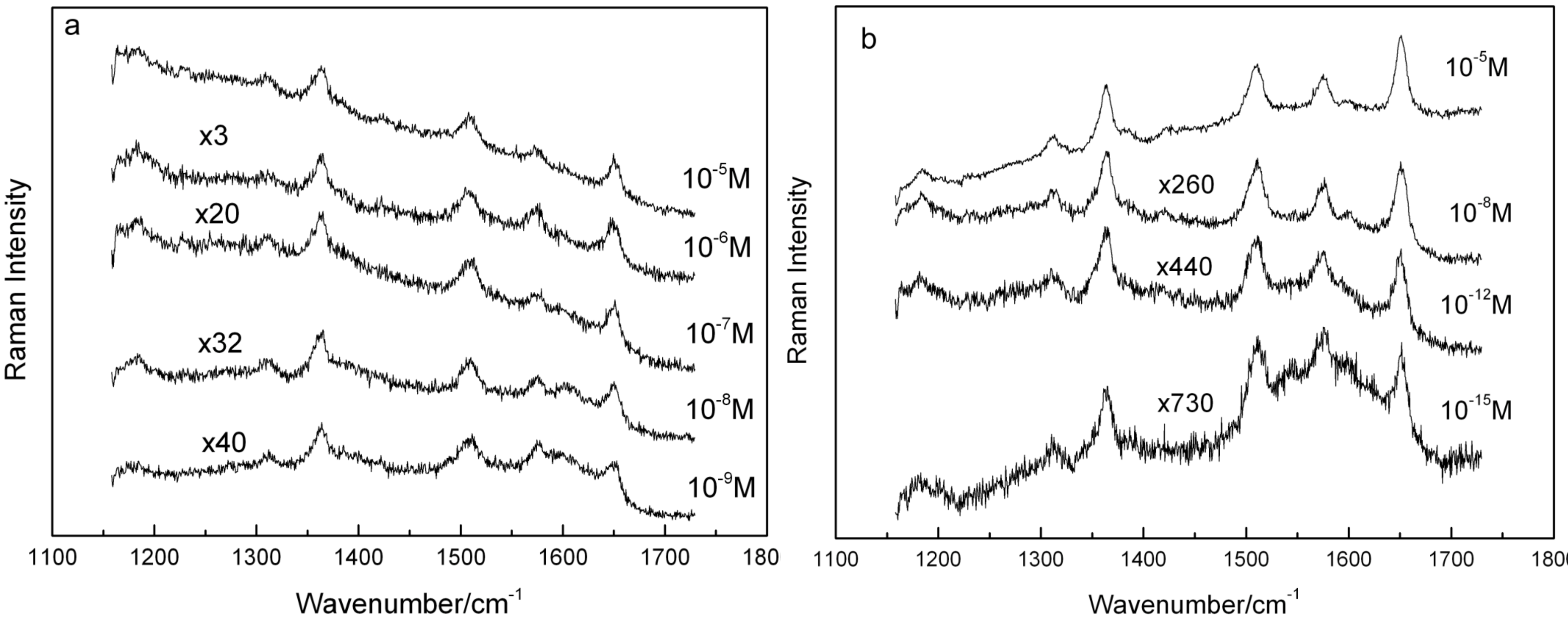


UV/Vis spectra recorded in total reflectance mode



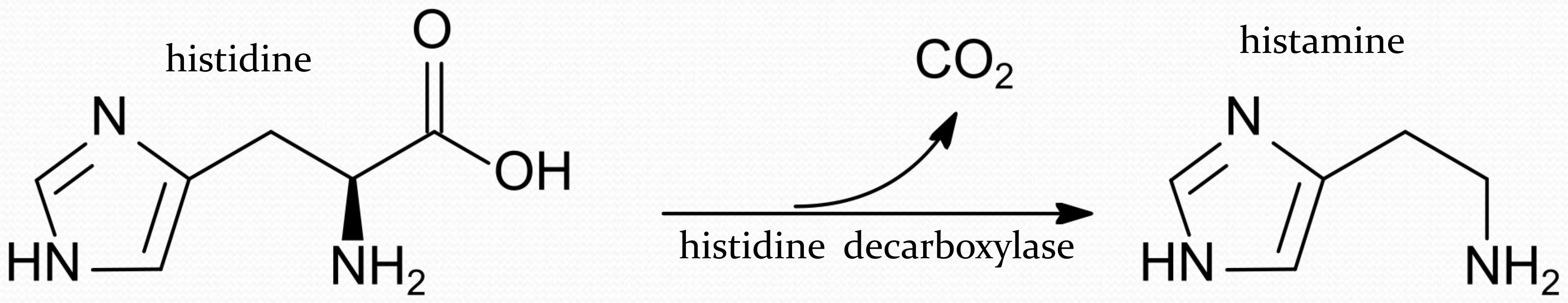
The SERS spectra of R6G for substrates

S1 S2



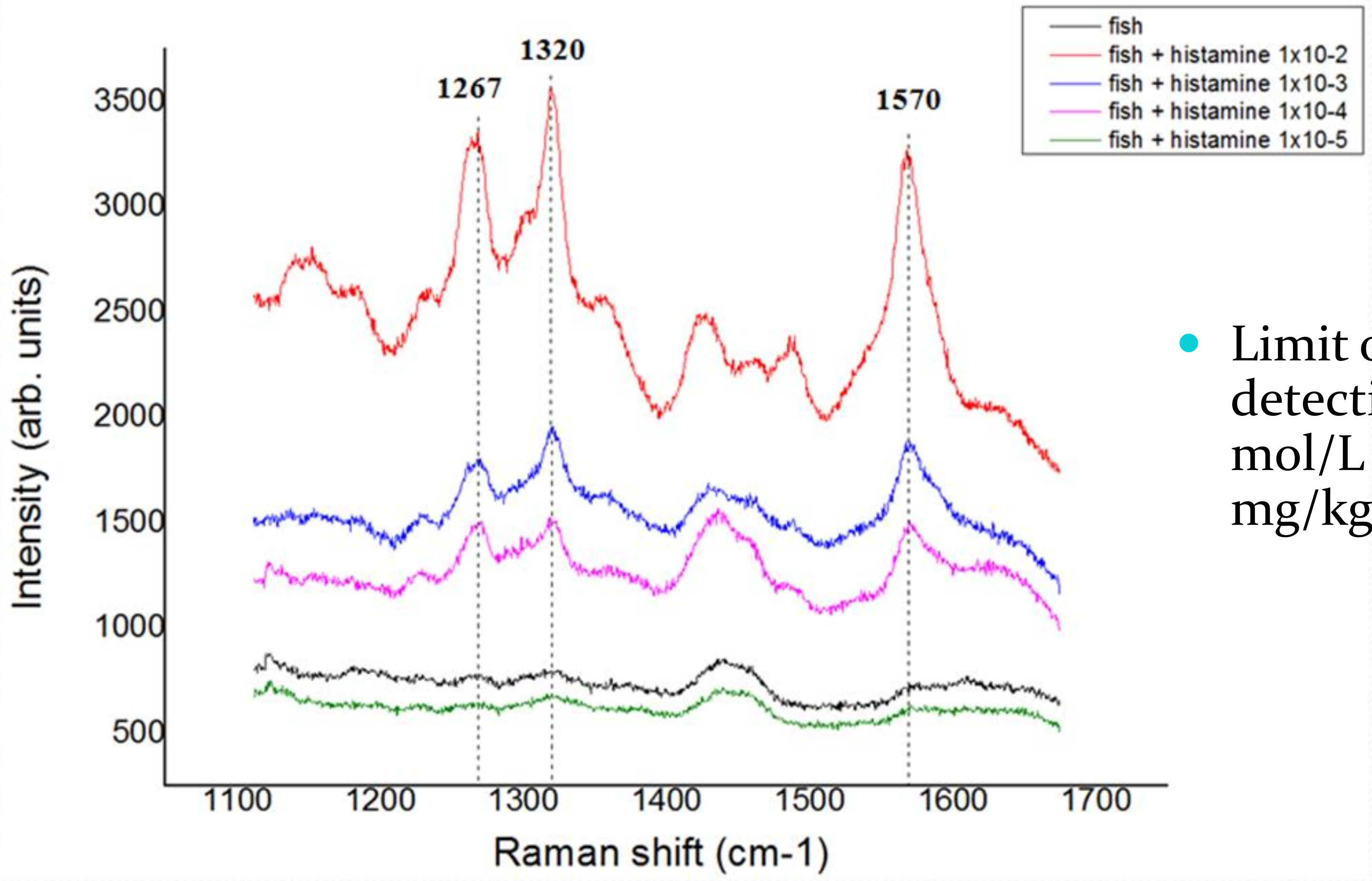
M. Kosović et al., Porous Silicon Covered with Silver Nanoparticles as Surface-Enhanced Raman Scattering (SERS) Substrate for Ultra-Low Concentration Detection. // Applied spectroscopy. 69 (2015) , 12; 1417-1424

SERS of Histamine



- Most frequent cause of health problems associated with seafood consumption
- Wide array of analytical methods – complex, expensive, long analysis time
- Need for simpler, faster methods adequate for „on field" analysis
- Legislative set limits:
  - 50 mg/kg of fish – USA
  - 100 mg/kg of fish - EU

SERS measurements – fish extracts



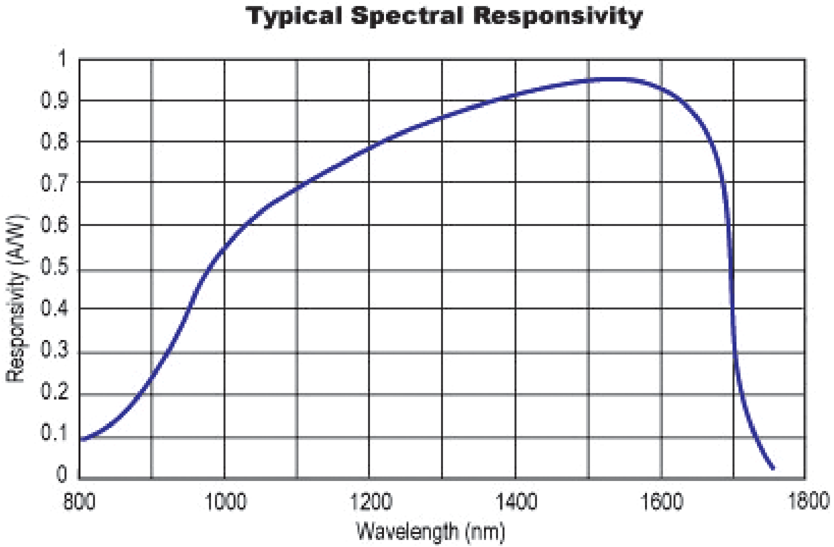
- Limit of detection: 1×10^{-5} mol/L ≈ 11.5 mg/kg of fish

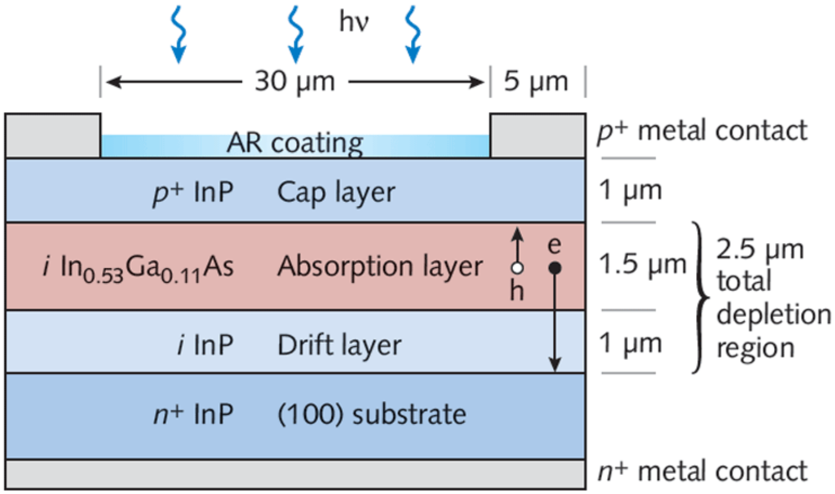
T. Janci et al., Optimization of parameters for histamine detection in fish muscle extracts by Surface Enhanced Raman Spectroscopy using silver colloid SERS substrates, Journal of Raman Spectroscopy, 2016.

State of the art in IR detection – InGaAs photodiode

- Tunable band-gap
  - GaAs (1.42 eV) to InAs (0.34 eV)
- Typical range 900nm to 1700nm
- 1.3 micron and 1.55 micron sensitivity
- High Responsivity
- Both Small Area (High Speed) and Large Area

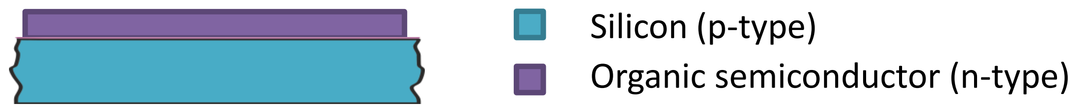
- Not Si CMOS compatible
- Expensive (MBE)
- Toxic precursors





*http://goo.gl/hz2Q6Q
http://goo.gl/W7f1rI
http://goo.gl/H89sZG

Silicon/organic hybrid heterojunction



Silicon

- well- developed Si CMOS technology

if micro/nano structured:

- large surface area
- light trapping
- nano-scale phenomena

Organic semiconductor thin films

- electronics with carbon-based materials
- chemically **tunable electronic properties**
- easy and cheap processing
- low environmental impact
- low material usage

Hybrid electronics

integrating advantages of organics with silicon-based electronics - **going beyond Si**

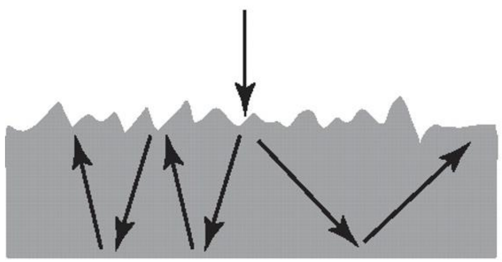
+ advantages of nanostructuring of Silicon

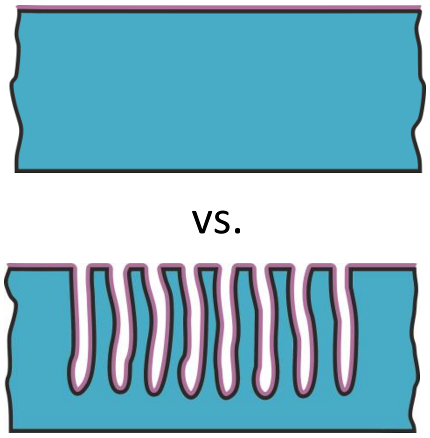
Optimization of Si in hybrid heterojunction

Micro- and nano-structuring of the Si surface

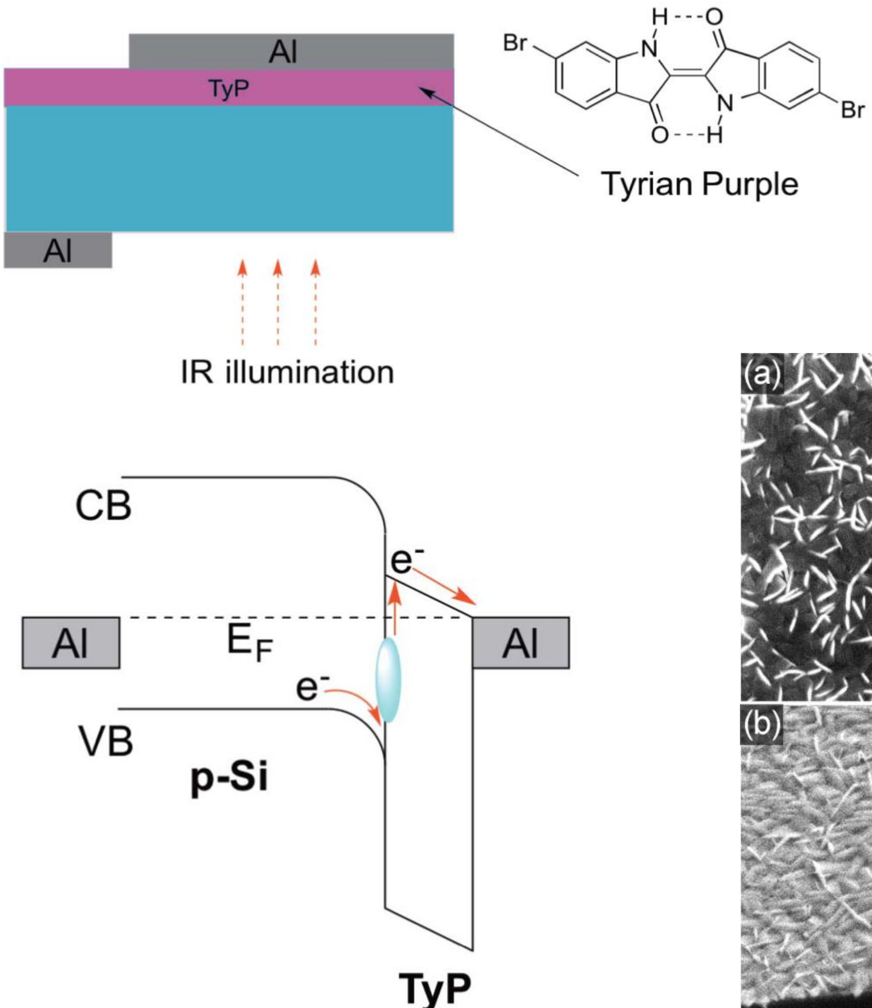
LIGHT TRAPPING

> EFFECTIVE JUNCTION AREA

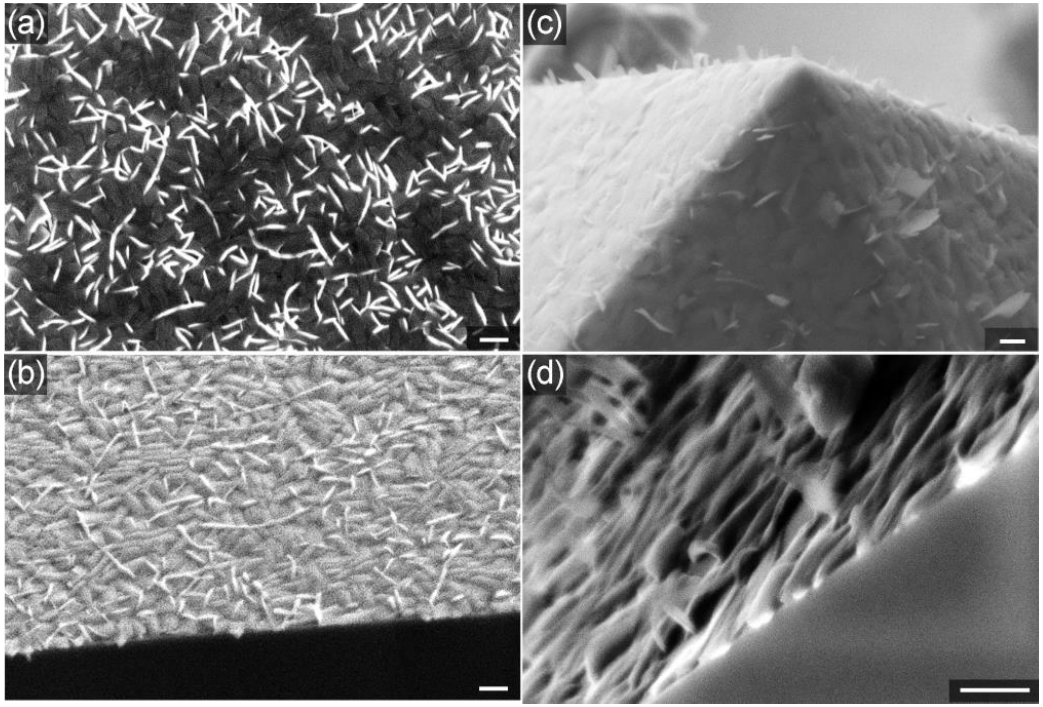




Structured Si/Tyrian Purple photodiode



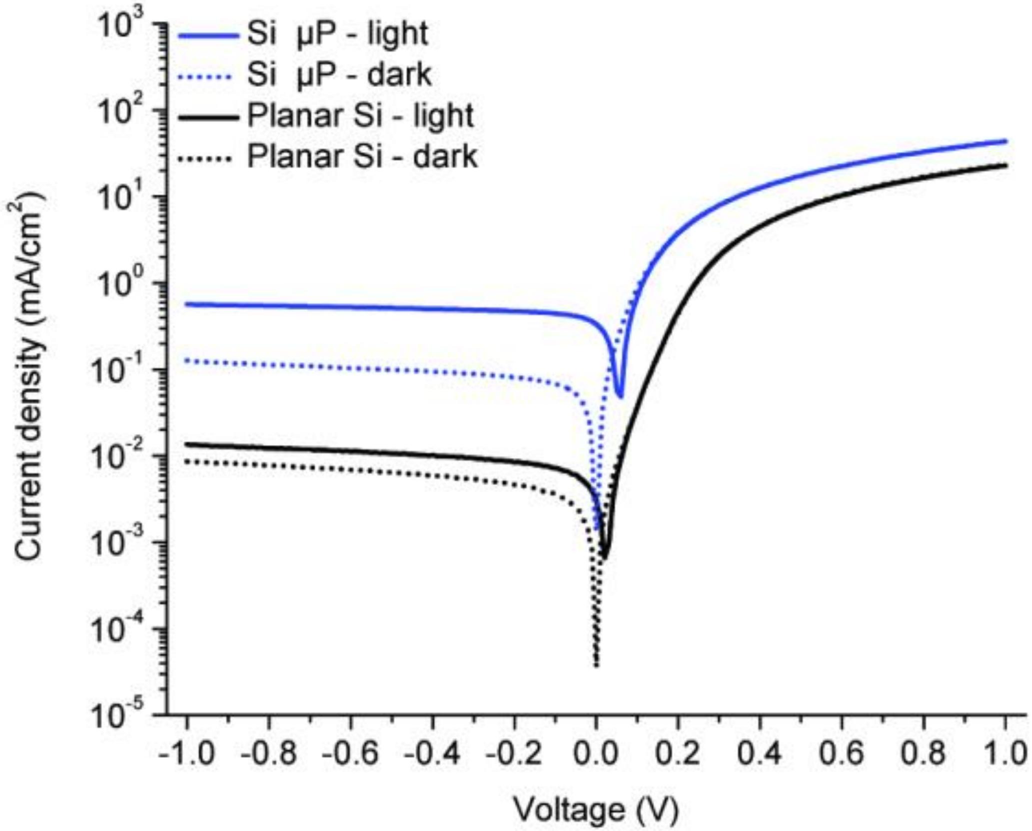
- 6,6′-dibromoindigo – Tyrian Purple
- Hydrogen-bonded pigment
- n-type organic semiconductor
- Thin films by hot-wall epitaxy



200 nm

Structured Si/Tyrian Purple photodiode

- Up to **700-fold** increase in short-circut photocurrent over planar diodes
- Highest responsivity:
  silicon micropyramids/TyP
- Responsivity: **4 mA/W** at 1,55 µm (room temperature, -1 V biased)
- InGaAs: max 1A/W



light = 1,48 µm laser diode (200 mW/cm^2)

V. Đerek, E. D. Głowacki, M. Sytnyk, W. Heiss, M. Marciuš, M. Ristić, M. Ivanda, and N. S. Sariciftci, Enhanced near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors, Appl. Phys. Lett. 107, 083302 (2015).

Structured Si/Tyrian Purple photodiode

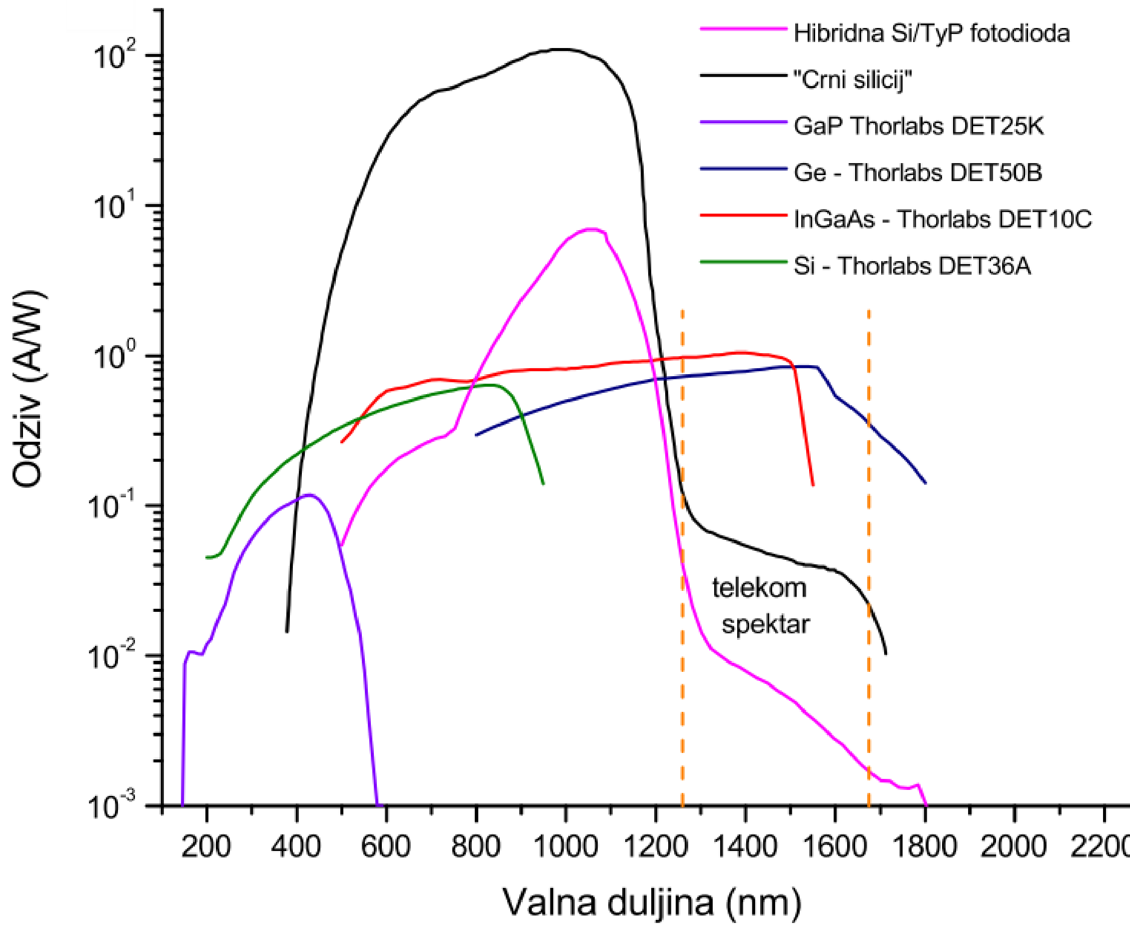
- Up to **700-fold** increase in short-circut photocurrent over planar diodes
- Highest responsivity: **silicon micropyramids/TyP**
- Lower responsivity than competing technologies (black Si, InGaAs)

Advantages:

✓ broader spectral response

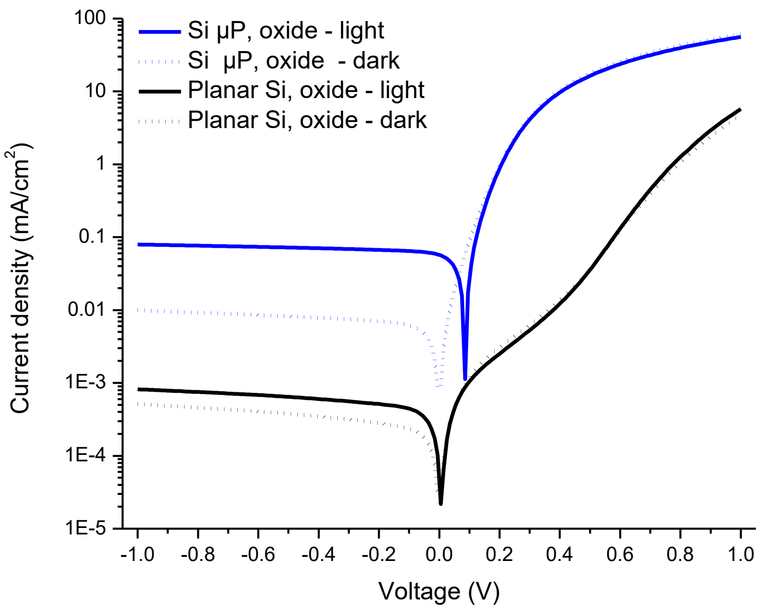
✓ one order of mangitude cheaper manufacture

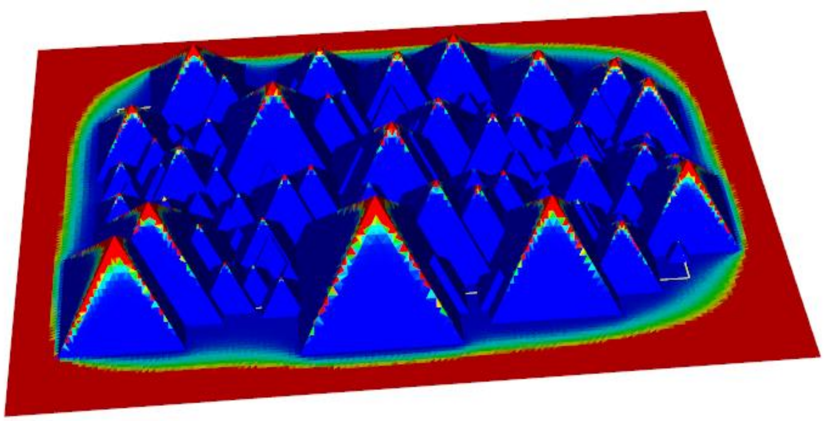
✓ preserved electronic properties of Si



V. Đerek et al., Near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors, Appl. Phys. Lett. 107, 083302 (2015)

Mechanisims of improvement - speculative





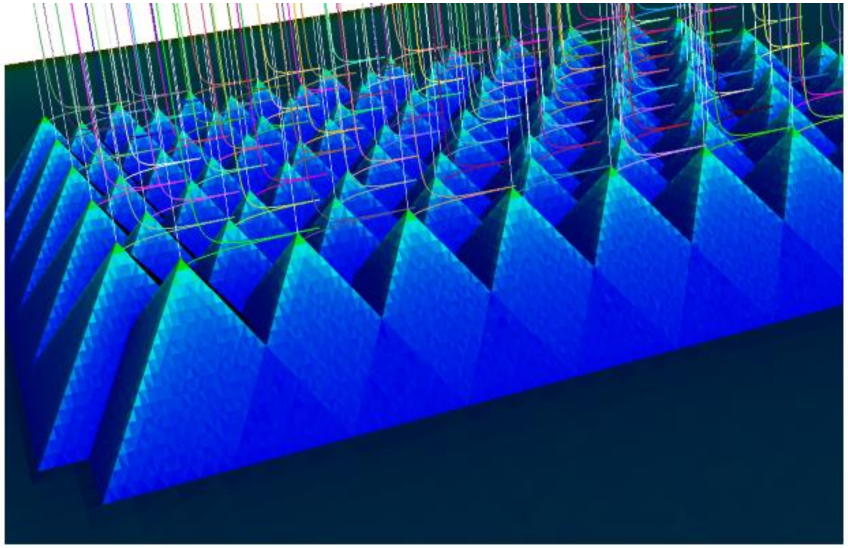
- Largest increase in J_{SC} (x 700) observed on micropyramid-Si with thin (1-3 nm) SiO_2 between
 Si and TyP

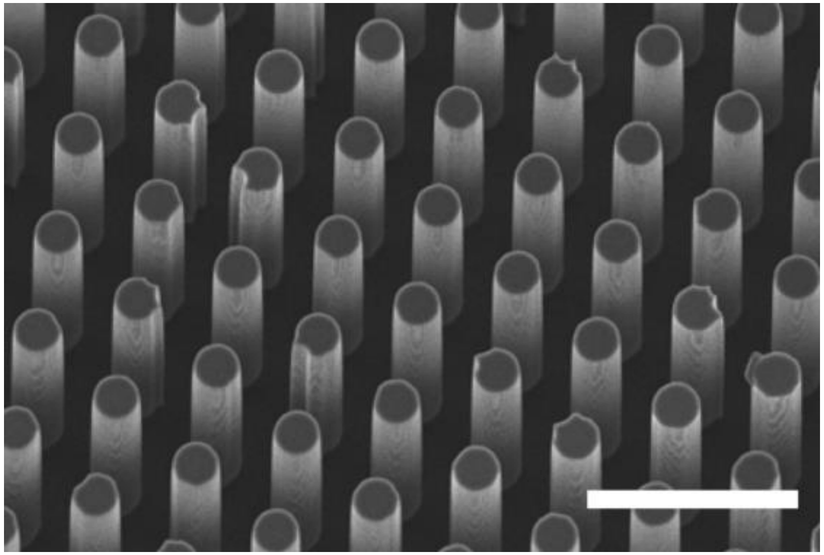
- High current densities possible on pyramid tips due
to Fowler–Nordheim type field electron emission
across the barrier?

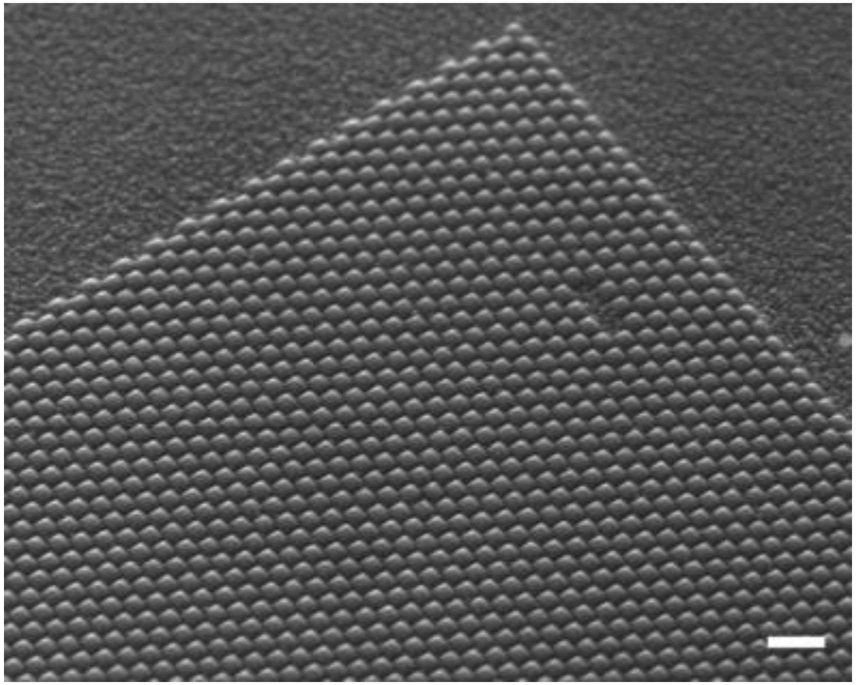
$$J = A\,E^2 e^{-\frac{B\varphi^{\frac{3}{2}}}{E}}$$

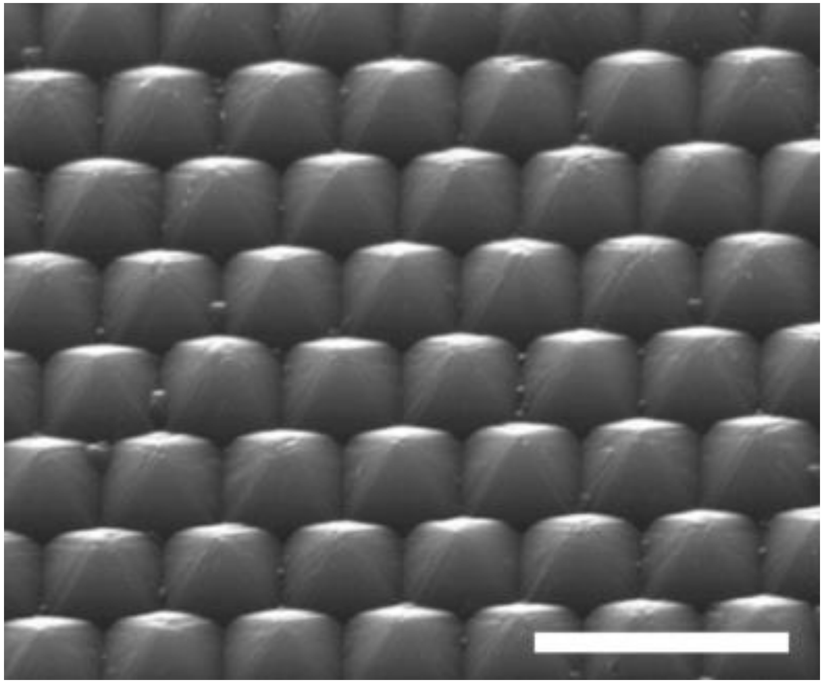
Nordheim-Fowler tunneling current density – strongly dependand on electric field

Regular field of micropiramids









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Hrvatska zaklada za znanost

Thank you!

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