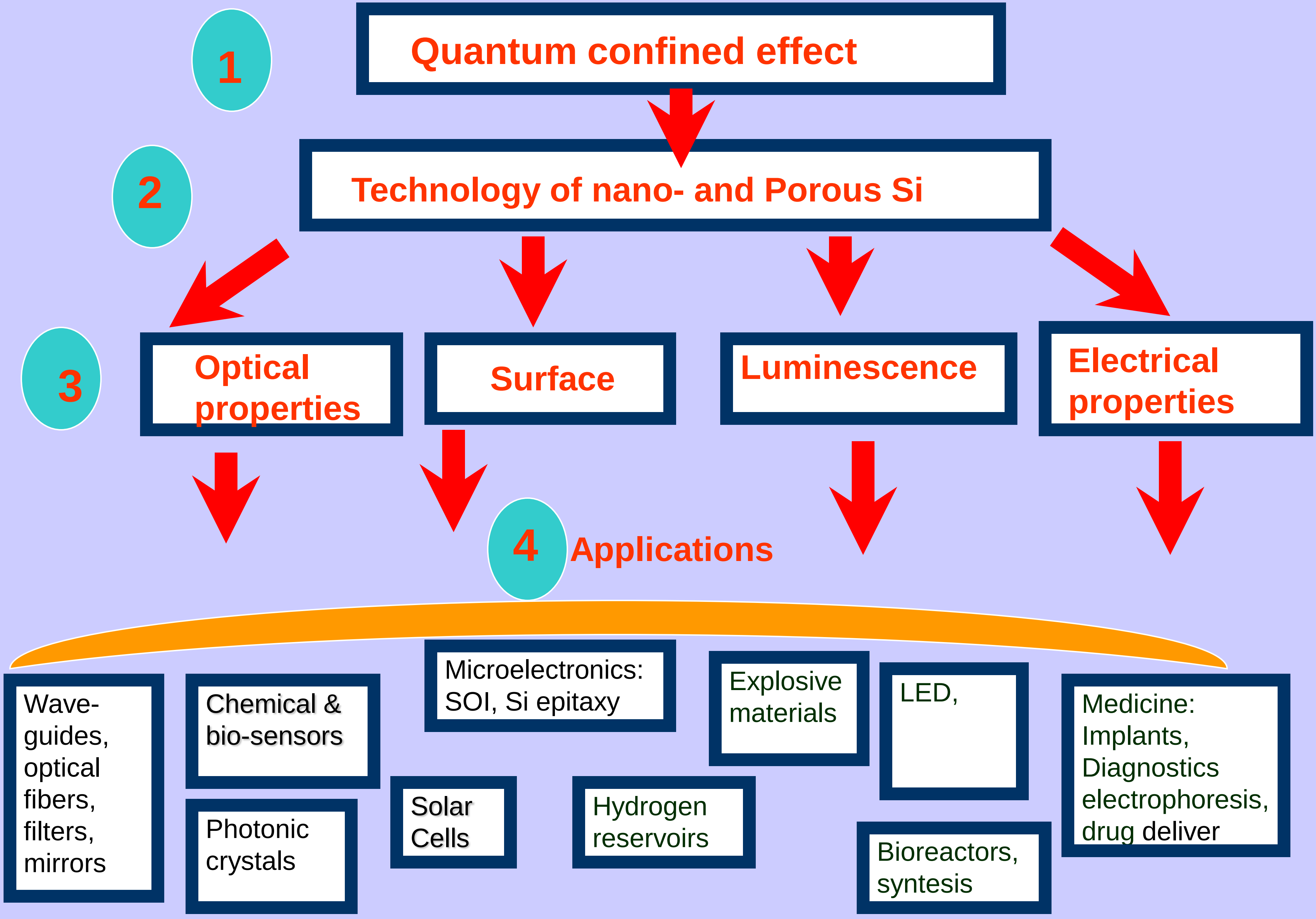
Porous silicon and Si nanoparticles: new photonic and electronic materials

Technologies and physics properties

проф. В.А.Скришевський

OUTLINE

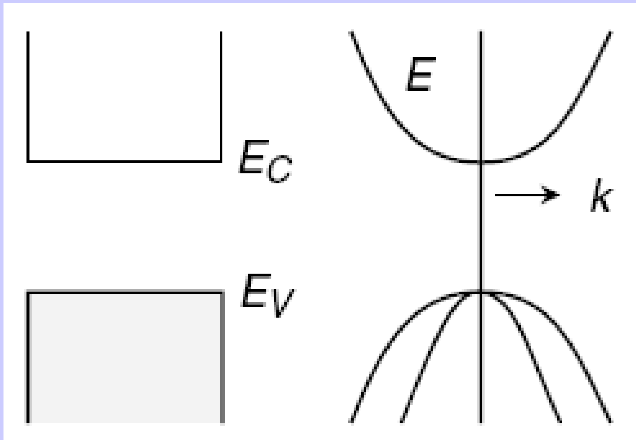

1
Quantum confined effect
2
Technology of nano- and Porous Si
3
Optical properties
Surface
Luminescence
Electrical properties
4
Applications
Wave-guides, optical fibers, filters, mirrors
Chemical & bio-sensors
Photonic crystals
Solar Cells
Microelectronics: SOI, Si epitaxy
Hydrogen reservoirs
Explosive materials
LED,
Bioreactors, syntesis
Medicine: Implants, Diagnostics electrophoresis, drug deliver

Evolution of modern semiconductor physics: *from bulk to nano*

- Band theory + doping
- Effective mass theory

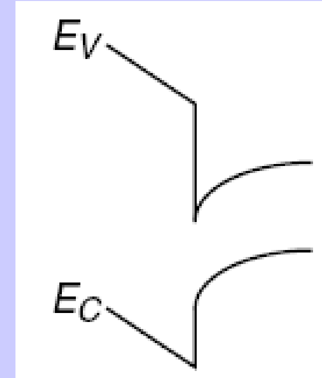
$$\mathbf{p} = \hbar \mathbf{k}$$

$$E = \frac{\hbar^2 k^2}{2m_0}$$



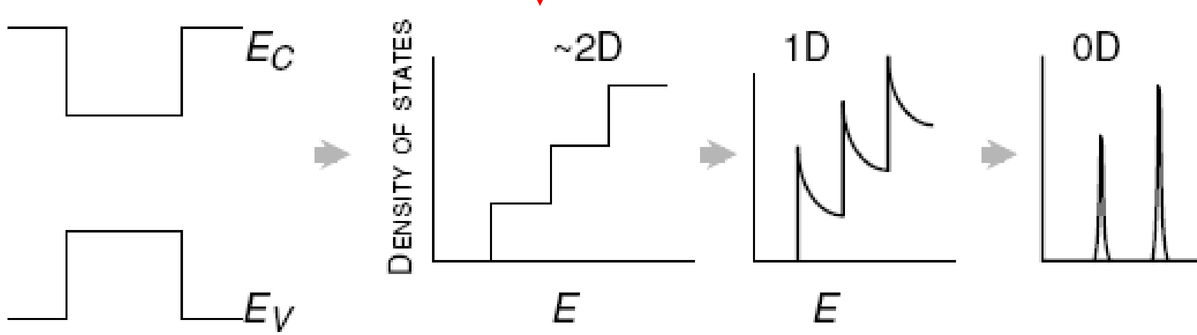
Semiconductor transistor

Semiconductor laser

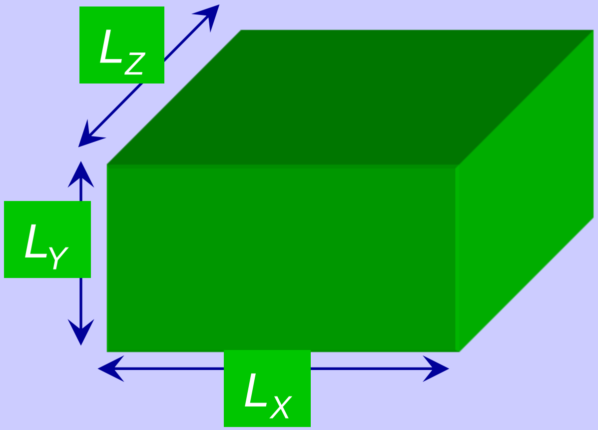


HETEROSTRUCTURES
Heteroepitaxy, strained epitaxy, self-assembly

- carrier confinement
- low-dimensional systems



Why nano ?



Move of electron in periodic field of lattice
Schrodinger equation

$$\left[\frac{-\hbar^2}{2m_0}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = \mathbf{E}\psi(\mathbf{r})$$

$$\psi(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$

Quantum effects for electron in Si:
λ ~ 3 nm

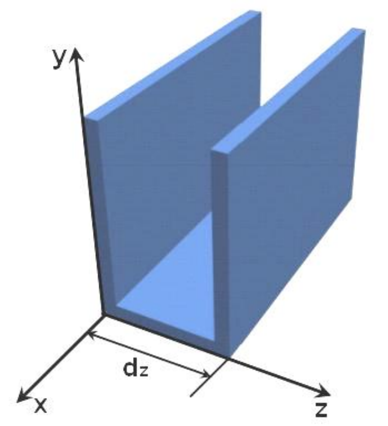
de Broglie wavelength (λ) – quantum phenomena

$$\lambda \approx L_i$$

Geizenberg equation

$$\lambda = \frac{h}{p} = \frac{h}{m^* \upsilon} \qquad m_e^* \sim 0.2 m_0$$

Quantum confined effect



$$V(z) = \begin{cases} 0, & 0 \le z \le d_z \\ \infty, & \text{autrement} \end{cases}$$

Quantum well

Figure 1. 1 *Modèle d'un puits quantique infini : l'électron est confiné dans la direction z, sur une épaisseur de largeur d_z.*

$$E = E_n^{\infty} + \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2\right) \qquad E_n^{\infty} = \frac{\hbar^2}{2m^*}\left(\frac{n\pi}{d_z}\right)^2, \qquad n \in N$$

Quantum wire

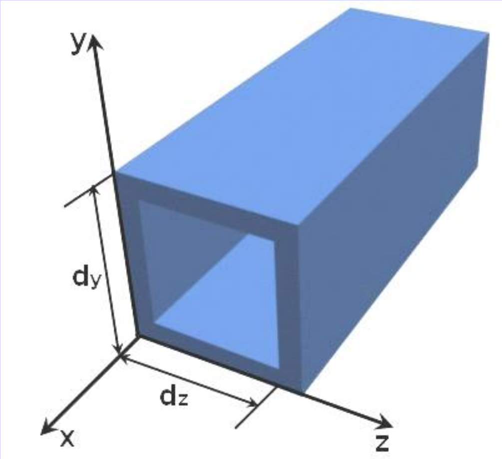


Figure 1. 1 *Modèle de fil quantique infini : l'électron est confiné dans les directions z et y.*

$$E = \frac{\hbar^2\pi^2}{2m^*}\left[\left(\frac{n_y}{d_y}\right)^2 + \left(\frac{n_z}{d_z}\right)^2\right] + \frac{\hbar^2 k_x^2}{2m^*}$$

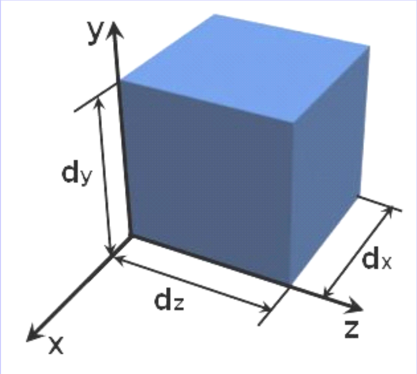


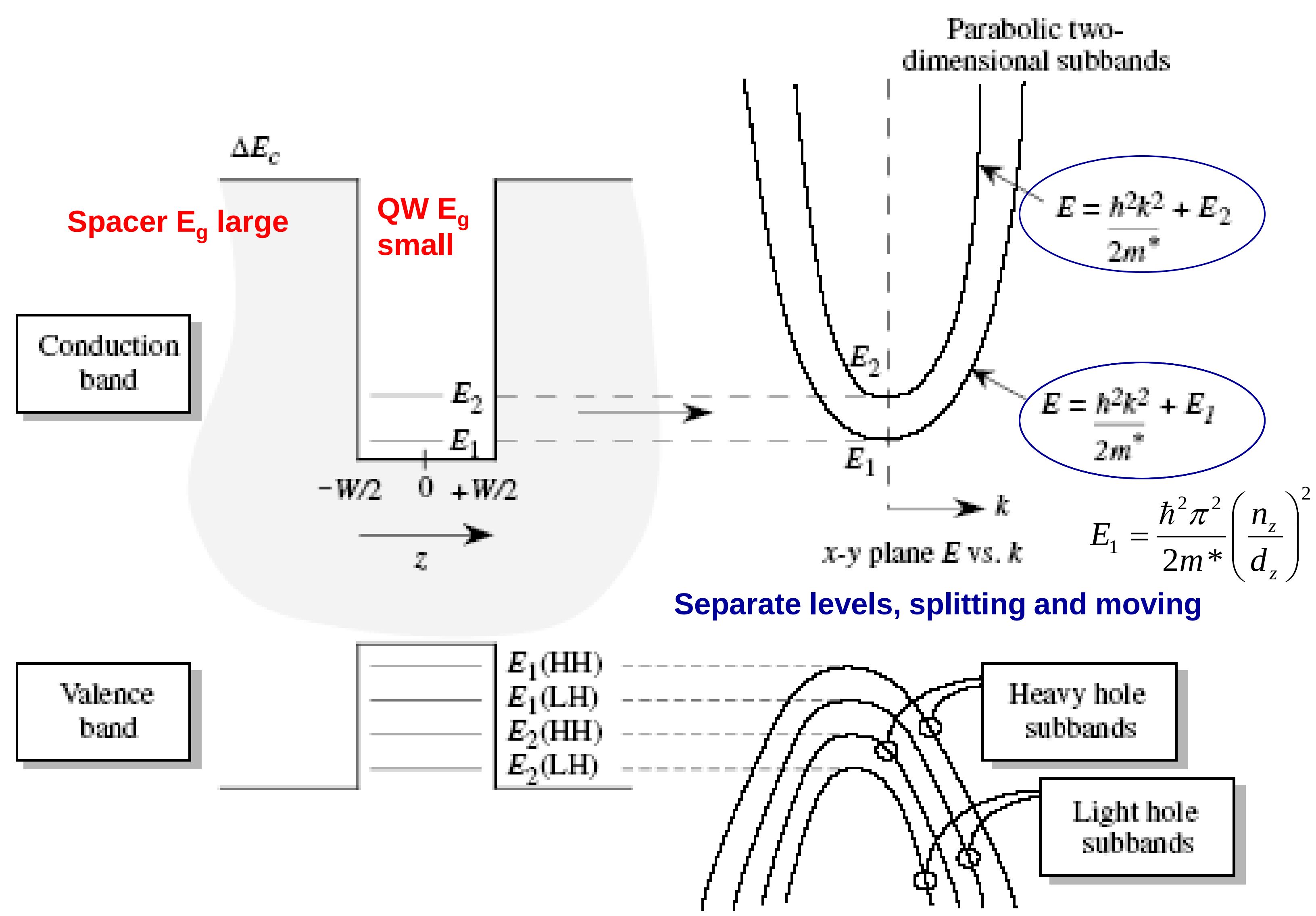
Figure 1. 1 *Modèle de boîte rectangulaire : l'électron est confiné dans trois directions.*

$$E = \frac{\hbar^2\pi^2}{2m^*}\left[\left(\frac{n_x}{d_x}\right)^2 + \left(\frac{n_y}{d_y}\right)^2 + \left(\frac{n_z}{d_z}\right)^2\right]$$

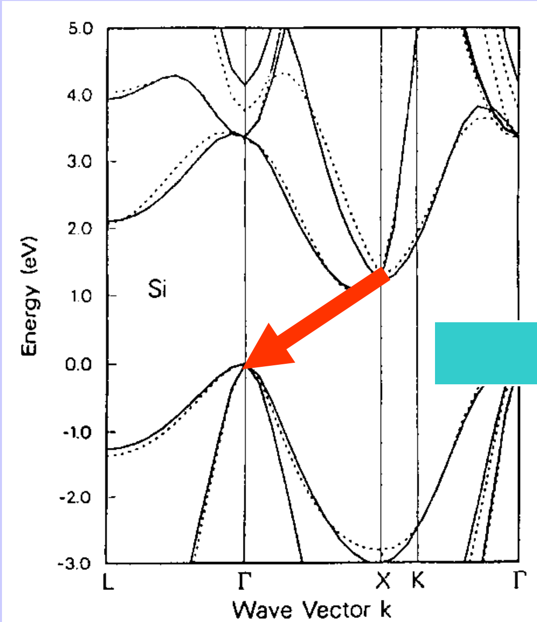
Quantum dot

Electronic spectra – series of levels like in atom !

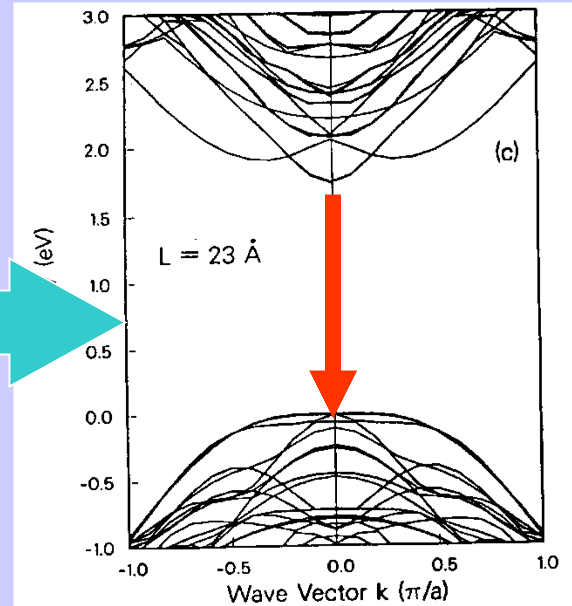
Quantum well



Band structure of nano-Si: two possibilities



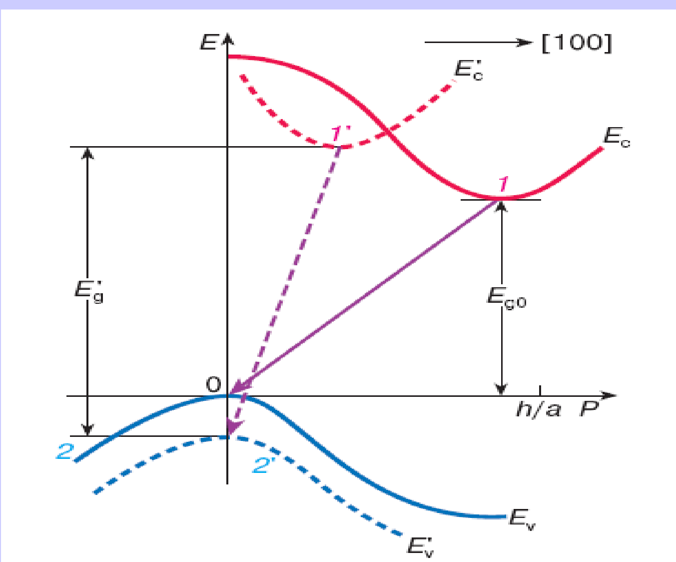
Band structure of bulk Si



Si quantum wires , L= 2.3 nm

Si Qwires:
Indirect- direct band gap transformation,
E_g increases

Si Qdot:
Indirect band gap,
E_g increases,
Electron-wall collision



$$E_c - E_v = h\nu$$

law of conservation of energy

$$\Delta\hbar k >> \frac{\hbar\omega}{c}$$

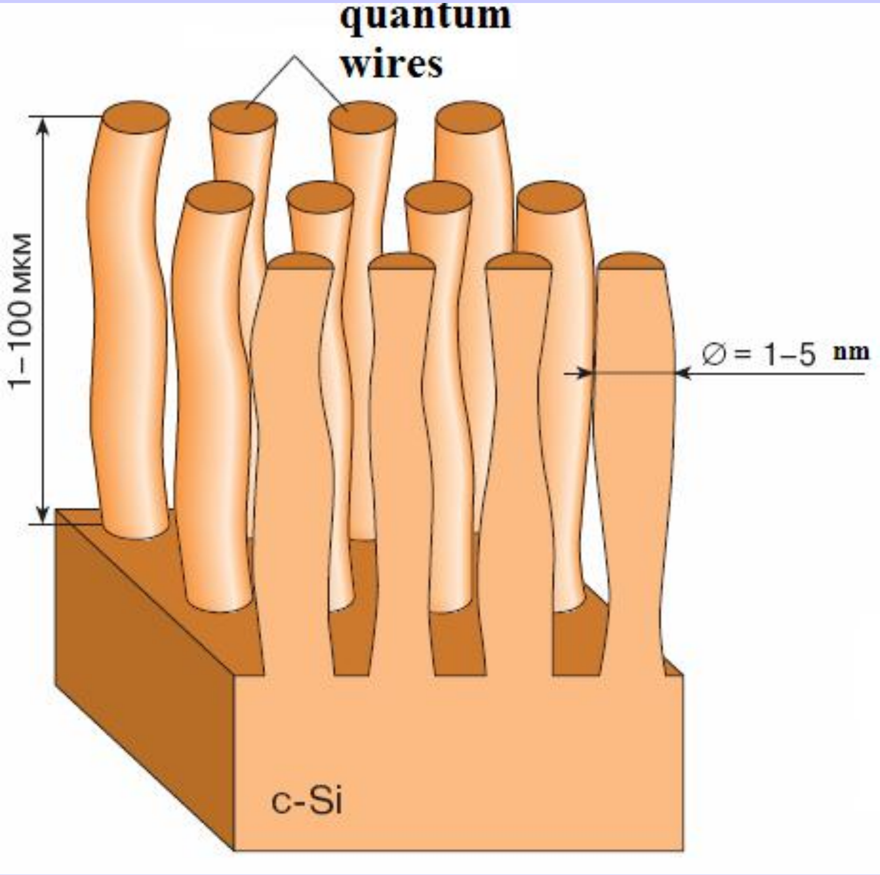
$$\Delta\hbar k = \frac{\hbar\omega}{c} + mv_{collision}$$

law of conservation of impulse in indirect semiconductor
(need phonon mv_{ph})
and QW (collision with well)

Nomenclature of pores

(International Union of Pure and Applied Chemistry, IUPAC) standard

Micropore, with pore diameters and pore distances ≤2 nm.
Mesopores, with geometries in the 2-50 nm region.
Macropores, with geometries in the >50 nm region.



Technology of nano- and Porous Si

Criteria for choice of pore formation methods

Preparation Methods:

High quality
Expensive

lasers, LED, FET,…

Targets
advantages and disadvantages

Low -cost
Nongomogeneous
Mass production

Sensors, hydrogen storage, explosive materials,…

- Ion implantation
-Low-pressure CVD
- Annealing of induced precipitation from SiO_2 layers
- Laser ablation of Si target
- Laser pyrolysis of silanes

-Electrochemical anodization
-Stain etching

High Si nanotechnologies

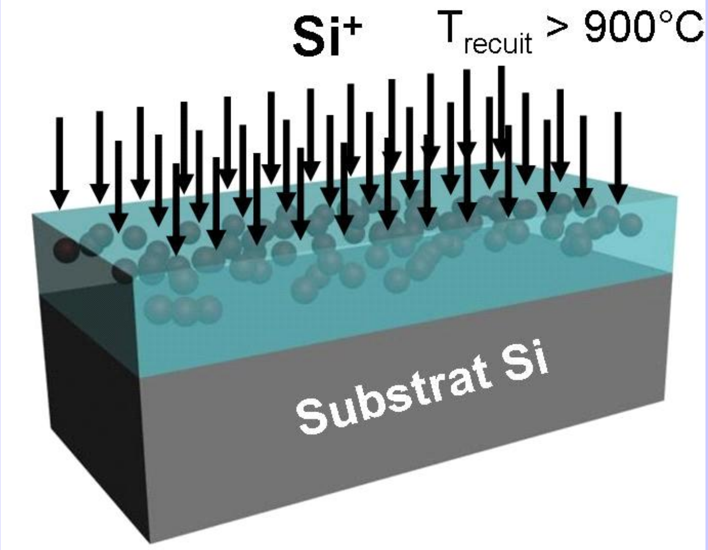


Schéma du processus de fabrication de nanostructures de Si par implantation ionique

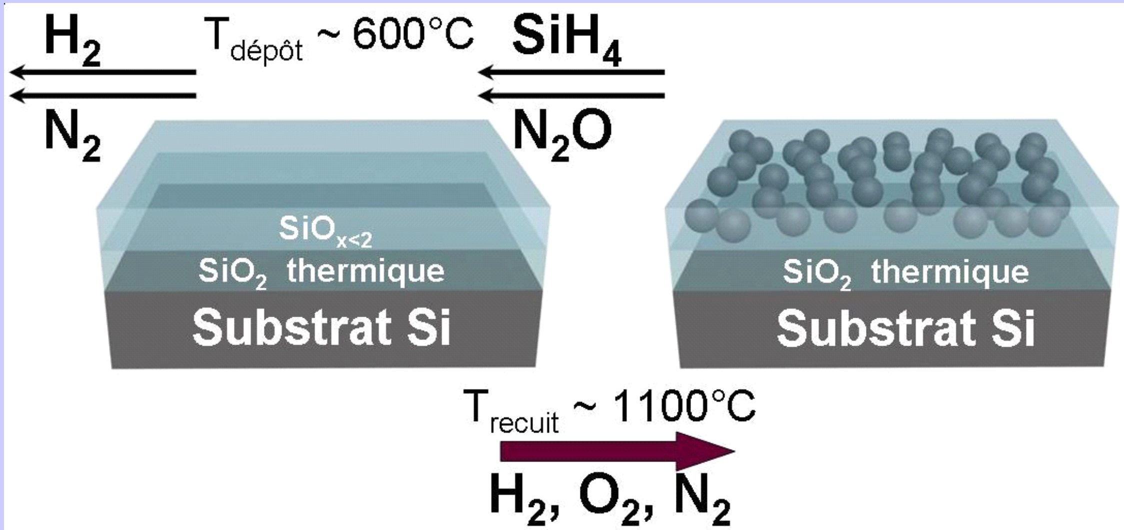
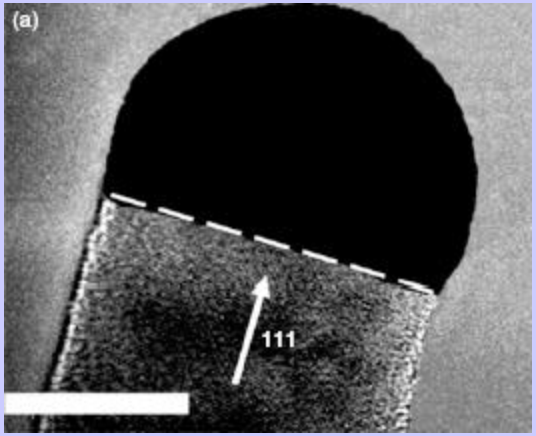
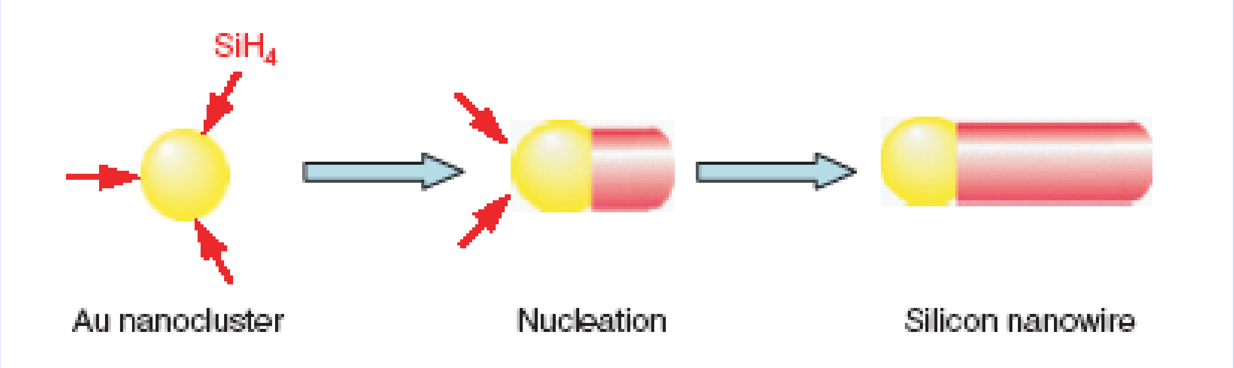


Schéma du processus de fabrication de nanostructures de Si par LPCVD : précipitation dans une couche d'oxyde.



scale bar 20 nm



A nanoclaster catalysed SiNW growth by CVD

High nano Si technologies

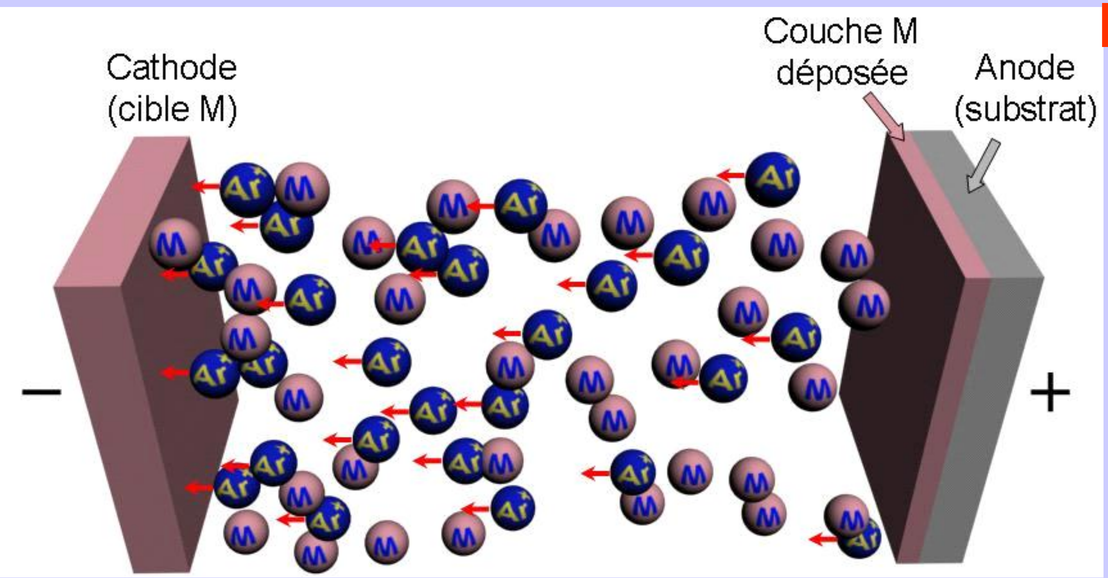


Schéma de principe de la pulvérisation cathodique.

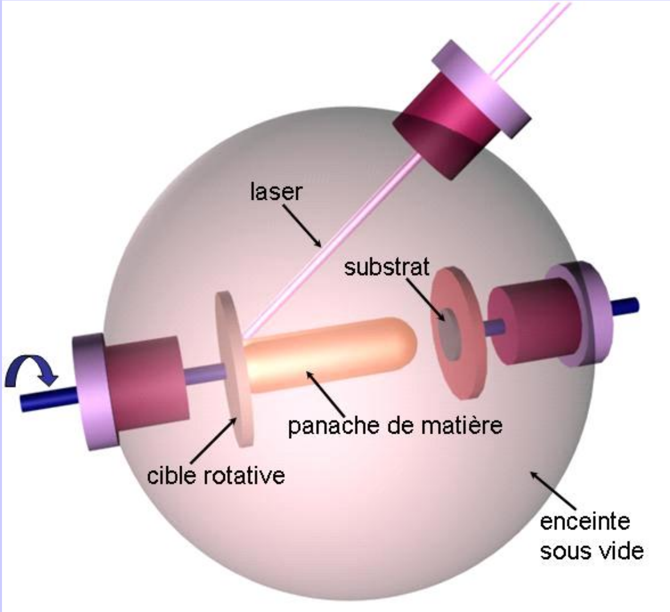


Schéma de principe de l'ablation laser.

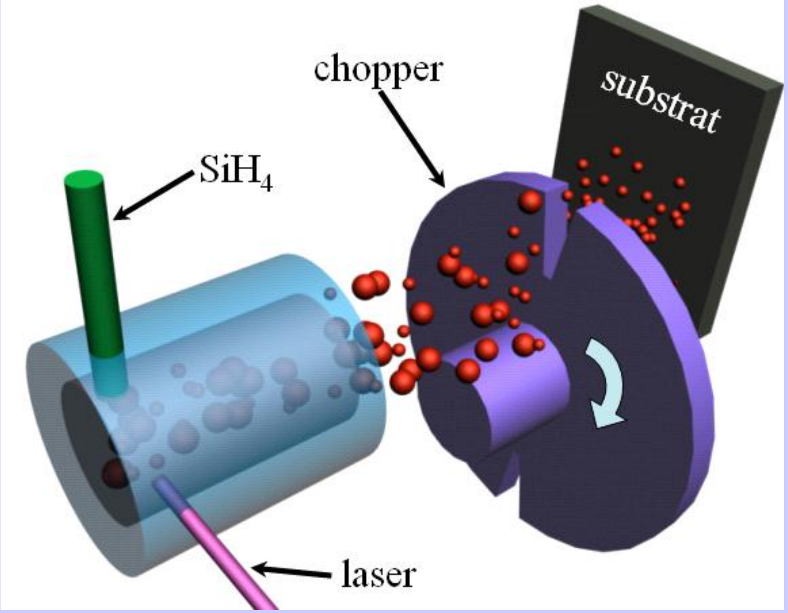
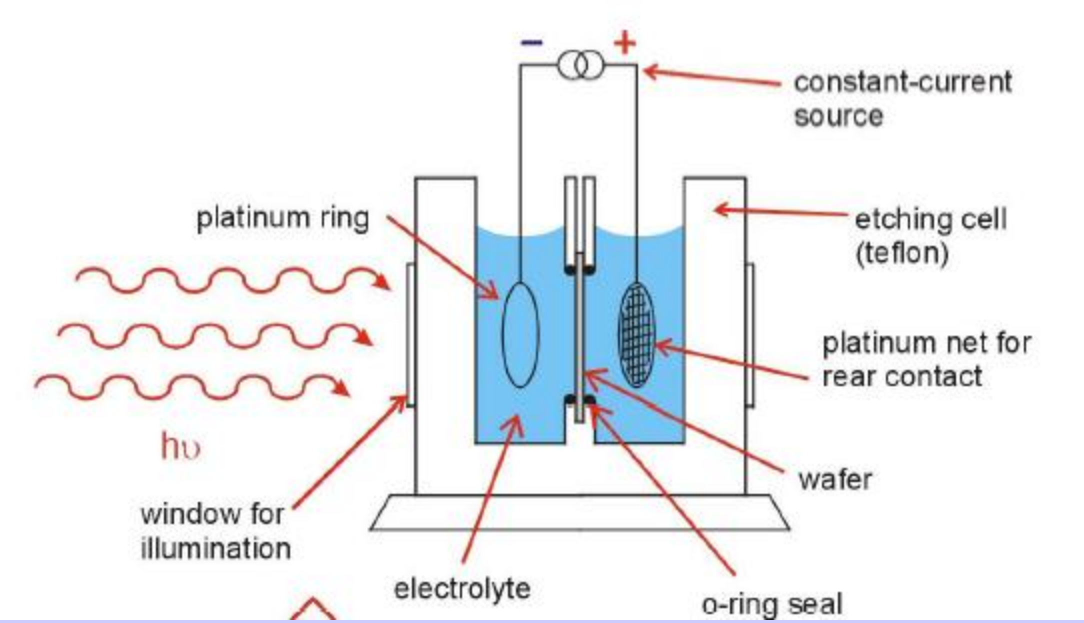


Schéma de principe du pyrolyse laser.

Electrochemical formation

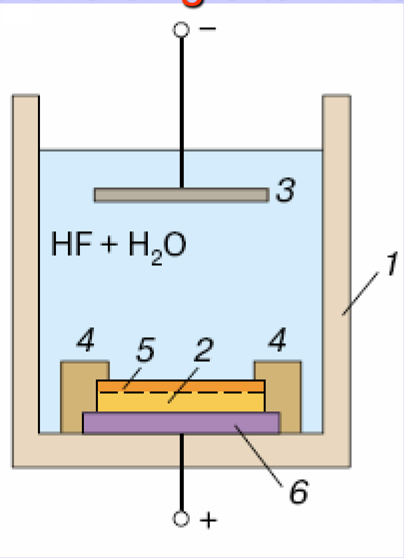


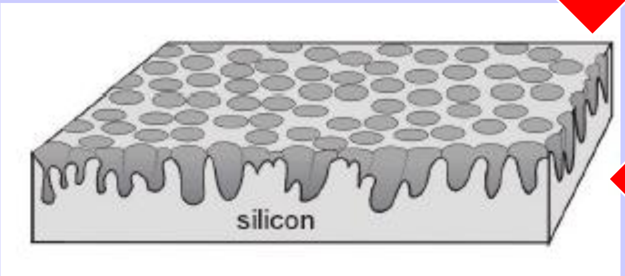
Key parameters:

Si surface- hydrophobic!

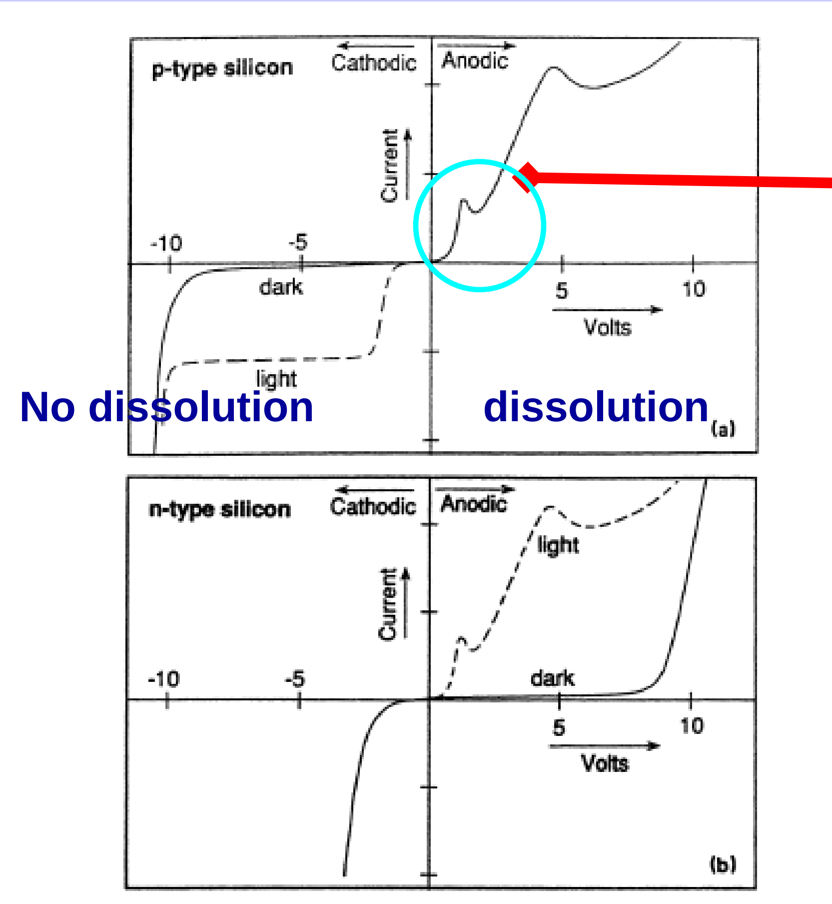
- Electrolyte type (C_2H_5OH for wettability, org. for homogeneity)
- HF concentration (<50%)
- Doping level (n, n+, p, p+)
- Illumination state
- Anodical current (constant I mode=control porosity)
- Cell: H_2 bubble remove!

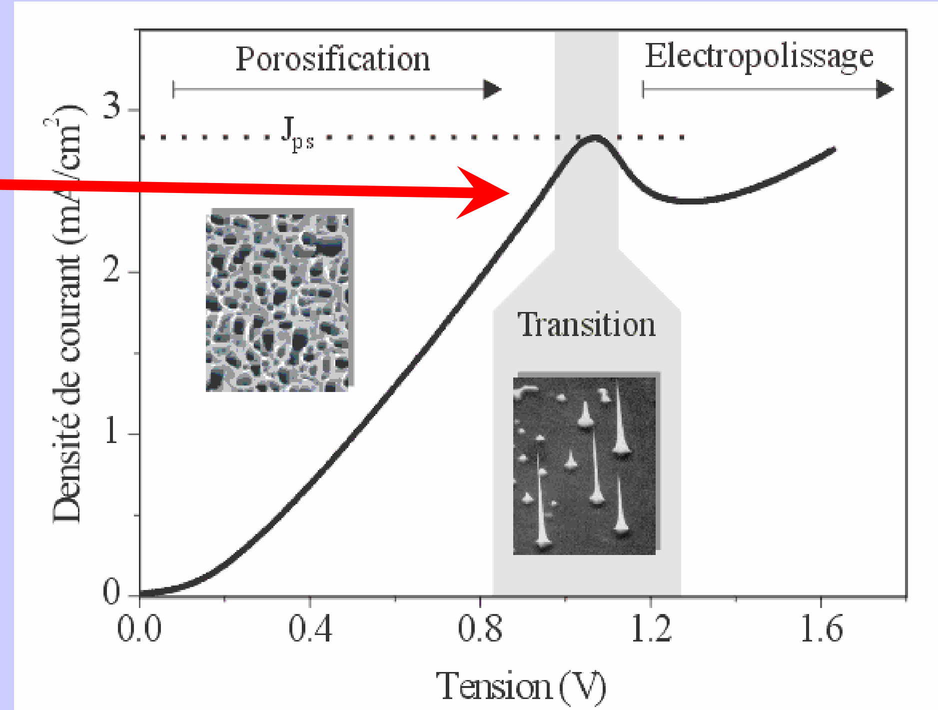
Double and single tank cells





Electrochemical formation





$$J = J_0\left[e^{\frac{eV}{nkT}} - 1\right]$$

(Schottky diode behavior)
Change from electronic to ionic current due to specific redox reaction on Si surface

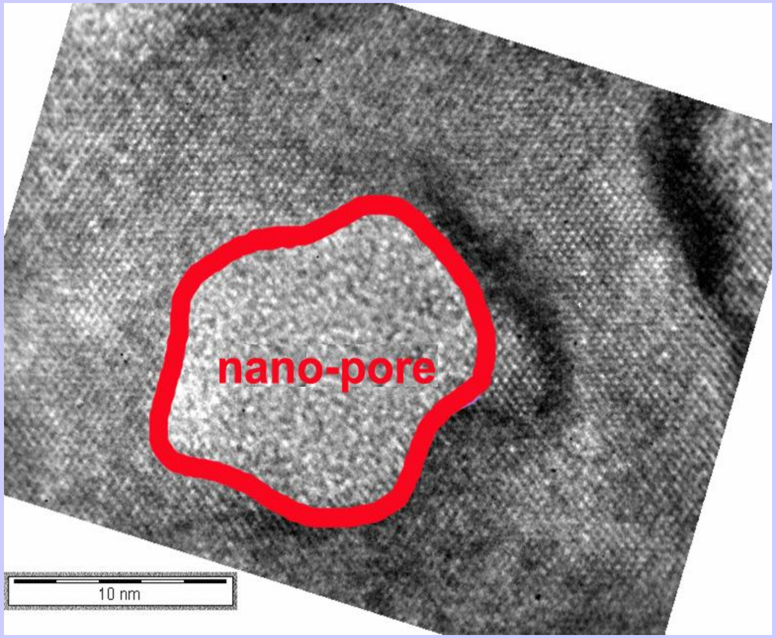
Dissolition chemistry:

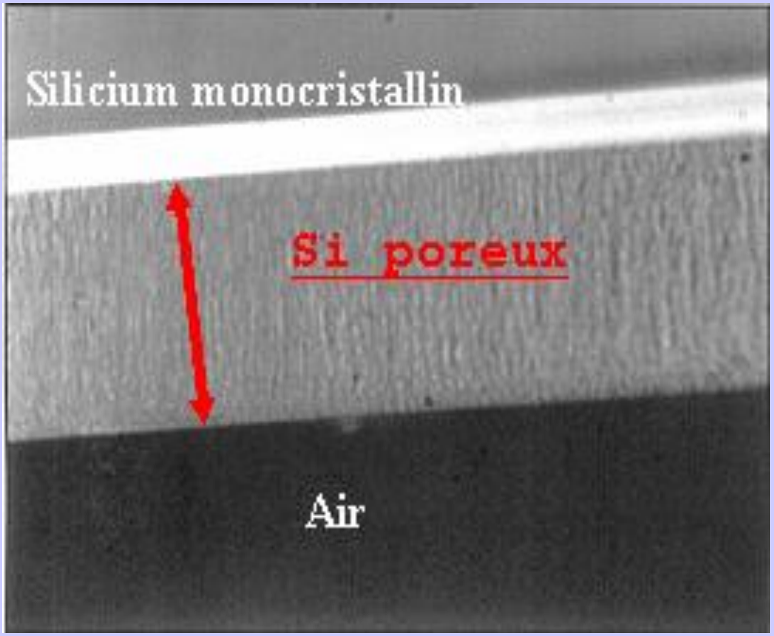
Pore formation $Si + 6HF \rightarrow H_2SiF_6 + H_2 + 2H^+ + 2e^-$

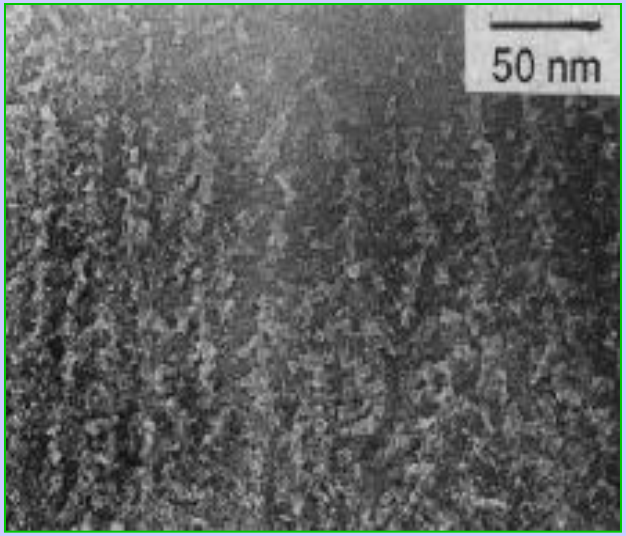
Electropolishing $Si + 6HF \rightarrow H_2SiF_6 + 4H^+ + 4e^-$

O.Bisi, S.Ossini, L.Pavesi, Surf.Sci.Rep, 38(2000)1

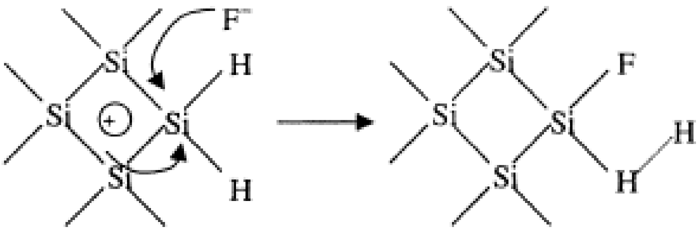
Pore formation domain



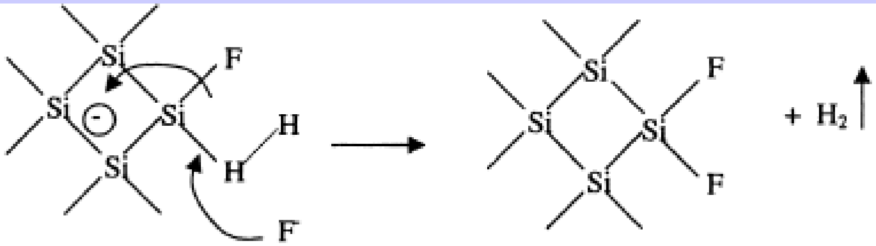




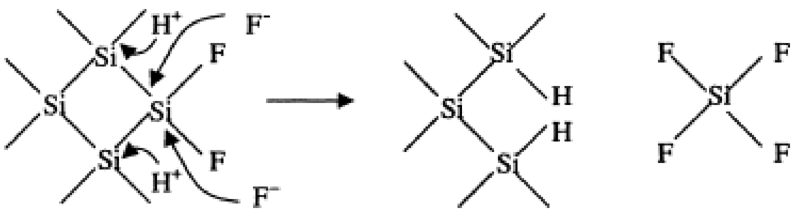
Mechanism of Si dissolutions



Hole injection and attack on a Si-H bond by a fluoride ion



Second attack by a fluoride ion with hydrogen evolution and electron injection into the substrate



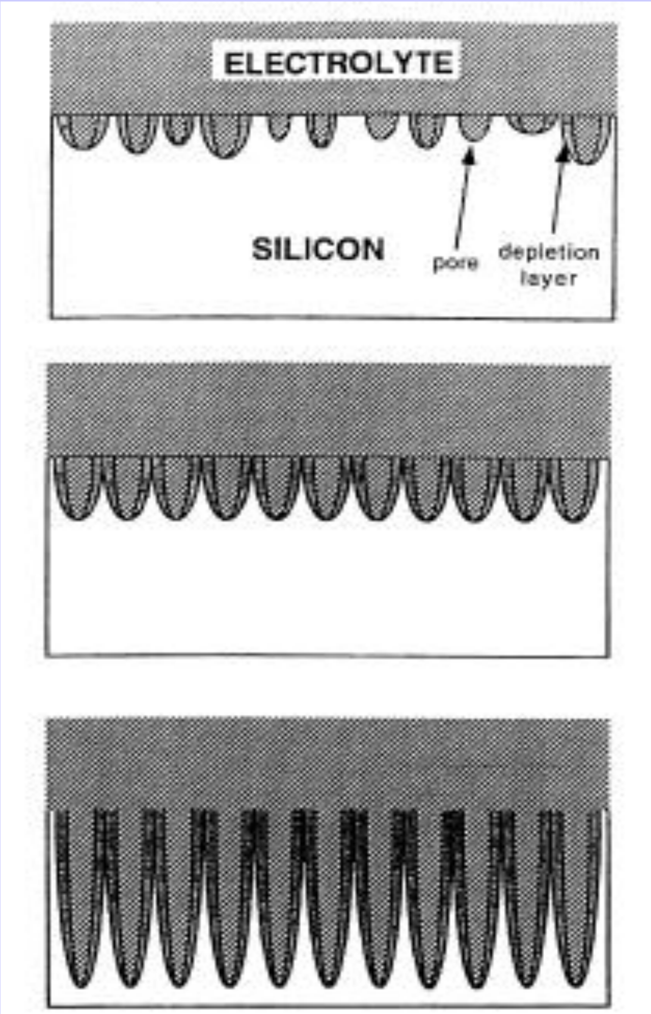
HF attack to the Si-Si backbonds. The remaining Si surface atoms are bonded to the H atoms and a silicon tetrafluoride molecule is produced

To dissolve 1 Si atom:
$2h^+ + H_2O$.
One H_2 molecule forms on the surface
Process of replacing:
Si-H $\rightarrow$ Si-OH$\rightarrow$Si-F &
settling-out of SiF_4

Silicon dissolution scheme, Lehmann and Gosele

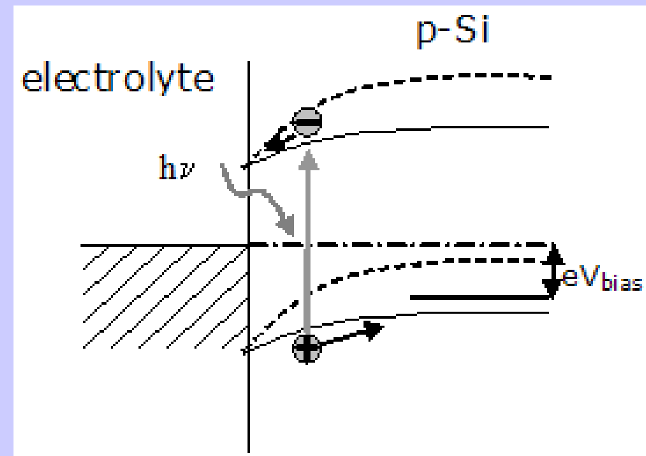
The silicon tetrafluoride reacts with two HF molecules to give H_2SiF_6 and then ionizes.

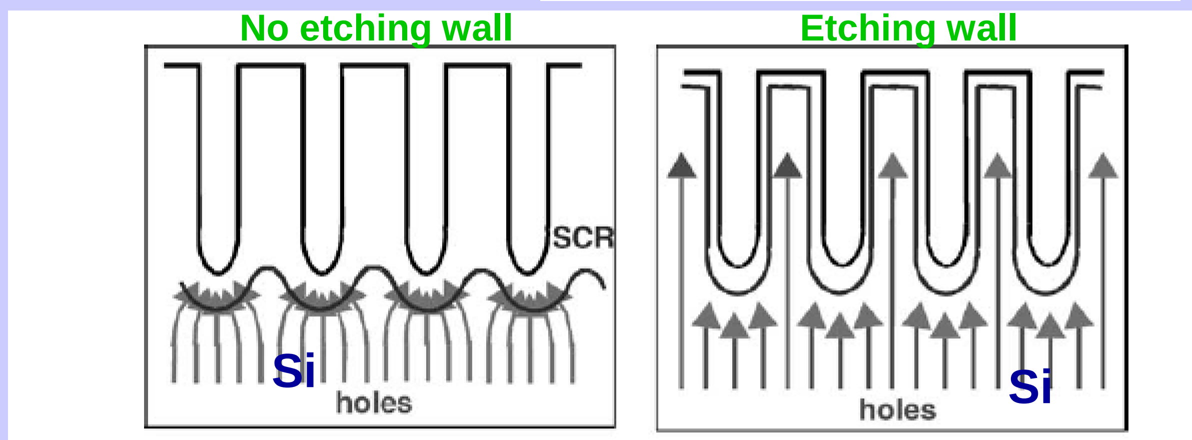
Why pore formation?



-There are initial roughness or pores
-A surface region depleted in mobile carriers at Si/electrolite interface (Schottky contact).
-The thickness of depleted region depends on doping level.
-The size of pore is related both to the depletion layer and mechanism of charge transfer
(breakdown, tunneling, overcome the barrier PS-Si…)

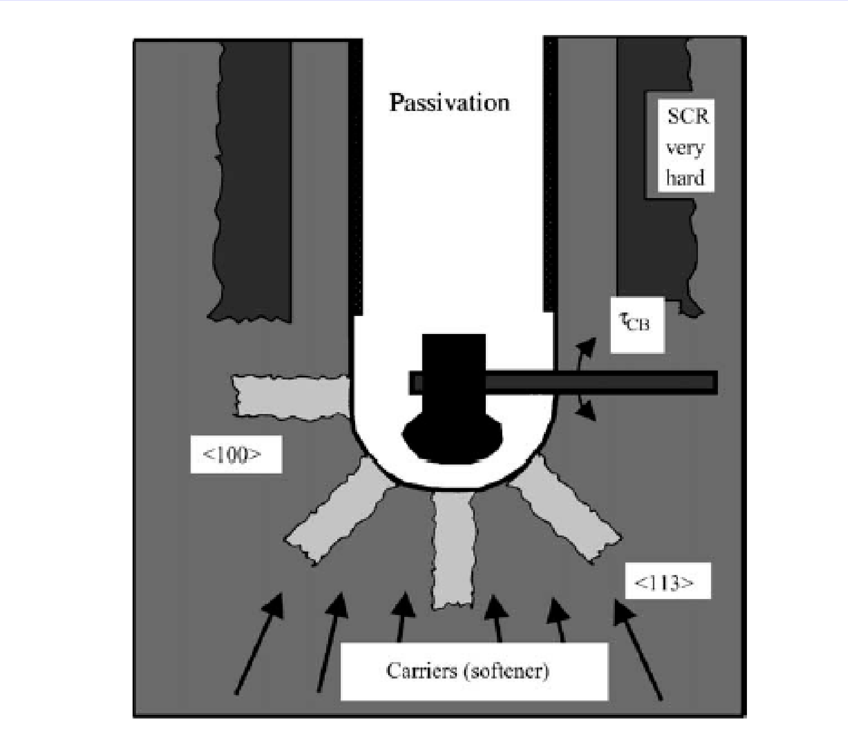
$$x_0 = \sqrt{\frac{2\varepsilon\varepsilon_0 e\psi_s}{e^2 N_A}}$$



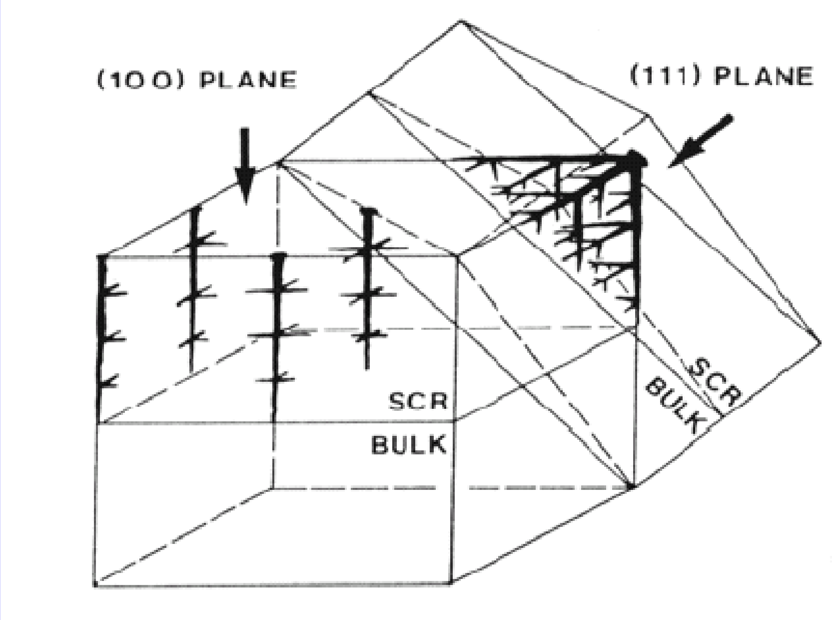


Large SCR and small SCR

Hummer model of pore formation

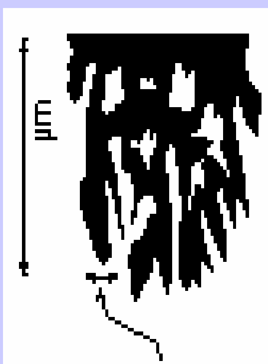


Si is always removed in patches corresponding to the domain size of system!

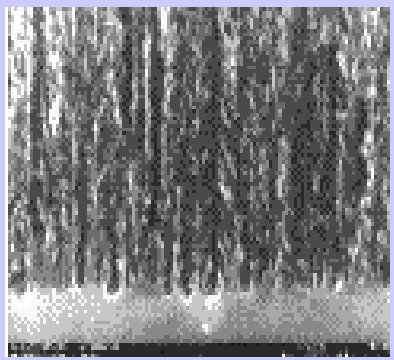


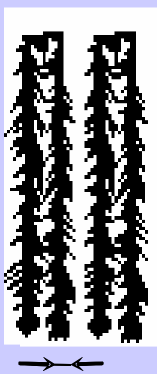
Pore formation region

Nano-porous Si P-type	Meso-porous Si P+-type	Macro-porous Si N-type + light
- « nano-sponge » morphology	- « nano-column » morphology	- « nano-wells » morphology
- nanocristallites sizes: **1 - 5 nm**	- column width: **5 - 20 nm**	- inter-well space: **0.1 - 1 µm**



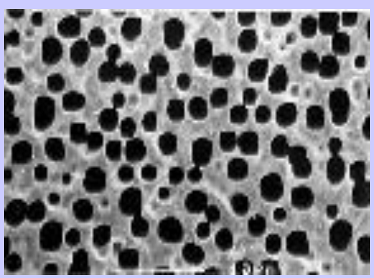
<5 nm



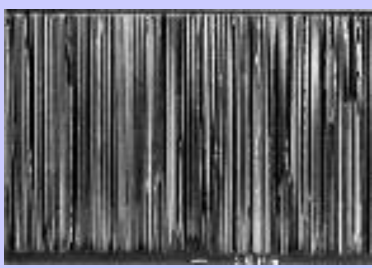


5 nm

Top view



Cross-section



Bomchil *et al.*, Appl. Surf. Sci. **65/66**, (1993) pp. 394-407

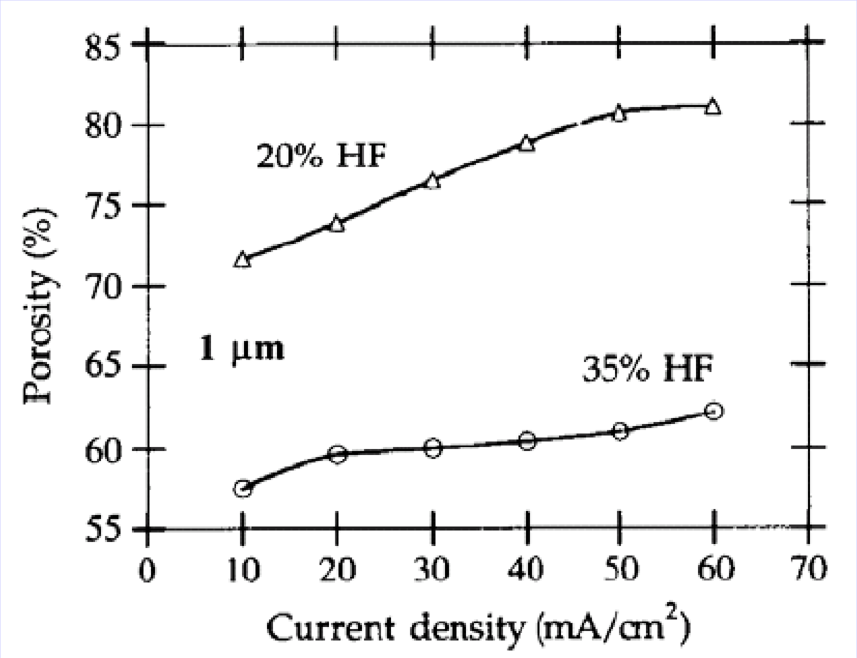
WWW-Server, Faculty of Engineering Christian-Albrechts University of Keil

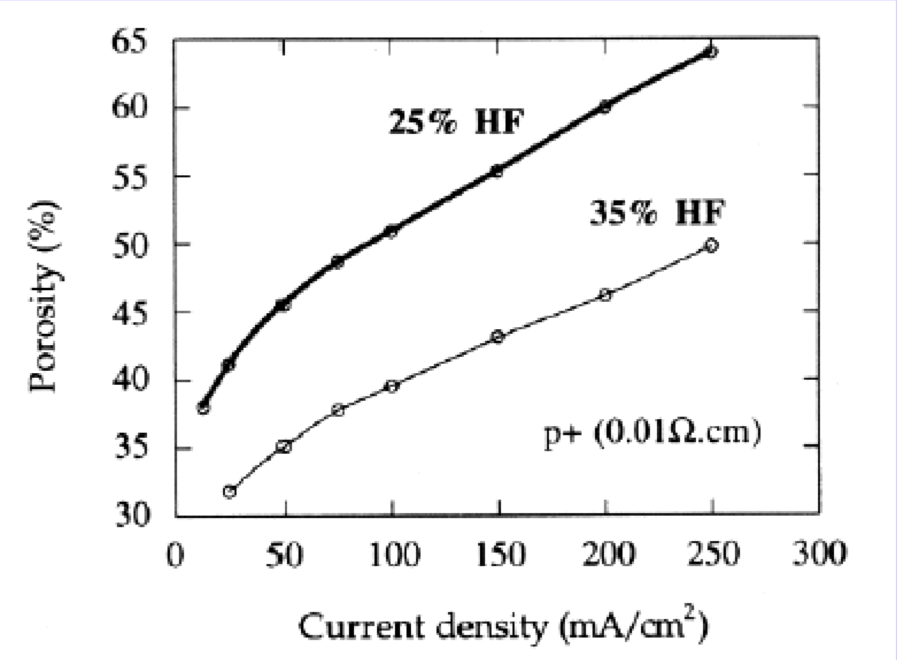
WWW-Server Max-Planck-Institut für Mikrostrukturphysik Halle, Germany

Porosity

Nano-porous Si P-type

Meso-porous Si P+-type



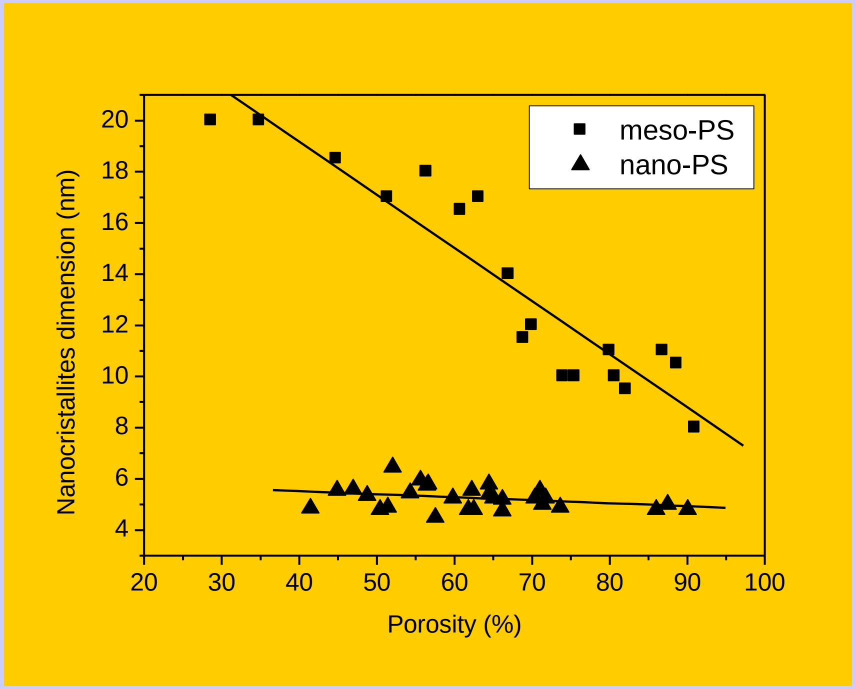


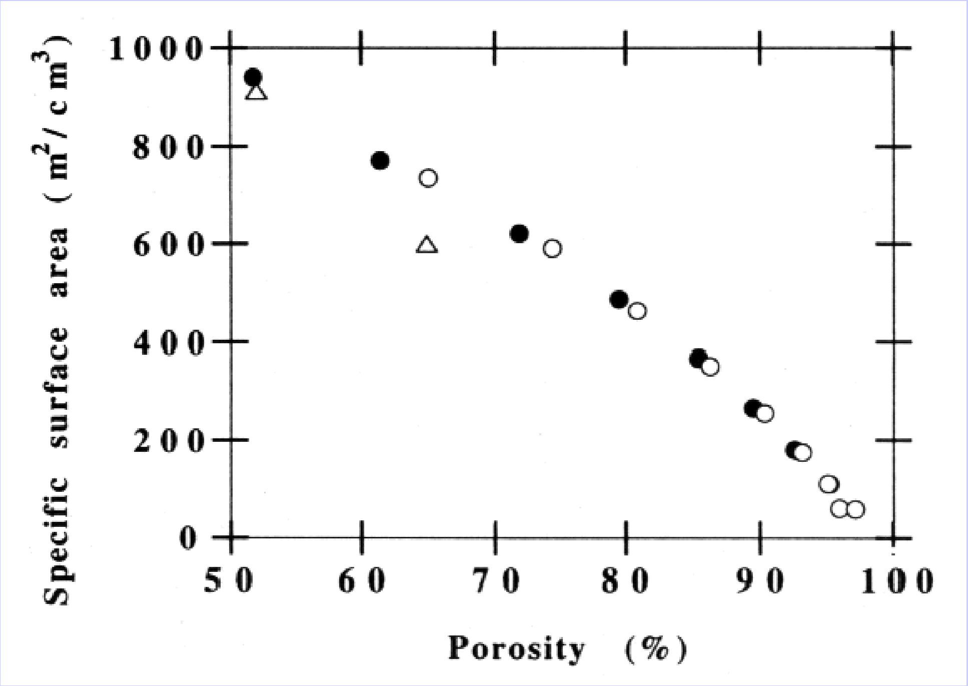
Porosity

$$P = \frac{V_{pore}}{V_{pore} + V_{Si}} = \frac{m_1 - m_2}{m_1 - m_3}$$

m_1- weight before anodization, m_2- after, m_3- after rapid dissoluion of PS in KOH

Porosity, particles dimension, specific surface



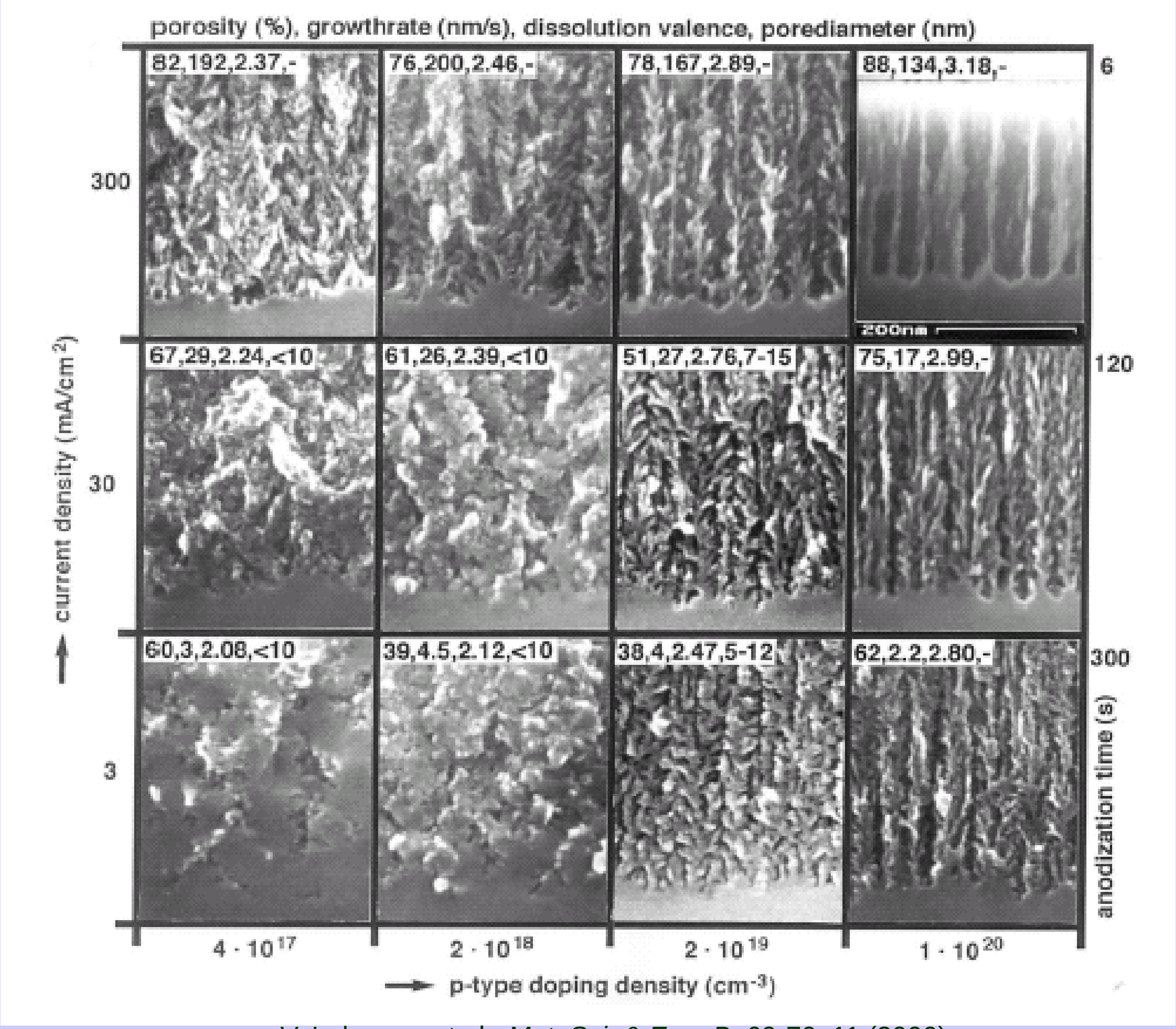


Specific surface

Nano-PS (sponge type)
meso-PS (column type)

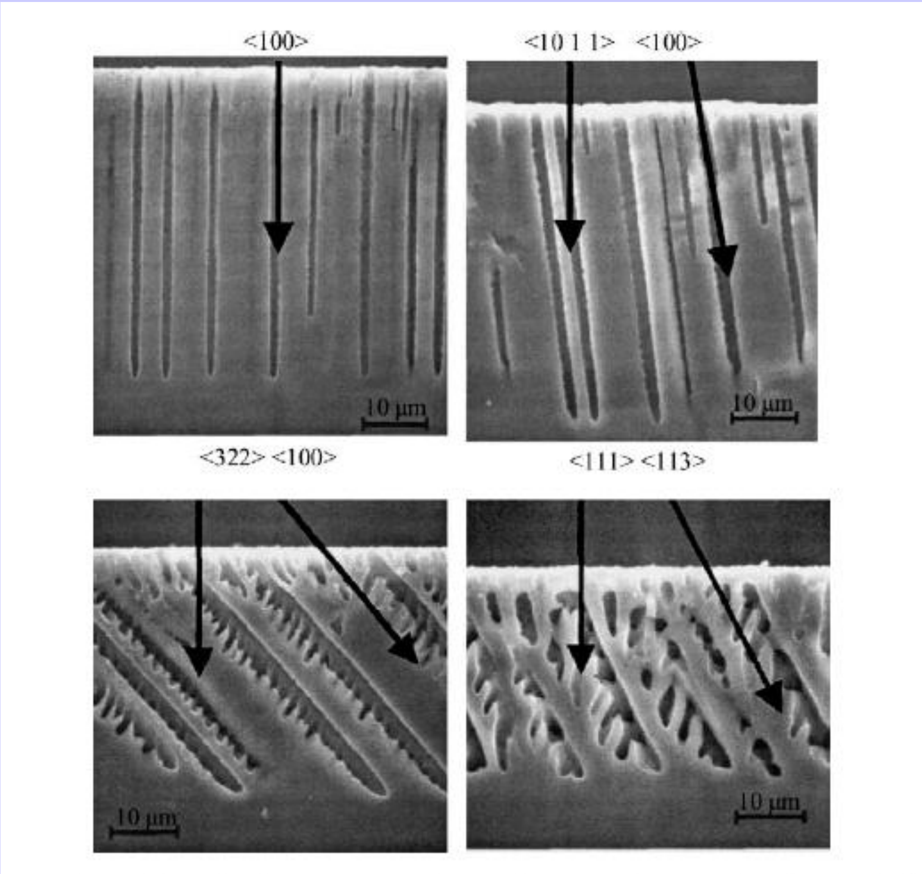
Particle dimension vs Porosity

Pore formation region (current & doping level)

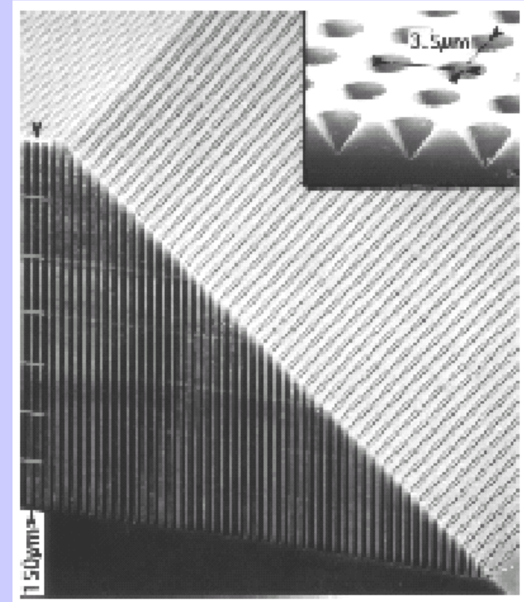


V. Lehmann et al., *Mat. Sci. & Eng. B*, 69-70, 11 (2000)

Macrpores



V. Lehmann, Kluwer Acad. Publ., 1, (1993)



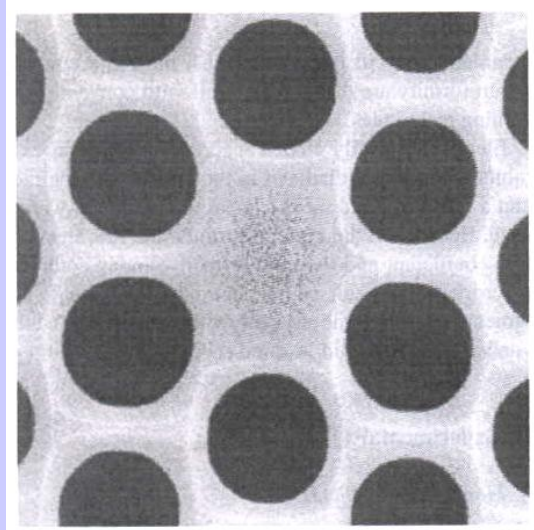
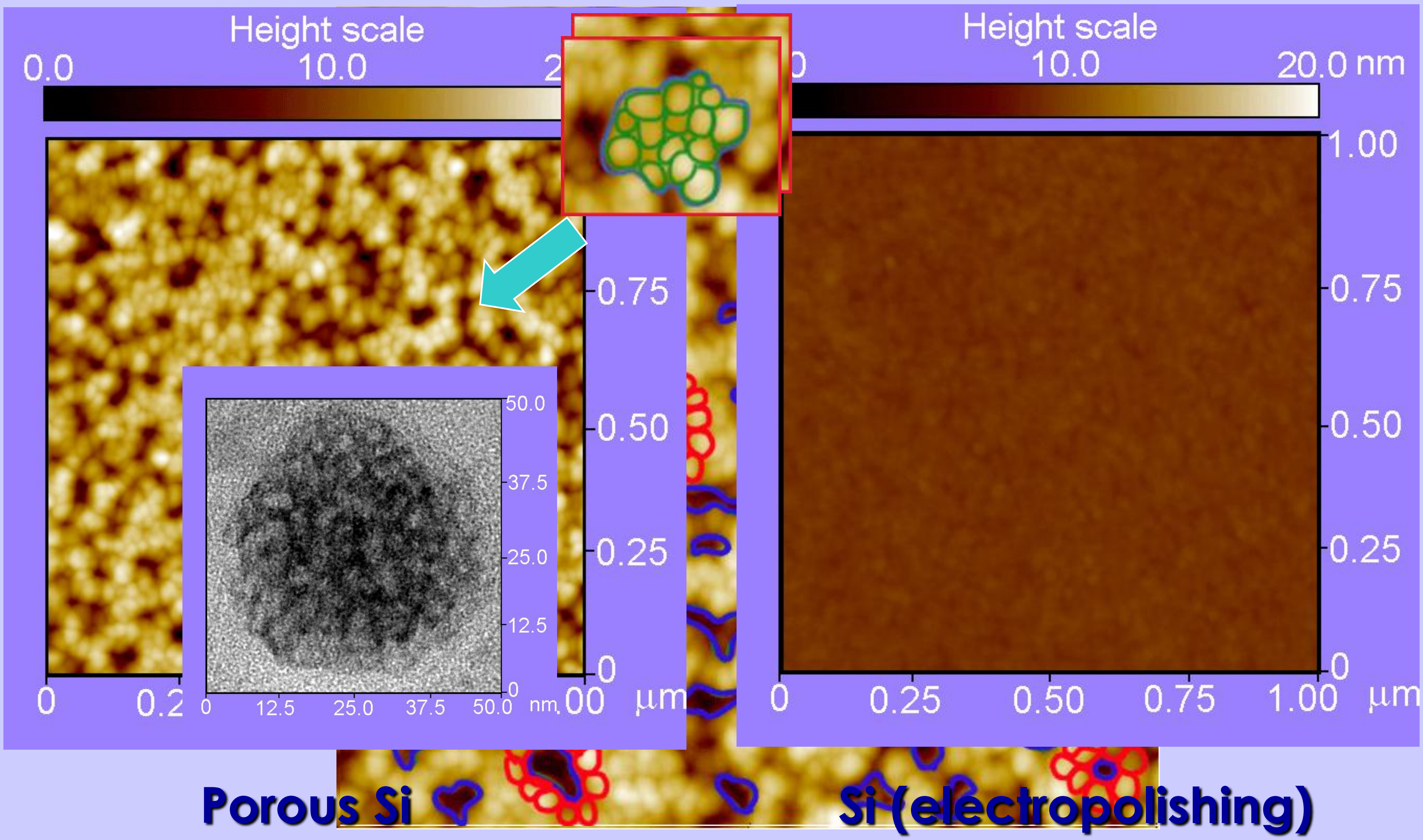


Figure 1. SEM image of the region around a missing etch pit after electrochemical pore growth and subsequent pore widening by oxidation/etching steps. The distance between the pores is 1.5 μm, pore diameters are 1.15 μm.

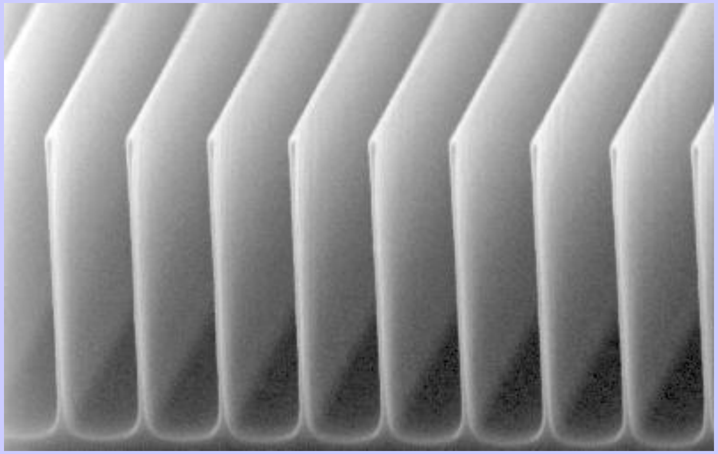
Nano-porous nanostructures



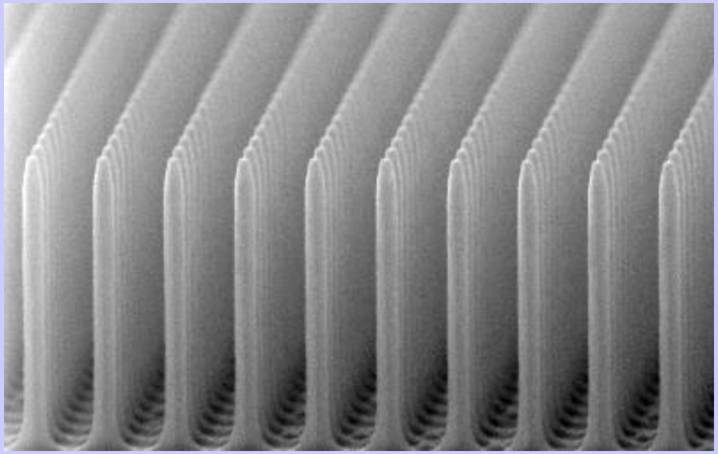
Porous Si

Si (electropolishing)

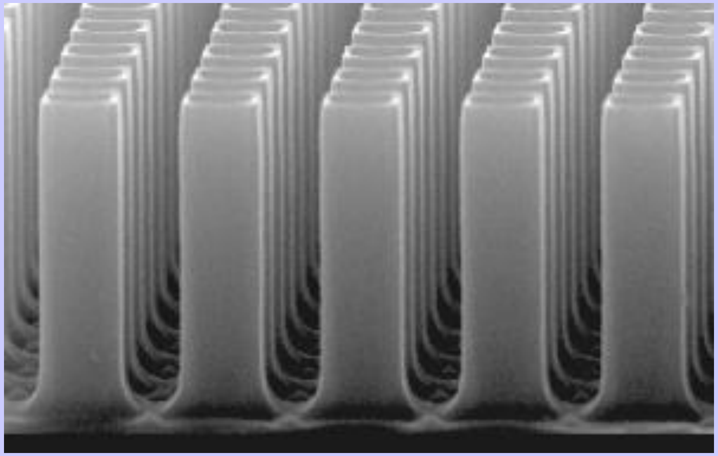
Transient anodization regime



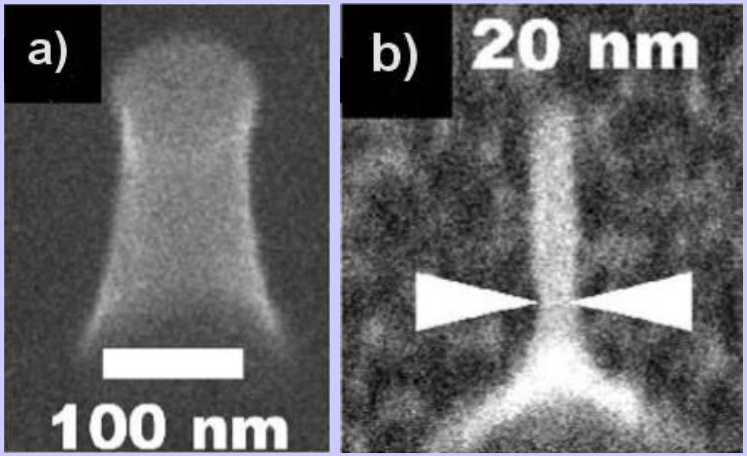
Réseau de Murs
Période 1.6 µm ; Largeur 110 nm ; hauteur 7 µm



Réseau de Piliers
Période 1.6µm ; Largeur 450 nm ; hauteur 7 µm

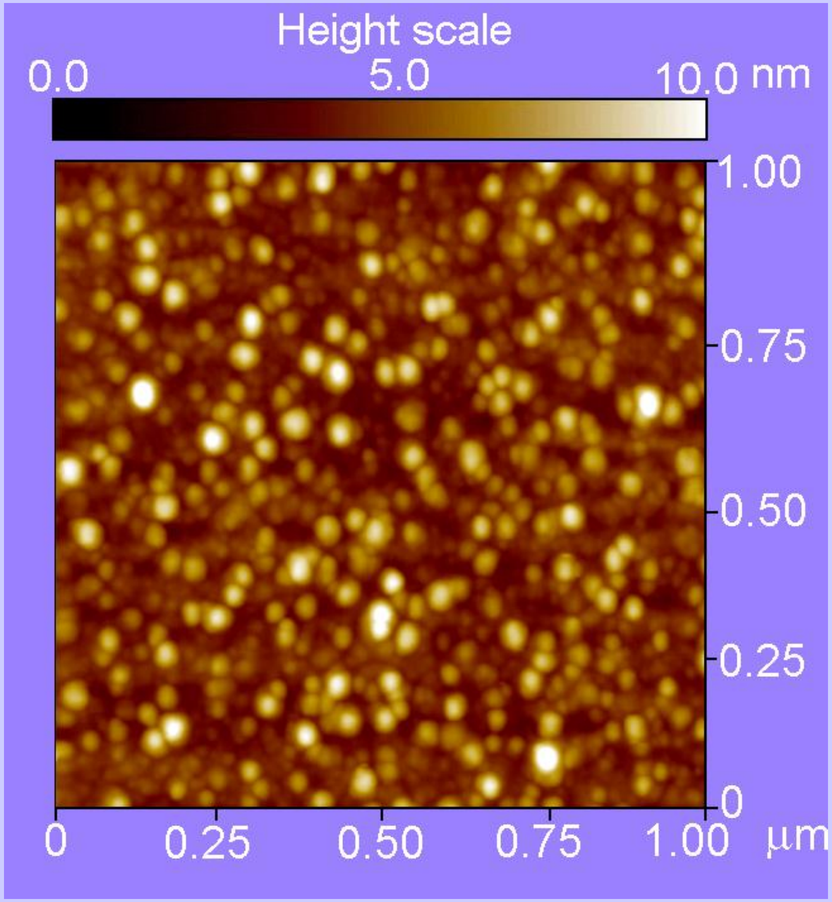


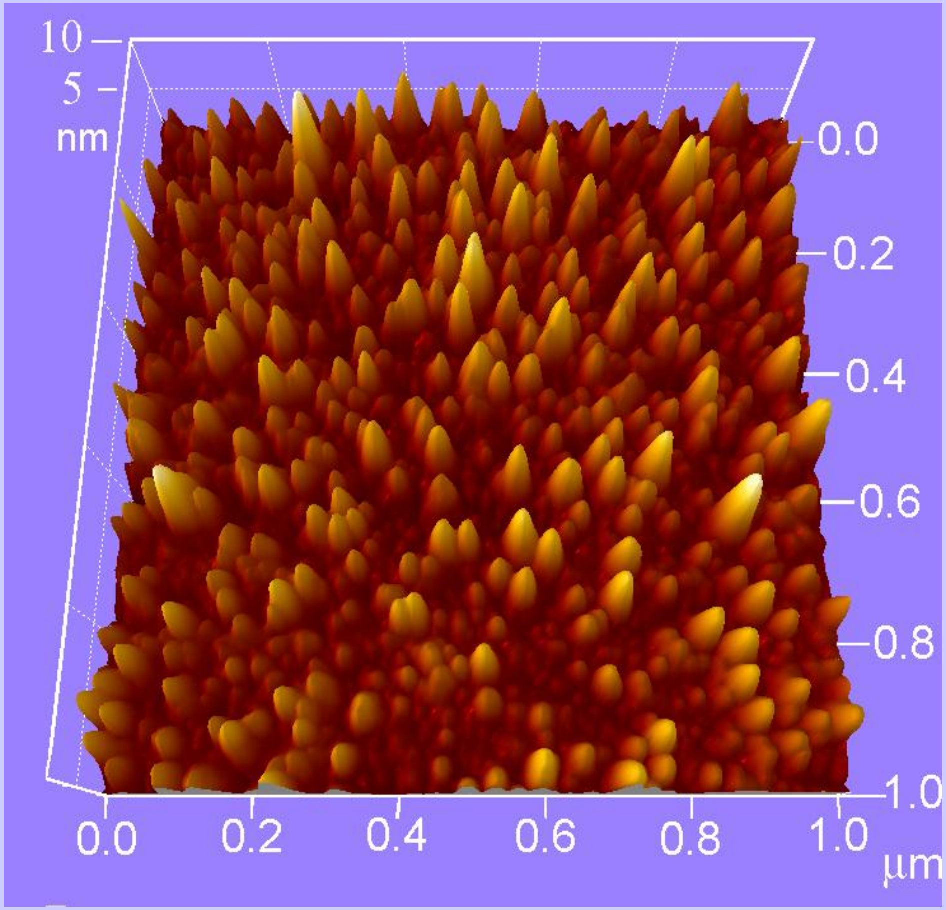
Réseau de Tubes
Période 3.2 µm ; Murs 220 nm ; hauteur 7 µm



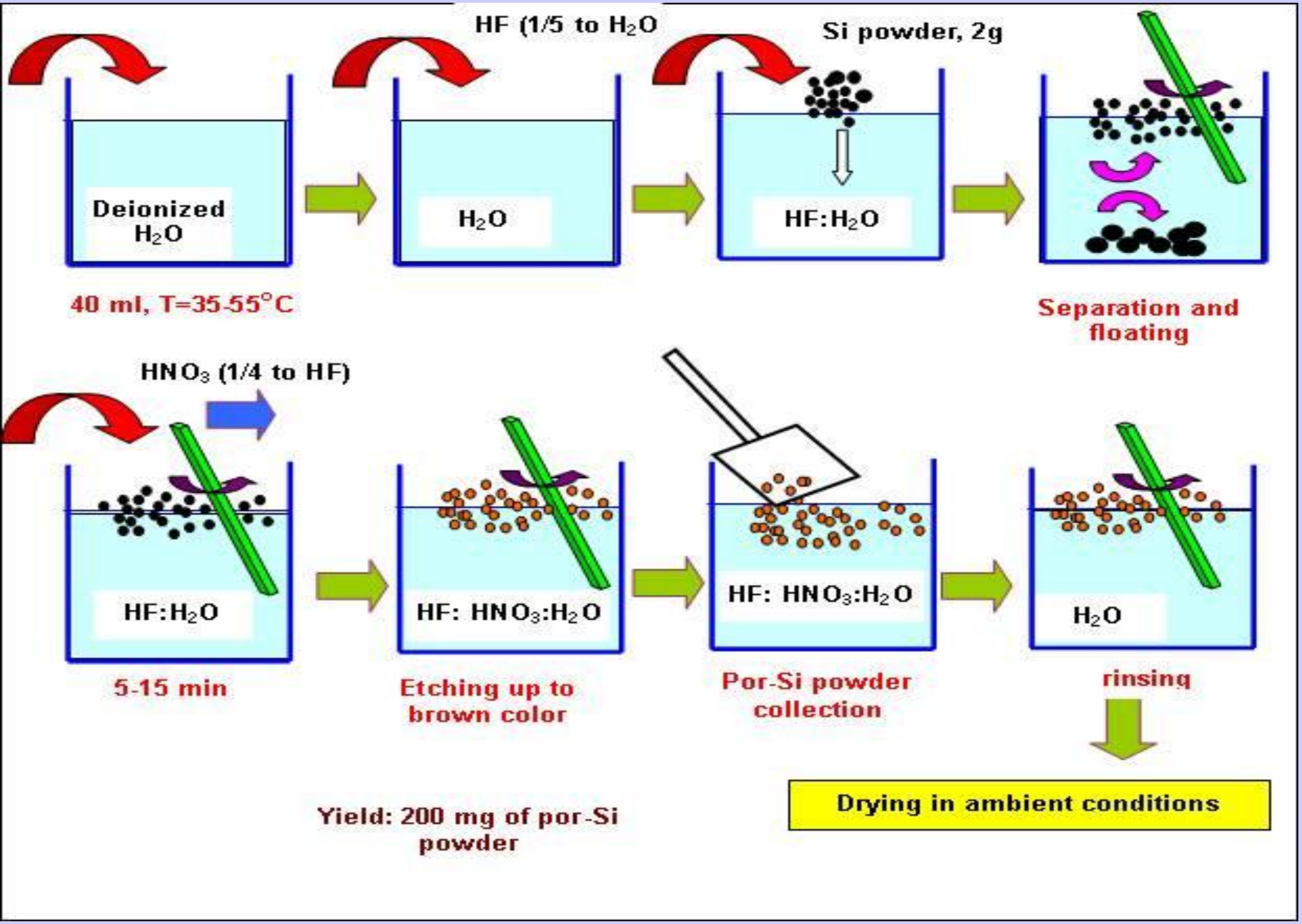
a) Pilier obtenu par gravure plasma puis b) aminci par gravure électrochimique

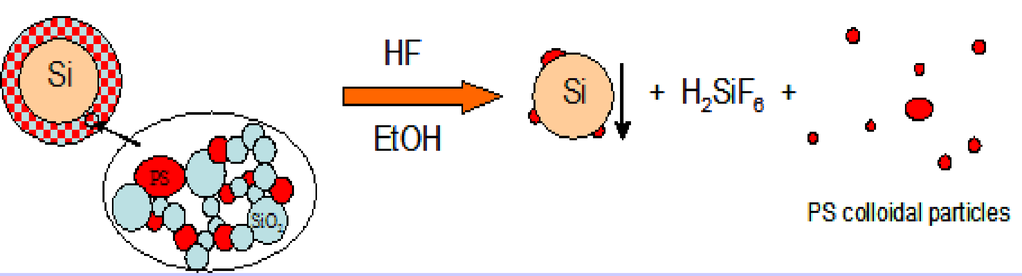
Time-resolved transient anodization regime: nanoparticle formation





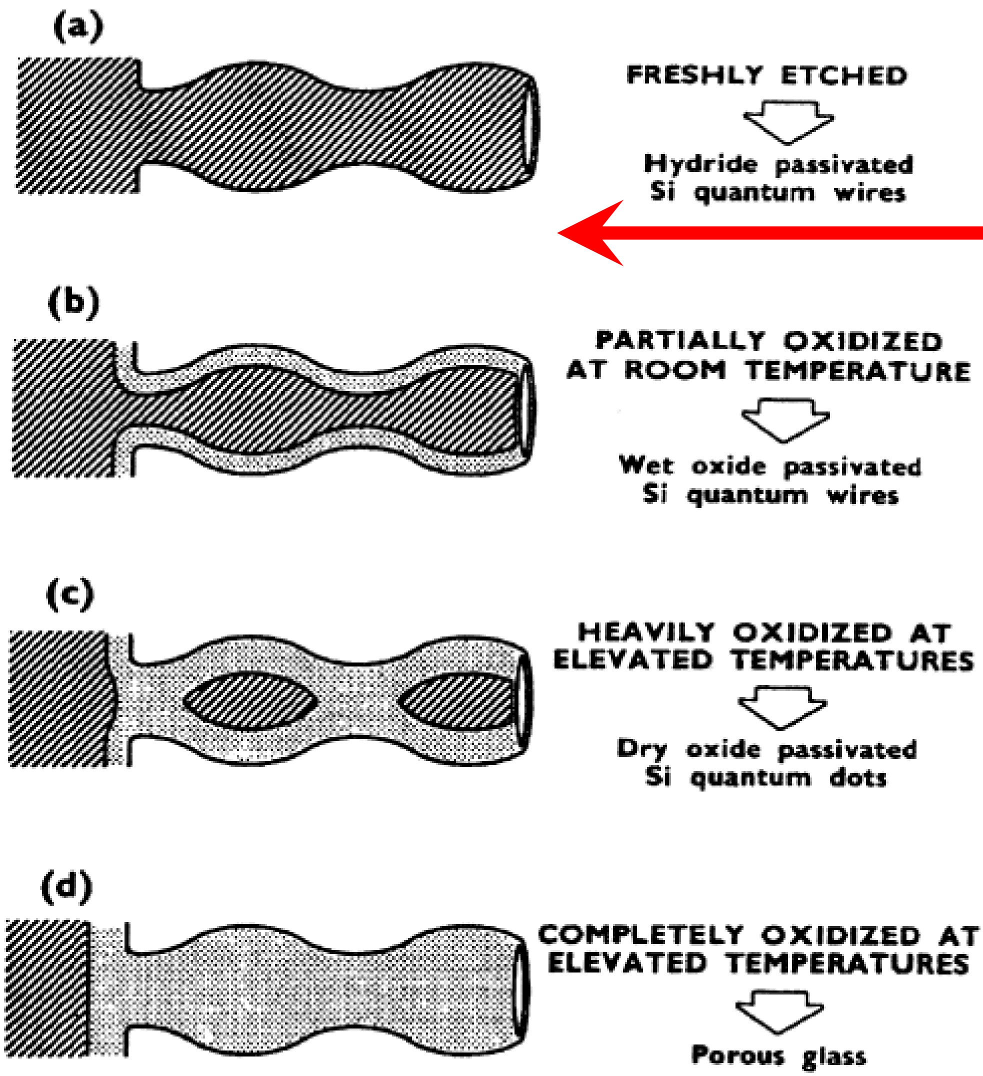
Stain etching of Si powder: method

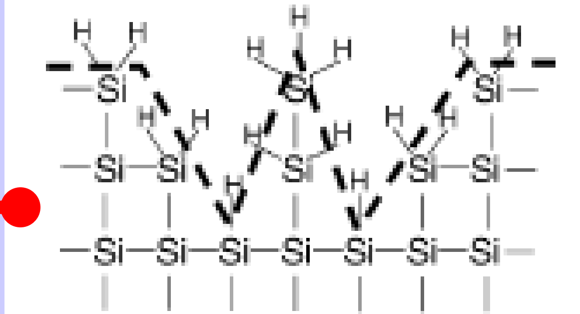


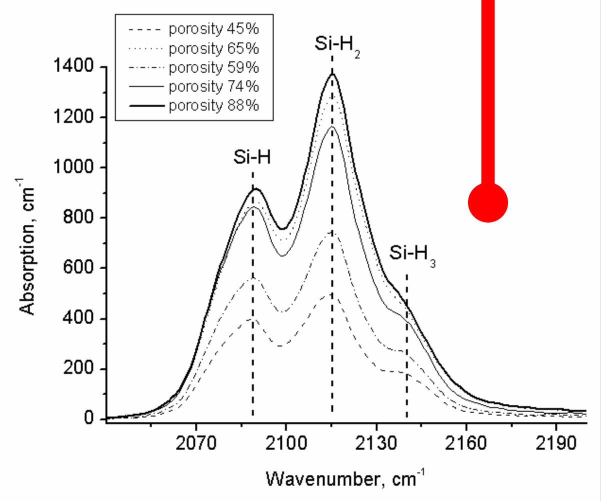


$$
\begin{cases}
HNO_3 + 3H^+ \rightarrow NO + 2H_2O + 3e^+ \\
ne^+ + Si + 2H_2O \rightarrow SiO_2 + 4H^+ + (4-n)e^- \\
SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O
\end{cases}
$$

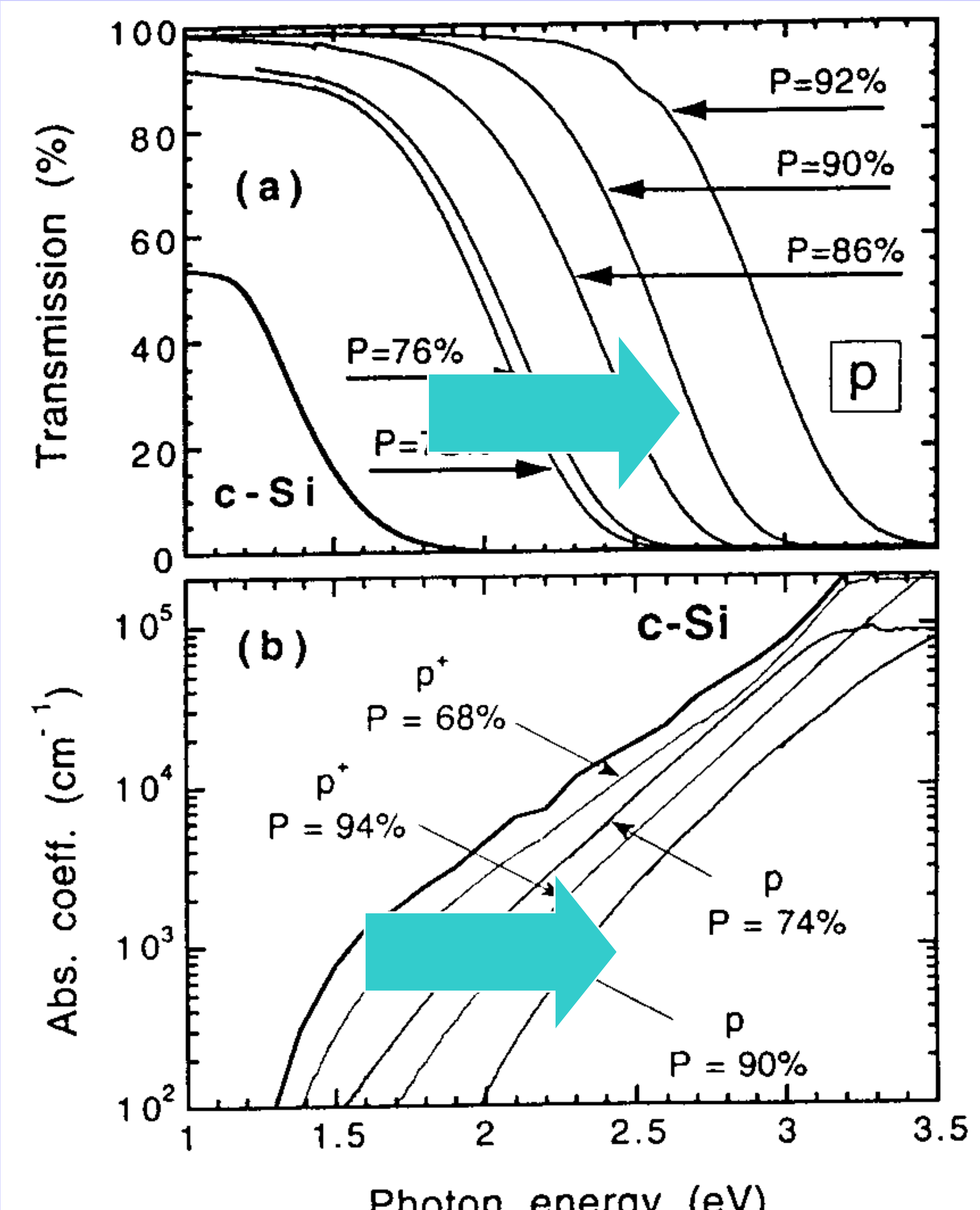
Idealized schematic steps in the oxidation process of highly PS

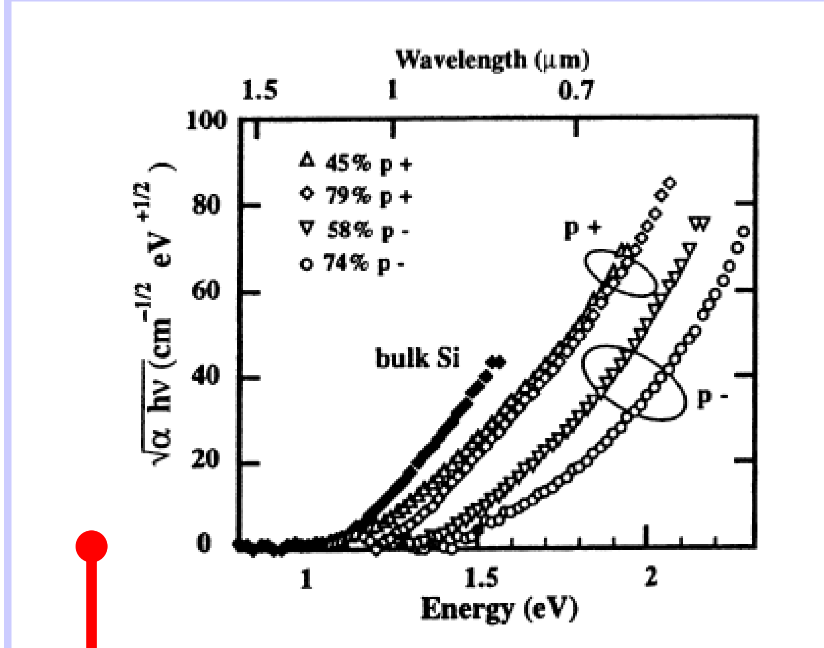






Optical properties of nano- porous Si



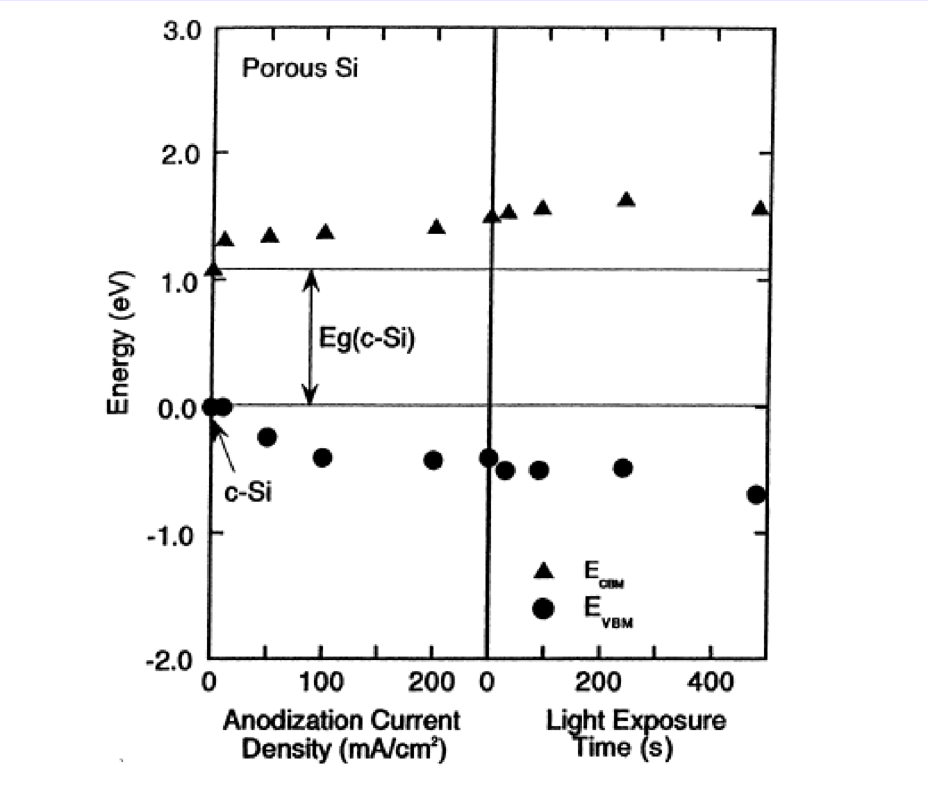


Square root of the absorption coefficient times photon energy *vs* photon energy

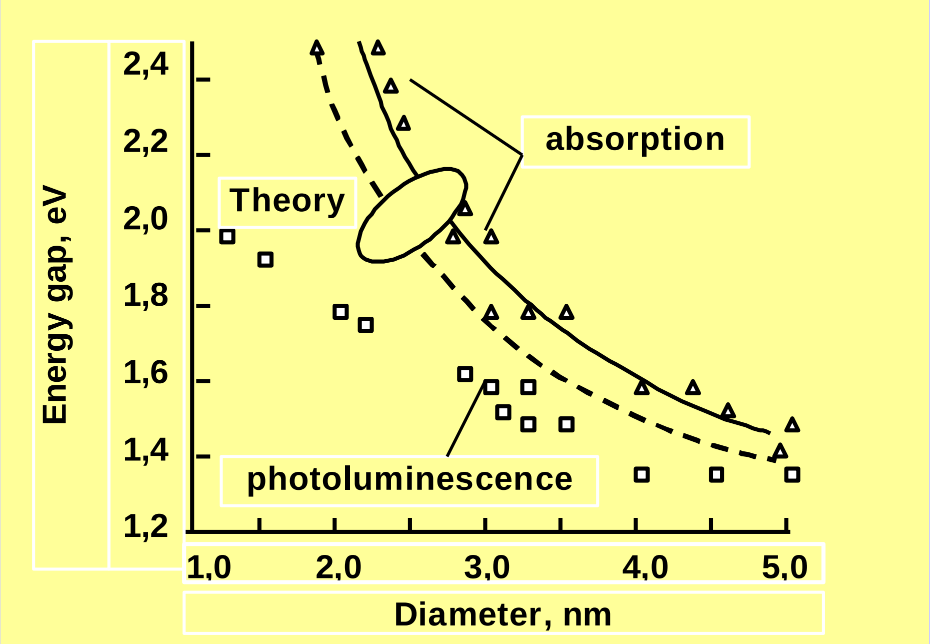
$$\alpha = \left(h\nu - E_g \pm E_{ph}\right)^2$$

/P.M.Fauchet, In: "Properties of porous silicon", ed.L.Canham, Emis, N18, 1997

Energy band of nano- porous Si

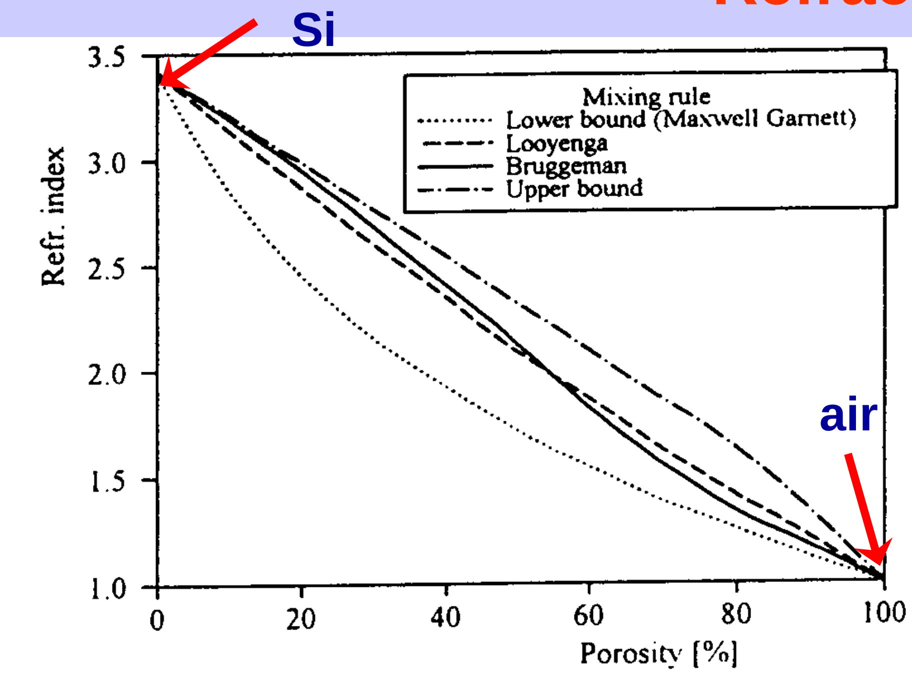


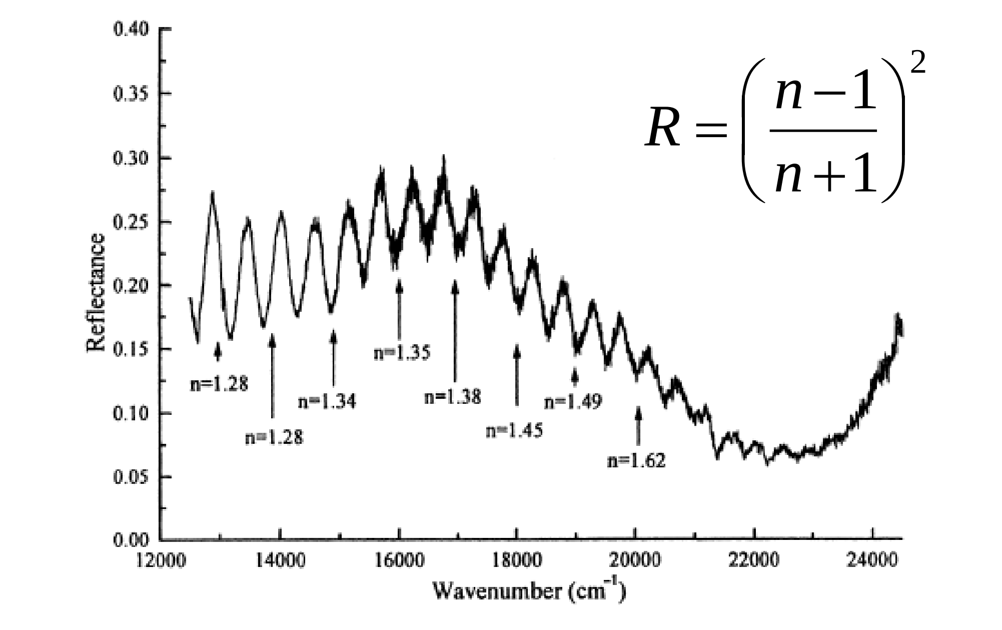
Energy position of c-band minimum and v-band maximum vs anodization current



Energy bend gap vs diameters on of Si particles

Refractive index





$$R = \left(\frac{n-1}{n+1}\right)^2$$

Bruggeman effective medium approximation

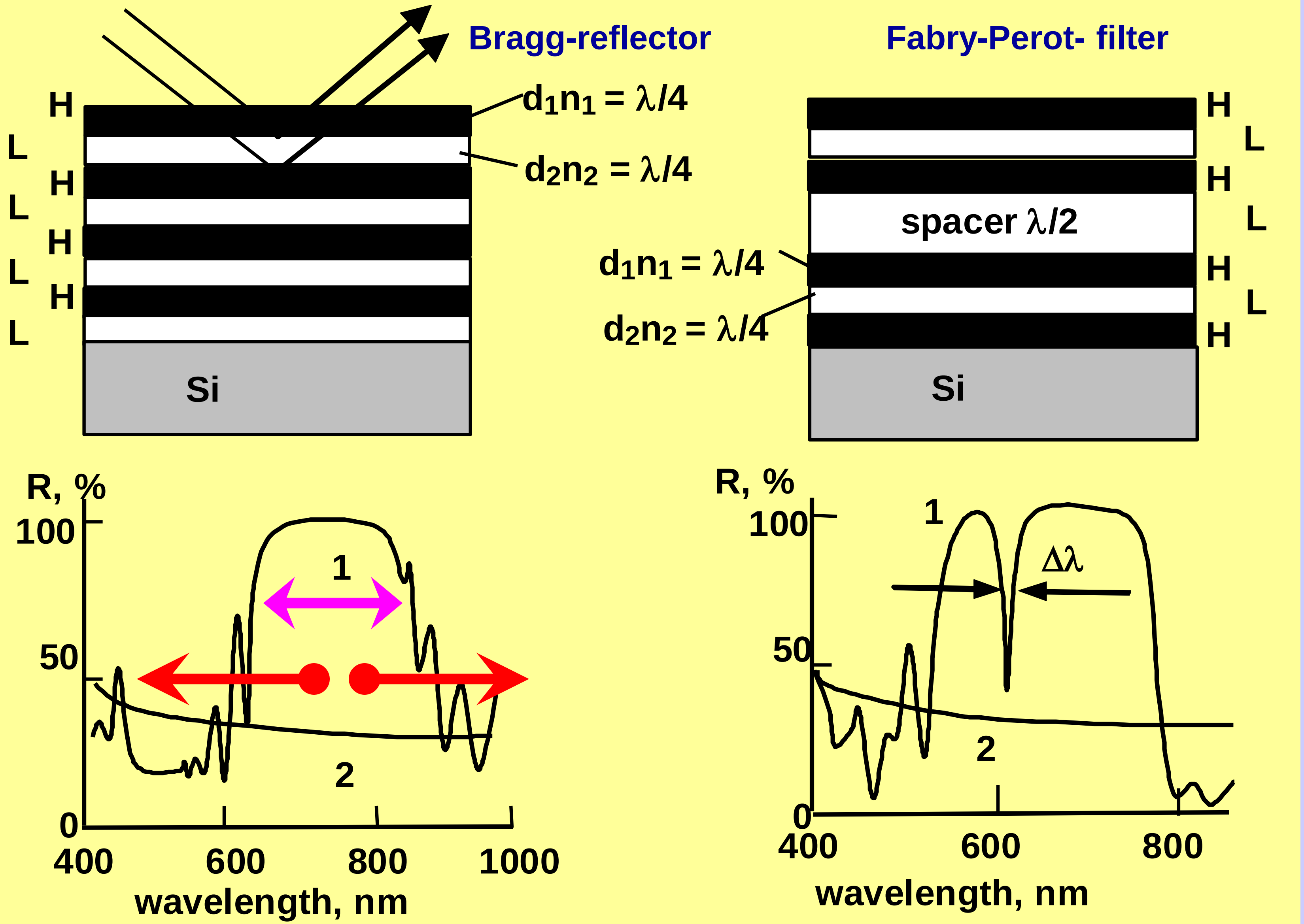
$$P\left(\frac{1-\hat{\varepsilon}}{1+2\hat{\varepsilon}}\right)+(1-P)\left(\frac{\hat{\varepsilon}_{Si}-\hat{\varepsilon}}{\hat{\varepsilon}_{Si}+2\hat{\varepsilon}}\right)=0$$

$$n = \frac{1}{2d}\left(\frac{1}{\lambda_k}-\frac{1}{\lambda_{k+1}}\right)^{-1}$$

$$\hat{n} = \sqrt{\hat{\varepsilon}} \qquad \hat{\varepsilon} = \varepsilon_1 + i\varepsilon_2 \qquad P = \frac{V_{pore}}{V_{pore}+V_{Si}}$$

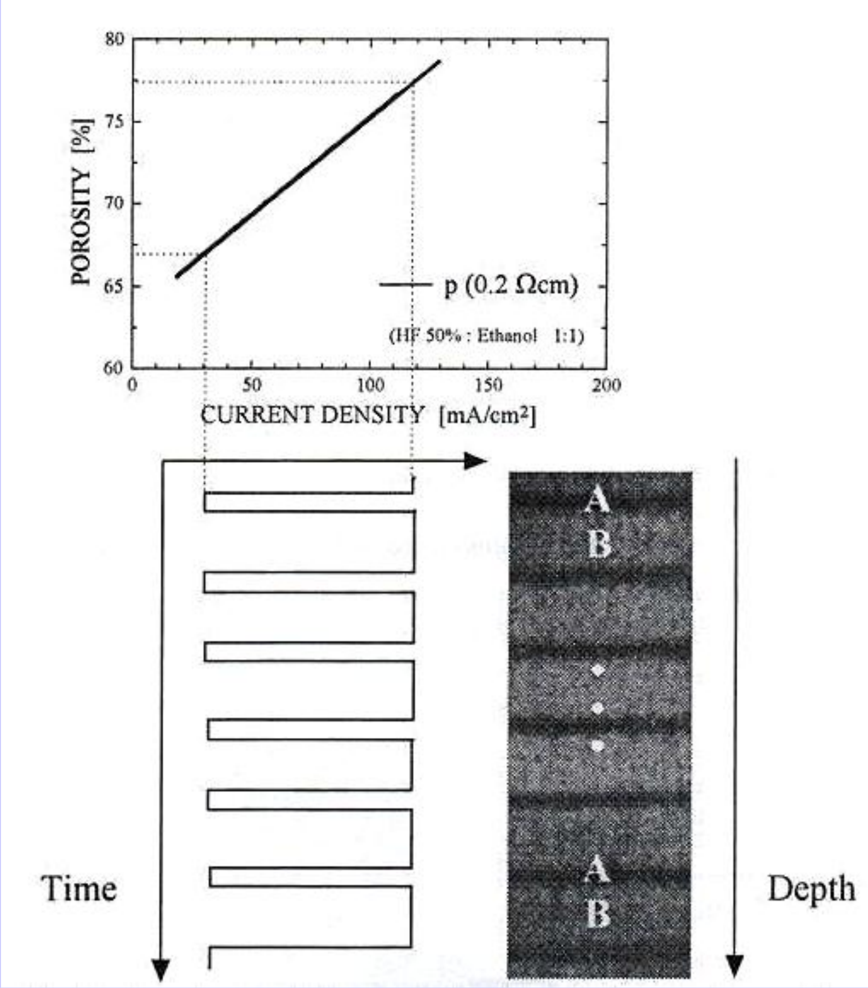
$$\varepsilon = (1-P)\varepsilon_{Si} + P\varepsilon_{air}$$

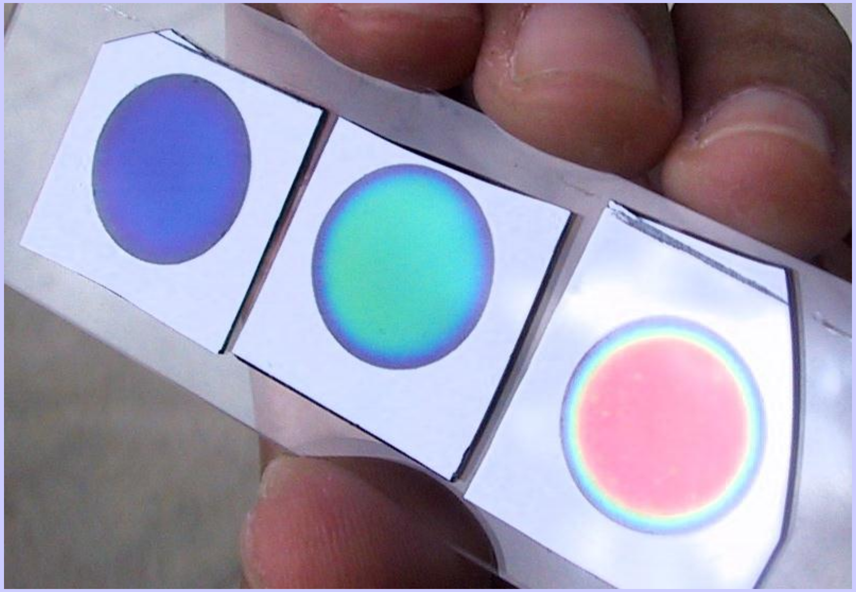
Optical multi-structures



/M.Thonissen, In: "Properties of porous silicon", ed.L.Canham, Emis, N18, 1997, p.349/

Bragg's reflectors



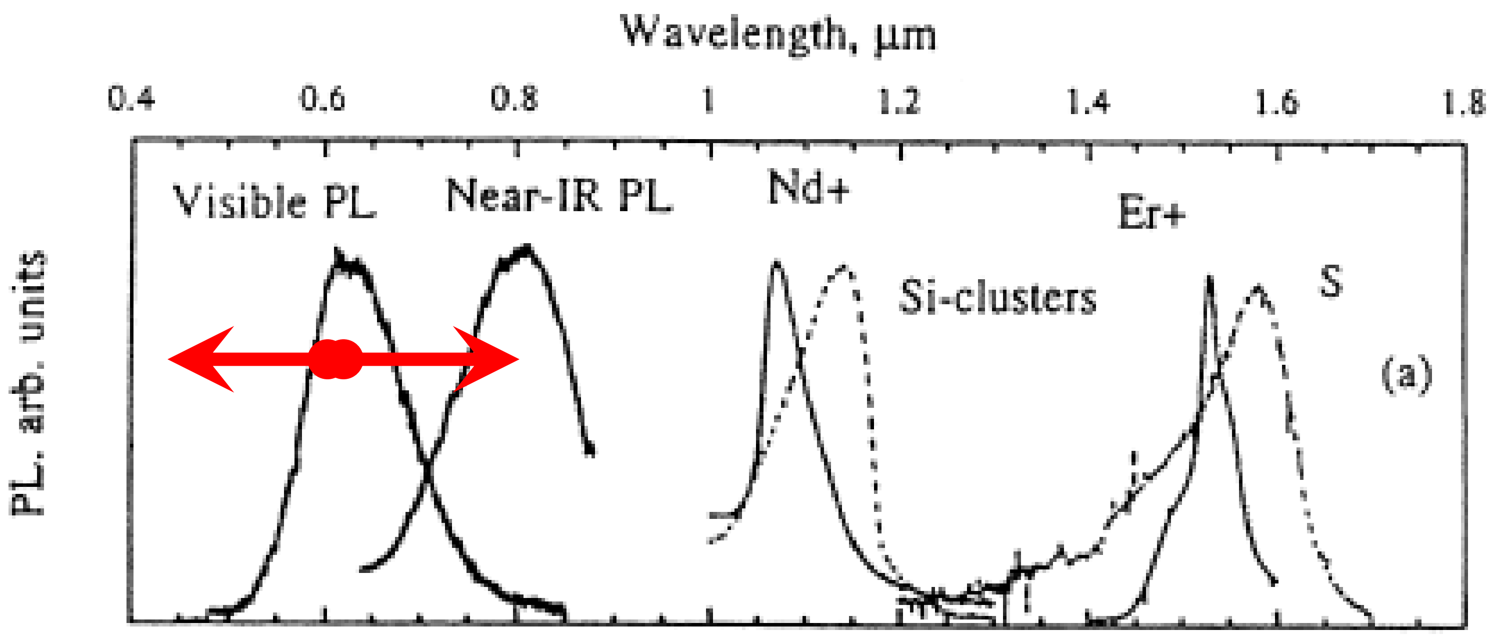


$$m\lambda_{Bragg} = 2(d_1 n_1 + d_2 n_2)$$

$$\lambda_{Bragg} \uparrow \Rightarrow d_{12} \uparrow n_{12} \uparrow$$

Hilbrich et al., Thin Solid Films 297, (1997) pp. 250-253

Photoluminescence of nano- porous Silicon at UV illumination at T_{room}



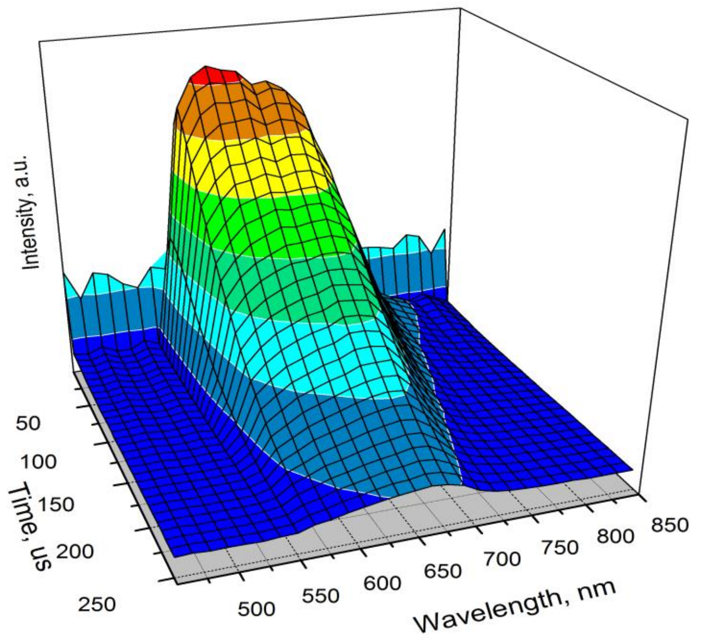
Spectral range	Peak wavelength	Label
UV	~350 nm	UV band
Blue–green	~470 nm	F band
Blue–red	400–800 nm	S band
Near IR	1100–1500 nm	IR band

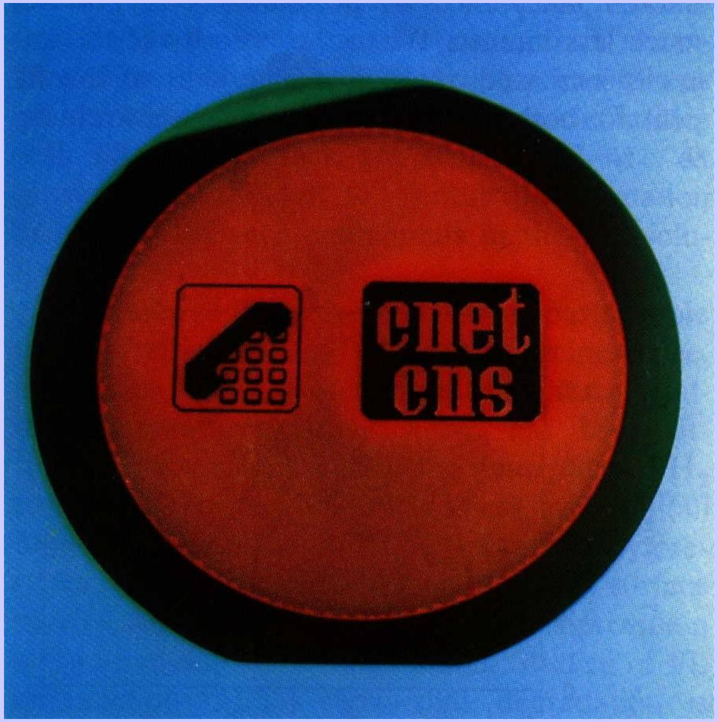
O.Bisi, S.Ossini, L.Pavesi, Surf.Sci.Rep, 38(2000)1

Photoluminescence of nano- porous Silicon

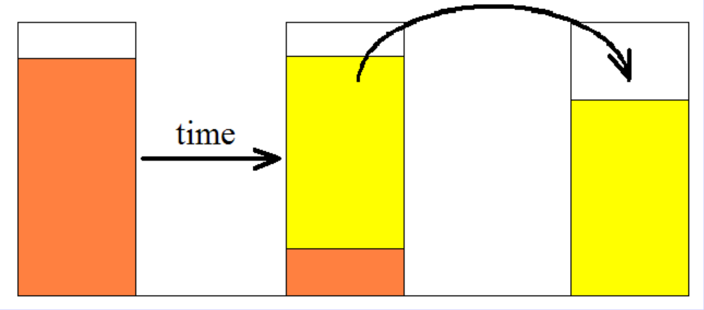
Some spectral characteristics of the S-band (adapted from Ref. [459])

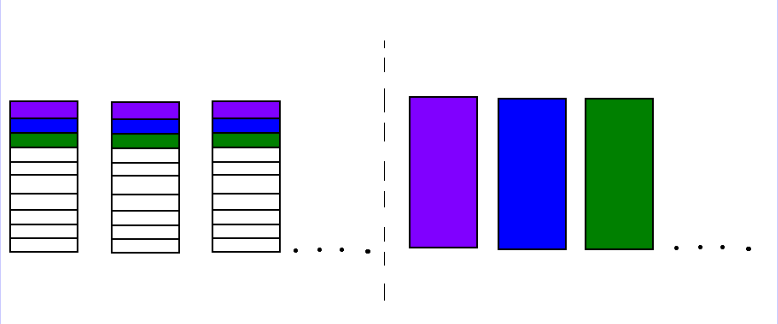
Property	Typical values	Comments
Peak wavelength	1100–400 nm	At 300 K
PL efficiency	$\geq 5\%$	At 300 K and for external quantum efficiency
FWHM	0.3 eV	At 300 K (8 meV in porous silicon microcavities)
PL decay times	$\simeq 10\ \mu s$	Strongly dependent on wavelengths, temperature and aging condition
Polarizability ratio	$P \leq 0.2$	
Fine structure under resonant excitation	Phonon replica at 56 and 19 meV	Heavily aged PS, energies typical of Si phonons

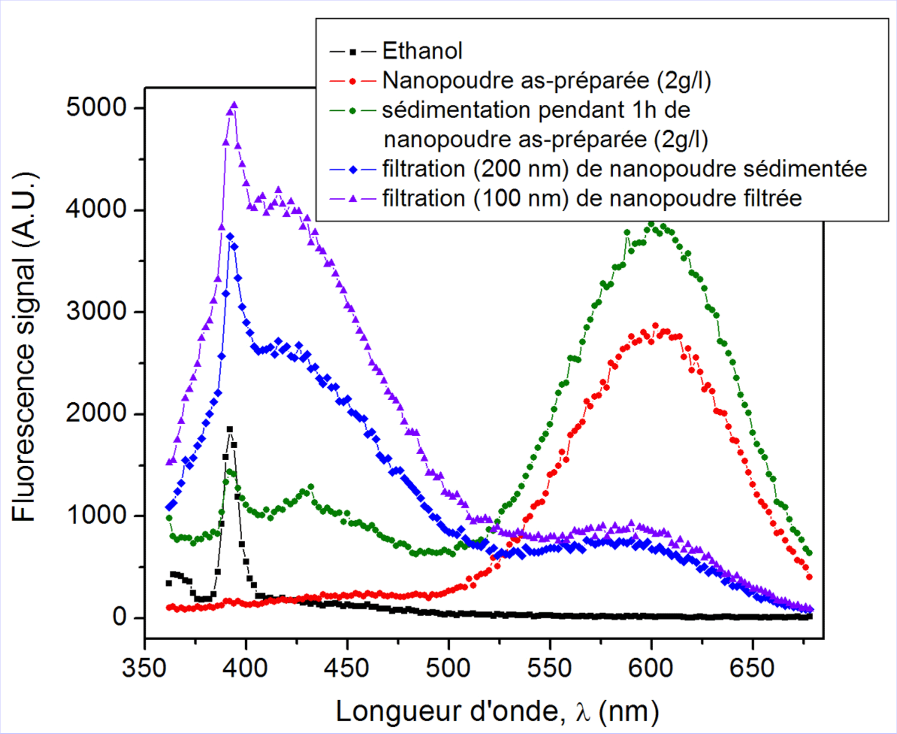


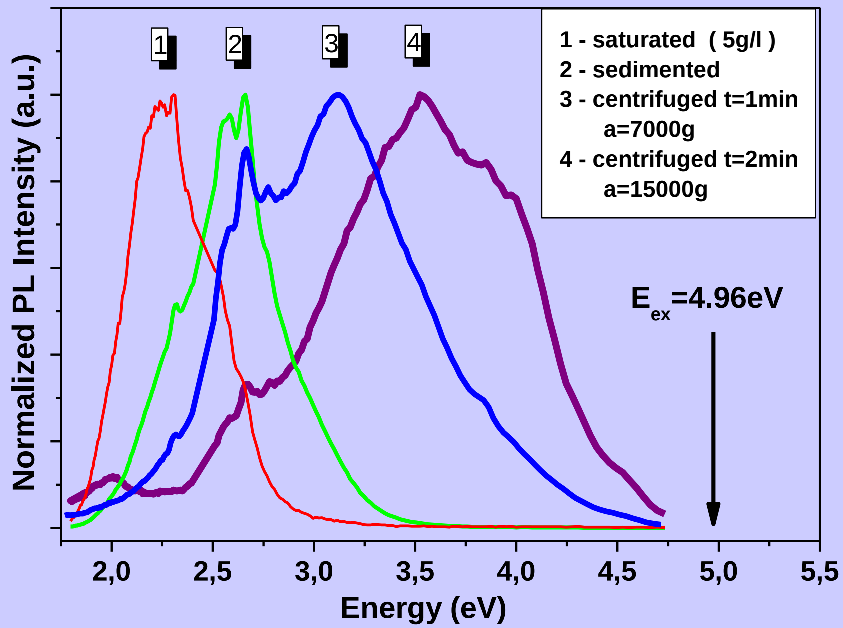


Photoluminescence of sediment Si nanoparticles



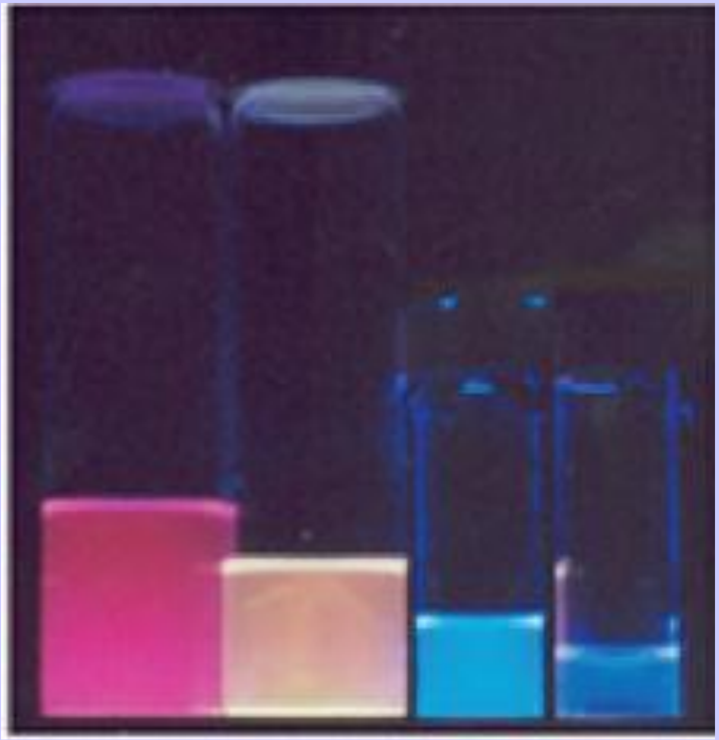




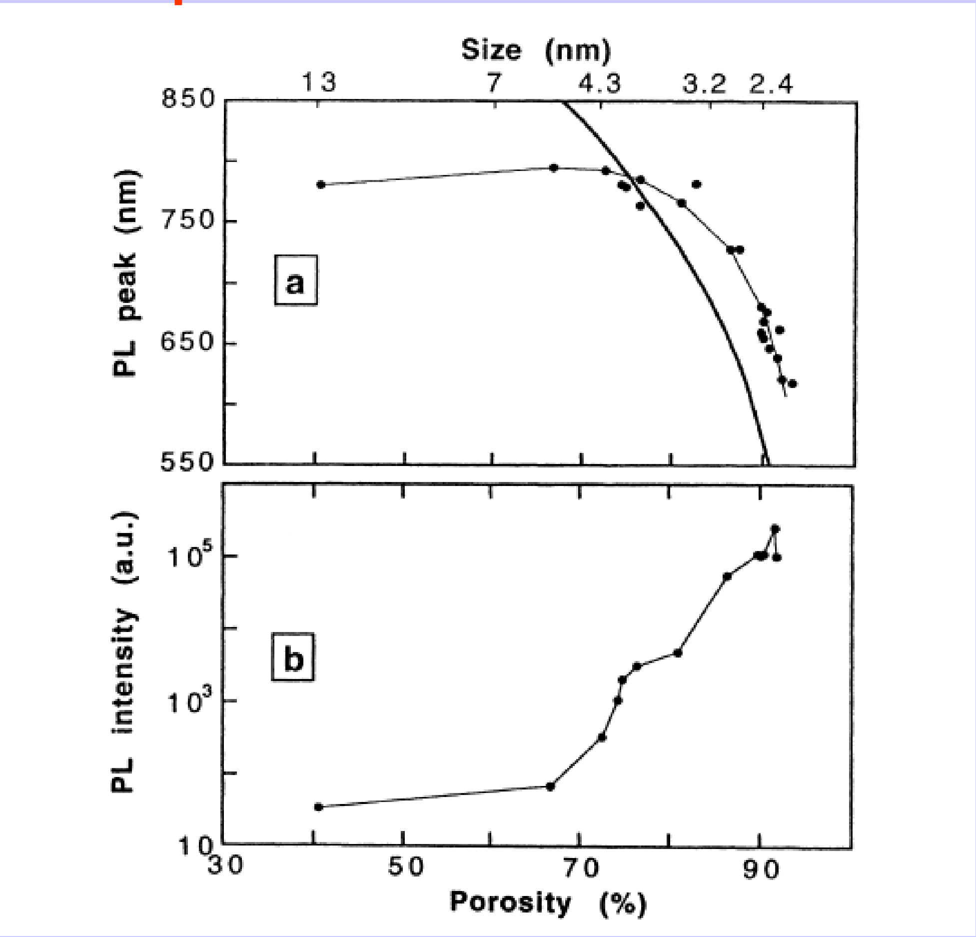


Sedimentation of ethyl solutions of Si nanoparticles + centrifugation

Photoluminescence of nano- porous Silicon



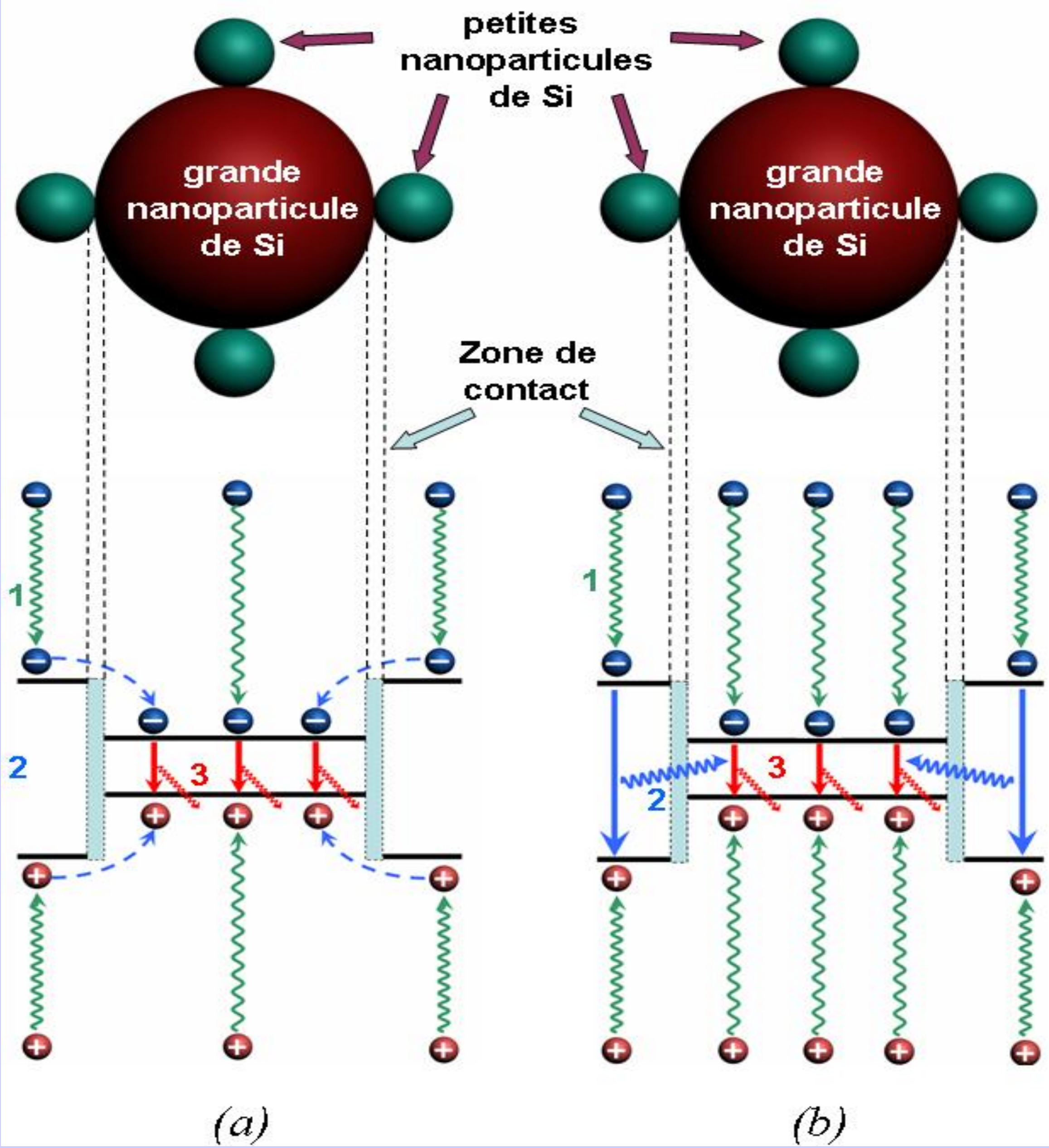
Emission of colloids of 4 members of the magic family 2.9, 2.15, 1.7 and 1.0 nm in diameter, after they have been separated, excitation 365 nm



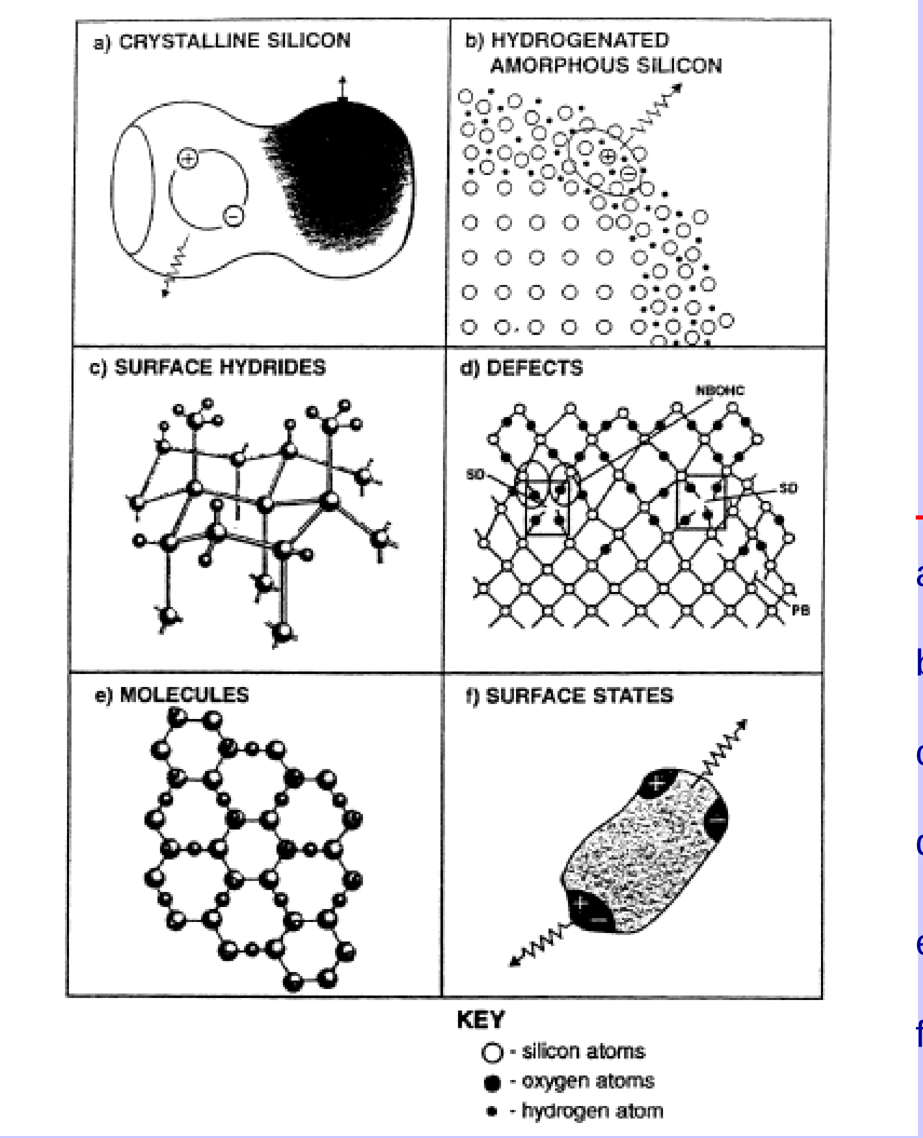
Emission peak and intensity vs size and porosity

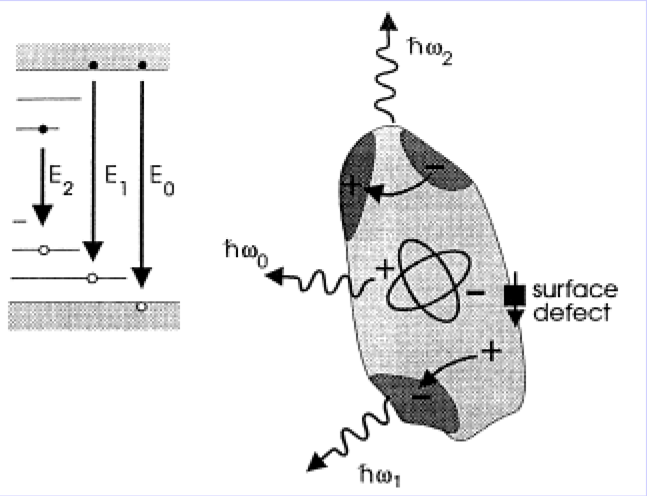
V.Kumar, Nanosilicon, Elsevier, 2007

Why UV Photoluminescence is not observed in solid PS?



Photoluminescence models



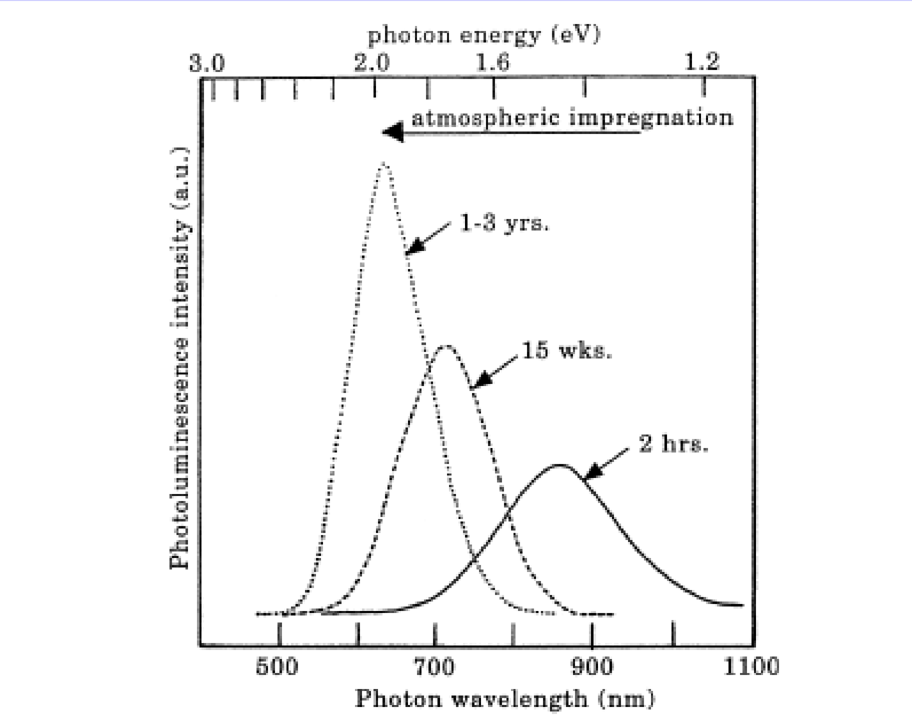


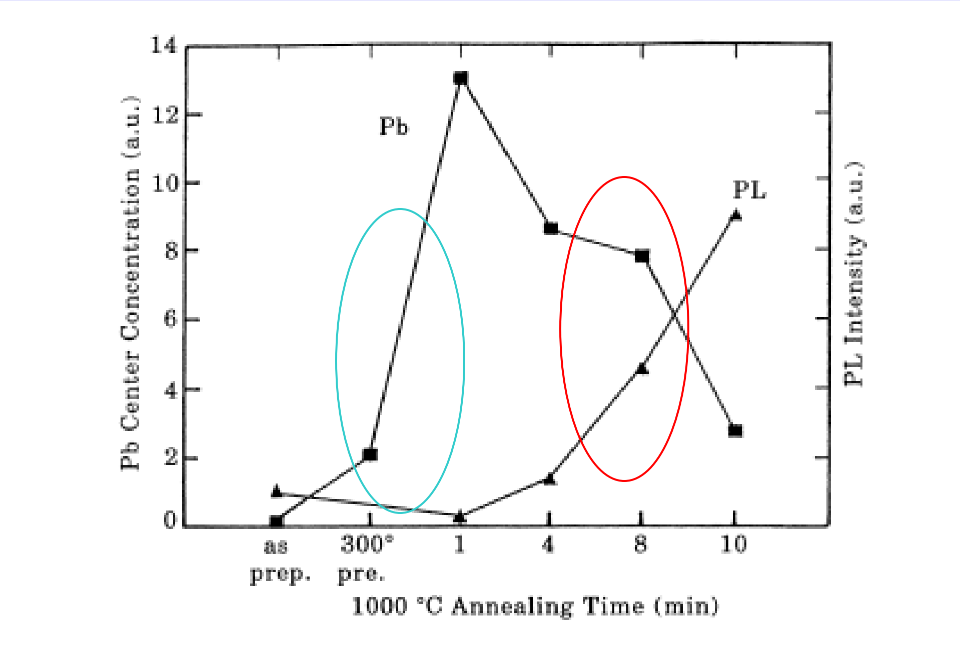
Hierarchy of transition in the SS model. The indices 0,1,2 indicate the number of SS involved

The six group of models proposed to explain PS PhL

a) Crystalline QW. Localized on SS or free exciton recombination
b) c-Si covered by layer of hydrogenated a-Si, where recombination occurs
c) Si surface passivated by SiHx terminations. Radiative recombination occurs at the Si-H bonds
d) Partially oxidized Si containing defects proposed as radiative centers
e) Siloxene molecule $Si_6O_3H_6$ is proposed to exist on the large inner PS surface and act as luminescence center
f) Si dot with SS that localize carriers and holes separately (upper part) or together (lower part, radiative recombination)

Photoluminescence aging and alternative model of PhL





Aging: blue shift of emission due to reduce of nanoparticle size

Dangling bond (Pb centers) concentration and PhL vs annealing time at 1000°C in O_2

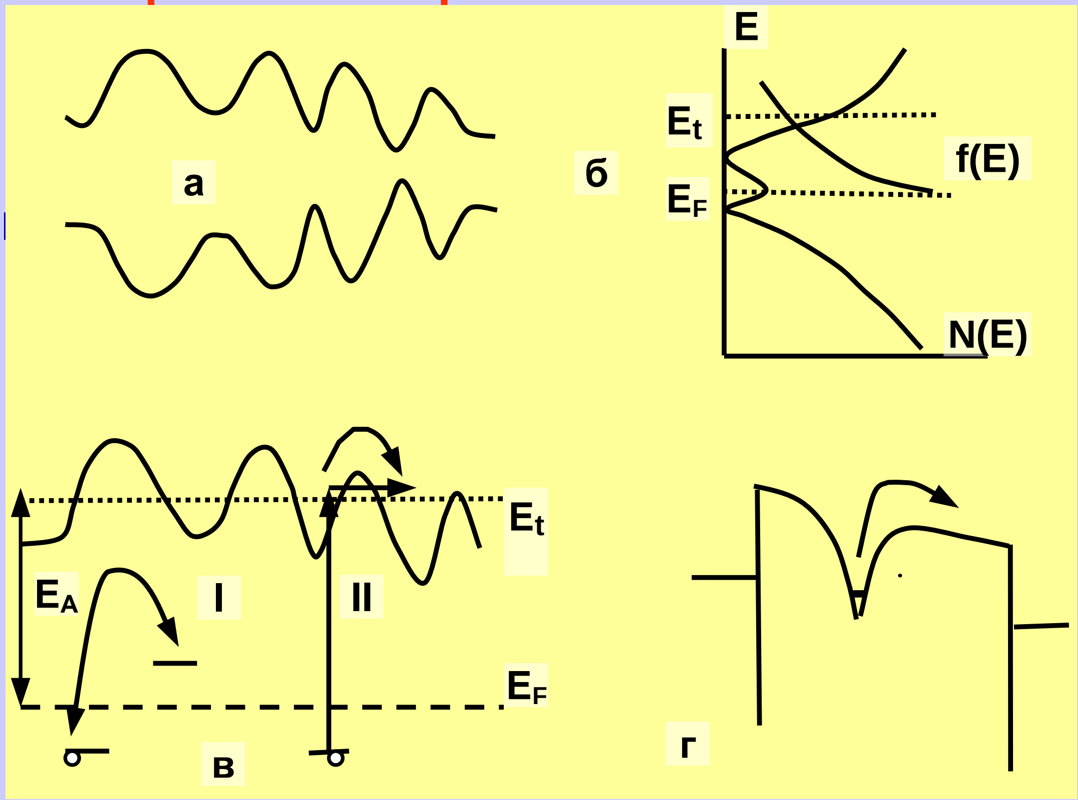
Dangling bonds- most important paramagnetic defect centers: in Si/SiO_2 interface

$\cdot Si\equiv Si_3$ (Pb centers)

in hydrogen depleted oxide layer **$\cdot Si\equiv SiO_3$ (E\` center)**

Electrical transport in microporous Si

a. Bandgap fluctuation due to variation of nanocrystalline size,
b. density of states in forbidden band, Et- level of current leaking, f(E) –distribution function
c. transport mode: hopping on surface states(I), thermogeneration, thermoionic or tunneling across state tails
d. Poole-Frenkel mechanism



Surface states:

Density >10^{12}-10^{14} cm^{-2}eV^{-1}

Free carriers:

Density <10^{10}-10^{13} cm^{-3}

Mott law for jump (hopping):

$$\sigma(T) = \sigma_0 \exp(T/T_0)^m, m = 4$$

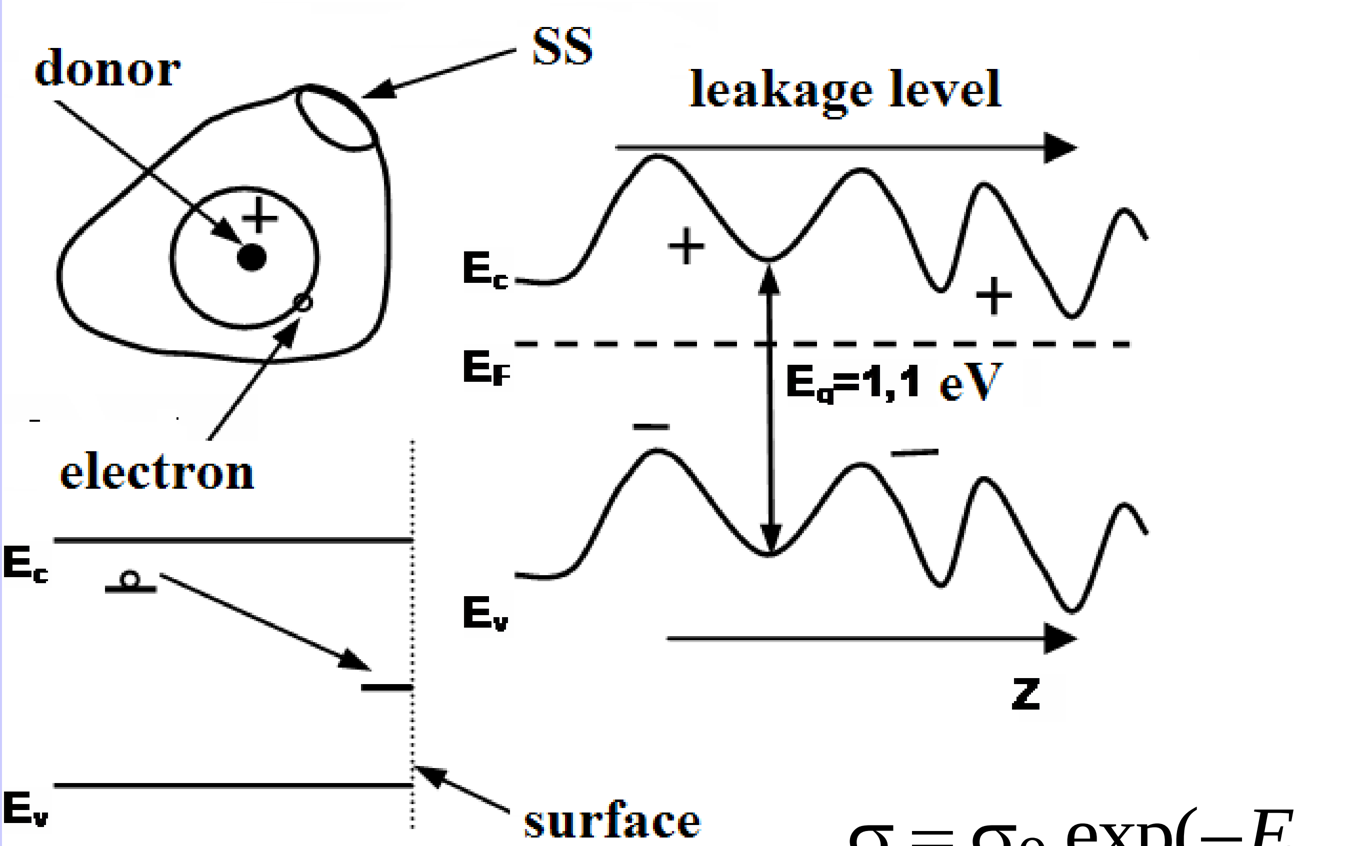
Poole-Frenkel ionisation:

$$\sigma(V,T) = \sigma_0 \exp(\frac{E_a}{kT}) \exp(\beta \sqrt{\frac{V}{V_0(T)}})$$

Space charge limited current:

$$I = \gamma(T) \frac{V^n}{d^m}, \quad n\sim 2$$

Electrical transport in macroporous Si



$$\sigma = \sigma_0 \exp(-E_a / kT)$$

Initial Si is heavy doped, but meso-PS is high resistive!

a) Cross-section of Si microwire that shows the process of free electron capture on surface state of acceptor type, b) energetic sketch of process, b) band modulation due to electric field between D+ and negatively charged SS. Z- direction along Si microwire

New perspectives:Other stable Si nanoparticles

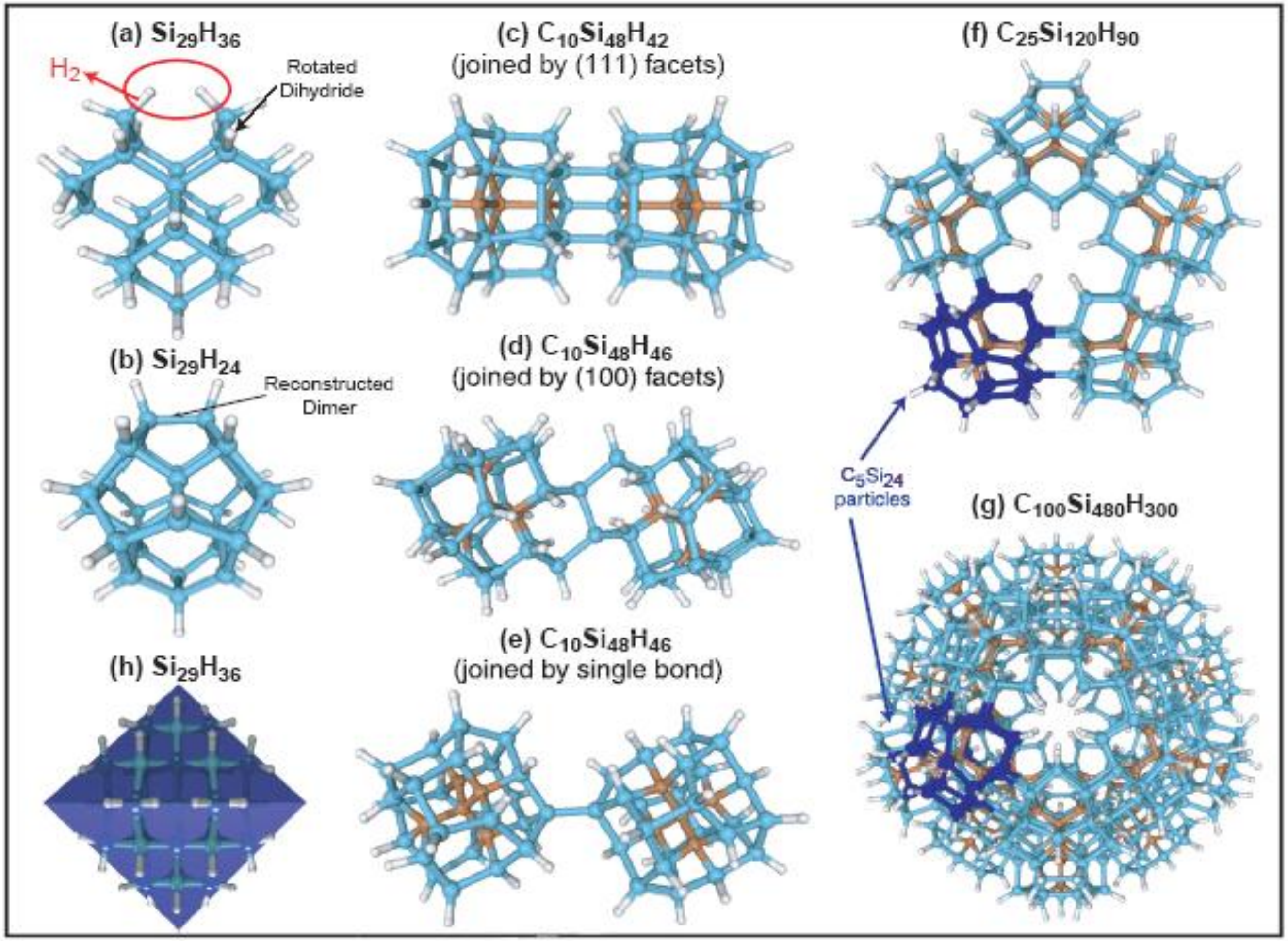


FIG. 1: Calculated atomic structures of single, double, 5-fold and 20 nanoparticles structures. Si, C and H atoms are colored blue, brown and white. In (f) and (g) atoms in a single C_5Si_{24} particle are highlighted in dark blue.

Properties of Micropores or nanocrystalline Si. Summary

Features:

- Surface area – 200- 500 m^2/cm^3
- E_g = 1.1- 3.0 eV
- Resistivity $\rho = 10^8$-10^{12} Ω.cm
- Carrier mobility 10^{-3} – 10^0 $cm^2/V.s$
- Quantume efficiency of PL- more than 10 %
- Quantume efficiency of EL - 1 %
- Chemical composition (Cullis A.G.,Canham L.T, J.Appl.Phys, 82(1997) 909).

Condition of porous Si	Chemical composition
1. In situ in HF during and after formation	SiF_xH_y
2. Freshly etched in inert ambient	SiH_x
3. Chemically or anodically oxidized 4. Rapid thermally oxidized at high temperatures	SiO_xH_y
5.Aged in ambient air for months to years	$SiO_xH_yC_z$