# 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

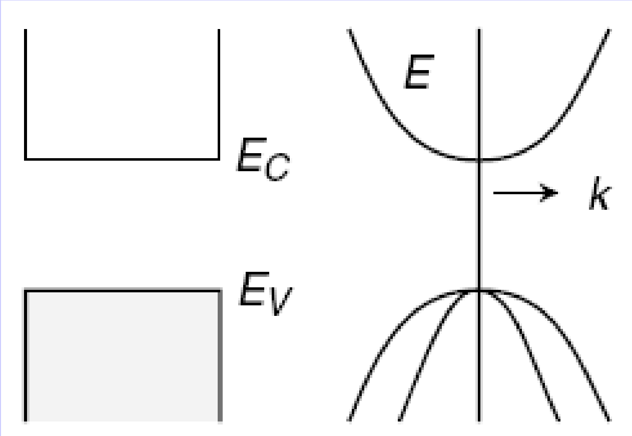
4 Applications

- Wave-guides, optical fibers, filters, mirrors
- Chemical & bio-sensors
- Photonic crystals
- Microelectronics: SOI, Si epitaxy
- Solar Cells
- Hydrogen reservoirs
- Explosive materials
- LED,
- Bioreactors, syntesis
- Medicine: Implants, Diagnostics electrophoresis, drug deliver

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

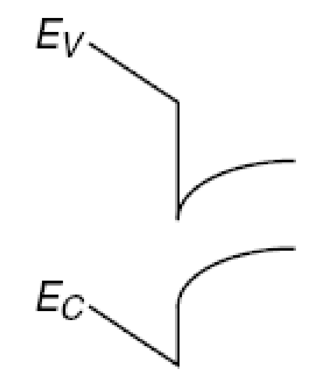
- Band theory + doping
- Effective mass theory

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

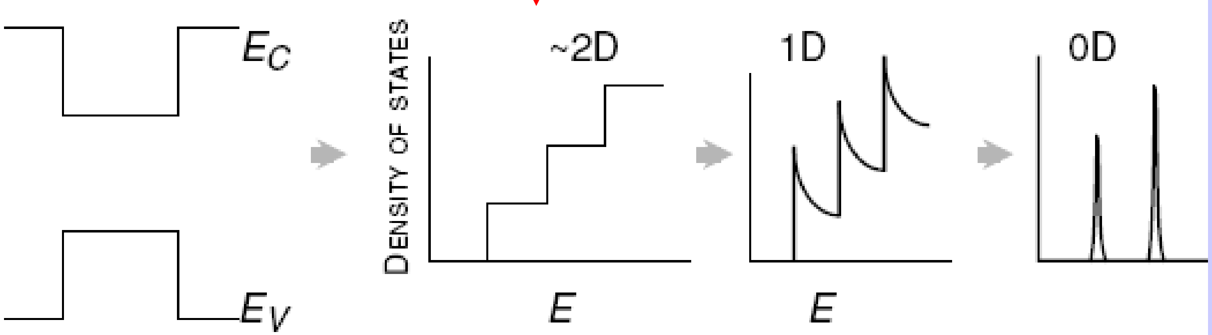



Semiconductor transistor

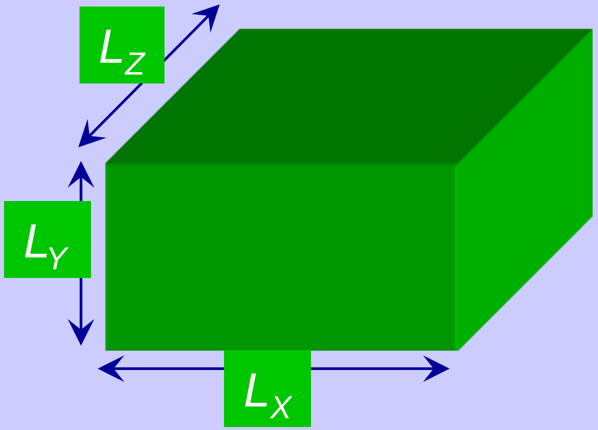
Semiconductor laser




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:***
***$\lambda$ ~ 3 nm***

de Broglie wavelength ($\lambda$) – quantum phenomena

$$\lambda \approx L_i$$

***Geizenberg equation***

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

# Quantum confined effect

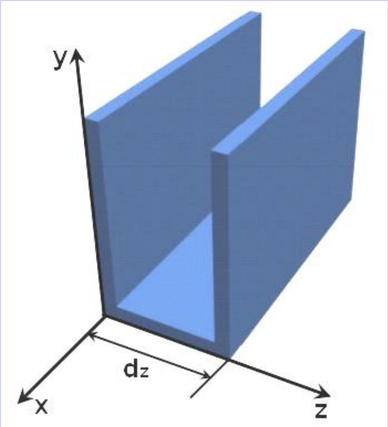



*Figure 1. 1* Modèle d'un puits quantique infini : l'électron est confiné dans la direction z, sur une épaisseur de largeur $d_z$.

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

## Quantum well

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

## Quantum wire

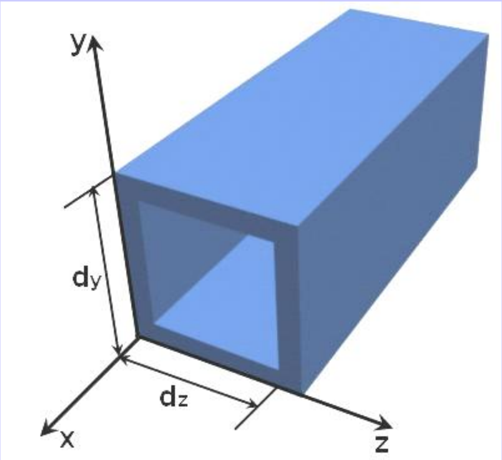



*Figure 1. 1* Modèle de fil quantique infini : l'électron est confiné dans les directions z et y.

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

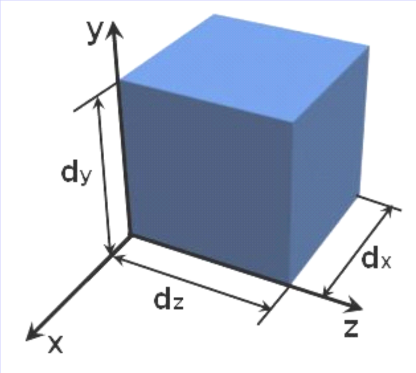


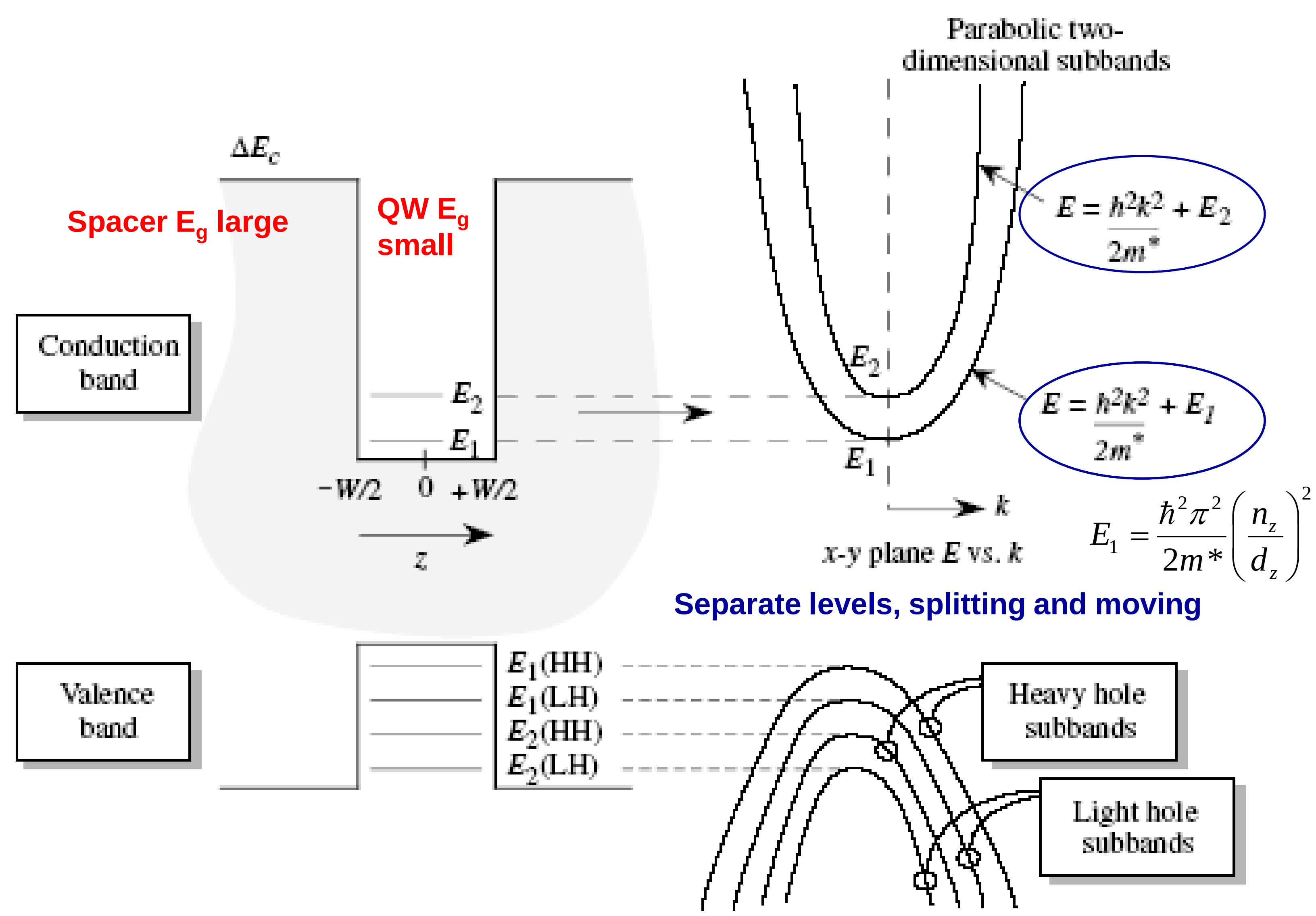

*Figure 1. 1* Modèle de boîte rectangulaire : l'électron est confiné dans trois directions.

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

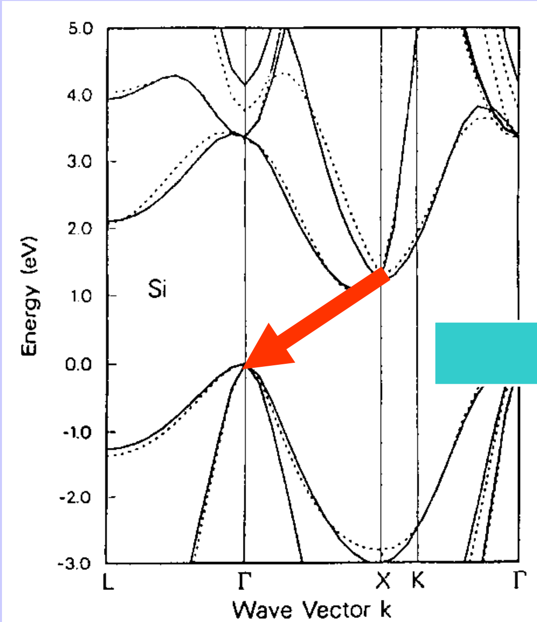
## Quantum dot

**Electronic spectra – series of levels like in atom !**

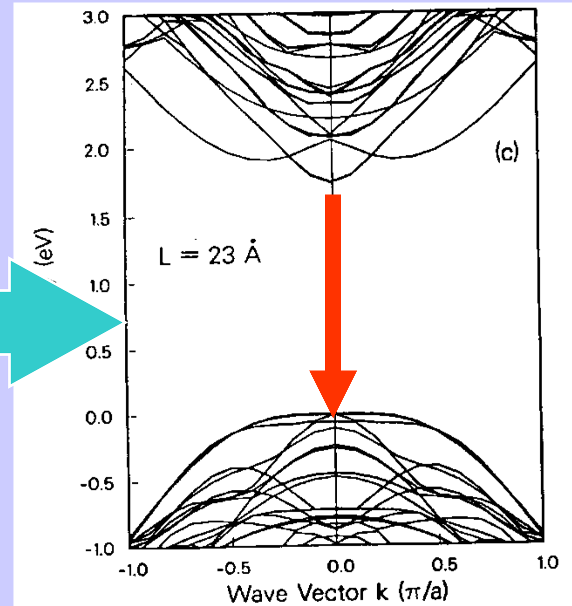
# Quantum well



# Band structure of nano-Si: two possibilities



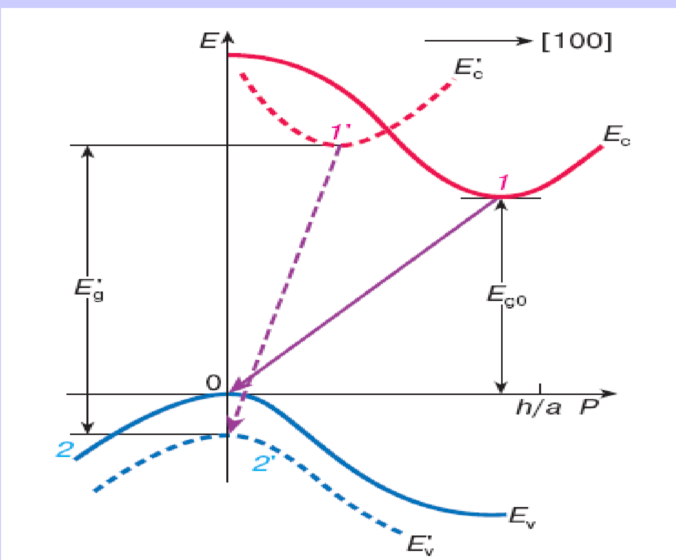

Band structure of bulk Si




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**

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

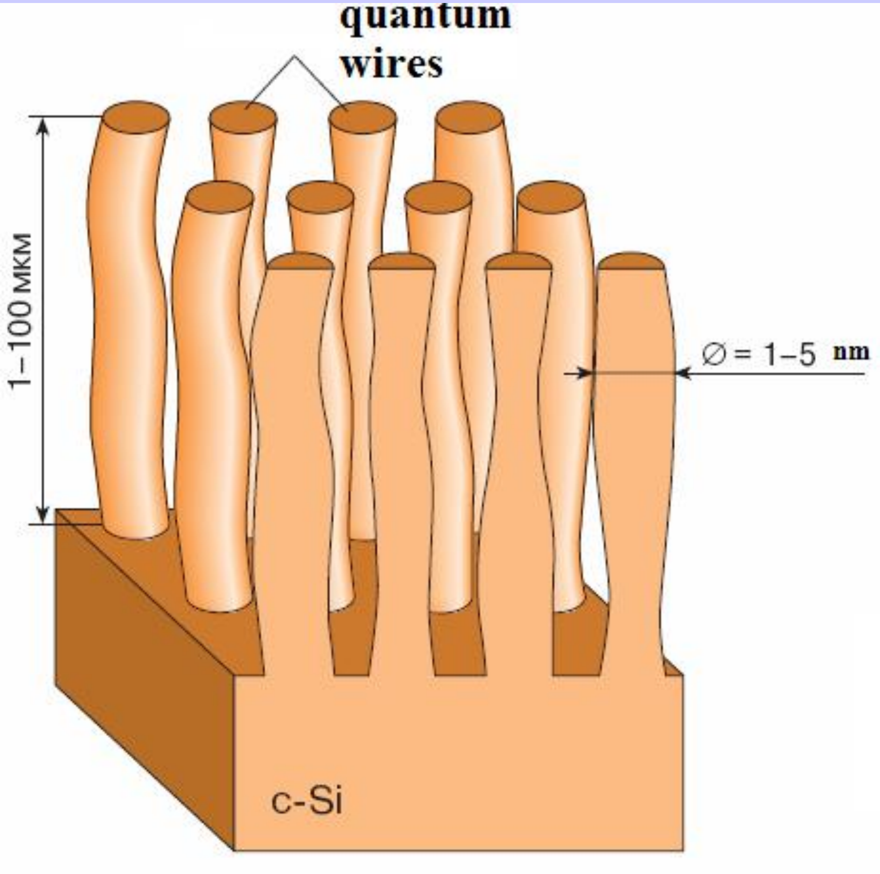
$$\Delta\hbar k = \frac{\hbar\omega}{c} + mv_{collision}$$

**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 $\leq$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

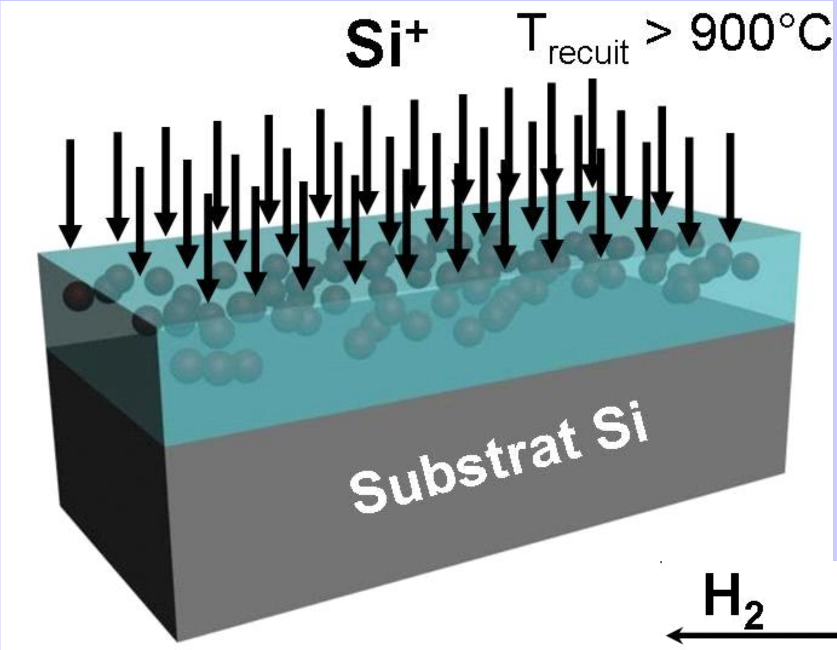



Schéma du processus de fabrication de nanostructures de Si par implantation ionique

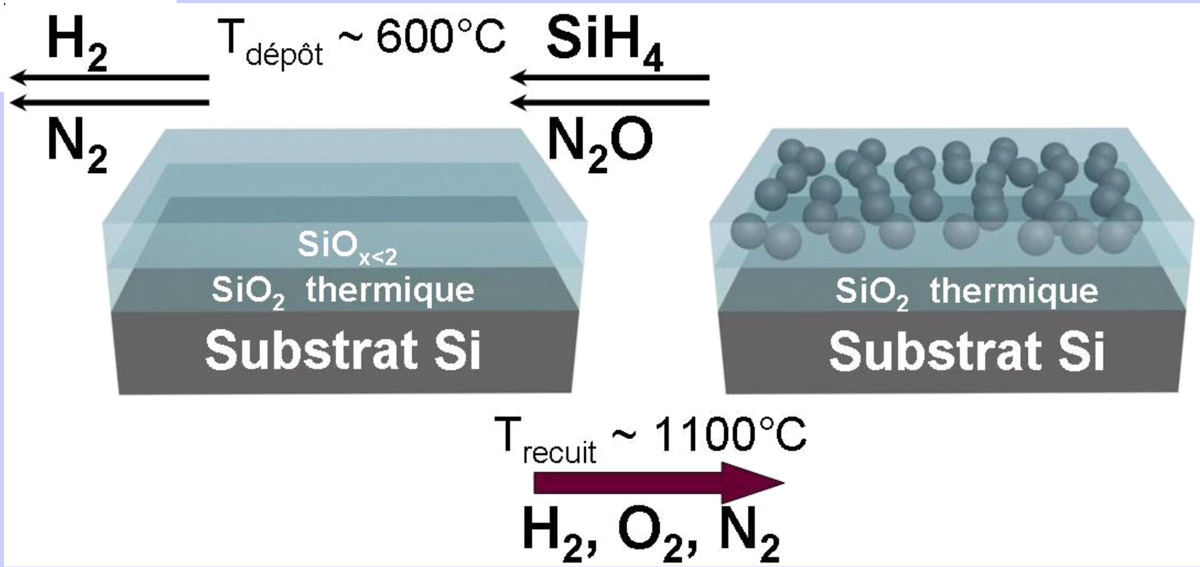
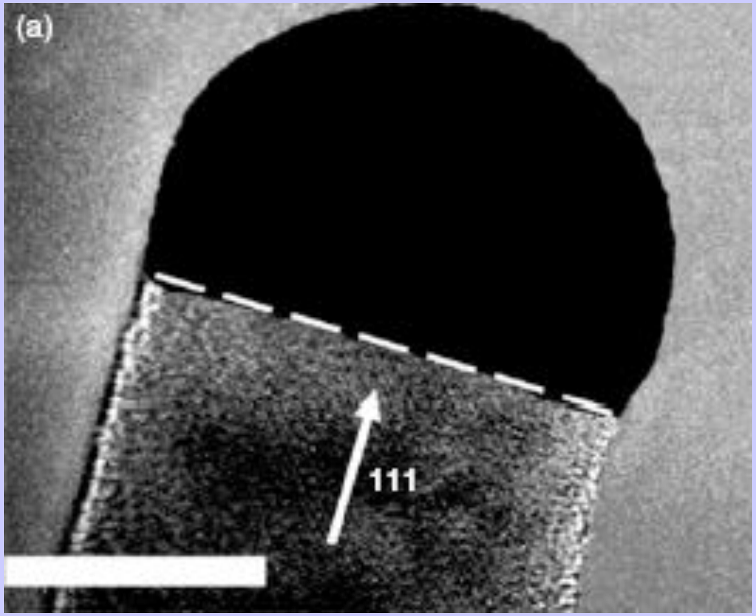
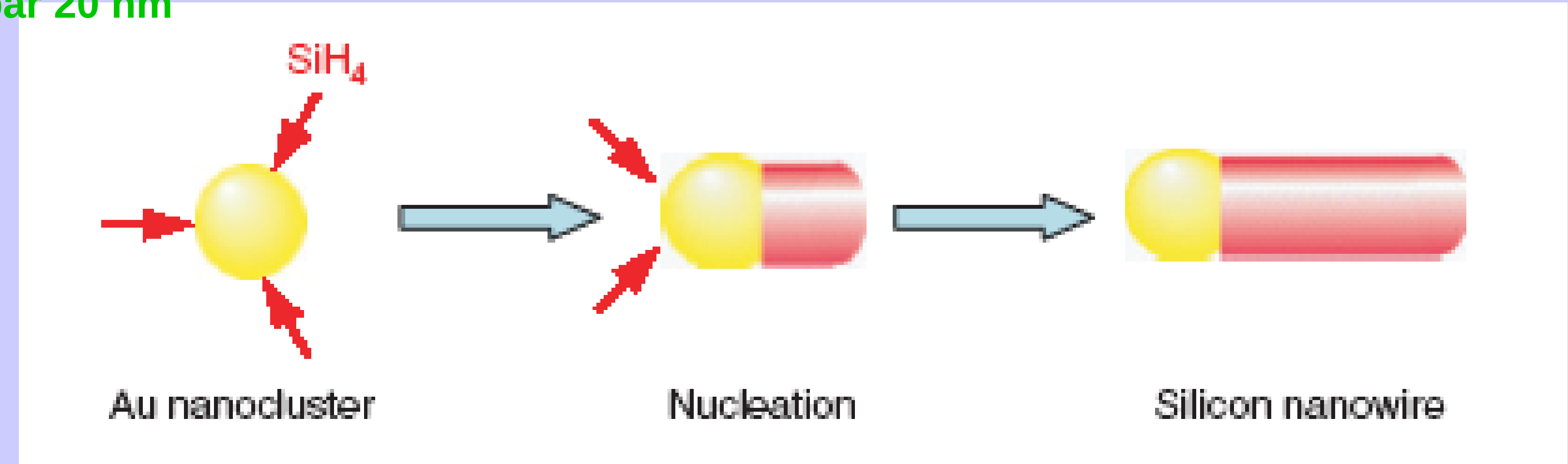



Schéma du processus de fabrication de nanostructures de Si par LPCVD : précipitation dans une couche d'oxyde.

# A nanoclaster catalysed SiNW growth by CVD

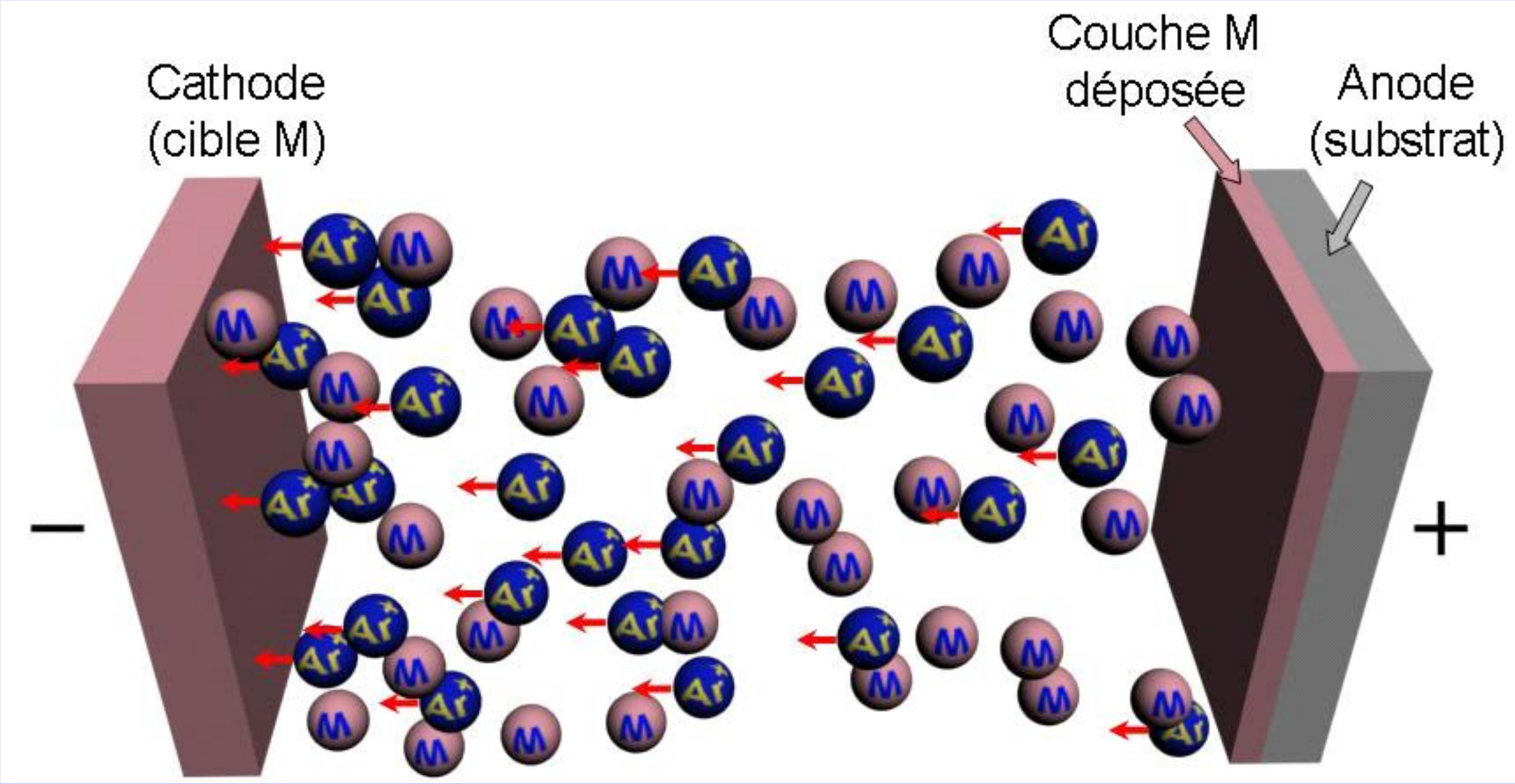



scale bar 20 nm

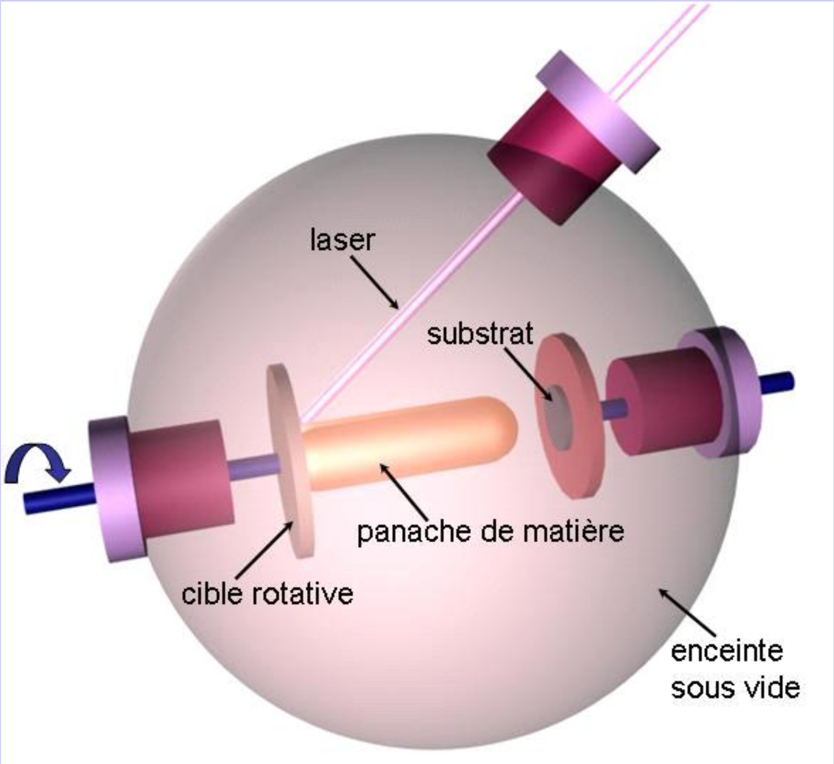


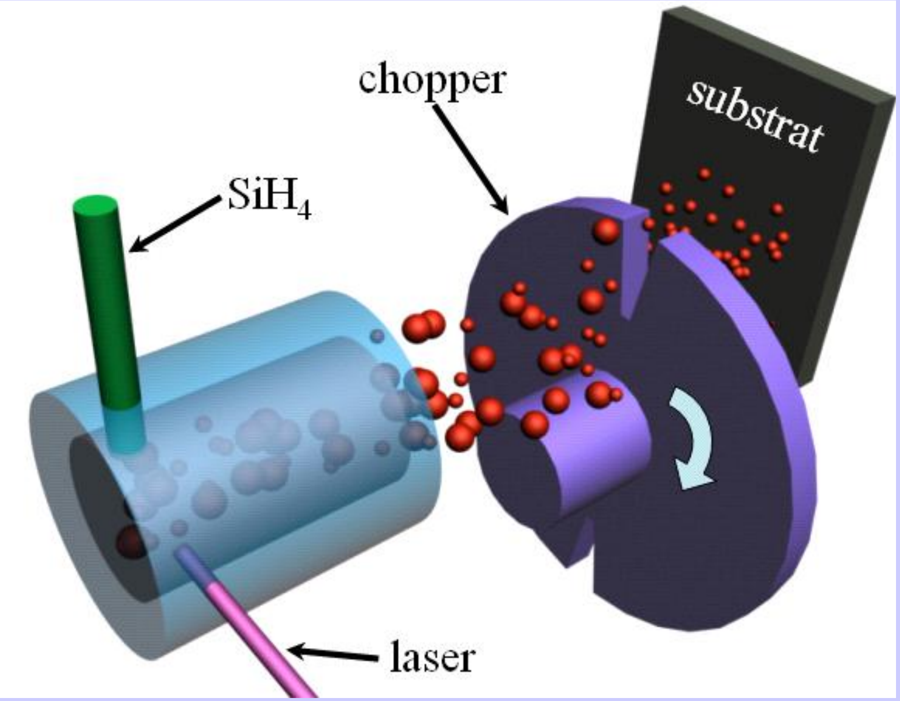
# High nano Si technologies

**Schéma de principe de la pulvérisation cathodique.**



## Schéma de principe de l’ablation laser.



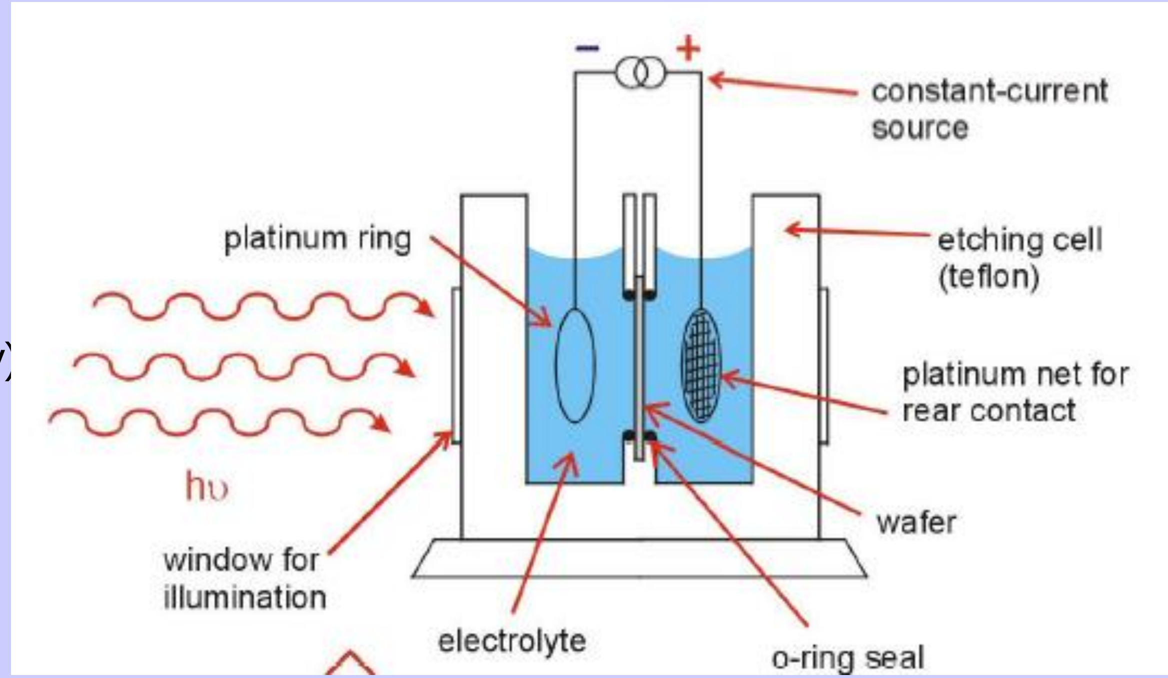

## Schéma de principe du pyrolyse laser.

# Electrochemical formation

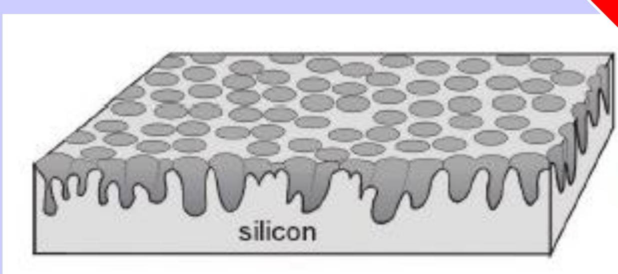
**Key parameters:**

***Si surface- hydrophobic!***

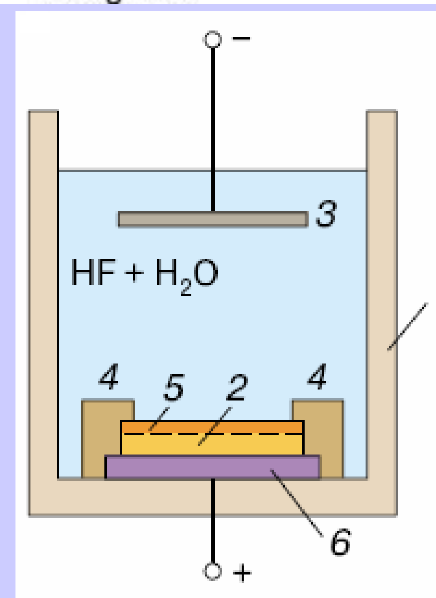
- Electrolyte type ($C_2H_5OH$ for wettability, org. for homogeneity)
- HF concentration (<50%)
- Doping level (n, n+, p, p+)
- Illumination state
- Anodical current (constant I mode=control porosity)
- Cell: $H_2$ bubble remove!



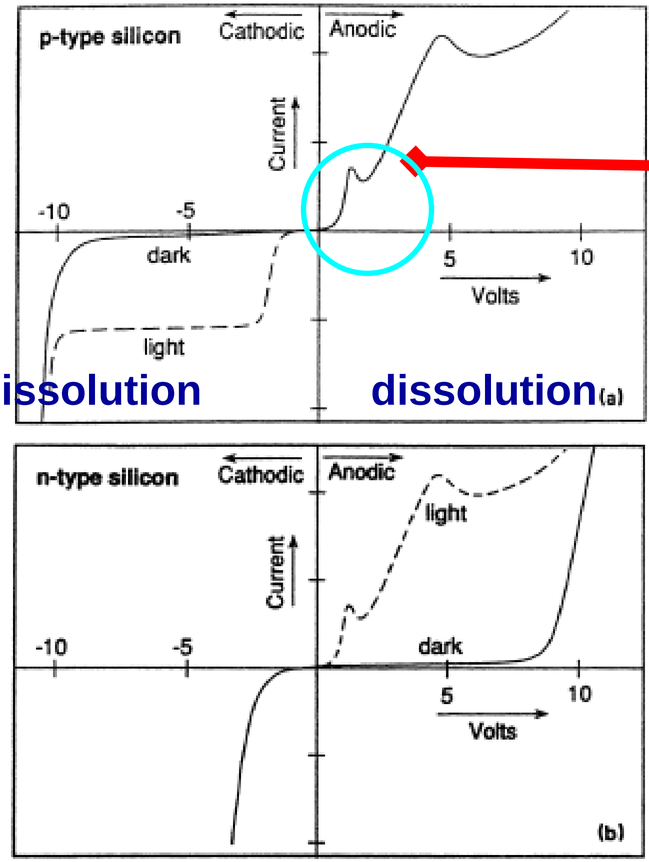

Double tank cell




single tank cells

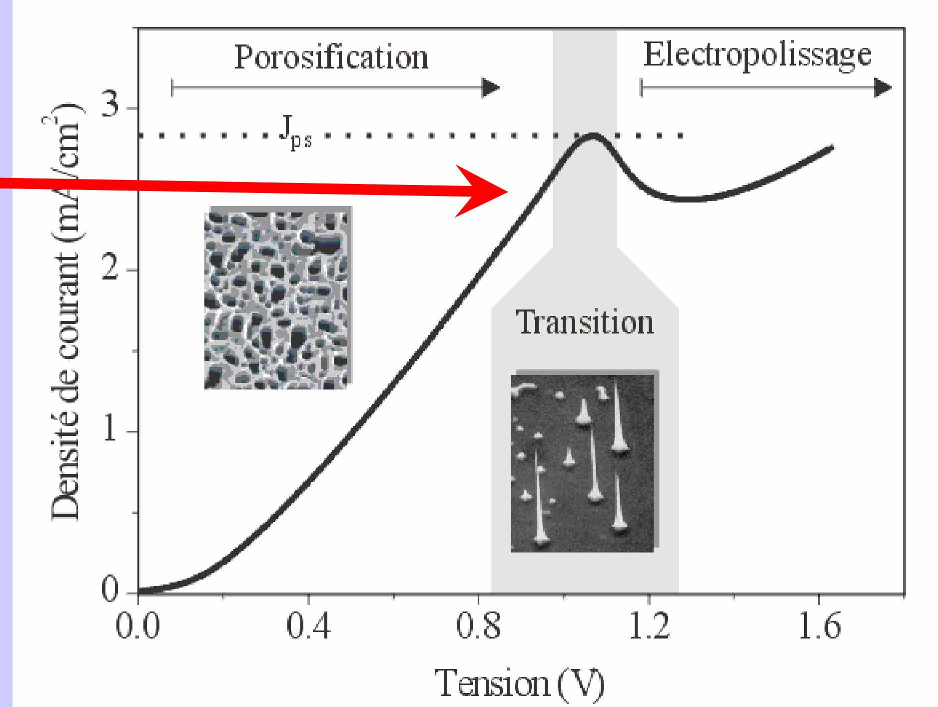


# Electrochemical formation




No dissolution

dissolution




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

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

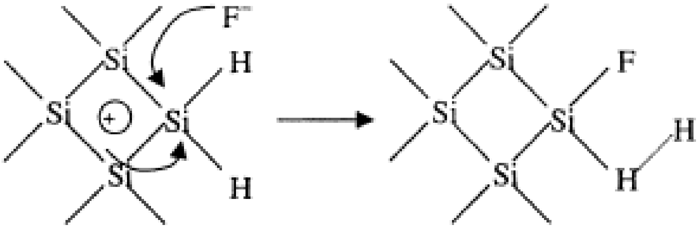
Dissolition chemistry:

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

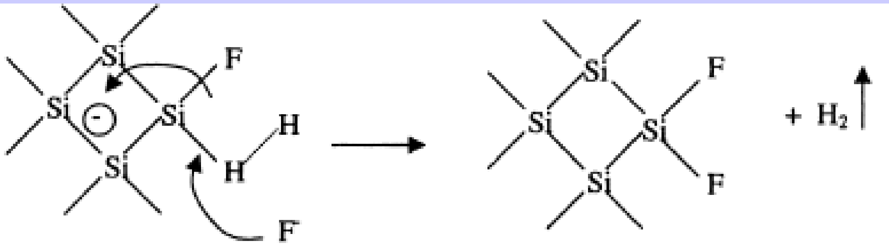
**Electropolishing** $Si + 6HF \rightarrow H_2SiF_6 + 4H^+ + 4e^-$

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

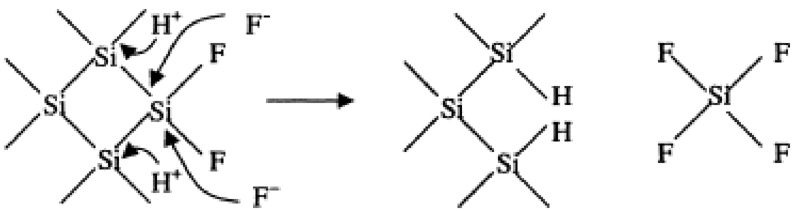
# Mechanism of Si dissolutions



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



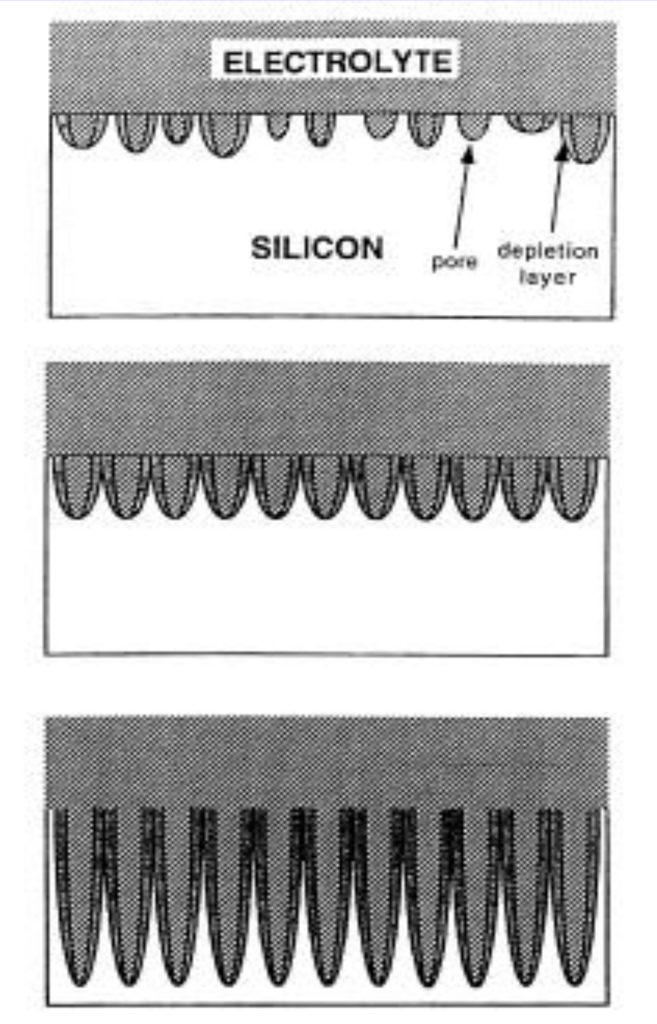
HF attack to the Si-Si backbonds. The remaining Si surface atoms are bonded to the H atoms and a silicon tetrafluoride molecule is produced

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


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

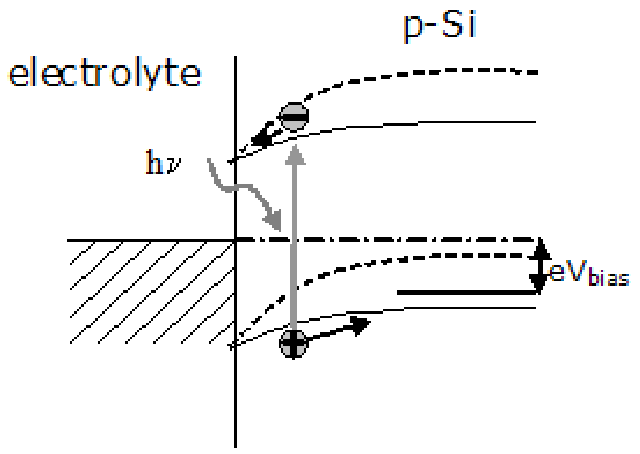
**Silicon dissolution scheme, Lehmann and Gosele**

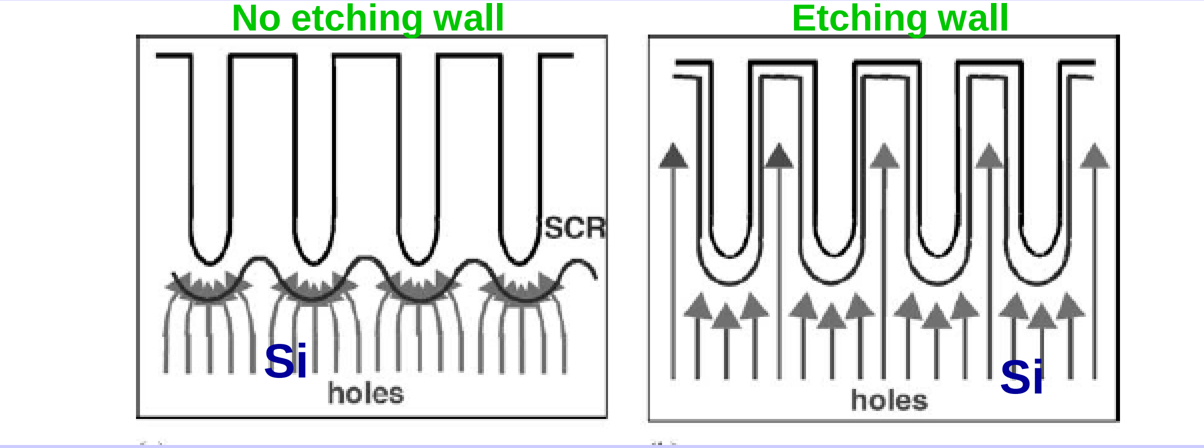
# Why pore formation?




-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…)

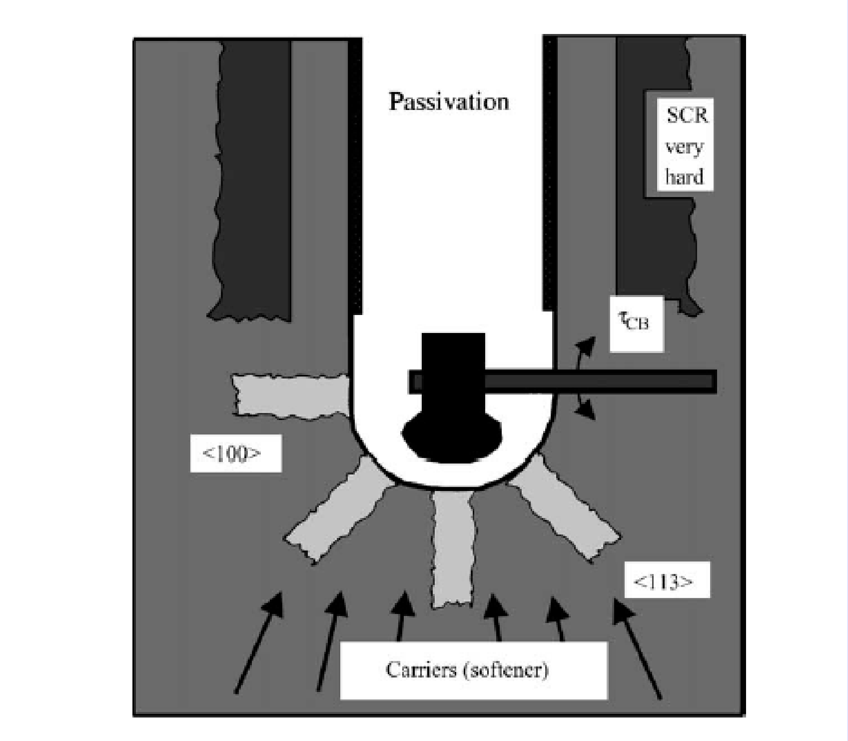
$$x_0 = \sqrt{\frac{2\varepsilon\varepsilon_0 e\psi_s}{e^2 N_A}}$$



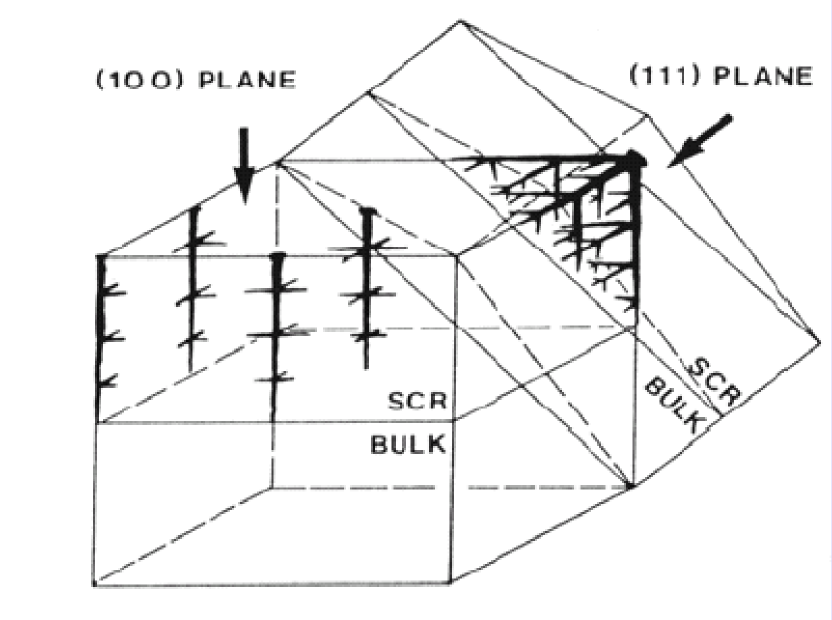




Large SCR and small SCR

# Hummer model of pore formation



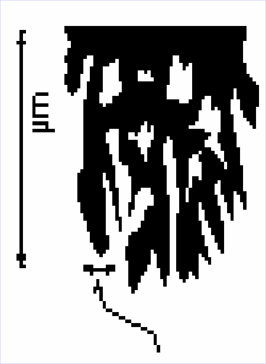

Si is always removed in patches corresponding to the domain size of system!



# Pore formation region

## Nano-porous Si
## P-type

- « nano-sponge » morphology
- nanocristallites sizes: **1 - 5 nm**

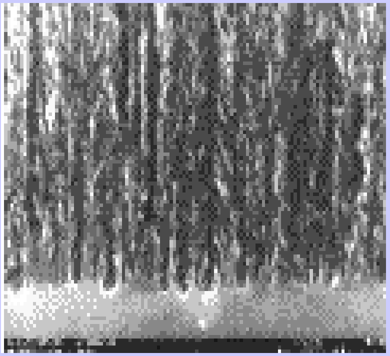



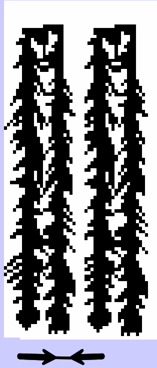

**<5 nm**

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

## Meso-porous Si
## P+-type

- « nano-column » morphology
- column width: **5 - 20 nm**





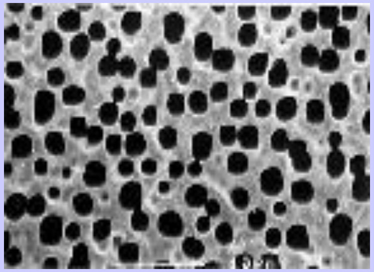
**5 nm**

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

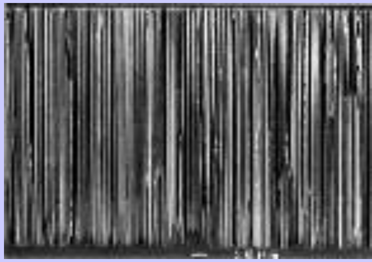
## Macro-porous Si
## N-type + light

- « nano-wells » morphology
- inter-well space: **0.1 - 1 µm**

**Top view**



**Cross-section**

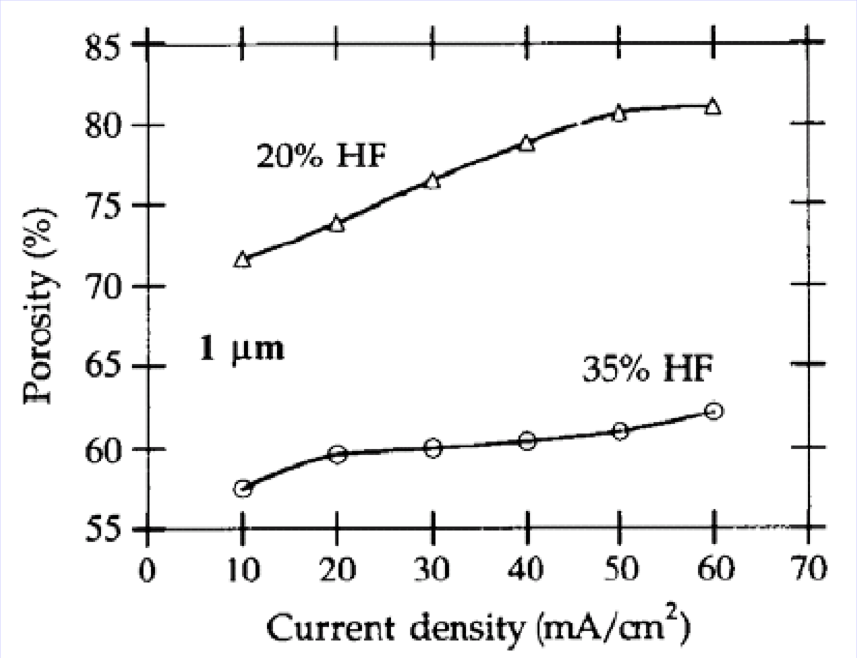


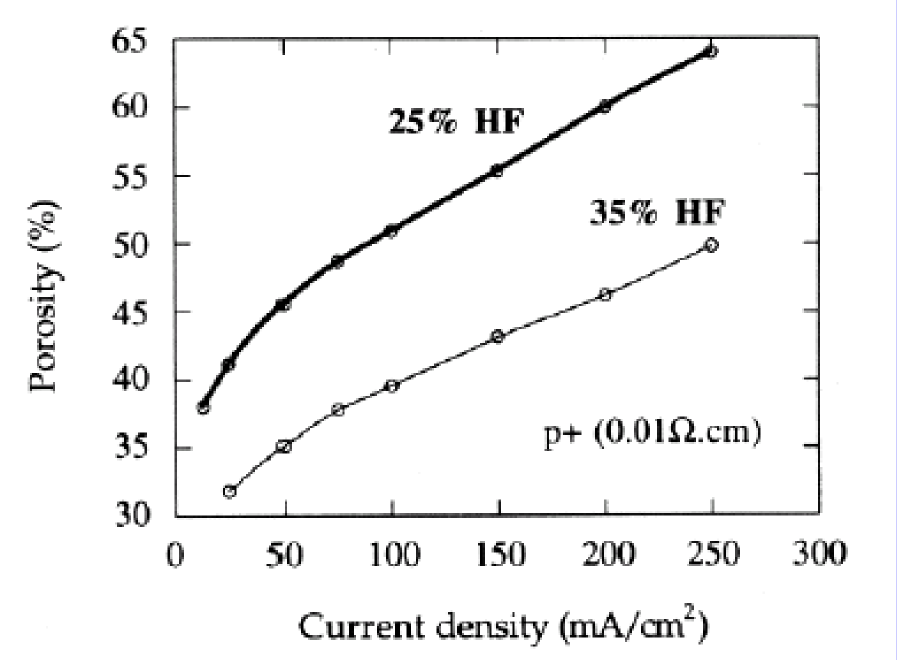
WWW-Server Max-Planck-Institut für Mikrostrukturphysik Halle, Germany

# Porosity

**Nano-porous Si P-type**

**Meso-porous Si P+-type**



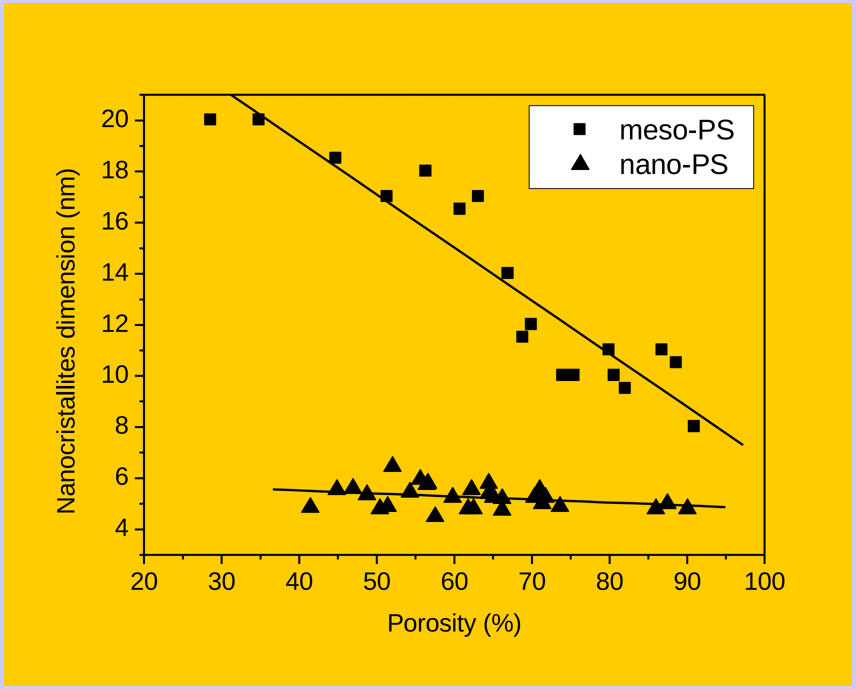



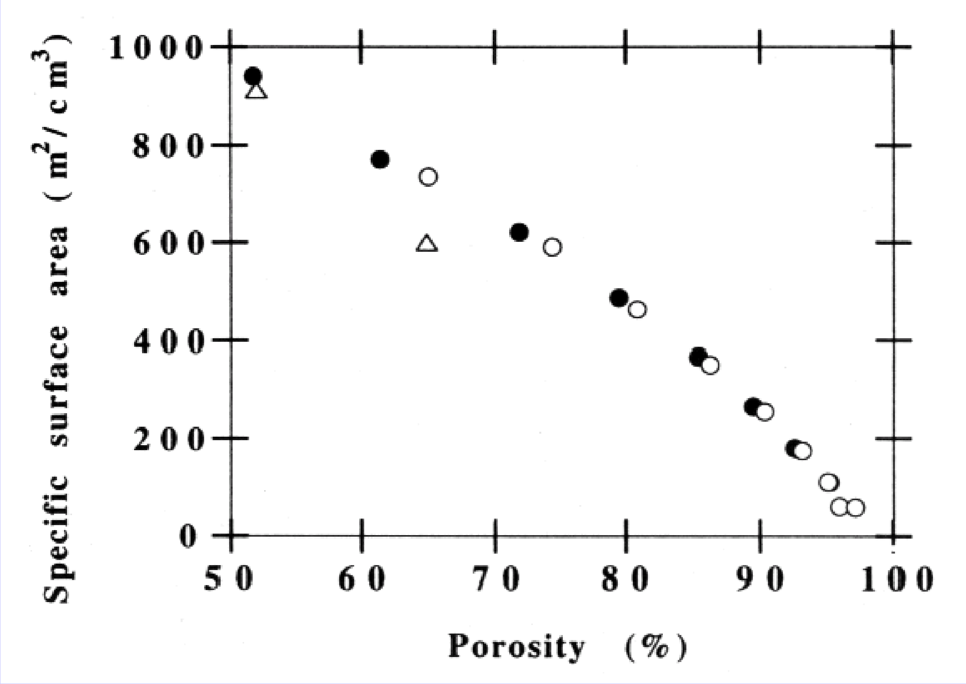

Porosity

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

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

# Porosity, particles dimension, specific surface



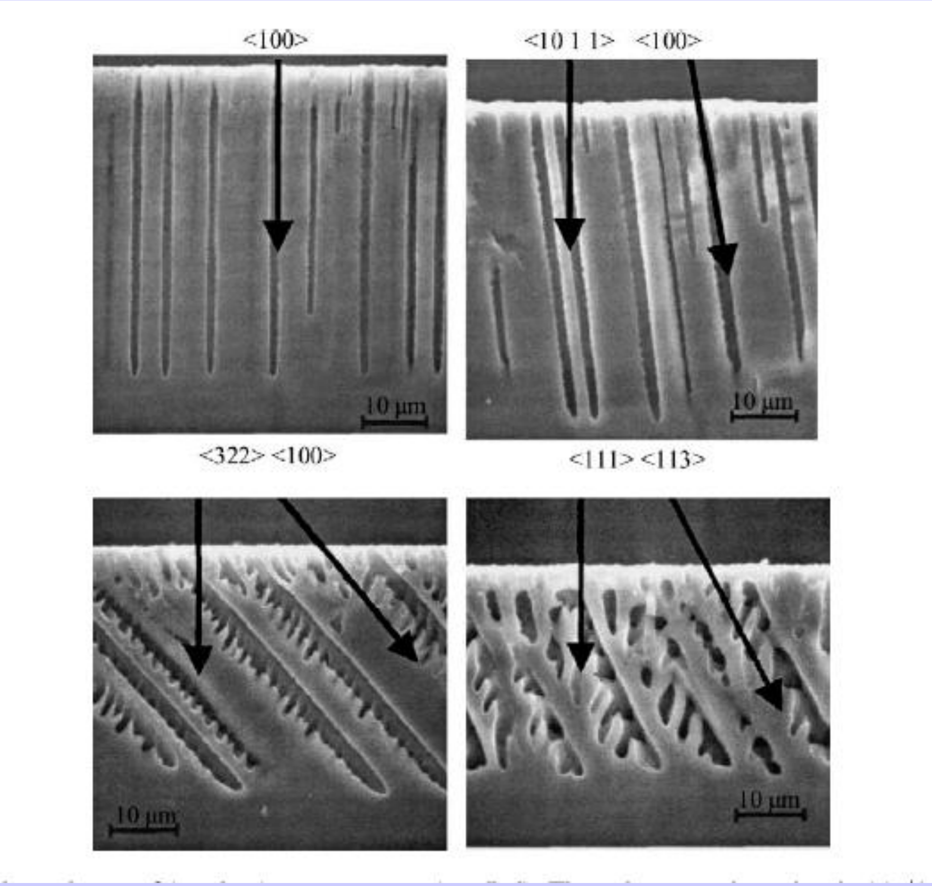



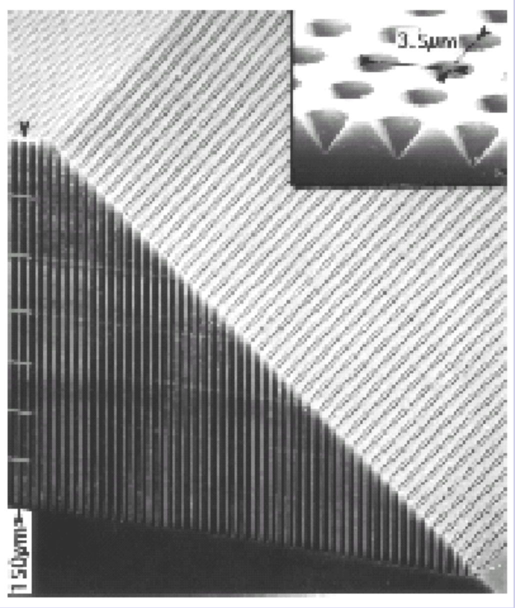

Specific surface

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

Particle dimension vs Porosity

# Macrpores



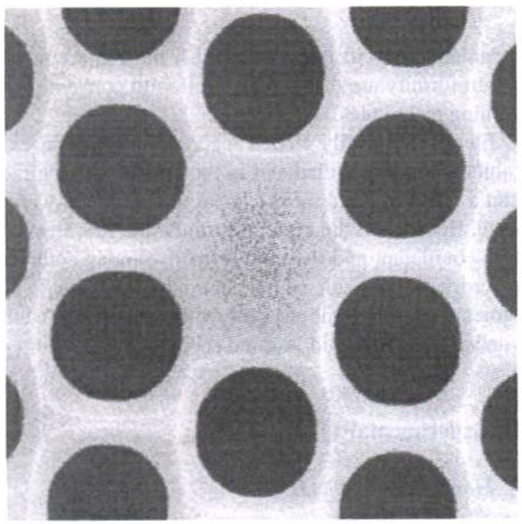
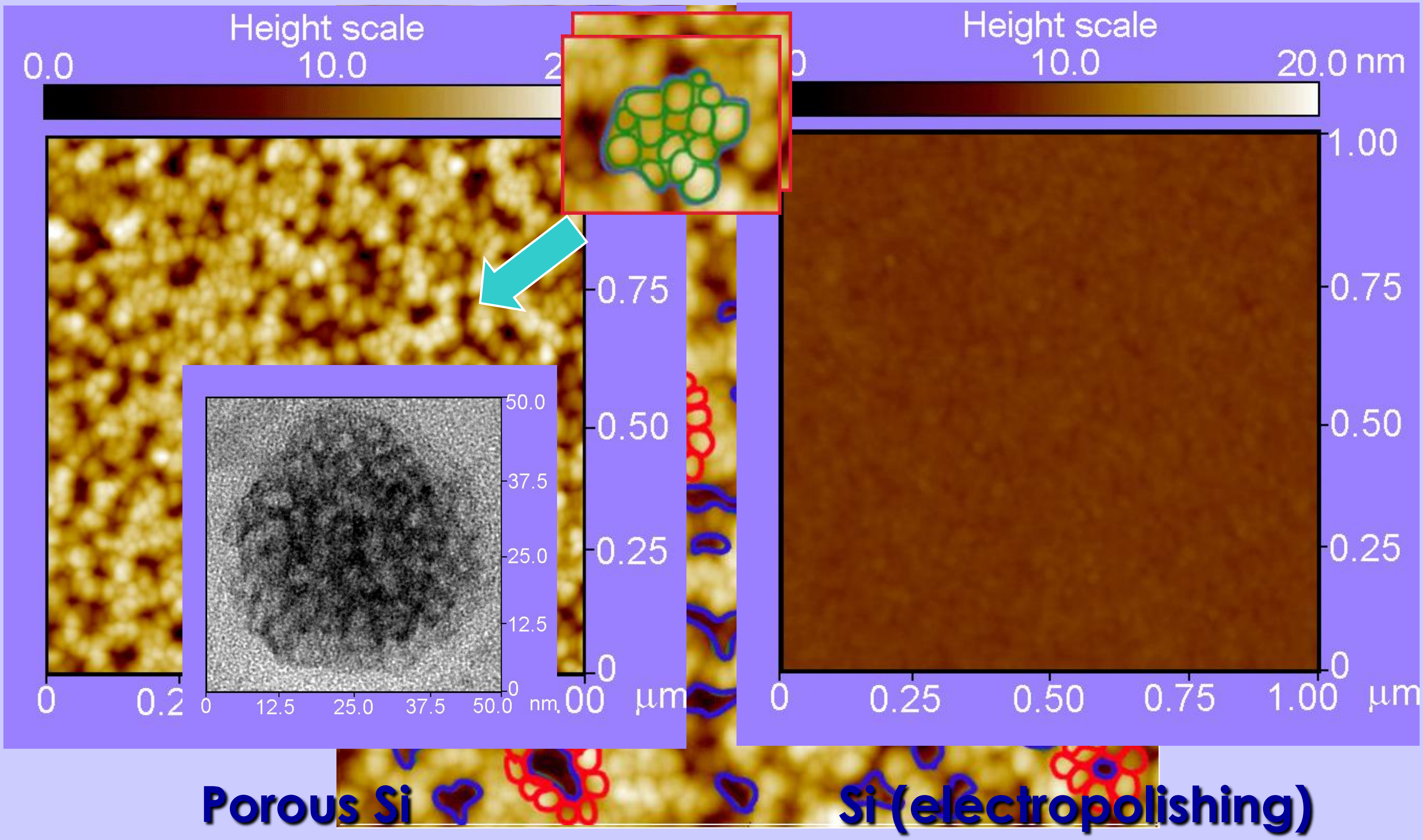



*Figure 1.* SEM image of the region around a missing etch pit after electrochemical pore growth and subsequent pore widening by oxidation/etching steps. The distance between the pores is 1.5 $\mu$m, pore diameters are 1.15 $\mu$m.

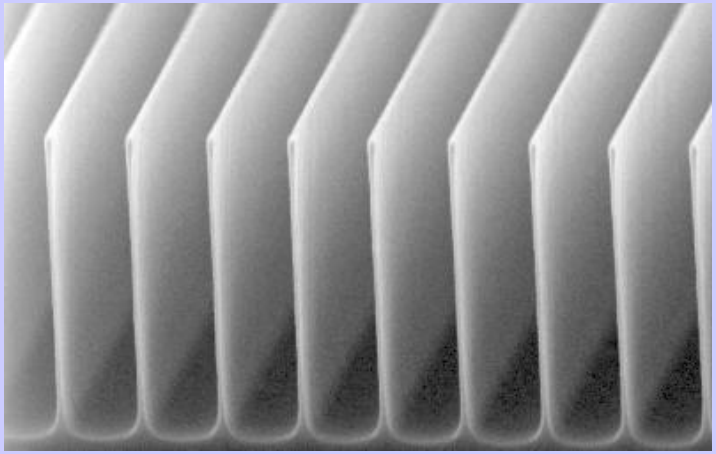
V. Lehmann, Kluwer Acad. Publ., 1, (1993)

# Nano-porous nanostructures

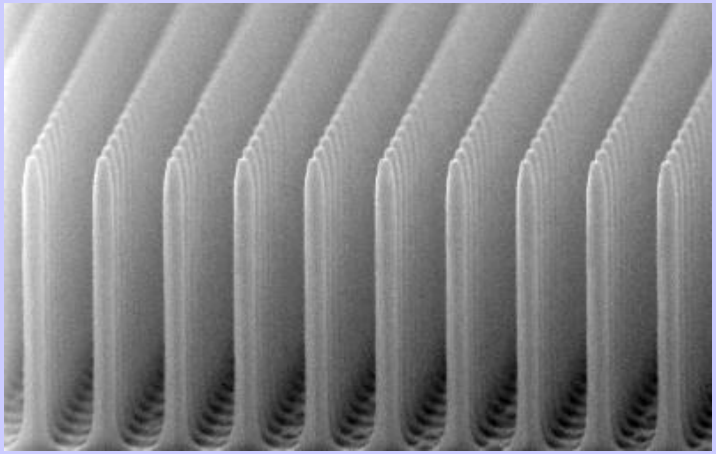



**Porous Si** **Si (electropolishing)**

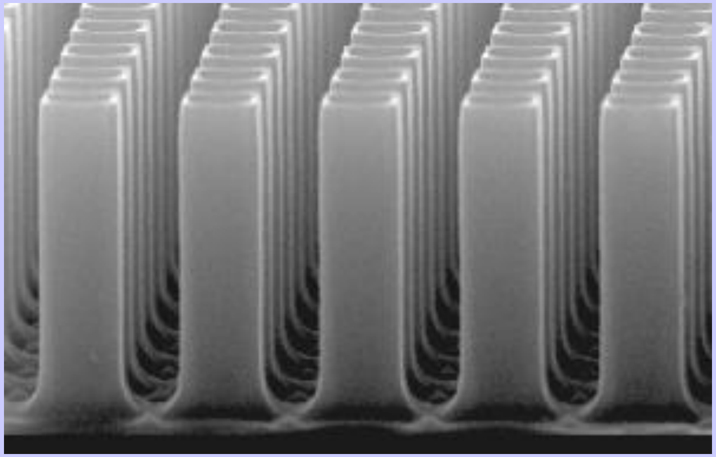
# Transient anodization regime



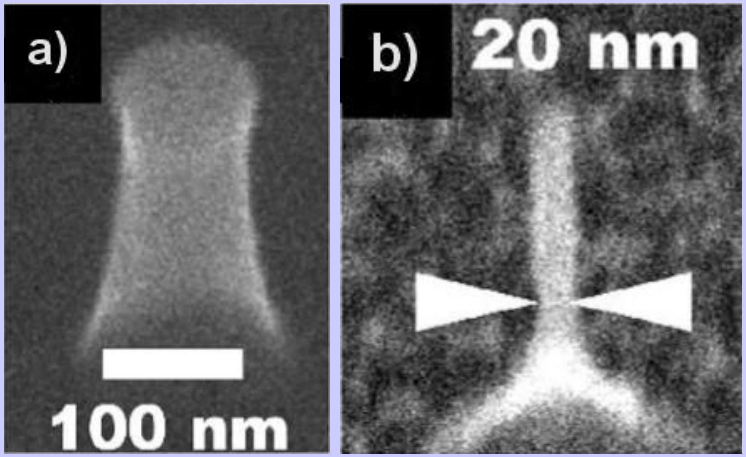
Réseau de Murs
Période 1.6 µm ; Largeur 110 nm ; hauteur 7 µm



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

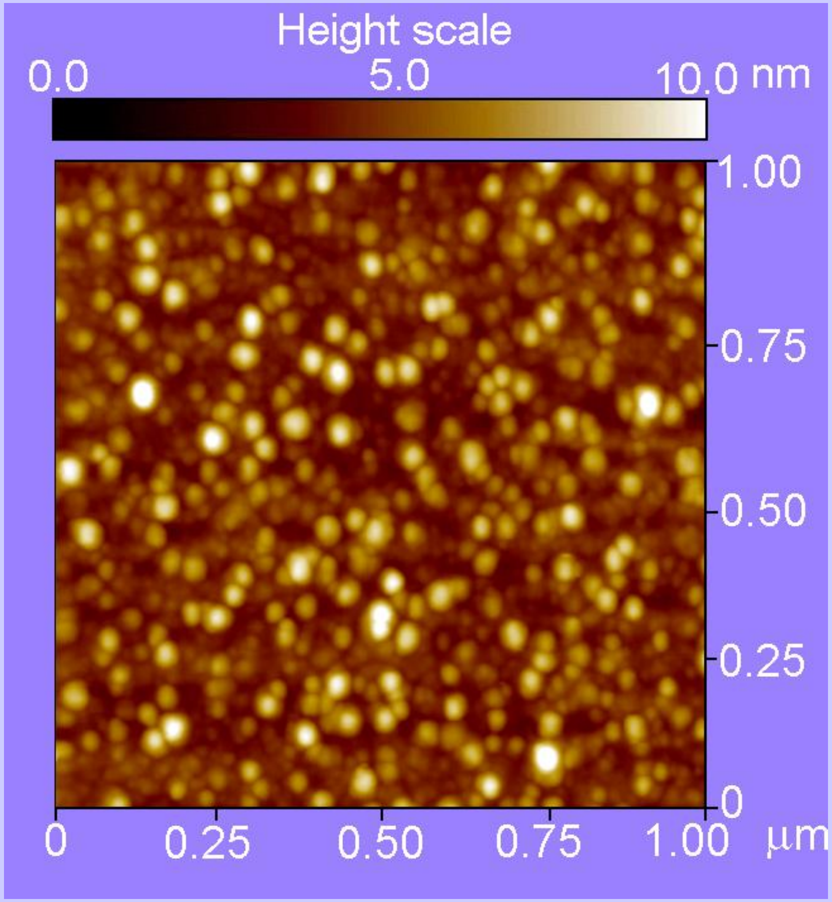


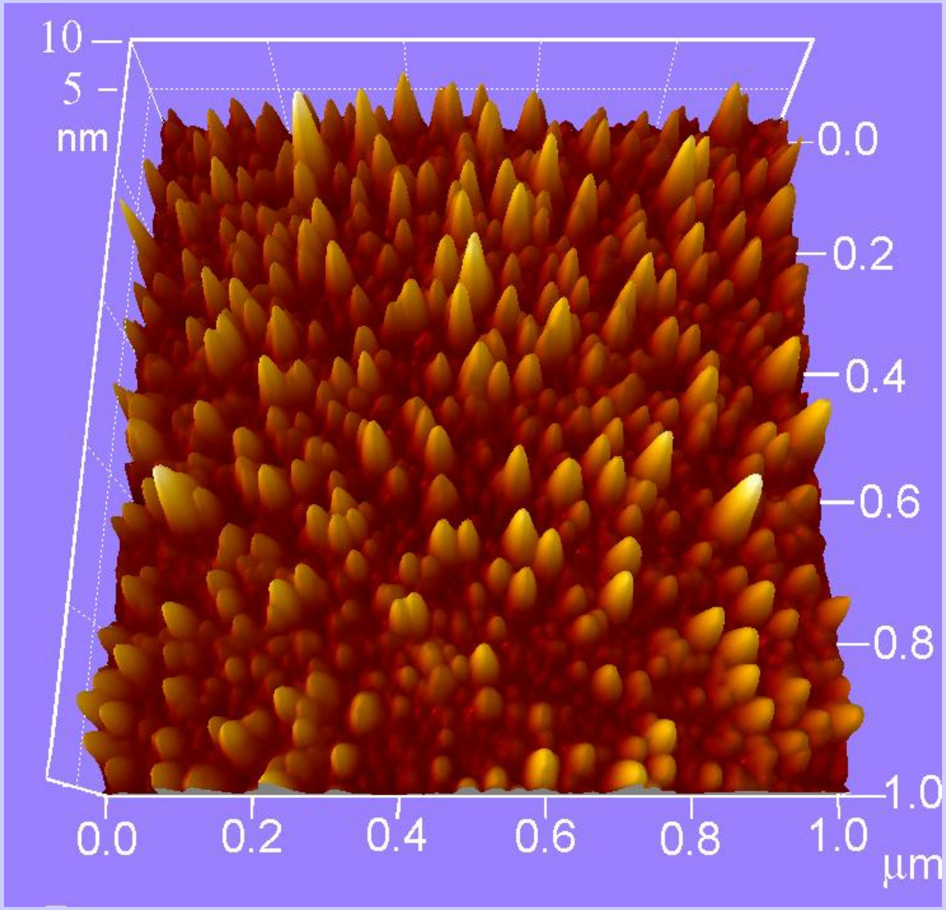
Réseau de Tubes
Période 3.2 µm ; Murs 220 nm ; hauteur 7 µm



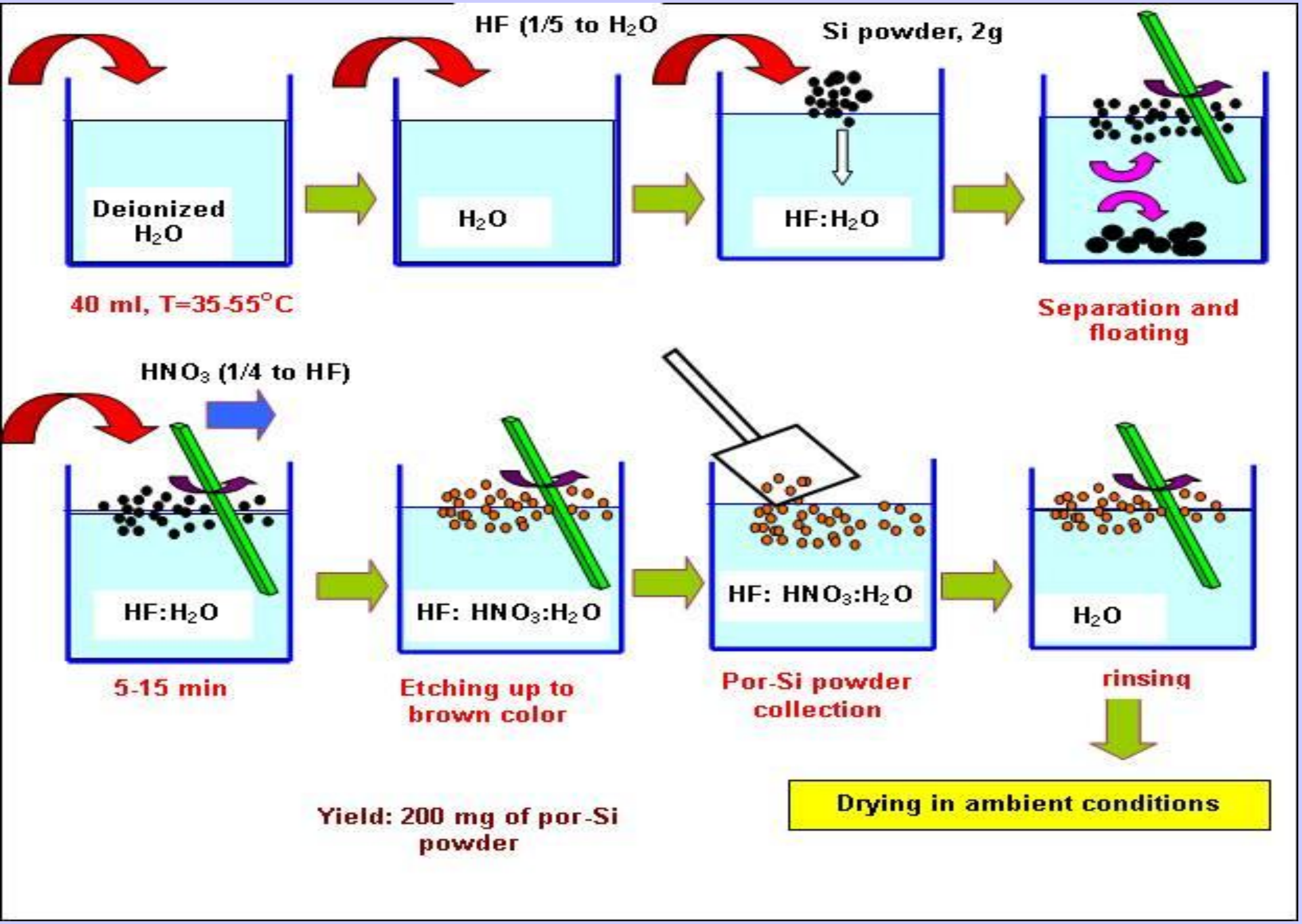

a) Pilier obtenu par gravure plasma puis b) aminci par gravure électrochimique

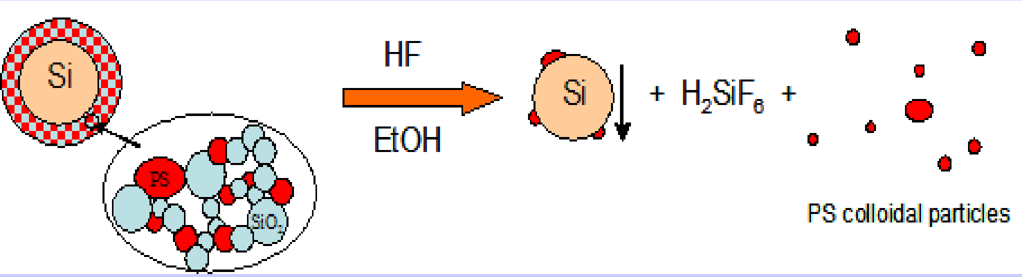
# Time-resolved transient anodization regime: nanoparticle formation



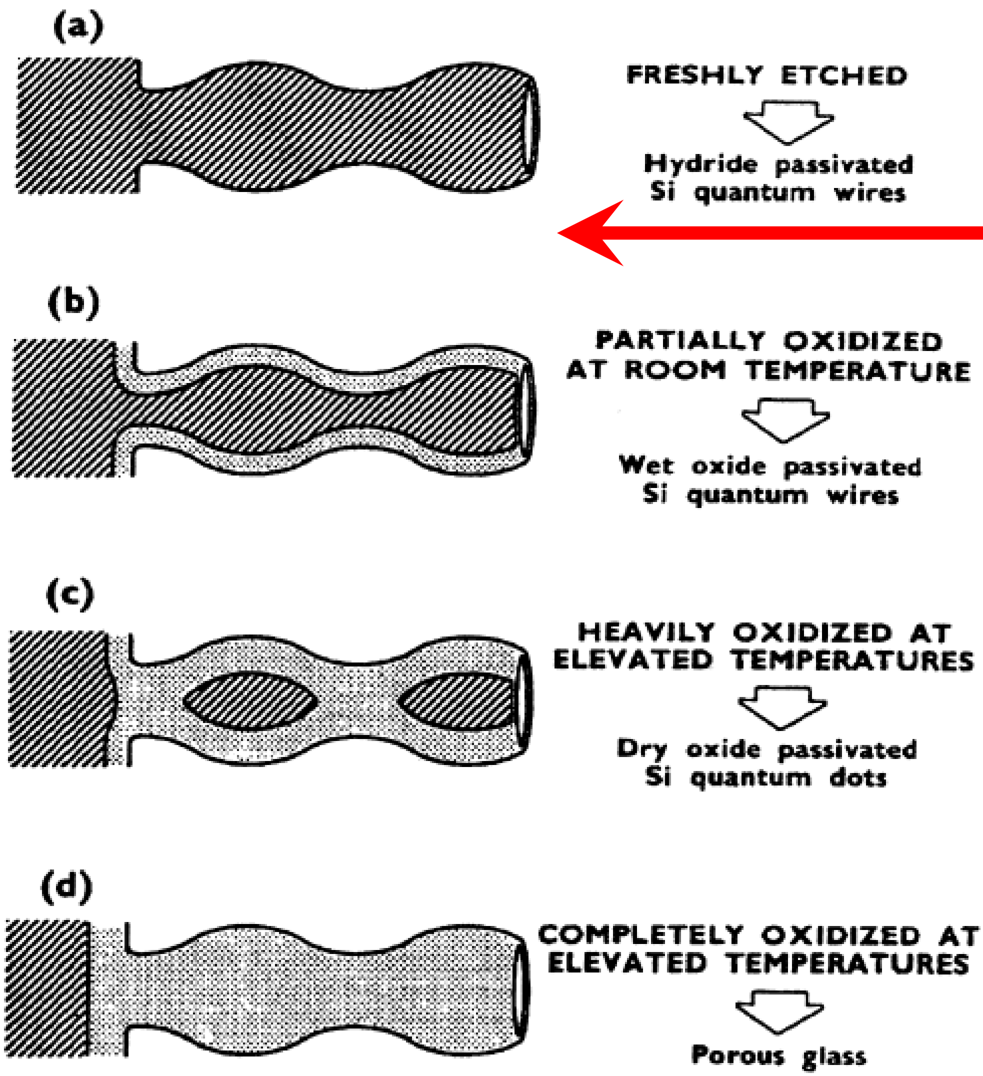
## Stain etching of Si powder: method

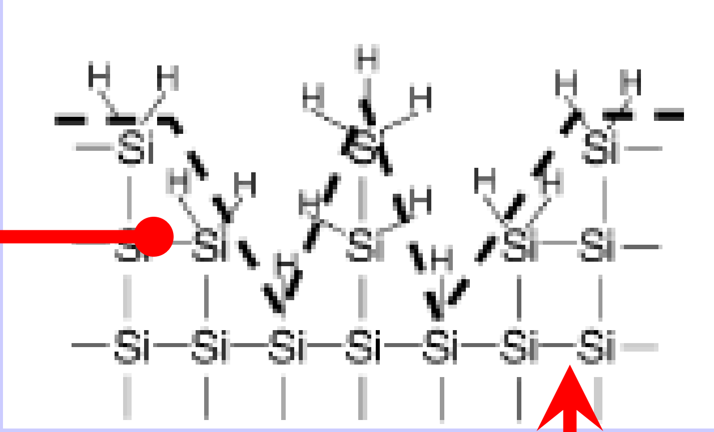


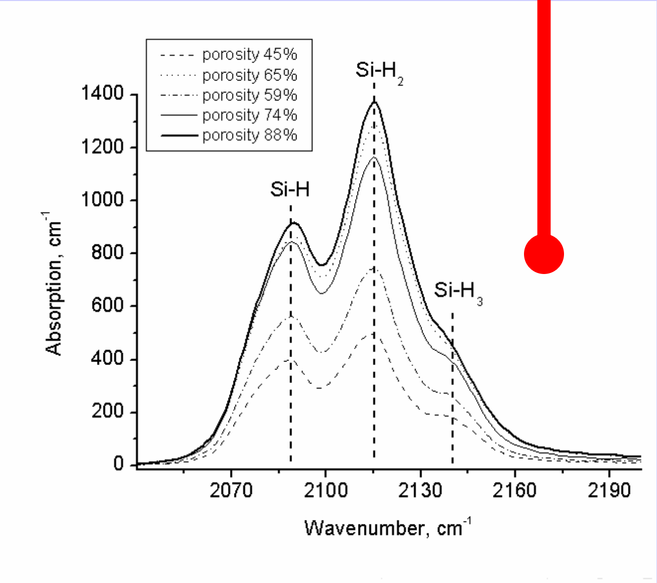




$$
\begin{cases}
HNO_3 + 3H^+ \rightarrow NO + 2H_2O + 3e^+ \\
ne^+ + Si + 2H_2O \rightarrow SiO_2 + 4H^+ + (4-n)e^- \\
SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O
\end{cases}
$$

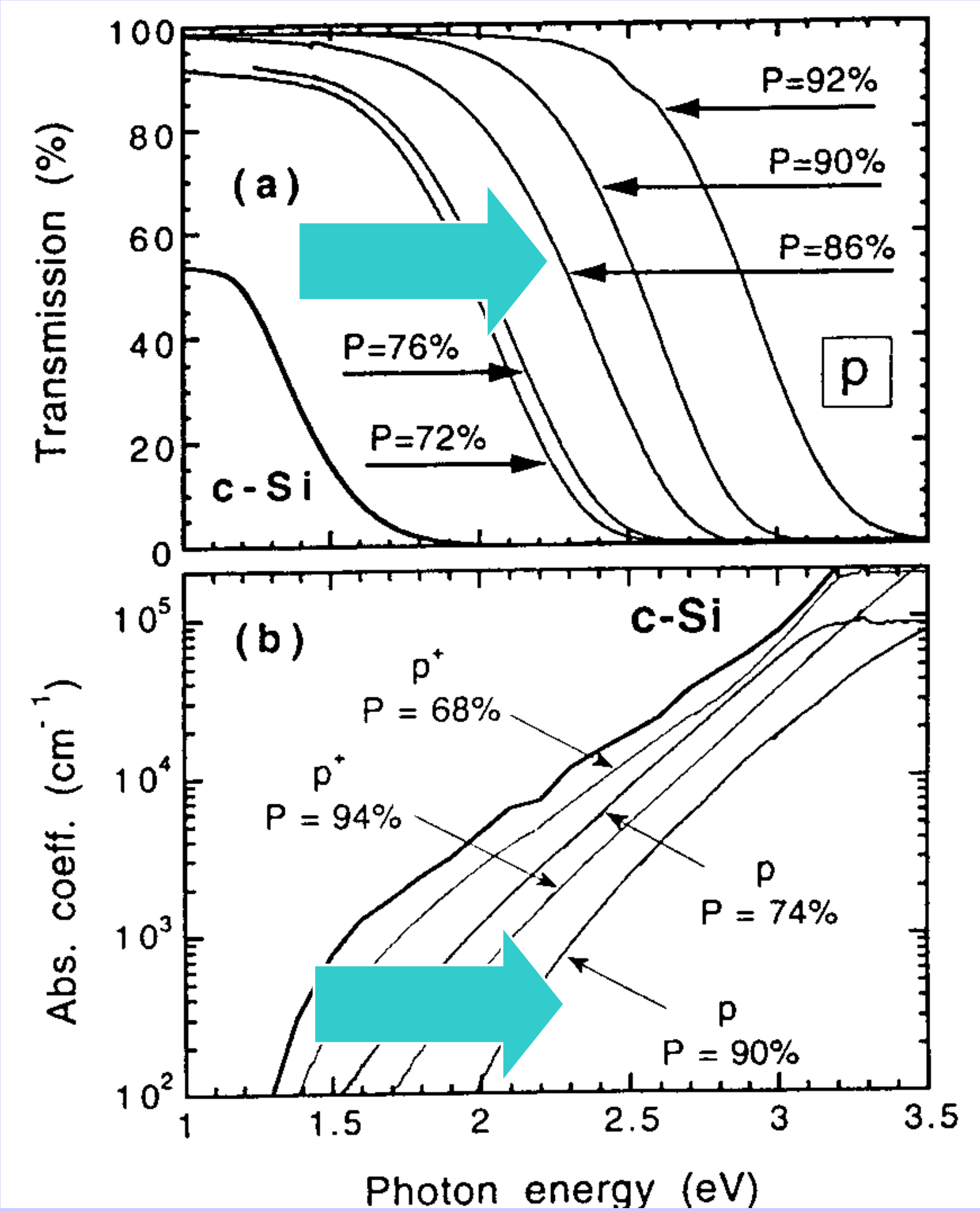
# Idealized schematic steps in the oxidation process of highly PS

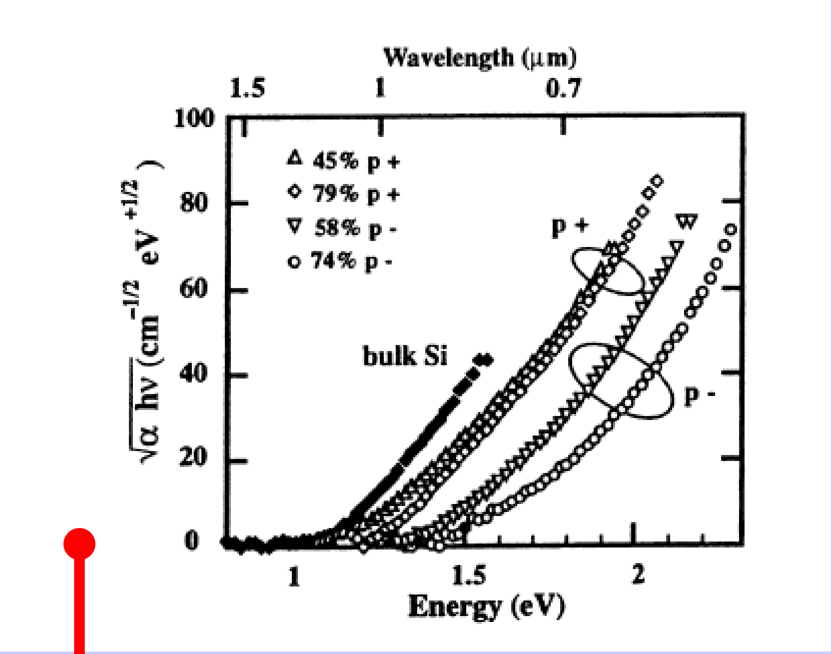




# Optical properties of nano- porous Si



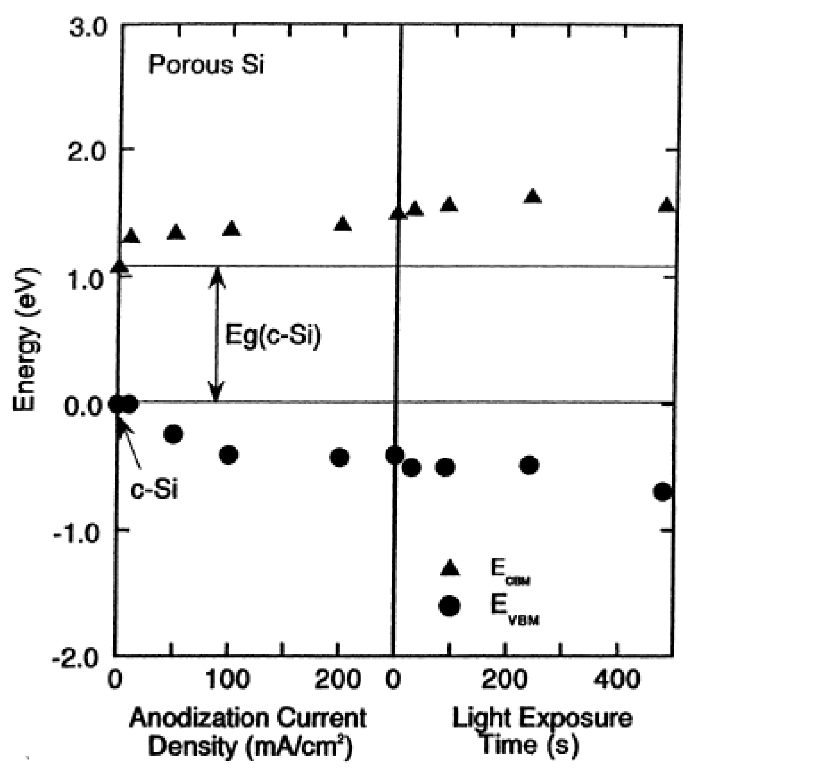




Square root of the absorption coefficient times photon energy *vs* photon energy

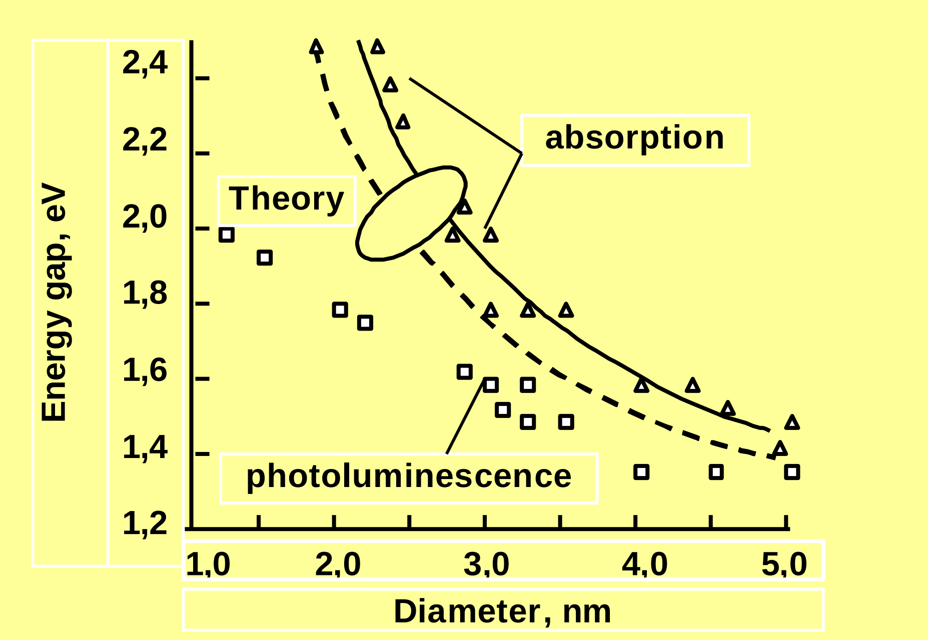
$$\alpha = \left(h\nu - E_g \pm E_{ph}\right)^2$$

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

# Energy band of nano- porous Si

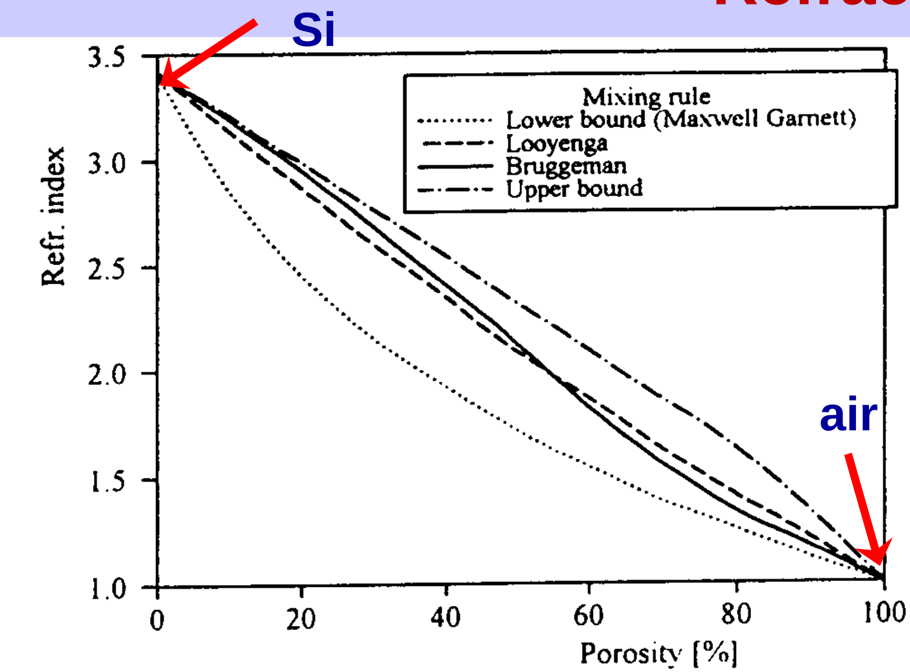


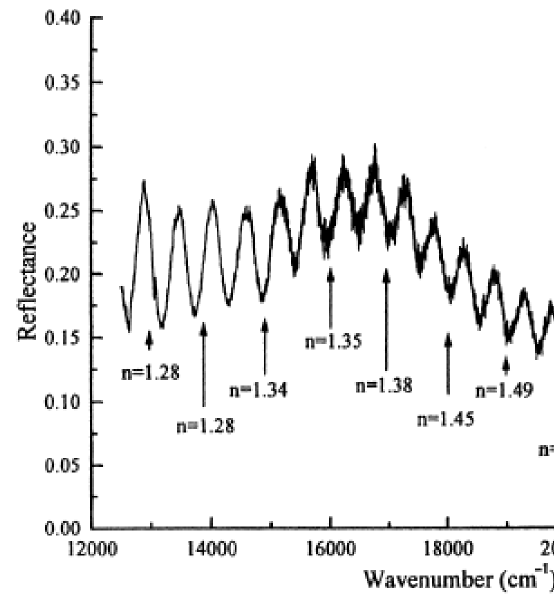

Energy position of c-band minimum and v-band maximum vs anodization current




Energy bend gap vs diameters on of Si particles

# Refractive index




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

**Bruggeman effective medium approximation**

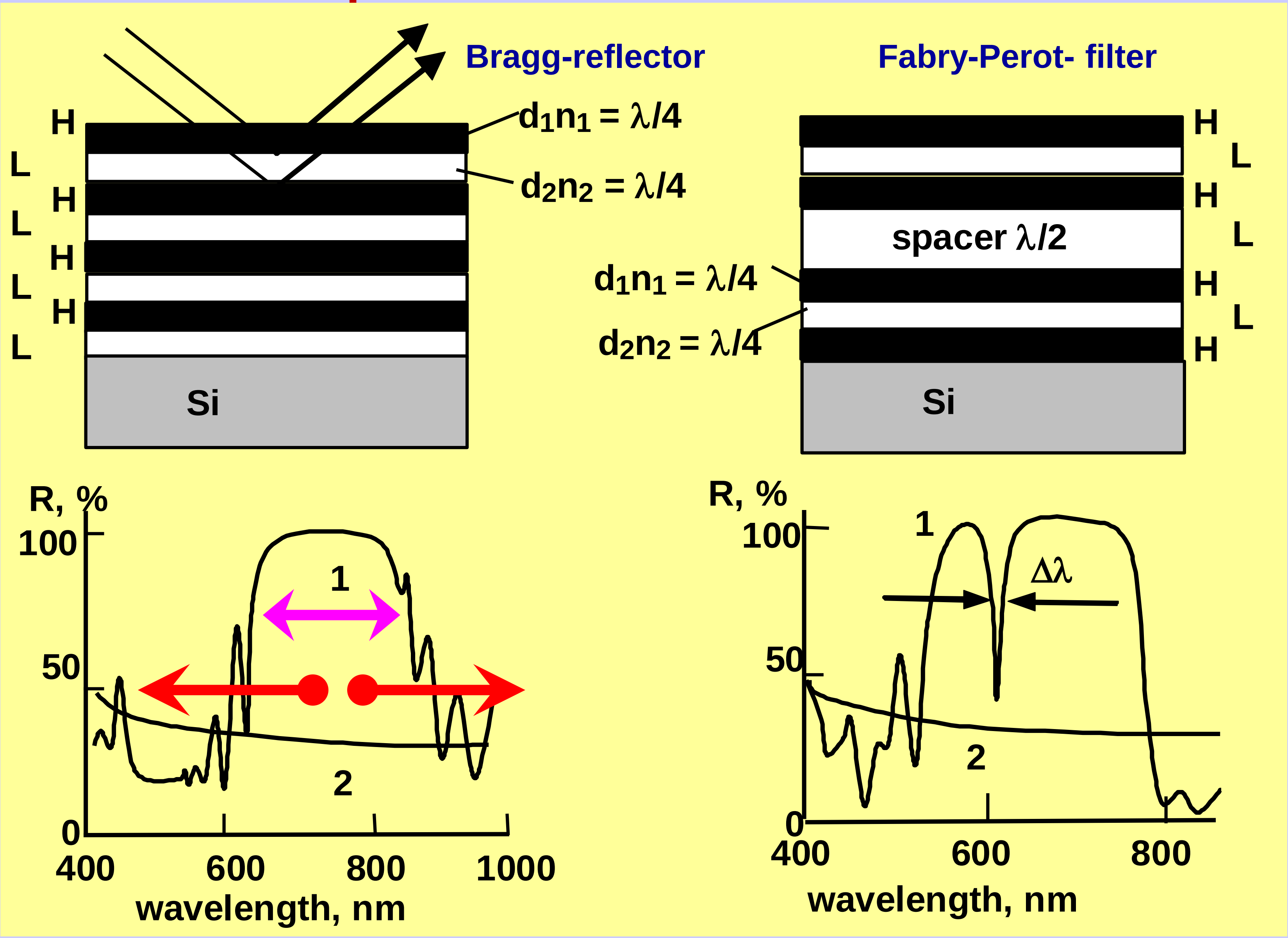
$$P\left(\frac{1-\hat{\varepsilon}}{1+2\hat{\varepsilon}}\right) + (1-P)\left(\frac{\hat{\varepsilon}_{Si} - \hat{\varepsilon}}{\hat{\varepsilon}_{Si} + 2\hat{\varepsilon}}\right) = 0$$

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

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

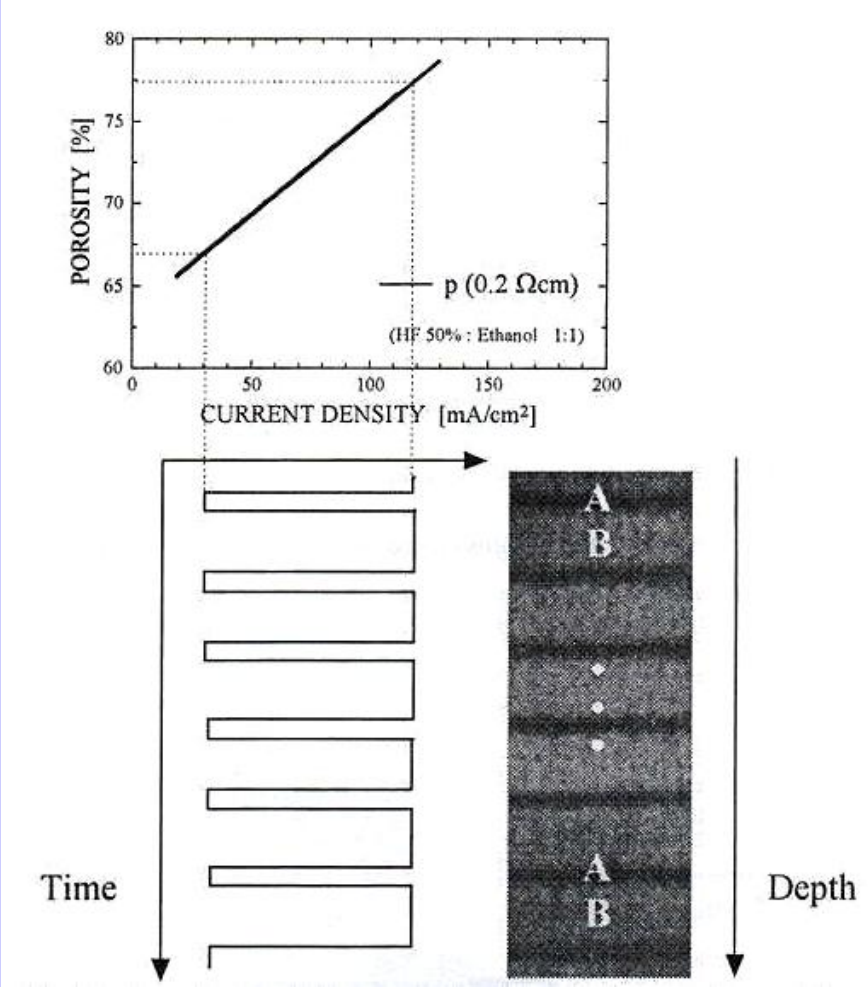
$$\varepsilon = (1-P)\varepsilon_{Si} + P\varepsilon_{air}$$

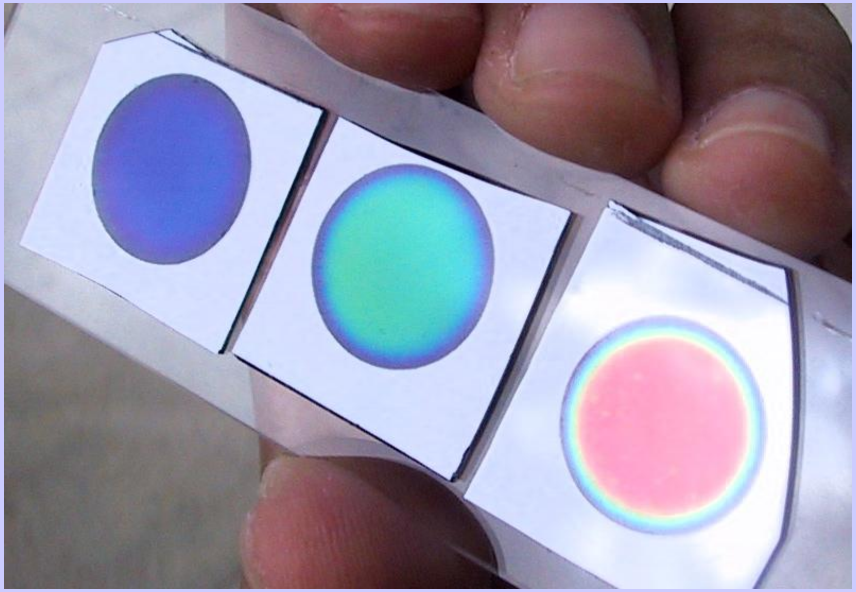
# Optical multi-structures




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

# Bragg's reflectors



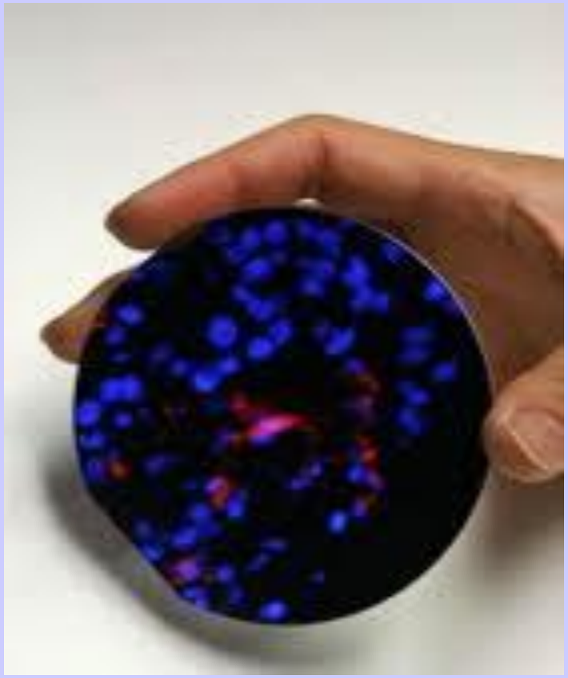



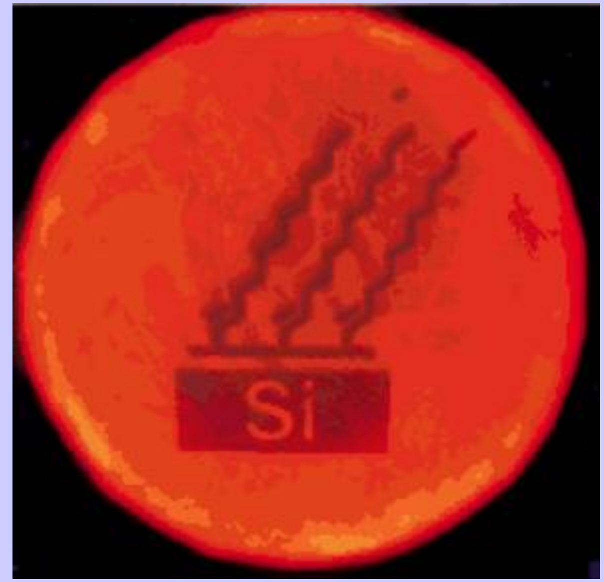
$$m\lambda_{Bragg} = 2(d_1 n_1 + d_2 n_2)$$

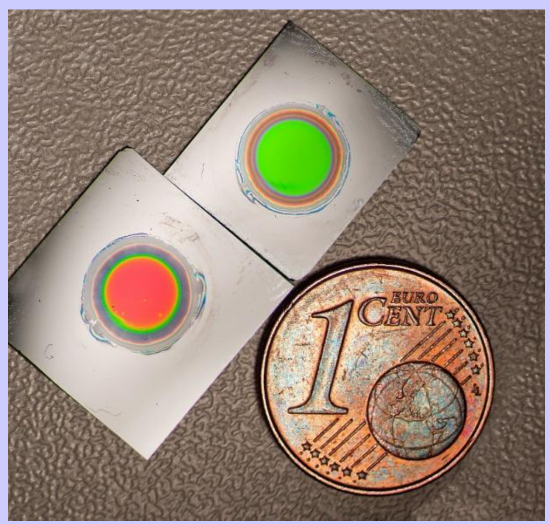
$$\lambda_{Bragg} \uparrow \Rightarrow d_{12} \uparrow n_{12} \uparrow$$

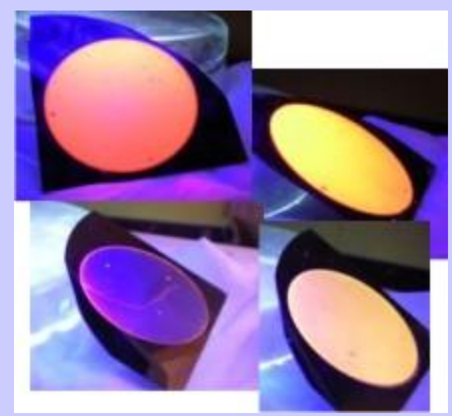
Hilbrich et al., Thin Solid Films 297, (1997) pp. 250-253

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

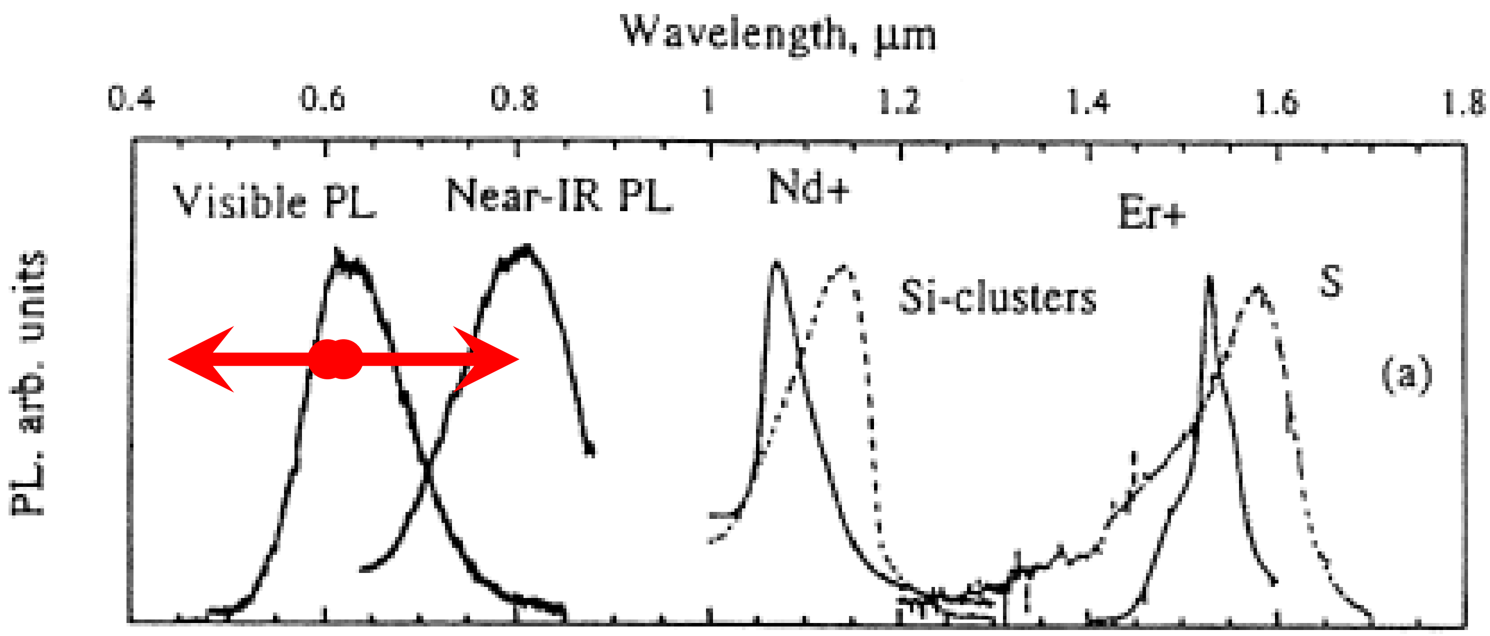




# Photoluminescence of nano- porous Silicon at UV illumination at $T_{room}$



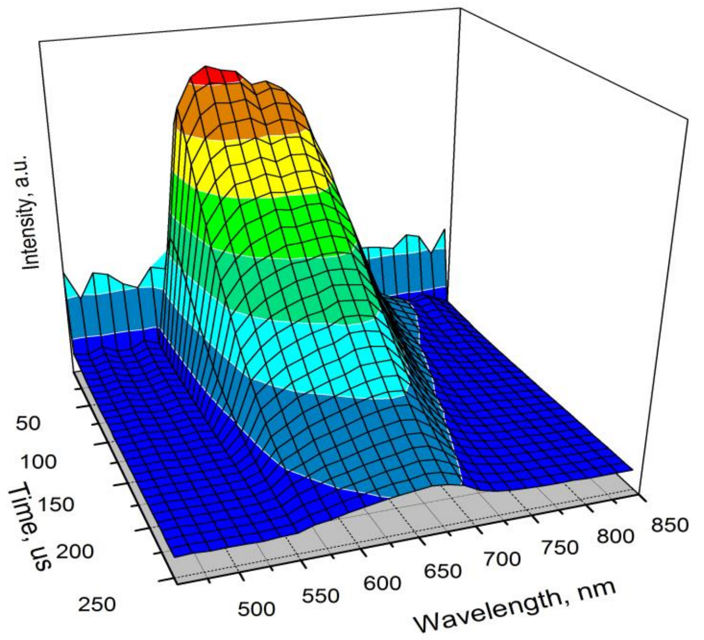

| Spectral range | Peak wavelength | Label |
|---|---|---|
| UV | ~350 nm | UV band |
| Blue–green | ~470 nm | F band |
| Blue–red | 400–800 nm | S band |
| Near IR | 1100–1500 nm | IR band |

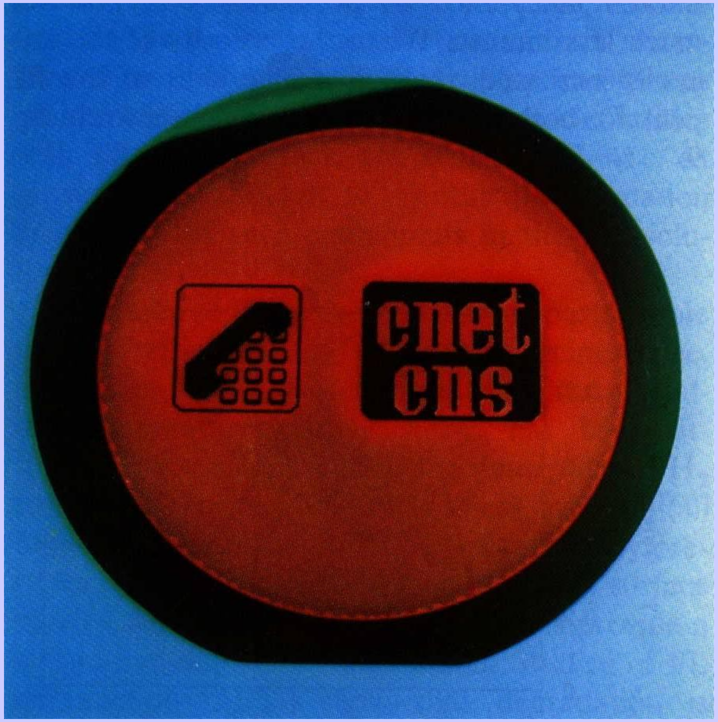
O.Bisi, S.Ossini, L.Pavesi, Surf.Sci.Rep, 38(2000)1

# 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 μs | 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 |



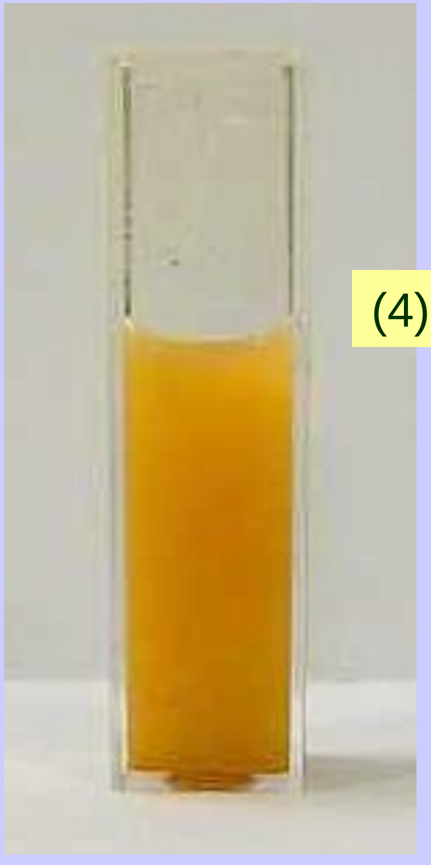



# Si QDs preparation in colloidal solution

2) Grinding of layer
3) Few times washing in pure ethanol, drying and formation of homogeneous micro powder
4) Dissolvation in pure ethanol **2-5 mg/mL**

(2)

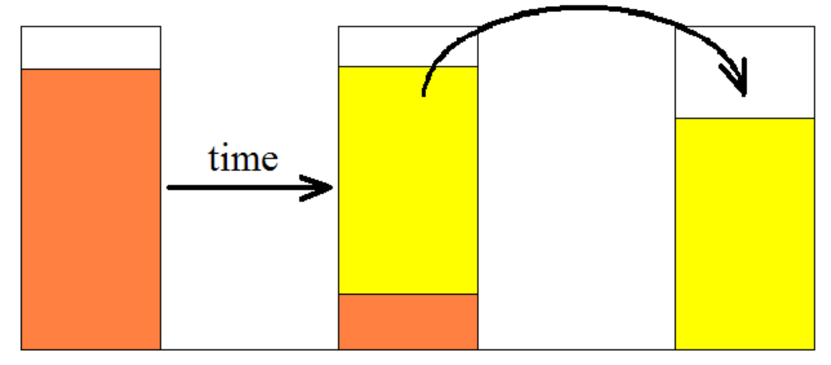
(3)

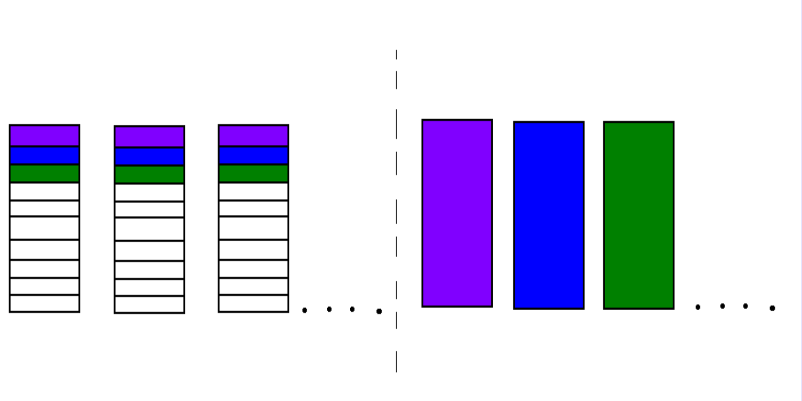


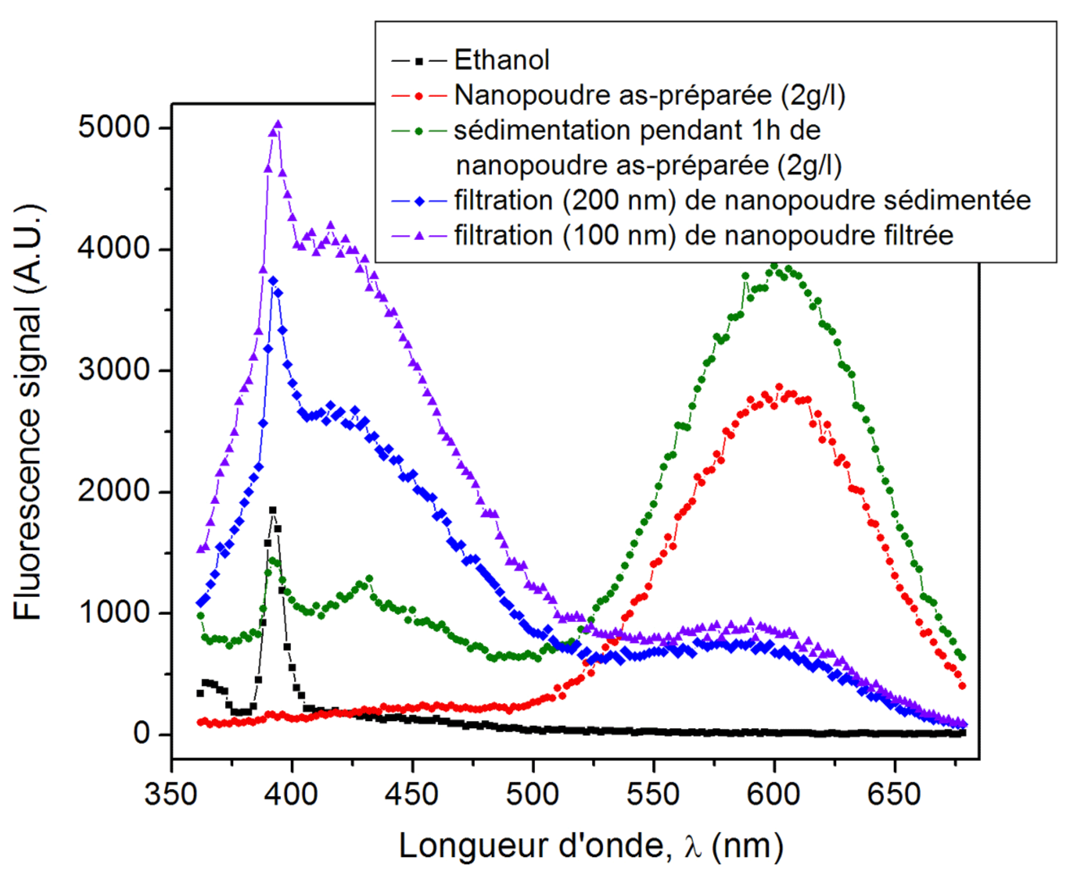
(4)

# Sedimentation+ filtration

(5)



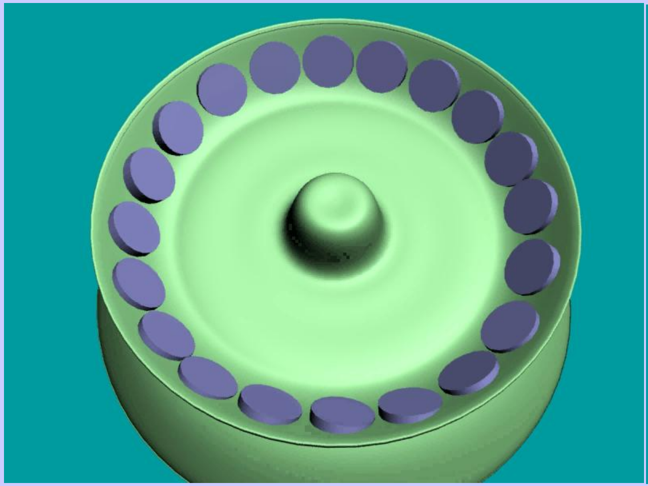


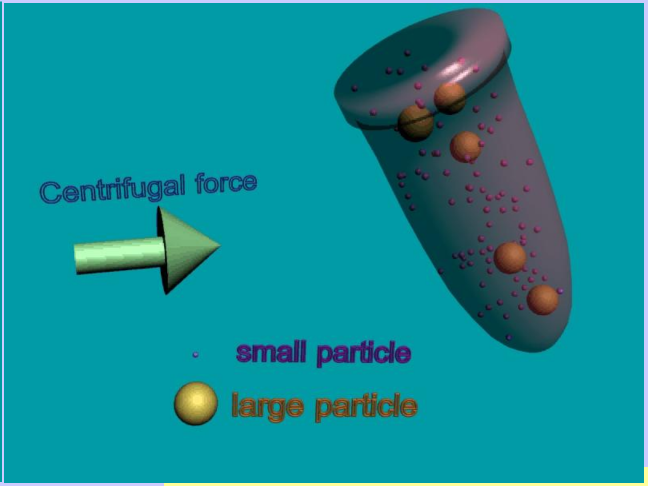

**PhL of different sedimented layers**

**V.Lysenko, V.Onyskevych, O.Marty, V.Skryshevsky, Y.Chevolot, C.Bru-Chevalier, Appl.Phys.Lett, 92(2008) 251910**

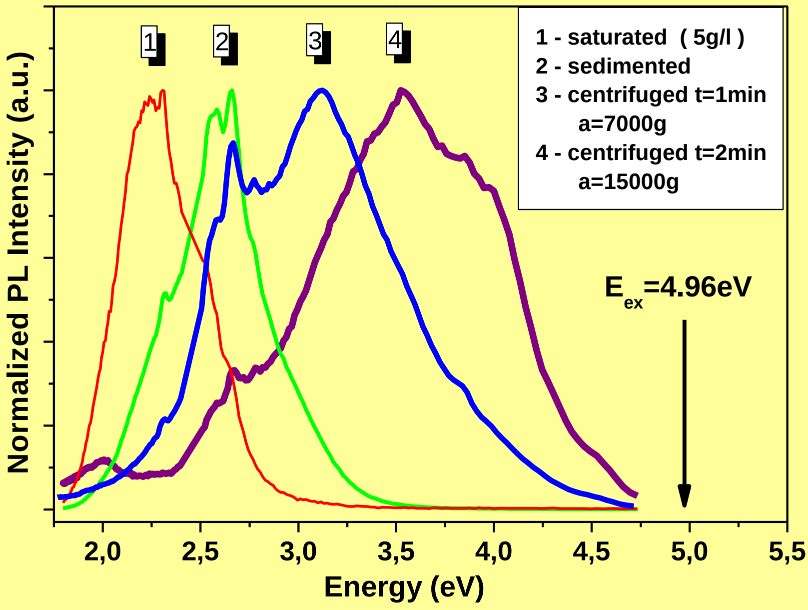
# Centrifugation

(6)

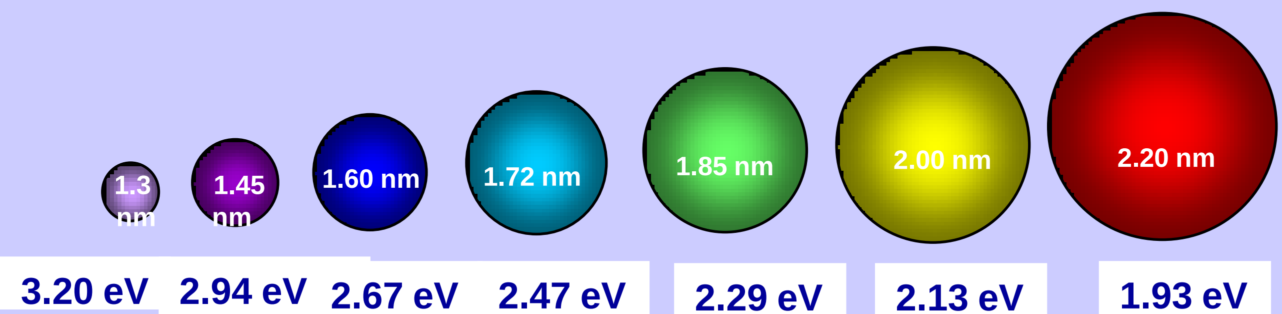


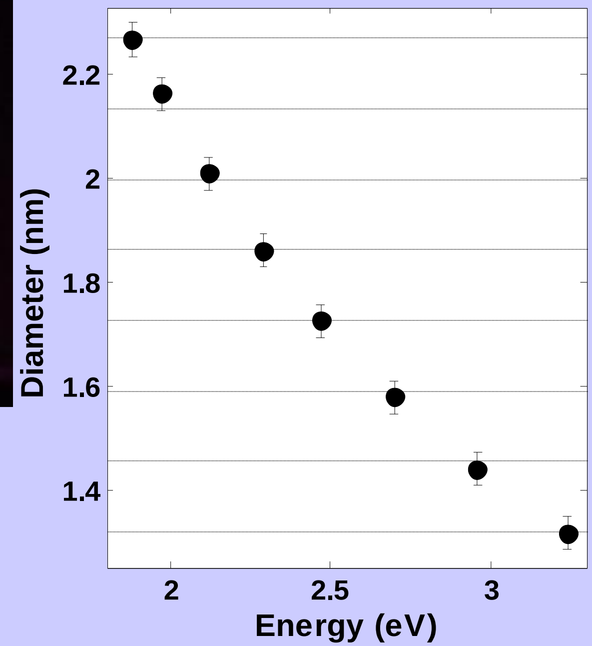



PL spectrum of the initial PS nanopowder in ethanol solution and its evolution upon sedimentation and moderate centrifugation



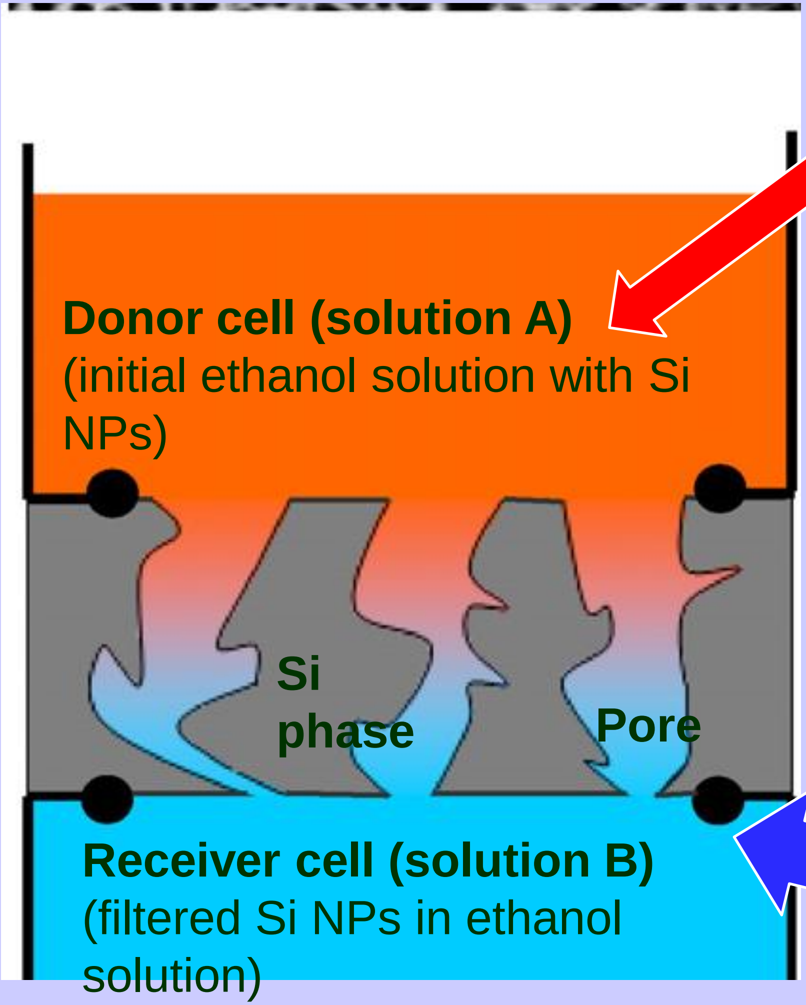
# Semiconductor nanoparticles

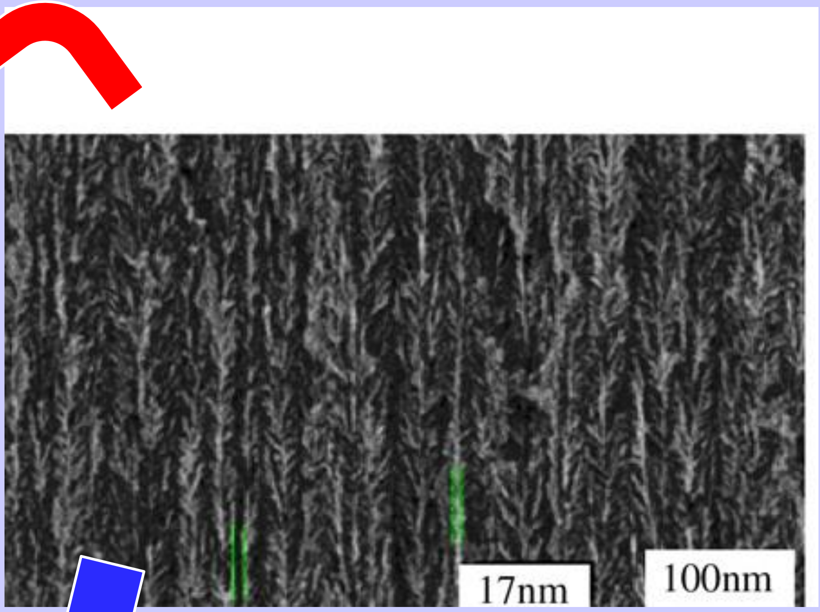


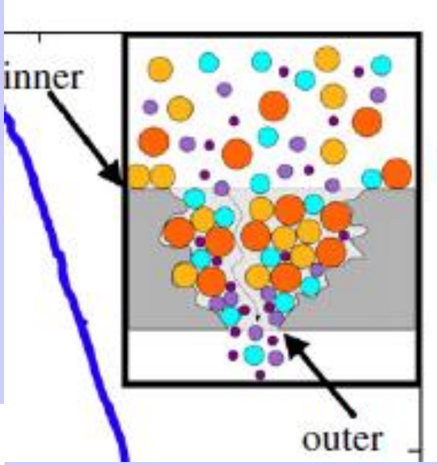




J.K. Jaiswal, S. M. Simon, *Trends in cell biology*, vol 14, 497-504 (2004)

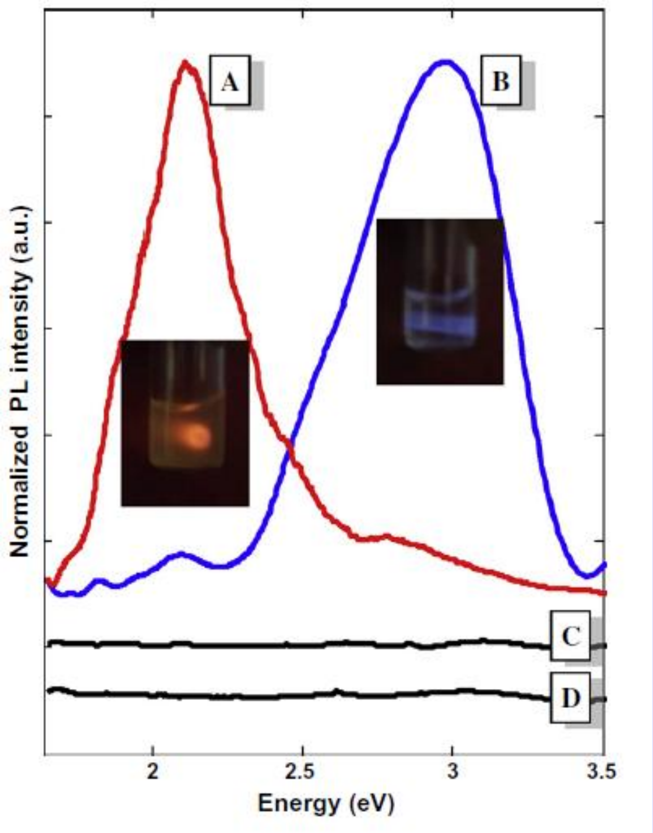
# Authofiltaration of nano-Si particles




*T. Serdiuk et al. / Journal of Colloid and Interface Science 364 (2011) 65–70*




PL spectra with corresponding photos of initial (curve A) and filtered (curve B) ethanol solutions with dispersed Si NPs.

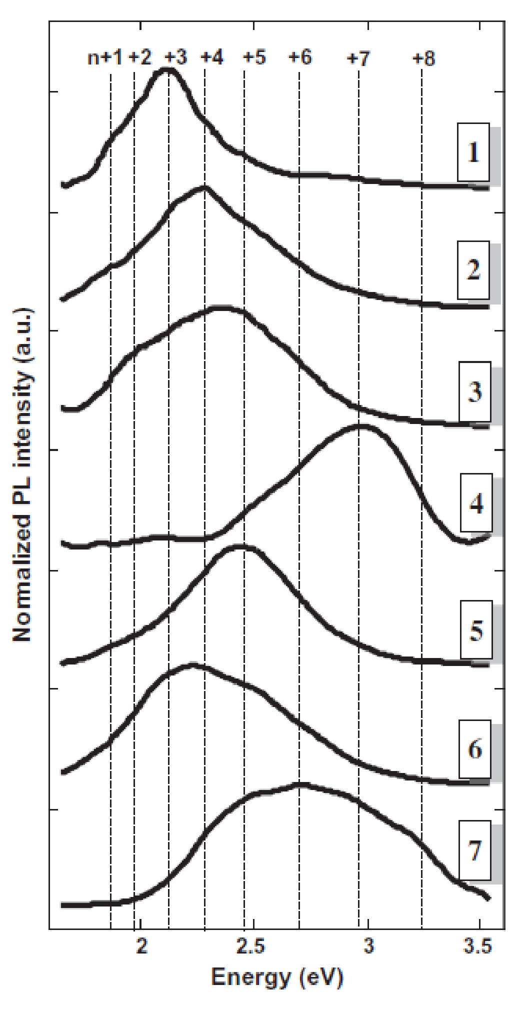
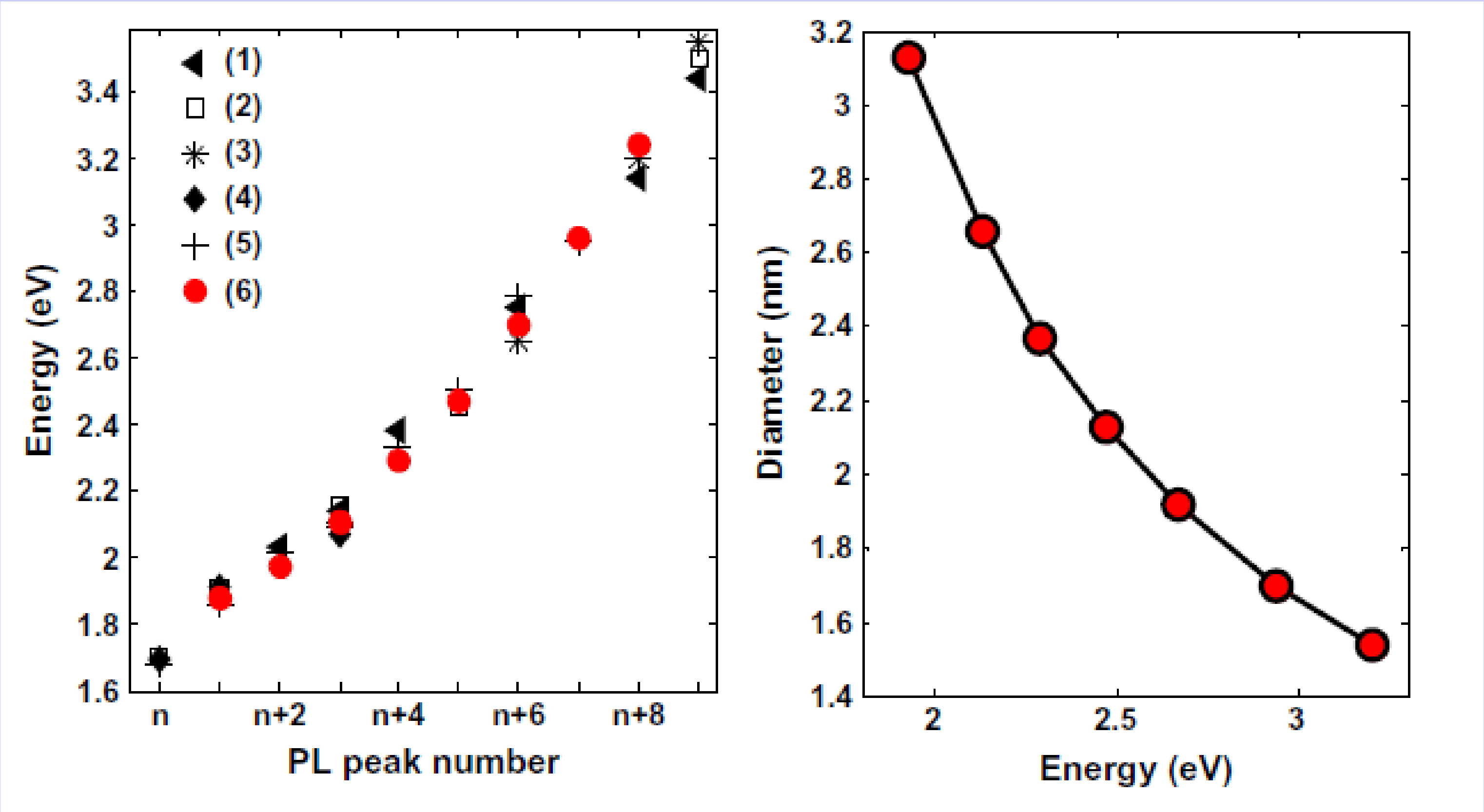


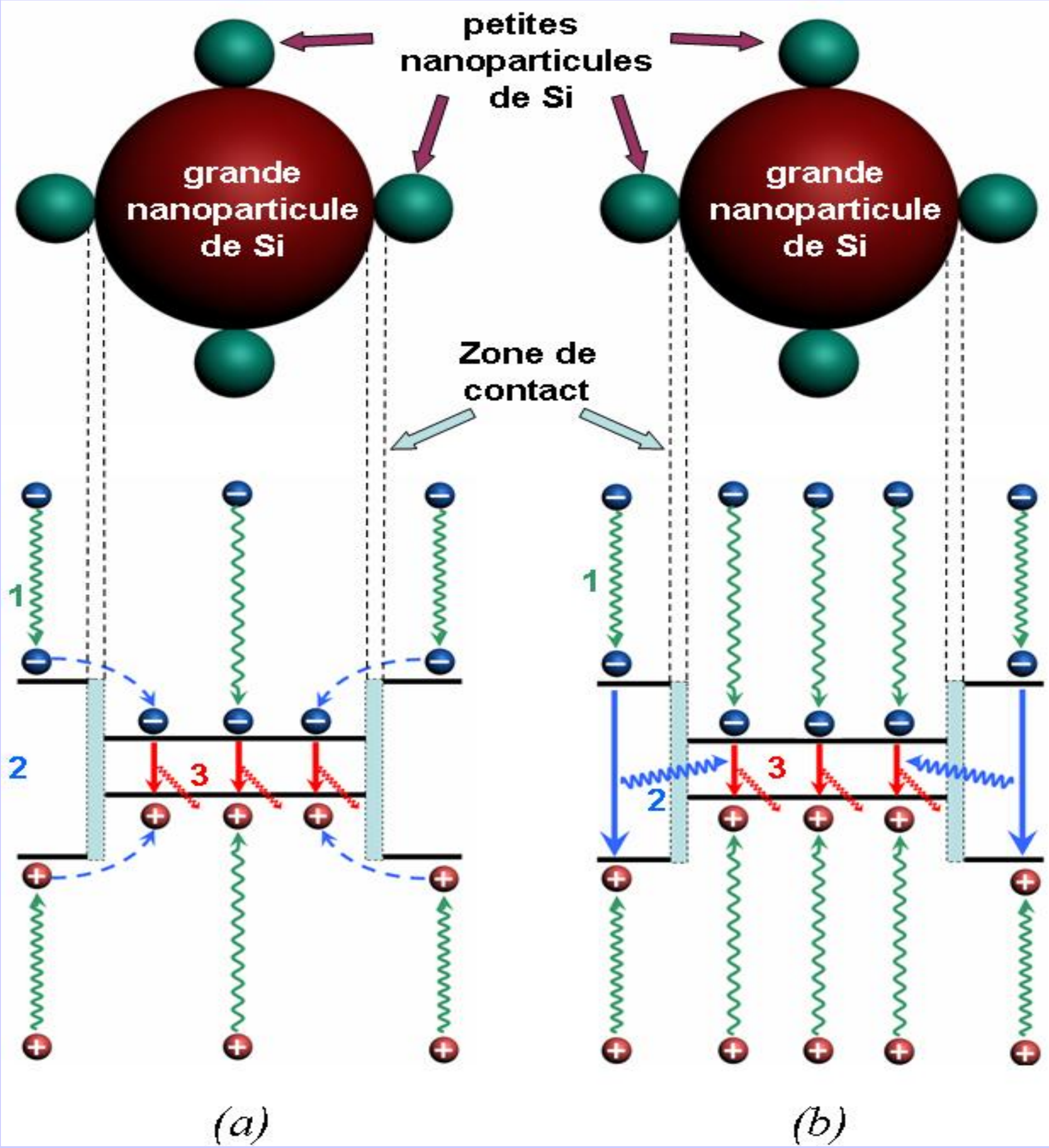

**Fig. 6.** PL spectra of Si NPs dispersed in initial (curve 1) ethanol solutions, filtered with the use of 23-μm thick free-standing meso-PS membrane (curve 2), filtered with the use of 37-μm thick free-standing meso-PS membrane before (curve 3) and after (curve 4) oxidation in 1:1 volume mixture of deionized water and ethanol at about 320 K during 15 min, filtered with the use of 246-μm thick free-standing meso-PS membrane before (curve 5) and after (curve 6) etching in 1:10 volume mixture of HF and deionized water at room temperature during 10 min, filtered with the use of 350-μm thick free-standing meso-PS membrane (curve 7).



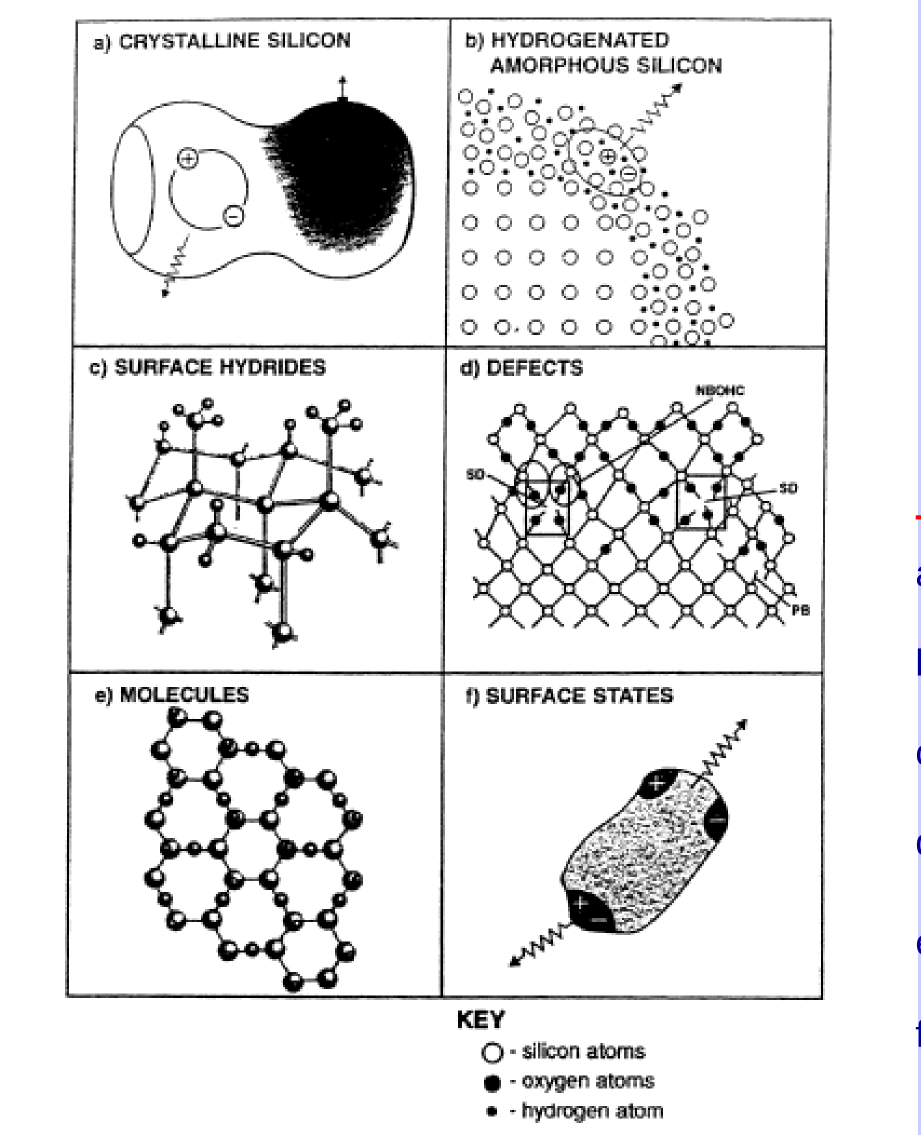

: Dependence of Si NPs size calculated according to the model described in [24] on the PL peak energies reported in this work.

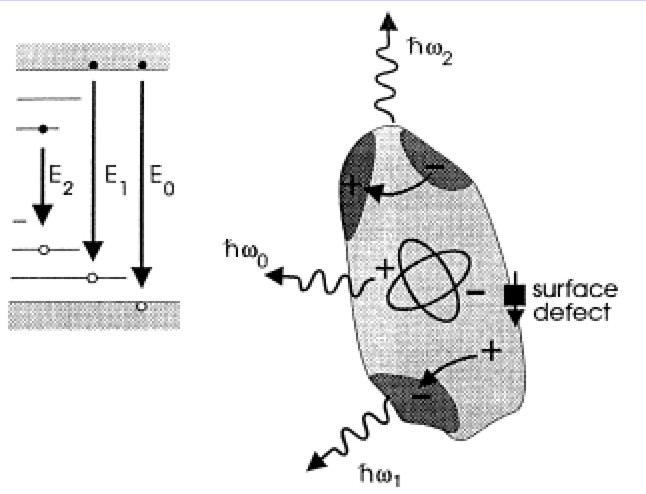
$$Eg(d) = 1.167 + 3.73 * d^{-1.39}$$

# 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

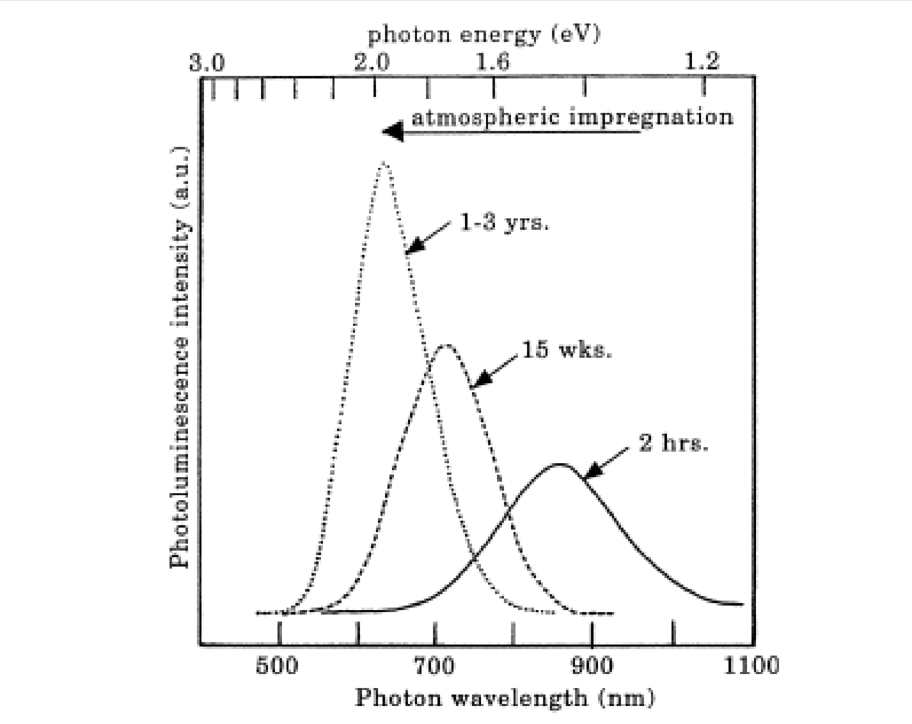
c) Si surface passivated by SiHx terminations. Radiative recombination occurs at the Si-H bonds

d) Partially oxidized Si containing defects proposed as radiative centers

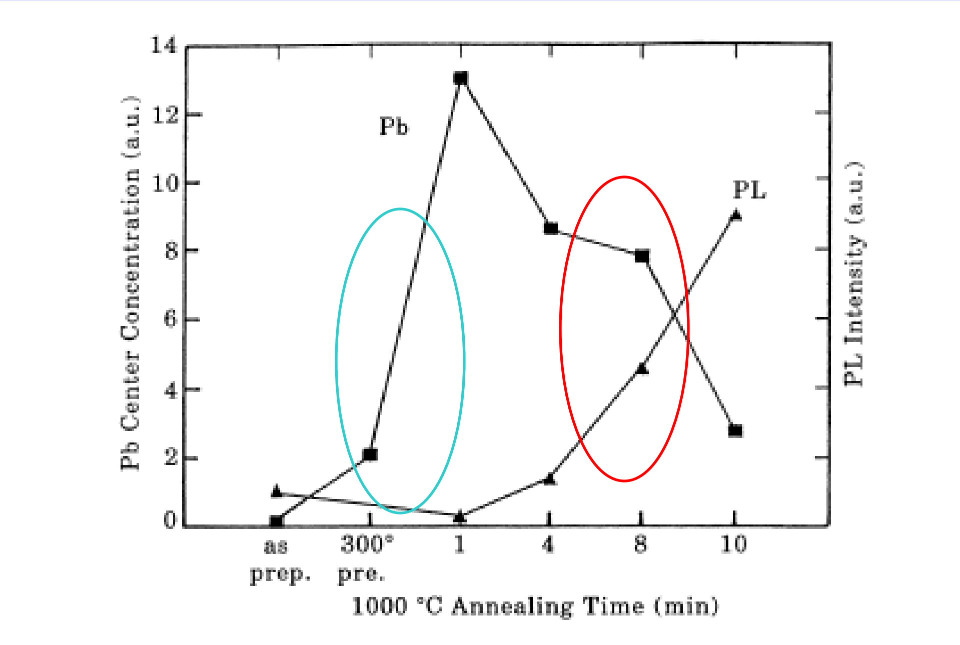
e) Siloxene molecule $Si_6O_3H_6$ is proposed to exist on the large inner PS surface and act as luminescence center

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$^o$C in $O_2$**

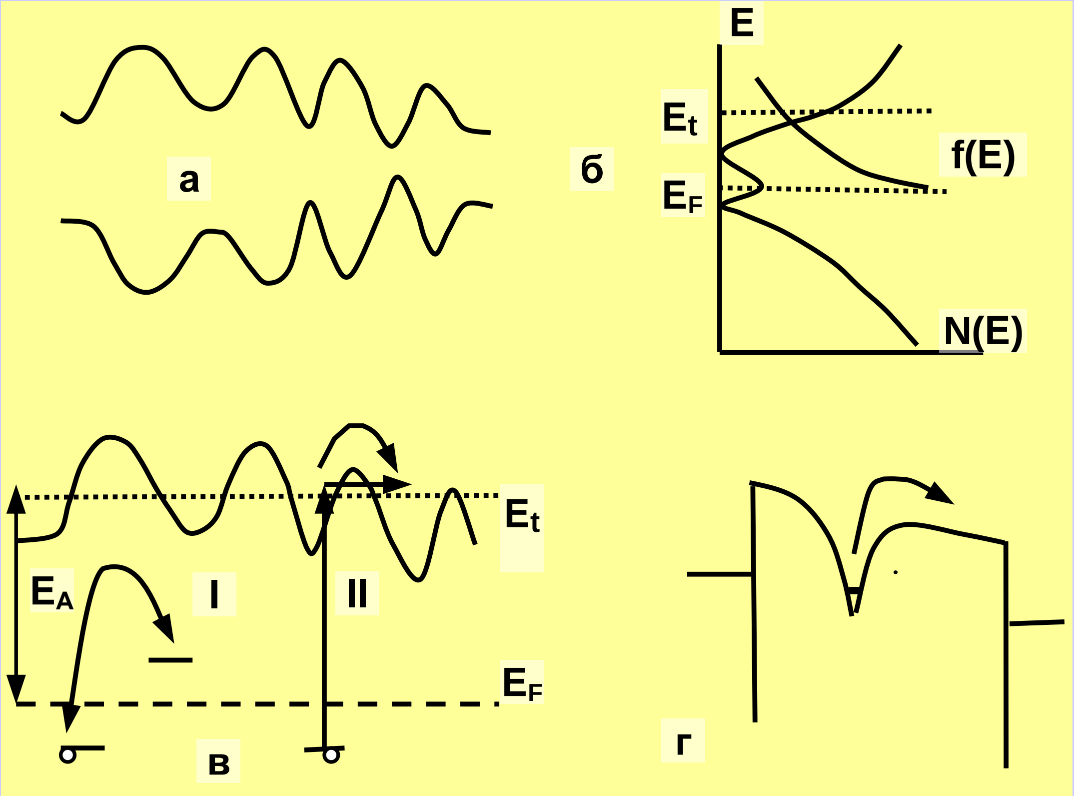
Dangling bonds- most important paramagnetic defect centers: in $Si/SiO_2$ interface

**·Si≡$Si_3$ (Pb centers)**

in hydrogen depleted oxide layer **·Si≡$SiO_3$ (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):**

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

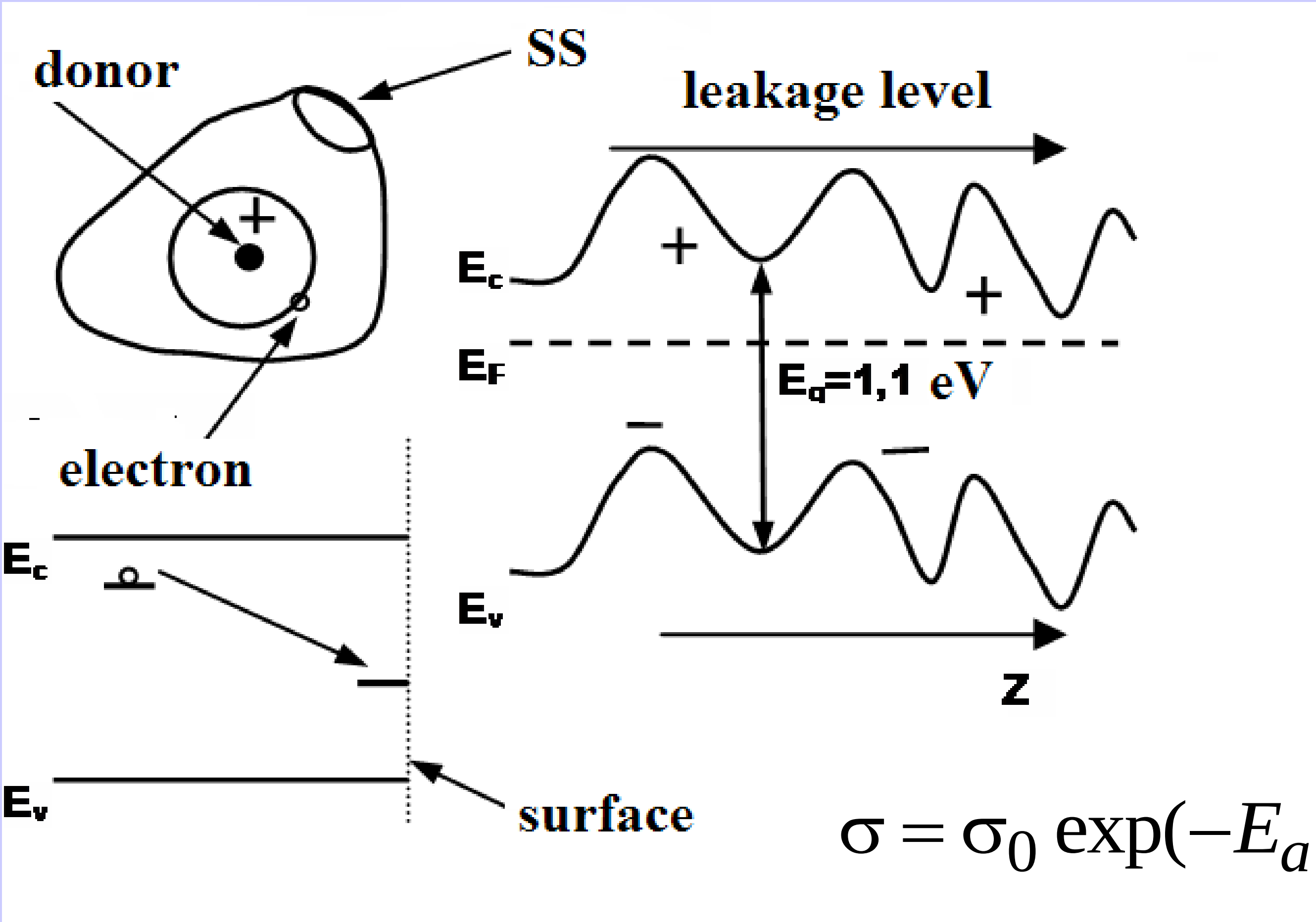
**Poole-Frenkel ionisation:**

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

**Space charge limited current:**

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

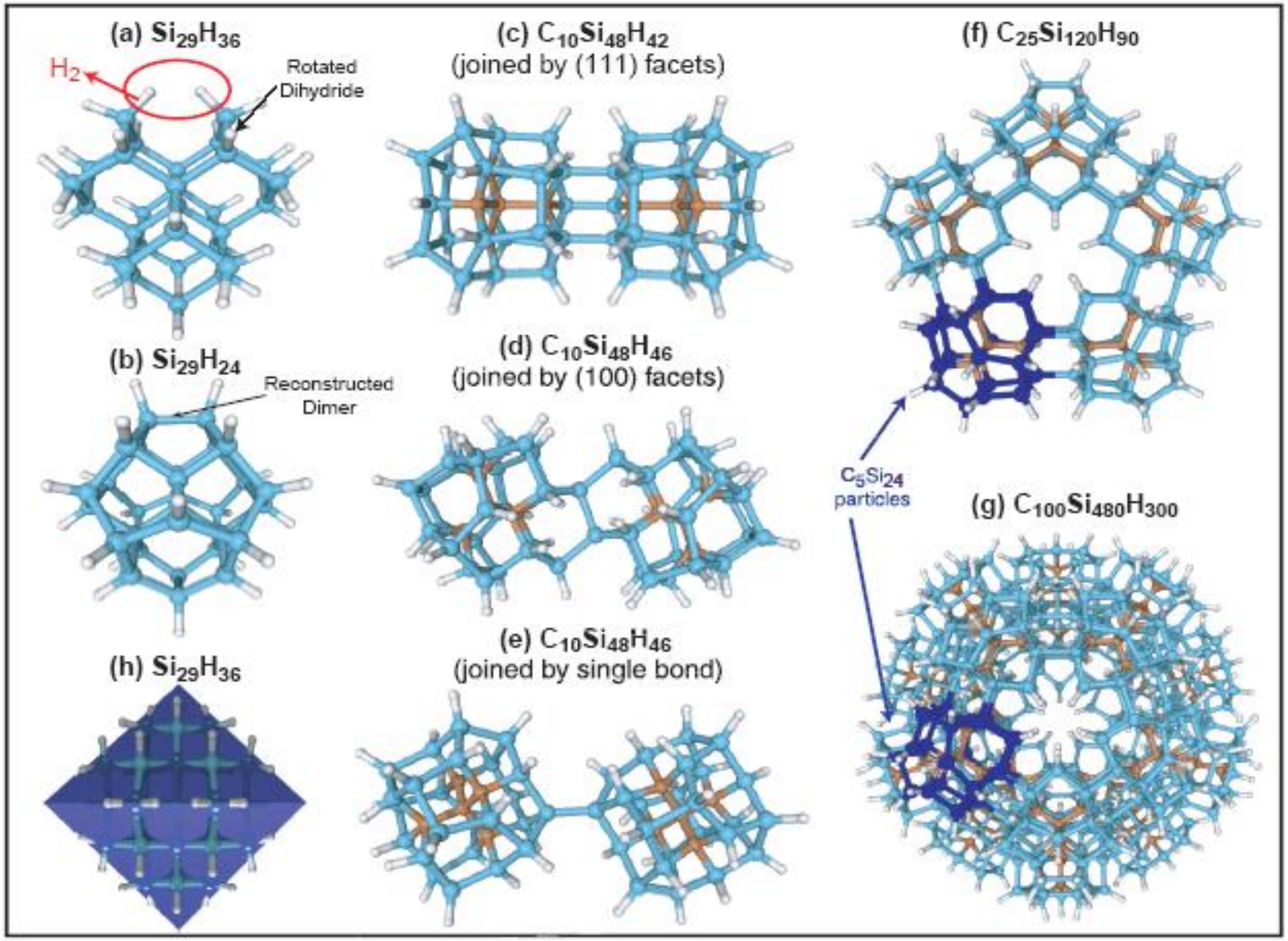



FIG. 1: Calculated atomic structures of single, double, 5-fold and 20 nanoparticles structures. Si, C and H atoms are colored blue, brown and white. In (f) and (g) atoms in a single $C_5Si_{24}$ particle are highlighted in dark blue.

# Properties of Micropores or nanocrystalline Si. Summary

**Features:**

- **Surface area – 200- 1000 $m^2/cm^3$**
- **$E_g$ = 1.1- 3.0 eV**
- **Resistivity $\rho = 10^8$-$10^{12}$ $\Omega$.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**<br>**4. Rapid thermally oxidized at high temperatures** | **$SiO_xH_y$** |
| **5.Aged in ambient air for months to years** | **$SiO_xH_yC_z$** |