

# Nanotecnologie: materiali e metodi di produzione

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**L**aboratory «**R**oberto **B**oscaino»  
of **A**dvanced **M**aterials

Web: [www.unipa.it/lamp/](http://www.unipa.it/lamp/)

*Palermo, 16/05/2018*

# Sommario

## Introduzione:

Proprietà peculiari dei materiali nanometrici

Alta superficie specifica --- Confinamento quantistico

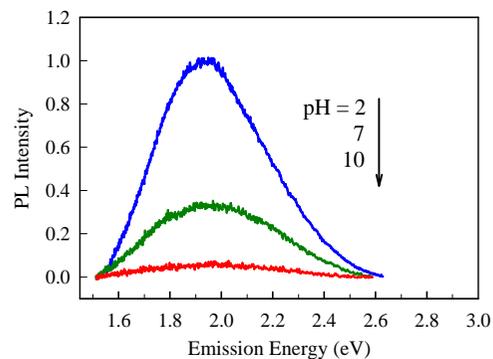
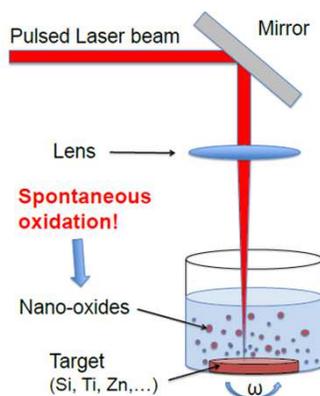
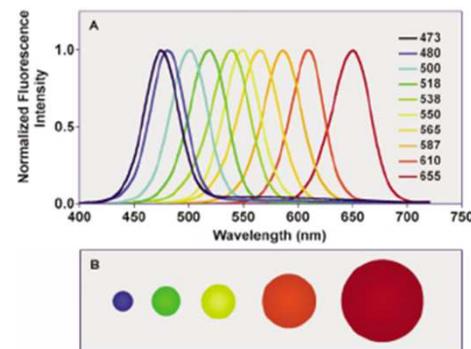
## Metodi di produzione

Pulsed Laser Ablation (PLA)

## Applicazioni di PLA:

Nanocristalli di Silicio «ossidato»

Nanoparticelle di ZnO



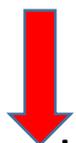
# Introduzione



Il controllo delle proprietà ottiche/elettriche di un materiale è il principale **goal** delle moderne nanotecnologie

Controllo della morfologia (dimensione, forma) e della composizione chimica (volume, superficie)

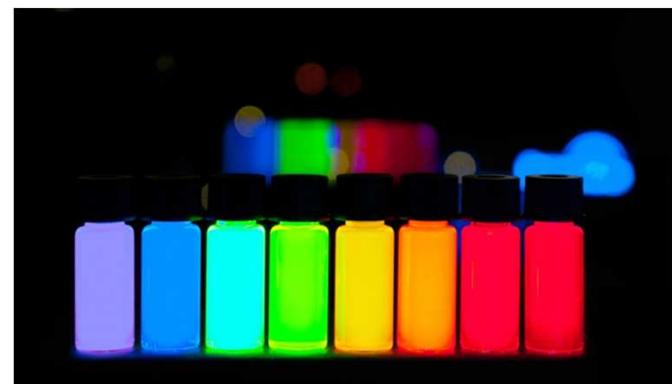
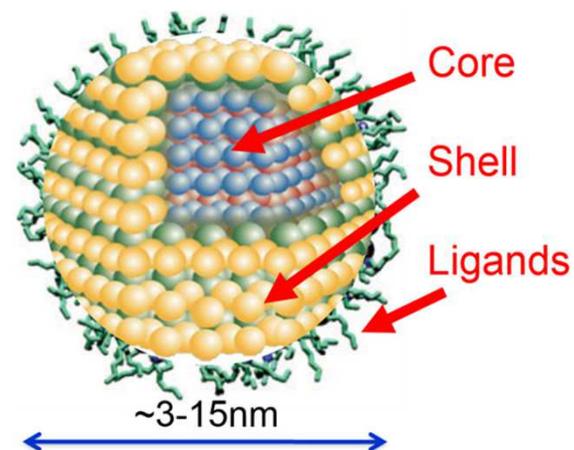
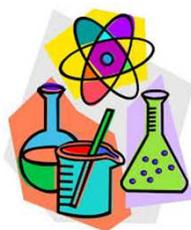
Attraverso processi di sintesi



Proprietà peculiari dei materiali nanometrici

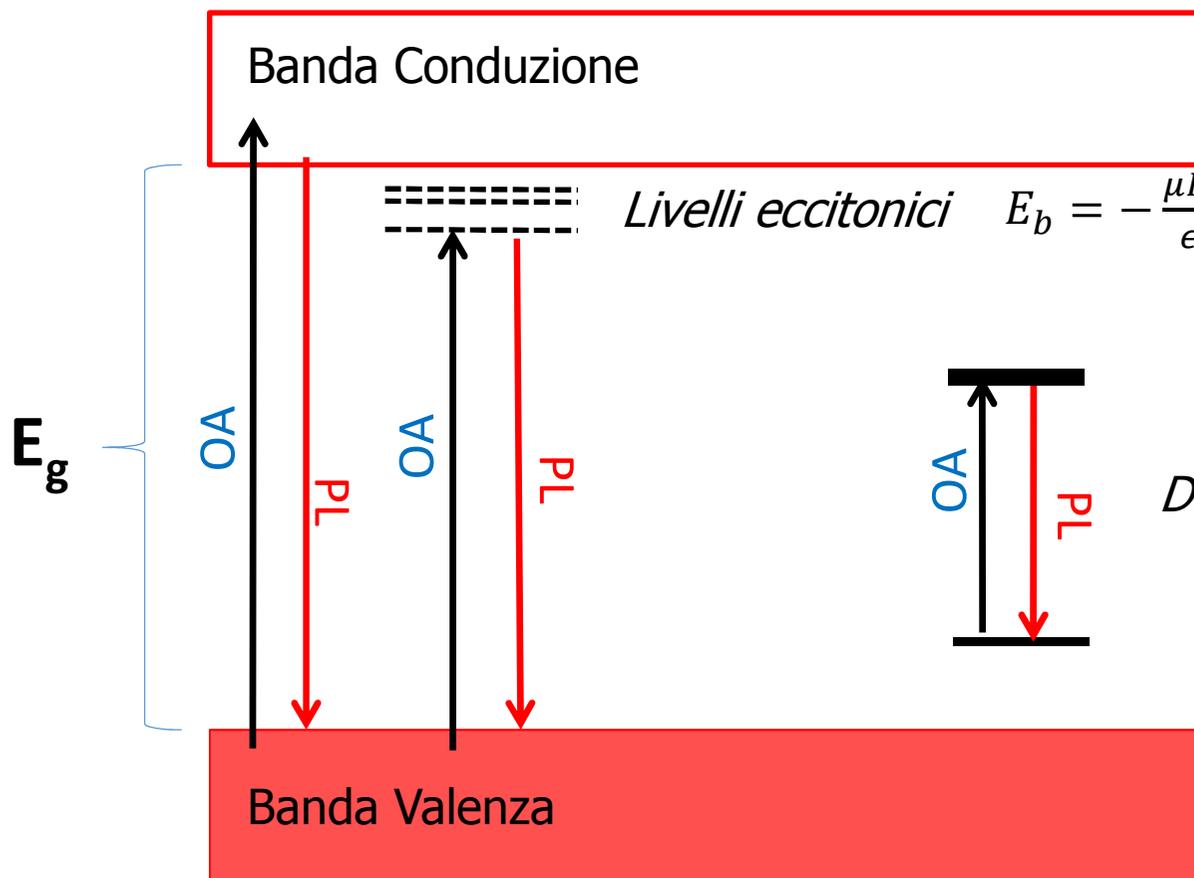
*che non dipendono esclusivamente dalla loro composizione*

**missione di luminescenza:** tunabilità, stabilità, brillantezza



# luminescenza

Proprietà ottica di Semiconduttori/Isolanti  
Materiali con gap ottica  $E_g \sim 1-10$  eV



- $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_b^*}$  massa ridotta
- $\epsilon$  costante dielettrica di mezzo
- $R_H = 13.6$  eV costante di Rydber

# 1/2 Proprietà peculiari dei materiali nanometrici (geometria)



macro



nano

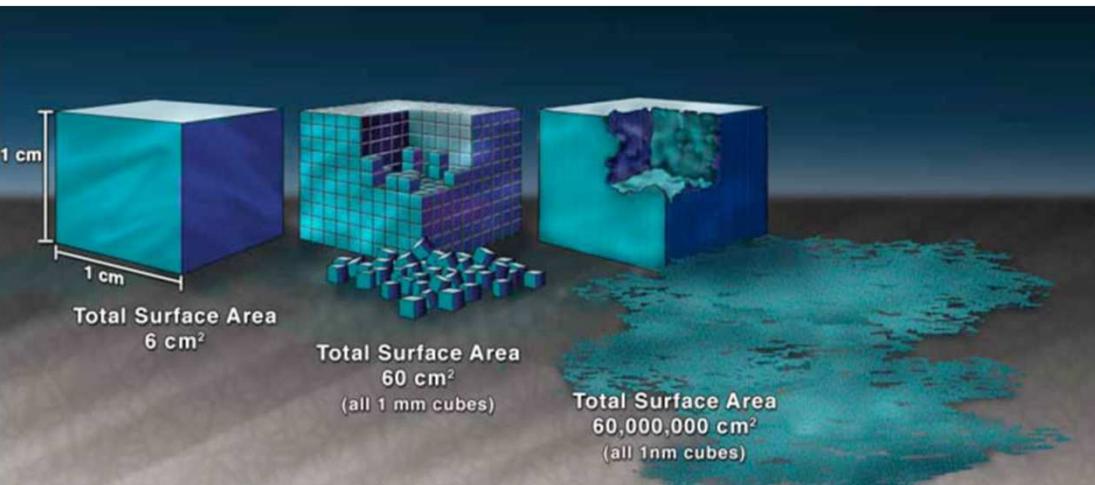
Superficie specifica

$$\sigma = \text{sup}_{\text{tot}}/\text{massa} [\text{m}^2/\text{g}]$$

dimensioni delle particelle (r)

$$\sigma \propto 1/r$$

r ~ nm: nanoparticelle (NP)  $\sigma \sim 100 \text{ m}^2/\text{g}$

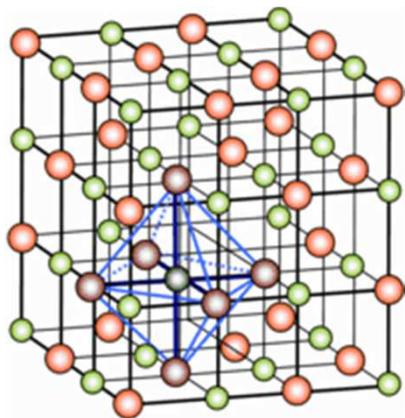


~10 g di NP



2

**Superficie** è *per definizione* un'interruzione del network cristallino



Prop. Elettr. (volume)  $\neq$  Prop. Elettr. (superficie)  
*inv. traslazionale 3D*

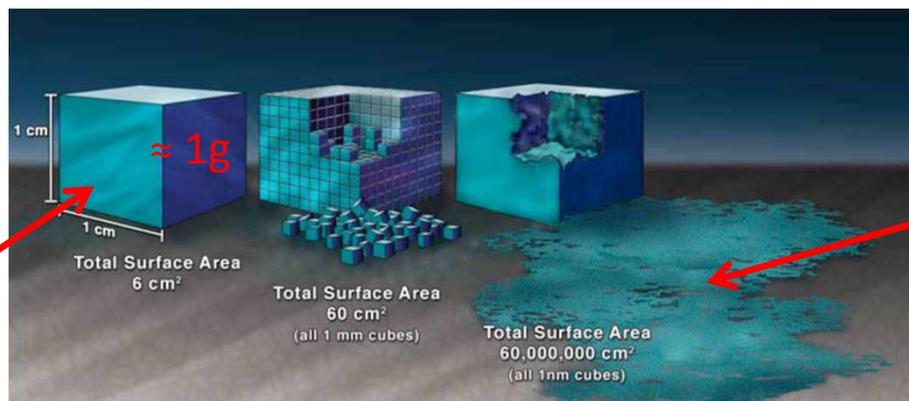
Superficie è:

- 1) Interfaccia fra il solido e l'ambiente esterno
- 2) Un «contenitore» di difetti (*dangling bonds...*);  
densità superficiale  $\phi \geq 10^{16} / \text{m}^2$

difetti/massa =

$$\phi \cdot \sigma \propto 1/r$$

$$\geq 6 \cdot 10^{12} / \text{g}$$



$$\geq 6 \cdot 10^{19} / \text{g}$$

**I difetti di superficie dominano  
le proprietà ottiche dei sistemi nanom**

Superficie poco estesa



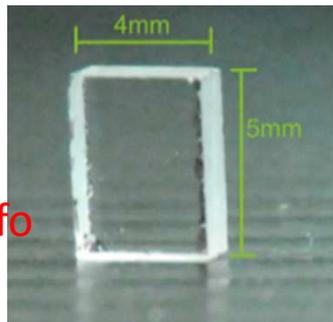
Superficie molto estesa



macro ( $\sigma \sim 10^{-4} \text{ m}^2/\text{g}$ )



Carbonio (grafite, diamante)



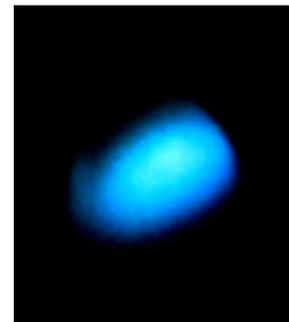
Silice -  $\text{SiO}_2$  amorfo

nano ( $\sigma \sim 10^2 \text{ m}^2/\text{g}$ )



Carbonio (nanoparticelle)

Laboratory «Roberto Boscaino»  
of Advanced Materials



Silice (nanoparticelle)

# 2 Proprietà peculiari dei materiali nanometrici (confinamento quantistico)

Confinamento Quantistico (QC)  $\longleftrightarrow$  Nanoparticelle: Quantum Dots (QDs)

L'importanza della scala nanometrica si capisce attraverso il confronto con le dimensioni dell'**eccitone** (coppia elettrone-buca)

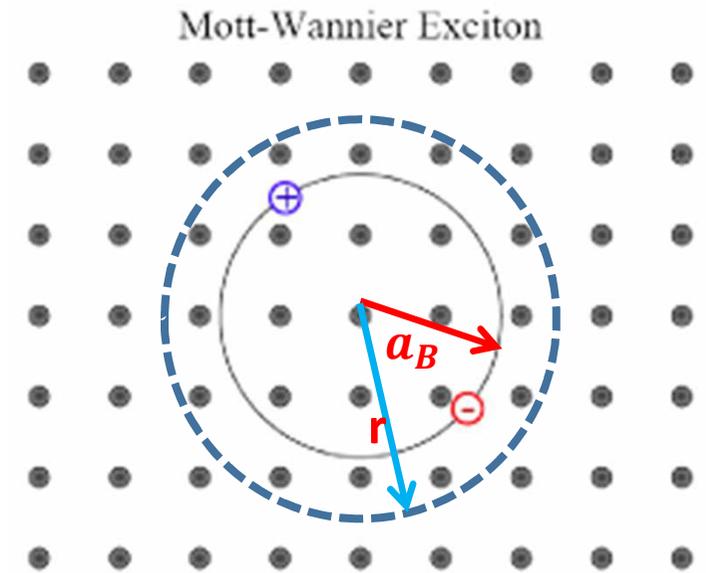
$$a_B(n) = \frac{a_0 \epsilon}{\mu/m_e} \cdot n^2; \quad E_n = -\frac{\mu/m_e R_H}{\epsilon^2} \cdot \frac{1}{n^2}$$

$a_0 \approx 0.53 \text{ \AA}$  raggio di Bohr;  $a_B(n=1)$  raggio \_eccitone

$a_B(\text{Ge}) \approx 24.3 \text{ nm}; E \approx 3 \text{ meV}$

$a_B(\text{Si}) \approx 4.9 \text{ nm}; E \approx 15 \text{ meV}$

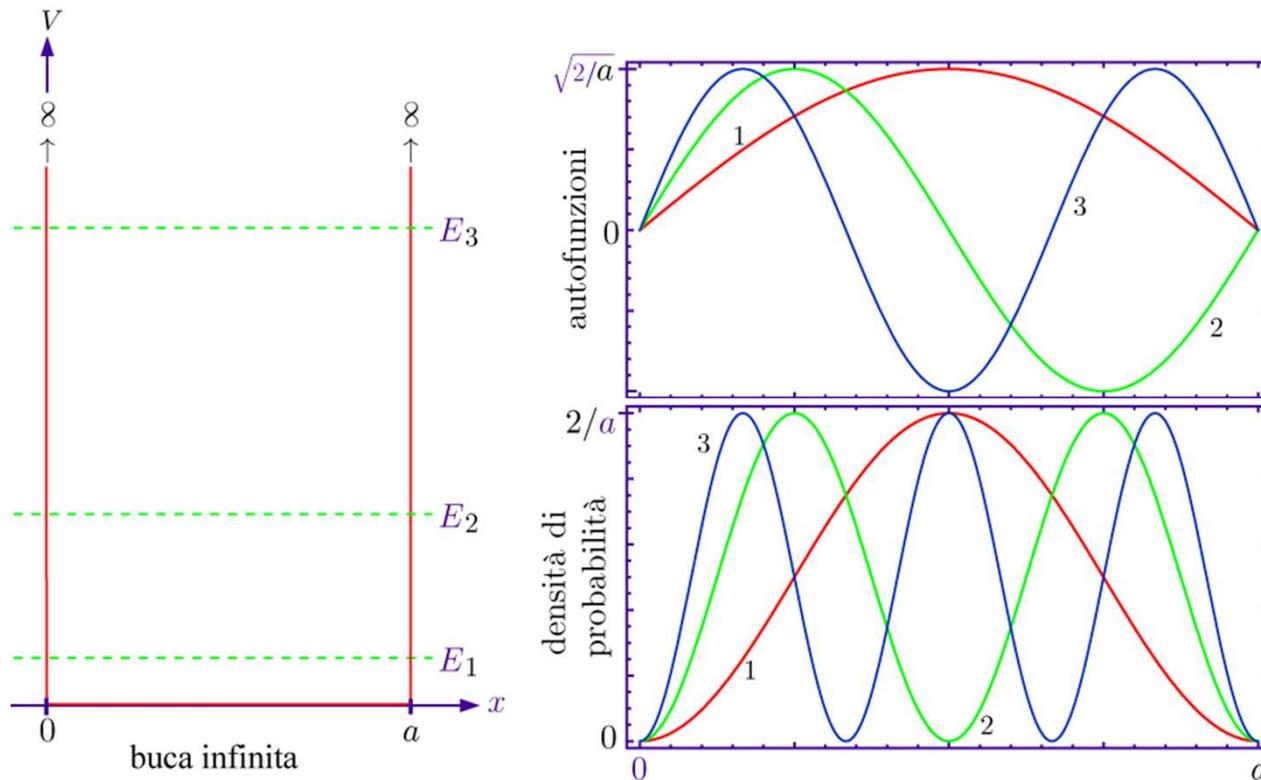
$a_B(\text{ZnO}) \approx 2.3 \text{ nm}; E \approx 60 \text{ meV}$



QC si osserva se le dimensioni delle NPs e dell'eccitone sono confrontabili  $(r \sim a_B)$

# Confinamento Quantistico (QC)

$r | a_B$ ): il sistema può essere studiato qualitativamente utilizzando il modello di una particella (eccitone) all'interno di una **buca di potenziale a pareti infinite**



buca sferica (raggio  $r$ )

$$\text{QC: } E_m = \frac{\hbar^2 \pi^2 m^2}{2\mu r^2}$$

$$E_m = \frac{\hbar^2 \pi^2 m^2}{2\mu a^2}; \quad \psi(x) = \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{m\pi x}{a}\right); \quad m = 1, 2, 3, \dots$$

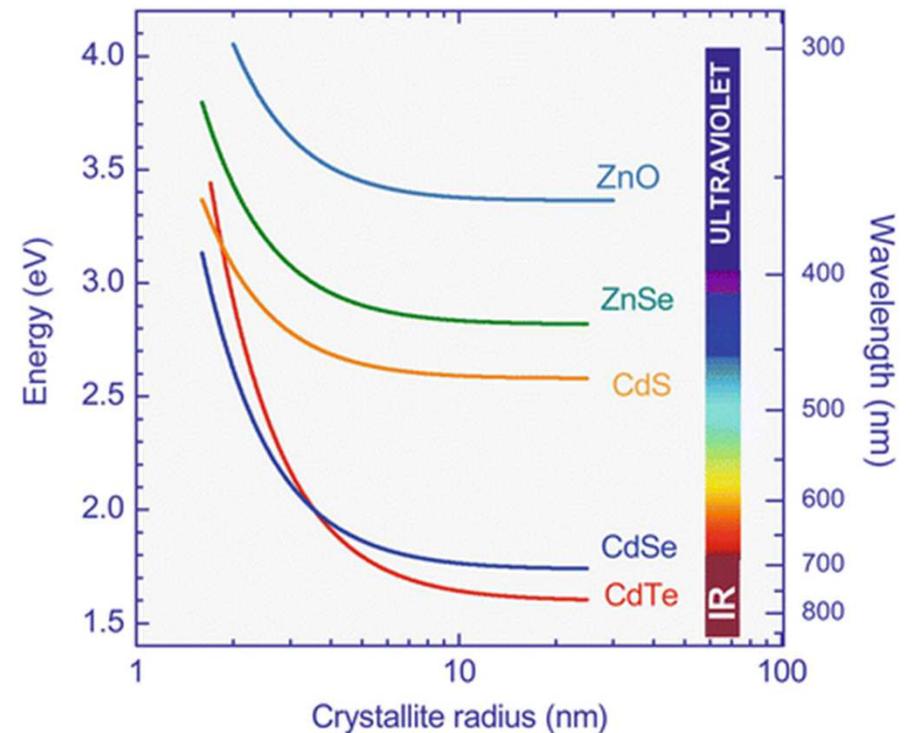
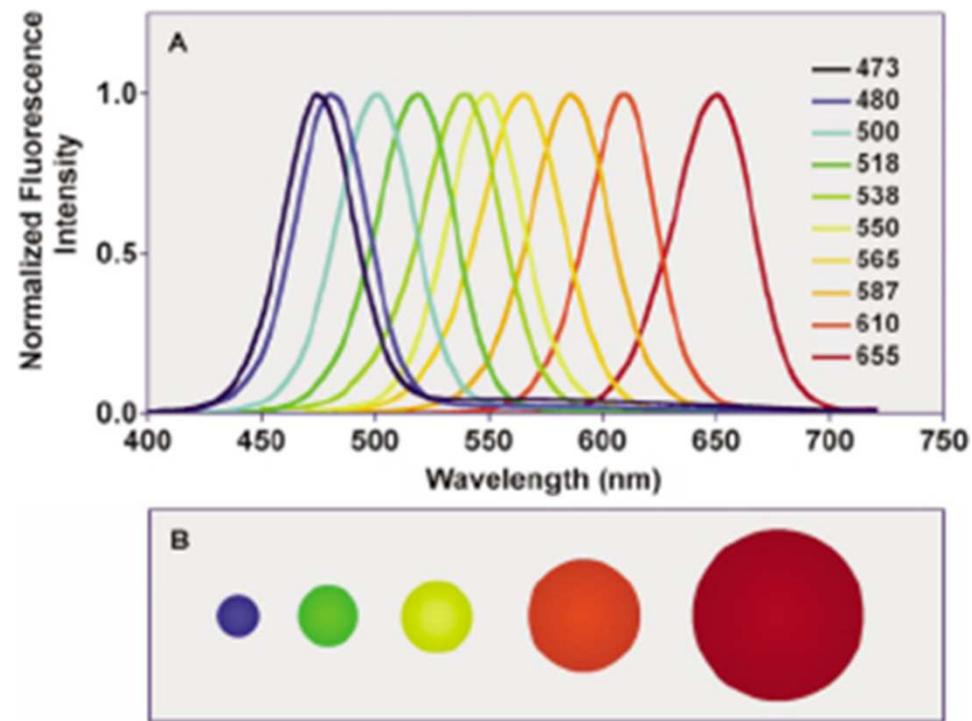


## QC: come si osserva?

Spettro di emissione degli eccitoni

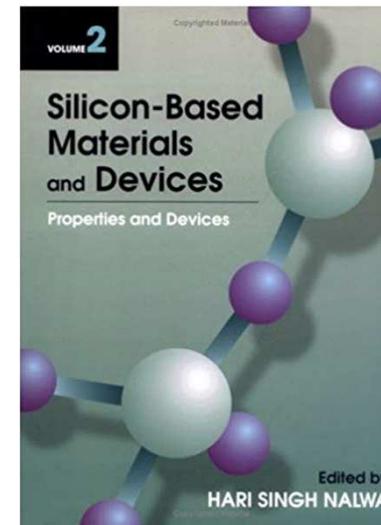
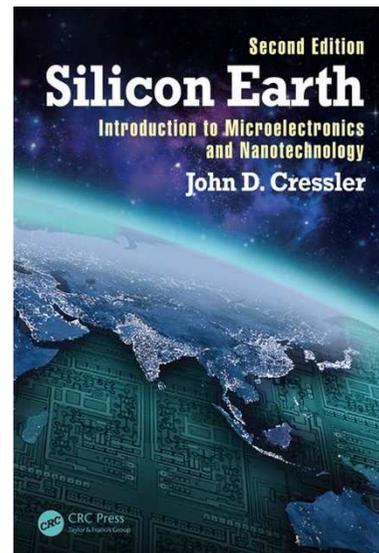
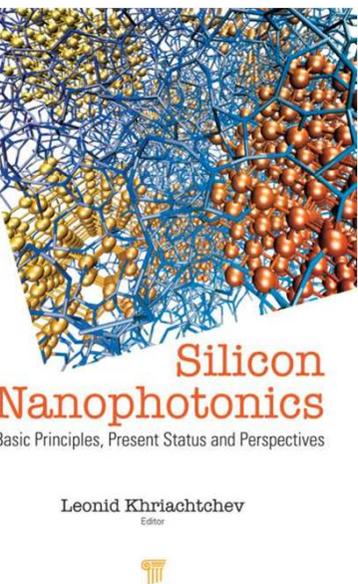
$$E_{exc} = E_g^{Bulk} - \frac{\mu/m_e R_H}{\epsilon^2} \cdot \frac{1}{n^2} + \frac{\hbar^2 \pi^2}{2\mu r^2}$$

$E_g$  vs. dimensioni - semiconduttore



QC: esempio

**Silicon nanocrystal Si-NC:**  
*milestone in the development of nanotechnology*



# Silicio

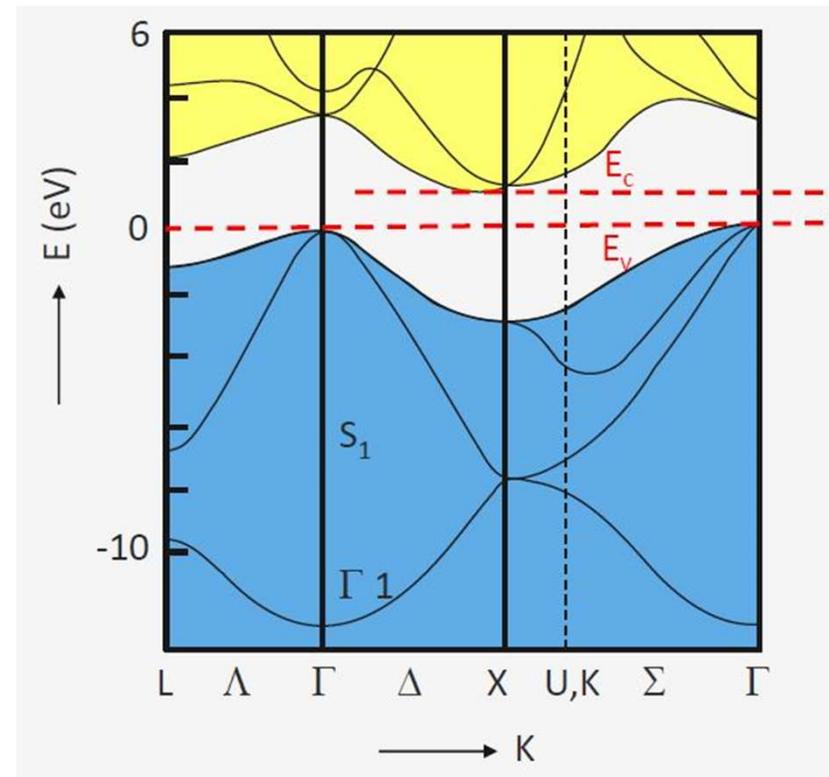
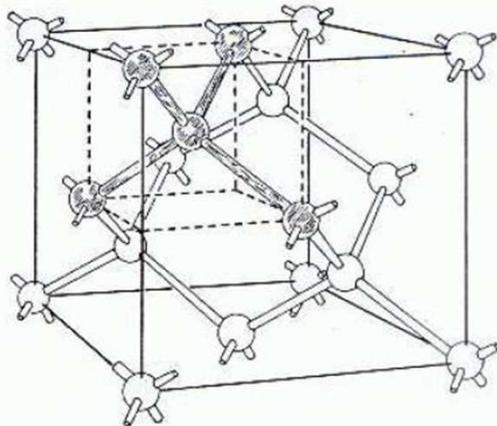
IV gruppo della tavola periodica

struttura cristallina covalente cubica

facce centrate

Semiconduttore a gap indiretta

	IIIA	IVA	VA	VIA
	5 B Boro	6 C Carbonio	7 N Azoto	8 O Ossigeno
	13 Al Alluminio	14 Si Silicio	15 P Fosforo	16 S Zolfo
30	Zn Zinco	Ga Gallio	Ge Germanio	As Arsenico
48	Cd Cadmio	In Indio	Sn Stagno	Sb Antimonio
80	Hg Mercurio	Tl Tallio	Pb Piombo	Bi Bismuto
				84 Po Polonio

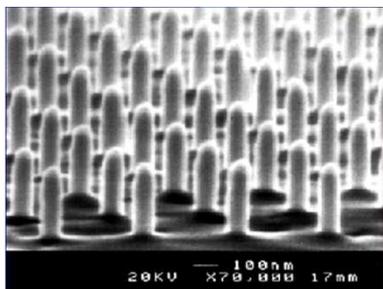
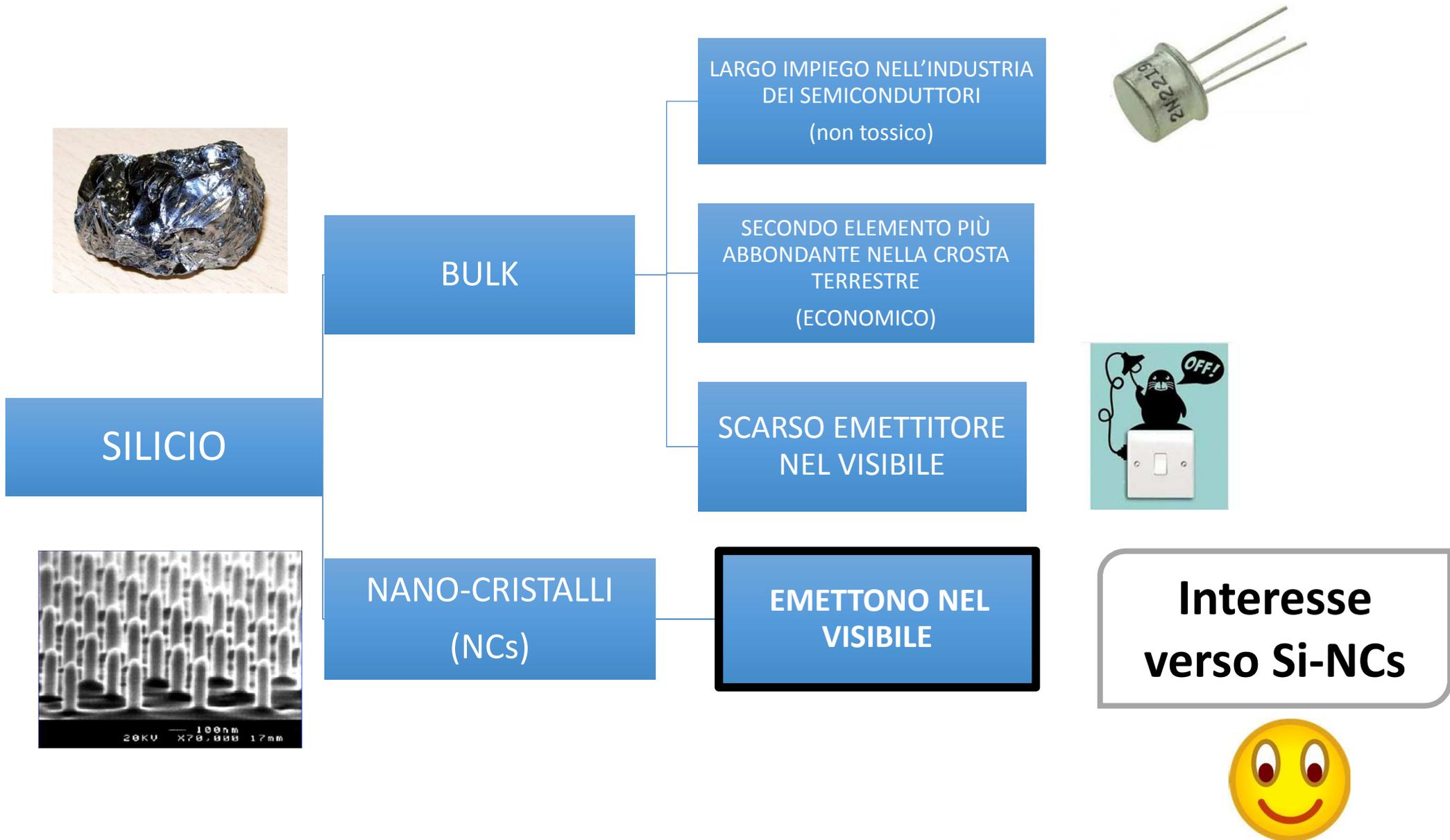


$E_g \approx 1.1$

conduttori  $\rho < 10^{-5} \Omega m$  (rame:  $3 \cdot 10^{-8} \Omega m$ )  
 $10^{-5} < \rho < 10^3 \Omega m$  (silicio:  $2300 \Omega m$ )  
 $\rho > 10^3 \Omega m$  (diamante:  $10^{14} \Omega m$ )

$\Gamma$  ( $K=\{0,0,0\}$ ); X ( $K=\{1,0,0\}2\pi/a$ ); L( $\{1/2,1/2,1/2\}2\pi/a$ )

# Proprietà BULK E NANOCRISTALLI



# Si-NCs

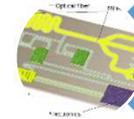
Hamers (1990):

Prima osservazione delle  
proprietà di  
**luminescenza** nel range  
visibile in silicio poroso.

Ha aperto la possibilità di  
sviluppo di dispositivi  
**optoelettronici** di Silicio!

Cristalli che hanno  
le dimensioni dei  
nanometri

A  
P  
P  
L  
I  
C  
A  
Z  
I  
O  
N  
I



**OPTOELETTRONICA**  
(laser, LED, OLED)



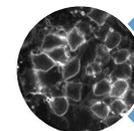
**NANOELETTRONICA**  
(dispositivi di memoria)



**FOTOVOLTAICO**

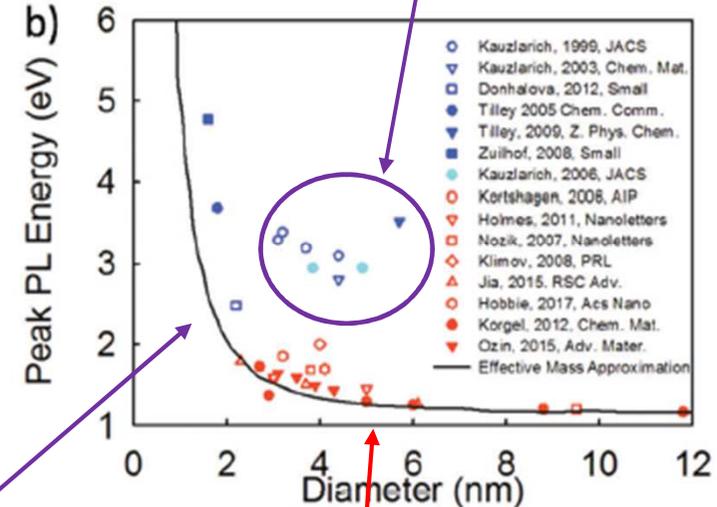
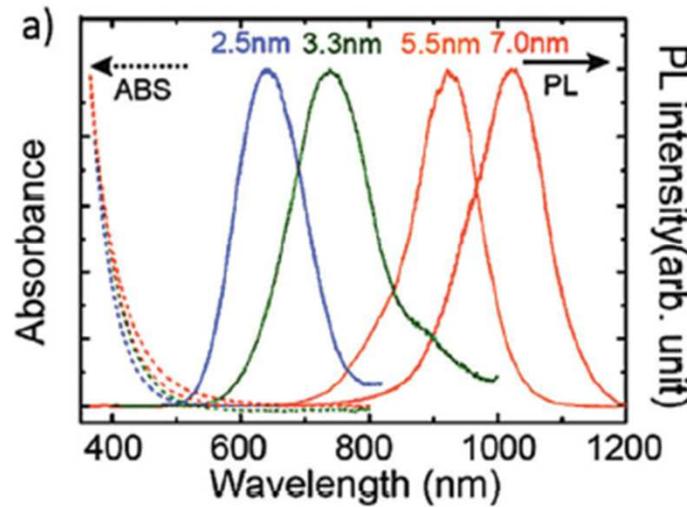
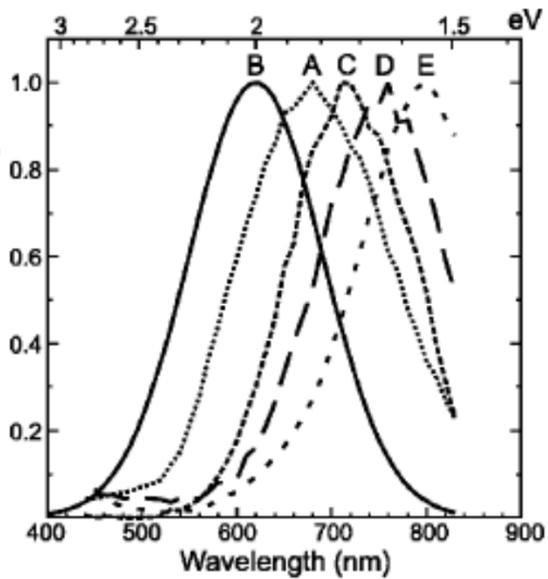


**BATTERIE**



**APPLICAZIONI  
BIOLOGICHE**

# -NCs: prime evidenze sperimentali del confinamento Quantistico (QC)



Difetti sulla superficie dei Si-MCNCs

*ux et al. Phys. Rev. B* **62** (2000) 15942

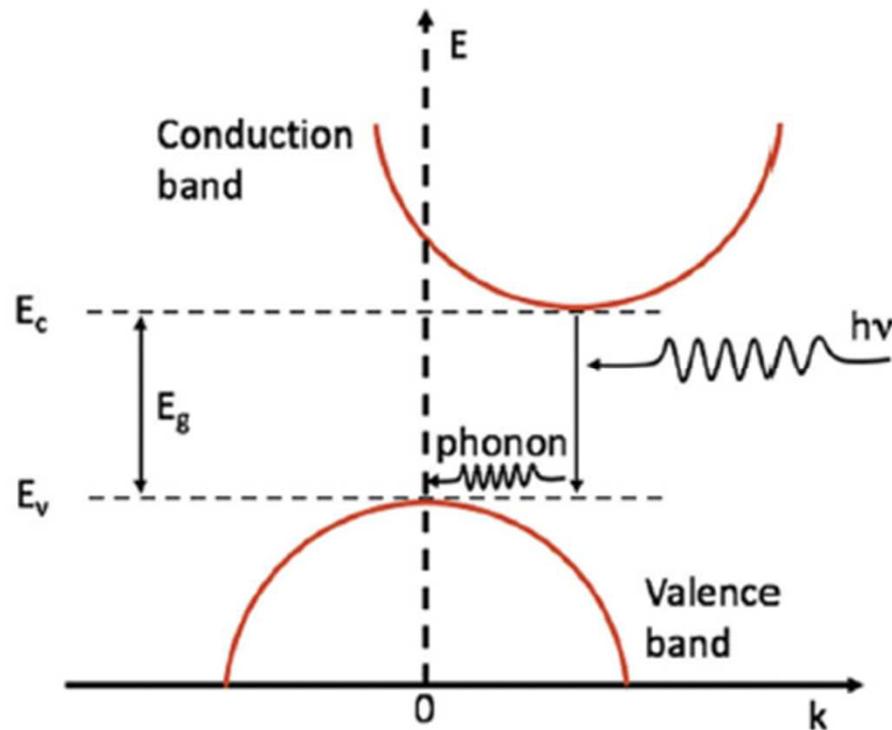
Se  $r \ll a_B$ : forte confinamento limita l'emissione degli eccitoni

$a_B$

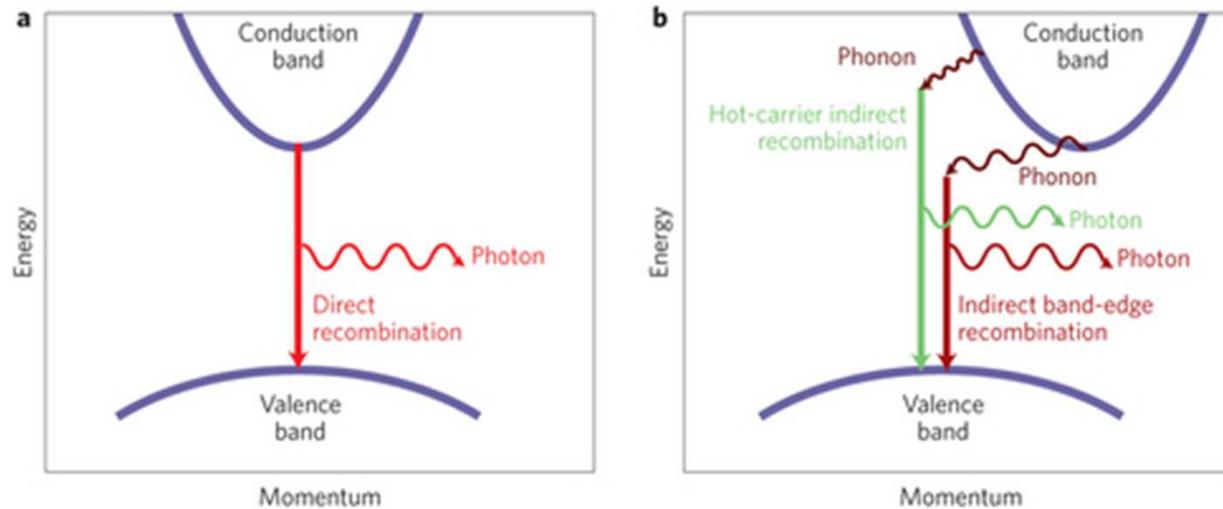
# Proprietà sorprendenti rispetto al Si-Bulk

Il Silicio (Si) è un semiconduttore a gap indiretta.

A temperatura ambiente ( $T=300\text{ K}$ ) l'energia-gap vale:  $E_g \approx 1.1\text{ eV}$



Nei semiconduttori a gap indiretta, il processo di fotoluminescenza avviene con probabilità minore (tempo di vita maggiore) rispetto ai semiconduttori a gap diretta.

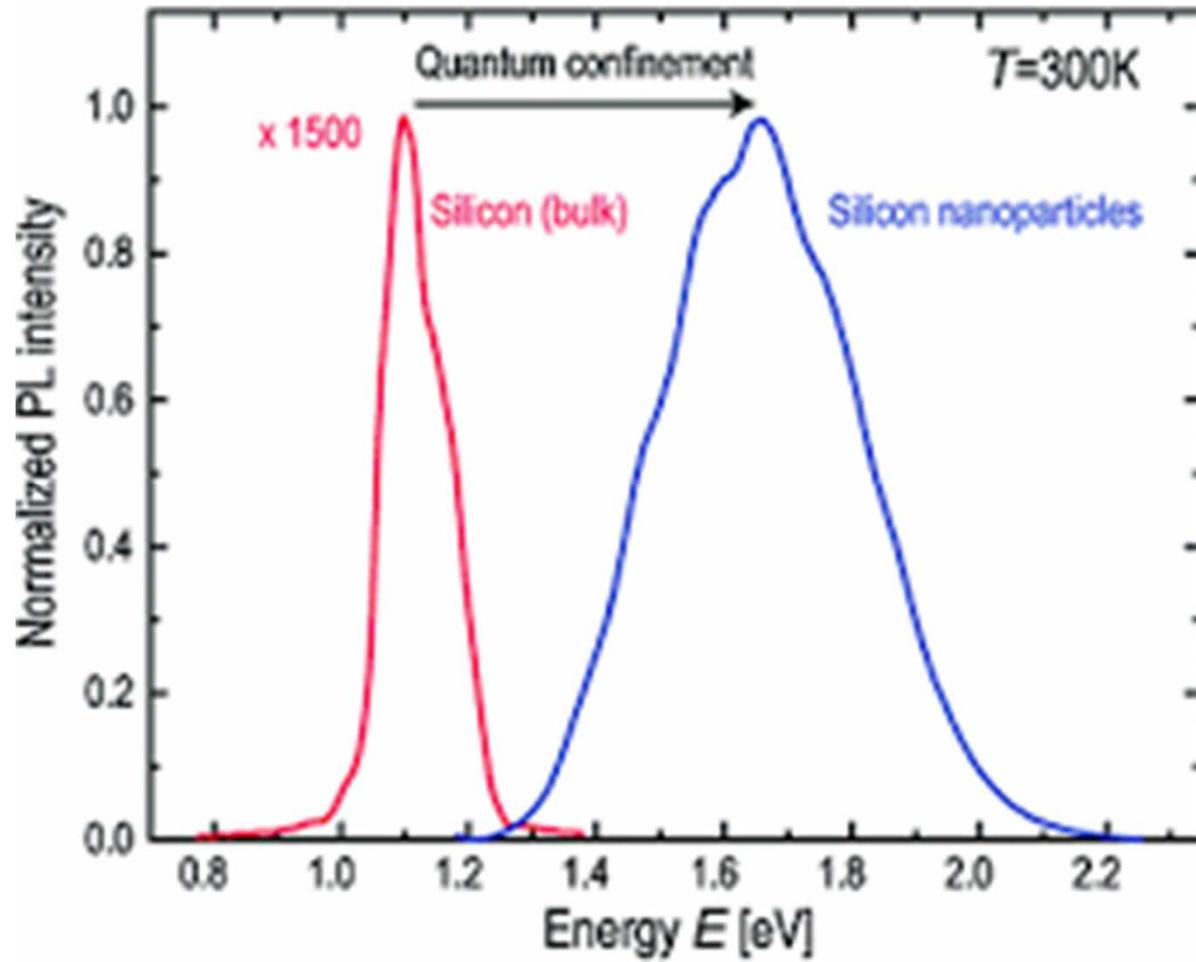


Semiconduttori a gap diretta (ZnO; GaN..) :  $\tau \sim 10^{-9} - 10^{-8} \text{ s}$

Semiconduttori a gap indiretta (Si; Ge..) :  $\tau \sim 10^{-5} - 10^{-3} \text{ s}$

Le proprietà ottiche di un semiconduttore a gap diretta cambiano completamente se questo viene ridotto a dimensioni nanometriche.

## Aumento del rate di emissione



# Aumento del rate di emissione

$$\Delta x \cdot \Delta p \sim \hbar$$

$$\Delta x \cdot \Delta k \sim 1$$

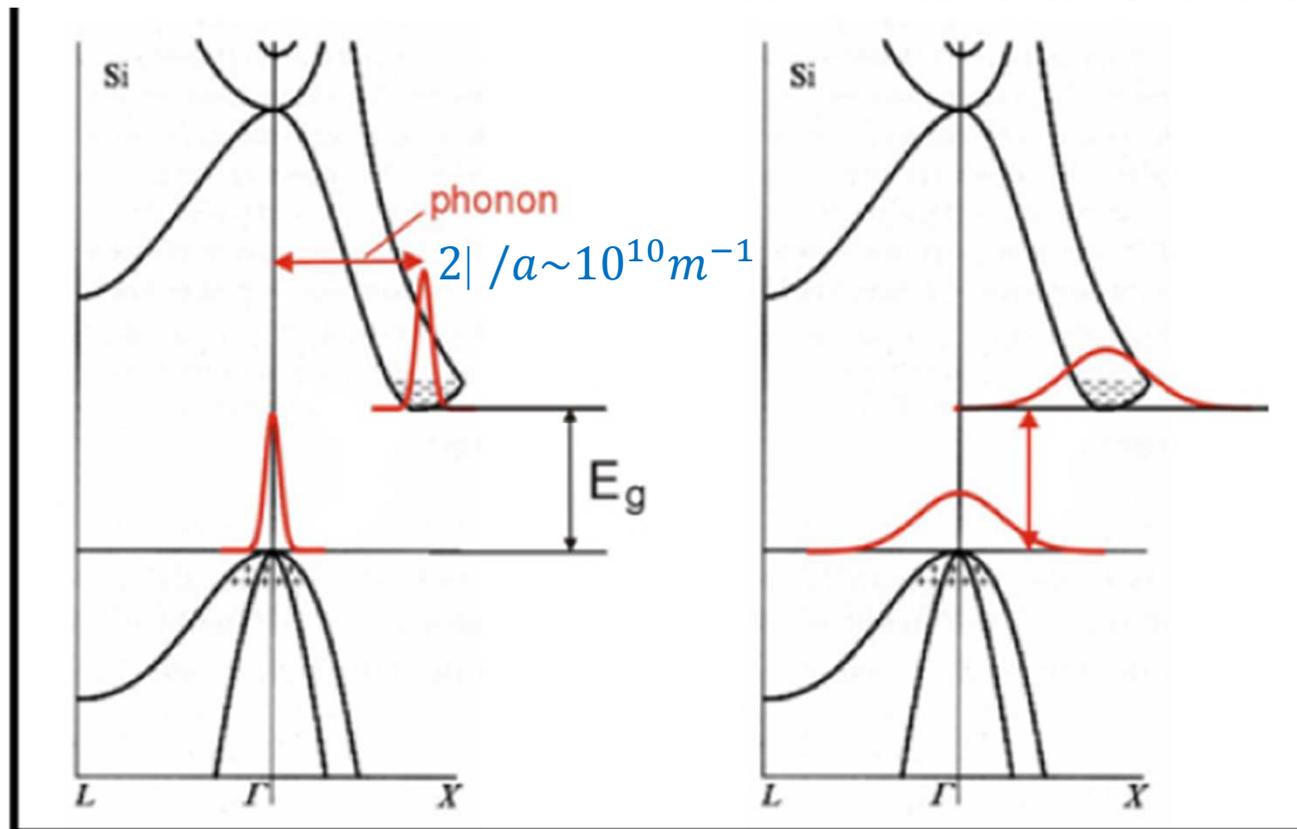
Principio d'indeterminazione

$\Delta x \rightarrow grande (\sim 10^{-2}m) \Rightarrow \Delta k \rightarrow piccolo (\sim 10^2 m^{-1})$

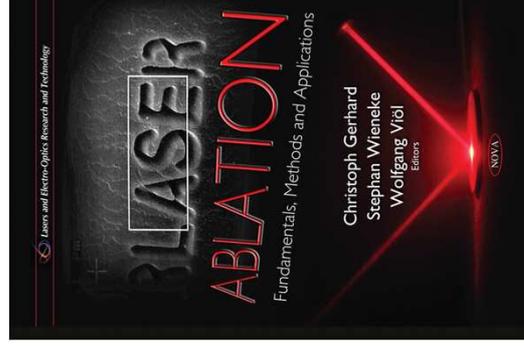
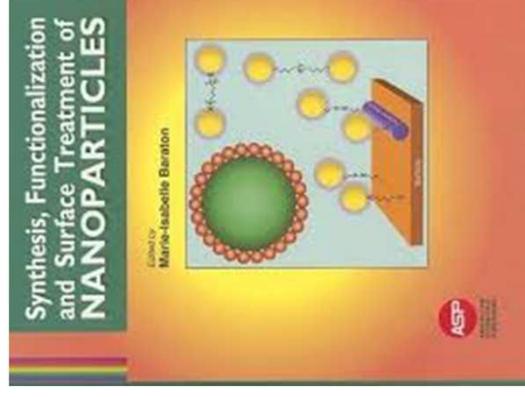
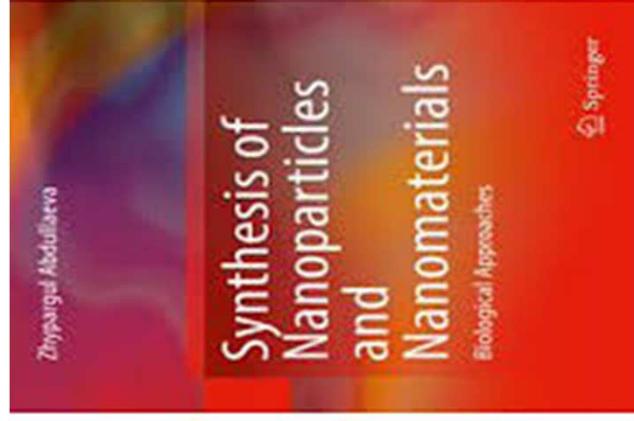
$\Delta x \rightarrow piccolo (\sim 10^{-9}m) \Rightarrow \Delta k \rightarrow grande (\sim 10^9 m^{-1})$

Fonone reticolare necessario alla ricombinazione

Funzioni d'onda di elettrone e buca si allargano.  
Transizione *direct-like* favorisce la ricombinazione senza l'intervento del fonone

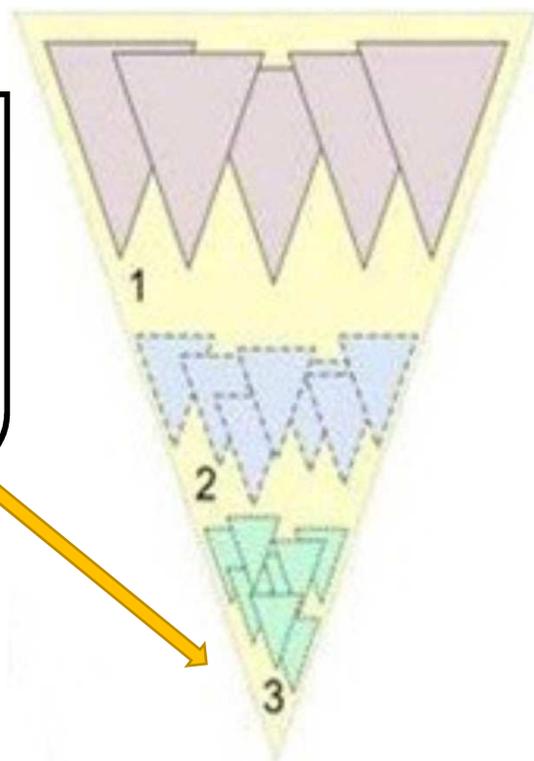


# Metodi di produzione



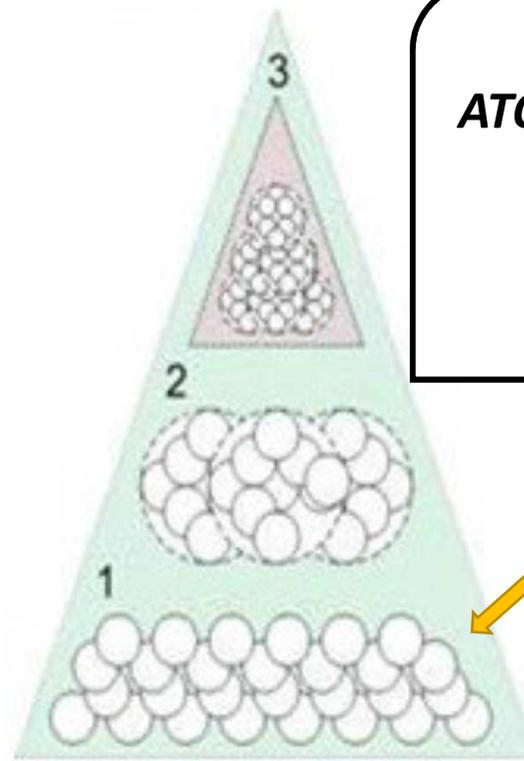
# TECNICHE DI PRODUZIONE

AL BULK VERSO I  
NANOCRISTALLI  
(riduzione di materiale)



Top-down

DA  
ATOMI / MOLECOLE VERSO I  
NANOCRISTALLI  
(aggregazione)



Bottom-up

# TECNICHE DI PRODUZIONE

## **TOP-DOWN**

**ABLAZIONE LASER**

**IMPIANTAZIONE IONICA**

**ETCHING**

**POLVERIZZAZIONE CATODICA**

## **BOTTOM UP**

- 1. DEPOSIZIONE CHIMICA DA VAPORE**
- 2. OSSIDAZIONE / RIDUZIONE IN SOLUZIONE**
- 3. EPITASSIA DA FASCI MOLECOLARI**

# TECNICHE DI PRODUZIONE

## TOP-DOWN

ABLAZIONE LASER

IMPIANTAZIONE IONICA

ETCHING

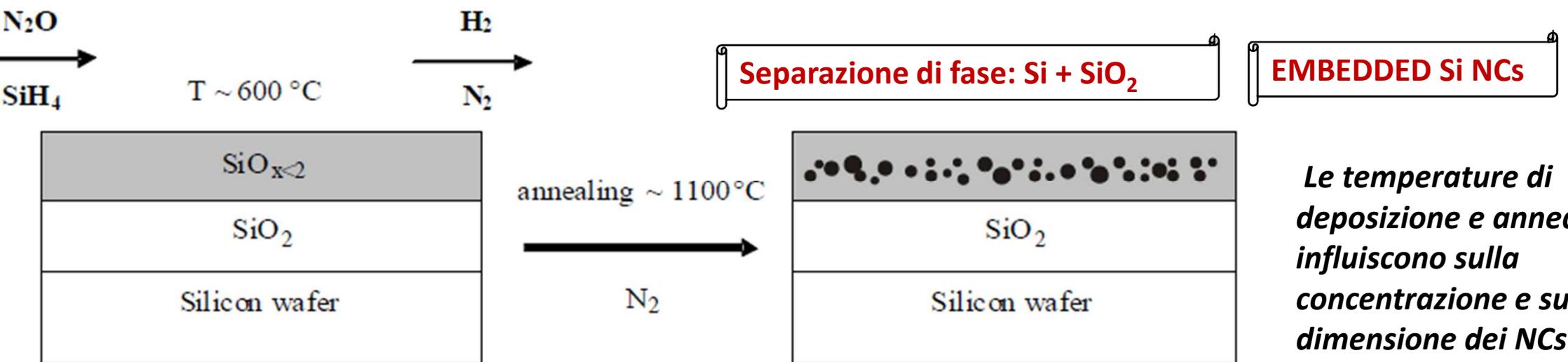
POLVERIZZAZIONE CATODICA

## BOTTOM UP

1. **DEPOSIZIONE CHIMICA DA VAPORE**
2. **OSSIDAZIONE / RIDUZIONE IN SOLUZIONE**
3. **EPITASSIA DA FASCI MOLECOLARI**

# DEPOSIZIONE CHIMICA DA VAPORE (bottom-up)

**PECVD** (*Plasma-enhanced chemical vapor deposition*)



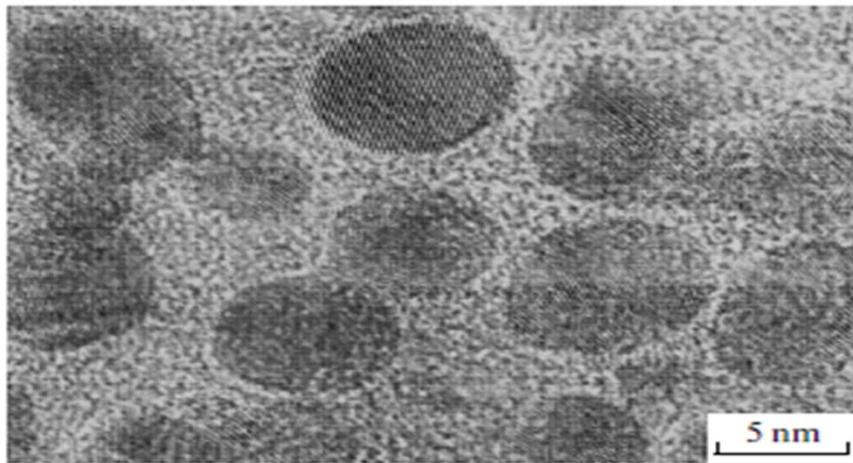
# amples

$\text{SiO}_x/\text{SiO}_2$  multi-layers grown on a p-type crystalline Si substrate.

$\text{SiO}_x$  produced by evaporation of SiO powder.

$\text{SiO}_2$  produced by electron beam evaporation of fused quartz

Sample	$\text{SiO}_x/\text{SiO}_2$ thickness (nm)	Ann. Temp ( $^{\circ}\text{C}$ )	Layers number
1	2.2/2.8	---	64
2	2.2/2.8	1100	64
3	4.4/2.8	1100	32
4	8.4/2.8	1100	50

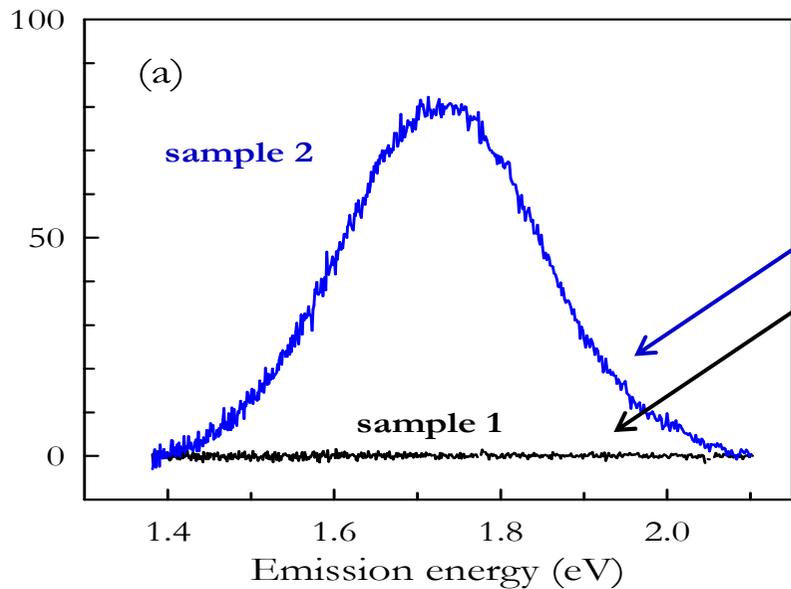


*2 hours annealing at 1100  $^{\circ}\text{C}$  induces the formation of Si-NCs*

**Fig. 2.** HR TEM image of a cross section of the 4/3 nm MNS annealed at 1100 $^{\circ}\text{C}$ .

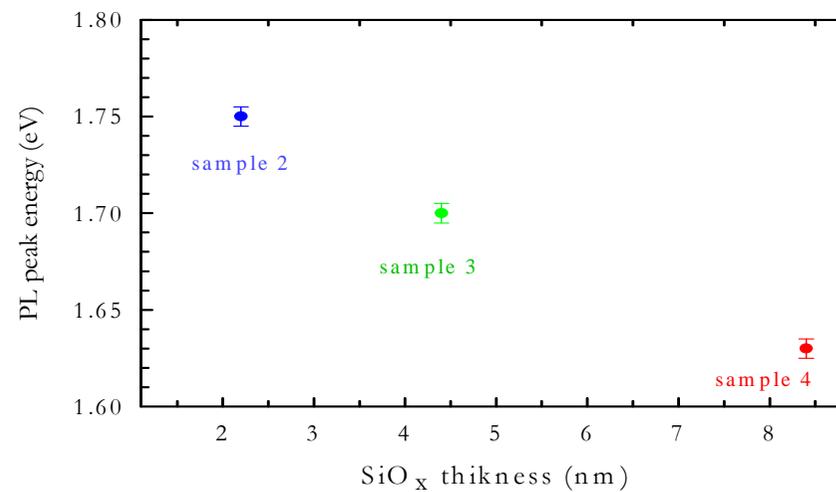
# Luminescenza

$E_{exc} = 4.6 \text{ eV}$

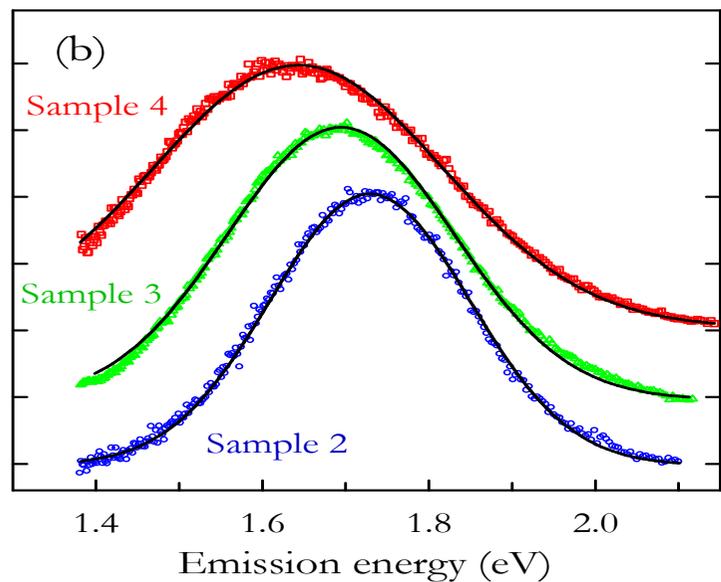


After annealing

No annealing



Normalized PL Intensity



QC effect

$$E_{PL}(d) = E_0 + \frac{3.73}{d^{1.39}}$$

Sample	$E_{PL}$ (eV)	Si-NC size (nm)
2	$\approx 1.73$	$d \approx 3.8$
3	$\approx 1.69$	$d \approx 4.1$
4	$\approx 1.63$	$d \approx 4.5$

# TECNICHE DI PRODUZIONE

## TOP-DOWN

**ABLAZIONE LASER**

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## BOTTOM UP

1. **DEPOSIZIONE CHIMICA DA VAPORE**
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3. **EPITASSIA DA FASCI MOLECOLARI**

# Pulsed laser ablation (PLA) in liquid

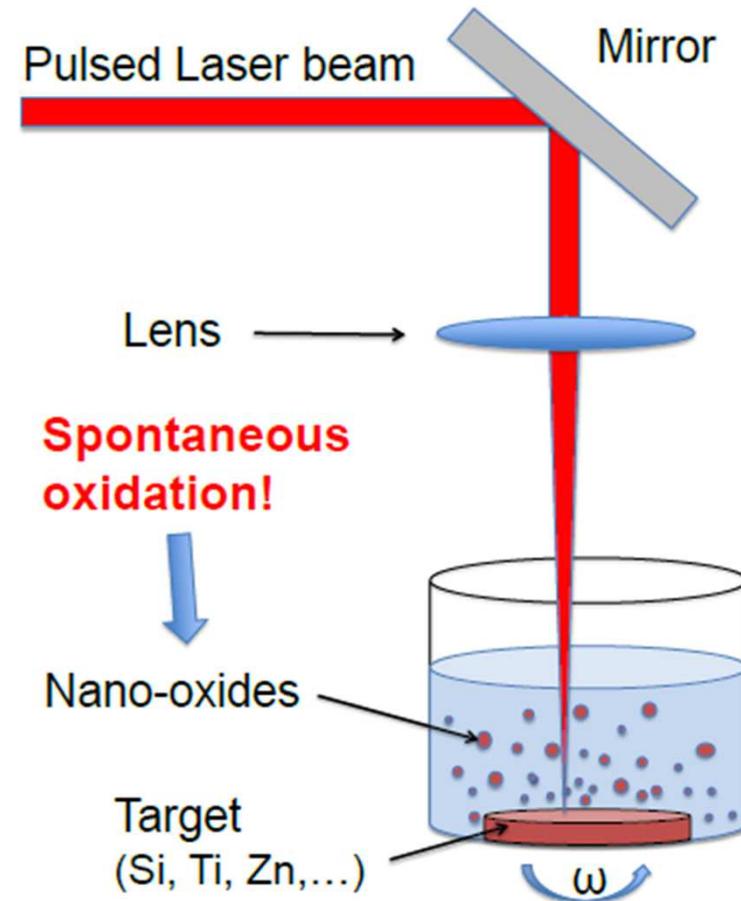
- Il fascio laser viene focalizzato sulla superficie del target.
- Il target viene ruotato o mosso per evitare che il laser colpisca sempre la stessa area.
- Fluenza ( $\text{J}/\text{cm}^2$ ): densità di energia fornita.

$$\Delta f = l \left( 1 - \frac{f}{\sqrt{n^2 f^2 + (n^2 - 1) r^2}} \right)$$

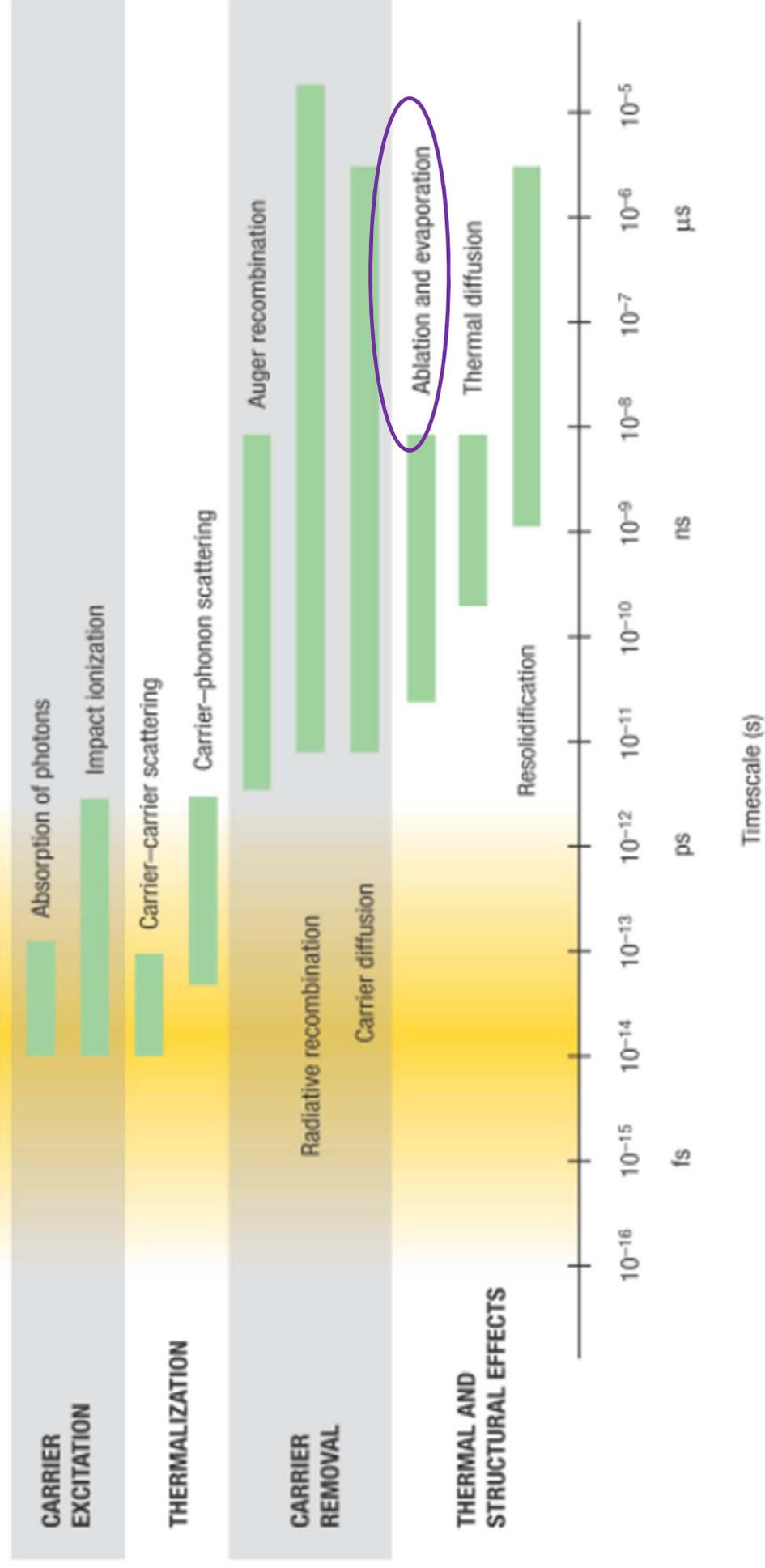
$$r \ll f, \quad \Delta f = l \left( 1 - \frac{1}{n} \right)$$

$r$  : raggio del fascio laser

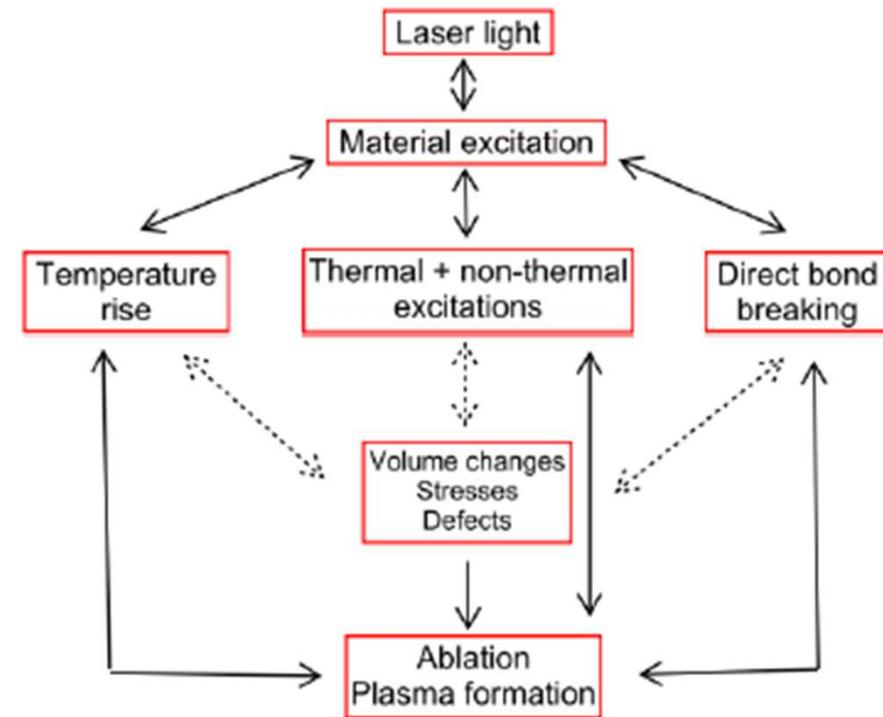
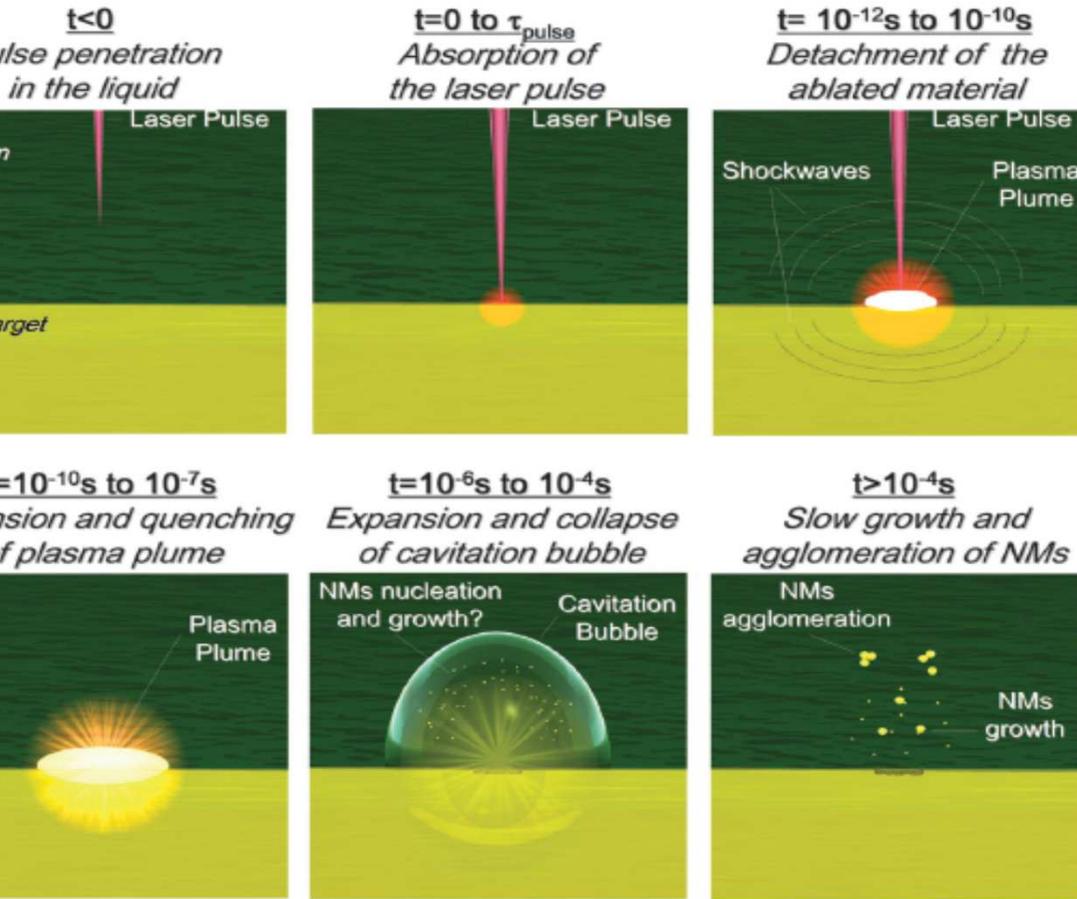
$n$  : indice di rifrazione del solvente



# Interazione laser/materia



# Principali step dell'ablazione



Parametri del plasma plume:

$$T \approx 10^3 \text{ K}$$

$$P \approx 10^9 - 10^{10} \text{ Pa}$$

L'ablazione in liquido si differenzia  
 dall'ablazione in gas dopo  $10^{-10} \text{ s}$

.A

# Vantaggi e svantaggi



• Semplicità e basso costo

• Metodo green

• Gran varietà di materiali ottenuti

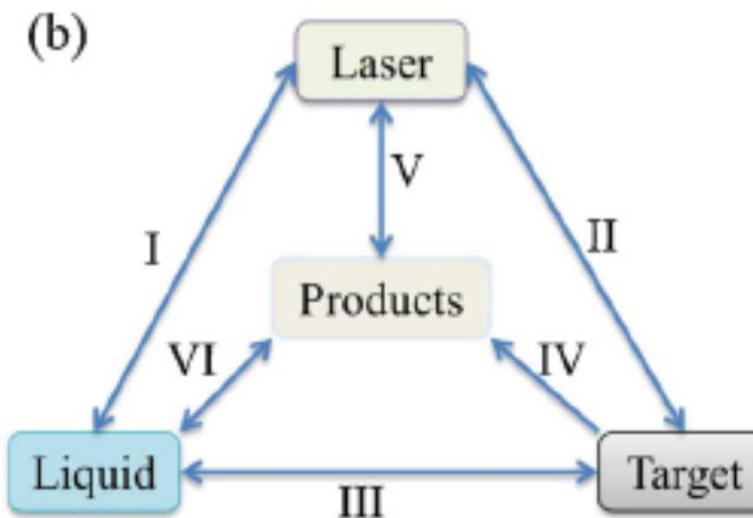
• Controllo dei parametri di sintesi:

laser, target, soluzione

• Non applicabile su larga scala (10 mg/ora)

• Scarso controllo della forma delle NP

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**																
		*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Tb		
		**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		



# Effetto dei parametri sperimentali



## Parametri del laser

- Lunghezza d'onda
- Numero di impulsi
- Energia dell'impulso
- Durata dell'impulso
- Repetition rate

## Parametri materiali

- Target bulk
- Solventi
- Soluti



# Parametri del laser: lunghezza d'onda (frequenza)

## Condizioni da soddisfare:

La soluzione deve essere trasparente al fascio laser

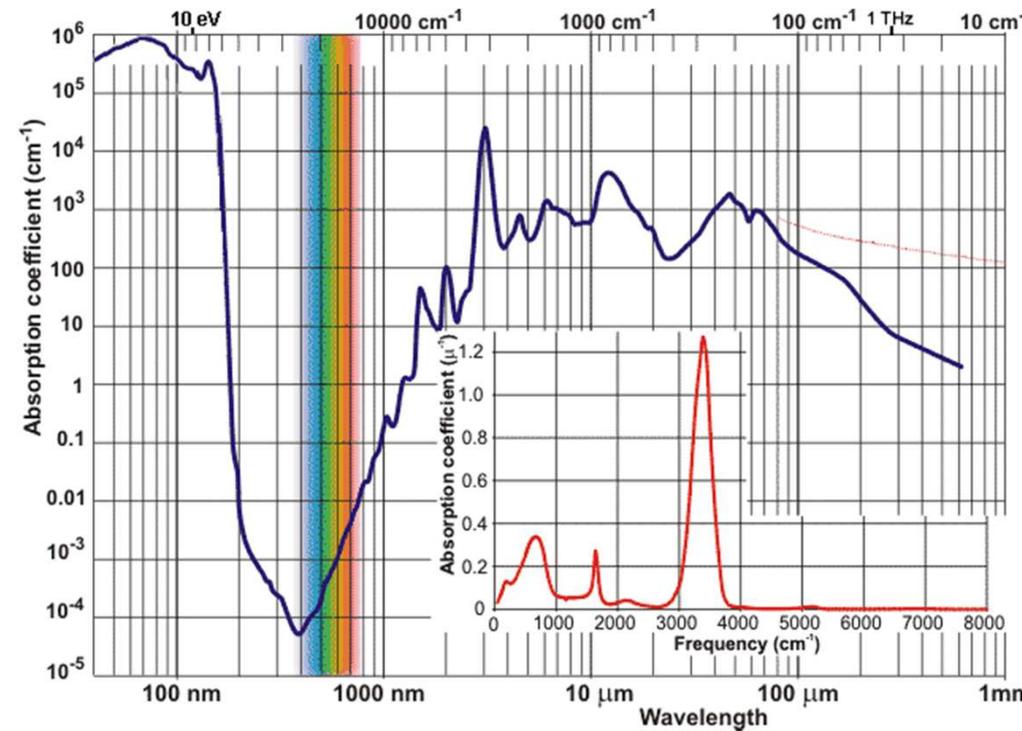
Il fascio laser deve essere assorbito dal target

«entro pochi nanometri»

$$\sigma_{target}(\nu_{laser}) \geq 10^7 \text{ cm}^{-1}$$

Valida per i metalli in un ampio range spettrale

Valida per isolanti e semiconduttori se  $h \cdot \nu_{laser} > E_g$

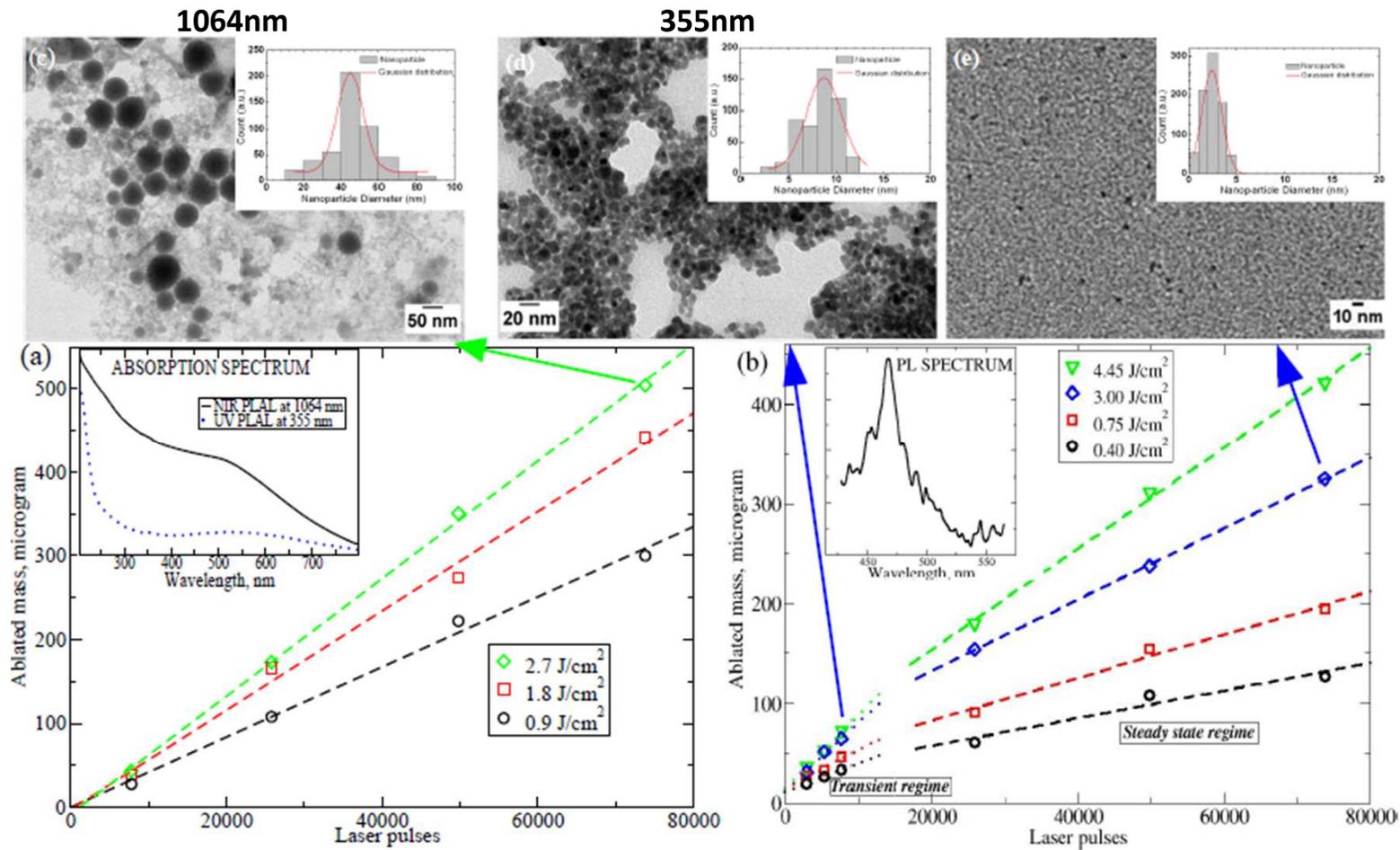


Esempio: Spettro assorbimento acqua distillata

# Parametri del laser: numero impulsi

**Laser:** Nd-YAG 1064 nm, 355 nm 60 ps RR=20Hz  $d_{\text{spot}}=0.2\text{mm}$

**Target:** Wafer di Silicio in 2 ml di acqua deionizzata (DIW)



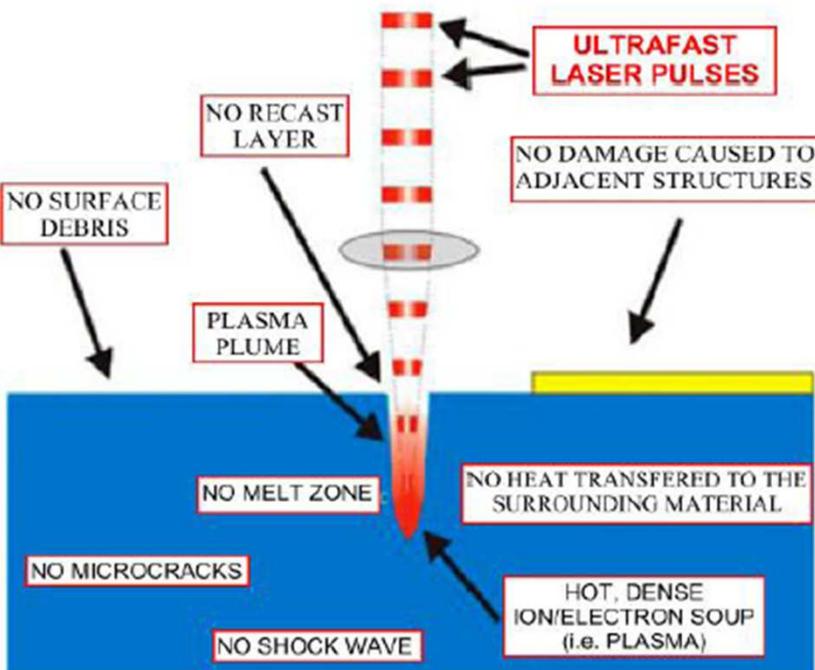
# Parametri del laser: durata dell'impulso ( $\tau_{laser}$ )

La criticità di questo parametro è legata al tempo di termalizzazione del target ( $\tau_{therm} \sim ps$ )

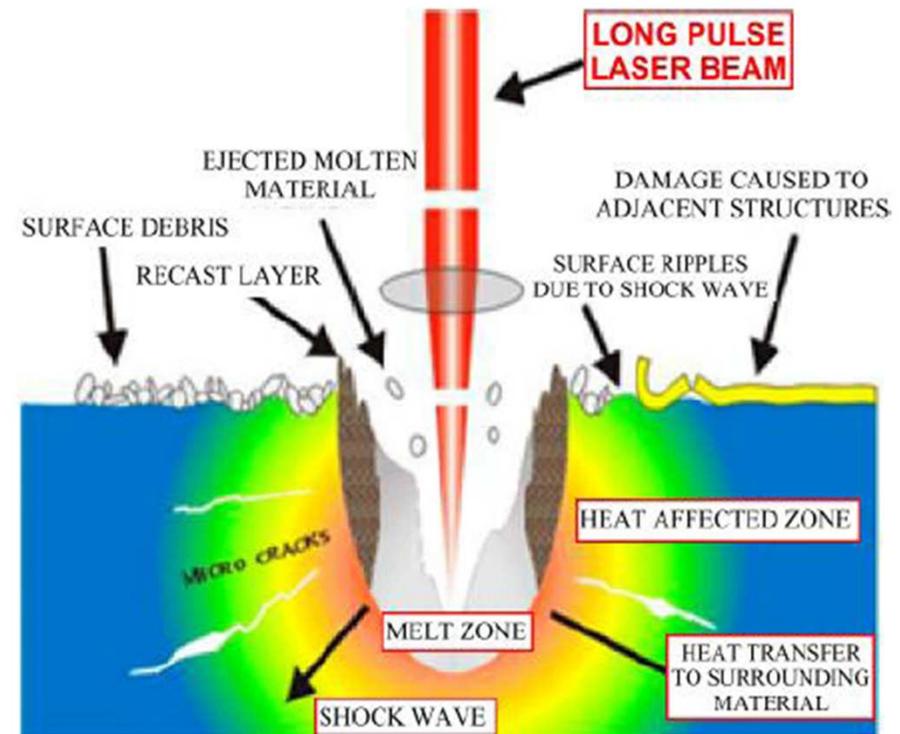
$\tau_{laser} \sim fs \ll \tau_{therm}$  gli elettroni non hanno il tempo di termalizzare col reticolo

$\tau_{laser} \sim ns \gg \tau_{therm}$  la termalizzazione coinvolge un'area grande dello spot laser

Non-thermal ablation



thermal ablation



# Parametri del laser: durata dell'impulso

thermal ablation

Non-thermal ablation

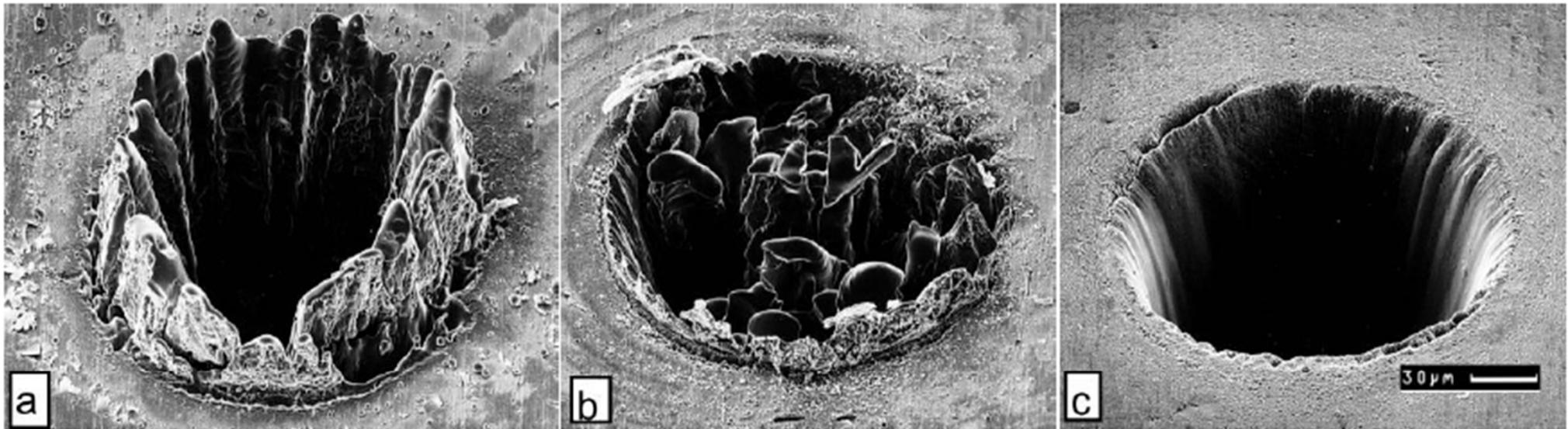
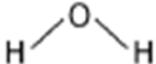
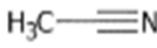
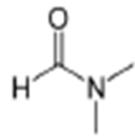
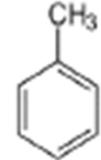
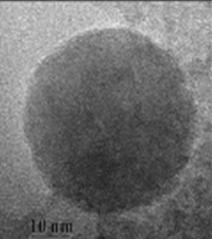
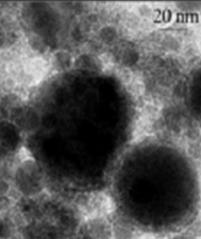
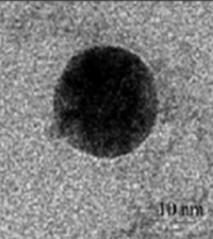
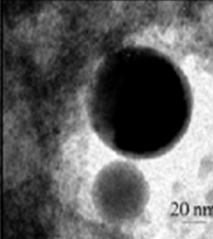
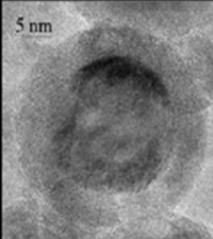
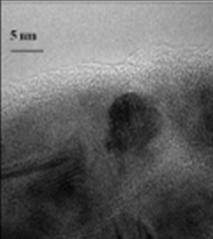
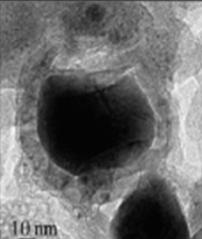


Figure 4: SEM photograph of a hole drilled in a steel foil with (a) 3.3 ns, 1mJ,  $\phi = 4.2 \text{ J cm}^{-2}$ ; (b) 80 ps, 900  $\mu\text{J}$ ,  $\phi = 3.7 \text{ J cm}^{-2}$ ; and (c) 200 fs, 120  $\mu\text{J}$ ,  $\phi = 0.5 \text{ J cm}^{-2}$  laser pulses at 780 nm [12].

# Effetto del solvente

- Viscosità, densità e tensione superficiale  $\longrightarrow$  Confinamento e dinamica del plume
- Interazione con le nanoparticelle  $\longrightarrow$  Capping e modifiche chimiche e strutturali

## Esempio

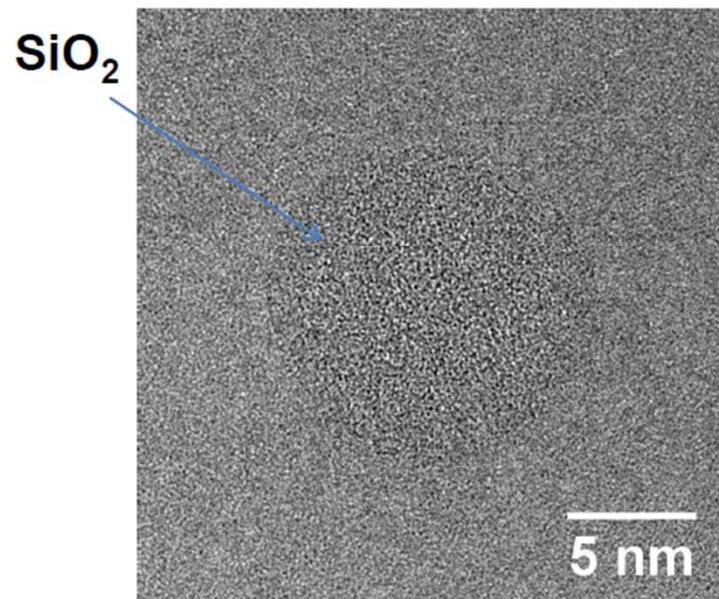
Target ↓	Solvent ↓	Water	Ethanol	Acetonitrile	Dimethyl- formamide	Tetra- hydrofuran	Dimethyl- sulfoxide	Toluene
								
<b>Fe</b>								
		<i>Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe(OOH)<sub>2</sub></i>	<i>Fe<sub>3</sub>O<sub>4</sub>, FeC<sub>3</sub></i>	<i>Fe<sub>3</sub>O<sub>4</sub>, Carbon</i>	<i>Fe<sub>3</sub>O<sub>4</sub>, Carbon</i>	<i>Metal Fe/ Fe<sub>3</sub>O<sub>4</sub></i>	<i>Metal Fe/ Carbon</i>	<i>Fe-Carbide/ Graphite</i>

# Effetto del solvente

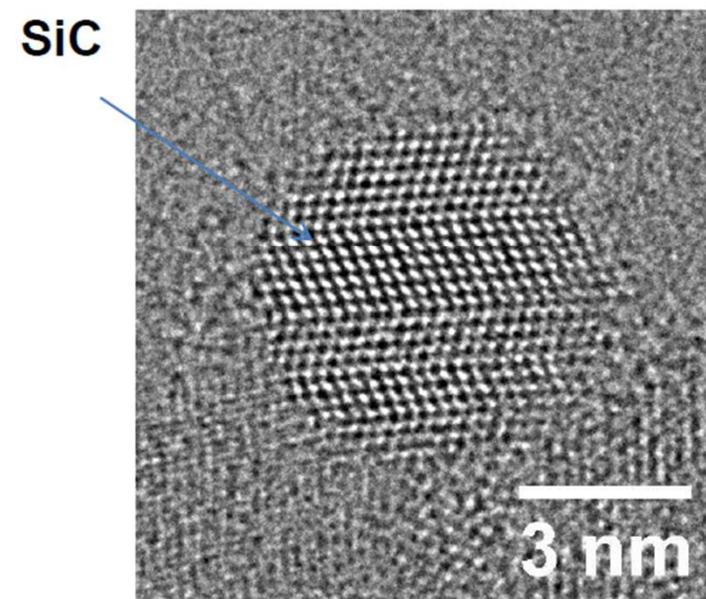
Esempio

Laboratory «Roberto Boscaino»  
of Advanced Materials

Ablazione di Silicio in acqua



Ablazione di Silicio in eptano C<sub>7</sub>H<sub>16</sub>



## Ossidi nano-strutturati sintetizzati con ablazione laser in liquido

1) Si/SiO<sub>2</sub>

2) ZnO

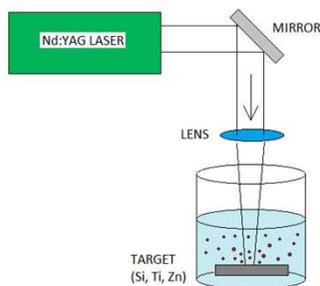
---

# Tecniche sperimentali

Dipartimento di Fisica e Chimica  
"Emilio Segrè" di Palermo

Karlsruhe Institute of Technology

- 1) Nd:YAG (1064 nm)  $\tau_{\text{laser}} \approx 5 \text{ ns}$ ;
- 2) Ti:Sapphire (800 nm)  $\tau_{\text{laser}} \approx 50 \text{ fs}$



PLA

OA and PL  
"online"

NP

Morphological  
Properties



AFM

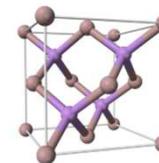
HRTEM;  
EDXS

Optical  
Properties

Optical  
absorption  
(UV-Vis.)

Time  
resolved PL

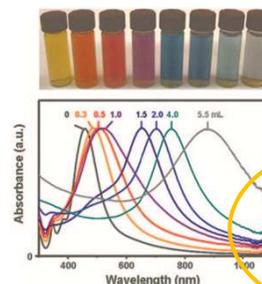
Structural  
Properties



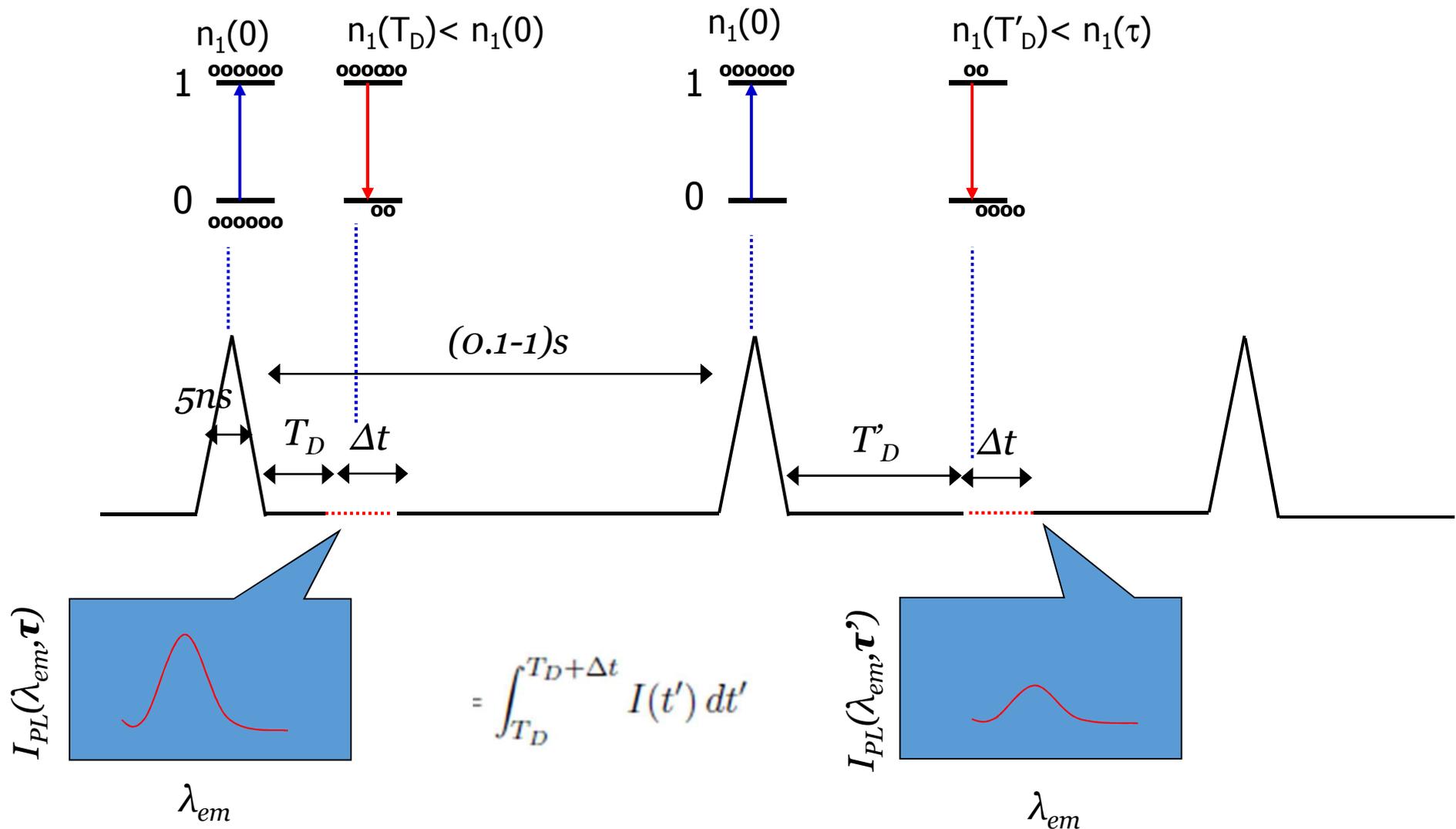
$\mu$ Raman

IR  
absorption

EPR



# Time-resolved PL re-interpretata!!



## Gating:

ritardo  $\tau$ , acquisizione  $\Delta t$  controllabili via computer (ns-ms)!!

possibilità di accumulare più spettri per ogni ritardo  $\tau$  (sulla CCD e via software)

# 1) Production of Si-nnc/SiO<sub>2</sub>



Applied Surface Science 302 (2014) 62–65



Contents lists available at ScienceDirect

Applied Surface Science

Journal homepage: [www.elsevier.com/locate/apsusc](http://www.elsevier.com/locate/apsusc)



luminescent silicon nanocrystals produced by near-infrared  
nanosecond pulsed laser ablation in water



JOURNAL OF APPLIED PHYSICS 120, 024303 (2016)



**Self-limiting and complete oxidation of silicon nanostructures produced  
by laser ablation in water**



Enhancing the luminescence efficiency of  
silicon-nanocrystals by interaction with H<sup>+</sup> ions†

Click for updates

J. Chem. Chem. Phys.,

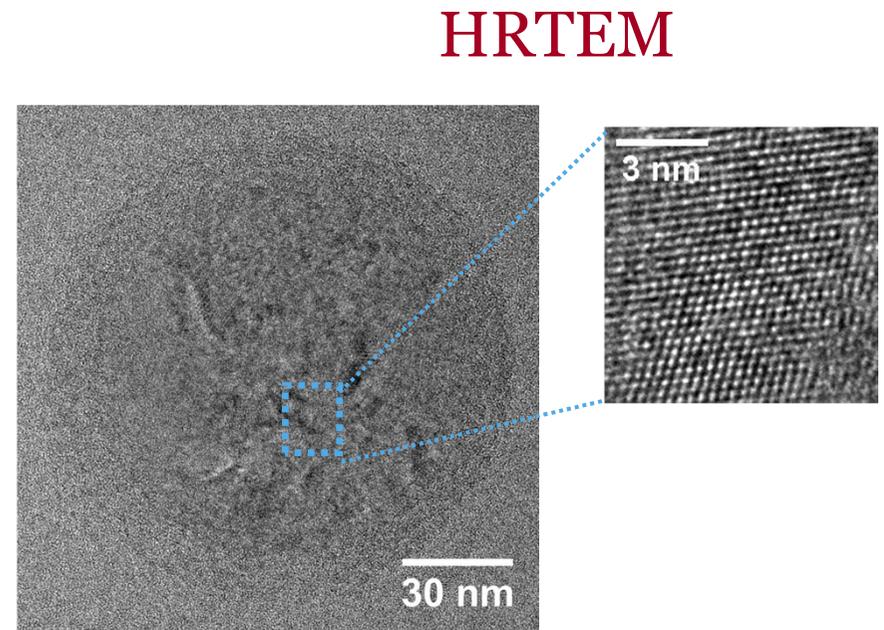
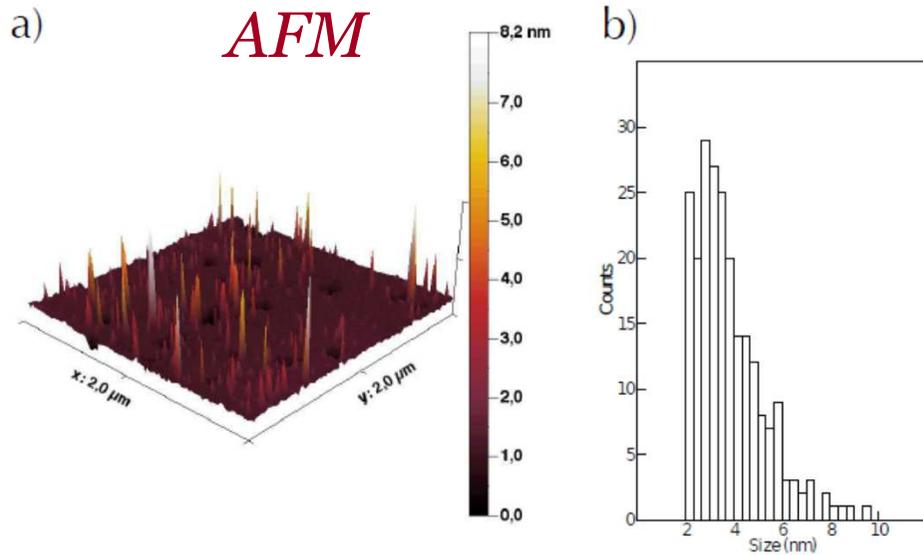
**ORIGINAL PAPER**

Si/SiO<sub>2</sub> Nanoparticles

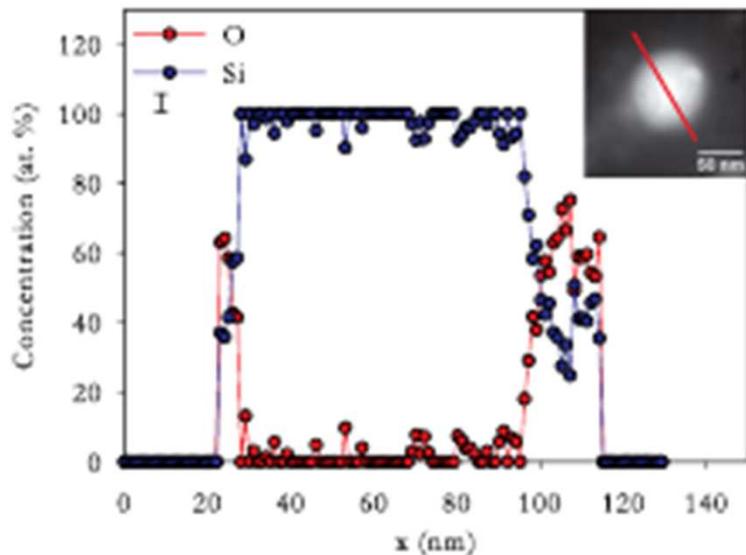
**Luminescence Efficiency of Si/SiO<sub>2</sub> Nanoparticles  
Produced by Laser Ablation**



# Proprietà morfologiche/strutturali



*EDXS*

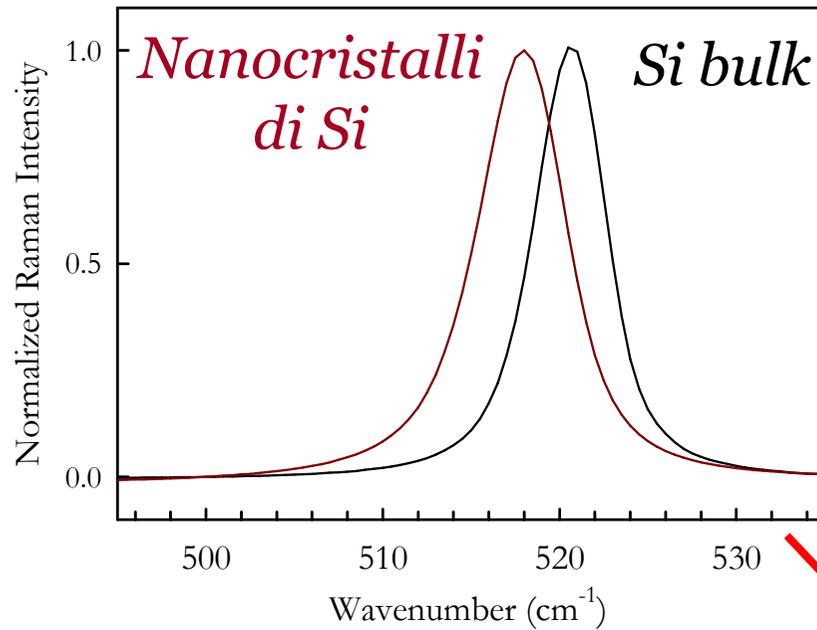


Si cubic structure:  
lattice parameter  $a=5.4305 \text{ \AA}$

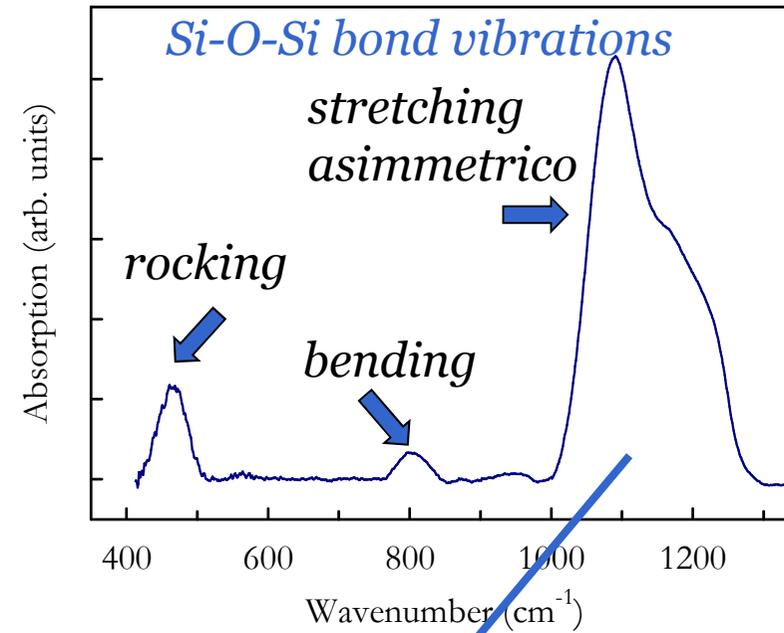
Si polycrystal surrounded by amorphous  $\text{SiO}_2$  layer  
with an interface mainly composed by  $\text{Si}_3\text{O}$

# Proprietà vibrazionali IR

## $\mu$ -Raman

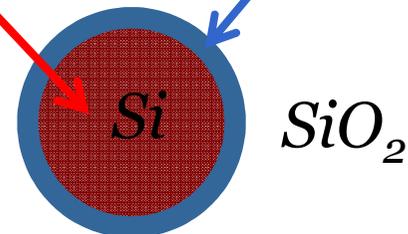


## Assorbimento



$\Delta v$ : quantum confinement (QC)

Size  $\sim 4$  nm

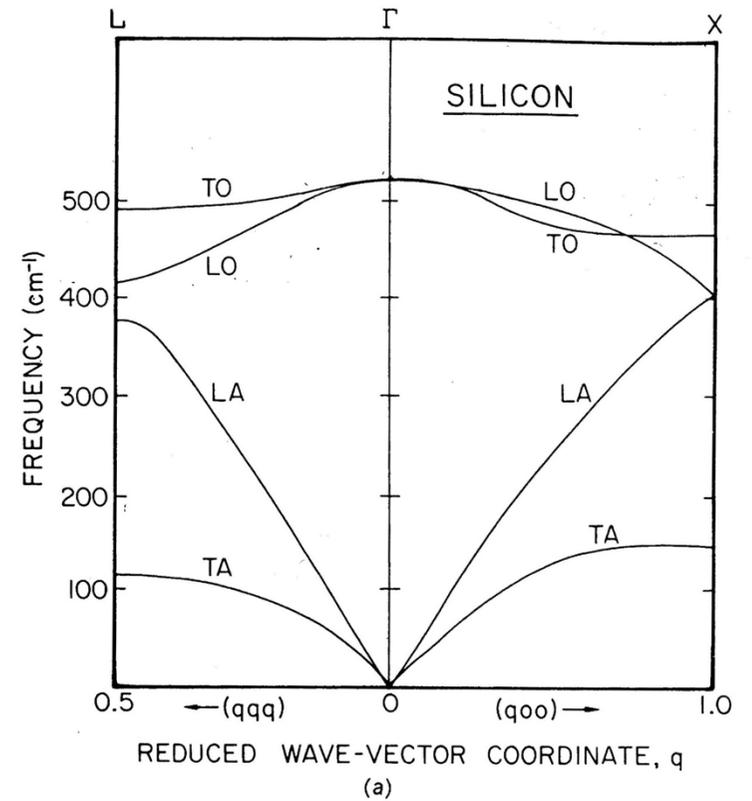
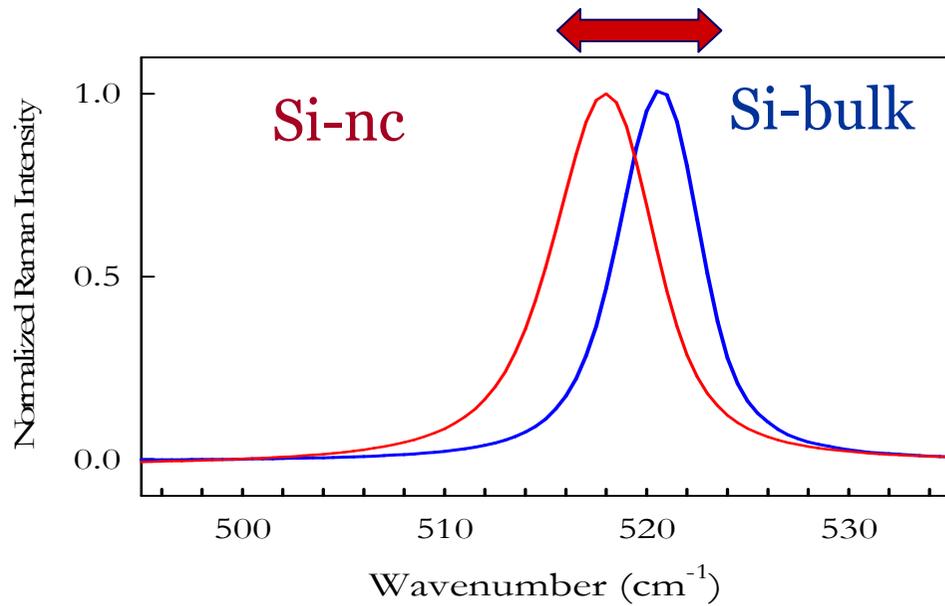


QC

$$\Delta x \cdot \Delta k \sim 1$$

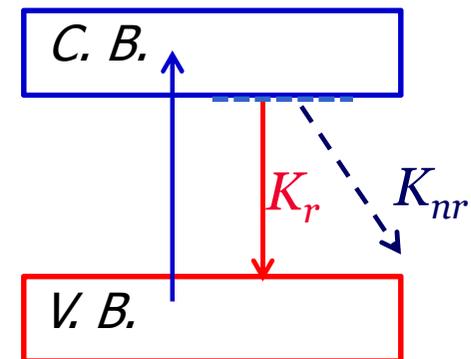
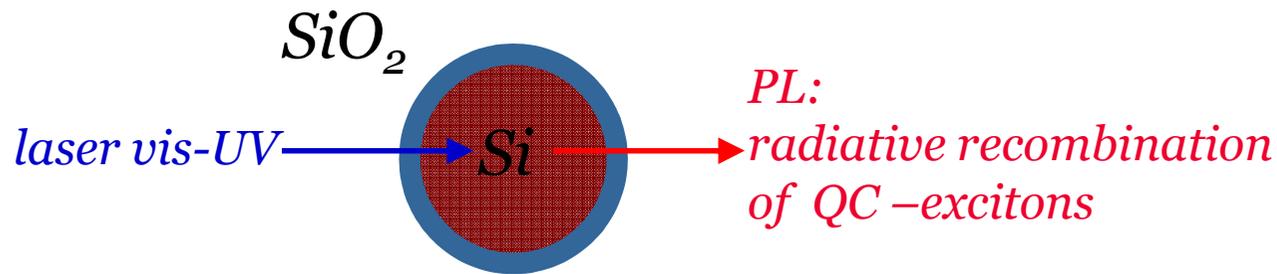
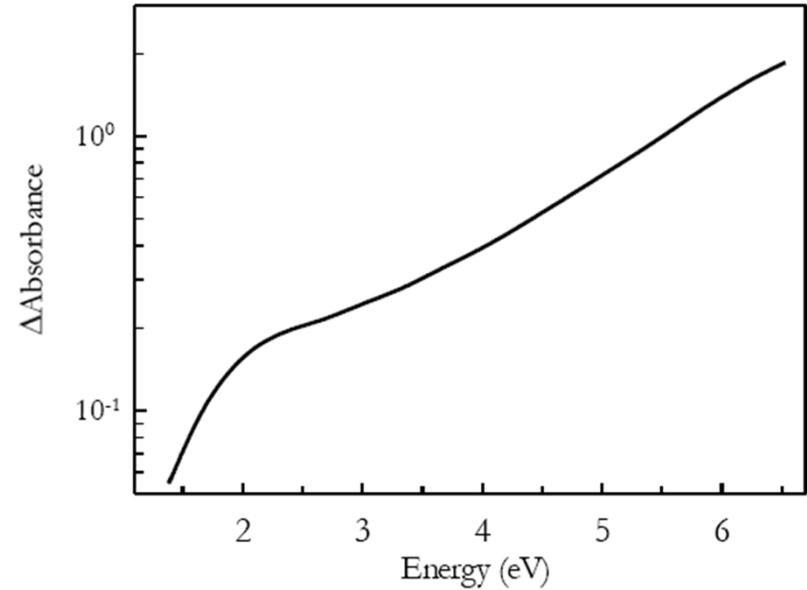
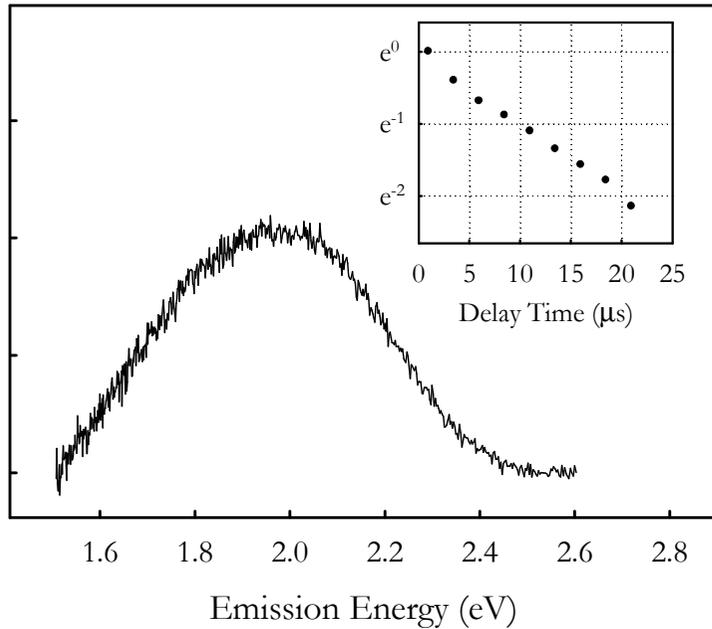
Bulk:  $\Delta x \rightarrow$  grande ( $\sim 10^{-2}m$ )  $\Rightarrow \Delta k \rightarrow$  piccolo ( $\sim 10^2m^{-1}$ )

NC:  $\Delta x \rightarrow$  piccolo ( $\sim 10^{-9}m$ )  $\Rightarrow \Delta k \rightarrow$  grande ( $\sim 10^9m^{-1}$ )



# Proprietà ottiche PL/OA

*PL a 1.9 eV*  $E_{exc}=4.13eV$   
 $t_D=1\mu s, \Delta_T=10ms$



# Goal!

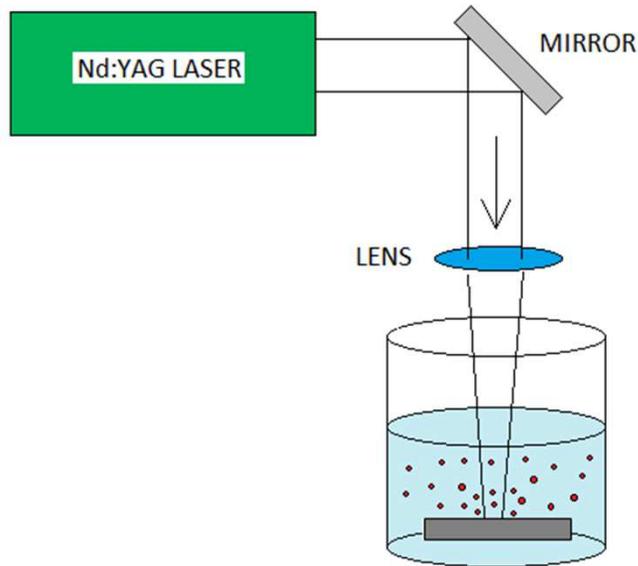
*Increase the brightness:*



*Enhancement of PL quantum efficiency*

# Experimental Methods

## *Laser Ablation*



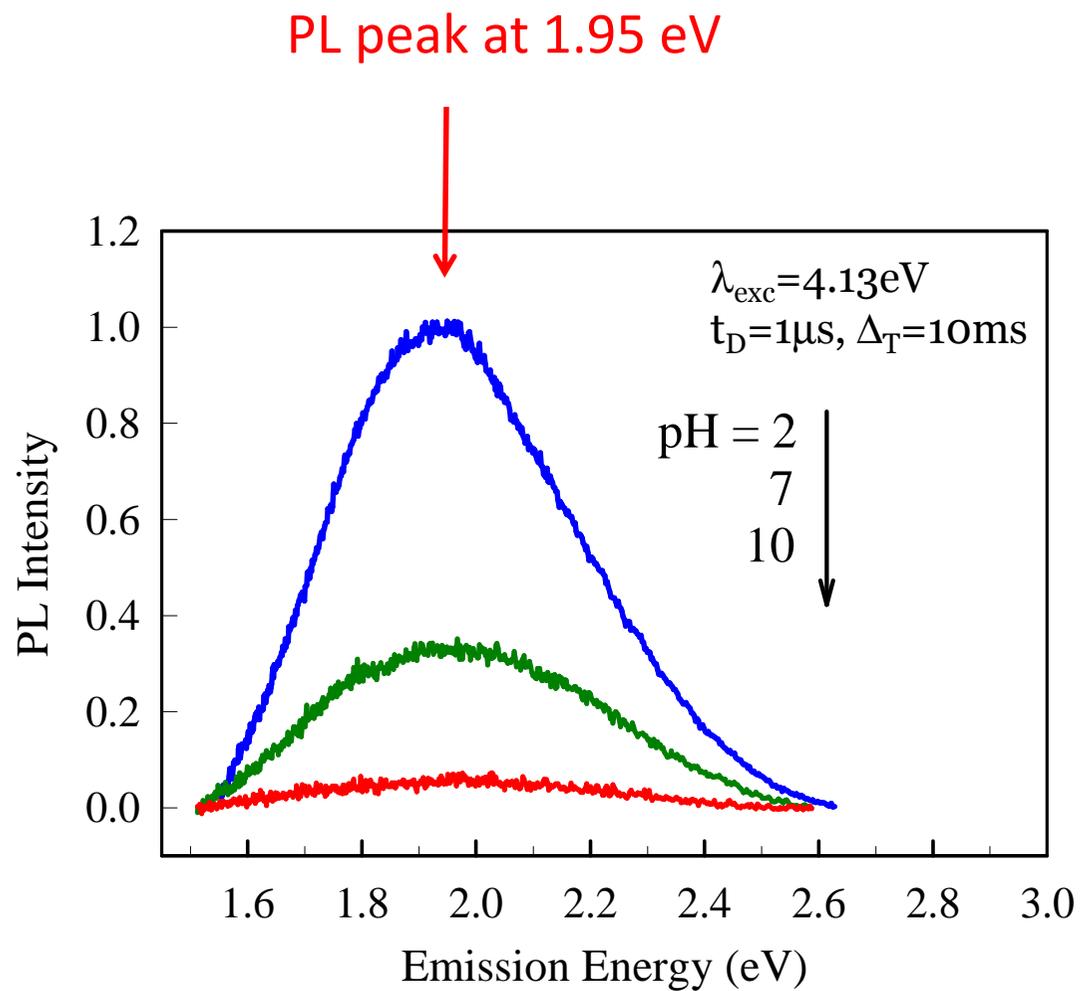
*Si-Target  
in deionized water*



*Soluzioni «acide» e «basiche»  
Al variare del pH da 1 a 10*

*Time-resolved PL  
IR absorption*

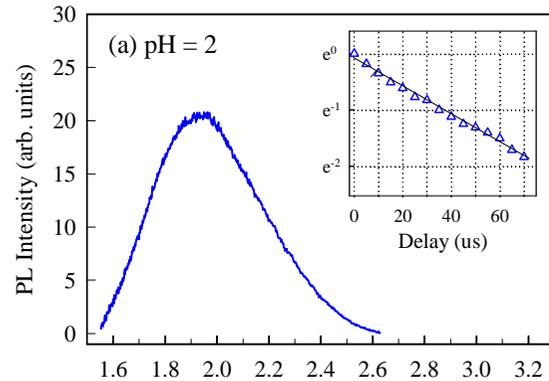
# Results PL dependence on pH



**PL intensity increases by a factor of  $\sim 20$  upon decreasing the pH from 10 to 2.**

# Results

## PL dependence on pH

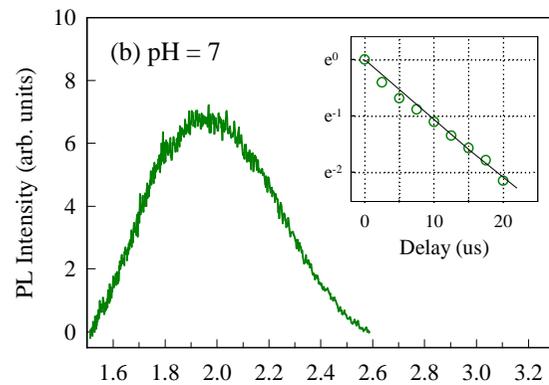


Exponential decay:  $\exp(-t/\tau)$   $\tau = 1_r / (k_r + k_{nr})$

$\tau \approx 35 \mu\text{s}$

$I_{\text{PL}}$  and  $\tau$  are correlated

$$I_{\text{PL}} \propto \eta = k_r / (k_r + k_{nr}) = k_r \times \tau$$

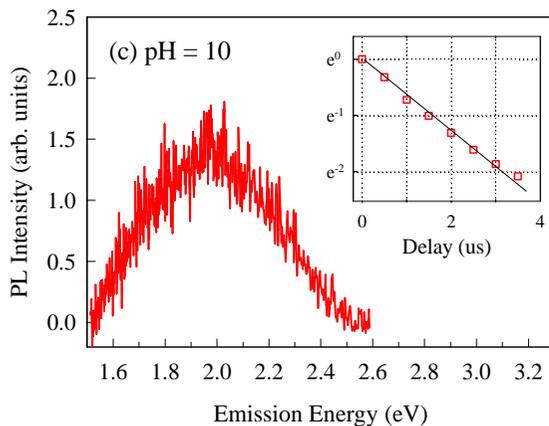


$\tau \approx 9.5 \mu\text{s}$

$I_{\text{PL}}$  is related to the variation of  $\eta$

Hypothesis:

*$\eta$  is limited by the existence of centers on which the excitons non-radiatively recombine (non-radiative defects)*

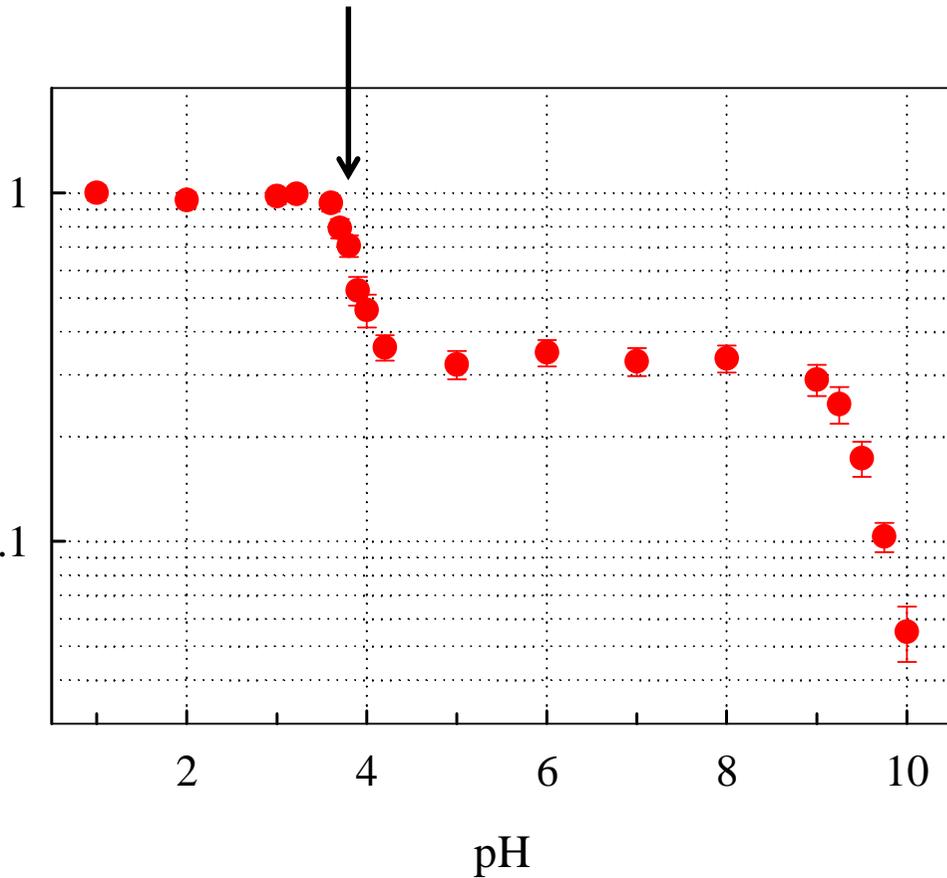


$\tau \approx 1.8 \mu\text{s}$

# Results

## PL efficiency: dependence on pH

pH  $\approx$  3.5;  $[H^+] \approx 2 \times 10^{17} \text{ cm}^{-3}$



Maximum efficiency:  $\eta_{\text{max}} = k_r \times \tau_{\text{max}}$

$$k_r \leq 1 / \tau_{\text{max}} \approx 3.6 \times 10^4 \text{ s}^{-1}$$

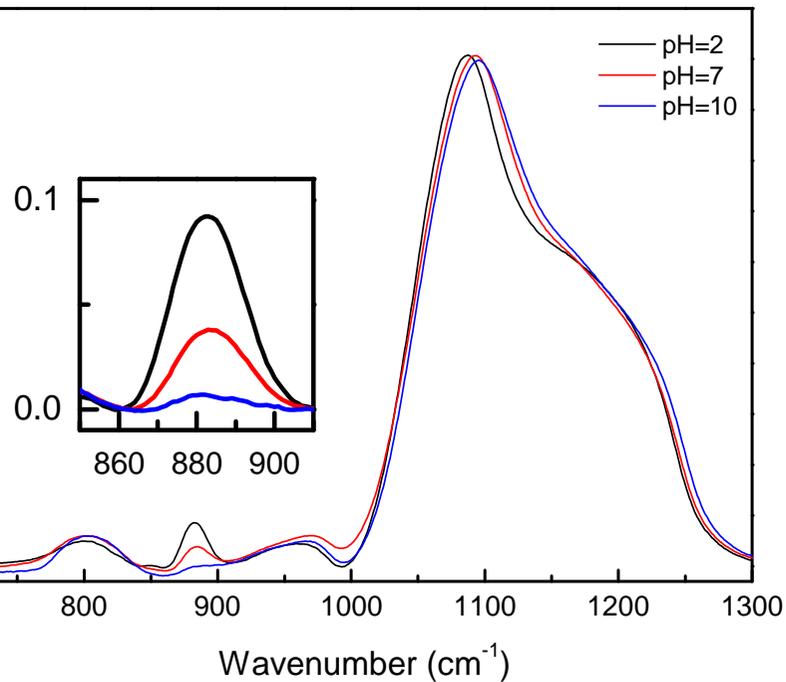
$$\eta = k_r / (1/\tau) = k_r / (1/\tau_{\text{max}} + \Delta k_{\text{nr}})$$

enhancement of  $\eta$  on increasing  $[H^+]$ ,  
consistently with the passivation non-radiative def

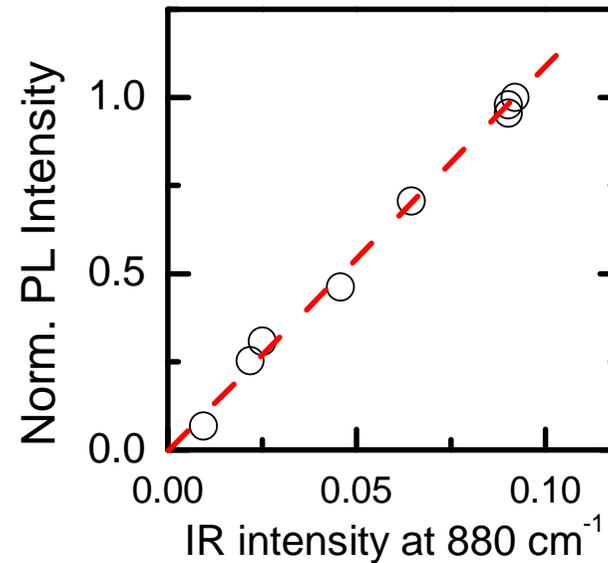
# Results IR absorption: dependence on pH



*What about the origin of non-radiative defects?*



## Linear correlation between [SiH] and $I_{PL}$



When diluted in solution  $[SiH]_{max} \sim 10^{17} \text{ cm}^{-3}$   
*in accordance with  $[H^+]$  that determines the saturation of  $\eta$*

First proposal:

*$H^+$  ions passivate the non radiative defects,  
thus increasing  $[SiH]$*

$0 \text{ cm}^{-1} \rightarrow SiH$  bending mode

et al. J. Non-Cryst. Solids **185** (1995) 249



*The exact structure of non radiative centers remains open!!*

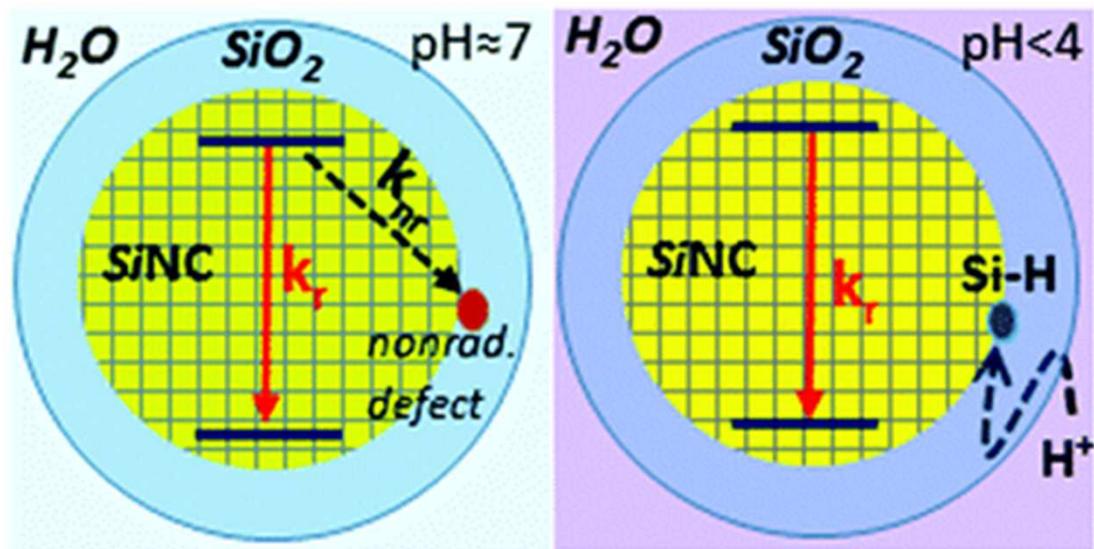
*Hypothesis!*

*Distorted Si—Si bonds and Si—O—Si bridging bonds at the Si/SiO<sub>2</sub> interface  
[Lee et al. Adv. Funct. Mater, 22, 3233 (2012): pseudopotential simulations]*

*In our system:*

*The interface (~3 nm) is Si<sub>3</sub>O ...*

*Distorted Si—Si bonds and Si—O—Si bridging bonds could be present!*



## 2) Production of ZnO-nc



Production of Zn nanoparticles probed by online optical spectroscopy during  
second pulsed laser ablation of a Zn plate in H<sub>2</sub>O

PCCP

PAPER



Cite this: *Phys. Chem. Chem. Phys.*,

Luminescence mechanisms of defective  
ZnO nanoparticles



Controlling the oxidation processes of Zn nanoparticles produced by pulsed laser  
ablation in aqueous solution

# Ossido di zinco (ZnO)

ZnO è un semiconduttore del II-VI gruppo

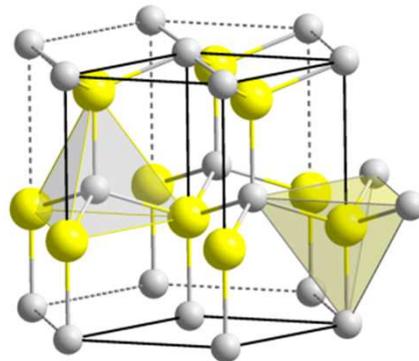
ZnO



**Proprietà:** Alta mobilità elettronica, ampio band gap, biocompatibilità, piezoelettricità e **intensa luminescenza a temperatura ambiente**

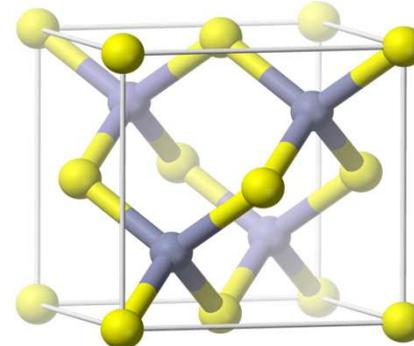
## Strutture cristalline

**Wurtzite**



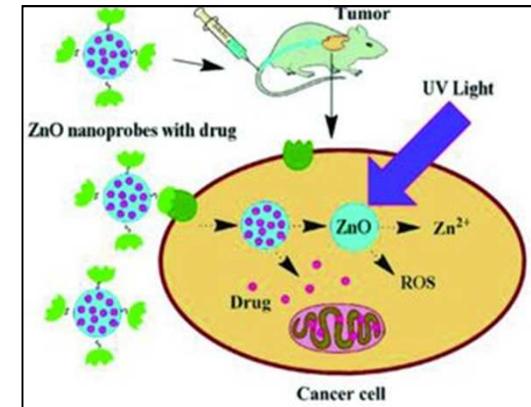
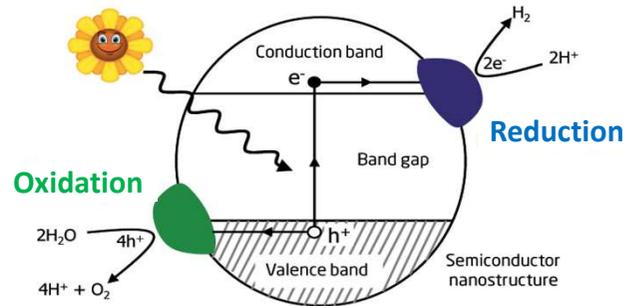
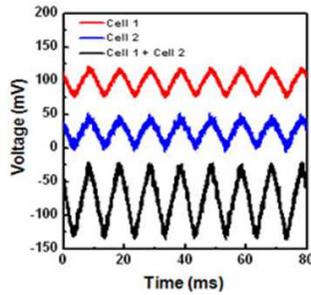
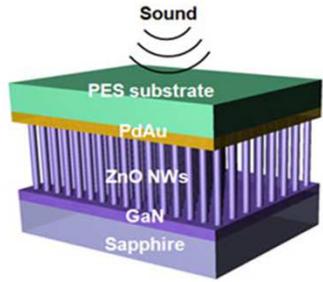
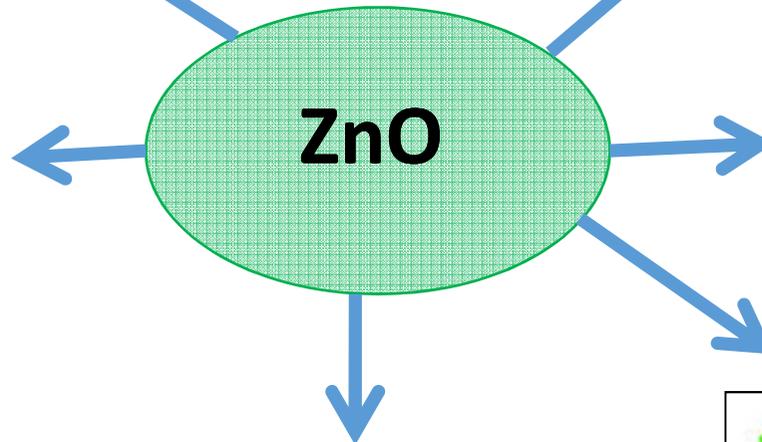
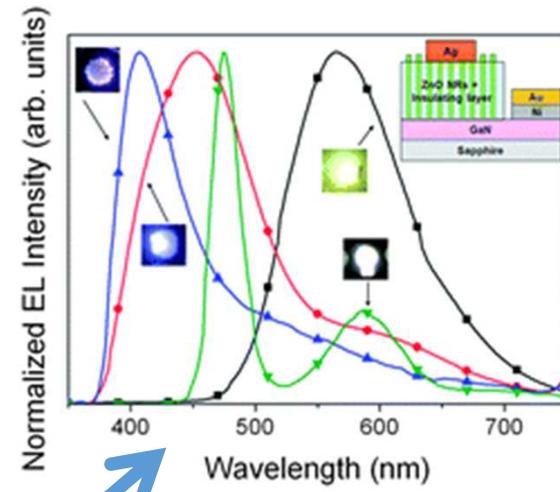
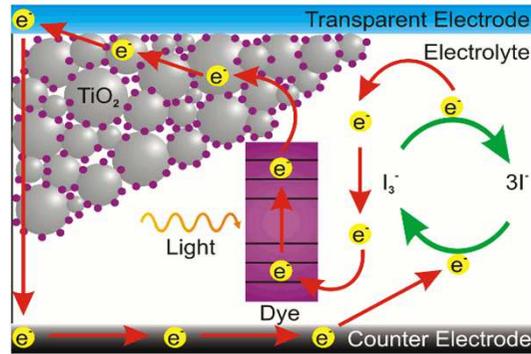
$E_g = 3.37\text{eV}$  (direct-bandgap)

**Zincoblenda**



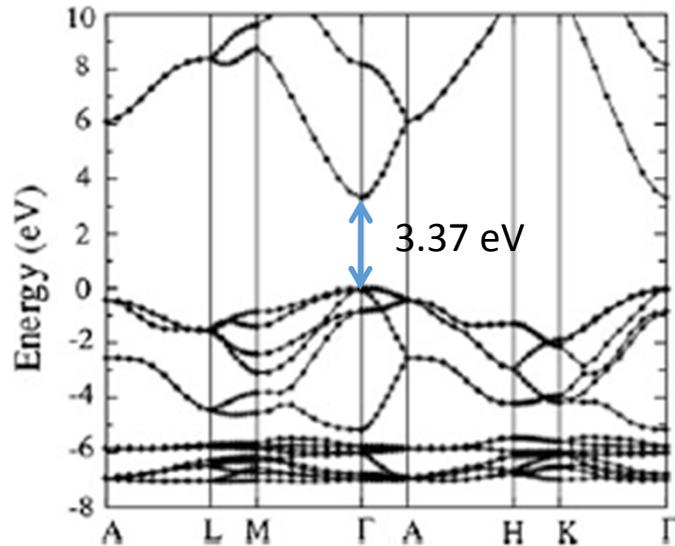
$E_g = 3.27\text{ eV}$  (direct-bandgap)

# D: Applicazioni



# Proprietà elettroniche e ottiche

Struttura bande ZnO wurtzite



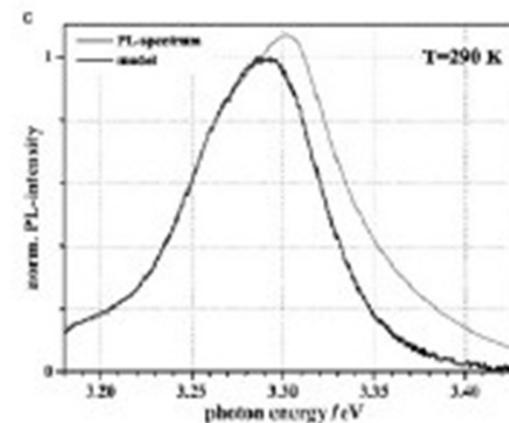
Rep. Prog.Phys 72, 126501 (2009)

BV: livelli O-2p pieni  
 BC: livelli Zn-3s vuoti

Table 1.1 Comparison of physical properties of some key compound semiconductors

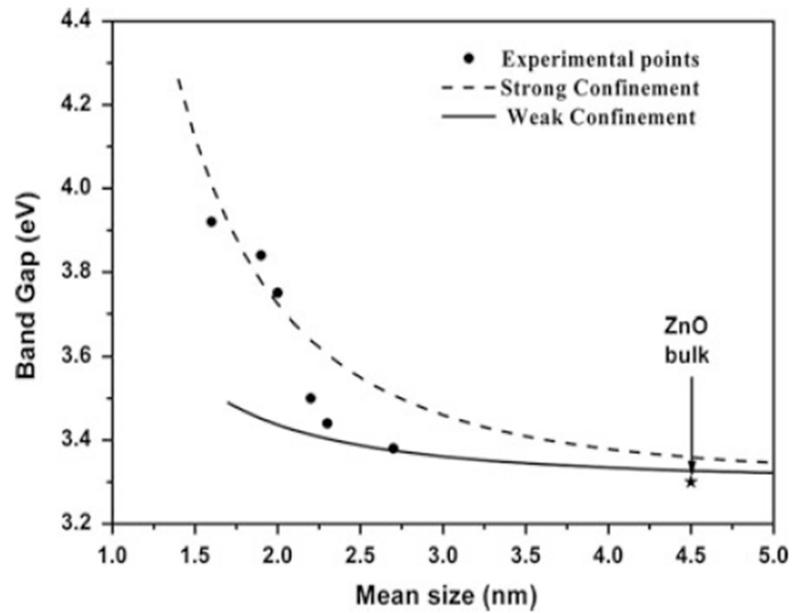
Material	Crystal structure	Lattice constants $a$ and $c$ (Å)	Band gap (eV)	Energy of fusion (K)	Exc. binding energy (meV)	Dielectric constant $\epsilon(0)$ and $\epsilon(\infty)$
ZnO	Wurtzite	3.25 5.21	3.37	2,248	60	8.75 3.75
ZnS	Wurtzite	3.82 6.26	3.8	2,103	30	9.6 5.7
ZnSe	Zinc blende	5.66	2.7	1,793	20	9.1 6.3
GaAs	Zinc blende	5.65	1.43		4.2	12.9 10.9
GaN	Wurtzite	3.19 5.19	3.39	1,973	21	8.9 5.35
SiC	Wurtzite	3.18 15.12	2.86	>2,100	-	9.66 6.52

Luminescenza eccitonica

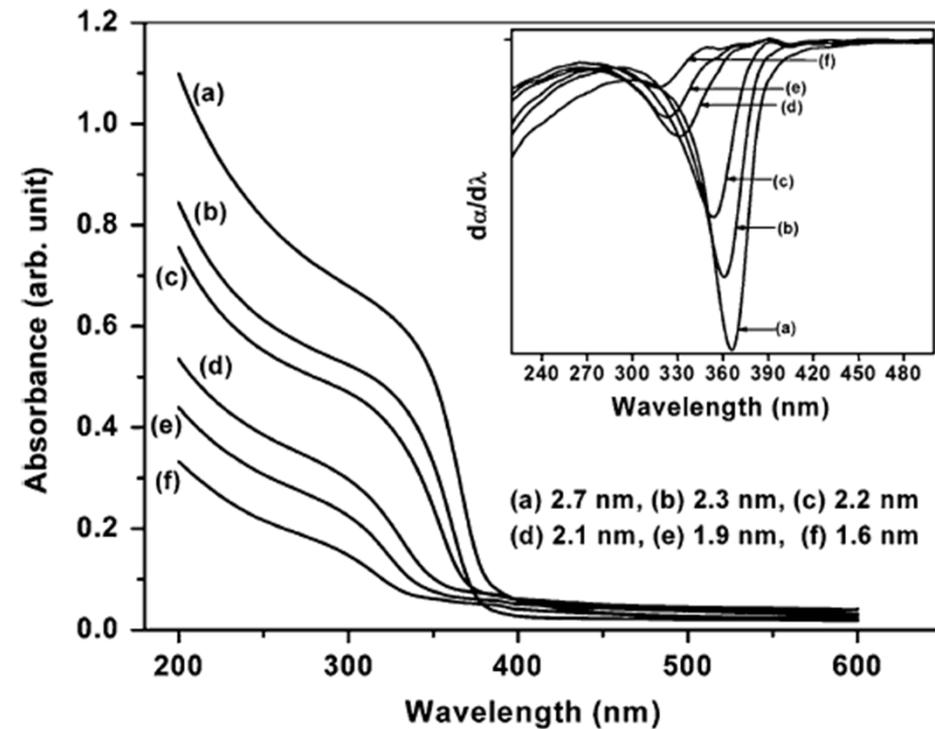


# ZnO NPs: effetti QC

$$R_B \text{ ZnO} = 2.23 \text{ nm}$$



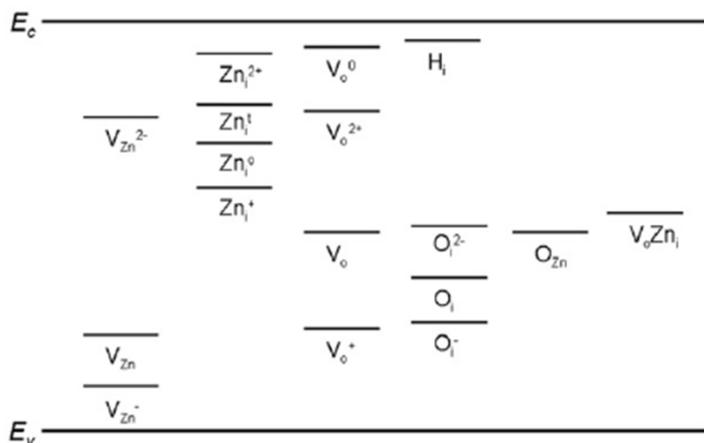
## Assorbimento UV-Vis



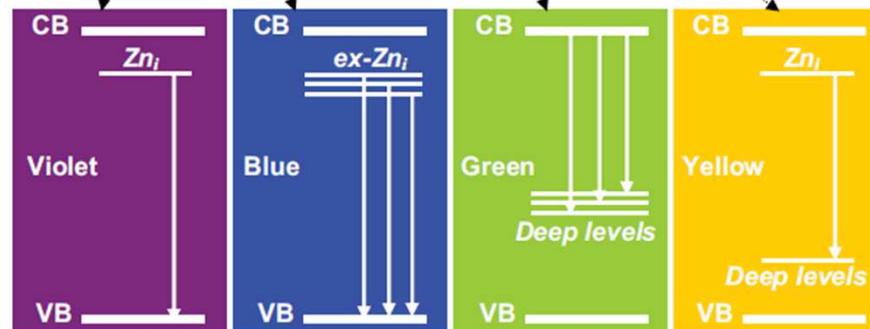
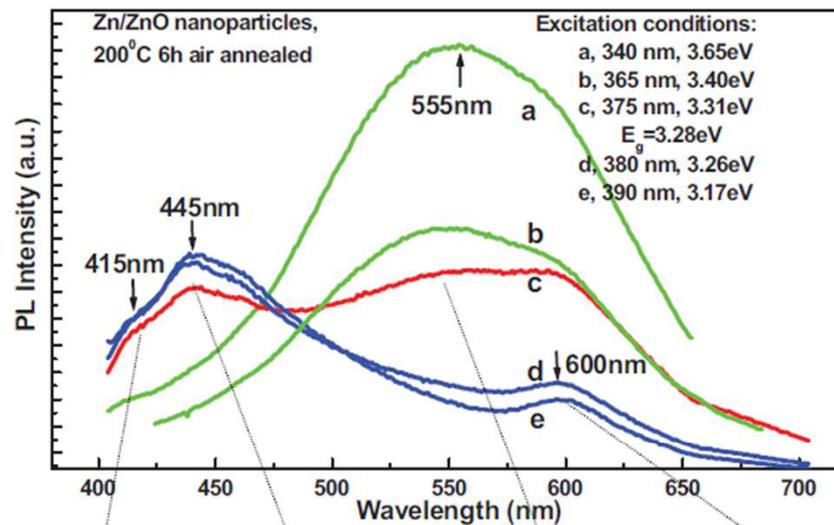
# Difetti ZnO nano-strutturato

## Difetti intrinseci

Livelli energetici calcolati tramite DFT



- $O_i$  : banda gialla (2 eV)
- $Zn_i$ : banda blu (2.8 eV)
- $V_o$ : banda verde (2.3 eV)
- $V_{Zn}$ : banda verde (2.5 eV)



# Ablazione di zinco in acqua

## Setup sperimentale:

Foil di Zn in 10mL di acqua deionizzata (becker 100mL)

Laser Nd-Yag (1064 nm),  $\approx 5$  ns;

Laser Ti:Sapphire (800 nm),  $\approx 50$  fs

Subito dopo l'ablazione

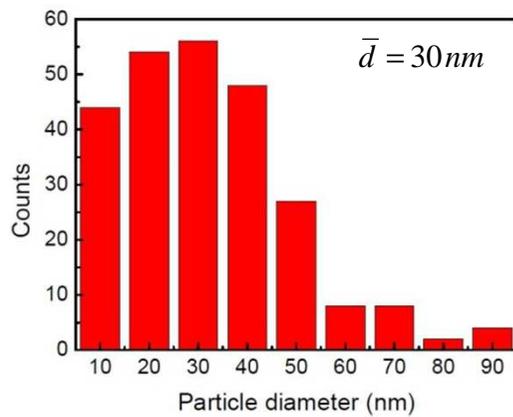
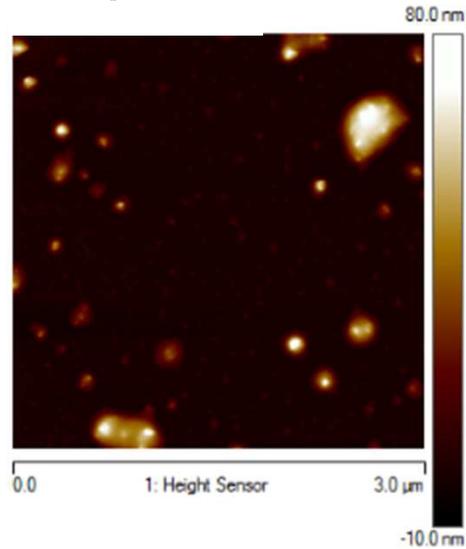


dopo un ora

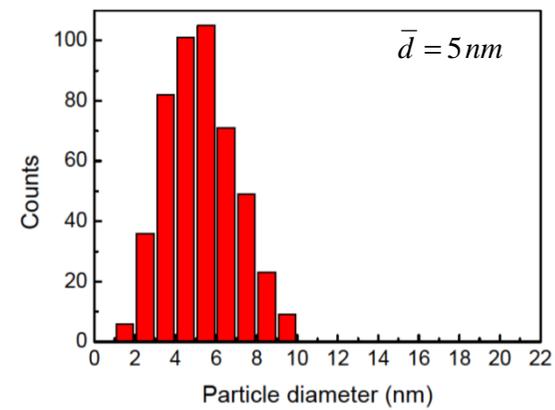
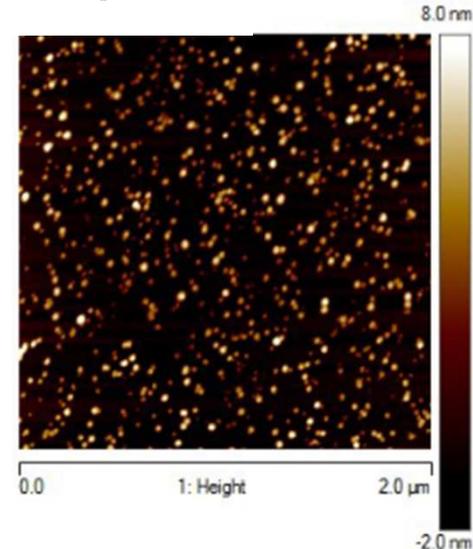


# Caratterizzazione microscopica: Effetto della durata dell'impulso

$$E_p = 90 \text{ mJ}, 5 \text{ ns}$$

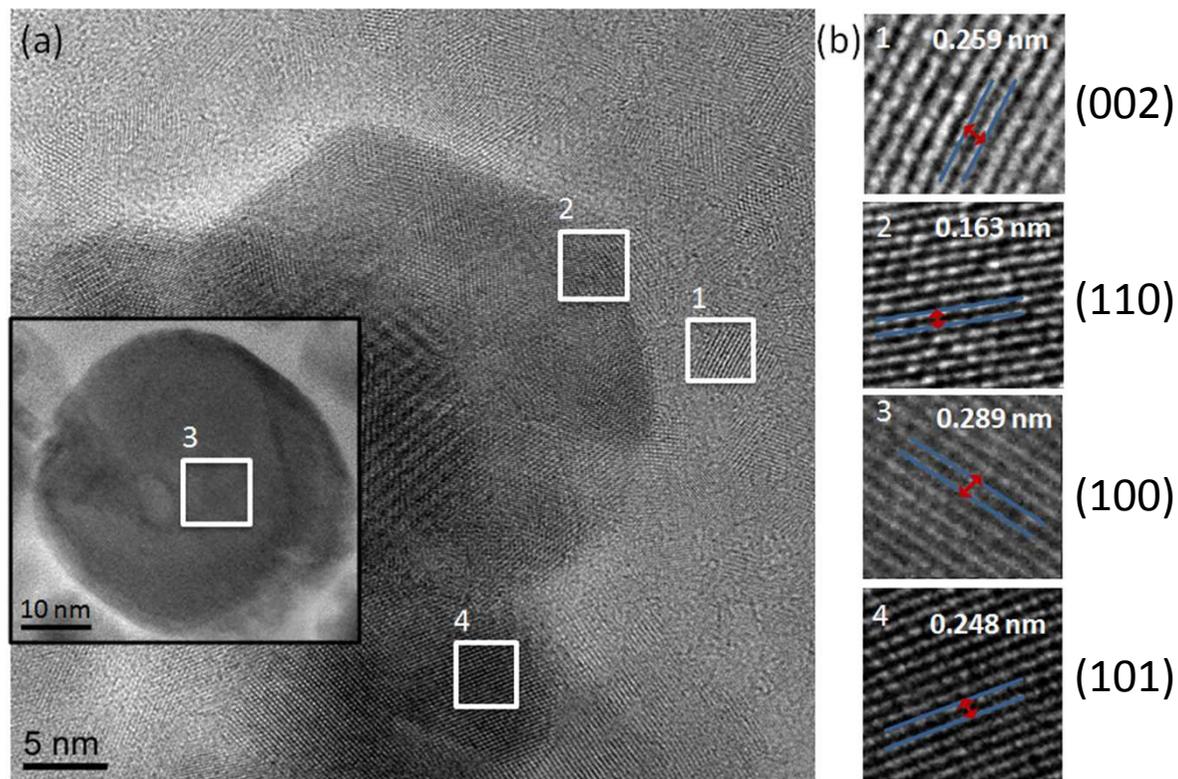


$$E_p = 150 \mu\text{J}, 60 \text{ fs}$$

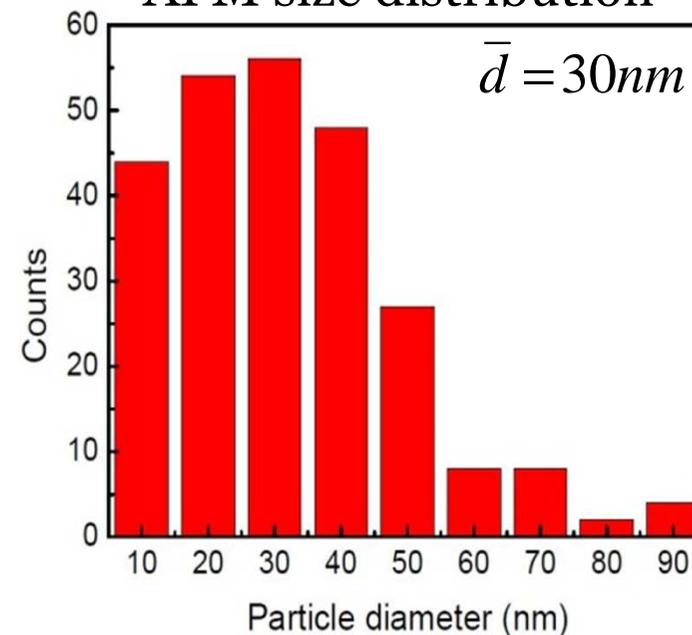


# Morphology and structure

## HRTEM



## AFM size distribution



Wurtzite ZnO  
 $a = 0.325 \text{ nm}$ ,  $c = 0.521 \text{ nm}$

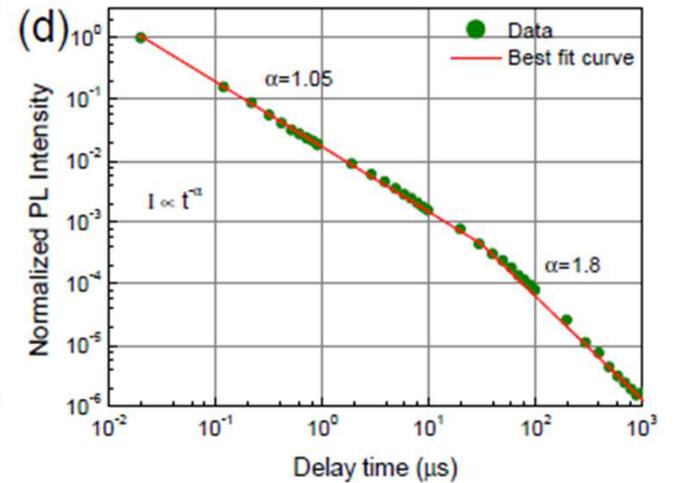
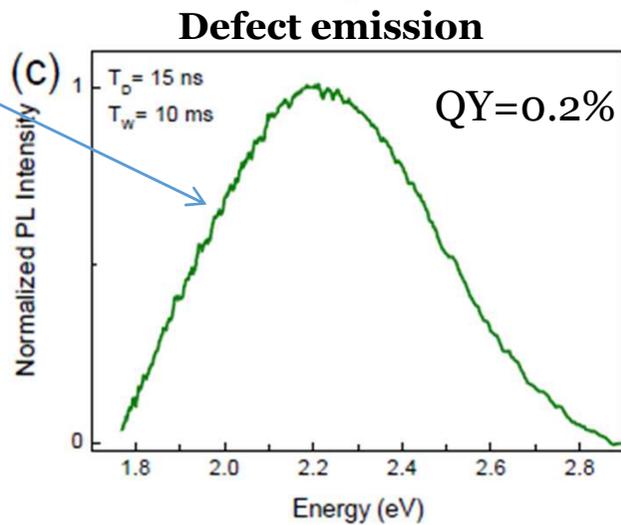
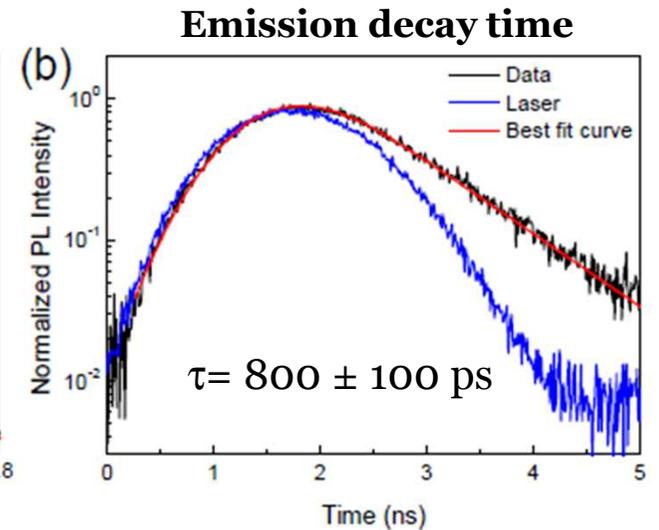
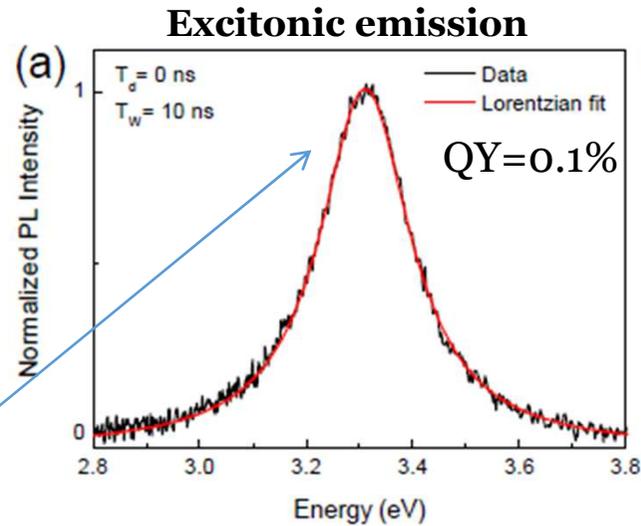
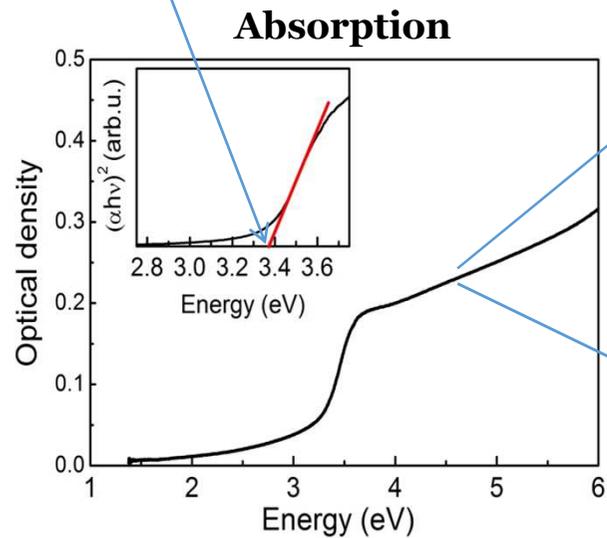
$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

$a_{\text{exp}} = 0.334 \pm 0.001 \text{ nm}$

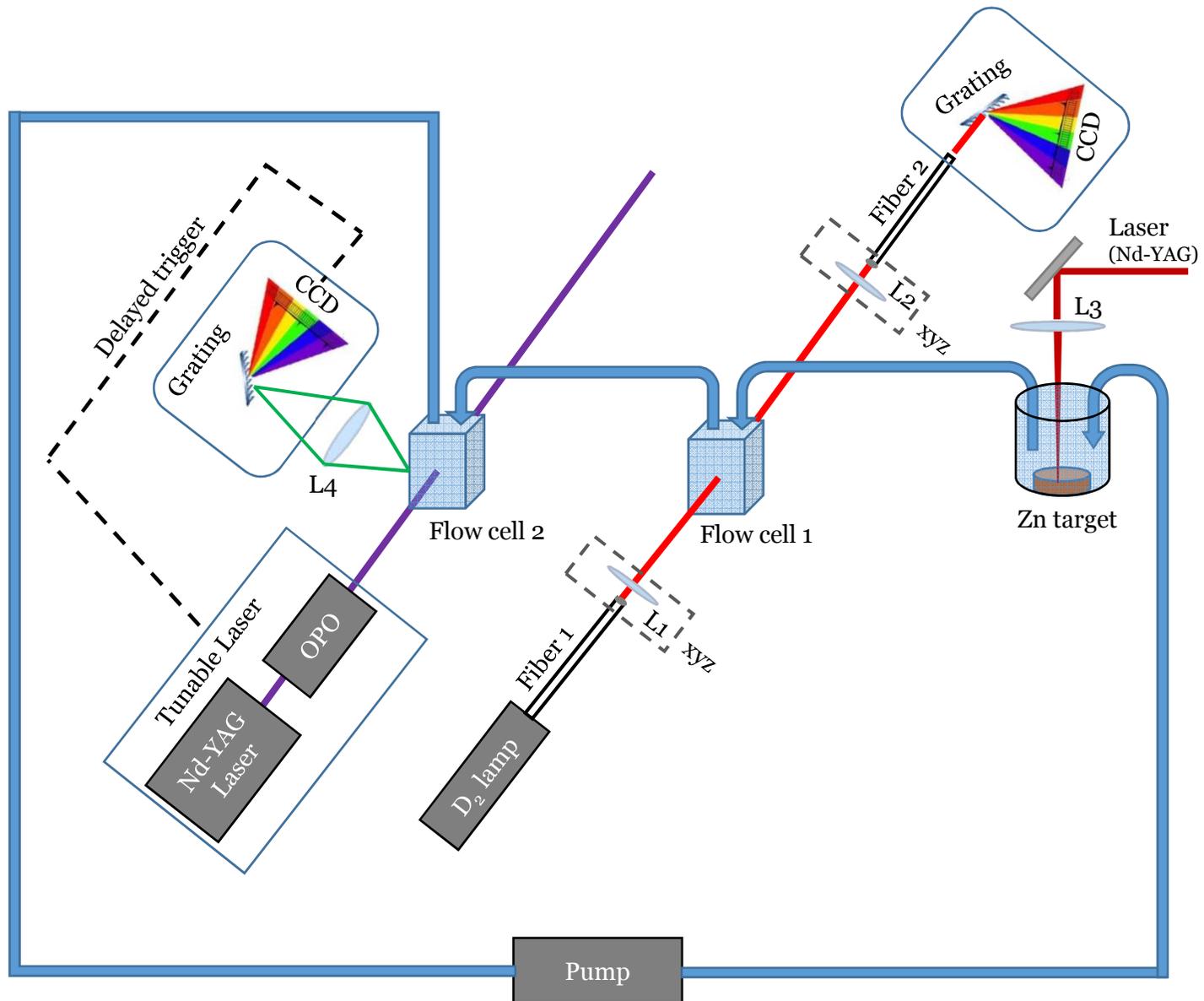
$(h \ k \ l)$	(0 0 2)	(1 1 0)	(1 0 0)	(1 0 1)
Measured $d(\text{nm})$	$0.259 \pm 0.001$	$0.1630 \pm 0.0006$	$0.289 \pm 0.001$	$0.248 \pm 0.002$
Reported $\bar{d}(\text{nm})$	0.2602	0.1625	0.2814	0.2476

# Optical properties

$E_g = 3.38$  eV which is consistent with wurtzite

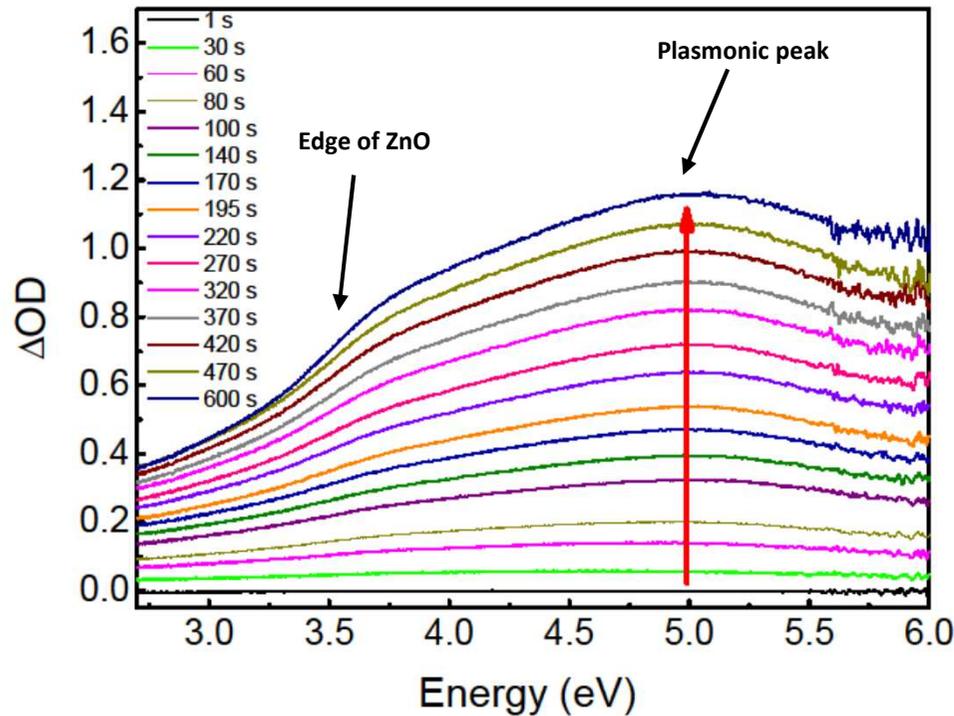


# Misure ottiche in situ

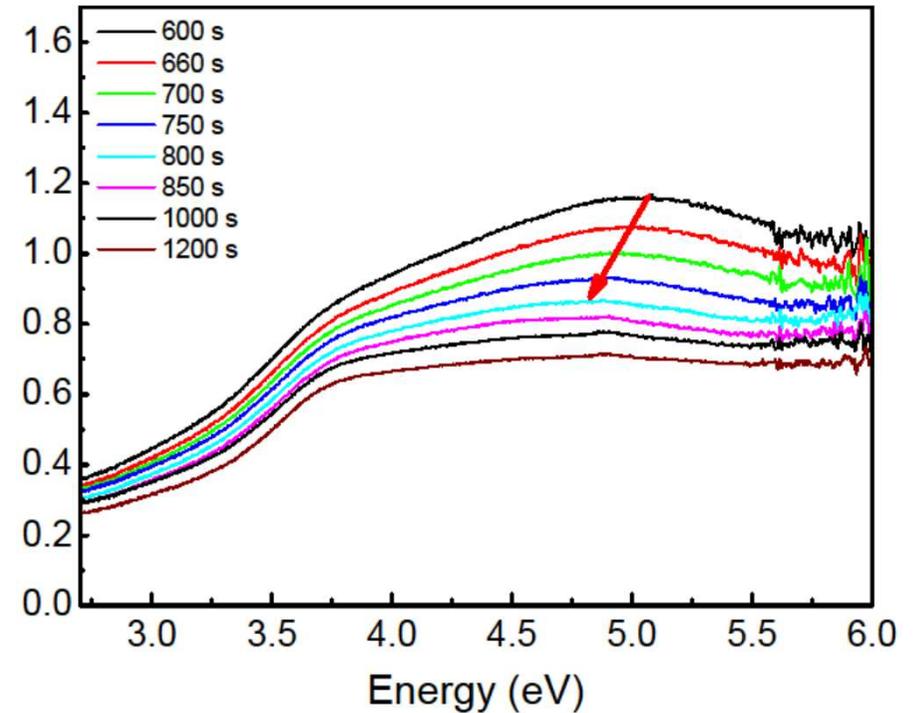


# Misure OA online

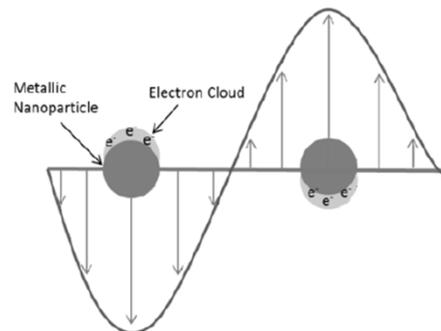
## Durante l'ablazione



## Dopo l'ablazione

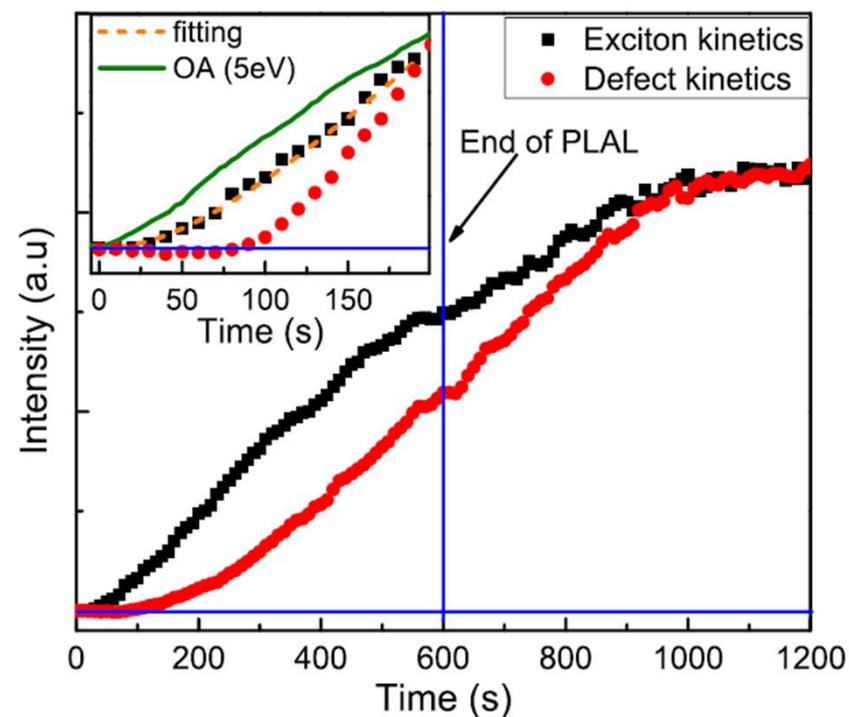
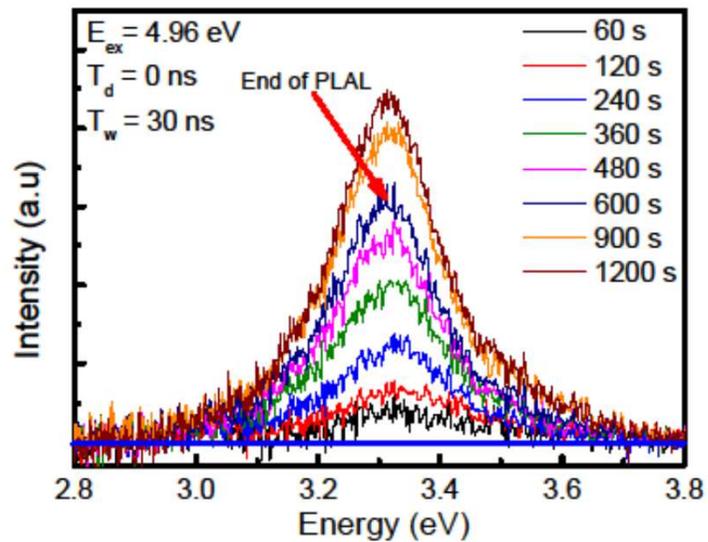
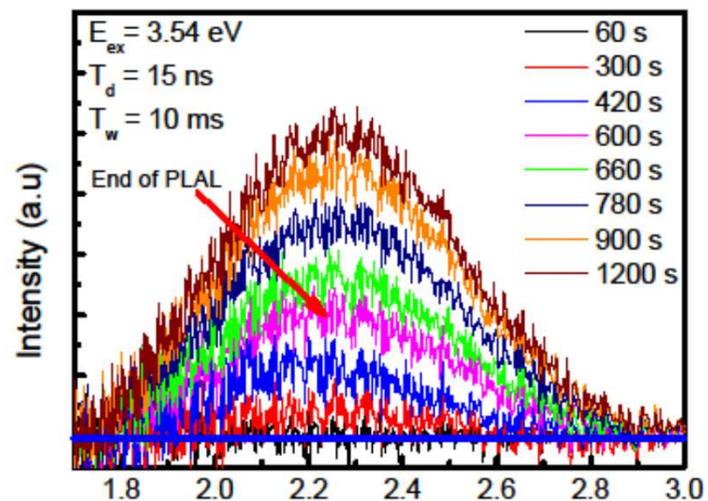


Edge ZnO :  
*Formazione di ZnO.*

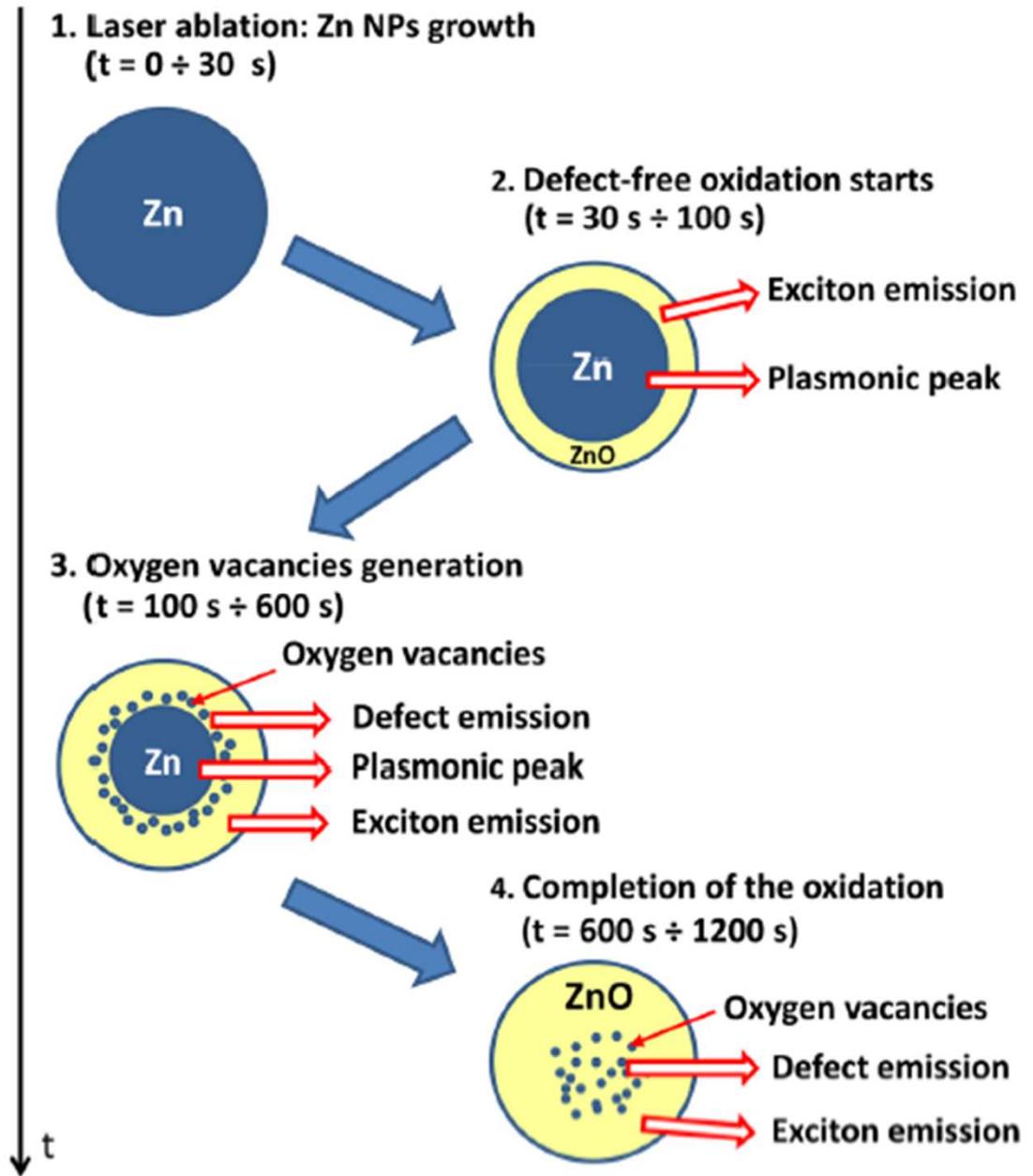


Plasmonic peak:  
*oscillazione degli elettroni del metallo  
Indotta dalla radiazione e.m.*

# Misure PL online



processo multi-steps  
l'ossidazione di Zn-NPs  
durante l'ablazione in acqua



MOJOTIC12 FESTIVAL

감사하십시오

Asante

choukran

bighmmi

谢谢

you

gracias

당신을 spasiba

Merci

ありがとう

obrigada

arigato

thank

Danke

grazie

per la vostra attenzione!!!

