

Nanotecnologie: materiali e metodi di produzione

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of **A**dvanced **M**aterials

Web: www.unipa.it/lamp/

Palermo, 16/05/2018

Sommario

Introduzione:

Proprietà peculiari dei materiali nanometrici

Alta superficie specifica --- Confinamento quantistico

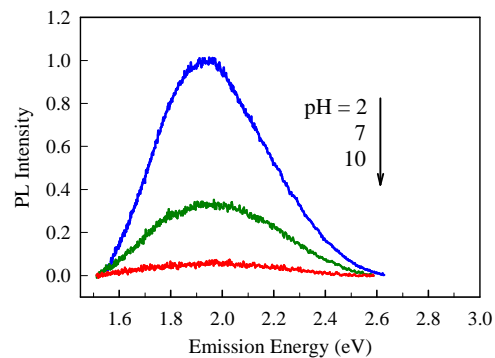
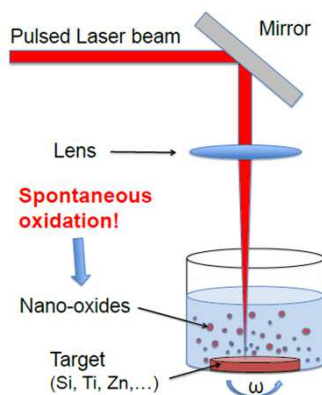
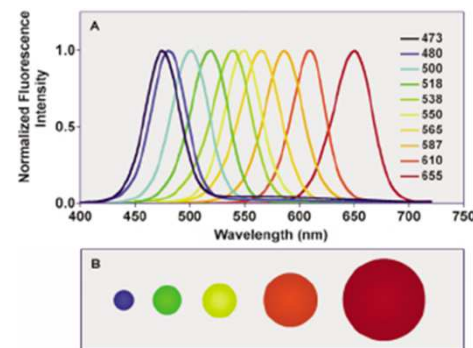
Metodi di produzione

Pulsed Laser Ablation (PLA)

Applicazioni di PLA:

Nanocristalli di Silicio «ossidato»

Nanoparticelle di ZnO



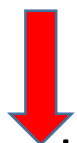
Introduzione



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)

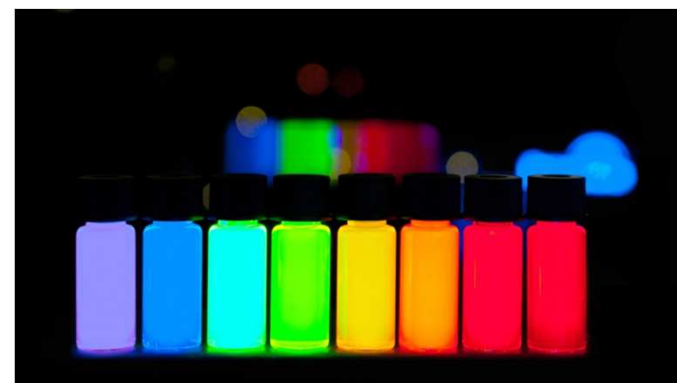
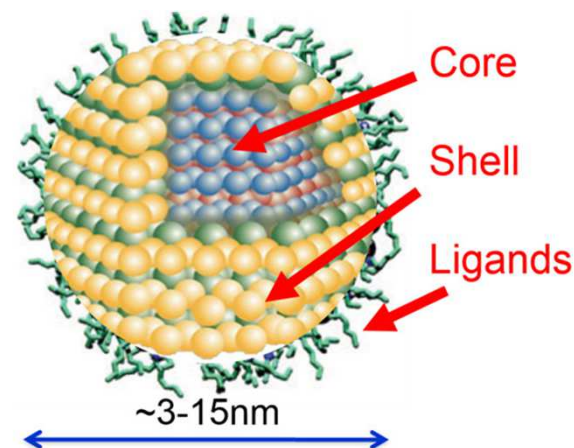
Attraverso processi di sintesi



Proprietà peculiari dei materiali nanometrici

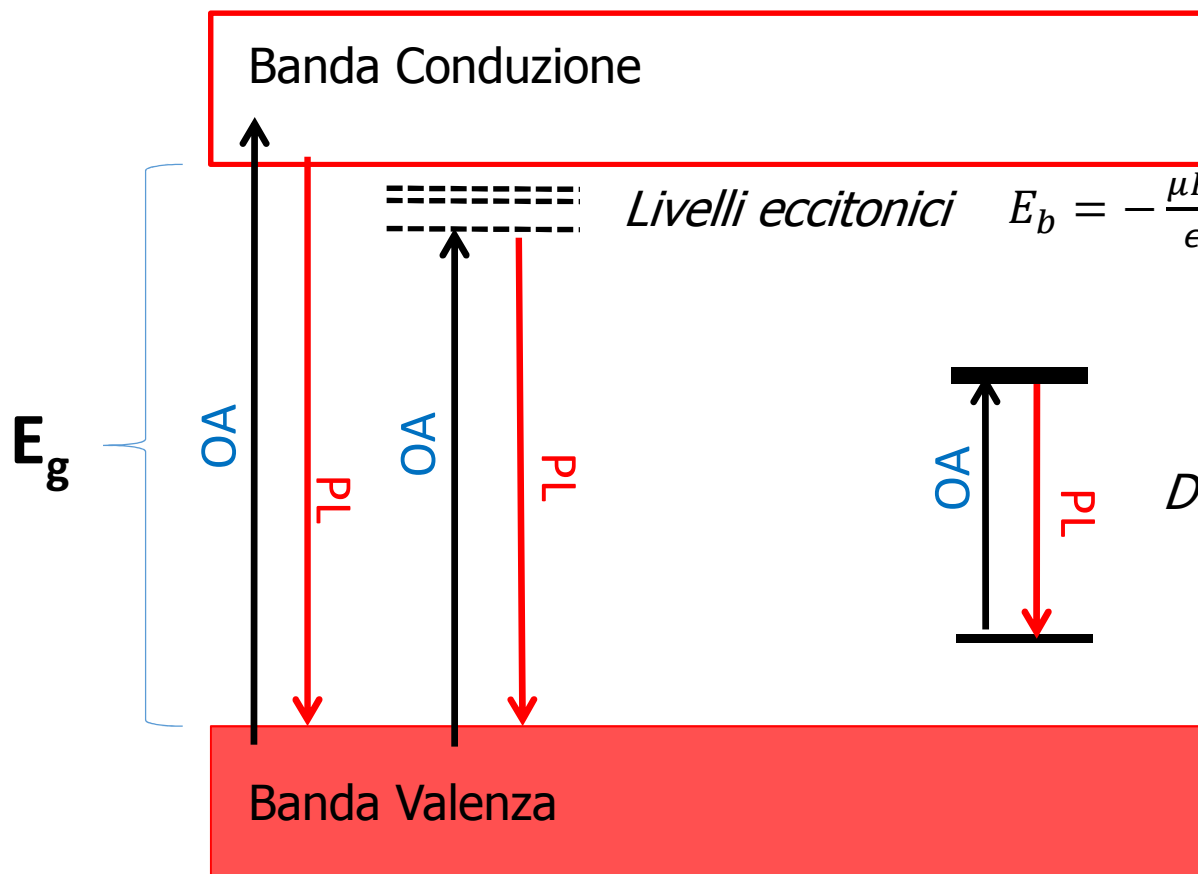
che non dipendono esclusivamente dalla loro composizione

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
- ϵ costante dielettrica di mezzo
- $R_H = 13.6$ eV costante di Rydber

Difetti (livelli localizzati)

1/2 Proprietà peculiari dei materiali nanometrici (geometria)



macro



nano

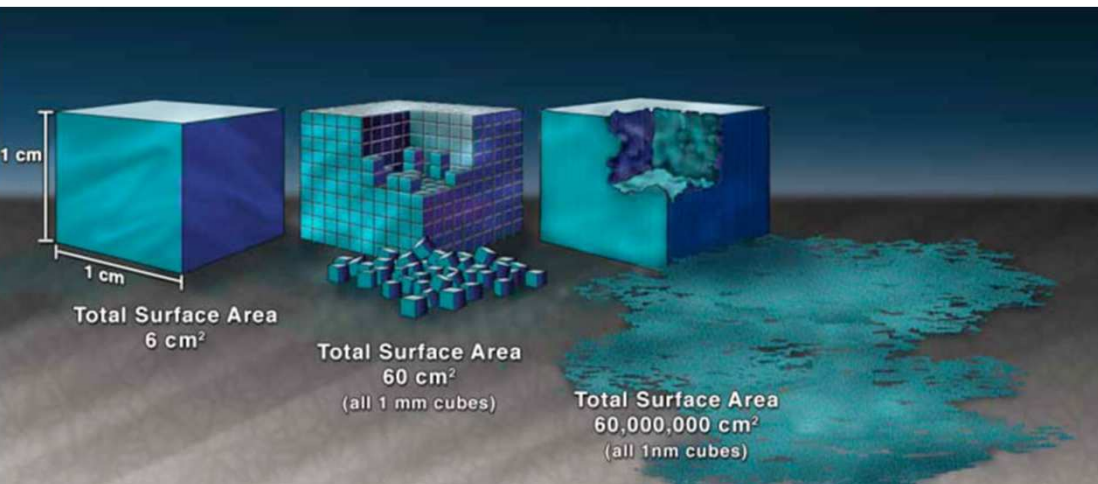
Superficie specifica

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

dimensioni delle particelle (r)

$$\sigma \propto 1/r$$

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

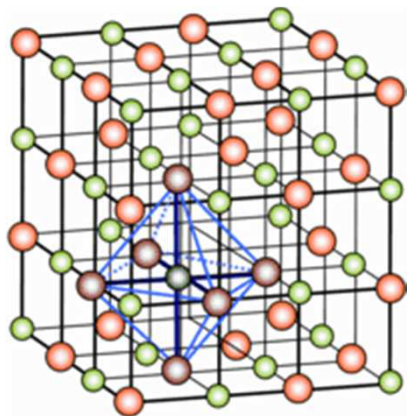


~10 g di NP



2

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



Propr. Elettr. (volume) \neq Propr. Elettr. (superficie)
inv. traslazionale 3D

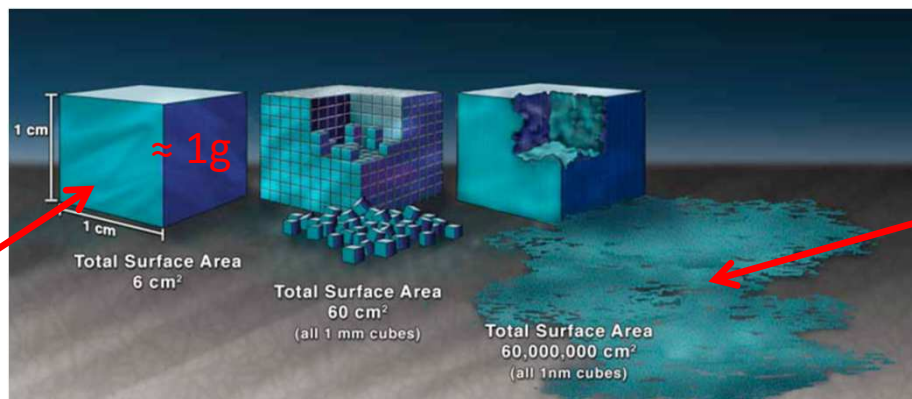
Superficie è:

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



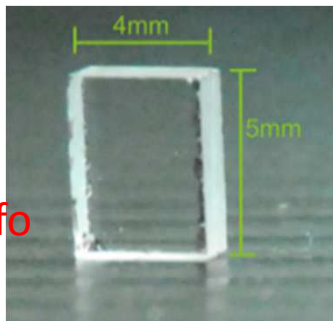
Carbonio (grafite, diamante)

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

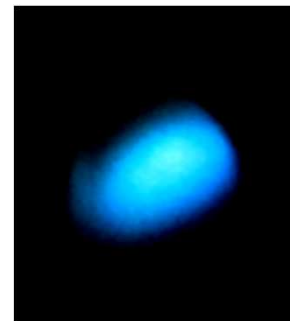


Carbonio (nanoparticelle)

Laboratory «Roberto Boscaino»
of Advanced Materials



Silice - SiO_2 amorfo



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)

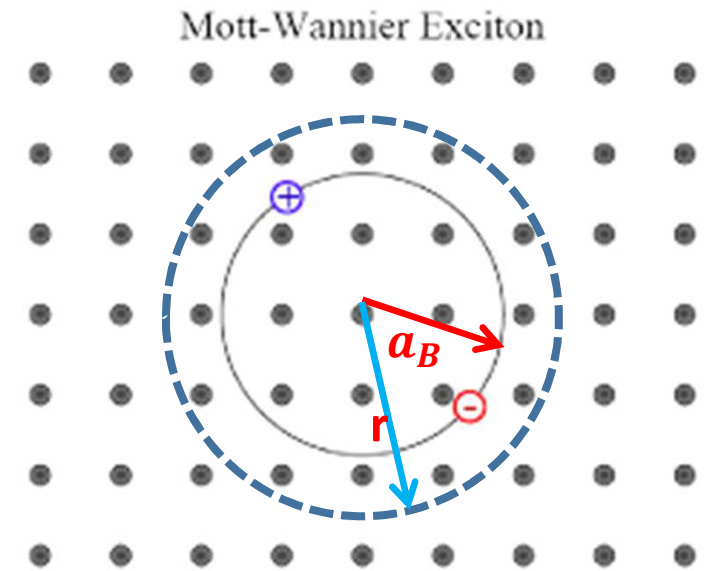
$$a_B(n) = \frac{a_0 \epsilon}{\mu/m_e} \cdot n^2; \quad E_n = -\frac{\mu/m_e R_H}{\epsilon^2} \cdot \frac{1}{n^2}$$

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

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

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

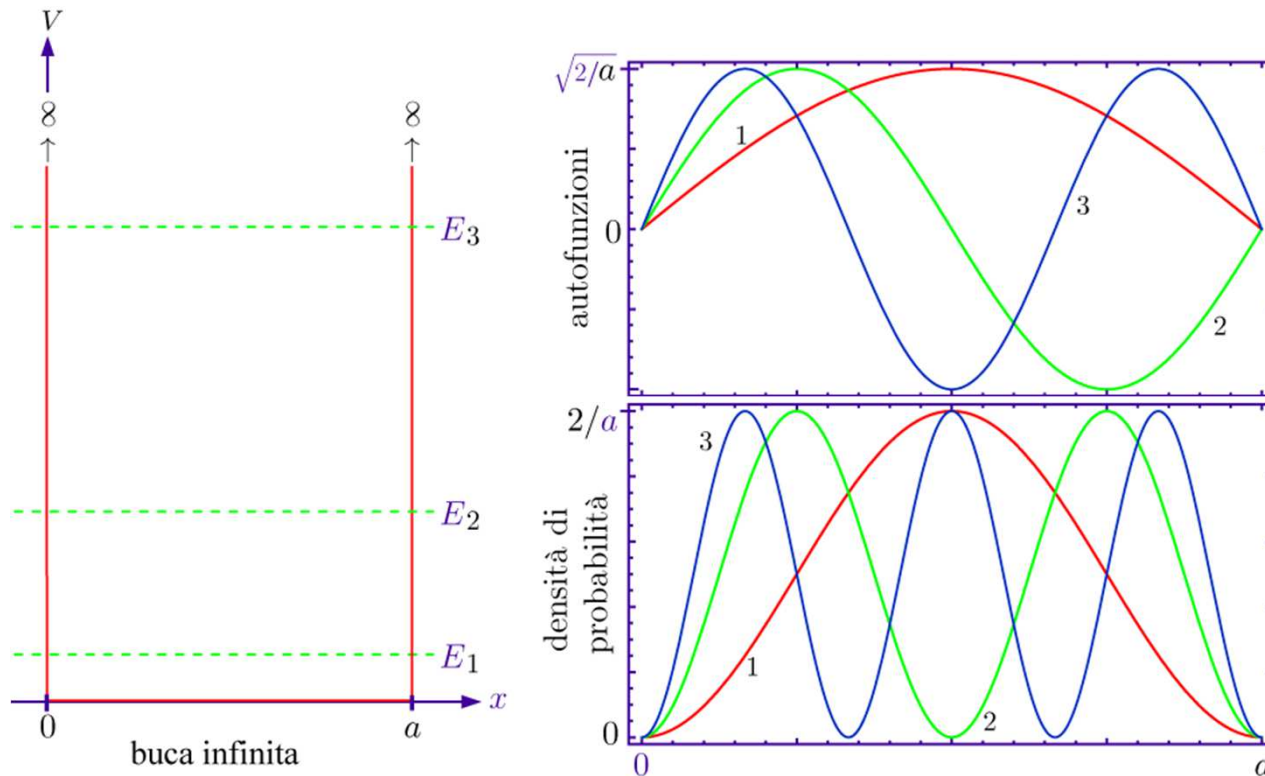
$a_B(\text{ZnO}) \approx 2.3 \text{ nm}; E \approx 60 \text{ meV}$



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**



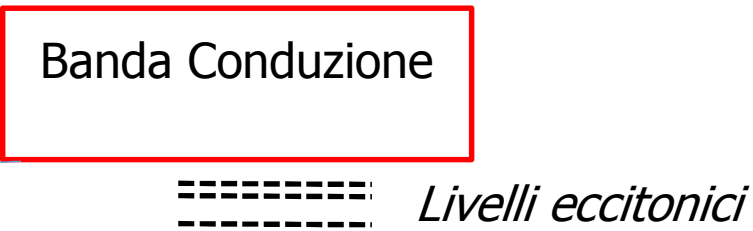
buca sferica (raggio r)

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

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

QC: il gap energetico aumenta

$$E_g^{nano} = E_g^{Bulk} + \frac{\hbar^2 \pi^2}{2\mu r^2}$$



E_g^{Bulk}

Banda Valenza

Banda Conduzione

Livelli eccitonici

Bulk «macro»

E_g^{nano}

Banda Conduzione

Livelli eccitonici

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

Banda Valenza

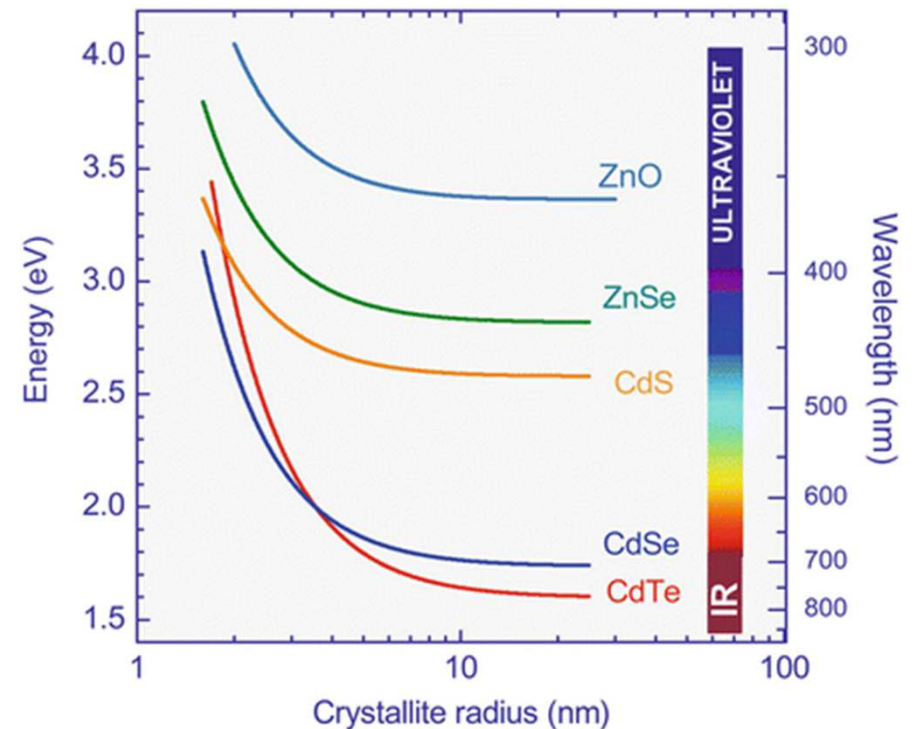
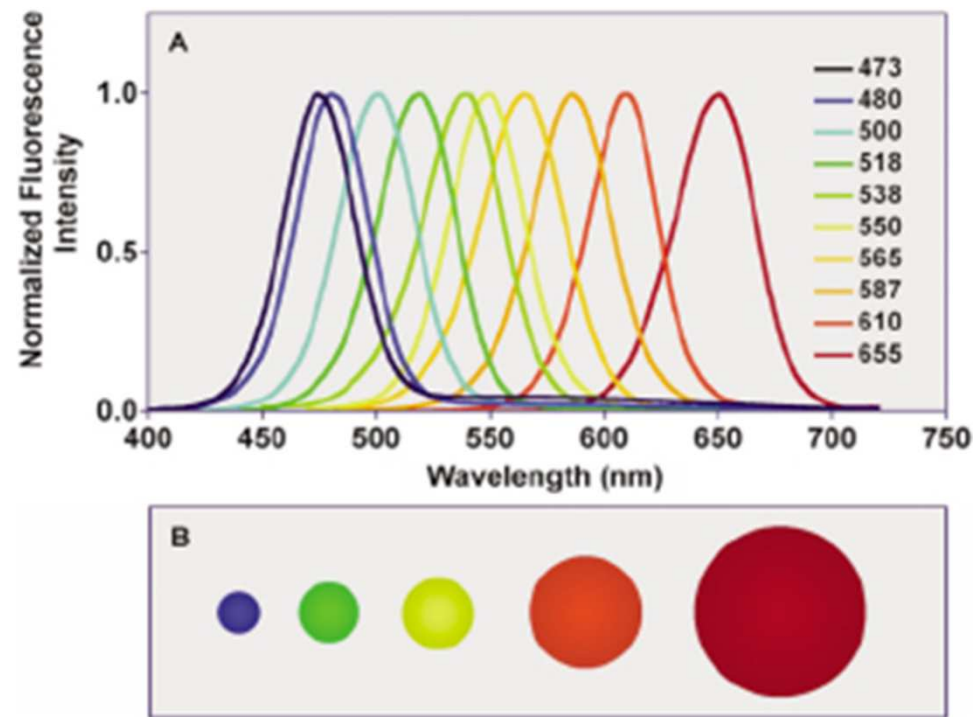
Nanoparticella (r~nm)

QC: come si osserva?

Spettro di emissione degli eccitoni

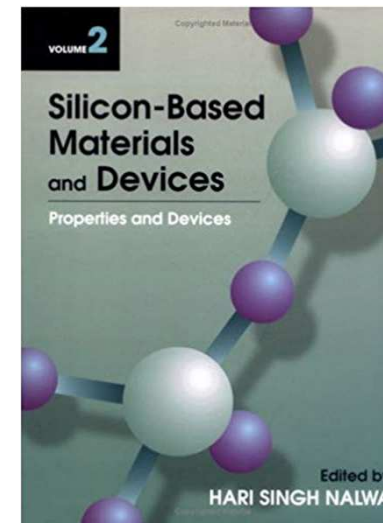
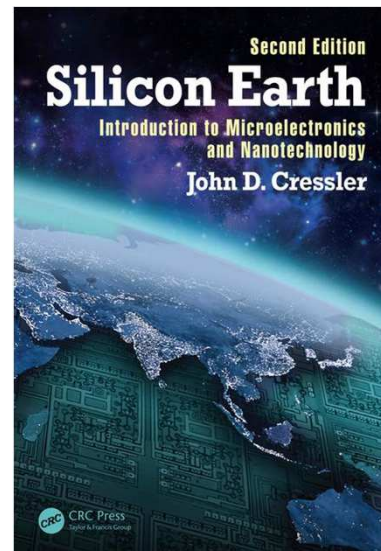
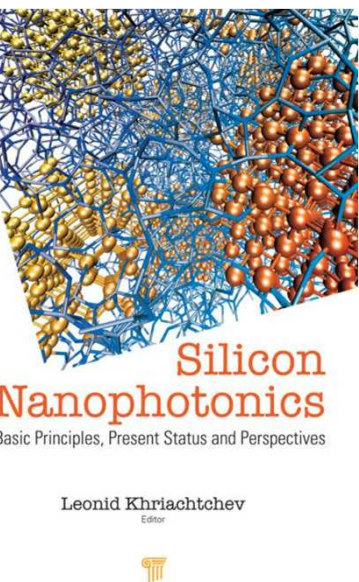
$$E_{exc} = E_g^{Bulk} - \frac{\mu/m_e R_H}{\epsilon^2} \cdot \frac{1}{n^2} + \frac{\hbar^2 \pi^2}{2\mu r^2}$$

E_g vs. dimensioni - semiconduttore



QC: esempio

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



Silicio

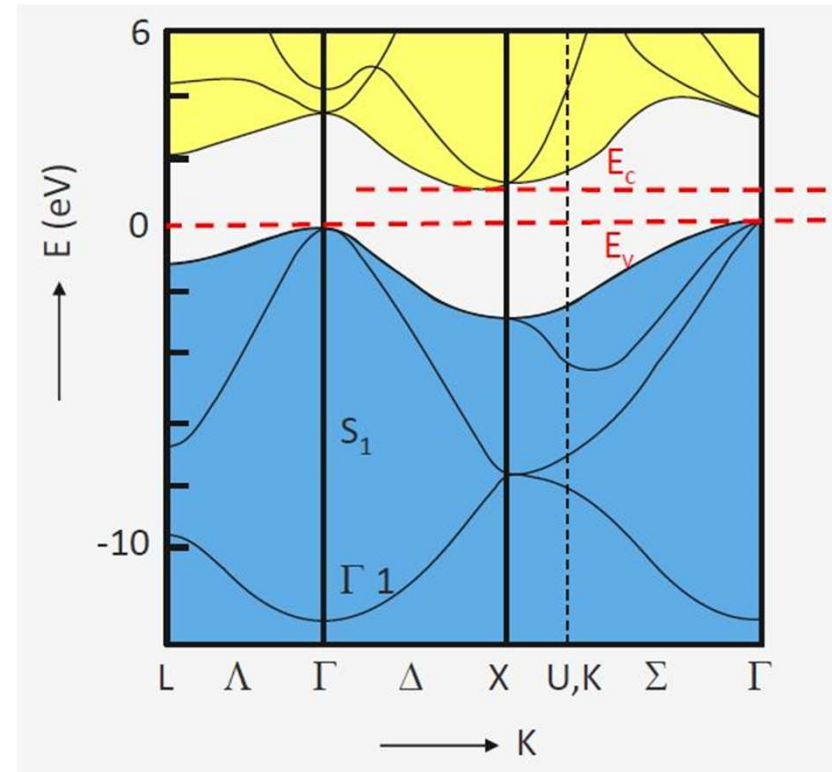
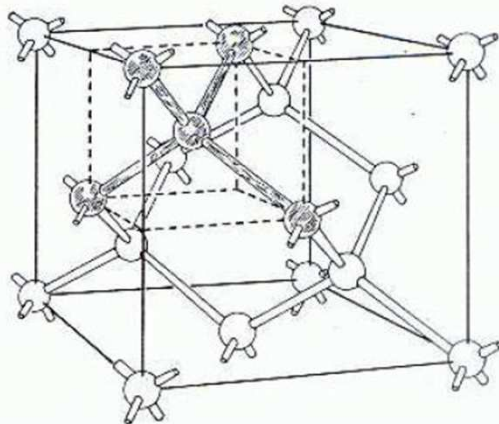
IV gruppo della tavola periodica

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	34 As Arsenico
48	Cd Cadmio	In Indio	50 Sn Stagno	52 Sb Antimonio
80	Hg Mercurio	81 Tl Tallio	82 Pb Piombo	84 Bi Bismuto

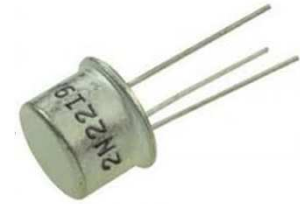
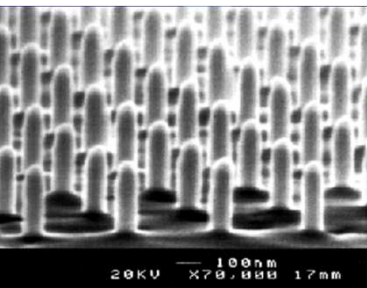
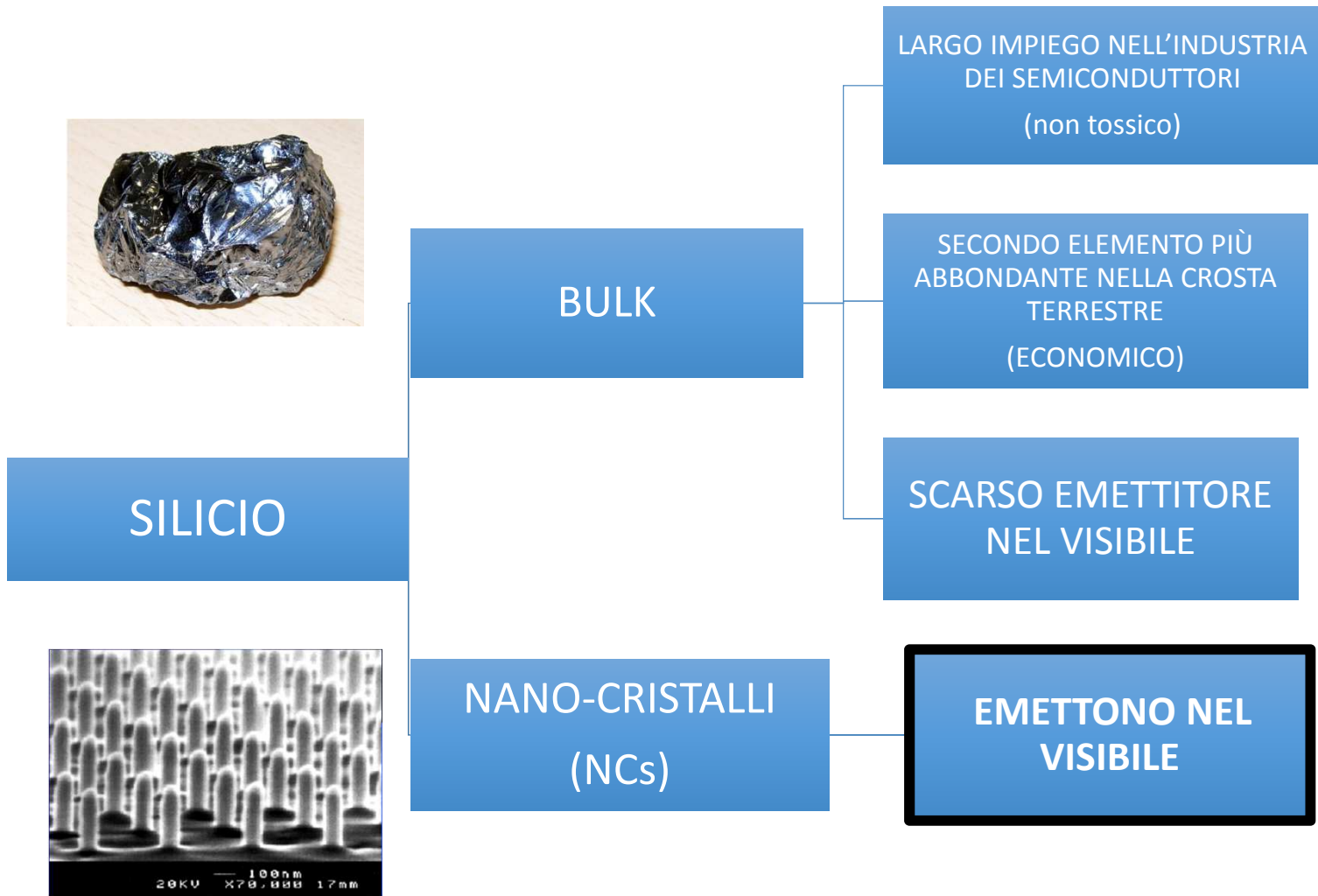


$E_g \approx 1.1$

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: $10^{14} \Omega m$)

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

Proprietà BULK E NANOCRISTALLI



Interesse verso Si-NCs



Si-NCs

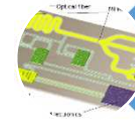
Hamers (1990):

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



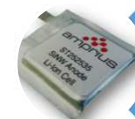
OPTOELETTRONICA
(laser, LED, OLED)



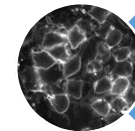
NANOELETTRONICA
(dispositivi di memoria)



FOTOVOLTAICO

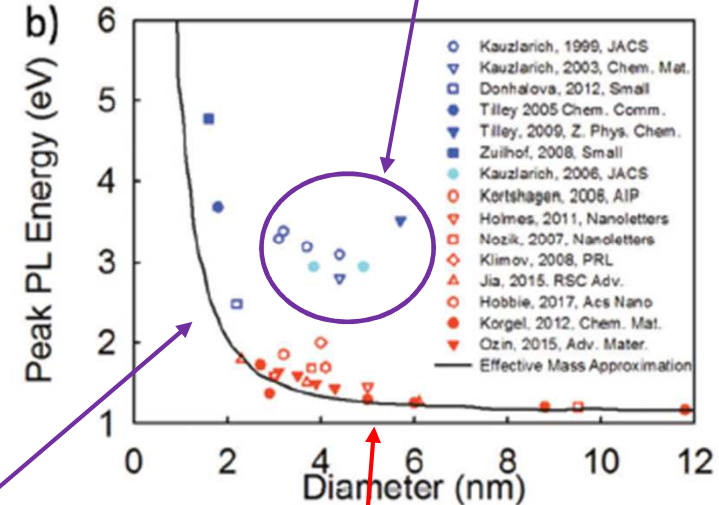
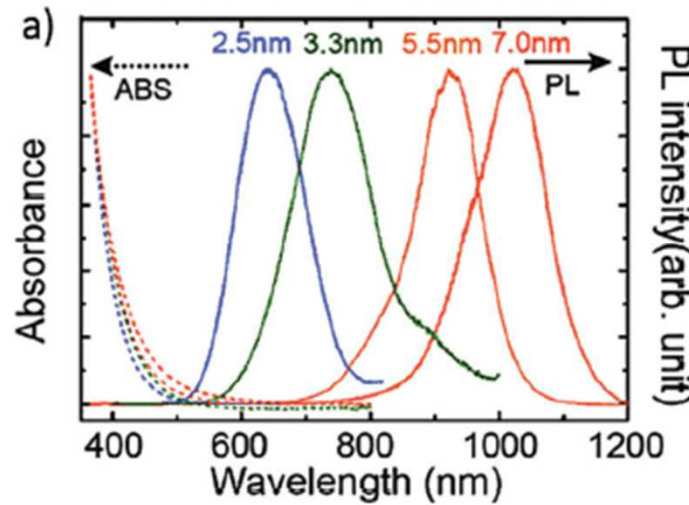
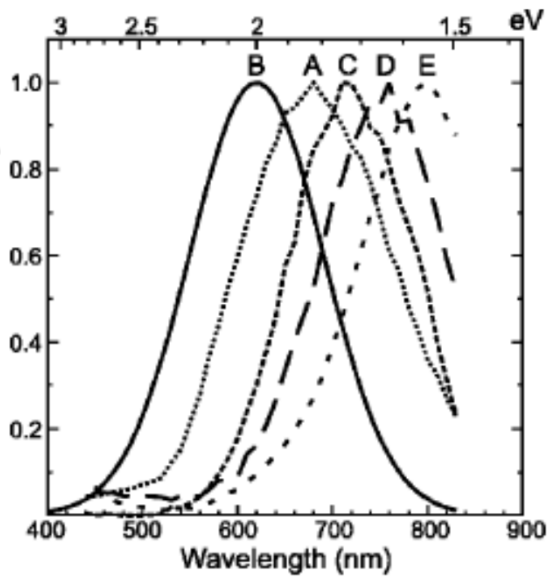


BATTERIE



**APPLICAZIONI
BIOLOGICHE**

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



Difetti sulla superficie dei Si-M

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

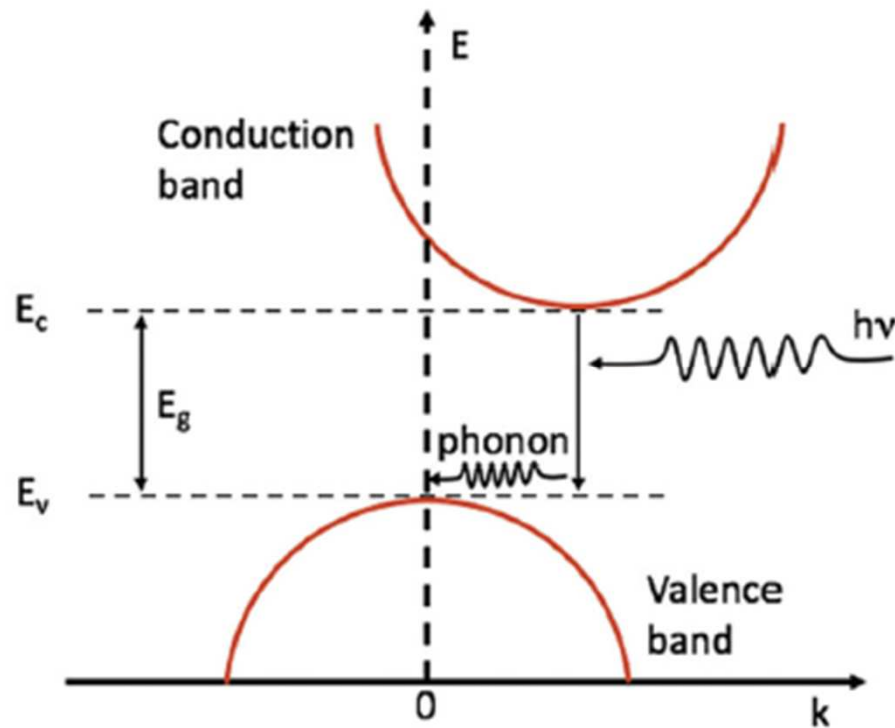
Se $r \ll a_B$: forte confinamento limita l'emissione degli eccitoni

a_B

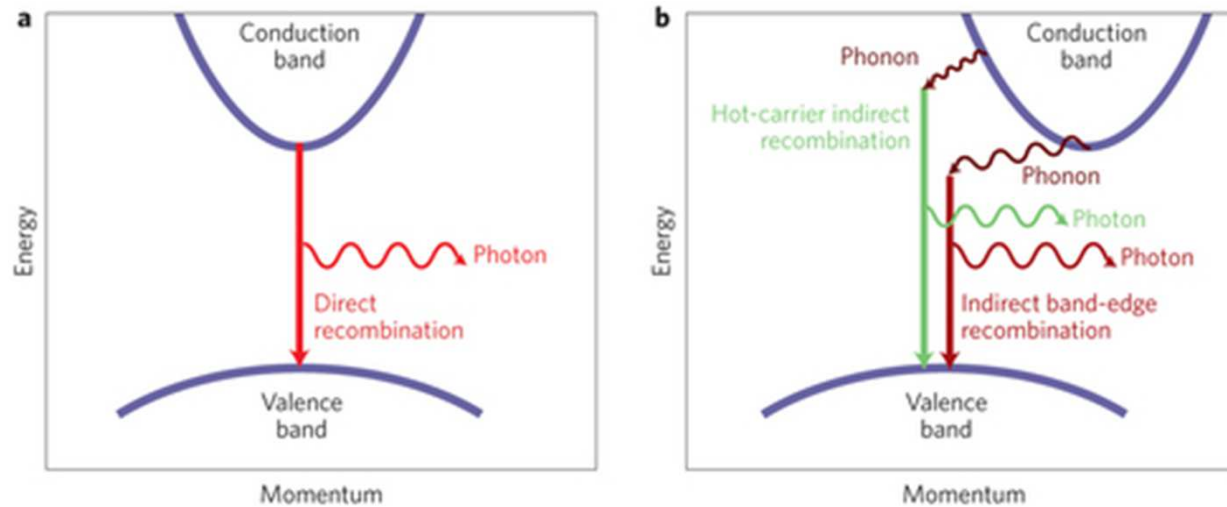
Proprietà sorprendenti rispetto al Si-Bulk

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.

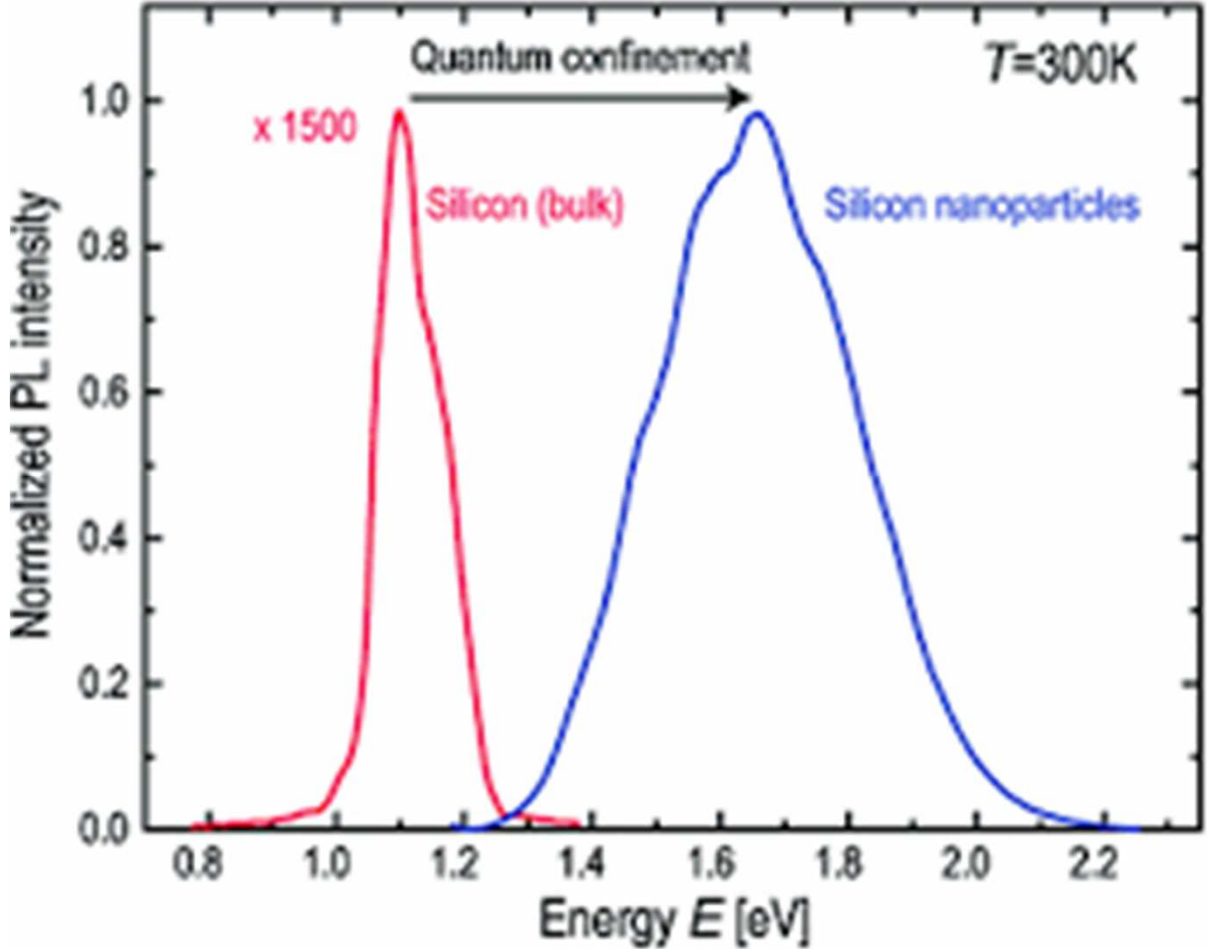


Semiconduttori a gap diretta (ZnO; GaN..) : $\tau \sim 10^{-9} - 10^{-8} \text{ s}$

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

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

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

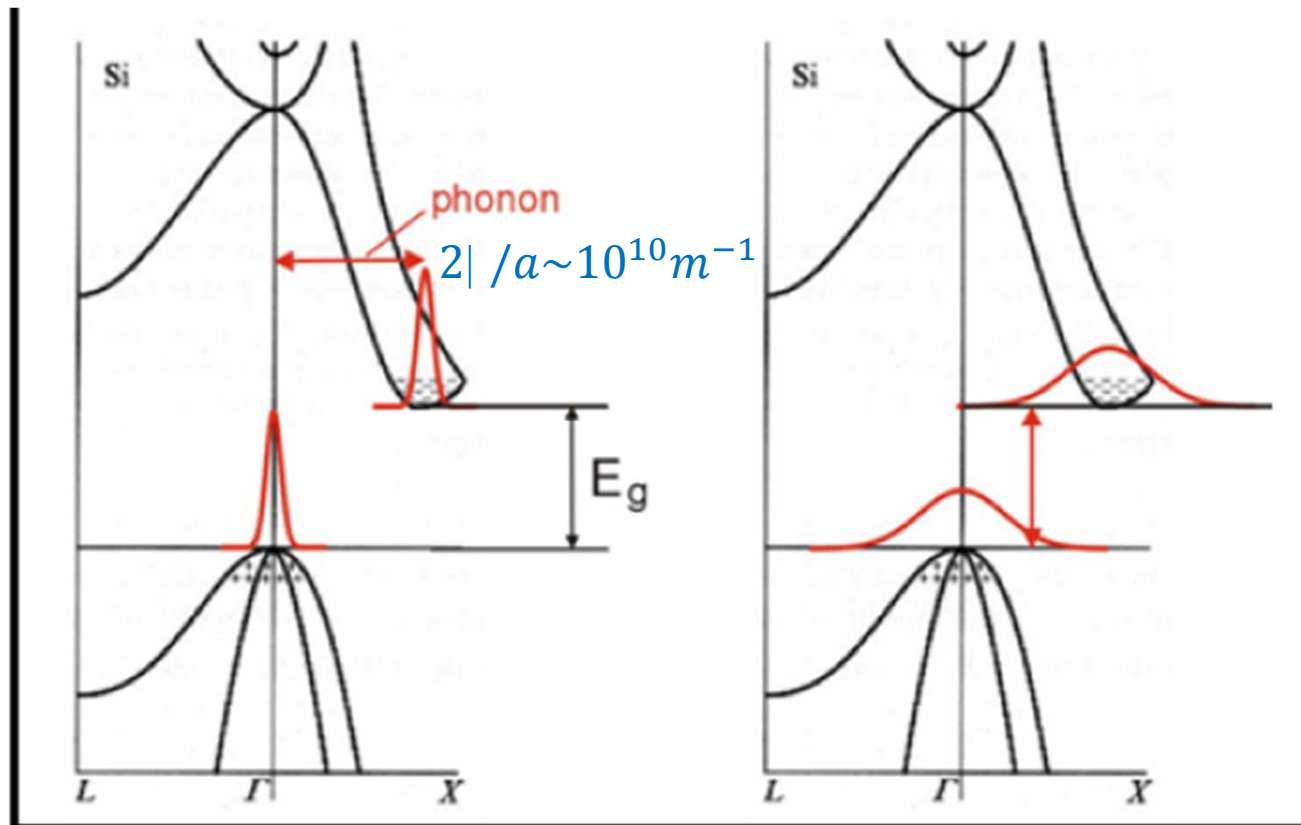
Principio d'indeterminazione

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

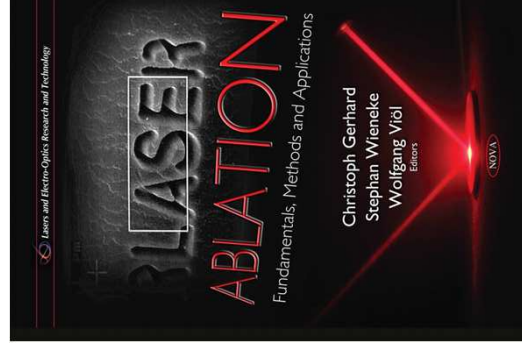
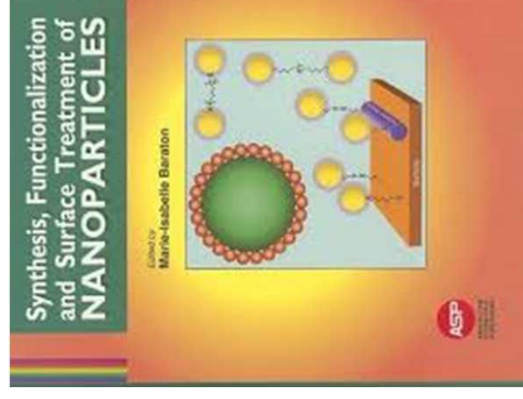
$\Delta x \rightarrow piccolo (\sim 10^{-9}m) \Rightarrow \Delta k \rightarrow grande (\sim 10^9 m^{-1})$

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

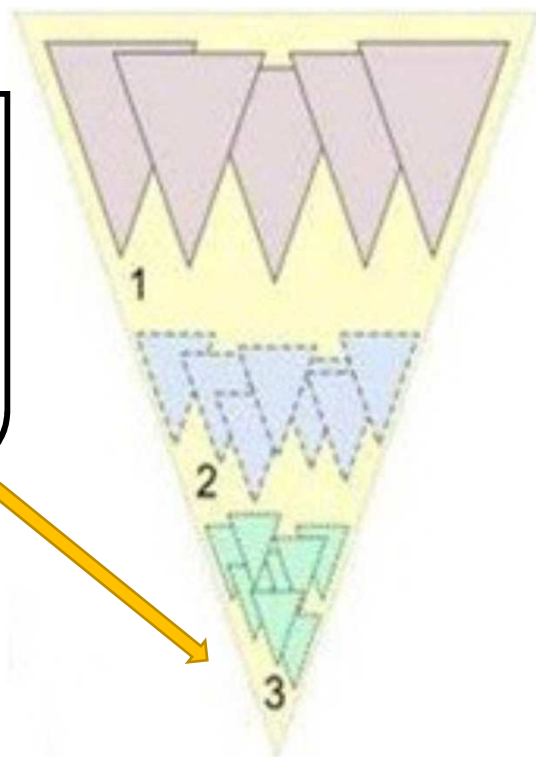


Metodi di produzione



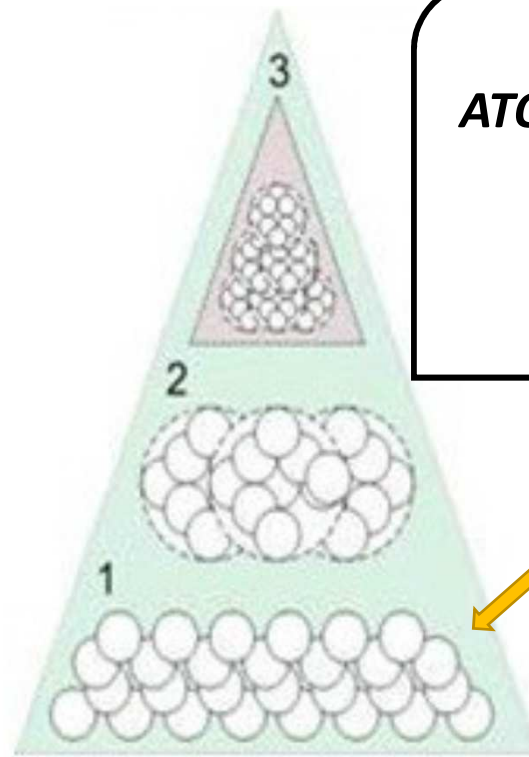
TECNICHE DI PRODUZIONE

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

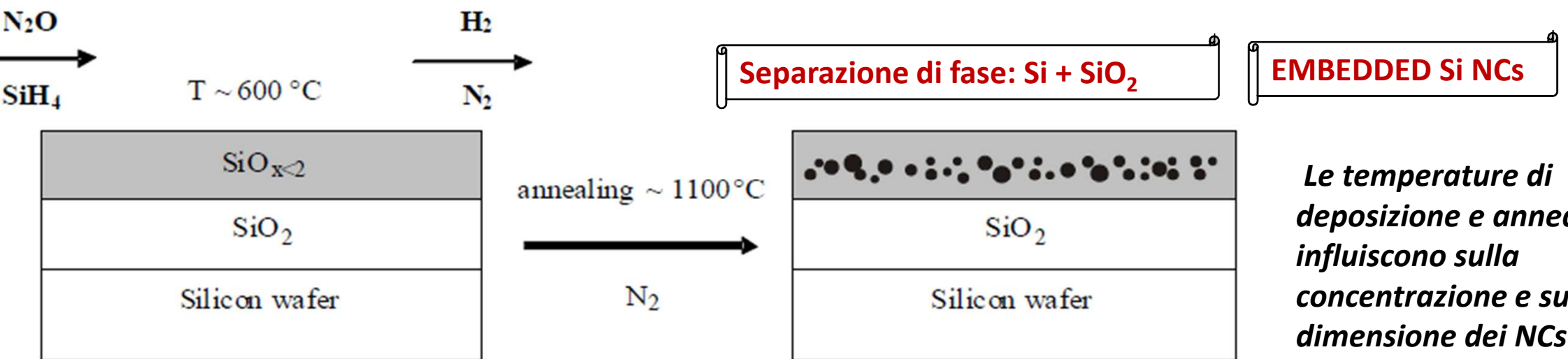
POLVERIZZAZIONE CATODICA

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*)



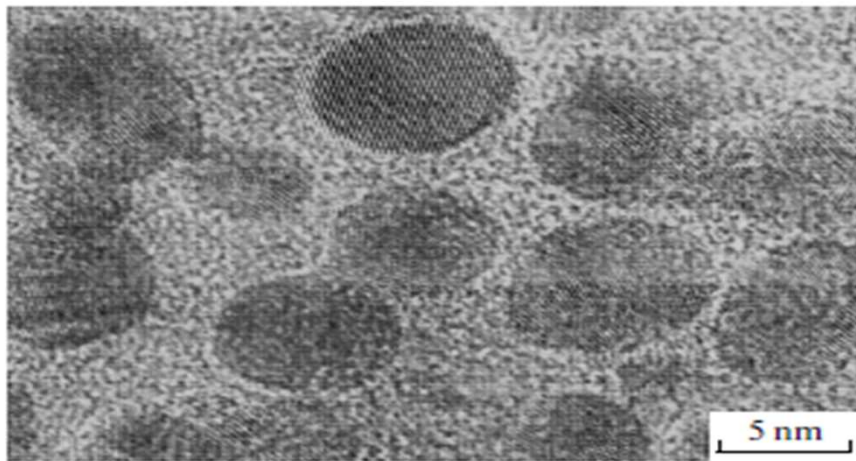
amples

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

SiO_x produced by evaporation of SiO powder.

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

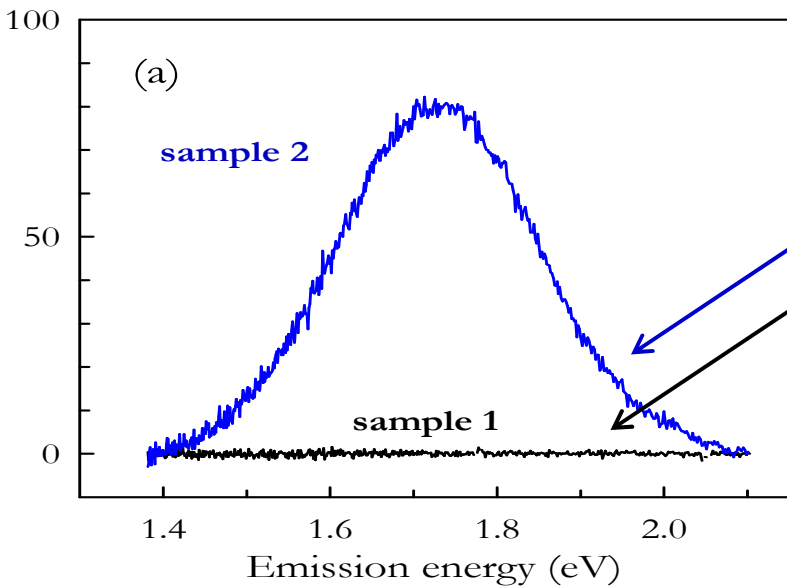


2 hours annealing at 1100 $^{\circ}\text{C}$ induces the formation of Si-NCs

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

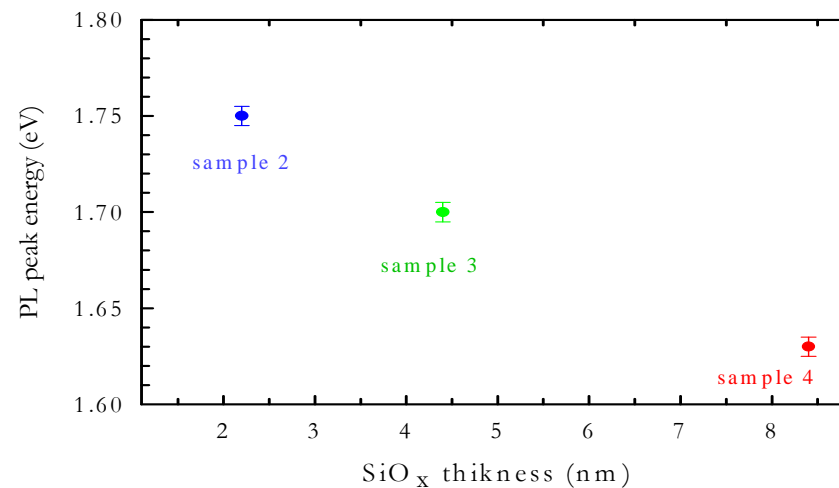
Luminescenza

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

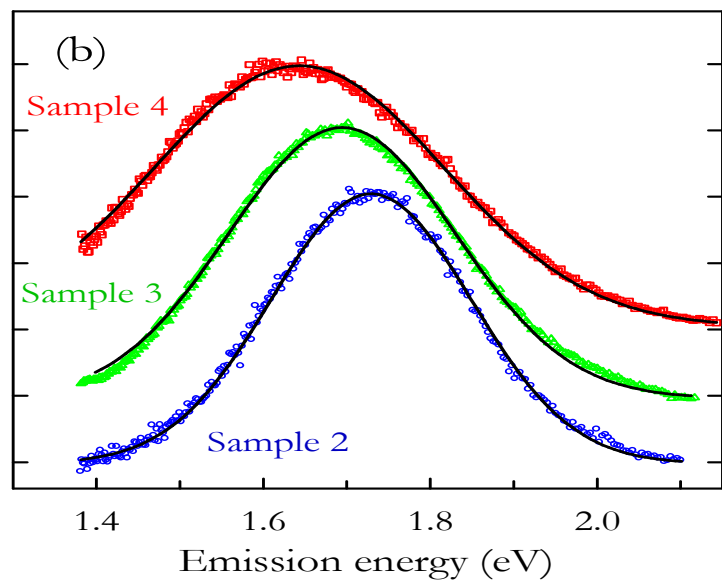


After annealing

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	≈ 1.73	$d \approx 3.8$
3	≈ 1.69	$d \approx 4.1$
4	≈ 1.63	$d \approx 4.5$

TECNICHE DI PRODUZIONE

TOP-DOWN

ABLAZIONE LASER

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BOTTOM UP

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

Pulsed laser ablation (PLA) in liquid

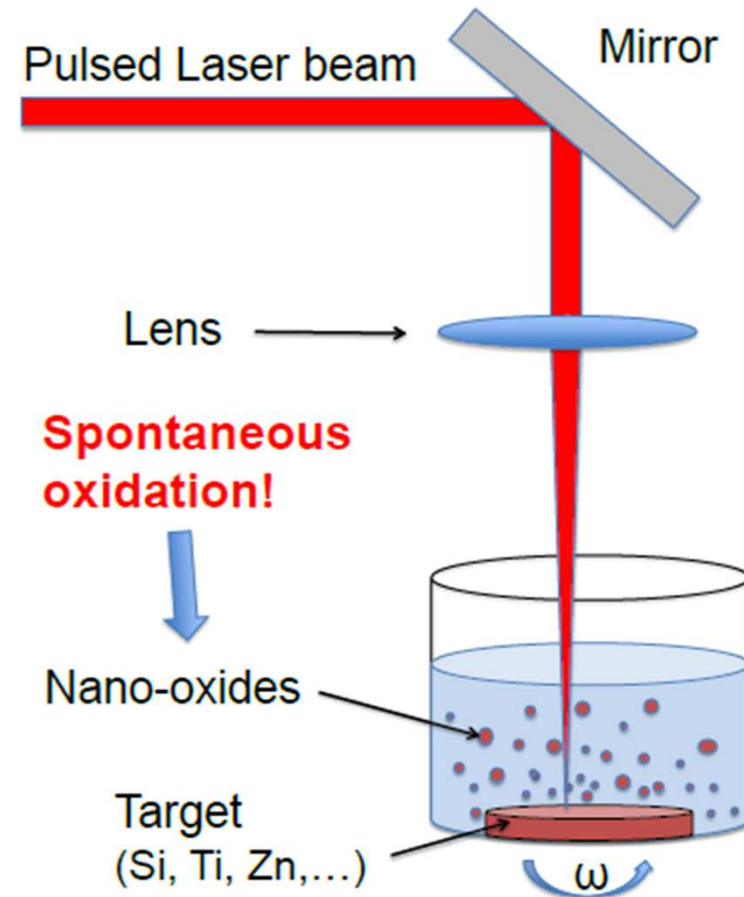
- Il fascio laser viene focalizzato sulla superficie del target.
- Il target viene ruotato o mosso per evitare che il laser colpisca sempre la stessa area.
- Fluenza (J/cm^2): densità di energia fornita.

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

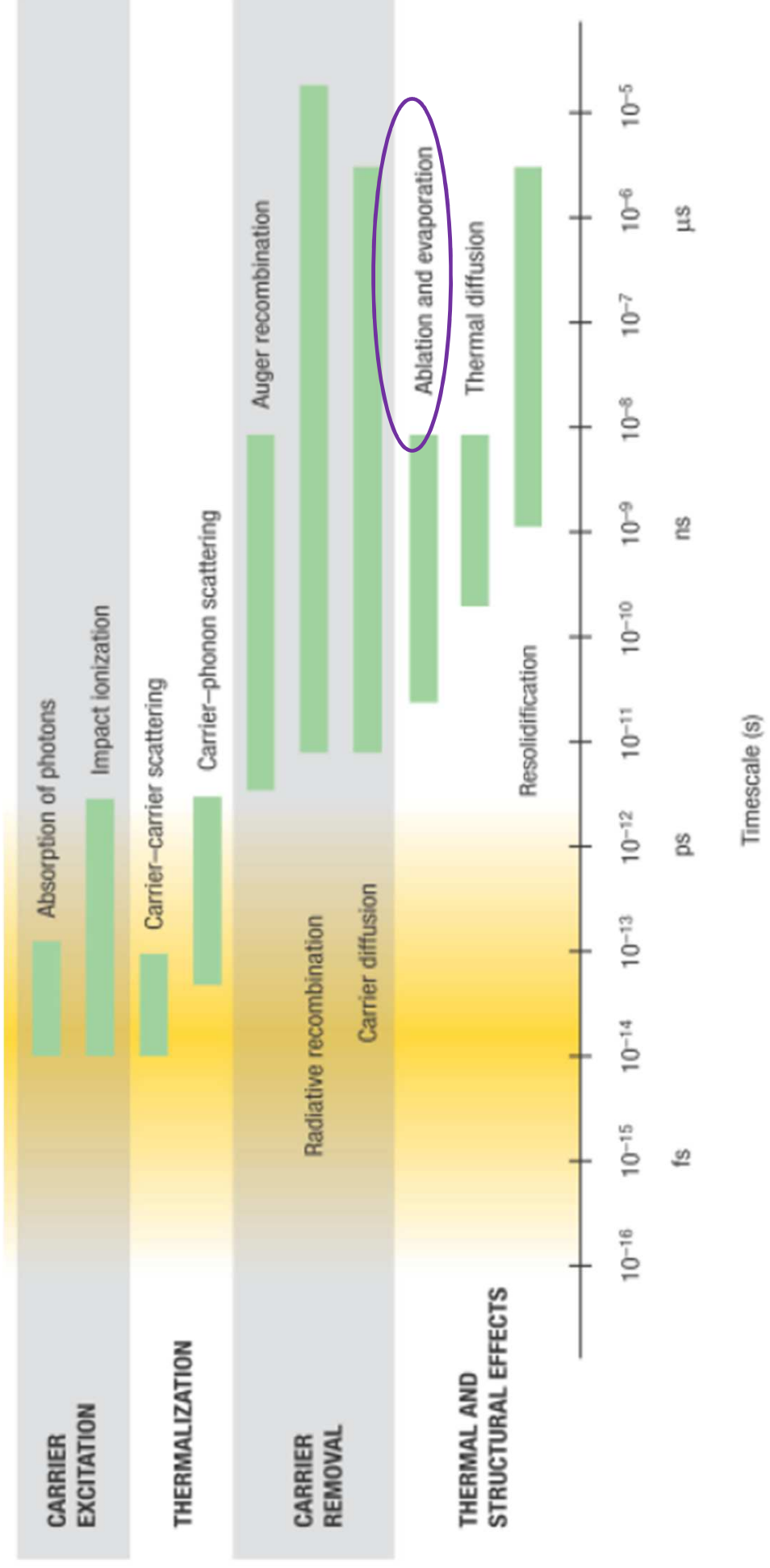
$$r \ll f, \quad \Delta f = l \left(1 - \frac{1}{n} \right)$$

r : raggio del fascio laser

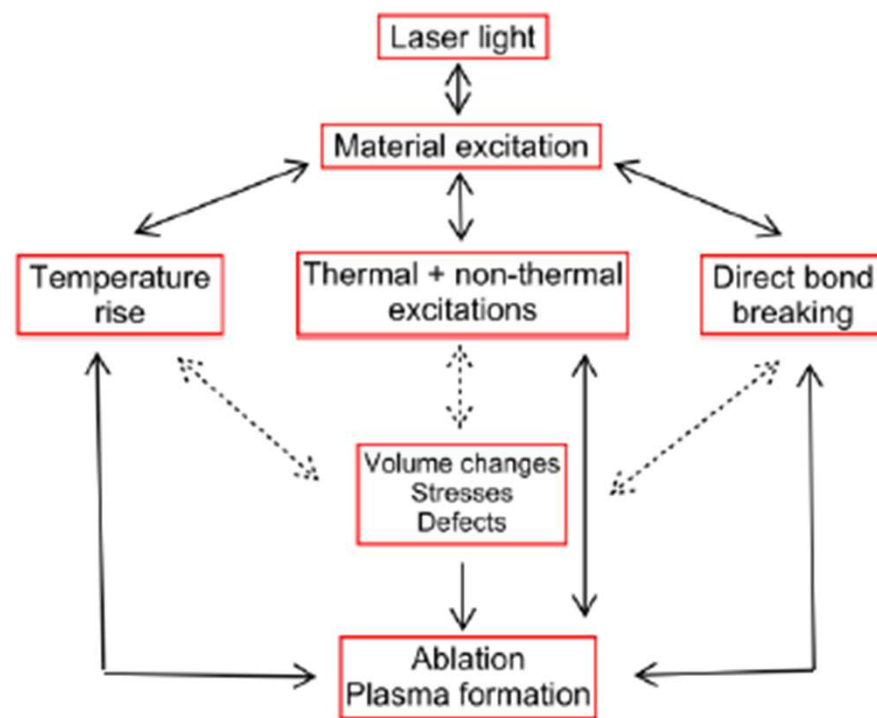
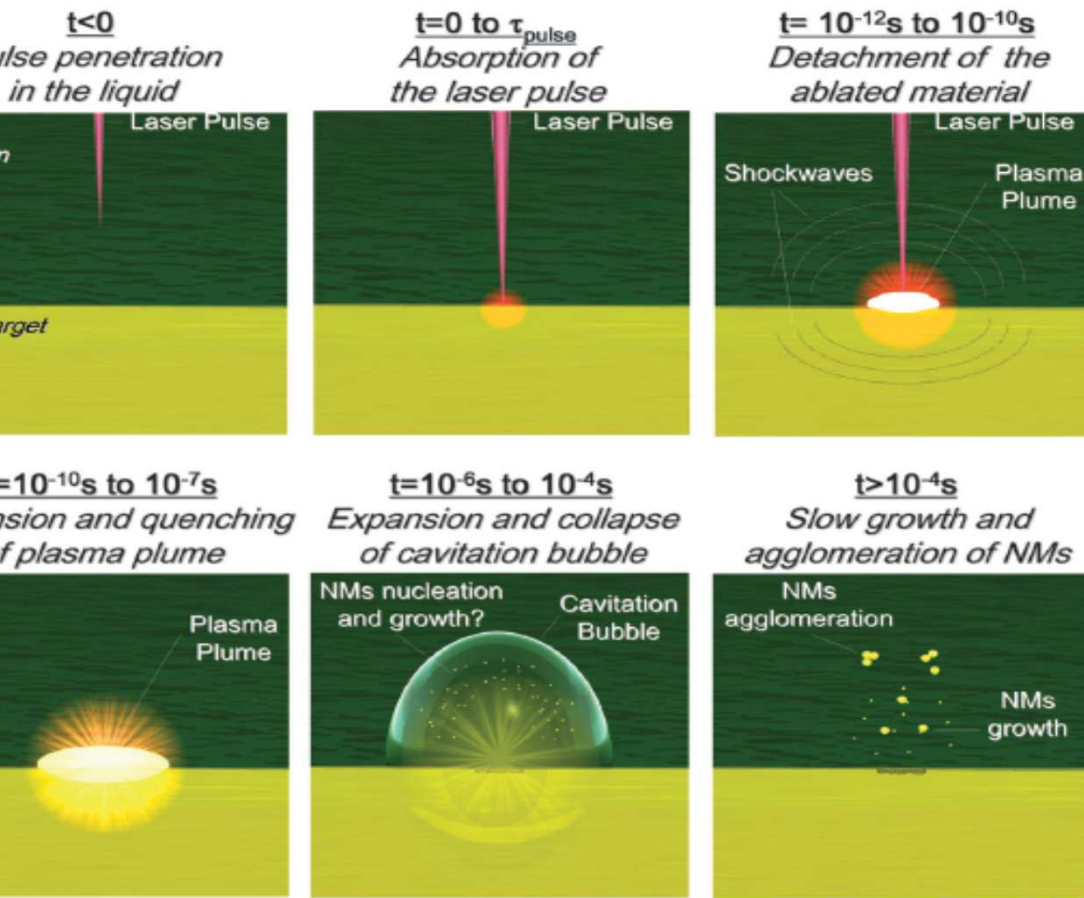
n : indice di rifrazione del solvente



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} s

.A

Vantaggi e svantaggi



• Semplicità e basso costo

• Metodo green

• Gran varietà di materiali ottenuti

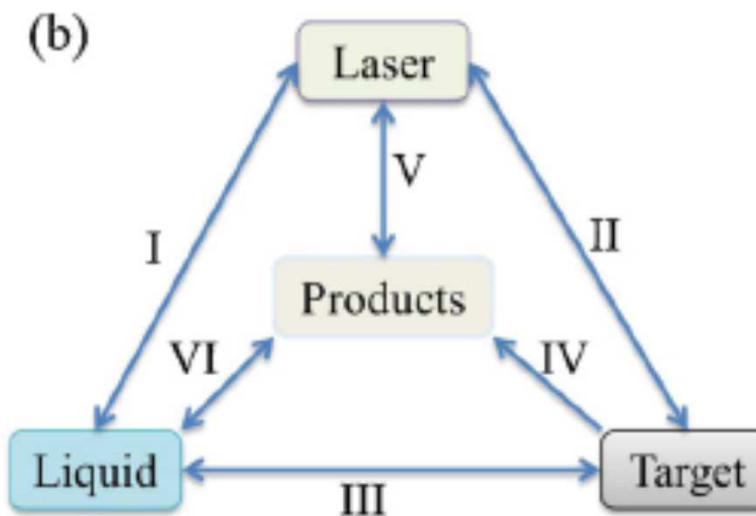
• Controllo dei parametri di sintesi:

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

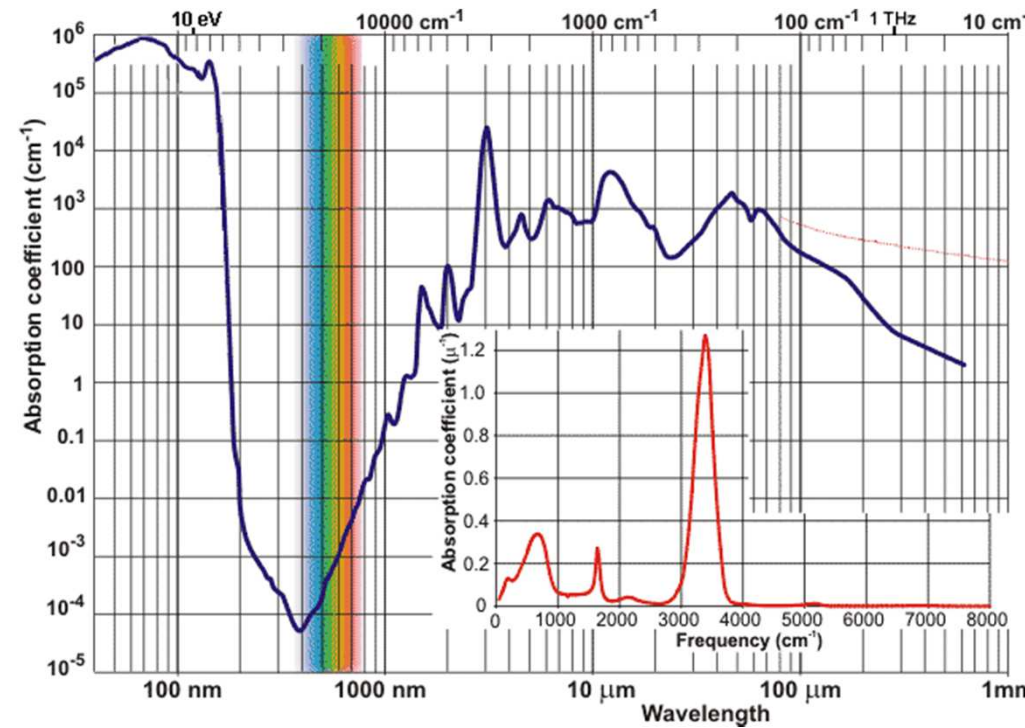
Il fascio laser deve essere assorbito dal target

«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 $h \cdot \nu_{laser} > E_g$

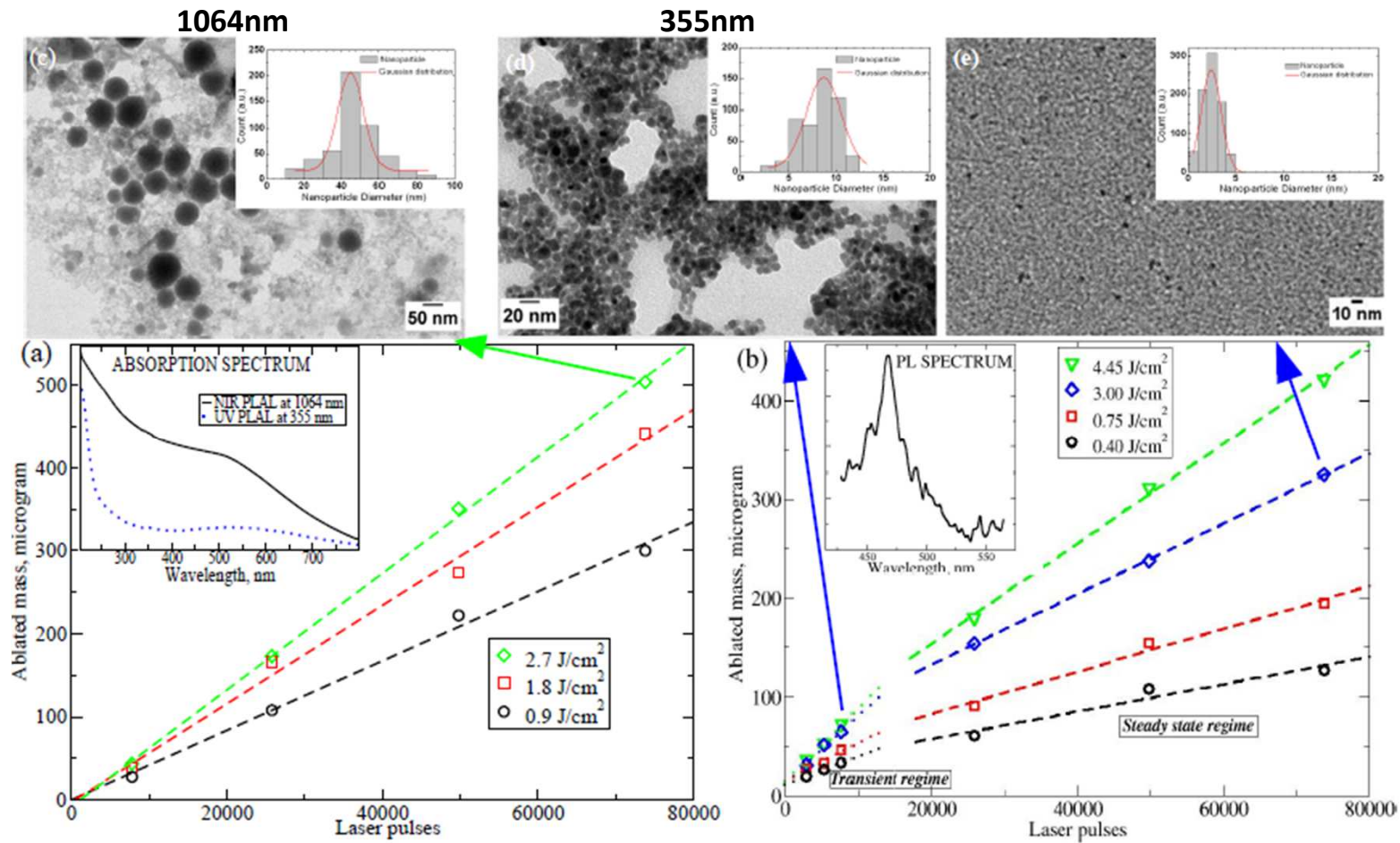


Esempio: Spettro assorbimento acqua distillata

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)



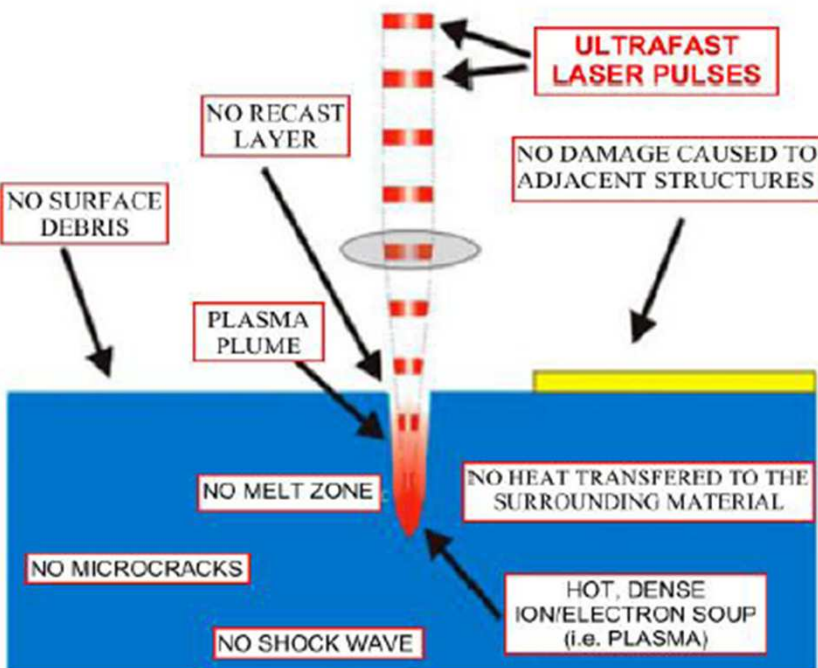
Parametri del laser: durata dell'impulso (τ_{laser})

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

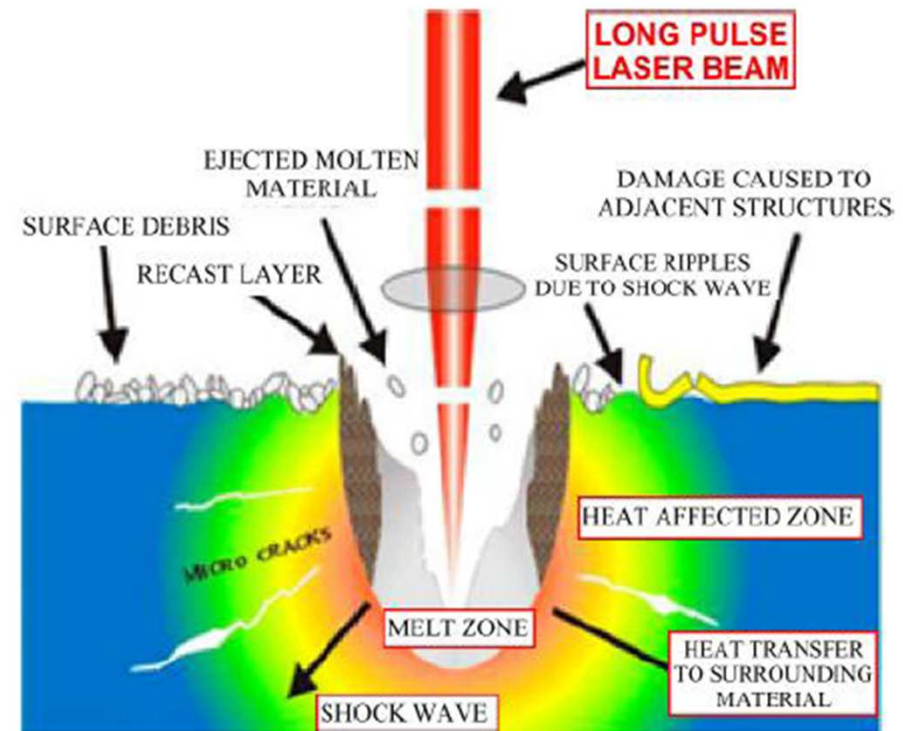
$\tau_{laser} \sim fs \ll \tau_{therm}$ gli elettroni non hanno il tempo di termalizzare col reticolo

$\tau_{laser} \sim ns \gg \tau_{therm}$ 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

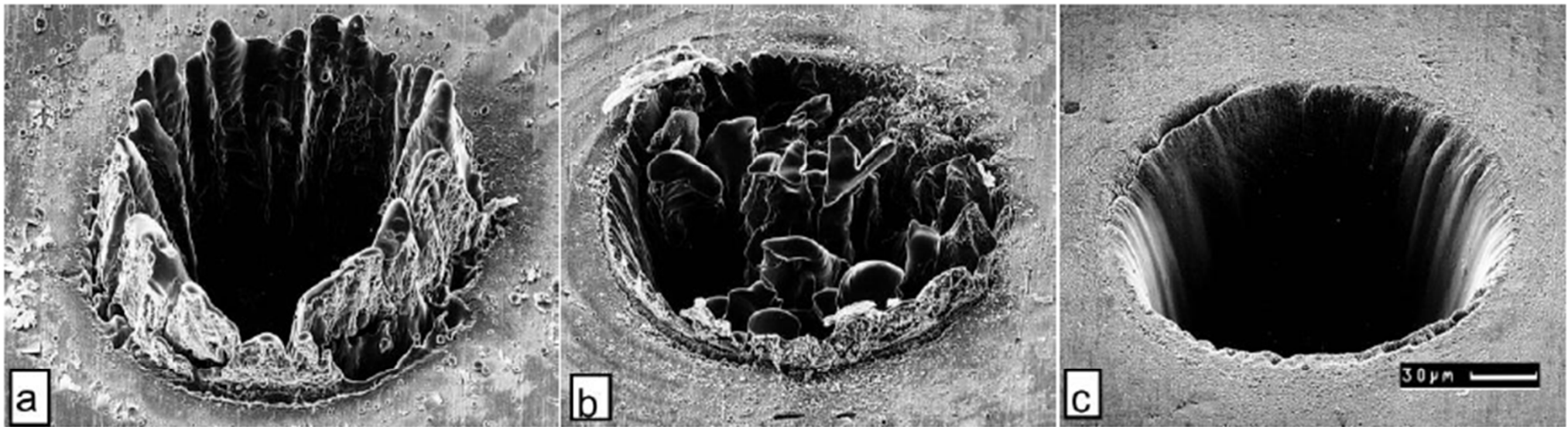
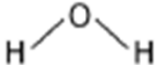
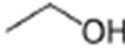
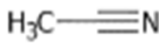
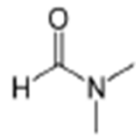


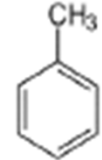
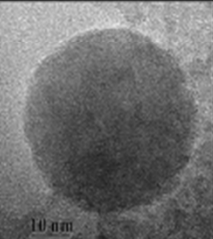
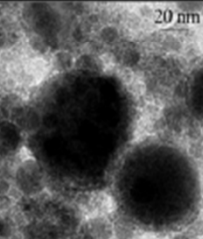
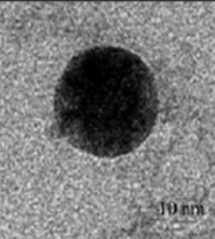
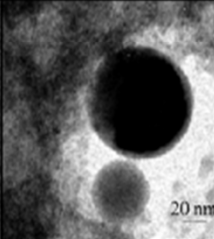
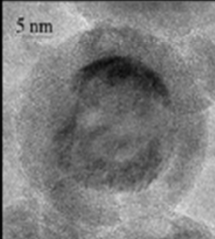
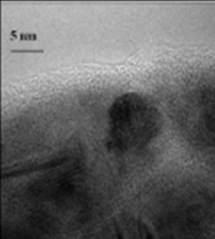
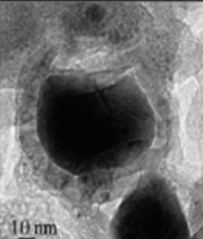


Figure 4: SEM photograph of a hole drilled in a steel foil with (a) 3.3 ns, 1mJ, $\phi = 4.2 \text{ J cm}^{-2}$; (b) 80 ps, 900 μJ , $\phi = 3.7 \text{ J cm}^{-2}$; and (c) 200 fs, 120 μJ , $\phi = 0.5 \text{ J cm}^{-2}$ laser pulses at 780 nm [12].

Effetto del solvente

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

Esempio

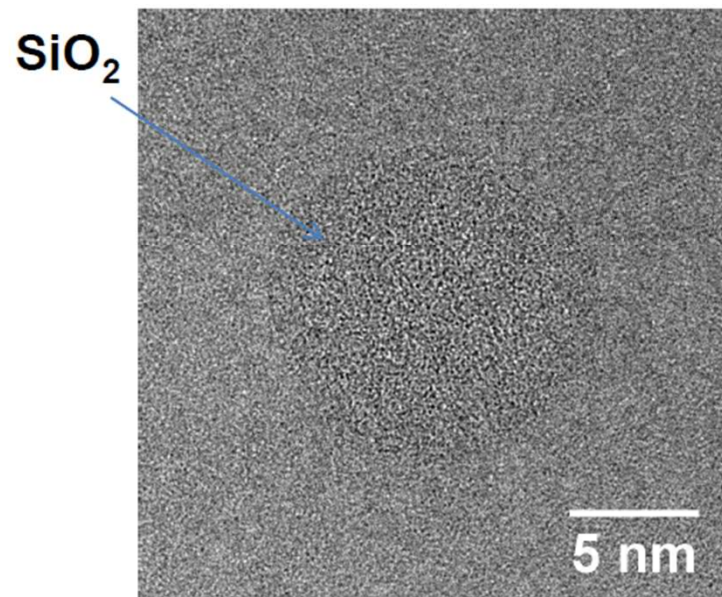
Target ↓	Solvent ↓	Water	Ethanol	Acetonitrile	Dimethyl- formamide	Tetra- hydrofuran	Dimethyl- sulfoxide	Toluene
								
Fe								
		<i>Fe₃O₄, Fe₂O₃, Fe(OOH)₂</i>	<i>Fe₃O₄, FeC₃</i>	<i>Fe₃O₄, Carbon</i>	<i>Fe₃O₄, Carbon</i>	<i>Metal Fe/ Fe₃O₄</i>	<i>Metal Fe/ Carbon</i>	<i>Fe-Carbide/ Graphite</i>

Effetto del solvente

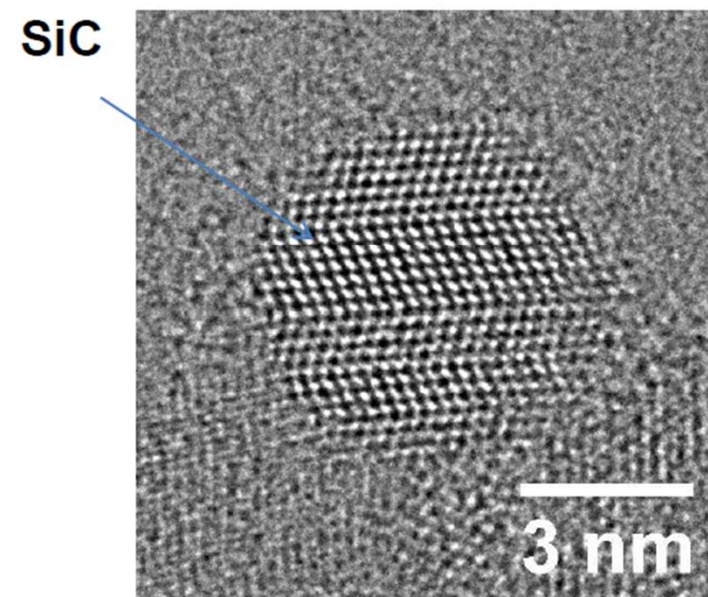
Esempio

Laboratory «Roberto Boscaino»
of Advanced Materials

Ablazione di Silicio in acqua



Ablazione di Silicio in eptano C₇H₁₆



Ossidi nano-strutturati sintetizzati con ablazione laser in liquido

1) Si/SiO₂

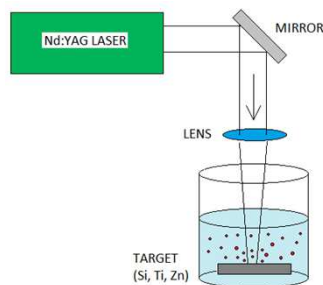
2) ZnO

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

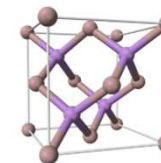
HRTEM;
EDXS

Optical
Properties

Optical
absorption
(UV-Vis.)

Time
resolved PL

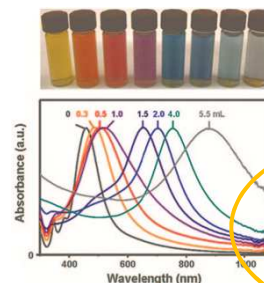
Structural
Properties



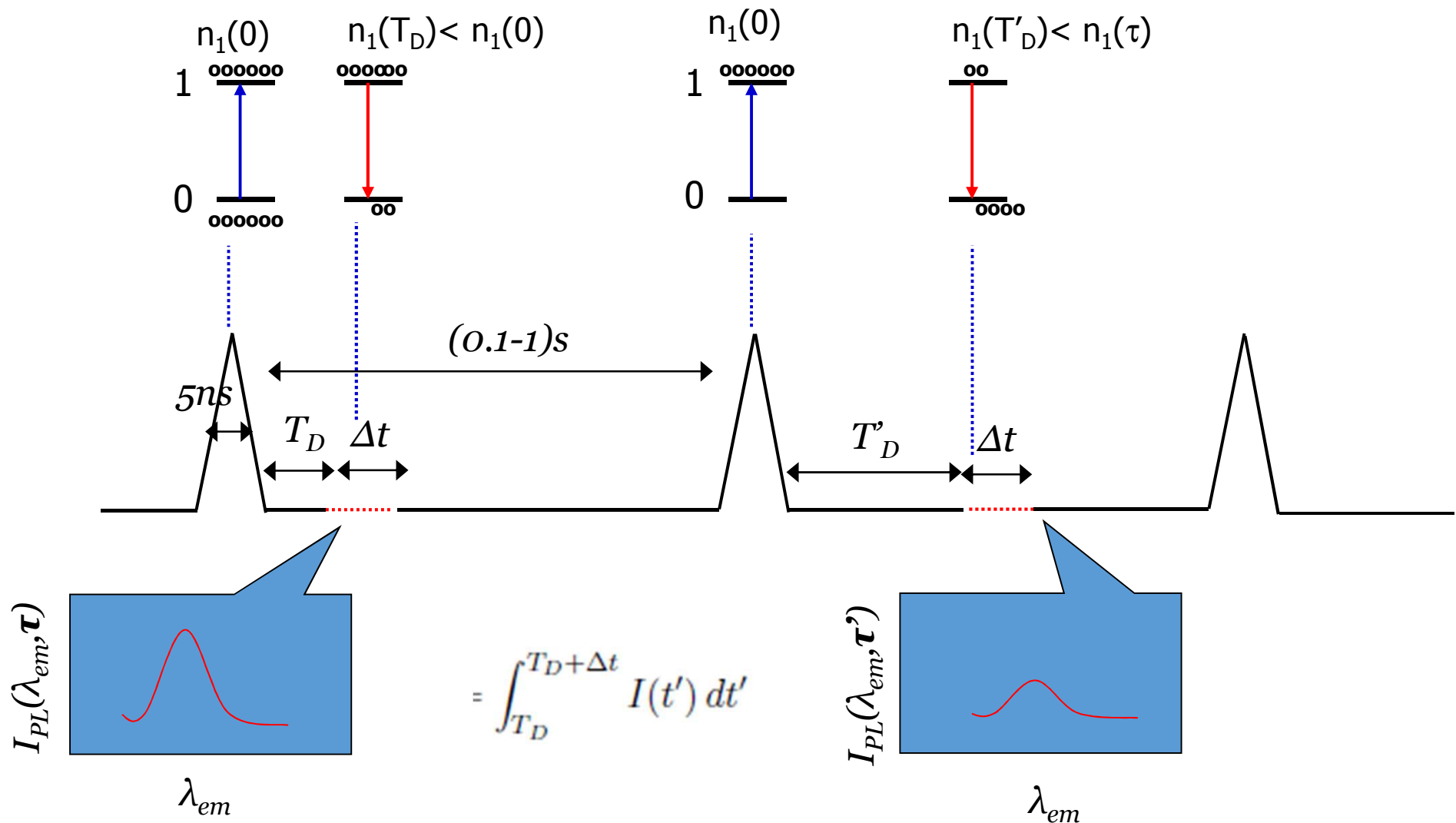
μ Raman

IR
absorption

EPR



Time-resolved PL re-interpretata!!



Gating:

ritardo τ , acquisizione Δt controllabili via computer (ns-ms)!!

possibilità di accumulare più spettri per ogni ritardo τ (sulla CCD e via software)

1) Production of Si-nnc/SiO₂



Applied Surface Science 302 (2014) 62–65



Contents lists available at ScienceDirect

Applied Surface Science

Journal homepage: 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⁺ ions†

Click for updates

J. Chem. Chem. Phys.,

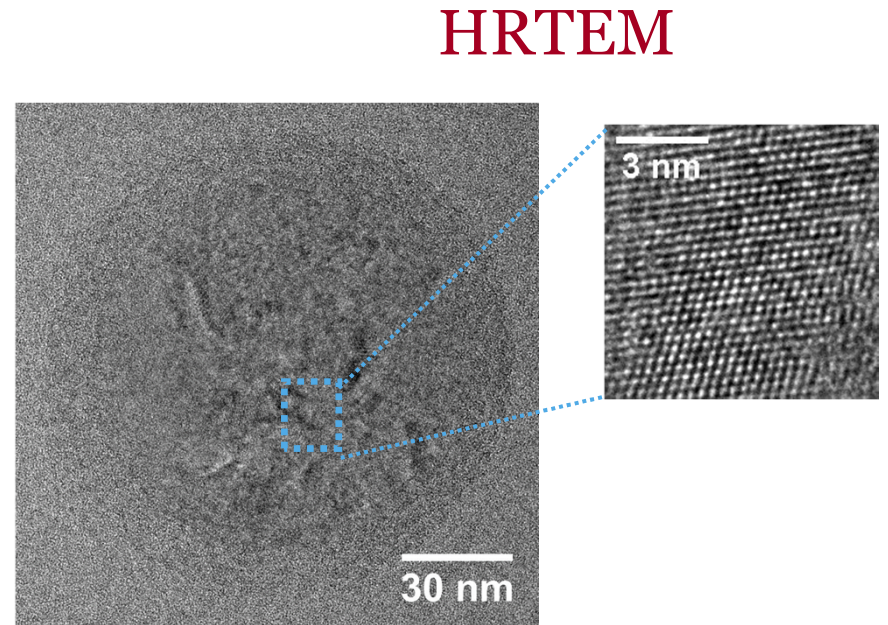
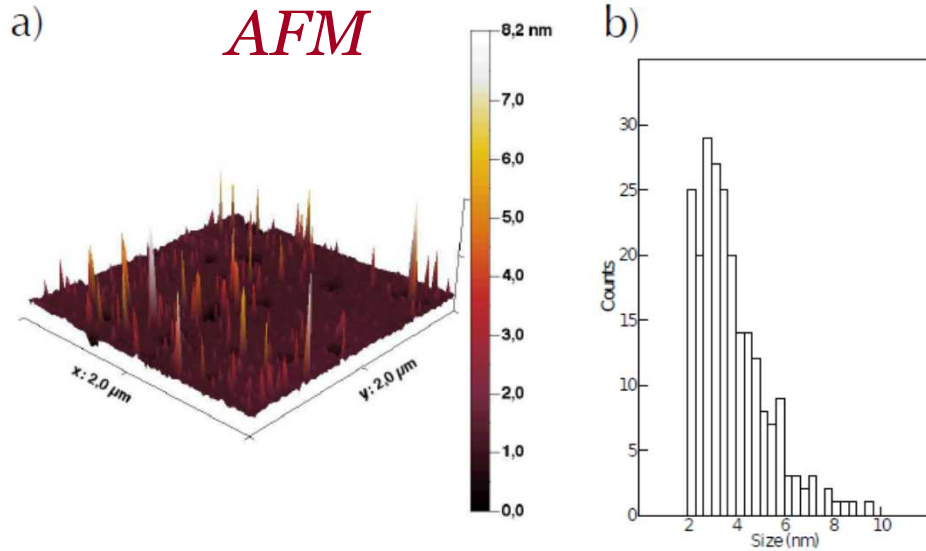
ORIGINAL PAPER

Si/SiO₂ Nanoparticles

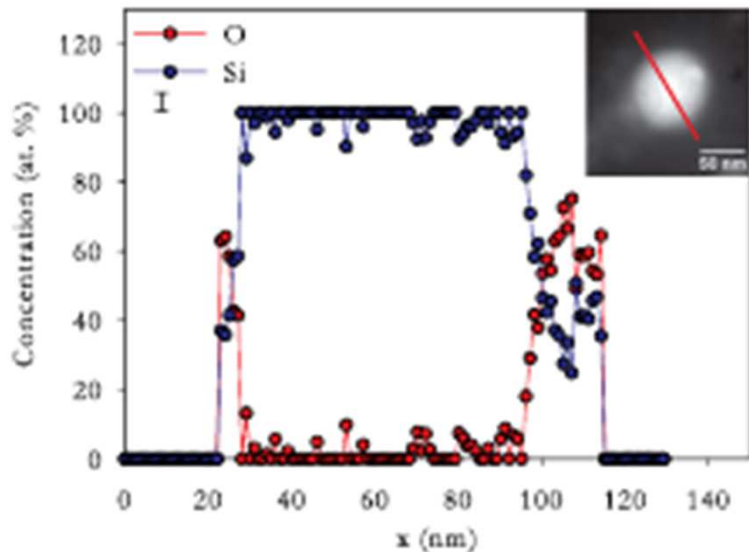
**Luminescence Efficiency of Si/SiO₂ Nanoparticles
Produced by Laser Ablation**



Proprietà morfologiche/strutturali



EDXS

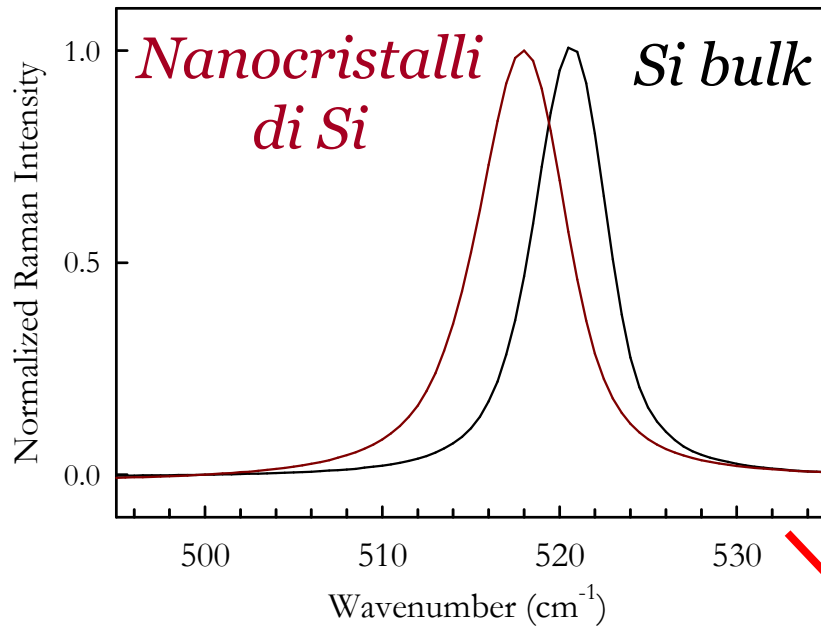


Si cubic structure:
lattice parameter $a=5.4305 \text{ \AA}$

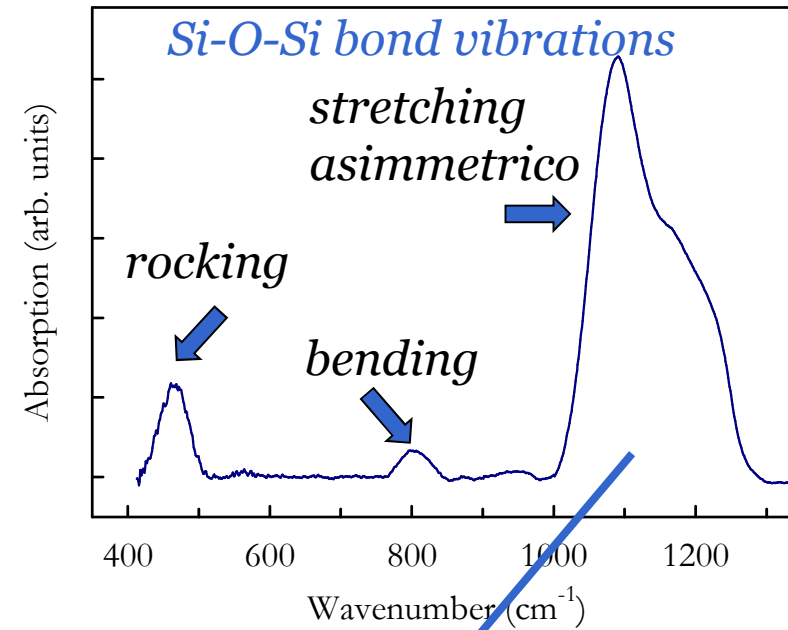
Si polycrystal surrounded by amorphous SiO_2 layer
with an interface mainly composed by Si_3O

Proprietà vibrazionali IR

μ -Raman

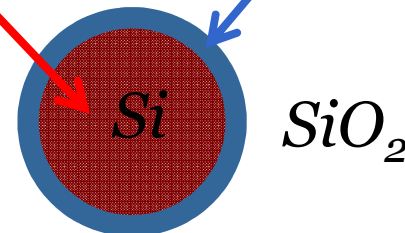


Assorbimento



Δv : quantum confinement (QC)

Size ~ 4 nm

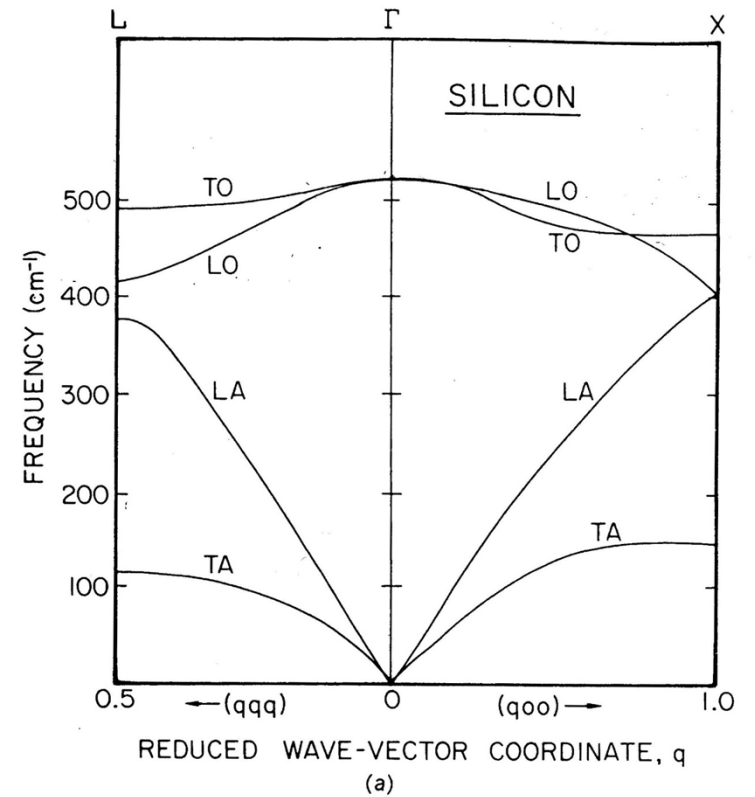
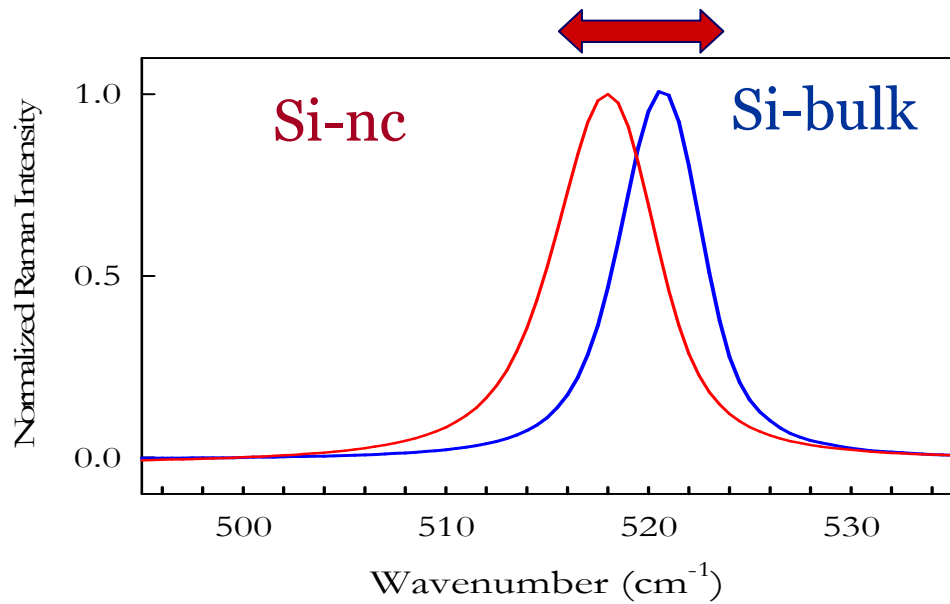


QC

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

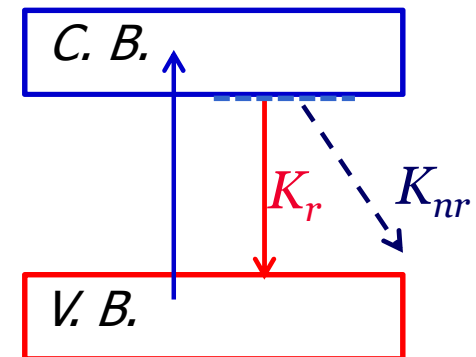
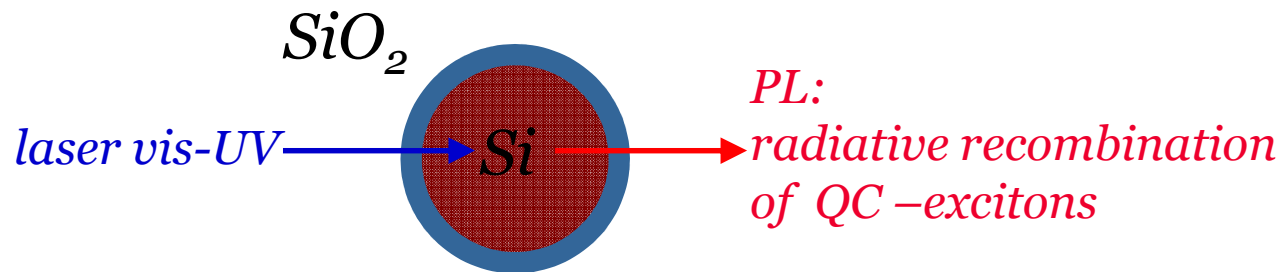
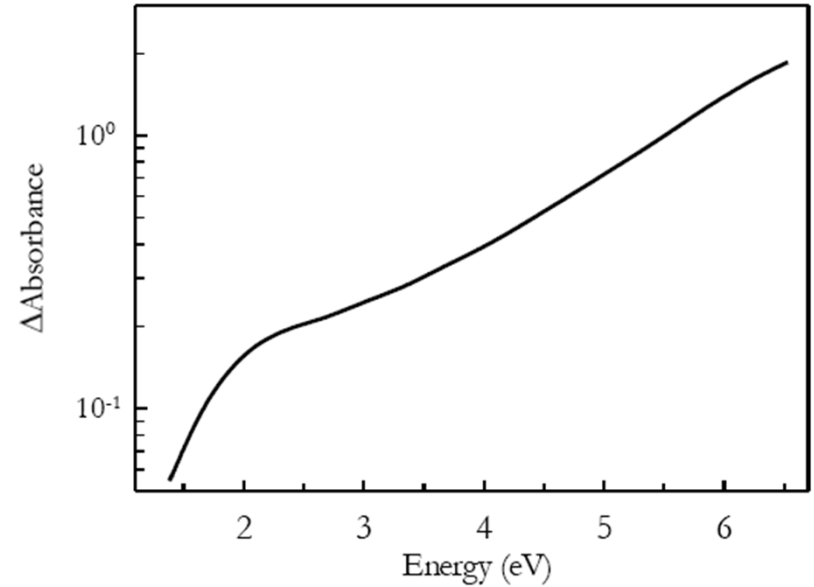
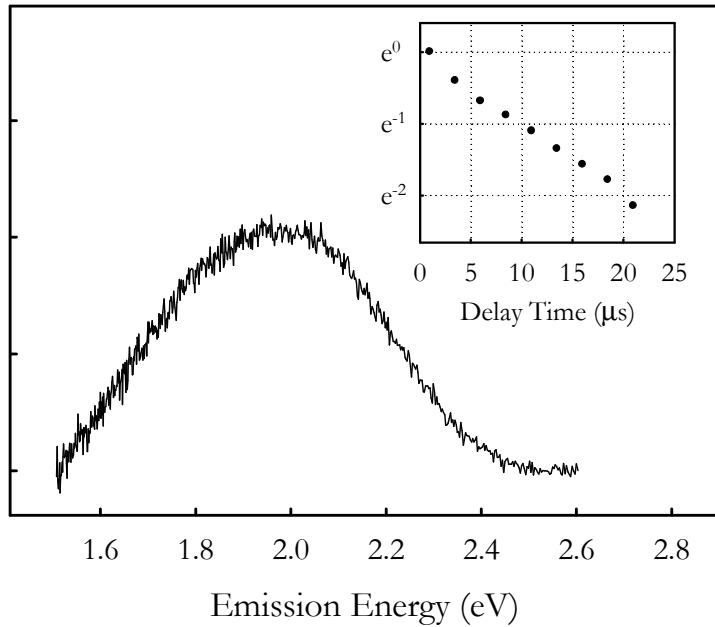
Bulk: $\Delta x \rightarrow$ grande ($\sim 10^{-2}m$) $\Rightarrow \Delta k \rightarrow$ piccolo ($\sim 10^2m^{-1}$)

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!

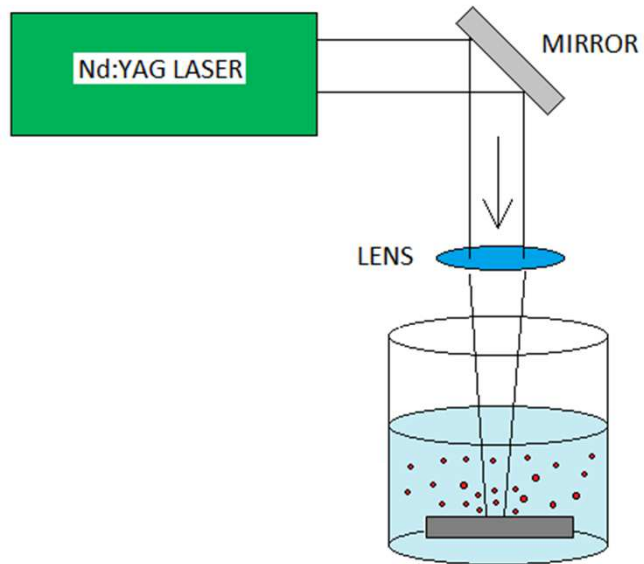
Increase the brightness:



Enhancement of PL quantum efficiency

Experimental Methods

Laser Ablation



*Si-Target
in deionized water*

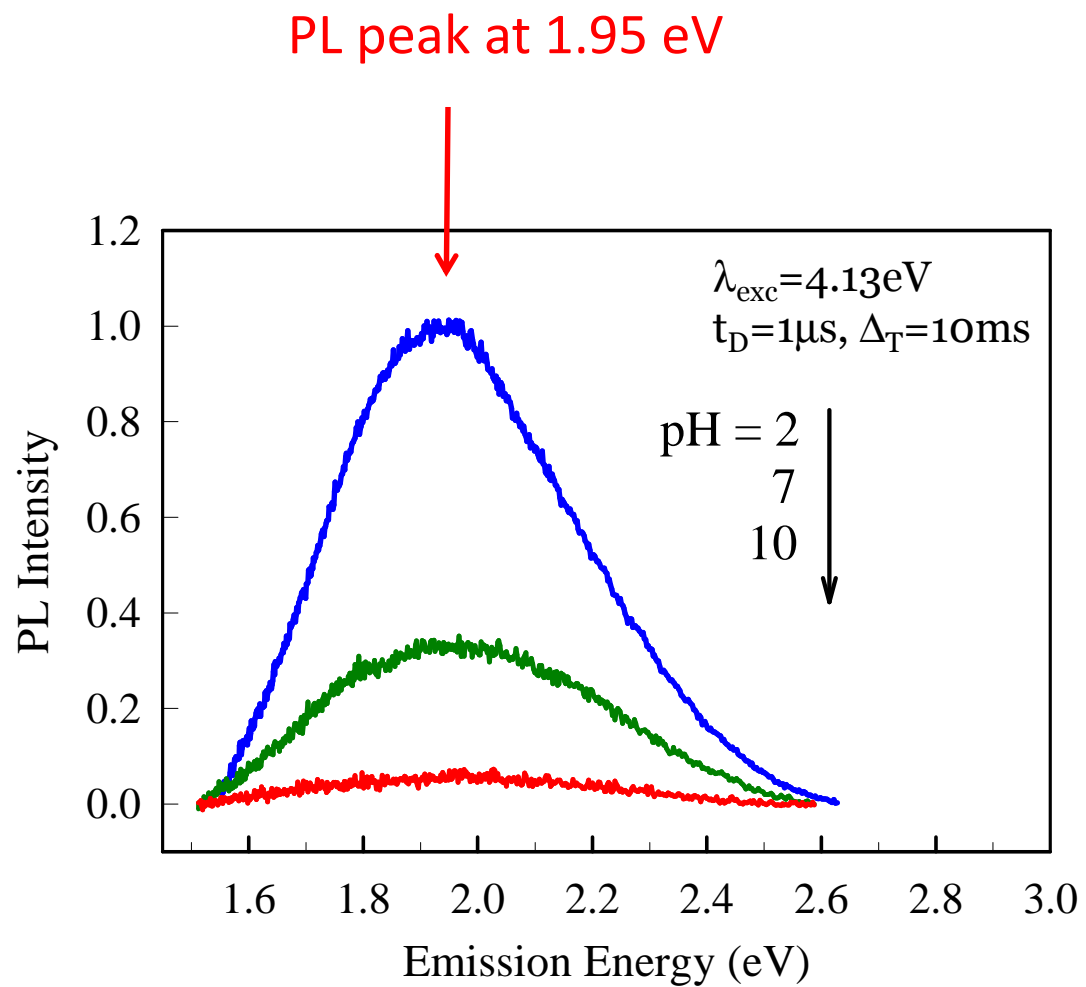


*Soluzioni «acide» e «basiche»
Al variare del pH da 1 a 10*

*Time-resolved PL
IR absorption*

Results

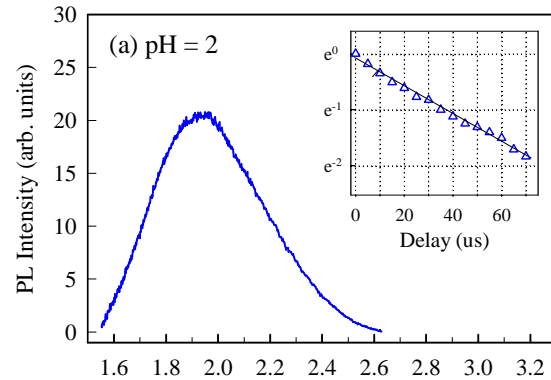
PL dependence on pH



PL intensity increases by a factor of ~ 20 upon decreasing the pH from 10 to 2.

Results

PL dependence on pH

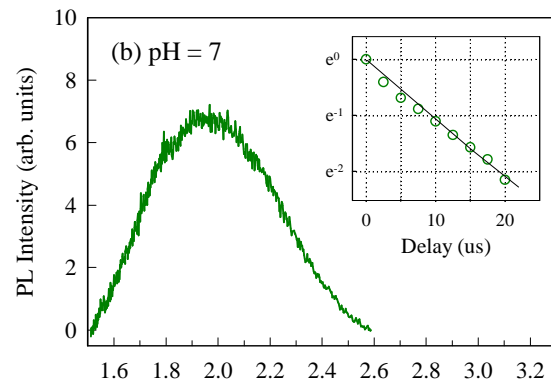


Exponential decay: $\exp(-t/\tau)$ $\tau = 1_r / (k_r + k_{nr})$

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

I_{PL} and τ are correlated

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

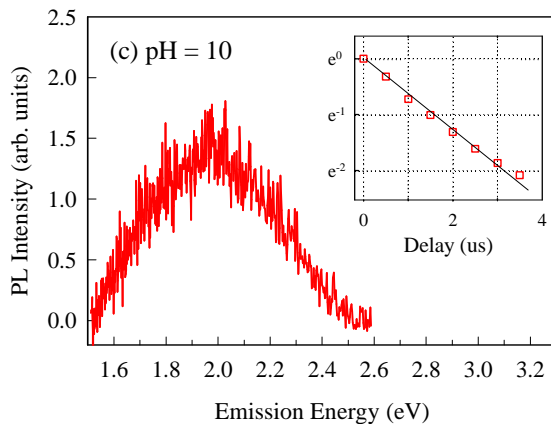


$\tau \approx 9.5 \mu\text{s}$

I_{PL} is related to the variation of η

Hypothesis:

η is limited by the existence of centers on which the excitons non-radiatively recombine (non-radiative defects)

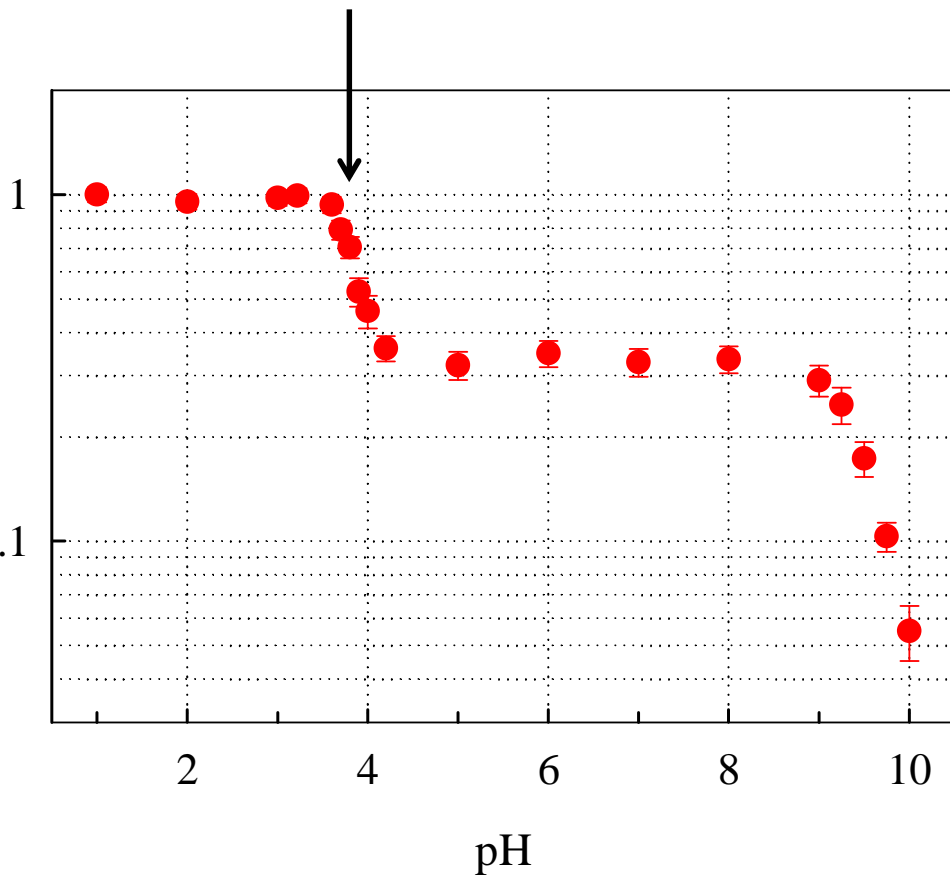


$\tau \approx 1.8 \mu\text{s}$

Results

PL efficiency: dependence on pH

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



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

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

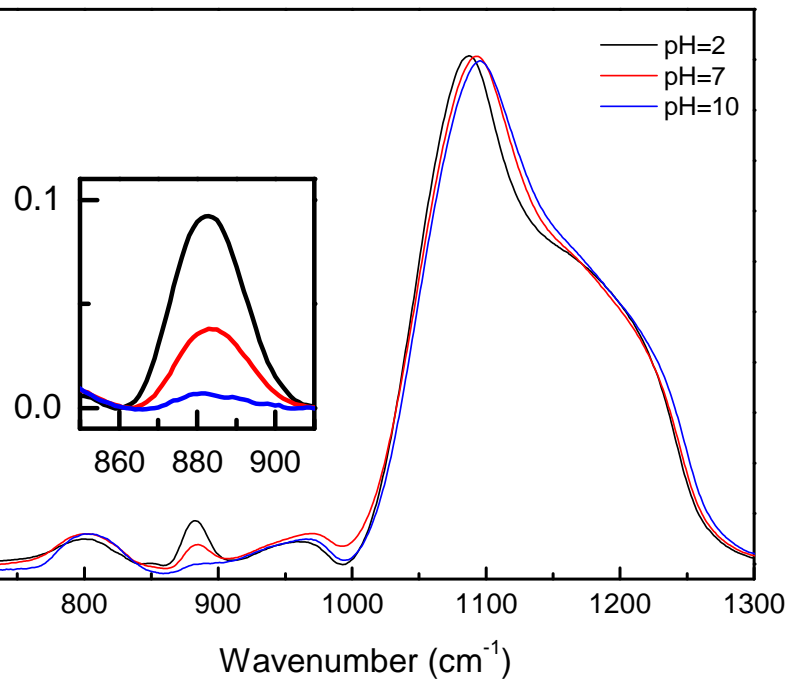
$$\eta = k_r / (1/\tau) = k_r / (1/\tau_{\text{max}} + \Delta k_{\text{nr}})$$

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

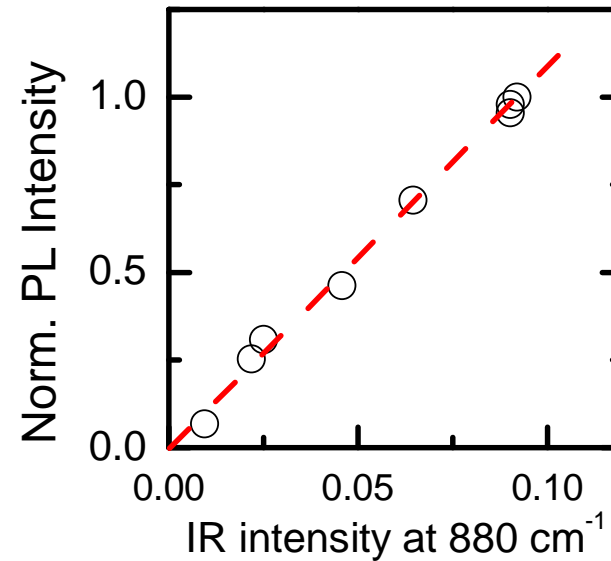
Results IR absorption: dependence on pH



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 η

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!!

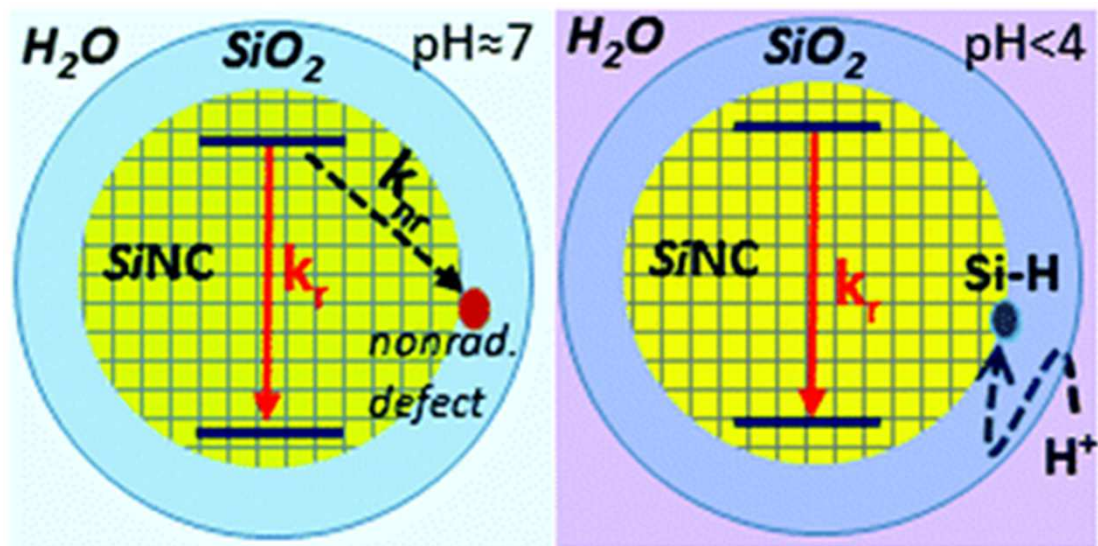
Hypothesis!

*Distorted Si—Si bonds and Si—O—Si bridging bonds at the Si/SiO₂ interface
[Lee et al. Adv. Funct. Mater, 22, 3233 (2012): pseudopotential simulations]*

In our system:

The interface (~3 nm) is Si₃O ...

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 H₂O

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

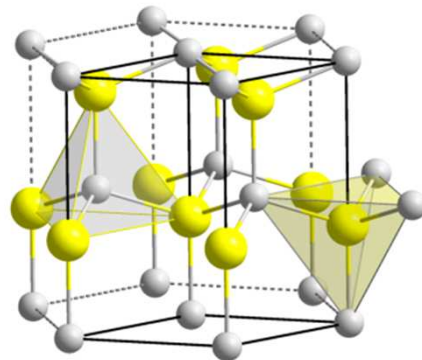
ZnO



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

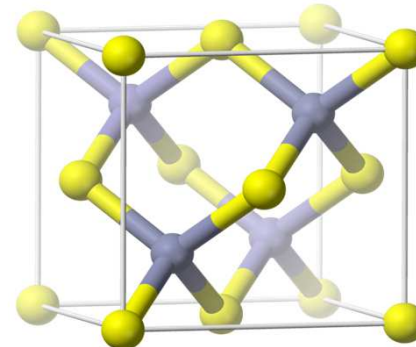
Strutture cristalline

Wurtzite



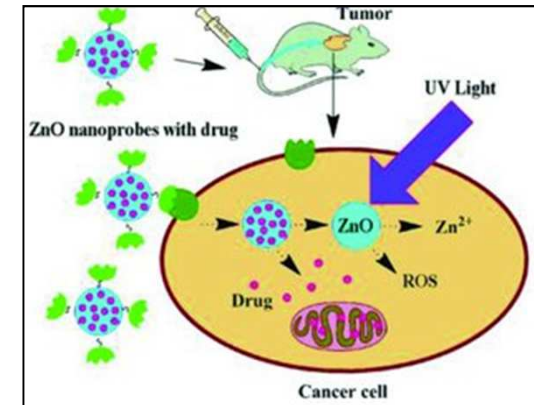
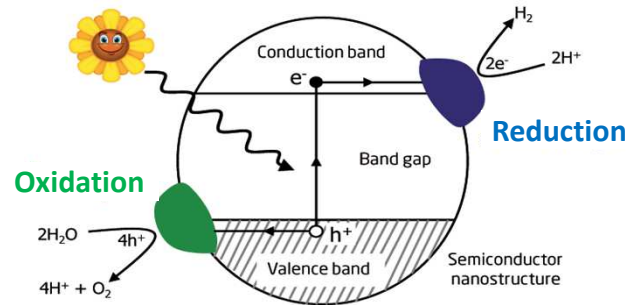
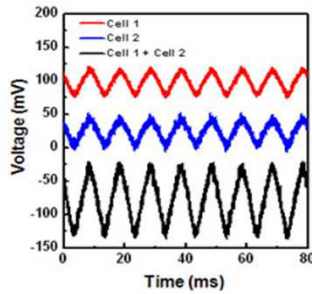
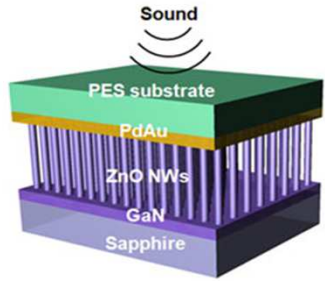
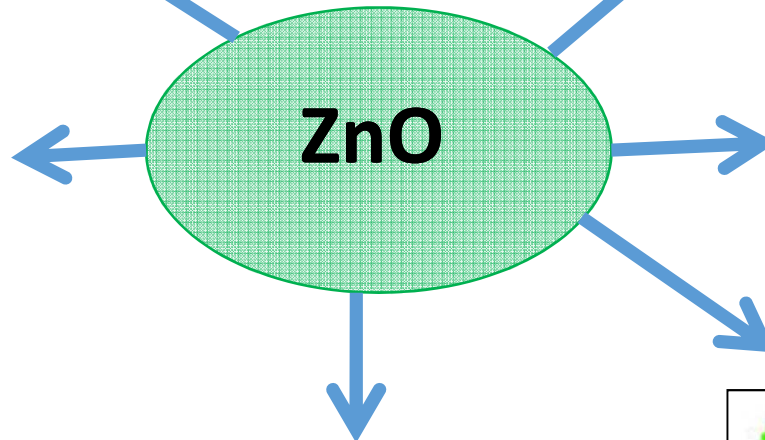
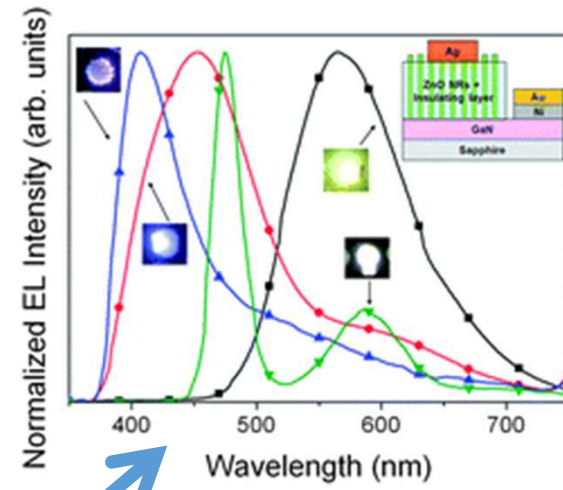
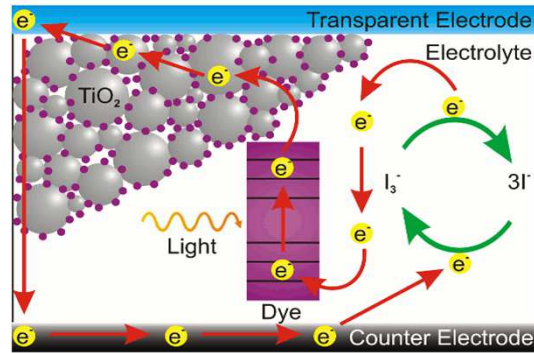
$E_g = 3.37\text{eV}$ (direct-bandgap)

Zincoblenda



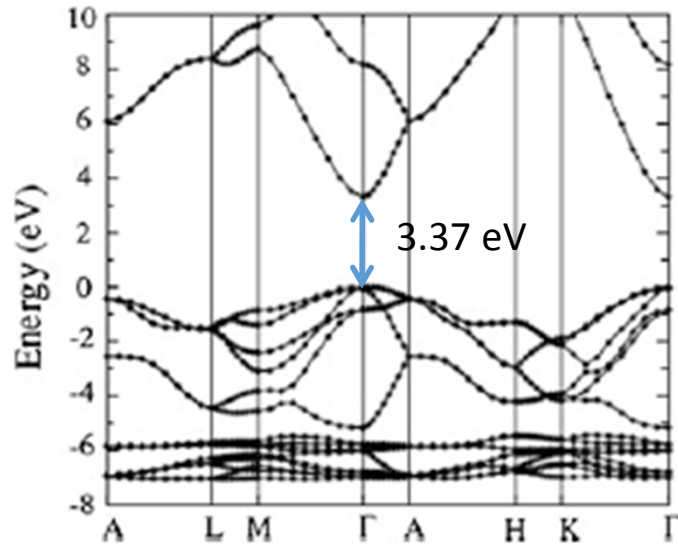
$E_g = 3.27\text{ eV}$ (direct-bandgap)

D: Applicazioni



Proprietà elettroniche e ottiche

Struttura bande ZnO wurtzite



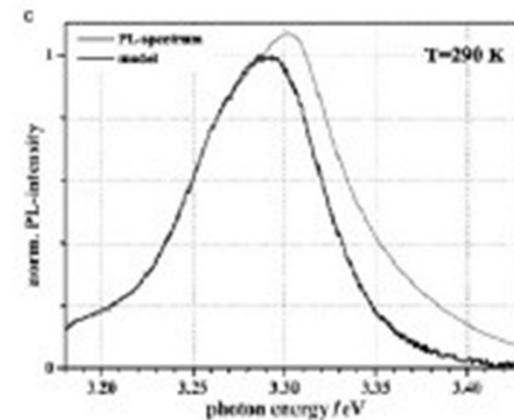
Rep. Prog.Phys 72, 126501 (2009)

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

Table 1.1 Comparison of physical properties of some key compound semiconductors

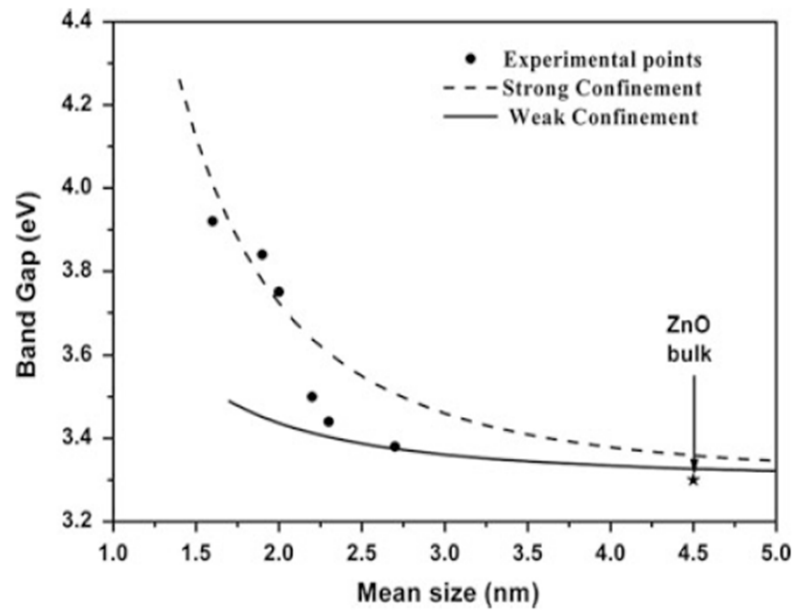
Material	Crystal structure	Lattice constants a and c (Å)	Band gap (eV)	Energy of fusion (K)	Exc. binding energy (meV)	Dielectric constant $\epsilon(0)$ and $\epsilon(\infty)$
ZnO	Wurtzite	3.25 5.21	3.37	2,248	60	8.75 3.75
ZnS	Wurtzite	3.82 6.26	3.8	2,103	30	9.6 5.7
ZnSe	Zinc blende	5.66	2.7	1,793	20	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

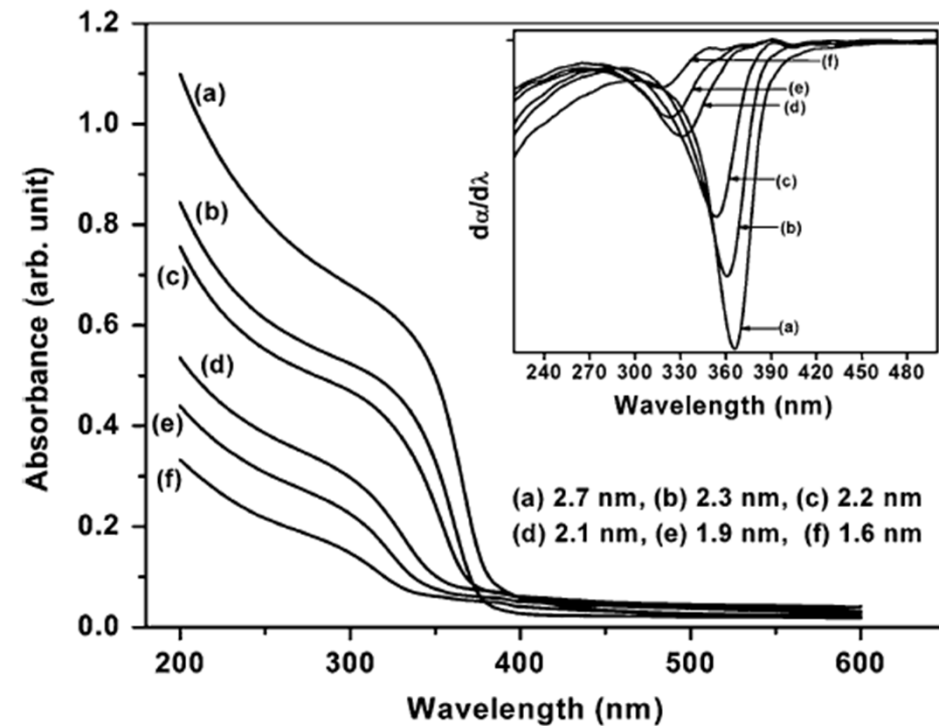


ZnO NPs: effetti QC

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



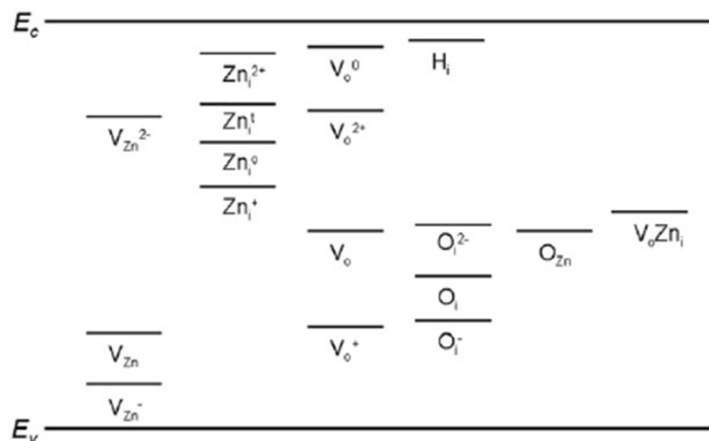
Assorbimento UV-Vis



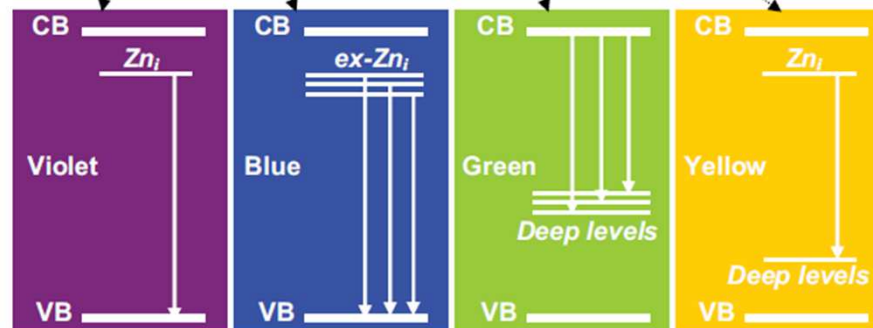
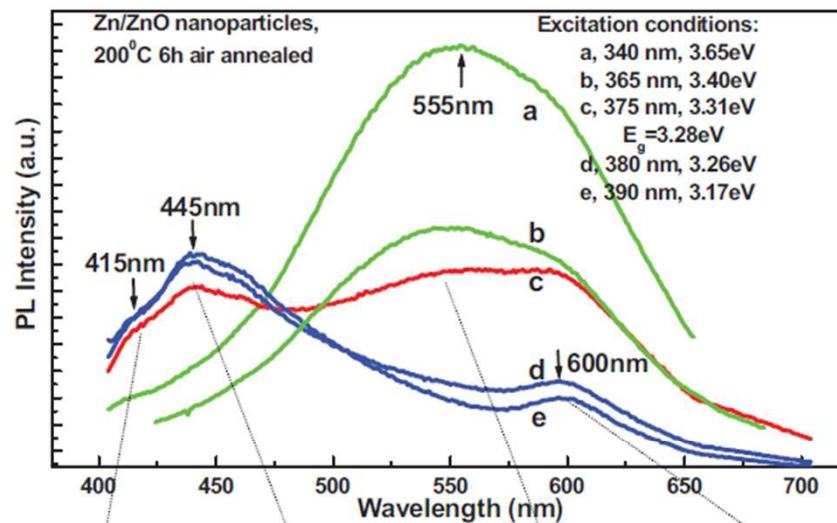
Difetti ZnO nano-strutturato

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)

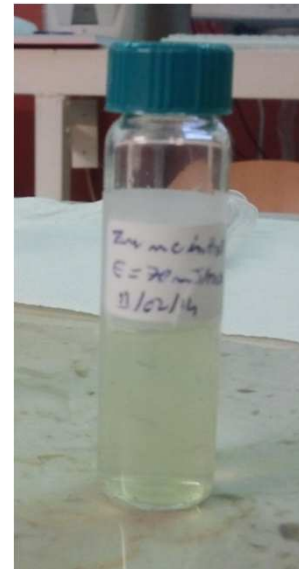
Laser Nd-Yag (1064 nm), ≈ 5 ns;

Laser Ti:Sapphire (800 nm), ≈ 50 fs

Subito dopo l'ablazione

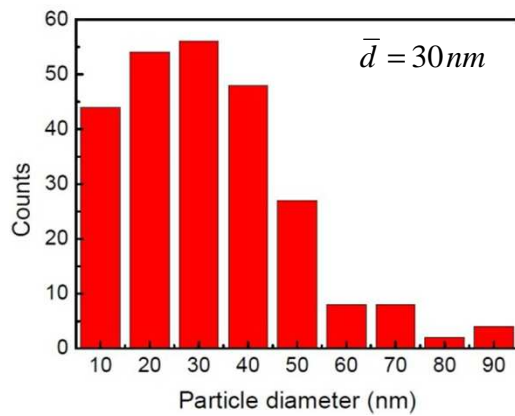
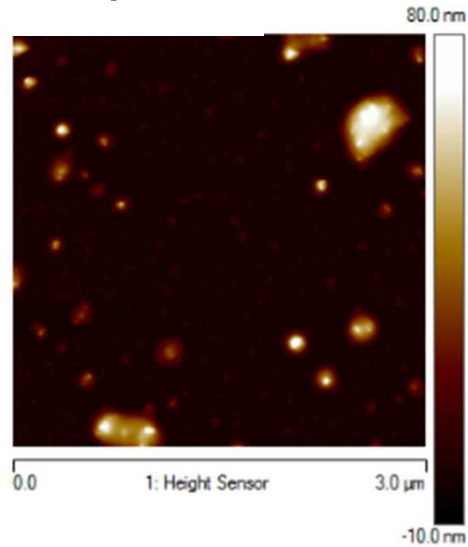


dopo un ora

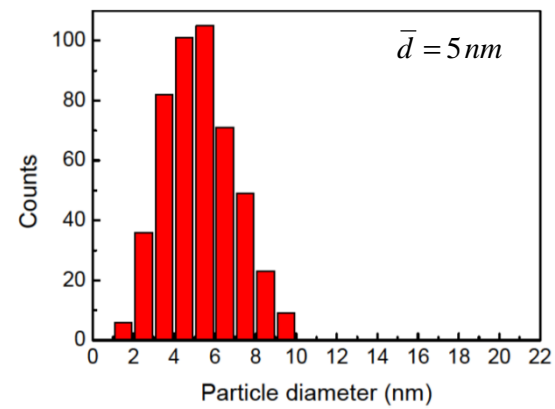
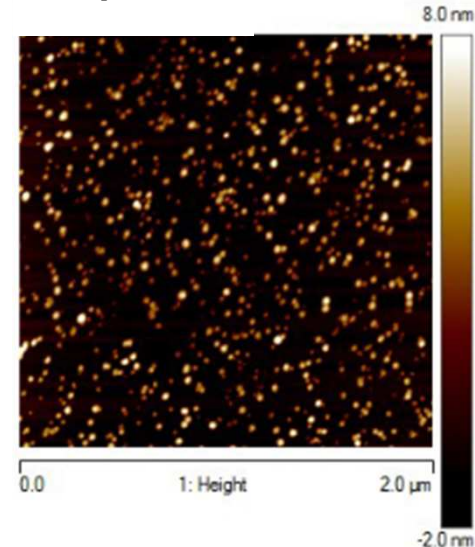


Caratterizzazione microscopica: Effetto della durata dell'impulso

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

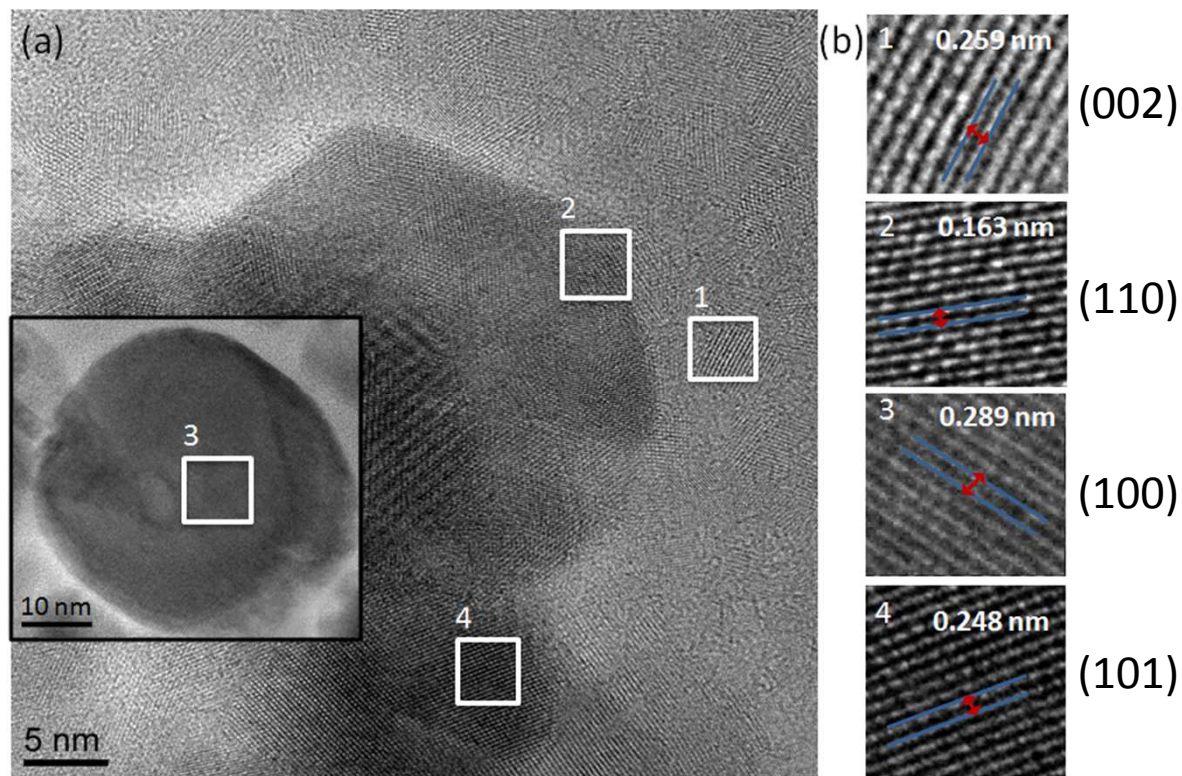


$$E_p = 150 \mu\text{J}, 60 \text{ fs}$$

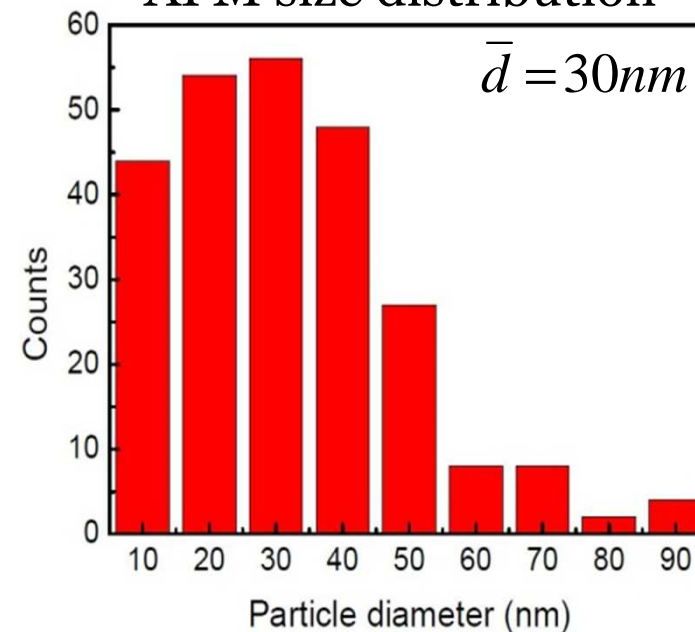


Morphology and structure

HRTEM



AFM size distribution



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

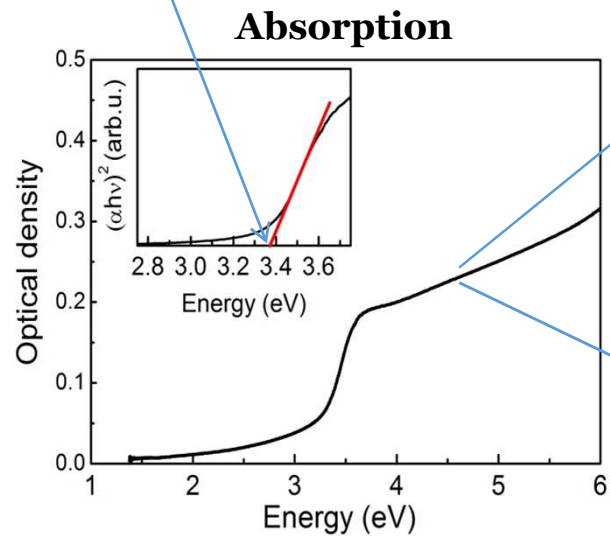
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

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

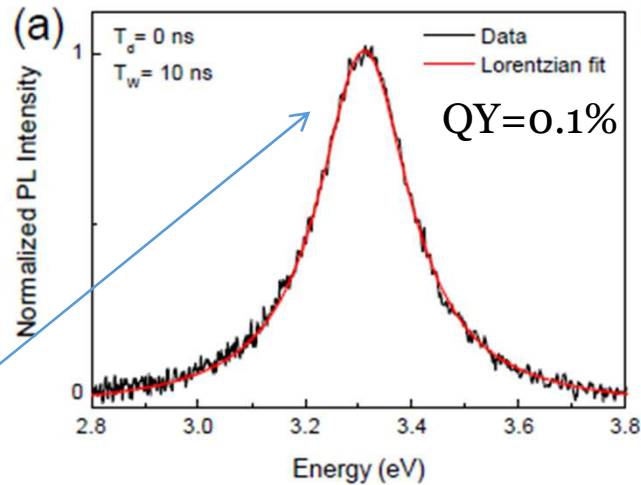
$(h \ k \ l)$	(0 0 2)	(1 1 0)	(1 0 0)	(1 0 1)
Measured $d(\text{nm})$	0.259 ± 0.001	0.1630 ± 0.0006	0.289 ± 0.001	0.248 ± 0.002
Reported $\bar{d}(\text{nm})$	0.2602	0.1625	0.2814	0.2476

Optical properties

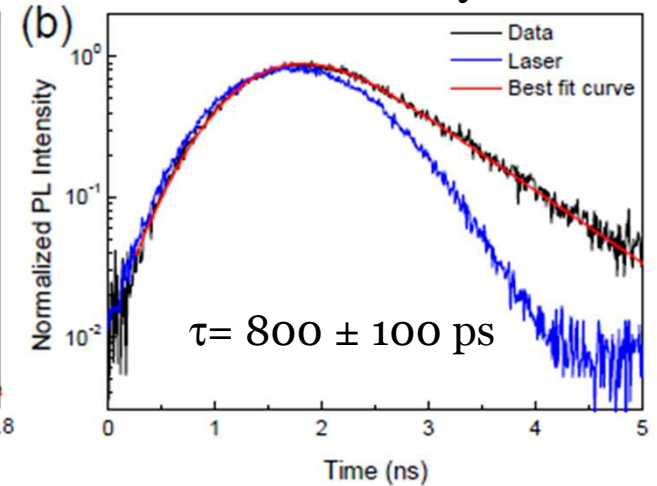
$E_g = 3.38$ eV which is consistent with wurtzite



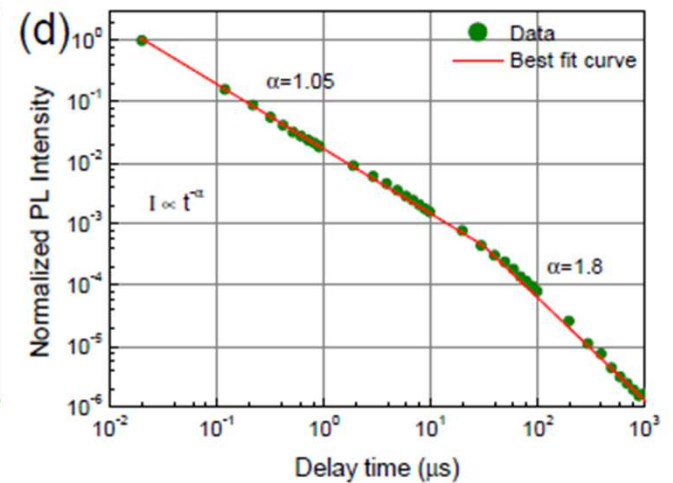
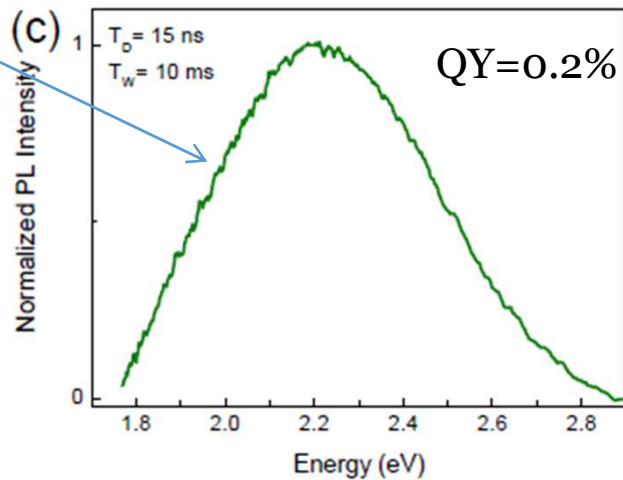
Excitonic emission



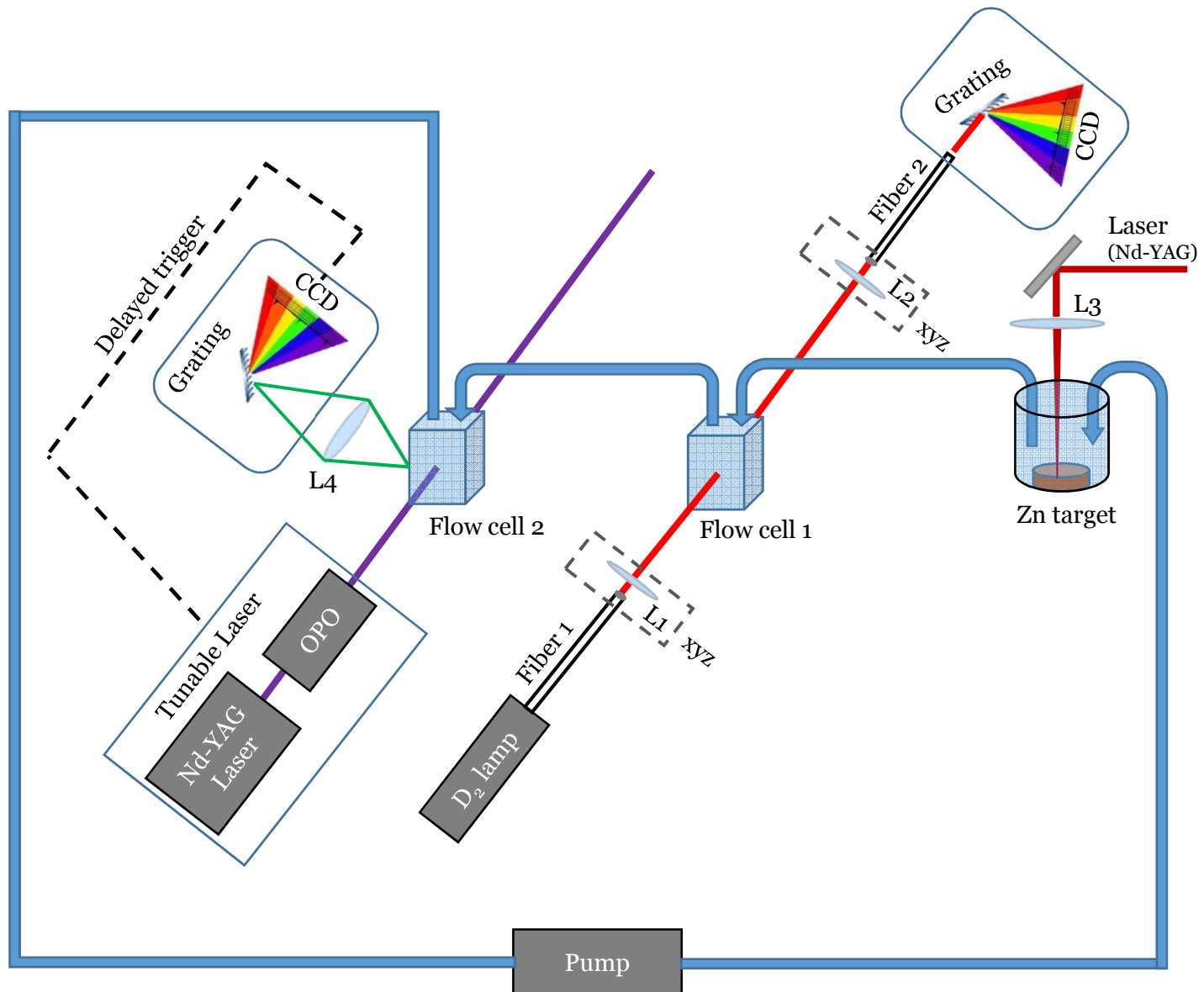
Emission decay time



Defect emission

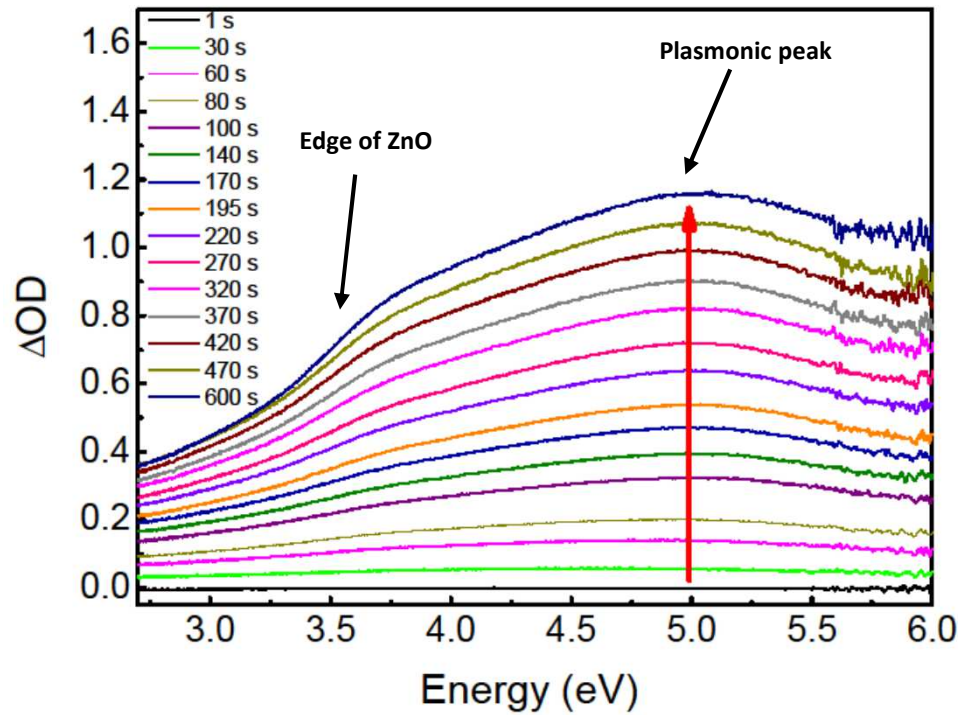


Misure ottiche in situ

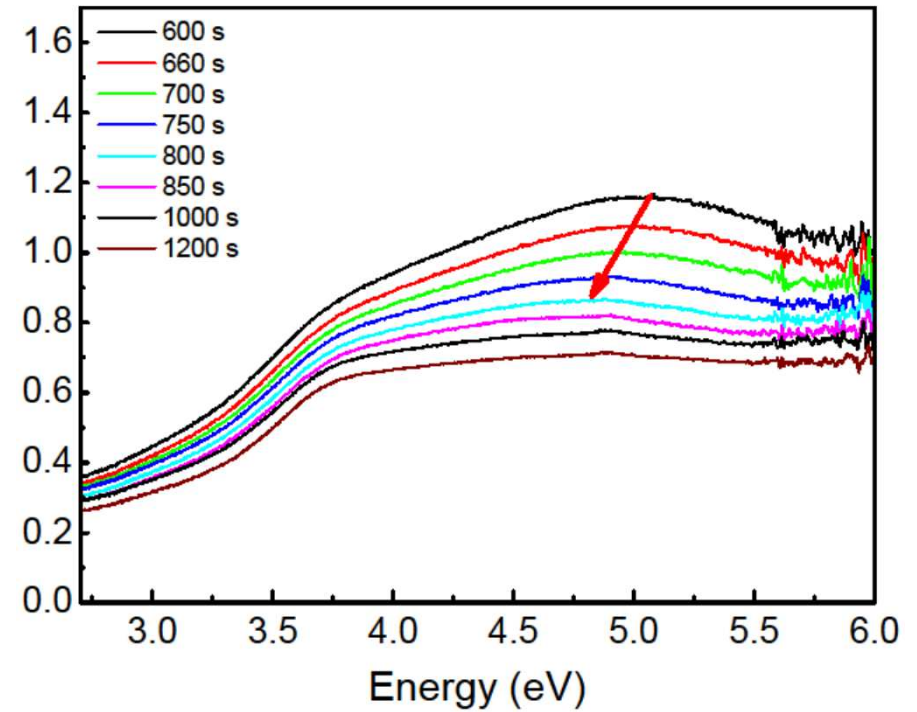


Misure OA online

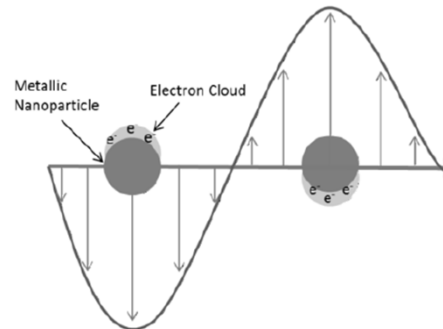
Durante l'ablazione



Dopo l'ablazione

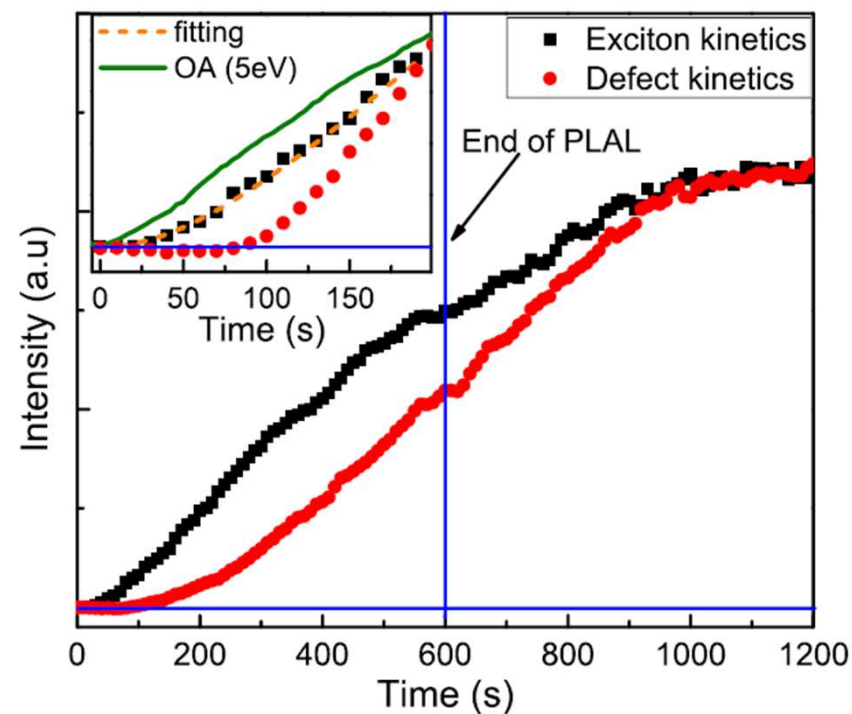
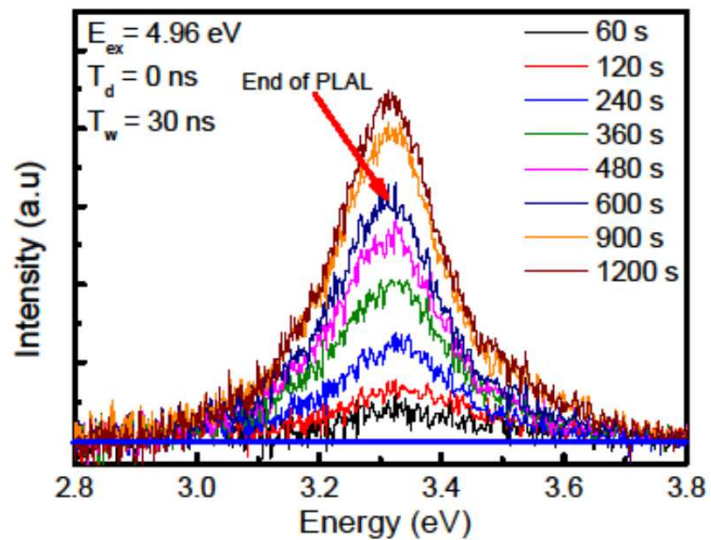
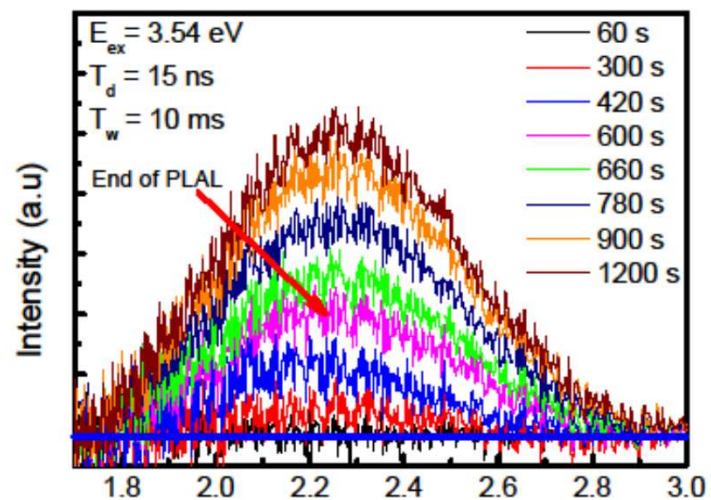


Edge ZnO :
Formazione di ZnO.

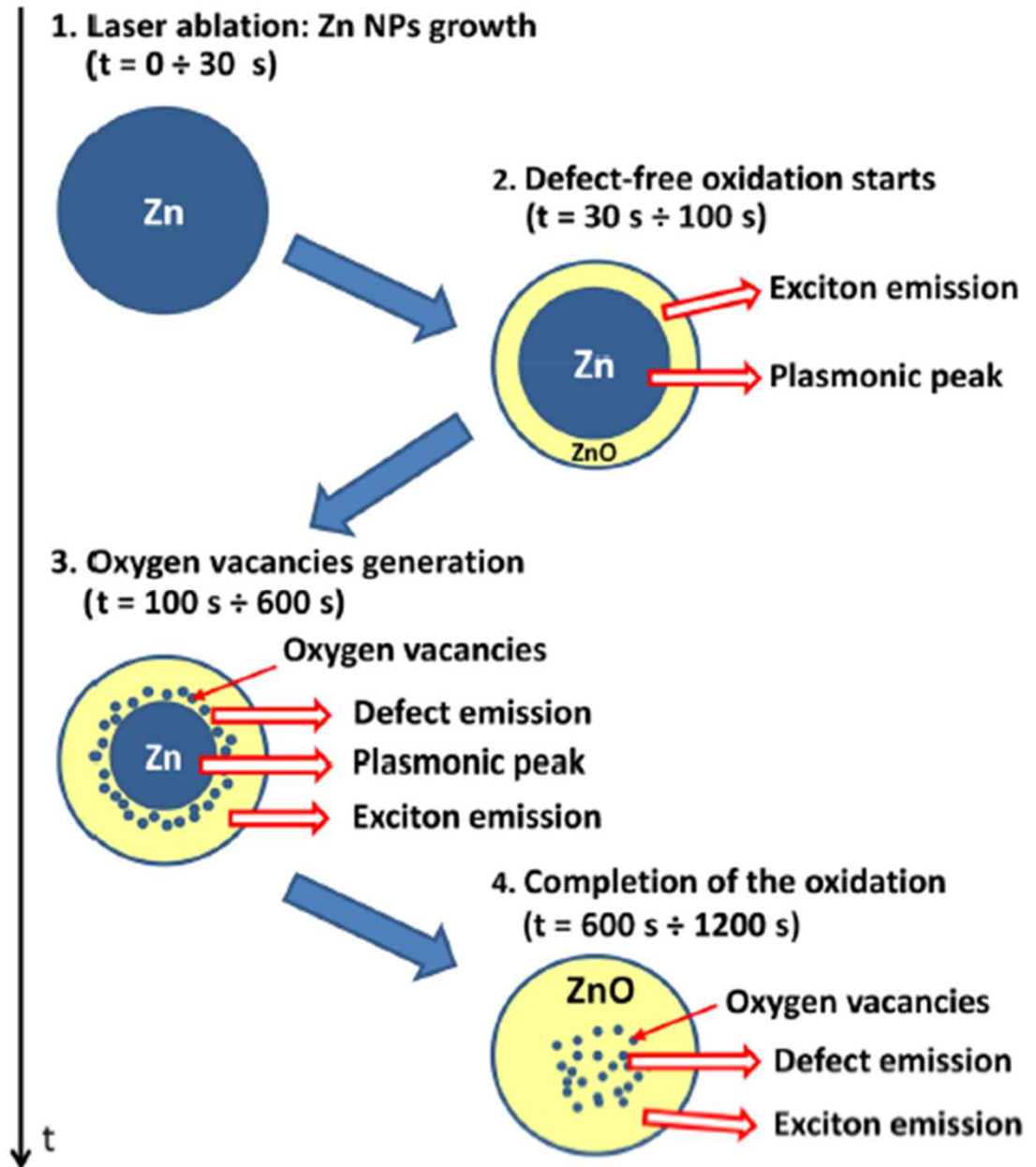


Plasmonic peak:
*oscillazione degli elettroni del metallo
Indotta dalla radiazione e.m.*

Misure PL online



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



MOJOTIC12 FESTIVAL
감사하십시오
Asante
choukran
bighmmi
you
Merci
ありがとう
obrigada
gracias
당신을 spasiba
grazie
arigato
Danke
thank

per la vostra attenzione!!!

