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# Ossidi per ottica ed elettronica: relazioni tra proprietà microscopiche ed applicazioni

# Sommario

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- > **Materiali ed applicazioni del  $\text{SiO}_2$**
- > **Preparativa e proprietà microscopiche**
- > **Conclusioni**

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- > **Materiali ed applicazioni del  $\text{SiO}_2$**
  - > **Preparativa e proprietà microscopiche**
  - > **Conclusioni**

# Applicazioni del $\text{SiO}_2$



**Vetri di alta purezza  
per applicazioni di  
ottica e fotonica**

**Fibre ottiche per  
telecomunicazioni  
e sensori**



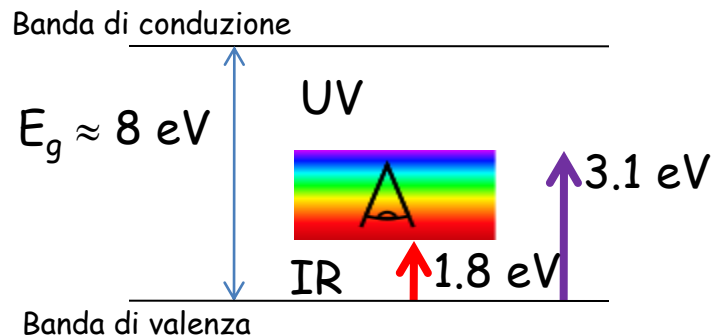
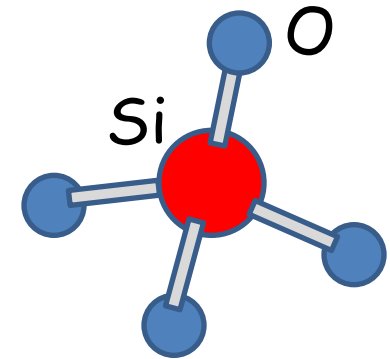
**Materiali isolanti in dispositivi  
MOS**

# I materiali di alta purezza

SiO<sub>2</sub> amorfa = Silice

(Contenuto di gruppi OH) ≤ 1000 ppm in peso

(Contenuto di altri elementi differenti da Si ed O) < ppm in peso



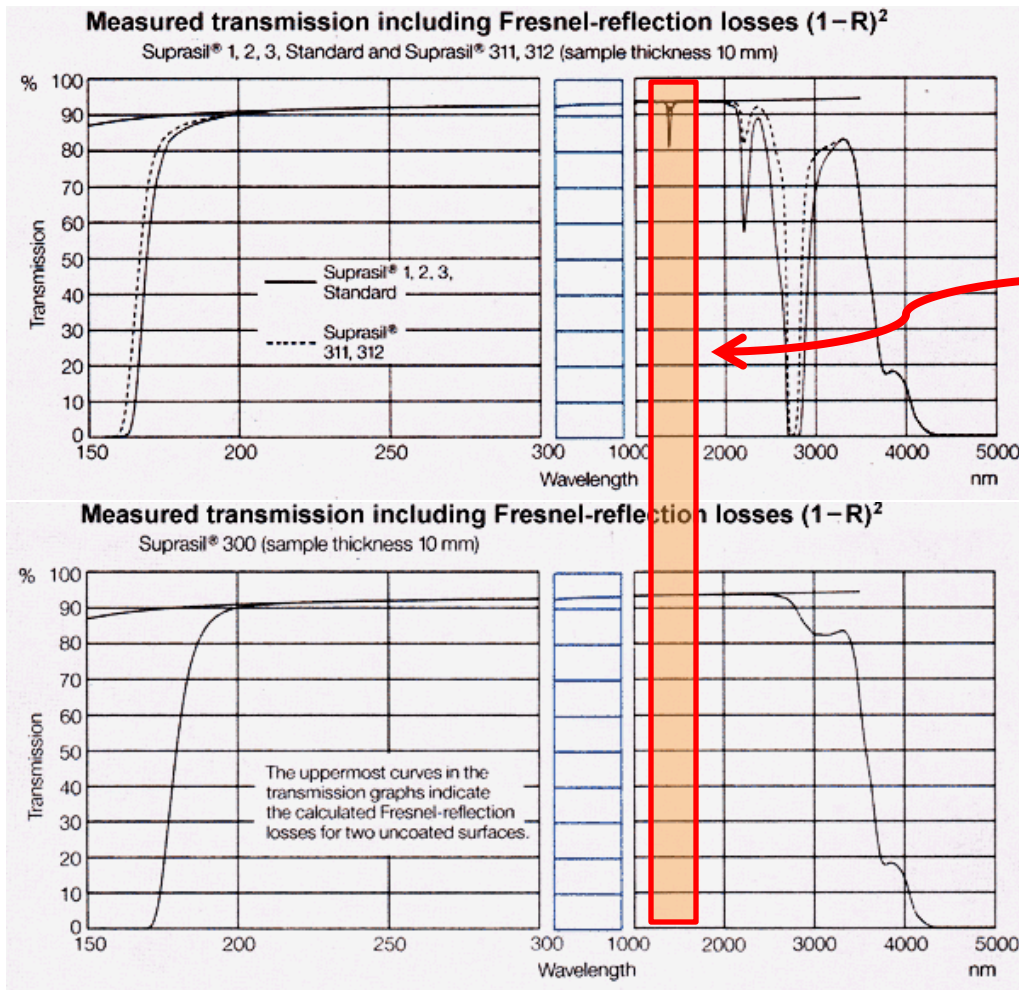
Indice di rifrazione  $n \approx 1.4 \div 1.6$

Elevata trasmissione nel visibile e nell'UV (>90%)

La presenza dei gruppi OH riduce la trasmissione nell'IR

Elevato potere isolante

# I materiali di alta purezza



# I materiali di alta purezza

Nelle fibre ottiche si utilizza  $\text{SiO}_2$

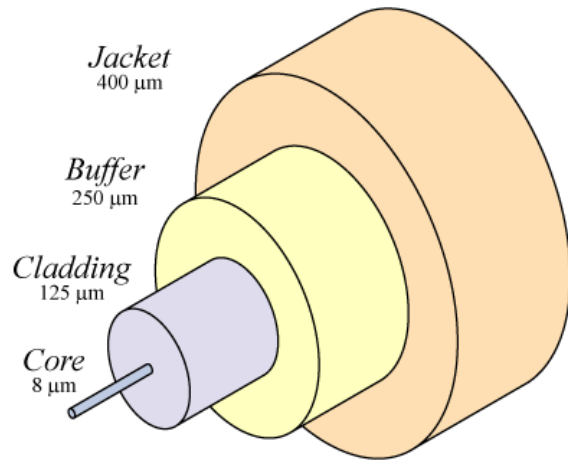
Tipicamente i segnali trasmessi sono in una regione di lunghezze d'onda corrispondente ad una delle seguenti "finestre per le telecomunicazioni":

- **Prima finestra**: 800–900 nm.
- **Seconda finestra** : lunghezze d'onda intorno a 1300 nm (1.3  $\mu\text{m}$ ).
- **Terza finestra** : lunghezze d'onda intorno a 1500 nm (1.5  $\mu\text{m}$ ).

Le perdite per assorbimento sono minime in quest'ultima regione, e sono disponibili amplificatori su fibra drogata con erbio che offrono la possibilità di estendere le distanze di trasmissione.

Band	Description	Wavelength range
O band	original	1260–1360 nm
E band	extended	1360–1460 nm
S band	short wavelengths	1460–1530 nm
C band	conventional ("erbium window")	1530–1565 nm
L band	long wavelengths	1565–1625 nm
U band	ultralong wavelengths	1625–1675 nm

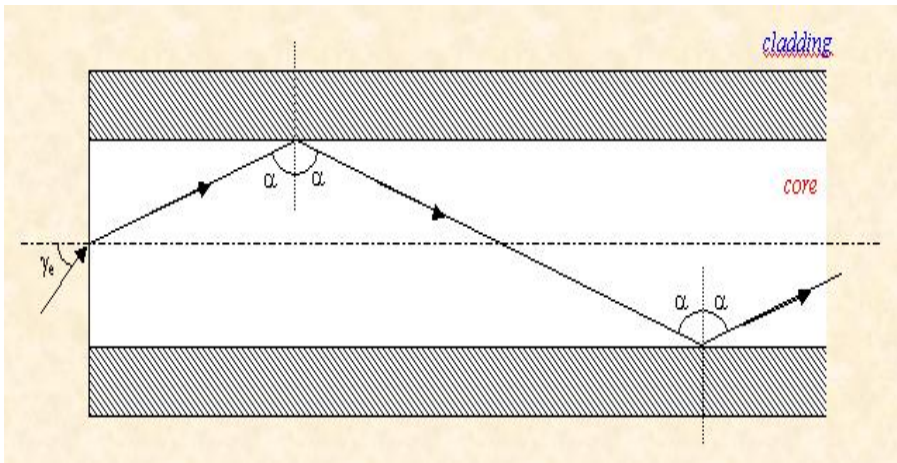
# Fibre ottiche



La trasmissione su OF è basata sul fenomeno della riflessione totale

$$n_{\text{core}} > n_{\text{cladding}}$$

$$\alpha > \alpha_{\text{limite}} = \arcsen(n_{\text{clad}} / n_{\text{core}})$$



Il valore dell'indice di rifrazione viene modificato attraverso l'inserimento di droganti (Ge, P, F, Cl) nel  $\text{SiO}_2$



# I materiali drogati



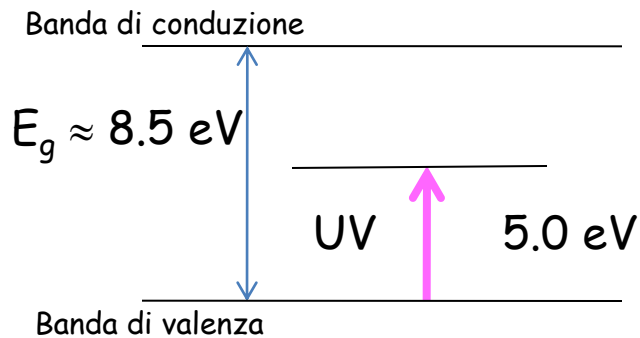
Contenuto di Ge ~1÷10%

Disperso e sostituzionale

Explore the **physics** of the chemical elements through this periodic table

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period	1	2																2	
1	H																		He
2	Li	Be											5	6	7	8	9	10	
3	Na	Mg											B	C	N	O	F	Ne	
4	K	Ca											13	14	15	16	17	18	
5	Rb	Sr											Al	Si	P	S	Cl	Ar	
6	Cs	Ba	*										21	22	23	24	25	26	
7	Fr	Ra	**										Sc	Ti	V	Cr	Mn	Fe	
													39	40	41	42	43	44	
													Y	Zr	Nb	Mo	Tc	Ru	
													71	72	73	74	75	76	
													Lu	Hf	Ta	W	Re	Os	
													103	104	105	106	107	108	
													Lr	Rf	Db	Sg	Bh	Hs	
													109	110	111	112	113	114	
													Uuo	Uut	Uuq	Uup	Uuh	Uus	
													57	58	59	60	61	62	
													La	Ce	Pr	Nd	Pm	Sm	
													89	90	91	92	93	94	
													Ac	Th	Pa	U	Np	Pu	
													95	96	97	98	99	100	
													Am	Cm	Bk	Cf	Es	Fm	
													101	102	103	104	105	106	
													Md	No	Lr				

\*Lanthanoids  
\*\*Actinoids



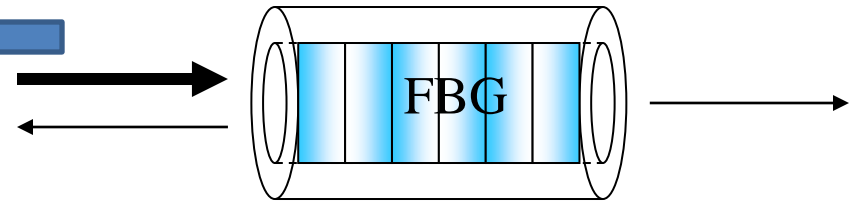
Introduzione di livelli energetici spuri all'interno della gap

**Fotosensibilità:** variazioni dell'indice di rifrazione indotte da esposizione a luce laser

$$\Delta n \approx 10^{-4} \div 10^{-3}$$

# Fiber Bragg Grating

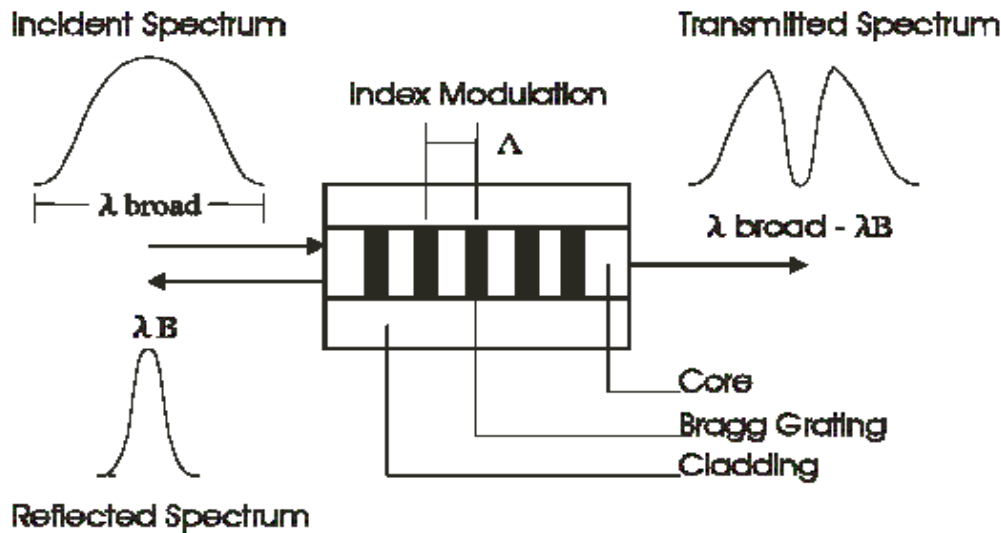
Un reticolo di Bragg in fibra è una perturbazione periodica o pseudo-periodica dell'indice di rifrazione del core di una fibra ottica



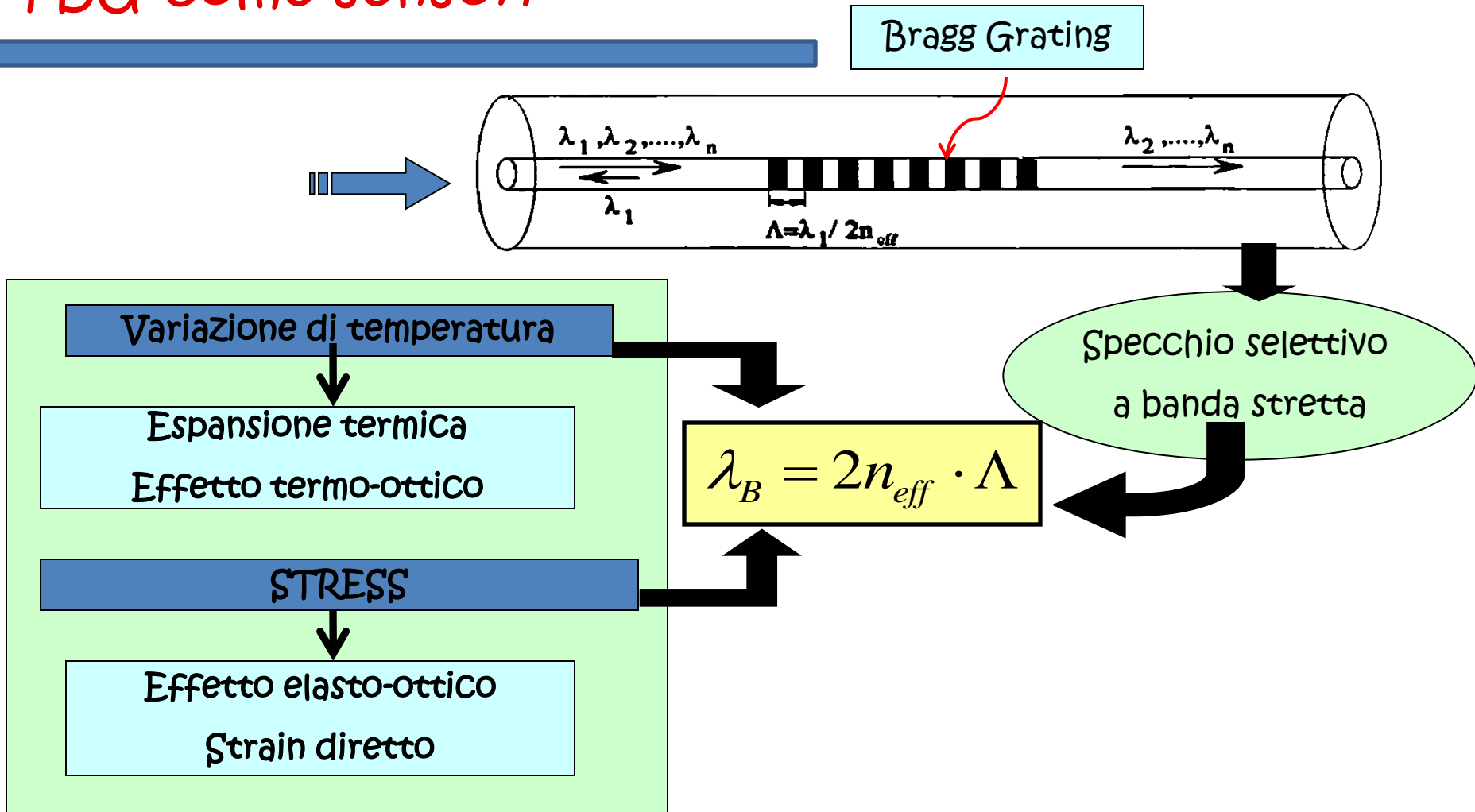
Un FBG è un filtro spettrale selettivo che riflette una banda della radiazione in ingresso intorno alla lunghezza d'onda di Bragg

$$\lambda_{\text{Bragg}} = 2n\Lambda$$

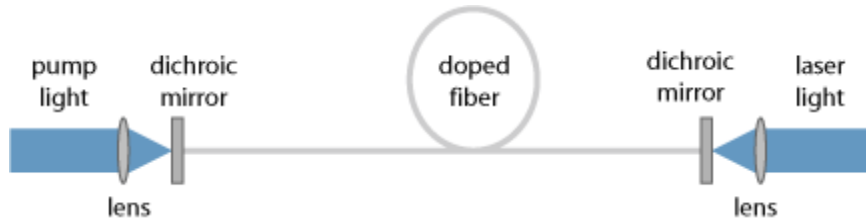
Es. :  $\lambda_{\text{B}} = 1.5 \mu\text{m}$  per  $\Lambda = 0.5 \mu\text{m}$



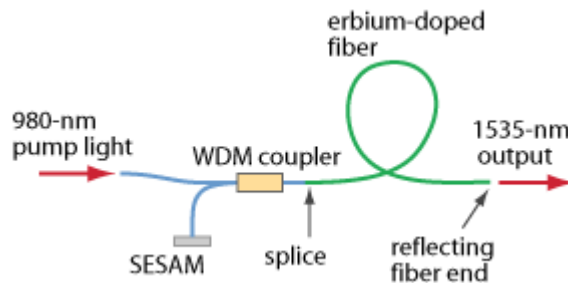
# FBG come sensori



# Fiber Lasers



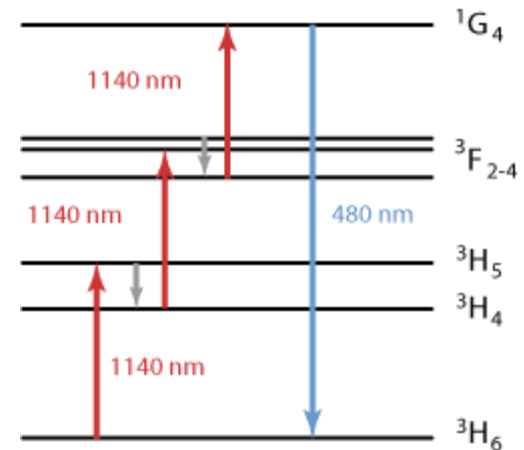
Setup of a simple fiber laser. Pump light is launched from the left-hand side through a dichroic mirror into the core of the doped fiber. The generated laser light is extracted on the right-hand side



A simple erbium-doped femtosecond laser, where the Fresnel reflection from a fiber end is used for output coupling

I Fiber lasers ( $P = 1 \text{ mW} \div 100 \text{ W}$ ) impiegano fibre ottiche come mezzo attivo

Si utilizza una fibra di  $\text{SiO}_2$  drogata con ioni delle terre rare come **erbio** ( $\text{Er}^{3+}$ ), **neodimio** ( $\text{Nd}^{3+}$ ), **itterbio** ( $\text{Yb}^{3+}$ ), **tulio** ( $\text{Tm}^{3+}$ ), o **praseodimio** ( $\text{Pr}^{3+}$ ), ed impiegando diodi laser per il pompaggio

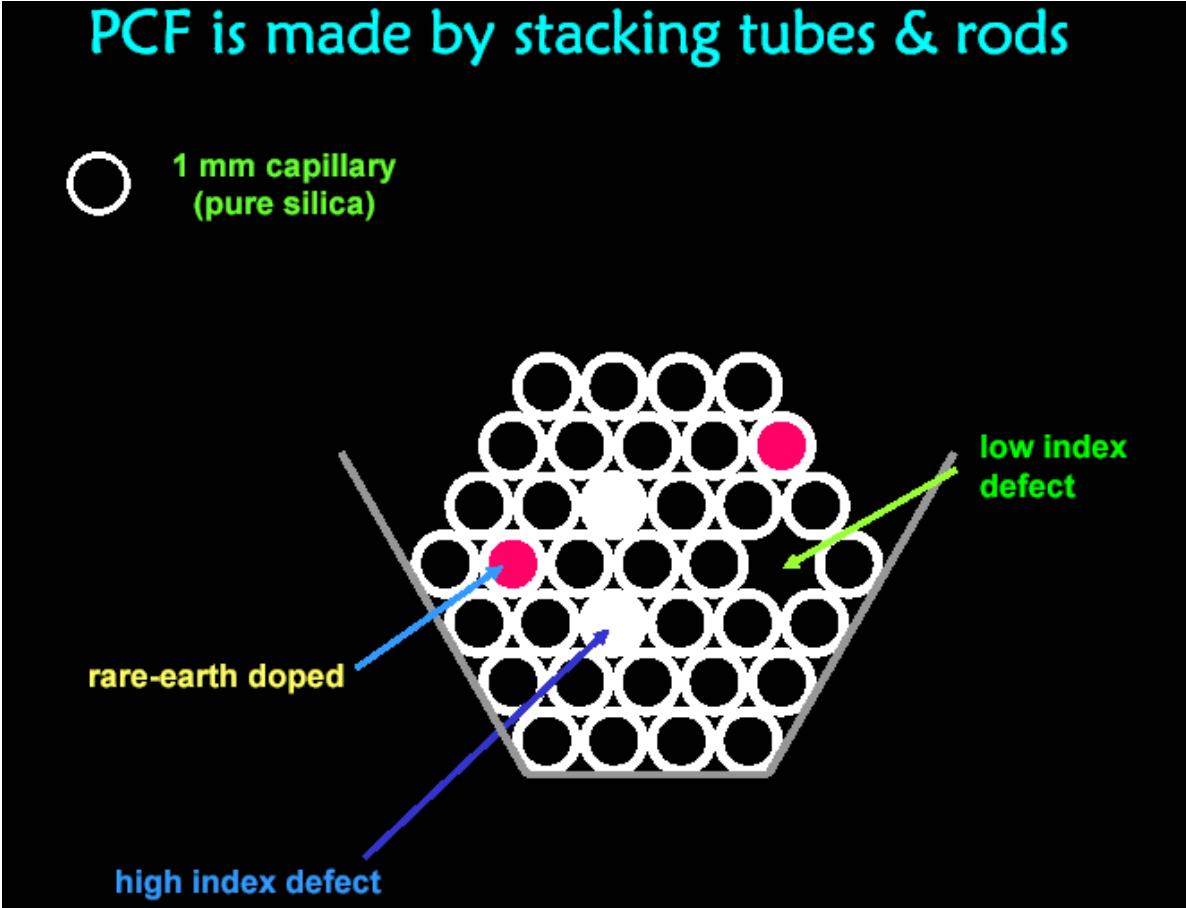


Level scheme of thulium ( $\text{Tm}^{3+}$ ) ions in ZBLAN fiber, showing how excitation with an 1140-nm laser can lead to blue fluorescence and laser emission

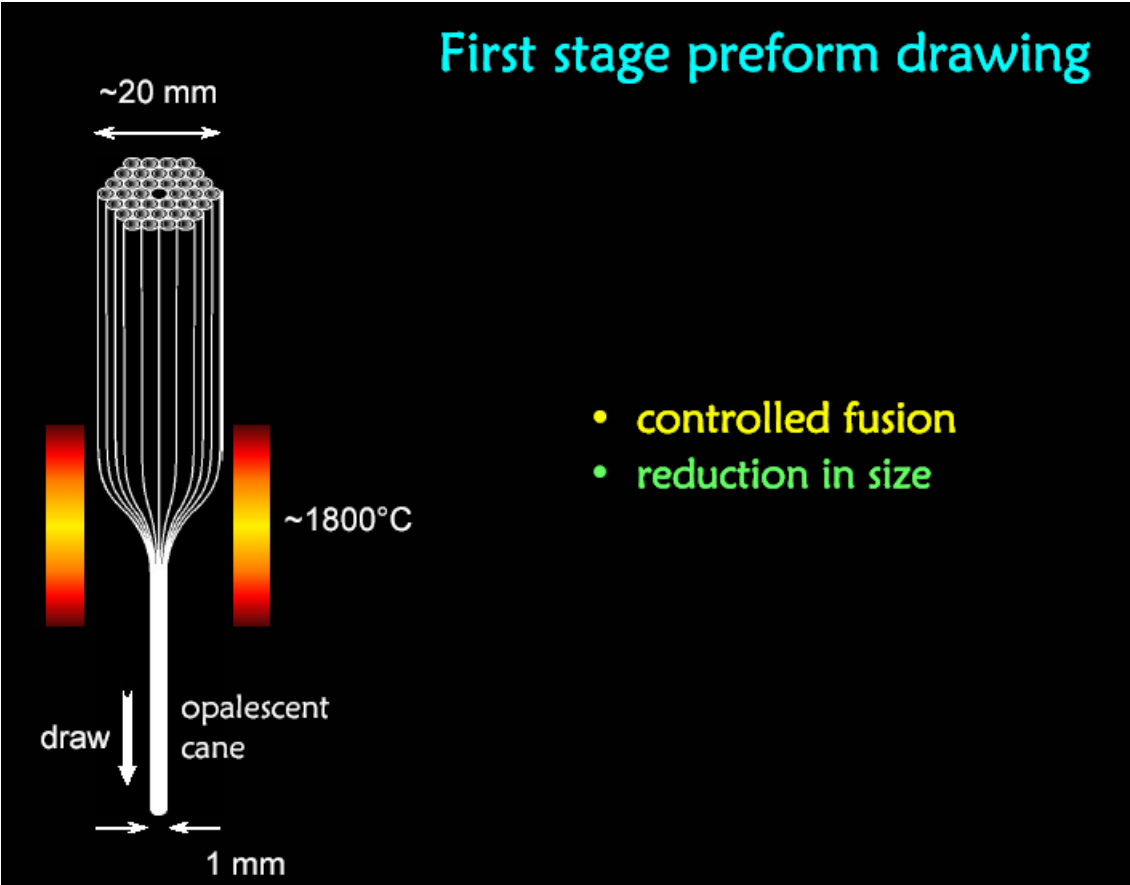
# Fiber Lasers

Ion	Common host media	Important emission wavelengths
<a href="#">neodymium</a> (Nd <sup>3+</sup> )	YAG, <a href="#">YVO<sub>4</sub></a> , <a href="#">YLF</a> , <a href="#">silica</a>	1.03–1.1 μm, 0.9–0.95 μm, 1.32–1.35 μm
<a href="#">ytterbium</a> (Yb <sup>3+</sup> )	YAG, <a href="#">tungstates</a> , <a href="#">silica</a>	1.0–1.1 μm
erbium (Er <sup>3+</sup> )	YAG, <a href="#">silica</a>	1.5–1.6 μm, 2.7 μm, 0.55 μm
thulium (Tm <sup>3+</sup> )	YAG, <a href="#">silica</a> , <a href="#">fluoride</a> glasses	1.7–2.1 μm, 1.45–1.53 μm, 0.48 μm, 0.8 μm
holmium (Ho <sup>3+</sup> )	YAG, YLF, <a href="#">silica</a>	2.1 μm, 2.8–2.9 μm
praseodymium (Pr <sup>3+</sup> )	<a href="#">silica</a> , fluoride glasses	1.3 μm, 0.635 μm, 0.6 μm, 0.52 μm, 0.49 μm
cerium (Ce <sup>3+</sup> )	YLF, LiCAF, LiLuF, LiSAF, and similar fluorides	0.28–0.33 μm

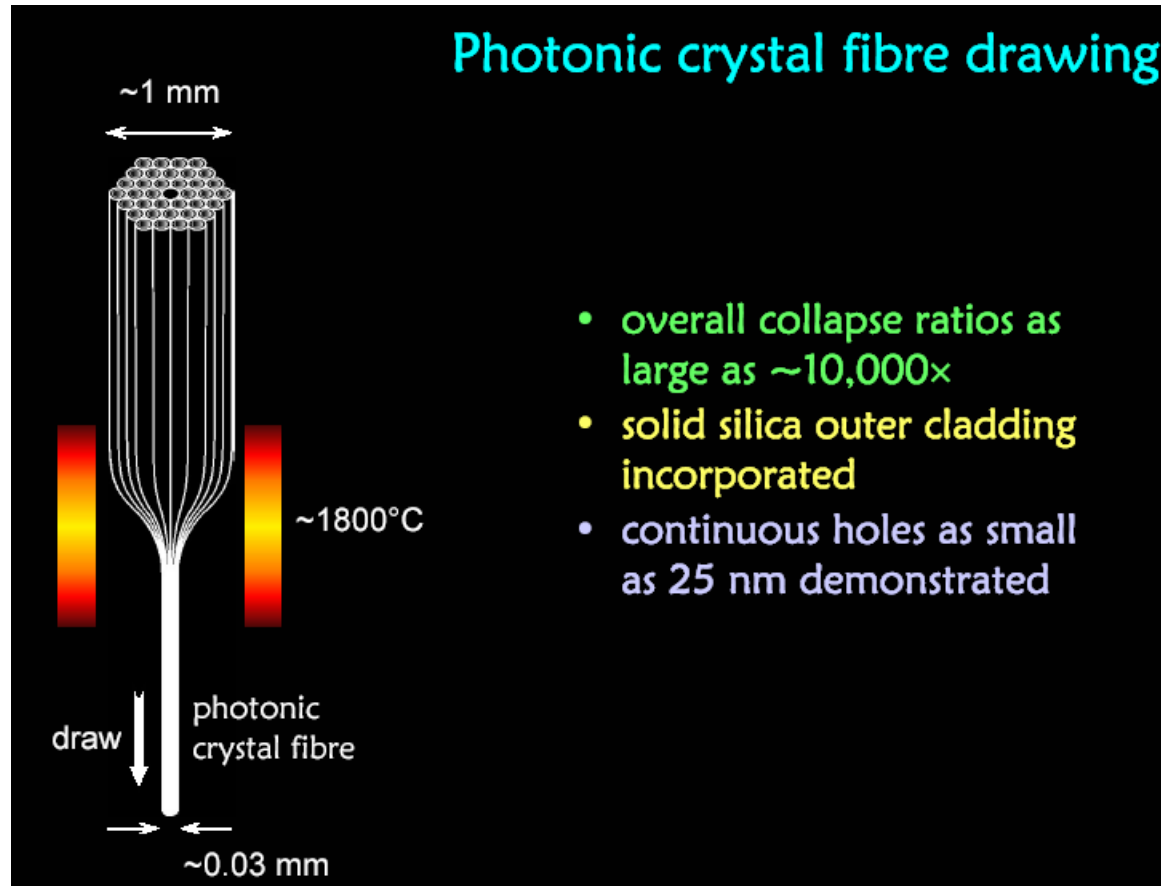
# Photonic crystal fibers: PCF



# Photonic crystal fibers: PCF

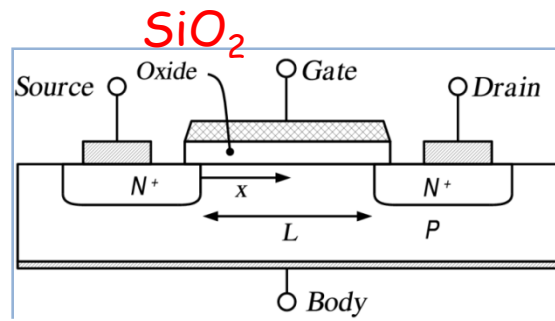


# Photonic crystal fibers: PCF





# MOS

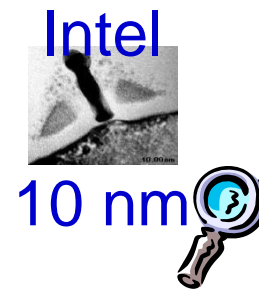
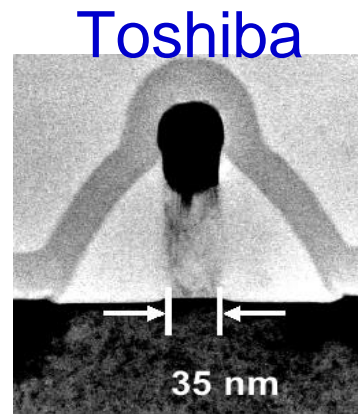
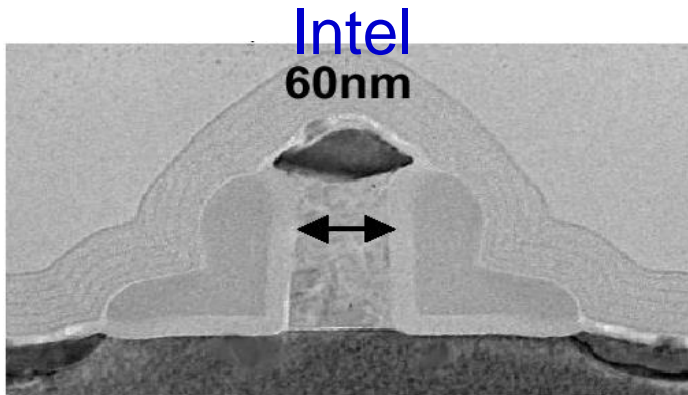


FET

- > La purezza e la stechiometria del  $\text{SiO}_2$  condizionano l'uso del materiale
- > La presenza di trappole di carica (*difetti di punto*) nell'ossido di gate ne modifica le proprietà dielettriche e causa il malfunzionamento del dispositivo.
- > Fasi di produzione o esposizione a radiazioni ionizzanti (UV, raggi X,  $\gamma$ ,  $\beta$ ) inducono trappole di carica

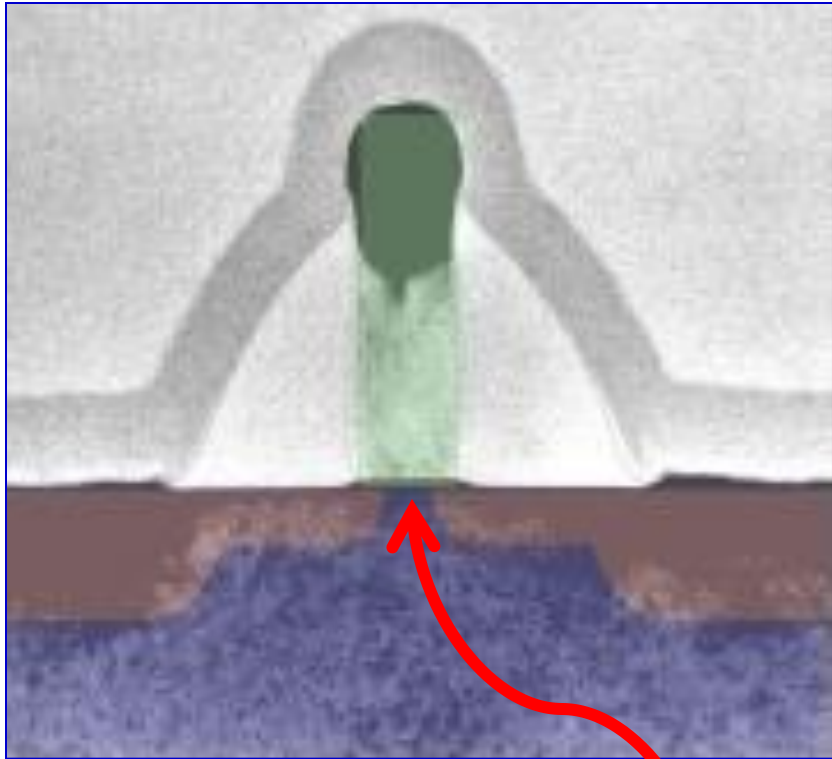
# MOS

## Miniaturizzazione



# MOS

## Miniaturizzazione



La miniaturizzazione dei componenti ha portato alla costruzione di strati di  $\text{SiO}_2$  (isolante del gate nei MOSFET) dello spessore di pochi nm

$\text{SiO}_2$

I MOSFET con lunghezze di canale molto minori del micrometro sono una sfida per la tecnologia. Negli anni recenti si è arrivati a poche decine di nanometri (35 nm) creando problemi operativi

### PROBLEMI

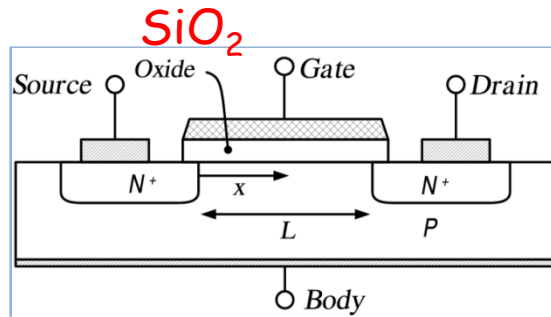
#### Conduzione sotto soglia maggiore

A causa delle ridotte dimensioni, il voltaggio che può essere applicato al gate deve essere ridotto

#### Aumento delle perdite gate-ossido

L'ossido di gate, che funge da isolante tra gate e canale, dovrebbe essere reso il più sottile possibile per aumentare la conducibilità nel canale e le prestazioni del transistor.

Tuttavia, con l'attuale spessore dell'ossido di gate in  $\text{SiO}_2$  (circa 1.2 nm, che in atomi di silicio è pari a  $\sim 5$  atomi) il fenomeno quantistico di effetto tunnel di elettroni che si verifica tra il gate ed il canale provoca un aumento del consumo di energia.



FET



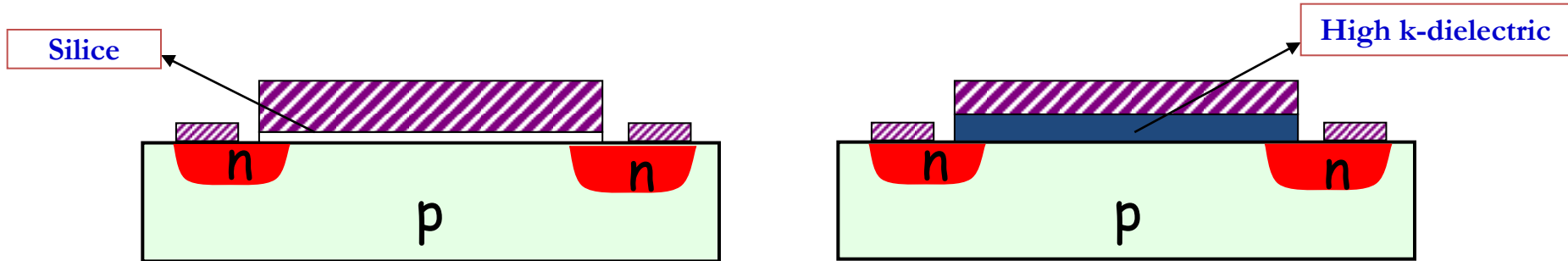
# MOS

## Miniaturizzazione

$$I_D = \mu_n C_{ox} \frac{W}{L} (V_{GS} - V_T - \frac{V_{DS}}{2}) V_{DS}$$

Il MOSFET è un elemento capacitivo

$$C_{ox} = k \frac{\epsilon_0 A}{t}$$



$$C_{SiO_2} = 3.9 \frac{\epsilon_0 A}{t_S}$$

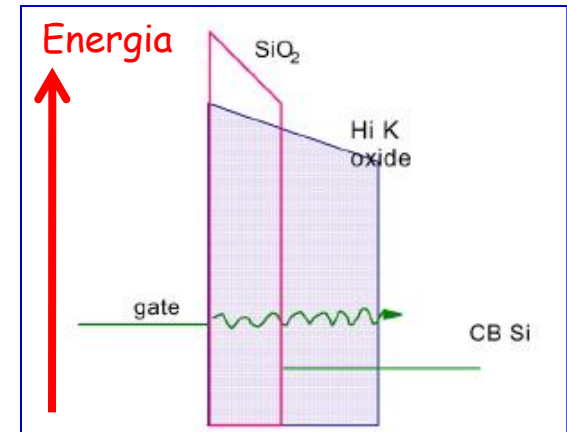
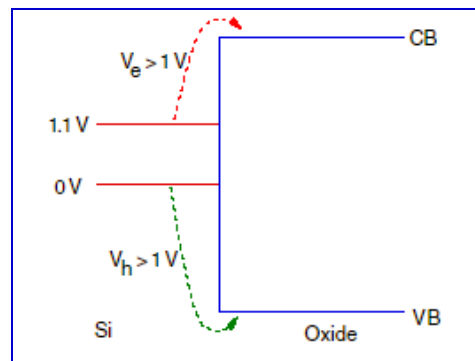
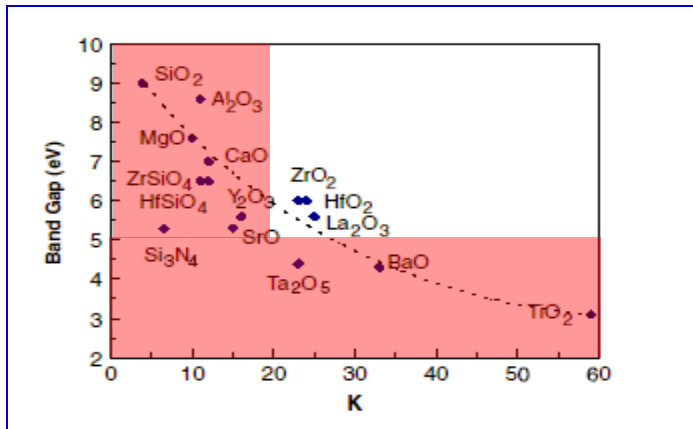
$$C_{SiO_2} = C_{H-k}$$

$$C_{H-k} = k \frac{\epsilon_0 A}{t_H}$$

# MOF

## MOSFET a dimensione ridotta

Isolanti che hanno una costante dielettrica più grande del biossido di silicio (denominati dielettrici ad alta-k), come metallo-silicati del gruppo IV, ad esempio silicati di afnio o di zirconio, ed ossidi di afnio o zirconio (afnia e zirconia) sono utilizzati per ridurre le perdite del gate nella tecnologia dai 45 nanometri in poi. Aumentare la costante dielettrica del dielettrico di gate consente di aumentarne lo spessore, pur mantenendo un'alta capacità fissate tutte le altre geometrie. Un più alto spessore dielettrico riduce la corrente di tunneling attraverso il dielettrico tra il gate e il canale.



In base alla stabilità termodinamica HfO<sub>2</sub> è risultato il materiale più adatto sul Si

I difetti nel materiale creano livelli energetici elettronici all'interno della gap

Le cariche che vi si intrappolano possono cambiare la  $V_T$

I difetti possono indurre instabilità temporale dei dispositivi

I difetti possono fare da precursori per il "breakdown"

Le cariche intrappolate possono divenire centri di scattering per gli elettroni in transito nel canale

## Pulsed ion-beam induced nucleation and growth of Ge nanocrystals on $\text{SiO}_2$

N. P. Stepina,<sup>9)</sup> A. V. Dvurechenskii, V. A. Armbrister, V. G. Kesler, P. L. Novikov, A. K. Gutakovskii, V. V. Kirienko, and Zh. V. Smagina  
Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, prosp.ekt Lavrent'eva 13, 630090 Novosibirsk, Russia

R. Groetzschel  
Forschungszentrum Rossendorf, D-01328 Dresden, Germany

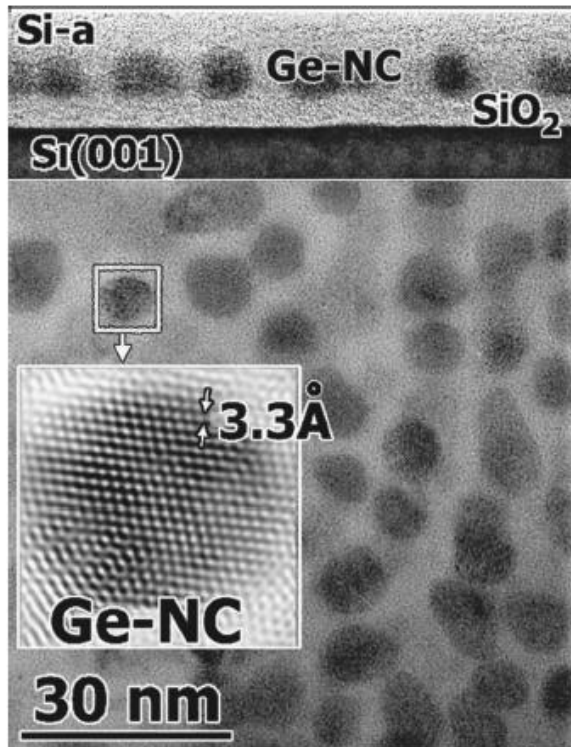


FIG. 2. HREM image (upper part, cross section; lower part, plan view) of nanocrystals on  $\text{SiO}_2$   $J_{\text{Ge}}=0.08$  ML/s,  $T=250$  °C.

Nanocrystals (NCs) in a dielectric matrix have attracted much attention as a promising candidate for a charging nodes in a single-electron memory device (SEMD). An advantage of the nanofloating gate memory over the continuous floating gate is its improved endurance due to preventing lateral charge movement. Faster writing/erasing time, lower operating voltage, and longer retention time have been demonstrated in memory device based on Si NCs embedded in  $\text{SiO}_2$ .<sup>1,2</sup> Recently, King *et al.* showed that Ge-based SEMD has the superior properties over Si-based SEMD in terms of the writing/erasing time and the operating voltage.<sup>3</sup> Since then different methods were used for fabrication of Ge NCs in dielectric matrix, such as ion-beam synthesis,<sup>4</sup> oxidation and reduction of Ge/Si NCs,<sup>5</sup> rapid thermal annealing of cosputtered,<sup>6</sup> molecular beam epitaxy deposited,<sup>7</sup> and chemical-vapor deposited<sup>3</sup> layers, and pulsed-laser deposition.<sup>8</sup> However, space distribution of NCs within dielectric created by most of these techniques is random. To suppress the tunneling distance fluctuation, one should form in-plane distribution of NCs. Moreover, when using NCs for charge storage devices, the general requirements that can be placed upon the control are the size of NCs and their density and homogeneity in growth plane. That is the problem for most of the above-mentioned growth methods. Our prelimi-



# Nanostrutture in $\text{SiO}_2$ : Semiconduttori

Il campo di ricerca delle nanostrutture (**cluster**) in silice e di silice si è rivelato promettente nella tecnologia delle telecomunicazioni e dei dispositivi su scala quantistica per applicazioni ottiche non-lineari.

Il piccolo numero di atomi che formano i cluster e la rilevante frazione di atomi sulla superficie del cluster rendono questi oggetti intrinsecamente differenti dalla fase bulk in termini sia di proprietà fisiche sia chimiche.

Per esempio, il valore della regione di energie proibite (**gap**) tra banda di valenza e di conduzione può essere modulato attraverso la variazione delle dimensioni dei cluster. Questa è una manifestazione dell'effetto di confinamento quantistico che avviene quando il diametro del cluster è minore delle dimensioni del raggio di Bohr (**raggio atomo idrogenoide**) dell'eccitone libero: tipicamente qualche nm.

Questi sistemi sono usualmente riferiti come *punti quantici* (**quantum dots**). In linea di principio, le proprietà fisiche del sistema nanostrutturato possono essere regolate finemente ed adattate per ottenere materiali con caratteristiche predefinite

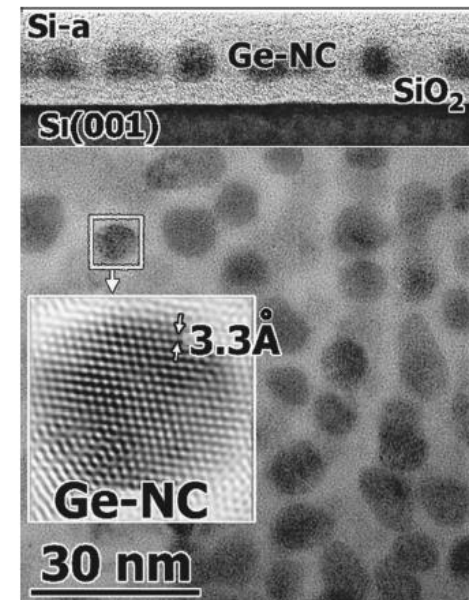


FIG. 2. HREM image (upper part, cross section; lower part, plan view) of nanocrystals on  $\text{SiO}_2$   $J_{\text{Ge}}=0.08$  ML/s,  $T=250$  °C.

# Nanostrutture in $\text{SiO}_2$ : Isolanti

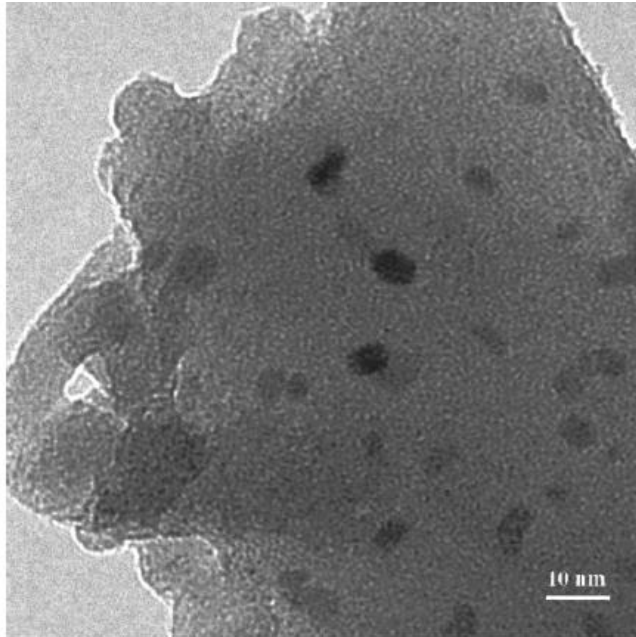


FIG. 1. TEM image of tin dioxide nanoclusters dispersed in  $\text{SiO}_2$  in a glass-ceramic sample prepared by the sol-gel technique.

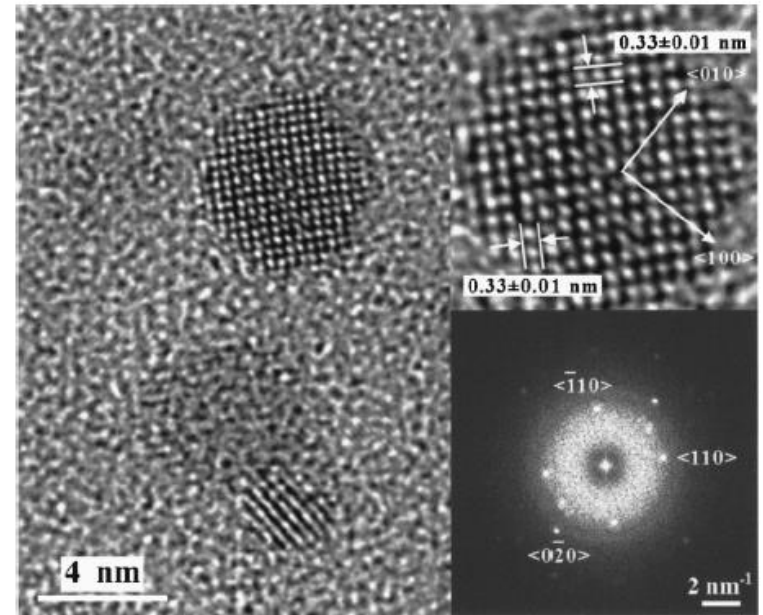
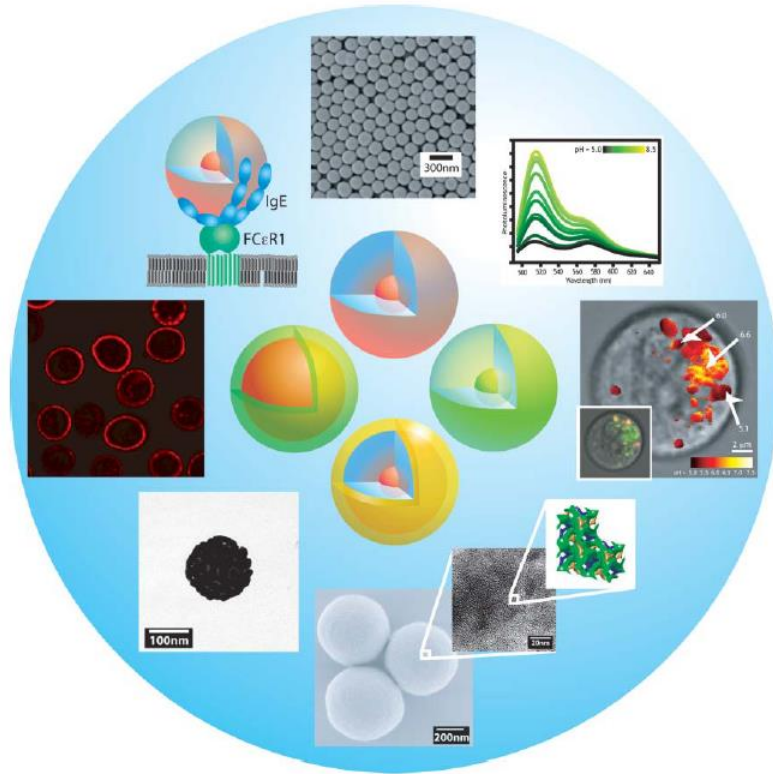
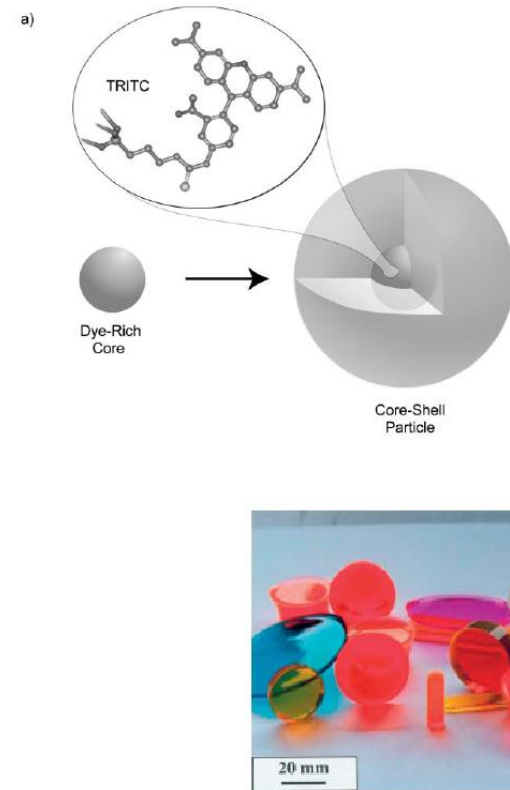


FIG. 2. HRTEM images of 2 mol %  $\text{SnO}_2$ -doped silica, showing the structural features of the crystalline nanophase; the upper inset shows a magnification of the image of a single  $\text{SnO}_2$  dot 5.6 nm in diameter in (001) projection with the measured lattice parameters; the lower inset shows the corresponding ED pattern.

# Nanostrutture di $\text{SiO}_2$



**Fig. 1** An overview of the versatility of the fluorescent core-shell silica nanoparticle platform: illustrations of single and dual-emission particles as well as gold-nanoshell encapsulated core-shell particles are shown at the heart of the figure, while a variety of applications including bioimaging, drug delivery, sensing and therapeutics are shown in the periphery.



**Fig. 1.** Hybrid organic-inorganic materials containing organic chromophores prepared at the Laboratoire de Physique de la Matière Condensée (Ecole Polytechnique) [10].

- 
- > **Materiali ed applicazioni del  $\text{SiO}_2$**
  - > **Preparativa e proprietà microscopiche**
  - > **Conclusioni**



a tetravalent metalloid, more reactive than germanium, the metalloid directly below it in the table. Controversy about silicon's character dates to its discovery. It was first prepared and characterized in pure form in 1823. In 1808, it was given the name silicium (from Latin: *silex*, hard stone or flint), with an **-ium** word-ending to suggest a **metal**, a name which the element retains in several languages. The present English name was first suggested in 1817 to conform with the physically similar elements, **carbon** and **boron**.

Silicon is the eighth most **common element** in the universe by mass, but very rarely occurs as the pure free element in the Earth's crust. It is most widely distributed in **dusts**, **sands**, **planetoids**, and **planets** as various forms of **silicon dioxide** (silica) or **silicates**. Over 90% of the Earth's crust is composed of **silicate minerals**, making silicon the **second most abundant element** in the Earth's crust (about 28% by mass) after **oxygen**.<sup>[9]</sup>

Most silicon is used commercially without being separated, and often with little processing of the natural minerals. Such use includes industrial construction with **clays**, **silica sand**, and **stone**. Silicate is used in **Portland cement** for mortar and **stucco**, and mixed with silica sand and **gravel** to make **concrete** for walkways, foundations, and roads. Silicates are used in whiteware **ceramics** such as **porcelain**, and in traditional **quartz-based soda-lime glass** and many other specialty **glasses**. Silicon

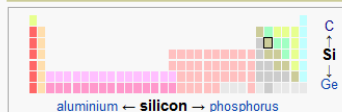


Spectral lines of silicon

### General properties

<b>Name, symbol</b>	silicon, Si
<b>Appearance</b>	crystalline, reflective with bluish-tinged faces
<b>Pronunciation</b>	<i>/ˈsɪlɪkən/ or /ˈstɪlɪkən/</i> <i>SIL-ə-ken or SIL-ə-kon</i>

### Silicon in the periodic table



<b>Atomic number (Z)</b>	14
<b>Group, block</b>	group 14 (carbon group), p-block

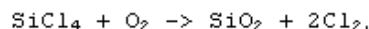
# Il biossido di silicio amorfo: $\alpha$ -SiO<sub>2</sub>, o silice

## Silice

Da Wikipedia, l'enciclopedia libera.

La **silice** /silice/ (o anche **anidride silicica**, IUPAC **biossido di silicio**) è un composto del **silicio** la cui formula chimica è SiO<sub>2</sub>.

La silice purissima per applicazioni ad alta tecnologia viene ottenuta dalla reazione in fiamma fra il **tetracloruro di silicio** e l'**ossigeno**




e a seconda del contenuto finale di gruppi OH, la silice viene comunemente distinta in silice dry e silice wet (rispettivamente, basso o elevato contenuto di gruppi OH).

Pura, è una polvere cristallina bianca che impartisce all'acqua una lieve **acidità**: una **sospensione** di 40 g in un litro di acqua ha **pH** compreso tra 3,7 e 4,7.

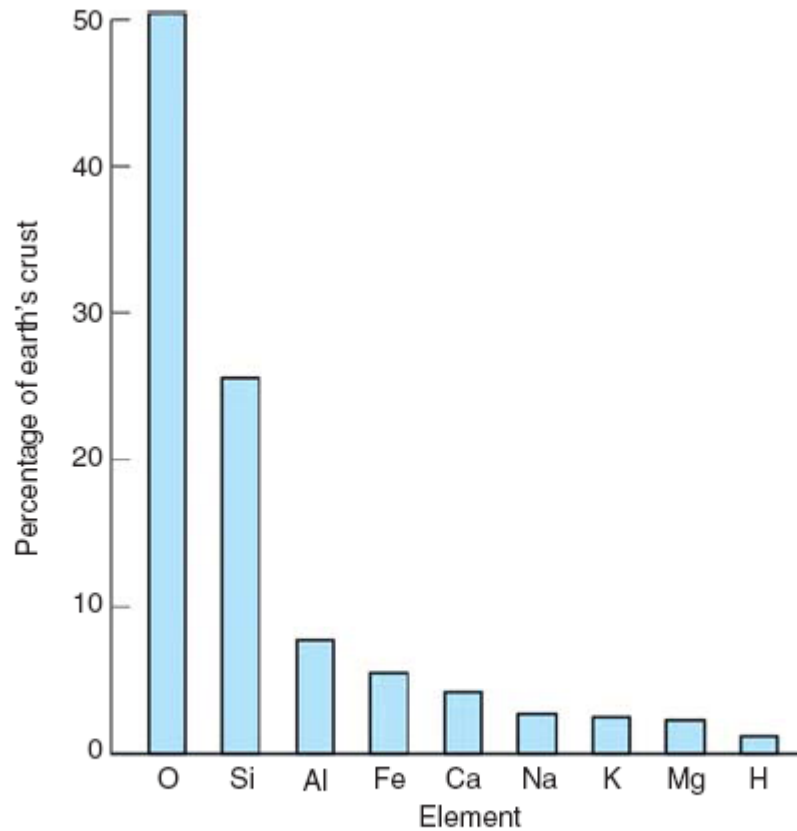
Lo stato fisico più comune in natura è quello solido cristallino, in **minerali** come il **quarzo** e i suoi **polimorfi**, e più raramente quello amorfo, come nell'**opale**; la silice cristallina è il costituente principale di diverse **rocce sedimentarie** (ad es. **sabbia**, **radiolariti**, **quarzareniti** e **pelle di leopardo**). Talvolta si rinviene cristallizzata da fluidi di segregazione all'interno di **rocce metamorfiche** e **magmatiche** e all'interno di **rocce carbonatiche** sotto forma di **selce** di origine **metasomatica**.

Moltissimi animali e piante utilizzano la silice presente come ione silicato sia nell'acqua dolce sia in quella salata purché al di sotto dei 18 °C. Le **diatomee**, i **radiolari**, le **spugne** silicee, moltissimi **cereali** ed altre piante come la **canna da zucchero** e l'**equiseto** utilizzano questo materiale come impalcatura per lo sviluppo di strutture scheletriche.

Esistono comunque anche 15 **solidi cristallini** composti esclusivamente di silice, tra i quali il più famoso è certamente il **quarzo** o le sue forme di alta e altissima temperatura **tridimite** e **crystalite**, oltre a solidi criptocristallini quali il **calcedonio**.

Silice	
	
Nome IUPAC	
diossido di silicio	
Caratteristiche generali	
Formula bruta o molecolare	SiO <sub>2</sub>
Peso formula (u)	60,08
Aspetto	solido cristallino bianco
Numero CAS	[7631-86-9]
Proprietà chimico-fisiche	
Densità (g/cm <sup>3</sup> , in c.s.)	2,2
Solubilità in acqua	0,15 g/l a 298 K
Temperatura di fusione (K)	1999 (1726 °C)
Proprietà termochimiche	
$\Delta_f H^0$ (kJ·mol <sup>-1</sup> )	-910,7
$\Delta_f G^0$ (kJ·mol <sup>-1</sup> )	-856,3
$S_m^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	41,5
$C_{p,m}^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	44,4

# Il biossido di silicio amorfo: $\alpha\text{-SiO}_2$ , o silice



**Fig. 1** The relative abundance of elements in the earth's crust illustrates the common availability of quartz and the silicas [1]

# Il biossido di silicio amorfo: $\alpha\text{-SiO}_2$ , o silice

• Batteriologicamente pura alla sorgente • Oligominerale NAT

ANALISI CHIMICA E CHIMICO FISICA  
UNIVERSITÀ DEGLI STUDI DI CATANIA  
DIPARTIMENTO DI IGIENE E SANITÀ  
DETERMINAZIONI CHIMICO-FISICHE  
EVALUTAZIONI CHIMICHE DIVERSE

UNIVERSITY STUDY CATANIA  
CHEMICAL ANALYSIS

Temperatura dell'acqua	11,6°C	Water temp. at spring	11,6°C
Cond. Elest. Spec. A 20°C (k20)	100uS/cm <sup>-1</sup>	Conductivity 20°C	100uS/cm <sup>-1</sup>
(Ph)	6,6	(Ph)	6,6
Residuo fisso a 180°	70 mg/l	Residue 180°	70 mg/l
Azoto ammoniacale	<0,03 mg/l	Ammonium	<0,03 mg/l
Nitriti (NO <sub>2</sub> )	<0,002 mg/l	Nitrites (NO <sub>2</sub> )	<0,002 mg/l
Nitrati (NO <sub>3</sub> )	2,70 mg/l	Nitrates (NO <sub>3</sub> )	2,70 mg/l

Gas disciolti in un litro d'acqua  
Anidride carbonica libera (CO<sub>2</sub>) 0,016 g/l  
Ossidabilità (O<sub>2</sub>) 1,40 mg/l

Dissolved gas per litre of water  
Carbon dioxide at the source (CO<sub>2</sub>) 0,016 g/l  
Oxidability (O<sub>2</sub>) 1,40 mg/l

Sostanze disciolte in un litro d'acqua


CALCIO	CA <sup>++</sup>	3,60 mg/l
SODIO	NA <sup>+</sup>	0,013 g/l
MAGNESIO	Mg <sup>++</sup>	4,60 mg/l
POTASSIO	K <sup>+</sup>	0,23 mg/l
BICARBONATI	HCO <sub>3</sub>	42,70 mg/l
SOLFATI	SO <sub>4</sub>	4,86 mg/l
CLORURI	CL	3,90 mg/l
SILICE	SiO <sub>2</sub>	26,43 mg/l

Mineral content per litre

CALCIUM	CA <sup>++</sup>	3,60 mg/l
SODIUM	NA <sup>+</sup>	0,013 g/l
MAGNESIUM	Mg <sup>++</sup>	4,60 mg/l
POTASSIUM	K <sup>+</sup>	0,23 mg/l
BICARBONATE	HCO <sub>3</sub>	42,70 mg/l
SULPHATE	SO <sub>4</sub>	4,86 mg/l
CHLORIDE	CL	3,90 mg/l
SICON	SiO <sub>2</sub>	26,43 mg/l

Catania, 05/11/2010  
MANAGER - Prof. S. Sciacca

Classificazione Acqua Oligominerale  
Catania, 05/11/2010  
Il RESPONSABILE - Prof. S. Sciacca

Silice	
	
Nome IUPAC	
diossido di silicio	
Caratteristiche generali	
Formula bruta o molecolare	SiO <sub>2</sub>
Peso formula (u)	60,08
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$C_{p,m}^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	44,4



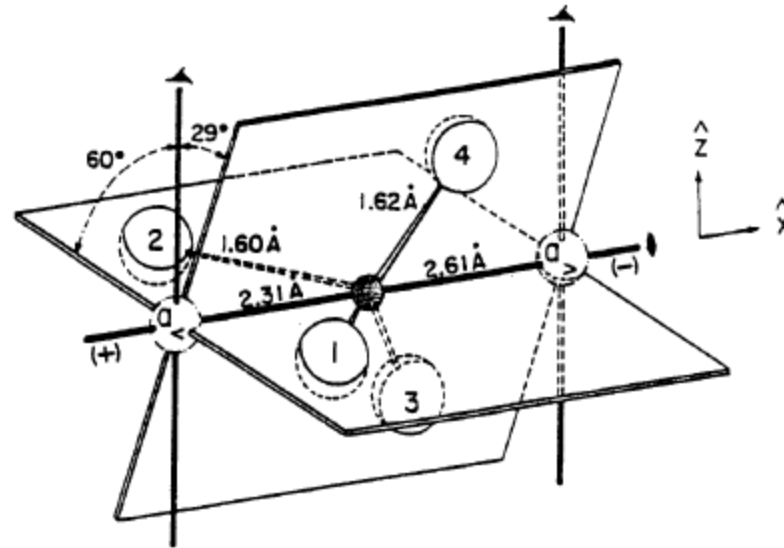


Figure 2 – Details of a SiO<sub>4</sub> tetrahedron in right  $\alpha$ -quartz ( See Fig. 1 ). Symbols  $a_{<}$  and  $a_{>}$  locate possible sites for an interstitial atom/ion in the middle of a large  $c$ -axis channel at its intersection with the two-fold axis  $a_1 = x$ -axis. Symbols  $\pm$  give the sign of the electrical charge developed on  $a_1$  when the crystal is compressed along this direction (  $-$  charge on  $+$  side of  $a_1$  ). Reproduced from Fig. 7 of [6].

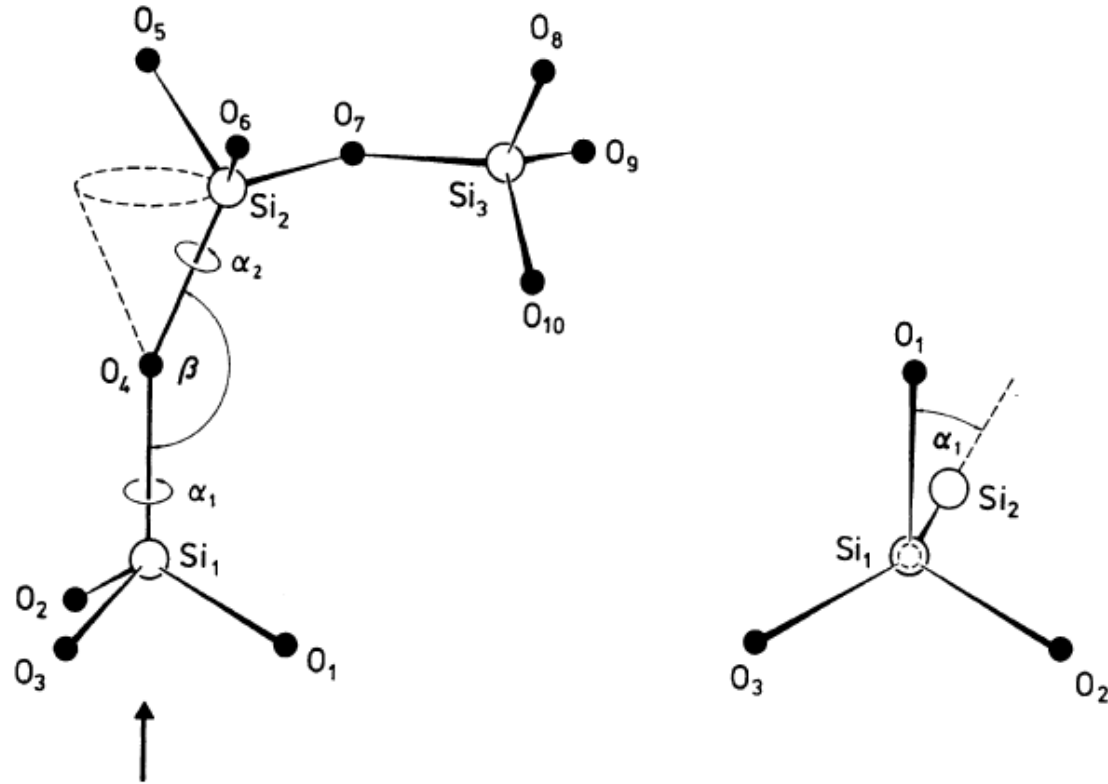
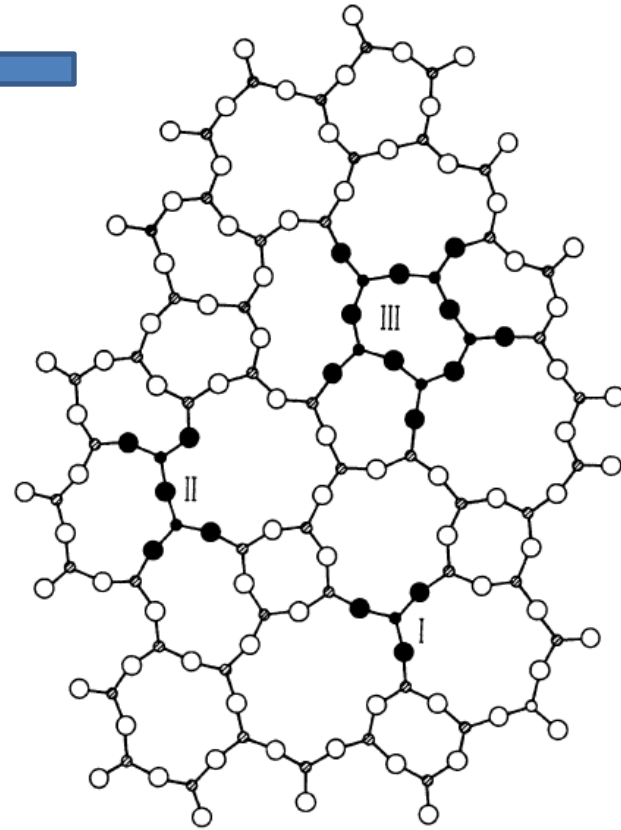


Figure 2. Definition of the bond angle,  $\beta$ , and the torsion angles,  $\alpha_1$  and  $\alpha_2$ , for vitreous SiO<sub>2</sub>.

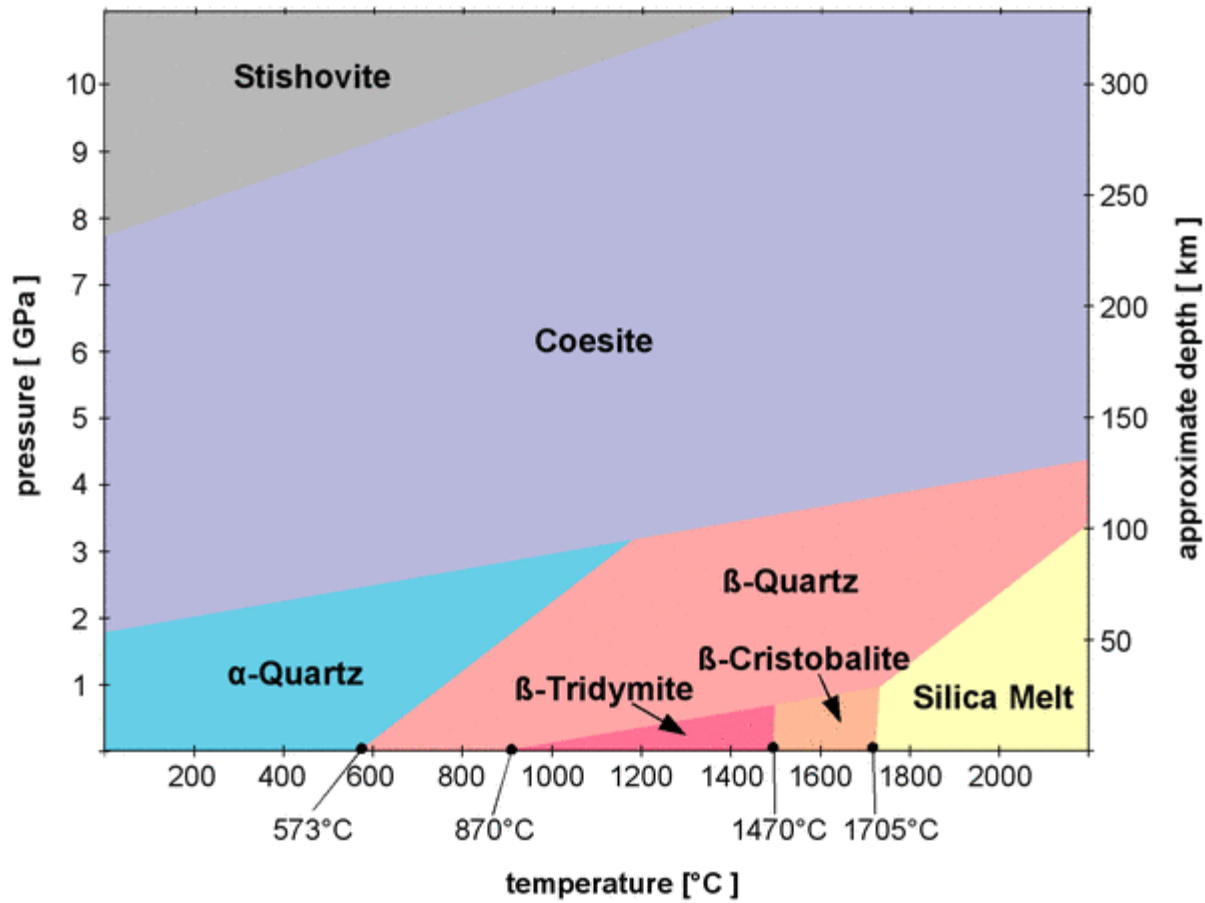


**Figure 1.** Zachariasen's original random network diagram (retraced) for a glass of composition  $\text{A}_2\text{O}_3$  [8], with structural units shaded to indicate range I, II and III order. Small atoms, A and large atoms, O. Note the regularity of the  $\text{AO}_3$  structural units.

Polymorph/Regrowth	Avg. Si-O-Si Angle $\theta$ ,°	Avg. Ring Size	Avg. Local Cluster Size	Density, $\times 10^3$ kg/m <sup>3</sup>
HP-Tridymite	149.5	6	27	2.18*
$\beta$ -Cristobalite	148.0	6	29	2.21*
$\alpha$ -Cristobalite	145.3	6	29	2.33*
Keatite	154.1	6.9	39	2.50*
$\alpha$ -Moganite	138.5	7.4	41	2.62*
$\alpha$ -Quartz	143.6	7.7	63	2.65*
$\beta$ -Quartz	150.9	7.7	63	2.77*
Coesite	150.8	10.0	78	3.01*
Vitreous Silica	145	~6	?	2.21*

Polymorph	Stability Regime	Density	Primitive Ring Content
Cristobalite	high temperature (1743-2001 K)	$\alpha$ 2.33	12 6-rings
		$\beta$ 2.21	
Tridymite	high temperature (1140-1743 K)	HP 2.18	12 6-rings
		MC 2.26	
Vitreous Silica	high temperature ( $T_g \sim 1333$ K)	2.21	$n \approx 6?$

In "Defects in SiO<sub>2</sub> and related dielectrics: Science and Techn. "  
Ed. G.Pacchioni, L.Skuja, D.L. Griscom, Kluwer 2000



C. Koike et al. The Astroph. Journ. (2013) 778, 60

<http://www.quartzpage.de>

# Produzione di $\text{SiO}_2$

## Overview: Synthetic $\text{SiO}_2$ Products

### 1. Thermal or pyrogenic or fumed silica

Silica by flame hydrolysis

Arc silica

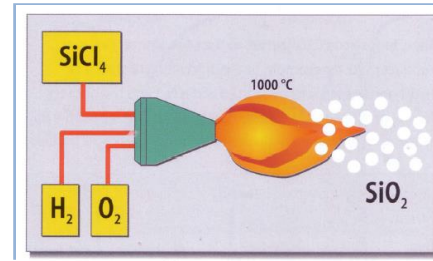
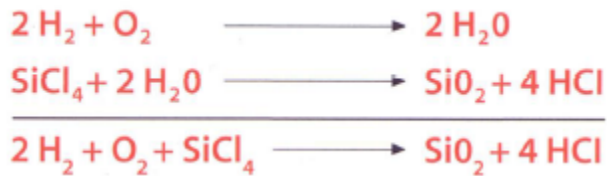
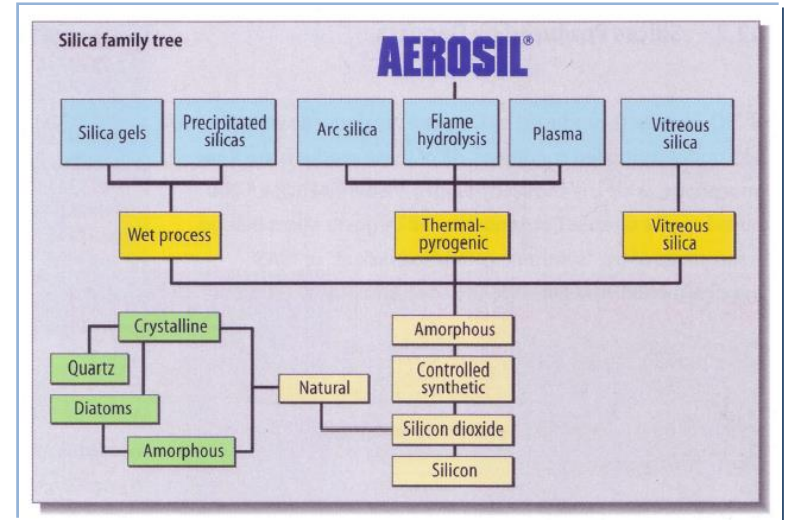
Plasma silica

### 2. Wet process silica

Precipitated silica

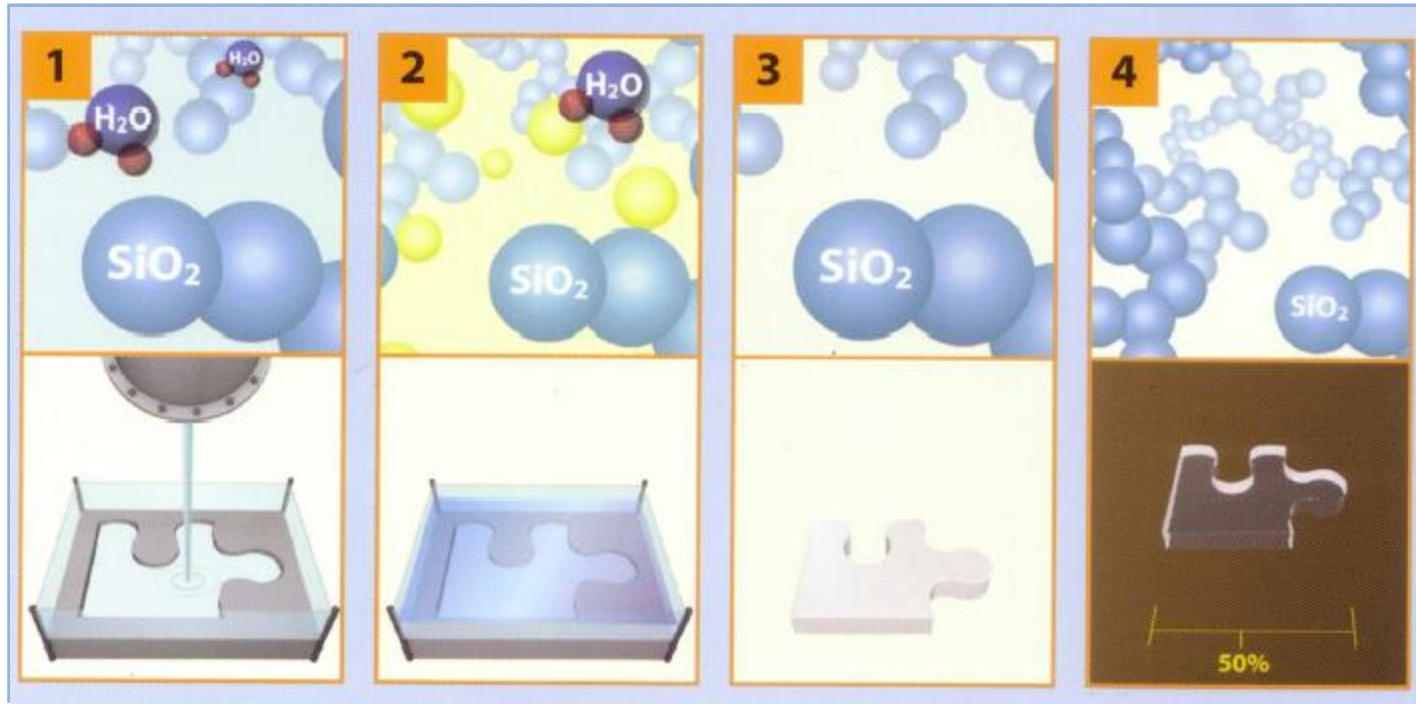
Silica gel

### 3. Vitreous silica



By varying the concentration of the coreactants, the flame temperature, and the dwell time of the silica in the combustion chamber, it is possible to influence the particle size, the particle size distribution, the specific surface, and the surface properties of the silicas within wide boundaries.

# SiO<sub>2</sub> sol-gel



# SiO<sub>2</sub> nanostrutturata

## Polveri nanostrutturate di SiO<sub>2</sub>

- Preparazione attraverso la tecnica **sol-gel** a temperatura ambiente: idrolisi e condensazione di tetraetoxisilano (TEOS) o tetrametoxisilano (TMOS)
- Preparazione di polveri nanostrutturate **fumed silica**: idrolisi di SiCl<sub>4</sub>

**Superficie specifica maggiore di 400 m<sup>2</sup>/g**

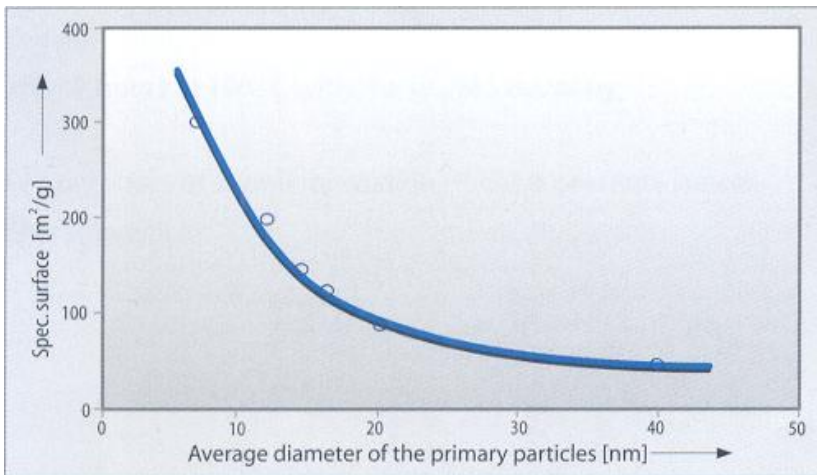
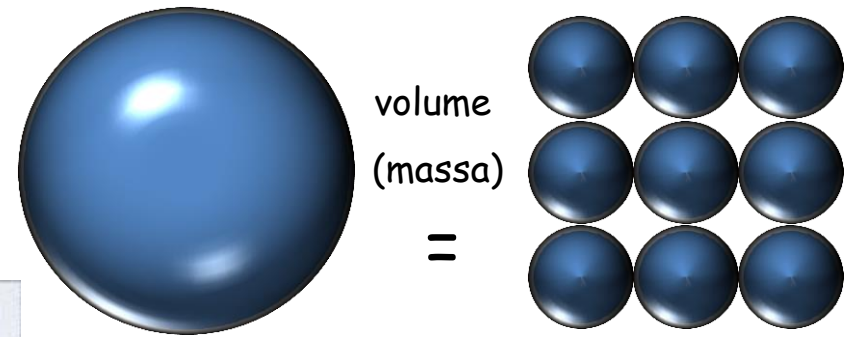
L'auto aggregazione delle particelle è un attrattiva di notevole interesse per costruire nanostrutture. Particelle di silice nanoporosa sono di dimensioni dell'ordine del micrometro (**1/10 di un capello umano**), e posseggono canali di dimensioni nanometriche.



# Produzione di SiO<sub>2</sub>

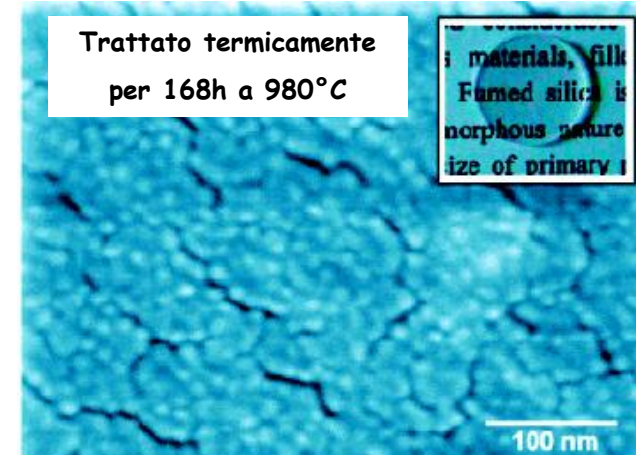
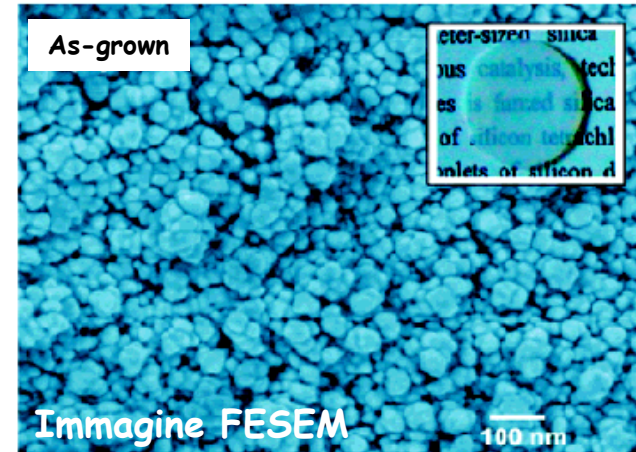
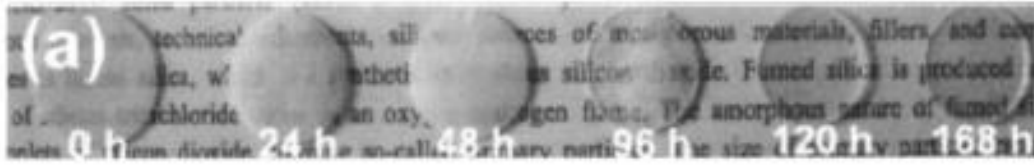
Aerosil							
	OX 50	90	130	150	200	300	380
Diametro particella primaria (nm)	40	20	16	14	12	7	7
Superficie specifica (m <sup>2</sup> /g)	50	90	130	150	200	300	380

**Superficie  
specifica**  
(superficie/massa)



$$\frac{\text{Superficie}}{\text{Volume}} \propto \frac{1}{r}$$

# SiO<sub>2</sub> nanostrutturata



# SiO<sub>2</sub> nanostrutturata

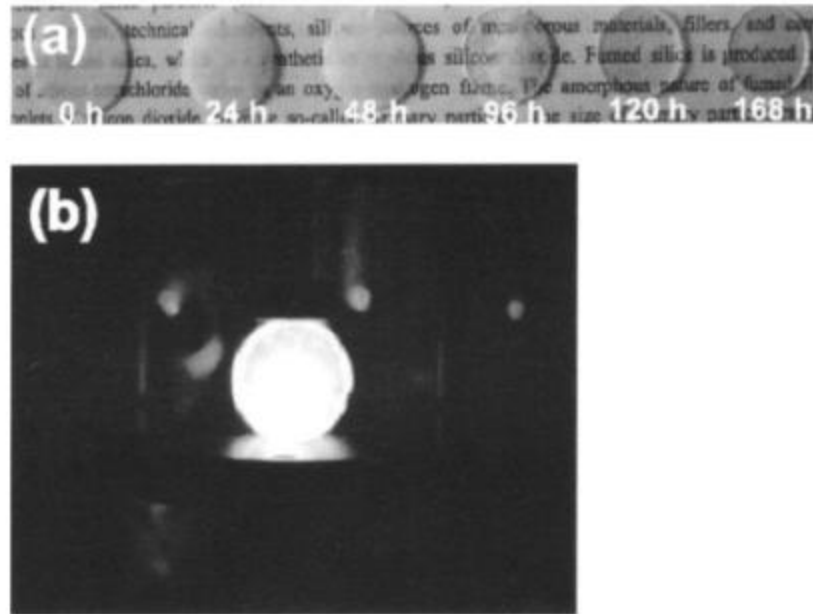
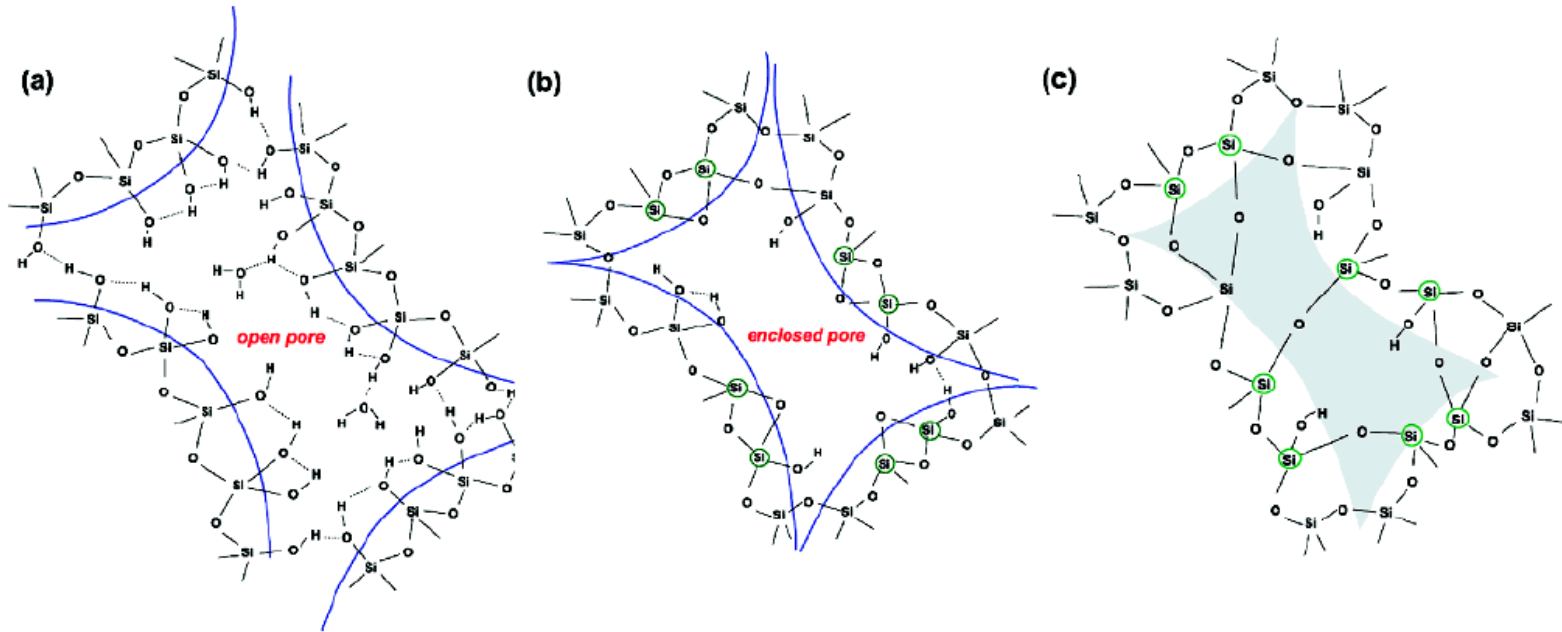


FIG. 1. (a) The sintering process for the disk shaped samples; heating times are indicated below the respective samples. (b) A photograph of photoluminescent silica glass, which was prepared by heating fumed silica at 980 °C for 168 h, excited with a pulsed Nd:YAG laser light ( $\lambda_{\text{exc}} = 266 \text{ nm}$ ;  $\sim 3 \text{ mJ/cm}^2$  per pulse). A bright part corresponds to the irradiated area with the laser (beam diameter  $\sim 10 \text{ mm}$ ).

# SiO<sub>2</sub> nanostrutturata



**Figure 10.** Schematic atomic arrangements of (a) a non-heat-treated sample with open pores, (b) a heat-treated sample with macroscopic enclosed pores, and (c) a heat-treated sample with no macroscopic enclosed pores. Broken lines represent hydrogen bonds. The Si atoms involved in and derived from the edge-sharing tetrahedral units are circled in (b) and (c), respectively. The shaded part in (c) indicates the region in which the interfacial atomic arrangements are not fully relaxed and are hence highly deformed.

# Struttura delle particelle di $\text{SiO}_2$ nanometrica

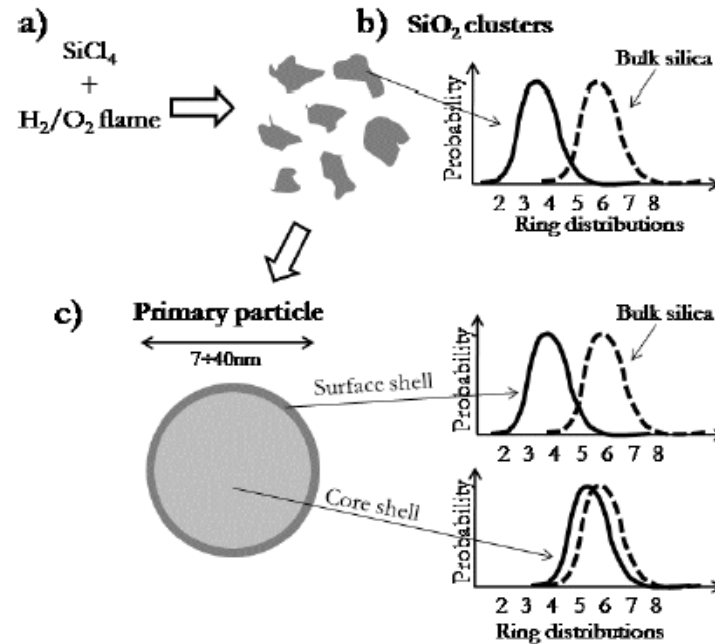
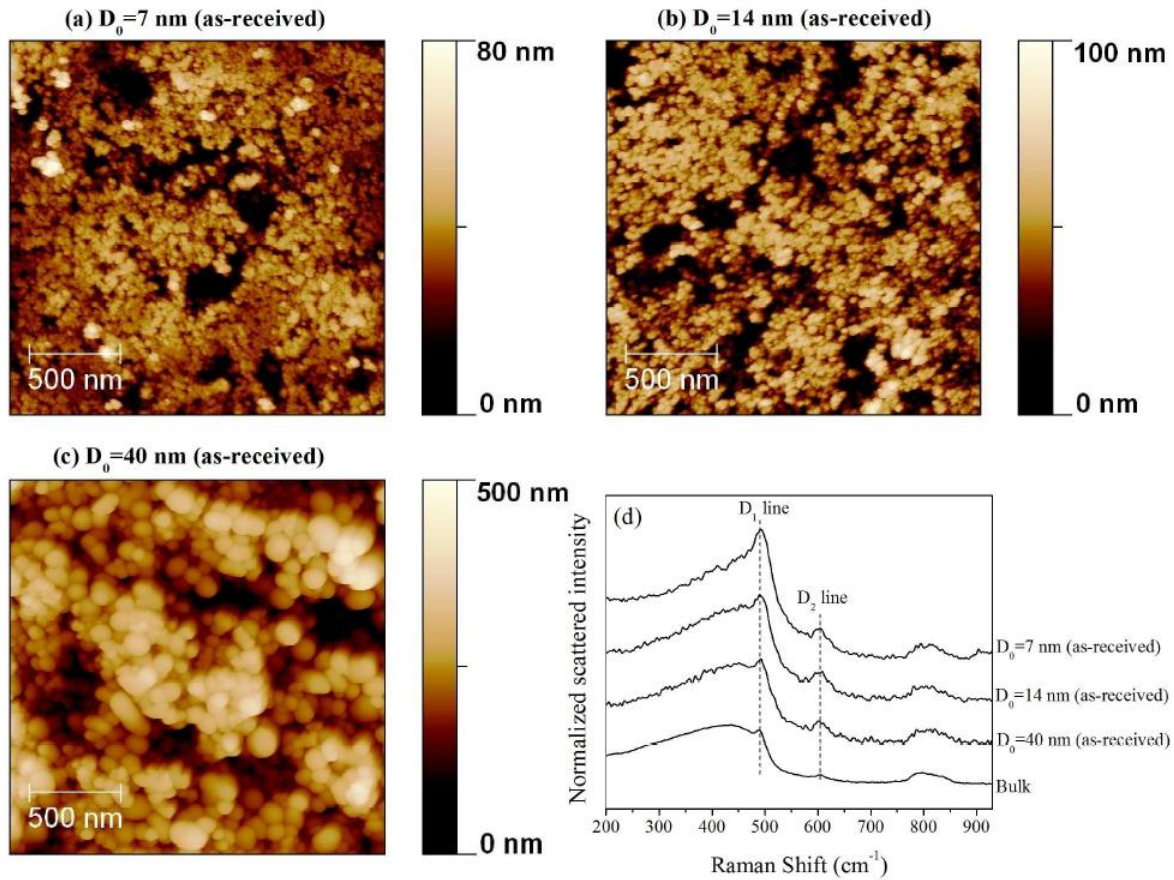


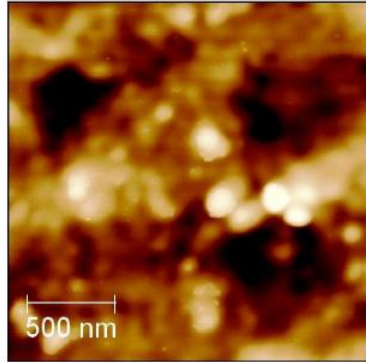
Figure 7: Schematic representation of the formation of fumed silica primary particles:  $\text{SiCl}_4$  hydrolysis in  $\text{H}_2/\text{O}_2$  flame a), formation of small  $\text{SiO}_2$  clusters b) and, finally, the primary particle c). The shell model of this latter with a core and surface region is shown. The rings distribution of small clusters, bulk silica, core and surface shells primary particle, are qualitatively reported.

# SiO<sub>2</sub> nanostrutturata

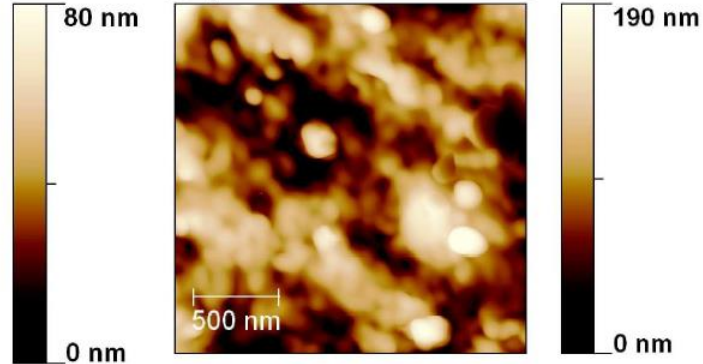


# SiO<sub>2</sub> nanostrutturata

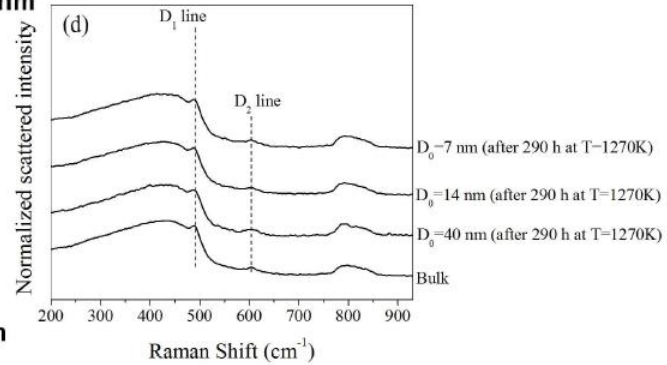
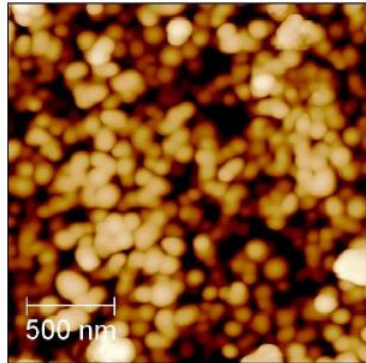
(a) D<sub>0</sub>=7 nm (after 290 h at T=1270K)



(b) D<sub>0</sub>=14 nm (after 290 h at T=1270K)



(c) D<sub>0</sub>=40 nm (after 290 h at T=1270K)



# SiO<sub>2</sub> nanostrutturata

## Proprietà di emissione di nanoparticelle di silice

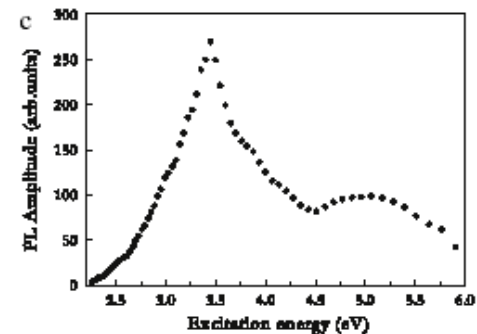
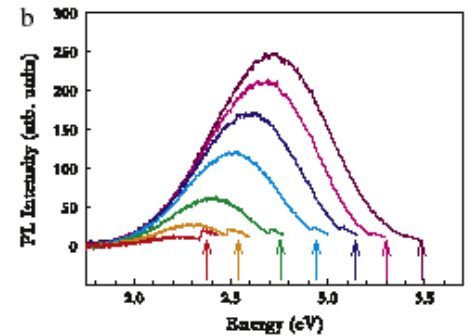
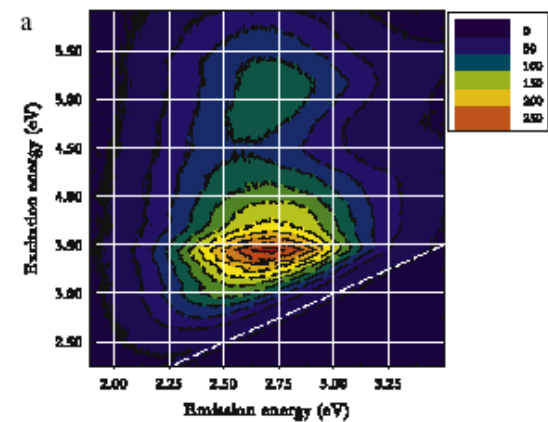
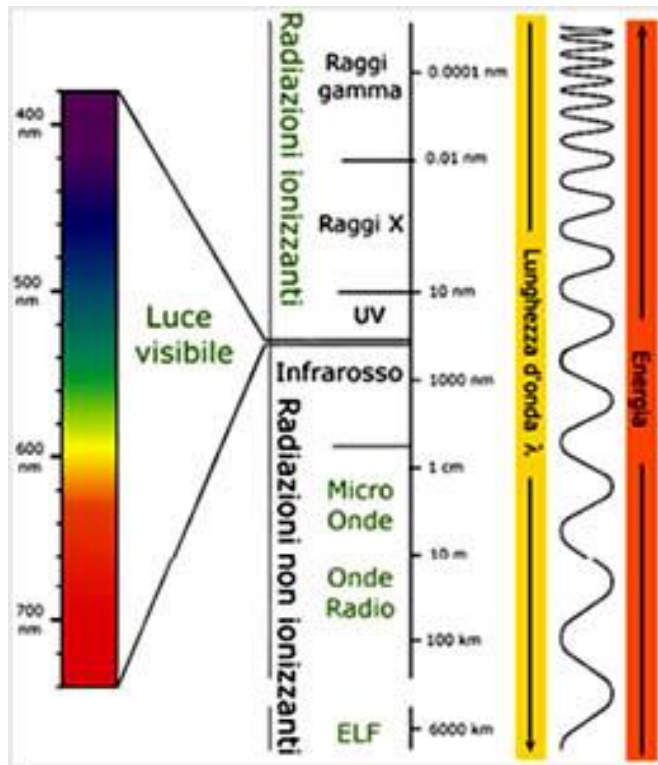


Fig. 1. (a) Contour plot of the emission spectra collected at various  $E_{ex}$  ranging from 2.25 to 5.90 eV with  $\Delta T = 200$  ns and  $T_D = 3$  ns; the dashed line represents  $E_{em} = E_{ex}$ . (b) PL spectra detected under different  $E_{ex}$  indicated by the arrows, the scattered laser light is also evident in the tails at high energies. (c) Excitation energy dependence of the PL amplitude measured at the peak of each spectrum.



# Processo di diffusione in $\text{SiO}_2$ nanostrutturata

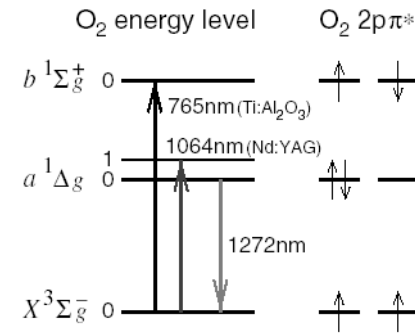
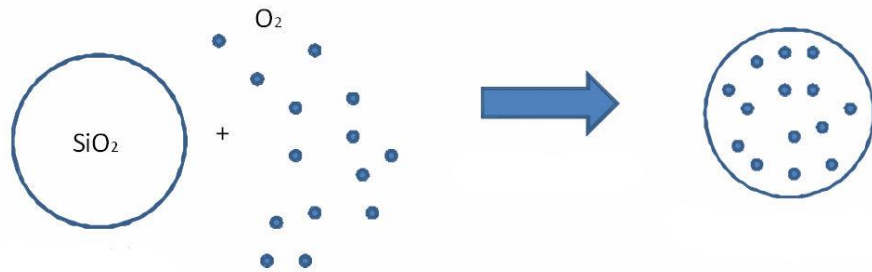


Fig. 1. Schematic diagram of low-lying electronic states and electronic transitions of interstitial  $\text{O}_2$  in a- $\text{SiO}_2$ .

*Nature Nanotechnology* **4**, 710 - 711 (2009)  
doi:10.1038/nnano.2009.326

Subject term: [Nanomedicine](#)

## Bioimaging: Second window for *in vivo* imaging

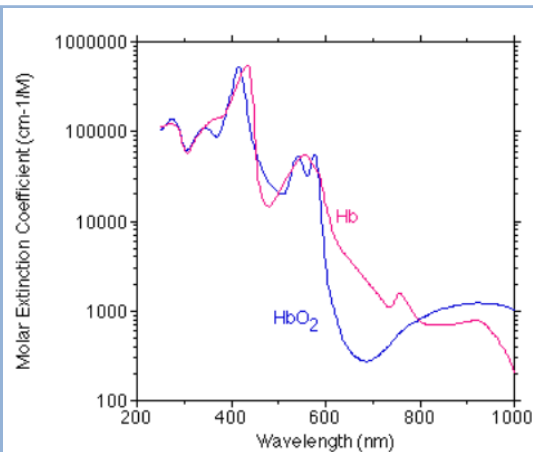
Andrew M. Smith<sup>1</sup>, Michael C. Mancini<sup>1</sup> & Shuming Nie<sup>1</sup>

1. Andrew M. Smith, Michael C. Mancini and Shuming Nie are in the Departments of Biomedical Engineering and Chemistry, Emory University and Georgia Institute of Technology, 101 Woodruff Circle Suite 2007, Atlanta, Georgia 30322, USA.

Correspondence to: Shuming Nie<sup>1</sup> e-mail: [snie@emory.edu](mailto:snie@emory.edu)

**Enhanced fluorescence from carbon nanotubes and advances in near-infrared cameras have opened up a new wavelength window for small animal imaging.**

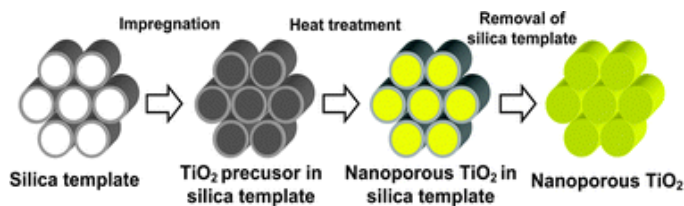
Near-infrared light (700–2,500 nm) can penetrate biological tissues such as skin and blood more efficiently than visible light because these tissues scatter and absorb less light at longer wavelengths. Simply hold your hand in sunlight and your fingers will glow red owing to the preferential transmission of red and near-infrared light.



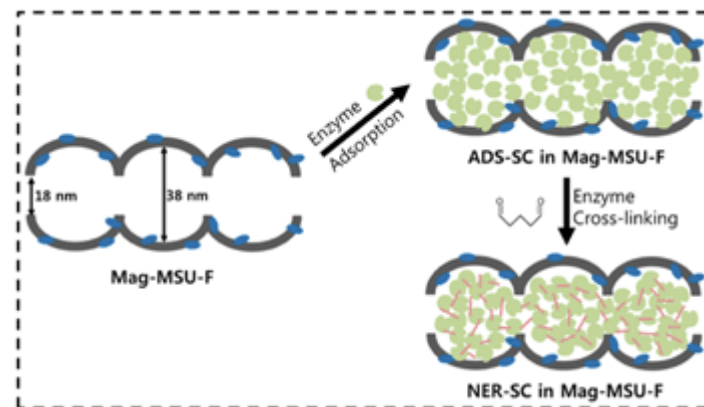
A best estimate of the spectrum of Hb and  $\text{HbO}_2$  from a variety of sources by Scott Prahl. [A tabulation of the data is available.](#)

## MESOPOROUS SILICA SYSTEMS

These materials can be functionalized and are of large interest in different technological fields, for catalysts, as adsorbents, for fixing bioactive molecules such as enzymes and drugs, and as hard template or fillers.



*New J. Chem.*, 2012,36, 2094-2100



*Green Chem.*, 2012,14, 1884-1887

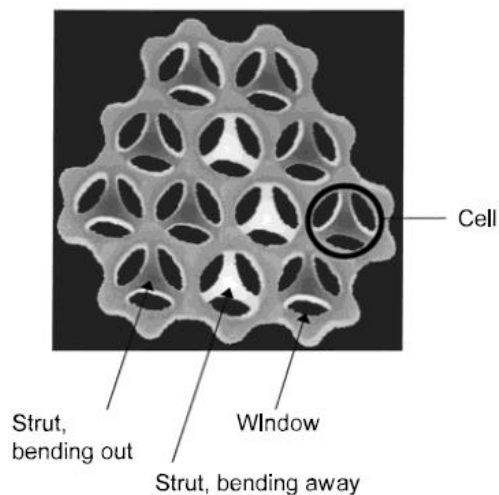


*Nanoscale*, 2011,3, 2801-2818

## MESOPOROUS SILICA STRUCTURES

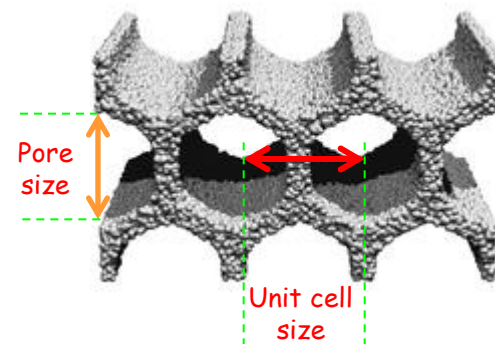
Different structures have been suggested, constituted by  $\text{SiO}_2$  walls of specific thickness and porosity

### Cellular Foam



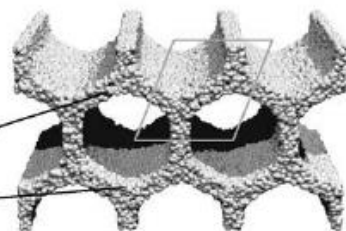
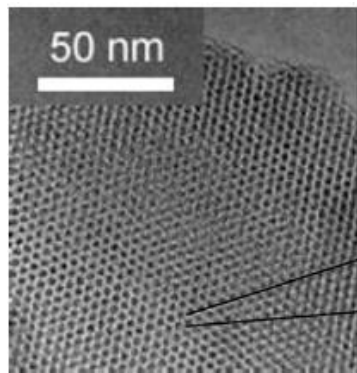
*Chem. Mater.* 2000, 12, 686-696

### 2D hexagonally ordered



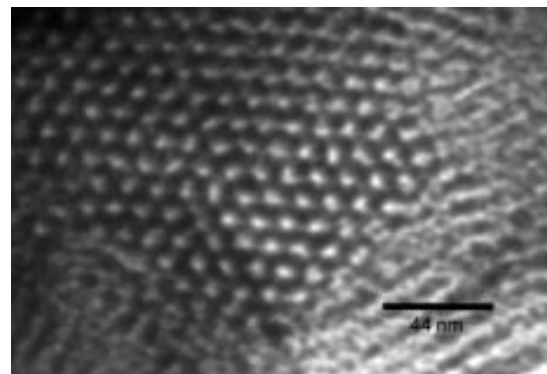
*Phys. Chem. Chem. Phys.*, 2008,10, 347-360

## MESOPOROUS SILICA STRUCTURES (TEM)



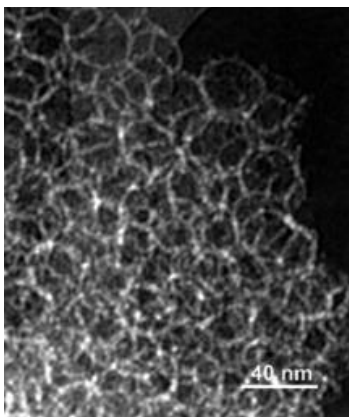
**MCM-41 (2D hexagonal)**

V. Meynen et al., *Micropor. Mesopor. Mat.* 2009, 125, 170-223



**MSU-H (large pore 2D hexagonal)  
Porous walls**

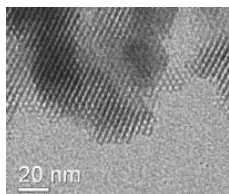
**MSU-F (cellular foam)**



Seong-Su Kim et al. *Chem. Commun.*, 2000, 17, 1661-1662

# Commercial mesoporous materials (Sigma Aldrich)

## POWDERS



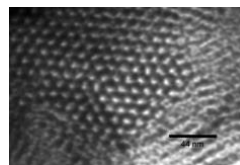
### MCM41

2D hexagonal type

unit cell of 4.5-4.8 nm

pore size of 2.1-2.7 nm

specific surface  $\sim 1000 \text{ m}^2/\text{g}$



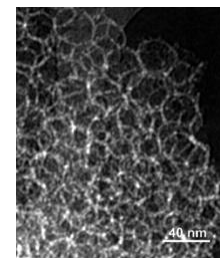
### MSU-H

2D hexagonal type

unit cell of  $\sim 11.6 \text{ nm}$

pore size of  $\sim 7.1 \text{ nm}$

specific surface  $\sim 750 \text{ m}^2/\text{g}$



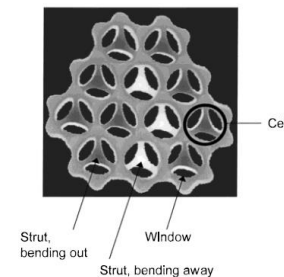
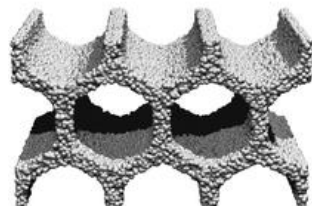
### MSU-F

cellular foam

unit cell of  $\sim 22 \text{ nm}$

cell window of  $\sim 15 \text{ nm}$

specific surface  $\sim 562 \text{ m}^2/\text{g}$



# SiO<sub>2</sub> nanostrutturata

## Applicazioni non ottiche

Alta purezza → wafer polishing

Grande superficie specifica → applicazioni catalitiche

Adattabilità → coating, rivestimenti

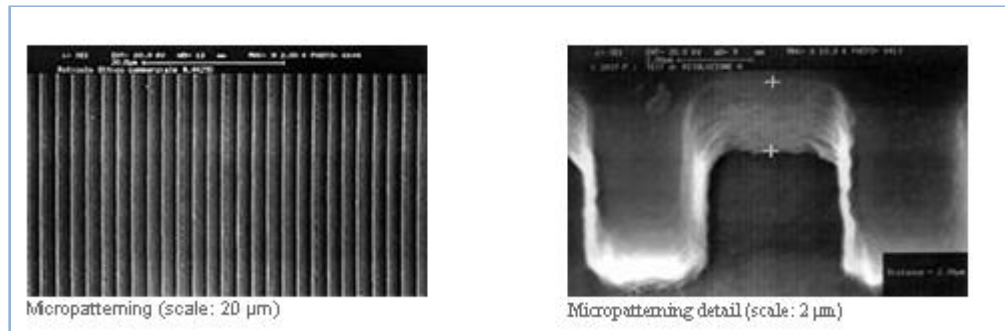
## Applicazioni ottiche-elettroniche

fibre → preforme alta purezza

lenti → omogeneità, modellabilità

semiconduttori → film sottili per dispositivi

Quantum computing → Quantum dots



# I difetti di punto

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Invarianza delle proprietà fisiche dei materiali durante il loro utilizzo:

Esposizione alla radiazione ionizzante (UV, raggi X, raggi  $\gamma$ )

Applicazioni in ambienti radioattivi o in applicazioni spaziali (lenti, fibre, strati isolanti nei MOS)

Investigazione delle strutture microscopiche che danno luogo a specifiche proprietà:

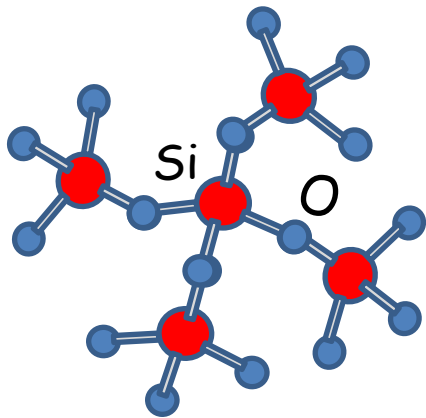
Sensibilità-resistenza alla radiazione

Centri di colore per applicazioni fotoniche: FBG, Laser, dispositivi non lineari

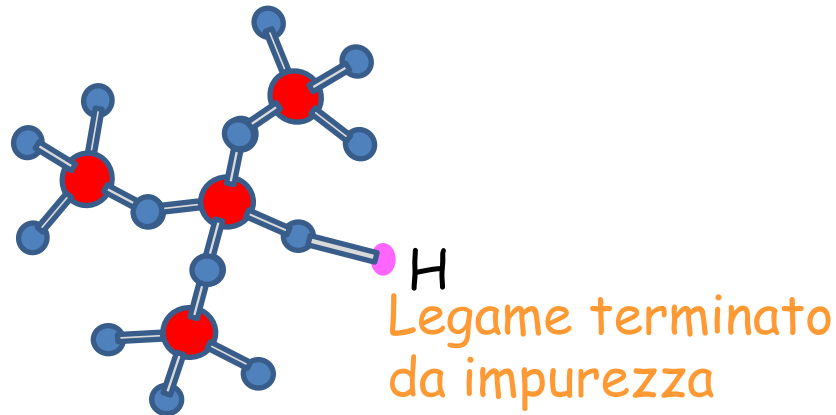
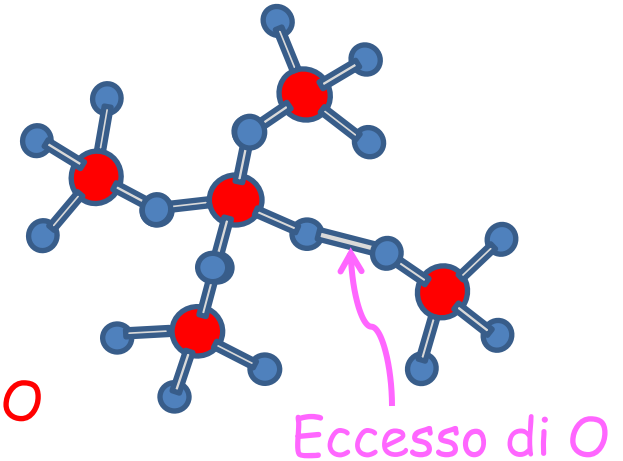
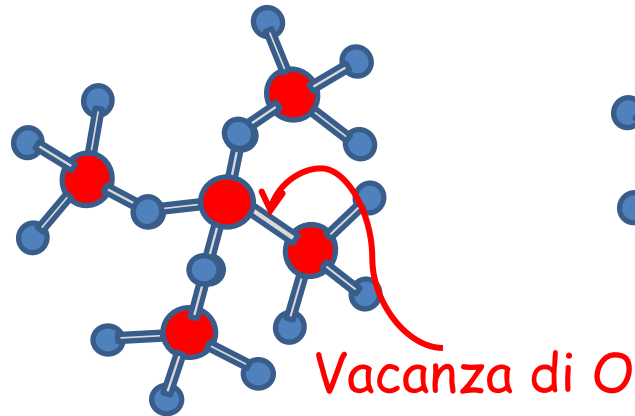
Difetti di punto in applicazioni elettroniche

# I difetti di punto

Difetto di punto = distorsione a livello atomico della silice



Frammento regolare





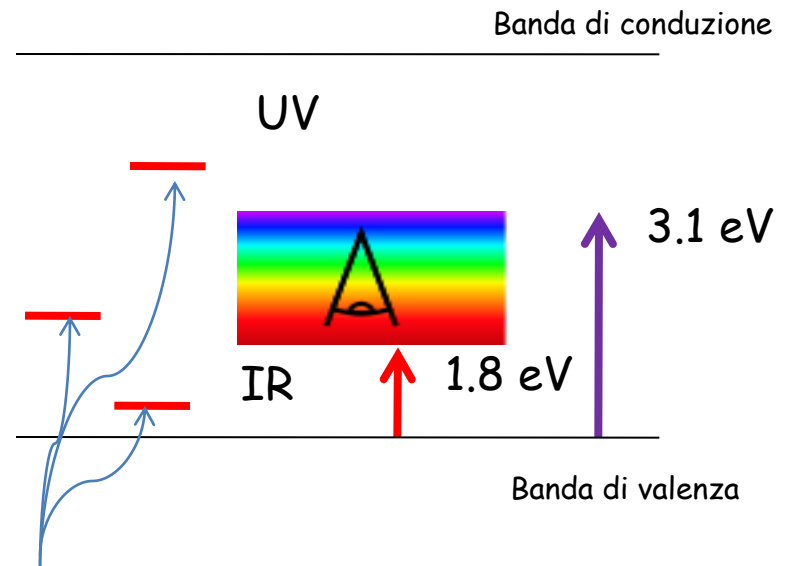
# I difetti di punto

Difetto di punto = comparsa di livelli energetici nella regione di energie proibite

## Effetti causati:

Perdita di trasparenza con assorbimento ed emissione di luce

Possibilità di intrappolare cariche con modifica delle proprietà elettriche

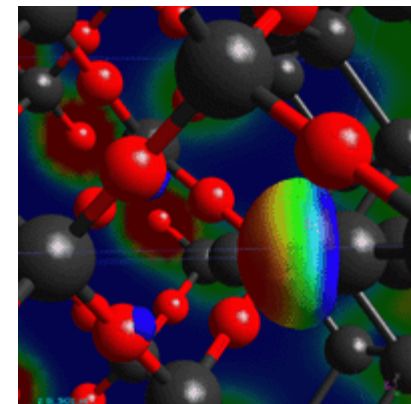
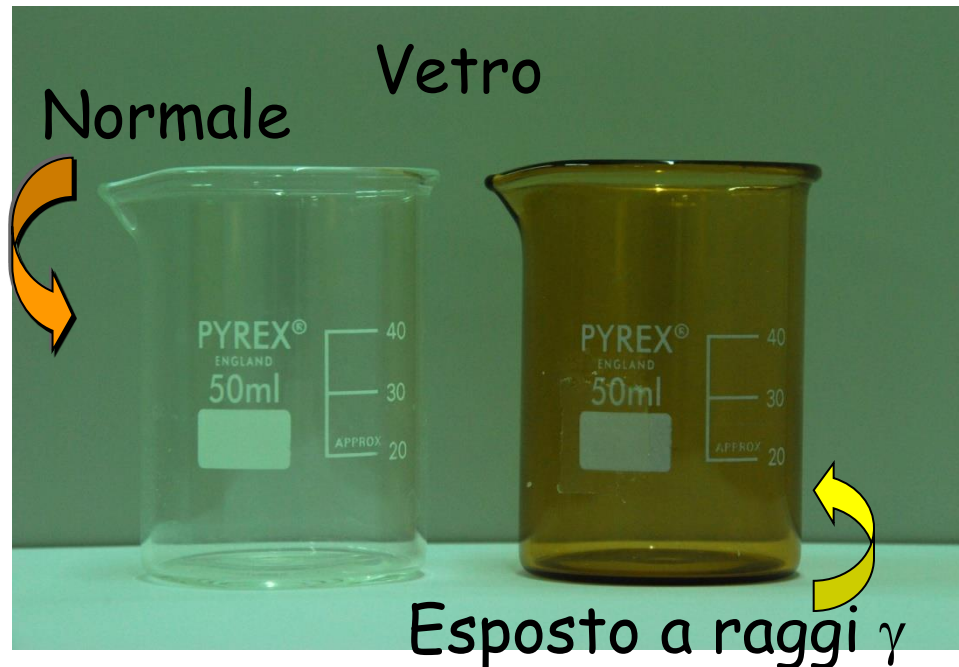


livelli energetici dovuti ai difetti

# Studio "microscopico" del $\text{SiO}_2$

Effetti della radiazione ionizzante

(Laser, raggi X, raggi  $\gamma$ , raggi  $\beta$ ,...)  
generazione di centri di colore

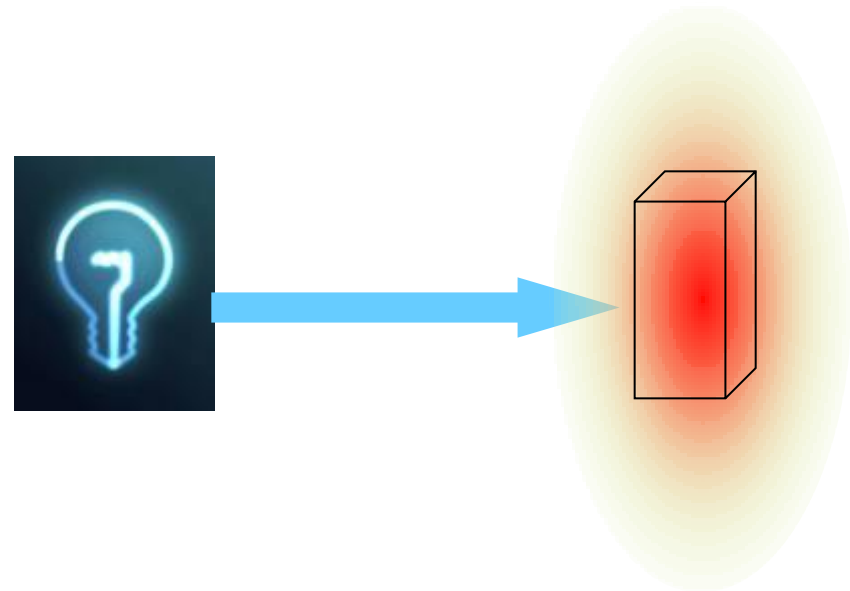
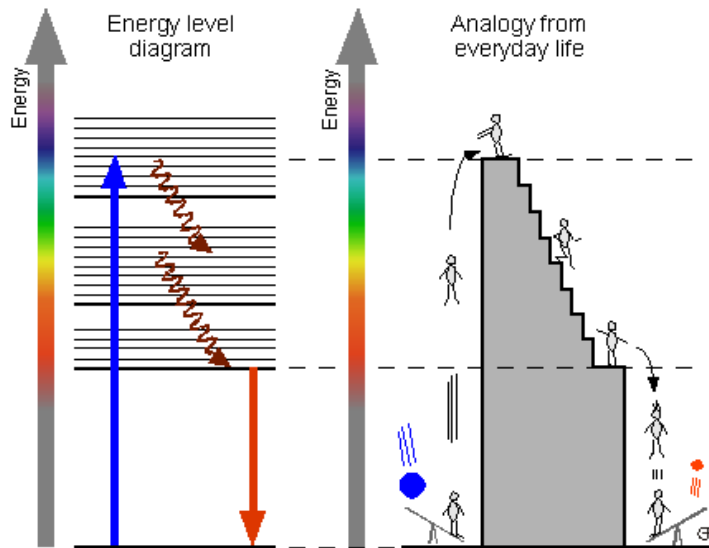


Determinazione delle  
strutture atomiche e dei  
processi di formazione dei  
centri di colore

# Tecniche: Spettroscopia Ottica

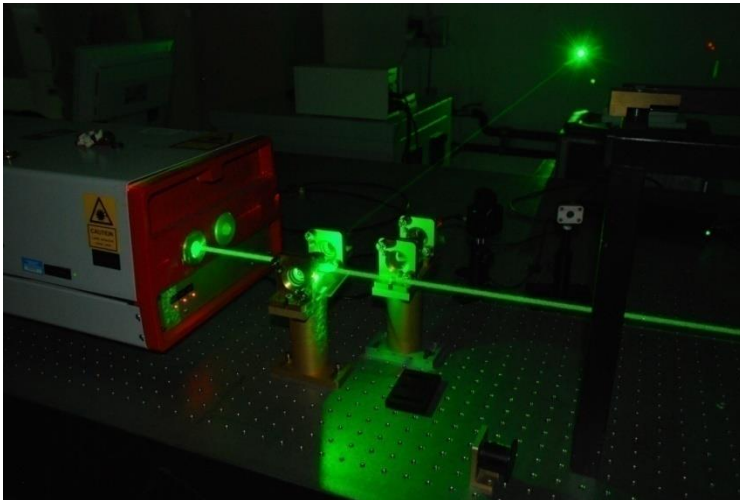
## Absorption, Nonradiative Relaxation and Luminescence

Making **heat** and 1x **red** out of 1x **blue**

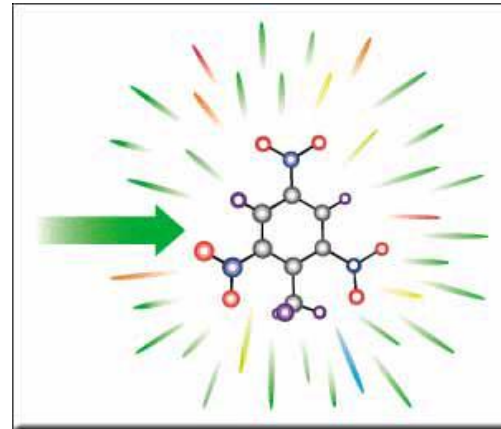
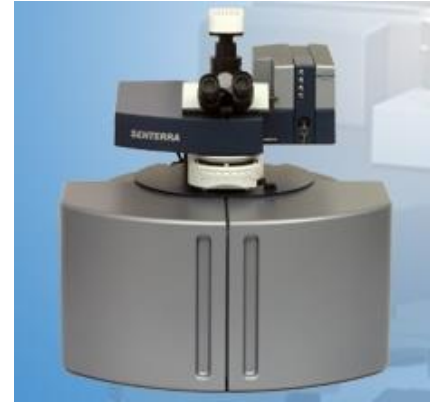


# Tecniche: Spettroscopia Ottica

Laser UV-visibile, Emissione risolta in tempo

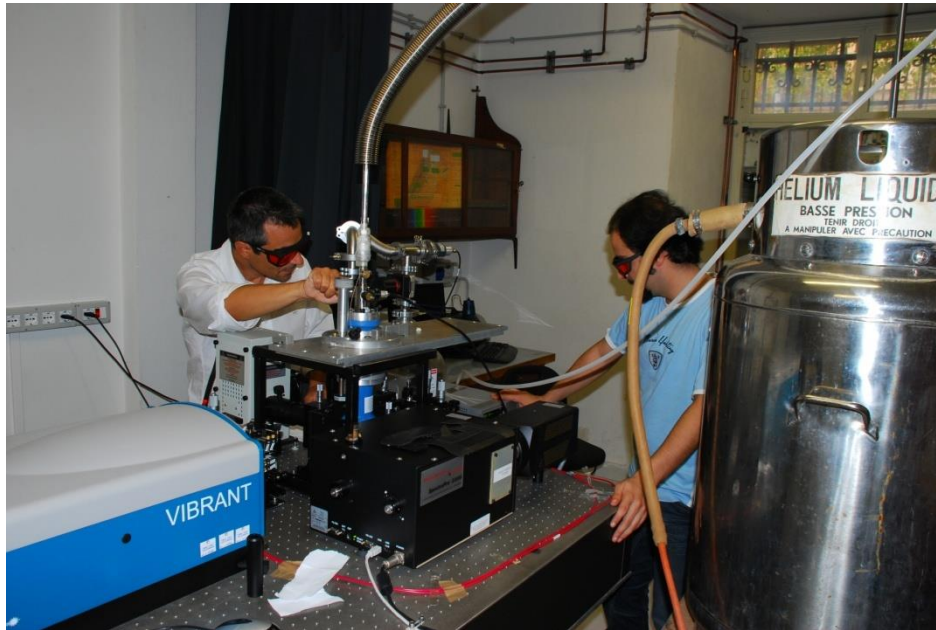


Spettroscopia  
Raman, Micro-Raman

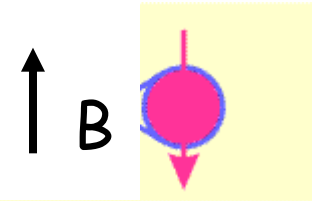


# Tecniche sperimentali

Misure fino a  $-270^{\circ}\text{C}$  (bassa temperatura)



Risonanza di spin elettronico



# Conclusioni

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- > Il biossido di silicio seppur un materiale di “vecchia data” costituisce ancora un sistema di avanguardia nella fotonica e nell’elettronica.
- > Le novità riguardano applicazioni di materiali di nuova sintesi o sistemi basati su  $\text{SiO}_2$ .
- > Sono in corso ricerche su materiali che possano sostituire l’ $\text{SiO}_2$  in alcune applicazioni standard.
- > La ricerca sui difetti di punto mira a chiarire gli aspetti microscopici che da un lato contrastano l’applicabilità del  $\text{SiO}_2$  e dei suoi sostituti, mentre dall’altro sono alla base delle nuove applicazioni (FBG, Fiber Lasers, nanocristalli).