

NANOTECNOLOGIE

esperienze, esperimenti, applicazioni

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Cose e loro dimensioni (arancio = cose fatte dall'uomo)

Millimeters

Microns

Nanometers

Ball of a ball point pen

0.5

Thickness of paper

0.1

100

Human hair

0.02 - 0.2

20 – 200

Talcum Powder

40

Fiberglass fibers

10

Carbon fiber

5

Human red blood cell

4 – 6

E-coli bacterium

1

1000

Visible Light Wavelength:

0.40 – 0.75 microns

400 – 750 nm

Size of a modern transistor

0.25

250

Transistor Gate

35

Size of Smallpox virus

0.2 – 0.3

200 – 300

Electron wavelength: Upper upper limit ~ 10 nm

Diameter of Carbon Nanotube

3

Diameter of DNA spiral

2

Diameter of C60 Buckyball

0.7

Diameter of Benzene ring

0.7

Size of one Atom

0.1

**Fisica
quantistica**

**Scienza dei
materiali**

Dispositivi nanomeccanici

Nanoelettronica

Nanotubi al carbonio

*Autoassemblaggi
inorganici*

Elettronica Organica

Nano-compositi

Nano-tribologia

Nanotecnologia per dispositivi

**Nanomateriali,
ricoprimenti e plastiche**

Foto-voltaico

*LED e laser tramite
nanosemiconduttori*

*Ricoprenti
per attrezzi*

Trasporto

*Processamento di dati
bio-molecolari*

*Dispositivi
Magneto-resistivi*

Electronica, informatica

Aerospazio

Sospensioni ed inchiostri

Miniaturizzazione

Cosmetica

Tessile

Nanofabbricazione

Coloranti

Catalizzatori nanostrutturati

Impianti micro-nano

*Distribuzione
di medicinali*

Farmaceutica

*Sintesi di
materiali*

Nano-filtrazione

Alimenti e bevande

Chimica

Ambiente

Energia

Sensori DNA

**Nanotecnologie per la
chimica e l'ambiente**

Nanobiotecnologia

Batterie

Bio-sensori

*Immagazzinamento
dell'idrogeno*

Biochip

Autoassemblaggio Biologico

Bio-catalisi

Auto-assemblaggio supra-molecolare

Biologia molecolare

**Chimica
supramolecolare**

SCIENZA

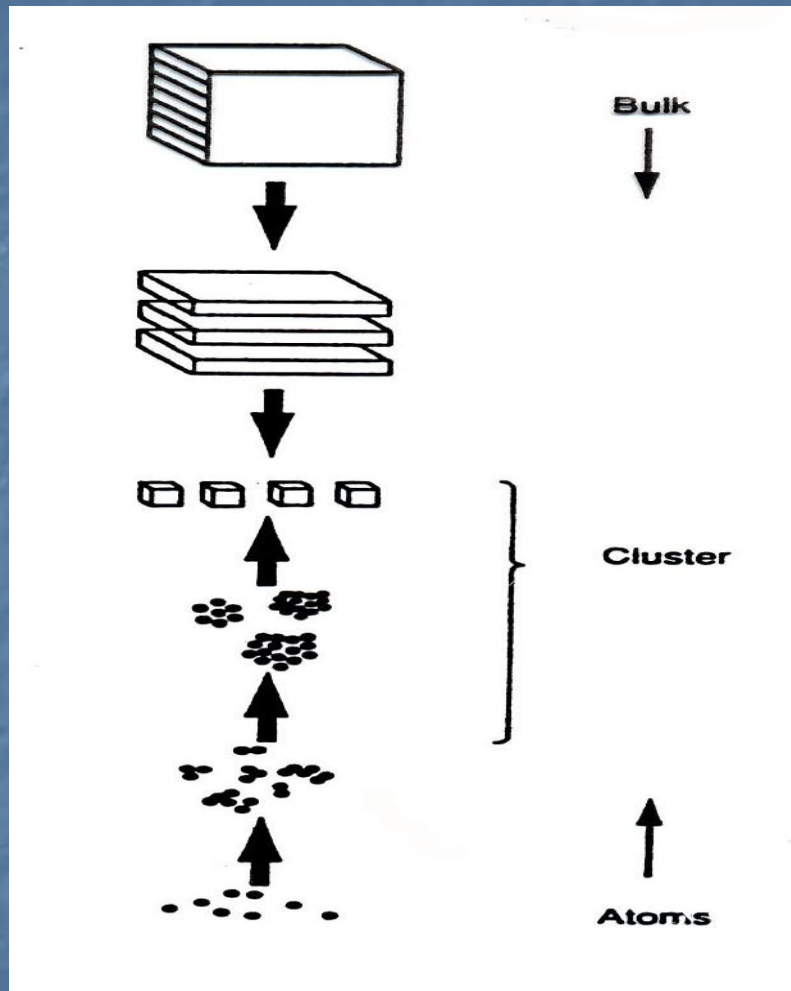
complesso organico e sistematico delle conoscenze che si posseggono intorno a un determinato ordine di fenomeni

TECNOLOGIA

studio dei materiali, delle macchine e dei procedimenti tecnici da impiegarsi nella produzione di beni e servizi

- La nanoscienza fornisce uno strumento concettuale estremamente potente ed innovativo, che apre orizzonti nuovi e vastissimi.
- Le nanotecnologie forniscono gli strumenti per lo sfruttamento pratico di questi nuovi concetti, consentendo la realizzazione di materiali nanostrutturati, di nanocompositi, di nanodispositivi.
- Al di là delle definizioni più o meno discusse su ciò che può essere considerato "nanotecnologia", le attività avviate sotto questa etichetta sono comunque una realtà importante, che avrà importanti conseguenze sul nostro mondo tecnologico.

Sintesi di nanostrutture



Top-down



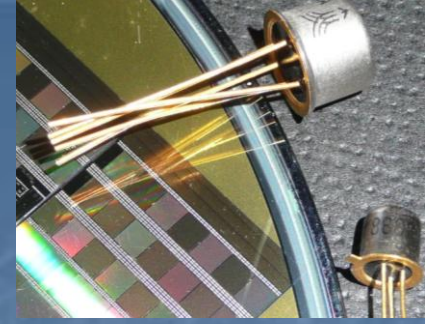
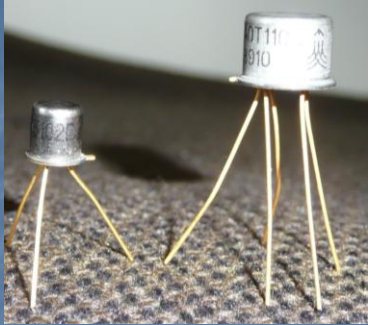
Bottom-up



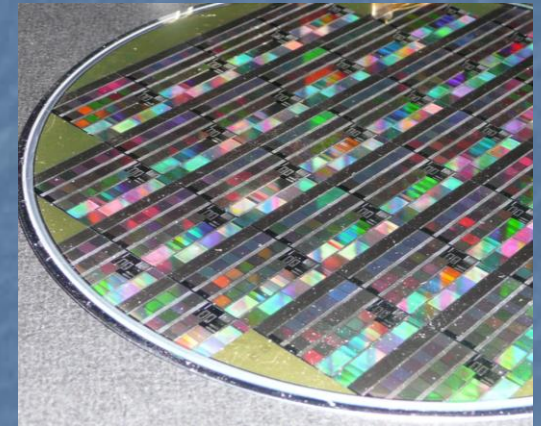
SCENARIO DI RIFERIMENTO - nanofabbricazione



La nanofabbricazione è destinata a diventare un elemento costitutivo nella sequenza di sviluppo definita da ricerca, trasferimento tecnologico, industrializzazione e commercio

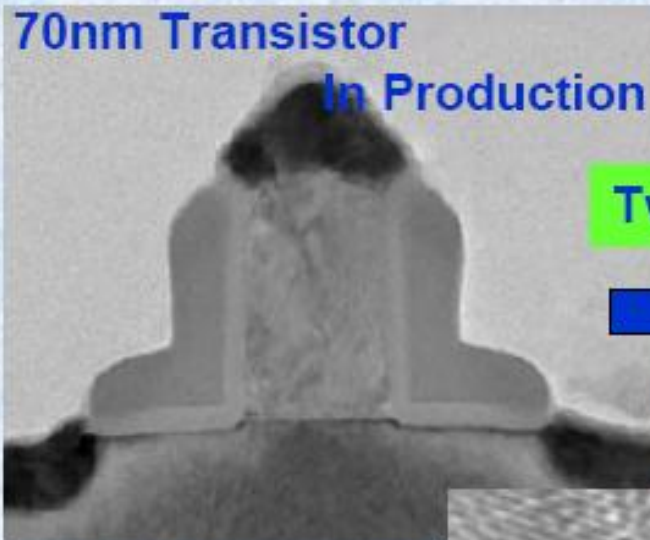


dal MACRO al MICRO al NANO



caso della MICROELETTRONICA

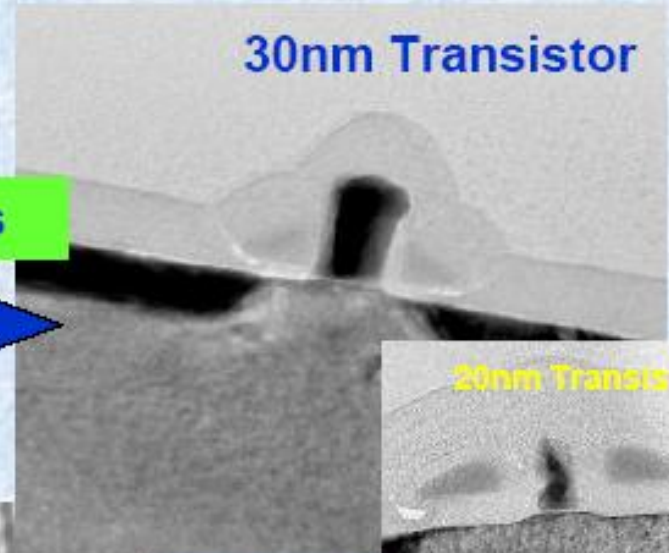
70nm Transistor
In Production



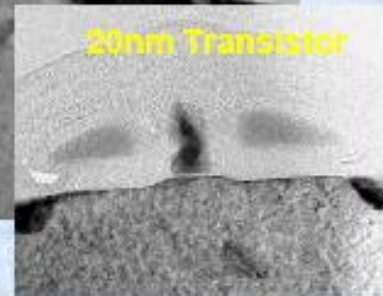
Two Generations



30nm Transistor



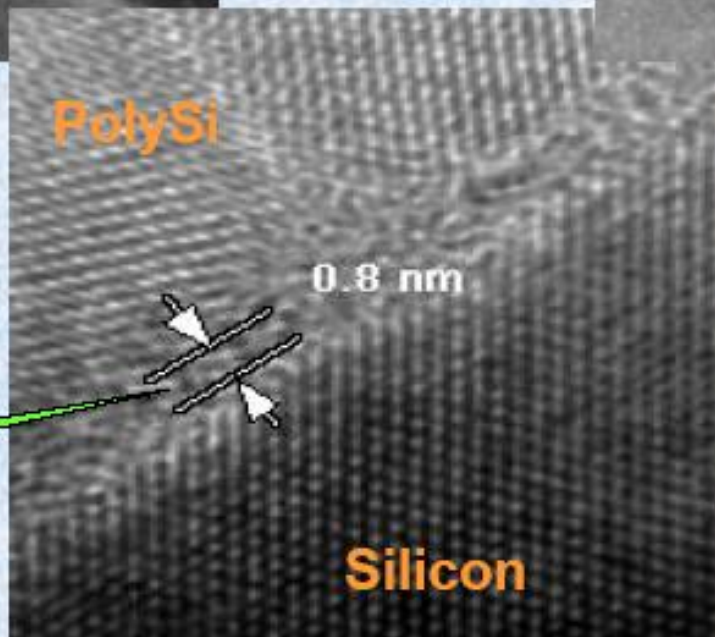
20nm Transistor



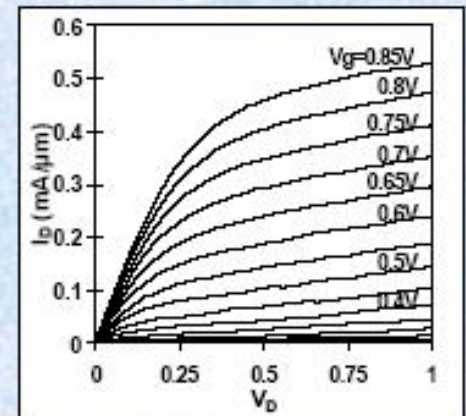
PolySi

0.8 nm

Silicon



Gate Oxide less
than 3 atoms thick

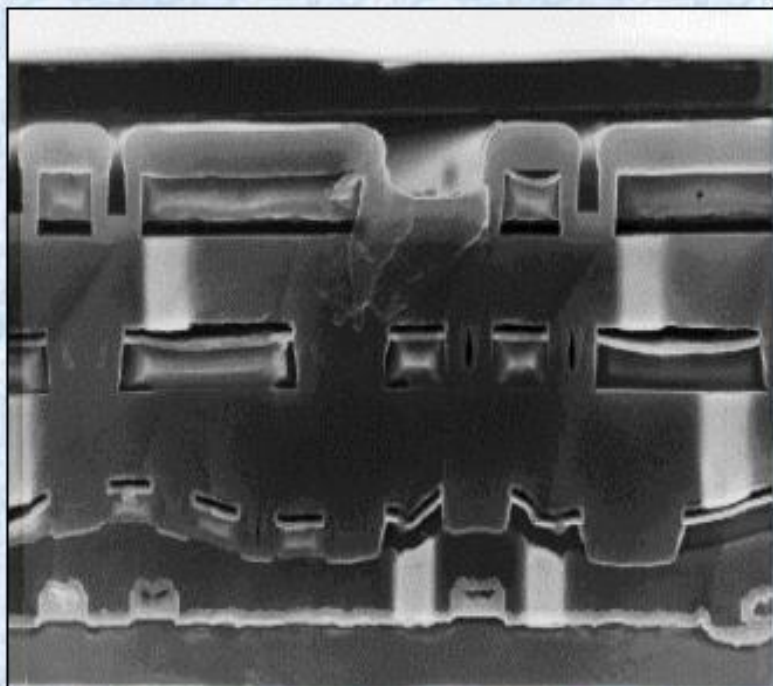




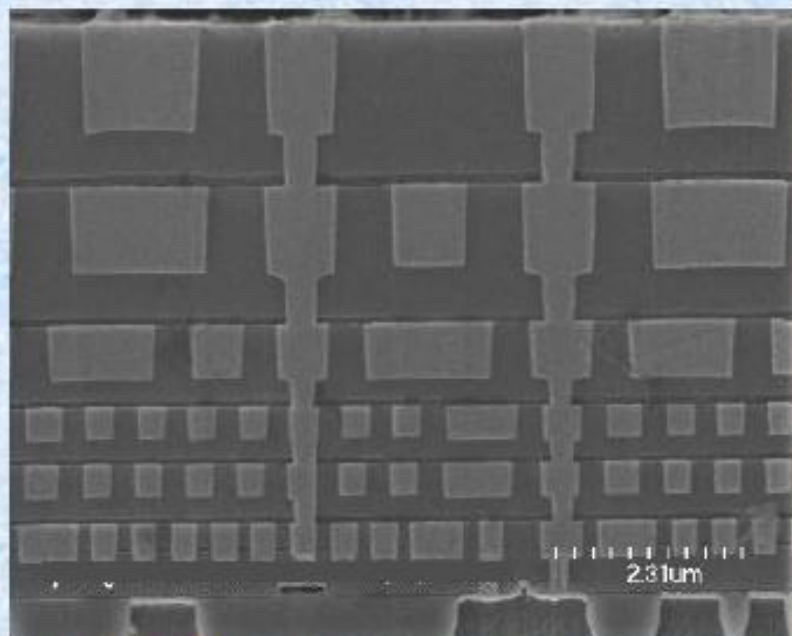
Continued Progress on Interconnects

8

500nm Interconnects



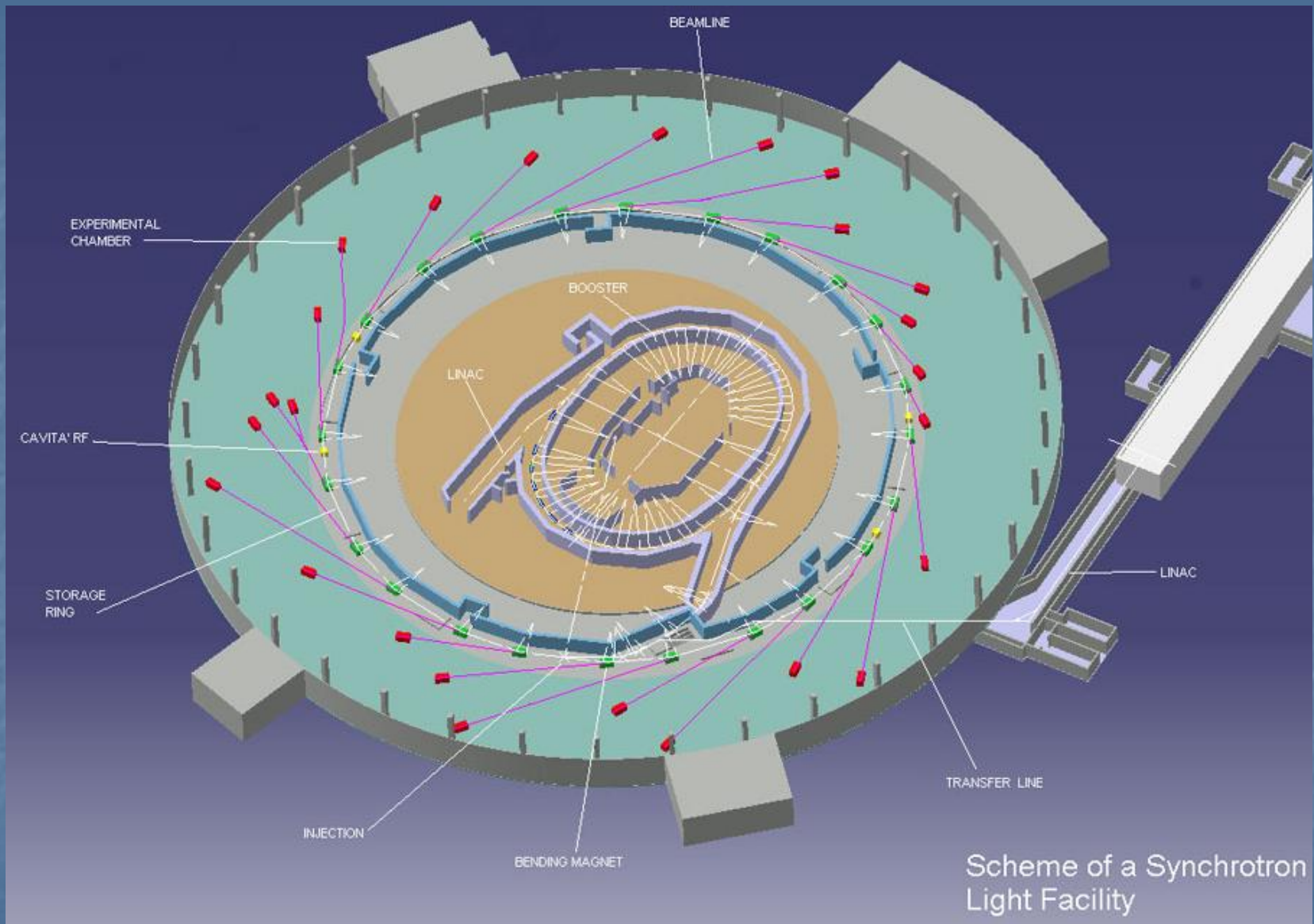
130nm Interconnects



Four Generations of
Interconnect Progress



Determinazione delle proprietà elettroniche di superficie (primi piani atomici)



CALIFORNIA-Stanford

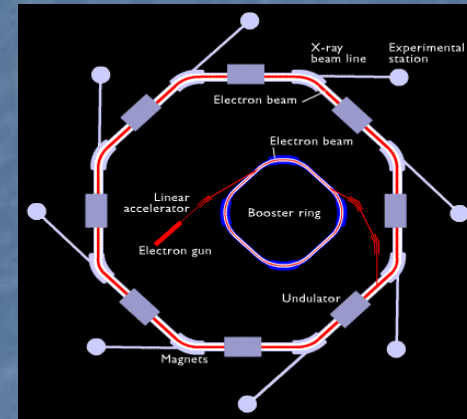
WISCONSIN-Madison

La fabbrica europea di Luce (ESRF)



La luce dagli elettroni

- La luce è prodotta facendo circolare gli elettroni all'interno di un circuito di magneti.
- La radiazione emessa viene estratta attraverso appositi canali (linee di luce)



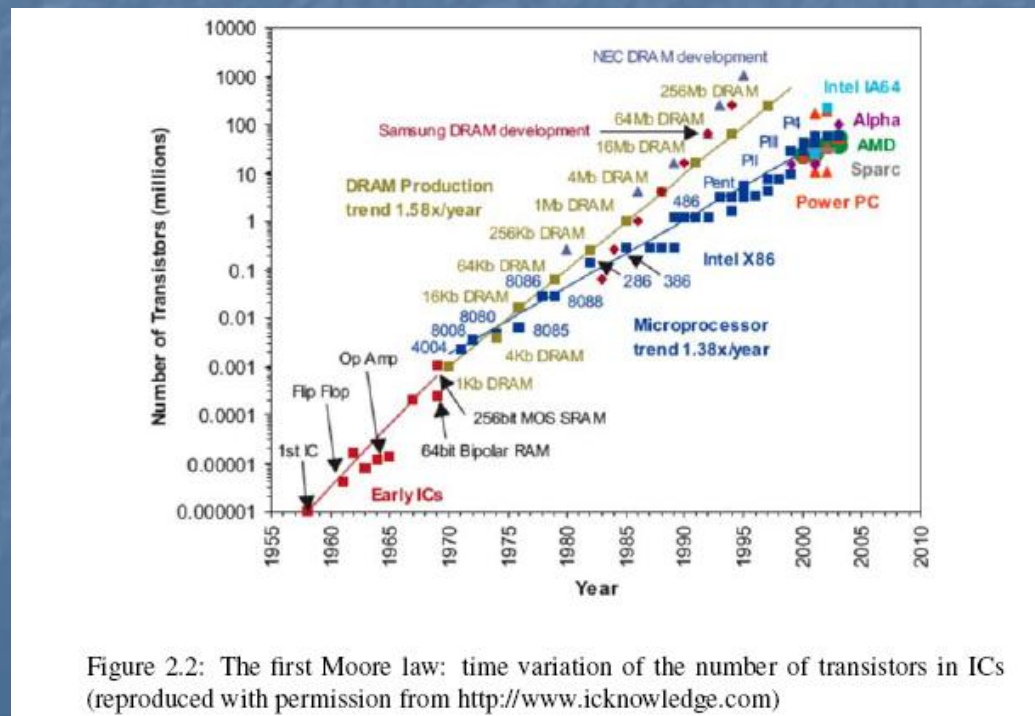
Inoltre, con la microtecnologia si realizzano prodotti che ogni anno divengono sempre più piccoli

MOORE'S LAW: (INTEL-1965) ogni 18-24 mesi il numero di transistor in un dispositivo raddoppia

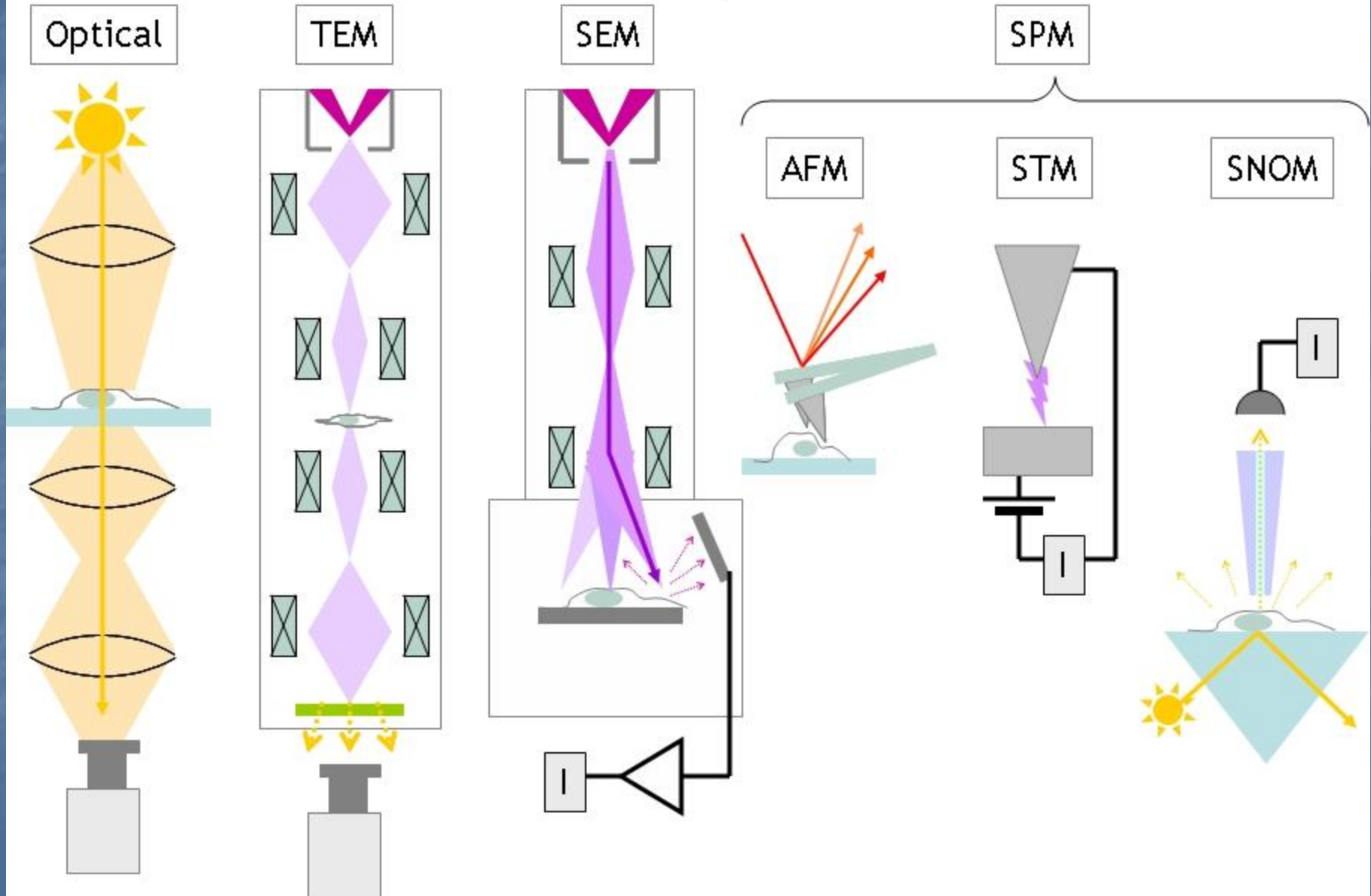
IC's era stato inventato solo 7 anni prima!

(by Moore, his Fairchild/Intel colleagues, and Texas Instrument's Jack Kilby)

La sua legge ha predetto lo sviluppo per 40 anni:

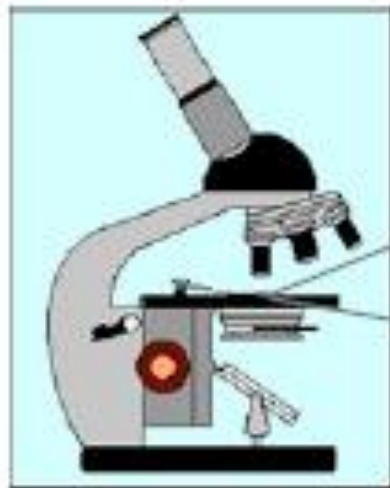


Microscopes

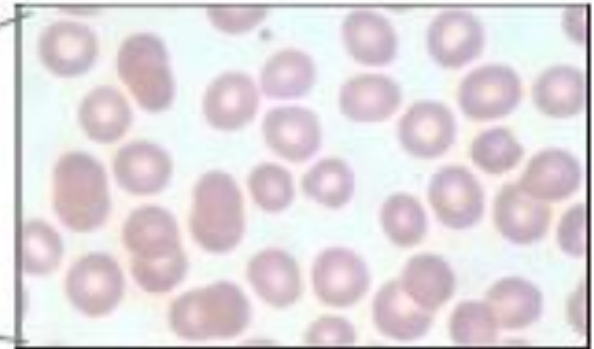


Using Light to See

- **The naked eye can see to about 20 microns**
 - A human hair is about 50-100 microns thick
- **Light microscopes let us see to about 1 micron**
 - Bounce **light** off of surfaces to create images



Light microscope
(magnification up to 1000x)

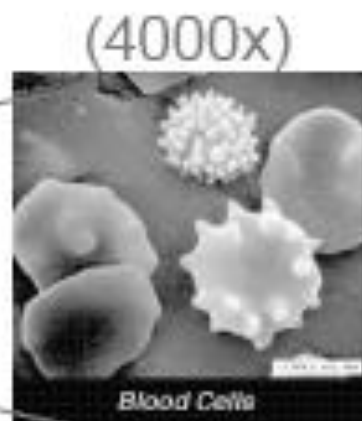


to see red blood cells
(400x)



Using Electrons to See

- **Scanning electron microscopes (SEMs),** invented in the 1930s, let us see objects as small as 10 nanometers
 - Bounce electrons off of surfaces to create images
 - Higher resolution due to small size of electrons



Greater resolution to see things like blood cells in greater detail



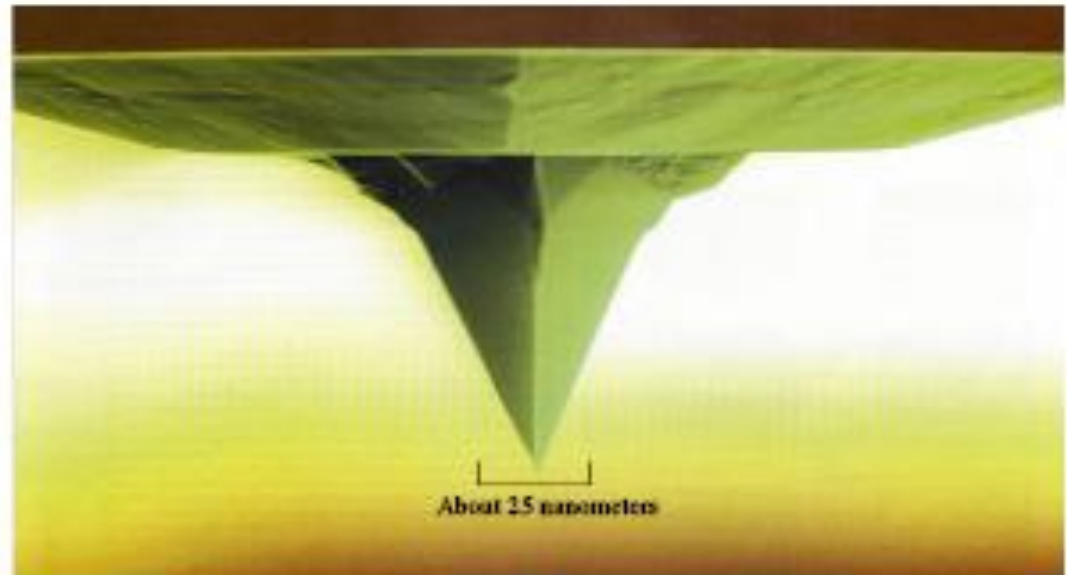
Scanning Probe Microscopes

- **Atomic Force Microscope (AFM)**
 - A tiny tip moves up and down in response to the **electromagnetic forces** between the atoms of the surface and the tip
 - The motion is recorded and used to create an image of the atomic surface
- **Scanning Tunneling Microscope (STM)**
 - A flow of **electrical current** occurs between the tip and the surface
 - The strength of this current is used to create an image of the atomic surface



Touching the Surface

- Scanning probe microscopes, developed in the 1980s, give us a new way to “see” at the nanoscale
- We can now see really small things, like atoms, and move them too!



This is about how big atoms are compared with the tip of the microscope



Sviluppo di tecniche di sintesi:

Espansione libera in fasci molecolari supersonici

Tecniche laser di vaporizzazione

Sputtering

Atomic Layer Deposition

Chemical vapor deposition (plasma assisted)

Impianto ionico

Sol-gel

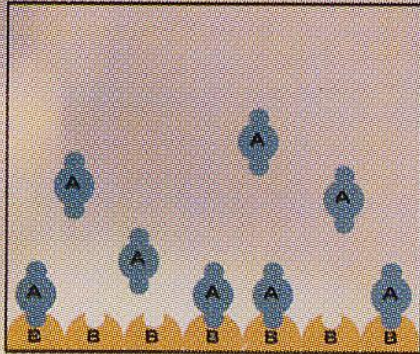
Ball-milling

Litografia, reactive ion etching...

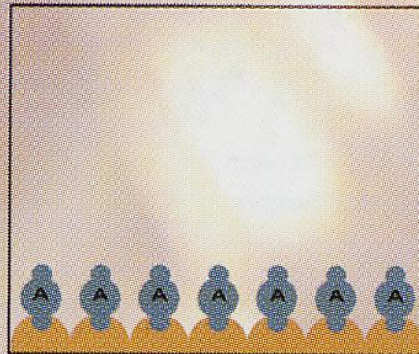
Atomic-Layer Chemical Vapour Deposition

Based on sequential saturated chemical reactions on the surface, this growth method has been called by various names: Atomic Layer Epitaxy (ALE), Atomic Layer Deposition (ALD), digital chemical vapour deposition (D-CVD) or atomic-layer chemical vapour deposition (ALCVD).

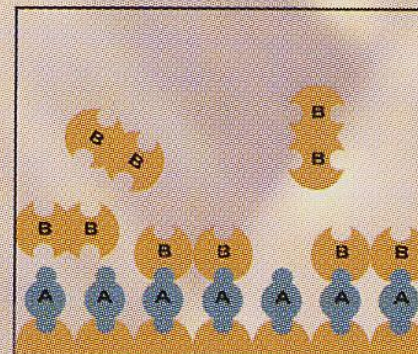
In Chemical Vapour Deposition (CVD) precursor chemicals are introduced simultaneously by a carrier gas into the reaction chamber where the precursors chemically react, depositing a thin film. However, in ALCVD, deposition is based on chemical reactions on the substrate surface. Also, in contrast to other CVD processes, ALCVD is divided into sequential saturated steps - growth takes place step-by-step, layer-by-layer - hence the name Atomic-Layer Chemical Vapour Deposition.



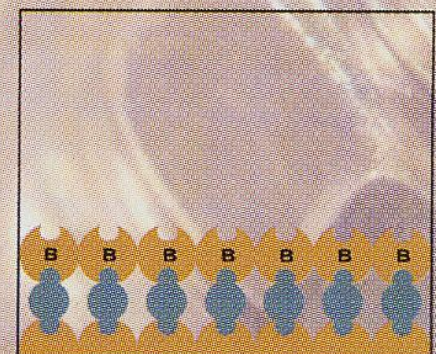
Vapour A chemisorbs on a surface covered by atoms B. The reaction proceeds until saturation, i.e. all bonding sites available to atoms A are filled.



After the saturation of the reaction, the surface is covered with atoms A, which makes the surface reactive to atoms B. Excess vapour is removed.



Vapour B chemisorbs on a surface covered by A. The reaction proceeds until all bonding sites available to atoms B are filled.



Reaction re-establishes the coverage with atoms B, which activates the surface to the next sequence of surface reaction with gas containing atoms A.

Breve storia dei nanomateriali

- 1861: Thomas Graham conia il termine colloide per descrivere una soluzione contenente particelle di diametro inferiore a 100 nm in sospensione; (Faraday, Ostwald,...)
- fine 1800 - inizio 1900: Rayleigh, Maxwell e Einstein studiano i colloidi (proprietà ottiche);
- 1908: Gustav Mie, calcolo elettrodinamico esatto della risposta ottica di nanocluster metallici
- 1930: metodo di Langmuir-Blodgett per deporre monostrati atomici;
- 1960: Uyeda studia con la microscopia e la diffrazione elettronica singoli nanocluster;
- 1970: nanocluster di lega metallica;
- 1985: Smalley & Kroto scoprono il C_{60} (fullerene)
- 1991: Iijima studia i nanotubi di C;
- 1993: Creato negli Usa il primo laboratorio di nanotecnologie (Rice University)
- 2000: manipolazione e posizionamento di singoli atomi (STM, AFM) nanotecnologia.
- 2002 L'Europa stanZIA 700 milioni € in quattro anni.
- ...la storia continua... ...Sistemi biologici...

Materiali Nanostrutturati

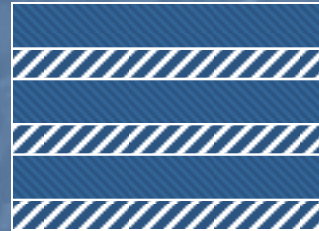
(dimensioni caratteristiche < 100 nm)

1.



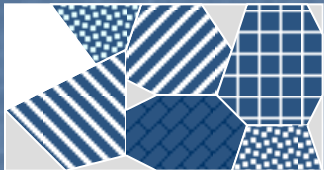
Materiali
Massivi (3D)

4.



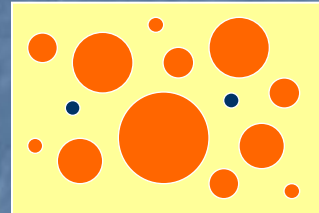
Multi-strati
(1D-2D)

2.



Materiali Nanofasici
(3D)

5.



Nanoclusters (~ 0D)
(metalli,
semiconduttori,
nanotubi, fullereni...)

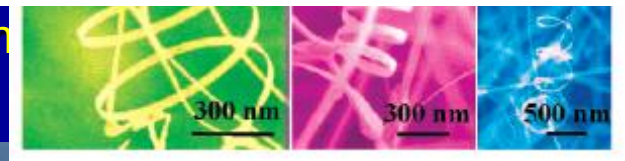
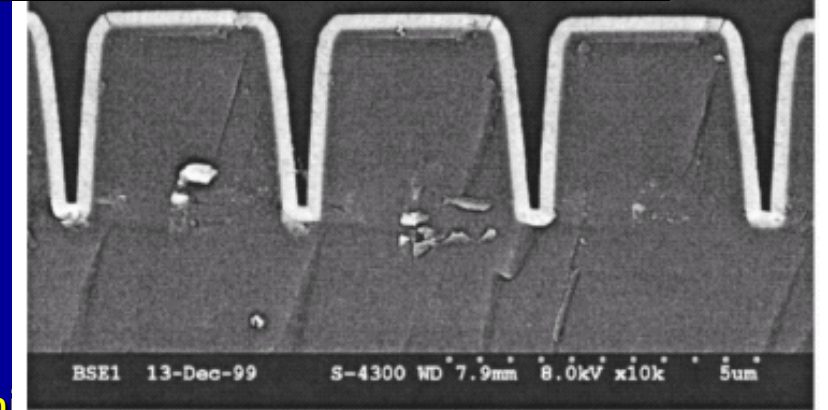
3.



Film nanofasici
(1D-2D)

Cosa sono (1 nm

- Nanoparticelle (0 D)
- Nanofili, nanofibre, nanocavi
- Film sottili (2 D)
- Nanomateriali massivi (3 D)
 - Materiali Mesoporosi
 - Ibridi organico-inorganici
 - Materiali Nanostrutturati (nanogran
 - Nanocompositi (nanoparticelle o nanofibre in



Attività di Ricerca & Sviluppo (R&D) sui nanomateriali

1) Ricerca sui nanomateriali:

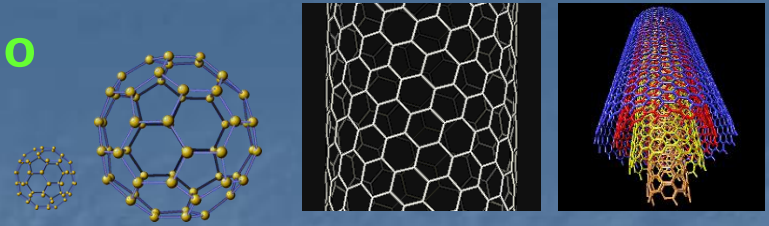
Nuove proprietà chimico-fisiche (diverse dal bulk)

2) Sviluppo di tecniche di sintesi:

- Espansione libera in fasci molecolari supersonici
- Tecniche laser di vaporizzazione
- Sputtering
- Impianto ionico
- Sol-gel
- Chemical vapor deposition
- Ball-milling
- Litografia, reactive ion etching...

3 Nanomateriali a base di carbonio

3.1 Nanotubi di carbonio



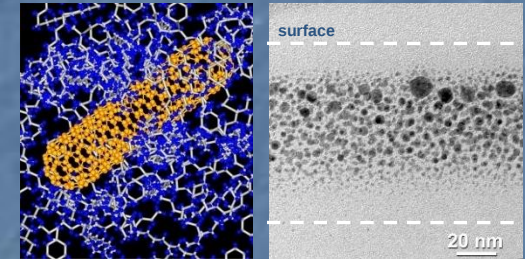
4 Nanomateriali a base polimerica

4.1 Compositi a matrice polimerica

4.1.1 Sensoristica

4.1.2 Fotonica

4.1.3 Ricoprimenti

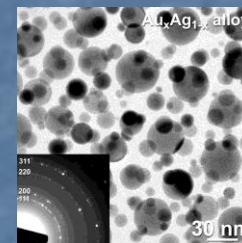


5 Nanomateriali a base vetrosa

5.1 Vetri e vetroceramici

5.1.1 Vetri tecnici

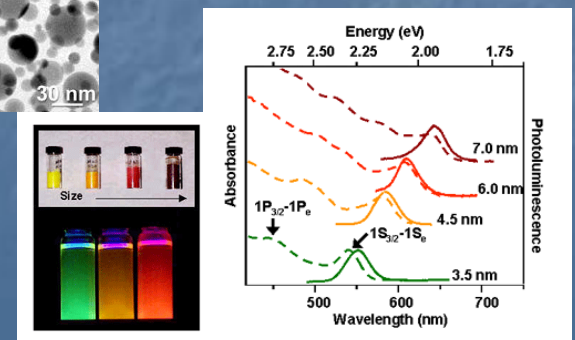
5.1.2 Vetroceramici



6 Nanomateriali e quantum dots

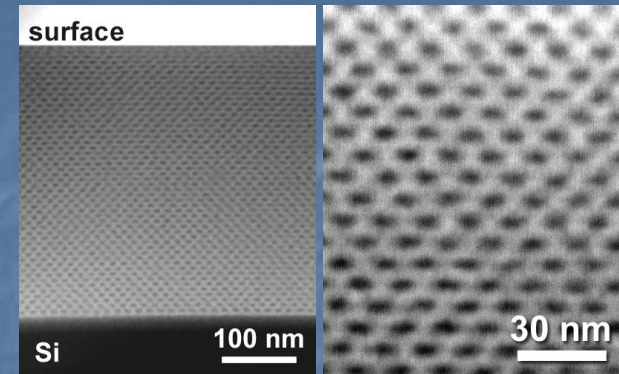
6.2 Nanofotonica

6.2.1 Ottica nonlineare



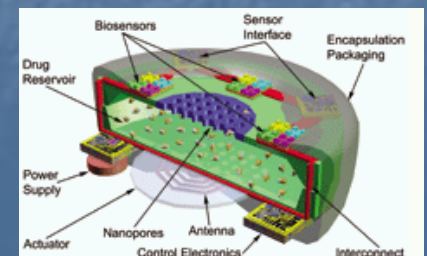
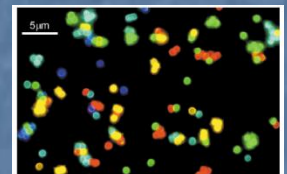
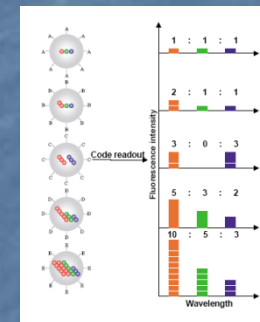
7 Nanomateriali per la sensoristica

- 7.1 Sensori chemio-resistivi
- 7.2 Sensori a lettura ottica (opto-chimici).
- 7.3 Sensori a film sottile mesoporoso
- 7.4 Sensori a matrice polimerica



8 Nanomateriali per la biotecnologia e l'ambiente

- 8.1 Diagnostica medica: il lab-on-chip
- 8.2 Nanoparticelle come biosensori
- 8.3 Ingegneria tissutale
- 8.4 Biocapsule
- 8.5 Le nanotecnologie per l'ambiente
 - 8.6.1 Nanoparticelle di oro come catalizzatori
 - 8.6.2 Nanoparticelle di oro funzionalizzate



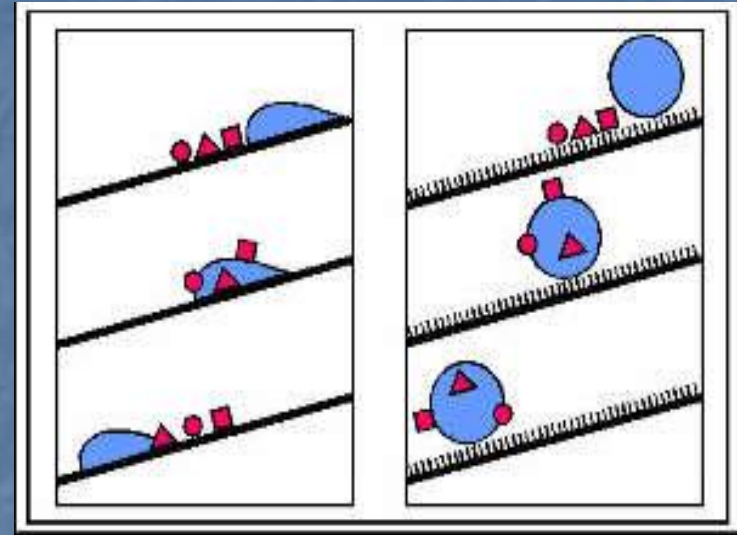
Un esempio dove l'uomo copia la natura:

Il controllo chimico e morfologico consente di ottenere superfici super-idrofobiche con proprietà auto-pulenti sfruttando il cosiddetto "Effetto Loto"

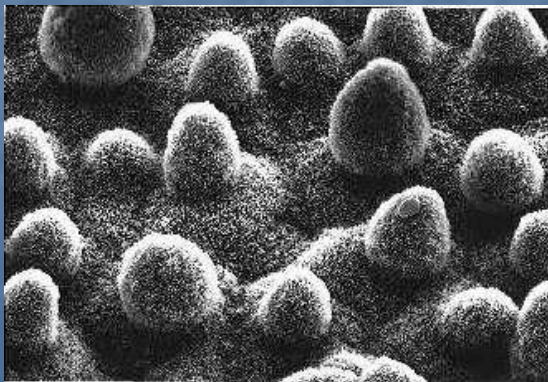
Superfici auto-pulenti: Effetto Lotus



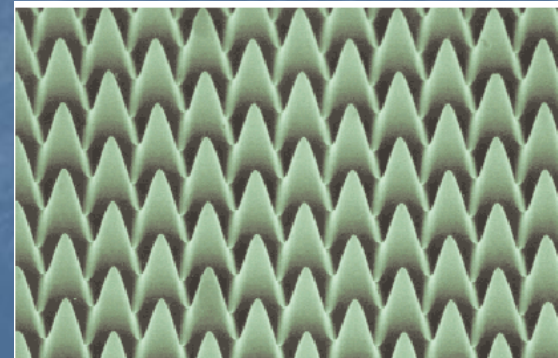
10 μm



W. Barthlott, Univ. di Amburgo



Cera cuticolare



REM recording of a
holographically produced
self-cleaning
surface.
© Fraunhofer ISE

Tensione Superficiale

Forze di Adesione

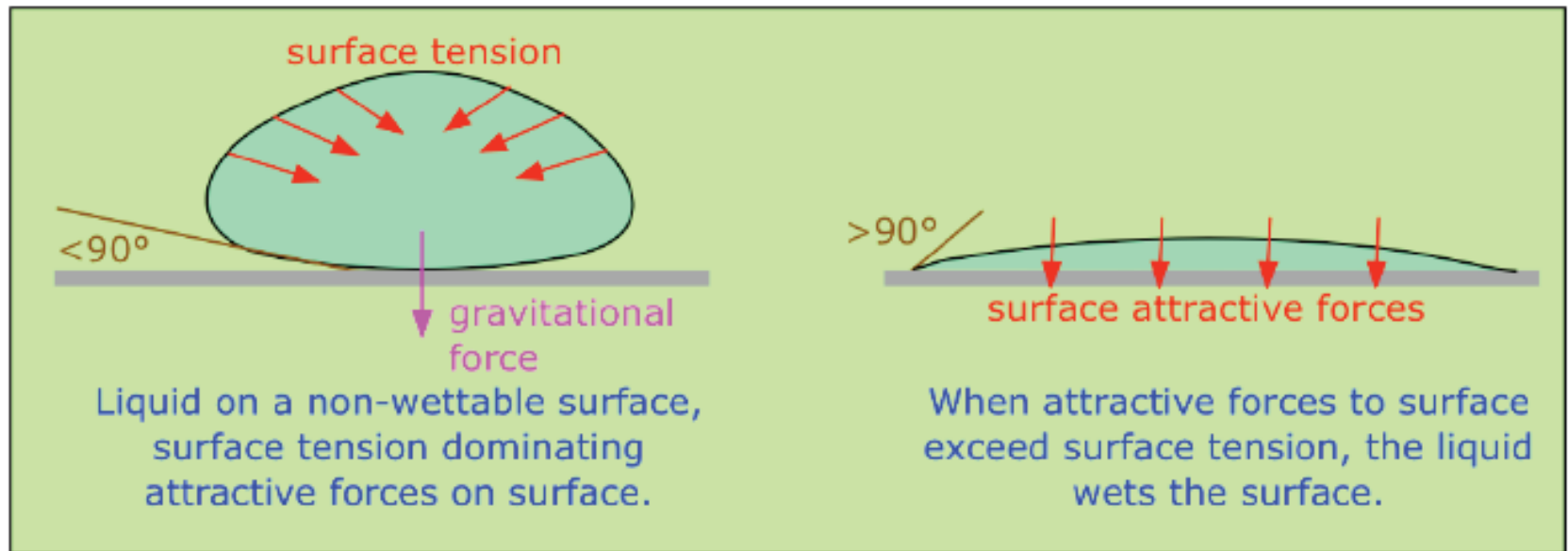
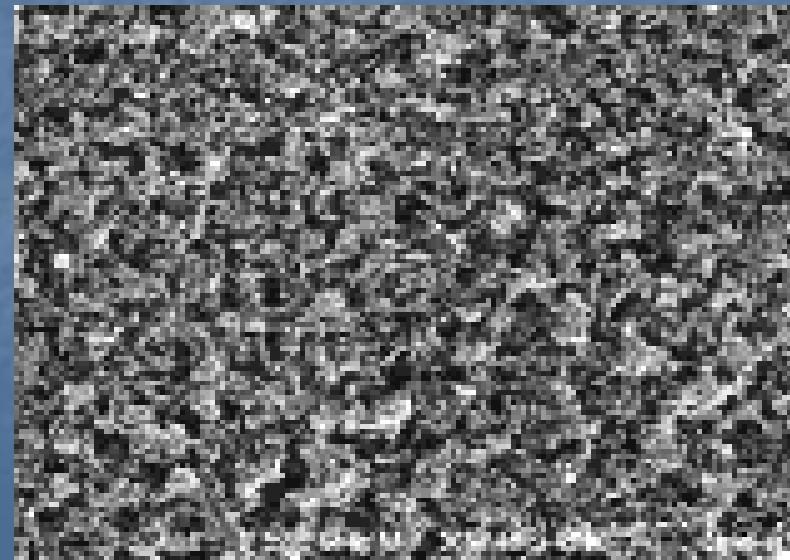
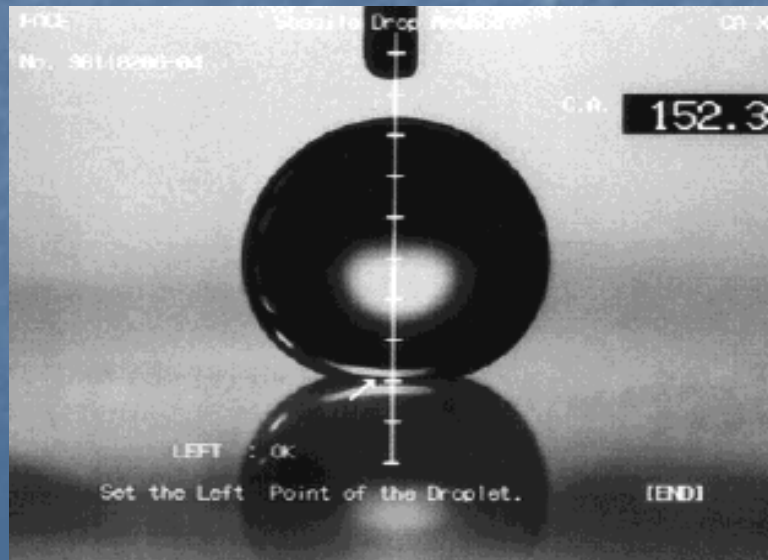
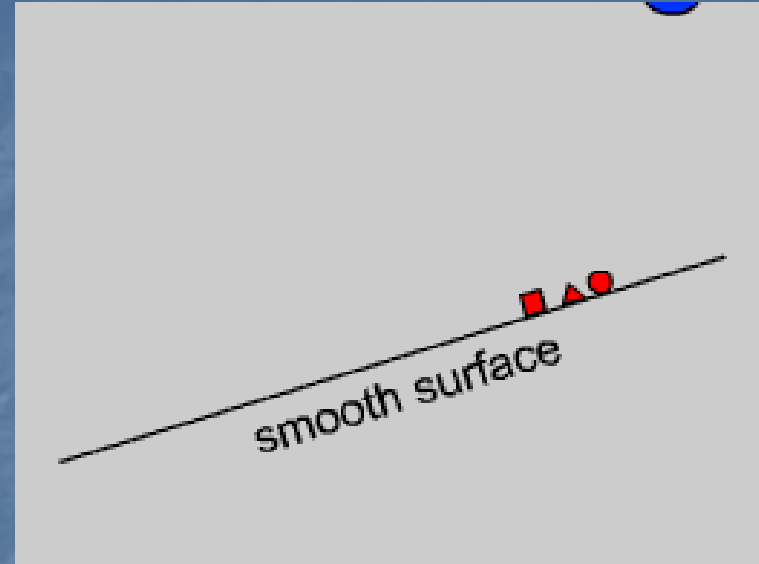
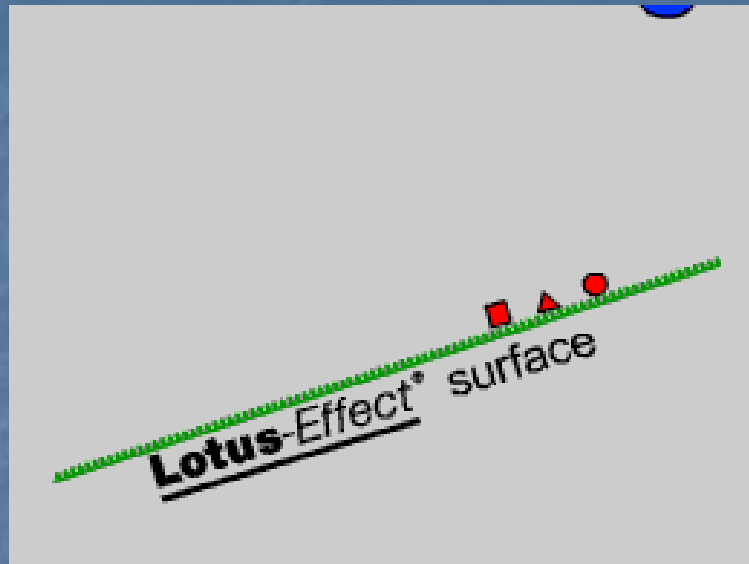
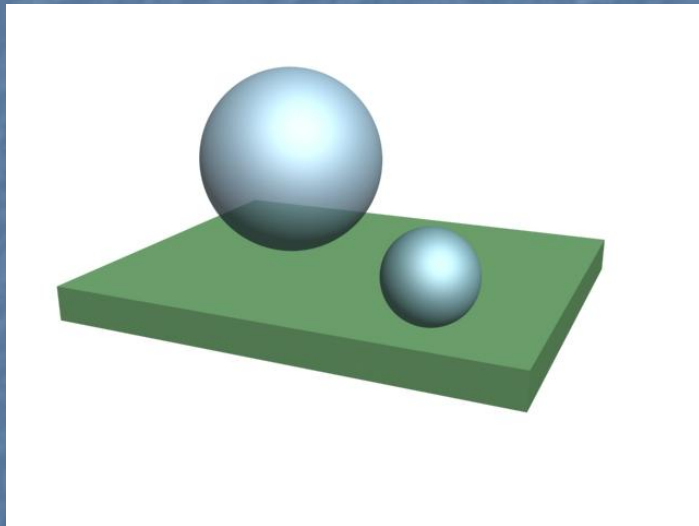


Figure 1. Surface tension and surface attractive forces for a drop of water on a non-wettable surface like glass (left), or a more attractive surface (right) [1].

Lotus Effect

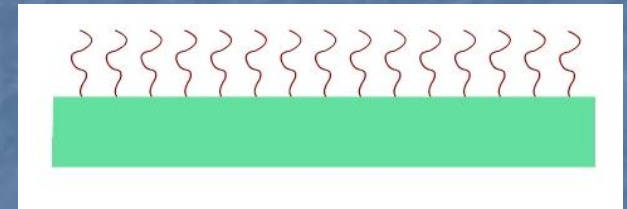


Film autopulente superidrofobico



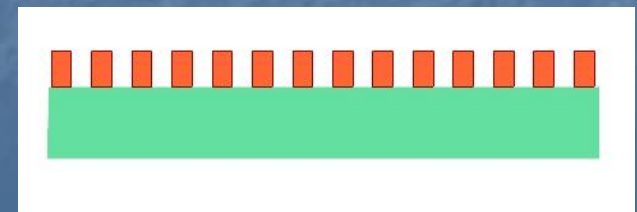
**Contributo
chimico**

Innesto di alchilfluorosilani
Molecole idrofobiche



**Contributo
geometrico**

Morfologia





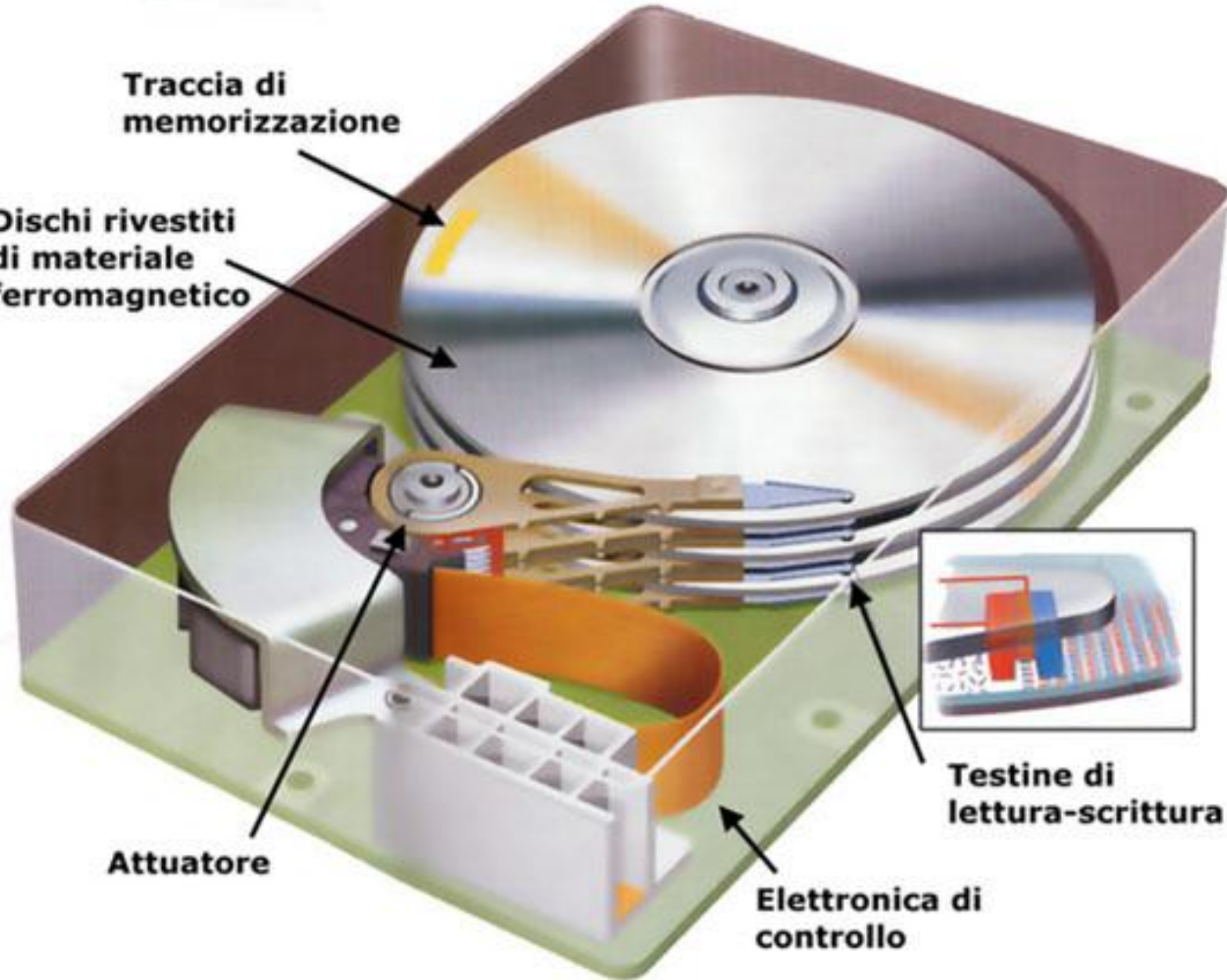
Disco Rigido
HITACHI DK23EA-60
da 60 GB su 2 piatti,
4200 giri/minuto.
Peso 95 grammi. Proveniente da
PC portatile, circa anno 2005.

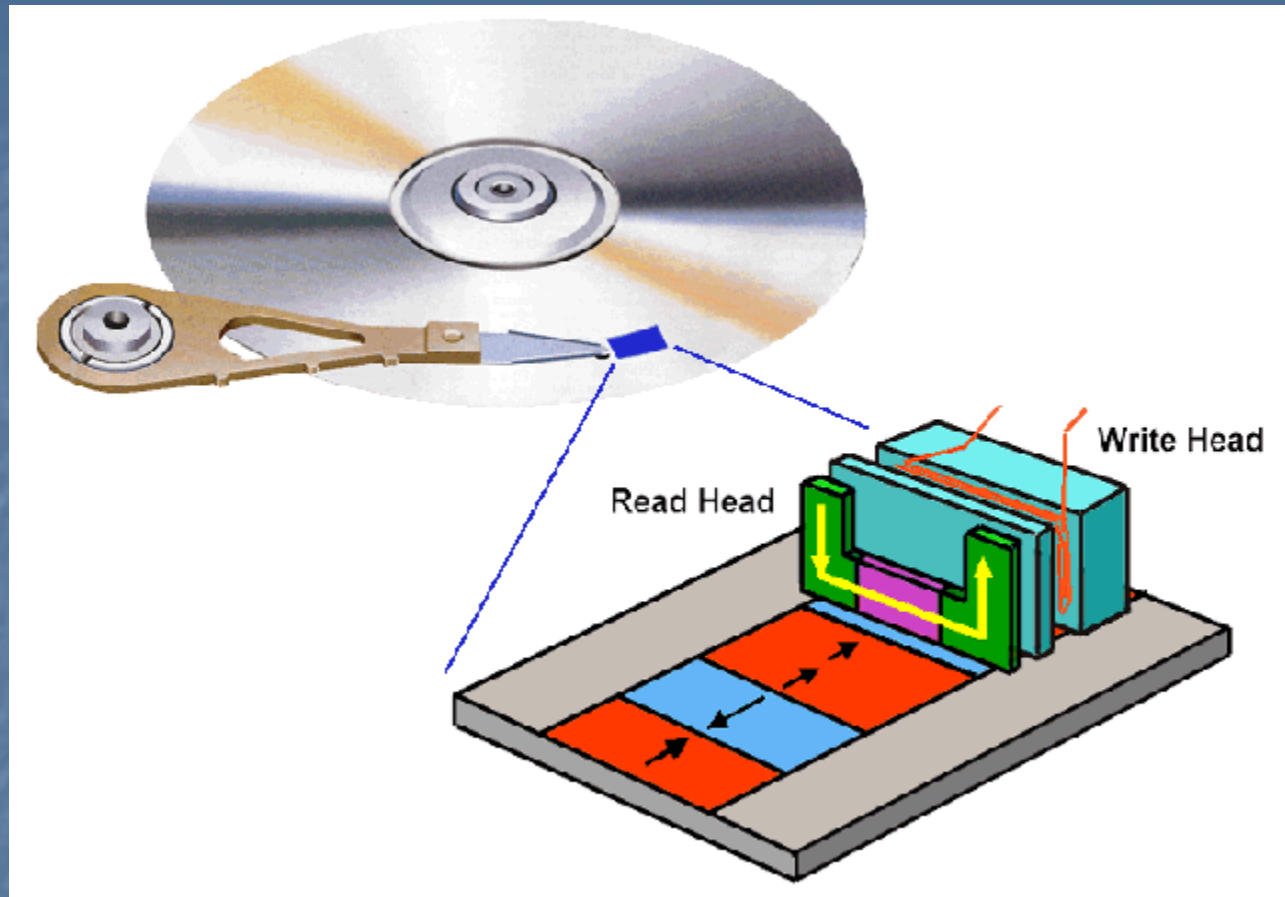




Traccia di memorizzazione

Dischi rivestiti di materiale ferromagnetico



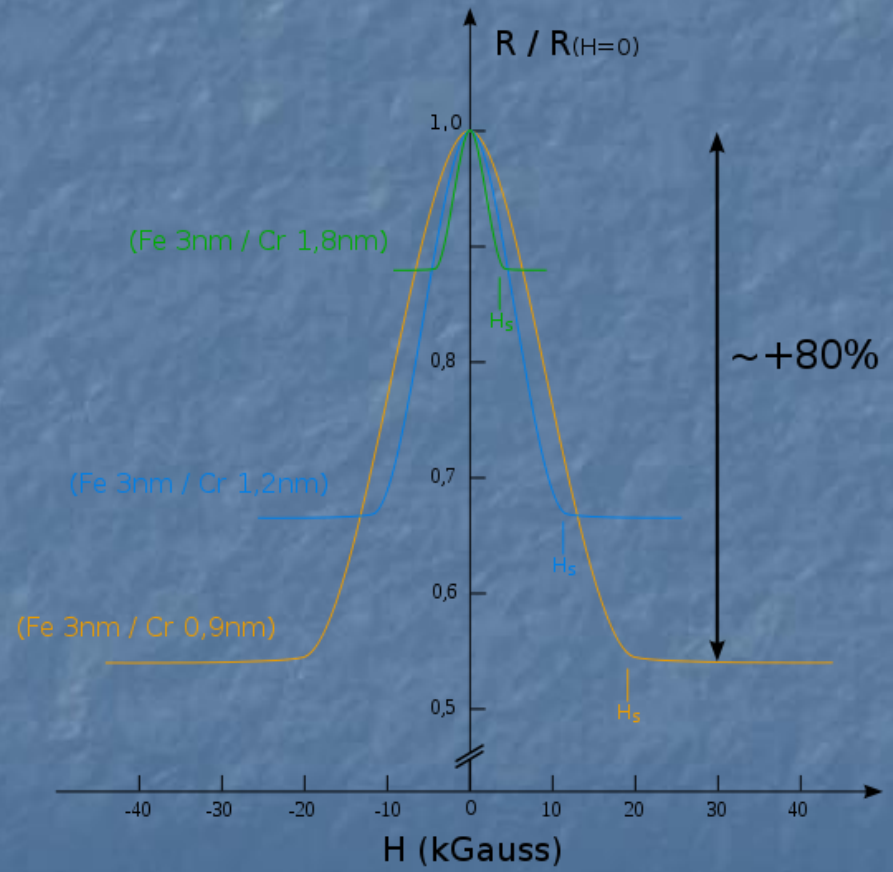
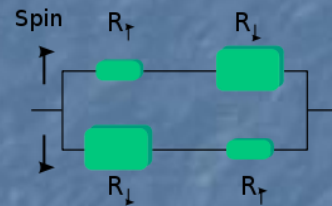
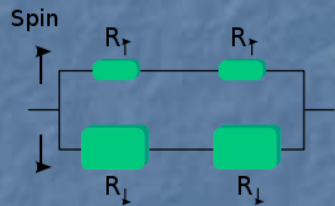
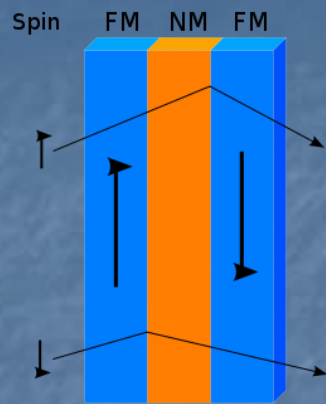
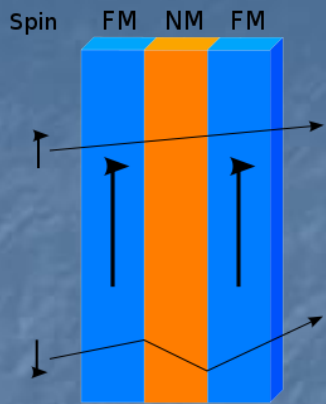


Giant magnetoresistance (GMR) (1988) is a [quantum mechanical magnetoresistance](#) effect observed in thin film structures composed of alternating [ferromagnetic](#) and nonmagnetic layers.

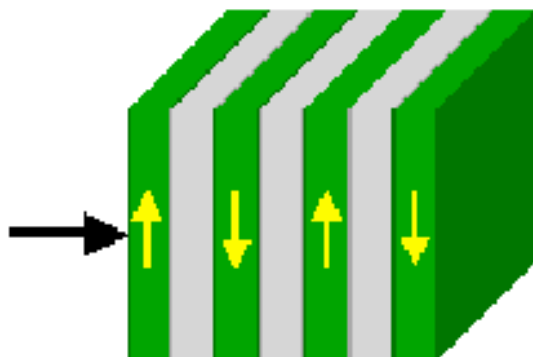
The effect manifests itself as a significant decrease (typically 10–80%) in [electrical resistance](#) in the presence of a magnetic field. [In the absence of an external magnetic field](#), the direction of [magnetization](#) of adjacent [ferromagnetic](#) layers is [antiparallel](#) due to a weak anti-ferromagnetic [coupling](#) between layers. The result is high-resistance magnetic scattering as a result of electron spin. When an external magnetic field is applied, the magnetization of the adjacent ferromagnetic layers is parallel. The result is lower magnetic [scattering](#), and lower resistance.[\[1\]](#)

The effect is exploited commercially by manufacturers of [hard disk drives](#).

The 2007 [Nobel Prize in physics](#) was awarded to [Albert Fert](#) and [Peter Grünberg](#) for the discovery of GMR.



a.

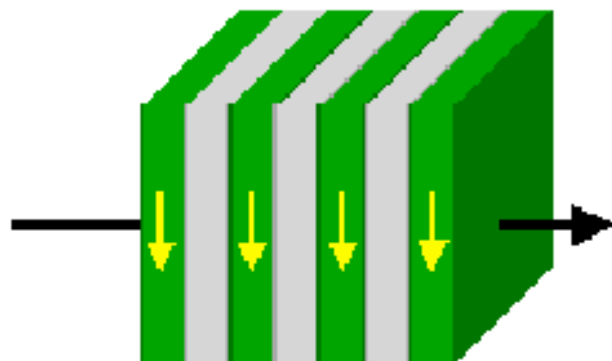


Magnetic layer

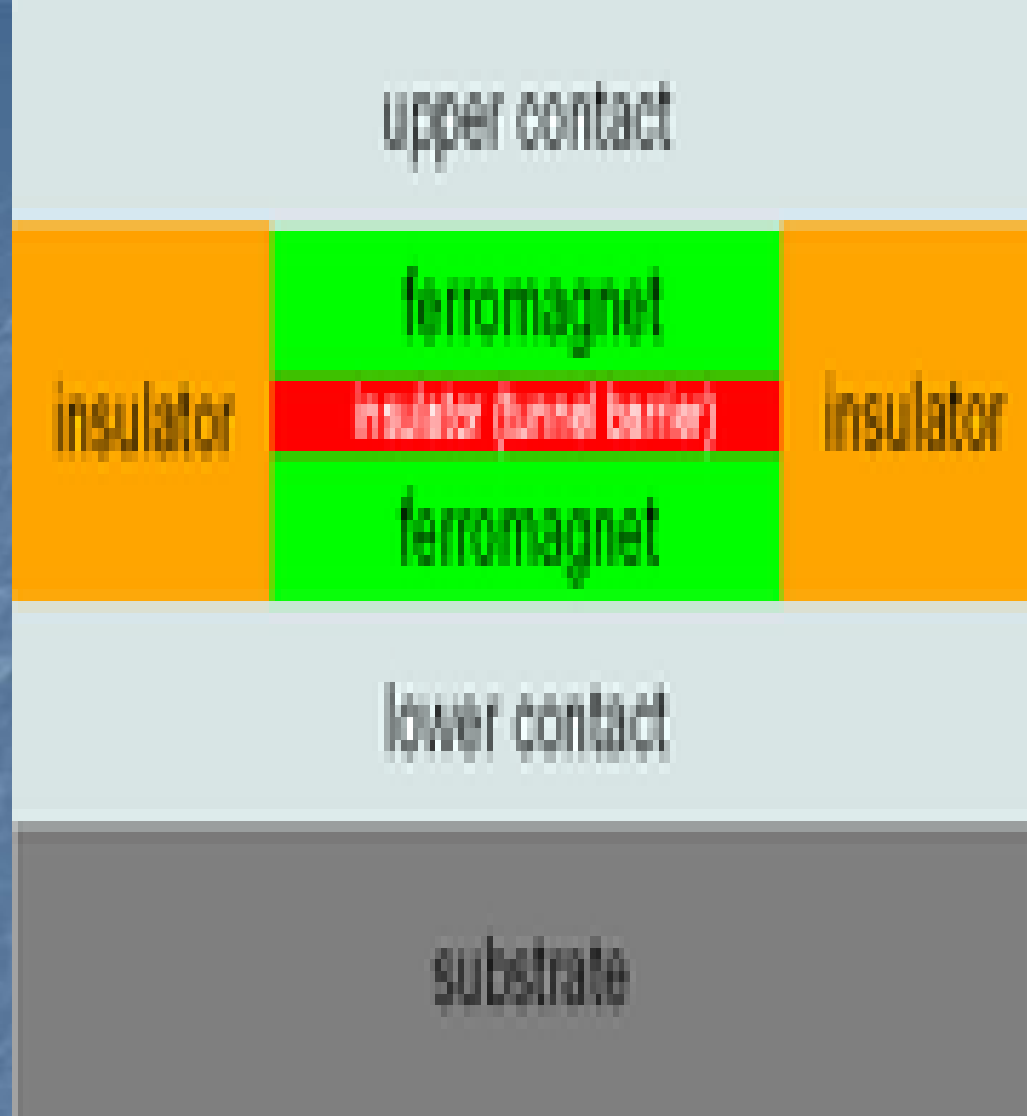


Non-magnetic layer

b.

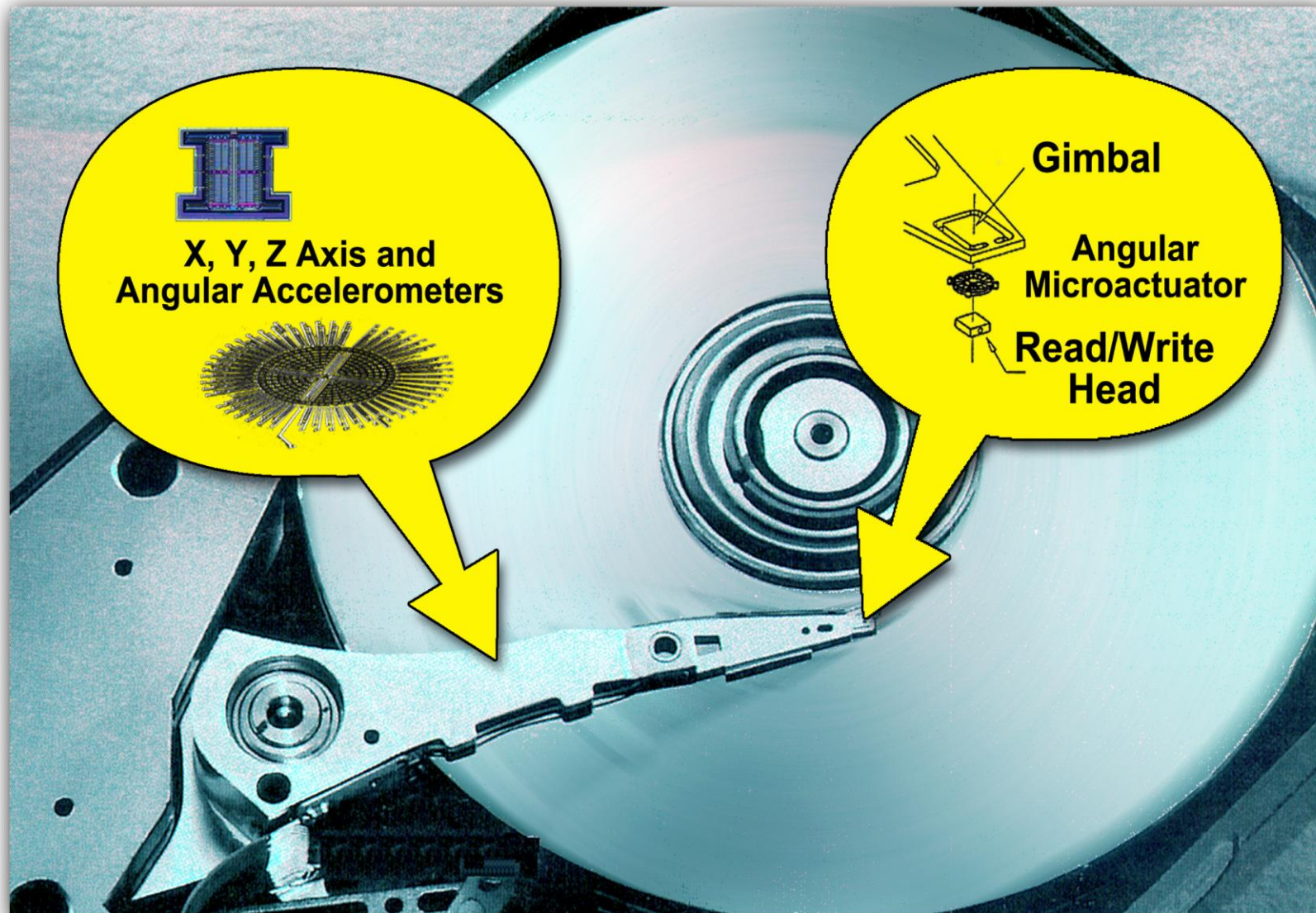


Magnet

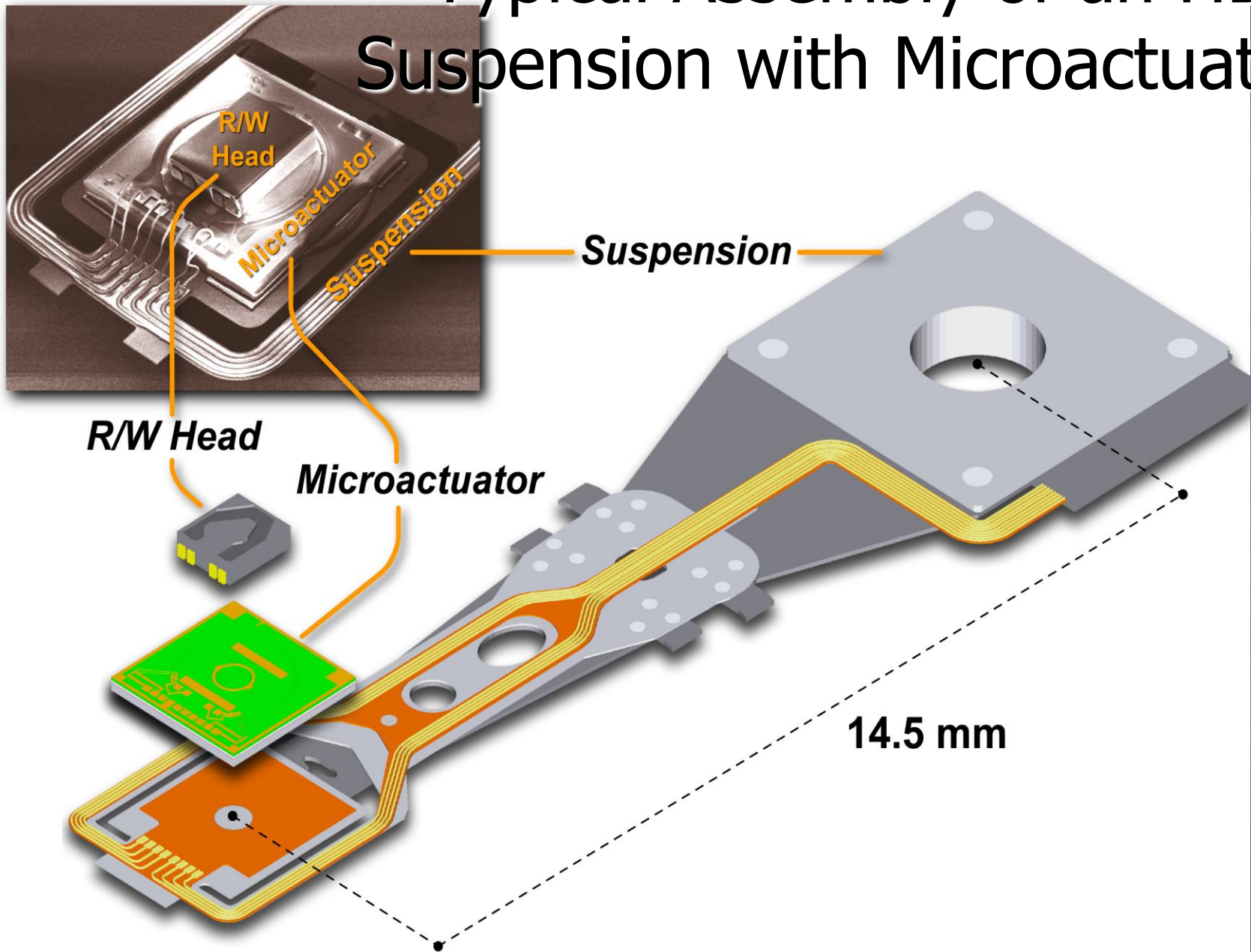


Tunnel magnetoresistance (TMR)

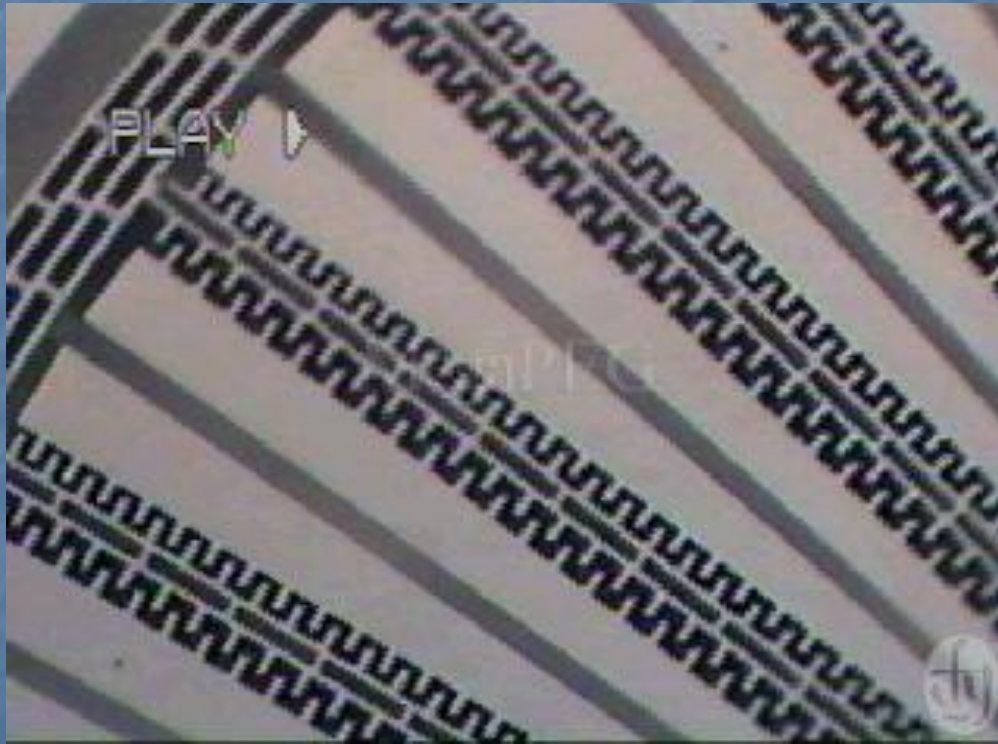
Silicon Microstructures in Future HDD



Typical Assembly of an HDD Suspension with Microactuator

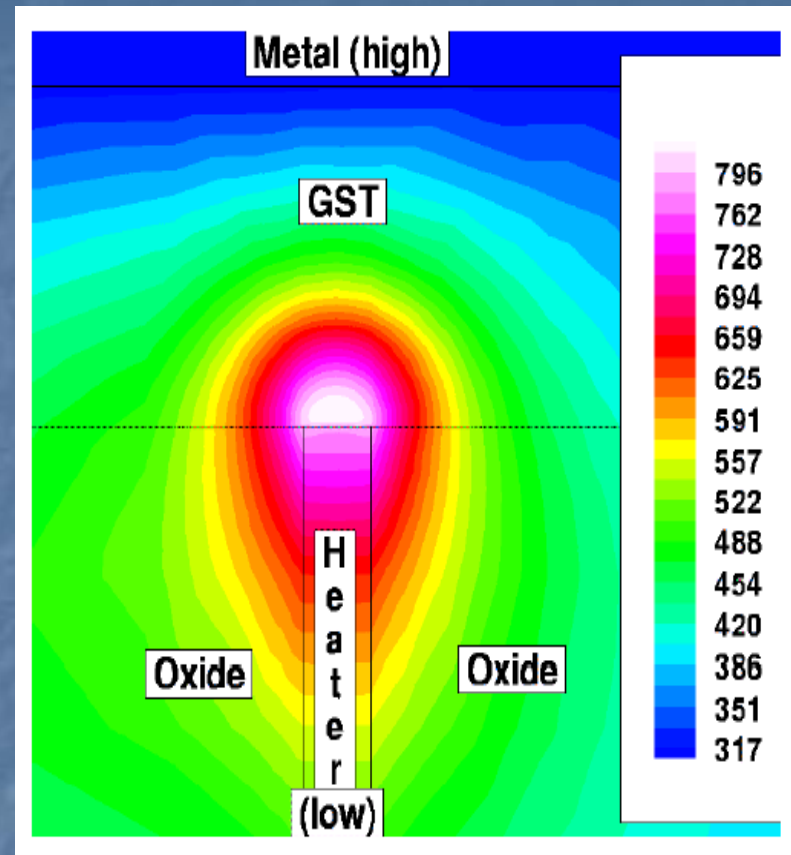
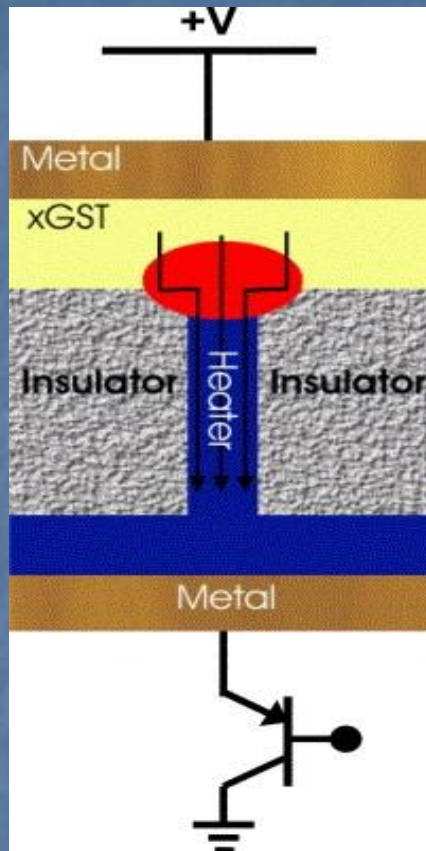


Microactuator without Cap Movie



MEMORIE ELETTRONICHE DI NUOVA GENERAZIONE A CAMBIAMENTO DI FASE REVERSIBILE

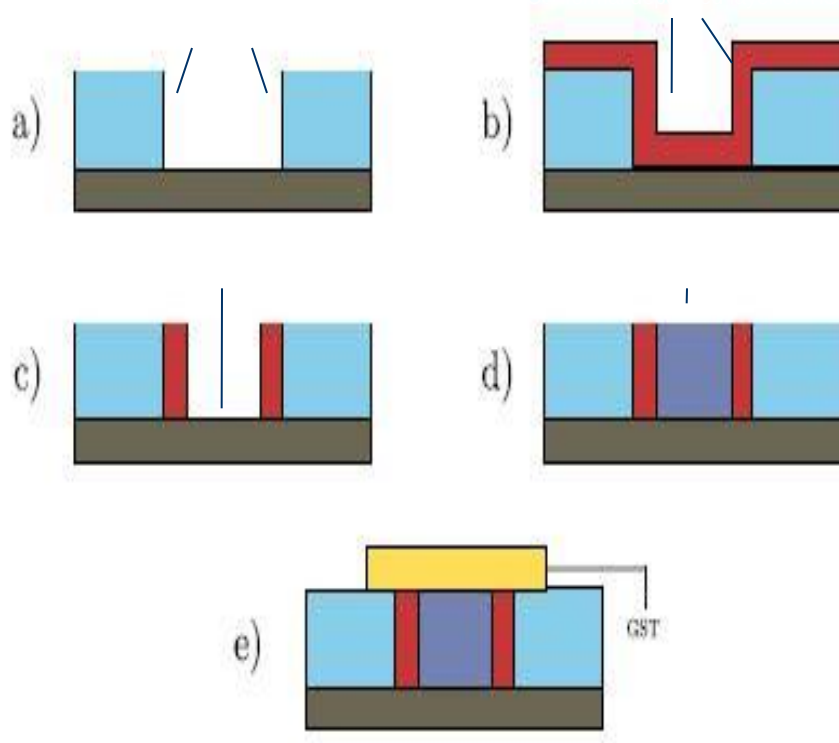
PCM = Phase Change Memories



- Maximum temperature at the GST/Heater interface: $\sim 800^{\circ}\text{C}$
- Maximum temperature at Metal/GST interface: $300 \div 400^{\circ}\text{C}$

Sample Deposition Process

No Lithographic process



SiO₂ deposition on Si

SiO₂ surface degas

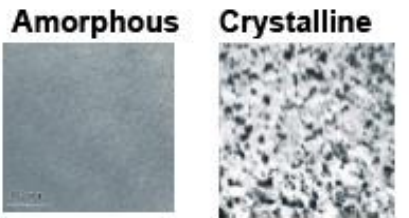
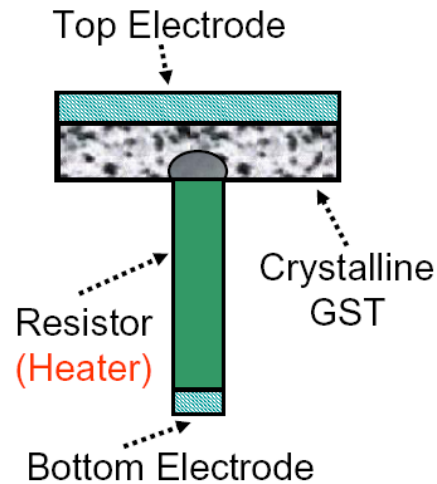
MOCVD TiN deposition

H₂/N₂ RF plasma

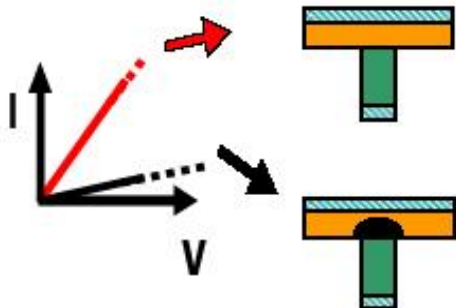
SiH₄ soak

Cella di Memoria Elettronica non-volatile con materiale con cambiamento di fase reversibile

From Concept ...



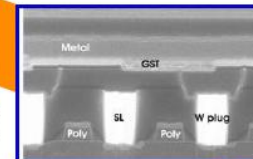
High resistivity Low resistivity



...to Integration



Storage Element



Memory Cell



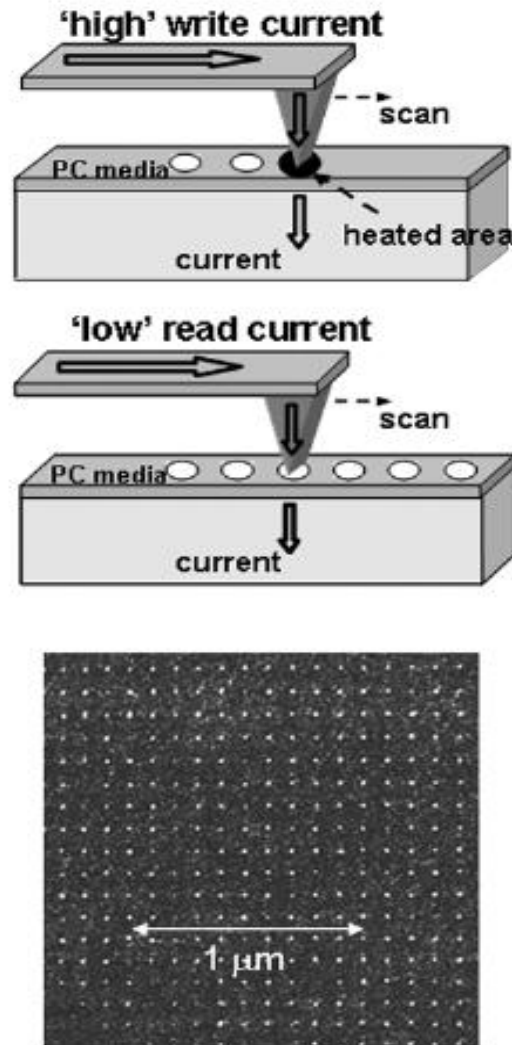
Memory Cell Array

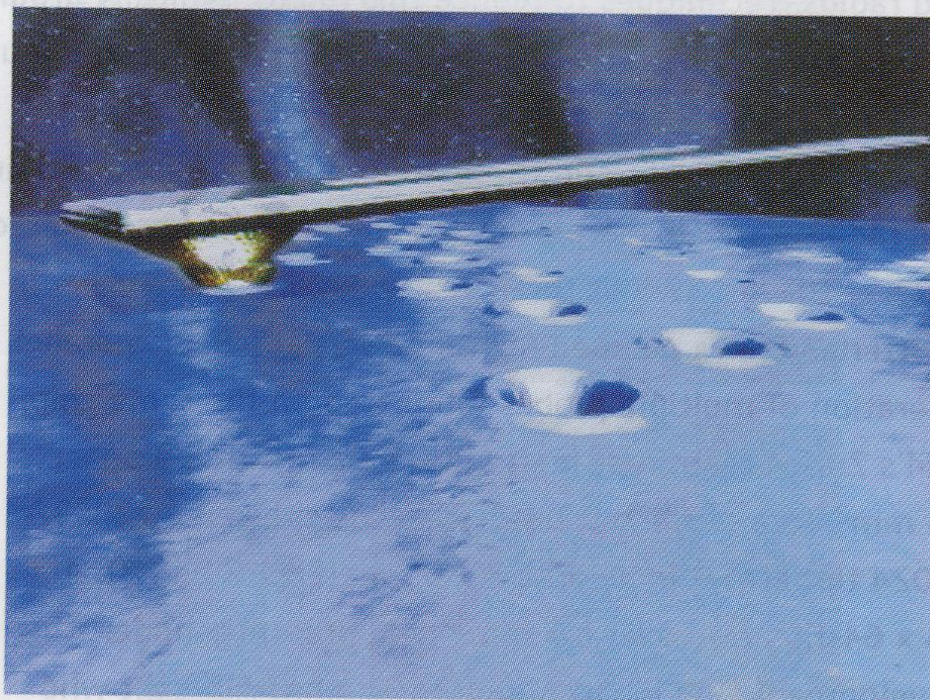
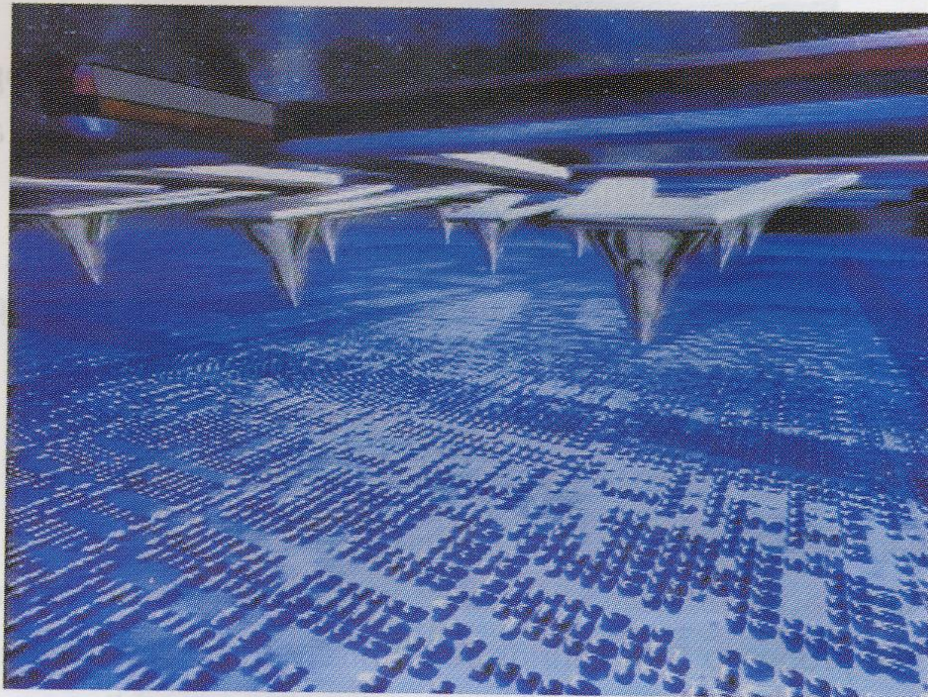


128Mb
PCM Chip

NUOVI TIPI DI MEMORIE

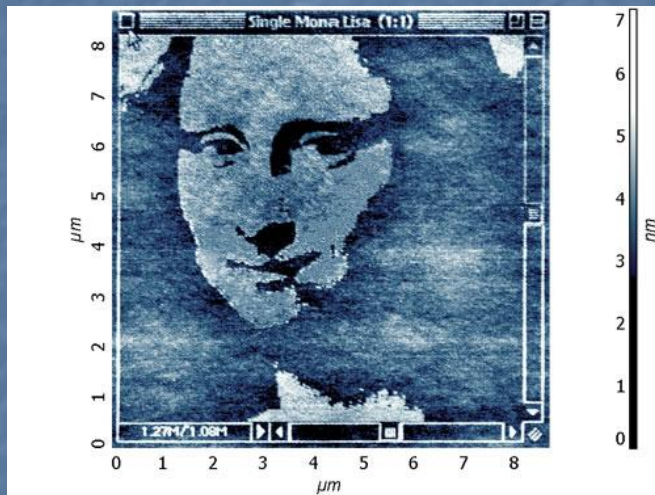
BASATI SU AFM e MATERIALI A VARIAZIONE DI FORMA REVERSIBILE



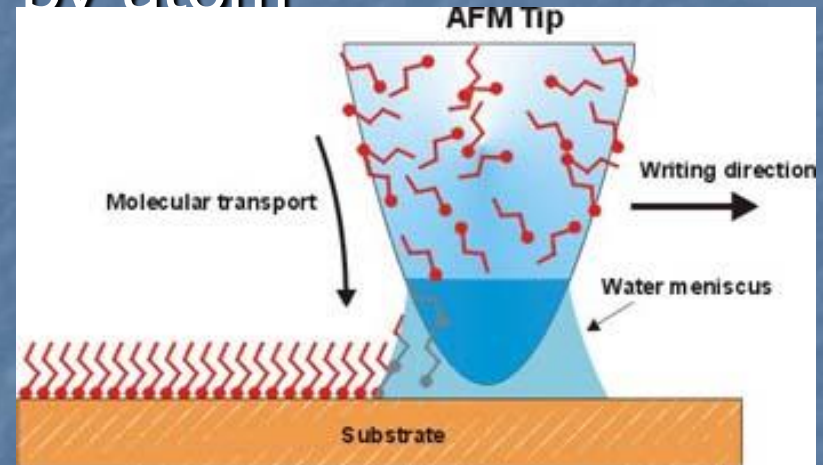


Technology: Building Smaller Devices and Chips

- Nanolithography to create tiny patterns
 - Lay down “ink” atom by atom



Mona Lisa, 8 microns tall, created by AFM nanolithography



Transporting molecules to a surface by dip-pen nanolithography

EFFETTO SEEBECK

(THOMSON)

L'effetto Seebeck è un effetto termoelettrico per cui, in un circuito costituito da conduttori metallici o semiconduttori, una differenza di temperatura genera elettricità

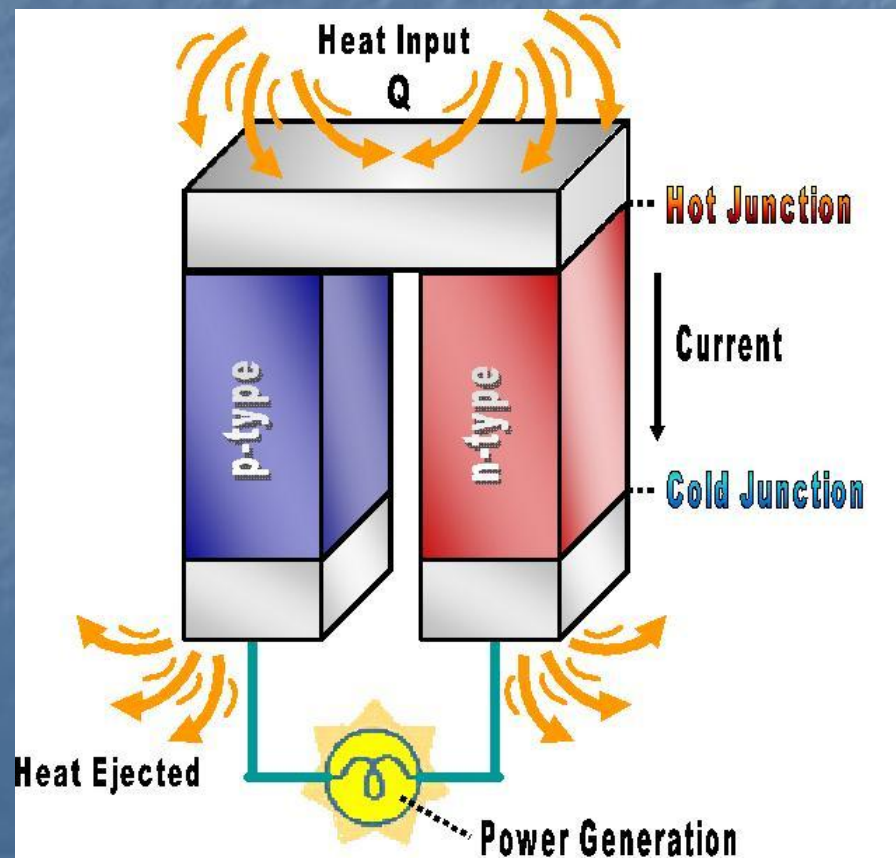


Figura di merito Seebeck

Rapporto tra:

Conducibilità elettrica e Conducibilità termica

Dipende dal materiale attraverso il coefficiente Seebeck

Valori Figura di Merito:

Bi_2Te_3 circa 1 (materiale generalmente usato)

Metalli circa 10^{-4} - 10^{-5}

Silicio poly circa 3×10^{-2}

In fili nanocristallini di silicio la conducibilità termica diminuisce di un fattore 100 dovuto allo scattering dei fononi sulle superfici

Effetto Seebeck nanofili di silicio



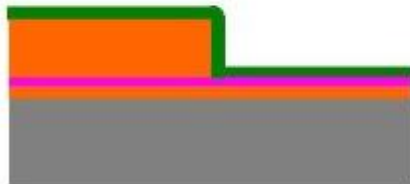
a) Silicio massivo



b) Deposizione della membrana
 $\text{SiO}_2/\text{Si}_3\text{N}_4$



c) deposizione e definizione
del SiO_2



d) Deposizione del polisilicio

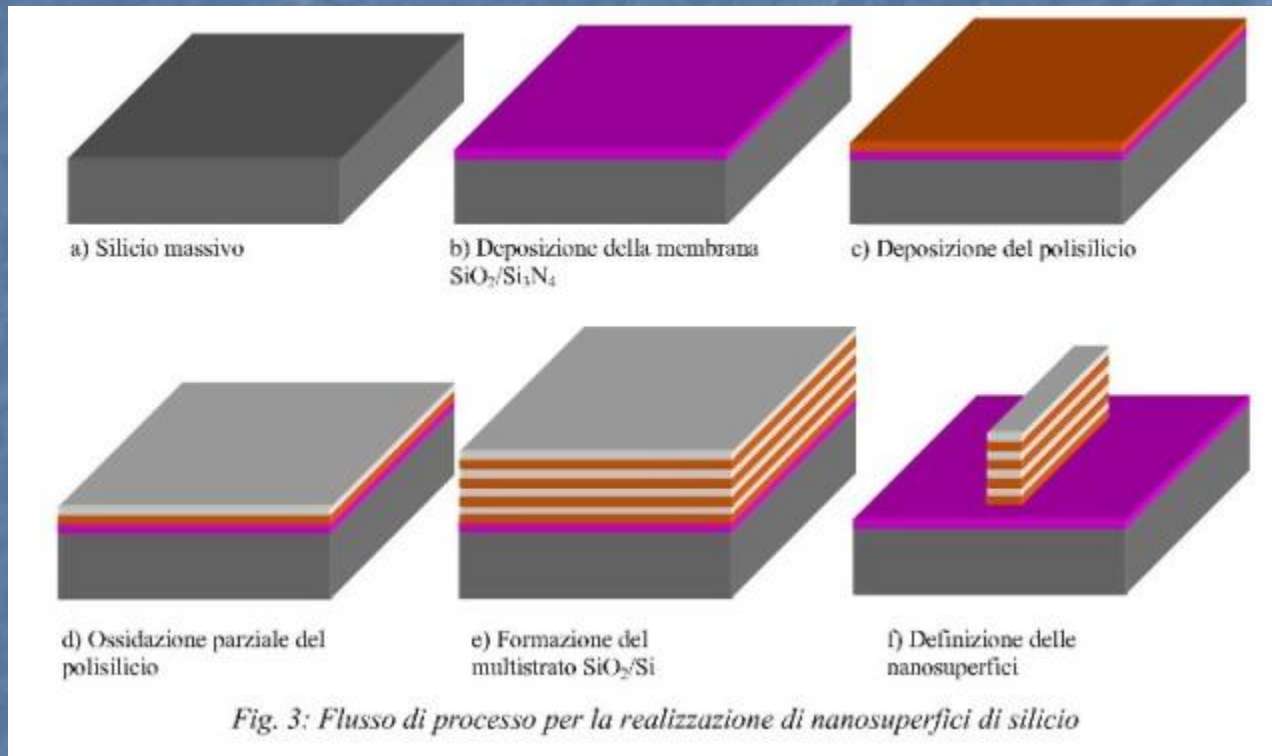


e) Attacco al plasma direzionale del
polisilicio

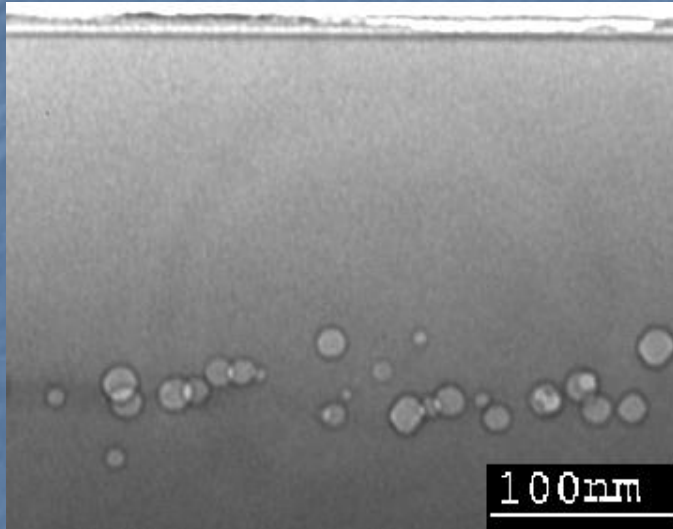


f) Rilascio dei nanofili di silicio

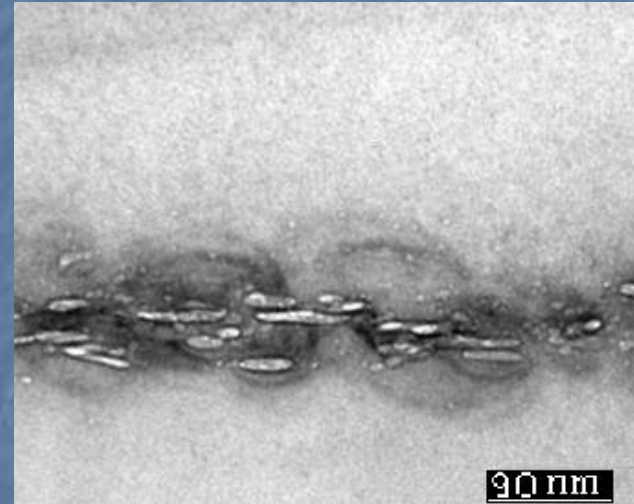
Effetto Seebeck nanosuperfici di silicio



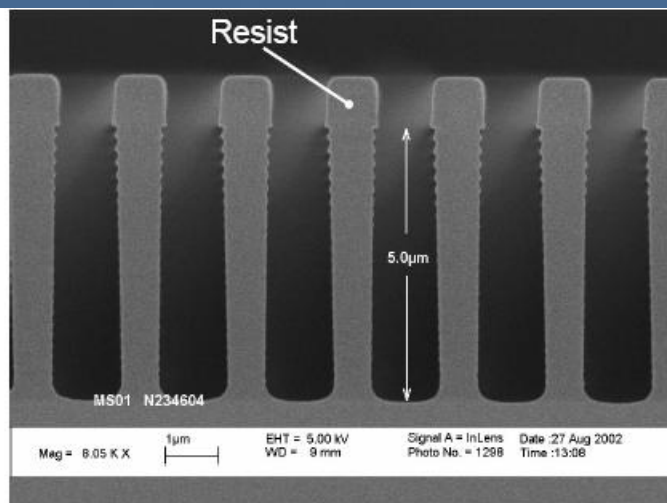
Helium Implanted Silicon



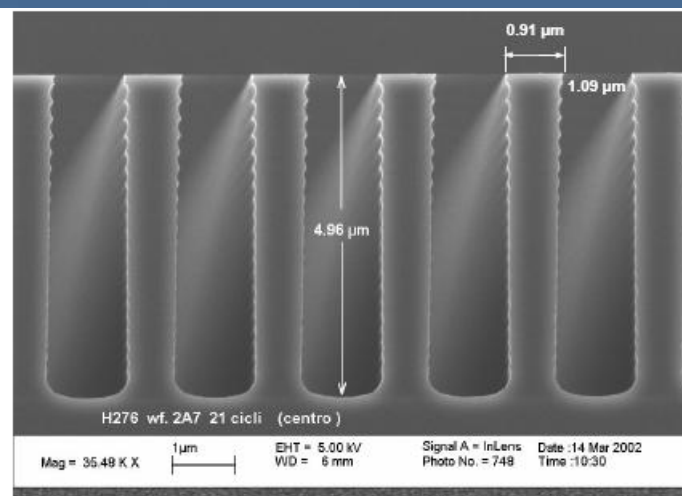
800 C 2 hours



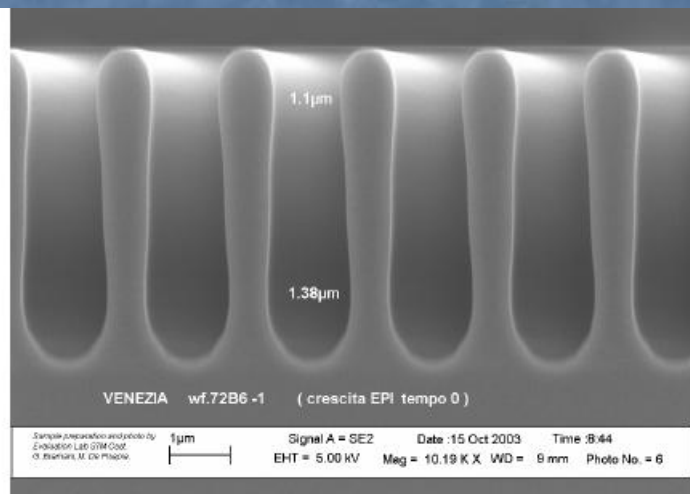
500 C 2 hours



After trench etch

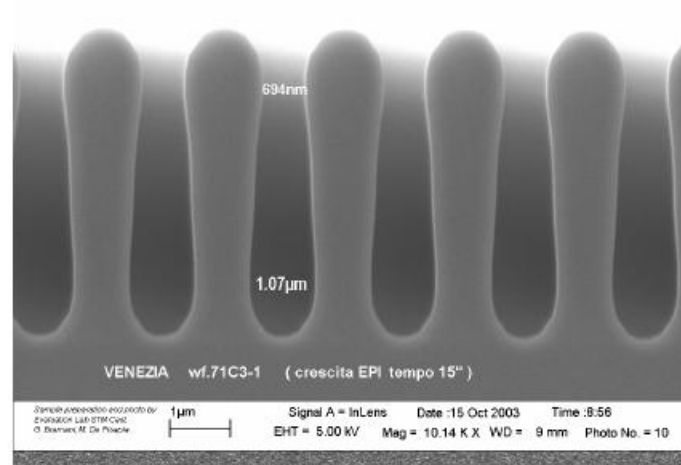
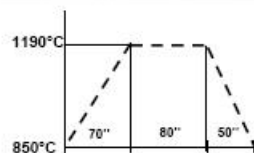


After resist strip



Atmospheric pressure

H₂ flow: 70 l/m

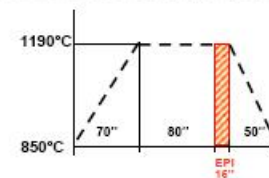


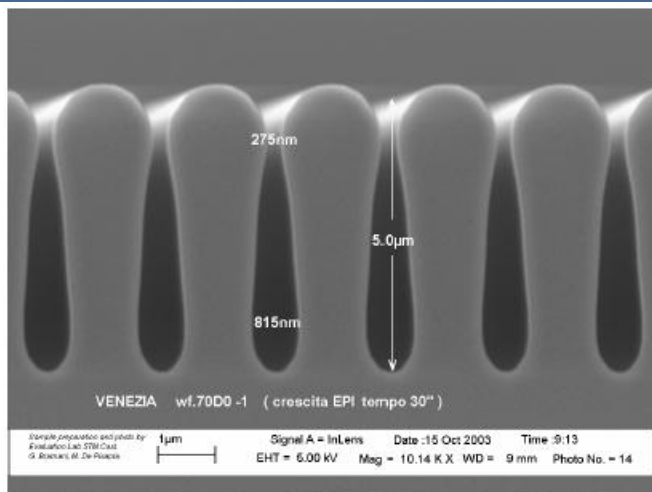
Atmospheric pressure

H₂ flow: 70 l/m

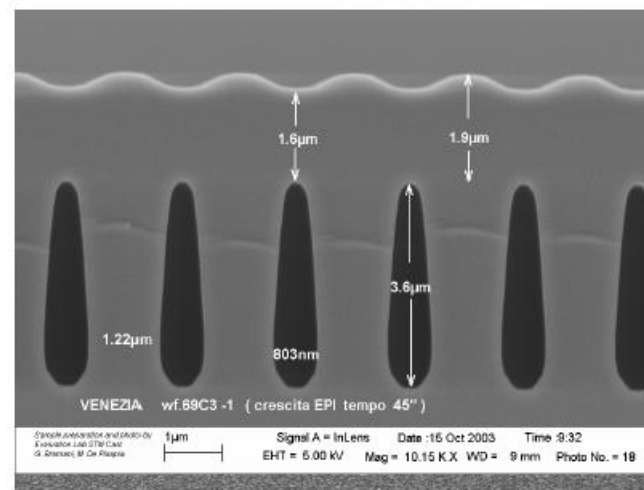
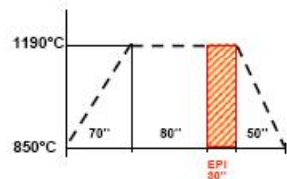
SiHCl₃ flow: 9.7 g/m

Dep rate: 54.7 nm/s

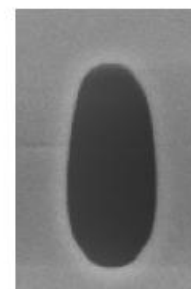
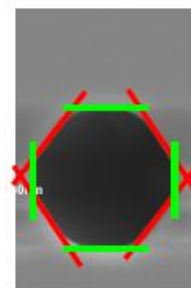
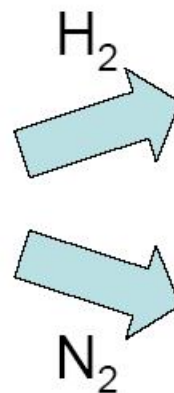
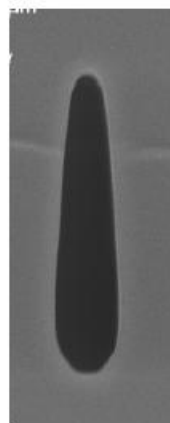
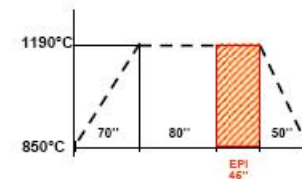


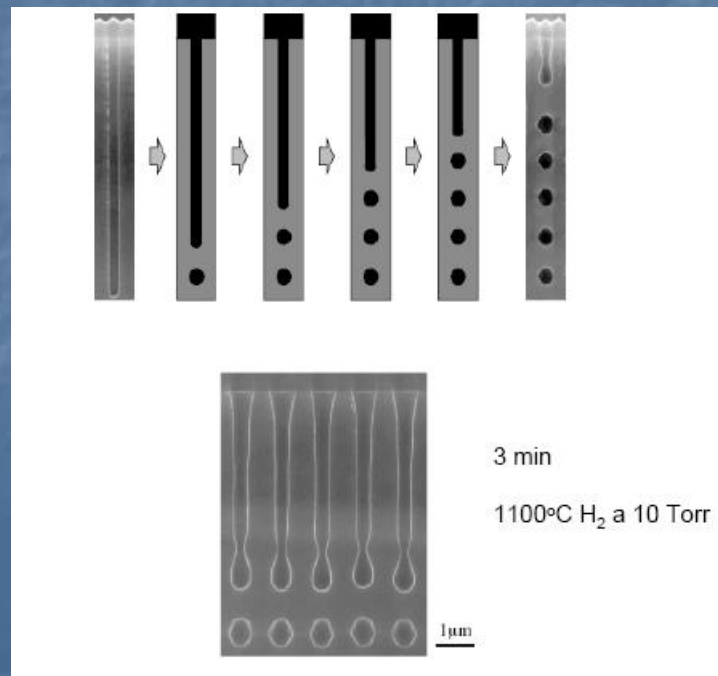
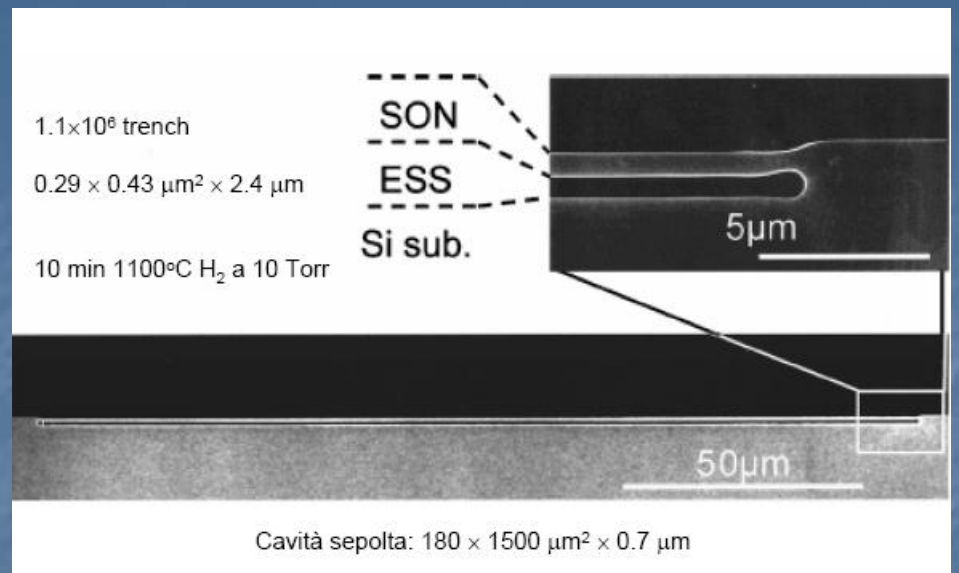
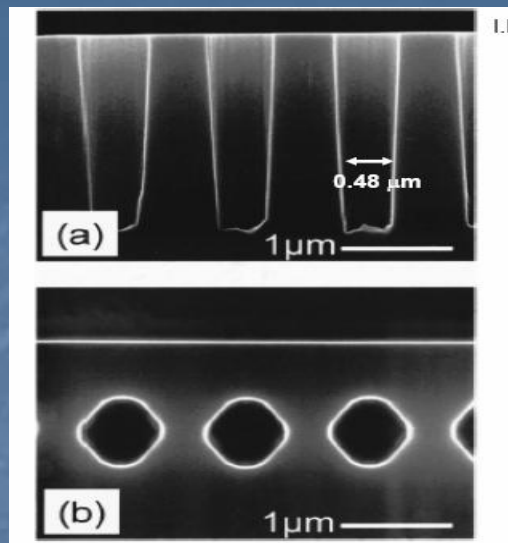


Atmospheric pressure
 H_2 flow: 70 l/m
 $SiHCl_3$ flow: 9.7 g/m
 Dep rate: 54.7 nm/s

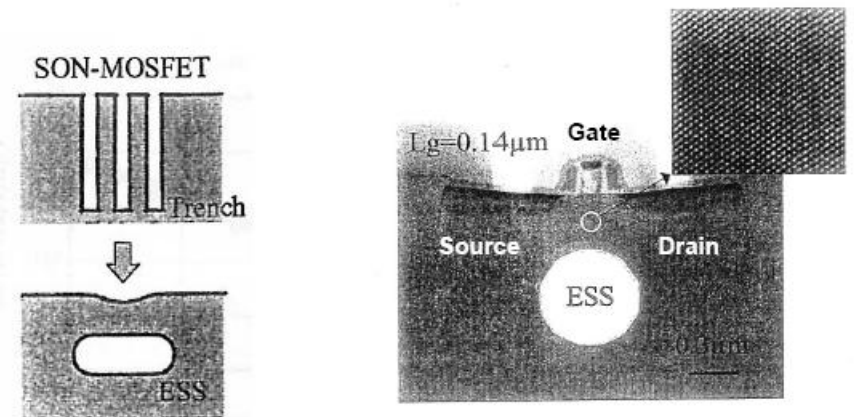


Atmospheric pressure
 H_2 flow: 70 l/m
 $SiHCl_3$ flow: 9.7 g/m
 Dep rate: 54.7 nm/s

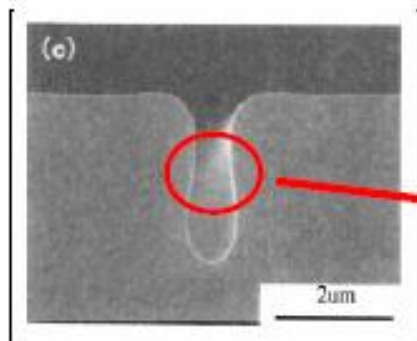




APPLICAZIONI...

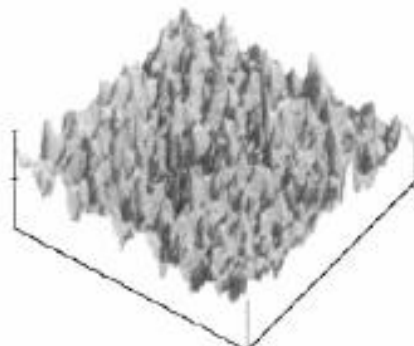


Parete laterale
interna del
trench circa a
metà
profondità

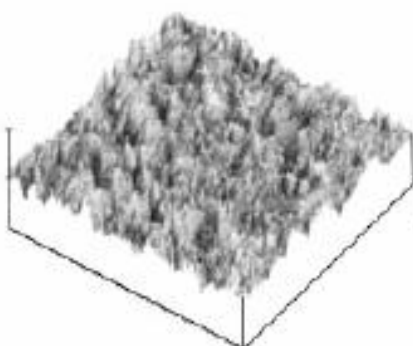


3 min 900°C

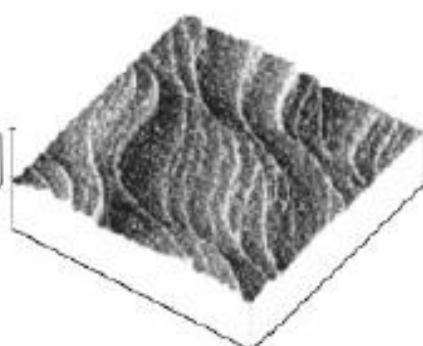
1 min 1000°C



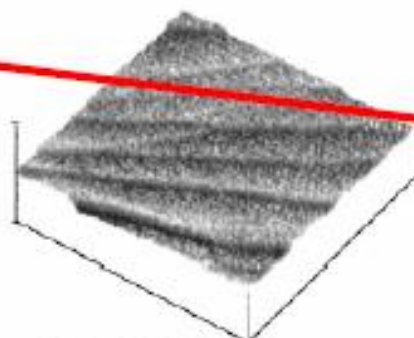
(a) RMS: 1.72nm



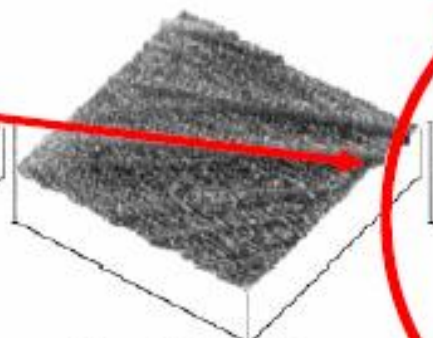
(b) RMS: 1.36nm



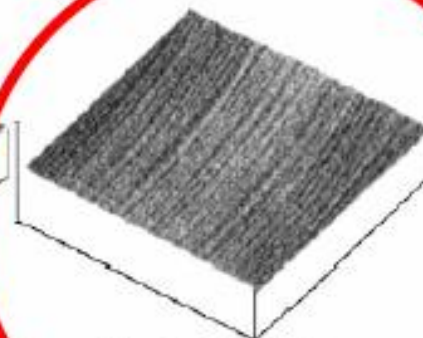
(c) RMS: 0.38nm



(d) RMS: 0.31nm
3 min 1000°C



(e) RMS: 0.42nm
10 min 1000°C



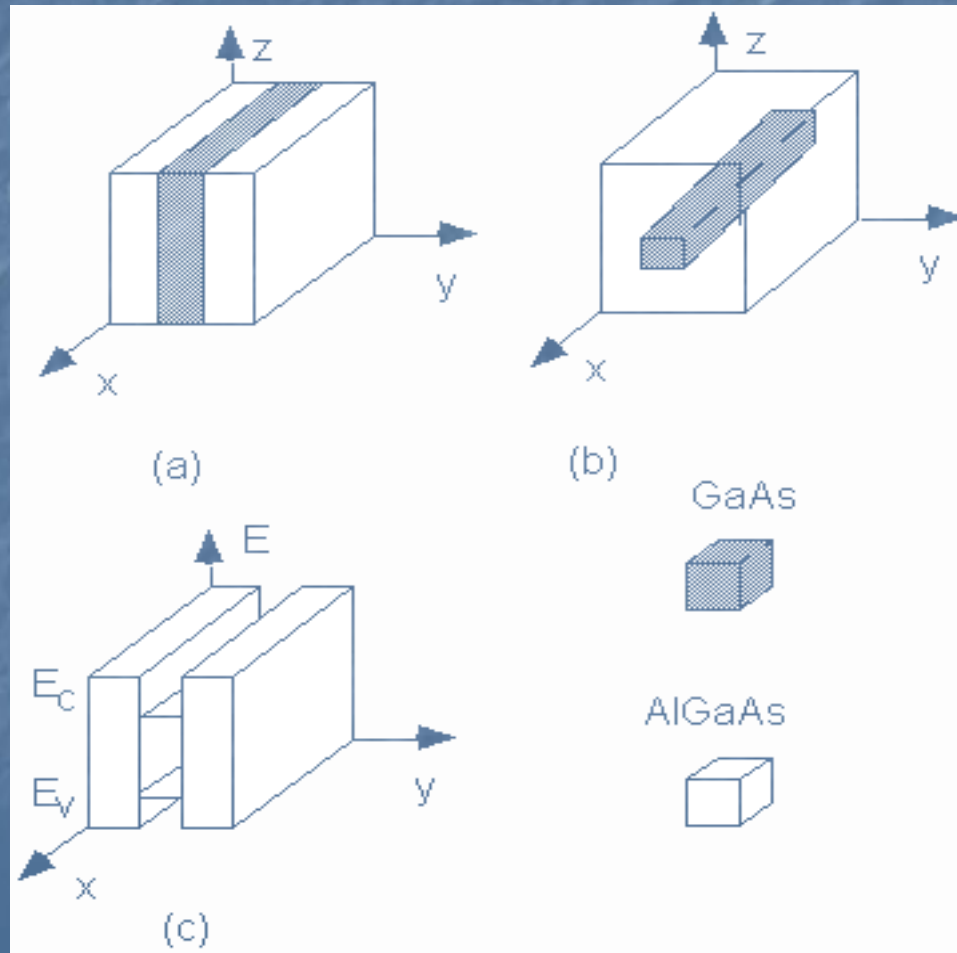
(f) RMS: 0.11nm
3 min 1100°C

$P_{H_2} = 40 \text{ Torr}$

[001] direction

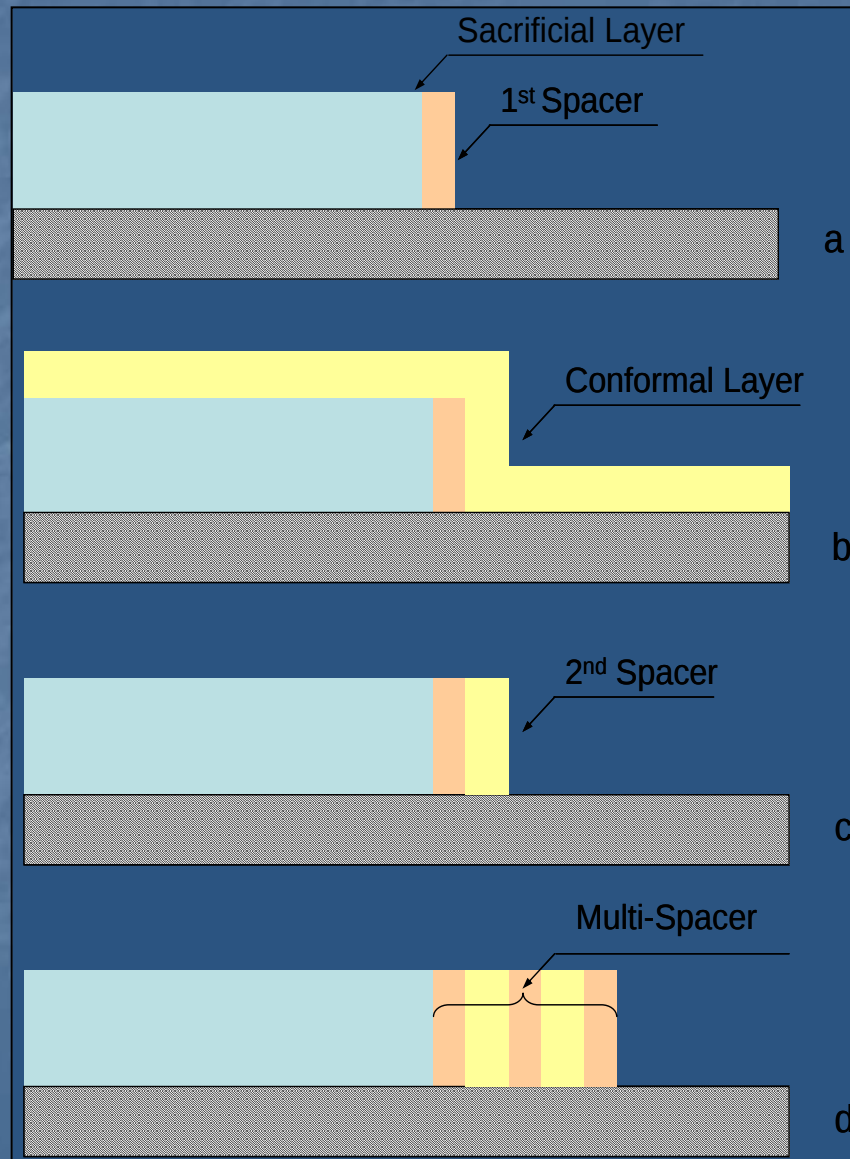
[110] direction

il confinamento quantico



ELETTRONICA MOLECOLARE UNA POSSIBILITA'

The Multi Spacer Technology



**35 nm a-Silicon
multiple spacers**

TEOS

Poly

Field oxide

Multispacer



EHT = 5.00 kV
WD = 2 mm

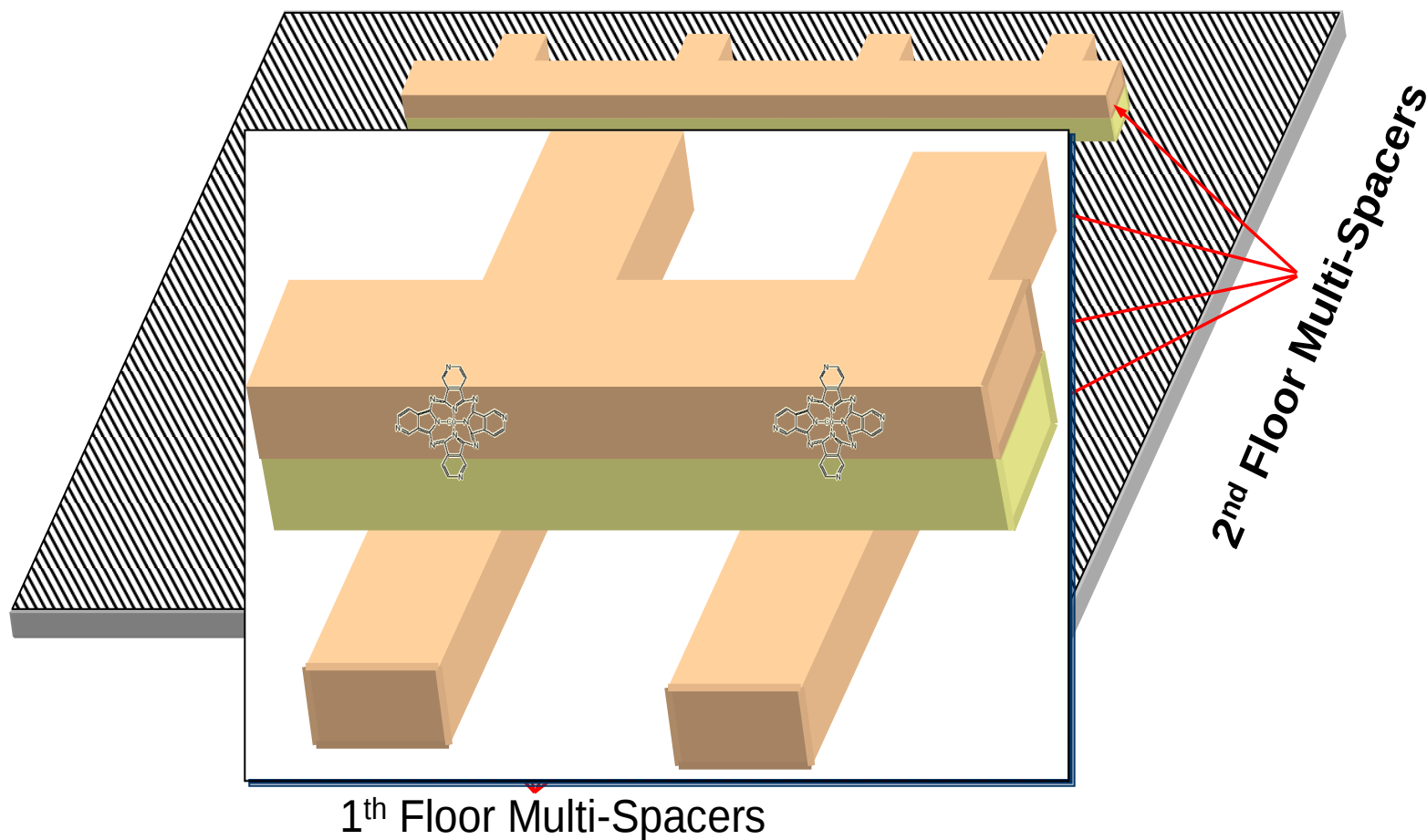
Date : 13 Apr 2004

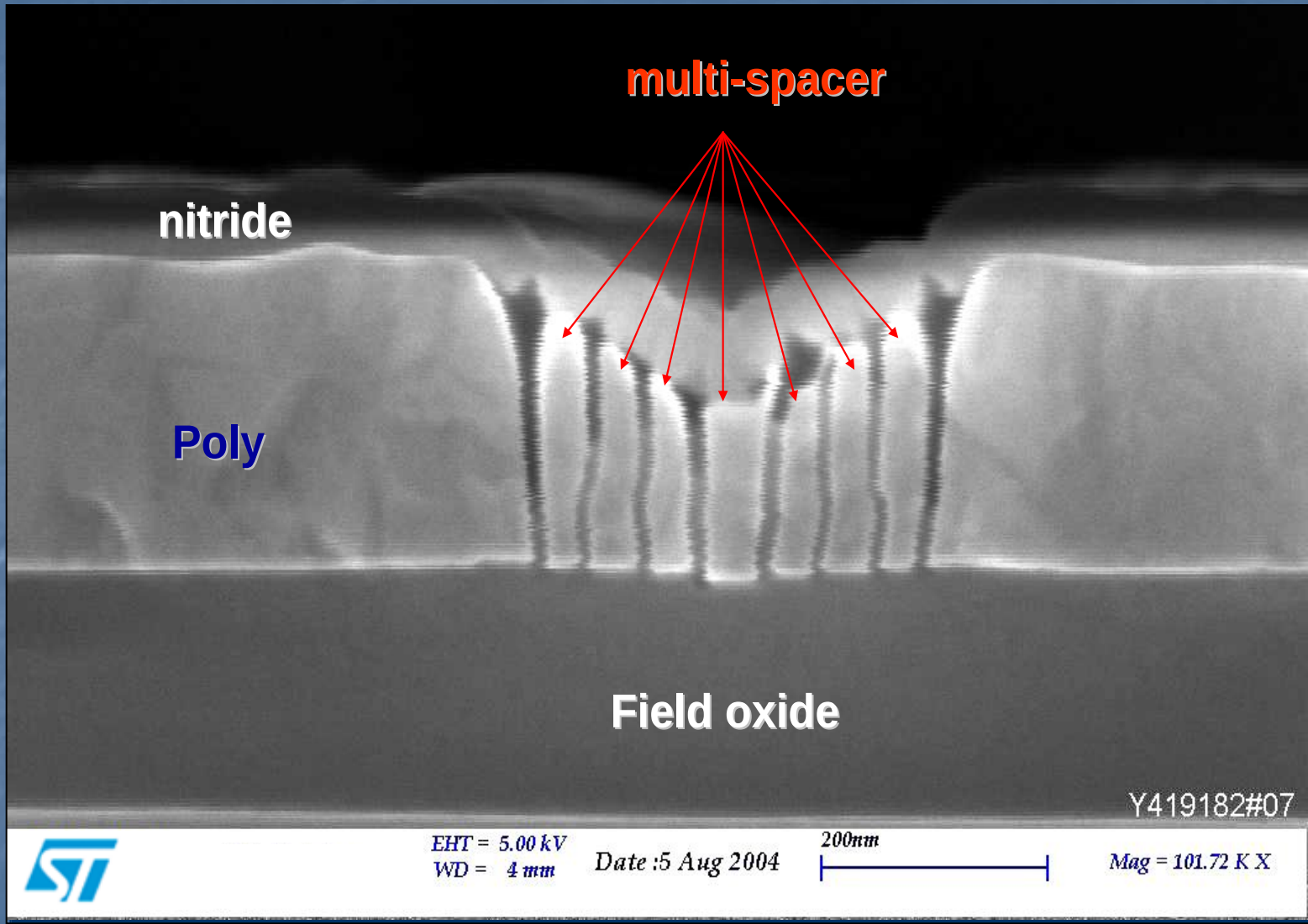
200nm



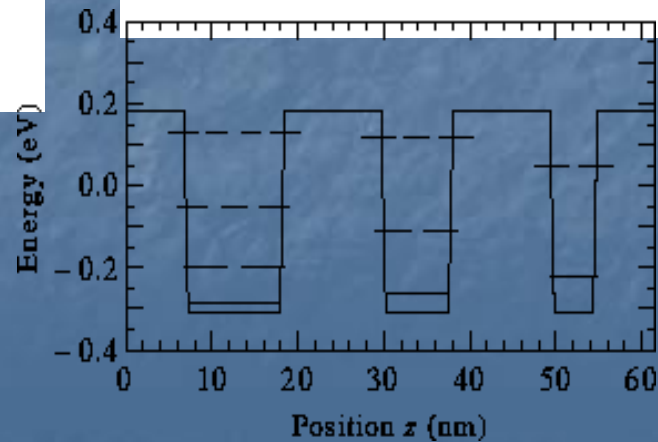
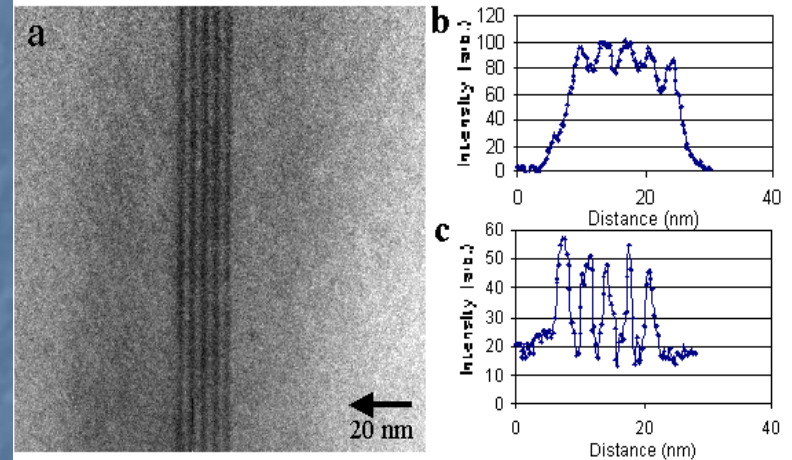
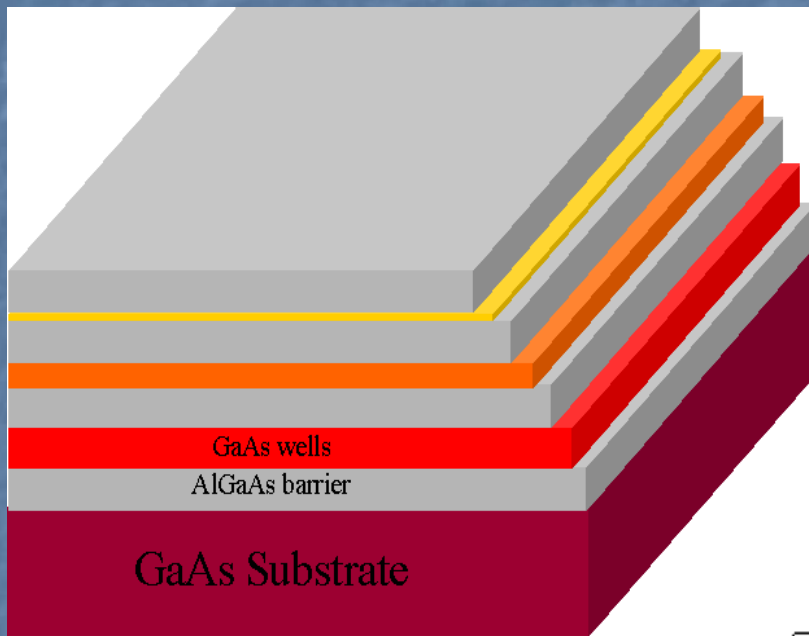
Mag = 83.53 K X

Silicon Host – Molecular Guest

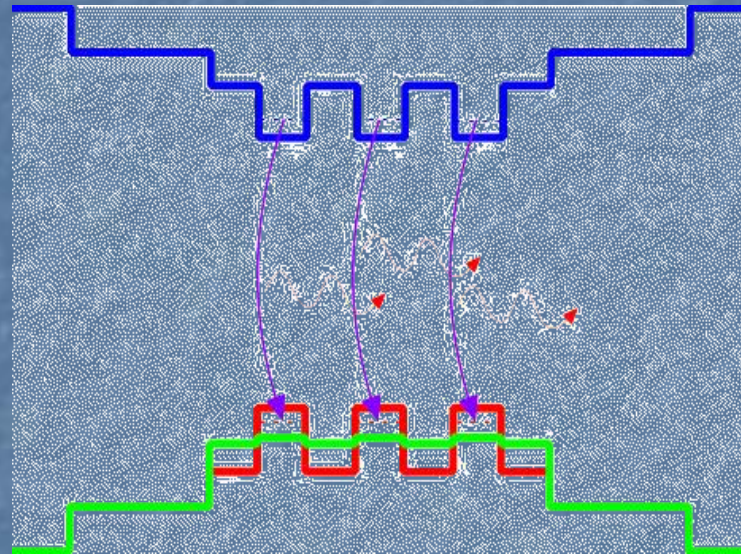




Buche quantiche

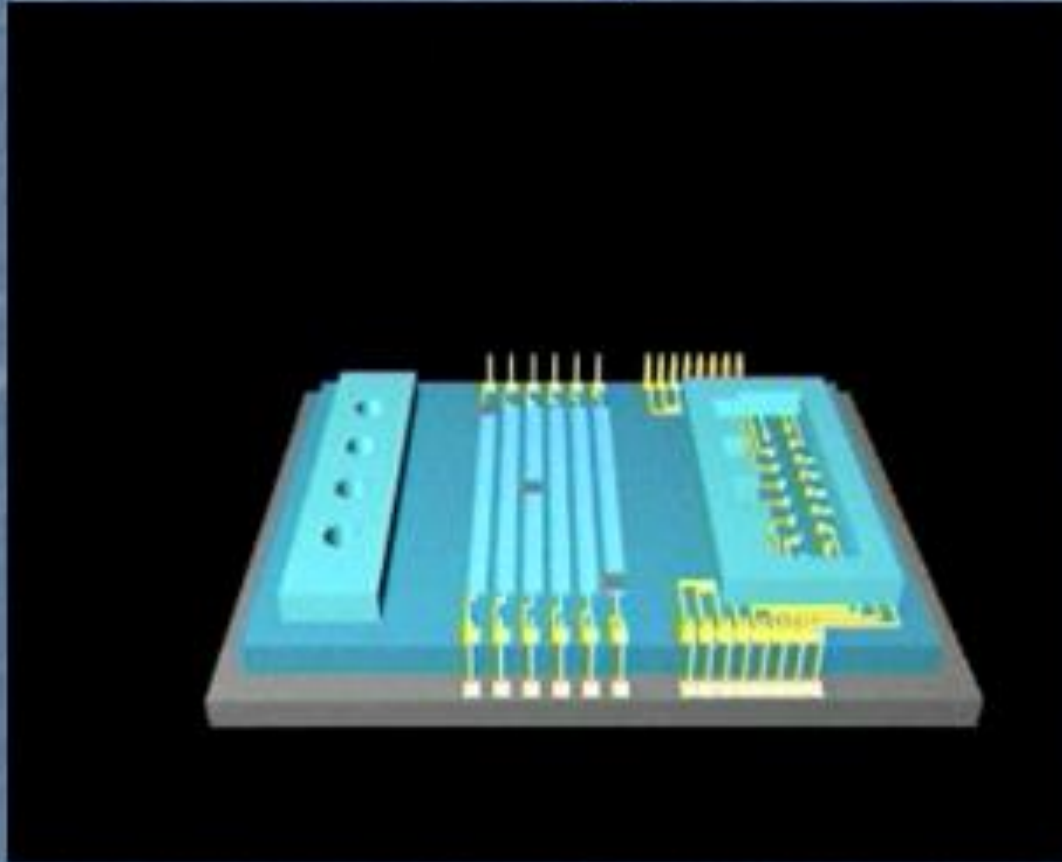


Buche quantiche

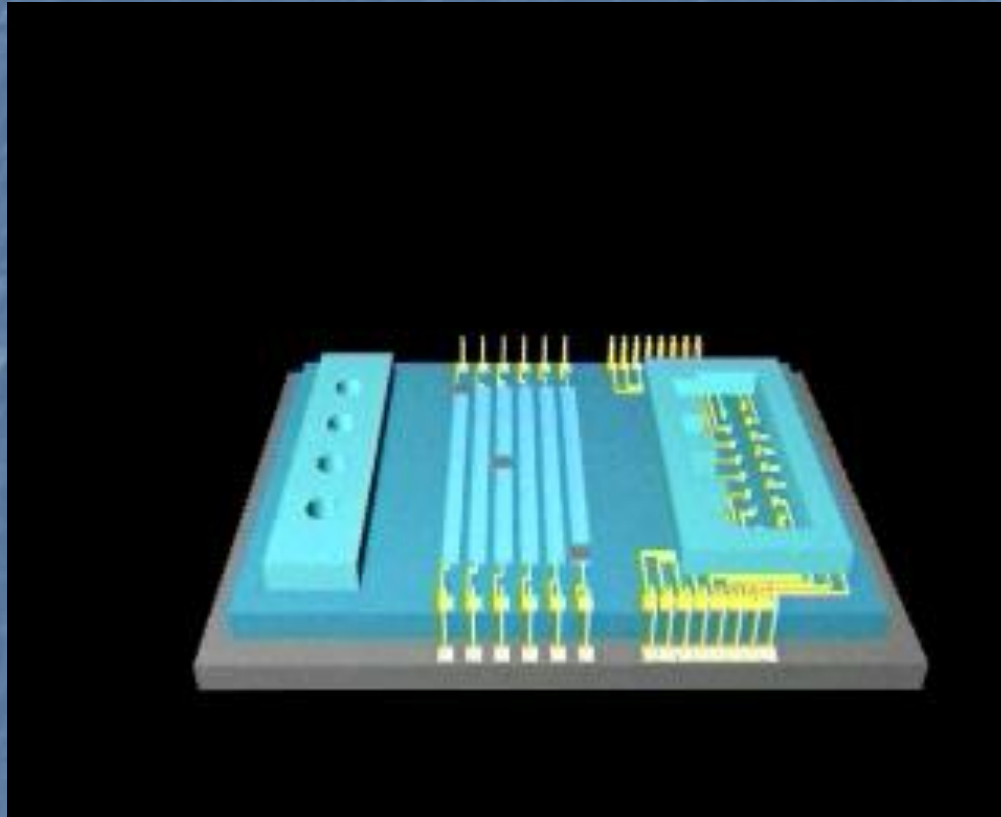


**Esempio di
realizzazione di un LED**

LAB on CHIP

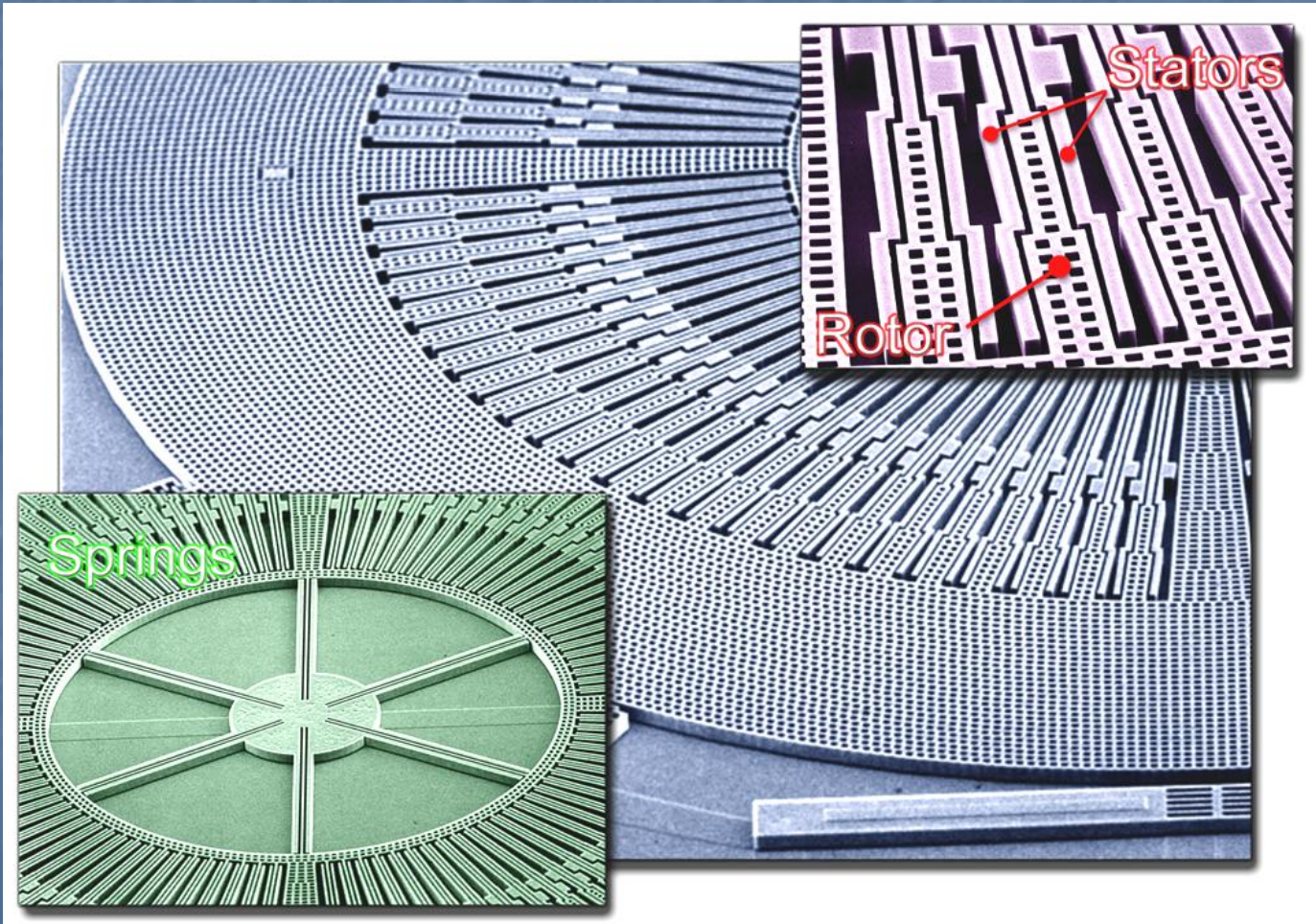


Lab on Chip Movie

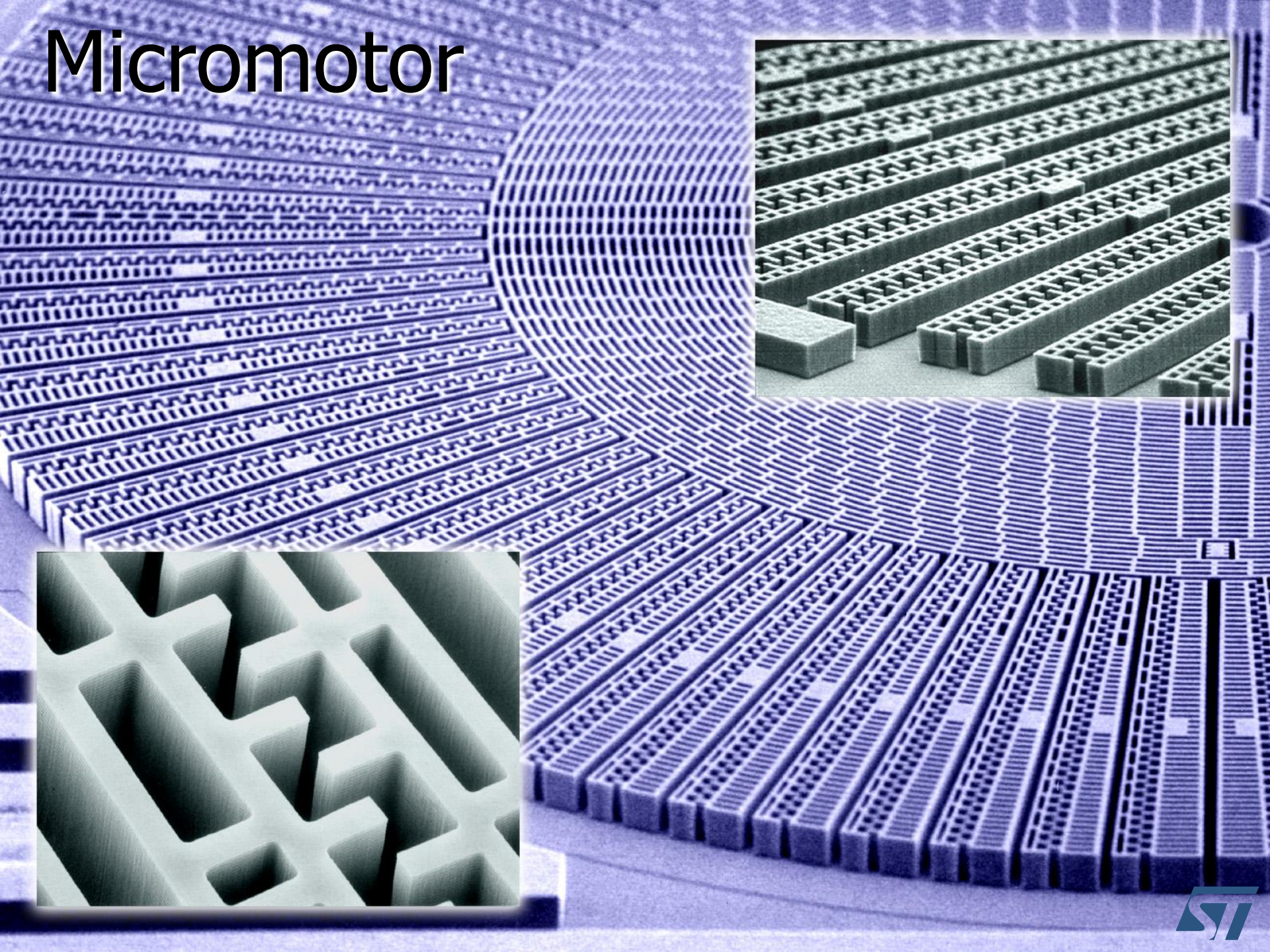


Sensing Element

- ▶ **MEMS** (**M**icro **E**lectro **M**echanical **S**ystem) Structure
- ▶ Angular acceleration is converted into a differential capacitive change

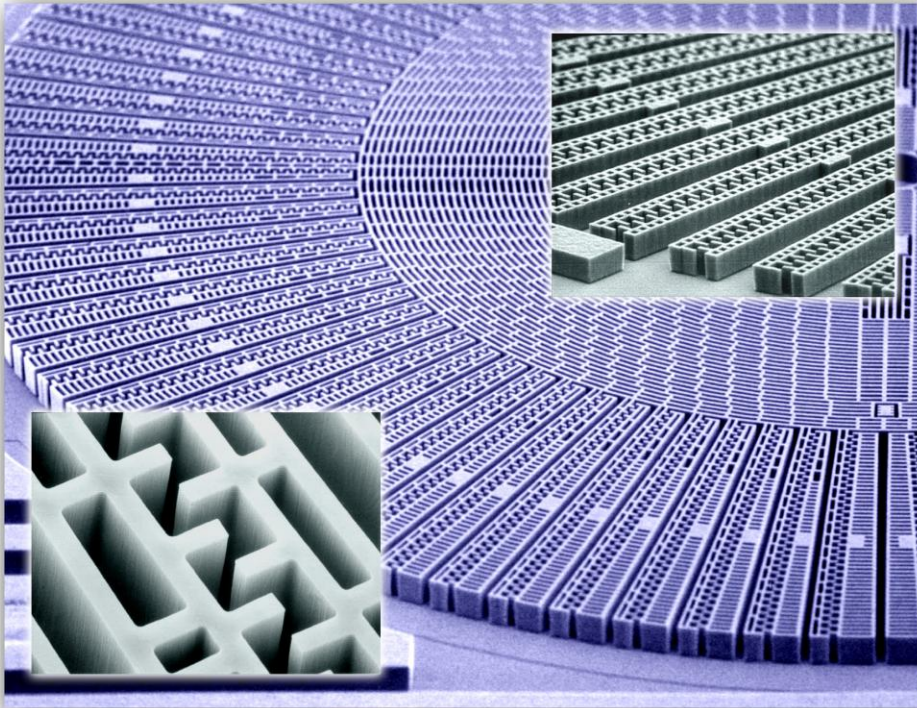


Micromotor

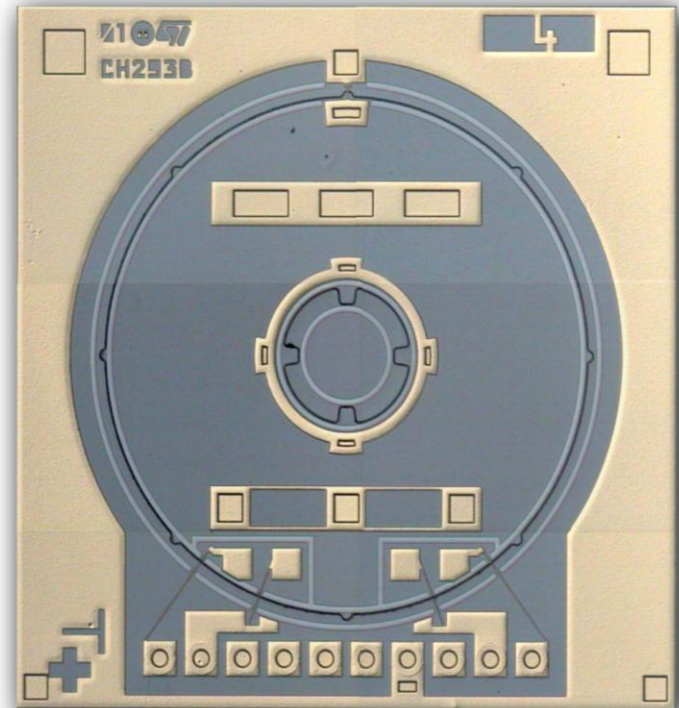


Microactuator Chip

without Cap



with Cap



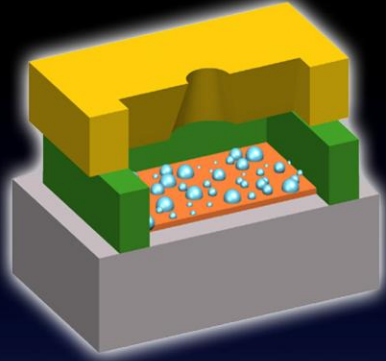
Die Size = 2.5 x 2.5 mm

Epipoly Thickness = 35 μm

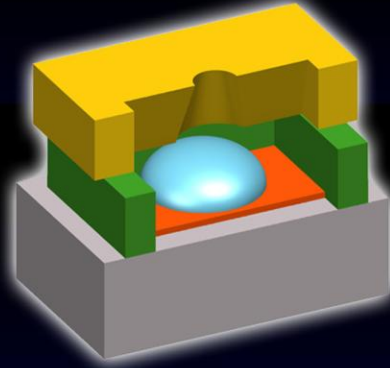
Electrostatic Micromotor



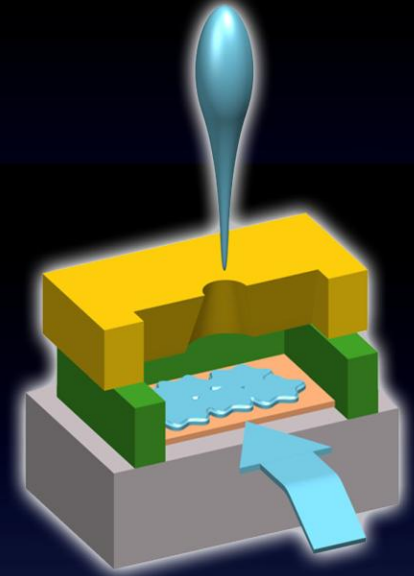
Ink Jet Cartridge



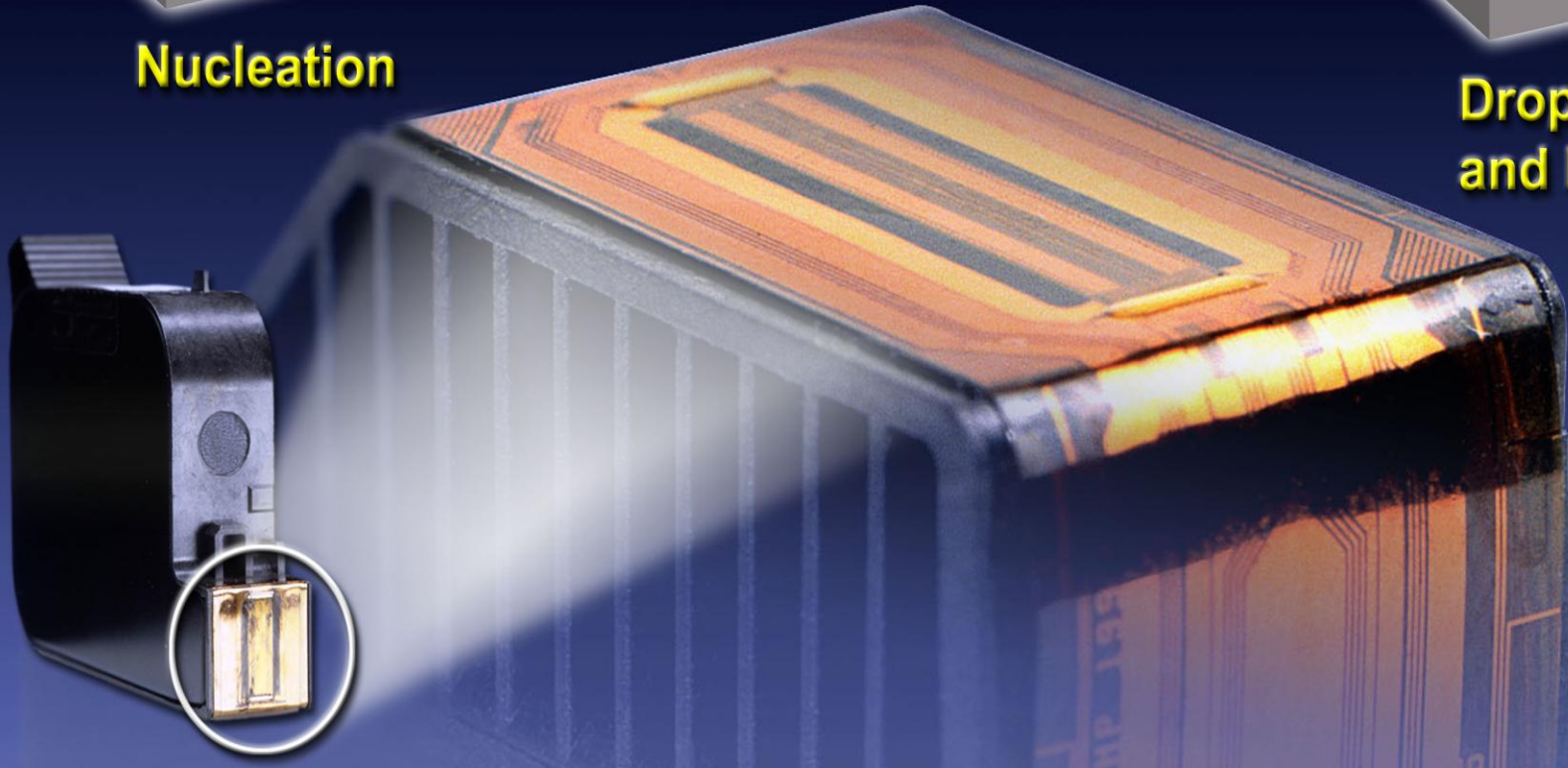
Nucleation



Bubble Growth



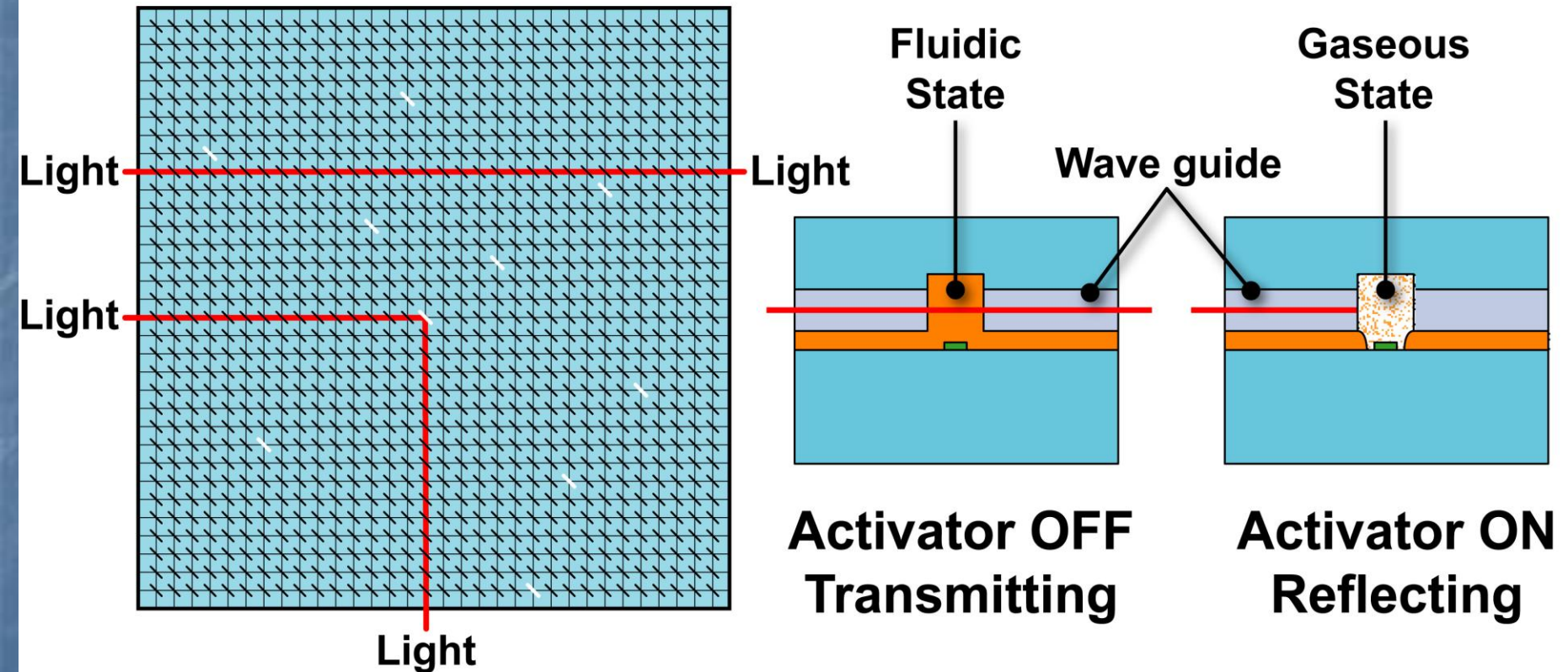
**Drop Ejection
and Refill**



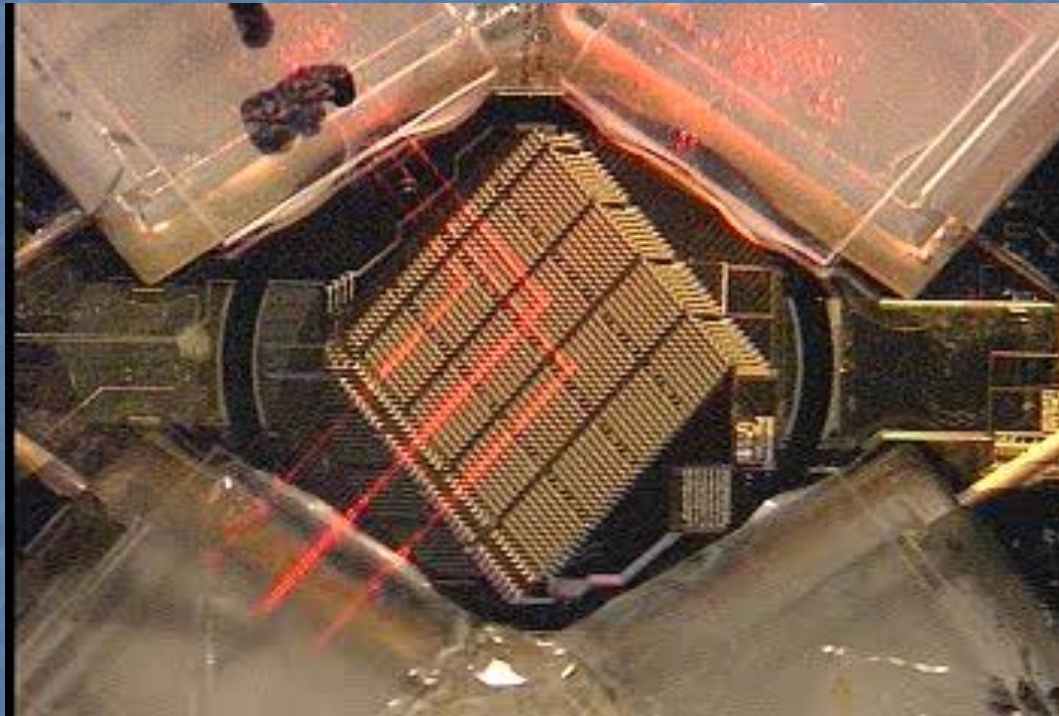
Photonic Switching Concept

Top-Down View - 32 x 32

Diagonal Cross-Sections



ST/AGILENT Bubble Switch Movie



NEGLI STATI UNITI ESISTONO ESEMPI DI DISTRETTI IN VIA DI SVILUPPO SPECIALIZZATI SULLE NANOTECONOLOGIE

Silicon Valley

\$100 milioni di finanziamenti statali nei prossimi 4 anni
Infrastrutture focalizzate sull'alta tecnologia con una miriade di aziende preminenti nel settore tecnologico
Non esiste un organismo di governo del distretto

Illinois Northwestern

Consolidata tradizione di ricerca sulle nanotecnologie
Distretto fondato nell'agosto 2002

Massachusetts Harvard

Consolidata reputazione nel creare imprese in nuovi settori industriali
Elevato numero di potenziali imprenditori
Non esiste un organismo di governo del distretto

California meridionale

\$100 milioni di finanziamenti statali nei prossimi 4 anni
Il California NanoSystems Institute sta incoraggiando le collaborazioni tra università e imprese
Distretto fondato nel giugno 2001

Texas Rice

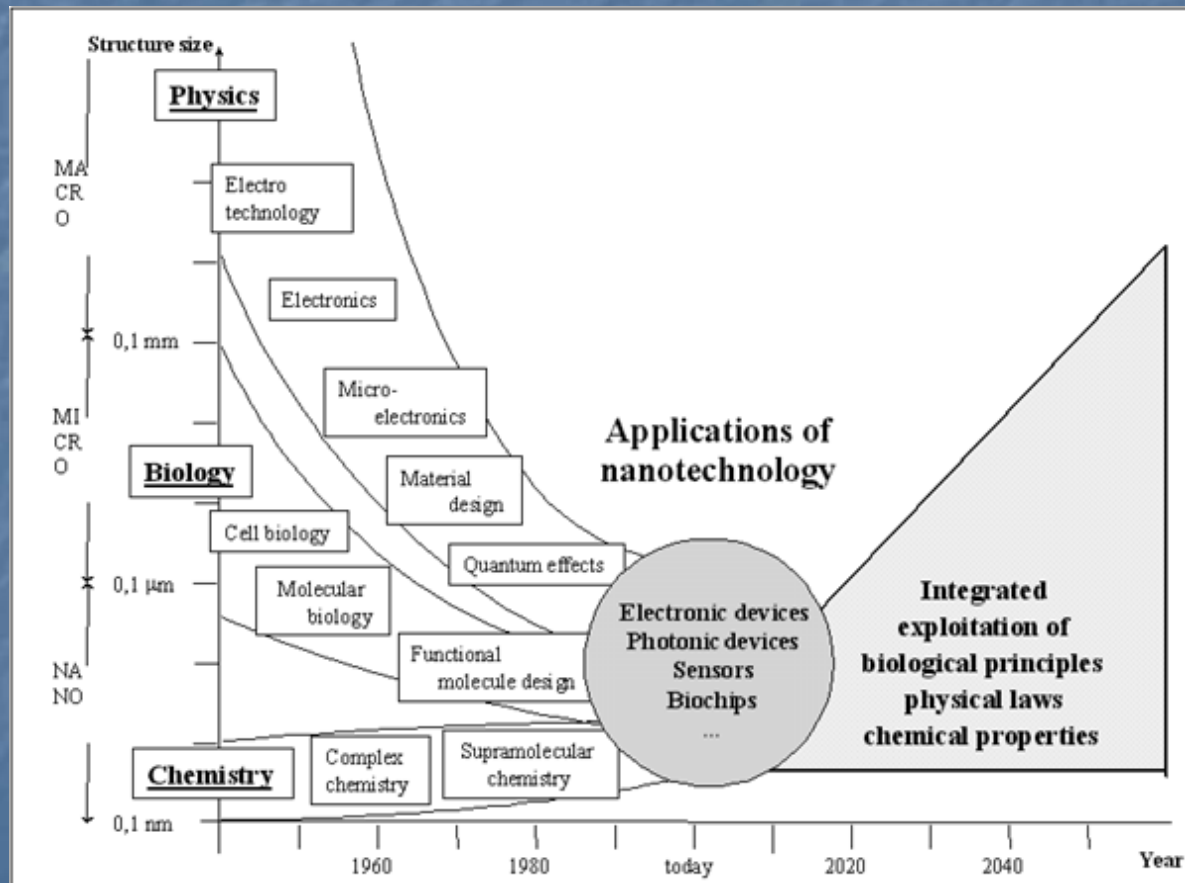
La Texas Nanotechnology Initiative sta promuovendo le collaborazioni tra università, imprese e amministrazioni locali
Il tessuto locale ha dimostrato elevata capacità di attrarre imprese con contenuti tecnologici
Distretto fondato nell'ottobre 2000

New York/New Jersey

Columbia, Cornell

Oltre \$150 milioni da fondi statali e dell'IBM per il Center for Excellence in Nano (SUNY at Albany)
Lo Stato del New Jersey incentiva le partnership tra università e imprese
Distretto fondato nell'ottobre 2001

Un mondo di applicazioni



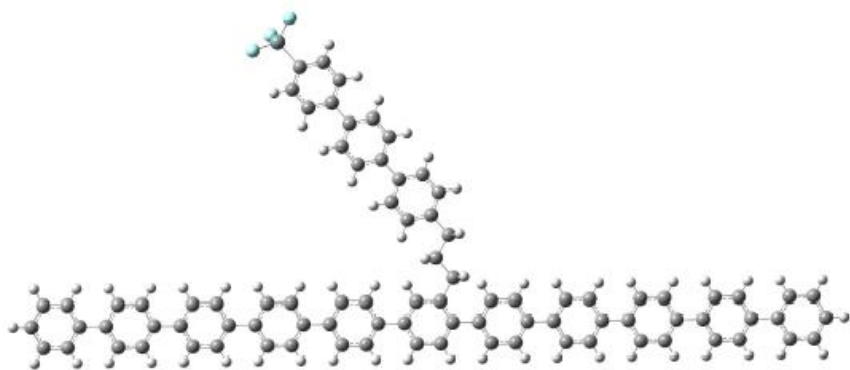
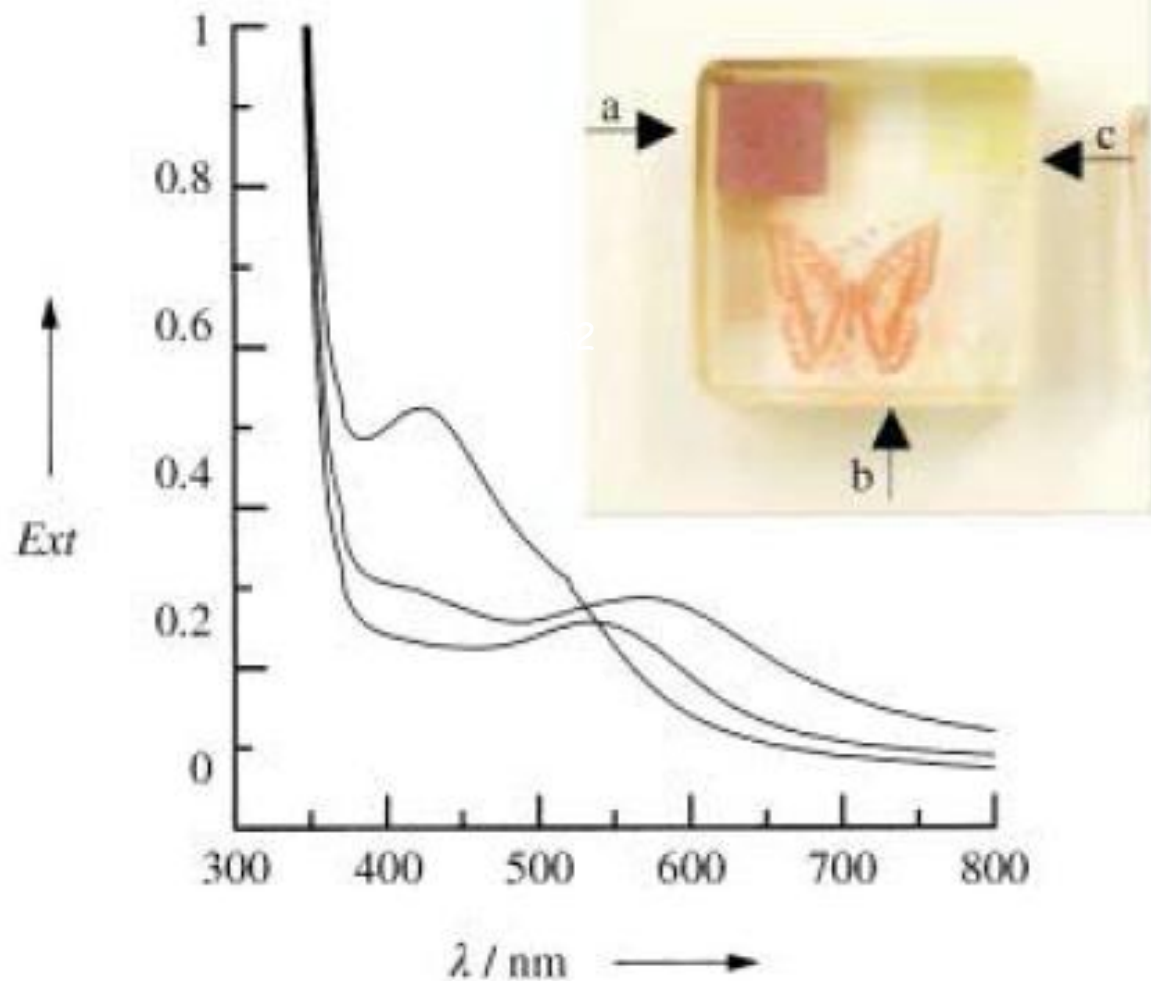


FIG. 1: A molecule characterized by a wire whose conduction state may be controlled by a side redox state

Irraggiamento a diverse intensità,
a) $6.5 \times 10^{13} \text{ W/cm}^2$,
b) $2.3 \times 10^{14} \text{ W/cm}^2$,
c) $5 \times 10^{16} \text{ W/cm}^2$, e in diverse zone.

Trattamento termico
 550°C , 1 ora



All'aumentare dell'intensità di irradiazione il colore delle aree irraggiate passa dal violetto al rosso, al giallo. Il picco d'assorbimento si sposta da 520 nm (risonanze delle particelle d'oro, lo shift da 568 a 534 nm legato alla variazione di dimensione delle particelle d'oro) a 422 nm (Au_{11} ?).

All'aumentare dell'intensità si riducono le dimensioni delle particelle.

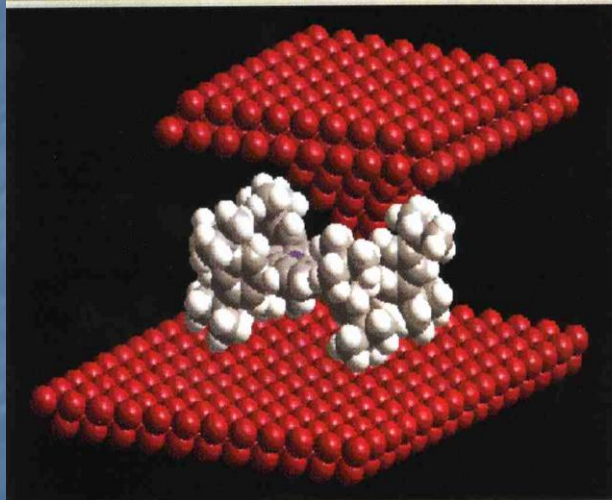


Tecniche di analisi di superfici e interfacce



Microscopia a scansione di sonda

2 How to move a molecule



Computer simulation by Christian Joachim (CEMES-CNRS) showing how an STM tip can push a molecule. The point of the tip (top) is lowered between the bulky legs of the molecule, which are repelled as the tip approaches. A rounded molecule would be more difficult to move, because it could slide away from the tip.

Risoluzione atomica

