Scuola di Dottorato in Ingegneria Leonardo da Vinci – a.a. 2009/10

PROPRIETÀ MECCANICHE, OTTICHE, ELETTRONICHE DEI MATERIALI ALLE PICCOLE E PICCOLISSIME SCALE

Versione 1 – Settembre 2010 – http://www.df.unipi.it/~fuso/dida

Parte 1
Introduzione:
alcuni esempi, definizioni e casi di interesse

Lu 06.09.10 9.30-11.30 aula DIC

Outlook

- *Small and ultra-small*: range of physical size of our interest
- A few examples of physical *properties depending on size* (and shape)
- Natural and historical examples of small and ultra-small objects used to attain *specific functions*
- Technological aspects and *nanotechnology*
- Popular *driving forces* for the progress of miniaturization and related scientific and technical problems
- (Almost) comprehensive perspectives of the forthcoming seminars

Small and ultra-small scale…

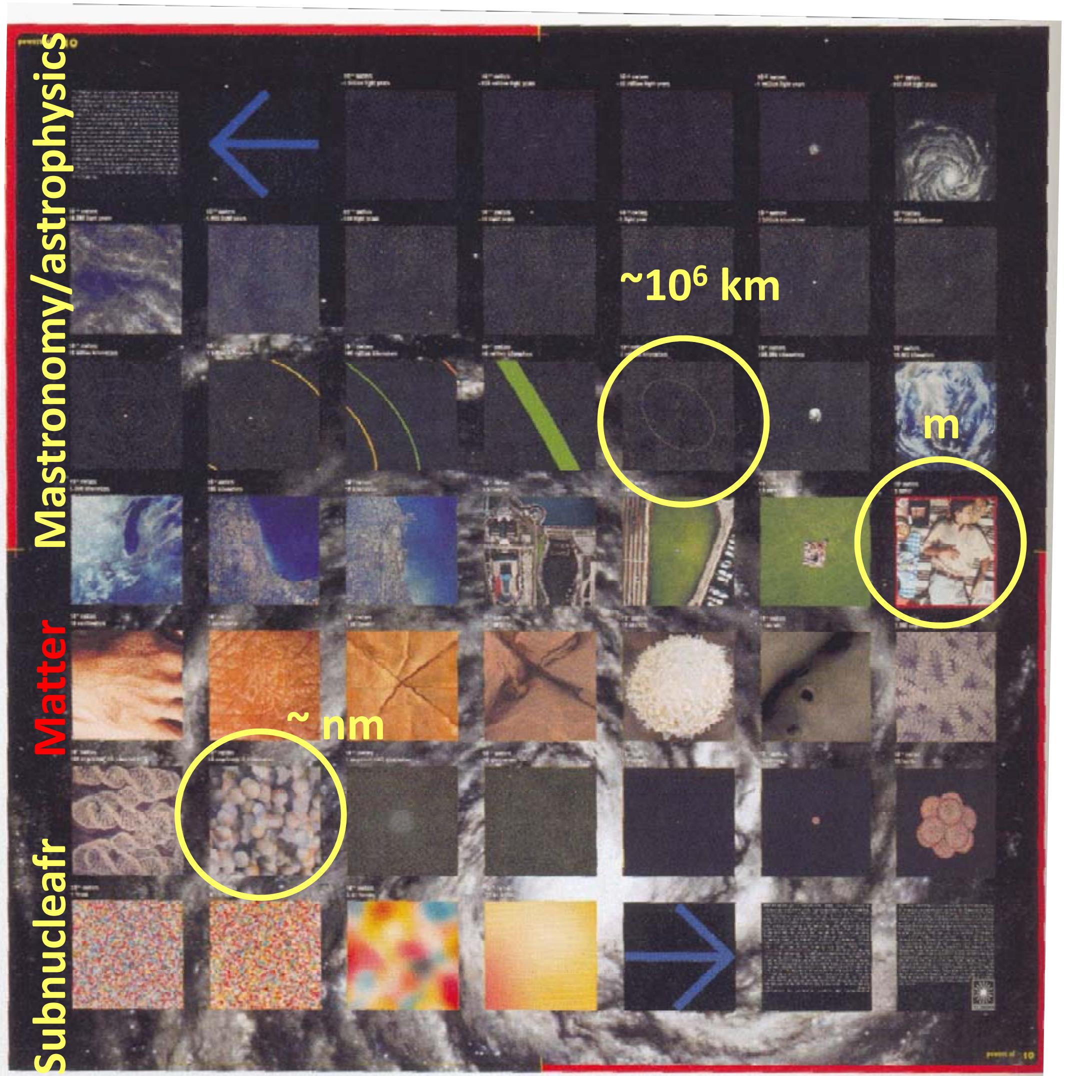
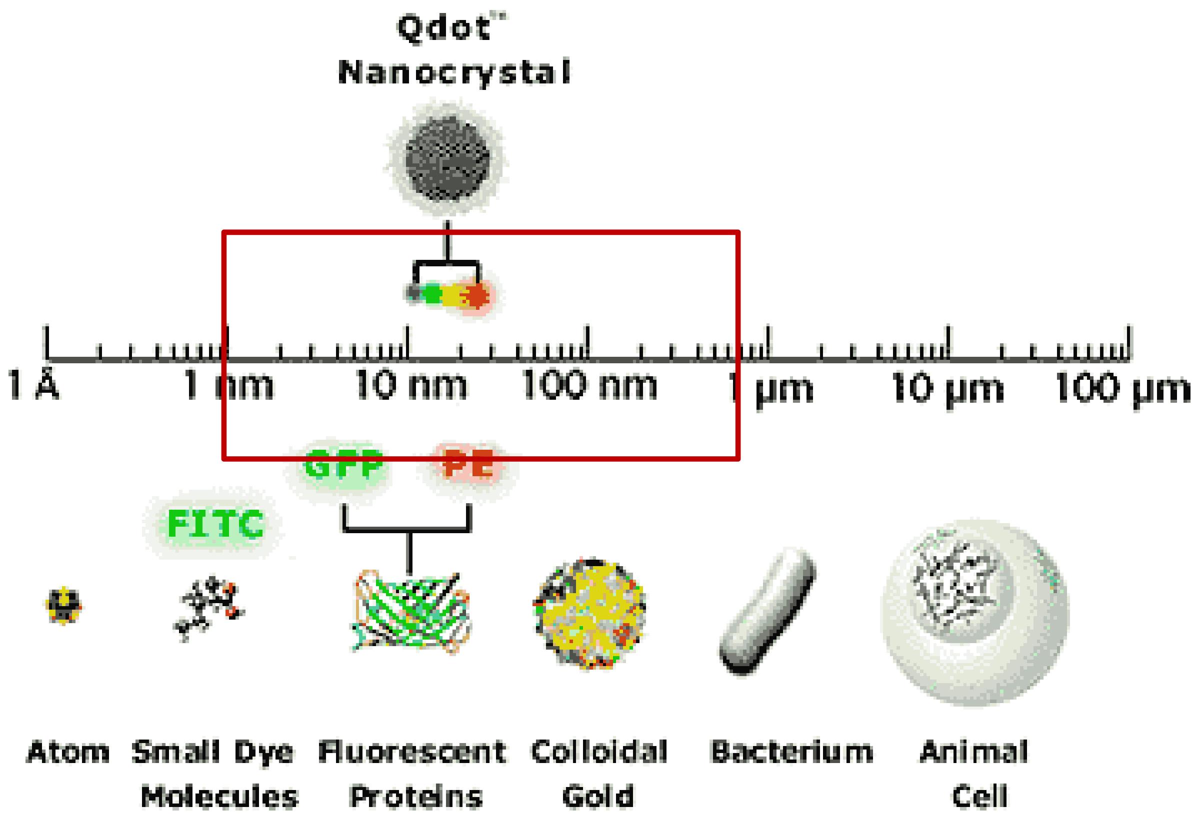


Figure 1.2
This image shows the size of the nanoscale relative to things we are familiar with. Each image is magnified 10 times from the image before it. As you can see, the size difference between a nanometer and a person is roughly the same as the size difference between a person and the orbit of the moon.

Natural and artificial phenomena of interest in science (namely, in physics) involve objects with a physical size spanning over many decades

Our point of view: Small/ultra-small means something placed at the bottom of the physical scale relevant for matter and devices

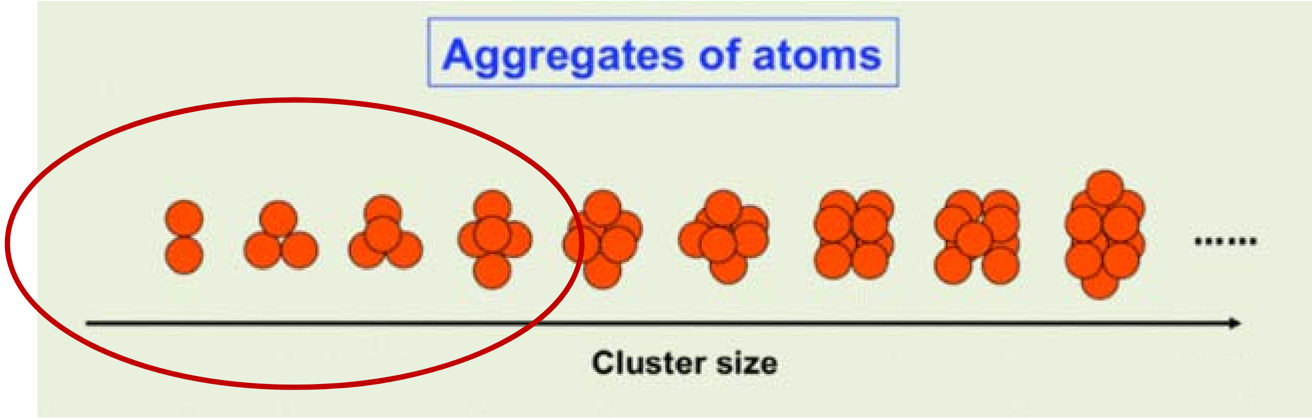
The world of small and ultra-small



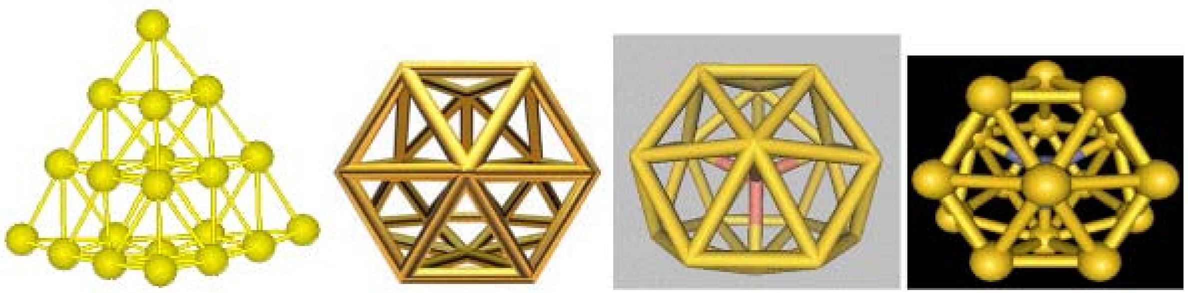
Typical range of our interest:
not too large to be "visible at the naked eye" (or with a magnifing lens)
not too small to directly entail the strcuture of the matter

From atoms to clusters

Few atoms: "everything" can be predicted by extending the rules of quantum physics/chemistry used for small molecules



At some point, very complex structures can appear: predictions get much more difficult to achieve (calculation problems, behavior no more governed by simple atomisitic laws)



Au_{20} Au_{16} $Cu@Au_{16}$ $Zn@Au_{16}$

The example of fullerenes and carbon nanotubes

Carbon atoms can form molecules and <u>nanostructures</u> with a large variety of bond lengths and angles

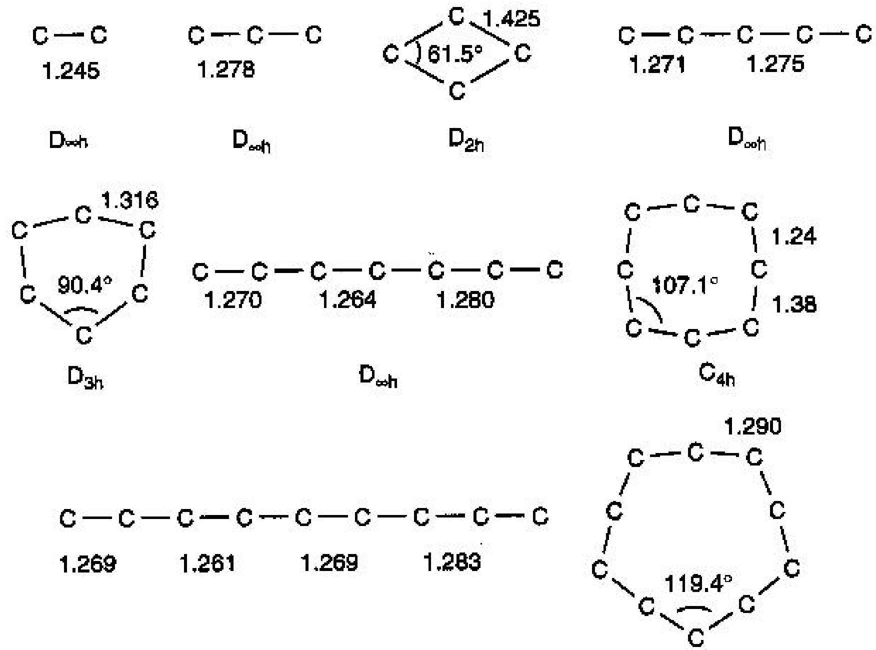
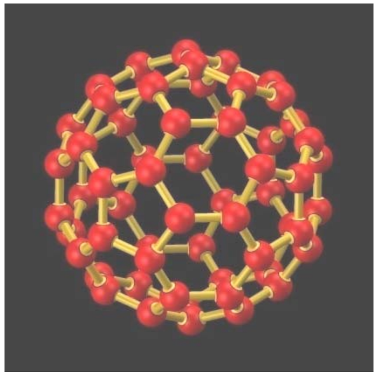


Figure 5.4. Some examples of the structures of small carbon clusters. [With permission fro Raghavacari et al., *J. Chem. Phys.* **87**, 2191 (1987).]

~ 1 nm

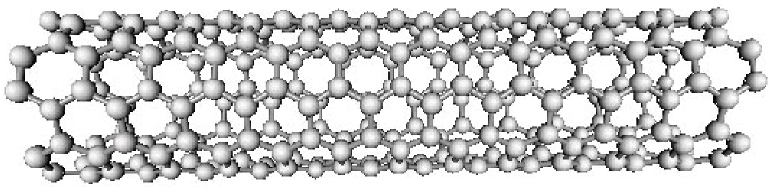


Fullerene (C_{60})

(Nobel Prize, mid 90's)

Carbon NanoTubes (CNT-single wall)

~ 1_100 nm

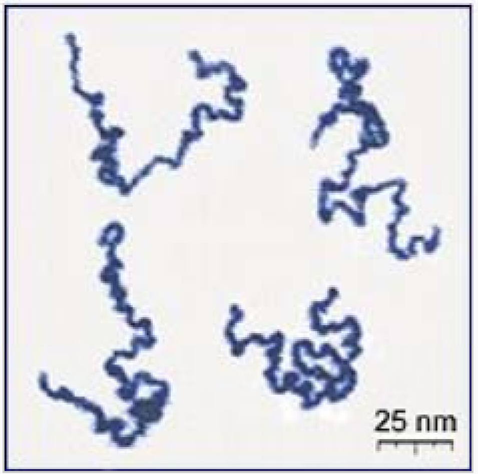


Up to hundreds of micrometers

A more “controversial” example: polymers/macromolecules

A **polymer** is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. While *polymer* in popular usage suggests plastic, the term actually refers to a large class of natural and synthetic materials with a wide variety of properties.

Because of the extraordinary range of properties of polymeric materials,[2] they play an essential and ubiquitous role in everyday life[3], ranging from familiar synthetic plastics and elastomers to natural biopolymers such as DNA and proteins that are essential for life. A simple example is polyethylene, whose repeating unit is based on ethylene (IUPAC name *ethene*) monomer. Most



Appearance of real linear polymer chains as recorded using an atomic force microscope on surface under liquid medium. Chain contour length for this polymer is ~204 nm; thickness is ~0.4 nm.[1]

Polymer properties are:
typically understood within the frame of macromolecule chemistry
typically exploited in materials (very many polymers “packed” together)

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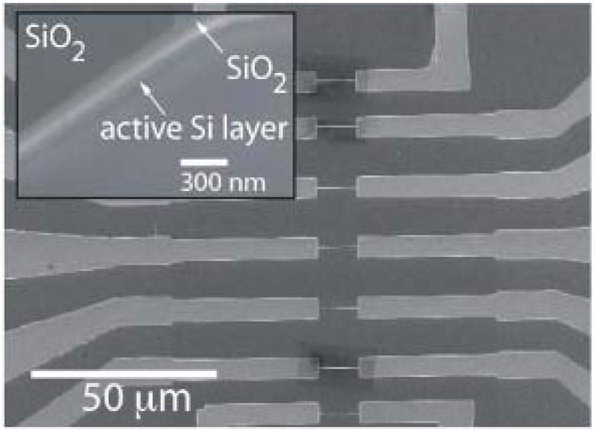
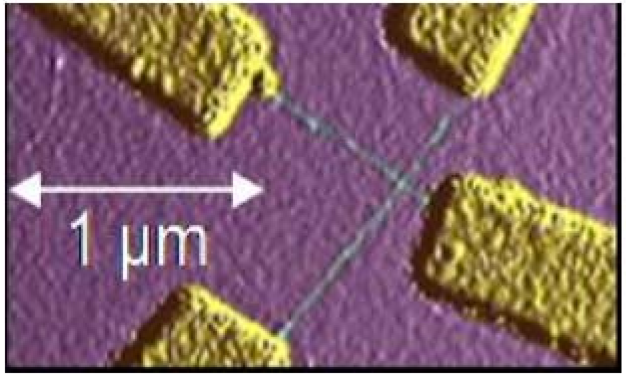
a little bit out of our interest range

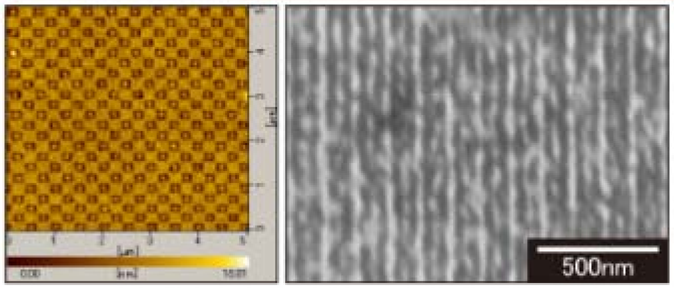
A less “obvious” example: nanostructured surfaces



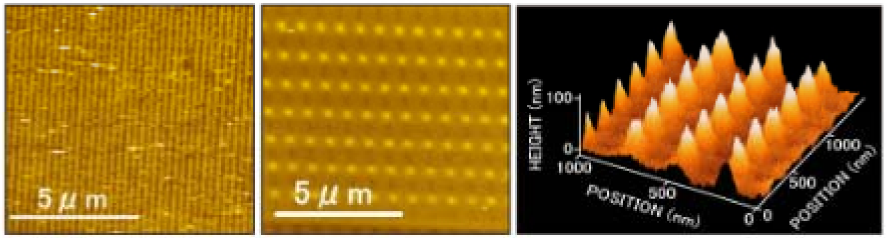
SEM picture of seven Si nanowires and leads, all etched into the silicon device layer of a Silicon-on-Insulator wafer. The metallic contacts are not visible. The inset shows a single nanowire still capped with its SiO2 layer acting as an etch-mask.



AFM image of a carbon nanotube device made using lithography to contact individual nanotubes



2次元リング（直径 100nm）　　32nm Line & Space

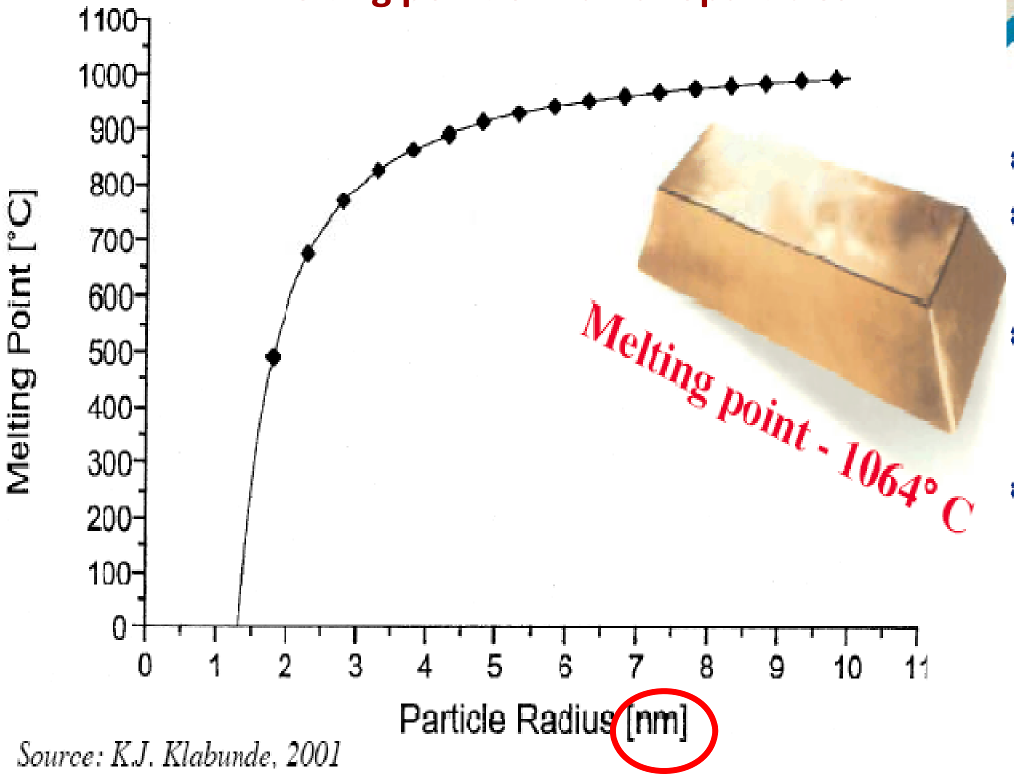


多重露光

Often, practical applications require nanosized objects to be singularly addressable and anchored to a (rigid) substrate

Nontrivial properties of nano-objects I

Melting point of Au nanoparticles



Source: K.J. Klabunde, 2001

Prova a fare questo

eSercizio:

- Quanti lati ha un cubo?
- Se il lato misura 1 cm, qual è la superficie totale del cubo?
- Tagliando il cubo tre volte (verticalmente, orizzontalmente e trasversalmente), quanti cubi si ottengono?
- Qual è la misura di ogni nuovo cubo? Qual è la superficie totale di tutti i cubi ottenuti?

Vedrai che a parità di peso (o, meglio, di massa), ***più piccolo significa maggior superficie***

Melting/evaporation depend on size:

In the phase trasnformation material at the surface or bulk contributes differently to the process

⇩

Melting point (e.g., in the case of metals) depends on the surface/volume ratio, hence on size and geometry

Nontrivial properties of nano-objects II

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa)[17]. (This, for illustration, translates into the ability to endure tension of a weight equivalent to 6422 kg on a cable with cross-section of 1 mm^2.) Since carbon nanotubes have a low density for a solid of 1.3 to 1.4 $g \cdot cm^{-3}$,[18] its specific strength of up to 48,000 $kN \cdot m \cdot kg^{-1}$ is the best of known materials, compared to high-carbon steel's 154 $kN \cdot m \cdot kg^{-1}$.

Comparison of mechanical properties[20][21][22][23]

Material	Young's modulus (TPa)	Tensile strength (GPa)	Elongation at break (%)
SWNT	~1 (from 1 to 5)	13–53^E	16
Armchair SWNT	0.94^T	126.2^T	23.1
Zigzag SWNT	0.94^T	94.5^T	15.6–17.5
Chiral SWNT	0.92		
MWNT	0.27^E[17]–0.8^E[24]–0.95^E[17]	11^E[17]–63^E[17]–150^E[24]	
Stainless steel	0.186^E[25]–0.214^E[26]	0.38^E[25]–1.55^E[26]	15–50
Kevlar–29&149	0.06^E[27]–0.18^E[27]	3.6^E[27]–3.8^E[27]	~2

^{E}Experimental observation; ^{T}Theoretical prediction

Mechanical properties depend on size (and shape):

Mechanical response (in particular, elasticity) is mostly ruled by bond strength and by the "distribution" of stress/strain in the structure

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Strongly anisotropic and well bond nanostructures can exhibit excellent properties

Nontrivial properties of nano-objects III

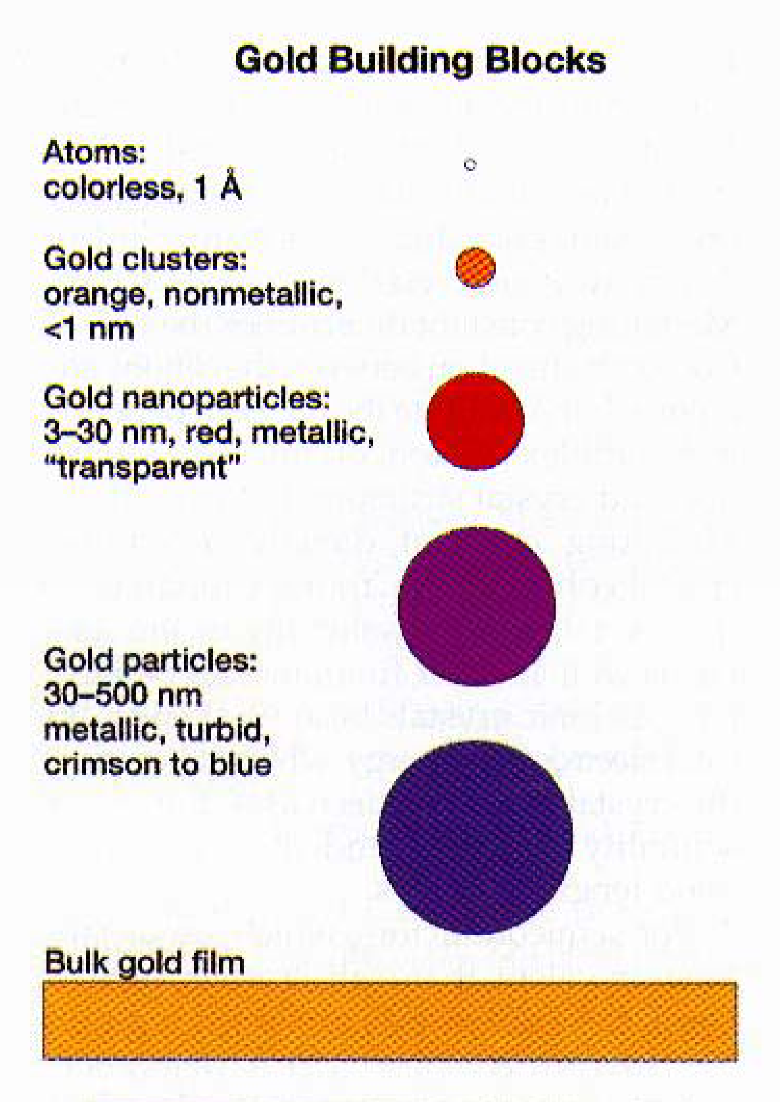

Figure 1. Gold building blocks, from the atomic to the mesoscopic, and their changing colors.

Color depends on size:

the color of an object results from the interaction between (white) light and the optical properties of the material

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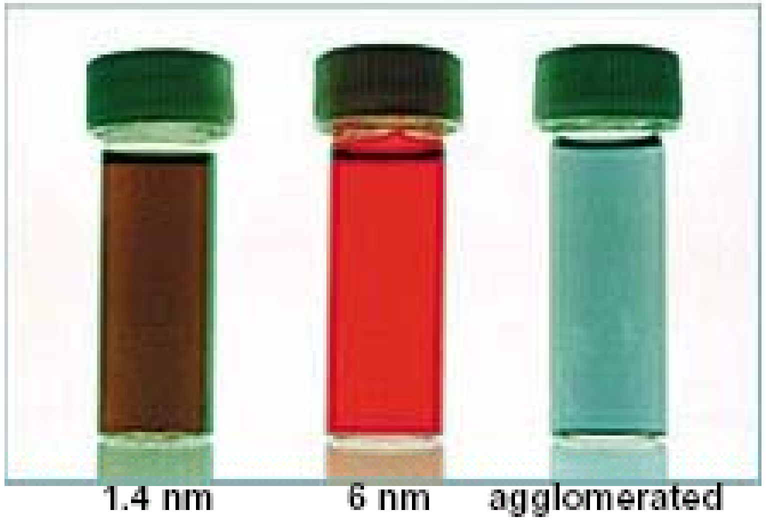
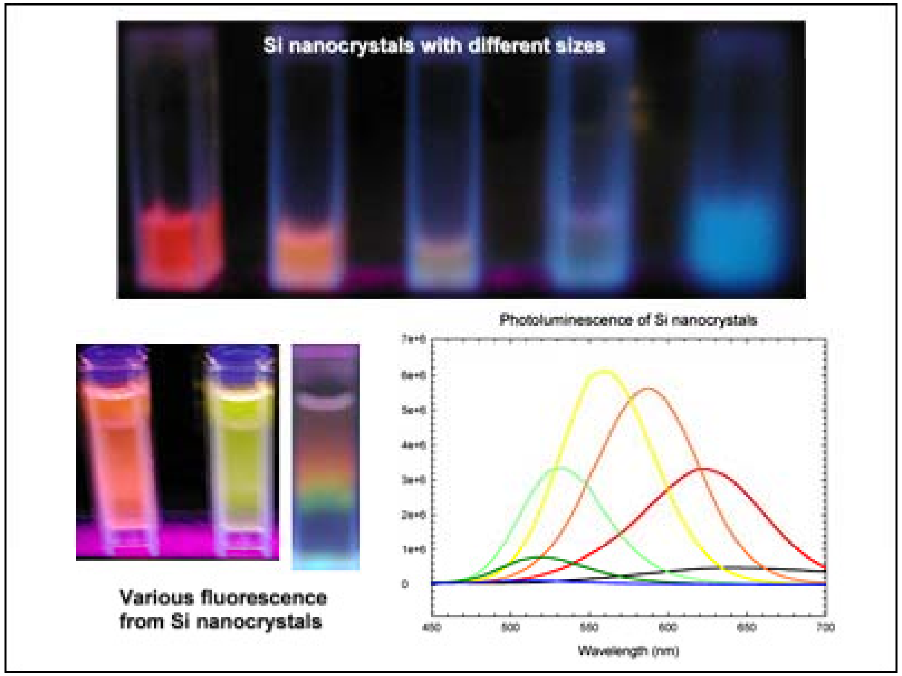
Optical properties (e.g., in the case of metal nanostructures) can strongly depend on size

Au nanoparticles
in solution



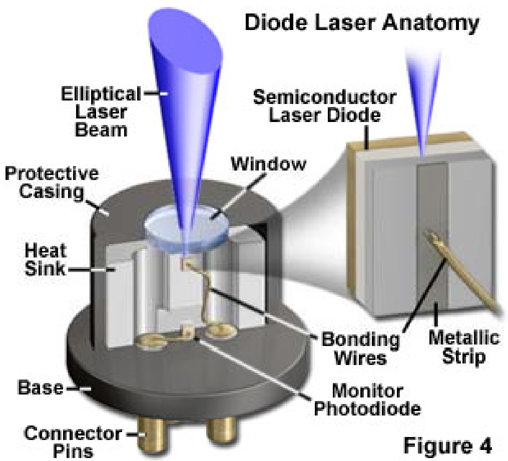
Nontrivial properties of nano-objects IV

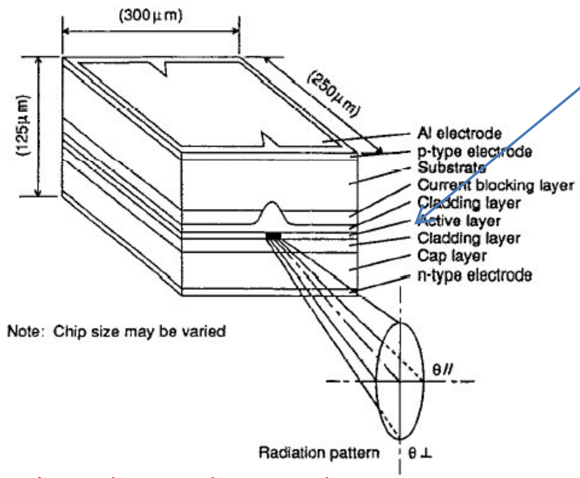


Also in semiconductors, optical properties (luminescence) can dramatically depend on size

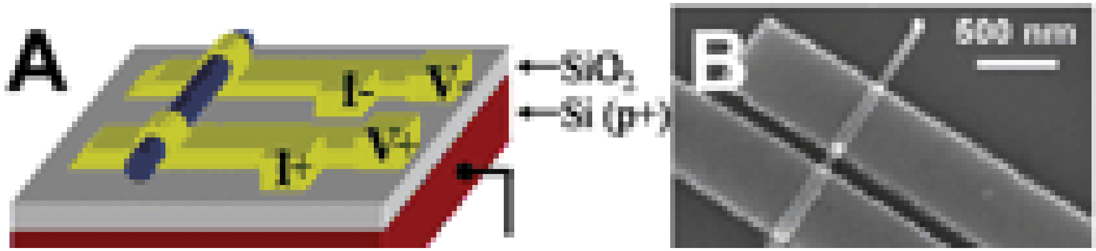
(but this is now due to purely quantum physics effects!)

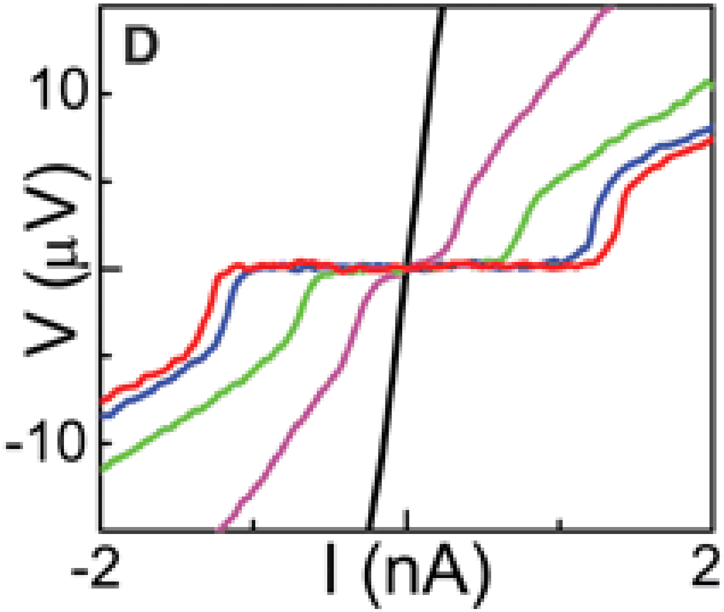
Extremely popular devices such as, LEDs and diode lasers, produce electroluminescence thanks to nano-sized objects (layers)





Nontrivial properties of nano-objects V





Clearly non-ohmic behavior!

Electrical properties (e.g., conductance) depend on size:

The electrical trasnport mechanisms are ruled by the material properties, but also by its shape and size

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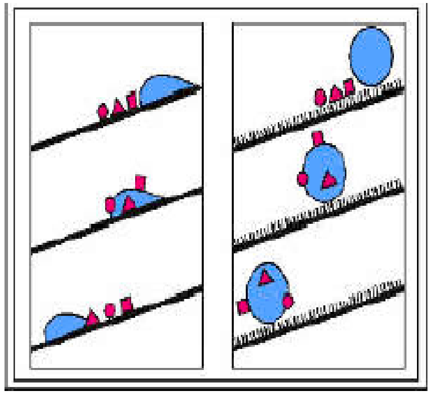
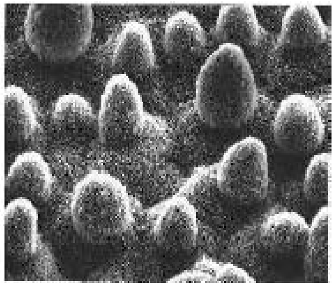
Electrical conductivity can be dramatically affected by size when specific geometries are concerned (e.g., nanowires, nanodots)

Small and ultra-small in the nature I

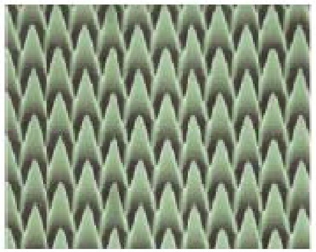


W. Barthlott, Univ. of Hamburg

On a smooth surface the contaminating particles are only moved by the water droplet (left). In contrast to that, on a rough surface they stick to the droplet rolling off the leaf thus being washed off (right).



Epicuticular wax



(Source: Metin Sitti, CMU)

A functional property (hydrofobicity) depends on the structural surface arrangement at the nanoscale

Small and ultra-small in the nature II

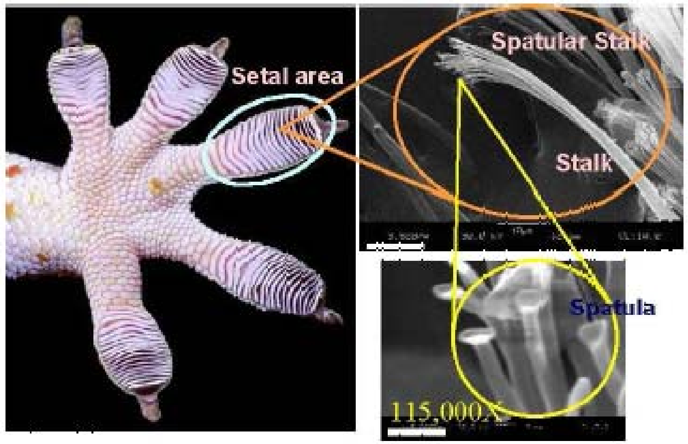
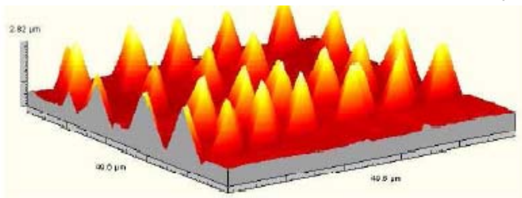


Figure 1: *Tokay* gecko foot-hair images: gecko foot bottom view (left image); zooming into one of the stalks (right upper image, bar indicates 10 μm), and zooming into spatulae and spatular stalks at the end of a stalk under SEM (right lower image, bar indicates 300 nm) (courtesy of Kellar Autumn).



(b)

Figure 3: 3-D AFM tapping mode image of (a) the AFM probe based indented flat wax surface, (b) molded and peeled off silicone rubber nano-hairs.

Synthetic Gecko Foot-Hair Micro/Nano-Structures for Future Wall-Climbing Robots

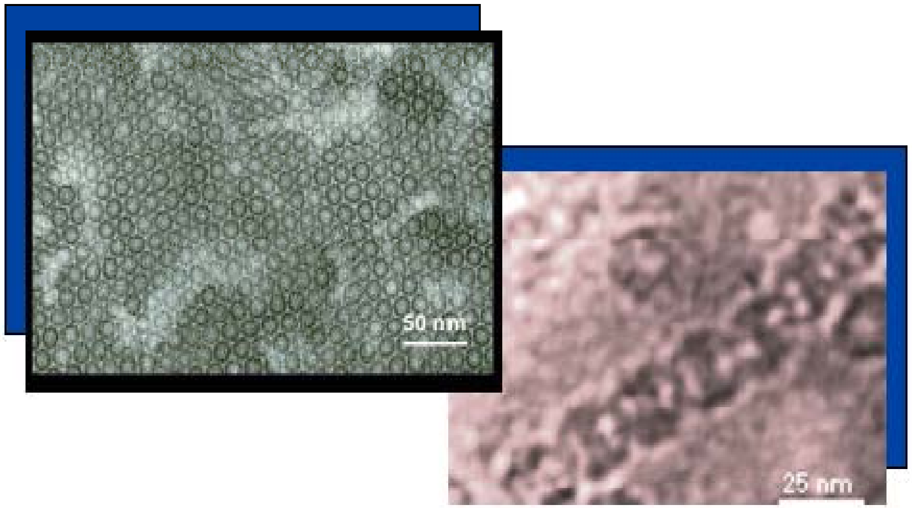
Metin Sitti[1] and Ronald S. Fearing[2]
[1] Dept. of Mechanical Engineering and Robotics Institute, Carnegie Mellon University, USA
[2] Dept. of EECS, University of California at Berkeley, USA

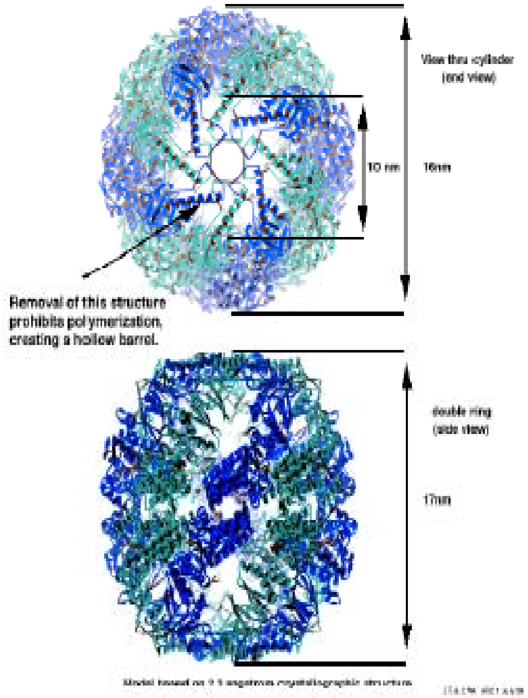
A functional/structural property (adhesion) depends on surface nanostructures (their artificial fabrication is under way)

Small and ultra-small in the nature III

- Heat shock protein (HSP 60) in organisms living at high temperatures ("extremophiles") is of interest in astrobiology

- HSP 60 can be purified from cells as a double-ring structure consisting of 16-18 subunits. The double rings can be induced to self-assemble into nanotubes.



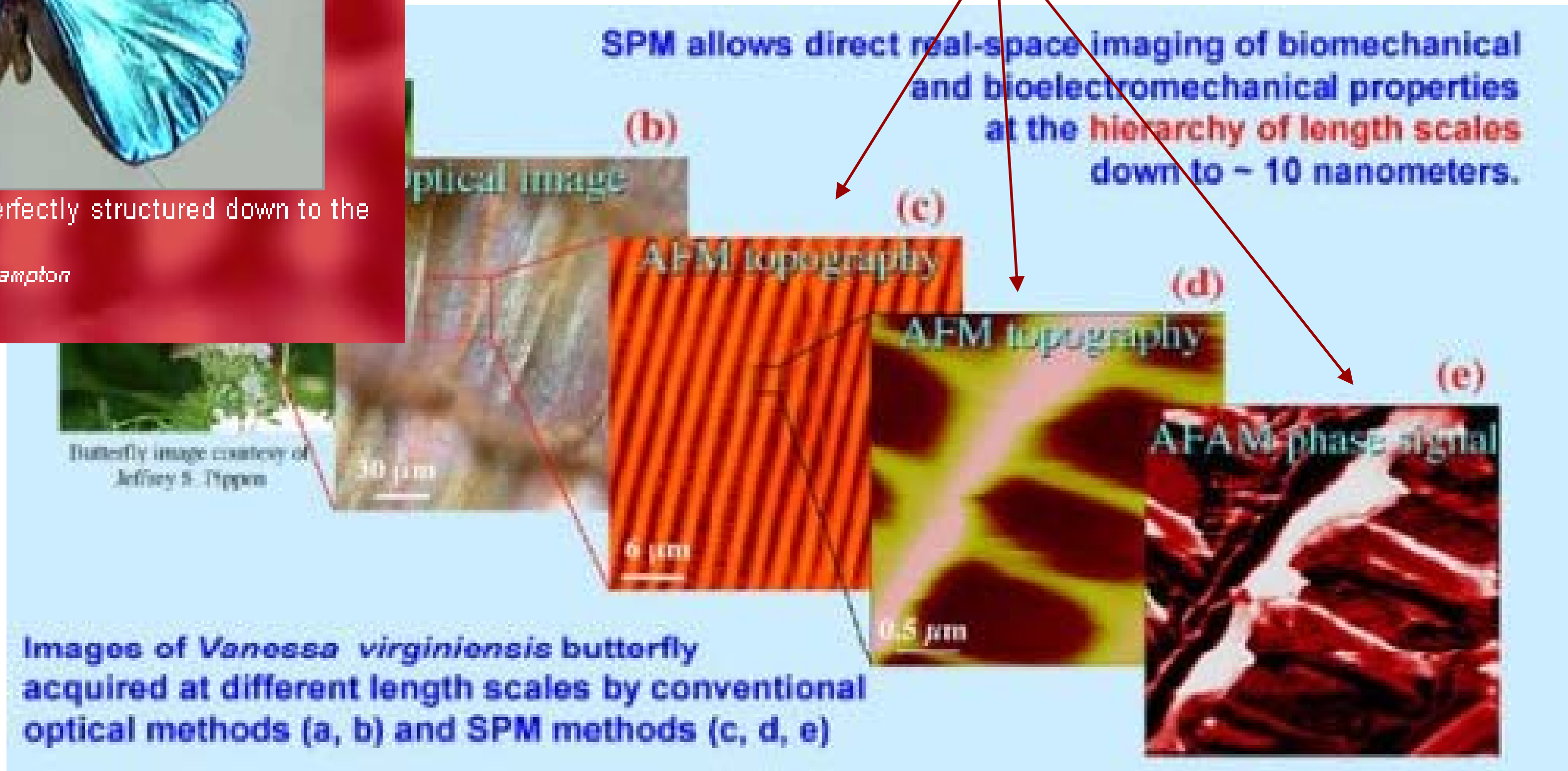


Termo-mechanical properties are enhanced when specific geometries are attained (at the nanoscale)

Small and ultra-small in the nature IV

Butterfly wings are perfectly structured down to the nano-scale.
Image: University of Southampton

Observations made possible thanks to the availability of new techniques



Very diverse features can be explained when considering the structure/morphology at the nanoscale

An historical example of small ultra-small objects

Lycurgus Cup in Roman times

Dr. Juen-Kai Wang

The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

Interpretation:
“Nanostructured” glass
(i.e., containing gold and silver nanoparticles)

The Lycurgus Cup, Roman (4th century AD), British Museum *(www.thebritishmuseum.ac.uk)*
F. E. Wagner et al., Nature ***407****, 691 (2000).*

Technological aspects

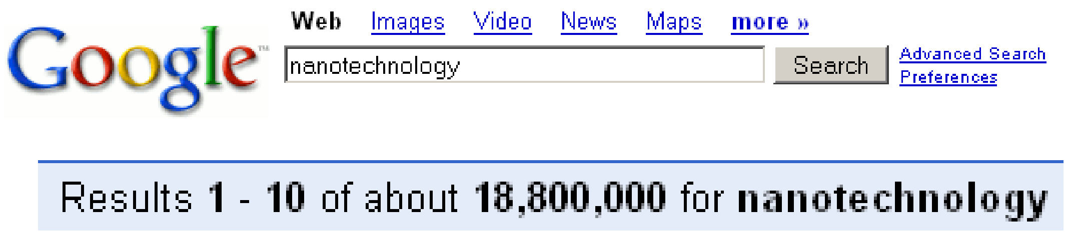
- We have (more or less) defined the range of interest, i.e., what is small or ultra-small
- We have seen that:
  - ✓ Nanosized objects can possess unique properties (we will explain some of them in the future!)
  - ✓ Nature knows how to exploit such properties to achieve specific functions

Since from many decades, technology has been interested in <u>producing, using, analyzing</u> nano-objects to.

- ➢ Miniaturize devices
- ➢ Improve their performance (power, efficiency, diffusion, reliability, …)
- ➢ Find practical applications for novel functions, specifically related to the nanosized character

Technology with (or for) small objects is known as nanotechnology

(Nano)technology



Technology: the ability to fabricate systems **useful** for some applications
Nano: fabricated systems are "small"-sized (*hard to figure out how small…)*

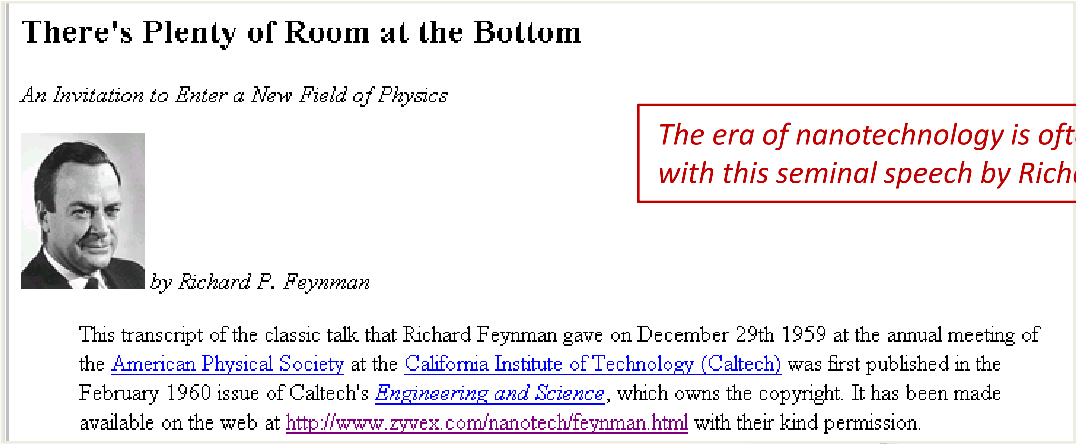
i.e., the ability to manipulate matter in order to fabricate systems (or structures, or devices) with a size in the **sub-micrometer** range

Technology uses techniques, but **it is not just a technical application**: basic science is involved as well in designing new techniques and new structures with improved functionalities

(Nano)technology is strictly connected with basic science, but **it is not just investigation/interpretation** of processes in the nano-world

[concepts from M.Wilson et al., Nanotechnology (Chapman&Hall, 2002)]

There is plenty of room at the bottom…I



There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics

by Richard P. Feynman

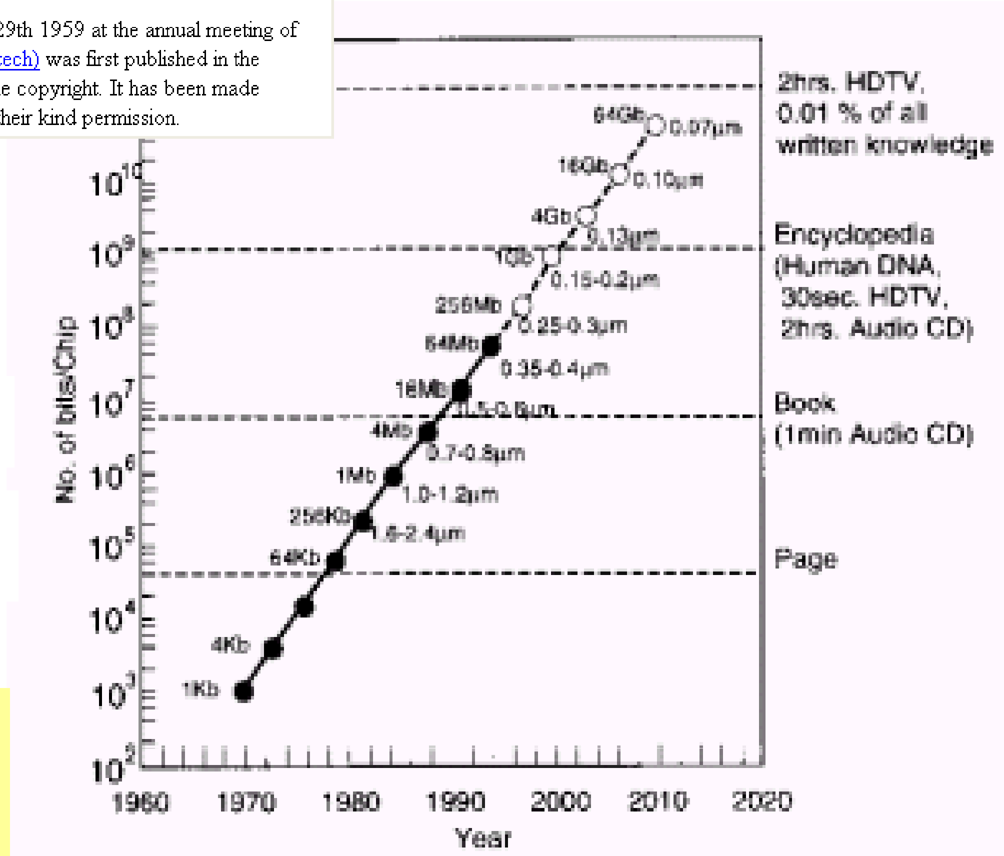
This transcript of the classic talk that Richard Feynman gave on December 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech) was first published in the February 1960 issue of Caltech's *Engineering and Science*, which owns the copyright. It has been made available on the web at http://www.zyvex.com/nanotech/feynman.html with their kind permission.

The era of nanotechnology is often considered to start with this seminal speech by Richard Feynman

How do we write small?

Information on a small scale

Miniaturizing the computer



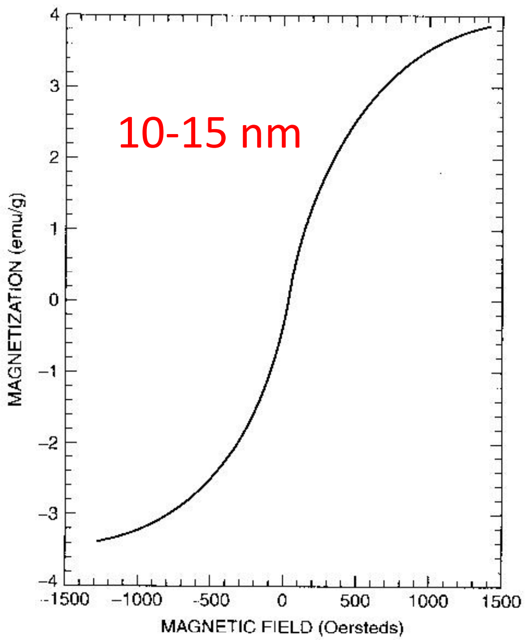
Miniaturization means increase of "power" in Information Technology

Increasing the information density: an example

Hard disk technology

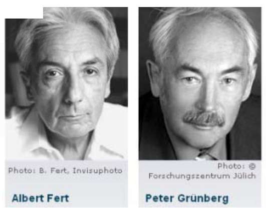
In hard disks (magnetic), information is retained in the magnetization status of nanosized systems

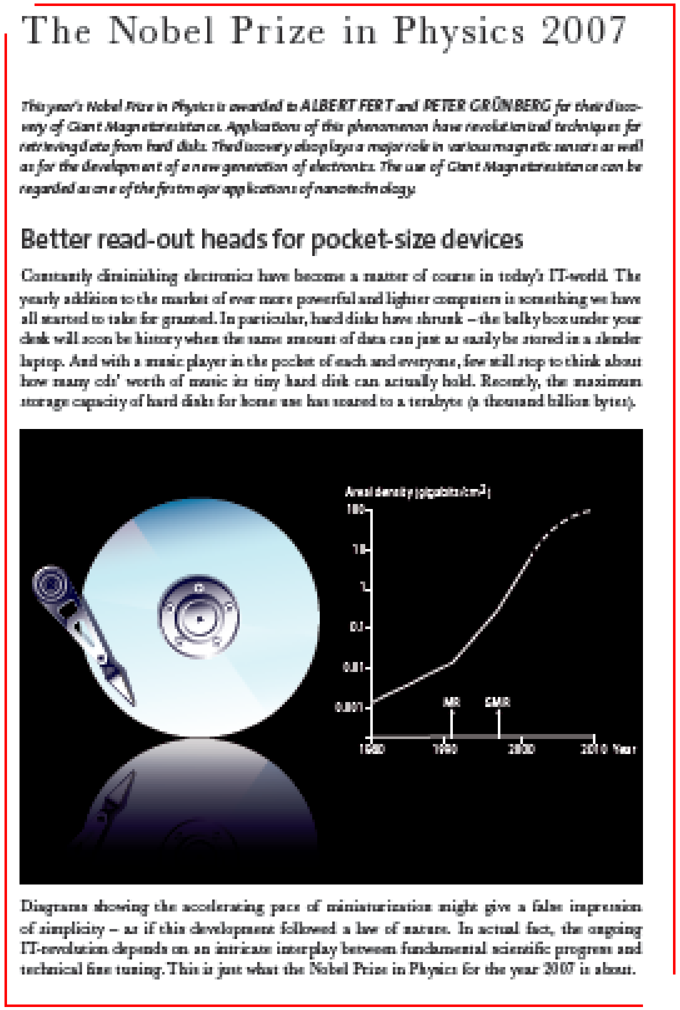
Reading small magnetic field variations requires sensitive systems based on nanostructured materials (GMR)



Magnetization vs magnetic field for a Co salt nanoparticle system

"for the discovery of Giant Magnetoresistance"





The Nobel Prize in Physics 2007

This year's Nobel Prize in Physics is awarded to ALBERT FERT and PETER GRÜNBERG for their discovery of Giant Magnetoresistance. Applications of this phenomenon have revolutionized techniques for retrieving data from hard disks. The discovery also plays a major role in various magnetic sensors as well as for the development of a new generation of electronics. The use of Giant Magnetoresistance can be regarded as one of the first major applications of nanotechnology.

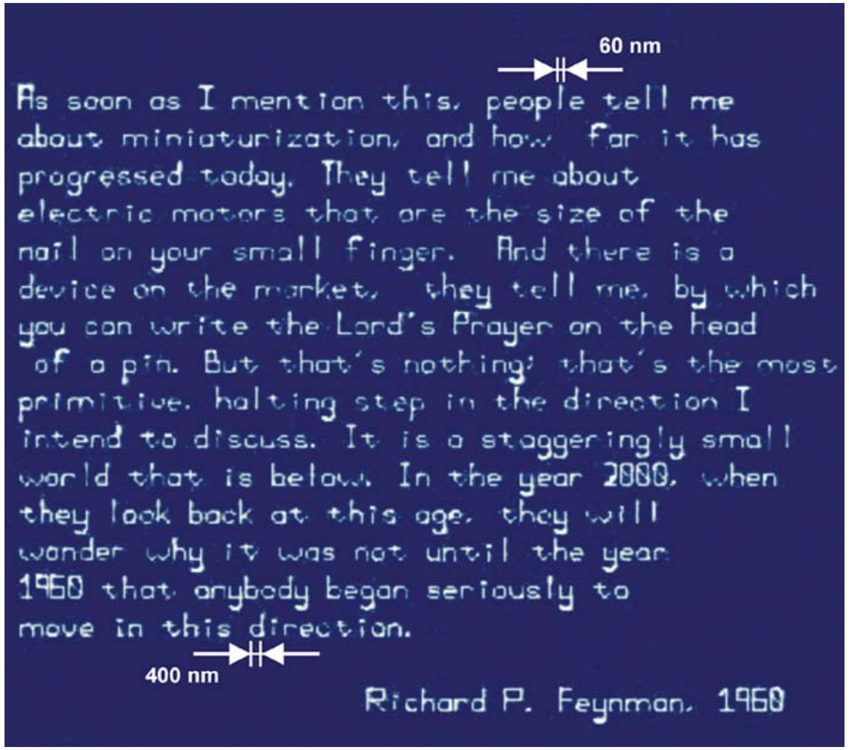
Better read-out heads for pocket-size devices

Constantly diminishing electronics have become a matter of course in today's IT-world. The yearly addition to the market of ever more powerful and lighter computers is something we have all started to take for granted. In particular, hard disks have shrunk – the bulky box under your desk will soon be history when the same amount of data can just as easily be stored in a slender laptop. And with a music player in the pocket of each and everyone, few still stop to think about how many cds' worth of music its tiny hard disk can actually hold. Recently, the maximum storage capacity of hard disks for home use has soared to a terabyte (a thousand billion bytes).

Diagrams showing the accelerating pace of miniaturization might give a false impression of simplicity – as if this development followed a law of nature. In actual fact, the ongoing IT-revolution depends on an intricate interplay between fundamental scientific progress and technical fine tuning. This is just what the Nobel Prize in Physics for the year 2007 is about.

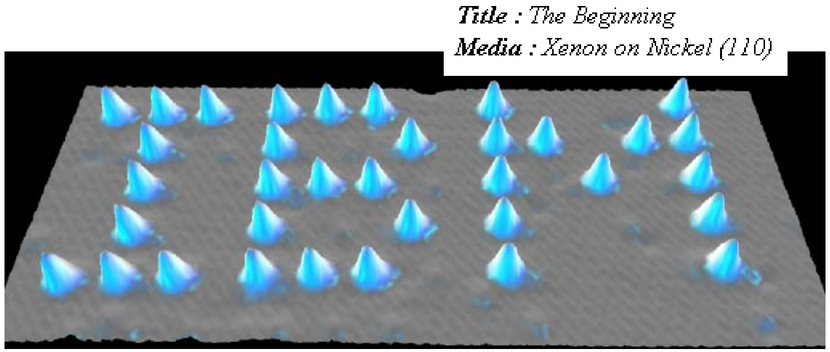
Towards less conventional implementations

Dip pen lithography



"Nanosized microfilm" displaying the initial part of the Feynman's speech

Single atom manipulation by STM



D.M. Eigler, E.K. Schweizer. Positioning single atoms with a scanning tunneling microscope. Nature 344, 524-526 (1990).

Strict interplay between basic science (e.g., fundamental phenomena occurring at the nanoscale) and applicative implementations

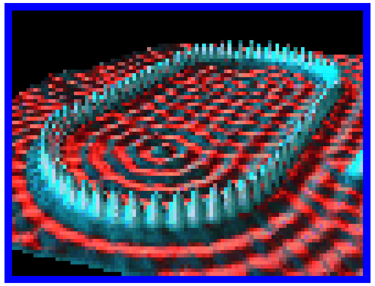
There is plenty of room at the bottom…II

Miniaturization by evaporation

Better electron microscopes

Atoms in a small world

Rearranging the atoms

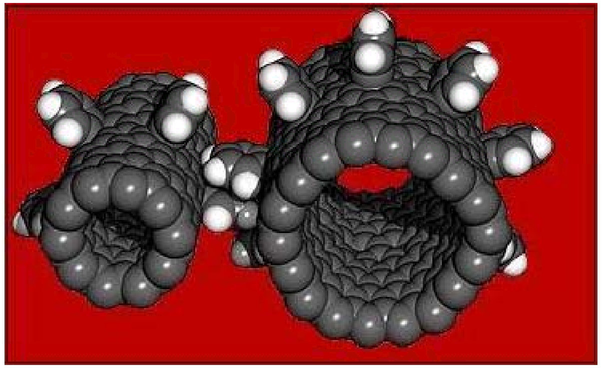


Title : Stadium Corral

Media : Iron on Copper (111)

IBM

Miniaturization means new (*quantized*) functionalities exploitable in novel applications



A representation of nanogears made from graphitetubes billionths of a meter wide. (Picture from the NanoGallery, see references)

Nanomachines for, e.g., computation, drug dispensing, nanofluidics, …

4 • NANOTECHNOLOGY

'nanotechnology is the principle of atom manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom-by-atom precision, yielding a variety of nanomachines.'

Eric Drexler (1990)

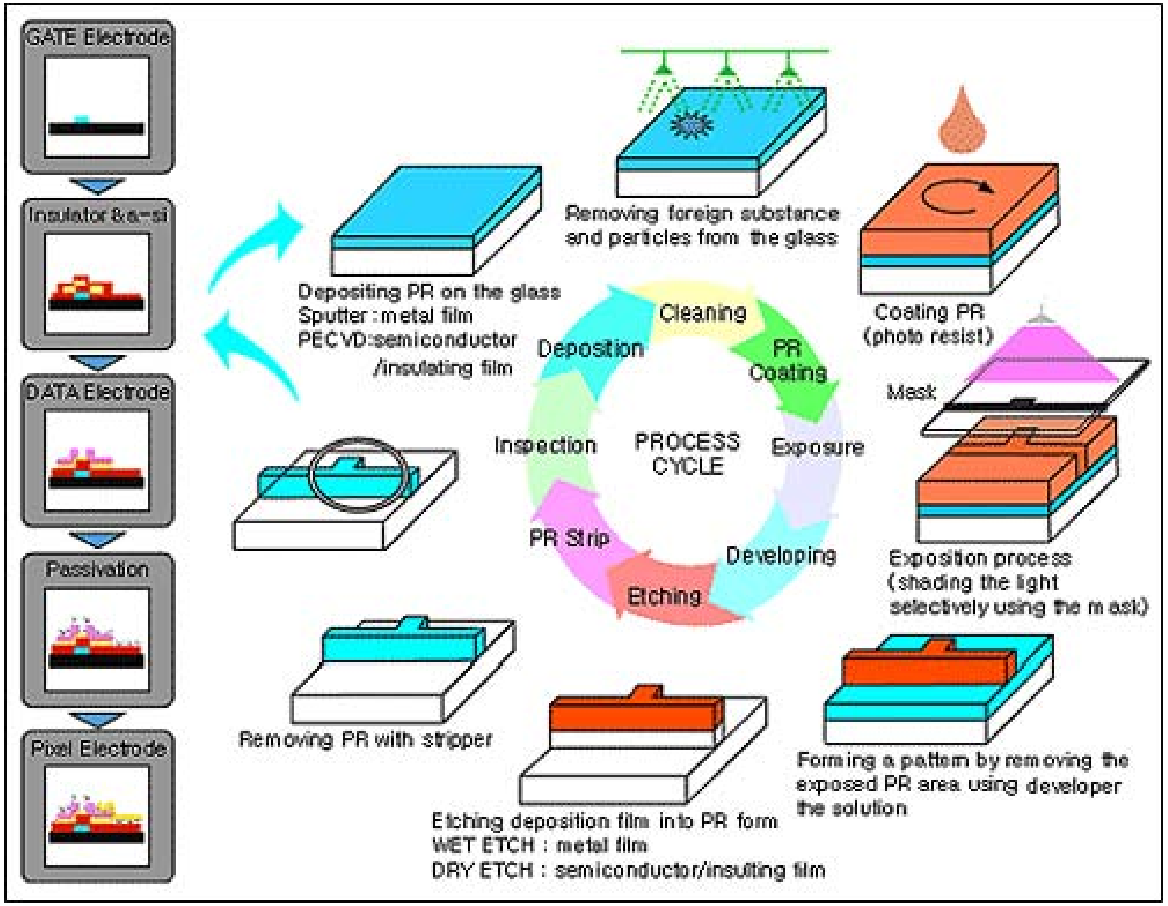
Manipulation and control of the matter at the single atom level made possible by new techniques and methods

Main driving forces for nanotechnology

Electronics devices:
they are typically (and *traditionally*) made of "small" structures

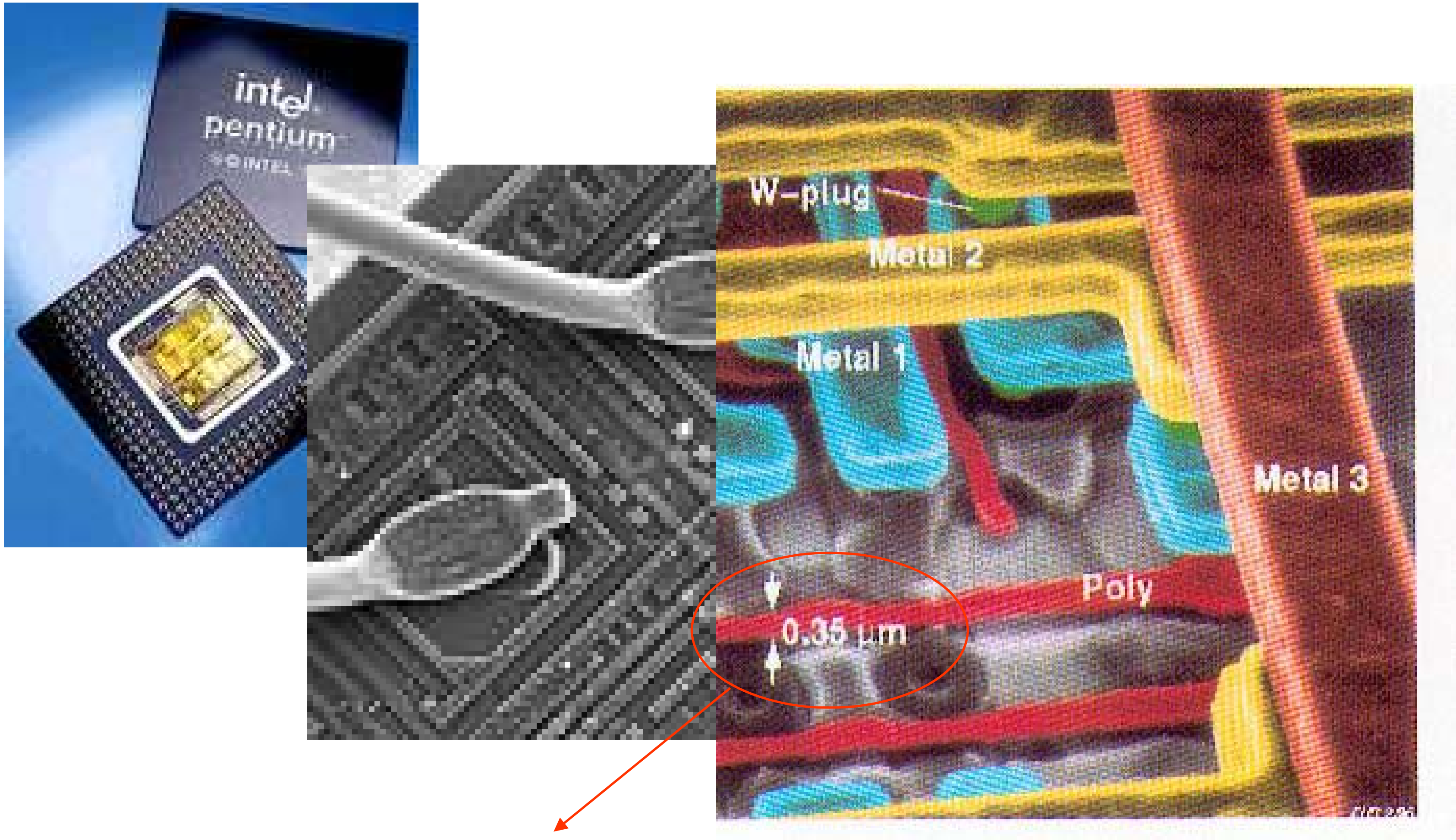
1. Thin films are deposited
2. A pattern is tranferred to the multilayered structure

Device components (resistors, capacitors, transistors, …) are so defined in an *integrated* structure



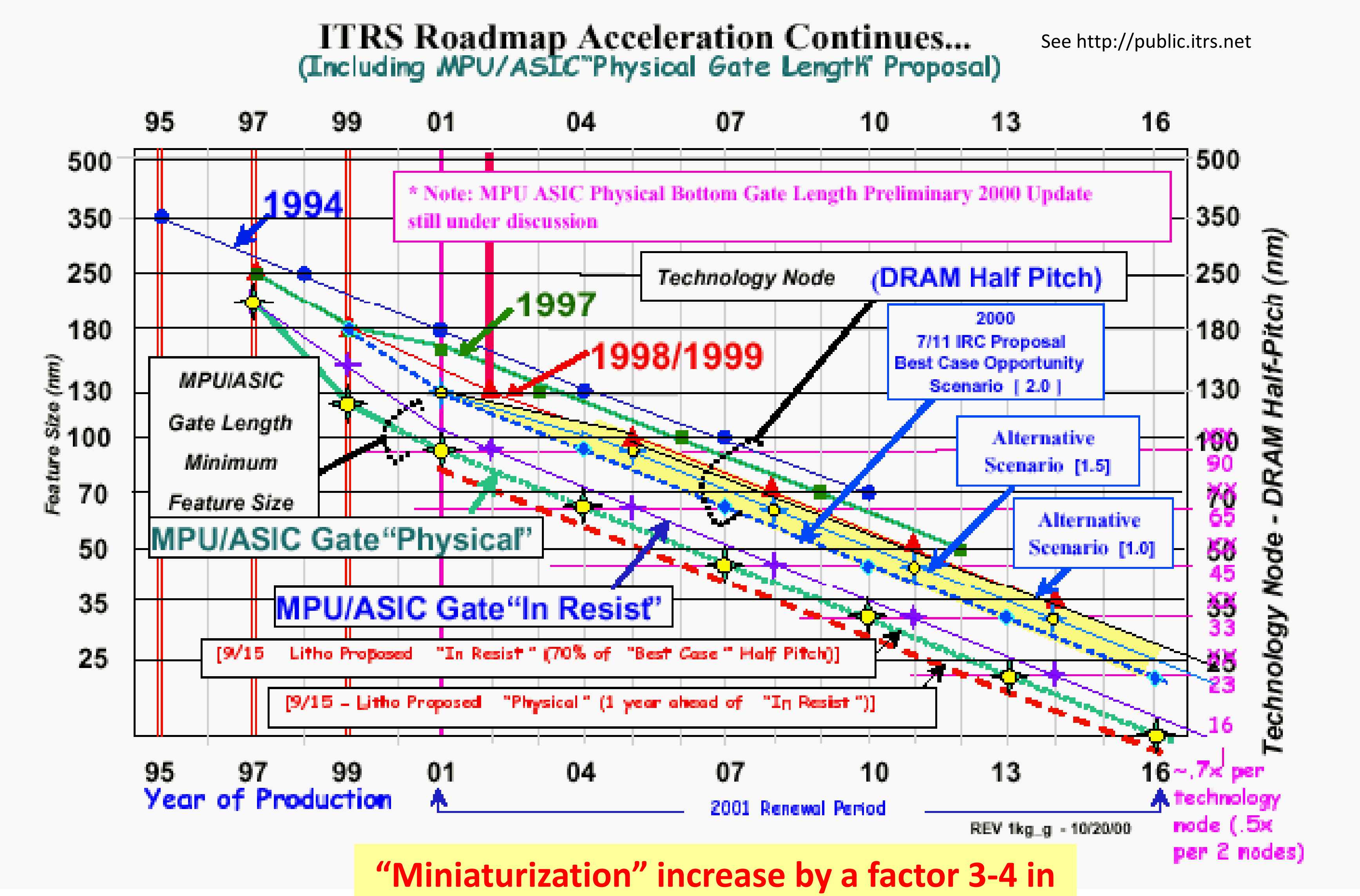
Traditionally, a *top-down* approach is adopted

Driving forces for nanotechnology II



Feature size
(typ., fwhm of the smaller device features)

The “Moore’s law”

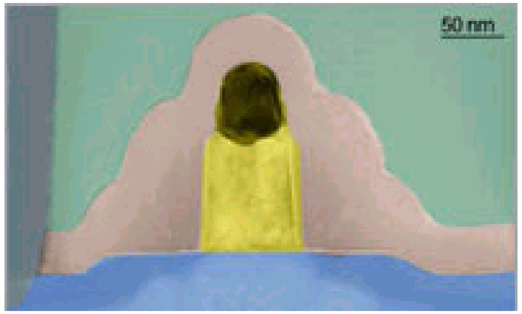


“Miniaturization” increase by a factor 3-4 in a 3-4 year period (still true?)

The 2004 status of miniaturization (commercial)

How many transistors can dance on the head of a chip only 66 millimeters square? Over 58 million, thanks to IBM's sophisticated process technology that builds them just 90 nanometers wide. Such superior technology developments turbo-charge the G5 processor to speeds of up to 2.5GHz.

To get electronics so small requires miniaturization breakthroughs, and IBM's dedication to basic scientific research makes these advances possible. For instance, the company began researching copper as an interconnect method over 25 years ago, but the technique wasn't practical until just recently.



One in 58 Million. A transistor just 90nm wide (yellow) on substrate of SOI (blue) with copper interconnects (gray). Layers of nitride (brown) and oxide (green) insulate it from its brethren. Magnified 146,000 times.

So Small

Transistors on the PowerPC G5 hold a charge to let the system make logic decisions based on whether the transistor is on or off. Using a 90nm process for even greater performance, IBM builds these devices just .00000009 meters wide on a layer of silicon on insulator. The 58 million transistors themselves are connected by over 400 meters of copper wire that's less than 1/1000th the width of a strand of your hair. Tiny paths mean less time to complete a sequence, since the

http://www.apple.com

Feature size below 100 nm (nanoelectronics)

The 2008/09 status of miniaturization (commercial)

45 nanometer

From Wikipedia, the free encyclopedia

Per the International Technology Roadmap for Semiconductors, the **45 nm** technology node should refer to the average half-pitch of a memory cell manufactured at around the 2007-2008 time frame.

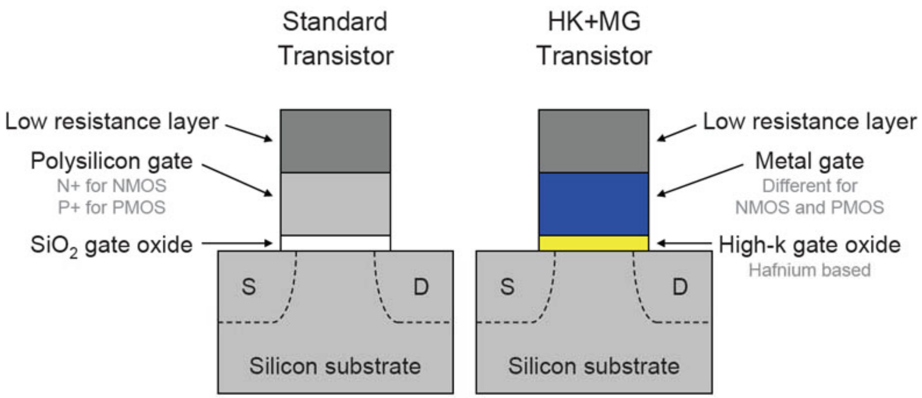
Matsushita and Intel started mass producing 45 nm chips in 2007, and AMD is targeting 45 nm production in 2008, while IBM, Infineon, Samsung, and Chartered Semiconductor have already completed a common 45 nm process platform. By the end of 2008, SMIC will be the first China-based semiconductor company to move to 45 nm, having licensed the bulk 45 nm process from IBM.

Many critical feature sizes are smaller than the wavelength of light used for lithography, i.e., 193 nm and/or 248 nm. A variety of techniques, such as larger lenses, are used to make sub-wavelength features. Double patterning has also been introduced to assist in shrinking distances between features, especially if dry lithography is used. It is expected that more layers will be patterned with 193 nm wavelength at the 45 nm node. Moving previously loose layers (such as Metal 4 and Metal 5) from 248 nm to 193 nm wavelength is expected to continue, which will likely further drive costs upward, due to difficulties with 193 nm photoresists.

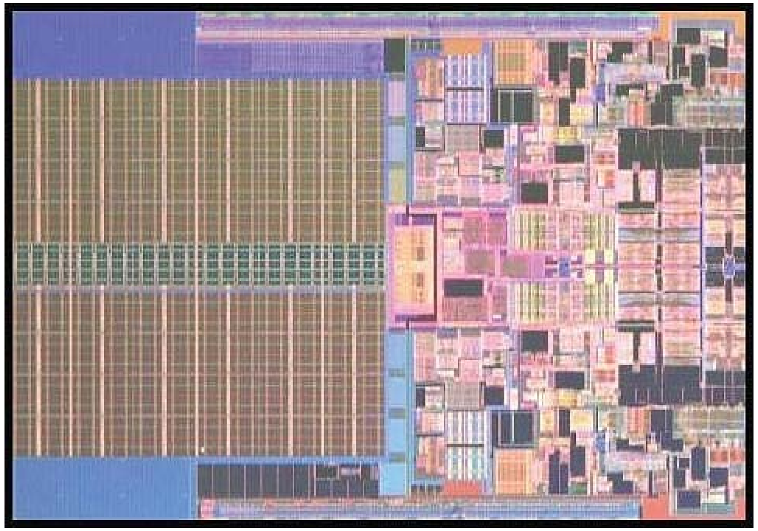
Intel demonstrates first 32nm chip

Explore the first 32nm logic process with functional SRAM packing more than 1.9 billion transistors.

» **Learn more**



High-k + metal gate transistors provide significant performance



Skilled and smart fabrication and material processing

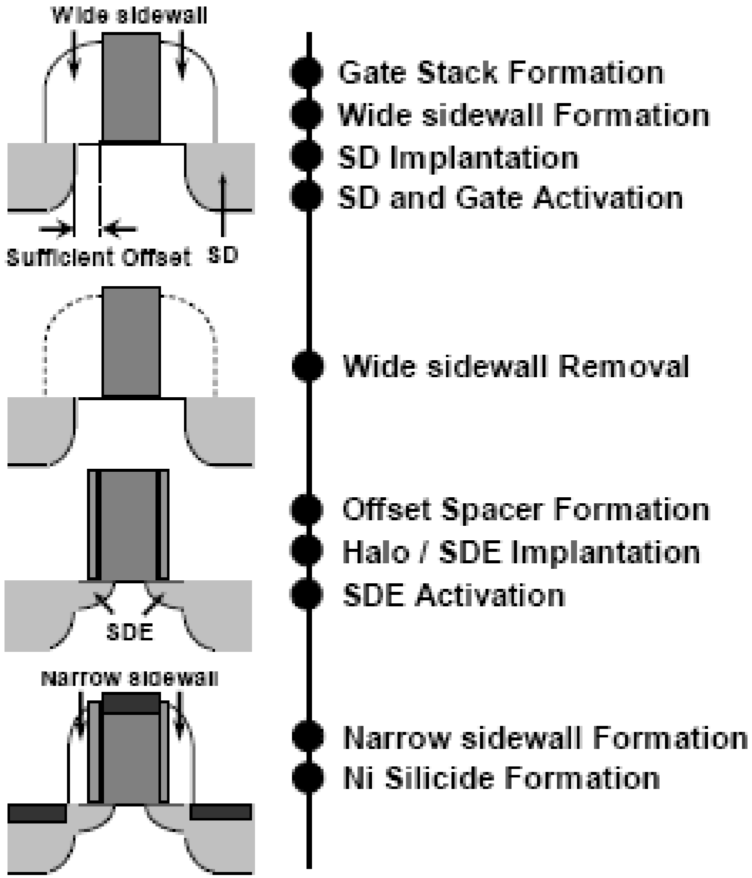


Fig.2 Process flow of reverse ordered SD/SDE formation. SD is formed by using wide sidewall which is disposed after SD formation. Narrow sidewall is formed for Silicide spacer after SDE formation.

High Performance CMOSFET Technology for 45nm Generation and Scalability of Stress-Induced Mobility Enhancement Technique

A.Oishi, O.Fujii, T.Yokoyama[***], K.Ota[***], T.Sanuki, H.Inokuma[*], K.Eda[*], T.Idaka[*], H.Miyajima[*], S.Iwasa[*], H.Yamasaki[*], K.Oouchi[**], K.Matsuo[*], H.Nagano[*], T.Komoda, Y.Okayama, T.Matsumoto[***], K.Fukasaku[***], T.Shimizu[*], K.Miyano[*], T.Suzuki[*], K.Yahashi[*], A.Horiuchi[***], Y.Takegawa, K.Saki[*], S.Mori[*], K.Ohno[***], I.Mizushima[*], M.Saito[***], M.Iwai, S.Yamada, N.Nagashima[***] and F.Matsuoka
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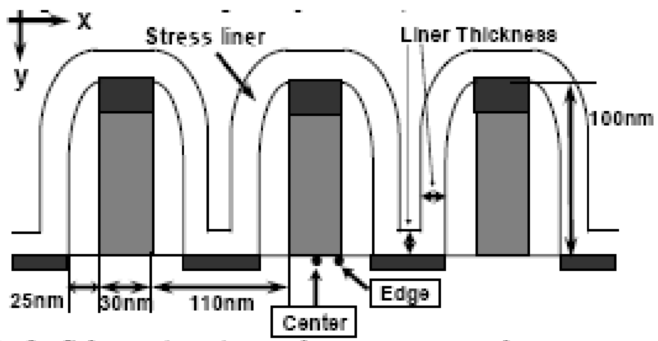


Fig.6 Schematic view of a structure for stress simulation. Minimum gate pitch which is often used for stacked gate circuit is assumed. It is assumed that stress liner deposition is conformal.

Striking results require combinations of different fabrication technologies

Technical and fundamental problems

- In order to maintain the progress of Moore's Law, the 2001 ITRS envisions **more aggressive scaling than projected in prior roadmaps**. For example, dynamic random access memory chips will feature critical dimensions of 90 nanometers in 2004, which is both smaller and sooner than the 100 nanometers projected for 2005 in the roadmap published just two years ago. Similarly, microprocessor transistor gate lengths -- a critical dimension that affects the processor's speed -- will be just 25 nanometers in 2007, six years sooner than expected in the 1999 version of the roadmap. (Note: a nanometer is one-billionth of a meter. A human hair is 100,000 nanometers in width, and a red blood cell is 5,000 nanometers in width.)

- **We are beginning to reach the fundamental limits of the materials used in the planar CMOS process**, the process that has been the basis for the semiconductor industry for the past 30 years. Further improvements in the planar CMOS process can continue for the next five to ten years by introducing new materials into the basic CMOS structure. However as the ITRS looks forward 10-15 years, it becomes evident that even with the introduction of new materials, most of the known technological capabilities of the CMOS device structure will approach or have reached their limits. In order to continue to drive information technology advances, it becomes necessary to investigate new devices that may provide a more cost-effective alternative to planar CMOS in this timeframe.

Da www.sia-online.org

The rate of increase in miniaturization has been growing fast
in information technology

Main motivations:
- Increase of "power" (computing efficiency, information storage, time response, …)
- Decrease of power consumption, usually associated with miniaturization
- Commercial reasons (a huge market!)

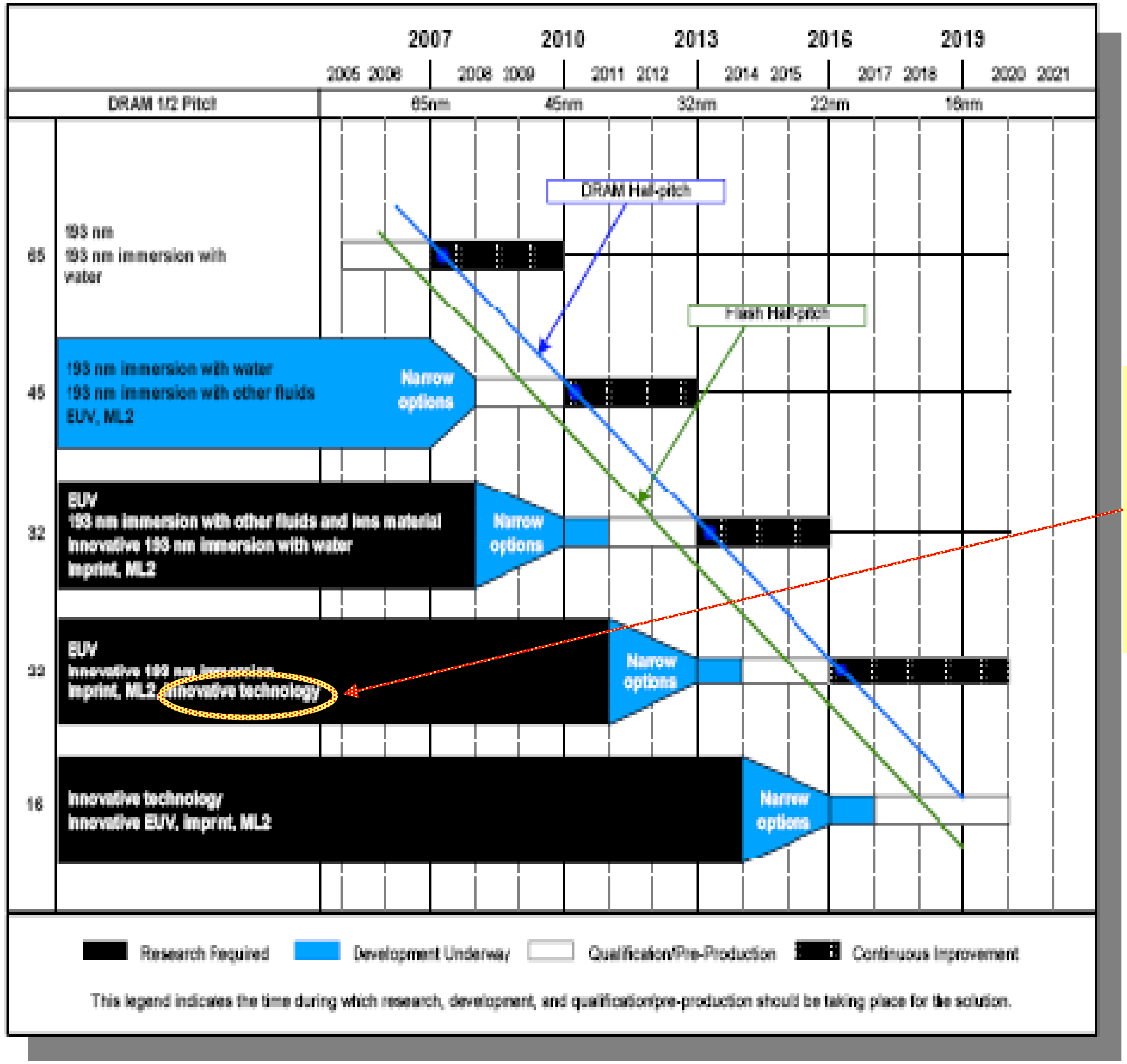
Technical limitations: lack of control in the manipulation, limitations inherent to the materials

Fundamental limitations: in the **techniques** (e.g., optical diffraction in lithography), in the **system operation** (e.g., *quantum* behavior)

Need for novel approaches

Need for new...

International Semicon Technol Roadmap

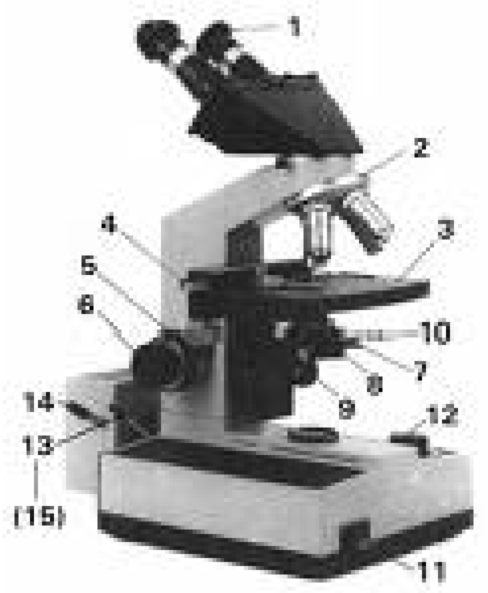


http://public.itrs.net

Alternative (new) technologies required simply to keep the pace of miniaturization

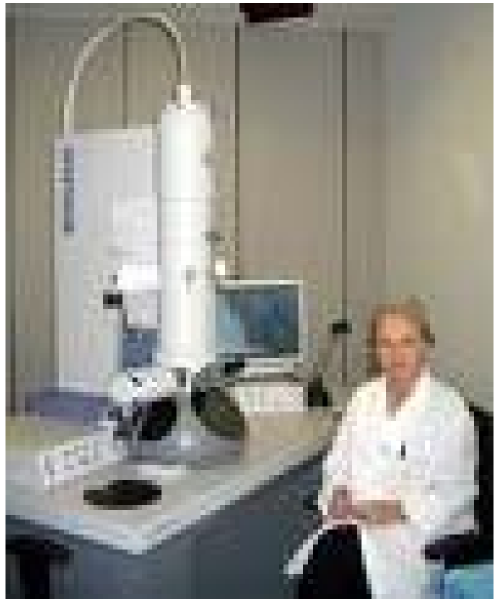
Need for suitable diagnostics

Part of nanotechnology is the development of tools able to catch the physical properties with a spatial resolution in the nanometer range



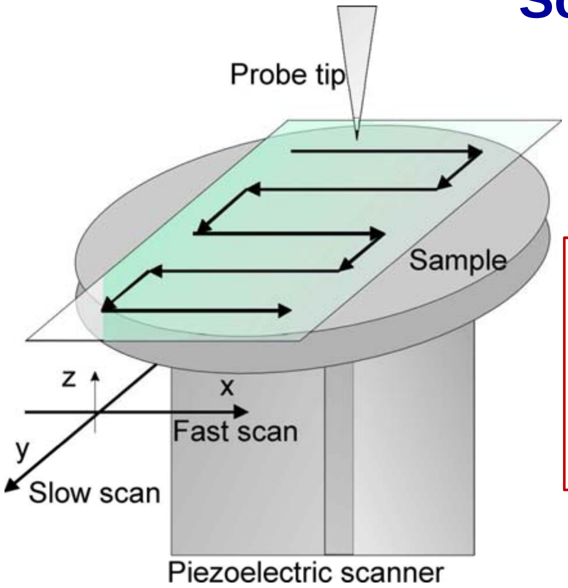
An optical microscope is fundamentally limited in resolution (down to 200-300 nm, typ) due to optical diffraction

An electon microscope can often outreach nm resolution (but it requires often cumbersome specimen preparation)

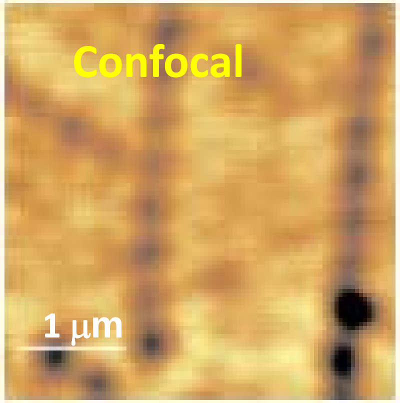


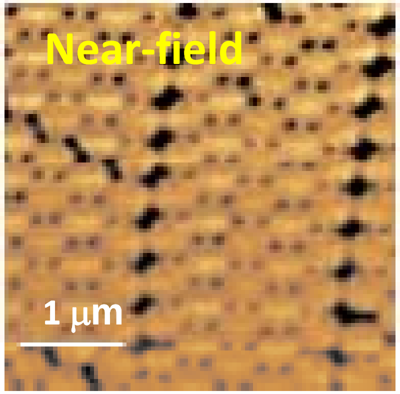
Staring ftom the eighties (Nobel prize 1985), technology has strongly searched for alternative methods able to **measure** physical quantities at the local scale (usually, without the need for sample preparation)

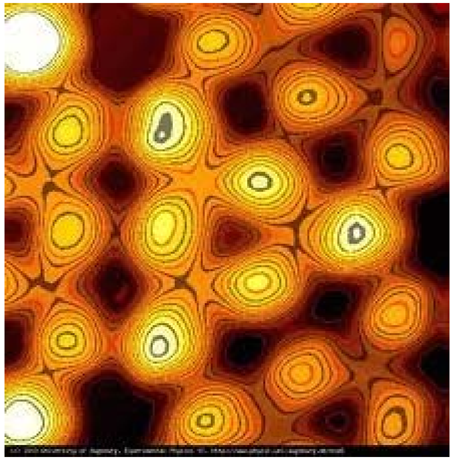
Scanning probe techniques



A small or ultra-small probe is used to measure **local** quantities
Surface scan is adopted to reconstruct the image







AFM (Atomic Force) image of Silicon surface (scan size 3.3nm x 3.3nm)

Alos, improvements of the spatial resolution in optical imaging can be achieved (by using “near-fields”))

Conclusions

✓ The world of small and ultra small is plenty of peculiar effects and opportunities:
- new physical effects associated to *surface/volume and geometry*;
- new physical effects associated to *quantum* phenomena

✓ *Nature and history* know how to exploit such effects

✓ *(Nano)technology* has been strongly developed in the last decades to use small and ultra small in practical devices:
- *electronics* is the main driving force for extreme miniaturization;
- *optical and mechanical* features can also be specific in the nano-world

✓ Fabrication, manipulation, design of nanosized systems has brought the need for *novel diagnostics* at the nano-scale, which we will mention

✓ Before looking at them, however, we will spend a few words on the theoretical tools to describe solid-state matter and nanosized objects, that is, *quantum physics*