



Nanotechnology

Introduction to Micro System Technology Lecture N

Quan Zhou

What is nano and nanotechnology?

Macro, Micro, Nano

How small is a nanometer? Stepping down in size by powers of 10 takes you from the back of a hand to, at one nanometer, a view of atoms in the building blocks of DNA. The edge of each image denotes a length 10 times longer than its next smallest neighbor. The black square frames the size of the next scene inward.

HAND



10 centimeters



1 centimeter



1 millimeter



100 microns

WHITE BLOOD CELL



10 microns



1 micron



100 nanometers



10 nanometers



1 nanometer

From the classic book *Powers of Ten*,
by Philip and Phyllis Morrison and the
office of Charles and Ray Eames.

- ❖ What is nano?
 - ⇒ 1 billionth
- ❖ Nanotechnology
 - ⇒ Science?
 - ⇒ Technology?

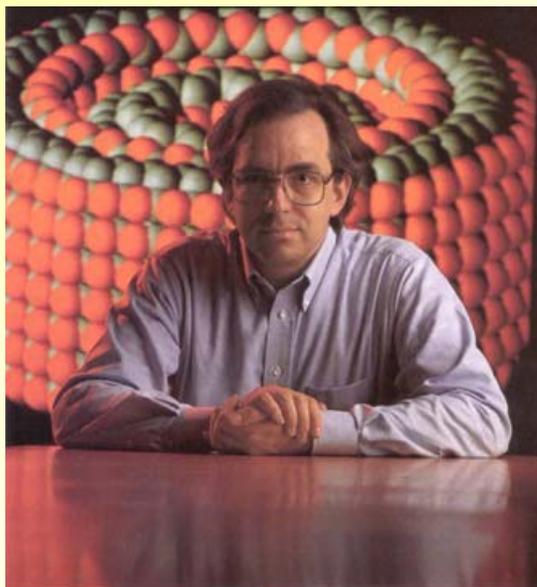


People you should know



RICHARD FEYNMAN predicted the rise of nanotechnology in a landmark 1959 talk at Caltech. "The principles of physics," he said, "do not speak against the possibility of maneuvering things atom by atom." But he also anticipated that unique laws would prevail; they are finally being discovered today.

← Table of Contents



NANOSCRIBE K. Eric Drexler conceived the concept of molecular machine systems

K. Eric Drexler, author of *Nanosystems, Molecular Machinery, Manufacturing, and Computation*, 1992



What is nanotechnology? A technology of making things small?

SOFT LITHOGRAPHY

Printing, molding and other mechanical processes carried out using an elastic stamp can produce patterns with nanoscale features. Such techniques can fabricate devices that might be used in optical communications or biochemical research.

MAKING AN ELASTIC STAMP

- A liquid precursor to polydimethylsiloxane (PDMS) is poured over a bas-relief master produced by photolithography or electron-beam lithography.
- The liquid is cured into a rubbery solid that matches the original pattern.
- The PDMS stamp is peeled off the master.

MICROCONTACT PRINTING

- The PDMS stamp is inked with a solution consisting of organic molecules called thiols and then pressed against a thin film of gold on a silicon plate.
- The thiols form a self-assembled monolayer on the gold surface that reproduces the stamp's pattern. Features in the pattern are as small as 50 nanometers.

MICROMOLDING IN CAPILLARIES

- The PDMS stamp is placed on a hard surface, and a liquid polymer flows into the recesses between the surface and the stamp.
- The polymer solidifies into the desired pattern, which may contain features smaller than 10 nanometers.

← Table of Contents, Slide 4

Nanofabrication: Comparing the Methods

Researchers are developing an array of techniques for building structures smaller than 100 nanometers. Here is a summary of the advantages and disadvantages of four methods.

<p>Photolithography</p> <p>Advantages: The electronics industry is already familiar with this technology because it is currently used to fabricate microchips. Manufacturers can modify the technique to produce nanometer-scale structures by employing electron beams, x-rays or extreme ultraviolet light.</p> <p>Disadvantages: The necessary modifications will be expensive and technically difficult. Using electron beams to fashion structures is costly and slow. X-rays and extreme ultraviolet light can damage the equipment used in the process.</p>	<p>Soft Lithography</p> <p>Advantages: This method allows researchers to inexpensively reproduce patterns created by electron-beam lithography or other related techniques. Soft lithography requires no special equipment and can be carried out by hand in an ordinary laboratory.</p> <p>Disadvantages: The technique is not ideal for manufacturing the multilayered structures of electronic devices. Researchers are trying to overcome this drawback, but it remains to be seen whether these efforts will be successful.</p>
<p>Scanning Probe Methods</p> <p>Advantages: The scanning tunneling microscope and the atomic force microscope can be used to move individual nanoparticles and arrange them in patterns. The instruments can build rings and wires that are only one atom wide.</p> <p>Disadvantages: The methods are too slow for mass production. Applications of the microscopes will probably be limited to the fabrication of specialized devices.</p>	<p>Bottom-Up Methods</p> <p>Advantages: By setting up carefully controlled chemical reactions, researchers can cheaply and easily assemble atoms and molecules into the smallest nanostructures, with dimensions between two and 10 nanometers.</p> <p>Disadvantages: Because these methods cannot produce designed, interconnected patterns, they are not well suited for building electronic devices such as microchips.</p>

DIP-PEN LITHOGRAPHY

PYRAMIDAL TIP of an atomic force microscope (AFM) is coated with a thin film of thiol molecules. A minute drop of water condenses between the microscope's tip and a gold surface. The thiols migrate from the tip to the surface, where they form a self-assembled monolayer.

What is nanotechnology? A science of understanding the tiny?

Quantization electrical conductance and thermo conductance are discoveries of 1987 and 1990s!

ONE STEP AT A TIME

THE QUANTIZATION OF ELECTRICAL CONDUCTANCE

In 1987 Bart J. van Wees and his collaborators at the Delft University of Technology and Philips Research Laboratories (both in the Netherlands) built a novel structure (micrograph) that revealed a basic law governing nanotech circuits. Gold gate electrodes (bright areas) were placed atop a semiconductor substrate (dark background). Within the substrate, a planar sheet of charge carriers, called a two-dimensional electron gas, was created about 100 nanometers below the surface. The gates and the gas acted like the plates of a capacitor.

When a negative voltage bias was applied to the gates, electrons within the gas underneath the gates, and slightly beyond the gates' periphery, were pushed away. (The diagram shows this state.) When increasing negative voltage was applied, this "depletion edge" became more pronounced. At a certain threshold, carriers on either side of the constriction (between points A and B) became separated, and the conductance through the device was zero. From this threshold level, conductance did not resume smoothly. Instead it increased in stepwise fashion, where the steps occurred at values determined by twice the charge of the electron squared, divided by Planck's constant. This ratio is now called the electrical conductance quantum, and it indicates that electric current flows in nanocircuits at rates that are quantized.



NANOBIDGE DEVICE: allowed Caltech physicists to first observe the quantization of thermal conductance—a fundamental limit to heat flow in minute objects. Four holes (black) etched into a silicon nitride membrane defined an isolated thermal reservoir (central green square) suspended by four narrow bridges. One gold transducer (yellow) electrically heated this reservoir; the second measured its temperature. Thin superconducting films (blue) on top of the bridges electrically connected the transducers to off-chip instrumentation but carried no heat. The reservoir therefore cooled only through the silicon nitride bridges, which were so narrow that they passed only the lowest-energy heat waves.

Table of Contents, Slide 5

What is nanotechnology? Something called nanoelectronics?

NANOTRANSISTORS

MOLECULAR TRANSISTORS

could be the building blocks of electronics on the nanometer scale. Each of the two molecules shown here conducts electricity like a tiny wire once a chemical reaction—oxidation reduction—alters its atomic configuration and switches it on. In the diagram, each stick represents a chemical bond; each intersection of two sticks represents a carbon atom; and each ball represents an atom other than carbon.

ROTOXANE

TAKING CHARGE

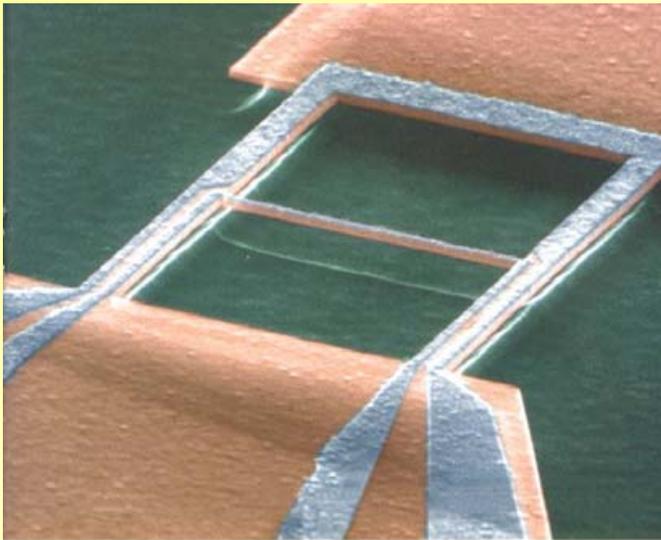
SINGLE ELECTRONICS

Advances in nanofabrication allowed Theodore A. Fulton and Gerald J. Dolan to build a single-electron transistor at Bell Laboratories in 1987 (micrograph). In this structure the controlled movement of individual electrons through a nanodevice was first achieved. At its heart was a coulomb island, a metallic electrode isolated from its counter-electrodes by thin insulating oxide barriers (diagram). The counter-electrodes led up to the macroscale laboratory instrumentation used to carry out the experiments. An additional gate electrode (visible in the diagram but not the micrograph) was offset from the coulomb island by a small gap; it allowed direct control of the charge introduced to the island. Electric current flowed through the device from one counter-electrode to another, as in a conventional circuit, but here it was limited by the stepwise hopping of electrons onto and off the coulomb island.

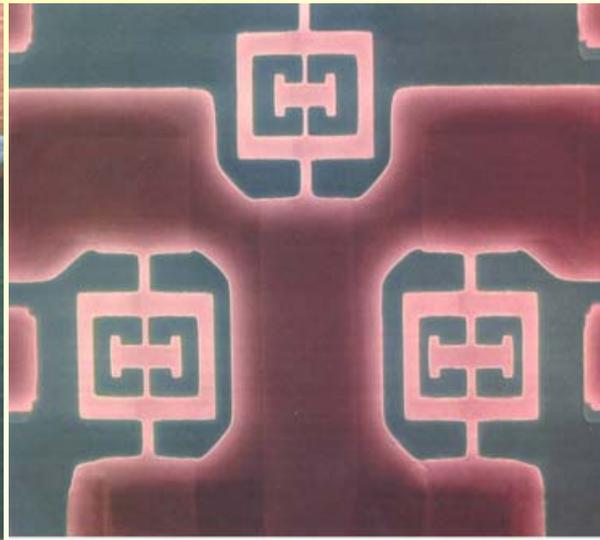
Fulton and Dolan's experiments demonstrate both the fundamental physics of single-electron charging and the potential of these devices as ultrasensitive electrometers: instruments that can easily detect individual electron charges. Circuits that switch one electron at a time could someday form the basis for an entirely new class of nanoelectronics. The advent of such single electronics, however, also presages problems that will have to be faced as conventional electronic circuits are shrunk to the nanoscale.

Table of Contents, Slide 6

What is nanotechnology? Some nano mechanism that works?



NANOMECHANICAL AMPLIFIER overcomes the vexing problem of communication with the macroworld by providing up to 1,000-fold amplification of weak forces. Two suspended bridges (left and right) of monocrystalline silicon carbide support the central crossbridge, to which the signal force is applied. Thin-film electrodes (silver) atop these structures provide very sensitive readouts of nanoscale motion.



NOVEL NANOTECH DEVICES, such as these nanoelectromechanical resonators, are enabling scientists to discover the laws of physics that regulate the unique properties of matter at the mesoscale.

← Table of Contents, Slide 7

DNA Computing

WHY LIMIT OURSELVES TO ELECTRONICS? Most efforts to shrink computers assume that these machines will continue to operate much as they do today, using electrons to carry information and transistors to process it. Yet a nanoscale computer could operate by completely different means. One of the most exciting possibilities is to exploit the carrier of genetic information in living organisms, DNA.

The molecule of life can store vast quantities of data in its sequence of four bases (adenine, thymine, guanine and cytosine), and natural enzymes can manipulate this information in a highly parallel manner. The power of this approach was first brought to light by computer scientist Leonard M. Adleman in 1994. He showed that a DNA-based computer could solve a type of problem that is particularly difficult for ordinary computers—the Hamiltonian path problem, which is related to the infamous traveling-salesman problem [see “Computing with DNA,” by Leonard M. Adleman; *SCIENTIFIC AMERICAN*, August 1998].

Adleman started by creating a chemical solution of DNA. The individual DNA molecules encoded every possible pathway between two points. By going through a series of separation and amplification steps, Adleman weeded out the wrong paths—those, for example, that contained points they were not supposed to contain—until he had isolated the right one. More recently, Lloyd M. Smith’s group at the University of Wisconsin–Madison implemented a similar algorithm using gene chips, which may lend themselves better to practical computing [diagram].

Despite the advantages of DNA computing for otherwise intractable problems, many challenges remain, including the high incidence of errors caused by base-pair mismatches and the huge number of DNA nanoelements needed for even a modest computation. DNA computing may ultimately merge with other types of nanoelectronics, taking advantage of the integration and sensing made possible by nanowires and nanotubes.

—C.M.L.



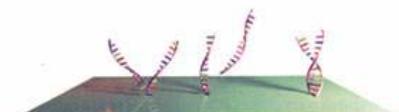
1 Single DNA strands are attached to a silicon chip. They encode all possible values of the variables in an equation that the researchers want to solve.



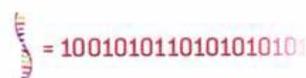
2 Copies of a complementary strand—which encodes the first clause of the equation—are poured onto the chip. These copies attach themselves to any strand that represents a valid solution of the clause. Any invalid solutions remain a single strand.



3 An enzyme removes all the single strands.



4 Other processes melt away the added complementary strands. These steps are repeated with all the clauses of the equation.



← Table of Contents

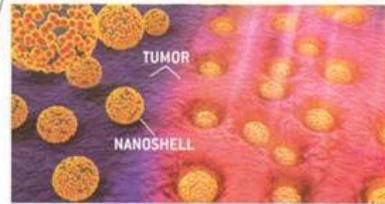
A GRAND PLAN FOR MEDICINE

The National Nanotechnology Initiative includes among its goals, or "grand challenges," a host of futuristic improvements in the detection, diagnosis and treatment of disease. Some are depicted here. The goals, many of which are far from being realized, also feature new aids for vision and hearing, rapid tests for detecting disease susceptibility and responses to drugs, and tiny devices able to find problems—such as incipient tumors, infections or heart problems—and to relay the information to an external receiver or fix them on the spot.



1 GOAL: Improved Imaging
Improved or new contrast agents would detect problems at earlier, more treatable stages. They might, for instance, reveal tumors [red] only a few cells in size.

2 GOAL: New Ways to Treat Disease



Nanoparticles would deliver treatments to specifically targeted sites, including places that standard drugs do not reach easily. For example, gold nanoshells [spheres] that were targeted to tumors might, when hit by infrared light, heat up enough to destroy the growths.

3 GOAL: Superior Implants



Nanometer-scale modifications of implant surfaces would improve implant durability and biocompatibility. For instance, an artificial hip coated with nanoparticles might bond to the surrounding bone more tightly than usual, thus avoiding loosening.



1

TECHNOLOGY
laboratory

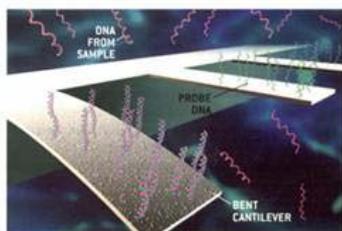
BIO-NANOTECH IN ACTION

The items here could one day enhance the speed and power of biomedical tests, such as those used to screen small samples of material for the presence of particular genetic sequences. For clarity, the images have not been drawn to scale.



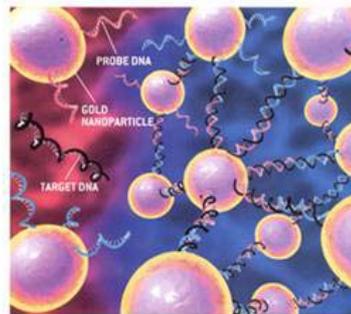
MAGNETIC TAGS

Many tests reveal the presence of a molecule or disease-causing organism by detecting the binding of an antibody to that target. When antibodies labeled with magnetic nanoparticles bind to their target on a surface [foreground], brief exposure to a magnetic field causes these probes collectively to give off a strong magnetic signal. Meanwhile unbound antibodies tumble about in all directions, producing no net signal. This last property makes it possible to read the results without first washing away any probes that fail to find their target.



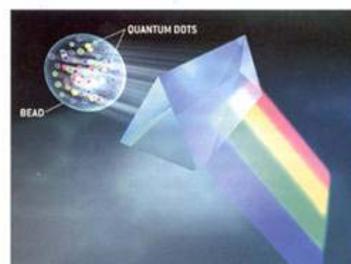
CLEVER CANTILEVERS

Biological samples can be screened for the presence of particular genetic sequences using small beams [cantilevers] of the type employed in atomic force microscopes. The surface of each cantilever is coated with DNA able to bind to one particular target sequence. A sample is then applied to the beams. Binding induces a surface stress, which bends the affected beams by nanometers—not much, but enough to reveal that the bent beams found their specific targets in a sample.



GOLD PARTICLES

Gold nanoparticles studded with short segments of DNA could form the basis of an easy-to-read test for the presence of a genetic sequence (black) in a sample under study. DNA complementary to half of such a sequence [red] is attached to one set of particles in solution, and DNA complementary to the other half [blue] is attached to a second set of particles. If the sequence of interest is present in the sample, it will bind to the DNA tentacles on both sets of spheres, trapping the balls in a dense web. This agglomeration will cause the solution to change color [from red to blue].



NANO BAR CODES

Latex beads filled with several colors of nanoscale semiconductors known as quantum dots can potentially serve as unique labels for any number of different probes. In response to light, the beads would identify themselves (and, thus, their linked probes) by emitting light that separates into a distinctive spectrum of colors and intensities—a kind of spectral bar code.

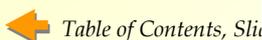
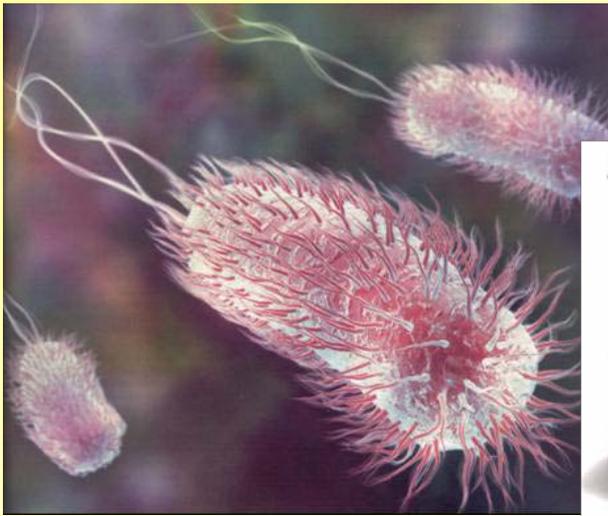


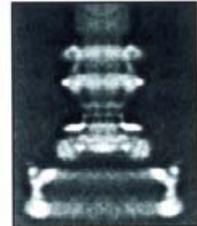
Table of Contents, Sli

UNIVERSITY OF TECHNOLOGY
Engineering Laboratory

What is nanotechnology? Even tiny tiny motors?



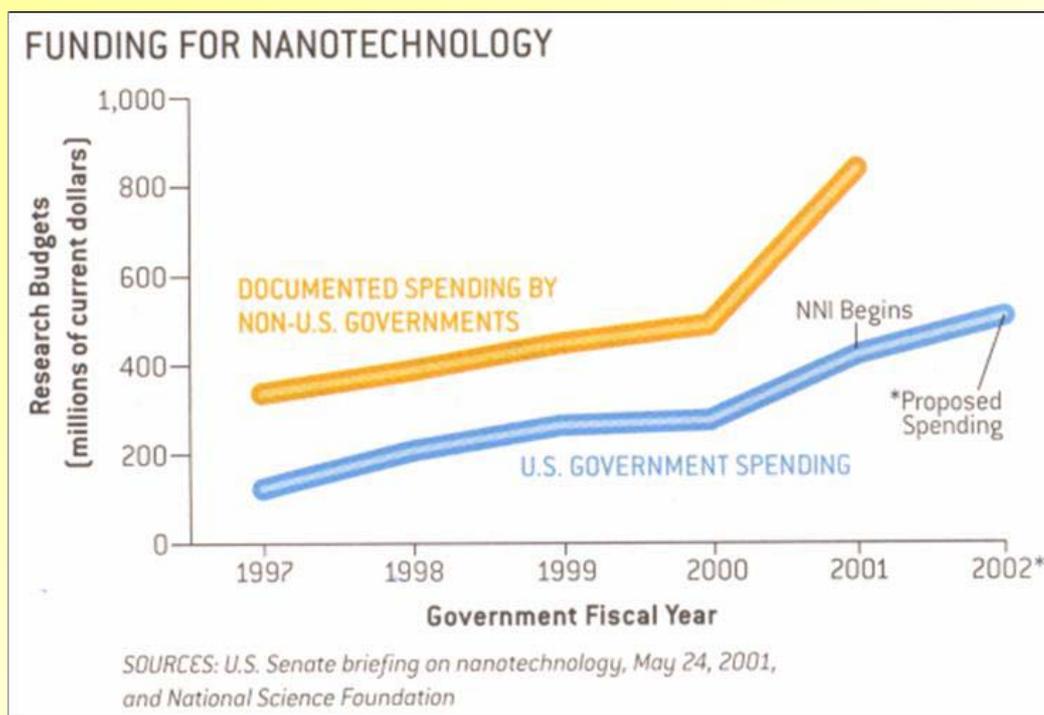
A TALE OF TWO MOTORS



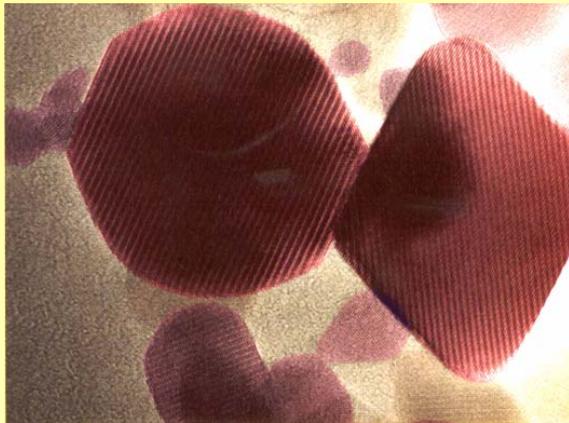
STANDARD-ISSUE electric motor bears a superficial—albeit striking—resemblance to the biochemical rotary motor (top right) that turns the flagella in a bacterium.

← Table of Contents, Slide 11

Funding?



← Table of Contents, Slide 12



NANOPARTICLES are made by Nanophase Technologies.

- ❖ Is nanotechnology
 - ⇒ Distant basic research?
 - ⇒ Physics, chemist, material people's job?
 - ⇒ Biomedical people's work?
 - ⇒ Or something might affect what I am doing

← Table of Contents, Slide 13



HELSINKI UNIVERSITY OF TECHNOLOGY
Control Engineering Laboratory

Nanotechnology Classification

- ❖ "Wet" nanotechnology, is the study of biological systems that exist primarily in a water environment. Nanometer-scale structures: genetic material, membranes, enzymes and other cellular components.
- ❖ "Dry" nanotechnology, derives from surface science and physical chemistry, focuses on fabrication of C structures (e.g. C60 and nanotubes), silicon ...
- ❖ Computational nanotechnology, permits the modeling and simulation of complex nanometer-scale structures. The predictive and analytical power of computation is critical to success in nanotechnology.



Want need to know?

- ❖ Overall picture of nanotechnology
- ❖ Some results and expectation in some field
 - ⇒ Nanofabrication
 - ⇒ Nanomanipulation
 - ⇒ Nanomachines
 - ⇒ Modeling and simulation
 - ⇒ Market and applications

← Table of Contents, Slide 15

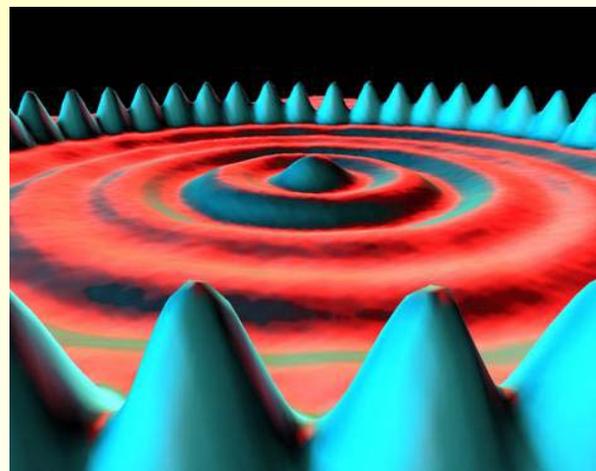


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Control Engineering Laboratory



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Control Engineering Laboratory

Nanofabrication

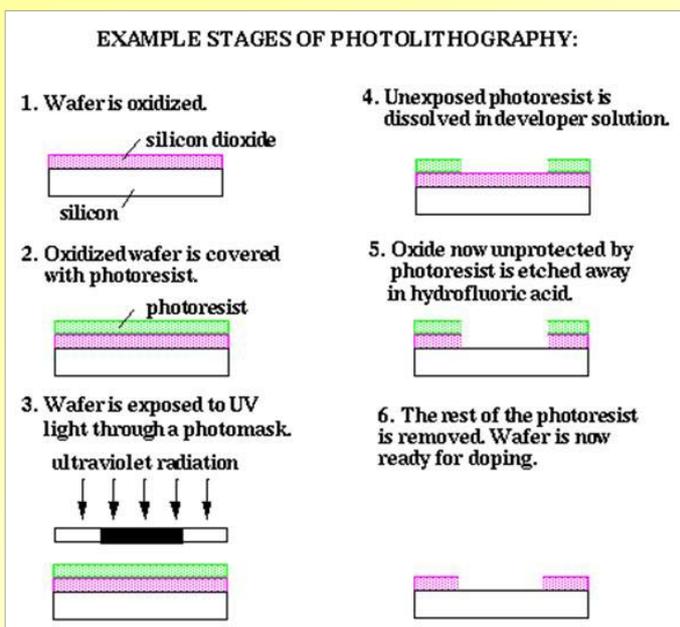


Nanofabrication

- ❖ Nowadays researchers examine extremely wide range of various fabrication techniques in order to produce nanostructures → structures smaller than 100 nm
- ❖ Nanofabrication techniques:
 - ⇒ top-down methods remove or add material to a surface
 - photolithography, soft lithography, scanning probe methods
 - ⇒ bottom-up methods construct nanostructures from molecules or atoms

← Table of Contents, Slide 17

Photolithography

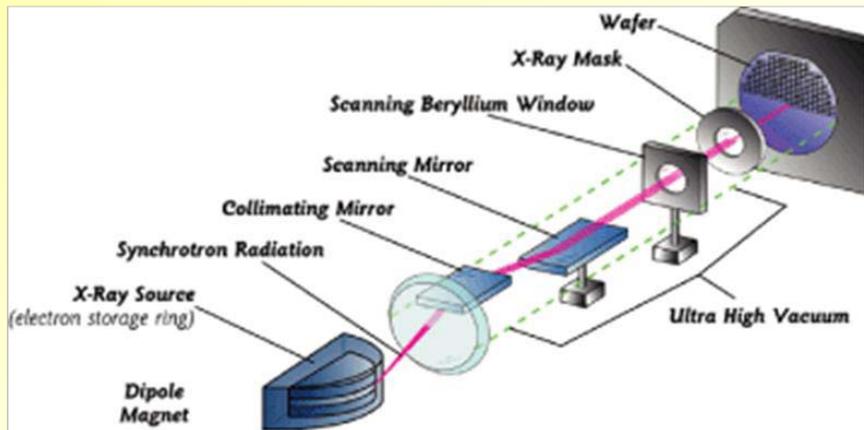


- ❖ Uses light to etch features onto a silicon surface
- ❖ Mass production
- ❖ Expensive mask
- ❖ Min. line width 70 nm

← Table of Contents, Slide 18

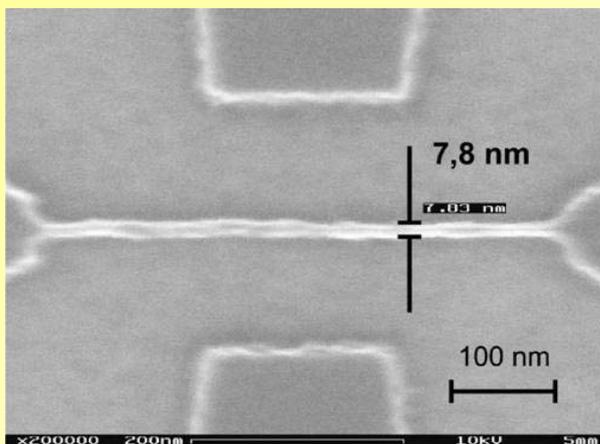
X-ray lithography

- ❖ Like ordinary optical lithography
 - ⇒ wavelengths involved are much shorter: 0.1 - 10 nm
 - ⇒ parallel processes, in which the surface of a photo-sensitive resist-coated wafer is exposed to radiation through a photomask - min. line width 20 nm
 - masks are more difficult to fabricate
 - high intensity x-ray source



← Table of Contents, Slide 19

Electron beam lithography

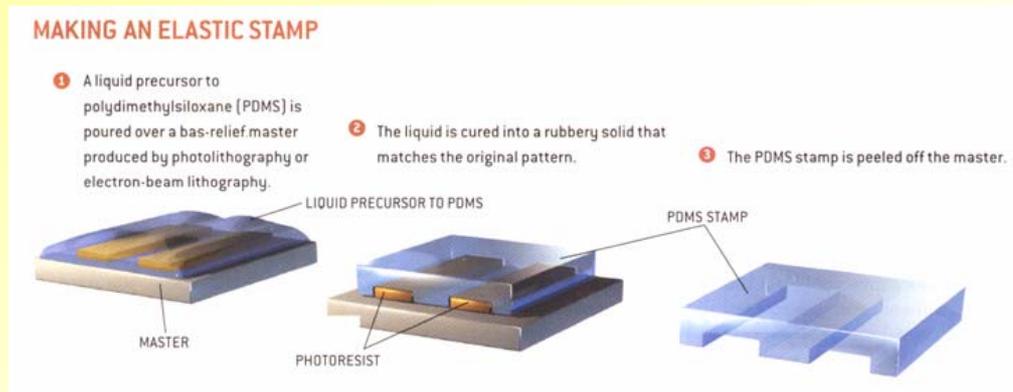


- ❖ Circuit pattern is written directly onto an electron-sensitive resist by serially scanning an electron beam across the wafer in the desired pattern → no mask
- ❖ Rarely used, but utilized in creating photomasks, of which only a few, necessarily highly accurate, master copies are needed

← Table of Contents, Slide 20

Soft lithography

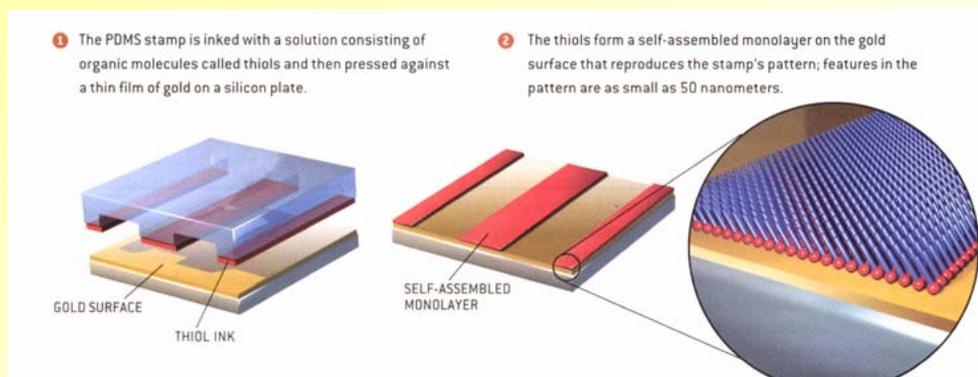
- ❖ Uses flexible rubber stamps to fabricate devices with nanoscale features
- ❖ Elastic stamp
 - ⇒ producing of bas-reliefing stamp by electron beam lithography is expensive, but the copying of the pattern on PDMS stamps is simple and inexpensive



← Table of Contents, Slide 21

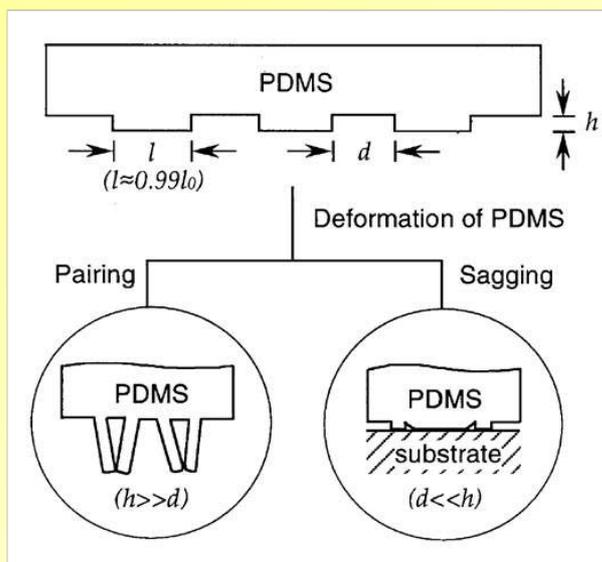
Soft lithography

- ❖ Microcontact printing
 - ⇒ elastomeric stamp is used to generate patterns by printing the thiol molecules onto solid substrate that is usually a thin gold or silver coating → SAM
 - ⇒ simple, straightforward, inexpensive, flexible



← Table of Contents, Slide 22

Soft lithography

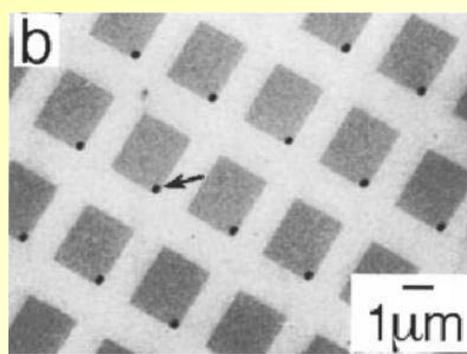
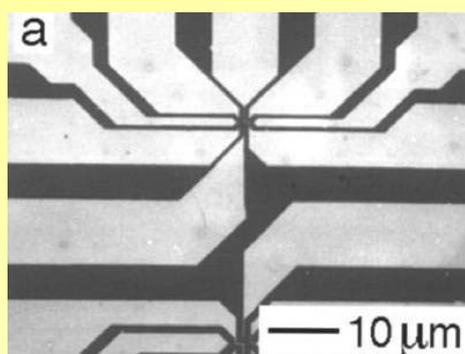


❖ Microcontact printing

- ⇒ Two possible distortions that are usually associated with an elastomer:
 - pairing of raised structures
 - sagging of recessed regions during microcontact printing

← Table of Contents, Slide 23

Soft lithography

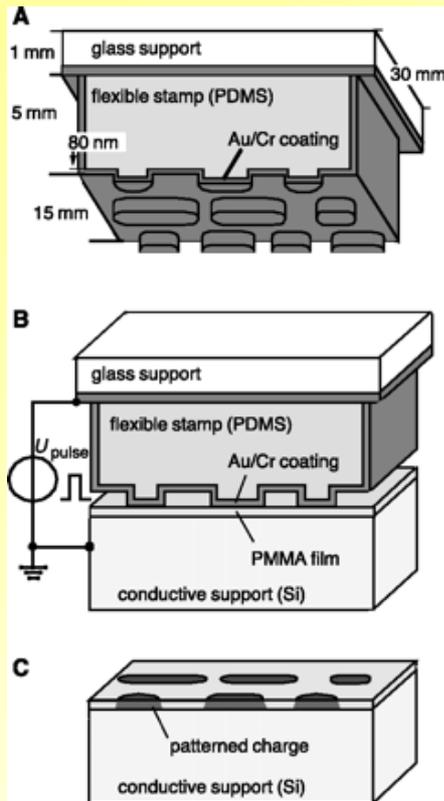


❖ Examples of micro contact printing

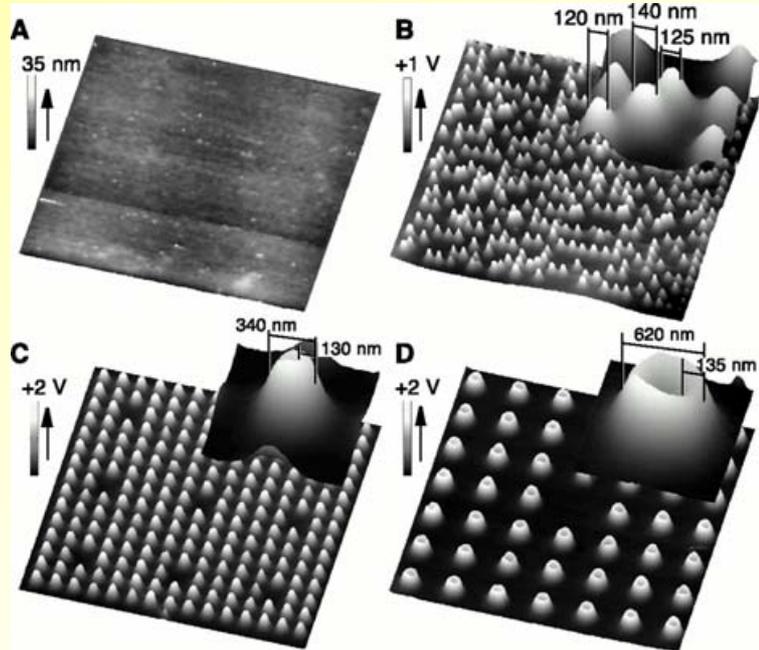
- ⇒ a) SEM image of fibronectin selectively adsorbed on a SAM-patterned gold surface
- ⇒ b) SEM image of patterned microstructure fabricated with printed SAMs as templates: CuSO_4 particles (arrow) formed by selective dewetting and crystallization

← Table of Contents, Slide 24

Soft lithography



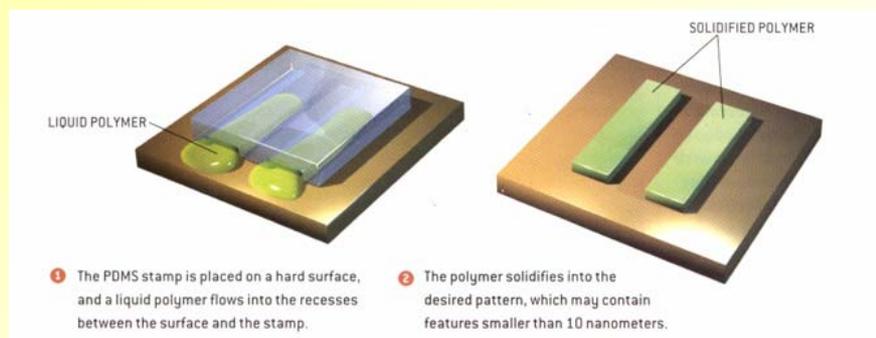
❖ Electrical microcontact printing



Soft lithography

❖ Micromolding in capillaries

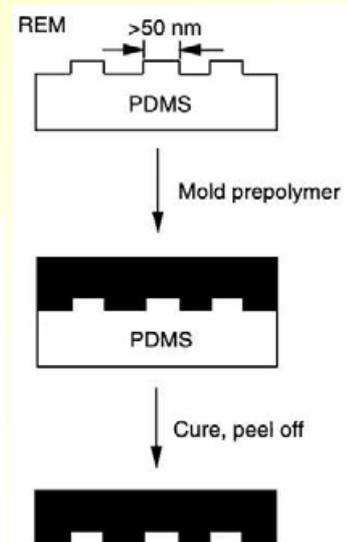
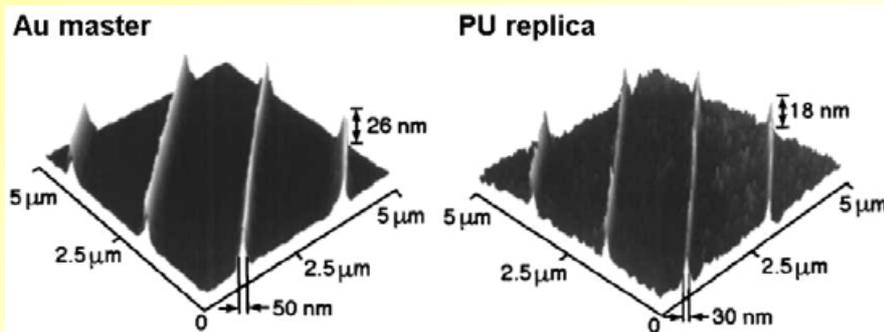
- ⇒ low-viscosity prepolymer is placed at the open ends of the channels formed by PDMS stamp → liquid spontaneously fills the channels by capillary action
- ⇒ after curing the PDMS mold is removed to reveal patterned microstructures of the polymer



Soft lithography

❖ Replica molding

- ⇒ efficient method for the duplication of the shape and morphology from the mold surface
- ⇒ allows duplication of 3D topologies in a single step
- ⇒ reliability of this process determined by wetting and filling of the mold.



← Table of Contents, Slide 27

Soft lithography - related methods

❖ Rigid stamp → structures with multiple layers

❖ Step-and-flash imprint lithography

- ⇒ quartz master is used as stamp
- ⇒ master is pressed against a thin liquid polymer film, which fills the master's recesses
- ⇒ polymer cured with UV light
- ⇒ about 60 nm features has been produced

❖ Nanoimprint lithography

- ⇒ embossing process is facilitated by a film of polymer that is heated above T_g
- ⇒ 6 nm features has been produced
- ⇒ non-flat surfaces has been printed

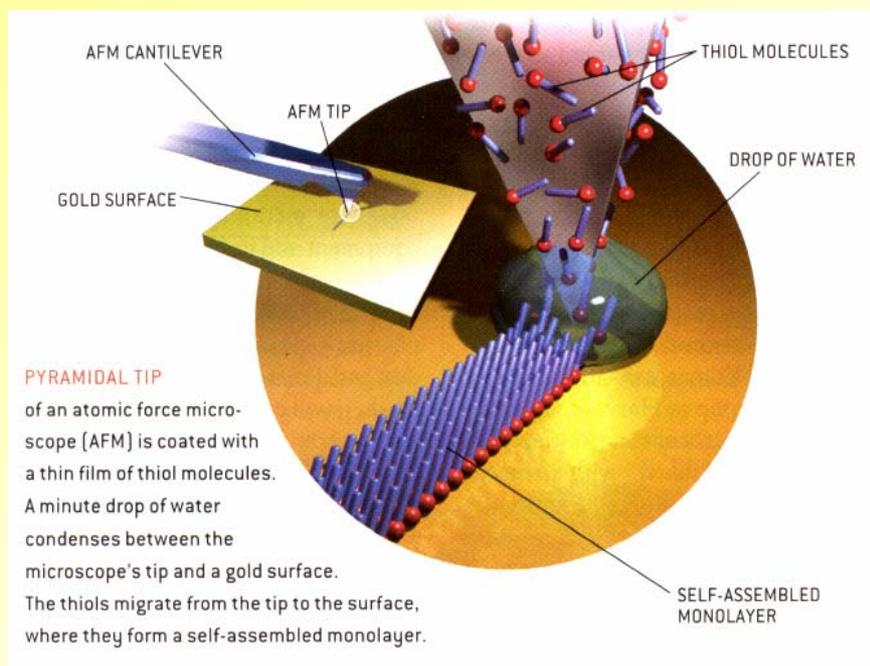
← Table of Contents, Slide 28

Scanning probe methods

- ❖ Promising and really versatile area
 - ⇒ maybe too slow for mass production
- ❖ Few examples:
 - ⇒ Dip-pen nanolithography
 - ⇒ Assembly tool for molecular structures
 - ⇒ STM nanofabrication of electronic industry compatible thermal silicon oxide
 - ⇒ Semiconducting Nanostructures Patterned by AFM
 - ⇒ Positioning single atoms with STM
 - ⇒ Positioning nanoparticles with AFM
 - ⇒ Single-Bond Formation and Characterization with a STM

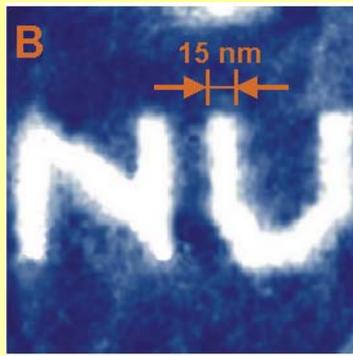
← Table of Contents, Slide 29

Dip-pen nanolithography

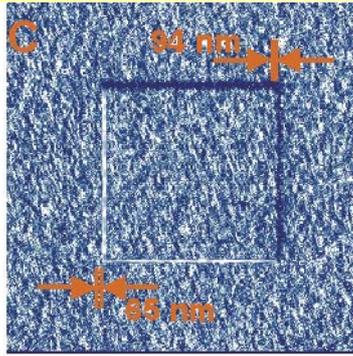


← Table of Contents, Slide 30

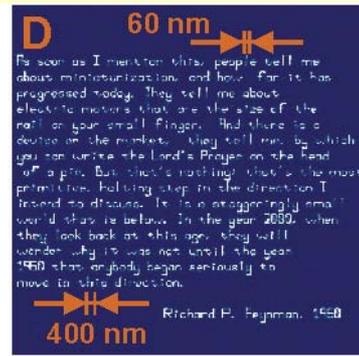
Dip-pen nanolithography



0 nm 180

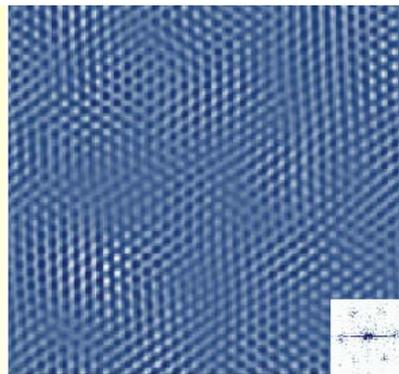


0 μm 8



Richard P. Feynman, 1959

- B) Ultra-high resolution pattern on gold surface
- C) Two aligned alkanethiol patterns
- D) Feynmann's speech written using the DPN nanoplottter

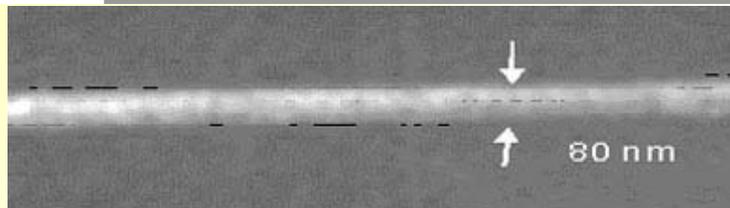
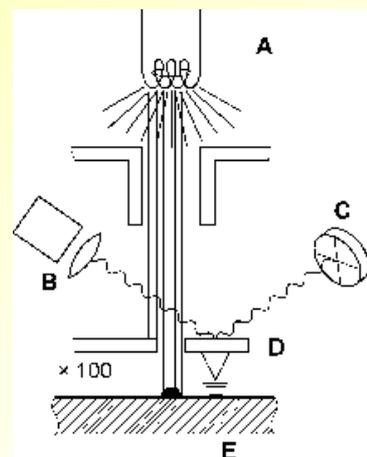
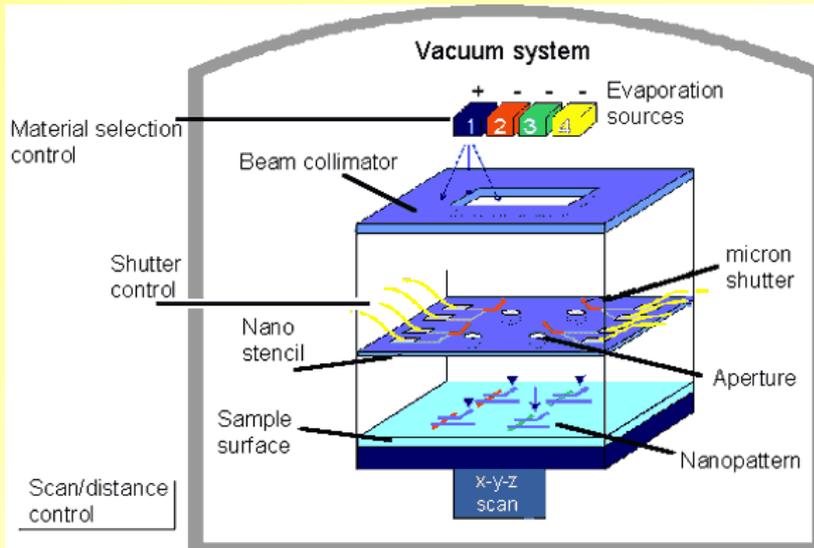


0 nm 15

Lattice-resolved monolayer of octadecanethiol patterned on gold

← Table of Contents, Slide 31

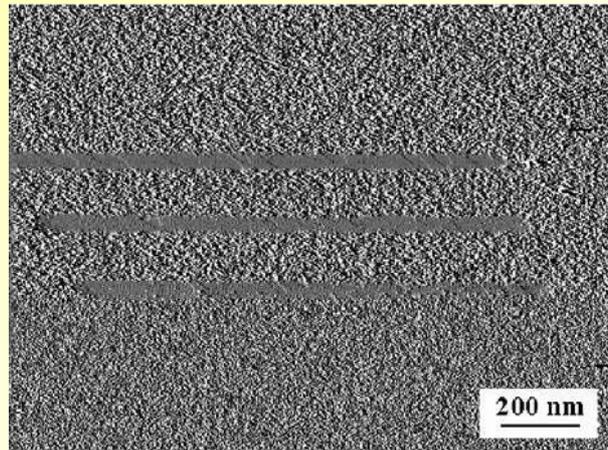
Assembly tool for molecular structures



← Table of Contents, Slide 32

STM nanofabrication of electronic industry compatible thermal Si oxide

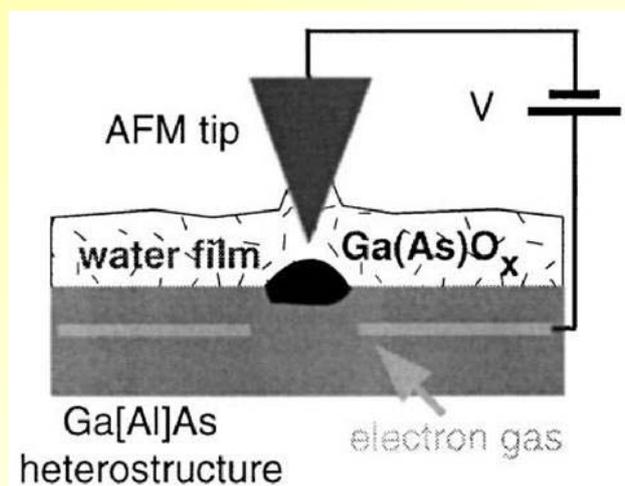
- ❖ In the field emission mode a low-energy electron beam can be extracted from the STM tip
- ❖ By irradiating the electron beam to the surface of a Si oxide layer reaction can be stimulated and windows can be cut through the oxide layer.



← Table of Contents, Slide 33

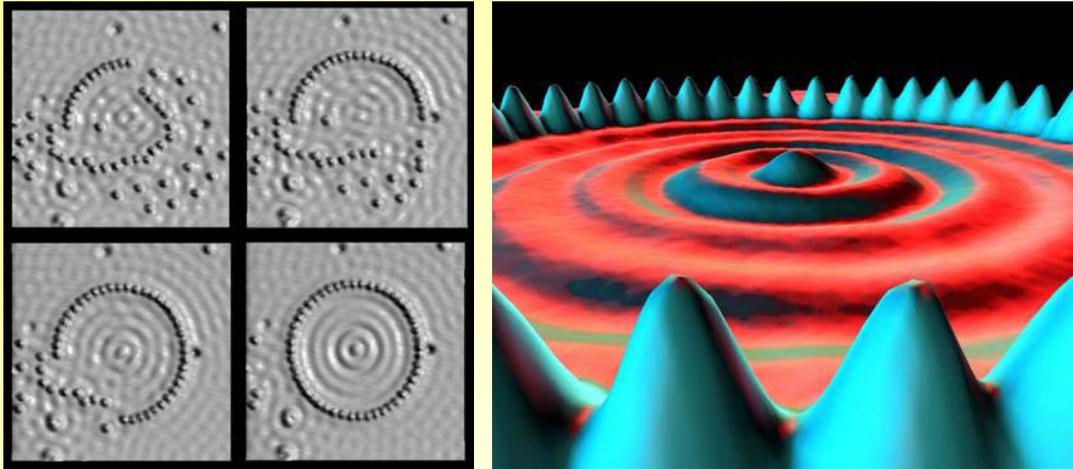
Semiconducting Nanostructures Patterned by AFM

- ❖ Tunable nanostructures can be patterned in Ga[Al]As heterostructures with AFM
 - ⇒ oxidizing the GaAs cap layer locally by applying a voltage to the AFM tip leads to depletion of the electron gas underneath the oxide.



← Table of Contents, Slide 34

Positioning single atoms with STM

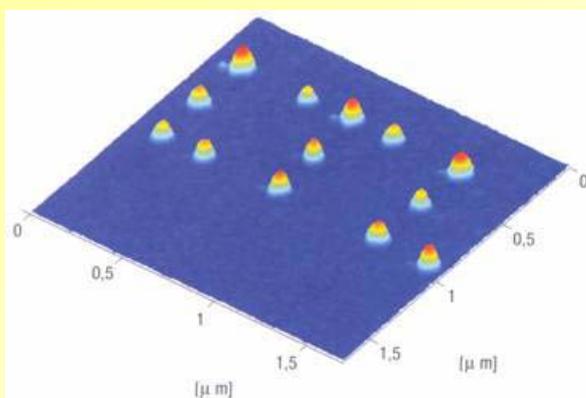


- ❖ STM tip can pull an atom across a surface while the atom remains bound to it
- ❖ 48 iron atoms on copper surface positioned into a circular ring in order to "corral" some surface state electrons and force them into "quantum" states of the circular structure

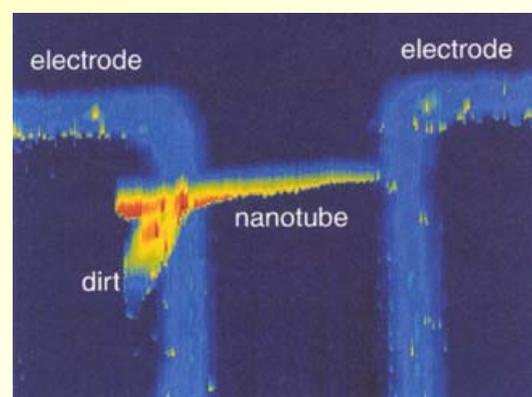
← Table of Contents, Slide 35

Positioning nanoparticles with AFM

- ❖ AFM based method to move metallic nanoparticles and nanotubes with the AFM tip (HUT)
 - ⇒ NC-AFM is used to monitor particles during the procedure



45 nm silver particles moved by AFM tip

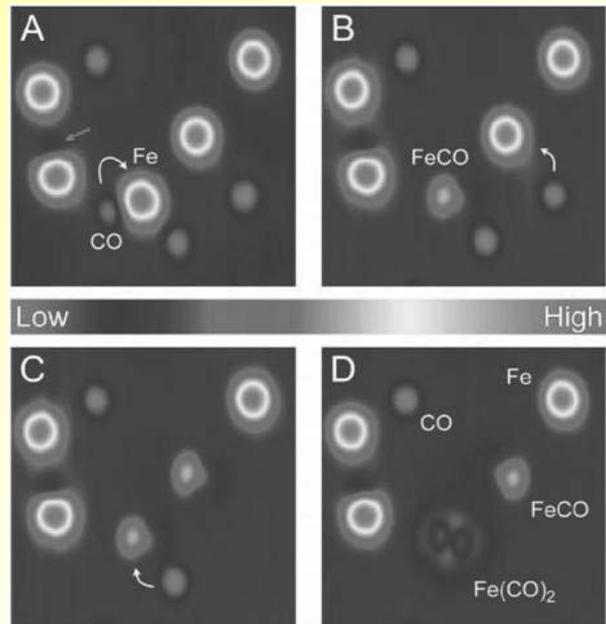


Electrical testing configuration of single electron transistor made out of a nanotube

← Table of Contents, Slide 36

Single-Bond Formation and Characterization with a STM

- ❖ STM tip can be used to deliver CO molecules one at a time to an Fe atom, forming $\text{Fe}(\text{CO})$, then $\text{Fe}(\text{CO})_2$
- ❖ STM was used to form chemical bonds, to image reactants and products, and to measure single-molecule vibration spectra

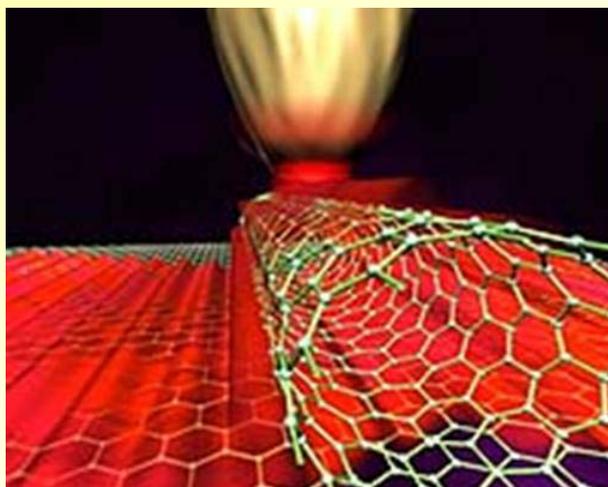


Fe and CO on Ag surface (scan size 6.7 nm x 6.7 nm)

← Table of Contents, Slide 37

Bottom-up methods

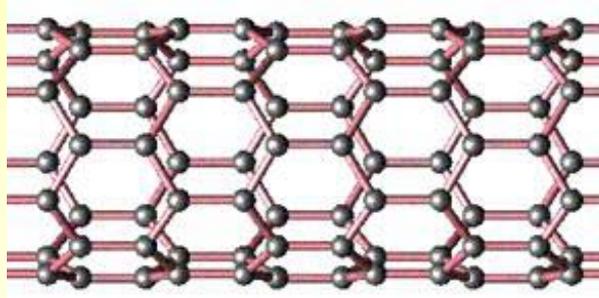
- ❖ Hard to draw a line between top-down and bottom-up methods
- ❖ Two most prominent bottom up methods:
 - ⇒ nanotubes
 - ⇒ quantum dots



← Table of Contents, Slide 38

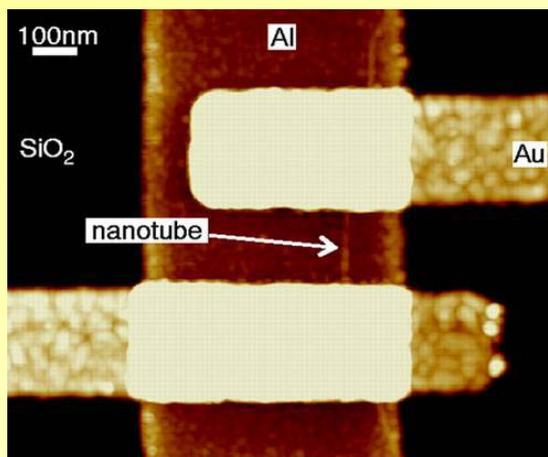
Nanotubes

- ❖ Single-wall fullerene nanotubes (SWNT) are produced by condensation of a laser-vaporized carbon/Ni/Co mixture at 1200°C
- ❖ Carbon nanotubes hold promise as basic components for nanoelectronics
 - ⇒ conductors, semiconductors and insulators
- ❖ Variations of carbon nanotubes using B, C, and N should provide interesting building blocks and phenomena for nanoscience and nanotechnology

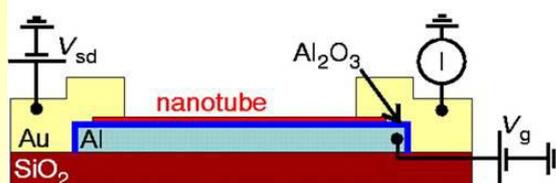


← Table of Contents, Slide 39

Logic Circuits with Carbon Nanotube Transistors



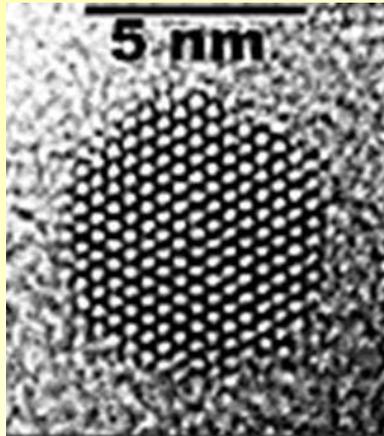
- ❖ Semiconducting nanotube is contacted by two Au electrodes
- ❖ An Al wire, covered by a few nanometers thick oxide layer, is used as a gate



← Table of Contents, Slide 40

Quantum dots

- ❖ Nanometer-scale particles that are neither small molecules nor bulk solids
- ❖ Their composition and small size give these dots extraordinary optical properties that can be readily customized by changing the size or composition of the dots
- ❖ Quantum dots absorb light, then quickly re-emit the light but in a different color



TEM image shows the crystalline arrangement of atoms in a 5 nm CdSe quantum dot particle

← Table of Contents, Slide 41

Summary

Nanofabrication: Comparing the Methods

Researchers are developing an array of techniques for building structures smaller than 100 nanometers. Here is a summary of the advantages and disadvantages of four methods.

Photolithography

Advantages: The electronics industry is already familiar with this technology because it is currently used to fabricate microchips. Manufacturers can modify the technique to produce nanometer-scale structures by employing electron beams, x-rays or extreme ultraviolet light.

Disadvantages: The necessary modifications will be expensive and technically difficult. Using electron beams to fashion structures is costly and slow. X-rays and extreme ultraviolet light can damage the equipment used in the process.

Scanning Probe Methods

Advantages: The scanning tunneling microscope and the atomic force microscope can be used to move individual nanoparticles and arrange them in patterns. The instruments can build rings and wires that are only one atom wide.

Disadvantages: The methods are too slow for mass production. Applications of the microscopes will probably be limited to the fabrication of specialized devices.

Soft Lithography

Advantages: This method allows researchers to inexpensively reproduce patterns created by electron-beam lithography or other related techniques. Soft lithography requires no special equipment and can be carried out by hand in an ordinary laboratory.

Disadvantages: The technique is not ideal for manufacturing the multilayered structures of electronic devices. Researchers are trying to overcome this drawback, but it remains to be seen whether these efforts will be successful.

Bottom-Up Methods

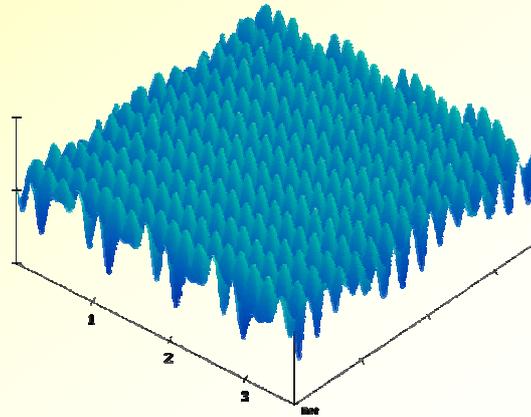
Advantages: By setting up carefully controlled chemical reactions, researchers can cheaply and easily assemble atoms and molecules into the smallest nanostructures, with dimensions between two and 10 nanometers.

Disadvantages: Because these methods cannot produce designed, interconnected patterns, they are not well suited for building electronic devices such as microchips.

← Table of Contents, Slide 42



Scanning probe microscopy in nanotechnology



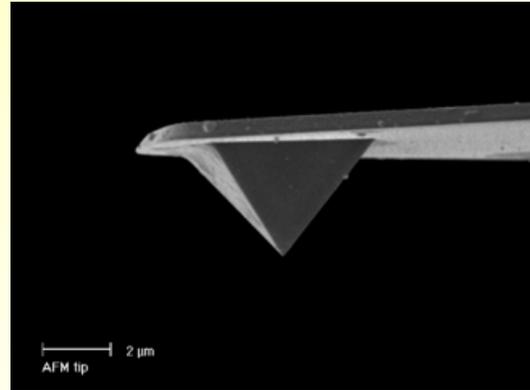
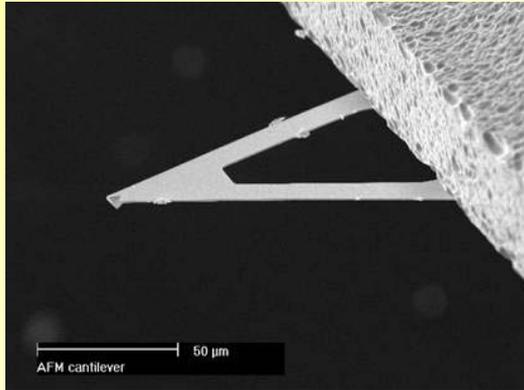
Scanning probe microscopy in nanotechnology

- ❖ Scanning probe microscopes are basic tools in nanotechnology
 - ⇒ huge amount of various applications in this area
 - ⇒ some examples: peek of the possibilities of SPMs
- ❖ Principle of AFM and STM
- ❖ Other SPM techniques
 - ⇒ lateral force microscopy (LFM)
 - ⇒ force modulation microscopy (FMM)
 - ⇒ phase detection microscopy (PDM)
 - ⇒ magnetic force microscopy (MFM)
 - ⇒ electrostatic force microscopy (EFM)



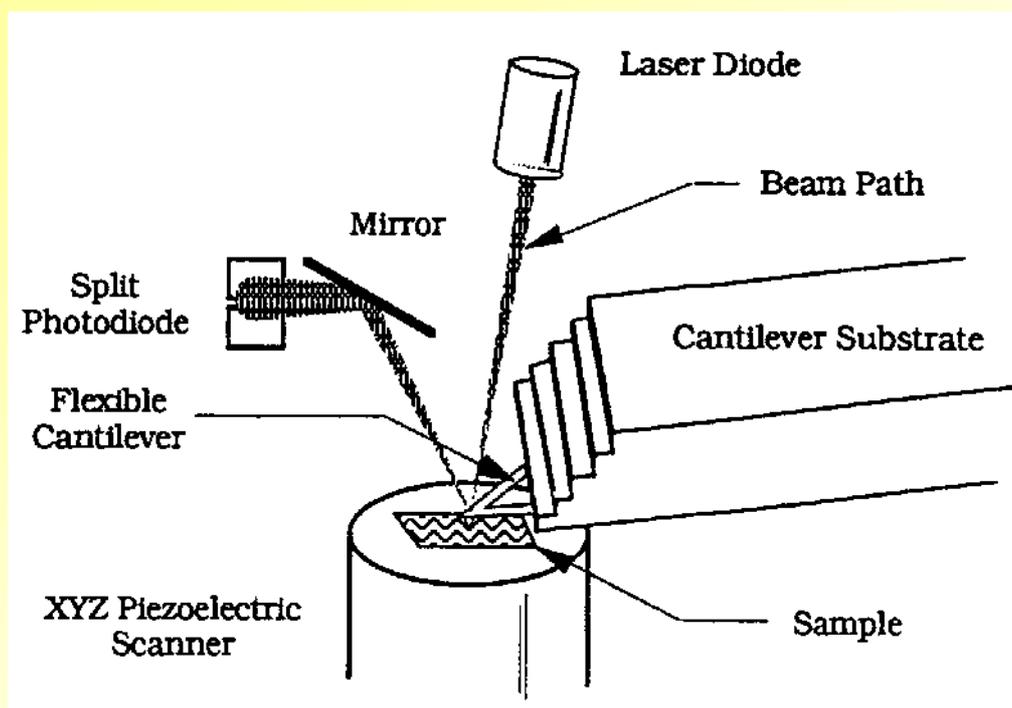
Atomic force microscopy, AFM

- ❖ The surface of the sample is scanned by a very sharp tip, which is attached to the end of the flexible cantilever
 - ⇒ cantilever bends due to forces between the tip and the surface of the sample
 - ⇒ sample or tip is moved by piezoelectric tube scanner



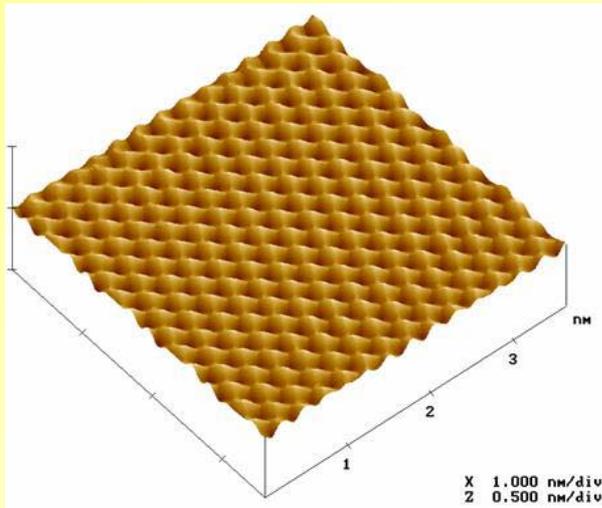
← Table of Contents, Slide 45

Atomic force microscopy, AFM



← Table of Contents, Slide 46

Scanning tunneling microscopy, STM



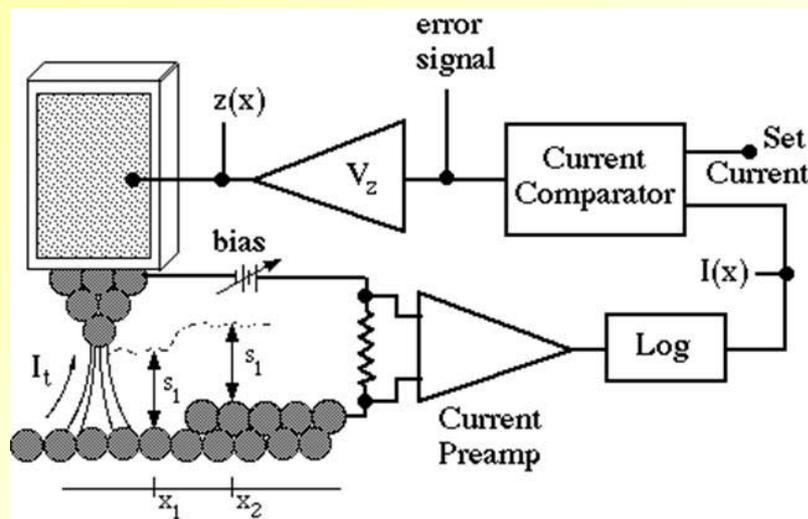
Graphite

- ❖ The first SPM
- ❖ Atomic resolution capability in 1981
- ❖ The tunneling current maps the electronic density of states at the surface
- ❖ Unlike AFM, cannot image insulating materials
- ❖ Scanning tunneling spectroscopy (STS) characterizes the local electronic structure of surface

← Table of Contents, Slide 47

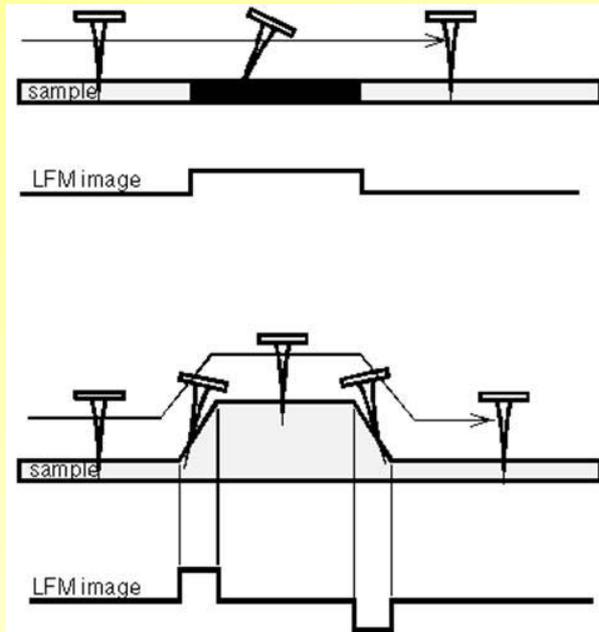
Scanning tunneling microscopy, STM

- ❖ Electrons from the sample begin to "tunnel" through the 1 nm gap into the tip
- ❖ Resulting tunneling current varies with tip-to-sample spacing → STM image



← Table of Contents, Slide 48

Lateral force microscopy, LFM

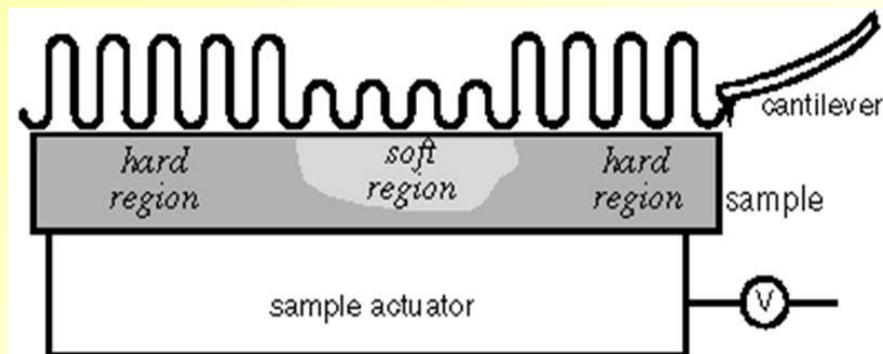


- ❖ Force acting on the tip parallel to the plane of the surface → twisting of the cantilever → lateral deflections
- ❖ Atomic scale images of lateral ('frictional') forces

← Table of Contents, Slide 49

Force modulation microscopy, FMM

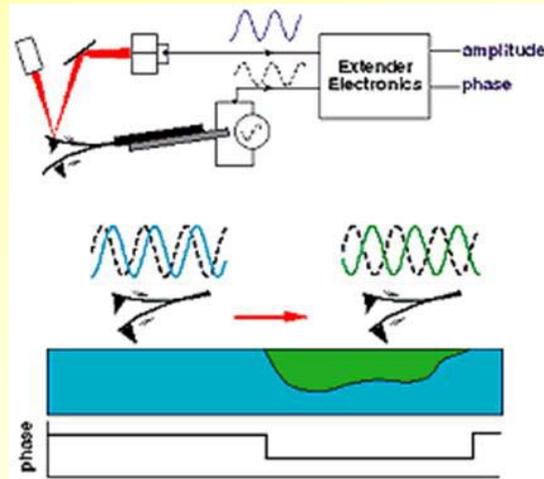
- ❖ Variations in the surface stiffness or elasticity initiate variations in cantilever deflection amplitude
- ❖ Differences in elasticity in the surface of the sample in contact-mode



← Table of Contents, Slide 50

Phase detection microscopy, PDM

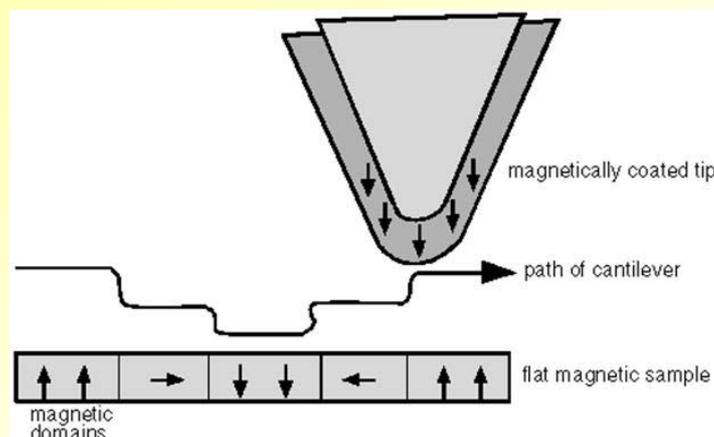
- ❖ System monitors the phase lag of the cantilever oscillation output signal relative to the signal that drives the cantilever to oscillate
 - ⇒ detects variations in composition, adhesion, friction and viscoelasticity



← Table of Contents, Slide 51

Magnetic force microscopy, MFM

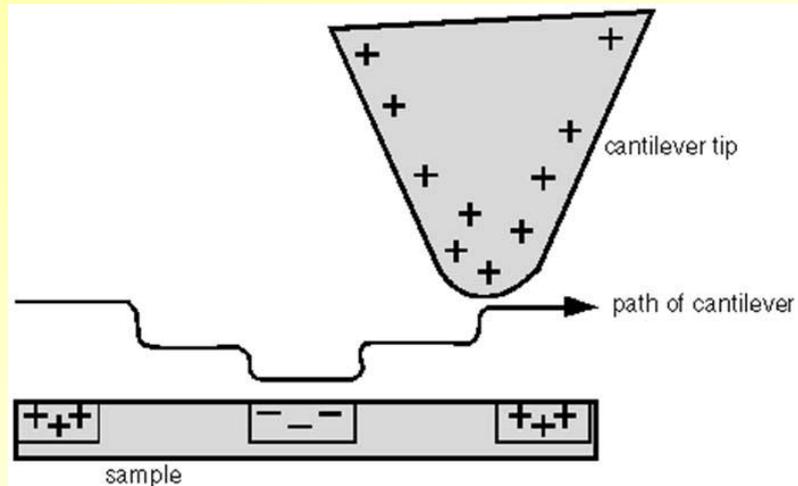
- ❖ Gradients in the magnetic forces on the tip induce changes in the resonant frequency of the cantilever
 - ⇒ images the stray magnetic fields on a sample surface



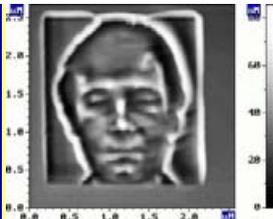
← Table of Contents, Slide 52

Electrostatic force microscopy

- ❖ Measures electric field gradient and distribution above the sample surface
 - ⇒ detection of charges as small as single electron

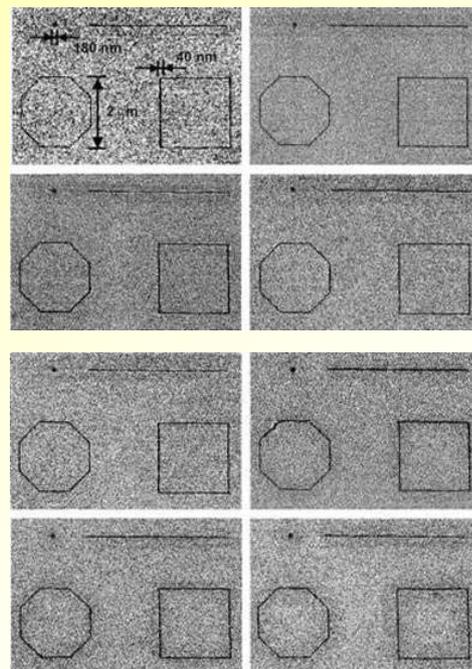


← Table of Contents, Slide 53



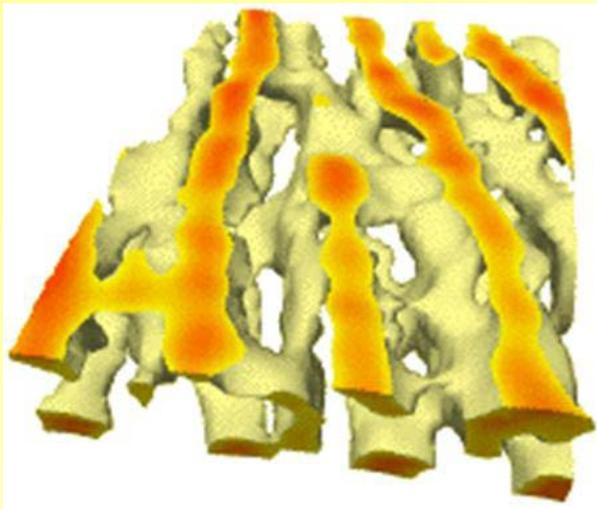
Nanolithography

- ❖ Surface is modified atom by atom
- ❖ Operated by applying either excessive force with an AFM or high-field pulses with an STM
- ❖ LFM images of nanolithography patterns, which were formed using an eight-pen nanoplotter capable of doing parallel dip-pen nanolithography



← Table of Contents, Slide 54

Nanotomography

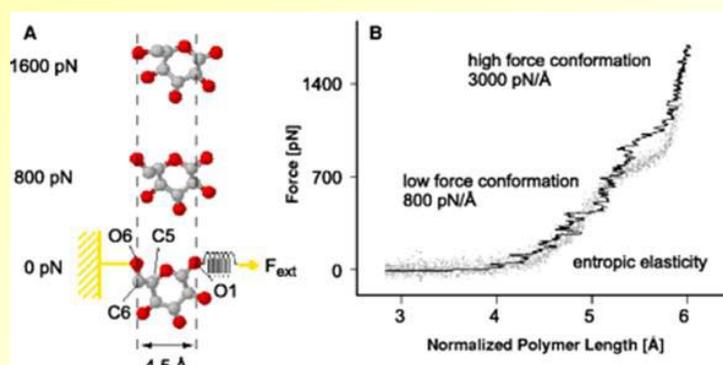


- ❖ Polymer surface first depicted by AFM and then repeated 13 times, shaving away a 7.5 nm layer of the sample with a beam of oxygen ions before each step
- ❖ From a series of images, the 3D distribution of polystyrene and polybutadiene was reconstructed

← Table of Contents, Slide 55

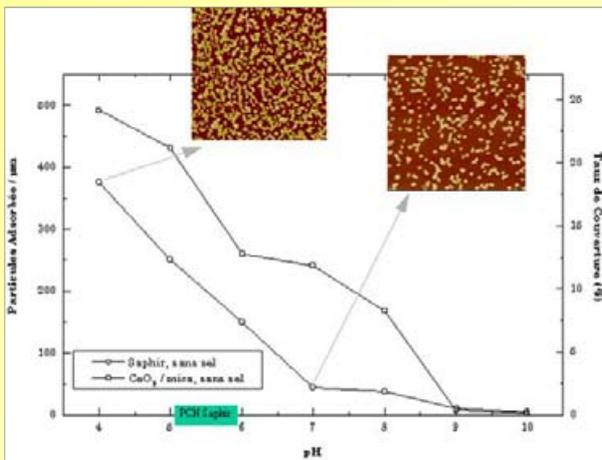
Single molecule force spectroscopy on polysaccharides by AFM

- ❖ Recent developments in piconewton instrumentation allow the manipulation of single molecules and measurements of intermolecular as well as intramolecular forces
- ❖ Dextran filaments linked to a gold surface were probed with the AFM tip by vertical stretching



← Table of Contents, Slide 56

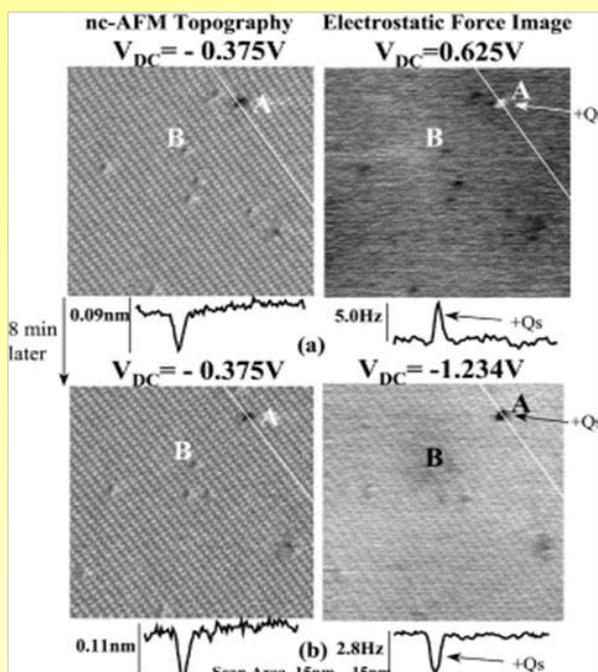
Adhesion of nanolatex on mineral surfaces



- ❖ The coating of mineral particles with anionic nanolatex improves their dispersion in concentrated regimes → homogeneous coatings
- ❖ Characterization the structure of the adsorbed layer of nanolatex (\varnothing 25 nm) and the interactions between two layers.
- ❖ Figure presents the pH dependence of the amount of nanolatex adsorbed on two mineral substrates.

← Table of Contents, Slide 57

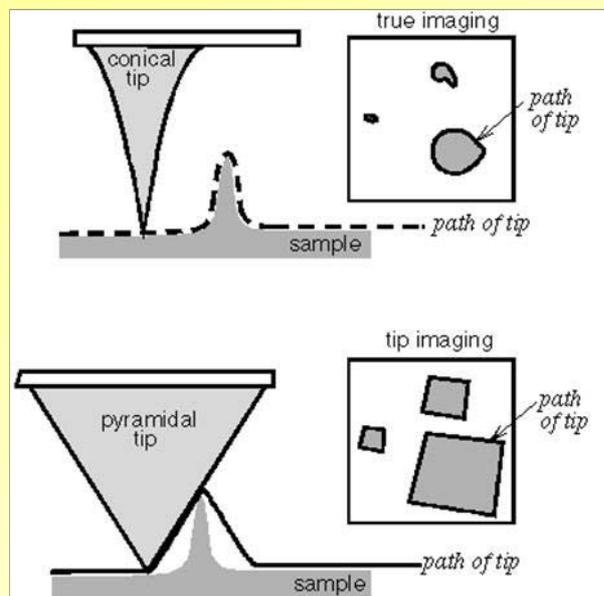
Atomic Scale EFM Study of GaAs Surfaces



- ❖ Point charges on n^+ -GaAs(110) cleaved surfaces imaged by a modified non-contact UHV-AFM with an EFM function
- ❖ This method enables the investigation of the charge-related phenomena on an electron-by-electron and ion-by-ion basis

← Table of Contents, Slide 58

Image artifacts



- ❖ Important to remember the influence of the tip geometry on the image
- ❖ Tip convolution could be decreased by using conical tip instead of pyramidal tip

Comparison between true imaging and tip imaging

← Table of Contents, Slide 59

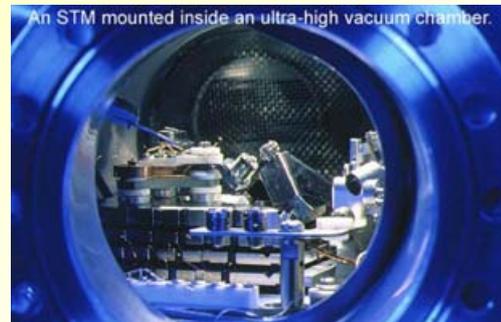
Summary

- ❖ Work in this research area encompasses novel applications of scanning probe methods and related techniques with which one can manipulate individual atoms and molecules to construct nanometer-sized structures
- ❖ Increasing efforts have been dedicated to the development of sensors for chemical and biological interactions, stress, magnetization, etc. in extremely minute amounts of materials as well as into the development of such SPM techniques as microscopy based on chemical interactions, nuclear magnetic resonance or dynamic forces.

← Table of Contents, Slide 60



Nanomanipulation



Nanomanipulation

- ❖ Nanomanipulation: The process of manipulating items at an atomic or molecular scale in order to produce precise structures.
- ❖ The gap between the top-down strategy and bottom-up strategy to build NEMS (nanometer-sized electromechanical structures) and MEMS (microelectromechanical systems) is gradually reduced.
 - ⇒ Powerful tools to manipulate nanometer-sized objects are emerging
- ❖ Nanomanipulator serves:
 - ⇒ As a prototype for manufacturing device of NEMS
 - ⇒ As a significant tool for investigating the mesoscopic phenomena occurring in the nano world

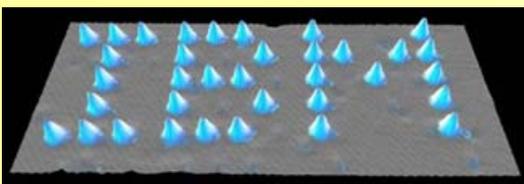


Demands

- ❖ We are entering the new stage to build NEMS and MEMS based on the nanotechnology.
- ❖ Innovative strategies required at present are summarized as follows:
 - ⇒ Downsizing of the component: Micro to Nano
 - ⇒ Higher precision of machining accuracy
 - ⇒ 3D manipulation and assembly technique
 - ⇒ Method and theory to overcome difference between the model and practice
 - ⇒ Nano-structured and functional materials
 - ⇒ Utilization of the self-organization phenomenon
- ❖ Among them, the 3D manipulation and assembly technique and theory to explore the nano world will play an important role in near future.

← Table of Contents, Slide 63

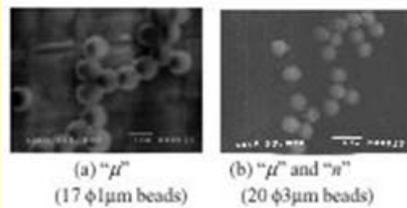
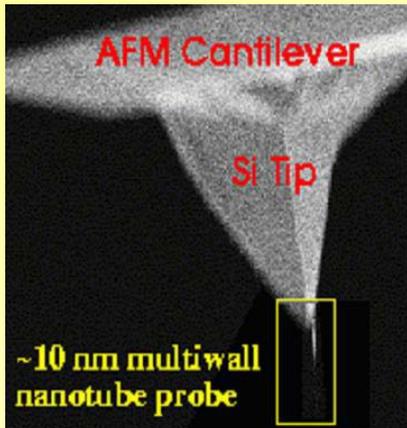
Background of Nanomanipulation



- ❖ Difficulties of exploring the nano world:
 - ⇒ Theoretically, nano systems are in a size regime about whose fundamental behavior we have little understanding.
 - ⇒ Experimentally, the particles are too small for direct measurements.
- ❖ First practice on nanomanipulation was performed by Eigler and Schweizer at IBM
- ❖ Since that, more researchers have used STM or other versions of nanomanipulators to create letters, pictures, etc, on surfaces one atom at a time

← Table of Contents, Slide 64

Strategies for Nanomanipulation: Contact Manipulation



- ❖ Two types of contact Manipulation:
 - ⇒ Mechanically Contact Manipulation
 - Pushing or pulling nanometer objects on a surface with an AFM cantilever is a typical manipulation using this method
 - ⇒ Contact Manipulation by Controlling Intermolecular and/or Surface Forces.

← Table of Contents, Slide 65

Strategies for Nanomanipulation: Non-Contact Manipulation

- ❖ Presently, relative large nanometer scale particles and molecules are generally manipulated with contact way.
- ❖ However, for atom or small molecules, non-contact manipulation is preferred.
- ❖ Other cases to apply non-contact manipulations include in liquid environment, bio-samples or other objects that are not suitable or impossible to be attached in order to avoid destructive.
- ❖ Two ways are leading among others:
 - ⇒ STM or non-tapping SPM (electrostatic or magnetic field forces are applied)
 - ⇒ Laser trapping (optical pressure is used)

← Table of Contents, Slide 66

Nanomanipulation Systems: Tools



(IBM)

← Table of Contents, Slide 67

- ❖ Vision tools:
 - ⇒ Scanning tunneling microscope (STM)
 - ⇒ Atomic force microscope (AFM)
 - ⇒ Scanning Probe Microscopes.
 - ⇒ Optical Techniques: Optical techniques are continuously developing, for example recently the use of interferometry
- ❖ other tools and techniques that operate on the nanoscale
 - ⇒ nuclear magnetic resonance
 - ⇒ molecular beam epitaxy
 - ⇒ laser tweezers (laser beams are used to hold and manipulate molecules)
- ❖ Computer Modeling



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Control Engineering Laboratory

Nanomanipulation Systems

- ❖ Manipulators (Positioning Devices)
 - ⇒ There are mainly two families of nanomanipulators: SPM (including STM, AFM, and other type SPMs), and robotic type.
- ❖ SPM Nanomanipulators
 - ⇒ After they were invented, STM and AFM or other type local probe microscopes had also been used as positioning devices.
 - ⇒ The advantages of this family are their incomparable resolution (tenths of an angstrom) for 3-D surface topology observation.
 - ⇒ However, for truly three-dimensional manipulation, they have not yet proven very useful.
- ❖ Nanorobotic Manipulators
 - ⇒ It is much significant to manipulate nano scale objects in 3-D space for constructing nano structures and devices.
 - ⇒ This kind of manipulators need microscopes as the real time observation systems.

← Table of Contents, Slide 68



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Control Engineering Laboratory

Nanomanipulation Systems

- ❖ Microscopes (Sensing Systems)
 - ⇒ The recent rapid advances in nanomanipulation are due in large part to the development of microscopes.
 - ⇒ Scanning probes, optical tweezers, high-resolution electron microscopes, or other new tools, now permit to create new structures, measure new phenomena, and explore new applications.
- ❖ Control Systems
 - ⇒ Since the lack of knowledge about micro/nano world, telemanipulation based on master-slave way is still the only method for control the manipulators.
- ❖ Human-Machine Interface
 - ⇒ Providing a virtual-environment interface to a SPM gives the virtual telepresence on the surface.

 [Table of Contents, Slide 69](#)

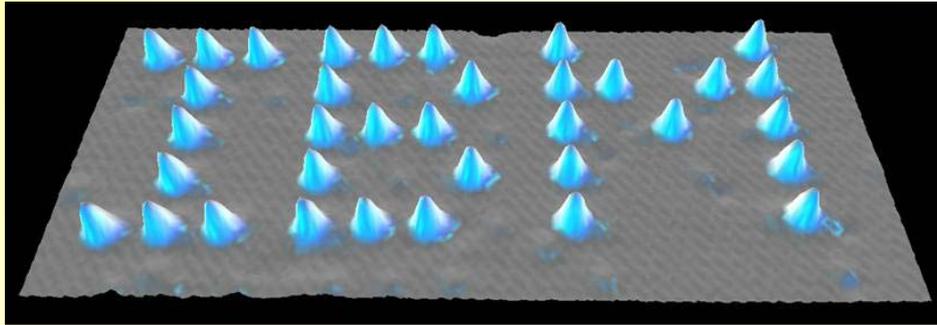
Nanomanipulation Applications

- ❖ Assembly and modification of several kinds of molecules have been tried. Fabrication of simple nanometer scale structures and even mechanism has also been achieved.
- ❖ Nanomanipulation may find application in many other fields:
 - ⇒ Molecular biotechnology: DNA exploring, gene explanation, protein manipulation, etc.
 - ⇒ Material science
 - ⇒ Information technology: Memory storage, nanometer scale IC fabrication, etc.
 - ⇒ Chemistry: Catalysis understanding, mesoscopic chemistry, etc.
 - ⇒ Medicine: Nanomedical robot

 [Table of Contents, Slide 70](#)

Positioning single atoms with STM

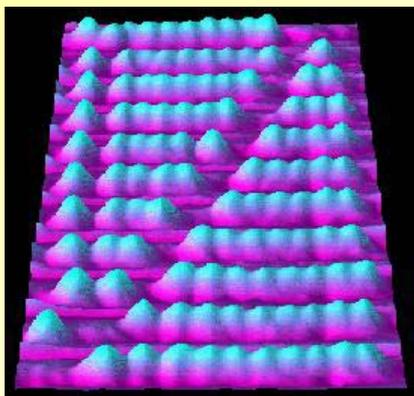
- ❖ The magnitude and direction of the force, which the STM tip exerts on an adsorbate atom, may be tuned by adjusting the position and voltage of the tip → positioning single atoms
- ❖ Individual xenon atoms on a single-crystal nickel surface positioned by UHV STM at 4 K



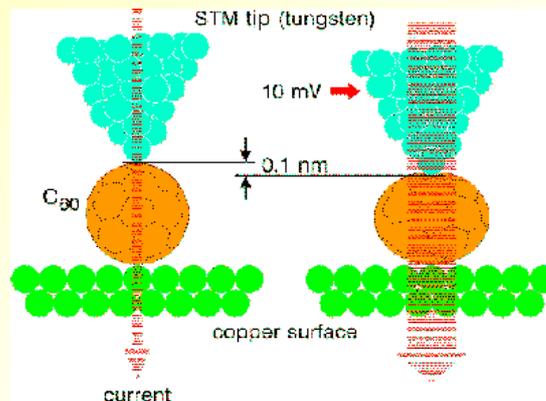
← Table of Contents, Slide 71

The world's smallest abacus and a molecular amplifier

- ❖ Individual fullerene molecules are approached by the STM tip and pushed back and forth
- ❖ Electrical conductance of fullerene molecules can be changed continuously and reversibly by applying a mechanical force to a single molecule



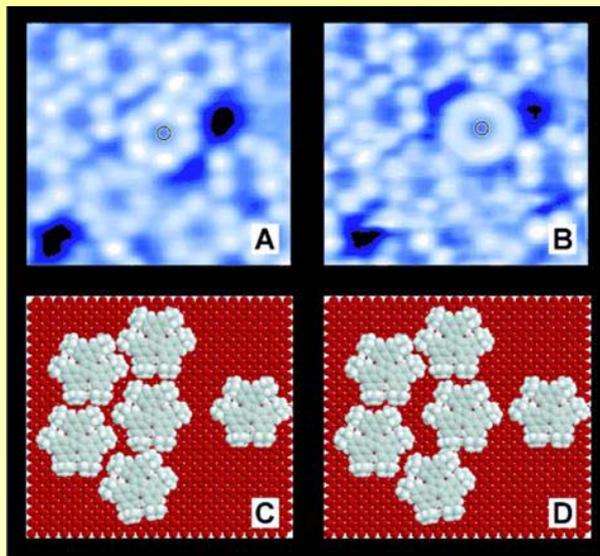
The world's smallest abacus



A molecular amplifier

← Table of Contents, Slide 72

Rotation of a single molecule within a supramolecular bearing

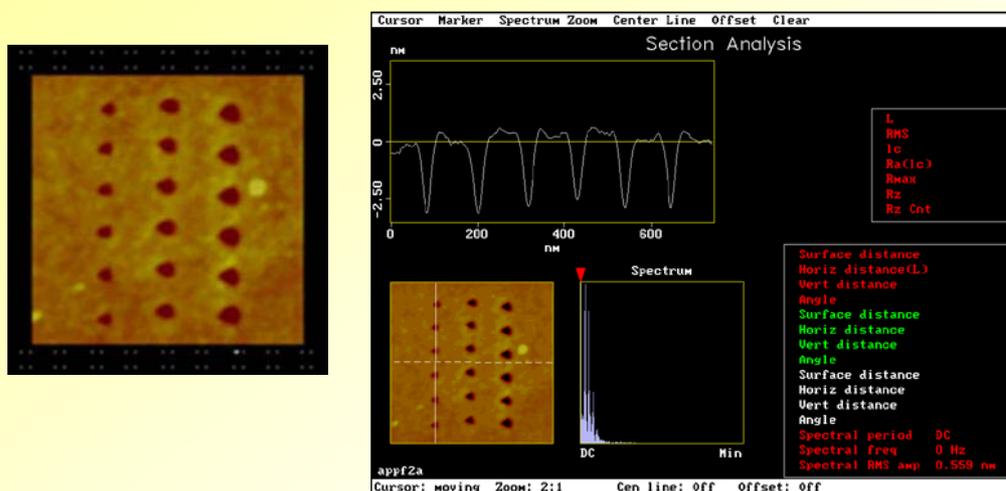


- ❖ Evidence of high-speed rotation of single molecules, driven by thermal energy at room temperature was obtained by STM
 - ⇒ A) molecule immobilized at a high-symmetry site defined by the surrounding molecules
 - ⇒ B) molecule is imaged as a torus, indicating rotation
 - ⇒ C, D) snapshots of the molecular mechanical simulations based on the molecular coordinates taken from the STM data

← Table of Contents, Slide 73

Nanoindenting, scratching and wear testing by SPM

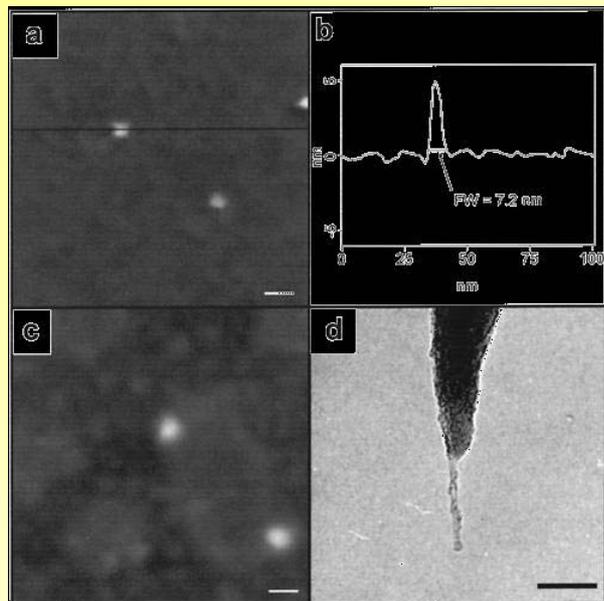
- ❖ Using a diamond tip mounted to a metal-foil cantilever, it is possible to indent a surface and immediately image the indentation and even to perform scratch and wear tests using the same cantilevers



15 nm thick diamond-like carbon film indented 6 times with 3 forces

← Table of Contents, Slide 74

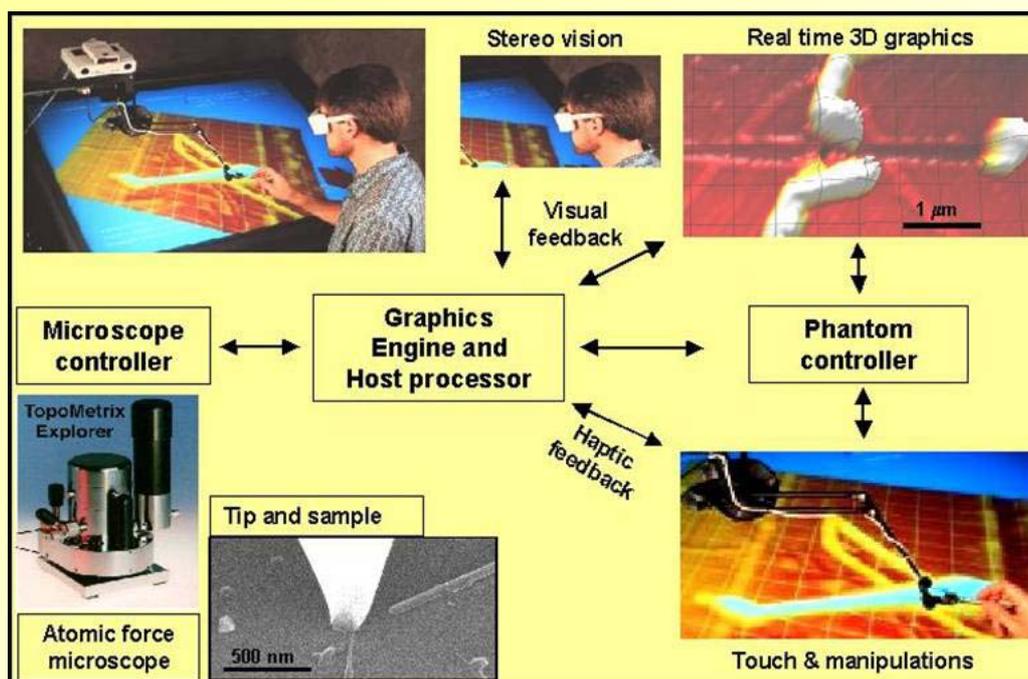
Nanotubes as Nanoprobes in SPM



- ❖ One of most promising applications of carbon nanotubes is the use of nanoprobes in SPM
 - ⇒ a) Tapping mode AFM image of 5.2 nm gold colloids recorded in air. (scale bar 10 nm)
 - ⇒ b) A cross section from (a) demonstrates that the full width of the colloid is 7.2 nm
 - ⇒ c) AFM image of 5.2 nm gold colloids recorded in water
 - ⇒ d) TEM image of a glued nanotube tip capable of being used in fluid imaging (scale bar 25 nm)

← Table of Contents, Slide 75

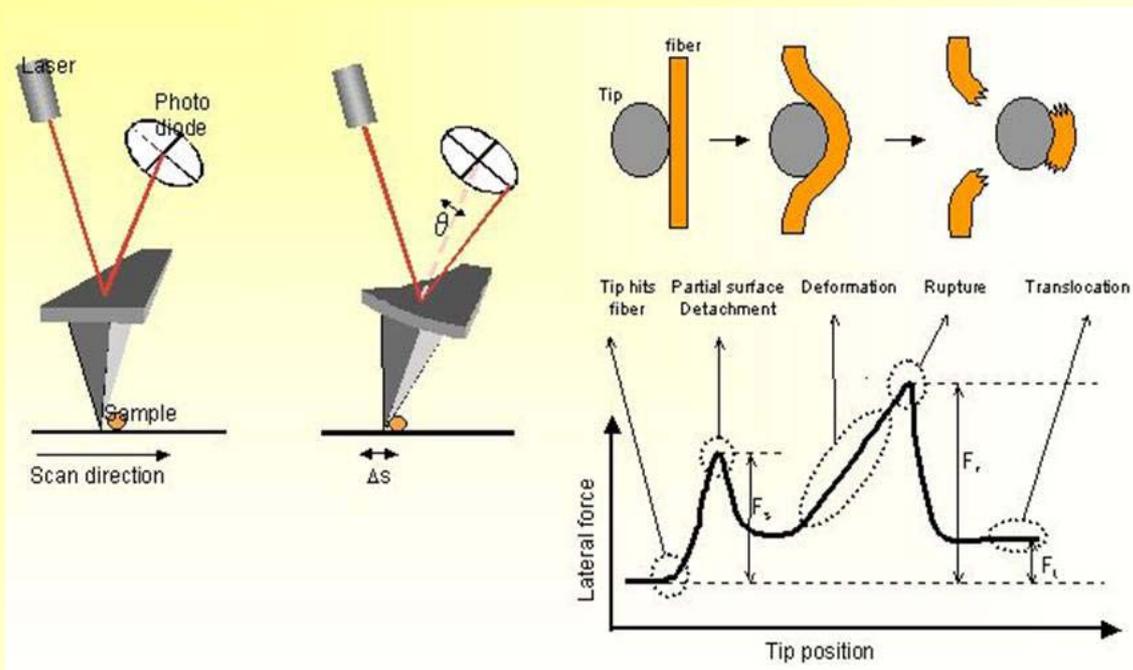
NanoManipulation of Individual Fibrin Fibers University of North Carolina



← Table of Contents, Slide 76

NanoManipulation of Individual Fibrin Fibers

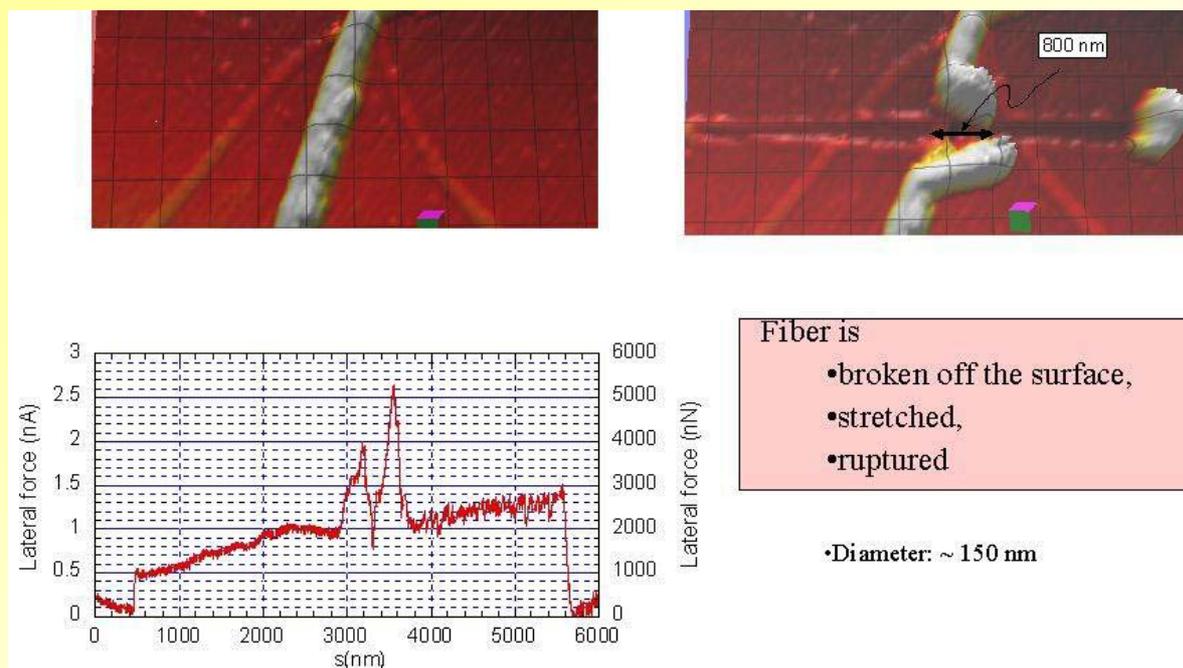
Lateral Force Measurement



← Table of Contents, Slide 77

NanoManipulation of Individual Fibrin Fibers

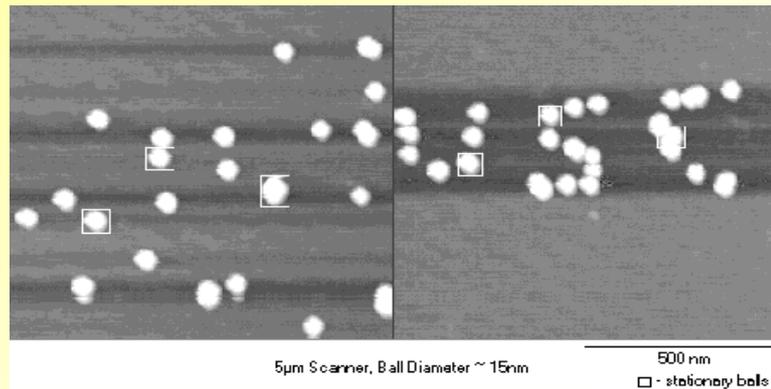
Manipulation of Fibrin



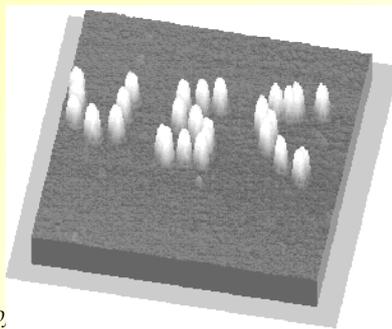
← Table of Contents, Slide 78

Nanomanipulation with the SPM

- ❖ Done by Becker and co-workers at Bell Labs, who managed to create nanometer-scale germanium structures on a germanium surface by raising the voltage bias of an STM tip.



The initial pattern of 15 nm Au balls (left) and the "USC" pattern obtained by nanomanipulation (right).

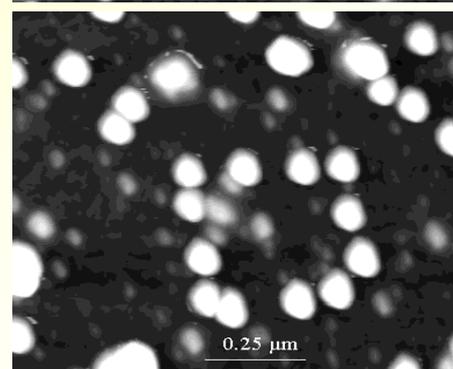
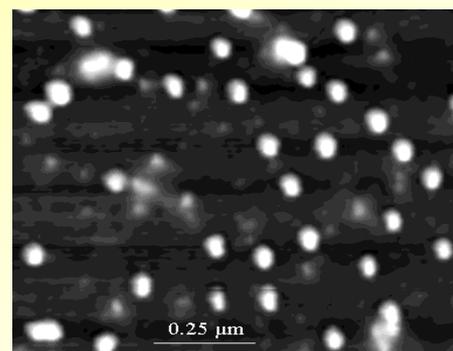


The "USC" pattern viewed in perspective

← Table of Contents

Nanomanipulation on Silicon

- ❖ The images demonstrate an attempt of positioning colloidal Au particles on a Si substrate.
- ❖ The first image shows the initial (and random) arrangement of the particles.
- ❖ The final square arrangement shown on the second was produced by pushing the Au nanoparticles with the AFM tip.



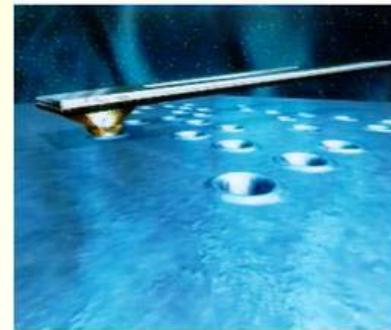
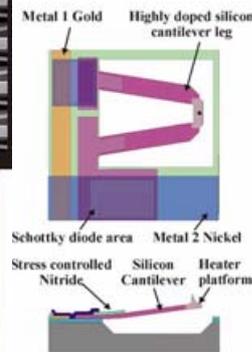
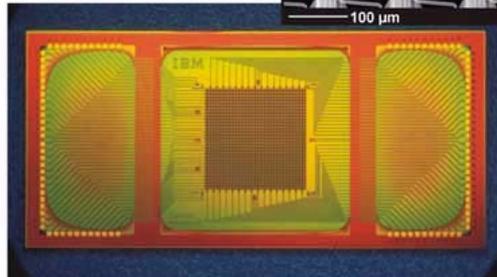
← Table of Contents, Slide 80

Thermal Chemical Storage

Fabricated "MILLIPEDE" Chip

Integration in a $7 \times 14 \text{ mm}^2$ chip size of:

- An array of 32×32 (1024) Cantilever
- Approaching, leveling sensors (4)
- Thermal sensors (4)
- Heaters



Stored bits: indentations at a "pitch" (distance between centers of neighboring indentations) as high as 40 nm, leading to areal density of ca. 400 gigabits per square inch.

← Table of Contents, Slide 81

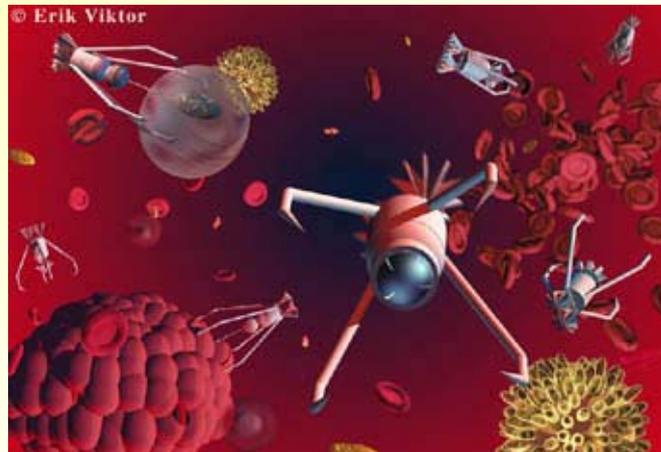
Summary

- ❖ Nanomanipulation provides a unique pathway to micro and nanomanufacturing that is unobtainable otherwise.
- ❖ There are two main types, that depend on the objects, the environment and the observation devices:
 - ⇒ Contact manipulation
 - ⇒ Non-contact manipulation
- ❖ A typical nanomanipulation is composed of:
 - ⇒ A manipulator(s) for positioning the end-effector(s)
 - ⇒ A sensing system and/or a measurement system to facilitate the manipulation and determine the properties of the object.
 - ⇒ A user-friendly human-machine interface is also desired.
- ❖ Applications of nanomanipulation include many fields such as physics, chemistry, biotechnology among others.

← Table of Contents, Slide 82



Nanomedicine



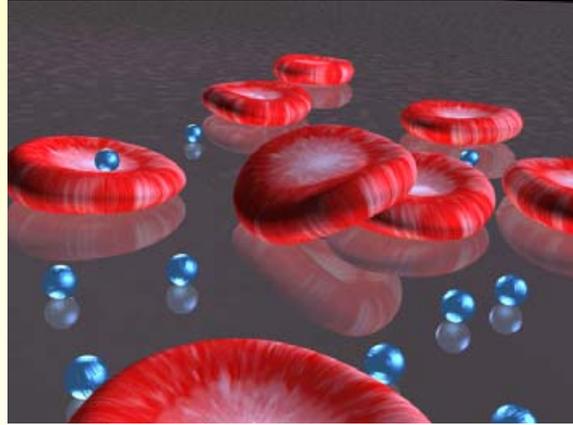
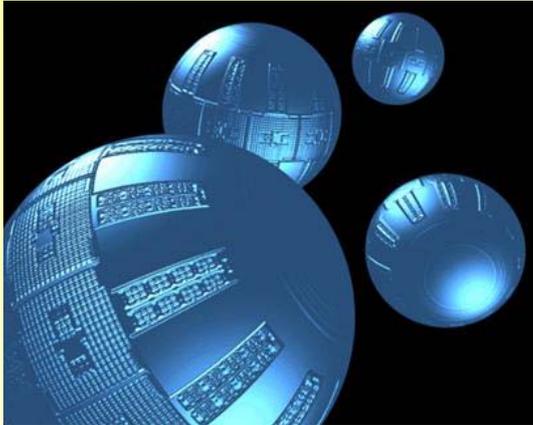
Nanomedicine, overview

- ❖ Nanomedicine is an interdisciplinary field of science, even a simple project needs contributions from physicists, engineers, material chemists, biologists and end users, such as an orthopaedic surgeon.
- ❖ A mature nanomedicine will require the ability to build structures and devices to atomic precision, hence molecular nanotechnology and molecular manufacturing are key enabling technologies for nanomedicine.
- ❖ Medicine must catch up with the technology level of the human body before it can become really effective. The result will be the ability to analyse and repair the human body as completely as we can repair a conventional machine today.
- ❖ If the nanoconcept holds together, it could be the groundwork for a new industrial revolution.
- ❖ BUT: can all different scientists and engineers work together to achieve crossover dreams?



History

- ❖ Despite the importance of nanotechnology, literature review of robotics in 1993 included not a single reference to nanotechnology or nanomedicine.
- ❖ The first nanomedical device design technical paper in 1998 by Freitas: Respirocyte – an Artificial Red Cell.



← Table of Contents, Slide 85

Nanostructures in nature

- ❖ Nature has created nanostructures for billions of years. Biological systems are an existing proof of molecular nanotechnology.
- ❖ Biology is an ingenious form of nanotechnology, even very simple living cells are able to duplicate. So far there is no machine of any size or type, which could do the same.

← Table of Contents, Slide 86

Replication

- ❖ Replication is a basic capability for molecular manufacturing. Still some scientists think that medical nanorobots need not ever replicate.
- ❖ It is unlikely that the FDA would ever approve a use of a medical nanodevice that was capable of in vivo replication. Replicators will be very tightly regulated by governments everywhere. In practice you would not want anything that could replicate itself to be turned loose inside your body.

← Table of Contents, Slide 87

Nanodreams

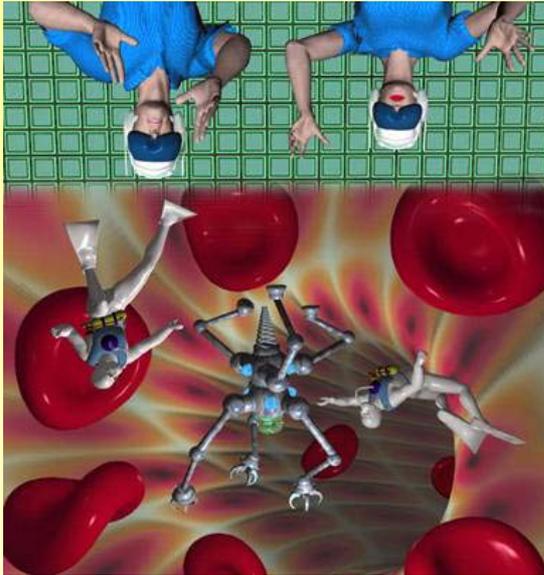


Pollution-free industry will guarantee the well-being for the nature.

- ❖ Nanomedicine will eliminate virtually all common diseases, all medical pain and suffering => theoretically eternal life.
- ❖ Extension of human capabilities.
- ❖ New era of peace. People who are well-fed, well-clothed, well-educated, healthy and happy will have little motivation to make war.

← Table of Contents, Slide 88

Nanohorrors



- ❖ Self replicating nanorobots could become massive chemical and biological weapons.
- ❖ Changes to human properties, such as brains, respiration, muscles and DNA will be uncontrolled and may threaten the existence of human being.

← Table of Contents, Slide 89

Risks and remedy at a nanomedical procedure

- ❖ Risk
 - ⇒ The incompetence or negligence of medical personnel.
 - ⇒ Biocompatibility, computers.
 - ⇒ Malfunction involved with unexpected machine-machine interaction that has not been tested in advance.
- ❖ Remedy
 - ⇒ Fail-stop protocols and fail-safe design.
 - ⇒ The doctor must always have control on the nanomachines. This will probably become a universal requirement for all medical nanodevices.

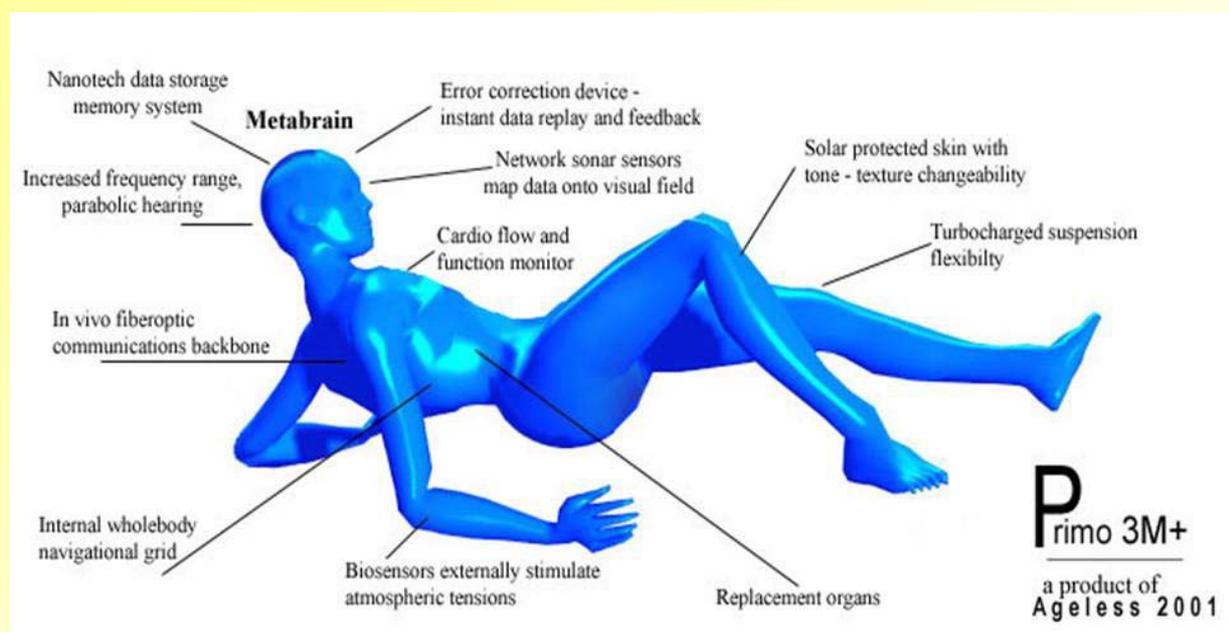
← Table of Contents, Slide 90

Potential applications of nanomedicine

drug delivery	implant materials
improved imaging	artificial tissues
DNA analyses	improving brains
nanobarcode® technique	cleaning teeth, lungs and arteries

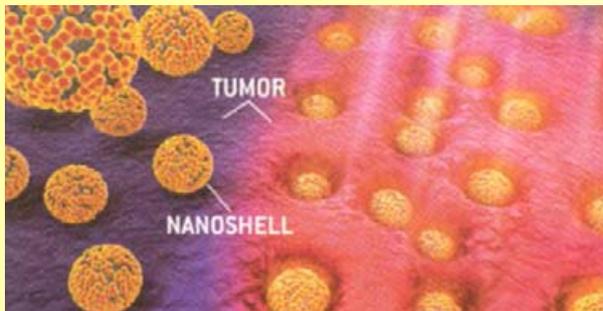
← Table of Contents, Slide 91

Human targets



← Table of Contents, Slide 92

Drug delivery I

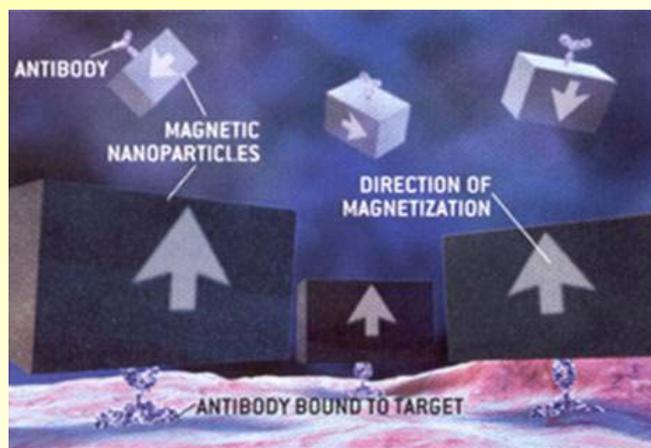


- ❖ Nanoparticles can deliver drugs in a sophisticated ways, like target specific and trigger based drug dose.
 - ⇒ Target specific delivery enables the use of lower doses, because the whole body is not saturated with the drug.
 - ⇒ The side effects will be minimized, and it is possible to use stronger drugs, which could not be used by conventional drug delivery.
- ❖ The use of gold particles in cancer healing is an example target specific action.
 - ⇒ Gold plated spheres are linked to tumor cells. Nanoshells can be heated from the outside using an infrared source. Heating the shells destroy the cancerous cells, leaving the surrounding tissue unharmed.

← Table of Contents, Slide 93

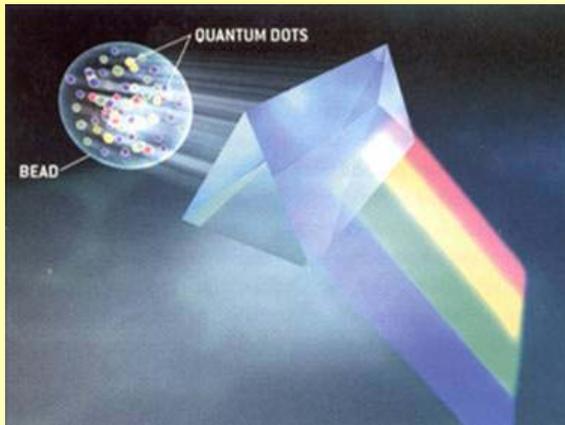
Improved imaging

- ❖ Using magnetic nano particle can Improve imaging with better contrast agents and helps to diagnose diseases more sensitively.
- ❖ The method enables the detection of very small tumors and other organisms which cause disease. When the diagnostics is improved the healing will also be easier.



← Table of Contents, Slide 94

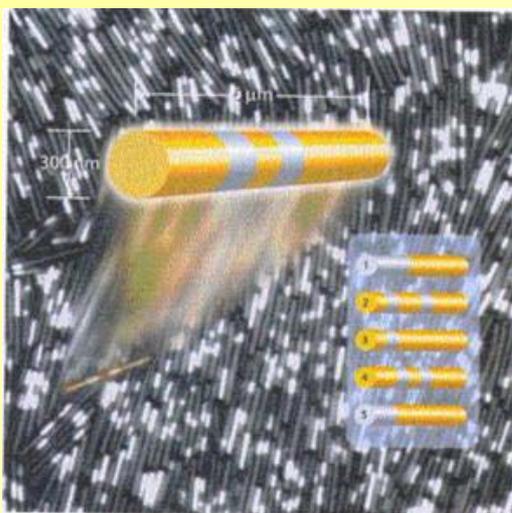
DNA analyses



- ❖ Semiconductor nanocrystals, quantum dots, absorb only photons of light omitting just the right wavelength for their size.
- ❖ Use of a variety of sizes and concentrations of quantum dots produces a spectral bar code with distinct spectral lines. Such method allows multiple labels.
- ❖ Fast and accurate DNA testing, comparison of genetic material, rewriting DNA sequences in vivo, and even home DNA test systems.

← Table of Contents, Slide 95

Nanobarcode® technique I



- ❖ SurroMed company is developing nanobarcode® technique with researchers from the Penn State University.
- ❖ The idea is to use little metallic bars. Consecutively alternating gold- and silver-bands on a bar are interpreted as individual bits.
- ❖ Twenty bands equal twenty bits $\approx 10^6$ alternatives.
- ❖ The bands can be interpreted with an optical microscope.

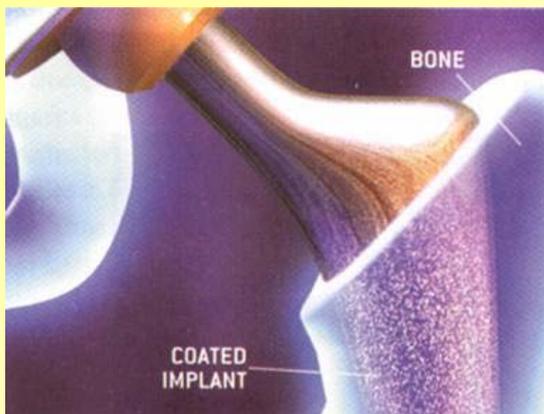
← Table of Contents, Slide 96

Nanobarcode® technique II

- ❖ Numerous DNA-testers can be attached to a single bar, the testers combine with receptor molecules. The complex formation results a multiple DNA-sequence analysis. Also antibody molecules can be attached to a surface of a bar, after an immunologic reaction peptide hormones can be analysed.
- ❖ Hundreds of components can be measured from one milliliter of serum, multiple test tubes and plentiful blood samples become unnecessary.

← Table of Contents, Slide 97

Superior implant materials

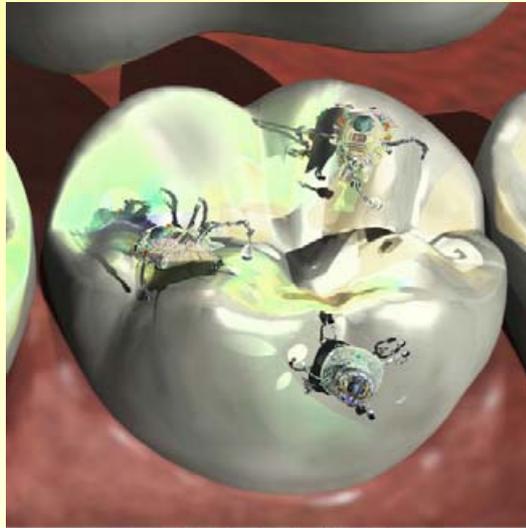


- ❖ The connection between implant material and bone/ surrounding tissues is a key factor to a successful and long-term use of prostheses.
- ❖ Nano-scale modifications of implant surfaces would improve implant durability and biocompatibility.

← Table of Contents, Slide 98

Cleaning robots I

Teeth cleaning robots collect harmful bacteria from the mouth.



Copyright 2001 American Dental Association

◀ Table of Contents, Slide 99

Cleaning robots II

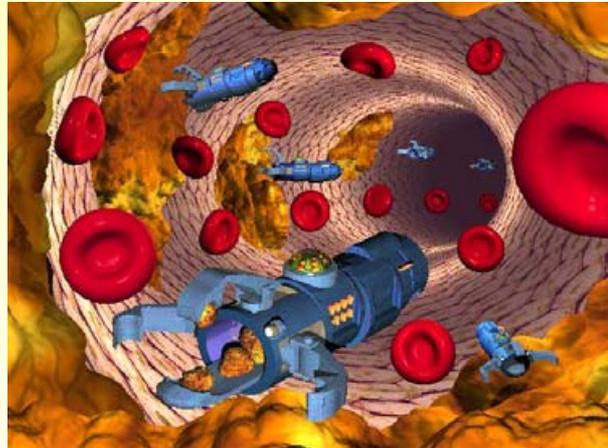
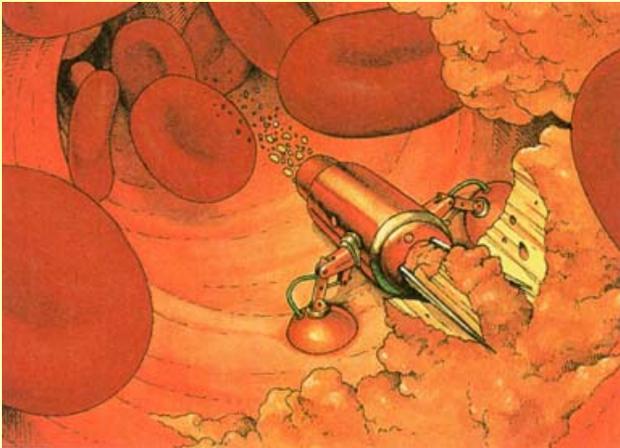
- ❖ Similar cleaning robots can be used in lungs. We have natural macrophages in alveoli, but they are not able to metabolize foreign particles like fibers of asbestos and toxic effects of smoking from the lungs.



◀ Table of Contents, Slide 100

Cleaning robots III

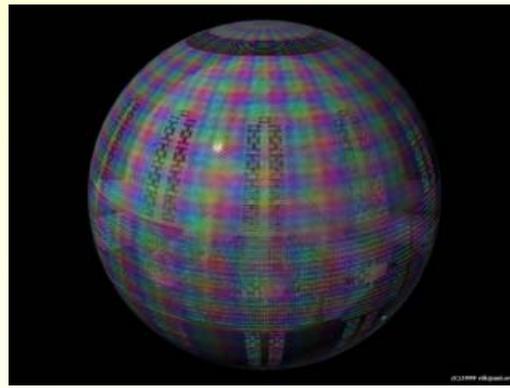
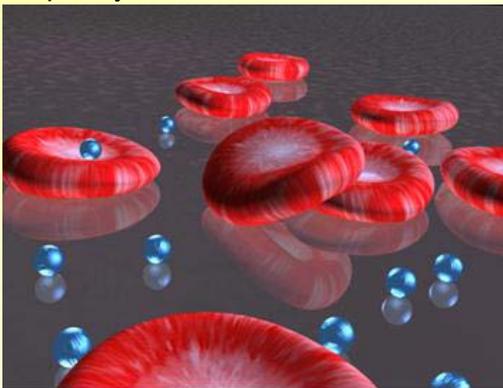
Extra fat can be removed from the arteries with cleaning robots.



← Table of Contents, Slide 101

Respirocyte

- ❖ It is an artificial mechanical red blood cell floating along in the bloodstream. A spherical ($d = 1 \mu\text{m}$) nanomedical device is made of 18×10^9 atoms (mostly carbon).
- ❖ The design of respirocyte was the first technical paper on nanomedical device design. It was published in 1998 by Robert A. Freitas.
- ❖ It is important to notice that molecular nanotechnology violates no physical laws and there are technical paths leading to useful results.
- ❖ Respirocyte device cannot be built today



← Table of Contents, Slide 102

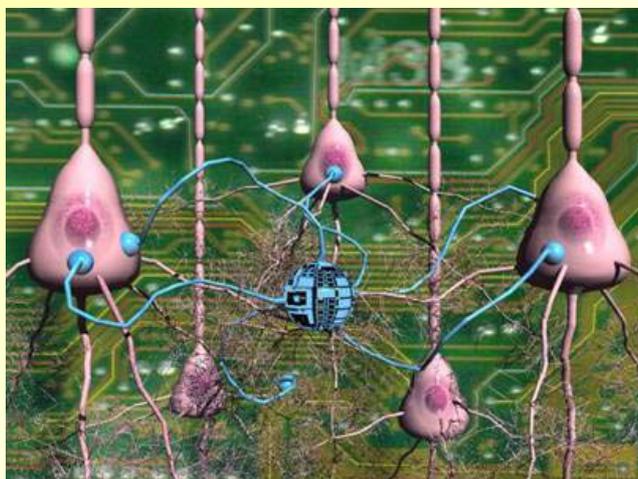
Gas transport

- ❖ Pressure tank can be pumped full of up to $9 \cdot 10^9$ oxygen (O_2) and carbon dioxide (CO_2) molecules. The gases can be released from the tank in a controlled manner.
- ❖ Continuous oxygen release throughout the body.
- ❖ Systems responsive to local O_2 partial pressure or the ability to precisely control saturation curve profiles independently for O_2 and CO_2 .
- ❖ Respirocytes can deliver 236 times more oxygen to the tissues per unit volume than natural red cells while simultaneously managing carbonic acidity. Efficiency is mainly due to a much higher operating pressure (up to 1000 atm). The operating pressure of the natural red blood cell is the only about 0.51 atm.
- ❖ Injection of a 5 cm³ dose of 50% respirocyte aqueous suspension into the bloodstream can replace the entire O_2 and CO_2 carrying capacity of the patient's entire 5 000 cm³ of blood.

← Table of Contents, Slide 103

Improving brains

- ❖ A nanostructured data storage device measuring a volume about the size of a single human liver cell can store an amount of information equivalent to the entire library.



← Table of Contents, Slide 104

Artificial tissues and organs

- ❖ Researchers hope to figure out ways to regenerate skin, bone and more sophisticated organs.
- ❖ At present auto-, allo- and xenografts plus some artificial materials are being used for reconstruction of damaged tissues and organs.
- ❖ The amount of auto- and allografts is limited, and allo- and xenografts carry a risk of infection (HIV or BSE).
- ❖ So the need and interest for artificial regeneration definitely exists!

← Table of Contents, Slide 105

Properties of medical nanodevices

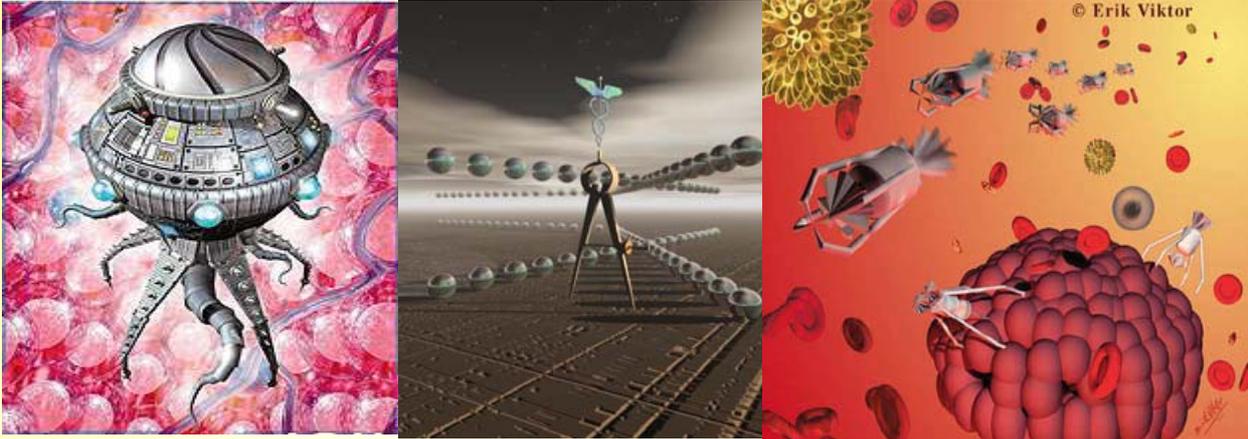


- ❖ Shape and size
- ❖ Biocompatibility
- ❖ Powering
- ❖ Communication
- ❖ Navigation

← Table of Contents, Slide 106

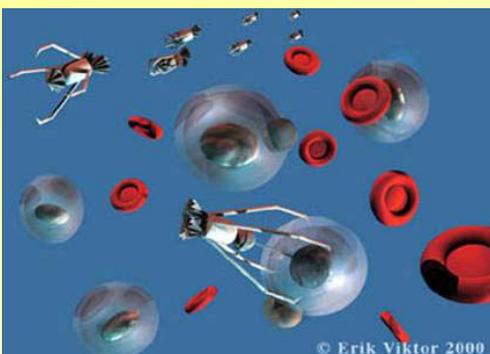
Shape and size

- ❖ The optimum nanorobot shape varies according to the function the device is designed to perform, and the environment in which the device must operate.



← Table of Contents, Slide 107

Summary

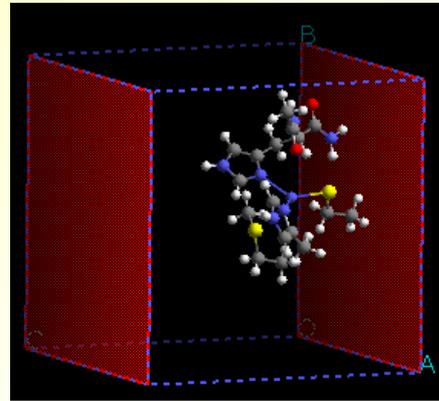


- ❖ In the medical field the neck of the bottle is not always the lack of methods and results. In fact, there are plenty of results. The problem is how to understand and interpret for instance DNA-sequences and how to define which are the best targets for new drug-molecules?
- ❖ The history of nanomedicine is brief, but the future is promising.
- ❖ In developing nanotechnology medical and pharmaceutical applications are one of the main target areas. In the field of nanomedicine there is a big basket full of ideas, quite few of those have been accomplished so far in practise.
- ❖ It is reasonable to expect several and significant advantages of nanotechnology in health care in the future.

← Table of Contents, Slide 108



Molecular Modeling of Nanosystems



Molecular Modeling

- ❖ Selection of the model
- ❖ Selection of the method
 - ⇒ quantum mechanical (ab initio and semiempirical)
 - ⇒ molecular mechanics (empirical)
- ❖ The calculation itself
 - ⇒ single point calculation
 - ⇒ energy minimisation
 - ⇒ conformational search
 - ⇒ molecular dynamics



Ab initio methods

- ❖ Quantum mechanics states that the energy and other related properties of a molecule can be obtained by solving the Schrödinger equation: $H\Psi = E\Psi$.
- ❖ Ab initio → no empirical data are used except masses and charges of nuclear particles, c , Planck's h .
- ❖ Most accurate, no limitation on a certain class of comp.
- ❖ Drawback: computational demand (limited to hundreds of atoms).

 [Table of Contents, Slide 111](#)



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Control Engineering Laboratory

Semiempirical methods

- ❖ Solving the Schrödinger equation.
- ❖ Approximations: only valence electrons are considered explicitly.
- ❖ Parameters derived from experimental data → system dependent.
- ❖ Less computational demanding.

 [Table of Contents, Slide 112](#)



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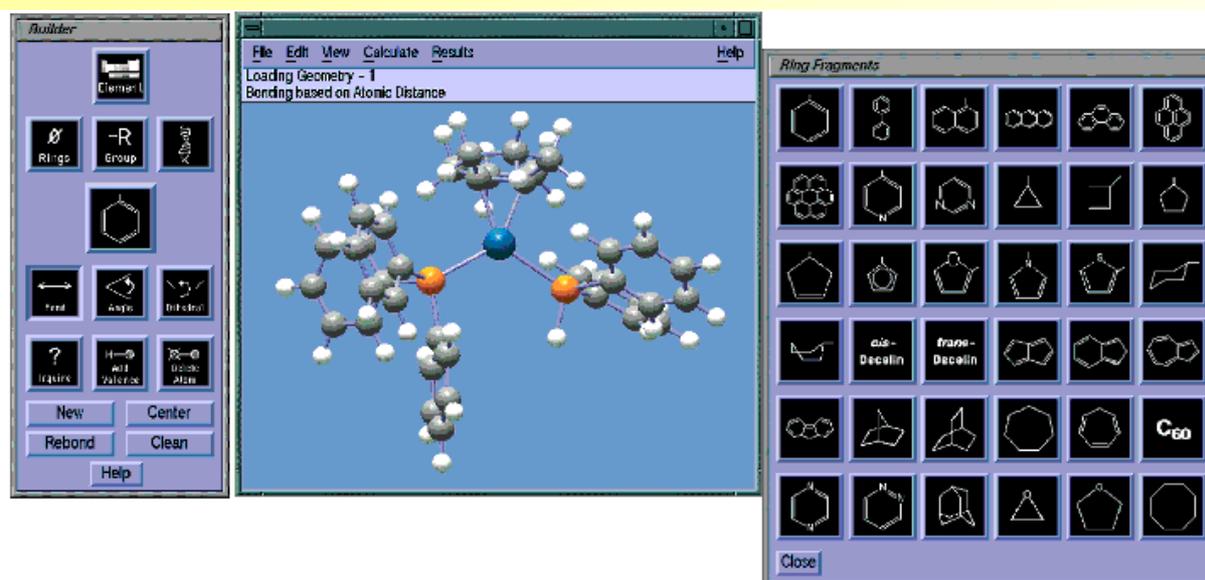
Software for computational chemistry

- ❖ Very large number of software: commercial, cheap or free.
- ❖ Various platforms.
- ❖ Parallel implementations.
- ❖ With or without graphical interface.
- ❖ Classification of the software:
 - ⇒ Ab initio electronic structure
 - Gaussian, Q-Chem, Spartan, Jaguar, Gamess, ADF, Turbomol, Dmol3...
 - ⇒ Relativistic electronic structure
 - ⇒ Semiempirical
 - ⇒ Molecular Modeling
 - ⇒ Molecular Dynamics/ Monte Carlo
 - ⇒ Visualization and analysis

← Table of Contents, Slide 113

Gaussian (Schrödinger. Inc)

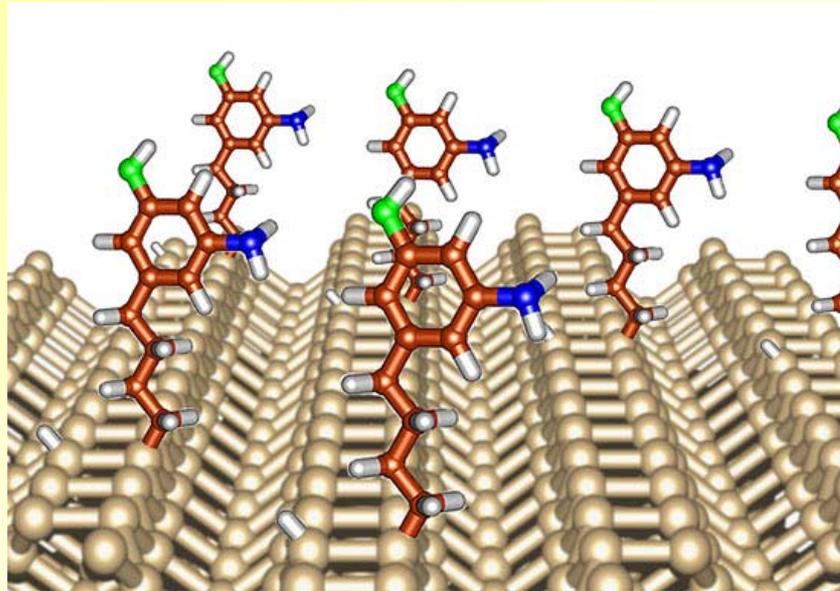
Building the model



← Table of Contents, Slide 114

Examples

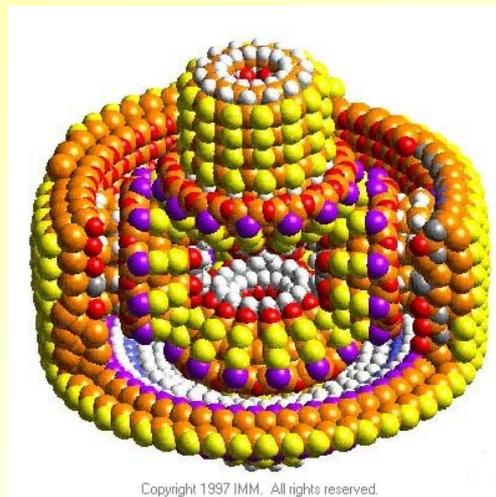
- ❖ Modification of semiconductor surfaces



← Table of Contents, Slide 115

Examples

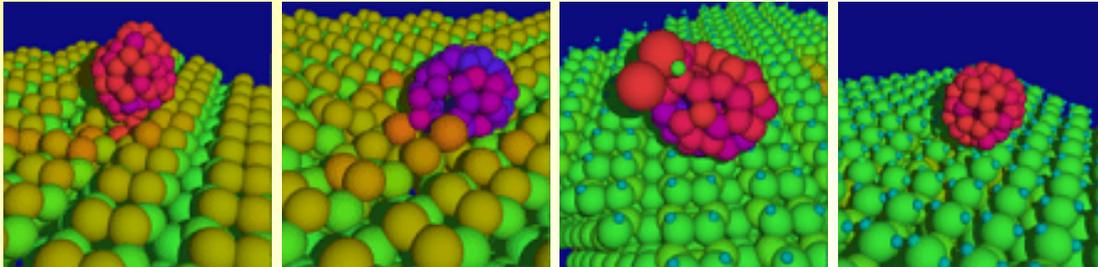
- ❖ Molecular Mechanics analysis of Drexler-Merkle Gear



← Table of Contents, Slide 116

Examples

- ❖ Molecular dynamics simulations of C60 interaction with bare and hydrogenated Si surface

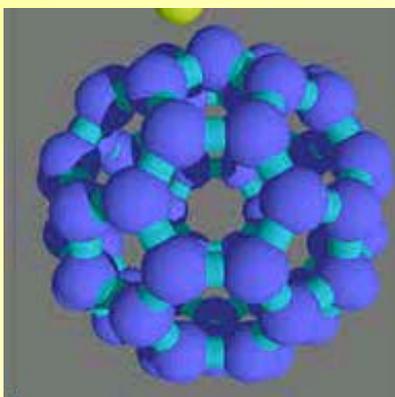


Substrate, angle, time dependent

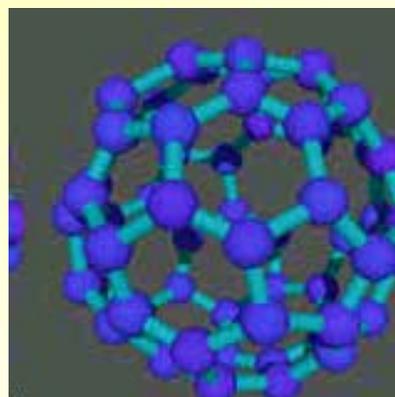
← Table of Contents, Slide 117

Examples

- ❖ Hydrogen implantation into C60



cold fullerene

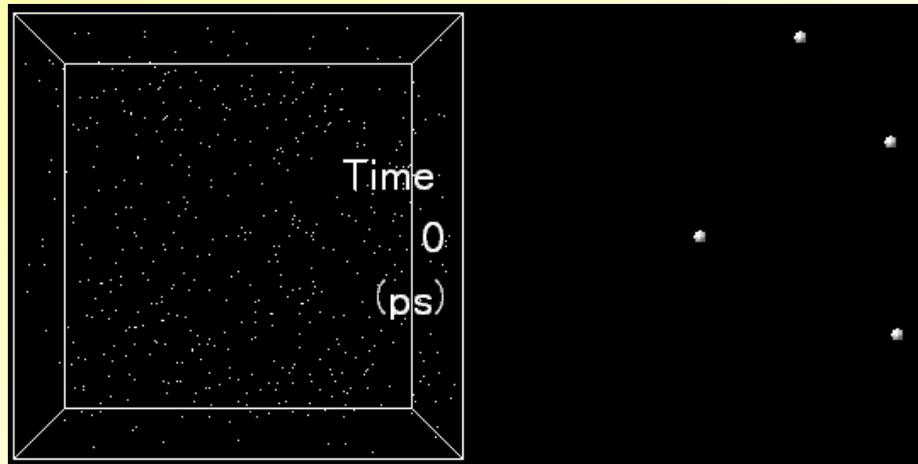


25 degrees Celsius fullerene

← Table of Contents, Slide 118

Examples

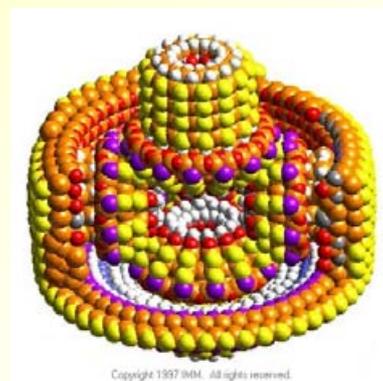
- ❖ C60 formation under laser irradiation



← *Table of Contents, Slide 119*



Molecular Devices



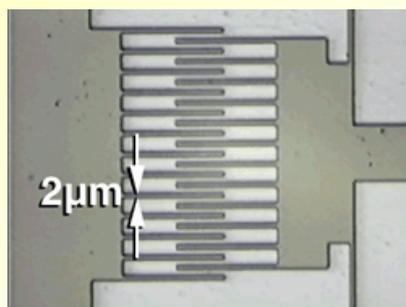
Molecular Nano-devices

- ❖ Molecular Nano-devices are manufactured products are made from atoms.
- ❖ The properties of those products depend on how those atoms are arranged.
 - ⇒ If we rearrange the atoms in coal we can make diamond.
 - ⇒ If we rearrange the atoms in sand (and add a few other trace elements) we can make computer chips.
- ❖ Conclusion: it would be nice if we could operate at atomic scale (nano-scale) and arrange atoms in any physical and chemical allowed position
 - ⇒ any desired property can be obtained.

← Table of Contents, Slide 121

Top Down Devices

- ❖ A example of top-down approach: Diamond combs
 - ⇒ Sandia National Laboratories researchers have created the world's first diamond micromachine in a comb drive that drives a tiny diamond piston. The drive is powered by a tiny alternating electrical current.
- ❖ Technology:
 - ⇒ Etching from an amorphous diamond surface



← Table of Contents, Slide 122

Molecular Nano-devices (Bottom-up)

- ❖ There are many categories of molecular nano-devices with applications in : medicine, electronics, biology, mechanics, computers... Some important achievements would be:
 - ⇒ *Fabrication and demonstration of conducting molecular wires:*
 - Prof. J. Tour (univ. South Carolina) and Prof. D. Allara and P. Weis (Penn State University) have been able to successfully make a molecular wire that works.
 - It is made out of a single chain molecule, where the ends are absorbed to the surface of a gold lead.
 - ⇒ *Fabrication of a self-assembled molecular electronic circuit array*
 - At Purdue University, scientists and engineers fabricated a regular extended array of functioning molecular-scale circuit elements.
 - They used many 2 nanometer diameter gold balls where each one was affixed to the top ends of several molecular wires of the type invented by Professor James Tour.

← Table of Contents, Slide 123

Molecular Nano-devices (Bottom-up)

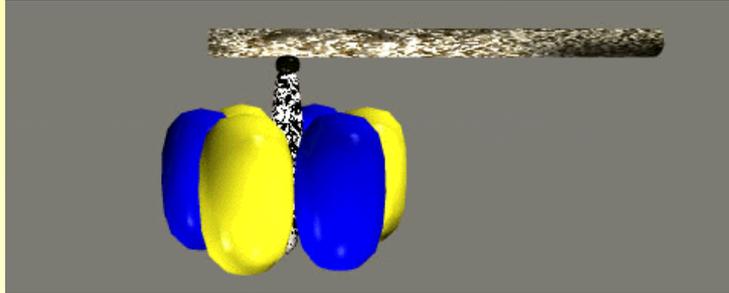
- ⇒ *Invention of the Quantum Dot Cell and "wireless" electronic computing*
 - Prof. C. Lent and W. Porod at University of Notre Dame invented a nanometer-scale switch out of five quantum dots in cruciform arrangement.
 - Using quantum-mechanical modeling and simulations, they were able to show that two neighboring cruciform molecules are able to interact: these molecules send a signal along a line of cells without any current flowing.
- ⇒ *Fabrication and testing of "quantum corrals"*
 - This was achieved by D.M. Eigler at IBM Almaden Research Laboratory in northern California, who lead an investigated team.
 - A quantum corral is a primitive nanometer-scale device that manipulates electronic charges on solid surfaces
- ⇒ *Construction and demonstration of the Nanomanipulator*
 - developed in a joint effort at university of North Carolina Department of Computer Science and the Chemistry Department at the University of California at Los Angeles (UCLA).
 - This new achievement allows scientists now to interact with atoms.

← Table of Contents, Slide 124

Molecular Nano-devices

❖ The molecular model-T

- ⇒ Engineers at Cornell univ. desined and produced a nano-motor which rotated for 40 minutes at 3 to 4 revolutions per second.

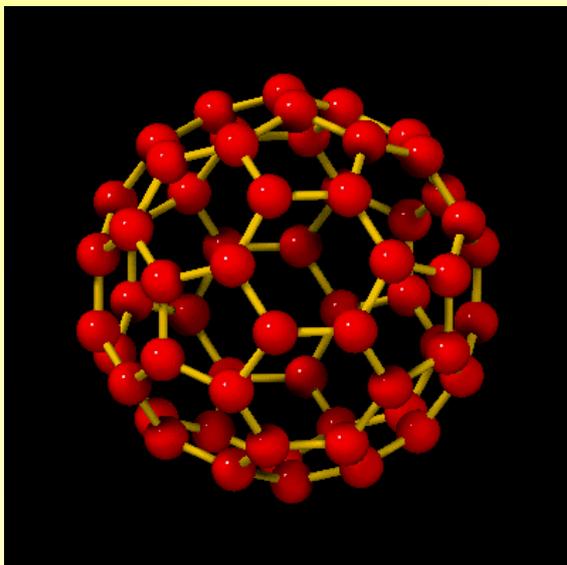


<http://falcon.aben.cornell.edu/rickyTest.htm>

<http://www.sciam.com/exhibit/1999/092099molecularmotor/index.html>

← Table of Contents, Slide 125

Fullerens and Nanotubes

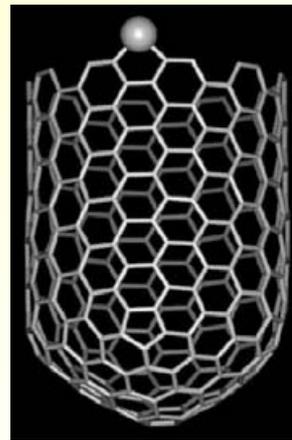
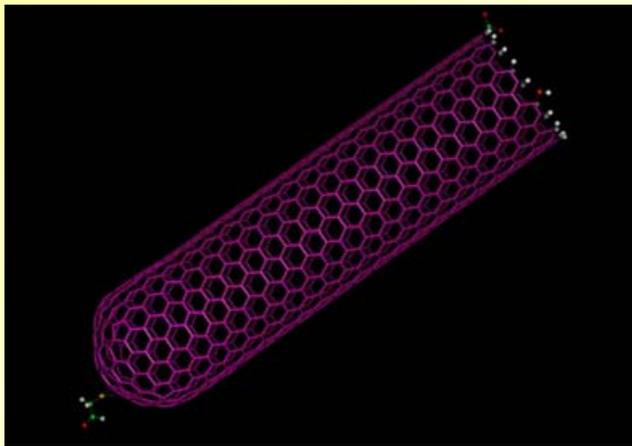


- ❖ In the 80's when an astronomer noticed an absorption line in the spectrum of some stars that could only be explained by carbon forming in an unheard of arrangement Fullerene C60 (the ball).
- ❖ Smally, Kroto and coworkers were the ones to prove experimentally the existence of this structure
 - ⇒ Nobel price awarded 1996.
- ❖ The next breakthroughs came in 1990 when the synthesis of
 - ⇒ macroscopic C60 quantities succeeded.

← Table of Contents, Slide 126

Fullerens and Nanotubes

- ❖ In 1991, scientists at NEC Corporation in Japan discovered that graphitic carbon needles grew on the negative carbon electrode of the arc-discharge apparatus used for the mass production of C₆₀.
- ❖ The structure of these tubes, having nanometer lengths



← Table of Contents, Slide 127

Fullerens and Nanotubes

- ❖ These tubes are the strongest possible material that can be made with known matter (not considering some theoretical possibilities of carbon nitride).
- ❖ Their strength is predicted to be between 1.2 and 2 times that of a diamond fiber, or a whopping 100 - 150 times as strong as steel at less than one fourth the weight.
 - ⇒ This is a dramatic improvement over carbon fiber, now used in the highest performance composites.
 - ⇒ A tube epoxy composite should have such a high strength to weight ratio as to defy human experience.
 - ⇒ Airplanes could be about one fifth their present weight with structural members like wings that seem impossibly thin.

← Table of Contents, Slide 128

Prospective Applications and Dreams

- ❖ Nanomachine.
- ❖ Electronic components (at least two ways to make a nanocomputer with tubes; one mechanical and one electronic).
- ❖ A fiber so strong as to be difficult to explain in human terms.

 [Table of Contents, Slide 129](#)



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Nanomachines dreams

- ❖ Smart materials would be made of nanomachines.
 - ⇒ Such machines would have more or less, the same components as macro, or familiar "normal" sized machines with recognizable gears, bearings, motors, levers and belts... (except for all the nanocomputers).
 - ⇒ Smart materials with a myriad of functions like shape changing and distributing fluids and gas, say for environmental control in a paper-thin space suit that actively moves with the body or Drexler's smart paint.
 - ⇒ Open a can and splat some on a wall. The paint spreads itself across the surface using microscopic machines and changes color on command or becomes a wall sized 3-D television...
 - ⇒ Then again, the whole wall may as well be smart material changing texture or windows on command.

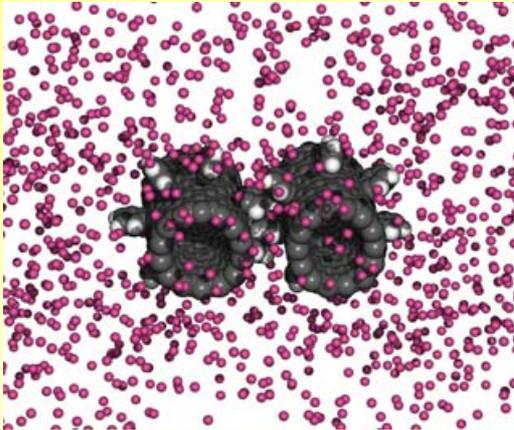
 [Table of Contents, Slide 130](#)



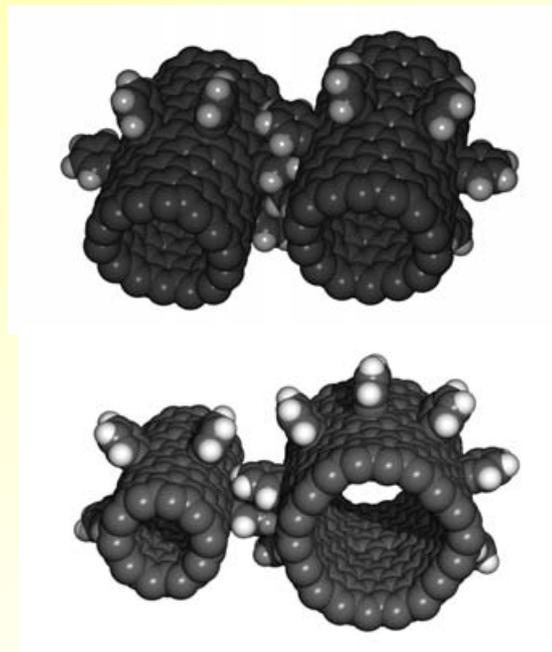
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Nanomachines

They aren't real yet



Cooling them with Helium.

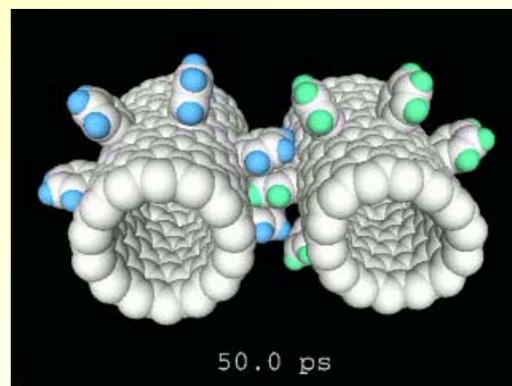
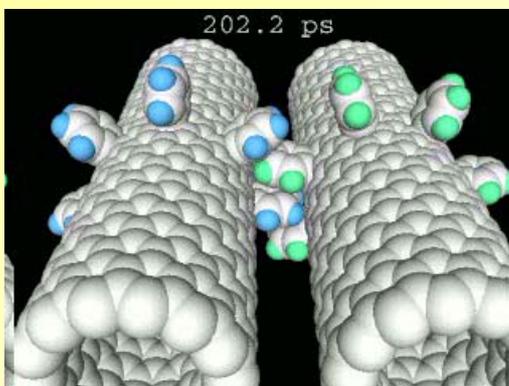


Gears rotating under laser action. Calculations predict 6 trillion rotations per min.

← Table of Contents, Slide 131

Nanomachines

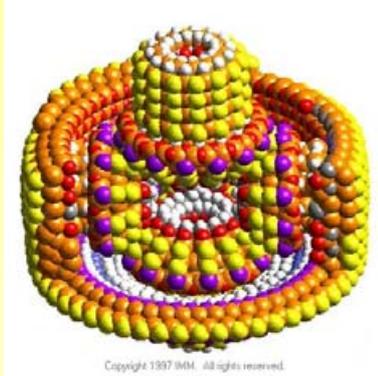
❖ Simulations of nanotube rotating gears.



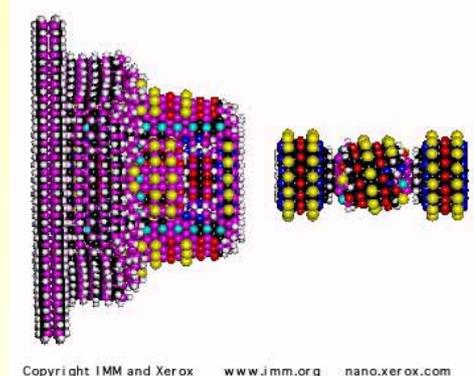
← Table of Contents, Slide 132

Nanomachines

- ❖ The *Institute for Molecular Manufacturing* is currently pursuing studies on the molecular machine parts:



Differential gear.



The pump and segment of chamber wall pictured here contain 6165 atoms.

← Table of Contents, Slide 133



Nanotechnology: Market Outlook and Future Prospects

Development of Technologies

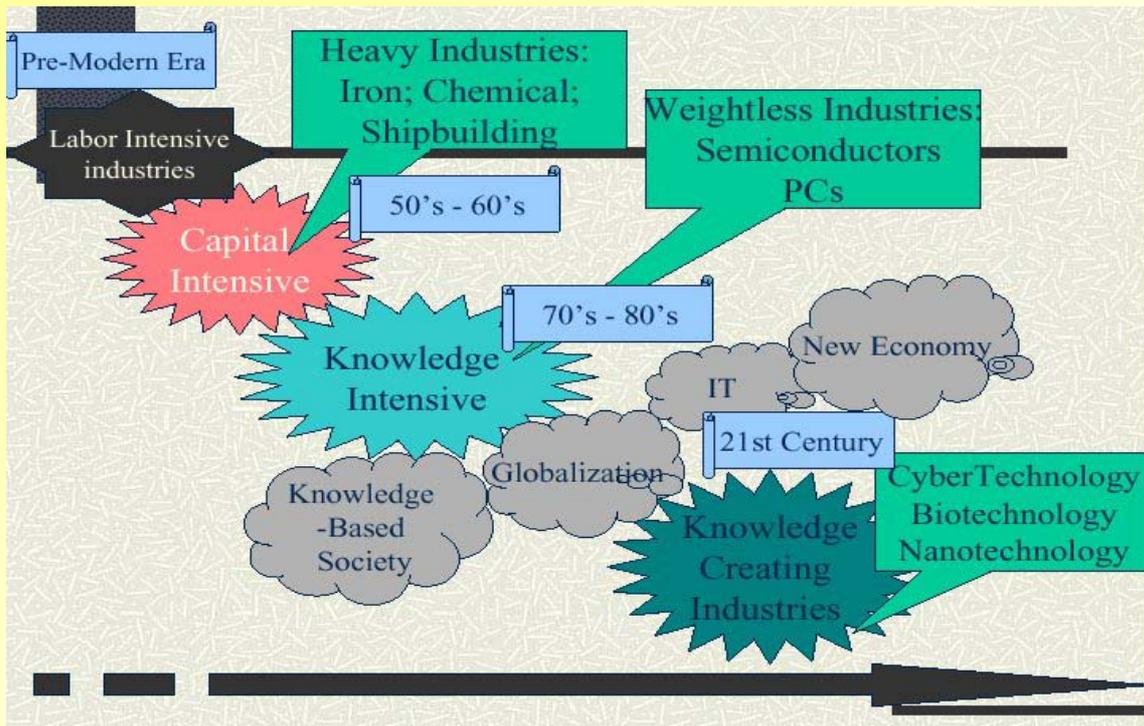


Table of Contents, Slide 135

Micro and Nanotechnology Application Areas

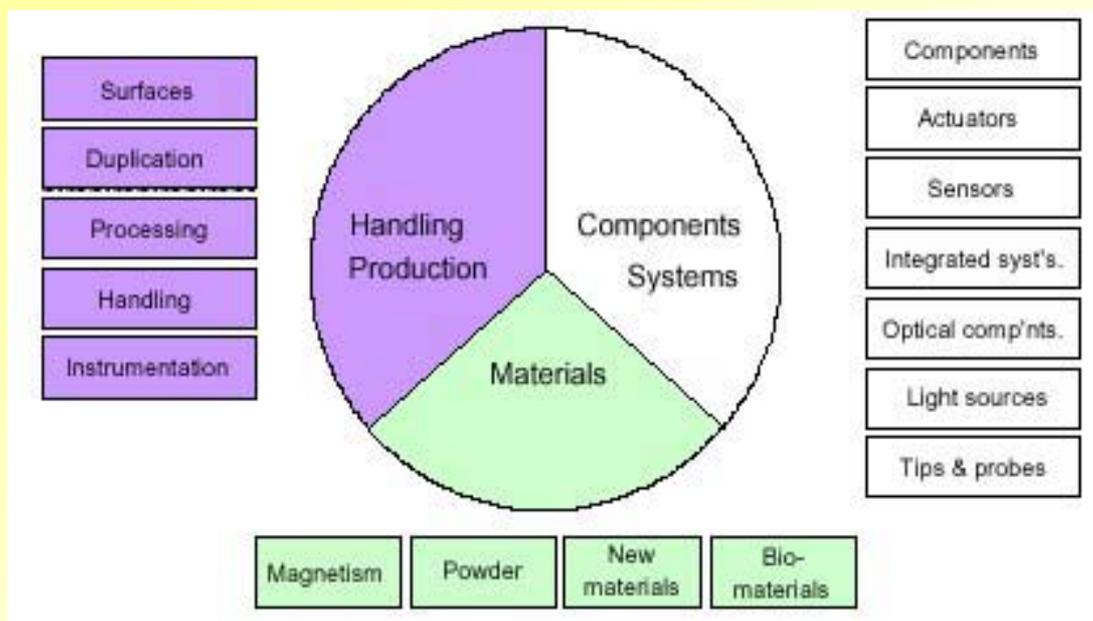


Table of Contents, Slide 136

Current Applications of Nanotechnology

- ❖ Current applications include:
 - ⇒ New semiconductor lasers
 - ⇒ Random Access Memories
- ❖ Novel materials are already being marketed, such as:
 - ⇒ Sunburn lotions containing ultraviolet-absorbing nano-particles
 - ⇒ Spectacles with scratch-resistant nano-coating
- ❖ The bio-chip arrays are a powerful diagnostic product of nanotechnology and biotechnology and are currently used in:
 - ⇒ High throughput screening for detecting diseases
 - ⇒ In gene sequencing in the Human Genome Project

← Table of Contents, Slide 137

World Scene

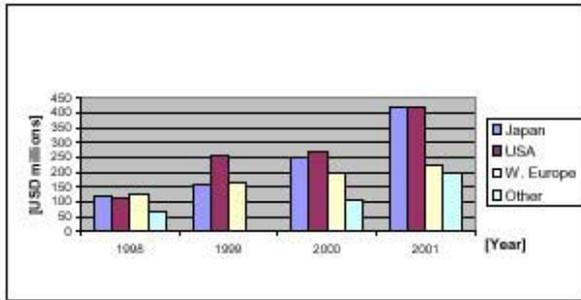
- ❖ The importance of nanotechnology is evident from the interest shown by governments around the world.
- ❖ The world investment in nanotechnology has been dominated by the United States and Japan. This is expected to continue.
- ❖ Increasing investment is expected by European countries such as the UK, Germany and Switzerland and Asian countries such as China and Korea.

Country	Annual budget for nanotechnology research (US\$ million)
<i>Japan</i>	120
<i>USA</i>	116
<i>Western Europe</i>	128
<i>Other Countries</i>	70
TOTAL	432

Government Expenditures on Nanotechnology Research in 1997

← Table of Contents, Slide 138

Research spending: Micro and nanotechnology



- ❖ USA is strong in the rapid implementation of scientific findings.
- ❖ However, particularly in the field of micro and nanotechnology, Europe has tremendous competency.
- ❖ When it comes to microsystems, optics, precision mechanics and production technologies, Europe is in the lead.

← Table of Contents, Slide 139

Foreseen applications & links with industries

- ❖ (Opto) electronics (main area of application)
 - ⇒ General electronics, optics and photonics (devices)
 - optical information storage
 - molecular electronics
 - waveguide devices, rectifiers and switches
 - nanoscale integrated circuits
 - fiber optics
 - magnetic recording and storage devices (video, computers)
 - optical devices (mirrors and lenses)
 - ⇒ Quantum electronics
 - Single electron tunneling devices
 - ⇒ Superconductors and hard & soft magnets

← Table of Contents, Slide 140

Foreseen applications & links with industries

❖ (Opto) electronics

- ⇒ Sensors and actuators
 - information processing in sensors
 - actuators (linear motors)
 - piezo actuators
 - magnetoresistance sensors
 - bio-molecular devices including sensors
- ⇒ Displays
 - large area displays
 - new generations of low power consumption, high brightness flat screen displays for (e.g.) computers, TV's virtual reality headsets, camcorders, etc
- ⇒ Micro-lasers and vertical emitters & injection lasers

 [Table of Contents, Slide 141](#)

Foreseen applications & links with industries

❖ Life sciences

- ⇒ pharmacy
 - drug delivery / controlled release
- ⇒ medical technology
 - diagnostic tools
- ⇒ biotechnology
 - biocompatible micromechanics

❖ Environment

- ⇒ air
 - ambient air control
- ⇒ energy
 - combustion technologies
- ⇒ catalysis
 - catalysis: new clean process technology

 [Table of Contents, Slide 142](#)

Foreseen applications & links with industries

- ❖ Industrial technologies
 - ⇒ corrosion technology
 - ⇒ industrial hygiene
- ❖ Materials
 - ⇒ ceramics
 - ceramic nanocomposites
 - functional ceramics
 - ceramics based on monodisperse particles
 - ⇒ concrete
- ❖ Mechanical technologies
 - ⇒ precision engineering in cars, aircrafts
 - ⇒ ultra precision machines to improve accuracy
 - ⇒ diamond grinding / turning

← Table of Contents, Slide 143

Market Forecast of Nanotechnology

Year	2005	2010
Molecular Electronics Materials	26	2214
Quantum Devices	380	1380
Magnetic Materials for HD Memory	27075	95812
Materials for Optic Memory	10312	17062
Manufacturing Devices of Thin Films	1885	1885
Semiconductors Manufacturing Devices	24450	31950
Ultra Precise Processing Devices	2036	2986
Micromachines	5019	7723
Fullerene, Nanotubes	145	291
Optic Catalysts Materials	576	1810
Bio Reactors	609	1380
Genetic medicine	4696	5581
Medical devices	649	2390
Total:	84810	191159

(100 Million Yen)

- ❖ According to a study conducted by the Mitsubishi Research Institute, the size of the nanotechnology market will expand rapidly to ¥8 trillion in 2005 and ¥19 trillion in 2010.

← Table of Contents, Slide 144

Nanomaterials

- ❖ The applications in nanomaterials vary from use in polymers, batteries, electronics, cosmetics, sensors, fuel cells, and catalysis to coatings on metals and computer screens and other displays.
- ❖ The most cost-effective nanomaterials available are layered, often chemically modified, clays consisting of nanometer-thick platelets of up to 1,000 nm in diameter.
- ❖ Current global demand for nanoclay reinforcements may be only a few thousand tons
 - ⇒ By 2010 global markets for nanoclays will be in the hundreds of millions of dollars
- ❖ Carbon nanotube polymer composites are gaining interest.
 - ⇒ The market for these composites will reach about 80,000 tons by 2009.

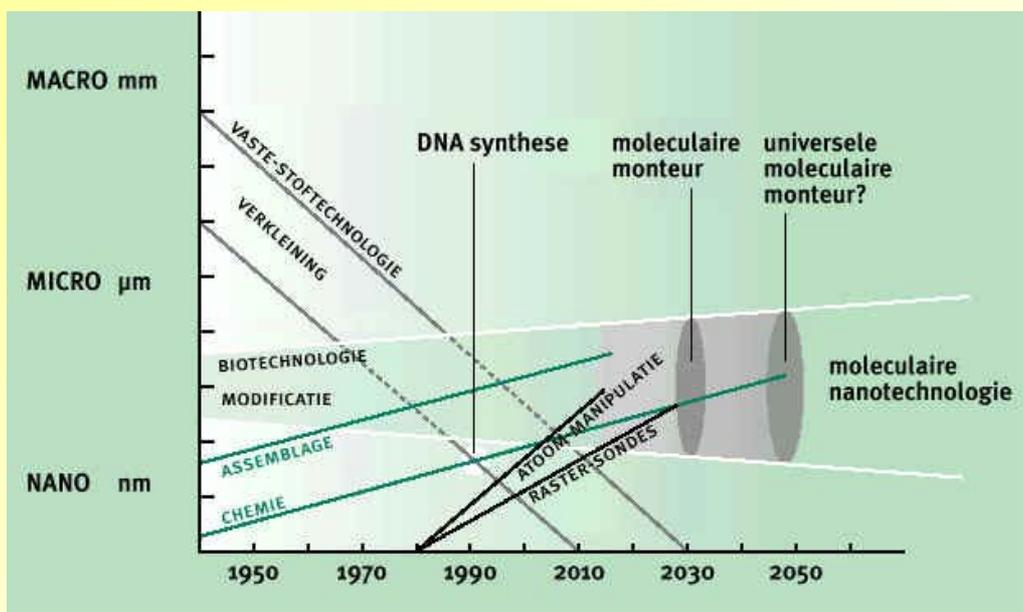
 *Table of Contents, Slide 145*

Nanotechnology Situation in Europe

- ❖ Nanotechnology related activity in Europe is increasing.
- ❖ There are several European networks regarding nanotechnology developments:
 - ⇒ Since 1992, PHANTOMS deals with the area of nano-electronics.
 - ⇒ The European society for precision engineering and nanotechnology (EUSPEN).
 - ⇒ The NANO-network from the European Science Foundation (ESF) focuses on materials.
 - ⇒ The European Consortium for NanoMaterials (ECNM)
 - ⇒ National networks
 - the French Club Nanotechnologie
 - the UK Institute of Nanotechnology
- ❖ National centres working on nanoscience are formed more and more.

 *Table of Contents, Slide 146*

Nanotechnology Situation in Europe

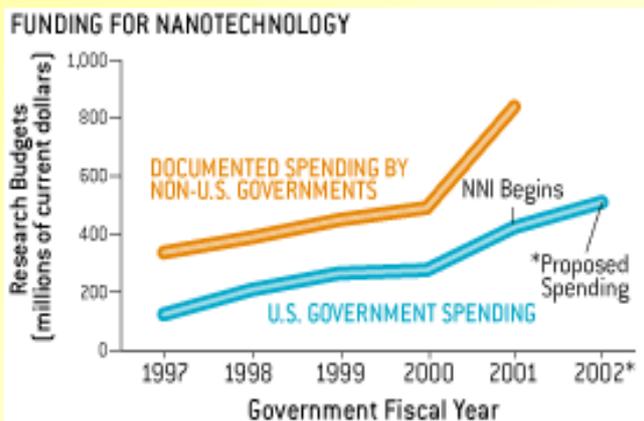


Nanotechnology future prospects in Europe

← Table of Contents, Slide 147

Nanotechnology Situation in USA

- ❖ The National Nanotechnology Initiative (NNI), helps to keep the U.S. competitive with world spending.
- ❖ United States has increased the NNI budget by 83%, from US\$270 million to US\$495 million, and it seems that the Bush Administration is maintaining the same position.



SOURCES: U.S. Senate briefing on nanotechnology, May 24, 2001, and National Science Foundation

← Table of Contents, Slide 148

- ❖ Commercial Impact (Potential Markets)
 - ⇒ Nanomaterials
 - ⇒ Information Technology Materials
 - ⇒ Nanobiotechnology

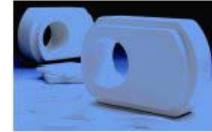
Nanotechnology Situation in USA

NANOMATERIALS



Q-Dot Contrast Enhancers; Frankel, MIT

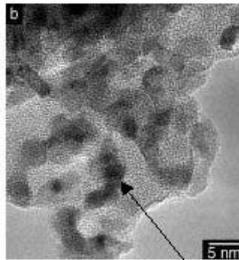
NANOSTRUCTURES



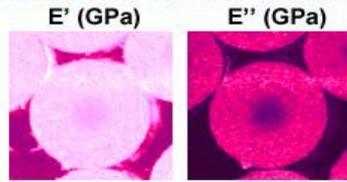
Netshape Formed Nanoceramics; Siegel, RI

CONSOLIDATED NANOSTRUCTURED MATERIALS

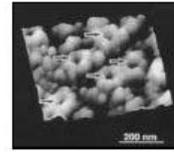
NANOCOMPOSITES



Nanocrystalline RuO₂ wire in Silica Aerogel; Rolison, NRL

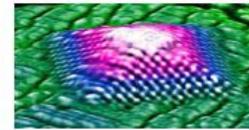


10 μ m
10 20 30 40 50 60 70 GPa
Composite Moduli Measurement; Wahl, NRL



Cell Membrane; Oberleithner, Münster

NANOPOROUS MATERIALS

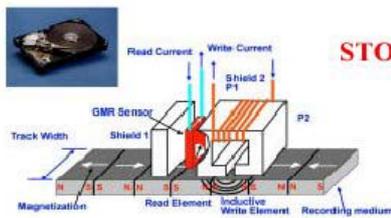


DIRECTED SELF ASSEMBLY

Table of Contents, Slide 149

Nanotechnology Situation in USA

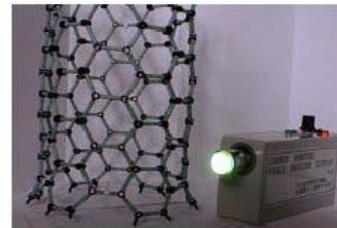
INFORMATION TECHNOLOGY MATERIALS



Magnetic recording process.
GMR Reading Head; IBM

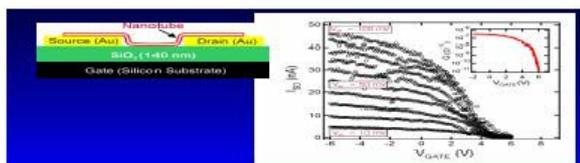
STORAGE

DISPLAY



CNT FED Display; Zhou, UNC

LOGIC



CNT FET; Avouris, IBM

TRANSMISSION



Superlattice VCSEL; Honeywell

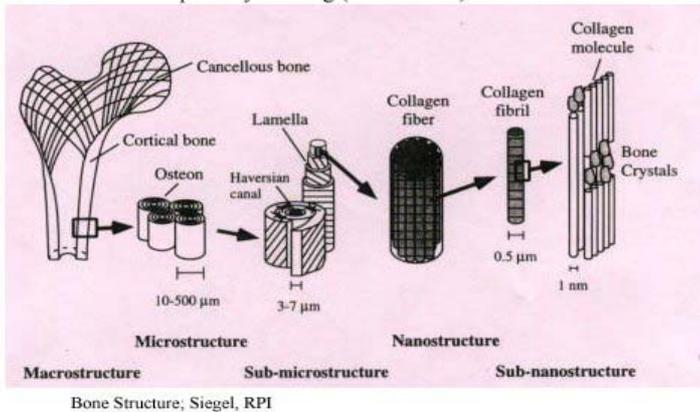
Table of Contents, Slide 150

Nanotechnology Situation in USA

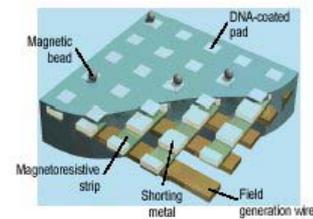
NANOBIOTECHNOLOGY

Earlier Detection and Treatment of Disease

Contrast Agents for Imaging
Sensors
Susceptibility Testing (DNA/RNA)

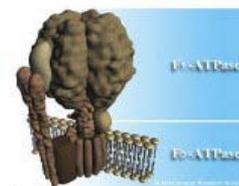


Bone Structure; Siegel, RPI



BARC Sensor; Colton, NRL

Improved Implants



Molecular Motor; Montemagno, Cornell

NSM06-2001-ETD

Therapeutic Delivery

Enhanced Solubility
Targeted, Local Delivery

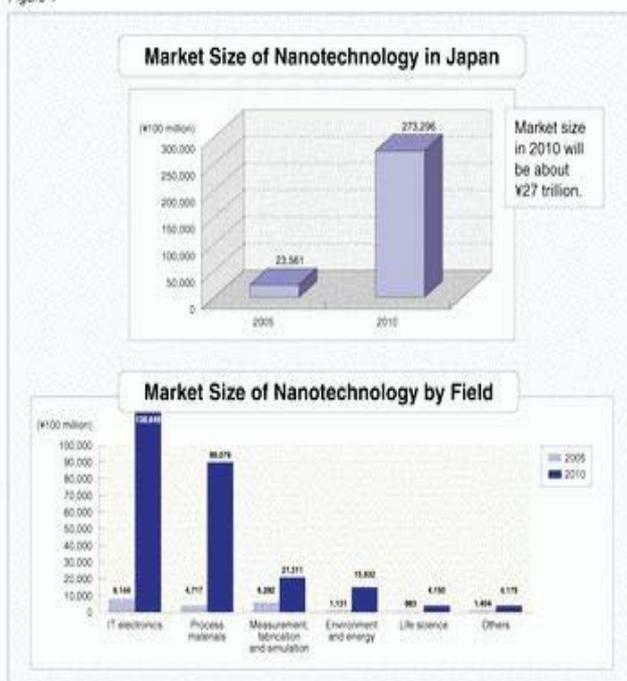
← Table of Contents, Slide 151



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Nanotechnology Situation in Japan

Figure 1



Note: 1. Based on preliminary calculations by the Hitachi Research Institute (HRI).
2. The life science field is limited to the narrow area where there is an integration of nanotechnology and biotechnology. It excludes what is known as biotechnology, which includes genome drugs and DNA chips.

- ❖ 2000 was the dawn of nanotechnology in Japan.
- ❖ Before then, Japan had become involved from an early stage in advanced research into nano fields including:
 - ⇒ A nano-mechanism project in 1985
 - ⇒ Discovery of carbon nanotubes by Dr. Iijima Sumio in 1991
 - ⇒ Atom technology in 1992.



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Nanotechnology Situation in Japan

- ❖ Nanotechnology's Applications in Environmental and Biotechnology Fields
 - ⇒ One example is a micro total analysis system that performs measurement, detection, analysis, diagnosis and other tasks as a whole on a single super-small chip.
 - ⇒ Other developments are also expected such as artificial photosynthesis and recyclable materials that are made of polymers
- ❖ Nanotechnology Materials
 - ⇒ Developing nanoparticle material is expected to dramatically increase properties and functionality.
 - ⇒ There is a wide range of applications for nanotechnology in the materials field including nanofilm that is only several nanometers thick and nanocomposites
- ❖ Measurement, Fabrication and Simulation Technology
 - ⇒ Measurement by beam techniques such as electron beams and X-rays is also crucial for nanotechnology.
 - ⇒ How to manufacture, as well as measure, in the nano world are the major issues to be solved.

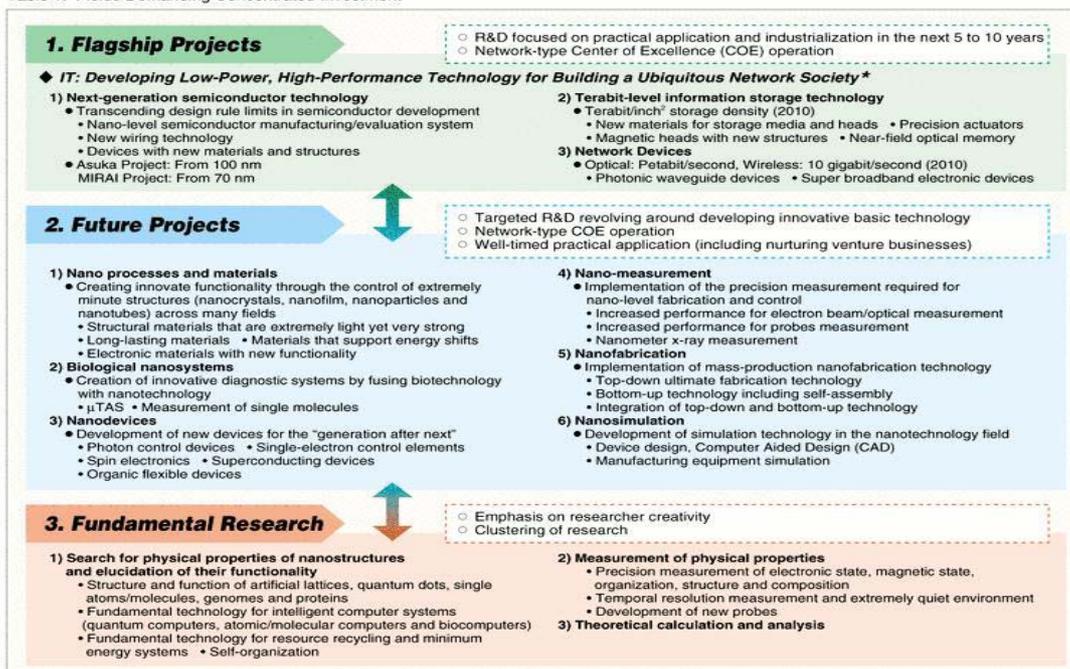
← Table of Contents, Slide 153



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Nanotechnology Situation in Japan

Table 1: Fields Demanding Concentrated Investment



Note*: In the Ubiquitous Network Society, the formation of a high-level information network infrastructure is achieved, and everyone can use network information terminals everywhere.

Concrete proposals to the Japanese government

← Table of Contents, Slide 154



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Global Trends in the Following 15 years

- ❖ The integration of continuing revolutions in information technology, biotechnology, materials science, and nanotechnology will generate a dramatic increase in investment in technology, which will further stimulate innovation within the more advanced countries.
- ❖ Discoveries in nanotechnology will lead to unprecedented understanding and control over the fundamental building blocks of all physical things.
 - ⇒ Developments in this emerging field are likely to change the way almost everything (from vaccines to computers to automobile tires) is designed and made.
 - ⇒ Self-assembled nanomaterials, such as semiconductor "quantum dots," could by 2015 revolutionize chemical labelling and enable rapid processing for drug discovery, blood content analysis, genetic analysis, and other biological applications.

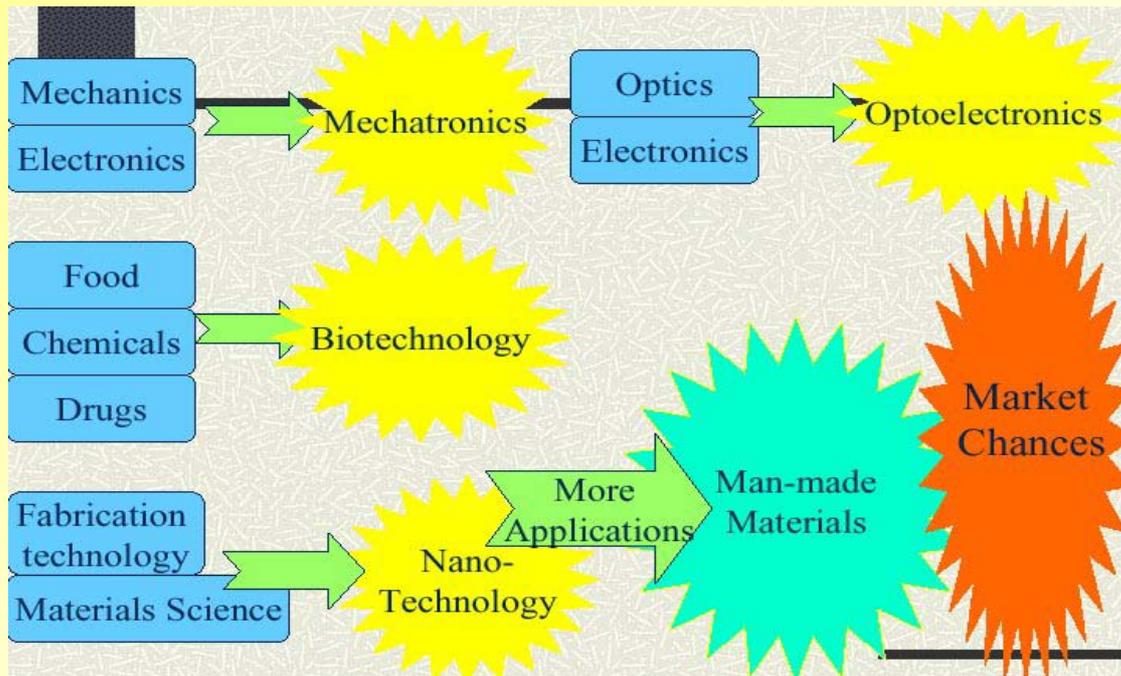
 *Table of Contents, Slide 155*

Opportunities in Nanotechnology

- ❖ Creating better Computing and Electronic Devices
 - ⇒ Nanotechnology will make it possible to develop computer processors and memory devices using physical or chemical phenomena.
 - ⇒ At Hewlett-Packard in the USA they are making progress toward developing a molecular computer.
- ❖ Nano Materials: more efficient, more environmental
 - ⇒ These new substances may be the first innovations of nanotechnological R&D to get to market
 - ⇒ Estimates for the market of polymeric nano-composites by 2009 are \$3 billion
- ❖ Nano Biology: A cleaner, more environmentally sound future
 - ⇒ Looking at genes, proteins, carbohydrates, and lipids from single cells will require nano-scale techniques.
 - ⇒ i-Stat, a Canadian company, has already established a significant market presence for its hand-held blood chemistry analysers.
 - Market forecasts for products such as this are up to 2 billion a year by 2004.

 *Table of Contents, Slide 156*

Future: Chances in Fusion and Innovations



- ❖ **Fusion** innovation (versus breakthrough innovation)
- ❖ The future is the fusion of different technologies

← Table of Contents, Slide 157

Future Challenges of Nanotechnology

- ❖ Nanostructured materials by design: stronger, lighter, harder, self-repairing and safer.
- ❖ Nanoelectronics, optoelectronics and magnetics.
- ❖ Advanced health care, therapeutics and diagnostics.
- ❖ Nanoscale processes for environmental improvement.
- ❖ Efficient energy conversion and storage.
- ❖ Microcraft space exploration and industrialization.
- ❖ Bio-nanosensors for biological threat detection.
- ❖ Applications to economical and safe transportation.
- ❖ Applications to national security.

← Table of Contents, Slide 158

Summary

- ❖ World market for nano-electronics alone will be worth many hundreds of billions of euros in products such as:
 - ⇒ More powerful computers
 - ⇒ Memories with higher storage densities for its use in phones, cars and consumer and industrial applications that are microprocessor-controlled
- ❖ The fabrication of nano-structures will create materials with new and improved properties for its use in:
 - ⇒ Organic solar cells
 - ⇒ Anti-corrosion coatings
 - ⇒ Tougher and harder cutting tools
- ❖ Nano-biotechnology will provide biosensors and biomaterials for its use in:
 - ⇒ Sophisticated DNA-chips
 - ⇒ Precision drug delivery systems

 [Table of Contents, Slide 159](#)



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