Outline – Nanotechnology part

I. Motivation:

- Nanotechnology, in general. Feynman lecture from today.
  Status of CMOS technology, End of Moore's law
- Small is different!
  Important length scales, quantum effects, fluctuations
  Different fields: electron transport, optics, mechanics, N/MEMS, microfluidics, biology,…
- Impact

II. Tools of Nano

- Microscopy and manipulation
  Scanning probe techniques: STM, AFM, MFM ….
  Electron microscopy: SEM, TEM, …
  Tweezers, nano techniques with fluorescence

III. Nanostructures with top-down

- Lithography: photo, electron
- MEMS
- Thin films, MBE, self-assembled mask
- Stamp techniques
- FIB…

Outline – Nanotechnology part

IV. Nanostructures with bottom-up
Self assembly, NWs, CVD, ALD, DNA nanotechnology…

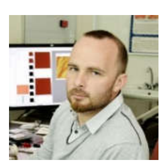
V. New concepts in electronics
Spintronics, memristors, quantum electronics

Optical techniques new directions in material science by Sandor Bordacs

Modern surface science techniques SIMS, SNMS, XPS, AES … by Gabor Dobos

MEMS, silicon technology by Peter Furjes (MTA EK MFA)

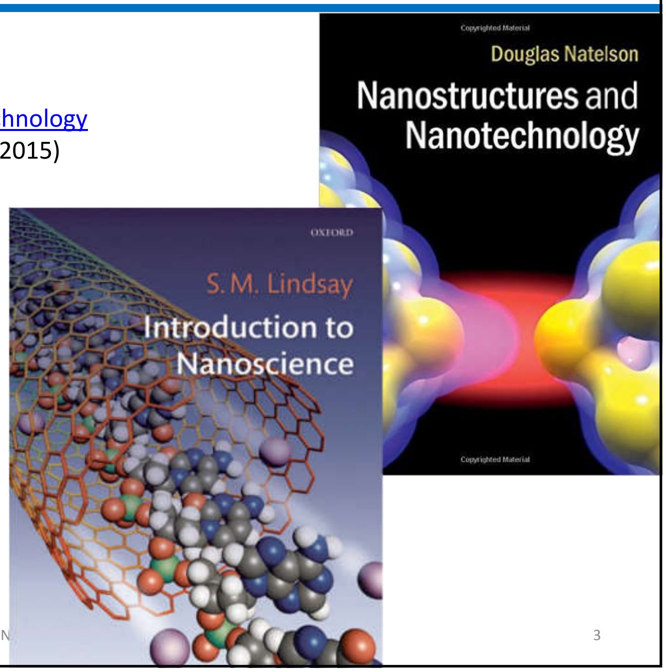
SPM by Levente Tapaszto (MTA EK MFA)



Nanotechnology and material science - 2019

Literature

- D. Natelson:
  Nanostructures and Nanotechnology
  Cambridge University Press (2015)
  ISBN-13: 978-0521877008
- S. M. Lindsay:
  Introduction to Nanoscience
  Oxford Uni. Press. (2010)
  ISBN: 978–0199544202
- T. Ihn: Semiconductor Nano-
  structures, Oxford Uni. P.
  ISBN-13: 978-0199534432
- Scientific papers
  see citations
- Wikipedia



Nanotechnology today, Following Feynman's ideas 1959

„There is plenty of room at the bottom"
There are several ideas, predictions from the talk of Feynman (1959), which have been realized. He has envisioned the birth of nanotechology and realized the great potential at nanoscale.

Examples from Feynman's suggestions:

- **Electron beam lithography (EBL)**

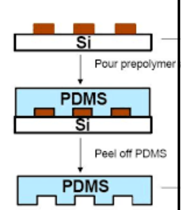
Using electron beams, demagnified in an electron microscope, to write small features: *"We can reverse the lens of an electron microscope in order to demagnify as well as magnify . . . This, when you demagnify it 25,000×, it is … 32 atoms across."* Sub 10nm accessible. → See top-down techniques

R (Up) principle of EBL

(Bottom) Principle of soft litography

- **Soft lithography ('98)**

"We would just have to press the same metal plate again into the plastic and we would have another copy." Stamping technology, leaving an imprint of the nano-features on the surface of the stamp. The stamp can then be used to print out multiple copies of the original (laboriously manufactured) nano-structure very rapidly. → See micro fluid.



After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology today, Following Feynman's ideas 1959

„There is plenty of room at the bottom"

- **Focused ion beam (FIB)**

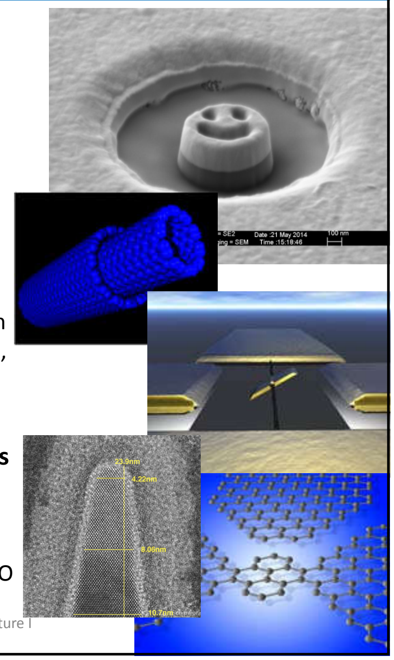
Use ions to etch structures. *"A source of ions, sent through the lens in reverse, could be focused to a very small spot."* Today it is used for nanoscale milling machine. (E.g. TEM preparation, etc…) → See top down techniques

- **Machines at the nanoscale**

"Consider the possibility that we too can make a thing very small, which does what we want—that we can manufacture an object that maneuvers at that level! " E.g. motor that rotates on a carbon nanotube shaft. Tiny molecular/biomotors have been constructed, but which operate on very different principles from the motors humans build.

- **Miniaturizing computer components → supercomputers**

"For instance, the wires could be 10 or 100 atoms in diameter . . .. If they had millions of times as many elements, they could make judgments . . . ." See COMS presently, 7nm node or results of molecular electronics, also achived possibilites as Deep Mind in GO (2016).



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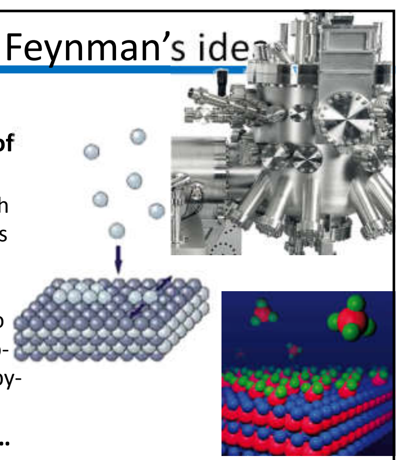
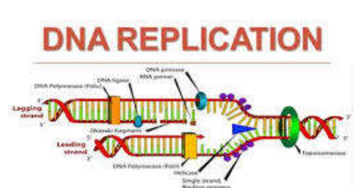
Nanotechnology today, Following Feynman's ideas

„There is plenty of room at the bottom"

- **Making atomic scale structures by evaporating layers of atoms (MBE, ALD):**
  "So, you simply evaporate until you have a block of stuff which has the elements . . . What could we do with layered materials with just the right layers?" **Molecular beam epitaxy** (MBE) layers of atoms are formed by projecting hot vapors onto a substrate in UHV. Different types of atoms can be projected to form layered structures with nanometer thickness. → See top-down. **Atomic layer depostion** (ALD): grow e.g. oxides layer-by-layer → See bottom-up, also van der Waals heterostructures
- **Manufacturing: machines that make machines and so…**
  "I let each one manufacture 10 copies, so that I would have a hundred hands at the 1/16 size." This idea, of making small machines, that make more even smaller machines etc. (Gray goo) Is not realised, but exponential growth through copying copies is what lies behind the amazing polymerase chain reaction, the biochemical process that yields macroscopic amounts (micrograms) of identical copies of just one DNA molecule. → see example later



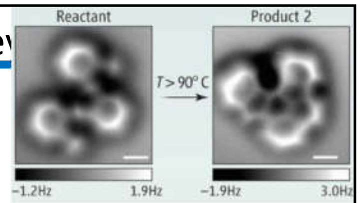


After Lindsay: Intro. to Nanosicence Section 1.3

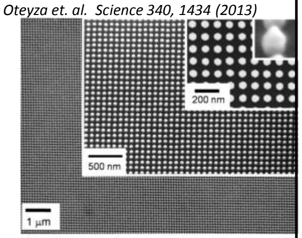
Nanotechnology today, Following Fe[…]

„There is plenty of room at the bottom"

- **Doing synthesis of complex organic molecules by "pushing atoms together":** *"We can arrange atoms the way we want."* With the invention of STM, we can image molecules and even induce reactions by pushing → See tools of nano
- **Resonant antennas for light emission and absorption:** *"It is possible to emit light from a whole set of antennas, like we emit radio waves."* This is the modern field known as "nanophotonics." For example, arrays of nanoparticles can be used to guide light. → See optics part
- **Using quantum phenomena in electronic devices:** *"We could use, not just circuits, but some system involving quantized energy levels, or the interaction of quantized spins."* Quantum mechanics offers us completely novel ways to do computations. Massive parallel computing based quantum entanglement. Field of Quantum Computing. QuantumManifesto 2017-2027. →See new concept in electronics

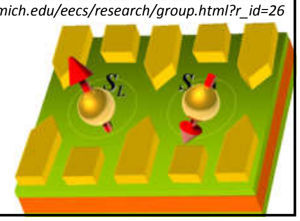


(Up) STM image of covalent bond structure of a chemical reaction on surface, Oteyza et. al. Science 340, 1434 (2013)



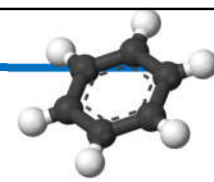
Site-controlled gallium nitride based (AlInGaN) quantum dots can enable novel applications in optoelectronics, nanoelectronics, and quantum information processing. These quantum dots, fabricated by metal-organic chemical vapor deposition, are optically active at room temperature.

https://www.cse.umich.edu/eecs/research/group.html?r_id=26&g_id=66

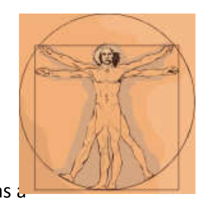


After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology



Nanotechnology:
Manipulation of matter with at least one dimension sized from 1 to 100 nanometers
Multidisciplinary field including physics, chemistry, biology and engineering.
Various applications: nanoelectronics, biomaterials, nanomedicines, energy production…, toxicity.



How small is nano?
Incredibly different scale: 1nm = 10^{-6}mm Thus a 1cm^3 = 10^{21} nm^3 Conversion between macro and nanoworld is ~ Avogadro-number
E.g. Caesar's last breath: 15th March -44. 1l of gas = 0.05mol of N_2 . Earth atmosphere has a mass of 10^{18}kg with 80% of N_2. I.e. it has 10^{20} mol of N_2. If N_2 from Ceasar's last breath diffused evenly through the atmosphere, we inhale all the time 10 molecule of Caesar's last breath!

Size matters in other way as well… - Length scales
Electronics, optics, mechanics, fluidics, bio …

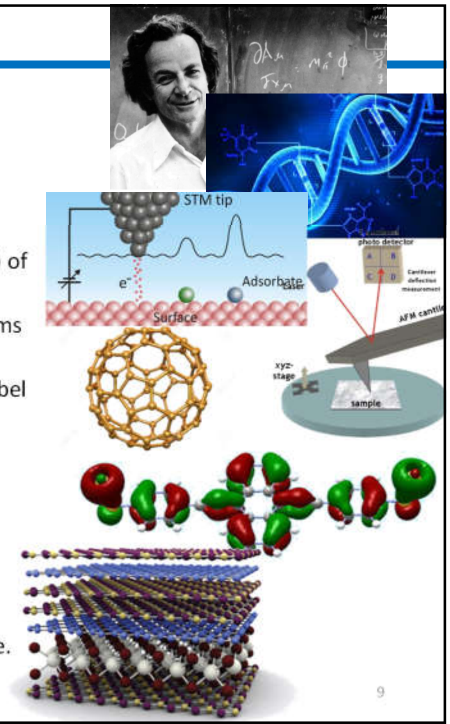
First example: Electronics
- Present status of CMOS
- Length scales in electron transport

Other examples…

History of nanotechnology

1959 An inspiration of Nano. Feynman famous talk There's Plenty of Room at the Bottom
1970 First sequencing of DNA
1974 N. Taniguchi has used first ‚nano-technology’
1981 STM unprecedented visualization (later manipulation) of individual atoms and bonds, (low cost tool) [Nobel 1986]
1986 AFM opened a way to explore chemical and bio systems as well
1985 Discovery of fullerenes → carbon nanostructures [Nobel 1996]
1990 DFT calculations get accurate by better exchange and correlation interactions. Various program packages.
2004 Graphene as the first 2D crystal extracted → van der Waals heterostructures [Nobel 2010]

Today nanotechnology is a common platform for modern physics, biology and chemistry. ‚Like’ plastic in everyday life.



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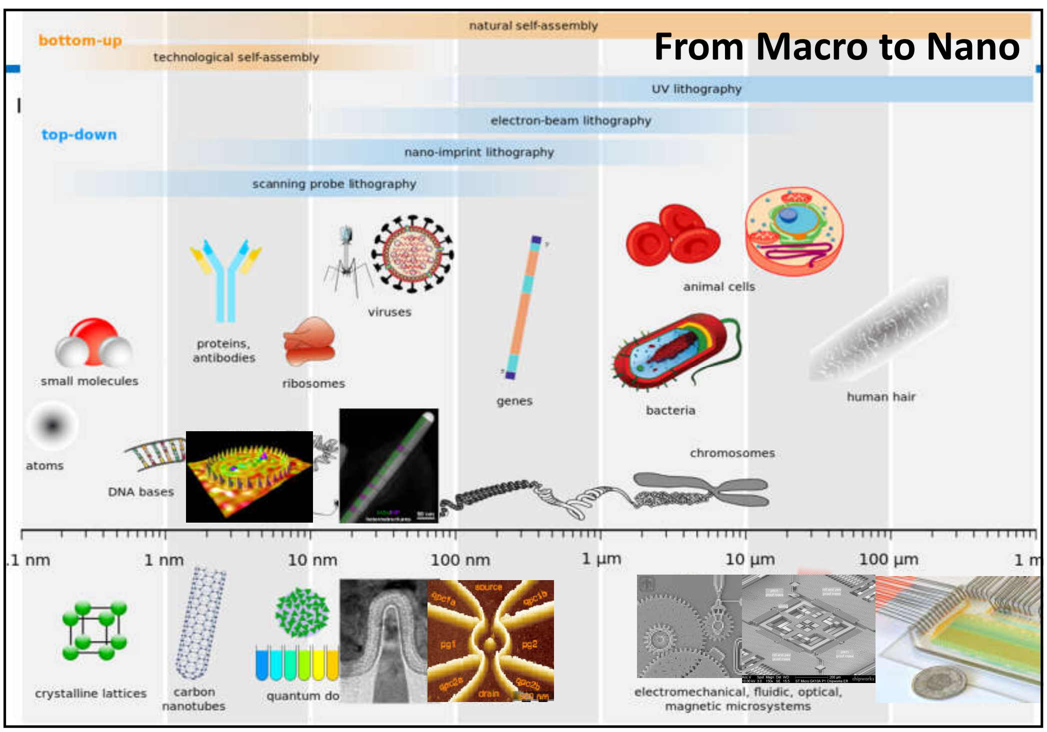
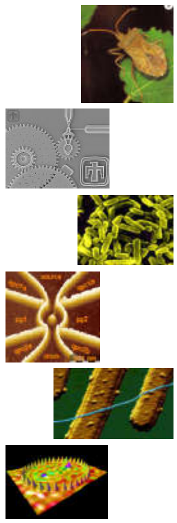
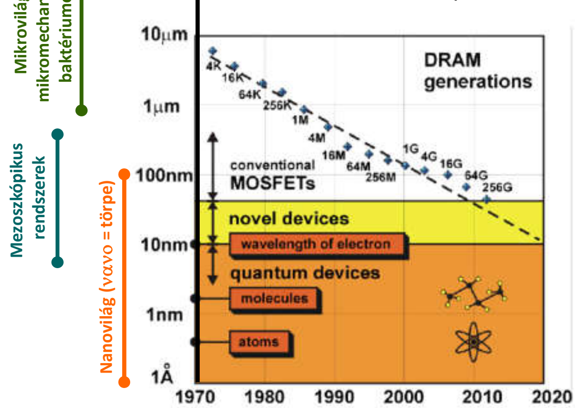
From Macro to Nano

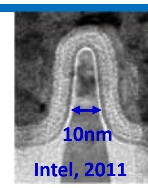


Moore's law, towards nano in electronics





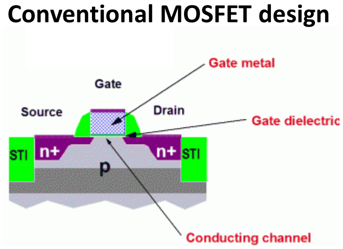
'Number of transistors on a chip doubles in every 18 months '



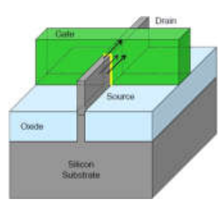
Gordon E. Moore,
Co-founder of Intel

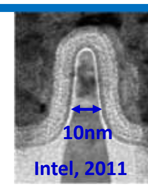
Intel MosFET

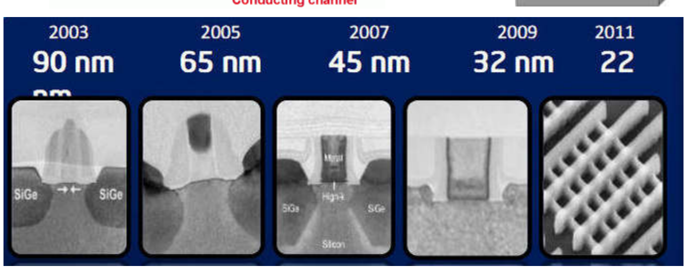
Conventional MOSFET design



22nm 3D Tri-gate technology

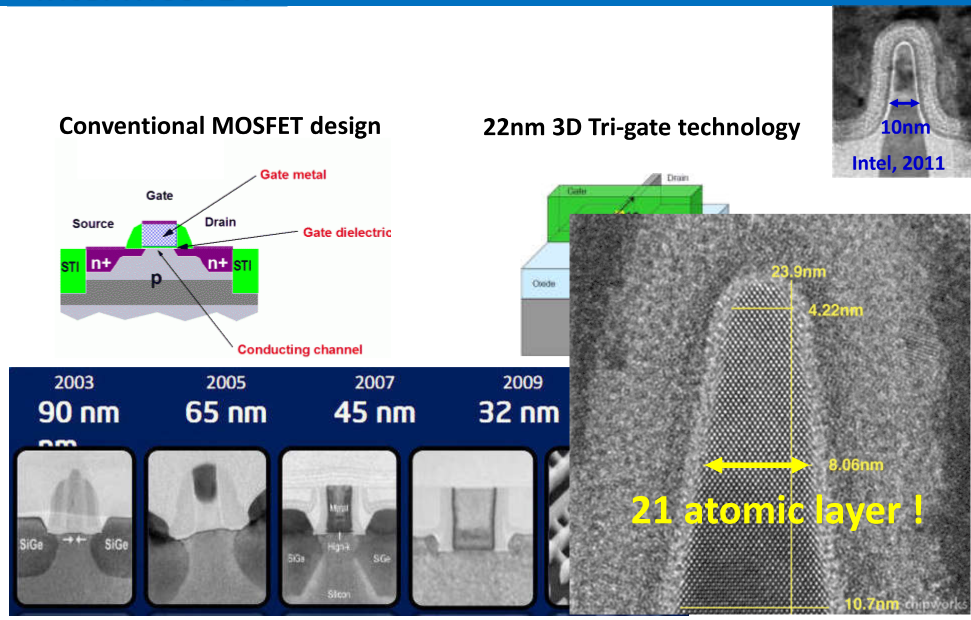






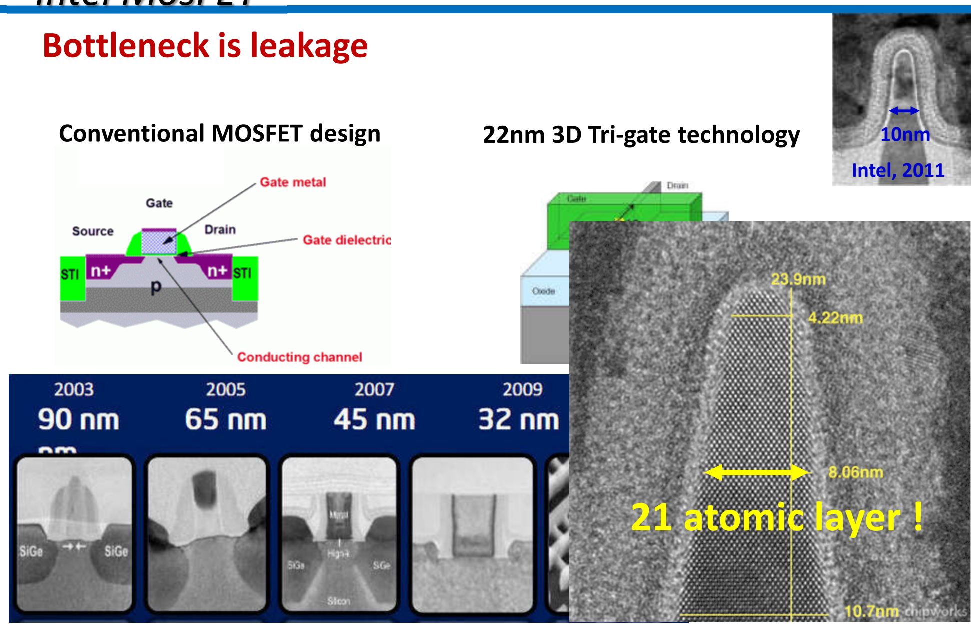
Gordon E. Moore,
Co-founder of Intel

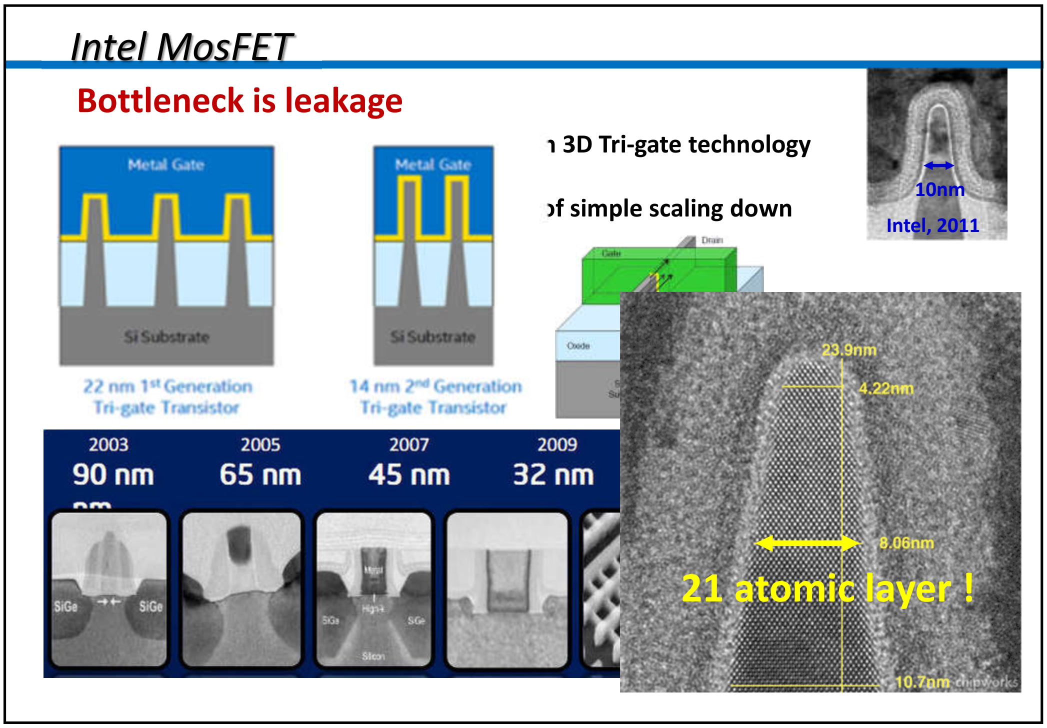
Intel MosFET

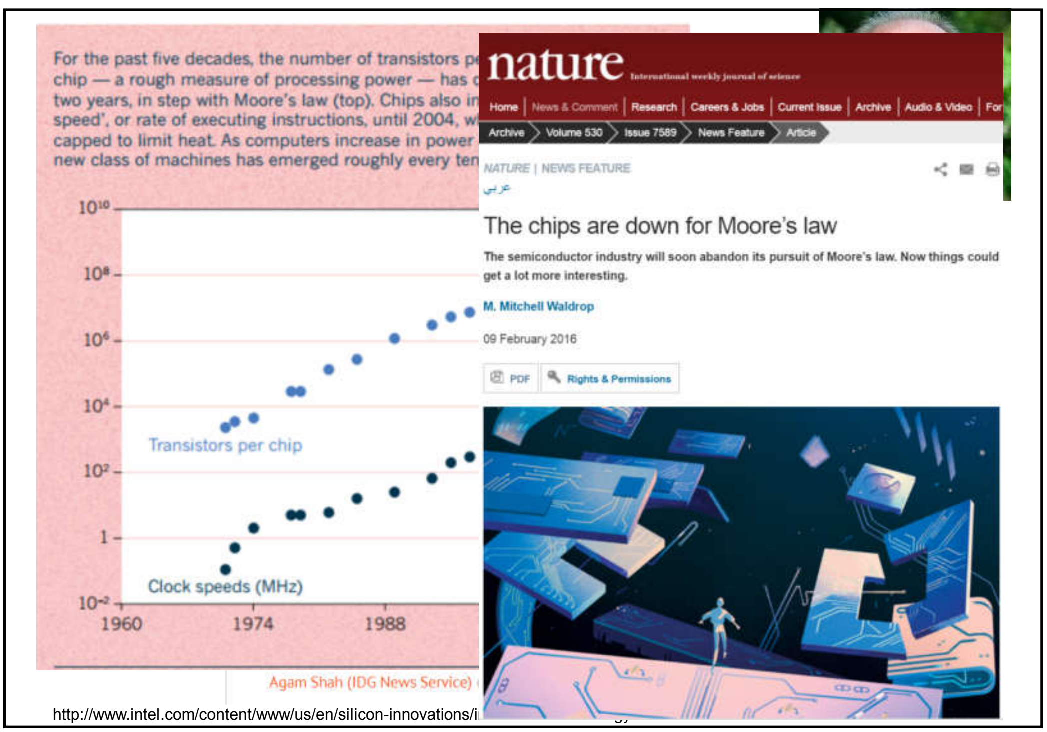


Intel MosFET

Bottleneck is leakage




Intel MosFET
Bottleneck is leakage
Metal Gate
Si Substrate
22 nm 1st Generation Tri-gate Transistor
14 nm 2nd Generation Tri-gate Transistor
3D Tri-gate technology
of simple scaling down
10nm
Intel, 2011
2003 90 nm
2005 65 nm
2007 45 nm
2009 32 nm
SiGe
23.9nm
4.22nm
8.06nm
21 atomic layer !
10.7nm


For the past five decades, the number of transistors p
chip — a rough measure of processing power — has
two years, in step with Moore's law (top). Chips also in
speed', or rate of executing instructions, until 2004, w
capped to limit heat. As computers increase in power
new class of machines has emerged roughly every ten
Transistors per chip
Clock speeds (MHz)
1960
1974
1988
Agam Shah (IDG News Service)
http://www.intel.com/content/www/us/en/silicon-innovations/i
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NATURE | NEWS FEATURE
The chips are down for Moore's law
The semiconductor industry will soon abandon its pursuit of Moore's law. Now things could get a lot more interesting.
M. Mitchell Waldrop
09 February 2016
PDF
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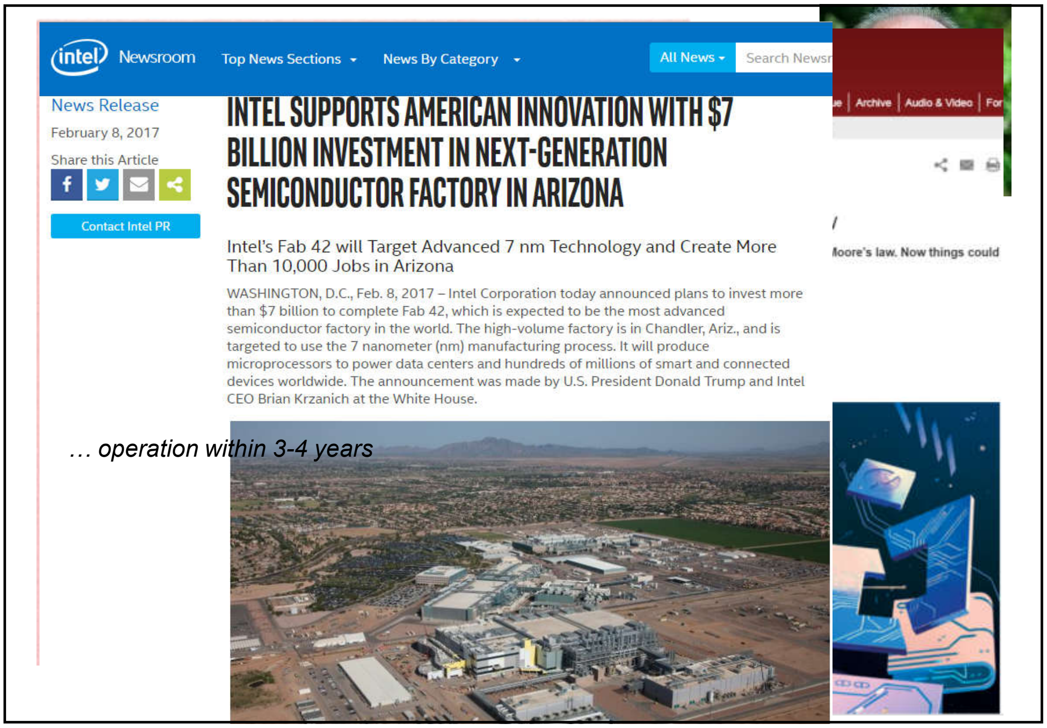
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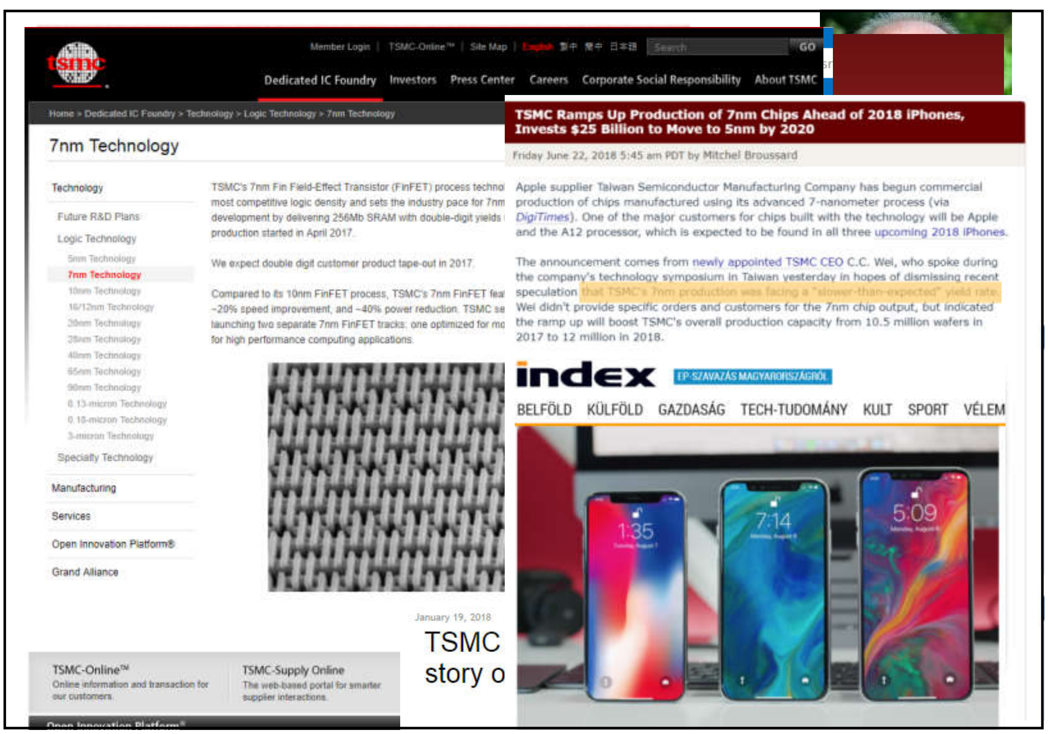
INTEL SUPPORTS AMERICAN INNOVATION WITH $7 BILLION INVESTMENT IN NEXT-GENERATION SEMICONDUCTOR FACTORY IN ARIZONA
Intel's Fab 42 will Target Advanced 7 nm Technology and Create More Than 10,000 Jobs in Arizona
WASHINGTON, D.C., Feb. 8, 2017 – Intel Corporation today announced plans to invest more than $7 billion to complete Fab 42, which is expected to be the most advanced semiconductor factory in the world. The high-volume factory is in Chandler, Ariz., and is targeted to use the 7 nanometer (nm) manufacturing process. It will produce microprocessors to power data centers and hundreds of millions of smart and connected devices worldwide. The announcement was made by U.S. President Donald Trump and Intel CEO Brian Krzanich at the White House.
… operation within 3-4 years
Archive
Audio & Video
loore's law. Now things could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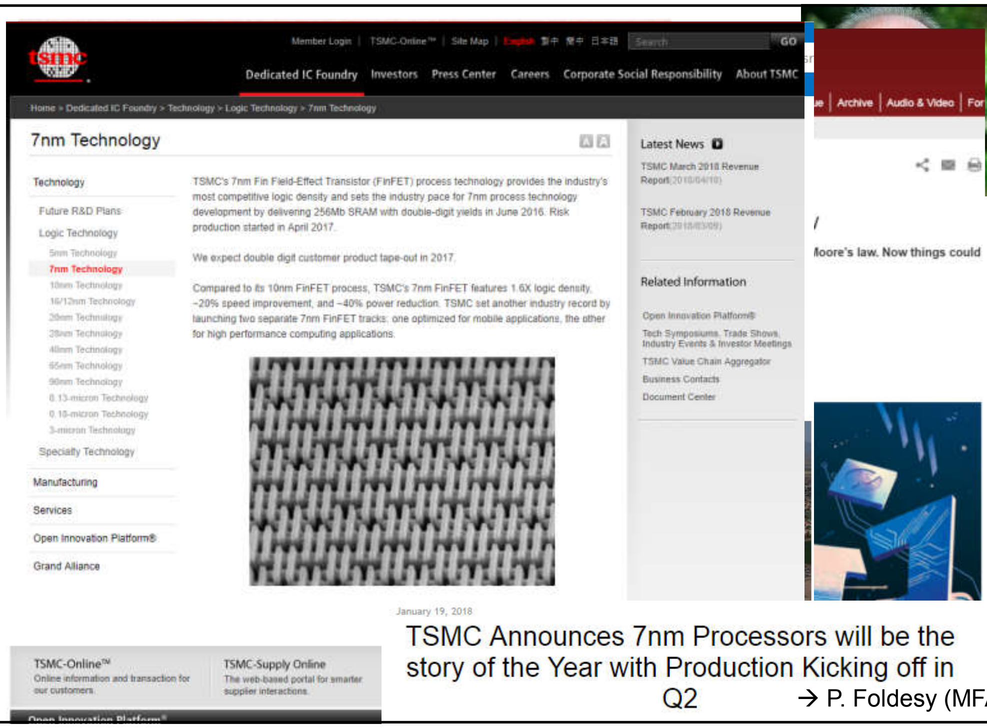
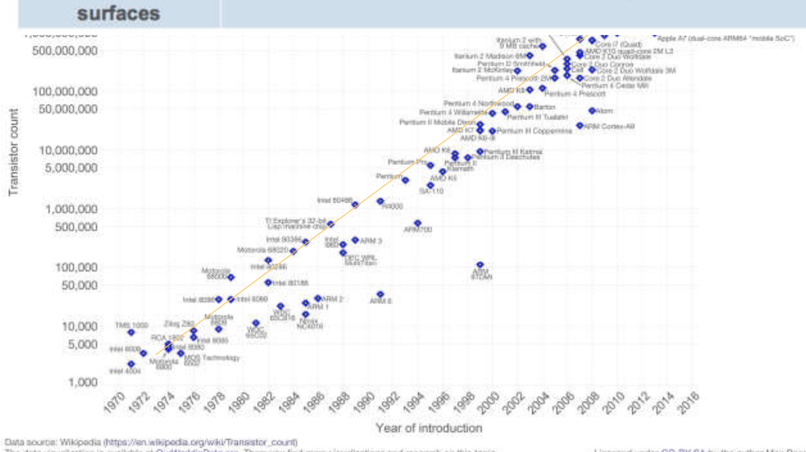
7nm Technology
Technology
Future R&D Plans
Logic Technology
5nm Technology
7nm Technology
10nm Technology
16/12nm Technology
20nm Technology
28nm Technology
40nm Technology
65nm Technology
90nm Technology
0.13-micron Technology
0.18-micron Technology
3-micron Technology
Specialty Technology
Manufacturing
Services
Open Innovation Platform®
Grand Alliance
TSMC's 7nm Fin Field-Effect Transistor (FinFET) process techno
most competitive logic density and sets the industry pace for 7nm
development by delivering 256Mb SRAM with double-digit yields
production started in April 2017.
We expect double digit customer product tape-out in 2017.
Compared to its 10nm FinFET process, TSMC's 7nm FinFET fea
~20% speed improvement, and ~40% power reduction. TSMC se
launching two separate 7nm FinFET tracks: one optimized for mo
for high performance computing applications.
January 19, 2018
TSMC
story o
TSMC-Online™
Online information and transaction for our customers
TSMC-Supply Online
The web-based portal for smarter supplier interactions
TSMC Ramps Up Production of 7nm Chips Ahead of 2018 iPhones, Invests $25 Billion to Move to 5nm by 2020
Friday June 22, 2018 5:45 am PDT by Mitchel Broussard
Apple supplier Taiwan Semiconductor Manufacturing Company has begun commercial production of chips manufactured using its advanced 7-nanometer process (via DigiTimes). One of the major customers for chips built with the technology will be Apple and the A12 processor, which is expected to be found in all three upcoming 2018 iPhones.
The announcement comes from newly appointed TSMC CEO C.C. Wei, who spoke during the company's technology symposium in Taiwan yesterday in hopes of dismissing recent speculation that TSMC's 7nm production was facing a "slower-than-expected" yield rate. Wei didn't provide specific orders and customers for the 7nm chip output, but indicated the ramp up will boost TSMC's overall production capacity from 10.5 million wafers in 2017 to 12 million in 2018.
index
EP-SZAVAZÁS MAGYARORSZÁGRÓL
BELFÖLD
KÜLFÖLD
GAZDASÁG
TECH-TUDOMÁNY
KULT
SPORT
VÉLEM
1:35
7:14
5:09



TSMC Announces 7nm Processors will be the story of the Year with Production Kicking off in Q2 → P. Foldesy (MFA)

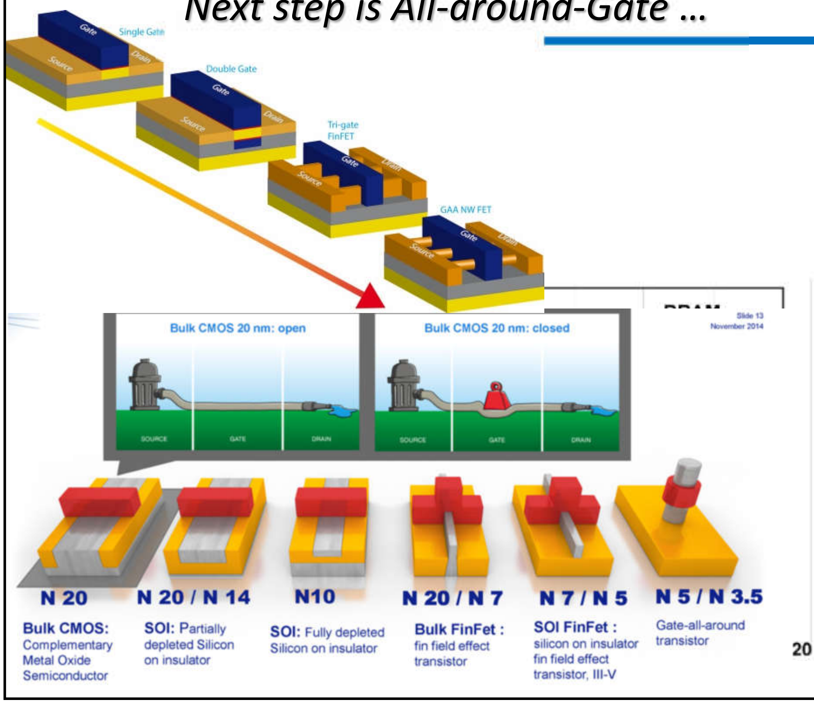
Ref: S.C. Song, Qualcomm; V. Moroz, Synopsys

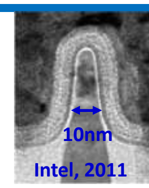
Traditional FinFET	Round/Square Wire	Horizontal Nanoslab/sheet/ multi-bridge channel	Hexagonal Nanowire	Nano-Ring
Three control surfaces	Four/All Around Control Surfaces Per Channel			



Gordon E. Moore, Co-founder of Intel

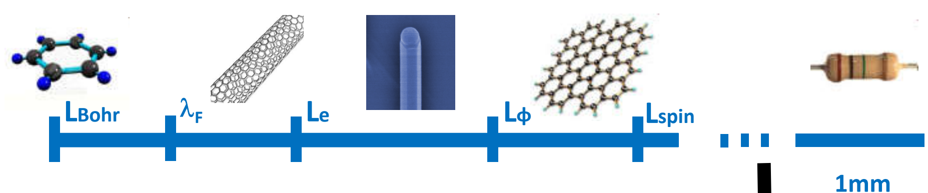
Next step is All-around-Gate …





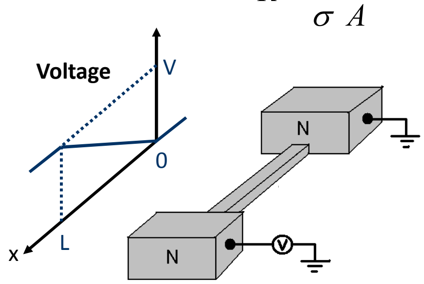
Gordon E. Moore, Co-founder of Intel

Length scales in electronics



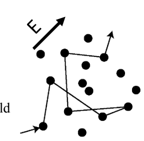
Macroscopic conductor

Ohm's law, Resistance $R = \frac{1}{\sigma}\frac{L}{A}$



Drude – model (1900)

$$\left[\frac{d\mathbf{p}}{dt}\right]_{\text{scattering}} = \left[\frac{d\mathbf{p}}{dt}\right]_{\text{electric field}}$$



average drift velocity

$$\frac{m\mathbf{v}_d}{\tau_m} = e\mathbf{E} \Rightarrow \mathbf{v}_d = \underbrace{\frac{e\tau_m}{m}}_{\text{mobility } (\mu)}\mathbf{E}$$

$$\mathbf{j} = ne\mathbf{v}_d = ne\mu\mathbf{E} \Rightarrow \sigma = ne\mu = \frac{ne^2\tau_m}{m}$$

L_e : elastic scattering length, distance between scattering events

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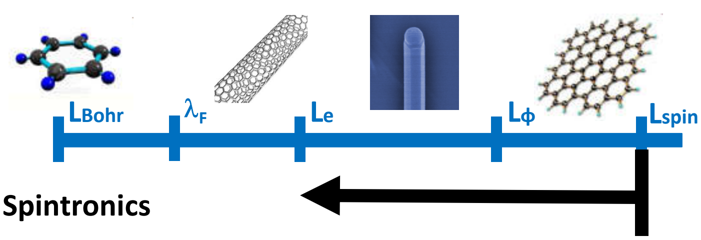
See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

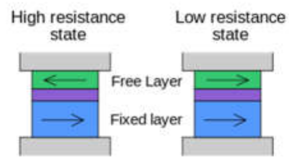
Length scales in electronics

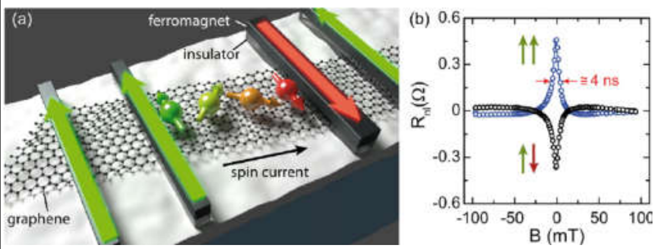
See Wikipedia: Spin valves, GMR effect



Spintronics

L_{spin}: spin relaxation length.
When size is < L_{spin} , the spin information of electron is not lost during travelling through.



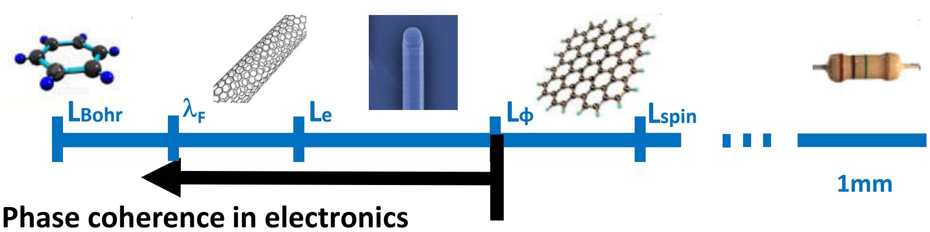


http://iopscience.iop.org/article/10.1088/2053-1583/2/3/030202/meta (2016)

(Up) Spin valve devices used in hard disk reader head as a spintronics device (Left) Graphene based spin valve, where ferromagnetic leads with magnetization pointing up (green) and down (red) are used to inject spin polarized current, which propagates thorugh graphene for several μm distances. (b) Influence of perpendicular B field, measured in non-local geometry.

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

Length scales in electronics

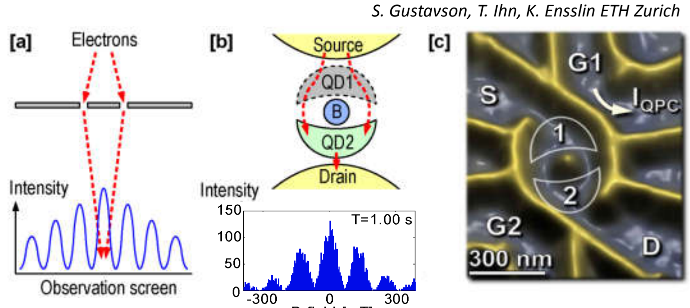


Phase coherence in electronics

L_ϕ: Phase coherence length When size is < L_ϕ phase coherent processes could take place. E.g. qunatum interference.

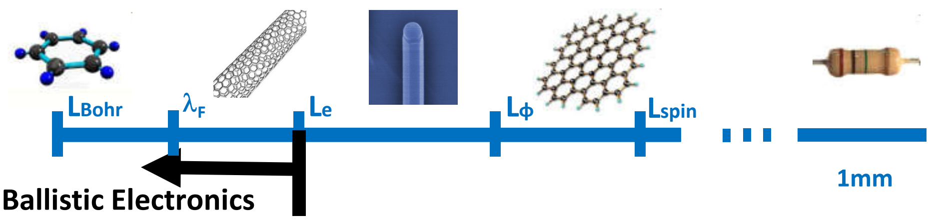
S. Gustavson, T. Ihn, K. Ensslin ETH Zurich

(a) Typical optical interference setup with two slits. (b) An analog interferometer for electrons. There are two paths where electrons can get from source to drain electrode. Phase difference between the two paths is induced by magnetic field. (i.e. Aharonov- Bohm effect) (c) Realization of the interferometer device in 2DEGs with AFM litography. Intensity corresponds to the transferred electrons, it is measured by QPC.



See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

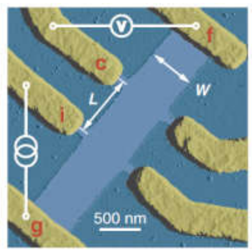
Length scales in electronics

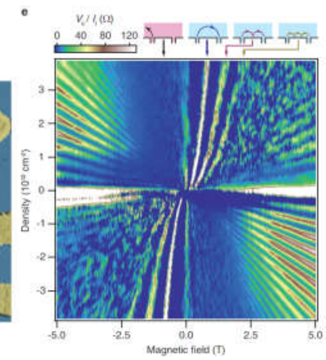


Ballistic Electronics

L_e: Elastic mean free path When size is < L_e , electrons propagate via the system without scattering. They have ballistic motion.

(Left) Ballistic graphene device, where graphene is stacked between hBN layers. Contacts are yellow, graphene is smooth blue region with a width of w.
(Right) ***Transfer magnetic focusing in graphene.*** *Electrons follow a circular trajectory in magnetic field, which sends electrons from contact to the other when the cyclotoron radius properly set.*

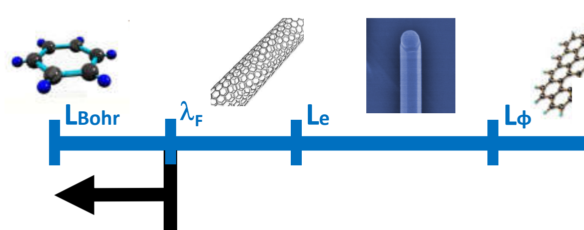


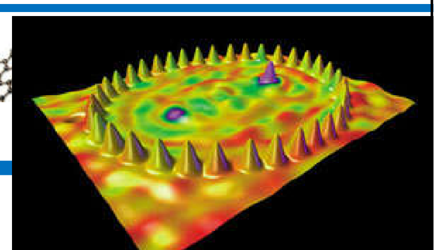


T.Taychatanapat et. al. , Nature Physics 9, 225 (2013)

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

Length scales in electronics

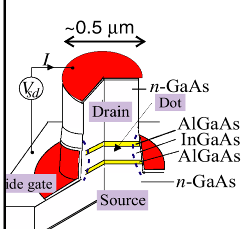


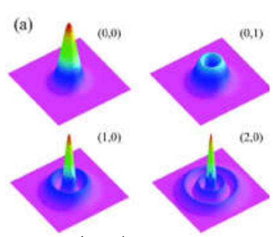


Manoharan, Lutz, Eigler, IBM ***Almaden (2000)***

Full quantum mechanical description

λ_F: Fermi wavelength When size is < λ_F L_ϕ electrons occupy separated discrete states linked to wavefunctions.





Kouwenhoven, Rep. Prog. Phys. 64, 701 (2001)

(Up) Quantum mirage: Electronic state of a Co atom (placed in a focal point of an ellipse) is projected to a remote location to the other focal point by the Cu atoms forming a corral. Created by manipulation atoms one-by-one with STM and performing STM measurements.

(Left) Artificial atoms Small confinement potential is generated in the InGaAs region with disk like shape in the semiconductor heterostructure. This confinement acts like an atom, in which fixed number of electron (few) is confined. Probability profile of the discrete wave functions solved for the cylindrical confinement.

See more details in A. Palyi: Quantumelectronics, Halbritter, Csonka: Fundamentals of Nanoelectronics

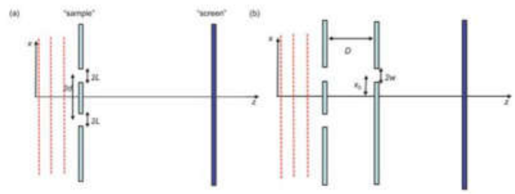
Near-field scanning optical microscopy (NSOM)

Resolution of optical microscope limited by λ
Nano objects can effect EMF on scale << λ
E.g. small opening with d<< λ. But evanescent field still gets through. NSOM probe this.
See example: a) Double slit experiment → diffraction pattern
b) Add an extra small sub-λ aperture (w<< λ) close by (i.e. z<< λ) and move its position → Double slit with sizes <<λ can be resolved.

Tip, aperture or particle in the near field of the sample can scatter the evanescent component into propagating component that survives to far field.

Contrast is system dependent.

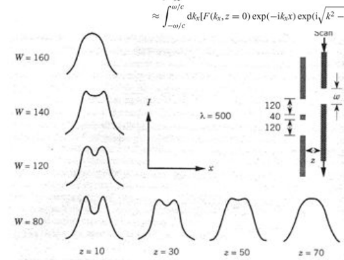
Principle of operation: small aperture very close to a double slit



Diffraction pattern for a double slit (Fourier transformation of slits)

$$F(k_x, z=0) = \int_{d-L}^{d+L} E_0 \exp(ik_x x)dx + \int_{-d-L}^{-d+L} E_0 \exp(ik_x x)dx$$
$$= 4E_0 \cos(k_x d)\frac{\sin(k_x L)}{k_x},$$

$$E(x,z) = \int_{-\infty}^{+\infty} dk_x[F(k_x, z=0)\exp(-ik_x x)]\exp(ik_z z)$$
$$\approx \int_{-\omega/c}^{\omega/c} dk_x[F(k_x, z=0)\exp(-ik_x x)\exp(i\sqrt{k^2-k_x^2}z)],$$

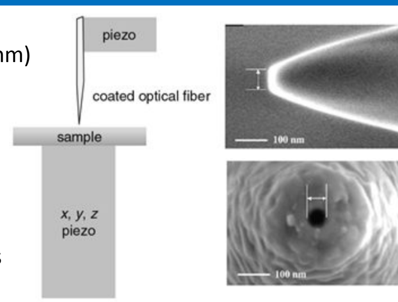


See Natelson Section 4.1.6 and 8.5
Wikipedia: NSOM

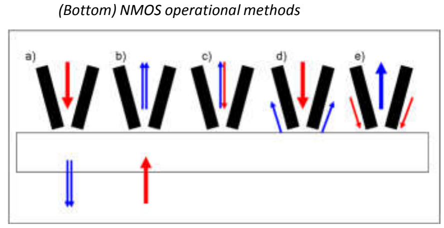
Near-field scanning optical microscopy (NSOM)

Setup:
- Coated optical fiber with a subwavelegth aperture ($\propto$10nm)
- Piezo positioning of the sample to achieve nm lateral resolution
- Tip-sample distance is kept constant by tuning fork like AFM configuration

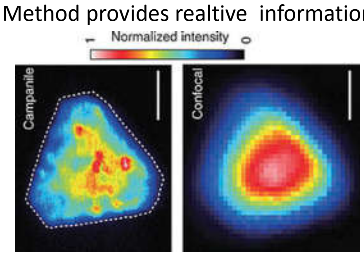
Various operation modes:
a) Illumination b) Collection c) Illumination/collection
d) Reflection e) Reflection/collection f) Aperture less modes (e.g. tip, metal particle)….
Used for biology, photonic chrystals, plasmonic structures



(Top left) Setup of NMOS, (Top right) End of optical fiber tip (Bottom) NMOS operational methods



Method provides realtive information.

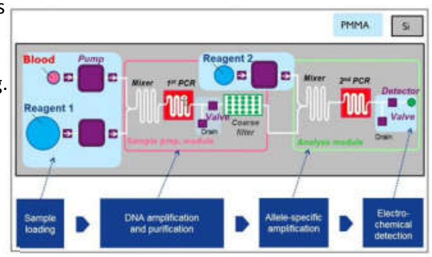


Example: Comparison of photoluminescence maps recorded from a MoS_2 flake using NSOM with a campanile probe (left) and conventional confocal microscopy (right). Scale bars: 1 μm

See Natelson Section 4.1.6 and 8.5
Wikipedia: NSOM

Micro-fluidics ‚Lab-on-chip'

(Top) lab-on-chip (LOC) devices that can be used at the "point of need." (Bottom) Sscheme of a silicon based LOC device for Blood testing



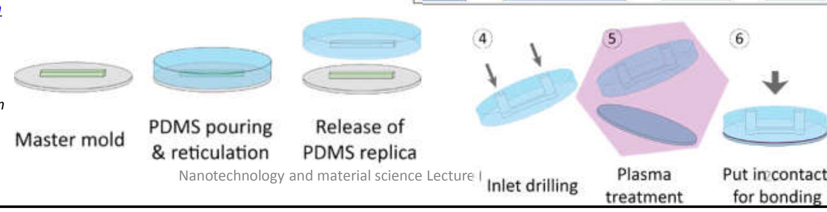
Simple example**: inkjet printers** micron scale droplets of ink through a microfabricated array of orifices. *(see P. Furjes' talk on MEMS)*

Future goal, "lab-on-a-chip" technologies:
More complex systems, enabling the circulation, routing, mixing, and storage of small quantities of fluids on demand, microfluidic systems can perform complex chemical and biochemical procedures using much more reduced amounts of analytes or reactants than traditional, "full size" bench approaches.
If mass production is cheap --> revolutional medical diagnostics (e.g. DNS check similar to pregnant test)

Typically based on planar semiconductor fabrication (similar to MEMS) or recently soft lithographic techniques involving PDMS. **Replica molding of various PDMS layers** on top. → cheap thus revolutional for LOC.

See
http://www.meddeviceonline.com/doc/silicon-a-material-with-huge-potential-for-lab-on-chips-0001
http://www.elveflow.com/microfluidic-tutorials/microfluidic-reviews-and-tutorials/the-poly-di-methyl-siloxane-pdms-and-microfluidics/

(Bottom) Fabrication of PDMS based microfluidics



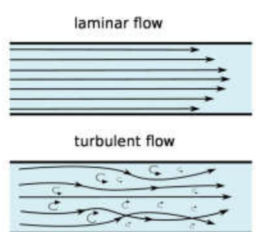
Micro-fluidics ‚Lab-on-chip'

(Top) While a macro scale swimmer can coast in water micron scale one can not!

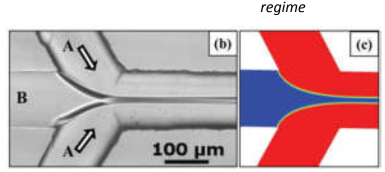
Reynold number (Re): ratio of inertial force and viscous forces
- Re large : turbulent flow, -Re small: laminar flow

Macroscopic world is in the **large Re** limit.
Consequences: Two examples:
- mixing coffee with milk is fast
- during swimming we can coast. (Momentum is enough to overcome comparatively weak viscous drag forces)

Micro and nano world is in **low Re** limit.
- Laminar flow → no turbulences. Mixing fluids is based on slow diffusion at interface. → challanging to mix fluids efficiently in micro-fluidic systems. Challenges for chemical or bio reactions
- Swimming for a bacterium. Its size ~1μm, initial velocity v ~30μm/sec, Re~ 10^{-5} . Coasting distance: 1nm!



(Left) Velocity profile of low Re, laminar flow typical in microfluidics system. And of high Re turbulent flow.
(Bottom) Special microfluidic arrangements for mixing liquids, which based on flow focusing. A liquid of interest may be "squeezed" down hydrodynamically to small (tens of nanometers) transverse dimensions. This small flow width leads to diffusive mixing times across the flow down to the microsecond regime



See Natelson Section 10.1 and 10.6, 10.7

Magnetic separation at nanoscale

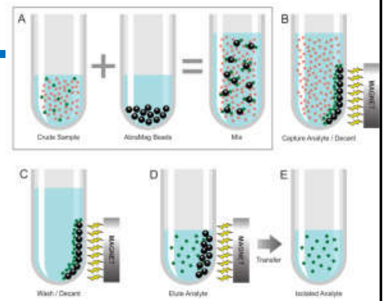
A multiple example showing differences at nanoscale

It is used for capturing or purifying e.g. proteins, antibodies, or DNA from diverse biological samples.

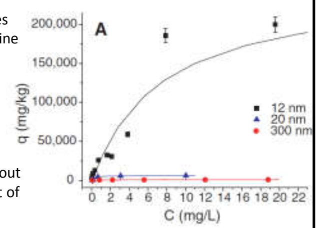
Principle: Targeted analyte connects to functionalized magnetic particles and removed by magnetic field gradient. Micron sized magnetic beads are widely used in biology

Recently magnetic nanoparticles can be synthesized chemically. Much larger surface! → Increased efficency.

However **issues at nanoscale**: force of B field ~ volume, viscous force ~ diameter, fluctuations i.e. Brownian motion ~$k_B T/d$. → Nanoscale is not preferable.
Still it works for 10nm scale particles with better sensitivity. . Reasons: a) Single domain particles -> large stray field ~M_{sat}/d and b) large interparticle force which order neighbouring particles → collective response of particles



(Up) Principle of magnetic separation. Functional magnetic beads are added to mixture under investigation (A) Mix beads (black spheres) with crude sample (red Xs) containing desired analyte (green squares); (B) capture analyte-bound beads with magnet; (C) wash away crude sample components; (D) elute analyte from beads; (E) transfer to new tube.
http://www.abraxiskits.com/products/magnetic-beads/



(Down) Arsenic adsorption studies with nanocrystalline (12 nm) and commercially available (20 and 300 nm) Fe3O4. 1000 times less 12nm scale NP is required to filter out the same amount of arsenic.

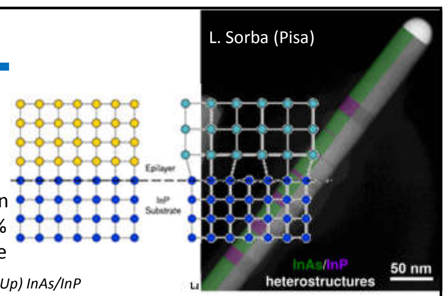
See Natelson Section 7.7

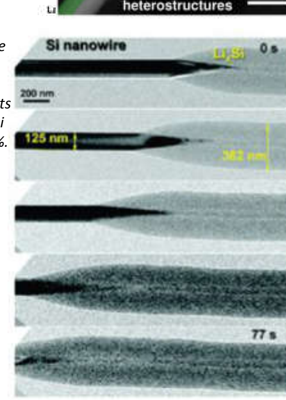
Cafer T. Yavuz Science 314, 964 (2006) DOI: 10.1126/science.1131475

Mechanics at nanoscale

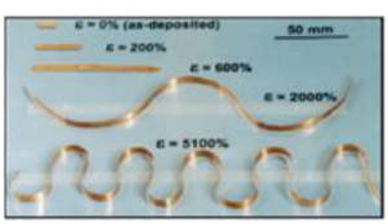
Examples:
Easier to accommodate strain at nanoscale…
- Novel heterostructures: Possible to relax lattice mismatch at nanoscale. E.g. InAs/InP heterostructures
- Huge strain before failure E.g. intercalation of lithium into silicon NWs for potential chargeable battery option. Strains up to 200% is possible! Nanowires can respond much more reversibly to the distortions associated with lithiation and delithiation

Superplasticity
Plastic deformation happens with displacement of dislocations
When grain size smaller than the length scale of formation/ propagation of dislocations (i.e. at the nanoscale) → different plastic deformation properties. Grain bonderies dominate.





(Up) InAs/InP heterostructures in nanowires, possible due to lattice mismatch relaxing at nanoscale.
(RIght) Si nanowire as its size increasing during Li intercalation over 200%. A reversible process.

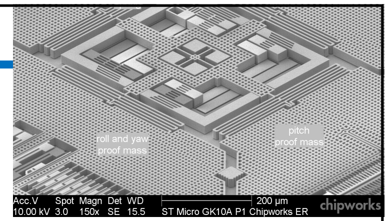


Superplasticity of nanocrystalline Cu: When grain size becomes small, significant fraction of atoms are at grain boundaries, remarkable deformations can be possible. See elongation over 5000%.

See D. Natelson Section 9.1.4

L. LU et al. ADVANCED ENGINEERING MATERIALS 2001, 3, No. 9, 663

NEMS/MEMS systems

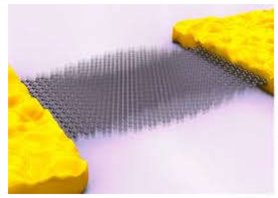


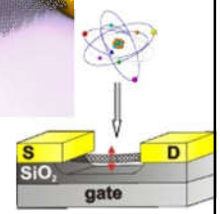
Nano/micro electro mechanical systems
Various applications: automative systems,sensing, electronics etc.
Huge market.

Planar techniques for semiconductor manufacturing.
Limited fabrication paths and materials

Used for: cantilevels, Inertial sensing, mass sensing, inkjet head, …

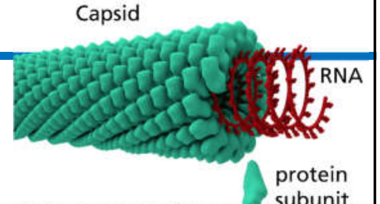
NEMS goals: ultimate limit of mass (or force) sensing, e.g. to detect a molecule by its mass.
Resonance freq: $f=\sqrt{D/m}$ → To increase mass sensitivity: m↘ , D↗ and also Q should be large.
Use: Carbon nanotubes or graphene
Achived resolution 1.7 yg (1 yg = 10^{-24} g) (2012) Mass of one proton.





Chastle Nature Nanotecnology **7**, 301–304 (201
See D. Natelson Section 9.4

BioNanoTechnology



(Up) Example of a virus goemetry. Tobacco mosaic virus. It has a helical protein shell (called capsid), which encloses the genetic material (RNA).

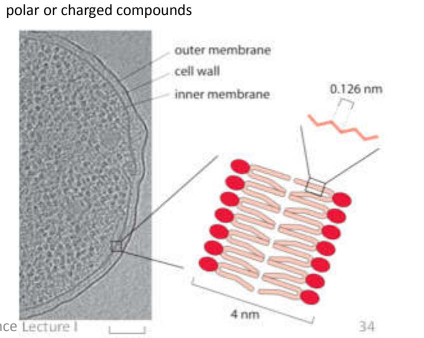
Biology operates truly at the nanoscale
There are nanoscale machines in our cells, e.g. they fabricate complex structures (molecules), they can act as motors, pumps, transducers to mechanical energy. Biological systems can build up complex structures from nano to macro scale.

Typical objects and their sizes
Viruses: E.g. Tobacco mosaic virus 18nm in diameter and 300nm long
Cells: their wall are at the ~10nm scale
Ion transporters, pumps etc.

Molecules and their interaction governed by electrostatic, van der Waals, hydrogen bonding & hydrophobic interactions at k_BT.

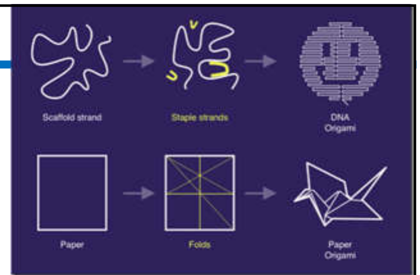
(Left) Sodium-potassium pump: It is an enzyme, which pumps sodium (Na) out of cells while pumping potassium (K) into cells, both against their concentration gradients.It as active element using energy from ATP. One of its application: nerve conduction.

(Down) Electron micrograph of a cell, with its wall. The membranes consist lipid bilayers. Red circle denotes the hydrophilic head, the pink lines represent the hydrocarbon chains forming a tight hydrophobic barrier excluding water, polar or charged compounds



Source: Wikipedia
http://book.bionumbers.org/what-is-the-thickness-of-the-cell-membrane/
See D. Natelson Section 11.1

Copying Biology…

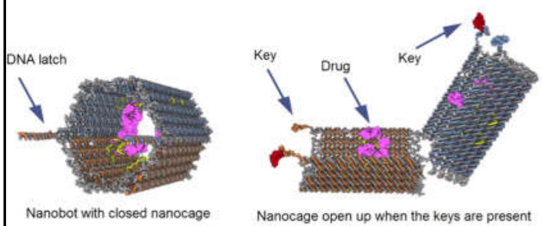


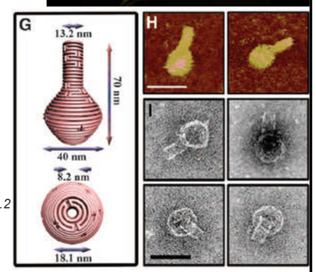
I. example: DNA origami

Nanoscale folding of DNA to create non-arbitrary two- and three-dimensional shapes at the nanoscale. Based on well established knowledge of DNA structures and possibility to set arbitrary base sequences, which then determines interactions and final shape. There are multiple smaller "staple" strands, which bind the longer in various place. First staples are designed by a program, then DNA is mixed, neated and cooled. During cooling, the various staples pull the long strand into the desired shape.

True **bottom-up self-assembly method**, which is considered promising alternatives that offer cheap, parallel synthesis of nanostructures under relatively mild conditions.
Possible to do 3D structures, used e.g for drug delivery.

(Up) Principle of DNA origami, (Right) Realization of 2D and also 3D structures (Bottom) Smart DNA nanobot for drug delivery, which opens and closes. The aim is to attack cancer cells. Size:35nm in width.

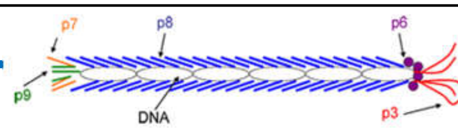




See D. Natelson Section 11.2.2
Source: Wikipedia

https://ninithi.com/2015/08/20/smart-dna-nanobots-mount-a-deadly-attack-on-cancer-cells-first-human-trial-this-year/

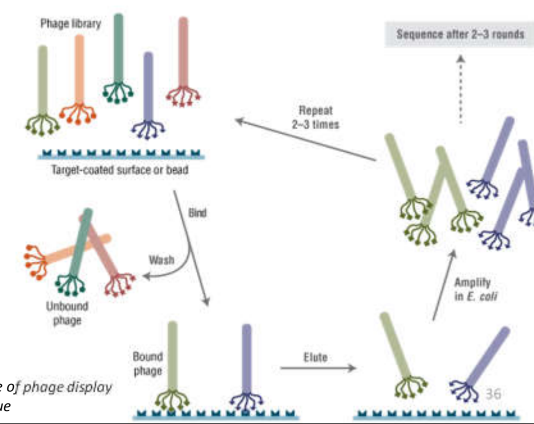
Copying Biology…



II. example: Virus enabled synthesis and assembly

Idea: Biological systems use proteins to manipulate inorganic materials like patterning bones, seashells. Try to program it do for us. **Phage display technique:**
Bachteriphages viruses pray upon bacteria
Special one called M13. Diameter 9nm Length 900nm. It contains a single DNA with 6407 bases, which encodes proteins that constitutes the phage's protein coat. It attracts E. coli bacteria, which reproduces them. Protein p3 is essential for binding to E. coli.
It is know which DNA segment codes the proteins in the coating. Try to modify them to have affinities to desired materials.

Procedure - bio amplification with spirit of evolution:
- Started with M13 with broad varying composites of P3 (or recently also P8) . - Expose test surface with desired material, - Wash away phages do not bind strongly, - Bound phages eluted separately and introduced to *E. coli* for reproduction for amplification,
- Repeat the process and DNA sequence the outcome. → try to understand binding mechanisms or motifs.

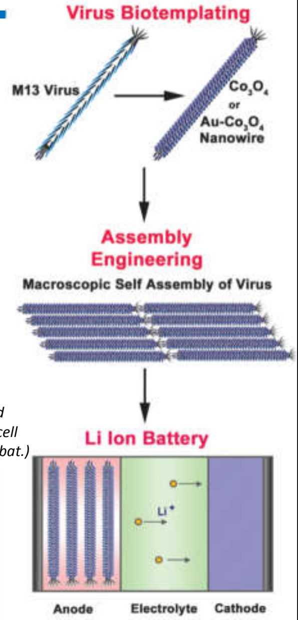


Principle of phage display technique

See D. Natelson Section 11.2.3 also Wikipedia

Copying Biology…

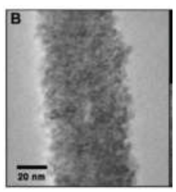
Principle of virus templated production of battery electrodes



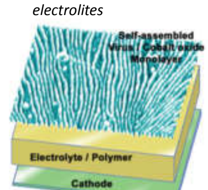
E.g.1: **Develop a library of peptides that bind selectively to semiconductors.** Start with 10^9 combinations of P3 . Genomes of best binders were analyzed to get trends. E.g. groups were found which selectively bind to GaAs(100) and not to Si.

E.g.2: **virus templated synthesis for electrodes of Li ion battery.**
Cobalt oxide has shown excellent electrochemical cycling properties and thus promising as an electrode for advanced lithium batteries. Try to use viruses and bio assembly to produce electrodes.
- Develop P8 with binding affinity for Co_3O_4 and Co_3O_4 -Au nanoparticles. → Cover M13 with Co_3O_4 and Co_3O_4 -Au .
- Two dimensional assembly of viruses on polyelectrolyte multilayers by liquid crystalline ordering → It works as a promising electrode with high surface area.

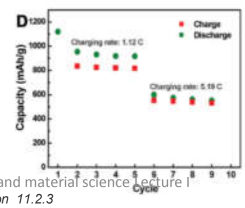
(Left) High resolution TEM image of a Co3O4 viral nanowire



(Down) AFM image of the naowire array on polimer electrolites



(Down) Capacity for the assembled monolayer of Co_3O_4 nanowires/Li cell (theoretical limit is 3800 for Li ion bat.)

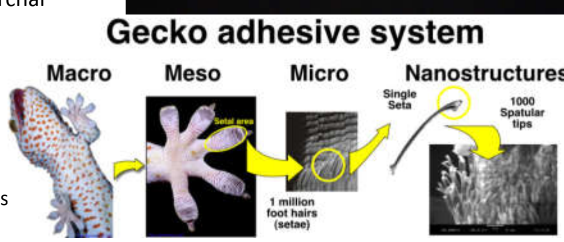


K.T. Nam et al. Science 312, 885 (2006)

See D. Natelson Section 11.2.3

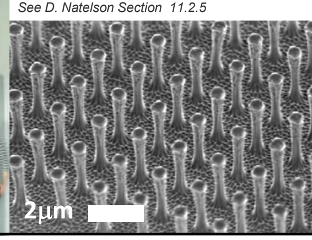
Copying Biology…

Gecko tape – Nanofabrication to mimic bio
Gecko's feet are coated with hear like structures (Seta scale ~µm) and all ended with nanoscale projections called spatulae.
Results in a remarkable adhesive property due to van der Waals and large contact area of this hierarchal structure. I.e. adhesion ~ $10 Ncm^{-2}$



Try to immitate with nanostructure. E.g. by using polimer nanorods (see image) or CNTs. Very strong reversible adhesion can be achieved.
See products e.g. nanoGripTech.com: Dry adhesives

See D. Natelson Section 11.2.5



(Top) Biological example, the micro and nanostructure of Gecko's feet.
(Left) Millions of synthetic setae from polimer nanorods and resulting adhesion experiment (Bottom) products from nanoGripTech

Chemistry at the nanoscale

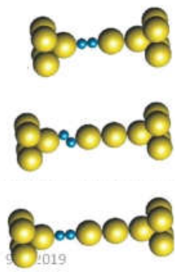
E.g. Nano-catalyst

- Role of Catalysts: - reduce the temperature of a transformation, -reduce reagent-based waste and - enhance the selectivity of a reaction → green chemistry

Catalysts play essential role in production of medicines, fine chemicals, polymers, lubricants …

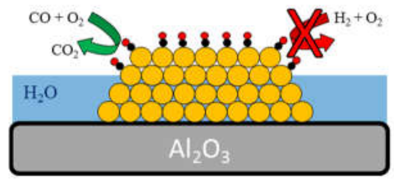
- Nano size: a) High surface to volume ration b) also different electronic and structural structure an nanoscale→ new chemical properies could show up.

Example1: Chemistry of gold. Au in bulk form know as chemically inert, but it has remarkable catalitic properties at nanoscale due to the the strongly modified electronic structure of gold nanoclusters /nanostructures as their size and/or dimensionality are reduced.



Example2:
H2 is important industrial product. However CO is also produced in such processes, which is highly undesired for e.g. ammonia production or in fuel cells. → Find a cheap way to remove CO down to 50pmm range. Way out: generate $CO+O_2$ → CO_2 reaction.

Au nanoparticles can catalyze $CO+O_2$ → CO_2 reaction while O_2+H_2→ HO_2 is efficiently blocked by using proper water pressure and flow velocity of the gas. (HO groups on Au surface helps.)

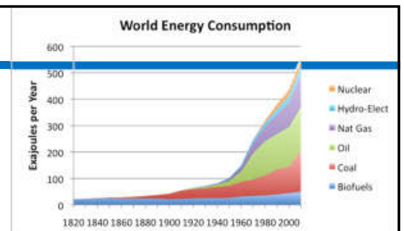


(Left) Interaction of gold and H2 molecule Au atoms with low cooridnation can bind so strongly to H2 that it can even pull a gold atomic chain. (Right) Set up for selective catalytic reaction for $CO+O_2$ → CO_2, which blocks O_2+H_2→ HO_2 using Au nanparticles (yellow) and water.

Read more at:
Johnny Saavedra et al., Nature Chemistry (2016). DOI: 10.1038/nchem.2494
http://phys.org/news/2016-05-tuning-gold-nanoparticle-catalyzed-carbon.html

Csonka et al. PRB 73, 075405 (2006)
www.researchgate.net/publication/284727255_Catalysis_A_brief_review_on_Nano-Catalyst

Potential future impact of Nano

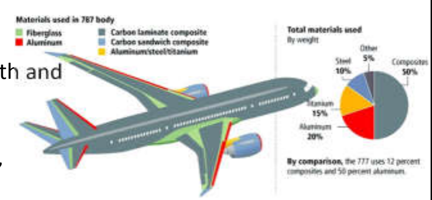


E.g. Energy sector

Sustainability of our need? – Strongly increasing consumption, - Oil, coal, gas are dominating …
How Nano does and will help?

Efficiency Reduce sharply the energy consumption:

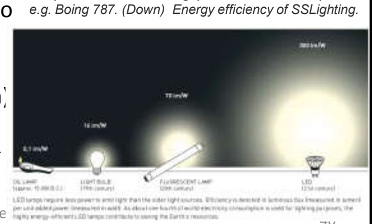
- Light, strong, multifunctional materials
Reducing mass while maintaining necessary structural strength and performance. E.g. carbon fiber composites demonstrate the potential (presently micro)
or multifunctional systems incorporating nanomaterials (e.g., windows that incorporate solar cells).



(Upup) World energy consuption vs. Time. (Up) Carbon composites as dominating parts of modern airplanes e.g. Boing 787. (Down) Energy efficiency of SSLighting.

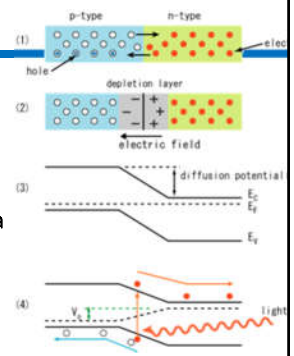
- Reduce loss during electrical transmission Use of nanomaterials to enable *local* generation and storage of electrical energy

- **Solid state lighting** (Lighting is 20% of overall energy consumption) Normal bulb: 15 lumens/W, LED ~300lumens/W. Nanostructuring the LED semiconductor materials as a photonic band gap system → possibility to further improve



Nattelson Section 12.1.

Potential applications of Nanotechnology



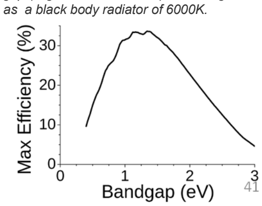
Power generation by solar cells:

Flux of energy from the Sun in the form of light 340W/m2 (direct sunlight). Energy demand of word: 24TW= 24 10^{12}W (continuous). E.g. with 10% conversion efficiency 7x10^{10} m2. This is ~ 75% of area of HU.
Most widely used silicon solar cells. PN junctions where built in E field separates electrons and holes.

(Up) Operation principle of pn-junction solar cell. (1-2) At the interface of a p and n dopped semiconductor depletion layer forms with electric field (3) in this region. This could separate electron and holes generated by photon absorption. (Down) Theoretical limit of efficiency of solar cells using pn jucntions created from a semiconducor with fixed band gap (E.g. for silicon 1.1eV.) assuming the Sun as a black body radiator of 6000K.

Schockley–Queisser limit on efficiency in *pn* junction cells: max. 34% (Taking into account blackbody radiation, thermalization of extra energy, and the spectrum of sunlight, (band gap 1.34eV), 1 photon → 1 e-h pair)
Goals: go beyond this limit or decrease fab price etc

(RIght) World biggest solar plant (2013) Mojave Desert of California, US. It has an installed capacity of 354MW and generates 662GWh of power annually. Area: 6.5 km^2. → 10000 such plants are rquired.

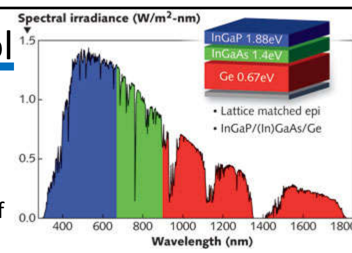


Potential applications of Nanotechnol

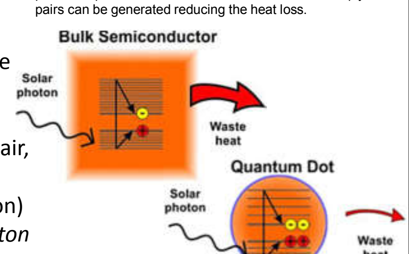
Power generation by solar cells:

Goals: go beyond SO limit or decrease fab price etc
Various strategies with ingredients from nanotechnology

- **Multijunction cells:** For Si pn-junctions the efficiency limit is 32% →try other III-V semiconductors and even a multilayer of them. First blue, later green then red absorption layers. Get them down to nano thicknesses. Efficiency: 43% (2015). Theoretical limit with infinite number of layers is 86.8% Expected efficiency: 50-70%
- **Hybrid organic/inorganic solar photovoltaics:** Chemically synthesized semiconductor nanocrystals with organic semiconducting polymers. Optical absorption can be tuned by quantum confinement.
  Nanocrystals for ***multiexciton generation and carrier multiplication****:* When $\hbar\omega > E_g$ photon generates a hot e-h pair, then with inelastic processes $\hbar\omega - E_g$ converts to heat. In nanoparticles (no translation invariance → no k conservation) collisional excitation or Auger scattering take place → *Photon with* $3E_g$ energy can generate 3 e-h pairs! Using narrow gap Semiconductor 1 photon→ >2 particles. → Go above Schockley-O. limit.

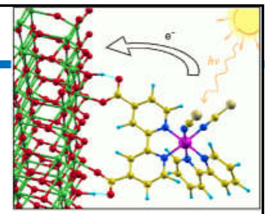


(Up) The spectrum of the Sun light with colored segments which is absorbed by different layers of a multilayered semicopnductor cell. (Down) Principle of multiexciton generation in nanocrystal quantum dots. In bulk semicondcutors $\hbar\omega$-E_g converts to heat after generating e/h pairs. In quantum dots without k conservation multiply e/h pairs can be generated reducing the heat loss.



C. Smith et. al. Nanomaterials ***2014****, 4(1), 19;*
A. Polman et al. Nat. Mat., 11, 174 (2012).

Potential applications of Nanotechnology



Power generation by solar cells:

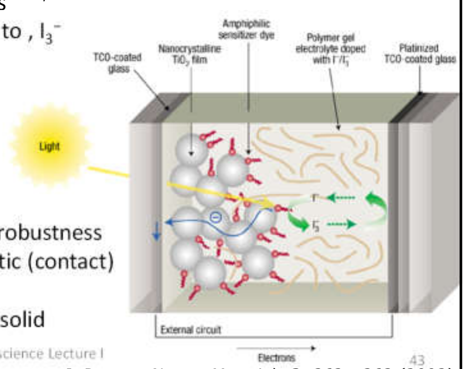
- Dye-sensitized or Grätzel solar cells (DSSC):

Efficiency: 10-12% Hope to get cheap manufacturing.
Steps of photon to current conversion:

- photon is absorbed by Ru complex photosensitizers on TiO_2 (or ZnO) nanoparticle surface
- photosensitizers are excited and e is injected to TiO2 conduction band
- Electron diffuses to TCO contact via TiO2 nanoparticles
- Oxidized photosensitizer from I^- ion, which is oxidized to , I_3^-
- I_3^- diffuses toward the counter Pt electrode and then it is reduced to I^- ions

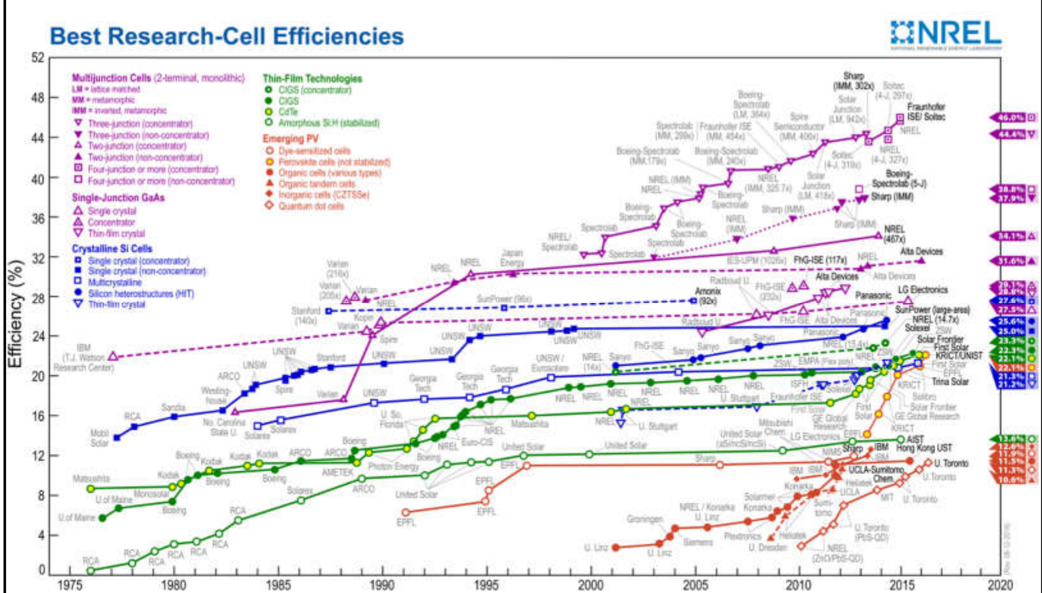
Nanoparticles with *large surface area* to contain large amount of dyes.
Pro/contras:
+ Inexpensive compared to the silicon solar cells,
+ no recombination due to e/h separation, + mechanical robustness
- costly Ru (dye), Pt (catalyst) and conducting glass or plastic (contact) are needed → Replace Pt by CoSx (2010), graphene …
Electrolyte has T instabilities (freeze , thermal expand) → solid electrolites since 2012

(Up) Molecular dye anchored to TiO nanoparticle. The Ru^{2+}-bipyridine complex can be excited by visible photon to a state where it inject an e to TiO2 nanoparticle http://www.ifm.liu.se/compchem/research/solarcells/ (Down) Structure of the DSSC: transparent conducting electrode TCO with nanocrystalline TiO2 film coated with dye molecules. It interacts with an electrolyte generating e transfer between dye and conter electrdes via redox processes.



Nattelson Section 12.1. also Wikipedia *J. Durrant Nature Materials **2**, 362 - 363 (2003)*

Potential applications of Nanotechnology



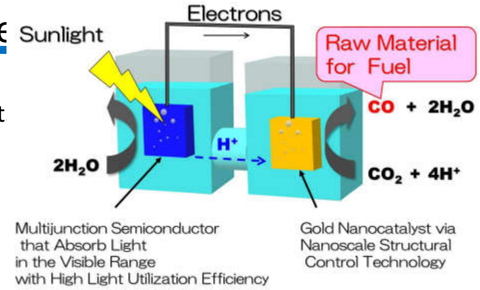
https://en.wikipedia.org/wiki/Multi-junction_solar_cell#/media/File:Best_Research-Cell_Efficiencies.png

Potential applications of Nanotechnology

- Artificial photosynthesis:

Idea: sunlight drives chemical reactions to store it energy in chemical form.
E.g. Convert $2H_2O$ into $2\ H_2 + O_2$
Or covert $CO_2 \rightarrow CO$
CO is a source for production of methanol, which can be used as a substitute for gasoline and for manufacture others (adhesives, medicines and PET …)
Clear advantage is volume energy density.
E.g. lithium-ion battery: ~2 MJ/L, gasoline: 36 MJ/L.

Operation principle: Photon absorbed in engineered e.g. nanostructure → e/h pairs. → spatially separated e.g. by band bending → e ends up at the surface where chemical species can be reduced
Role of nanostructures: high specific surface area, special surface sites for engineering



(Up) Highest Efficiency Artificial Photosynthesis Technology by Toshiba (2014) Efficiency: 1.5%
https://www.toshiba.co.jp/rdc/rd/detail_e/e1412_01.html
http://phys.org/news/2015-09-molecular-catalyst-artificial-photosynthesis-carbon.html

Nattelson Section 12.1. also Wikipedia

Potential applications of Nanotechnology

Storing energy

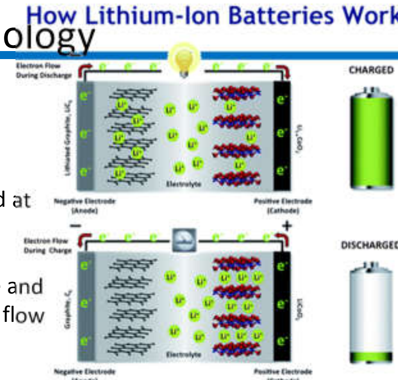
Nanostructured materials important in energy storing systems: Batteries and supercapacitors

- **Batteries**

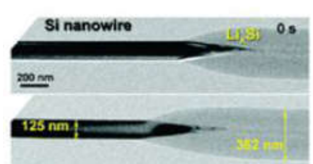
Energy is stored electrochemically through reactions performed at the two electrodes mediated by an electrolyte.
E.g. lithium ion batteries
Discharging process: Li^+ ions are deintercalated from the anode and transported to the cathode, where they are reduced. Electrons flow from the anode through the load to the cathode.
Charging process: positive voltage is applied to the cathode → current in the opposite direction
Structure: Li ion permeable separator between anode and cathode, graphitic carbon anode, $LiCoO_2$ cathode.
Important parameters:

- mass-specific capacity: e.g. graphite electrode 370 mAh/g
- Speed of charging/discharging - Many cycles without degradation

Ideas from nanotechnology:
- Silicon as anode: theoretical capacity 4000mAh/g. $Li_{4.4}Si$ alloy is a stable structure. But large lithium filling → 300% volume change. Bulk Si can not sustain, but nanostructured could!

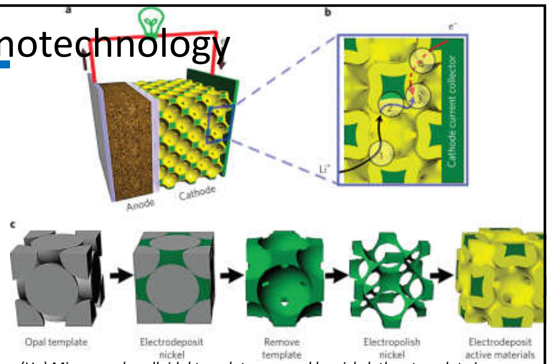


(Up) Structure and operation principle of Li ion batteries. Ion and electron flow are shown during discharging and charging process.
(Down) TEM image of Si nanowire as Li is intercallates and increase the volume. Large surface of Si nanowire allows the relaxation of the huge strain



Wikipedia *Nattelson Section 12.1.2*

Potential applications of Nanotechnology



E.g. lithium ion batteries

- Max. speed of charging/discarging important. High surface area electrodes → high speed operation
- E.g. inverse opal structures with open framework can be created by nanotech and coated with active electrode material. → Battery which can charge in seconds!

It out-power supercapacitors while retaining comparable energy density of batteries.

(Up) Micron scale colloidal template, covered by nickel, then template is removed. Electrodepsition of active electrode layer results an ultra high surface electrode where charging takes place fast.
H. Zang et. al. Nature Nanotechnology 6, 277–281 (2011)

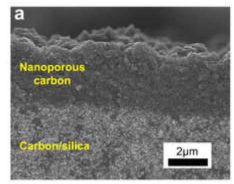
E.g. supercapacitors

Energy stored electrostatically through the arrangement of charge on two non-reacting electrodes and the polarization of a dielectric medium.

Used: cars to store breaking energy, trams, memory back-ups in electronics.

Important:
- Very high surface area of electrodes: ~m^2/g → nanostructured electrode materials
- Be fast: RC is small → good conducting material

Pro/contras
+ Rate is not limited by reaction kinetics + Lifetime is longer.
- Energy density is low: ~50kJ/l



(Down) Carbide derived carbon (CDC) electrodes which consist nm scale pores → Due to pores 75% more energy storage capacity using as electrode in supercapacitor.

Wikipedia *Nattelson Section 12.1.2* *C. Shen et. Al. Scientific Reports* **3**, Article number: 2294 (2013)

Potential applications of Nanotechnology

Environmental protection – with nanoparticles

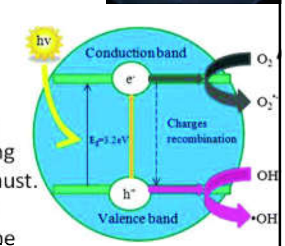
- **Automobile exhaust systems**: metal nanoparticle catalyst are widely used.

E.g. filter system of a Diesel engine

- Diesel oxidation catalysts (DOC): Role is to convert CO to CO_2 and remaining hydrocarbons to CO_2 and H_2O. (90% efficiency). → reduce such pollutants
  AlOx, palladium, platinum nanostructures are widely used
- Diesel particle filters (DPF): high levels of particulate matter (soot) consisting mainly carbon . One strategy to burn the soot. or e.g. nanoparticle platinum is also tried to convert
- **NOx filtering**: First step NOx absorber (e.g. zeolit trap). Second step: Selective catalytic reduction (SCR) Convert NOx to N_2 and H_2O. Adding gaseous reductant (called DEF) e.g. carbamide, ammonia to the exhaust. Diesel cars emit x10 more than gasoline cars → they convert to fine particles, serious health concerns! And also help in creation of ozone (45% from transportation)

- **Photocatalytic decomposition of hydrocarbon pollutants**

E.g. titania (TiO2) particles in water solution. Photons induce redoc process at the particle surface, generate reactive oxigene e.g. ozone, and also OH group. → oxidize organic contaminants. Used in urban air treatment (e.g. kill viruses, bacterias) or wastewater.



(Up) Automobile exhaust systems contain various catalists where metal nanoparticles are used. (Down) Principle of Photocatalitic decomposition with TiO2 nanoparticles Light generates e and h pairs in the particle. They induce reactions at the surface, like generation of reactive oxigen ions or OH groups.

Wikipedia *Nattelson Section 12.1.2*