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

VI. 2D materials

VII. Optical techniques new directions in material science by Sandor Bordacs

VIII. Modern surface science techniques SIMS, SNMS, XPS, AES ... by Ferenc Réti

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

SPM by Levente Tapaszto (MTA EK MFA)

Kahoot at the begining of the lectures from the previous topic. Exam:

10 quiz quastion, min. 60% to enter to the exam.

- 1 topic (20 minutes preparation time, notes, books can be used), - questions from other topics 11/14/2024 Nanotechnology and material science Lecture I









Nanotechnology and material science - 2023

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 Nanostructures, Oxford Uni. P. ISBN-13: 978-0199534432
- Scientific papers see citations

- Wikipedia

Douglas Natelson

Nanostructures and Nanotechnology

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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 clearly seen 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. \rightarrow See top-down techniques

- 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. \rightarrow See micro fluid.





R. Feynman (1918-1988)

- Mean field QED
- Path integral formulation
- Nobel prize (1965) QED
- Atomic bomb project
- Populizer of physics

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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...) \rightarrow 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, 3nm node or results of molecular electronics, also achieved possibilities as Deep Mind in GO (2016), ChatGPT (2022).

Nanotechnology and material science Lecture



11/14/2024

Nanotechnology today, Following Feynman's idea

"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. \rightarrow See topdown. **Atomic layer depostion** (ALD): grow e.g. oxides layer-bylayer \rightarrow 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







11/14/2024

After Lindsay: Intro. to Nanosicence Section 1.3

Nanotechnology and material science Lecture I

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 \rightarrow 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. \rightarrow 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. Quantum Manifesto 2017-2027. \rightarrow See new concept in electronics 11/14/2024

After Lindsay: Intro. to Nanosicence Section 1.3



(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 (AllnGaN) guantum dots can enab. novel applications in optoelectronics, nanoelectronics, and quantum information processing. These quantum dots, fabricated by metal-organi chemical vapor deposition, are optically active at room temperature

https://www.cse.umich.edu/eecs/research/group.html?r id=26 &g id=66



Nanotechnology and material science Lecture I

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 = 10⁻⁶mm Thus a 1cm³ = 10²¹ nm³ 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 ^{11/14/2024} Nanotechnology and **Other examples...**







History of nanotechnology

1959 An inspiration of Nano. Feynman's 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 \rightarrow 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 \rightarrow van der Waals heterostructures [Nobel 2010]

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





Moore's law, towards nano in electronics



Impact on society







MÚEGYETEM 1782



Impact on society







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Conventional MOSFET design Gate metal Gate Gate Drain Source Gate dielectric Source STI n+ n+ sti Oxide Silicon Substrate **Conducting channel** 2003 2005 2007 2009 2011 90 nm 65 nm 45 nm 32 nm 22 nm CXB SiGe SiGe SiGs. SGe Sleo

22nm 3D Tri-gate technology

Drain



10nm

Intel, 2011

Gordon E. Moore, Co-founder of Intel



Bottleneck is leakage

Conventional MOSFET design 22nm 3D Tri-gate technology **10nm** Intel, 2011 Gate metal Drain Gate Gate Drain Source Gate dielectric STI n+ n+ st -nmOxide **Conducting channel** 2003 2007 2009 2005 90 nm 65 nm 45 nm 32 nm 000 21 atomic layer SiGe SiGe SiGs. SGe ile:

Bottleneck is leakage





Moore-törvény – *Exponenciális technológiai fejlődés 50 éven át* Gordon Moore, az Intel társalapítója 1965-ben, ötven éve írta meg az Electronics magazinban, hogy a számítógépes csipekben az egy négyzetcentiméterre bezsúfolható tranzisztorok száma 1.5 évente megduplázódik. Úgy gondolta, hogy ez a fejlődési ütem legalább tíz évig tartható.





↑ News > As Moore's Law approaches 50, Intel battling to ke...

As Moore's Law approaches 50, Intel battling to keep up

Intel is facing more challenges to keep up with Moore's Law, which manifested in the 14-nanometer process

Agam Shah (IDG News Service) on 21 November, 2014 07:56

http://www.intel.com/content/www/us/en/silicon-innovations/intel-14nm-technology.html

For the past five decades, the number of transistors per microprocessor chip — a rough measure of processing power — has doubled about every two years, in step with Moore's law (top). Chips also increased their 'clock speed', or rate of executing instructions, until 2004, when speeds were capped to limit heat. As computers increase in power and shrink in size, a new class of machines has emerged roughly every ten years (bottom). *en át* a meg az az egy 5 évente ob tíz évig



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http://www.intel.com/content/www/us/en/silicon-innovations/intel-14nm-technology.html

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News Release February 8, 2017

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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.

Aoore's law. Now things could

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... operation within 3-4 years







onin reciniology

3nm Technology

TSMC's 3nm technology (N3) will be another full node stride from our 5nm technology (N5), and offer the most advanced...



5nm Technology

TSMC's 5nm Fin Field-Effect Transistor (FinFET) process technology is optimized for both mobile and high performance...

TSMC's 5nm (N5) Fin Field-Effect Transistor (FinFET) technology successfully entered volume production in the second quarter of 2020 and experienced a strong ramp in the second half of 2020.

TSMC's N5 technology is TSMC's second available EUV process technology, to enable our customers' innovations for both smartphone and HPC applications. As the foundry industry's most advanced solution with the best performance, power and area (PPA), N5 technology provides about 20% faster speed than N7 technology or about 40% power reduction. N5 technology further expands our customer product portfolio and increases our addressable markets.

In addition, TSMC plans to launch 4nm (N4) technology, an enhanced version of N5 technology. N4 provides further enhancement in performance, power and density for the next wave of N5 products. The development of N4 technology is on schedule with good progress, and volume production is expected to start in 2022.



TSMC Fab 18 is the main 5nm production facility



Moore's law, towards nano in electronics

Moore's Law: The number of transistors on microchips doubles every two years Our World





6

5



Gordon E. Moore, Co-founder of Intel

OurWorldinData.org – Research and data to make progress against the world's largest problems.

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Moore's Law is Dying









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MAR 9, 2018 @ 08:00 AM 4,175 @

Moore's Law Is Dying -- So Where Are Its Heirs? **≡ Forbes**

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solvable one, and that s the sliver mining to the death of Moore's Law. The industry's performance plateau creates a market space and opportunity for new ways of thinking, new designs and new inventions. We need radical, not incremental, change. We cannot afford to be bound by the dogma that has dictated traditional Silicon Valley product development (this dogma, by the way, is why the alternatives we've been promised are far behind schedule).







2 Free Issues of Forbes



TSMC still uses FinFET (3nm, 2023) 3 nm process nodes [edit]										
	Samsung ^{[43][66][67][68]}			TSMC ^[69]						Fin
Process name	3GAE	3GAP	3GAP+	N3	N3E	N3S				
Transistor type	MBCFET			FinFET						
Transistor density (MTr/mm ²)	150 ^[67]	195 ^[67]	Unknown	220 ^[46]	215.6 ^[70]	Unknown	224.2 ^[71]	224.2 ^[71]	Unknown	
SRAM bit- cell size (µm ²)	Unknown	Unknown	Unknown	0.0199 ^[59]	0.021 ^[59]	Unknown	Unknown	Unknown	Unknown	
Transistor gate pitch (nm)	40	Unknown	Unknown	45 ^[59]	48 ^[70]	Unknown	Unknown	Unknown	Unknown	
Interconnect pitch (nm)	32	Unknown	Unknown	Unknown	23 ^[59]	Unknown	Unknown	Unknown	Unknown	











Home > Computing

Samsung Struggling to Hit 70% Yields for 3nm GAA After One Year of Production

Qualcomm is reportedly demanding its yields hit 70% before it places any orders.

By Josh Norem October 4, 2023 🚦 💥 🚭



Samsuna 3nm node GAAFFT



Source: Intel's Ann Kelleher, "Enabling an exponentially better future", ITF 2023. The author circled the CFET for clarity.

The CFET builds on the gate-all-around concept of vertically stacked nanosheets, but makes for a taller design, **stacking a pair of transistors on top of each other to essentially create two transistors in one fin**. In one of its recent R&D updates, Intel noted that their experiments with CFETs have shown a 30 to 50% shrink in logic circuitry. Still, using these transistors in commercial manufacturing is still years away:



Length scales in electronics



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 the system.



High resistance Low resistance state state Free Layer Fixed layer

(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 through graphene for several µm distances. (b) Influence of perpendicular B field, measured in non-local geometry.

Nanotechnology and material science Lecture I

See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

Length scales in electronics



L_{ϕ}: **Phase coherence length** When size is < L_{ϕ} phase coherent processes could take place. E.g. quantum interference.

(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 lithography. Intensity corresponds to the transferred electrons, it is measured by QPC.



2024. 11. 14. Nanotechnology and material science Lecture I See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics
Length scales in electronics



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2024. 11. 14. Nanotechnology and material science Lecture I See more details in Halbritter, Csonka: Fundamentals of Nanoelectronics

Length scales in electronics



Le: Elastic mean free path When size is < Le, 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 cyclotron radius properly set.

2024.11.14.





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

Nanotechnology and material science Lecture I 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} . electrons occupy separated discrete states linked to wavefunctions.



(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 $<< \lambda$ E.g. small opening with d $<< \lambda$. But evanescent field still gets through. NSOM probe this. See example: a) Double slit experiment \rightarrow diffraction pattern

b) Add an extra small sub- λ aperture (w<< λ) close by (i.e. z<< λ) and move its position \rightarrow 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)



Near-field scanning optical microscopy (NSOM)

Setup:

- Coated optical fiber with a subwavelegth aperture (∞ 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 crystals, plasmonic structures







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



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 μ m

Micro-fluidics ,Lab-on-chip'

Simple example: inkjet printers micron scale droplets of ink through a microfabricated array of orifices. (see P. Furjes's 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 significantly reduced amount 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. \rightarrow cheap thus revolutional for LOC. (Bottom) Fabrication of PDMS based microfluidics

See: 6 4 5 http://www.meddeviceonline.co m/doc/silicon-a-material-withhuge-potential-for-lab-on-chips 0001 http://www.elveflow.com/microfl PDMS pouring Release of uidic-tutorials/microfluidic-Master mold & reticulation PDMS replica reviews-and-tutorials/the-poly-di-Nanotechnology and material science Lecture I Plasma Put intcontact methyl-silokane2pdms-and-Inlet drilling microfluidics/ treatment



(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



Micro-fluidics ,Lab-on-chip'

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. → challenging to mix fluids efficiently in microfluidic 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!



laminar flow



turbulent flow





(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



Nanotechnology and material science Lecture I

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! \rightarrow Increased efficiency.

However **issues at nanoscale**: force of B field ~ volume, viscous force ~ diameter, fluctuations i.e. Brownian motion $^{k}_{B}T/d$. \rightarrow Nanoscale is not preferable.

Still it works for 10nm scale particles with better sensitivity. Reasons: a) Single domain particles -> large stray field $^{M}M_{sat}/d$ and b) large interparticle force which order neighbouring particles \rightarrow 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) delute analyte from beads; (E) transfer to new tube.

http://www.abraxiskits.com/products/magnetic-beads/



11/14/2024

See Natelson Section 7.7

Nanotechnology and material science Lecture I

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

11/14/2024

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) \rightarrow different plastic deformation properties. Grain bonderies dominate.



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%.

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Lattice Constant (A)

(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.



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

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

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

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Mechanics at nanoscale

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



2.4

2.0

1.0

1.2

0.8

0.4

0.0 6.2

⁵⁰ See D. Natelson Section 9.1.4

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=VD/m \rightarrow To increase mass sensitivity: m \supseteq , D \nearrow 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.





BioNanoTechnology

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 lon transporters, pumps etc.

Molecules and their interaction governed by electrostatic, van der Waals, hydrogen bonding & hydrophobic interactions at $k_{B}T$.



Source: Wikipedia

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(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.

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http://book.bionumbers.org/what-is-the-thickness-of-the-cell-membrane/

protein subunit (Up) Example of a virus geometry. Tobacco mosaic virus. It has a

RNA

helical protein shell (called capsid), which encloses the genetic material (RNA).

Capsid

(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



I. example: DNA origami

Nanoscale folding of DNA to create non-arbitrary two- and threedimensional 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, heated 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 cancer cells. Size:35nm in width. G





and closes. The aim is to attack

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 p9 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. \rightarrow try to understand binding mechanisms or motifs.



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also Wikipedia See D. Natelson Section 11.2.3

Principle of phage display technique



Principle of virus templated production of battery electrodes



E.g.1: Develop a library of peptides that bind selectively to

semiconductors. Start with 10⁹ 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. \rightarrow Cover M13 with Co_3O_4 and Co_3O_4 -Au.

- Two dimensional assembly of viruses on polyelectrolyte multilayers by liquid crystalline ordering \rightarrow It works as a promising electrode with high surface area.



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

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



(Down) Capacity for the assembled monolayer of Co₃O₄ nanowires/Li cell (theoretical limit is 3800 for Li ion bat.)



Gecko tape – Nanofabrication to mimic bio

Gecko's feet are coated with hair like structures (Seta scale $\sim \mu m$) 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 ~ 10Ncm⁻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





Gecko adhesive system



(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

Best gripping material—especially to skin



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.





(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 $CO+O_2 \rightarrow CO_2$, which blocks $O_2+H_2 \rightarrow HO_2$ using Au nanparticles (yellow) and water.



Csonka et al. PRB 73, 075405 (2006)

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. \rightarrow Find a cheap way to remove CO down to 50pmm range. Way out: generate CO+O₂ \rightarrow CO₂ reaction.

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



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

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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).

- 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 \rightarrow possibility to further improve





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



LED lamps require less power to emit light than the older light sources. Efficiency is denoted in luminous flux (measured in lumen) per unit added power (measured in watt). As about one fourth of world electricity consumption is used for lighting purposes, the highly energy-efficient LED lamps contribute to saving the Earth's resources.

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Nattelson Section 12.1.

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 10¹²W (continuous). E.g. with 10% conversion efficiency 7x10¹⁰ 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.

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 km². \rightarrow 10000 such plants are rquired.





(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.



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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 \rightarrow no k conservation) collisional excitation or Auger scattering take place \rightarrow *Photon with* $3E_g$ energy can generate 3 e-h pairs! Using narrow gap Semiconductor 1 photon \rightarrow >2 particles. \rightarrow 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).

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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 TiO₂ (or ZnO) nanoparticle surface
- photosensitizers are excited and e is injected to TiO2 conduction band
- Electron diffuses to TCO contact via TiO2 nanoparticles^{redox processes.}
- 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 \rightarrow Replace Pt by CoSx (2010), graphene ...

Electrolyte has T instabilities (freeze, thermal expand) \rightarrow solid electrolites₂since 2012

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(Up) Molecular dye anchored to TiO nanoparticle. The Ru²⁺-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





11/14/2024 Nanotechnology and material science Lecture I https://en.wikipedia.org/wiki/Multi-junction_solar_cell#/media/File:Best_Research-Cell_Efficiencies.png

Potential applications of Nanote Sunlight

- Artificial photosynthesis:

Idea: sunlight drives chemical reactions to store it energy in chemical form.

E.g. Convert $2H_2O$ into $2H_2 + O_2$ Or convert $CO_2 \rightarrow CO$

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 \rightarrow e/h pairs. \rightarrow spatially separated e.g. by band bending \rightarrow e ends up at the surface where chemical species can be reduced

Role of nanostructures: high specific surface area,

special surface sites for engineering 11/14/2024

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Multijunction Semiconductor that Absorb Light in the Visible Range with High Light Utilization Efficiency Gold Nanocatalyst via Nanoscale Structural Control Technology

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

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 \rightarrow current in the opposite direction

Structure: Li ion permeable separator between anode and cathode, graphitic carbon anode, LiCoO₂ 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 \rightarrow 300% volume change. Bulk Si can not sustain, but nanostructured could!

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Wikipedia



(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



E.g. lithium ion batteries

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

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

Anode Opal template Electropolish Electrodeposit Remove Electrodeposit active materials template nickel

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: $\sim m^2/g \rightarrow$ nanostructured electrode materials

- Be fast: RC is small \rightarrow good conducting material

Pro/contras

- + Rate is not limited by reaction kinetics + Lifetime is longer.
- Energy₄density is low: ~50kJ/l

Wikipedia

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Nattelson Section 12.1.2

(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)

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

C. Shen et. Al. Scientific Reports 3, Article number: 2294 (2013)





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 CO₂ and remaining hydrocarbons to CO₂ and H₂O. (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 N₂ and H₂O. Adding gaseous reductant (called DEF) e.g. carbamide, ammonia to the exhaust. Diesel cars emit x10 more than gasoline cars → they are converted to fine particles in air, serious health concerns! And it also helps 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. \rightarrow oxidize organic contaminants. Used in urban air treatment (e.g. kill viruses,

bacterias) or wastewater.

Wikipedia





(Up) Automobile exhaust systems contain various catalists where metal nanoparticles are used. (Down) Principle of Photocatalitic docomposition 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.