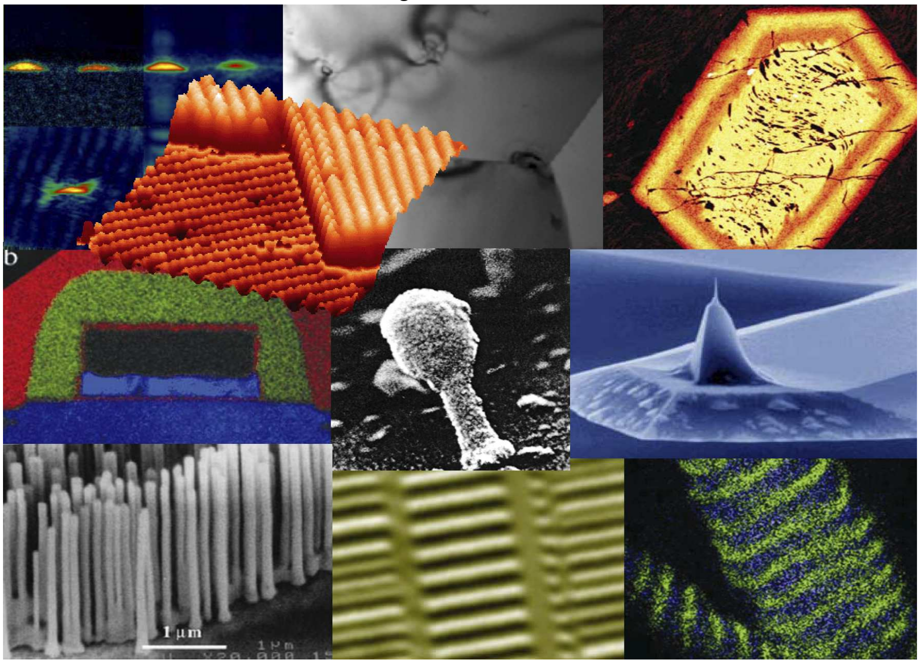
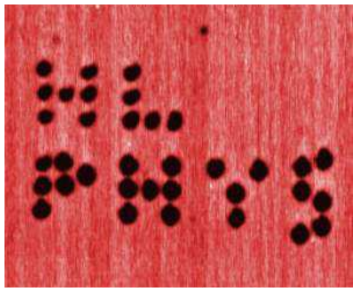
Nanocharacterization I – NanoMicroscopy

Vorlesung 322.229 und Praktikum 322.230, ECTS credits 3.0 + 1.5





Lecturer:
Gunther Springholz, Tel. 9681
email: gunther.springholz@jku.at

Curriculum: Mandatory course for Master „Nanoscience and Technology“, elective for Master/Bachelor „Technische Physik“.

Time and Location: **Do. 15:30 – 17:00, P004,** Starting from October

Labcourse (Praktikum): Block @ end of semester, 3 Exercises: Choice: SEM, TEM, µPL, XRD, MFM/PFM, STM
Groups of 3 students each

Course Information

Objectives:

Learn the ***different methods*** for ***characterization*** of nanomaterials and how they work:

- Learn which ***kind of probes*** can be employed:
  » Beam probes, photons, electrons, x-rays, scanning probes, …
- Learn ***how the probes interact*** with nanomaterials (mechanisms of interactions):
  » Elastic/inelastic scattering, absorption, excitations, secondary emission
- Know what ***kind of information*** can be obtained:
  Structure, morphology, shape, composition, electronic, magnetic properties, etc.
- Advantages, disadvantages and resolution limitations of the different methods.

Nanocharacterization I:

A. Fundamentals: Probes for Nanocharcterization and their interactions with samples.
Photons, electrons, x-rays, particles, ….

» Focus: What kind of information can be obtained with different techniques ?

B. *Imaging* of nanomaterials with high spatial resolution » ***“Nanomicroscopy”.***

Fundamental optics and instrumentation, » scanning versus imaging

» ***Resolution limits*** and **contrast**: How can it be enhanced and manipulated ?

» **Methods**: Optical microscopy, scanning probe microscopy, electron microscopy,

Nanocharacterization II: » ***“Nanoanalytics”***

» *Ion and Electron based Microscopy and Spectroscopy*

Contents of the Course

Part I: Introduction: Key issues of Nanoscience and Nanotechnology

Part II: Fundamentals: Probes for Nanocharacterization
- Photons, x-rays, Electrons: Properties and Instrumentation
- Probe–Sample Interactions and Generation Secondary Signals.
- Optical Spectroscopy, X-ray Methods, Electron based Methods

Part III: Fundamentals of Microscopy
- Microscopy Methods: Scanning versus Imaging,
- Optical / Electron / Scanning Probe Microscopy
- Basic Optics and Resolution

Part IV: Advanced Microscopy
- X-ray and EUV Microscopy
- Contrast Modification in Optical Microscopy
- 3D Imaging and Scanning Confocal Microscopy and Spectroscopy
- Deep sub-wavelength Fluorescence Microscopy: PALM, STED, STORM
- Transmission electron microscopy

Part V: Scanning Probe Microscopy
- Basic Properties, Methods, Scan Modes and Instrumentation
- Scanning Tunneling Microscopy, Scanning Force Microscopy

Nanocharacterization II (SS): Nanoanalytics using

Ion Scattering (RBS), SIMS, EDX, AES, XPS, Electron diffraction LEED..

Praktikum: Block at end of semester. Experiments: AFM, MFM, T(S) EM, Micro-PL ...

Curriculum Master „Nanoscience and Technology“

§ 4.2 Masterstudium „Nanoscience and -Technology“

1. Prüfungsfach „Pflichtfächer“		ECTS-Credits
Physik niedrigdimensionaler Systeme	3 VO + 1 UE	4,5 + 1,5
Nanofabrikation I	2 VO + 1 PR	3 + 1,5
Nanofabrikation II	2 VO + 1 PR	3 + 1,5
Nanocharakterisierung I	2 VO + 1 PR	3 + 1,5
Nanocharakterisierung II	2 VO + 1 PR	3 + 1,5
Thermodynamik und Grundlagen der Statistischen Physik	2 VO + 1 UE	3 + 1,5
Computational Physics I	2 VO + 1 UE	3 + 1,5
Seminar aus Nanoscience and -Technology	2 SE	3
Gesamt	24 SS	36

⇨ Masterstudium “Technische Physik”: Wahlfach aus dem LVA Katalog NST

⇨ Bacherlorstudium „Technische Physik“: Wahlfach Nanocharacterization I

Curriculum: Master Nanoscience and Technology

1. Semester		2. Semester		3. Semester		4. Semester	
Nanotechnology Nanocharacterization I Nanofabrication I	6	**Nanotechnology** NanocharacterizationII Nanofabrication II	6	**Masterarbeit** Theoretische oder Experimentelle Forschungsarbeit	12	**Masterarbeit** Theoretische oder Experimentelle Forschungsarbeit	21
Nanoscience Physics of Low-dimensional Systems Computational Physics I	10.5	**Wahlfächer** ComputationalPhys. II Nanoptik, Nanoelektronik, Advanced Microscopy, Optoelectronic Devices, Smart Materials, Quantum Computation, Wachstum & Epitaxie Organic Semiconductors, etc. ...	16.5	**Wahlfächer** Mikrosensorik Bionanostructures Laserpatterning Nanomagnetism ...	6		
Wahlfächer Cond. Matter Phys. Semiconductors Surface Physics, Strukturanalyse, Programmierung, etc.	9			**Spezialpraktikum**	9	**Spezialfächer zur Masterarbeit**	4.5
Nano-Praktikum	3	**Nano-Praktikum**	3			**Gesamtprüfung**	3
Freie Wahlfächer	1.5	Freie Wahlfächer	1.5	Freie Wahlfächer	1.5	Freie Wahlfächer	1.5
ECTS	**30**		**30**		**30**		**30**

Chapter I

II. Nanoscience:
A short Introduction

NSTL NanoScience and Technology Center Linz

Chapter I: Introduction

Content:

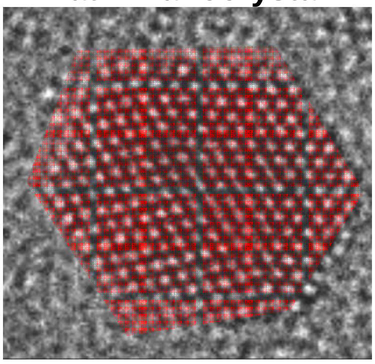
1.1 Nanoscience and Nanotechnology

Nanno = greek: „Dwarf "(Zwerg)

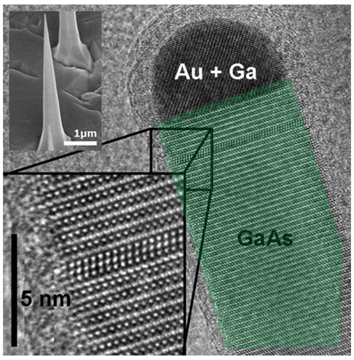
1 Nanometer = 10^{-9} m ~= 5 Atoms

⇨ **Nanostructures = Objects with a size from few up to about one thousand atoms in one direction**

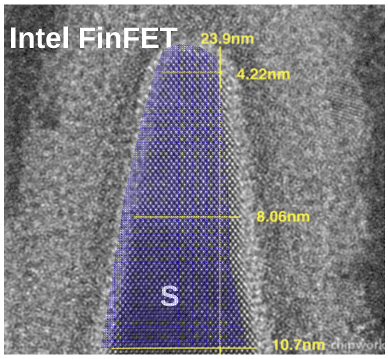
Platin Nanocrystal



GaAs Nanowire

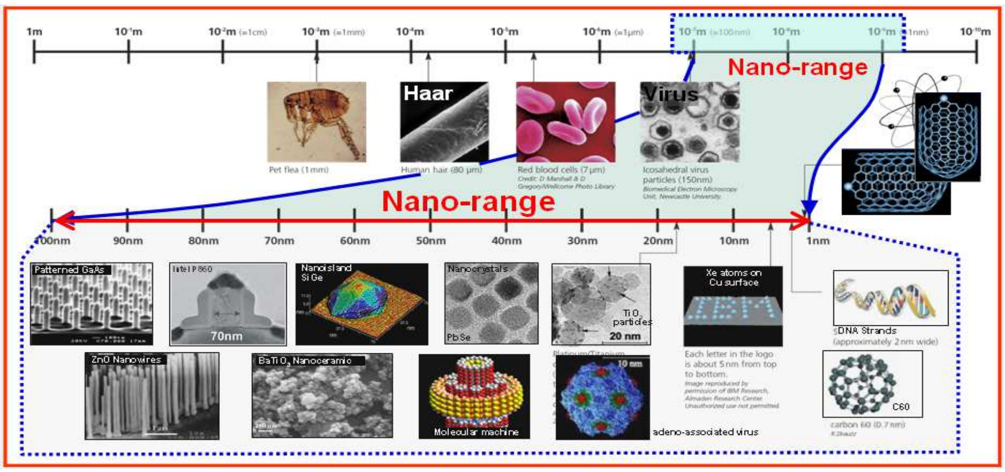


Silizium Nanotransistor



Nanoscience and Nanotechnology =

= To ***make, manipulate, measure***, ***see***, and ***predict* materials** on the scale of atoms & molecules in the **1 to 100 nm range**: Includes: Atom clusters, molecular structures, nanocrystals, nanoparticles, nanowires, thin films, etc.



Motivation: Properties of nanomaterials change with physical dimension. Thus, they differ strongly from those of single atoms as well as those of bulk materials.

Sub-fields:

1. Nanofabrication,
2. *Nanocharacterization* and *Nanoanalytics*,
3. Theoretical modeling and simulation,
4. Nanodevices and applications.

Curriculum: Master Nanoscience and Technology

1. Semester		2. Semester		3. Semester		4. Semester	
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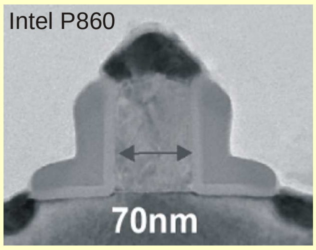
ECTS	**30**		**30**		**30**		**30**

1.2 What is so Interesting about Nanostructures ?

1. Miniaturization of electronic devices

Goals
- increase of integration density,
- increase of speed and functionality,
- lower costs.

Integrated Si circuits will soon contain devices < 20 nm

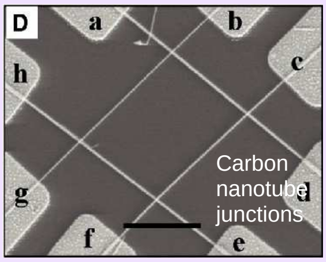


2. Realization of new functional materials

based on the new physical properties of nanostructures.

Goal: Realization of functions that cannot be achieved by conventional devices or materials.

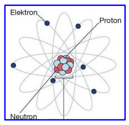
Examples: Optoelectronics (Laser, etc.), Quantum Computation, Spin electronics, Magnetic Memories, Single Electron Transistors und Nanotube Devices, Solar Cells, Ceramics, Single Molecule Biosensors, Medical Diagnostics, …,



3. Fundamentally new physics: Low dimensional systems, topological quantum effects, quantum transport, quantum optics, novel magnetic, electronic, chemical properties, ...

1.3 Physics on the Nanoscale

⇨ **Nanotechnology is not only about miniaturizing things !**



At the nanoscale:

- Different laws of physics come into play (quantum mechanics, etc.),
- Many properties of materials change due to the shrinking of the building blocks,
- Behavior of surfaces starts to dominate the behavior of bulk materials.

Novel effects in nanostructures:

1. ***Quantization of the Electronic Structure*** due to confinement of electrons to a small region in space.
   - continuum states of bulk materials become quantized in energy,
   - reduced dimensionality leads to low dimensional density of states
   - quantized energy levels are ***tunable*** by the nanostructure size: Emission and absorption can be spectrally tuned,
   - high performance of quantum devices such as lasers, LEDs, detectors, solar cells,…
2. ***Quantum Transport***: Quantum Hall effect, conductance quantization, Coulomb blockade …
3. ***Novel Structures*** not allowed in bulk form: Quasicrystals, fullerenes, molecular structures, …
4. ***Surface and interface effects***: High reactivity, chemical catalysis, surface reconstructions
5. ***Functionalization***: Bio-Nanostructures, fluorescence markers, …..

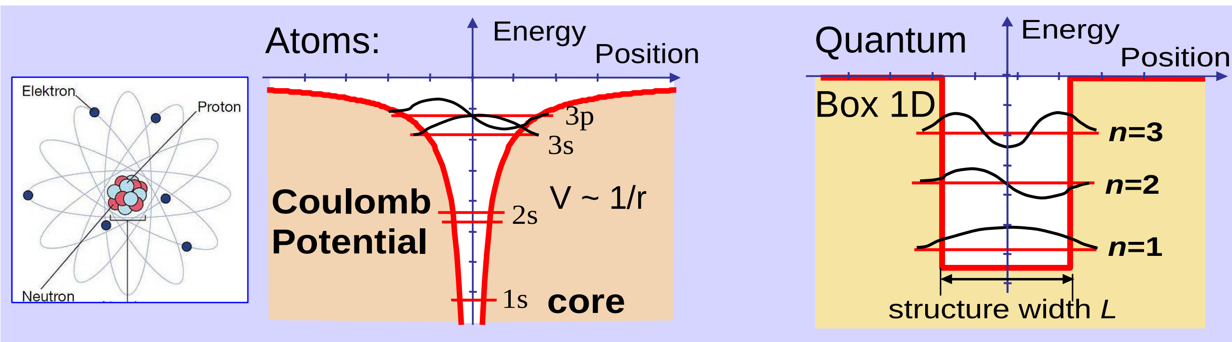
1.4 Size Quantization of the Electronic States

In nanostructures, electrons are bound to a narrow region of space by a ***confining potential*** similar as the electrons bound to the nucleus in an atom by the attractive Coulomb potential.

This leads to a quantization of the energy levels, which are determined by the

Schrödinger Equation:

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - V(x)\right) = 0$$



$$\lambda_e = h / m_e v = 2L$$

Atoms: Coulomb potential defined by nucleus charge
↳ different energy levels for different atoms.

Nanostructures:
↳ Confining potential defined by different energy gaps or work functions of inside/outside material, as well as size dimension
↳ Change of energy spectrum and of density of states
↳ ***blue shift*** of electronic transitions with decreasing structure size *L*.

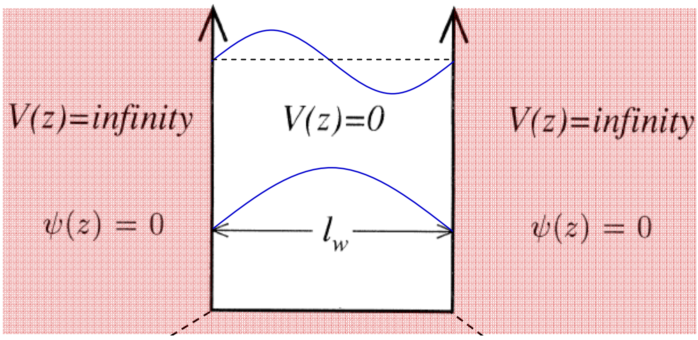
$$E_n = \frac{n^2 h^2}{8 m_e L^2}$$

infinite square potential well

Example: Quantum Wells & Infinite Square Potential Barriers in 1D

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\psi(z) + V(z)\psi(z) = E\psi(z)$$

Schrödinger Equation



Boundary condition:

$$\psi(z) = A\sin kz + B\cos kz$$

$$\psi(0) = \psi(l_w) = 0$$

$$k = \frac{\pi n}{l_w}$$

$$E_n = \frac{\hbar^2\pi^2 n^2}{2ml_w^2}$$

$$\psi(z) = A\sin kz + B\cos kz$$

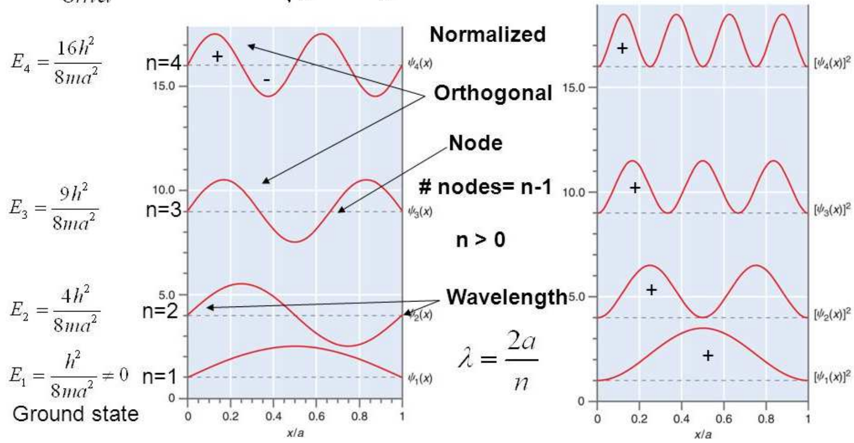
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\psi(z) = E\psi(z)$$

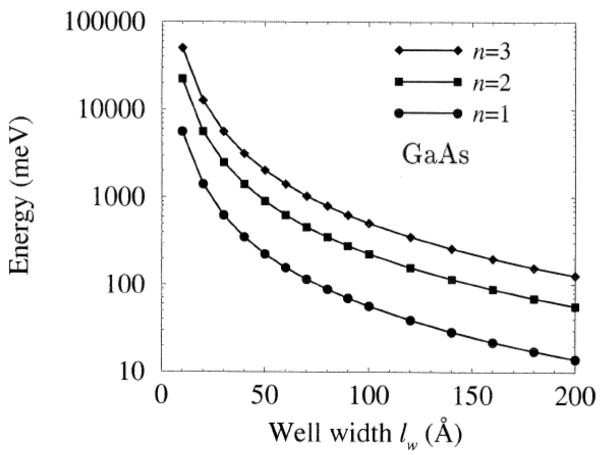
Plane wave Ansatz

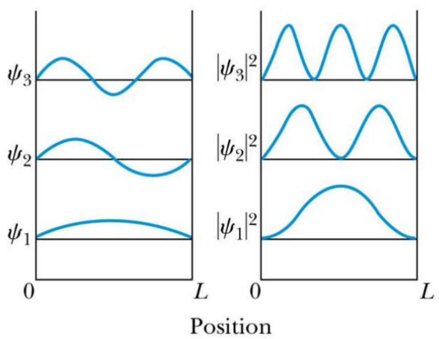
$$\frac{\hbar^2 k^2}{2m}(A\sin kz + B\cos kz) = E(A\sin kz + B\cos kz) \Rightarrow \frac{\hbar^2 k^2}{2m} = E$$

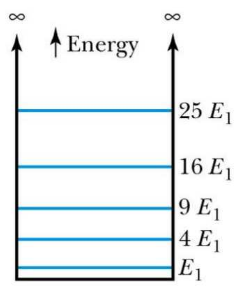
Solutions: Quantum Wells & Infinite Square Potential Barriers

$$E_n = \frac{n^2 h^2}{8ma^2} \quad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \quad P_n(x) = \frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right)$$



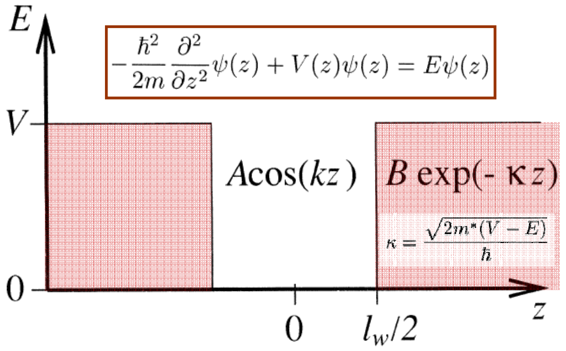


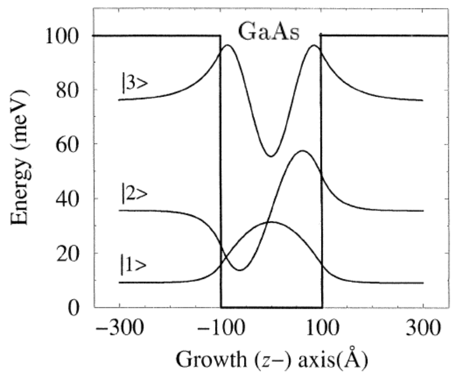




Real Potential Wells: Example GaAs/GaAlAs QWs

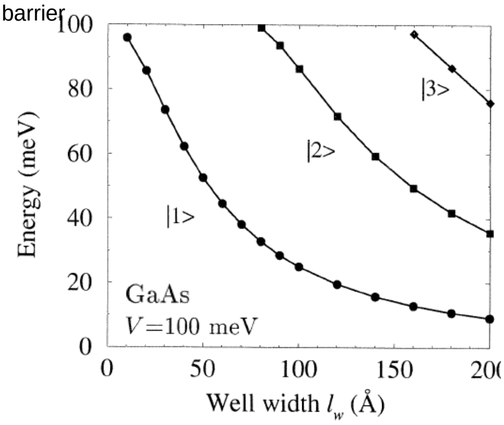
Finite barrier height, effective masses m_{eff} and band structure effects

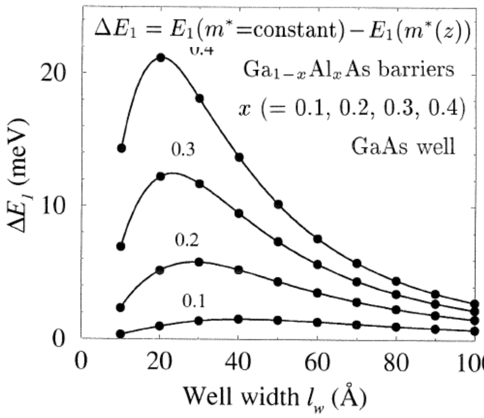




Ansatz: Plane waves inside quantum well,
Decaying exponential function in barrier

$$\psi(z) = B\exp(\kappa z), \qquad z \le -\frac{l_w}{2}$$
$$\psi(z) = A\cos(kz), \qquad -\frac{l_w}{2} \le z \le \frac{l_w}{2}$$
$$\psi(z) = B\exp(-\kappa z), \qquad \frac{l_w}{2} \le z$$





1.4.1 What is the *Size* required to see Quantum Effects ?

Quantization energies for an electron in an infinite 1D square potential well (n = 1,2,3…)**:**

» Energies in the 4 - 400 meV range for L < 10 nm

$$E_n(L) = \frac{h^2}{8m}\frac{n^2}{L^2} = \frac{0.38eV}{m_{eff}/m_0}\cdot\frac{n^2}{L(nm)^2}$$

Practical considerations: Conditions for notable quantum effects

(1) *L* < electron de Broglie wavelength: $\lambda_e = 2\pi/k_F \sim 1/n_e^{1/3}$ or $\sim 1/E_F^{1/2}$

(2) Filling of only few subbands $\Delta E_i \sim E_F$ and/or subband spacing $\Delta E_i > k_BT$

Metals:

$n_e = 10^{23}$ cm^{-3} ; E_F = 2 - 10 eV;

≈ $\lambda_e \sim$ 5 Å

Semiconductors:

$n_e = 10^{16\text{-}19}$ cm^{-3} ; E_F = 2 - 150 meV,

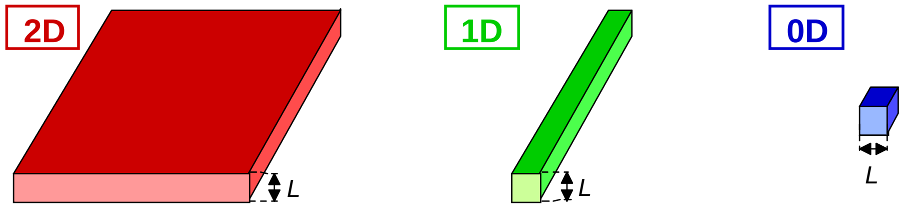
$\lambda_e \sim$ 100 -1000 Å

Example: GaAs/AlGaAs QW:
E_i= 56, 224, 504 .... meV for L = 100 Å,

⇨ **Quantization effects are much more pronounced in semiconductors** than in metals due to the much lower free carrier concentration and small effective masses**,**

⇨ **Few tens of nm in size** are sufficient in semiconductors for substantial quantum effects.

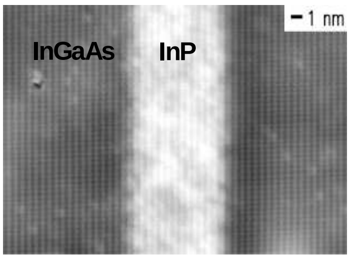
1.4.2 Dimensionality of Low Dimensional Systems

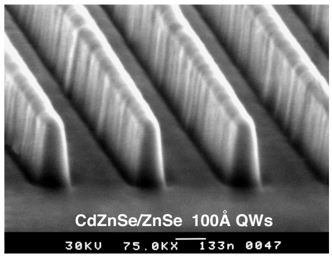


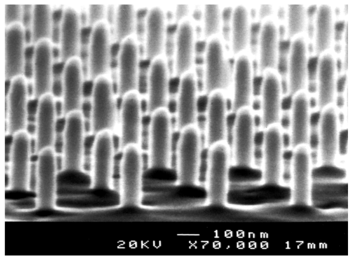
Size quantization

$$E_n = \frac{n^2 h^2}{8 m L^2}$$

"Quantum Wells" | "Quantum Wires" | "Quantum Dots"





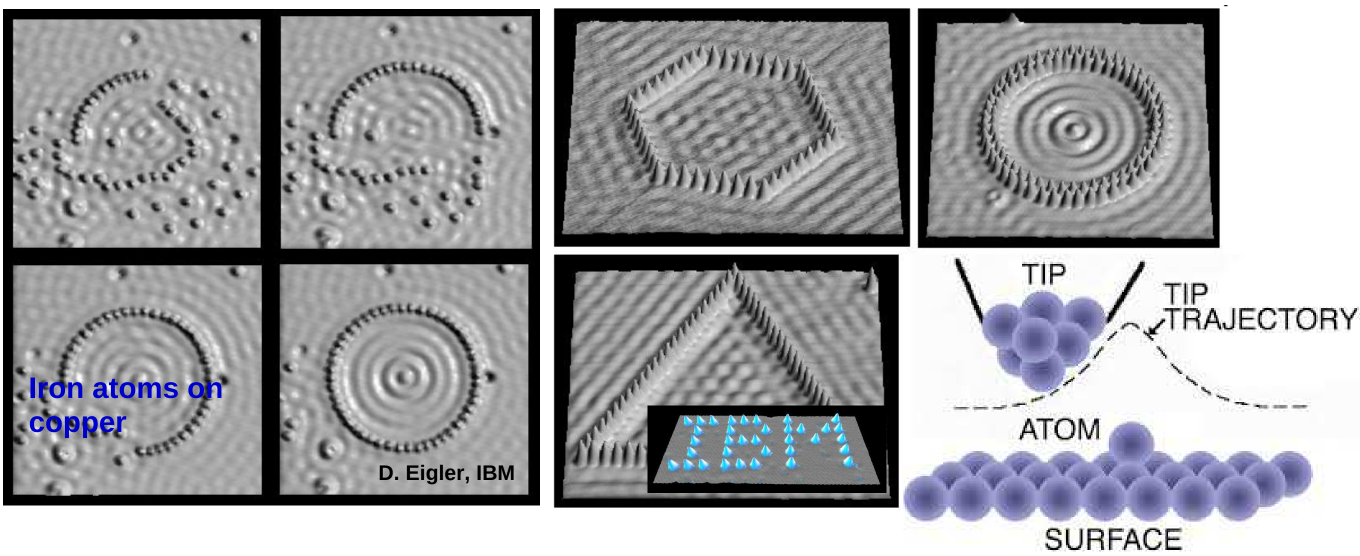


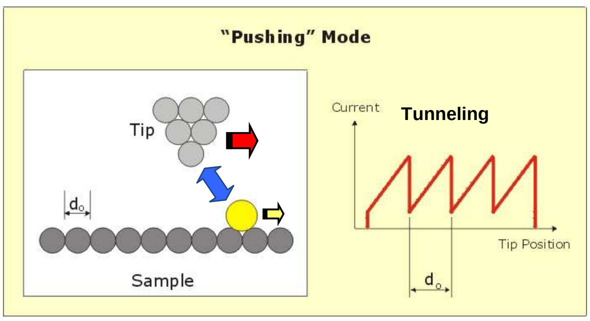
⇨ **Yields size quantization in 1, 2 or 3 Dimensions**

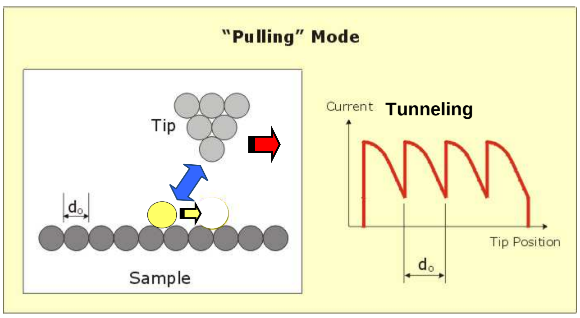
Realization: (see below)

- **2D:** Heteroepitaxy and deposition of ultra-thin layers, exfoiliation (graphene, etc.),
- **1D, 0D:** "**Top-down**" Lithography & etching, nanoimprinting, focused ion beam milling, "**Bottom-up**": molecular synthesis, colloidal growth, self-assembly, self-organization, epitaxial growth, phase separation, nano-crystallization, atom manipulation

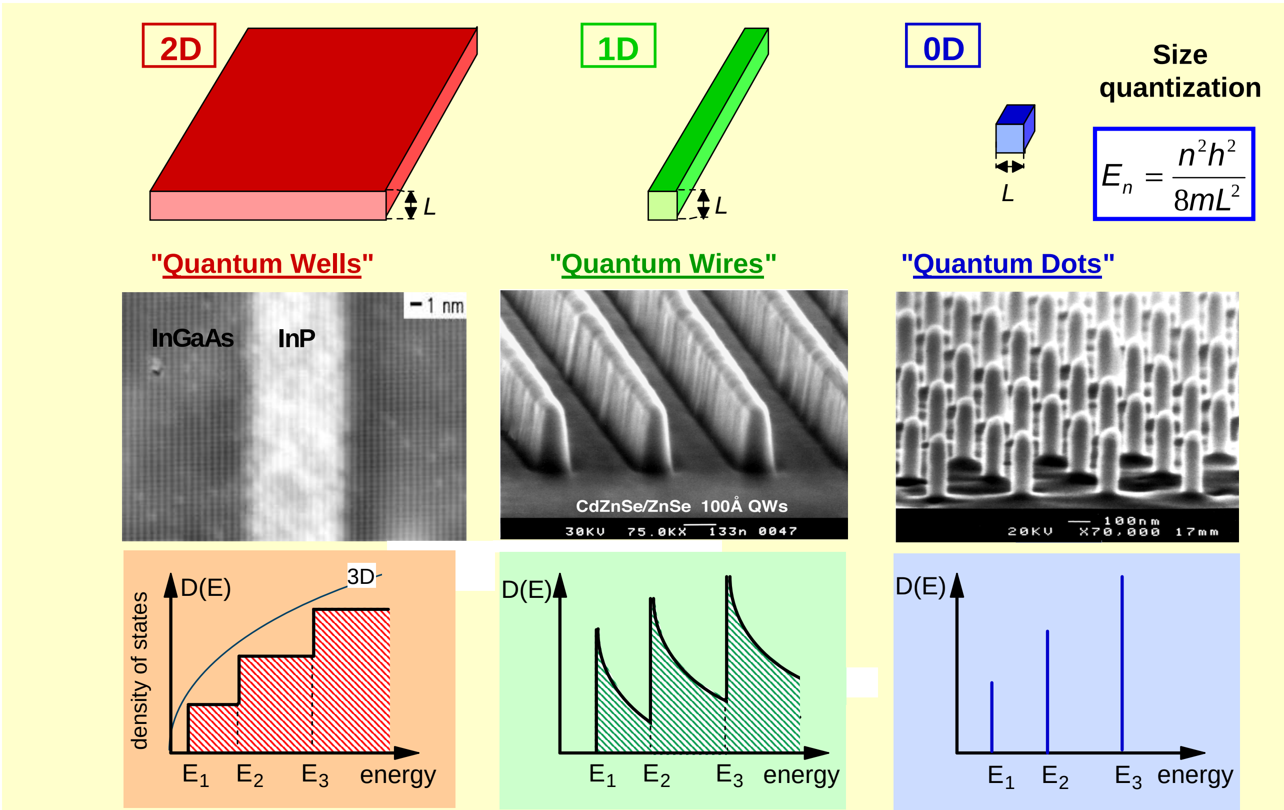
Example: Nanostructures formed by STM Atom Manipulation







1.4.3 Electronic Density of States in Low Dimensions



D(E) = const.

$D(E) = 1/\sqrt{E}$

$D(E) = \delta(E-E_i)$

Electronic Density of States in Low Dimensions

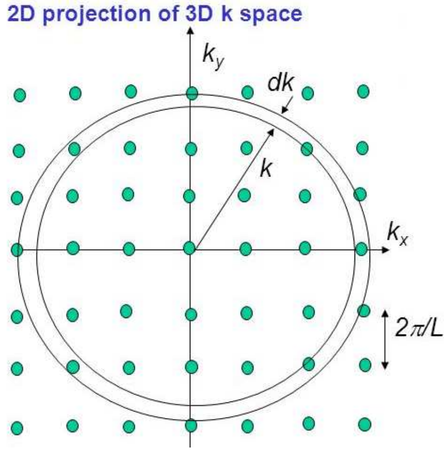
Density of states in a volume V per unit wave vector:

$$\frac{dn}{dk} = \frac{Vk^2}{2\pi^2}$$

For a free electron gas:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

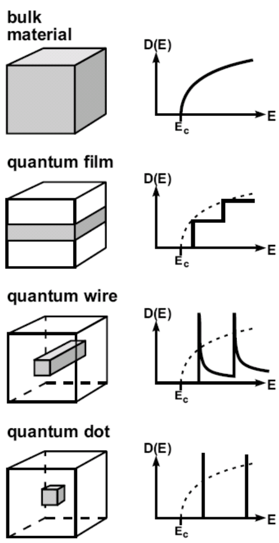
$$\frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{Vk^2}{2\pi^2}\frac{m}{\hbar^2 k} = \frac{Vm}{\hbar^2 2\pi^2}\sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}$$

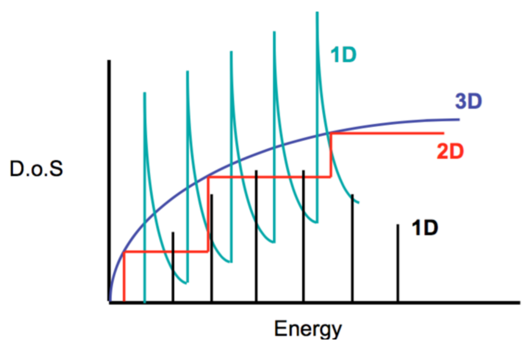


$$D_1(E) = \frac{1}{\sqrt{c_k(E-E_0)}}$$

$$D_2(E) = \frac{\pi}{c_k}$$

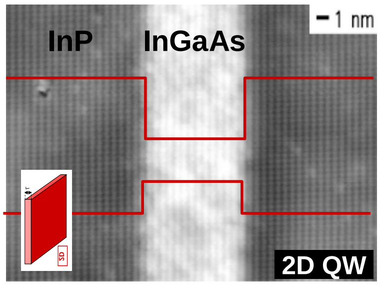
$$D_3(E) = 2\pi\sqrt{\frac{E-E_0}{c_k^3}}.$$

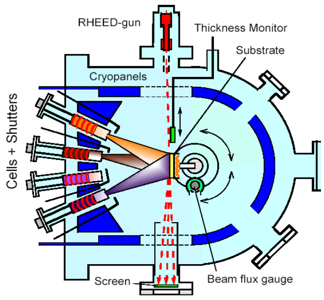


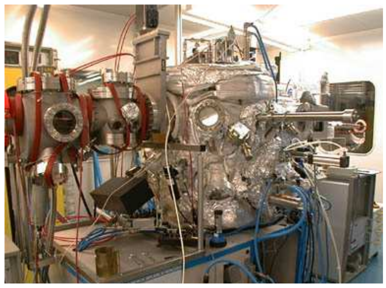


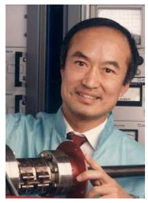
1.4.4 2D Systems: Design and Realization

Realization: Molecular Beam Epitaxy of **ultra-thin layers** with few nm thickness



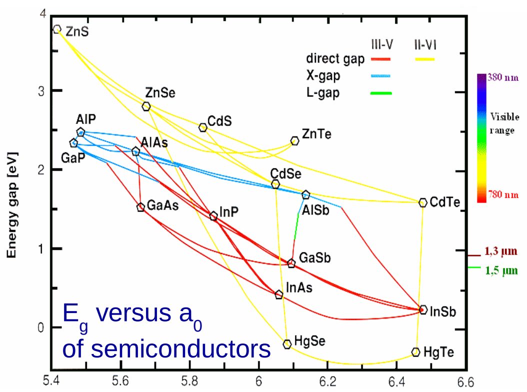




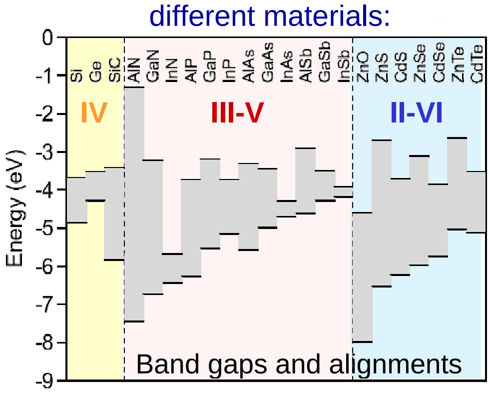


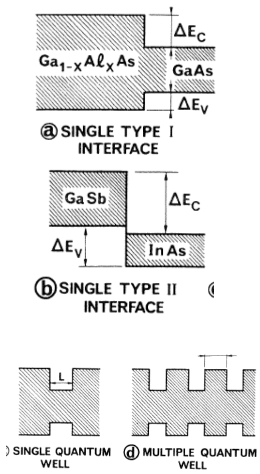
Al Cho
Bell Labs

"Band gap engineering:"



Band alignment between different materials:

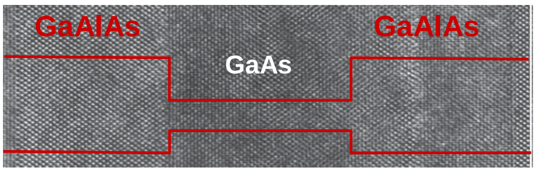




⇨ **MBE provides precise control of physical dimensions and potential profiles !**

Example: Epitaxially Grown GaAs/GaAlAs Quantum Wells

Optical transitions between 2D QW states in the CB and VB bands



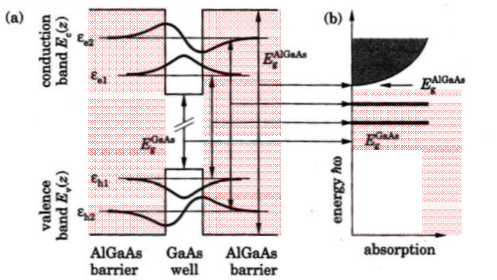
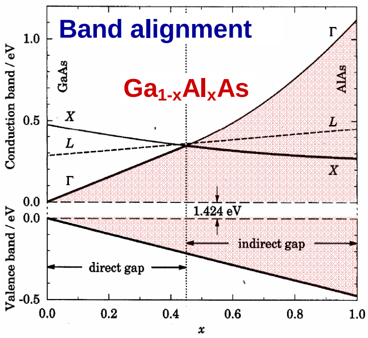


FIGURE 1.3. Optical absorption in a quantum well formed by a layer of GaAs surrounded by AlGaAs. (a) Potential well in conduction and valence band, showing two bound states in each; the energy gap of GaAs is really much larger than this diagram implies. (b) Transitions between states in the quantum well produce absorption lines between the band gaps of the GaAs well and AlGaAs barrier.



⇨ ***Blue shift*** of optical transitions with decreasing well width

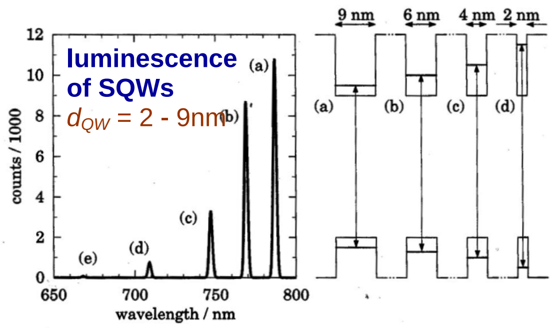
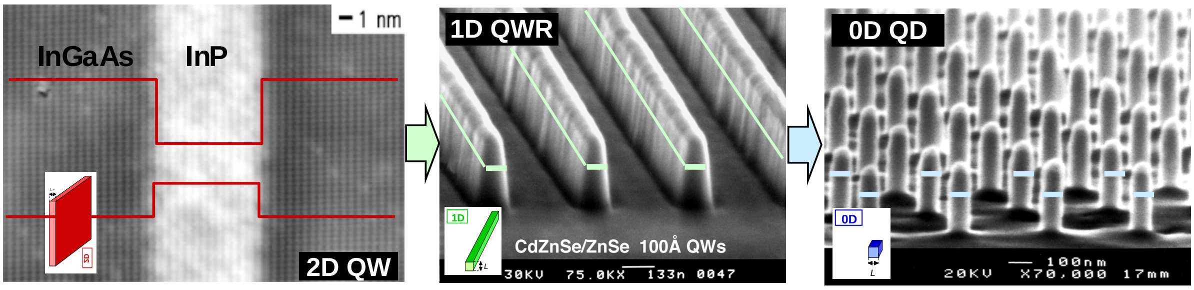


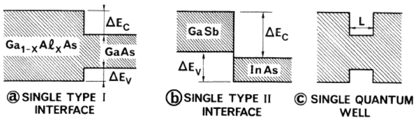
FIGURE 1.4. Photoluminescence as a function of wavelength for a sample with four quantum wells of different widths, whose conduction and valence bands are shown on the right. The barriers between the wells are much thicker than drawn. [Data kindly supplied by Prof. E. L. Hu, University of California at Santa Barbara.]

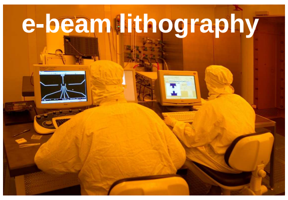
1.4.5 1D and 0D Systems: Realization and Size Quantization

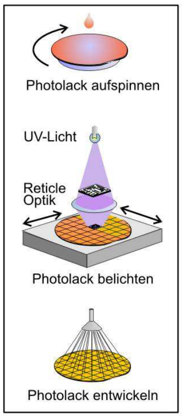
(1) Top down lithographic patterning starting from 2D heterostructures



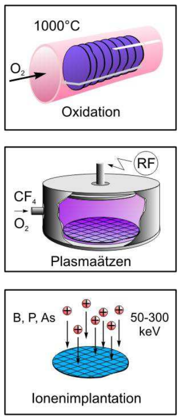
Band gap engineering







Lithographie



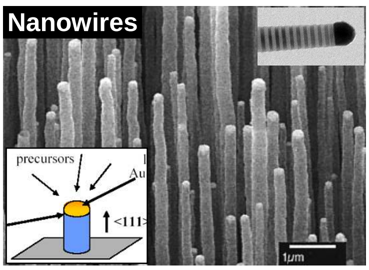
Strukturübertragung

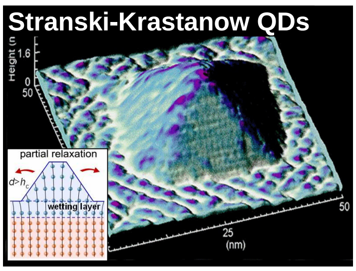
- ⇨ precise control of physial dimensions
- ⇨ arbitrary shapes and position control
- ⇨ combined with gap engineering

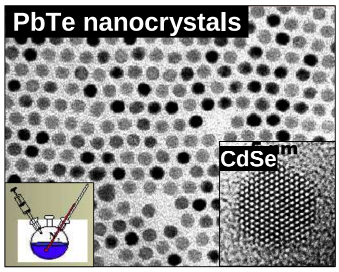
Draw back: High cost, size limitations, defect generation by patterning process

Realization of 1D and 0D Nanostructures

(2) Bottom up synthesis of "*self-assembled*" nanostructures by growth



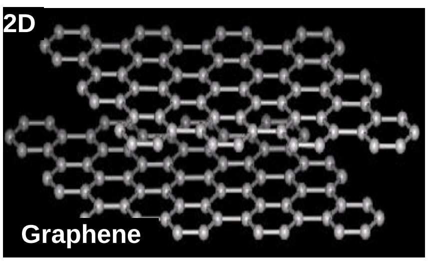


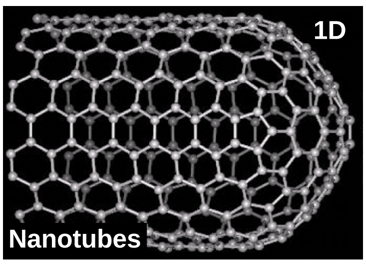


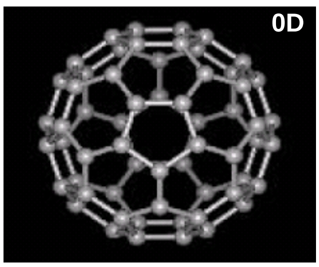
⇨ **High densities, low cost, but variation in size and shapes**

3. Realization of *molecular* nanostructures

(e.g. carbon-based, chemical synthesis, exfoilation .....

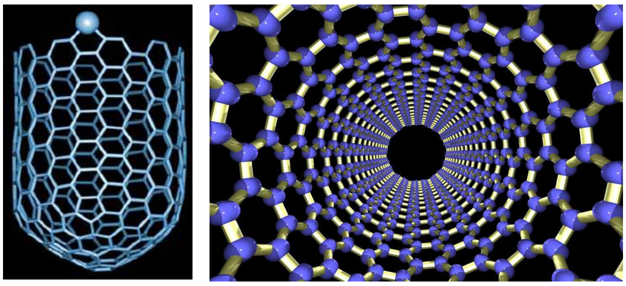


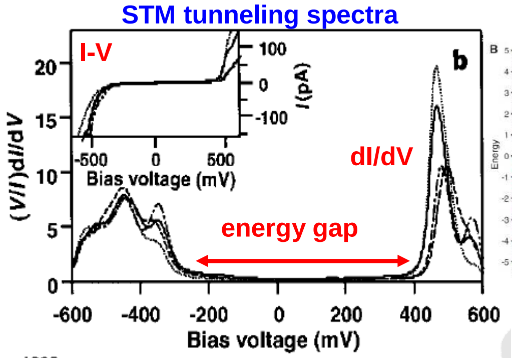


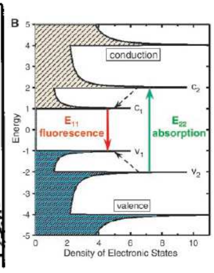


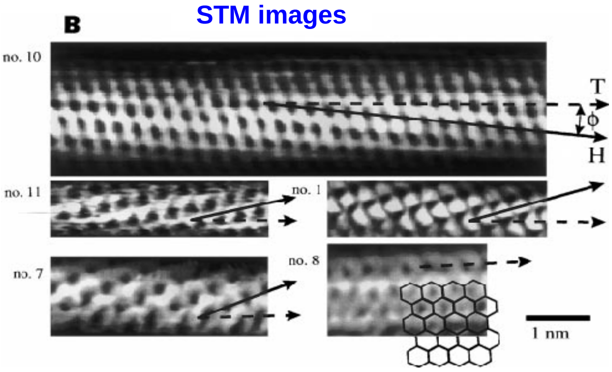
Size Quantization in 1D Nanowires

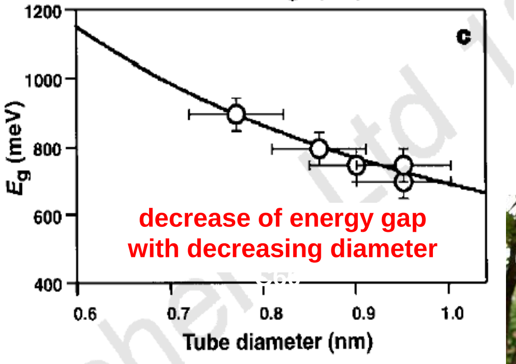
Example: Energy band gap of 1D carbon nanotubes vs. tube diameter

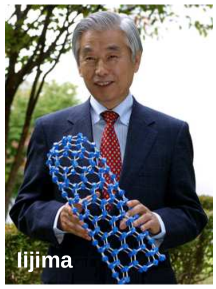












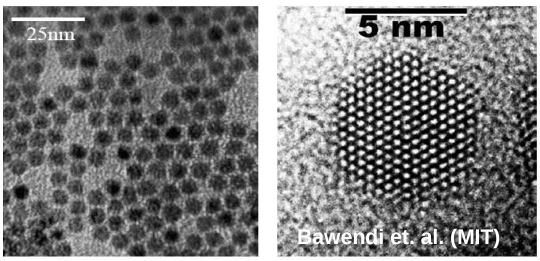
⇨ **Well-defined geometries, but mixtures of different structures**

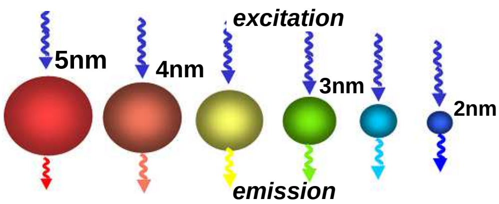
Teri Wang Odom & al; Nature Vol 391 January 1998

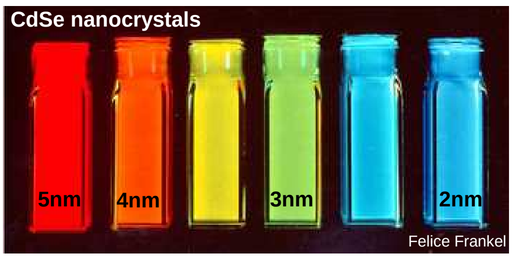
Size Quantization in 0D Quantum Dots

Example #1: Colloidal CdSe nanocrystals synthesized by reaction in liquid solutions

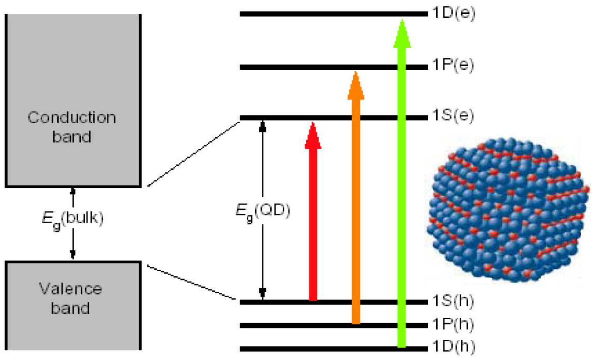
sizes ranging from 2 to 6 nm

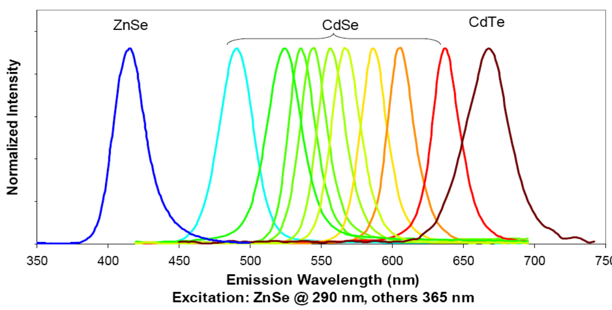




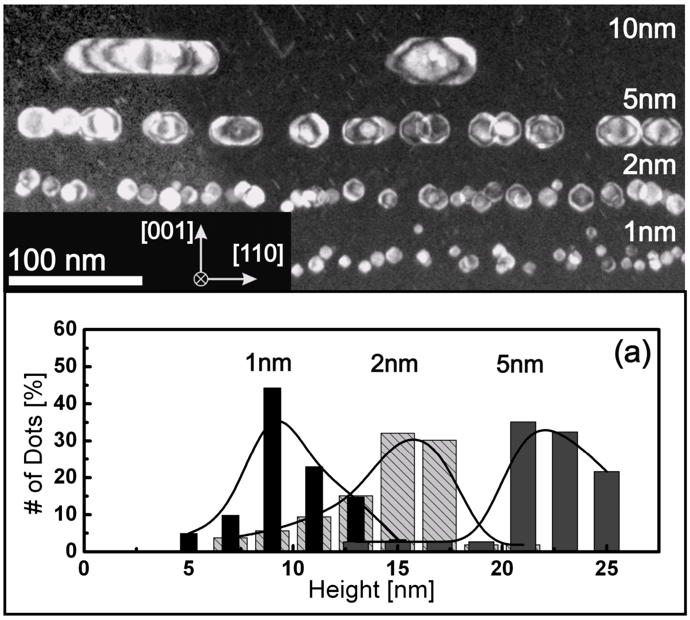


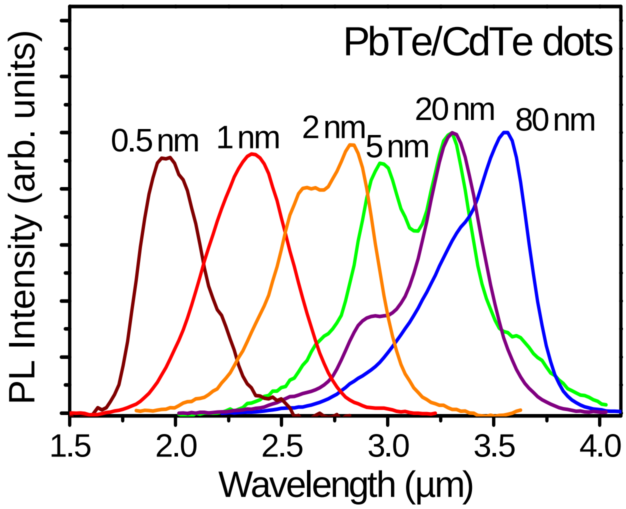
Bawendi (MIT), Murray (IBM), Alivisatos (Stanford), etc.





Example #2: Epitaxial PbTe quantum dots embedded in CdTe by phase separation



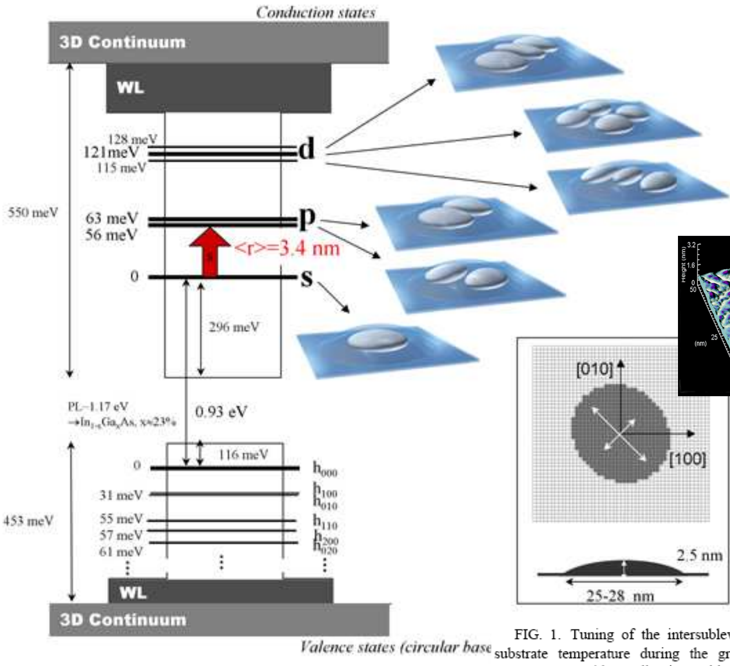


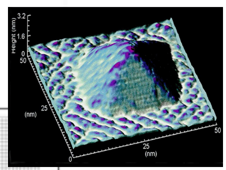
Size variation from ~5 to 30 nm

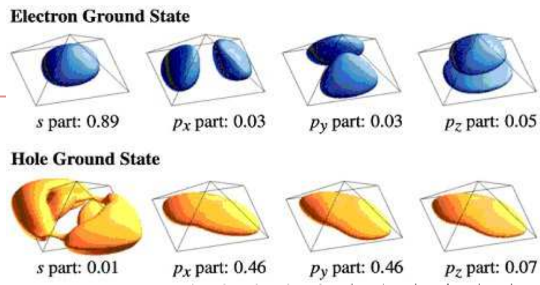
Photoluminescence Emission

⇨ **Solution of Schrödinger equation, envelope function or tight binding calculation**

Example: InAs quantum dots in GaAs







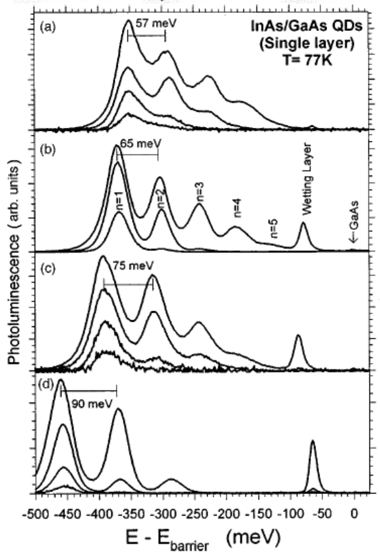
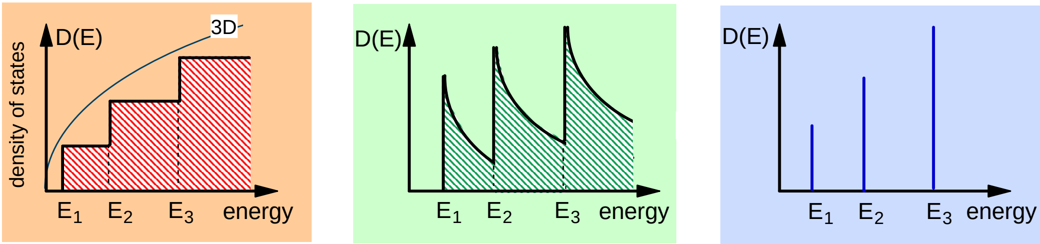


FIG. 1. Tuning of the intersublevel energy spacing with the substrate temperature during the growth of InAs/GaAs QD's. Larger QD's with smaller intersublevel energy spacings are obtained at higher temperatures: (a) Shows T_{growth}=535 °C, (b) T_{growth}=515 °C, (c) T_{growth}=500 °C, (d) T_{growth}~480 °C, giving an intersublevel energy spacings adjustable between 57 and 90 meV. The state-filling spectroscopy is obtained with the photoluminescence at 77 K, with the highest excitation of a few kW/cm^2 above the barrier energy.

Application for Optoelectronic Devices

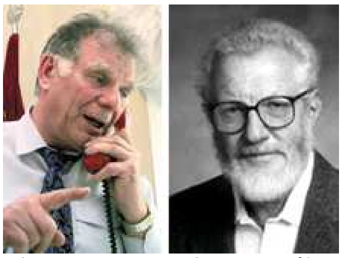
» **Tuning of the emission spectrum for particular applications**
» **Enhanced performance and efficiency due to peaked density of states**

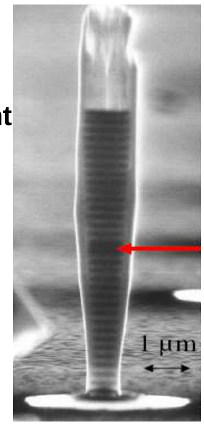


Examples:

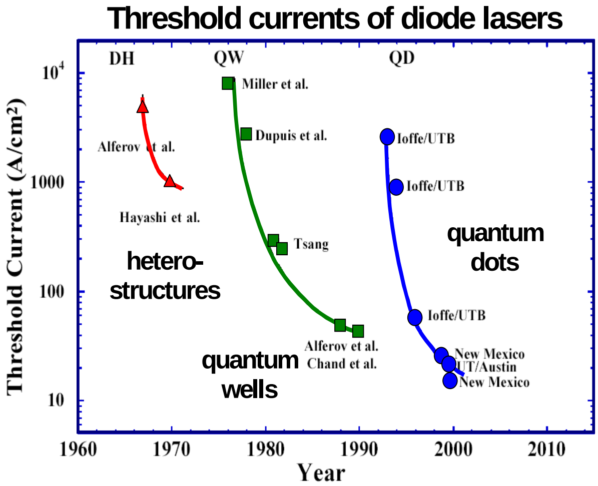
1. Quantum well and QD Lasers:
» **peaked density of states allows lower threshold current**

2. Single photon sources





Herber Krömer and Zores Alferov– Nobel prize 2000

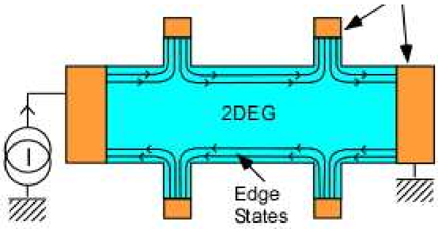


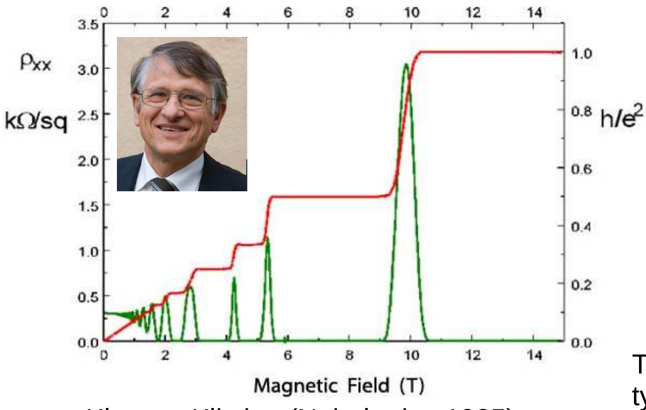
1.5 Quantum Transport in Nanostructures

⇨ ***Fundamentally differs*** from that in bulk materials where conductance linearly scales with size.

1.5.1 Quantum Hall Effect in 2D Structures

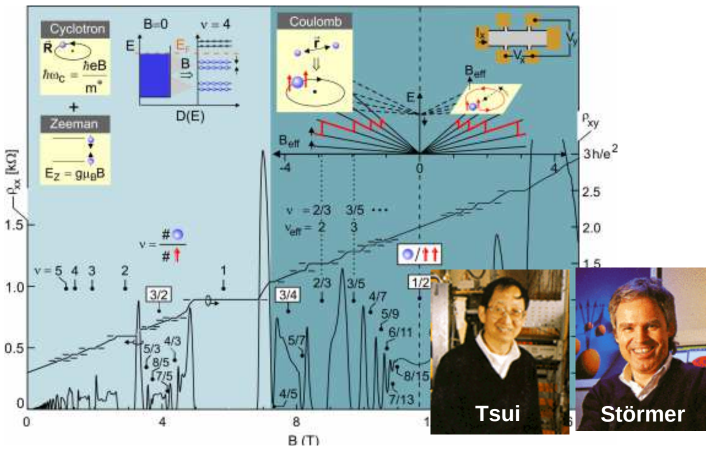
Quantized Hall resistance due to edge channels ***in magnetic fields***. Resistance plateaus at discreet values of fundamental constant h / e^2 = *independent* of geometrical dimensions





Klaus v. Klitzing (Nobel prize 1985)

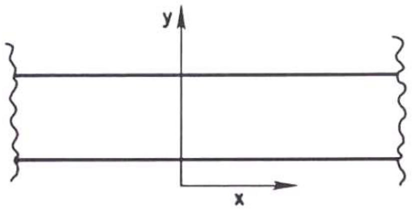
Fractional quantum Hall effect in very high mobility 2D structures and very low temperatures, (H. Störmer and D. Tsui, Nobel prize 1998).

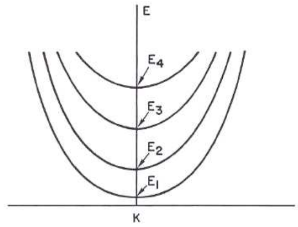


This was explained by J. Laughlin by the formation of a new type of composite fermions (Nobel prize 1998).

1.5.2 Quantized Conductance in 1D Nanowires

- In 1D nanowires, the **conductance is fundamentally quantized** even without magnetic field.
- The conductance is ***independent*** of the nanowire length, only depends on the discreet number of conducting channels:
  Landauer-Büttiger formula: Each populated1D subband contributes to the total conductivity with the **quantum conductance e^2/h**





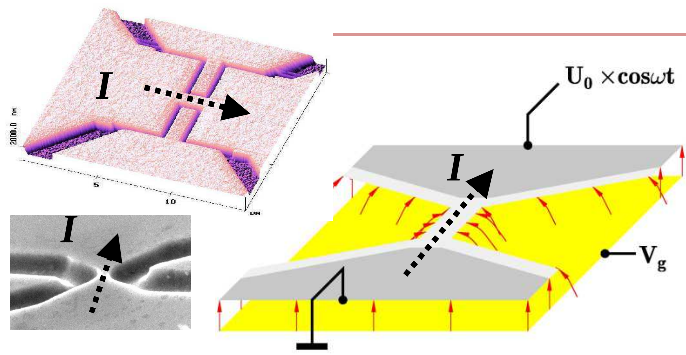
$$G = \frac{e^2}{h}\sum_n T_n = \frac{e^2}{h}N$$

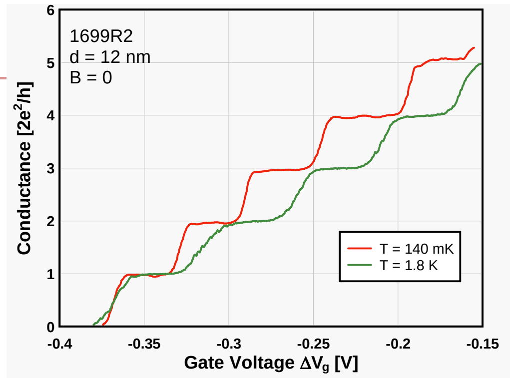
spin degeneracy

$$G = \frac{2e^2}{h}\sum_n T_n = \frac{2e^2}{h}N$$

Requirement: Wire length must be shorter than the inelastic mean free path (Ballistic transport)

Example: PbTe nanowire (quantum point contact)





Quantized Conductance in 1D Nanowires: Carbon Nanotubes

Example: Carbon nanotubes

Stefan Frank, *et al. Science* **280**, 1744 (1998

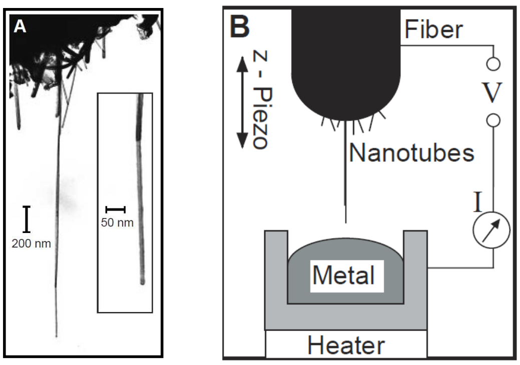


Fig. 1. Nanotube immersed in a liquid mercury metal. (**A**) TEM micrograph of the end of the nanotube fiber, from which several long and straight nanotubes protude. The nanotubes are very clean after they have been dipped in liquid metal. (**B**) Experimental setup: The current *I* is measured as the fiber is moved up and down into the liquid metal.

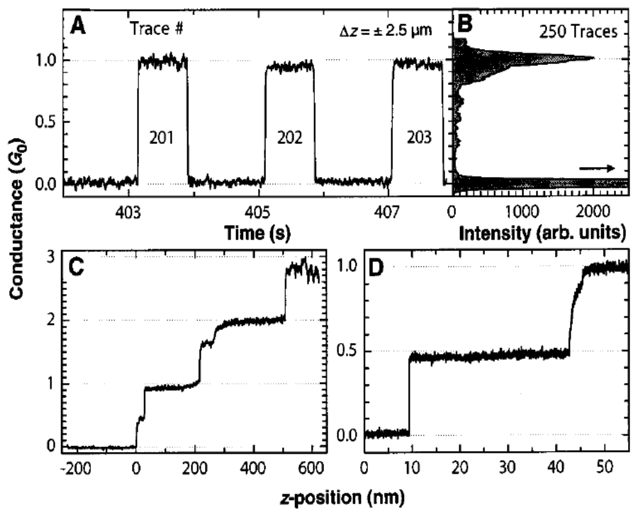
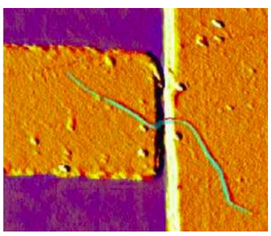
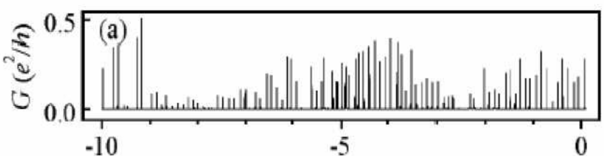


Fig. 2. (**A**) Measured conductance of a carbon nanotube that is moved in and out of the mercury liquid. The cycle is repeated 250 times to show its reproducibility. (**B**) Histogram of the conductance data of all 250 traces showing peaks at plateaus at $1G_0$ and at 0. (**C**) Trace of a nanotube contact with two major plateaus and minor pre-steps. This trace is interpreted as resulting from noninteger conductance interpreted to result from the nanotube tips. A clear example of this effect is shown in (**D**).

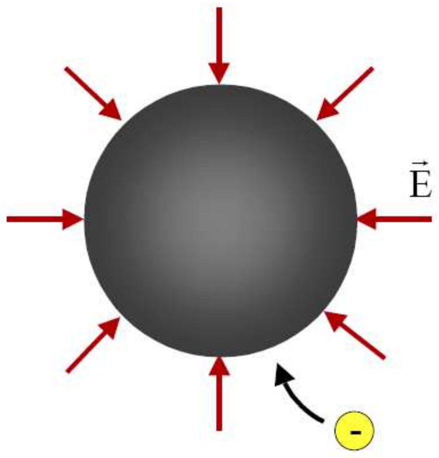


Nygård, Cobden, PRL 2002.



1.5.3 Coulomb Blockade in 0D Quantum Dots

COULOMB BARRIER = *discrete* energy for adding charge



$$\mathrm{div}\,\vec{E} = \frac{\rho}{\varepsilon_0} \qquad \vec{E} = -\mathrm{grad}\,U$$

$$\vec{E} = \frac{Q}{4\cdot\pi\cdot\varepsilon_0}\frac{1}{r^2} \qquad U = \frac{1}{4\pi\varepsilon_0}\frac{-Q}{r}$$

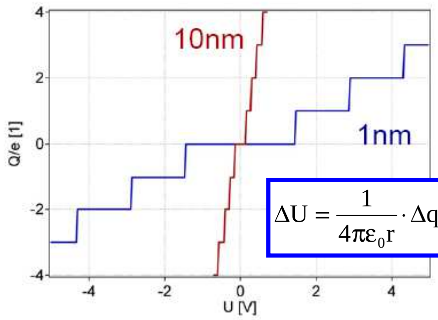
$$C = 4\cdot\pi\cdot\varepsilon_0\cdot r \qquad W = \frac{1}{2}\frac{Q^2}{C}$$

Single electron charging energy:

$$W_C = \frac{e^2}{8\cdot\pi\cdot\varepsilon_0\cdot r}$$

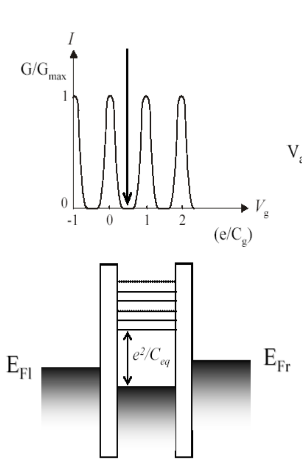
1nm cluster
W_C = 1eV

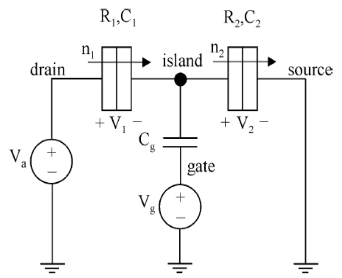
increases with decreasing dot size *r*

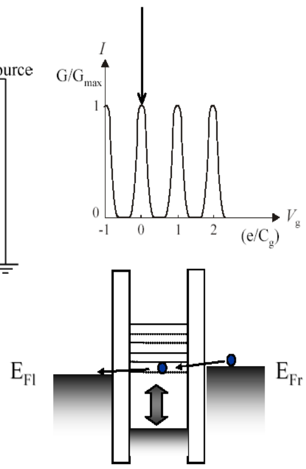


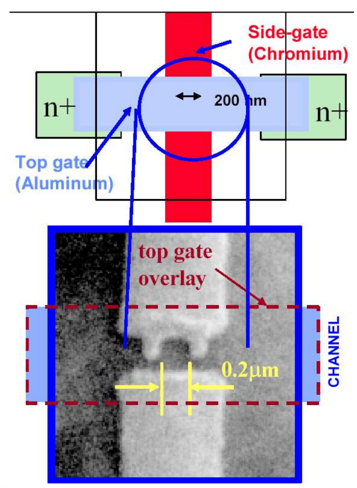
$$\Delta U = \frac{1}{4\pi\varepsilon_0 r}\cdot\Delta q = \frac{\Delta q}{C}$$

Single electron transistors based on the Coulomb blockade effect

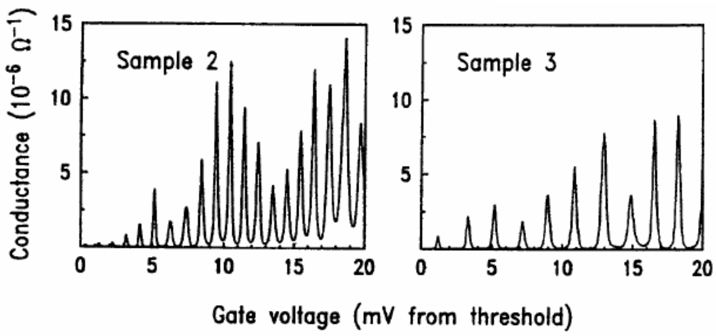








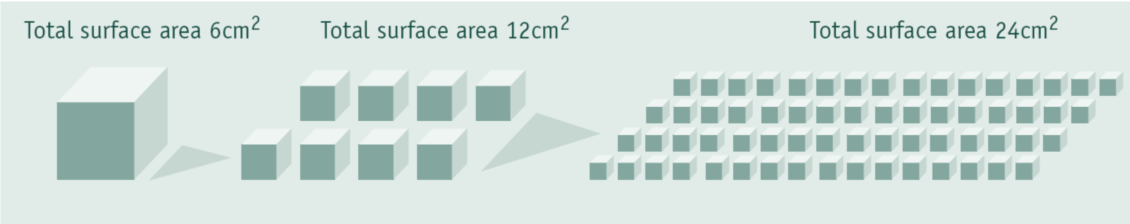
The system is biased off resonance.
A gap exists in the density of states of the island due to the Coulomb charging energy.



Kastner, Rev. Mod. Phys. 1992

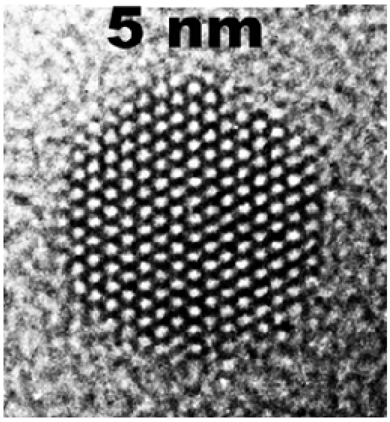
1.6 Strucural Properties: Nanocrystals & Surface Effects

» Nanostructures exhibit extremely large surface area to volume ratios



Ratio scales ~ linearly with physical dimensions !

Nano-crystals:	10 nm diameter:	~ 5 % of atoms are at the surface
	3 nm diameter:	~ 15 % of atoms are at the surface
	1 nm diameter:	~ 50 % of atoms are at the surface !



Consequences on the material properties:

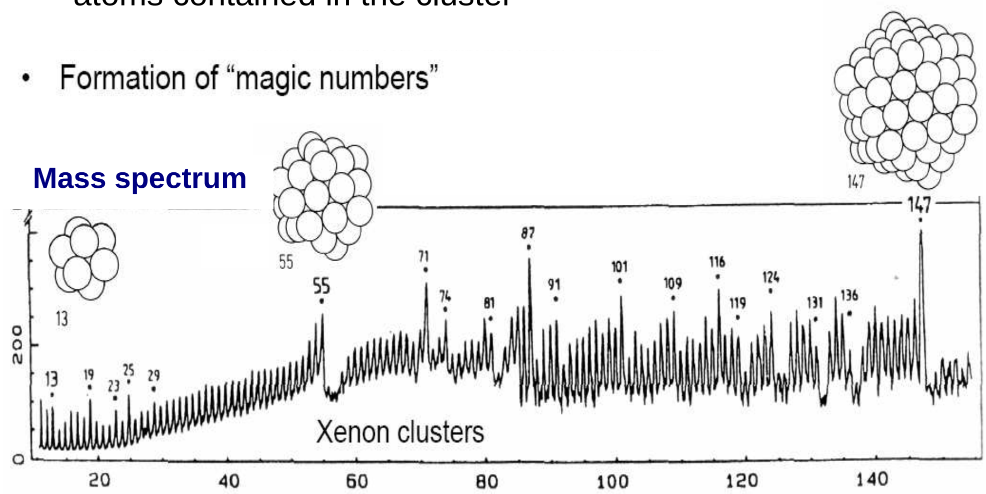
- ❖ Large number of broken bonds affects stability
  » Example: Reduction of melting point (up to 40%),
- ❖ Surface relaxation and changes in crystal structure: Novel structures can be formed.
- ❖ High surface reactivity & strong interaction with environment: » application for chemical catalysis and chemical and bio-sensors.

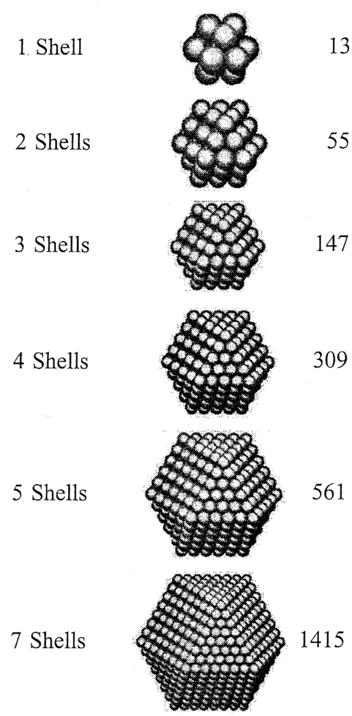
1.6.1 „Magic“ Sizes of Nanoclusters: Shell Model

Stability of atom clusters:

⇨ Depends on the number of individual atoms contained in the cluster

- Formation of “magic numbers”



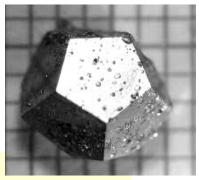


- Enhanced stability at *geometric shell* closings
- For rare gas clusters: formation of icosahedral shell structures

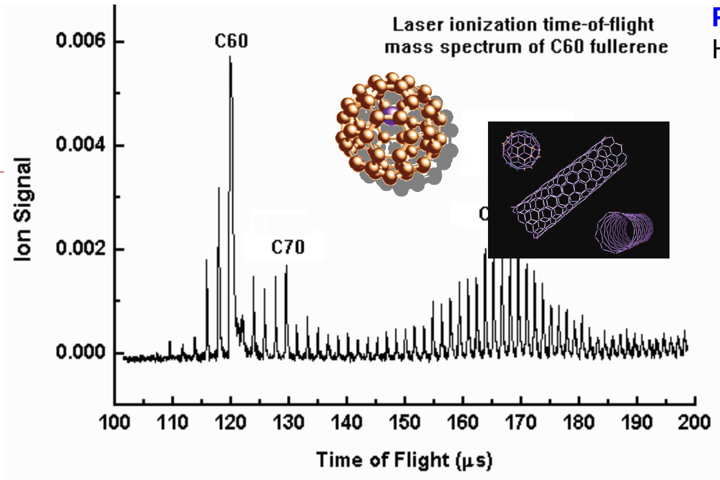
1.6.2 Icosahedral “Quasi-Crystals” & Molecular NanoStructures

Alternative bonding configurations due to finite atom numbers:

⇨ Formation of new structure types that are not stable in bulk material: “Quasi-Crystals” with no translational symmetry as required for bulk crystals (Shechtman, Nobel prize 2011)
Icosahedral structures with 5-fold symmetry typical for clusters with N = 13, 55, 147, 309 …

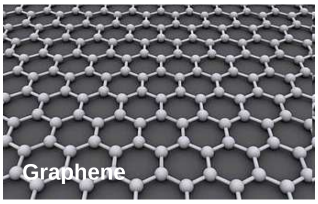


⇨ **Novel geometries/molecular Nanostructures**: Fullerenes, nanotubes, graphene, etc.



Fullerenes: Discovered 1985 by R. Smalley, R. Curl & H. Kroto (Nobel prize 1996)

Graphene: Discovered in 2004 by A. Geim and A. Novoselov, (Nobel prize 2010)



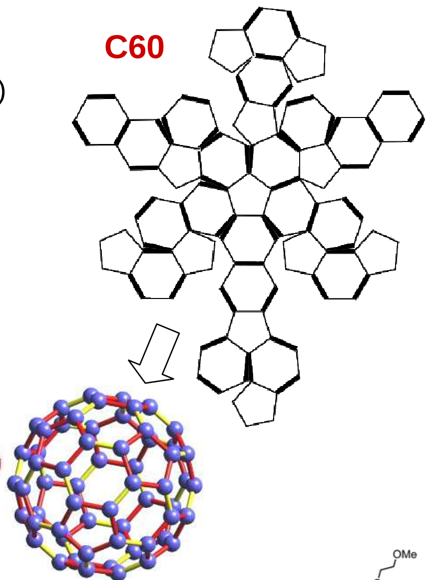
Carbon Fullerenes: Zoology of Different Structures

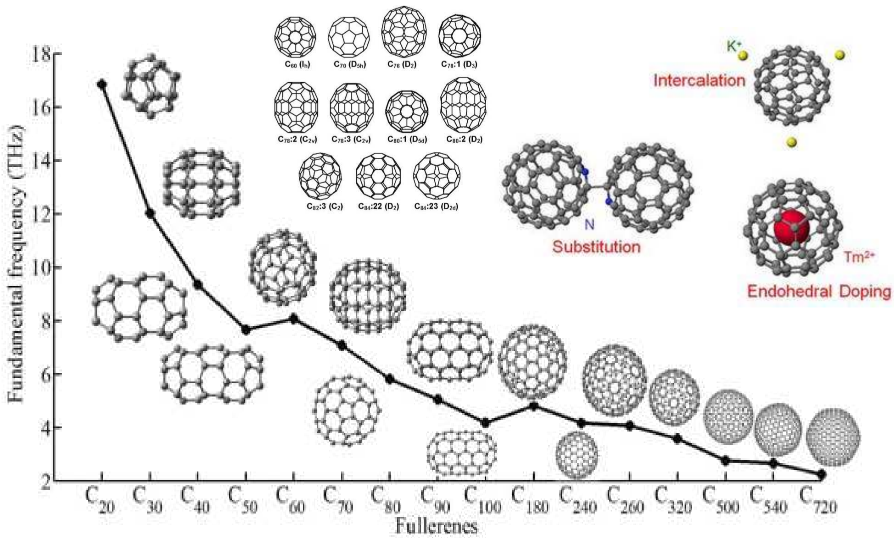
⇨ **Consists of 12 carbon pentagons joined together by a different number of hexagons.**

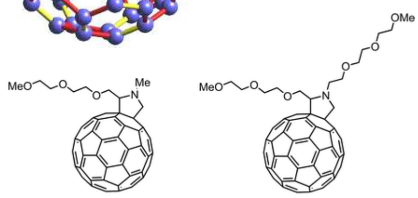
Based on Euler's theorem: 12 pentagons are always required for closure of a arbitrary atom network consisting of n hexagons.

C60 = 12 pentagons + 20 hexagons (= smallest Fullerene, d = 1.1 nm)
C70 = 12 pentagons + 25 hexagons
C80 = 12 pentagons + 30 hexagons & existence of several isomeres

C60



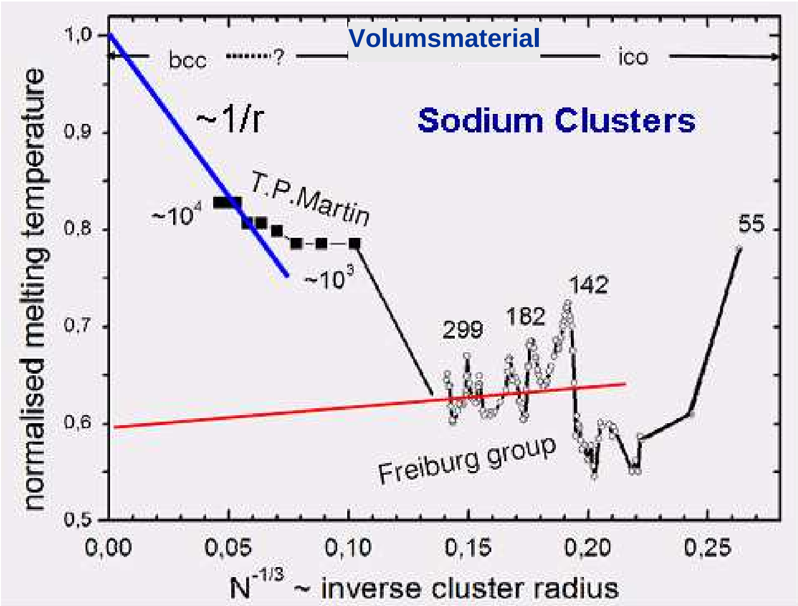


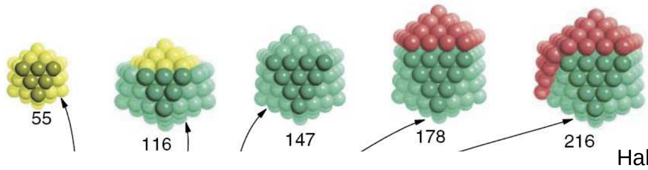


Most abundant species: C60, C70, C76, C80, C82, C84, C86, C90 and C94

1.6.3 Thermodynamic Size Effects

Example: Dependence of melting point on cluster size





Haberland, PRL 2005

- **Large clusters**: continous reduction of the melting point according to the Gibbs-Thomson Relation:

$$\Delta T = \frac{4\sigma M T_{bulk}}{\Delta H_m r \rho}$$

- **Small clusters**: magic sizes with increased thermodynamic stability.

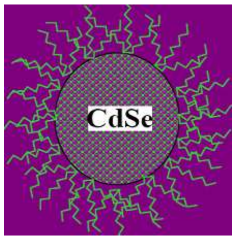
- **High reactivity** of unsaturated clusters, application for chemical catalysis.

1.7 Bio-Inspired Nanostructures

Example: Bio-functionalization of colloidal nanocrystals by attachment of bioactive proteins, antibodies, etc. ... to the organic shell.

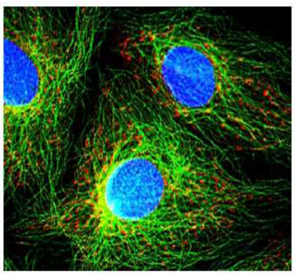
Applications: Medical diagnostics based on fluorescent bio-labels or magnetic nanoparticles.

Therapeutic applications for medical treatments.

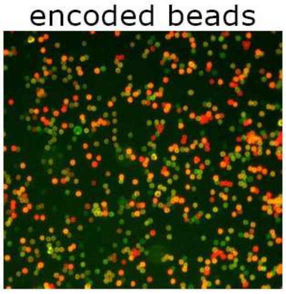


QBead™ encoded beads

Bio-labeling



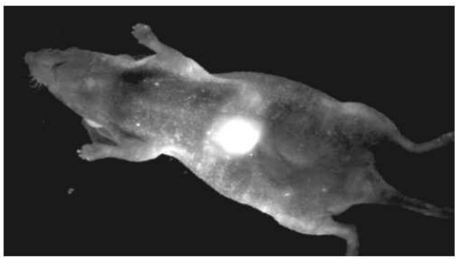
- Detection reagents for microscopy
- DNA chips
- flow cytometry
- immunoassays, ...



Platform for Multiplexed assays:

- proteomics
- genotyping
- gene expression)

Future applications



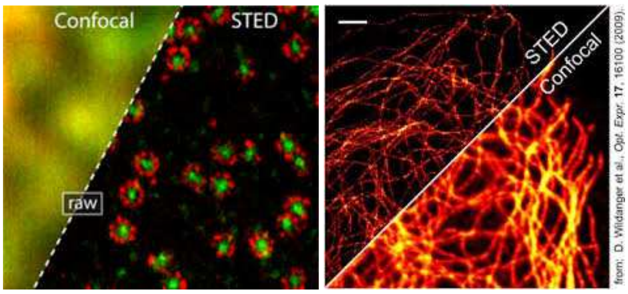
- Live cell imaging
- *in vivo* imaging,...

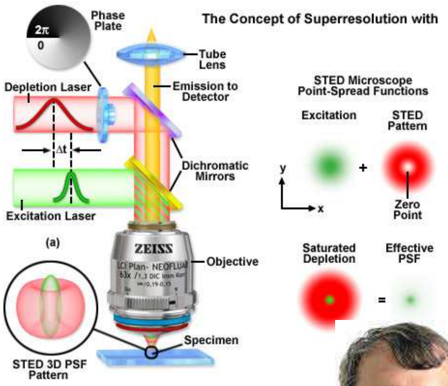
Imaging of Living Cells using Fluorescence Markers

Sub-wavelength fluorescence microscopy:

1999: Superresolution STED fluorescence microscopy
by Stefan Hell in Göttingen (Nobel prize 2014)

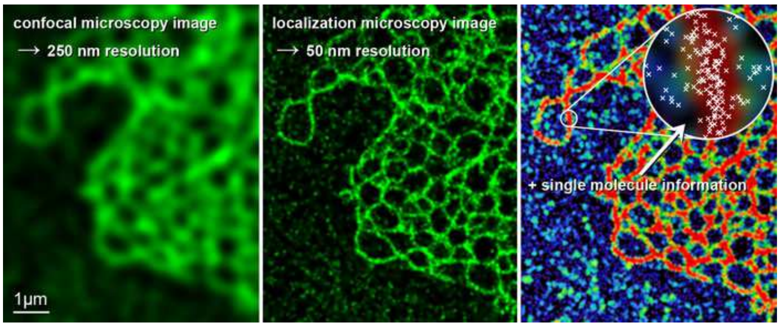
Example STED:

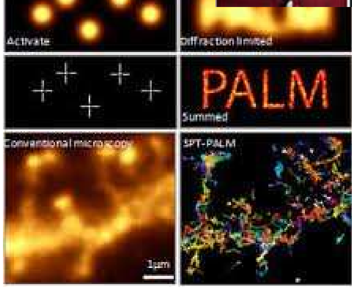




2006: New fluorescence microscopy methods (PALM, STORM, RESOLFT) invented
by Eric Betzig at Harvard and William Moerner at Stanford (Nobel prize 2014)

Example PALM:

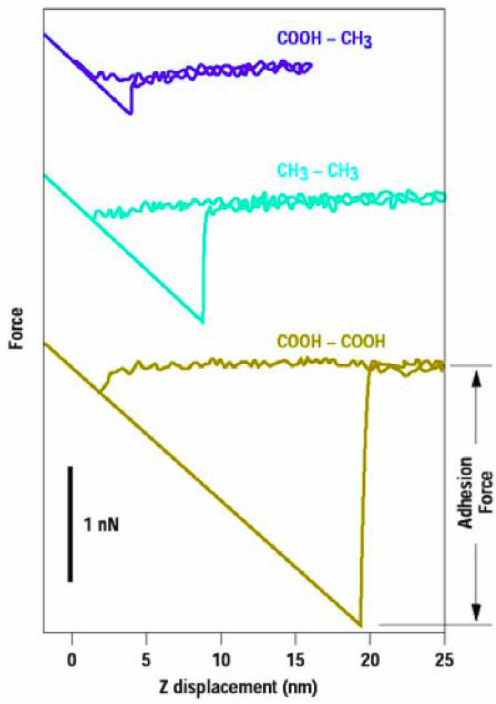


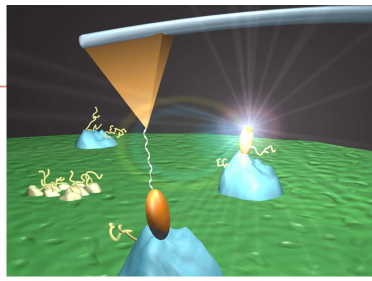


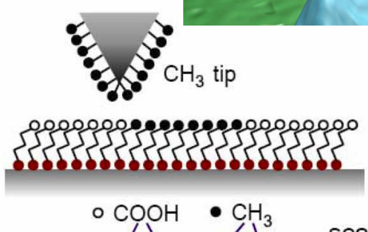
Biochemical Sensing with Functionalized AFM Tips

Example: Site specific bonding forces determined by force – distance measurements

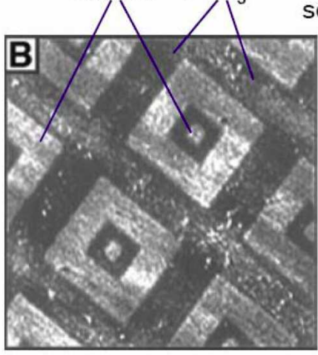
Chemical sensing by measuring the tip-surface adhesion force as a function of surface position





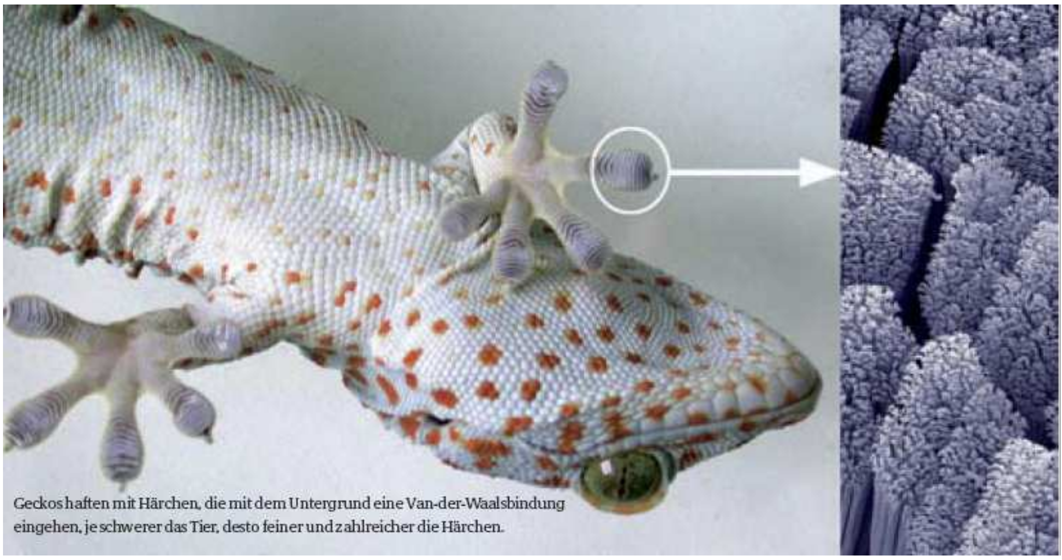


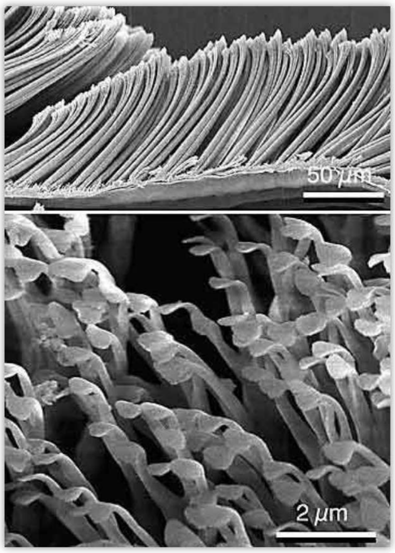
scanned in air



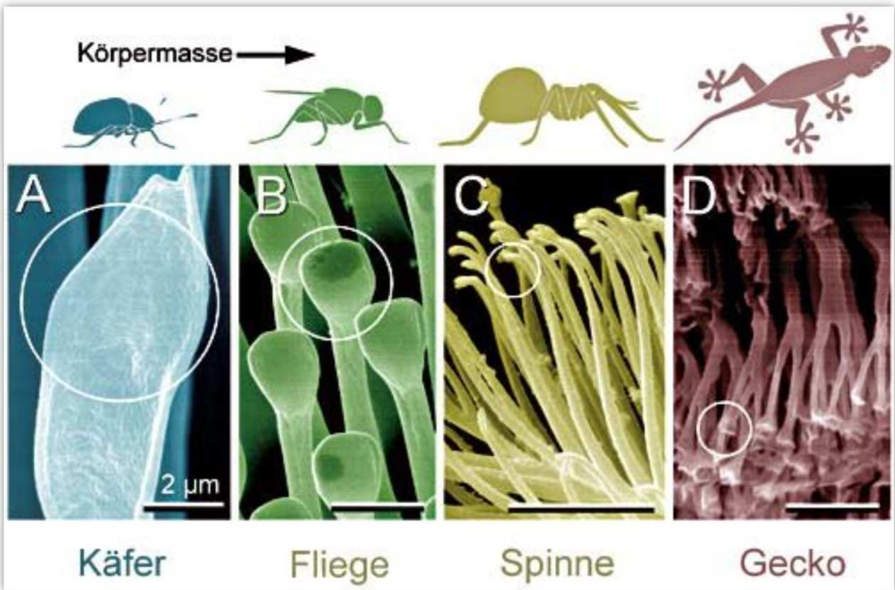
Nano in Nature

Gecko: Adhesion by Nanohairs

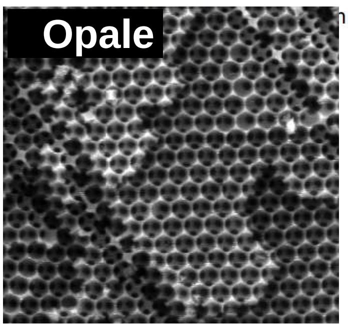




Elektronenmikroskopische Aufnahme der Setae (oben) und Spatulae (unten) des Tokee.

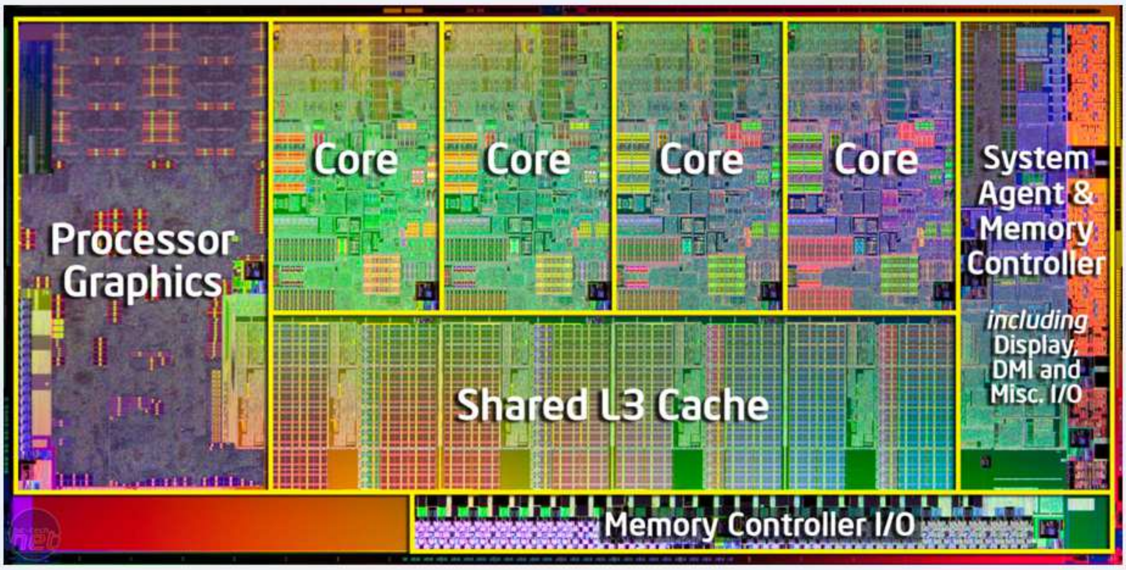


Das Elektronenmikroskop enthüllt die spatelförmigen Feinstrukturen, die an den Fußsohlen von Käfern, Fliegen, Spinnen und Geckos für Haftung an Decken
n.



1.8 NanoDevices: Downsizing of Silicon Transistors

Moderne Silicon Chips

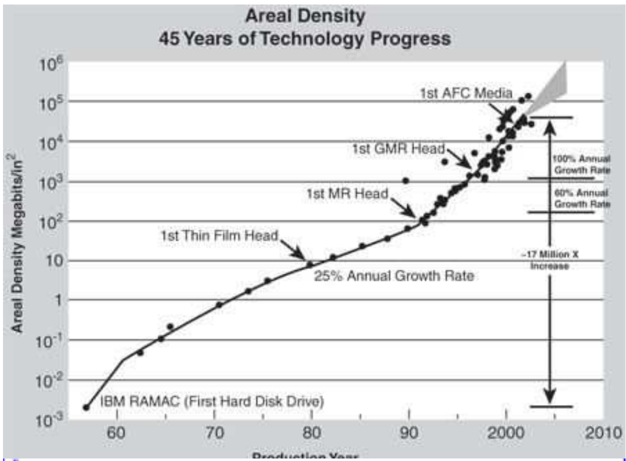


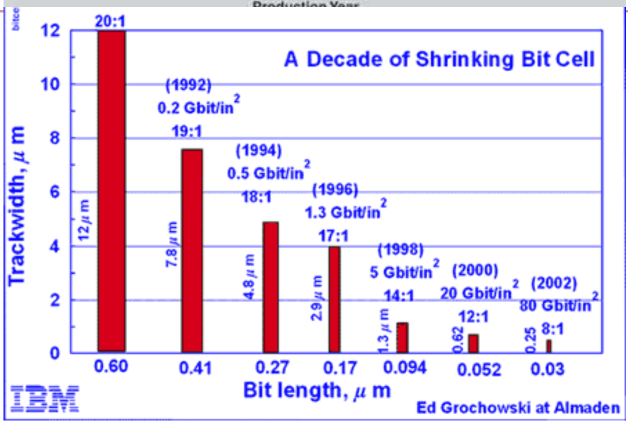
⇨ Complex architectures: Multicore processors, memory, readouts, etc.

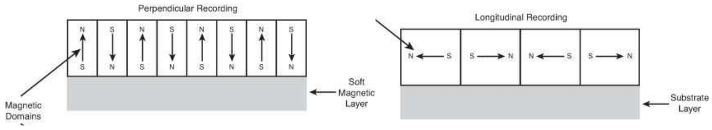
⇨ Contain more than 10 Billion (=10^{10}) transistors per chip !

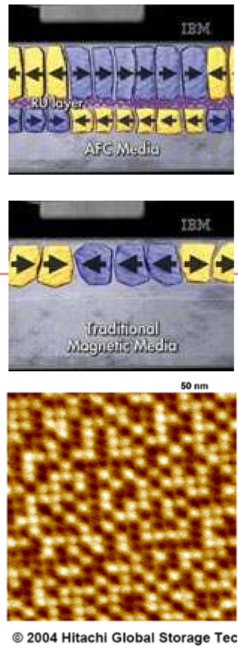
⇨ Current transistor sizes < 30nm: True Nanotechnology !

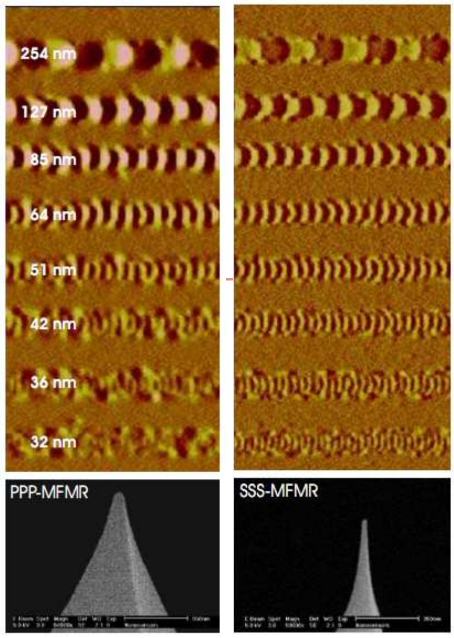
Data Density of Magnetic Storage Devices (Hard Disk Drives)





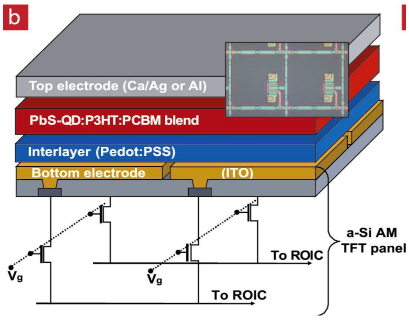




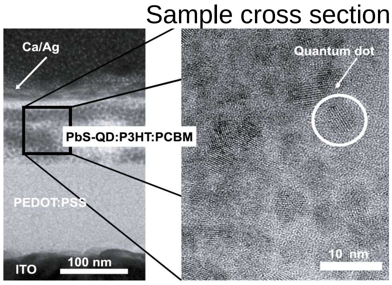


Optoelectronics

Infrared Camera using PbS Nanocrystals:



Sample cross section



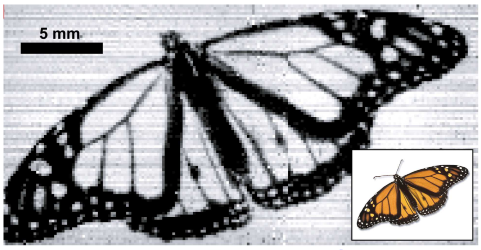
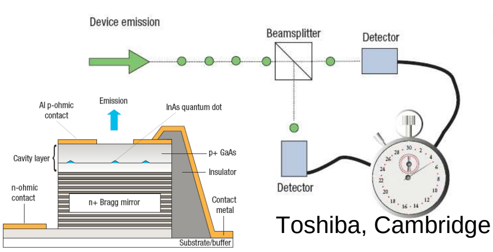


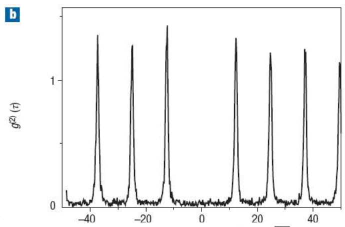
Image @ 1300 nm

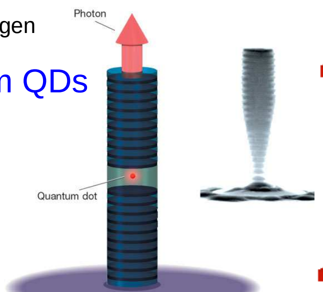
W. Heiss, in collaboration SIEMENS Erlangen

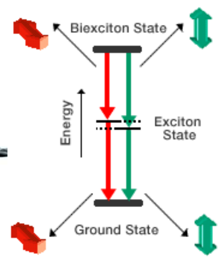
Single Photon & Entangled Two-Photon Sources from QDs



Toshiba, Cambridge

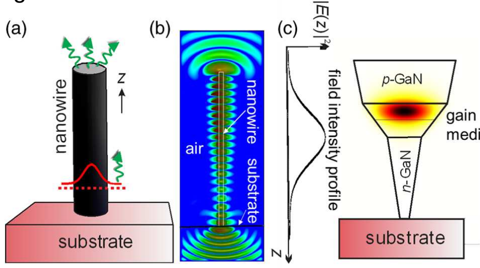


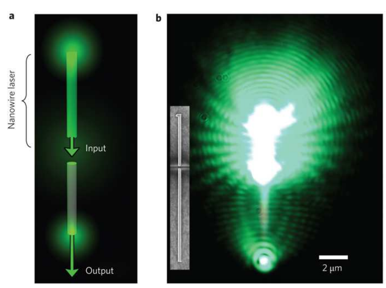




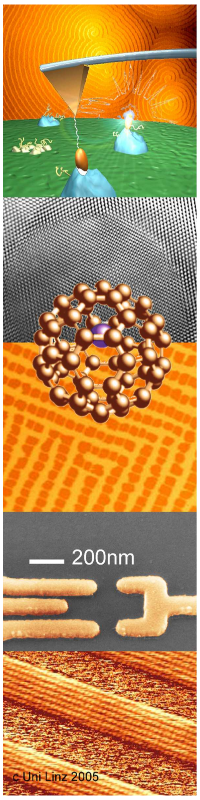
Nanowire Lasers:

Review: Arafin et al., J. Nanophotonics 2013





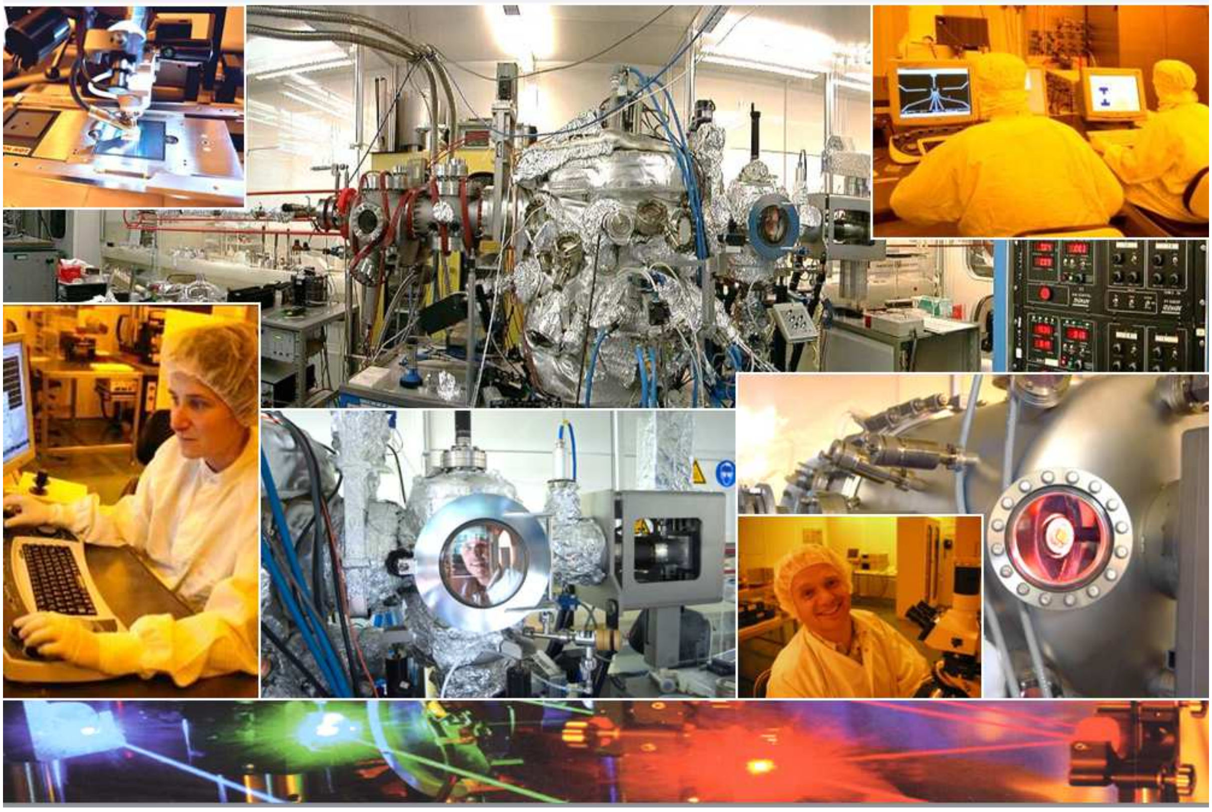
1.9 Nanoscience in Linz



Forschungsschwerpunkt der TNF

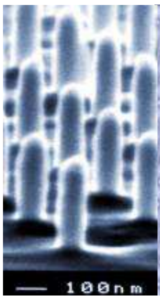
- **1990:** Erste Nanoforschung in Linz – Institut für HL-Physik
- **1996:** Doktoratskolleg „Niedrig-Dimensionale Nanostrukturen"
- **1998:** Wahlfachgruppe „Nanoscience" im Physikstudium
- **1998:** Zentrum Nanoscience & Technolgie in Linz
- **2000:** **Exzellenzschwerpunkt der JKU**
- **2005:** Forschungsnetzwerke: Öst. Nanoinitiative
  „Nanostructured Surfaces and Interfaces"
  Sonderforschungsbereich „Infrared-Optical Nanostructures"
- **2009:** **Masterstudium „Nanoscience & Technology"**
  einzigartiges Studium in Österreich,
  interdisziplinär und international ausgerichtet
- **2018:** **Baubeginn neuer Reinraum am LIT**

Reinraum @ Physik



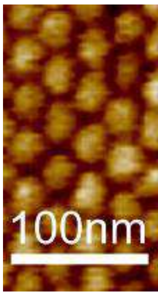
Nanoscience Research at JKU

Semiconductors



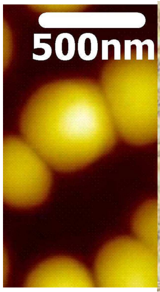
- Heteroepitaxy
- Nanostructuring
- Optical, Electronic, Magnetic Characterization
- Spintronics

Biophysical Systems



- Patch-Clamp-Technique
- Atomic Force Recognition
- Nano-Reader
- DNA-Sequencing

Polymers/Nanocomposites



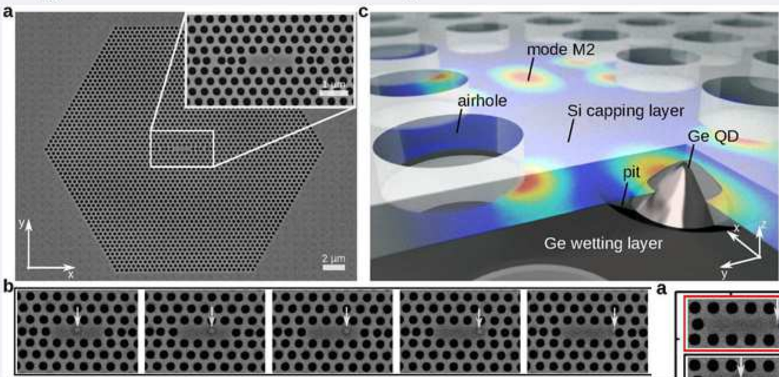
- Organic Electronics
- nano-electromechan. organic Sensors und Actuators
- Nanocomposites
- Carbon-Nanotubes

Surfaces/Interfaces

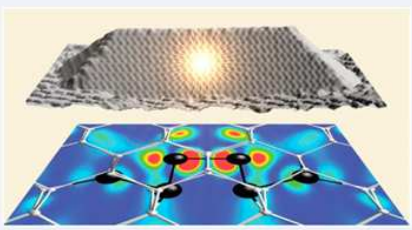
- Metallic Clusters
- Surface Reactions
- Optical, Ionenbeam- and Scanning-Probe-Characterization

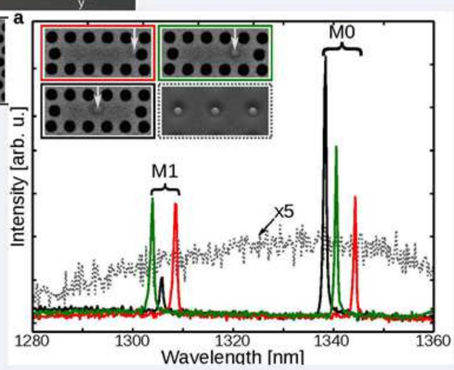
Nanophotonik @ JKU

Light emission from SiGe quantum dots embedded in photonic crystals



- Enhanced functionality of Si chips !

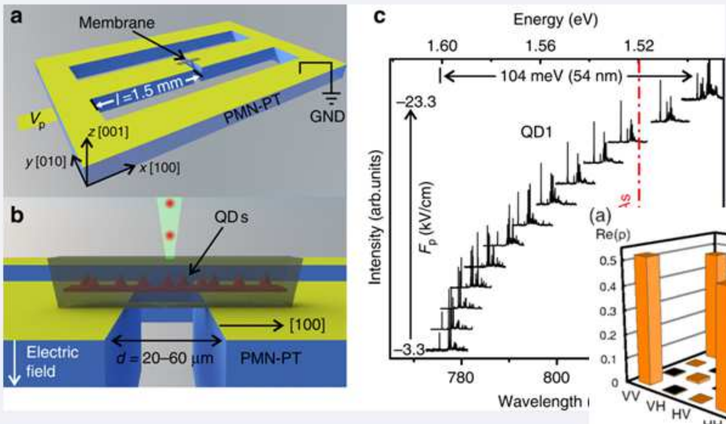




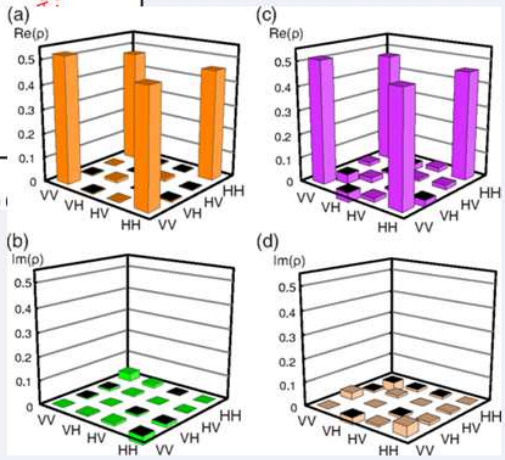
JKU, Institut für Halbeiterphysik, M. Brehm et al.

Quanten Communication @ JKU

Emission von quantenmechanisch verschränkten Photonenpaaren für Quantenkryptographie



Record fidelity of 97% !

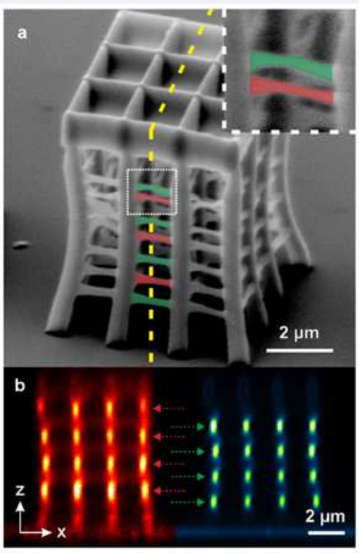


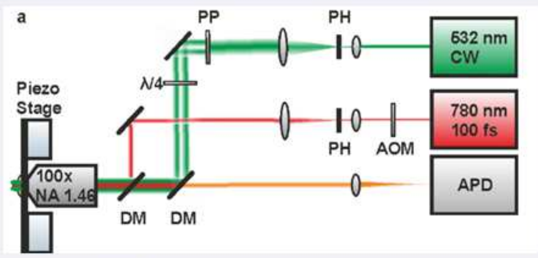
Piezo tunable double photon emission from single GaAs quantum dots

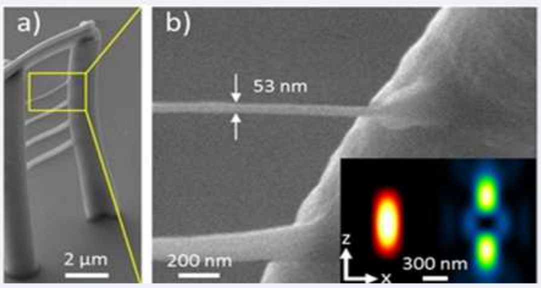
JKU, Institut für Halbeiterphysik, A. Rastelli et al.

3D Nanolithography @ JKU

Herstellung von 3D Nanostrukturen mittels 2 Photonen Belichtung







JKU, Institut für Angewandte Physik, T. Klar et al.

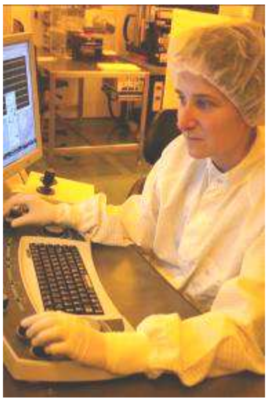
Experimental Nanoresearch Facilities at JKU

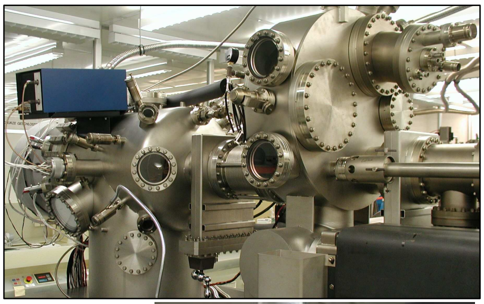
Fabrication of Nanostructures:

- ➪ Moleklularstrahlepitaxie
- ➪ Elektronenstrahlithographie
- ➪ Plasmaätzen
- ➪ Synthese von Nanokristalle

Nanoanalytics

- ➪ Rastertunnelmikroskopie
- ➪ Atomkraftmikroskopie
- ➪ Transmissionselektronenmikroskopie
- ➪ Rasterelektronenmikroskopie
- ➪ Hochauflösende Röntgenbeugung





Measurement Techniques

- ➪ Optische Spektroskopie
- ➪ Photolumineszenz und Kathodolumineszenz
- ➪ Elektronentransport im milli Kelvin Bereich und hohen Magnetfelder
- ➪ SQUID Magnetometrie und Suszeptometrie
- ➪ Spinresonanz
- ➪ TEM, SEM, etc. (Zona)

Nanodevices:

- ➪ Optoelektronik: Lasers, single photon sources, Detektoren, photonische Kristalle, etc.
- ➪ Einzelelektronentransistor, Spinelektronik
- ➪ Solar cells
- ➪ Nanosensors
- ➪ Quantum communication
- ➪ …..

1.10 Topics of this Course

➪ Nanocharacterization is an essential building block of NST !

Why ? We know that the properties of nanomaterials *strongly change* with size, shape, composition, surface and interface structure, … in contrast to bulk material.

➪ Many different parameters of the nanostructures must be known, such as:

- ➪ **Structure: Geometry, size, shape, morphology**
- ➪ **Chemical composition, and distribution of elements**
- ➪ **Bonding type, properties of surface and interfaces,**
- ➪ **Electronic properties: Band structure & energy levels**
- ➪ **Transport and optical properties: Absorption/emission, ..**
- ➪ **Magnetic properties, mechanical properties,**
- ➪ **Chemical & biological functionality, ..**

➪ Many different complementary experimental techniques must be employed in order to gain a *comprehensive* understanding of the complex behavior of nanostructures

Contents of Nanocharacterization - I

1.11 Summary

- **Nanostructures exhibit many interesting and novel properties.**

  These differ from macroscopic bulk materials and can be *tuned* by:

  - Quantum size effects,
  - Reduced dimensionality of density of states,
  - Surface to volume area,
  - Ballistic transport and Coulomb blockade,
  - Many body effects, etc. ….

  » Nanostructures provide **new functionalities** and **novel device applications.**

- For understanding and modeling, the **microscopic structure** of nanostructures must be known in detail to determine structure-properties relationship

  » Requires **advanced high-resolution nano-characterization techniques**

- **High spatial resolution** is provided by **microscopy** when using **small wavelengths and small probe sizes**:

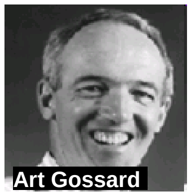
  » Photons, electrons, ions or scanning probes.

Appendix: Time Line of Nanoscience

- Nanoscience is a relatively new research field that developed only in the last 20 - 30 years.
- Development was driven by innovations and breakthroughs in nanomaterials & technologies that made the fabrication and investigation of nanomaterials feasible.

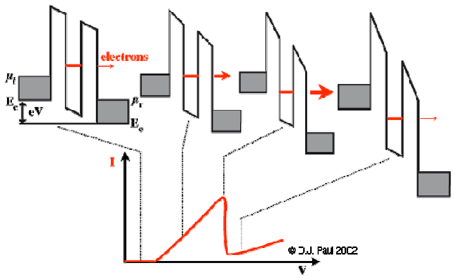
Early History: (1930 – 1980)

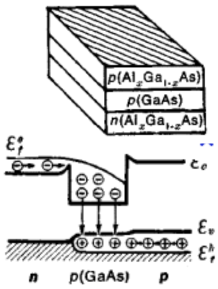
Microscopy: **Electron microscopy** invented 1931 by Ernst Ruska (Nobel prize 1985) and Max Knoll, **Scanning electron microscopy** developed by Max von Ardenne and Max Knoll in 1938. **Theory of electron optics** by Otto Scherzer and Donald Glaser in the 1940ties. Commercialization **of electron microscopes** staring from 1950ties First TEMs with nm resolution (1960ties).

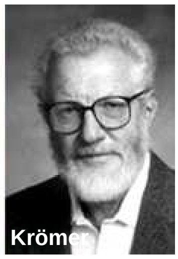


Nanofabrication: Development of **epitaxial growth techniques** for deposition of nm-thin layers for quantum wells and superlattices by molecular beam epitaxy (A. Cho, J. Arthur, A. Gossard). **Lithography & processing** of microelectronic devices (Intel, Bell Labs, RCA,Texas Instruments, … (Jack Kilby – Nobel prize 2000)

Novel devices: **Devices** based on low-dimensional semiconductor heterostructures, quantum wells and superlattices: » Resonant tunnelling diodes: L. Esaki - Nobel prize 1973, » Heterostructure lasers, high mobility transistor, .. : Herber Krömer and Zores Alferov– Nobel prize 2000.

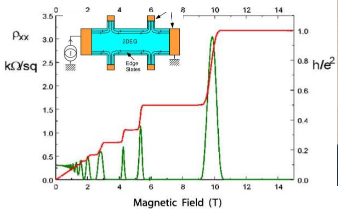






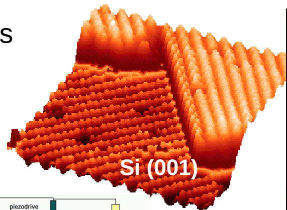
Breakthroughs in the 1980ies: Birth of Nanoscience

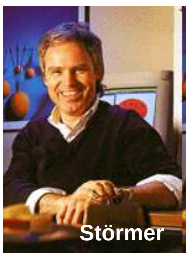
1980: Quantum Hall effect = quantized Hall conductance in high mobility 2D heterostructures in magnetic fields, discovered by Klaus v. Klitzing (Nobel prize 1985)

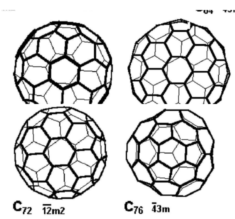


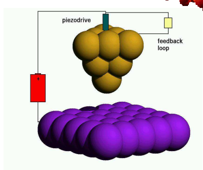
1981: Scanning tunneling microscope invented by H. Rohrer & G. Binnig (Nobel prize 1986): Enables real space imaging of atoms on surfaces.

1983: Fractional Quantum Hall effect & composite Fermions discovered by Tsui, Störmer and Laughlin (Nobel prize 1998)

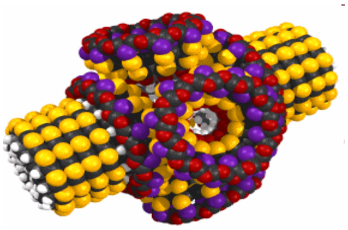








1985: Buckyballs of carbon atoms discovered by R. Smalley, R. Curl & H. Kroto (Nobel prize 1996) » New building blocks of molecular nanostructures

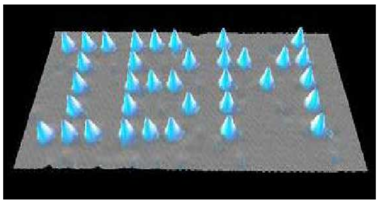
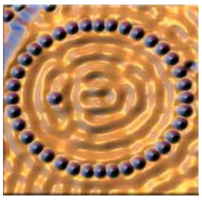


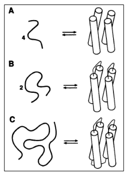
1986: "Engines of Creation" composed of molecular nanostructures proposed by E. Drexler

1986: Atomic force microscope invented by G. Binnig, C. Gerber and R. Quate. Enables atomic resolution of arbitrary nonconducting surfaces under ambient conditions

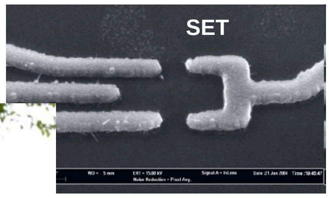
Breakthroughs in the 1980/1990ties:

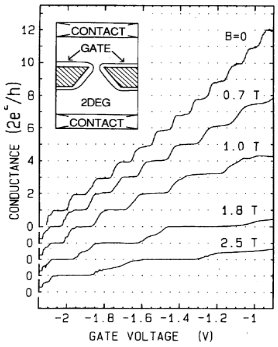
1988: First **designer protein** “alpha 4” created from scratch by W. deGrado at DuPont
1989: **Manipulation** of individual Xe atoms on Ni (110) by Don Eigler at IBM using STM

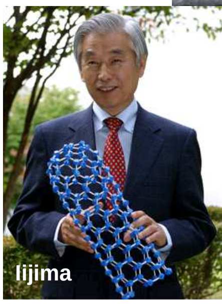



1987: **Quantization of electrical conductance** in 1D nanowires , **single-electron transistor** created by Bell Labs and groups in Holland & UK



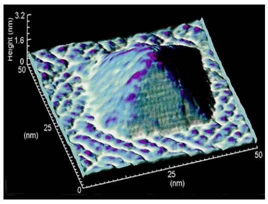
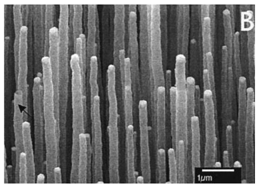


1991: **Carbon nanotubes** discovered by S. Iijima, Japan



New materials: Colloidal nanocrystals, Self-assembled quantum dots, Nanowires, hybrid nanostructures,

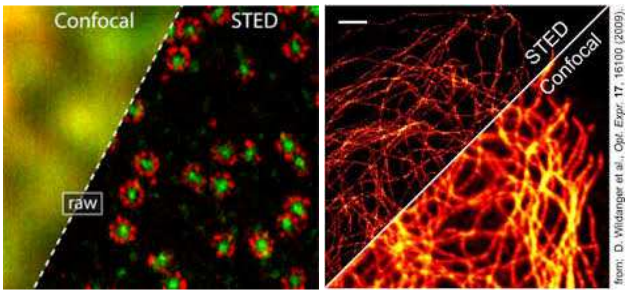
Fabrication methods:
Nanoimprinting, exfoliation, nano-chemistry ….

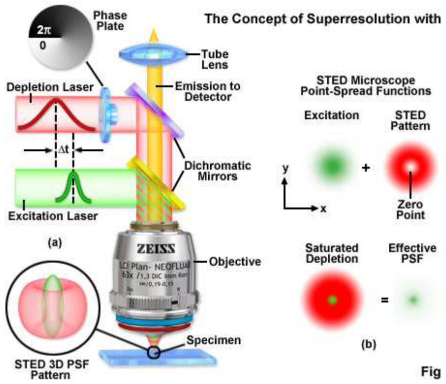



Improved nano-characterization methods:
Super-high resolution TEMs, atomic resolution scanning force microscopy, sub-wavelength microscopy, single dot spectroscopy, 3D tomography, etc. ….

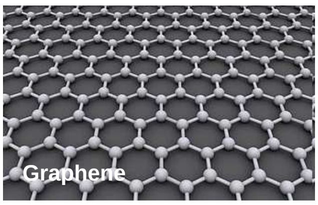
Recent developments:

1999: Superresolution STED fluorescence microscopy by Stefan Hell in Göttingen (Nobel prize 2014)

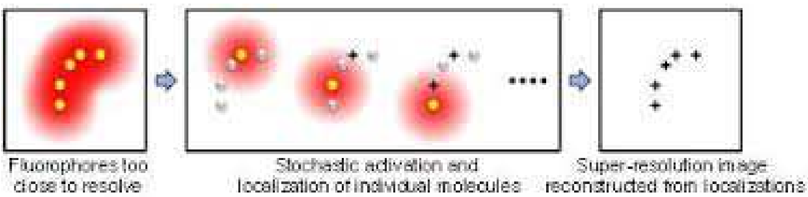




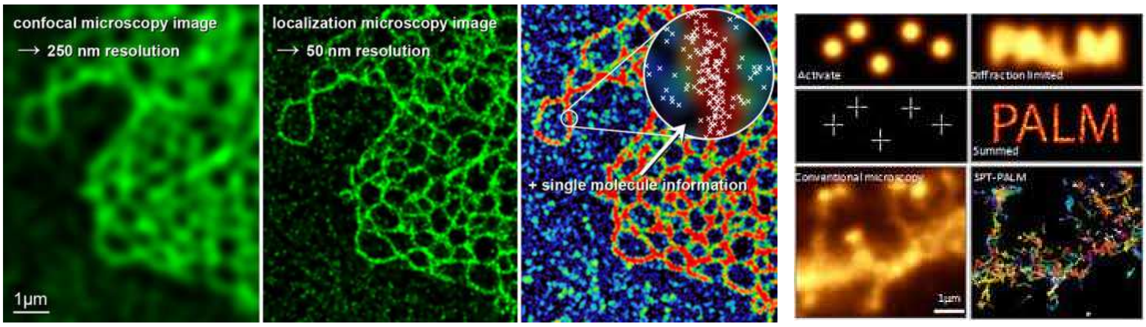
2004: Discovery of graphene (2D form of carbon) by A. Geim and Novoselov (Nobel prize 2010) featuring extraordinary properties



2006: New fluorescence microscopy methods (PALM, STORM, RESOLFT) invented by Eric Betzig at Harvard and William Moerner at Stanford (Nobel prize 2014)

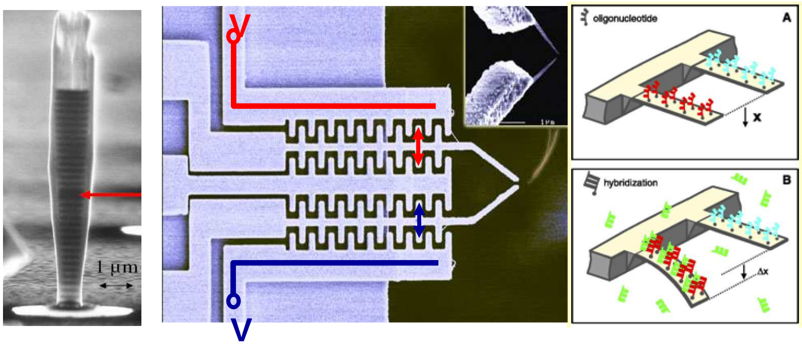


Example for PALM microscopy:



Last 10 years: Many new nanostructures and device applications developed**:**

- Nanophotonic devices
- Nanosensors
- Quantum dot and NWR lasers
- Single photon sources & detectors
- Bio-markers, biosensors
- Solar cells
- Nanofilters
- Si chips with sub-100 nm devices
- ……



⇨ Foundation of **nanoscience research centers**, nano-conferences and nanoscience journals

⇨ New nanoscience and nanotechnology **master, bachelor, PhD programs** in many Universities

Current state: Nanoscience is an established scientific field with a large scientific community and many new dedicated research journals and conferences

Examples: