Nanostrukturphysik (Nanostructure Physics)

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Vorlesung: Wednesday 9:00 – 10:30, C 108
Übung: Friday, 9:00 – 10:30, C 108 (U)

UTAM-prepared free-standing one-dimensional surface nanostructures on Si substrates: Ni nanowire arrays (a) and carbon nanotube arrays (b).
Contents of Class 1

A general introduction of fundamentals of nano-structured materials

Definition of nanostructures or nano-structured materials

Significance of nano-structured materials

Structural aspects

Optical aspects

One-dimensional nanostructures
Definition of nanostructures or nano-materials

The word ‘nanometer’ has been assigned to indicate the size of $10^{-9}$ meter

Structures with at least one dimension within 1-100 nanometer (nm)

called ‘nanostructures’ (Prof. H. Gleiter 1986-1988)

The word ‘nano’ derived from the Greek word ‘nanos’, means ‘dwarf’ (small)

Nanostructures have received high research interest because of their peculiar and fascinating properties, as well as their unique applications superior to their counterparts - bulk materials.

Nowaday, nanomaterials and nanostructures are not only at the forefront of the hottest fundamental research, but also gradually intrude into our daily life.
From: J. Henk
*Introduction to the Theory of Nanostructures* (Lecture Notes 2006)
‘There’s plenty of room at the bottom,
the principles of physics, as far as I can see, do not speak against
the possibility of manoeuvring things atom by atom...’

By the legendary physicist Richard Feynman in 1959
(Feynman R., Eng Sci, 1960)

Progress made in past two decades has proven this statement by
the abysmal nature of nanomaterials, has achieved exciting
technological advancement for the benefit of mankind.
Nobel Prize Winners with research related to nanotechnology:

1986 Physics: G. Binnig, H. Rohrer: design of the scanning tunneling microscope (STM) → SPM systems;

1996 Chemistry: R. Curl, H. Kroto, R. Smalley: discovery of fullerenes (C60, bucky balls);


2010 Physics: A. Geim, K. Novoselov: for groundbreaking experiments regarding the two-dimensional graphene
1996: Curl, Kroto, Smalley
1985 or 1986: fullerenes (C60, bucky balls);

2010: Geim, Novoselov 2005-2007: 2D graphene

The allotropes of carbon: hardest naturally occurring substance, diamond one of the softest known substances, graphite.

For carbon nanotubes – CNT (by Ijima in 1991) and the equally important discovery of inorganic fullerene structures (by Tenne)

Allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d–f) fullerenes (C_{60}, C_{540}, C_{70}); g) amorphous carbon; h) carbon nanotube. from http://en.wikipedia.org/wiki/Carbon.
Why are nanostructures interesting?

- small is different: new properties of materials at nanometer scale
- look at quantum mechanics
- nanostructure + functions or properties: revolution in information technology, medicine, media .......
Many opportunities might be realized by making new types of nanostructures:

1. simply by down-sizing existing microstructures into 1-100 nm range:
   most successful example is microelectronics, where ‘smaller’ means greater performance (since the invention of integrated circuits): more components per chip, faster operation, lower cost, and less power consumption.

2. Miniaturization also represents a trend in a range of other technologies:
   Information storage, e.g., many efforts to fabricate magnetic and optical storage components with critical dimensions (feature size) as small as tens of nanometers.
Global funding status in nanotechnology

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Features of the nano-structured materials:

1. **Inventions:**
bucky balls and carbon fullerene
first TEM image of the CNT;
be termed as major breakthroughs in nanoscience and technology.

2. Different physical properties of these novel nano-materials have been ascribed to their characteristic structural features in between the isolated atoms and the bulk materials.

This course is try to overview this 21st century’s leading science and technology based on fundamental and applied research during the last 2 decades → Nano - World
Types of Nanostructure:

Two-dimensional nanostructure: nanowalls, quantum wells...

One-dimensional nanostructure: nanowires, nanotubes, nanorods, nanobelts...

Zero-dimensional nanostructure: quantum dots or nanoparticles
Structural aspects of nano-structured materials:

**Extremely large surface area** (very large surface/volume ratio):

when the dimensions decrease from micron level to nano level, the surface area increases by 3 orders in magnitude. This will lead to much improved and enhanced physical properties (sensing, optical, catalysis ...):

Cube – Cubic structures – divided into 8 pieces – surface area 2 times (doubled)
Cube – Cubic structures – divided into 1000 pieces – surface area 10 times

**Quantum confinement effect:**

It is widely accepted that quantum confinement of electrons by the potential wells of nanometer-sized structures provides the most powerful (and versatile) means to control the electrical, optical, magnetic, and thermoelectric properties of a solid-state materials.
Electronic properties:

The typical electronic properties of the nanostructures are a result of tunneling currents and coulomb blockade effects.

Dimensions of the system - comparable with de Broglie wavelength of electrons (which is comparable to nanowire diameter): energy bands may cease to overlap – discrete

However, owing to their wavelike nature, electrons can tunnel through between two closely adjacent nanostructures

If a voltage is applied between two nanostructures, which aligns discrete energy levels, resonant tunneling occurs – largely increases tunneling current
Medicine and biosciences

Many nano-materials and nanoscale systems for biological applications:

Bio-mineralization of nano-crystallites in protein matrix - highly important for the formation of bone and teeth;

Chemical storage and transport mechanisms within organs are also fields of major interest;

Bio-mimicry - process of using biological systems as a guide to synthesize nano-scale materials;

Learn from Nature to realize different nanostructures
The physical properties of functional nanostructure are different from those of the bulk materials, especially for optical properties:

**Quantum confinement effect** (size-reduction down to the nm-sized range) → a band-gap shift → adjust the optical properties of nanostructures.

Metallic nanostructures (especially Au and Ag) have unique optical properties → surface-enhanced plasmon resonance light-scattering and Raman scattering (SERS or SRR).

**Nanowire Lasing**: nanowires with flat end facets as optical resonance cavities to generate coherent light on the nanoscale.

Another important issue of the optical performance of nanostructures is the usage of inorganic semiconductor as field-emitters due to their low work functions, high aspect ratios and mechanical stabilities.

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Quantum confinement effect

When the feature size of a structure (e.g., particle) is comparable with the size of Bohr exciton radius (about 2–50nm, usually between 5-20 nm), electron becomes more confined in particle, quantum confinement effect lead to an increasing of energy band-gap. Furthermore the valence and conductive bands break into quantized energy levels.

Many exceptional physical properties of nano-materials are attributed to the changes in the total energy and structure of the system.

Band-gap shift due to the Quantum confinement effect:

\[ \Delta E_g = \frac{\hbar^2}{8R^2\mu} - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon R} \]
Quantum confinement in semiconductor nanoparticles

Fluorescence emission of CdSe spherical nanoparticles of various sizes.

The band gap emission is observed to shift through the entire visible region, from red emission for the largest particles, to blue emission for the smallest clusters.

Surface plasmon resonance: plasmons propagate in $x$- and $y$-directions along metal-dielectric interface (distances $\sim$ tens to hundreds microns), and decay in $z$-direction. The interaction between surface-confined EM wave and surface layer leads to shifts in the plasmon resonance condition.

Localized surface plasmons: light interacts with particles much smaller than the incident wavelength. This leads to a plasmon that oscillates locally around the nanoparticle with a LSPR frequency. The shape, size, material, and local dielectric properties—all of which determine the LSPR wavelength.

Schematic of (a) a surface plasmon resonance and (b) a localized surface plasmon resonance. (Katherine A., *Annu. Rev. Phys. Chem.* 2007. 58, 267.)
Surface plasmon resonance in noble metal nanoparticles (Au and Ag)
By adding gold nanoparticles, colored glass can be made with burgundy, red, or purple colors, and the color changes with the particle shape and size. This is due to the collective oscillation of the electrons in the conduction band, known as the surface plasmon resonance.

Fluorescence of Au nanoparticles with different size and shape.

The emission is changed with the size slightly, but changed with the shape (anisotropy) dramatically.

Nanowire Lasing

Nanowires with flat end facets can be exploited as optical resonance cavities to generate coherent light on the nanoscale. Room temperature UV lasing has been demonstrated for the ZnO and GaN nanowire systems.
The lasing action in the ZnO nanowire arrays are thought to originate from the fact that the single-crystal well-facetted nanowires act as natural lasing resonance cavities. Two mirrors of the resonance cavity are the epitaxial interface at the bottom of ZnO nanowire and the sharp (0001) plane at the top of the ZnO nanowires.

Schematic of the power-dependent emission (a) from ZnO nanowire arrays and a ZnO nanowire as a resonance cavity (b).
Field-emission (FE), is one of the main features of nanostructures, with great commercial interest in displays and other electronic devices.

Field-emission is a quantum tunneling in which electrons pass from an emitting material (negatively biased) to anode through a barrier (vacuum) with a high electric field - highly dependent both on properties of material and shape of particular cathode - materials with higher aspect ratios and sharp edges (nanowires or nanotubes) produce higher field-emission currents.

Recent progress in the synthesis and assembly of nanostructures has resulted in a considerable increase in current density and lowering of turn-on voltage for many nanomaterials.
Emission current strongly dependent on three factors:
(i) work function of an emitter surface,
(ii) radius of curvature of emitter end,
(iii) emission area.

A lower work function material produce a higher electron emission current. (not all low work function materials are ideal for constructing field-emission cathodes (the work function of caesium is 1.8 eV).

For a given material, emission current can be enhanced by increasing aspect ratio, assembling into arrays, or decorating isurface with lower work function material (the field-emission performance of ZnO nanowires can be significantly enhanced through decreasing density of nanowires, and increasing aspect ratio).

(a) Field-emission phenomenon: emission from a tip of an emitter.
(b) Emitter can have different emission currents depending on tip geometry: (i) round tip, (ii) blunt tip, (iii) conical tip.
Characterization of nano-structures

An appropriate characterization will play a crucial role in determining various structures and properties of nanostructures.

Three broadly approved aspects of characterization are
1. Morphology
2. Crystalline structure
3. Chemical analysis
**ATEM:** Analytical Transmission Electron Microscopy; **AES:** Auger Electron Spectrometer; **XRD:** X-ray Diffraction; **RBS:** Rutherford Backscattering Spectrometry; **XPS:** X-ray Photoelectron Spectrometer; (Kelsall et al., Nanoscale science and technology. 2005)
**SEM:** Scanning Electron Microscopy; **ATEM:** Analytical Transmission Electron Microscopy; **AEM:** Auger Electron Microscopy. **XRD:** X-ray Diffraction; **LEED:** Low-energy electron diffraction; **RBS:** Rutherford Backscattering Spectrometry (Kelsall et al., Nanoscale science and technology. 2005)
One dimensional (1D) nanostructure: nanowires, nanotubes, nanorods, nanobelts...

One dimensional nanostructure refers to the systems with the lateral dimension in the range of 1-100 nm.

In comparison with 0D nanostructures, 1D nanostructures provides a better model system to investigate the dependence of properties (electronic transport, optical, and mechanical) on size confinement and dimension. Nanowires, in particular, plays an important role as both interconnects and active components in preparing nanoscale devices (Nano-devices).
One-Dimensional Nanostructures

UTAM-prepared free-standing one-dimensional surface nanostructures on Si substrates: Ni nanowire arrays (a) and carbon nanotube arrays (b).
(Y. Lei et al., Chemistry of Materials, 2004)
A schematic summary of the kinds of one dimensional nanostructures already reported:

(A) nanowires and nanorods;
(B) core–shell structures;
(C) nanotubes/hollow nanorods;
(D) heterostructures;
(E) nanobelts/nanoribbons;
(F) nanotapes;
(G) dendrites;
(H) hierarchical nanostructures;
(I) nanosphere assembly;
(J) nanosprings.

Six different strategies for achieving 1D growth:

1. Anisotropic growth dictated by crystalline nature of a structure;
2. Use a liquid-solid interface to reduce symmetry of a seed;
3. Anisotropic growth by templates;
4. Use capping reagent to control growth rate of various facets of a seed;
5. Self-assembly of 0D nanostructures;
6. Size reduction of 1D microstructures.

(Xia et al., Adv Mater, 2003)
Properties and applications of 1D nanostructures:

Major advantages with the 1D nanostructures are their extraordinary lengths, flexibility and structure that can allow them to be physically manipulated into various shapes according to the design requirements.

Quantum effects are unique in 1D structures resulting in new electronic properties:

Mechanical strength of the 1D structures has not only been attributed to the size but also to the extremely low dislocation density. Recently scientists have produced nanotubes of peptides with a Young’s modulus of 19 GPa;
Surface charge dependent in the conductance of nanostructures is the major basis of functioning of the metal oxide nanowire based device configurations.

The main reason behind the high interest in the use of 1D nanostructures is the large surface-to-volume ratio rendering the ability for more surface atoms to participate in the surface reactions.

The electronic, chemical, and optical processes occurring on metal oxides concerning the sensing, which is benefit from reduction in size to the nano range (Kolmakov et al., Annu Rev Mater Res 2004)
Schematic describing the different forms of semiconductor oxides investigated in the literature for the gas sensing applications (Meyyappan et al., Interface 2005).
‘There’s plenty of room at the bottom’
By the legendary Richard Feynman in 1959

Dream statement has been realized in half a century by consistent efforts and large contributions from the scientific community across the globe.
Thank you and have a nice day!
Next course:

Vorlesung: April 25th (Wed), 9:00 – 10:30, C 108
Übung: April 27th (Fri), 9:00 – 10:30, C 108 (U)