Nanostrukturphysik (Nanostructure Physics)

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Vorlesung: Thursday 13:00 – 14:30, F 3001
Übung: Friday (G), 11:00 – 12:30, C 110

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 nanostructured materials
Definition of nanostructures or nanostructured materials
Significance of nanostructured materials
An outline of all the 12 lectures
Characterization of nanostructures
3 types of nanostructures
Definition of nanocrystalline materials
‘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 three decades has proven this statement by the amazing nature of nanomaterials, has achieved exciting technological advancement for the benefit of mankind.
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’ comes from a 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.

Nowadays, nanomaterials and nanostructures are not only one of the hottest fundamental research topics, but also gradually intrude into our daily life.
Nobel Prizes 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
Nobel Prizes with research related to nanostructures:

Gerd Binnig (German) & Heinrich Rohrer (Swiss)
Nobel Prize 1986 Physics
Designing of the scanning tunneling microscope (STM) → SPM systems

G. Binnig also designed AFM with other 2 scientists, and started the company 'Definiens' in 1994.
He worked as honorary professors in some universities, e.g., Uni-München.
Konstantin Novoselov & Andre Geim (Russian)
Nobel Prize 2010 Physics
for groundbreaking experiments regarding the two-dimensional graphene
1996: Curl, Kroto, Smalley
1985 or1986: **fullerenes** (C60, bucky balls);

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

The allotropes of carbon: hardest natural 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) Ionsdaleite; d–f) **fullerenes** (C_{60}, C_{540}, C_{70}); g) amorphous carbon; h) **carbon nanotube**.

Why are nanostructures interesting?

**Small is different:** extremely large surface area (very large surface/volume ratio):

- Miniaturization
- Quantum confinement effect
- **Electronic properties:** e.g., tunneling currents
Miniaturization represent the trend in different technologies:

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

Information storage, e.g., many efforts to fabricate magnetic and optical storage components with critical dimensions (feature size) as small as tens of nanometer – device miniaturization
The physical properties of nanostructure are different from those of the bulk materials, especially for optical properties:

**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 below 10-15 nm), electrons are more confined in a particle, quantum confinement effect lead to an increasing of optical energy band-gap.

Band-gap shift due to the Quantum confinement effect:

\[
\Delta E_r = E_{gap} + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*} - \frac{1}{m_h^*} \right)
\]
Radiation shift between the two edges of visible spectra

$\Delta E_{\text{nano}} > \Delta E_{\text{bulk}}$
Quantum confinement in semiconductor nanoparticles

Optical fluorescence of CdSe nanoparticles of different sizes.

The band gap emission is observed to shift through the entire visible range, from red emission of largest particles, to blue emission of smallest particles. (B. O. Dabbousi, J. Phys. Chem. B, 1997, 101, 9463)
Electronic properties:

The typical electronic properties of the nanostructures are a result of **tunneling currents**. Owing to their wavelike nature, electrons can tunnel through between two closely adjacent nanostructures. An electron's penetration of an energy barrier, even though the electron's energy is below the height of barrier.
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Global funding status in nanotechnology

This course is try to overview this 21st century’s leading science and technology based on fundamental and applied research during the last 3 decades → Nano - World
• Class 1: A general introduction of fundamentals of nano-structured materials
• Class 2: Structures and properties of nanocrystalline materials
• Class 3: Graphene
• Class 4: 2D atomic-thin nanosheets
• Class 5: Optical properties of 1D nanostructures and nano-generator
• Class 6: Carbon nanotubes
• Class 7: Solar water splitting I: fundamentals
• Class 8: Solar water splitting II: nanostructures for water splitting
• Class 9: Lithium-ion batteries: Si nanostructures
• Class 10: Sodium-ion batteries and other ion batteries, and Supercapacitors
• Class 11: Solar cells
• Class 12: Other nanostructures
Class 2: Structures and properties of nanocrystalline materials

• Structures
  Chemical composition, density, micro-structure, thermal stability, etc.

• Properties
  Enhanced solubility, specific heat, electrical resistivity, etc.
Class 3: Graphene

- Introduction (exfoliation)
- Brief history
- Characterizing graphene flakes
- Devices with graphene
- Alternatives to mechanical exfoliation
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"
Prof. Andre Geim (from: en.wikipedia.org/wiki/Andre_Geim)

obtained first tenured position in 1994, associate professor at Uni-Nijmegen, one doctoral student at Nijmegen was Novoselov.

He was offered professorships at Nijmegen and Eindhoven, but turned them down as he found the Dutch academic system too hierarchical and full of politics. "This can be pretty unpleasant at times," he says. "It's not like the British system where every staff member is an equal quantity."

In 2001 he became a professor at the University of Manchester, and was appointed director of the Manchester Centre for Mesoscience and Nanotechnology in 2002.
Class 4: 2D atomic-thin nanosheets

• Fabrication strategies
  • Layered structures
  • Quasi-layered structures
  • Non-layered structures

• Electronic structure regulation
  • Increased densities of state near Fermi level
  • Higher electric conductivity
  • Better electron transport

• Energy device construction
  • Thermoelectric
  • Transparent devices
  • Flexible devices
Class 4: 2D atomic-thin nanosheets
Class 5: optical properties of 1D nanostructures & nano-generator

- Features
- Quantum confinement
- Nanowire lasing
- Field emission display
When a ZnO NW is bent by a Pt-coated AFM tip, a strain is produced. Stretched side has positive potential and compressed side has negative potential. Schottky diode is formed (Pt/ZnO).

**Two processes:**

When tip contacts and bends NWs, interface of tip and stretched side is a reversely biased Schottky diode ($\Delta V = V_m - V_s^+ < 0$). Piezoelectric potential is created in NW, no charge flowing across Schottky diode although there is a piezoelectric potential in NW side (**charge creation and accumulation process**).

When tip reaches compressed side of NW, a forward biased Schottky diode formed at interface ($\Delta V = V_m - V_s^- > 0$), external electrons can flow across interface under driving of piezoelectric potential, resulting in a discharging. (**current output process**).
Class 6: carbon nanotubes

- History
- Fabrication
- Applications
The first ever observation of carbon nanotubes
1953, W. R. Davis: an unusual form of carbon from carbon monoxide at 450°C, but TEM can't reveal the architectures of such an unusual form of carbon.

letters to nature

Nature 171, 756 (23 April 1953); doi:10.1038/171756a0

An Unusual Form of Carbon

W. R. DAVIS, R. J. SLAWSON & G. R. RIGBY

British Ceramic Research Association, Queen’s Road, Parkhall, Stoke on Trent. Nov. 24.

In the course of experimental work on the deposition of carbon in the brickwork of blast furnaces (deposition which may cause the disintegration of the bricks), it has been found by electron micrography that the carbon is deposited as minute vermicular growths which can penetrate considerable thicknesses of brickwork. The carbon is formed by the interaction of carbon monoxide and iron oxide in the so-called iron-spots in the brick. It has been found possible to reproduce this reaction in the laboratory by exposing samples of brick containing iron spots to the action of carbon monoxide at an optimum temperature of about 450°C. Moreover, a similar form of carbon growth is observed if iron ore, magnetite or any form of iron oxide is substituted for the brick samples.
1991, a breakthrough in research of carbon nanostructures: Iijima reported arc-discharge synthesis and high-resolution TEM characterization of such ‘helical microtubules’. These microtubules, later known as carbon nanotubes (CNTs), are molecular-scale fibers with structures related to fullerenes.
Class 7: fundamentals of solar water splitting

- Related semiconductor physics
- Thermodynamic and kinetics of semiconductor-liquid interface
**Solar**

potential $1.2 \times 10^5$ TW; practical 600 TW

**Wind**

4% Utilization
Above 2-3 TW

**Solar**

potential $1.2 \times 10^5$ TW; practical 600 TW

**Wind**

4% Utilization
Above 2-3 TW

**Hydroelectric**

Gross: 4.6 TW
Technically Feasible: 1.6 TW
Economic: 0.9 TW

**Geothermal**

Continental Total Potential: 11.6 TW
Most of hydrogen production comes from fossil fuel! New renewable processes are necessary!
Possible scheme for large-scale H₂ production via solar water splitting
Class 8: nanostructures for solar water splitting

- Pros and cons
- Material designs and nanostructured architectures
Material designs and nanostructured architecture to improve photoelectrochemical activity

**Light absorption**

- Absorbance
  - Single band gap
    - Band structure modification
      - Inhomogeneous doping
    - Branched structure
  - Multi band gap
    - Heterostructure modification
      - Co-catalysts sensitization
    - Plasmonic assist
      - Quantum dot sensitization

**Charge separation and transportation**

- Water splitting
  - Carrier transportation
    - Dye sensitization
    - Graphene-based assist
Class 9: nanostructured Si anodes for lithium-ion batteries

- Principle of lithium-ion batteries
- Opportunities and challenges of Si anodes
- Nanostructured Si anodes
Class 10: Sodium-ion batteries and other ion batteries, and Supercapacitors

- Abundant
- Similar electrochemistry to Li system
- High ion conductivity of Na\(^+\)-based electrolyte

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<td>(-3.04) V</td>
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<tr>
<td>97.7 °C</td>
<td>180.5 °C</td>
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<tr>
<td>$150 per ton</td>
<td>$5000 per ton</td>
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<tr>
<td>At $2000–2500 per ton</td>
<td>Cu $7000–8500 per ton</td>
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<tr>
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<td>Octahedral and prismatic</td>
<td>Octahedral and tetrahedral</td>
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Class 11: nanostructures for enhancing light absorption in solar cells

- Semiconductor nanostructures
- Metal nanostructures: surface plasmons
Different fabrication process for large scale nano-particles.

Chem. Rev. 2011, 111, 3736–3827
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
Types of Nanostructure:

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

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

Zero-dimensional nanostructure: quantum dots or nanoparticles
Graphene is a 1-atom thick sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Graphene is easily visualized as an atomic-scale wire made of carbon atoms and their bonds. Graphite consists of many graphene sheets stacked together.
(http://en.wikipedia.org/wiki/Graphene)
One dimensional (1D) nanostructures

1D nanostructure: nanowires, nanotubes, nanorods...
1D nanostructure refers to the systems with the lateral dimension in the range of 1-100 nm.

Compared to 0D nanostructures, 1D nanostructures provides a better model system to investigate the dependence of properties (electronic transport, optical & 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)
Templates with large-scale (1 mm$^2$) perfect rectangular pore arrays without defect
Perfect regular 1D nanostructure arrays with different wire configuration
1D 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.

Zero-dimensional nanostructure: quantum dots or nanoparticles

UTAM surface nano-patterning technique