Nanostrukturphysik (Nanostructure Physics)

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Vorlesung: Thursday 7:00 – 8:30, F 3001 (Faradaybau)
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).
• 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 atomically 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
Contents of Class 2
Structures and properties of nanocrystalline materials
New methods & new structures

Development of solid state physics and material science are made in many cases by one of the following two approaches:

- Developing and applying new methods of investigation
  
  \textit{TEM, SEM, STEM, etc.} \textit{(Techniken der Oberflächenphysik)}

- Preparing materials with novel structural features and/or properties

  \textbf{Nanocrystalline materials:} solids with \textit{new atomic structures} and their properties decided by the \textit{atomic arrangements in the cores of defects}. \textit{(Nanostrukturphysik)}
Nanocrystalline materials
(proposed by Prof. Herbert Gleiter in 1988)

Perfect crystals vs. disordered crystals

**Perfect crystals**: 3D periodic or quasi-periodic array of atoms

![Hard sphere model of a perfect crystal (hexagonal array of atoms).](image1)

**Disordered crystals**: solids deviating from perfectly ordered structures

![Hard sphere model of a glassy structure with changed atomic density and neighbor coordination.](image2)
Two types of deviation

- **Thermally disordering** crystalline structure of a material and by **freezing in** the disordered state by means of quenching, e.g. glass.
Two types of deviation

- **Incorporating defects** such as dislocations, grain or interphase boundaries, vacancies.

Edge **dislocation** in a simple cubic crystal. In the dislocation core, the atomic density and coordination is changed in comparison to the perfect cubic lattice.

Atomic structure of **grain boundary** in NiO deduced from the high resolution electron image shown later.
Comparing the two types

- The atomic density in the core of grain boundaries is reduced typically of ~15 to 30%, which is almost an order of magnitude more than the density difference between the glassy and crystalline state materials.
Grain boundary in NiO. *Small vertical displacement of the boundary plane* in section A relative to the section B results in two different core structures although all other parameters (crystal misorientation, boundary inclination, etc.) are not changed.
What’s like in conventional polycrystals?

Conventional polycrystals: grain size typically ≥ 1 μm

The atomic structures of the boundary cores are not noticed in most structural investigations such as XRD, because the fraction of atoms located in the core of the boundaries is $10^{-4}$ or less.
Basic idea of nanocrytalline materials

What if one generates a material that contains a high density of defects?

• Nanocrystalline materials is a new class of disordered solids by introducing such a high density of defect cores that 50% or more of the atoms (molecules) are situated in the core of these defects (typically $10^{19}$ per cm$^3$).

• Types of defects: grain boundaries, interphase boundaries, dislocations, etc.
Sphere model of a 2D nanocrystalline material. The atoms in the center of the “crystals” are indicated in black, while those in the boundary core regions are indicated by open circles.

Common feature of nanocrystalline materials: a large volume fraction of defect cores and (strained) crystal lattice regions!
If the thickness of interfacial region is assumed to be about 1 nm, an estimation shows that the volume fraction of the interfaces becomes comparable to the volume fraction of the crystalline regions when the crystal size is in the range of 5-15 nm.
Basic idea of nanocrystalline materials

• Atomic structure of the core regions of different boundaries between crystals are different because their structures depend on the crystal misorientations and boundary inclinations - **structure heterogeneity**

• This featured structure of heterogeneity is not formed in thermally induced disordered solids such as glasses.
Beyond single-component nanocrystalline materials

- Nanocrystalline alloys

Sphere model of a mixture of nanometer sized crystals. Open or closed circles represent atoms of the two chemically different crystals. The dashed lines mark boundary regions between adjacent crystals.
(1) Body-centered cubic (b.c.c.) $\alpha$-Fe crystals
(2) b.c.c. $\alpha$-Fe crystals with incorporated Ag atoms
(3) Face-centered cubic (f.c.c.) Ag crystals with incorporated Fe atoms
(4) f.c.c. Ag crystals, indicated by the X-ray scattering data

Mössbauer spectrum of a nanocrystalline Ag-Fe alloy at $T = 10$ K, showing three components.
Enhanced sphere model of a mixture of nanocrystals; atomic rearrangement in the boundary regions are considered.
Pure Si (5 nm crystal size)

Si-Fe (5% Fe)
Fe: 10% larger than Si in size

Si-Au (25% Au)
Au: 20% larger than Si in size

• The decreasing number of the diffraction peaks indicates a reduction of the range of atomic order with increasing alloy content.

Sphere model of a 2D nanoglass consisting of elastically distorted crystallites. Near the large solute atoms, the lattice planes are curved as indicated in the crystallite on the lower left side. This is not so if all atoms have the same size.

The distortion results from the incorporation of large solute atoms.

Beyond single-component nanocrystalline materials

- Imperfect (Distorted) crystallites – nanoglasses
- Containing two types of defects: the grain boundaries (as in the previously discussed cases) and the defects inside crystallites
- Examples: crystallites contain large solute atoms that largely distort their lattices
Transition between nanocrystalline and nanoglassy materials

- Nanocrystalline materials that are generated by *consolidating small defect-free crystals*
- Nanoglassy materials synthesized from nanometer-sized particles with *highly distorted atomic bonds*
- Possible to tune the atomic arrangements in nanostructured materials from one side to the other side or vice versa.
1. Self diffusion

- Numerous interfaces in nanocrystalline materials provide a high density of short circuit diffusion paths.
- Nanocrystalline materials exhibit an enhanced self diffusivity in comparison to single crystals or conventional polycrystals with the same chemical composition.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Nanocrystalline copper (8 nm)</th>
<th>Grain boundary diffusion*</th>
<th>Lattice diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>393</td>
<td>$1.7 \times 10^{-17}$</td>
<td>$2.2 \times 10^{-19}$</td>
<td>$2 \times 10^{-31}$</td>
</tr>
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* Assumed boundary width about 1 nm.
1. Self diffusion

The measured diffusivity in nanocrystalline Cu are about 14 to 20 orders of magnitude higher than lattice diffusion and about 2 to 4 orders of magnitude larger than grain boundary self diffusion.

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2. Solute diffusion

- In amorphous alloys, non-periodic structure results in a spectrum of trapping sites - account for observation of hydrogen diffusion
- In nanocrystalline materials, similar effect is observed, and the structure of the interfaces of nanocrystalites makes a distribution of sites of different trapping energies for a solute
- An example: hydrogen solubility and diffusion in nanocrystaline Pd
**Function of concentration**: diffusion coefficients of hydrogen at 293 K as a function of $\text{H}_2$ concentration in single-crystaline & nanocrystalline Pd.

**Low diffusivity at low $\text{H}_2$ concentration**: H atoms are trapped in the boundaries at sites of low energy.

**Increased diffusivity with increasing $\text{H}_2$ concentration**: deep traps are filled and diffusivity involves migrations between very shallow traps.

**Decreased diffusivity at high $\text{H}_2$ concentration**: an increase of the H-H interaction impeding the diffusion of $\text{H}_2$. 

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[Diagram with labels: Single crystalline, Nanocrystalline, Fitted curve, Experimental curve, Decreased diffusivity at high $\text{H}_2$ concentration, Increased diffusivity with increasing $\text{H}_2$ concentration.]
3. Enhanced solubility of solute

- The solubility of a solute A in a solvent B, is controlled by the chemical potential $\mu_A$ of A in B.
- If the atomic structure of B is changed, the chemical potential and hence the solubility of A in B may be enhanced (or reduced).
4. Specific heat

Enhancement ($\Delta C_p$):
- nanocrystalline/polycrystalline = 29~53%
- metallic glass/polycrystalline

Heat insulating (barrier) material
5. Thermal expansion (enhanced)

- Nanocrystalline Cu (8 nm crystal size): $31 \times 10^{-6} \text{ K}^{-1}$ @ 110 K vs. $16 \times 10^{-6} \text{ K}^{-1}$ @ 293 K.
- A similar enhancement in nanocrystalline Pd (10 nm crystal size)
- **Crystalline component** (crystalline component + boundary component = a nanocrystalline material) has small contribution to the enhancement of thermal expansion coefficient
- Average thermal expansion of **boundary component** is about **four times larger** than the lattice expansion to the exhibited expansion coefficient
6. Electrical resistivity

Specific electric dc-resistivity of nanocrystalline Pd as a function of temperature and crystal size.

Temperature ↘, resistivity ↗, crystal size ↗, resistivity ↘
• The observed trend can be understood in terms of electron scattering inside crystallites and by boundaries.
• The scattering may either be described in terms of the reflection of electrons by boundaries or the transmission through the boundaries.
• If the crystal size is smaller than the electron mean free path, grain boundary scattering dominates and hence the conductivity decrease.
• If the crystal size is larger than the electron mean free path, electron scattering by scattering effects inside of crystal becomes the dominant scattering mode.
7. Magnetic properties

- The saturation magnetization ($M_s$) of nanocrystalline Fe (6 nm crystal size) is reduced by 40% than bulk Fe.
- The Curie temperature ($T_c$) of nanocrystalline Ni (70 nm crystal size) is lowered by 40°C relative to that of bulk Ni.

The interior of the crystals has the same $T_c$ as a single crystal of Ni, but the $T_c$ of the grain boundary regions is reduced.

Scheme of the superfine-grained material structure.
• The magnetic microstructure of nanocrystalline Fe differs from the one of crystalline and amorphous Fe and Fe alloy: ferromagnetic domains separated by domain walls in the latter, whereas no domain structure in the former.
• Every crystallite of a nanocrystalline Fe is a single ferromagnetic domain.
• The magnetization of neighboring crystallites is controlled by the crystal anisotropy (to align the magnetization of every crystallite in one of the easy directions) and the magnetic interaction between neighboring crystallites (to align the magnetization of adjacent crystals into a common direction).

Paramagnetic & superparamagnetic
Large-scale free-standing Ni nanowires: (Left): top view of nanowire array of an area of about 775 μm². (Right): nanowire arrays with tunable length, diameter, spacing.
Magnetic easy axis along the axis of the nanowires due to their shape anisotropy.

8. Mechanical properties

8.1 Elastic deformation (stiffness - rigid)

- Due to free volume of grain boundary, average interatomic spacing in boundary regions are increased relative to perfect lattice.
- The elastic constants of a nanocrystalline material is reduced due to the reduced elastic modulus (Young’s modulus) of boundaries.

<table>
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<tr>
<th>Material</th>
<th>Crystal size (nm)</th>
<th>Young’s modulus $E$ (1,000 N/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>8</td>
<td>88 (123)*</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>39 (41)*</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td></td>
<td>38 (111)*</td>
</tr>
</tbody>
</table>

Elastic properties of nanocrystalline and conventional materials (* Conventional polycrystal)
8.2 Internal friction

Internal friction $Q^{-1}$ in nanocrystalline Pd below 300 K is about 2 to 3 times smaller than coarse-grained Pd.

Internal friction is interpreted in terms of viscous sliding of interfacial boundaries, and may also due to dislocation movement in grain boundaries.

Temperature variation of the internal friction of nanocrystalline Pd with a heating rate of 150 K/h.
8.3 Hardness

The hardness of nanocrystalline TiO$_2$ is about 2 or more times the hardness of the two other samples.

Vickers microhardness in kp mm$^{-2}$ to TiO$_2$ (rutile) measured at room temperature as a function of 1.5 h sintering at successively increased temperature.

The value of hardness after sintering at 800-900$^\circ$C is typical of bulk ceramics, indicating that good mechanical properties can be achieved in nanocrystalline TiO$_2$ after low temperature sintering, comparing with two other samples.

(Standard ceramic processing method)
8.4 Plastic deformation

If the load is removed, a reversible strain recovery of about 3% is noticed, irrespective of the number of loading cycles.

Work hardening occurs during deformation.
Plastic deformation of materials

- Plastic deformation in polycrystalline solids occurs by movement of lattice dislocations. The dislocation movement mechanism predominates in most conventional materials at relatively low temperatures.

- The strain-hardening effect often restricts the mechanical processing of metals, which must be eliminated by thermal annealing in order to perform further deformation without cracking.
• The diffusion creep rate ($\dot{\varepsilon}$), which is dominated by grain boundary diffusion, is related to grain size

$$
\dot{\varepsilon} = \frac{B\Omega_0 \sigma \delta D_{gb}}{d^3 kT}
$$

where $\sigma$ is tensile stress, $\Omega$ is atomic volume, $d$ is average grain size, $B$ is a numerical constant, $D_{gb}$ is grain boundary diffusivity, $\delta$ is grain boundary thickness, and $k$ is Boltzmann’s constant.

• Accordingly, **Gleiter** et al. predicted that a nanocrystalline (nc) material, one in which the crystallite size is in the nanometer regime, would make it amenable to high creep rates and large-scale deformation at much lower homologous temperatures, so that ductile ceramics and diffusional creep of pure metals would be possible even at room temperature. *(Scripta Metallurgica, 1989, 23, 1679)* This possibility may significantly facilitate the fabrication process for producing components with complex shapes.
Superplastic extensibility of nanocrystalline copper at room temperature

As-prepared nanocrystalline copper

Superplastic extensibility of nanocrystalline Cu dominated by grain boundary activities rather lattice dislocation.

Nanocrystalline copper with a deformation degree of 4800 %

*Science* 2000, 287 (5457), 1463-1466.
Classical methods for strengthening materials

Strengthening strategies are to control the generation and interactions among internal defects. Such defects include:

• atomic vacancies (point defects)

• dislocations (line defects)

• grain, interphase boundaries (planar defects)

• strengthening precipitates and dispersed particles (volume defects) of a different phase or material than the surrounding matrix.
Classical methods for strengthening materials

Forming alloys with impurity elements is a routine method for modifying the properties of metals.

- Strengthening via solute, whereby solute atoms strain the matrix to impede the movement of a dislocation (red line) through the lattice;
- Strengthening via precipitates that interact with movable dislocations, leading to overall strengthening of material;
- Strengthening via elastic interactions between intersecting dislocations (blue and red lines)
• Dislocation (red ⊥ symbol) movement is blocked by grain boundaries (GBs).
• The high concentration of incoherent GBs provides barriers to transmission of dislocations from one grain to the next. A higher stress is needed to deform a polycrystalline metal with a smaller grain size (more GBs).
• Strengthening with grain refinement is observed for grain sizes as small as ~10 to 15 nm.

Science 2009, 324 (5925), 349-352.
Disadvantages of classical methods and GB for strengthening materials

These classical approaches suffer from the undesirable consequence that an increase in strength, will also causes reduced plastic extensibility and increased brittleness.
Grain and interphase boundaries

Nanocrystalline materials
Nanoscale twin boundaries (TBs) strengthening

- Twin boundaries (TBs) effectively hinder dislocation motion and can thus act as stable interfaces for strengthening metals.
- TB strengthening based on dislocation/TB interactions - mobile dislocations could be generated, either in neighboring domains (twin or matrix) or at TBs. Gliding of dislocations along TBs is feasible because of its coherent structure. Higher strength and higher plastic extensibility are achieved with a smaller twin thickness $\lambda$ in the nanometer scale.

*Science 2009, 324 (5925), 349-352.*
A bright-field TEM image and the electron diffraction pattern (inset) show roughly same-sized submicrometer grains with random orientations separated by high-angle GBs.

Electron diffraction patterns [inset in (D)] indicate that the twins in each grain are parallel to each other, and high-resolution TEM images (E) show that the twins follow a sequence of ATATA with twinning elements.
The tensile strength $\sigma_y$ (at 0.2% offset) reached as high as 900 MPa, and the ultimate tensile strength ($\sigma_{UTS}$) was 1068 MPa; these values are at least one order of magnitude larger than those of the coarse-grained (grain size 100 $\mu$m) Cu samples.
Effect of mean twin thicknesses ($\lambda$) on tensile stress-strain curve for Cu sample with nano-twins

Grain size: 400 – 600 nm
(A)$\lambda = 96$ nm.
(B)$\lambda = 15$ nm.
(C)$\lambda = 4$ nm

Science 2009, 323 (5914), 607-610.
Effect of mean twin thicknesses ($\lambda$) on tensile stress-strain curve for Cu sample with nano-twins

Two distinct features are observed with respect to the $\lambda$ dependence of the mechanical behavior of Cu sample with nano-twins (nt-Cu).

*Science* 2009, 323 (5914), 607-610.
Nanotwins in diamond

A Vickers hardness of 200 GPa, even higher than that of natural diamond, was reported for synthetic bulk nanotwinned diamond.
Zentralbau des Deutschen Museums

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Thanks for your attention