Preparation of Nanostructures
(Příprava Nanostruktur)

Jaroslav Hamrle

jaroslav.hamrle@vsb.cz

December 16, 2014
Outline

1 Content
2 Relation between symmetry of crystals and crystal properties
3 Introduction
4 Bulk crystal growth
5 Thin film preparation
6 Lateral structures
7 ATR / Surface plasma resonance

Preparation of Nanostructures (Příprava Nanostruktur)
Překrytí obsahu přednášky s jinými předměty:

- MBE, napařování (sputtering) -> Hlubina (vakuová fyzika)
- absorbce, desorbce molekul na površích -> Hlubina (vakuová fyzika)
- tenké vrstvy (napařování, sputtering, CVD) -> Postava
- techniky studia tenkých vrstev (XRD, SEM, AFM, RHEED, LEED) -> jiné předměty
<table>
<thead>
<tr>
<th>Content</th>
<th>Relation between symmetry of crystals and crystal properties</th>
</tr>
</thead>
</table>


- Jaroslav Hamrle
- Rudolf Sýkora
- Illa Ramakanth
- Radek Ješko

Preparation of Nanostructures (Příprava Nanostruktur)
Illa Ramakanth (3 lessons)

1. Chemical deposition methods for the formation of thin films
   - Chemical approach (preparation)
   - Chemical Vapor Deposition (CVD) process (chemical method)
   - Electrodeposition and solid phase method (chemical method)
   - Co-precipitation approach (chemical method)
   - Sol-gel (chemical method)
   - Hydrothermal synthesis / Solvothermal method (chemical method)
   - Ultrasonic assisted wet chemical route
   - Spin coating (chemical method)
   - Lithography

2. Fullerenes: Structure, Preparation, Properties & applications

3. Carbon Nanotubes: Structure, Preparation, Properties & applications
Nabízený obsah přednášky:

**Rudolf Sýkora**
- krystalografie, 2D krystalografie, pocitani vzdalenosti rovin
- relaxace povrchu,
- elektronova struktura povrchu (kap 2 ze surface science)
- kap. 8. + 9. rekonstrukce povrchu; atomova struktura povrchu
- kap. 11. elektronova struktura povrchu

**Radek Ješko**
- fyzikální depozice: MBE, naprašování (sputtering) [bude upřesněno]
Nabízený obsah přednášky:

- Jaroslav Hamrle
  - symetrie krystalů a jejich vliv na vlastnosti materiálů
  - absorbce, desorpce, teorie růstů krystalů a tenkých vrstev (?)
  - charakterizační techniky podle zájmu (např. NMR, surface plasmons a ATR, MOKE ?)
Dvě možnosti jak proběhne praktikum:

1. exkurze nebo
2. příprava a charakterizace feritů:

- např. CrFe$_2$O$_4$, ZnFe$_2$O$_4$, CuFe$_2$O$_4$, NiFe$_2$O$_4$, BiFeO$_3$
- 8 vzorků (2 tloušťky, 4 žíhací teploty), připraveno pomocí dipping
- charakterizace: XRD, VSM, AFM (případně SEM), případně elipsometrie a magento-optická spectroskopie, případně XPS
- reálná šance opublikovat výsledky (yní studujeme podobnou sadu vzorků)

Jaroslav Hamrle
Preparation of Nanostructures (Příprava Nanostruktur)
Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance
Types of structures

- bulks (including bulk superstructures)
- layers
- 2D structures (lithography, self-organizing growth)
- 3D structures (special lithography, 3D printing)
Basic material structures

Basic material structures from material point of view:
- single crystal (also known as monocrystals or epitaxial)
- polycrystals (small single crystals randomly oriented)
- amorphous (e.g. glass)
Crystal growth techniques I: using one solvent

- slow cooling of the solvent (*rozpouštědlo*): substances that are much more soluble in a solvent at high temperature than at low temperature

slow evaporation of the solvent [solvent evaporates $\rightarrow$ crystal growth]

- solvent can be also liquid metal (e.g. Sn-tin)

Crystal growth techniques I: using two solvents

Two solvents (substances that are very soluble in one solvent and insoluble in a second solvent. The two solvents must be miscible, i.e. soluble in each other in all proportions):

- **two solvent evaporation** [dissolve substance in good solvent → add bad solvent → good solvent evaporates → crystal growth in bad solvent]
- **two solvent liquid diffusion** [dissolve substance in good solvent → add bad solvent → crystal growth in mixture of bad and good solvent].
- **two solvent vapour diffusion** [dissolve substance in good solvent → add bad solvent to surrounding → bad solvent mixes with good through diffusion of vapours → crystal growth in bad solvent]
Crystal growth techniques II: Czochralski process

- high quality crystal growth of single crystals, to very large size (length 1-2 m, industrial diameter for wafers upto 450 mm)
- semiconductors (e.g. Si, Ge, GaAs), metals (e.g. Pd, Pt, Ag, Au), salts, etc.
- defects later removed by subsequent zone recrystallization.
Crystal growth techniques III: Laser Heated Pedestal Growth (LHPG)

- similar to Czochralski process, but no crucible needed
- heating by power laser
- high purity and low stress crystals
- allows to growth materials with very high melting points
- when heating starts with single crystal on top, can produce single crystal
Polycrystal growth: arc melting/remelting

- melting or remelting in week vacuum (usually Ar residual atmosphere)
- creation of metal polycrystals, with defined composition
- allows to melt small amounts of materials
- vacuum remelting and slow cooling: removal of residual gas and high vapour pressure elements (C,S,O,Mg), larger crystal size, stable structure obtained.

1. Crystal nucleation:

- small particle of crystal is created (nucleated), with random crystallographic orientation.
- homogenous/heterogenous (without/with influence of the external particle).
- nucleus appears slowly (then crystal may growth quickly).
- external crystal can be used as a seed.
2. Crystal growth:

- In ideal case, crystal grows layer by layer added to the nucleated seed. The interface between crystal and vapour/solvent is atomically sharp.

- Non-uniform lateral growth: The surface advances by the lateral motion of steps which are one interplanar spacing in height.

- Uniform lateral growth: The surface advances normal to itself without the necessity of a stepwise growth mechanism.
Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance

Jaroslav Hamrle
Preparation of Nanostructures(Příprava Nanostruktur)
Thin film preparation

Techniques of thin film preparation

- physical techniques (usually physical vapour deposition, differing by source of vapour (MBE, sputtering, ion plating))
- chemical techniques (spin coating, chemical solution deposition (sol-gel), chemical vapour deposition)
Physical deposition techniques: physical vapour deposition (PVD)

PVD involves: **Vapour formation → vapour transformation → film formation**

<table>
<thead>
<tr>
<th>Vapour phase creation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>evaporation</td>
</tr>
<tr>
<td>sputtering</td>
</tr>
<tr>
<td>ion plating</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vapour transportation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>collisions (can be related with cluster formation)</td>
</tr>
<tr>
<td>ionizations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condensation on substrate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>nucleation, growth, ion bombardment, redeposition etc.</td>
</tr>
</tbody>
</table>

**Source (Solid / Liquid)**

- Evaporation

**Gas phase**

- Transport & Deposition

**Solid phase**

(Changes in physical morphology)
Example of molecular beam epitaxy, (M. Jourdan, Mainz)
Sources of vapours I: electron beam evaporators

Local heating by electron bombardment → evaporation of the target material → clean deposition of the target

www.mbe-components.com
Source of vapours II: Effusion cells (Knudsen Cell)

Thermal evaporation out of a heated crucible (T_{max} \approx 1800^\circ C)

www.mbe-components.com
Problem of PLD: droplets (μm-sized balles deposited together with vapour).
Control of the deposition

Deposited thickness gauge

Oscillating Crystal Monitor
[change of mass $\rightarrow$ change of resonance frequency]

Mass Spectrometer
Sputtering:

- ejection of atoms from target due to bombardment of energetic particles \((E \gg 1 \text{ eV})\).
- commonly use for thin-film deposition, etching or analytical material study.
  1. create plasma (dc, rf, mw)
  2. plasma looses energy to surroundings (bombardment)
  3. for plasma, atoms of noble gas of similar weight as target is used (e.g. Ar for 3d metals)
dc-sputtering

http://www.ajaint.com/whatis.htm
dc-sputtering: Glow Discharge

Crookes
Dark space

Negative
glow

Faraday
dark space

Positive
column

Accumulated ions
-> electric field

Low electron energy
-> no ionization

Screened ions
-> almost field free
Sputtering: example
Sputtering: industrial sputtering of glass

**Figure 1:** Horizontal inline sputter coater for architectural glass; annual throughput up to 8,000,000 m²
Sputtering: magnetron

Diagram showing the process of sputtering with a magnetron cathode. The diagram includes labels for the substrate, coating, substrate area to be coated, surface atom ejected from target, argon ions accelerated to target, electric field, primary magnetic field, target, magnet assembly, and magnetron sputtering cathode.
Sputtering: magnetron

Added magnetic field drives free electrons:
- electrons do not touch the target, and hence do not heat it
- electrons are localized above the target, and hence enhancing probability of ionization of noble gas \( \Rightarrow \) increases deposition rates
- recombination of free electrons and ions \( \Rightarrow \) glowing plasma
Sputtering: magnetron

Diagram showing the components of a magnetron, including:
- Clamped/Bonded Target
- Anode Shield Lid
- Target Clamp
- Backing Plate
- Magnet Assembly
- Cathode Body
- Insulator
- Anode Shield
- STEM
Sputtering: rf sputtering

- Plasma is generated by radio-frequency (rf) field (MHz).
- Rf-sputtering avoids charge build-up on insulating targets (e.g. allows to sputter oxides).
Atoms of target are ionized, to increase their speed prior the deposition → atom can penetrate deeper into the substrate

**Goal (1):** placement of atoms into substrate:
- gold plating
- steel hardening (e.g. layer of TiN)

**Goal (2):** crystal defects caused by atom irradiation:
- interface roughness control (magnetization anisotropy control)
- defects in AFM/FM interface ⇒ exchange bias control
- …
PVD techniques - comparison

http://www.eclatcoating.com/learn/pvdcoating.php
Chemical deposition

- Involves chemical change at a solid surface
- Unidirectional deposition
  - electroplating (Although very cheap, very high quality Au/Co layers with atomically sharp interface has been demonstrated.)
  - chemical solution deposition (CSD), or sol-gel (transformation of colloidal solution (sol) into solid layer (gel))
  - spin-coating: liquid precursor is spread on a thin plate by spinning.
  - chemical vapour deposition (CVD): gas precursor.
  - dip coating
  - electrospray deposition
Chemical vapour deposition (CVD)

- Film components bound in gas molecules
- Gas molecules directed on heated substrate
- Chemical reaction creates film material
- Gaseous by-products

GaN deposition
\( (\text{NH}_3+\text{TriMetylGalium}) \)

http://thermodynamik.uni-duisburg.de/mitarbeiter/atakan/cvd_intro.htm
CVD - reactors

http://www.timedomaincvd.com
gallium nitride – industrial CVD reactor

The C(lose) C(ouple) S(hower) Head reactor

![Diagram of a Gallium Nitride CVD Reactor](image)
gallium nitride – industrial CVD reactor
gallium nitride – industrial CVD reactor

CCS MOCVD System
Electrospray deposition

- Strong electric field extracts droplets from Taylor cone containing solute ions ($M^+$); most counter ions remain in capillary
- Solvent evaporates, droplets shrink, charge density increases
- Solute ions are ejected from the shrinking droplets; substrate
- Solute molecules form thin film on a plume
Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance
Photolithography: top-down approach

- First, entire layered structure is grown. Then part of it is etched.
- Lateral limit given by optical resolution (can be overcome UV light, extreme UV, X-ray etc, sub-wavelength diffraction masks, immersion photolithography)
- Instead of mask and subsequent optical illumination, exposure can be done by e-beam.
- Current lateral resolution cca 16 nm.
Lithography: standard and lift-off process

Lift-off: mainly to have good metal/metal interface.
Advantages:
• do not need etching.
Disadvantages
• Retention: not all (usually metallic) layer is washed out and stays on the wafer.
• Ears: When the metal is deposited, and it covers the sidewalls of the resist, "ears" can be formed.
• Redeposition: it is possible that particles of metal will become reattached to the surface, at a random location.
Focused ion beam (FIB):  
1. source of ions (usually $\text{Ga}^+$ or $\text{He}^+$)  
2. beam optics (similar to scanning electron microscopy)  
3. ions are focused to sample surface (focus diameter down to 1 nm)  
4. local removal of atoms by ions (FIB-milling)

http://web2.ges.gla.ac.uk/~mlee/FIBtec.htm
FIB nanostructures examples

http://nano.aalto.fi/en/research/groups/mqs/research/micro_and_nanofabrication/

www.raith.com
Bottom-up approach

- The opposite of the top-down approach.
- Instead of taking material away to make structures, the bottom-up approach selectively adds atoms to create structures.

http://idol.union.edu/~malekis/ESC24/KoskywebModules/sa_topd.htm
Nature uses the bottom up approach.

- Cells
- Crystals
- Humans

Chemistry and biology can help to assemble and control growth.

http://www.csacs.mcgill.ca/selfassembly.htm
Why is Bottom-Up Processing Needed?

- Allows smaller geometries than photolithography.
- Certain structures such as Carbon Nanotubes and Si nanowires are grown through a bottom-up process.
- New technologies such as organic semiconductors employ bottom-up processes to pattern them.
- Can make formation of films and structures much easier.
- Is more economical than top-down in that it does not waste material to etching.

http://courses.ee.psu.edu/ruzylllo/ee518/EE518_Top-down%20and%20Bottom-up1.ppt
Self Assembly

- The principle behind bottom-up processing.
- Self assembly is the coordinated action of independent entities to produce larger, ordered structures or achieve a desired shape.
- Found in nature.
- Start on the atomic scale.
Example 1: self-assembled nanodots

1) Self-assembled monolayer of 340 nm-diameter polystyrene spheres
2) Ni film deposited and balls removed

AppliedSurfaceScience257,8712,(2011)
Example 2: Self-assembled Monolayers (SAMS)

- Molecules are deposited molecule-by-molecule to form a self-assembled monolayer.
- Creates a high quality layers.
- Layers are deposited one layer at a time.
- Organic molecules can’t be deposited using extreme conditions because it would damage the organic molecules.
- SAMS technique does not damage organic molecules.
- SAMS films are nearly defect free.
- Used to deposit organic semiconductors.

http://www.mtl.kyoto-u.ac.jp/english/laboratory/nanoscopic/nanoscopic.htm

http://www.seas.upenn.edu/
Other examples of self assembly

- carbon nanotubes
- ...
Outline

1. Content
2. Relation between symmetry of crystals and crystal properties
3. Introduction
4. Bulk crystal growth
5. Thin film preparation
6. Lateral structures
7. ATR / Surface plasma resonance
Reflection and total reflection

Snell law:

\[ \sqrt{\varepsilon_1} \sin \varphi_1 = \sqrt{\varepsilon_2} \sin \varphi_2 \]

Critical angle:

\[ \sin \varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}} \]
Light reflection on the interface

1. Maxwell equations

2. solution as plane wave
   \[ E = E_0 \exp(i(\vec{k} \cdot \vec{r} - \omega t)) \]

3. boundary conditions at the interface:
   \( \vec{E}, \vec{H} \) fields: continuous transverse \((x, y)\) components
   \( \vec{D}, \vec{B} \) fields: continuous normal \((z)\) components

4. for total reflection, solution of transverse wave is in form so called evanescent wave, non-propagating in \( z \)-direction
   \[ E = E \exp(-k_z z) \]
Light reflection on the interface

s-polarized light:

$$r_\perp = \frac{n_i \cos(\theta_i) - n_\perp \cos(\theta_i)}{n_i \cos(\theta_i) + n_\perp \cos(\theta_i)}$$

$$t_\perp = \frac{2n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_\perp \cos(\theta_i)}$$

p-polarized light:

$$r_\parallel = \frac{n_i \cos(\theta_i) - n_\parallel \cos(\theta_i)}{n_i \cos(\theta_i) + n_\parallel \cos(\theta_i)}$$

$$t_\parallel = \frac{2n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_\parallel \cos(\theta_i)}$$

And, for both polarizations:

$$n_i \sin(\theta_i) = n_\parallel \sin(\theta_i)$$

Light reflection on the interface

Reflection on glass/air

![Graph showing reflection on glass/air](image-url)
**Total reflection**

Critical angle:

\[
\sin \varphi_c = \sqrt{\frac{\varepsilon_2}{\varepsilon_1}} = \frac{n_2}{n_1}
\]

Evanescent wave:

\[
E = E_t \exp(-z/\delta - i\omega t)
\]

Penetration depth:

\[
\delta = \frac{1}{k_0 \sqrt{(n_1 \sin \varphi_1)^2 - (n_2^2)}}
\]

Example: glass\((n_1)\)/water\((n_2)\) interface; \(n_1 > n_2\)

http://www.tirftechnologies.com/principles.php
Attenuated total reflectance (ATR)

(Zeslabený úplný odraz)

- probes sample by evanescent wave

⇒ sensitive to surface of the sample

- sample modifies evanescent wave → partial absorption or transmission of light in sample → total reflection is decreased (attenuated).

- reflected beam does not follow exactly geometrical optics → The Goos-Hänchen shift
Attenuated total reflectance (ATR): gap effect

Gap thickness (refractivity of gap=1):

Absorption in gap (gap thickness 960 nm):

[Graphs showing the relationship between gap thickness and angle of incidence for different gap thicknesses and refractive indices.]
Electric field in the vicinity of the interface:

\[ E = E_0 \exp[i(k_x x + k_z z - \omega t)] \]

where

\[ k^2 = k_x^2 + k_z^2 = \epsilon (\omega/c)^2 = \epsilon k_0^2 \]  \hspace{1cm} (1)

At the interface of two materials \( \epsilon_1 \) and \( \epsilon_2 \):

(a) \( k_x \) continuous over the interface;

\[ k_{x1} = k_{x2} \]  \hspace{1cm} (2)

(b) \( D_z \) and \( E_x \) continuous over the interface

\[ k_{z1}/\epsilon_1 = k_{z2}/\epsilon_2 \]  \hspace{1cm} (3)

\[ \beta = k_0 \sqrt{\frac{n_1^2 n_2^2}{n_1^2 + n_2^2}} \]

http://www.physics.uwo.ca/~smittler/
From Eqs. (1–3) follows dispersion relation for surface plasmon:

$$ k_x = k_0 \sqrt{\left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) }, \quad (4) $$

where $k_0 = \omega / c$.

Surface plasmon appears only for p-polarized (TM) wave, as this mode has normal (z) component of $D = \varepsilon \varepsilon_0 E$ field.
Example: assuming $\epsilon_1 = 1$ (air) and $\epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$ (metal as free electron model of an electron gas). Then

$$k_x = \frac{\omega}{c} \sqrt{\left( \frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2} \right)} \quad (5)$$

Hybridization between photon ($\omega = ck_0$) and plasmon $\omega_{SP} = \omega_p/\sqrt{2}$. 

![Graph showing hybridization between photon and plasmon](image)
Surface plasma resonance (SPR) I

- Resonance between incident wave photon and surface plasmon. Resonance means that both (pseudo)-particles have equal $\omega$ and $k_x = k_{x,\text{inc}} = \Re(k_{x,\text{sp}})$.
- Description of incident wave from material $\epsilon_1$ under angle $\varphi$:

$$k_{x,\text{inc}} = \frac{\omega}{c} \sqrt{\epsilon_1 \sin \varphi} \quad (6)$$

- Description of surface plasmon:

$$k_{x,\text{sp}} = \left(\frac{\omega}{c}\right) \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}, \quad (7)$$

Condition for existence of the resonance: $\Re(\epsilon_2) < -\epsilon_1$ (i.e. $\Re(\epsilon_2)$ must be negative; fulfilled by coinage metals, Au, Ag, Cu). Here, $\epsilon_1$ is assumed to be non-absorbing material (i.e. $\Im(\epsilon_1) = 0$).
Surface plasmons are very sensitive to slight perturbations within the skin depth ⇒ surface plasmons are often used to probe tiny changes of refraction index near the interface (extreme sensitive detector of small changes of the refraction index). ⇒ Readout of many bio-sensors based on this detection technique.

http://www.bionavis.com/technology/spr/
• presence of resonance increases absorption and reduces reflectivity.
• position of reflection minima very sensitive to refractivity index in position of the evanescent wave.
• presence of resonance increases absorption and reduces reflectivity.
• position of reflection minima very sensitive to refractivity index in position of the evanescent wave.
SPR: how to couple surface plasmon and photon?

- couple light by high-refraction index prism
- lateral modulation of the interface (roughness or structuring)

\[
\frac{\omega}{c} \sin \varphi + \frac{2\pi}{b} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_2}{\varepsilon_2 + 1}}
\]
SPR: bio sensors

http://www.bionavis.com/technology/spr/