Growth and Properties of Semiconductor Nanowires

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Outline

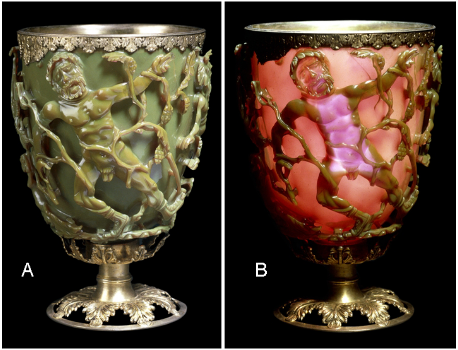
Introduction

There's Plenty of Room at the Bottom

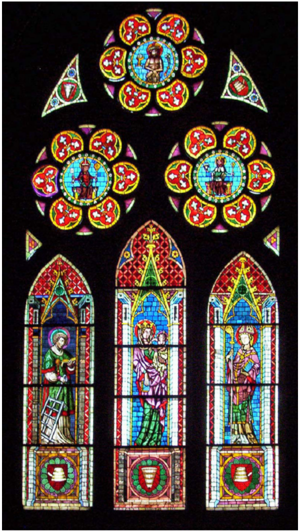
Richard P. Feynman
(1918-1988)

Lecture given at an American Physical Society meeting at Caltech on December 29 in 1959.

From Vases to Church Windows



Lycurgus cup (British Museum):
A) illumination from the front, B) from behind



Cathedral of Freiburg

What is nano?

Nanotechnology: from the atom to structures of up to 100 nm

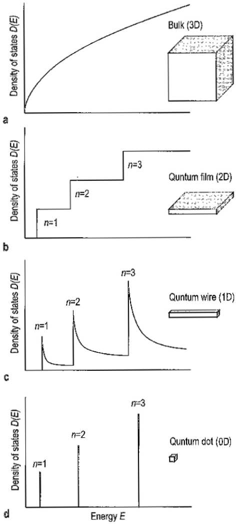
nano from *nanos* (greek: dwarf)

Quantum size effects:

- confinement leads to quantum effects (e.g. energy states become quantized)
- density of states:

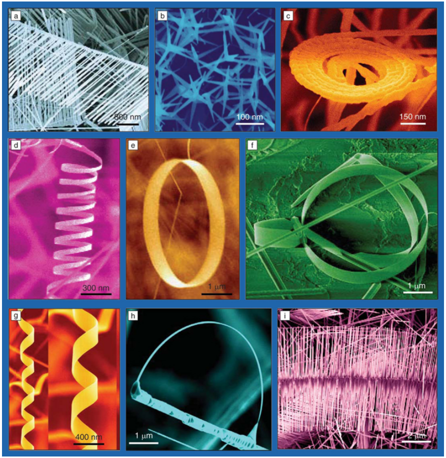
  DOS 3D: $D_{3D} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \cdot E^{\frac{1}{2}}$

  DOS 1D: $D_{1D} = \frac{(2m^*)}{\pi\hbar} \cdot \frac{1}{E^{\frac{1}{2}}}$



Density of states from 3D to 0D

Synthesis



Synthesis Overview

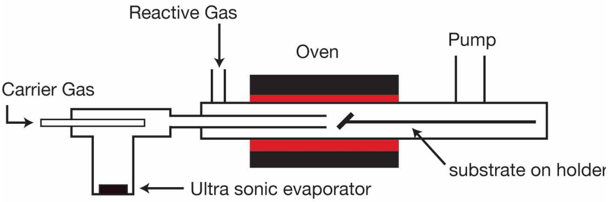
1. Vapor Phase Epitaxy
2. Vapor-Liquid-Solid Method
3. Solution-Liquid-Solid Method
4. "Pseudo"-Nanowires
5. ...

Vapor Phase Epitaxy

- most extensive explored approach for whiskers, nanorods and belts
- possible for any solid material by controlling the supersaturation, which influences the form and morphology (low: whiskers, medium: bulk crystal, high: powder)
- observation as early as 1921 by Volmer and Estermann: Hg nanofibers
- most products are oxides due to inevitable amounts of O_2 in the system
- major advantage: simplicity and accessibility

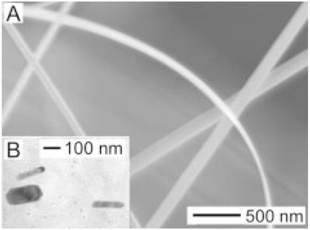
Vapor Phase Epitaxy

- typical process:
  - generation of vapor species (evaporation, reduction,...)
  - transport of this species to the surface of the substrate with lower temperature
  - with proper control of the supersaturation one can obtain 1D nanostructures



Examples

- Si_3N_4, SiC, Ga_2O_3 and ZnO nanowires by heating commercial powder of these materials (circular or square cross-section)
- nanobelts or -ribbons with rectangular cross-section: evaporation of commercial metal oxide powder at elevated temperatures
- diameter: 30-300 nm, length: several mm



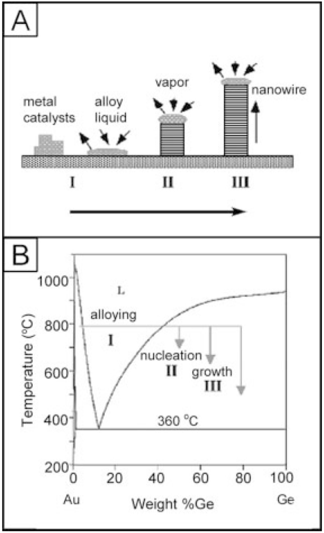
SnO_2 nanobelt: A) SEM image, B) XTEM image

Vapor-Liquid-Solid Method

- most successful method for generating nanowires with single-crystalline structures
- developed by Wagner et. al. in 1960s for micrometer-sized whiskers
- typical VLS process:
  - dissolution of gaseous reactants in nanosized liquid droplets of a catalysts metal
  - generation of vapor species (laser ablation, thermal evaporation, arc discharge)
  - nucleation
  - growth of single-crystalline rods and then wires

Vapor-Liquid-Solid Method

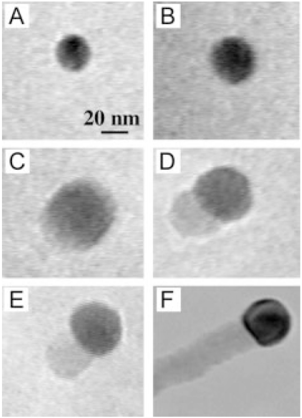
- growth is induced and dictated by the liquid catalyst droplet
- size remains unchanged during growth
- droplet strictly limits lateral growth
- requirement: good solvent capability between liquid alloy and target material (formation of eutectic compound)
- after supersaturation of liquid droplet growth at solid-liquid interface starts
- vapor pressure low enough to suppress secondary nucleation



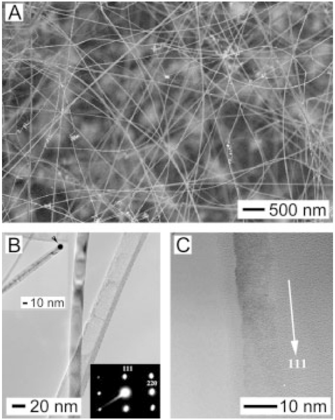
Vapor-Liquid-Solid Method

Ge nanowires on Au nanocluster:

- diameter of the order of 10 nm and length scale over 1 μm



in-situ TEM



A) SEM, B) TEM (inset: AU tip), C) atomically resolved TEM

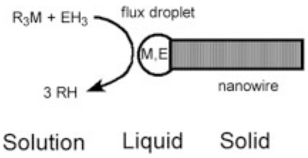
Vapor-Liquid-Solid Method

Problems of VLS:

- selection of the appropriate catalyst
- impossible to apply VLS to metals
- metal as a catalyst may contaminate the nanowires

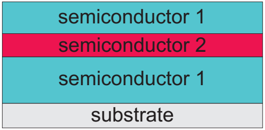
Solution-Liquid-Solid Method

- similar to VLS
- developed for highly crystalline nanowires of III-V semiconductors at low temperatures
- procedure:
  - metal (e.g. In, Sn, Bi) with low melting point as catalyst
  - decomposition of organometallic precursors to get desired species
- whiskers or filaments are produced (lateral dimension: 10-150 nm, length: several μm)

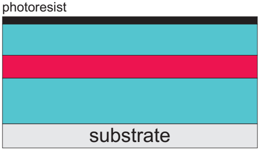


"Pseudo"-Nanowires

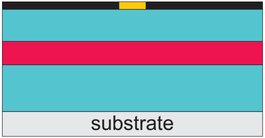
Top-down approach: formation via lithography and etching:



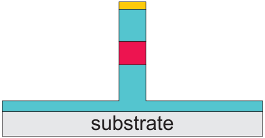
formation of 2D quantum well



coating with photo-resist

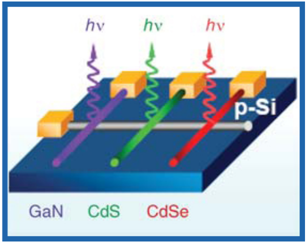


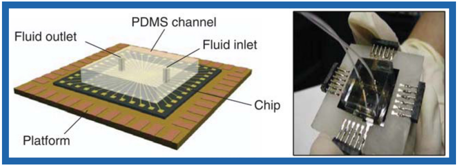
creation of pattern



subsequent etching

Properties and Applications

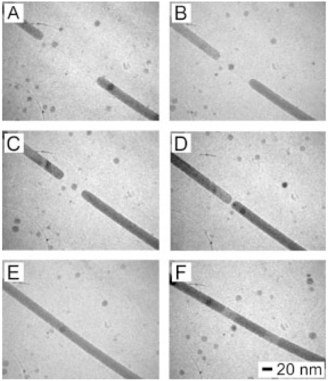




Thermal Stability

- melting point is reduced with decreasing size
- consequence:
    - annealing temperature much lower for healing
    - integration in functional devices and circuitry (cutting, interconnecting, welding)
    - sensitivity to environmental changes (e.g. temperature or stress fluctuation)

Welding of two Ge nanowires (TEM images, 10-100 nm thickness)

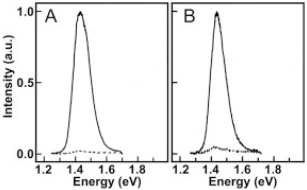


Electron Transport Properties

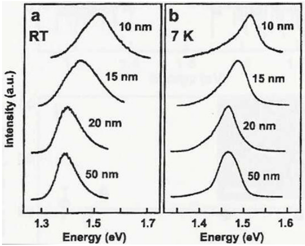
- due to the decrease of the critical dimensions the electron transport properties become an important issue for study
- because of size reduction extra quantum effects arise
- some metal NW undergo a transition to become semiconducting as their diameter is reduced (e.g. Bi)
- conductivity is much less than bulk material and quantized ($\frac{2e^2}{h}$)
- ballistic transport occurs in nanowires

Optical Properties

- light emitted from nanowires is strongly polarized along their longitudinal axis
- absorption edge of nanowires is blue-shifted (higher energies) with decreasing diameter
- additionally there are sharp, discrete features in absorption spectra
- a possible explanation include quantum-confined effects (although surface states may contribute additional features)

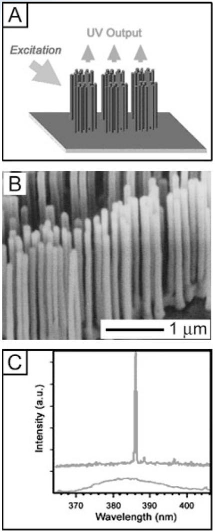


A) Excitation and B) emission spectra from InP nanowire (15nm diameter)



blue-shift

Lasing in Semiconductor Nanowires



- nanowires with flat ends are utilized as optical resonance cavities

Example: room-temperature UV lasing of ZnO

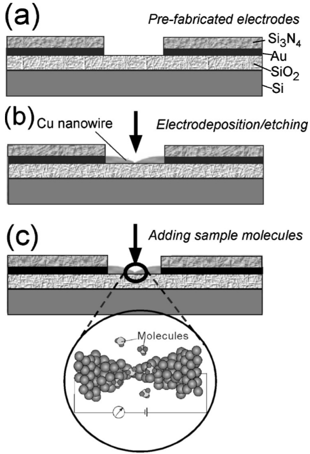
- ZnO grown on sapphire with VLS
- high exciton binding energy, wide bandgap
- nanorod serves as good optical cavity because of the refractive index of sapphire, ZnO (highest) and air
- nanowire is pumped by a Nd:YAG laser
- light emission occurs normal to the end of the wire

Sensing Applications

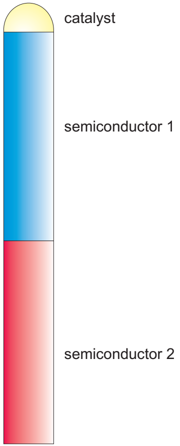
- sensing of important molecules
- high electrical sensitivity due to high surface-to-volume ratios

Example: Copper sensor

- arrays of Cu nanowires containing nanoscale gaps
- adsorption of organic molecules reduced the quantized conductance
- reason: scattering of the conduction electrons by the adsorbate



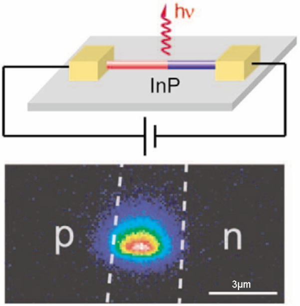
Axial NW Heterostructures I



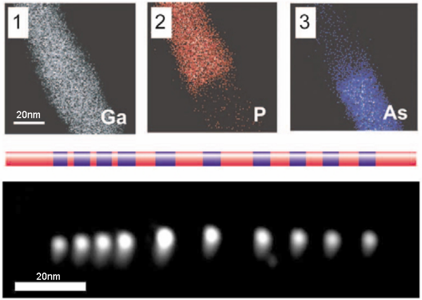
- variation of the composition and/or doping modulation along the axis
- integrating controlled device functions into nanowires
- no additional lithography steps are necessary
- procedure: switching the reacting species during growth

Axial NW Heterostructures II

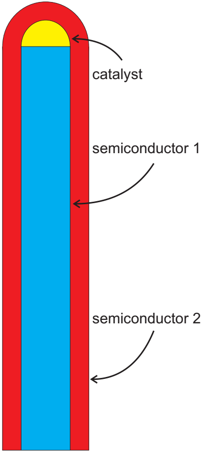
Nanoscale LED (n-InP/p-InP)



Modulation of GaAs and GaP



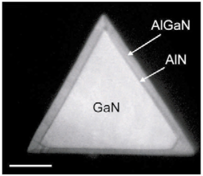
Radial NW Heterostructures I

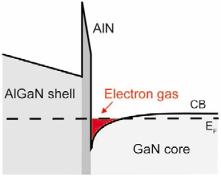


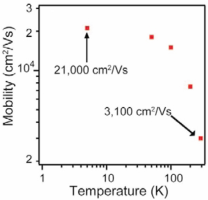
- radial composition/doping may enhance the performance
- first, growth of a nanowire
- second, change the conditions in order to favor shell growth

Radial NW Heterostructures II

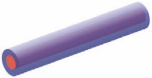
GaN/AlN/AlGaN NWFETs

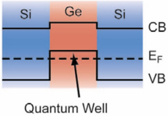




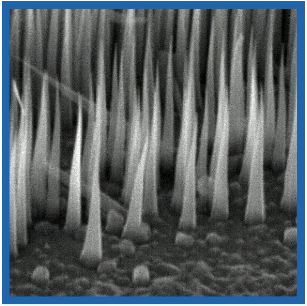


Ge/Si core-shell NWFETs



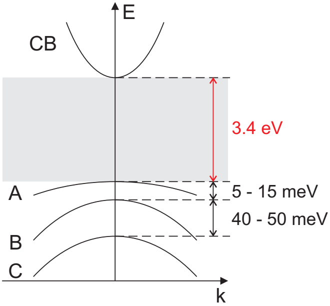


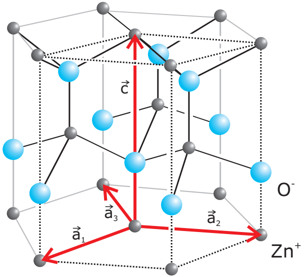
Catalyst-free self-assembled Growth of ZnO Nanoneedles



Properties of ZnO

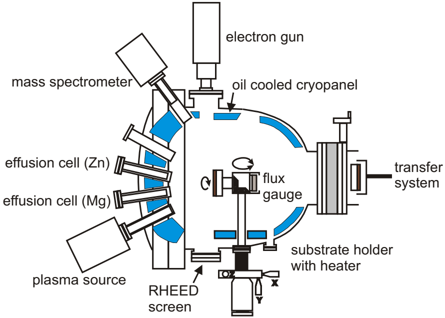
- II-VI semiconductor
- Wurtzite structure





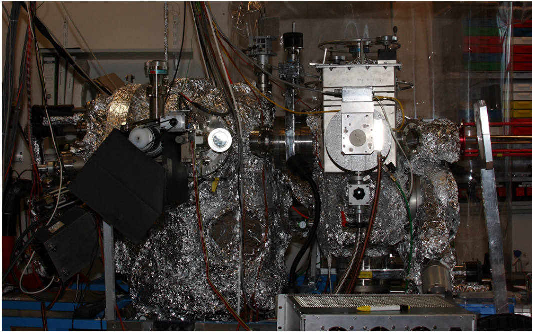
- direct wide bandgap of 3.4 eV
- high exciton binding energy ($\approx 60\,\text{meV}$)
- strong tendency to selforganized growth due to polar surfaces

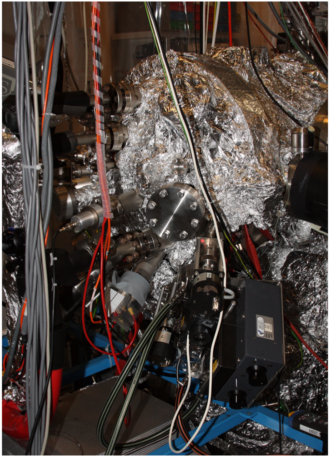
PAMBE Growth



- substrate temperature $T_S = 350\ ^\circ\mathrm{C}$
- a-plane sapphire
- Zn beam equivalent pressure $BEP(Zn) = 2 \cdot 10^{-6}$ mbar
- plasma power $P(\mathrm{O}_2) = 250$ W @ 0.5 sccm

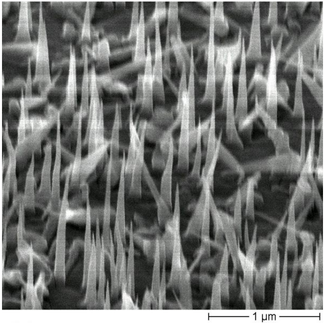
Our PAMBE System

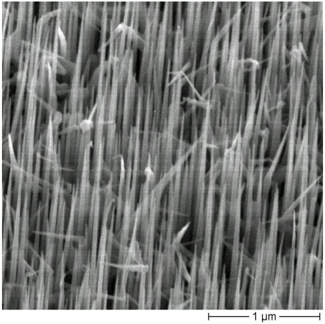




Scanning Electron Microscopy (SEM)

increased Zn flux

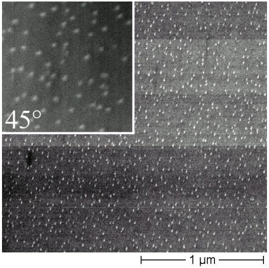




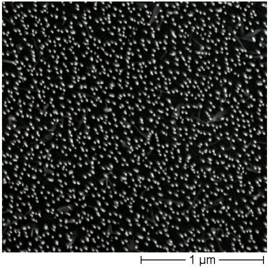
- influence on nucleation and shape

Growth Time

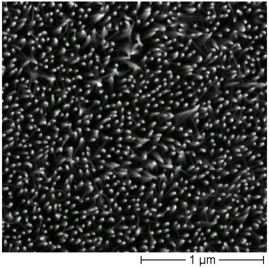
Scanning Electron Microscopy (SEM)



t = 1.5 min



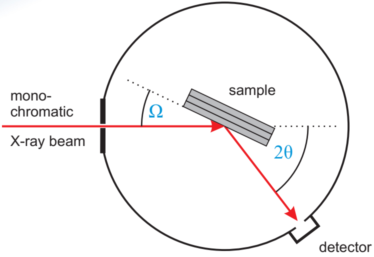
t = 10 min

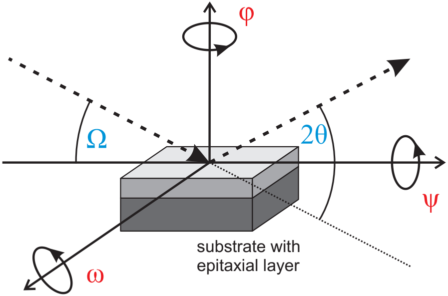


t = 40 min

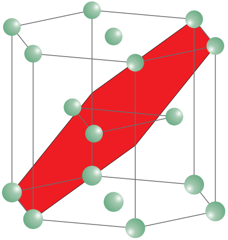
- immediate nucleation
- almost constant density
- time-dependent growth rate

High Resolution X-Ray Diffraction

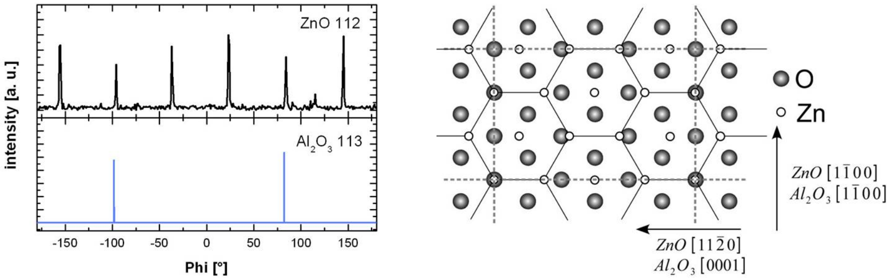




$$n \cdot \lambda = 2d \cdot \sin\theta$$

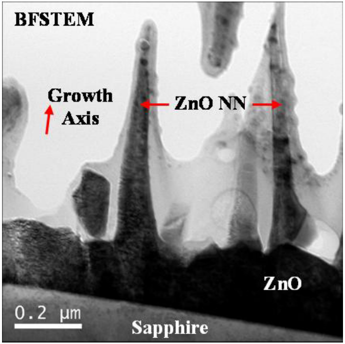


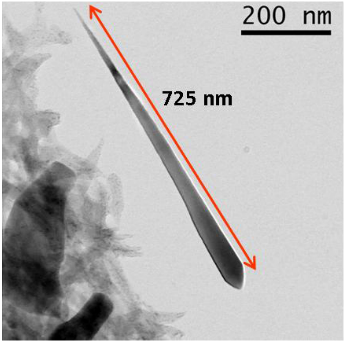
High Resolution X-Ray Diffraction (HRXRD)



- $\mathrm{Al_2O_3[11\bar{2}0] \parallel ZnO[0001]}$ and $\mathrm{Al_2O_3[0001] \parallel ZnO[11\bar{2}0]}$
- same as for continuous layer

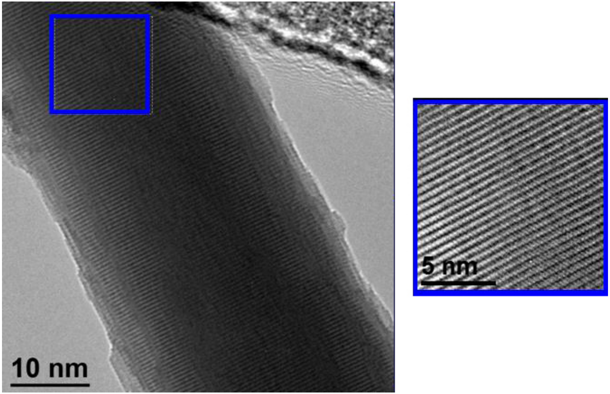
Transmission Electron Microscopy (TEM)





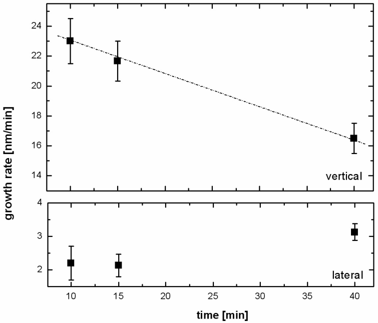
- wetting layer is formed during growth process
- isolated nanoneedles show tapered basis

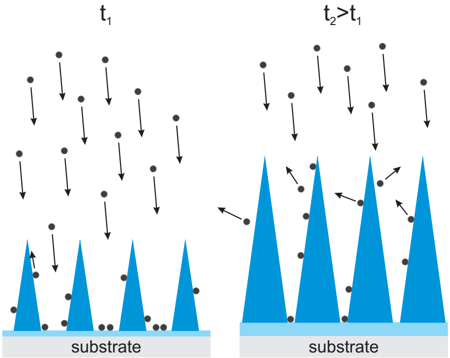
TEM Part II



- walls of the nanoneedles relatively rough
- good structural quality
- tip diameter ($\approx$ 3 nm)

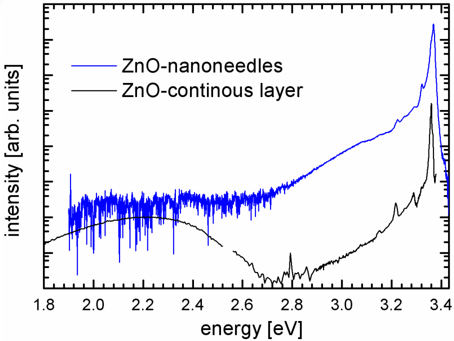
Growth Rate and Model

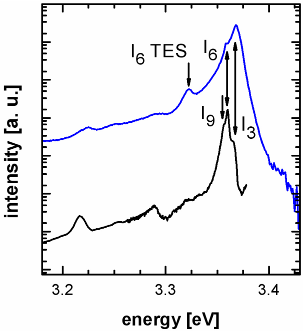




- high vertical growth rate compared to continuous layer (2-3 nm/min)
- low lateral growth rate due to high mobility on side-walls and Zn-rich conditions
- decrease in growth rate with increasing growth time due to limited desorption time

Photoluminescence (PL)





- relative intensity of bound excitons change
- weak deep luminescence

Round Up

- Synthesis:
  - bottom-up: CVD, VLS, SLS, MBE, ...
  - top-down: lithography and etching, ...
- Due to the different properties there are plenty of applications:
  - semiconducting devices (FETs, p-n junctions, ...)
  - gas sensors
  - lasing
  - light emitting diodes
- Our current research: ZnO nanoneedles

спасибо

(Thank you for your attention!)