Nanocrystals, superlattices/mesocrystals and nanowires

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• nanocrystals
  – semiconductors
  – metals
• superlattices & mesocrystals
• nanowires
some useful references

Nano

- nanotechnology remains hot
- nano = at least one dimension < 100 nm
- famous lecture of Richard Feynman: “there’s plenty of room at the bottom” (1959)
- real start: scanning probe microscopy (>1990)
- control matter at the atomic scale
  - top down: lithography
  - bottom up: self-assembly
- many potential applications of bottom up

Fe on Cu(111), Eigler, IBM
Two approaches

This lecture: bottom-up approach

from http://www.aist.go.jp
Nanocrystals

- crystallisation = self-assembly
- nanoparticle: small
- nanocrystal: small & crystalline
  - often true single crystal (no grain boundaries)
- why small? bulk properties change and can be tailored
Nanocrystals/particles from many materials

- **semiconductors**
  - Si, CdTe, ... (‘quantum dots’)
- **metals**
  - Ag, Au, ...
- **oxides**
  - SiO₂, ZnO
Tunable properties: band structure

- **Metal** atom, nano, bulk
- **Semiconductor** atom, nano, bulk

Fermi level

Stronger effect for semiconductors
Surface passivation

- large relative surface area, thus large influence of so-called surface states
  - will influence electronic properties for semiconductors
  - cover with large bandgap material
  - of course: can also use this
- prevent aggregation
  - cover with organic molecules to keep nanocrystals in solution
Tunable properties

- CdS from molecule to bulk
  - bandgap from 4.5 to 2.5 eV
  - melting point from 400 to 1600°C
- light-emitting diodes (LED’s)
- lasers
- quantum dots for solar cells
- biological labels (are really used!)
Nanocrystal morphology

• more-or-less the same as growing big crystals
• determined by the growth rate in different directions
  – facets are the directions that grow slowest

• time and length scale usually such that thermodynamic equilibrium shape is *not* formed
  – even for nanocrystals!
Morphology

• ‘only’ need to know the growth rate for each (major) direction
• this depends on many parameters
  – supersaturation
  – solvent
  – defects
  – impurities/additives
  – ...
• often empirical knowledge
Growing semiconductor nanocrystals

• three components
  – precursors
  – organic surfactants
  – solvents
• example CdSe
• dissolve dimethylcadmium and selenium powder in butyl phosphine.
• inject in trioctyl phosphine oxide (TOPO, acts as surfactant) at 350°C: rapid nucleation
• let it grow at 290°C
• stop at the right moment
  – possible to get narrow size distribution
How to get narrow size distribution?

- Under normal conditions: nucleation and growth leads to particles with many different sizes

1. Normal growth + selection afterwards
   - ‘size-selective’ sedimentation
   - precipitate out the larger crystals by adding poor solvent
   - each step gives different size
   - tedious, low yield

2. size-distribution focussing
   - predicted in 1951, Reiss
Gibbs-Thomson effect

- small crystals have relatively large surface energy
  - less stable than large crystals
  - solubility depends on size
  - THE solubility is for ‘infinitely’ large crystal
- small crystal will only grow if concentration is above it’s own solubility
- if you wait very long time: one big single crystal
  - Ostwald ripening (big crystals will growth at the expense of smaller ones)
size-dependent growth

- Critical size
- Growth rate: geometrical effect: more atoms needed for larger crystals
- Solubility
- Monomer concentration
size distribution focussing

all particles should be larger than for maximum growth rate

From: Yin and Alivisator, Nature 437 (2005) 664
requirements for size focussing

- separate nucleation from growth step
  - you don’t want new small particles
- maintain sufficiently high monomer concentration
- stop growth abruptly
  - otherwise you go though broadening regime

TEM of CdSe nanocrystals
From: Yin and Alivisator, Nature 437 (2005) 664
Role of surfactants

- prevents agglomeration
- determines solubility
  - makes surface often hydrophobic
- but also: huge influence on growth
- organic-inorganic interface very important
  - bonding can be facet dependent
  - change morphology
  - many unknowns
- similar to biomineralization, where biomolecules can determine the morphology
Fancy morphologies

• branched crystals of CdSe
  – start with zincblende core using high supersaturation (metastable, Ostwald rule of stages)
  – grow wurtzite branches

and now some metal nanocrystals

- first documented solution-phase synthesis: Michael Faraday, 1857, Au colloids
- last two decades: sufficient control over size, morphology and quantity
- ingredients
  1. metal salt precursor (AgNO₃)
  2. solvent (ethylene glycol)
  3. reducing agent (ethylene glycol)
  4. capping agent (poly(vinyl pyrrolidone), PVP)
growth of metal nanocrystals

• Three steps
  1. nucleation
  2. seeds (stable)
  3. growth

• the exact growth route is not known!
  – cluster + neutral atoms, or
  – cluster + metal-ligand complex?

• metals have simple structure (often fcc), with full-shell geometries with high stability

Xia et al., Angew. Chem.Int. Ed. 48 (2009) 60
seeds

- typically, after the nucleation phase, seeds with different structures are formed

- in order to get uniform nanocrystals, better to have single type of seeds
  - allow for oxidative etching (e.g. add NaCl, + O$_2$ from air)
  - seeds with defects are less stable, etch faster
nanocrystal morphologies

- defects (permanent step) lead to faster growth
  - anisotropic morphology

Xia et al., Angew. Chem. Int. Ed. 48 (2009) 60
capping agents (like in semiconductors)

- addition of compounds that preferentially bind to specific facets will change crystal morphology
  - PVP bind to \{100\} facets of Ag and Pd: \{111\} disappear
- can be separately added
- can be side product
- could be (unknown) impurity
- still: trial-and-error
- would be called ‘habit modifier’ clascally
**shapes achieved so far**

<table>
<thead>
<tr>
<th>Structures</th>
<th>Shapes</th>
<th>Schematic drawings</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>single-crystal</td>
<td>perfect/truncated cube$^{\text{HI}}$</td>
<td><img src="image1" alt="Diagram" /></td>
<td>Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe</td>
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<tr>
<td></td>
<td>perfect/truncated octahedron$^{\text{II}}$</td>
<td><img src="image2" alt="Diagram" /></td>
<td>Pd, Ag, Au, Pt</td>
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<tr>
<td></td>
<td>perfect/truncated tetrahedron$^{\text{III}}$</td>
<td><img src="image3" alt="Diagram" /></td>
<td>Ag, Au, Pt, Rh</td>
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<tr>
<td></td>
<td>rectangular bar</td>
<td><img src="image4" alt="Diagram" /></td>
<td>Pd, Ag, Pt</td>
</tr>
<tr>
<td></td>
<td>octagonal rod</td>
<td><img src="image5" alt="Diagram" /></td>
<td>Pd, Au, Fe, Co, Ni</td>
</tr>
<tr>
<td></td>
<td>rectangular or octagonal wire</td>
<td><img src="image6" alt="Diagram" /></td>
<td>Pb, In, Sn, Sb, Fe, Co</td>
</tr>
<tr>
<td>singly twinned</td>
<td>right bipyramid</td>
<td><img src="image7" alt="Diagram" /></td>
<td>Pd, Ag</td>
</tr>
<tr>
<td>multiply twinned</td>
<td>decahedron$^{\text{IV}}$</td>
<td><img src="image8" alt="Diagram" /></td>
<td>Pd, Ag, Au</td>
</tr>
<tr>
<td></td>
<td>icosahedron$^{\text{II}}$</td>
<td><img src="image9" alt="Diagram" /></td>
<td>Pd, Au</td>
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<tr>
<td></td>
<td>five-fold twinned pentagonal rod</td>
<td><img src="image10" alt="Diagram" /></td>
<td>Pd, Ag, Au, Cu</td>
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<tr>
<td></td>
<td>five-fold twinned pentagonal wire</td>
<td><img src="image11" alt="Diagram" /></td>
<td>Ag, Au, Cu</td>
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<tr>
<td></td>
<td>triangular/hexagonal plate</td>
<td><img src="image12" alt="Diagram" /></td>
<td>Pd, Ag, Au, Cu, Pb, Bi, Co, Ni</td>
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<tr>
<td></td>
<td>disc</td>
<td><img src="image13" alt="Diagram" /></td>
<td>Sn, Co</td>
</tr>
</tbody>
</table>

*Xia et al., Angew. Chem.Int. Ed. 48 (2009) 60*
some examples

Pd

Ag

Y. Xia et al.
Tunable properties: metals

- electron in normal electronic states
- interaction of free electrons in flat surface with light: in phase oscillation called surface plasmon resonance (SPR)
  - high reflectivity of metals
- for nanocrystals, plasmons are confined: localized surface plasmon resonance (LSPR)
  - very strong electric fields within nanometers of the surface
  - much stronger Raman scattering: surface-enhanced Raman scattering (SERS)
    - makes fingerprinting of molecules much easier
shape-dependent properties

- Ag nanocrystals
- simulation, but experiments show similar results

metal nanocrystals for catalysis

• basic: high surface-to-volume ratio
• aim use shape and size to increase
  – activity (many edge/corner atoms)
  – selectivity (facets)
• some promising results
  – however: shape may get lost during catalysis
metal nanocrystals as magnets

- single magnetic domain
- however: ‘superparamagnetic limit’: if too small, already spin flipping at room temperature
- to be continued...
• nanocrystals
  – semiconductors
  – metals
• superlattices & mesocrystals
• nanowires
crystals of nanocrystals

• if the nanocrystals are sufficiently homogeneous, they can form ordered structures
  – nanocrystal superlattices
  – mesocrystals (non-spherical)
• nanocrystal = artificial atom
• massive playground
  – different sizes
  – different shapes
  – different materials (metals + semiconductors)
• even quasi-crystals have been grown
PbSe (11 nm) + CdSe (5.8 nm)

Vanmaekelbergh, Nano Today 6 (2011) 419
PbSe (7.8 nm) + CdSe (5.8 nm)

Vanmaekelbergh, *Nano Today* 6 (2011) 419
nanocrystal superlattice formation

• similar to normal crystals
  – adding anti-solvent
  – solvent evaporation

• entropy can be dominant contribution in free energy (for semiconductor nanocrystals)
  – entropy ≠ disorder
  – entropy = maximum number of possibilities (*freedom”)
  – in ordered state, there can be more room per particle than in disordered state (at high densities)
  – computer simulations for hard spheres + experiment
    • no (attractive) force needed to form a crystal
Novel materials

Vanmaekelbergh, Nano Today 6 (2011) 419
Mesocrystals

- building block is (non-spherical) nanocrystal
  - not single atom/molecule
  - similar to biomineralization (amorphous blocks)

mesocrystals

Li et al., Nature 402 (1999) 393

BaCrO₄

Wang et al., JACS 127 (2005) 3246

CaCO₃
another type of mesocrystal

- oriented attachment, ‘epitaxial sintering’
  - ‘pearl string’
- need to sample many orientations
  - possible for mobile nanocrystals

TiO$_2$ (anatase), Penn & Banfield, 1999
and finally, some flowers!

- mutual interaction between the growth of barium carbonate (crystalline) and silicate (amorphous) and CO₂
- see talk of Garcia-Ruiz

Noorduin et al, Science 340 (2013) 832

Vlieg, Science 340 (2013) 822
• nanocrystals
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  – metals
• superlattices & mesocrystals
• nanowires
Growth of nanowires

• VLS growth: vapour-liquid-solid
  – Wagner & Ellis, 1964
• growth using metal-organic vapour phase epitaxy (MOVPE)
• gold ‘catalyst’ determines diameter
  – 5-200 nm (metal nanocrystal!)
• here: III-V semiconductor
  – InP, GaP

soft nano imprint lithography
Pierret et al., Nanotechnology 21 (2010) 065305
VLS and lateral growth

1) Mass transport through gas phase
2) Dissociation reaction
3) Diffusion through metal particle
4) Growth at the liquid-solid interface
5) Adsorption of precursor molecules on the substrate or the nanowire surface
6) Surface diffusion
7) Thin film growth on the nanowire side walls
8) Thin film growth on the substrate surface
MOVPE

MOVPE Parameters:
- temperature
- gas flow
- doping

Aixtron 200 MOVPE reactor
Potential applications

- Three-terminal devices
- PN junctions (LED’s)
- Sensors
- Solar cells
  - misfit no problem in multi-junction cells
- ?
Growth stages

- Core growth
- Faceting
  - fast, because of length scale
- Lateral growth
  - possibly heteroepitaxial
Morphodrome of GaP

- Different facets, twins and crystal structure
- Wurtzite + zinc blende
Crystallographic structure InP

• in bulk
  – zinc blende structure
  – [111] direction
  – ABC stacking

• in nanowires
  – often wurtzite structure
  – [001] direction
  – ABAB stacking
  – (size effect?)
Wurtzite versus zinc-blende in InP

zinc-blende if sufficient Zn doping
Zinc-blende regime: regular twinning

period depends on diameter

Algra et al., Nature 456 (2008) 369

10 nm  20 nm  50 nm  100 nm

420 °C
Twinning superlattice: why?

• **Interfacial energies**
  – shape/angle gold droplet
  – side facets
  – hexagon ↔ triangle
Model for superlattice period

- Take all interfacial energies into account
  - nucleation probabilities for different stacking

\[ N = AD - 2 + \frac{D}{B} \ln(e^{2B/D} - 1) \]

L.F. Feiner, Philips
twins in GaP

\[ \{11\bar{2}\} = \{100\} + \{111\} \text{ nanofacets} \]

*Algra et al., Nanoletters 10 (2010) 2349*
facets of twin pairs

\{111\} facets after first random twin
then: second twin
mechanism

- analogous to InP
- difference: \{111\} versus \{112\} side facets
- twin: \{111\} → two routes

Algra et al., Nanoletters 10 (2010) 2349
Model

- nucleation probability of different stackings depend on droplet contact angle
Twinning superlattice as template: nanotubes

Algra et al., Nano Lett. 11 (2011) 1690
Wurtzite template

- GaP wurtzite nanowire gives wurtzite Si shell
  - non-equilibrium (non-diamond) Si structure
Conclusions

- huge progress has been made in the controlled growth of nanocrystals and nanowires
- up to now: fundamentals
- applications will come
  - already quantum dots as biomarkers