Cadmium chalcogenides – important II – VI semiconductors

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Syllabus

- Introduction:
  - Fundamental terms about semiconductors: energy bands, band gap
  - Doping, p– and n– type semiconductors
  - Semiconducting materials by groups

- II – VI type semiconductors
- Cadmium chalcogenides, traditional and modern methods of preparation
- Use of sonochemical method in the synthesis of CdS and CdSe

Introduction

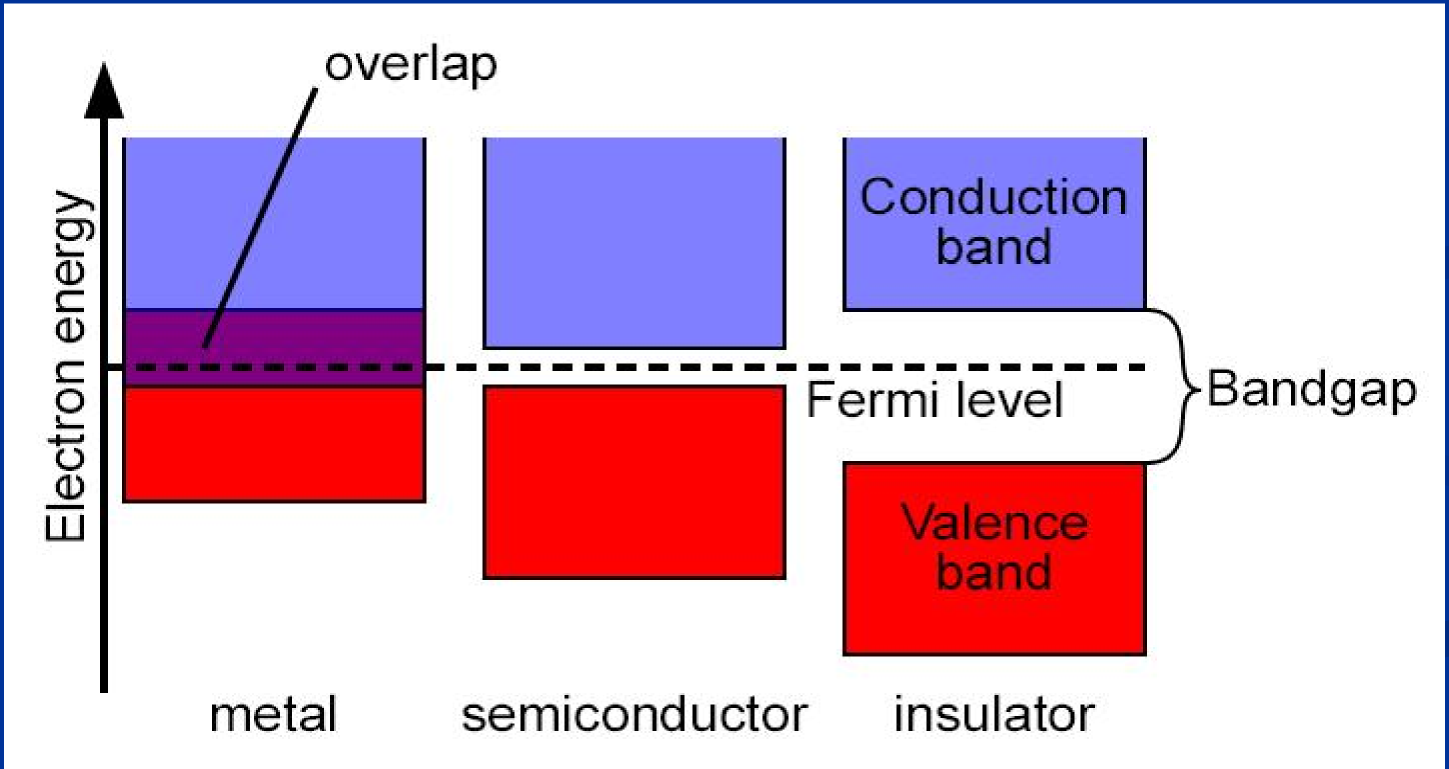
- **Semiconductor:** material that has a resistivity value between that of a conductor and an insulator
- The conductivity of a semiconductor material can be **varied** under an external electrical field
- Devices made from semiconductor materials are the foundation of modern electronics: including radio, computers, telephones, and many other devices.
- Semiconductor devices: transistor, diodes including the light-emitting diode (LED), integrated circuits
- **Solar photovoltaic panels**: large semiconductor devices that directly convert light energy into electrical energy.

Energy bands, band gaps

- Electrons of a single isolated atom occupy atomic orbitals, which form a discrete set of energy levels.
- If several atoms are brought together into a molecule, their atomic orbitals split - the number of molecular orbitals proportional to the number of atoms
- When a large number of atoms are brought together to form a solid, the number of orbitals becomes exceedingly large, and the difference in energy between them becomes very small, so the levels may be considered to form continuous ***bands*** of energy rather than the discrete energy levels

- Some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming *band gaps*

Semiconductors: $E_g < 3$ eV



Doping

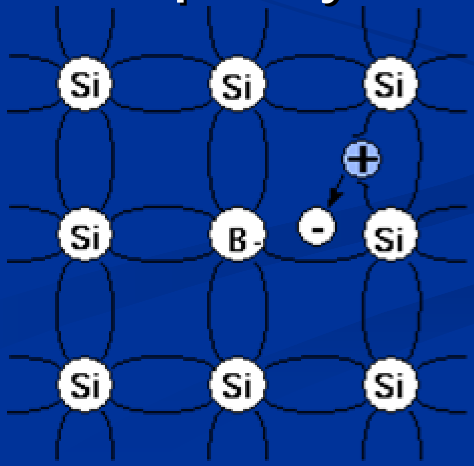
Intrinsic (undoped) semiconductor: conductivity due to crystal defects or thermal excitations, n = p

- n – type doping: adding an impurity of valence 5 element to a valence 4 semiconductor, typically

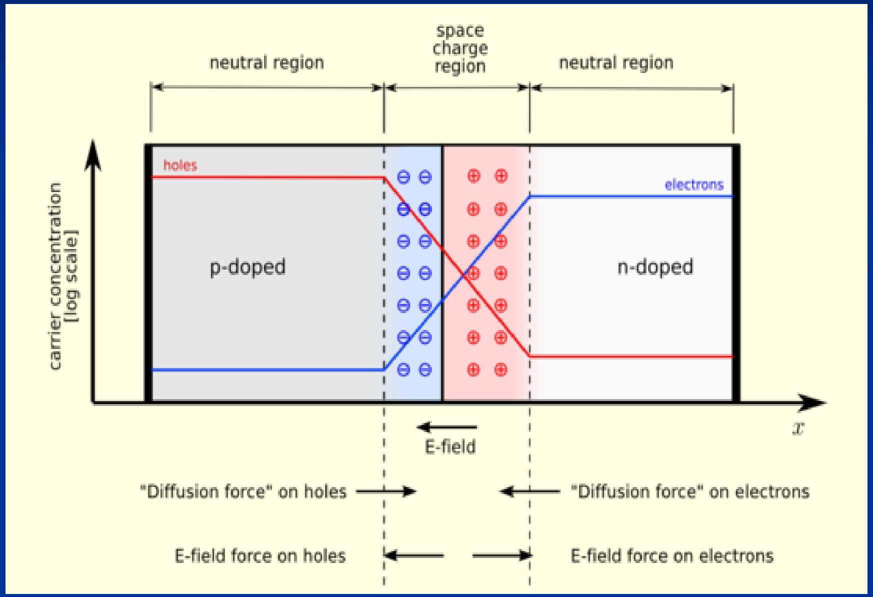
  Si + P
- p – type doping: adding an impurity of valence 3 electron to a valence 4

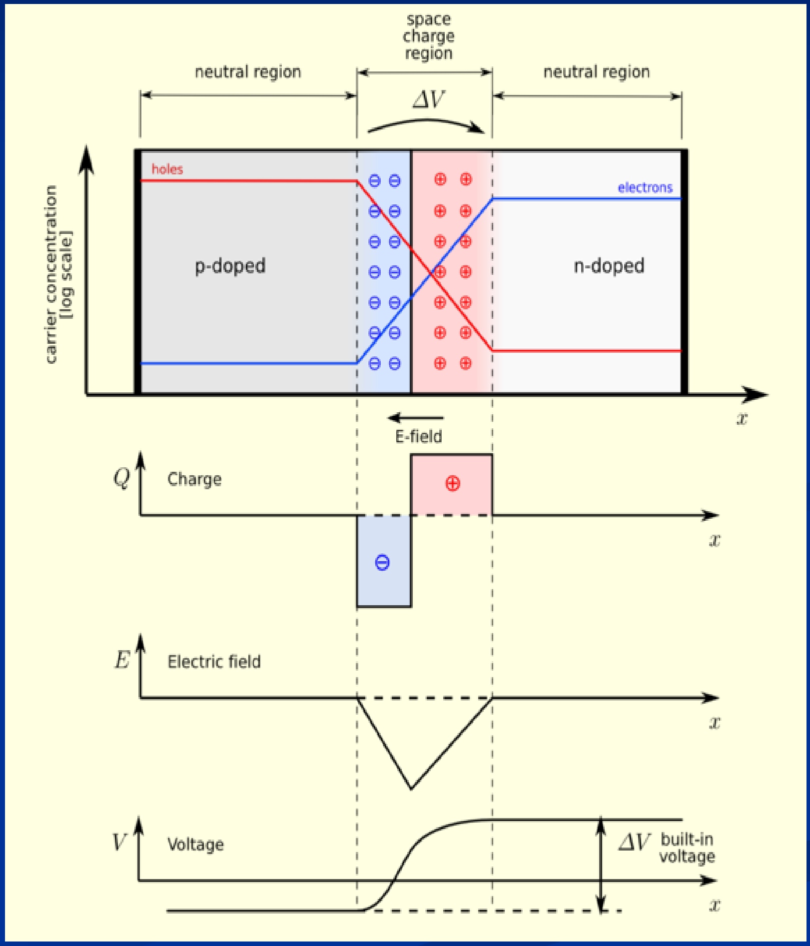
  semiconductor,

  typically Si + B:



Scheme of basic principle of semiconductors





Intrinsic (undoped) semiconductor:

- n = p
- Conductivity due to crystal defects or thermal excitations

Doped semiconductors:

- Classical Si cell: p – n (p – doped Si + n – doped Si)

Recent designs:

- p – i – n Si cells: the middle layer is intrinsic (undoped) silicon
- n – i – p cells:

Common types of semiconducting materials

- Group IV elmental SC: Si, Ge
- Group IV compound SC: SiC, SiGe
- III – V semiconductors: GaAs
- II – VI semiconductors: **CdS, CdSe, CdTe**

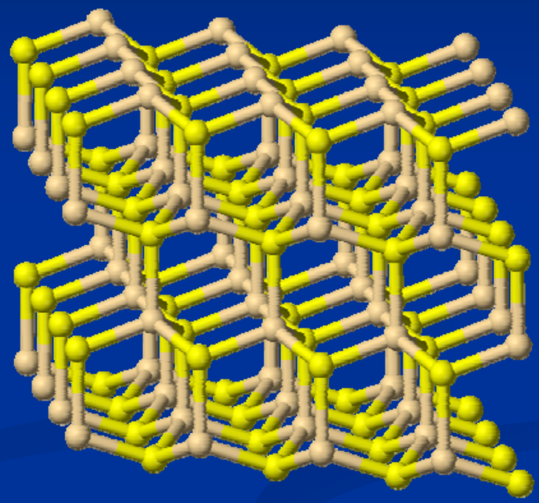
  ZnO, ZnS, ZnSe, ZnTe

  ternary compounds, e. g. CdZnTe

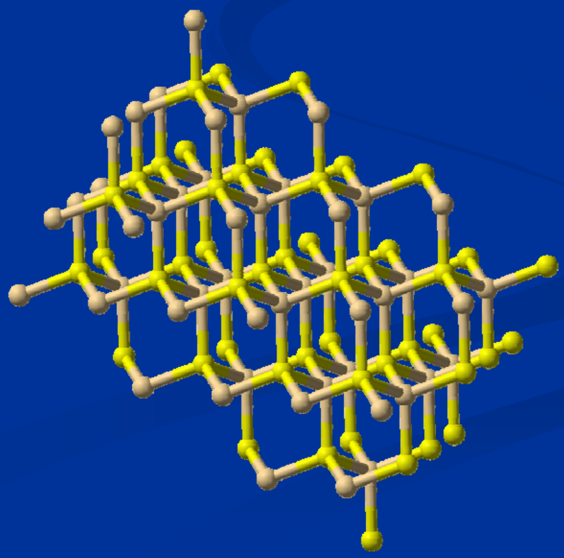
Cadmium sulfide, CdS

Two naturaly occuring crystalline modifications:

- Greenockit (hekxagonal UC):



- Hawleyit (cubic UC):

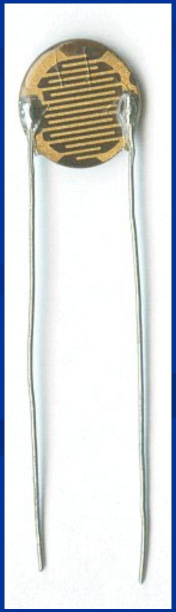


Applicatons of CdS

- Known as **cadmium yellow** (CI pigment yellow 37): pigments valued for good thermal stability, light and weather fastness and high opacity
- Pigment in plastics and in art: *Van Gogh, Monet*

Direct band gap semiconductor: band gap = 2.42 eV at 300 K (bulk), up to 4 eV with nanoparticles

- conductivity increases when irradiated → photoresistor
- Both polymorphs are piezoelectric
- Solid state laser
- When combined with a p - type semiconductor: **photovoltaic** (solar) **cell**: (CdS/Cu_2S , 1954)



Applications of CdSe

- Thermally stable pigment: CdS + CdSe = **orange** to **red** colours

Semiconducting material: band gap = 1.74 eV at 300 K

- Laser diodes
- Size dependent fluorescence spectrum (*quantum confinement*): properties of CdSe are tunable based on their size
- Tested for use in high – efficiency **solar cells**

Cadmium telluride, CdTe

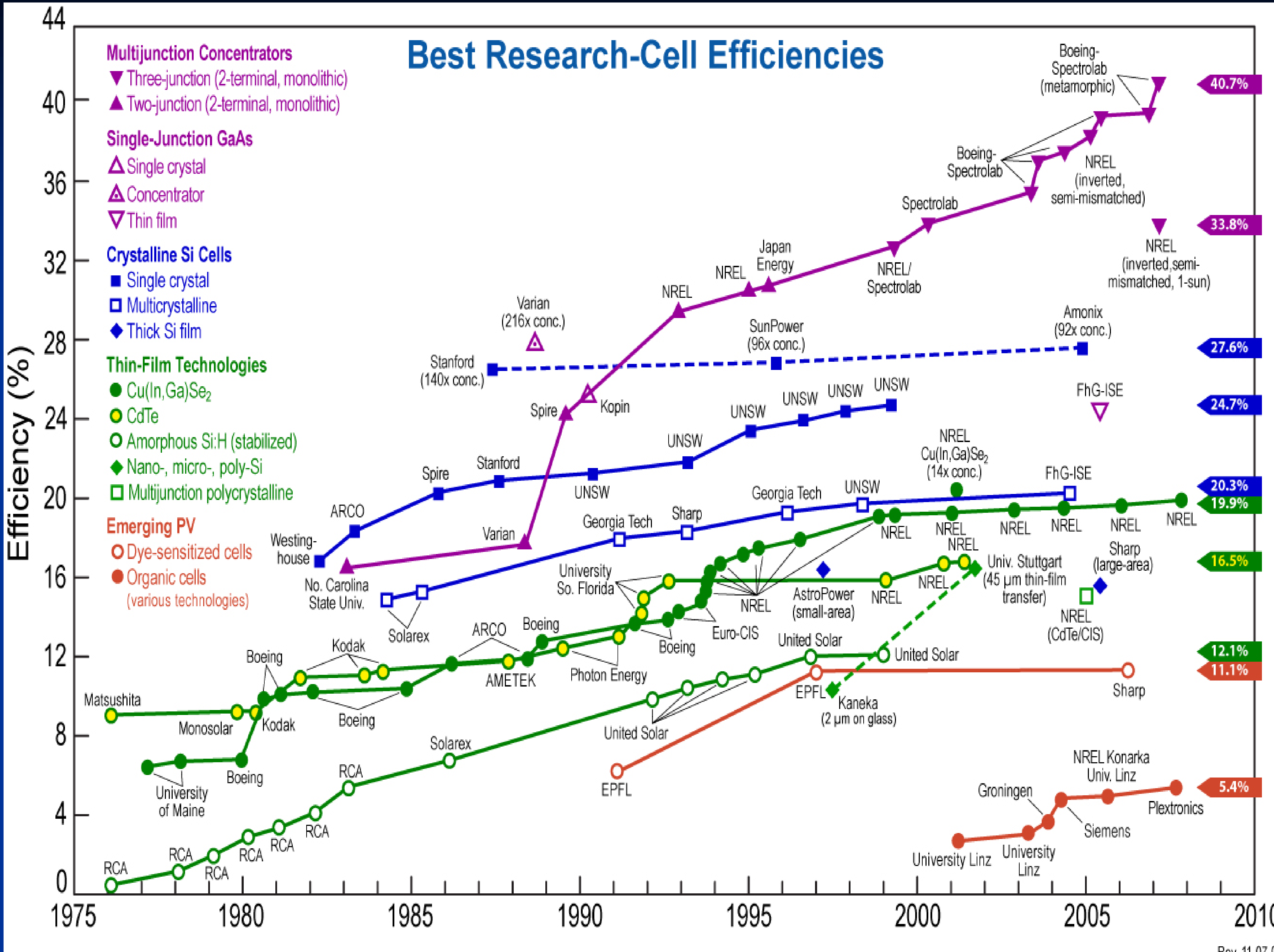
- Crystalline compound, zinc blende (cubic) crystal structure
- Direct band gap semiconductor: band gap = 1.56 eV at 300 K, strong solar cell material
- Highly usefull in making thin – film photovoltaic modules
- Alloyed with mercury: verstile IR detector material
- Alloyed with zinc: x-ray and gamma ray detector
- IR optical material for optical windows and lenses

CdTe photovoltaics

- First and only photovoltaic technology to overtake silicon in cheapness

Since the beginning: the dominant solar cell technology has been based on crystalline Si

- Research in CdTe: late 1950s
- Band gap: around 1.5 eV, perfect match to distribution of photons in the solar spectrum
- 1960s: simple heterojunctions, p-type CdTe + n – type CdS



Best Research-Cell Efficiencies
Efficiency (%)
Multijunction Concentrators
Three-junction (2-terminal, monolithic)
Two-junction (2-terminal, monolithic)
Single-Junction GaAs
Single crystal
Concentrator
Thin film
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells
(various technologies)
Boeing-Spectrolab (metamorphic)
Boeing-Spectrolab
NREL (inverted, semi-mismatched)
Spectrolab
NREL (inverted, semi-mismatched, 1-sun)
NREL/Spectrolab
Japan Energy
NREL
Varian (216x conc.)
Stanford (140x conc.)
SunPower (96x conc.)
Amonix (92x conc.)
FhG-ISE
Spire
Kopin
Varian
UNSW
Stanford
ARCO
Westing-house
No. Carolina State Univ.
Georgia Tech
Sharp
NREL Cu(In,Ga)Se2 (14x conc.)
University So. Florida
AstroPower (small-area)
Univ. Stuttgart (45 µm thin-film transfer)
Sharp (large-area)
NREL (CdTe/CIS)
Euro-CIS
Boeing
Photon Energy
AMETEK
Solarex
Kodak
Matsushita
Monosolar
University of Maine
RCA
United Solar
EPFL
Kaneka (2 µm on glass)
Sharp
NREL Konarka Univ. Linz
Groningen
Siemens
Plextronics
University Linz
40.7%
33.8%
27.6%
24.7%
20.3%
19.9%
16.5%
12.1%
11.1%
5.4%
0 4 8 12 16 20 24 28 32 36 40 44
1975 1980 1985 1990 1995 2000 2005 2010
Rev. 11-07-07

Main concerns connected with CdTe cells

Te supply:

- Recently 800 t / year
- Coproduct with Cu production
- Few uses – few exploration (new places in China)

Toxcicity of Cd:

- CdTe is toxic, but only if ingested or inhaled
- Securely encapsulated, can be rendered harmless
- Recycling of modules at the end of their lifetime
- More environmental friendly than any other use of Cd

Classical methods of synthesis

- Solid – state reactions
- Reaction between aqueous solutions of Cd - salts and gaseous H_2S / H_2Se
  - In the past: gravimetric analysis of cadmium: using gaseous, highly toxic reactant!
- Pyrolysis
- CdS thin films: from Cd – salts and thiourea or from volatile Cd - alkyls
- CdSe: preparation of bulk material by high pressure vertical zone melting

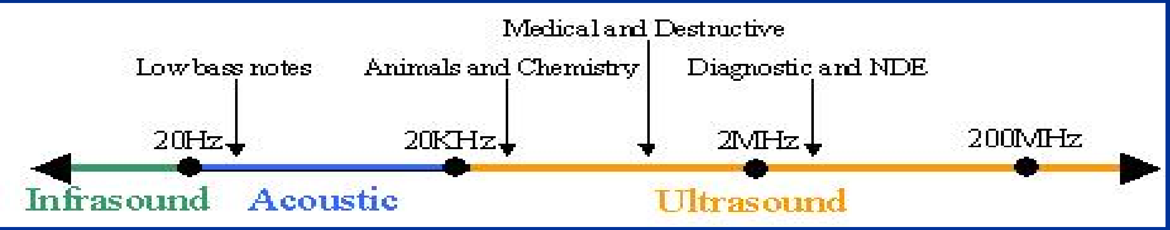
Modern methods for the synthesis of cadmium chalcogenides

- Safer, avoiding toxic reactants
- Milder reaction condidtions → easier to control

- Reverse (inverse) micells method
- Microwave synthesis
- Synthesis in liquid ammonia (amorphous product!)
- Bacterial biosynthesis
- Mechanochemial method (mechanical alloying, high – energy milling)

Basic principles of sonochemical reactions

- Ultrasound: cyclic sound pressure with fequencies between 20 kHz and 10 MHz



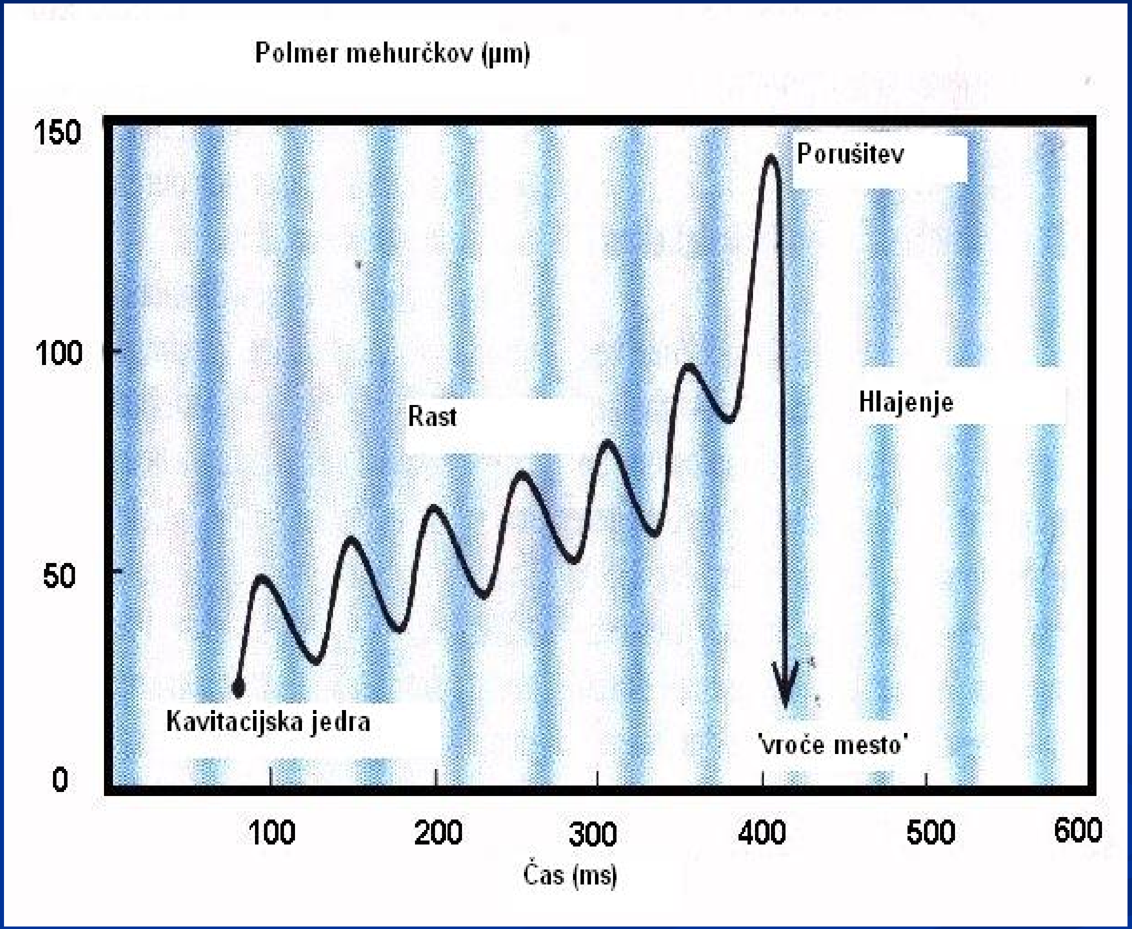
- Effect of ultrasound to molecules: indirect, most probable through the mechanism called **acoustic cavitation**: formation, growth and implosive collapse of gas/vapour bubbles inside the liquid
- Extreme conditions at the collapse[1] ('hot – spot') :

$$T > 5000^0C, P > 2000 \text{ bar}, \Delta T / \Delta t \approx 10^9 \text{ K/s}$$

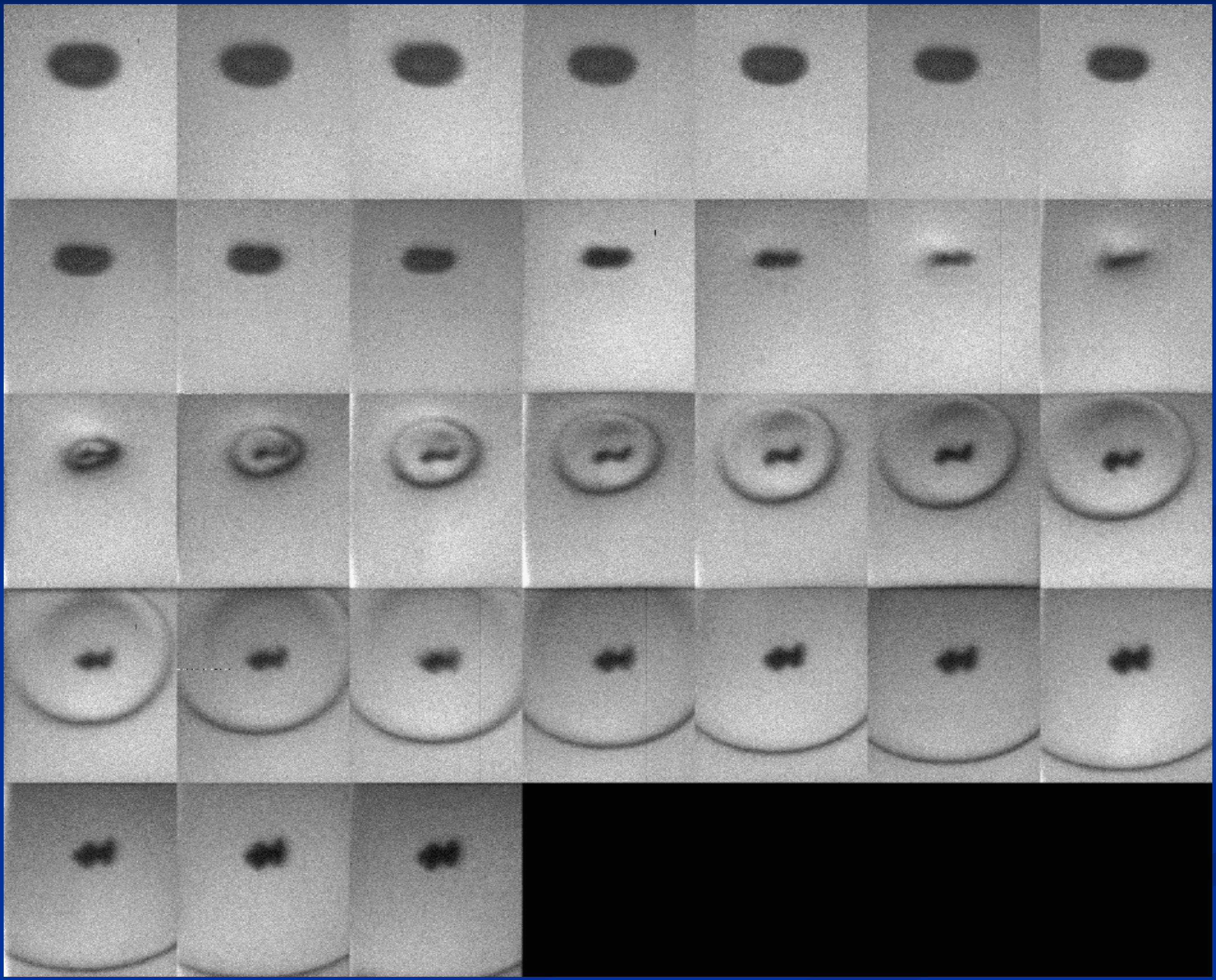
1: K. S. Suslick, Science 247 (1990), 1439

Bubble dynamics inside a liquid

- Formation, growth and implosive collapse of gas bubbles inside a liquid

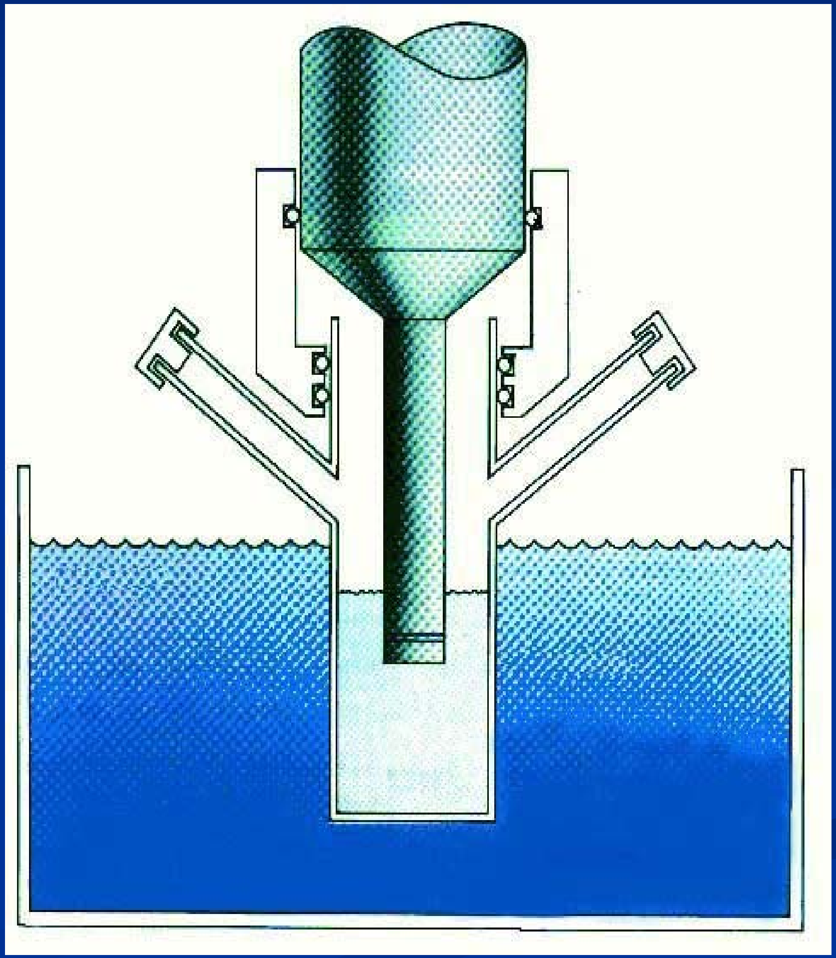


Photograph of a collapsing bubble during acoustic cavitation, 20 million frames / s



Used ultrasonisc system:

- Sonics & Materials VCX 750
- 1.25 cm^2 Ti – probe
- 20 KHz
- 100 W/cm^2
- 50 mL beaker



Conclusion:

- Simple sonochemical methods, suitable for preparation of semiconducting CdS and CdSe
- Nanocrystalline particles with average particle size 4,54 – 9,66 nm
- Confirmation by X – ray powder diffraction, electrone microscopy and EDS
- Detailed thermal analysis in air and N_2 flow
- Further investigations underway: attempt to prepare **CdTe** nanoparticles in similar way!

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