MATERIALS SYNTHESIS

Bulk Materials

- ***Solid state synthesis – "shake & bake"***
- ***Chemical vapor transport***
- ***Sol Gel Synthesis***
- ***Melt growth***

Thin Films

- ***Chemical Vapor Deposition***
- ***Laser Ablation***
- ***Sputtering***
- ***Molecular Beam Epitaxy***

Nanomaterials

- ***Nanocrystals***
- ***Carbon Nanotubes***
- ***Nanowires***

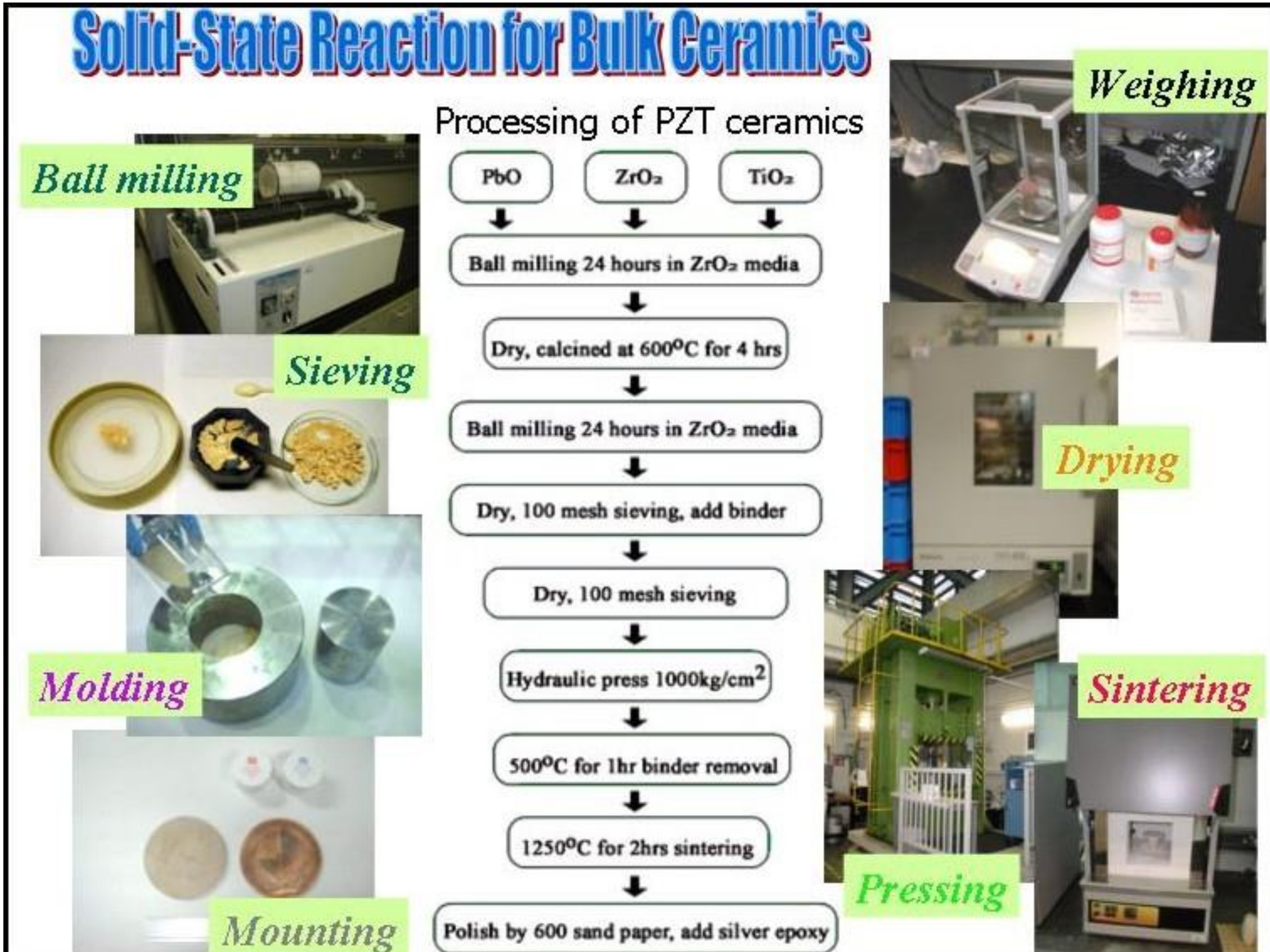
Just a few of the huge number of different methods!

Reading: West 4

SOLID STATE SYNTHESIS

Mix starting materials, heat, compress …. presto!

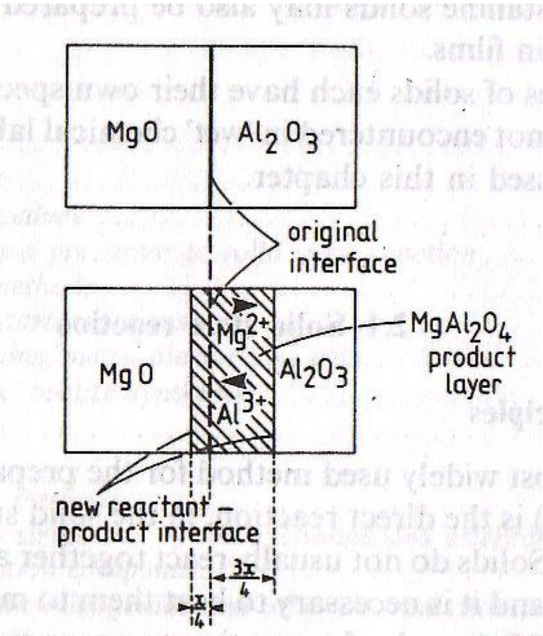
- Historically the most common method to make polycrystalline samples.



SOLID STATE SYNTHESIS

relies on enhanced solid-state diffusion at high temps.

$$4MgO + 4Al_2O_3 \rightarrow 4MgAl_2O_4$$



at $MgO/MgAl_2O_4$ interface:

$$2Al^{3+} - 3Mg^{2+} + 4MgO \rightarrow MgAl_2O_4$$

at $Al_2O_3/MgAl_2O_4$ interface:

$$3Mg^{2+} - 2Al^{3+} + 4Al_2O_3 \rightarrow 3MgAl_2O_4$$

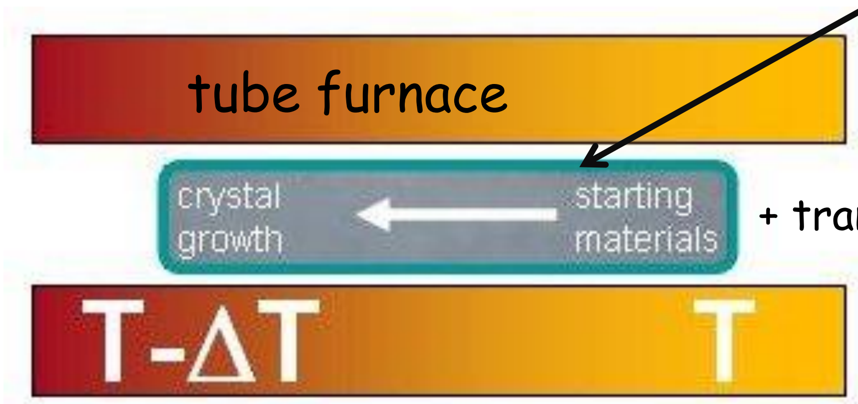
factors:
1. area of contact between the reacting solids
2. the rate of nucleation of the product phase
3. the rates of ion diffusion through the various phases

CHEMICAL VAPOR TRANSPORT (CVT)

Crystal growth by the thermal transport of volatile compounds generated from nonvolatile elements or compounds.

- Popularized by Schafer (1971).

sealed quartz tube



+ transport agent (often I_2)

$$Ti + S_2 \longrightarrow TiS_2$$

$$Ti(s) + 2I_2(g) \rightleftarrows TiI_4(g)$$

$$TiI_4(g) + S_2(g) \longrightarrow TiS_2(s) + 2I_2(g)$$

1. synthesis of new compounds
2. growth of large single crystals
3. purification of compounds

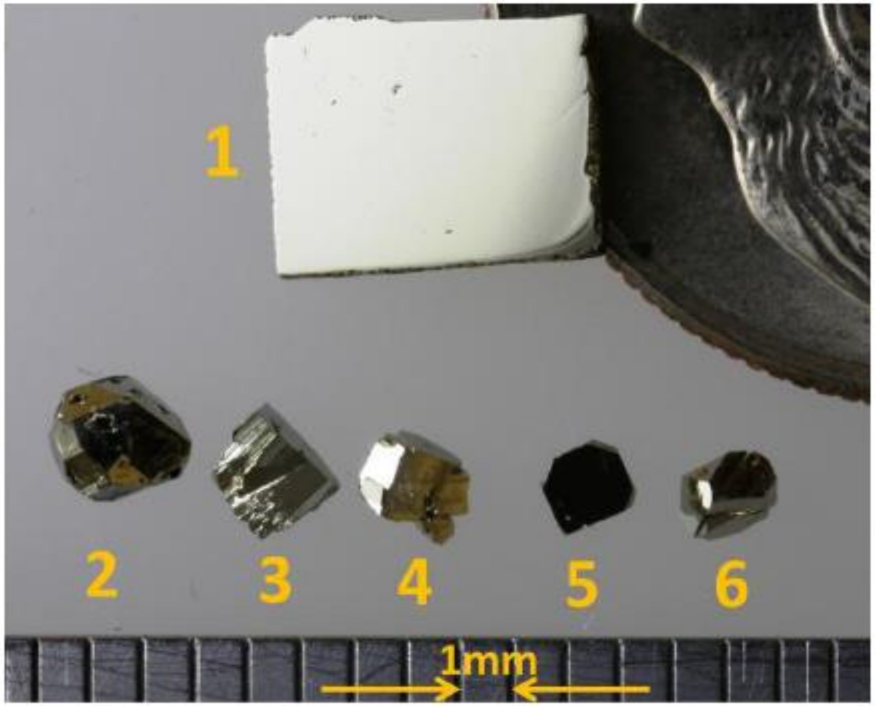
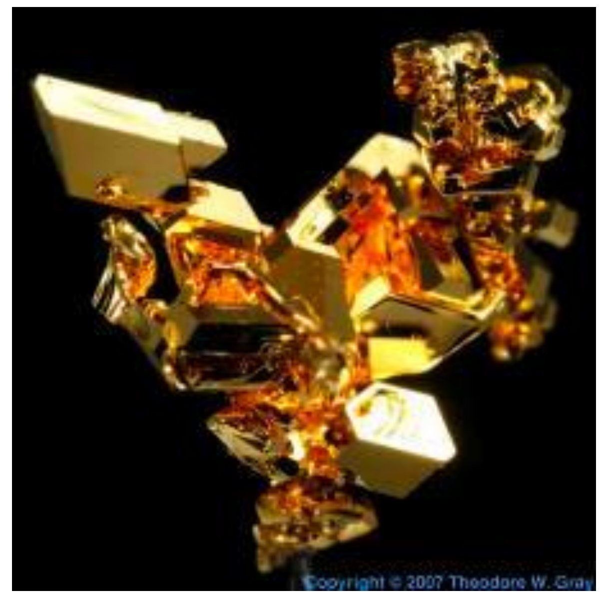


Figure 1: Pyrite crystals used in preliminary studies: Slice from natural crystal, polished to atomic flatness (1), synthetic crystals from flux growth (2) and chemical vapor transport (3-6).

Ti (using I_2)



Au (using I_2)

Typical transporting agents include:
I_2, Br_2, Cl_2, HCl, NH_4Cl, H_2, H_2O, $TeCl_4$, $AlCl_3$, CO, S_2

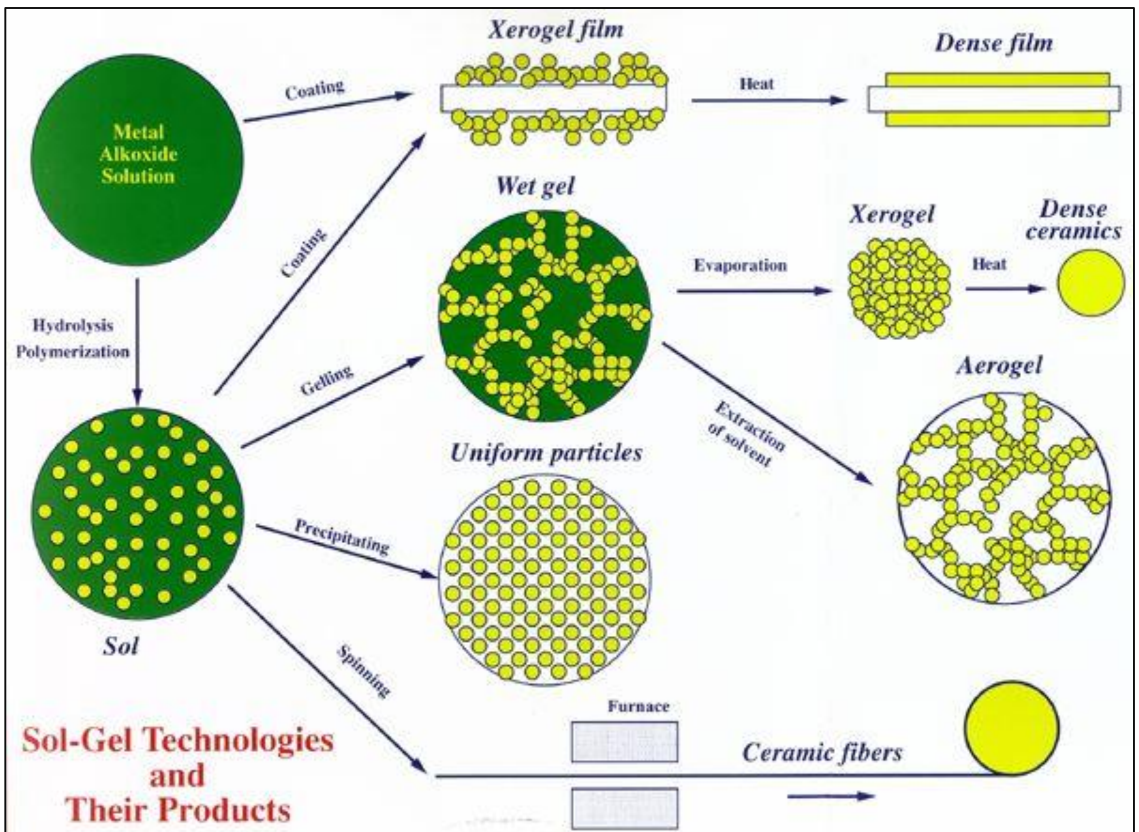
SOL GEL (solution-gelation) PROCESS

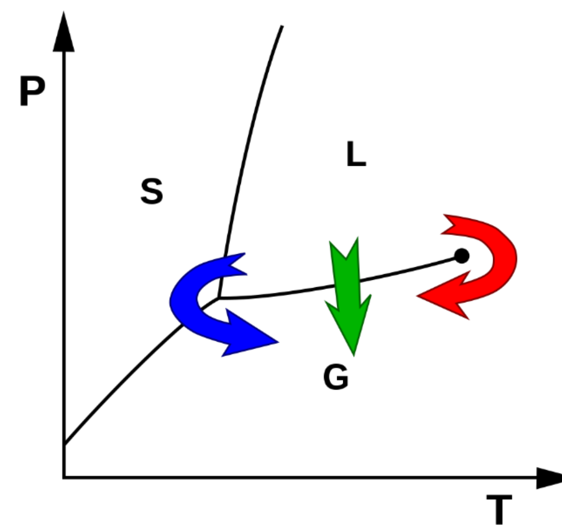
Low-temp, solution phase method that uses hydrolysis and polycondensation reactions to form an inorganic network solid.

- *makes ceramic and glassy materials, usually from $M(OR)_x$ solutions.*

$$M\text{-}OR + H_2O \longrightarrow M\text{-}OH + ROH \quad \text{(hydrolysis)}$$

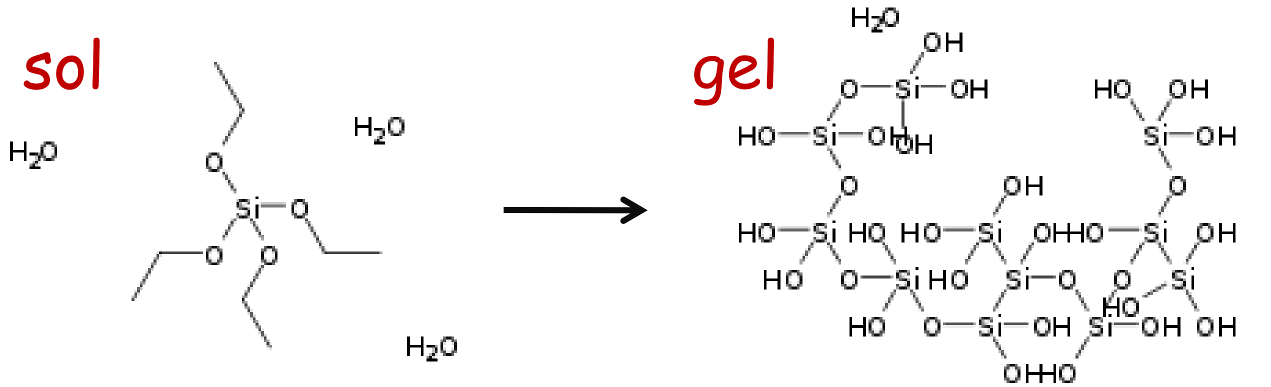
$$M\text{-}OR + M\text{-}OH \longrightarrow [M\text{-}O\text{-}M]_n + ROH \quad \text{(condensation)}$$



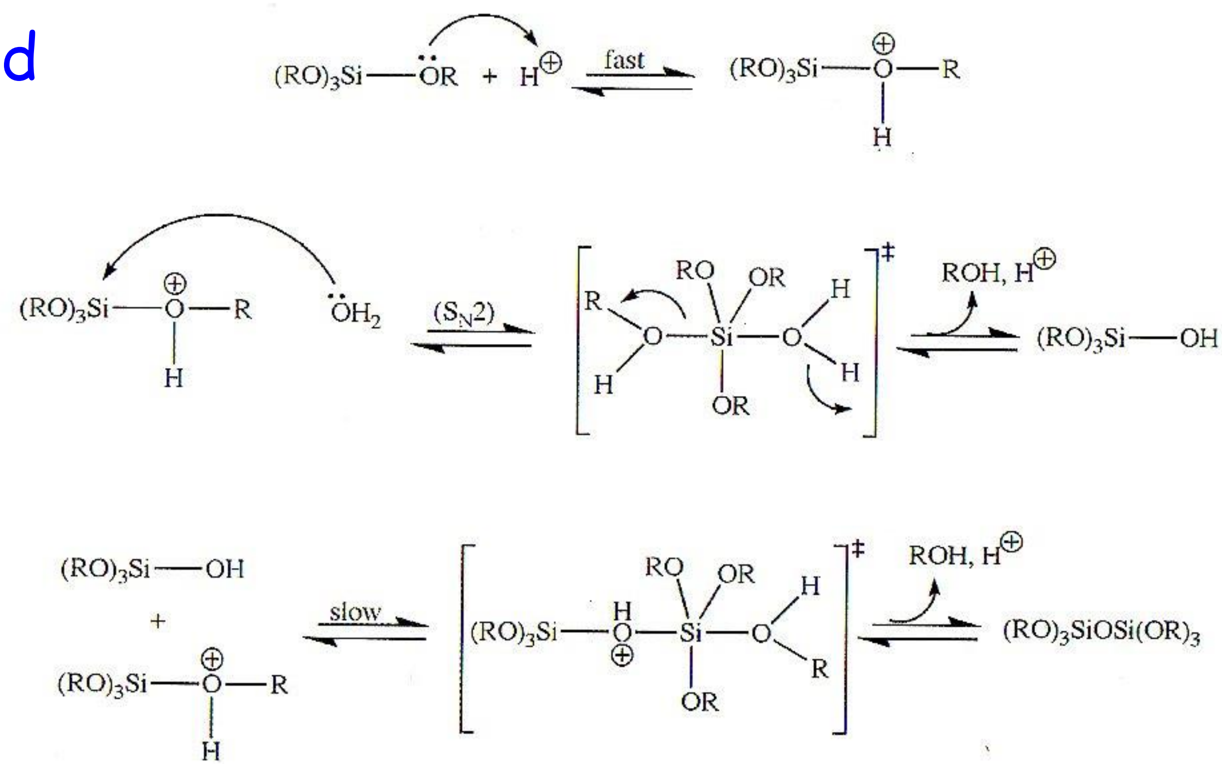


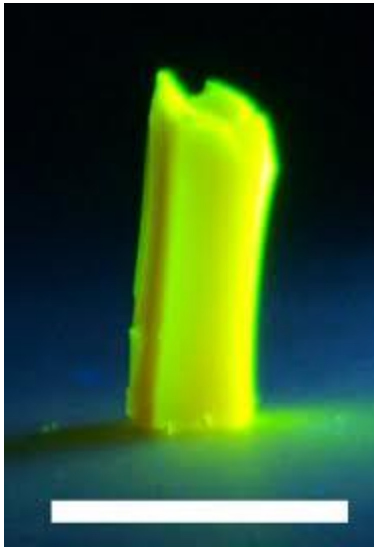
Green: normal drying
Blue: freeze drying
Red: supercritical drying

SiO_2 from tetraethyl orthosilicate (TEOS)



acid-catalyzed reaction mechanism:

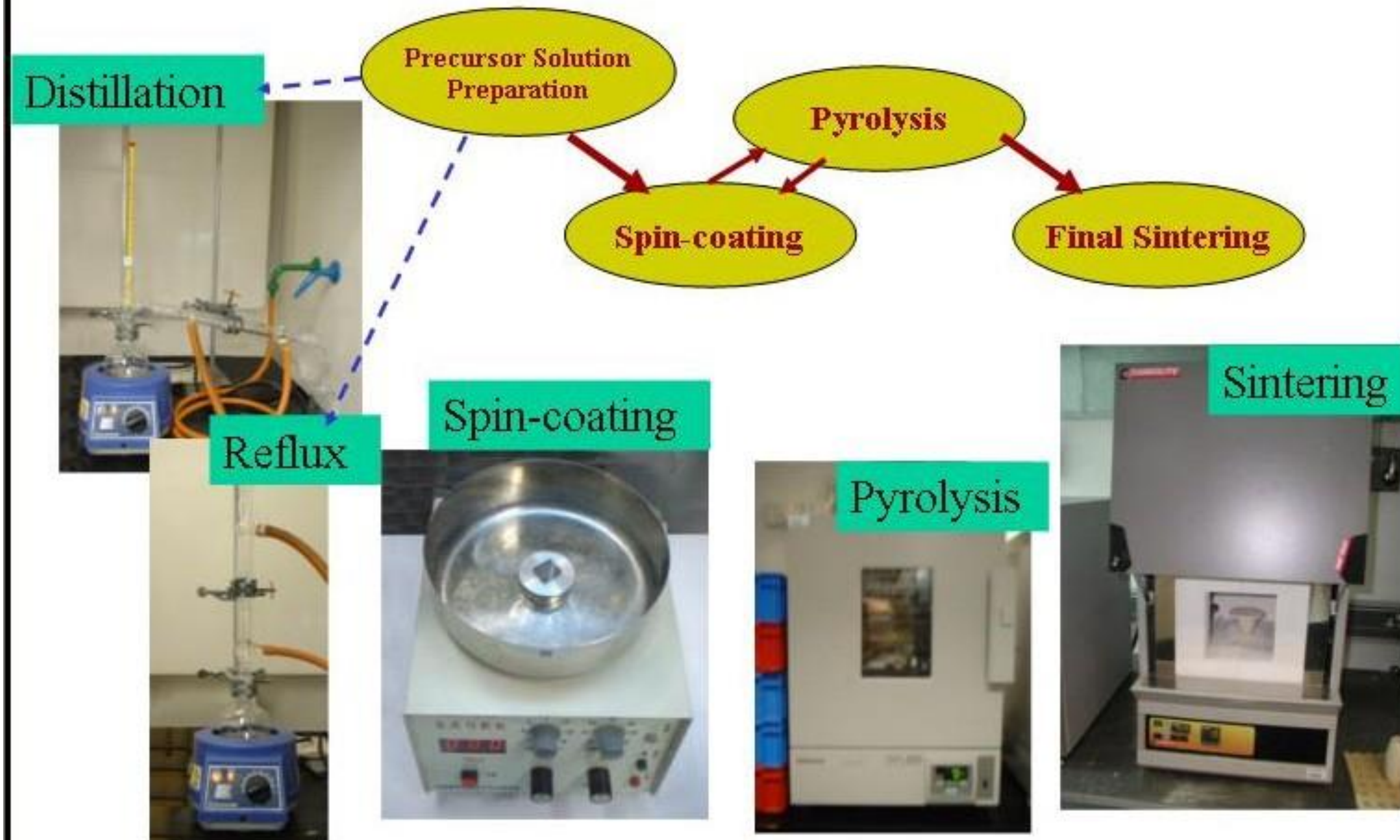




xerogel containing CdSe/CdS quantum dots

aerogel

Sol-Gel Deposition of Thin Films



MELT GROWTH

Crystallization from the liquid, without solvent.

→ Production of semiconductor grade silicon from silica (sand).

The Siemens process

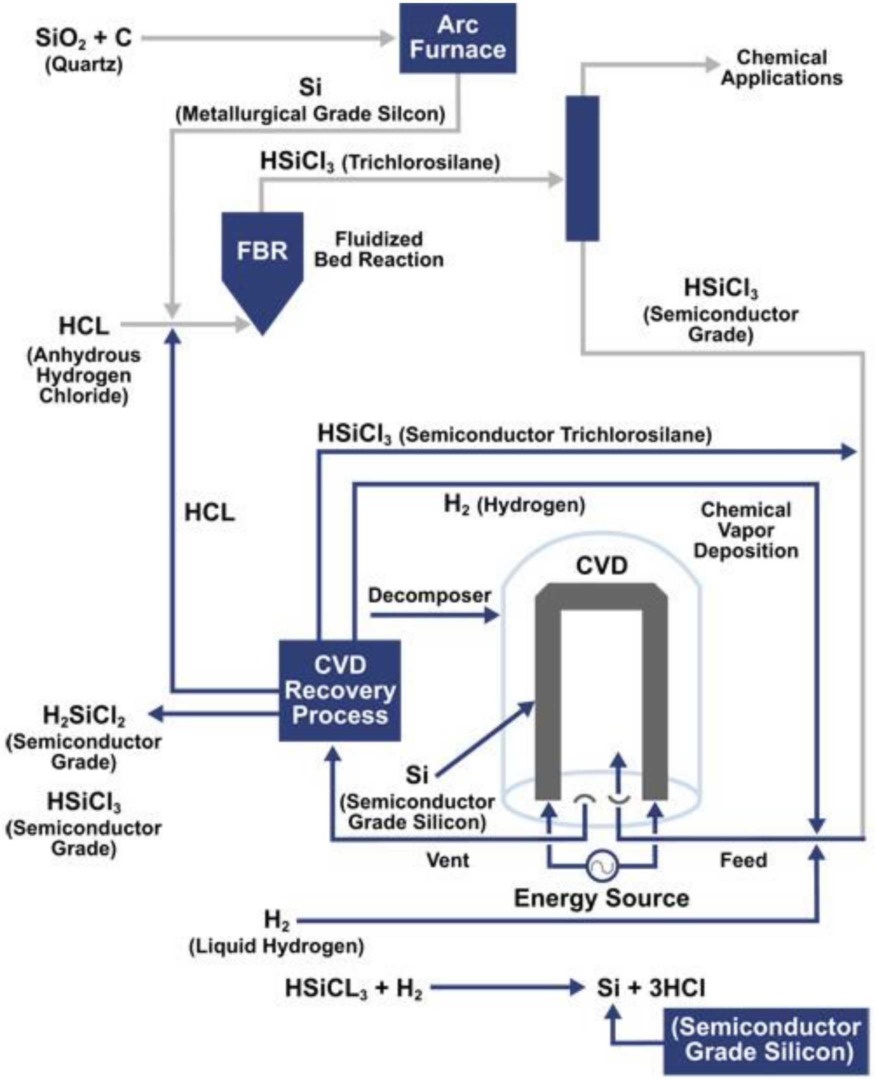
$$SiO_2 + 2C \xrightarrow{2250°C} Si + 2CO$$

98-99%
(metallurgical grade)

$$Si + 3HCl \xrightarrow{300°C} SiHCl_3 + H_2$$

$$2SiHCl_3 \xrightarrow{1150°C} Si + 2HCl + SiCl_4$$

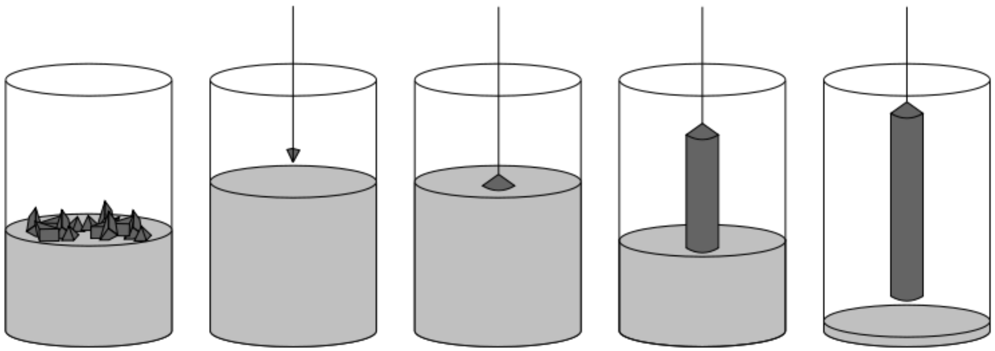
99.999999999%
(semiconductor grade)



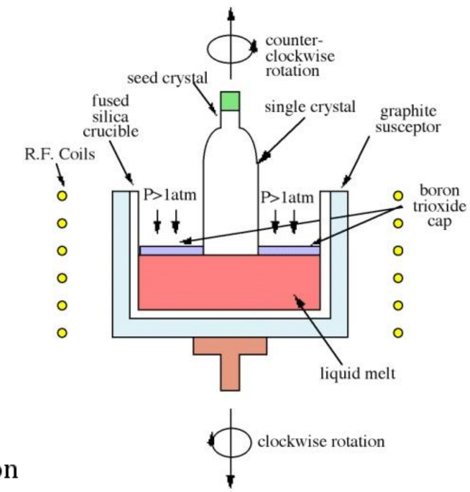
Siemens process makes
polycrystalline SG-Si

Czochralski (cho-HRAL-ski) process

makes single crystal ingots from polycrystalline SG-Si

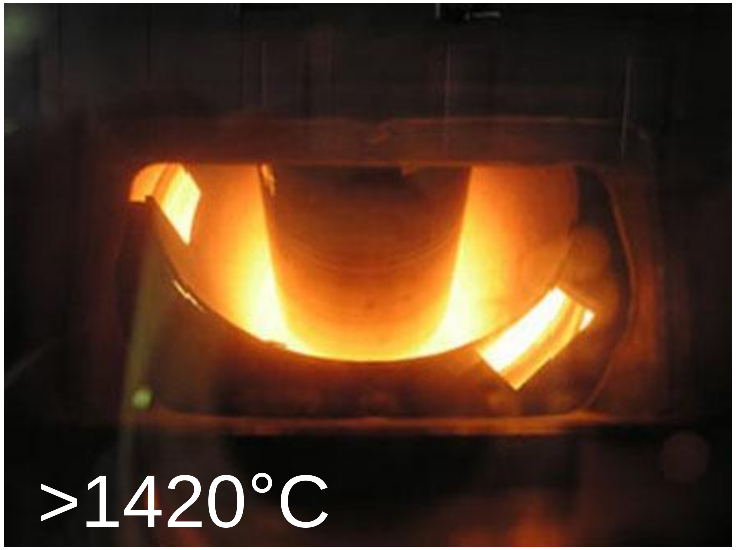


Melting of polysilicon, doping | Introduction of the seed crystal | Beginning of the crystal growth | Crystal pulling | Formed crystal with a residue of melted silicon



- good for making doped Si

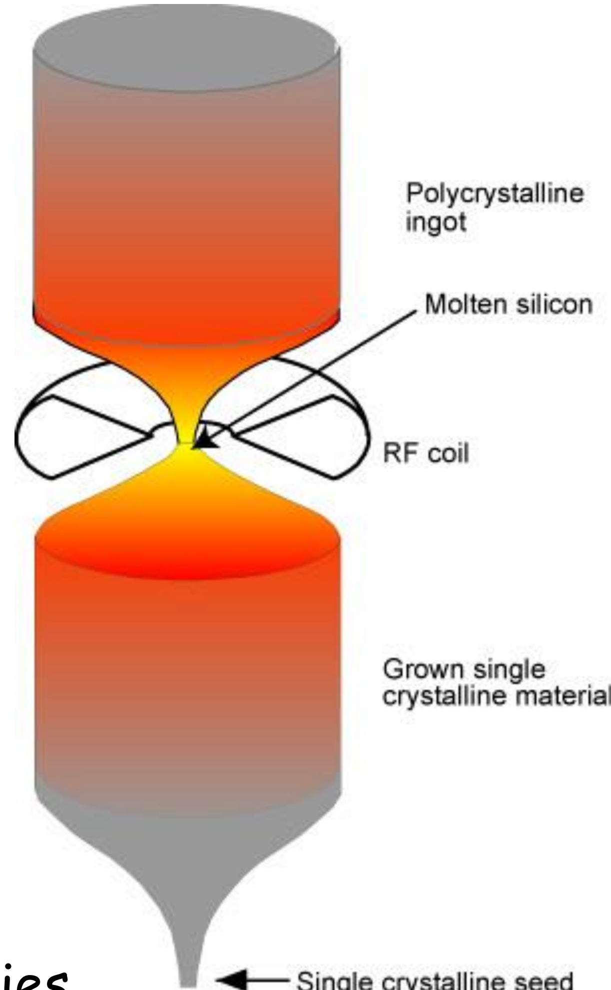
- suffers from O and C impurities from the crucible

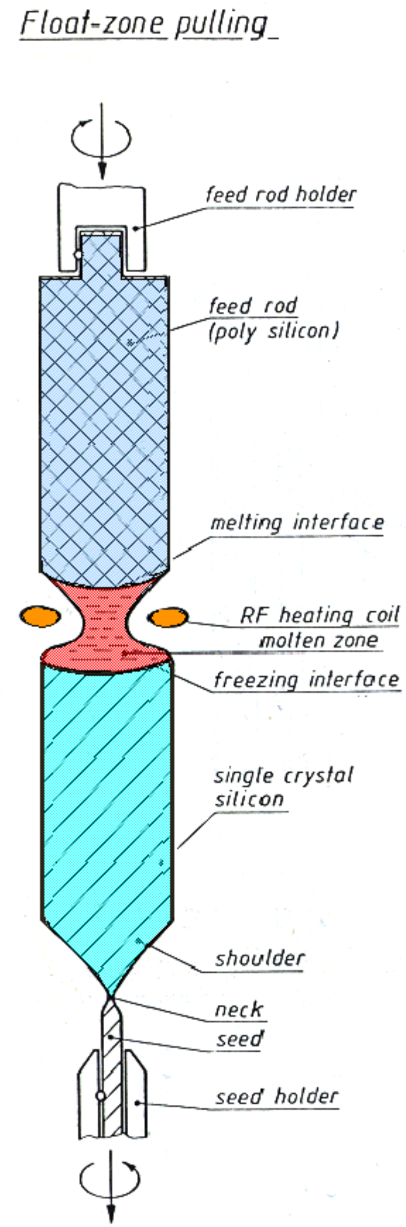


CZ-Si

Bridgman-Stockbarger and float zone techniques

makes use of the greater solubility of impurities in the melt than the crystal

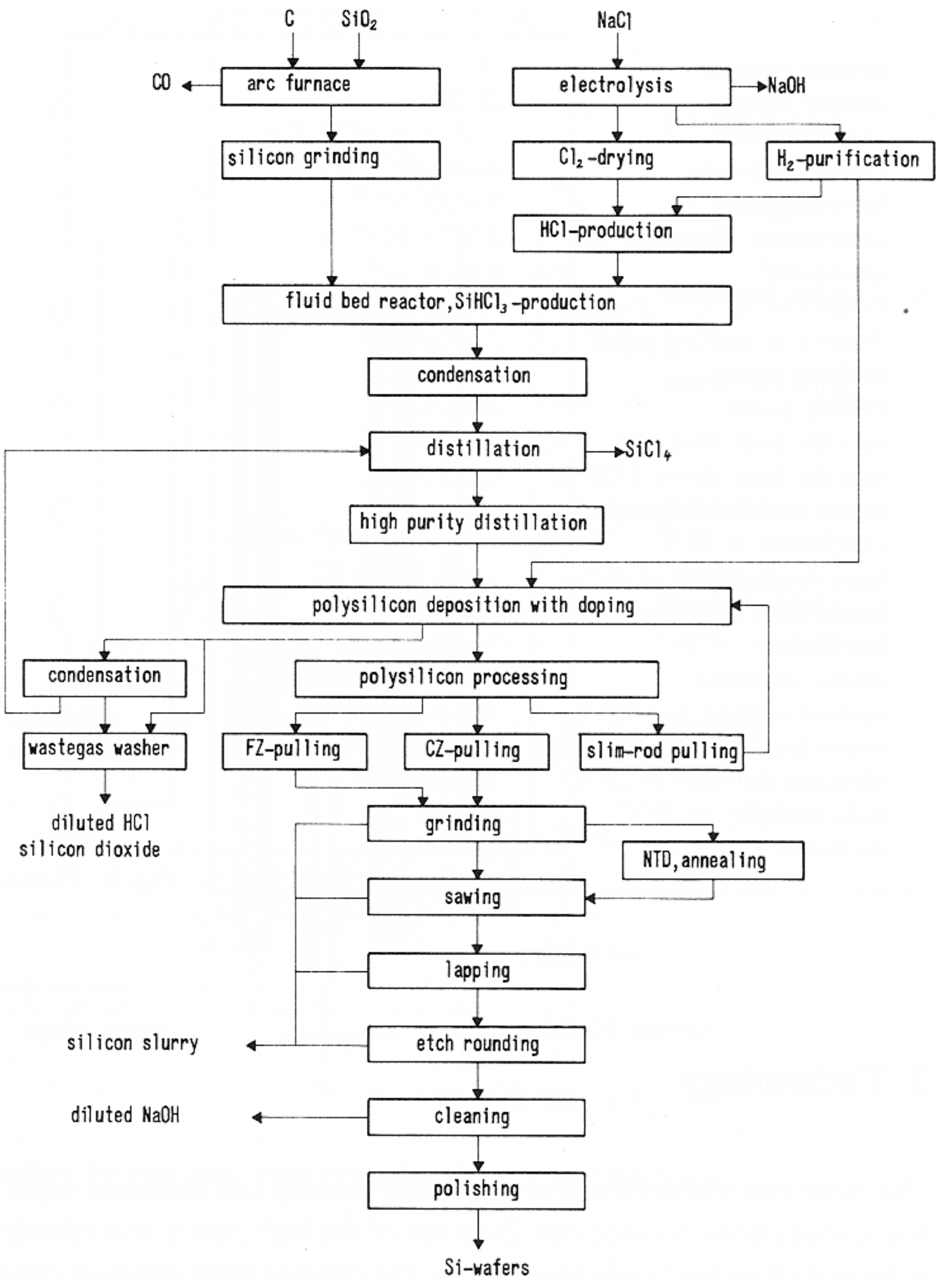


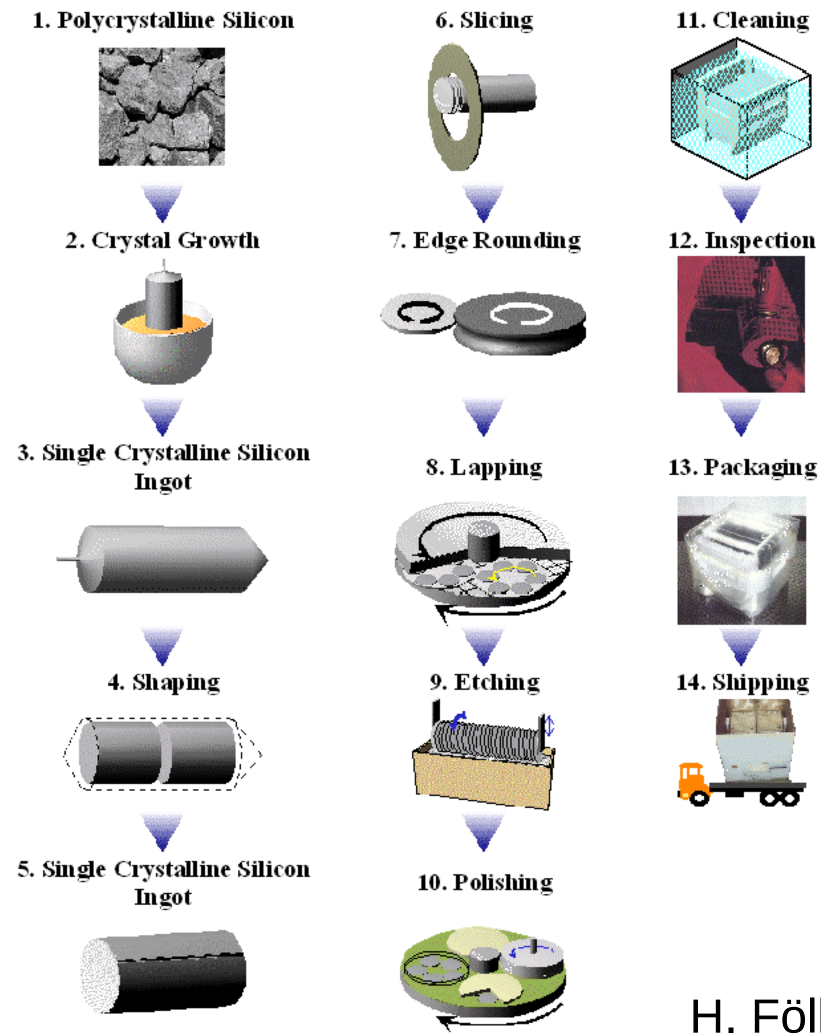


- melt touches nothing
→ fewer O and C impurities

- FZ ingots limited to ~200 mm

SAND TO SILICON



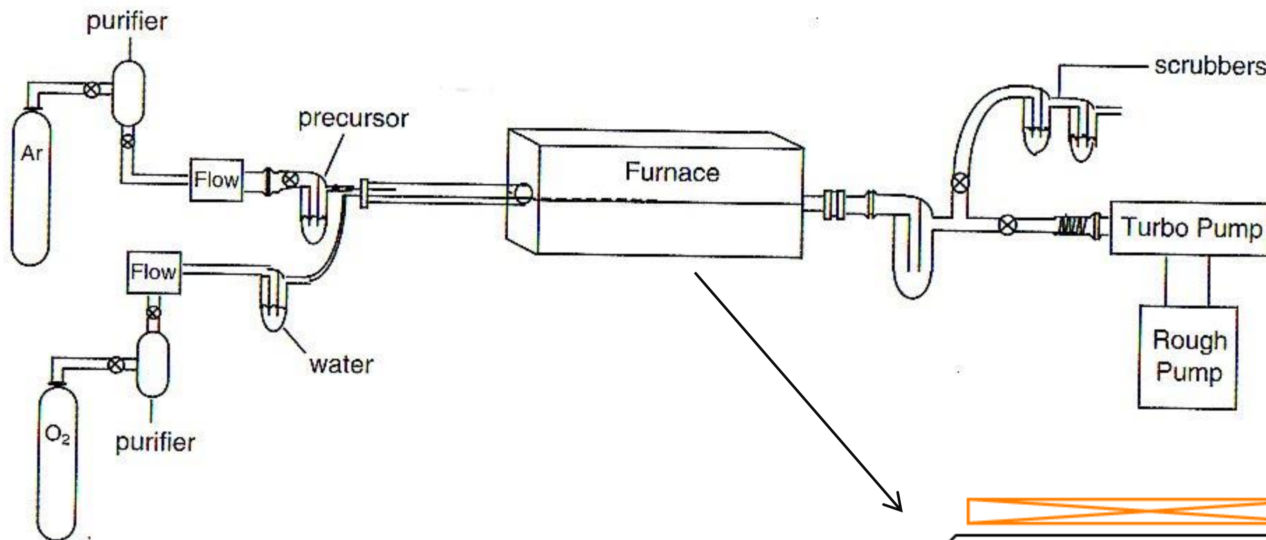


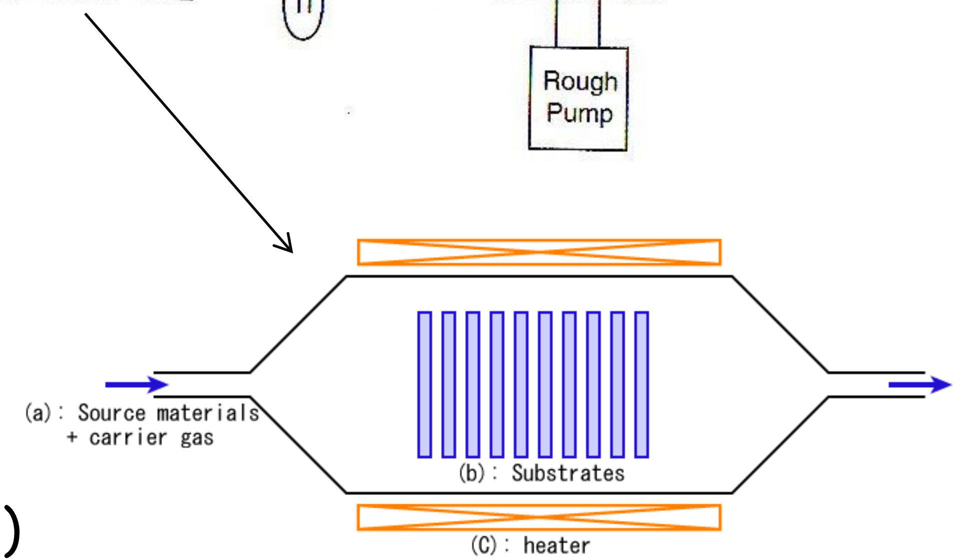
H. Föll

CHEMICAL VAPOR DEPOSITION (CVD)

Reactive thermolysis of volatile molecular precursors to grow a thin film layer.

a hot wall low-pressure CVD (LP-CVD) reactor:





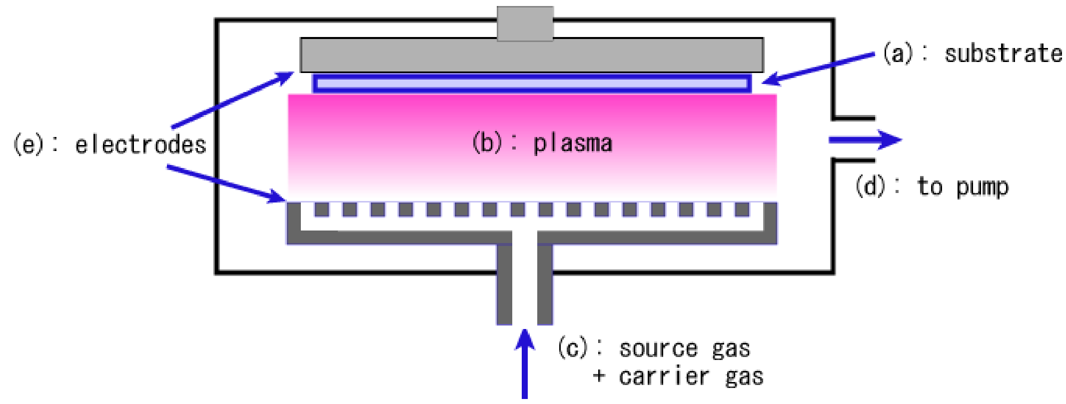
- metals
- alloys
- oxides, nitrides, carbides
- semiconductors (III-V, II-VI)
- carbon (even diamond!)
- many others

TYPES OF CVD

by reactor type:

- hot wall
- cold wall

plasma system



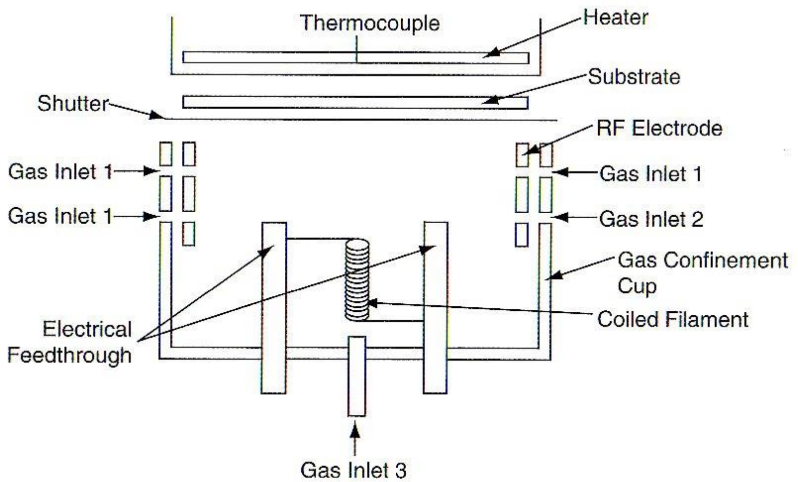
by pressure:

- atmospheric pressure CVD (AP-CVD)
- LP-CVD >10^{-6} Torr
- ultrahigh vacuum (UHV-CVD) <10^{-8} Torr

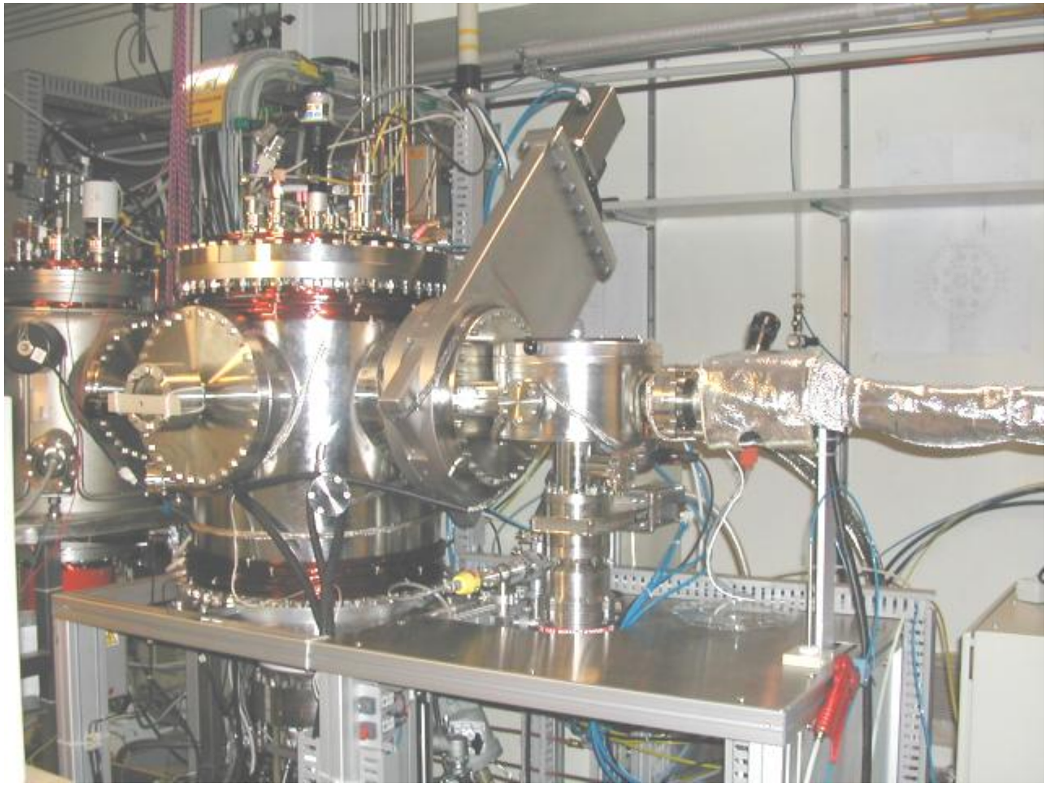
by precursor degradation method:

- plasma enhanced CVD (PE-CVD)
- laser-assisted CVD (LA-CVD)
- hot-wire CVD (HW-CVD)

hot wire system

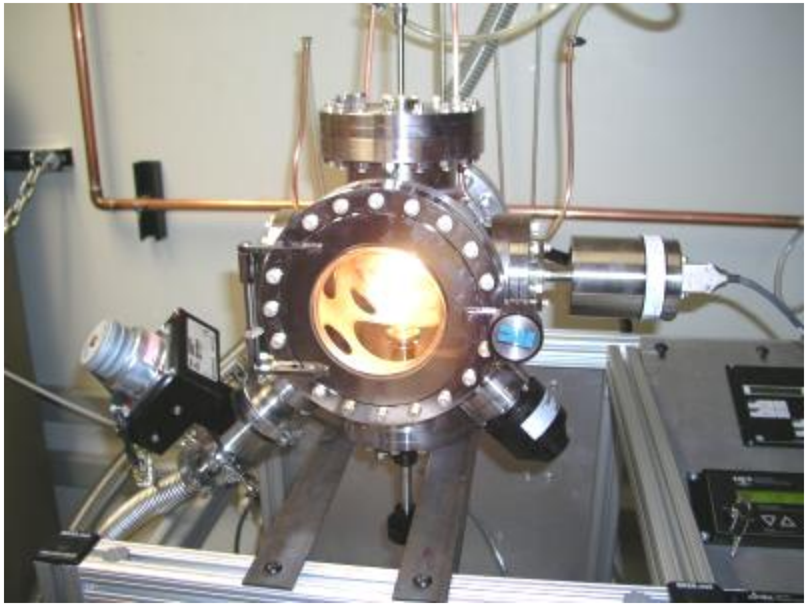


PE-CVD for SiGe growth



Danny Chrastina

Hot wire CVD for a-Si



EXAMPLES

polysilicon

$SiH_4 \rightarrow Si + 2H_2$ LP-CVD, 600-1000°C, 10-100s of nm min^{-1}

silicon nitride (Si_3N_4)

$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$ LP-CVD, 600-800°C, 10s of nm min^{-1}

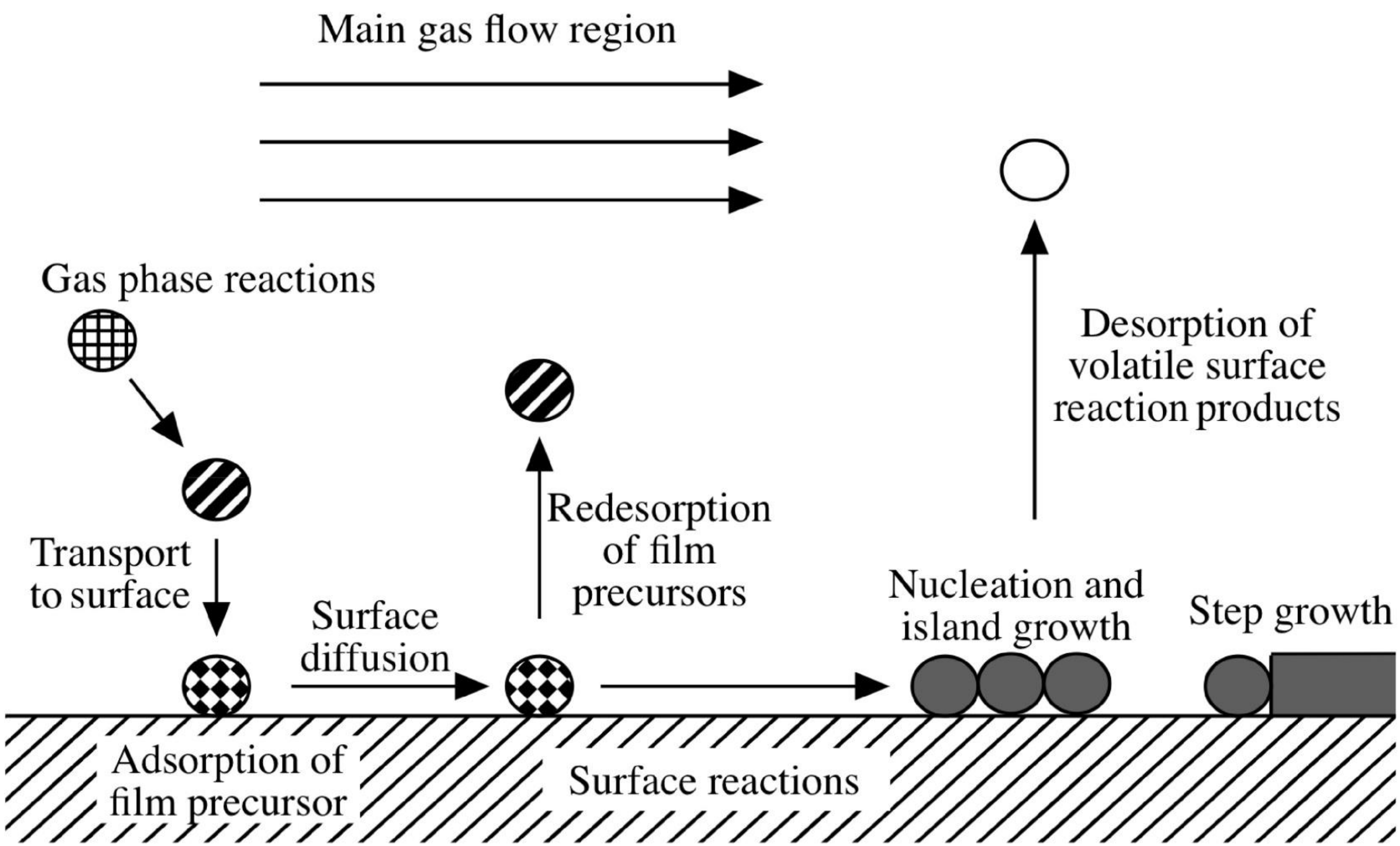
gallium arsenide (GaAs)

$Ga(Me)_3 + AsH_3 \rightarrow GaAs + 3CH_4$ LP-CVD, 400-800°C in H_2 carrier gas

- example of metal organic CVD (MO-CVD)

IMPORTANT STEPS IN CVD

physisorption, chemisorption → reaction → nucleation → growth



GaAs: Overall Reaction Pathway (350-500°C)

$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3$	(low energy, gas phase)

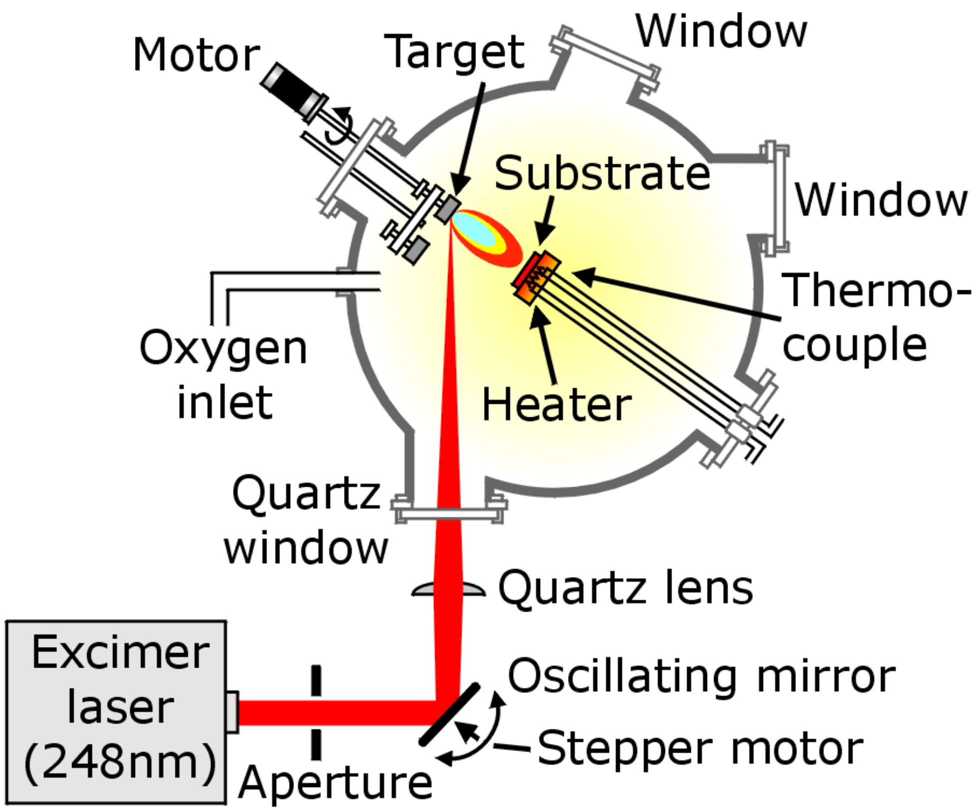
$Ga(CH_3)_2 \rightarrow GaCH_3 + CH_3$	(gas/surface)
$GaCH_3 \rightarrow Ga + CH_3$	(surface)
$Ga(CH_3)_2 \rightarrow Ga + H_3C\text{-}CH_3$	(reductive elimination)

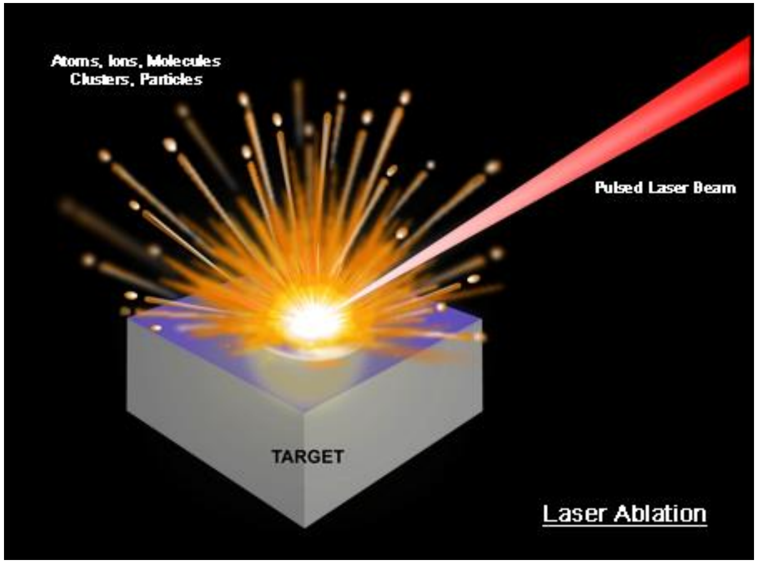
$AsH_3 \rightarrow AsH_2$	
$AsH_2 \rightarrow HAs + H$	(surface)
$HAs \rightarrow As + H$	(surface)

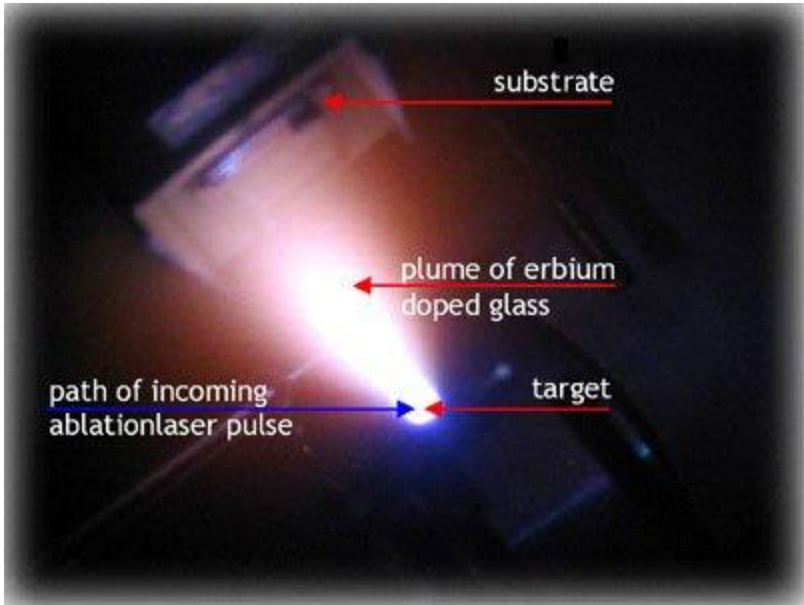
$H + CH_3 \rightarrow CH_4$	(surface)

PULSED LASER DEPOSITION (PLD)

Stoichiometric mass transfer by ablation of a solid target using a pulsed laser in HV or UHV.

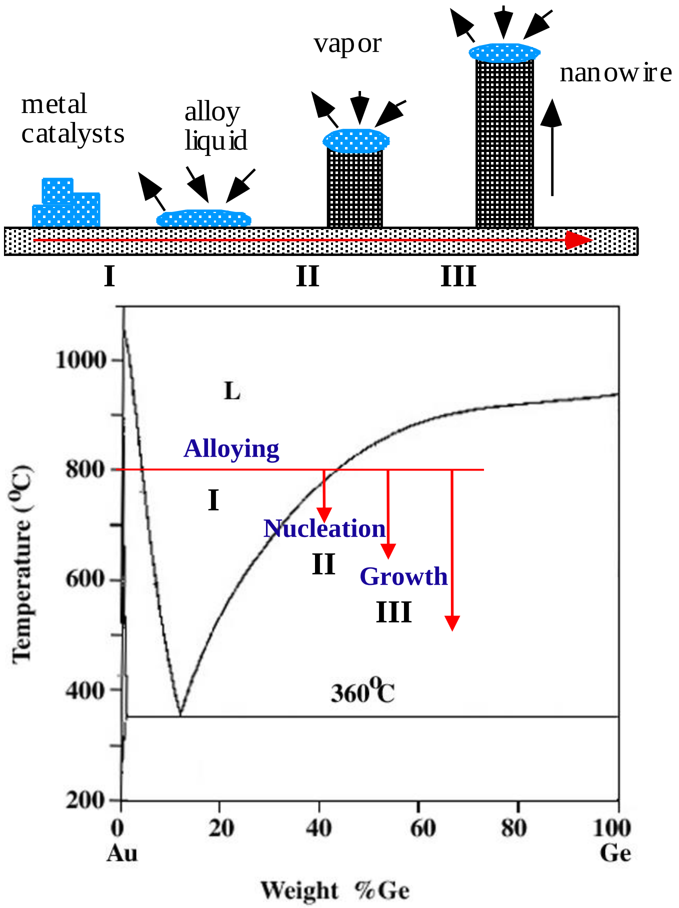




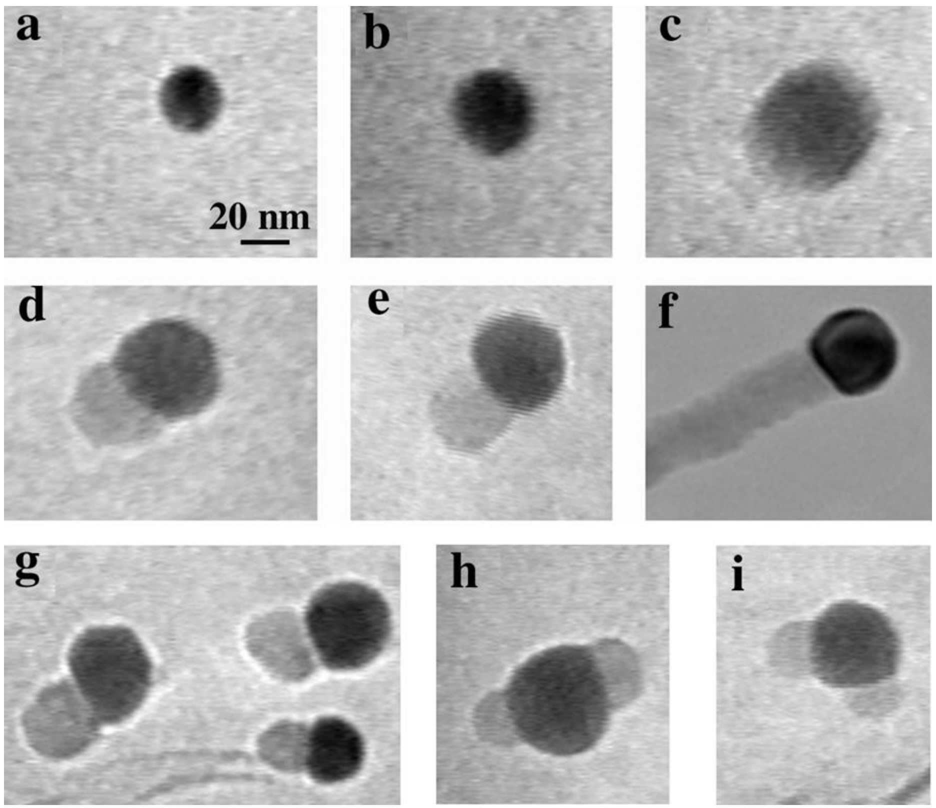


good for materials of complex stoichiometry

Vapor-Liquid-Solid Nanowire Growth

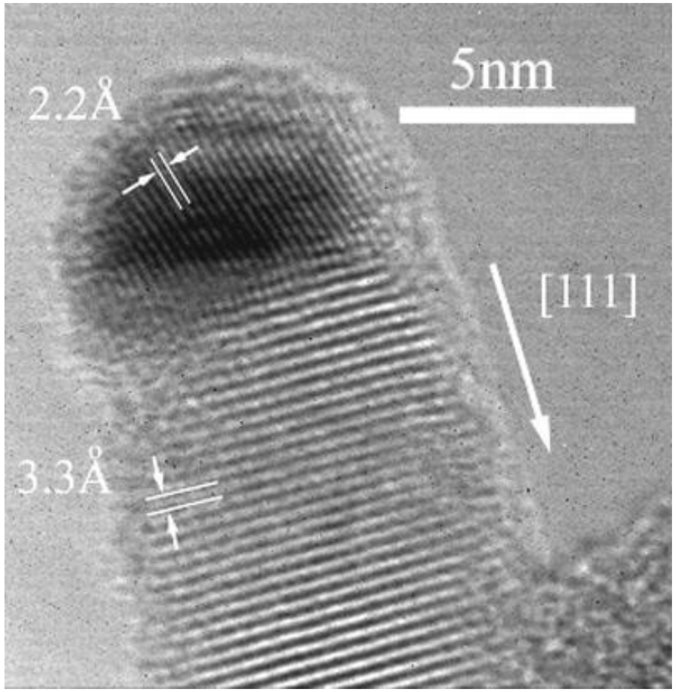


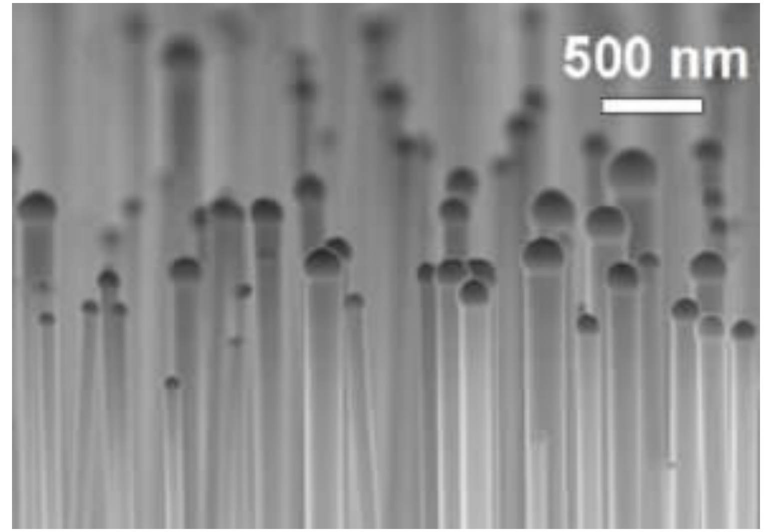
800 deg. In-situ TEM

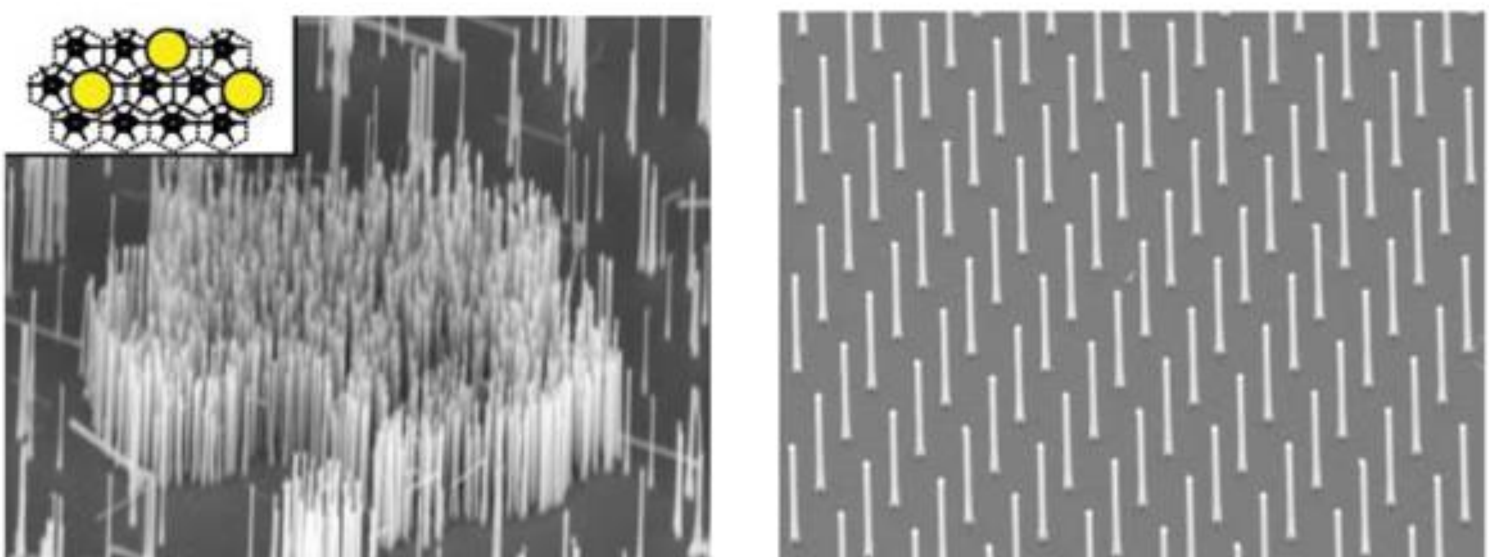


Unidirectional growth is the consequence of an anisotropy in solid-liquid interfacial energy.

Y. Wu et al. *J. Am. Chem. Soc*. **2001**, *123*, 3165







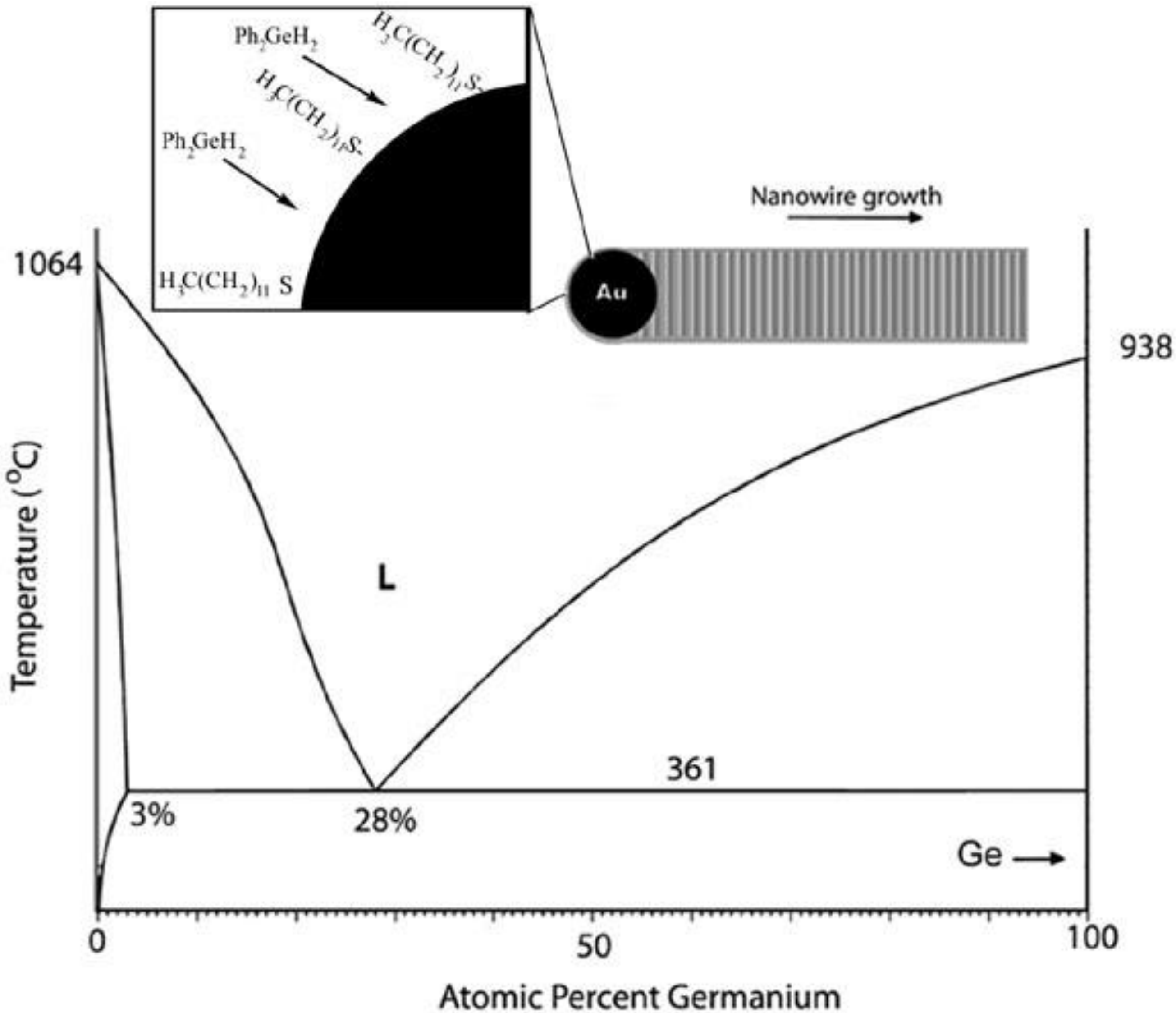
a b

Nanowires grown by PLD

Table 1. Summary of single crystal nanowires synthesized. The growth temperatures correspond to ranges explored in these studies. The minimum and average nanowire diameters were determined from TEM and FE-SEM images. Structures were determined using electron diffraction and lattice resolved TEM imaging: ZB, zinc blende; W, wurtzite; and D, diamond structure types. Compositions were determined from EDX measurements made on individual nanowires. All of the nanowires were synthesized using Au as the catalyst, except GaAs, for which Ag and Cu were also used. The GaAs nanowires obtained with Ag and Cu catalysts have the same size distribution, structure, and composition as those obtained with the Au catalyst.

Material	Growth Temperature [°C]	Minimum Diameter [nm]	Average Diameter [nm]	Structure	Growth Direction	Ratio of Components
GaAs	800–1030	3	19	ZB	<111>	1.00 : 0.97
GaP	870–900	3–5	26	ZB	<111>	1.00 : 0.98
$GaAs_{0.6}P_{0.4}$	800–900	4	18	ZB	<111>	1.00 : 0.58 : 0.41
InP	790–830	3–5	25	ZB	<111>	1.00 : 0.98
InAs	700–800	3–5	11	ZB	<111>	1.00 : 1.19
$InAs_{0.5}P_{0.5}$	780–900	3–5	20	ZB	<111>	1.00 : 0.51 : 0.51
ZnS	990–1050	4–6	30	ZB	<111>	1.00 : 1.08
ZnSe	900–950	3–5	19	ZB	<111>	1.00 : 1.01
CdS	790–870	3–5	20	W	<100>, <002>	1.00 : 1.04
CdSe	680–1000	3–5	16	W	<110>	1.00 : 0.99
$Si_{1-x}Ge_x$	820–1150	3–5	18	D	<111>	$Si_{1-x}Ge_x$

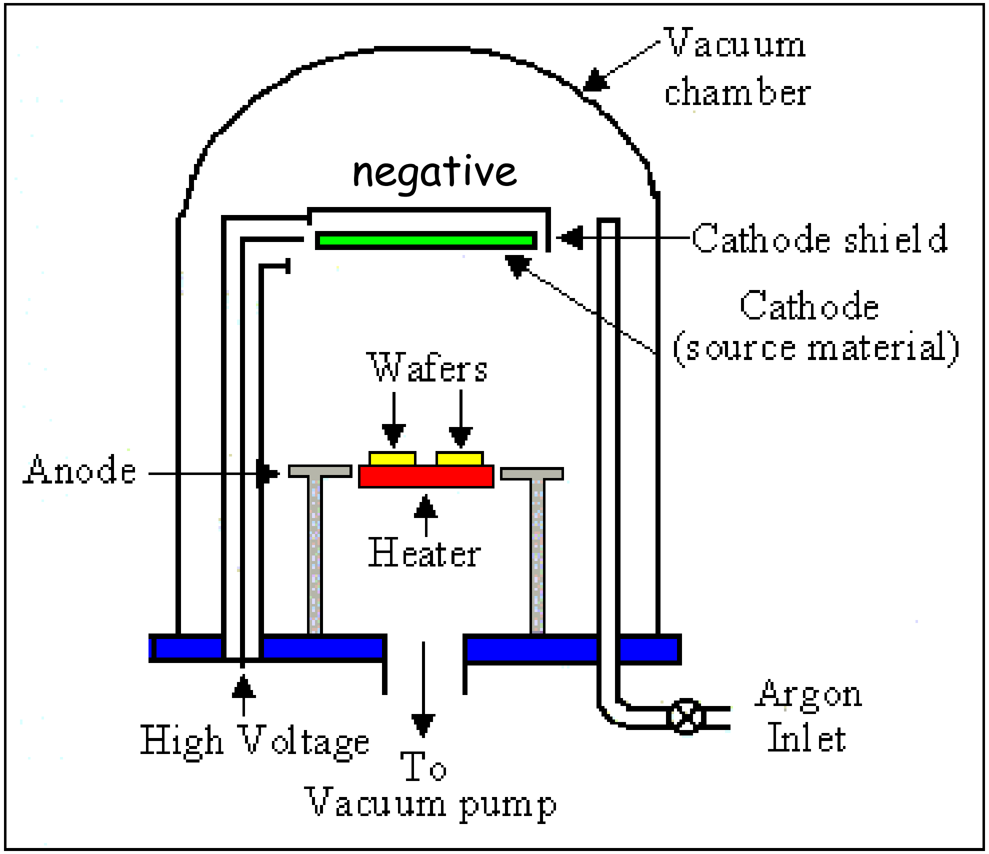
Solution-liquid-solid (SLS) nanowire growth



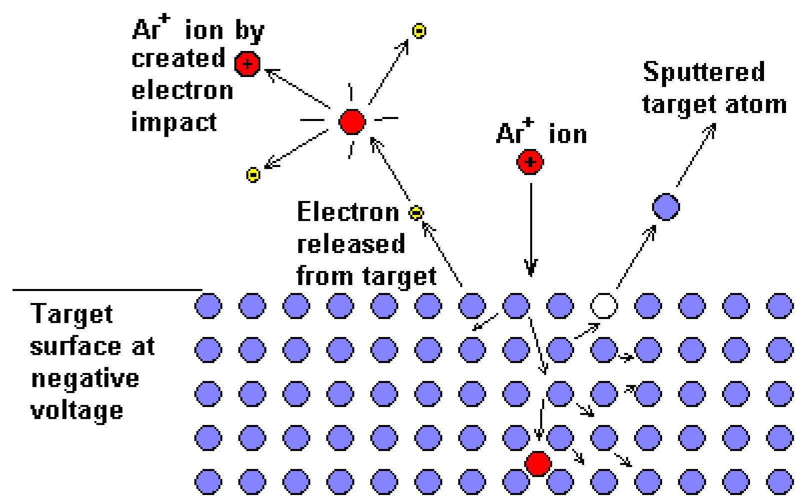
Korgel Group, UT, Austin, Department of Chemical Engineering

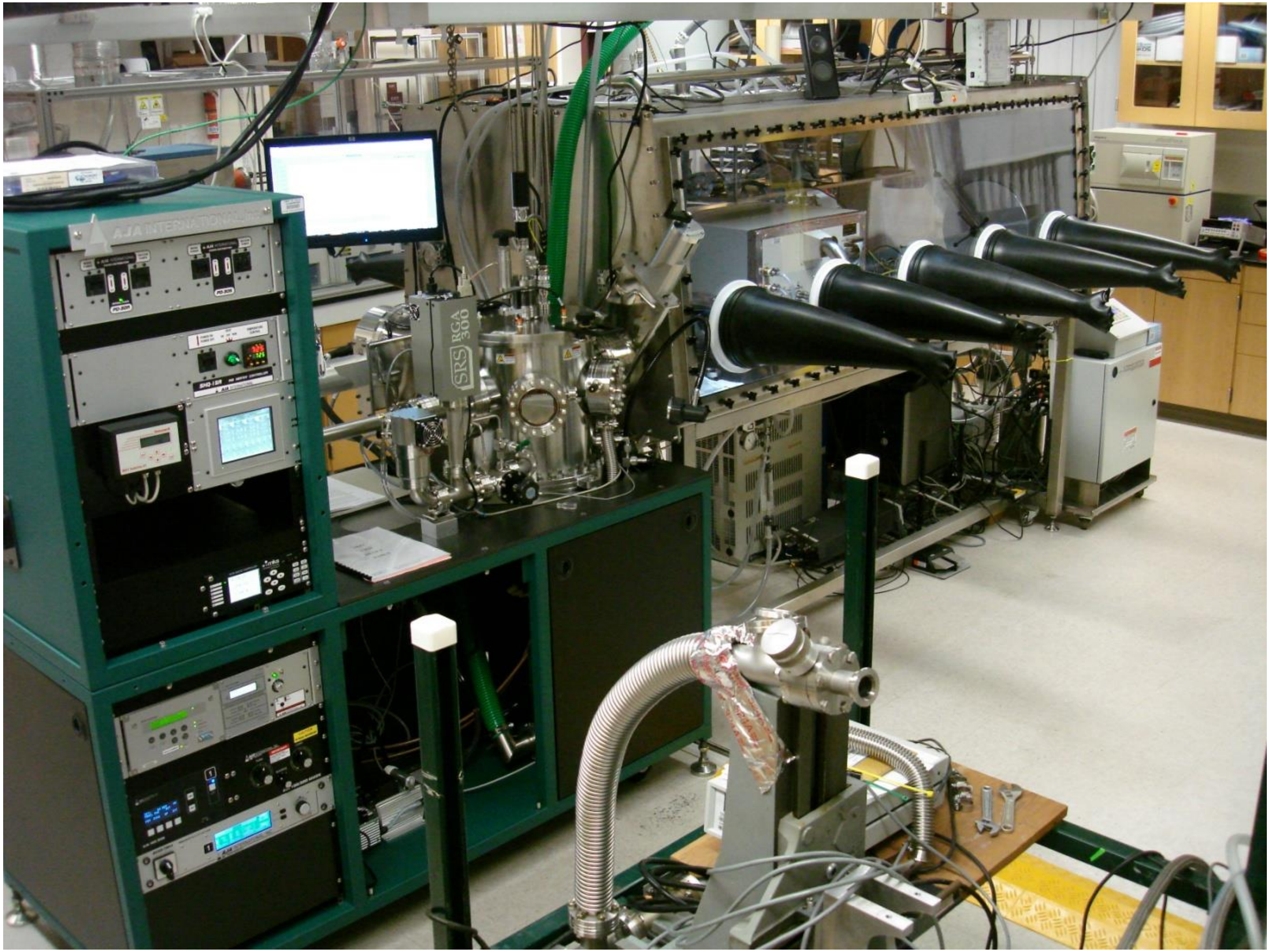
SPUTTERING

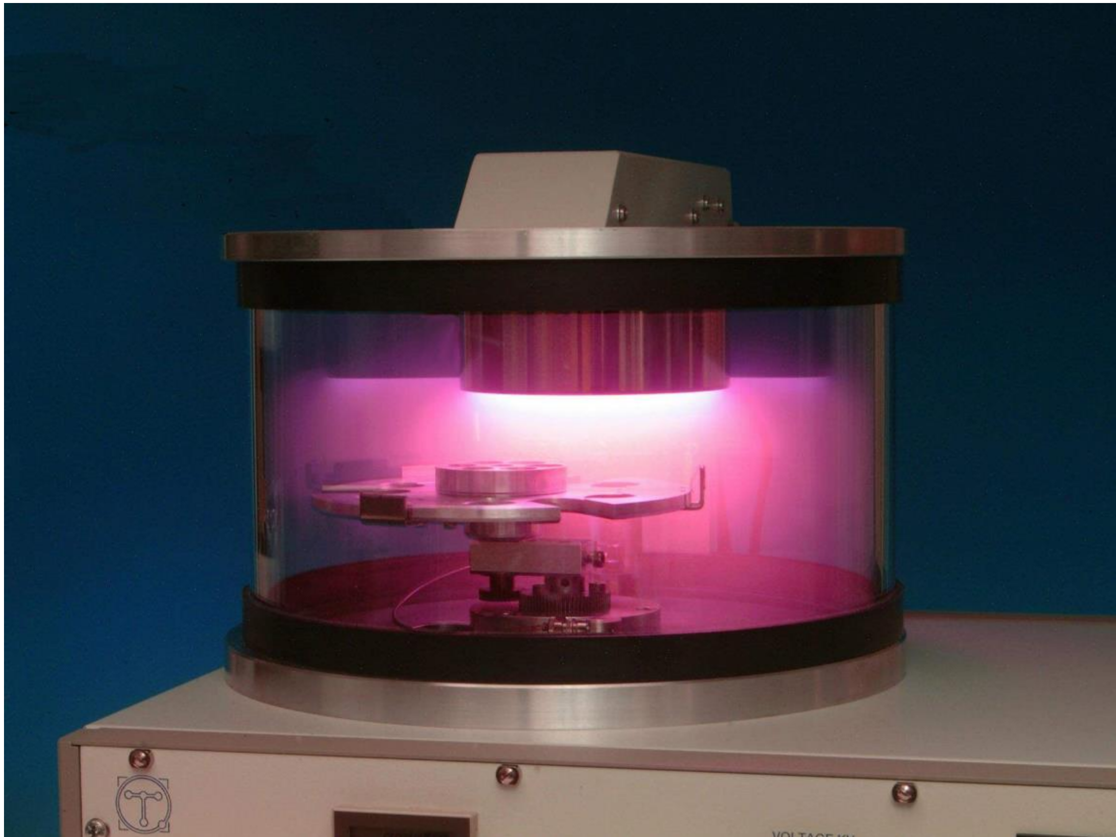
Bombardment of high-energy ions (usually argon) ejects atoms from a negatively-charged source to create a thin film coating.

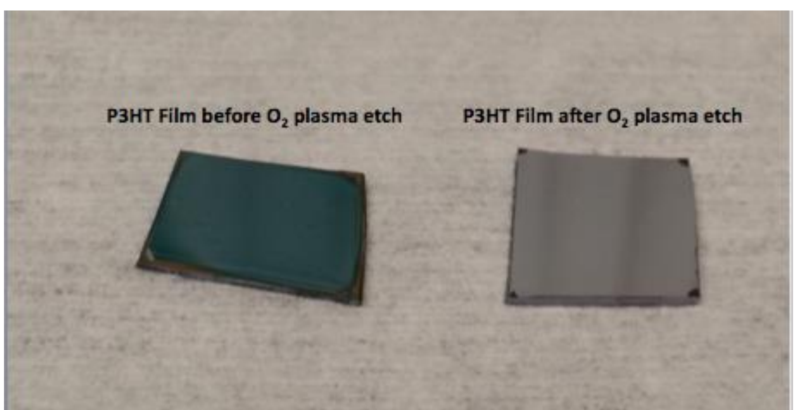


- vacuum (10^{-7} T), line-of-sight method
- argon ions created by high voltage dc or rf plasma
- produces hard, dense coatings




AJA INTERNATIONAL
SRS RGA 300




P3HT Film before O$_2$ plasma etch
P3HT Film after O$_2$ plasma etch


PC-2000
PLASMA CLEANER

MOLECULAR BEAM EPITAXY (MBE)

UHV technique for producing very high quality epitaxial layers with monolayer thickness control.

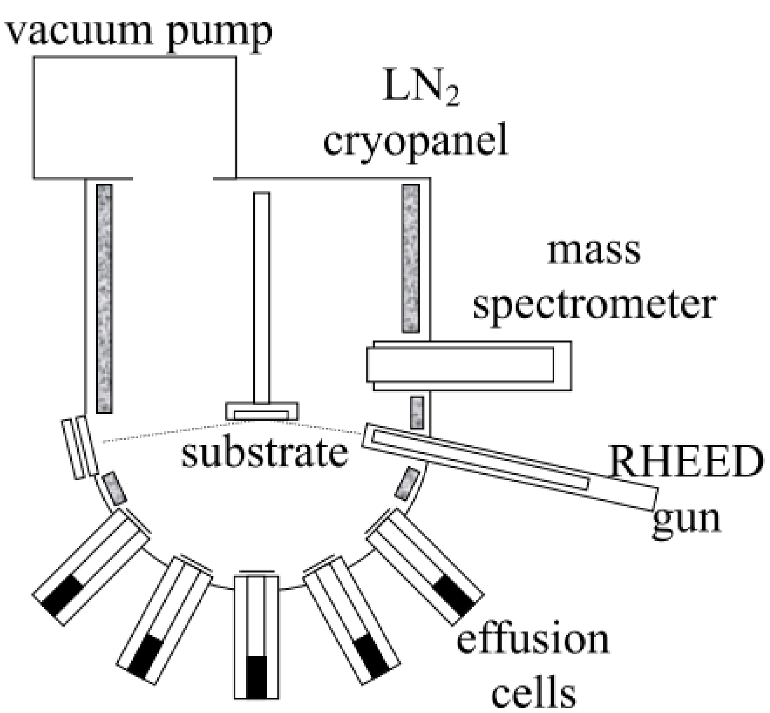
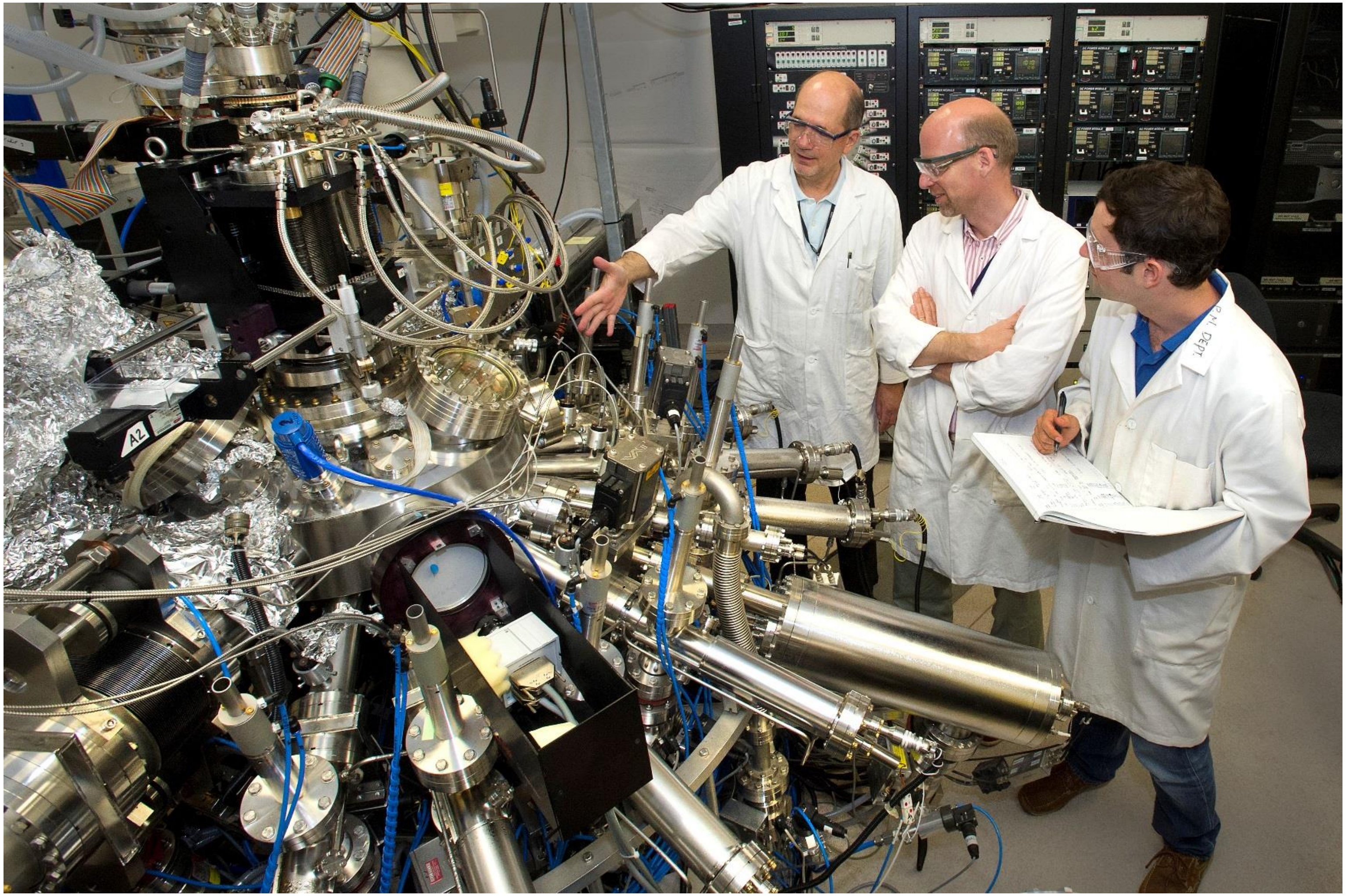


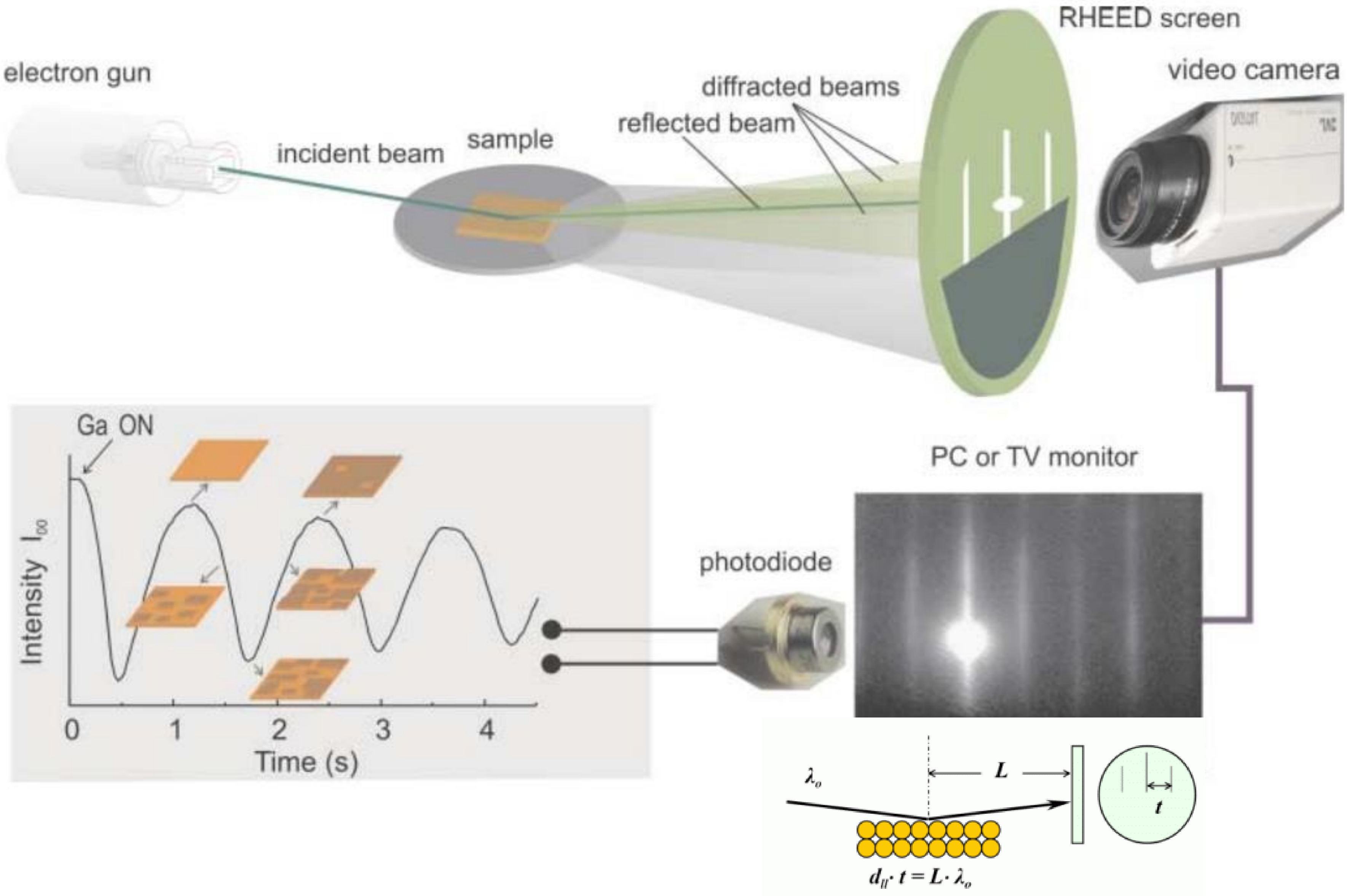
Fig. 1: A typical MBE system.

- ultrahigh vacuum (10^{-10} Torr), medium temp, line-of-sight method
- UHV gives long mean free path → "molecular beams" and ultrapure crystals
- slow growth rate (1 ML s^{-1}) promotes extremely high quality crystals
- very expensive



Brookhaven Nat'l Lab

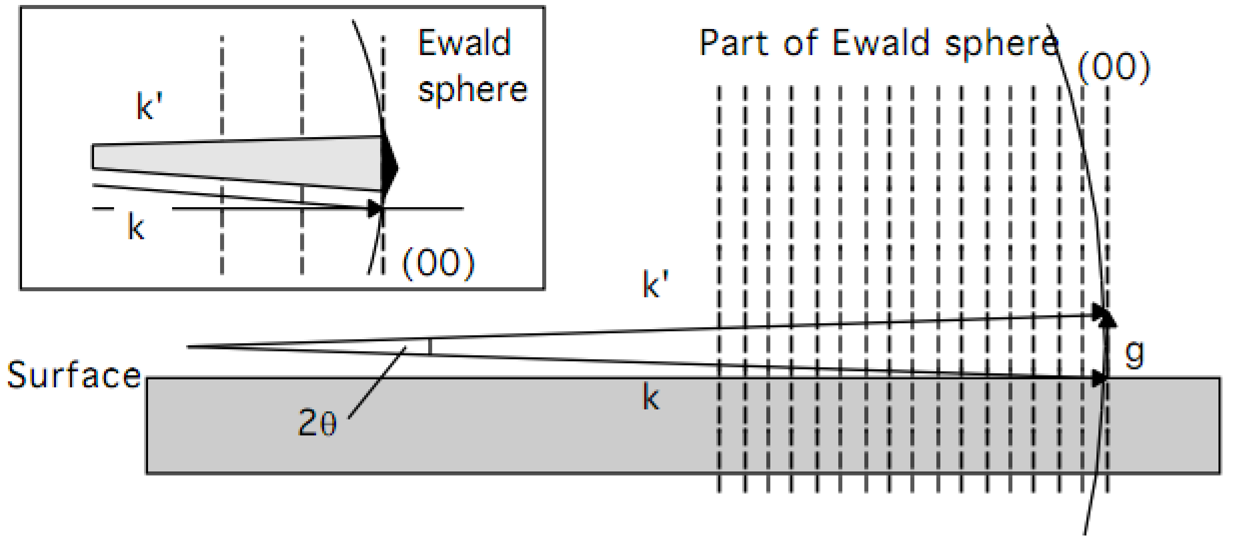
Reflection high-energy electron diffraction (RHEED)



3-100 keV electrons used to monitor monolayer growth wave vector of 50 keV electron ~120 $Å^{-1}$ → large Ewald sphere

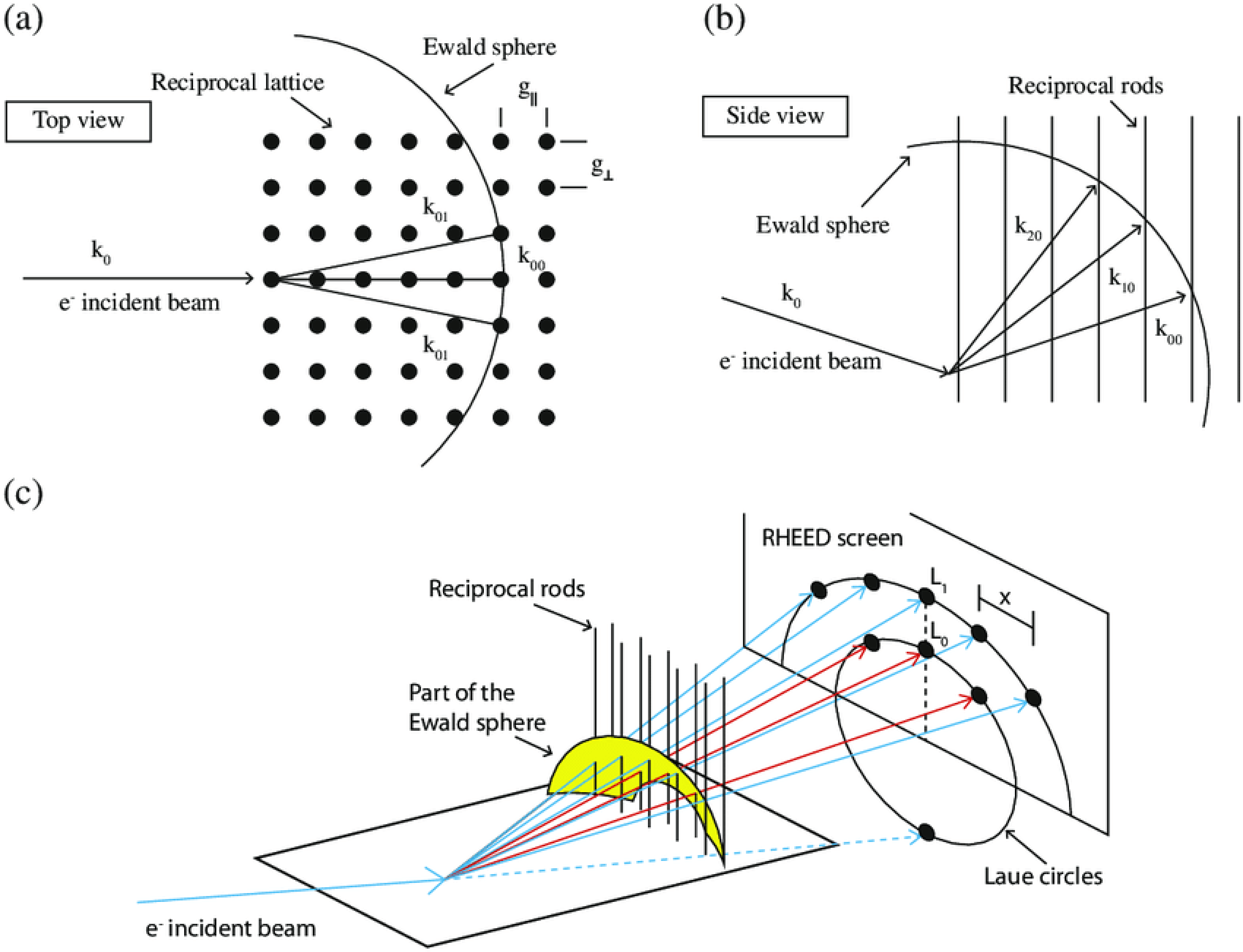
no diffraction condition in 3rd dimension → reciprocal lattice rods

Draw Ewald sphere for an incidence angle of 88°:

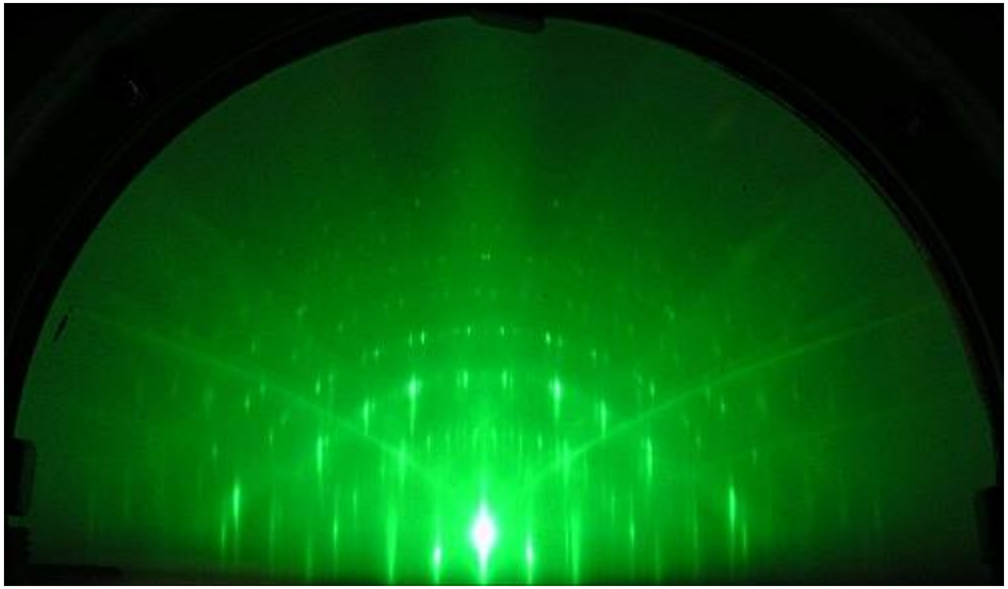


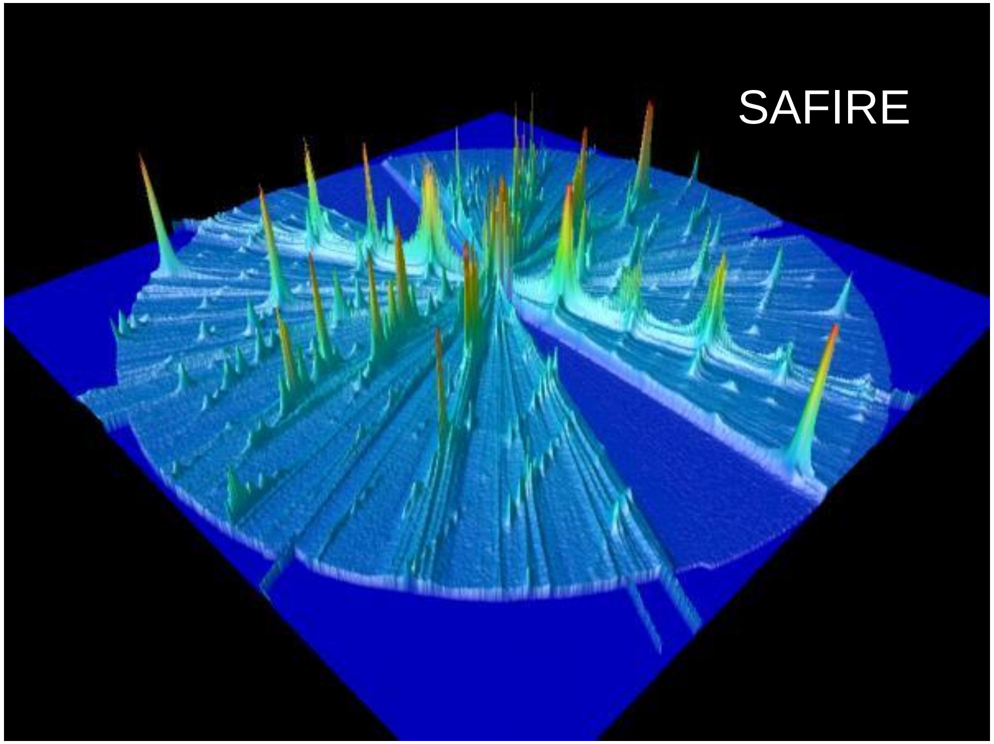
- Ewald sphere crosses many lattice rods, resulting in many spots separated by small diffraction angle differences. However, few of these are close to the grazing exit angles, so only a few spots are seen on the RHEED screen.

- The crossing of Ewald sphere with lattice rod can be very poorly defined → RHEED spots are broadened into vertical streaks

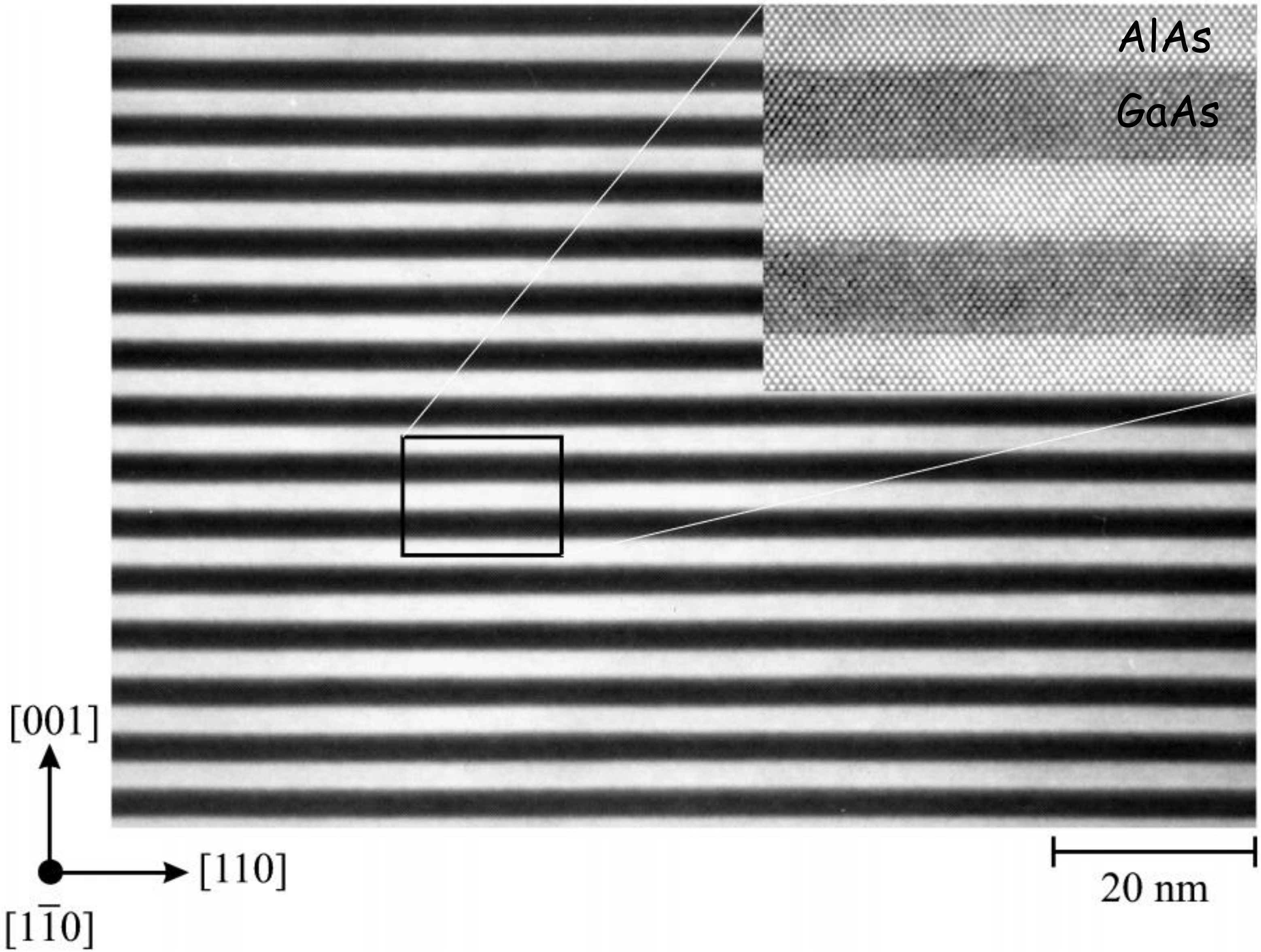


https://en.wikipedia.org/wiki/Reflection_high-energy_electron_diffraction




SAFIRE

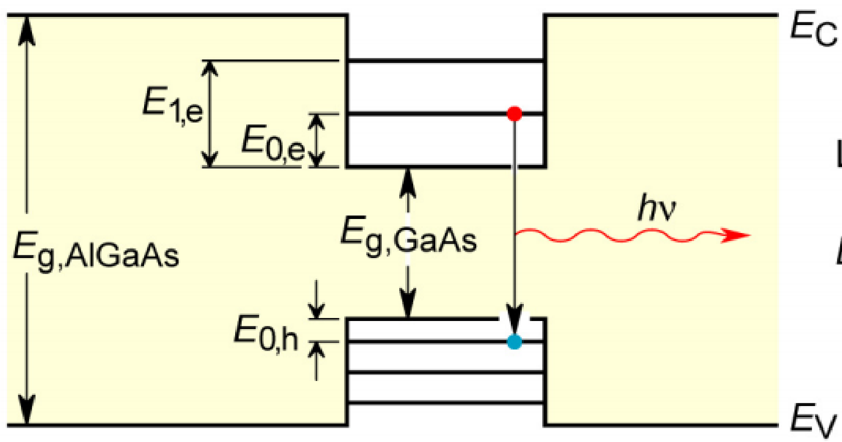
SC multilayer stack – “multiple quantum well” – grown by MBE



QUANTUM WELLS

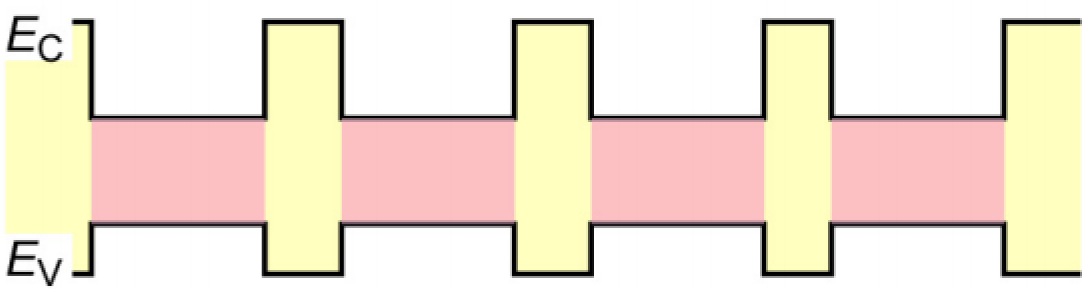
GaAs QWs

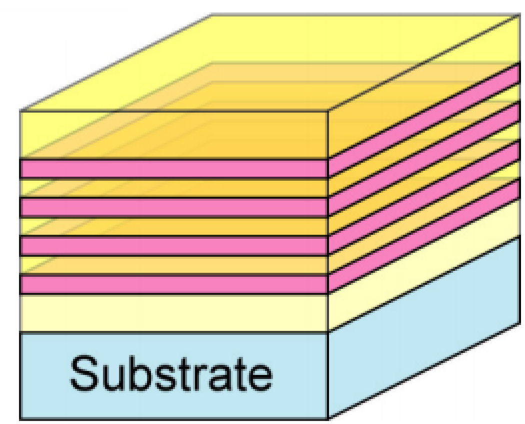
A finite potential well with only discrete energy levels.



Lowest transition energy:

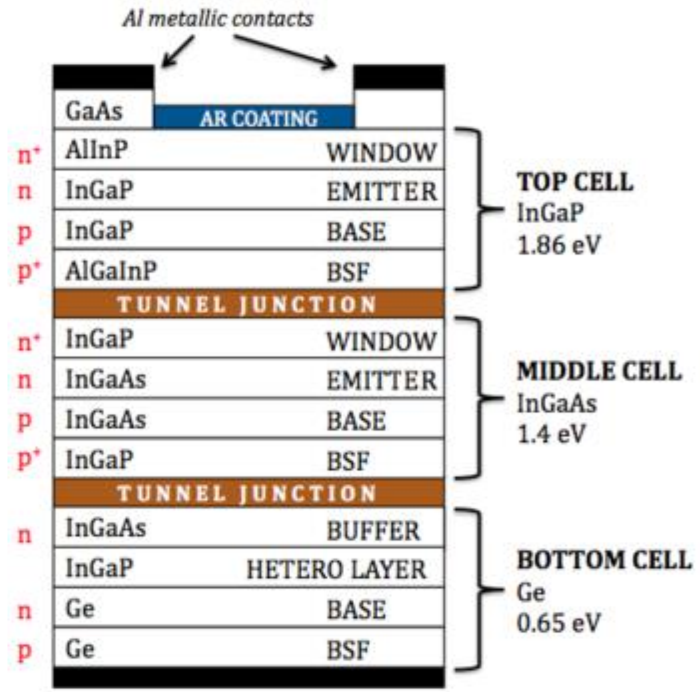
$$E = h\nu$$
$$= E_{g,GaAs} + E_{0,e} + E_{0,h}$$

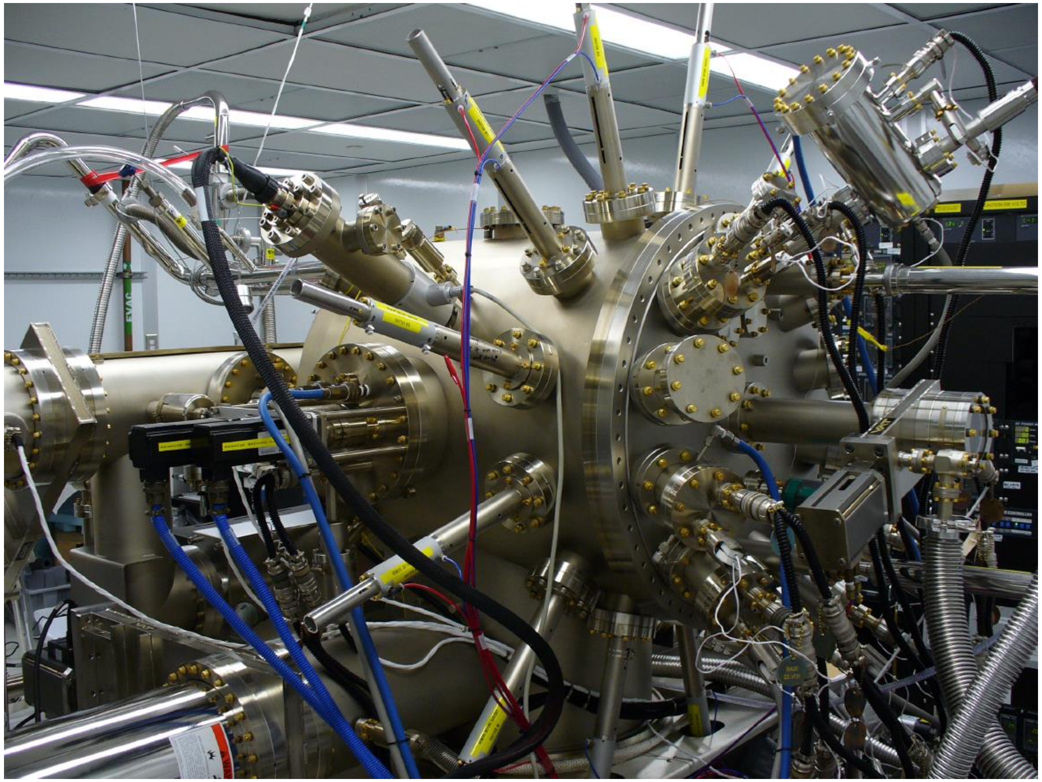


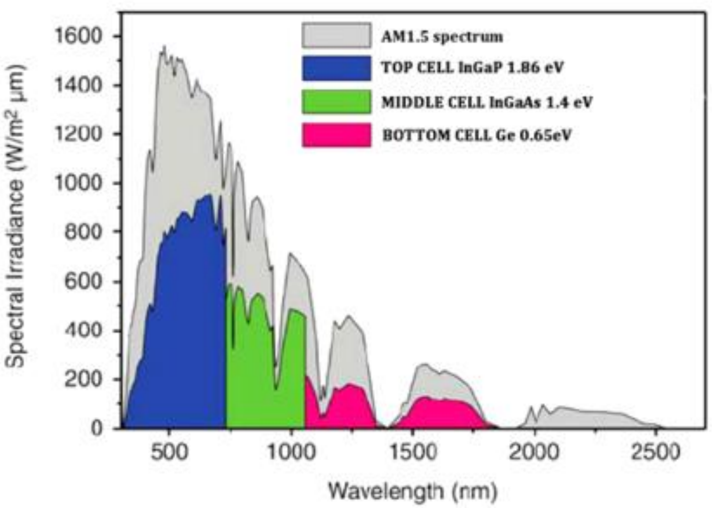


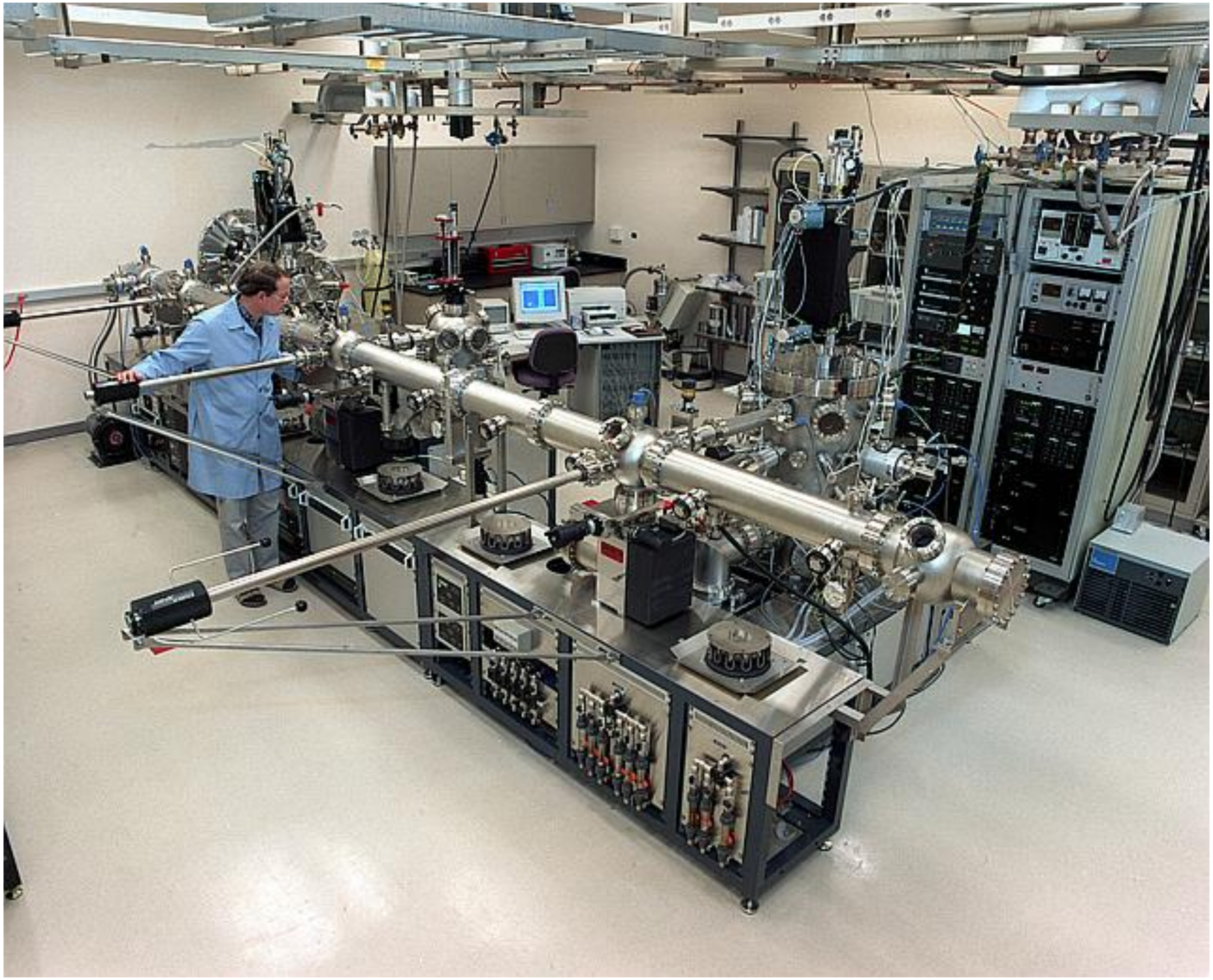
- can design transition energies
- high radiative efficiency
- low laser thresholds
- low surface recombination

MULTIJUNCTION SOLAR CELLS





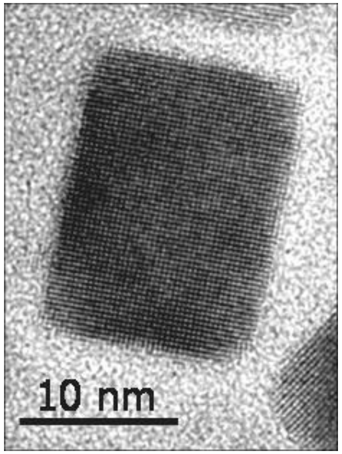


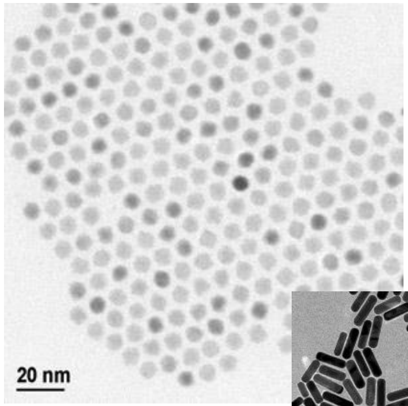


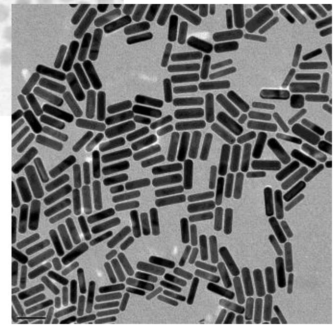
William R. Wiley Environmental Molecular Sciences Laboratory (PNNL)

SEMICONDUCTOR QUANTUM DOTS

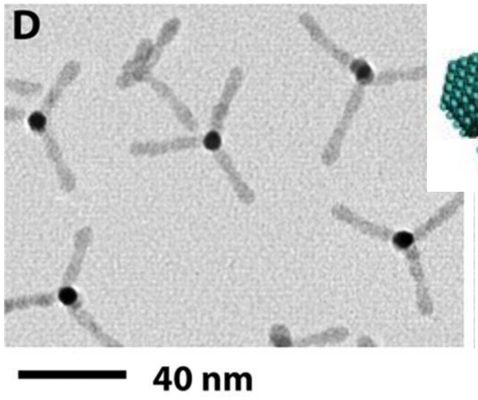
Nanometer size crystals with size-dependent properties.

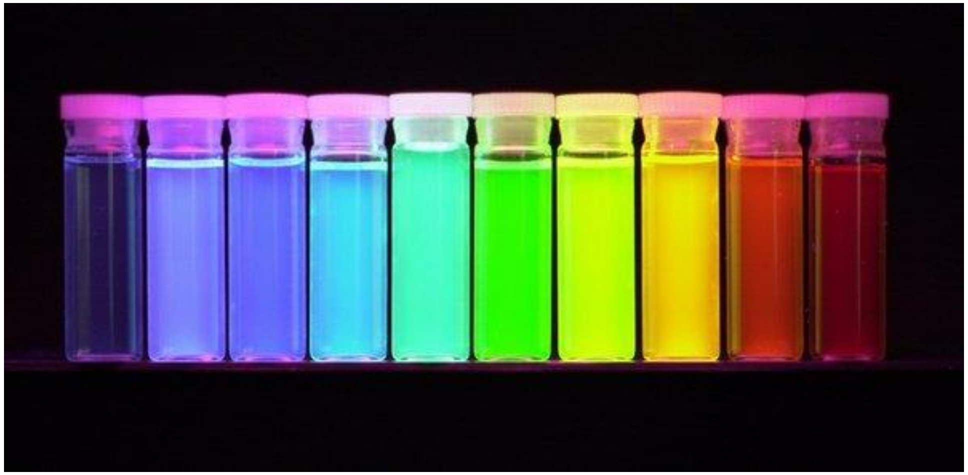


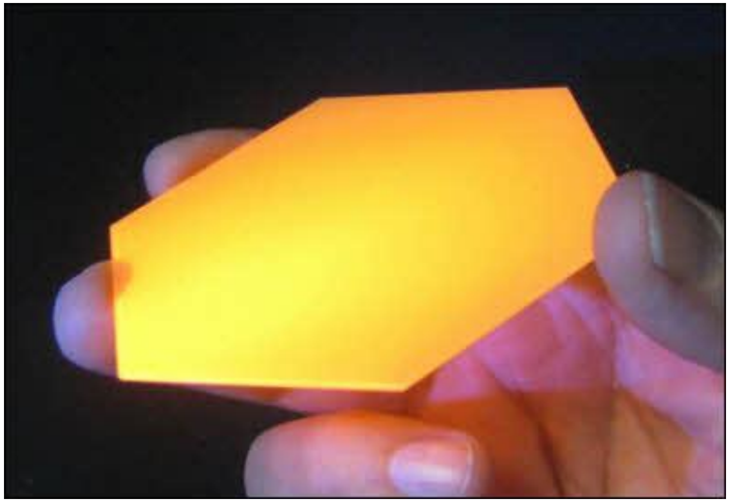




Initial CdTe tetrapods



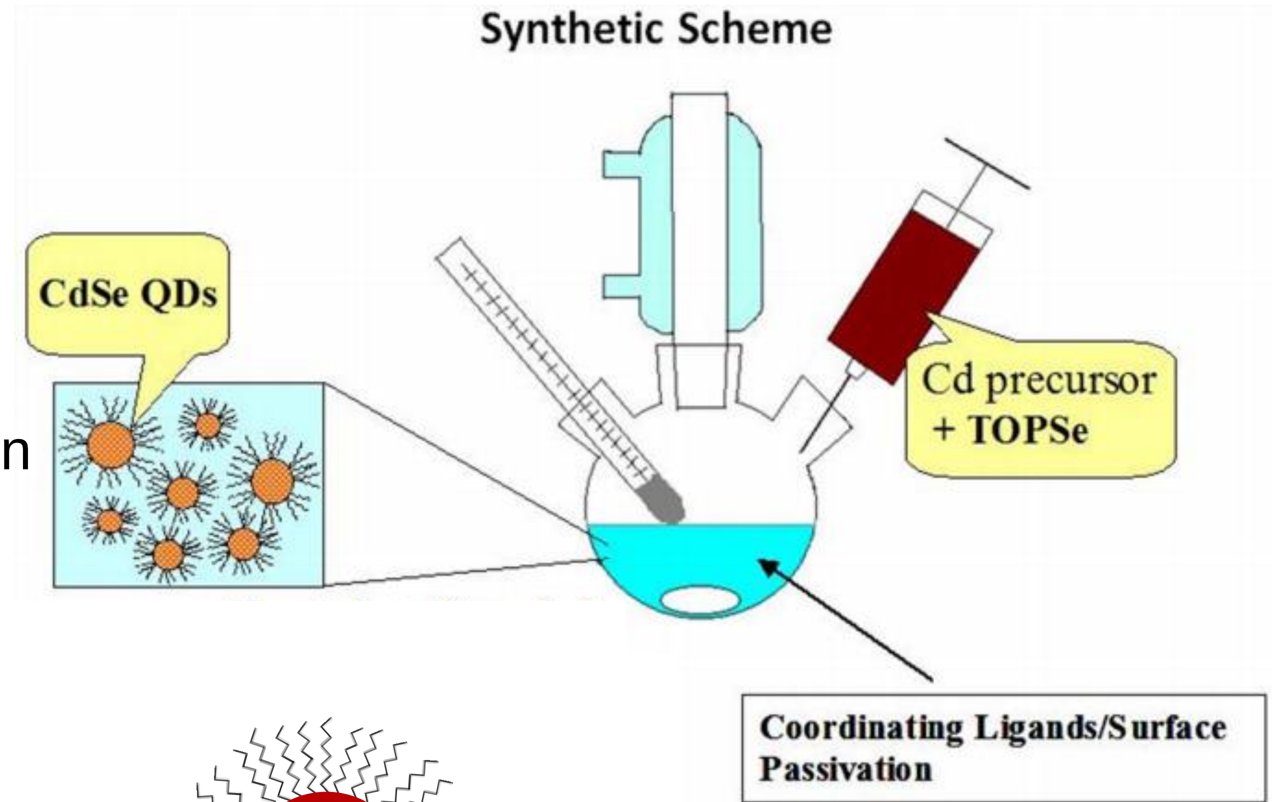


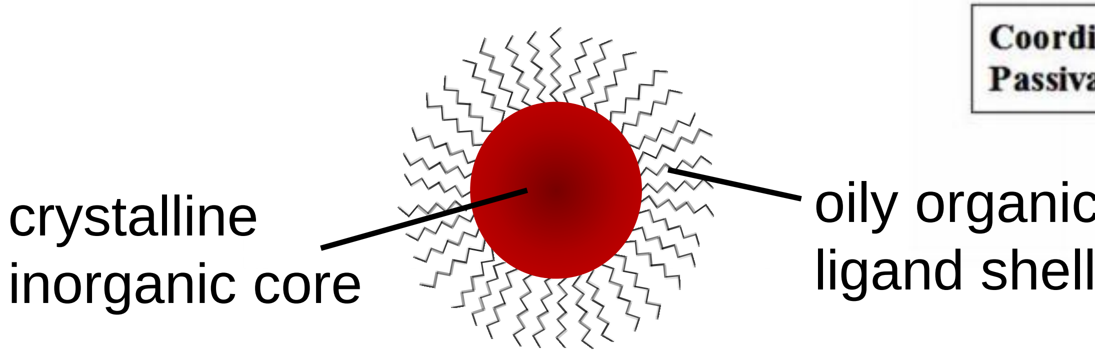


Synthesis of colloidal QDs

Synthesis Goals:

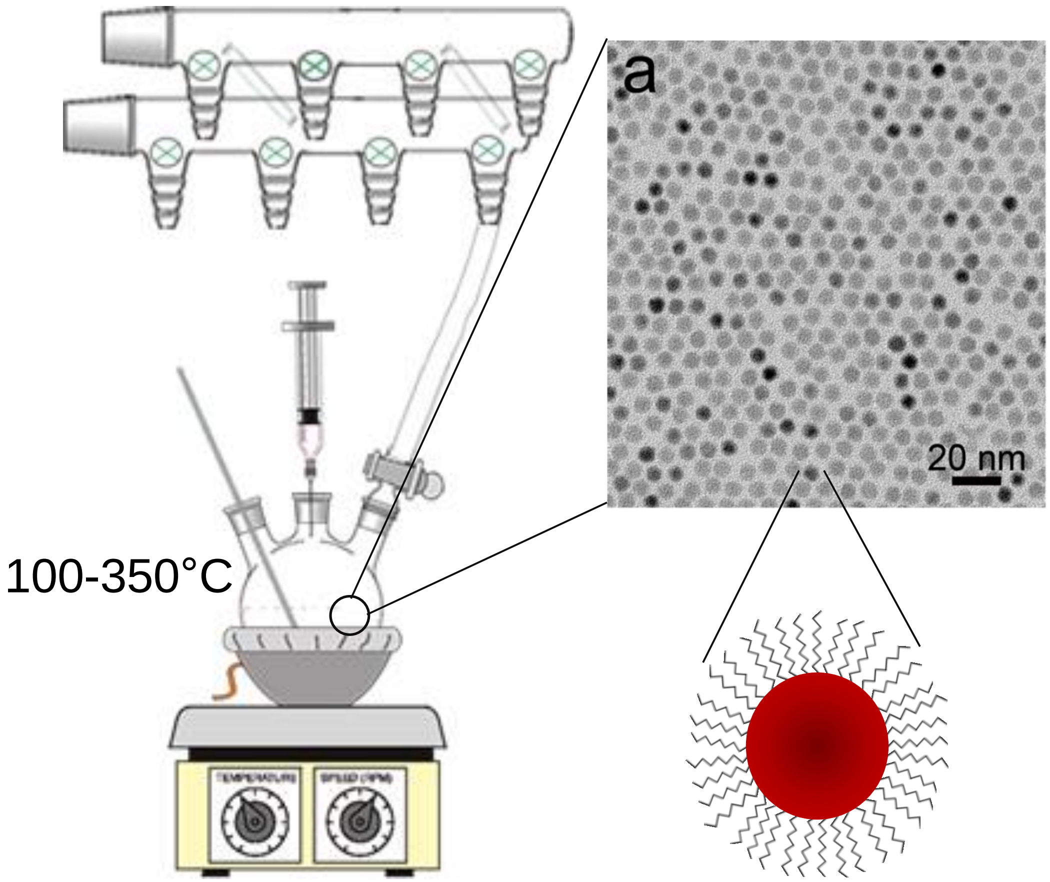
- monodispersity
- crystallinity
- size control
- shape control
- doping
- surface passivation
- colloidal stability





http://nanocluster.mit.edu/research.php

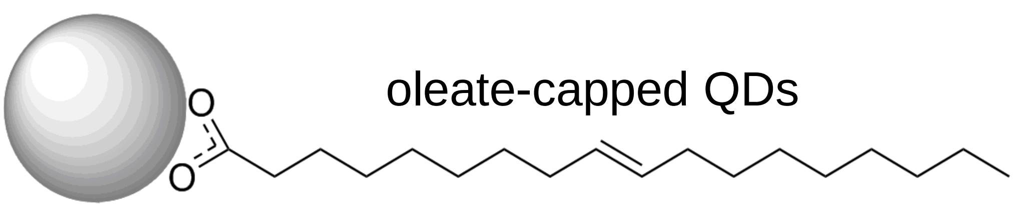
COLLOIDAL SC QUANTUM DOTS



<u>for PbSe quantum dots</u>

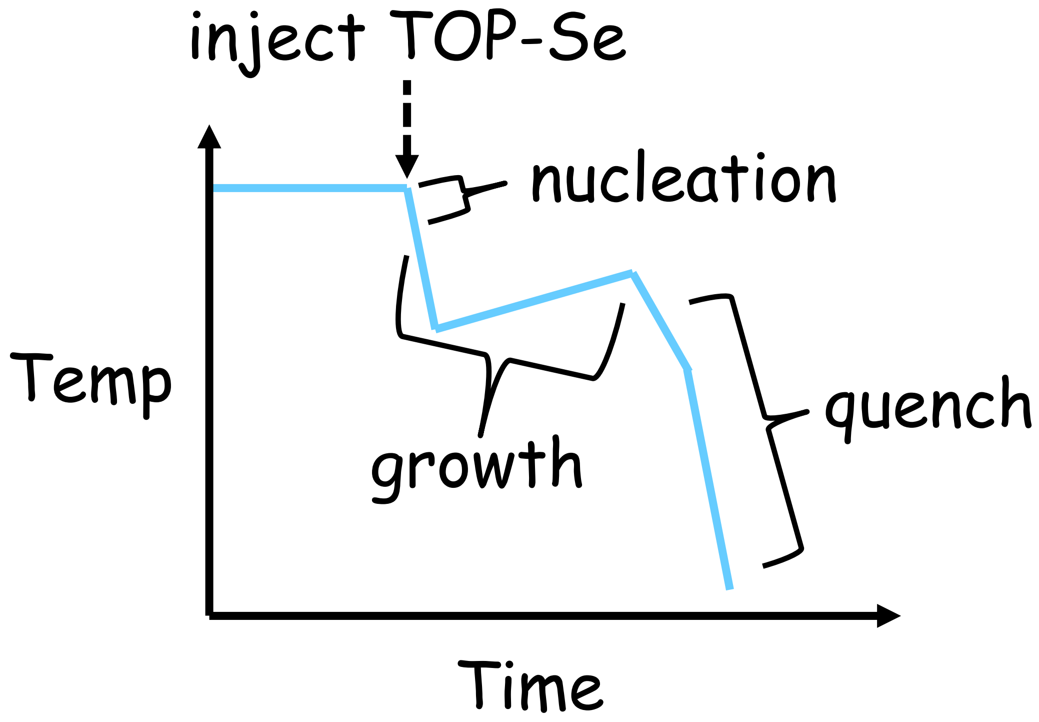
$PbO + 2OA \rightarrow Pb(OA)_2 + H_2O$

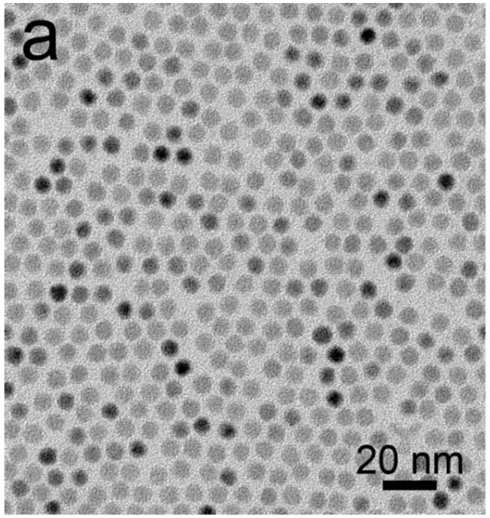
$Pb(OA)_2 + TOP\text{-}Se \rightarrow PbSe$
$+ \text{by-products}$



Hot injection method

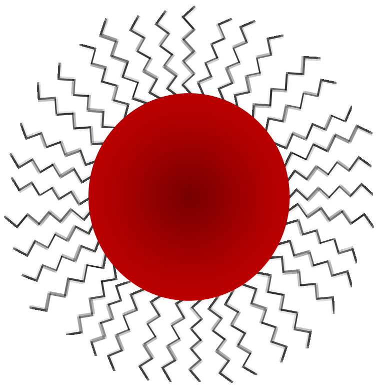
$$Pb(OA)_2 + (C_8H_{17})_3PSe \xrightarrow[180°C]{ODE} \text{PbSe dots}$$



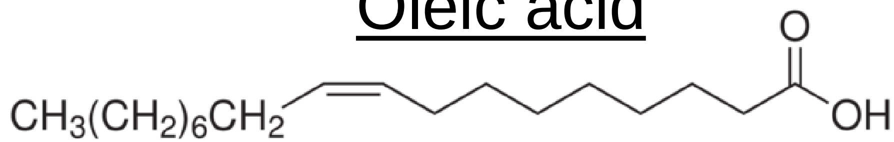


5% polydispersity
(unit cell roughness)

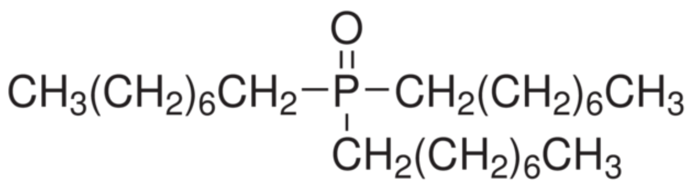
Native surface ligands



Oleic acid



TOPO



DDT

$CH_3(CH_2)_{10}CH_2SH$

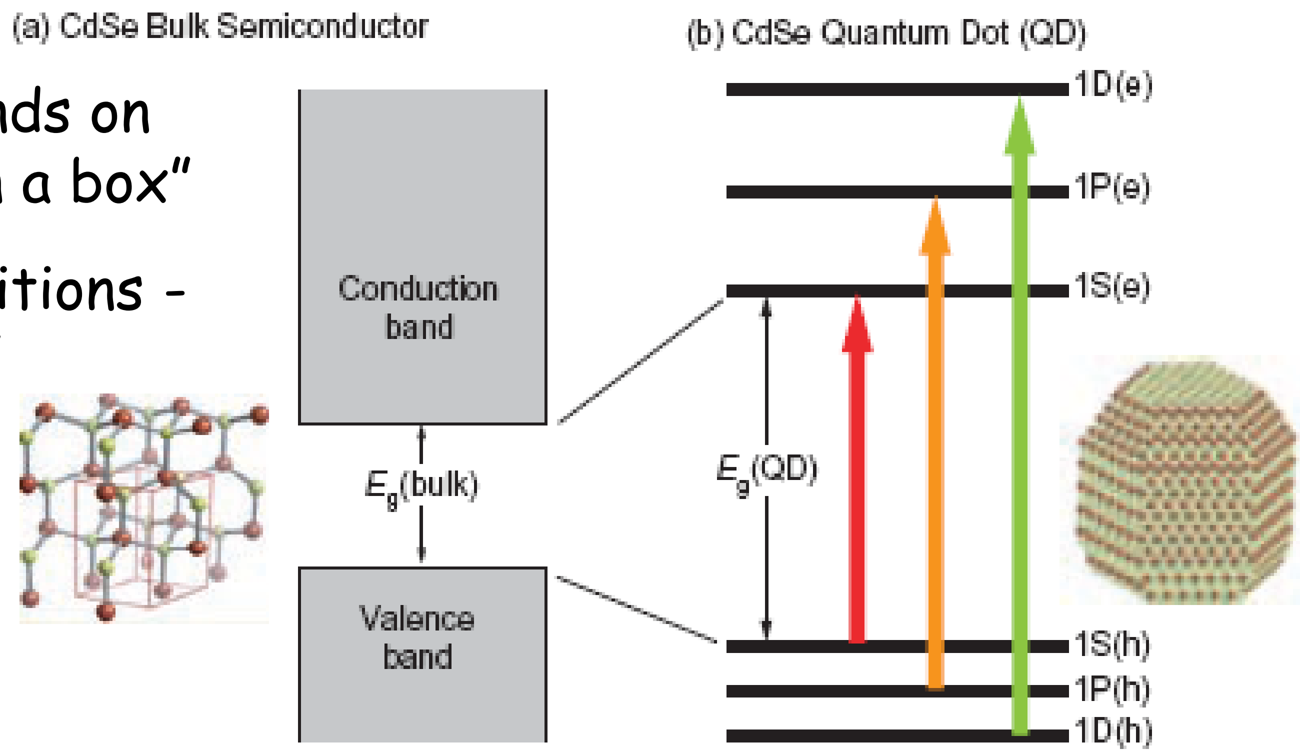
Functions:

- control size and shape
- prevent aggregation
- passivate surface states → strong PL
- doping?
- isolate QD from its environment (chemical stability)

QUANTUM CONFINEMENT

energy gap depends on size - "particle in a box"

discrete e^- transitions - "artificial atoms"



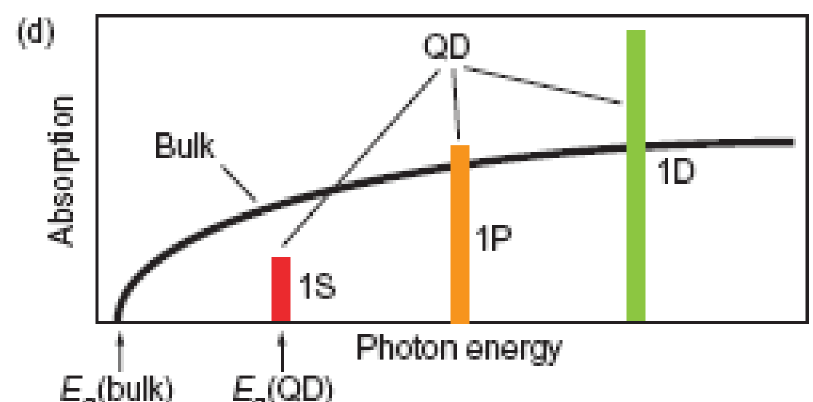
(c)

$$E_g(\text{QD}) \approx E_{g0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

$$m_{eh} = \frac{m_e m_h}{m_e + m_h}$$

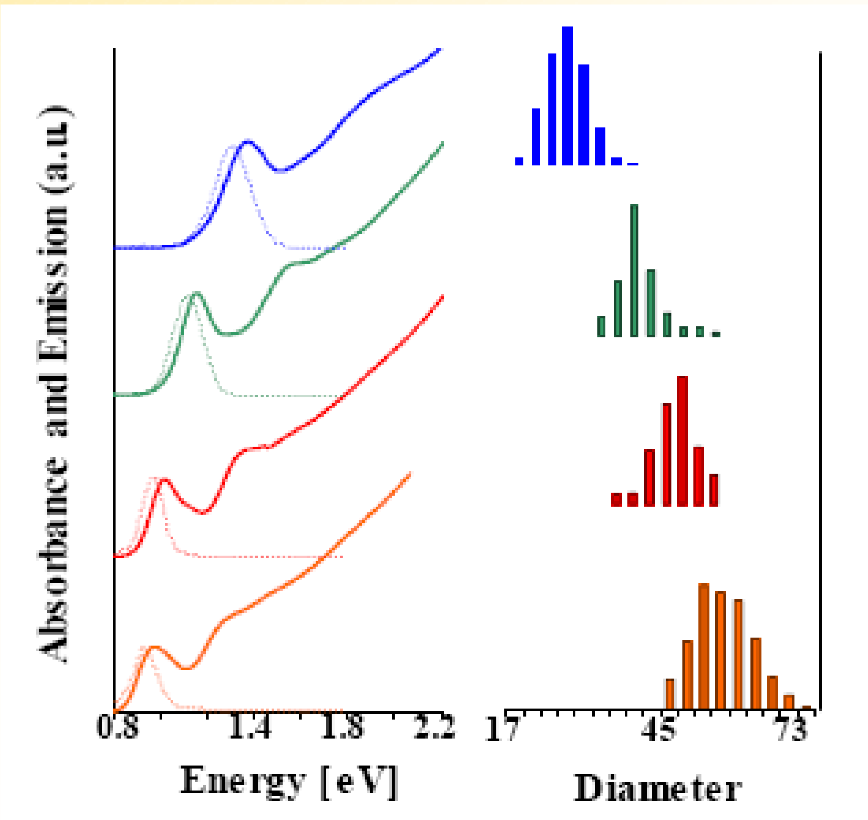
m_e = effective electron mass

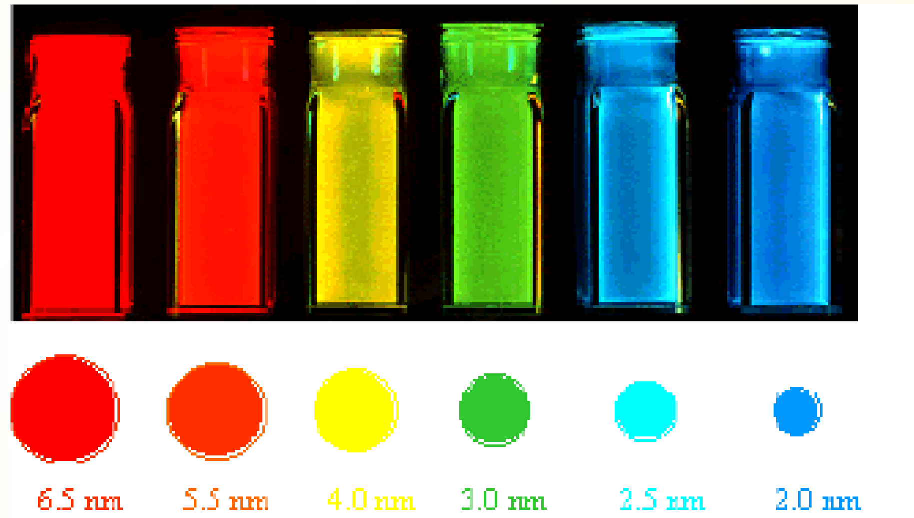
m_h = effective hole mass



smaller dots → larger bandgap → bluer absorption & emission

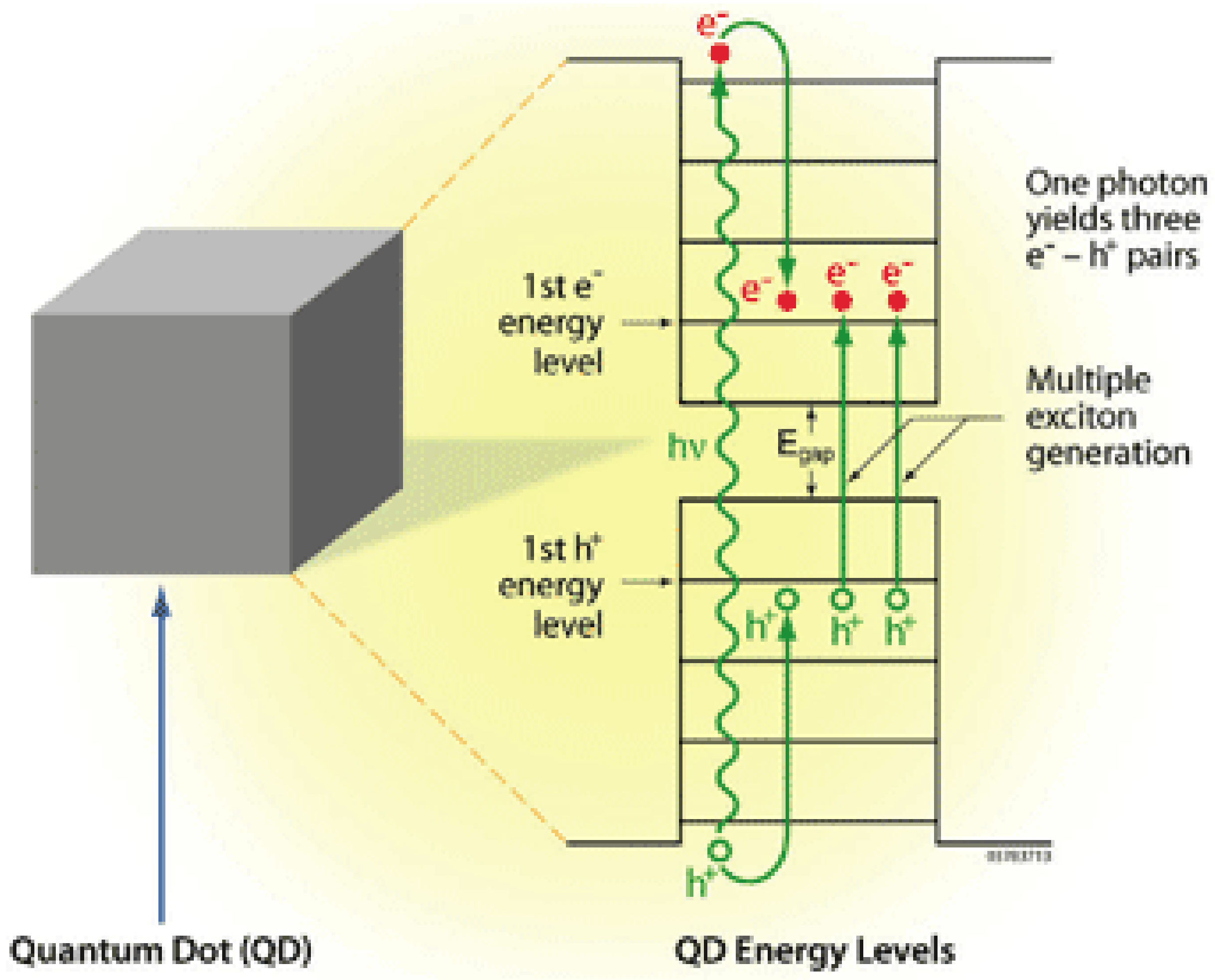
InAs nanocrystals (Banin group)





CdSe nanocrystals
(Bawendi group)

MULTIPLE EXCITON GENERATION



larger currents for solar cells

NUCLEATION

Nucleation = localized creation of a distinct thermodynamic phase.

<u>simple examples</u>: liquid in gas, solid in liquid, solid in gas, ZB in WZ

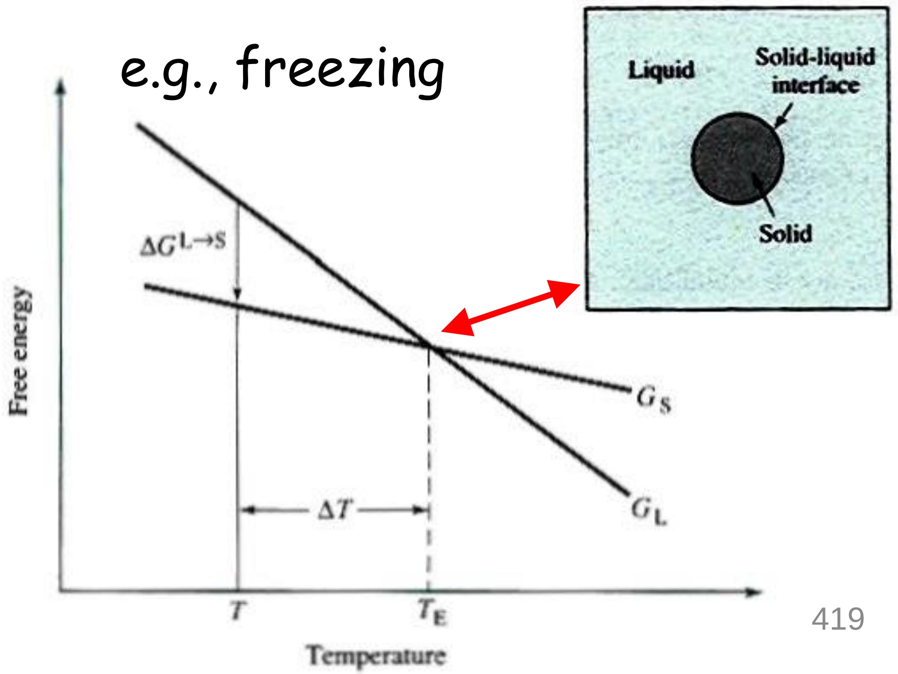
heterogeneous nucleation: nucleation assisted by a nucleation site, usually a surface (e.g., substrate, suspended particle, dust, etc.)

homogeneous nucleation: nucleation without a nucleation site. Harder to achieve than heterogeneous nucleation.

e.g., freezing

The driving force for nucleation is the lowering of free energy.

$$\Delta G = \Delta H - T\Delta S$$



SUPERCOOLING

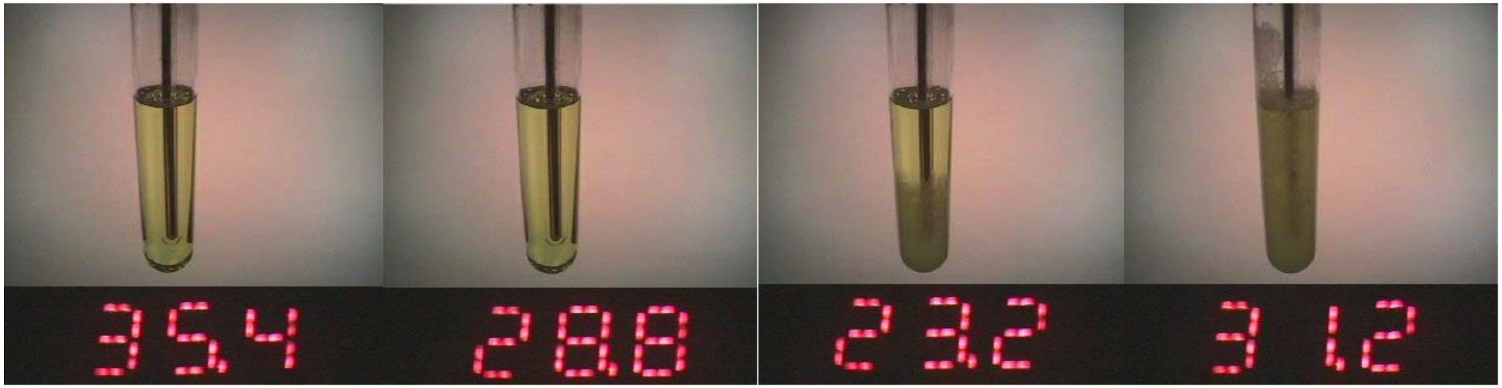
Nucleation and Growth

supersaturation
energetics
kinetics

Liquids are supposed to freeze when cooled to the freezing point

However, many liquids remain liquid below the freezing point because the freezing process is exceptionally slow

Example: 1-chlorine-2-nitrobenzene with $T_{freezing}$ = 35.4°C

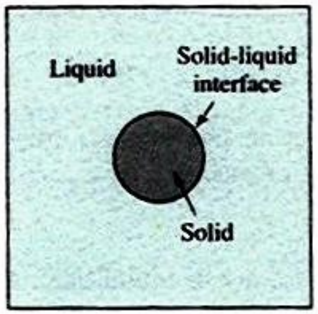


Liquid at $T_{freezing}$	Liquid below $T_{freezing}$	Liquid below $T_{freezing}$	Freezes & releases heat

Freezing of supercooled liquids is ***thermodynamically favored*** but ***kinetically hindered***

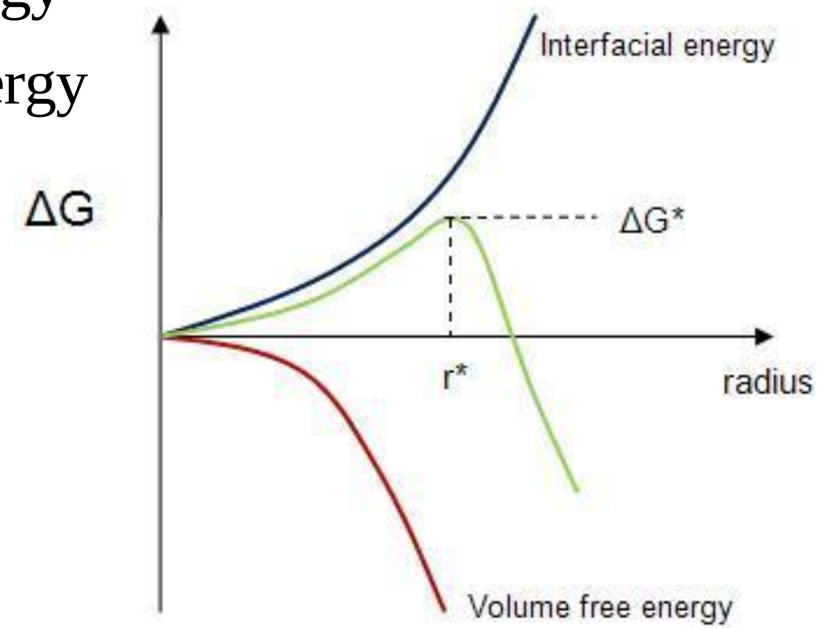
NUCLEATION and GROWTH

consider a spherical amorphous solid nucleating from a homogeneous supersaturated liquid:



$G_v =$ volume free energy

$\sigma =$ interfacial free energy



$$\Delta G(r) = \frac{4}{3}\pi \Delta G_v r^3 + 4\pi\sigma r^2$$

energy liberated by forming volume (-)

energy required to form interface (+)

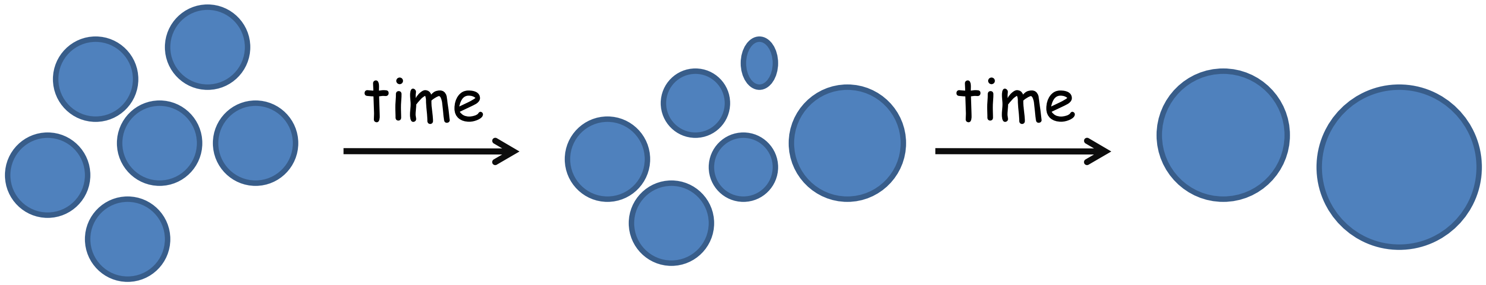
critical nucleus r*: $r^* = -\frac{2\sigma}{\Delta G_v}$

$r<r^*$ - nucleus dissolves

$r>r^*$ - nucleus grows

OSTWALD RIPENING

Initially the solid particles draw their material from the solution/melt. Later, as the solution/melt becomes depleted, the particles compete with each other for growth. In Ostwald ripening, small particles shrink and supply atoms to larger particles, which grow.



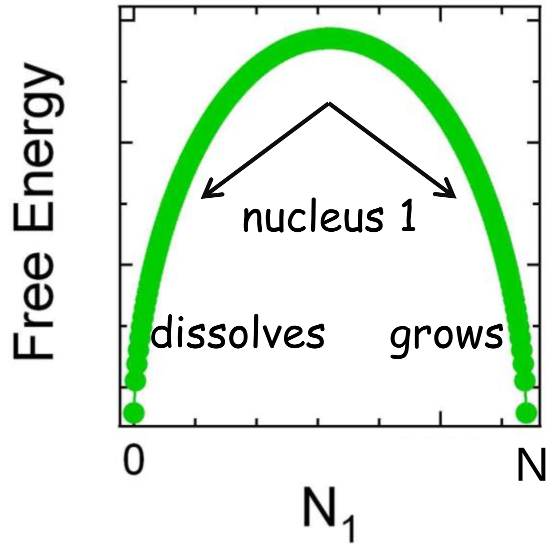
thermodynamically driven - atoms on surface are less stable than atoms in the bulk b/c lower coordination number (poorer bonding), so system can lower energy by reducing surface area.

OSTWALD RIPENING

consider two spherical nuclei w/ N_1 and N - N_1 atoms (N constant):

with $\Omega \equiv$ atomic volume,

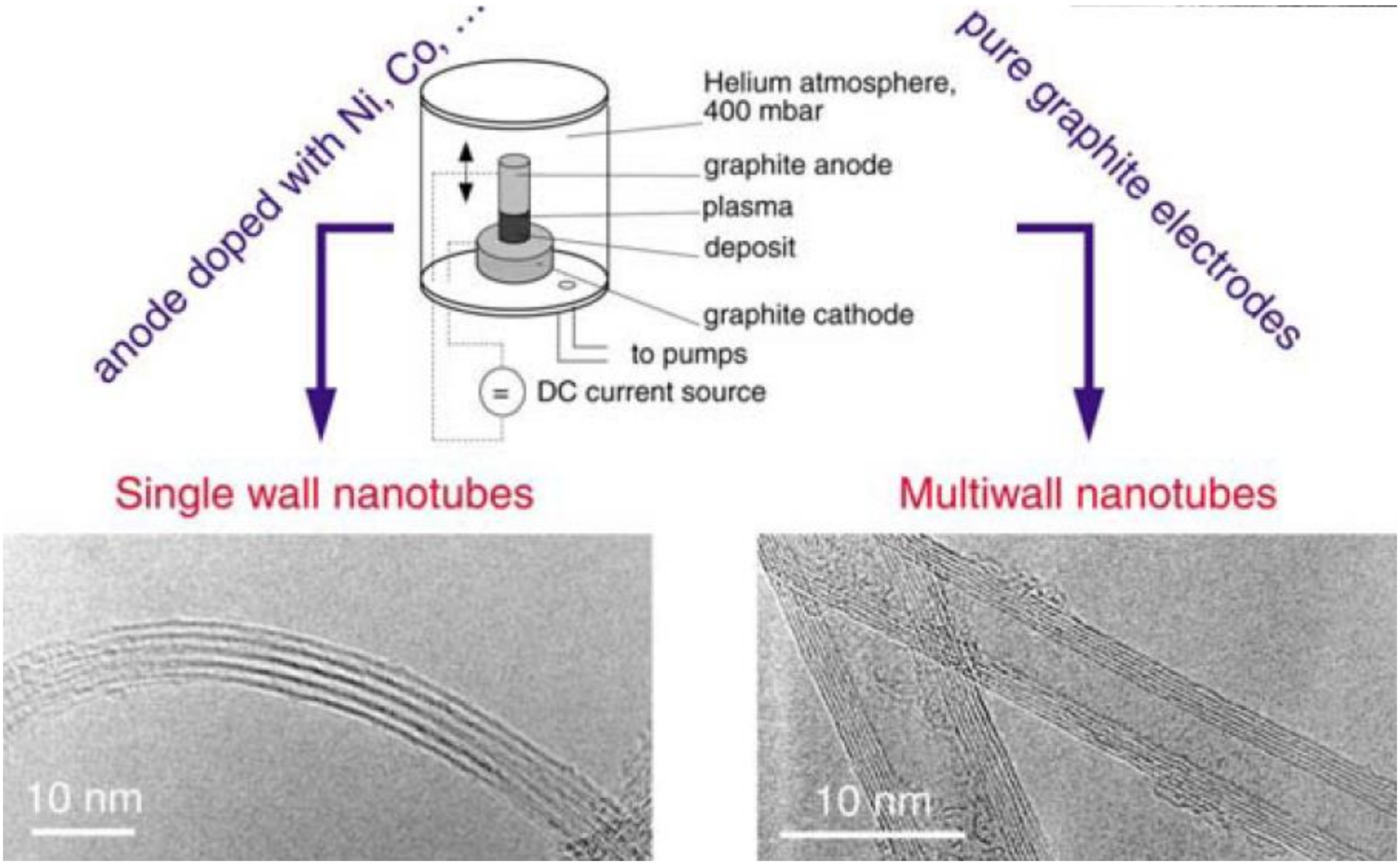
$$G(N_1, N-N_1) = N\Omega G_v + 4\pi\sigma\left(\frac{3\Omega}{4\pi}\right)^{2/3}\left[N_1^{2/3} + (N-N_1)^{2/3}\right]$$



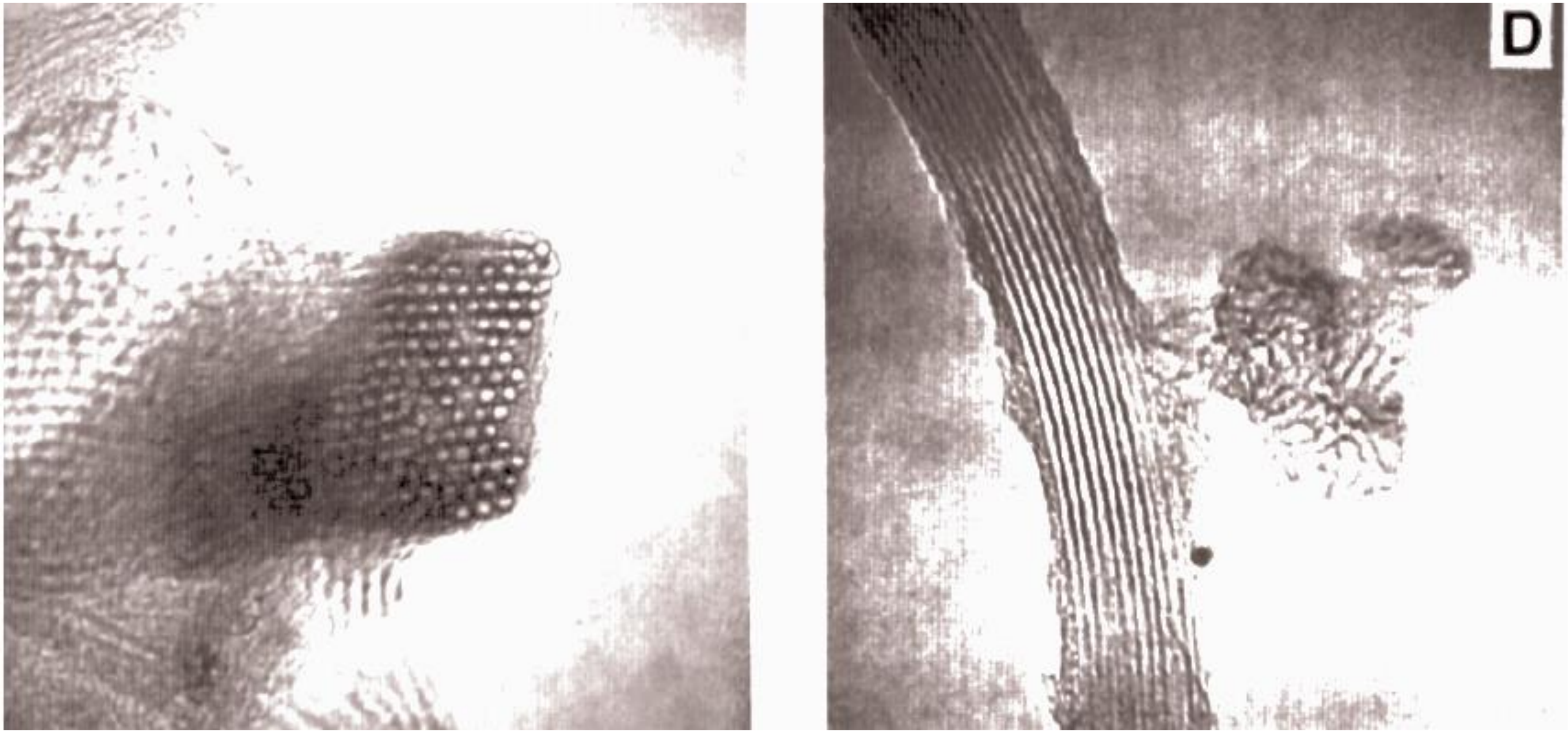
minimum G occurs when the two equal spheres combine into one big sphere:

$$\Delta G = -4\pi\sigma\left(\frac{3\Omega}{4\pi}\right)^{2/3}(2^{1/3}-1)N^{2/3}$$

CARBON NANOTUBES: ARC DISCHARGE

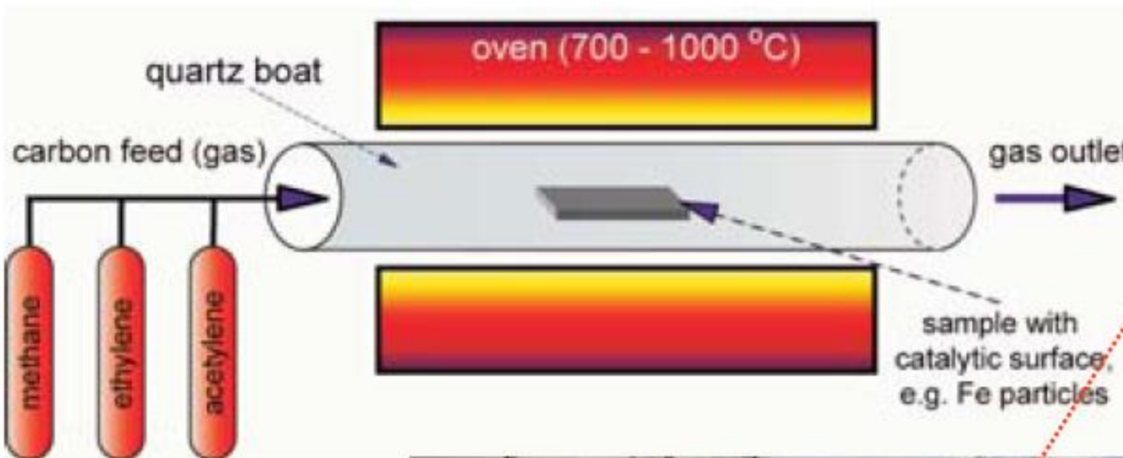


LASER ABLATION of CNTs

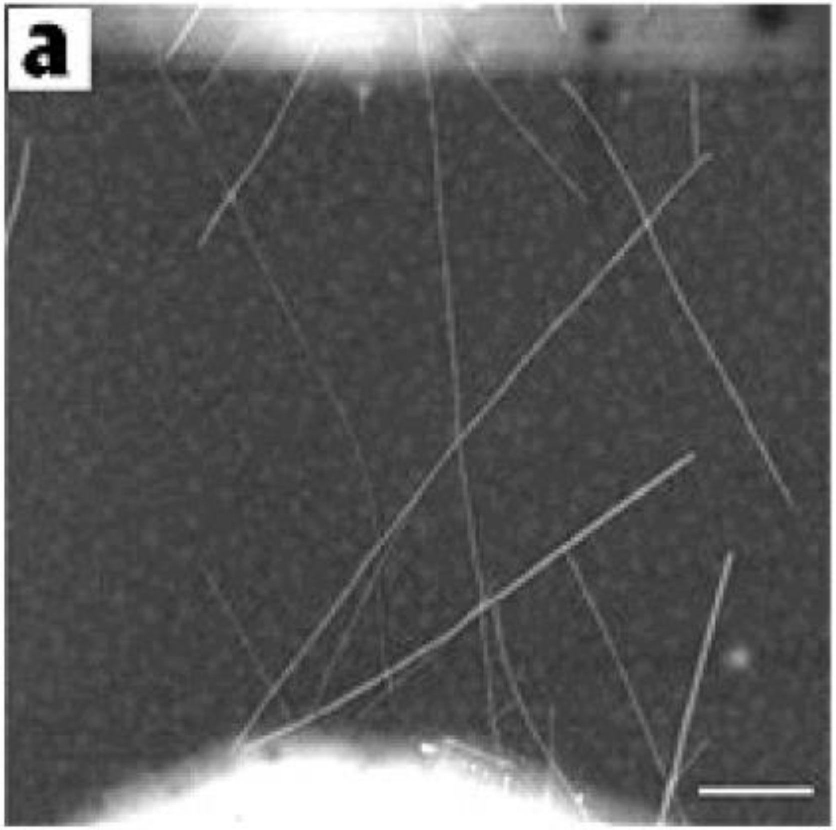


Thess et al., Science 273, 483 (1996)

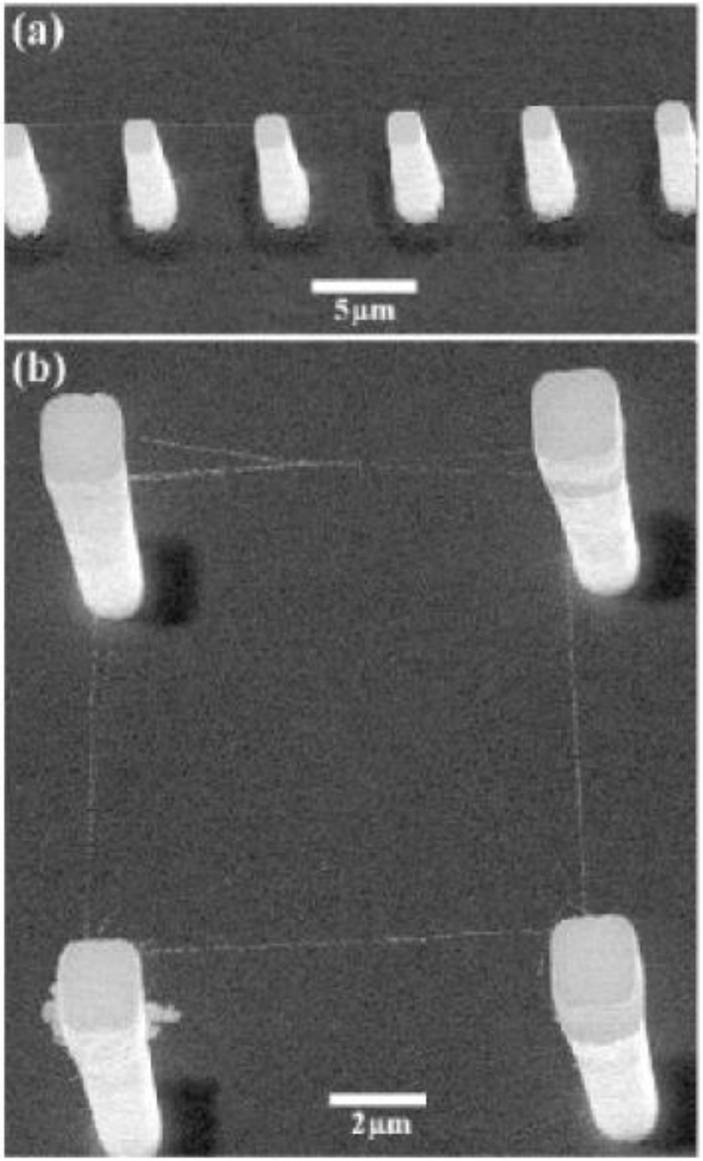
CVD of CNTs



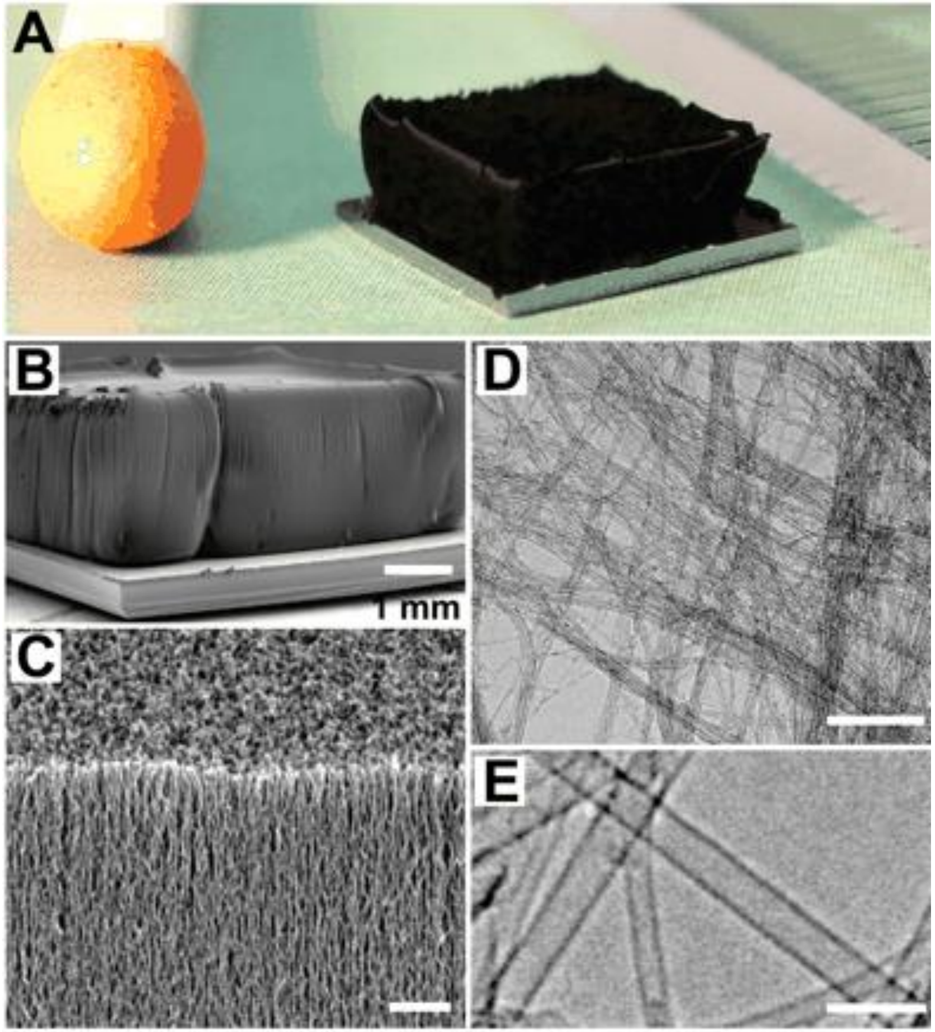
(CH_4, C_2H_4, C_2H_2...)



from the DaiLab @ Stanford



Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes



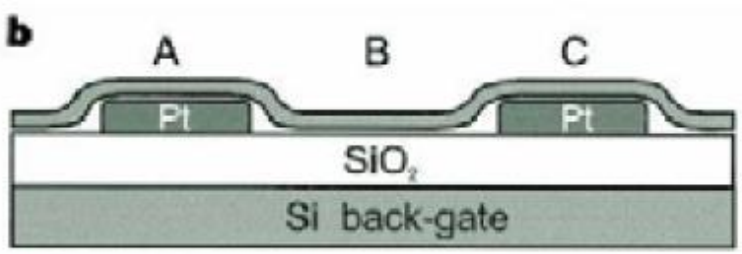
Science 19 November 2004:
Vol. 306. no. 5700, pp. 1362 - 1364

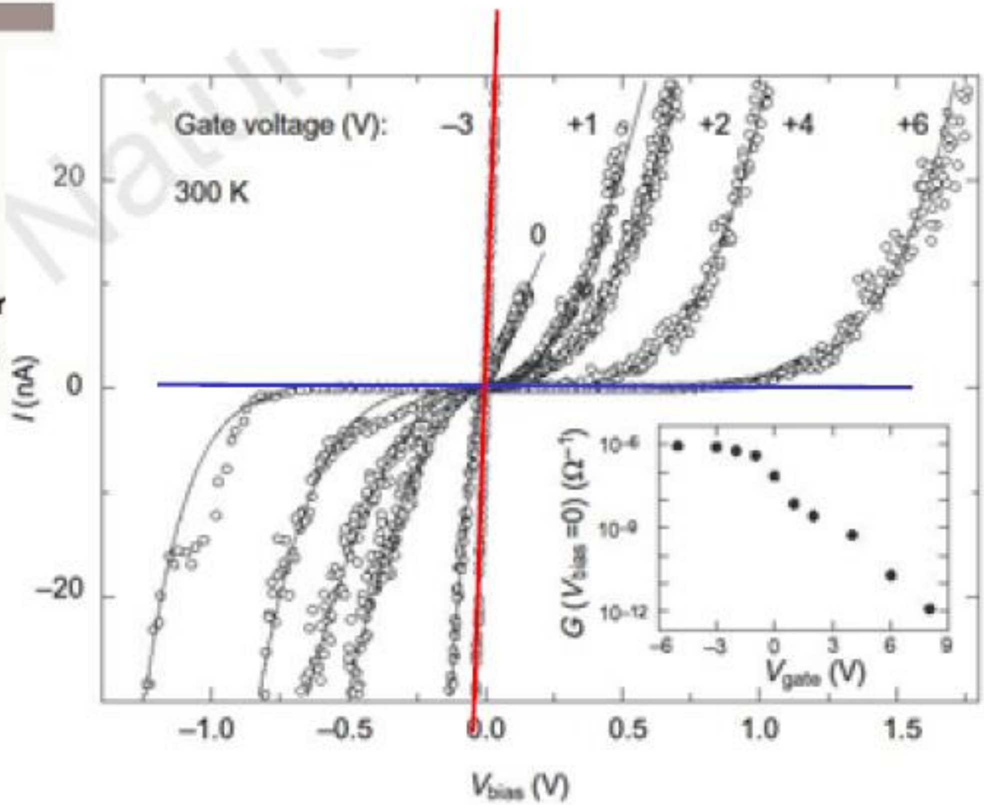
CNT DEVICES: FIELD EFFECT TRANSISTOR

Room-temperature transistor based on a single carbon nanotube

Sander J. Tans, Alwin R. M. Verschueren & Cees Dekker

Department of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands





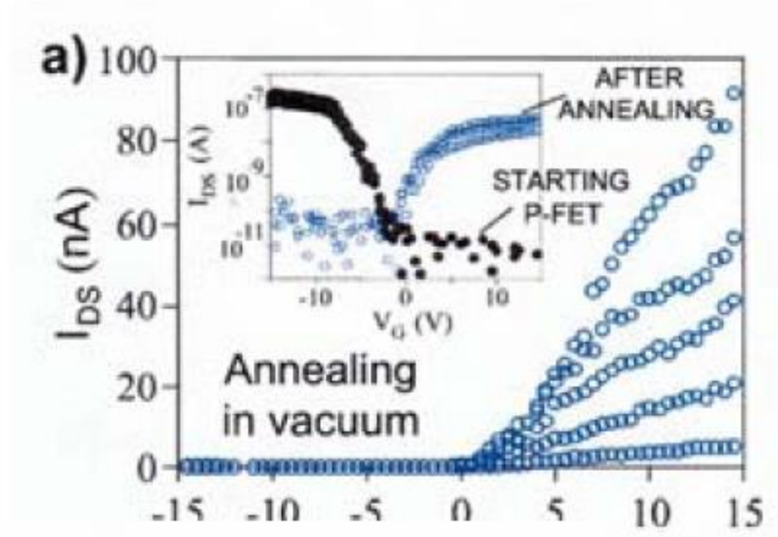
p-type behaviour !

CNT-BASED LOGIC

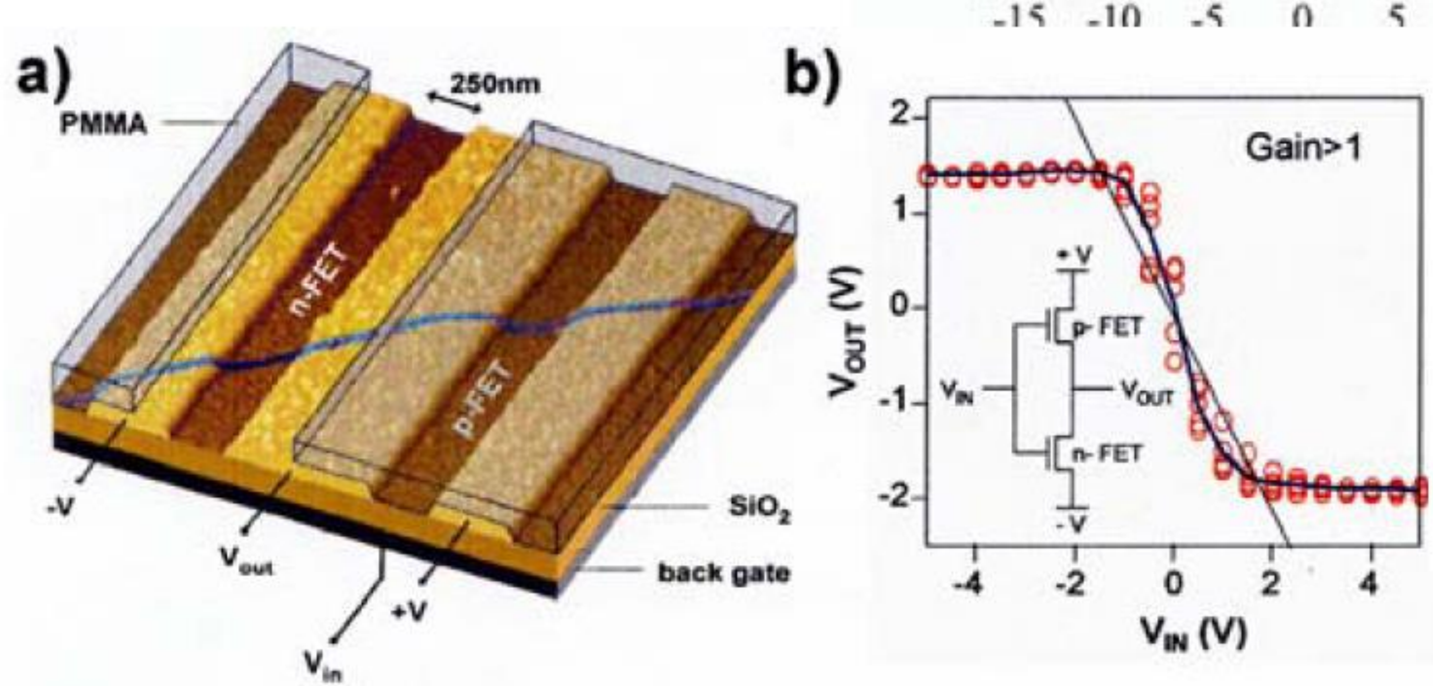
Carbon Nanotube Inter- and Intramolecular Logic Gates

V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris*

IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

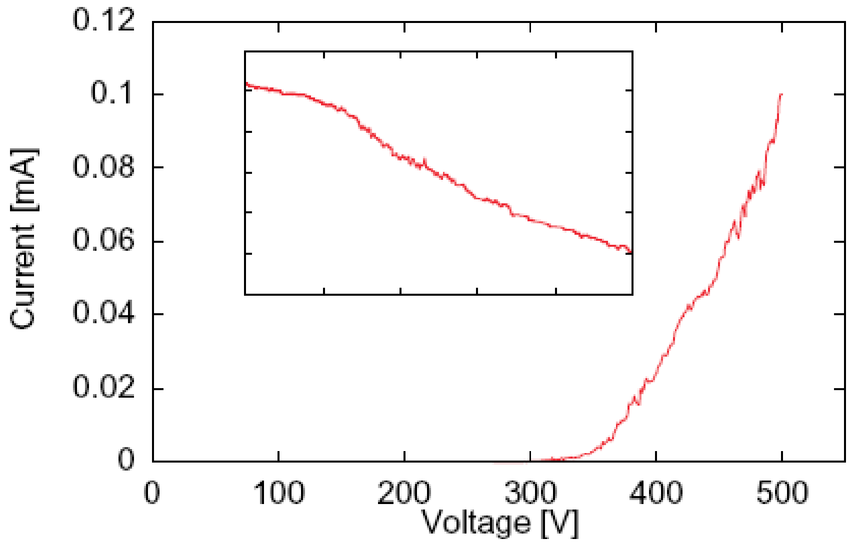


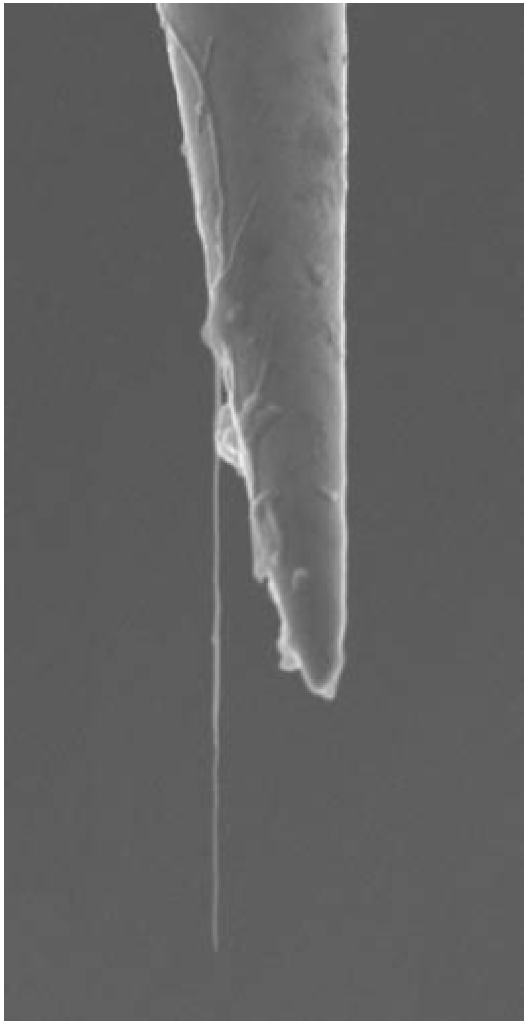
complementary logic based CNT inverter

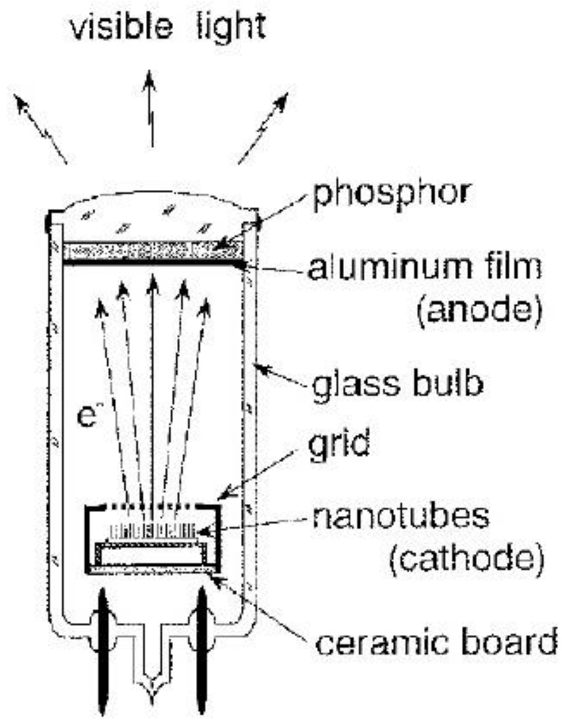


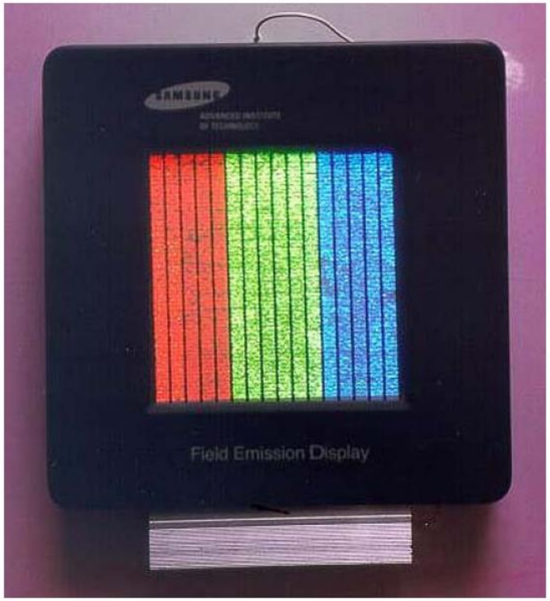
CNT FIELD EMITTERS

- low voltage (100V @ 1mm)
- high currents (0.2 mA)
- stable emission









SONY

Samsung

Motorola ...