Week 1-12

Purity and Crystal Growth

Materials purification
Crystal Growth
Thin film growth

Chapter 5.1 – 5.4.2.3

Objectives

- Provide a “hands-on” description about how devices are made
- Describe material purification methods
- Describe the various techniques for high quality materials growth
    - Single crystals
    - Solution deposition
    - Vapor phase deposition
- Discuss post-growth film preparation (annealing)
- Describe methods of device patterning
- Understand packaging, and why it is needed

Material Purity

To achieve high quality optoelectronic properties, materials must be purified

Impurities take many different forms:

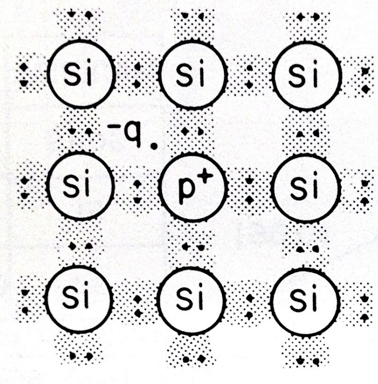
- ➢ Extrinsic defects
    - Dopants and “dirt”
    - Substitutional
    - Interstitial
- ➢ Intrinsic defects
    - Vacancies
    - Stacking faults

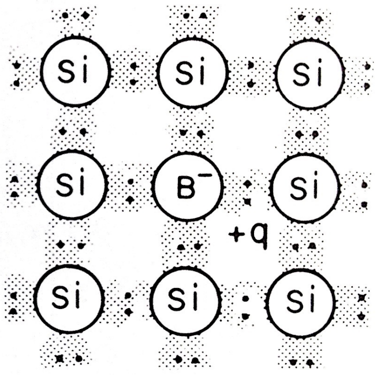
Due to lack of bonds in vdW solids, impurities have different effects

- Create stacking faults
- React with molecular constituents
    - ✧ Create unwanted bonds
    - ✧ Create fragments

In all cases, the inclusion of <u>unwanted</u> impurities leads to undesirable outcomes

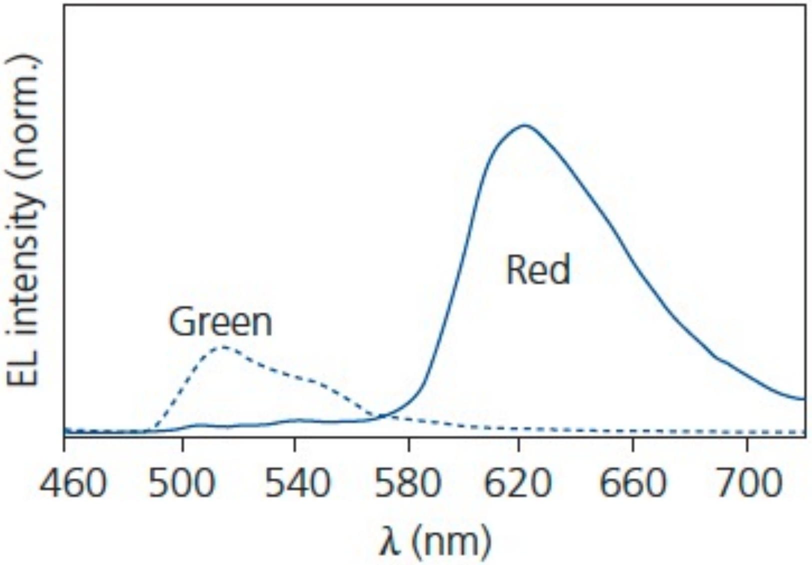
This is different from doping to change the conductivity of a semiconductor





Example of dopant cross contamination

Contaminated green PHOLED emission



- A green phosphorescent OLED contaminated with *1/500 monolayer* of a red phosphor shows relatively higher red emission.
- Both phosphors doped in the same host in the light emitting layer
- Indicates extreme sensitivity of organic devices to impurities
- Not all impurities have equally strong effects (triplet trapping by lower energy red phosphor is highly favored)
- Similar sensitivities to impurities found in many inorganic devices
- Impurities impact performance and device lifetime

McGraw & Forrest, Adv. Mater. 25, 1583 (2013).

Common Methods of Purification

- Purification done primarily by selection of molecular weight and physical size
  ⇒ Small molecules achieve higher purity than polymers due to their Mw monodispersity
- Thermal methods “cleaner” than solution methods since no 3rd agent (the solvent) is introduced

- Thermal methods

  (Most appropriate for small molecules deposited from the vapor phase)

  - Zone refining
  - Gradient sublimation

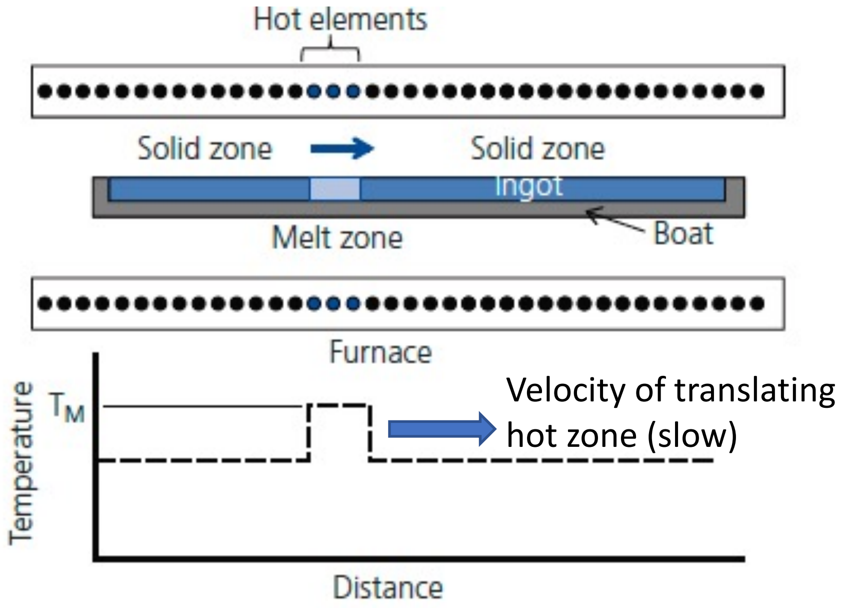
- Solution methods

  (Most appropriate for solution deposited small molecules and polymers)

  - Column chromatography
  - Size exclusion
  - Solvent washing
  - Centrifugation

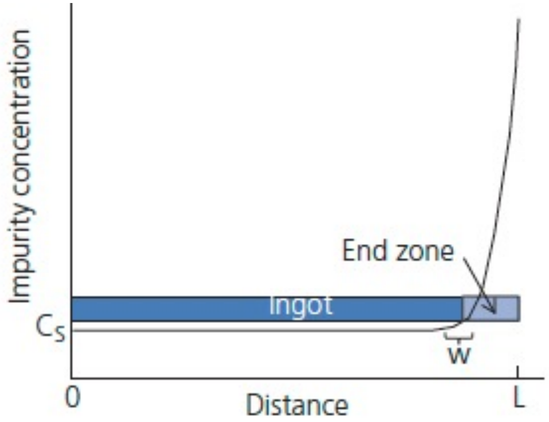
Zone Refining

- Useful for small molecules that have a solution phase at high T
- Purest crystals achieved using this method. but...
- Complicated and slow (impurities must have time to diffuse from solid to melt)



Velocity of translating hot zone (slow)

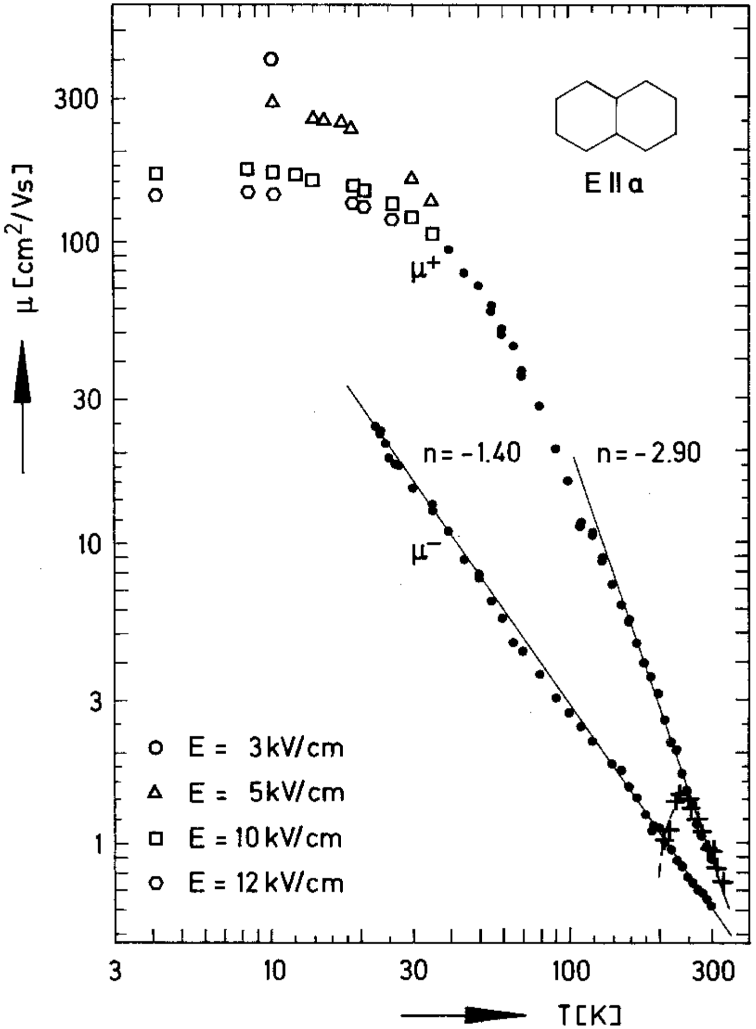
Ingot profile after zone refining sweep

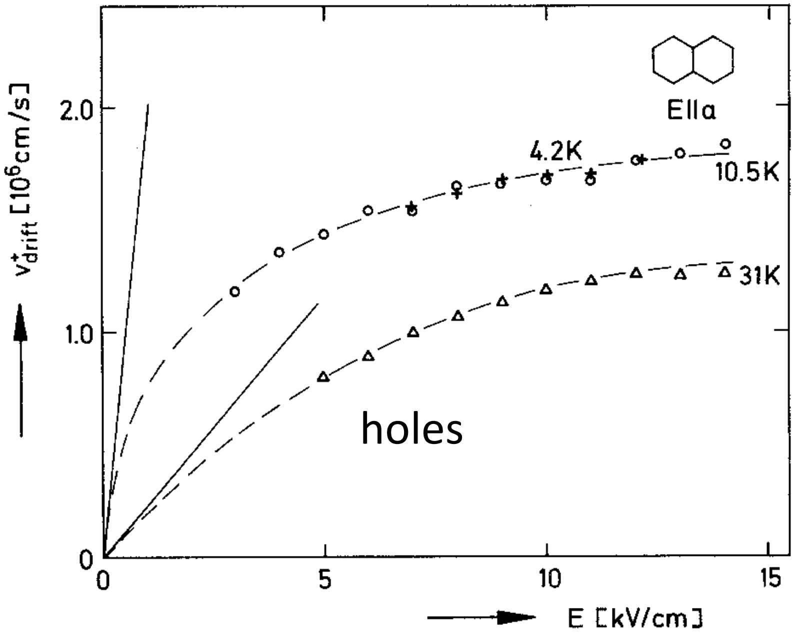


- If the distribution coefficient, $k=c_S/c_L > 1$ for impurities, then impurities will separated into a hot melt zone swept along the length of the ingot.
- Once the thermal sweep is complete, remove the end section with all the impurities
- Repeat until as pure as possible
- If $k < 1$, the impurities are trapped in the melt and the reverse process is used/

Band Transport Observed in Ultrapurified Naphthalene and Parylene

- Ultra-purified naphthalene (see Ch. 4)



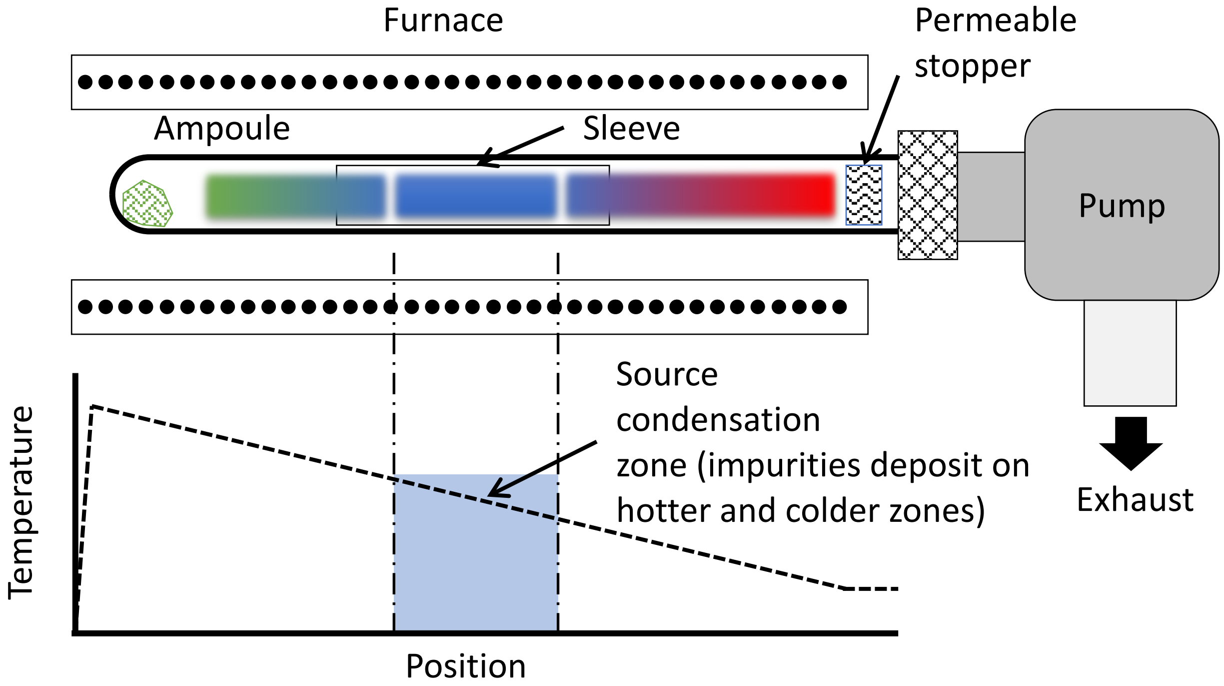


Band-like behavior: charge velocity saturation

Zone refined single crystals show properties of conventional, band-like inorganic semiconductors

Purification by Thermal Gradient Sublimation

Useful for obtaining very high purity small molecule materials



Furnace

Permeable stopper

Ampoule

Sleeve

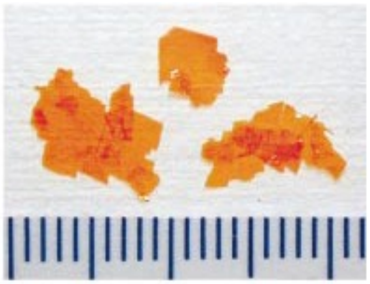
Pump

Exhaust

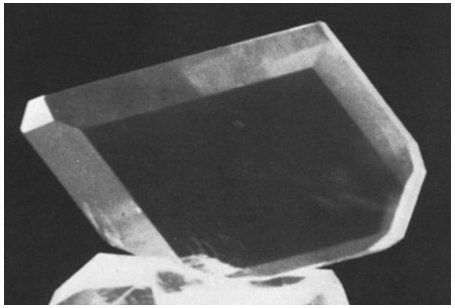
Source condensation zone (impurities deposit on hotter and colder zones)

Temperature

Position



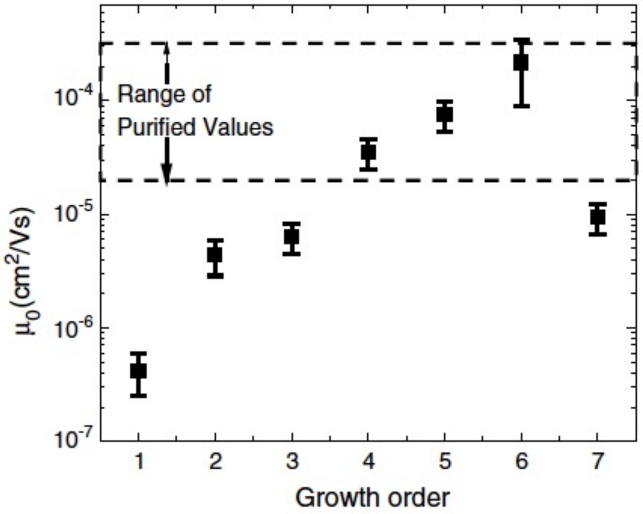
Tetracene after sublimation



Pyrene

- Reasonably fast and simple
- Material must be sublimable
- Multiple cycles result in higher purity
- Can occur in vacuum or under inert gas flow
- Small crystal growth on chamber walls possible

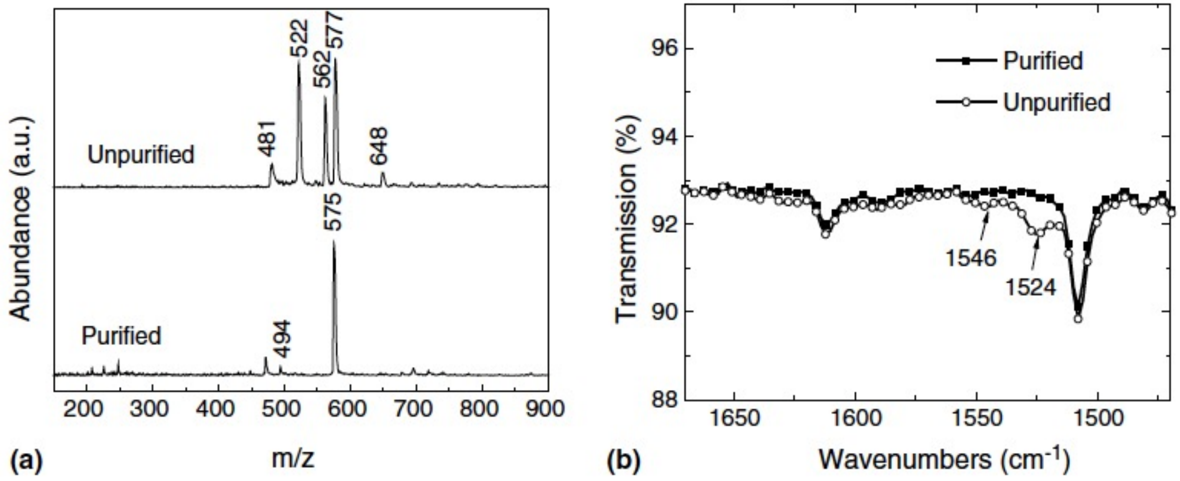
Purification of CuPc via Multi-cycle Sublimation in Vacuum



Mobility increases with sublimation cycle due to increased purity

reduction of impurity signatures

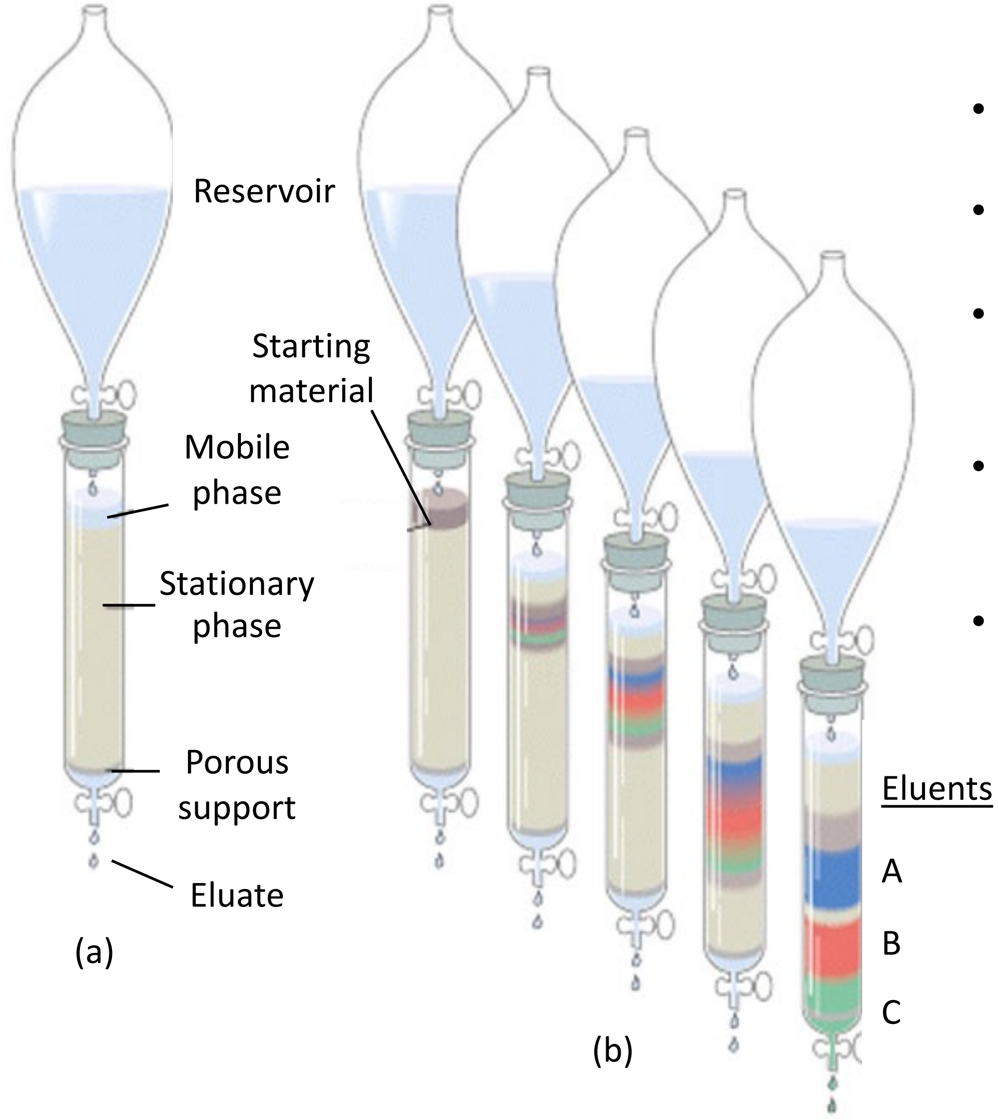
H_2Pc main impurity



Salzman, et al., Organ. Electron. 6, 242 (2005)

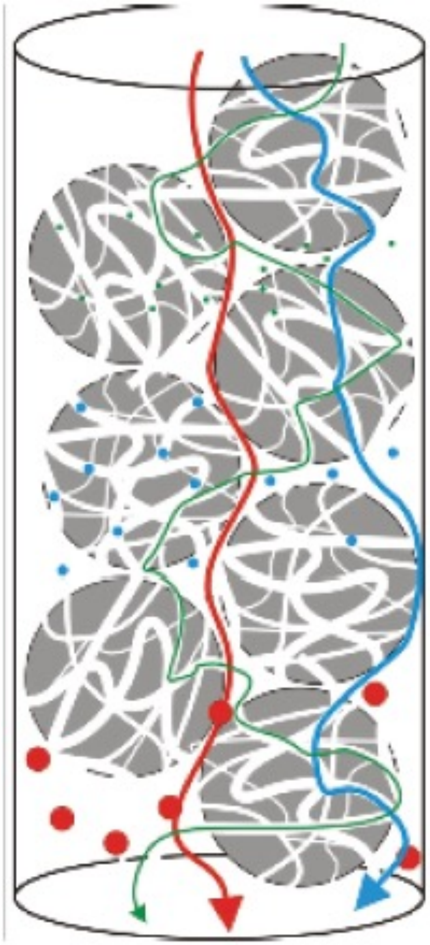
Purification via Solution

Column High Pressure Liquid Chromatography (HPLC)



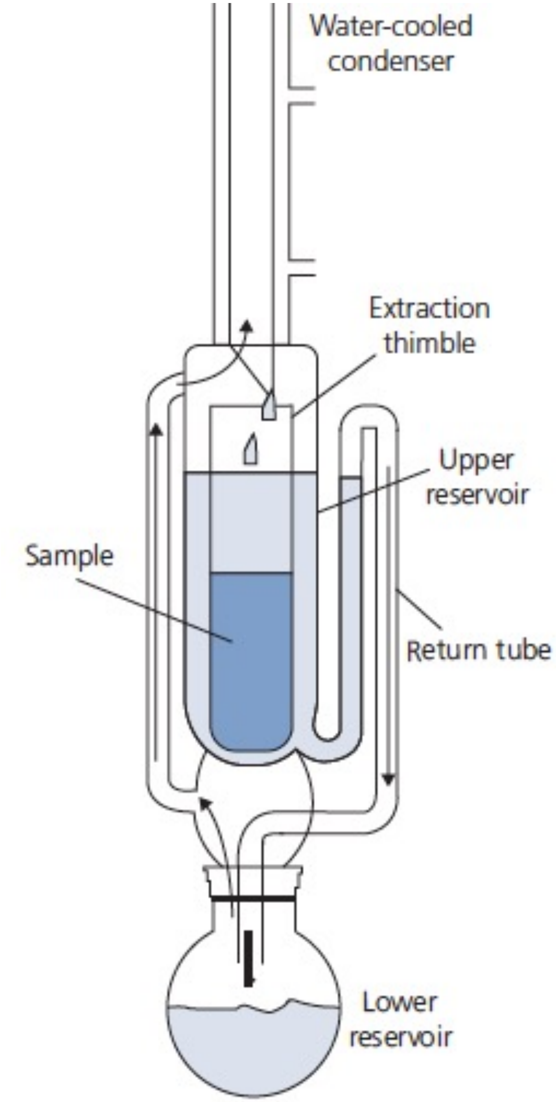
- Crude material (mobile phase) placed in reservoir
- Moves through column packed with material that impedes flow (stationary phase)
- Smaller impurities (C) move faster than larger (A). Material of interest (B) moves at intermediate rate.
- Selectively collect the material of interest (the eluent) when it arrives at bottom of column.
- Pressure applied to the solution makes the process move faster.

Size Exclusion Chromatography



- Column filled with porous beads
- Small particles flow through pores, large particles flow between beads
- Rate at which the solute is collected depends on length of path travelled
- Separate source from impurities by selecting their times of arrival at output

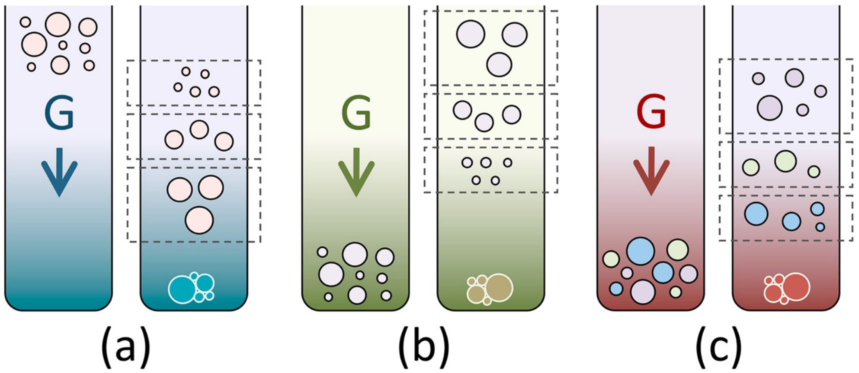
Solvent Washing via Soxhlet

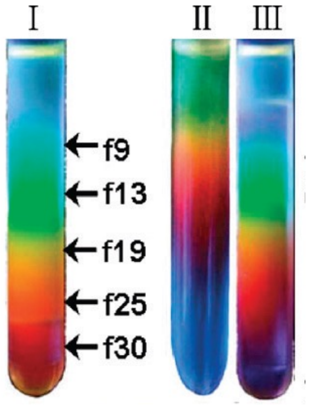


- A solvent reflux process
- High bp solvent placed in lower reservoir and heated
- Vapors condense and wash sample material in porous thimble
- After sufficient solution collects, it siphons back to lower reservoir
- Process repeats until (a) material clean or (b) solvent contaminated and replaced

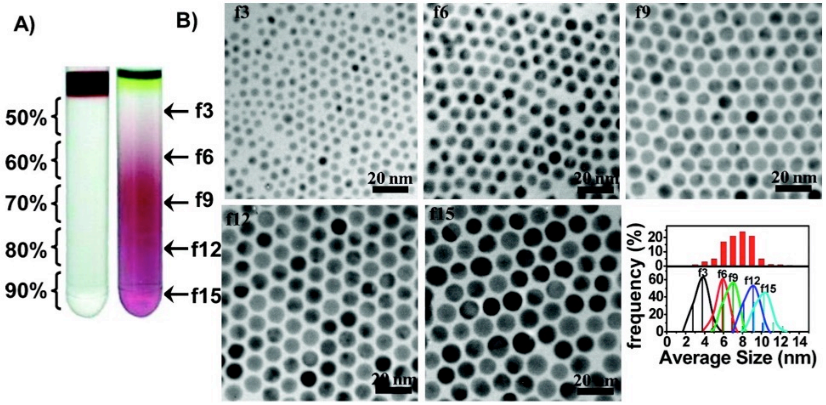
Purification via Centrifugation

Density gradient centrifugation



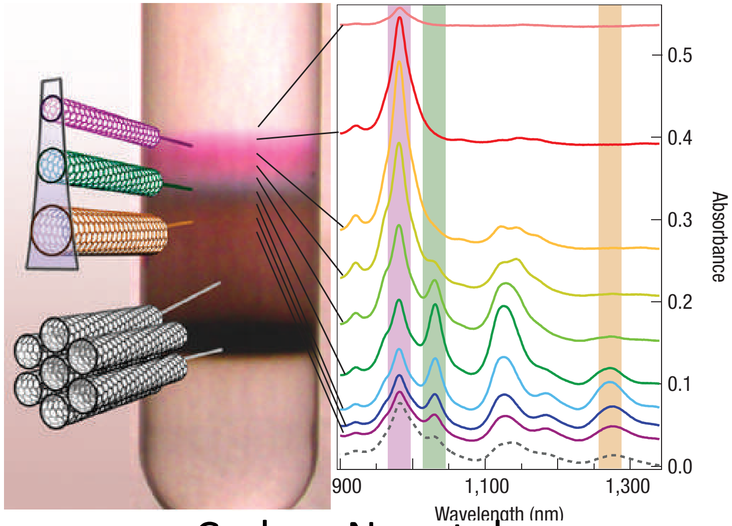


- Solvent density is graded from top (low density) to bottom (high density)
- Centripetal force (G) applied at 20 – 80K rpm. (a) Heavier particles float to bottom, (b) lighter to the top. (c) Particles of different particles separate independent of size.
- Micropipette extracts particles of desired size and density



Quantum Dots: 2 Solvent Mixture

Bai et al., J. Am. Chem. Soc. 132, 2333 (2010)



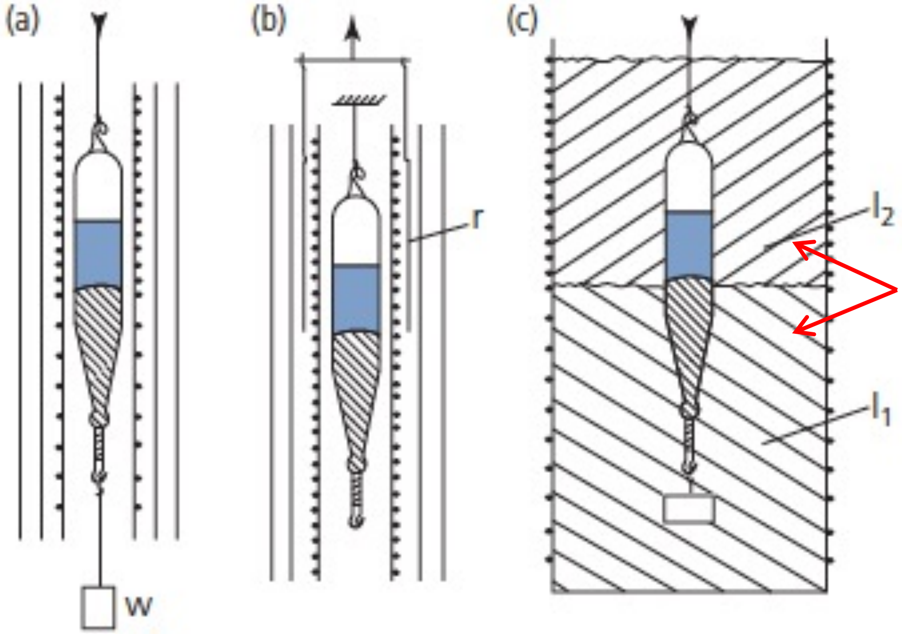
Carbon Nanotubes

Arnold et al., Nat. Nanotech. 1, 60 (2006)

Crystal Growth: Bridgeman Process

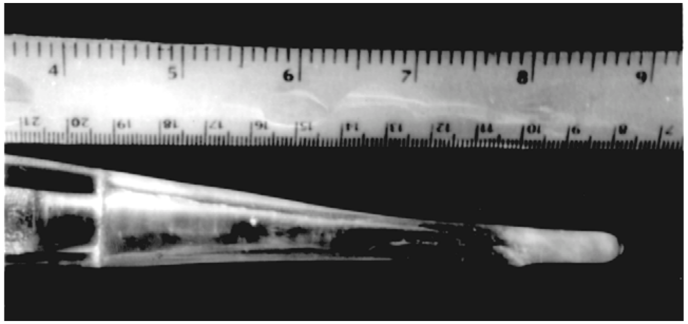
Material has to have a solution (melt) phase

Growth front moved from position of seed



Two different, immiscible liquids

Three ways to manage the growth front temperature
(a) bias-wound heating coil, (b) reflective shield around top coils, (c) immersion into a fluid with two immiscible liquids to conduct heat

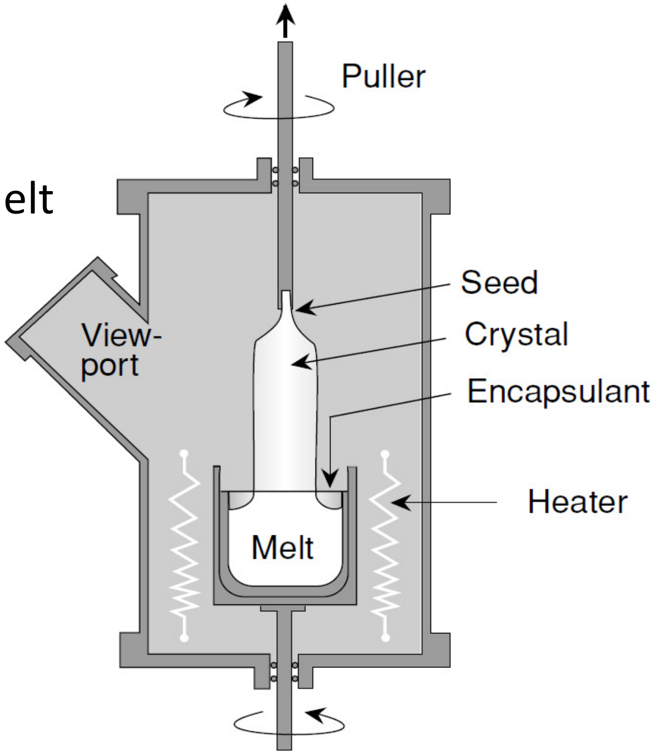


anthracene single crystal

Crystal Growth: Czochralski Process

Material has to have a solution (melt) phase

Seed slowly pulled from melt



Benzophenone crystal boules

Sankaranarayanana and Ramaswamy J. Cryst. Growth 280, 467 (2005)

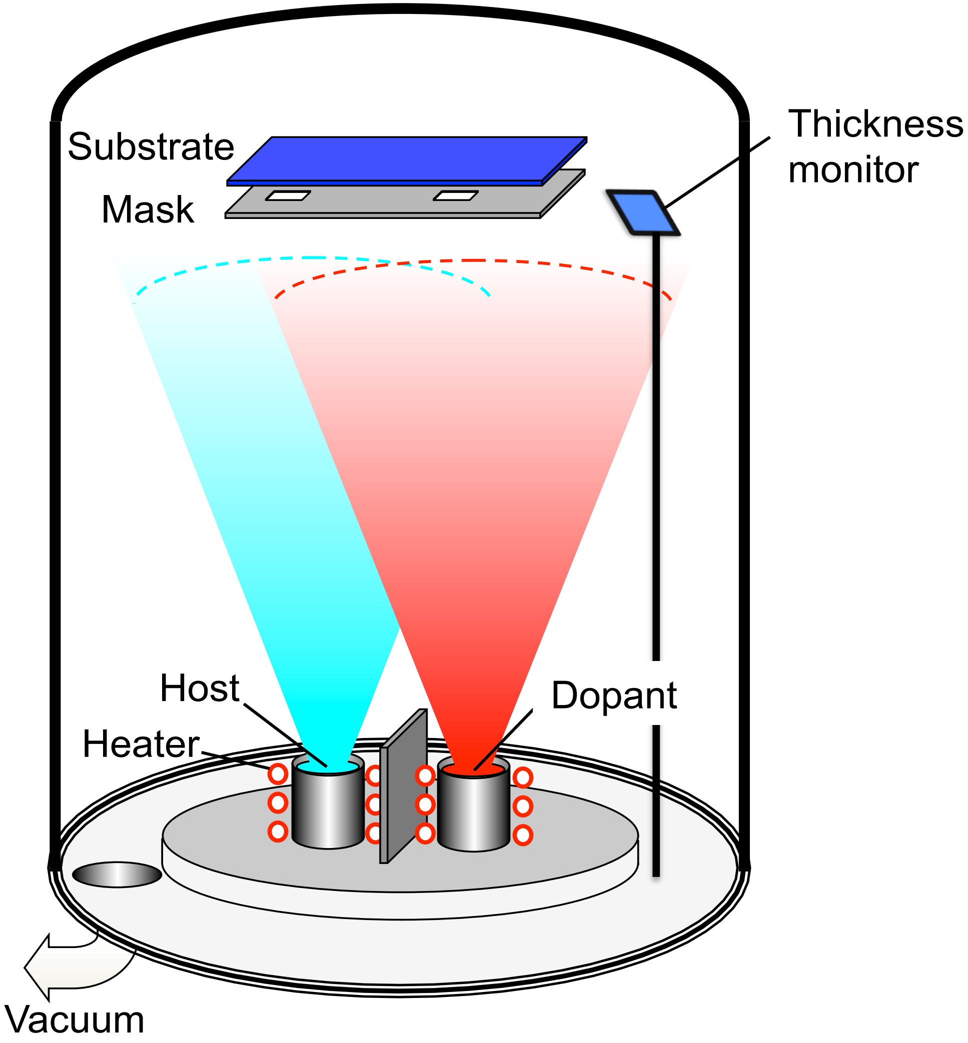
Film Deposition Techniques

Main objective: To deposit high purity materials with precise thickness control and a uniform morphology (i.e. no clusters, tears, dust, etc.)

- Two principle methods
  - ➢From the vapor phase - employs evaporation of small molecules
    - ✓Vacuum thermal evaporation
    - ✓Organic vapor phase deposition
  - ➢From the solution phase – employs solvation and drying of polymer or small molecule solutes
    - ✓Spin on
    - ✓Spray on
    - ✓Spread on

Vacuum Thermal Evaporation (VTE)

- Most common method to date
- Simple
- Precise
- Multilayer structures possible
- Small molecules, not polymers
- Wasteful of materials
- High vacuum: 10^{-7} torr
- Oil-free pumps



In-line VTE for Mass Production

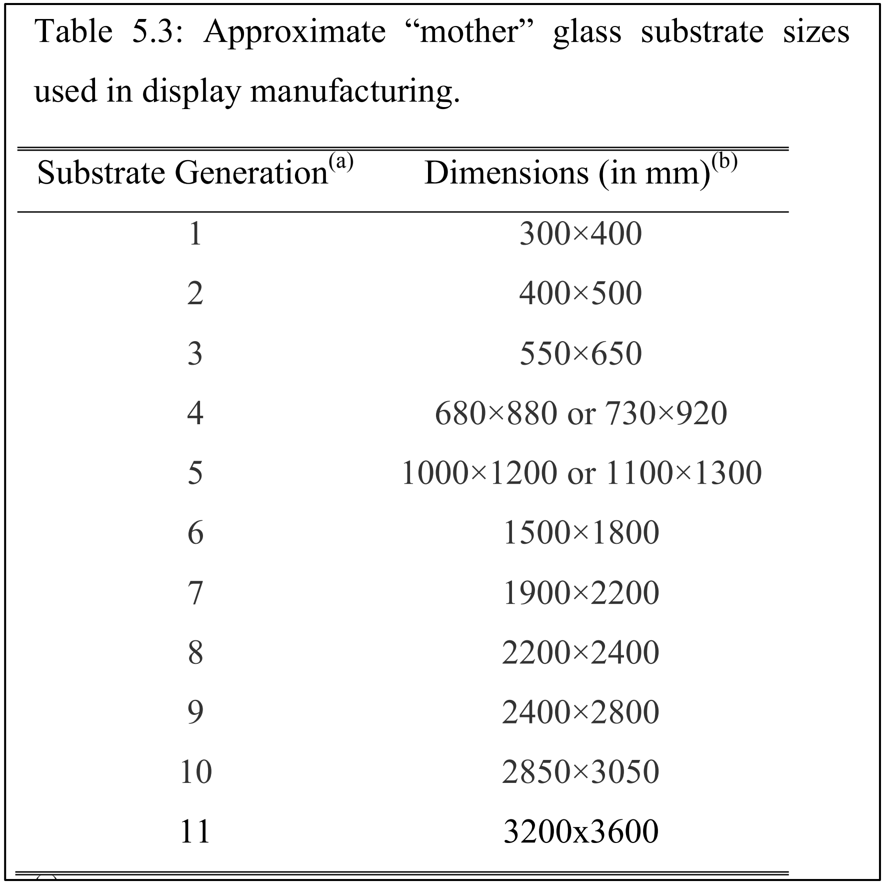
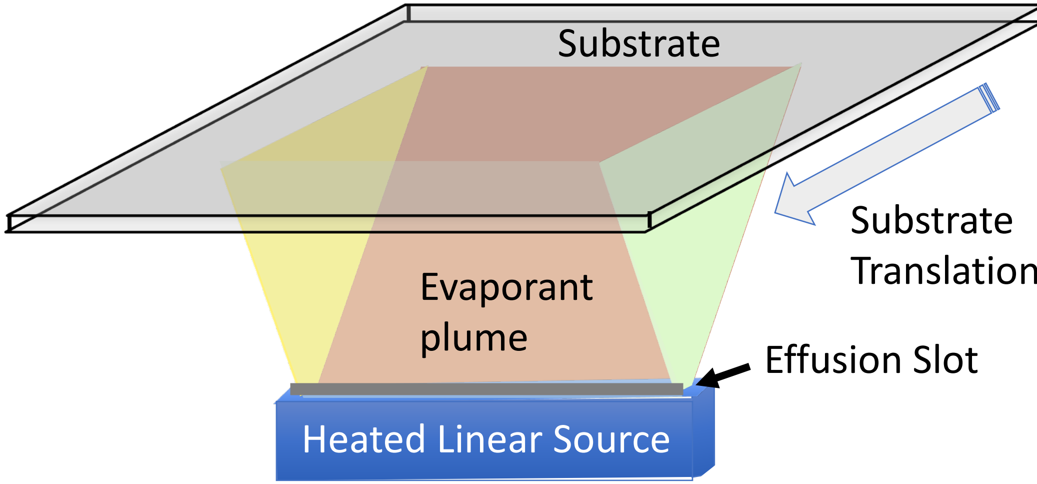


Table 5.3: Approximate “mother” glass substrate sizes used in display manufacturing.

Substrate Generation[(a)]	Dimensions (in mm)[(b)]
1	300×400
2	400×500
3	550×650
4	680×880 or 730×920
5	1000×1200 or 1100×1300
6	1500×1800
7	1900×2200
8	2200×2400
9	2400×2800
10	2850×3050
11	3200x3600



- Display manufacturing lines ~100-125 m in length!
- Glass substrate thickness ~0.3-0.7 mm
- Precise doping requires coincident fluxes from >1 linear source

Organic Molecular Beam Deposition (OMBD)

Ultrahigh Vacuum Environment: ~10^{-10} torr

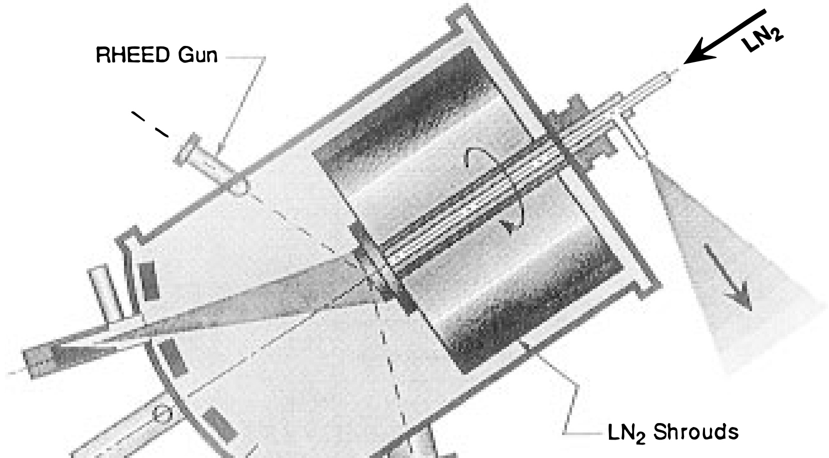
Extremely low impurity concentrations

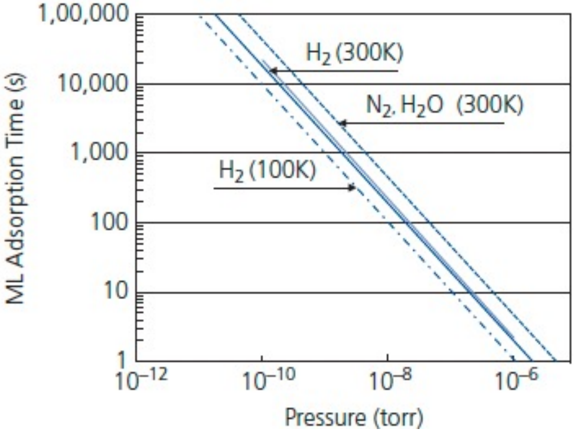
Scientific exploration

Monolayer growth control

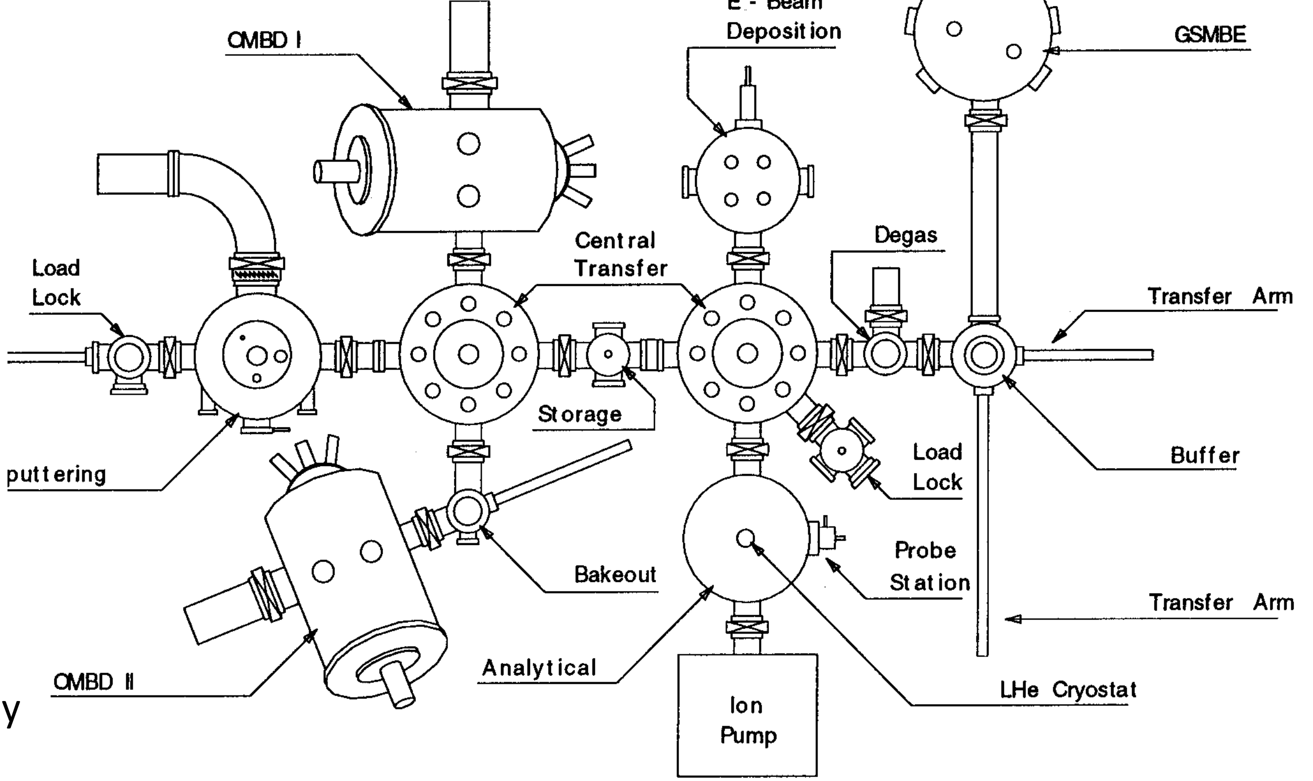
In-situ diagnostics

- RHEED, PES, I-V…



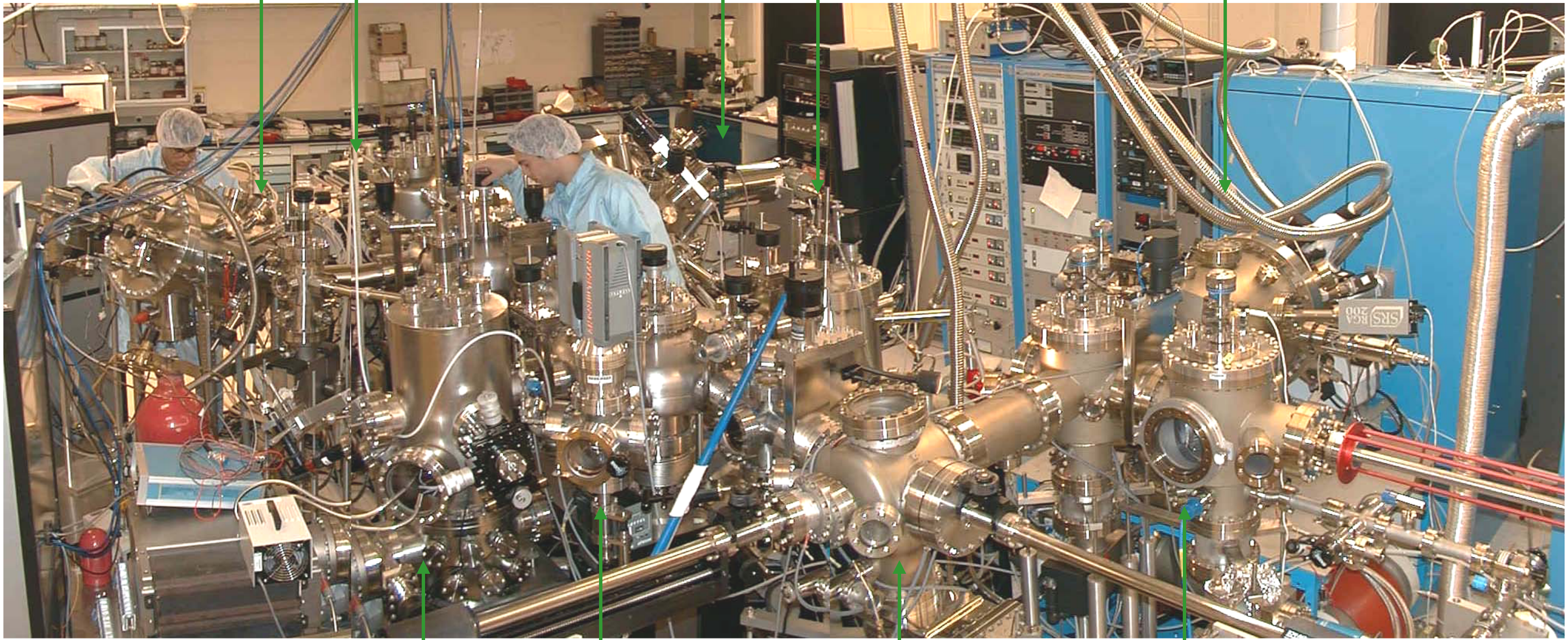


Time to adsorb a ML of impurity gas vs. bkgrd. pressure



Organic Materials Growth Laboratory

Base Pressure 10^{-9} ~ 10^{-11} Torr



OMBD II

Sputtering

OMBD I

Metal e-Beam

III-V MBE

Analysis Chamber

Load Lock

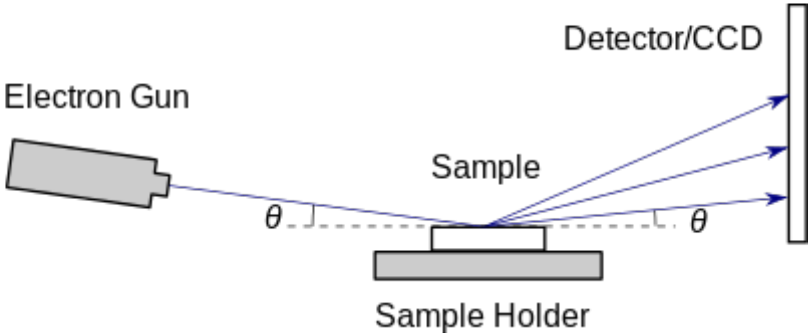
Transfer Chamber

Load Lock

RHEED: An important growth diagnostic

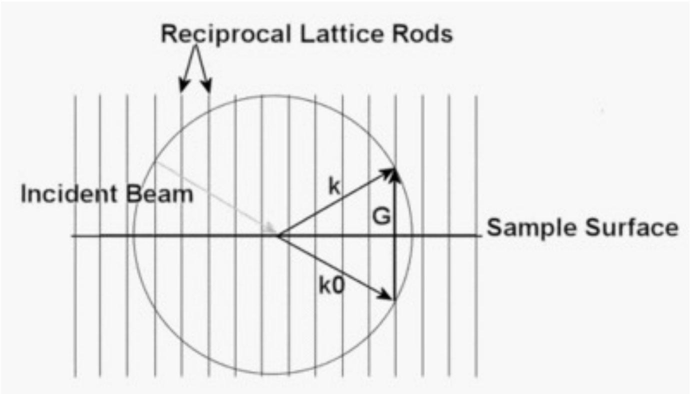
RHEED: Reflection High Energy Electron Diffraction

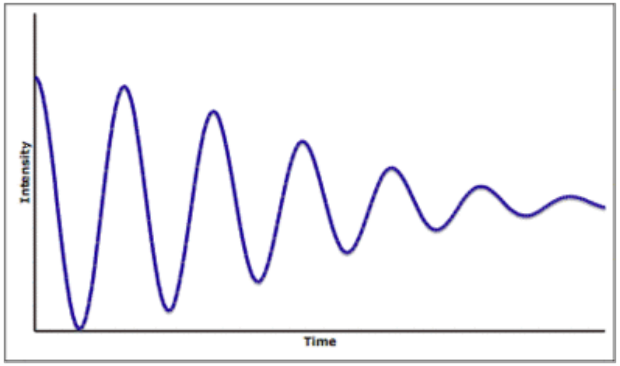
- Uses electron diffraction to monitor development of crystal structure during growth
- Employed in both OMBD and OVJP
- Analogous to glancing incidence x-ray diffraction: only monitors surface layers (e- penetration depth only 1 or 2 MLs



Experimental set up
Beam angle: $\theta = 1 – 2^{o}$

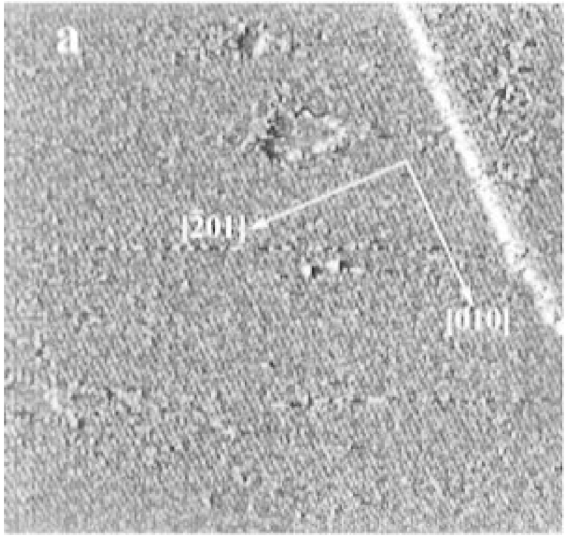
- 2D lattice "surface mesh" projects diffraction lines compared to spots in 3D
- Line spacing = surface mesh lattice constant
- Rotation of sample under beam gives surface lattice symmetry
- Intensity oscillation number = number of MLs deposited (partially filled layers are more 3D and hence reduce diffracted beam intensity)



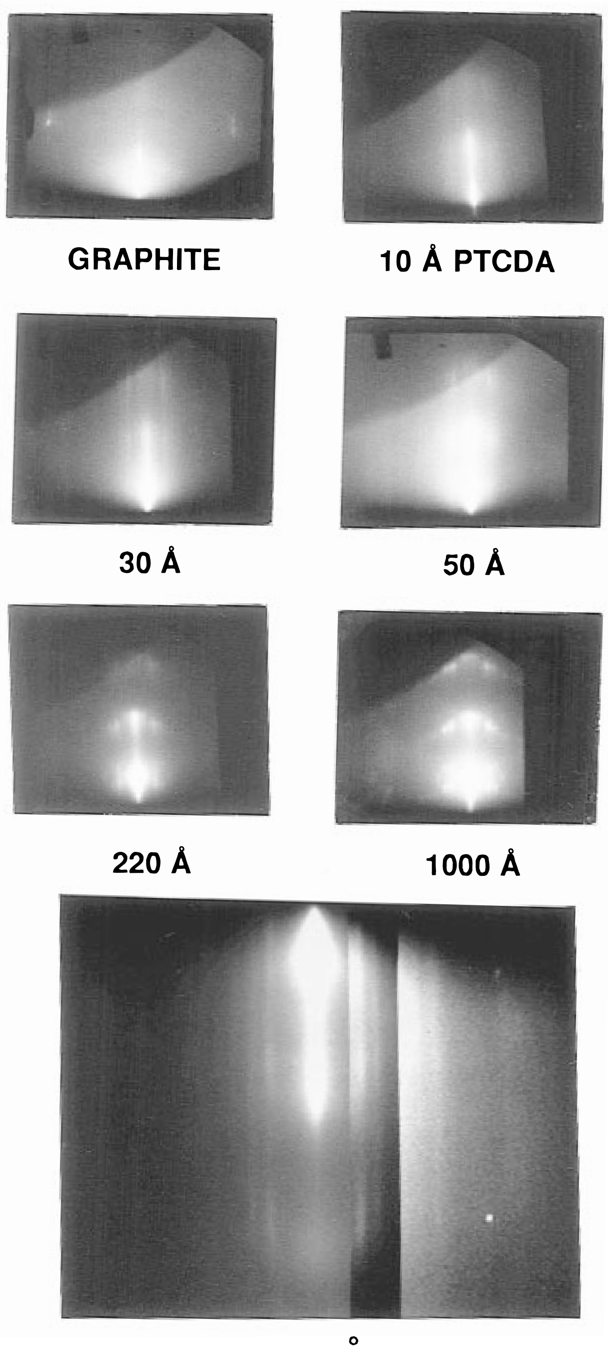


Specular beam intensity with growth time

Near Perfect Growth by OMBD



STM image of PTCDA on Graphite:
Layer by layer growth without epitaxial matching

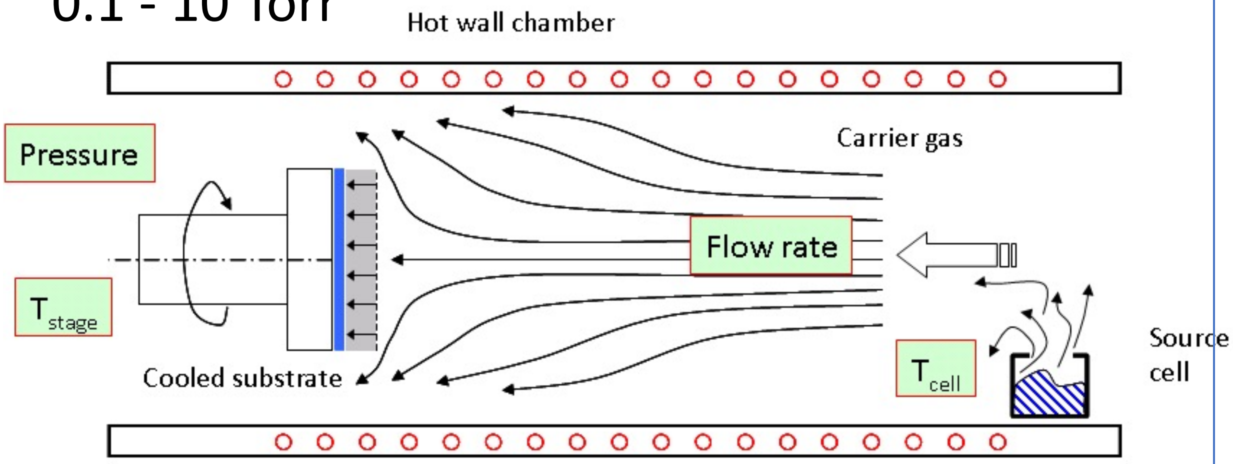

GRAPHITE
10 Å PTCDA
30 Å
50 Å
220 Å
1000 Å

20 Å

RHEED of PTCDA on Graphite:
Flat and ordered

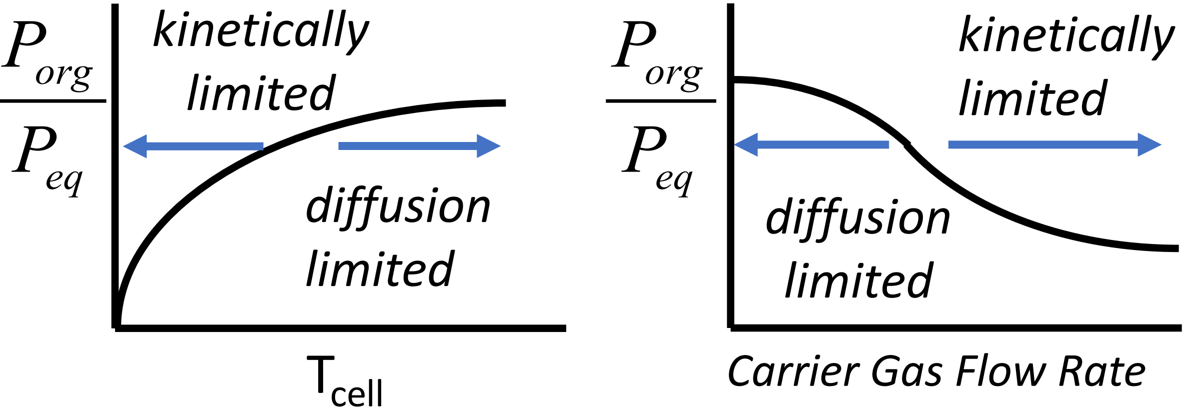
Organic Vapor Phase Deposition: Concept

0.1 - 10 Torr



- **Controlled and accurate doping** **(gas saturated with organics ~ equilibrium)**
- **Dust free chamber**
- **Efficient materials use**
- **Control of film crystal structure**

Constant Flow Rate *Constant Temperature*

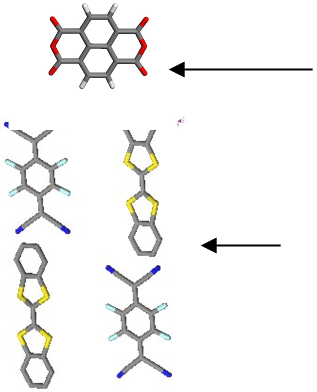


$$r_{out} = \frac{\dot{V}_{src}}{RT_{cell}} \cdot \frac{P_0 \exp(-\Delta H / RT_{cell})}{1 + \dot{V}_{src} / A_{evap} D_{org}}$$

M. Shtein, et al., J. Appl. Phys., 89, 1470 (2001).

Precision Growth by OVPD

RHEED is possible by minimizing e-beam path in the low pressure chamber



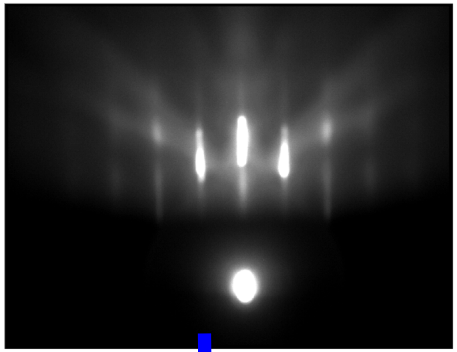
NTCDA

(20nm)

DBTTF-TCNQ

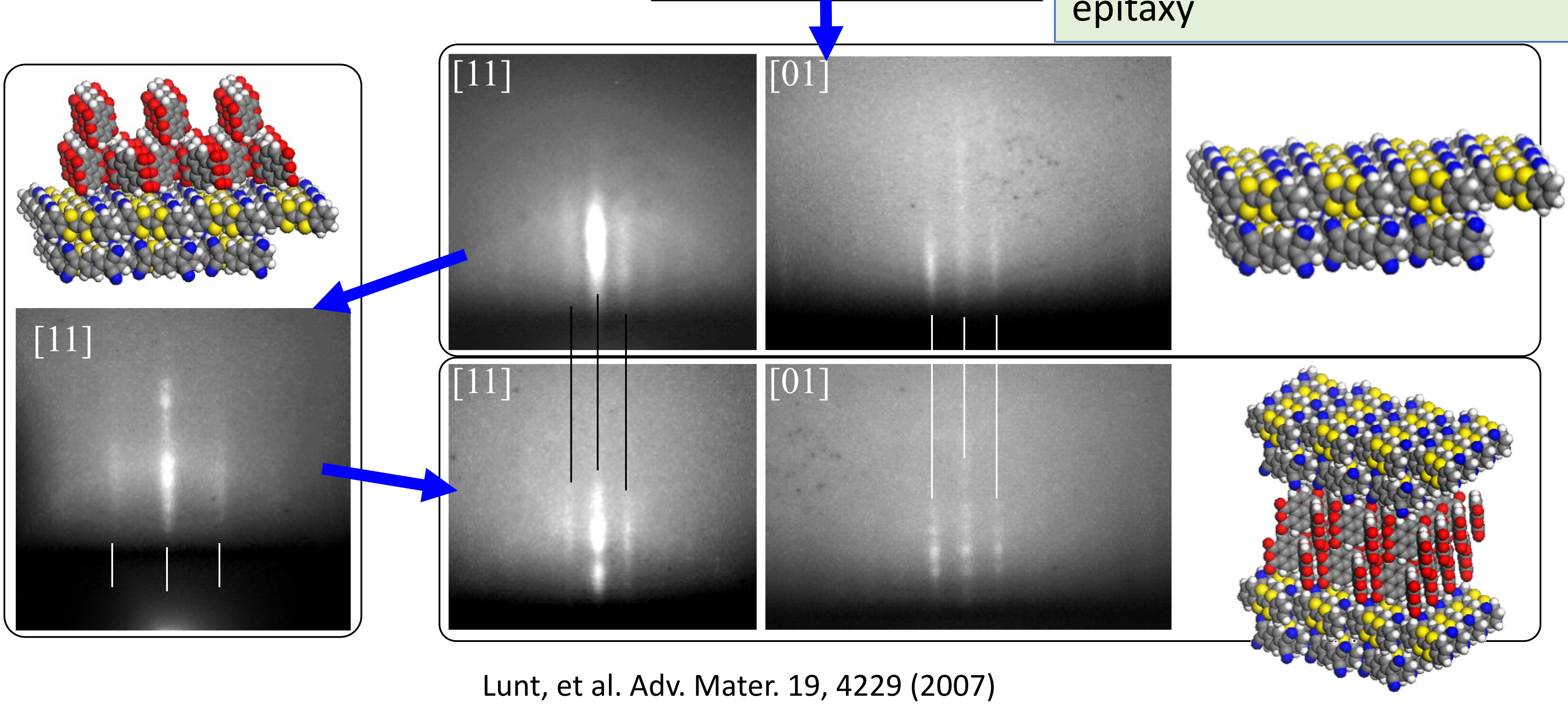
(20nm)

Substrate: KBr



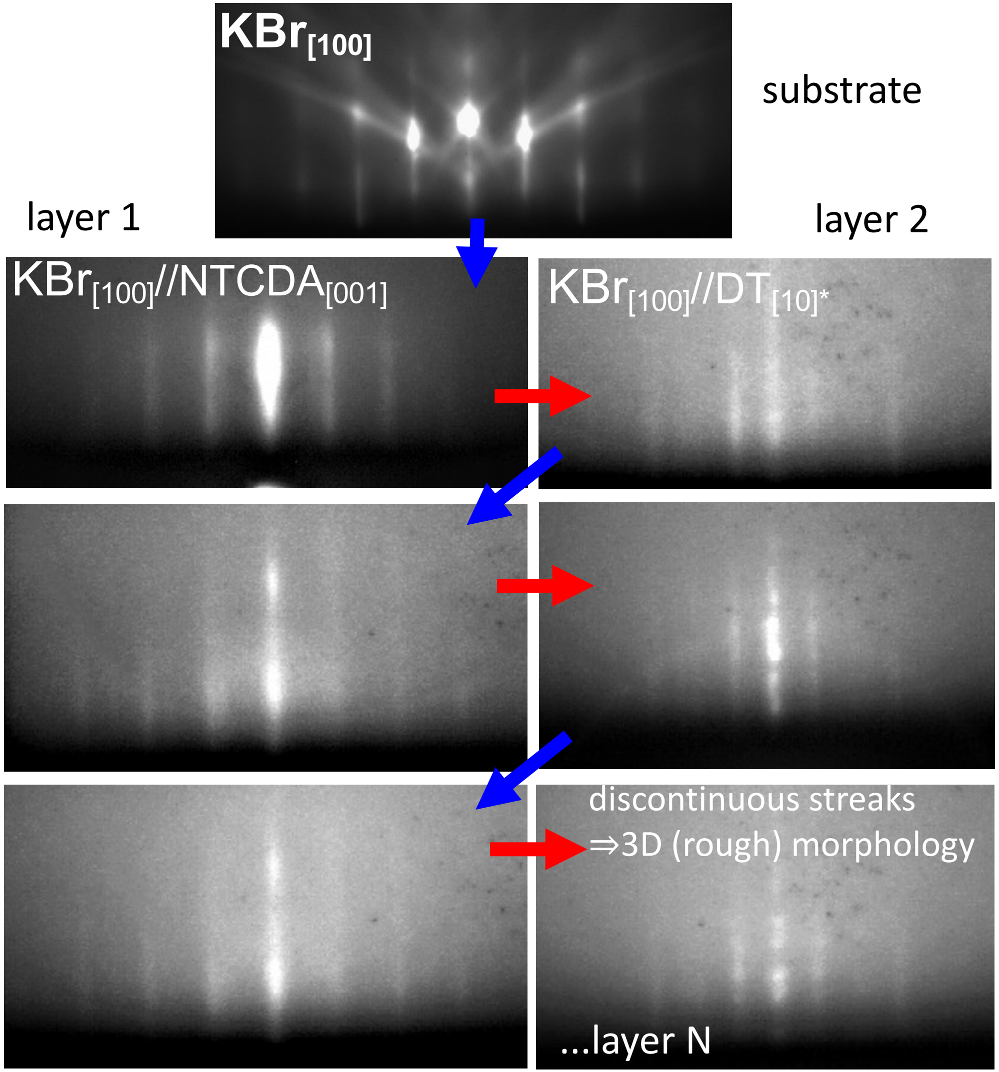
Combined Charge-Transfer Salts / Small Molecule Multilayer

Clear orientation to substrate w/o lattice match = quasi-epitaxy



Lunt, et al. Adv. Mater. 19, 4229 (2007)

6 Layer Multilayer QW Growth in OVPD



substrate

layer 1

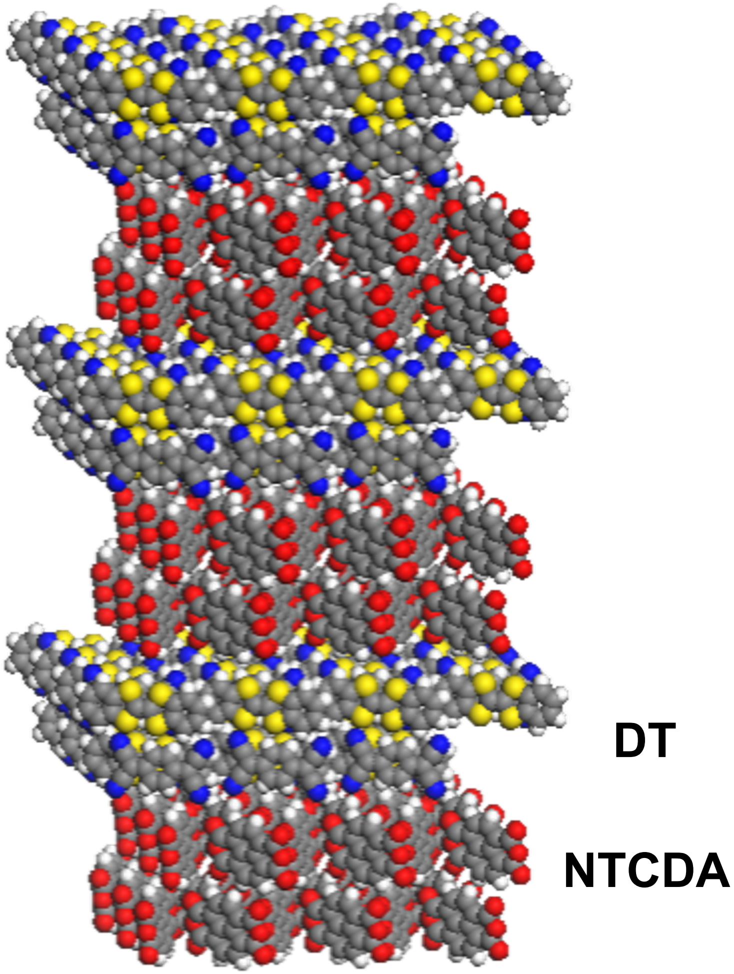
layer 2

discontinuous streaks

⇒3D (rough) morphology

...layer N

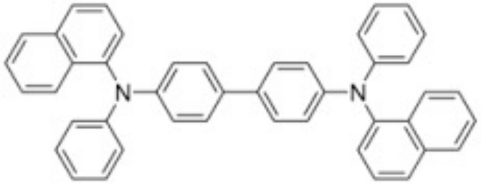
* $KBr_{[210]}$ ~ // $DT_{[01]}$ (surface mesh)



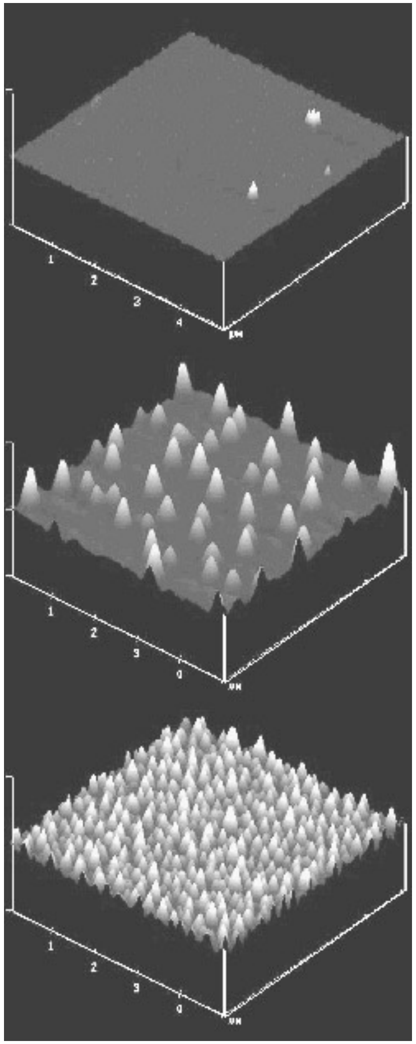
Crystallinity continues up to 12 layers of (5nm/5nm)

Lunt, et al. Adv. Mater. 19, 4229 (2007)

Morphology Controlled by Gas Flow and Temperature Conditions



α-NPD
(hole conductor)



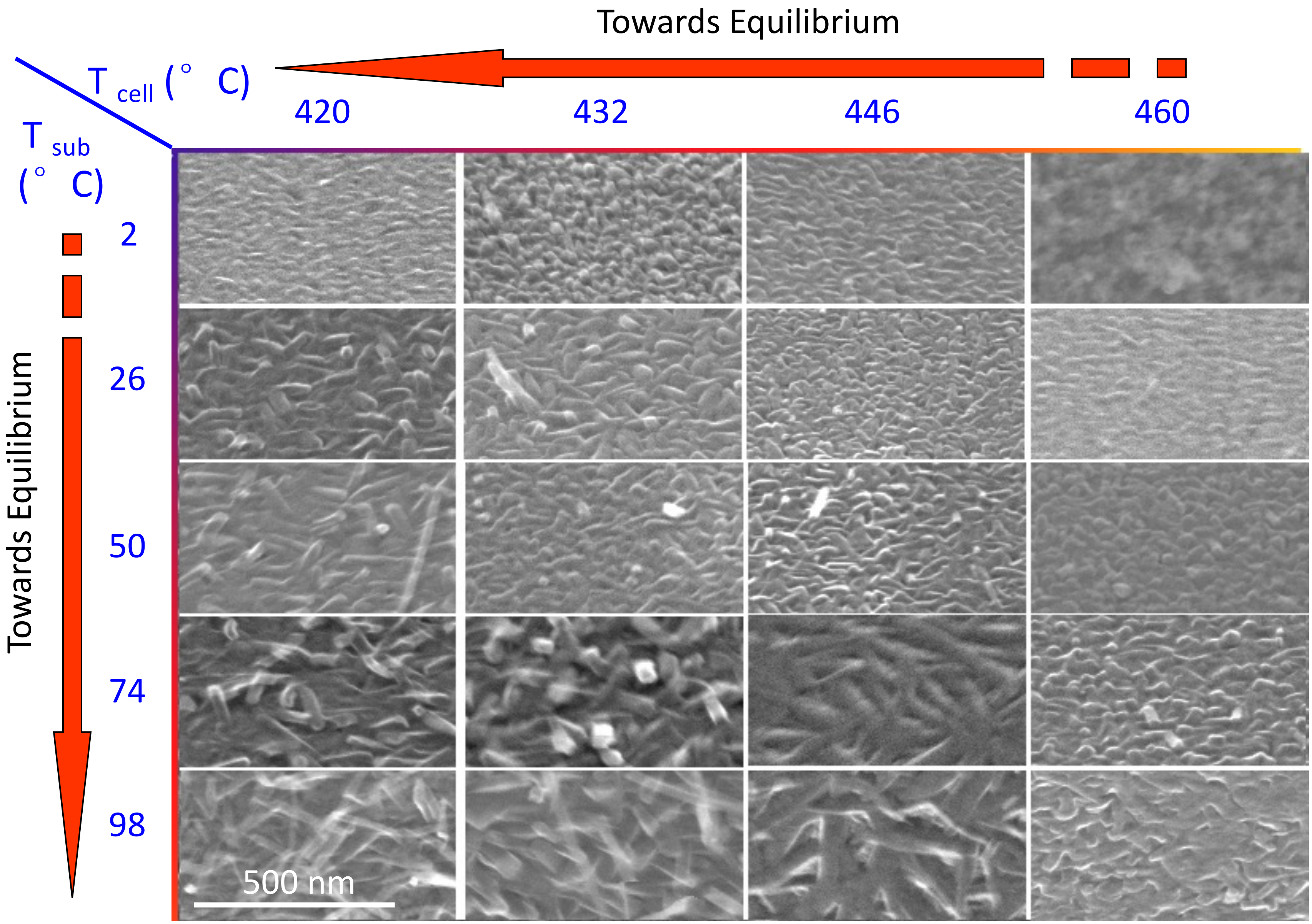
0.8 nm/s

1 nm/s

1.2 nm/s

Gas phase nucleation ensues at high deposition rates (“snowing”)

Nanomorphology control by temperature

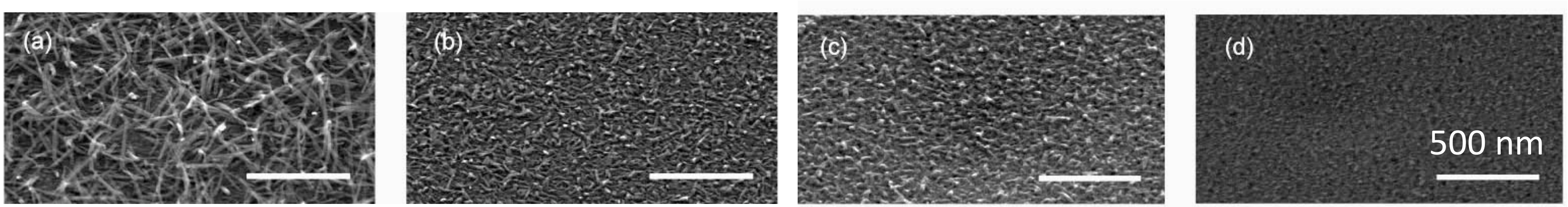


(flowrate = constant, pressure = constant)

Nanomorphology control by flow rate

(fixed source and substrate temperatures)

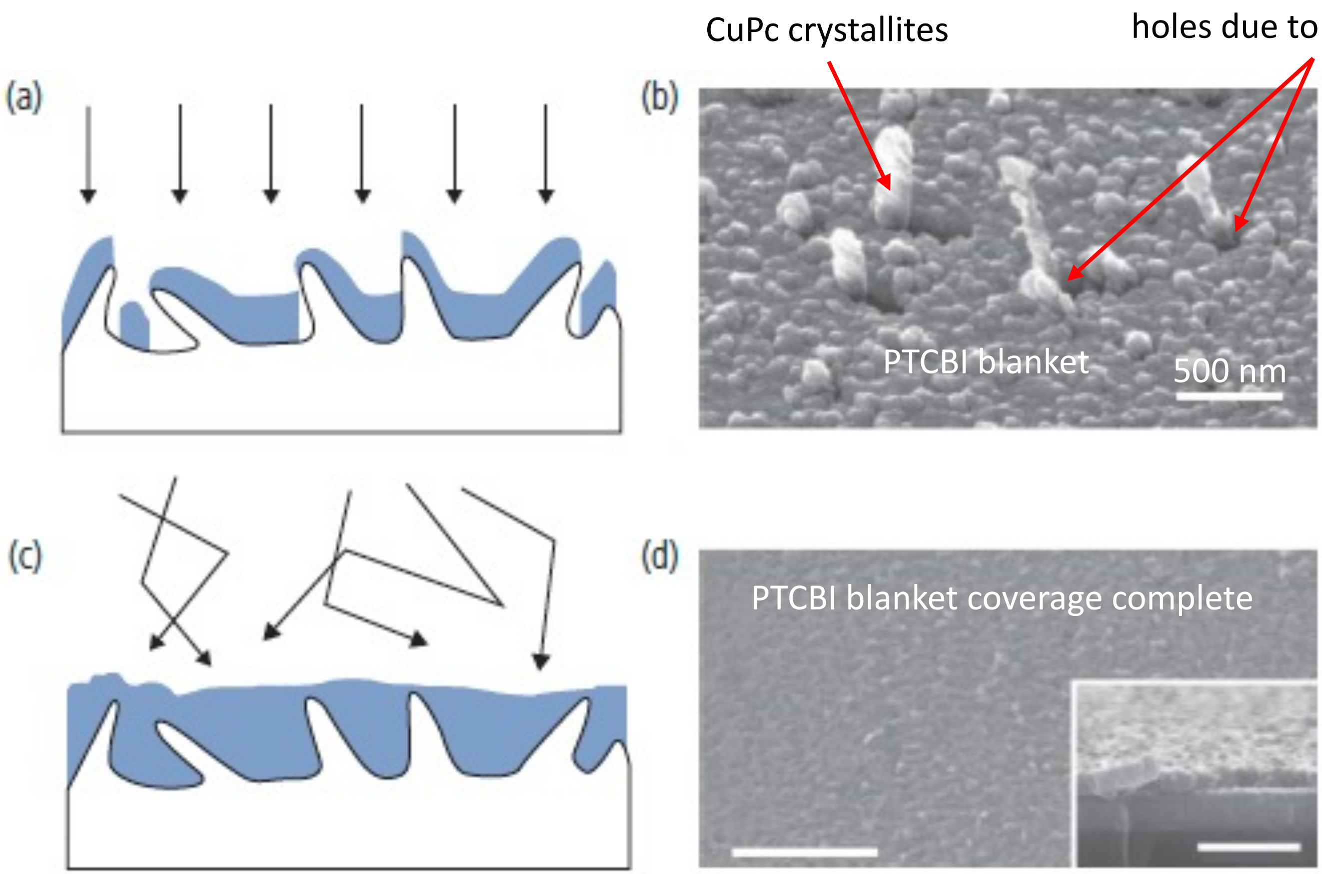
N_2 flow rate: 100 sccm 125 sccm 150 sccm 200 sccm



Increasing carrier gas flow rate

Crystals	Needle morph. Long, large	Flat morph. Uniaxial, small
Source temperature	Low	High
Substrate temperature	High	Low
Carrier gas flow rate	Low	High
Chamber pressure	Low	High

Differences between kinetic (VTE) and diffusion (OVPD) driven growth

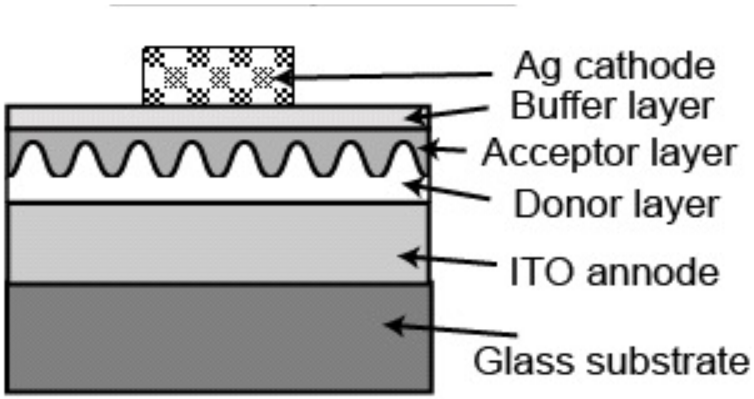


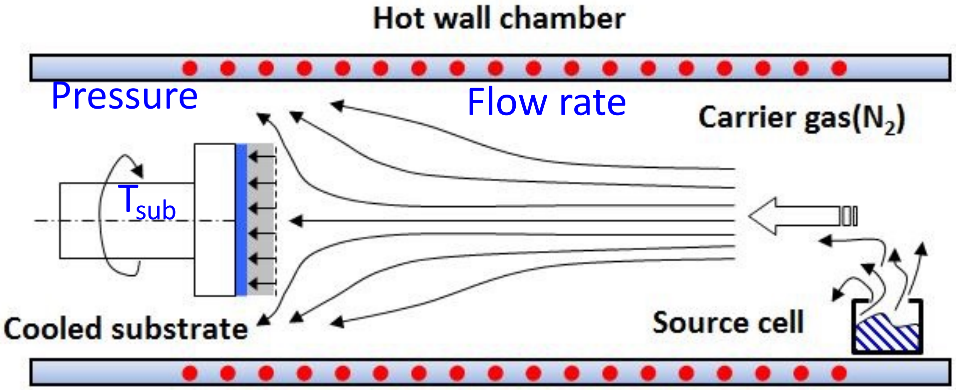
Kinetic regime: molecules follow line-of-sight trajectories
Mean-free-path >> chamber size

Diffusive regime: molecules random trajectories due to collisions with background gas
Mean-free-path << chamber size

Yang, et al. Nat. Mater. 4, 39 (2005)

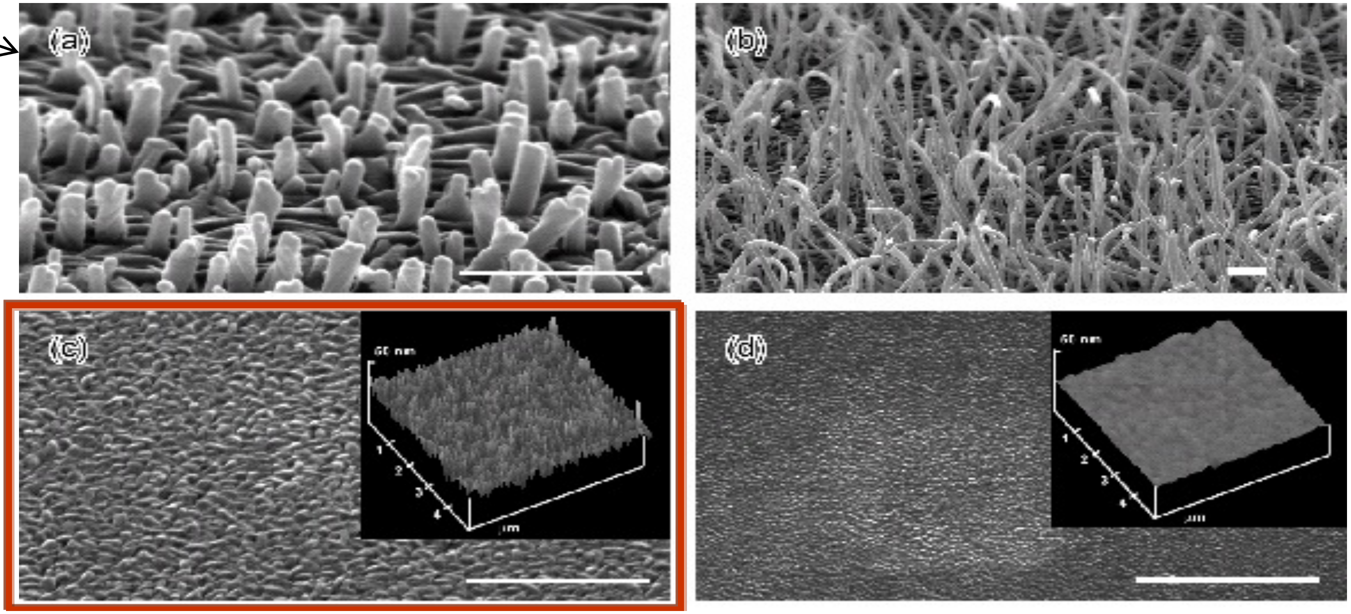
Controlled growth of a Bulk HJ by OVPD





Stranski-Krastonow growth

F. Yang, et al. Nature Mater., **4**, 39 (2005)



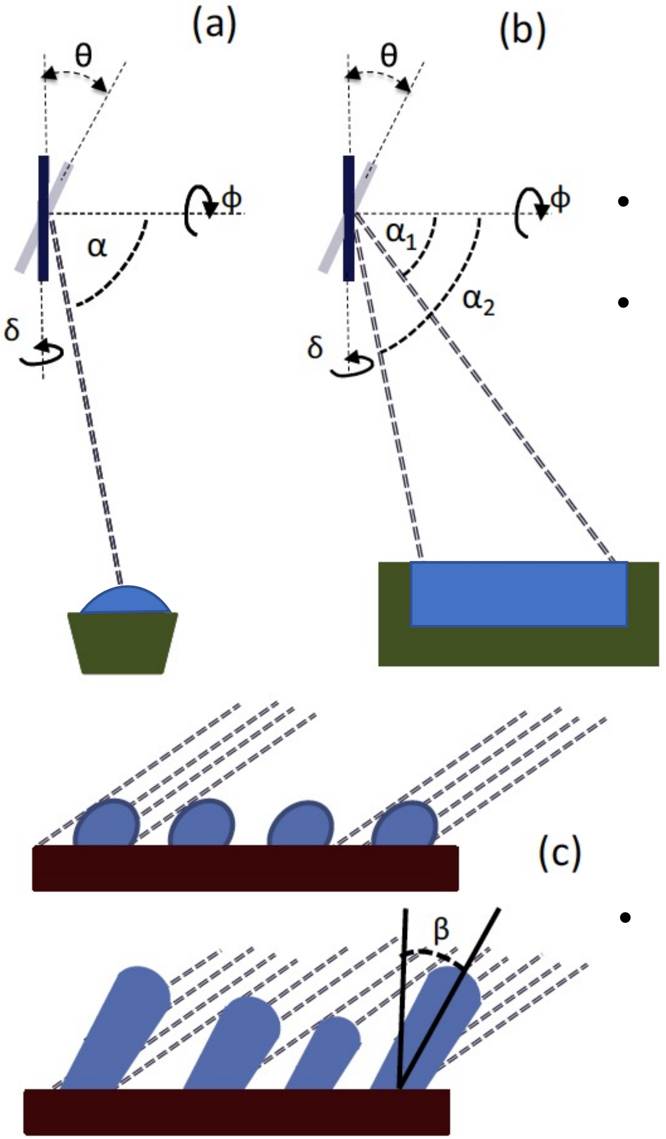
OVPD
rms~3.5nm

VTE
rms~0.3nm

Different strain and growth conditions result in different structure

Glancing Incidence Deposition Controls Deposit Structure

(see Ch. 6)



- Distributed and point evaporation sources.
- Point sources limit angles of incidence, controlling deposit morphology

- At glancing angles, initial nucleation sites shadow subsequent deposit, creating “pillars”

Substrate reversed once during deposition, creating angular pillars