Organic Electronic Materials

Deposition

Deposition process

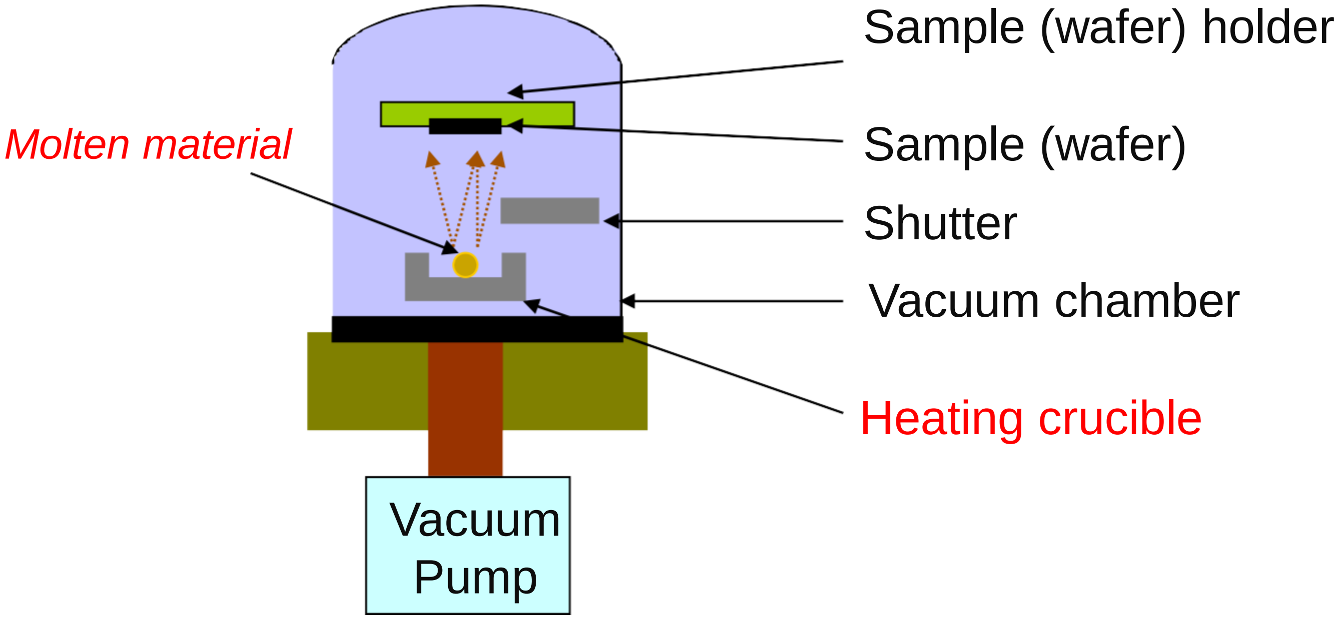
- Source
- Transport
- Condensation on substrate

- The nature of the film deposited on process parameters
  - Substrate, deposition temperature, gaseous environment, rate of deposition, etc.

- Favorable conditions are created to transfer the material from the source (target) to the destination (substrate)
  - In PVD process, the transfer takes place by a physical means such as evaporation or impact
  - In CVD process films are deposited through a chemical reaction

- Physical vapor deposition (PVD)
  - Evaporation : requires high Temp.
  - Sputtering: DC sputtering/ RF sputtering
- Chemical vapor deposition (CVD)
  - Source contains the materials
  - High quality films

Thermal evaporation



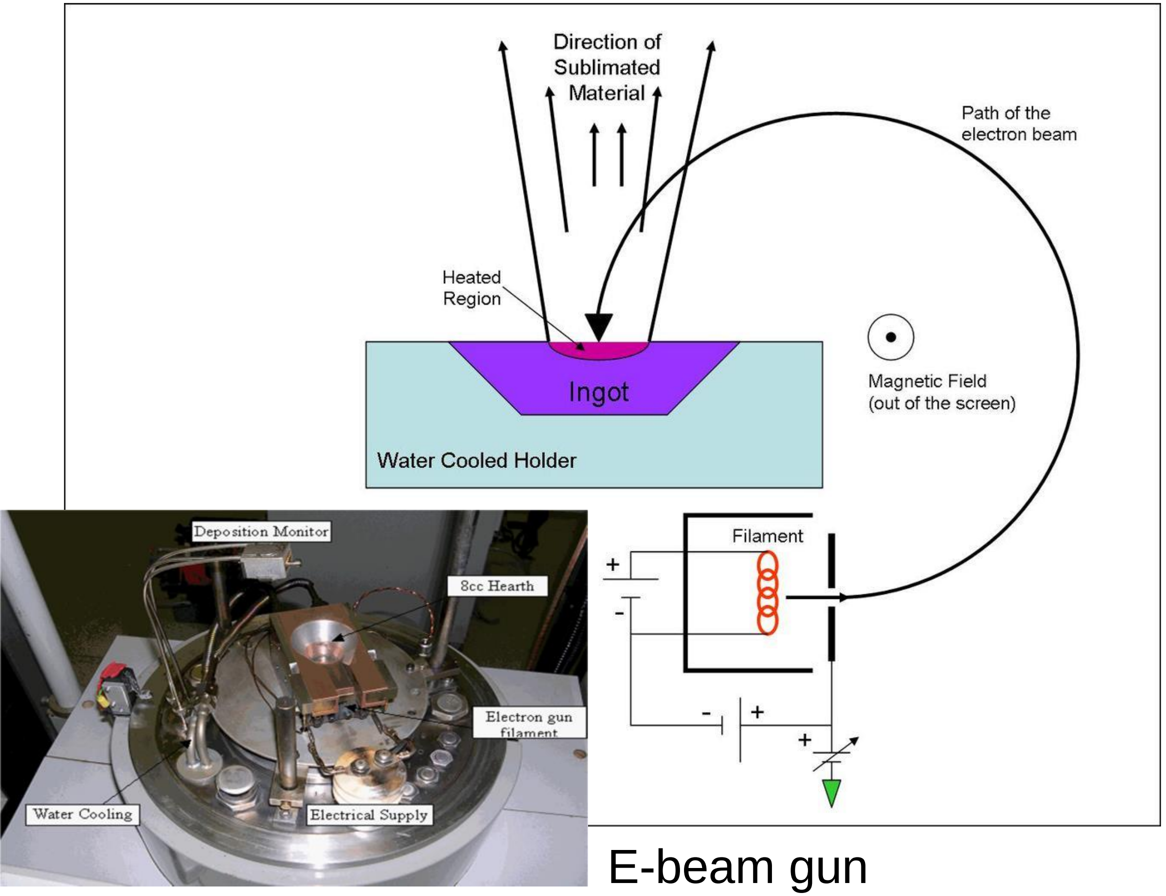
- Procedure
  - metal to be deposited is placed in an inert crucible
  - chamber is evacuated to a pressure of 10^{-6} – 10^{-7} Torr
  - crucible is heated using a tungsten filament or an electron beam to flash-evaporate the metal from the crucible and condense onto the cold substrate
- The evaporation rate is a function of the vapor pressure of the metal

Methods for heating

- Resistive heating
  - Tungsten boat/filament as containment structure
  - Filament life limits thickness (for industrial use)

E-beam evaporation

- Focused beam of electrons are used to locally heat the Source
- Can be used to heat / evaporate even high melting point materials
- Alloys could be deposited without dissociation of constituent elements
- Ideally suited for reactive evaporation (Oxides, Nitrides etc.,)



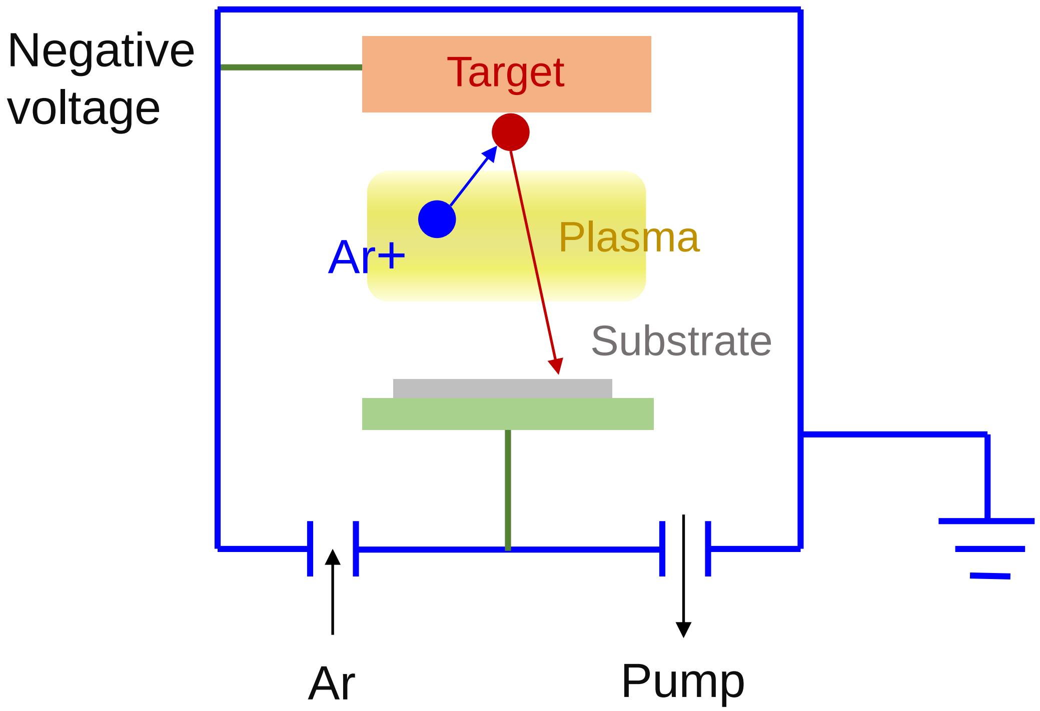
E-beam gun

- High intensity electron beam gun (3 ~ 20 kev) is focused on the target material that is placed in a copper (water cooled)
- The electron beam is magnetically directed onto the evaporant, which melts locally.
- No contamination from crucible.
- High quality films.
- High deposition rate 50 ~ 500nm/min.
- Disadvantages:
    - Process might induce x-ray damage and ion damage at the substrate.
    - At high energy(> 10kev), the incident electron beam causes x-ray emission.
    - Deposition equipment is more costly.

https://en.wikipedia.org/wiki/Electron-beam_physical_vapor_deposition#/media/File:Electron_Beam_Deposition_001.jpg

Sputtering

- A physical phenomenon involving
  - ✓ The creation of plasma by discharge of neutral gas such as helium or Ar
  - ✓ Acceleration of ions via a potential gradient and the bombardment of a ‘target’ or cathode
  - ✓ Through momentum transfer atoms near the surface of the target metal become volatile and are transported as vapors to a substrate
  - ✓ Film grows at the surface of the substrate via deposition
- For ion sputtering, the source material is put on the cathode (target); for sputter deposition, the substrates to be coated on the anode.
- The target, at a high negative potential is bombarded with positive argon ions created in a (high density) plasma. Condensed on to substrate placed at the anode.



http://shodhganga.inflibnet.ac.in/bitstream/10603/79579/12/12_chapter%202.pdf

- Sputtering yield is the average number of atoms ejected from the target per incident ion depends
  - Ion incident angle
  - Energy of the ion
  - Masses of the ion and target atoms
  - Surface binding energy of atoms in the target
- Sputter yields for various materials at 500ev Argon
  - Al 1.05 Cr 1.18
  - Au 2.4 Ni 1.33
  - Pt 1.4 Ti 0.51

Advantages of sputtering over evaporation:

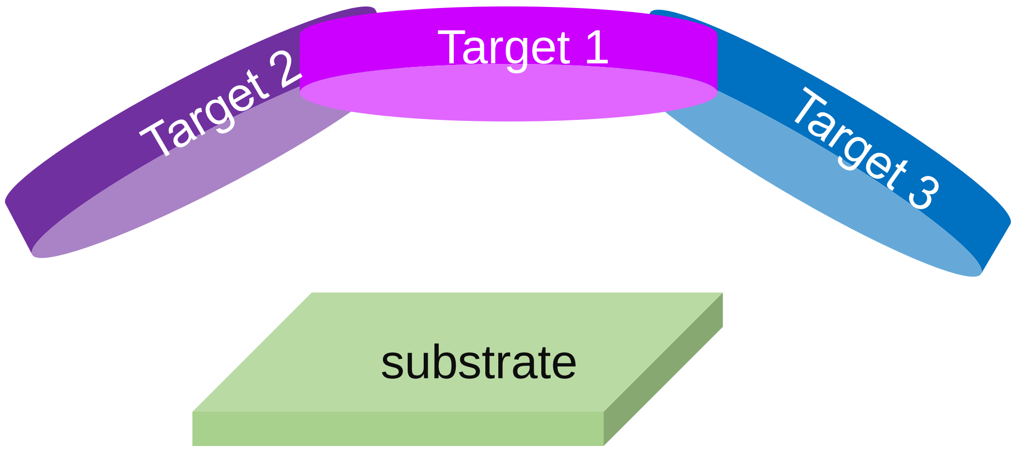
- Wider choice of materials.
- Better adhesion to substrate.
- Complex stoichiometries possible.
- Films can be deposited over large wafer (process can be scaled)
- Sputter yield= #of atoms removed per incident ion
- Deposition rate is proportional to yield for a given plasma energy

Disadvantages:

- High cost of equipment.
- Substrate heating due to electron (secondary) bombardment.
- Slow deposition rate. (1 atomic layer/sec).

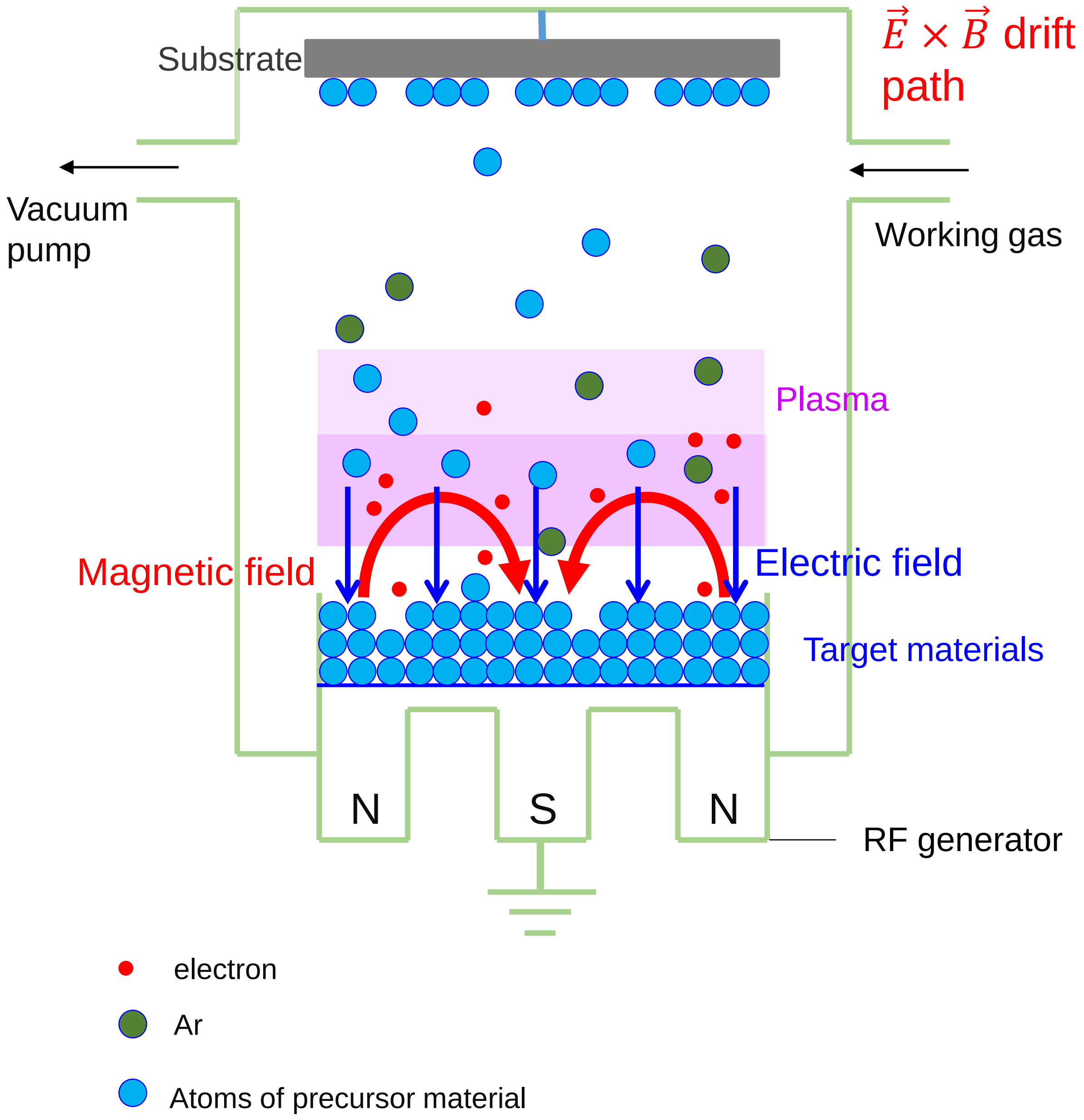
Co-sputtering

- More than one magnetron target
- Composition controlled by the power to individual targets
- Substrate rotation is required for composition uniformity.



RF Magnetron Sputtering

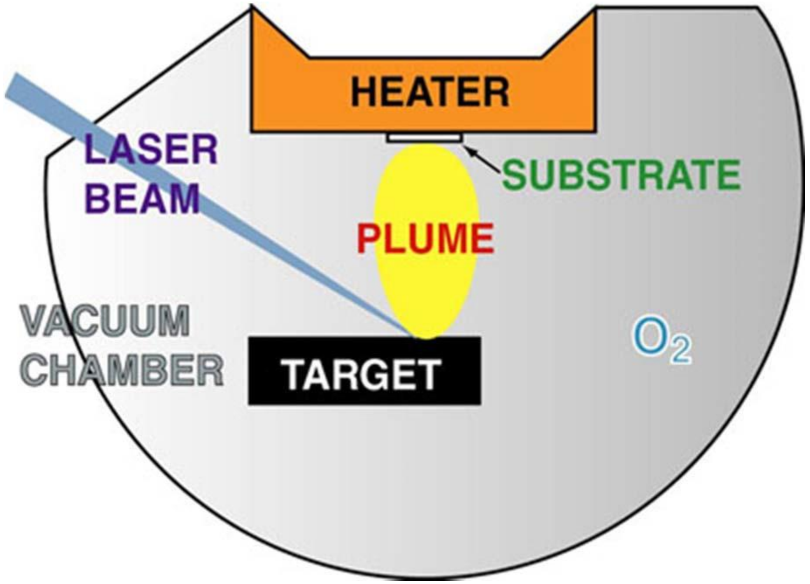
- For Dielectrics/insulators
- Advantages
  - Electron Confinement
  - High ionization
  - Low pressure sputtering
  - High purity of the films
- Disadvantages
  - Non uniform erosion
  - Thickness uniformity



	Evaporation	Sputtering
Rate	1000 atomic layer/sec (thickness control is difficult)	1 atomic layer/sec (thickness control possible)
Choice of material	Limited (to those with low melting point)	Almost unlimited
Purity	Better	Possibility of incorporating impurity
Alloy composition	Little or no control	Can be tightly controlled
Changes in source material	Easy	Expensive
Decomposition of material	High	Low
Adhesion	Often poor	Very good

Laser ablation

- Uses LASER radiation to erode a target, and deposit the eroded material onto a substrate.
  - The energy of the laser is absorbed by the upper surface of the target resulting in an extreme temperature flash, evaporating a small amount of material.
  - Usually pulsed laser is used.
- Material displaced is deposited onto the substrate without decomposition.
- The method is highly preferred when complex stoichiometries are required.
  - Thin film keeps the same atomic ratio as the target material.



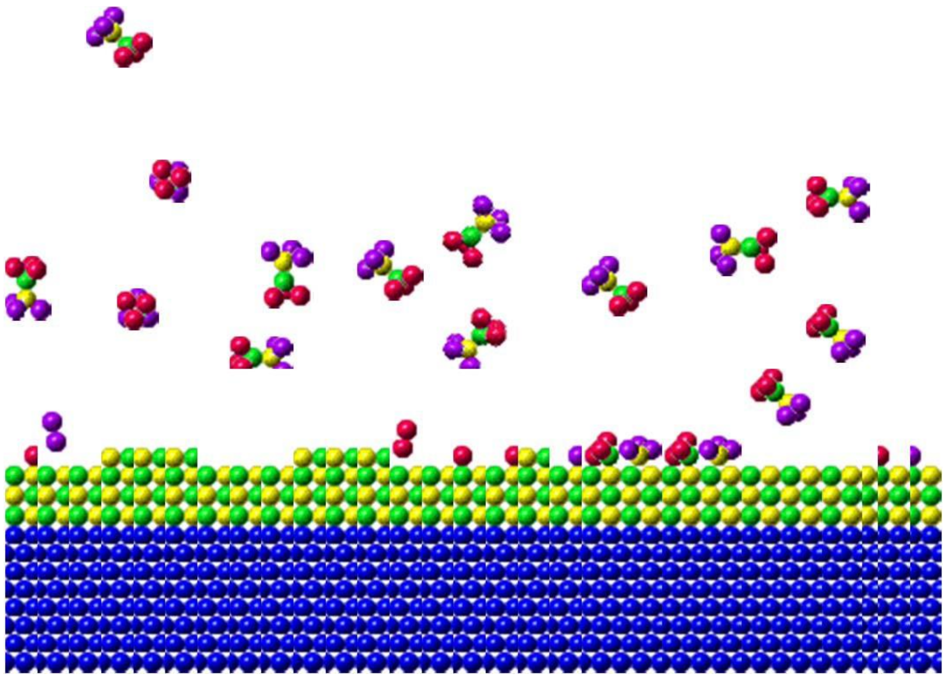
Pulsed Laser Ablation deposition (PLD)

- Used for high quality thin films
  - e.g., superconducting materials such as $YBa_2Cu_3O_{7-y}$
  - short-wavelength lasers such as the KrF or XeCl excimer laser in a non-equilibrium process.
- Ease of operation and reproducibility.
- Films do not require post-deposition annealing

- Processing variables
  - laser energy
  - laser pulse repetition rate
  - substrate temperature
  - oxygen background pressure

Chemical vapor deposition

- Chemical Vapor Deposition is chemical reactions which transform gaseous molecules, called precursor, into a solid material, in the form of thin film or powder, on the surface of a substrate



Constituents of a vapor phase, often diluted with an inert carrier gas, react at the hot surface to deposit a solid film.

Film-forming by

Heterogeneous reactions

Occurring at or close to heated surface

Homogenous reactions

Occurring in gas phase

Result in stoichiometric–correct film Used for

very thin Si deposition, copper,

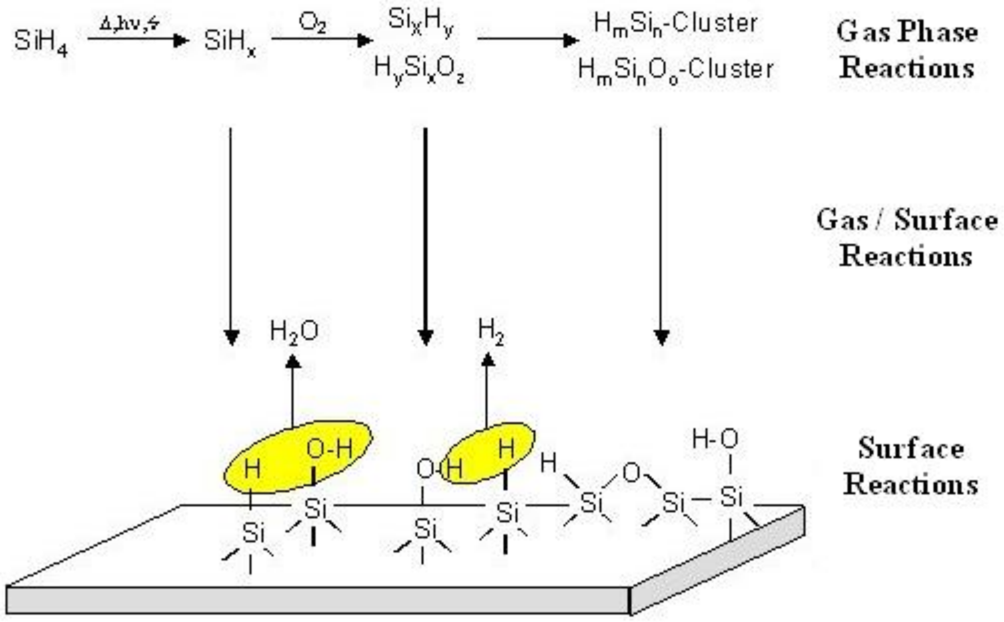
low dielectric insulators

- Common thin films deposited by CVD are
  - Polysilicon
  - Silicon Nitride, Silicon oxide
  - Ti, W, Ta, Cu
  - Nitrides of W & Ti & Ta
  - Low permittivity dielectric insulators

- Parameters that significantly influence the rate of chemical vapour deposition are:
  - temperature
  - pressure of carrier gas
  - velocity of gas flow
  - distance along the direction of gas flow

- Plasma enhanced (PECVD)
- Atmospheric pressure (APCVD)
- Low pressure (LPCVD)
- Very low pressure (VLCVD)
- Metallographic (MOCVD)

CVD Procedure



- Mass transport of reactant (and diluent gases) in the bulk gases flow region from the reactor inlet to the deposition zone
- Gas phase reactions leading to film precursors and by-products.
- Mass transport of film pre-cursors and reactants to the growth surface.
- Adsorption of film precursors and reactants on the growth surface.
- Surface reactions of adatoms occurring selectively on the heated surface.
- Surface migration of film formers to the growth sites.
- Incorporation of film constituents into the growing film.
- Desorption of by-products of the surface reaction.
- Mass transport of by-products in the bulk gas flow region away from the deposition zone towards the reactor exit

Molecular beam epitaxy

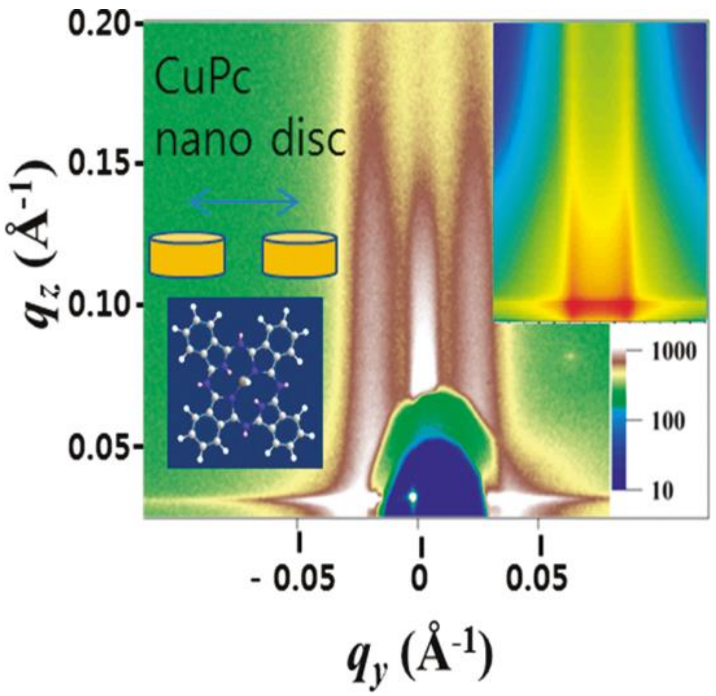
- Epitaxy: deposition of crystalline overlayer on a crystalline substrate
    - Homoepitaxy
        - Crystalline film is grown on a substrate or film of the same material
    - Heteroepitaxy
        - Crystalline film grows on a crystalline substrate of film of a different material

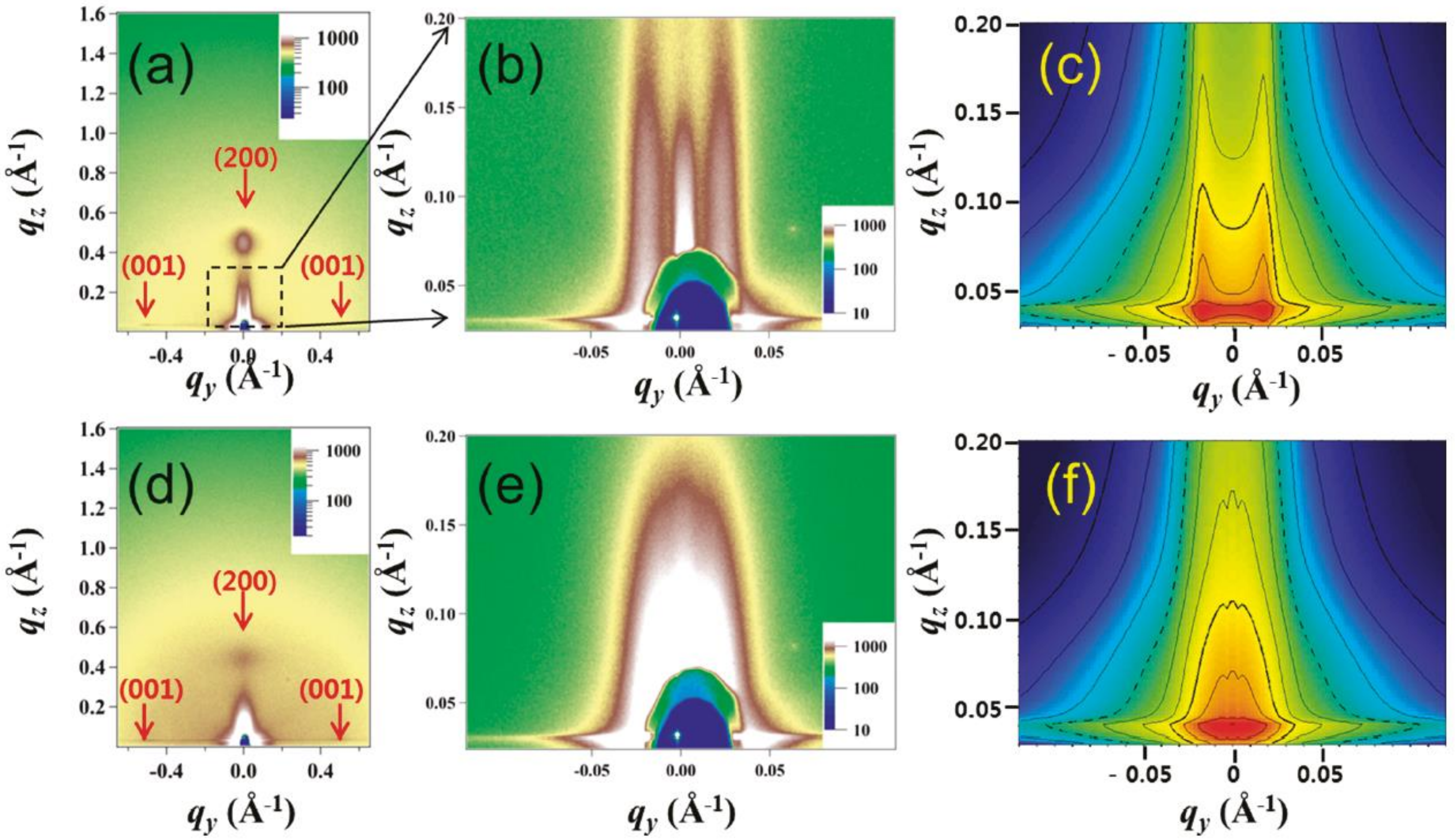
- Enable deposition of single crystal films.
- Also used for the deposition of some types of organic semiconductors ← molecules, rather than atoms, are evaporated and deposited onto the wafer.

- Key features
    - Low Deposition Rate
    - Better vacuum
    - Higher substrate temperature
    - Directed atomic beams (Effusion cell)

Organic small molecule thin films from thermal evaporation

- Small molecules
- Advantage
    - Easy to fabricate multi-layered structure
    - Control of molecular arrangement or crystallinity
        - Substrate temperature
        - Substrate treatment: surface E engineering, insertion layer (MTG)





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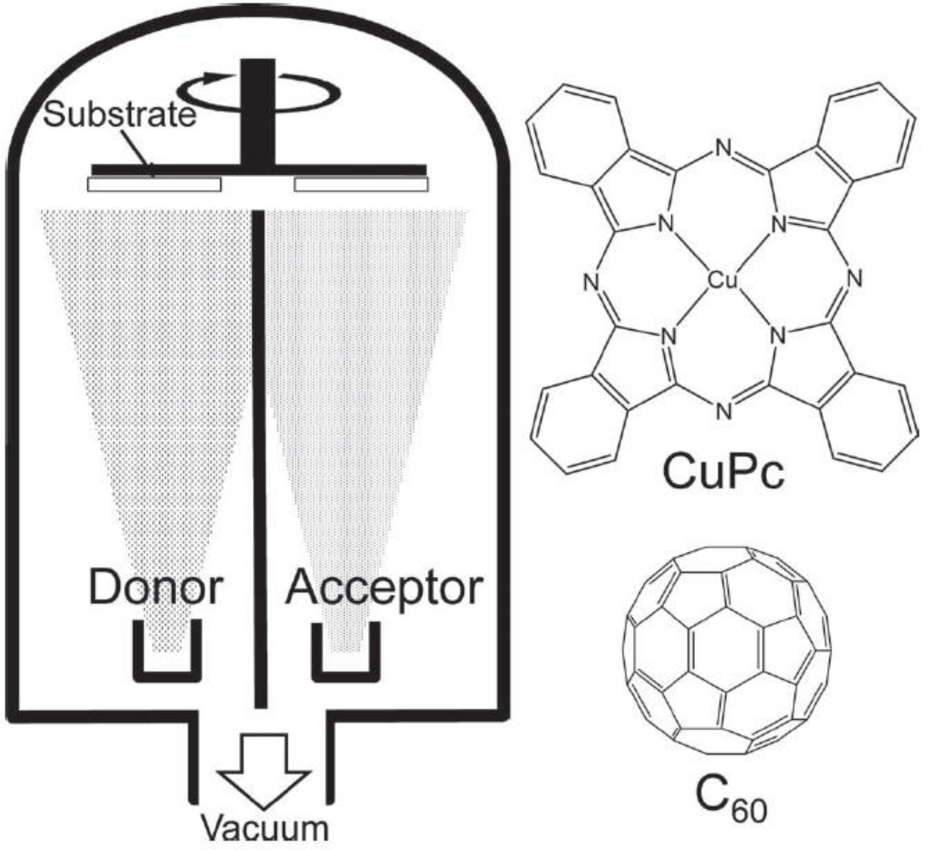
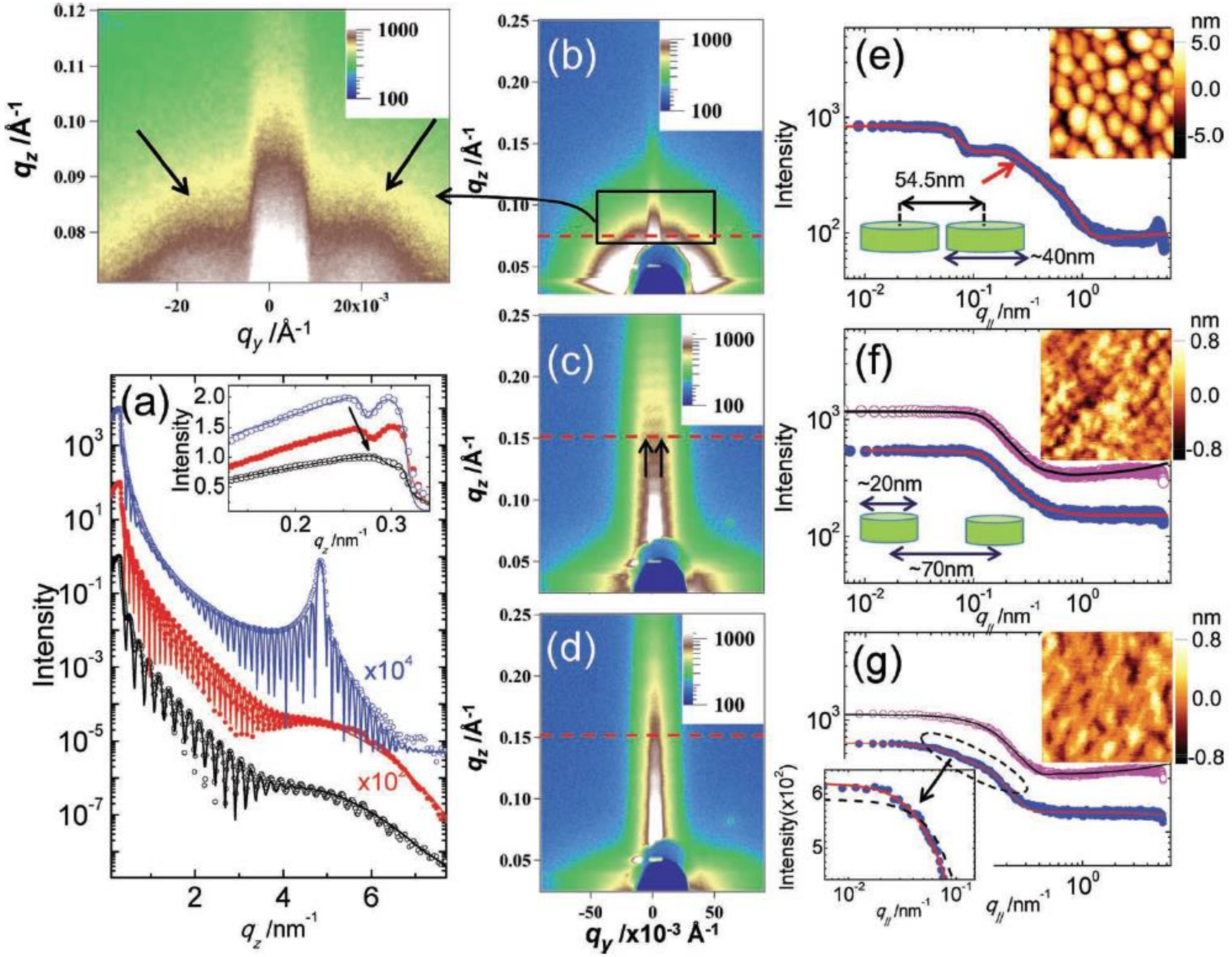
BHJ formation from co-evaporation





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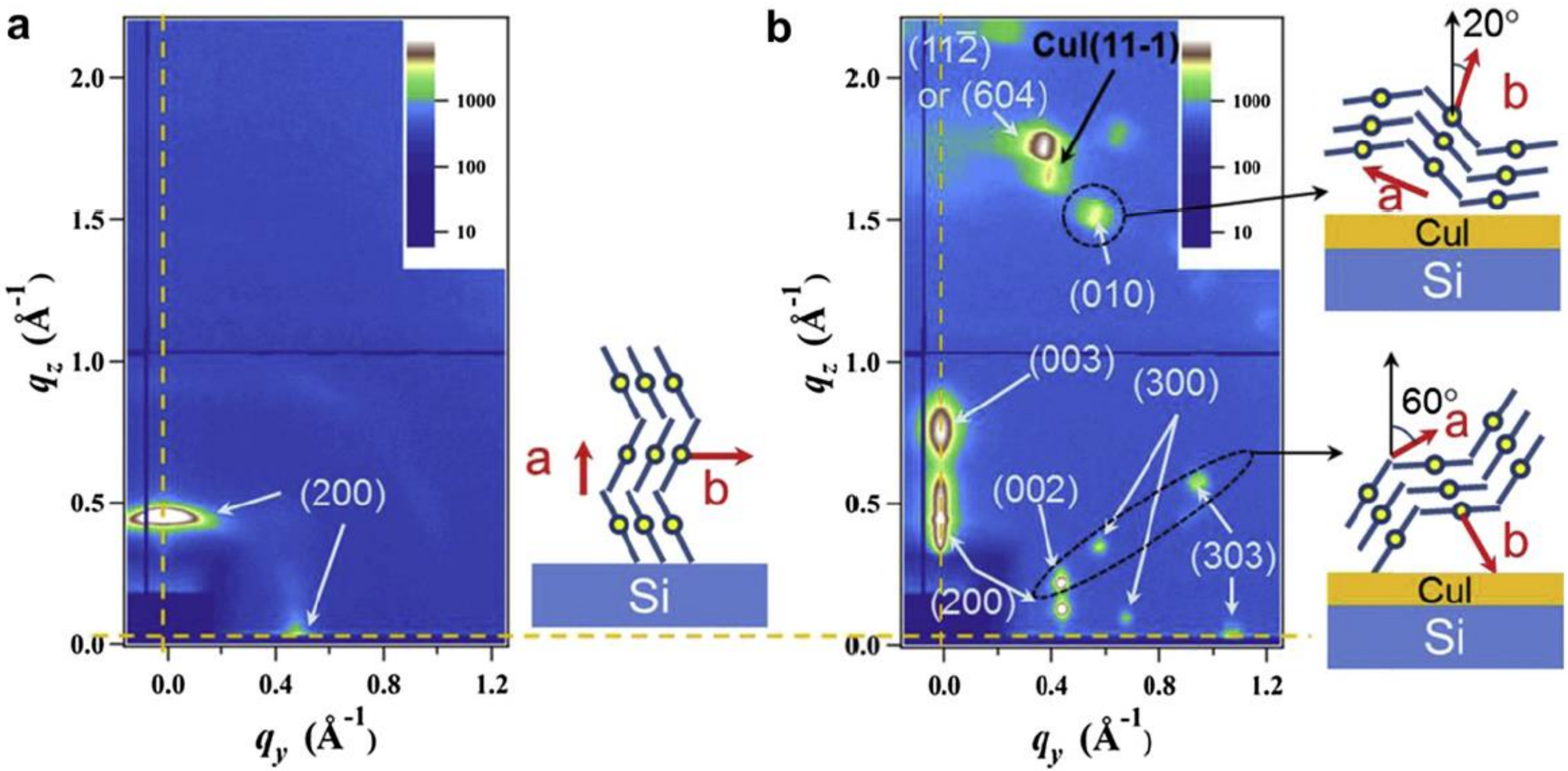
MTG (molecular templating growth)



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