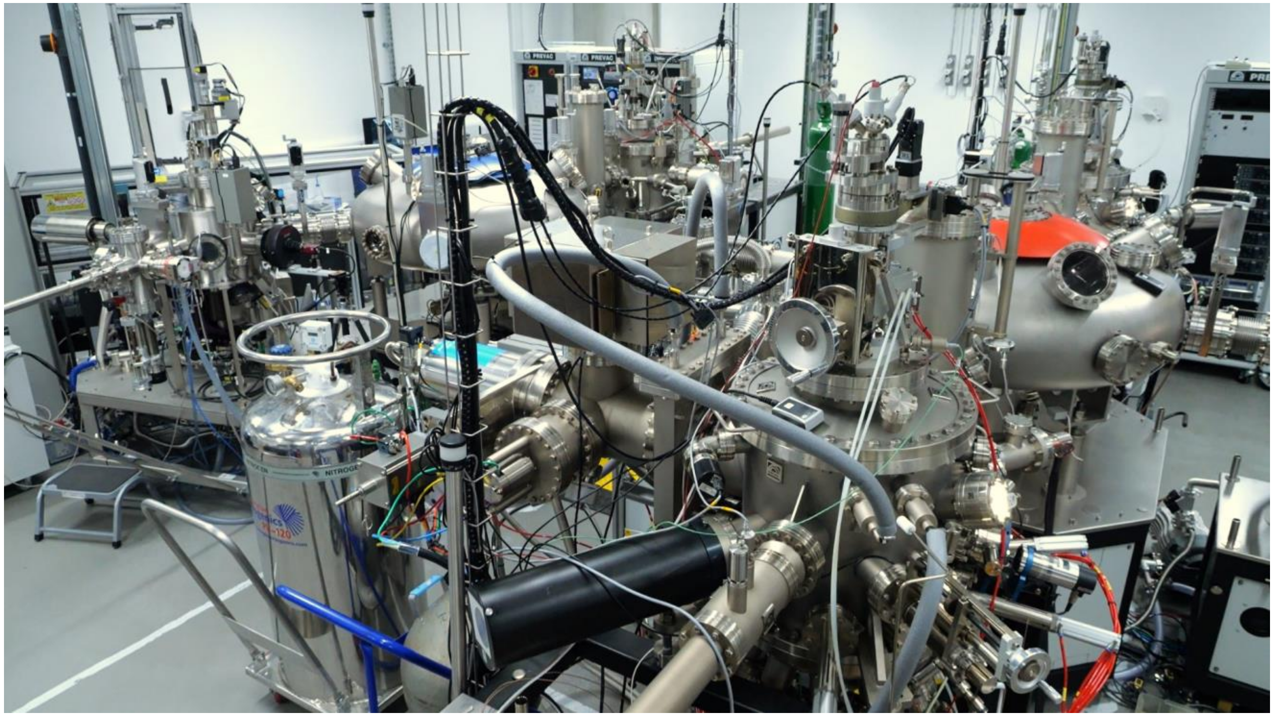
Growth Techniques

IOP Magnetism Winter School Lecture

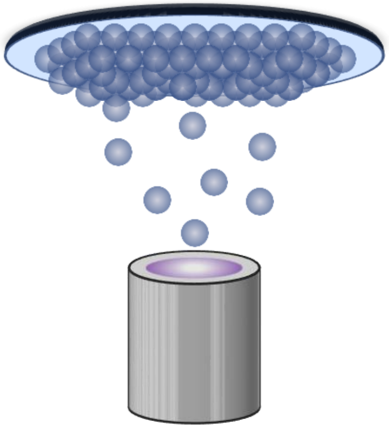
Dr Philippa Shepley

Royce Deposition System

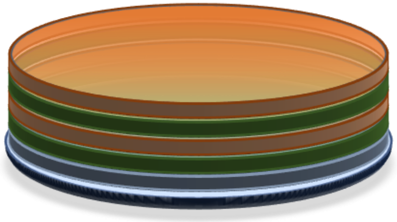


- We combine layers of different materials in “multilayers”.
- Multilayers allow us to study the interfaces between materials.

Thin film materials



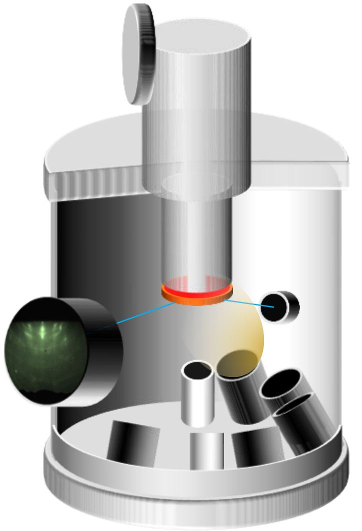
<1 nm to 100 nm



Royce Deposition System

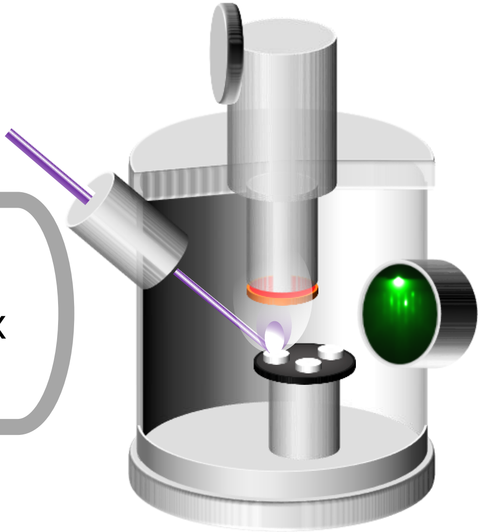
HENRY ROYCE INSTITUTE

UNIVERSITY OF LEEDS

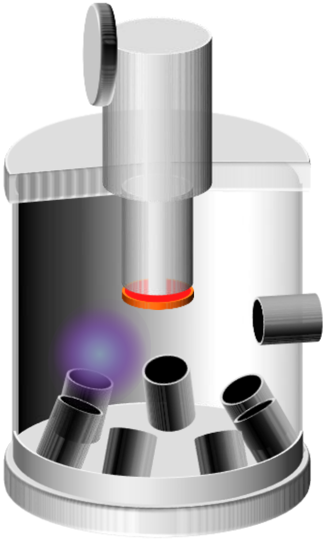


MBE
(topological insulators)

PLD
(Complex oxides)

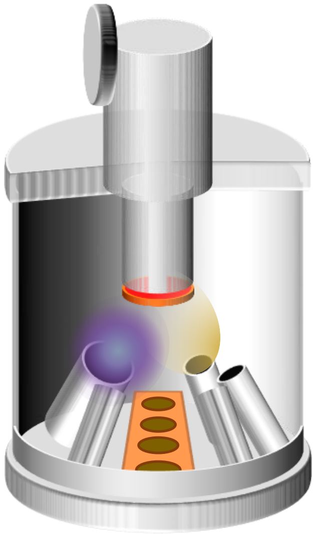


- Chambers linked under UHV
- Multilayer thin film deposition
- Physics at interfaces



Sputtering
(Metals and oxides)

MBE
(Organics and metals)



condensed-matter.leeds.ac.uk

Outline

- How do we achieve, maintain and measure vacuum?
    - Vacuum-compatible materials
    - Seals
    - Cleaning
    - Baking
    - Load locks
    - Pumps
    - Gauges
- Thin film deposition processes and techniques
    - Sputtering
    - Pulsed Laser Deposition
    - Molecular Beam Epitaxy
- In situ measurements

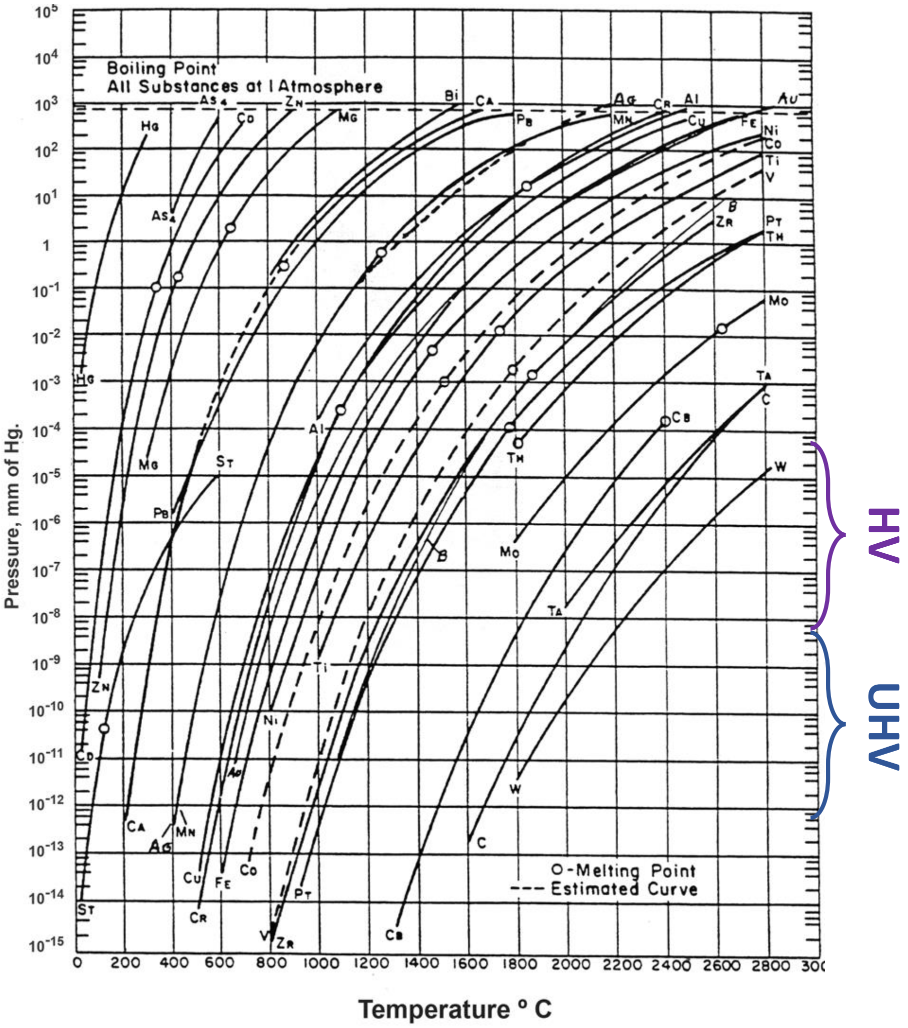
Atmosphere to UHV

- **Vacuum-compatible materials**
  - Use materials with low vapour pressures to limit evaporation into the chamber
  - Different materials are suitable for different levels of vacuum and temperatures

- Stainless steel (chamber walls)
- Oxygen-free copper (gaskets)
- High melting point metals

  e.g. molybdenum, tantalum, tungsten
- High melting point ceramics

  e.g. alumina, boron nitride

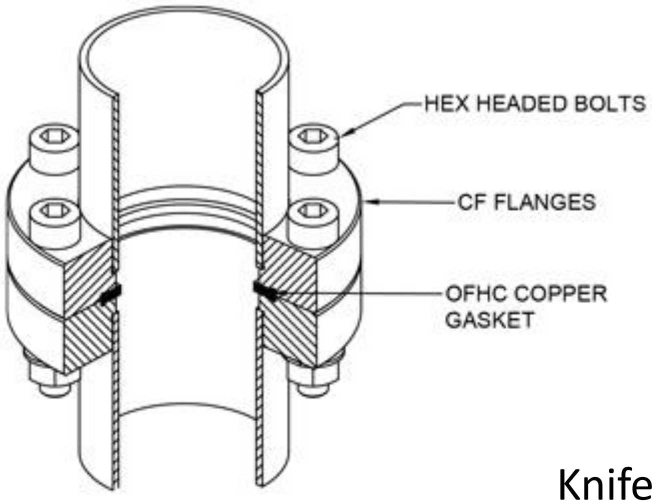


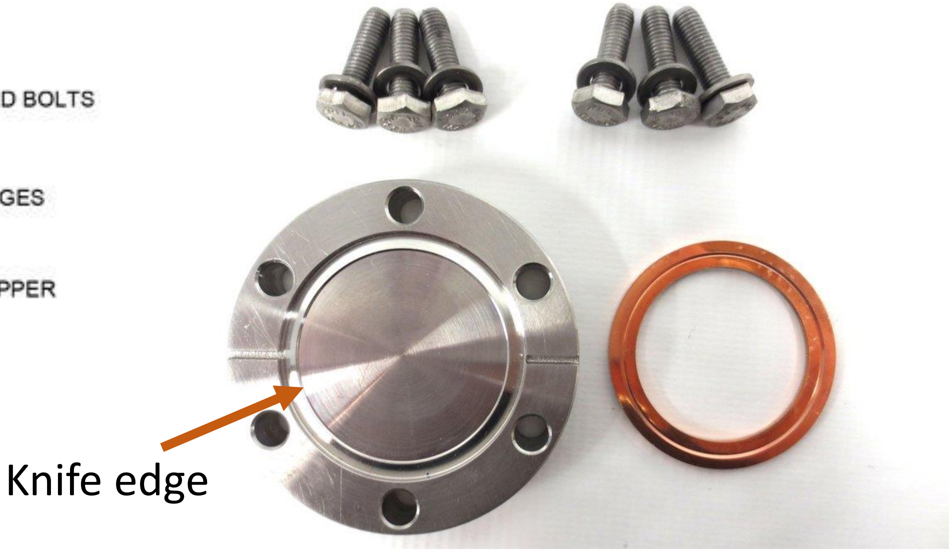
Vapor pressure vs. temperature

Atmosphere to UHV

- **Seals**
    - Prevent gas leaking into the chamber from atmosphere
    - Different seals for different levels of vacuum

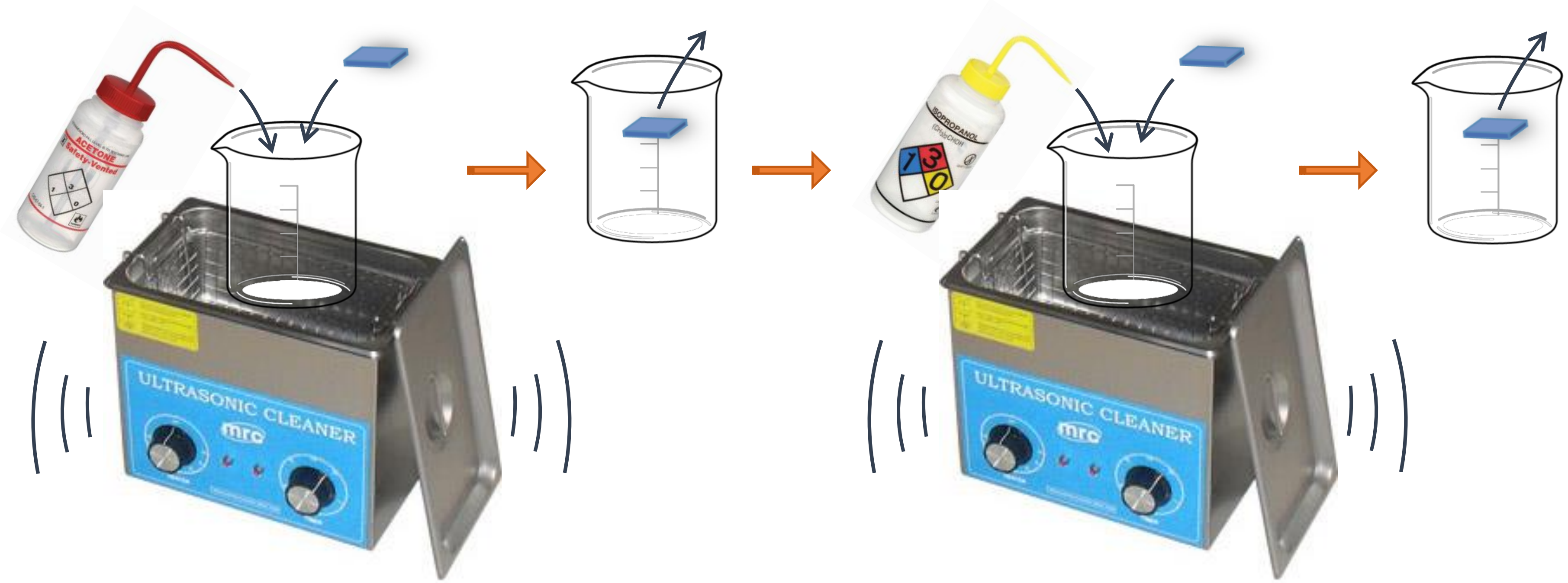
- Copper gaskets for UHV seals
- Knife edge on flange cuts into copper as bolts are tightened





Atmosphere to UHV

- **Cleaning**
  - Clean all components and substrates by sonicating in acetone to remove organic residues, then isopropanol to remove the acetone
  - Use gloves and tweezers to handle components and substrates



- An ultrasound bath introduces high frequency vibration to help dislodge dirt, grease etc

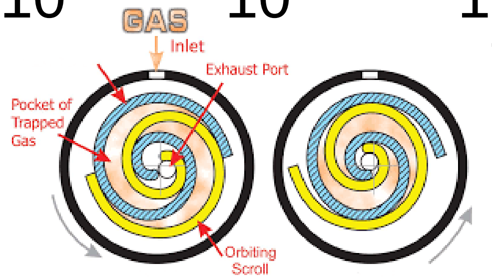
Pumps

- **Pumps**
    - Remove gas molecules from the system
    - Different pumps used for different levels of vacuum
    - Different pumps for different applications and gases

0.75 Torr
= 1 mbar
= 100 Pa

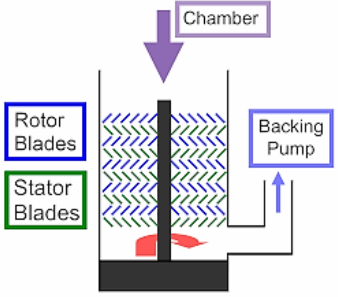
Low Vacuum | Moderate Vacuum | High Vacuum | UHV

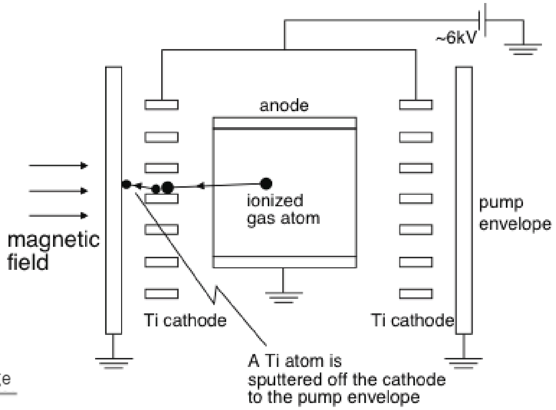
10^{3} 10^{1} 10^{-1} 10^{-3} 10^{-5} 10^{-7} 10^{-9} 10^{-11} mbar



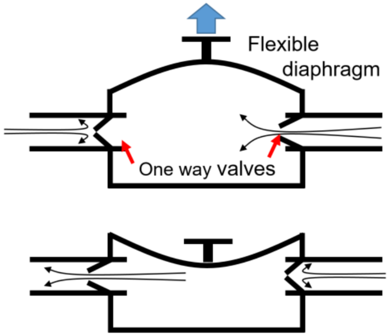
Scroll pump 10^{3}-10^{-3}

Turbomolecular pump 10^{-2}-10^{-10}



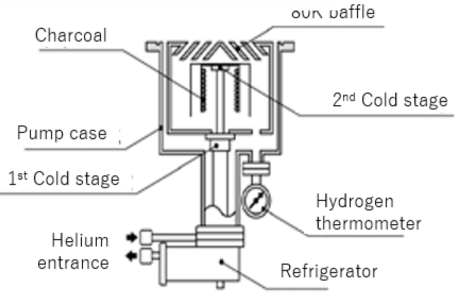


Ion pump 10^{-7}-10^{-11}

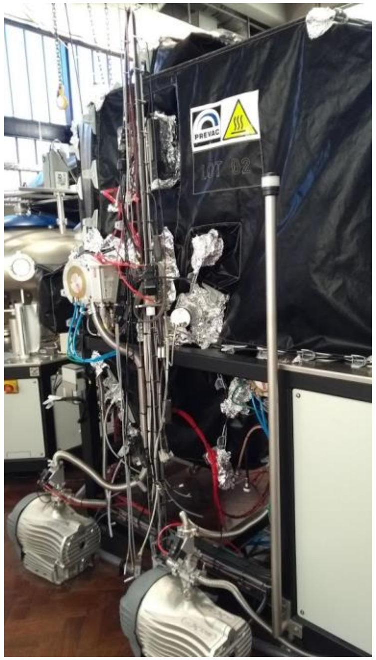


Diaphragm pump $>10^{3}$-10^{-1}

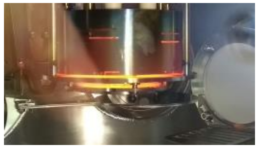
Cryogenic pump 10^{-3}-10^{-9}



Atmosphere to UHV



- **Baking**
  - Heat the entire chamber to >100°C to speed up evaporation of volatile molecules (e.g. H_2O) from the chamber walls
  - After baking, individual components can be slowly heated to **outgas**

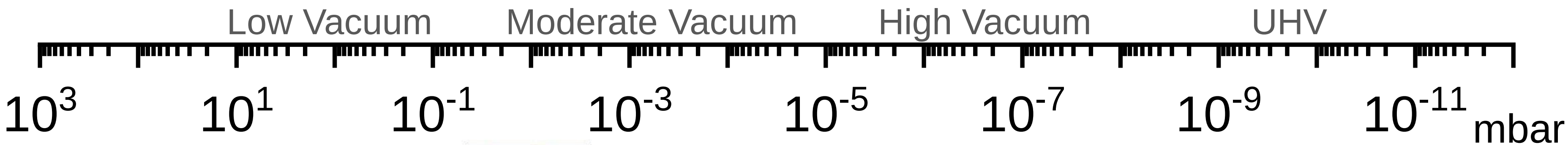


- **Load locks**
  - Using separate air-lock chambers to load and unload samples means we don’t regularly vent the whole chamber

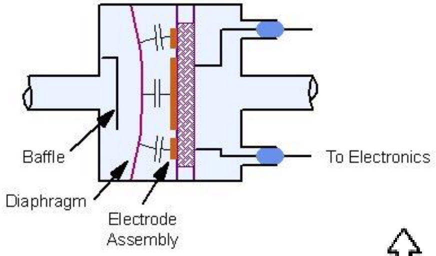
Pressure gauges

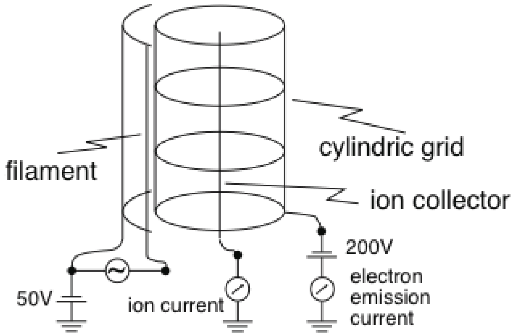
- **Gauges**
    - Measuring pressure to understand processes
    - Measuring pressure to take action to get the right pressure
    - Different gauges used for different levels of vacuum

0.75 Torr
= 1 mbar
= 100 Pa

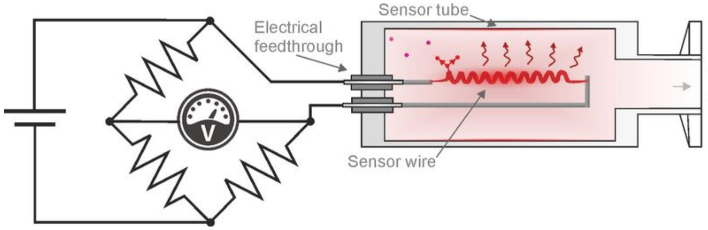


Baratron 10^{-1}-10^{-4}

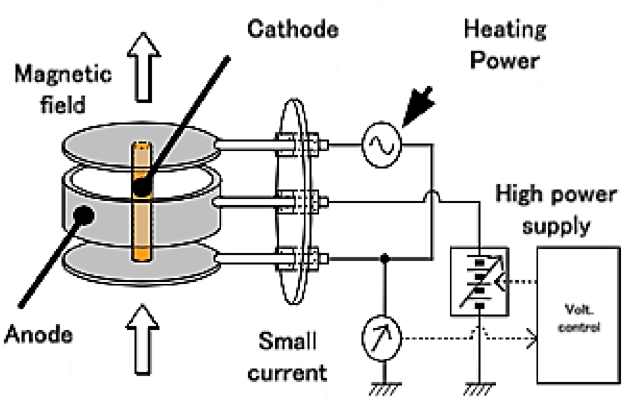




Ion gauge 10^{-6}-10^{-11}



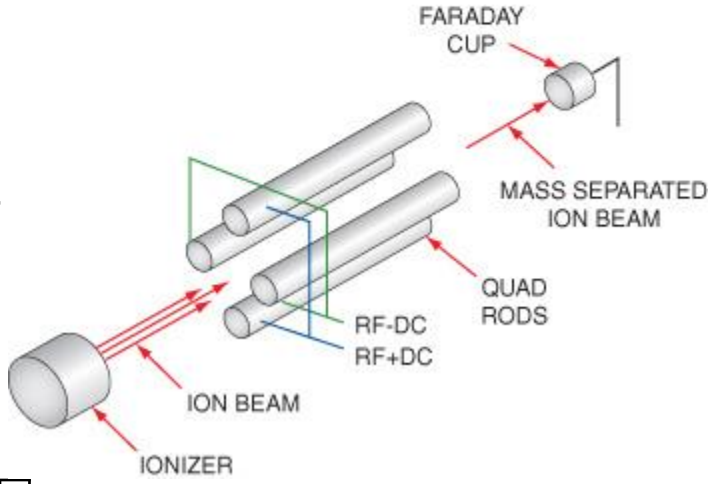
Pirani gauge 10^3-10^{-3}

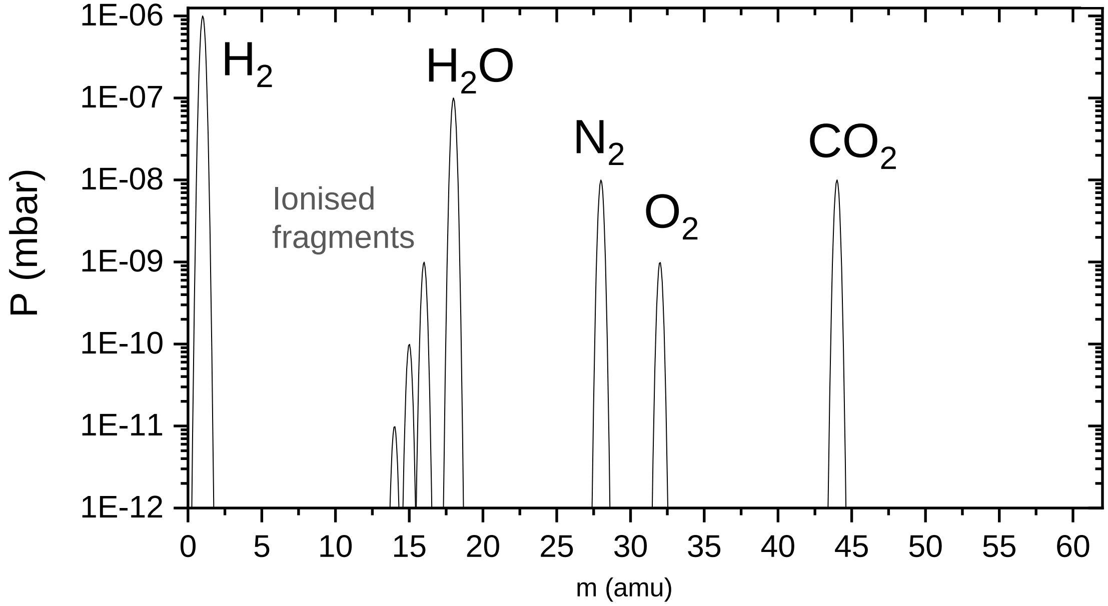


Cold cathode gauge 10^{-2}-10^{-9}

Residual Gas Analysis

- Mass spectroscopy of residual gases
- Gives partial pressures of different gases by mass
- Can check to leaks by applying He outside chamber monitoring He partial pressure





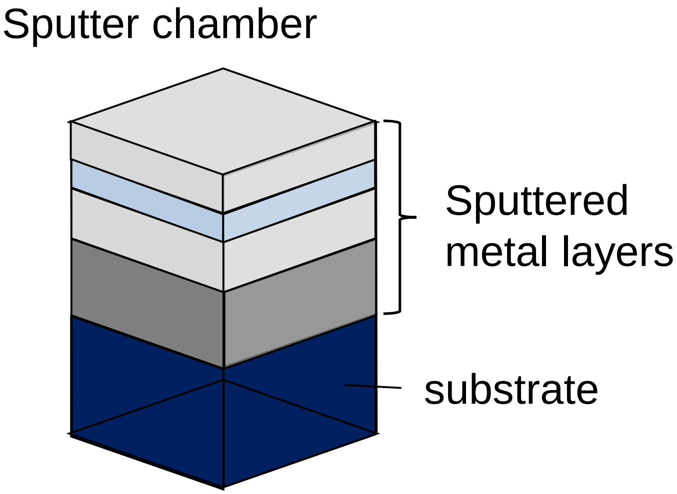
Pressure range 10^{-4}-10^{-11} mbar

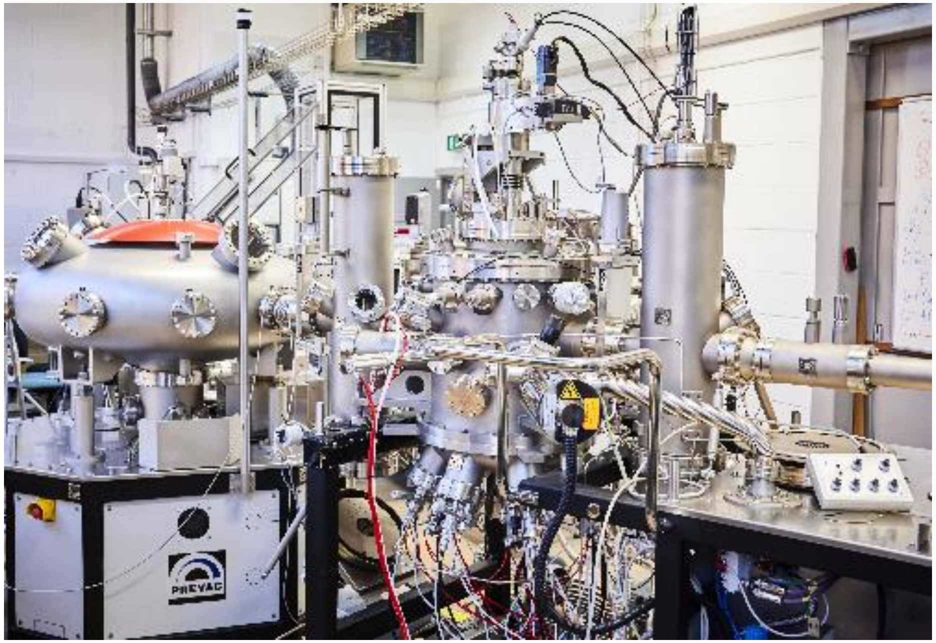
Deposition techniques

- Different techniques are useful for different materials and applications.

- Sputtering
    - Magnetron
    - dc/rf
    - Off axis sputtering
- Pulse laser deposition (PLD)
- MBE
    - Thermal evaporation
    - Electron-beam

Magnetron sputtering

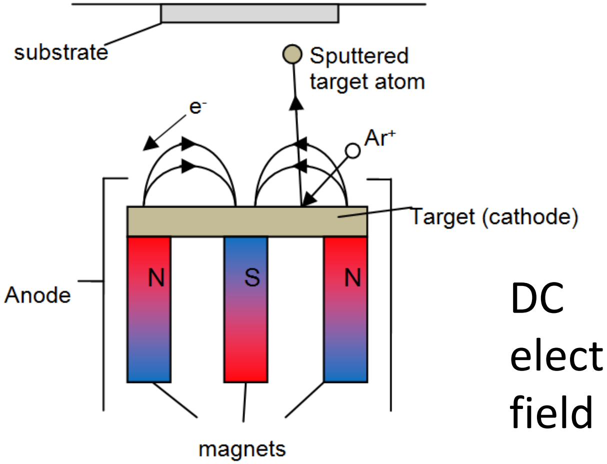




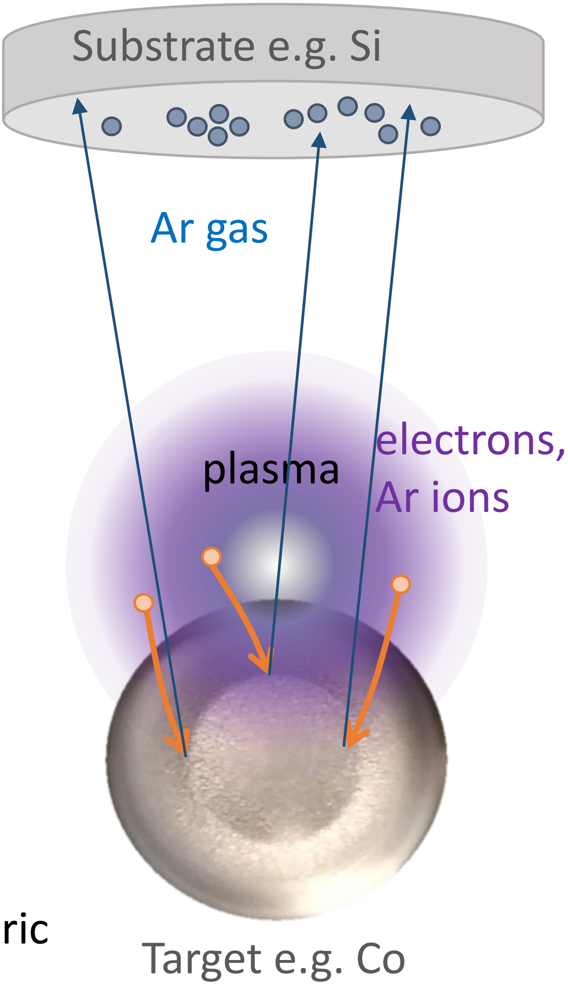
- Metals, oxides, nitrides
- Ideal for polycrystalline or textured films, but epitaxy is possible
- Atoms impinge on substrate with high energy
- Typical growth rates Å/s
- Very scalable and common across many industries

Magnetron sputtering

- A dc voltage between the target and shield ignites an Ar plasma e.g. voltage 340 V (current 0.24 A, power 82 W)
- Permanent magnets behind the target create a magnetic field that confines the plasma into a torus
- Ar ions from the plasma hit the target, ejecting ("sputtering") atoms and small clusters of atoms
- Sputtered particles are deposited onto the substrate to form a thin film e.g. rate of deposition 1 Å/s
- The rate of deposition and (crystal) structure of the film depend on the gun power, process gas and T-S distance (pressure x distance), the target material and the substrate temperature

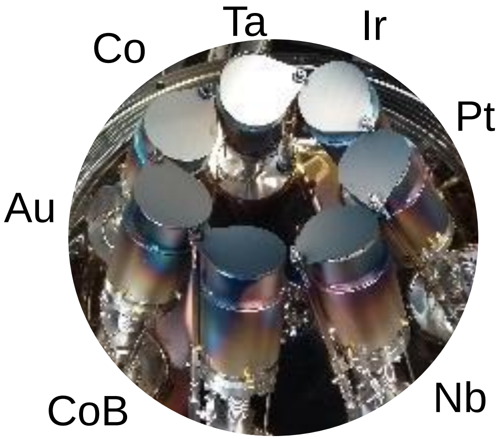


DC electric field

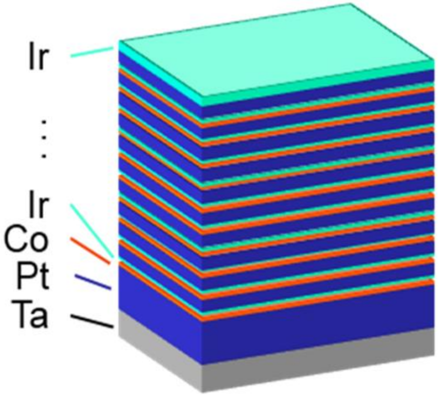


Magnetron sputtering

- Vacuum chamber at 10^{-8} to 10^{-10} mBar
- Load a substrate plate into the load-lock chamber and pump
- Transfer the substrate to the main chamber
- Set the substrate temperature e.g. 25°C
- Fill the main chamber with process gas e.g. Ar ~3 µBar



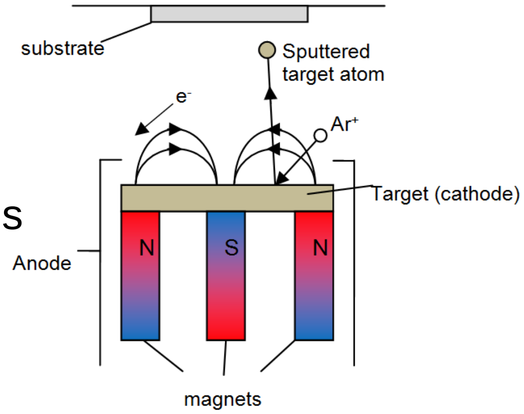
- Apply voltage between the target and shield of the magnetron
- Open the magnetron shutter for a set deposition time
- Deposit a multilayer thin film by using different magnetrons
- Ensure the sample is at room temperature
- Move the sample to the load-lock and out of the system



Sputtering

Radio frequency (rf) sputtering

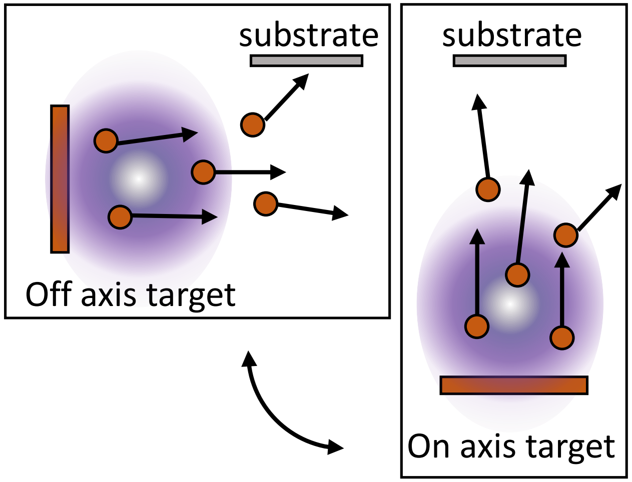
- Use an rf voltage to create a plasma
- Avoid build up of charge on insulating targets
- Typically used for insulating targets e.g. oxides



AC electric field between cathode and anode
kHz - MHz

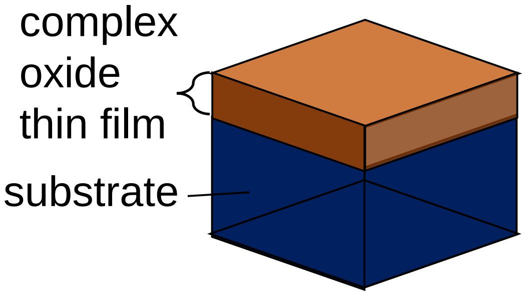
Off-axis sputtering

- Capture atoms that are scattered out to the side
- Lower energy atoms impinging on the substrate
- Low energy -> low damage -> better epitaxy
- Slower growth rates ~0.01 Å/s



Pulsed Laser Deposition

Pulsed laser deposition (PLD)

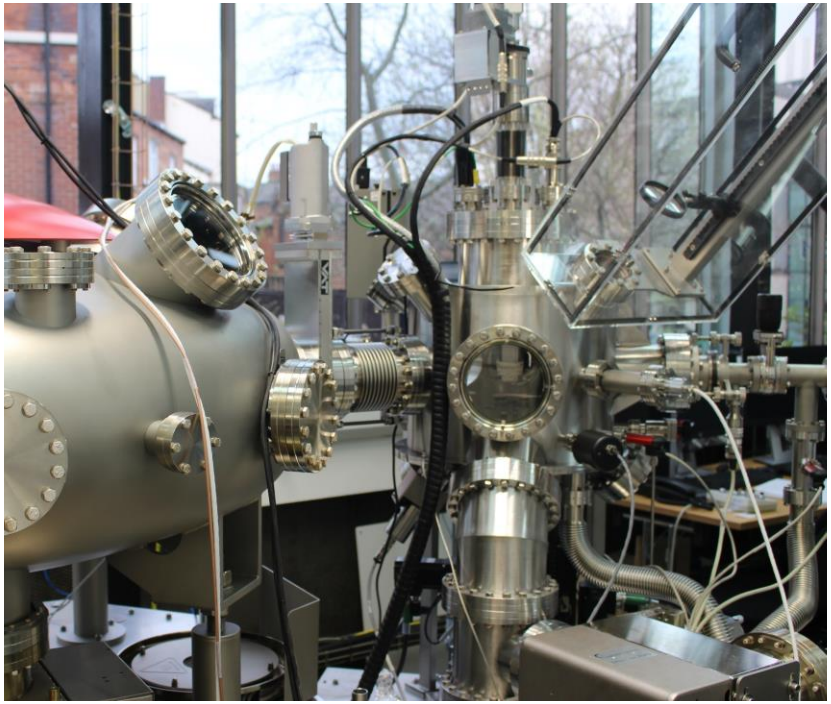


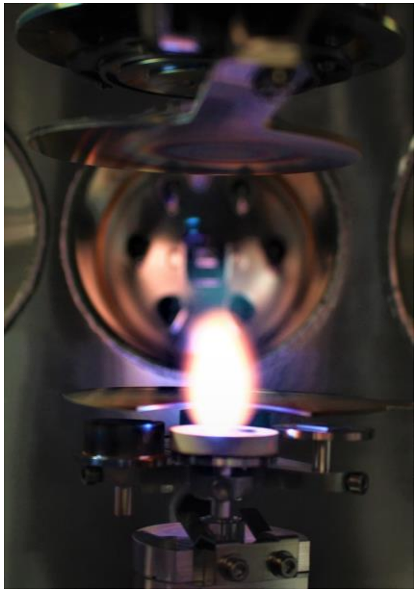
$SrTiO_3$

$SrRuO_3$

$BiFeO_3$

- multi-target stage for multilayer capability





- Good transfer of stoichiometry
- Can be used to grow a range of materials, but commonly used for complex oxides
- Epitaxial films over a small area
- Typical growth rates 0.1 Å/s

Pulsed Laser Deposition

- A pulse of laser light transfers energy to the target surface
- The temperature of the target surface increases
- Material from the target surface evaporates or sublimes
- The vaporised ("ablated") material forms a plasma
- The plasma expands in a "plume"

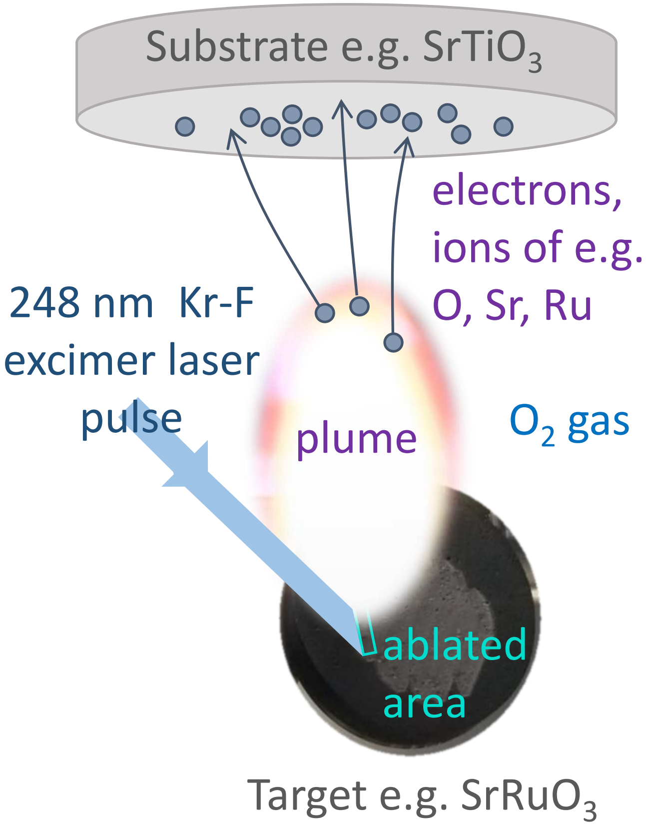
- There are a lot of processes happening at the target surface and in the plume!

- The properties of the plume depend on the **target material**, **laser fluence** and **process gas pressure**

- Ions and small particles of target material from the plume hit the substrate surface to form a thin film

  e.g. rate of deposition 0.1 Å/pulse
- The rate of deposition and (crystal) structure of the film depend on the properties of the plume, T-S distance and the temperature of the substrate

The ablation process



Substrate e.g. $SrTiO_3$

electrons,
ions of e.g.
O, Sr, Ru

248 nm Kr-F
excimer laser
pulse

plume

O_2 gas

ablated
area

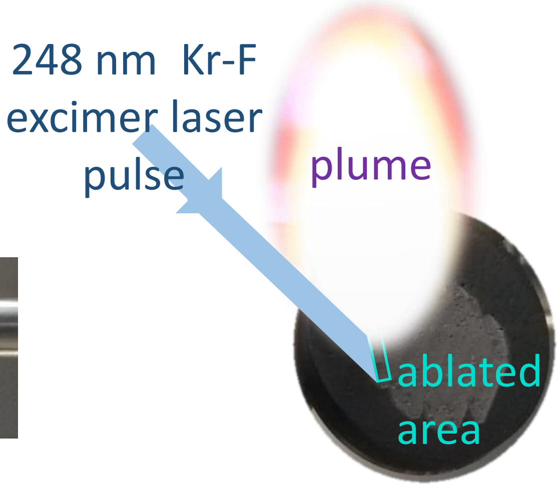
Target e.g. $SrRuO_3$

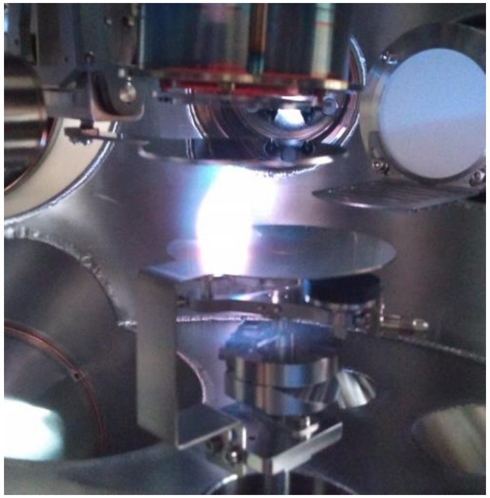
Pulsed Laser Deposition

- Vacuum chamber at 10^{-8} to 10^{-10} mBar
- Load a substrate plate into the load-lock chamber and pump
- Transfer the substrate to the main chamber
- Fill the main chamber with process gas e.g. O_2 ~0.1 mBar
- Heat the substrate to the growth temperature e.g. 700°C
- Measure the fluence of the laser with an energy meter

$$\text{e.g. fluence} = \frac{\text{pulse energy}}{\text{area on target}} = \frac{30\ \text{mJ}}{0.02\ \text{cm}^2} = 1.5\ \text{J/cm}^2$$

- Fire the laser to pre-ablate the target (clean the target surface)
- The target is scanned during ablation so that we use the whole surface





Pulsed Laser Deposition

- Open the shutter and ablate the target to deposit material onto the substrate

  e.g. 21000 pulses at a pulse rate of 5Hz

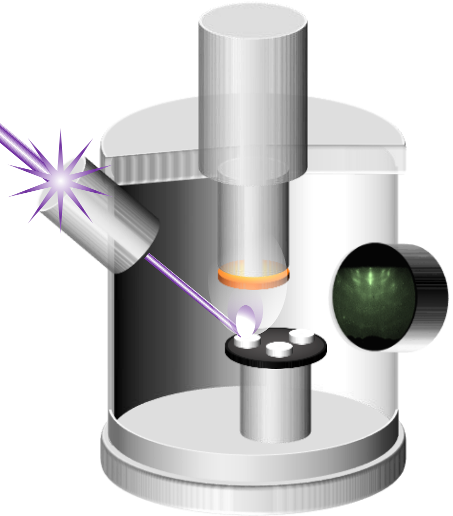
- The substrate sits at the edge of the plume

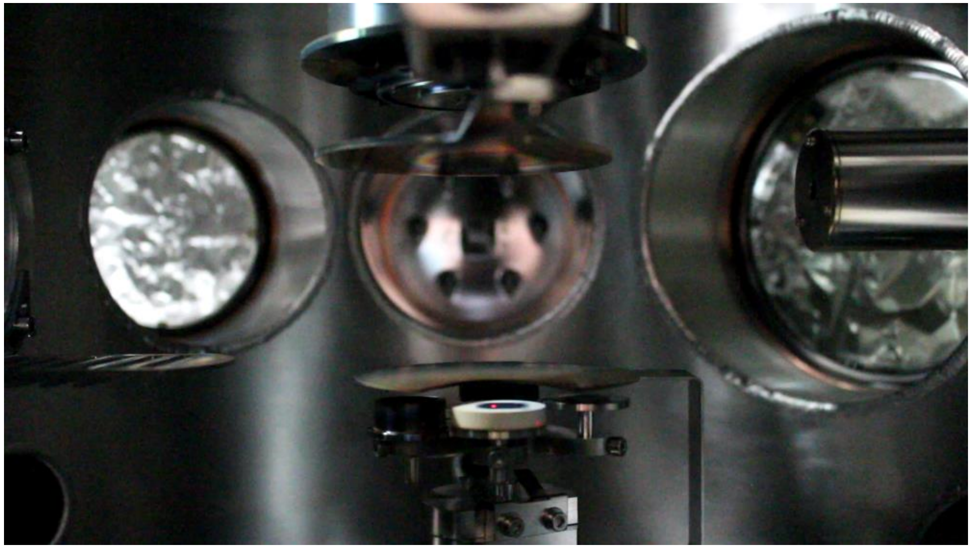
  e.g. target-sample distance (T-S) 55 mm

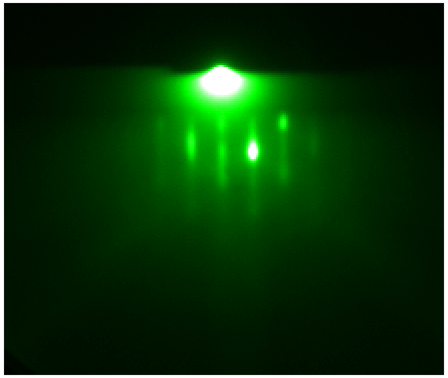
- We can measure the crystal structure of the surface during growth using RHEED
- Cool the sample in a process gas

  e.g. O_2 at 200mBar

- Transfer the sample to the load-lock and out of the system



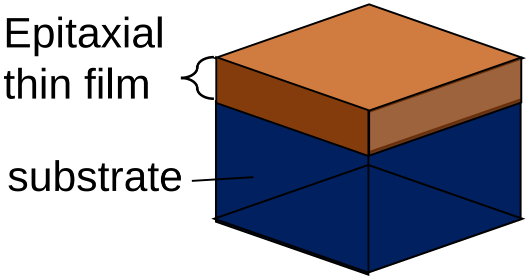




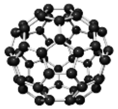
Molecular Beam Epitaxy

UNIVERSITY OF LEEDS

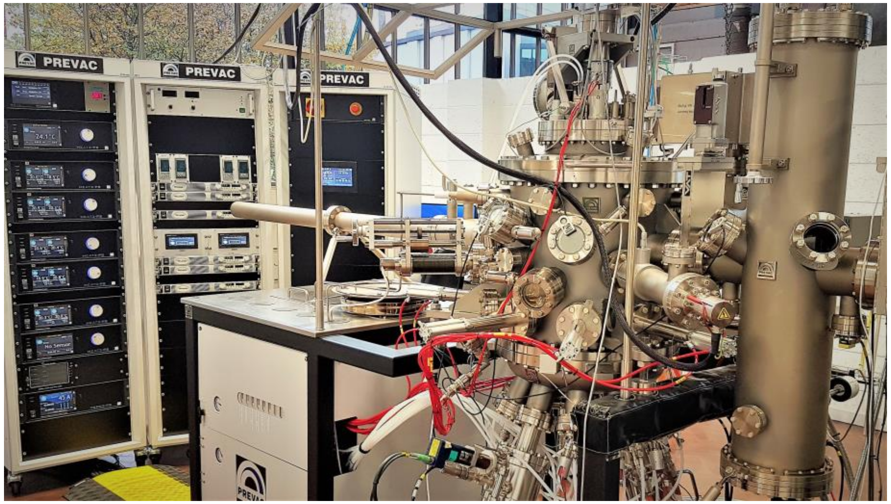
Molecular Beam Epitaxy (MBE)



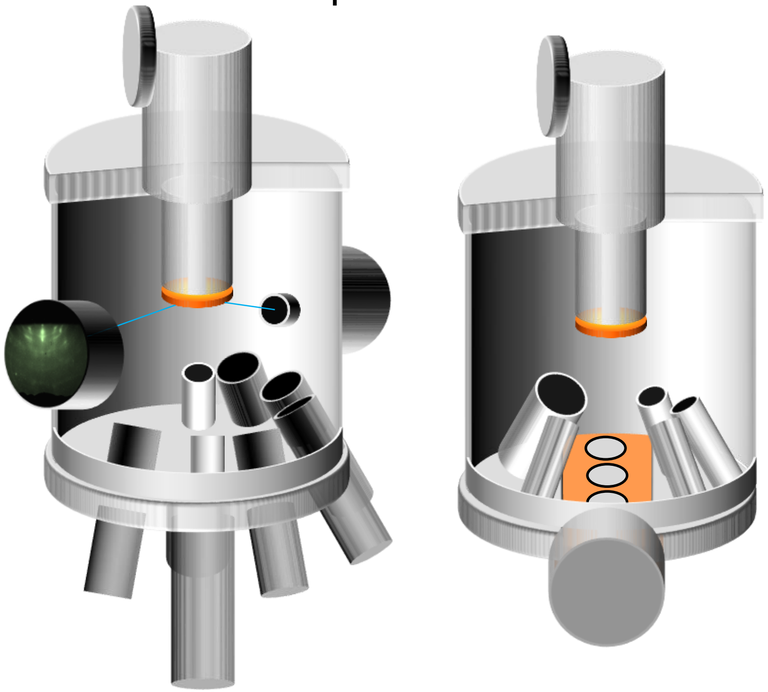
Bi_2Se_3



Cu/C_{60} multilayers



- Beam of evaporated/sublimed material



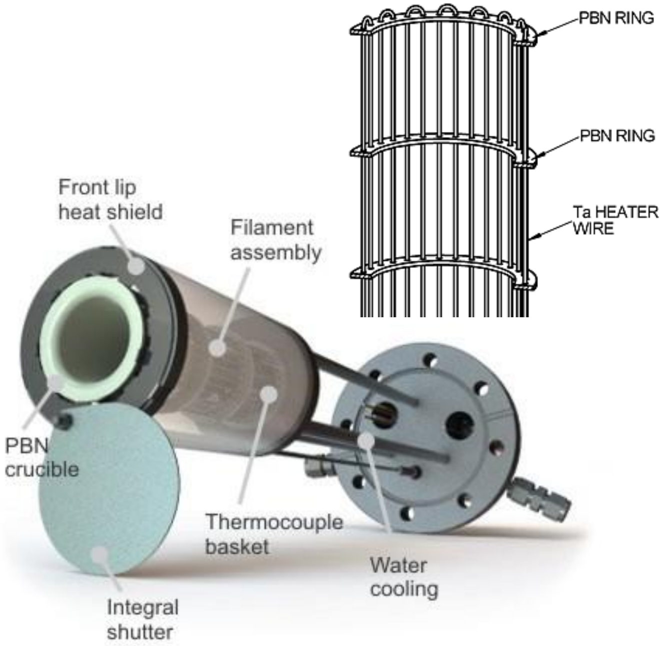
- Wide range of source materials: metals, organics
- Very specialized chambers dedicated to a few materials
- Alloys are made by combining different sources,
- Stoichiometry can be challenging
- Very slow growth rates often <0.1 Å/s
- Potential for very good epitaxy and high degree of crystallinity

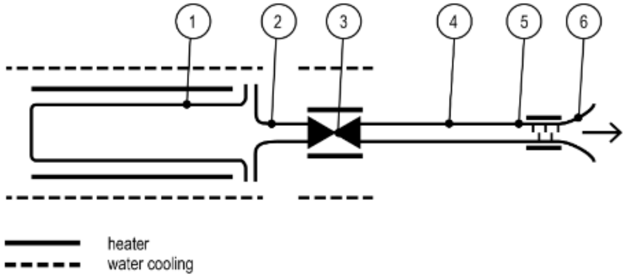
MBE: effusion cell

- Thermal evaporator with a crucible made of e.g. boron nitride, tungsten, graphite, quartz
- The material in the crucible is heated using resistive heating elements until a vapour forms
- “effusion” is the process of atoms/molecules a the vapour exiting an aperture
- Cells designed for higher temperatures are needed for materials with low vapour pressures
- Can include multiple heaters e.g. heat the crucible lip to a higher temperature to prevent vapour from condensing there
- Option to introduce reactive gas or plasma for e.g. oxide growth

Cracker cell

- Some materials tend to be evaporated as molecules from standard effusion cells
- Use a heated valve to control vapour output
- Use a heated cracking tube to break up molecules



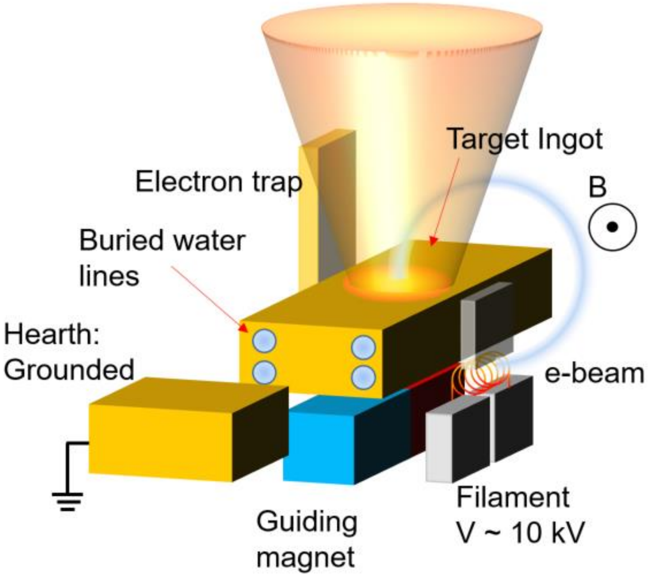


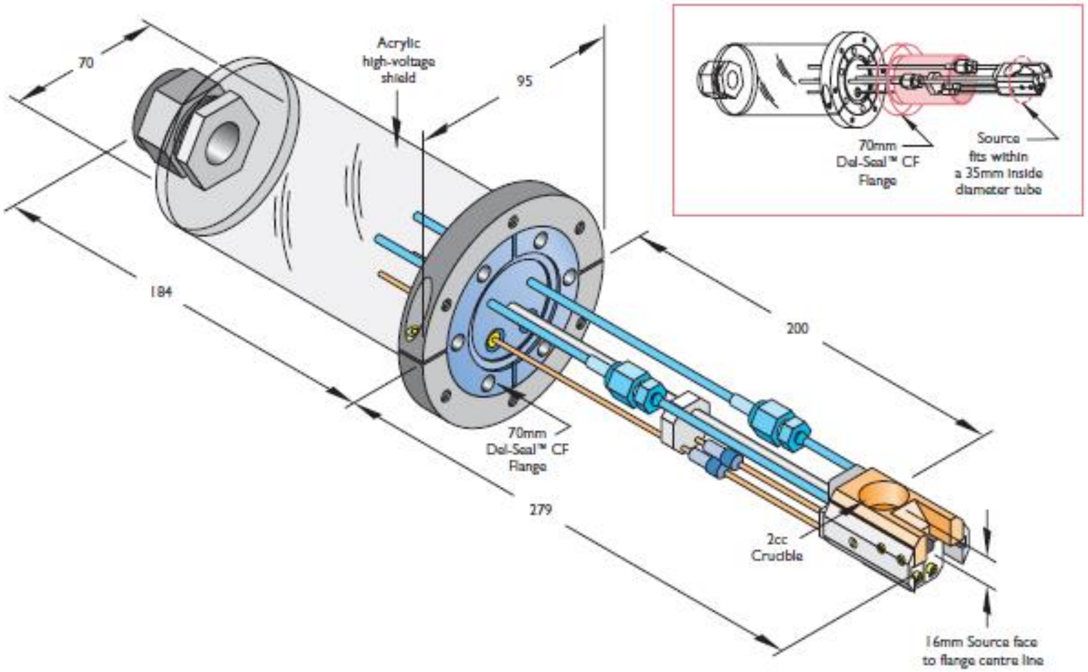
Schematic sketch of the VCCS building blocks. The PBN-funnel (2) connects the PBN reservoir (1) with the full-PBN valve (3). The evaporant is guided to the cracking stage (5) by a PBN injector tube (4). For better homogeneity there is a beam shaping funnel (6) on the orifice of the VCCS.

MBE: e-beam evaporation

- Electron beam emitted from a filament
- Beam steered onto the target material with magnetic field
- Electron bombardment heats and melts the target

- Works well for high melting point materials

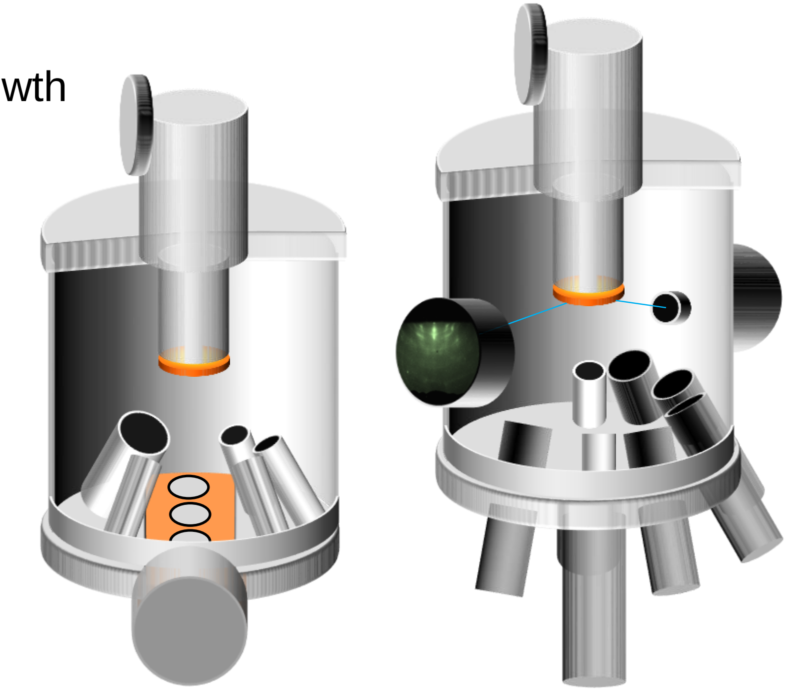




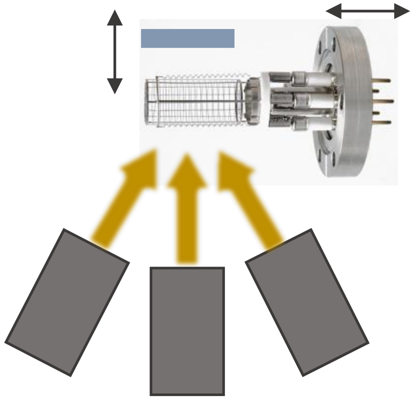
- Hearth can contain multiple pockets for different target materials

MBE

- UHV technique 10^{-8}-10^{-11} mbar
- Prepare chamber – sources have to be pre-heated to so that unwanted gases can be pumped away
- Heat substrate to outgas
- Might flash-anneal to reconstruct the substrate surface
- Shutter covers the substrate
- Heat sources (effusion/e-beam) until the right flux of material is being emitted
- Open the shutter to start depositing
- RHEED is often used to monitor growth
- Close the substrate shutter
- Cool sources and substrate



In situ measurement

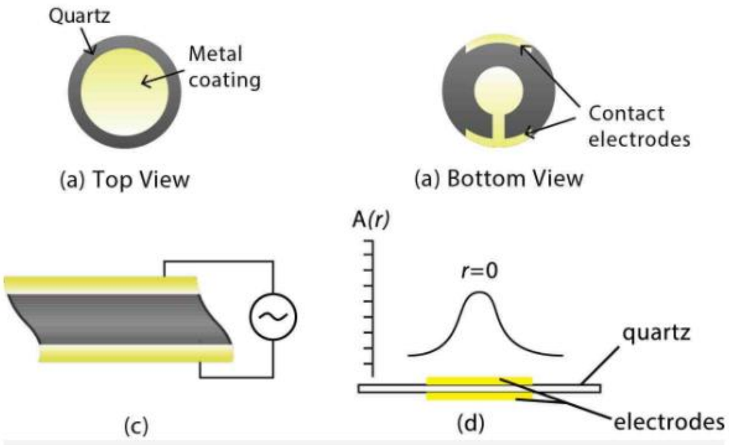


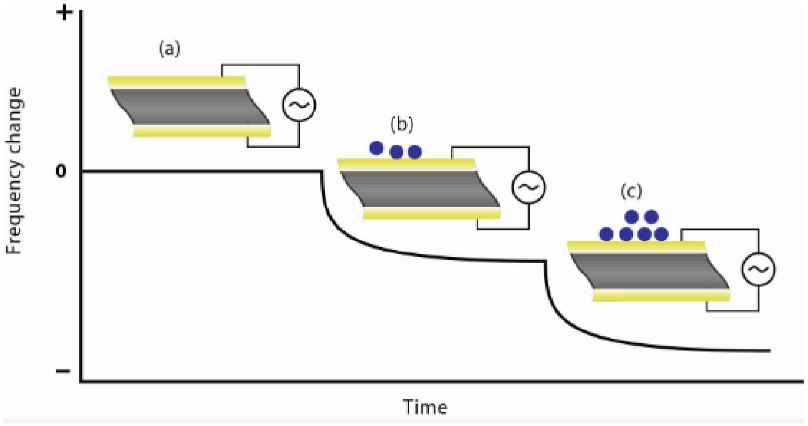
Flux monitors

- Measuring the partial pressure of material vapour
- Ion gauge filament
- Used for MBE in UHV conditions
- Position at the source focal point
- Retract flux monitor and move substrate down for growth

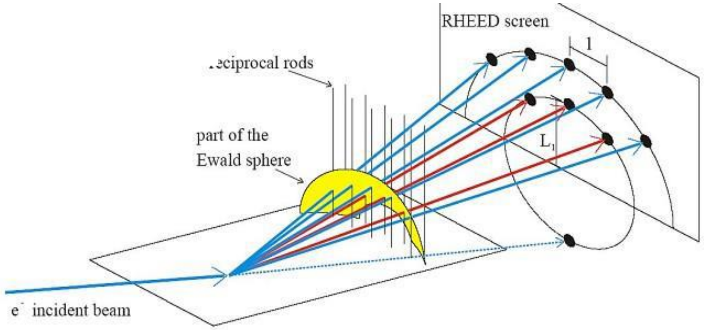
Quartz crystal microbalance

- Measuring thickness quantity of deposited material
- Apply ac voltage to oscillate quartz
- Measure frequency shift due to deposited material



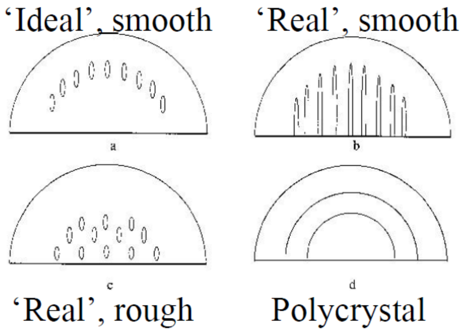


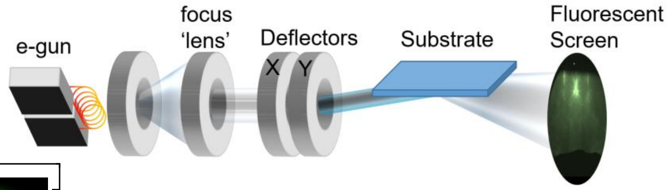
In situ measurement - RHEED

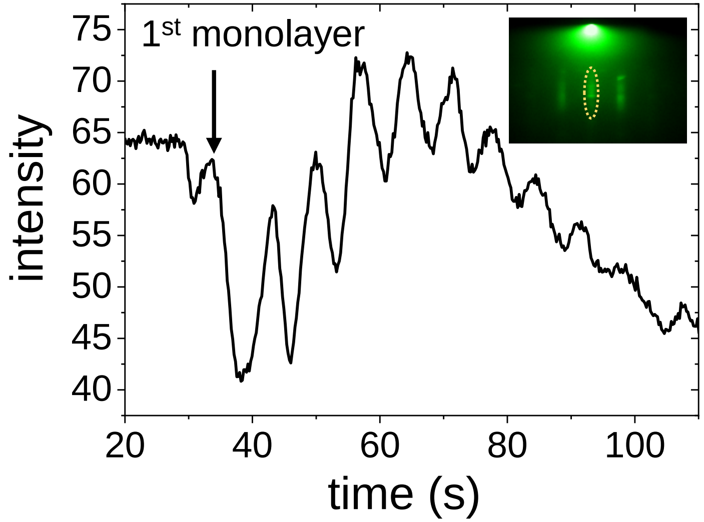


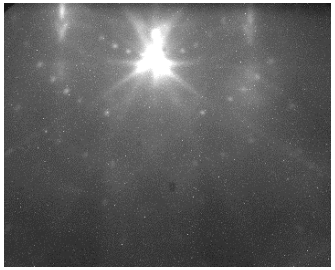
Reflection High Energy Electron Diffraction (RHEED)

- Electron diffraction at grazing incidence (2θ ~ 1°-5°)
    - Highly surface sensitive
- Typical accelerating voltages 10-30 kV
- Electron wavelength << 1 Å
    - Sensitive to atomic length scales
- Real-time monitoring of layer formation



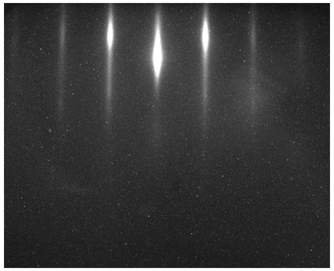






Si(7x7) surface pattern

sub 1ML pattern gone



Epi-film, streaks

Summary

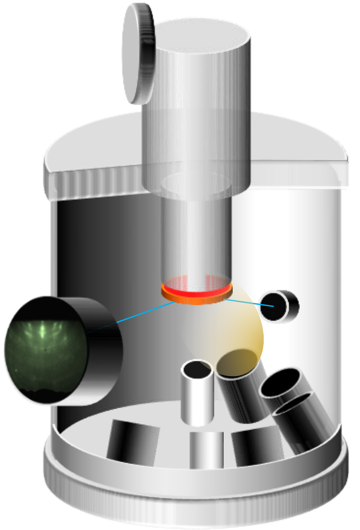
- How we achieve, maintain and measure vacuum
    - Cleaning
    - Vacuum-compatible materials
    - Seals
    - Baking
    - Load locks
    - Pumps
    - Gauges
- Thin film deposition processes and techniques
    - Sputtering
    - Pulsed Laser Deposition
    - Molecular Beam Epitaxy
- In situ measurements

Royce Deposition System advice and access:
Dr. Philippa Shepley p.m.shepley@leeds.ac.uk
condensed-matter.leeds.ac.uk

Royce Deposition System

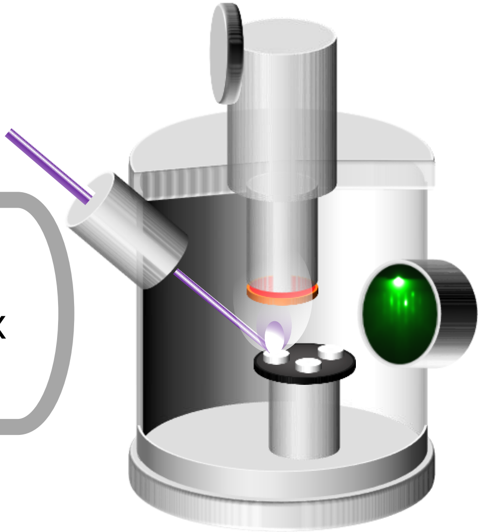
HENRY ROYCE INSTITUTE

UNIVERSITY OF LEEDS

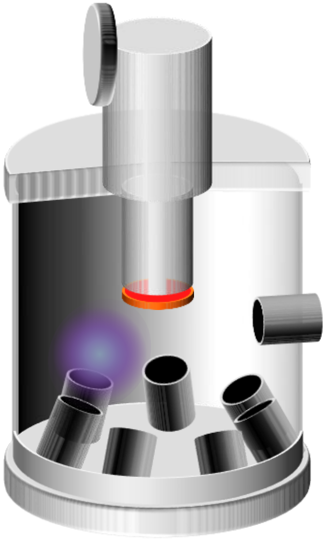


MBE
(topological insulators)

PLD
(Complex oxides)

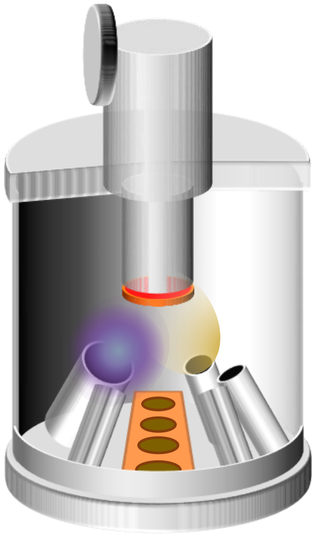


- Chambers linked under UHV
- Multilayer thin film deposition
- Physics at interfaces



Sputtering
(Metals and oxides)

MBE
(Organics and metals)



condensed-matter.leeds.ac.uk

Capabilities

- Thin film deposition with precise control of layer thickness (<1 nm to ~100 nm)
- Substrates sizes of a few mm up to 2 inch diameter wafers
- Wide range of materials (metals, oxides, organics) with best suited deposition techniques (sputtering, pulsed laser deposition, molecular beam epitaxy)
- Temperature control of substrates -100 to 1000°C
- Ultra high vacuum transfer between chambers for clean interfaces between different materials
- RHEED for in-situ characterisation of surfaces

Access for samples via the Royce Access Schemes: **www.royce.ac.uk/access-schemes/**
Contact me to discuss access: **p.m.shepley@leeds.ac.uk**

Royce Deposition System

17th-20th March, Imperial College London

ROYCE TRAINING: THIN-FILM DEPOSITION

Applications opening soon! www.royce.ac.uk/events/