MAX PLANCK INSTITUTE
OF MICROSTRUCTURE PHYSICS

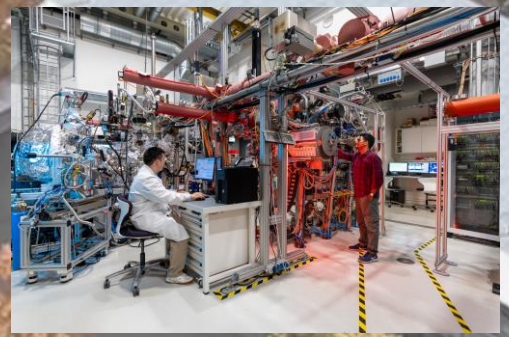
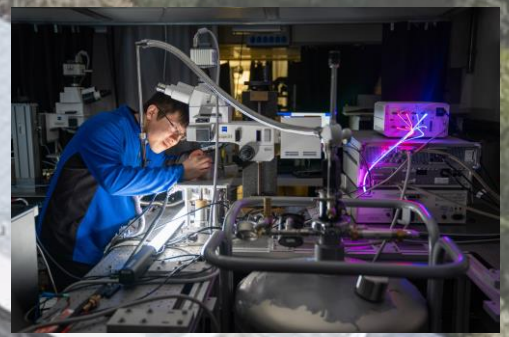
Nano-Systems from Ions, Spins and Electrons
Stuart S. P. Parkin, director

MOLECULAR BEAM EPITAXY

Pierre-Jean Zermatten

FUNLAYER Summer School, July 2025, ALBA



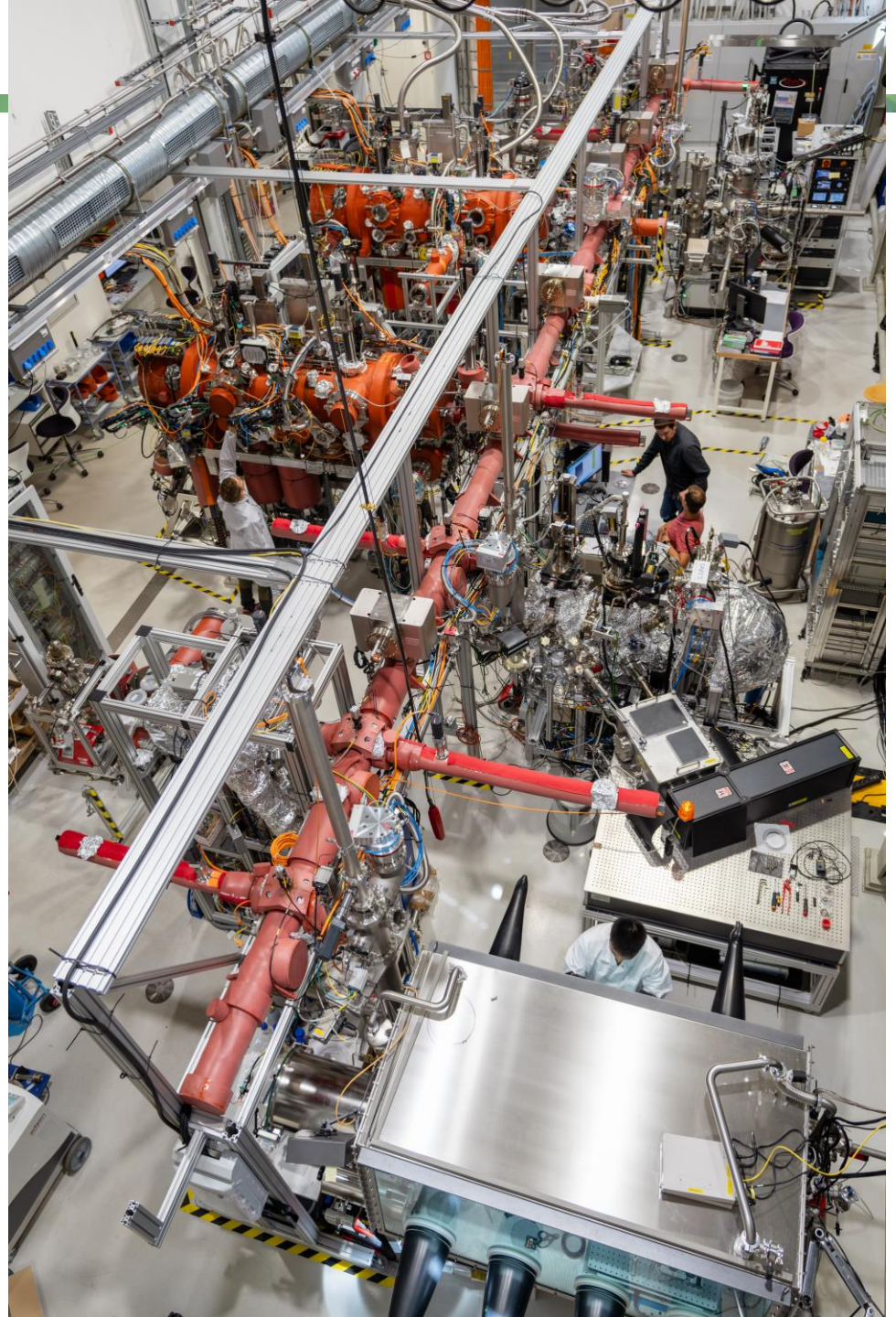

Deposition cluster

Oxide & Nitride MBE cluste

IBD / Magnetron sputtering x2

X-ray Photoelectron spectroscopy (XPS)

UHV sample transport tunnel



Oxide PLD

ARPES with Spin detecto

Exfoliation under N2 atmosphere – glove box

Rob Lavinsky, iRocks.com – CC-BY-SA-3.0

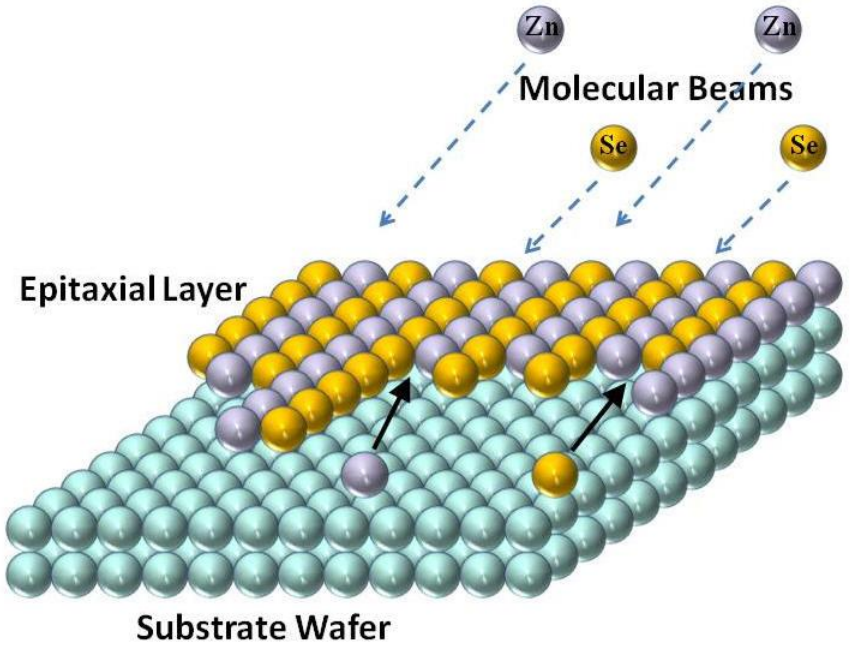
Epitaxy comes from Greek roots
epi – above
taxis – an ordered manner

Homoepitaxy growth – films grown and substrate are the same

Heteroepitaxy growth – films grown and substrate are different

MBE is the most powerful deposition technique for EXPLORING novel materials

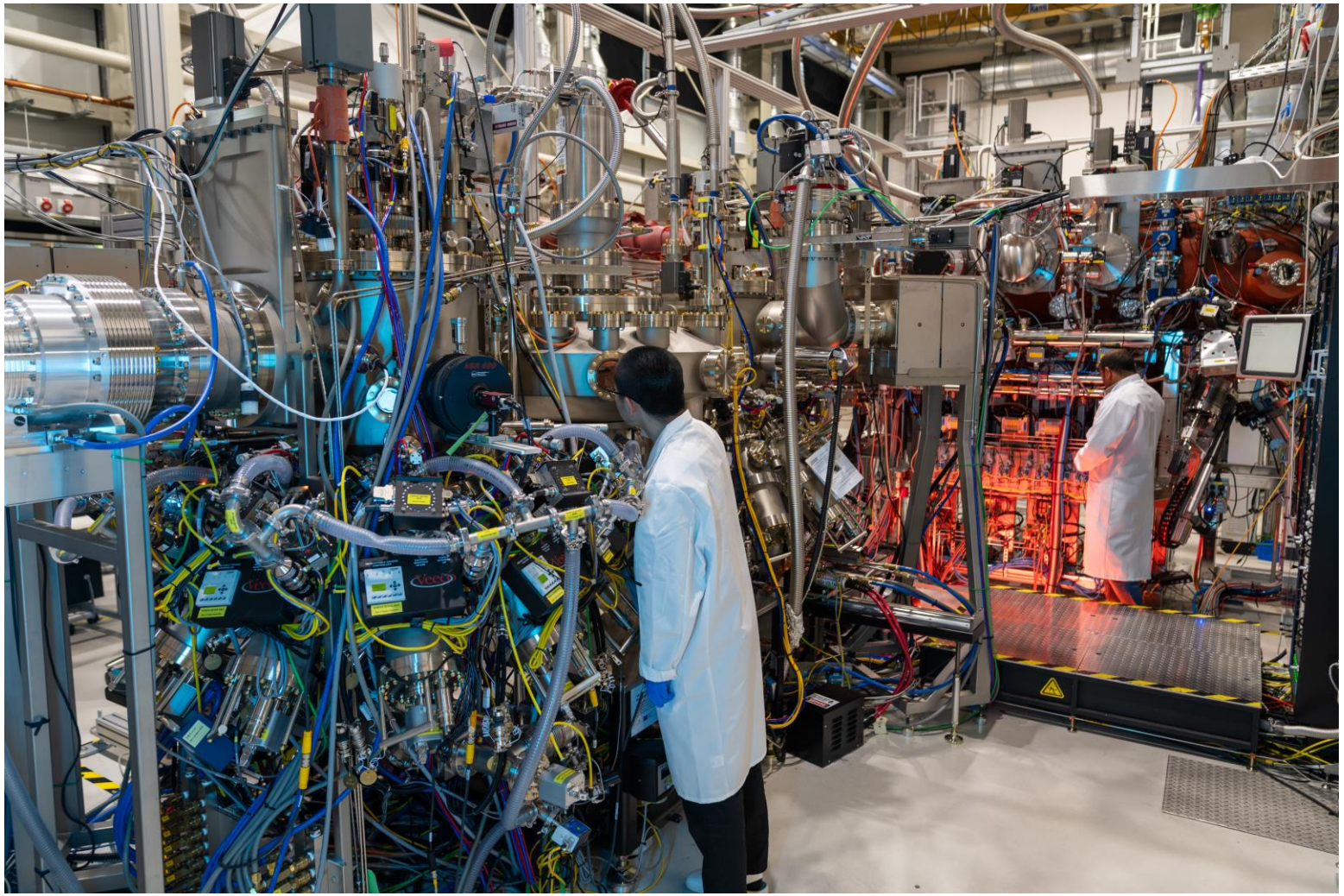
- **High-purity epitaxial growth -** UHV clean environment
- **Atomic-layer precision in thickness and composition** – Low and precisely controlled growth rate
- **Rich in-situ monitoring techniques** — such as RHEED and mass spectrometry for real-time observation.
- **Almost every elements available** — capable of growing semiconductors, oxides, magnetic materials, and more.
- **Ideal for complex heterostructures**



advantages — precise control and high-quality epitaxial growth
limitations — low growth rate, long setup time and high cost

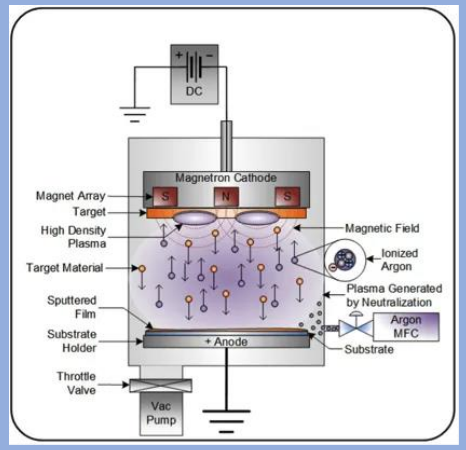
Objectives – introduction to MBE

- Vacuum
- Material sources type
- In-situ analysis technique – RHEED
- Few example on the growth of 2D materials



Physical vapor deposition - PVD

DC/RF Magnetron Sputtering

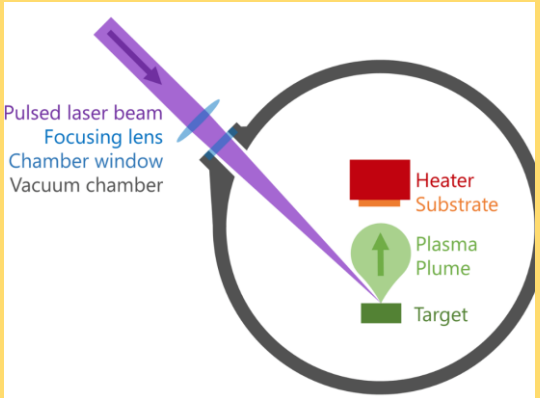


+ Co-deposition

+ Easy and unexpensive tech.

- “high” deposition rate
- use Argon gas (@1mbar)

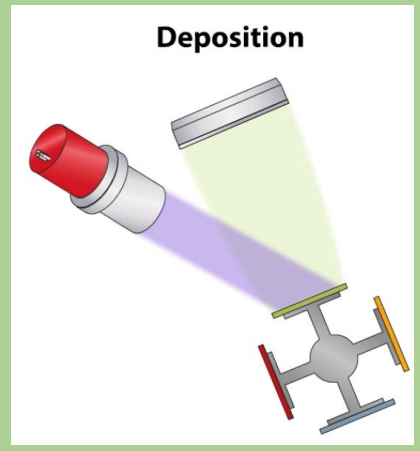
Pulsed Layer deposition



+ Epitaxial growth - Laser ablation generates a high-energy plume, which can enhance film crystallinity at lower substrate temperatures.

- Complex plume dynamics
- Target degradation that affects reproducibility
- No co-deposition

Ion beam sputtering

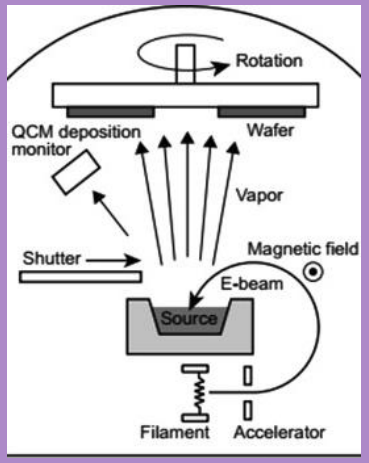


+ Use gas (Ar, Kr, Xe)

+ Works with almost every materials

- High flux can bombard the substrate and impacts film quality

E-beam sputtering



+ No gas needed – compatible with UHV

+ Can deposit material with high melting point

+ Deposition rate can be varied in a wide range

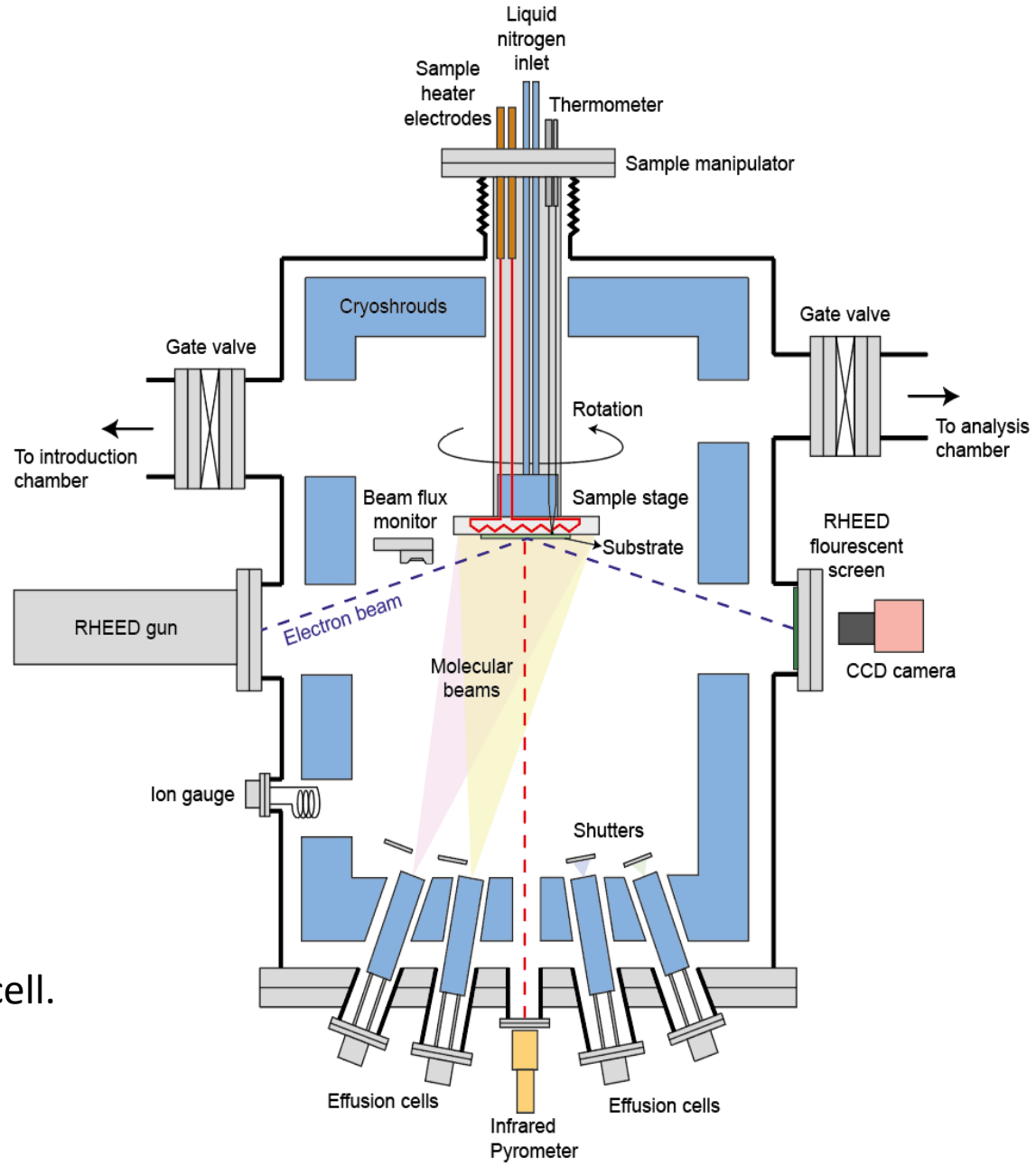
- Deposition rate varies during process

MBE system

HEATER
Usually up to 1000 C
Stable and reproducible
PID with thermocouple

RHEED
In situ analysis system

KNUDSEN CELLS
One pure material in each cell.
˜100 ms actuation shutter

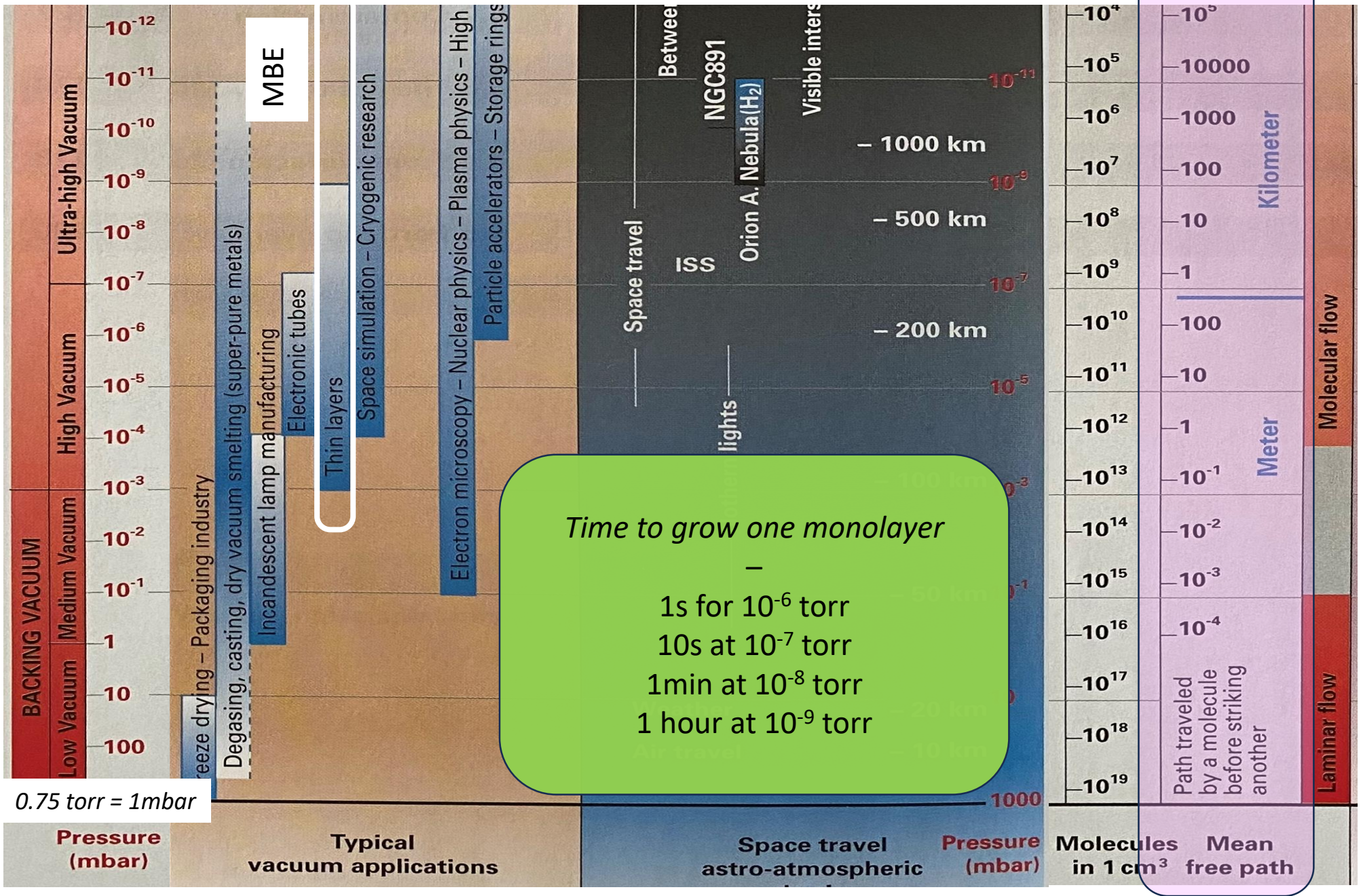


CRYOSHROUDS
Keeps the walls cool and thus avoid evaporation of previously deposited materials
LN2 or water when ozone gas is used (O3 becomes liquid @ 161K).

PUMPS
Purpose - reach 10^{-10} torr or better (see next slides)

Vacuum

Why do we need high vacuum?



Time to grow one monolayer

–

1s for 10^{-6} torr

10s at 10^{-7} torr

1min at 10^{-8} torr

1 hour at 10^{-9} torr

0.75 torr = 1mbar

CVD - Chemical **Vapor** deposition

PVD - Physical **Vapor** deposition

Elements to be deposited onto the surface come in a vapor phase. Sample surrounding must be evacuated / pumped prior to the deposition

Vacuum technology
Pfeiffer Know-how book

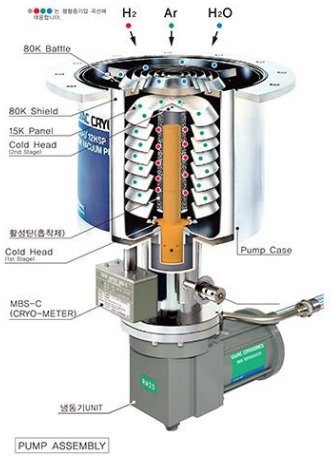
Types of pumps – Pumping speed and specifications

Turbo molecular pump

Water - ...
Air - 1250 litres/sec
Hydrogen - 1200 litres/sec
Argon - 1200 litres/sec

+ work with high gas load
- Ultimate pressure ~10^{-9} torr

Cryo pump



Water - 4000 litres/sec
Air - 1500 litres/sec
Hydrogen - 2500 litres/sec
Argon - 1200 litres/sec

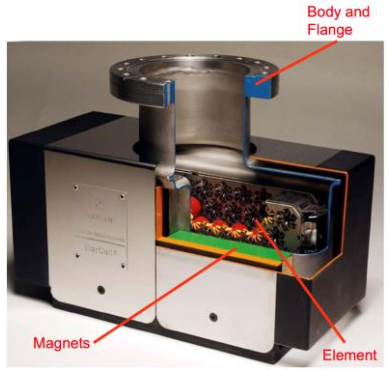
+ extremely good for pumping water
- Noisy / vibration
- Do not work with gas load

Titanium sublimation pump

Pumping speed depends on the surface

- Cannot pump noble gas
+ Unimitated ultimate pressure

Ion getter pump



N_2, O_2, H_2, CO_2, Water... – 200 l/sec

+ no moving parts
+ vacuum is kept even during electric shutdown
+ operate to 1E^{-12} torr
+ clean environment

-poor to pump noble gas

SOURCES

Different type of source depending on the evaporated element

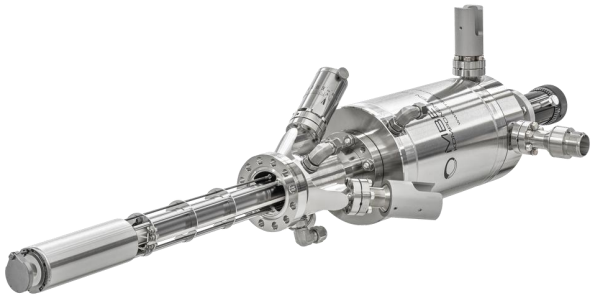
H																	He
Li	Be											B	C	N	O	F	Ne
													Spec.				
Na	Mg											Al	Si	P	S	Cl	Ar
													Spec.	Spec.	Spec.		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
															Spec.		
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
											Spec.						

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

- High temperature effusion cell
- Standard effusion cell
- Low temperature effusion cell

} K-cell

- Valved cracker source
- E-beam source



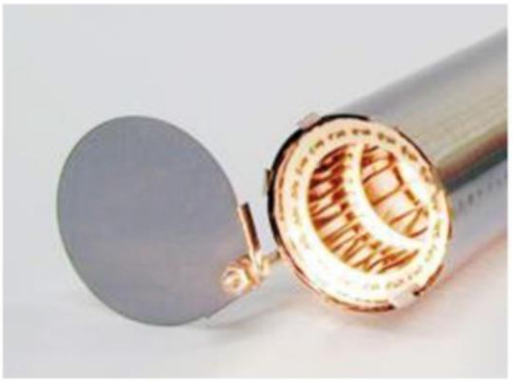
Source: https://www.mbe-komponenten.de/selection-guide/vapor-pressure.php

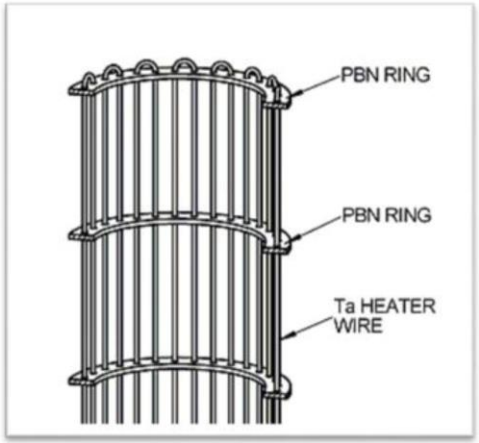
MBE Komponenten | Dr. Eberl

Knudsen cell also called K-cell

Insert -

Crucible –
Various materials (W, Ta, PBN, AlN,...)
Various designs for efficient material consumption and optimal uniformity





Heater filaments + Thermocouples
1 or 2 temperature zones
*PID to guaranty **0.1 C stability!***

MBE Komponenten | Dr. Eberl

Veeco

RIBER

DCA INSTRUMENTS

Total number of molecules emitted from a K-cell per second is proportional to the vapor pressure which depends strongly on the temperature.

For Co, @ 1000 C , a change of 1°C change the flux by ˜3%

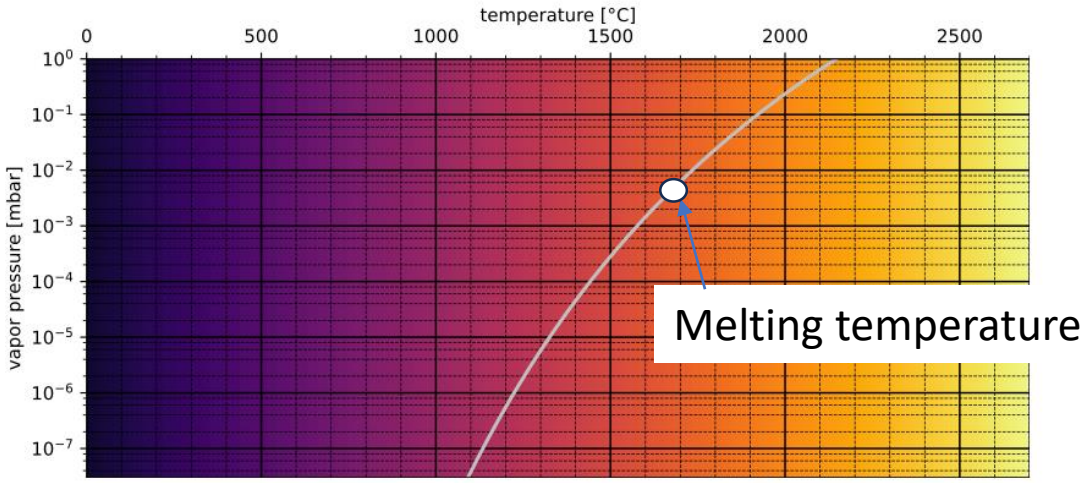
Deposition of Titanium with K-cell, doable but...

Titanium	$p_{vap}=10^{A-B/T[K]}[mbar]$	
^{22}Ti	A=9.735	B=23556
47.867	Transition	Tb=3287°C
	Tm=1670°C	ρ=4.51g/cm³

Isotope abundance:

46	47	48	49	50
8.00	7.30	73.8	5.50	5.40

MBE Komponenten | Dr. Eberl

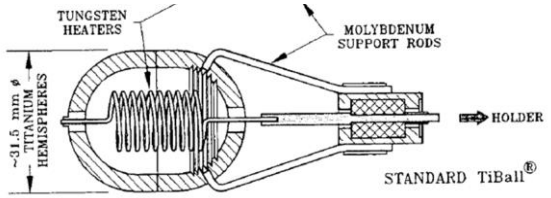


10cc crucible cost approx. 3000 EUR

Denser material that withstand high temperature (1670C) are needed.

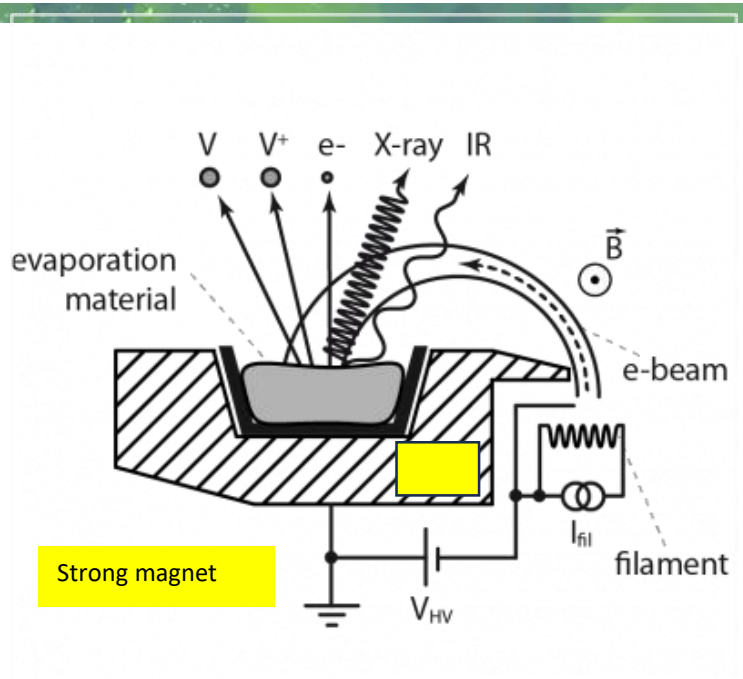
DCA INSTRUMENTS

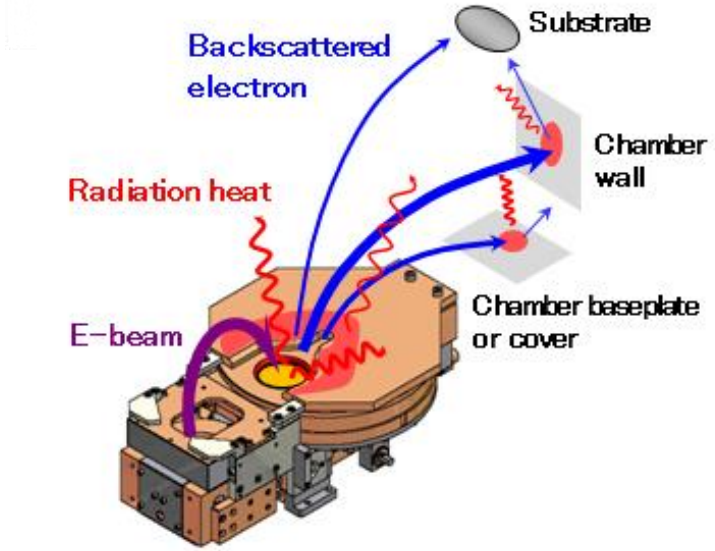
Veeco

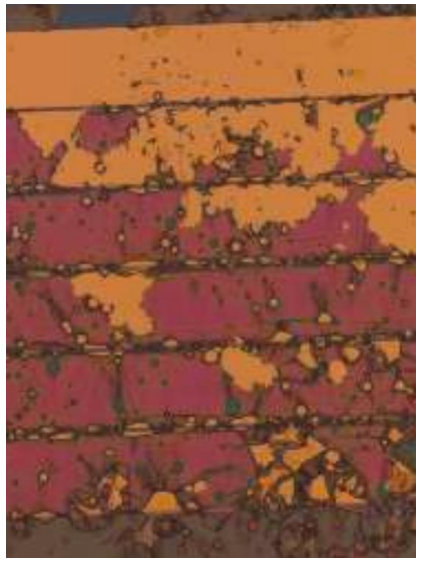


Ref. "A Radiant Heated Titanium Sublimator," Proc. 5th Int. Vacuum Congress, 1971, JVST 9 (1), 552 (1972)

E-beam evaporator







The E-beam flux is not perfectly stable + **arcing** possible that leads to spitting and particles on the substrate.

Radiation heat can burn the resist or affects the material already deposited on the substrate

Secondary electrons can cause

- Substrate damage
- Resist hardening
- Pin holes and flakes

What helps:

- Long source-sample distance (>500 mm)
- Set magnets along the way to deviate the electrons
- High-end supplier and proper grounding

"High" vapor pressure materials

MBE Komponenten | Dr. Eberl

Systems ~ Components ~ Equipment ~ Applications ~ Service ~ About ~ Product Finder ~

Home > Selection-Guides > Selenium

Selenium

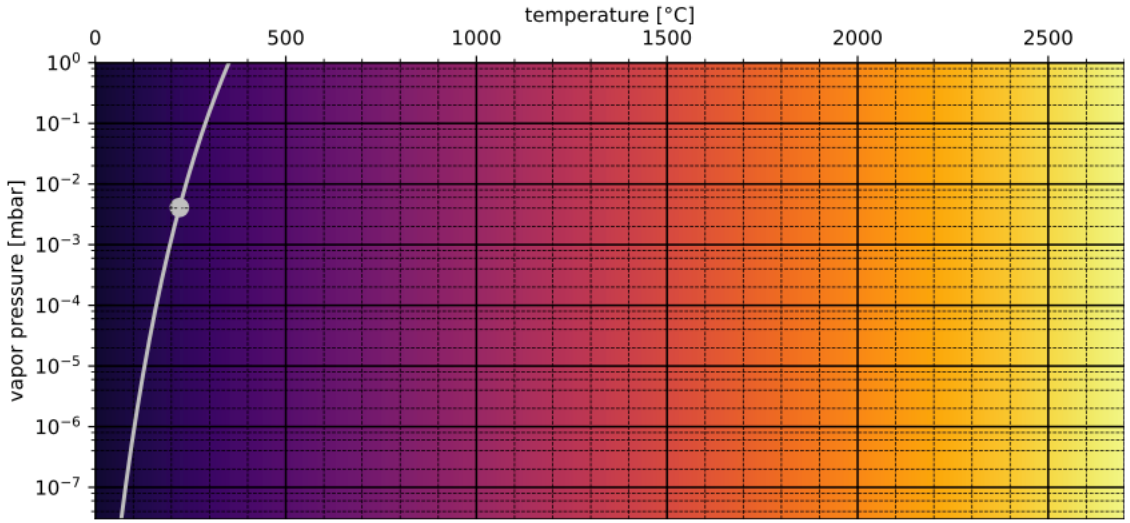
Vapor pressure of Selenium (Se)

Selenium	$p_{vap}=10^{A-B/T[K]}[mbar]$	
^{34}Se	A=9.108	B=5681
78.971	Nonmetal	Tb=685°C
	Tm=221°C	ρ=4.28g/cm³

Isotope abundance:

74	76	77	78	80	82
0.90	9.00	7.60	23.5	49.6	9.40

Antoine equation



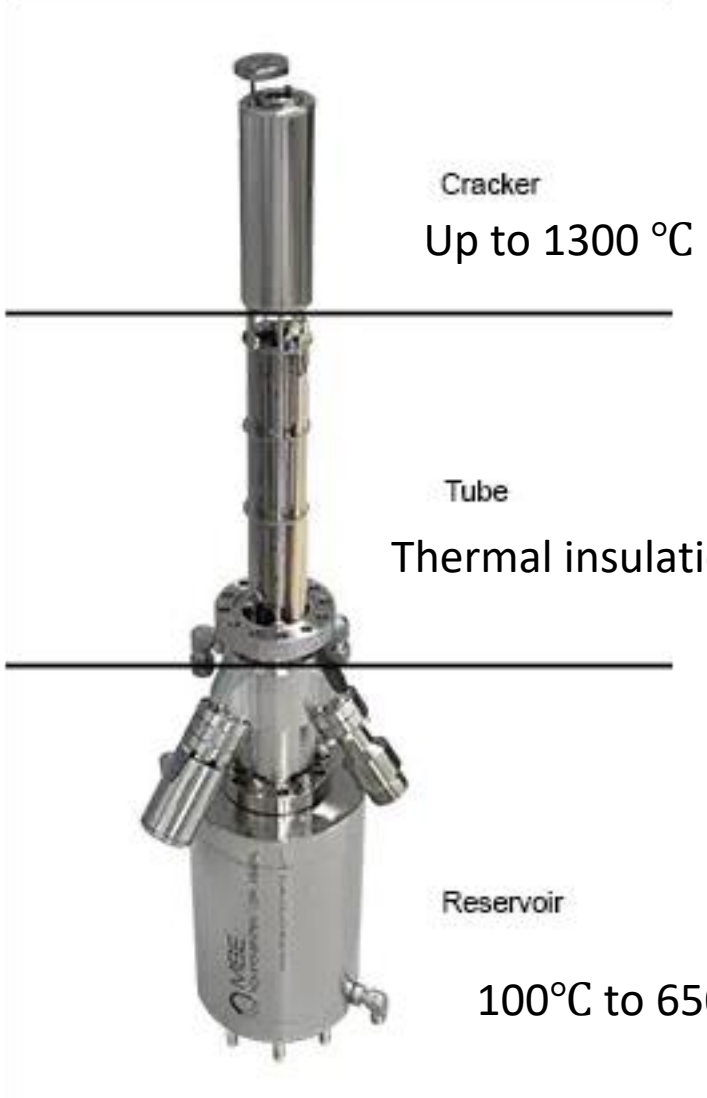
Temperature C	Vapor pressure mbar
20	5,2E-11
50	3,3E-09
80	1,0E-07
110	1,9E-06
140	2,3E-05

These materials are deposited everywhere in the chamber. If, for any reason, some part of the chamber are heated even a bit, then the base pressure increase tremendously.

That's contamination!

Think of WSe_2 for example.

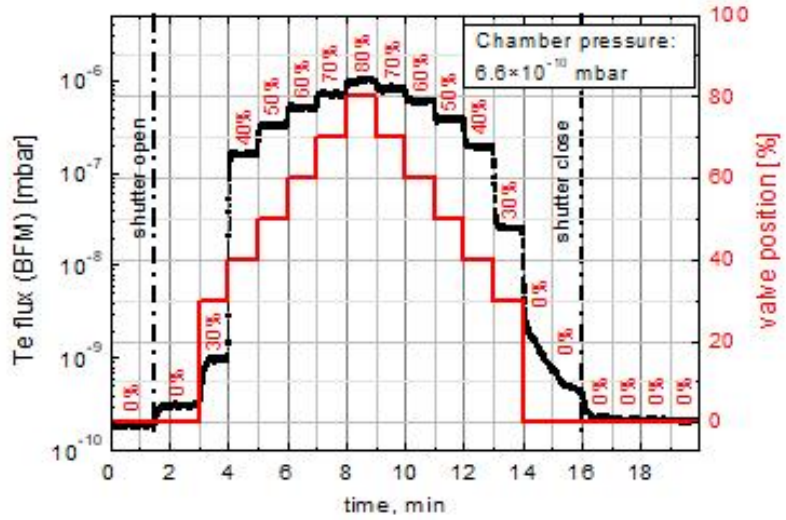
Valved cracker source - for As, Se, Te, Sb, Mg

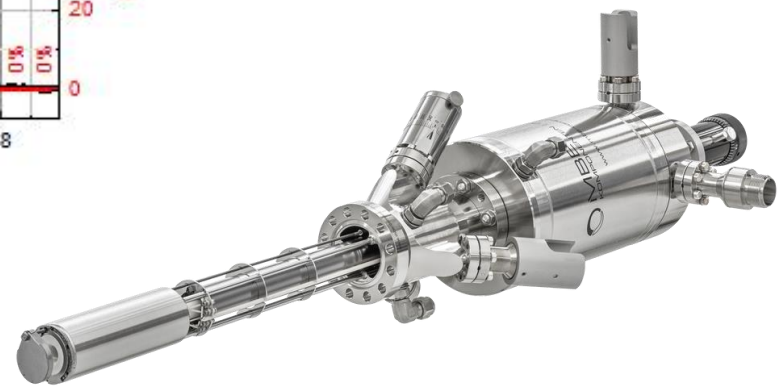


High vapor pressure materials forms atom clusters (poly-mers like Se_6 and Se_5, or Te_2).

The clusters are cracked into smaller form=> more reactive

An additional valve can help controlling the flux even more





RHEED

RHEED – reflection high-energy electron diffraction

Characterization of Materials, edited by Elton N. Kaufmann.
Chapter - REFLECTION HIGH-ENERGY ELECTRON DIFFRACTION by SHUJI HASEGAWA

Used to **analyse structures of crystal surfaces** at atomic levels and to **in-situ monitor growth** processes of thin films

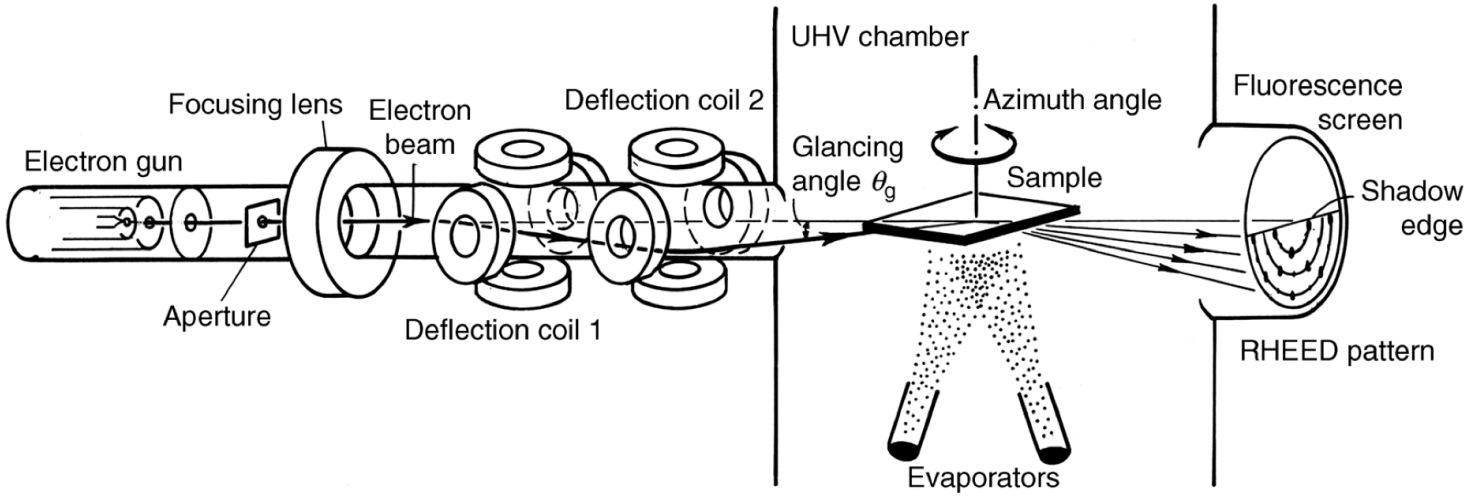
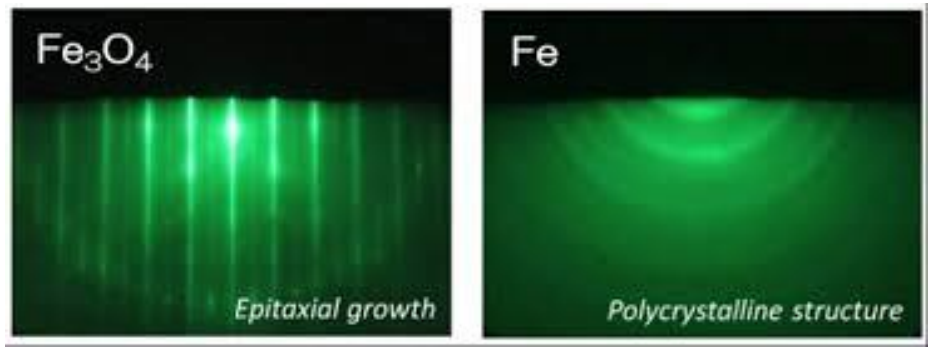


Figure 1. Schematic diagram of RHEED apparatus.



- Needs vacuum to work -> compatible with MBE
- Only the surface is probed - grazing angle ~1-5 degrees
- Compare to LEED (low-energy electron diffraction) where sample is facing the LEED, RHEED can be used during deposition.

Highly sensitive to magnetic field - Rules of Thumb

The earth's magnetic field may deflect a 10 kV electron beam by 20 mm over a travel distance of 500 mm

RHEED pattern evolution to understand the growth mode

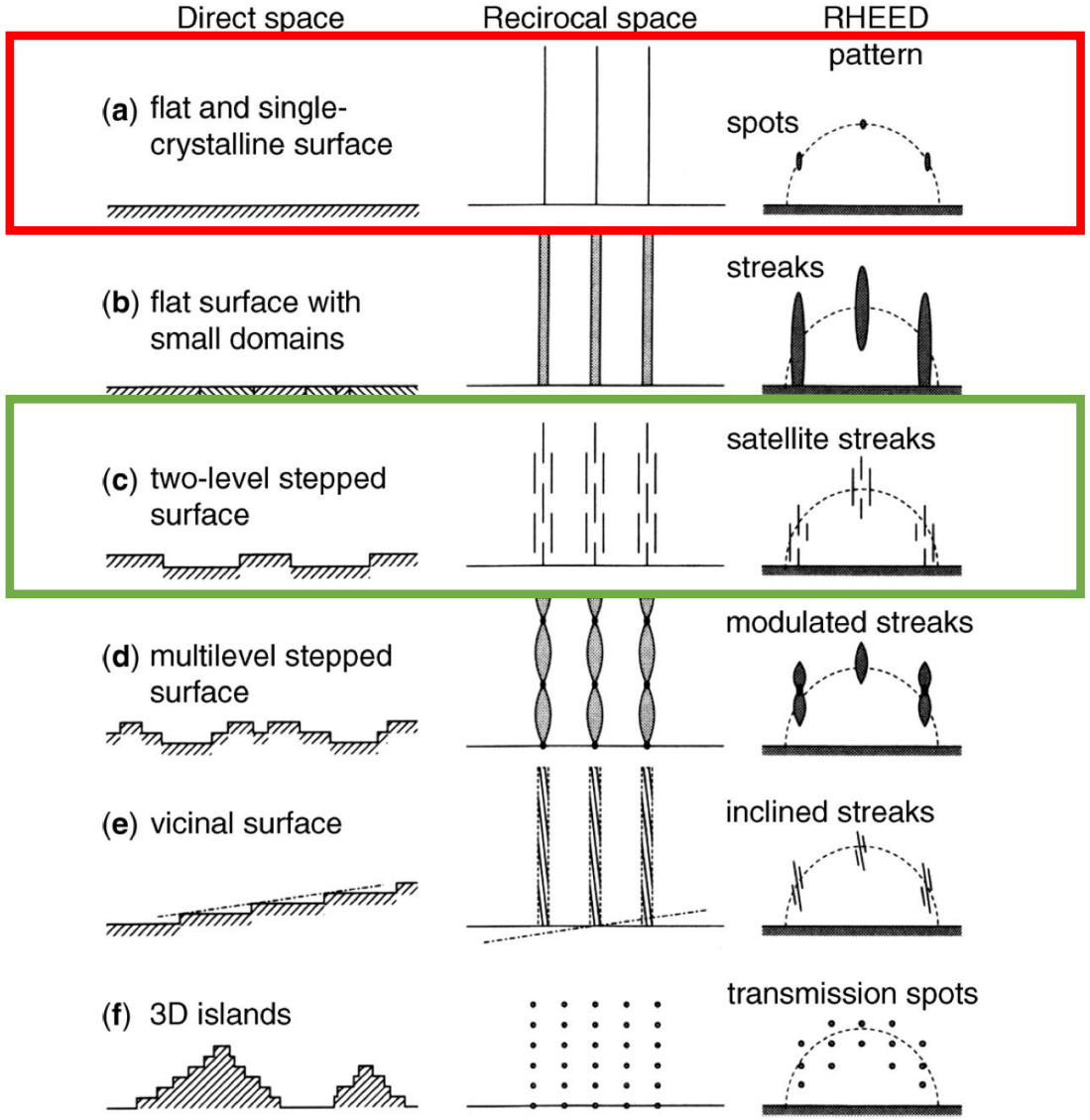
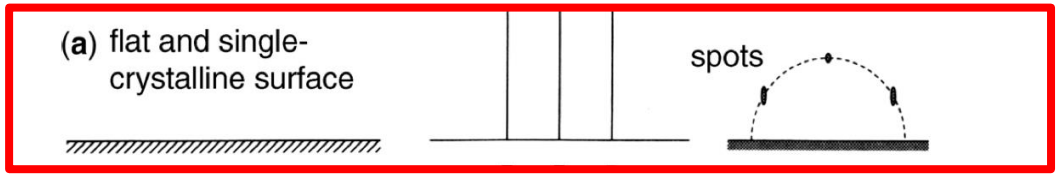


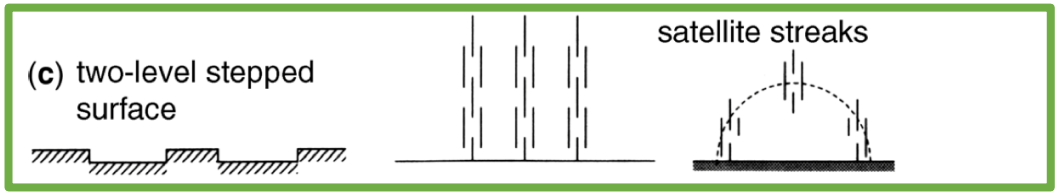
Figure 3. Schematics of various kinds of realistic surfaces, in real-space morphology, in reciprocal space, and their RHEED patterns (courtesy by Yoshimi Horio).

Looking at the evolution of the RHEED pattern during the growth can help understanding the growth mode.

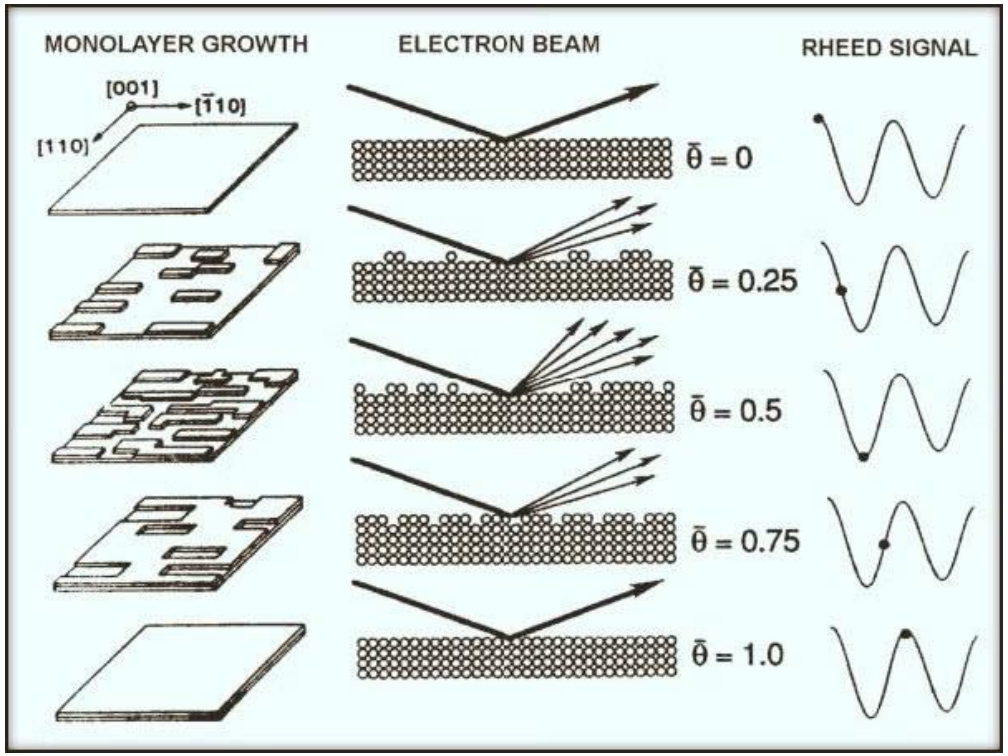
Characterization of Materials, edited by Elton N. Kaufmann.
Chapter - REFLECTION HIGH-ENERGY ELECTRON DIFFRACTION by SHUJI HASEGAWA

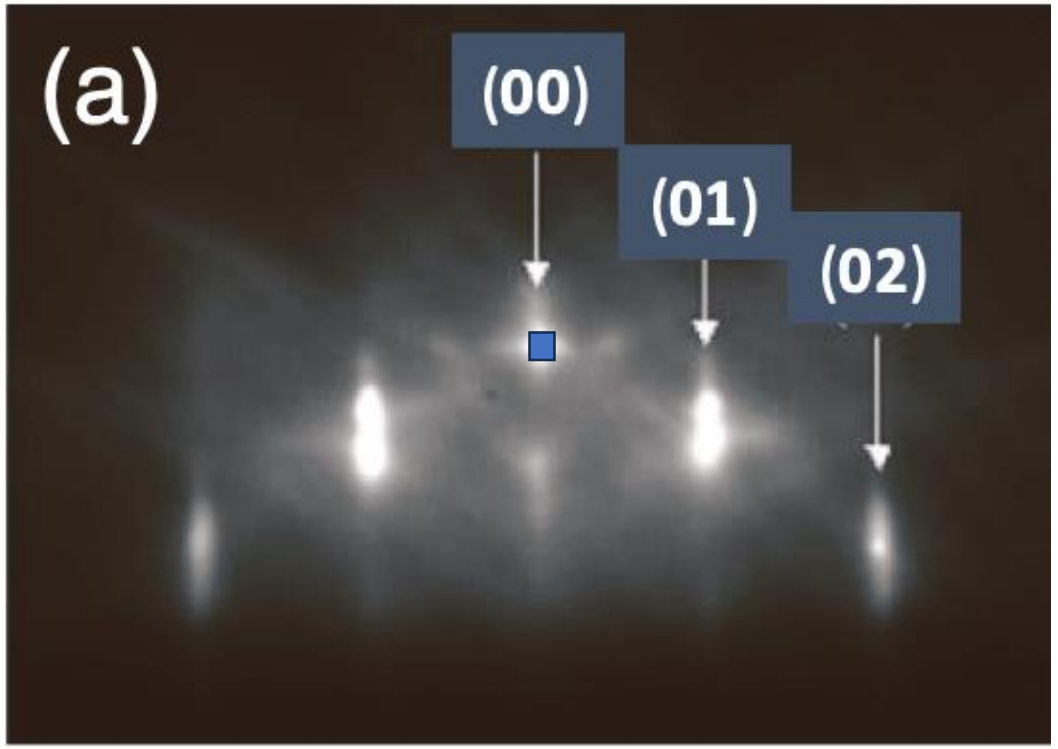
Counting the number of layers





If we plot over time the Intensity of a spot during the growth then here is what we will get if the growth alternate between a single crystalline surface and two-level stepped surface

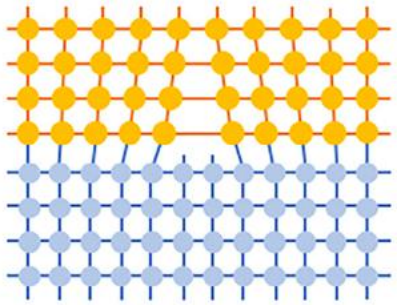




Van der Waals epitaxy

Conventional epitaxy

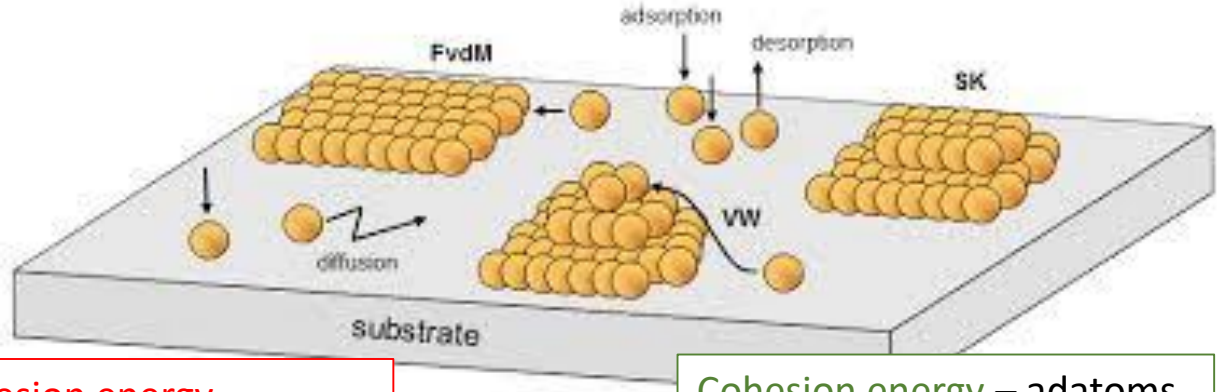
Huije Ryu et al., Appl. Phys. Rev. 9, 031305 (2022)
Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth



Conventional epitaxy
(Chemical interactions)

In-plane lattice parameters of the epi-layer MUST MATCH that of the substrate!

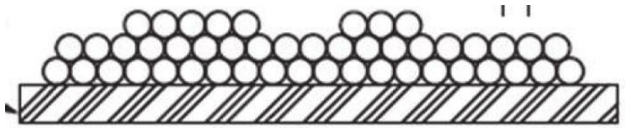
Diffusion barriers –
influenced by substrate defects, dangling bonds,..



Adhesion energy –
adatoms to substrate

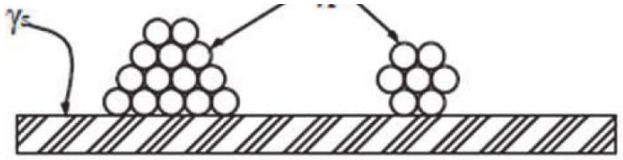
Cohesion energy – adatoms to adatoms

Layer-by-Layer Growth
(*Frank–van der Merwe Mode*)



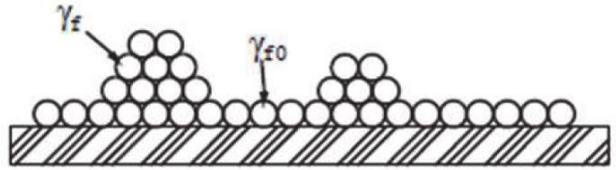
Diffusion barriers – low
E_{adh}/E_{coh} – high

Island Growth
(*Volmer–Weber Mode*)



Diffusion barriers – low
E_{adh}/E_{coh} – low

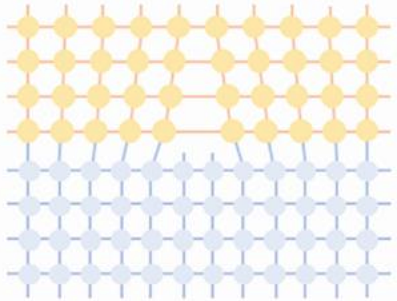
Layer-plus-Island Growth
(*Stranski–Krastanov Mode*)



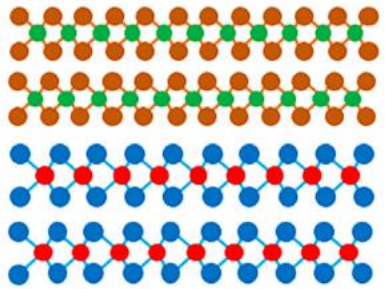
A mixture

van der Waals epitaxy

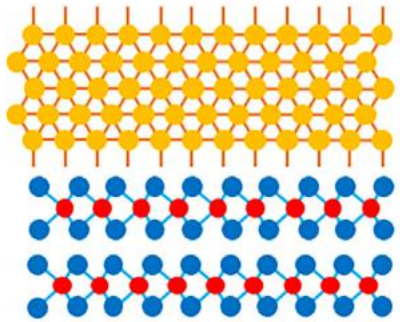
Huije Ryu et al., Appl. Phys. Rev. 9, 031305 (2022)
Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth



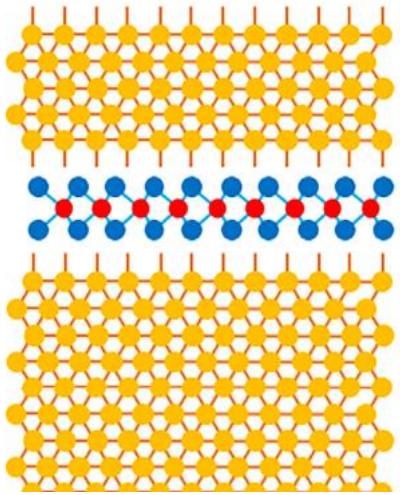
Conventional epitaxy
(Chemical interactions)



Van der Waals epitaxy
(Van der Waals interactions)



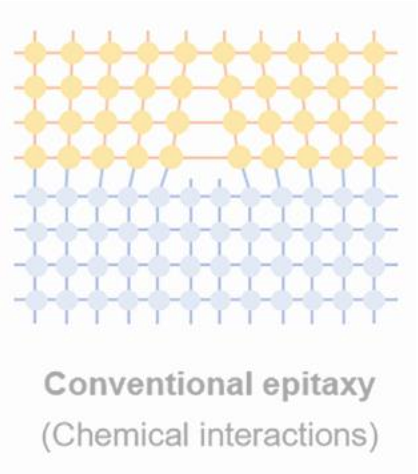
Quasi van der Waals epitaxy
(Quasi van der Waals interactions)

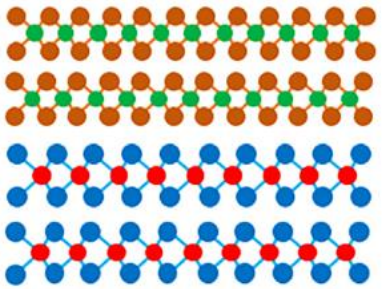


Remote epitaxy (exfoliation)

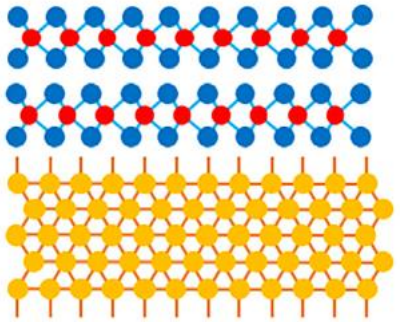
van der Waals epitaxy

Huije Ryu et al., Appl. Phys. Rev. 9, 031305 (2022)
Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth

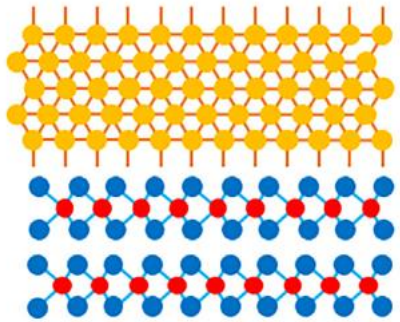




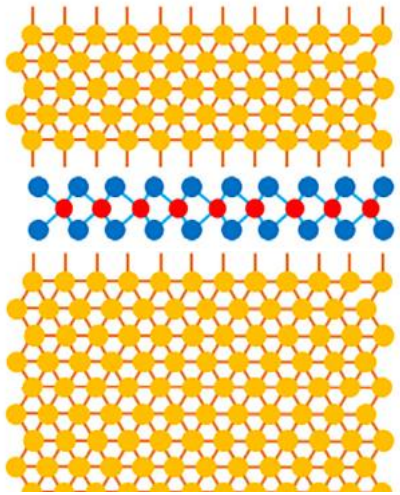
Van der Waals epitaxy
(Van der Waals interactions)



Epitaxy of 2D vdW films



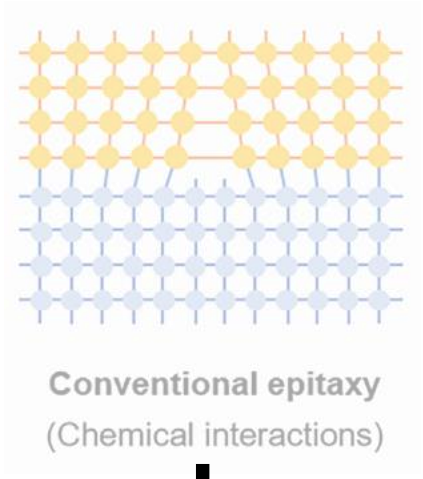
Quasi van der Waals epitaxy
(Quasi van der Waals interactions)

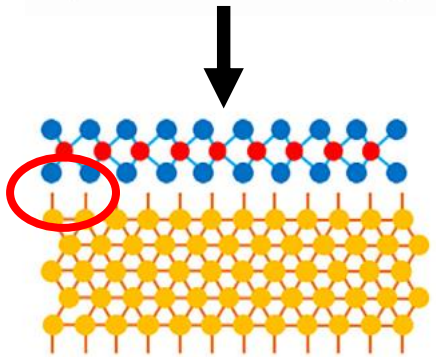


Remote epitaxy

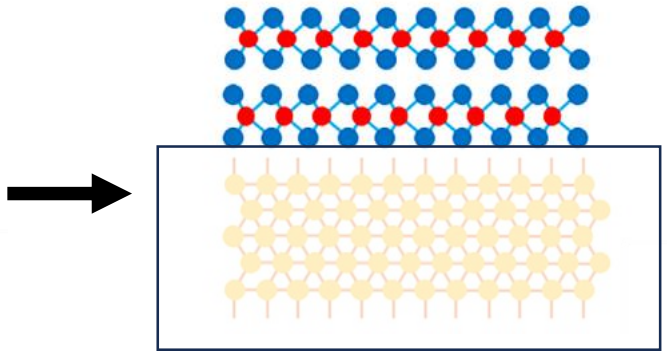
van der Waals epitaxy

Huije Ryu et al., Appl. Phys. Rev. 9, 031305 (2022)
Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth

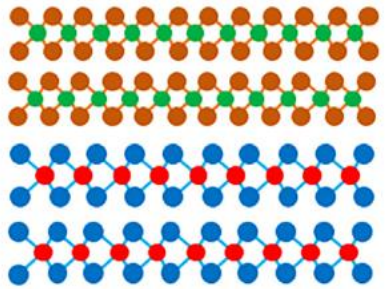




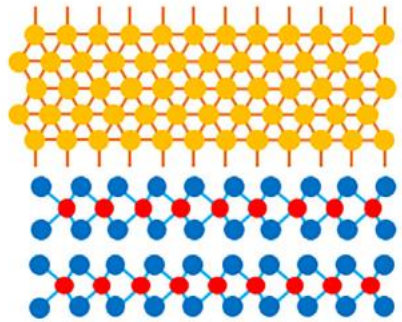
Epitaxy of 2D vdW films



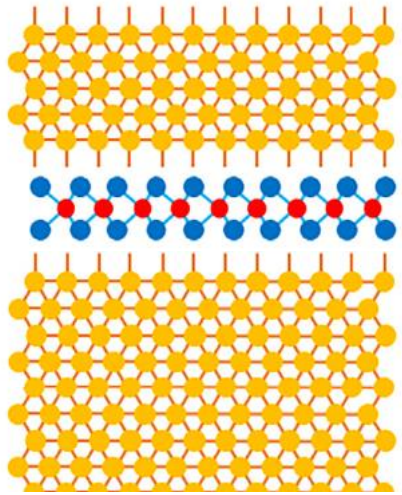
Van der Waals gap
=
Low adhesion energy



Van der Waals epitaxy
(Van der Waals interactions)



Quasi van der Waals epitaxy
(Quasi van der Waals interactions)

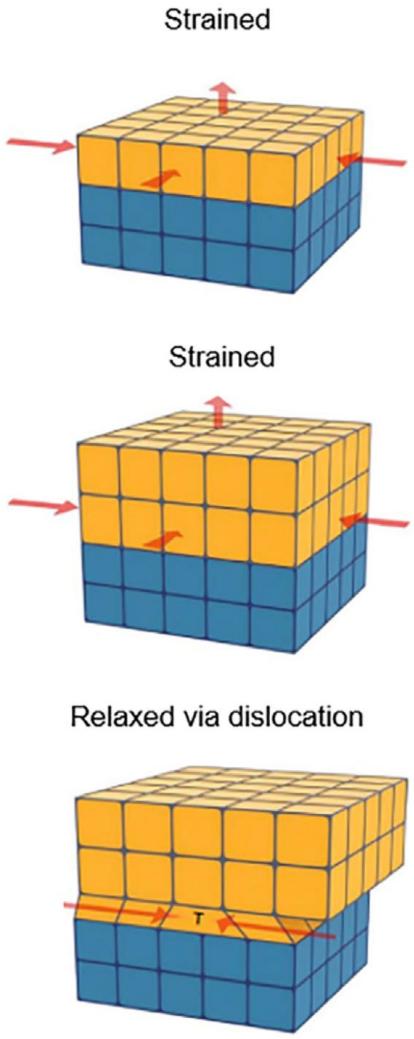


Remote epitaxy

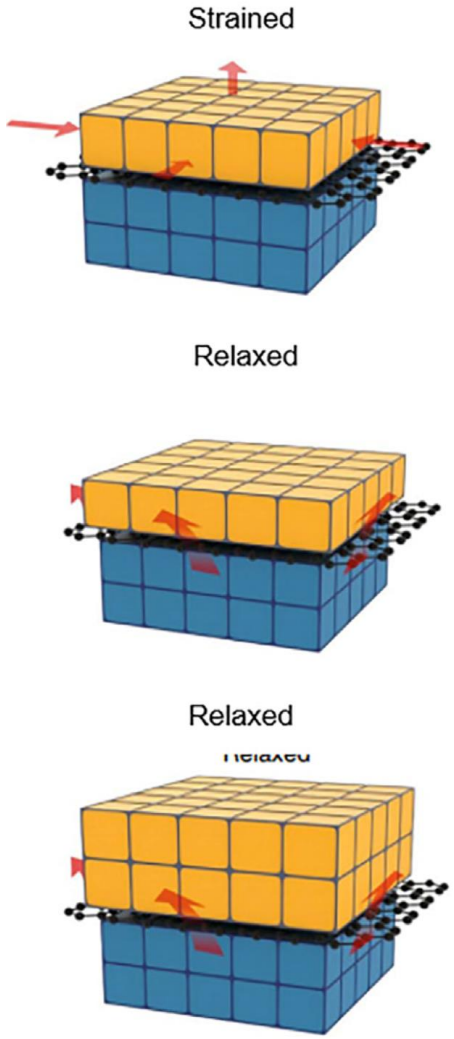
-> lattice parameters mismatch is allowed

van der Waals epitaxy

Huije Ryu et al., Appl. Phys. Rev. 9, 031305 (2022)
Two-dimensional material templates for van der Waals epitaxy, remote epitaxy, and intercalation growth



Conventional epitaxy

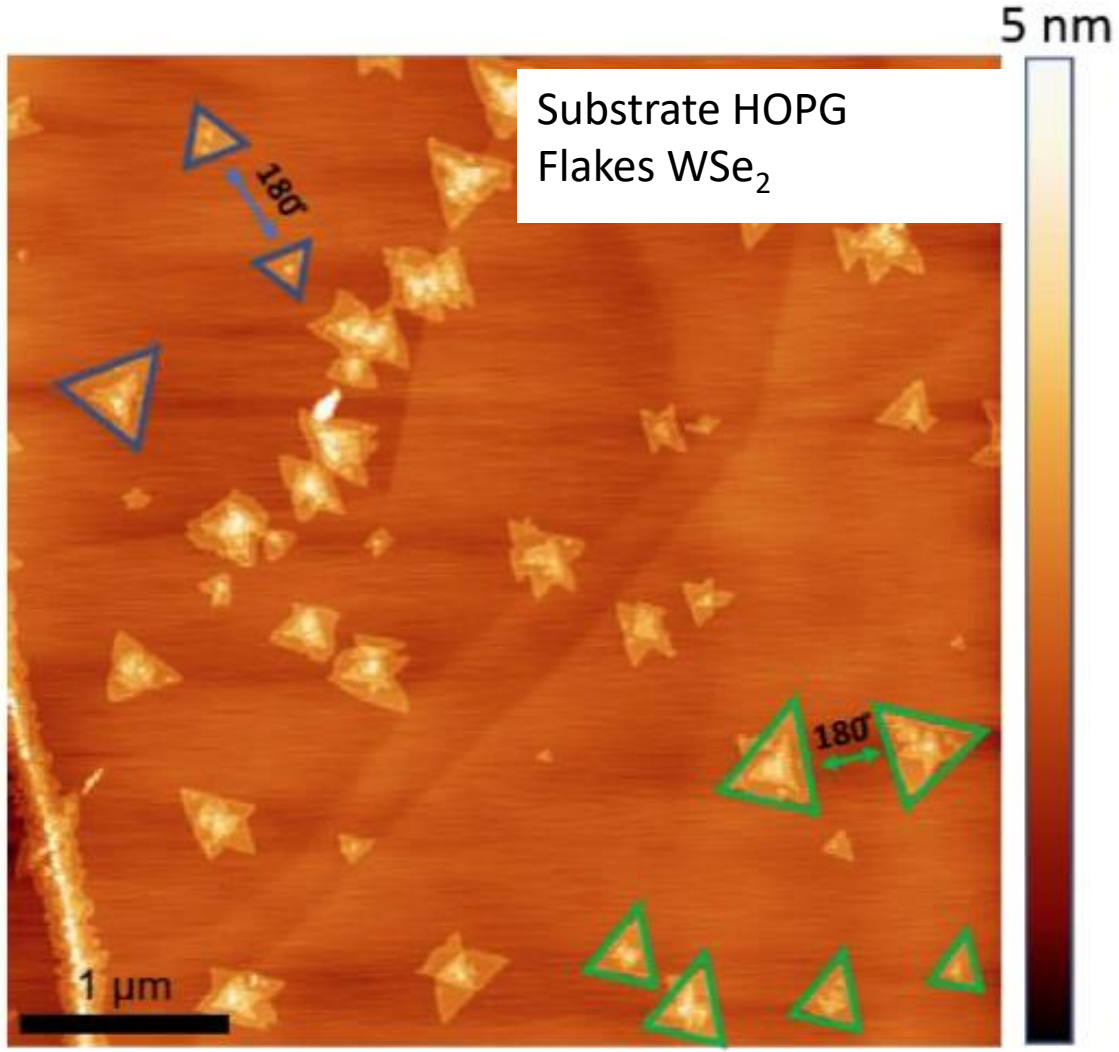


Van der Waals epitaxy

=> **Unstrained Growth:**
The weak van der Waals bonds between the epi-film and the substrate allows for strain-free epi-films.
Latice parameters mismatch is allowed.
Exfoliation possible!

van der Waals epitaxy

Ruoyu Yue *et al.*, 2017 **2D Mater**. 4 045019
Nucleation and growth of WSe : enabling large grain transition metal dichalcogenides



⇒ **Rotational Alignment**

Despite the lack of lattice matching, the grown layers exhibit a well-defined rotational alignment with the substrate's crystal structure.

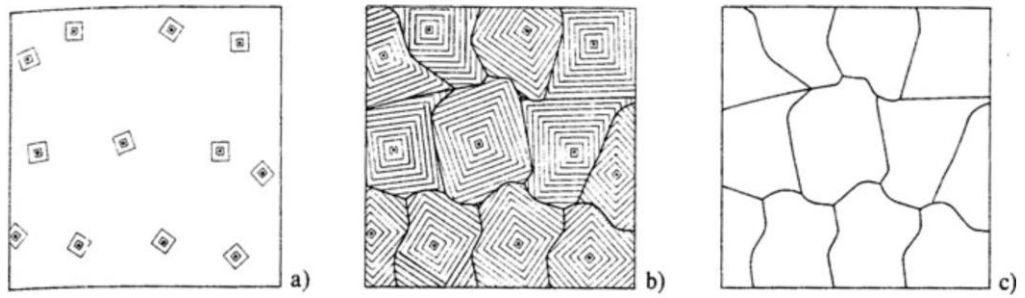
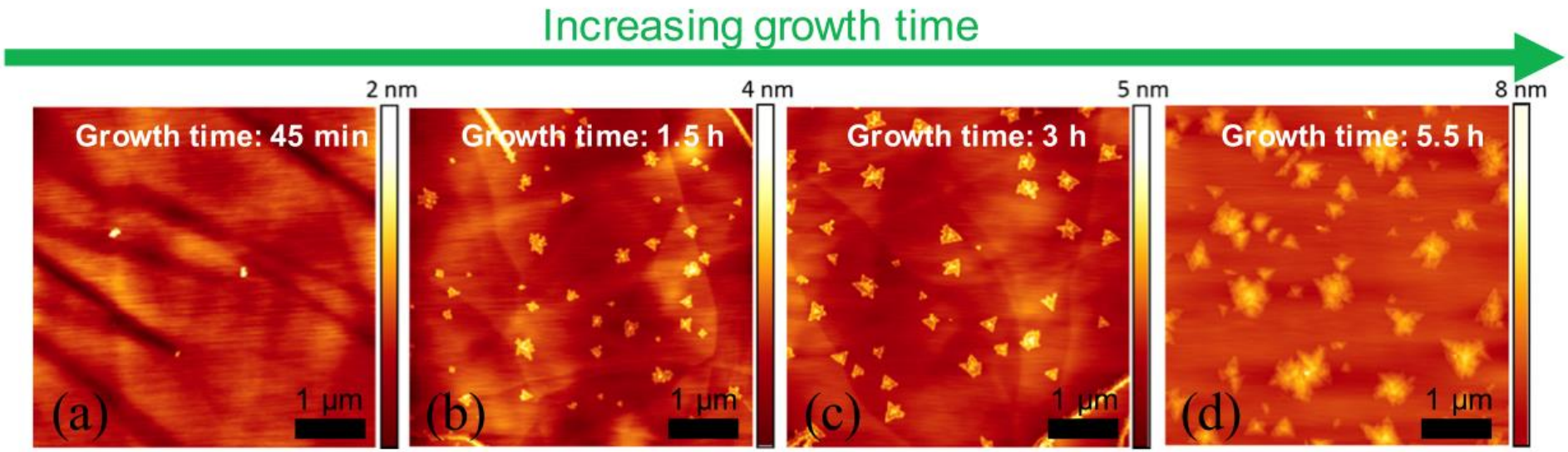


Fig. 5.8a–c Development of a crystal aggregate. (**a**) Formation of several nuclei, which initially can grow independently. (**b**) Collision of growing crystallites leads to interference and irregularity in growth of the polyhedra. Eventually, the polyhedral shape of the crystallites is entirely lost. (**c**) The single crystal domains of the aggregate with their grain boundaries

Crystallography: an introduction, Walter Borchardt-Ott, Springer 2012

Nucleation and growth

Ruoyu Yue *et al.*, 2017 **2D Mater**. 4 045019
Nucleation and growth of WSe : enabling large grain transition metal dichalcogenides



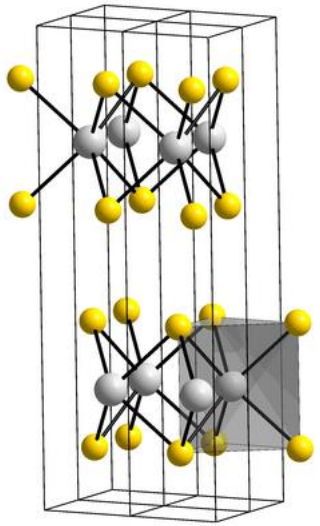
W flux of 5×10^{-9} mbar
Se flux of 7×10^{-7} mbar
Substrate temperature of 500 °C

Substrate HOPG
Flakes WSe_2

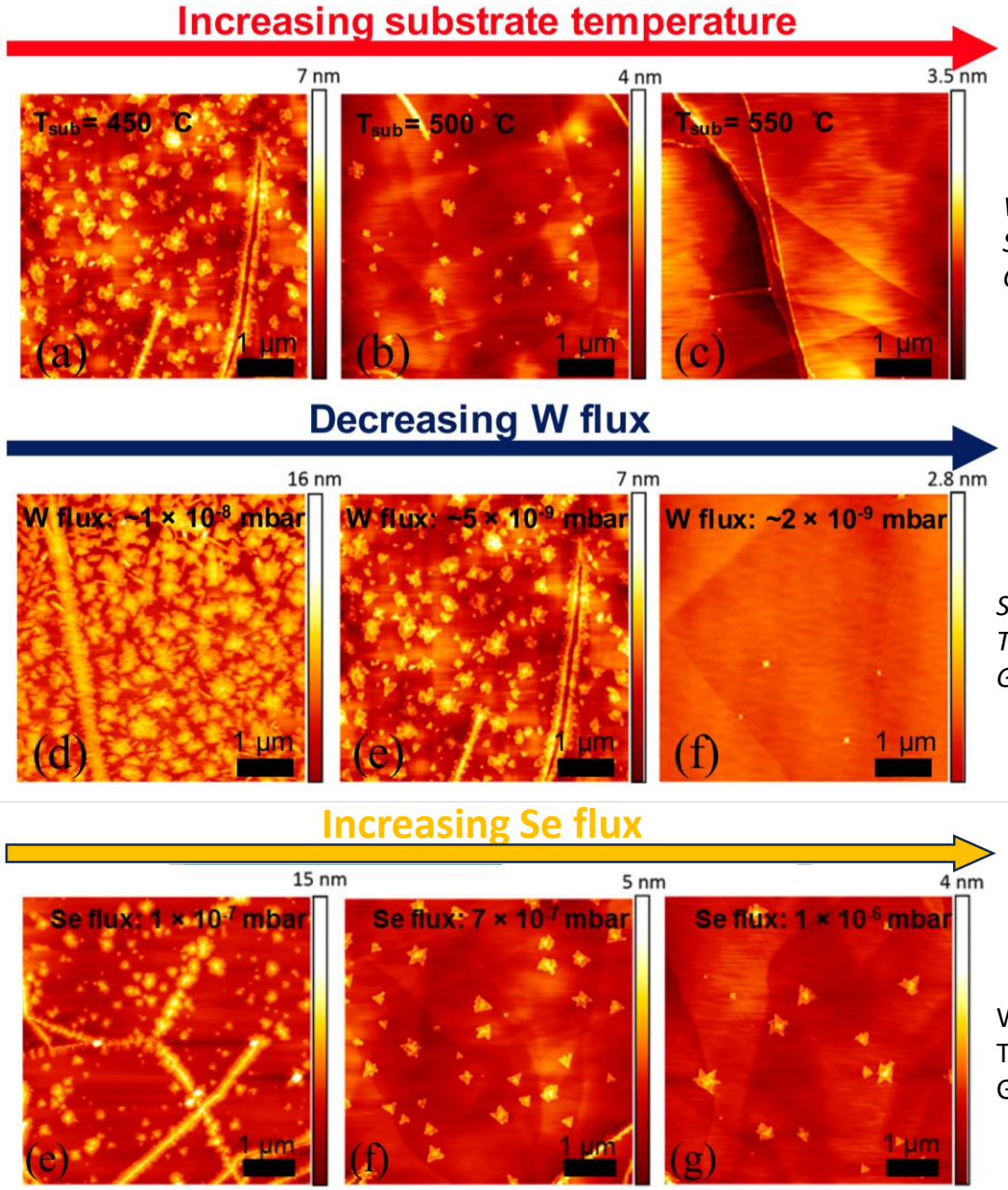
There is a competition between the nuclei density and the adatoms density

= an adatom has more chance to link itself to an existing nucleus than to form a new one when the distance to a nucleus is smaller than the distance to another adatom.

The substrate temperature, the W density (flux) and the Te flux are parameters we can play with



Independent parameters to control the growth

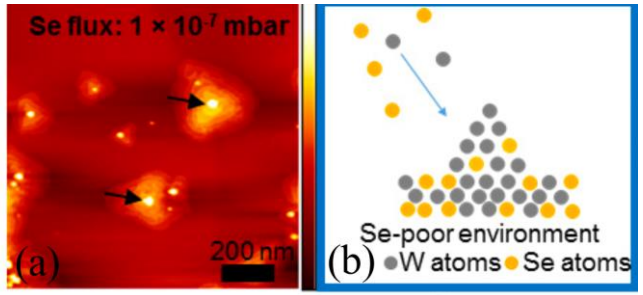


W flux: 5 × 10-9 mbar
Se flux: 7 × 10-7 mbar
Growth time: 1.5 h

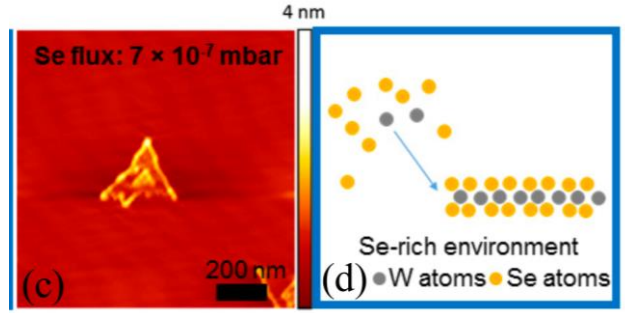
Se flux: 7 × 10-7 mbar
Tsub: 450°C
Growth time: 1.5 h

W flux of 5 × 10−9 mbar
Tsub: 500 °C
Growth time: 3 h

In a Se poor environment, W stick to the surface / create a lot of nuclei => island growth



In a Se rich environment, the excess of Se reduce the nuclei density and “stick” to the W to grow the WSe_2 epi-film => 2D growth



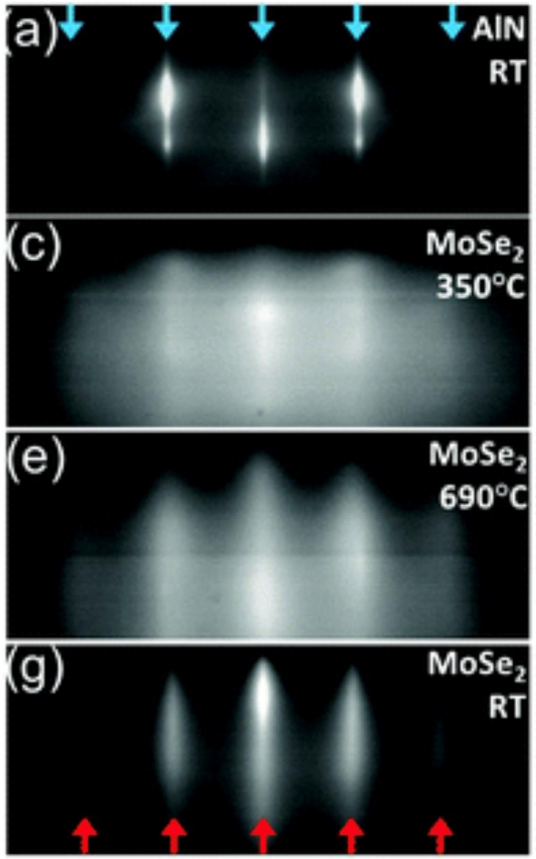
W flux of 5 × 10^{-9} mbar
Substrate temperature of 500 °C
Growth time of 3 h

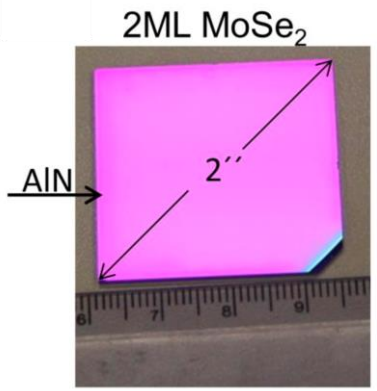
The growth of the TMDC - $MoSe_2$

P. Tsipas *et al.* ACS Nano Vol8 Issue 7 (2014)
E. Xenogiannopoulou *et al.*, Nanoscale, 2015, **7**, 7896-7905

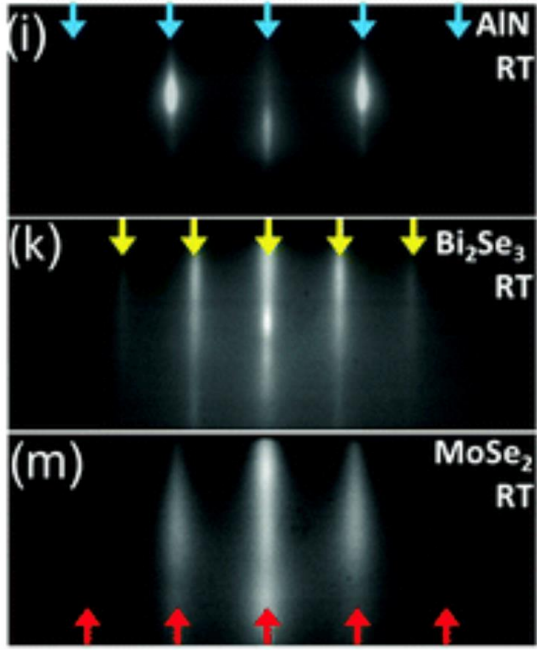
TMDCs : MX_2 (M = Mo, W; X = S, Se, Te)

SUBSTRATE - AlN/Si(111) with 200nm AlN grown by MOCVD





Deposition of Bi_2Se_3 as buffer layer.



Bi/Se flux ratio 1:20
Growth rate 1.5QL min^{-1}

Two steps process

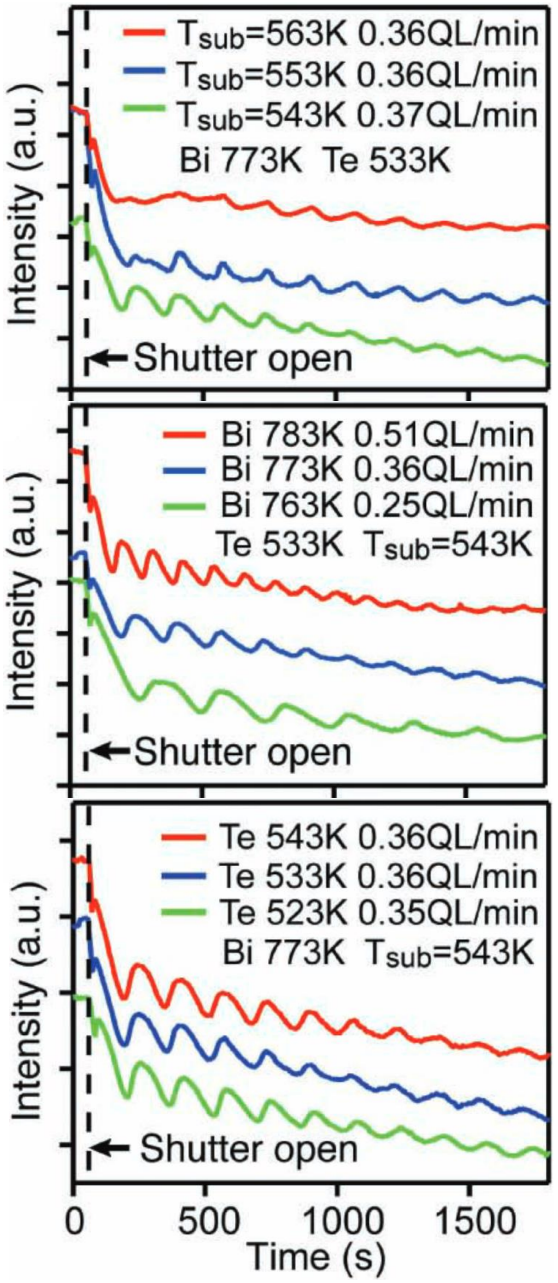
1. $MoSe_2$ grow at 350℃ in Se rich condition (1:10) using E-beam for Mo and K-cell for Se.
2. Post annealing at 650 ℃

Despite a mismatch of 20% of the lattice constant the epitaxial growth is successful
Growth temperature compatible with "Back-end-of-line".

Topological insulator Bi_2Te_3

Li, Y.-Y. *et al. Adv. Mater.* **22**, 4002–4007 (2010)

Substrate Si (111)



$T_{substrate}$ controls the growth mode

Bi flux control the growth rate

Te has no influence on the growth rate.

When Te lower than T substrate the growth in closer to a layer by layer growth

1. Te_2/Bi flux ratio = 13

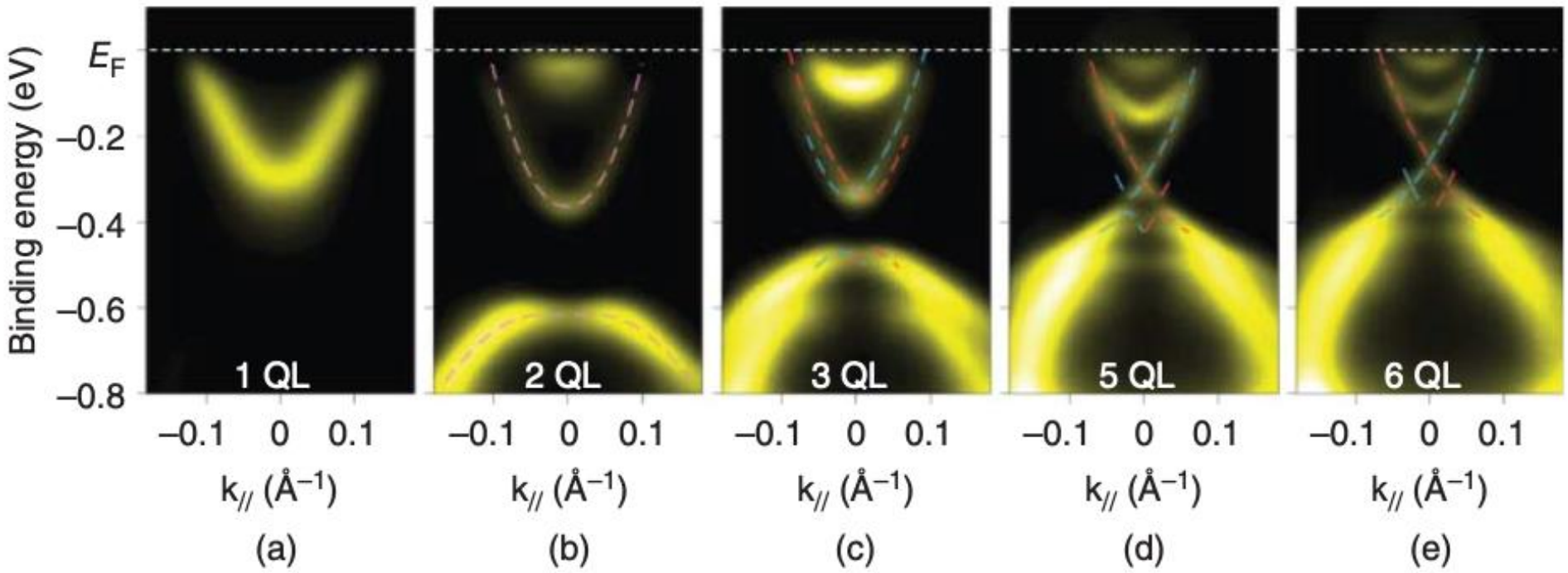
$\Rightarrow$ **There is always extra Te molecules available.**

+

2. $T_{substrate} > T_{Te}$

=> **Te not easily incorporated into the film but desorb**

Topological insulator Bi_2Te_3



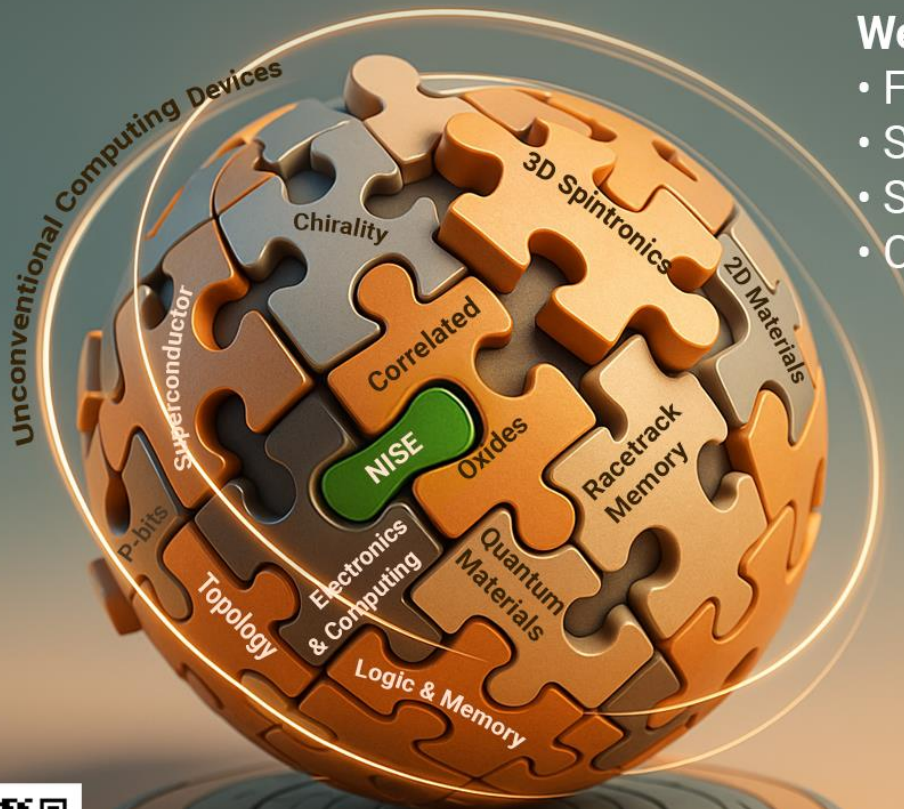
Li, Y.-Y. *et al. Adv. Mater.* **22**, 4002–4007 (2010)
Zhang, Y., He, K., Chang, CZ. *et al.* Crossover of the three-dimensional topological insulator Bi_2Se_3 to the two-dimensional limit. *Nature Phys* **6**, 584–588 (2010).

Thank you for your attention

IMPRS for Science and Technology of Nano-Systems
INTERNATIONAL MAX PLANCK RESEARCH SCHOOL

MAX-PLANCK-INSTITUT FÜR MIKROSTRUKTURPHYSIK

We are looking for excellent Postdocs and PhD students!



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- Freedom for independent research
- State-of-the-art research facilities
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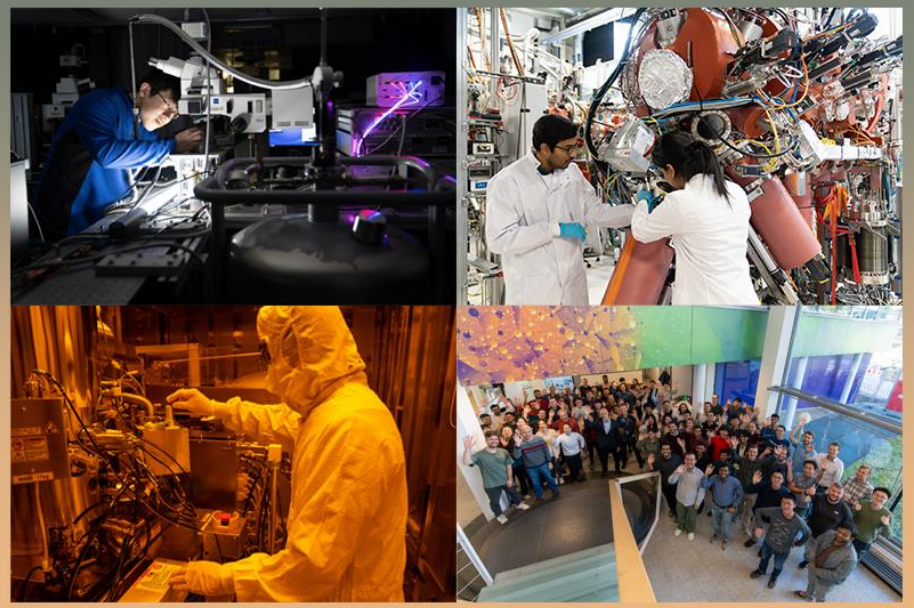
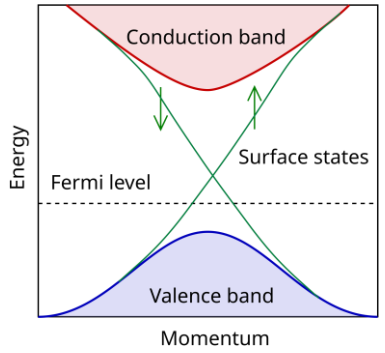
- Collaboration with a global network of renowned scientists

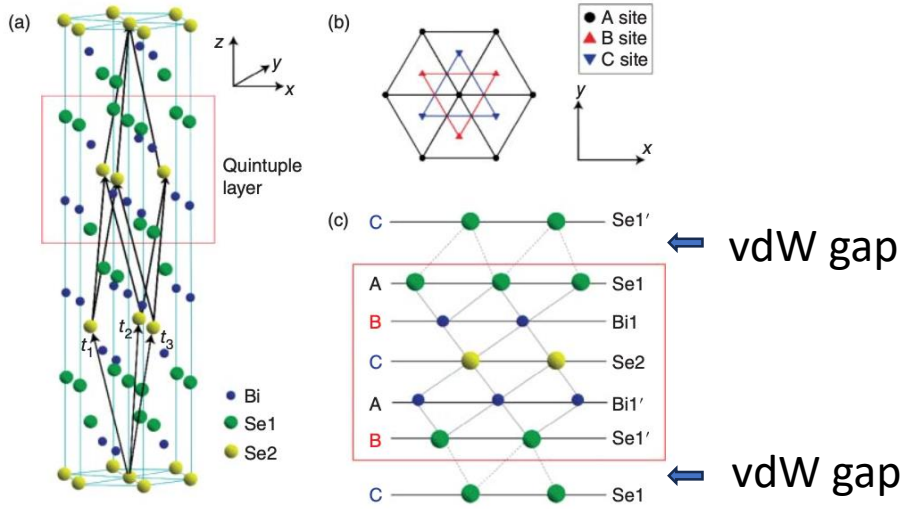


mpi-halle.mpg.de/nise/open-positions

Layer-by-layer vdWE of topological insulator on Si (111) substrate

Bi_2Te_3, Bi_2Se_3 are topological insulator material.





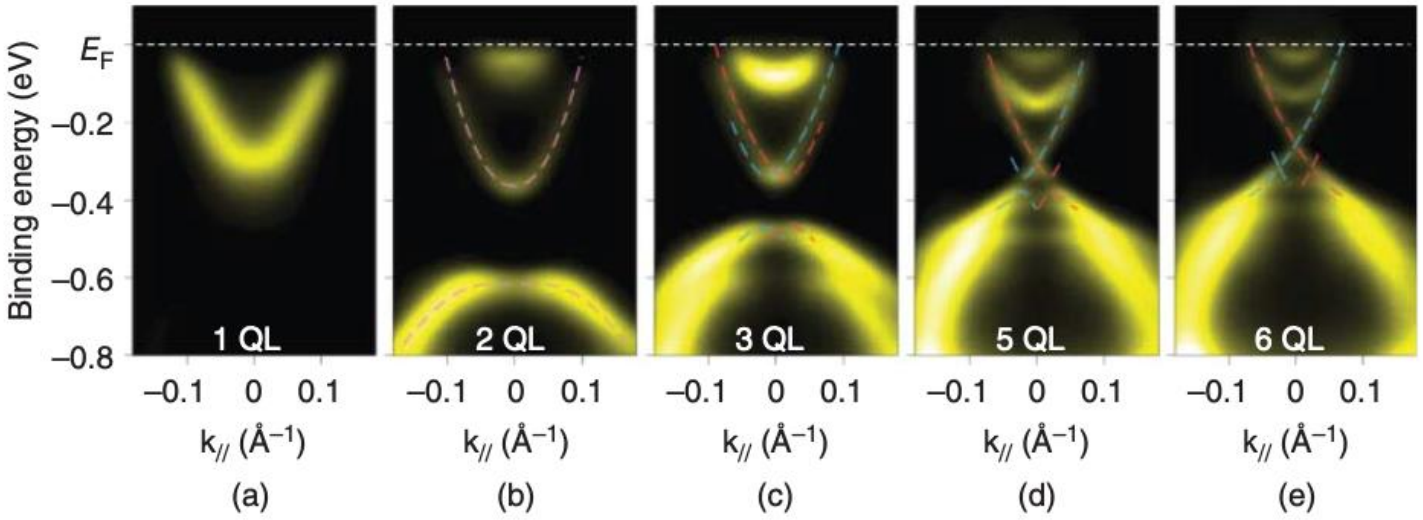
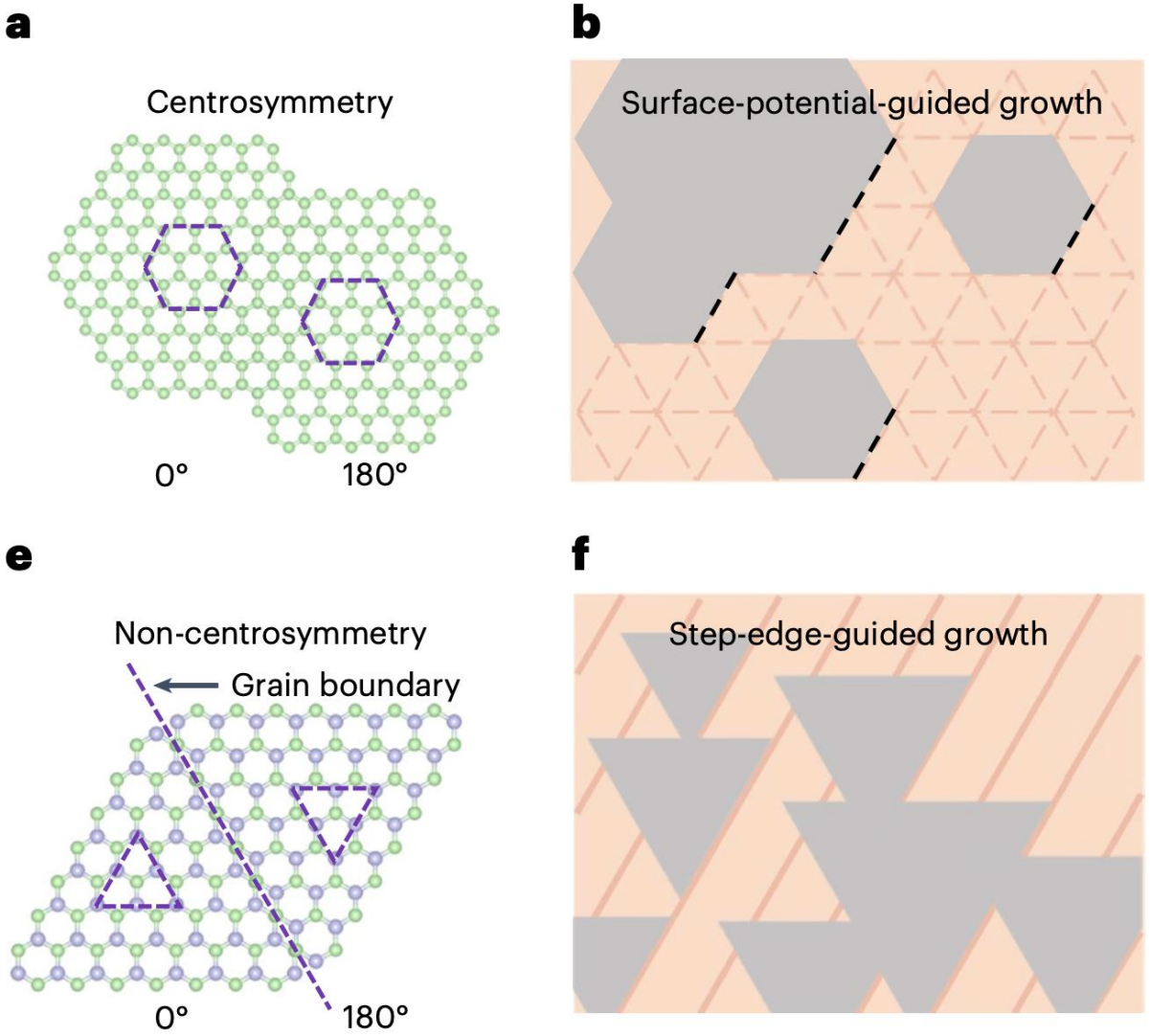


Figure 22.3 *Thickness-dependent ARPES of MBE-grown Bi_2Se_3 thin films from 1QL to 6QL (from Ref. [14]).*

Li, Y.-Y. *et al. Adv. Mater.* **22**, 4002–4007 (2010)
Zhang, Y., He, K., Chang, CZ. *et al.* Crossover of the three-dimensional topological insulator Bi_2Se_3 to the two-dimensional limit. *Nature Phys* **6**, 584–588 (2010).

Layer by layer growth BUT with slight miscut angle of the STO substrate (<0.1°)



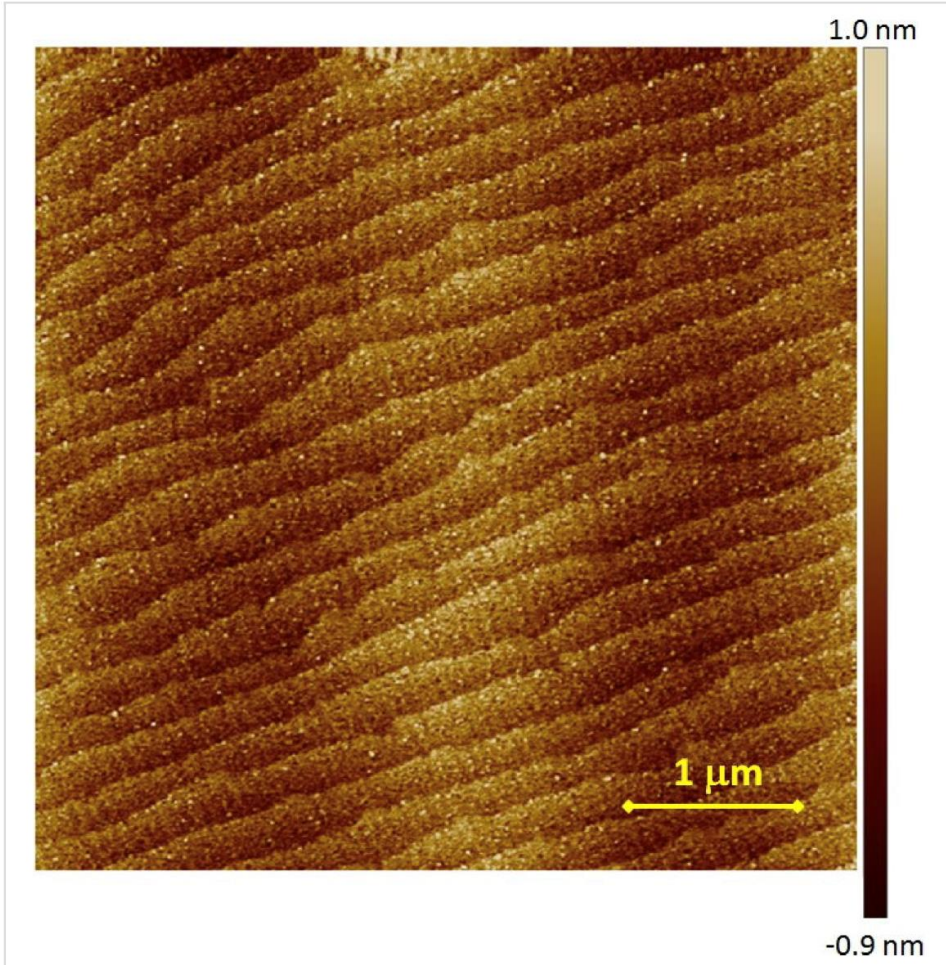
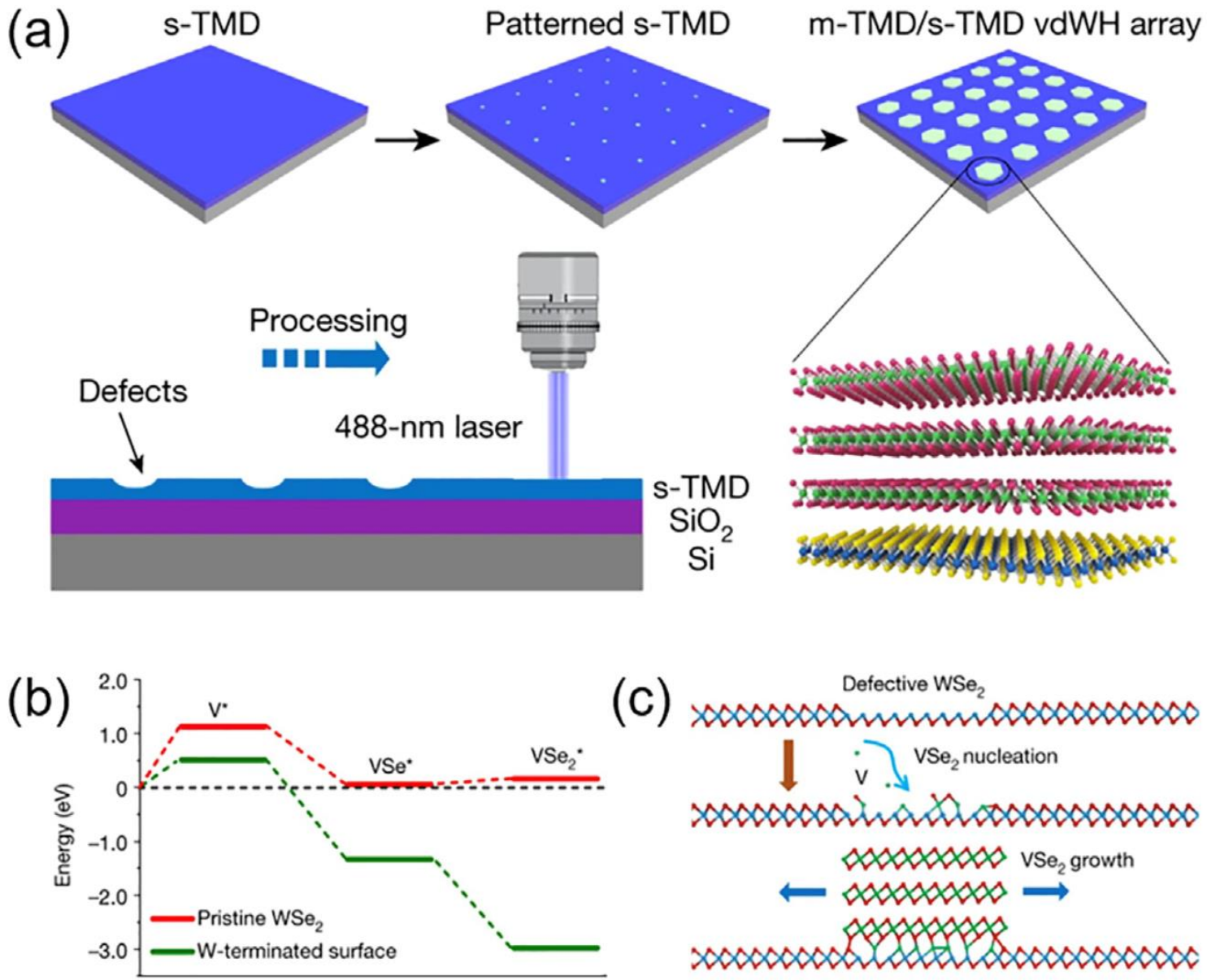
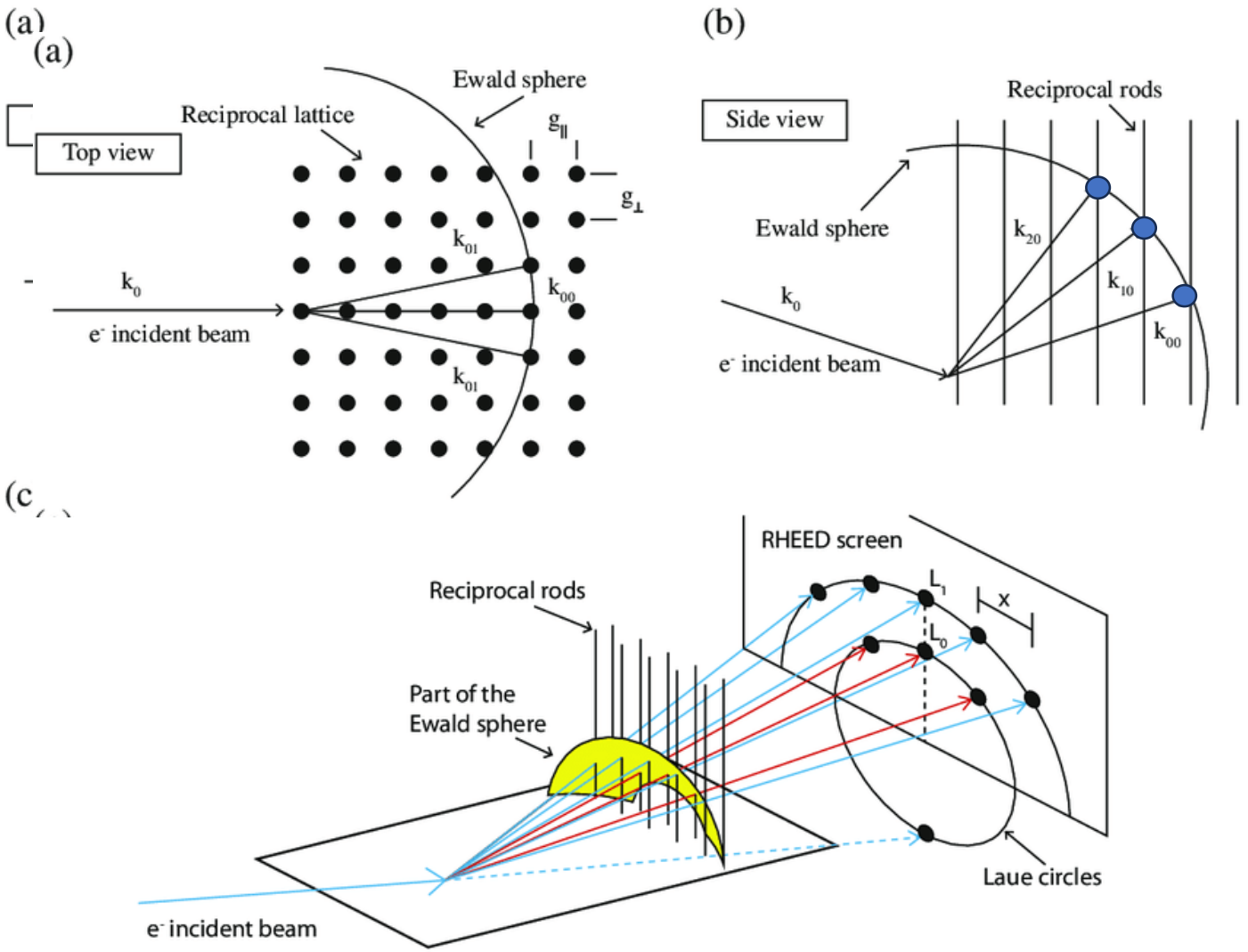


Figure 3: AFM image of 25 nm thick La_2NiO_4 film on STO substrate.


(a)
s-TMD
Patterned s-TMD
m-TMD/s-TMD vdWH array
Processing
Defects
488-nm laser
s-TMD
SiO2
Si
(b)
2.0
1.0
0
−1.0
−2.0
−3.0
Energy (eV)
V*
VSe*
VSe2*
Pristine WSe2
W-terminated surface
(c)
Defective WSe2
V
VSe2 nucleation
VSe2 growth

The Ewald sphere and the diffraction conditions



Structural, magnetic and electrical investigation of Iron-based III/V-semiconductor hybrid structures, Dissertation from Boris Landgraf, 2014, University of Hamburg

Diffraction conditions

$$\boldsymbol{k_{i0} - k_0 = a^*}$$

$$\|\boldsymbol{k_{i0}}\| = \|\boldsymbol{k_0}\|$$

The radius of the Ewald sphere is, for an acceleration voltage of 10kV,

$k_0 = \frac{2\pi}{\lambda} = 51\ \text{Å}^{-1}$

The spacing between the reciprocal nods of a Si (001) is $a^* = 2.314\ \text{Å}^{-1}$ (001)

$$\lambda = \frac{12.26}{\sqrt{U_0\left(1 + 0.9788 \times 10^{-6} U_0\right)}},$$

Wavelength in Angstrom
U_0 electron energy in eV

Deposition cluster

Oxide Nitride MBE cluster

2x growth modules
- 9x k-cell sources
- 4x 15cc pocket E-beam
- RHEED

Oxide chamber
- Pure ozone – shower head injection

Nitride chamber
- N2 plasma source

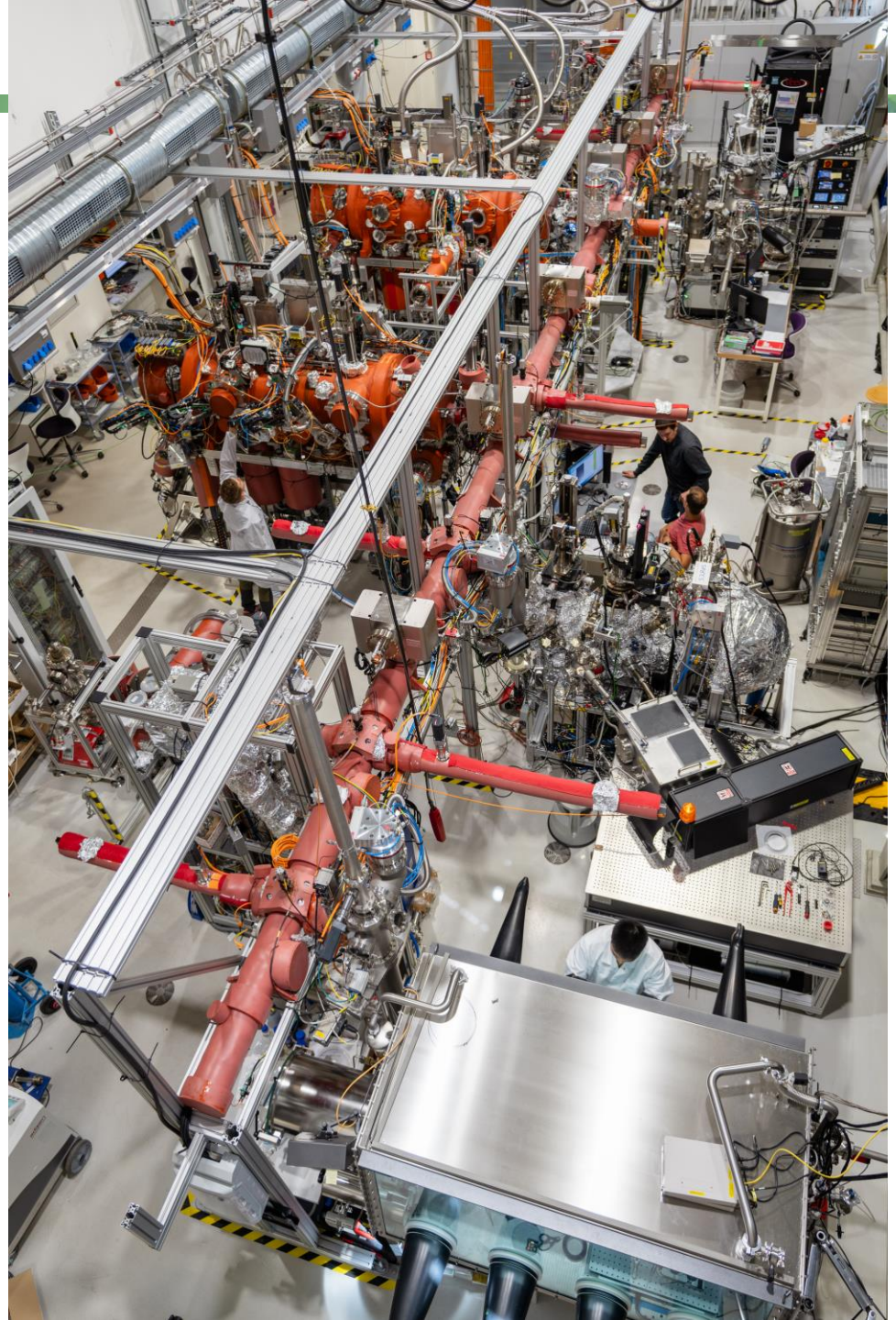
MANGO (sputtering)

- 3x {4x targets} IBD clusters. Co-deposition.
- 4x {3x magnetrons}. Co-deposition.
- 1x turret with x12 magnetrons. Single source deposition. Off-axis deposition possible.
- Radiative heater. Max 850 ˚C.
- RGA
- Ion beam cleaning/etching (0˚angle)

Under development
- Cryo-cooling of samples down to approx. 100K prior to deposition
- RHEED
- AUGER Electron spectroscopy for surface element analysis
- Annealing chamber (1000˚C) in presence of O2 [10-3 ;1] torr
- E-beam source

X-ray Photoelectron spectroscopy (XPS)

- PHOIBOS 150 CCD detector
  - max FWHM 0.44eV
- Flood gun
- Al and Mg X-ray source



Oxide PLD

- Samples load lock
- 6x targets in growth chamber + 6x targets in target load-lock
- Various slits. Min. beam spot size = 1x1.5mm. Fluence approx. = 10 J/cm2
- RHEED
- Radiative heater - max temperature 900 ˚C at 10-2 mbar O2.

ARPES with Spin detector

Manipulator – 5axis with open cycle Helium cooling

Sources
- VUV high flux source with monochromator
  - Line width <1meV
  - Spot size <500um spot size @ 10mm working distance
- Laser UV source

Detectors
- PHOIBOS 150 2D-CCD Energy analyser
  - ±15˚ in angle resolved and in transmission
  - Energy resolution <2meV
  - Angular resolution <0.1˚
- Spin detector

Exfoliation under N2 atmosphere – glove box

- Micromechanical exfoliation method - VdW pick-up method with PDMS stamps
- Spin coater & hot plate & 40kHz plasma cleaner
- Possibility to connect a vacuum taxi

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