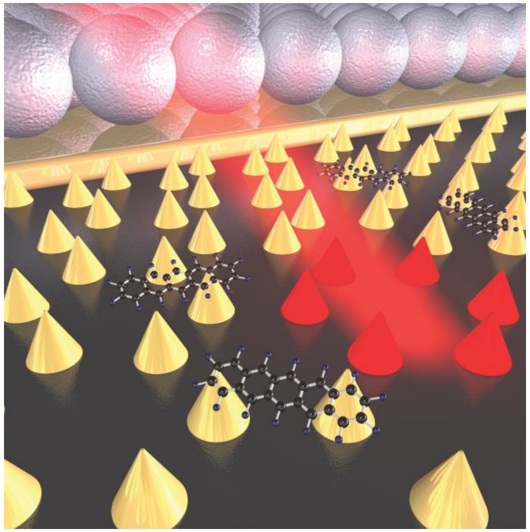
Basic module
Physics of Nanostructures

Summer term 2025



J. Meyer, D. Kölle, I. Zaluzhnyy,
Excercises: R. Löffler

Additional content

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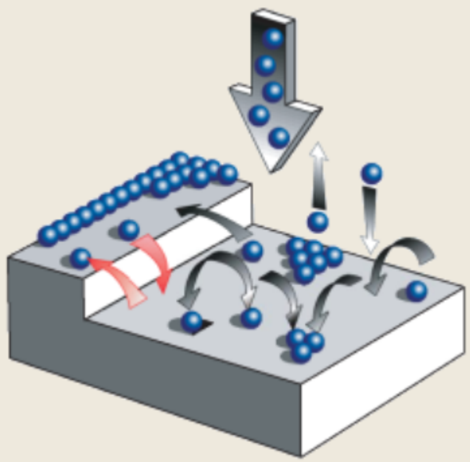
Physik der Nanostrukturen



Lectures in SoSe 2025 NEW

Prof. Dr. Jannik Meyer
Prof. Dr. Dieter Kölle
Dr. Ivan Zaluzhnyy

Mon. 10.15-12.00 in D4A19 and Thu. 14.15-16.00 in N4
Eintrag im **Alma-Portal** und in **Ilias**

Teaching Material Archive

www.soft-matter.uni-tuebingen.de ➔ teaching

Additional content

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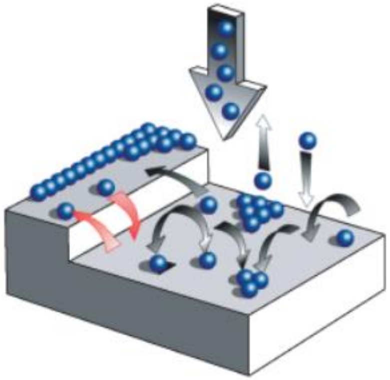
Physics of Nanostructures



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Link to **Alma-Portal**

Registration for this course in ILIAS

Materials for the lectures

(complete list of materials is posted on ILIAS)

Preparation (Chapter 6)

- Script
- Presentation
- Lecture notes

Characterization (Chapter 7)

- Script
- Presentation
- Lecture notes

login: soft
password: soft07

Plan for the next three weeks

6. Preparation of nanostructures:

07.07, 10.07 - Theoretical introduction into thin film growth

14.07 – Overview of various experimental techniques

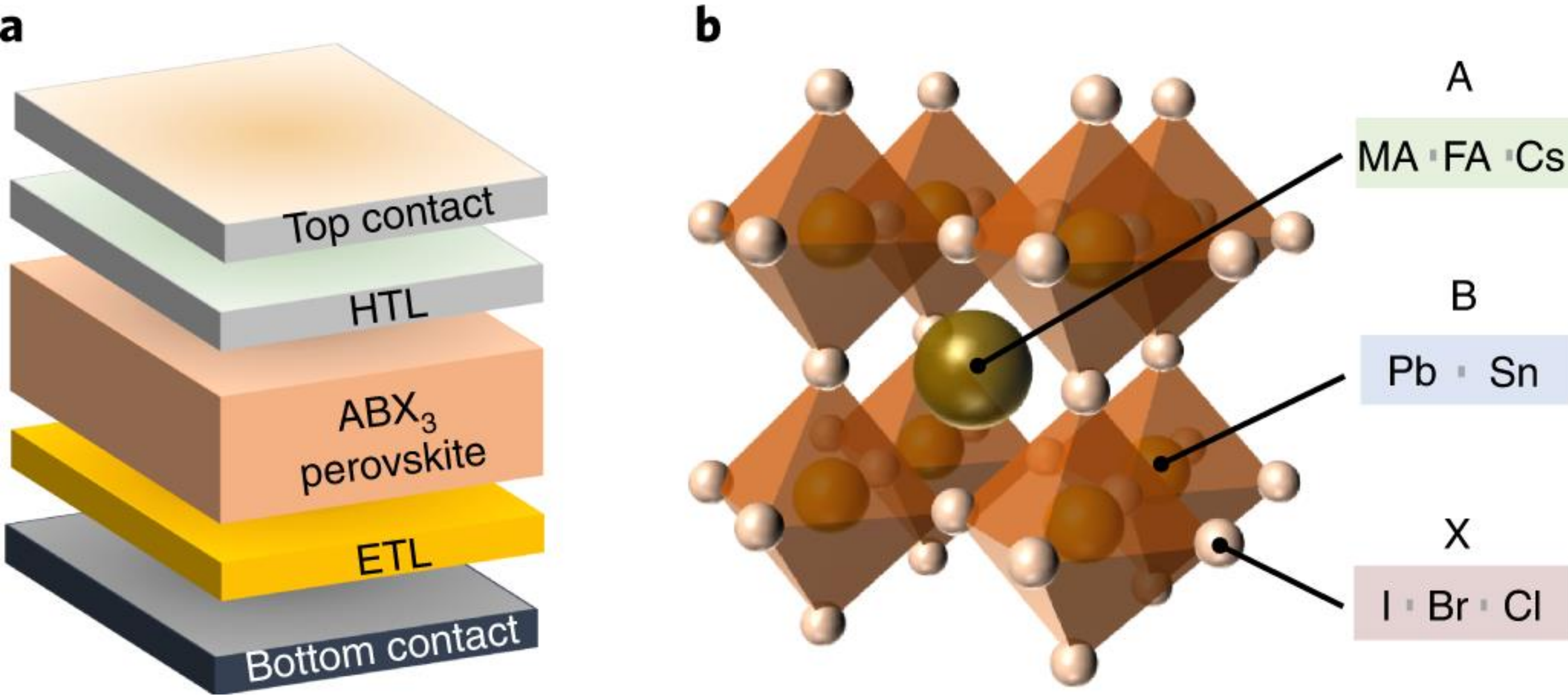
7. Characterization of nanostrucutres:

17.07, 21.07 – X-ray scattering from thin films

24.07 – Overview of various types of microscopy and spectroscopy

Why thin films?

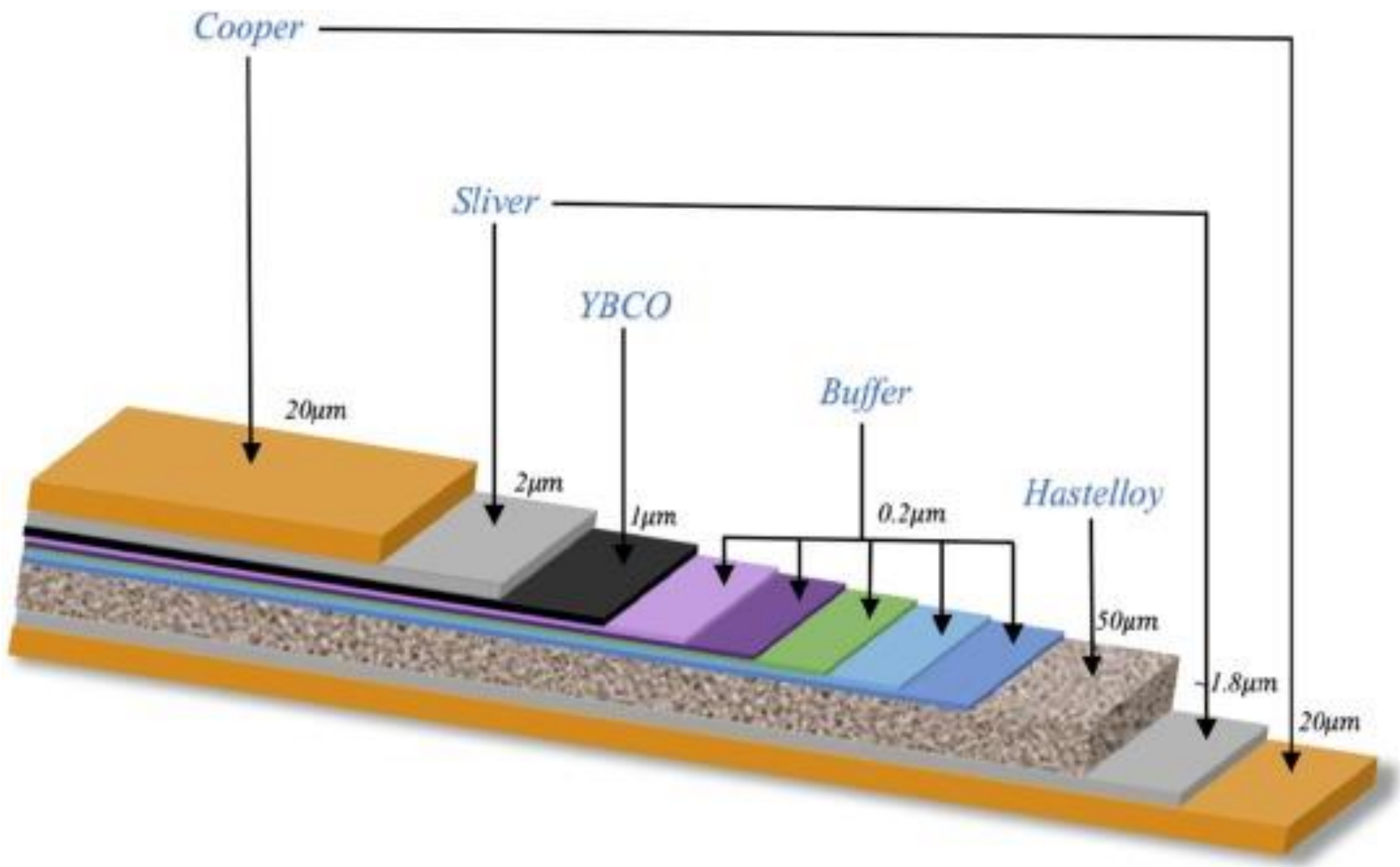
Perovskite-based solar cell



Y. Zhou, *et al. Nat Energy* **7**, 794–807 (2022).

Why thin films?

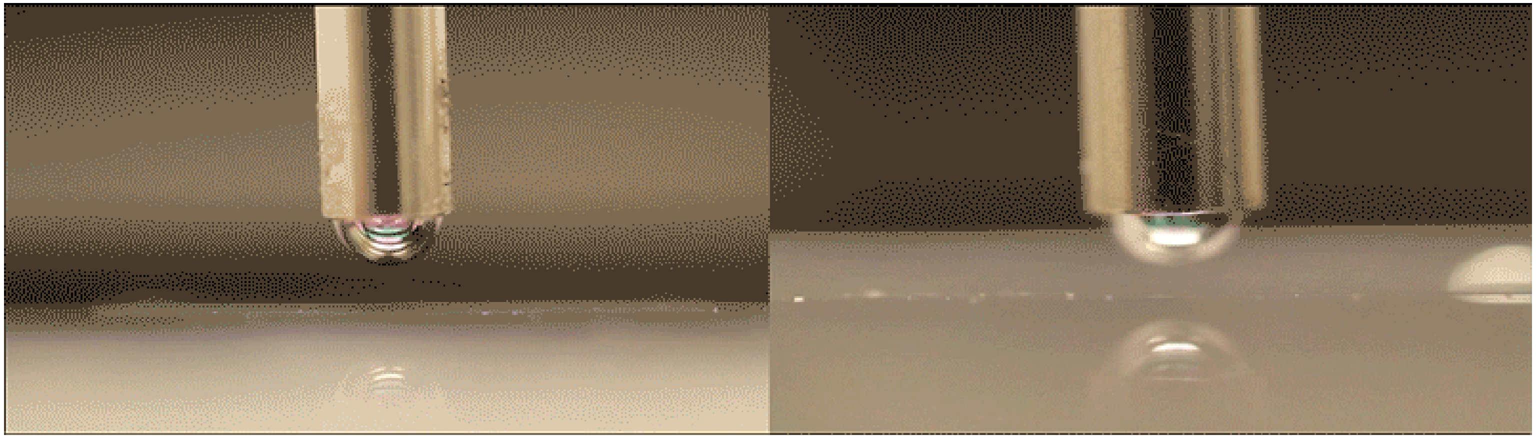
High-Temperature Superconducting tape



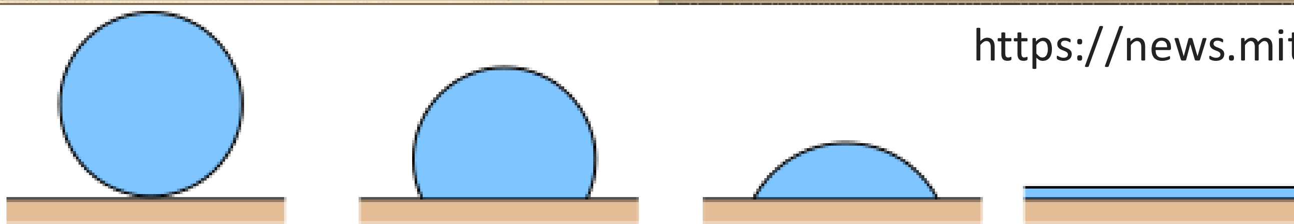
H. Chen, *et al. Compos. Struct.* **286**, 115336 (2022).

Droplet on a surface

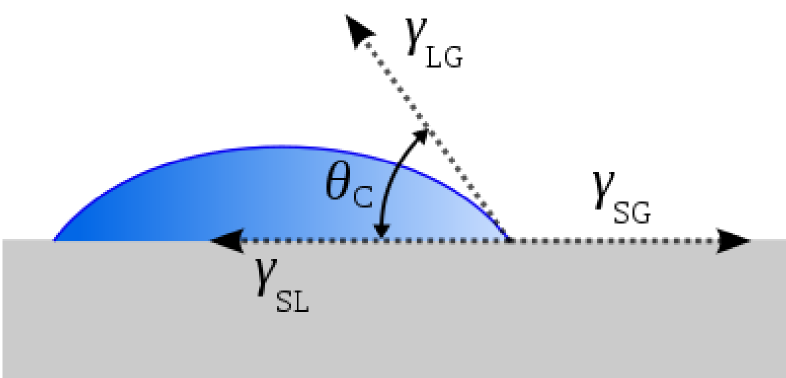
mercury on glass | water on glass



https://news.mit.edu/



perfect non-wetting | perfect wetting



γ_{SL} - surface tension between surface and liquid

γ_{LG} - surface tension between liquid and gas

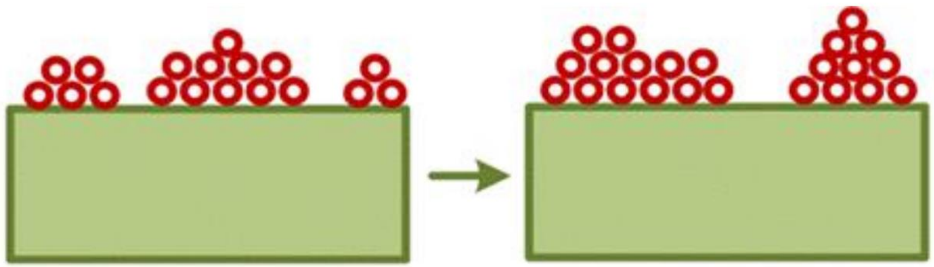
γ_{SG} - surface tension between surface and gas

θ_C - contact angle

the Young equation

$$\gamma_{SL} + \gamma_{LG} \cdot \cos\theta_C = \gamma_{SG}$$

Three categories of growth



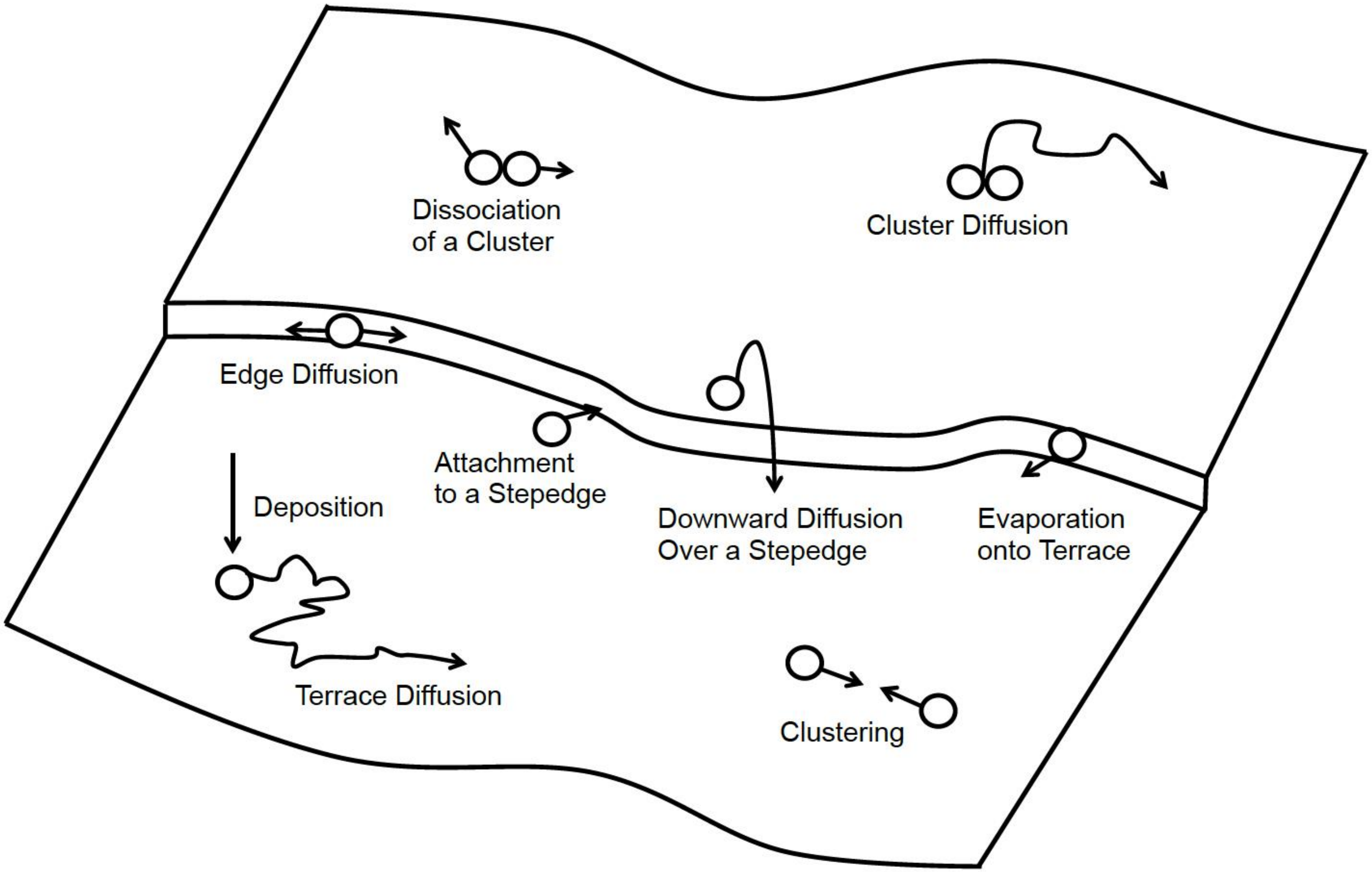
Volmer-Weber (islands)

Stanski-Krastanov (first layers, then islands)

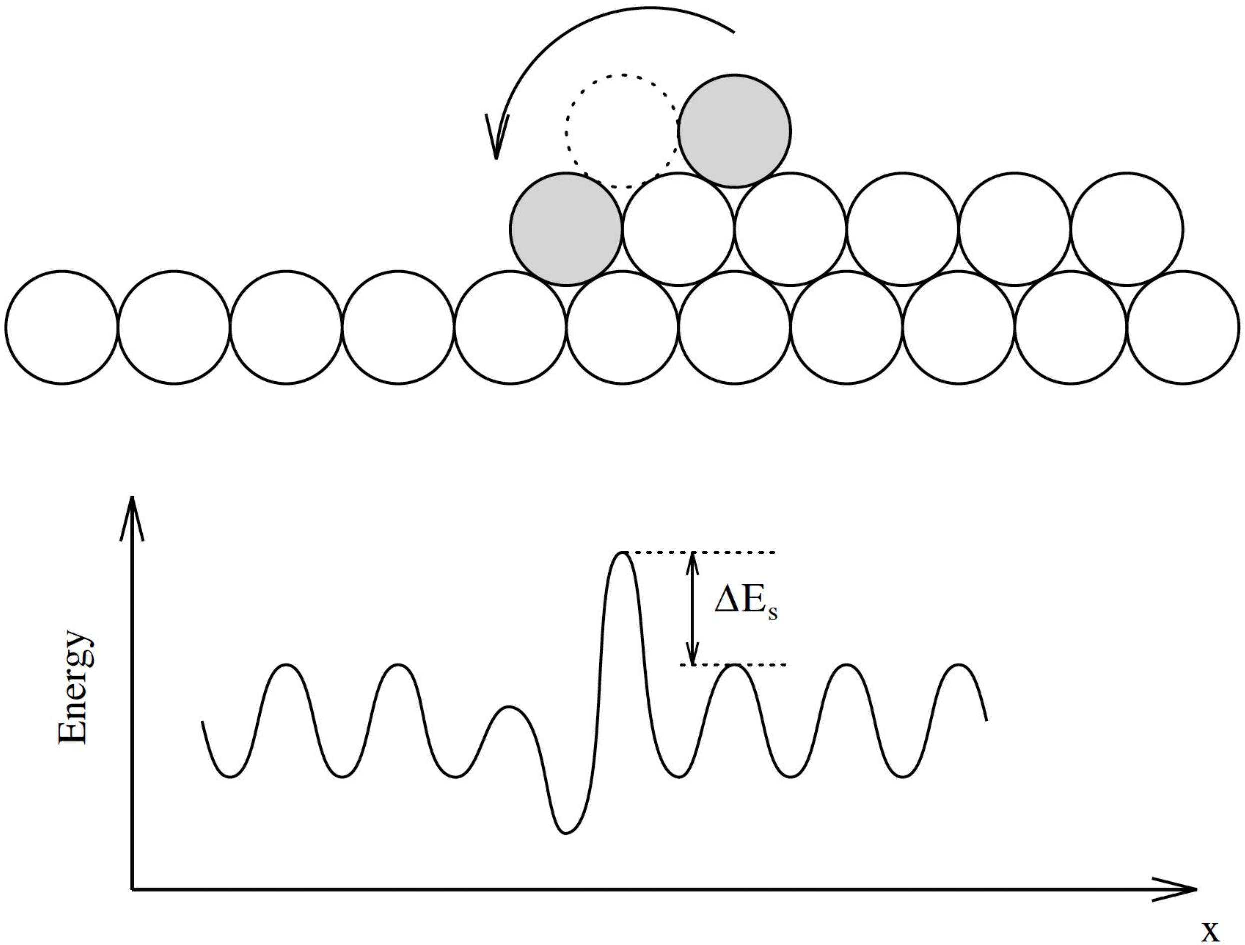
Frank-van-der-Merwe (layer-by-layer)

L. Aissani et al., Coatings, ***12*** *1746 (2022)*

How to describe growth?



Ehrlich-Schwöbel barrier



Pt adatom on Pt(111) surface: diffusion $E_D = 0.26$ eV
Ehrlich-Schwöbel barrier $\Delta E_S \approx 0.14$ eV

J. Krug, *Physica A* **313**, 47-82 (2002).

Adatom diffusion

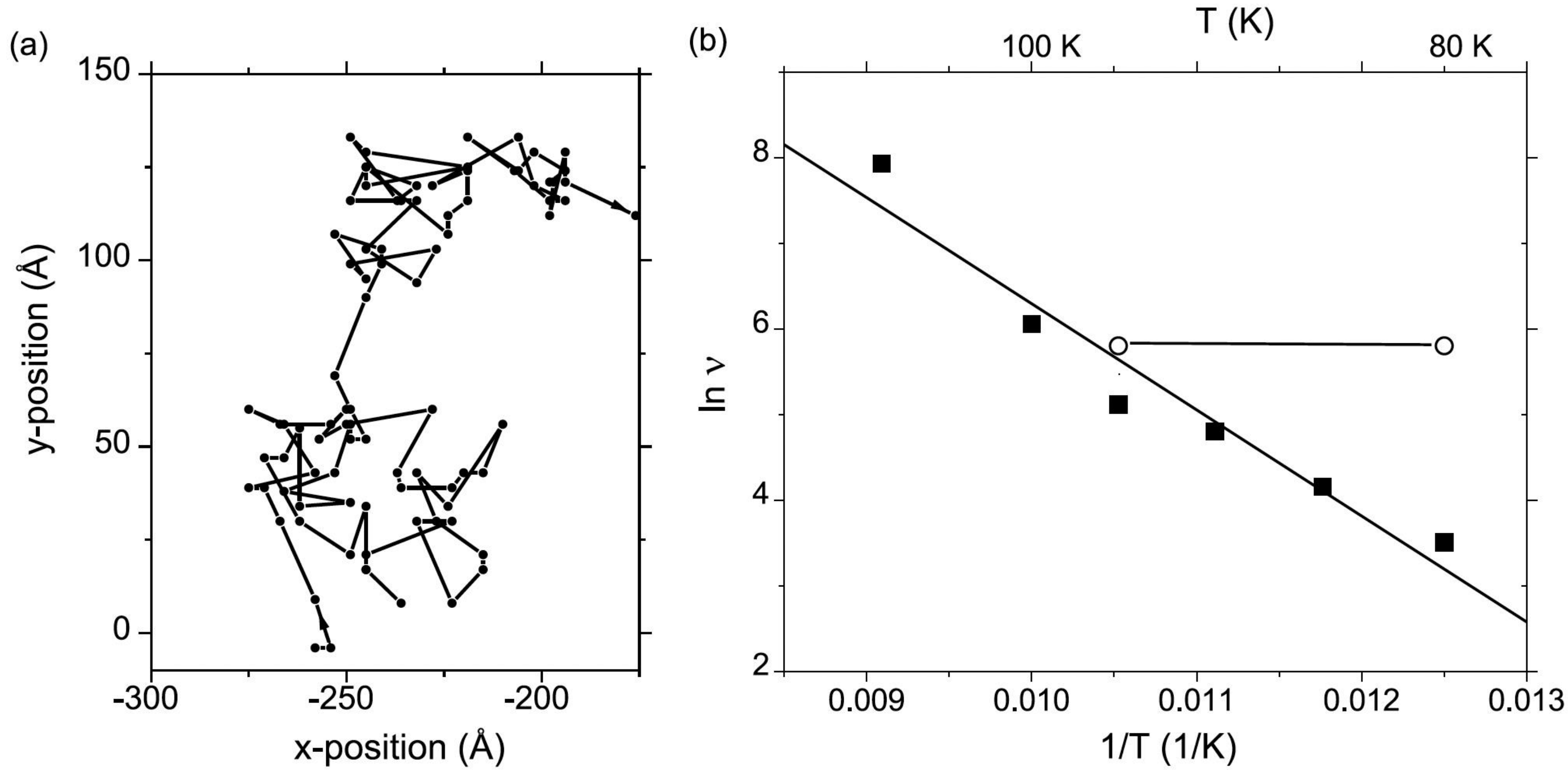
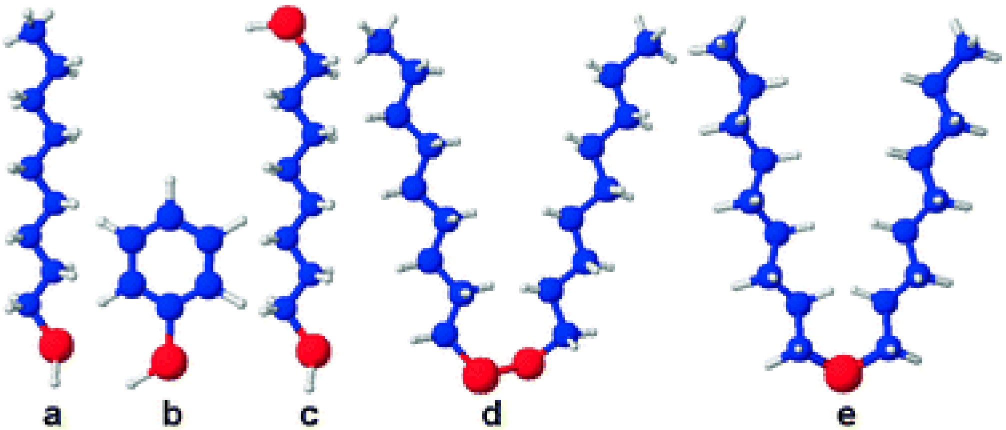
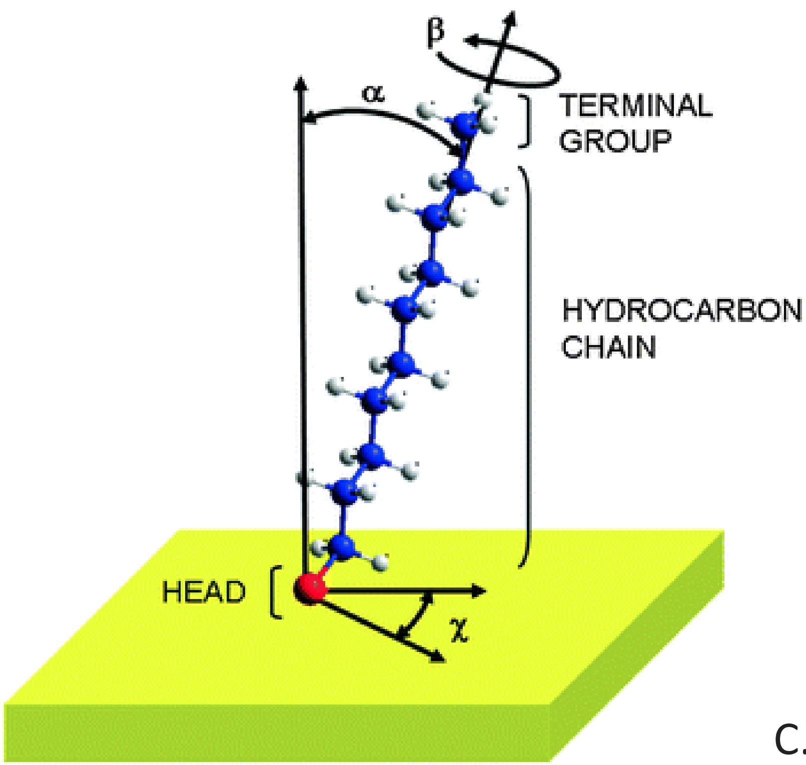


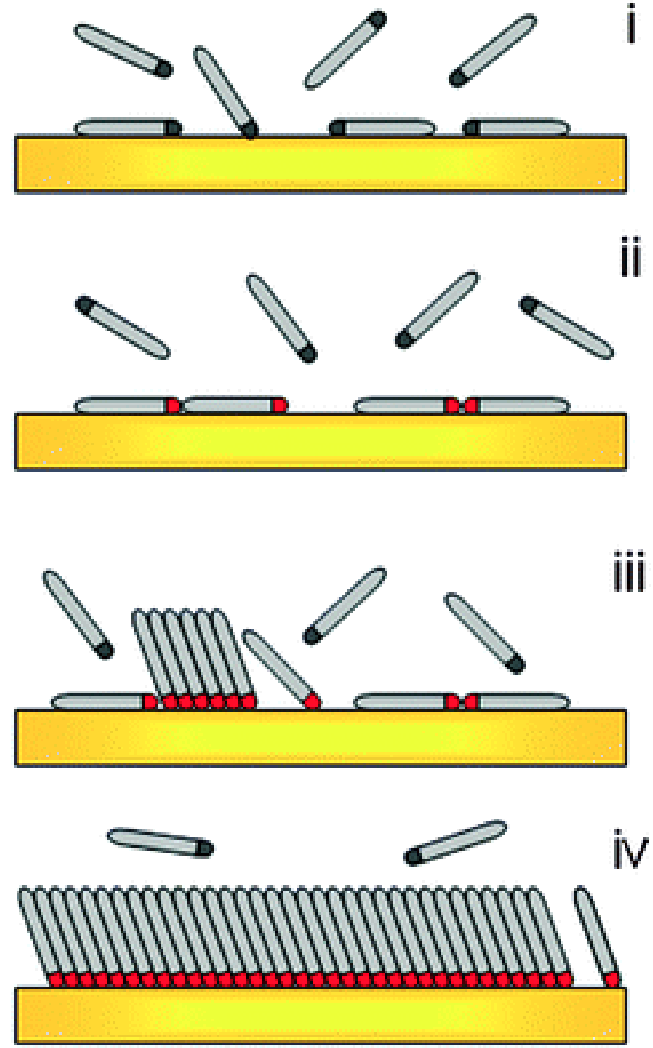
Fig. 2.3. (**a**) Map of consecutive adatom positions on STM topographs taken at 85 K in time intervals of 30 s. (**b**) Temperature dependence of the adatom hopping frequency ν determined by maps as in (**a**). *Full squares*: Data taken with a tunneling resistance of $R_t = 150\,\mathrm{M\Omega}$ ($U_t = 0.03\,\mathrm{V}$, $I_t = 0.2\,\mathrm{nA}$). *Full line*: Linear regression to the data. *Open circles*: Data with $R_t = 15\,\mathrm{M\Omega}$ ($U_t = 0.03\,\mathrm{V}$, $I_t = 2\,\mathrm{nA}$). Line to guide the eye

T. Michely & J. Krug (2004).

Thiols on gold







C. Vericat et al., Chem. Soc. Rev. **39** 1805 (2010).

Linear differential equations

Inhomogeneous linear differential equation of the first order with constant coefficients:

$$a_1 \frac{dy}{dt} + a_0 y = f(t)$$

Solution of this equation:

$$y = y_{homo} + y_{inhomo}$$

General solution of the corresponding homogeneous equation

$$a_1 \frac{dy}{dt} + a_0 y = 0$$

Look for a trial solution in the form

$$y = e^{\lambda t}$$

characteristic equation

$$a_1 \lambda + a_0 = 0$$

$$y_{homo} = C_1 e^{\lambda_1 t}$$

Any solution of the inhomogeneous equation

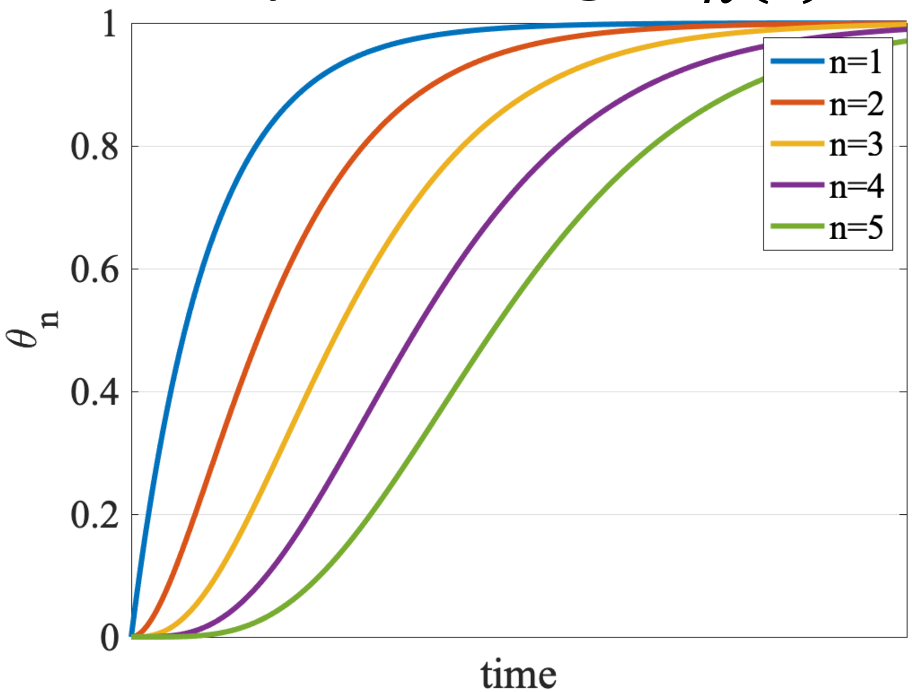
$$a_1 \frac{dy}{dt} + a_0 y = f(t)$$

Look for a trial solution in the form

$$y_{homo} = C_1(t) e^{\lambda_1 t}$$

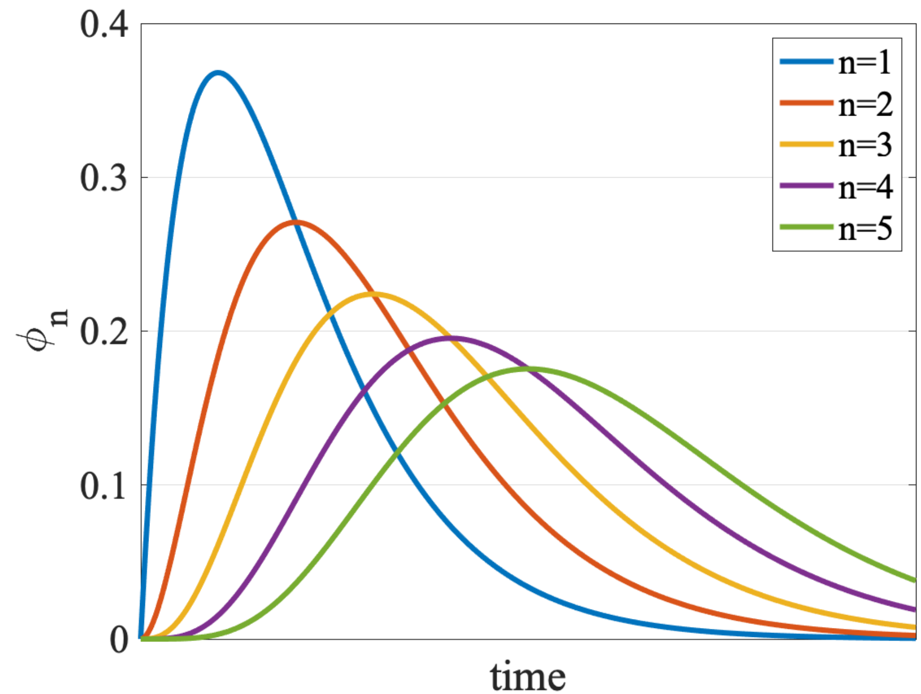
Statistical growth

Layer coverage $\theta_n(t)$

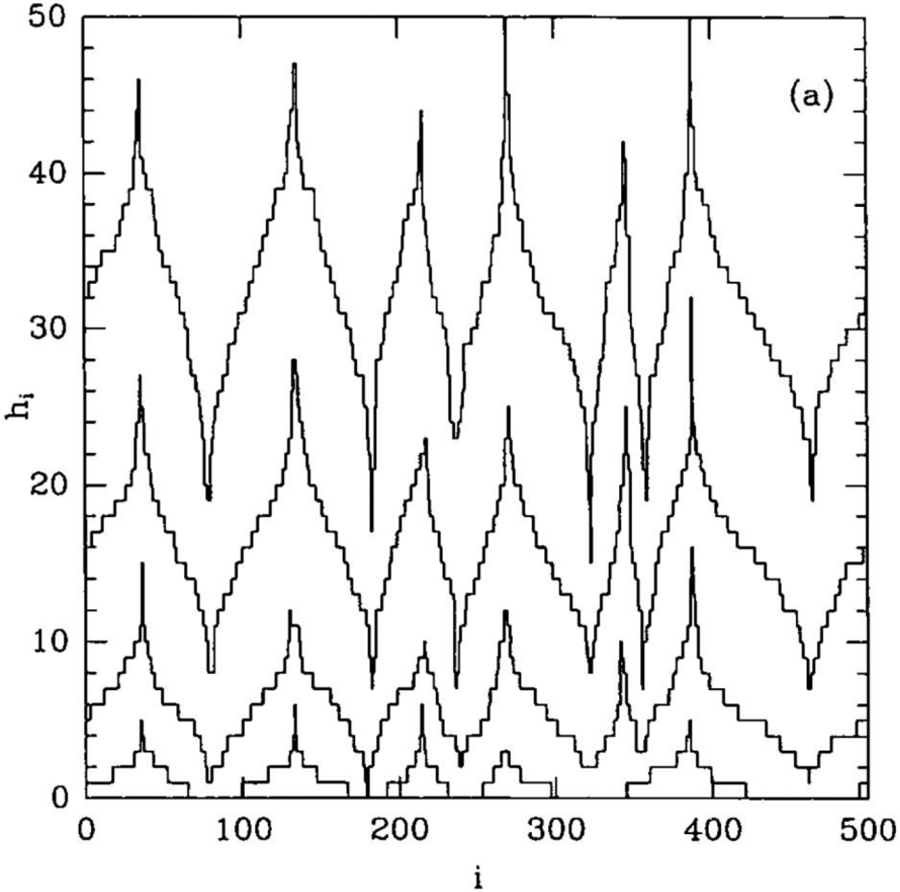


Exposed layer coverage

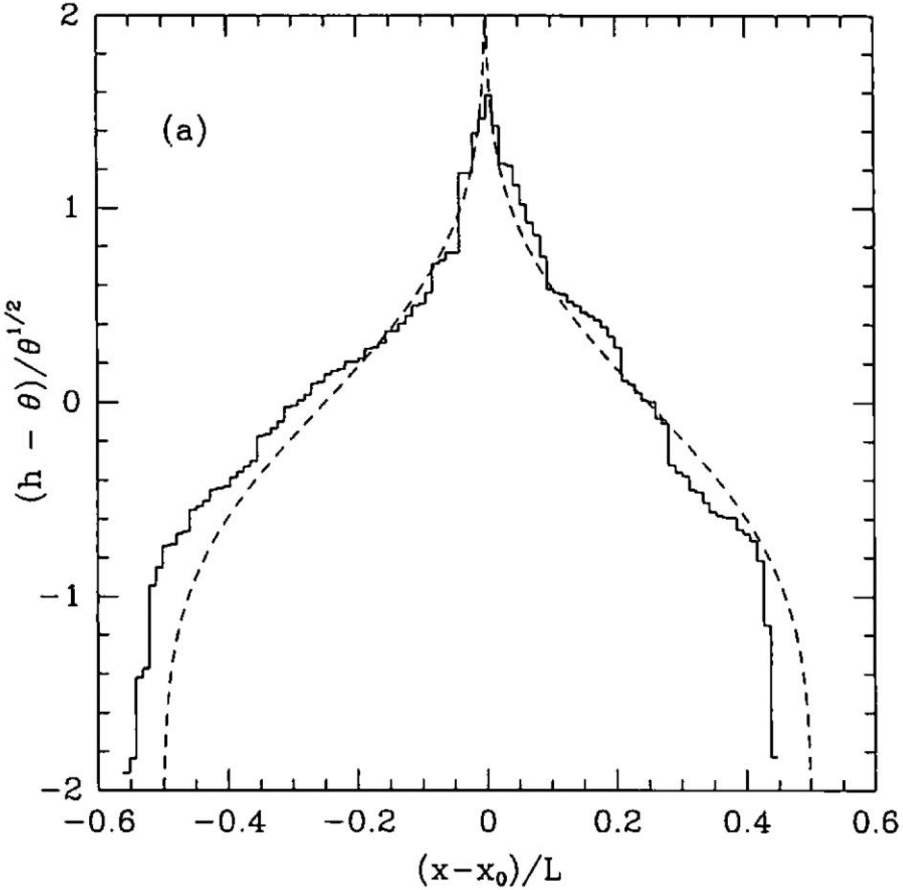
$$\varphi_n = \theta_n - \theta_{n-1}$$



Wedding cake shape



Line cut through the surface at different deposition times (simulations)



Fit of the ”wedding cake” profile with the error function

J. Krug, J. Stat. Phys. ***87*** *505 (1997).*

Wedding cake shape

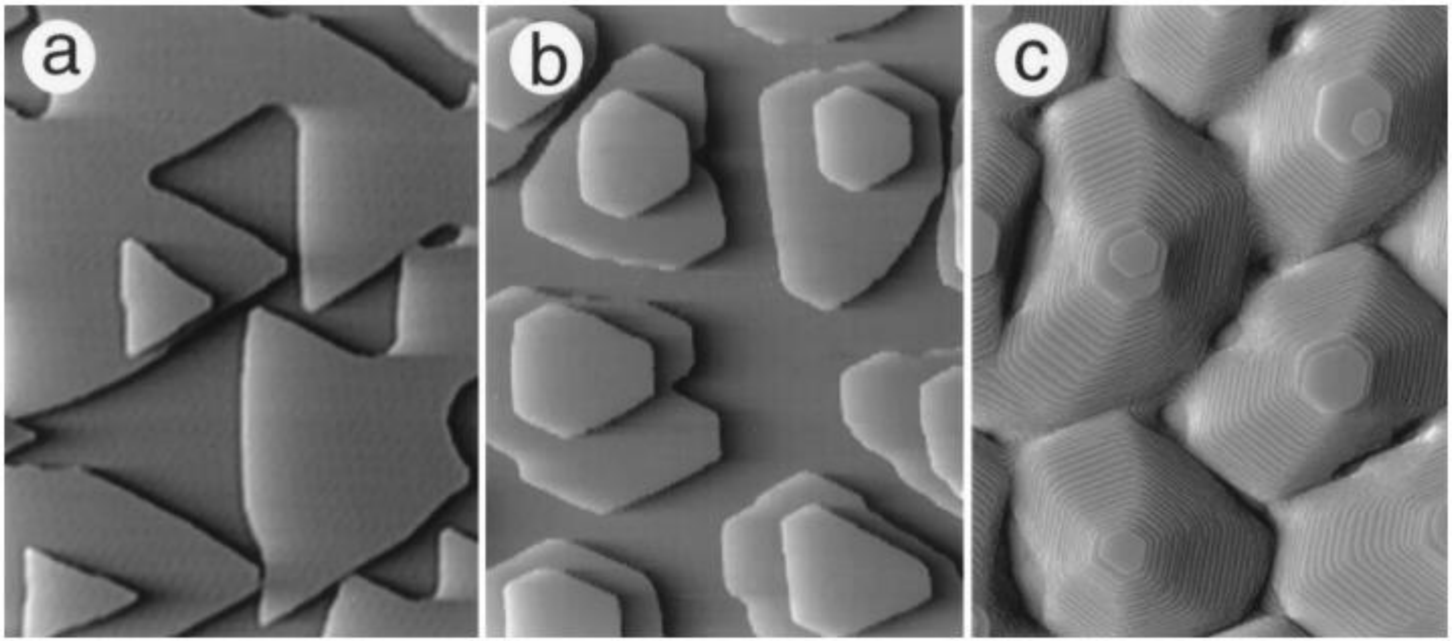


Fig. 4. STM topographs after deposition of (a) 0.78 ML, (b) 0.83 ML, and (c) 40 ML Pt at $T=440$. Deposition (a) under clean conditions and (b), (c) in the presence of 1.9×10^{-9} mbar of CO. Scan size 1610×1200 Å^2.

M. Kalff et al. Surf. Sci. 426 L447–L453 (1999)

Island size and shape

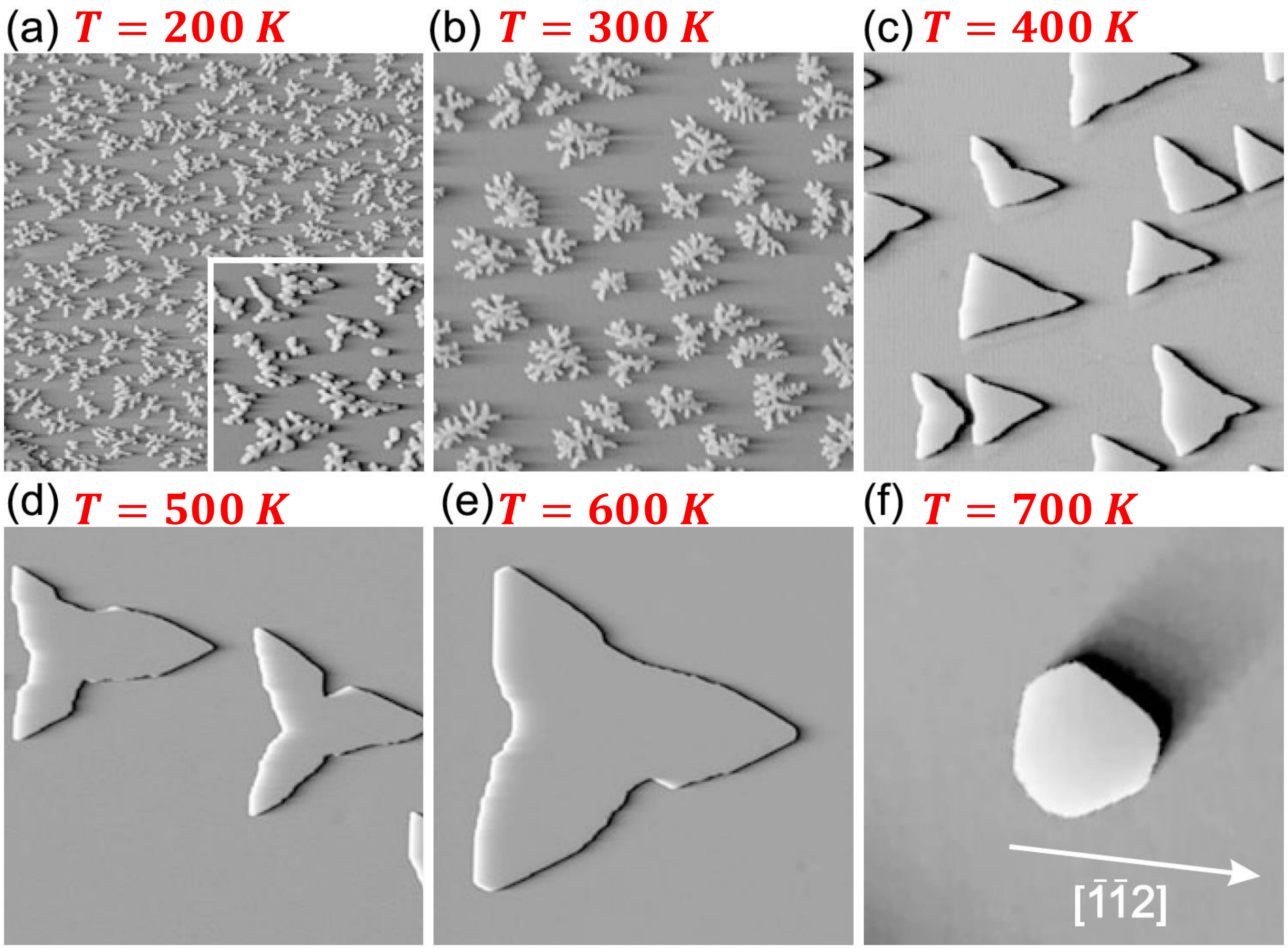
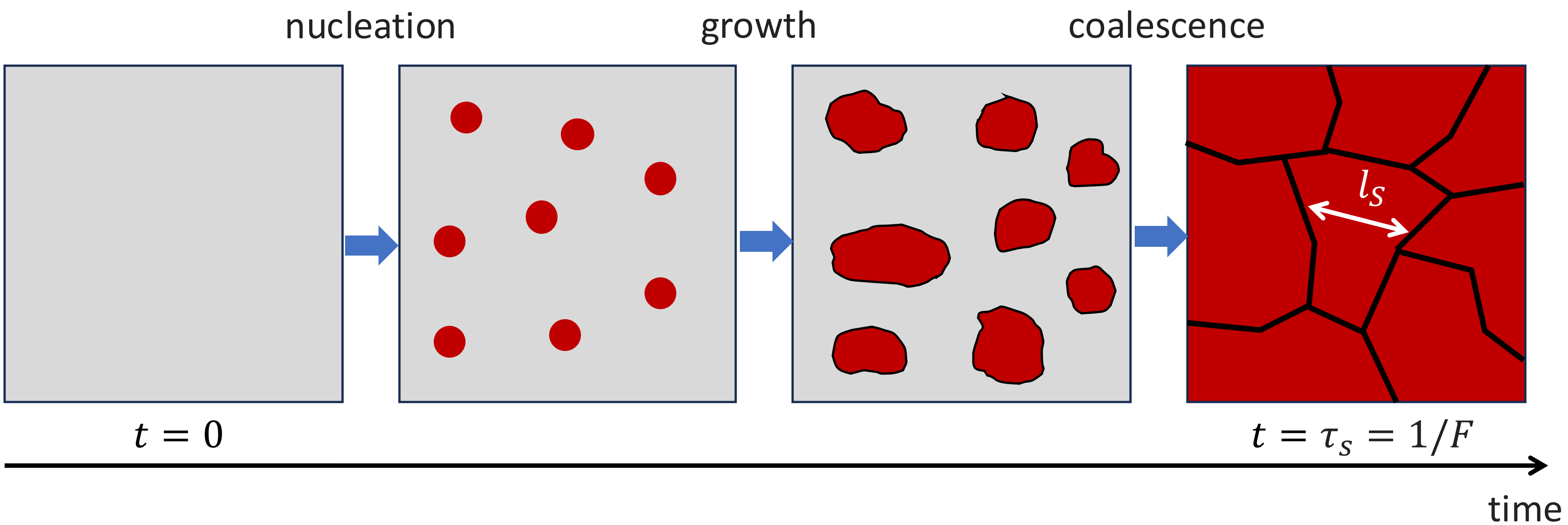


Fig. 3.1. STM topographs of adatom islands on Pt(111) after deposition of Pt at (**a**) 200 K, (**b**) 300 K, (**c**) 400 K, (**d**) 500 K, (**e**) 600 K and (**f**) 700 K. The deposited amount is 0.15 ML in (**a**)–(**e**) and 0.08 ML in (**f**), the deposition rate is 7×10^{-3} ML/s in (**a**)–(**e**) and 2.7×10^{-3} ML/s in (**f**). The topograph size is always 1560 Å × 1560 Å

T. Michely & J. Krug (2004).

Growth of 2D clusters



Deposition rate: $F\ [ML/sec]$

Time until coalescence: $\tau_s = 1/F\ [sec]$

size of a cluster: l_S

area of a cluster: l_S^2

number of a clusters per unit area: $1/l_S^2$

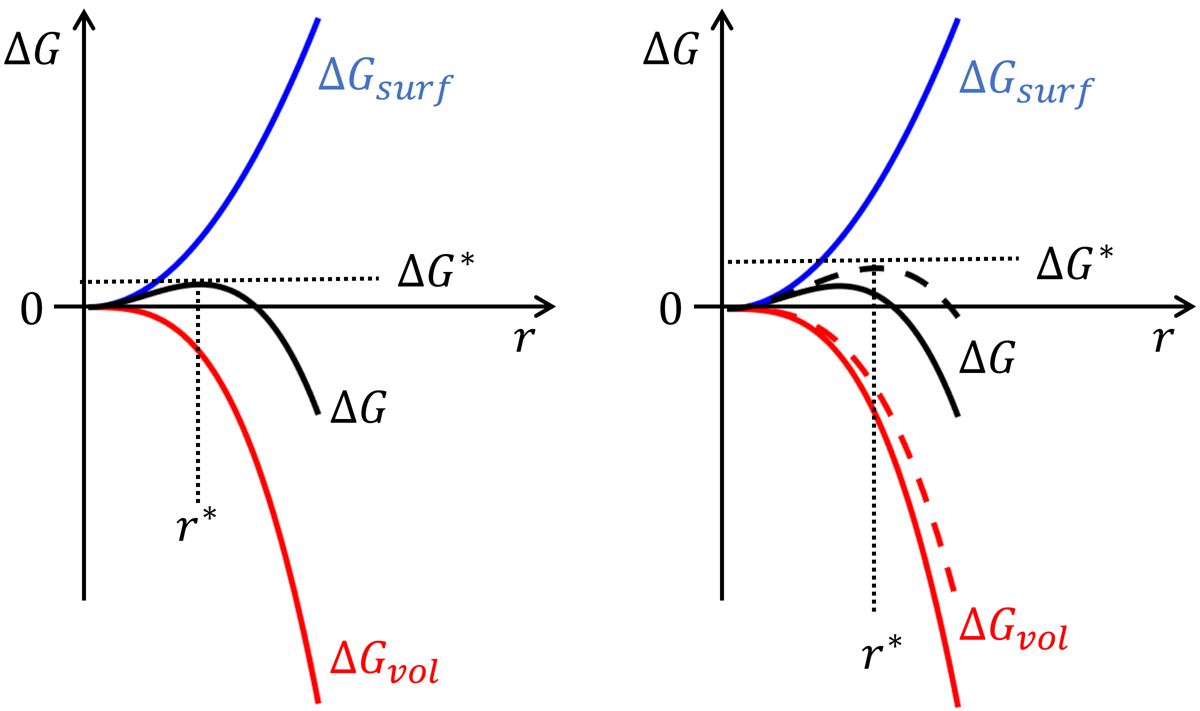
After A. Pimpinelli & J. Villain “Physics of crystal growth” (1998).

Classical nucleation theory (3D)

The change in Gibbs free energy when a nucleus is formed:

$$\Delta G = \Delta G_{vol} + \Delta G_{surf} = \tfrac{4}{3}\pi r^3 \cdot \Delta g_v + 4\pi r^2 \cdot \gamma$$

$$\Delta g_v \propto -\frac{k_B T}{v} \ln S \qquad (v \text{ – molar volume, } S \text{ - supersaturation})$$

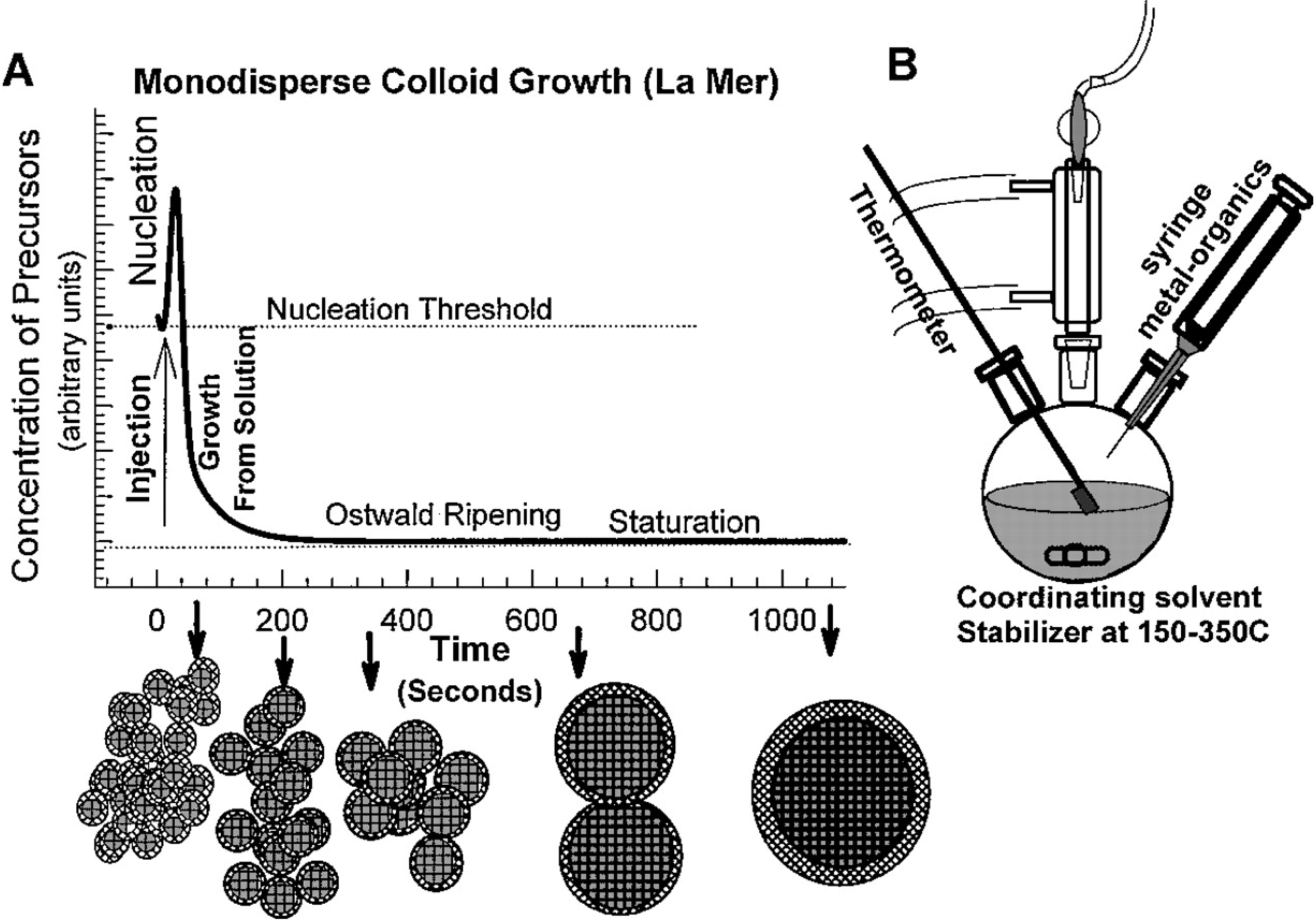


dashed lines – lower temperature (and a larger critical radius)

Nucleation rate:

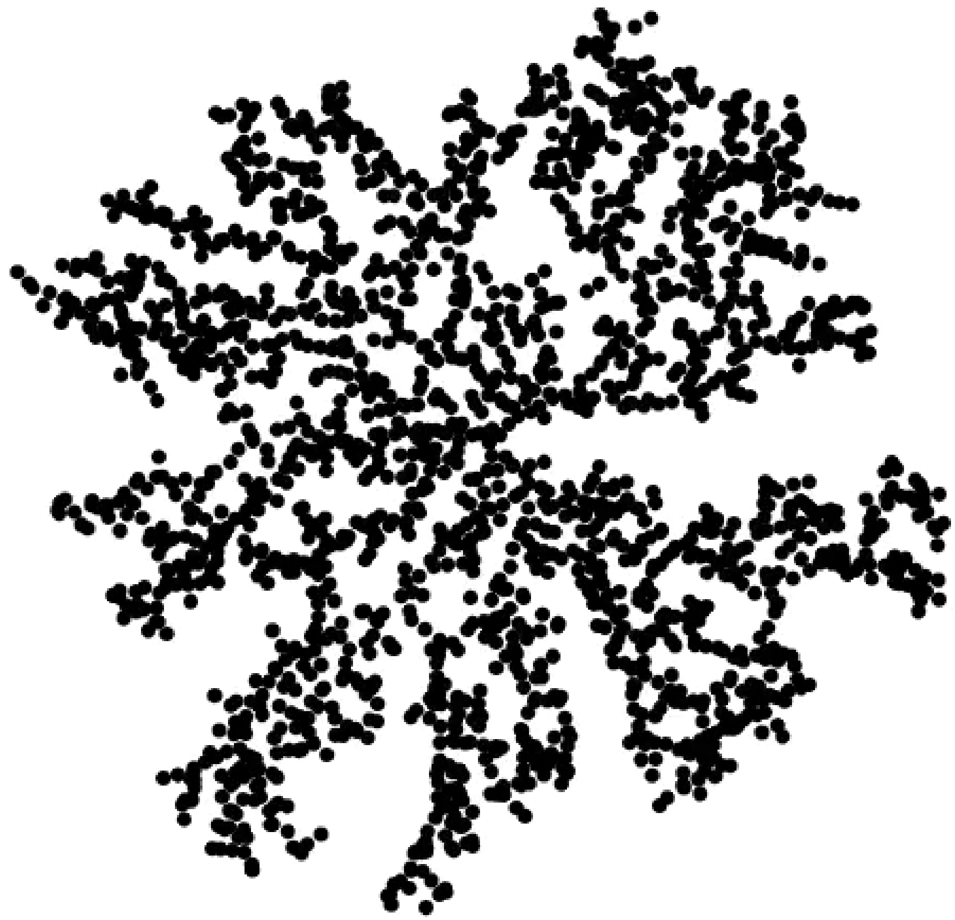
$$\frac{dN}{dt} \propto \exp\left[-\frac{\Delta G^*}{k_B T}\right]$$

N. Thanh et al., Chem. Rev. ***114****, 7610-7630 (2014)*



C. Murray et al., Annu. Rev. Mater. Sci. ***30****, 545-610 (2020)*

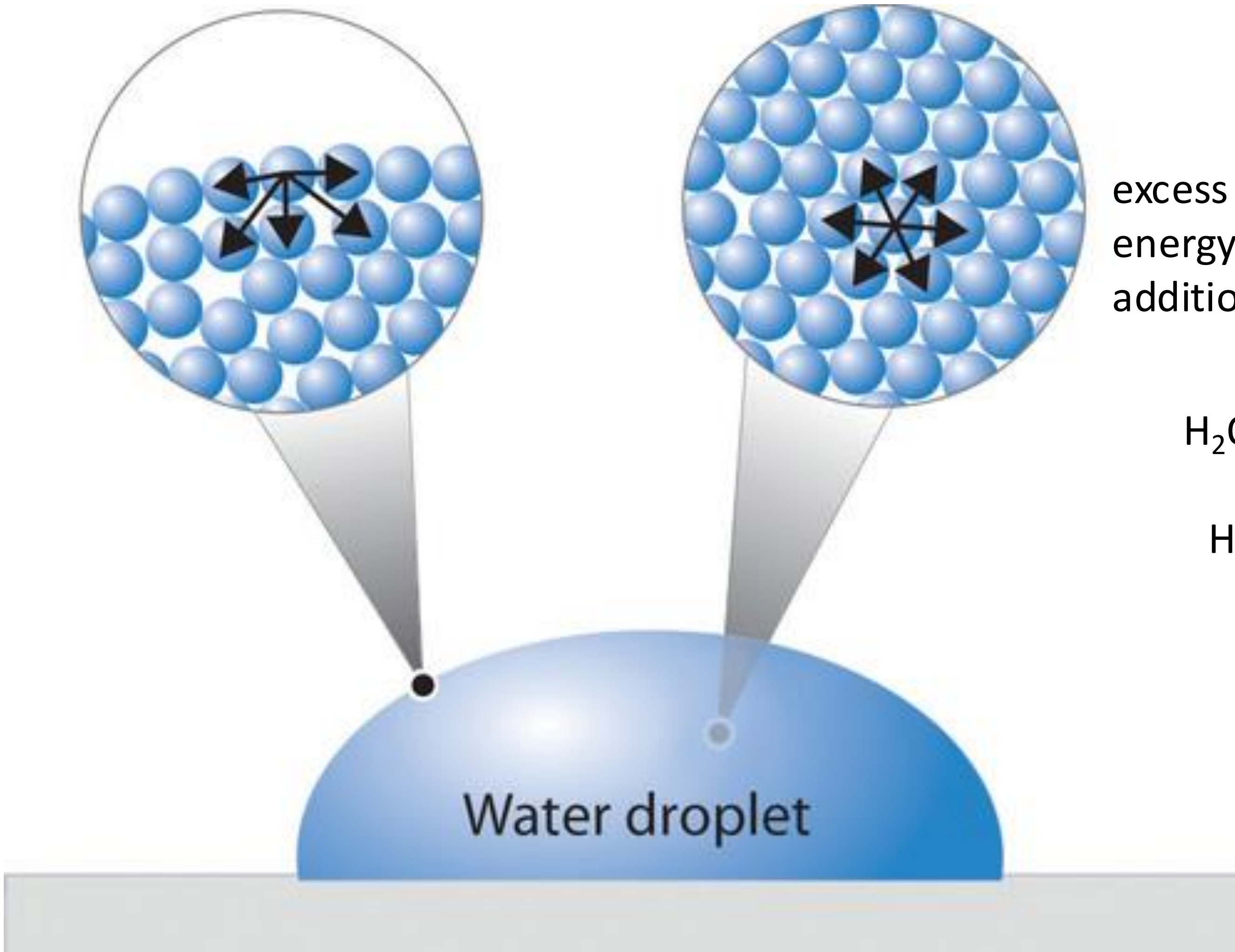
Diffusion limited aggregation



Pt adatom on Pt(111) surface: diffusion $E_D = 0.26$ eV
step edge diffusion $E_a \geq 0.6$ eV

https://flocc.network/model/diffusion-limited-aggregation

Surface tension



$$\gamma = \frac{\Delta E}{\Delta S}$$

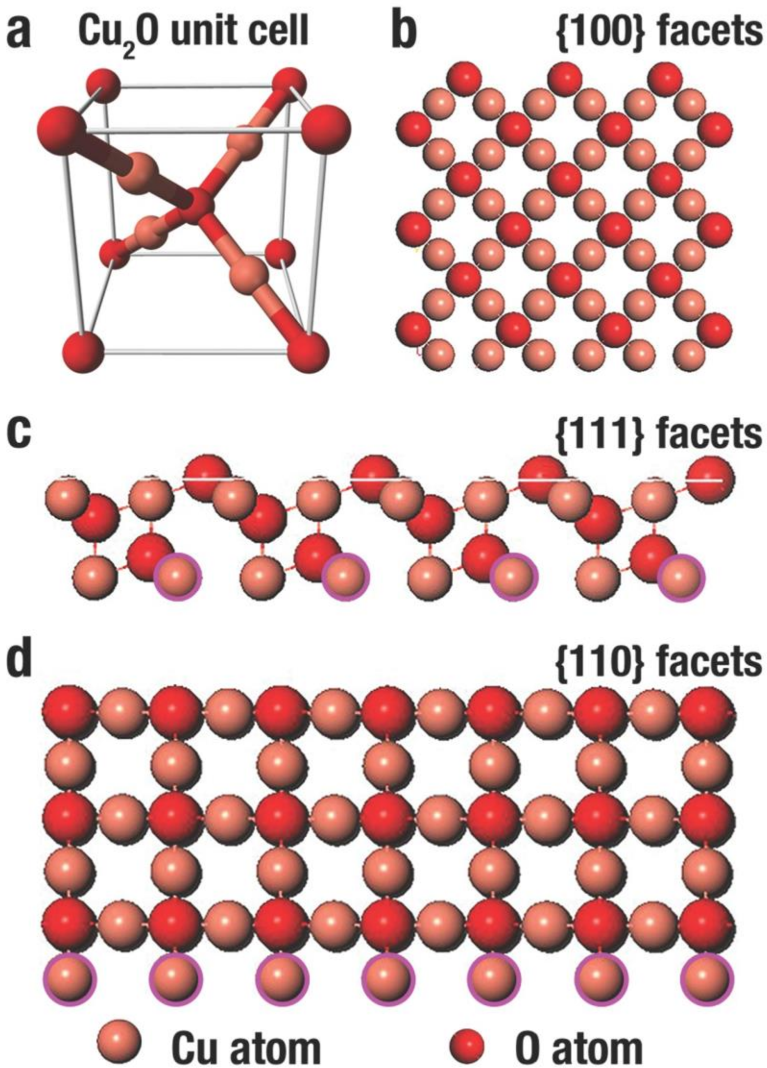
excess energy per surface area; energy that is needed to create additional surface with area ΔS

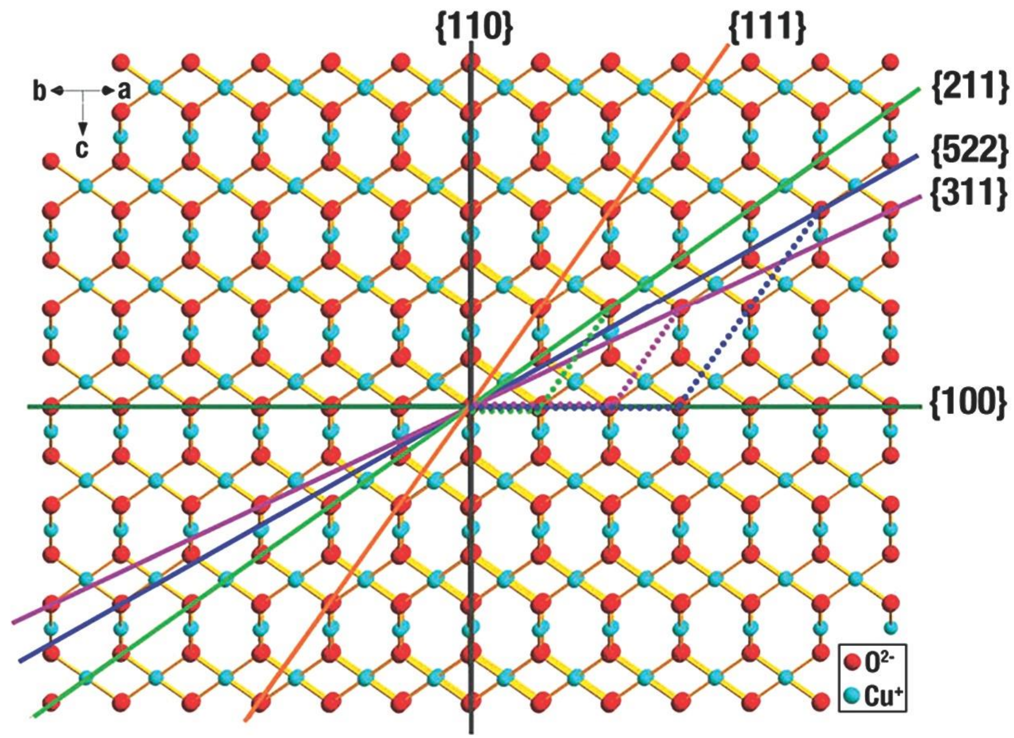
$$H_2O: \gamma = 72 \frac{mN}{m} = 4.5 \frac{meV}{Å^2}$$

$$Hg: \gamma = 487 \frac{mN}{m} = 30 \frac{meV}{Å^2}$$

https://chem.libretexts.org/

Equilibrium shape of an island





Y. Shang & Y. Guo, Adv. Sci., ***2*** *1500140 (2015)*

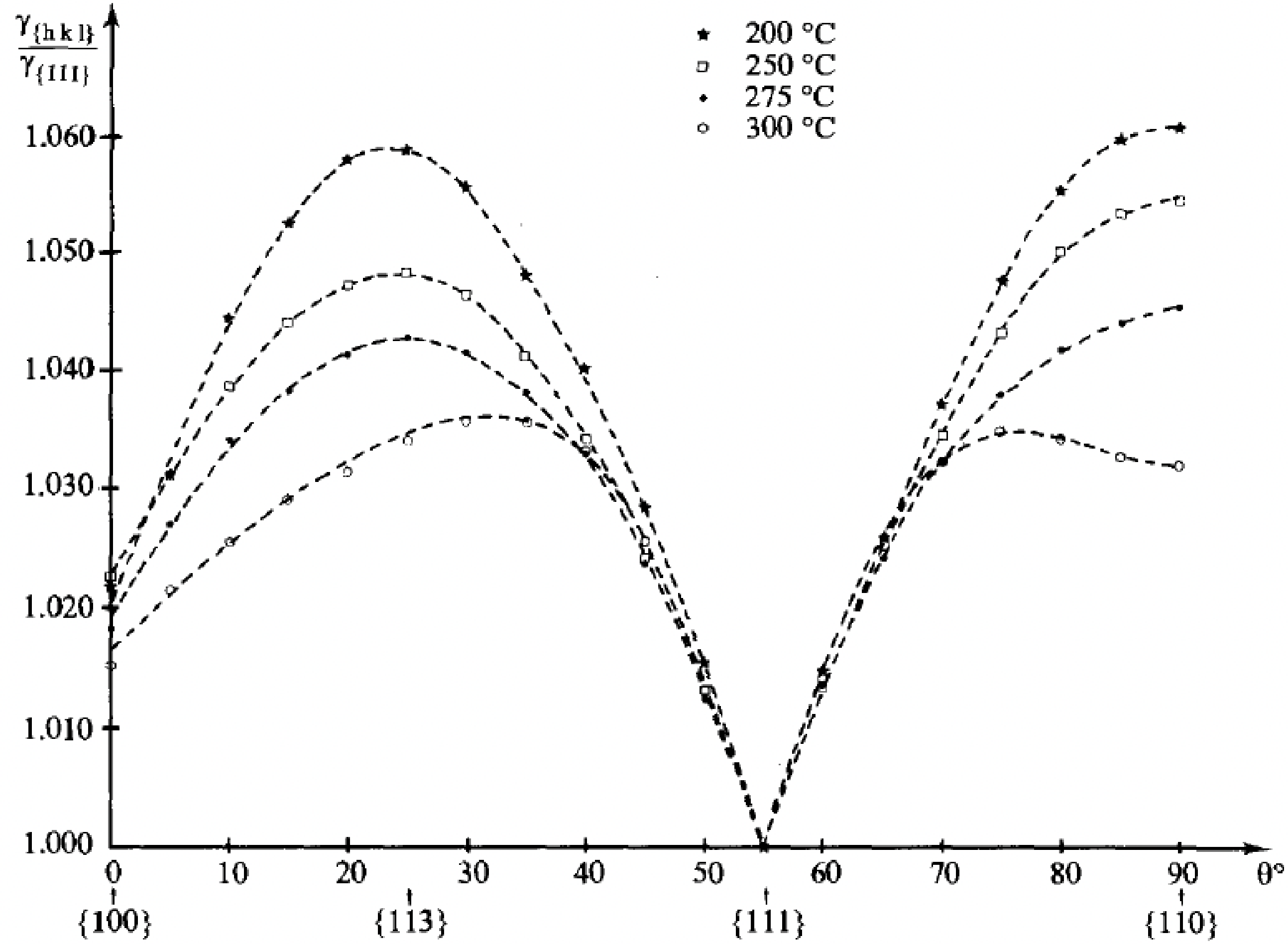
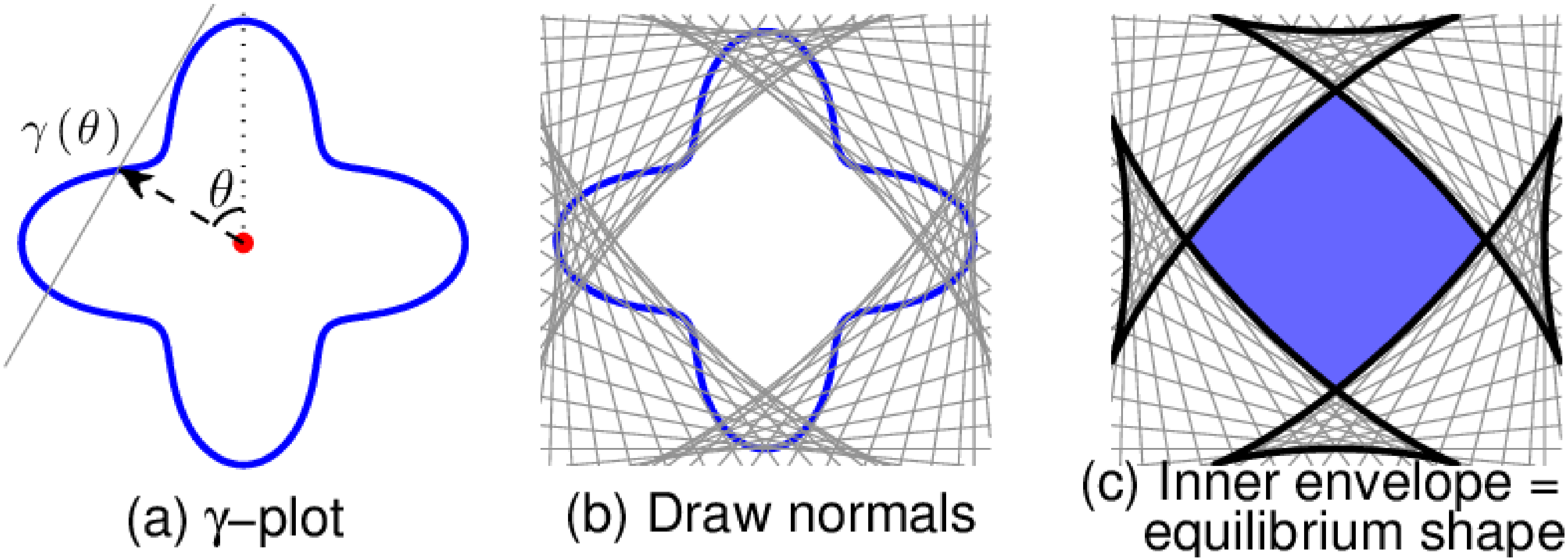


Fig. 2.2. The surface tension of indium at various temperatures, for the orientations $\{11k\}$, normalized to the value for $\{111\}$. Here, k is larger than 1 to the left and smaller than 1 to the right of the cusp. Note the weak variation (visually amplified by the choice of the normalization) and the roughening singularities (cusps) in the directions $\{100\}$ and $\{111\}$. The function ϕ has similar singularities (Heyraud & Métois 1986, with permission by the authors).

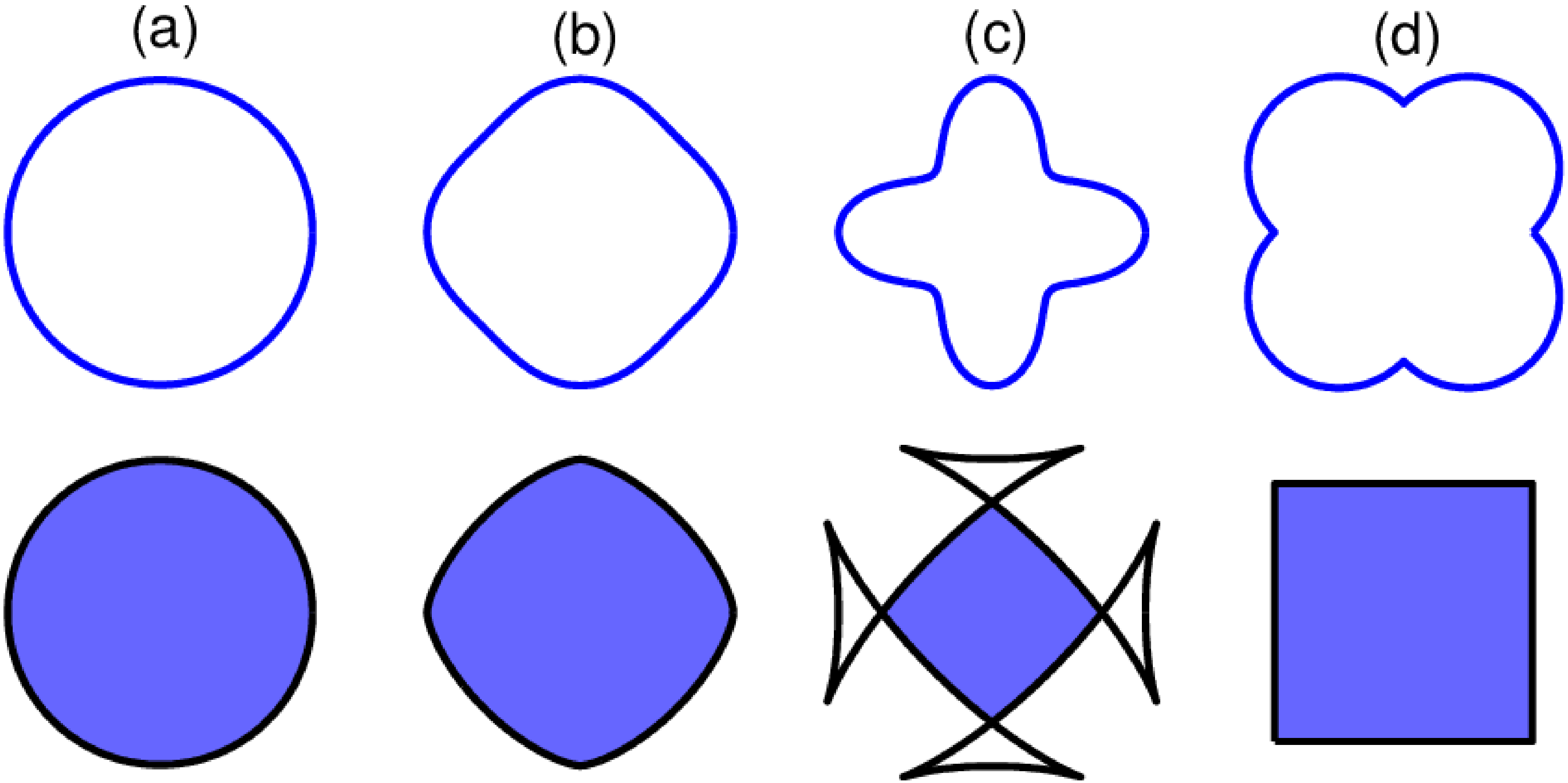
A. Pimpinelli & J. Villain "Physics of crystal growth" (1998).

Equilibrium shape of an island (Wulff construction)



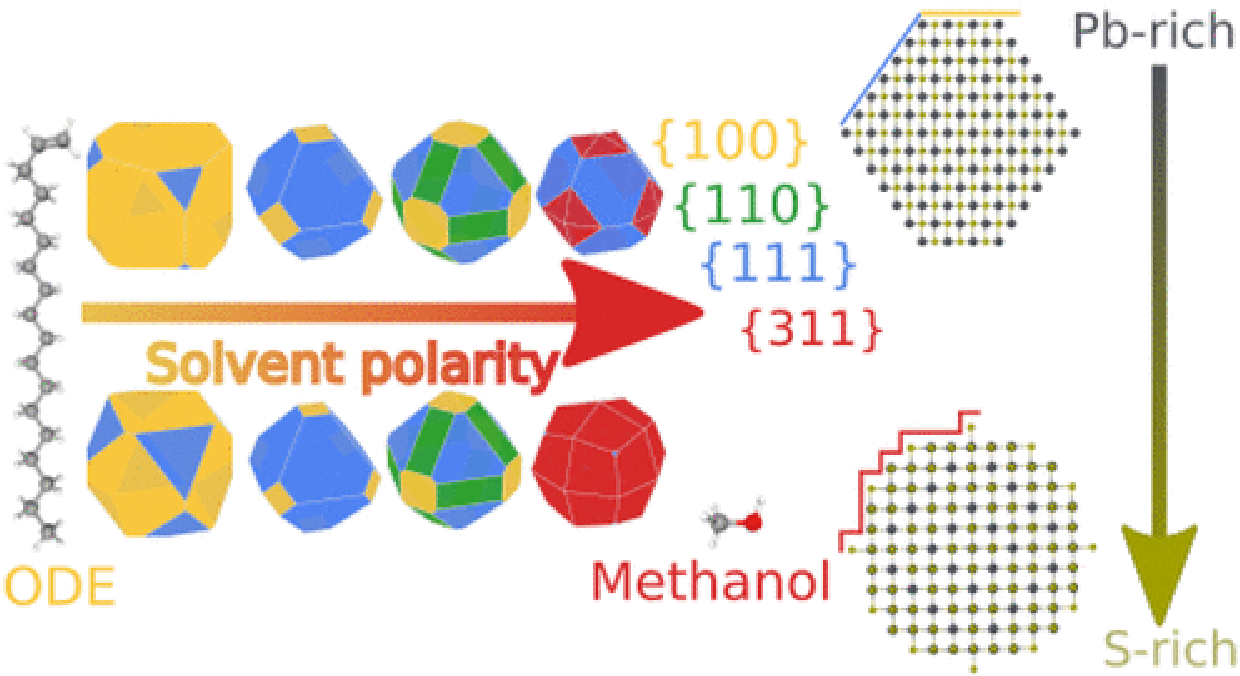
W. Bao et al., SIAM J. Appl. Math. ***77*** *2093 (2016)*

Equilibrium shape of an island (Wulff construction)

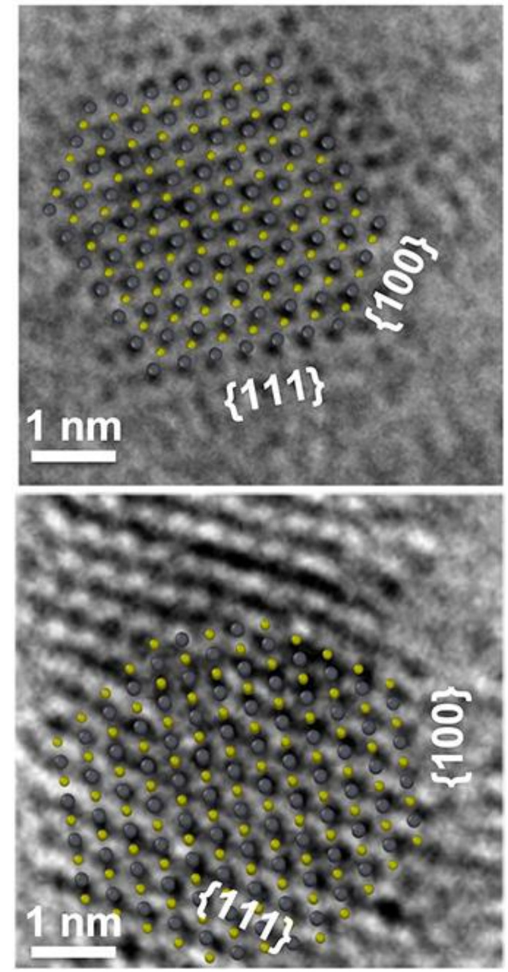


W. Bao et al., SIAM J. Appl. Math. ***77*** *2093 (2016)*

Equilibrium shape of nanoparticles

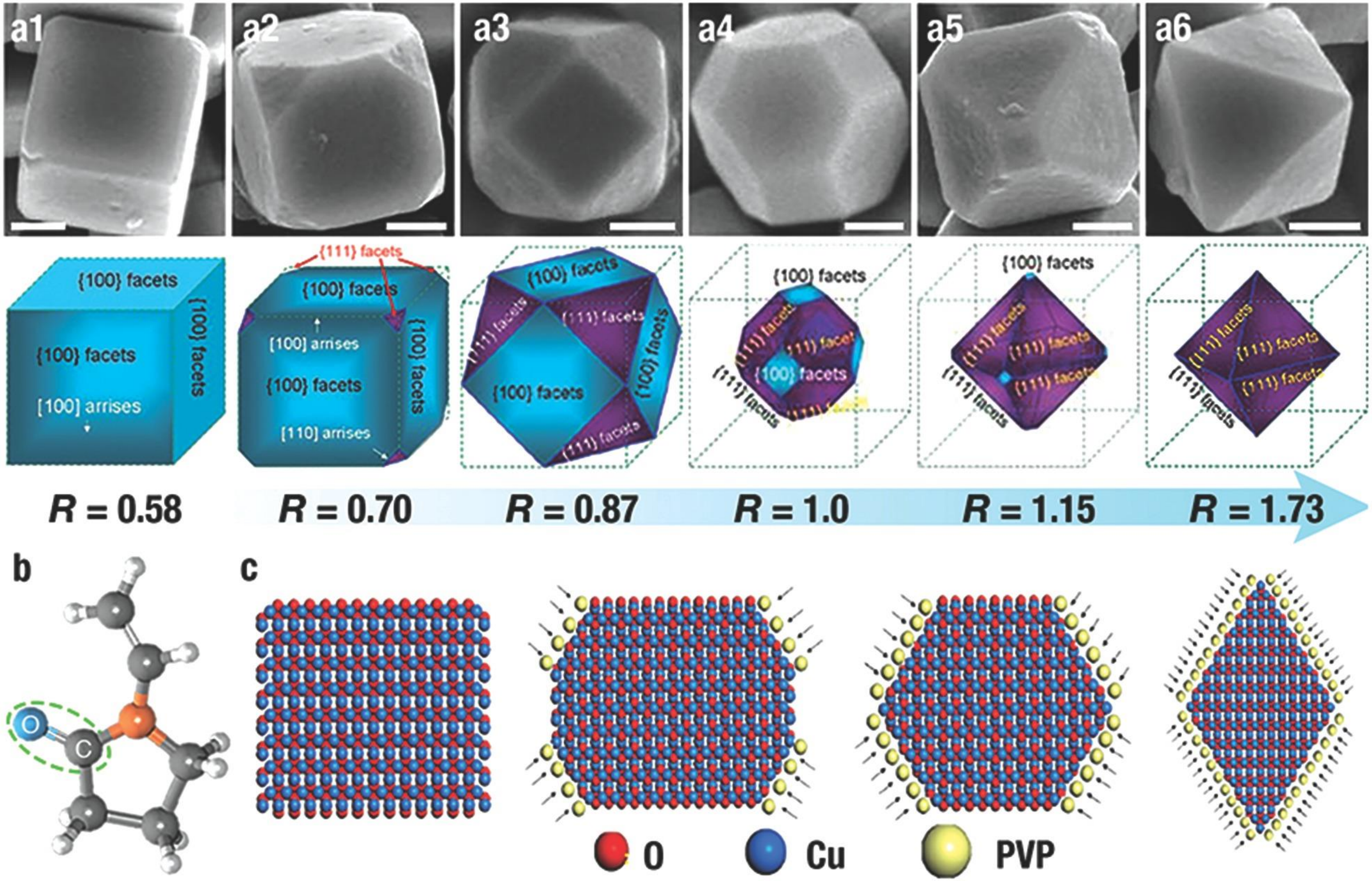


HRTEM of PbS/OA



B. Hou et al., Nano Lett. ***23***, *2277–2286 (2023).*

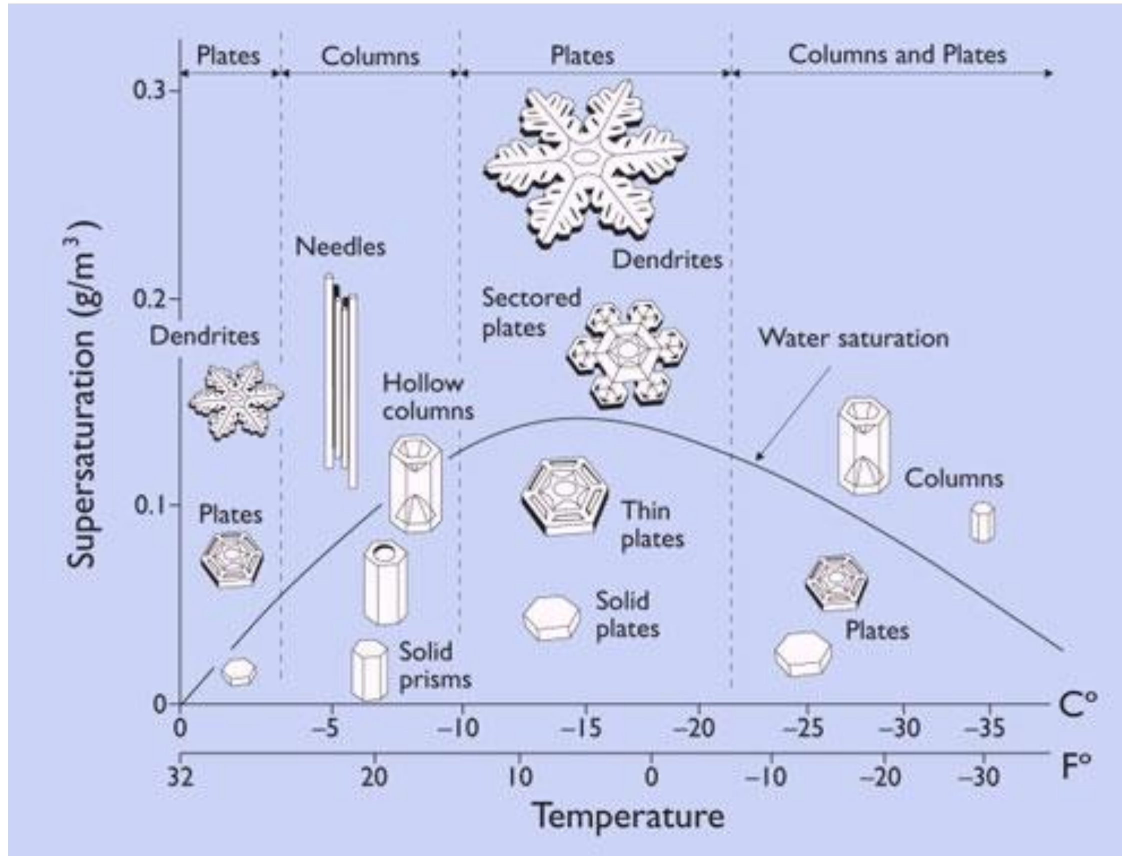
Kinetic control of the nanoparticle shape



Y. Shang & Y. Guo, Adv. Sci., ***2*** *1500140 (2015)*

Growth of snowflakes

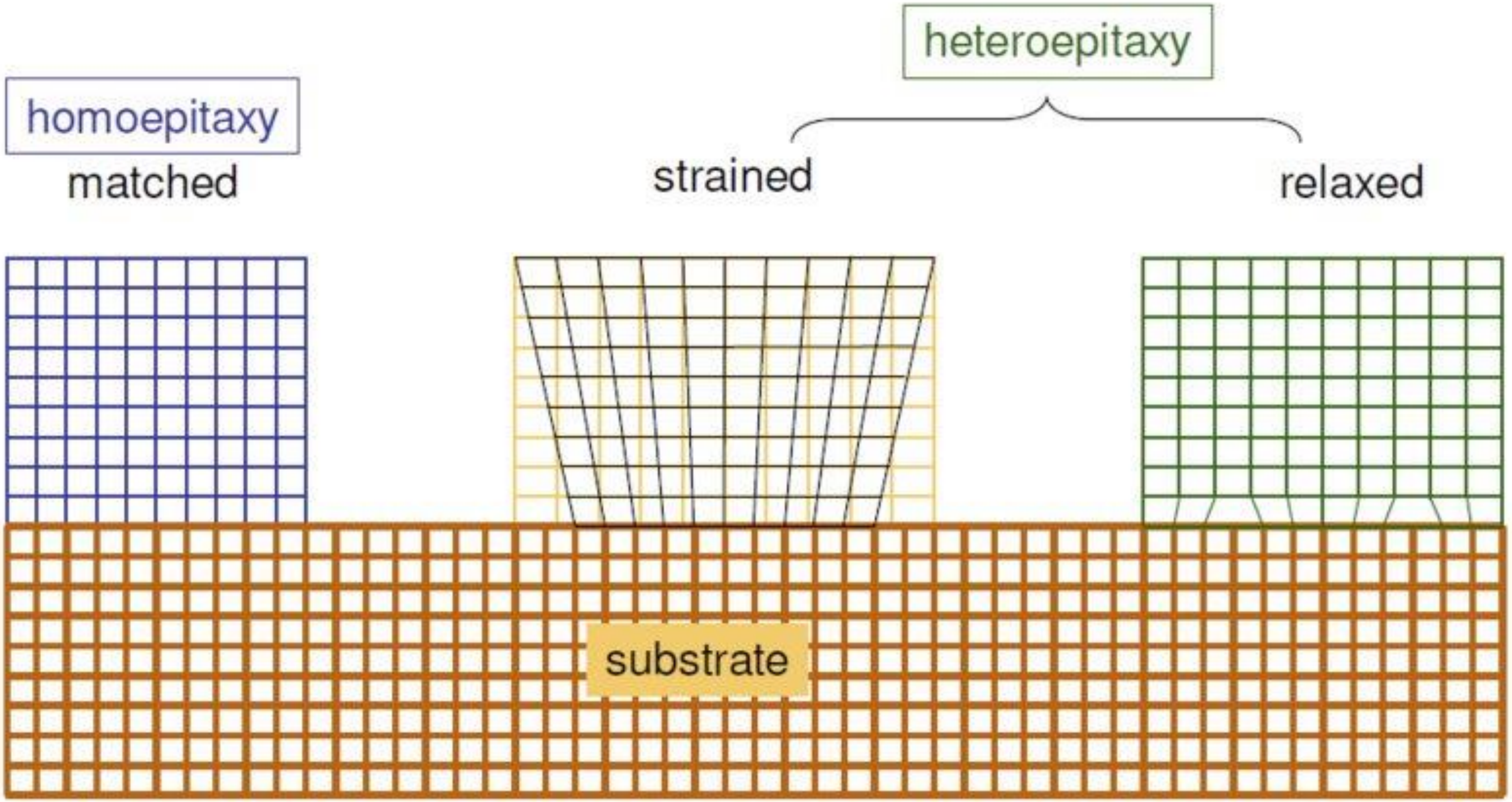
its.caltech.edu



earthsky.org

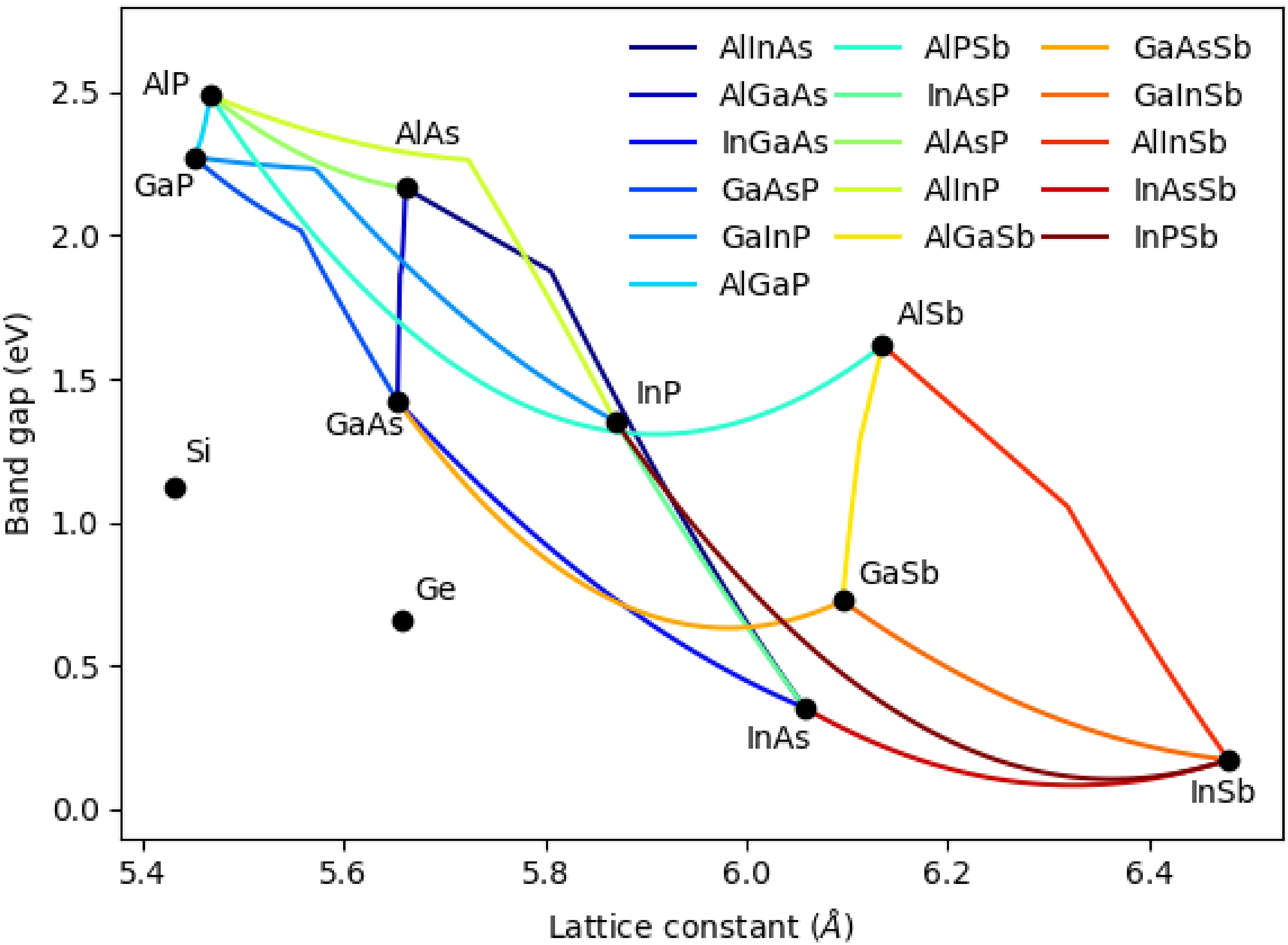
*G. Demange, et al. npj Comput Mater **3**, 15 (2017).*

Epitaxy



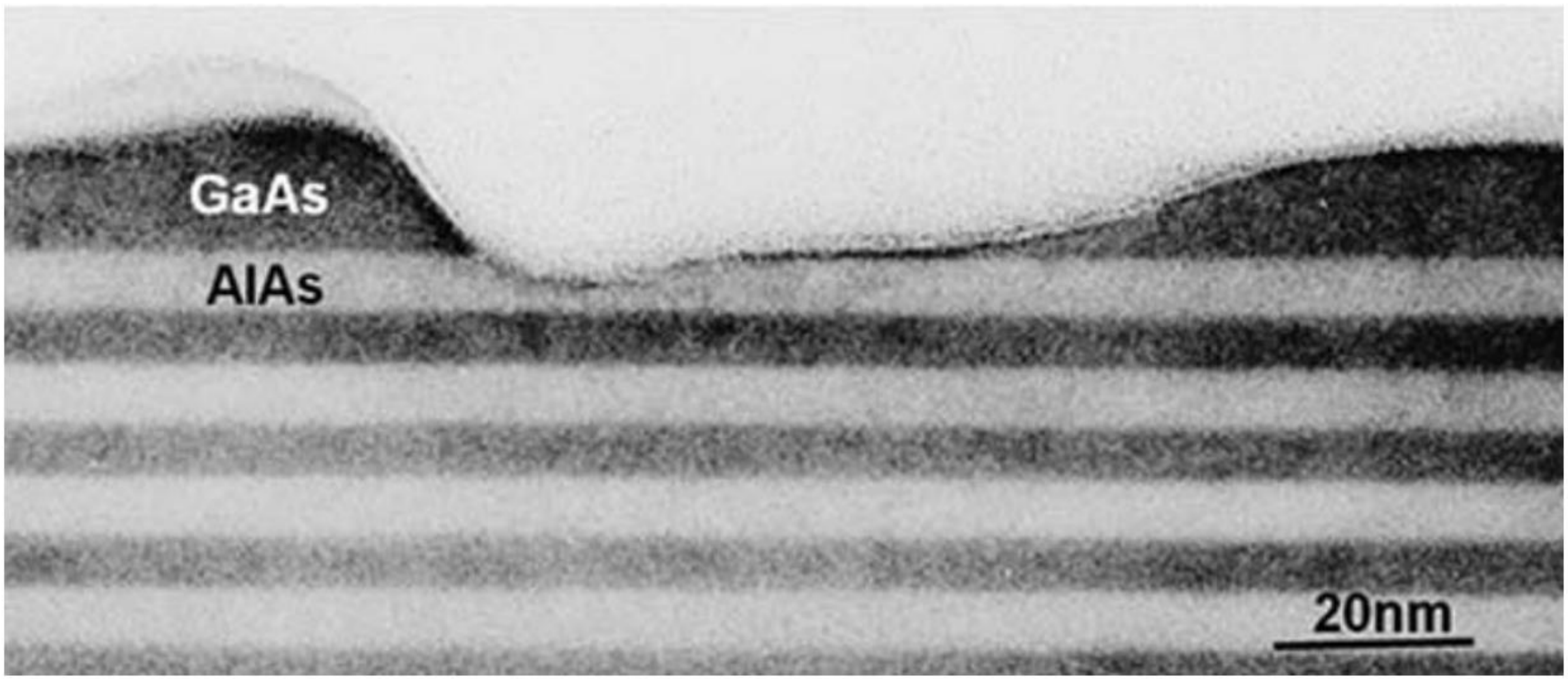
https://www.mks.com/n/silicon-epitaxial-thin-films

Band gap vs. lattice constant



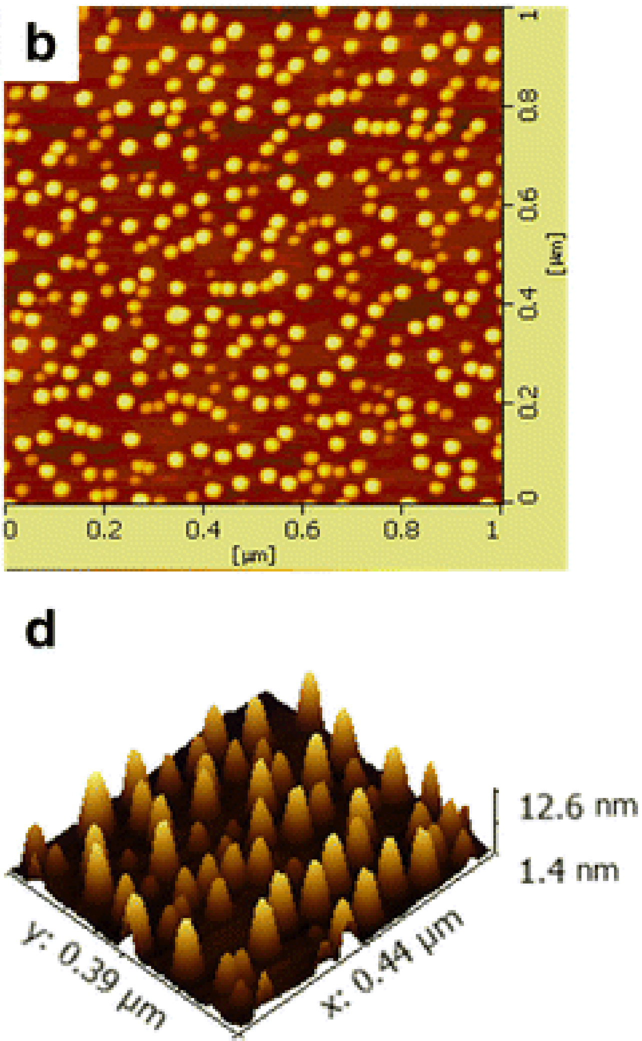
https://docs.solcore.solar/en/latest/Systems/Materials.html

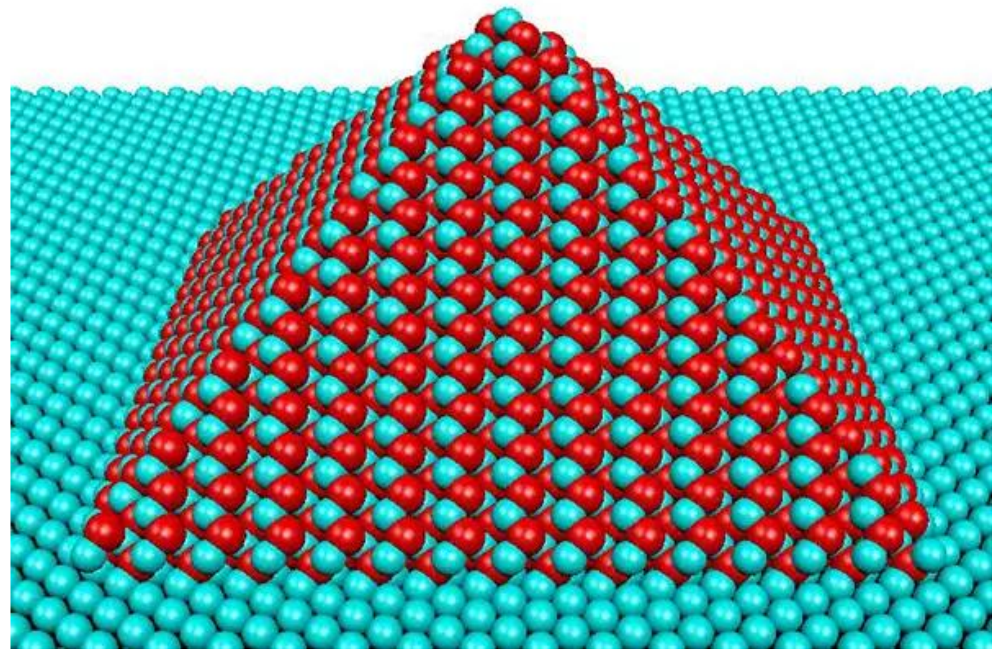
No strain – growth of thin films is possible



K.A. Sablon et al., Nanoscale Res. Lett. ***3*** *530-533 (2008)*

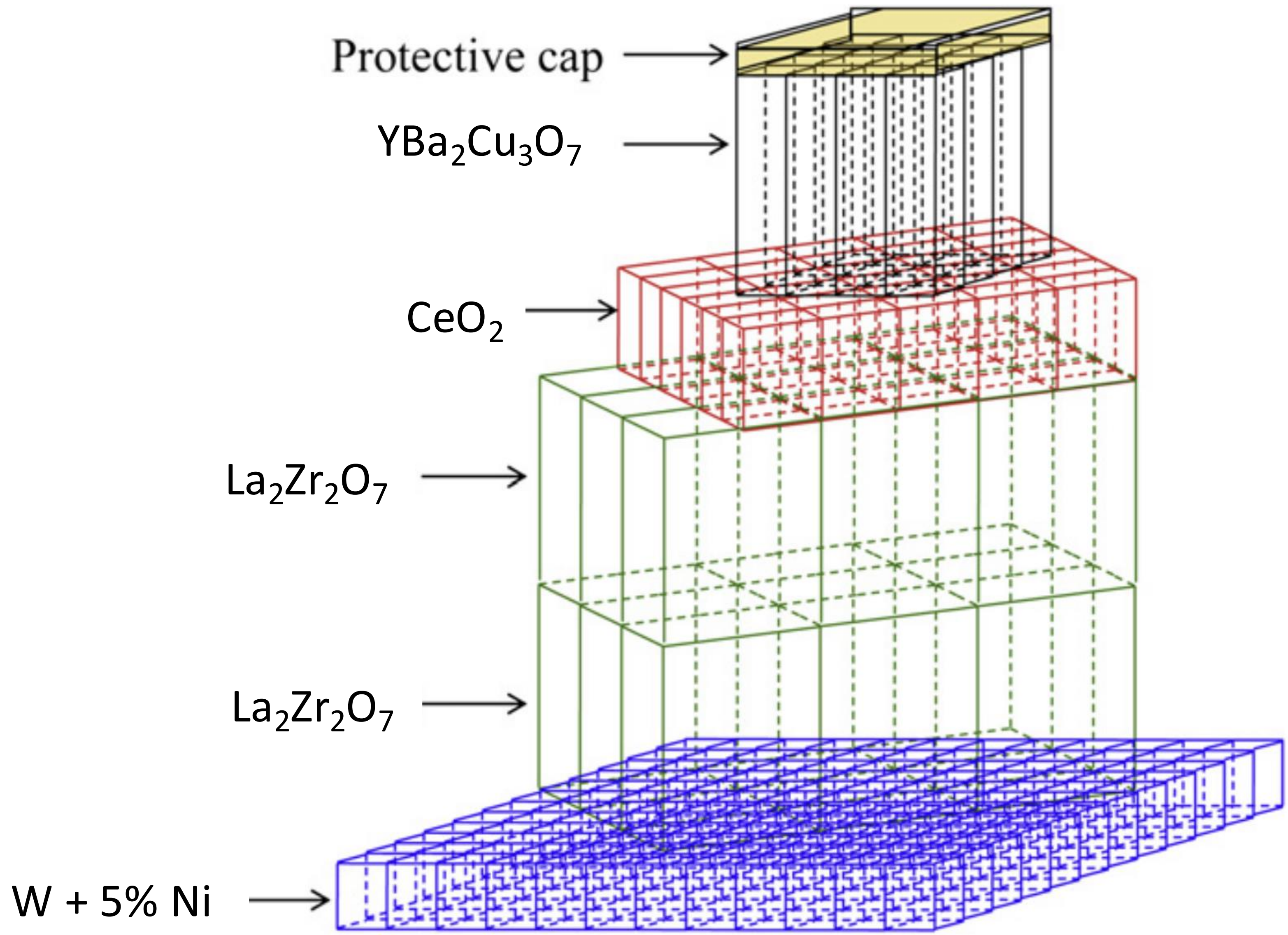
Strain leads to formation of dots





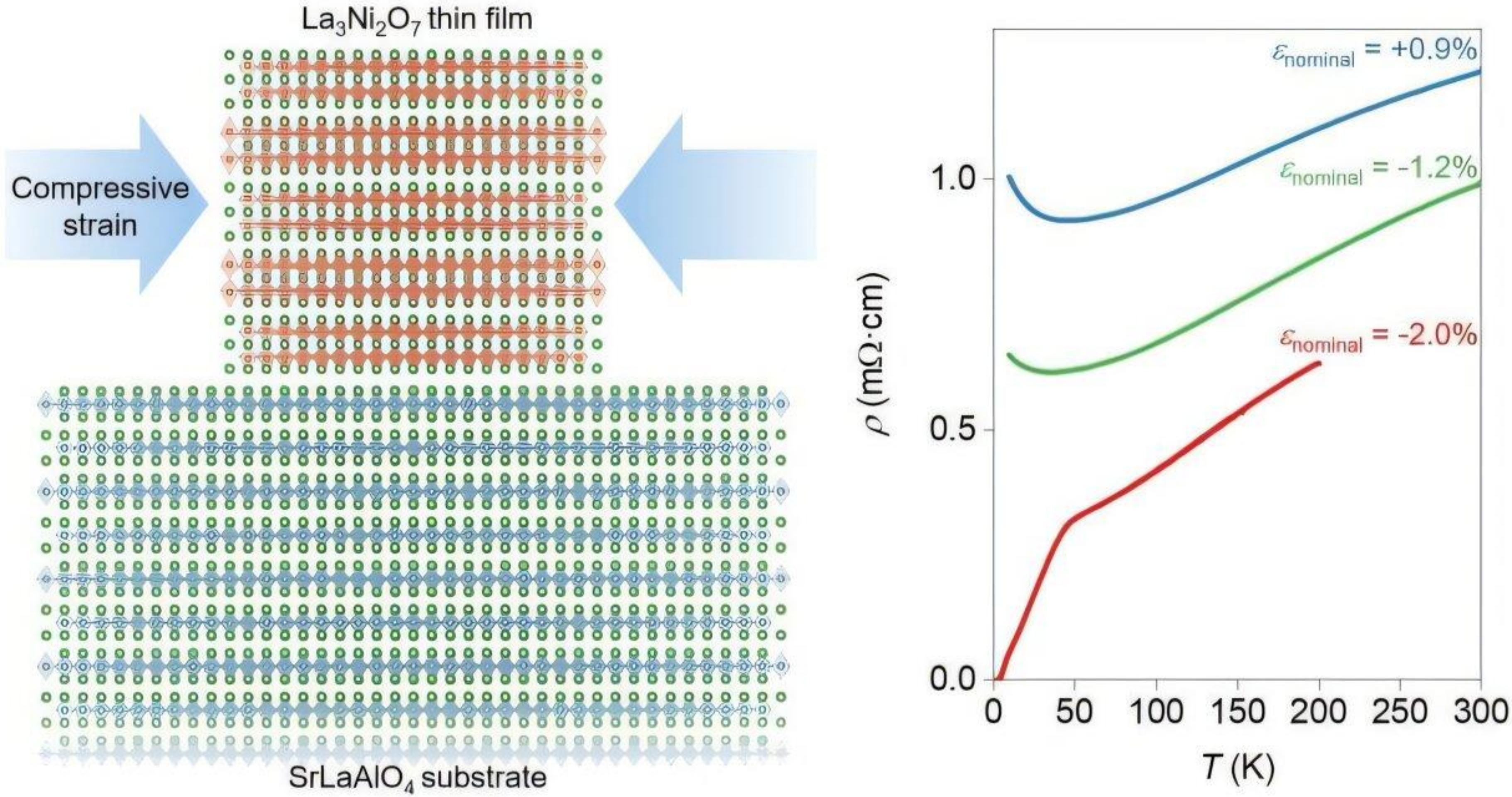
*X.B. Su et al. Nanoscale Res Lett **13**, 59 (2018)*

Buffer layer for epitaxial growth



V Narayanan et al. Prog. Solid State Chem. ***40****, 57 (2012)*

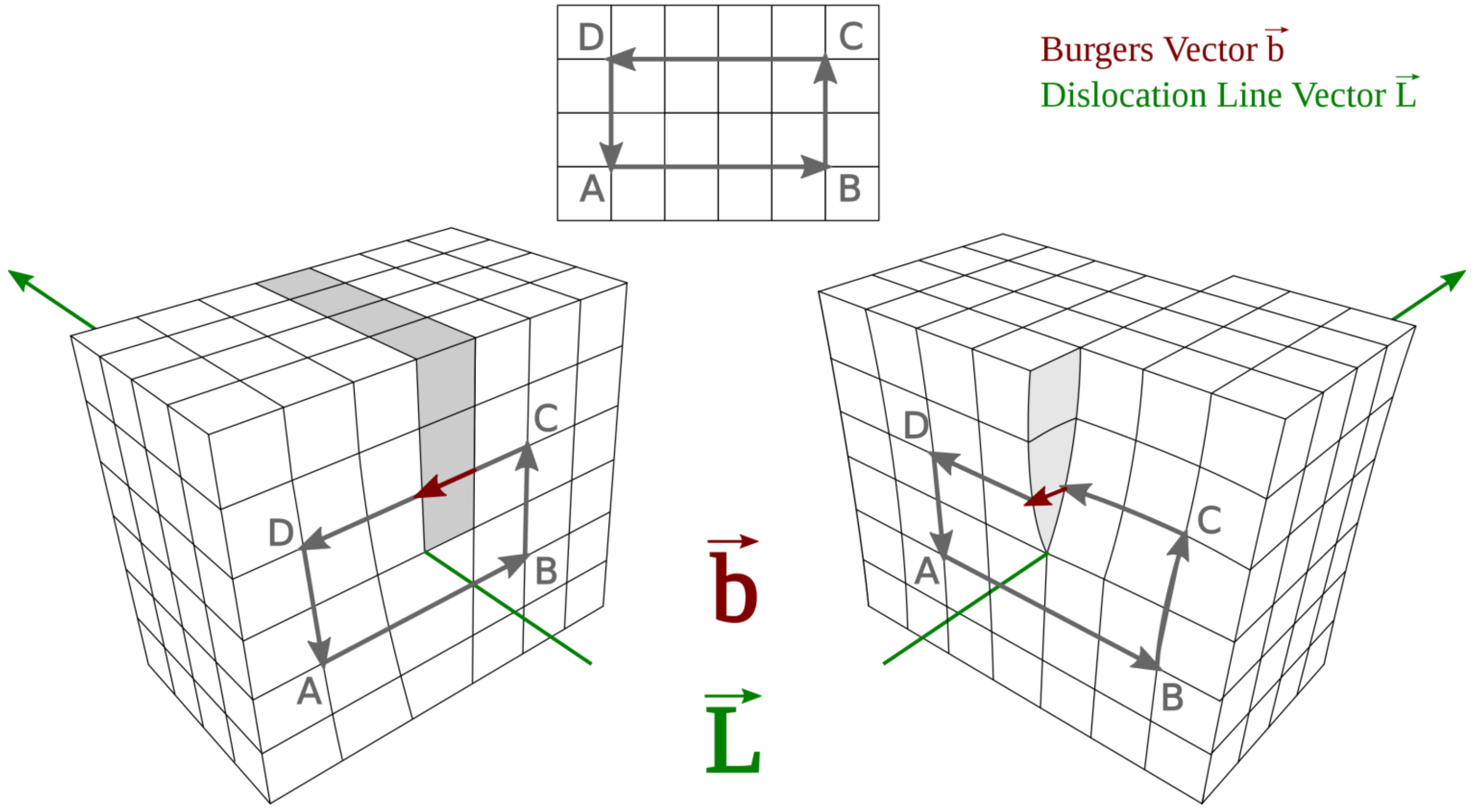
Strain to stabilize superconductivity



Eun Kyo Ko et al., Nature ***638****, 935-940 (2025)*

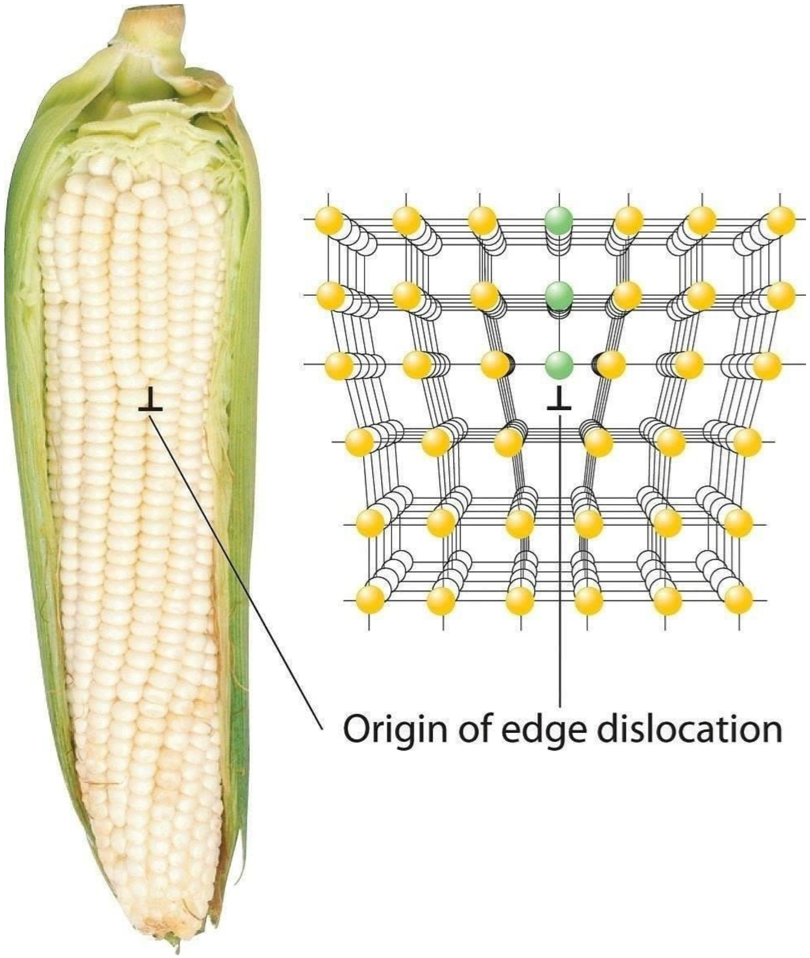
Dislocations

- Dislocation are linear defects which can be described by the Burgers vector



- Burgers vector can be perpendicular to the dislocation line (edge dislocation), parallel to the dislocation line (screw dislocation), or make an arbitrary angle with thee dislocation line (mixed dslocation)

Dislocations



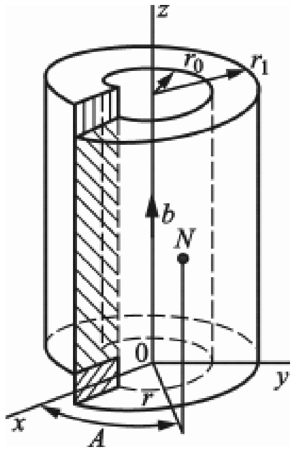
Dislocations

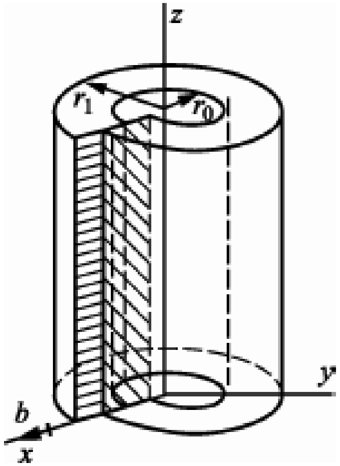
- By definition, the displacement field $\vec{u}(\vec{r})$ satisfies the following condition for any closed contour around the dislocation line

$$\oint d\vec{u}(\vec{r}) = \vec{b}$$

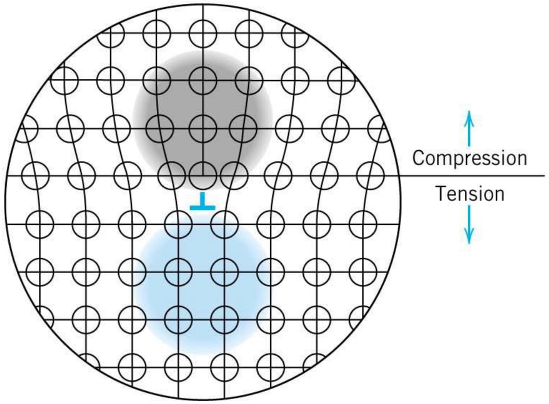
$$u(r) \cdot 2\pi r \sim b$$

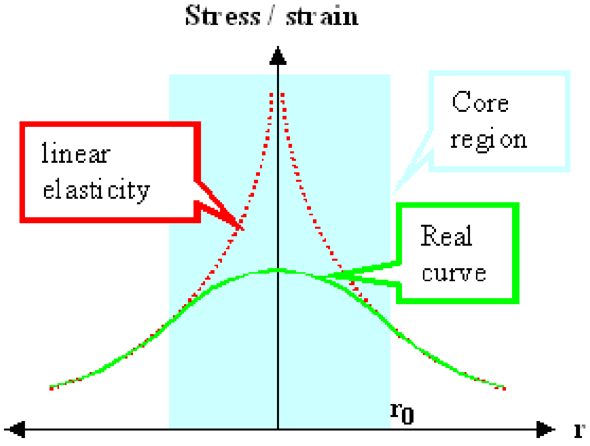
$$u(r) \sim \frac{b}{2\pi r}$$



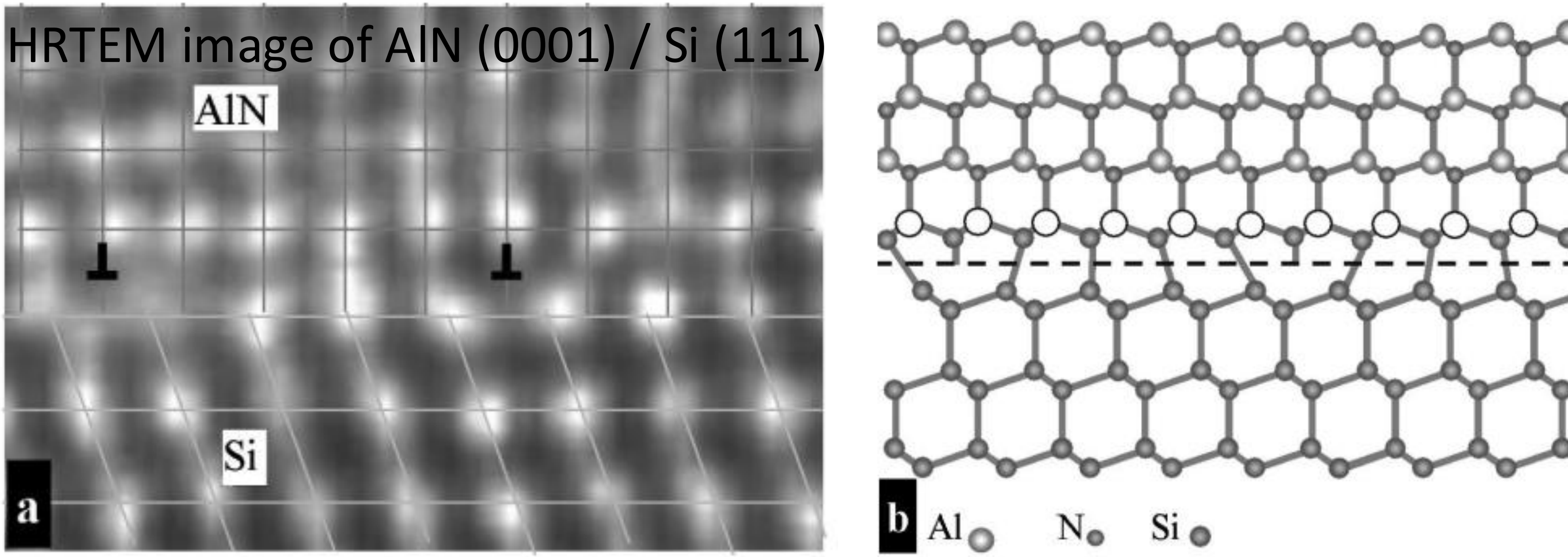


- Dislocations create slowly decaying displacement field $u \sim {}^{1}/_{r}$, so dislocations significantly distort the crystal lattice



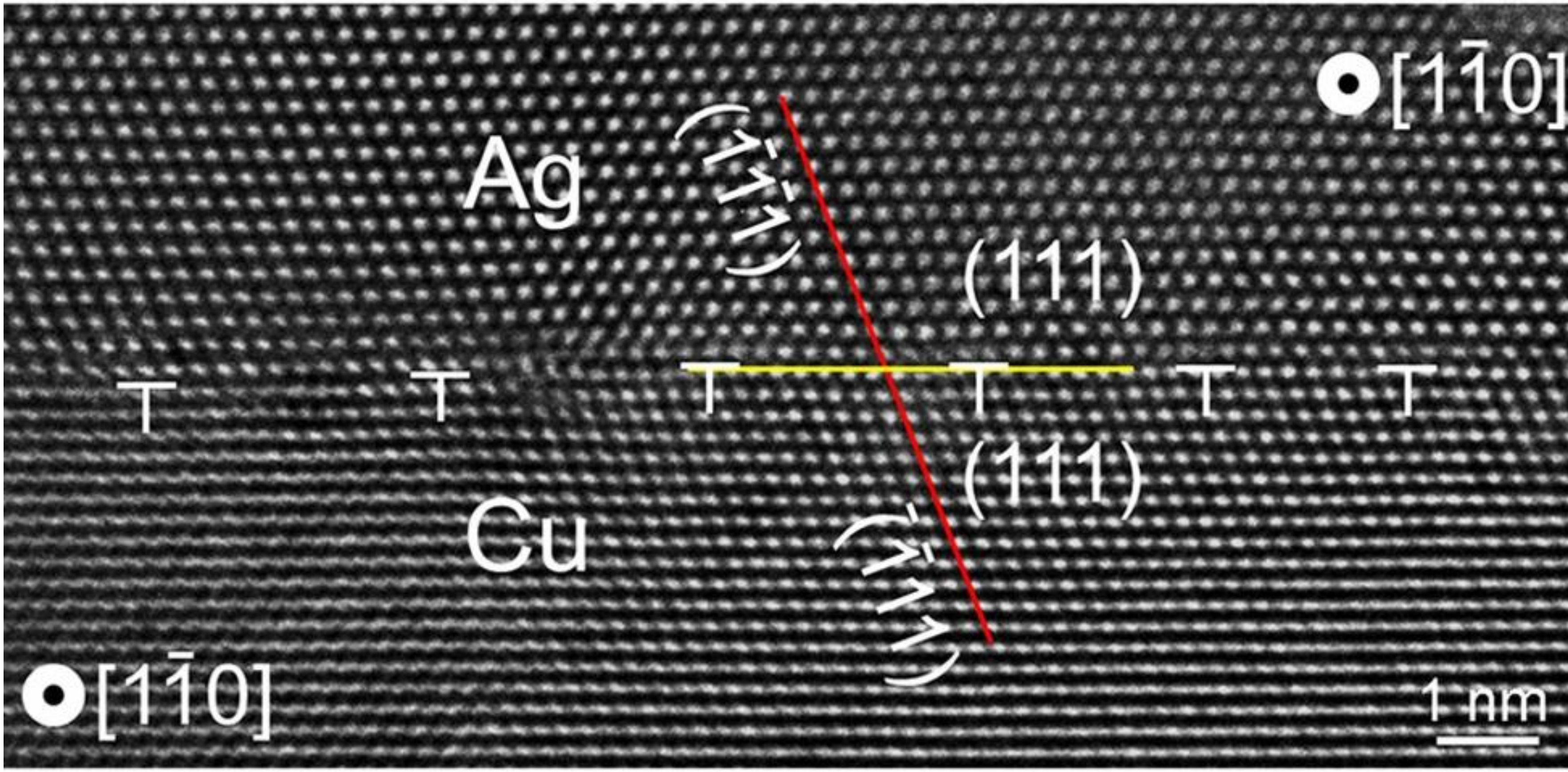


Misfit dislocations



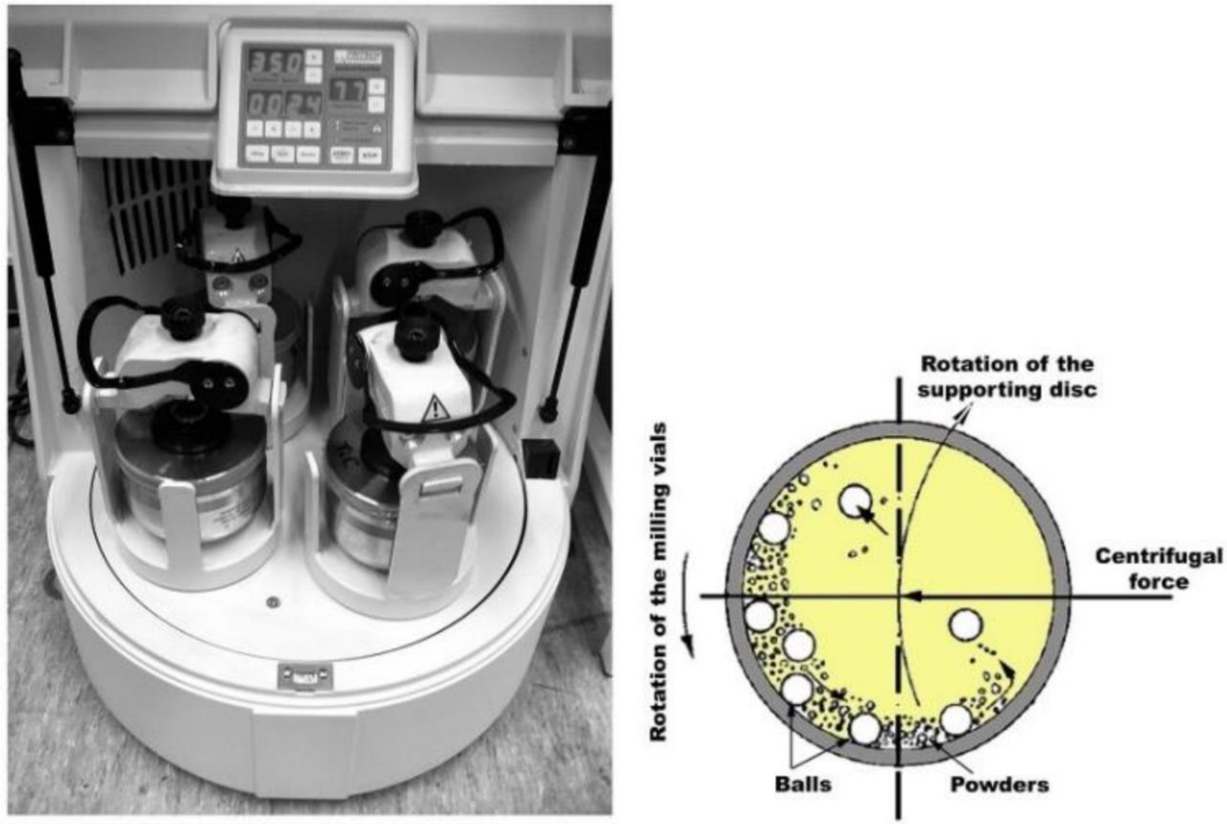
R. Liu, et al. Appl. Phys. Lett. ***83****, 860-862 (2003).*

Misfit dislocations



S. Zheng, et al. Sci. Rep. ***5****, 15428 (2015).*

Mechanical milling

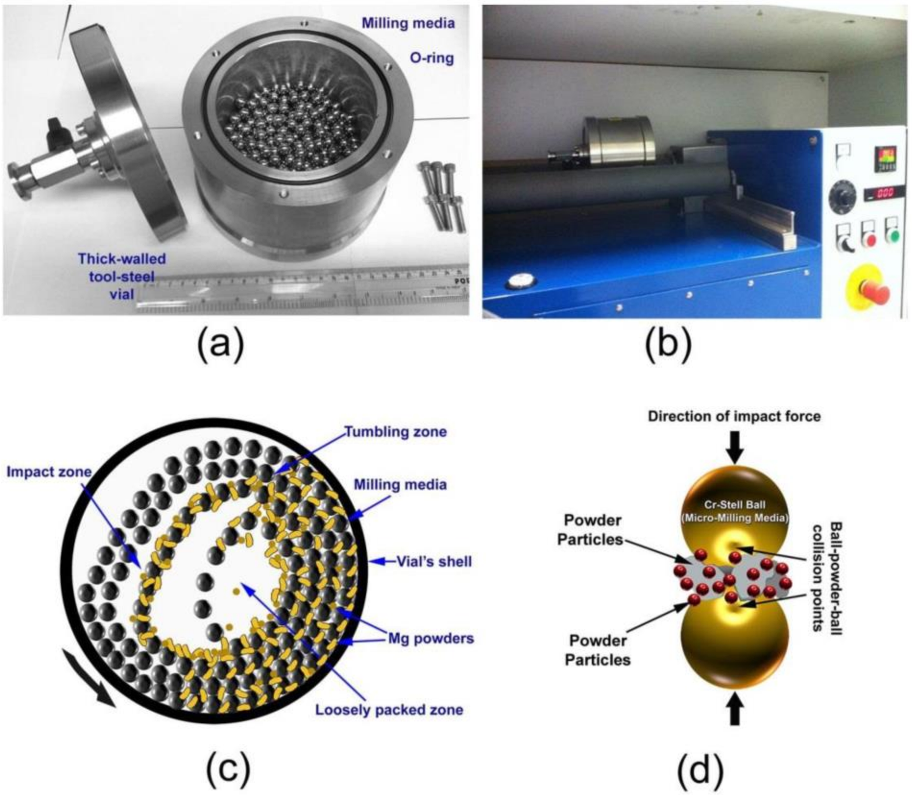


(a) (b)

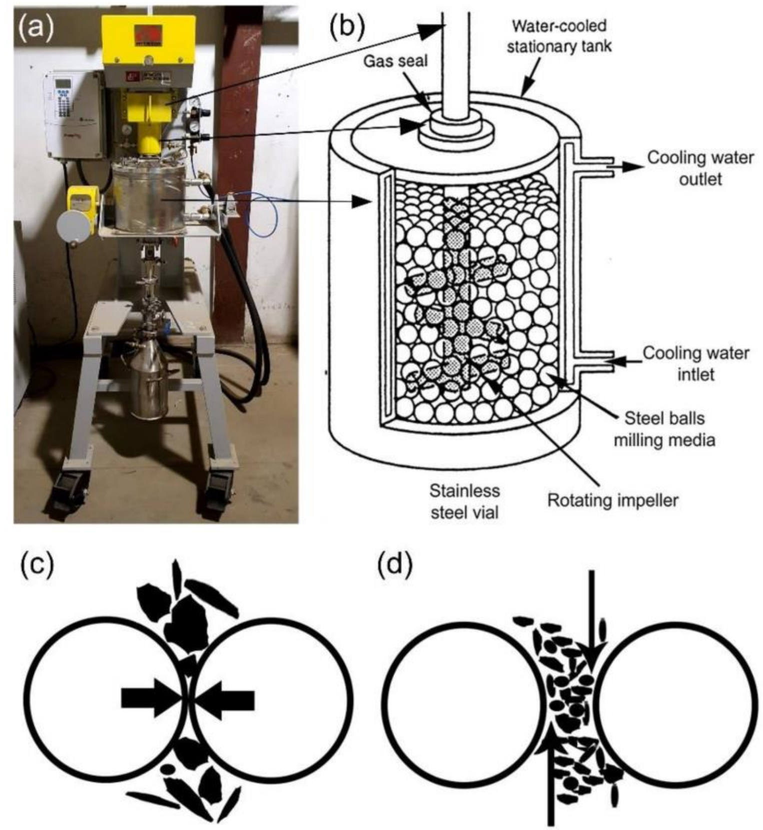
Planetary-type high energy ball mill

M. Sherif El-Eskandarany, et al. Nanomaterials ***11****, 2484 (2021).*

Mechanical milling



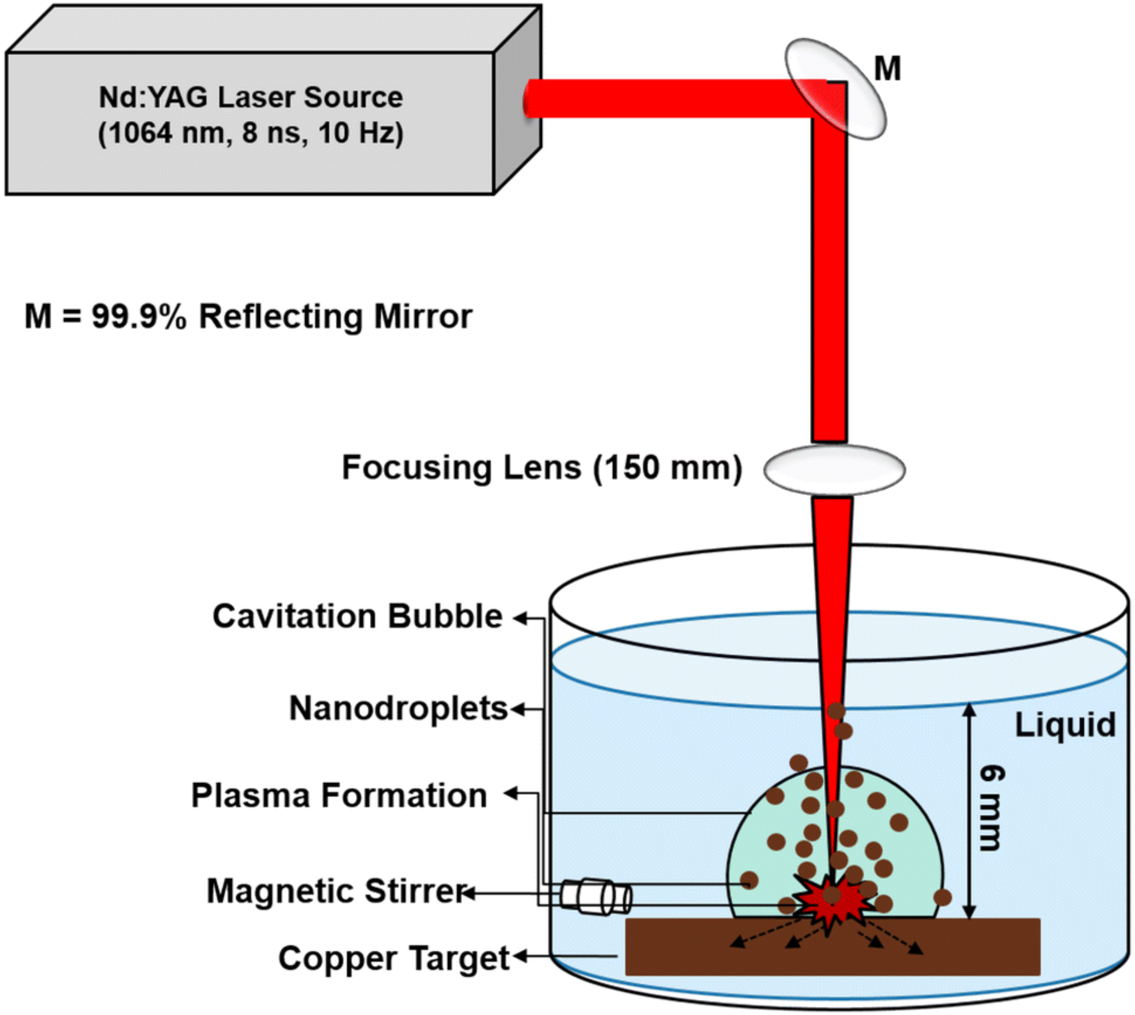
Tumbler Ball Mill

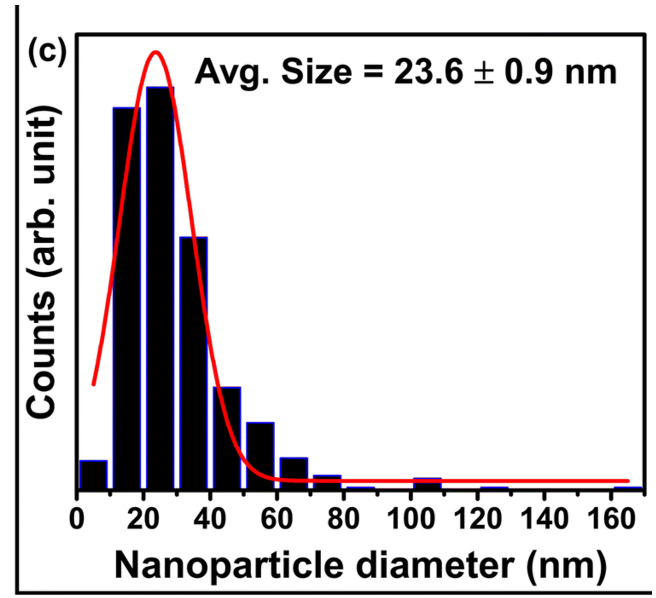


Attritor ball mill

M. Sherif El-Eskandarany, et al. Nanomaterials ***11****, 2484 (2021).*

Laser ablation

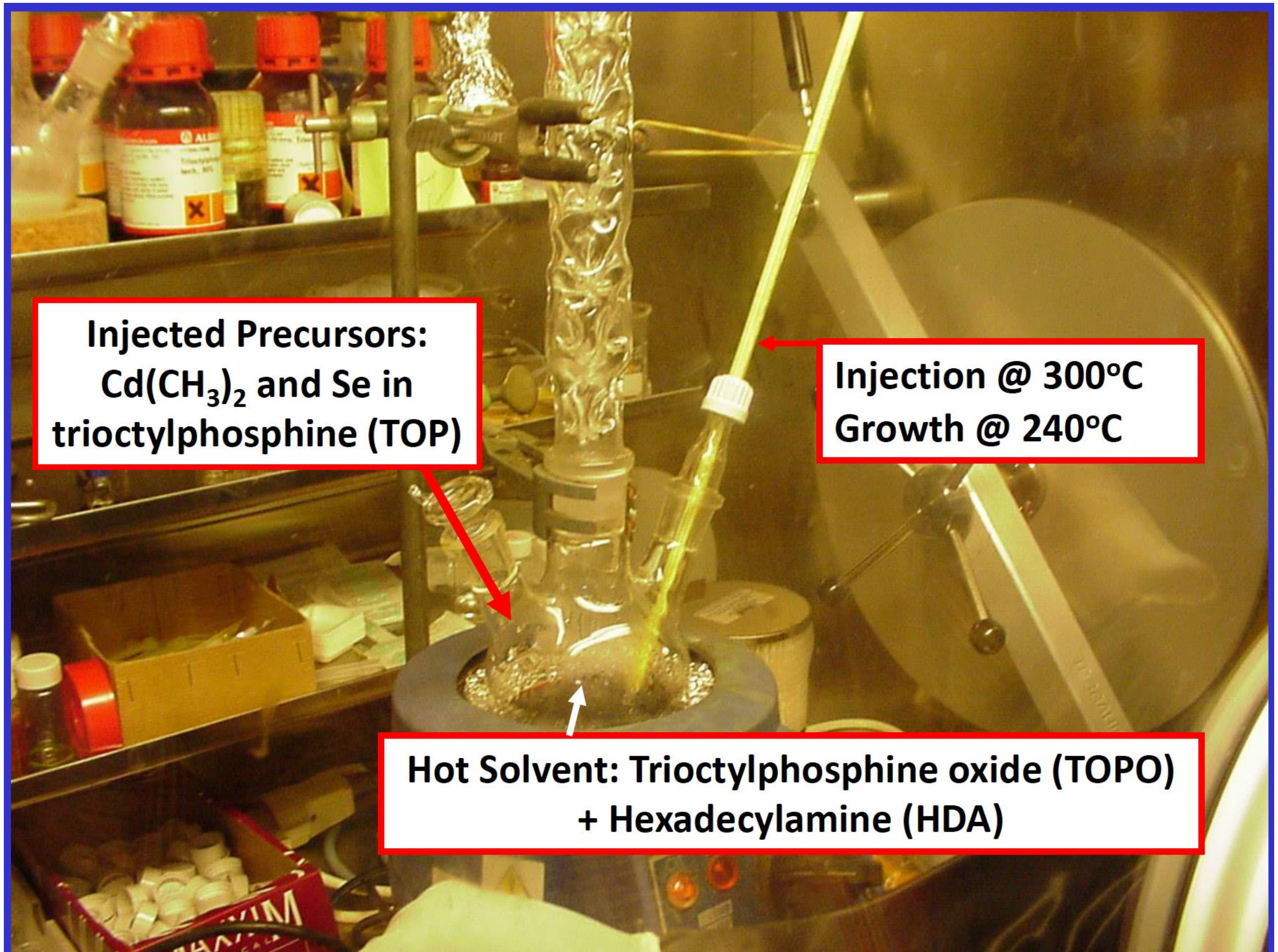




R. Rawat et al. Appl. Phys. A ***126****, 226 (2020).*

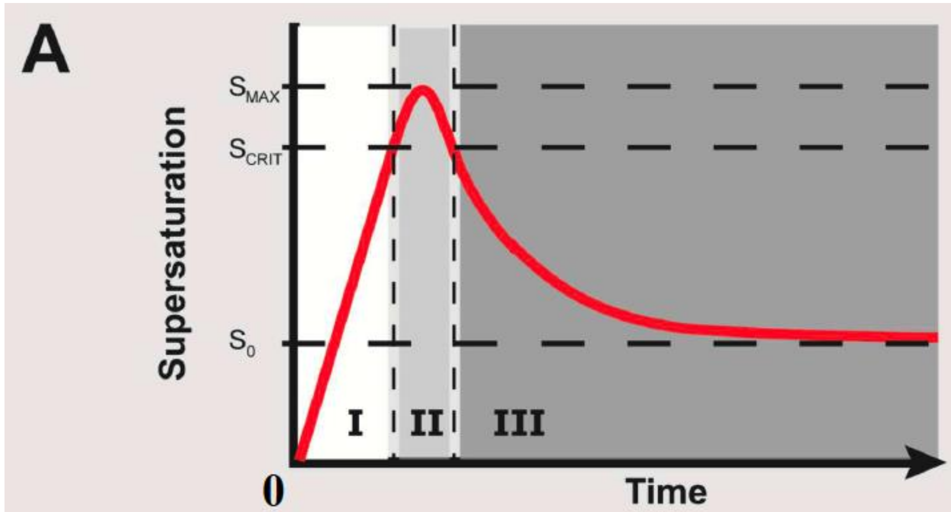
Synthesis in solution

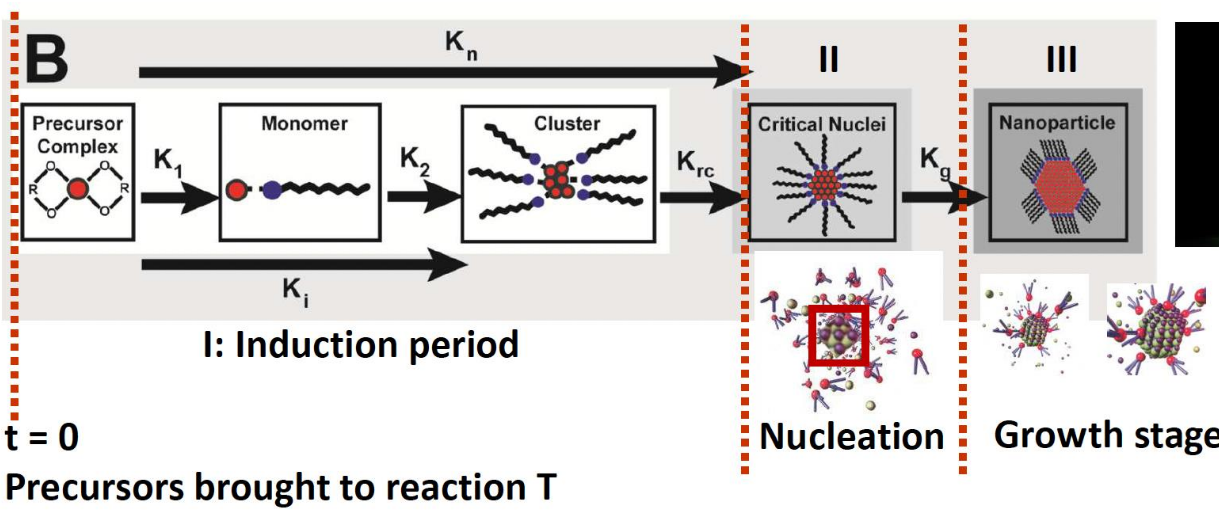
Hot-injection Synthesis of CdSe QDs

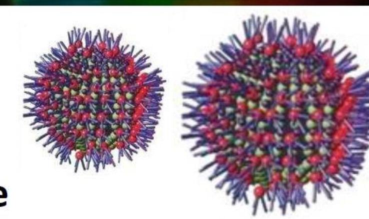


Courtesy of Celso de Mello Donega

Synthesis in solution



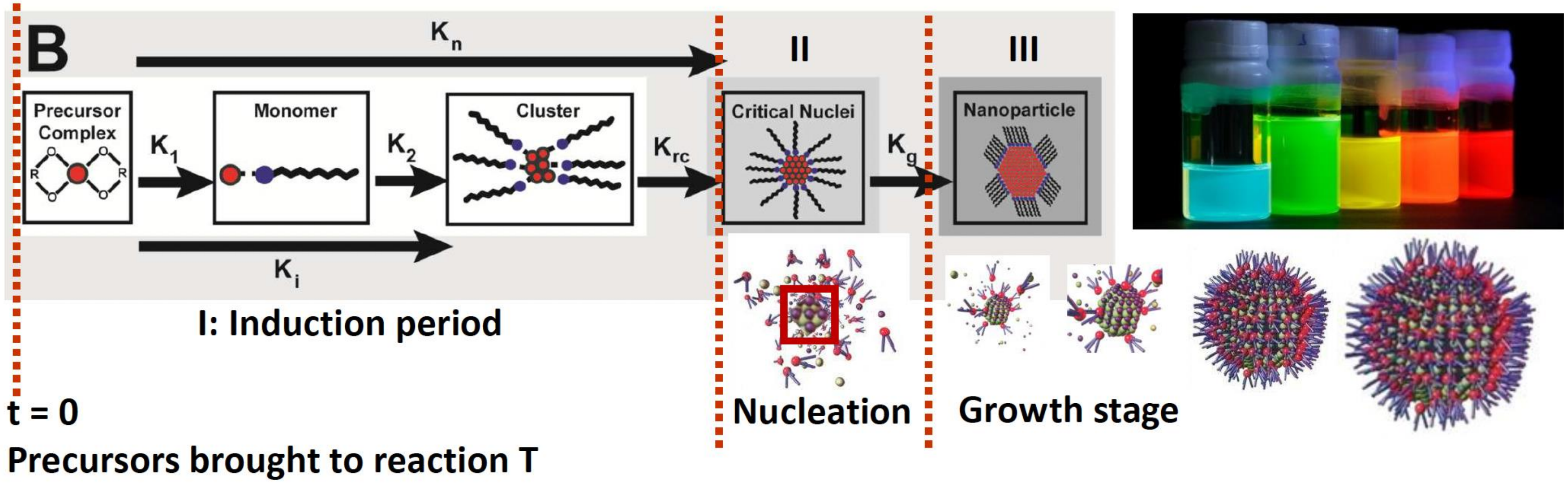


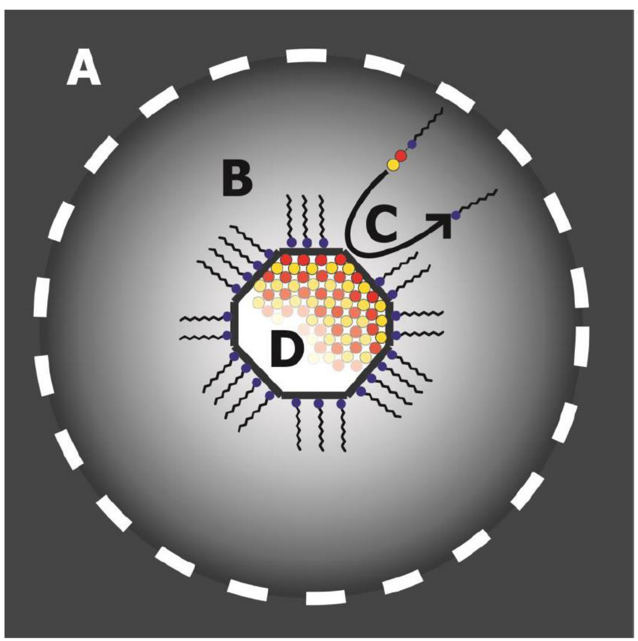


R. Viswanatha and D.D. Sarma in "Nanomaterials Chemistry: Recent Developments and New Directions" (Wiley-VCH, 2007)

*Donega, Chem. Soc. Rev., **40** (2011) 1512*

Synthesis in solution





Two kinetic growth regimes:

1. Diffusion-controlled growth: rate limiting step is the diffusion towards NC surface

2. Reaction-controlled growth: rate limiting step is the incorporation in the nanocrystal

Donega, Chem. Soc. Rev., ***40*** *(2011) 1512*

Self-assembly of nanodots

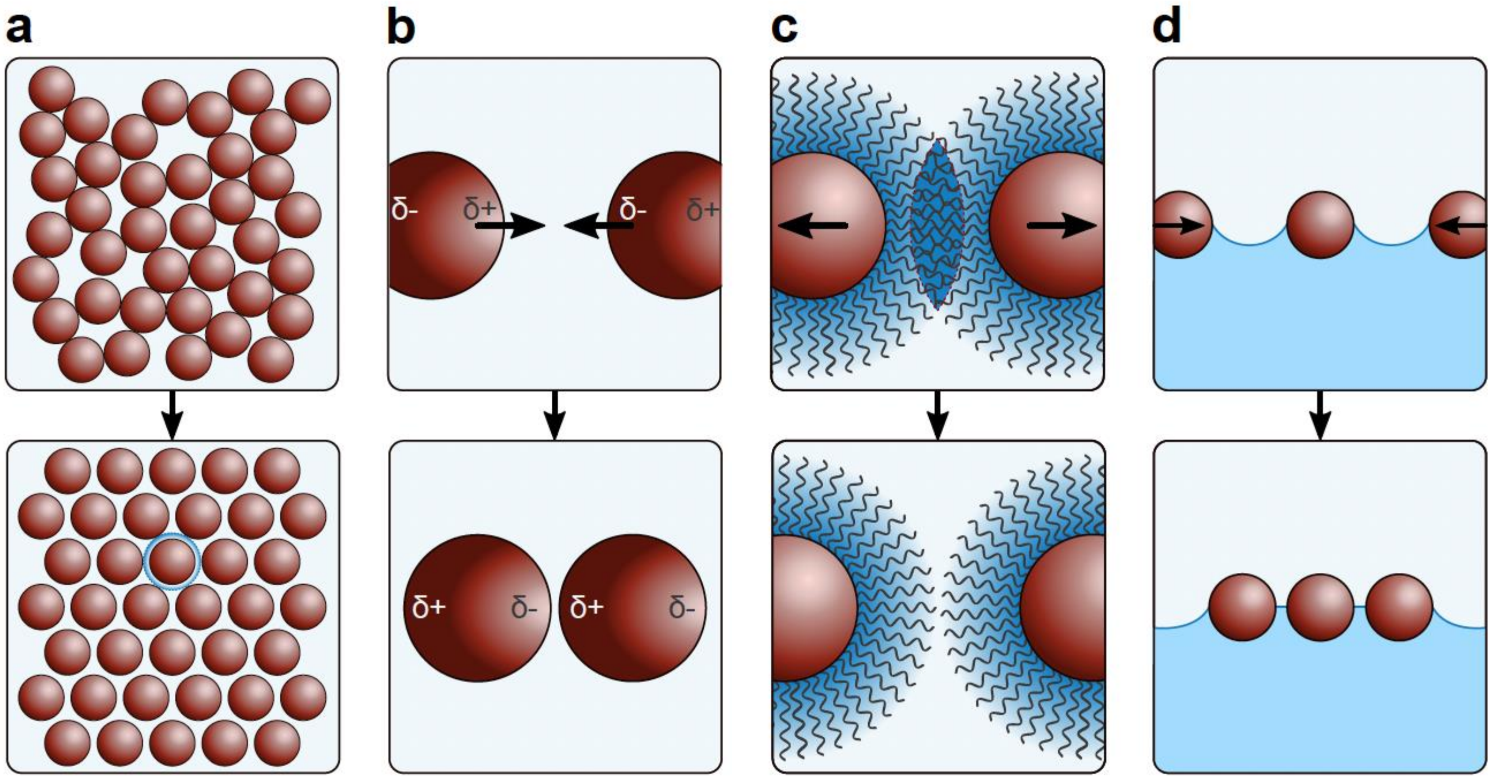


Figure 2.4: Schematic illustration of different interparticle interactions. (**a**) Entropic forces: For hard spheres the entropy is increased ($\Delta S > 0$) by assembling into crystalline state, caused by a gain in accessible free volume, indicated for one sphere in blue. (**b**) Van der Waals attraction: Charge density fluctuations create induced dipoles (δ^+ and δ^-), resulting in an attractive force of NCR cores. (**c**) Steric repulsion: Overlapping ligand shells of adjacent NCRs result in a repulsive force, preventing NCR agglomeration. (**d**) Capillary forces: Adsorption of NCRs at an interface cause distortion, resulting in an induced attractive force.

A. Meier, PhD thesis (2021)

Self-assembly of nanodots

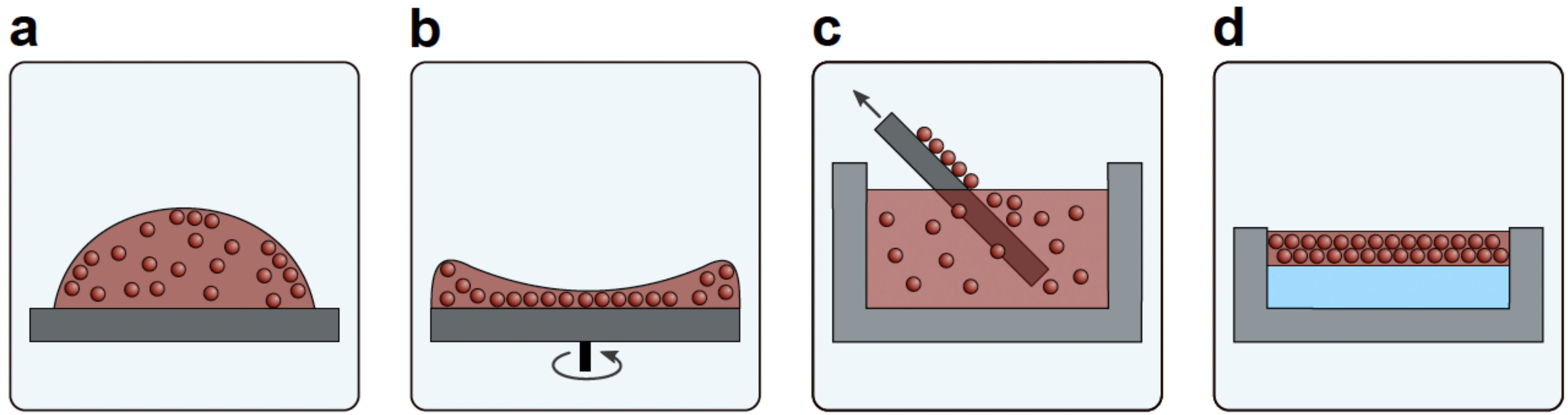
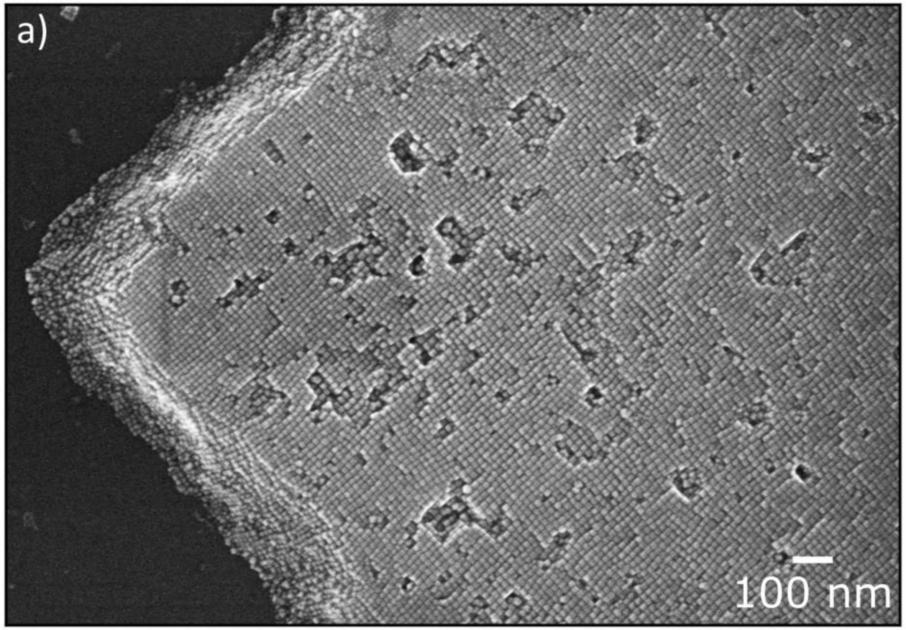
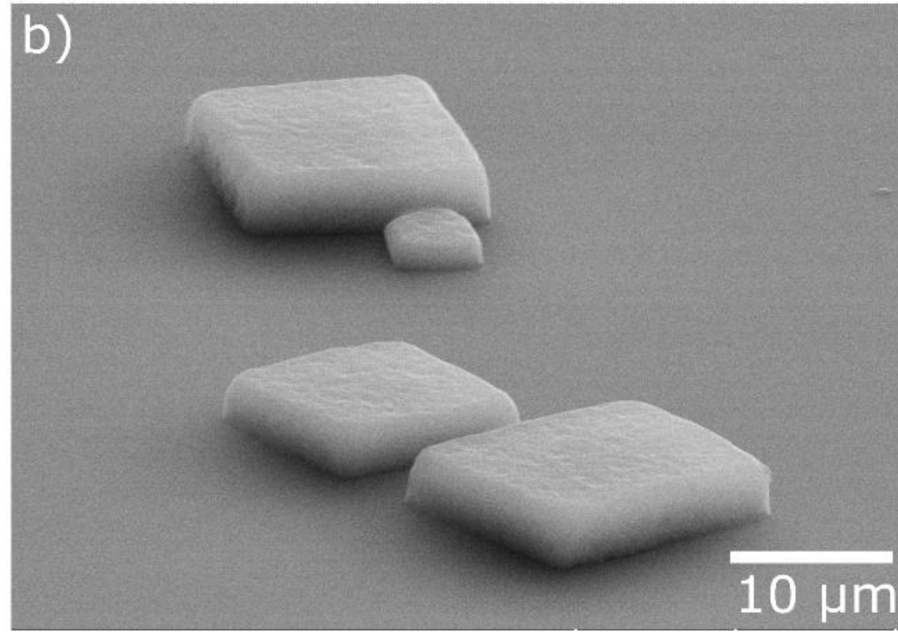


Figure 2.6: Schematic illustration of evaporation-based self-assembly methods: (**a**) drop-casting, (**b**) spin-coating, (**c**) dip-coating, (**d**) self-assembly at the liquid/air interface.

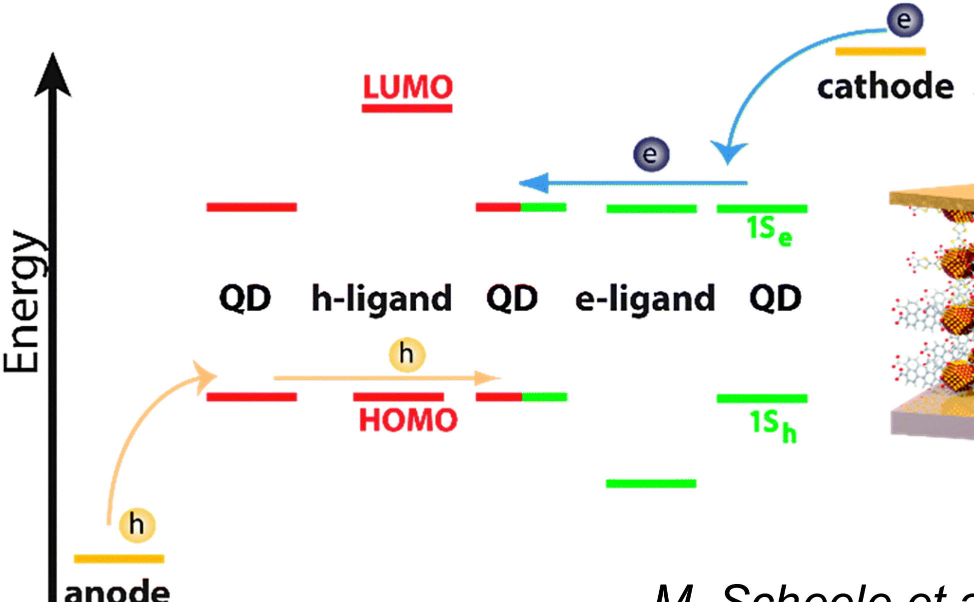
A. Meier, PhD thesis (2021)

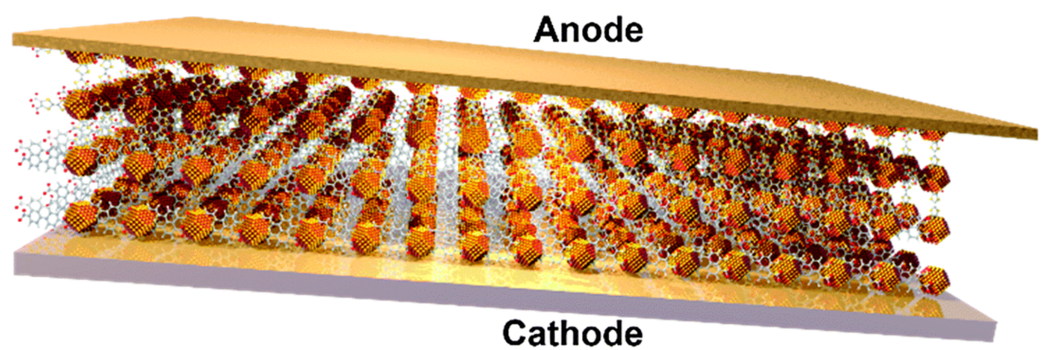
Self-assembly of nanodots





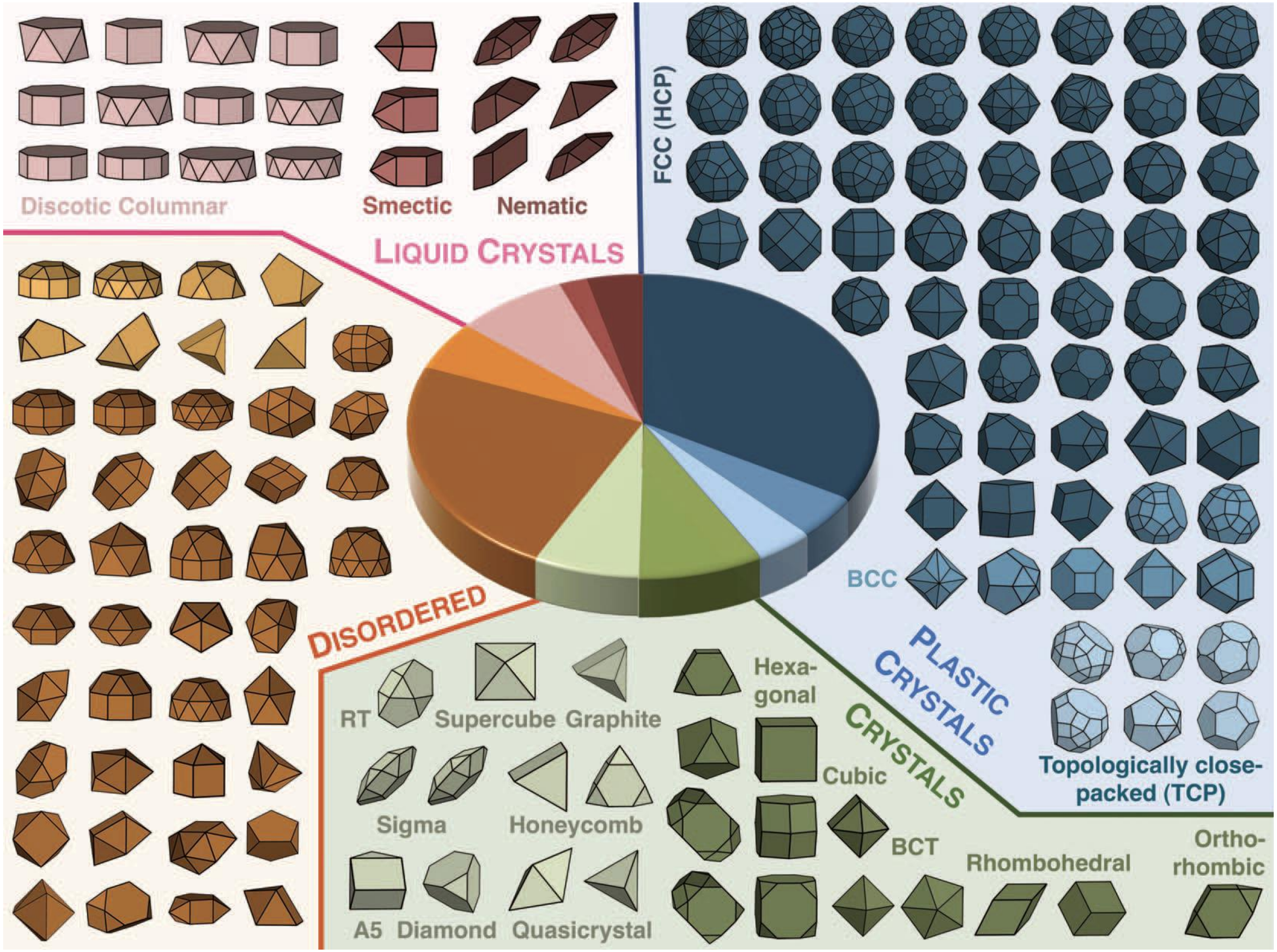
J. Hiller et al., ACS Nano (2025)





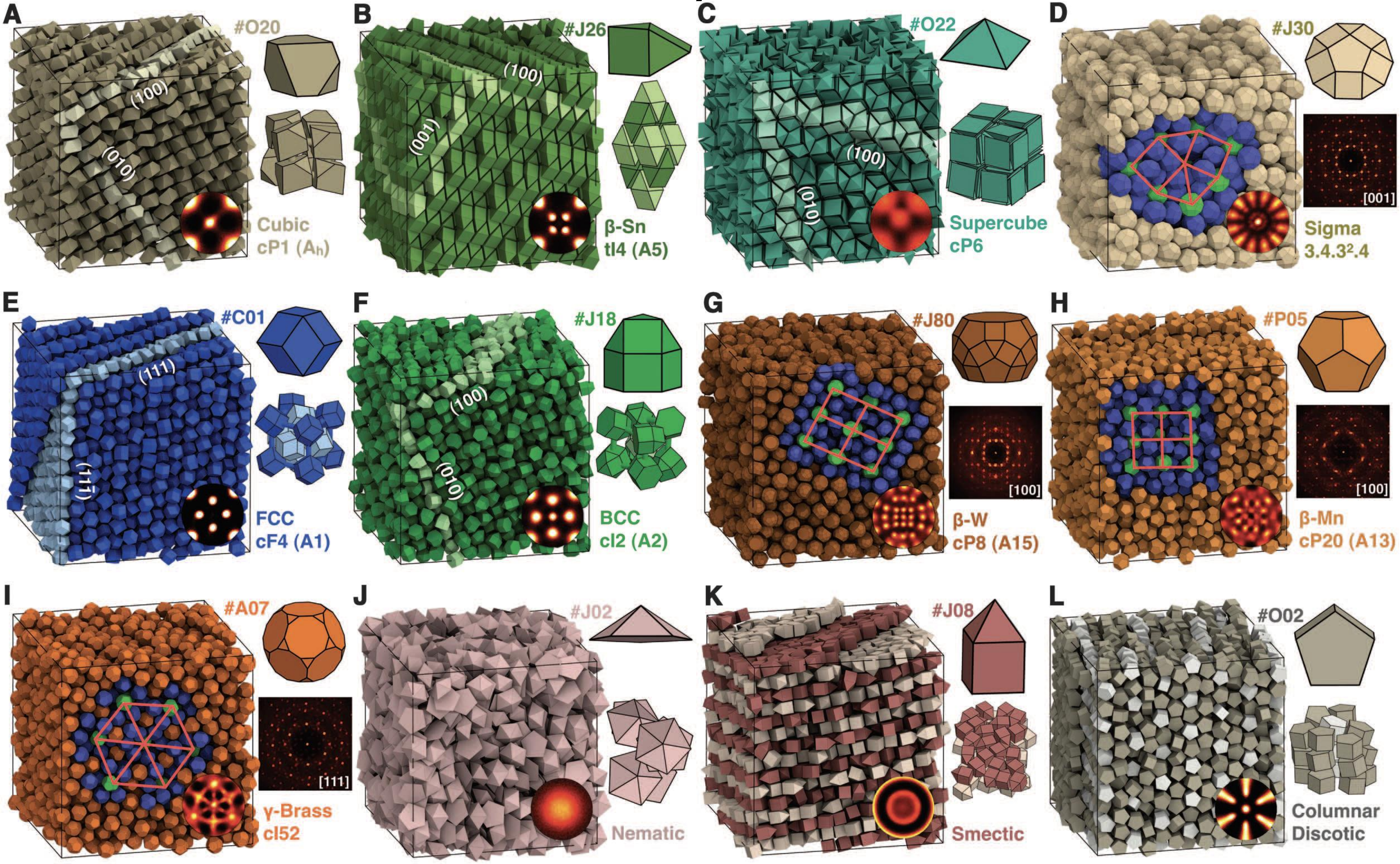
M. Scheele et al., Phys. Chem. Chem. Phys., **17** 97 (2015)

Self-assembly of nanodots



P.F. Damasceno et al., Science ***337****, 453 (2012)*

Self-assembly of nanodots



P.F. Damasceno et al., Science ***337****, 453 (2012)*

Liquid phase epitaxy

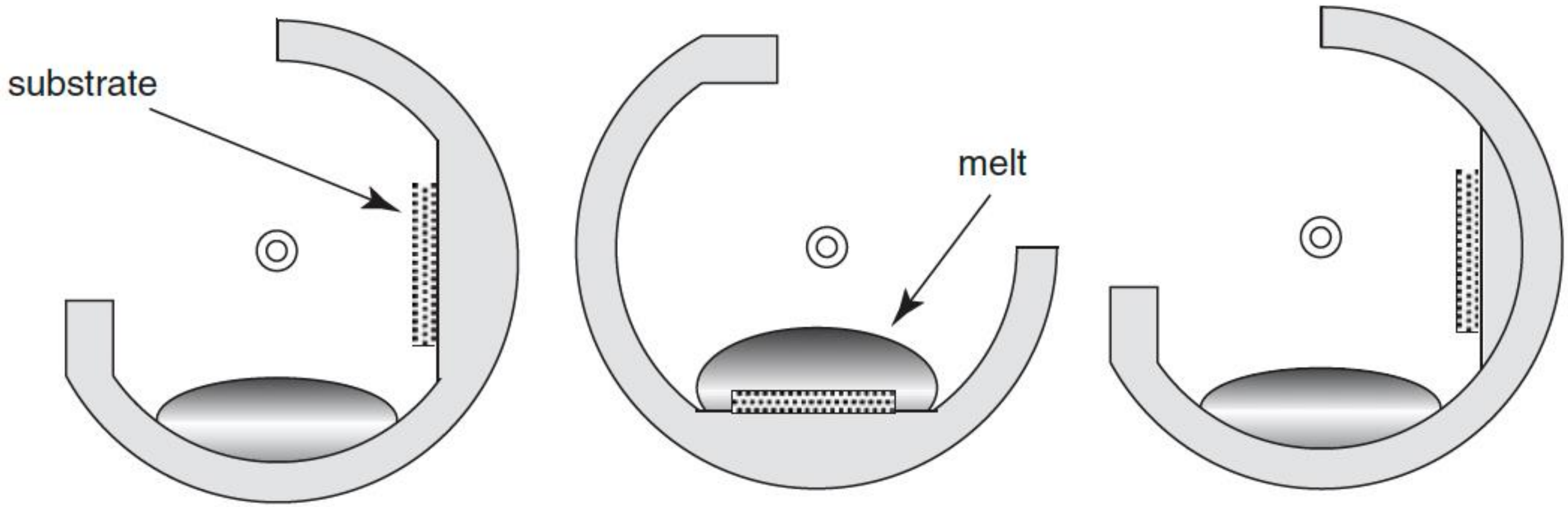
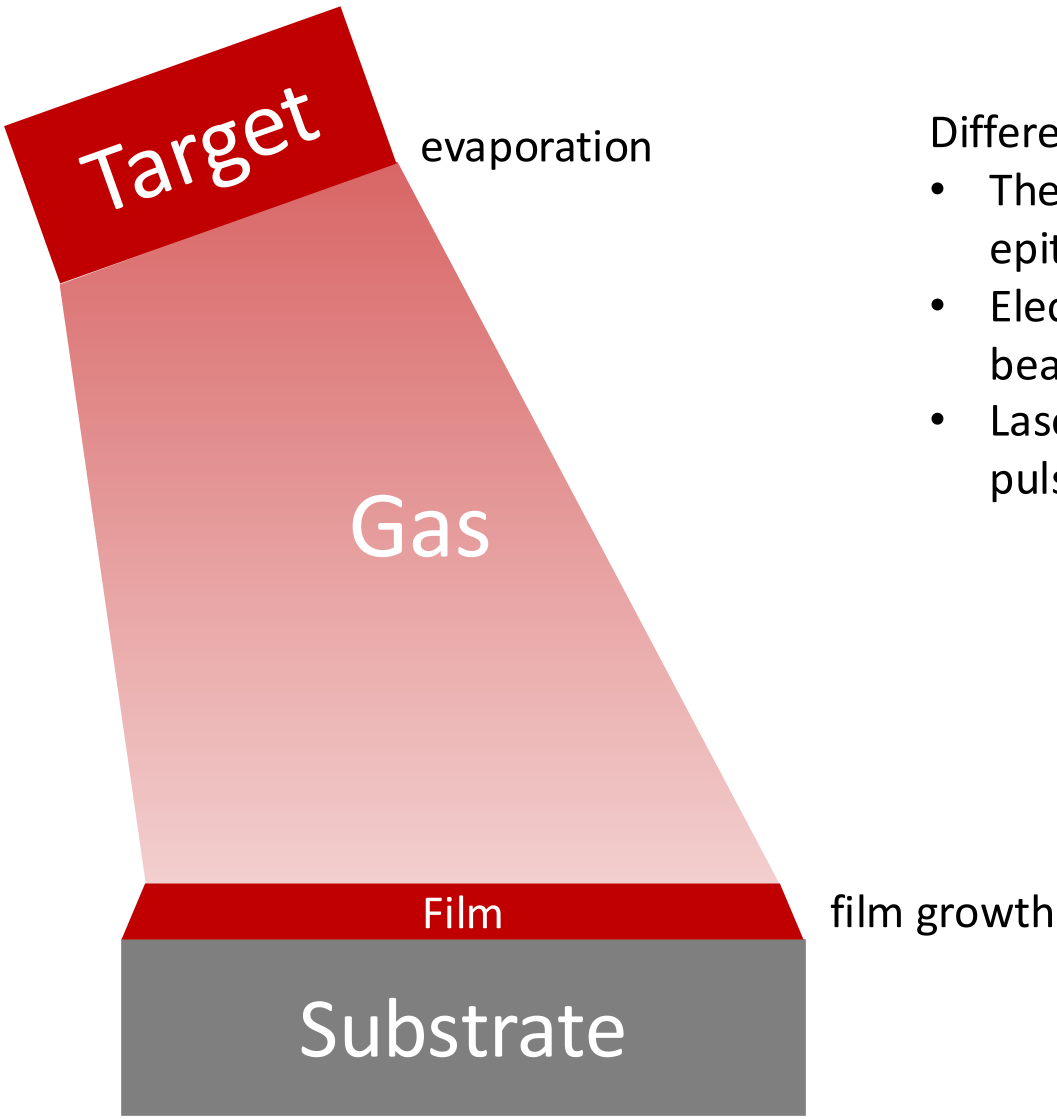


Figure 4.6 Rotating/tipping LPE apparatus. (After Arch *et al.*, 1992)

One of the schemes for liquid phase epitaxy (many other are possible)

Liquid phase epitaxy of electronic, optical and optoelectronic materials (ed. P. Capper, M. Mauk) (2007).

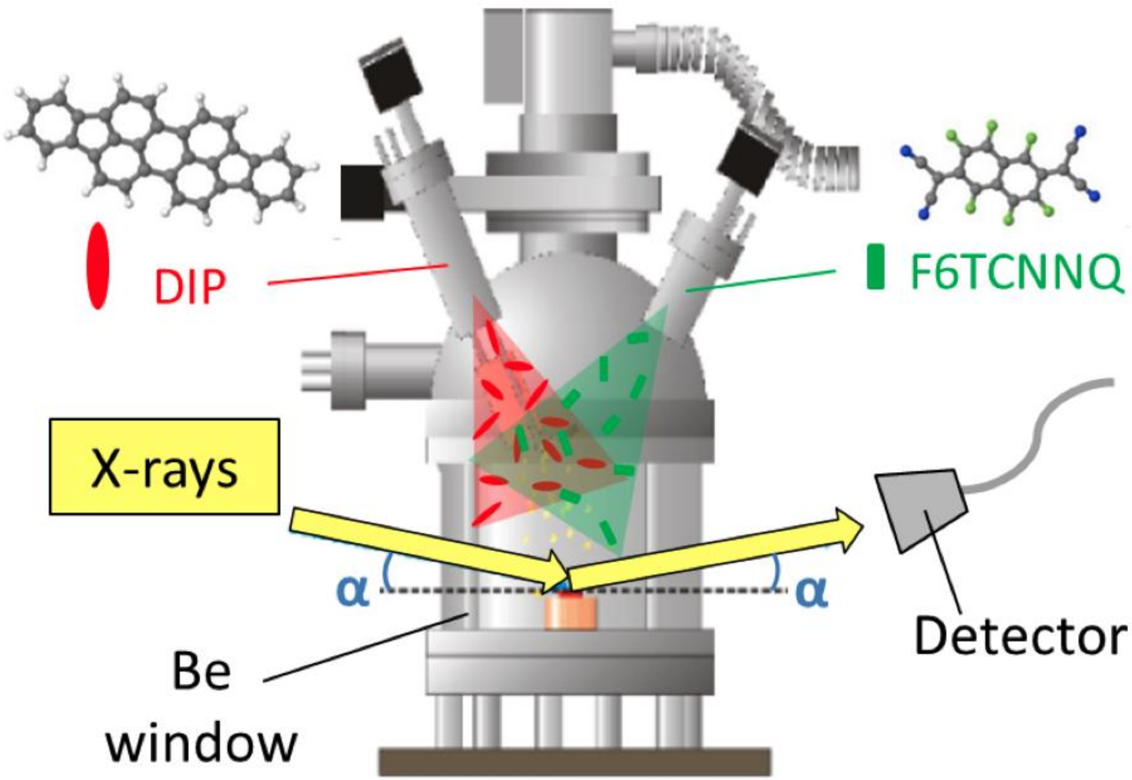
Physical vapor deposition (PVD)

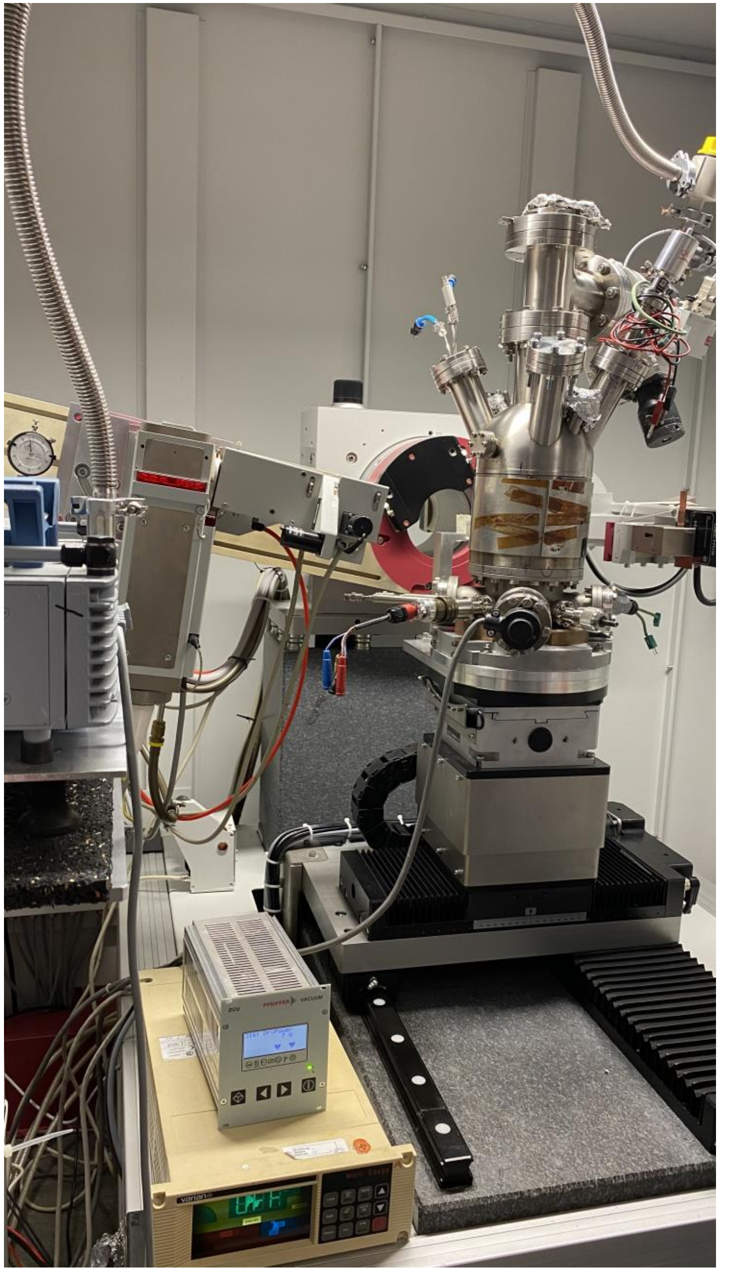


Different methods to create gas phase:

- Thermal evaporation (molecular beam epitaxy)
- Electron beam evaporation (electron beam epitaxy)
- Laser evaporation (thermal laser epitaxy, pulsed laser deposition)

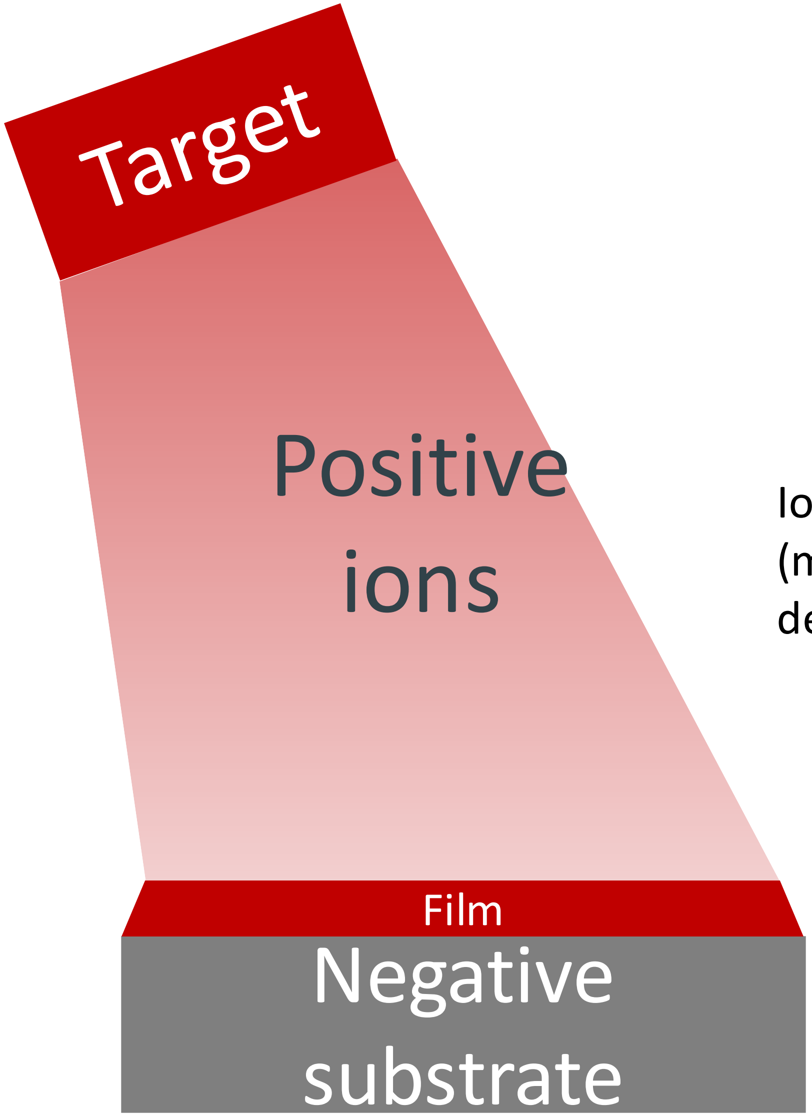
Organic molecular beam deposition





G. Duva, PhD thesis (2019)

Deposition from plasma

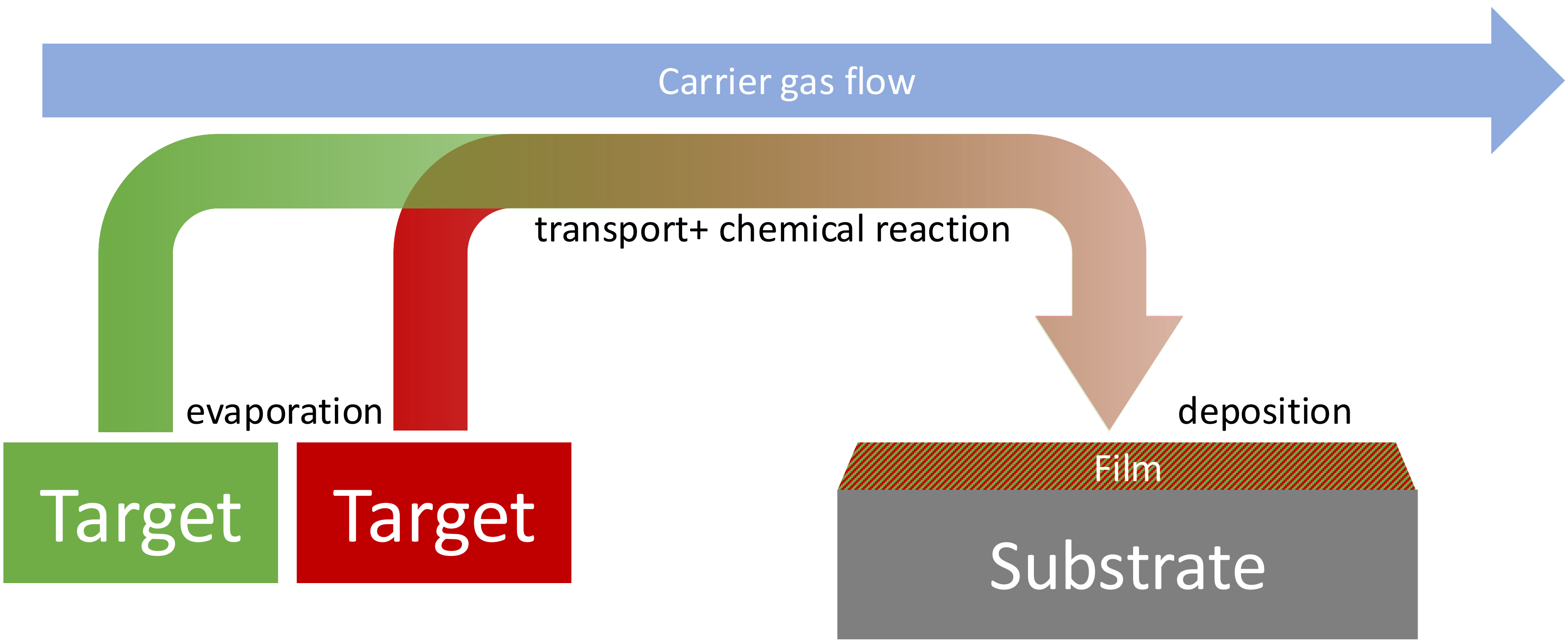


Different methods to create plasma

- Sputtering
- Cathode arc
- Laser pulses

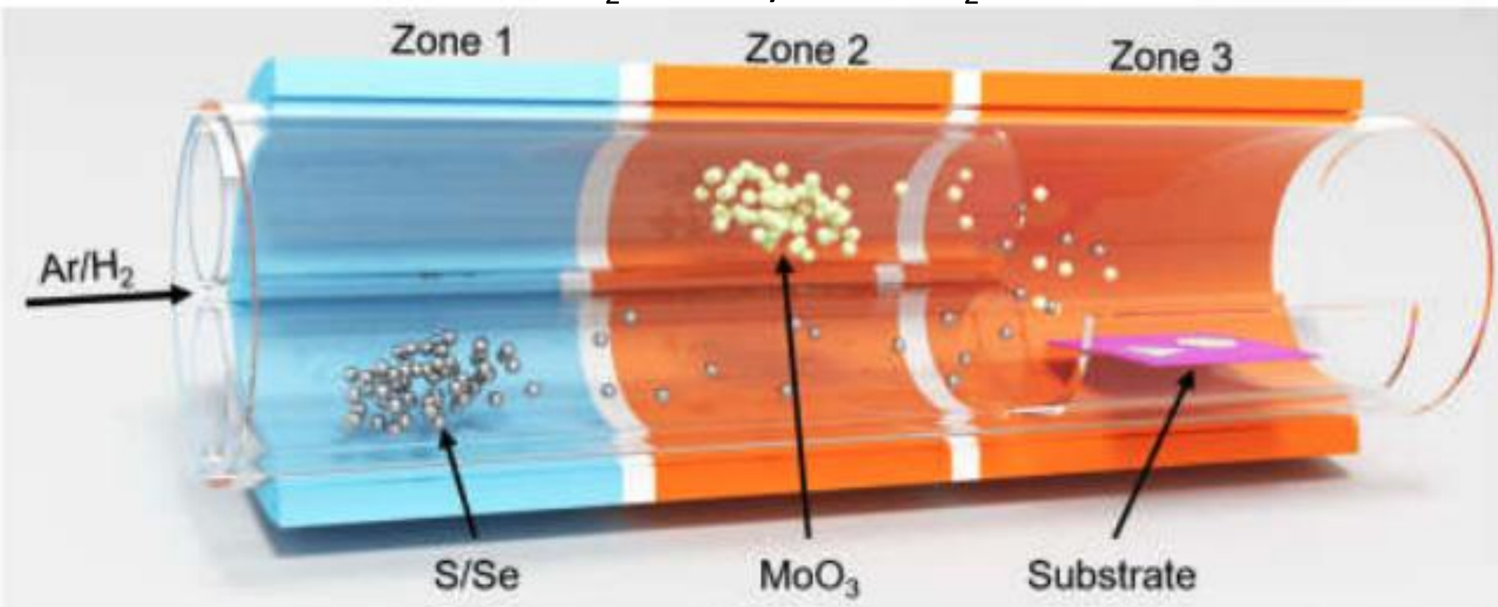
Ions can be guided by magnetic field (magnetron sputtering) or by gas flow (vapor deposition)

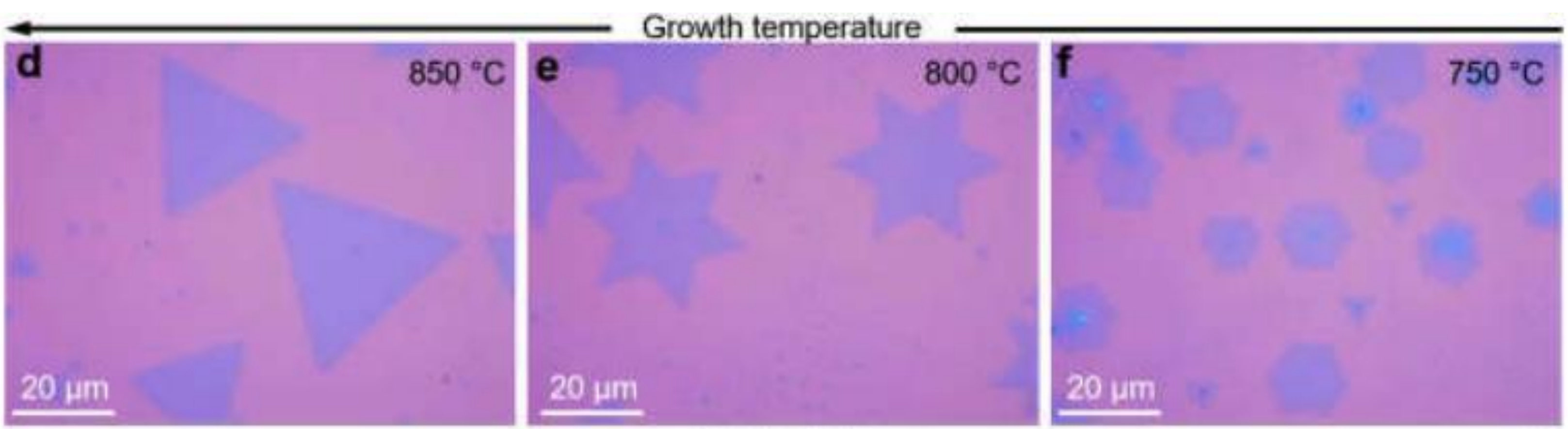
Chemical vapor deposition (CVD)



Chemical vapor deposition (CVD)

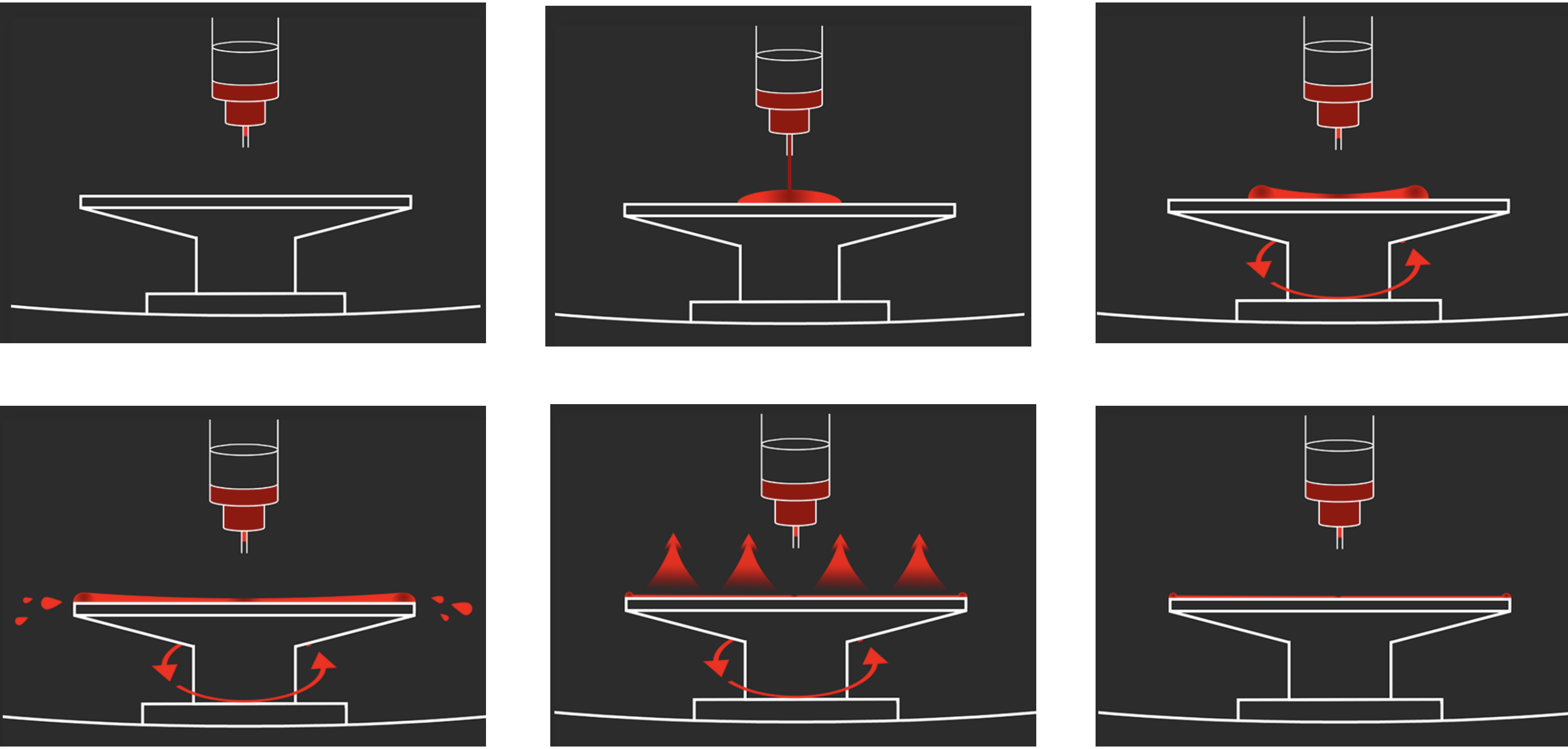
Growth of MoS_2 nanolayer on SiO_2 substrate





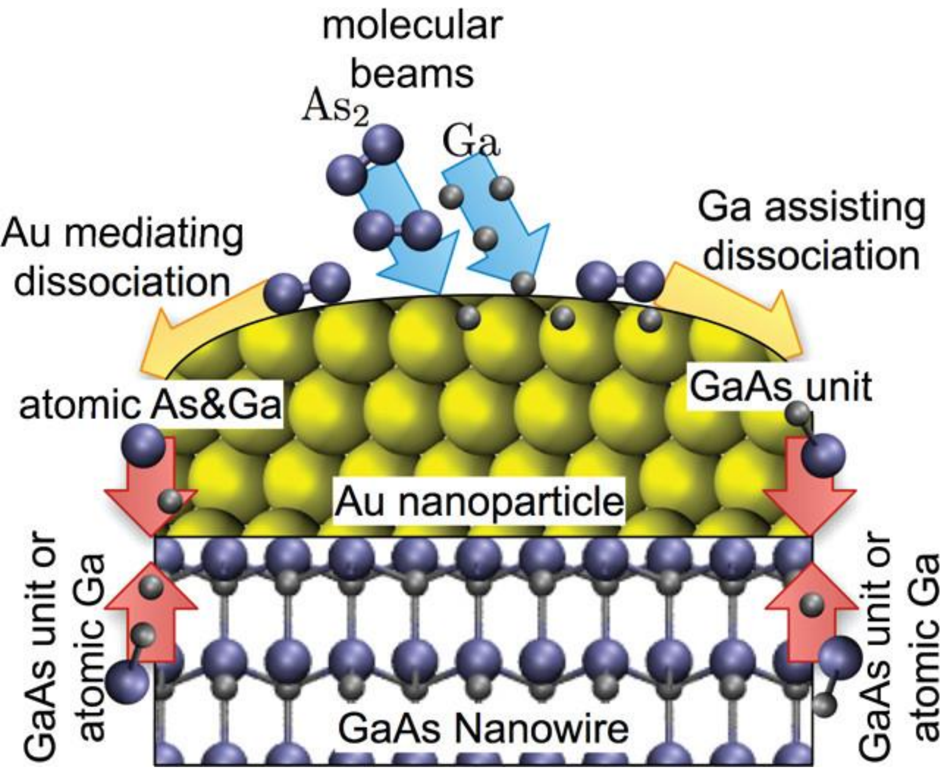
B. Zheng and Y. Chen, IOP Conf. Ser.: Mater. Sci. Eng. ***274*** *012085 (2017)*

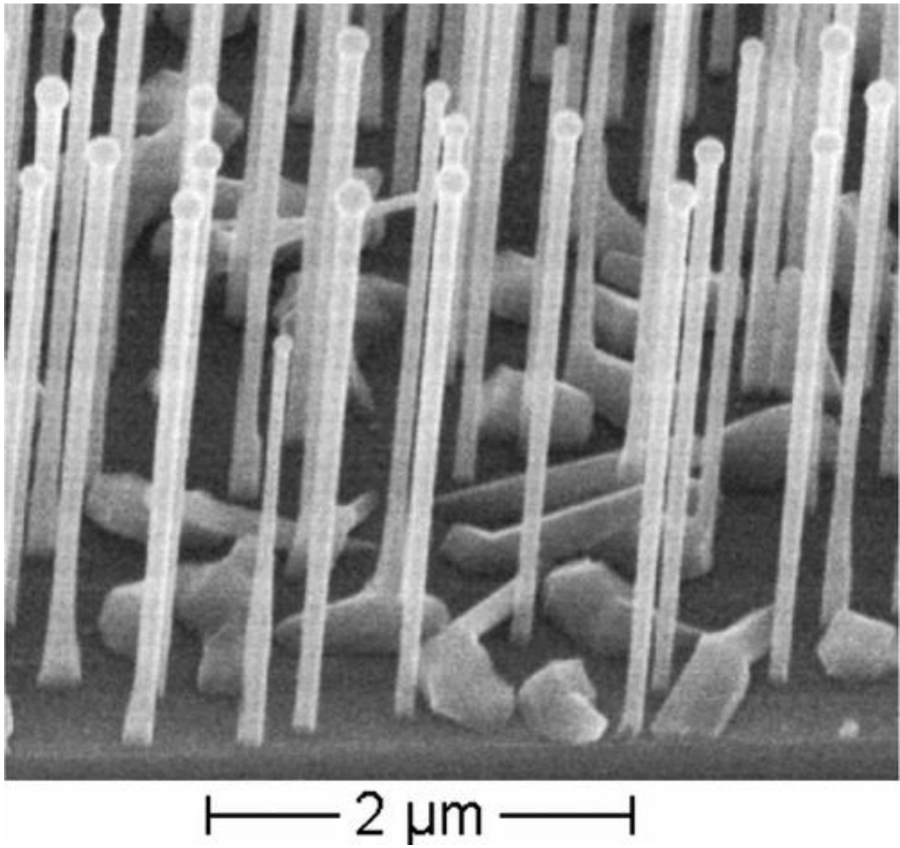
Spin coating



https://www.spincoater.com/what-is-spin-coating.php

GaAs Nanowires

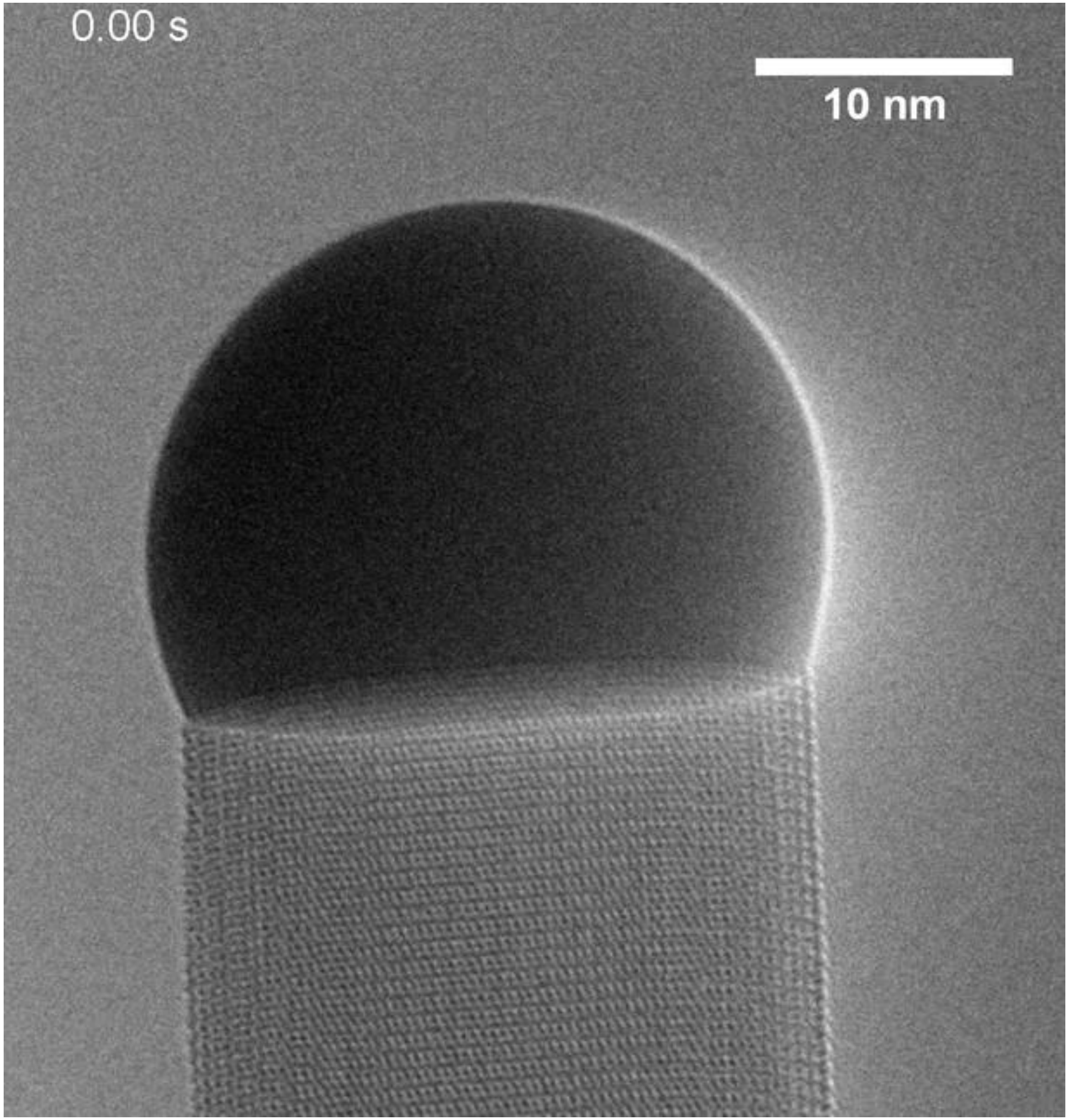




P. Kratzer et al., Nano Lett. ***12*** *943–948 (2012)*

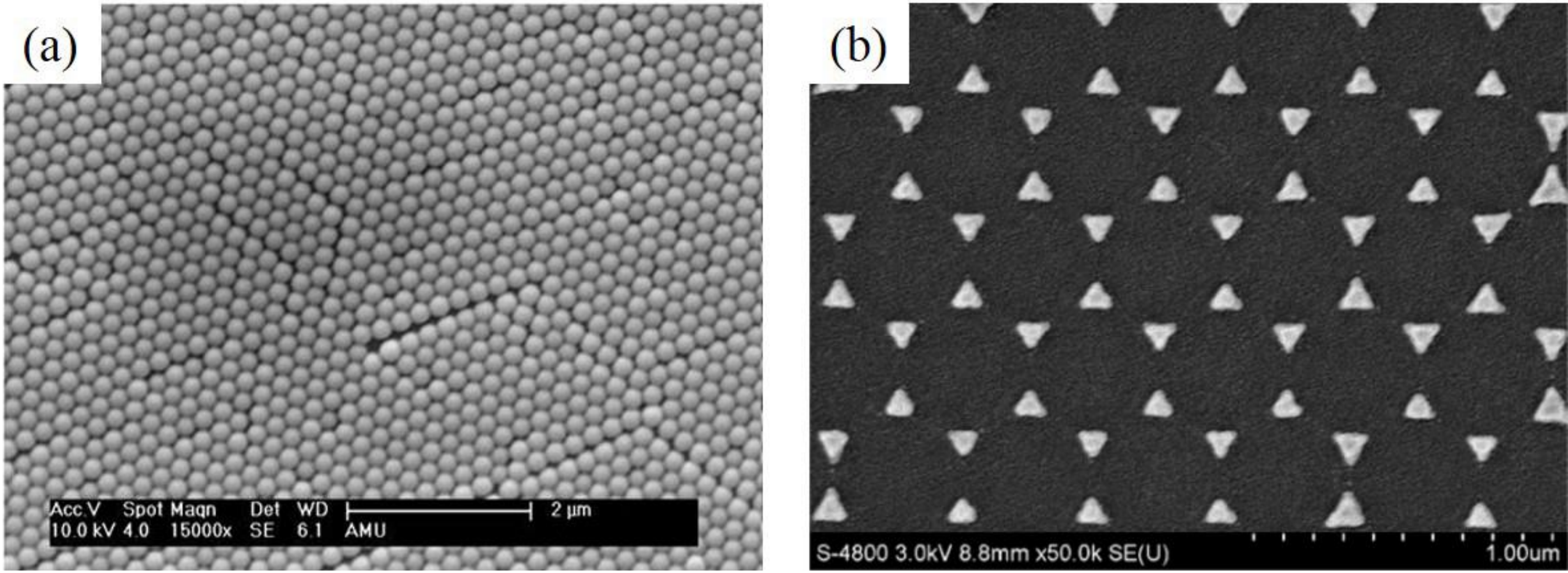
C. Colombo et al., Phys. Rev. B ***77*** *155326 (2008)*

GaAs Nanowires



J.-C. Harmand et al., Phys. Rev. Lett. ***121*** *166101 (2018)*

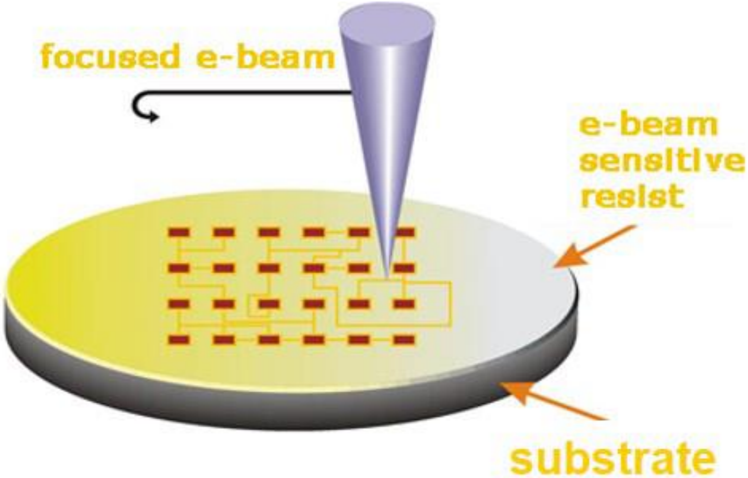
Nanosphere lithography



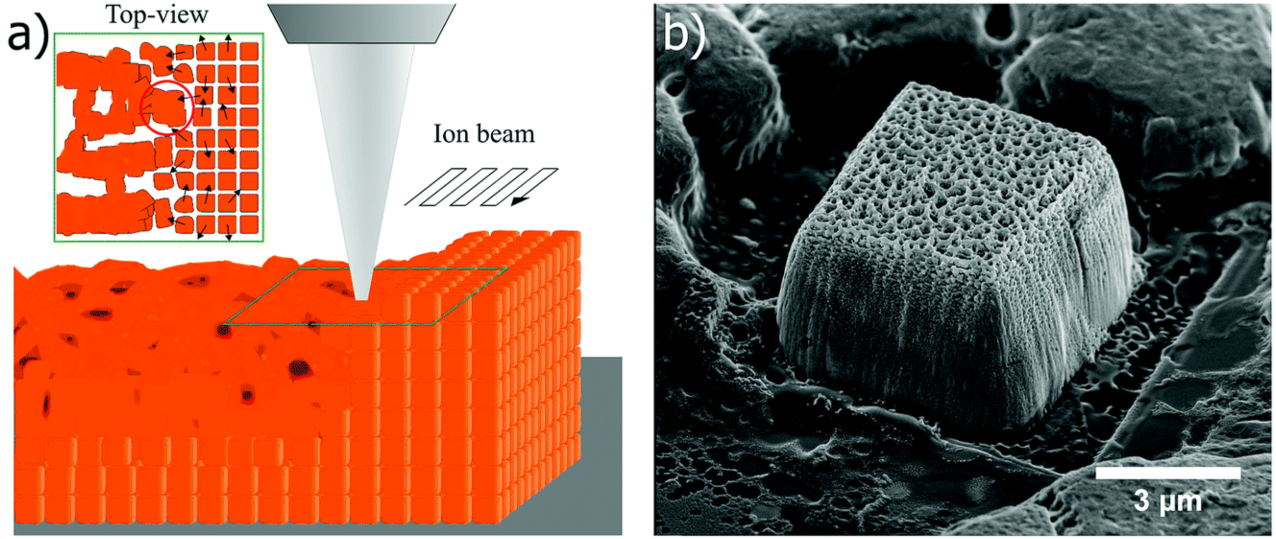
Courtesy of M. Fleischer

Nanopatterning

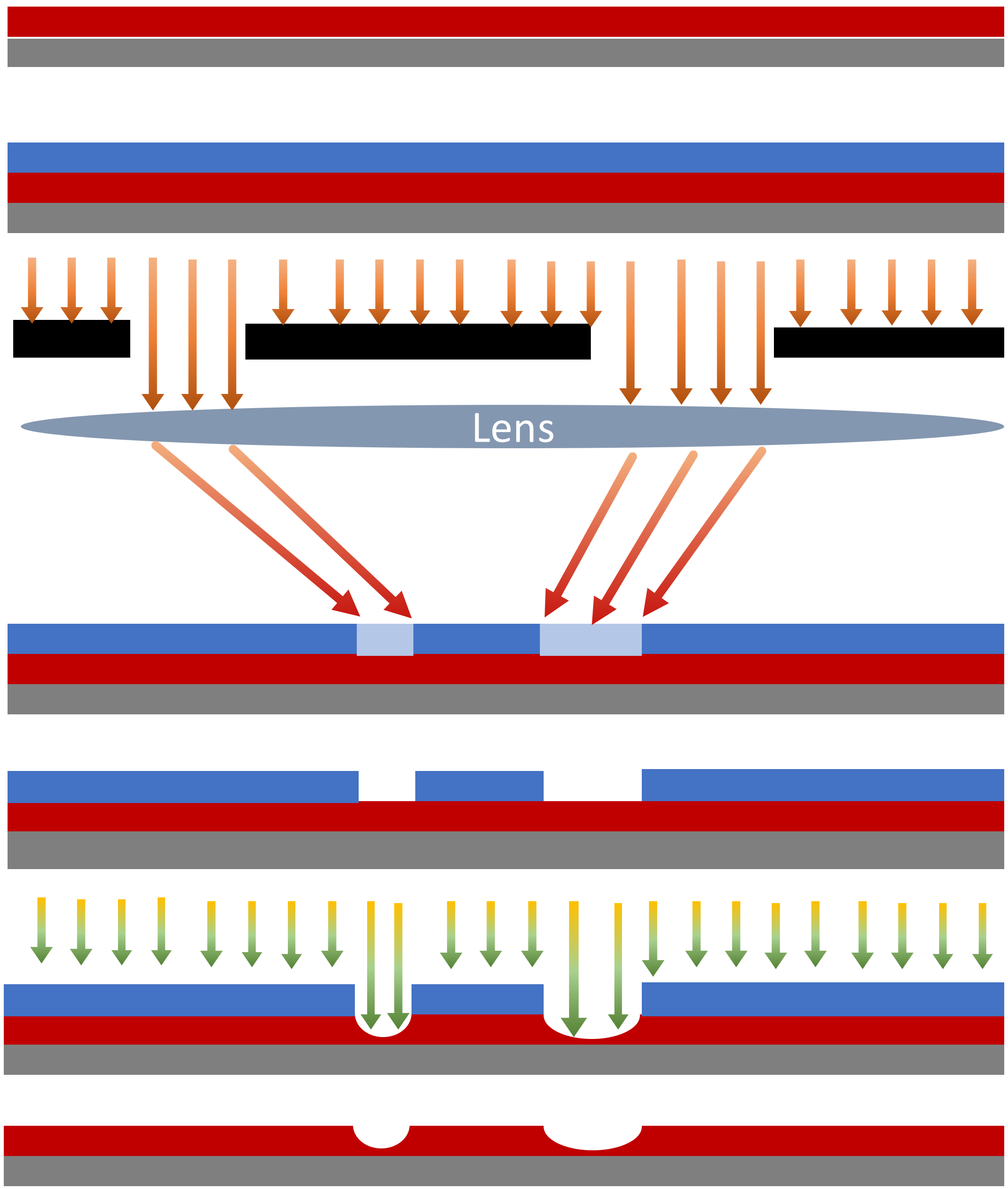
electron beam lithography



Focused Ion Beam (FIB) milling



Lithography



Substrate with a thin film

Coating with a (positive) resist via spin coating, dip coating, spray coating, etc.

Creating modified resist structure by

- Exposing resist **through mask** to light, electrons, ions, etc.
- Using focused ion / electron beam
- Pressing resist with a stamp

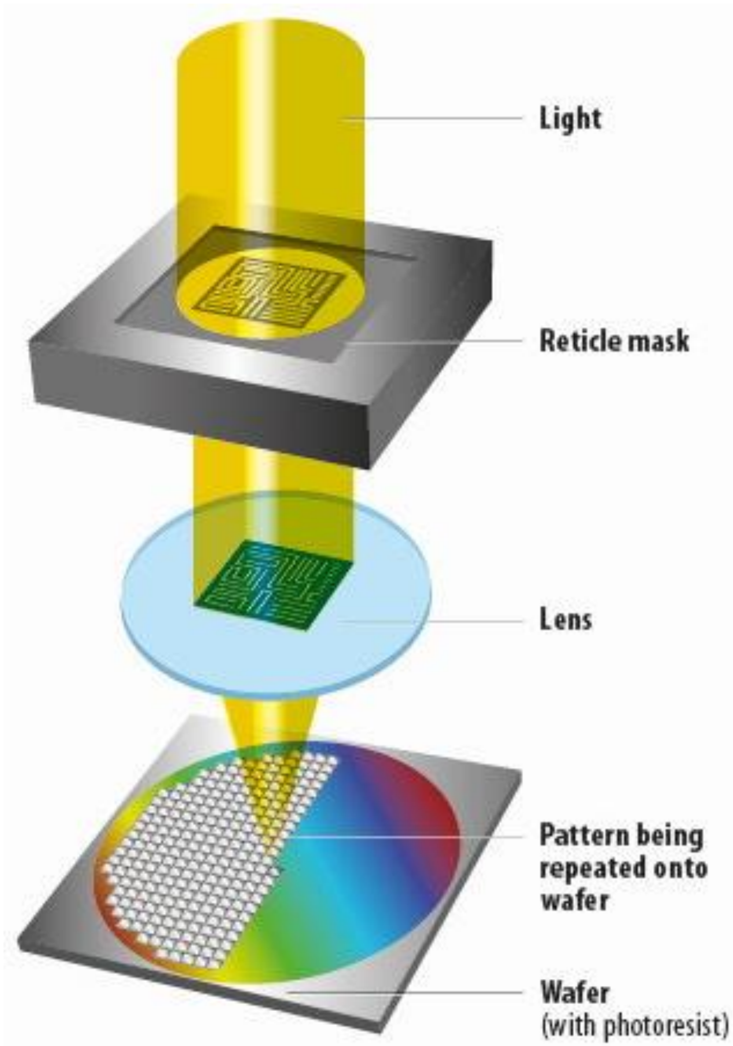
Removal of the modified resist structure (developing)

Etching or doping of the film not protected by the resist (chemical etching, dry etching, etc.)

Removal of remaining unmodified resist

Extreme Ultra Violet Photolithography

Rayleigh criterion equation (resolution): $\Delta = k_1 \cdot \frac{\lambda}{NA}$



k_1-factor, depends on the imaging and resist system (physical limit 0.25)

$NA = n \cdot \sin\theta$ - numerical aperture of the lens (by using ~1m large optical systems, NA=1.35)

λ - wavelength of light (currently $\lambda = 13.5$ nm)

https://bits-chips.nl/artikel/euv-for-dummies/

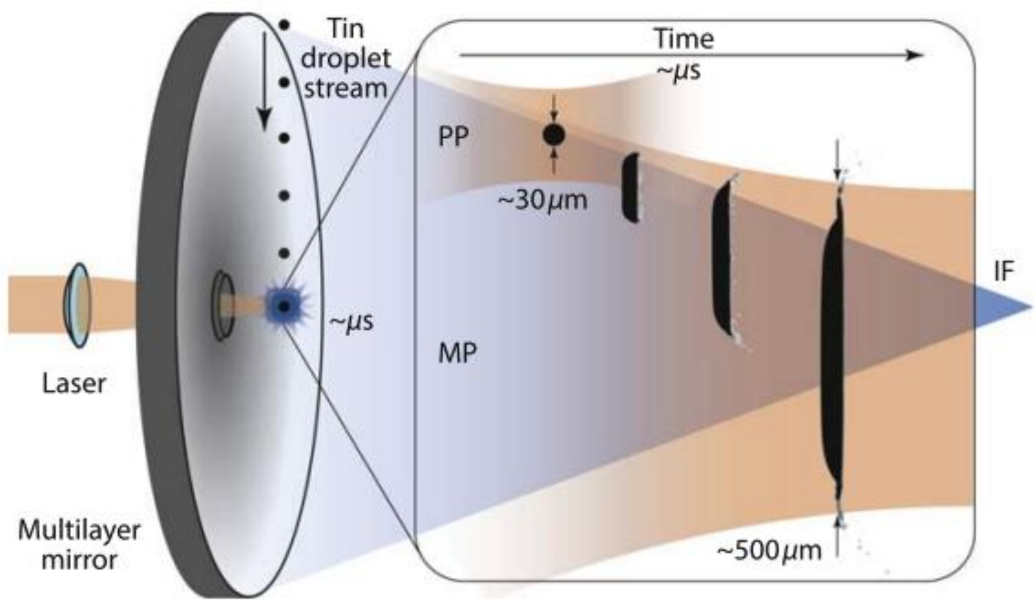
Generating EUV

Source of EUV light :

$4p^6\, 4d^m - 4p5\, 4d^{m+1} + 4d^{m-1}\, 4f$ in electron transitions in Sn^{8+}–Sn^{14+}

Prepulse forms flat disk of tin

Main pulse creates tin plasma



O. Versolato, Plasma Sources Sci. Technol. ***28*** *083001 (2019)*

Generating EUV

Source of EUV light :

$4p^6\,4d^m - 4p5\,4d^{m+1} + 4d^{m-1}\,4f$ in electron transitions in Sn^{8+}–Sn^{14+}

Prepulse forms flat disk of tin

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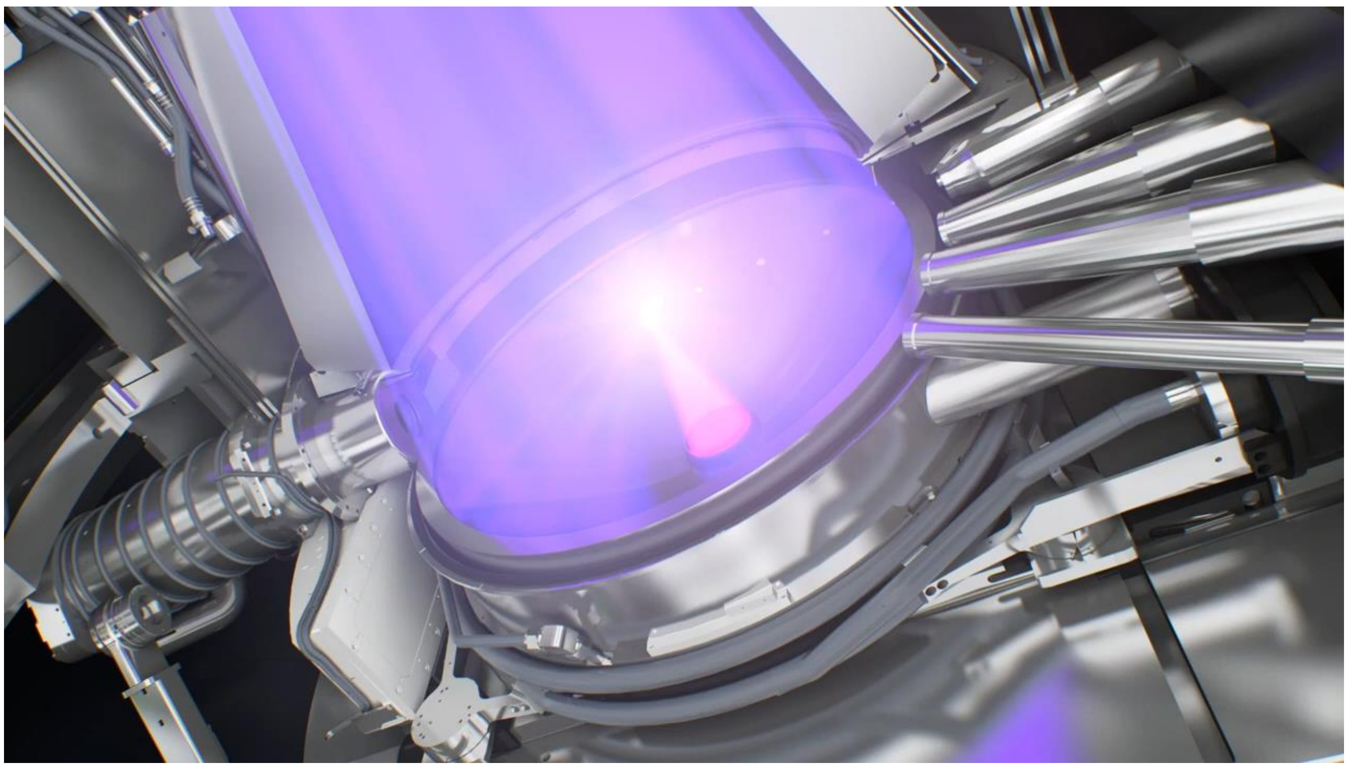
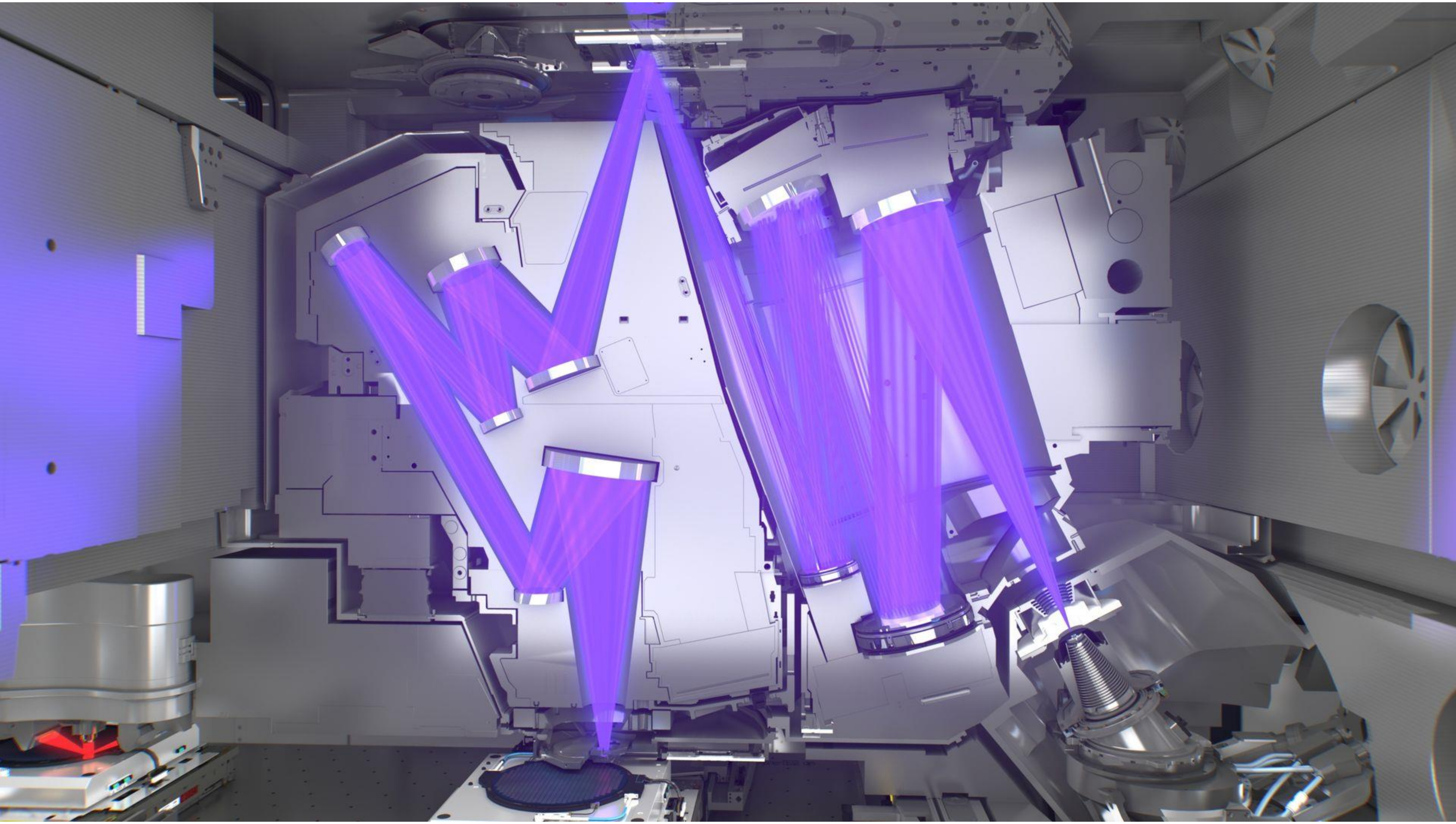


Source: ASML

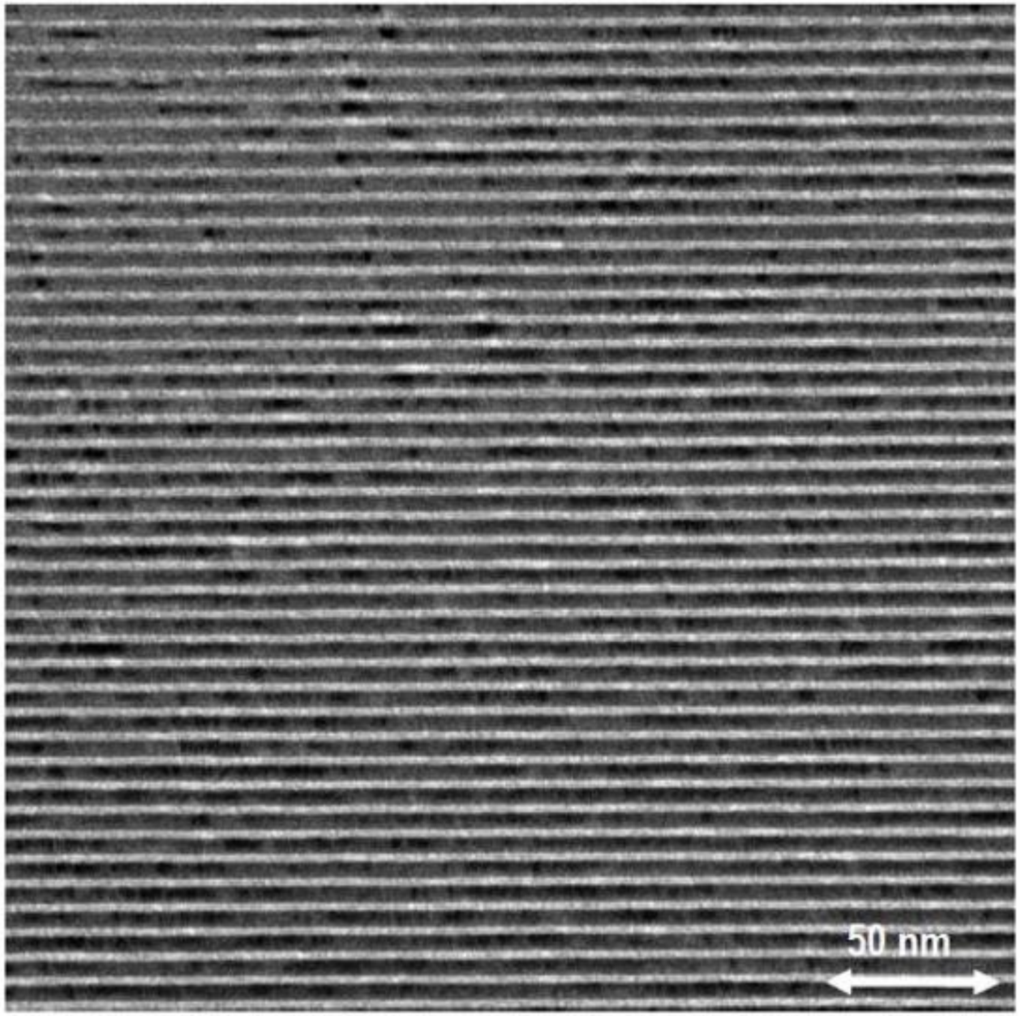
Handling EUV



Source: Zeiss & ASML

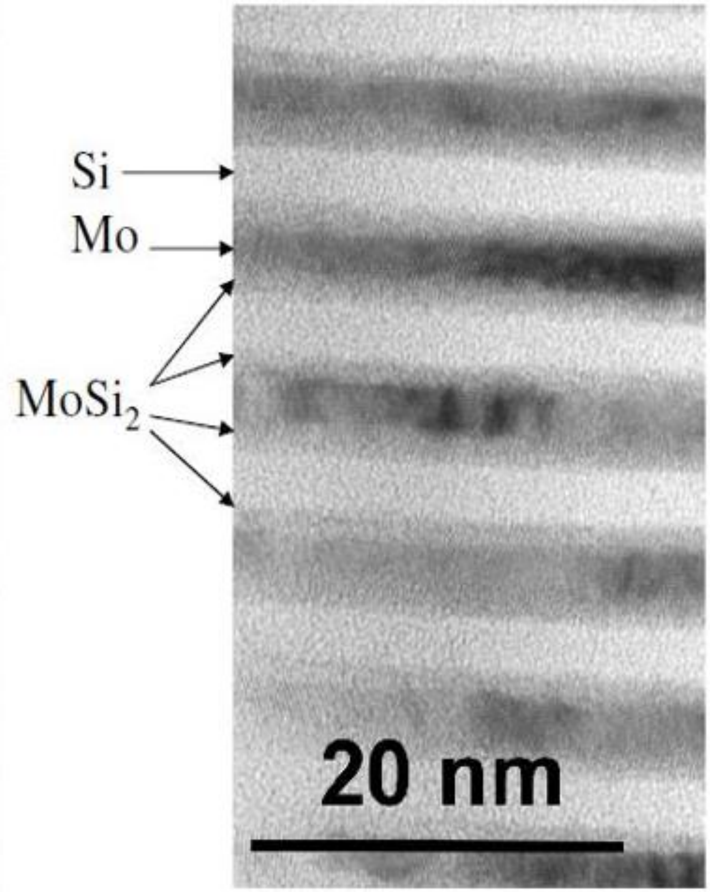
Multilayer mirrors for EUV

TEM of a Mo/Si EUV mirror, N=50, Λ=6.8 nm



Deposited by magnetron sputtering

HR TEM reveals interfacial $MoSi_2$



Source: Zeiss & ASML