Scanning probe microscopy of epitaxy of metal complex oxides

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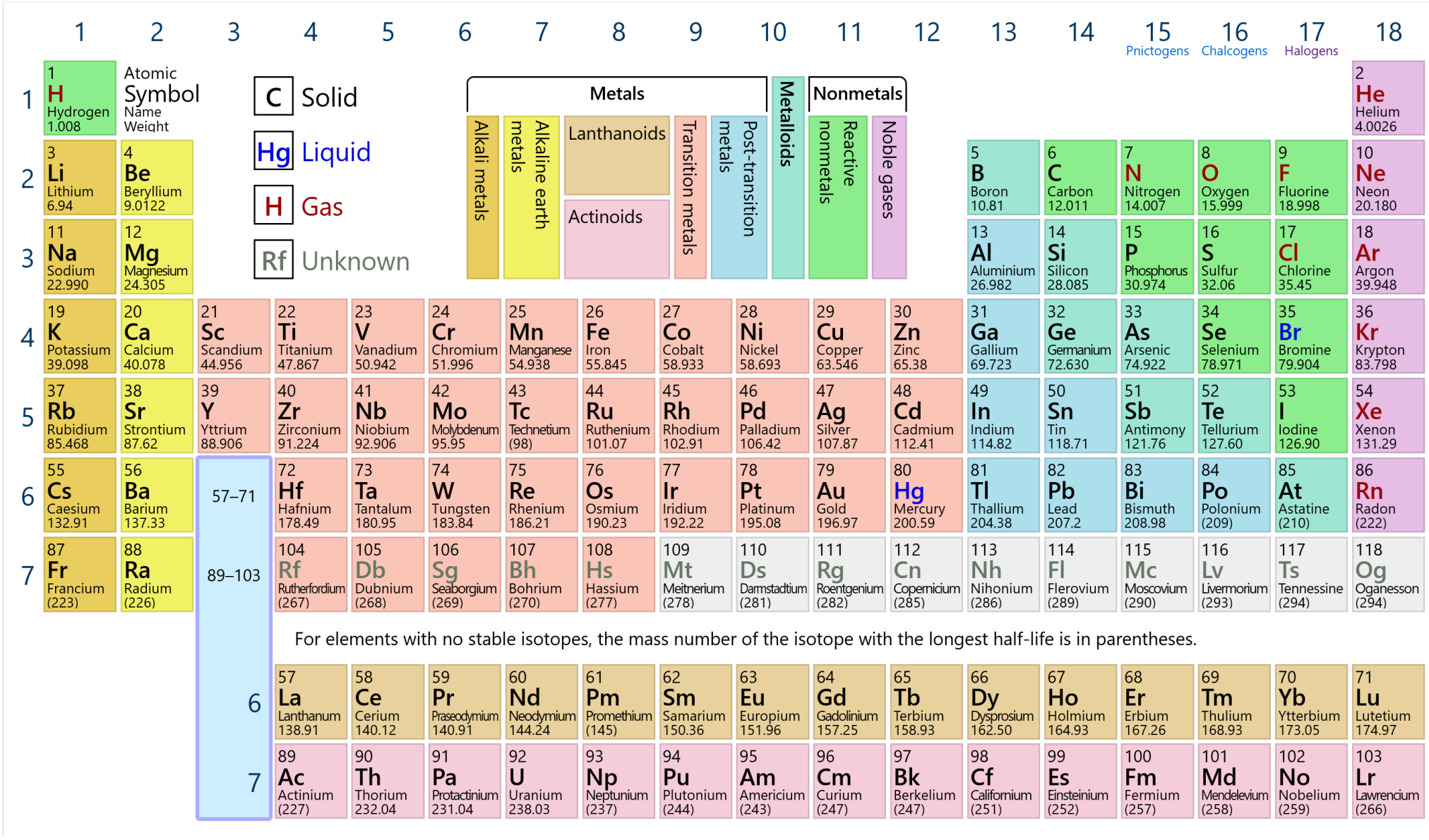
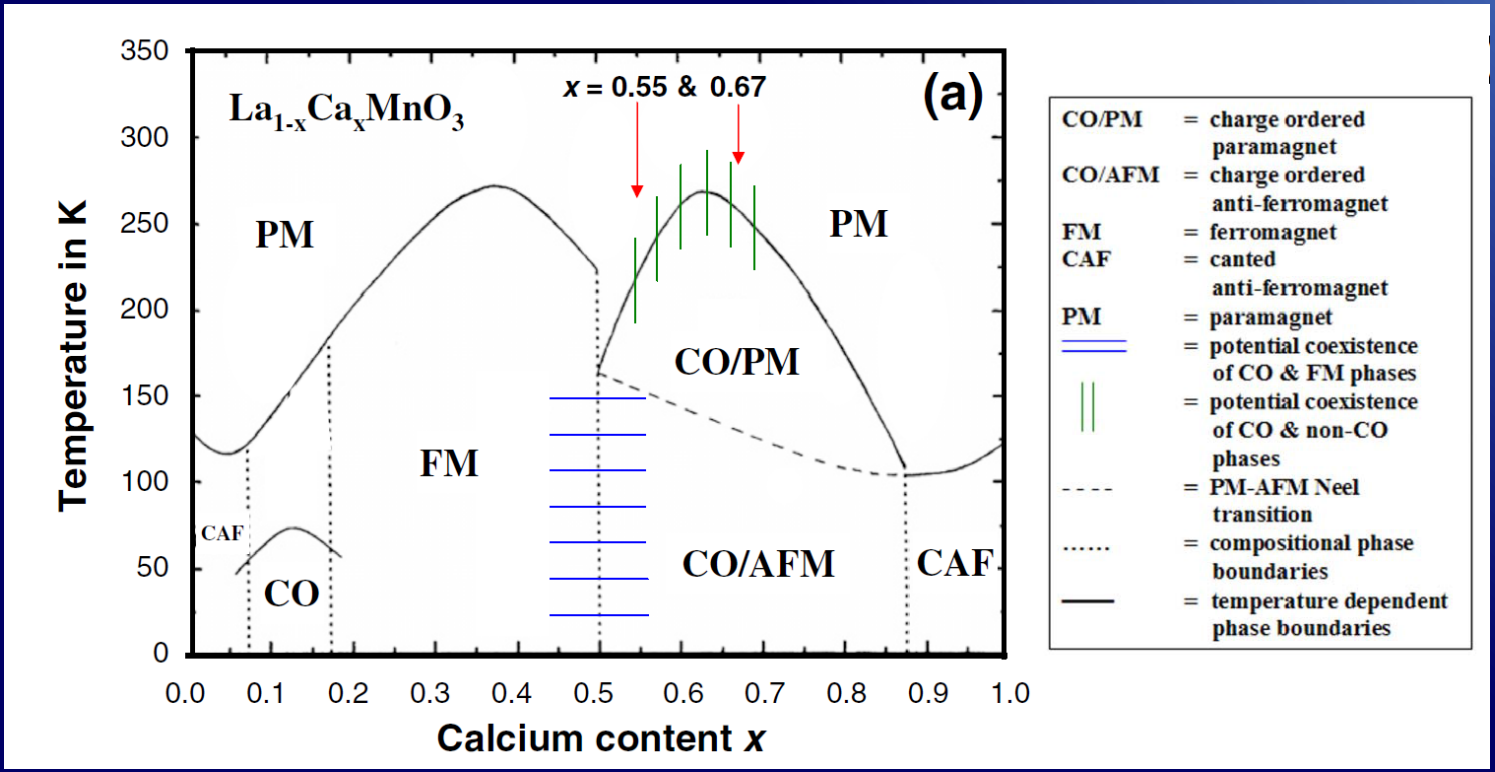
COMPLEX OXIDES



Phase diagram with phase coexistence



R. Schmidt, Phys. Rev. B **77**, 205101 (2008)

What complex oxides offer

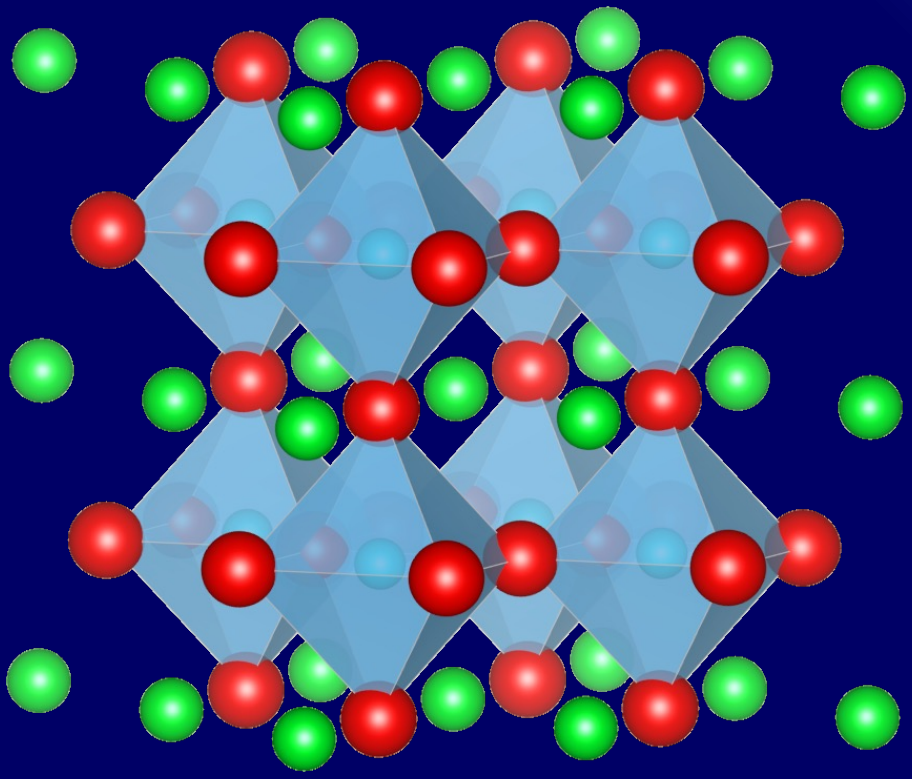
- Superconductivity
- Colossal magnetoresistance
- Ferromagnetism (spintronics)
- Ferroelectricity
- Multiferroism
- Metal-insulator transitions
- Tunability by strain
- Memristive behavior

Can be integrated with existing Si-based technologies

- Use in electrochemical energy storage and conversion systems

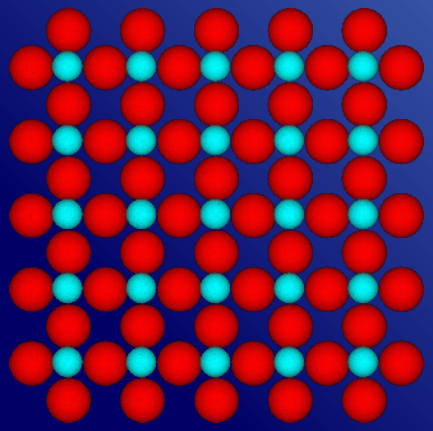
Perovskite structure

ABO_3

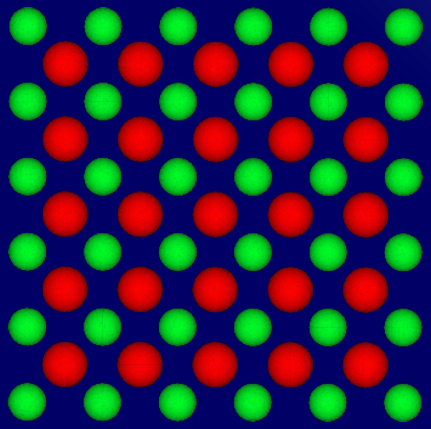


$SrTiO_3$

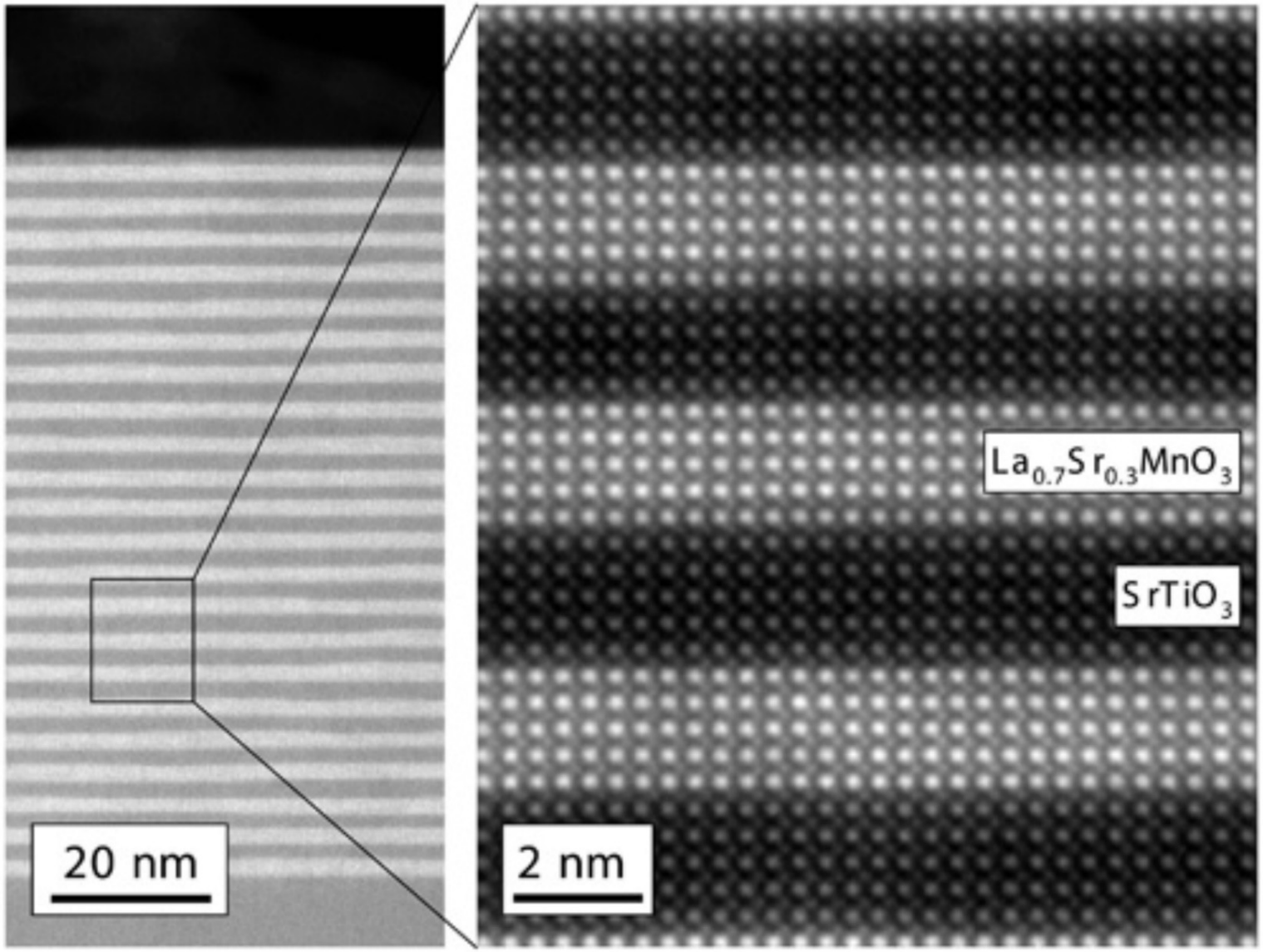
BO_2



AO



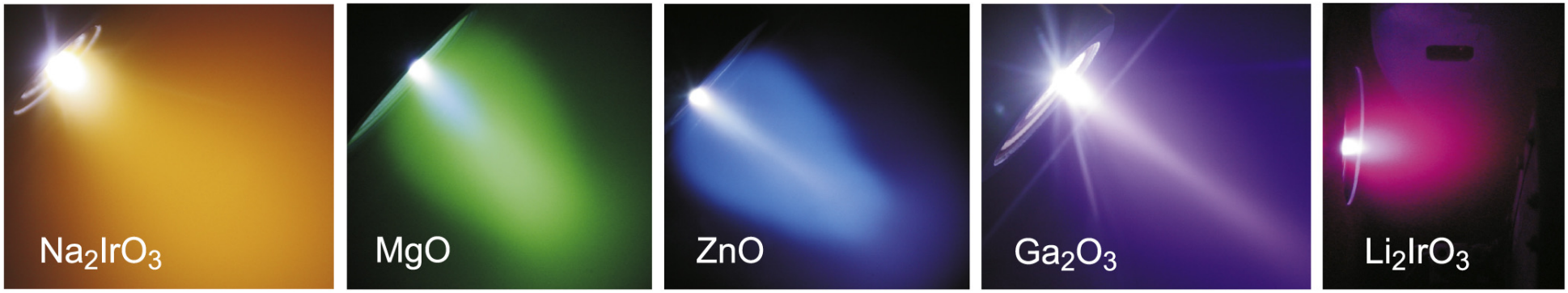
Structure example: LSMO/STO superlattice



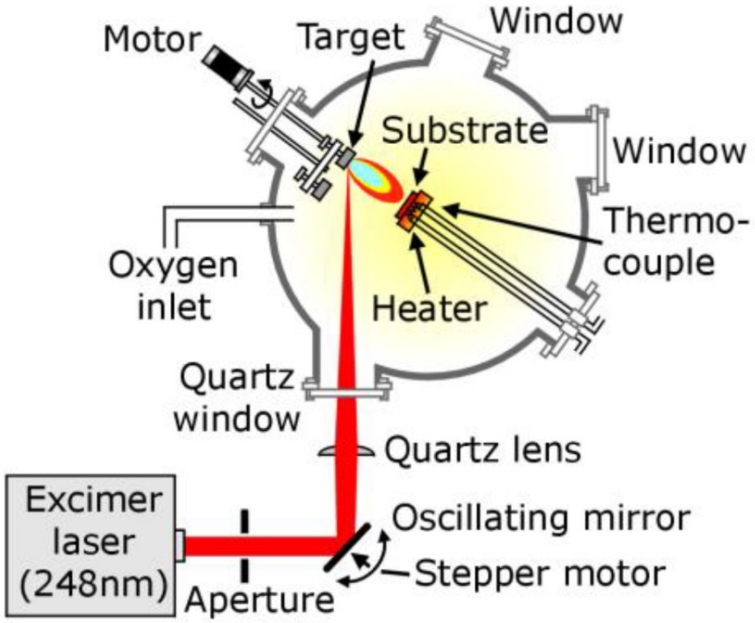
The structure was made using Pulsed Laser Deposition

PULSED LASER DEPOSITION

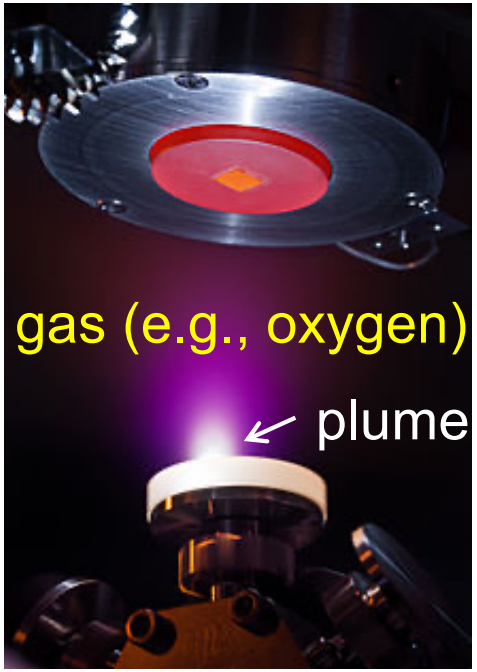
Pulsed laser deposition



Michael Lorenz et al Semicond. Sci. Technol. (2015)



At peak of laser pulse, temperatures on target can reach >10^5 K (> 40 eV!)
Electric fields > 10^5 V/cm
Plasma temperatures are 3000-5000 K
Ablated species are with energies 1 –100 eV (thermalization with a background gas)

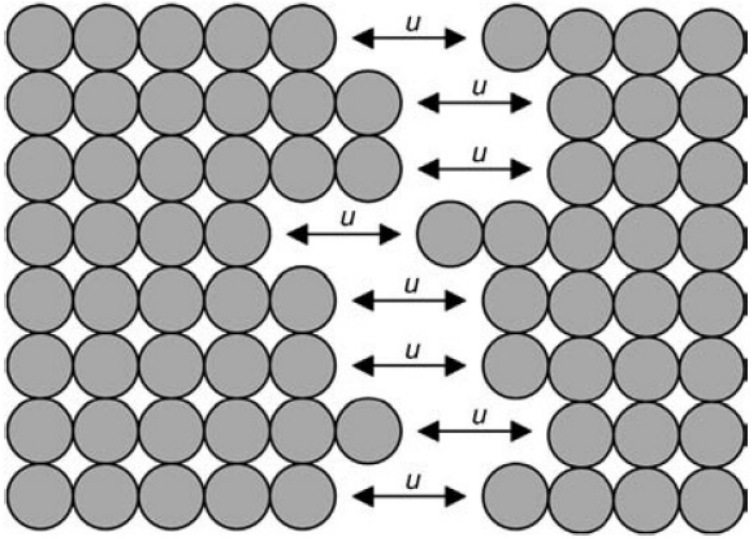


wikipedia.org

Substrate heating is used to promote adatom mobility and chemical reactions on the surface.

SURFACE ENERGY

Surface energy

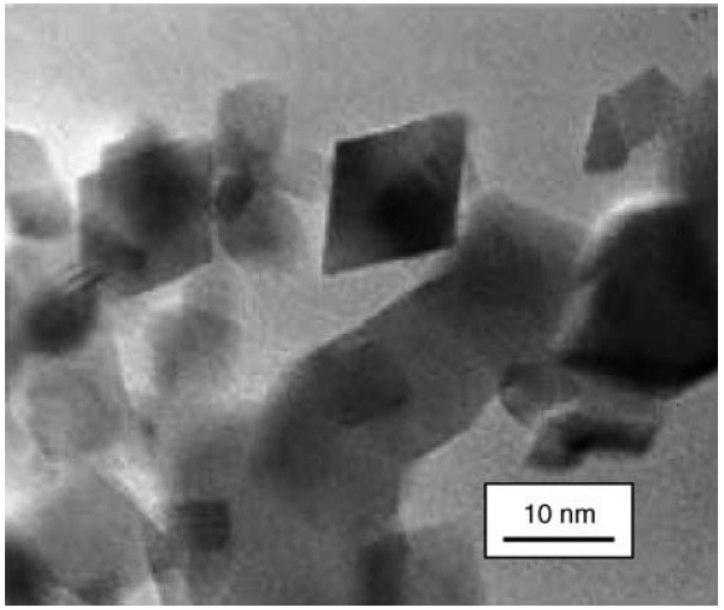


Gibb's energy with account of the surface energy term:

$G = U - TS + \underline{\gamma A}$, where

γ is the surface energy per unit area

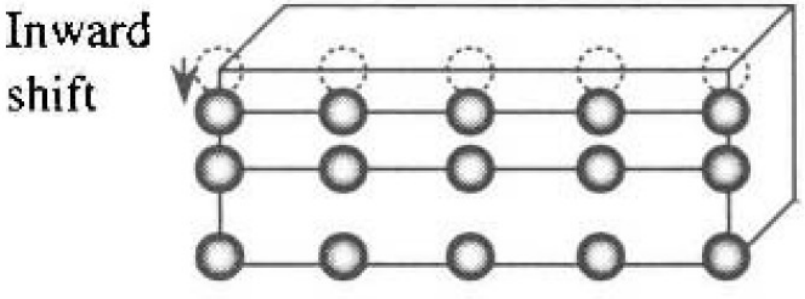
A is the surface area



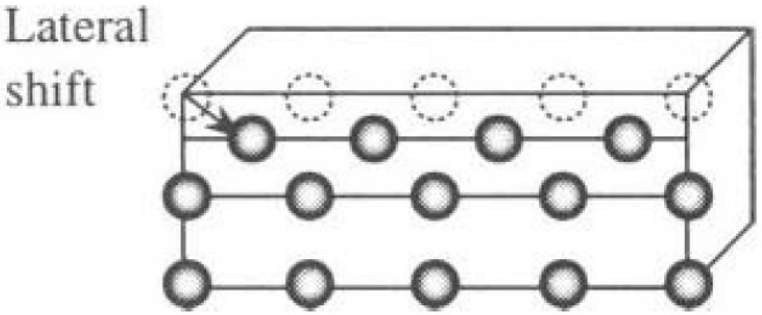
Facetted ceria (CeO_2) nanoparticles.

Note: *amorphous* particles are round!

Surface energy reduction mechanisms



relaxation



reconstruction

- *Due to the force of unbroken bonds, atoms shift towards inside of the crystal*

Surface reconstruction

Changes in bond length and interatomic arrangement on the surface

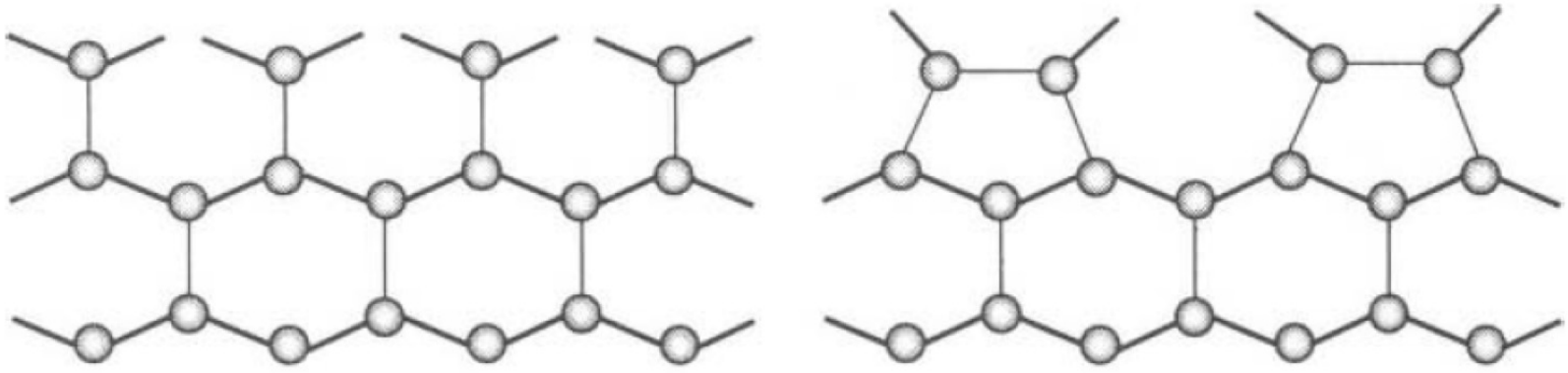
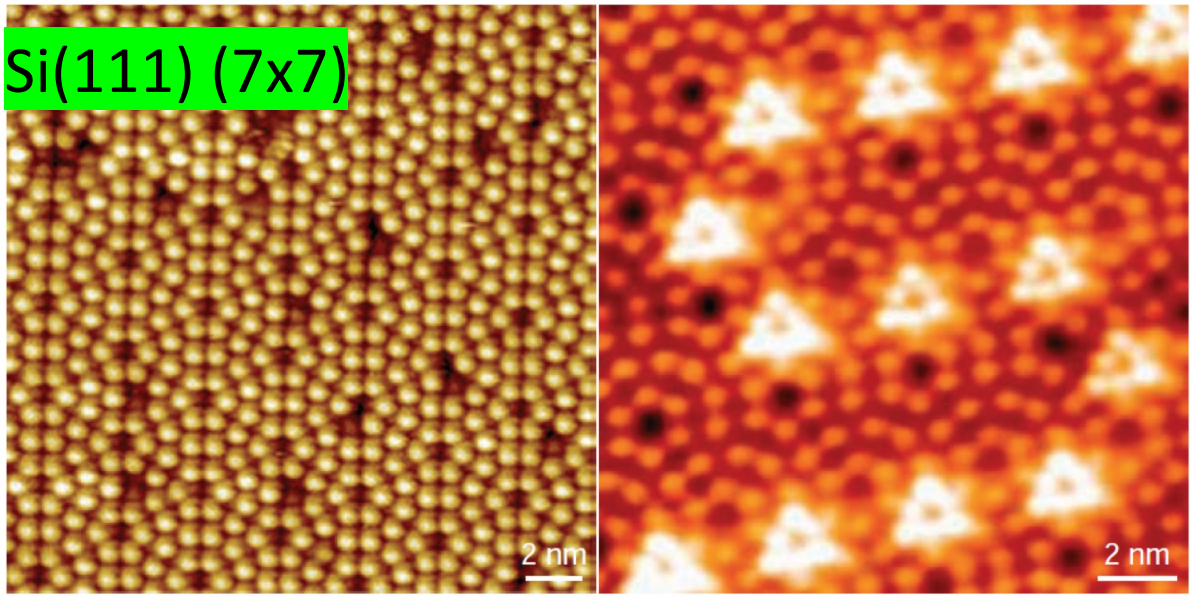


Fig. 2.5. Schematic illustrating the (2 × 1) restructure of silicon {100} surface.

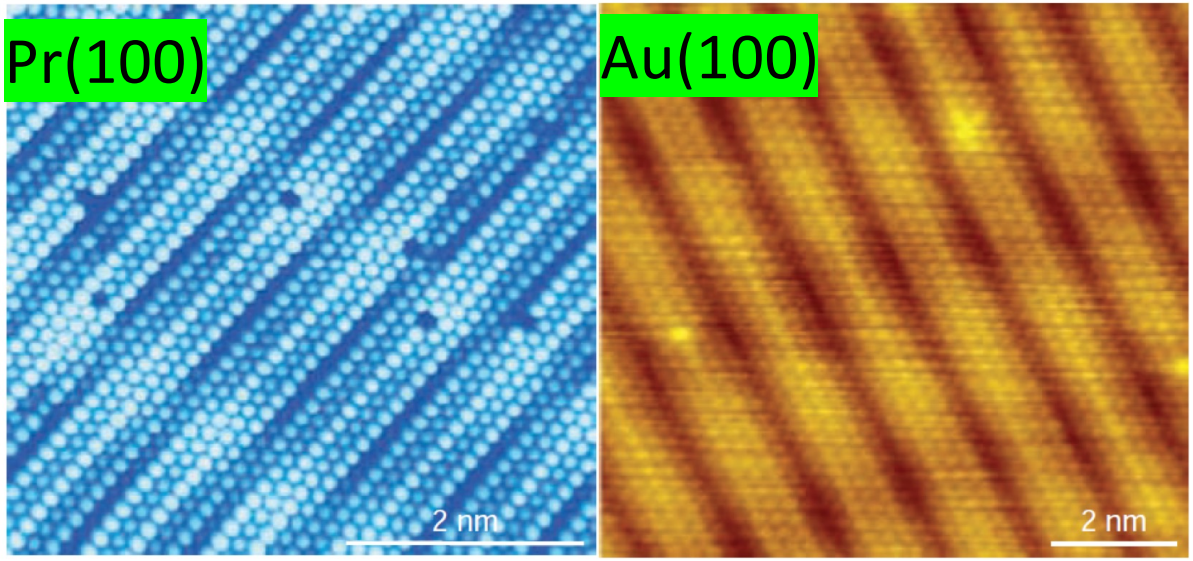
- Material properties are altered due to the presence of the surface up to a depth of a few interatomic distances: 0.5-1.5 nm

Surface reconstructions



Omicron NanoTechnology GmbH (http://www.omicron.de)

Phys. Rev. Lett . 88 (2002), 066101.



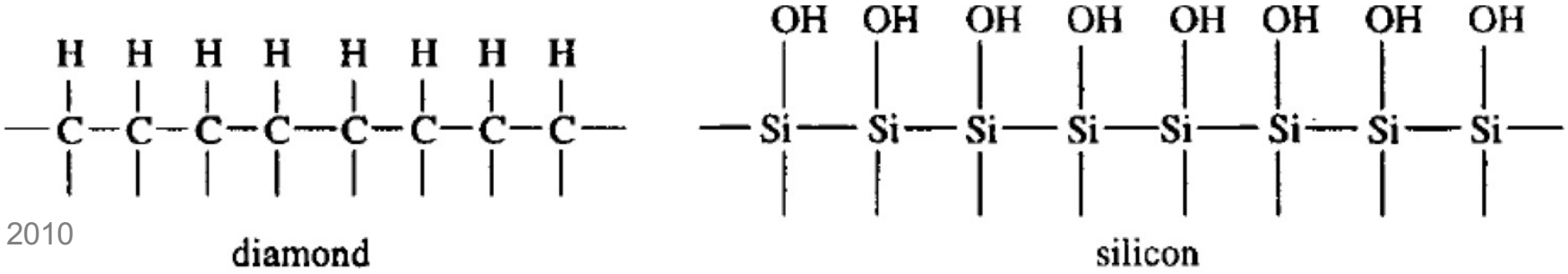
Surf. Sci . 306 (1994), 10–20

http://en.wikipedia.org/wiki/Scanning_tunneling_microscope

C. Binns, *Introduction to nanoscience and nanotechnology*, Wiley, 2010.

Surface adsorption and composition segregation

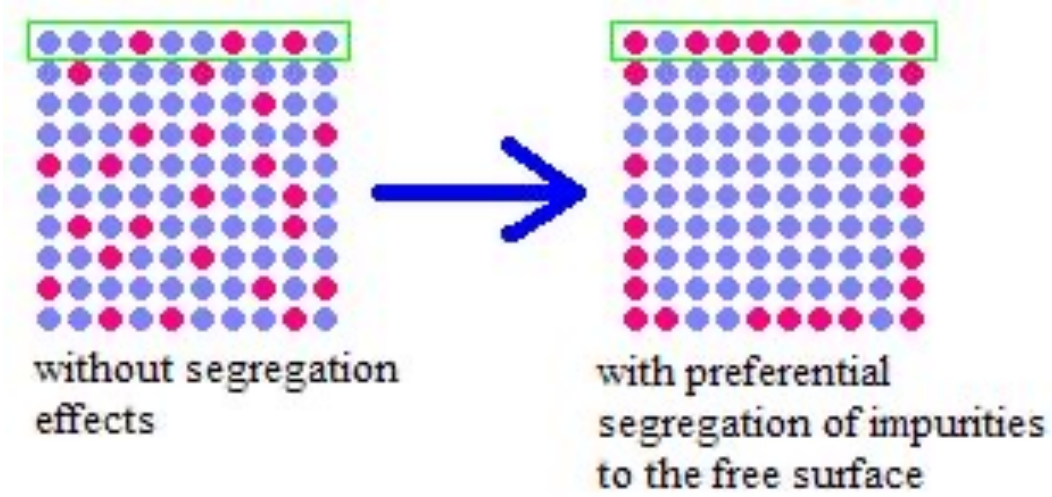
- surface adsorption through *chemical* or *physical* adsorption (from a gas of liquid):
  - forming chemical bonds or
  - weak attraction forces such as electrostatic or van der Waals forces



Cao 2010

diamond silicon

- composition segregation: dopant or impurity enrichment on the surface through solid-state diffusion (from a solid solution)

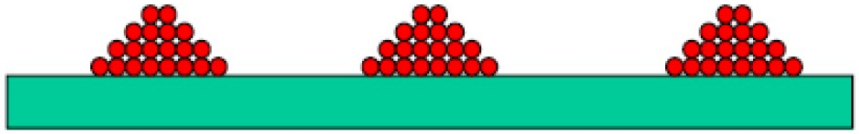


- Indirect evidences of "surface segregation" in nanomaterials: difficult to dope, and nearly perfect crystal lattice.

https://en.wikipedia.org/wiki/Segregation_(materials_science)

Nucleation and growth modes

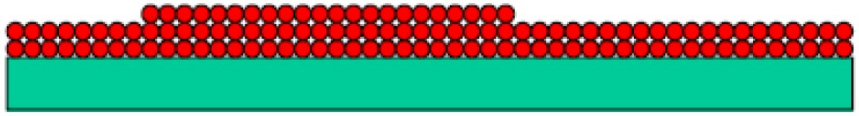
(1) Volmer-Weber: (island growth):



$\gamma_{sv} < \gamma_{fs} + \gamma_{fv}$

M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, p. 277 (1926).

(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):

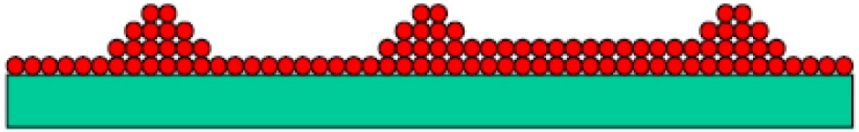


$\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv}$

F. C. Frank and J. H. Van der Merwe, *Proc. R. Soc. London*, Ser. A **198**, p. 205 (1949).

(3) Stranski-Krastanov: (layers + islands):

$\gamma_{sv} \approx \gamma_{fs} + \gamma_{fv}$



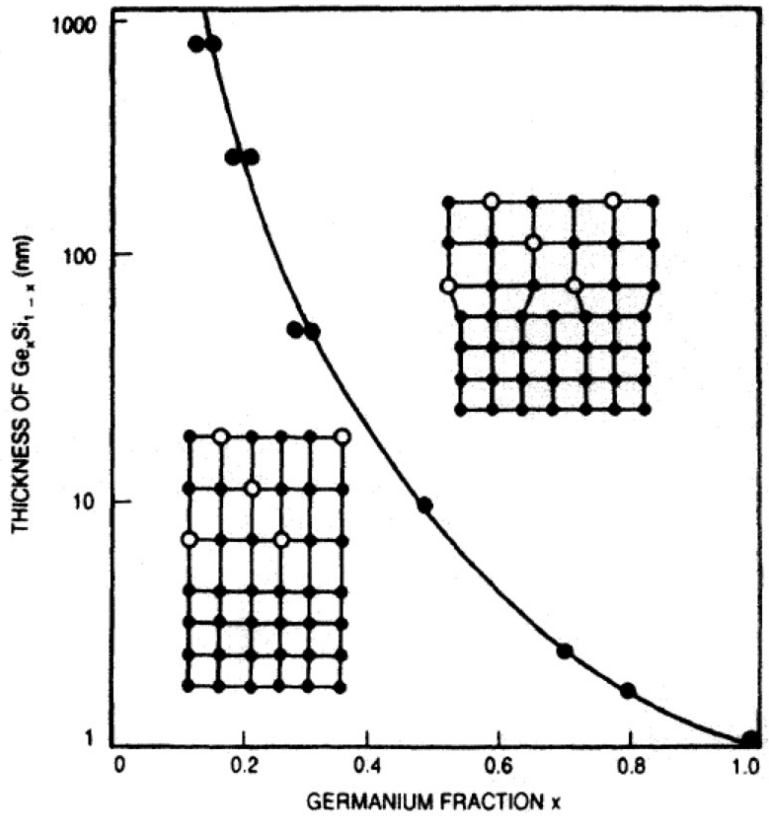
J. N. Stranski and L. Krastanov, *Ber. Akad. Wiss. Wien* **146**, p. 797 (1938).

Growth modes in PVD epitaxy

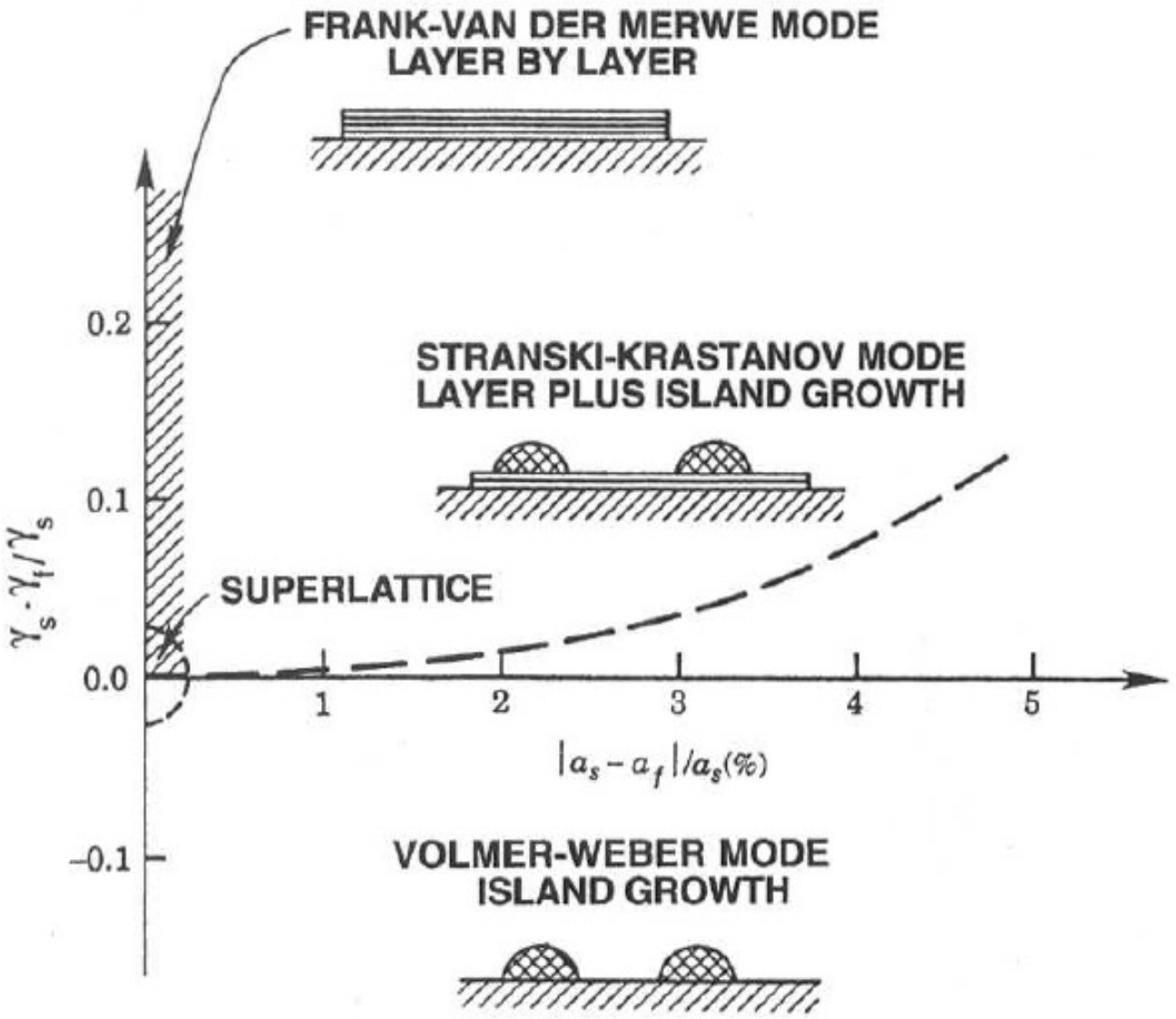
Lattice misfit

$$f = \frac{a_{s0} - a_{f0}}{a_{f0}} = \frac{\Delta a_0}{a_0}$$

$a_{0s,f}$ are unstrained lattice parameters of substrate and film



Thermodynamic aspects



A set of available substrates for perovskite oxides

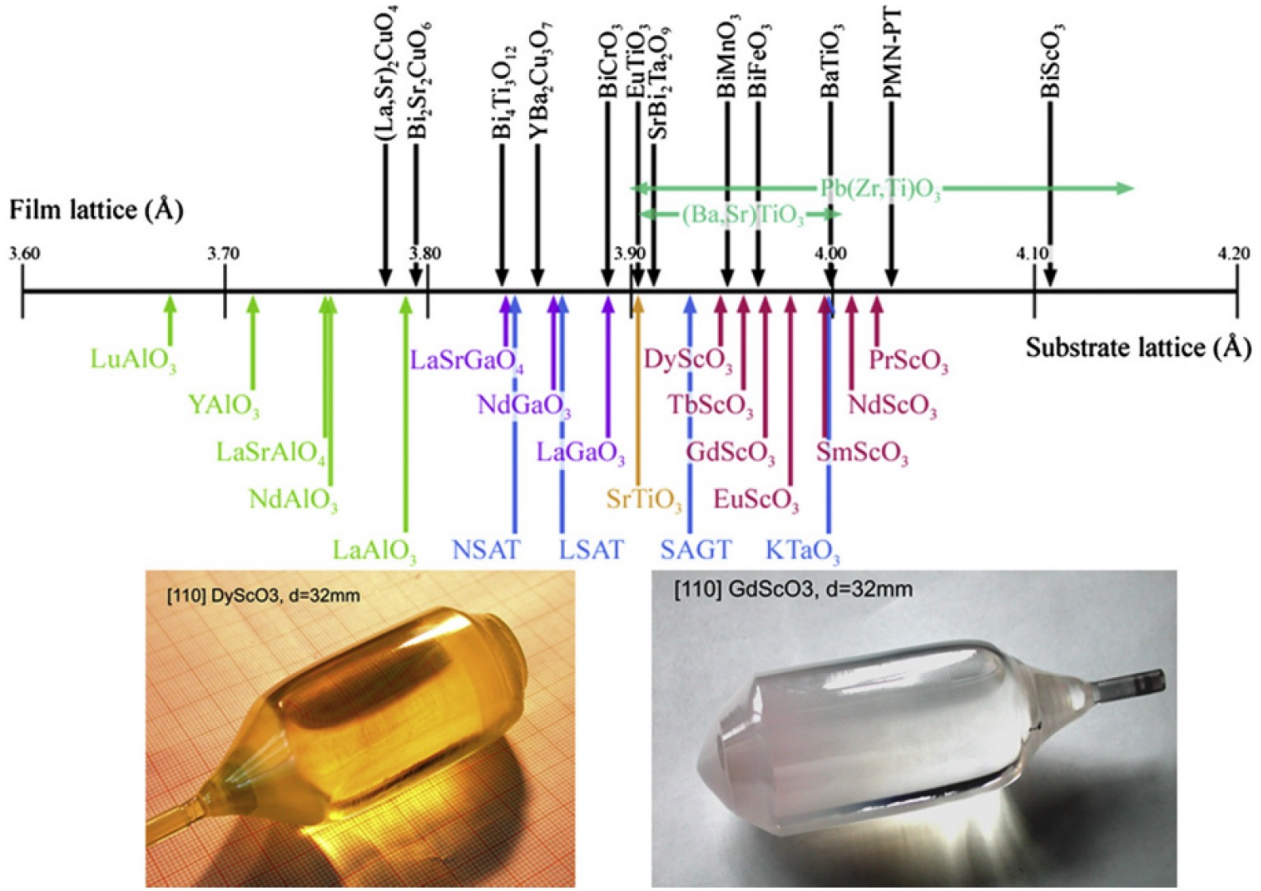
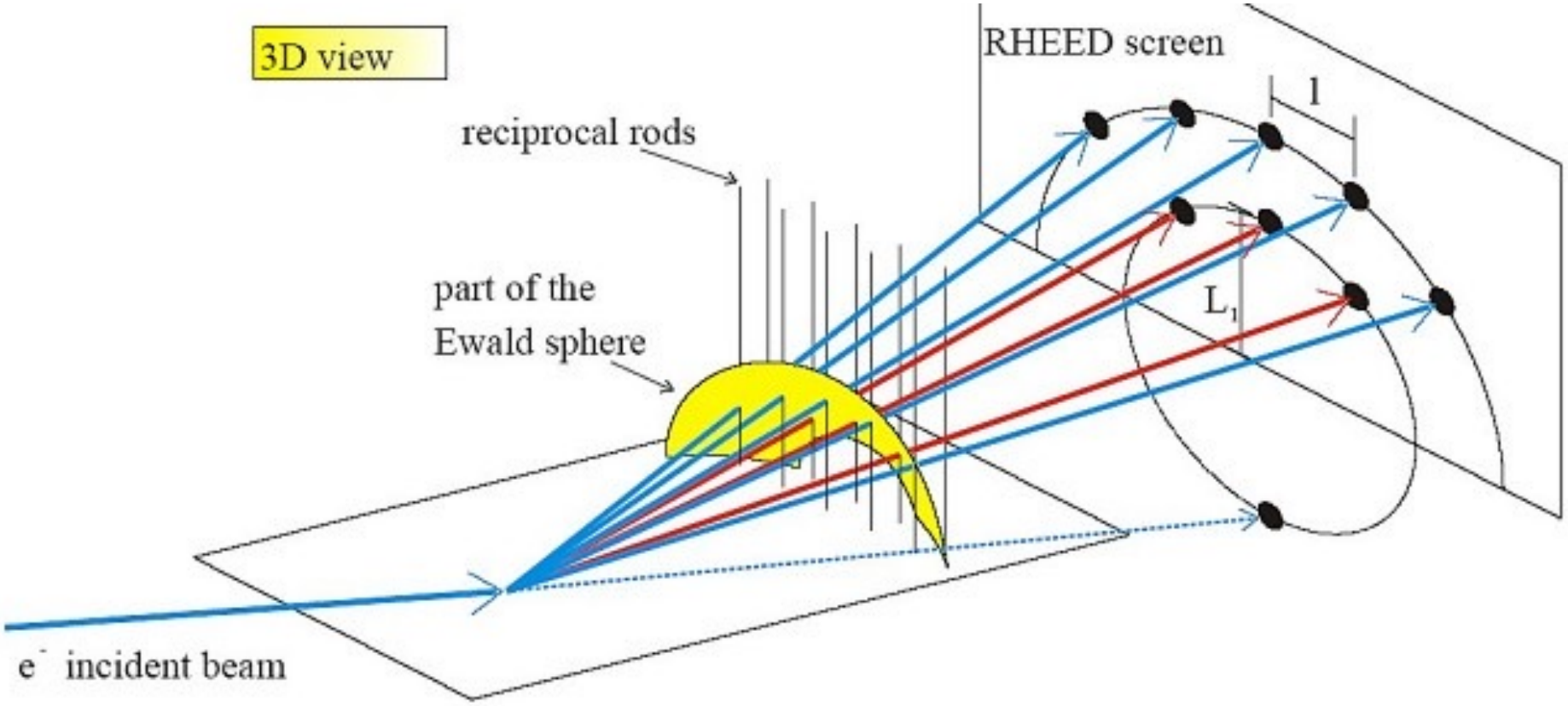


Fig. 3. A number line showing the pseudotetragonal or pseudocubic *a*-axis lattice constants in angstroms of some perovskites and perovskite-related phases of interest including multiferroics (above the number line) and of some of the perovskite and perovskite-related substrates that are available commercially (below the number line). The photos of exemplary single crystals used as substrates are from Ref. [96].

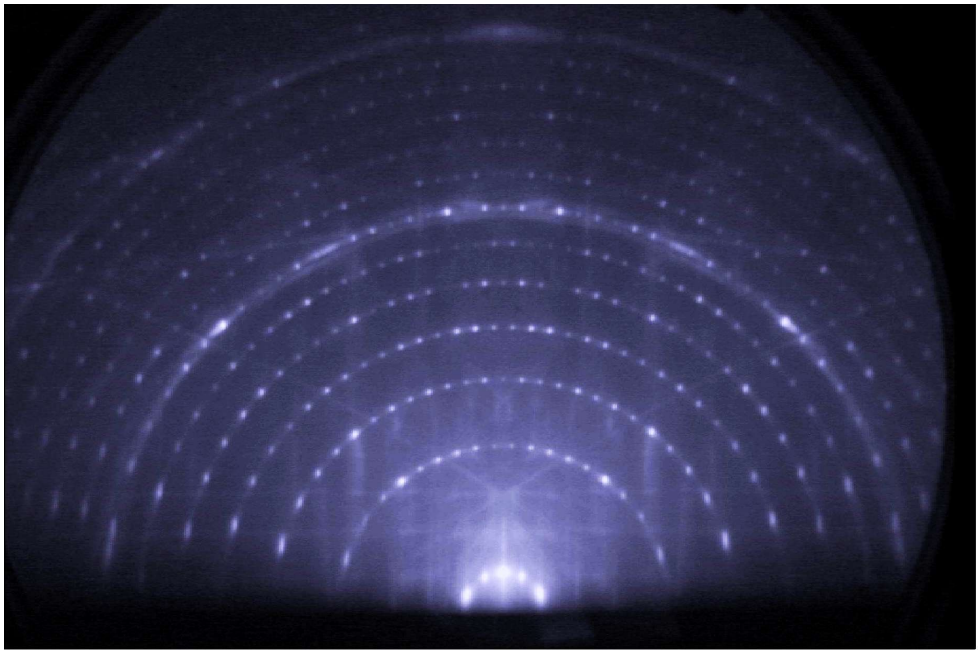
L.W.Martin and D.G.Schlom, *Current Opinion in Solid State and Materials Science* (2012)

REFLECTION HIGH-ENERGY ELECTRON DIFFRACTION

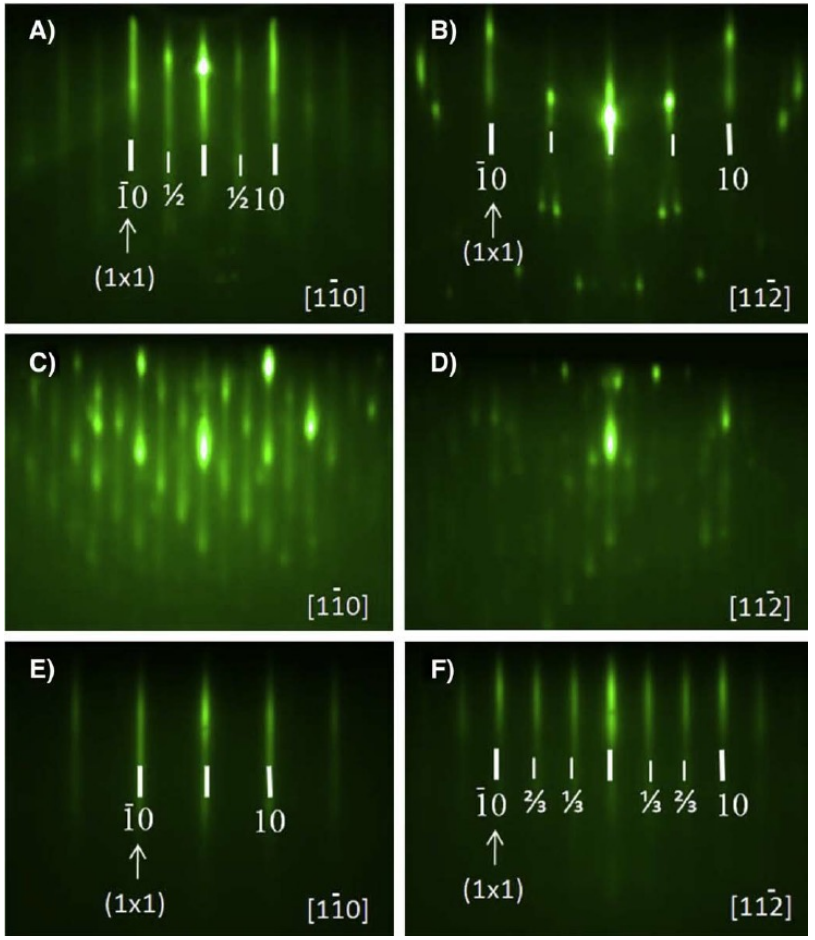
Reflection High-Energy Electron Diffraction (RHEED)



Example: RHEED patterns



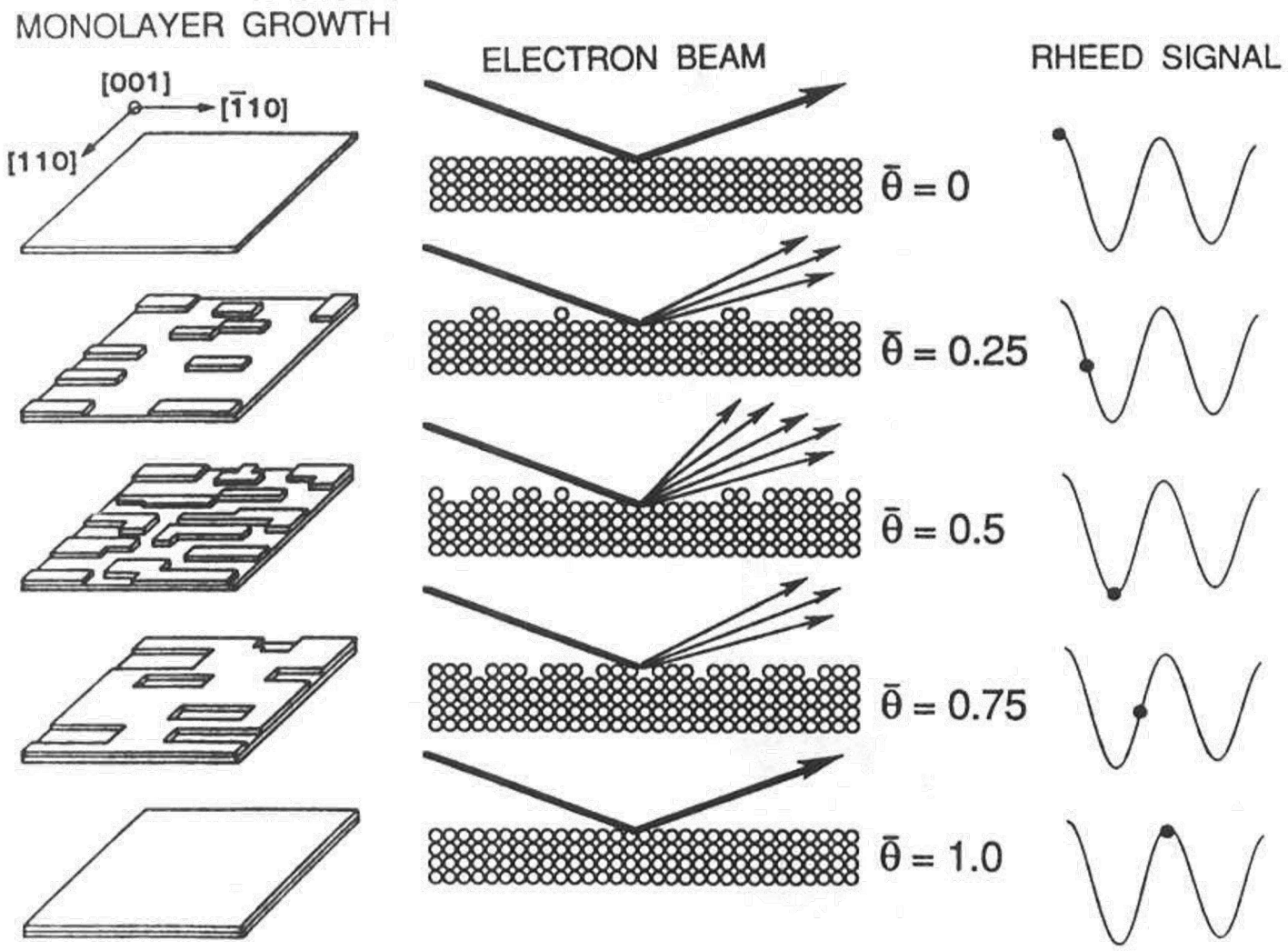
http://nano.umcs.lublin.pl/en-RHEED.php



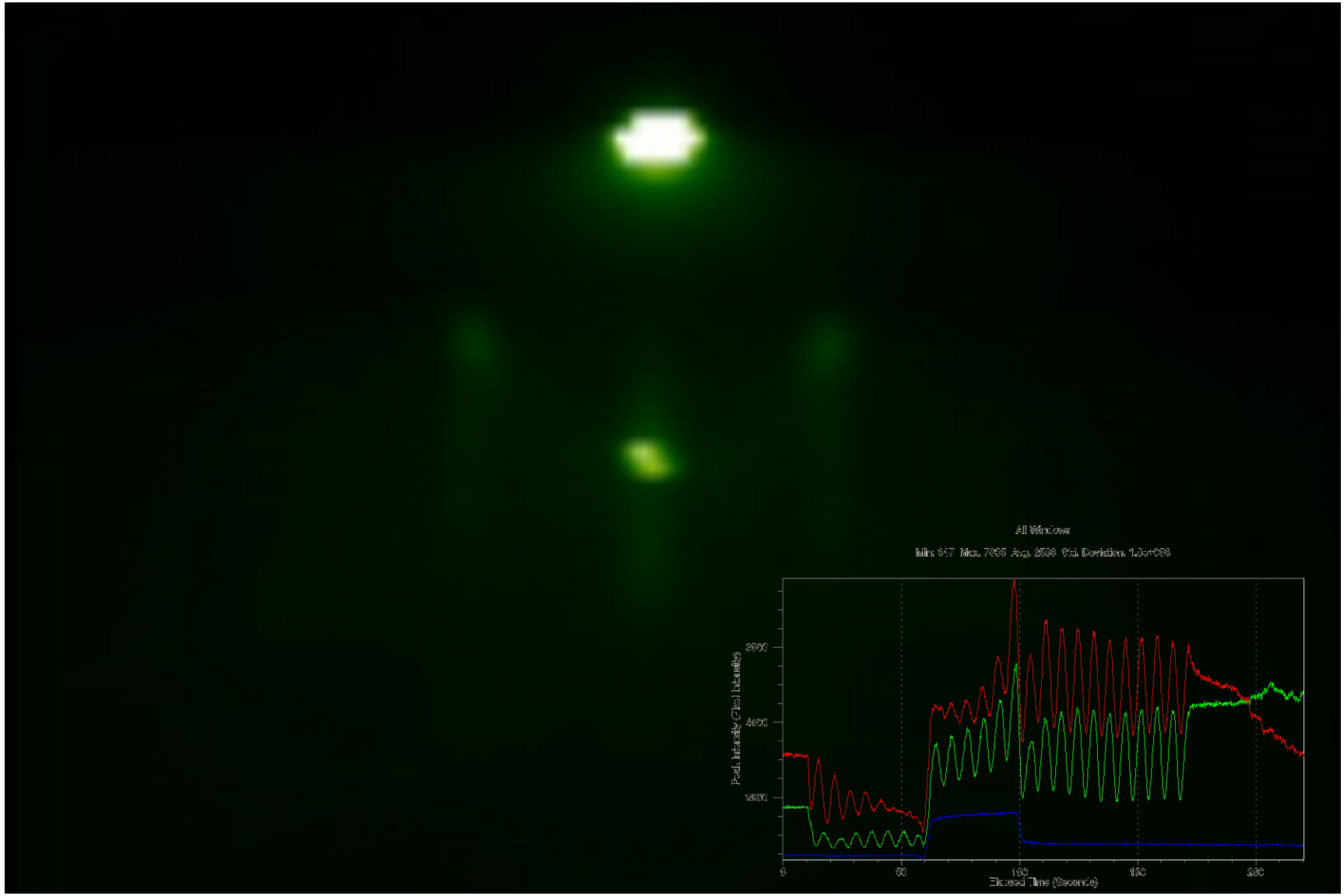
S. Olive-Mendez et al. *Thin Solid Films* (2008)

In situ control of film growth

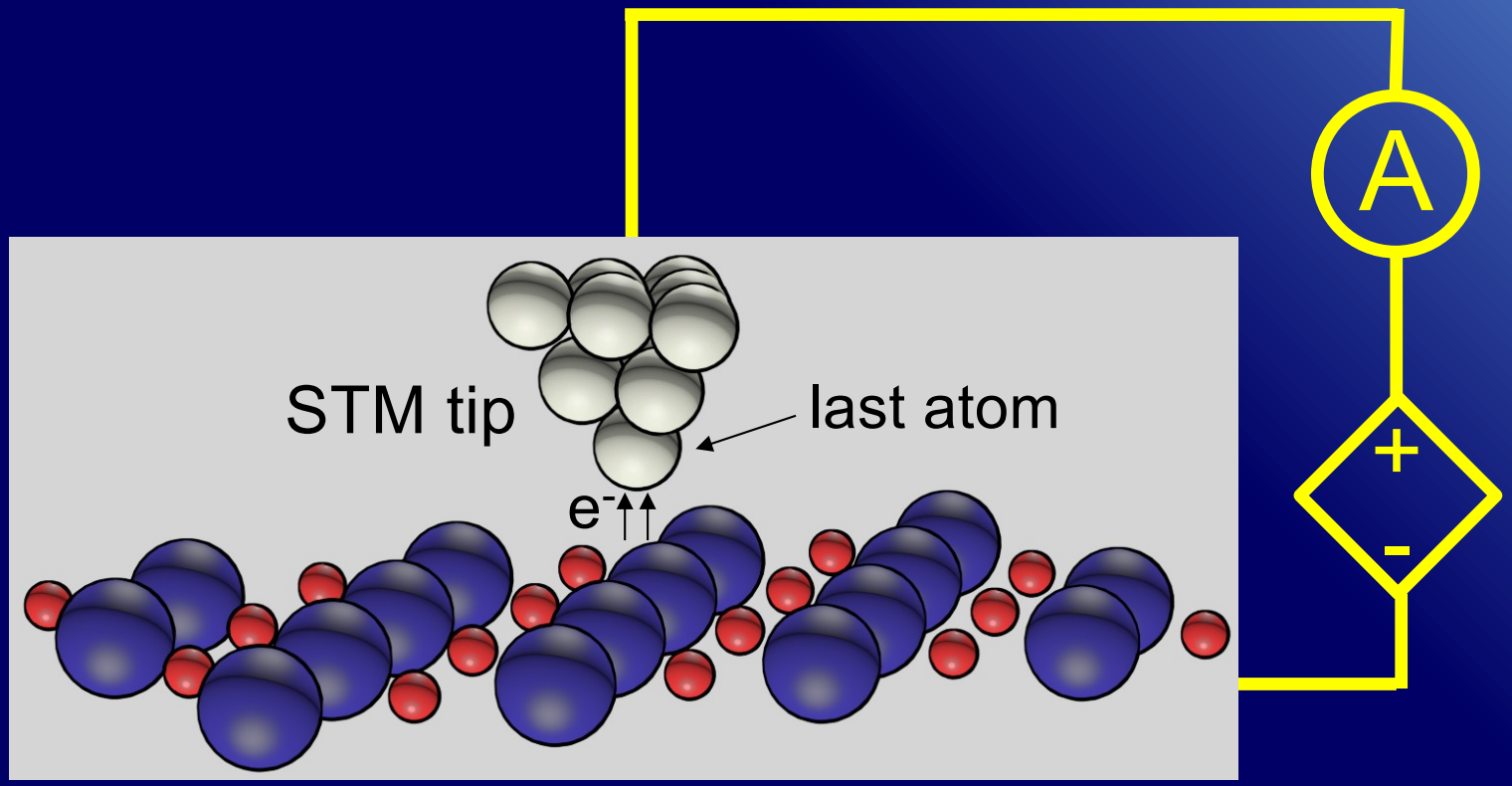
Reflection High-Energy Electron Diffraction



RHEED during a real deposition

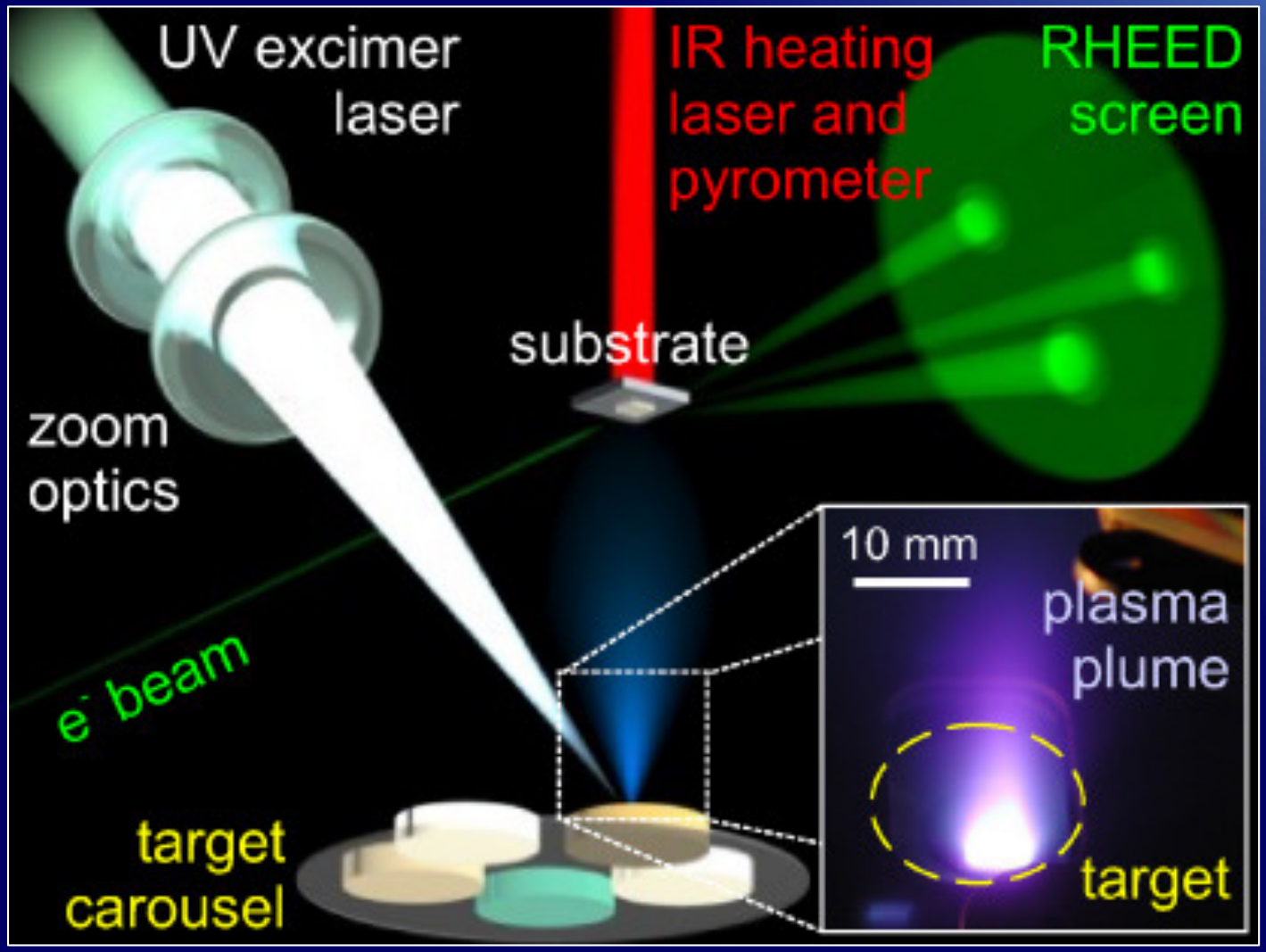


Scanning tunneling microscopy



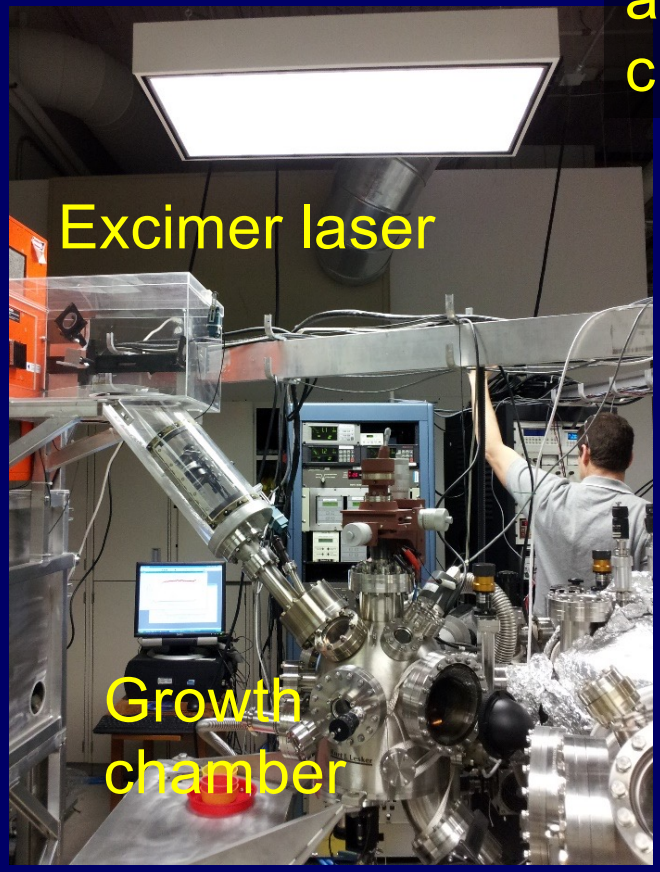
- *Atomic* resolution is generally *very difficult* to achieve on PLD-grown films

Pulsed Laser Deposition



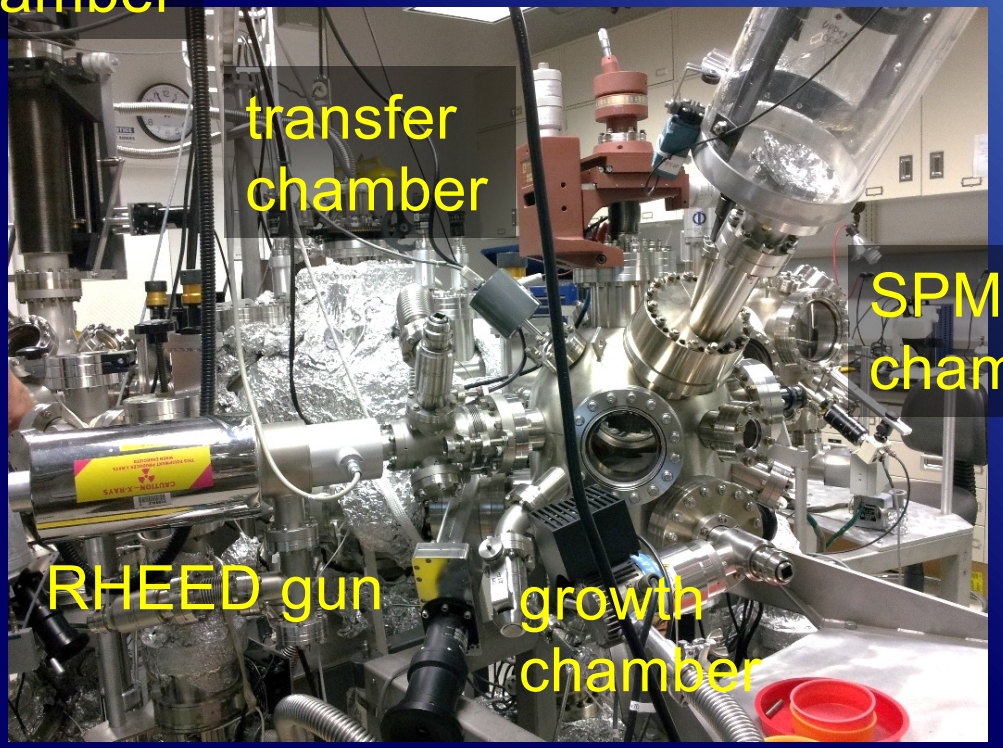
The schematic is from: M. Opel, J. Phys. D 45, 033001 (2012)

NanoTransport system at CNMS



analysis chamber

http://www.cnms.ornl.gov

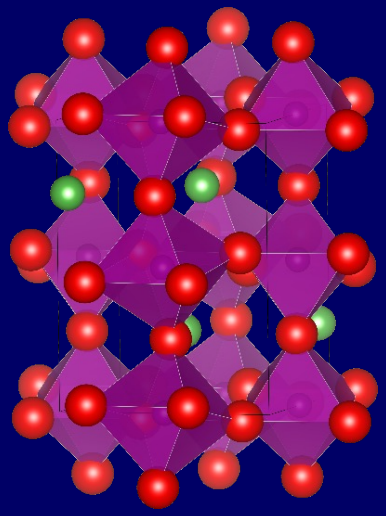


STM
AFM
in
UHV

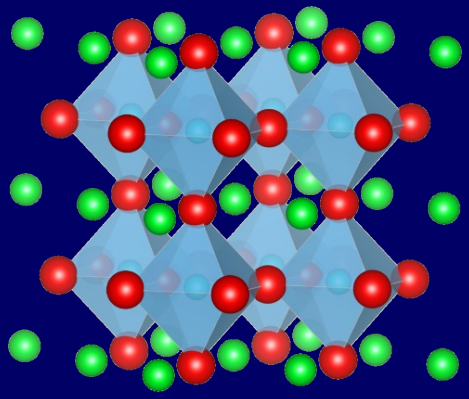
OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

Epitaxial film growth

$LaMnO_3$



$SrTiO_3$

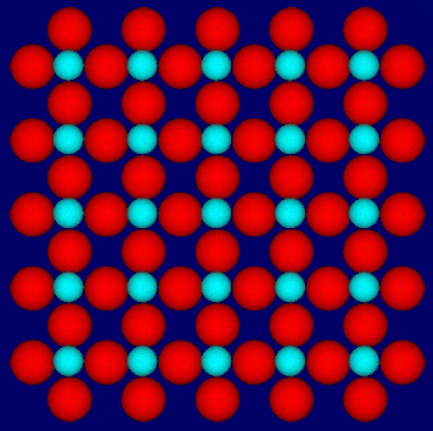


substrate

Growth at:
elevated substrate temperatures
650-850 °C &
in oxygen atmosphere 1-300 mTorr

B-terminated single-crystalline substrate

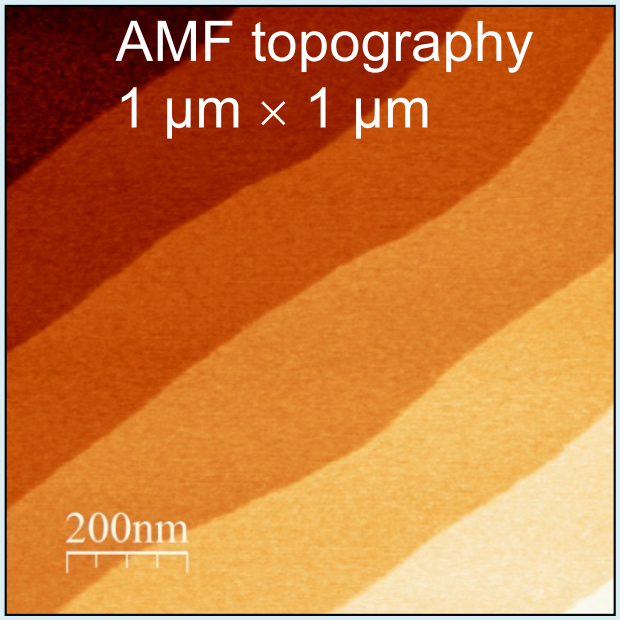
BO_2



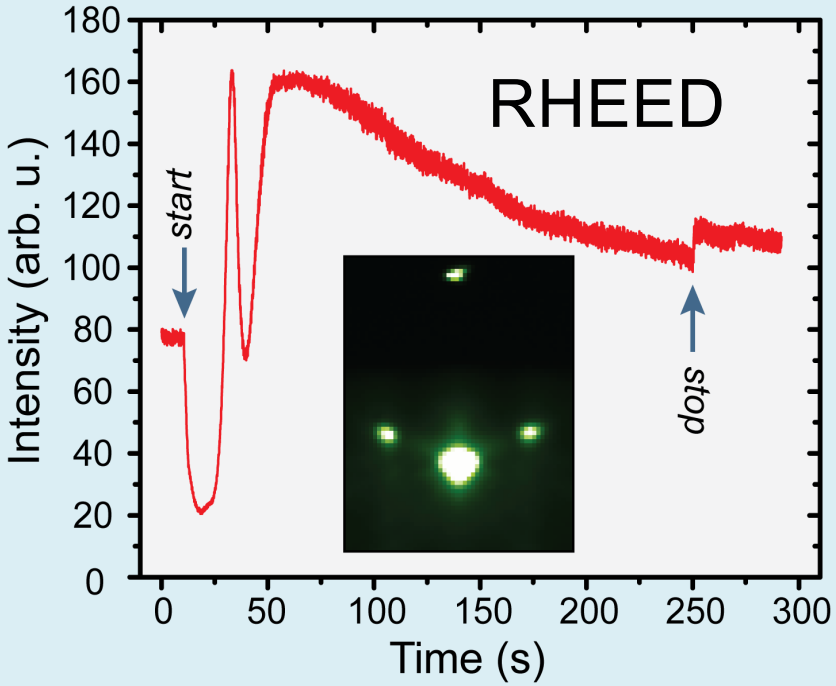
$SrRuO_3$

Widely used as a metal electrode

Film growth



RMS Roughness = 55 pm



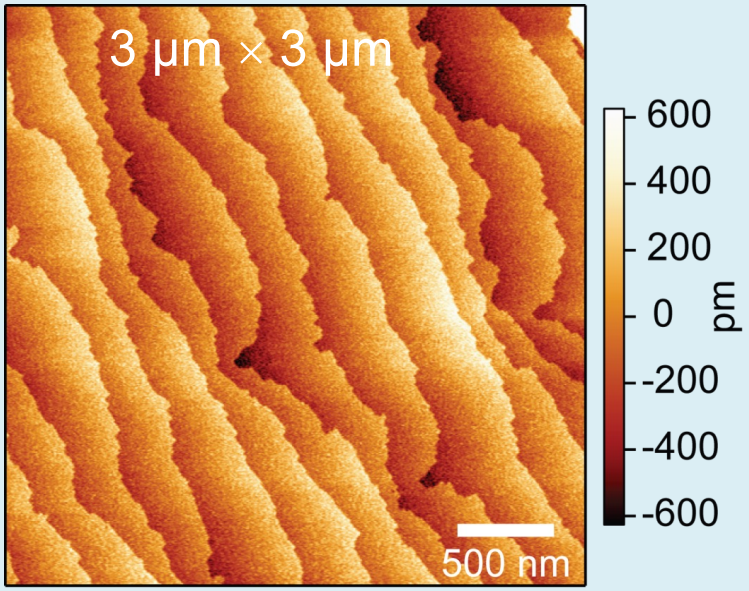
Substrate selection:
RMS roughness < 70 pm

Growth modes:

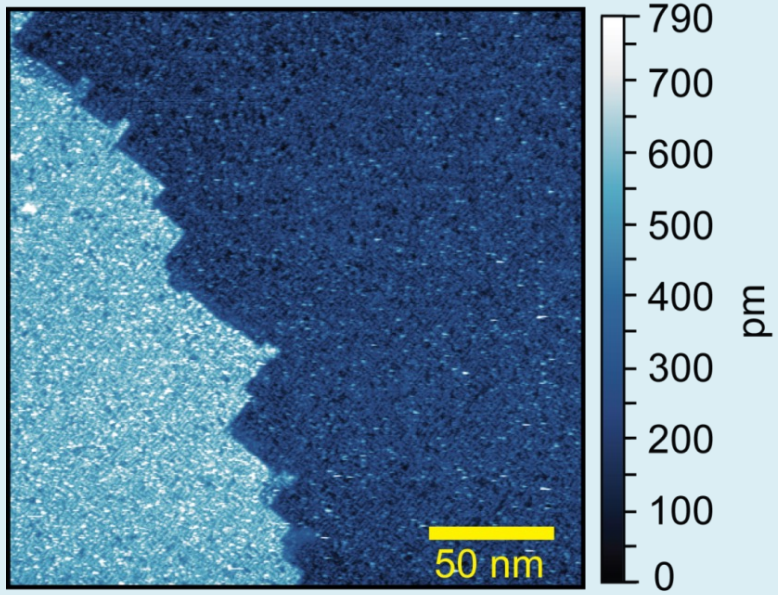
- 690 °C – step-flow
- 650°C – step-flow/island-formation

Film surface: larger scale

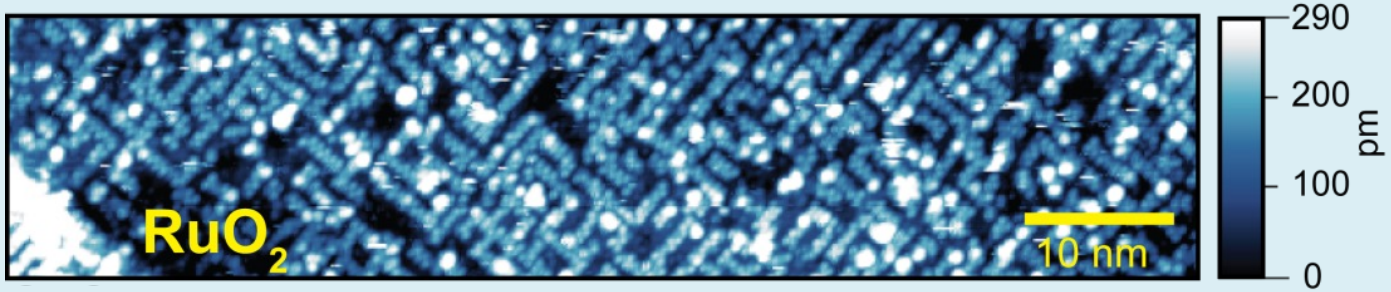
ex-situ AFM (topography)

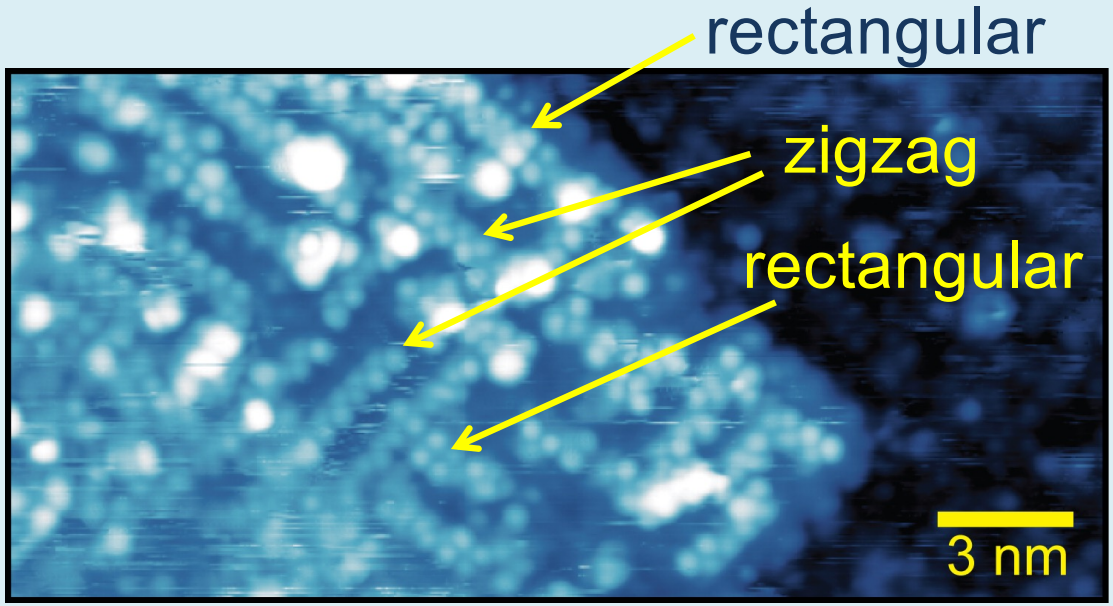


in-situ STM

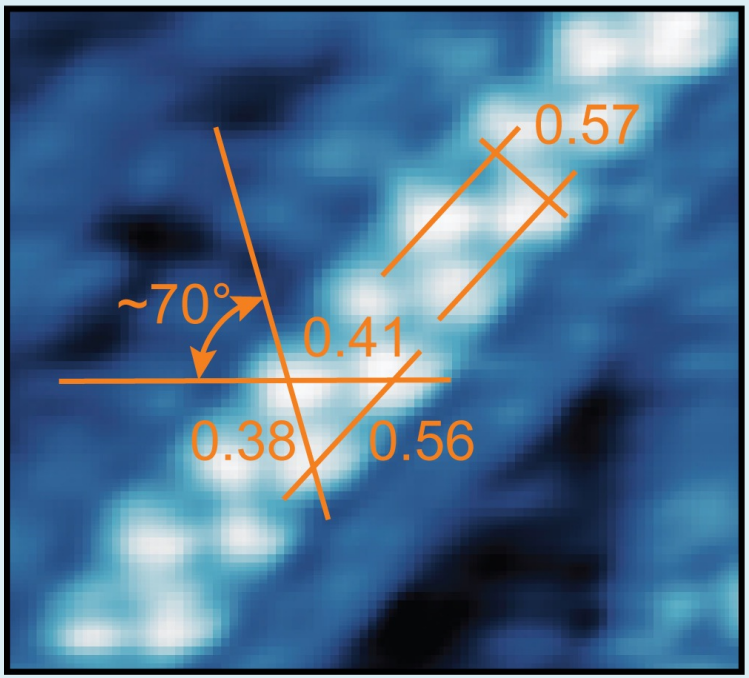


Competing surface patterns

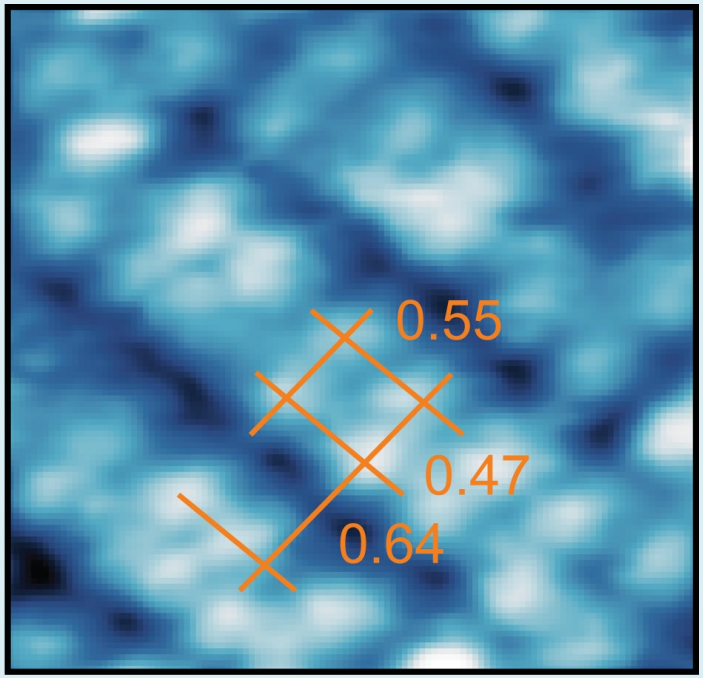




Zigzag and rectangular patterns



zigzag



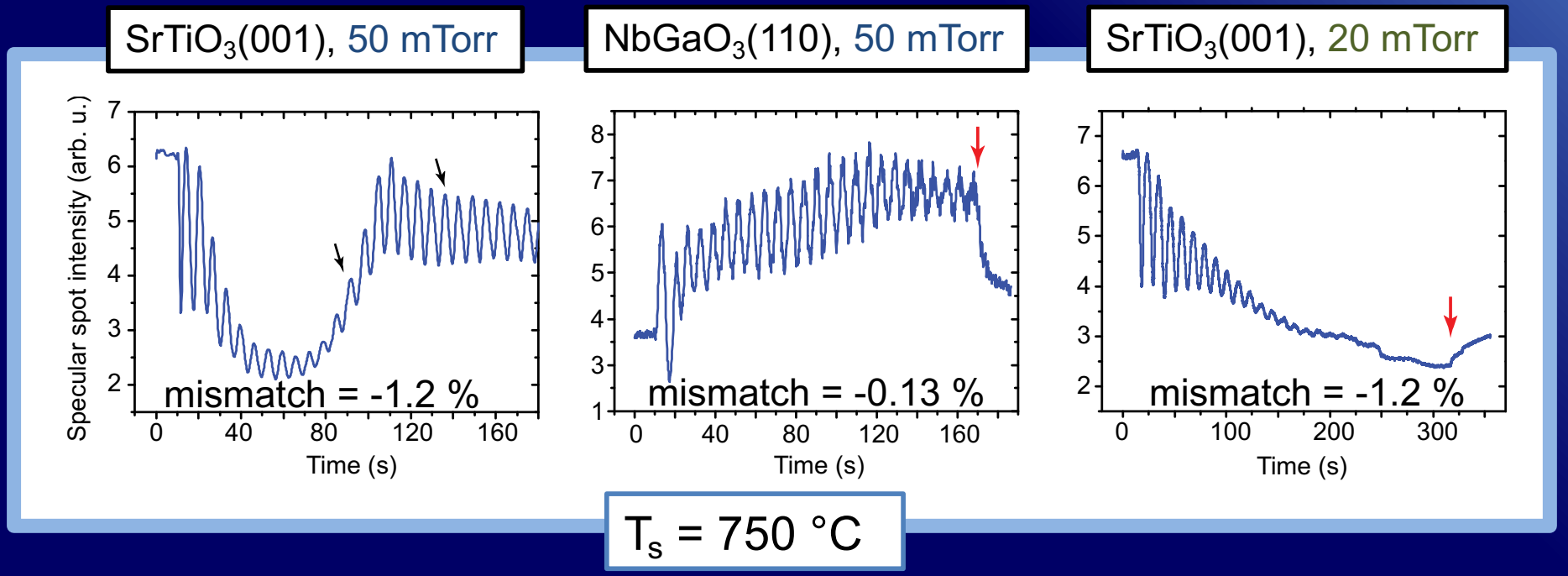
rectangular

$La_{5/8}Ca_{3/8}MnO_3$

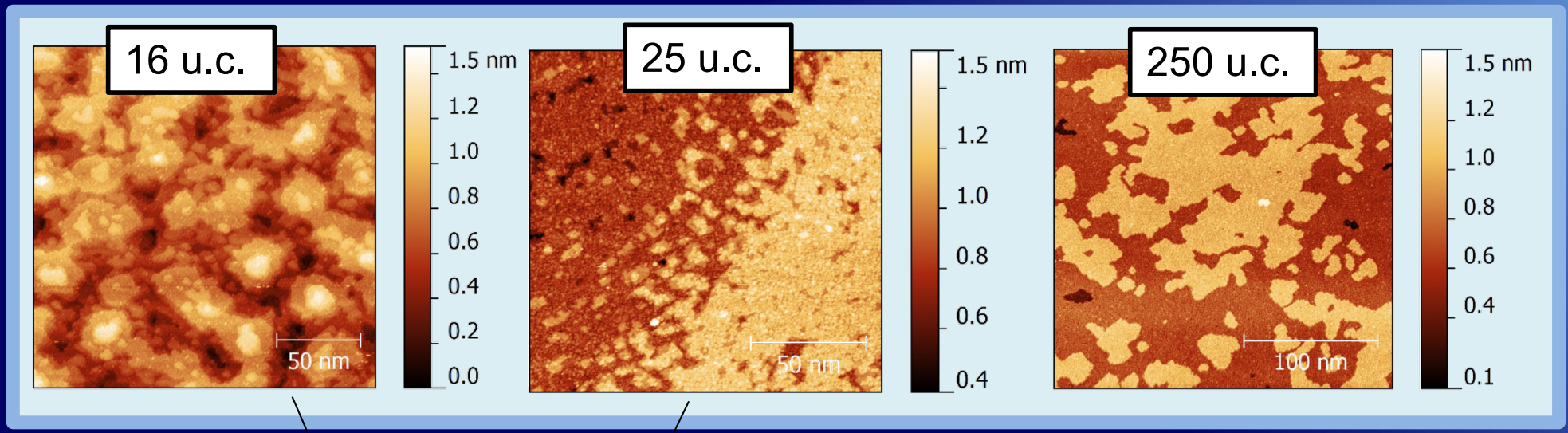
Classical *Colossal magnetoresistance* material

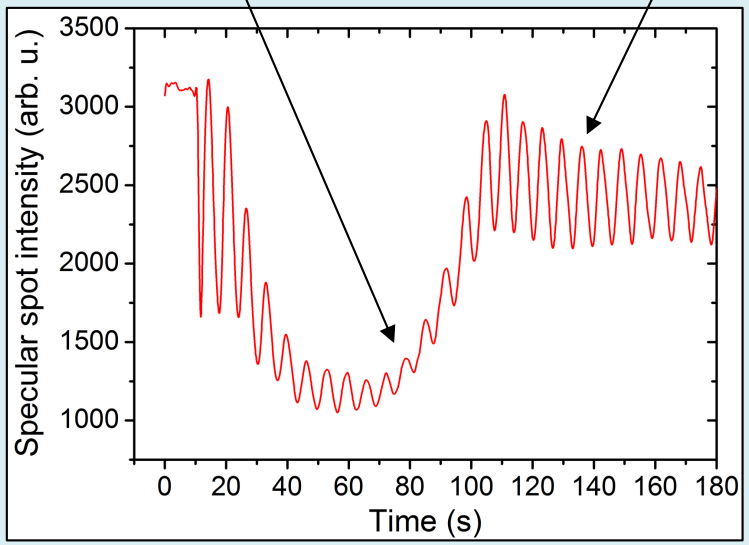
Growth dynamics vs. conditions

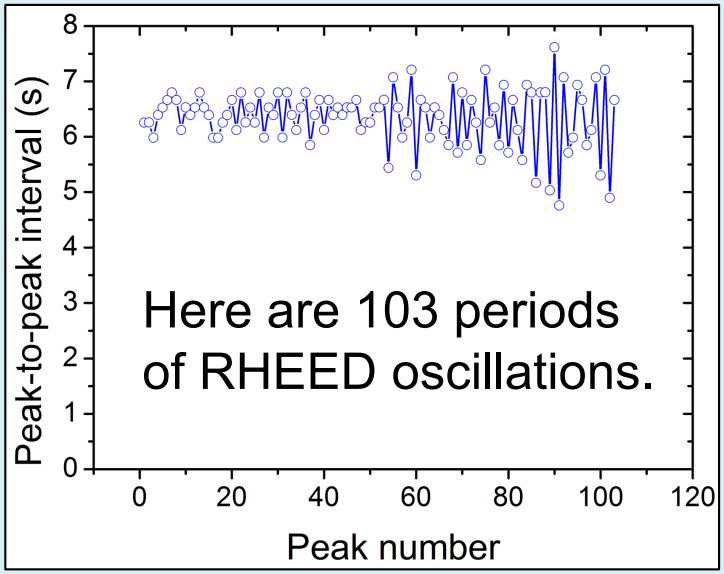
Growth behavior strongly depends on the substrate and relatively small variations of oxygen pressure.



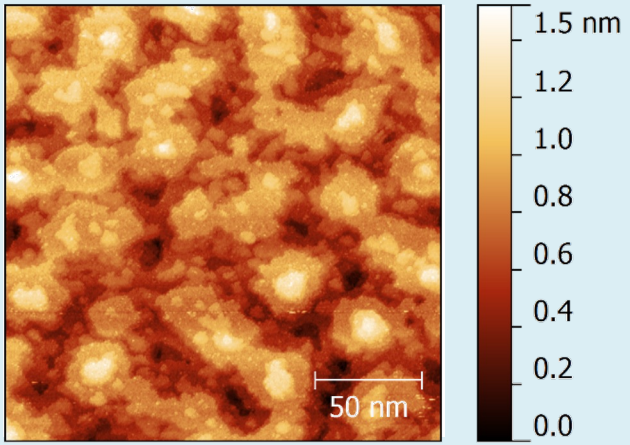
Evolution of surface morphology

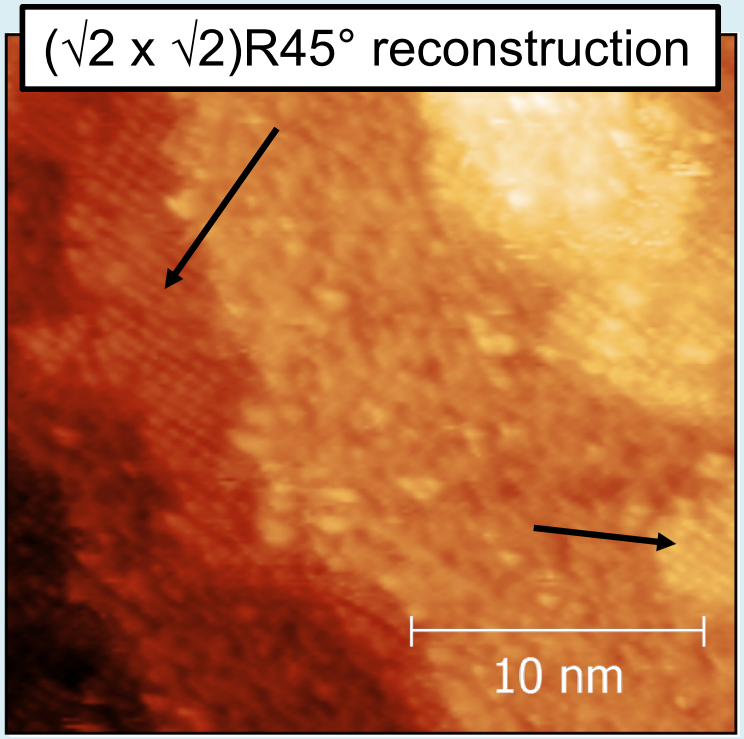


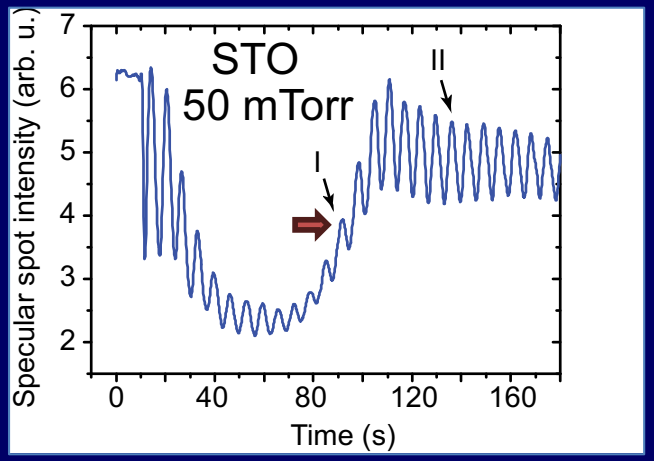




16 u.c. on $SrTiO_3$



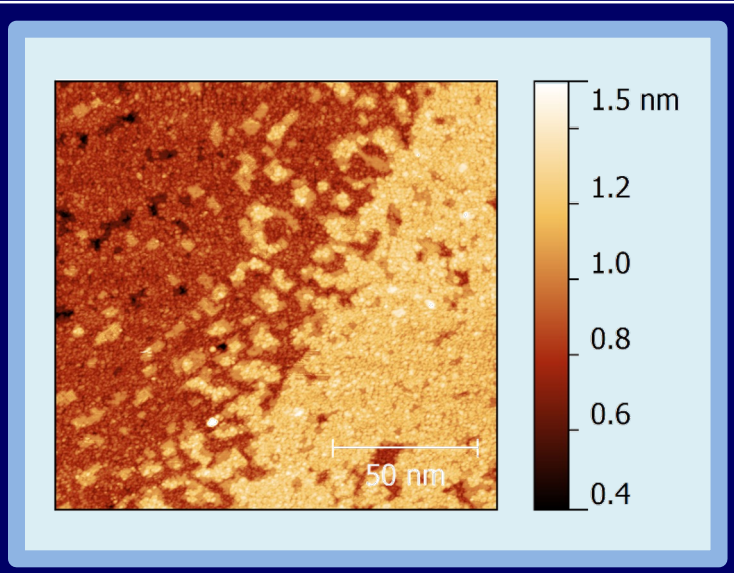


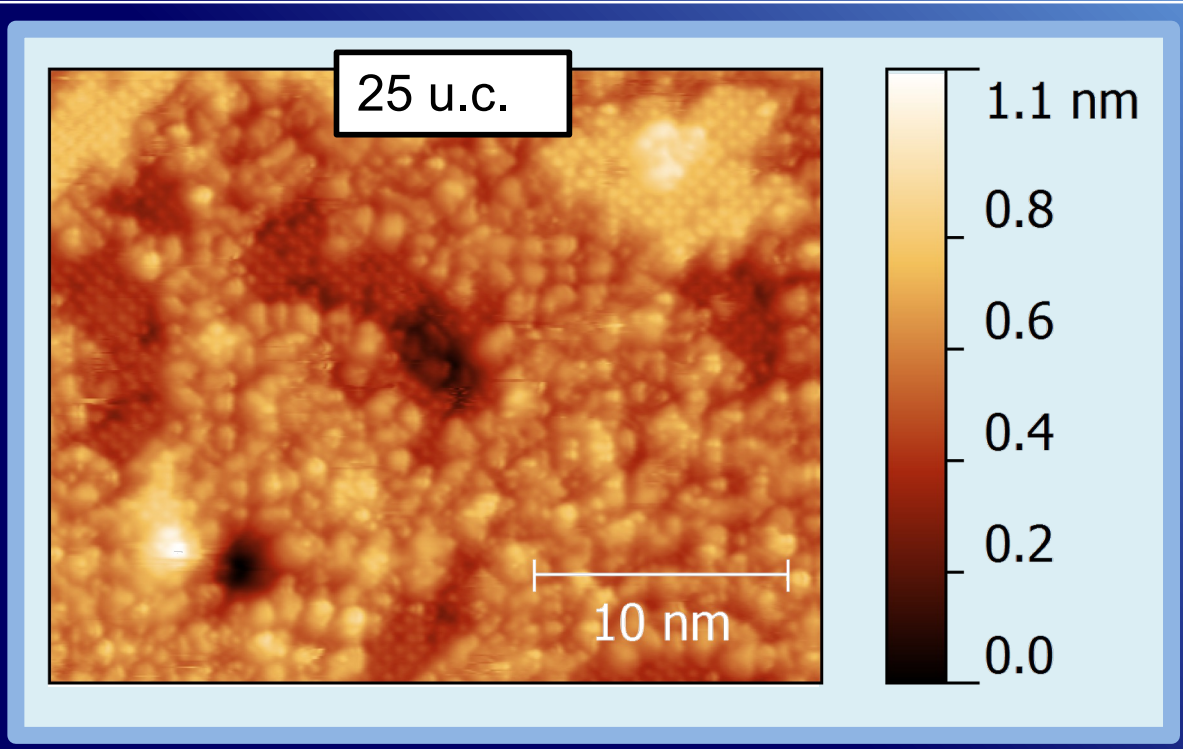


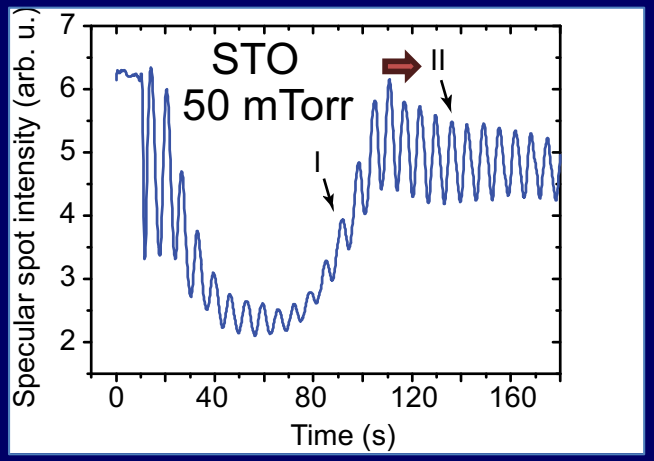
- Up to 7 u.c. layers can be seen
- Two terminations - *ordered* and *disordered*

V_t = -1.8 V, I_t = 40-90 pA, T = 297 K

25 u.c. on $SrTiO_3$

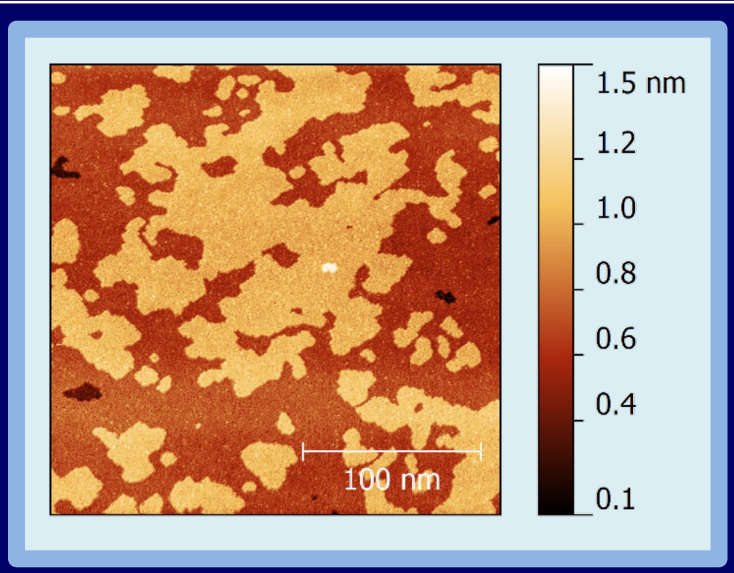


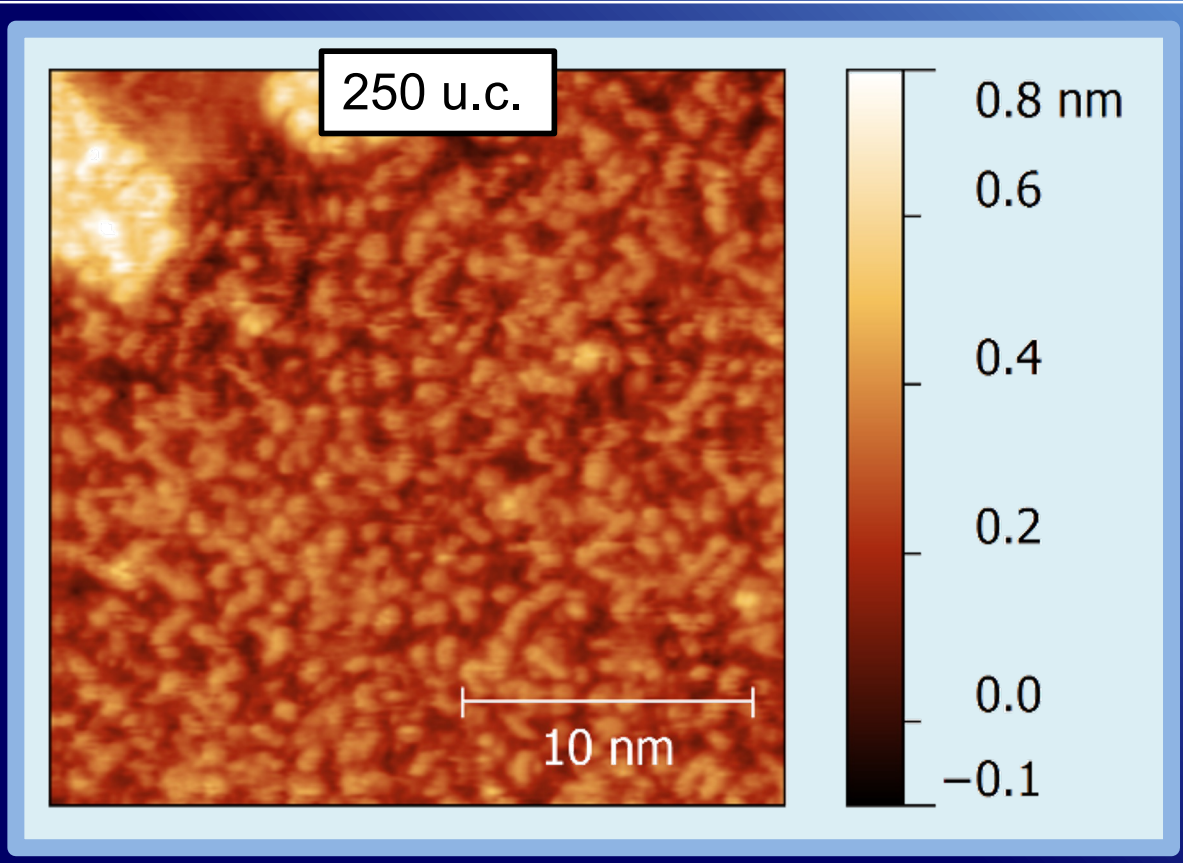




- Larger islands
- Up to 3 u.c. layers can be seen
- Two terminations: *ordered* and *disordered*.

250 u.c. on $SrTiO_3$

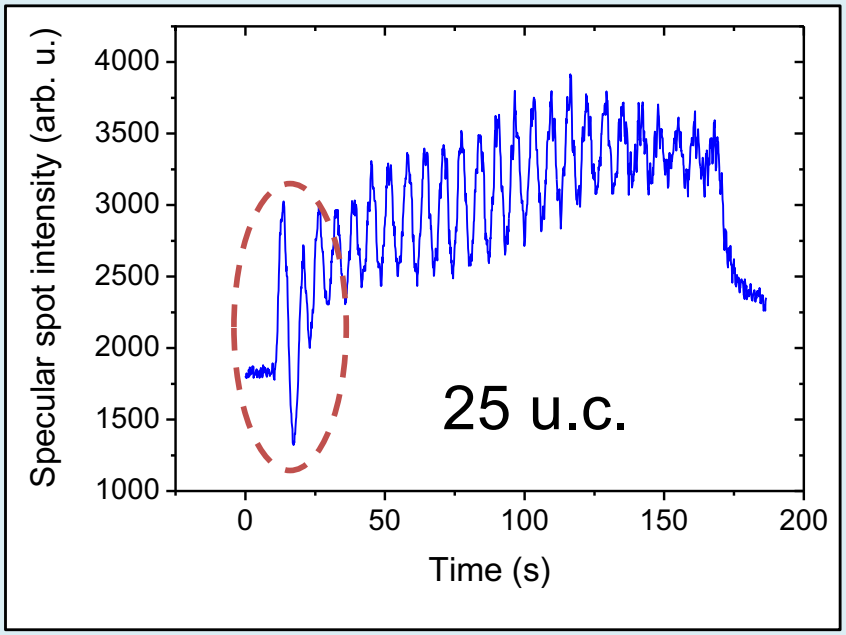


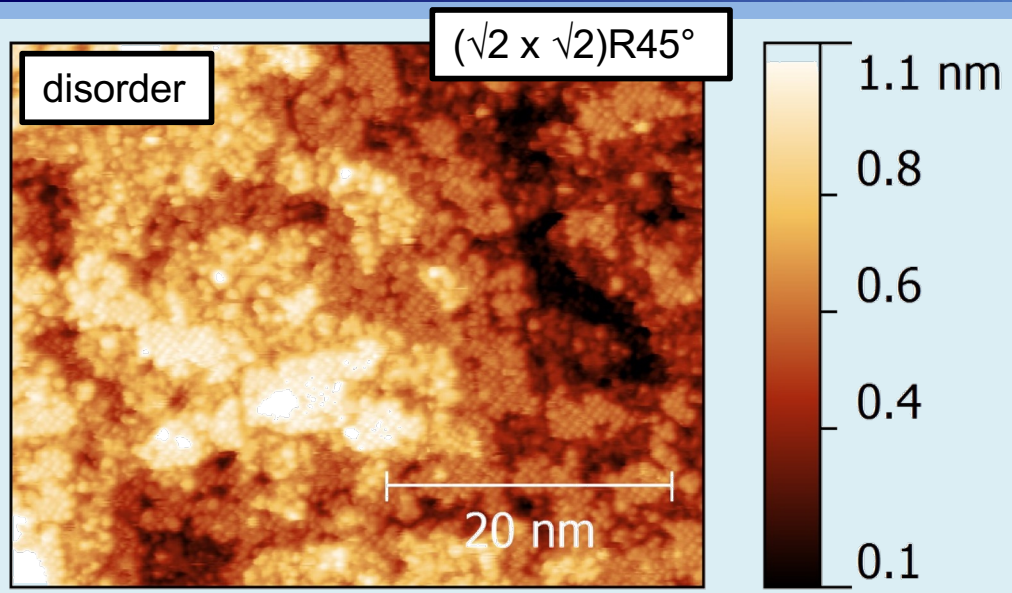


- Up to 3 u.c. layers can be seen
- One termination - *disordered*
- Nearly perfects layer-by-layer growth

Stable layer-by-layer growth on A/B-terminated NGO substrates

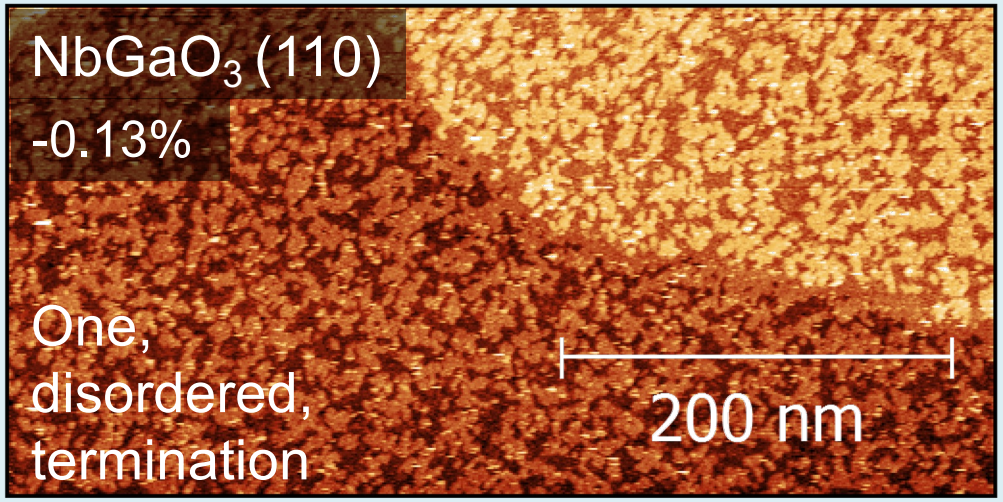
$NbGaO_3$ (110), lattice mismatch -0.13%

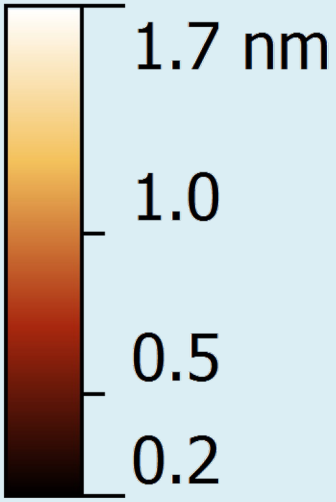


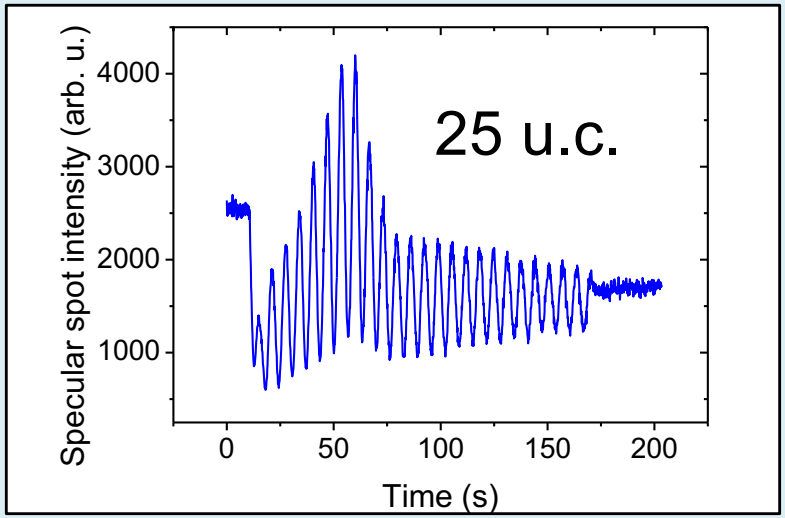


- The surface is doubly-terminated.
- A and B terminations are approximately equally present.

25 u.c. on B-terminated NGO substrate – single termination

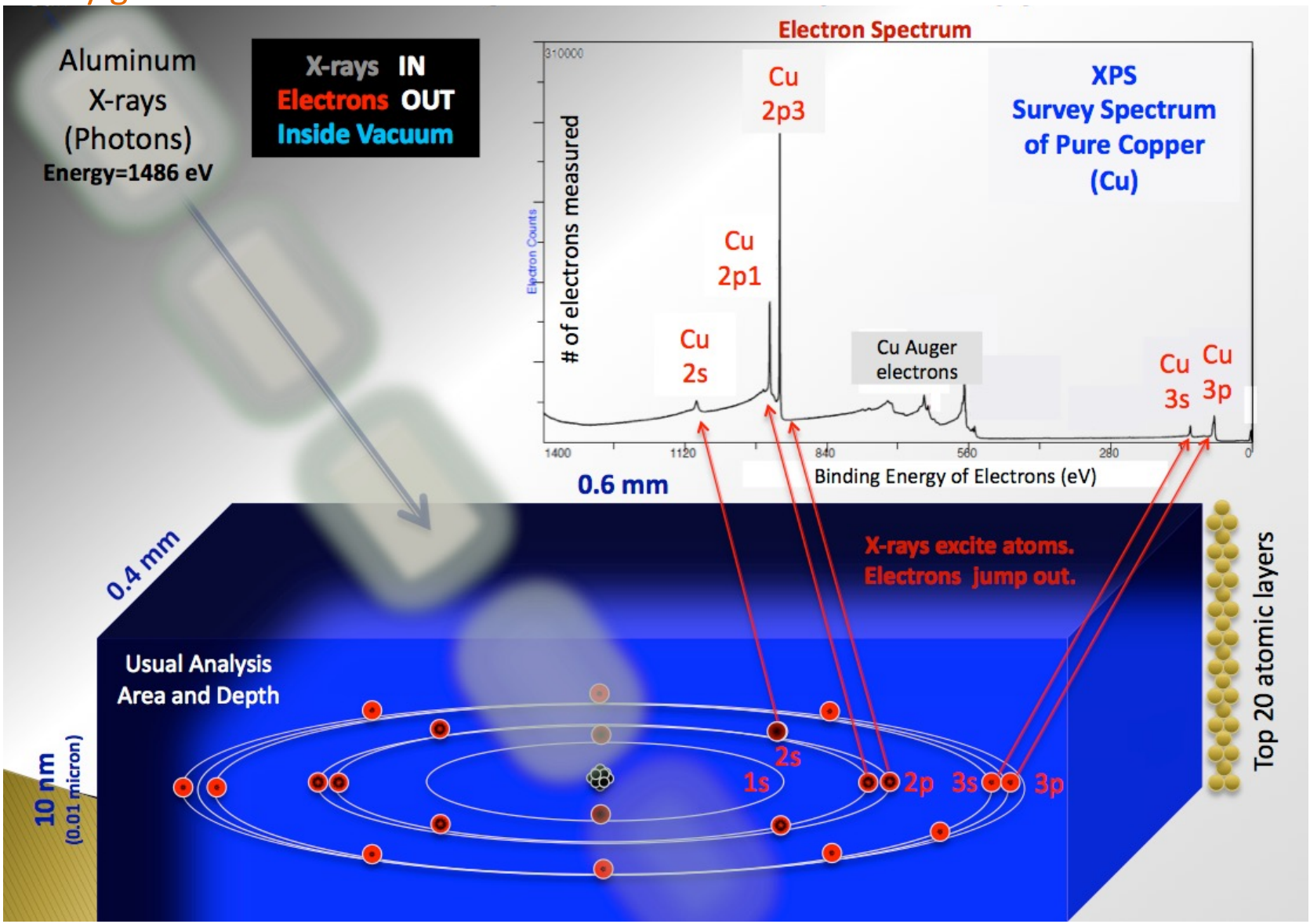




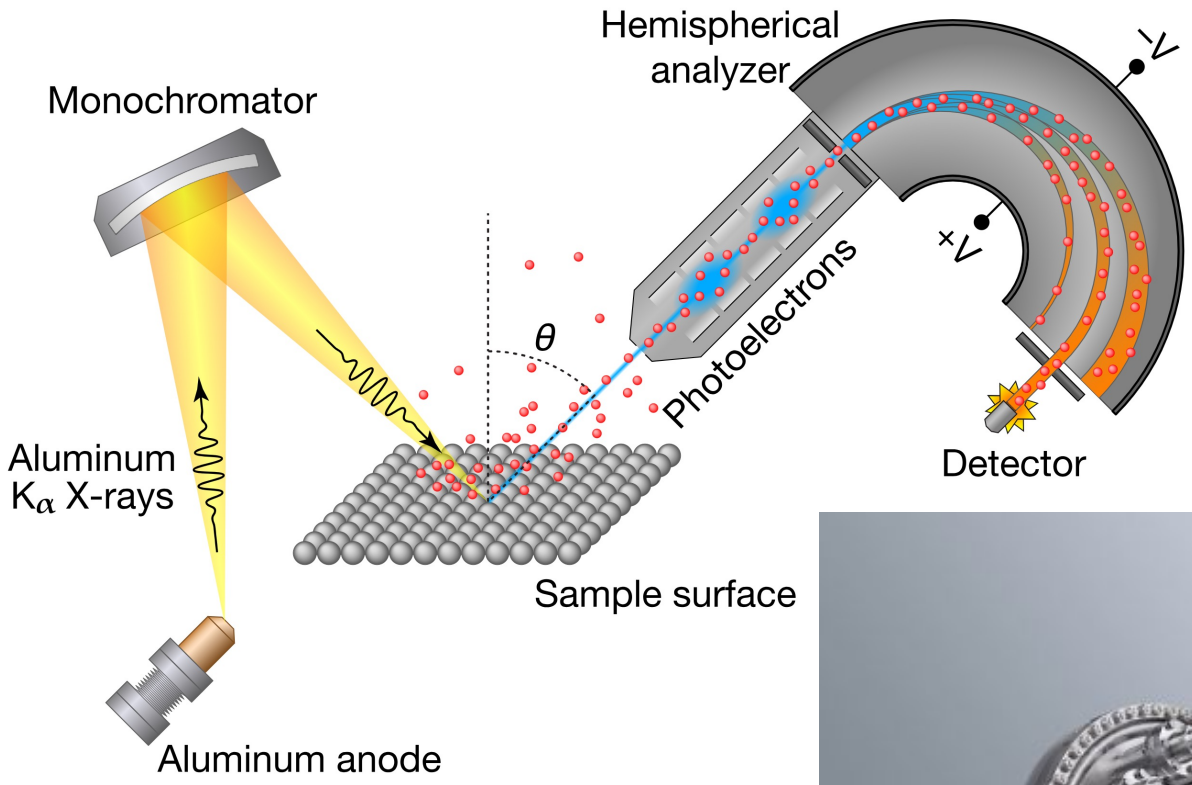


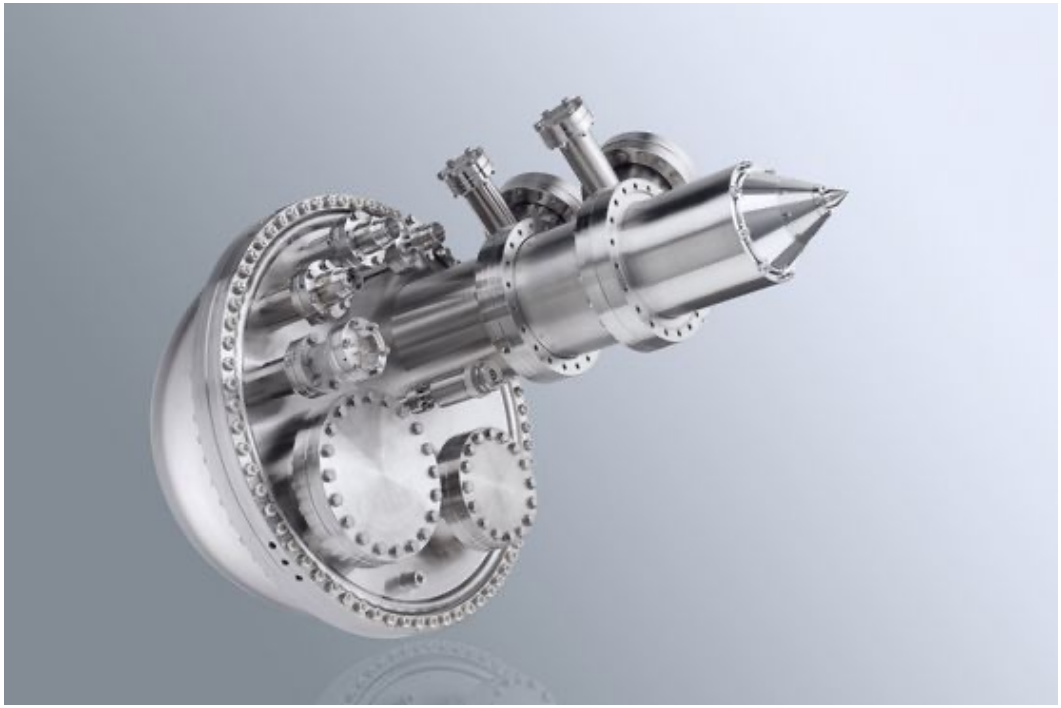
- The surface is single-terminated
- The termination is disordered, =>
- ***Disordered termination is B-termination***

XPS: X-ray Photo-electron Spectroscopy



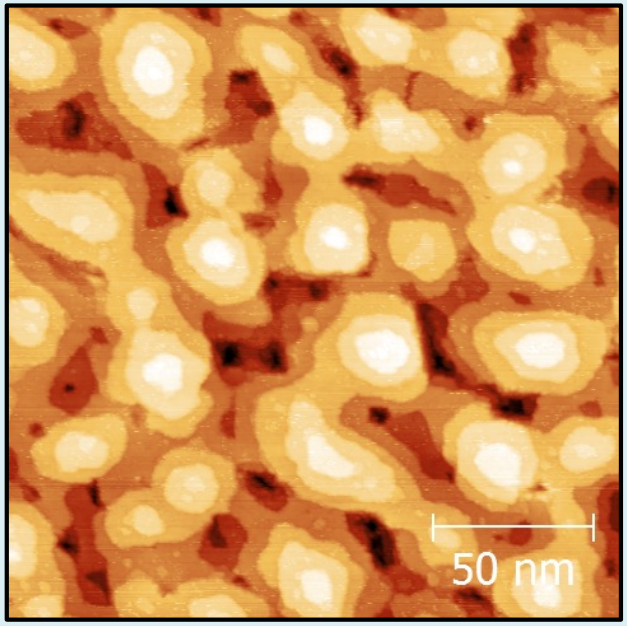
XPS: X-ray Photo-electron Spectroscopy

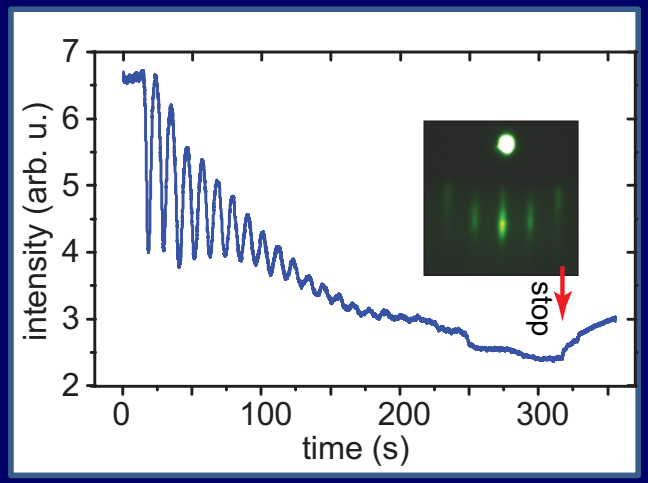


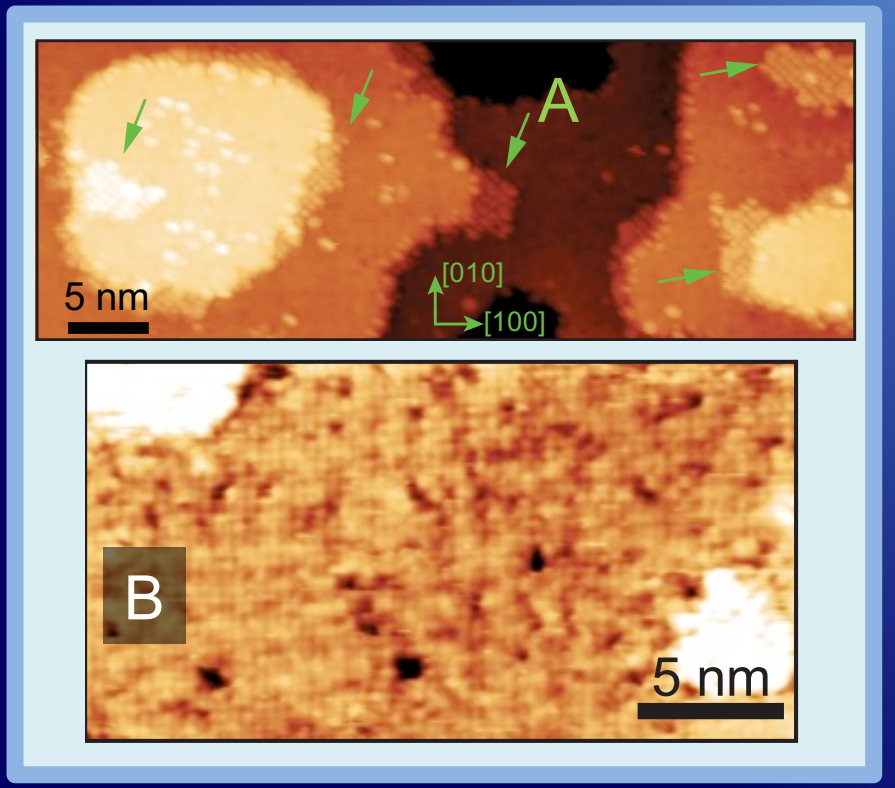


https://grimmgroup.net/research/xps/background/

Terminations: Mounded structure

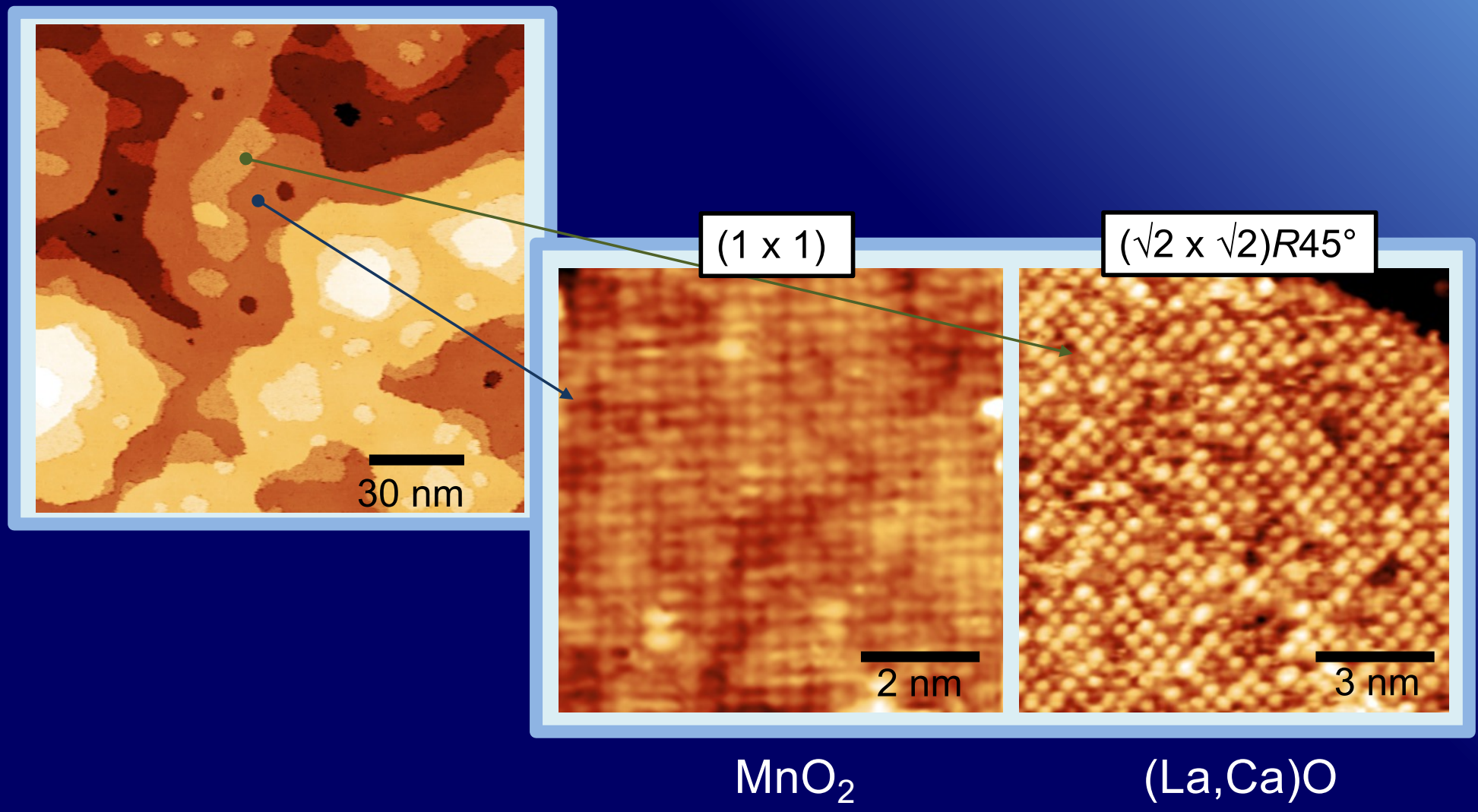




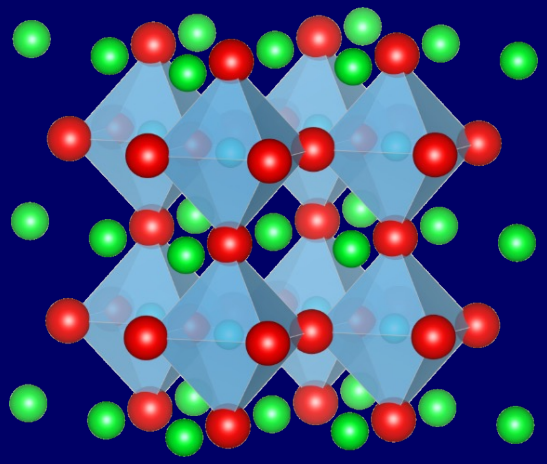


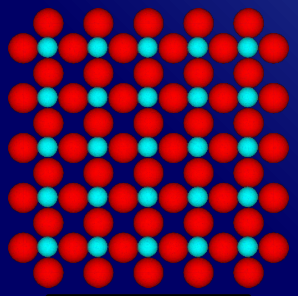
- A: (La,Ca)O
- B: MnO_2

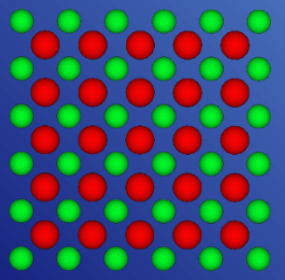
High-resolution images

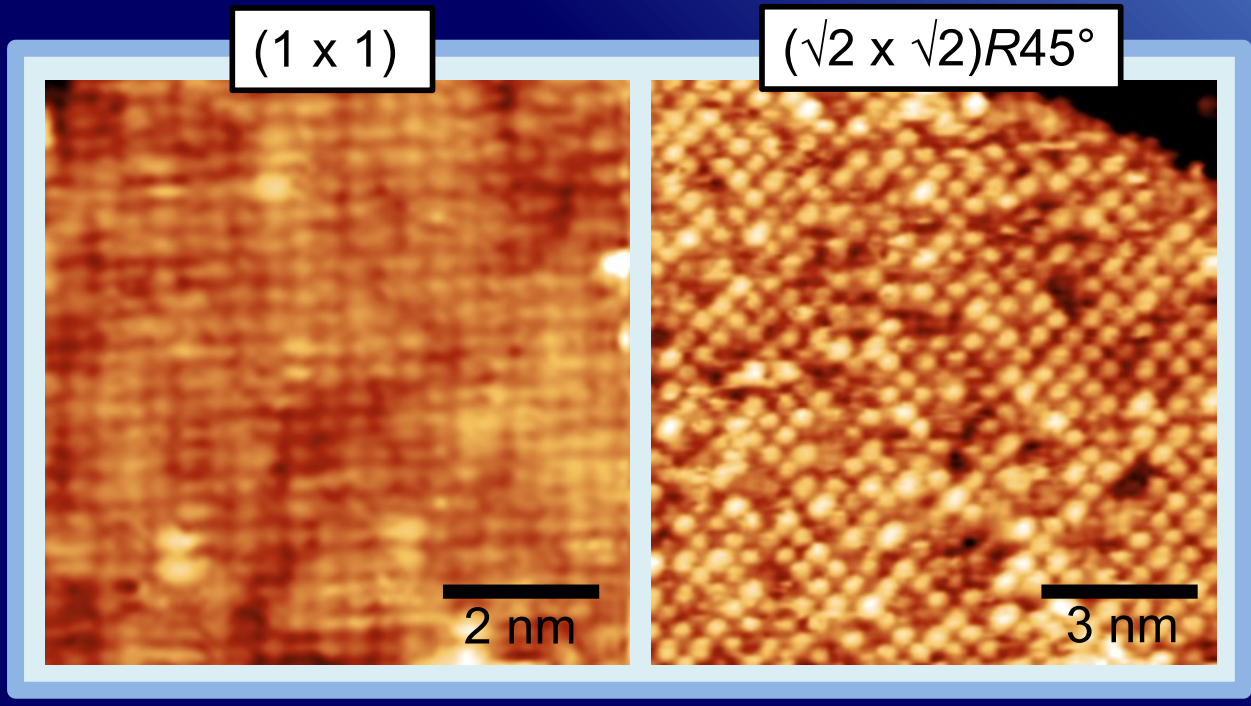


Meaning of the patterns





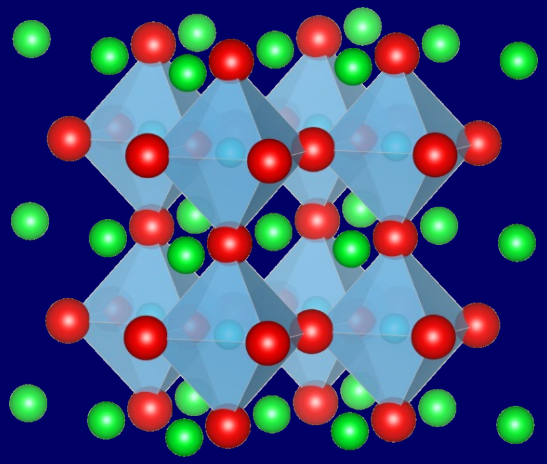


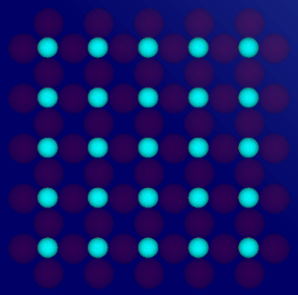


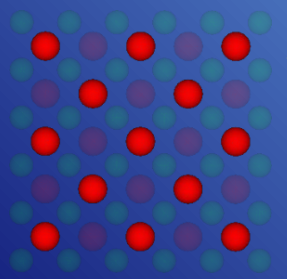
MnO_2

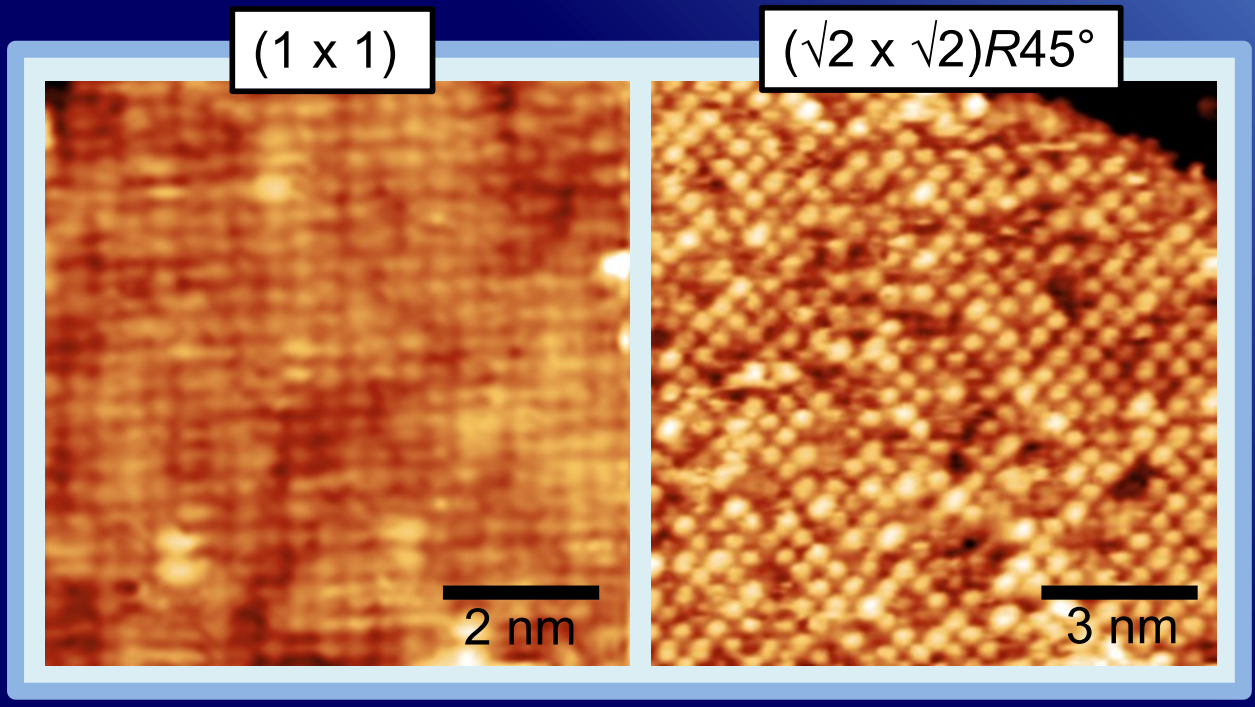
(La,Ca)O

Meaning of the patterns



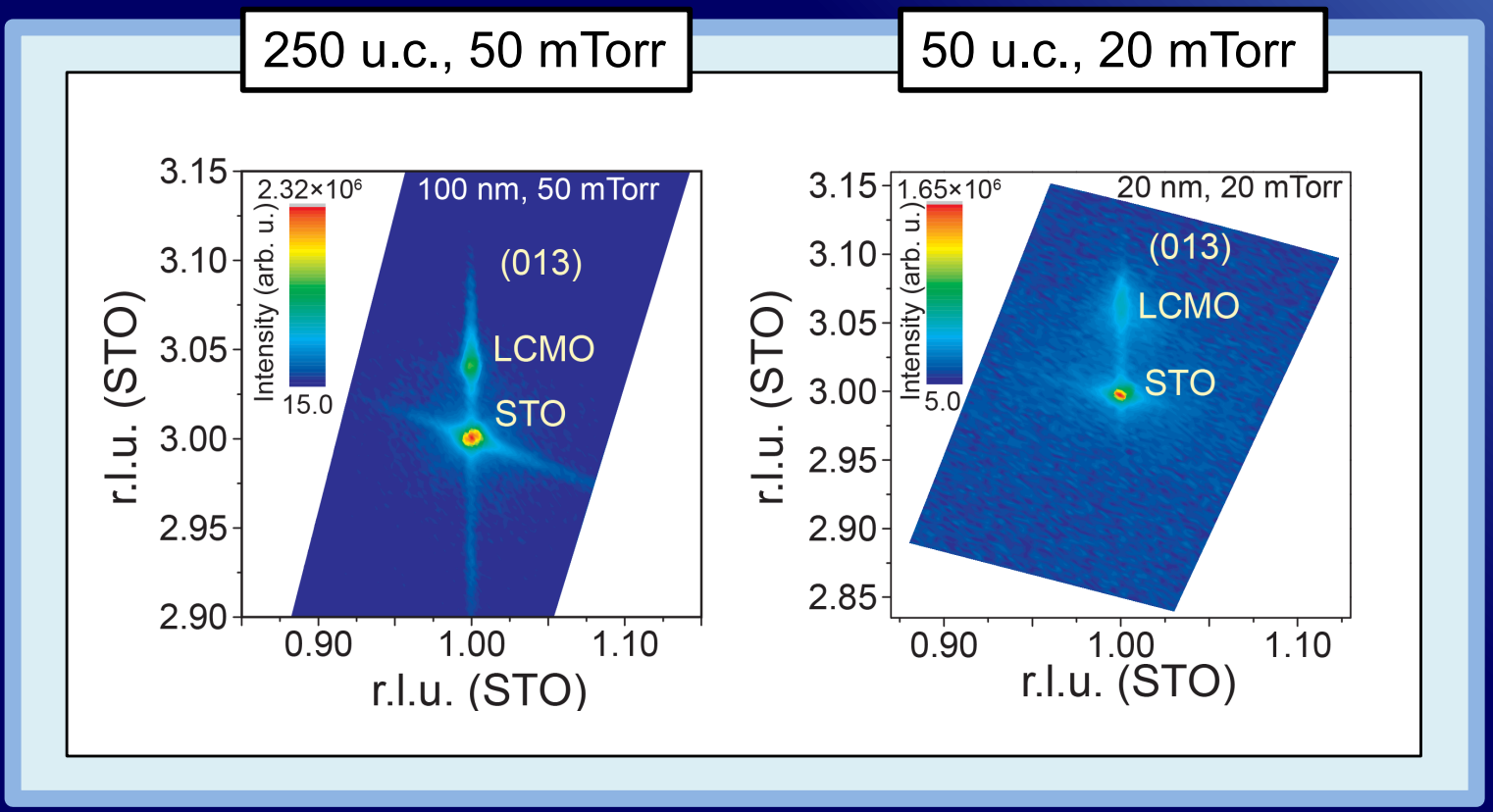






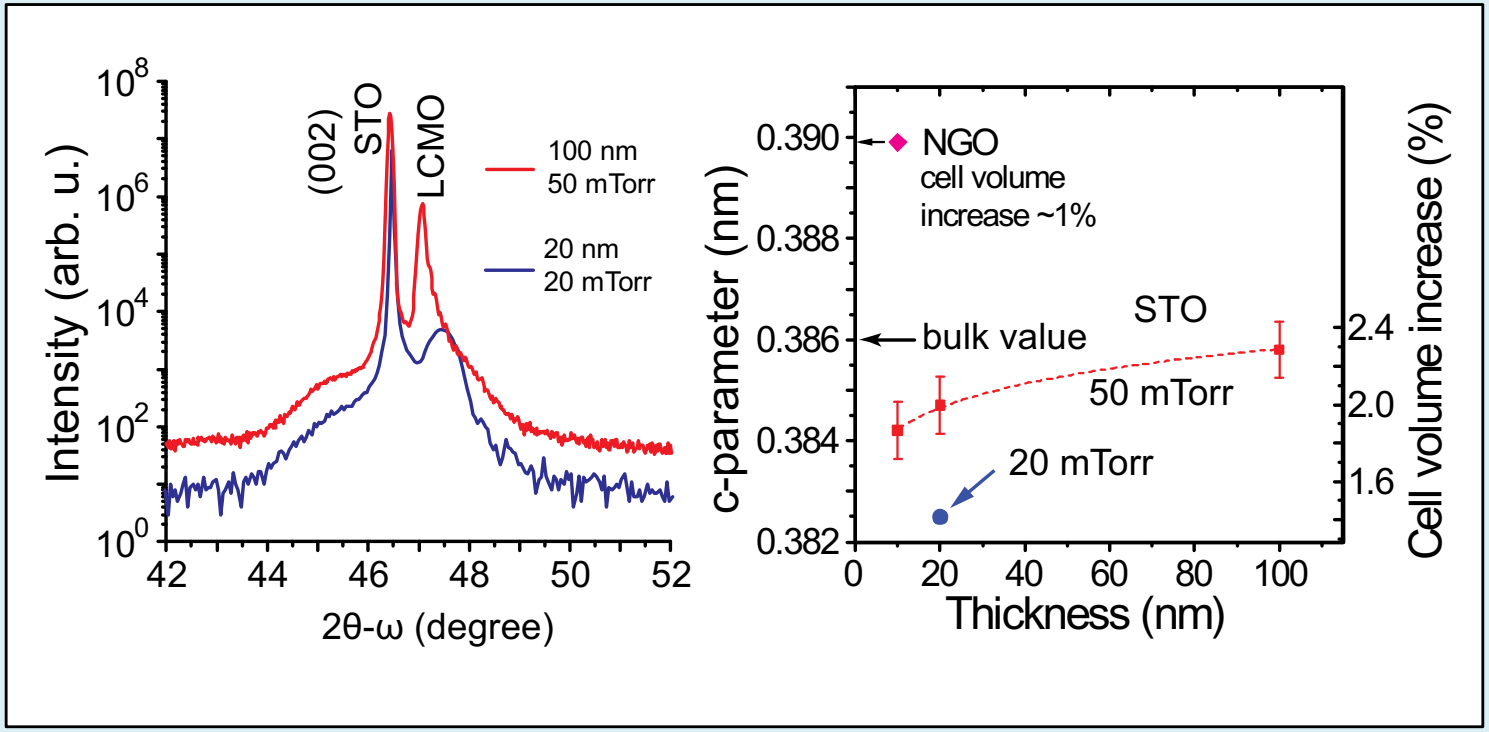
MnO_2 (La,Ca)O

XRD: q-space maps



All films are coherently strained to the substrate in plane

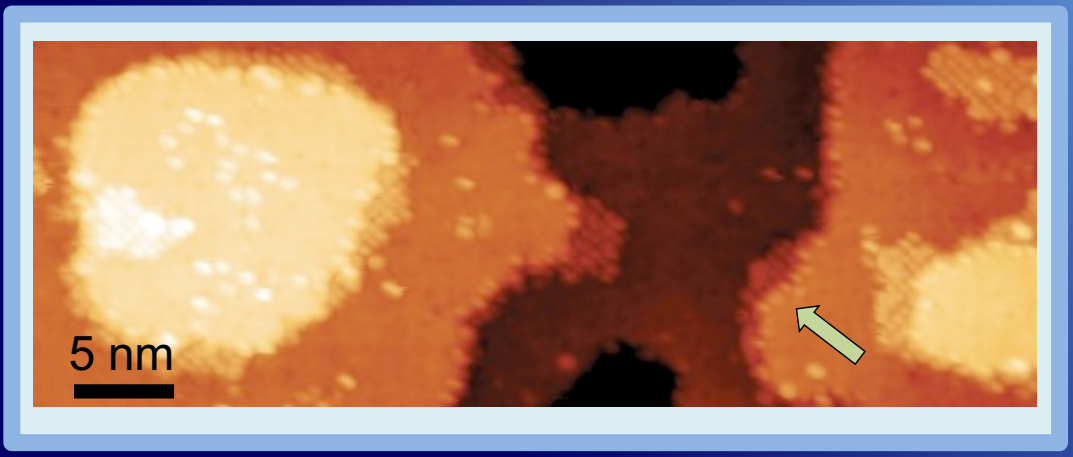
Out-of-plane lattice parameter



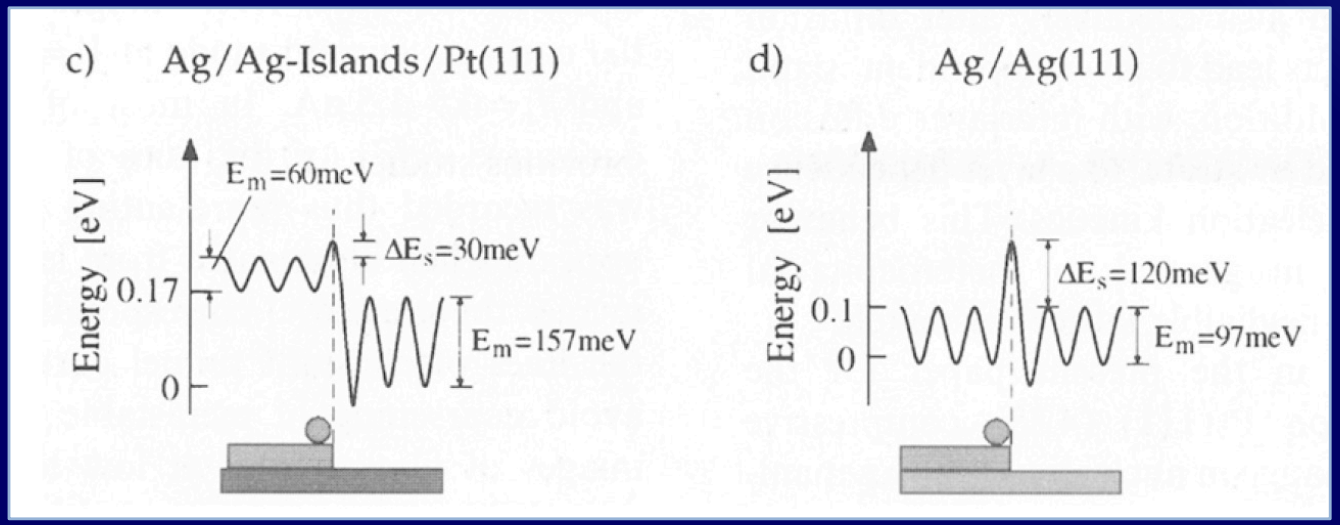
- 50 mTorr: out-of-plane lattice parameter increases with thickness
- 20 mTorr: film lattice is noticeably more compressed out-of-plane

Interpretation of the growth evolution

- Dependence of the barrier for interlayer adatom transport (Ehrlich-Schwoebel barrier) on strain.

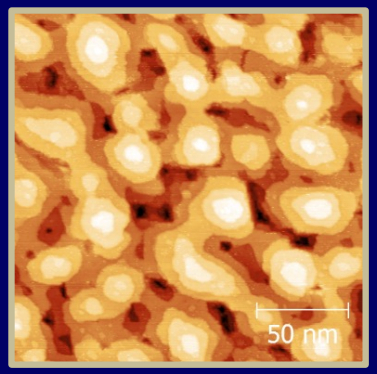


Ag-on-Pt (111) as an example



K. Bromann *et al.*, *PRL* 75, 677 (1995)

Cause-effect relationships



P_{O2}

Type of defects

substrate

Tensile strain

20 mTorr

50 mTorr

Reduced c-axis

Relaxed c-axis

Increased EB barrier

Reduced EB barrier

Mound instability

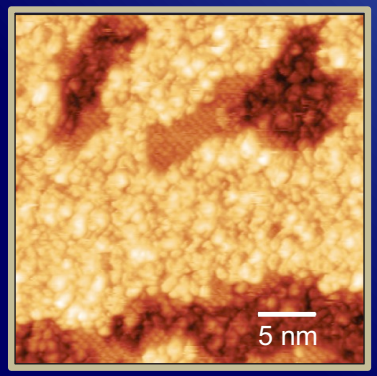
2D growth

Cationically *stoichiometric* terminations

Cationically *non-stoichiometric* B-termination

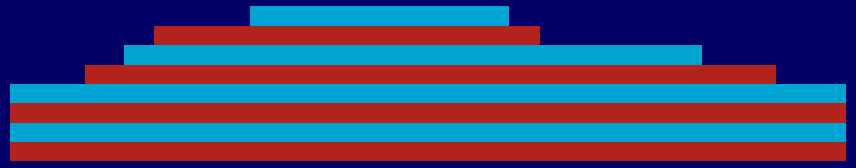
Increased adatom mobility

Reduced adatom mobility

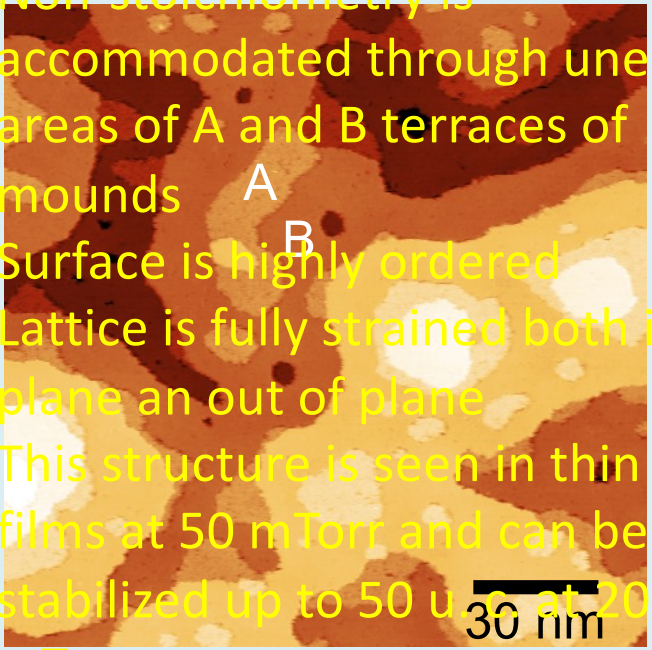


Film structure models

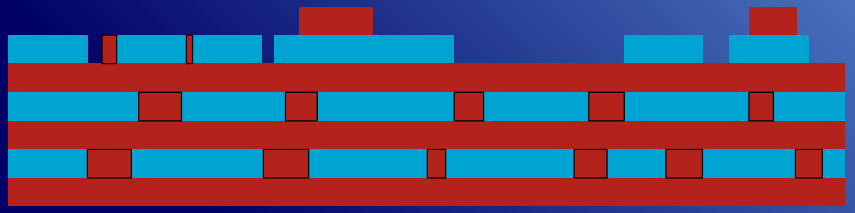
Mounded structure



- Non-stoichiometry is accommodated through unequal areas of A and B terraces of mounds
- Surface is highly ordered
- Lattice is fully strained both in plane an out of plane
- This structure is seen in thin films at 50 mTorr and can be stabilized up to 50 u. c. at 20 mTorr



Layer-by-layer growth



- Non-stoichiometry is accommodated via anti-site cation defects in the B sublattice
- Surface is disordered
- Lattice expands in the out-of-plane direction
- This structure is seen in all films >25 u. c. at 50 mTorr
- Apparent adatom mobility increases with increasing thickness