Pulsed Laser Deposition

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Nanomaterials for Energy Conversion and Storage

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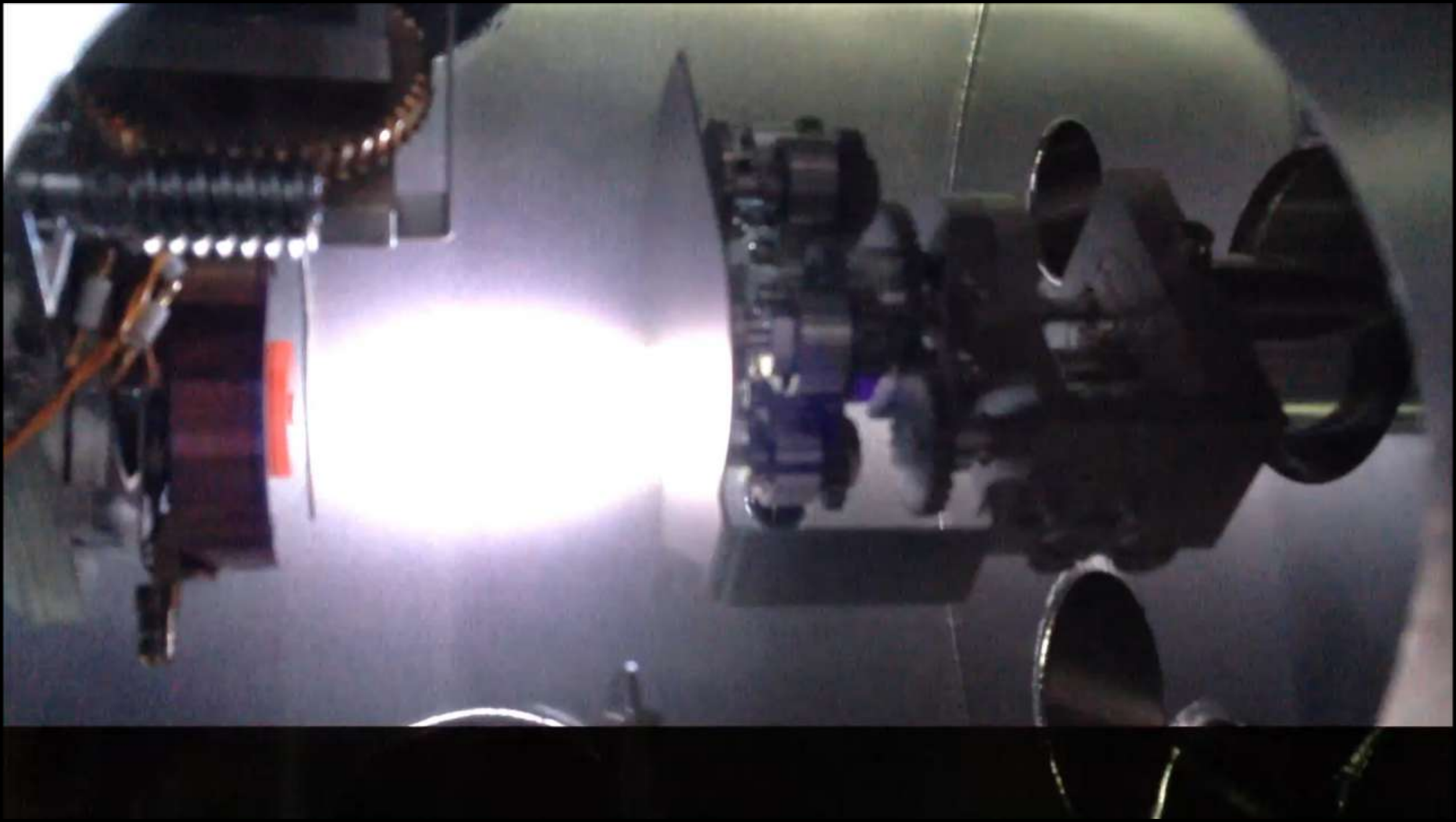
Pulsed Laser Deposition



Pulsed Laser Deposition (PLD) equipment

for thin film material science and nanotechnology

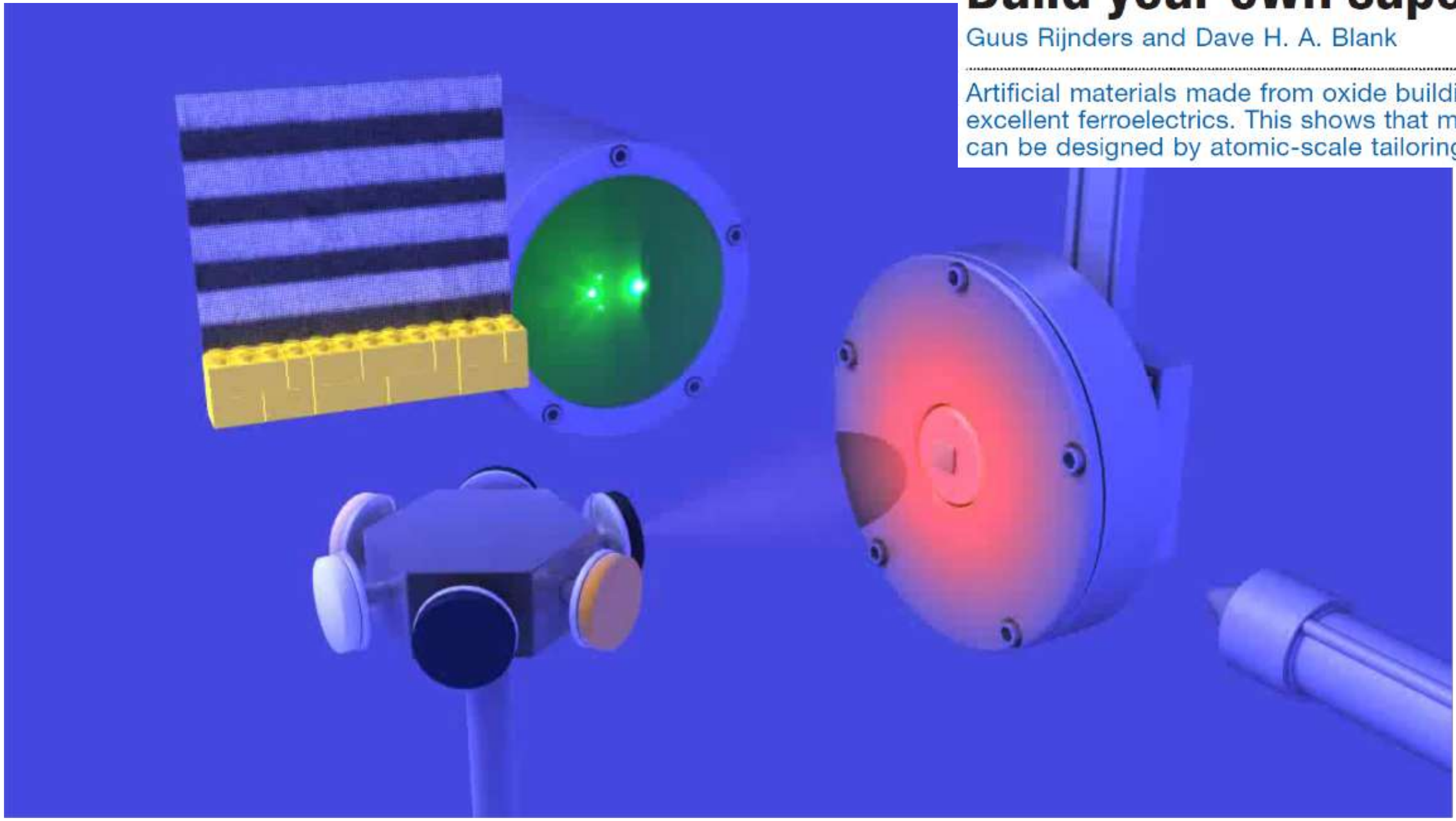
NATURE | VOL 433 | 27 JANUARY 2005 |

Materials science

Build your own superlattice

Guus Rijnders and Dave H. A. Blank

Artificial materials made from oxide building blocks turn out to be excellent ferroelectrics. This shows that materials with specific properties can be designed by atomic-scale tailoring of their composition.



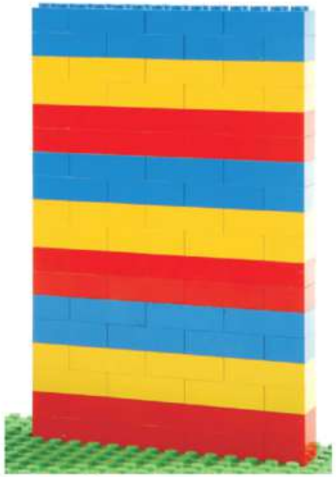


Figure 1 Building regulation — a Lego version of the superlattice structure shown in Fig. 1d (page 396)[2]. The base constitutes the substrate, including the $SrRuO_3$ electrode, and the Lego wall is made of layers of three different bricks: $SrTiO_3$ (red), $BaTiO_3$ (yellow) and $CaTiO_3$ (blue). Lee *et al.*[2] demonstrate that an artificial material with favourable ferroelectric properties can be constructed by using these three perovskite building blocks.

Materials for Oxide Electronics

Exploiting the wide range of physical properties available in (complex) oxide materials

(high K) Dielectrics for CMOS:
Al_2O_3-HfO_2-ZrO_2, $Ba_xSr_{1-x}O_y$

Magnetic (semi)conductors (ferromagnetic tunnel junctions):
$SrRuO_3$, Sr_2FeMoO_6

CMR and related materials:
$La_{0.7}(Ca,Sr)_{0.3}MnO_3$ $LaCaCu_3Mn_4O_{12}$

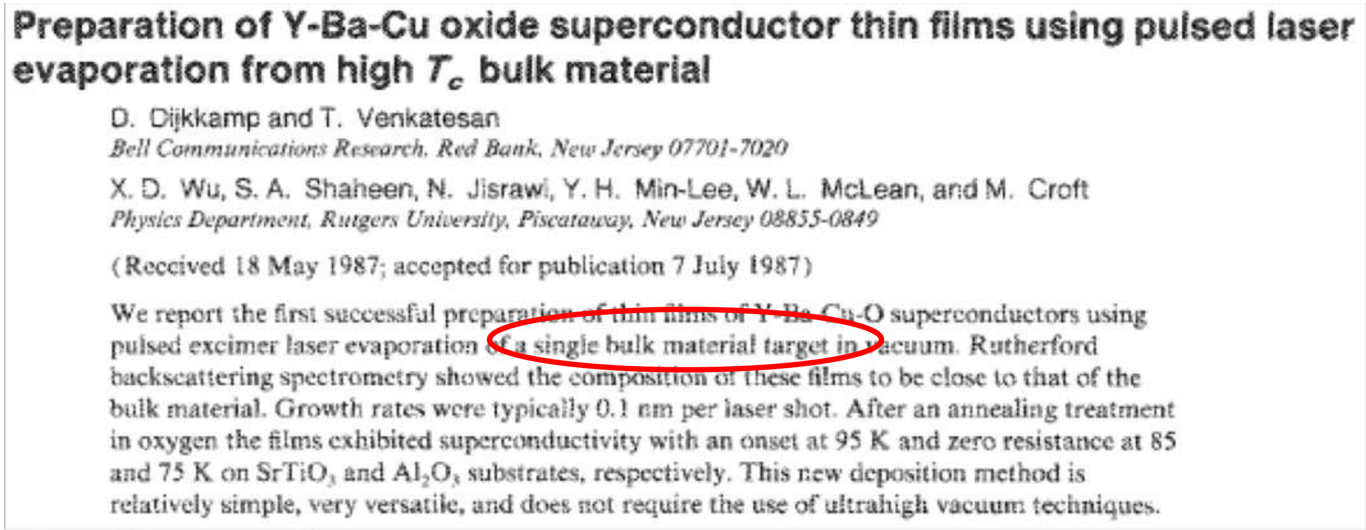
Non-linear optical and transparent conducting oxides:
$Sr_2CuO_xLa_{0.7}Ca_{0.3}MnO_3$, ITO, ZnO

Ferroelectric materials, multiferroics:
$BiFeO_3$, $(Ba,Sr)TiO_3$, Niobates, PZT

Superconducting materials:
YBaCuO, BiSrCaCuO

Important innovations for epitaxial complex oxide growth

(near)stoichiometric transfer of complex oxides



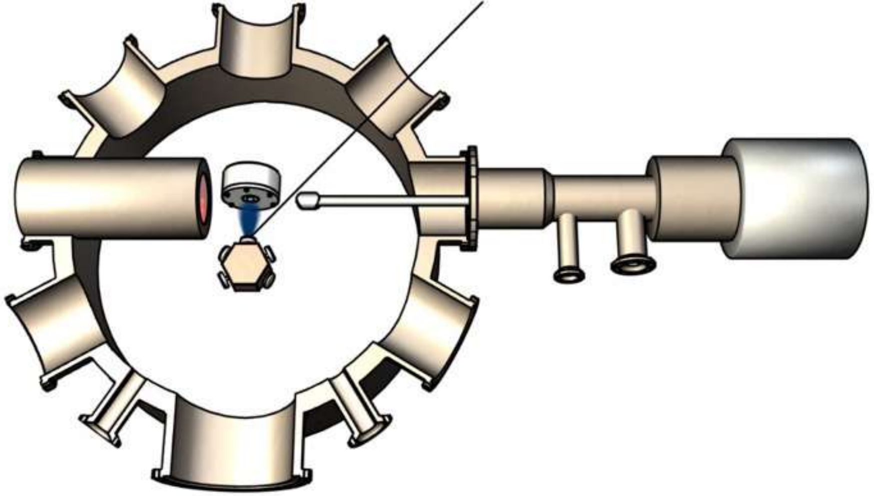
Preparation of Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high T_c bulk material

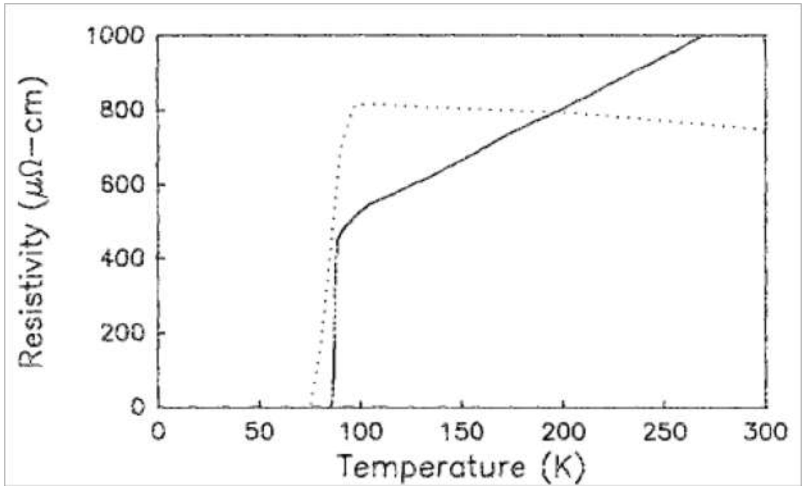
D. Dijkkamp and T. Venkatesan
Bell Communications Research, Red Bank, New Jersey 07701-7020

X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft
Physics Department, Rutgers University, Piscataway, New Jersey 08855-0849

(Received 18 May 1987; accepted for publication 7 July 1987)

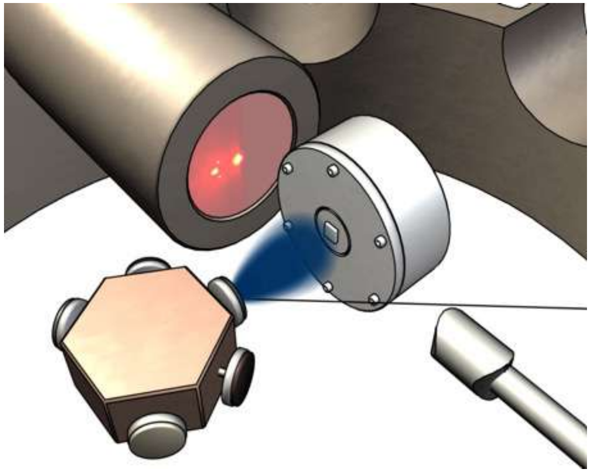
We report the first successful preparation of thin films of Y-Ba-Cu-O superconductors using pulsed excimer laser evaporation of a single bulk material target in vacuum. Rutherford backscattering spectrometry showed the composition of these films to be close to that of the bulk material. Growth rates were typically 0.1 nm per laser shot. After an annealing treatment in oxygen the films exhibited superconductivity with an onset at 95 K and zero resistance at 85 and 75 K on $SrTiO_3$ and Al_2O_3 substrates, respectively. This new deposition method is relatively simple, very versatile, and does not require the use of ultrahigh vacuum techniques.





Deposition technique : Pulsed laser deposition

Special features of Pulsed Laser Deposition



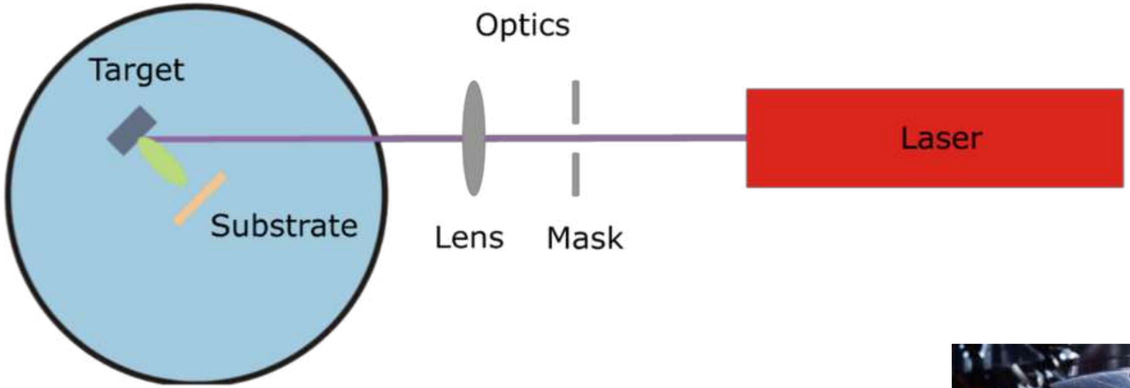
1. Stoichiometric transfer from target to film
2. Tunable kinetic energy of deposited particles
3. High supersaturation during deposition pulse
4. Instantaneous deposition

For complex oxides:
$E_A \sim 0.5 - 2$ eV
$T \sim 800 - 1100$ K
$t_{deposition} \sim 100\ \mu\text{sec}$

$$t_D = \nu^{-1} exp\left(\frac{E_A}{k_B T}\right)$$

$t_D > t_{deposition}$

Thin film growth; PLD parameters

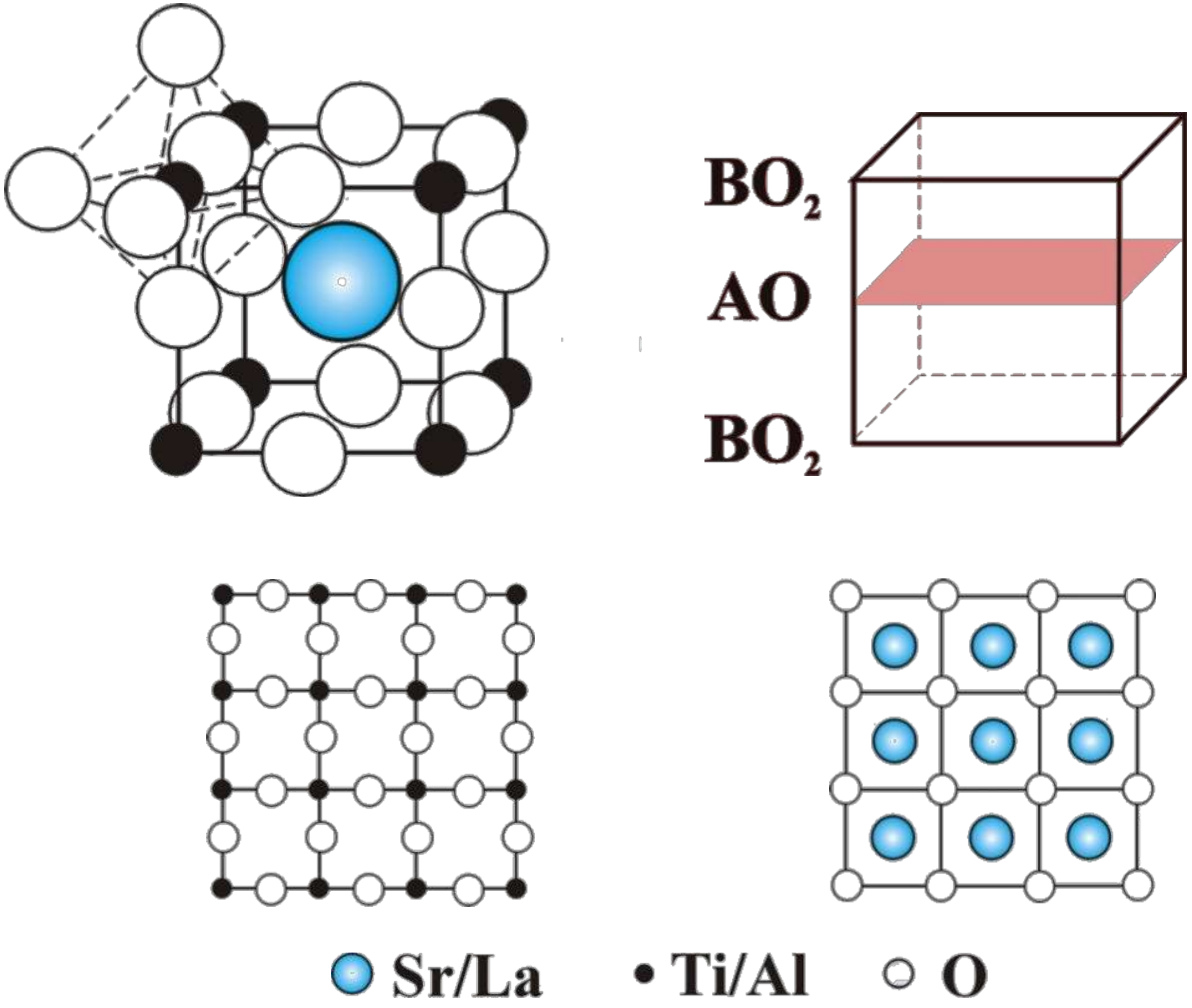


Growth parameters:

- Laser energy density (J/cm^2), ablation spot
- Pulse frequency
- Background gas
- Substrate temperature
- Spot size and shape

Control over parameters for reproducibility!

Schematic view of the ABO_3 perovskite structure

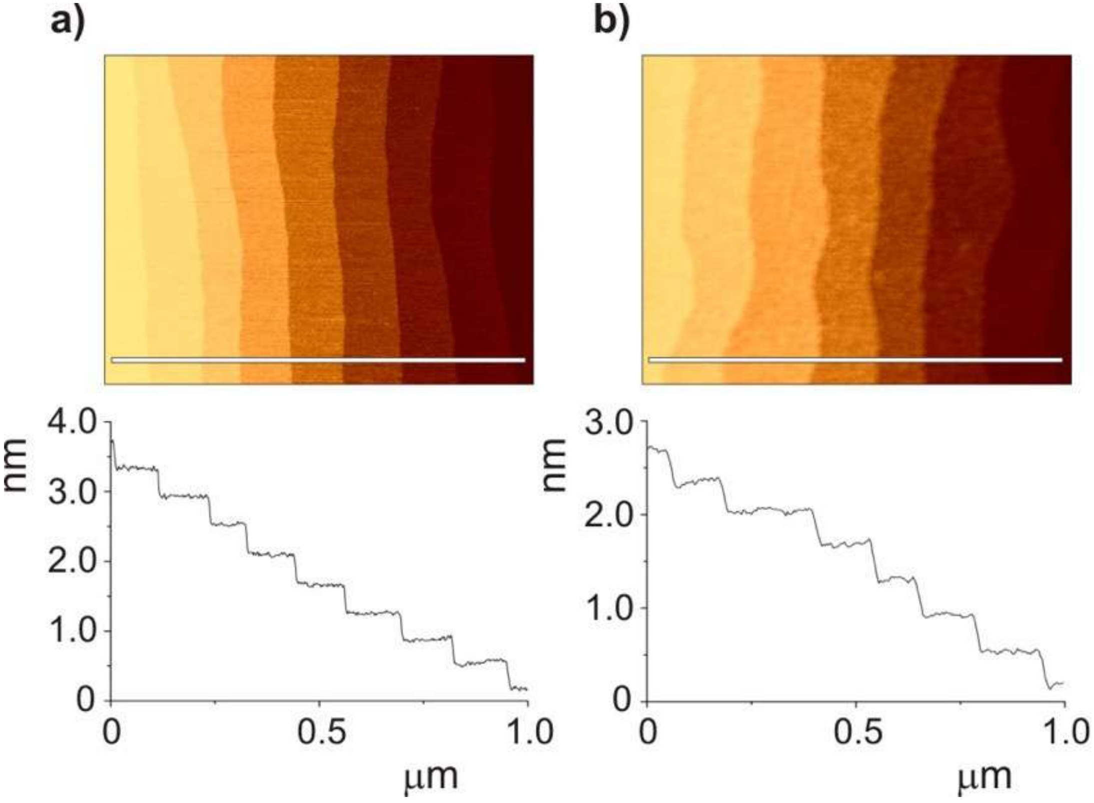


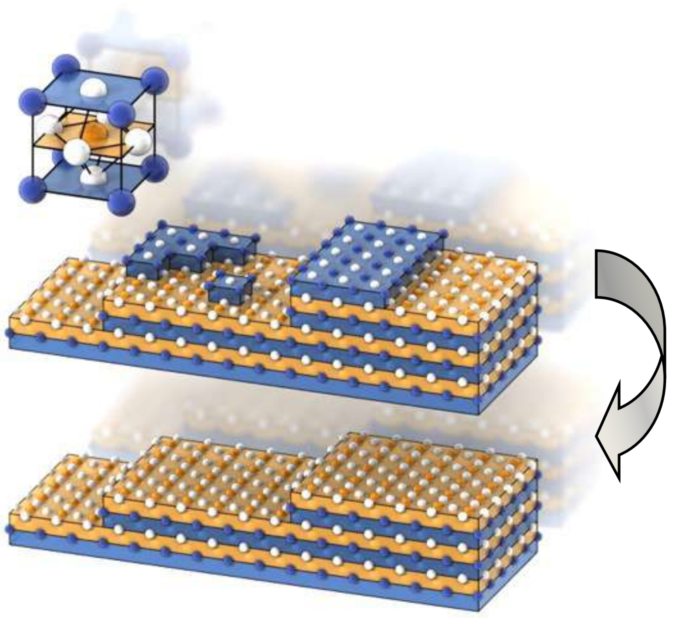
Cubic
$LaAlO_3$: 3.780 Å
$SrTiO_3$: 3.905 Å
$SrRuO_3$: 3.93 Å
$PbTiO_3$: 3.90Å

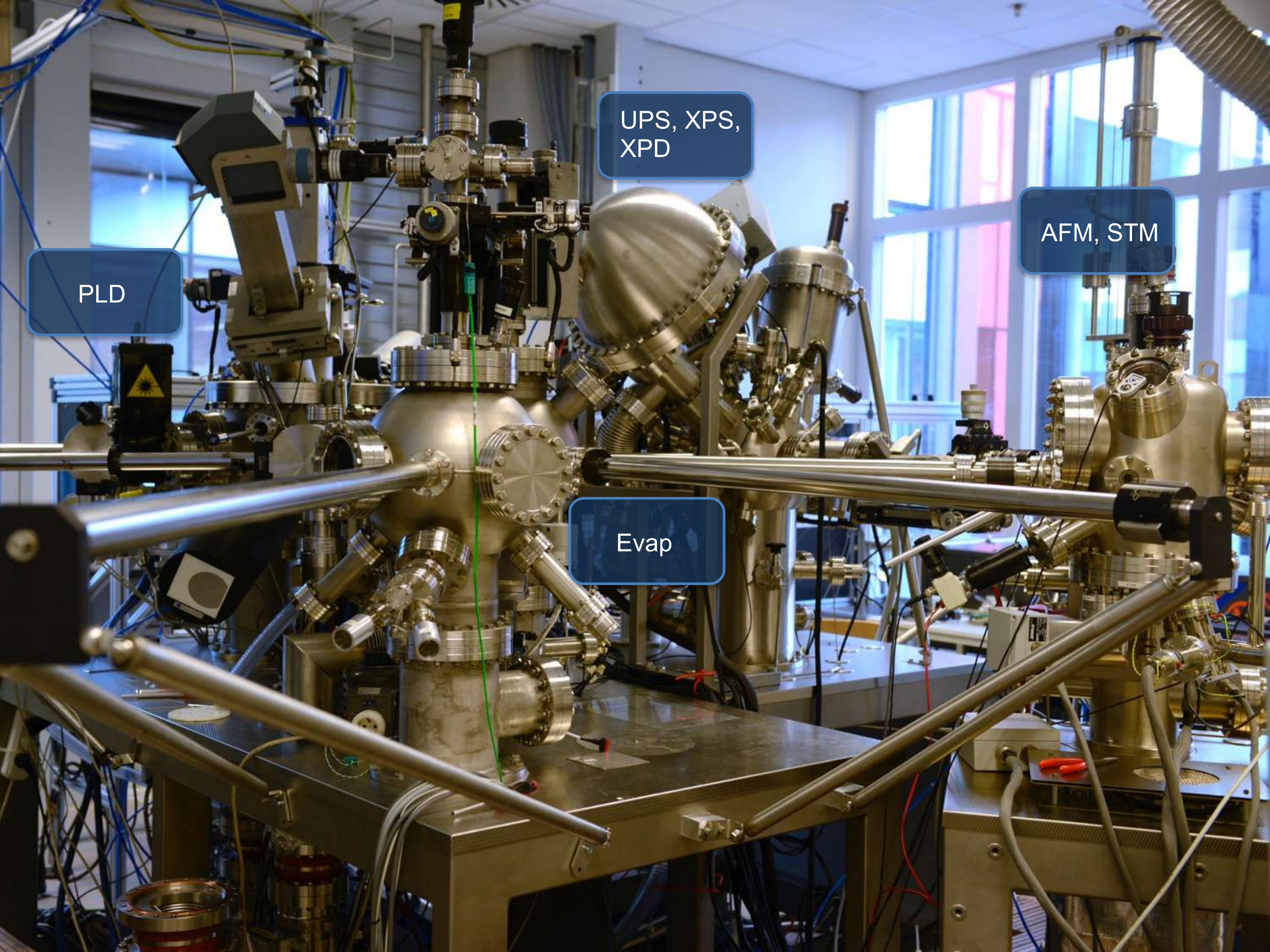
Single terminated substrates

TiO_2-terminated $SrTiO_3$: HF-acid/anneal treatment
G. Koster *et al.*, APL 73, 2920 (1998)

SrO-terminated $SrTiO_3$:
Subsequent deposition of single SrO layer by pulsed laser interval deposition
G. Koster *et al.*, APL 74, 3729 (1999)





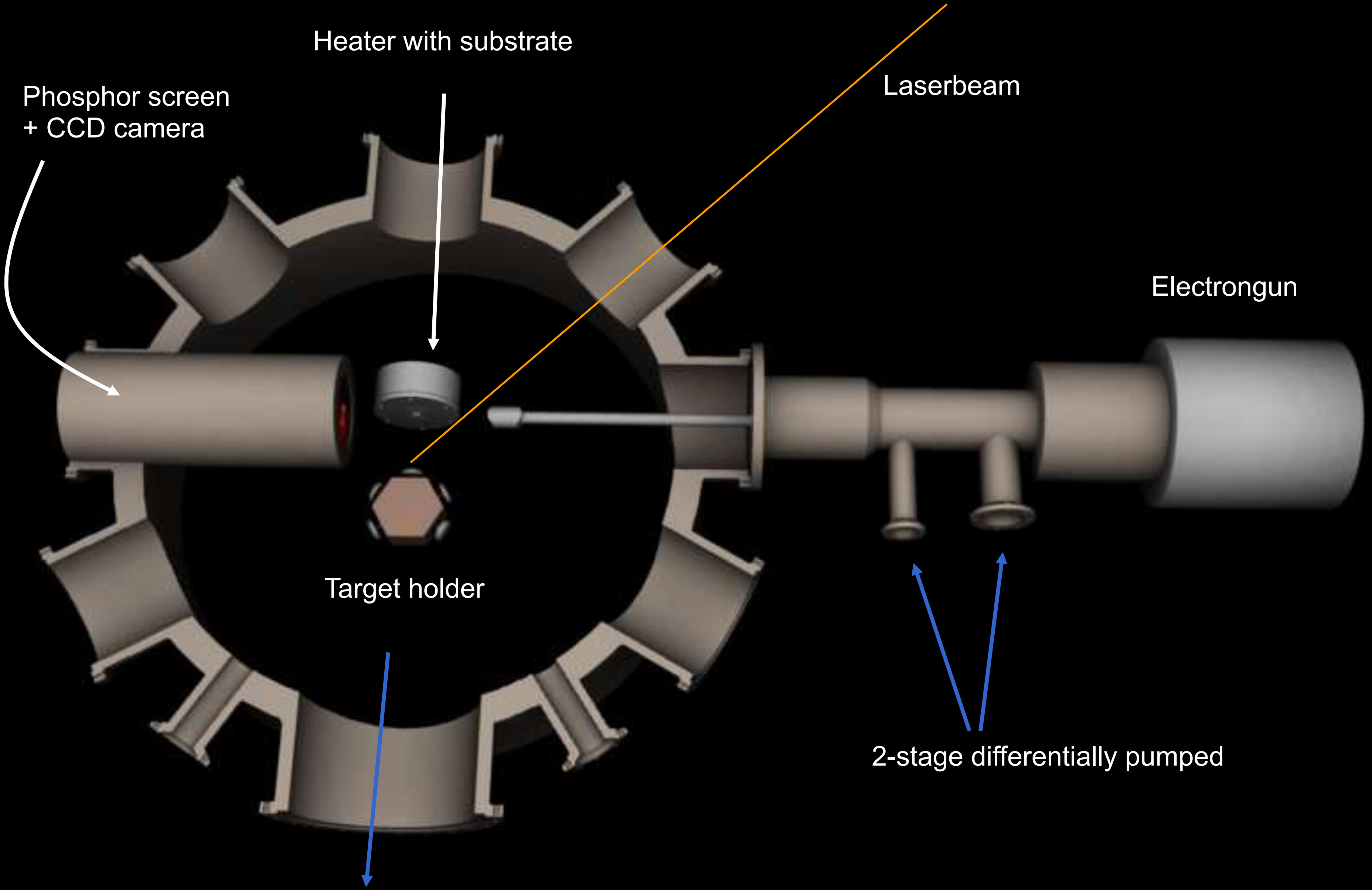


UPS, XPS, XPD

AFM, STM

PLD

Evap



Heater with substrate

Laserbeam

Phosphor screen
+ CCD camera

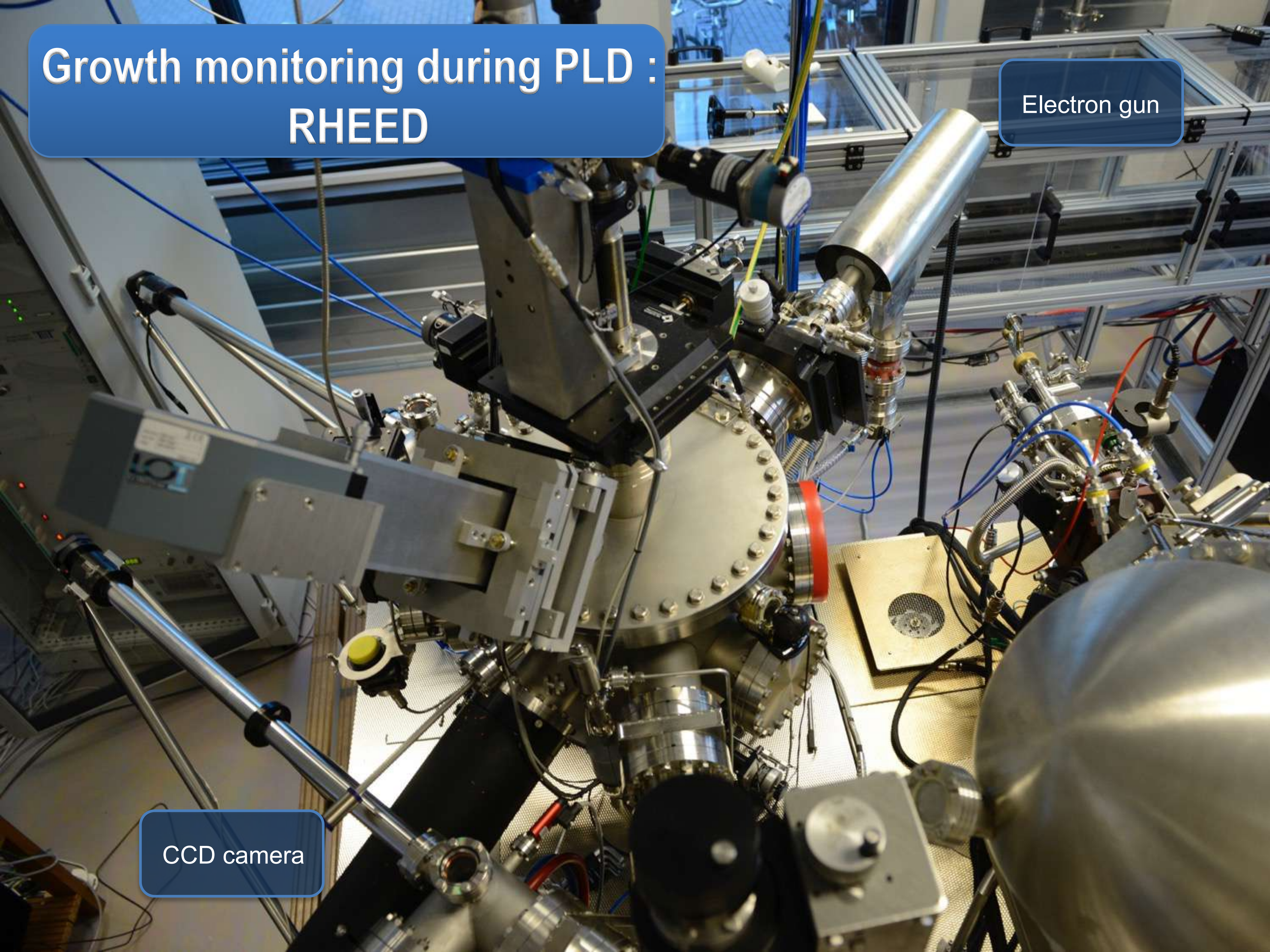
Electrongun

Target holder

2-stage differentially pumped

to main turbo pump

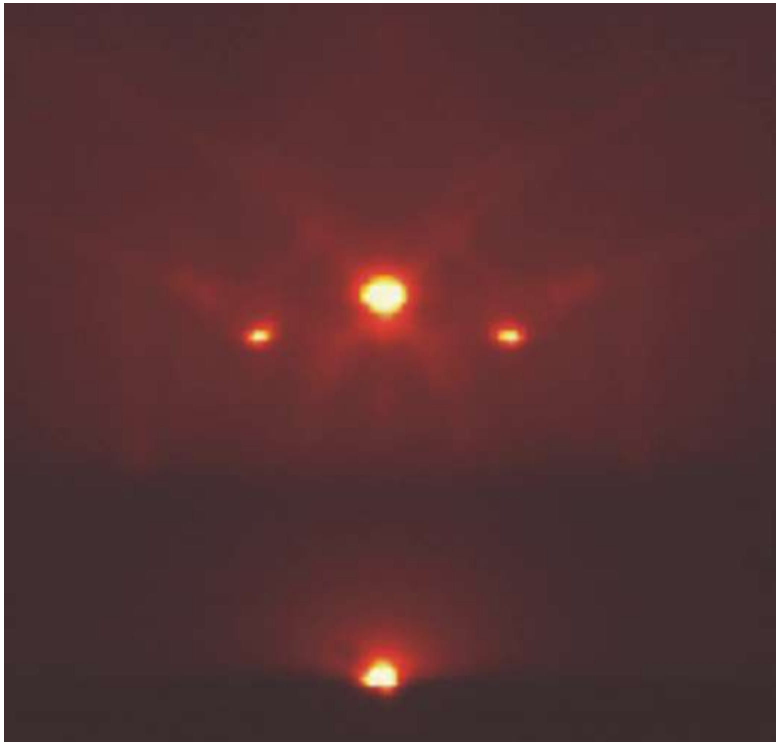
Growth monitoring during PLD : RHEED



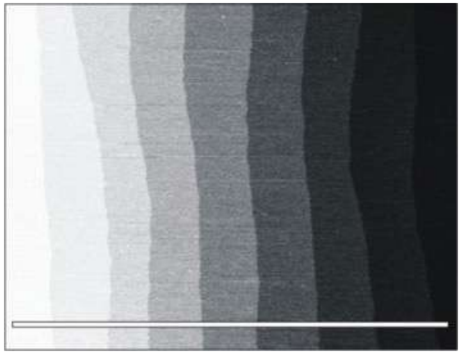
Electron gun

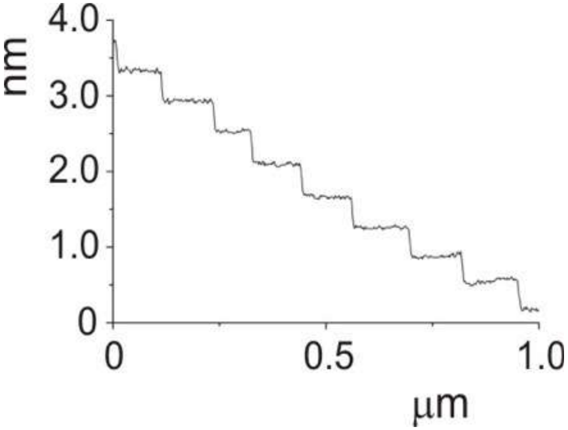
CCD camera

RHEED pattern

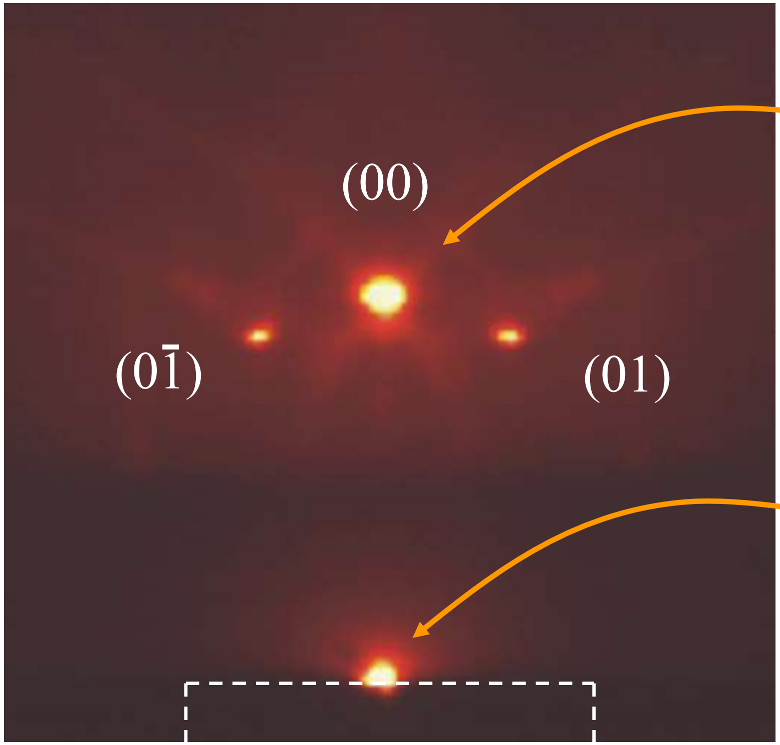


TiO_2-terminated $SrTiO_3$ substrate



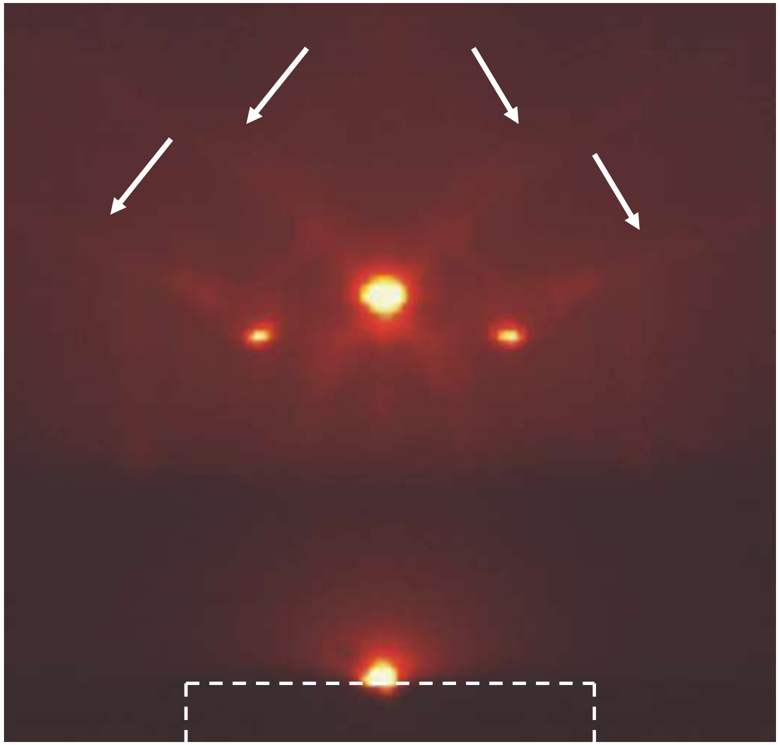


RHEED : Reflective High-Energy Electron Diffraction



Specular spot

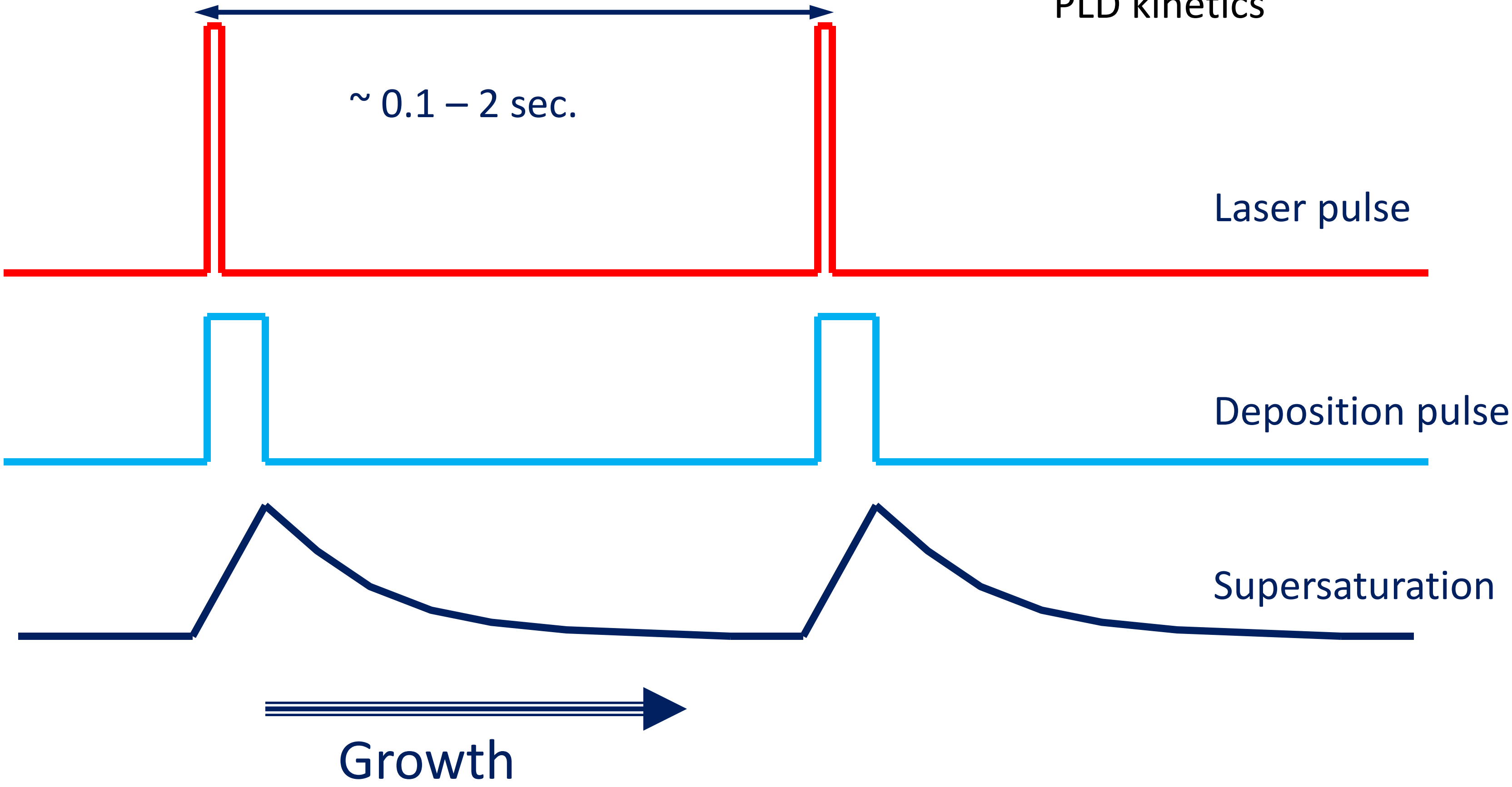
Direct beam



Kikuchi lines :

Indicating a
2-dimensional flat surface

PLD kinetics


~ 0.1 – 2 sec.

Laser pulse

Deposition pulse

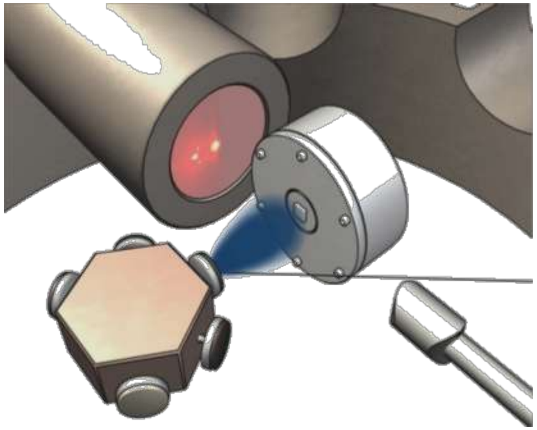
Supersaturation

Growth

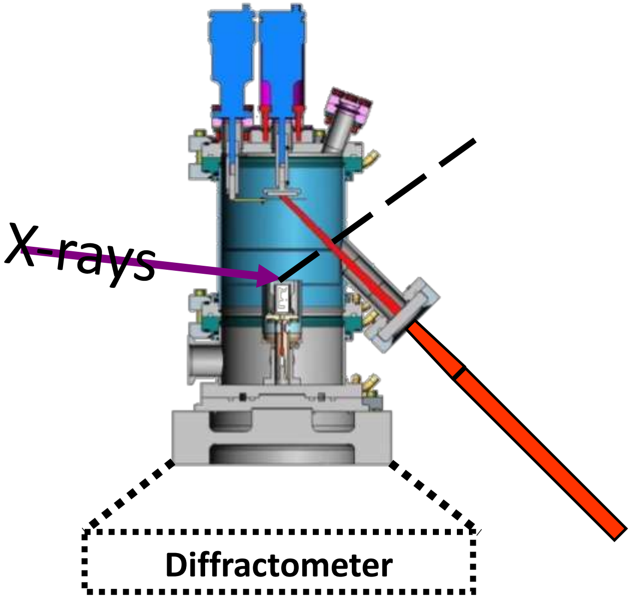
Deposition and Growth are separated in time:

This enables measurement of the kinetic parameters at growth conditions by monitoring the decay of the adatom density between the deposition pulses.

PLD with in-situ growth monitoring



RHEED



SXRD

RHEED provides information of the surface morphology and atomic arrangement at surface and is mainly used for growth monitoring.

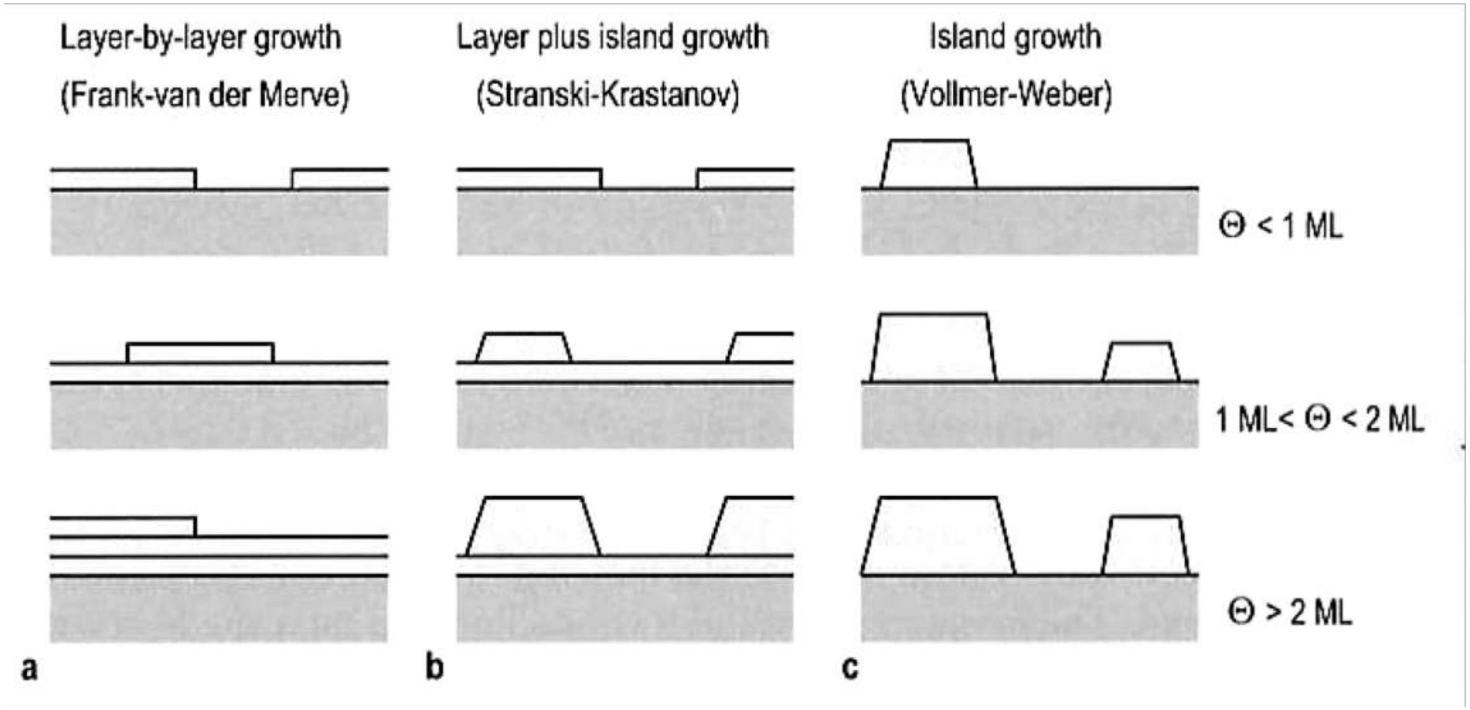
Surface XRD: X-rays interact only weakly with matter and modeling of the diffracted intensities provide also provides information on atomic structure & microstructure of the film grown.

Growth of Thin Films

controlled by the interplay of thermodynamics and kinetics.

Growth modes:

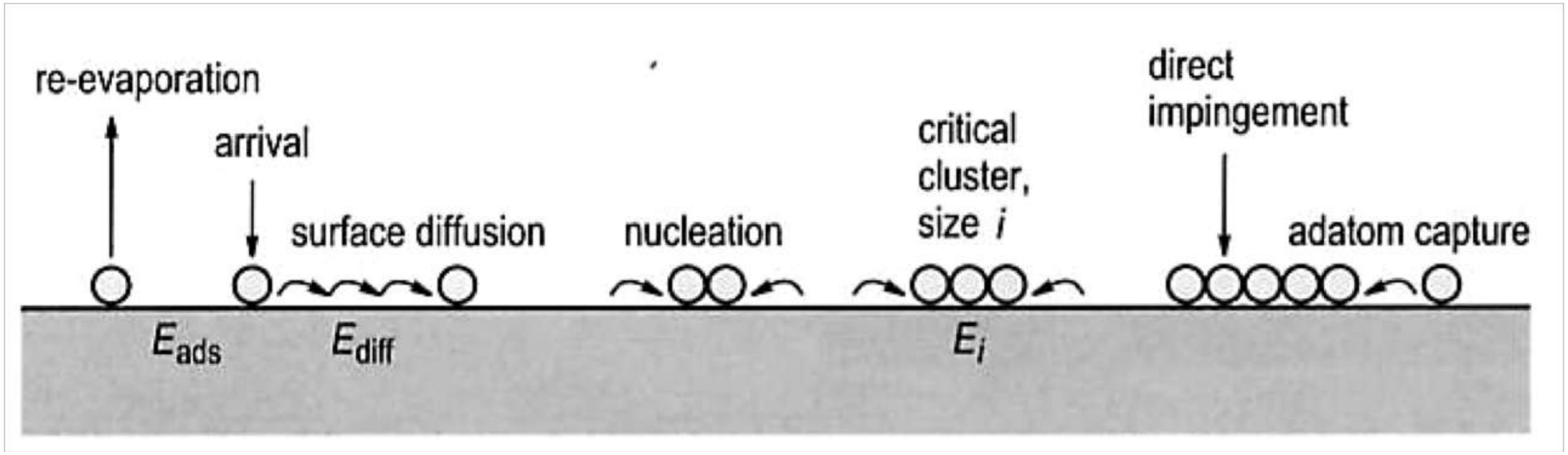
- Layer-by-layer, or Franck van der Merve (FM) growth
- Island, or Vollmer-Weber (VW) growth
- Layer plus island, or Stranski-Krastanov (SK) growth



The occurrence of the individual growth modes is governed by the bond strength between the atoms in the layer and the atom-substrate bonds.

Island number density

The following elementary processes take part at layer growth: Adsorption, surface diffusion, re-evaporation, capturing by defects and combination with other adatoms to form clusters (nucleation).

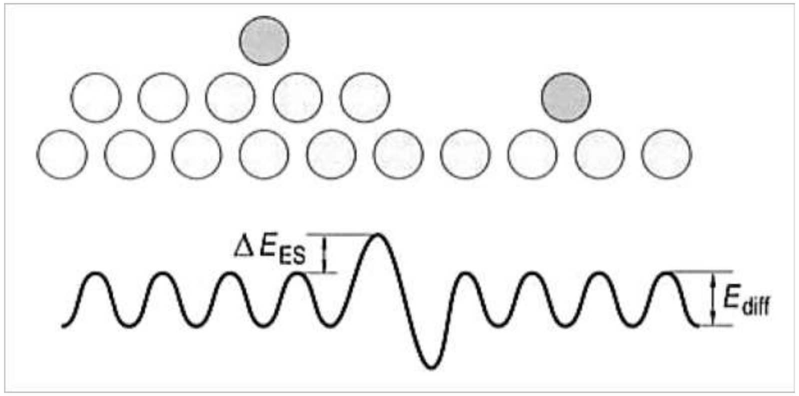


Small clusters are metastable but they become stable at a critical island size, determined by the energy gain for condensation and the energy cost to form new surfaces.

Kinetic effects during epitaxial growth

The actual growth is not only determined by thermodynamics
but also by kinetics.
In particular the mass transport on the surface determines the growth:

- Intralayer mass transport (diffusion on a flat terrace)
- Interlayer mass transport (diffusion across a step edge)

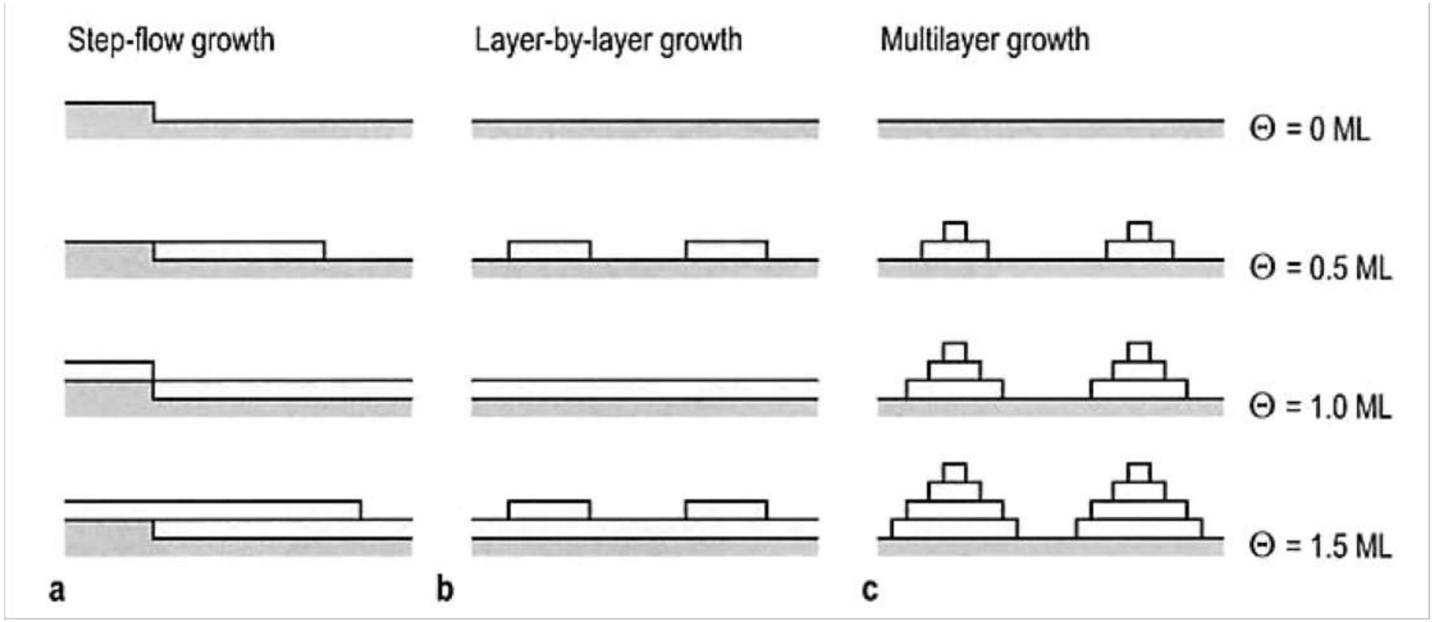


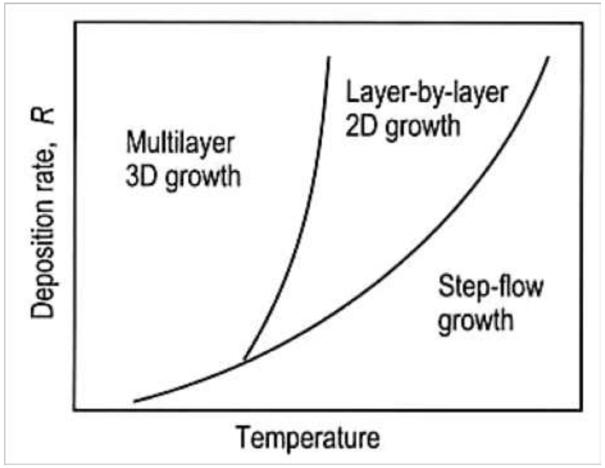
An atom approaching a lower step site will stick.
Coming from the high step site there may also be a barrier (Schwöbel-Ehrlich barrier, E_{ES}), because at the step the coordination is reduced.
The interlayer mass transport probability is given by:

$$s = \exp\left(-\frac{E_{ES}}{kT}\right)$$

Depending on the relative rate of intra and interlayer mass transport different growth modes exist:

- step-flow growth
- layer-by-layer growth
- multilayer growth



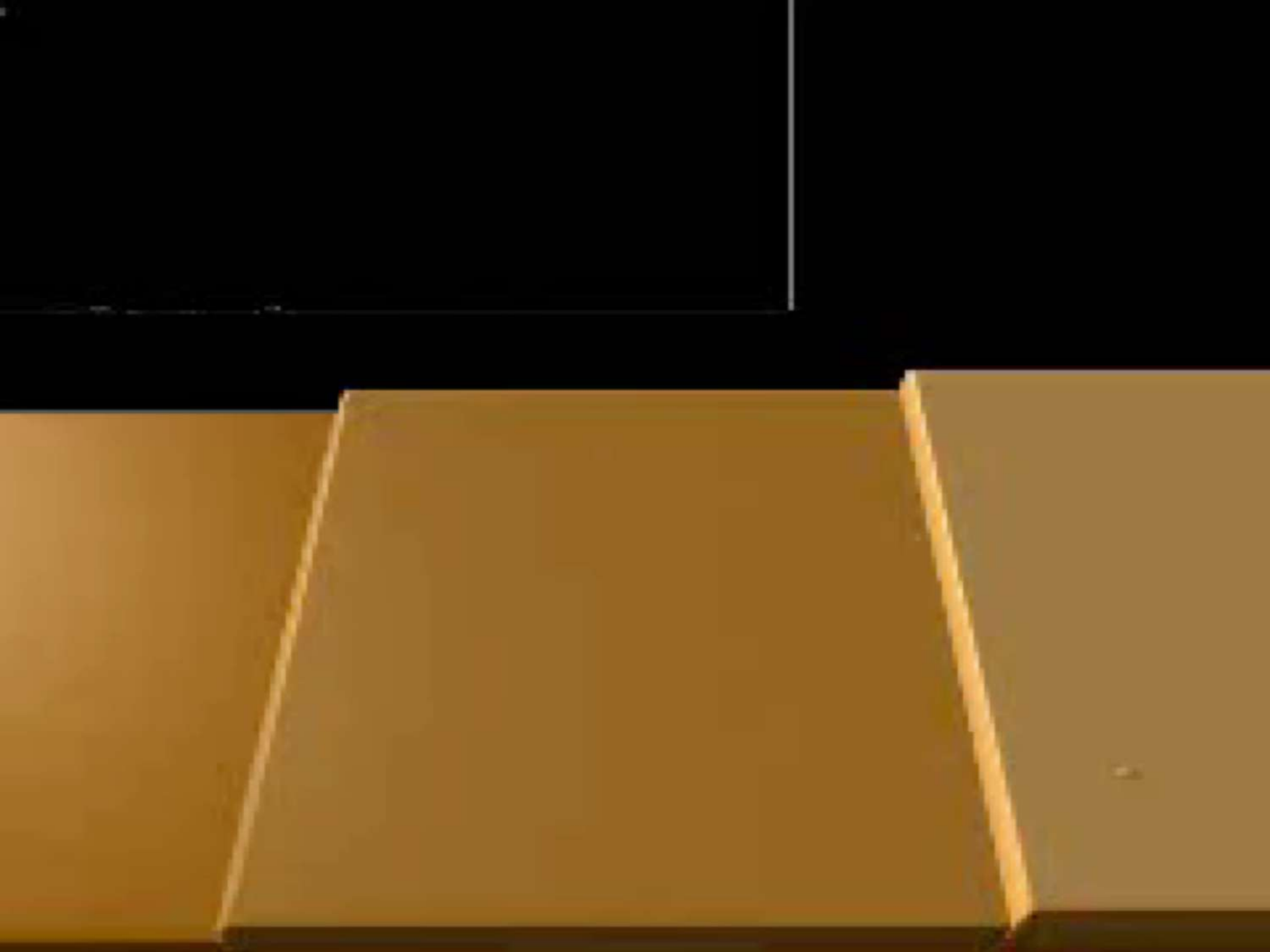


RHEED monitoring of homoepitaxial growth of $SrTiO_3$

Ideal
2-dimensional growth

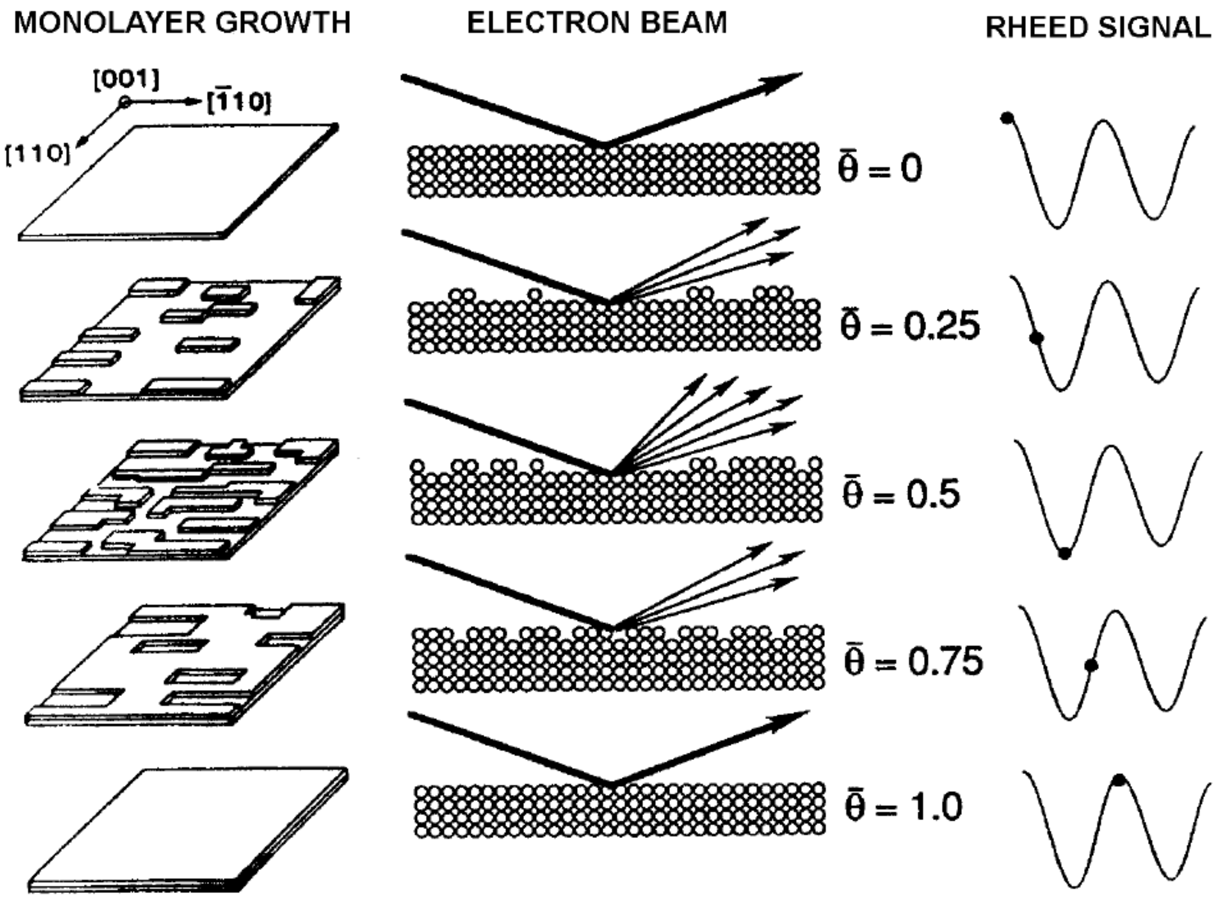
vs.

Non-ideal
3-dimensional growth

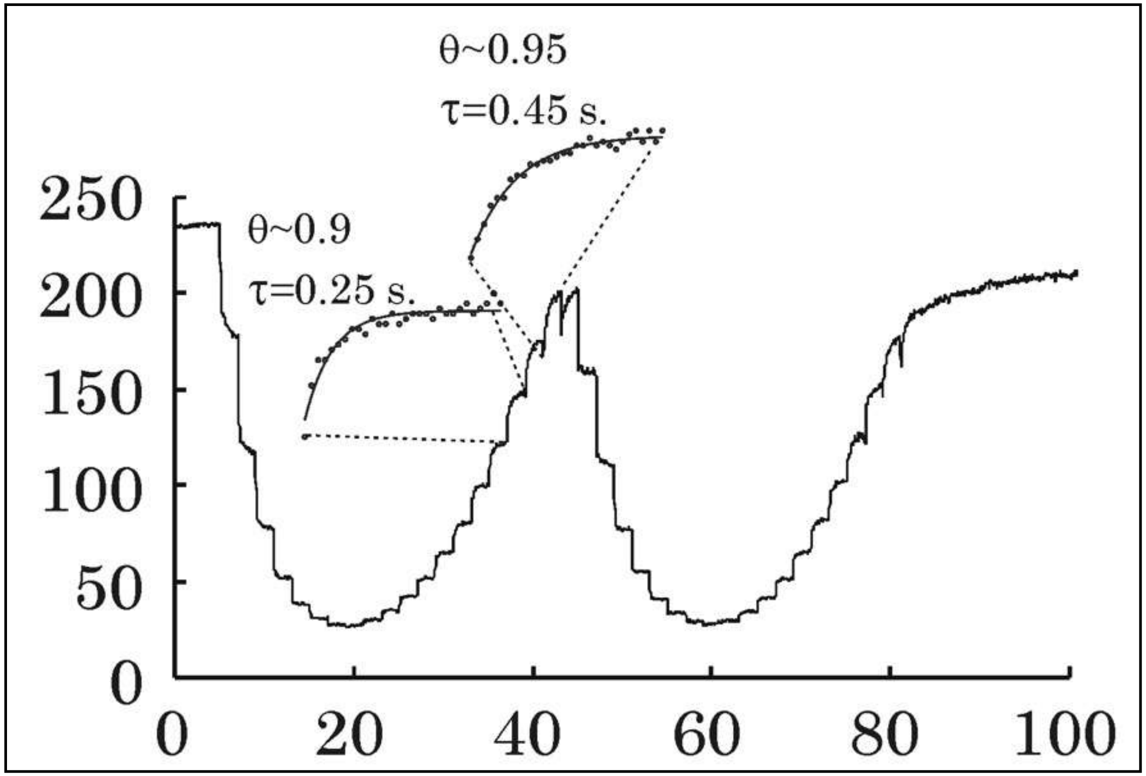


RHEED Oscillations

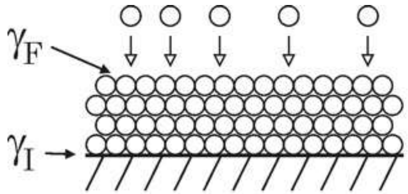
Indication of step density



Oxide thin film growth: Growth kinetics



RHEED intensity during homoepitaxial $SrTiO_3$ growth



layer-by-layer growth

Growth Kinetics

Diffusivity

$$D_S = \nu a^2\, exp\left(-\frac{E_A}{k_B T}\right)$$

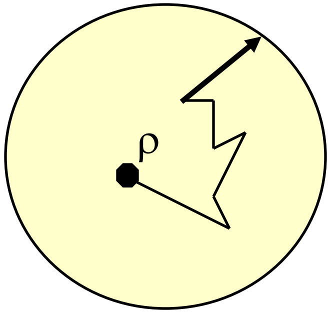
ν the attempt frequency for atomistic processes
a hopping distance
E_A the activation energy for diffusion
k_B Boltzmann's constant
T the temperature

Diffusion length $L_D \sim (D_S \tau)^{1/2}$

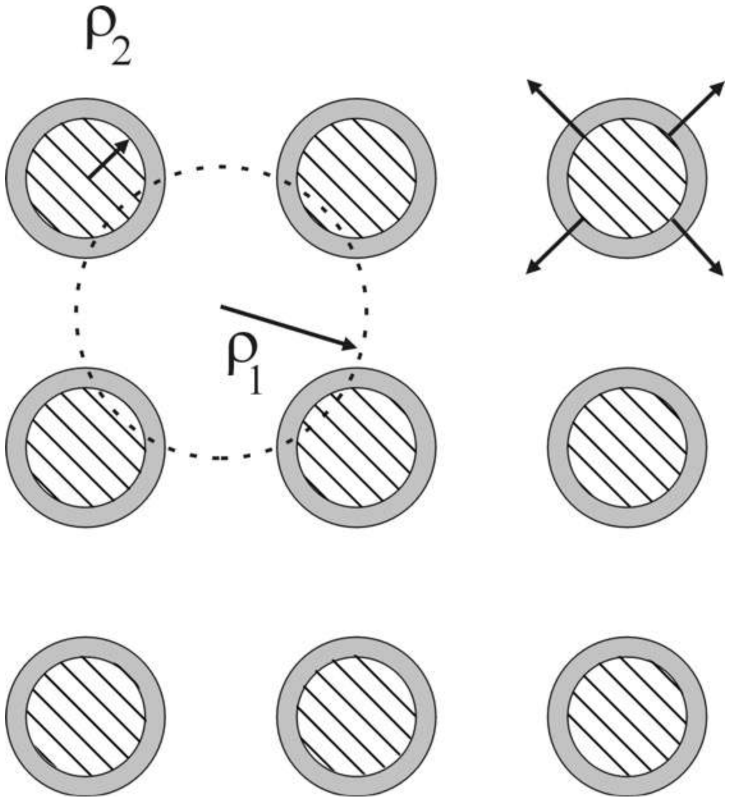
τ residence time

Diffusion time $\tau \sim \rho^2/D_S$

ρ radius island



Model for 2D layer-by-layer growth with island density N_S



$$\pi\rho_2^{\,2}(t) = \frac{\theta(t)}{N_S}$$

$$\tau_2 = \frac{\theta}{D_S\left(\mu_1^{(0)}\right)^2 \pi N_S}$$

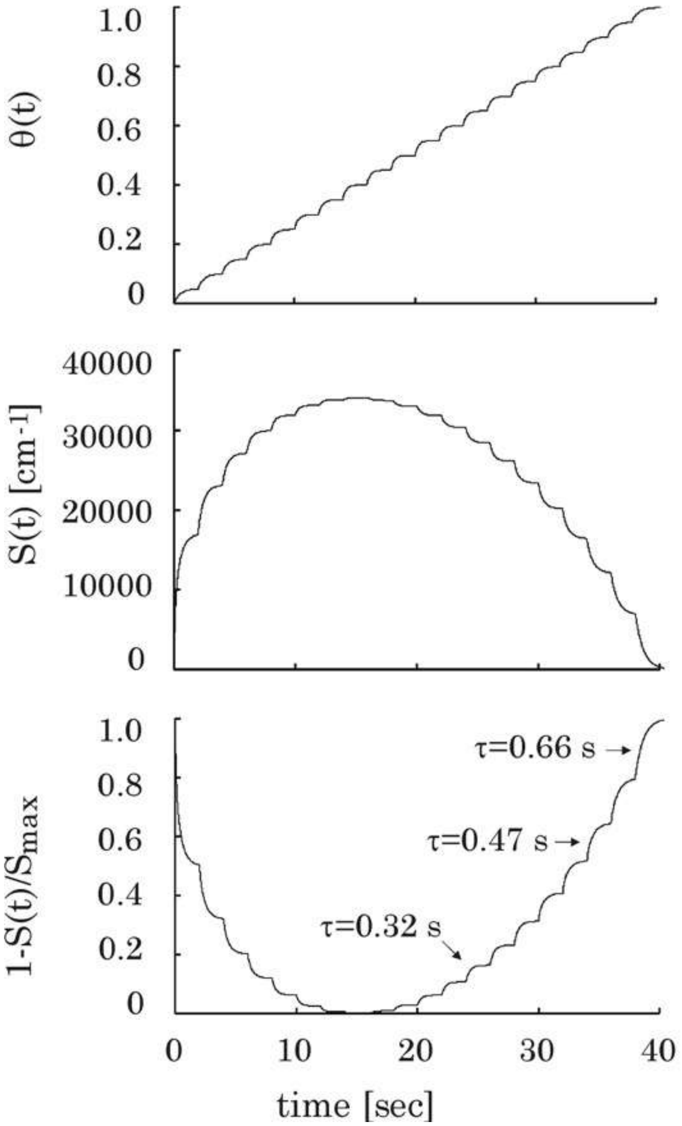
$$\pi\rho_1^{\,2}(t) = \frac{1-\theta(t)}{N_S}$$

$$\tau_1 = \frac{1-\theta}{D_S\left(\mu_1^{(0)}\right)^2 \pi N_S}$$

$$\Delta\theta_n(t) = \frac{\theta_{n-1}}{n_P}\left(1 - exp\left(-\frac{t}{\tau_2}\right)\right) + \frac{\left(1-\theta_{n-1}\right)}{n_P}\left(1 - exp\left(-\frac{t}{\tau_1}\right)\right)$$

A.J.H.M. Rijnders, *The initial growth of complex oxides: study and manipulation* (2001)

$N_S = 2\times10^{11}$ /cm^2, T = 850 ^{0}C, E_A = 2.2 eV, n_P = 20, f = 0.5 Hz



Coverage

Step density

$$S = 2\sqrt{\pi N_S}\,(1-\theta)\sqrt{-\,ln(1-\theta)}$$

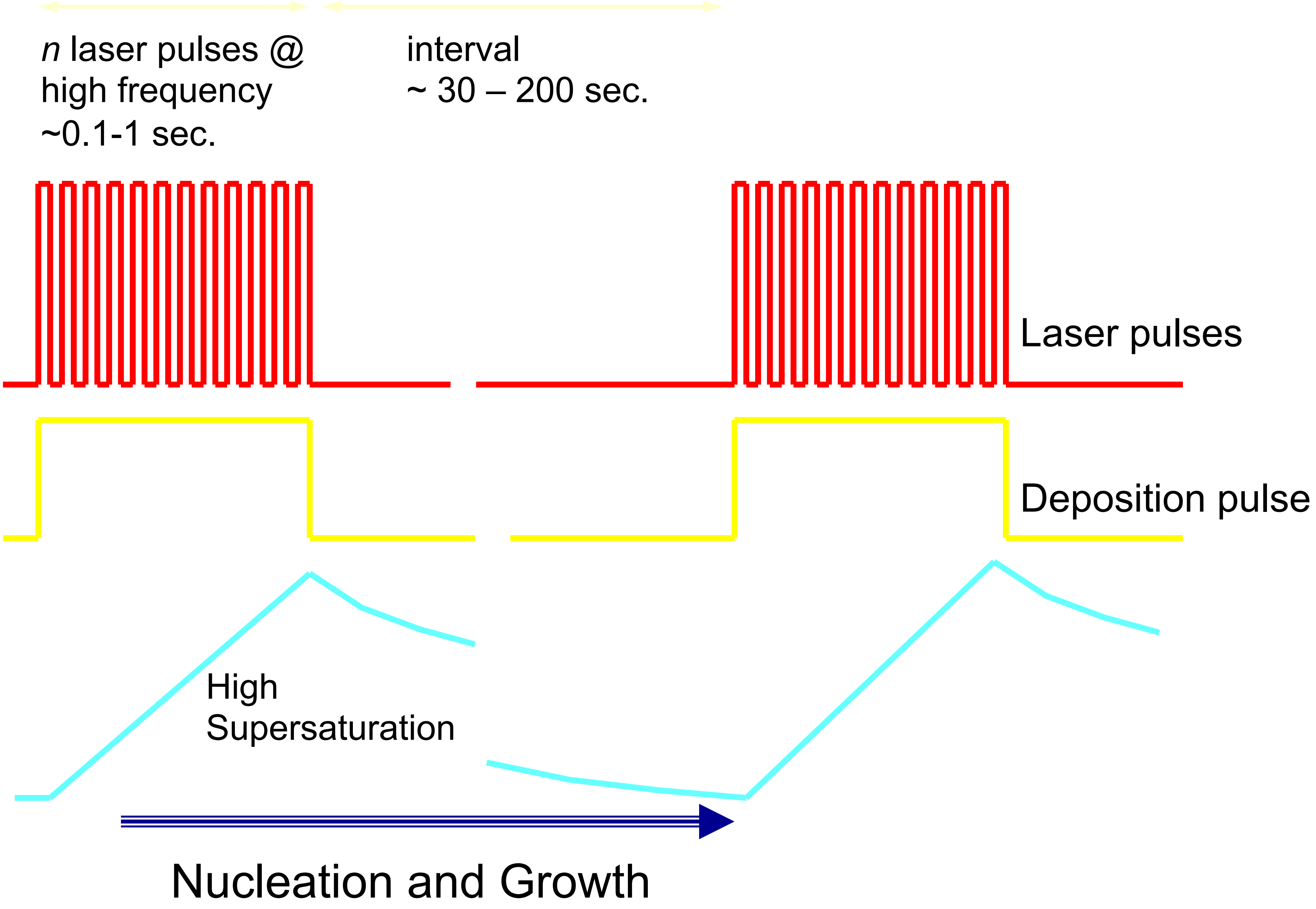
N_S is the number of nuclei per unit area

RHEED Intensity

Extra option for epitaxial growth

Artificial interval growth

Growth manipulation: Pulsed Laser *Interval* Deposition



n laser pulses @
high frequency
~0.1-1 sec.

interval
~ 30 – 200 sec.

Laser pulses

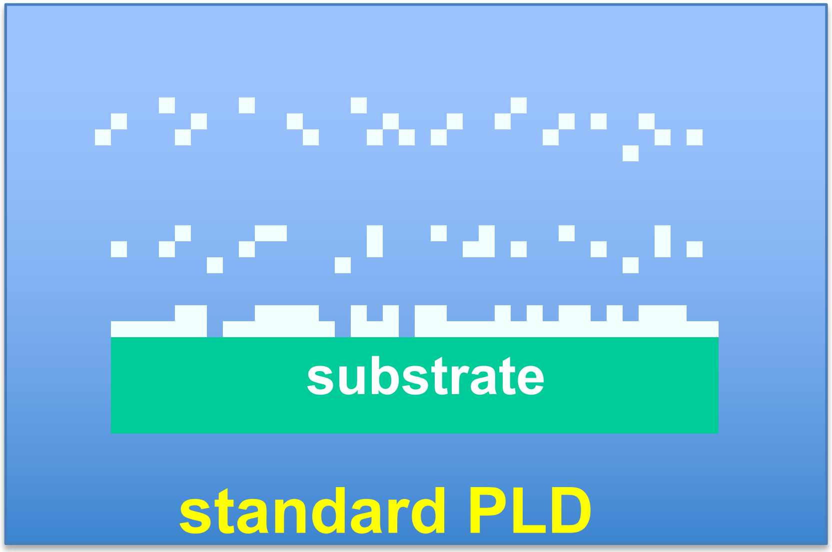
Deposition pulse

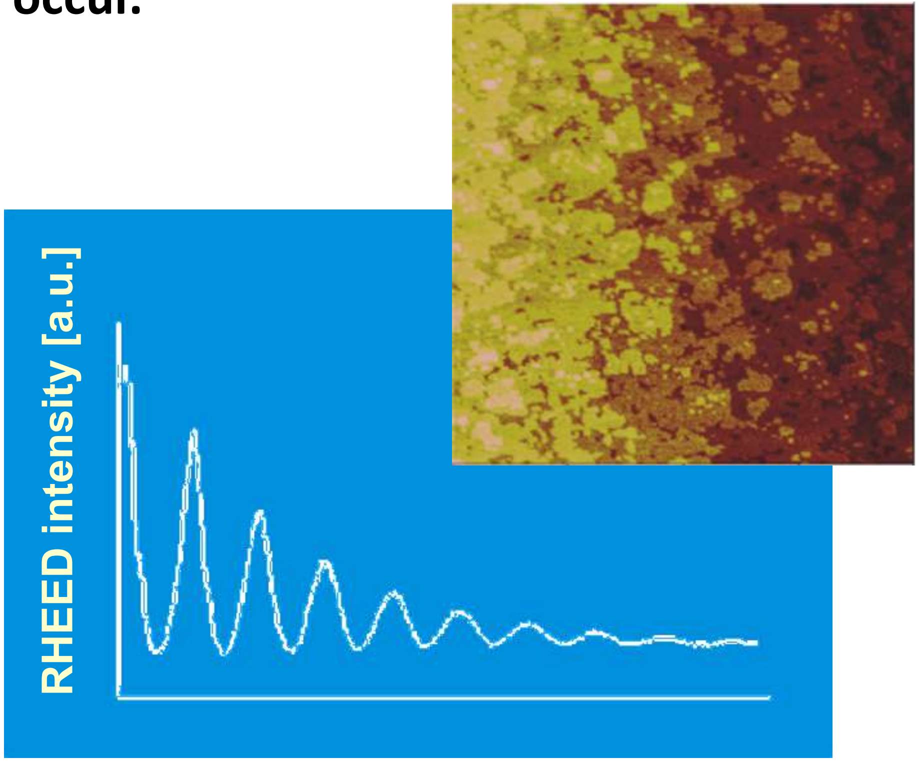
High
Supersaturation

Nucleation and Growth

Pulsed Laser Deposition

1. Fast deposition during one pulse.
   - high supersaturation leads to formation of small islands.
   - probability of nucleation on top of these small island is low.
   - material can rearrange after the pulse.
   - small islands promote interlayer mass transport.
2. During deposition in subsequent pulses nucleation and growth on top of the deposited islands can occur.

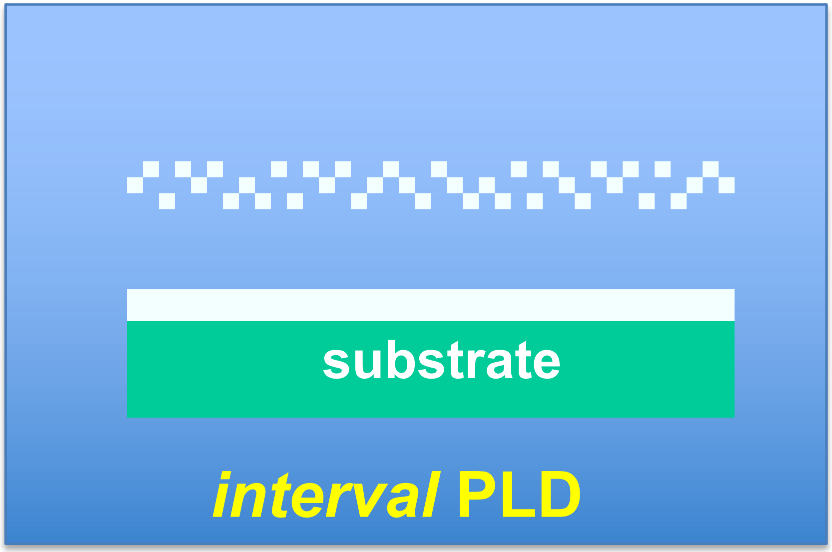


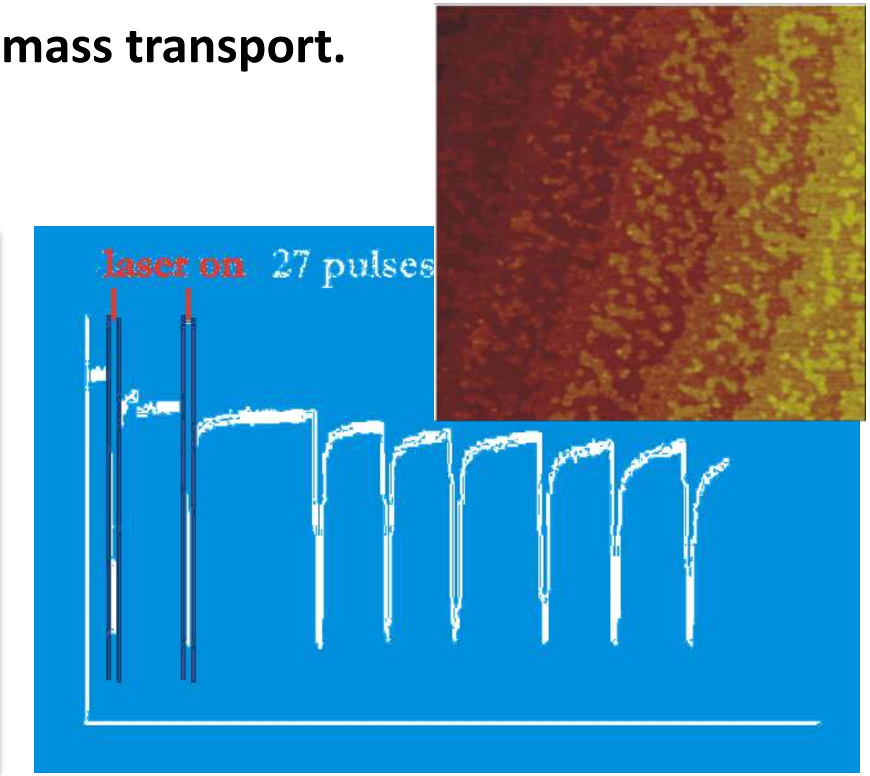


Pulsed Laser *Interval* Deposition

Gertjan Koster *et al*. Appl. Phys. Lett. **74** (1999) 3729

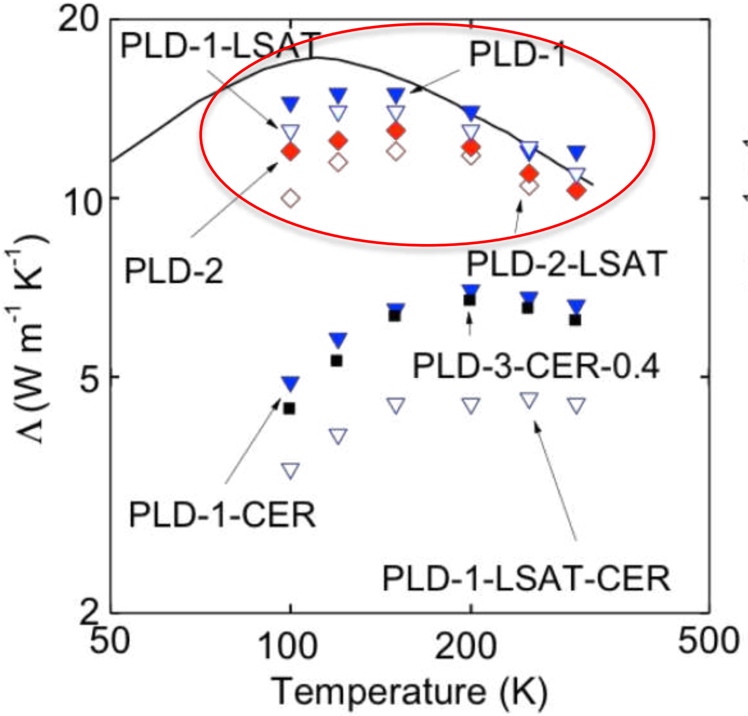
1. Fast deposition of enough material to complete just one monolayer.
   -high supersaturation leads to formation of small islands.
   -probability of nucleation on top of these small island is low.
2. Material can rearrange during interval.
   -small islands promote interlayer mass transport.

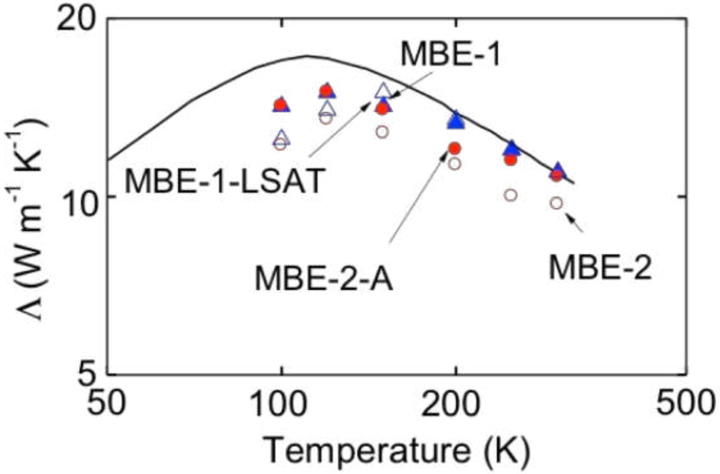




Density and purity of target : use single crystal !!

$SrTiO_3$ growth





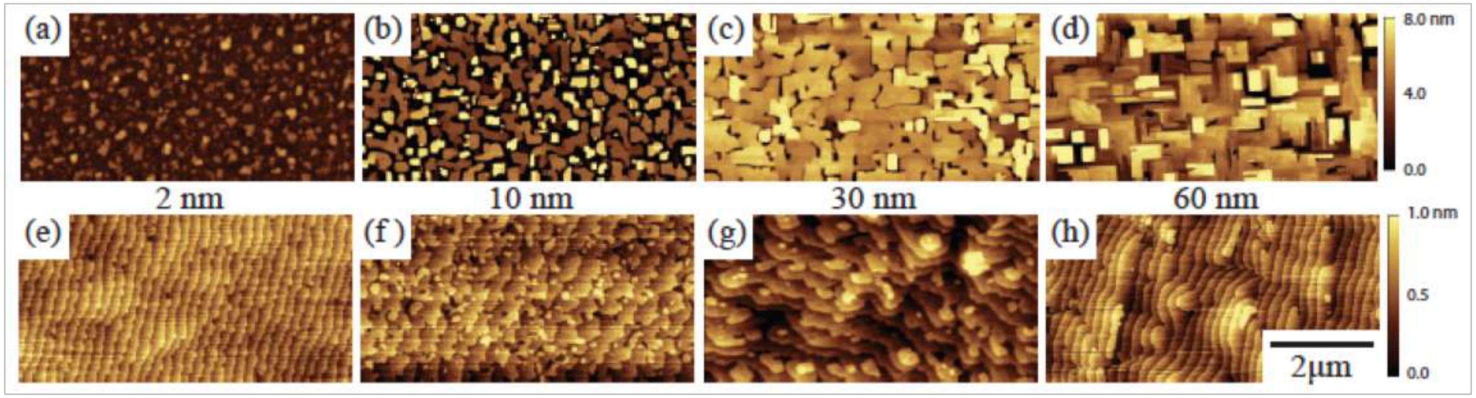
Oh et al., Appl. Phys. Lett. **2011**, 98, 221904.

Control of surface diffusion for enhanced thin film growth

BiFeO$_3$ growth on SrTiO$_3$ substrate:

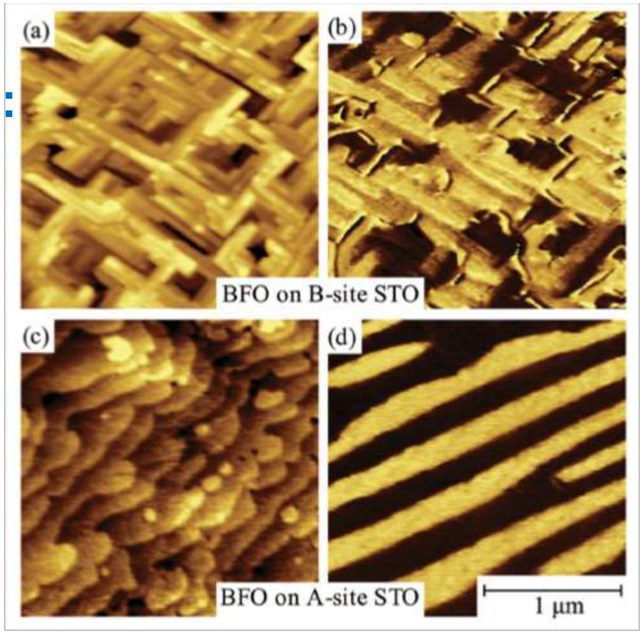
TiO$_2$ termination

SrO termination

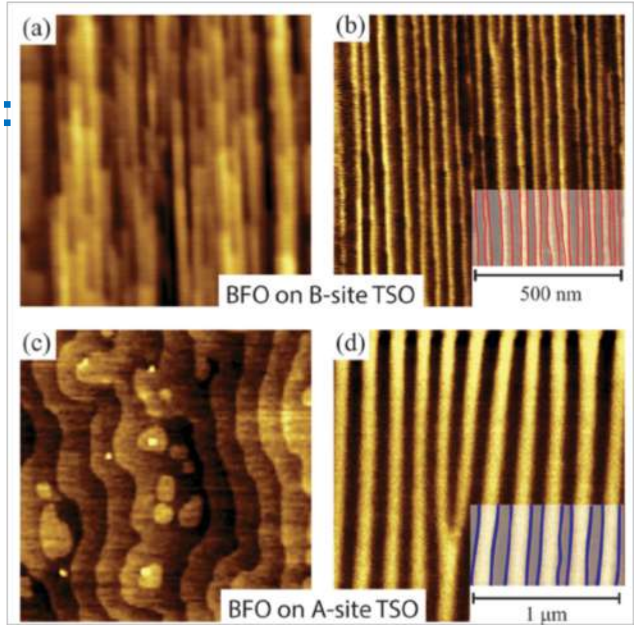


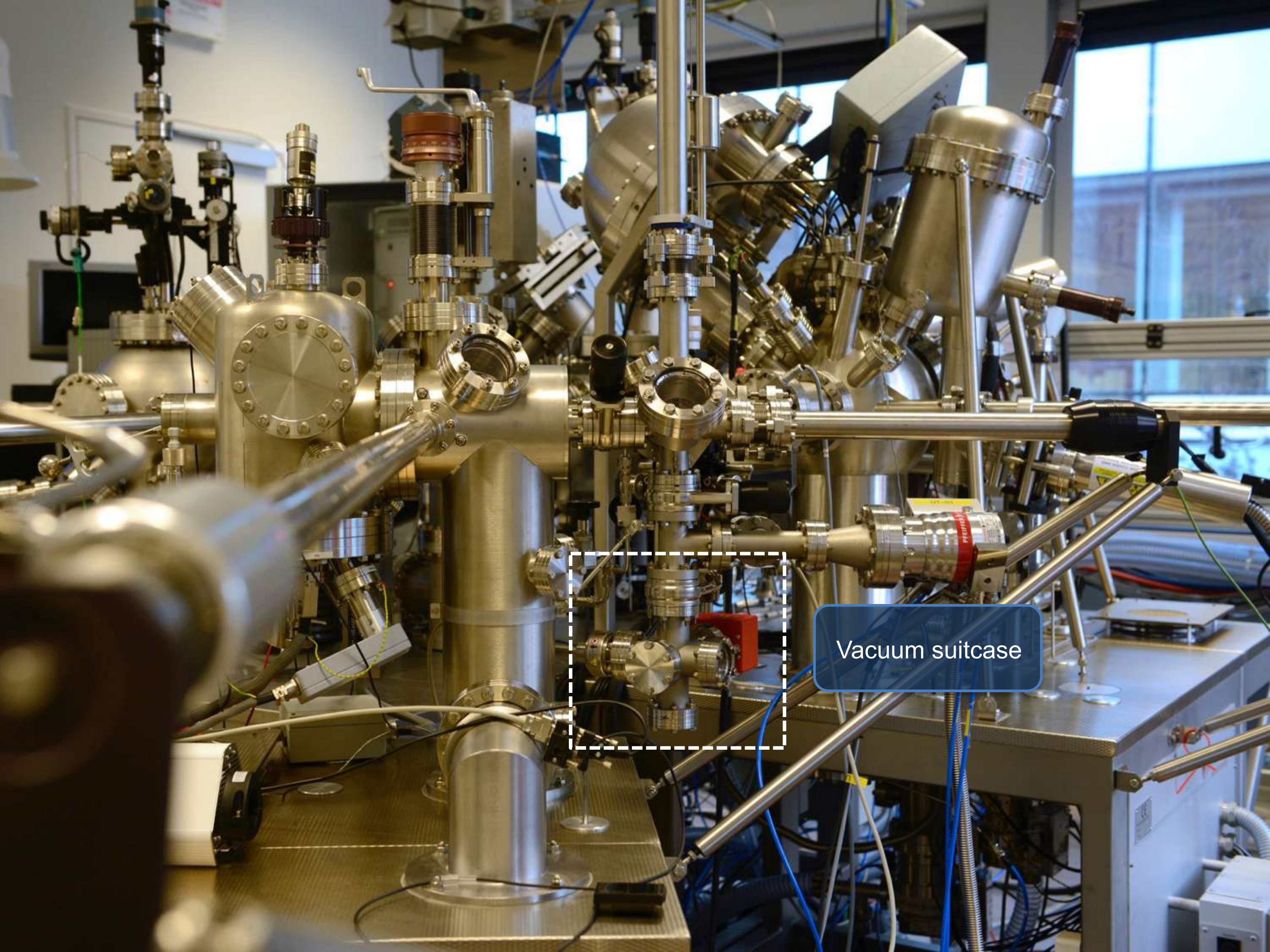
Solmaz et al., Adv. Funct. Mater. **2016**, 26, 2882–2889.

SrTiO$_3$ substrate:



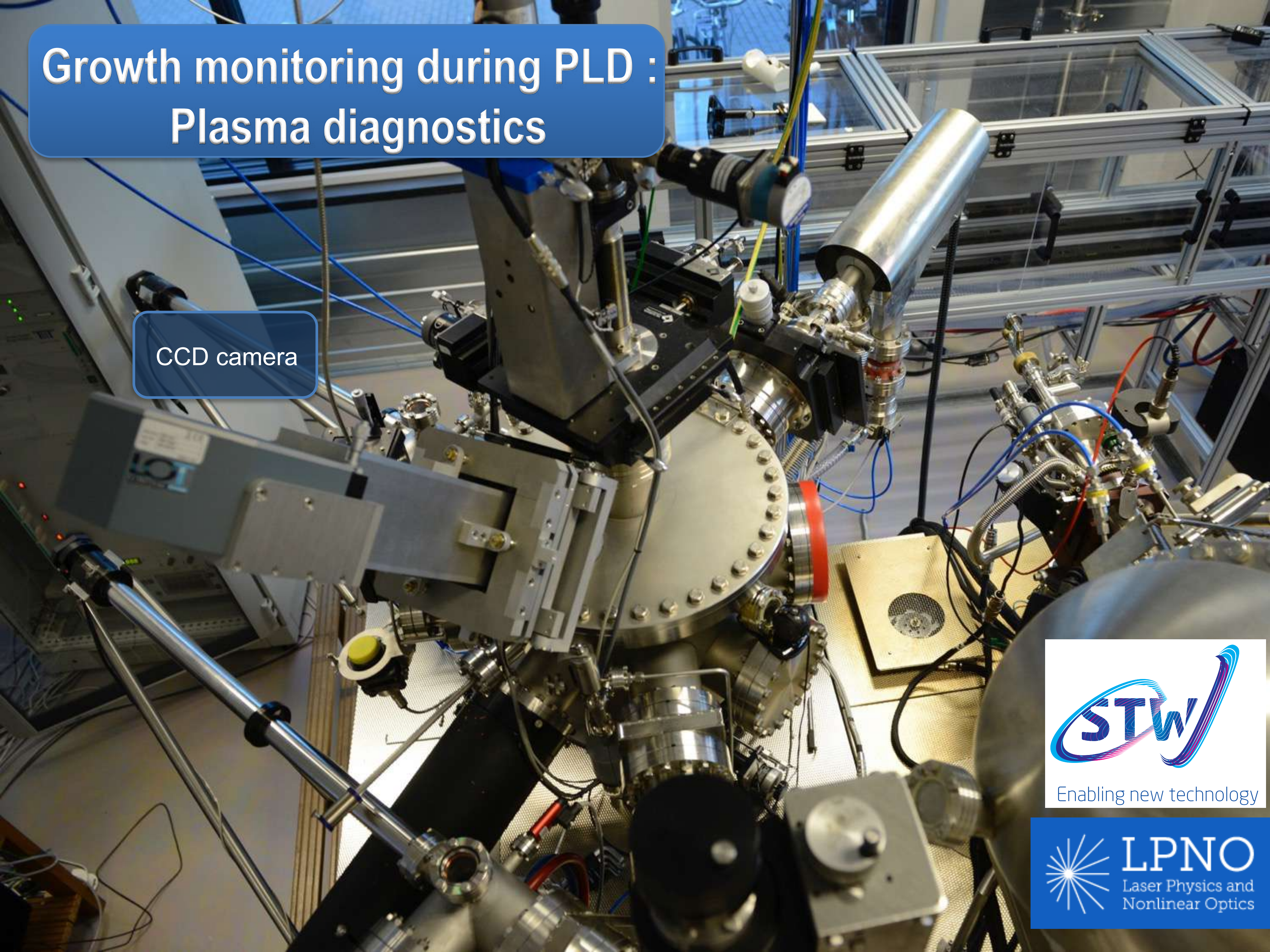
TbScO$_3$ substrate:





Vacuum suitcase

Growth monitoring during PLD : Plasma diagnostics



CCD camera

STW
Enabling new technology

LPNO
Laser Physics and Nonlinear Optics

Goal: Growth control

Stoichiometry → Properties

Control over film stoichiometry and morphology

Identify key mechanisms:

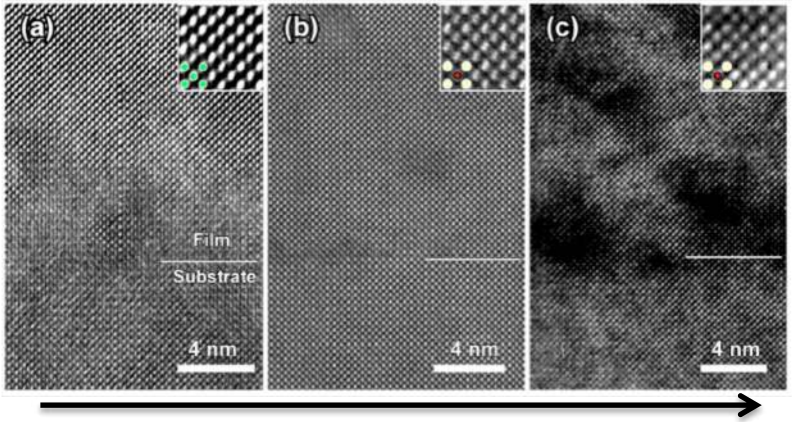
Fluence and pressure → Plasma characteristics → Film growth.

How, and why does PLD actually works?

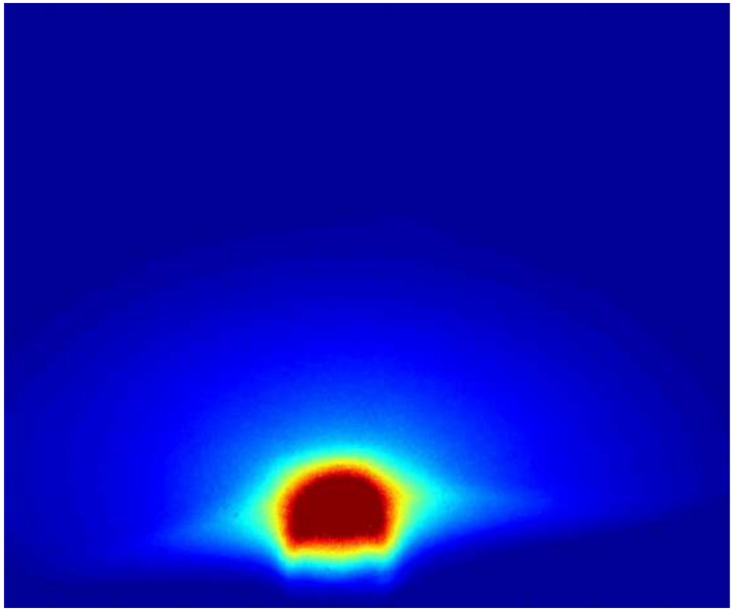
- PLD ‘paradigm’:

  species kinetics determine growth characteristics
- **It’s all about the plasma plume chemistry!**

Ohnishi, T., Shibuya, K., Yamamoto, T., & Lippmaa, M. (2008). Defects and transport in complex oxide thin films. *Journal of Applied Physics*, *103*(10), 103703



Fluence (J/cm^2)

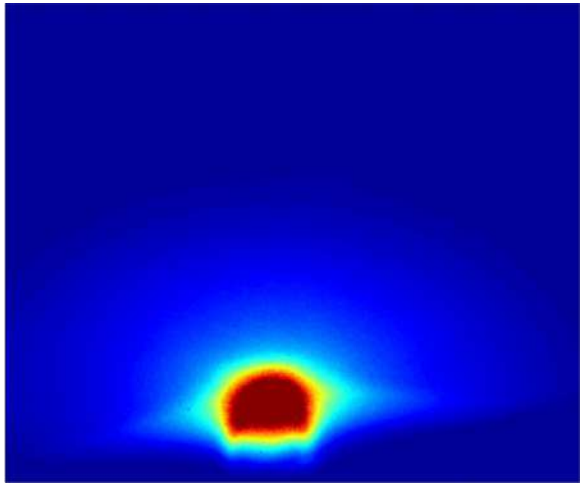


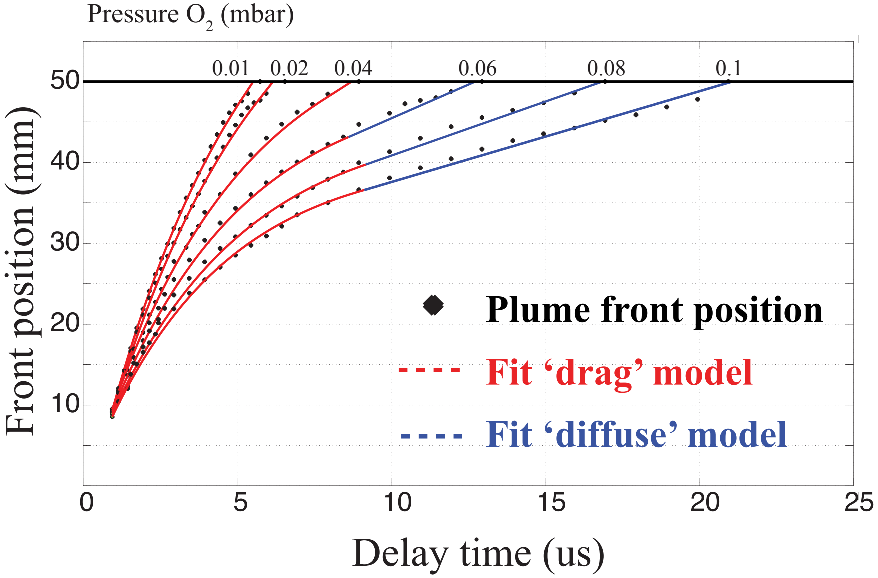
Data from R. Groenen

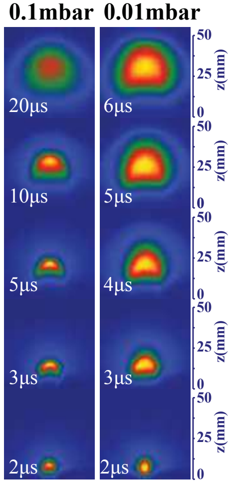
Plume characteristics

Transition in kinetics

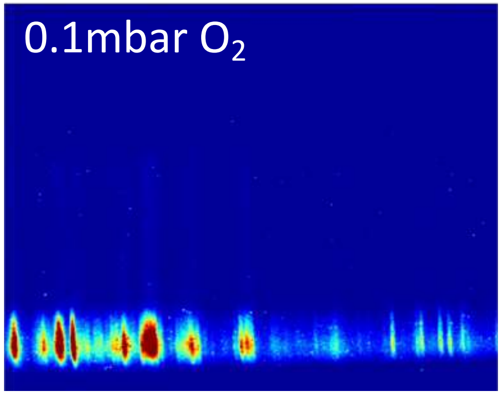
Plume propagation dynamics

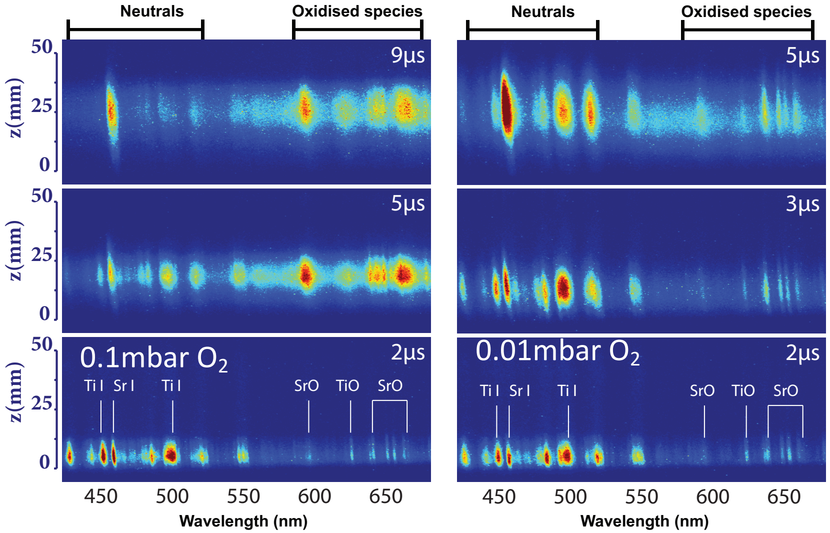






Plume composition



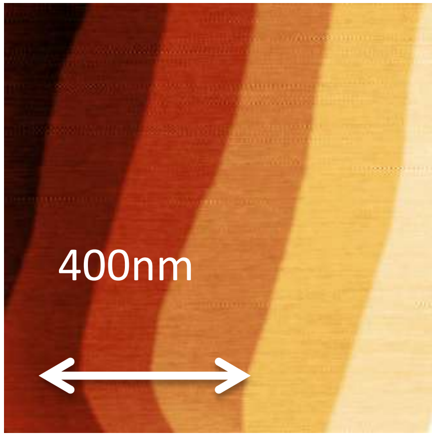


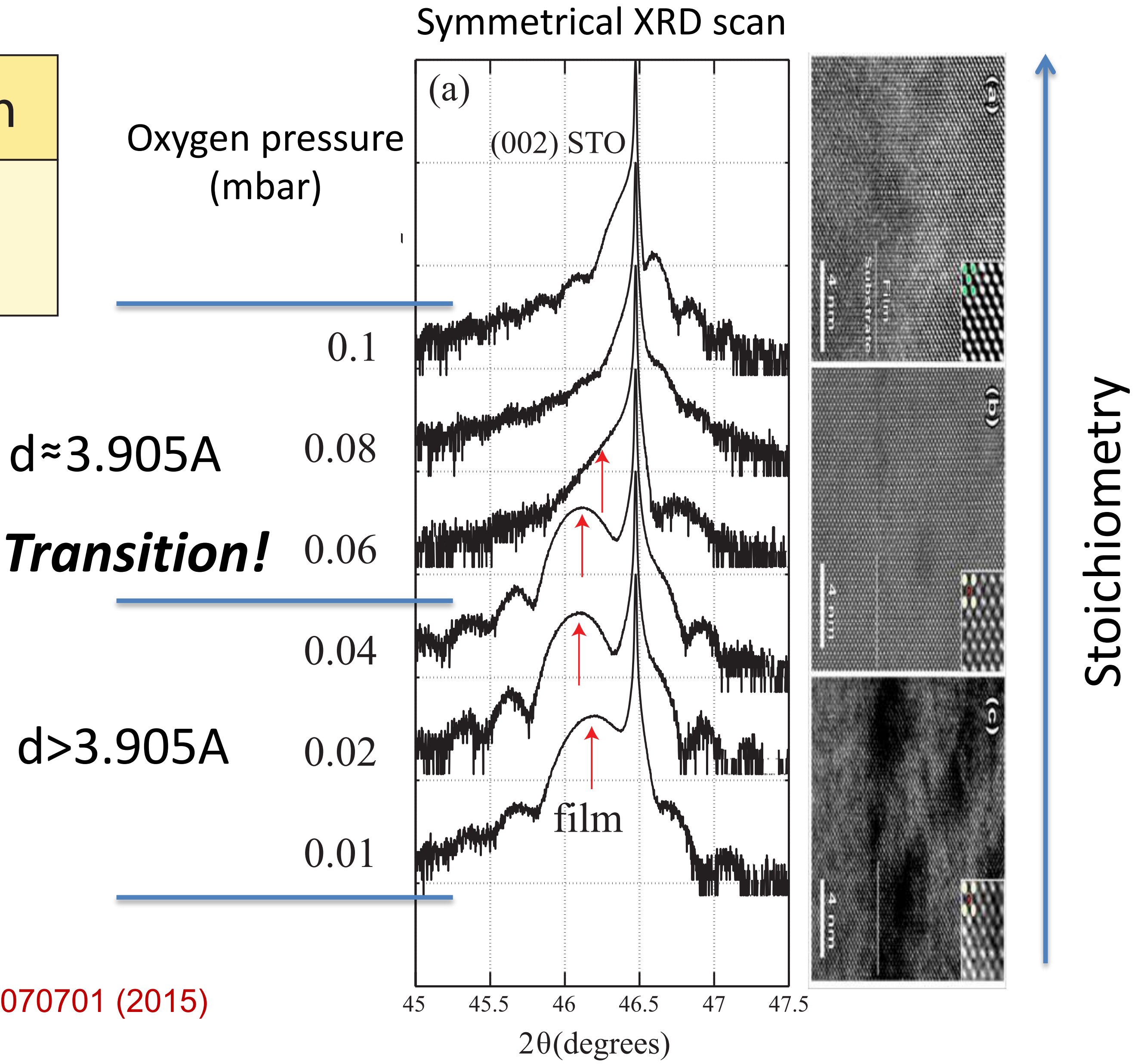
Transition in oxidation

Experiment

40nm $SrTiO_3$ film

$SrTiO_3$ substrate





d≈3.905A

Transition!

d>3.905A

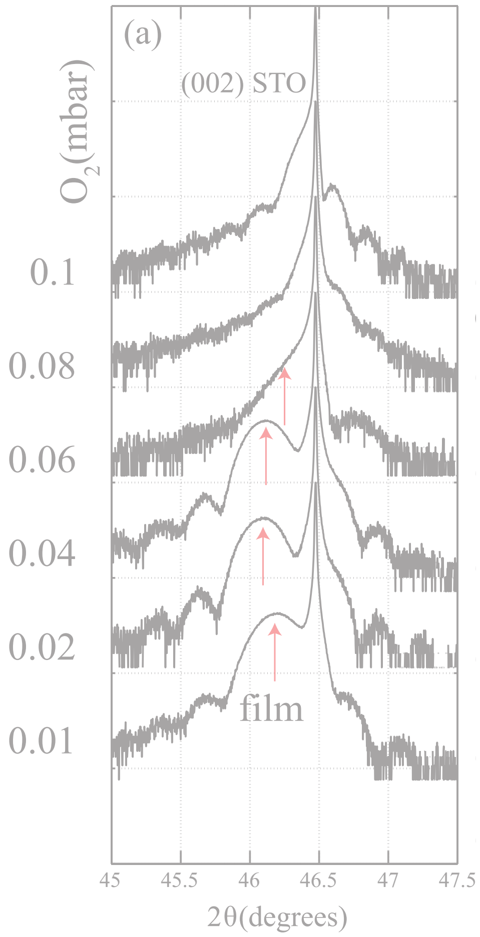
Groenen et al., APL Mater. 3, 070701 (2015)

Plume dynamics vs plume oxidation

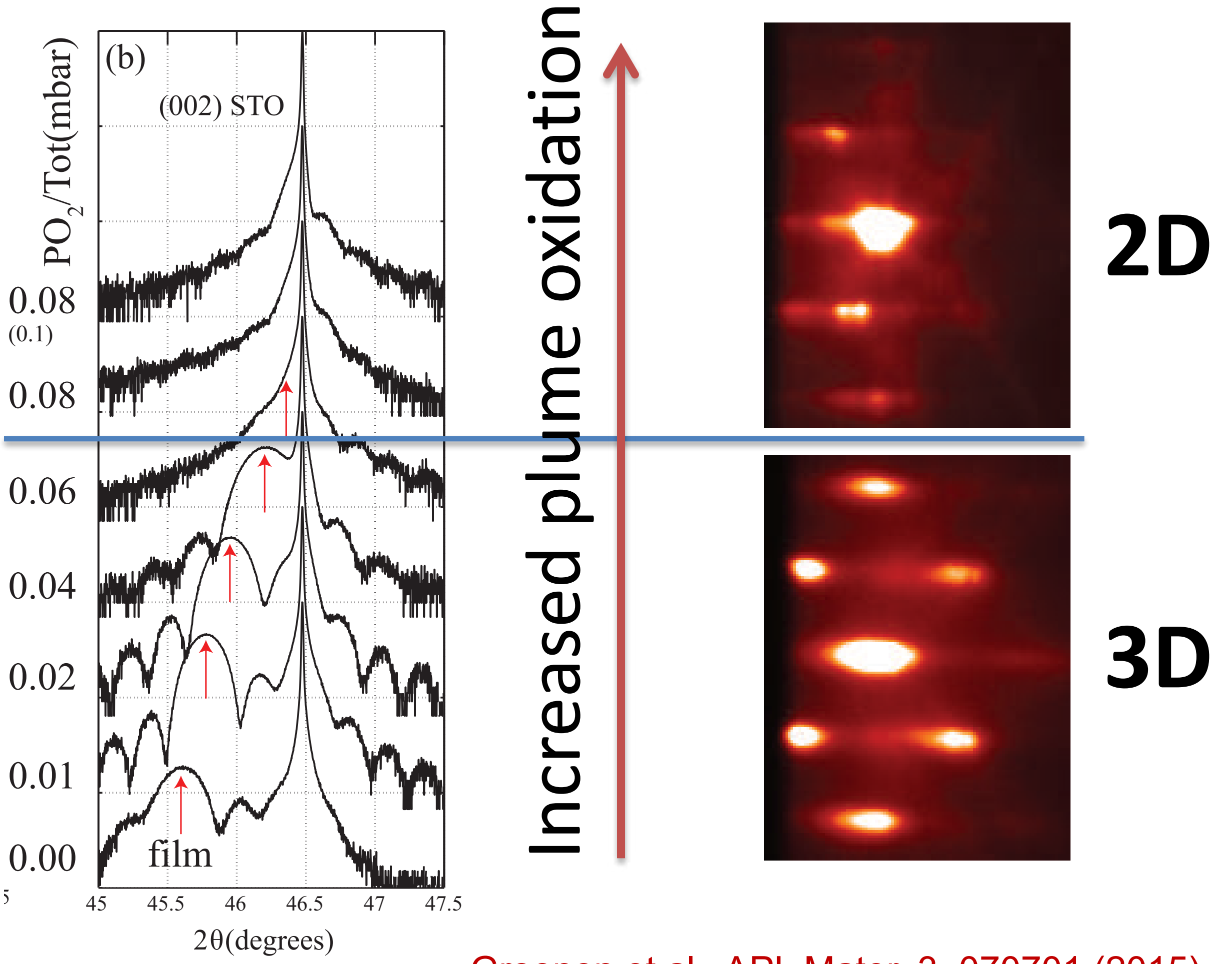
Stoichiometry

Growth kinetics

Oxygen



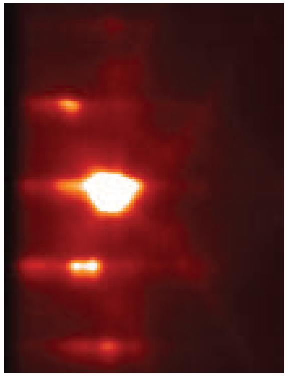
Oxygen/Argon mix

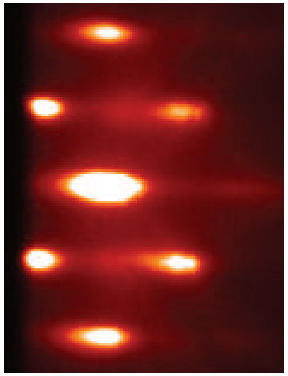


Groenen et al., APL Mater. 3, 070701 (2015)

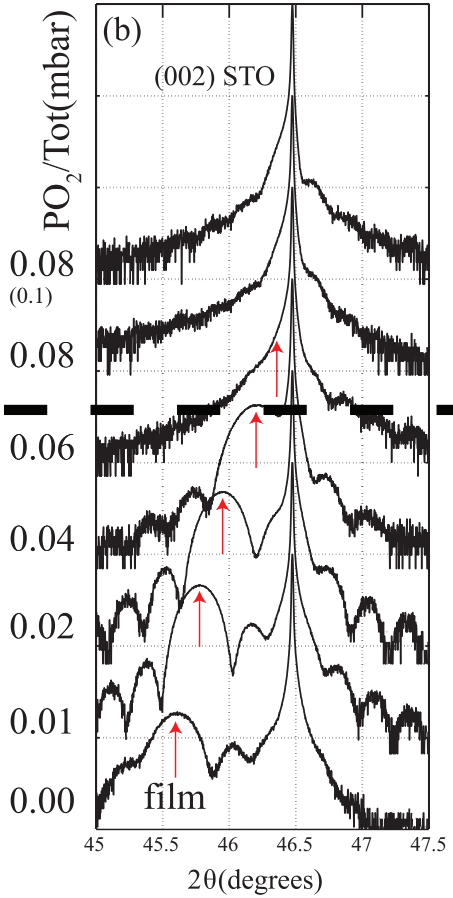
Growth → Plume

Improved growth kinetics

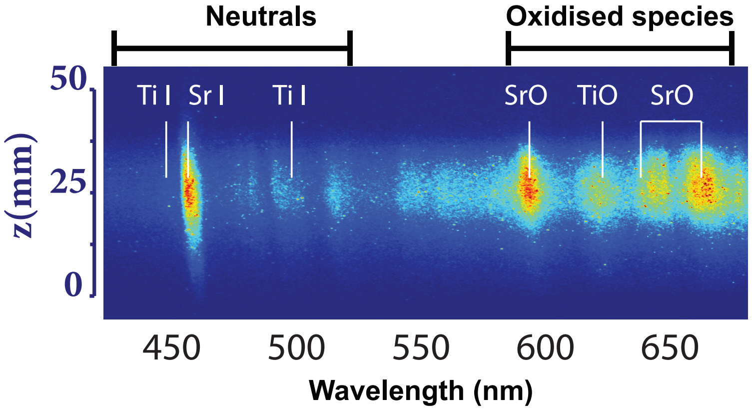


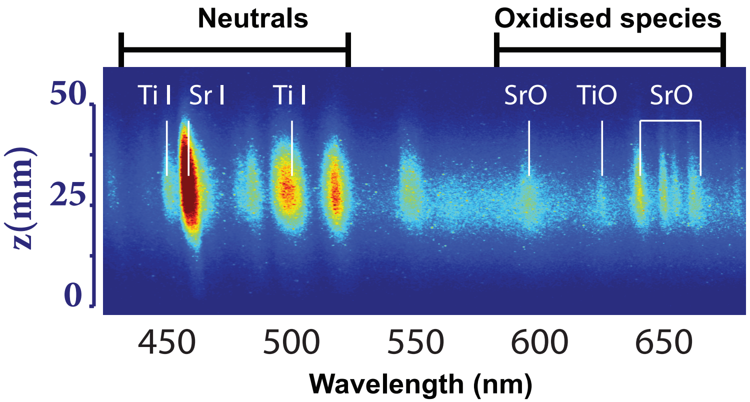


Improved stoichiometry



Increased plasma oxidation



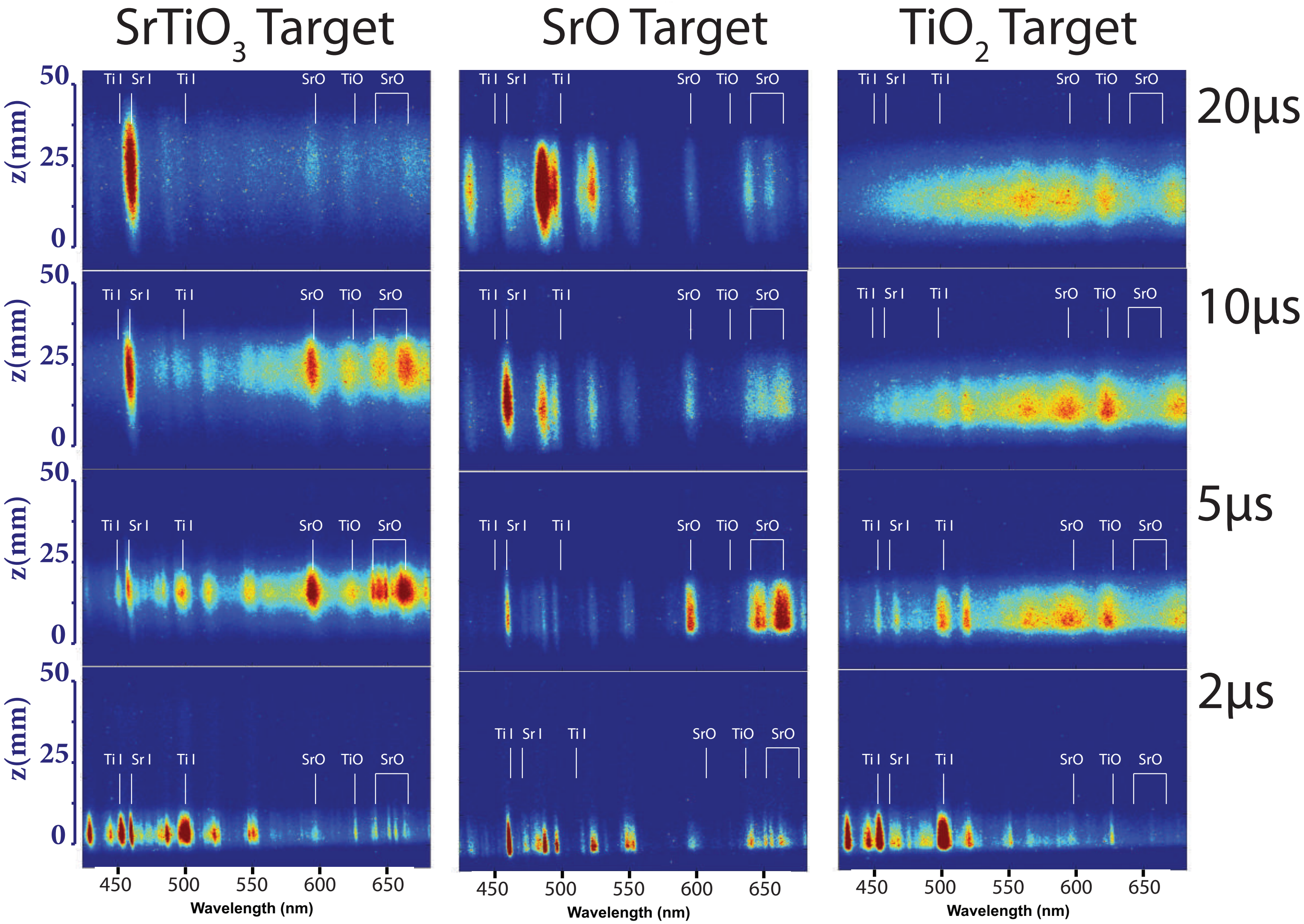


Bottleneck process in improved oxidation of plume and improved film stoichiometry?

Titanium vs Strontium

0.1mbar Oxygen

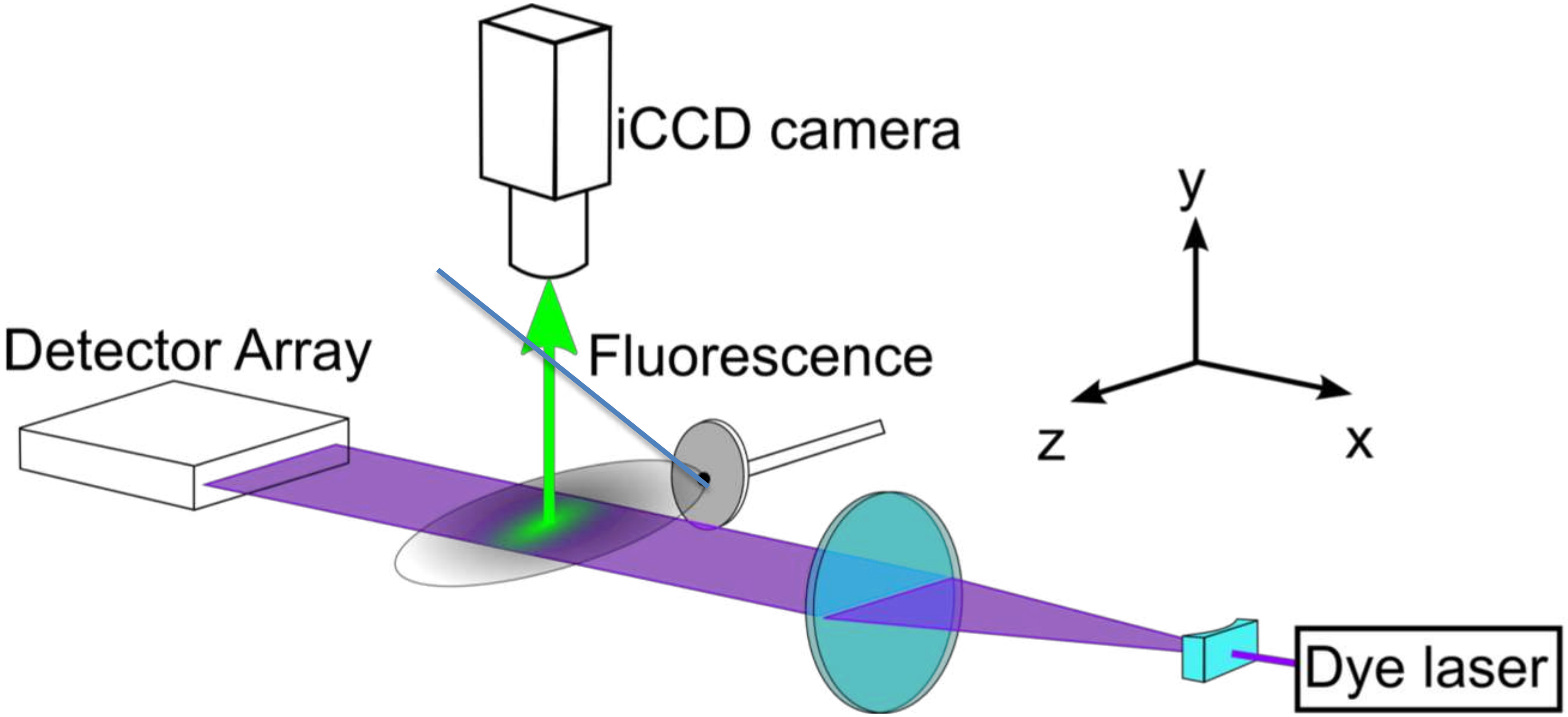
- $SrO + TiO_2 \neq SrTiO_3$
- Titanium seems to oxidize much stronger
- Complex plume chemistry



Important innovations for epitaxial complex oxide growth
Plasma characteristics

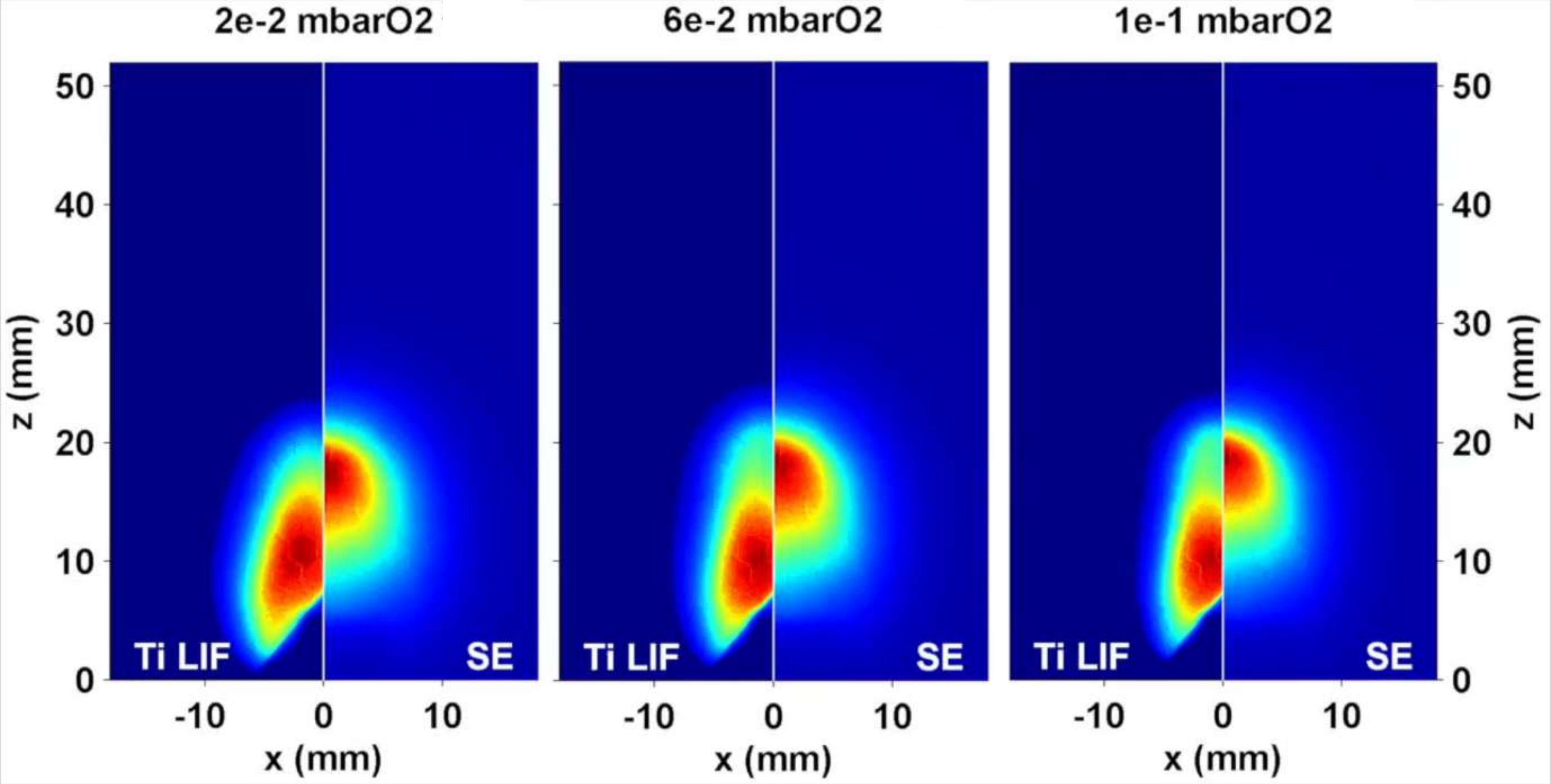
TSST designed system:

Laser Induced Fluorescence (LIF) for spatial and temporal element specific distribution



Important innovations for epitaxial complex oxide growth

Plasma characteristics



LIF = laser induced fluorescence
SE = self emission

Pulsed Laser Deposition: Important parameters

Laser Spot Parameters

Energy density influences the stoichiometry of ablated material;
Spot size and shape influences the homogeneity;
Repetition rate influences the deposition rate and growth mode.

Substrate temperature

Epitaxial growth is obtained at elevated temperatures.

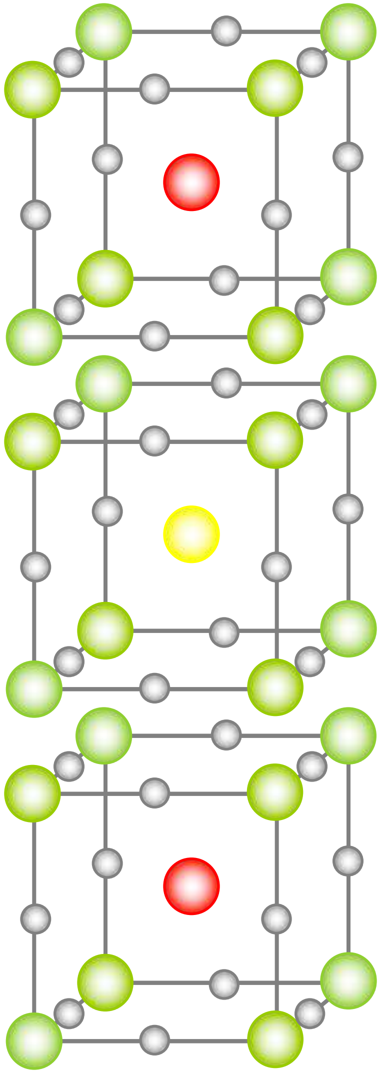
Deposition pressure

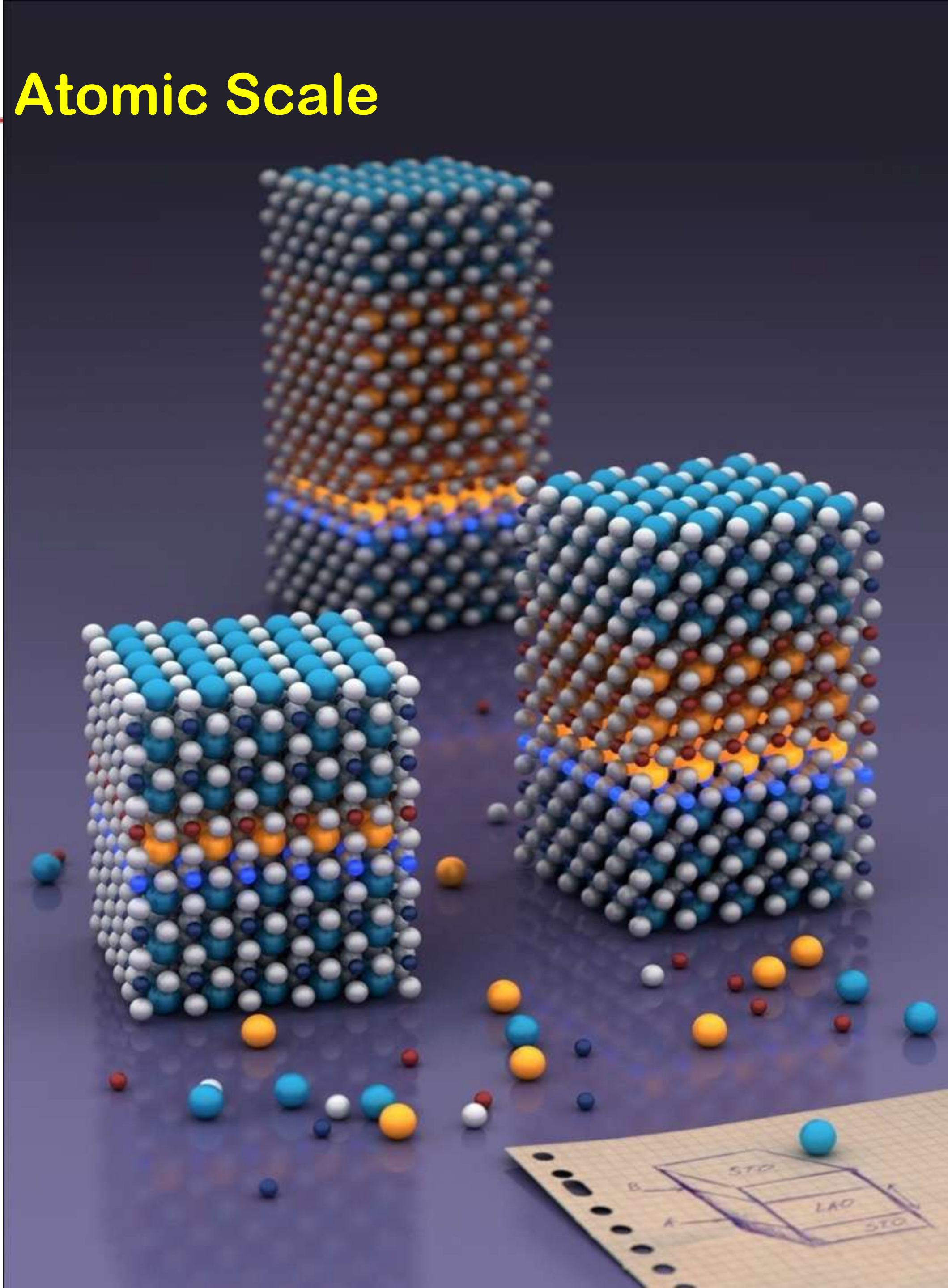
The shape and size of plasma is influenced by the pressure;
Energetic particles in plasma bombard the growing film;
This can lead to defects and stress.

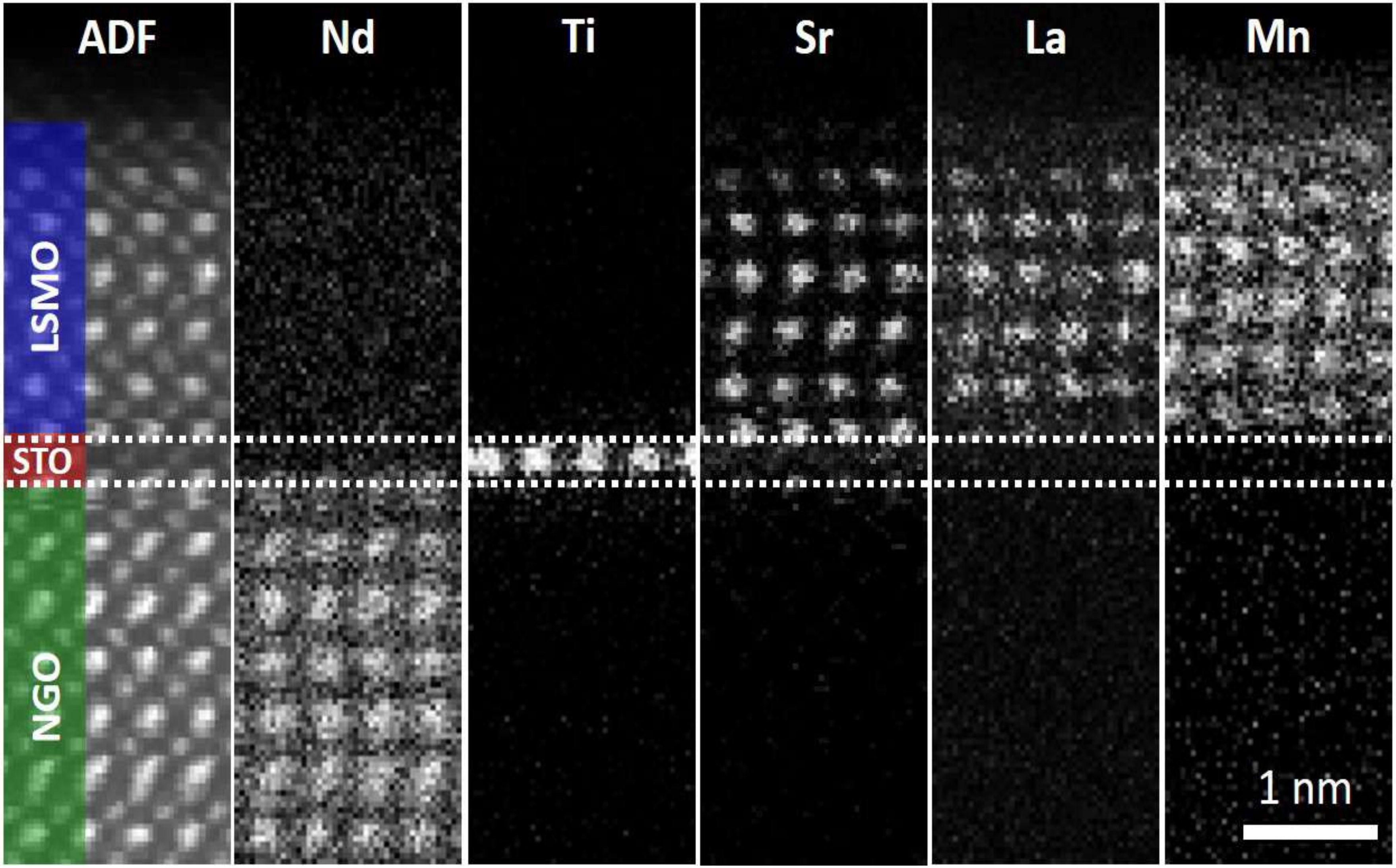
Oxygen pressure

Oxygen incorporation in the as grown film;
Oxidation power at high pressure allows for higher deposition temperature;
Deposition in stable regime to avoid decomposition.

Playing LEGO on Atomic Scale

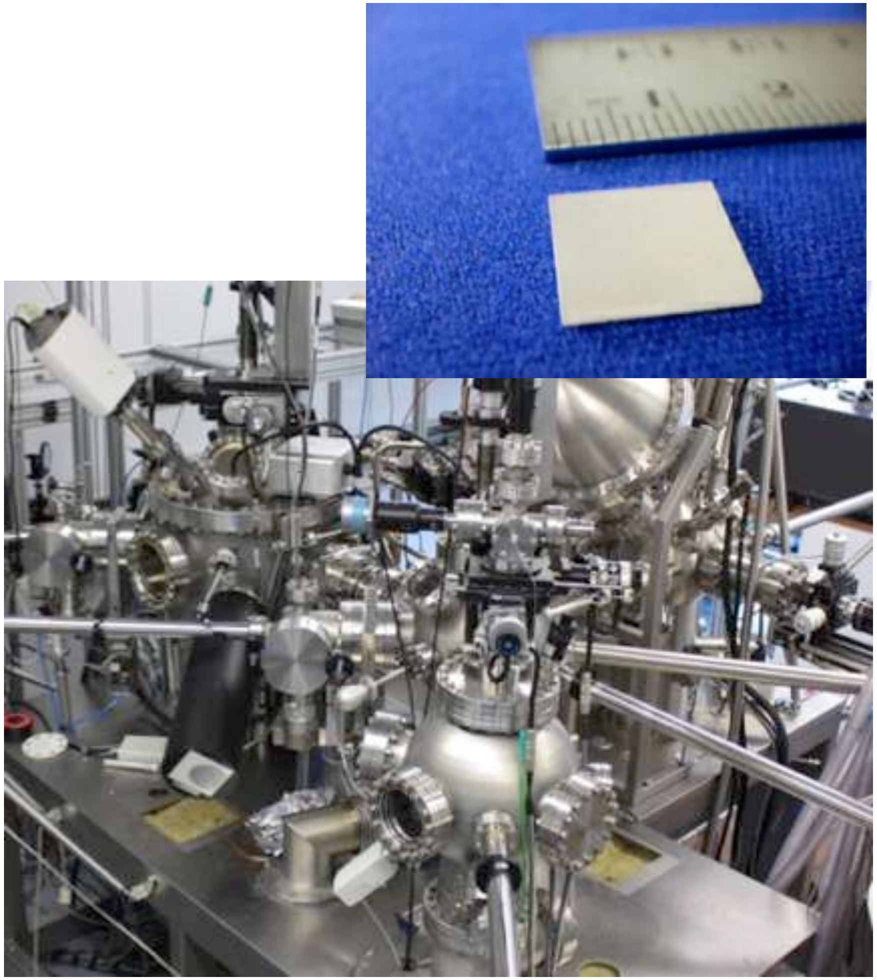






Liao et al, Nature Materials 15, 425 (2016)

Pulsed Laser Deposition: From Lab-scale to Industrial-scale



TSST

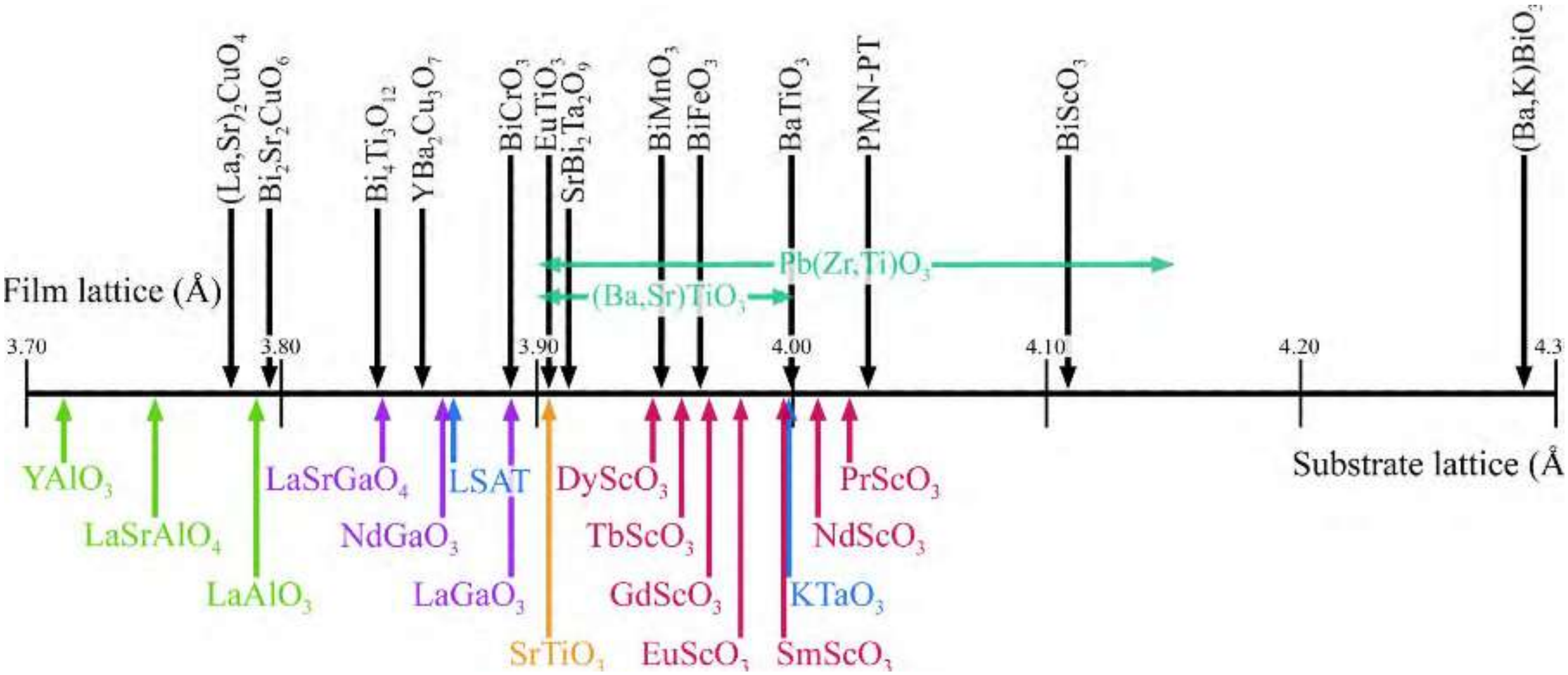
SolMateS
Solutions in Material Science

SolMateS
Solutions in Material Science

Equipment for PZT thin film production

Epitaxial Engineering of thin films:

Choosing ideal substrates

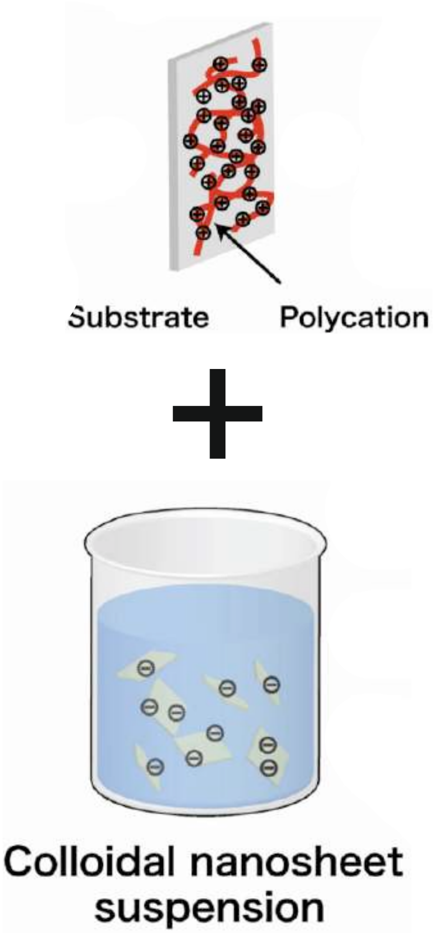


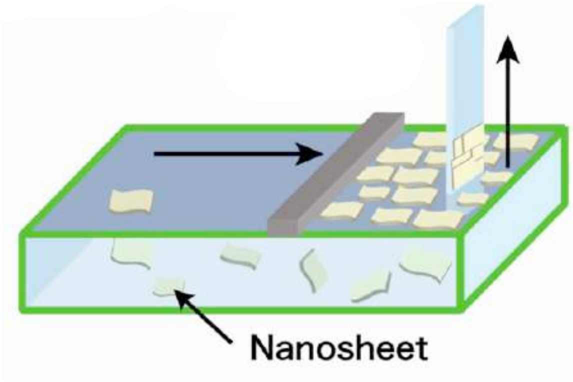
Schlom et al, JACS 91, 2429 (2008)

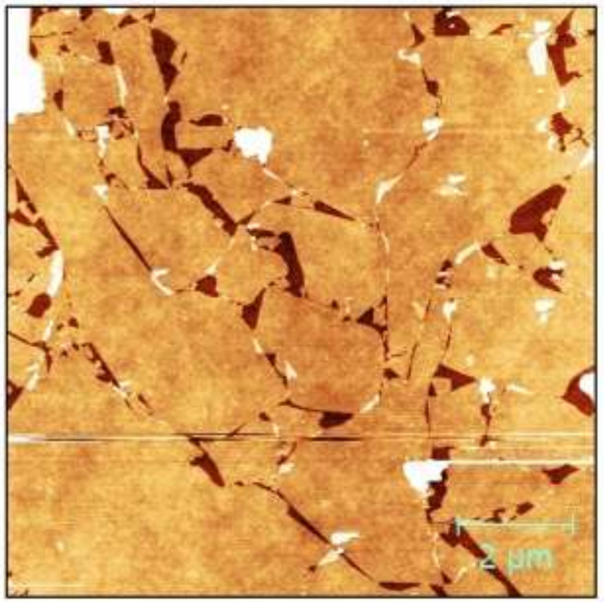
Epitaxy on Demand :

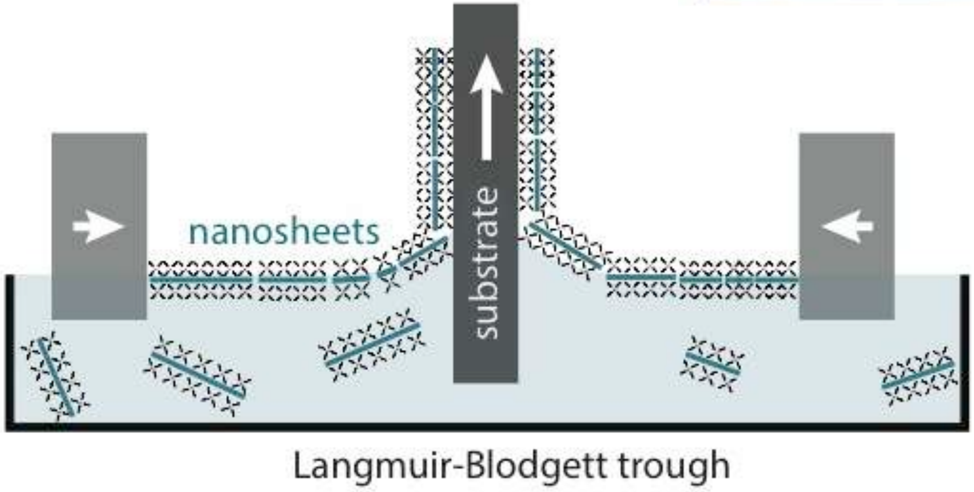
Nanosheets by Langmuir-Blodgett Deposition

Control of crystal structure on amorphous or polycrystalline substrates



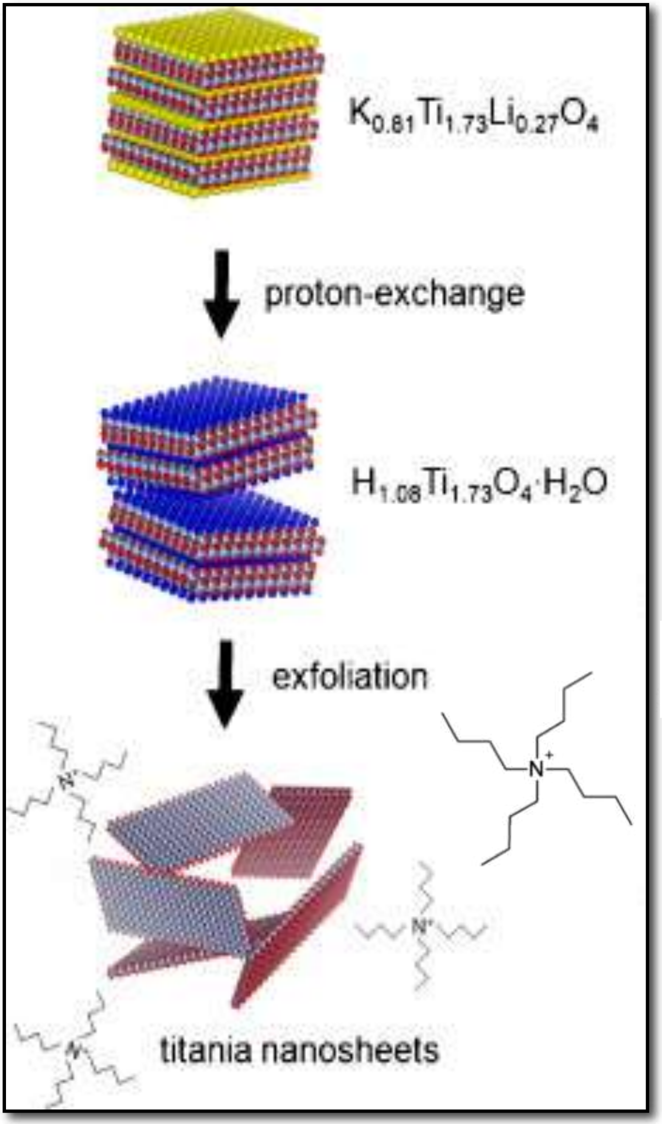






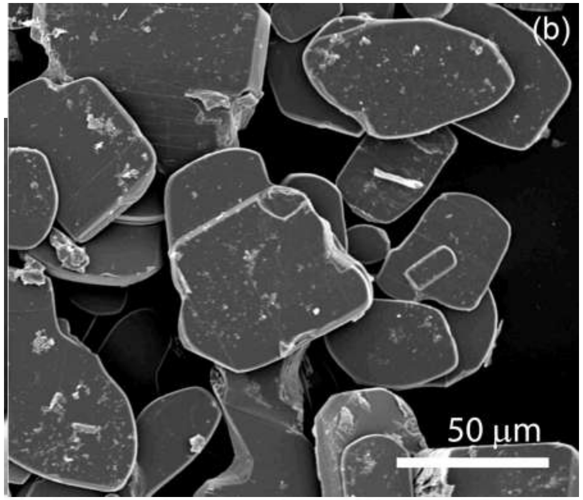
Epitaxy on Demand : TiO_x nanosheets

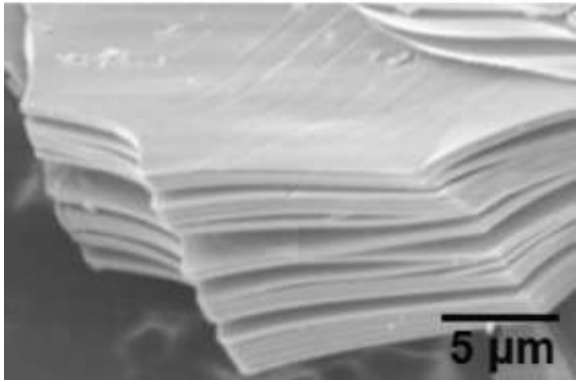
Formation of Titania Nanosheets



Gonzalez Rodriguez et al. (2016)

$K_{0.81}Ti_{1.73}Li_{0.27}O_4$



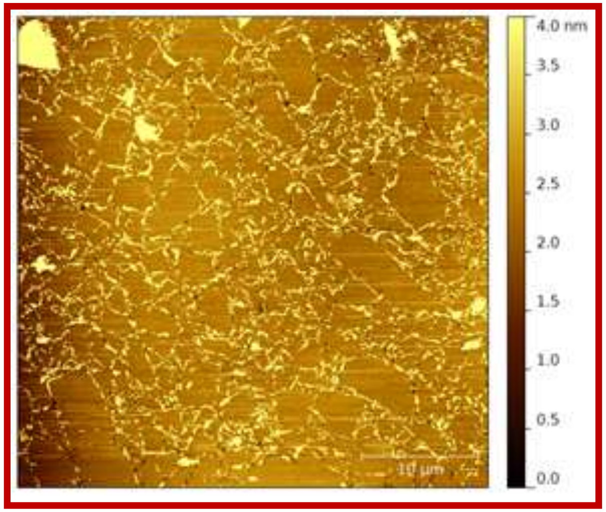


$H_{1.08}Ti_{1.73}O_4{\cdot}H_2O$

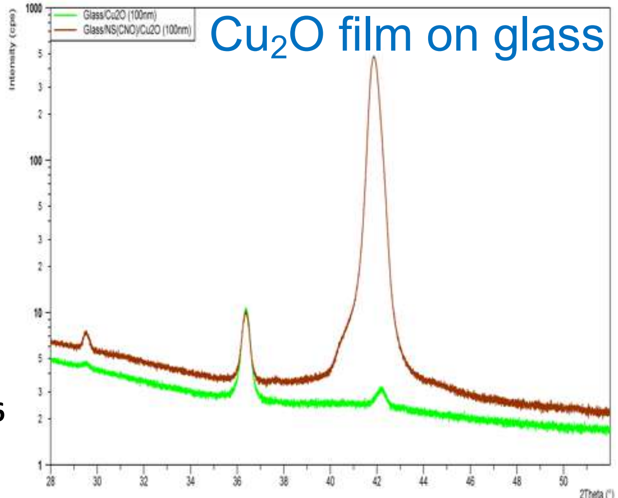
Kijima et al., J. Power Sources, 196 (2011) 7006

Formation Nanosheet Films

LB deposition

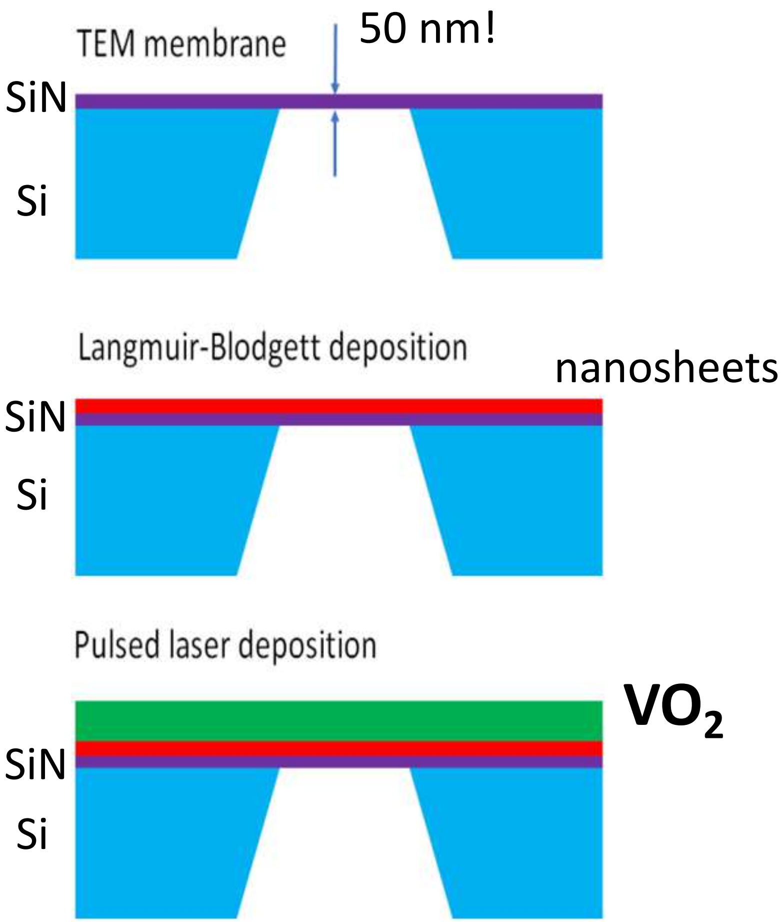


$Ti_{0.87}O_2$ layer (Coverage 97%)



Cu_2O film on glass

Epitaxy on Demand : VO_2 thin films on TEM grids



TEM membrane

50 nm!

SiN

Si

Langmuir-Blodgett deposition

nanosheets

SiN

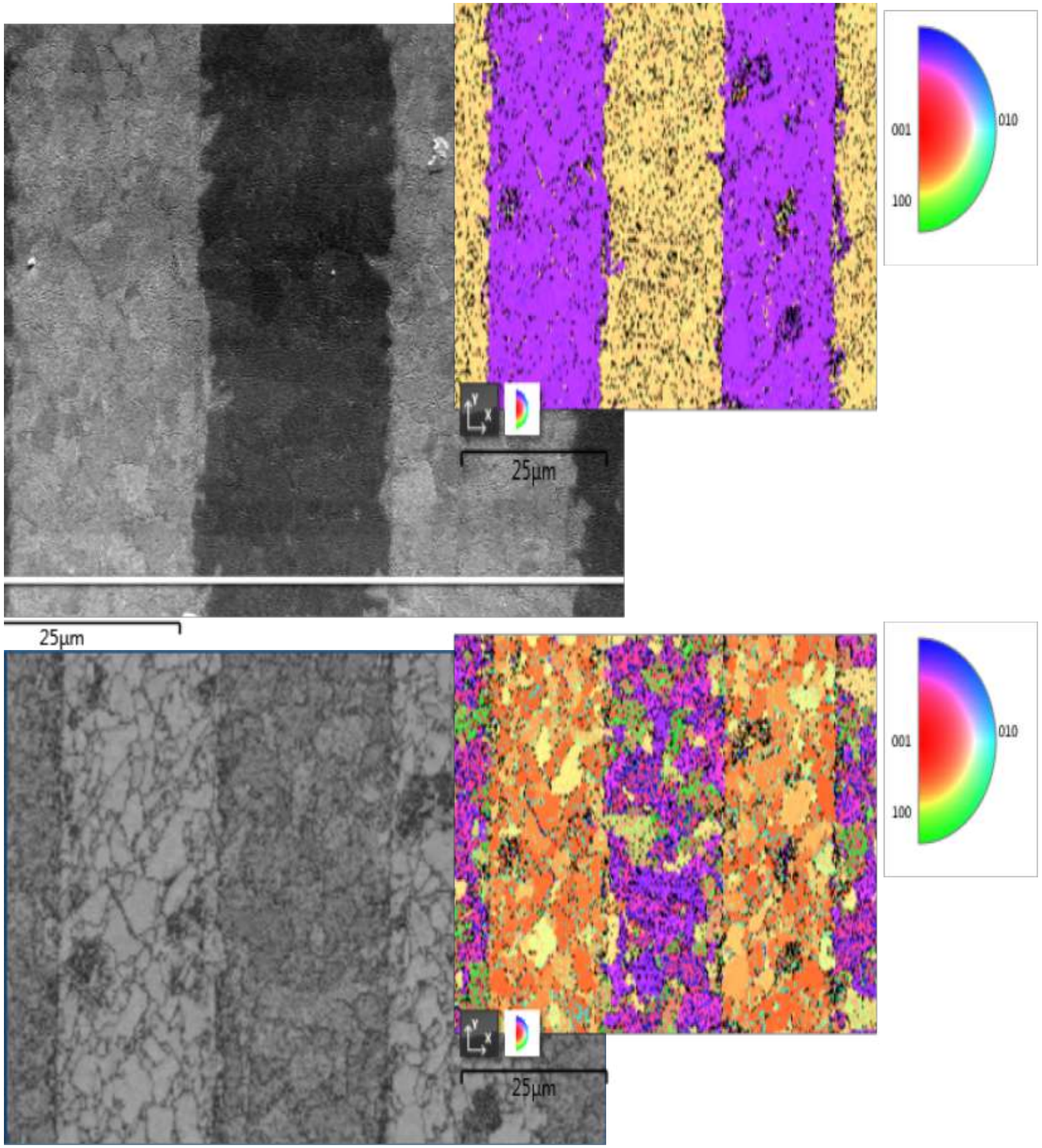
Si

Pulsed laser deposition

VO_2

SiN

Si



Examples of books on Pulsed Laser Deposition