



PSI Center for Neutron and
Muon Sciences

Pulsed Laser Deposition (PLD) of Oxide Materials

Fundamental Aspects Probed by Ablation Plume Analysis



Thomas Lippert
Venice, 16 July 2024

Affiliations



Laboratory for Multiscale Materials Experiments (LMX) and Thin Films and Interfaces Group, Paul Scherrer Institut

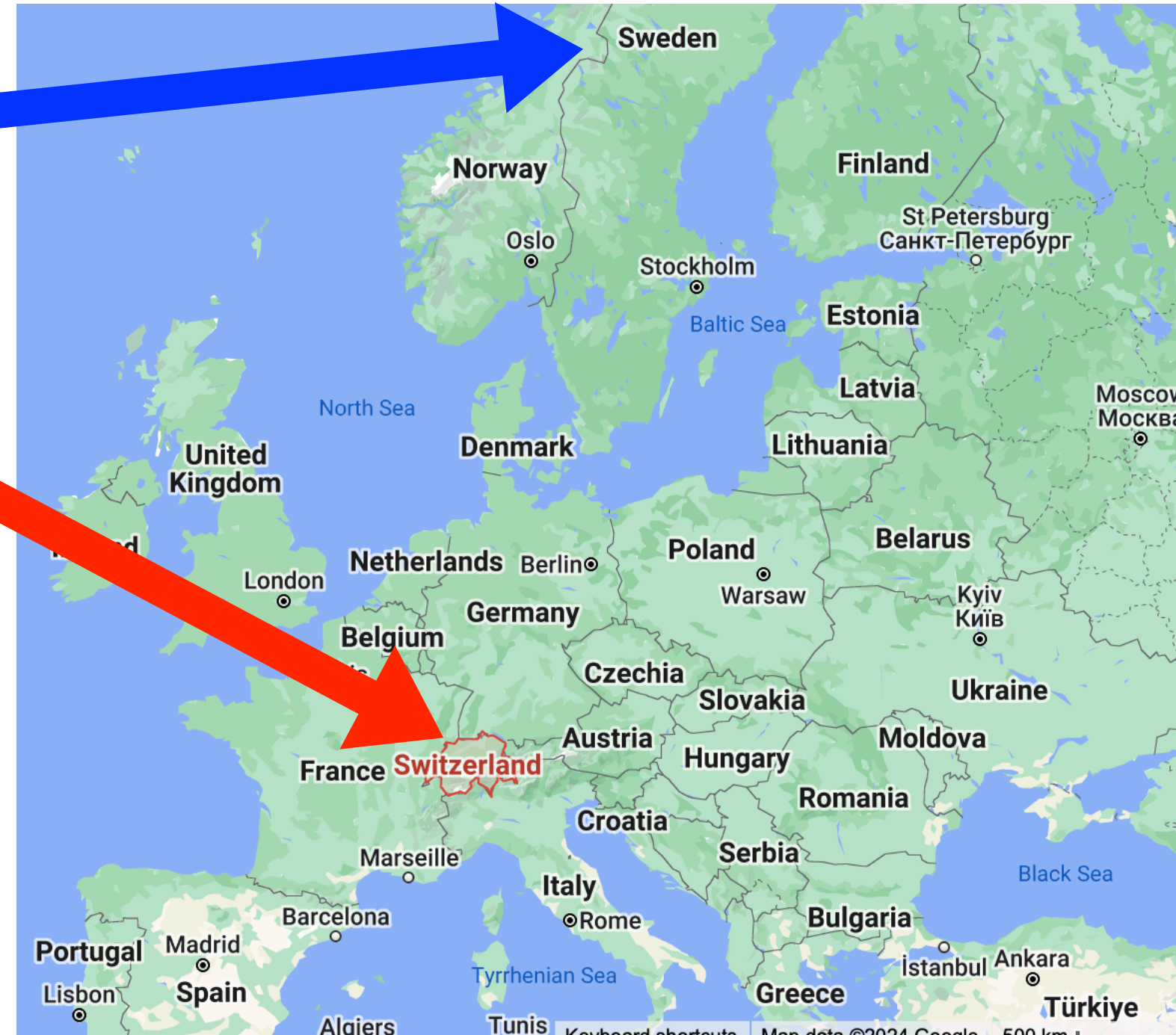


Laboratory of Inorganic Chemistry, ETH Zurich



PI at the International Institute for Carbon-Neutral Energy Research, Advanced Energy Conversion Systems Thrust, Kyushu University, Japan

Switzerland and it is
different to Sweden 😊



What is Switzerland famous for?

in addition to PSI and ETH 😊



Rolex Daytona



Thanks to:

- all students and scientists who have worked in my group on PLD, and especially on the fundamentals
 - M. Montenegro, S. Heule, I. Marozau, S. Heiroth, F. Simmen, Y. Hu, M. Bator, D. Stender, S. Temmel, M. Pichler, K. Shimamoto, A. Fluri, D. Pergolesi, C. Schneider, R. Pelaez, H. Tellez, D. O'Mahoney, T. Dumont, S. Canulescu, M. Esposito, J. Chen, A. Ojeda, X. Yao, N. Ohannessian, X. Huang, C. Schneider, A. Wokaun, N. Bulgakova, A. Bulgakov
- all cooperation partners and funding sources (SNF)

What I would like you to know/learn

- Why we want thin films.
- How to make thin film.
- What is PLD.
- What you need to know about PLD.
- What should you consider when you use PLD.
- What can happen (go wrong) during PLD.
- Conclusions.

Thin films

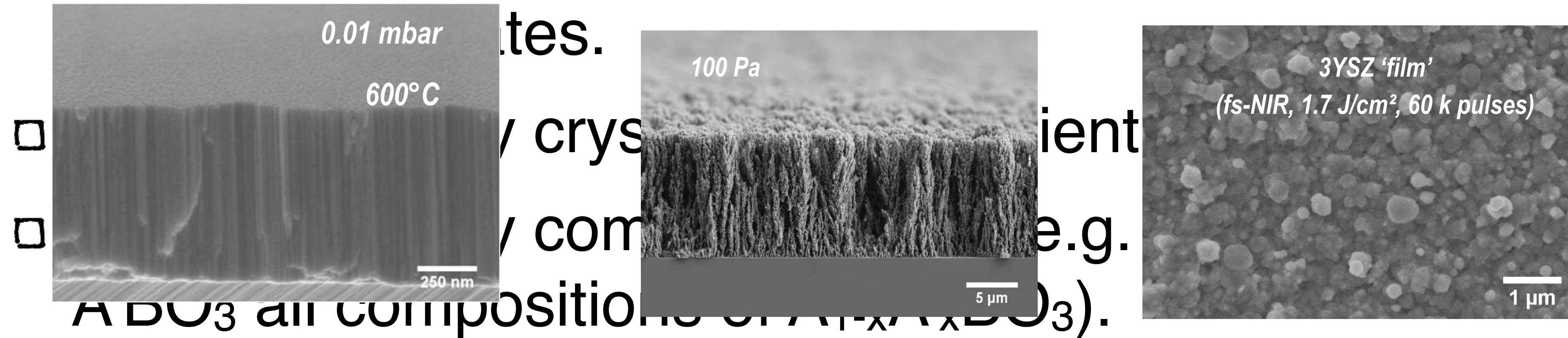
- Thin films are utilized in many applications as **active components**, but they are also often perfect **model systems** to study fundamental aspects of the materials, their properties, and functionality. **Which examples do you know?**
- For applications the “**cheapest**” or “**only**” deposition methods will be applied, but for fundamental studies the most “**flexible**” method with the highest control is often used → **PLD**.
- For achieving a high control over the films a **understanding of all processes** are required, i.e. from the first steps of the deposition method to the film growth.

Thin Films as model systems

- Possible to create well defined surfaces and materials on inert substrates.
- Possible to vary crystallinity and orientation.
- Possible to vary composition fast (e.g. out of ABO_3 + $A'BO_3$ all compositions of $A_{1-x}A'_xB O_3$).
- Possible to obtain phases which are difficult to obtain with other methods (metastable).
- Dense to porous films (even micro- to nano-particles are possible).

Thin Films as model systems

- Possible to create well defined surfaces and materials



- Possible to obtain phases which are difficult to obtain with other methods (metastable).
- Dense to porous films (even micro- to nano-particles are possible).

Short history of thin films. When?

- **Mechanically** (Au-beating) since 2650 BC in Egypt.
- **Gilding** (amalgam and fire) since 400 BC in China.
- **Electroless gold plating** 100 BC in Peru (Moche).
- **Electroplating** 18th century, but may be before in Egypt or Baghdad ca. 400 BC (Baghdad battery?).
- **Thermal evaporation and sputtering** 1872/1852 (related to vacuum/gauges and electricity) → **Physical Vapour Deposition**
- **Chemical Vapour Deposition** (HgS in China-1600-400 BC), later As (1650) and Si and Al (1876).
- **Chemical Solution Deposition** in 1835 (Ag and Au by Liebig)
- **Lasers and ions** only after 1965 and 1970.

How are thin films made?

CSD = chemical solution deposition:

- Spin coating
- Dip coating (with many variations)
- Spray coating
- Ink jet printing
- Laser direct writing

- Electroplating

PVD = physical vapour deposition:

- Evaporation:
 - Thermals
 - Electron beam
 - Electric arc
 - Molecular beam epitaxy (MBE)
- **Evaporation: Using photons-pulsed laser deposition (PLD)**
- Sputtering (*many variations*)
- Ion plating
- ICB (*ionized cluster beam*)

CVD = chemical vapour deposition:

- many variations, e.g. depending on pressure:
 - AP= atmospheric pressure-CVD
 - LP= low pressure-CVD
- with added parameter:
 - PE= plasma enhanced
 - HF= hot filament-CVD
 - MO= metal-organic CVD

To consider: geometry, conductivity, thermal properties of the film and substrate materials, the required quality, and **costs**.

PLD History



Vacuum Deposited Thin Films Using a Ruby Laser

1965

Howard M. Smith and A. F. Turner

Howard M. Smith is at the Institute of Optics, University of Rochester, Rochester, New York, and A. F. Turner is at Bausch & Lomb Inc., Rochester, New York.

Received 18 September 1964.

Partially sponsored by the U.S. Army Research Office, Durham, North Carolina. Paper TC18 presented at the Optical Society of America meeting, Rochester, New York, October 1962.

The vaporization of materials in air by a laser is a familiar phenomenon. It suggests the use of a laser beam to evaporate materials in vacuum for the deposition of optical thin films. The success of this technique cannot be predicted *a priori* since the constituent character of the vapor product, often visible in air as a plume, is still problematical and its film-forming potential unknown.

Table I. Powdered Materials Producing Optically Satisfactory Films

Material	nd/P	n	mp, °C	bp, °C
Sb ₂ S ₃	0.35	2.7	550	—
As ₂ S ₃	0.30	2.4	300	707
Fuchsine	0.25	—	—	—
Se	0.19	2.4	220	688
Ni-dimethyl glyoxime	0.12	—	250 subl.	—
ZnTe	0.09	2.7	1239	—
Te	0.05	5.0	452	1390
MoO ₃	0.04	2.0	795	subl.
PbCl ₂ (with carbon)	0.03	1.8	501	950
PbTe	0.03	5.0	917	—
Ge	0.01	3.8	959	2700

January 1965 / Vol. 4, No. 1 / APPLIED OPTICS 147

Vacuum Deposition by High-Energy Laser with Emphasis on Barium Titanate Films*

1969

Helmut Schwarz and H. A. Tourtellotte

Rensselaer Polytechnic Institute-Hartford Graduate Center, East Windsor Hill, Connecticut 06028
(Received 18 November 1968)

1969

A laser beam capable of energy outputs up to 500 Joule was directed through a glass window into a vacuum system onto fine grain powder of Cr, W, Ti, C, Sb₂S₃, ZnS, SrTiO₃, and BaTiO₃. A neodymium-doped glass laser of 1.06- μ wavelength was mostly used without Q spoiling. Sometimes the beam was focused. Films up to 2000 Å were achieved on glass with one laser burst only, which corresponds to deposition rates of up to 10⁶ Å/sec. The substrate was positioned between the vapor source and laser so that the laser beam passed through it, and therefore, also served as a shield. Electron micrographs were taken. From electron transmission diffraction patterns it appeared as if BaTiO₃ had not been decomposed. In order to evaluate electrical properties of the films, platinum-rhodium films were sputtered or "laser-deposited" onto glass slides to serve as base electrode. Then a barium titanate film was evaporated with a laser. On top of this, an array of thin aluminum dots were evaporated through a mask, so that it was possible to investigate different areas of the films. Values of up to 2.5 μ F/cm² at 1 kHz and relative dielectric constants of up to 1000 were measured. Dissipation factors were in a range from 1%–10%. The capacitance at 1 kHz was constant within 0.1% between 50° and 105°C as well as above 160°C. A sharp peak of the temperature dependence curve could be observed at about 125°C where the capacitance increased by 30%. For most films the onset of breakdown was observed at a field strength of around 5×10^6 Vcm⁻¹. Both the capacitance and dissipation factor decrease almost linearly when increasing the frequency from 60 Hz to 500 kHz with the capacitance reaching 90% of its 60-Hz value.

the journal of vacuum science and technology vol. 6 no. 3

Thin Solid Films, 29 (1975) 29–41
© Elsevier Sequoia S.A., Lausanne—Printed in Switzerland

1975

INTERACTION D'UN FAISCEAU DE LUMIÈRE COHÉRENTE PULSÉE AVEC UNE CIBLE COMPLEXE: APPLICATION À L'ÉLABORATION DE COMPOSÉS EN COUCHES MINCES

J. DESSERRE ET J. F. ELOY
C.E.A.-D.M.E.C.N., Département de Métallurgie de Grenoble, Laboratoire d'Etudes des Matériaux Minces, Grenoble (France)
(Reçu le 20 décembre 1974; accepté le 19 janvier 1975)

L'interaction d'un faisceau de lumière cohérente pulsée, émis par un laser relaxé ou déclenché, avec différentes cibles (Ni₃Mn, CdTe, ZrC, ReBe₂₂) a permis de réaliser la vaporisation congruente de celles-ci. L'étude des films minces obtenus par condensation sur un substrat de la vapeur et du plasma émis pendant l'interaction a montré que, dans certains cas, les couches élaborées avaient même composition et même structure que le matériau cible choisi, et ceci sans traitement thermique du dépôt après condensation.

SciTech Connect / Journal Article: Superconductivity of BaPb/sub 1-x/Bi/sub x/O/sub 3/ films prepared by laser evaporation method

Superconductivity of BaPb/sub 1-x/Bi/sub x/O/sub 3/ films prepared by laser evaporation method

Superconducting films of BaPb/sub 1-x/Bi/sub x/O/sub 3/ were prepared by laser evaporation and heat treatment of the resultant films in air. A study was made of the behavior of the film resistance in the course of evaporation and heat treatment, and also at low temperatures in magnetic fields up to 40 kOe. It was found that heat treatment at 550 /sup 0/C resulted in an irreversible fall of the resistance by more than 8--10 orders of magnitude and in the appearance of superconducting properties in films of compositions within the range 0.05< or=x< or =0.30. The temperature dependences of the resistance of films with rho approx. 1--10 /sup 4/ .cap omega. x cm had maxima associated with phase transitions. It was also found that in the case of the films with the compositions x = 0.25 and 0.30 the temperature dependences of the critical magnetic field differed considerably from those predicted by the BCS theory.

Authors: Zaitsev-Zotov, S.V.; Martynuk, A.N.; Protasov, E.A.

Publication Date: 1983-01-01

OSTI Identifier: 5926153

Resource Type: Journal Article

Resource Relation: Journal Name: Sov. Phys. - Solid State (Engl. Trans.); (United States); Journal Volume: 25:1

Research Org: Engineering-Physics Institute, Moscow

Country of Publication: United States

Language: English

Subject: 36 MATERIALS SCIENCE; 75 CONDENSED MATTER PHYSICS, SUPERCONDUCTIVITY AND SUPERFLUIDITY; BARIUM COMPOUNDS; FABRICATION; HEAT TREATMENTS; SUPERCONDUCTIVITY; BISMUTH COMPOUNDS; LEAD COMPOUNDS; OXYGEN COMPOUNDS; CHEMICAL COMPOSITION; CRITICAL FIELD; EVAPORATION; HIGH TEMPERATURE; IRREVERSIBLE PROCESSES; LASER-RADIATION HEATING; PHASE TRANSFORMATIONS; SUPERCONDUCTING FILMS; TEMPERATURE DEPENDENCE; ALKALINE EARTH METAL COMPOUNDS; ELECTRIC CONDUCTIVITY; ELECTRICAL PROPERTIES; FILMS; HEATING; MAGNETIC FIELDS; PHYSICAL PROPERTIES; PLASMA HEATING 360204* -- Ceramics, Cermets, & Refractories-- Physical Properties; 656102 -- Solid State Physics-- Superconductivity-- Acoustic, Electronic, Magnetic, Optical, & Thermal Phenomena-- (-1987)

1983

373

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

D. Dijkamp 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. Crc
Physics Department, Rutgers University, Piscataway, New Jersey 08855-0849

1987

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

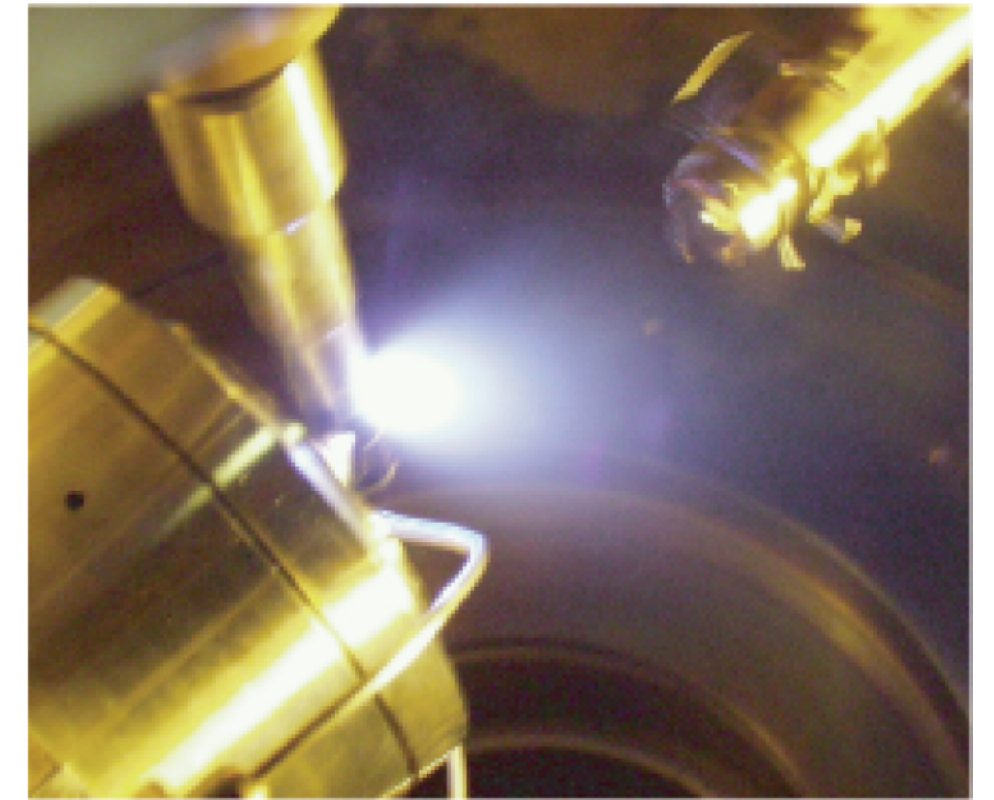
We report the first successful preparation of thin films of Y-Ba-Cu-O superconductors using pulsed excimer laser evaporation of a single bulk material target in vacuum. Rutherford backscattering spectrometry showed the composition of these films to be close to that of the bulk material. Growth rates 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 SrTiO₃ and Al₂O₃ substrates, respectively. This new deposition method is relatively simple, very versatile, and does not require the use of ultrahigh vacuum techniques.

Main start of PLD

Pulsed Laser Deposition (PLD)

PLD is often described as a three-step process consisting of

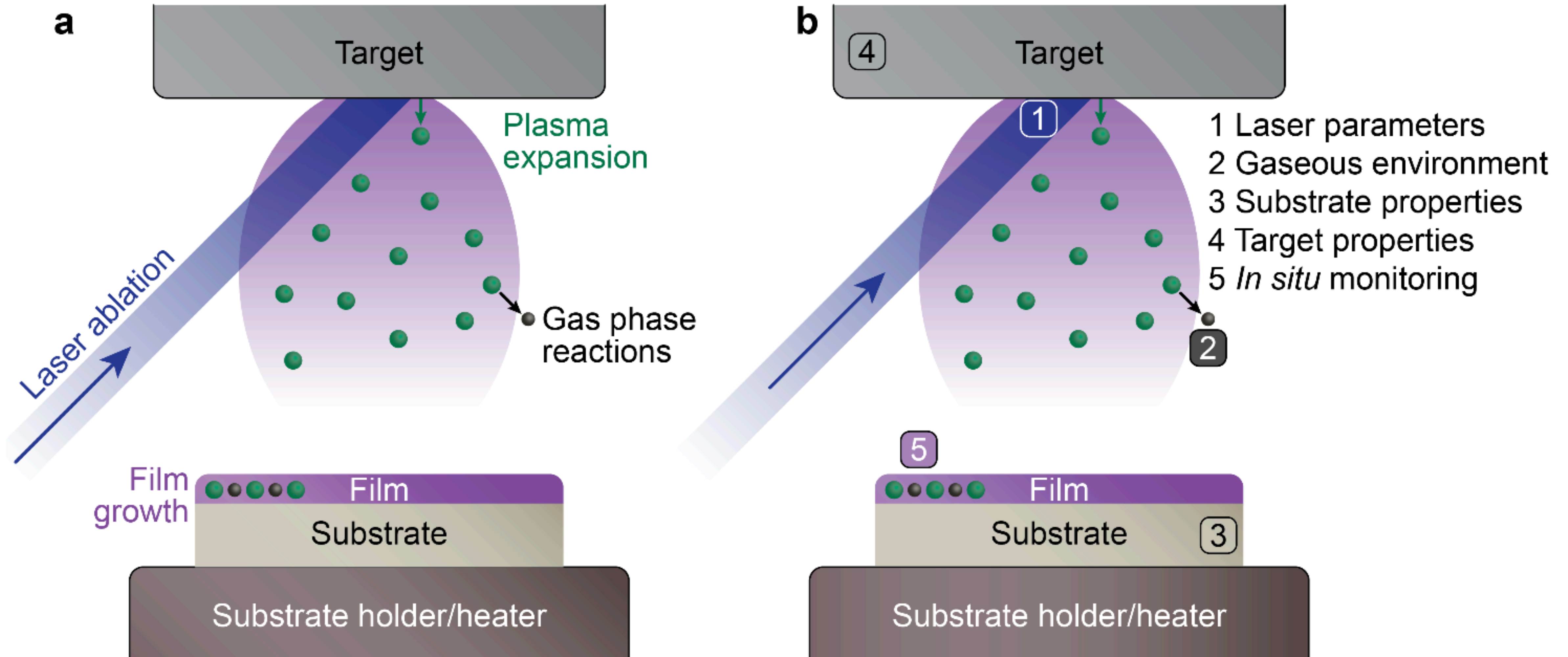
- vaporization of a target material
- transport of the vapor plume (plasma plume)
- film growth on a substrate
- **but the basis is that the light must be absorbed**



The short interaction times and the strong non-equilibrium conditions in PLD allow some *unique applications (metastable materials, nano-crystalline etc.)*.

The major disadvantage is the relatively low throughput that can be achieved (but deposition on tapes is possible). The particulates are another problem, especially with thin epitaxial films.

Pulsed Laser Deposition



Question

How many of you use PLD or PLD films?

How many of you think, that they understand PLD completely?

Pulsed Laser Deposition (PLD)

- Advantages:

1. **Very flexible** **my opinion**
2. In principle, **all materials** can be deposited (sub mono layer to..)
3. High quality films, **similar to MBE**, but also nanoparticles, amorphous, or porous films, and even surface termination is possible
4. **Separation** of energy source from deposition
5. etc.

- Disadvantages:

1. **Very flexible** **opinion of my students**
2. Metals are more difficult, as **droplets** may be formed
3. Fracture of target may result in the deposition of **particulates**.
4. **Congruent transfer** (film has same composition as target) is not really a given.
5. Homogeneity (thickness and composition) and **large areas** can be problematic
6. etc.

The PLD Process: Parameter

Ablation

Material

- Which elements
- Absorption coefficient (α), e.g. metals vs. oxide (or polymer)
- Stable during ablation or is α changing?
- Melting (sublimation) temperature (vapor pressure)
- Density
- Brittleness
- etc.

Laser

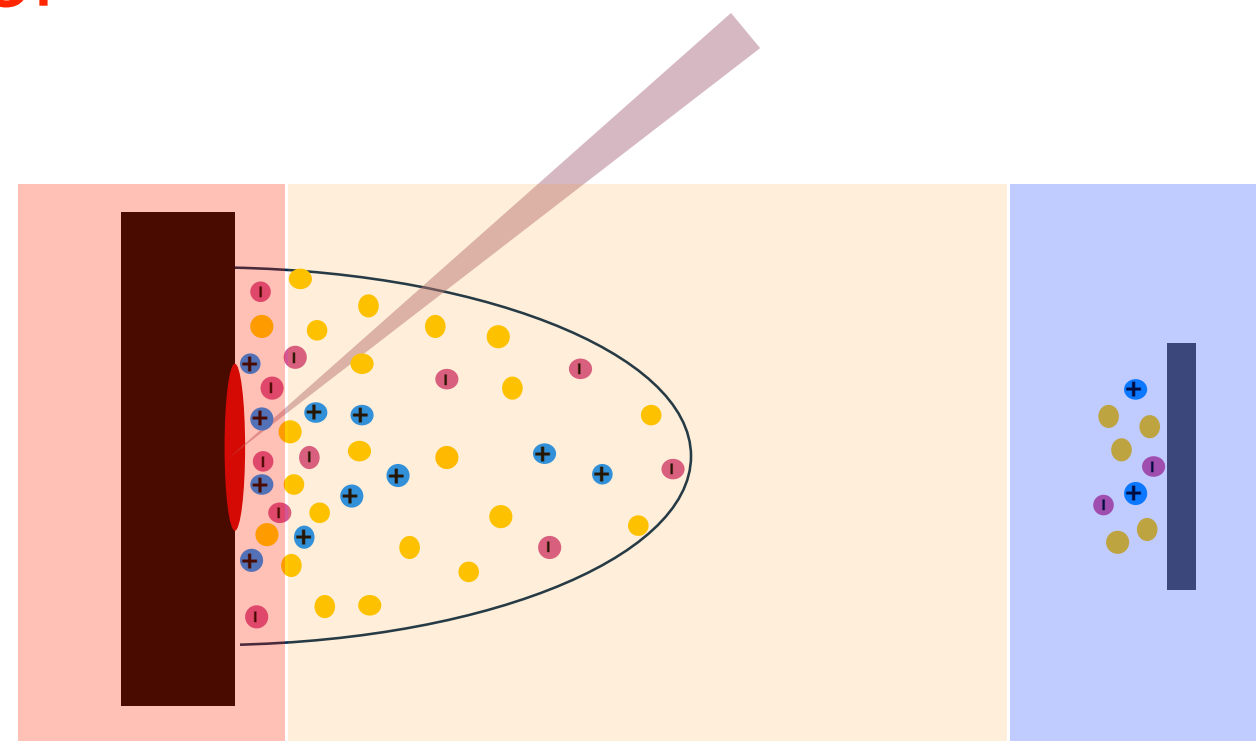
- Wavelength
- Fluence
- Pulse length
- Repetition Rate
- Spot size and shape,
- etc.

Plasma

- Kinetic energy of species
- Type and state of species
- Pressure in chamber (background gas)
- Type of background gas: collisions and reactions
- Which species are formed and are stable, etc.

Growth

- Substrate material and type (possible oxygen source)
- Temperature
- Distance to target
- Size of holder
- Lattice matching to growing film
- Interaction with arriving species, etc.



The PLD Process: Parameter

Ablation

Plasma

Growth

Material

- Which elements
- Absorption coefficient
- α
- (or
- Sta
- is a changing?
- Melting (sublimation) temperature (vapor pressure)
- Density
- Brittleness
- etc.

Laser

- Wavelength
- Fluence
- Shape,
- etc.

- Kinetic energy of species
- Type and state of

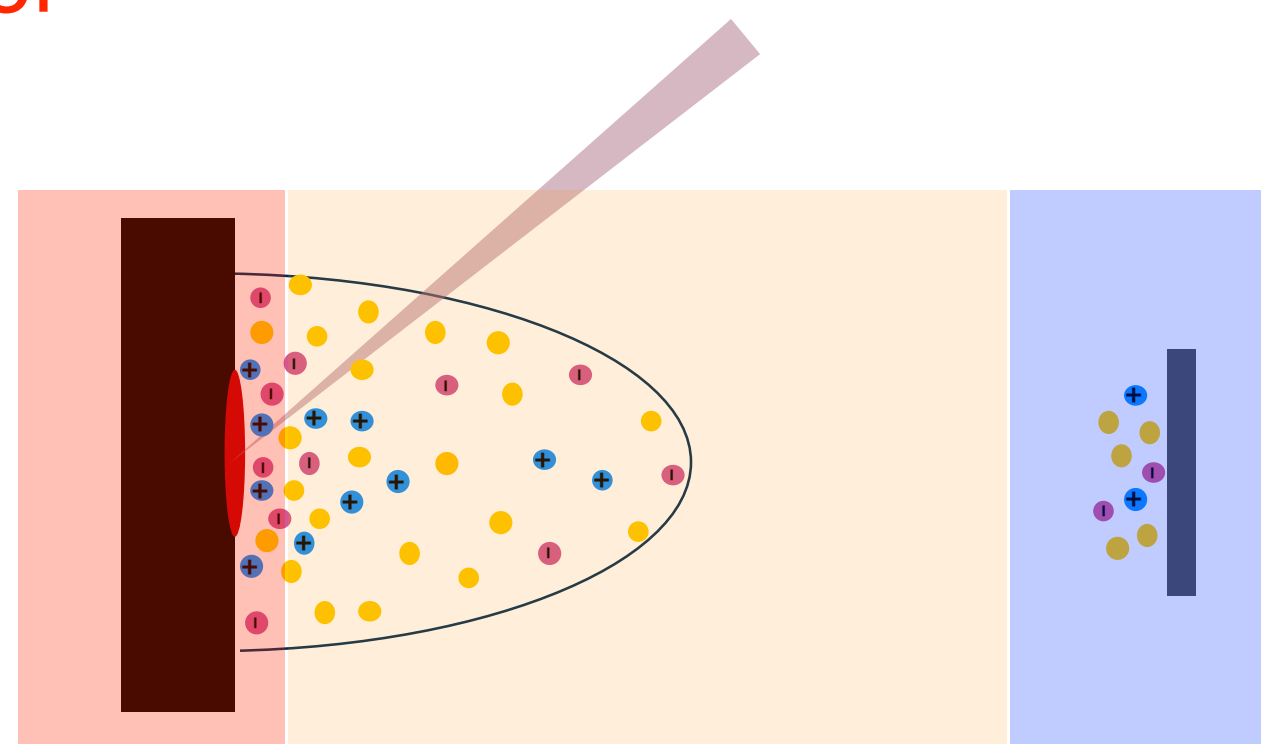
- Substrate material and type (possible oxygen source)
- Temperature

and many of the parameter are interrelated

(and many things can happen-remember the talk by N. Bulgakova)

- Type of background gas: collisions and reactions
- Which species are formed and are stable,
- etc.

- growing film
- Interaction with arriving species,
- etc.



Why Fundamentals of PLD?

- You can do wonderful things with PLD (from atomic sharp interfaces/surfaces, single crystals, strained materials, etc.), but it is dangerous to assume that this is a given. There may be problems! And I will show you some possible problems you should be aware of.
- Many people “assume” that PLD is always a method that allows the “congruent (same) transfer of materials from a target to a substrate” (in a chapter of the first book on PLD edited by Chrisey and Hubler-1994). But is this true?
- Thin film materials show sometimes different properties than bulk materials (of course some are related to mean free path of electrons/defect number/optical light penetration, etc.). Why?
- Could the composition be a problem?

Possible Problems with PLD Films (mainly oxides)

Oxygen content: directly after deposition too low, e.g. for a perovskite it can be between 2.5 up to > 3 . May be not a problem, if you can do annealing in oxygen, but if you want to do strain engineering then this may not be possible. What is the result of an **oxygen deficiency**:

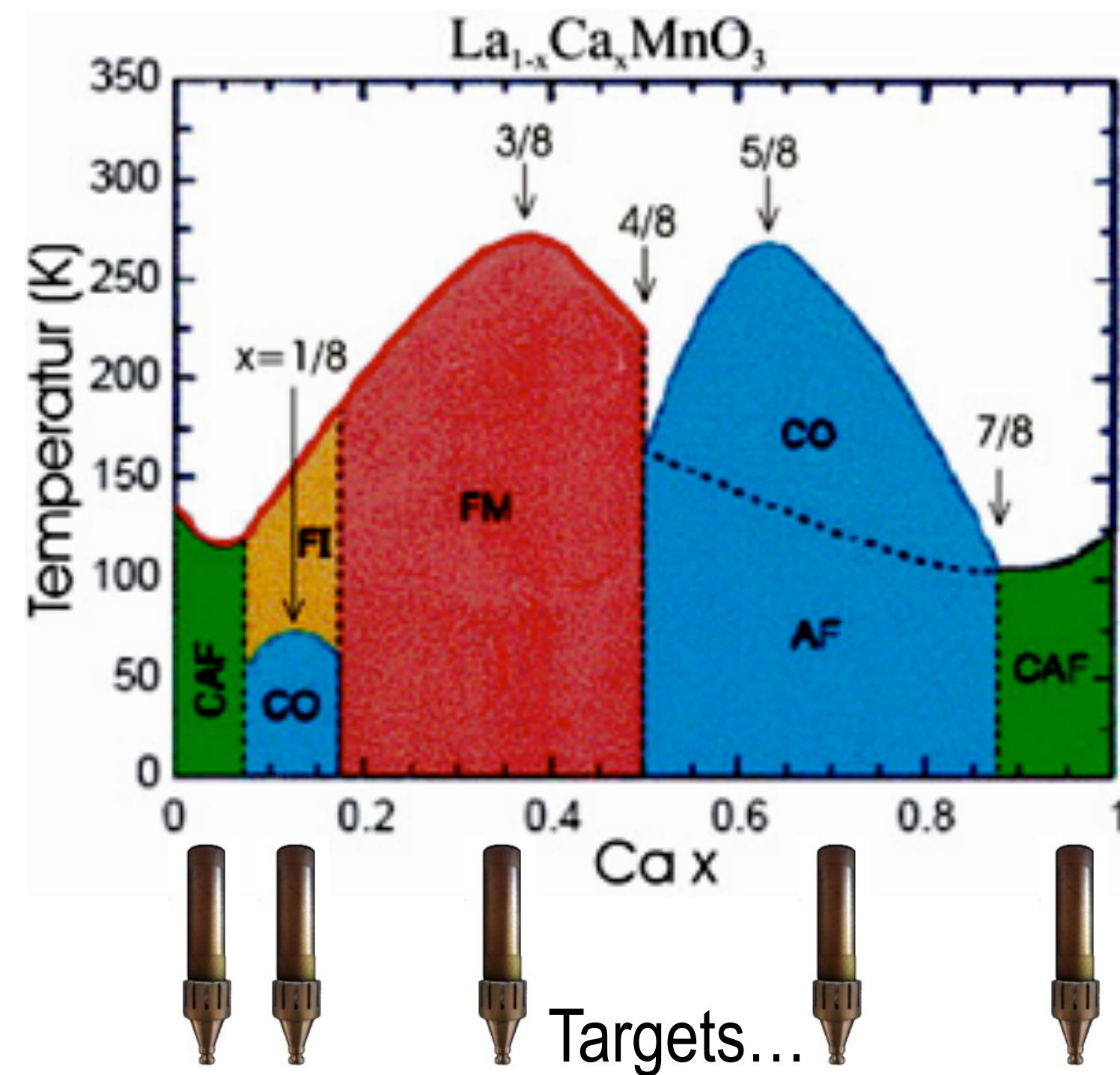
- **Vacancies** instead of oxygen ions \Rightarrow size of vacancy is typically smaller \rightarrow **strain** (chemo-mechanical strain) \Rightarrow different properties.
- **Cations** have to balance this, i.e. has to **change oxidation state**, which means very often a different size (and properties, e.g. the double exchange mechanism for manganites with mixed Mn oxidation states \rightarrow CMR), e.g. Fe^{2+} with 77 pm while Fe^{3+} is 63 pm \rightarrow **strain** (chemo-mechanical strain) e.g. for DyFeO_{3-x} .

Change of the ratio A/B of the 2 metals (ABO_3 in a perovskite). What does this mean?

- It is a different compound with possibly different properties (see LCMO e.g. with 0.5).

To know/understand this we need to measure the film composition quantitatively

Possible Problems with PLD Films (mainly oxides)

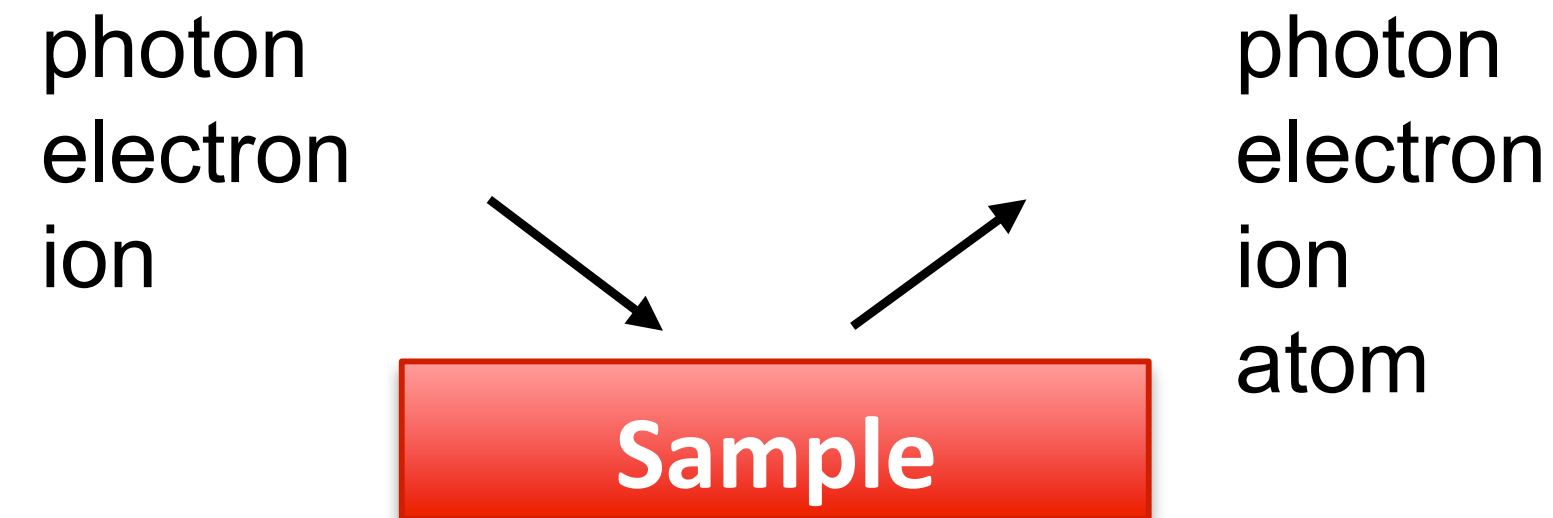


A.J. Millis, Nature 392, 147 (1998)

The horizontal axis shows the value of x in the formula. Phases include **charge-ordered (CO)**, **anti-ferromagnet (AF)**, **canted antiferromagnet (CAF)**, **ferromagnetic metal (FM)**, **ferromagnetic insulator (FI)**. The unlabelled region of the phase diagram has neither magnetic nor charge order.

To know/understand this we need to measure the film composition quantitatively

Quantitative composition of thin films

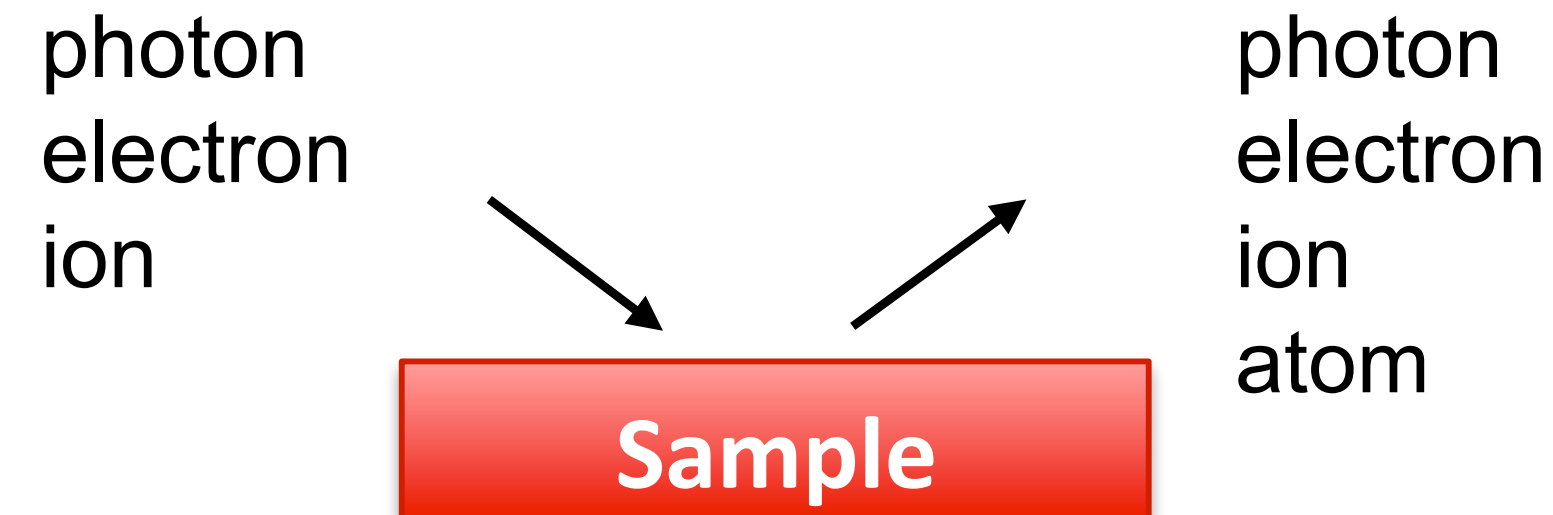


Method	RBS	ERDA	XRF	SEM-EDX	AES	XPS	SIMS
Elements accessible	Be-U	H-U	Be-U	B-U	Li-U	Li-U	H-U
Destructive	No	No	No	No	No	No	Yes
-Lateral resolution	1mm	20'000nm	0.1mm	300nm	7nm	10'000nm	10'000nm
-Depth resolution	5nm	5nm	5nm	500nm	2nm	2nm	0.5nm
Accuracy	0.5% (rel.)	3% (rel.)	2-10%	1-20%	4-30%	4-30%	4-30%
Standards req.?	No	No	Yes	Y/N	Yes	No	Yes

(low numbers are often for dedicated analytical instruments with expert operators and standards).

Also possible: dissolving the films and ICP-emission or mass spectrometry (standards required, and oxygen is not possible)

Quantitative composition of thin films



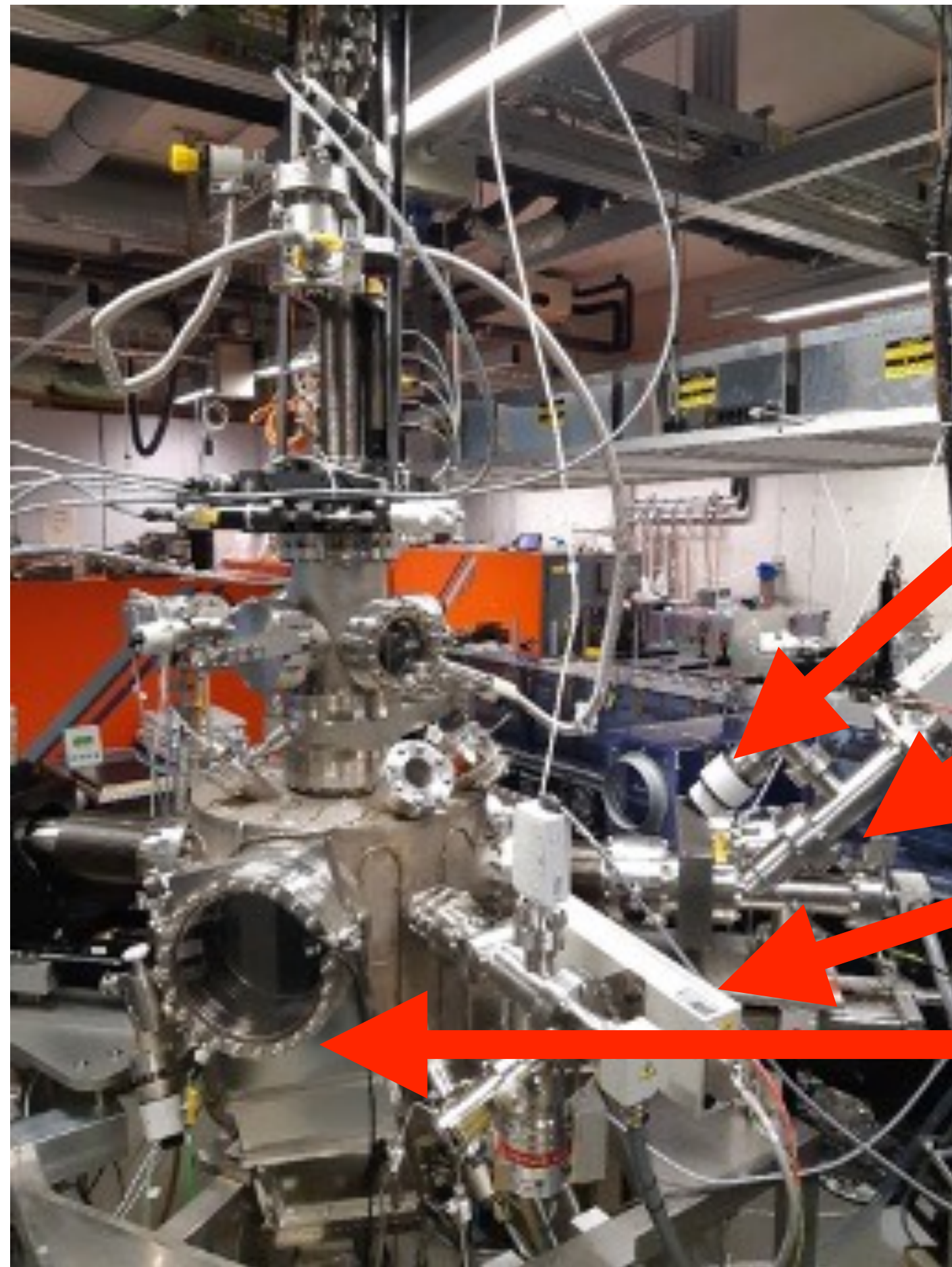
Method	RBS	ERDA	XRF	SEM-EDX	AES	XPS	SIMS
Elements accessible	Be-U	H-U	Be-U	B-U	surface composition, which can be different to bulk composition and we have to consider surface contaminations and for bulk analysis there may be preferential sputtering		
Destructive	No	No	No	No			
-Lateral resolution	1mm	20'000nm	0.1mm	300nm			
-Depth resolution	5nm	5nm	5nm	500nm			
Accuracy	0.5% (rel.)	3% (rel.)	2-10%	1-20%	4-30%	4-30%	4-30%
Standards req.?	No	No	Yes	Y/N	Yes	No	Yes

(low numbers are often for dedicated analytical instruments with expert operators and standards).

Also possible: dissolving the films and ICP-emission or mass spectrometry (standards required, and oxygen is not possible)

What we do to understand “problems”

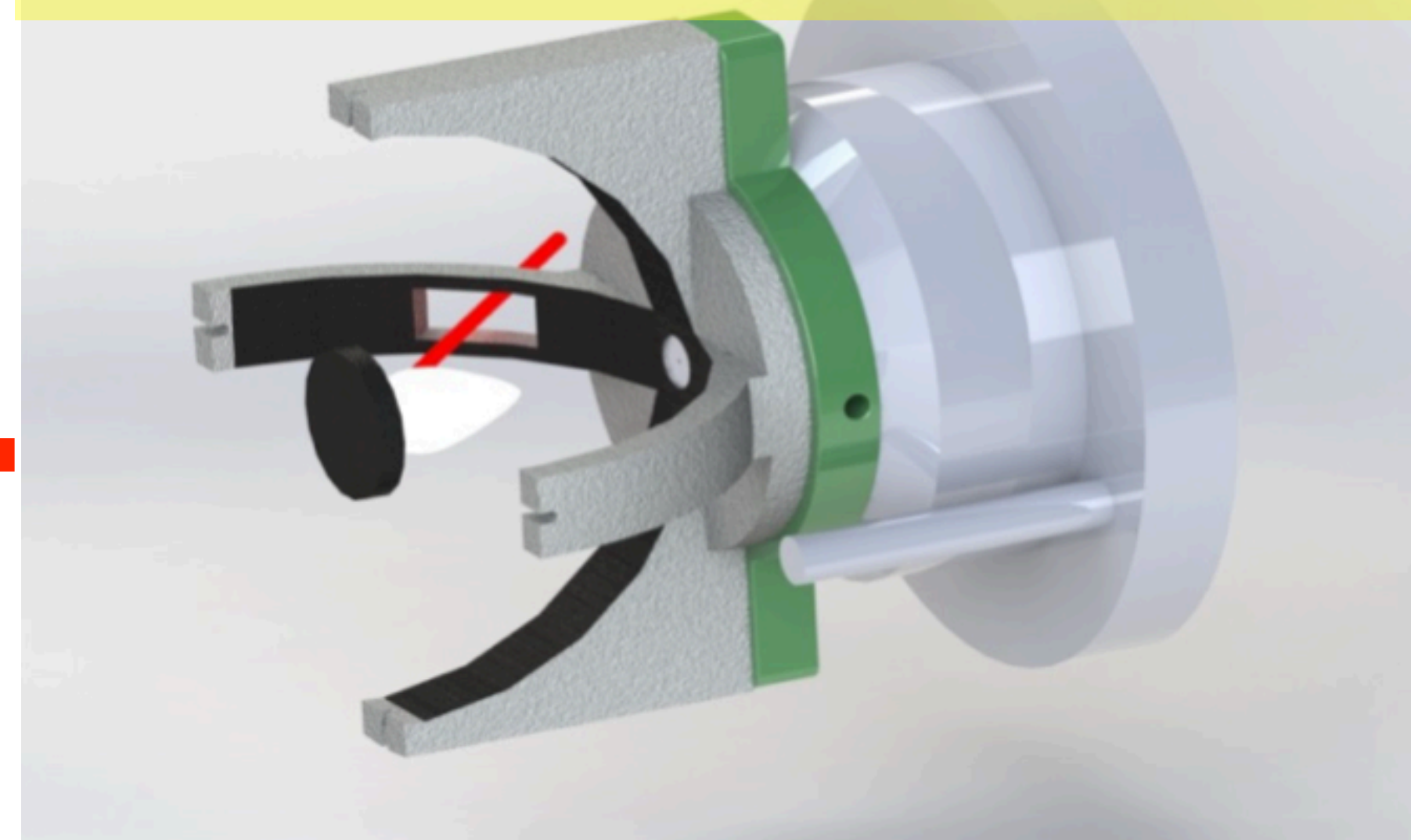
Plasma analysis by mass spectrometry, emission spectroscopy and ion probes
Compositional analysis by ion beam methods (RBS, ERDA, PIXE) and in-situ SIMS



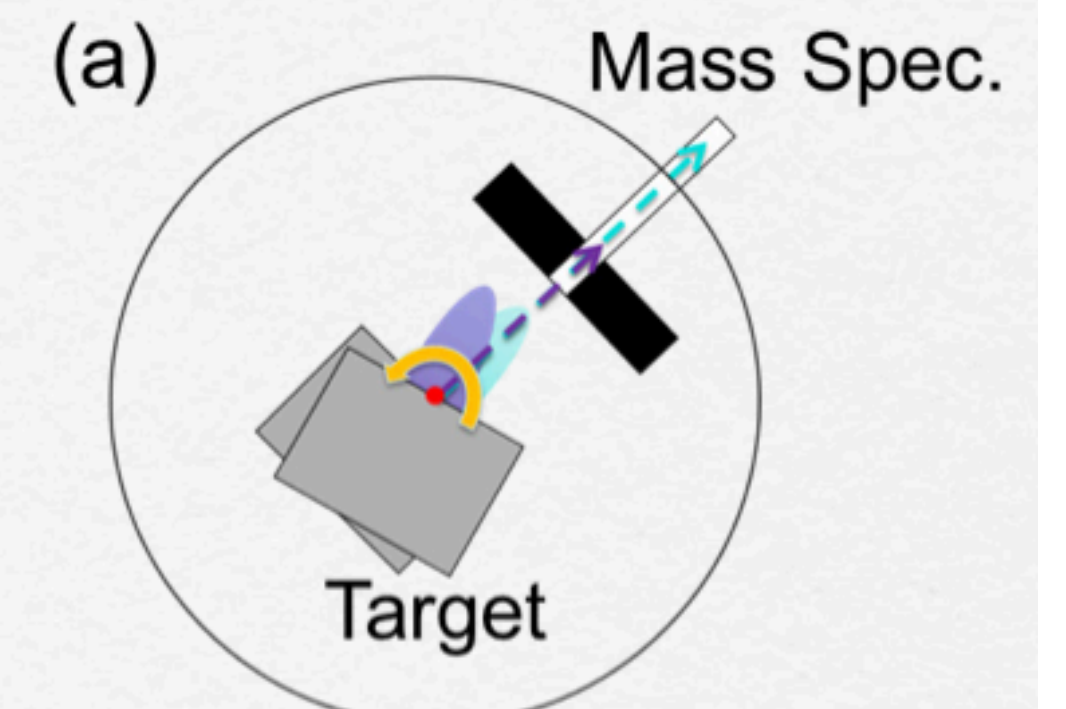
Dedicated PLD chamber for plasma analysis with film deposition:

Plasma Mass Spectrometer (positive/negative **ions**, and neutrals) with **angle**, **distance** and **kinetic energy** resolution

substrate mount for angle resolved compositional analysis at constant distance

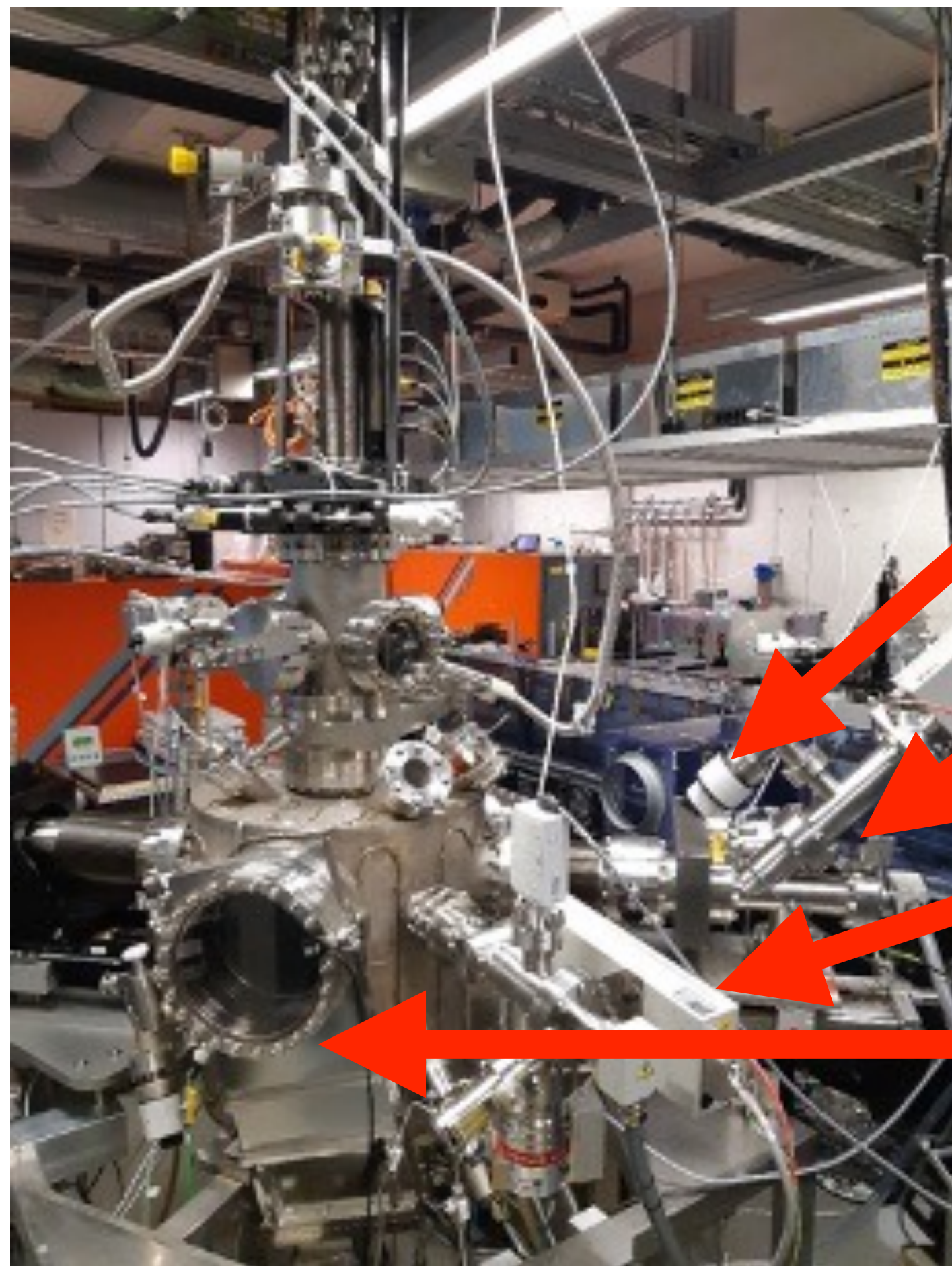


for angle resolved mass spectrometry we tilt our target and adjust laser spot size to be constant



What we do to understand “problems”

Plasma analysis by mass spectrometry, emission spectroscopy and ion probes
Compositional analysis by ion beam methods (RBS, ERDA, PIXE) and in-situ SIMS



Dedicated PLD chamber for plasma analysis with film deposition:

Plasma Mass Spectrometer (positive/negative **ions**, and neutrals) with **angle**, **distance** and **kinetic energy** resolution

We have also a **Langmuir probe array** for **ions** (and electrons) which we can mount on the nozzle of the mass spectrometer

Ion gun for **in-situ SIMS**, allowing **film analysis** (and special sample (substrate holders) for angle resolved deposition

Optical window, where we can mount:

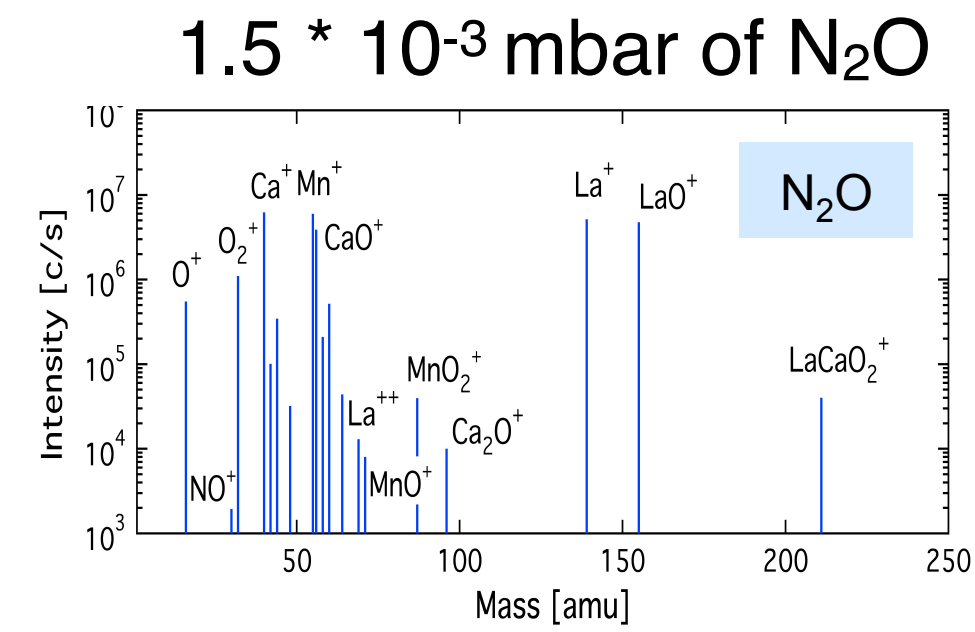
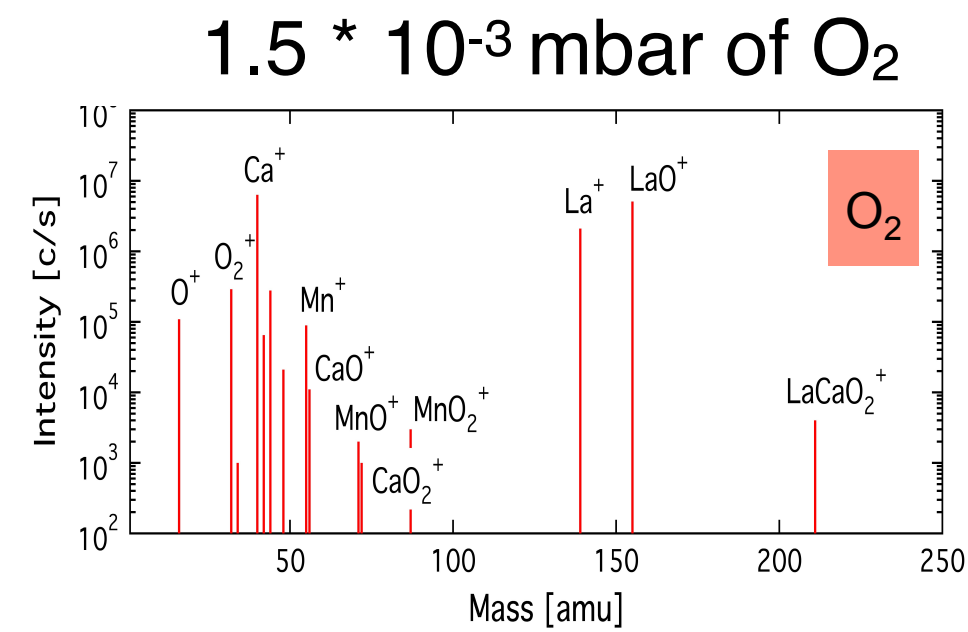
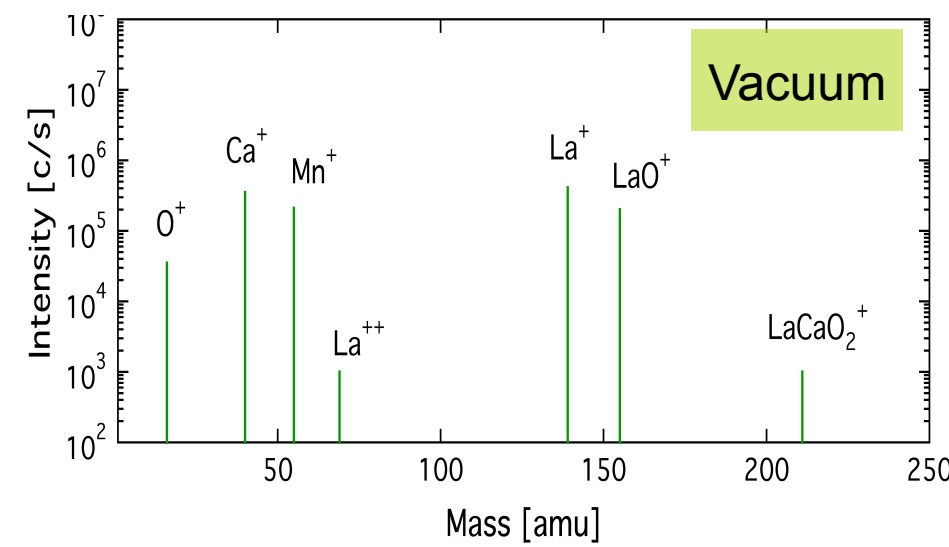
- a **plasma imaging** for **excited state neutrals** (and ions) setup with spectral and time resolution (2 AOTF's with 1.1-2.4 nm resolution in the range of 550-1000 nm and 0.7-2.1 nm resolution in the range of 400-650 nm).
- a **high resolution spectroscopy** setup, where we image the plume onto the monochromator slit.

Plasma composition: Mass Spectrometry

La_{0.4}Ca_{0.6}MnO₃

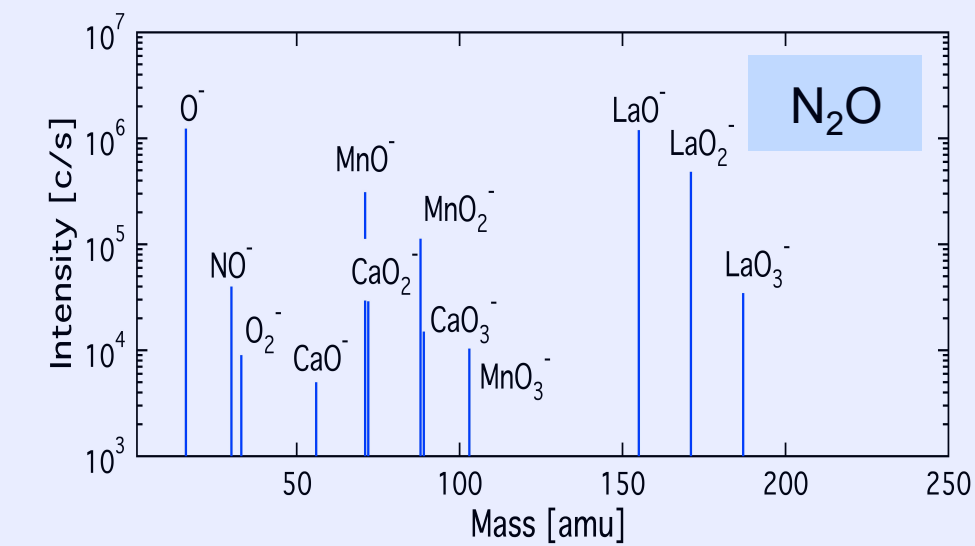
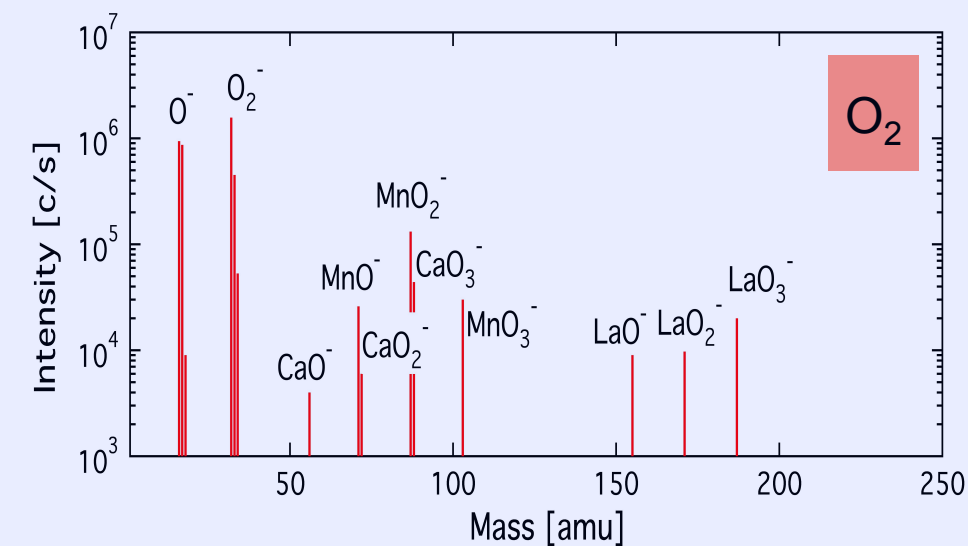
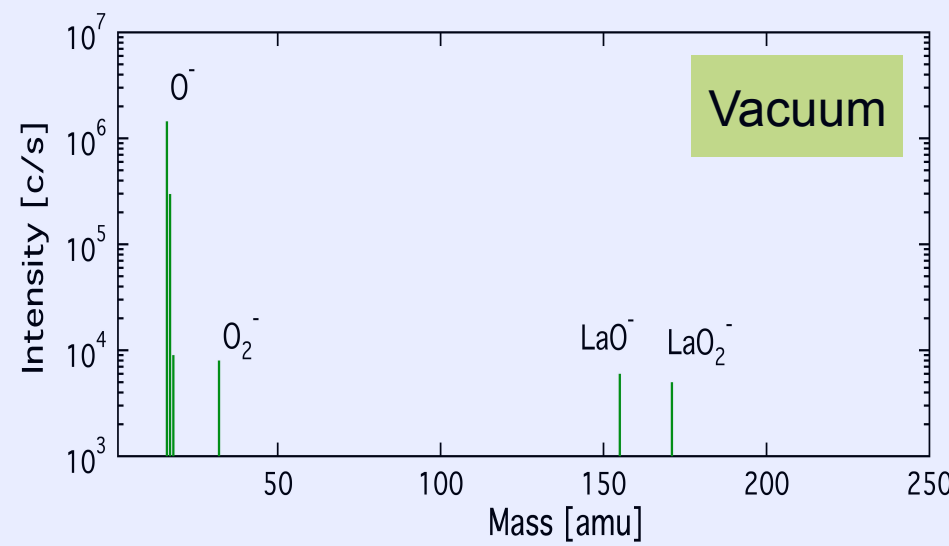
1.5 J cm⁻² at 193 nm: vacuum: 2*10⁻⁷ mbar

Positive



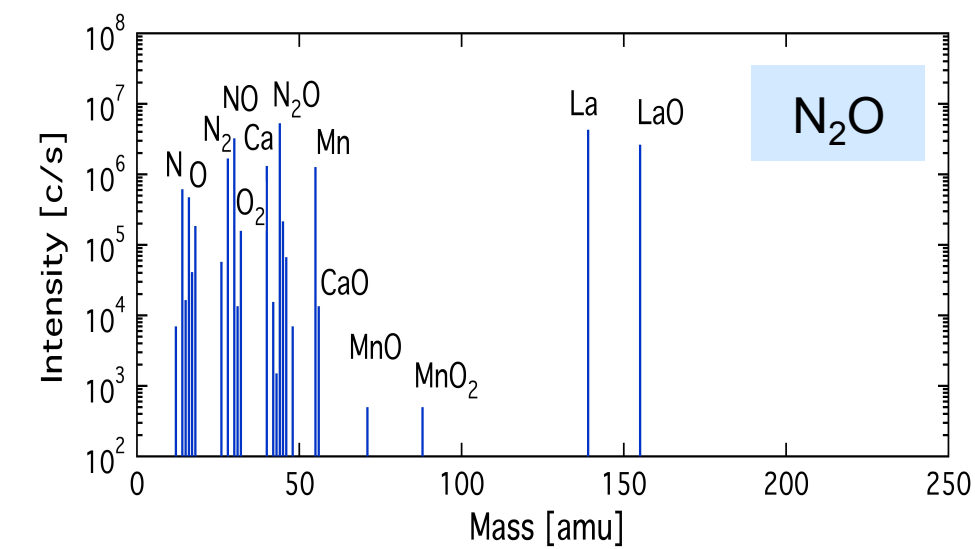
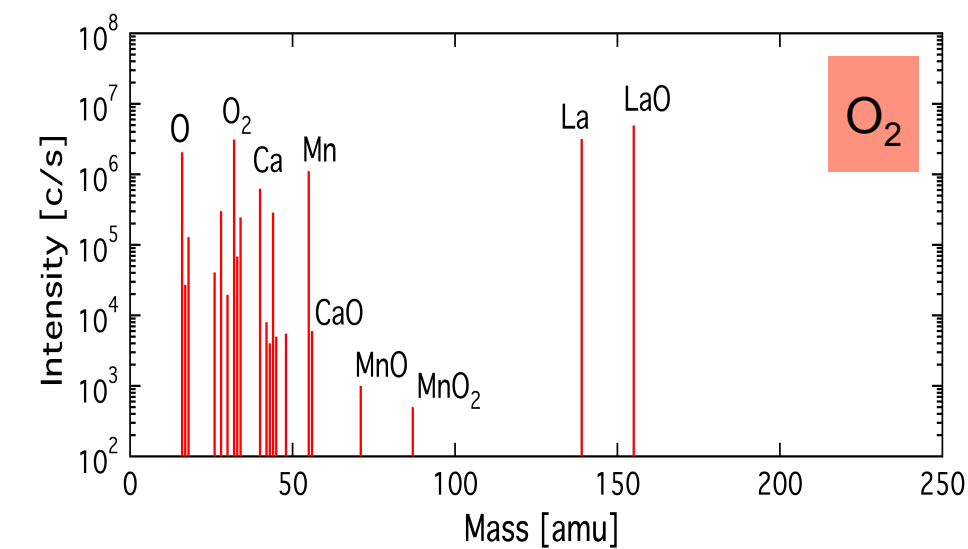
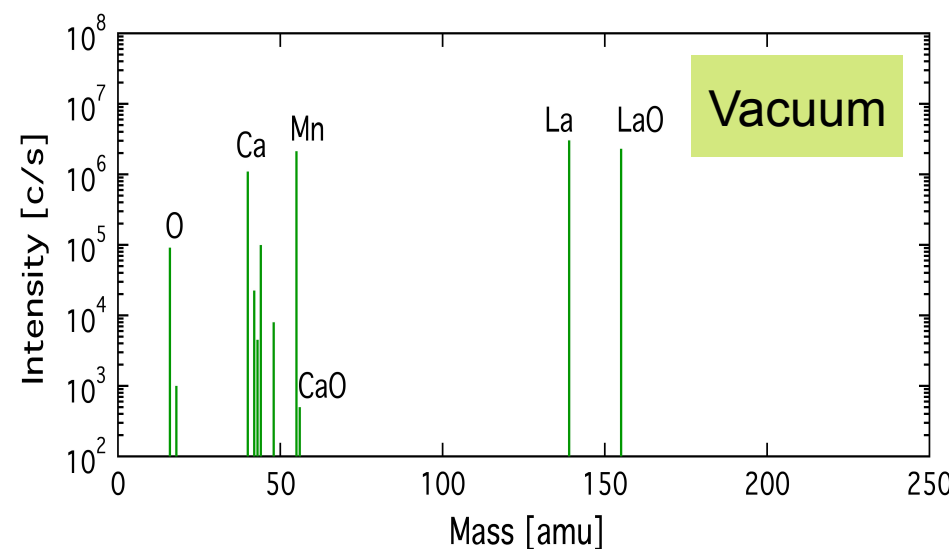
quantitative

Negative



quantitative

Neutrals



not quantitative
(ionisation efficiency as function of kinetic energies is not known)

What is interesting:

There is quite a large amount of **negative ions**, mainly related to “oxygen”, and they are in the case above, **mainly observed for O and La** (much less for Ca and Mn) and **increase in the presence of a oxygen** containing background gas.

- Is this important for the film composition?
 - yes, we find a **higher oxygen content** in the films when we find a **larger amount of negative ions** (**overlap with other species, such as MeO**).

Findings:

- ▶ **Films with different composition have various oxygen contents for the same deposition conditions!**
- ▶ **Films with different composition have various cation contents (ratios) for the same deposition conditions!**
- ▶ **Why???**
- ▶ **How to understand: one approach-plasma analysis combined with film analysis**

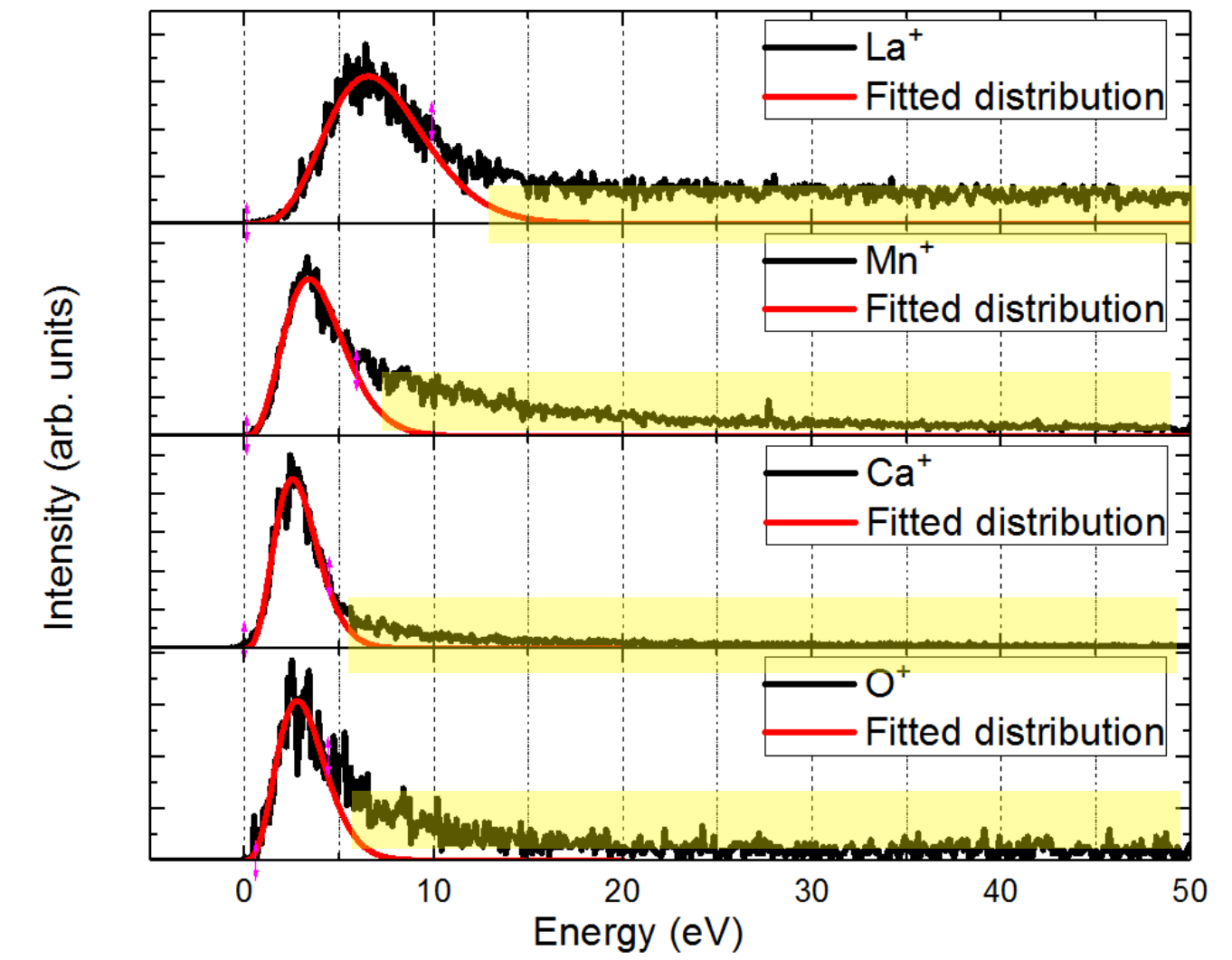
Plasma: Kinetic Energy

The plasma properties depend on many parameter and influence the composition and thickness (measured by energy resolved plasma mass spectrometry):

- 2 kinetic energy distributions.

For $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ as target:

- **Peak kinetic energies** (up to 20% of species) reach for a KrF laser values of up to 750 eV (if we think about velocities, then oxygen arrives prior to metals-one oxygen loss mechanism, in vacuum—-scaled with mass).



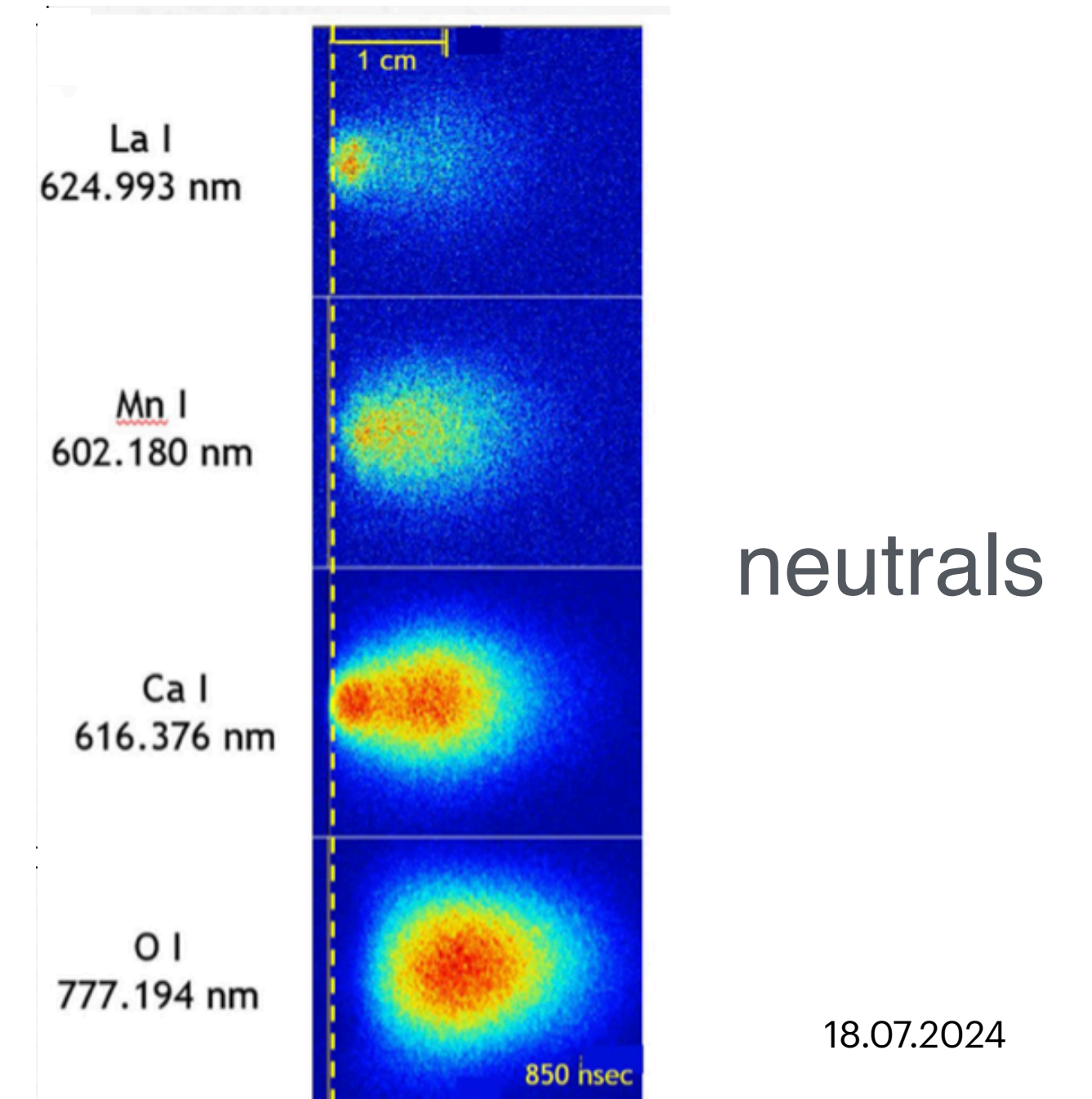
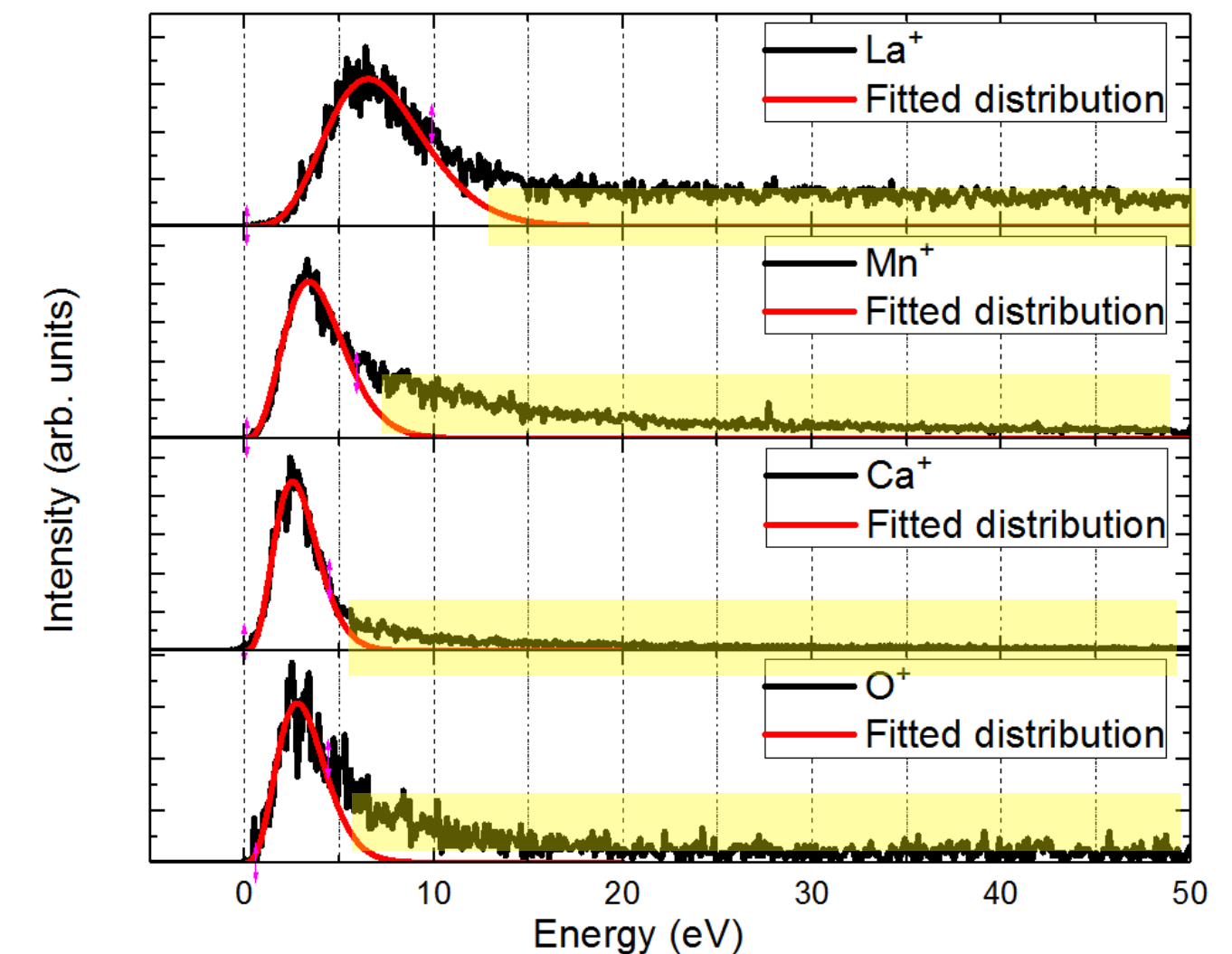
Plasma: Kinetic Energy

The plasma properties depend on many parameter and influence the composition and thickness (measured by energy resolved plasma mass spectrometry):

- 2 kinetic energy distributions.

For $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ as target:

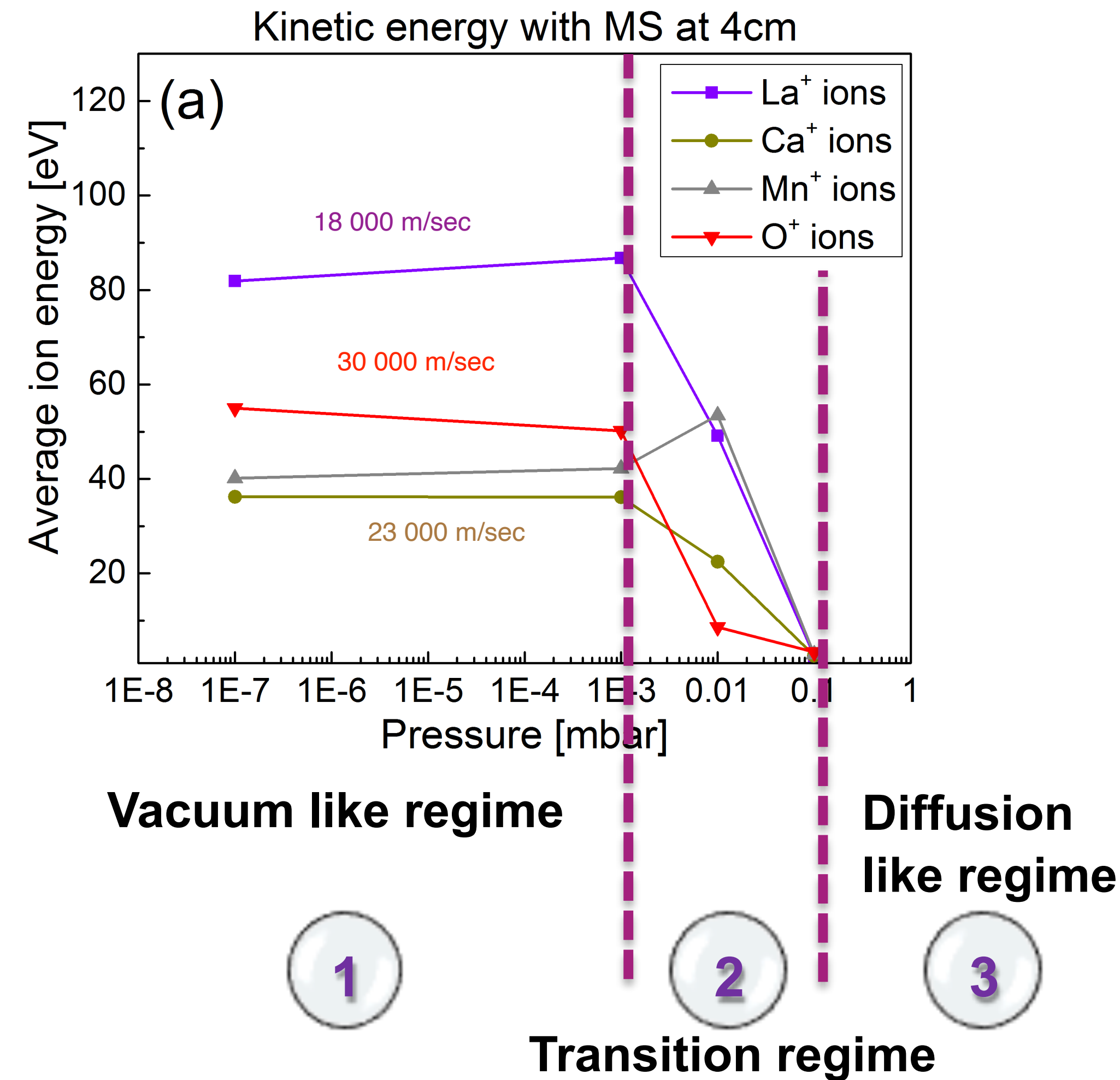
- **Peak kinetic energies** (up to 20% of species) reach for a KrF laser values of up to 750 eV (if we think about velocities, then oxygen arrives prior to metals-one oxygen loss mechanism, in vacuum—scaled with mass).



Plasma: Kinetic Energy

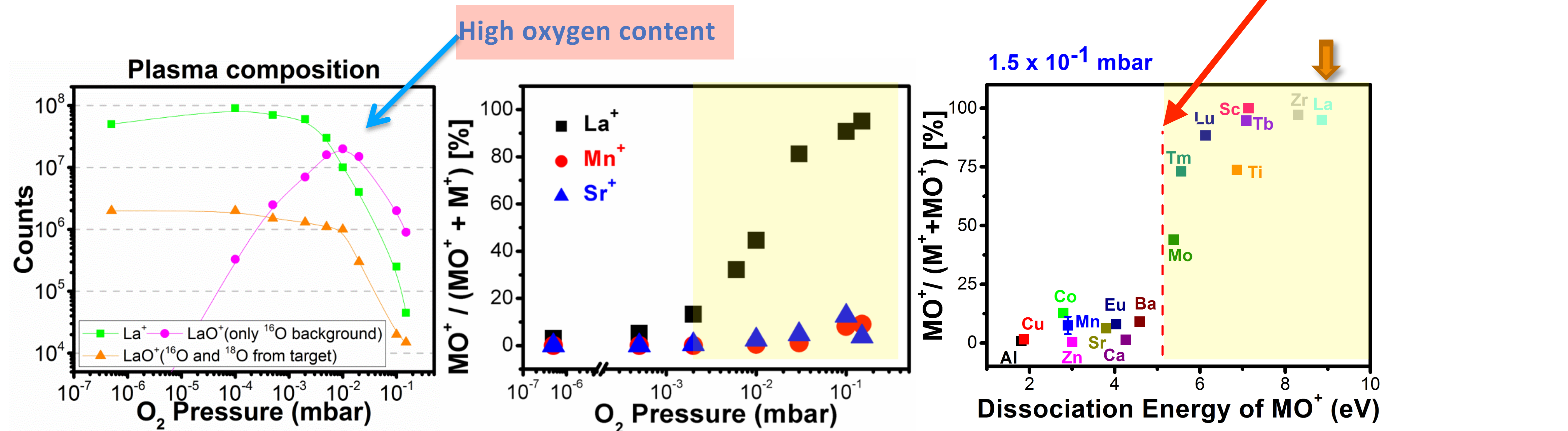
Background pressure (kinetic energies) and type of gas (**consider sputtering or bouncing**) will modify E_{kin} (also F , τ and λ):

- **vacuum like regime (mfp)**
- **transition regime (very often used for PLD)**
- **diffusion like regime**



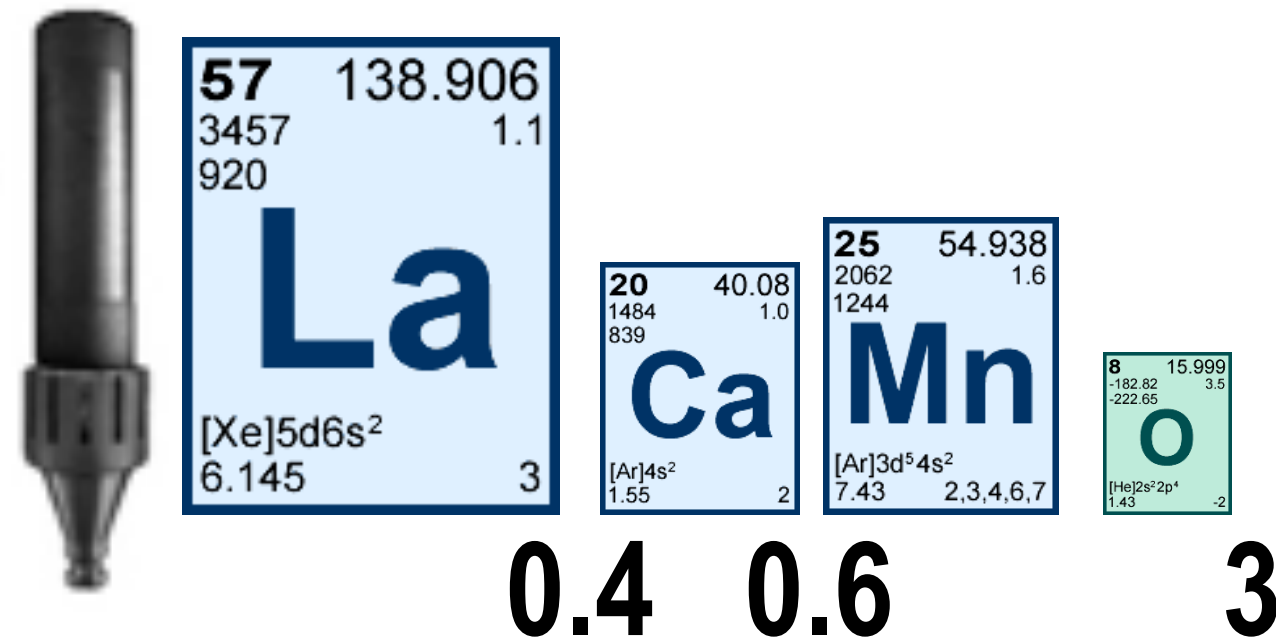
Plasma: Background gas

- With increasing background pressure metal-oxygen species with **large dissociation energies** (e.g. **LaO⁺**, and not **MnO⁺** or **SrO⁺**) are preferentially formed in the plasma as a consequence of plasma interactions with the oxygen background (mass or size of metals are not correlated, but **dissociation energy**).
- The **oxygen content in the films** is higher when we **maximise the amount of metal-oxygen** species (also higher amount of the **related metal**)



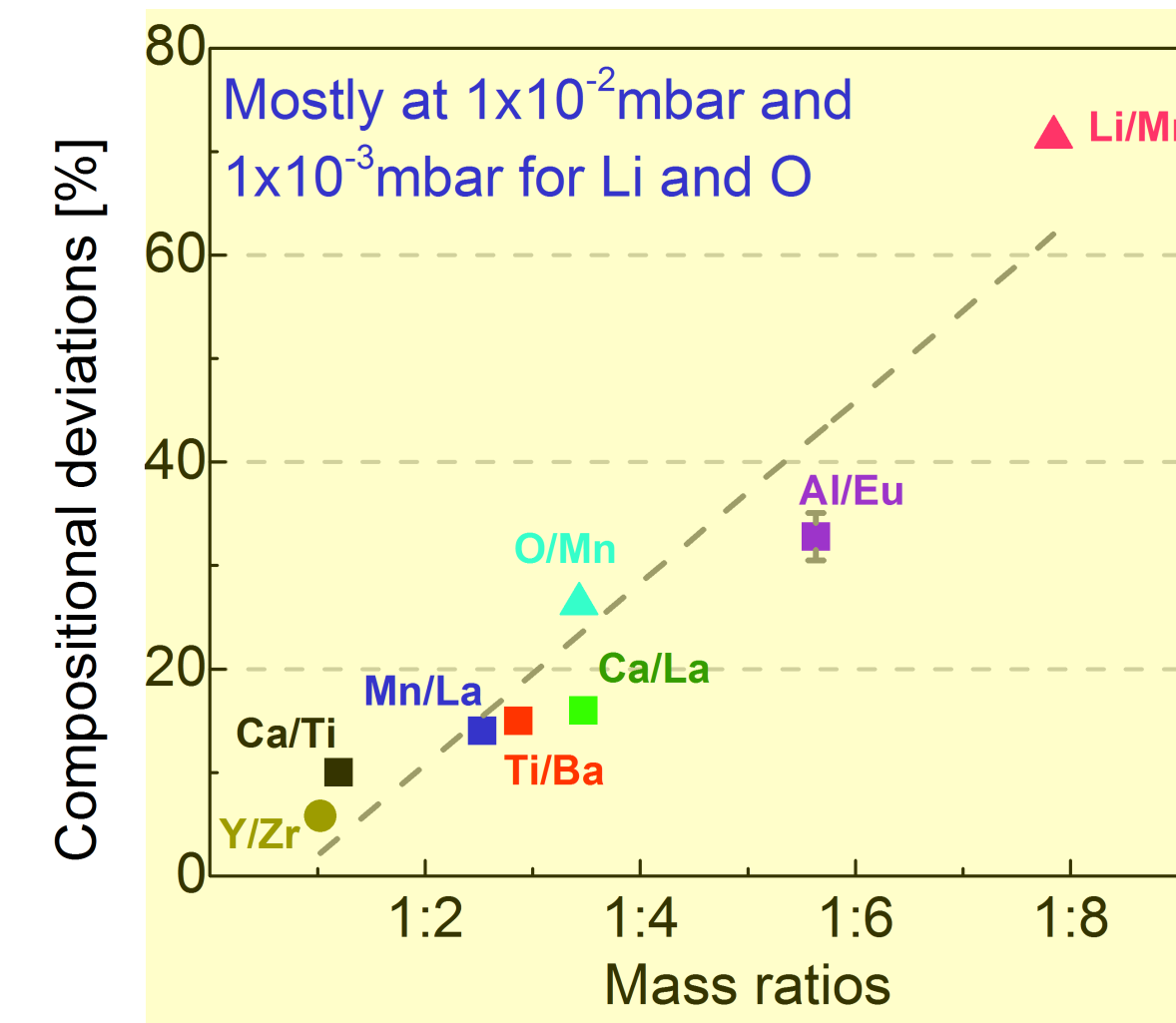
Film Composition: Influence of mass ratios in target

Mass ratio (1:2.5 - 1:3.5)



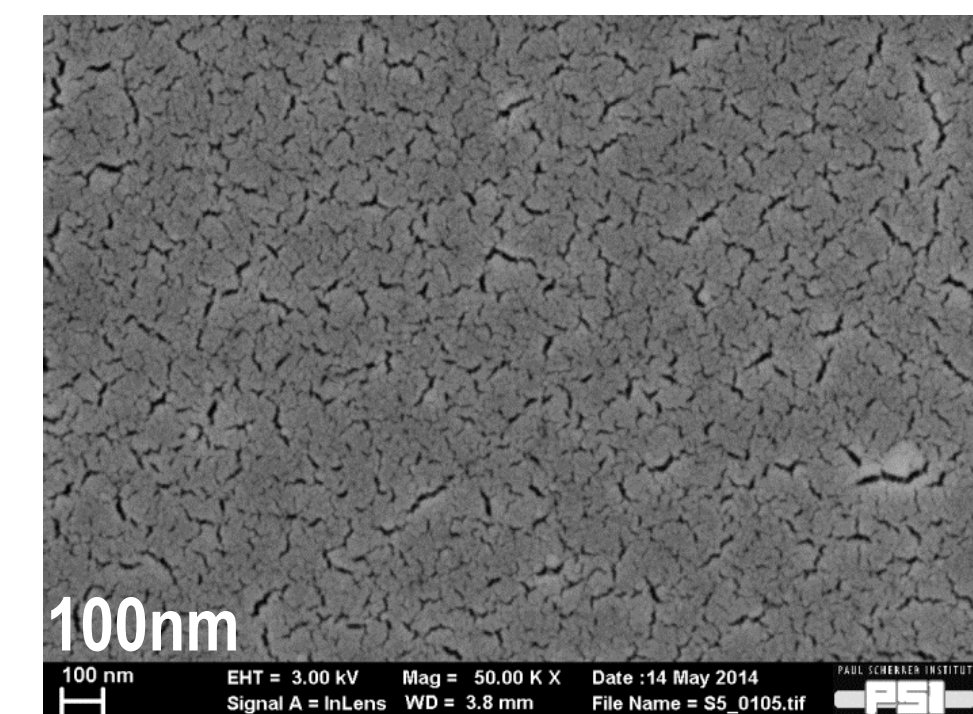
*Target composition verified by RBS

Note: areas of pictures scaled to match element masses



Note: error bars are too small to be seen

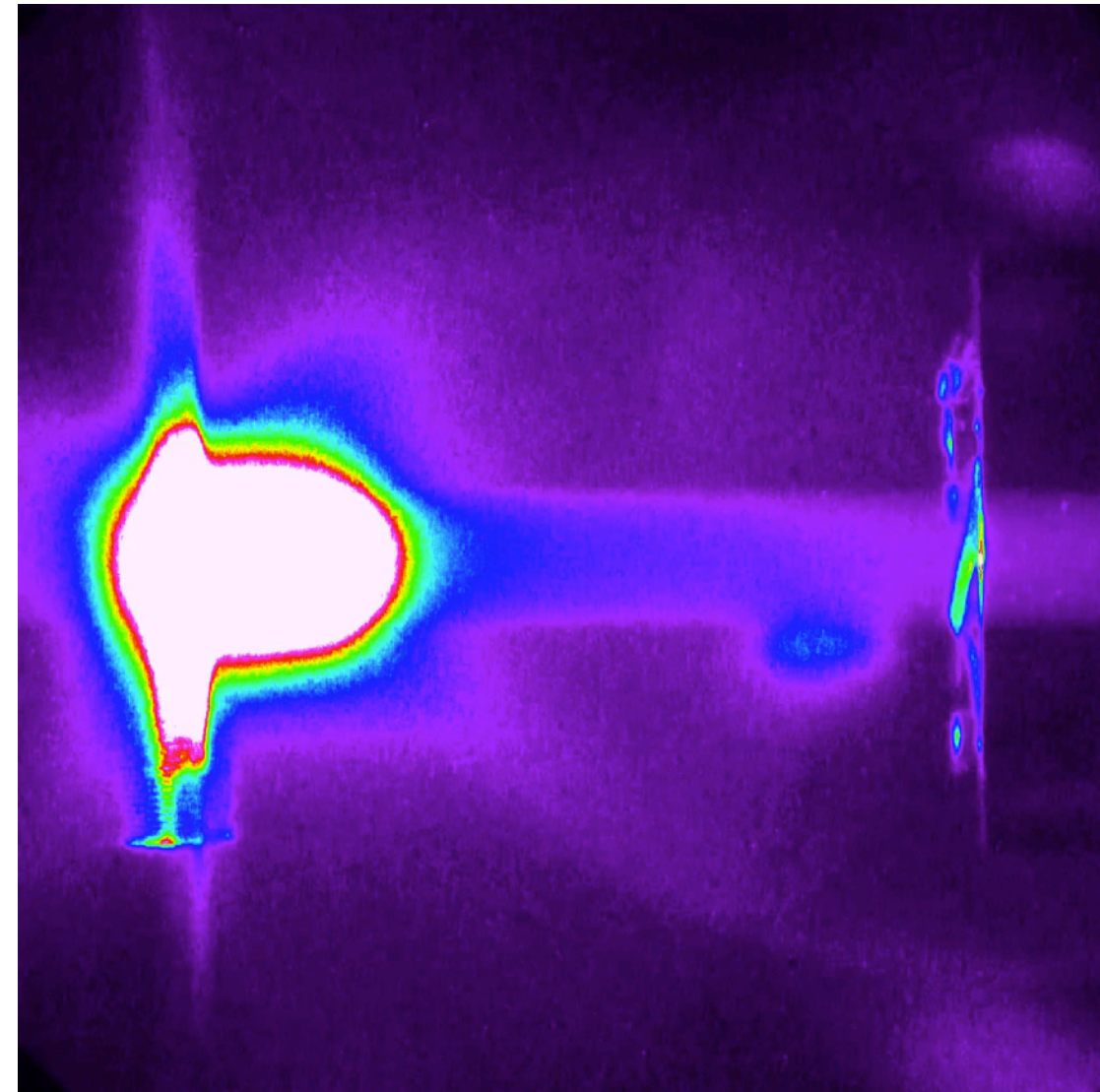
- Higher mass ratios result in larger deviations in the transition regime (2), which is often used in PLD ($\Rightarrow E_{kin}$ and scattering). For large mass ratios targets with an **excess of the of the light element** must be used.
- Compositional changes are very sensitive to the background pressure.
- Why are the intermediate pressures with the highest deviations used so often? Higher pressures result in porous films, while the low pressure gives often problems with crystallinity (too low oxygen content).



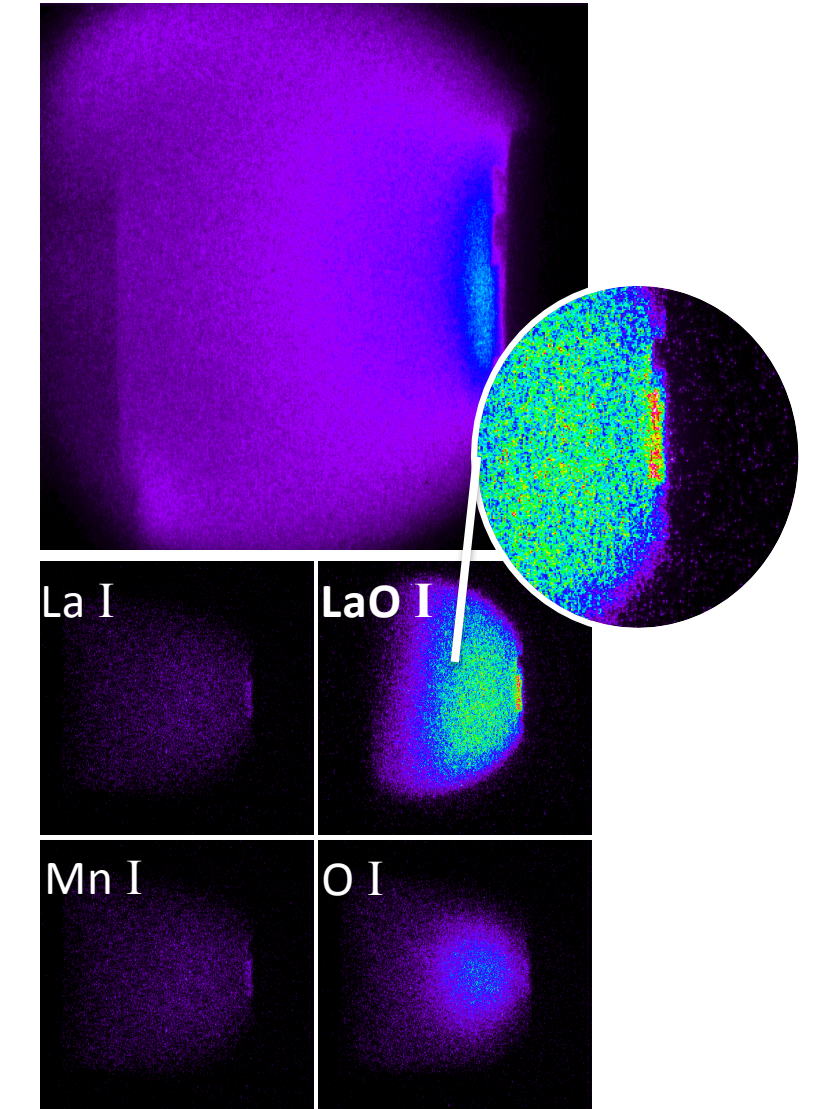
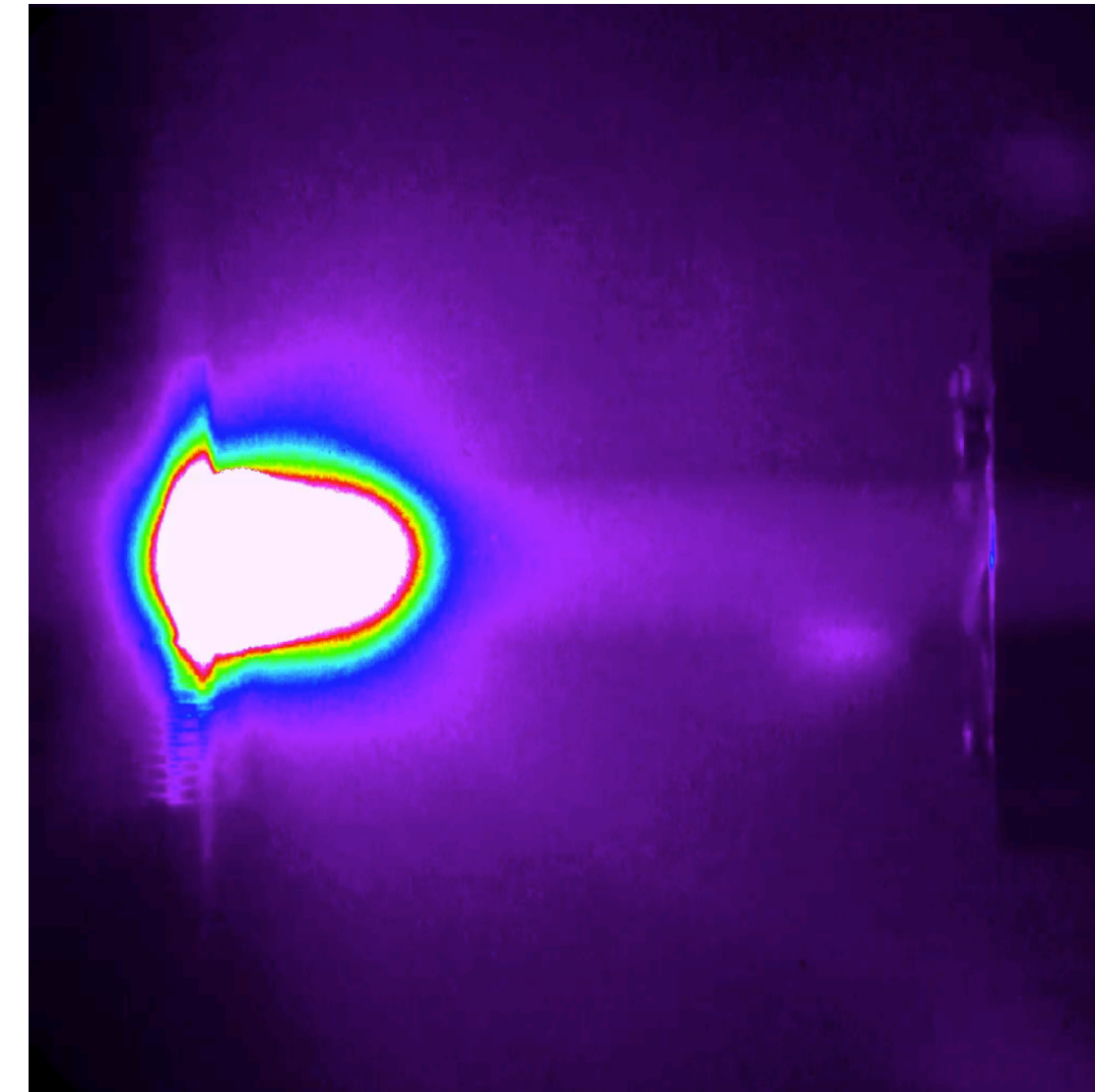
Plasma Imaging and Growth: Influence of Substrate

We have observed, that for some perovskites **it is beneficial when the excited state species reach the substrate** (better crystallinity for $\text{La}_{0.4}\text{Ca}_{0.6}\text{CoO}_3$). Consider the additional energy of the excited state species, or.....

Silver ablation in **Ar** at 1×10^{-1} mbar



Silver ablation in **O₂** at 1×10^{-1} mbar



Ag species do **not really reach the substrate, but bounce back with higher velocity** (slightly, Ar acts like a spring, is compressed 10 times). Consider: **Coating of target, and changes of composition.**

Less observable bouncing, but **high amount of emitting species above the substrate (could not be related to AgO, as we found no clear line for this)**. Checked with $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$, and the emitter is LaO.

Growth: Effects of Rebound on Composition



Substrate BEHIND the target

Growth: Effects of Rebound on Composition



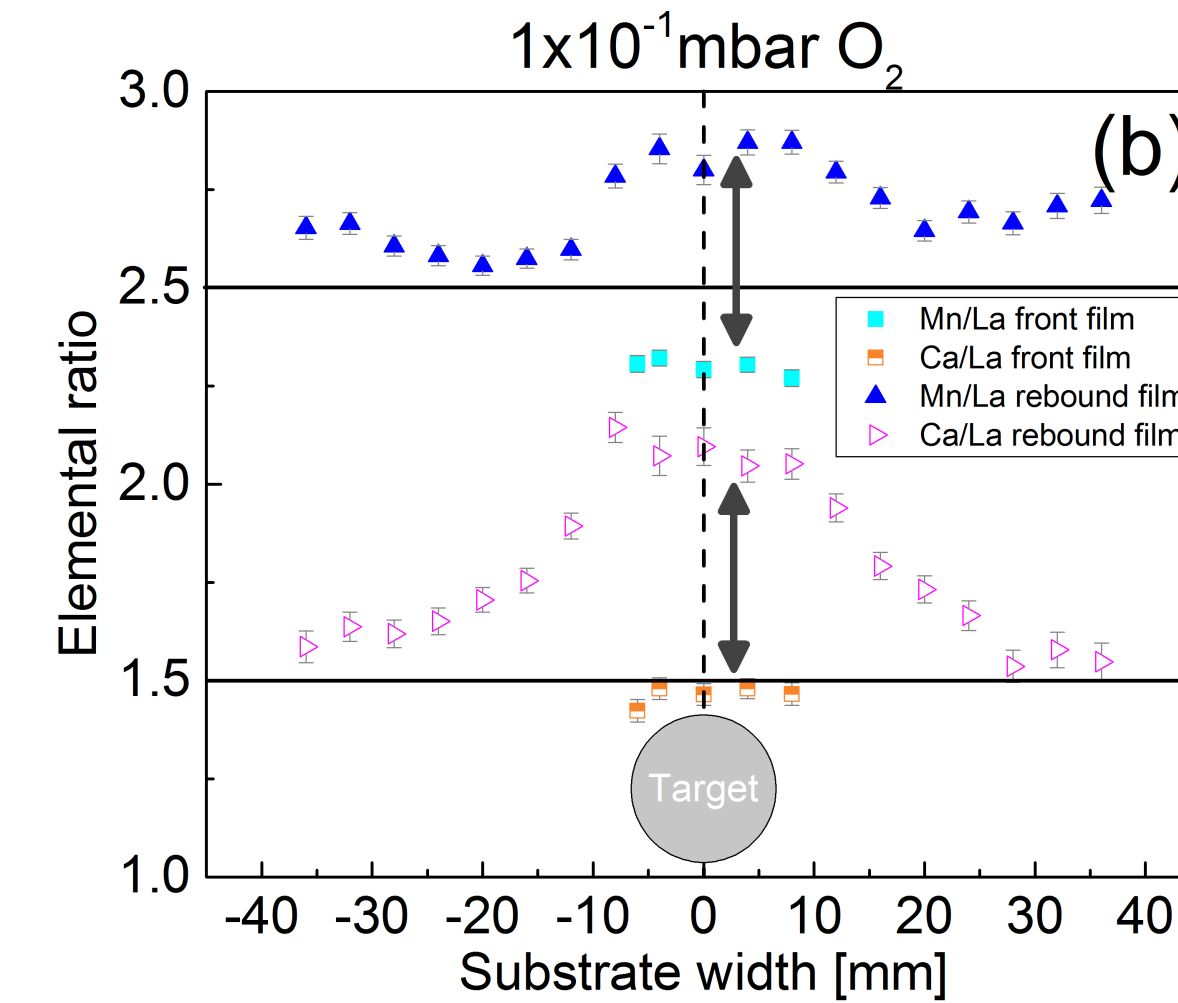
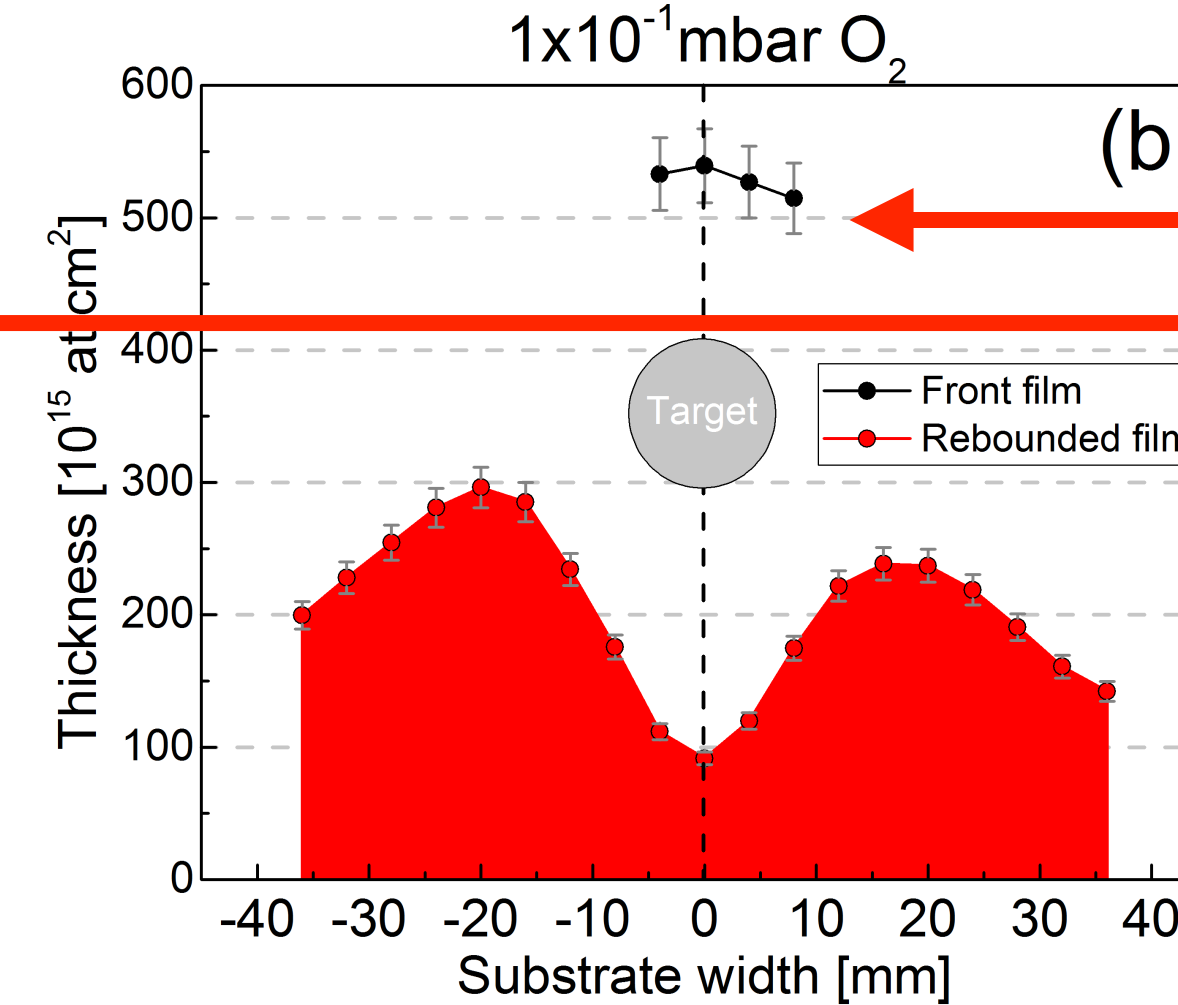
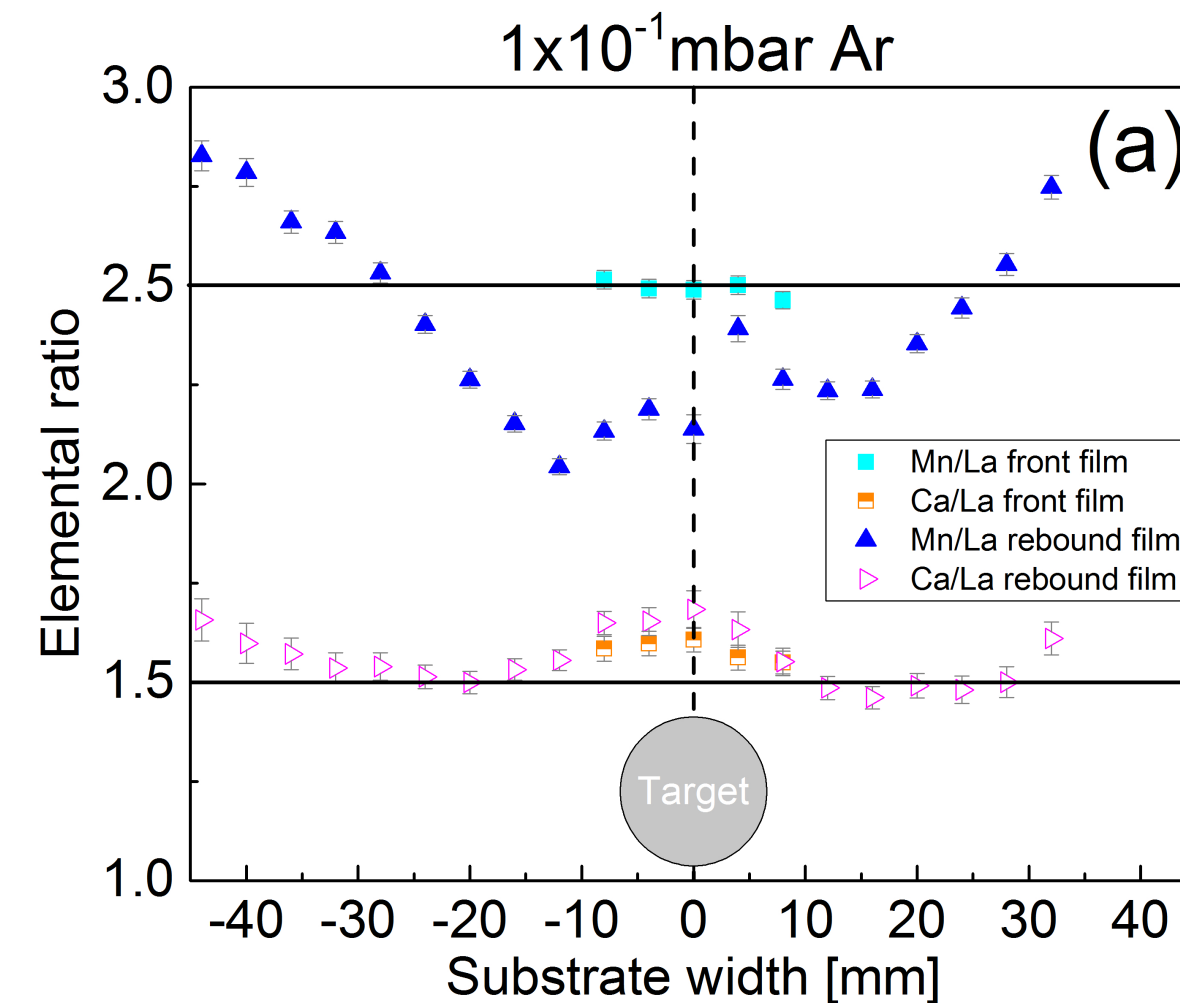
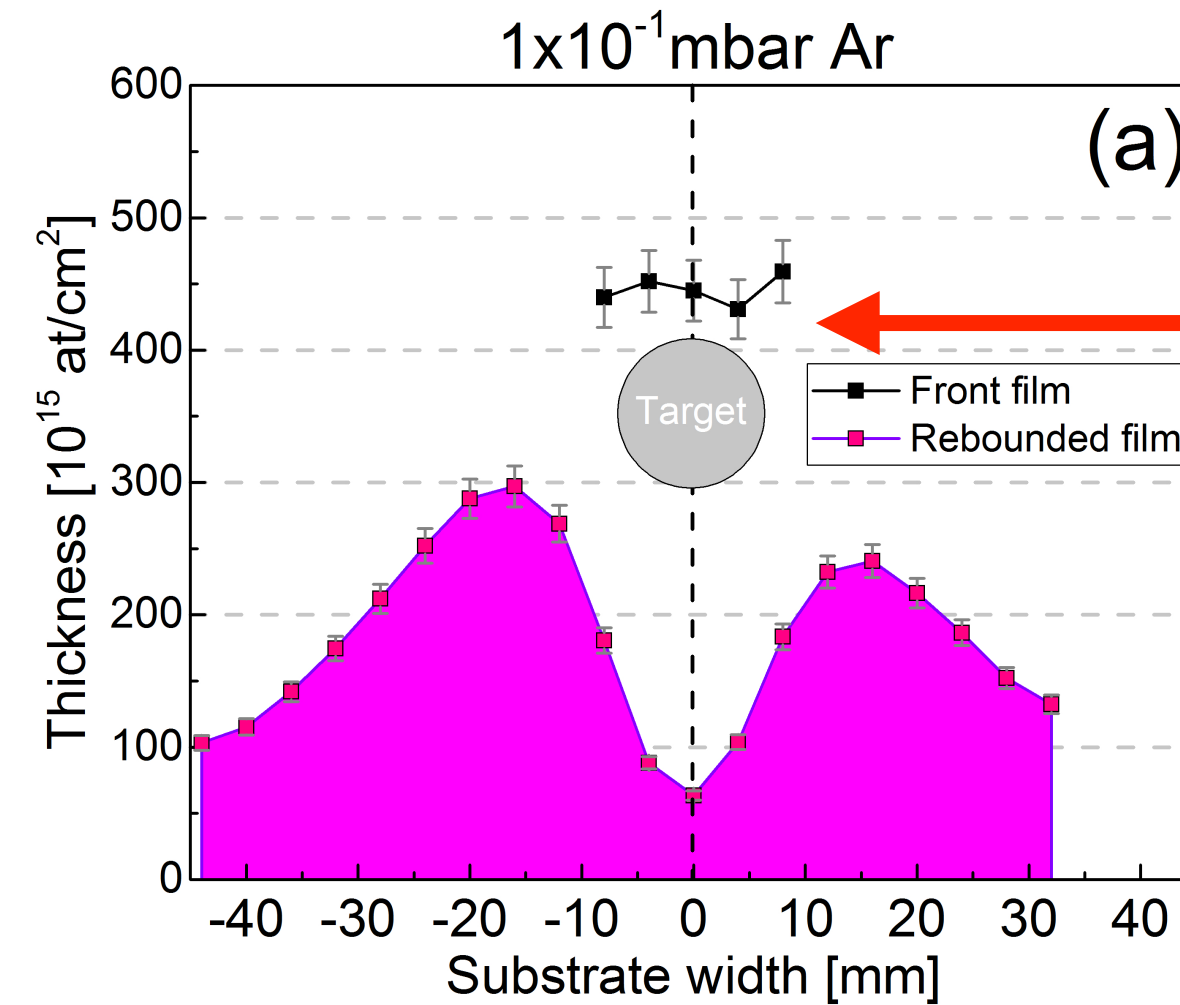
In Ar:

Rebound film is deficient in light elements close to the target position.

In O_2 :

Rebound film is deficient in La close to the target position. La stays (enriched) at the substrate (due to LaO ?)

Result: the composition of the target is constantly changing (up to 30% of the ablated material can come from rebound)



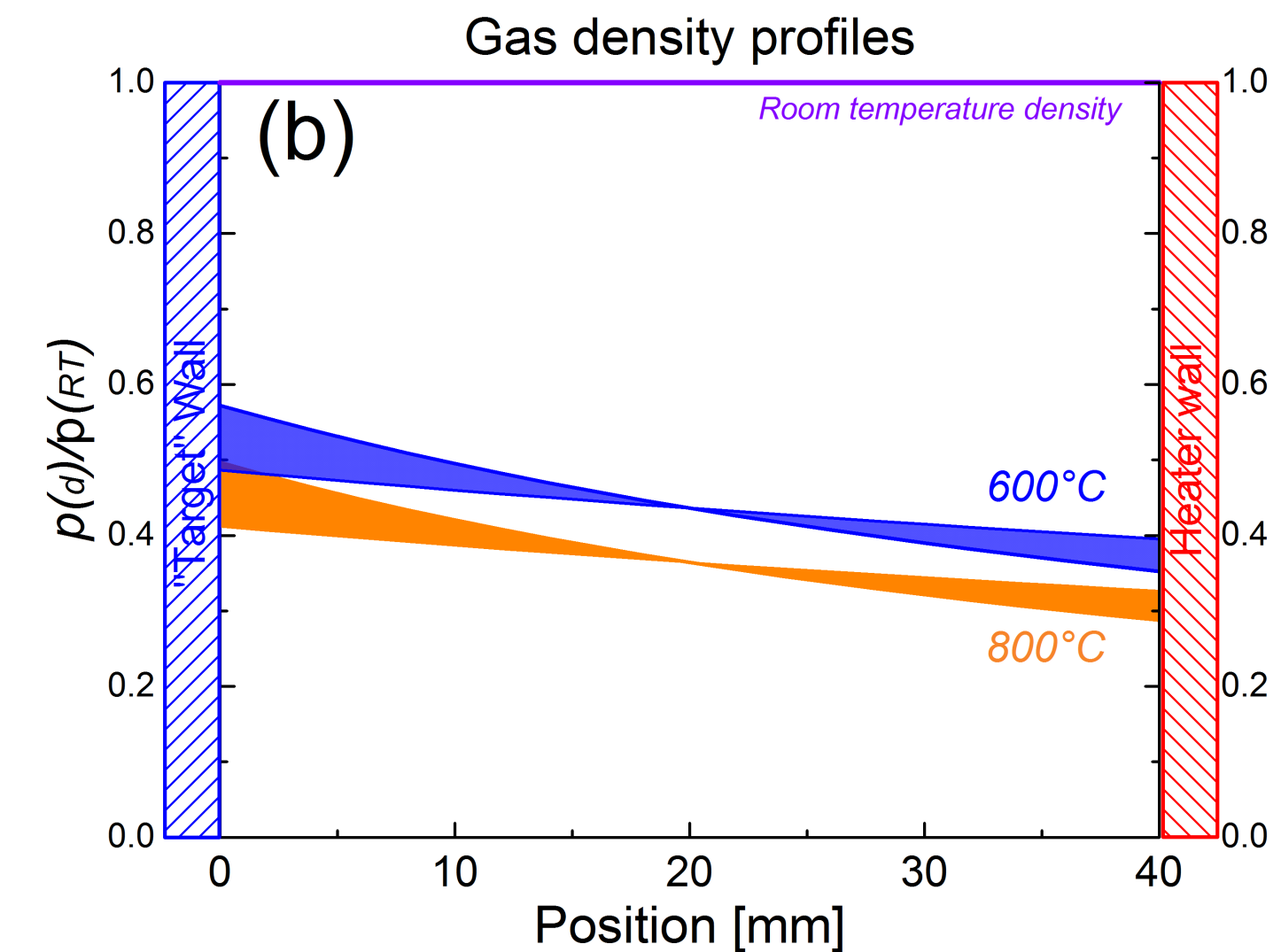
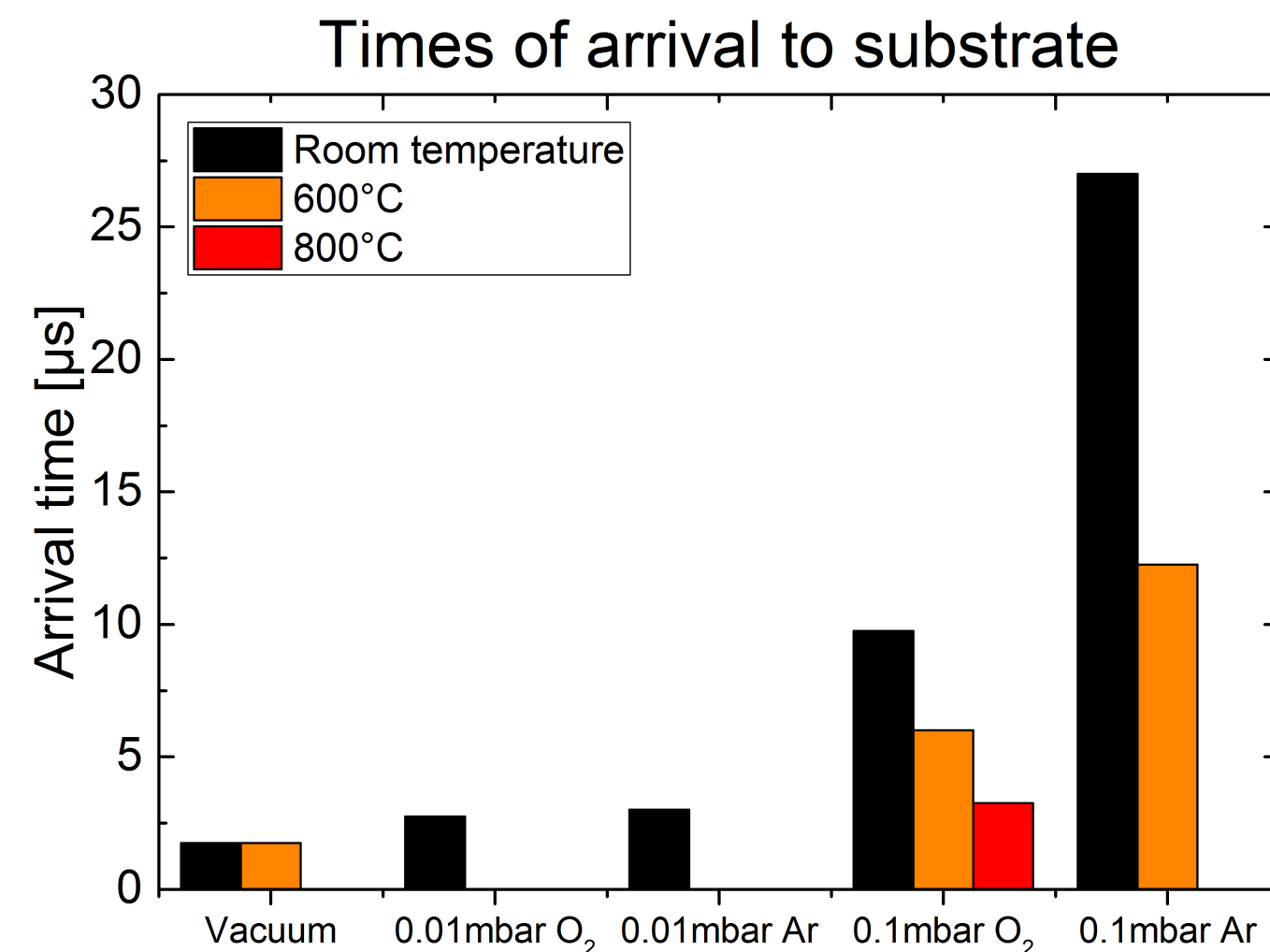
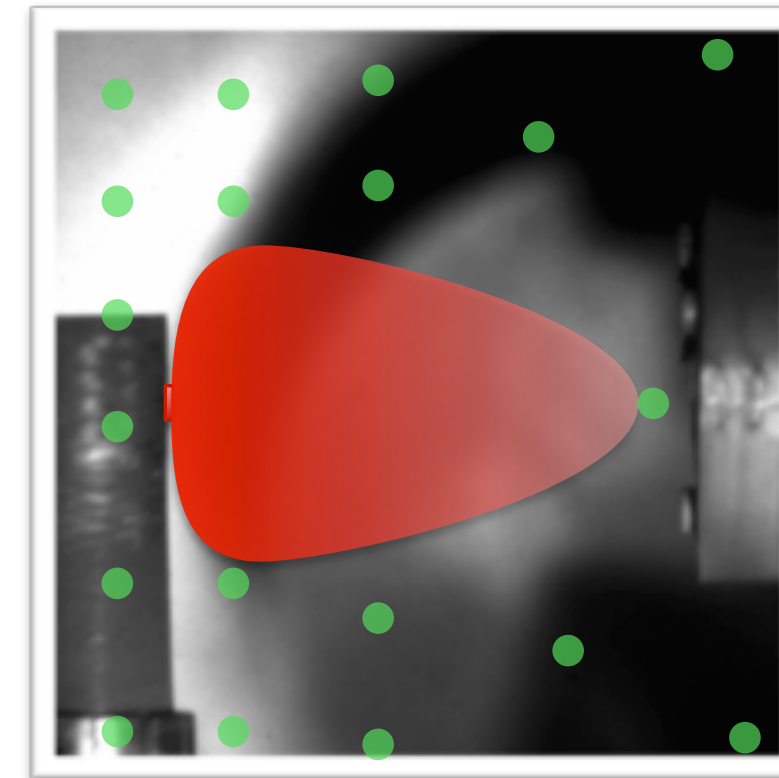
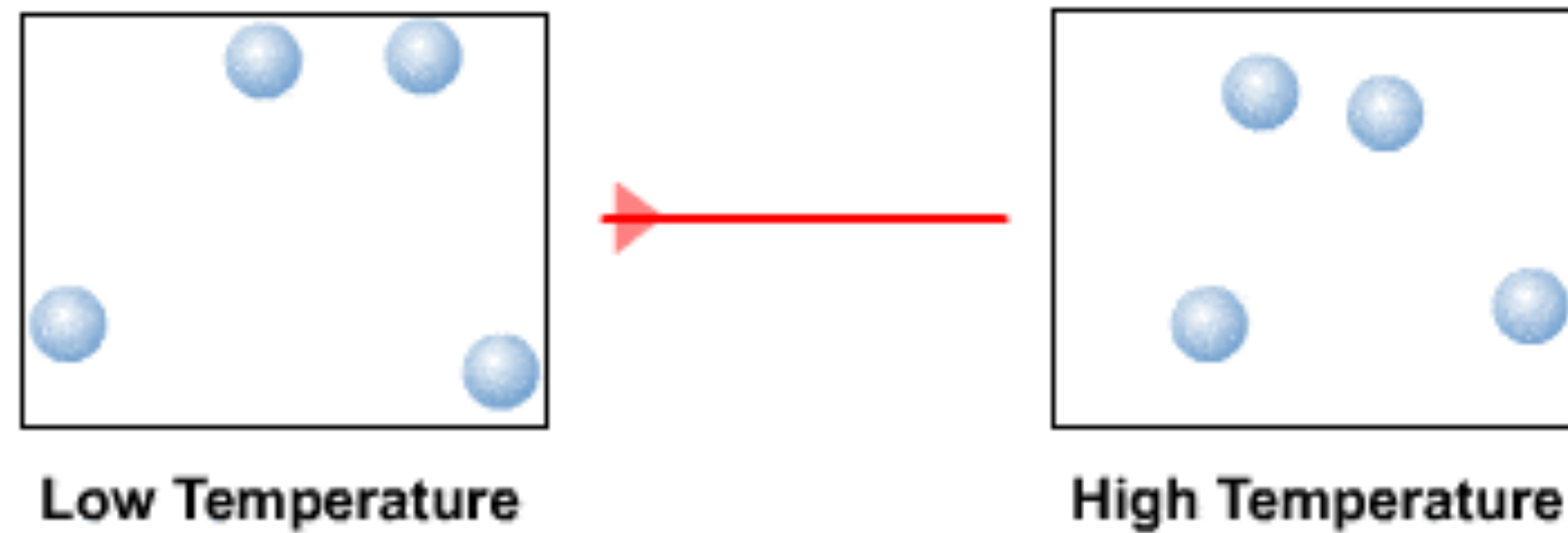
Front film is thicker in O_2 , remember stable MeO species tend to stay on substrate

nominal composition Mn/La

nominal composition Ca/La

Another influence of the substrate (holder), if heated

Effect of **temperature** (here for Ag) and **type/size of heater**:
 → **gas density gradient**



Another influence of the substrate (holder), if heated

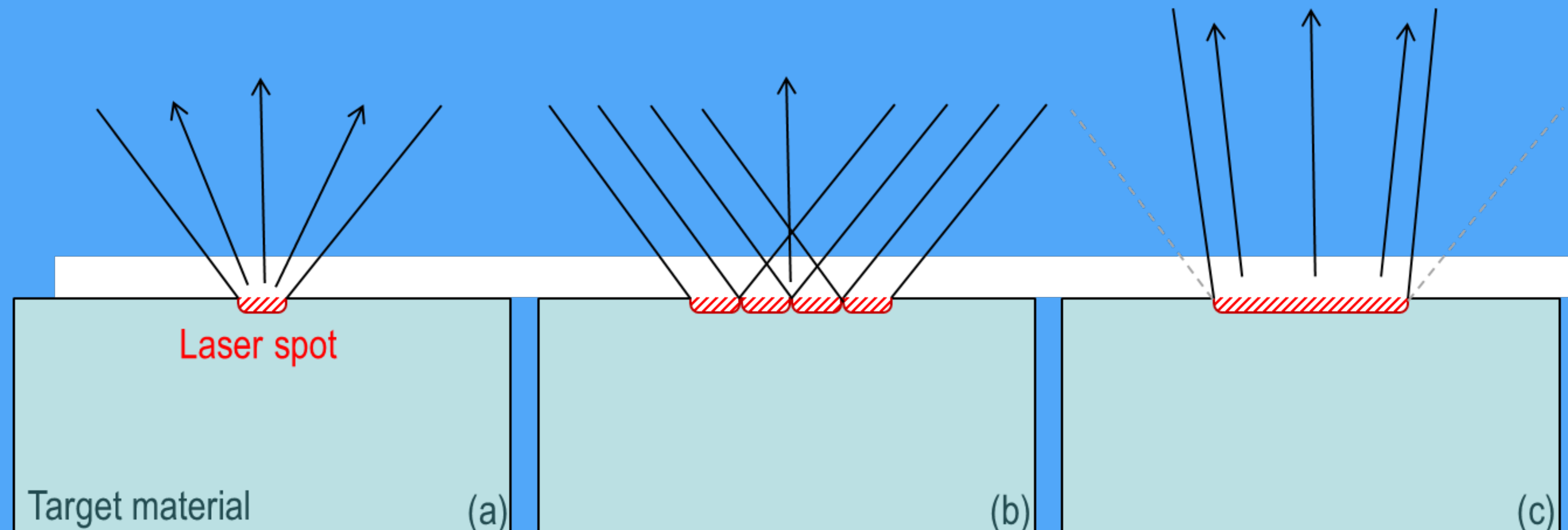
What happens if you change your substrate temperature?

Same plume expansion dynamics at higher temperature requires higher pressures

- At 600° → 45% RT gas density (~2.2x pressure)
- At 800° → 37% RT gas density (~2.7x pressure)

You need to change the background pressure to have the same conditions!

Be also careful if you change the fluence by changing the size of your laser spot (plasma expansion changes (and if you have not a spherical spot-consider flip over effect)!

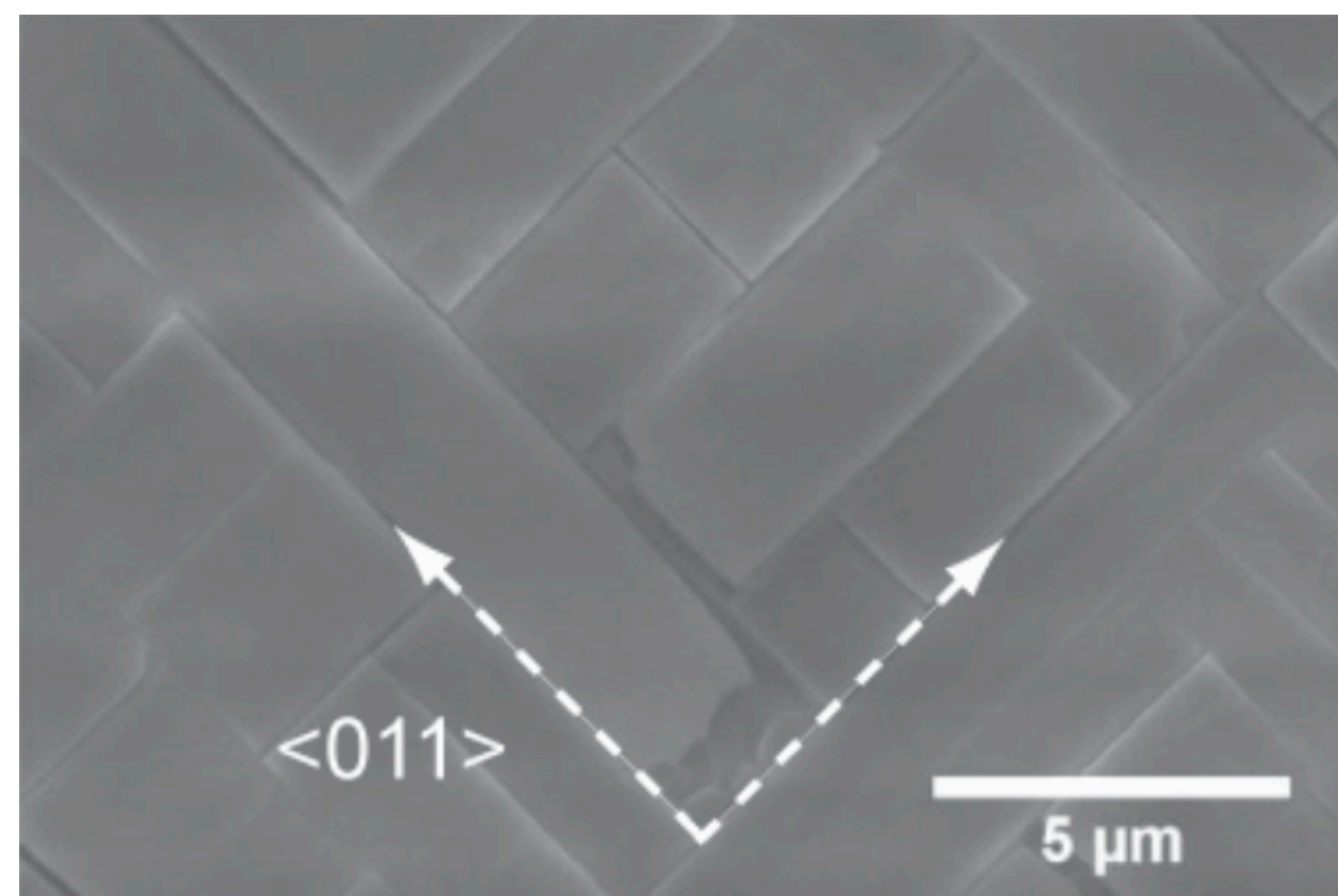
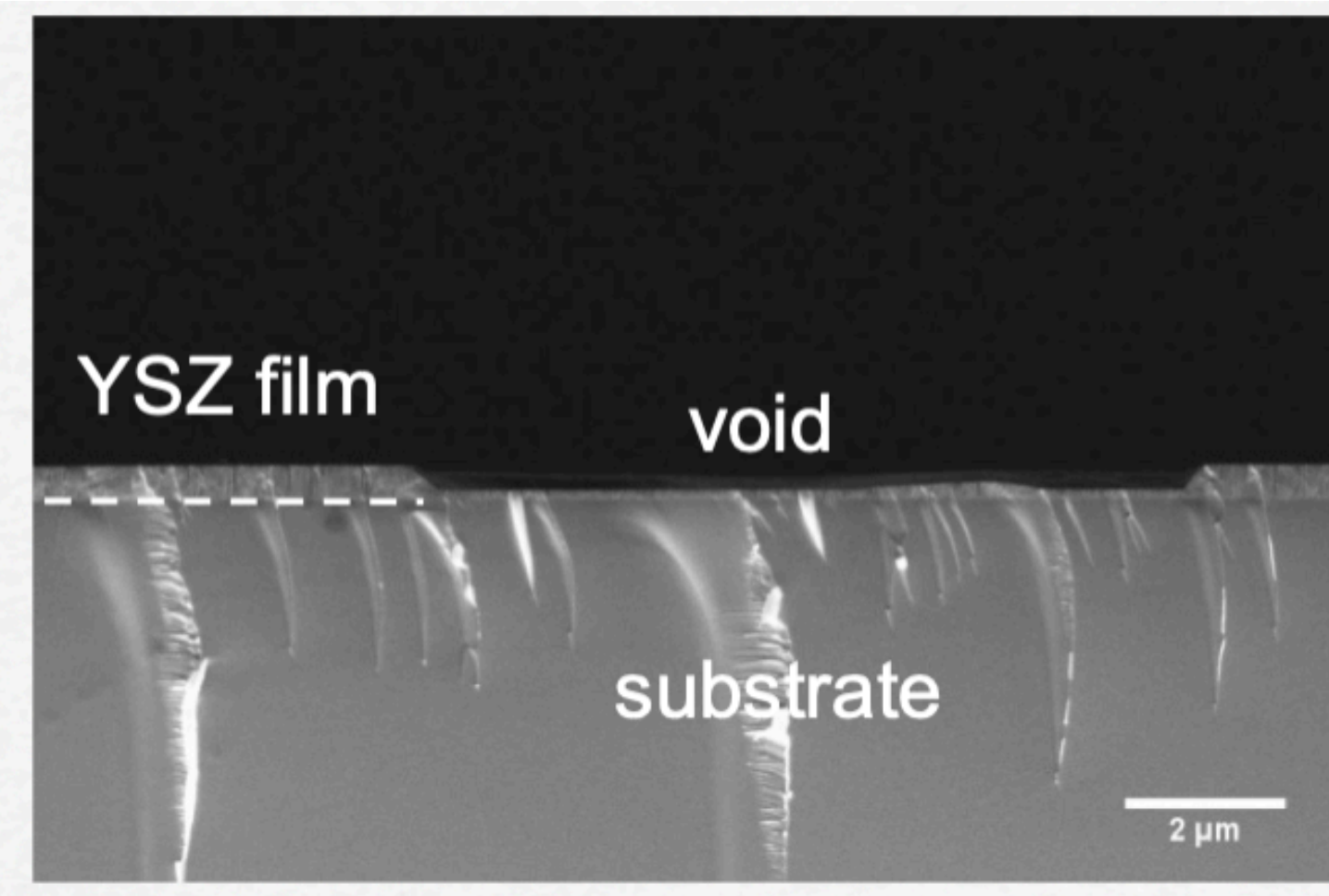
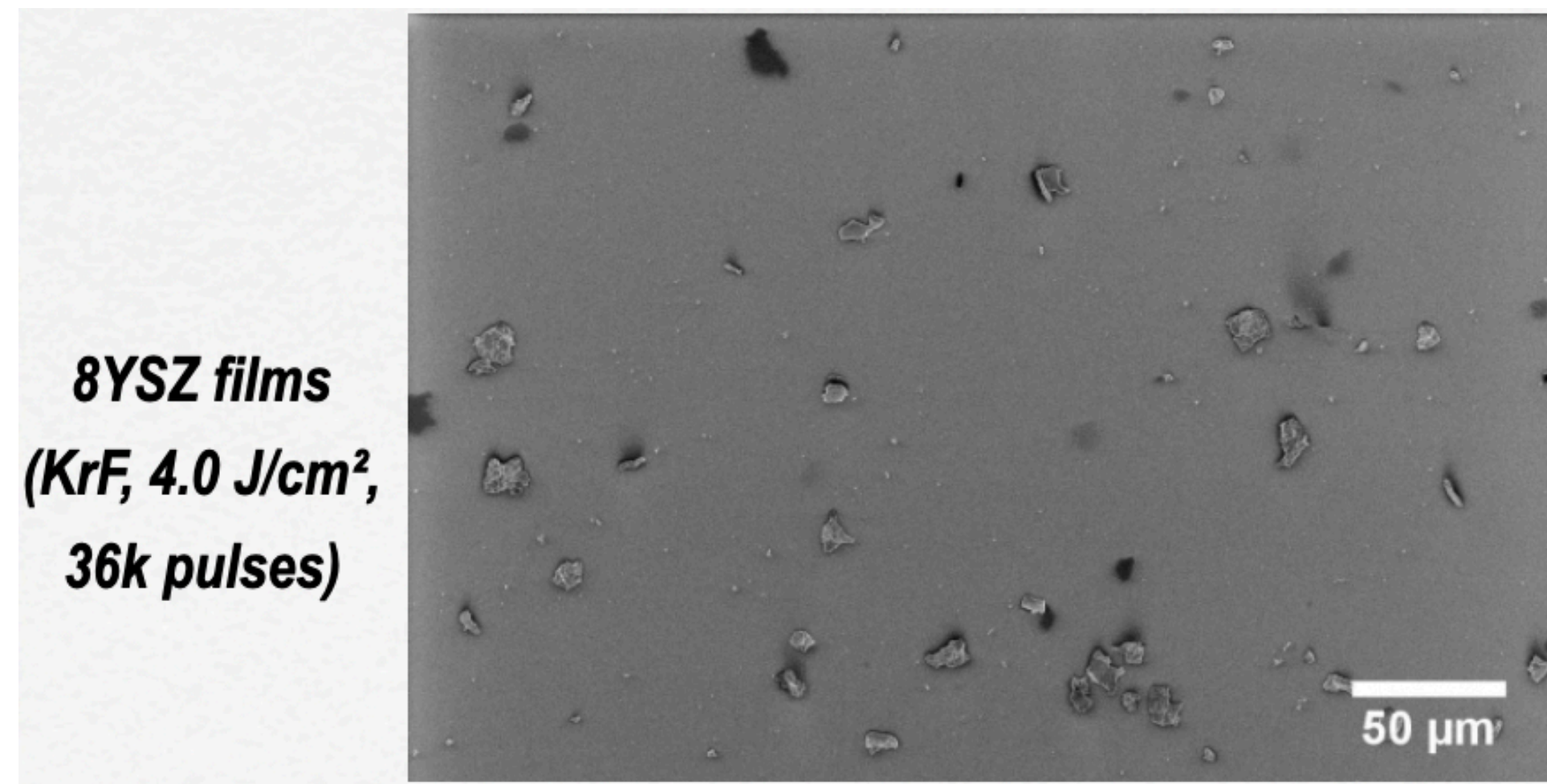


Finding:

Particulates or holes in film of 8YSZ.

Why?

Particulates and Holes in the Films of 8YST



- Particles on surface and voids **in the film**
- Extensive laser-induced formation of surface cracks **on the target** (not related to density of target)

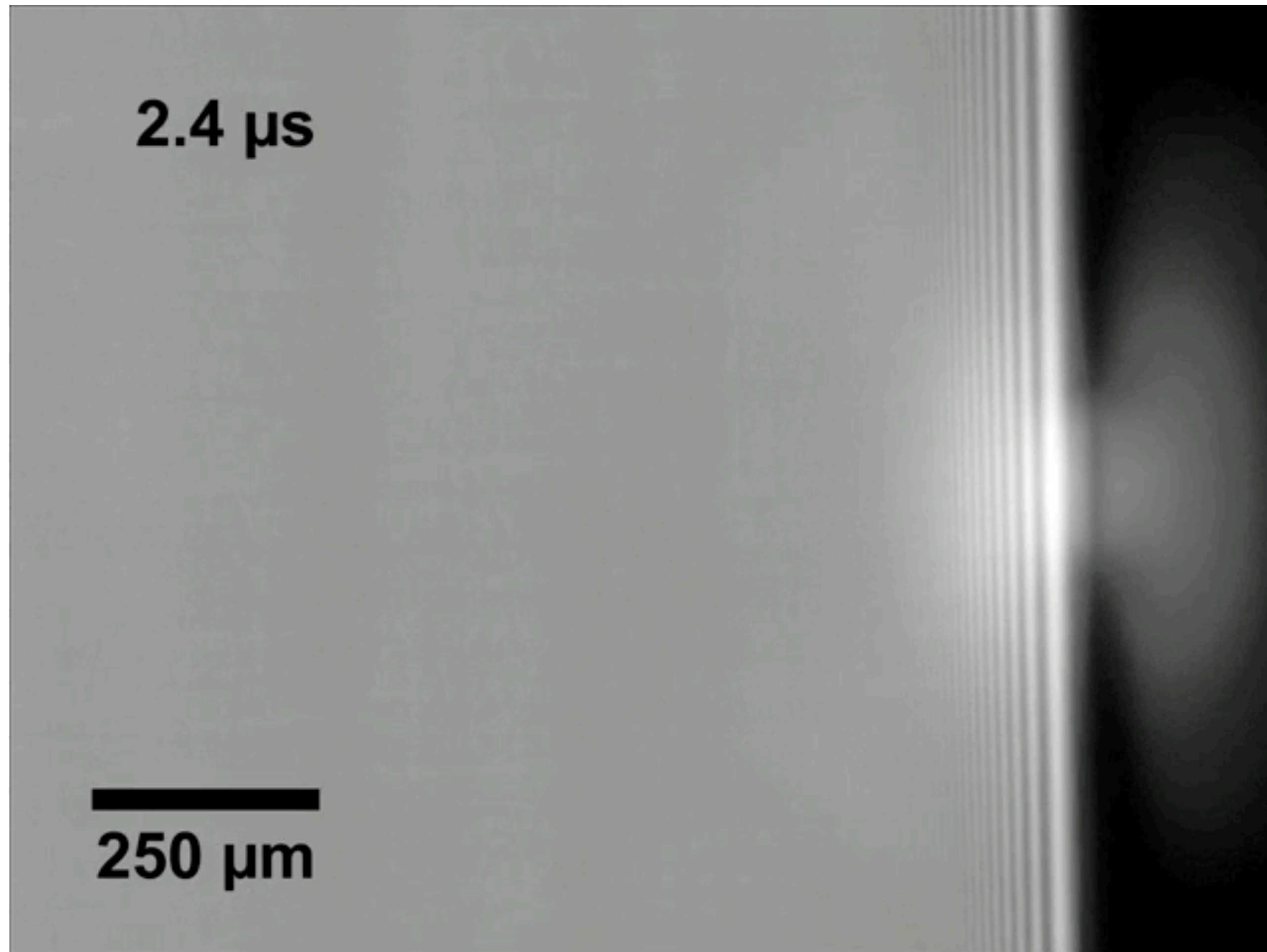
8 YSZ: Particulates

0 ns

250 μm

- ◆ Ejection of μm -sized fragments on the μs time scale, v_{max} : 350 km/h
- ◆ We could not find any solution how to avoid particulates (density, laser wavelength, pulse length, and fluence, etc.).
- ◆ Only approach: synchronised gas pulse to blow away particulates

3 YSZ: No Particulates

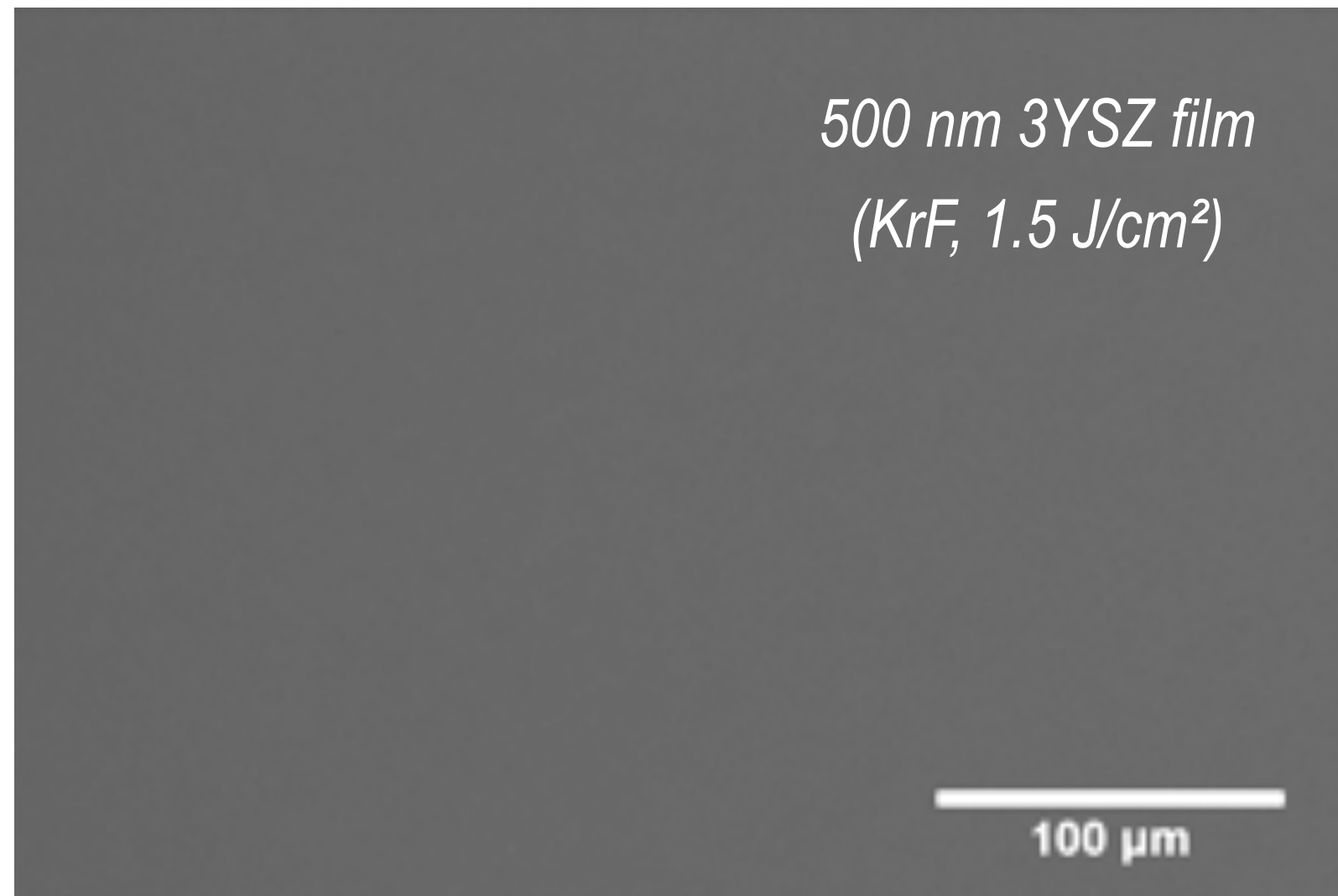


Why so different behavior?

This is a very similar material (a ceramic where the cubic crystal structure of zirconium dioxide is made stable at RT by an addition of yttrium oxide) :

- 3 mol% of Y_2O_3 in ZrO_2 (partially stabilized) vs
- 8 mol% of Y_2O_3 in ZrO_2 (fully stabilized)

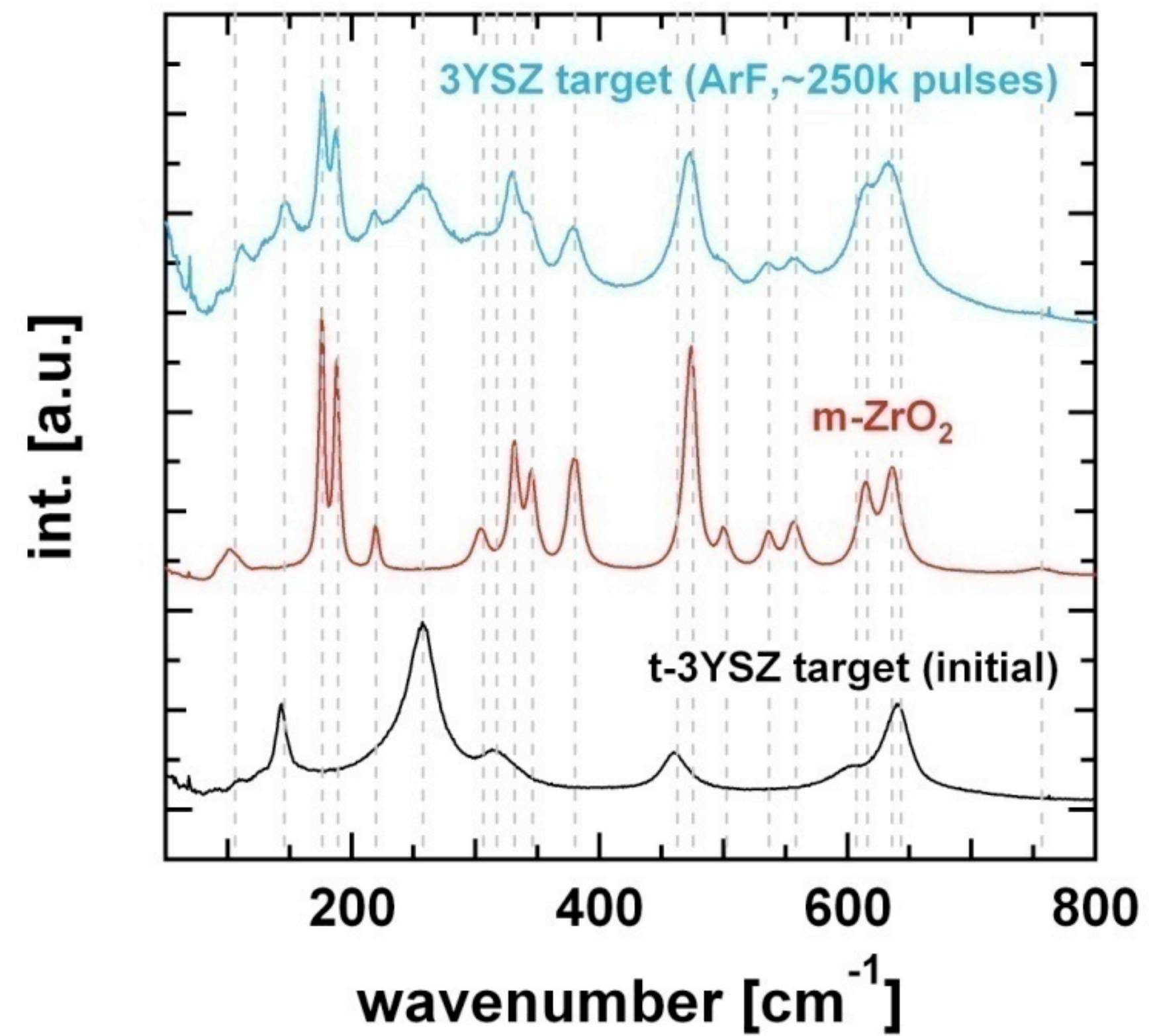
Material Dependence: 8YSZ vs. 3 YSZ



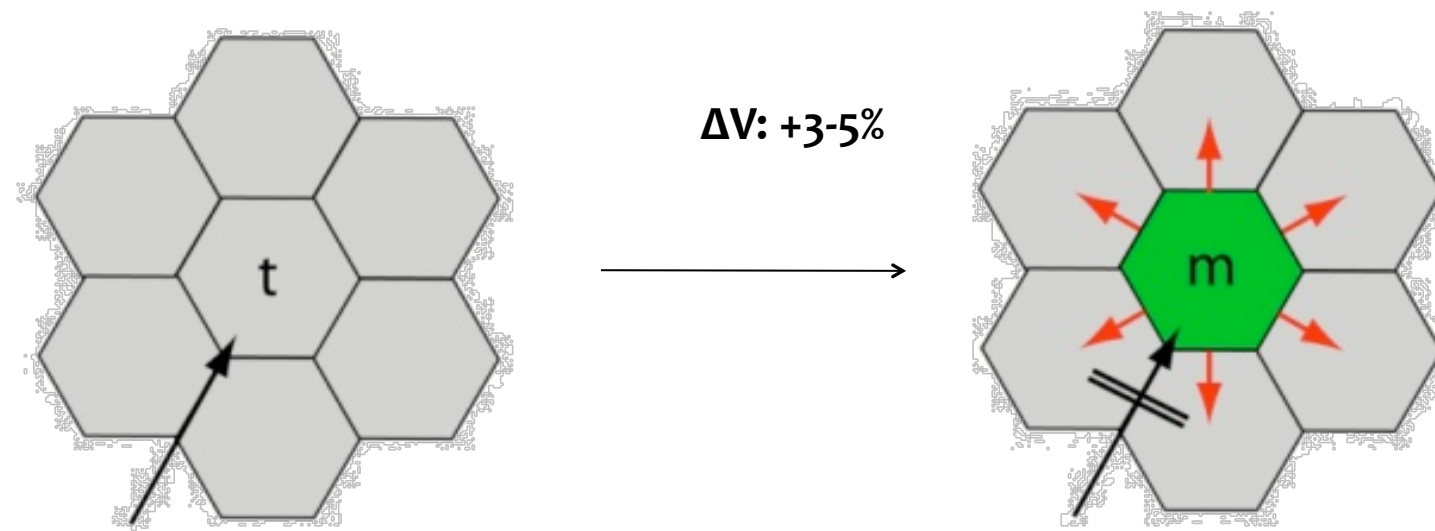
No fragmentation



Particle-free films



Enhanced fracture toughness by laser-induced partial phase transition:



Stress-field generated around transforming grains counteracts crack propagation

Findings:

- ▶ **SrTiO₃ (STO) deposited on SrTiO₃ and MgO shows an apparently 5-times higher conductivity on STO for the same deposition conditions.**

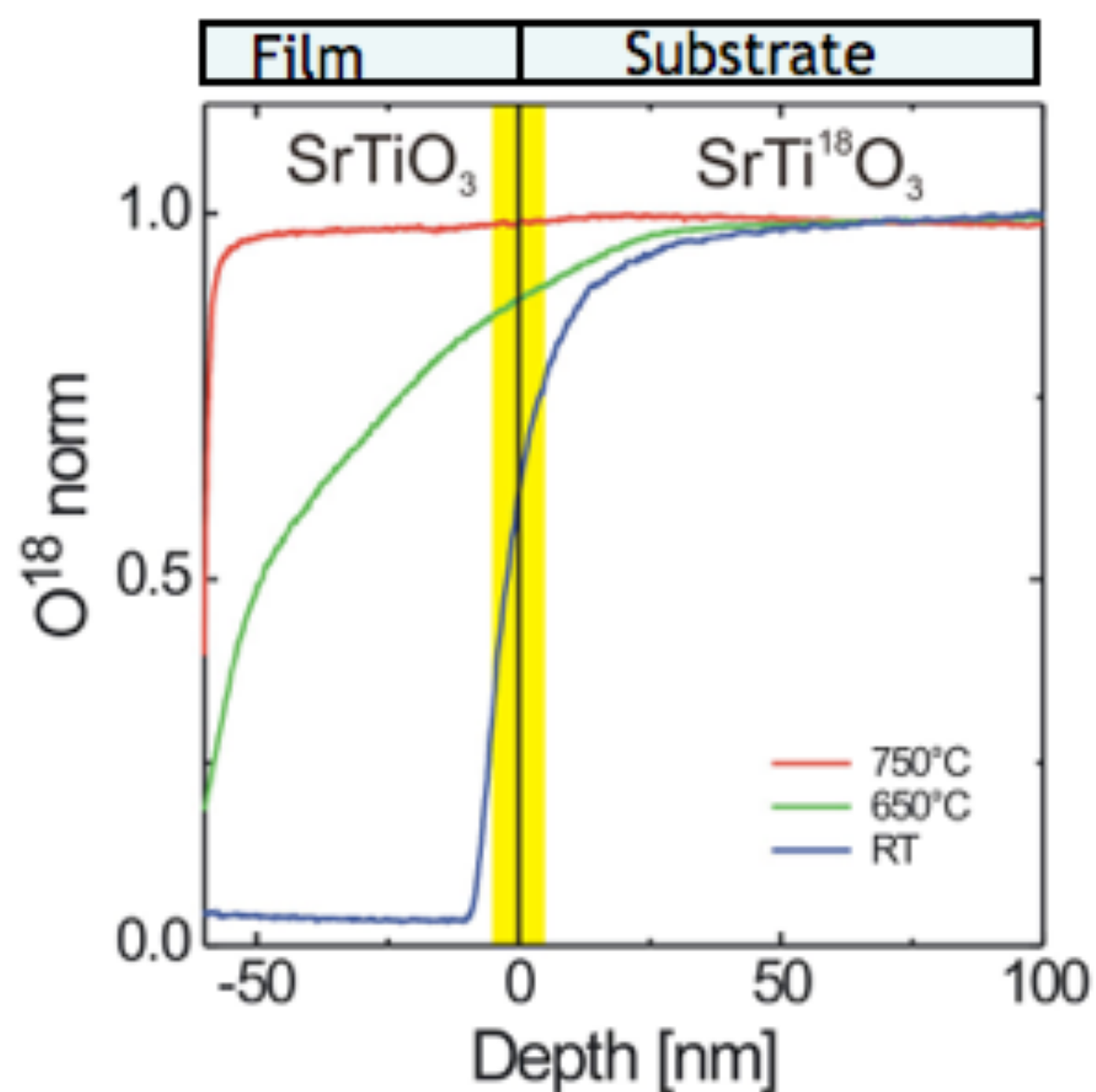
Why?

Hypothesis: related to growth and oxygen

Hypothesis: Oxygen can also come from the substrate which may change properties.

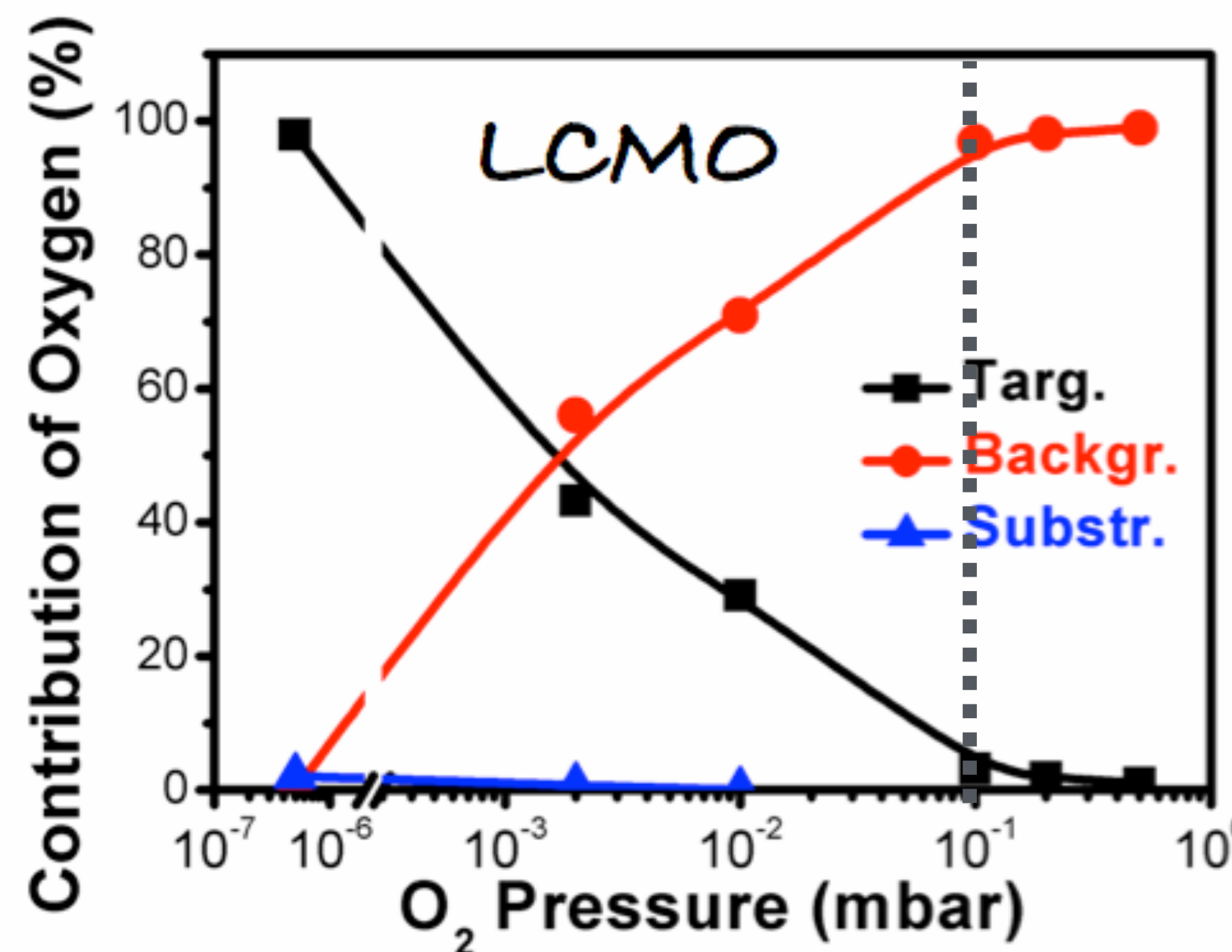
How to probe: use mass spectrometric methods (SIMS) and ^{18}O (single crystal substrates with ^{18}O , or even targets)

From: Secondary Ion Mass Spectrometry (SIMS)



All oxygen in the film comes from the substrate at 750°C

From: Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA)



on STO
(LCMO=La_{0.4}Ca_{0.6}MnO₃)

In addition to substrate, also a target with ^{18}O was used

Most oxygen in films originates from background for LCMO (at $p > 10^{-1}$ mbar).

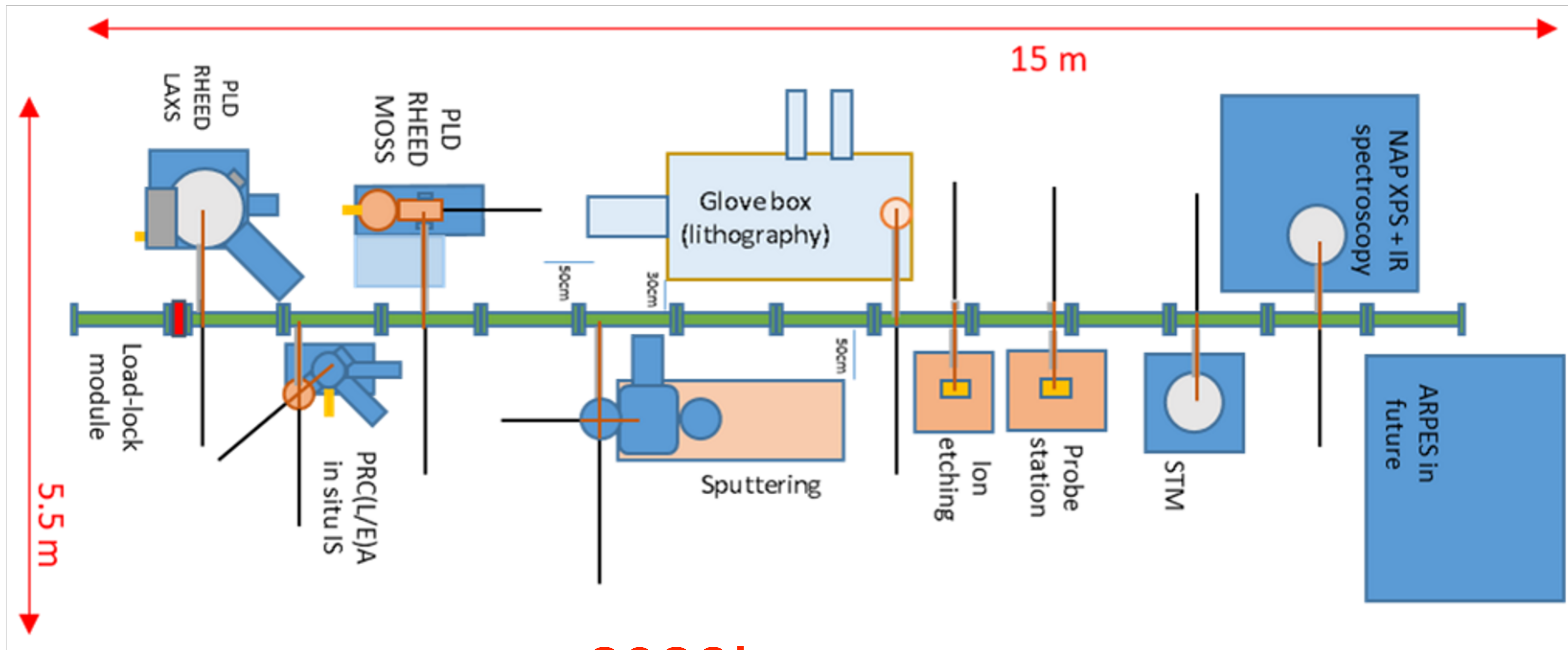
- Reduced STO is an electronic conductor, which results in huge apparent differences (we had up to 5 orders of magnitude for MgO vs. STO) in conductivity of thin films (but in reality it is the substrate).
- Annealing would help, but strain is often released during annealing.

Why do we care so much?

We prepare thin films for:

- ▶ Strain engineering of properties (in-situ stress monitoring during growth of 5-20 nm thick films):
 - ▶ ferroelectric and
 - ▶ multiferroic materials.
- ▶ Ion conductors (solid state Li^+ , with in-situ impedance spectroscopy-coming soon)
- ▶ Model systems for photo-electro-catalysis for water splitting (using large scale facilities)
- ▶ For all of these studies we need well defined films with high quality and desired composition

“Our” Future: the material innovation cluster (MIC)



2026!

Conclusions-Take Home Message

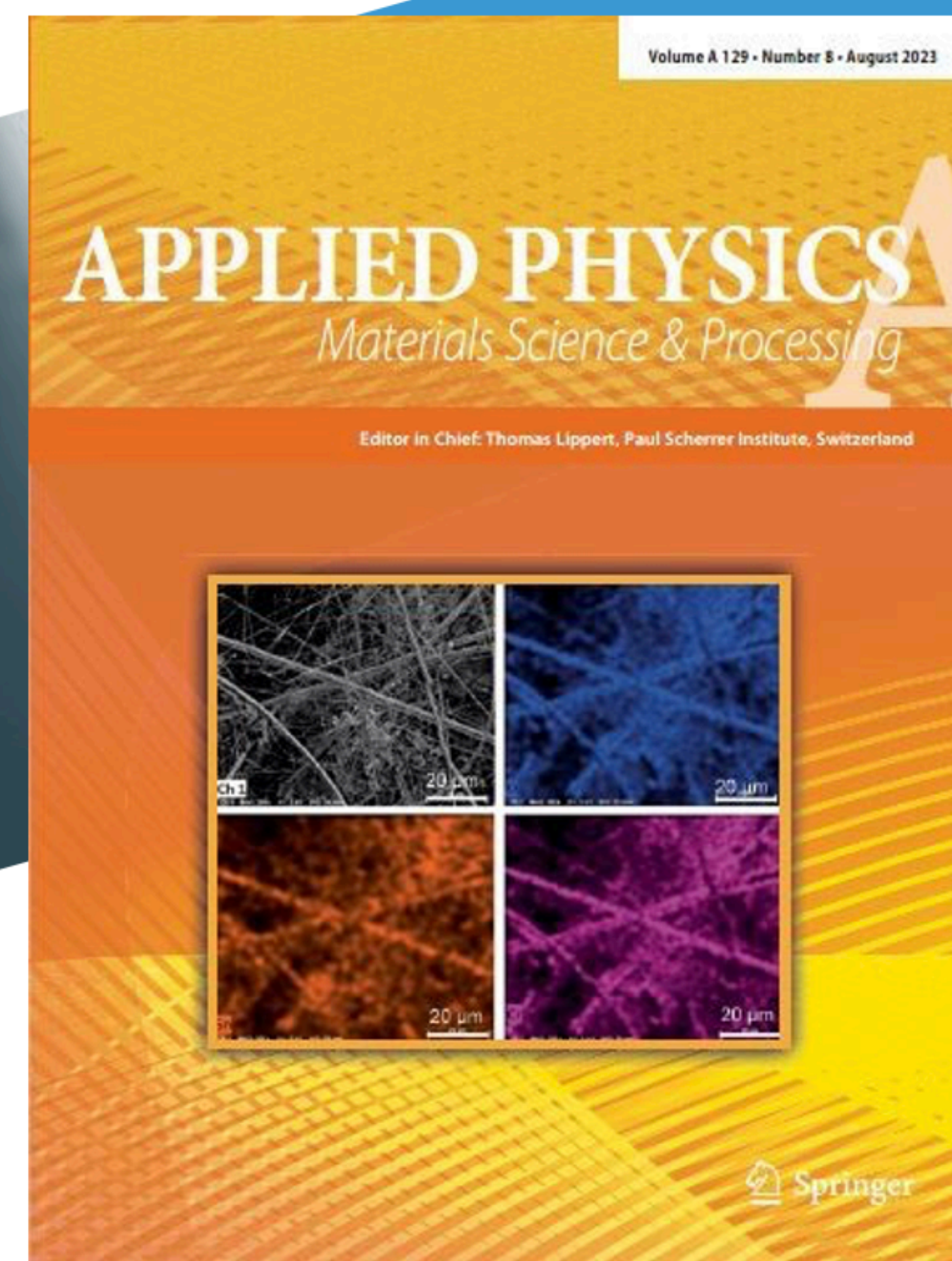
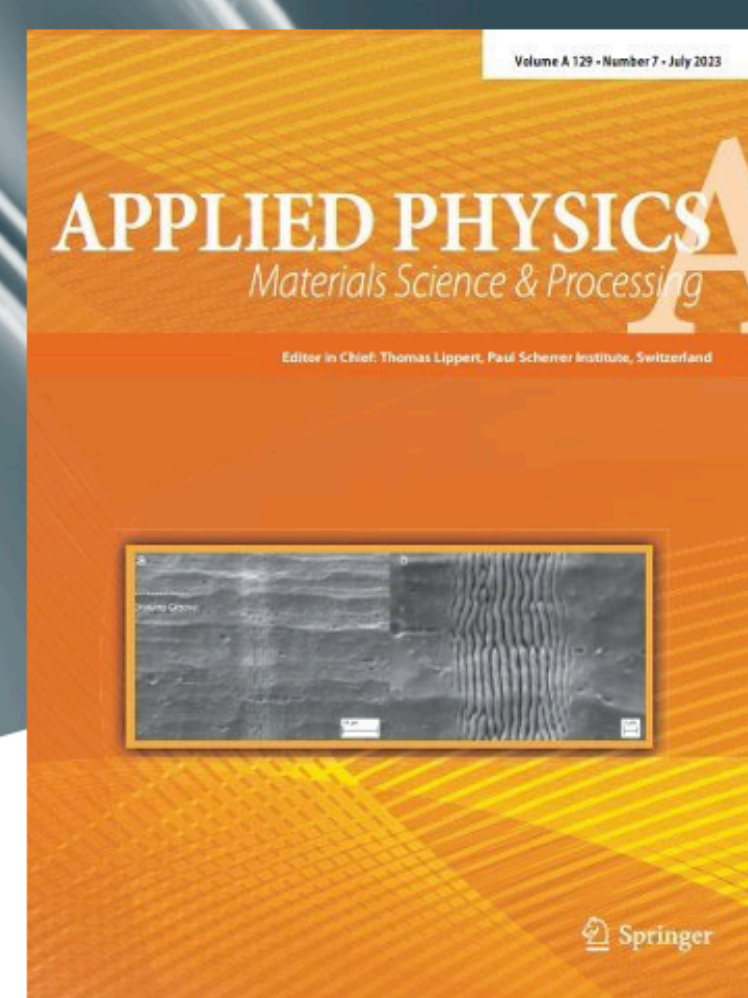
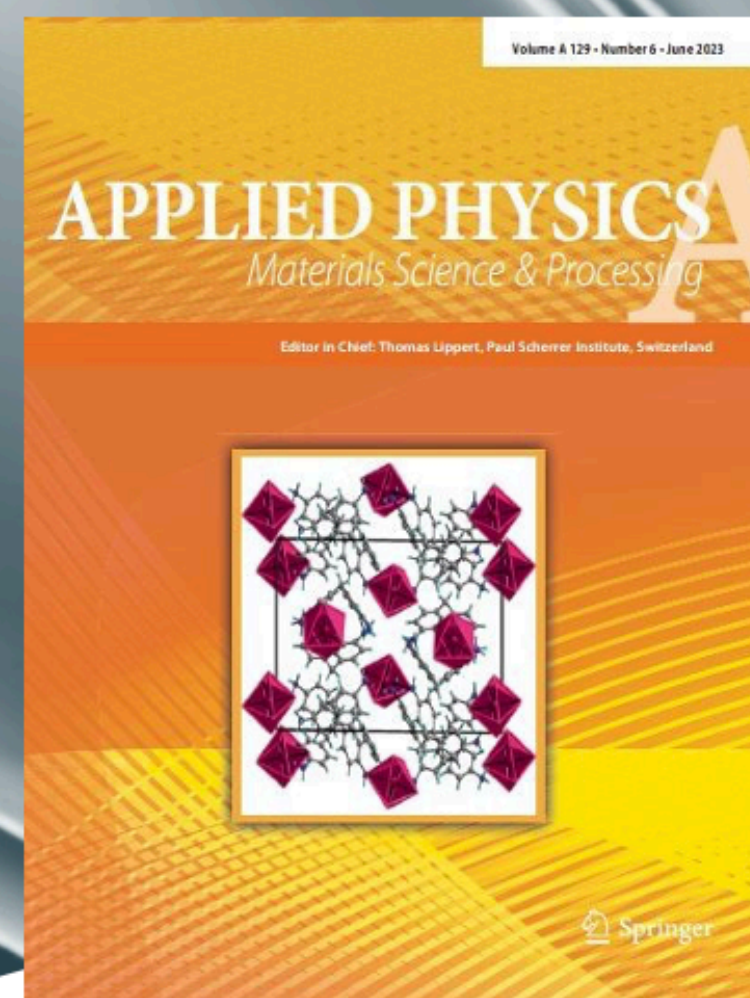
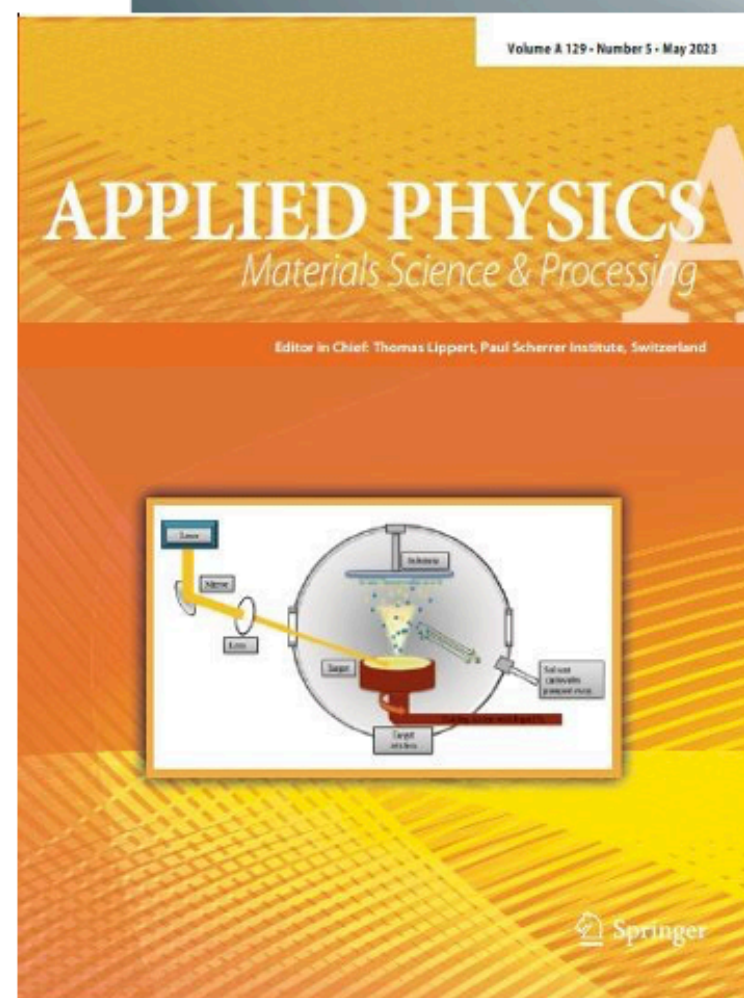
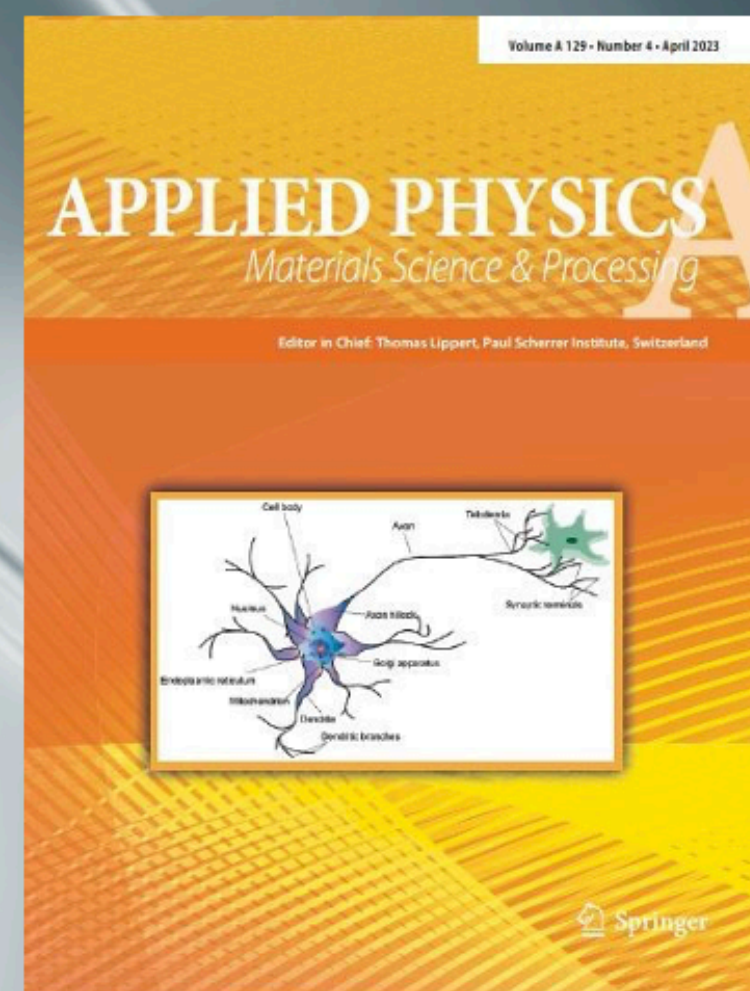
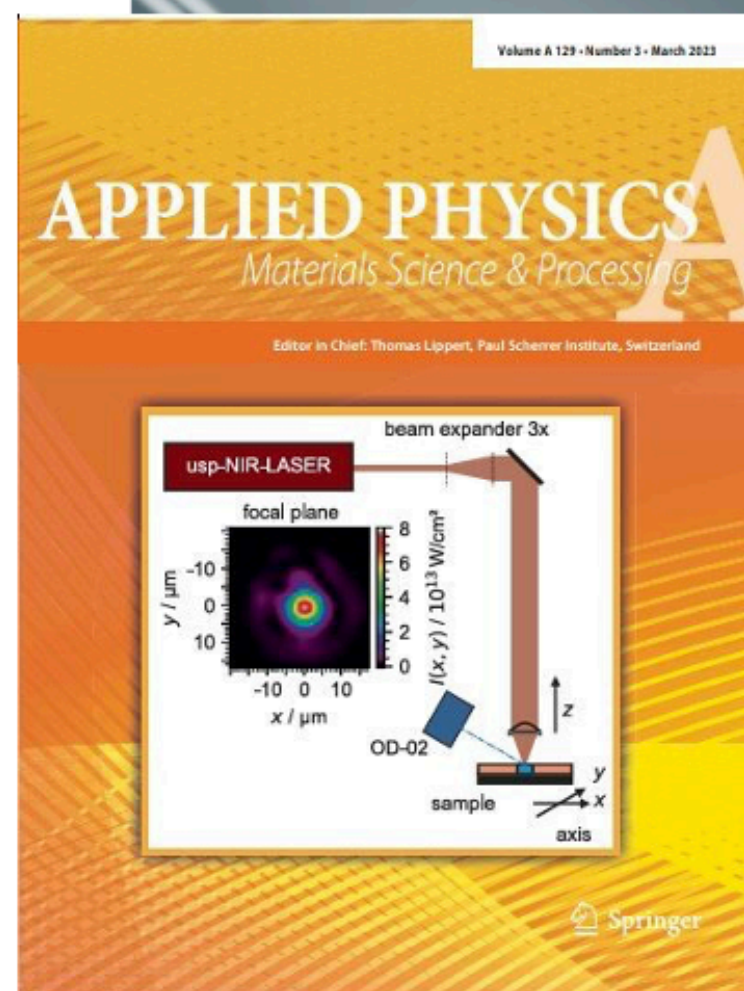
- ◆ **Despite all the problems I have mentioned, PLD is a very good methods for thin film deposition (we have 6+1 chambers, and more are coming), but you need to know what you are doing.**
- ◆ **The need of quantitative analysis of thin films is often neglected. Many processes causes deviations in composition: scattering in plume, sputtering, bouncing, evaporation, reactions, etc.**
- ◆ **We understand some of these processes, and can use some of them to optimise film composition and quality-and you should be aware of these processes.**
- ◆ Most likely problems will be encountered for materials with **high mass ratios**.
- ◆ **Thin films are wonderful model systems for in-situ or operando studies** using (neutron, photon or muons), but well defined films are needed→ This gave us already new insights for photo-electro-catalysis.
- ◆ **There is still room for fundamental studies on PLD.**
- ◆ **Future: Automated, ML/AI-controlled with feed back loops (in-situ “probes”, such as plasma analysis, film growth/composition/properties, etc.). We will be doing this in our new setup.**

Talk by Dave Geohegan

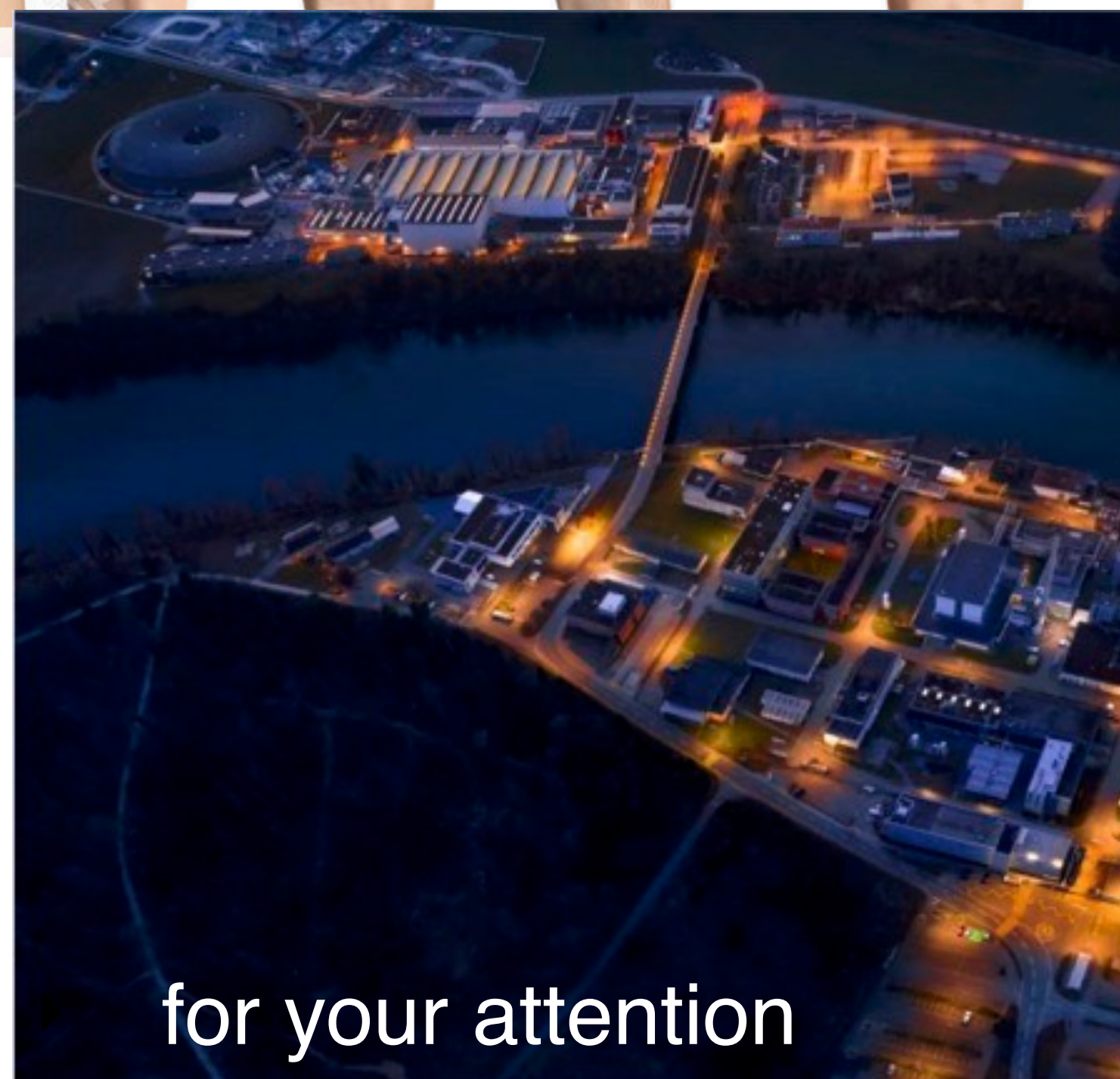
Springer Journal
Applied Physics A
Materials Science & Processing

Editor-in-Chief: Thomas Lippert

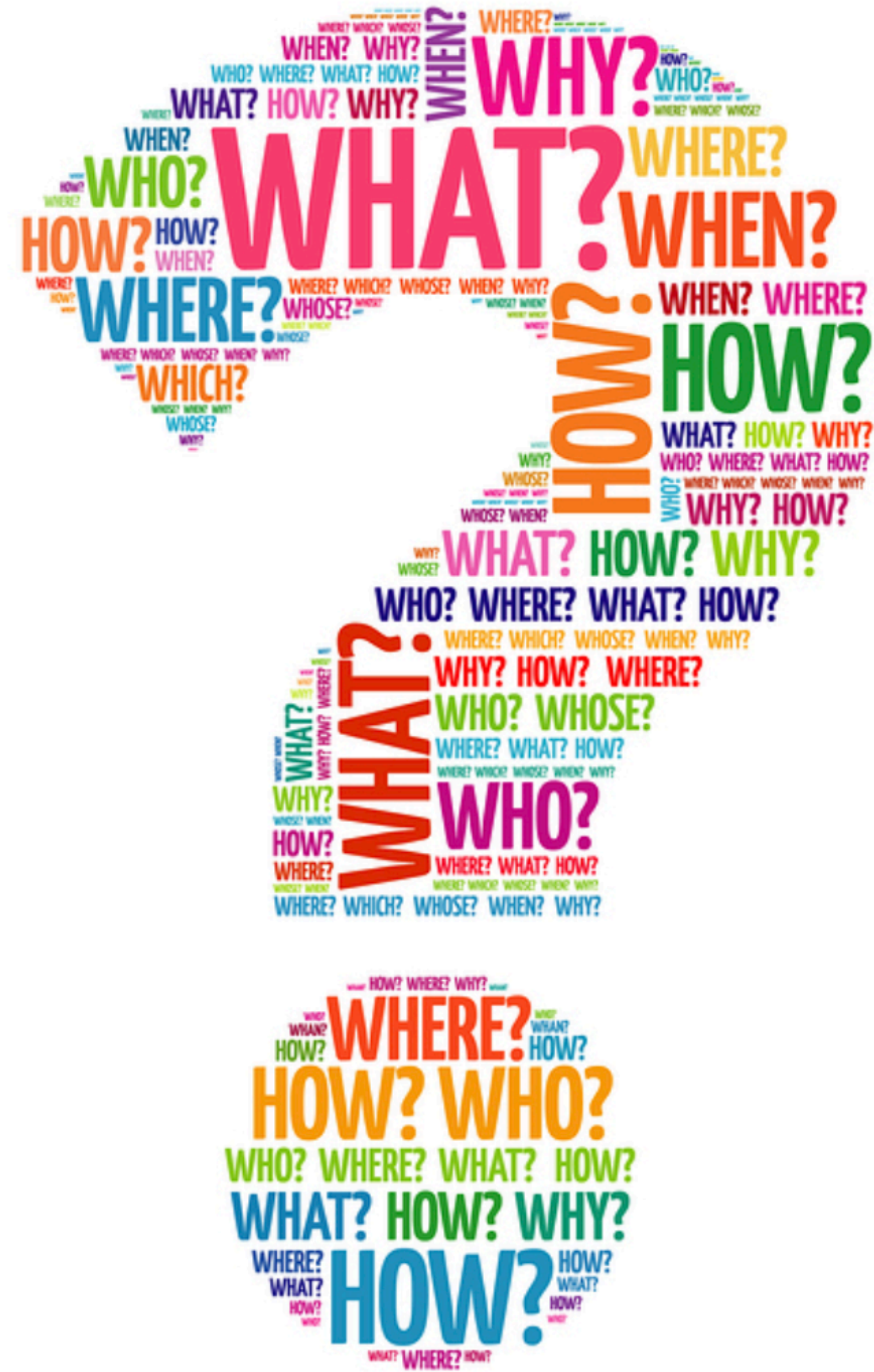
www.springer.com/339



THANK YOU



for your attention



References (most recent)

Reviews

- A. Ojeda, M. Döbeli, T. Lippert, *Influence of plume properties on thin film composition in pulsed laser deposition*, Adv. Mat. Interfaces 1701062, **(2018)**.
- C. W. Schneider, T. Lippert, *PLD plasma plume analysis: a summary of the PSI contribution*, Appl. Phys. A 129, 138 **(2023)**.
- N. Shepelin, Z. P. Tehrani, N. Ohannessian, C. W. Schneider, D. Pergolesi, T. Lippert, *A practical guide to pulsed laser deposition*, Chem. Soc. Rev. 52, 2294 **(2023)**.

Additional papers

- X. Yao, C. W. Schneider, N. M. Bulgakova, A. V. Bulgakov, T. Lippert, *Ion expansion dynamics of laser induced plasmas*, J.Phys. D: Appl.Phys. 56, 345202 **(2023)**
- X. Yao, C. W. Schneider, N. M. Bulgakova, A. V. Bulgakov, T. Lippert, *Double layer acceleration of ions with differently charged states in a laser induced plasma*, Appl. Phys. A 129, 590 **(2023)**.