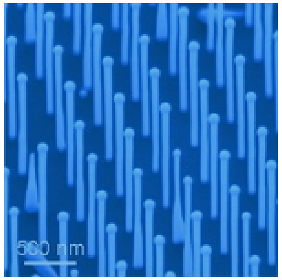

ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

11-16 Jun 2023 Aussois (73500) (France)

Pulsed laser deposition

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Institut des Sciences Chimiques de Rennes
UMR CNRS 6226

NAMe
GDR Nanomaterials for Energy Applications

El Nano 11-16 june 2023

Université de Rennes

cnrs

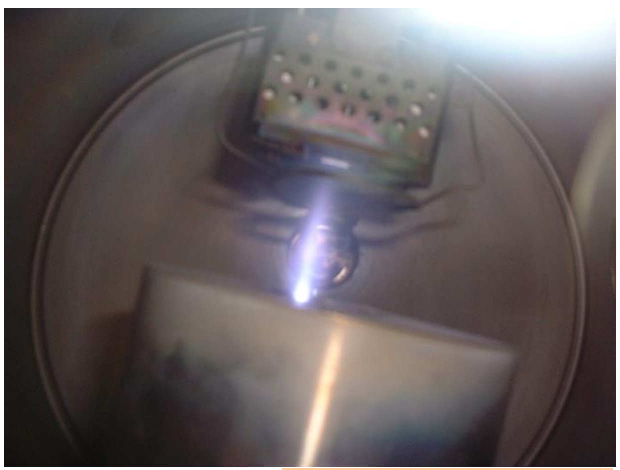
Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Thin film preparation

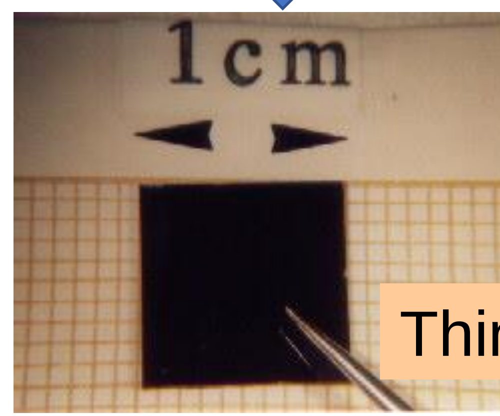
Laser ablation via a pulsed laser and deposition

Target

substrate



deposition



Thin film

PULSED LASER DEPOSITION EVOLUTION

Sixties : the “ laser age ”

1960 : paper of T.H. Maimon (ruby laser)

1965 : first thin films : *H.M. Smith, A.F. Turner, Appl. Opt.,* ***4****, 147 (1965)*

CdTe, PbTe, ZnTe … : under vacuum (10^{-4} Torr), ruby laser, 1 ms pulses

1968 : metals, oxides ($BaTiO_3$) …*H. Schwarz, H.A. Tourtelotte, J. Vac. Sci. Technol.,* ***6****, 373 (1968)*

Seventies : short pulses lasers, peak power > 10^6 W

⇒ congruent evaporation : possibility to grow thin films with the same composition and the same structure as the starting target

J. Desserre, J.F. Eloy, Thin Solid Films, ***29****, 29 (1975) (CdTe…)*

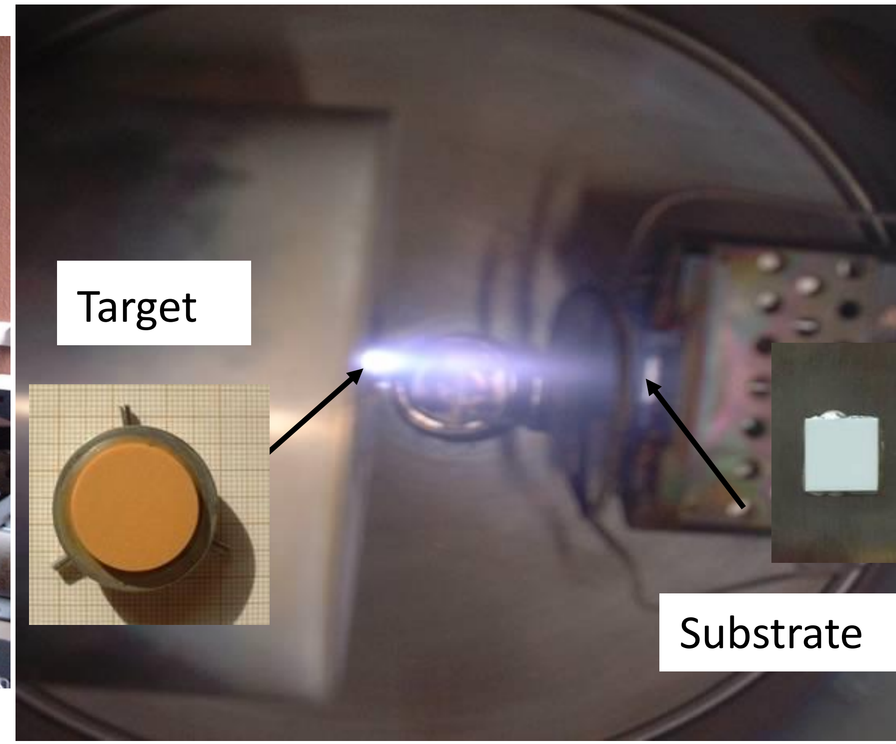
Eighties : short wavelengths (UV excimers) , high power pulses …

advantages of PLD : versatility, congruence …

Oxides : first high quality films of $YBa_2Cu_3O_7$ as soon as 1987

D. Dijkkamp, T. Venkatesan et al., Appl. Phys. Lett., ***51*** *, 619 (1987)*

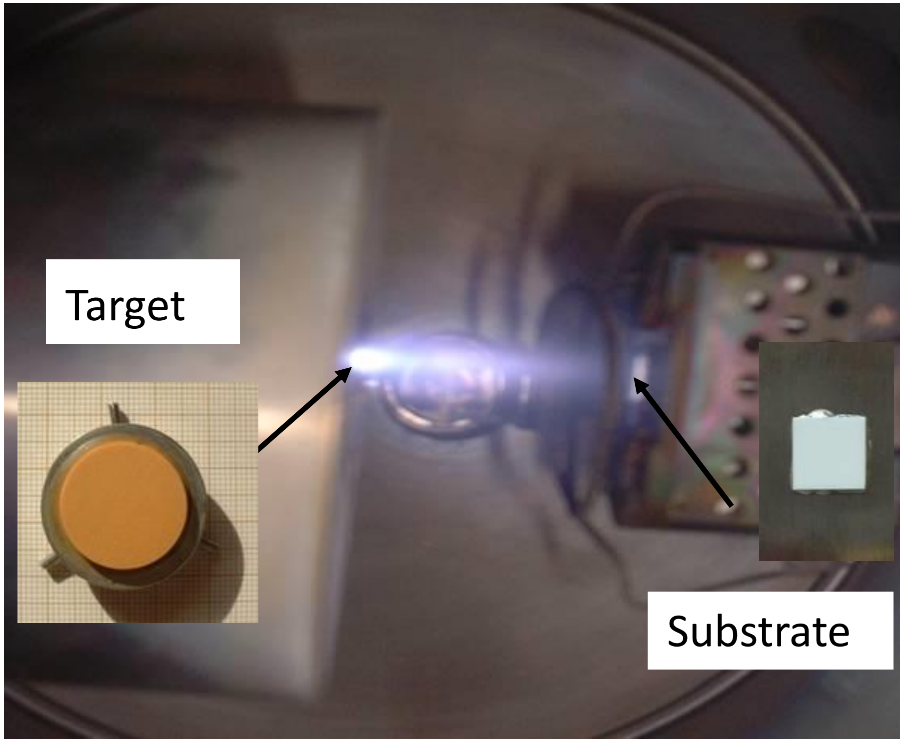
Pulsed Laser Deposition system



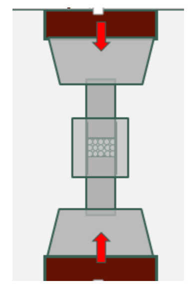
Excimer laser KrF
λ = 248 nm
Pulses 20 ns, 2 Hz
Fluence 1 - 4 J/cm^2

Institut des Sciences Chimiques de Rennes UMR CNRS 6226 CSM

Pulsed Laser Deposition system

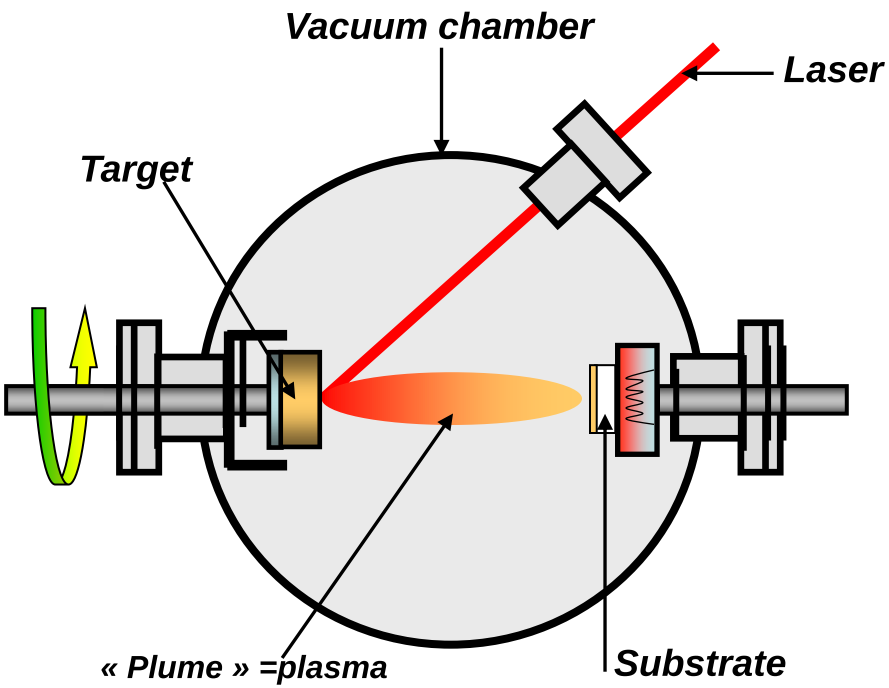


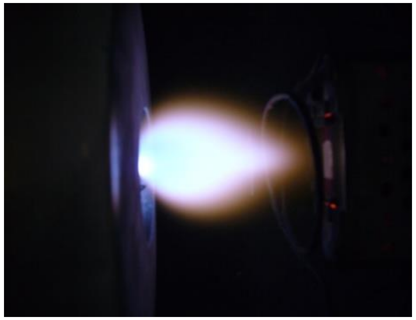
SPS
Spark Plasma Sintering

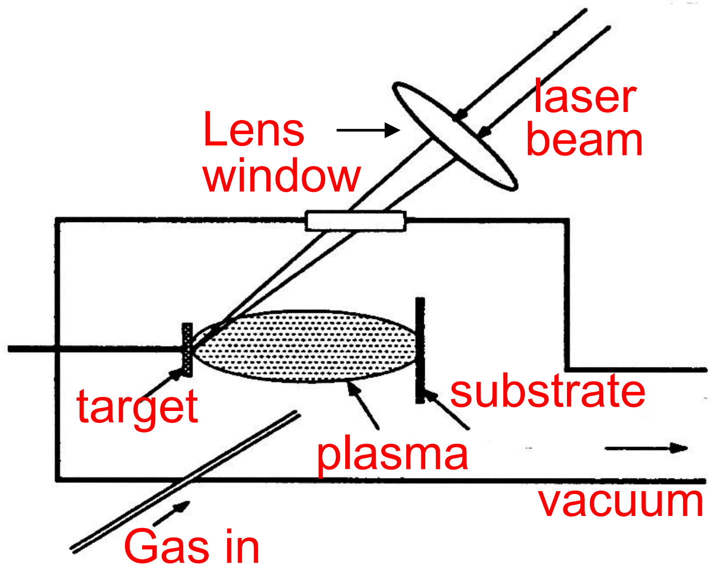


Ceramic target by
Natural sintering
or SPS
Metallic foil
etc

PLD Principle







Excimer Laser XeCl (308nm), ArF (193nm), Nd:YAG triple (354nm)…

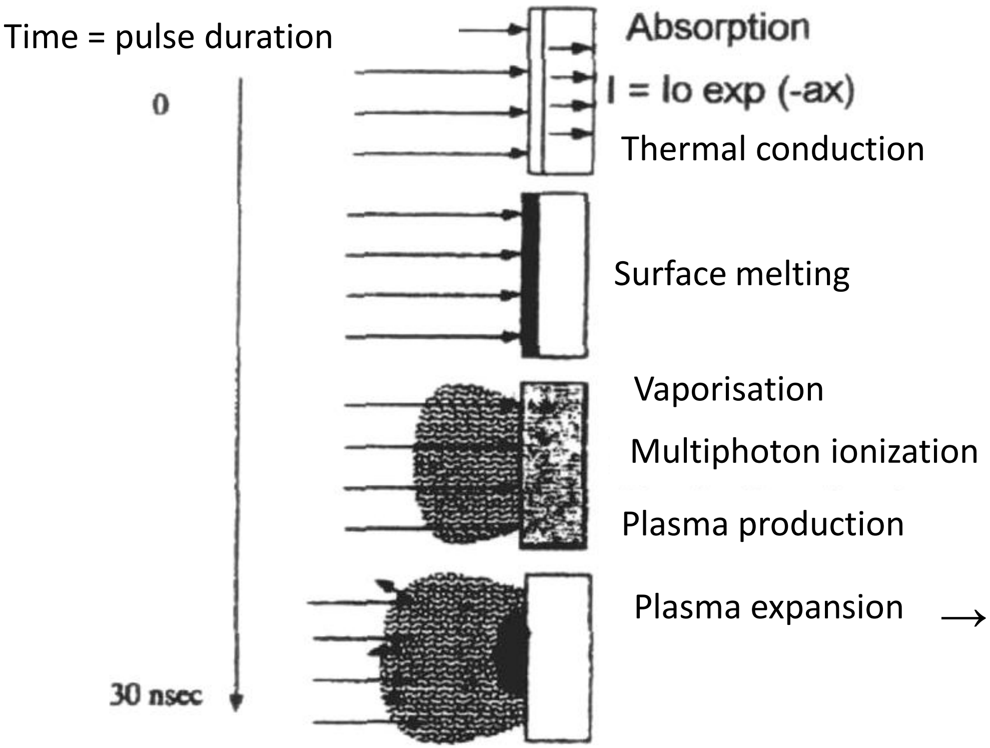
KrF - λ= 248 nm
Pulses 20 ns, 1-3 Hz
Fluence ~ 2 - 3 J/cm^2

PLD Principle

- **Main parameters**
- **Laser:**
  - Wavelength
  - Pulse duration
  - Repetition rate (frequency)
  - Fluence: E/interaction surface on the target J/cm^2
- **Deposition conditions:**
  - Deposition temperature
  - Deposition atmosphere: pressure and nature of gas
  - Target / substrate separation
  - .....

Laser ablation principle

PLD



"Sublimation"

↓

Melting then vaporization

T_{max} ~ several 1000 K

→ the mechanism depends strongly on the material

PLD Principle

➔ ***2 regimes***

1- at low fluence: production of vapor ≅ less dense environment

Main mechanisms: thermal conduction, melting, target vaporization

2- at high fluency : excitation and ionization

→ the incident laser beam is partially absorbed by the environment ; plasma formation

Main mechanisms : the process is influenced by the laser-plasma coupling and the plasma kinetic

→ evaporation process +

→ photoexcitation – photochemical effect, ionization, etc

→ Important role of the fluence

→ a threshold fluence for each material

Pulse duration

An important parameter: the pulse duration

- Most of studies: nanosecond (1- 40 ns mainly)
- pico- et femto-second
- If an extremely short pulse: thermal expansion more or less negligible
- femto- and pico-second: in 1^{rst} approximation : direct solid-vapor transfer (*in fact more complicated)*
- *Femto-second: athermic process*
- Case of standard nanosecond ablation of metals:

  absorbed E heats the target up to T_m then T_{vap}

  → evaporation from the melting liquid

photon – target interaction
Laser wavelength

- ***Depends on optical and thermal characteristics of the target :***
  - R : reflection coefficient
  - α : absorption coefficient
  - K : thermal diffusivity

- ***Depends on the laser :***
  - wavelength: λ
  - Pulse duration: τ
  - Energy density on the target (= fluence): F

laser beam : a part is reflected by the target,
another part is absorbed

Laser beam absorption

Classical Beer-Lambert law

$$I(z)= I_0.(1-R).e^{-\alpha(\lambda)z}$$

R : reflection coefficient

I(z) : wave intensity at z deep

α : absorption coefficient

I_0 : incident wave intensity

thickness of the target penetrated by the wave z_0 :

$$z_0=\frac{1}{\alpha(\lambda)}$$

α : absorption coefficient in m^{-1} , cm^{-1}

R : reflection coefficient

- R depends on the electromagnetic wavelength: R(λ)
- R depends also:
  - On the electrical conductivity of the target material
  - On the target surface quality

K= target thermal diffusion coefficient (« diffusivity »)

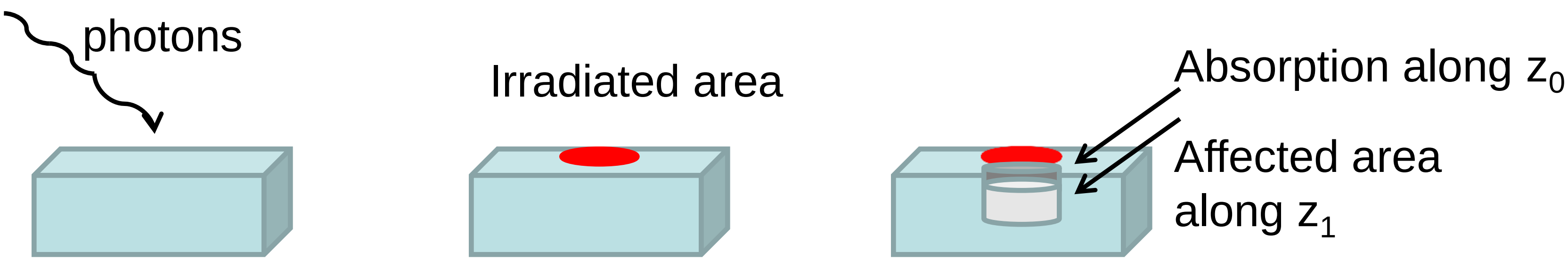
$$K=K_{th} /\rho C$$

K_{th} thermal conductivity, K_{th} : in $W.m^{-1}.K^{-1}$ and K : $m^2 s^{-1}$
ρ volumic mass, C calorific capacity $J.g^{-1}. K^{-1}$ if ρ in $g.m^{-3}$

Depth affected by radiation in the target

- Estimation of the thickness of the target's layer thermally affected by the irradiation:

$$z_1 = \sqrt{(Kt)}$$



→ Depending on the material : z_1 may be larger than z_0 or close to z_0

Interest of a UV laser

- To limit thermal effect → short wavelength
  ➔ most often: excimer laser with λ< 500 nm

  ArF: 193 nm (excimer)
  KrF: 248 nm (excimer)
  Nd:YAG (solid) (1064 nm, 532 nm, 355 nm, 266 nm)

- Prerequisite: absorption of the laser beam by the target's material at this wavelength

  → high α

- + roughness of the polycrystalline target enables to increase absorption

- Target irradiation can promote 2 phenomena:
  - Thermal evaporation
  - Photochemical interaction

in practice: both : i.e. an intermediate situation

→ PLD is not only evaporation

➔ In all cases, to promote matter ejection: F has to be larger than a threshold value that depend on :

- λ, τ
- target composition

Generally : 0,1- 2 J/cm^2 for oxides

A few tens of J/cm^2 for glassy carbon

Example of the ferroelectrics $KTa_{1-x}Nb_xO_3$ (KTN) and $K_xNa_{1-x}NbO_3$ (KNN)

Q. Simon et al., Appl. Phys. Lett. 99, 092904 (2011)
B. Aspe et al., Journal of Alloys and Compounds 827 (2020) 154341
B. Aspe, et al. Journal of Alloys and Compounds, 856 (2021) 158138
B. Aspe, et al. IEEE Antennas and Wireless Propagation Letters, 20 (2021), 1414-1418

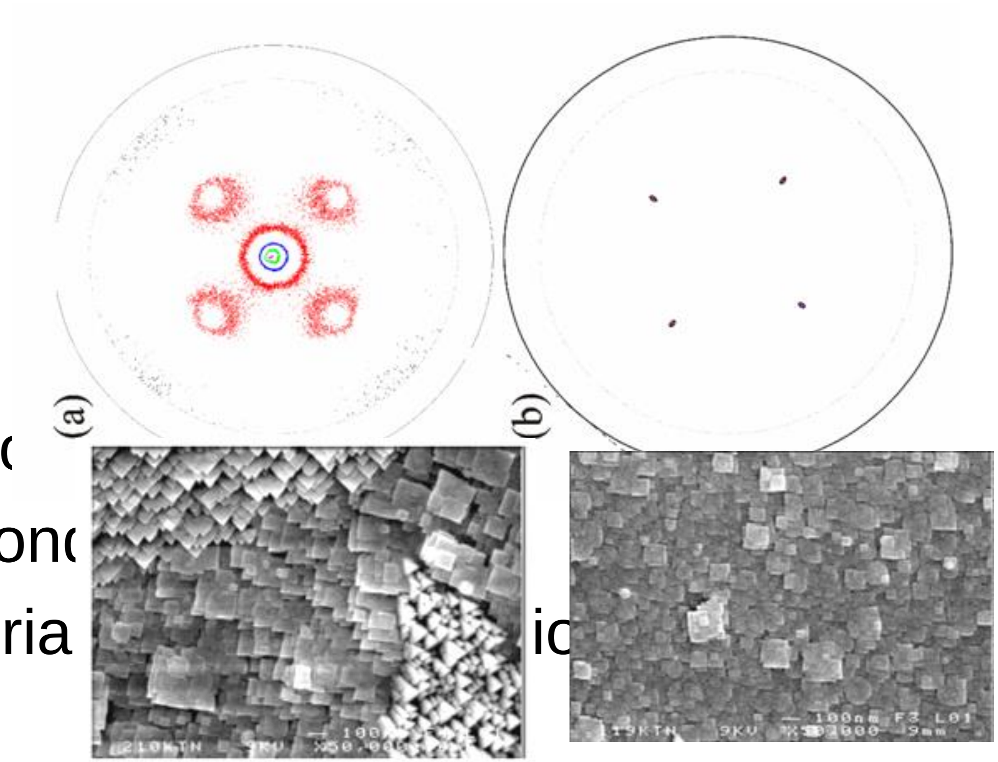
- « Thin film »

- Nano-objects i.e. nanor(

→ role of the deposition cond

→ importance of the materia … ic

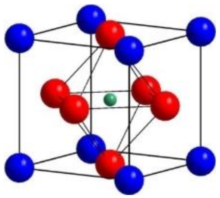
crystalline structure)

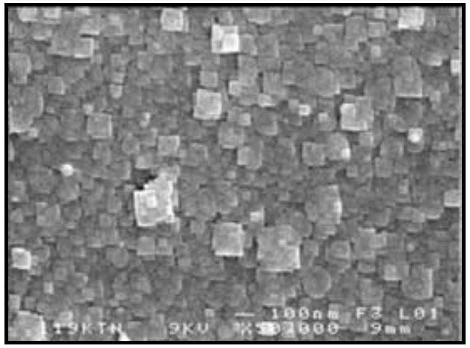


W. Peng, et al.
Integrated Ferroelectrics, 93, 126-132, (2007)

In the K-Ta-Nb-O system (piezoeletric phases) From perovskite to Tetragonal Tungsten Bronze (TTB) phase

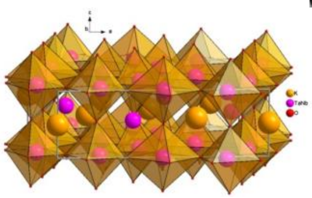
Perovskite

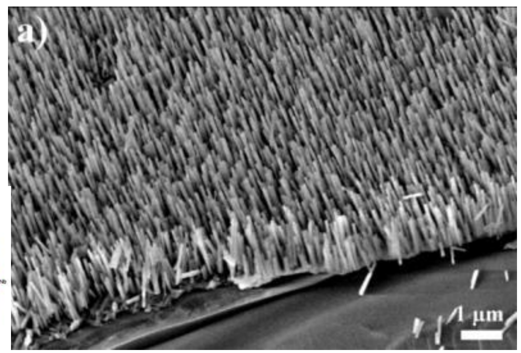


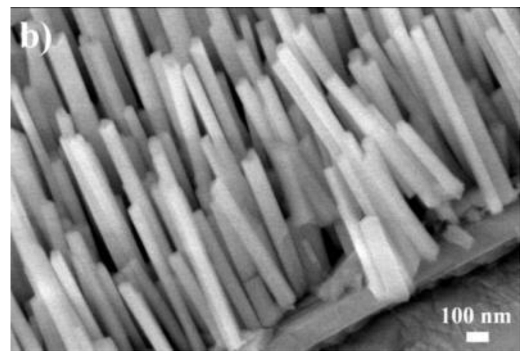


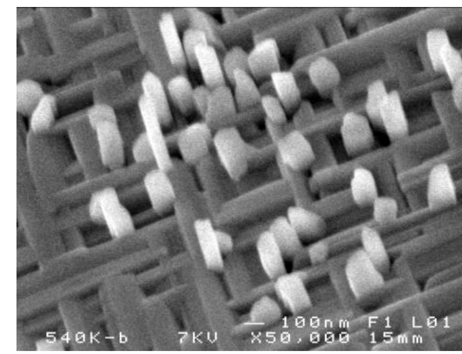
→ From thin film to nanorods

TTB





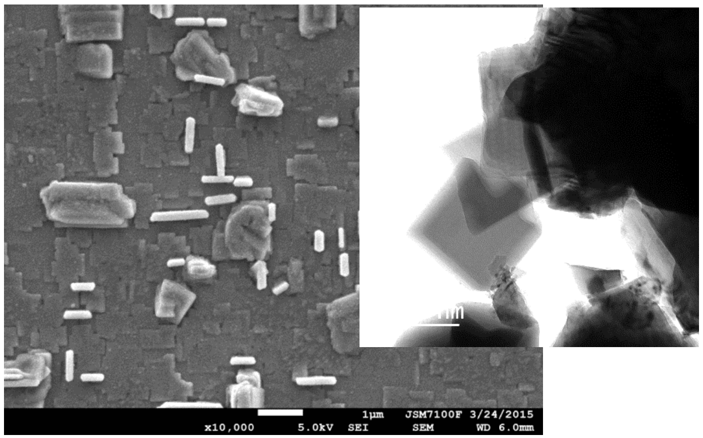


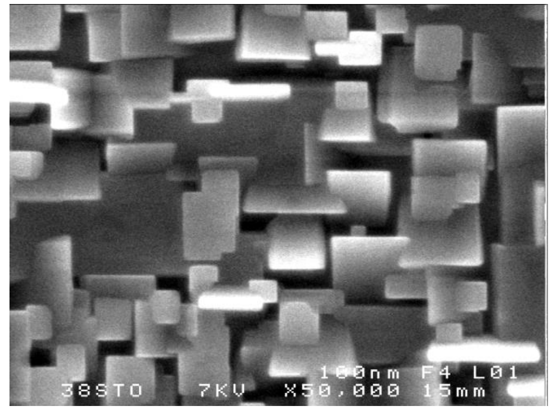


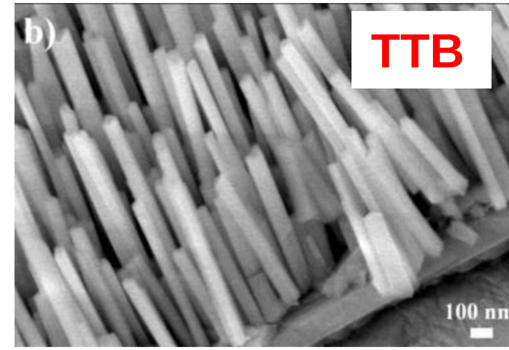
→ Variation of K content → variation of the crystalline phase
→ evolution of the morphology

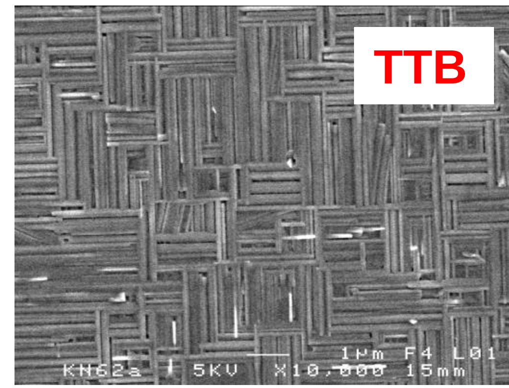
Q. Simon, V. Dorcet , P. Boullay, V. Demange, S. Députier, V. Bouquet, M. Guilloux-Viry.
Chem. Mater. **25** (2013) 2793

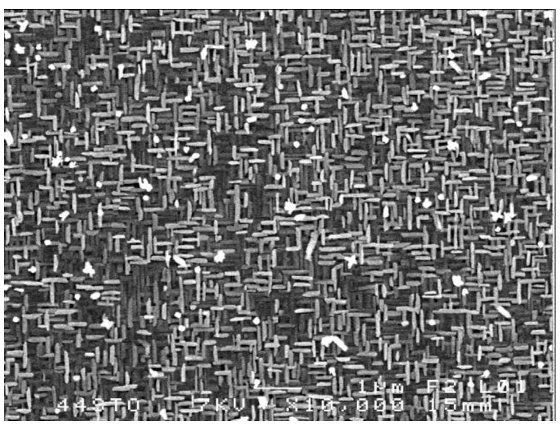
Composition, structural and epitaxial effects

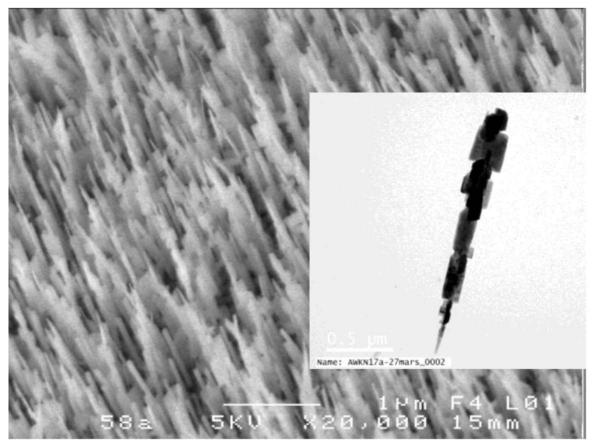












V. Demange, et al.
Crystal Growth & Design, 20 (2020) 2356-2366

SEM and TEM @ SCAN MAT

https://scanmat.univ-rennes.fr/

Control of thin films composition

- Some examples to illustrate how to control the composition of multi-element materials in thin films by PLD

- PLD is well – known for the good transfer of composition, but it can vary with the target composition

  BUT chemistry has to be taken into account

Superconducting $YBa_2Cu_3O_7$ (YBaCuO) thin films

- Stoichiometric targets → near stoichiometric films **(no volatil cation)**
  - **YBa_2Cu_3**O_x
- Oxygen content controlled by deposition and cooling atmosphere :

$P(O_2)$ deposition	cooling	T_c
0.3 mbar	300 mbar	86-90 K
~ 0.3 mbar	~ 0.3 mbar	~ 60-70 K

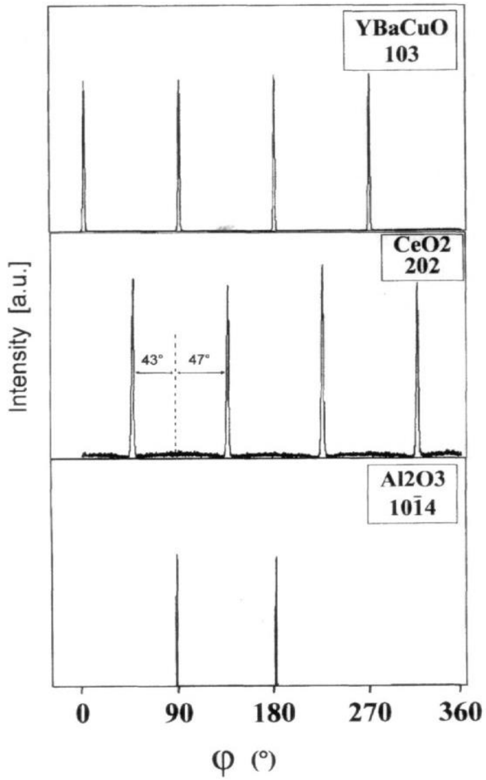
- Epitaxial thin films on various substrates

M. Guilloux-Viry et al. J. Cryst. Growth, 132, 396, (1993)
C. Perrin et al. J. Alloys & Compounds, 195, 339 (1993)

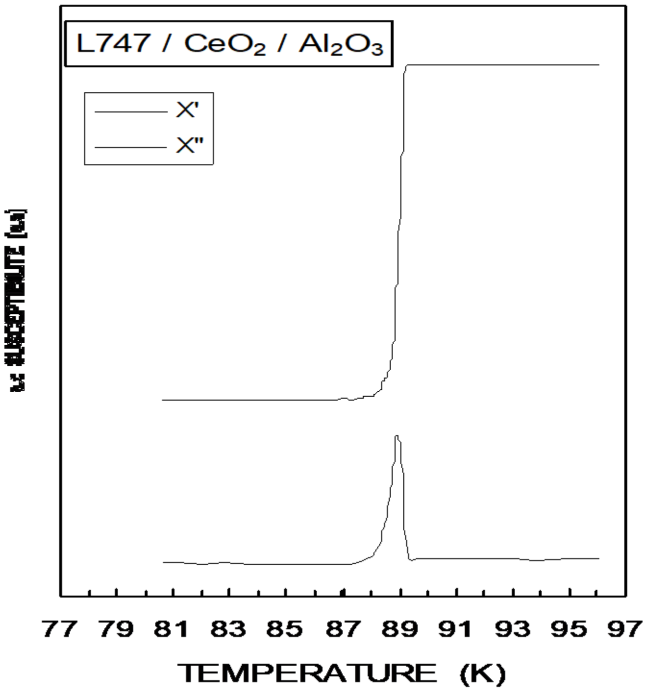
C-axis oriented $YBa_2Cu_3O_7$ epitaxial films on substrates suitable for microwaves

X-ray diffraction φ-scans

→ epitaxy on CeO_2 / R-Al_2O_3



On CeO_2 / R-Al_2O_3



R_s (10GHz, 77 K) = 0.5-1 mΩ

C. Le Paven-Thivet et al. Physica C, 244, 231, (1995)
X. Castel et al. J. of Crystal Growth, 187, 211 (1998)

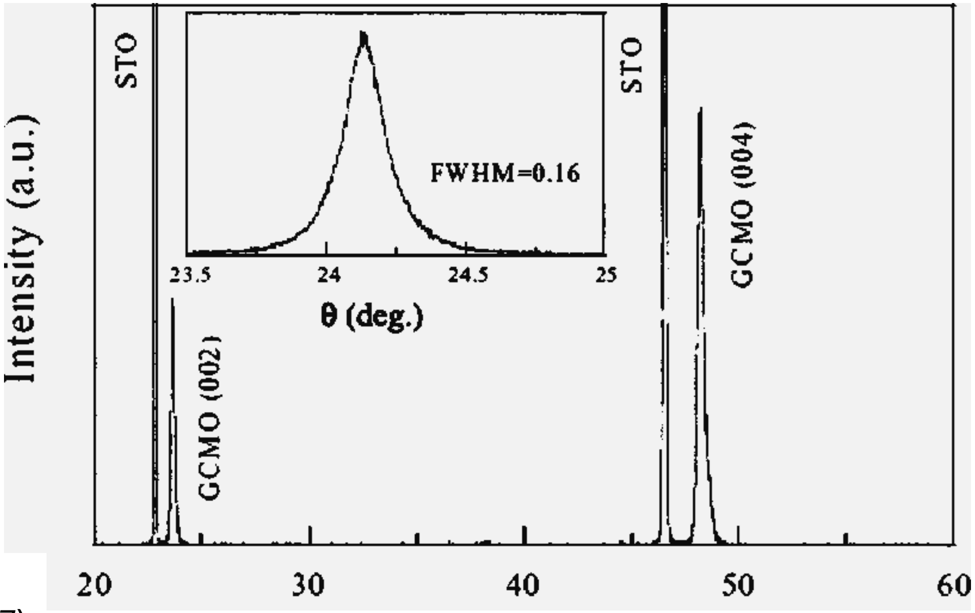
example without volatil cation ➔ Magnetic oxides : $Gd_xCa_{1-x}MnO_3$

- Stoichiometric target → stoichiometric films for cations
- Control of oxygen content with deposition pressure and post-annealing
- T_d = 740° C, $P(O_2)$ = 0.2-0.6 mbar

Θ-2θ X-ray diffraction

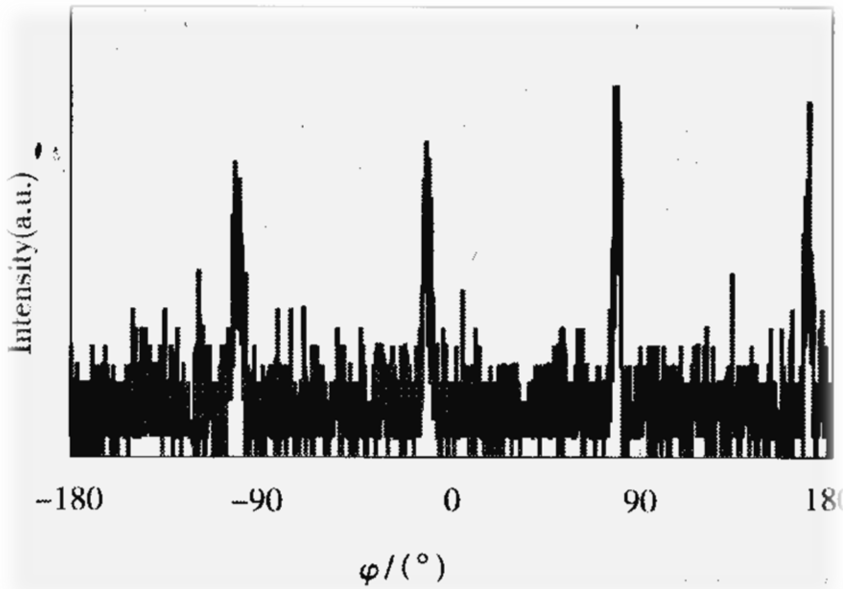
→ higly oriented films

Out of plane orientation

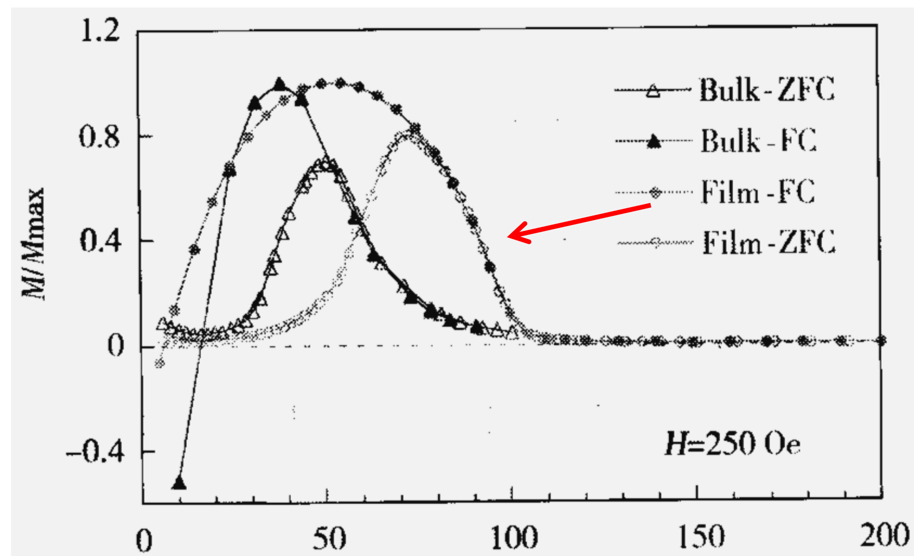


O. Peña, Y. Ma, M. Guilloux-Viry, C. Moure
Appl. Surf. Sci., doi : 10.1016/j.apsusc.2007.07.061, (2007)

$Gd_{0.67}Ca_{0.33}MnO_3$ thin films



- XRD φ-scan ⟶ epitaxial growth
- In-plane orientation



- ⟶ Magnetic ordering

Y. Ma, M. Guilloux-Viry, P. Barahona, O. Peña, C. Moure
Appl. Phys. Let., 86, 062506 (2005)

Functional oxides containing volatil cations: examples of ferroelectric materials

$PbZr_{0.52}Ti_{0.48}O_3$ simple perovskite structure

$SrBi_2Nb_2O_9$ layered perovskite-like structure

$KTa_xNb_{1-x}O_3$ perovskite structure – solid solution

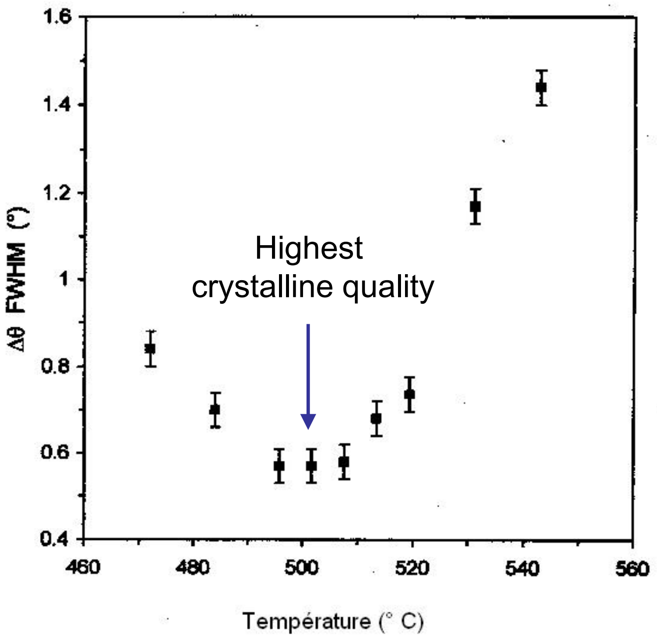
$\textcolor{red}{Pb}Zr_xTi_{1-x}O_3$ (PZT)

- $\textcolor{red}{Pb}Zr_xTi_{1-x}O_3$: deposition temperature compatible with composition ~ stoichiometry from a target slightly enriched in Pb

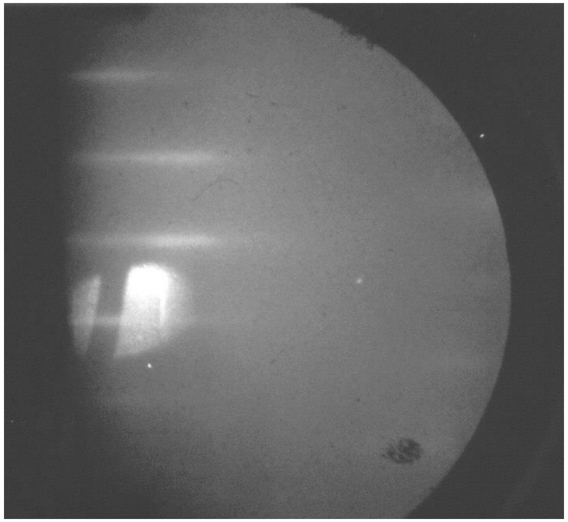
On (100)LiF

$\Delta\ \theta = f(T_d)$

FWHM rocking curve



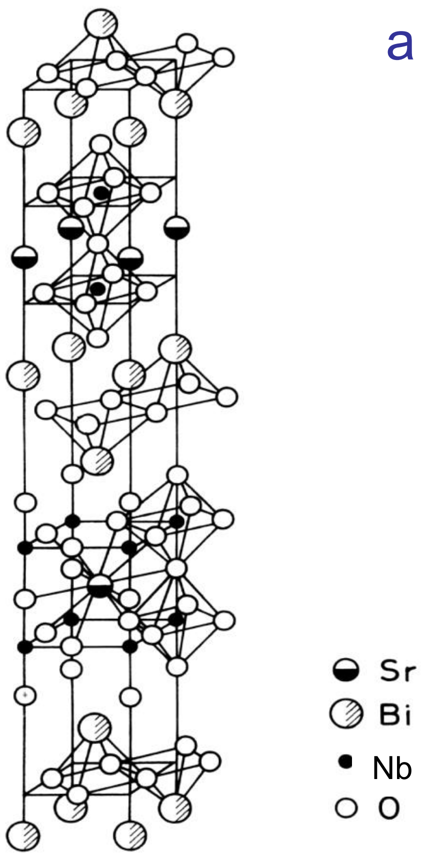
RHEED → epitaxy



L'H. Hamedi, M. Guilloux-Viry, A. Perrin, G. Garry, Thin Solid Films, 352, 66 (1999)

SBN : $SrBi_2Nb_2O_9$

- layered structure « Aurivillius phase »
- orthorhombic structure : a = 5.519 Å, b = 5.515 Å, c = 25.11 Å



a ($SrTiO_3$) x √2 = 5.52 Å → Δa/a = 0.05 %

$(Bi_2O_2)^{2+} (A_{m-1}B_mO_{3m+1})^{2-}$

m=2, A=Sr, B=Nb

Ferroelectric characteristics :

T_{curie} ~ 440° C

P_r ~ 10 - 20 mC/cm^2

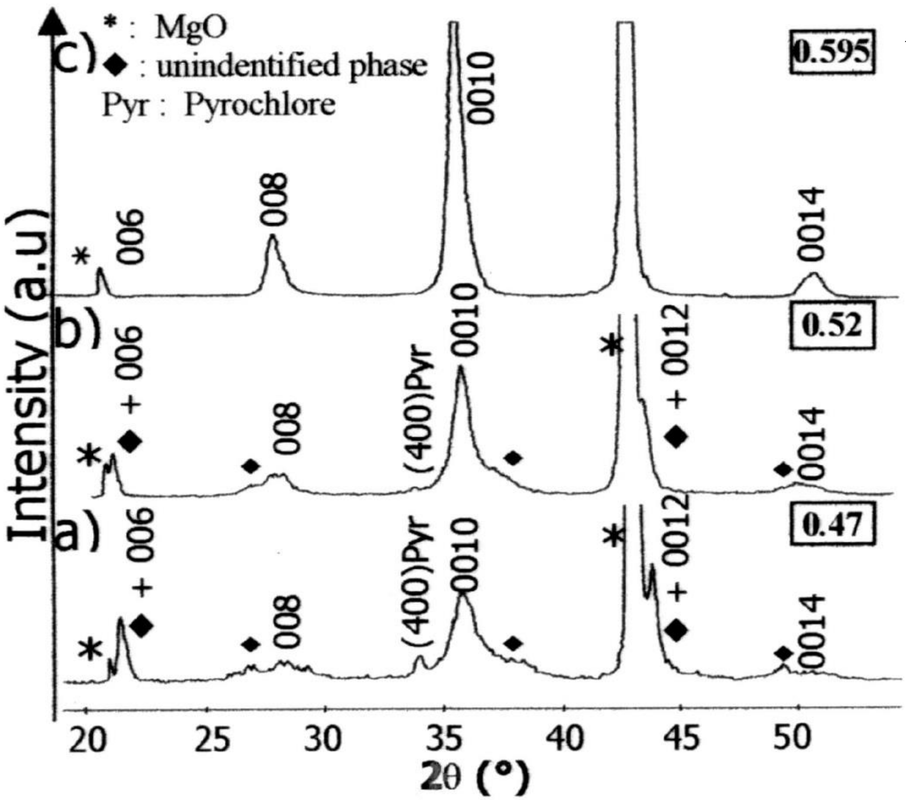
E_c ~ 60 kV/cm

Polarisation : ab plane

Fatigue resistant

Deposition from Bi_2O_3 enriched Sr-Bi-Nb-O targets

At 700° C, $P(O_2)$ = 0.3 mbar → Bi deficiency due to Bi volatility



Bi/(Sr+Nb)

+ 20 % Bi_2O_3

+10% Bi_2O_3

stoichiometric target

SBN + 30 % Bi_2O_3

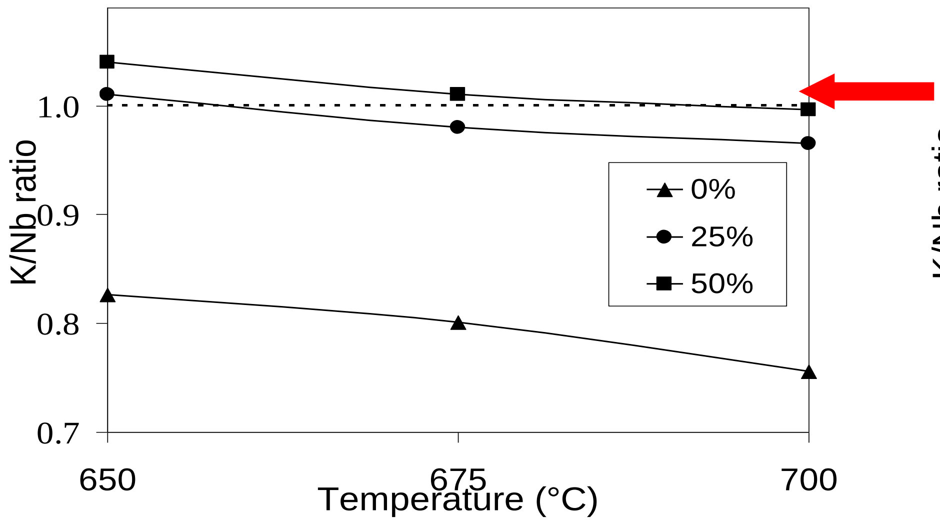
Stoichiometric epitaxial

$SrBi_2Nb_2O_9$ films grown at 700° C

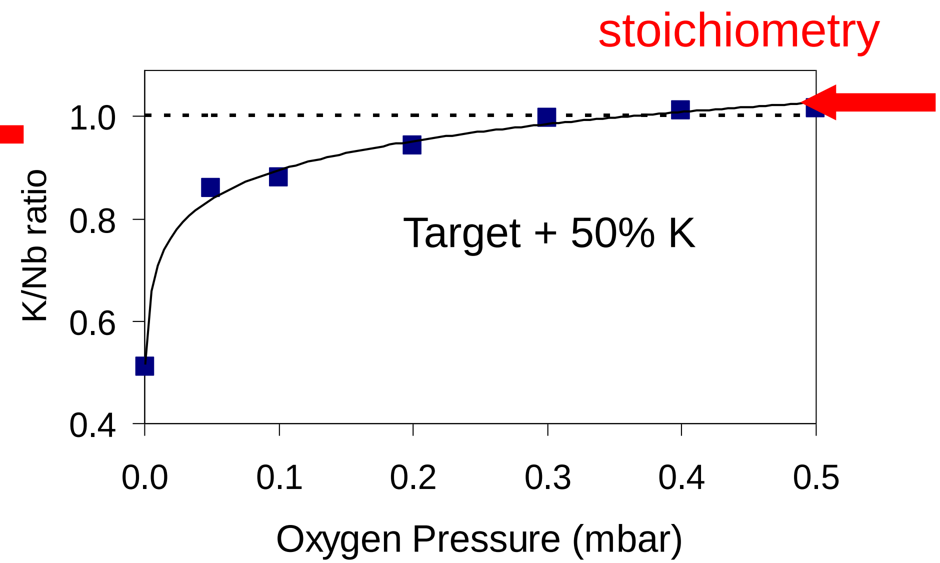
J.R. Duclère et al. Appl. Phys. Lett., 83, 5500 (2003)

Deposition of $KNbO_3$ and KTN from potassium enriched targets

K/Nb = f(T_d) – P (O_2) = 0.3 mbar
3 different targets



K/Nb = f(P (O_2)) – Td = 700°C



Potassium enriched targets : + KNO_3, molar content

→ K/Nb = 1: target + 50%, 0.3 mbar (O_2), 700° C

KTN → K/(Nb+Ta) ~ 1 ; Ta/Nb (film) ~ Ta/Nb (target)

K volatility + K preferential backscattering during plasma expansion *[M.J. Martín, et al J. Mater. Res., 12 (1997) 2699]*

A. Rousseau et al. Thin Solid Films *<u>515</u>* *(2006) 2353–2360*

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Thin films composition

Mo_6S_8 - $Cu_4Mo_6S_8$: solid solution

$Cu_2Mo_6S_8$, $Cu_3Mo_6S_8$:

→ superconducting material

→ insertion material ; potential interest as electrode for battery

PLD → films composition close to the target one

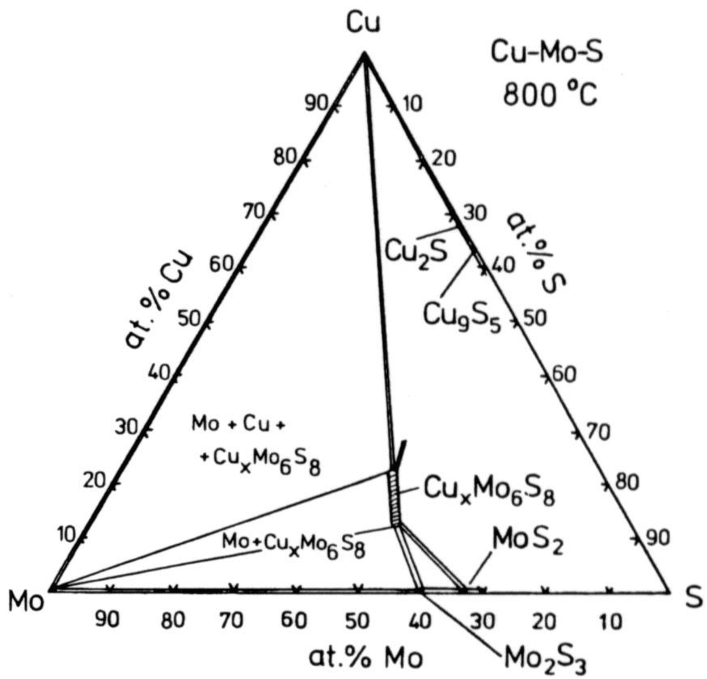
$Cu_4Mo_6S_8$:

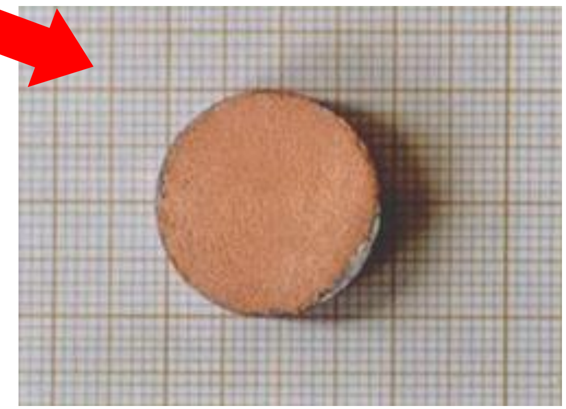
→ semiconductor ; potential interest for thermoelectricity

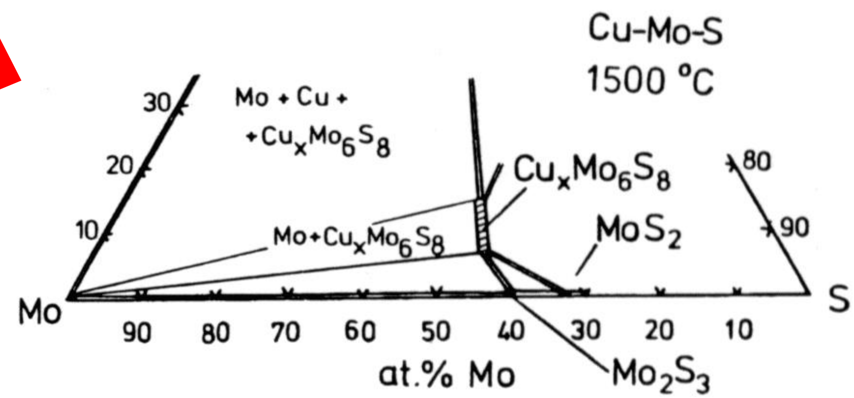
PLD → Cu and Cu_2S secondary phases (**very high excess of Cu**)

WHY ? → metastability of this composition

Expulsion of Cu : in relation with the metastability of $Cu_4Mo_6S_8$







(phase diagrams : R. Flükiger et al.)

PLD of high interest for the control of complex materials

- **High entropy oxide: an example**

Potential application in batteries (electrochemical reaction interfaces) and catalysis

"Growth of nanoporous high-entropy oxide thin films by pulsed laser deposition"

H. Guo, X. Wang, A.D. Dupuy, J.M. Schoenung, W. J. Bowman, J. of Mat. Res., 2022, 37 (1), 124

Ceramic target: $(Co_{0.2}Ni_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2})O$

- PLD using Nd:YAG, with 266 nm, 10 ns

✓ PLD → 3D island morphology → nanoporous thin films

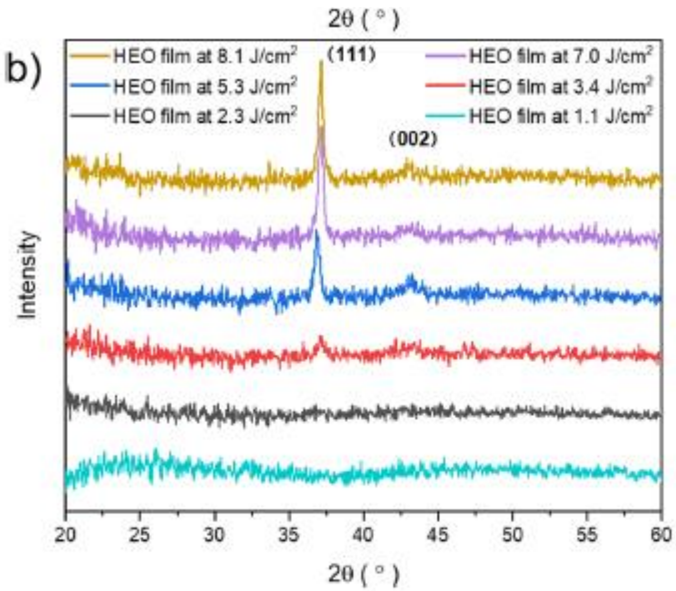
✓ Same structure as the target and homogeneous composition

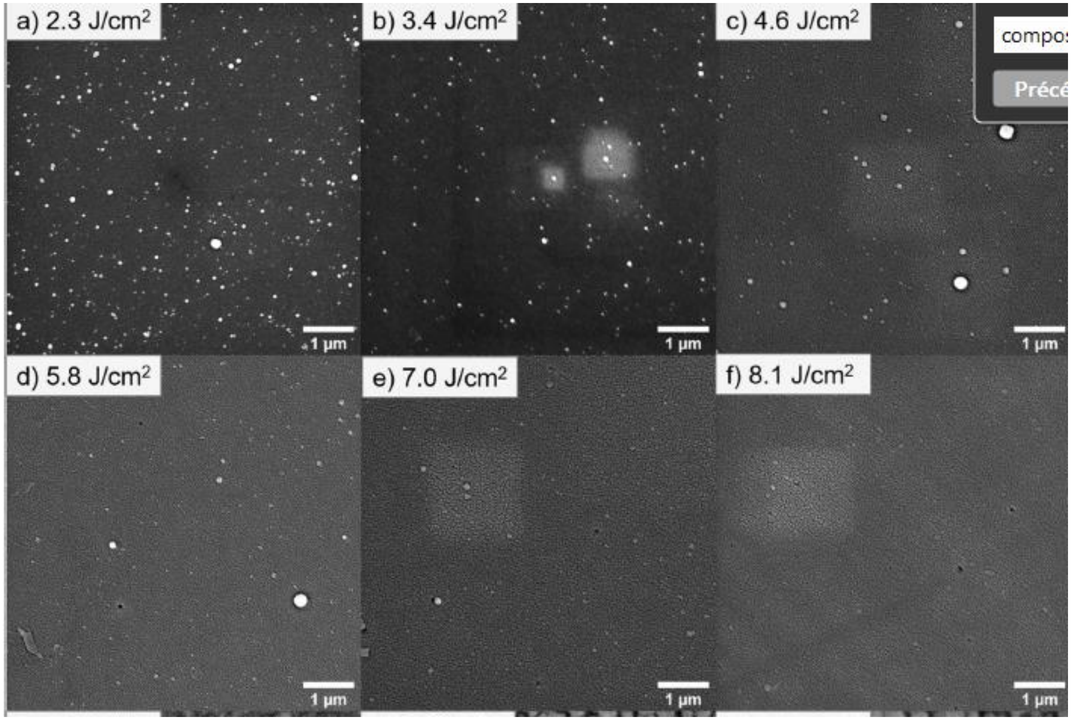
✓ Study of the effect of the fluence:

Increasing the fluence:

High entropy oxide

- Facilitates the crystallization
- Increases the thickness (60-140 nm)
- Influences the nanopores morphology and size
- Decreases the number of **droplets**





$T_d = 300°C$

From "Growth of nanoporous high-entropy oxide thin films by pulsed laser deposition" , H. Guo, X. Wang, A.D. Dupuy, J.M. Schoenung, W. J. Bowman, J. of Mat. Res., 2022, 37 (1), 124

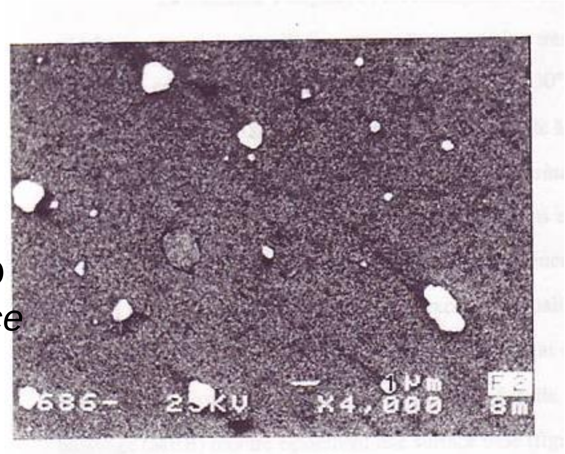
Droplets formation

At the edge of the vaporization area, the high temperature is not so high as in the center of this area but T is generally enough for melting ➔ *creation of a melted bath*

At the violent plasma expansion, with the effect of the backward pressure: expulsion of droplets from the target that can arrive on the growing film

Droplets diameter: ~ 1- 5 μm

Example: $YBa_2Cu_3O_7$ film on MgO
Formation of droplets on the surface



➔ High fluence, short wavelength, highly densified / sintered target contribute to reduce the number of droplets

→ Some illustrations of PLD in the context of nanomaterials for energy applications

PLD combinatorial approach
Dr J. Wolfman

GREMAN

- Shadow mask between the substrate and the target → deposition in selected area on the substrate
- Targets selection, control of laser shots with one or two laser (dual PLD) to modulate the composition on the surface of the substrate

https://greman.univ-tours.fr/english-version/research-topics/oxydes/combinatorial-and-dual-pld-thin-films-synthesis

PLD combinatorial approach
Dr J. Wolfman
illustration

- *Electrical property modulation of Au/$Ba_{0.6}Sr_{0.4}TiO_3$/$La_{0.7}Sr_{0.3}MnO_3$ structure by continuous composition spread Mn doping*
  J. Qiu, G. Liu, J. Wolfman, J. Xing, Ceramics International 48 (2022) 11786–11792
- Targets used for the BSTMx films in the Comb-PLD: BST and $Ba_{0.6\rightarrow}Sr_{0.4}Ti_{0.95}Mn_{0.05}O_3$ (BSTM) ceramics.

→ PEPR DIADEM

Plate-forme µELEC

Ceramics International 48 (2022) 11786–11792

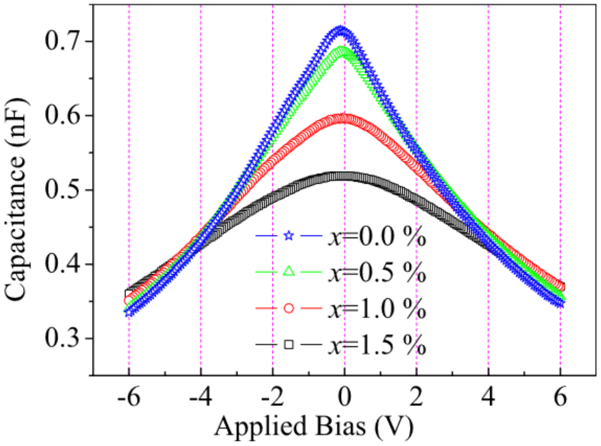


Fig. 3. The capacitance-bias curves of the Au/BSTMx/LSMO structure.

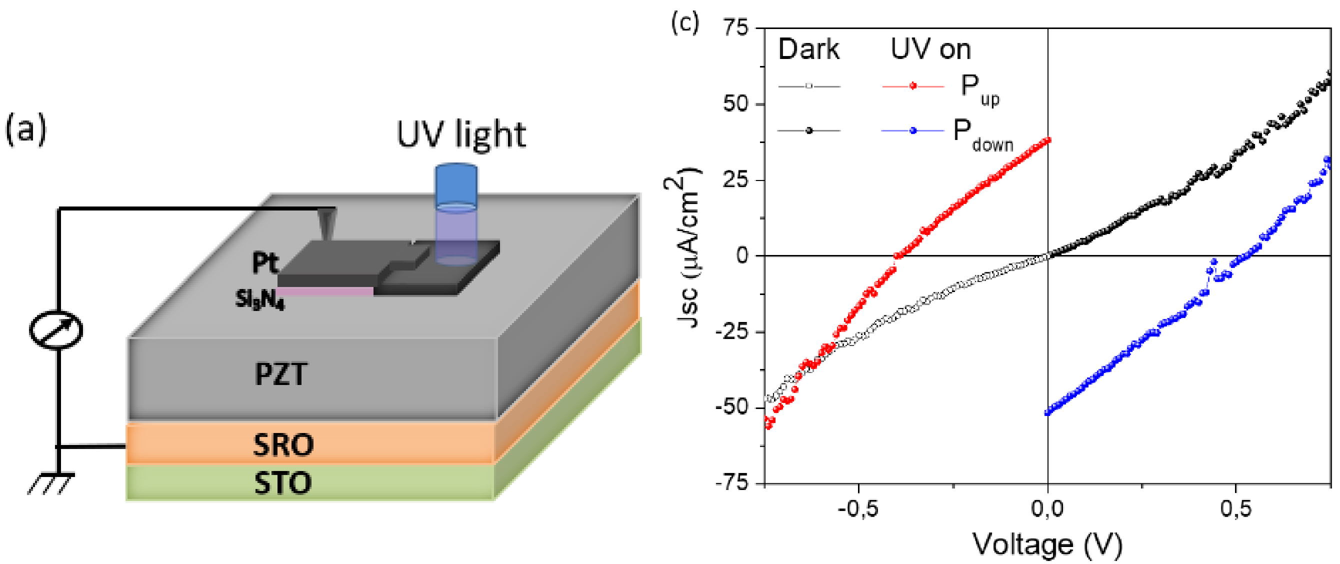
nanomaterials for energy applications

Quantitative investigation of polarization-dependent photocurrent in ferroelectric thin films

K. Rani, S. Matzen, S. Gable, T. Maroutian, G. Agnus, P. Lecoeur

Condensed Matter, 2021, 34 (10), pp.104003.

- Study of the switchability of the photocurrent according to the direction of the ferroelectric polarization



Epitaxial PZT (100 nm) thin films on 30 nm $SrRuO_3$

PLD: KrF excimer laser, 3J/cm² $P(O_2)$ = 120 mTorr, T_d = 630°C

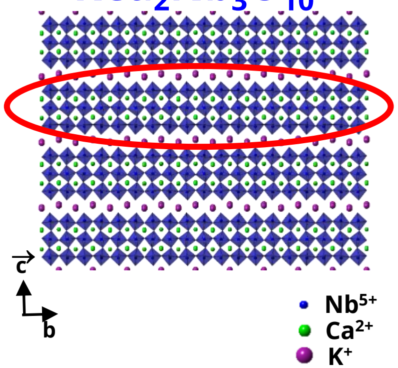
Integration of oxide functional thin films in devices requirements

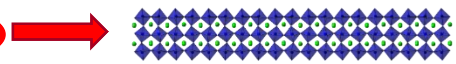
- High performance:
  - Cristalline quality
  - Properties suitable for the targeted application
  - Substrate: low cost, suitable for the growht of high quality thin films
- Possible limitations for oxides thin films:
  - Requirement of single crystal oxides substrate:
    - Cost
    - Limitation of large size availability
    - Thermal budget for the growth

Highly Transparent and Conductive Indium-Free Vanadates Crystallized at Reduced Temperature on Glass Using a 2D Transparent Nanosheet Seed Layer

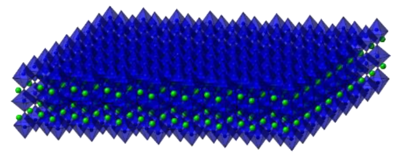
A. Boileau et al., Adv. Funct. Mater. **2021**, 2108047

Layered Oxide
$KCa_2Nb_3O_{10}$

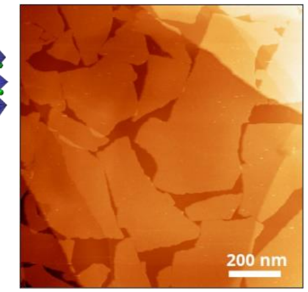




Exfoliation
in solution



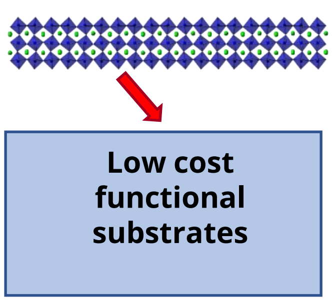
2D Oxides on Si

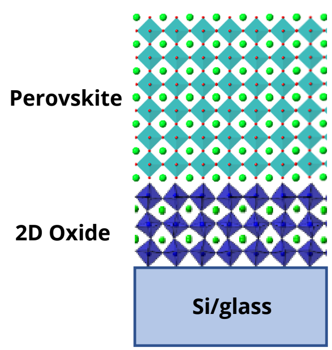


ISCR (Rennes)
Dr V. Demange, CNRS

→ PEPR DIADEM
Plate-forme µELEC

→oxides nanosheets as germination layer for thin films integration on various substrates (Si, glass, silica, flexible, ...)



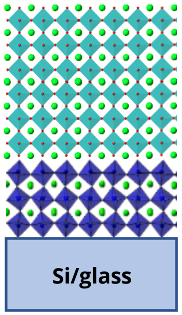


anr® **PolyNash (CRISMAT, ISCR, GEMAC)**

Université de Rennes

Highly Transparent and Conductive Indium-Free Vanadates Crystallized at Reduced Temperature on Glass Using a 2D Transparent Nanosheet Seed Layer

A. Boileau et al., Adv. Funct. Mater. **2021**, 2108047



ISCR (Rennes)

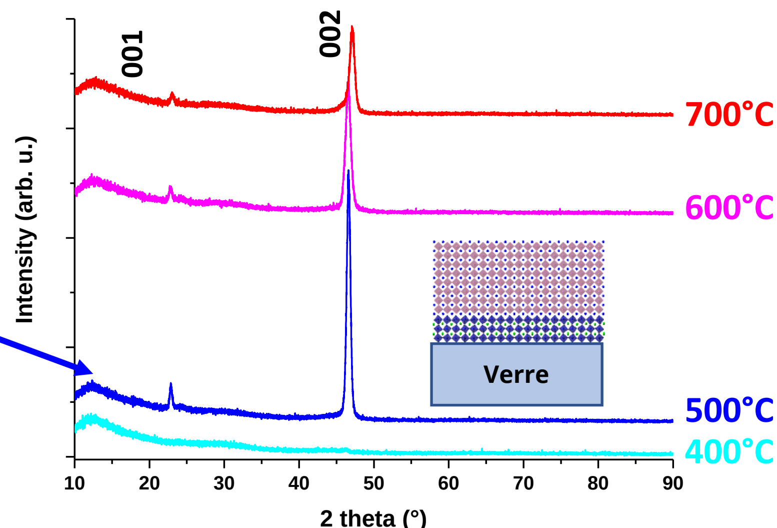
CRISMAT (Caen)

GEMAC (Versailles)

Deposition by PLD of $CaVO_3$ or $SrVO_3$ layer (40 nm) by pulsed laser deposition (PLD) between 400 and 700 °C

$SrVO_3$/glass : Amorphous and insulating

$SrVO_3$/oxide nanosheets (2-3 nm) /glass : cristallised, transparent and conducting

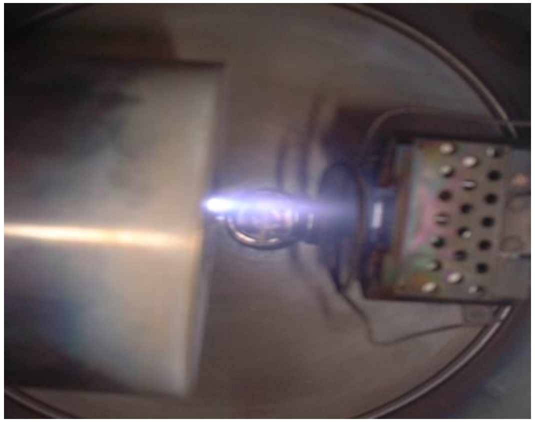


Among the best TCO
@T_{Growth} = 500°C
ρ = 3.81 x 10^{-4} Ω cm
T > 70 %

PolyNash (CRISMAT, ISCR, GEMAC)

Plasma expansion

→ brutal plasma expansion
→ brutal matter ejection towards areas with a lower local pressure
→ pressure gradient = motive force
→ the particles jet is then directional
→ more directional than in classical evaporation methods



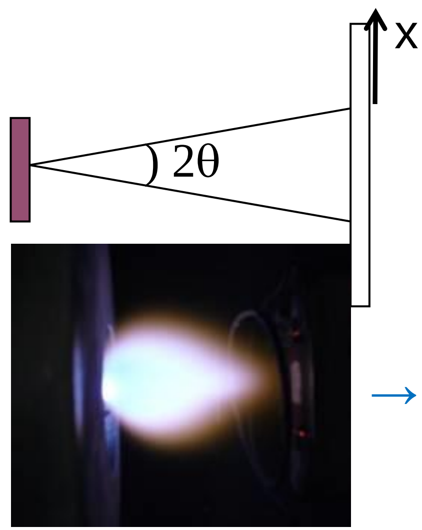
plasma expansion

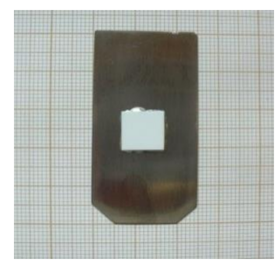
- Acceleration along the normal at the target >> to the one in the plane
  → *directional plasma*

Typical dimensions of the plasma formation at the laser beam – target impact:

- *// target (target plane): same dimensions as the laser spot (i.e: 1-2 mm^2)*
- *along target thickness: ~ 1-10 μm*

- *Thickness distribution :* $A\cos^4\theta + B\cos^n\theta$
- *High value for n: n ~ 7-20 : large thickness distribution along x*

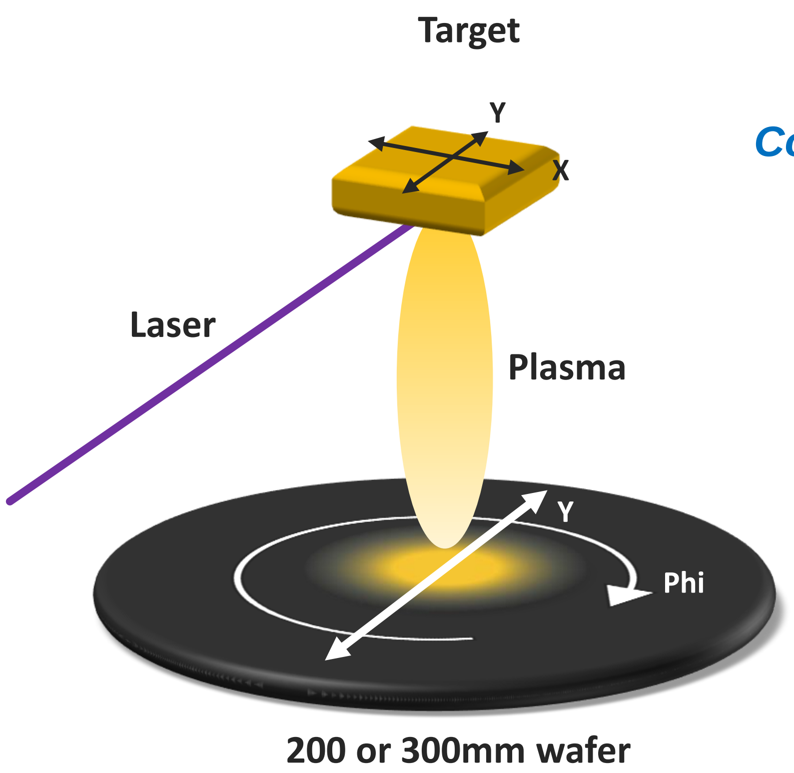




→ Large size area of deposition ?

Towards large area PLD thin films

Uniformity control on wafer area



Courtesy of Florian Dupont, CEA LETI

Deposition scan:

→ **Excellent thickness and stress uniformity** of deposited thin film

Towards large area PLD thin films

- SOLMATES 200 mm wafer PLD equipment at CEA LETI

deposition of KNN on 200 mm wafer by PLD at CEA LETI

Collaboration ISCR – CEA LETI (Dr G. Le Rhun) : PhD Hugo KUENTZ (2020-2023)

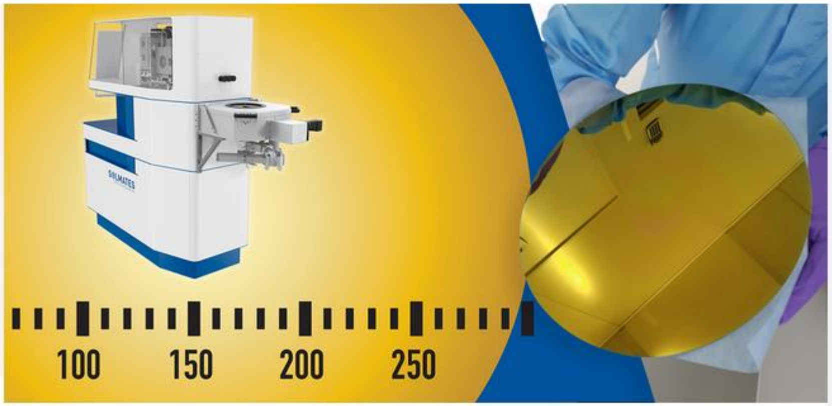
Lead free piezoelectric transducers and reliability

ANR TILPAC (2023-2026) (Coord. Dr G. Le Rhun)

Towards an Industry compatible high performances Lead free Piezoelectric thin film material for MEMS ACtuator applications

→ 300 mm wafer

https://www.solmates-pld.com/about-us/history-of-solmates/



Upscaling wafer size from 200 to 300 mm

We proudly showed our first ever 300 mm wafer coated by Solmates-PLD thin film equipment to the public. A small engineering step for Solmates, but a giant leap forward for thin-film manufacturing. Utilizing the intrinsic local nature of Pulsed Laser Deposition and innovative Solmates 'bridge tool' design, the scale-up from 200 to 300 mm was simply a matter of increasing the wafer scanning area, without the need for a larger target. This milestone was achieved at CEA-Leti and marks a bright future for PLD materials in automated 300 mm wafer device manufacturing.

SOLMATES
THIN FILM EQUIPMENT
A Lam Research Company

cea leti

300mm deposition by PLD

PLD, from sample-scale to 300mm-compatible process

Concluding remarks

- PLD of high interest for deposition of multielement materials
- PLD suitable for nanomaterials elaboration for energy applications
- Evolution towards large size area wafer

→ ***A specificity: kinetic energy during deposition***

Thin films growth – Crystallization

↕

deposition method

Crucial parameter

energy of particles on the surface of the substrate

Precursor → Transfer → substrate and surface

Deposition process
$\rightarrow E_k$

(emitted particles)

Deposition pressure (atmosphere)
$\rightarrow \Delta E_k$

Substrate temperature :
ΔE_k, diffusion ...

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Specific features of PLD compared to other techniques

Technique	Energy (Ek)	Evaporation (MBE…)	Sputtering	PLD
Deposition process	Energy of emitted particles	~ 0.1 eV	~ 10-100 eV	1-100 eV
Deposition pressure	Function of atmosphere nature → Δ Ek	ultra-high-vacuum 10^{-10} - 10^{-7} Torr	10^{-3} - 10^{-1} Torr E_k can decrease	***wide range*** UHV to 10^{-1} Torr E_k can be maintained or can decrease

Institut des Sciences Chimiques de Rennes UMR CNRS 6226

Concluding remarks

- PLD of high interest for deposition of multielement materials
- PLD suitable for nanomaterials elaboration for energy applications
- Evolution towards large size area wafer

→ ***A specificity: kinetic energy during deposition***

- The chemistry and the cristalline structure of the material are always of first importance
- Not presented in this course: « MBE PLD » *cf Romain Bachelet presentation on MBE*

Acknowledgements

- ISCR : V. Demange, S. Deputier, V. Bouquet, S. Ollivier, C. Derouet, V. Le Cam, JL. Cercus
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- F. Gouttefangeas, L. Joanny, Rennes University, SEM /EDS
  V. Dorcet, L. Rault, Rennes University MET
- In CEA LETI G. Le Rhun, F. Dupont, C. Poulain, H. Kuentz (thesis in progress)

supp

Thank you for your attention !