

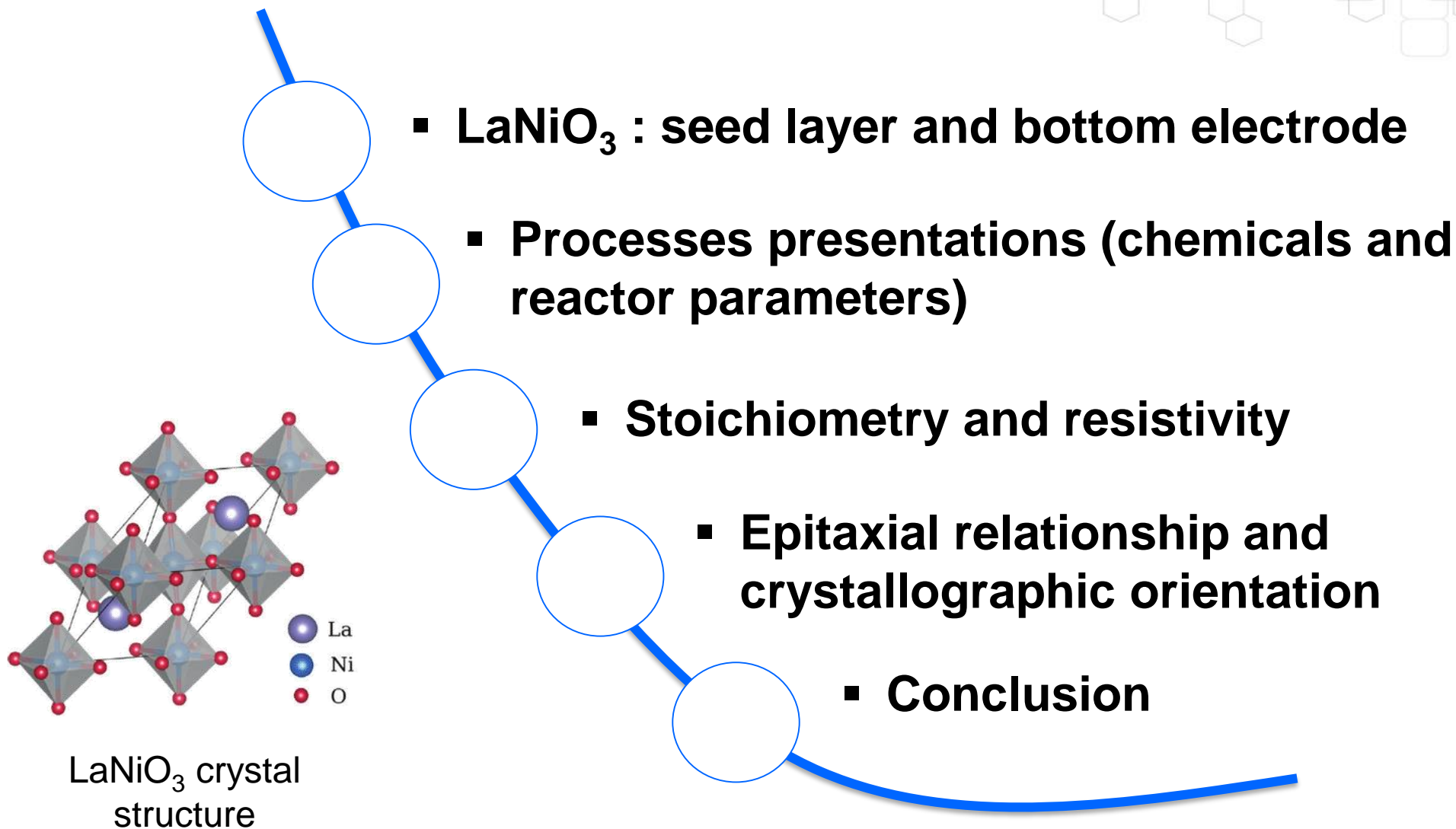
Relationship Processing-Composition- Structure-Resistivity of LaNiO_3 Thin Films Grown by Chemical Vapor Deposition Methods

Sabina Kuprenaite^{1,2}, Vincent Astié^{1,3}, Samuel Margueron¹, Cyril Millon¹, Jean-Manuel Decams³, Zita Saltyte², Valentina Plausinaitiene², Adulfas Abrutis², and Ausrine Bartasyte^{1,*}

¹ FEMTO-ST Institute, University of Bourgogne Franche-Comté, CNRS (UMR 6174), ENSMM, 26 rue de l'Épitaphe, 25030, Besançon, France;

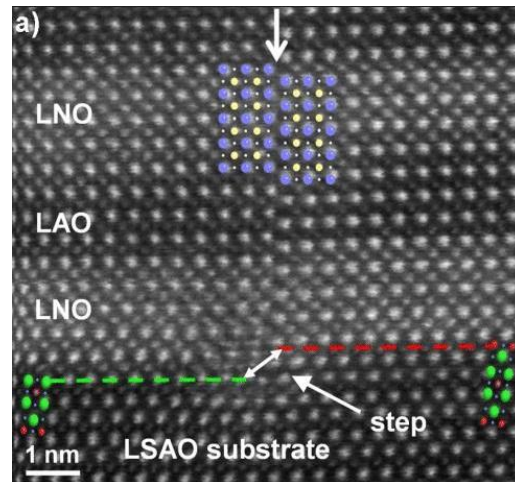
² Vilnius University, Faculty of Chemistry, Naugarduko 24, Vilnius, Lithuania; adulfas.abrutis@chf.vu.lt

³ Annealsys, 139 rue des Walkyries, Montpellier, France; jmdecams@annealsys.com



LaNiO₃ : Seed layer and bottom electrode

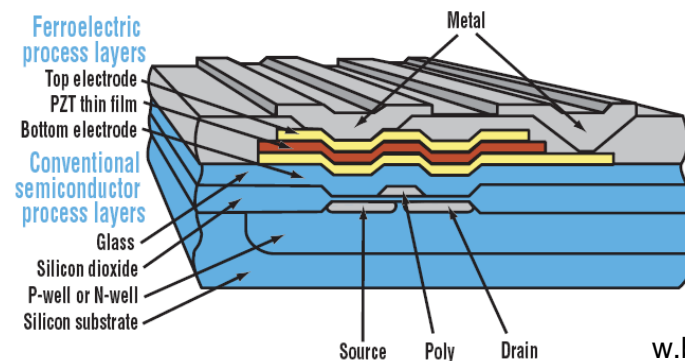
LNO-LAO superlattices (SLs)



- Intriguing phenomenon at the interface unattainable in bulk

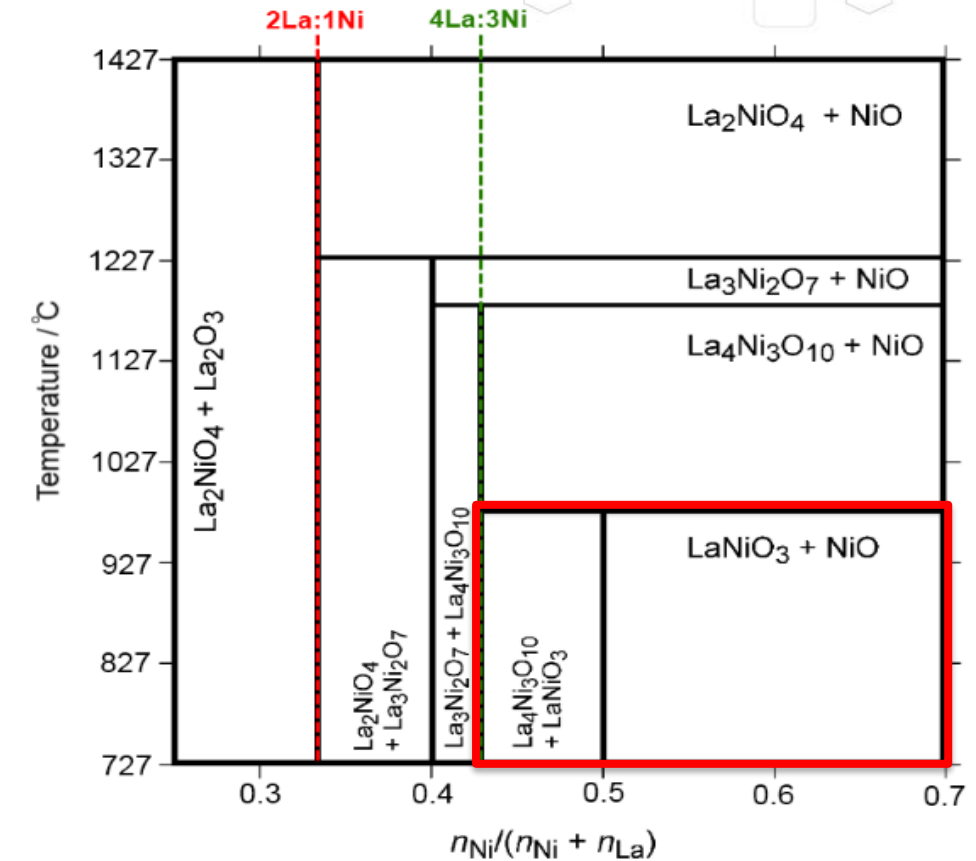
Detemple, E. et al. *Microscopy and Microanalysis* 19.S2 (2013): 1888-1889.

Pb(Zr,Ti)O₃ Ferroelectric RAM



- Perovskite conducting oxide as an electrode

w.baike.com



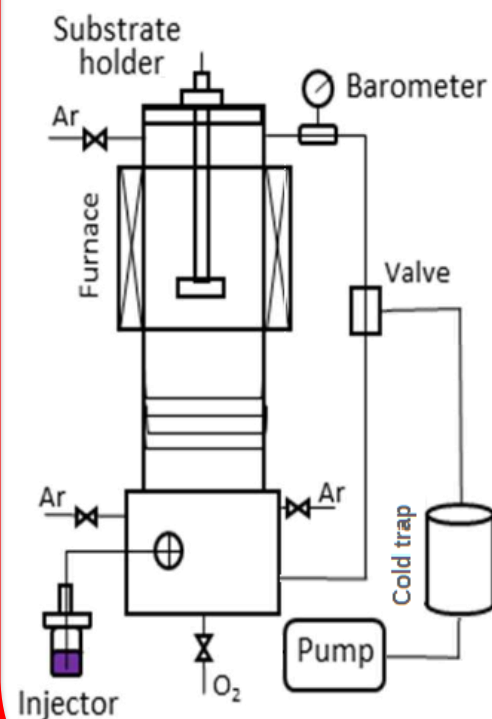
La₂O₃ – NiO phase diagram

Woolley, R. J., et al. *Journal of Power Sources* 243 (2013): 790-795.

Apparatus

➔ **Three different MOCVD methods** : PI-MOCVD, DLI-MOCVD and AP-MOCVD

Pulsed Injection-MOCVD

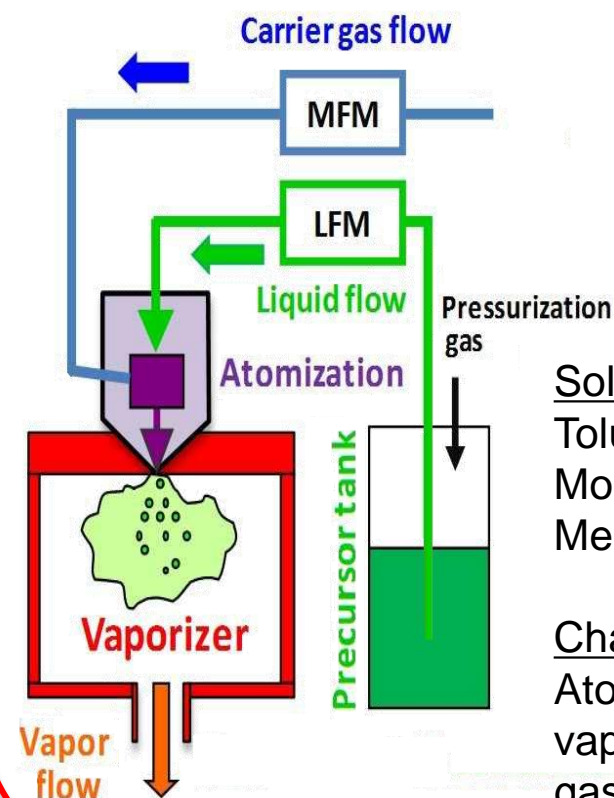


boschautoparts.com

Solvent:
1,2-dimethoxyethane
(monoglyme)

Characteristic:
Atomization and
fast vaporization of
a liquid precursor.

Direct Liquid Injection-MOCVD



kemstream.com

Solvent (+ Lewis Base):
Toluene (+ monoglyme)
Monoglyme
Mesitylene (+ TMEDA)

Characteristic:
Atomization and fast
vaporization of a mixture of
gas and liquid precursor.

Chemical Vapor Deposition study



Liquid

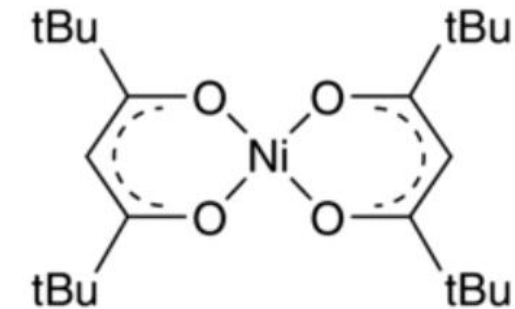
- Adding a Lewis Base (monoglyme, TMEDA etc.) helps to control the coordination sphere of the metallic center and/or its oxidation state.



Limit aggregation and oligomerization of the precursor to enhance vaporization

CVD parameters mapping

- Set precursors : β -diketonates – $\text{La}(\text{thd})_3$ and $\text{Ni}(\text{thd})_2$
- Ratio of $\text{La}(\text{thd})_3$ to $\text{Ni}(\text{thd})_2$ in solution : 1 – 2,2
- Evaporation temperature : 150 – 300 °C
- Deposition temperature : 425 – 750 °C
- Pressure : 2 – 15 Torr



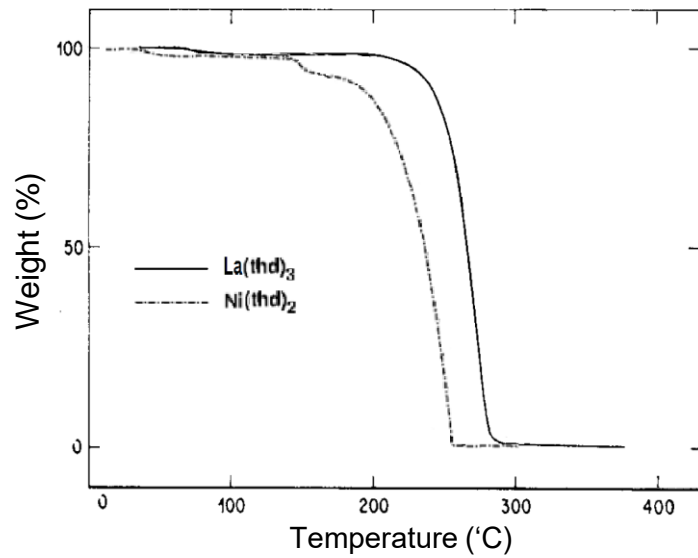
Solid is purple

Film properties

- Stoichiometry
- Resistivity
- Crystallographic orientation

Turns green in coordinating solvents. Otherwise remains purple.

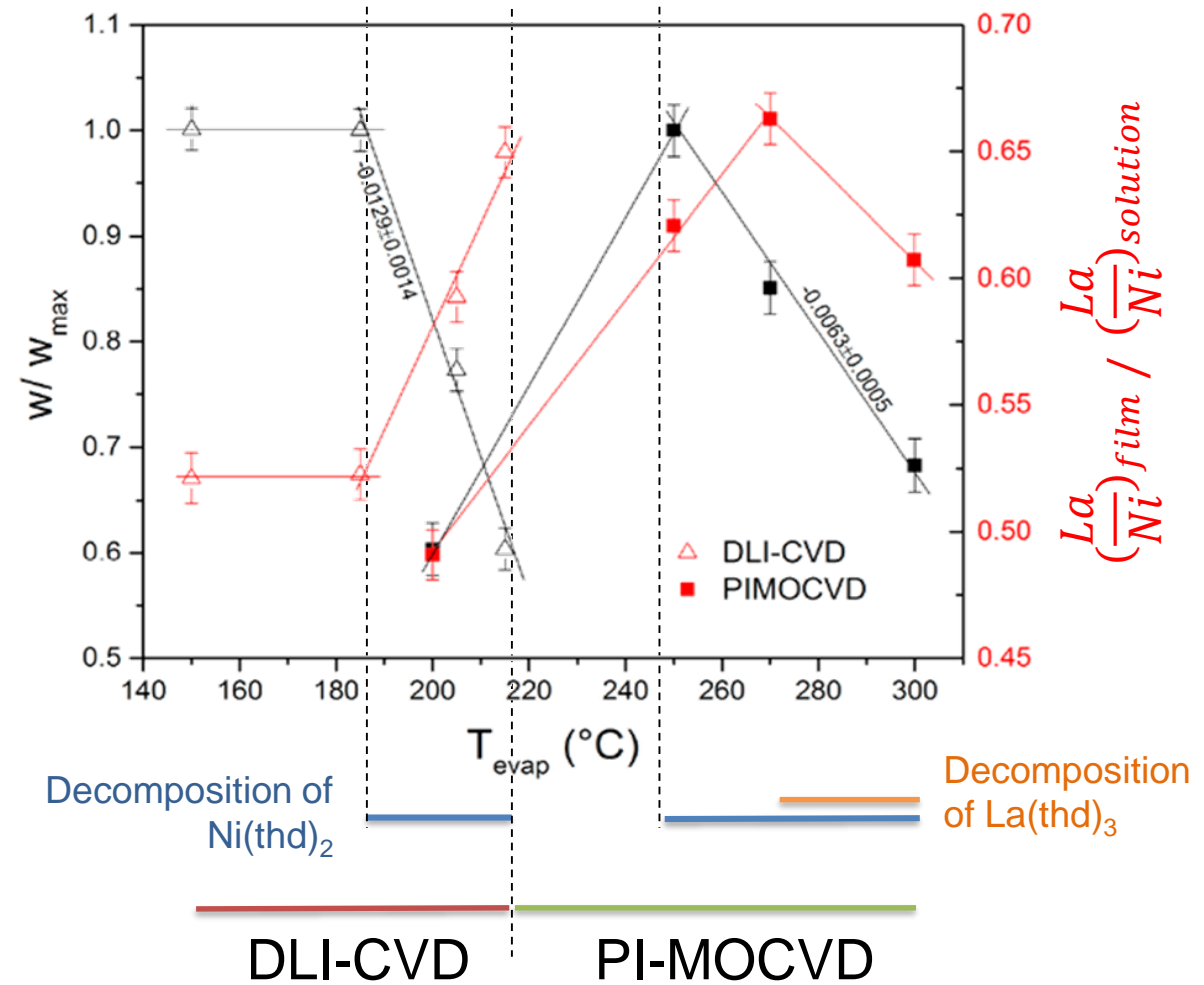
Evaporation conditions



- La(thd)₃ is less volatile than Ni(thd)₂
- Residues negligible
- Temperature can be brought down in vacuum conditions

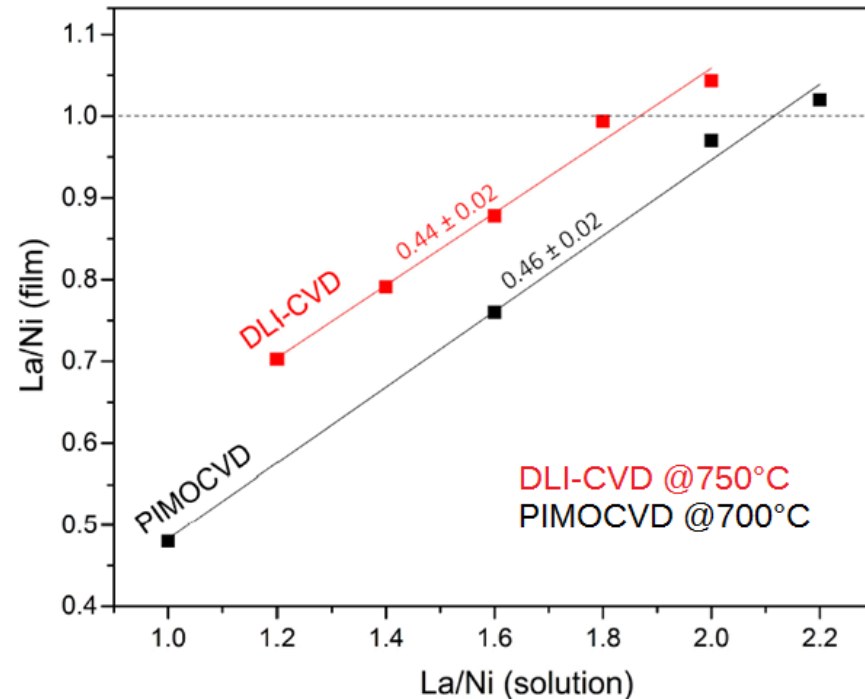
Eisentraut, K. *Journal of Inorganic and Nuclear Chemistry* 29.8 (1967): 1931-1936.
 Jones, A.C. *Chemical Vapor Deposition*, 1998.
 4(5): p. 169-179.

Normalized growth rate and molar ratio between La/Ni in the film and in the solution as a function of evaporation temperature



Solution and film stoichiometry

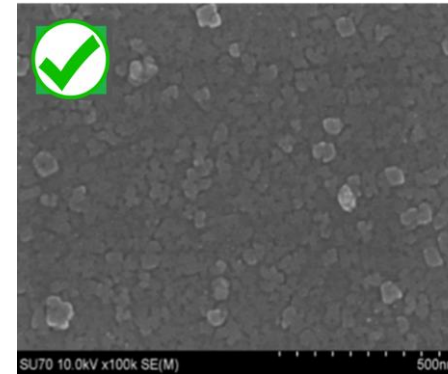
Relationship between La/Ni molar ratios in the LNO film and in the solution of precursors at deposition temperatures of 750 °C and 700 °C in DLI-CVD and PIMOCVD, respectively;



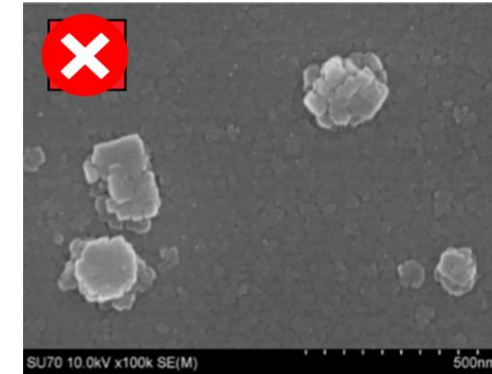
Both vacuum methods show a similar slope !

$$\left(\frac{La}{Ni}\right)_{film} \approx 0,45 * \left(\frac{La}{Ni}\right)_{injection}$$

- Hillocks formation on the surface when above 50% La_2O_3



Nearly stoichiometric



La_2O_3 -rich

- La_2O_3 is unstable in air and thus AP-MOCVD showed lanthanum hydroxide or carbonate

Crystallographic orientation

Note: LNO, Rhombohedral, $R\text{-}3c$ ($a = 5,454 \text{ \AA}$ and $c = 13,106 \text{ \AA}$)

Substrates considered :

- **Strontium Titanate SrTiO_3** : Cubic, $Pm\text{-}3m$ ($a = 3,905 \text{ \AA}$)
- **Lanthanum Aluminate LaAlO_3** : Rhombohedral, $R\text{-}3c$ ($a = 5,365 \text{ \AA}$ and $c = 13,112 \text{ \AA}$)
- **Corundum Al_2O_3** : Rhombohedral, $R\text{-}3c$ ($a = 4,758 \text{ \AA}$ and $c = 12,993 \text{ \AA}$)

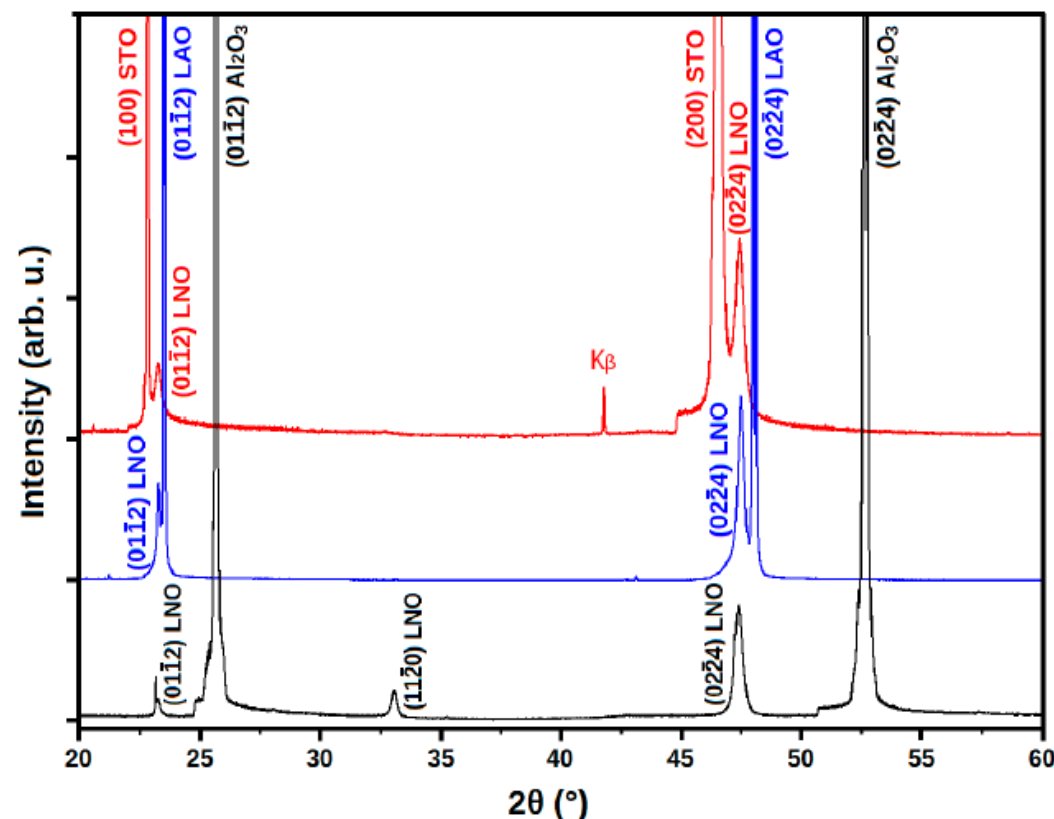
Lattice mismatch

$(01\bar{1}2)_{\text{LNO}} \parallel (100)_{\text{STO}}$
mismatch : <3%

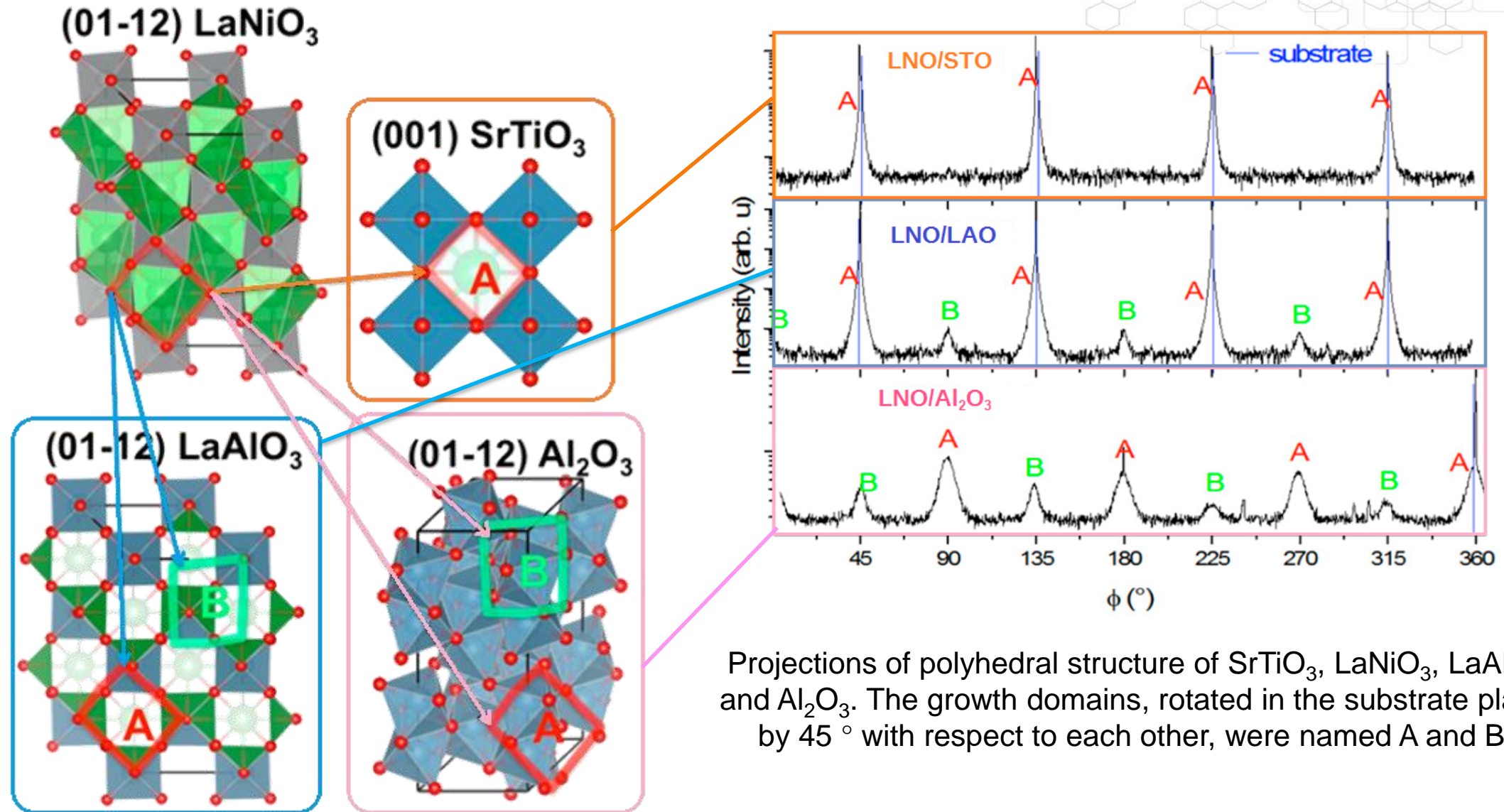
$(01\bar{1}2)_{\text{LNO}} \parallel (01\bar{1}2)_{\text{LAO}}$
mismatch : <2%

$(01\bar{1}2)_{\text{LNO}} \parallel (01\bar{1}2)_{\text{Al}_2\text{O}_3}$
mismatch : <13%

$(11\bar{2}0)_{\text{LNO}} \parallel (01\bar{1}2)_{\text{Al}_2\text{O}_3}$
mismatch : <3%

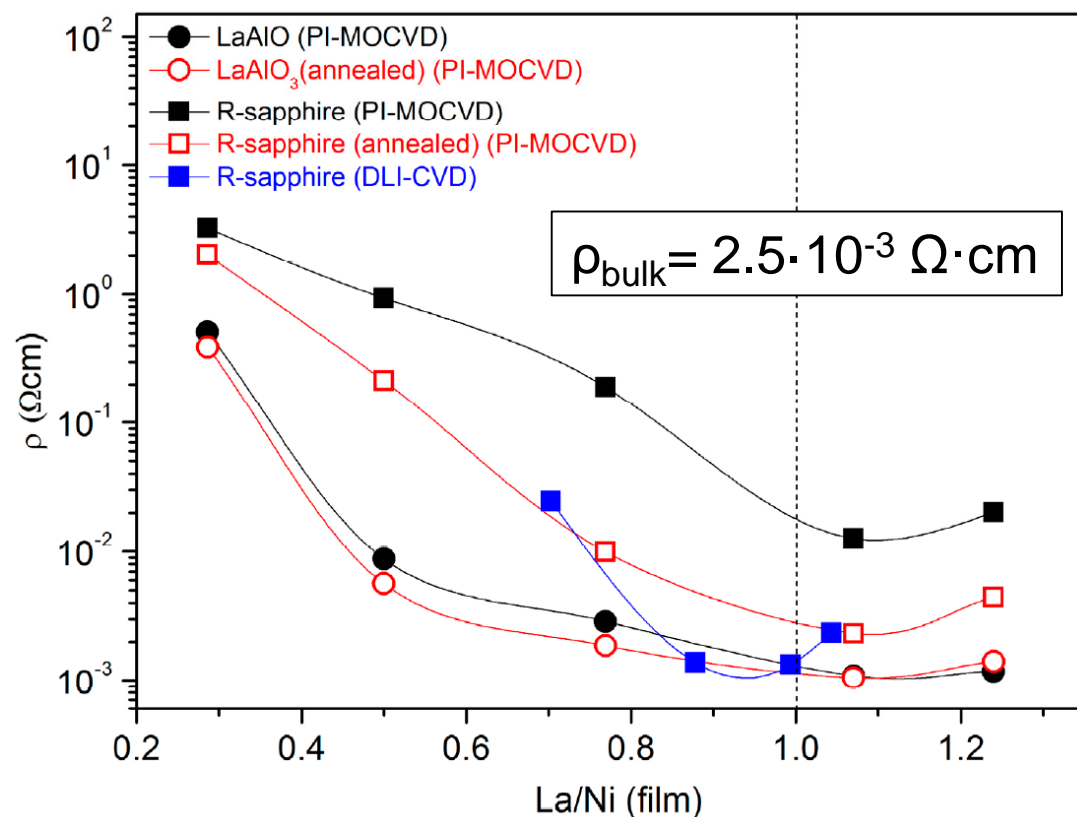


Crystallographic orientation



Resistivity

Key parameter : Stoichiometry in oxygen, structural defects and La_2O_3 -NiO ratio



Composition dependence of resistivity of as-deposited and annealed LaNiO_3 films on LaAlO_3 and R-sapphire substrates.

- **Annealing at 750 · C in air** significantly reduced resistivity in $\text{LNO}/\text{Al}_2\text{O}_3$ structures (down to $2.3 \cdot 10^{-3} \Omega \cdot \text{cm}$)
 - Recrystallization
- $1.26 \cdot 10^{-3} \Omega \cdot \text{cm}$ by direct growth on Al_2O_3 **at 750 · C !**
- La_2O_3 -NiO stoichiometry also impacts resistivity

$$\begin{aligned}\rho_{(\text{LNO}/\text{Al}_2\text{O}_3)} &= 1.26 \cdot 10^{-3} \Omega \cdot \text{cm} \\ \rho_{(\text{LNO}/\text{LAO})} &= 1.05 \cdot 10^{-3} \Omega \cdot \text{cm}\end{aligned}$$

Conclusion



- Fine control of the deposition parameters allows fine tuning of the LaNiO_3 layer properties
- LaNiO_3 was epitaxially grown by MOCVD on SrTiO_3 , LaAlO_3 and Al_2O_3 at 650-750°C, and X-Ray diffraction showed that 2 families of growth domains coexisted in the two later substrates
- Nearly stoichiometric composition and annealing in air drastically reduces resistivity in LNO layers though reduction of micro defects
- Resistivity as low as $1.05 \cdot 10^{-3} \Omega \cdot \text{cm}$ were obtained on high quality epitaxial LNO/LAO structures and $1.26 \cdot 10^{-3} \Omega \cdot \text{cm}$ on LNO/ Al_2O_3 (bulk $\sim 2.5 \cdot 10^{-3} \Omega \cdot \text{cm}$) without any post-annealing

Acknowledgments

FEMTO-ST Institute:

G. Clementi, S. Oliveri, S. Kuprenaite,
A. Almirall, V. Astié, A. Borzi, A.
Cavallaro

Colleagues:

C. Millon

University of Lorraine:

S. Margueron, P. Boulet

University of Vilnius:

Z. Saltyte, V. Plausinaitiene, A. Abrutis

Annealsys:

J.M. Decams, F. Laporte

Kemstream:

H. Guillon



Thank you for your attention



Any questions ?

