Structural, Chemical and Electronic State on $(La,Sr)MnO_3$ (LSM) Dense Thin-film Surfaces

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Key results

- Thickness, synthesis temperature, and substrate of cathode films influence surface topography, composition and electron transfer.
  - For textured LSM on YSZ:

    $T_{deposition}$ ↓ Thickness ↑,
    → A/B ↓ and σ_{tunnel} ↑

- Surface structure on epitaxial LSM:

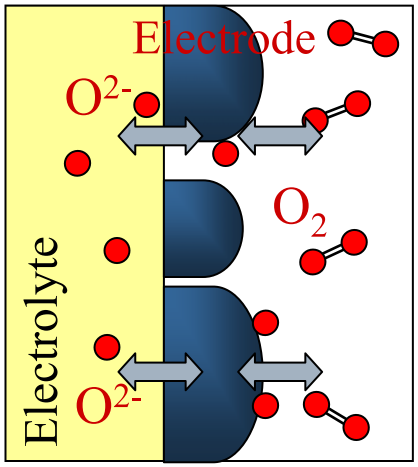
  AO-terminated perovskite surface, Sr-increase on A-site.

- LSM surfaces evolve in electronic and chemical state such that:

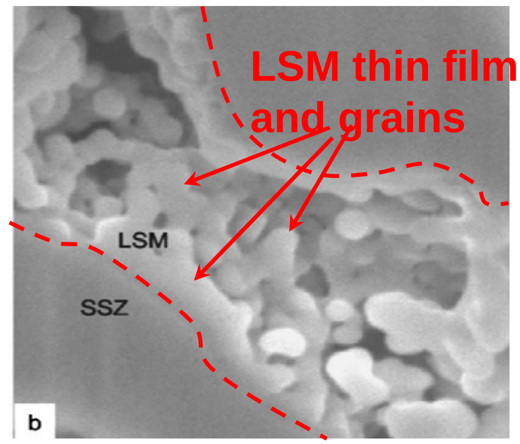
  T ↑: Insulator → Metallic
  PO_2 ↑: σ_{tunnel} ↑
  PO_2 ↑: Sr ↓

Motivation: Transport and reactivity at interfaces of SOFC cathodes

Chemical reactivity ←→ electronic structure of reactants.



Oxygen reduction
Surface structure



T. Sholklapper et al. *ESSL*, 10 (2007)

Inhomogeneities can favor/disfavor fast charge transport.

$D_{gb} >> D_{bulk}$

R.A. De Souza et al., *Mater. Lett.*, 43 (2000)

M. Petitjean et al., *J. Eur. Cer. Soc.*, 25 (2005)

Complexity of electrode microstructure → challenge in probing the structure-chemistry-transport on surfaces.

Approach

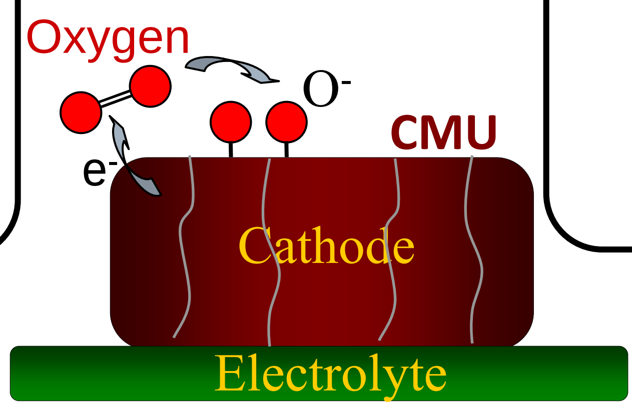
Isolate key parameters using model systems in reaching to surface structure and chemistry.

MIT

Surface electronic structure spatially resolved: Scanning Tunneling Microscopy/Spectroscopy (STM/STS)

UNLV

Surface chemical and electronic structure, laterally averaged; X-ray and Electron spectroscopies

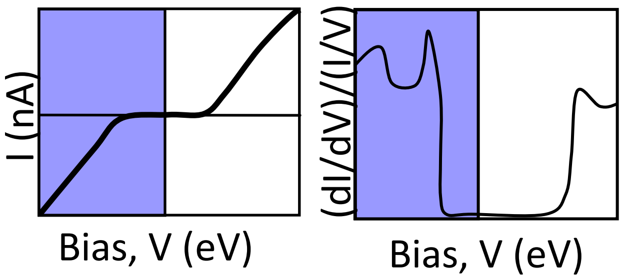


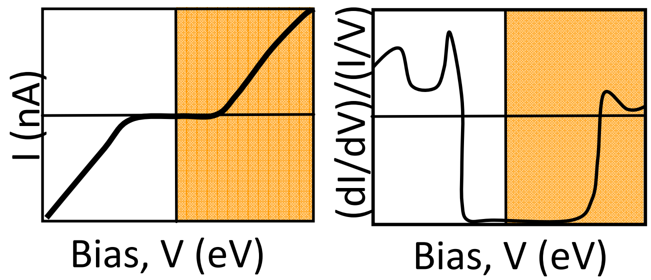
Understand the electronic and chemical behavior on SOFC cathode surfaces for electrocatalysis of oxygen

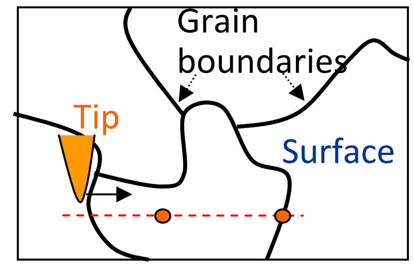
Scanning Tunneling Microscopy and Spectroscopy (STM / STS)

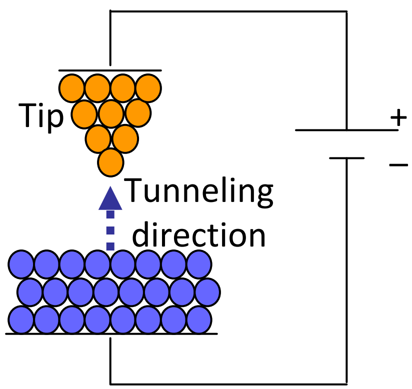
@ MIT

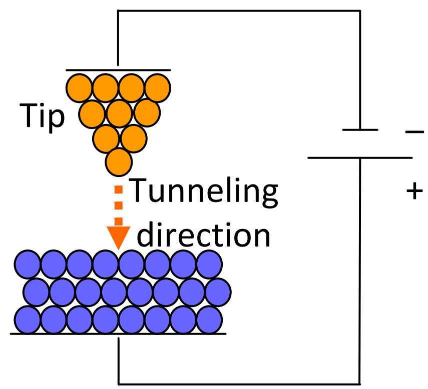
+ X-ray photo-electron spectroscopy (XPS)
+ Auger electron spectroscopy (AES)

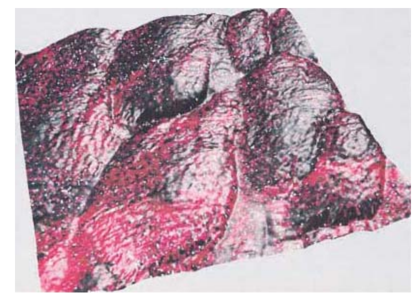










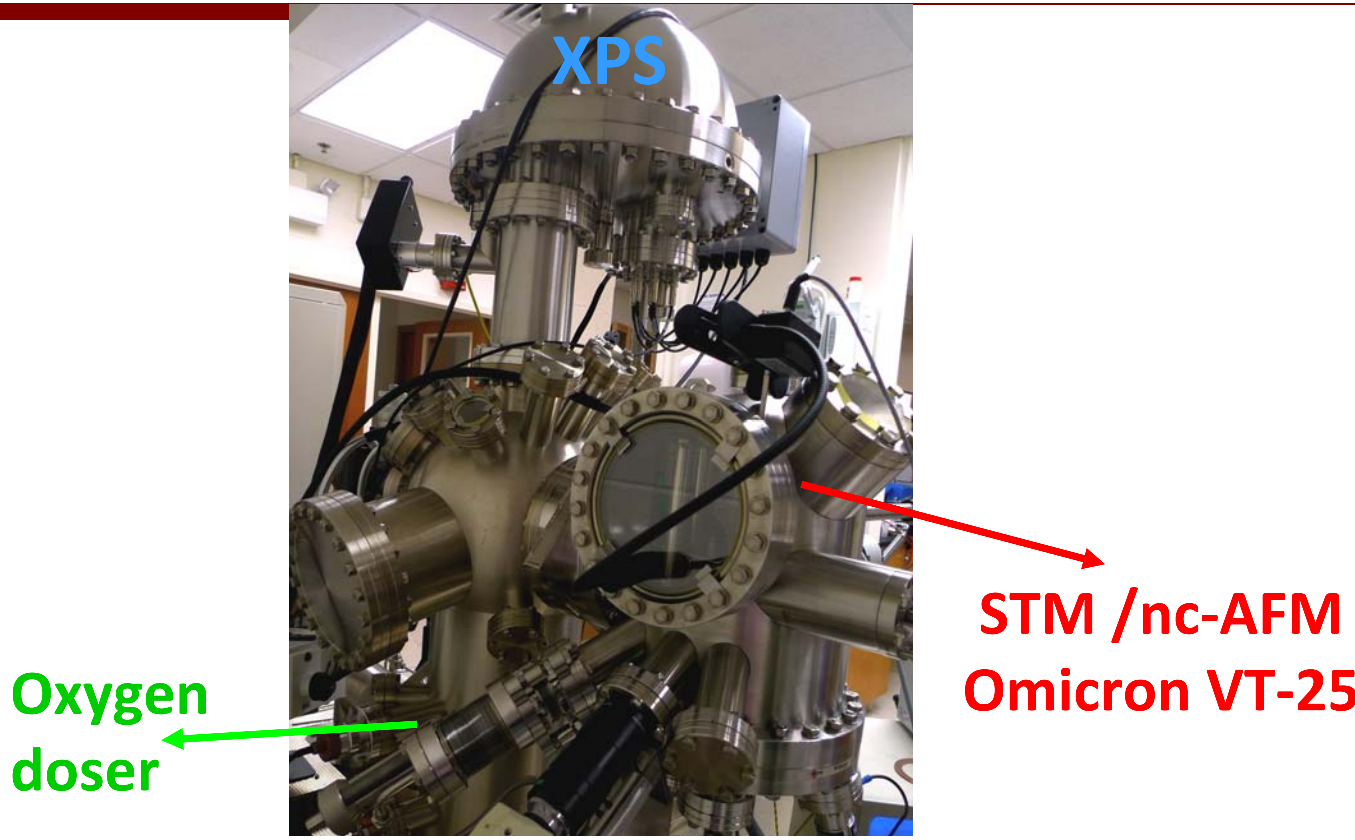


- ☐ Probing the filled (valence band) electronic states.
- ☐ Probing the empty (conduction band) electronic states.

Fermi-level tunneling conductance map on $La_{0.8}Ca_{0.2}MnO_3$.

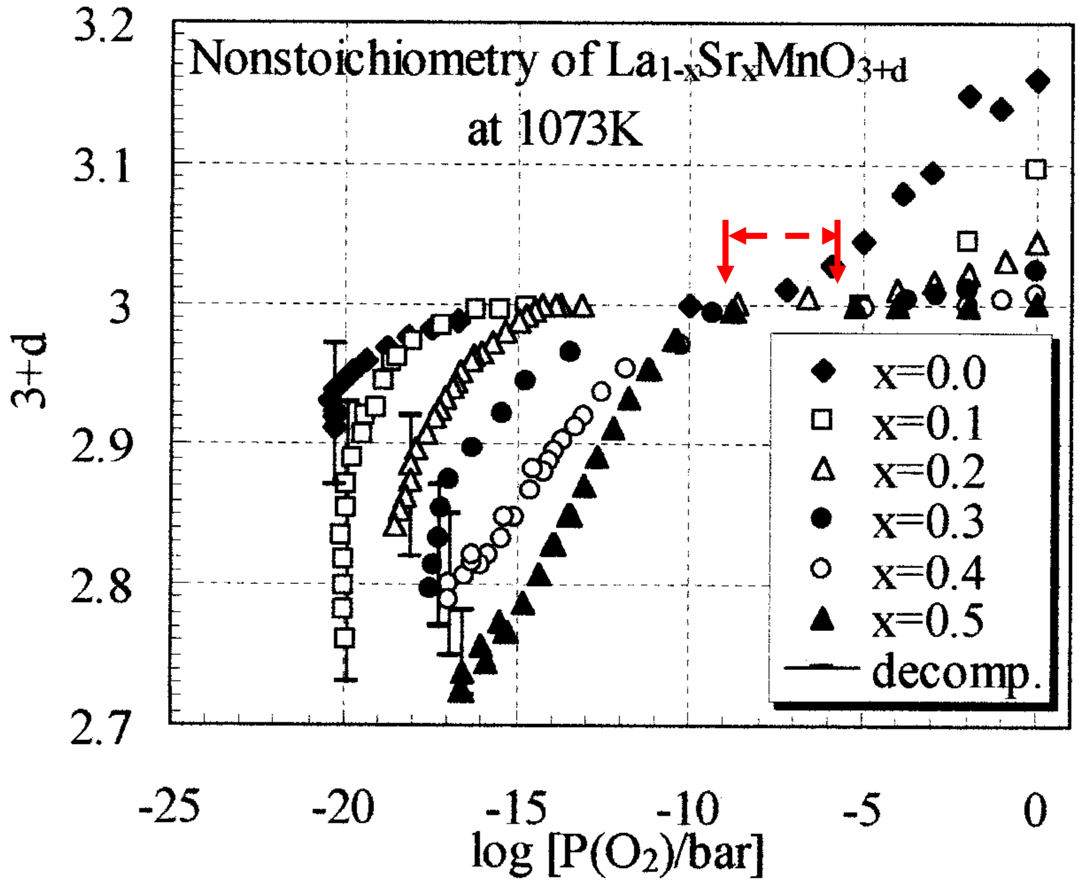
T. Becker, C. Streng, Y. Luo, et al., *Phys. Rev. Lett*. 89 (2002).

STM / STS set-up and experiment conditions



Surface cleaning conditions	T = 500 ^{o}C P_{O2} = 10^{-5} mbar t = 20-30 min
Measurement conditions	T = 23 – 580 ^{o}C $P_{O2\text{-}base}$ = 10^{-10} -10^{-6} mbar, $P_{O2\text{-}surface}$ ~ 10^{-4} - 10^{-3} mbar. (Tested up to 20 mbar, 500^{o}C.)

$La_{1-x}Sr_xMnO_{3+d}$ defect chemistry, $f(P_{O2})$



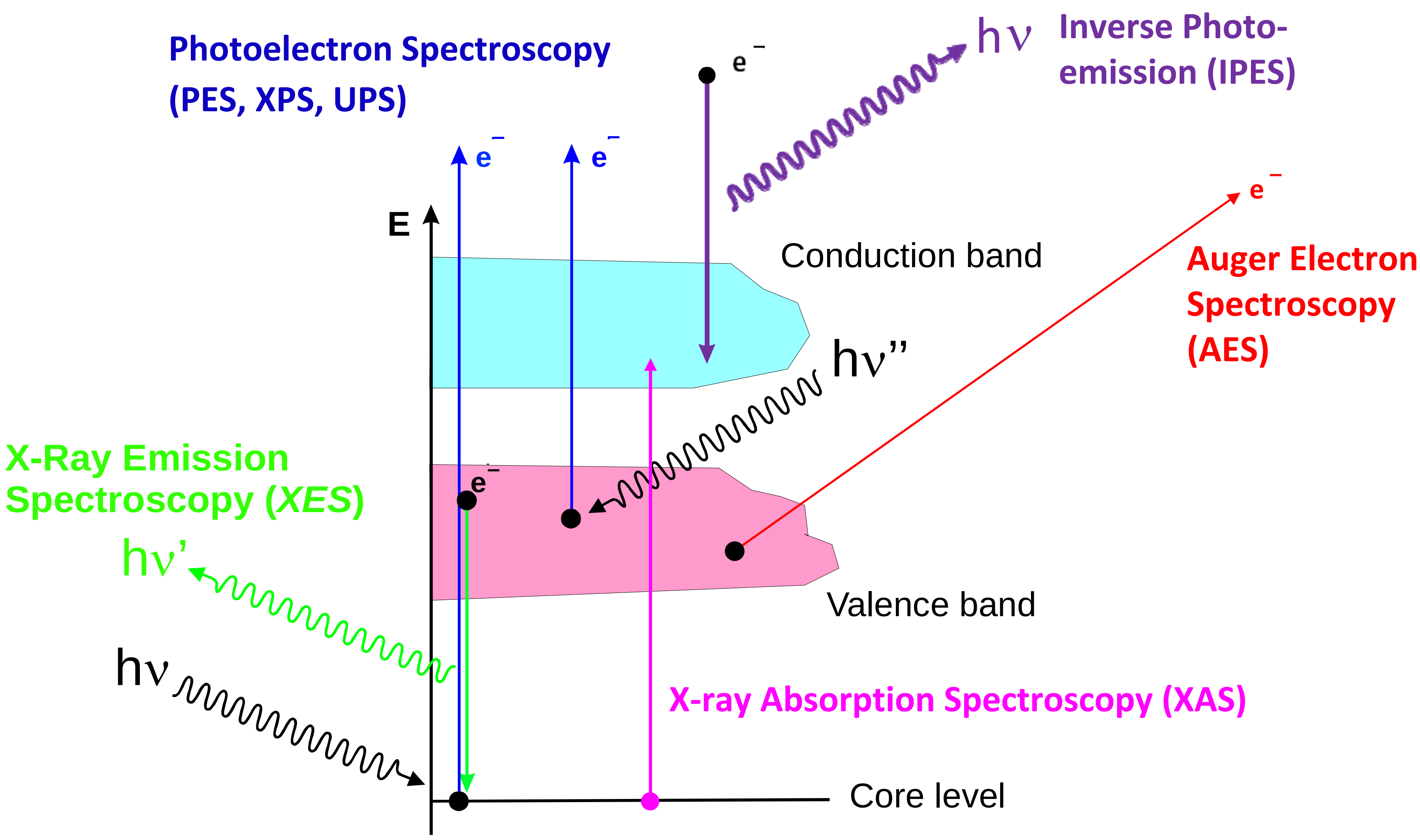
Nonstoichiometry, $La_{1-x}Sr_xMnO_{3+d}$ (x=0-0.5) as a function of P_{O2}.

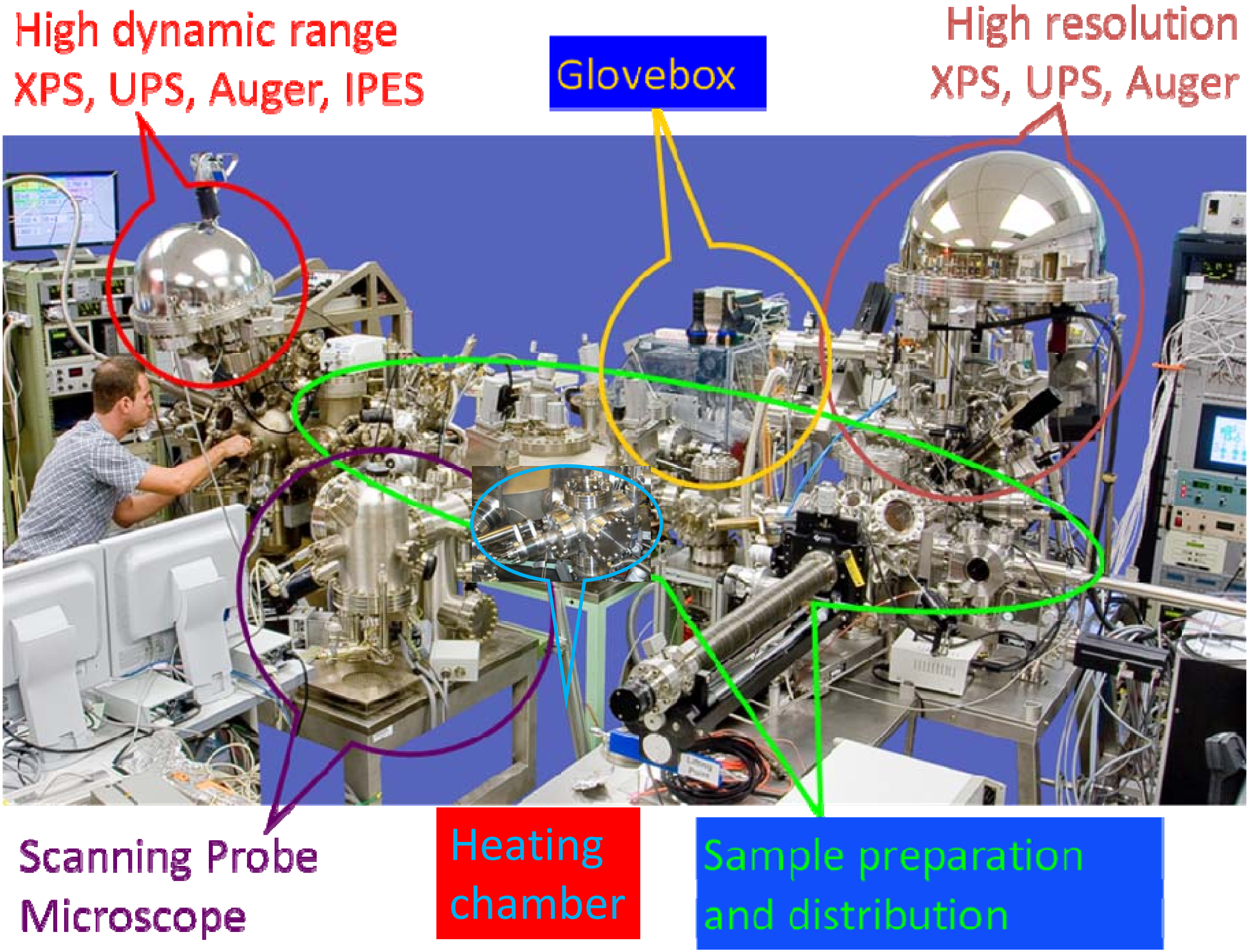
J. Misuzaki et al. *SSI*, **132**, 2000, pp.167

LSM bulk should not reduce in our experiment conditions.

UV/Soft X-ray Spectroscopies

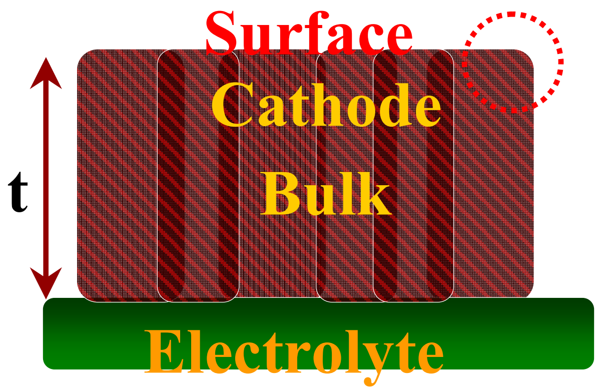
@ UNLV



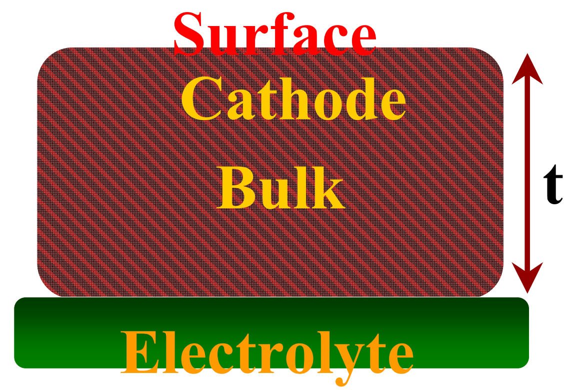

High dynamic range
XPS, UPS, Auger, IPES
Glovebox
High resolution
XPS, UPS, Auger
Scanning Probe
Microscope
Heating
chamber
Sample preparation
and distribution

Model dense thin-film cathode structures

@ CMU



A- Textured polycrystalline
Grain boundaries present
(Similar to cathode microstructure)



B- Epitaxial, single crystal
No grain boundaries

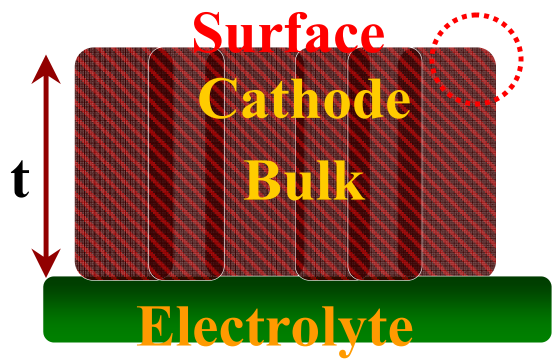
$La_{0.7}Sr_{0.3}MnO_3$ (LSM), Pulsed Laser Deposited (PLD) on:

$8\%Y_2O_3$-ZrO_2 (111) → LSM (110) film polycrystalline

$NdGaO_3$, $SrTiO_3$ (100) → LSM (100) film epitaxial

Questions to highlight

- What is the effect of thickness, synthesis temperature, and substrate of the dense thin-film cathodes on surface topography, composition and electron tunneling?
- What is the structural nature of A-site rich, Sr-rich, surfaces on LSM?
- How do the surfaces evolve in electronic and chemical state with temperature in oxygen environment?

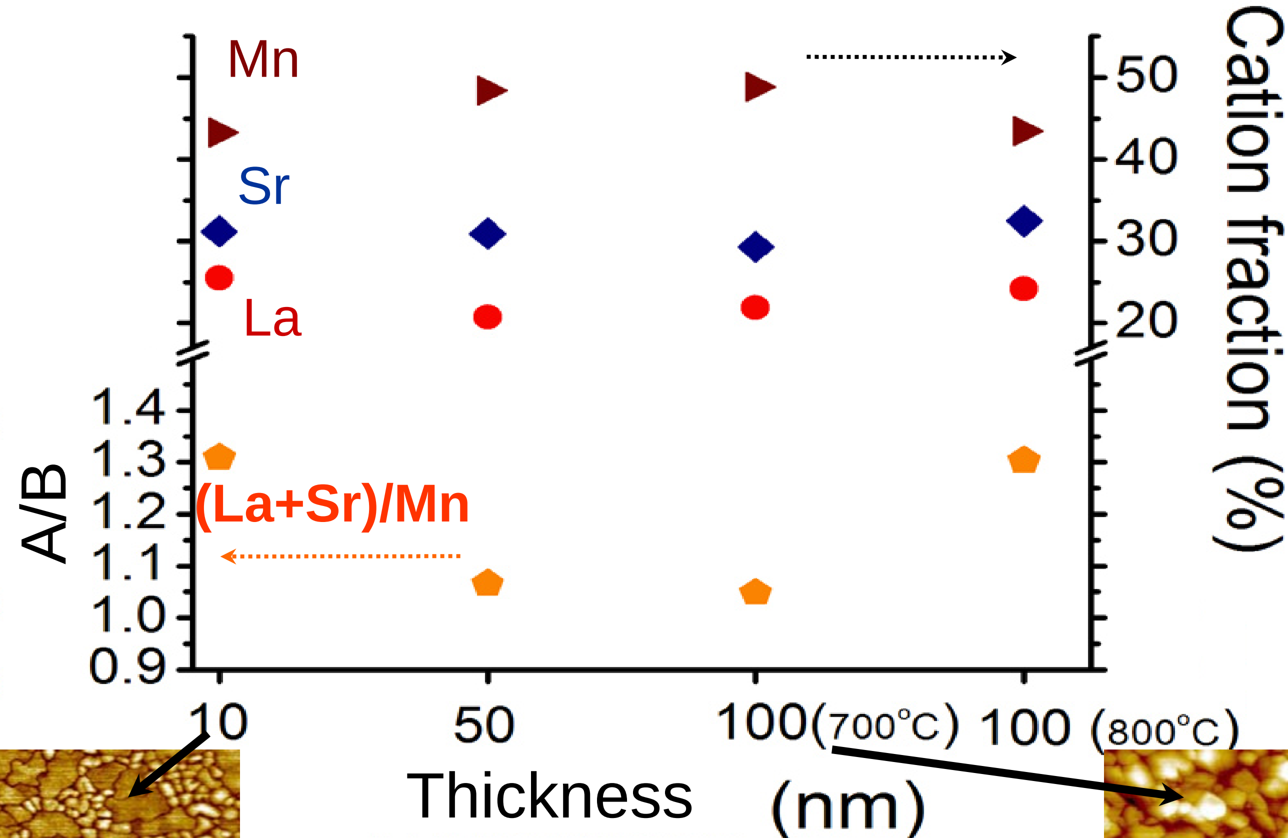


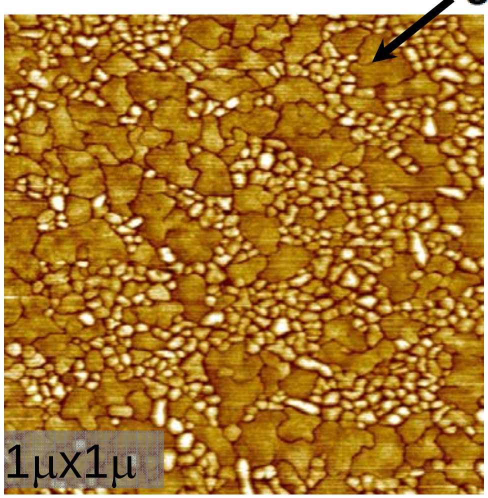
Textured polycrystalline

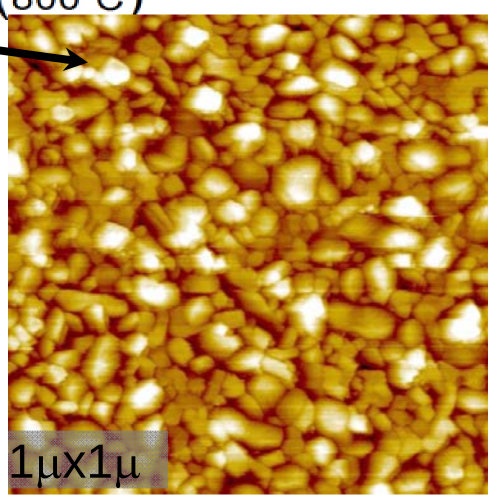
Grain boundaries present

- What is the effect of thickness, synthesis temperature, and substrate of the dense thin-film cathodes on surface topography, composition and electron tunneling?
  - Substrate: YSZ (111)
  - T_{dep}: 700 °C vs. 800 °C.

Surface of LSM on YSZ, *f(t)*



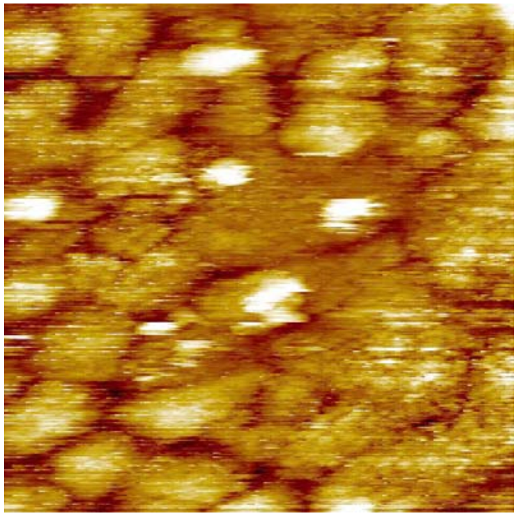




- Thickness ⬆, A/B ⬇.
- $T_{deposition}$ ⬆, A/B ⬆.
- Lattice strain?
- Substrate effect?

Tunneling current correlated with boundaries and/or domains?

Topography map
150x150nm^2

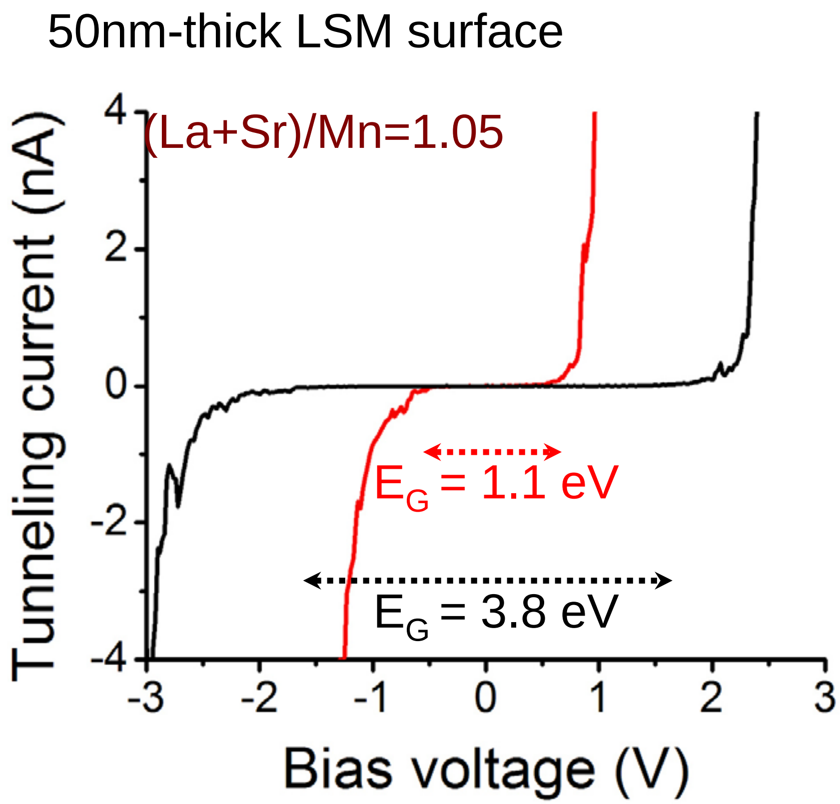


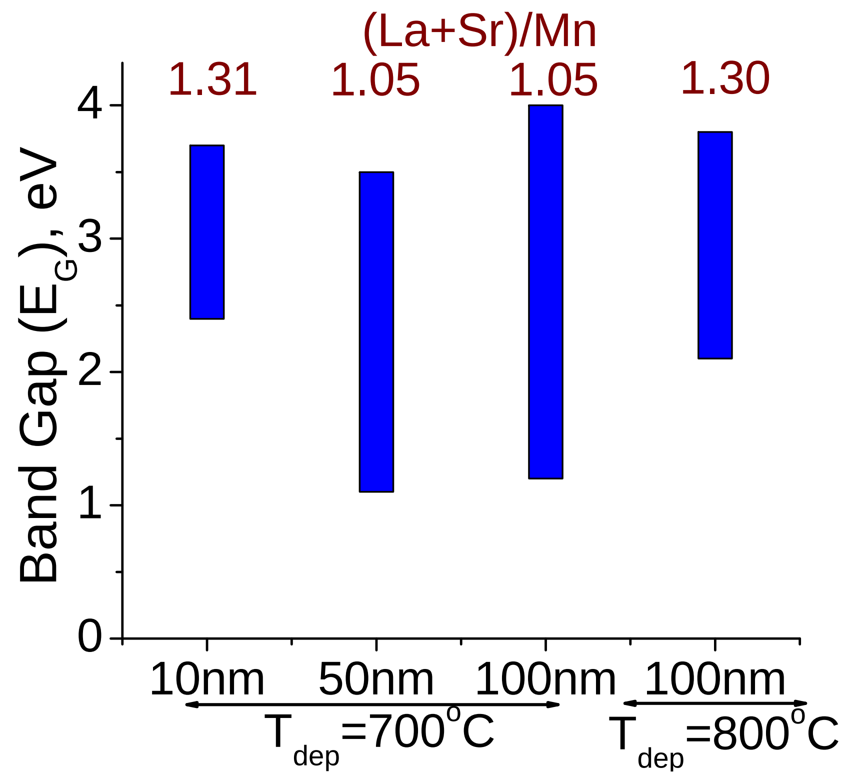
I_{tunnel} map, at -2.2V

- Higher electron tunneling rate at select grain boundaries compared to grain surfaces.
- Inhomogeneities also on grain surfaces.

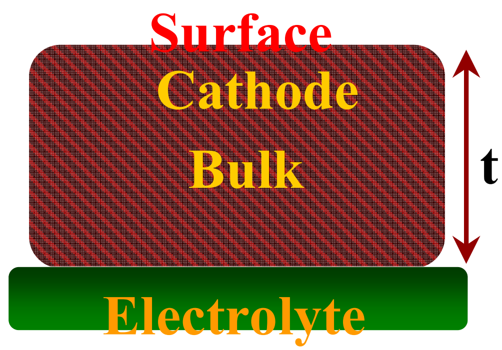
K. Katsiev, B. Yildiz et al.,
ECS Trans. 25 (2009) 2309.

Variation in the electronic behavior probed by STS





- "Smaller thickness" and "higher $T_{deposition}$" lead to:
  - larger A/B ←→ large E_G, more insulating in STS.



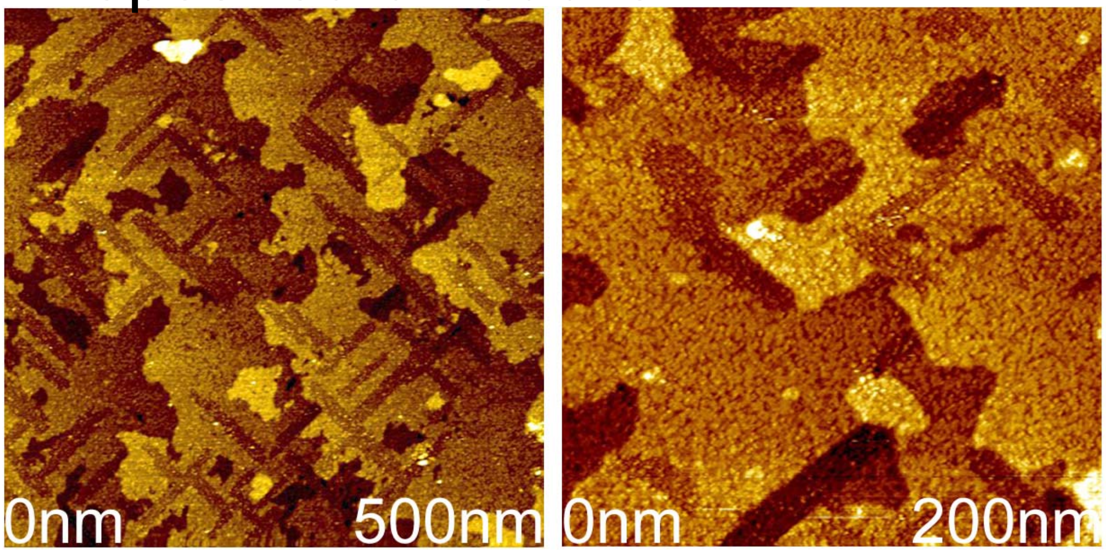
Epitaxial, single crystal

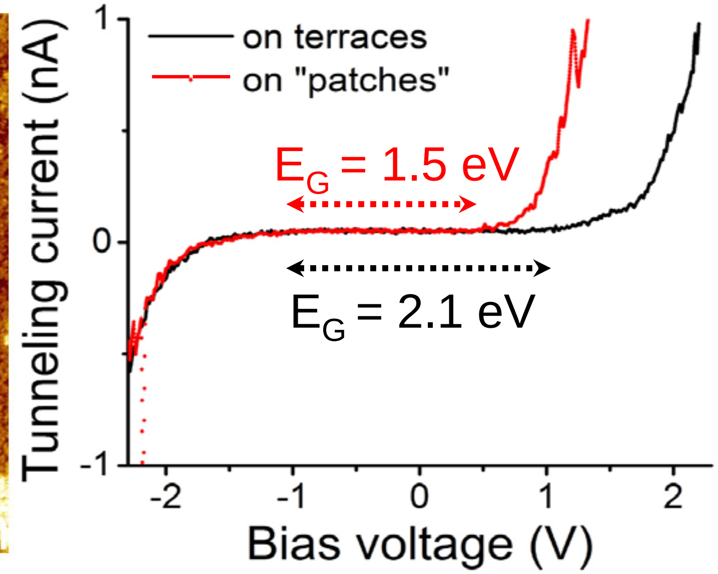
No grain boundaries

- What is the effect of thickness, synthesis temperature, and substrate of the dense thin-film cathodes on surface topography, composition and electron tunneling?
  - Substrate: $NdGaO_3$, $SrTiO_3$ (100)
  - T_{dep}: 700 ^oC vs. 800 ^oC.

10nm-thick epitaxial LSM on $NdGaO_3$

Deposited at 800^{o}C





- "Patches" exhibiting higher electron tunneling rate on the surface

Co-existence of (Sr,La)O-terminated and MnO_2-terminated surfaces.

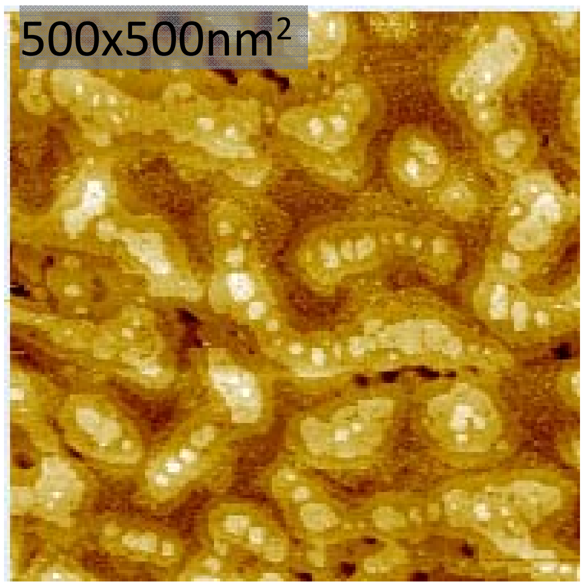
(Piskunov et al, *Phys. Rev. B* **78** (2008))

Partial surface oxidation and reconstructions during annealing in O_2.

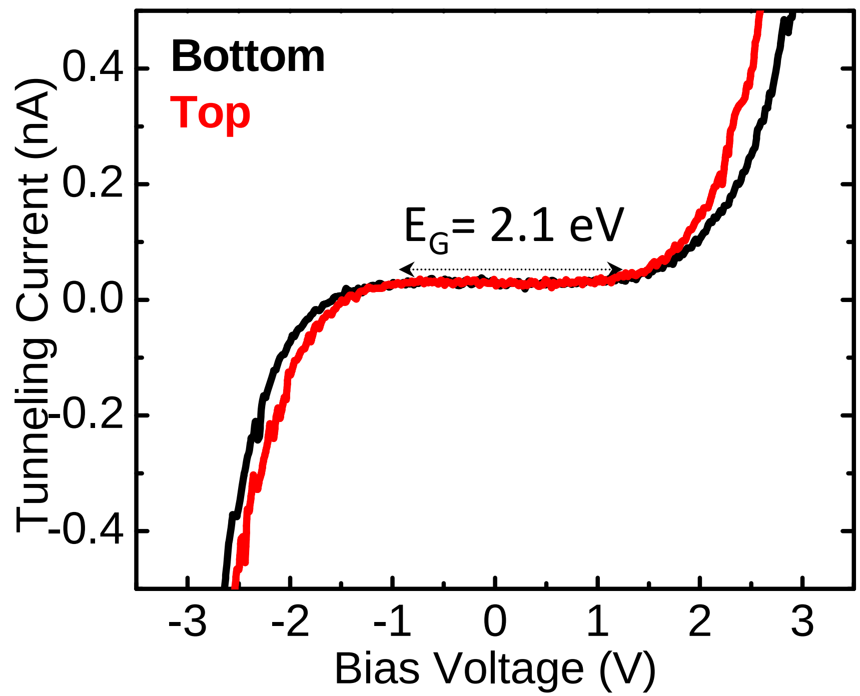
(Fuchigami et al., *Phys. Rev. Lett.,* **102** (2009))

10nm-thick epitaxial LSM on $SrTiO_3$

Deposited at 800°C



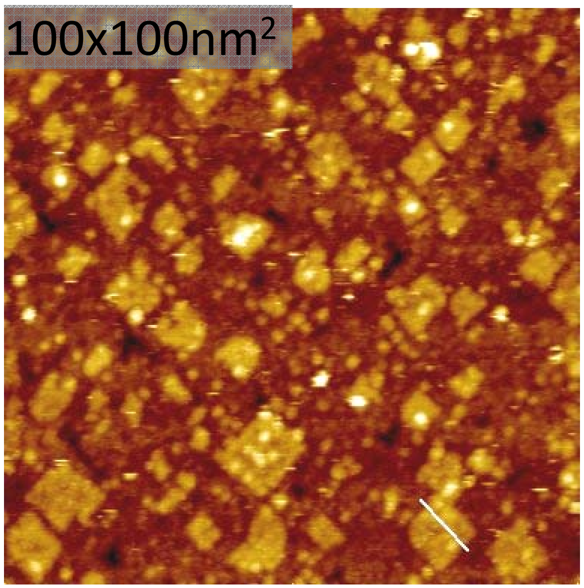
RT, P_{O2}= 10^{-10} mbar

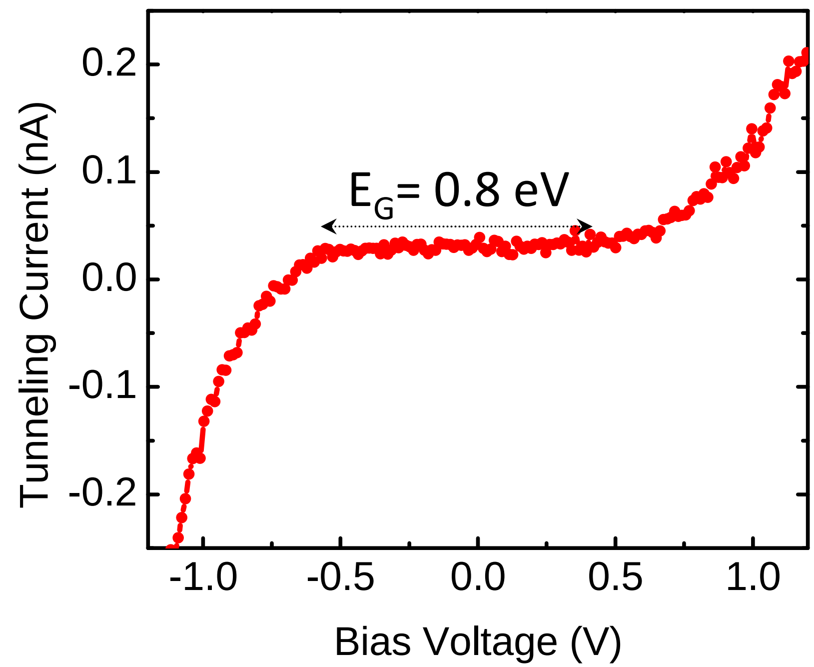


Tunneling spectra reproducible.
No evident phase separation at RT, UHV.

10nm-thick epitaxial LSM on $SrTiO_3$

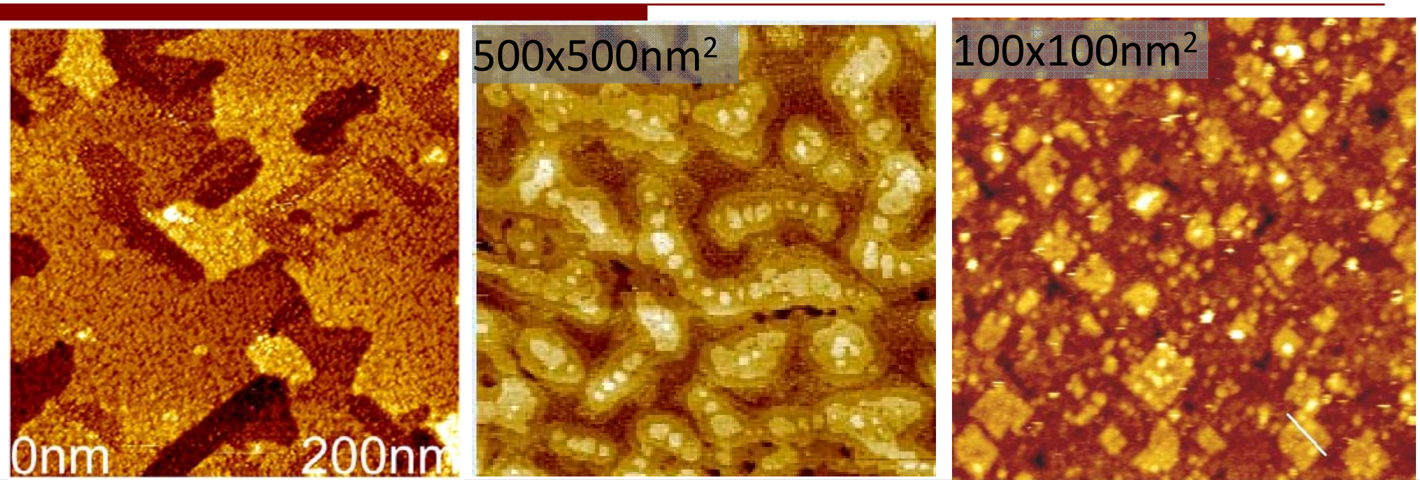
Deposited at 700^{o}C





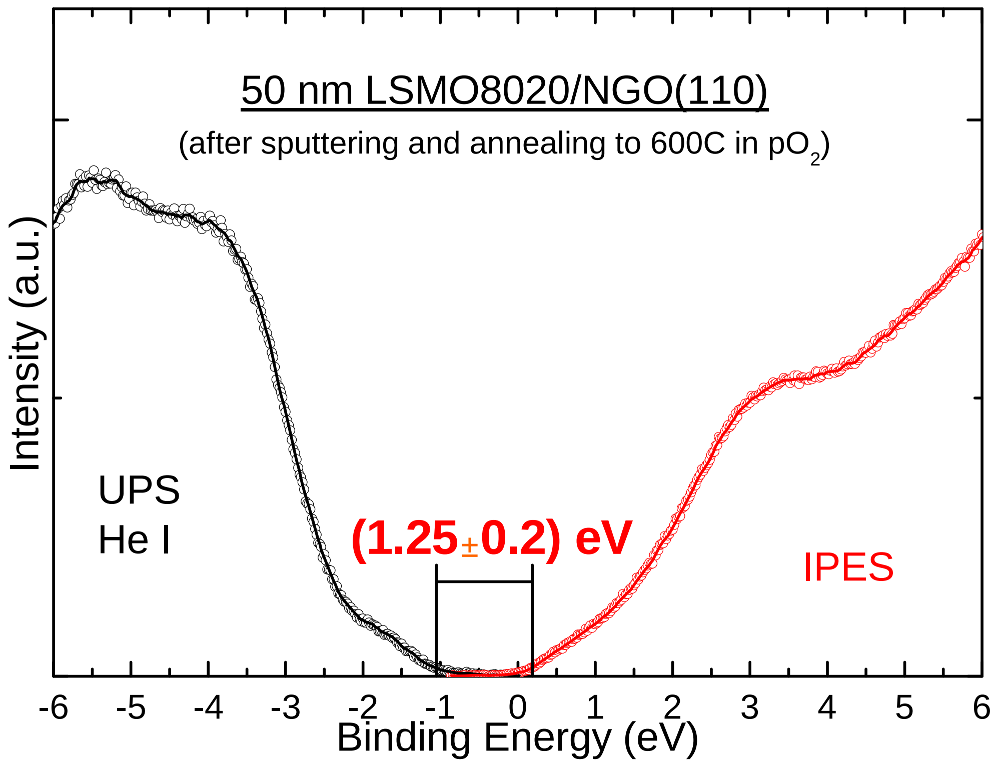
Tunneling spectra reproducible.
No evident phase separation at RT, UHV.

Comparison of epitaxial LSM films



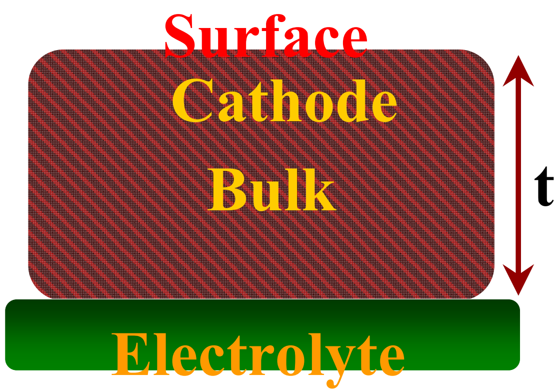
	LSM/NGO (c) T_{dep}= 800 °C	LSM/STO (t) T_{dep}= 800 °C	LSM/STO (t) T_{dep}= 700 °C
(La+Sr)/Mn	2.87	1.41	2.36
Sr/(La+Sr)	0.29	0.46	0.47
E_G (± 0.1 eV)	1.5 - 2.1 eV	2.1 eV	0.8 eV

Surface band gap on a 50 nm-thick LSM film



- C cleaned.
- Cr found in XPS.

- First combined UPS and IPES.
- Smallest gap found:
  - 1.25 (±0.20) eV
  - Consistent with the STS, 1.5 (±0.10) eV
- Measurements for different thicknesses, preparations and substrates → comprehensive comparison.



B- Epitaxial, single crystal
No grain boundaries

- What is the structural nature of A-site rich, Sr-rich, surfaces on LSM?
  - Segregation?
  - Phase separation?

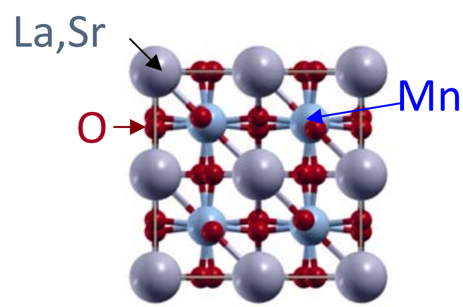
Epitaxial LSM films on STO

Surface composition and structure – nature of A-site rich surface?

Surface segregate structures:

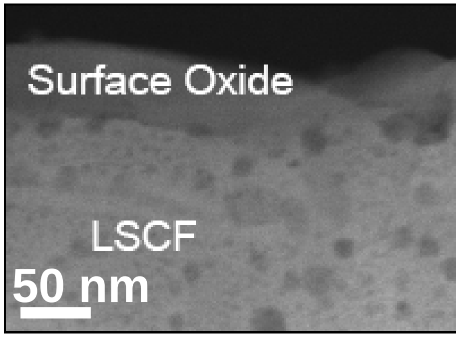
- Sr enrichment on A-site

Fister et al.
Appl. Phys. Lett. **93** (2008)



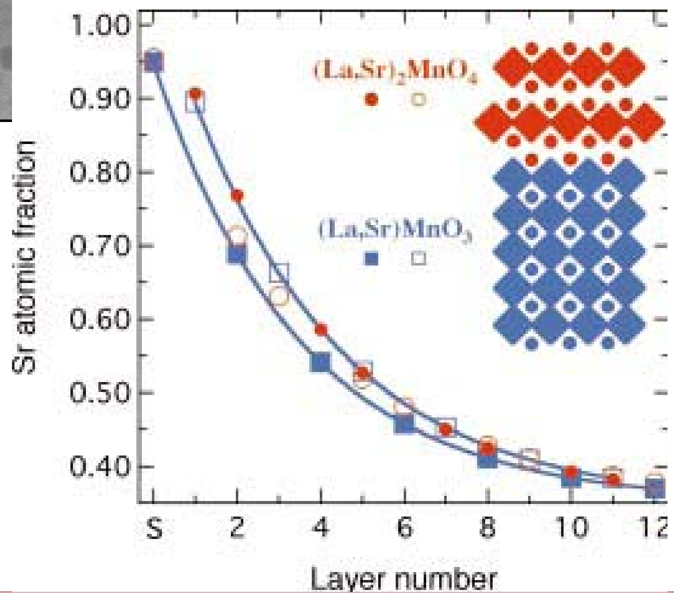
- Formation of (Sr,La)O

Courtesy of
Prof. Meilin Liu,
Georgia Tech, 2010

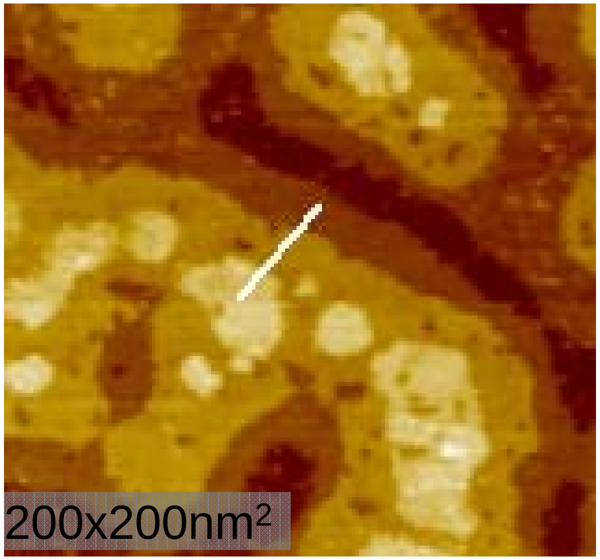


- Formation of $(La,Sr)_2MnO_4$

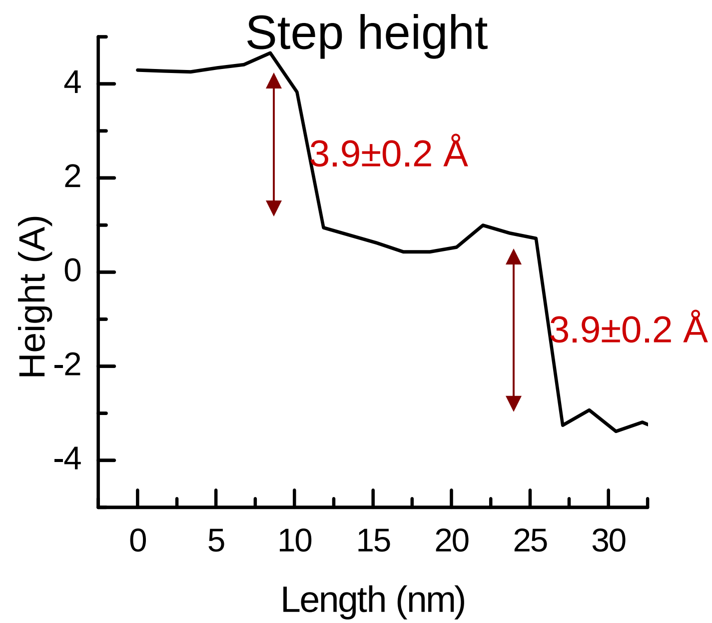
Dulli et al. *PRB* **62** (2000)



10nm-thick LSM/STO; surface topography



RT, P_{O2}= 10^{-10}mbar



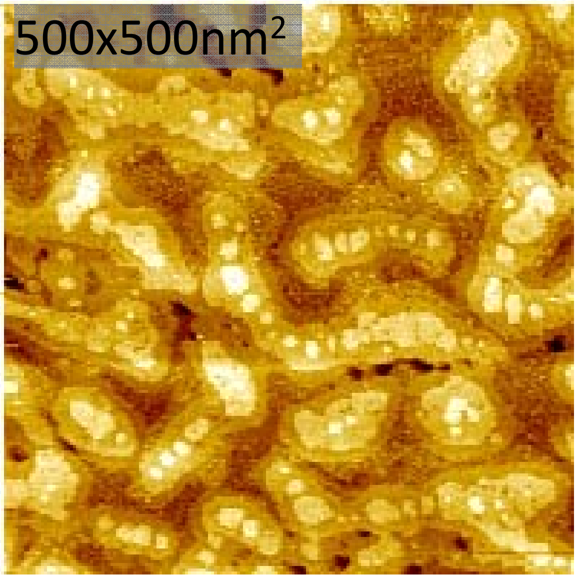
Difference in topography:
Top flat terraces, step height of 3.9±0.2 Å
Bottom layer defected

Compound	Lattice parameters
[1]$La_{0.7}Sr_{0.3}MnO_3$	a=b=c= 3.88 Å
[2]SrO	a=b=c=5.16 Å
[3]$SrCO_3$	a=5.1, b=8.4, c=6.0 Å
[4] La_2O_3	a=b= 3.4, c=6.1 Å
[5]$(La,Sr)_2MnO_4$	a=b=3.84 , c=12.5 Å

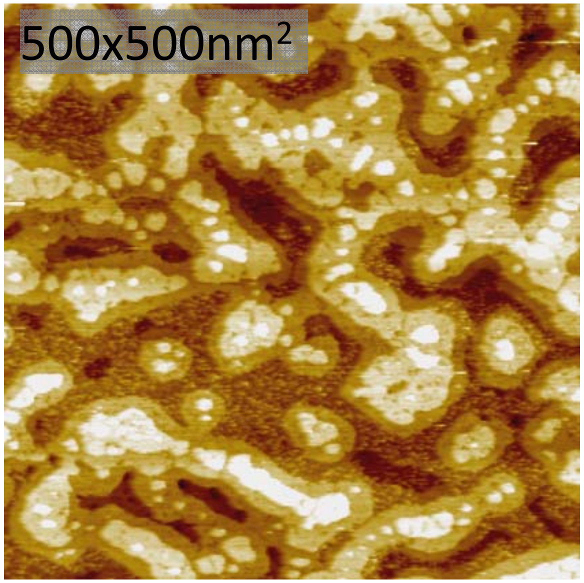
[1] Martin *Phys. Rev. B* 53 (1996)
[2] Bertacco et al. *Surf. Sci*. 511 (2002)
[3] Thongtem et al. *Mater. Lett.* 64 (2010)
[4] Hu et al. *Adv. Mater.* 19 (2007)
[5] Zheng et al. J. *Electrochem. Soc* 146 (1999)

10nm LSM/STO; surface topography $f(T, P_{O2})$

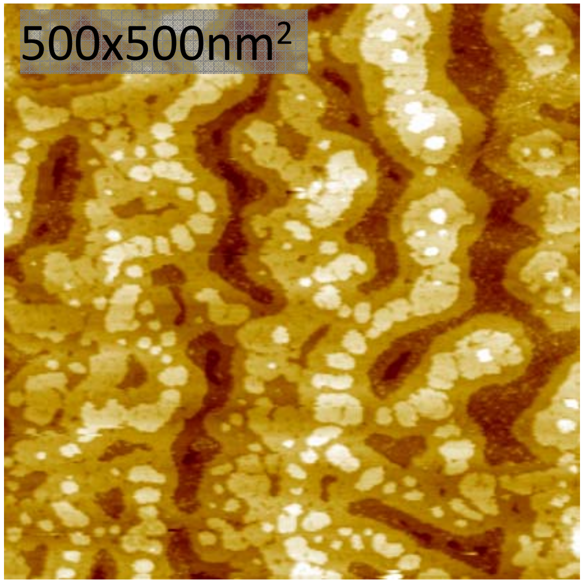
Measure of phase separation with T and PO_2



RT, $P_{O2}= 10^{-11}$mbar



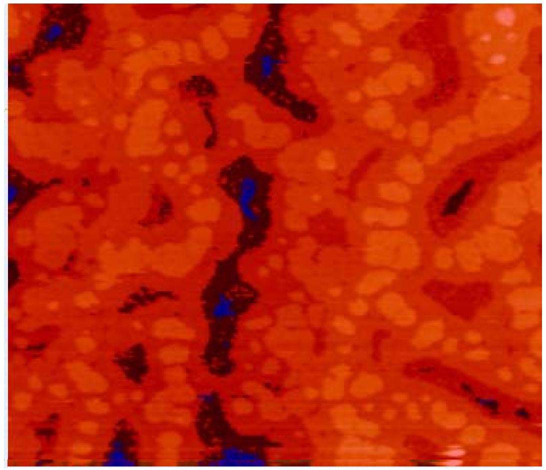
500^{o}C, $P_{O2\text{-surface}}$~10^{-3} mbar

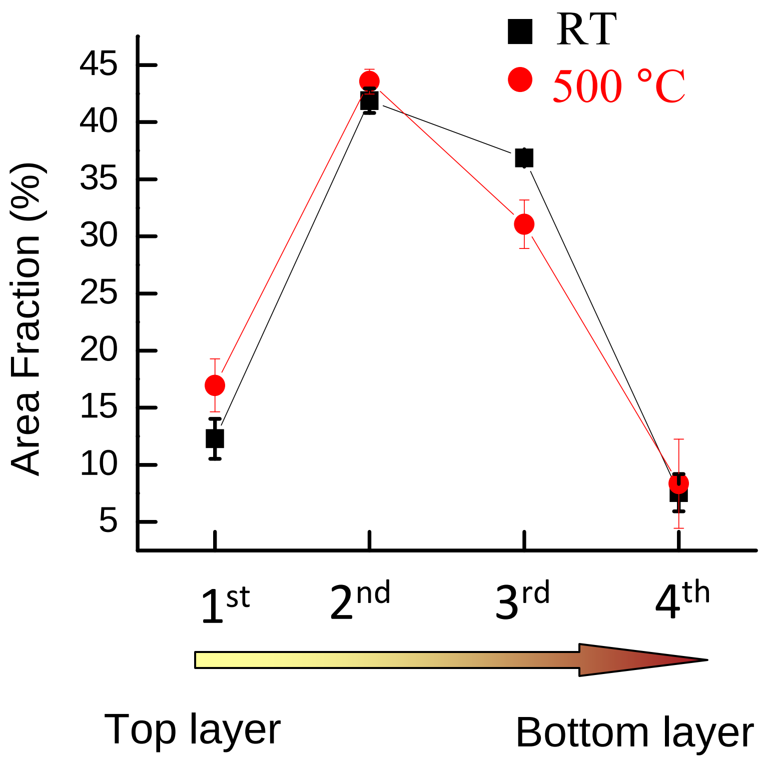


500^{o}C, $P_{O2} = 10^{-10}$ mbar

Surface layered structure remains stable at elevated temperatures

Size distribution of surface islands

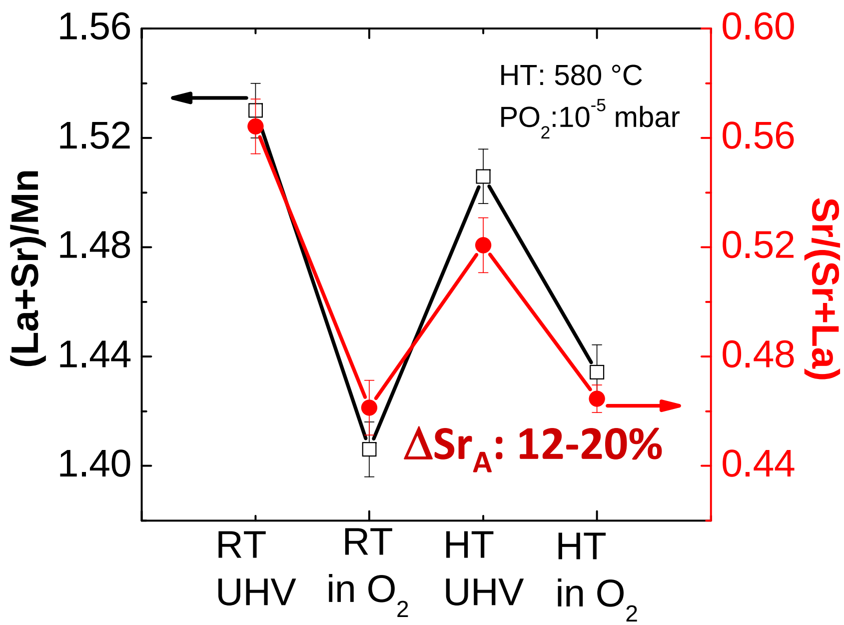




At 500 °C, only small changes in surface layers.
No new features arise.

Nature of A-site rich surface on LSM?

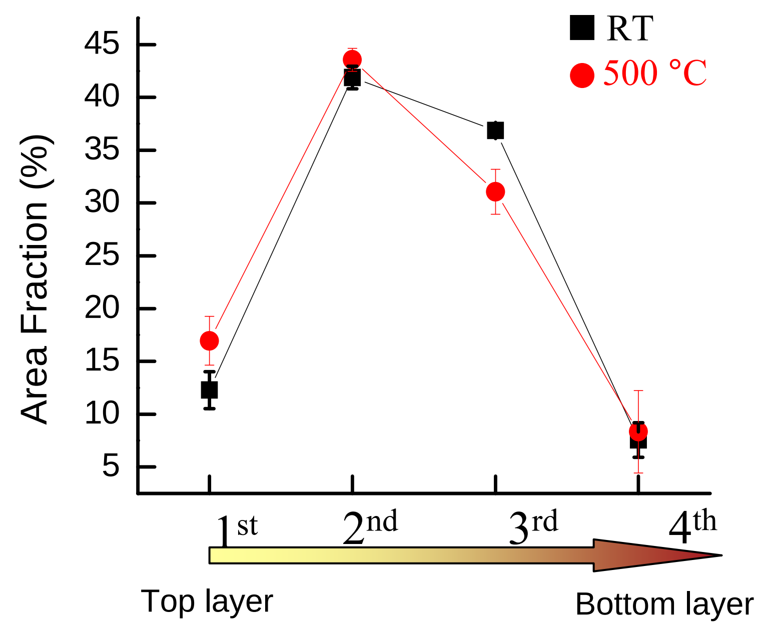
Surface composition



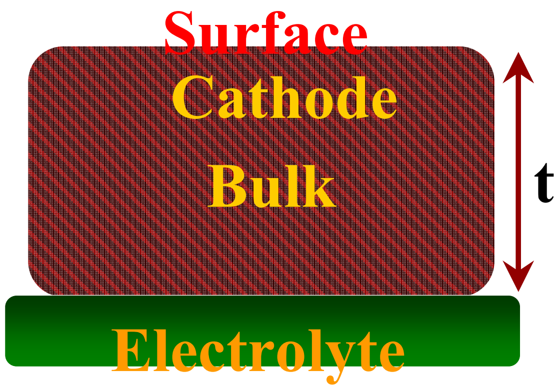
PO_2 ↓ Sr/(Sr+La) ↑

- Formation of A-O :
  a_{SrO} = 5.16 Å,
  c_{La2O3} = 6.1 Å ≠3.9 Å
- Formation of RP phase
  c_{RP} = 12.8 Å

Size of surface features



- Dominant surface:
  AO-terminated perovskite surface, Sr-increase on A-site.



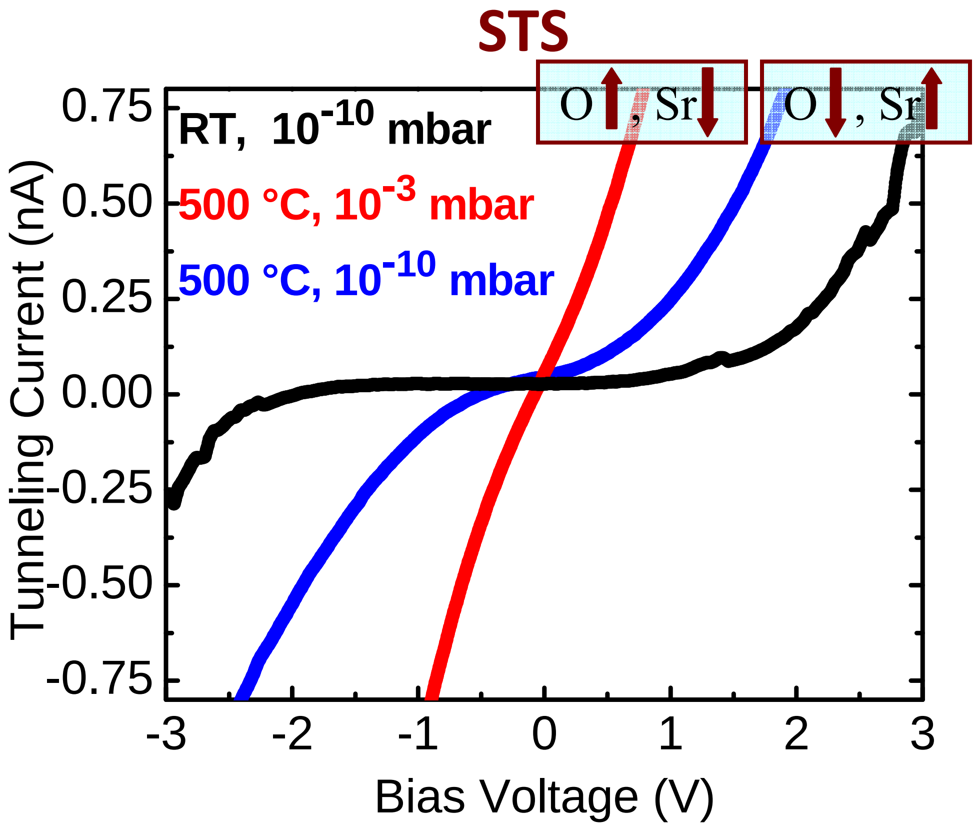
B- Epitaxial, single crystal

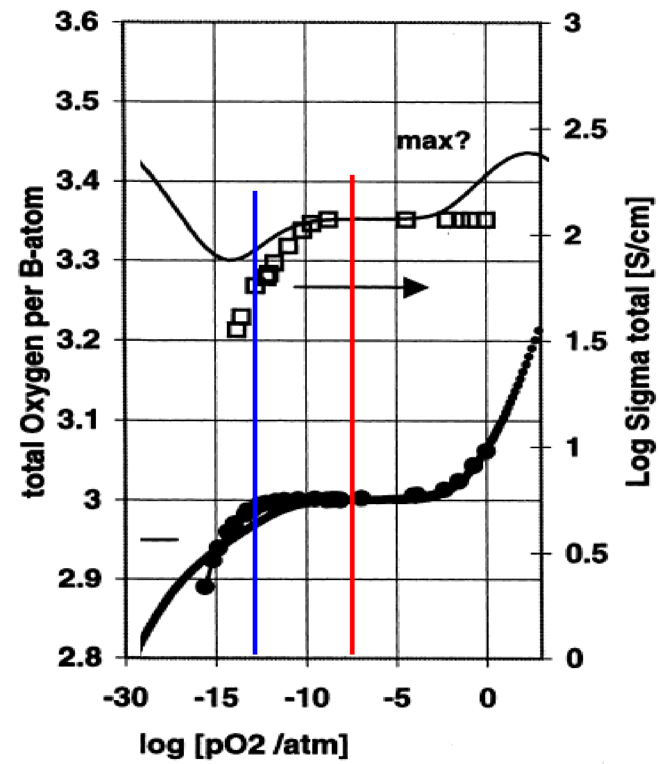
No grain boundaries

- How are the surfaces evolving with temperature and oxygen environment?
  - Structure
  - Composition
  - Electronic structure

Epitaxial LSM films on STO

Electronic state of LSM/STO; $f(T,P_{O2})$





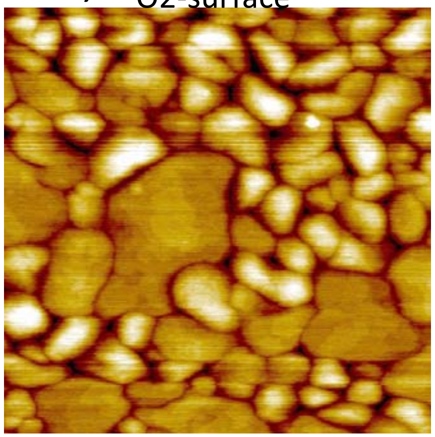
- T ↑ :Insulator → Metallic
- PO_2 ↑: $\sigma_{tunneling}$ ↑

Small polaron model: $\sigma \alpha P_{O2}$

F.W. Poulsen et al. *Solid State Ionics* **129** (2000)

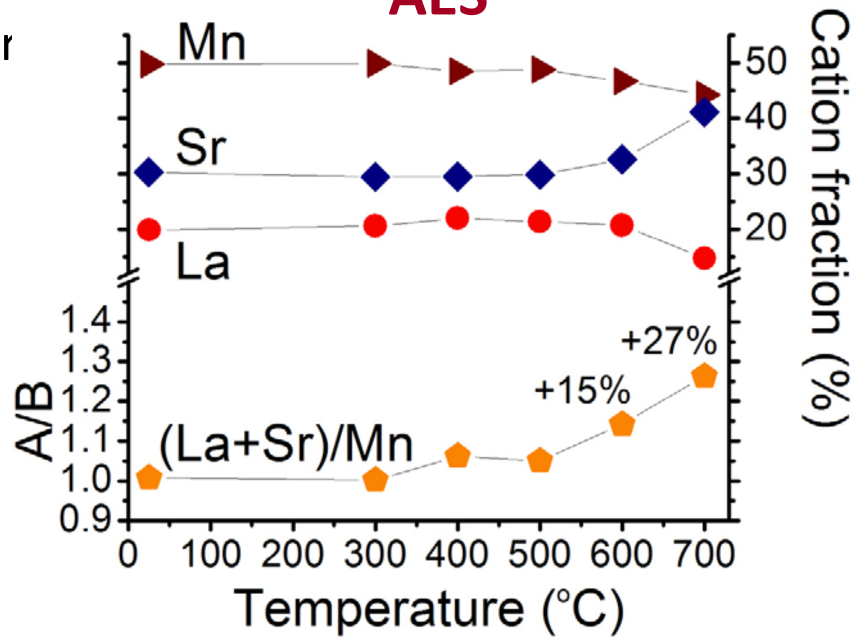
Surface of LSM/YSZ; *f(T)*

580°C, $P_{O2\text{-}surface}$ ~ 10^{-3} mbar



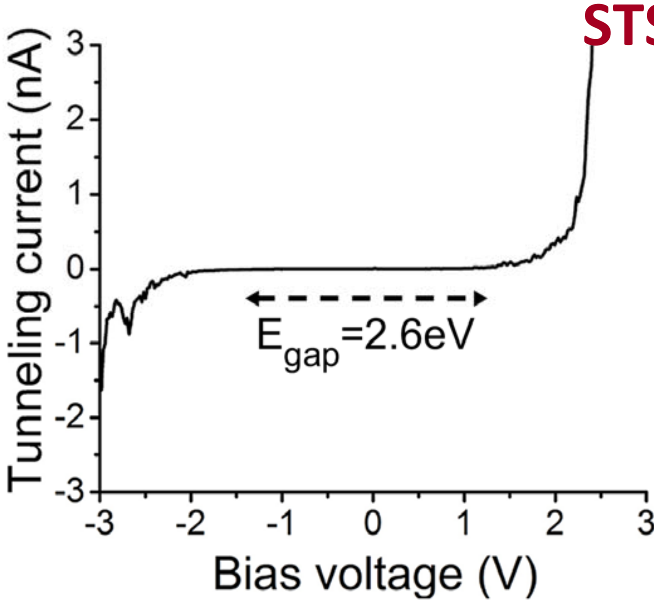
250x250nm²

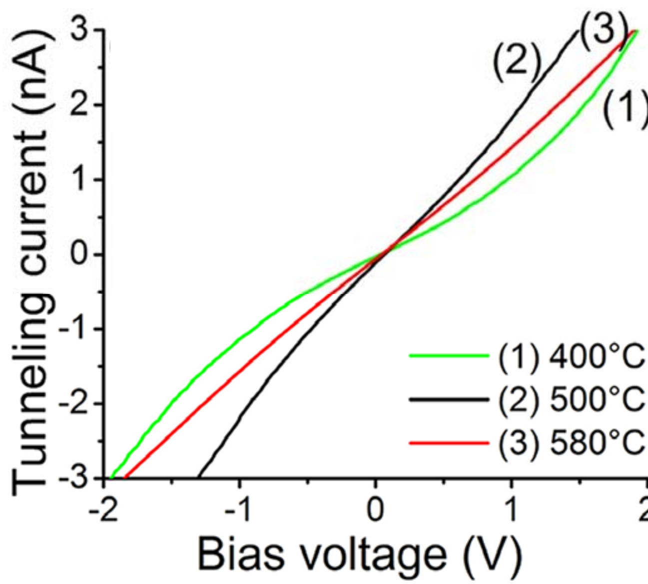
AES



T > 500°C → Sr⬆ → σ_{tun} ⬇

STS

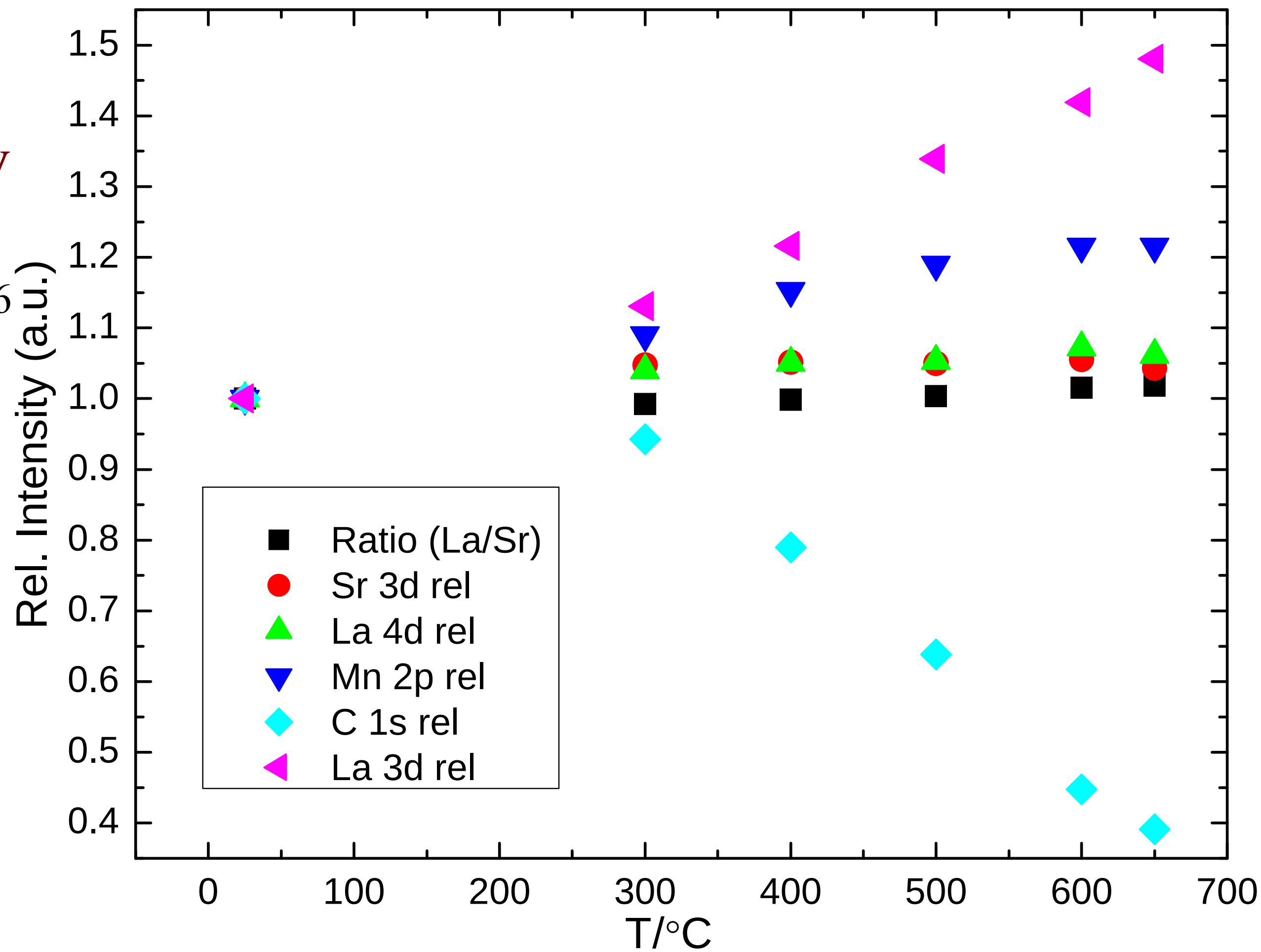




Katsiev and Yildiz et al., *Appl. Phys. Lett.* 95 (2009)

Surface of ex-situ annealed LSM/NGO; *f(T)*

- La/Sr ratio constant up to 500 °C, increases by 3-4% above 500 °C, quenched at $P_{O2}=1\cdot10^{-6}$ mbar. (corroborates with earlier annealing experiment to 800°C in air, 20% increase)
- Mn 2p and La 3d increase due to C 1s decrease and energy dependent signal attenuation by the carbon overlayer.



Relative (normalized to as-received state) change of the XPS lines measured after each step of ex-situ annealing

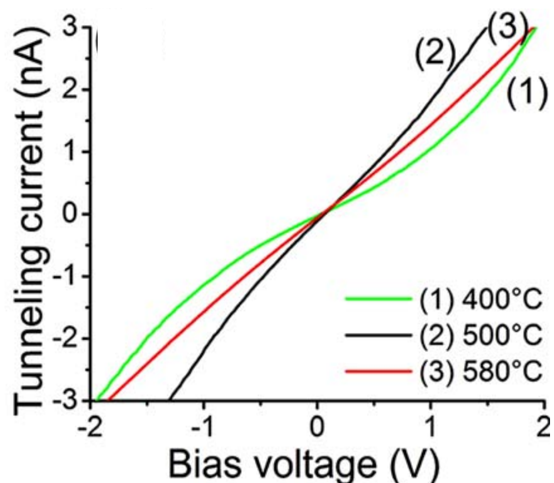
Summary Remarks

f (t, T, P_{O2})

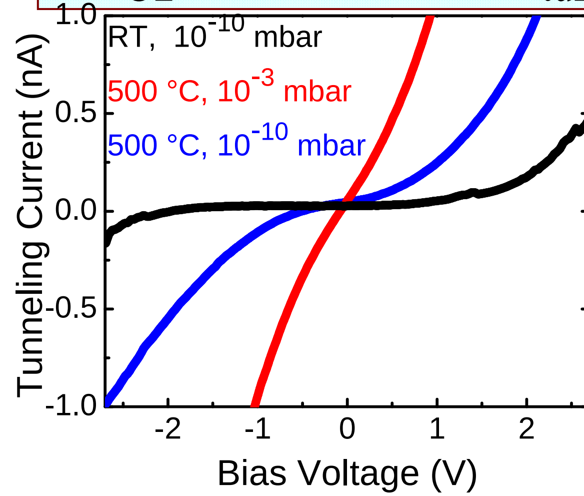
$T_{deposition}$⬇ Thickness⬆, → Sr ⬇ and σ_{tunnel} ⬆

Lattice strain? Vacancies?
Substrate effect?
Dense thin-films, but not so simple.

T⬆ → Sr⬆ → σ_{tun}⬇



P_{O2}⬇ → Sr⬆ → σ_{tun}⬇



Sr⬆ → AO-terminated perovskite surface, Sr-increase on A-site, within a limited P_{O2}-range

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