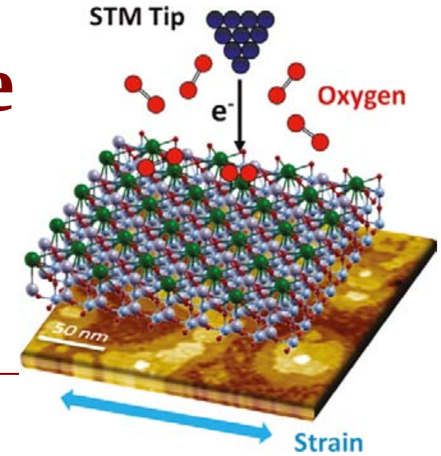
Surface Chemistry, Electronic Structure and Activity of SOFC Cathode Films – Effects of Temperature and Strain



Wonyoung Lee, Helia Jalili, Bilge Yildiz
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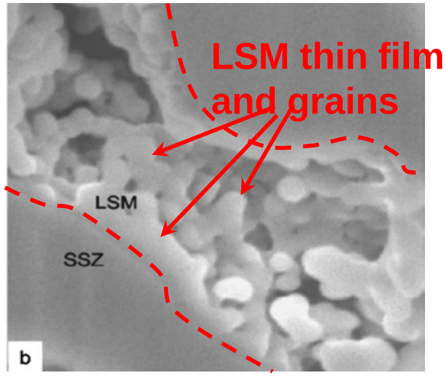
University of Nevada-Las Vegas

Lu Yan, Paul Salvador
Carnegie Mellon University

12th Annual SECA Workshop
July 27, 2011

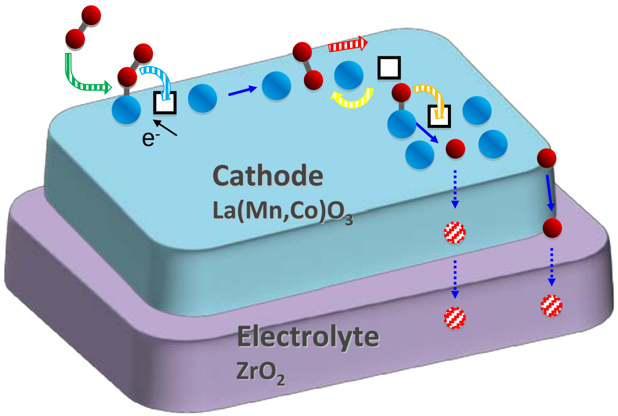
Oxygen Reduction @ Cathode

Structure, composition, electronic structure ←→ Oxygen reduction (OR) kinetics



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

→→→



Porous electrodes → **Dense thin-film electrodes** → **Simulations**

Porous electrodes

Oxygen reduction kinetics
- Rate constants
- Energy barriers

Dense thin-film electrodes

- Reaction pathways
- Surface segregation
- Grain boundary transport

Simulations

- Stable surface phases
- Energies (thermodynamic and kinetic) in OR steps

J. Van Herle et al., *Electrochim. Acta*, 41, 1996
M. J. Jorgensen et al., *J. Electrochem. Soc.* 148, 2001
Y. Arachi et al., *Solid State Ionics*, 121, 1999

J. Fleig, *Fuel Cells,* 8, 2008
Baumann et al. *J. Electrochem. Soc.* 152 , 2005
G.J. la O' et al., *J. Electrochem. Soc.*, 154 , 2007
R.A. De Souza et al., *Mater. Lett.,* 43, 2000

Piskunov et al., *Phys. Rev. B* 78, (2008)
Lee and Morgan et al., *Phys. Rev. B* 80, (2009)
Mastrikov et al., J. Phys. Chem. C 114 (2010)

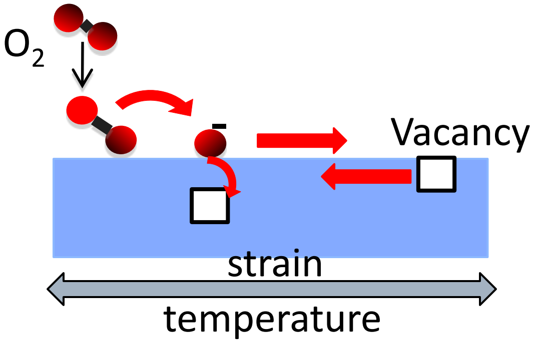
Probe surface ~ f (T, P_{O2}, V, ε)

Objective: assess governing factors of OR activity

Model "strained" systems:

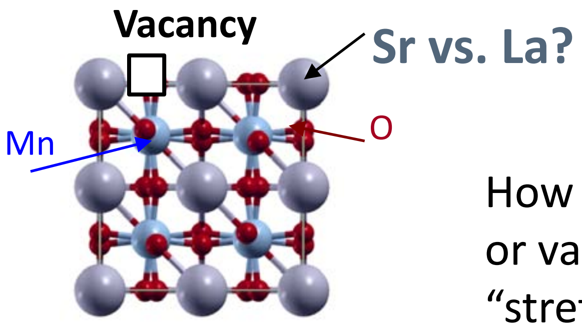
$La_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xCoO_3$

dense thin films, at high temperature



1) Chemical environment

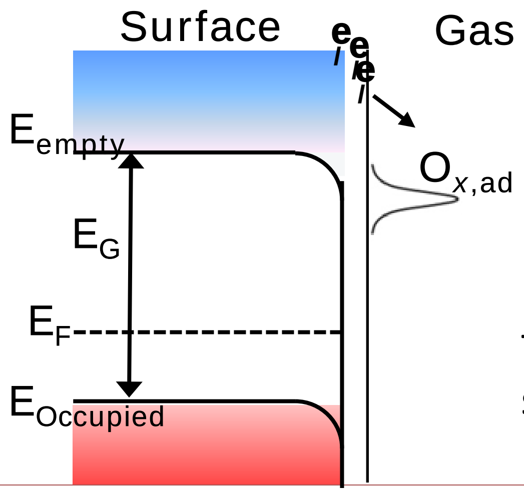
→ Sr segregation, and oxygen vacancies



How much more Sr, or vacancies on a "stretched" surface?

2) Electronic structure

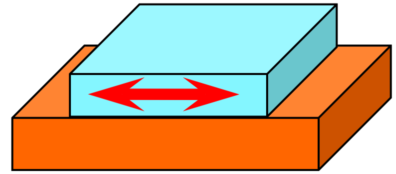
→ Energy gap, density of states (DOS) at E_F

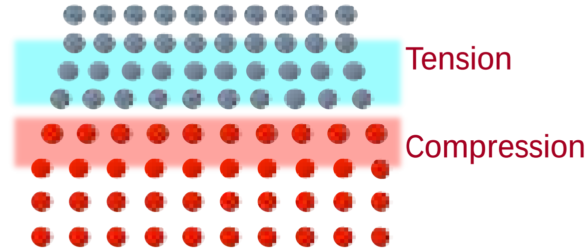


Facilitates electron transfer on the surface?

"Strain" in high temperature ionic materials?

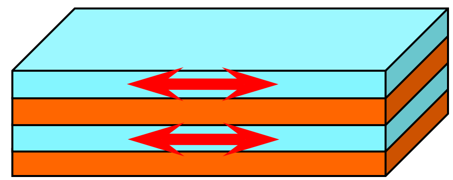
- Thin films
  - (Y_2O_3,ZrO_2)(YSZ) [1]
  - (Gd_2O_3,CeO_2)(GDC) [2]
  - $(La,Sr)CoO_3$ [3]



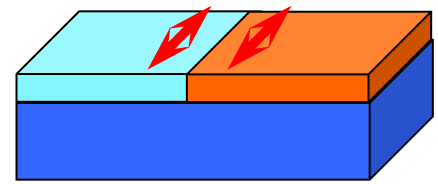


- Hetero-layer system
  - CaF_2/BaF_2 [4]
  - $YSZ/SrTiO_3$(STO) [5]
  - $Ce_{0.8}Sm_{0.2}O_2$/YSZ [6]
  - $(La,Sr)CoO_3/(La,Sr)_2CoO_4$ [7]

Ionic conductivity↑



Surface reactivity↑

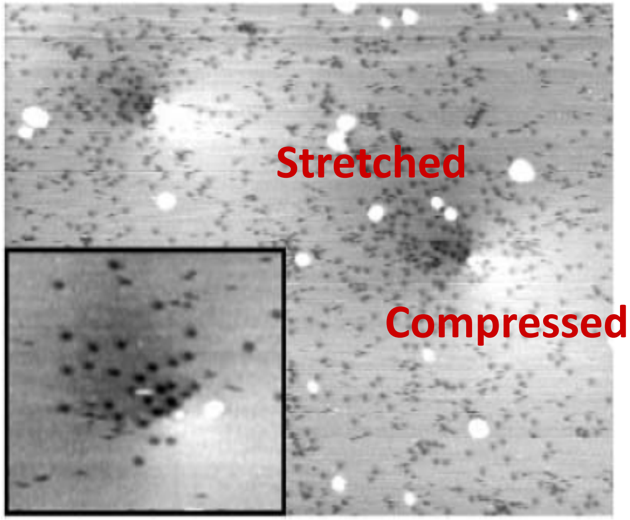


<u>Strain</u> as a driver of defect chemistry, ionic transport and oxygen reduction (OR) rates at the nano-scale interfaces?

[1] Korte et al., Phys. Chem. Chem. Phys., 10 (2008)
[2] Beckel, Rupp, Gaukcler et al., J. Pow. Sources (2007)
[3] Januchevsky and Fleig et al. Adv. Func. Mat. (2009)
La'O et al. Ang.Chem. Int. Ed. (2010)
[4] Sata and Maier et al., *Nature*, 408 (2000)
[5] Garcia-Barriocanal, *Science* 321 (2008)
Schichtel and Janek, PCCP., 11 (2009)
Kushima and Yildiz, J. Mat. Chem. 20 (2010)
[6] Sanna, Small, 6 (2010)
[7] Sase, *Solid State Ionics*, 178 (2008)

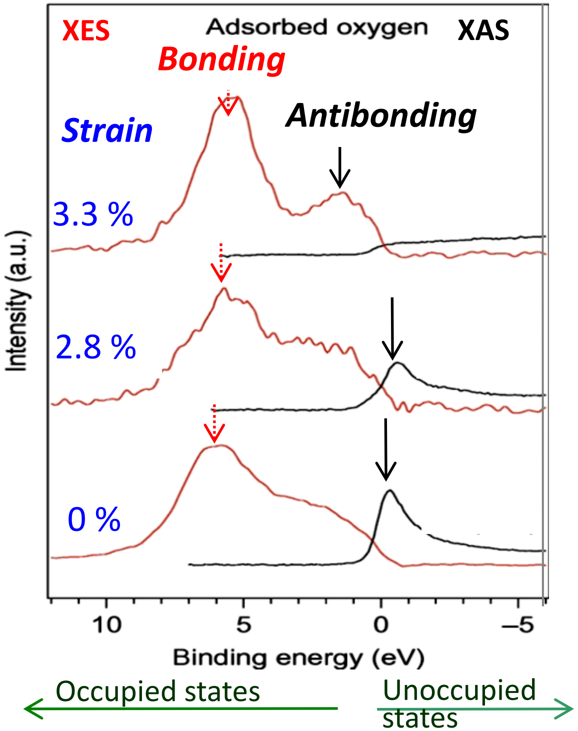
Lattice strain as a driver of oxygen reduction kinetics?

On low temperature metal electrocatalysts



- N adsorption enhanced by ~20x
- Attributed to decreased barrier for NO dissociation on the stretched surfaces

Wintterlin, J., et al.
Angew. Chem. Int. Ed. 2002 42 2850



Oxygen K-edge X-ray absorption and emission spectra (XAS, XES)

- shift in the d band center
- broader d band structure
- O 2p and Pt 5d antibonding downshift to higher occupancy

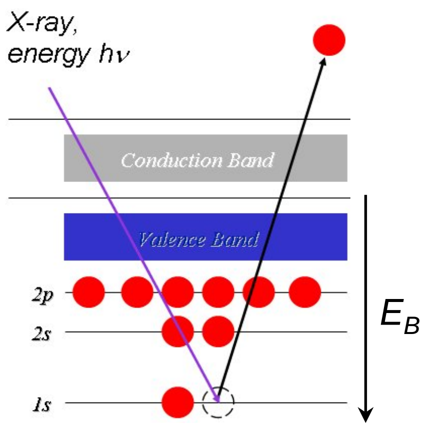
Mavrikakis, M., et al.
Phys. Rev. Lett. 1998, 81 2819.

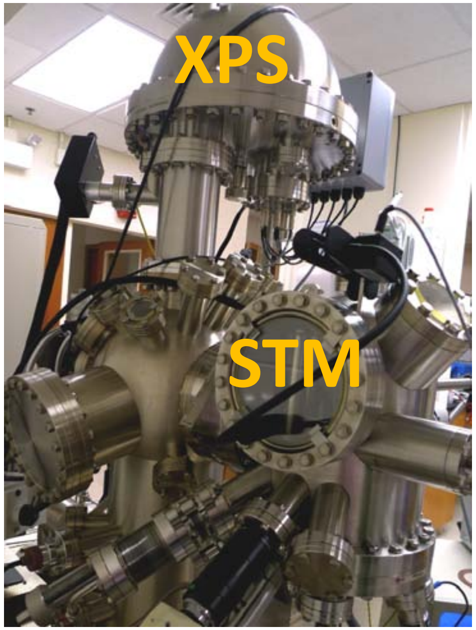
Strasser, P, et al.
Nat. Chem. 2010, 2 454.

Approach

Surface chemical state

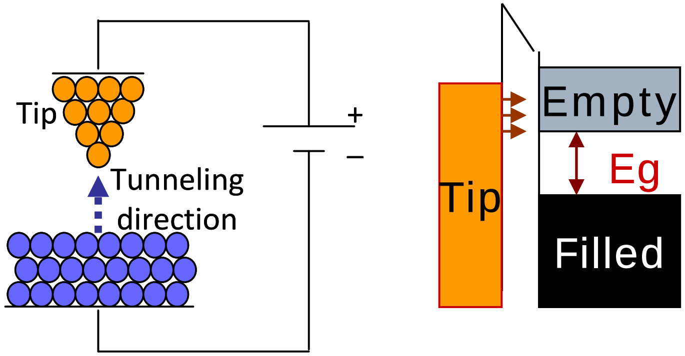
X-ray Photoelectron Spectroscopy (XPS)

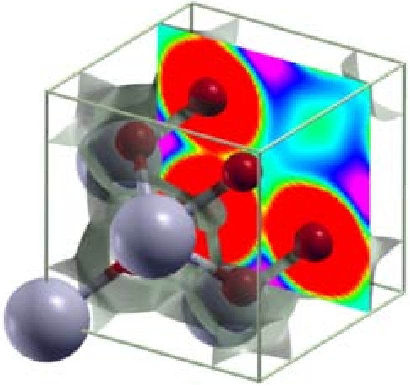




Surface electronic structure

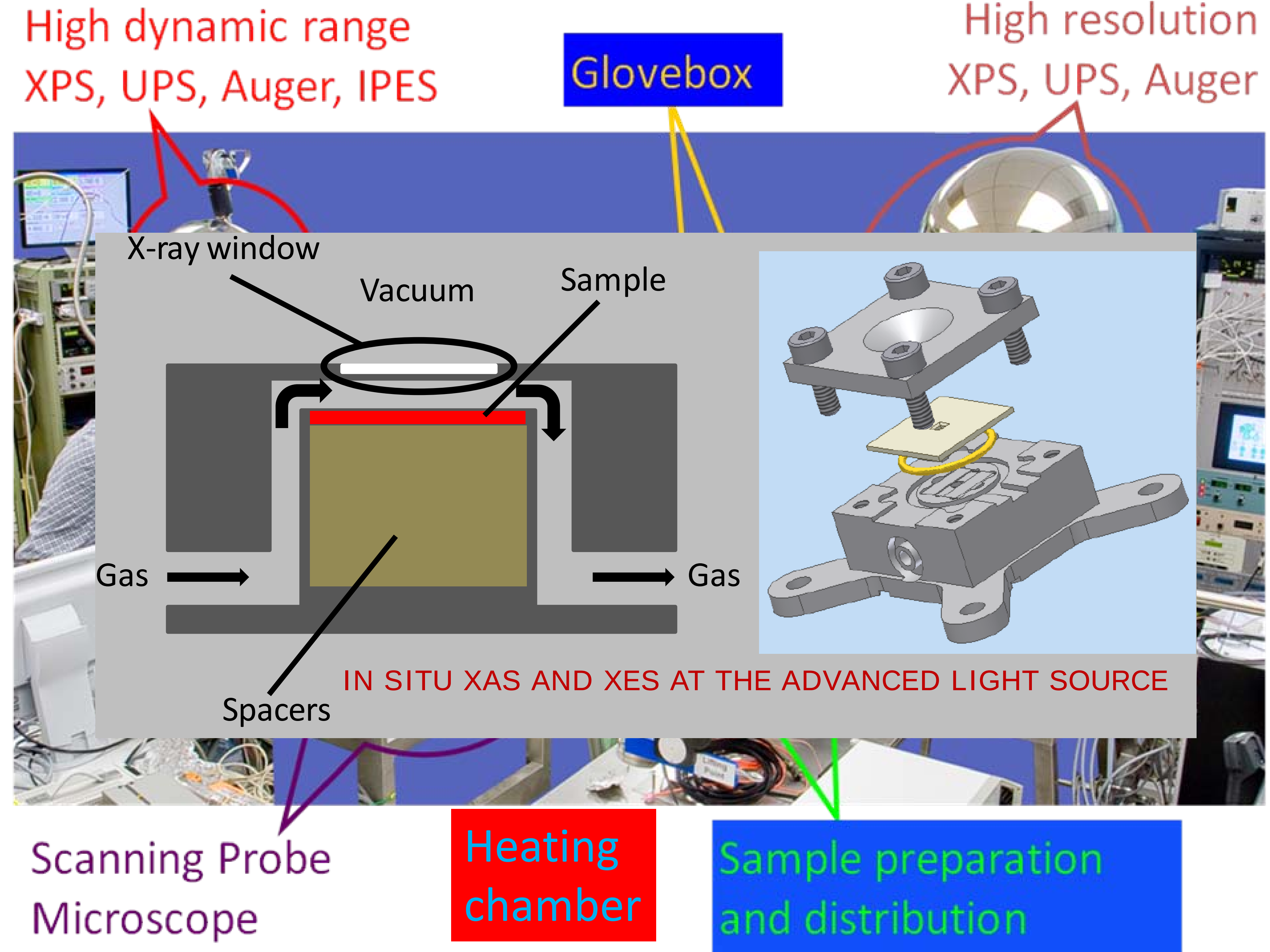
Scanning Tunneling Microscopy / Spectroscopy (STM/STS), ***in situ***





Mechanisms and kinetics of processes at the atomic-scale

Electronic structure (DFT+U)



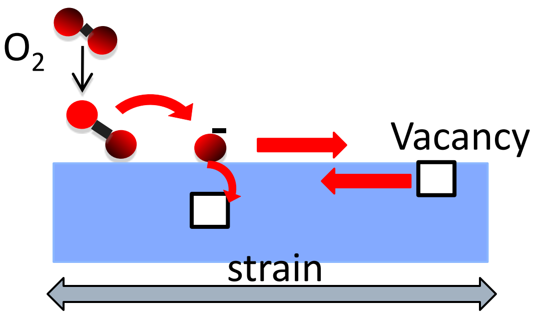
High dynamic range
XPS, UPS, Auger, IPES
Glovebox
High resolution
XPS, UPS, Auger
X-ray window
Vacuum
Sample
Gas
Gas
Spacers
IN SITU XAS AND XES AT THE ADVANCED LIGHT SOURCE
Scanning Probe
Microscope
Heating
chamber
Sample preparation
and distribution

Objective: assess governing factors of OR activity

Model "strained" systems:

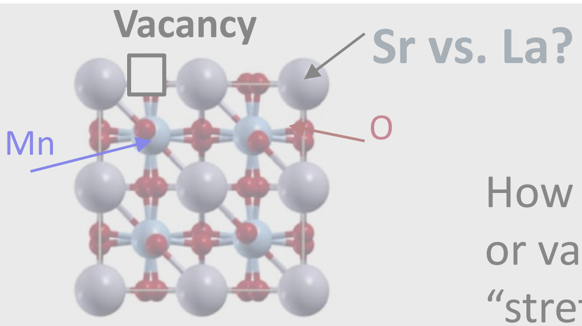
$La_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xCoO_3$

dense thin films, at high temperature



1) Chemical environment

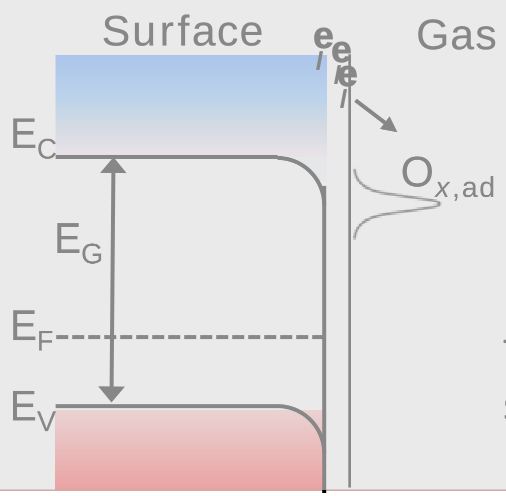
→ Sr segregation, and oxygen vacancies



How much more Sr, or vacancies on a "stretched" surface?

2) Electronic structure

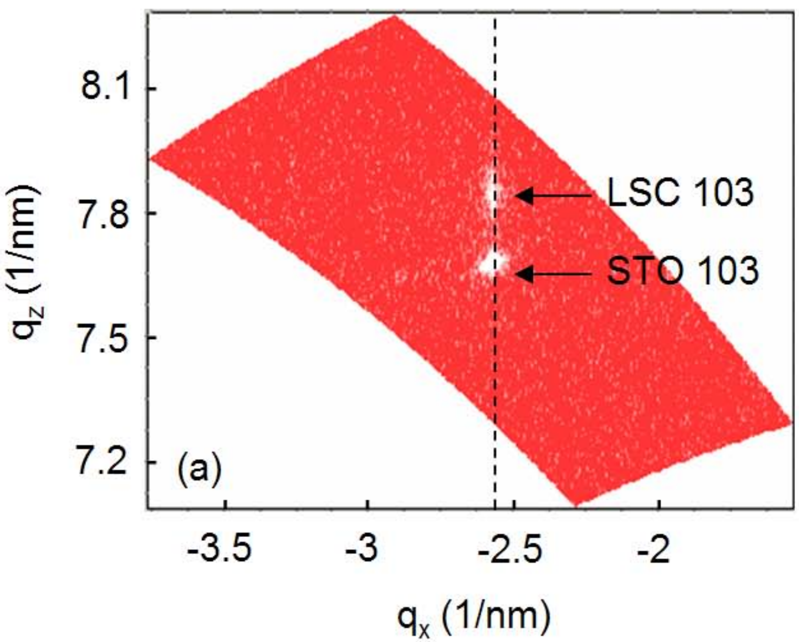
→ Energy gap, density of states at E_F

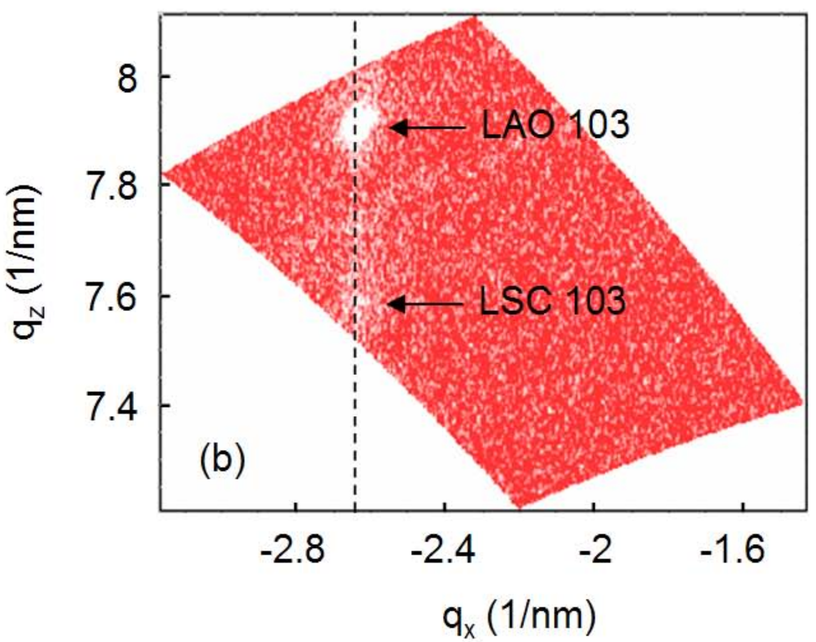


Facilitates electron transfer on the surface?

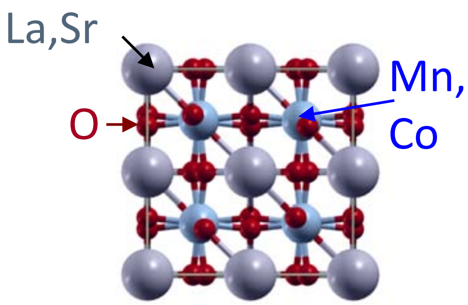
Model "strained" systems $La_{0.7}Sr_{0.3}MnO_3$, $La_{0.8}Sr_{0.2}CoO_3$

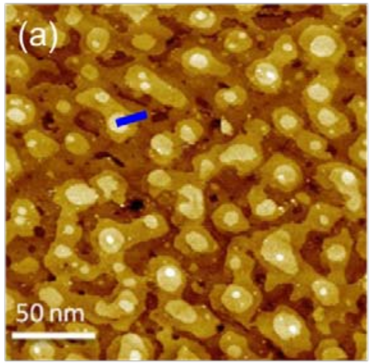
(100) epitaxial	Substrate	Abbr.	ε % (RT)	ε % (500 °C)
$La_{0.7}Sr_{0.3}MnO_3$	$SrTiO_3$ (100)	LSM/STO	+ 0.8	+ 0.6
$La_{0.7}Sr_{0.3}MnO_3$	$LaAlO_3$ (100)	LSM/LAO	-2.1	-2.3
$La_{0.8}Sr_{0.2}CoO_3$	$SrTiO_3$ (100)	LSC/STO	+1.4	+1.0
$La_{0.8}Sr_{0.2}CoO_3$	$LaAlO_3$ (100)	LSC/LAO	-1.5	-1.9

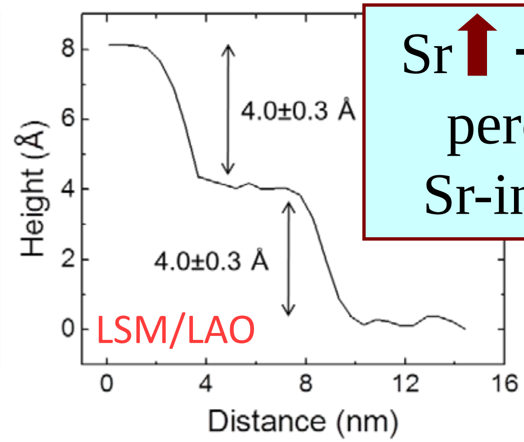




LSM and LSC thin film surface structure

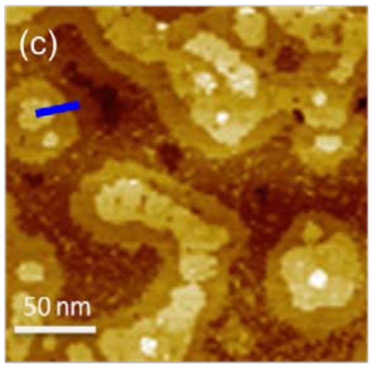


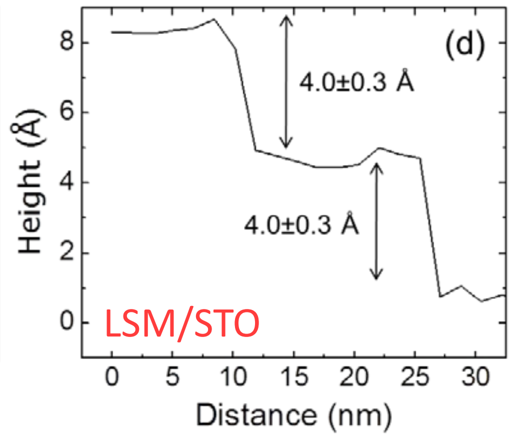




Sr⬆ → AO-terminated perovskite surface, Sr-increase on A-site

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





Jalili, Han et al., J. Phys. Chem. Lett. 2 (2011) 801-807

Cai et al. in review (2011)

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)

Objective: assess governing factors of OR activity

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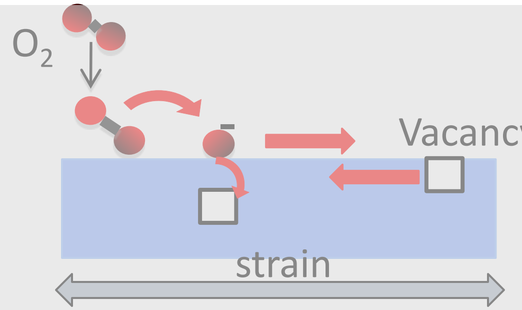
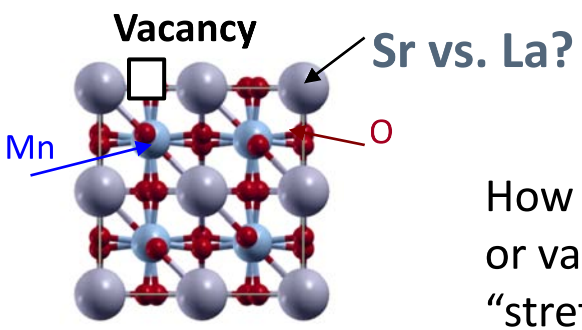
dense thin films, at high temperature



1) Chemical environment

→ a) Sr segregation,

b) oxygen vacancies

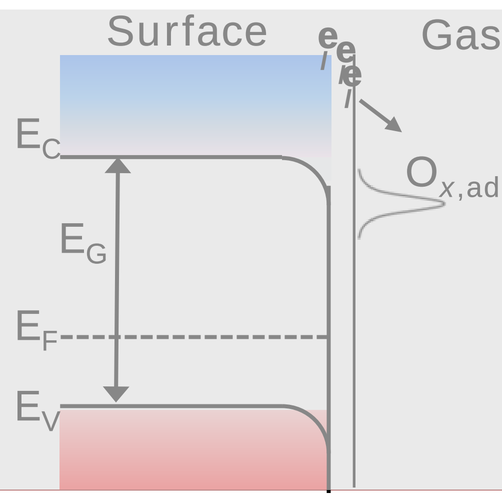


How much more Sr, or vacancies on a "stretched" surface?

2) Electronic structure

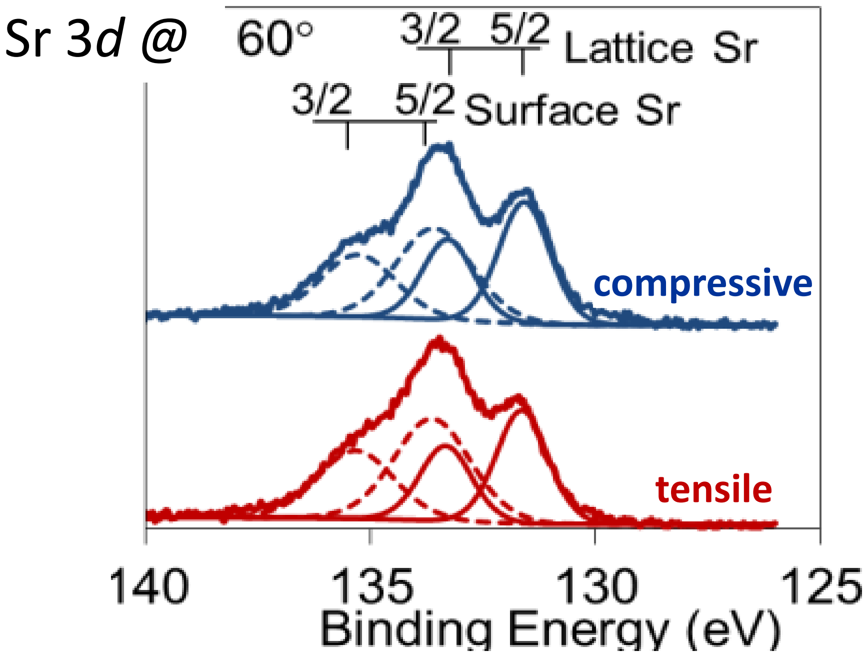
→ Energy gap,

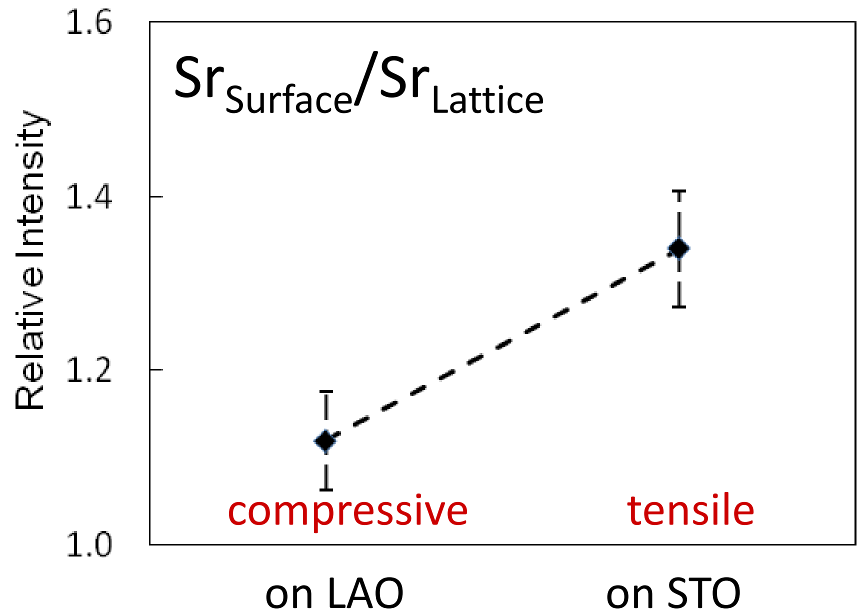
density of states at E_F



Facilitates electron transfer on the surface?

1-a) Strain-driven Sr enrichment on the A-site





- $Sr_{surface}$ on $La_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xCoO_3$
  Under-coordinated Sr on perovskite
  Sr-OH

van der Heide et. al
Chem. Phys. Lett. 1998, *297*.
Dupin, J.-C. et al.
Phys. Chem. Chem. Phys. 2000, *2*.
Hudson, L. et al.
Phys. Rev. B 1993, *47*.

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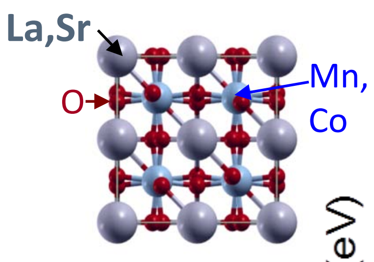
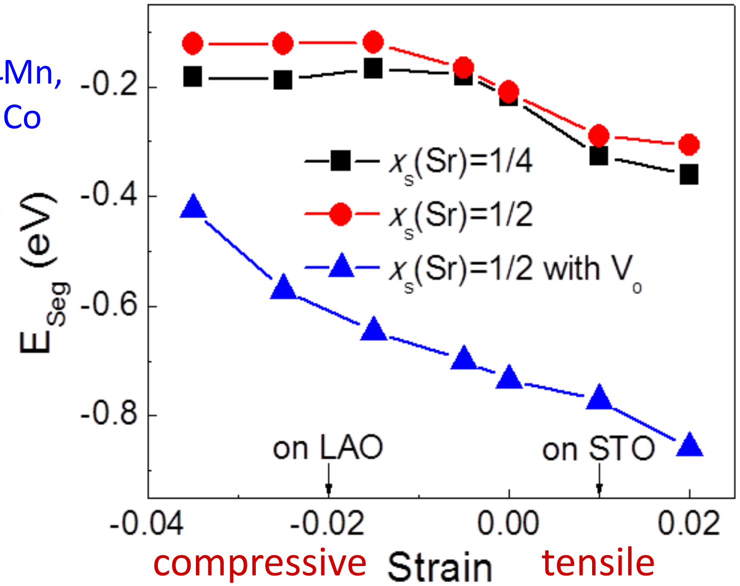
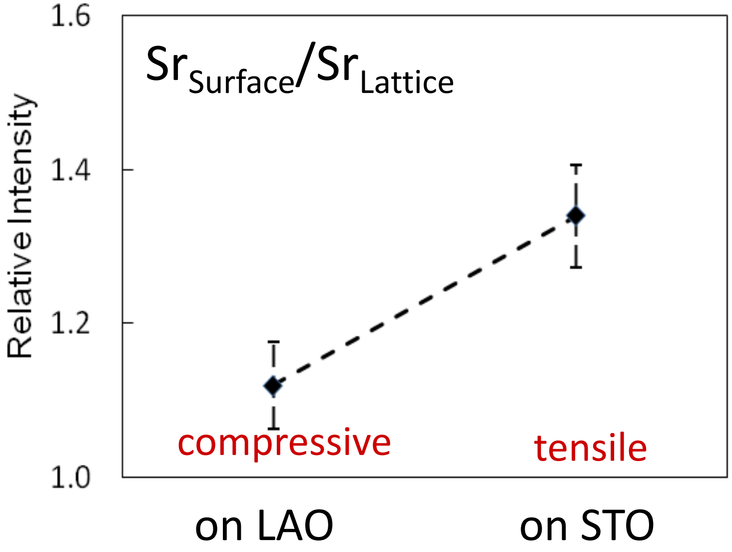


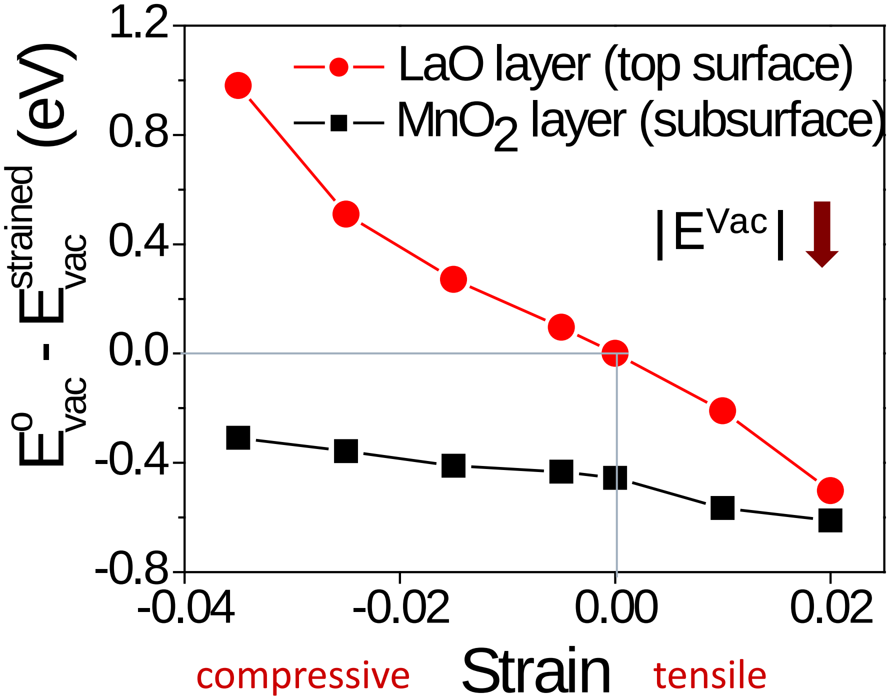
$|E^{Sr}_{seg}|$ ⬆

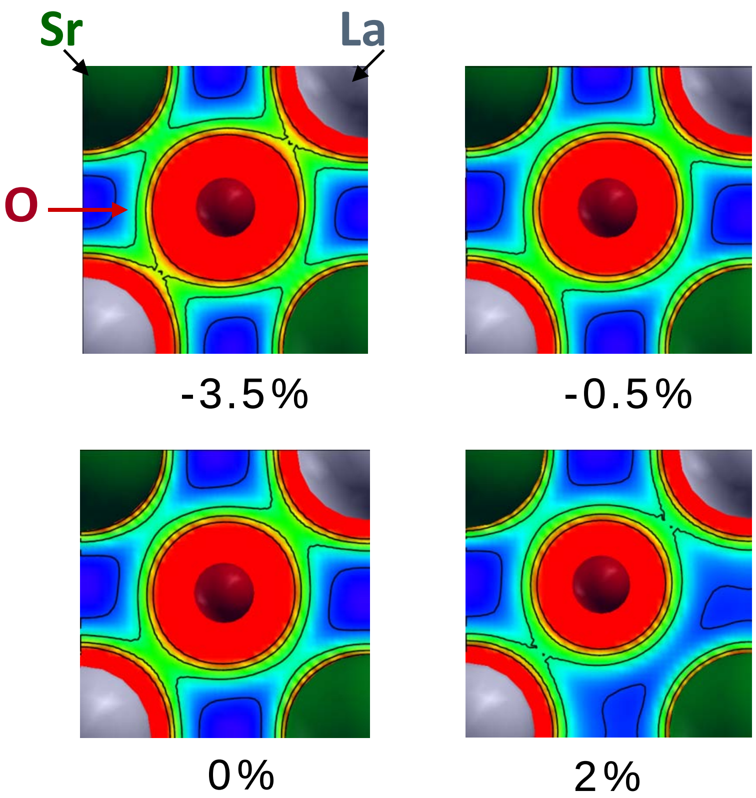




Jalili, Han et al., J. Phys. Chem. Lett. 2 (2011) 801-807

1-b) Strain-driven oxygen vacancy formation





- ☐ Vacancy formation is easier with tensile strain due to weaker cation-oxygen bonds in lattice.

Jalili, Han et al., J. Phys. Chem. Lett. 2 (2011) 801-807

Kushima, Yip and Yildiz, Phys. Rev. B. 82 (2010) 115435

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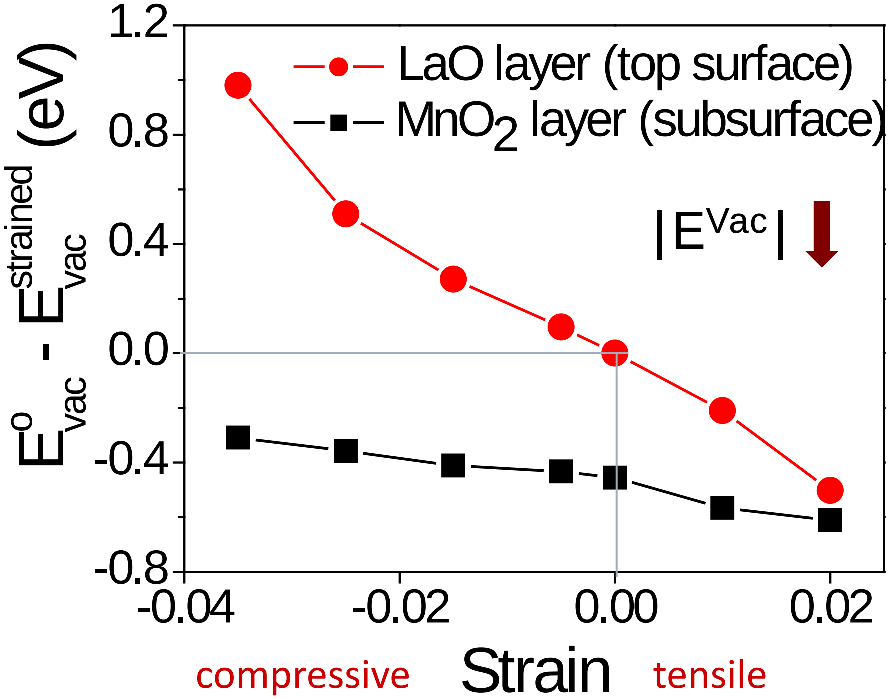

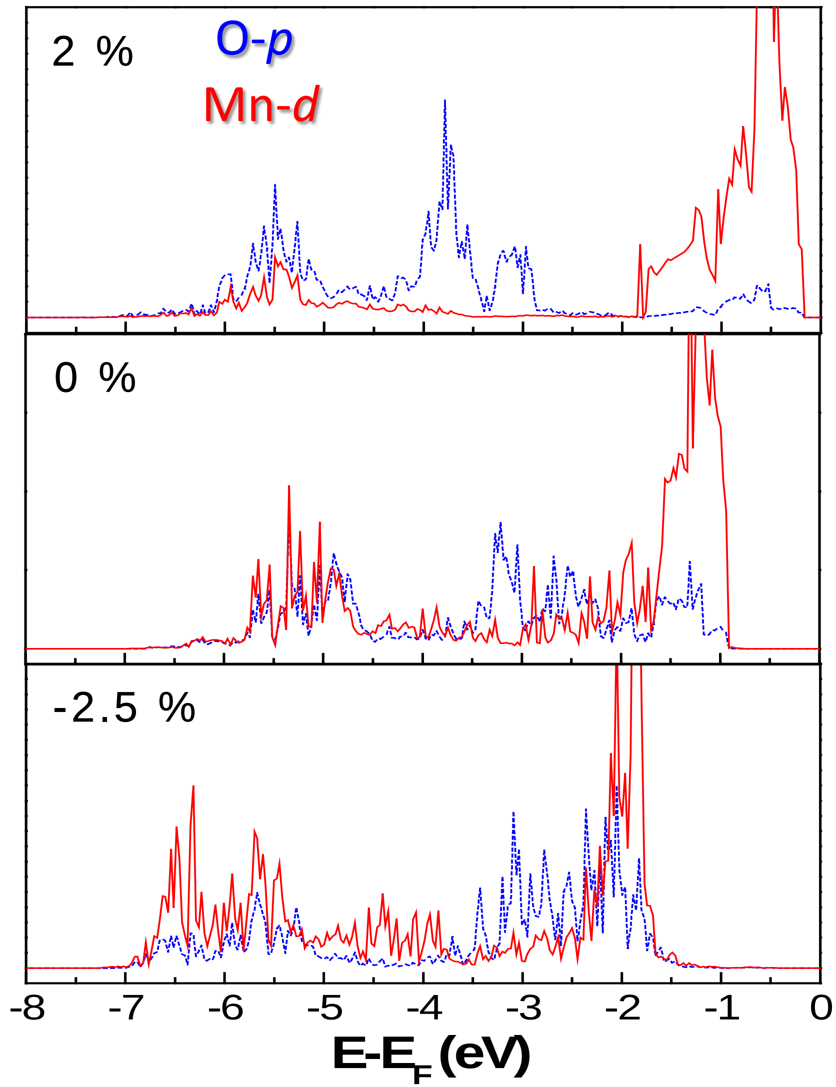

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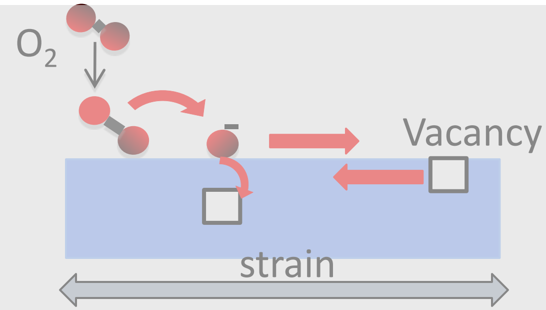

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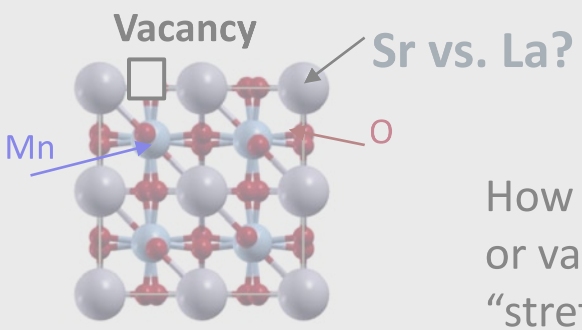

How much more Sr, or vacancies on a "stretched" surface?

2) Electronic structure

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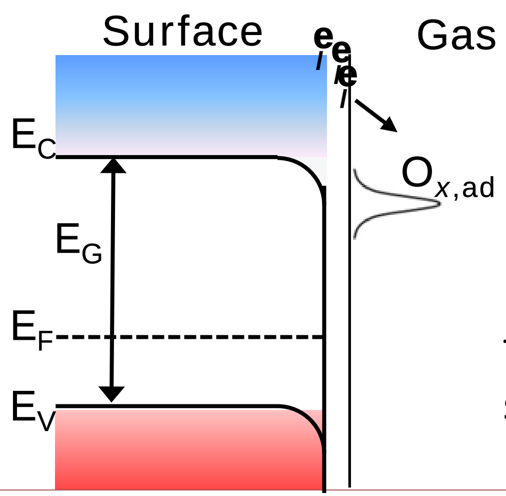
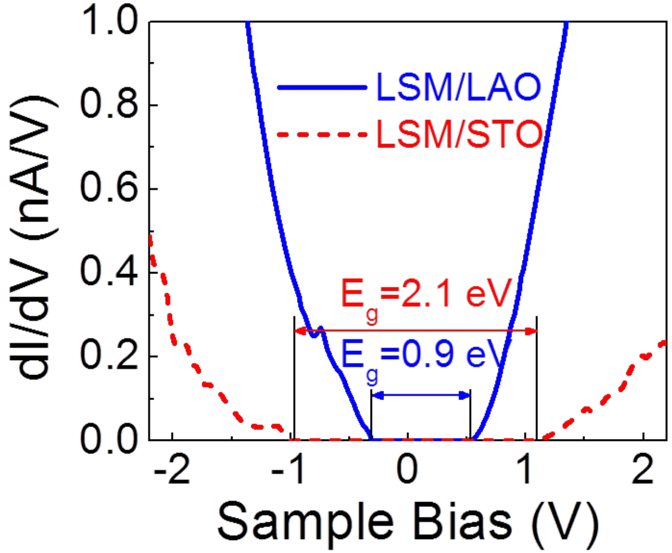


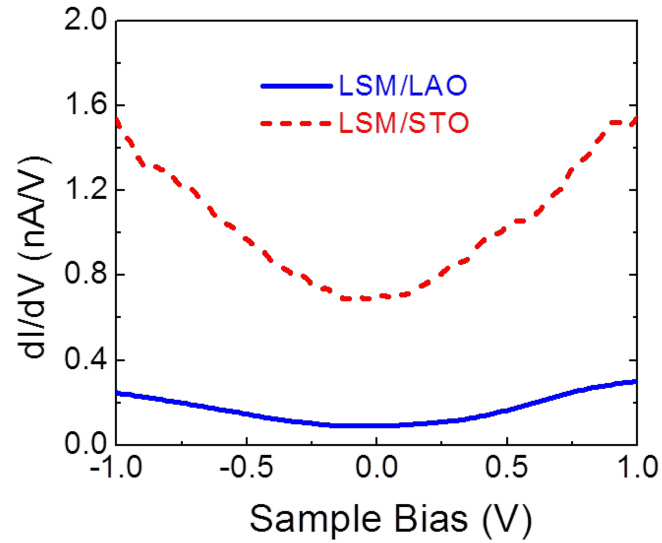
Facilitates electron transfer on the surface?

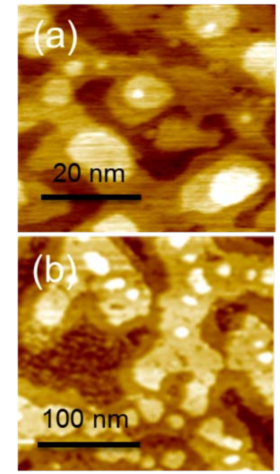
2) Surface electron transfer, reactivity; *f(T,ε)*

Tensile: E_g ⬆ **RT**



Tensile: DOS_{EF} ⬆ **500 °C**





A <u>reversible</u> gap-nogap transition at ~400 °C for LSM, at ~300 °C for LSC.

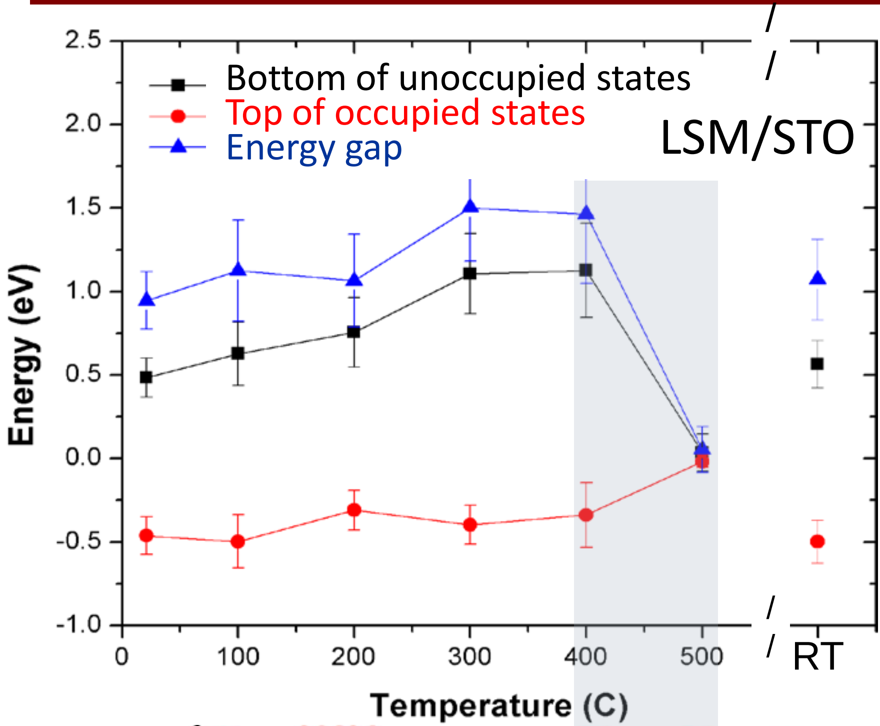
Larger density of states at E_f for tensile LSM and LSC.
→ reactivity favors tensile?

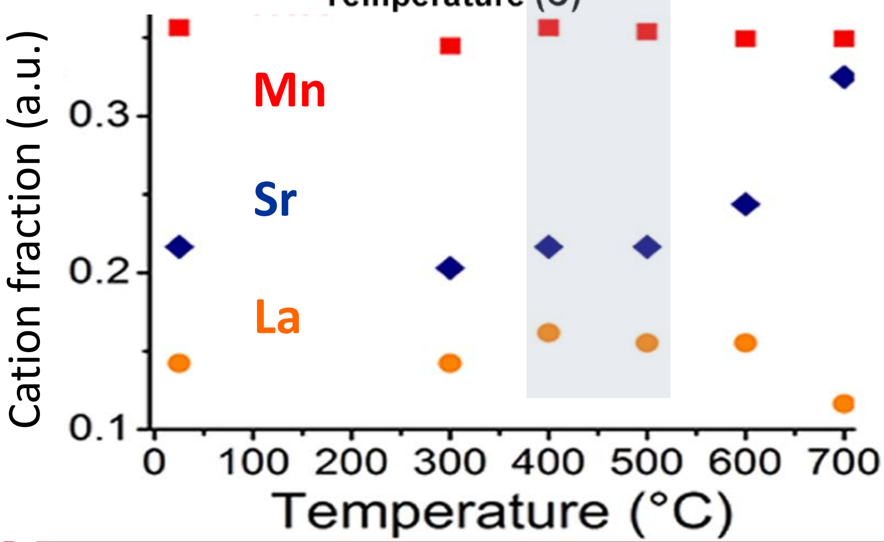
Feibelman and Hamann, Phys. Rev. Lett. (1984)
Yang and Parr, Proc. Nat. Acad. Sci. (1985).
Raccah and Goodenough, Phys. Rev. (1967).

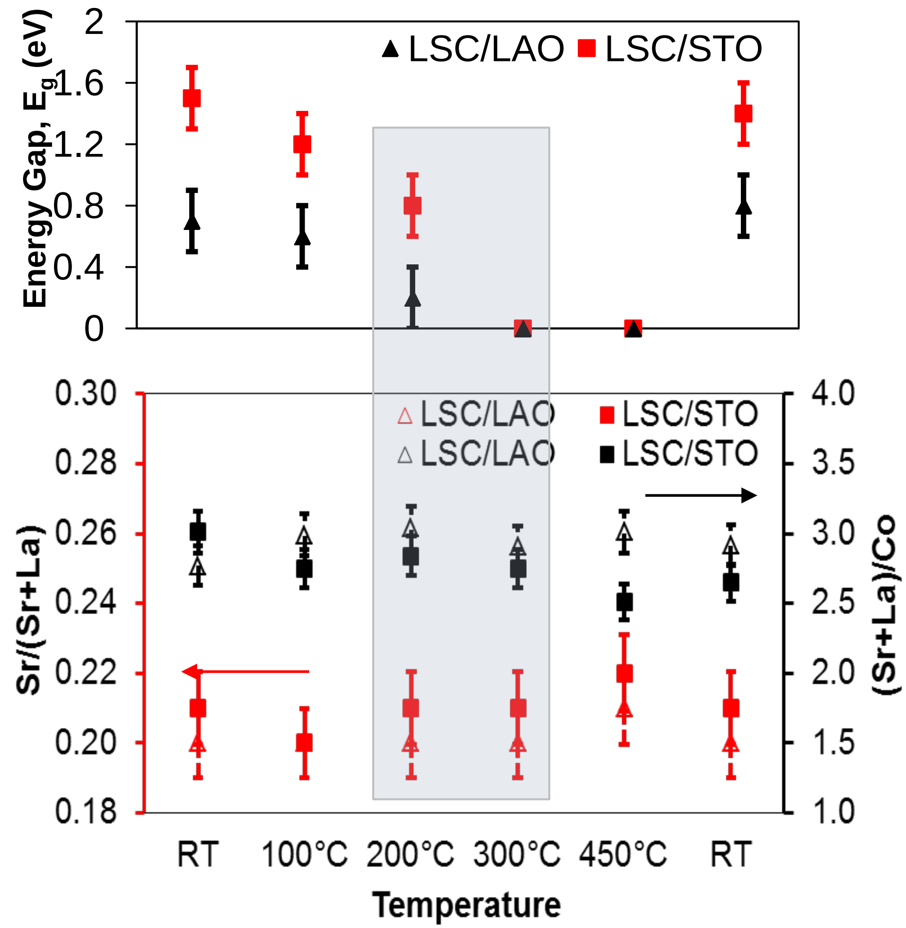
Role of the surface cation and anion chemistry? Restructuring?

Jalili, Han et al., J. Phys. Chem. Lett. 2 (2011) 801-807, Cai et al. in review (2011)

2) Surface electron transfer, chemistry; *f(T,ε)*







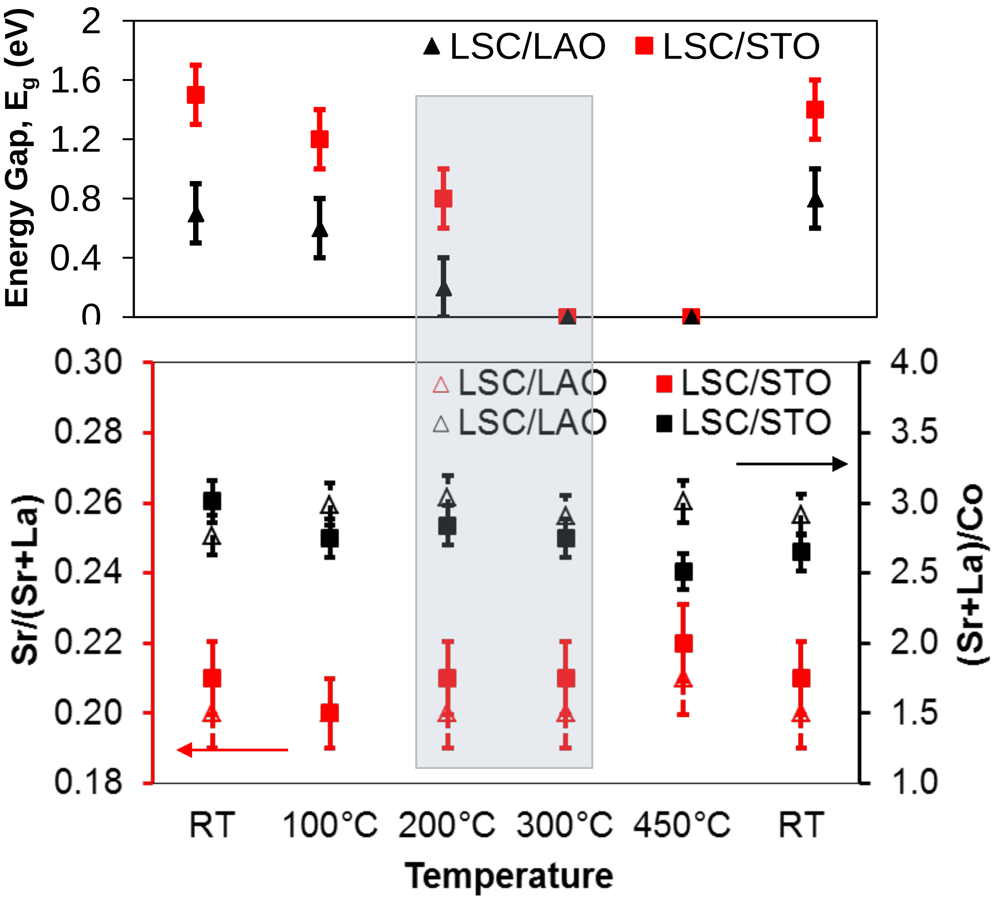
Cation chemistry same:

up to 300 ^{o}C for LSC

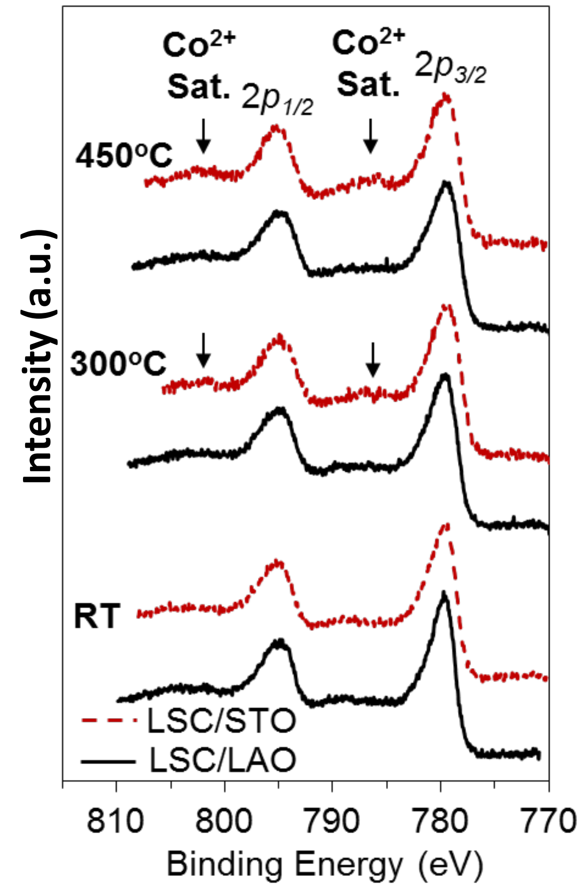
up to 500 ^{o}C for LSM

Cai et al. in review (2011)

2) Surface electron transfer, chemistry; *f(T,ε)*



Cation chemistry same up to 300 ºC.

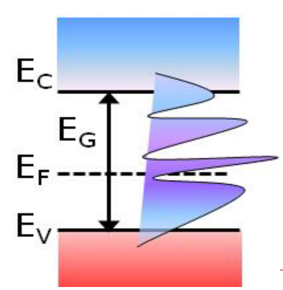


$Co^{3+/4+}$ → Co^{2+} favored for tensile.

Tensile: Vacancies ⬆

Oxygen vacancies → defect states in the gap.

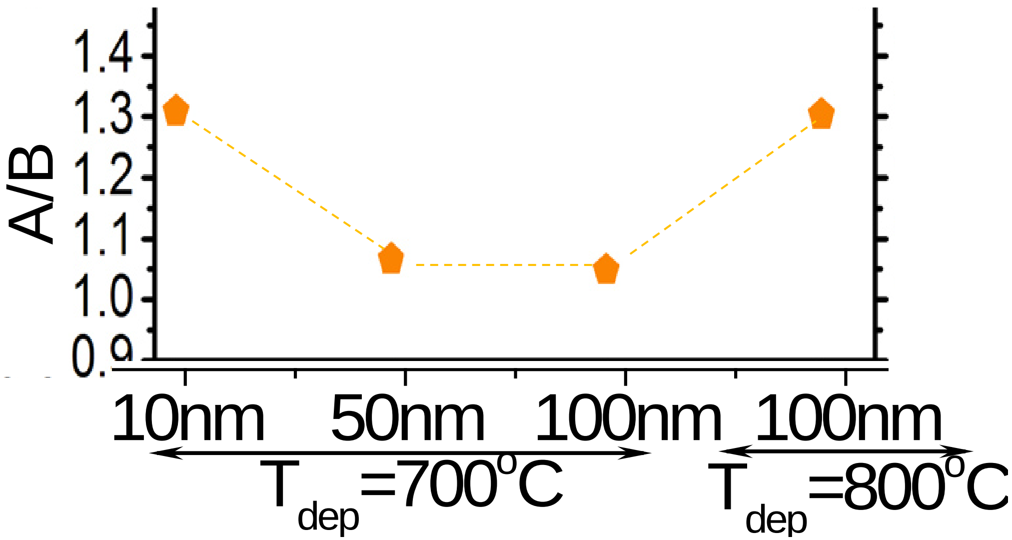
(Diebold et al., Ann. Rev. Phys. Chem. 61 (2010))

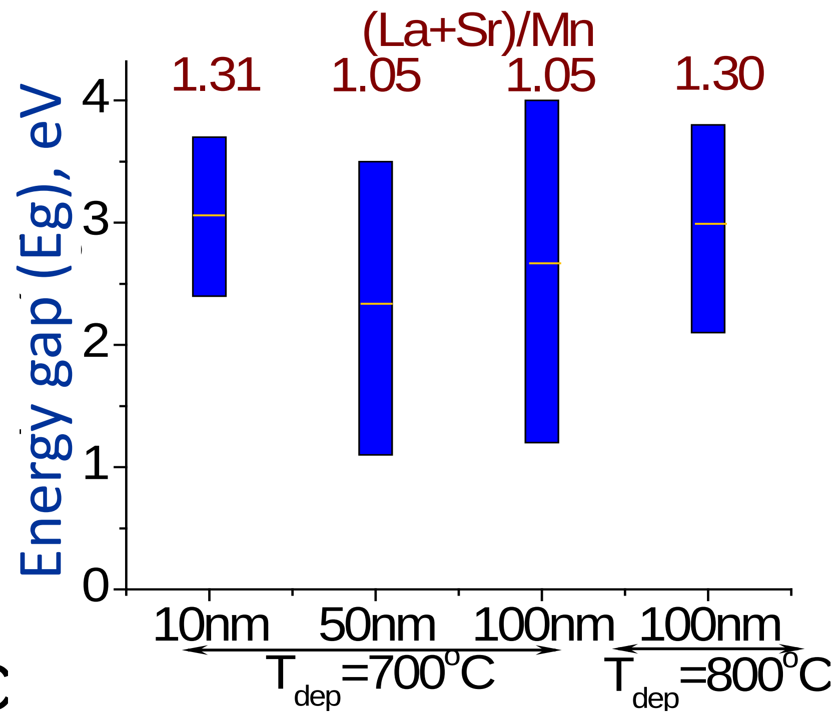


Cai et al. in review (2011)

Effect of thickness/strain on LSM/YSZ, *f(t,ε)*

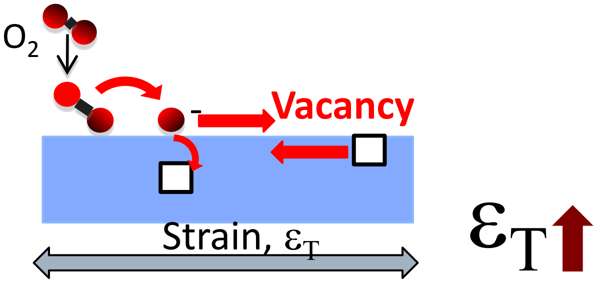
Surface cation chemistry, (La+Sr)/Mn



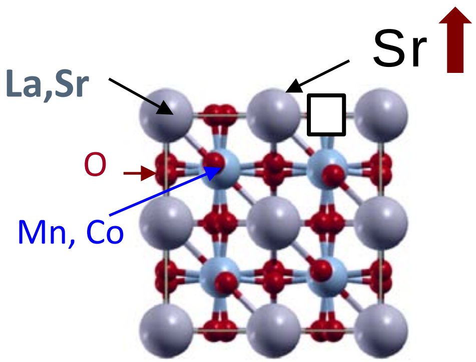


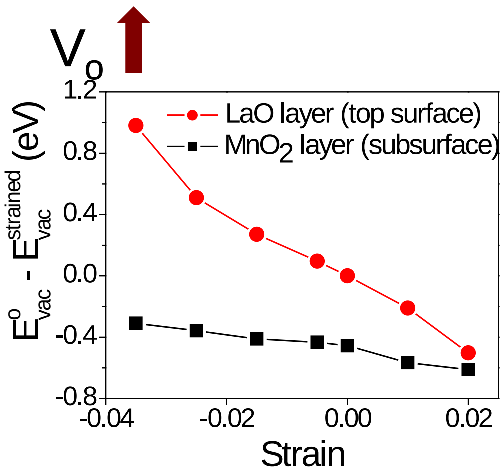
- Thickness↓, A/B↑, E_g↑.
- $T_{deposition}$↑, A/B↑, E_g↑.
- Lattice strain↑
- Substrate effect?

Surface chemistry, electronic structure, f(ε,T) – OR activity



- Sr enriches more with tensile strain on the A-site.





- Oxygen vacancy formation is easier with tensile strain.

300°C

tensile

compressive

- Electronic DOS at E_F is larger with tensile strain at high temperature; driven by oxygen vacancies.

Acknowledgements

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