Spectroscopic investigation of the impact of film thickness and post-growth treatment on the electronic structure of $La_xSr_{1-x}MnO-_3$ films

University of Nevada, Las Vegas
Department of Chemistry

S. Krause, T. Hofmann, and C. Heske, *Department of Chemistry, University of Nevada, Las Vegas, NV*
L. Yan, H. Du, B. Kavaipatti, and P. Salvador, *Carnegie Mellon University, Pittsburgh, PA*
H. Jalili, K. Katsiev, and B. Yildiz, *Massachusetts Institute of Technology, Cambridge, MA*

Objectives

CMU (sample growth) — MIT (local surface structure)

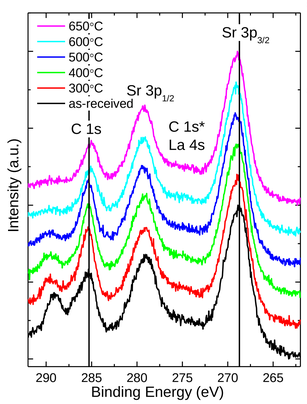
- samples
- information about growth conditions
- feedback on sample quality
- identification of contamination sources

- information on surface structure
- effect of heat and sputter treatment to surface
- chemical composition of surface vs. "bulk"
- valence level information (compare to STS)

UNLV (electronic structure, surface chemical composition)

- find a surface that allows study of occupied and unoccupied states with respect to a common reference (Fermi energy, vacuum level)
- investigate effect of temperature and pO_2 on surface chemical composition and electronic structure
- correlation with theory

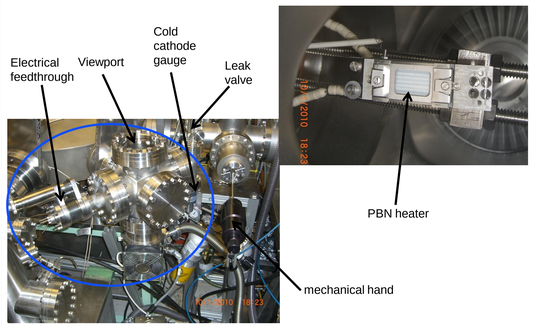
Ex-situ treatment

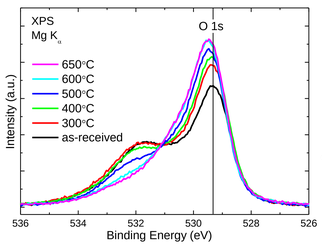


- Decrease of $SrCO_3$-related C 1s/O 1s peak
- Shift of about 0.2 eV for O 1s main peak and Sr 3p to higher E_B
- C 1s main peak shifts to lower E_B

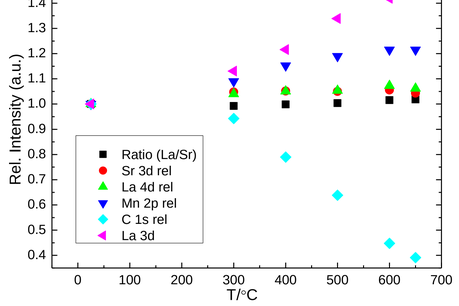
→ No complete reduction of C 1s
→ Combined with mild sputtering

Ex-situ treatment chamber

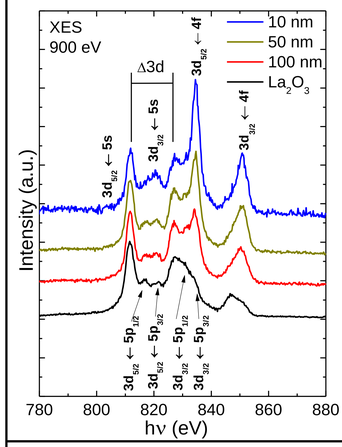




- La/Sr ratio stays constant up to 500°C, then it increases by 3-4%. (corroborates earlier annealing experiment to 800°C in air, 20% increase)
- Mn 2p and La 3d increase due to C 1s decrease and corresponding decrease in energy dependent signal attenuation due to carbon overlayer.

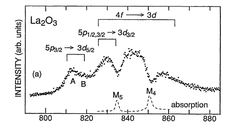


Thickness dependency

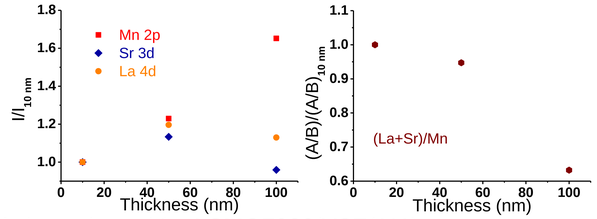


- Besides La M-edge, XES data shows no obvious thickness dependence
- Comparison to La_2O_3 shows mostly similar emission spectrum (two right peaks have different shape)
- Relative intensity between peak series 1 (800-830 eV) and 2 (830-860 eV) changes with thickness

→ possible self-absorption effect



Journal of the Physical Society of Japan
Vol. 64, No. 1, January, 1995, pp. 192–199

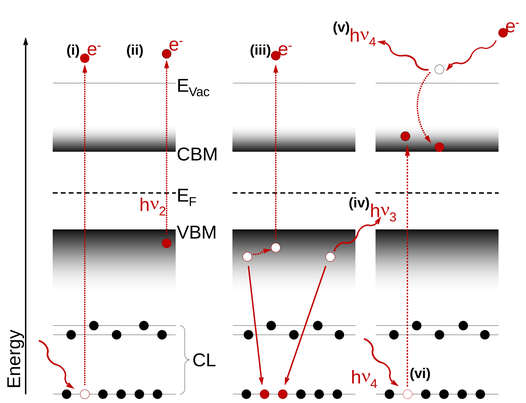


- Only investigated for LSMO7030/YSZ(111)
- Sr and La show only small variations with thickness
- Mn signal significantly increases with increasing film thickness
- A/B ratio decreases with increasing thickness

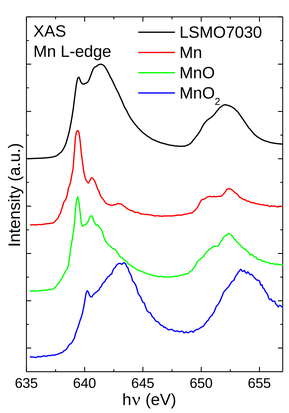
Experimental Methods

(i) XPS (X-ray Photoelectron Spectroscopy)
(ii) UPS (UV Photoelectron Spectroscopy)
(iii) AES (Auger Electron Spectroscopy)
(iv) XES* (X-ray Emission Spectroscopy)
(v) IPES (Inverse Photoemission Spectroscopy)
(vi) XAS* (X-ray Absorption Spectroscopy)

* performed at the Advanced Light Source, Lawrence Berkeley National Laboratory



Mn oxidation state



Mn_3O_4

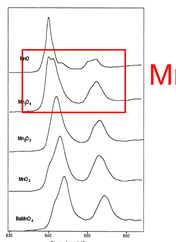


FIG. 3. Manganese $L_{2,3}$-edge spectra from five studied oxides after deconvolution of multiple loss events and background subtraction.

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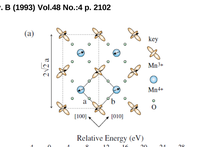
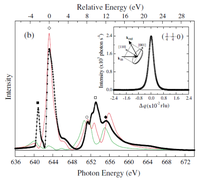
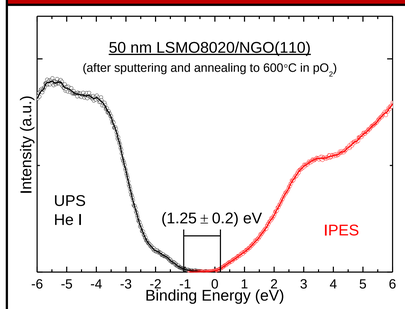




PRL (2004) Vol.92 No.:5 056403

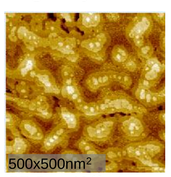
Ansatz:
Measurement of XAS spectra of various oxidation states of Mn and comparison
→ measurements corroborate literature data
→ Mixture of Mn^{3+} and Mn^{4+}

Valence Electronic structure – ex situ

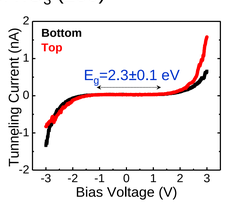


- First combined UPS and IPES spectrum
- Smallest gap found: 1.25 (±0.20) eV
- More measurements for different thicknesses, preparations and substrates needed

Single crystal LSMO on $SrTiO_3$ (100)



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

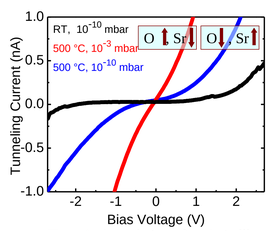


No phase separation

Repeatable electronic structure

→ Single crystal LSM surface is suitable for investigation of surface segregate structure using STM and XPS.

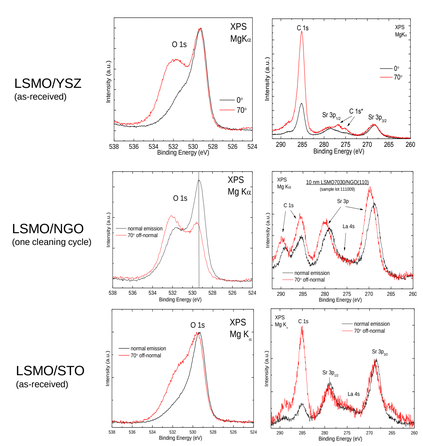
Ex-situ vs. in-situ



T ↑ Insulator → Metallic

PO_2 ↑ $\sigma_{tunneling}$ ↑

Surface termination



- All surfaces terminated with a strontium oxide, except for NGO substrate with strontium carbonate
- Different geometrical surface structure might be responsible → LEED