Thin-film Cathode Fabrication and Characterization

Paul A. Salvador

Department of Materials Science and Engineering,
Carnegie Mellon University, Pittsburgh, PA, 15213

Institute for Advanced Energy Solutions,
National Energy Technology Laboratory
Pittsburgh, PA, 15236
Morgantown, WV, 26507

SECA Review
July 15, 2009

RDS-NETL : Briggs White and Wayne Surdoval

Acknowledgements

K. R. Balasubramanian, Lu Yan, Shanling Wang, and Hui Du
Lam Helmick, Shen Dillon, R, Petrova, Sridhar Seetharaman, Greg Rohrer
Robin Chao, John Kitchin
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA

Randy Gemmen, Kirk Gerdes, Chris Matranga
Lane Wilson and Chris Johnson
National Energy Technology Laboratory, Morgantown WV and Pittsburgh, PA

Bilge Yildiz
Department of Nuclear Science and Engineering, Massachusetts Institute of Technology

Stefan Krause and Clemens Heske
Department of Chemistry, University of Nevada Las Vegas

Tim T. Fister, Dillon D. Fong, Jeffrey A. Eastman, Peter M. Baldo, Matthew J. Highland,
Paul H. Fuoss, Kee-Chul Chang, H. You, Terry Cruse, Brian Ingram, and Michael Krumpelt
Materials Science Division, Argonne National Laboratory, Argonne, Illinois

Special thanks to
Wayne Surdoval and Briggs White
DOE-SECA Programs

Outline

- Microstructural Characterization
  - Activity / Stability Issues
  - Oxygen Reduction Reaction

- Cathode Surface Fabrication / Characterization
  - Thin Film Geometry Synthesis
  - Combined Thin Film Property Measurements

- Electrical Conductivity Relaxation on LSM
  - Film Structures and Properties vs Bul
  - Orientation Dependence of oxygen uptake
  - Temperature Dependence of oxygen uptake
  - Substrate Dependence of oxygen uptake

Outline

- **Microstructural Characterization**
  - **Activity / Stability Issues**
  - **Oxygen Reduction Reaction**

- Cathode Surface Fabrication / Characterization
  - Thin Film Geometry Synthesis
  - Combined Thin Film Property Measurements

- Electrical Conductivity Relaxation on LSM
  - Film Structures and Properties vs Bul
  - Orientation Dependence of oxygen uptake
  - Temperature Dependence of oxygen uptake
  - Substrate Dependence of oxygen uptake

Solid Oxide Fuel Cells

•Performance of SOFCs depend on microstructure of electrochemically active regions

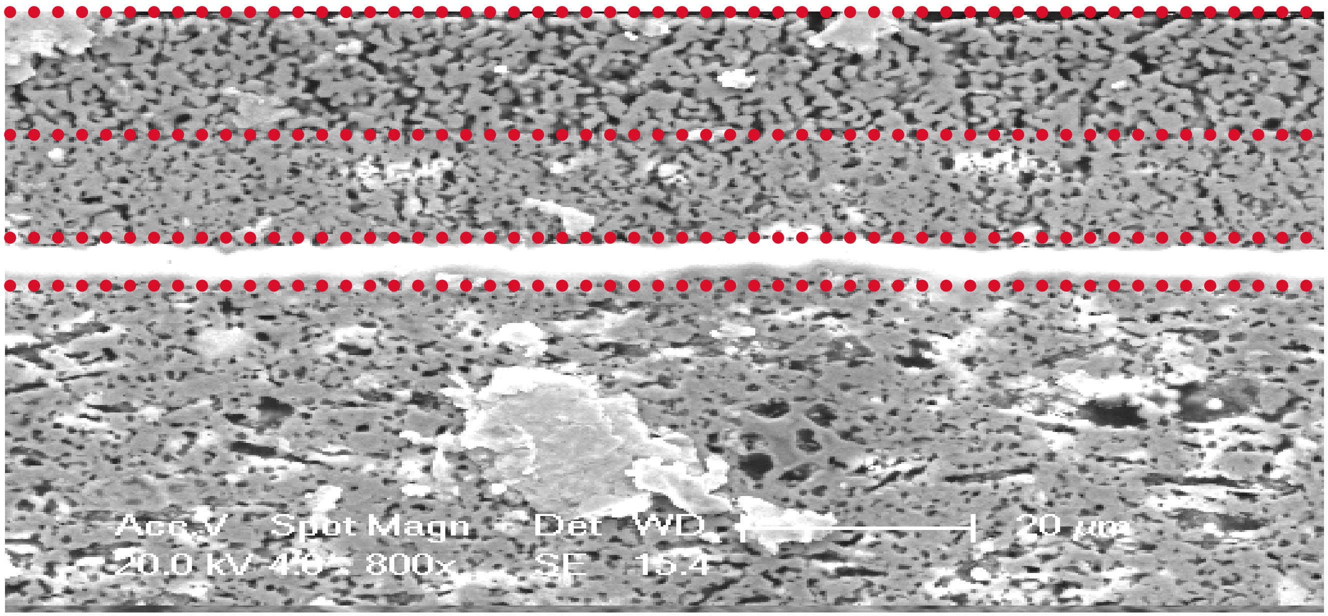
three-phase composite
each interpenetrating 3D-connected
electrochemical reaction occurs at or near triple points

Current Collector
Pores + (La,Sr)MnO_3

Active Cathode
P + LSM + YSZ

Electrolyte (YSZ)

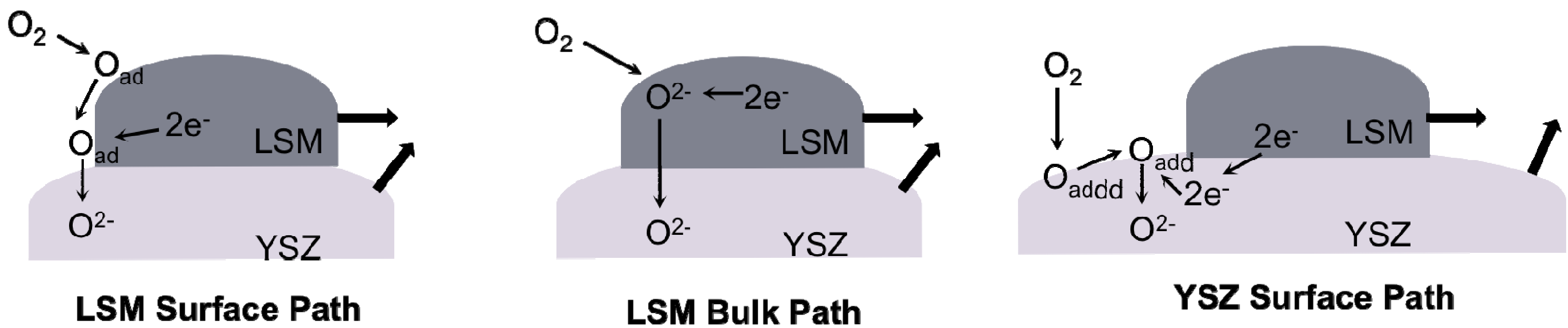
Anode
P + YSZ + NI



SEM from CMU of NETL prepared SOFC
R. Petrova, Y. Cao, S. Seetharaman, G. Rohrer, P. Salvador, R. Gemman, C. Johnson, L. Wilson

Oxygen Reduction Reaction

$1/2\ O_2(g)$	$+\ 2e^-$	$\rightarrow$	O^{2-}
pore	*conductor*		*ion conductor*



- ***Surface Processes***
  - ***Adsorption***
  - ***Electron Transfer***
  - ***Incorporation***

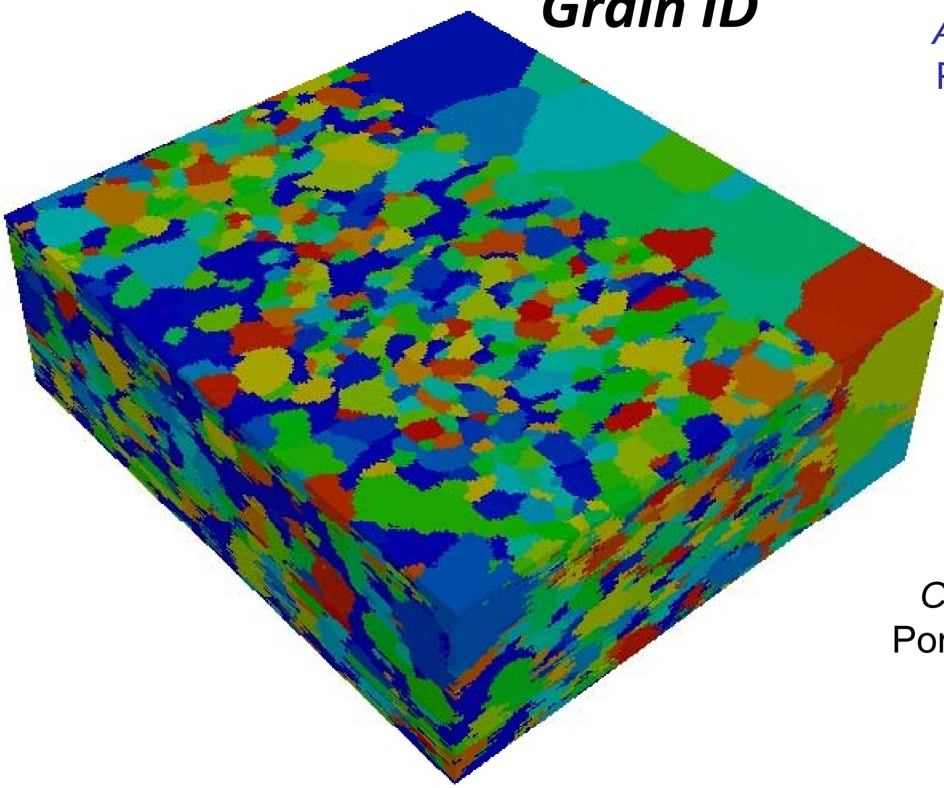
- ***Bulk Processes***
  - ***Electron Transport***
  - ***Ion Transport***
  - ***Long Term Stability***

Can we understand / engineer highly-active and stable surfaces?

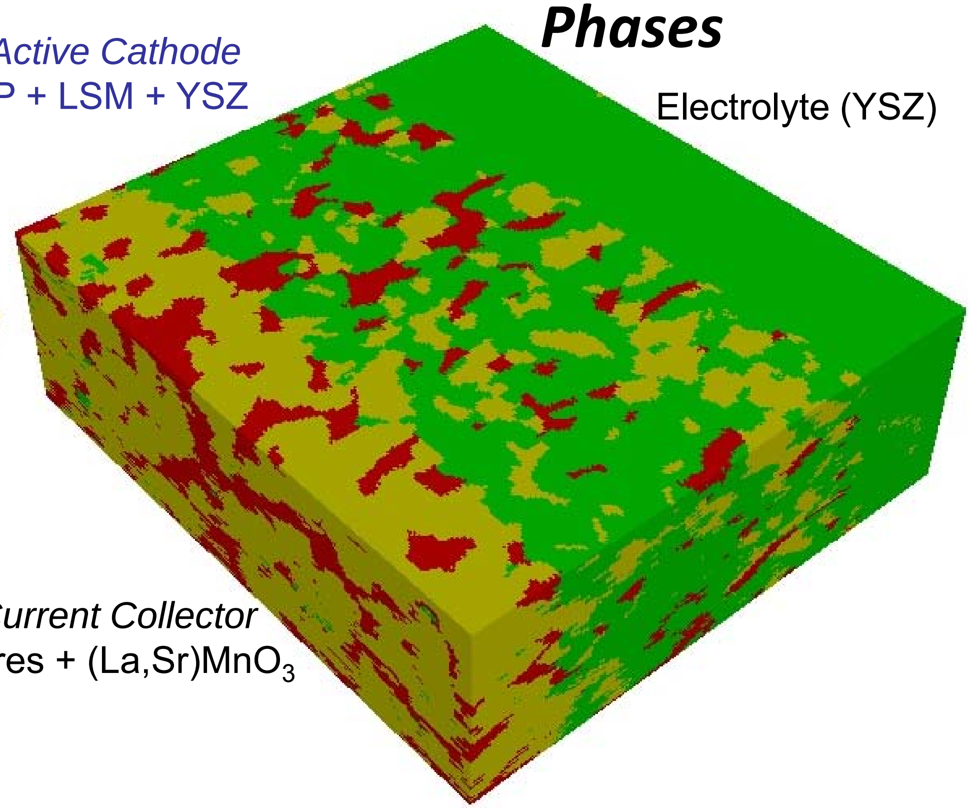
Solid Oxide Fuel Cell Microstructure

FIB with scanning electron microscope (SEM) and
electron backscattered detector (EBSD)
to acquire crystallographic orientation data in 3D

Grain ID

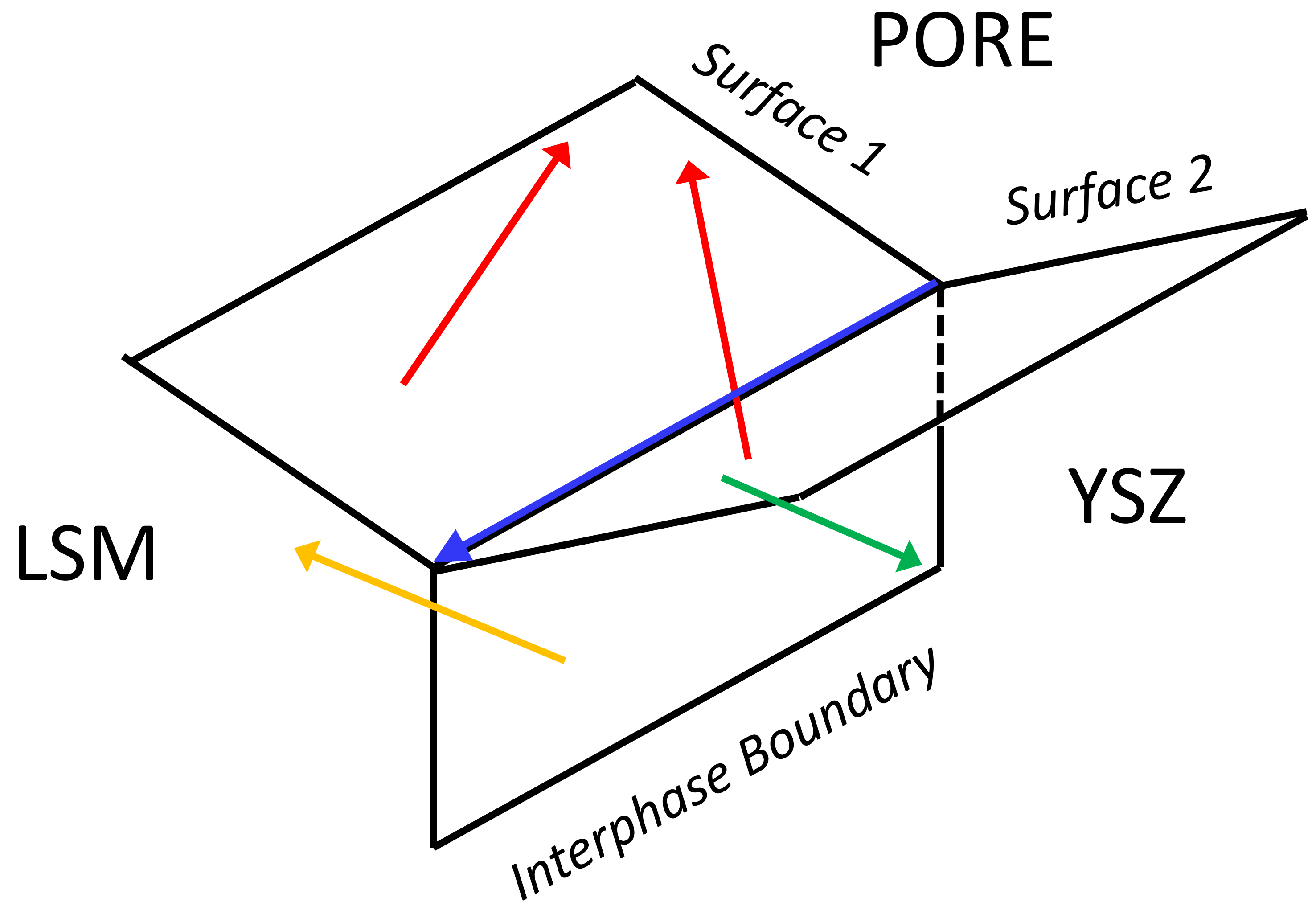


Phases

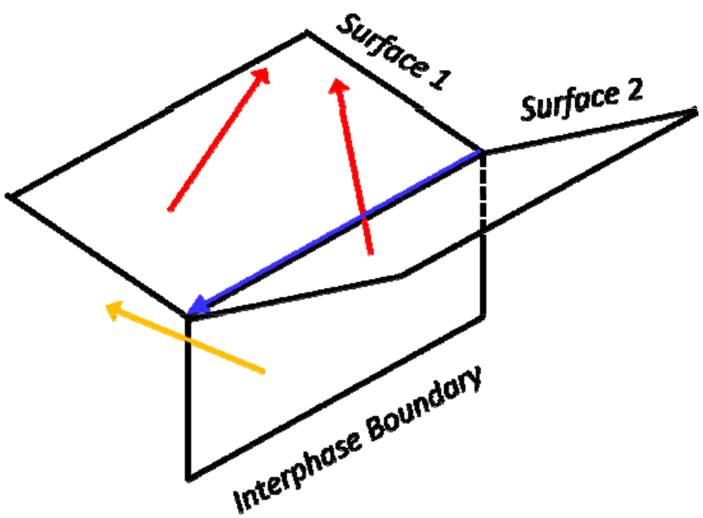


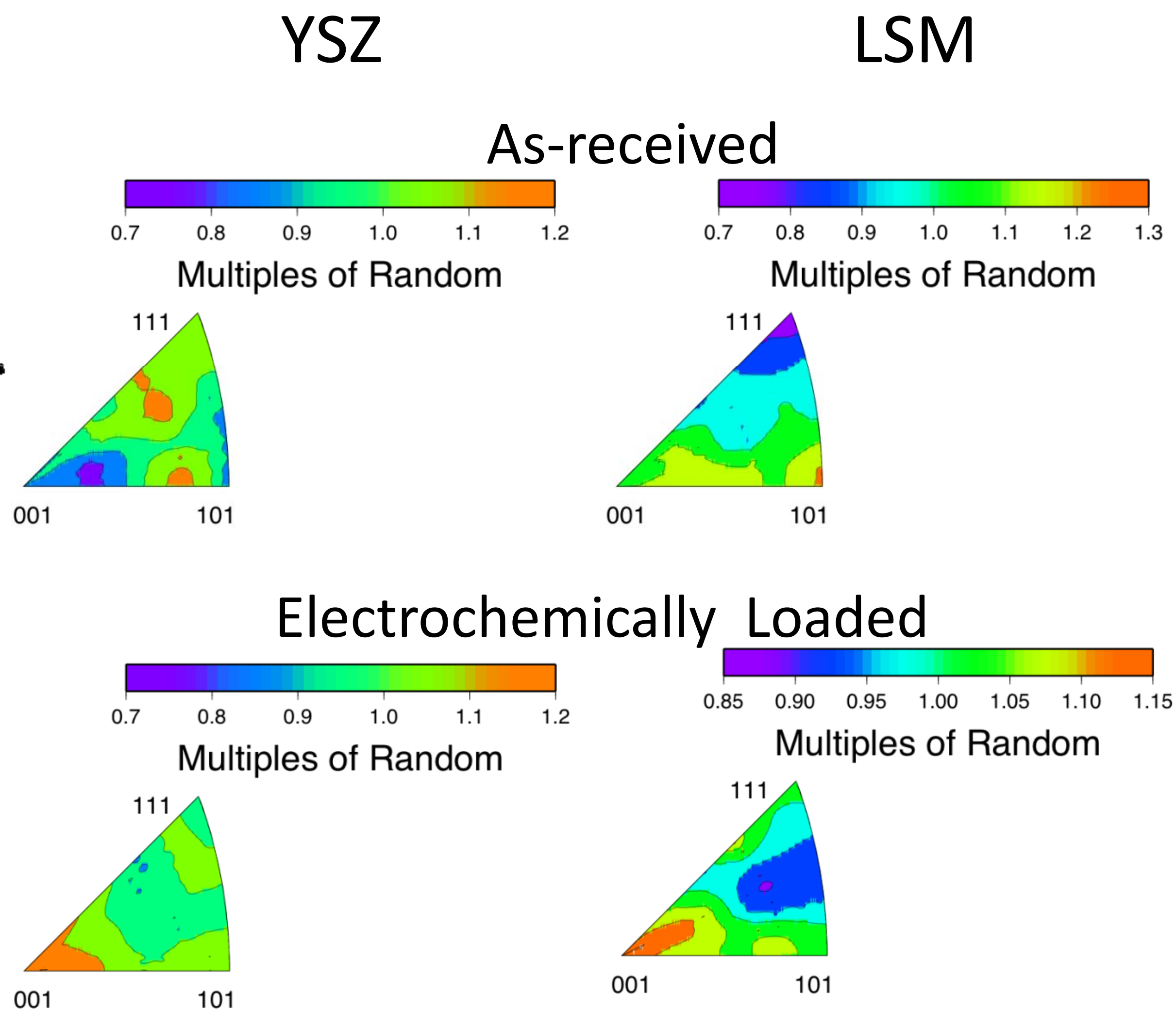
3D OIM from CMU of NETL prepared SOFC
S. Dillon, L. Helmick, G. Rohrer, P. Salvador, R. Gemman, C. Johnson, L. Wilson

Definitions near triple phase boundary



What kind of surfaces ARE present?

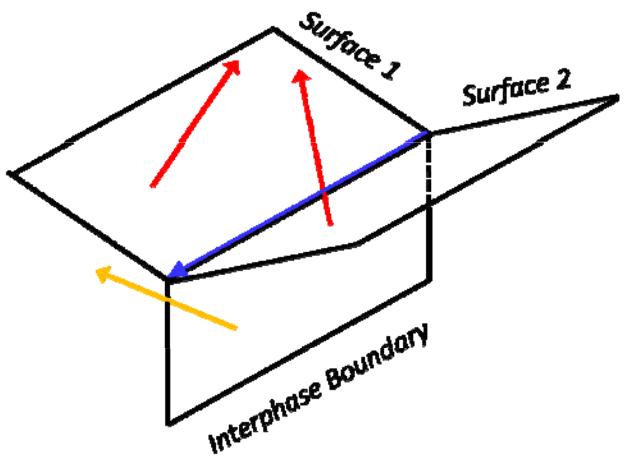




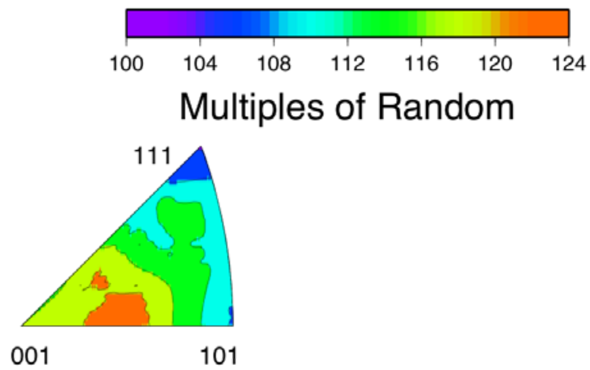
3D Analysis from CMU of NETL prepared SOFC

S. Dillon, G. Rohrer, P. Salvador, R. Gemman

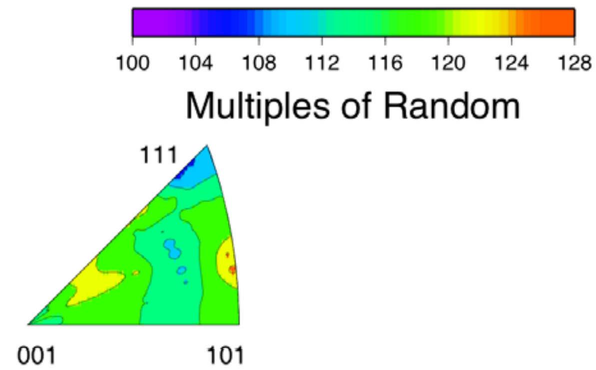
Why are those kinds of surfaces ARE present?



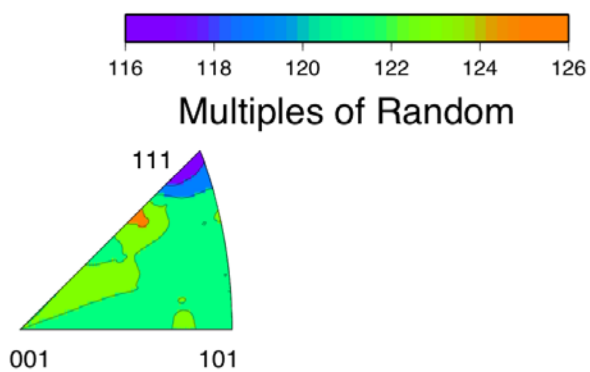
YSZ

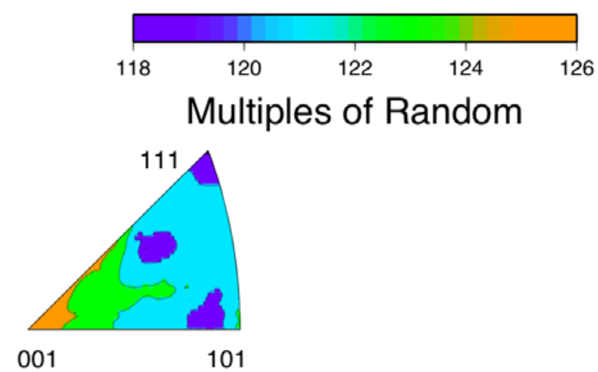


LSM



As-received





Electrochemically Loaded

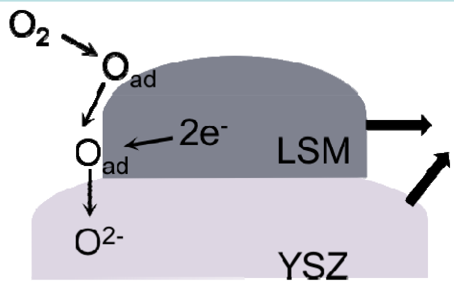
3D Analysis from CMU of NETL prepared SOFC

S. Dillon, G. Rohrer, P. Salvador, R. Gemman

Solid Oxide Fuel Cell Microstructure

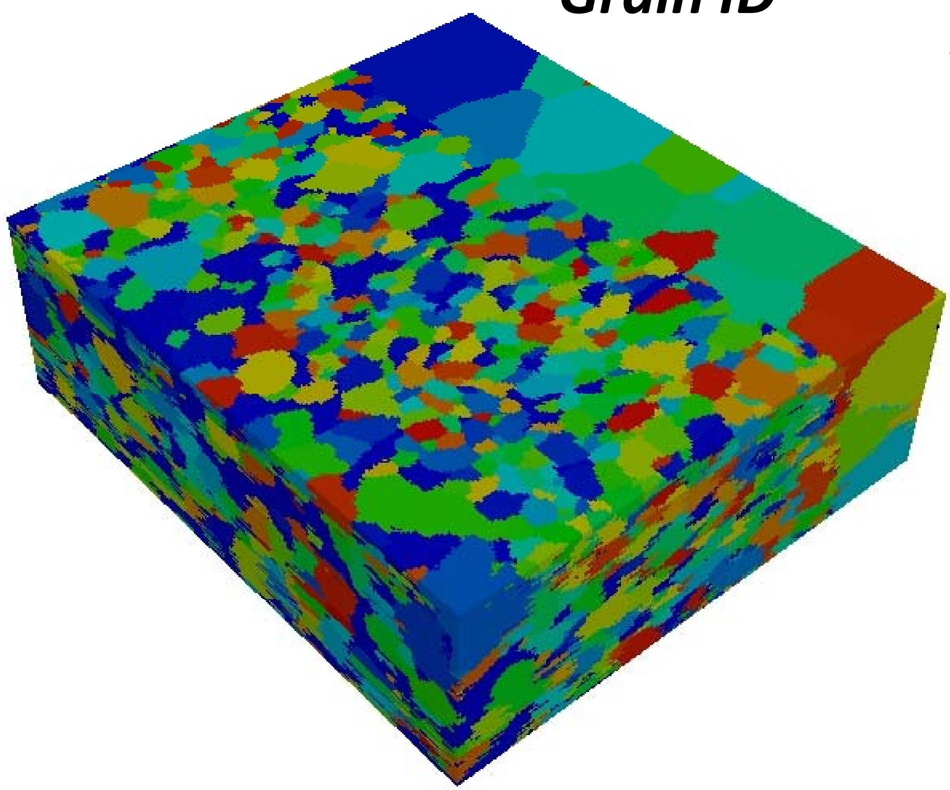
Can Map Crystallography AND Microstructures
in Complex Systems !

What are the local CONDITIONS and local Properties?

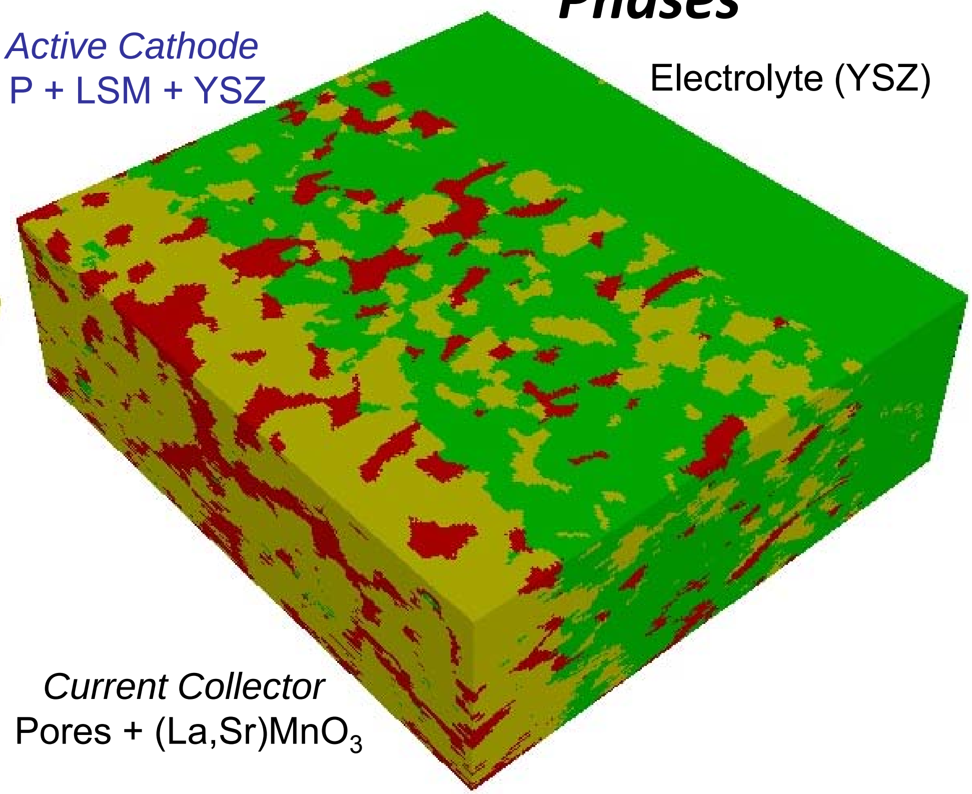


LSM Surface Path

Grain ID

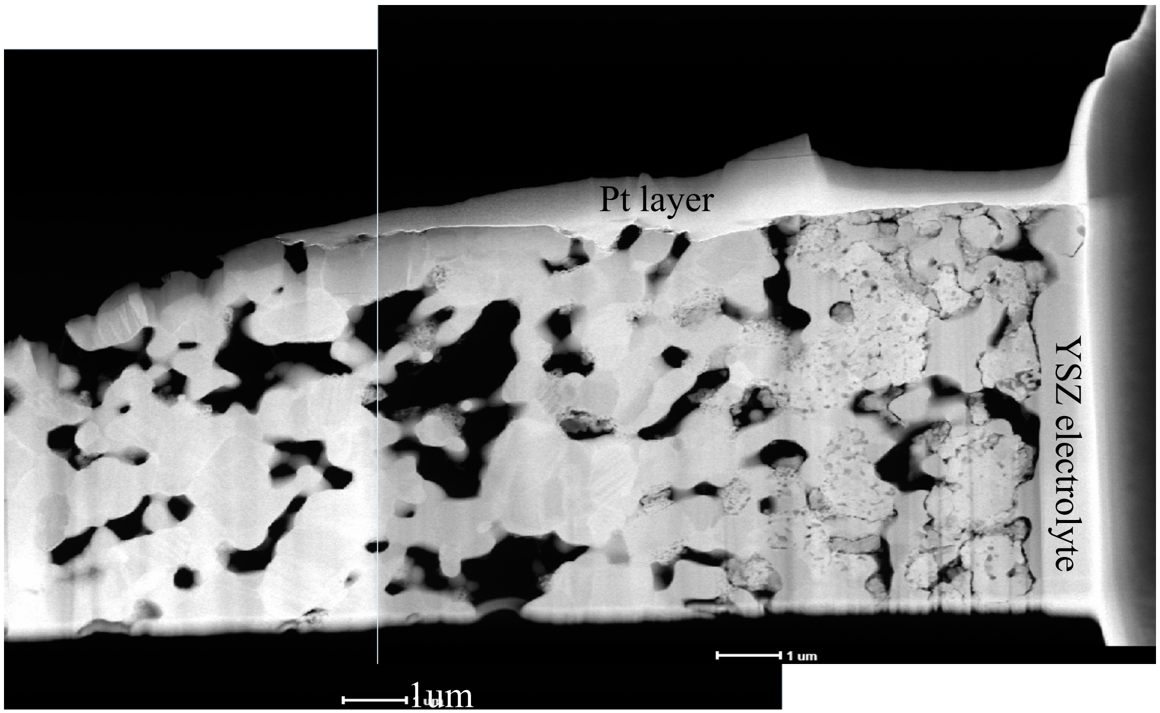


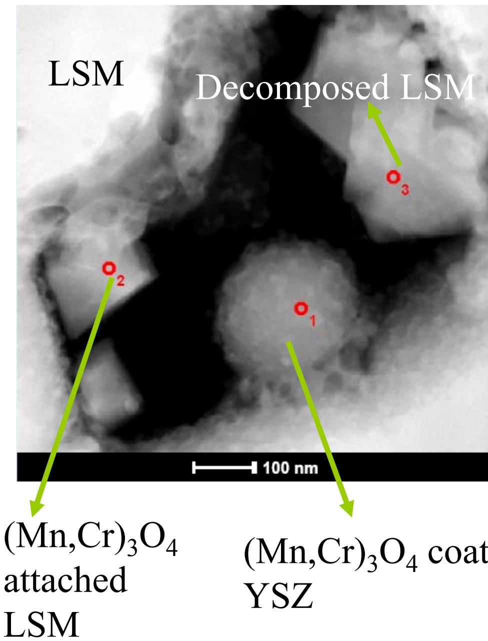
Phases



TEM Study of Degradation

- 700°C, E-brite, 2.3 A, 380% ΔV/10000hr, channel





TEM from CMU of ANL prepared SOFCs

S. Wang, P. Salvador, T. Cruse, B. Ingram, M. Krumpelt

Microstructure Degradation is Related to
Electrochemical Reaction of Chromium Vapors that is Spatially Varying

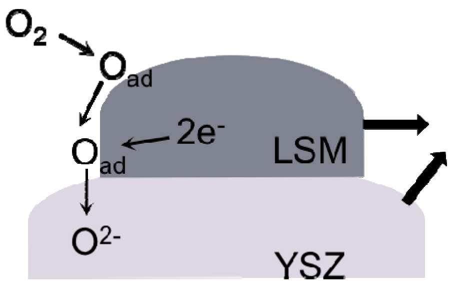
Cruse, T. A.; Krumpelt, M.; Ingram, B.; Wang, S.; Salvador, P. A.
In TMS 2008 Annual Meeting Proceedings Volume 1: Materials Processing and Properties, 2008; pp 571-580.

Solid Oxide Fuel Cell Microstructure

Long Term Basic Science Goal to

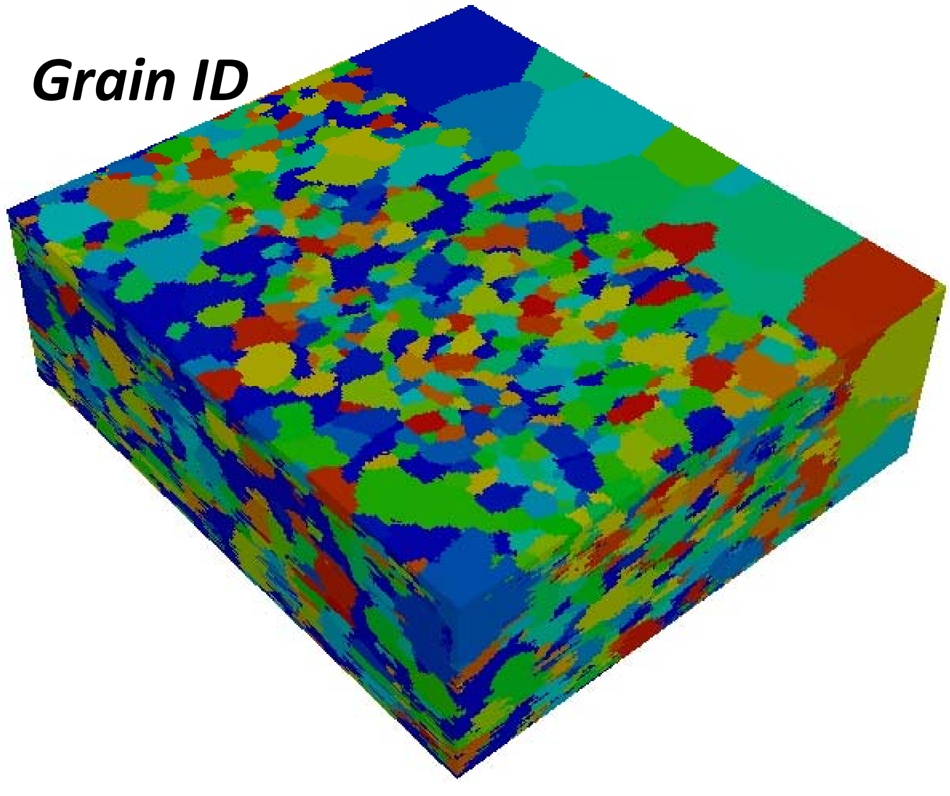
Predict/Model Performance using

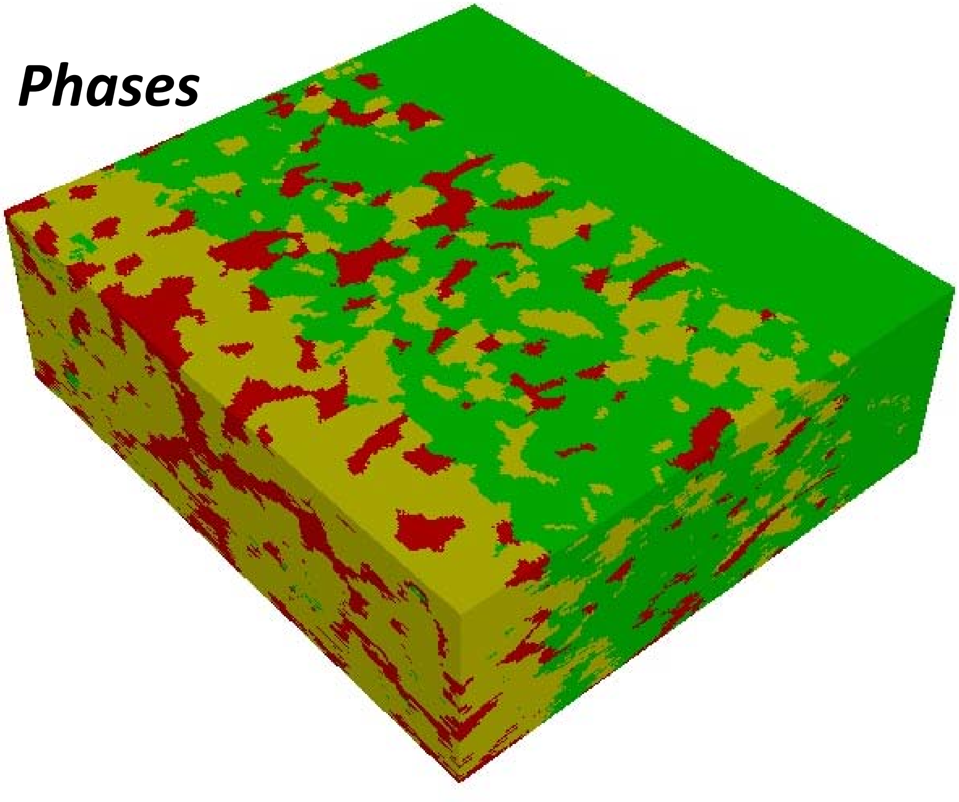
Structural and Material Parameters!



LSM Surface Path

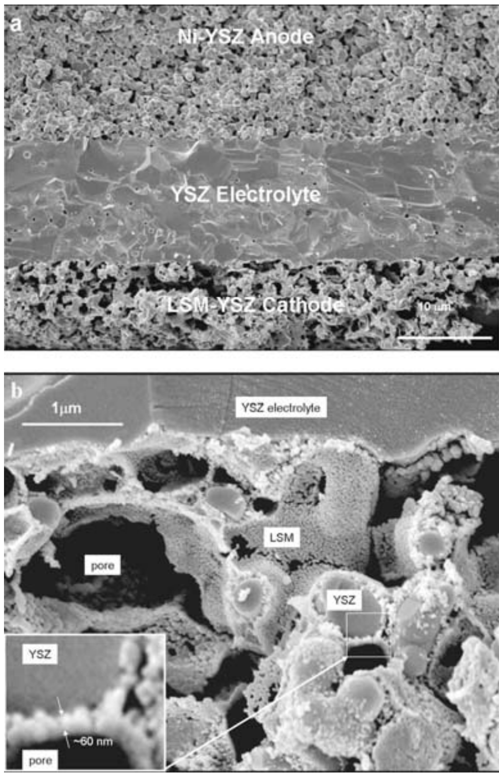
What are the surface related materials parameters?





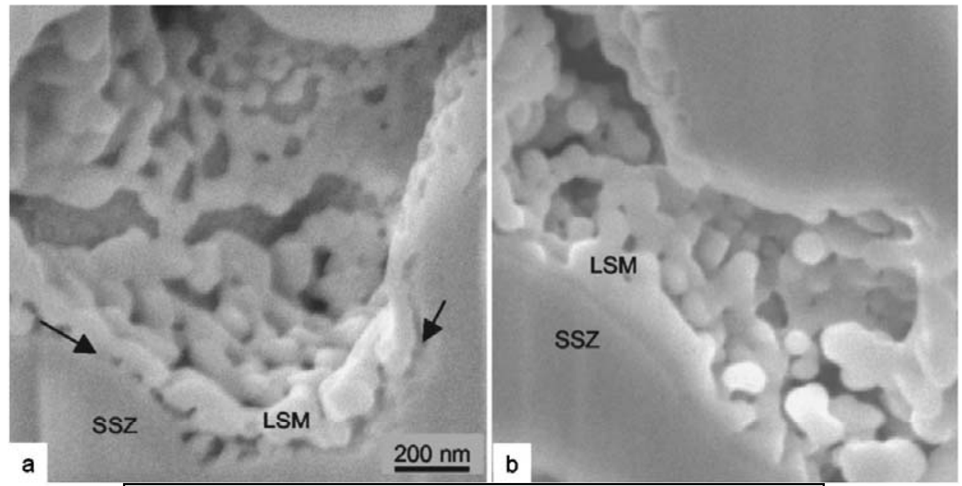
Nanoparticles can be used in Extreme Conditions

As-synthesized LSM nanoparticles in SOFC



Scholklapper et al. (LBL),
Electrochem. Solid-State Lett., **9**, A376 (2006)

As-synthesized LSM nanoparticles on SSZ | *Annealed at 650 for 500h at 150 m/cm^2*



Scholklapper et al. (LBL),
Electrochem. Solid-State Lett., **10**, B74 (2007)

What are the ideal materials to use as backbone or infiltrate?
How does high temperature electro-catalysis occur?
What is the stability of materials in extreme conditions?
How does the surface chemistry / electronic structure change in operation?

Outline

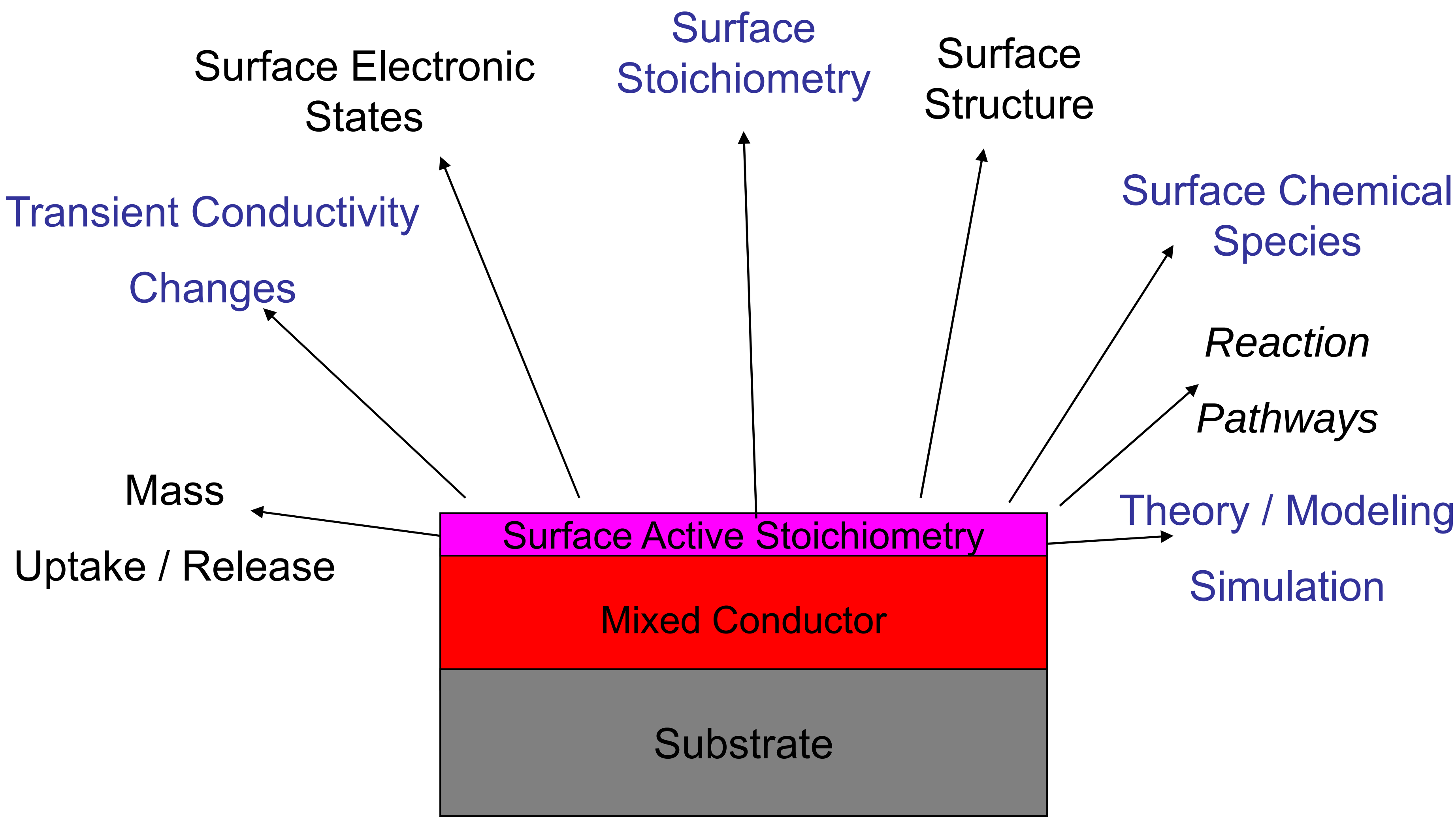
- Microstructural Characterization
  - Activity / Stability Issues
  - Oxygen Reduction Reaction

- **Cathode Surface Fabrication / Characterization**
  - **Thin Film Geometry Synthesis**
  - **Combined Thin Film Property Measurements**

- Electrical Conductivity Relaxation on LSM
  - Film Structures and Properties vs Bul
  - Orientation Dependence of oxygen uptake
  - Temperature Dependence of oxygen uptake
  - Substrate Dependence of oxygen uptake

Building a Team to Understand Oxygen Reduction: Thin Films Samples with "controlled" Surfaces

Probe the nature of atomic scale <u>surface chemistry</u> or <u>interface crystallography</u> <u>rather</u> than the device scale micro-structural perturbations.



Concepts partially developed by L. Wilson and P. A. Salvador

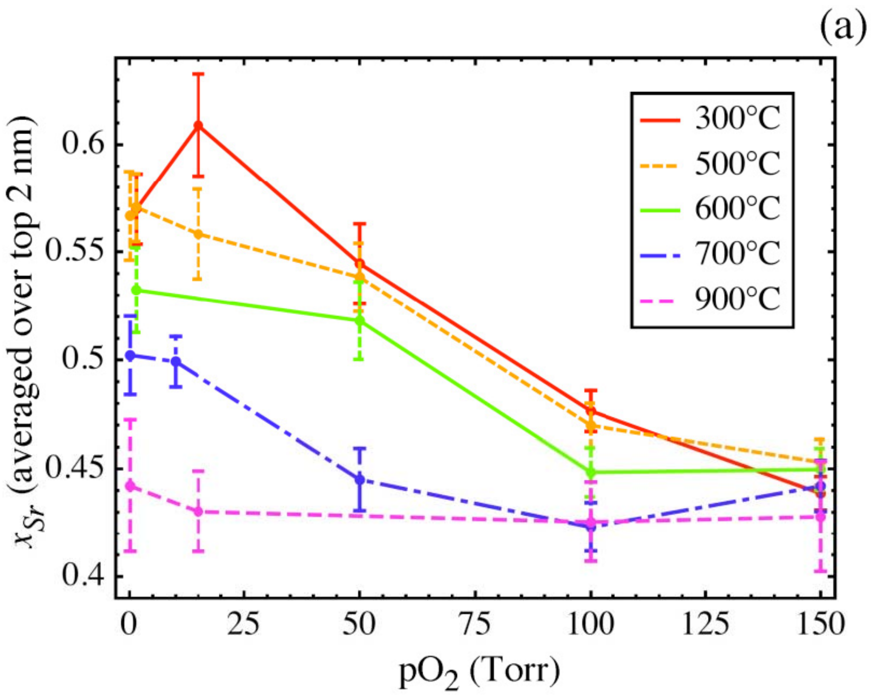
Strontium Segregation vs T an P for LSM Films on Perovskite Substrates

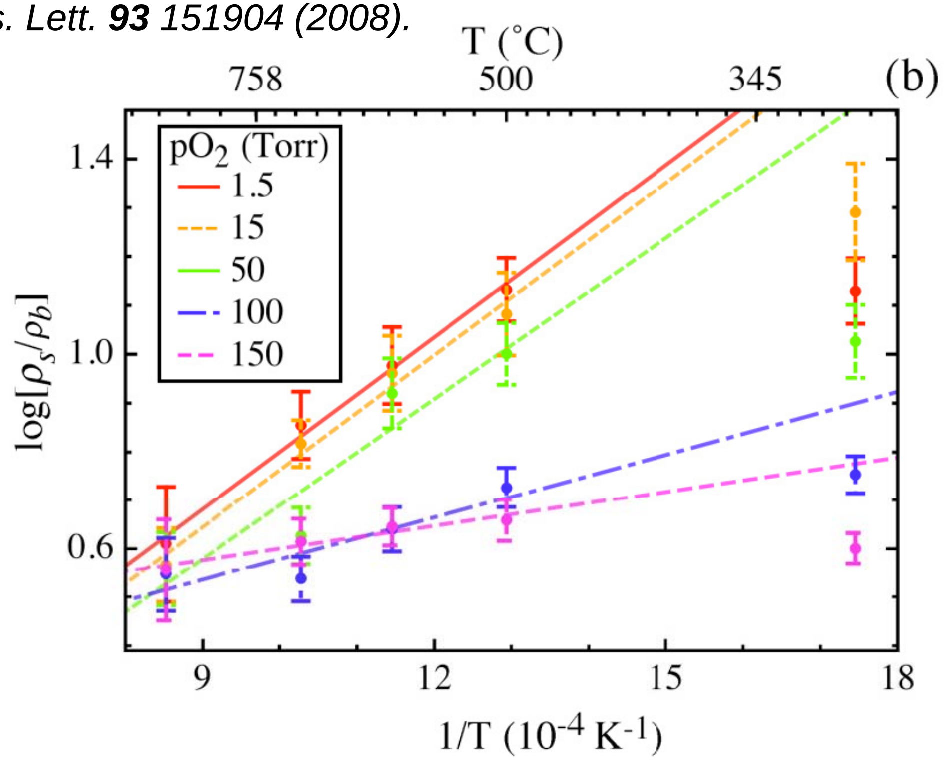
16 nm LSMO on DyScO3,

700°C, pO2 = 150 Torr

16 nm LSMO on DyScO3,

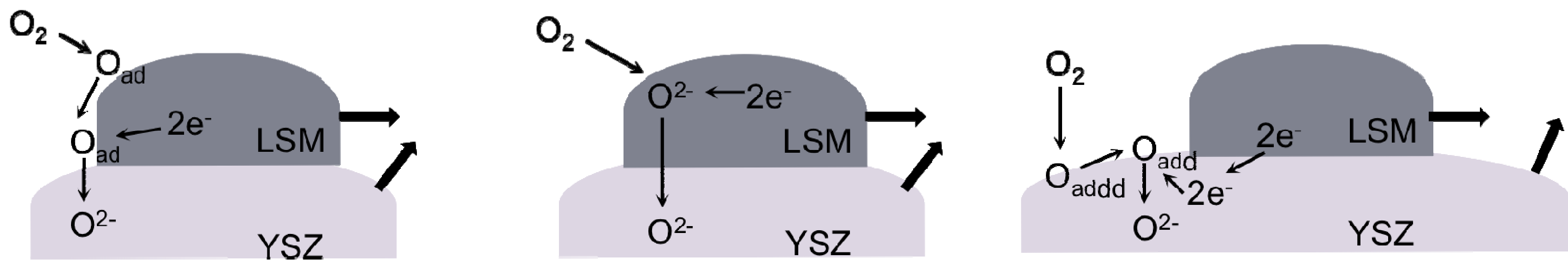
Fister et al., Appl. Phys. Lett. ***93*** *151904 (2008).*





- **Observe that Sr segregation depends on both T and pO_2**
  - plot shows average Sr composition in ~3 nm surface region (bulk composition = 0.3)
  - Enthalpy of segregation ≈ < .1 eV / atom and is pO_2 dependent.

What happens during oxygen uptake?



LSM Surface Path **LSM Bulk Path** **YSZ Surface Path**

- *Adsorption*
  - *Mass of Material* *(Gravimetry)*
  - *Surface Chemistry* *(Spectroscopy)*
  - *Surface Electronic Structure* *(Kelvin Probe, STS, Normal Conductivity)*

- *Electronic transfer*
  - *Consumption of holes* *(Parallel Conductivity / Thermopower)*
  - *Fermi Level Changes* *(Kelvin Probe / STS)*
  - *Surface chemistry* *(Spectroscopy)*

- *Oxygen Vacancy Consumption*
  - *Mass Change* *(Gravimetry)*
  - *Total charge density* *(Conductivity / Thermopower)*
  - *Surface Chemistry* *(Spectroscopy)*

CMU Work for Cathode Surface Science Project

- ***Growth of High-Quality Thin Film Samples***
  - *Perovskite / Perovskite Epitaxy and Surface Control*
  - *Perovskite / Fluorite Epitaxy and Surface Control*
  - *Generation of Surface-Modified Samples*

- ***Surface Kinetics for Oxygen Uptake***
  - *Electrical Conductivity Relaxation*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

- *Surface Thermodynamics of Oxygen Uptake*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

- *Electronic Structure*
  - *Kelvin Probe Spectroscopy*
  - *STM (MIT)*

- *Ex-situ Surface Characterization for Correlations*
  - *Scanning Auger / XPS*

“Ideal” Surface Science Sample

General Schematic	Example	Concept
1 - 2 Atomic or Unit Cell Monolayers	$SrMnO_3$	Gate
≈ 20 - 50 Unit Cells of Epitaxial Perovskite	(100)-terminated $(La,Sr)MnO_3$	Reservoir
Macroscopic, Single Crystal Perovskite Substrate of specific orientation / termination	(100)-terminated $SrTiO_3$	Support / Electrolyte

Control Microstructural Complexity and Surface Crystallography

Summary of Sample Preparation

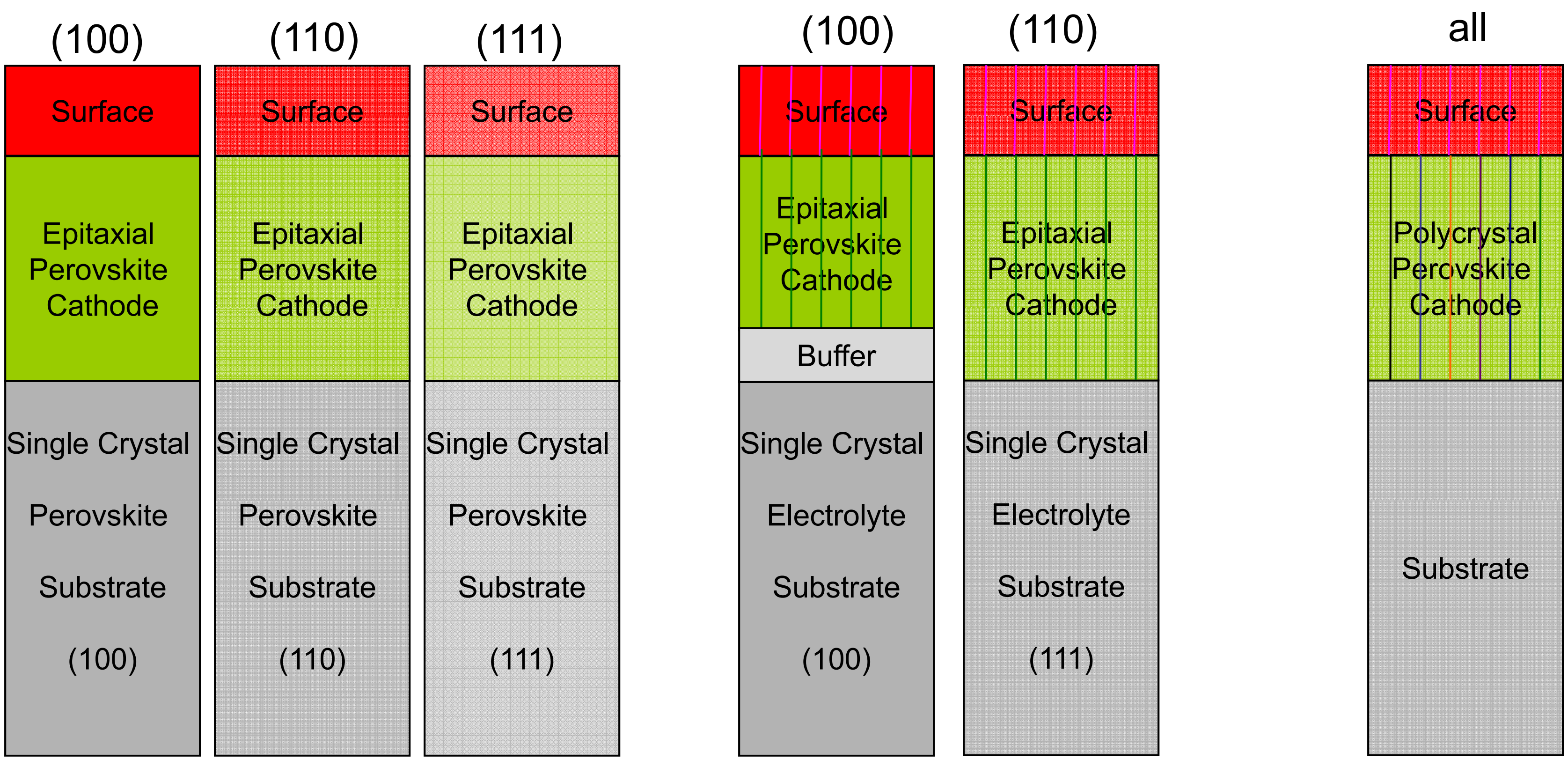
- *Growth of High-Quality Thin Films*
  - *Perovskite / Perovskite Epitaxy and Surface Control Achieved*
    - *LSM and LSC and LSCF (and LNO) deposited on many Perovskites*
    - *Cube-on-cube epitaxy on various orientations*
    - *Unit-cell roughness obtained*

  - *Perovskite / Fluorite Epitaxy and Surface Control Achieved*
    - *LSM and LSC and LSCF (110)[111] epitaxy on YSZ (111)[[11-2]*
    - *LSM and LSC and LSCF (100)[011]epitaxy on GDC-YSZ (100)[010]*
    - *Unit-cell roughness obtained*
    - *6 and 4 variants observed on (111) and (100) fluorites*

  - *Samples Provided to Collaborators*
    - *Measured Surface Chemistry at APS*
    - *Measured Electronic Properties at MIT*
    - *Measured Electronic Properties at UNLV*
    - *Measured Surface Properties at NETL*

Thin Film Samples Driving Surface Science

Films Allow for Surface / Microstructural Control



Single Crystal
Specific surface
BULK SURFACES

Multi-variant
Specific surface / boundaries

Poly-Xtal
Ensemble

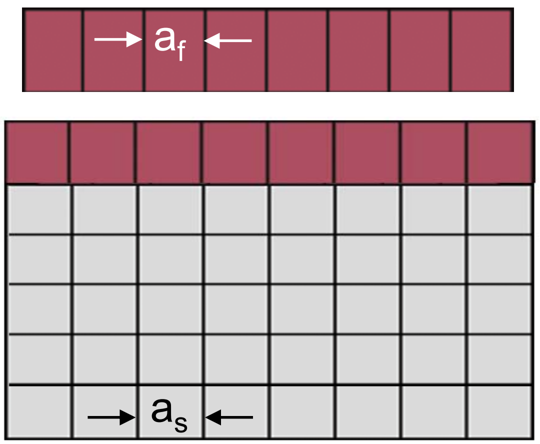
INFILTRATES

How do we synthesize these materials?

Cathode thin film growth – Substrate choice and orientation

Mismatch Strain

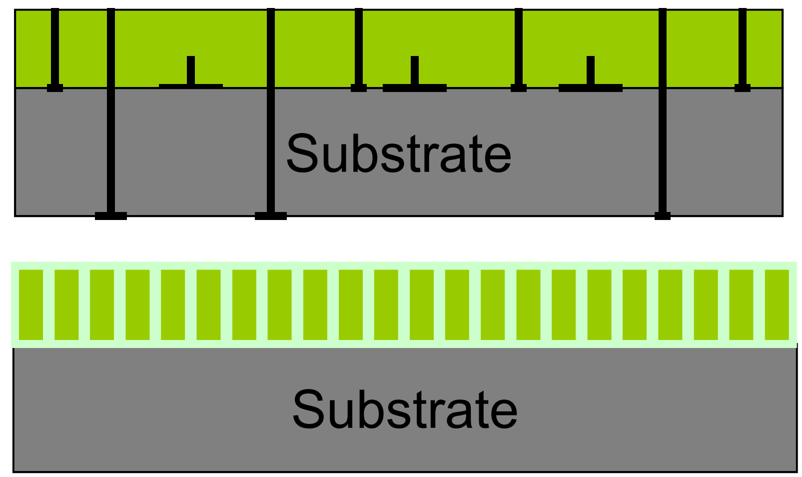
$$f = \frac{(a_s - a_f)}{a_f}$$



$$w_{strain}^{max} = \frac{2\mu(1+\nu)f^2}{(1-\nu)}$$

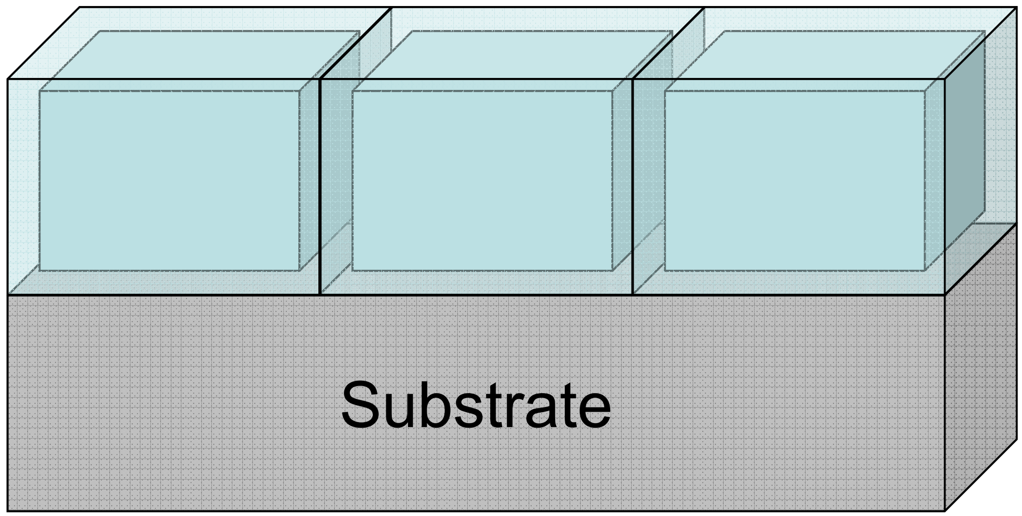
Dislocations

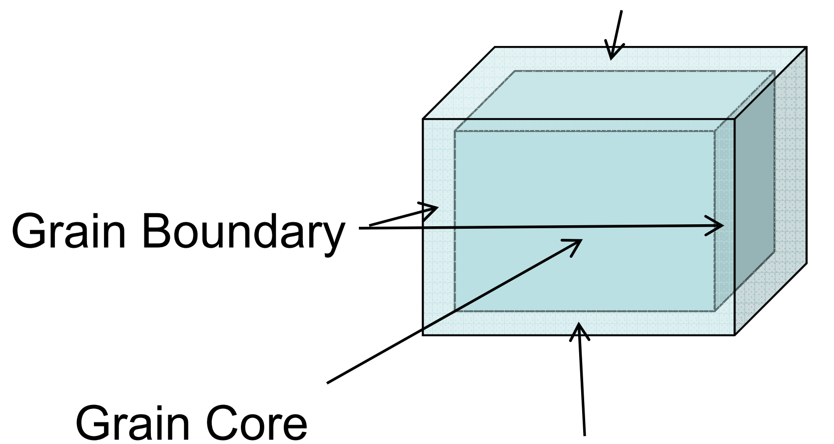
Misfit
Threading (relaxation)
Threading (inherited)



Substrates have different lattice mismatches and Different dislocation densities

Brick-Layer Type Model of Interaction





All Films have some level of Defects

How does the nature of the interfacial features affect performance?

- ***Surface***
- ***Grain Boundary***
- ***Interface***

Pulsed Laser Deposition
Laser MBE / MBE

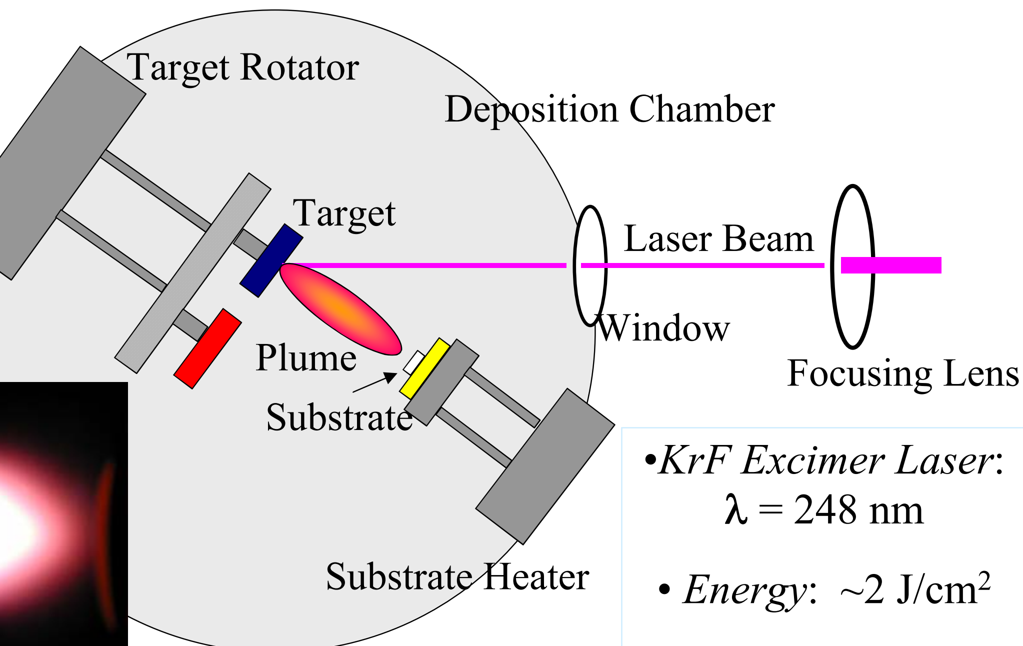
Advantages of PLD

- Targets made via standard methods.
- Stoichiometric transfer from target to film
- High-quality epitaxial films for complex oxides
- High-Quality Metal Films
- Simple, versatile, and relatively inexpensive
- House 6 targets at once

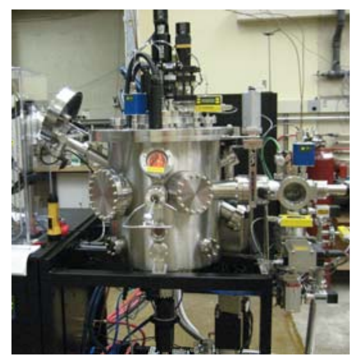
Deposition Parameters

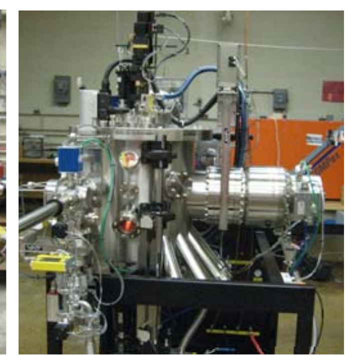
PRESSURE :	0.00001 - 0.2 Torr
TEMPERATURE:	RT - 950 °C
FLUENCE :	1-8 J/cm^2
FREQUENCY :	1-10 Hz
COOLING:	0.00001- 300 Torr
Depositions :	1- 4 hrs Max
	3 - 4 deps / day
	3 - 4 samples / dep

Pulsed Laser Deposition



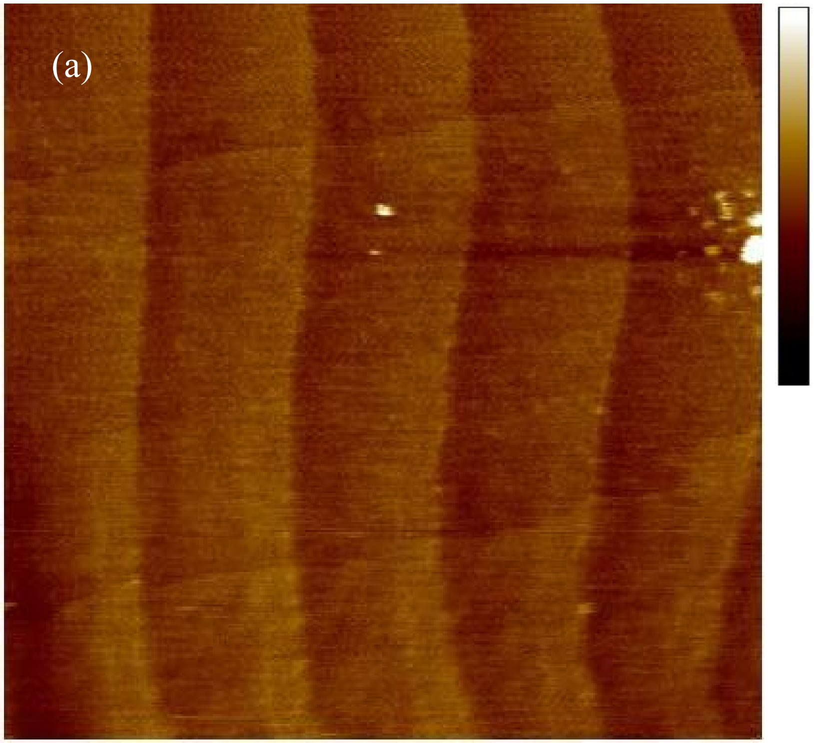
- *KrF Excimer Laser*: $\lambda = 248$ nm
- *Energy*: ~2 J/cm^2
- *Frequency: 3 Hz*



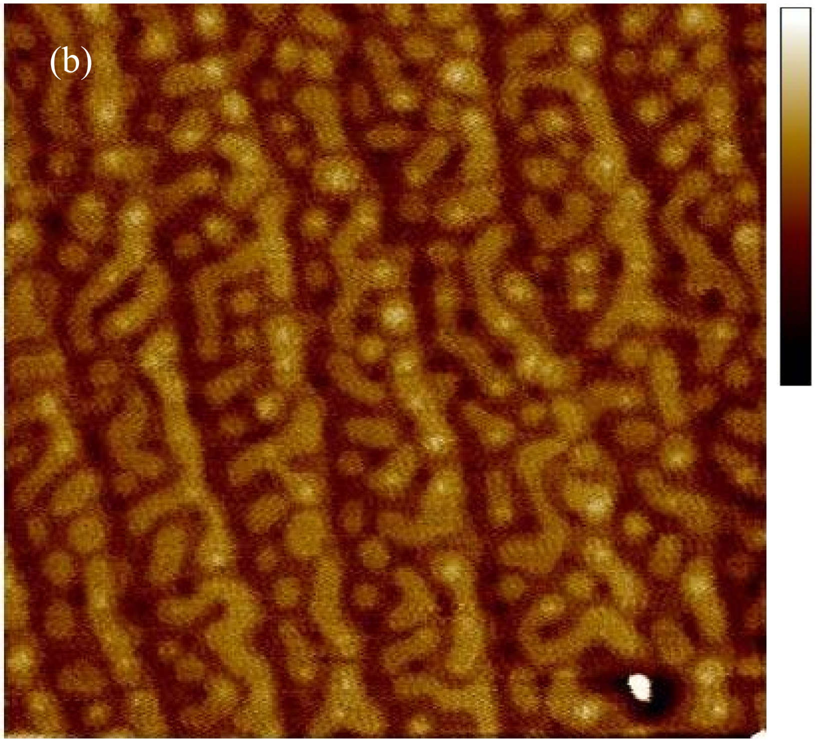


Surface Engineering
$SrTiO_3$ Crystals / (La,Sr)MnO_3 Films

$SrTiO_3$ Crystals
1 x 1 μm^2 (3 nm)
TiO_2 Terminated



10.8 nm (La,Sr)MnO_3 Film
1 x 1 μm^2 (3 nm)
MnO_2 Terminated ?

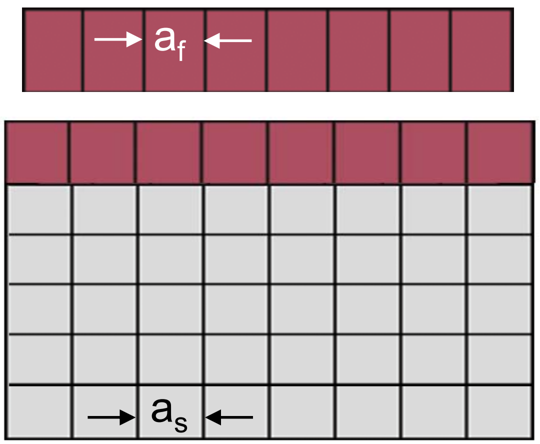


Atomically smooth surfaces by controlling growth minimize microstructure and can be used for STM / STS

Cathode thin film growth – Substrate choice and orientation

Mismatch Strain

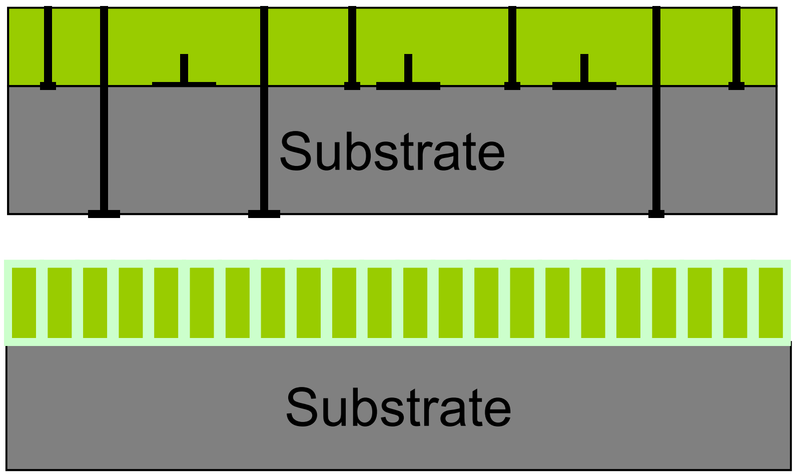
$$f = \frac{(a_s - a_f)}{a_f}$$



$$w_{strain}^{max} = \frac{2\mu(1+\nu)f^2}{(1-\nu)}$$

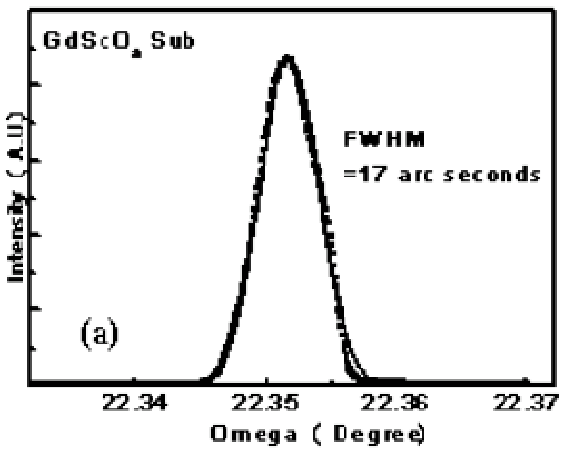
Dislocations

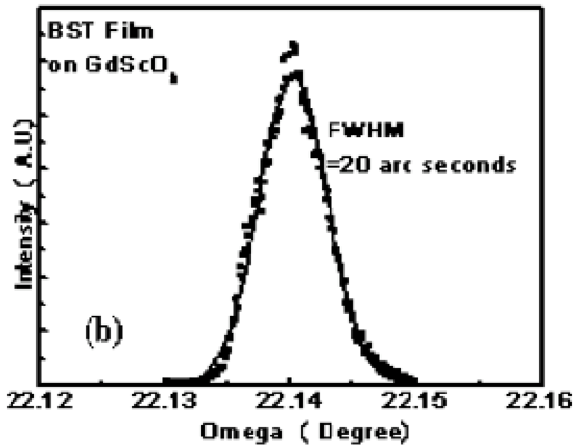
Misfit
Threading (relaxation)
Threading (inherited)



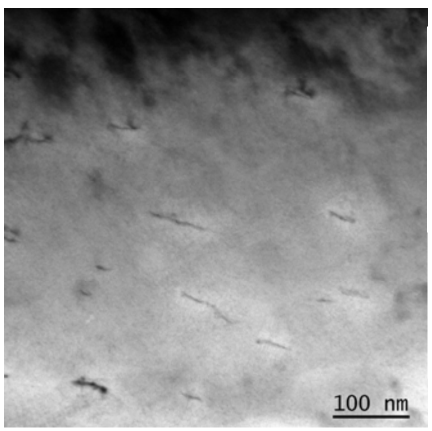
Substrates have different lattice mismatches and Different dislocation densities

Film Dislocation Densities: (Ba,Sr)TiO_3 Example

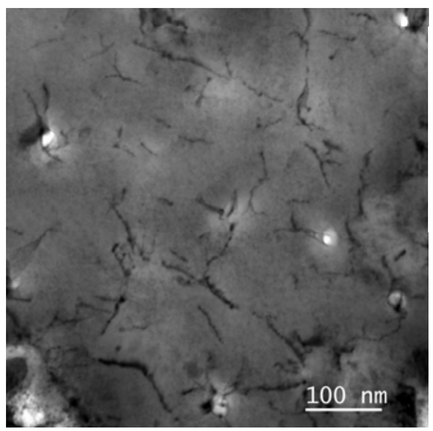




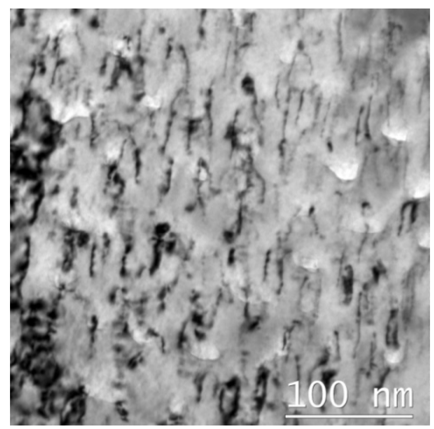
Substrate Material	FWHM of Film Rocking Curve (°)
MgO (100)	0.153
$GdScO_3$(110)	0.008
$DyScO_3$(110)	0.009
LSAT (100)	0.016
$LaAlO_3$(100)	0.183



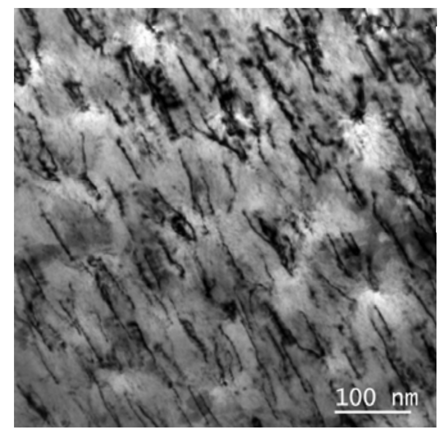
BST/$GdScO_3$
$6x10^9$/cm2



BST/$DyScO_3$(110)
$2x10^{10}$/cm2



BST/LSAT
$2x10^{11}$/cm2

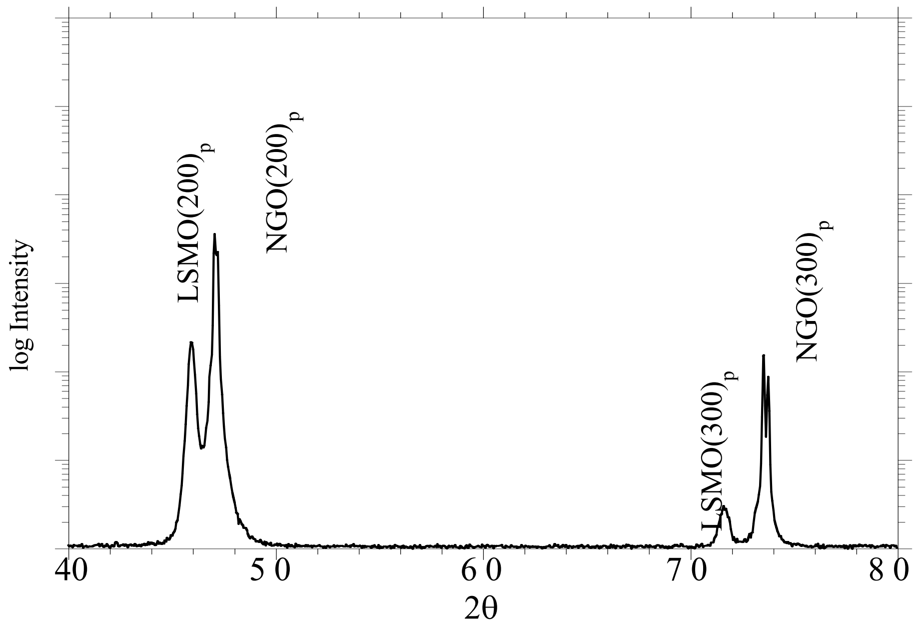


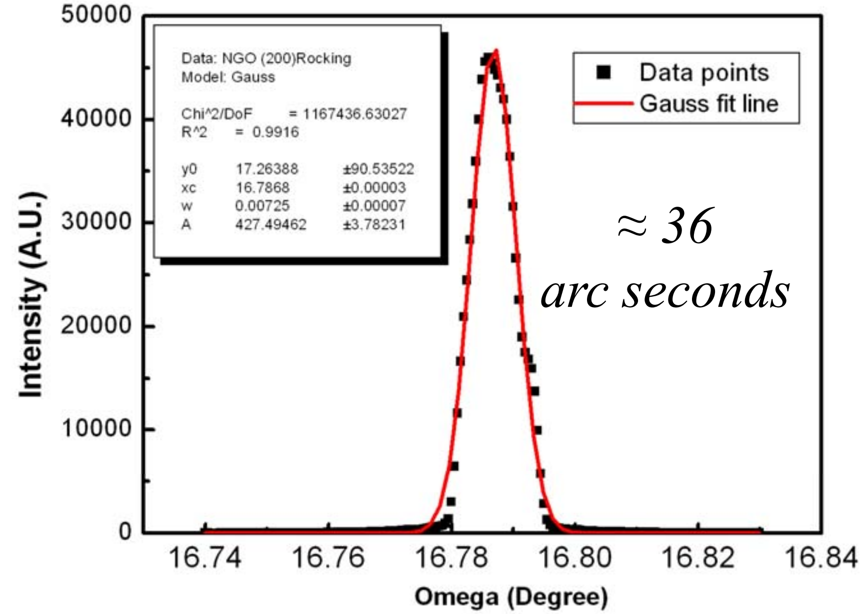
BST/LAO
$2.7x10^{11}$/cm2

Dislocation Control
(La,Sr)MnO_3 thin films on $NdGaO_3$

Very-high Quality Perovskite Crystals
No Overlapping Elements with Films
Highly Insulating (Good for ECR / PCM)

$La_{0.7}Sr_{0.3}MnO_3$ (54 nm) deposited on $NdGaO_3(100)_P$





Need Reasonable Perovskite Electrolyte(s) for Electrochemistry

CMU Work for Cathode Surface Science Project

- ***Growth of High-Quality Thin Film Samples***
  - ***Perovskite / Perovskite Epitaxy and Surface Control***
  - ***Perovskite / Fluorite Epitaxy and Surface Control***
  - *Generation of Surface-Modified Samples*

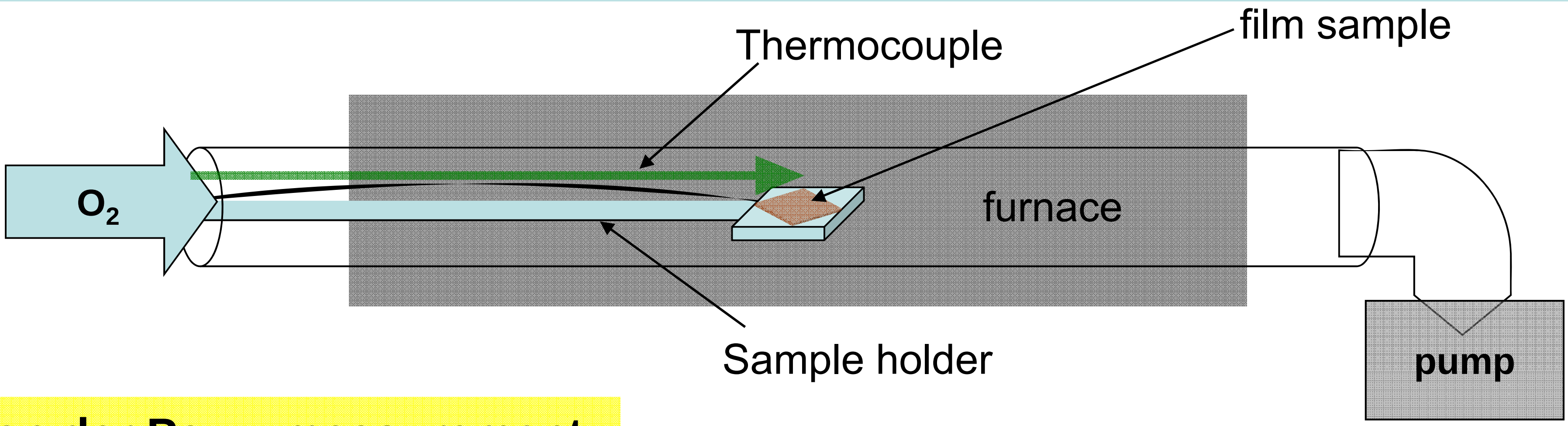
- ***Surface Kinetics for Oxygen Uptake***
  - ***Electrical Conductivity Relaxation***
  - ***Piezoelectric Crystal Microbalance Gravimetry***
  - ***Kelvin Probe Spectroscopy***

- *Surface Thermodynamics of Oxygen Uptake*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

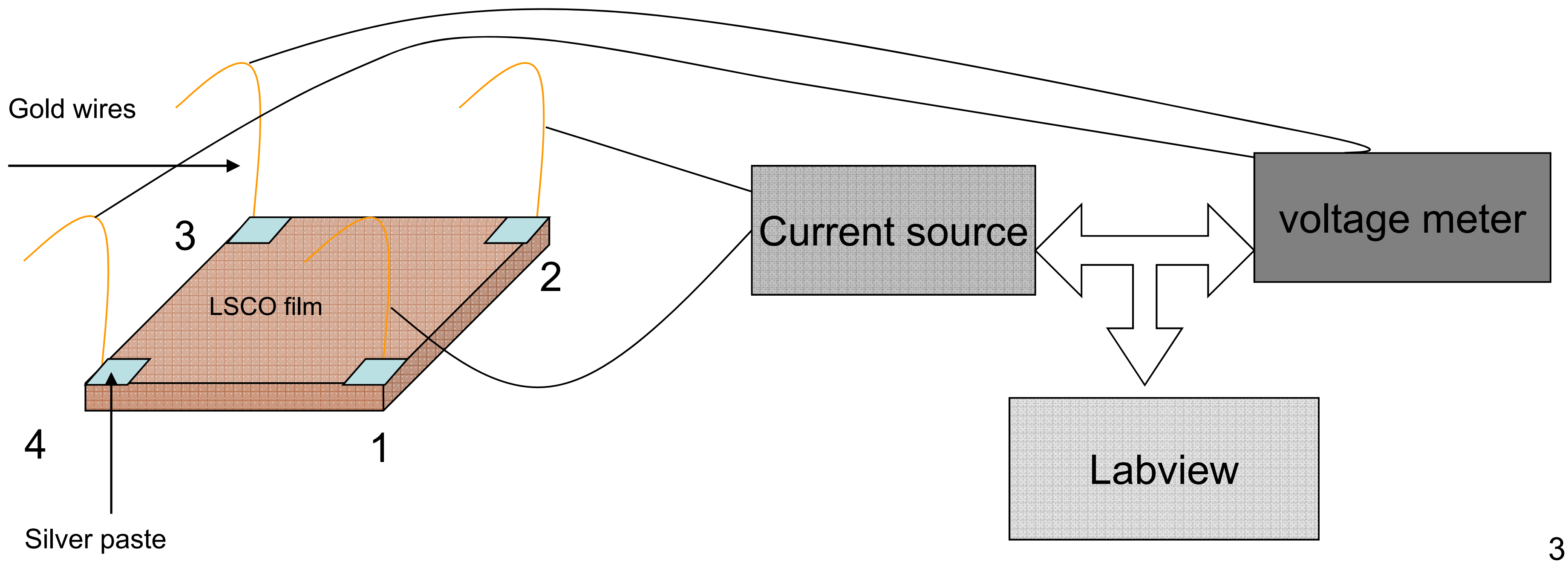
- *Electronic Structure*
  - *Kelvin Probe Spectroscopy*
  - *STM (MIT)*

- *Ex-situ Surface Characterization for Correlations*
  - *Scanning Auger / XPS*

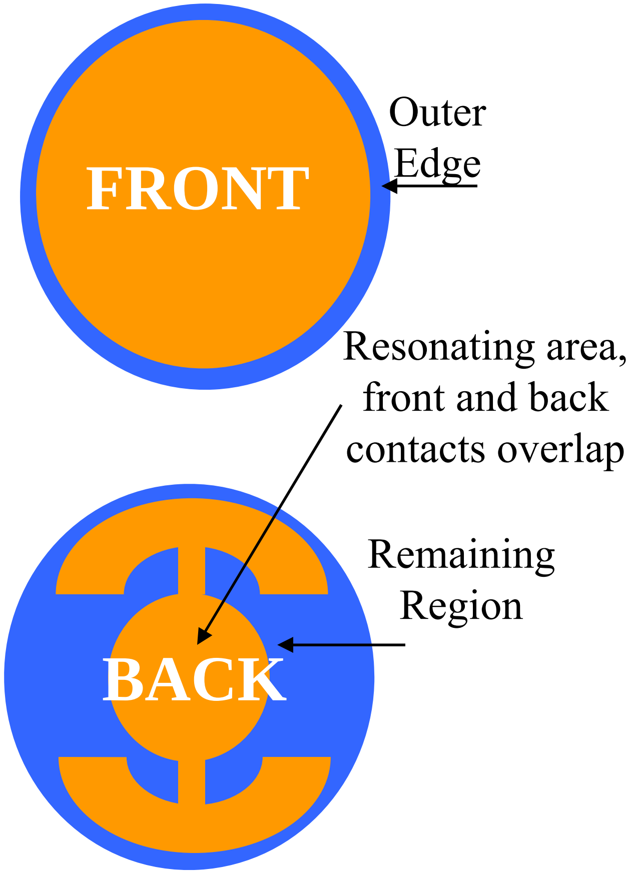
Experimental Approach for ECR: Determine surface exchange constant k_{chem}

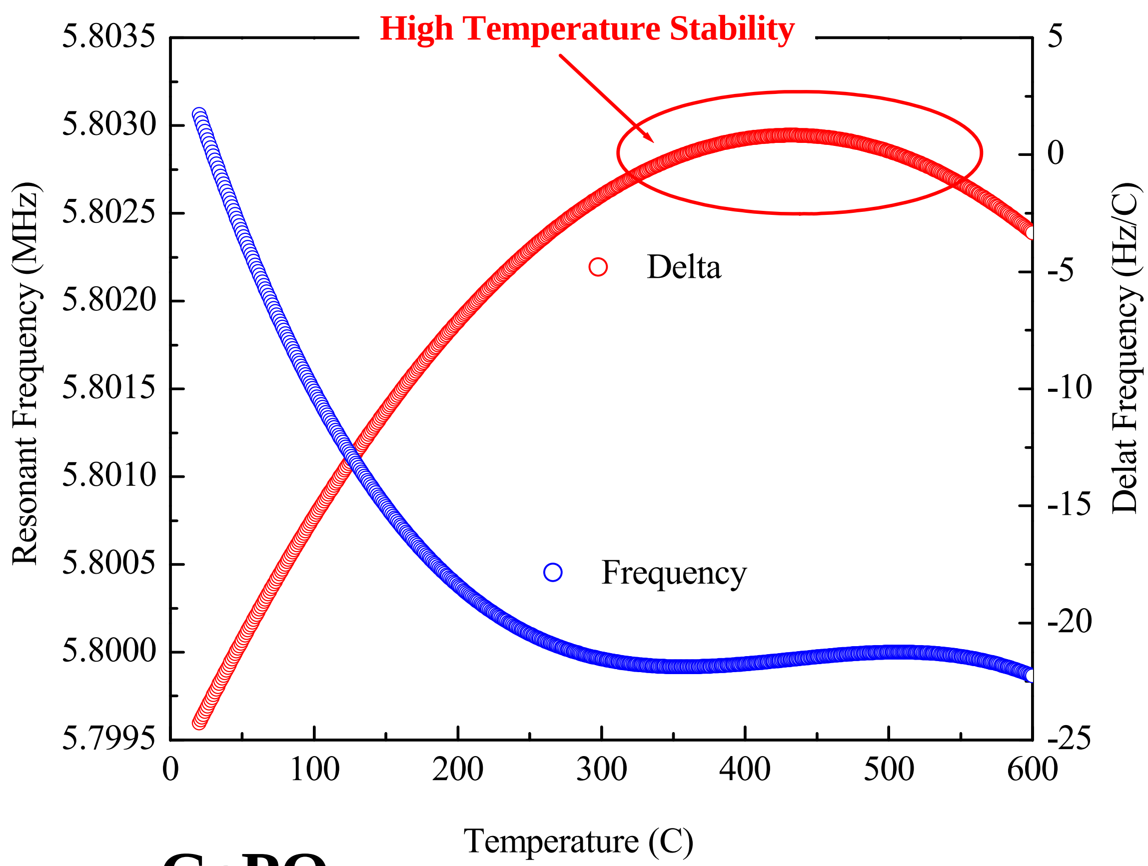


Van der Pauw measurement:



Gravimetry





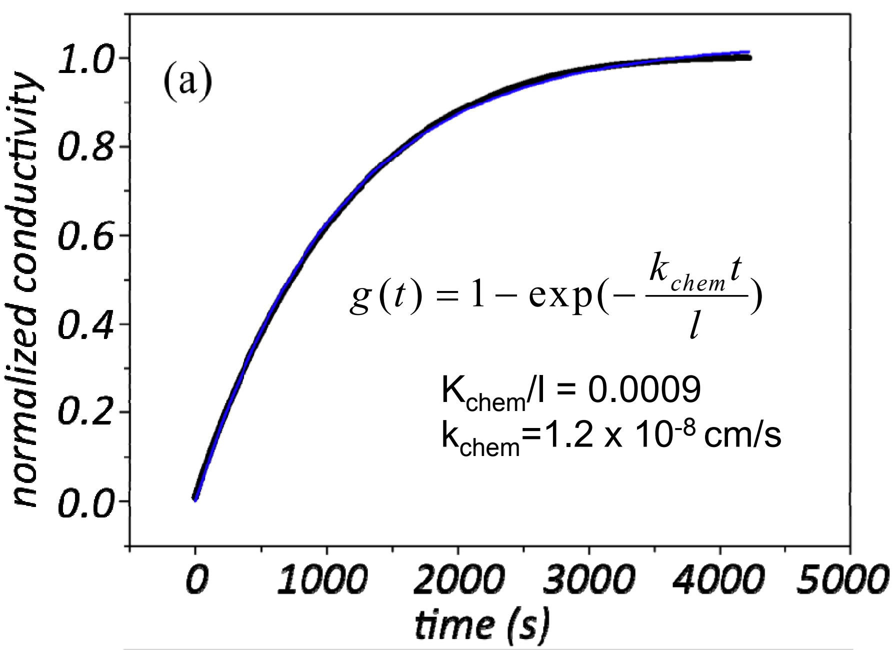
$GaPO_4$

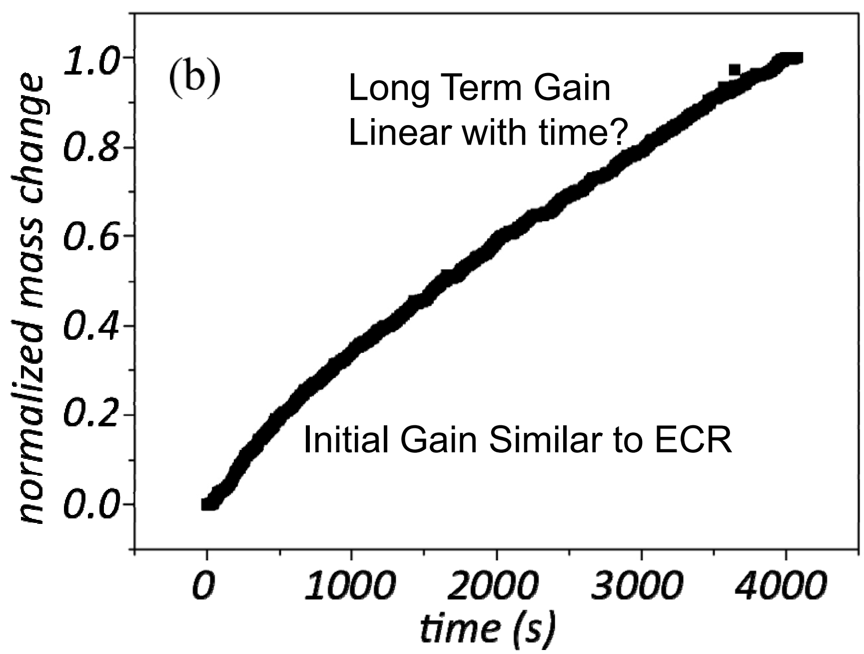
Diameter =0.55 inch; Thickness = 0.2 mm;

F_0 = 5.8 MHz, Sensitivity +/- 3 Hz

Combined ECR and PCM

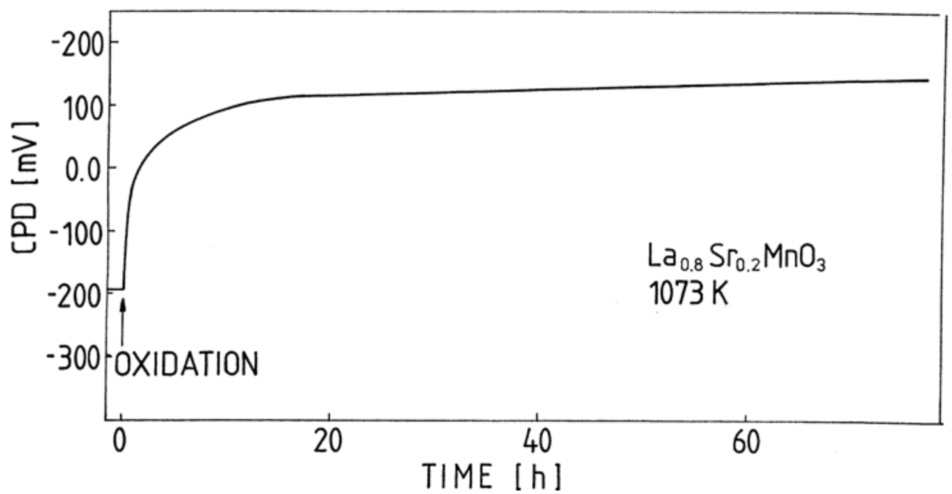
- $LaNiO_3$ is a well known conducting perovskite
- $LaNiO_3$ is suitable material for measurement of oxygen uptake range of 300-500^{o}C
- $LaNiO_3$ on grows on YSZ (100) and on STO (100) similar to LSM
- 3 mTorr O_2 to 10 mTorr O_2 in a total pressure of 220mTorr (nitrogen balance)

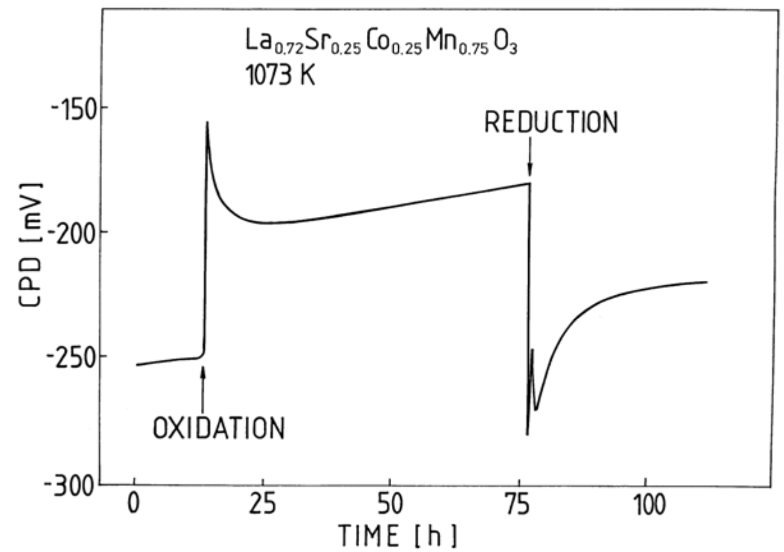




Kelvin Probe Spectroscopy

Badwal et al. J. Phys. Chem. Sol. ***62****, 723 (2001)*





Several Different Regimes Observed on PolyXtal Ceramics

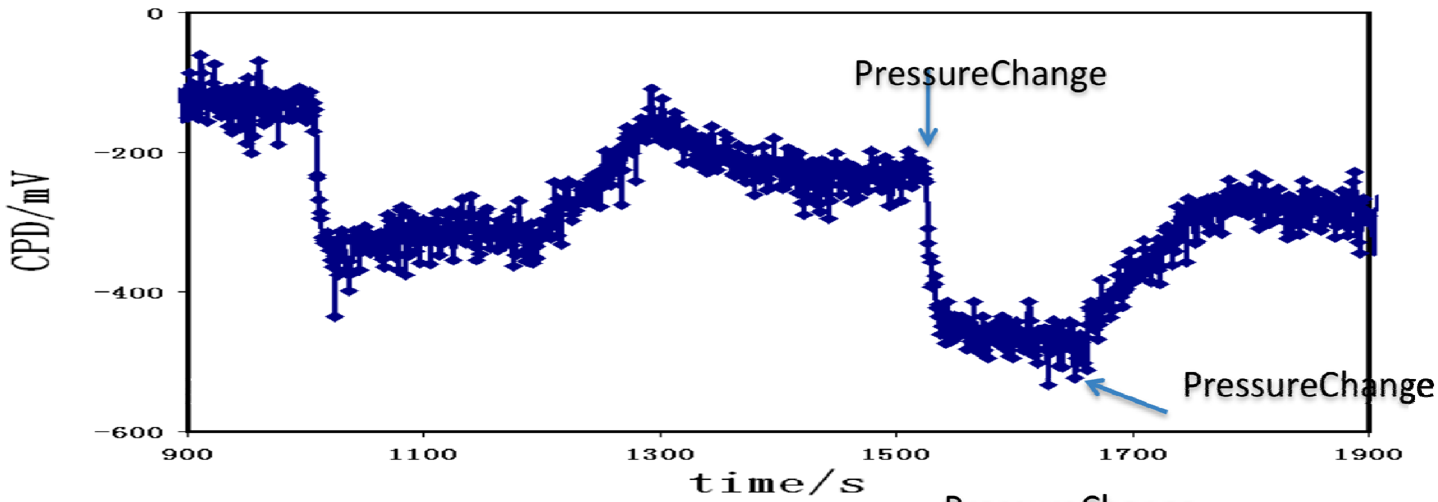
Should Correlate with conductivity AND sensitive mass measurements
deconvolute surface / bulk effects

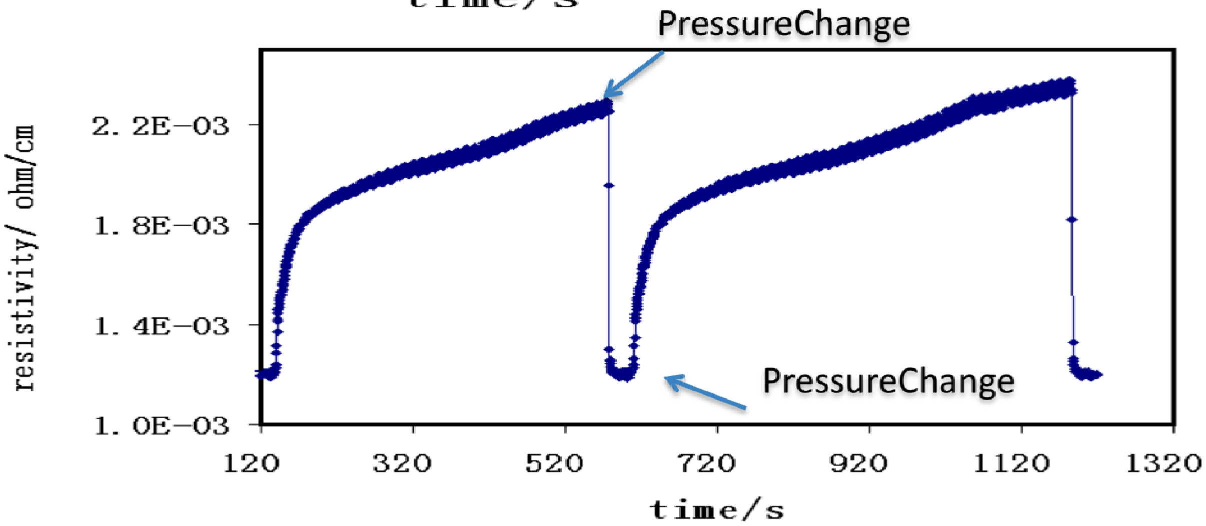
Requires Consistent surface engineered samples

Combined ECR and KPS

LSCO 100nm-YSZ(111)

800C; PO_2 : N_2 to O_2 1atm





Outline

- Microstructural Characterization
    - Activity / Stability Issues
    - Oxygen Reduction Reaction

- Cathode Surface Fabrication / Characterization
    - Thin Film Geometry Synthesis
    - Combined Thin Film Property Measurements

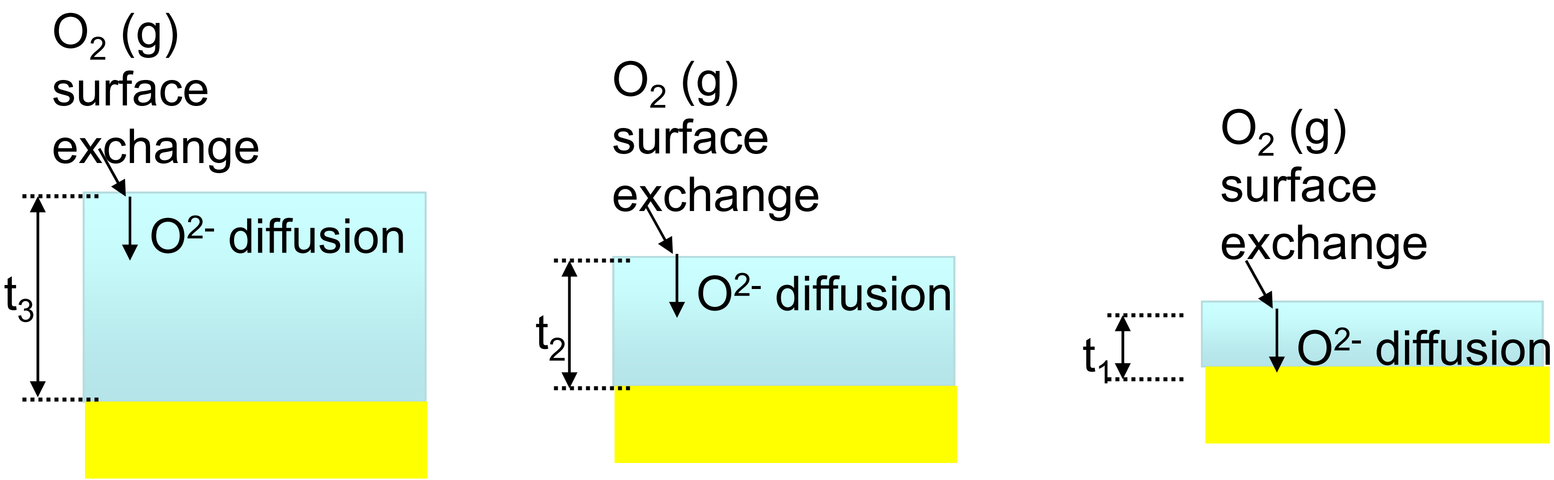
- **Electrical Conductivity Relaxation on LSM**
    - **Film Structures and Properties vs Bul**
    - **Orientation Dependence of oxygen uptake**
    - **Temperature Dependence of oxygen uptake**
    - **Substrate Dependence of oxygen uptake**

Thin film geometry selection

Characteristic length of the sample: $l_d = \tilde{D}/k$

$\tilde{D}$:chemical diffusion coefficient

k :surface exchange coefficient



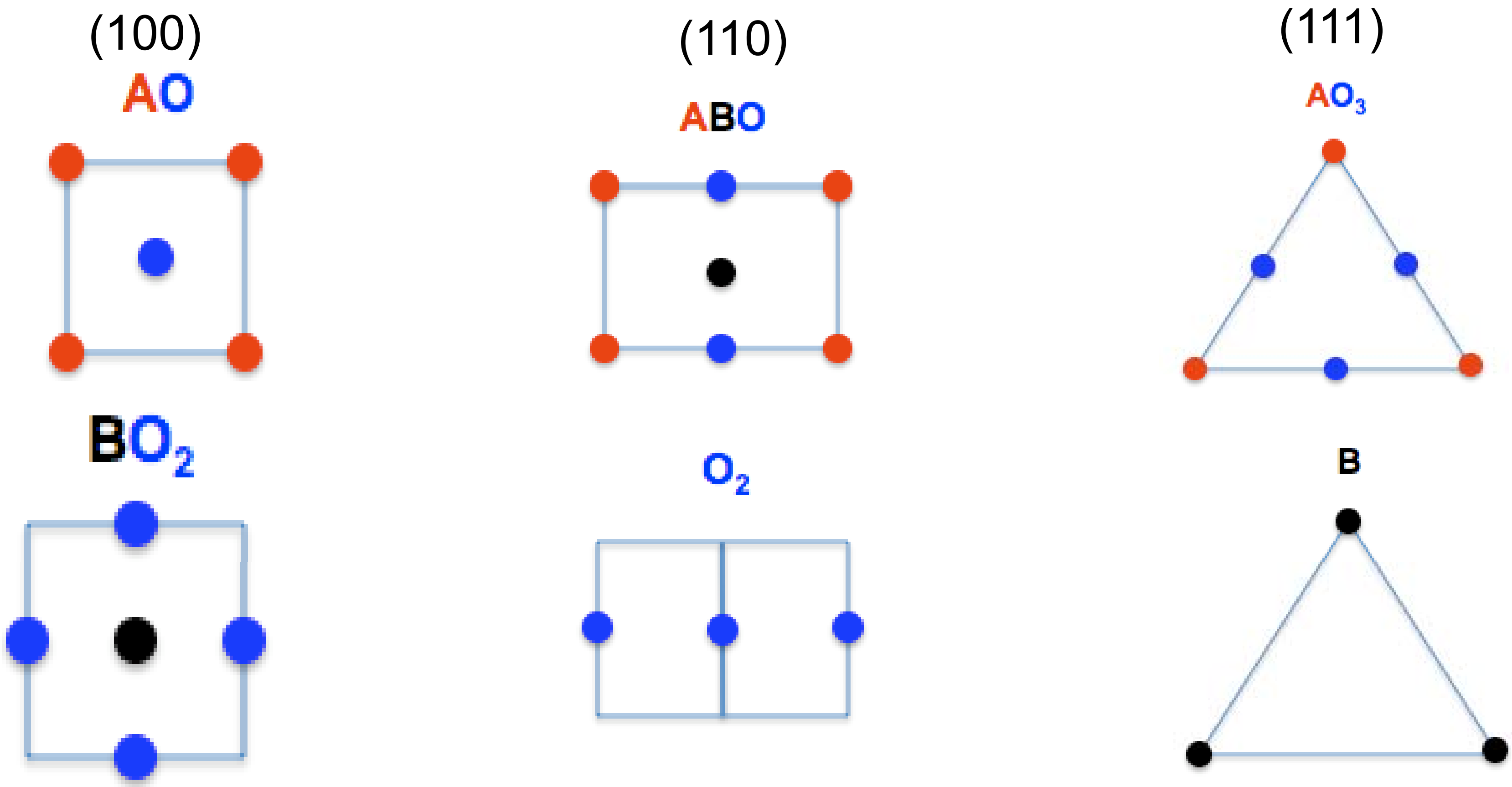
$t_3 \gg l_d$ — $\tilde{D}$

$t_2 \approx l_d$ — $\tilde{D}, k$

$t_1 \ll l_d$ — k

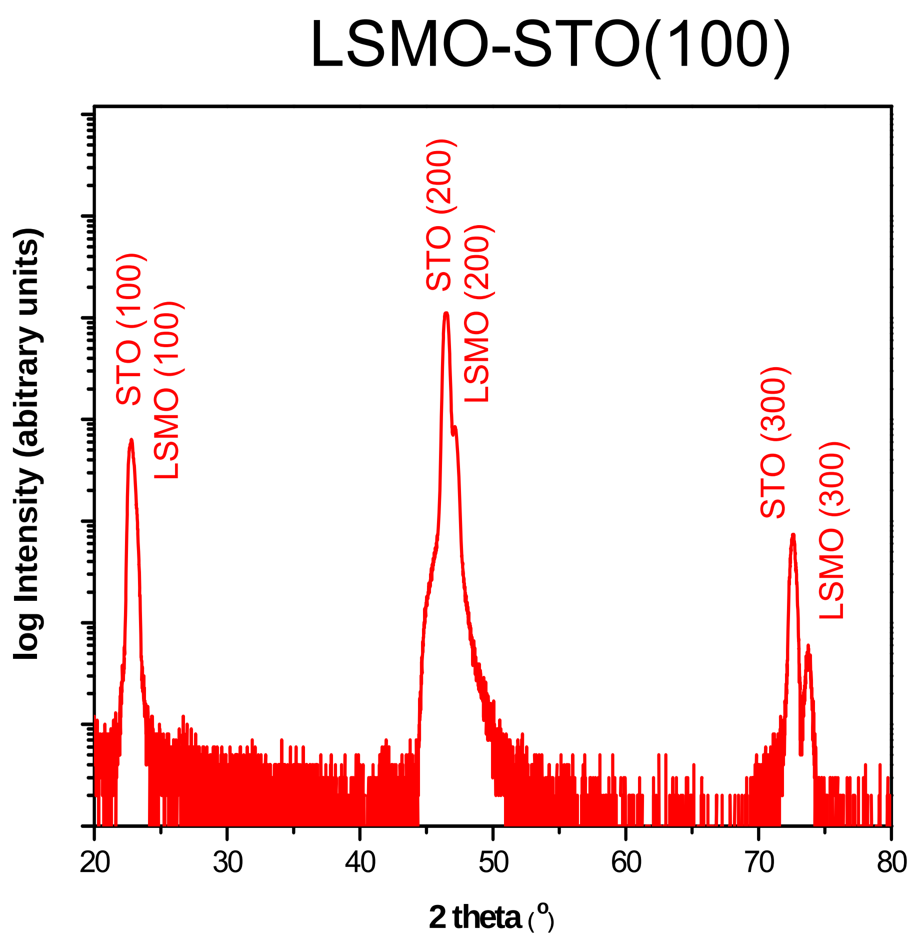
To isolate the surface influence on oxygen exchange process, film thickness should be smaller than critical value.

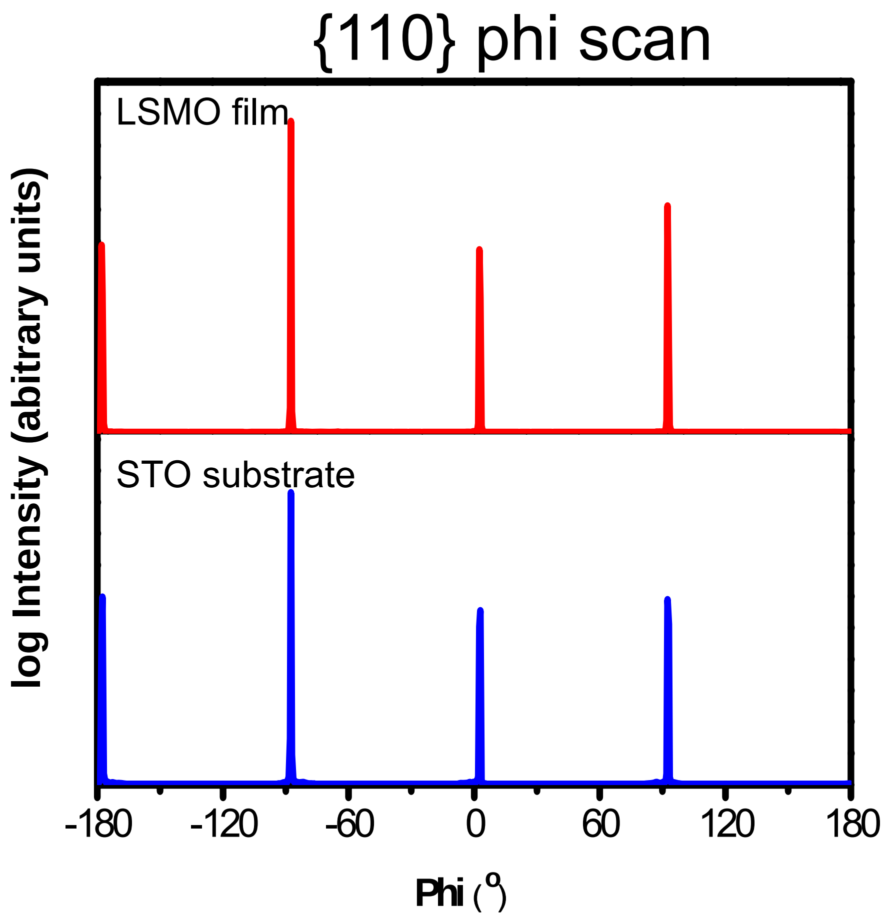
Ideal Surface Terminations



Different Types and Numbers of Broken Bonds on Surfaces

LSMO thin film growth on STO (100) substrates

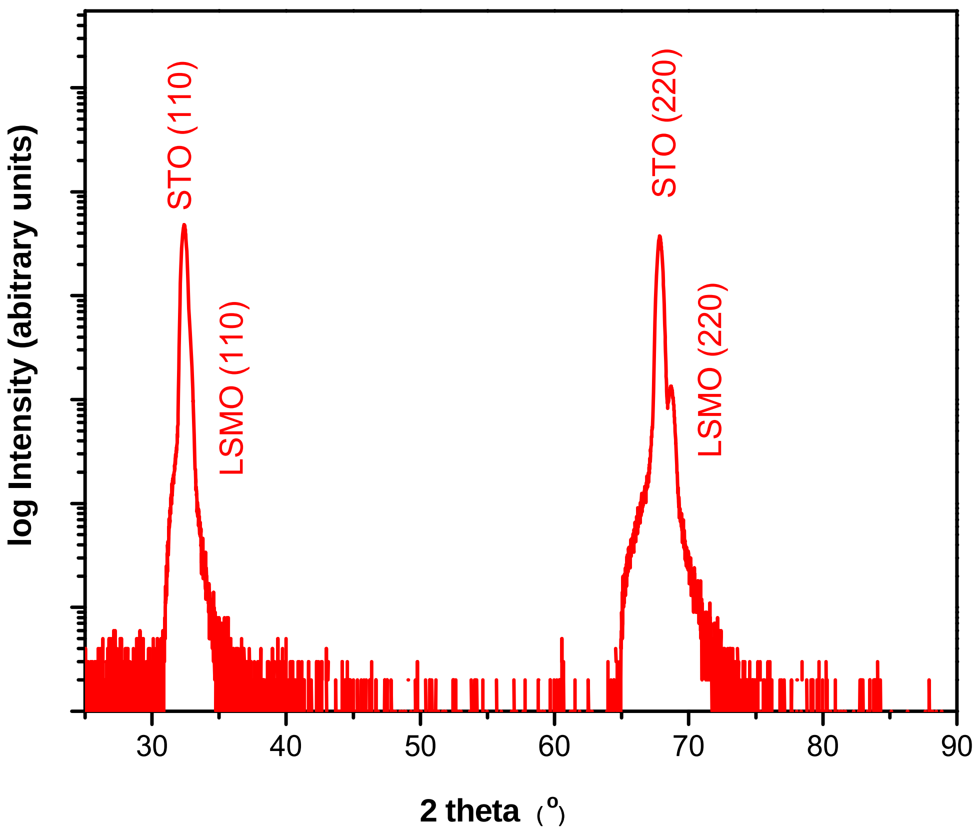




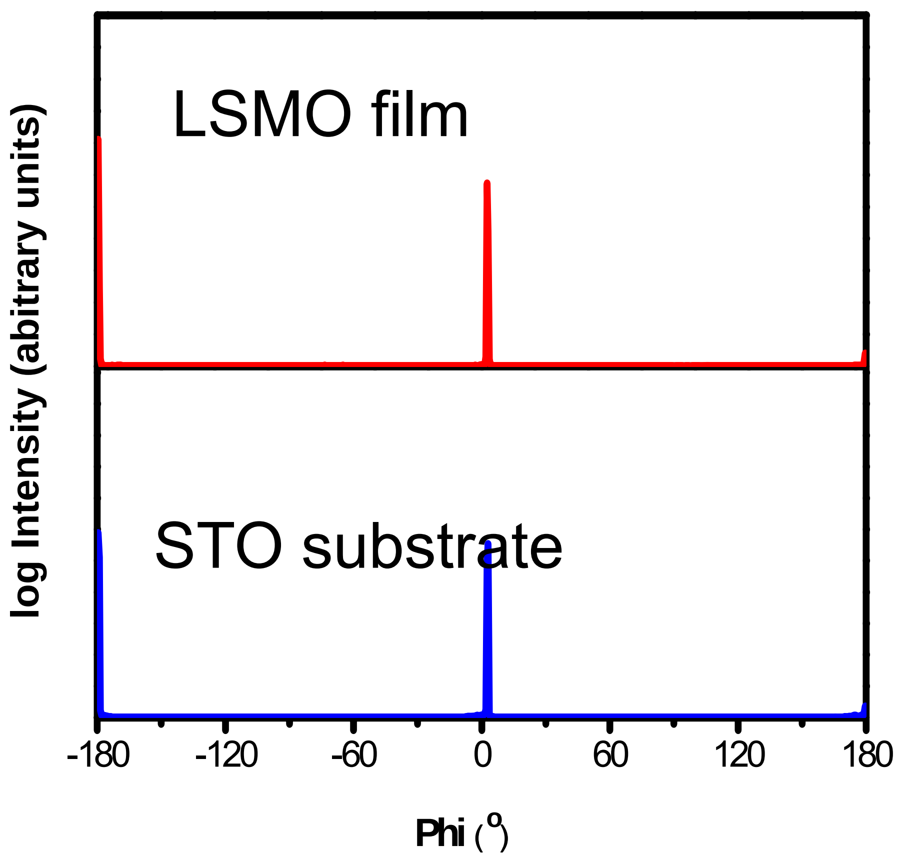
39

LSMO thin film growth on STO (110) substrates

LSM-STO(110)



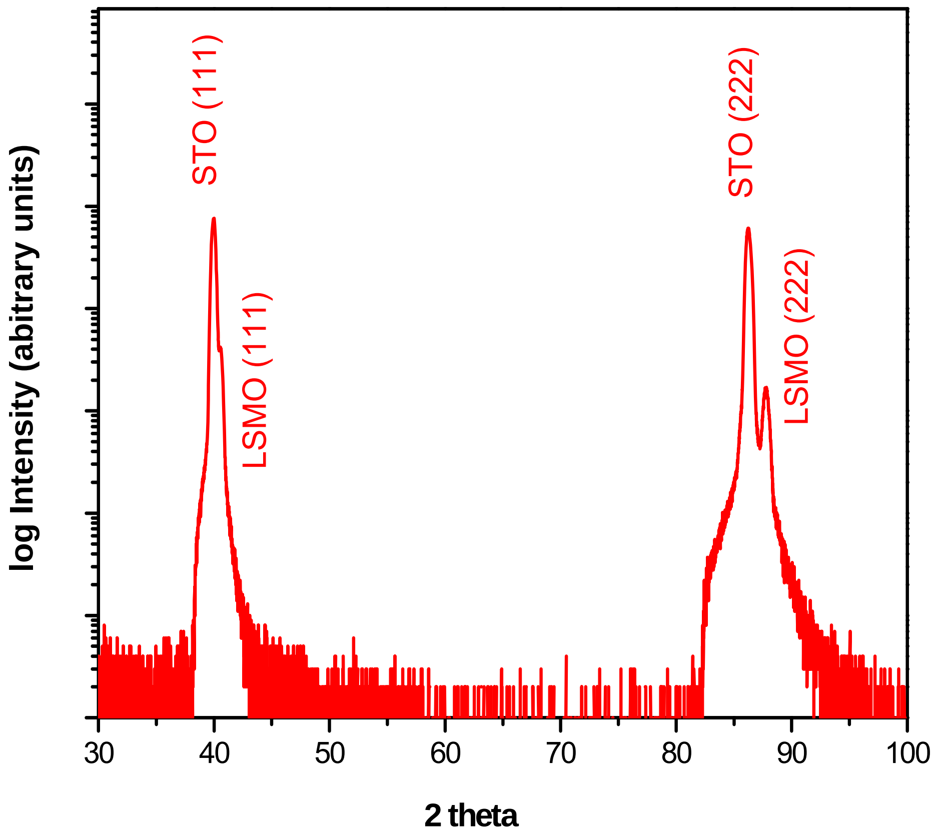
{100} phi scan



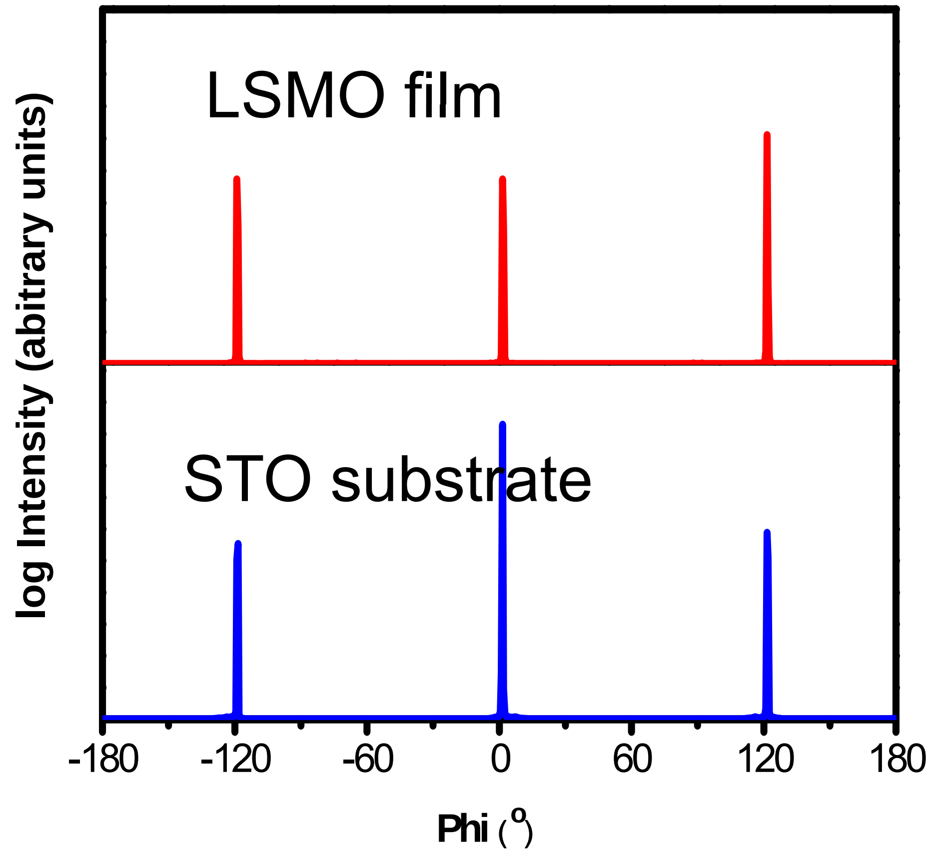
40

LSMO thin film growth on STO (111) substrates

LSMO-STO(111)

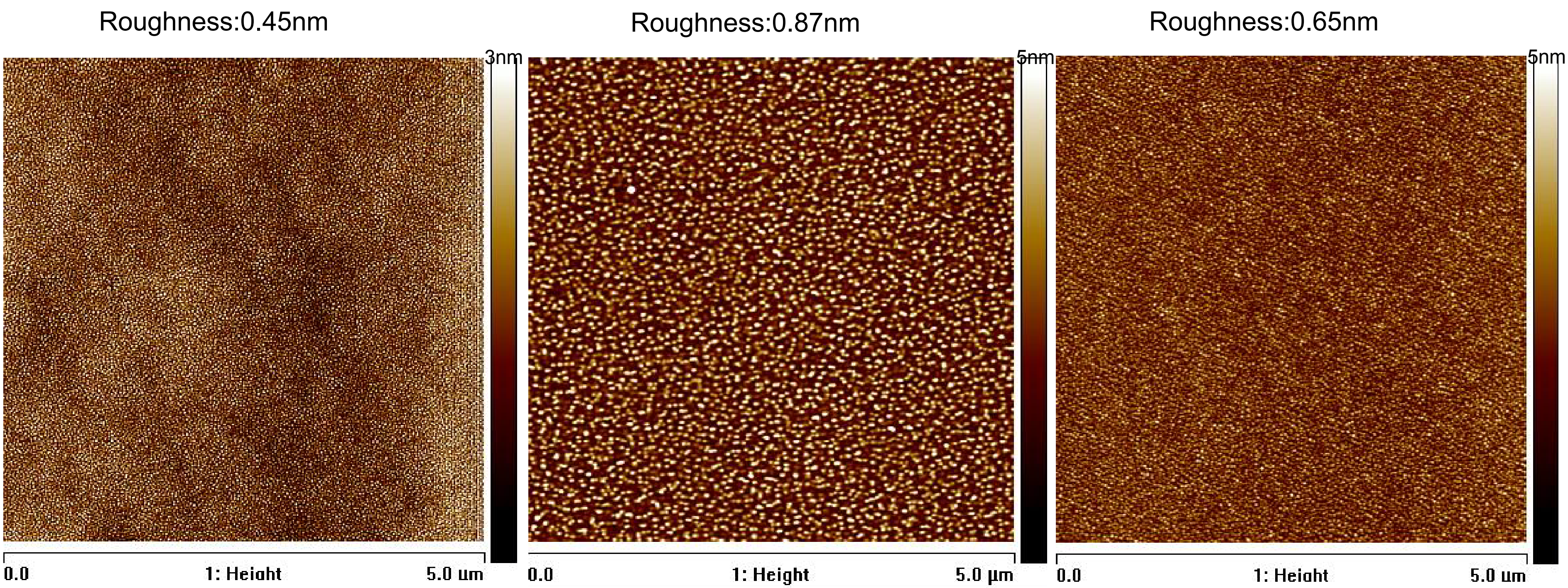


{110} phi scan



41

Cathode thin film surface on STO substrates



LSMO 100nm on STO(100) LSMO100nm on STO(110) LSMO 100nm on STO(111)

- Surface features are well defined.
- Films are unit-cell smooth.

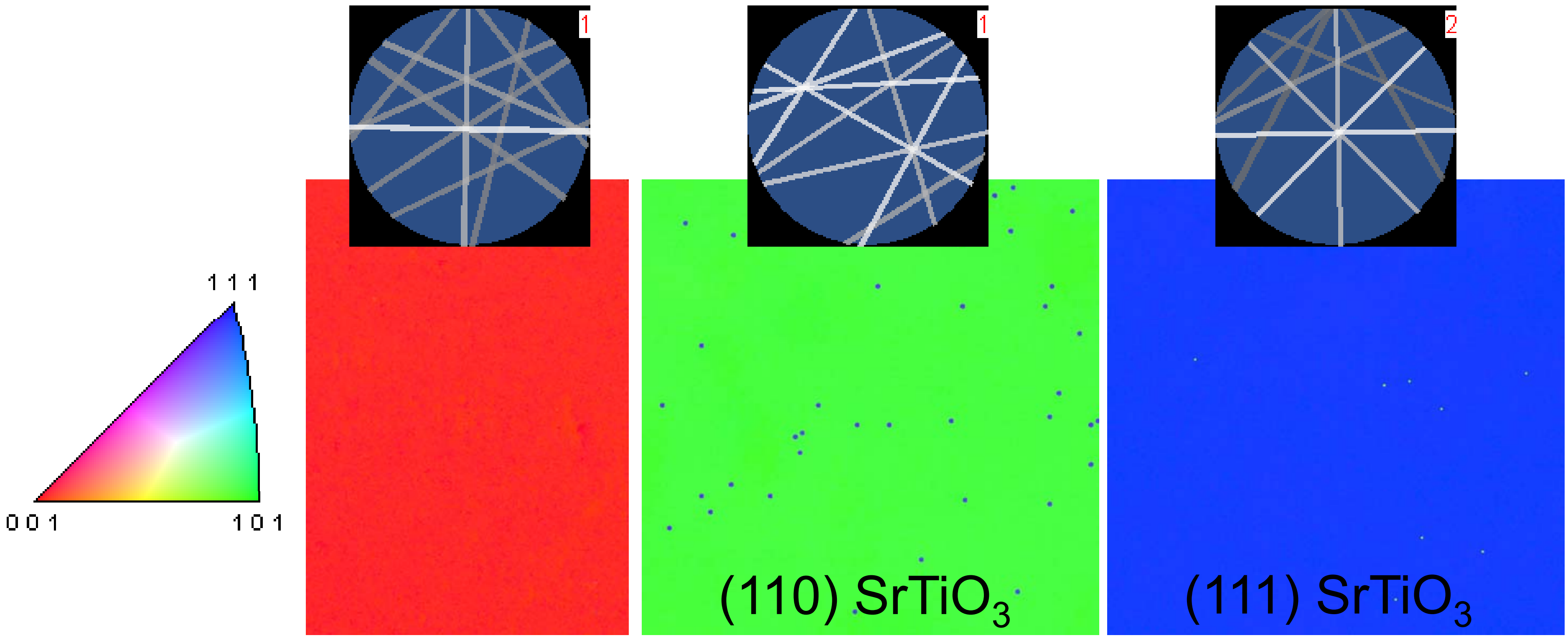
42

Epitaxy along various Orientations
Orientation Mapping / Surface Sensitivity

Electron Back-Scattered Diffraction used to Identify Local Orientations

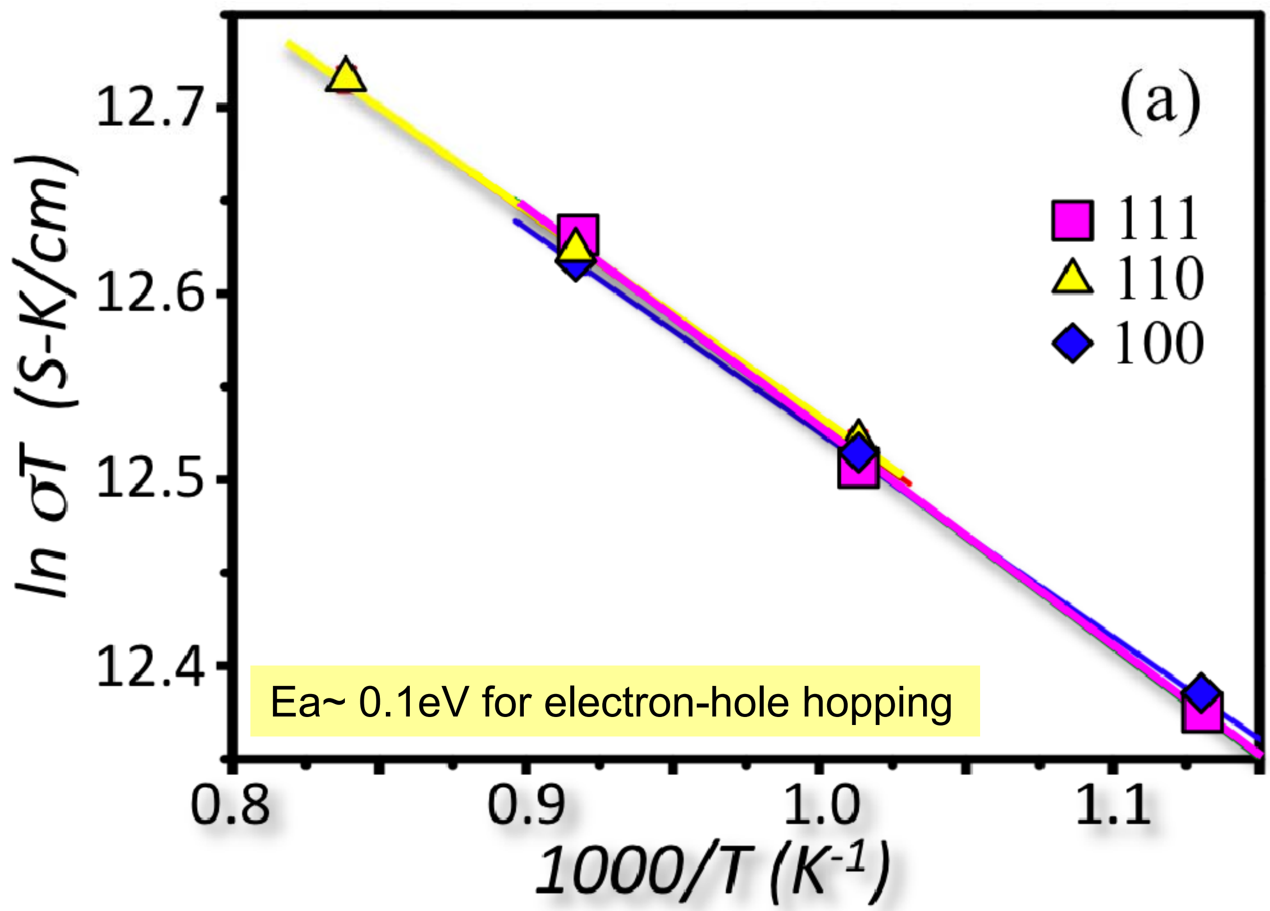
$La_{0.7}Sr_{0.3}MnO_3$ (50 nm) deposited on $SrTiO_3$

All scan areas > 20 x 20 micron^2



All three low-index surfaces are obtained as epitaxial films

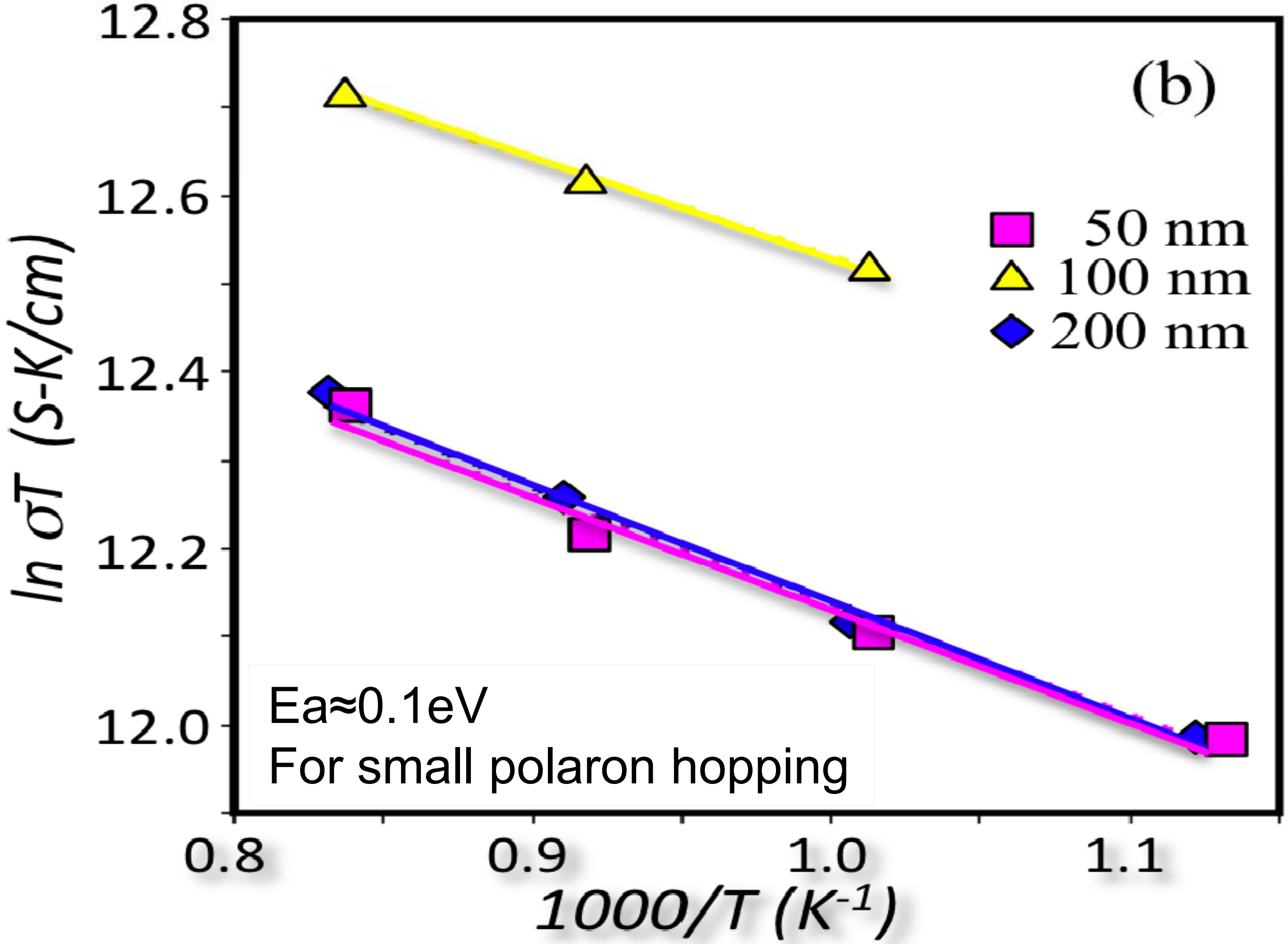
LSMO film conductivity dependency on temperature
PO_2=500mTorr



100nm thick LSMO films show resistivity ≈0.9 mΩ/cm, activation energy ≈0.1eV. Experimental data show good agreement with reported value for LSMO films.

Y. C. Liang and Y. C. Liang, *J. Cryst. Growth,* 304, 275-280 (2007).

(110) LSMO (70/30) conductivity change with temperature



50-200 nm thick LSMO films show resistivity ≈0.9 mΩ/cm, activation energy ≈0.1eV. Experimental data show good agreement with reported value for LSMO films.

Perovskite defect concentration vs PO_2

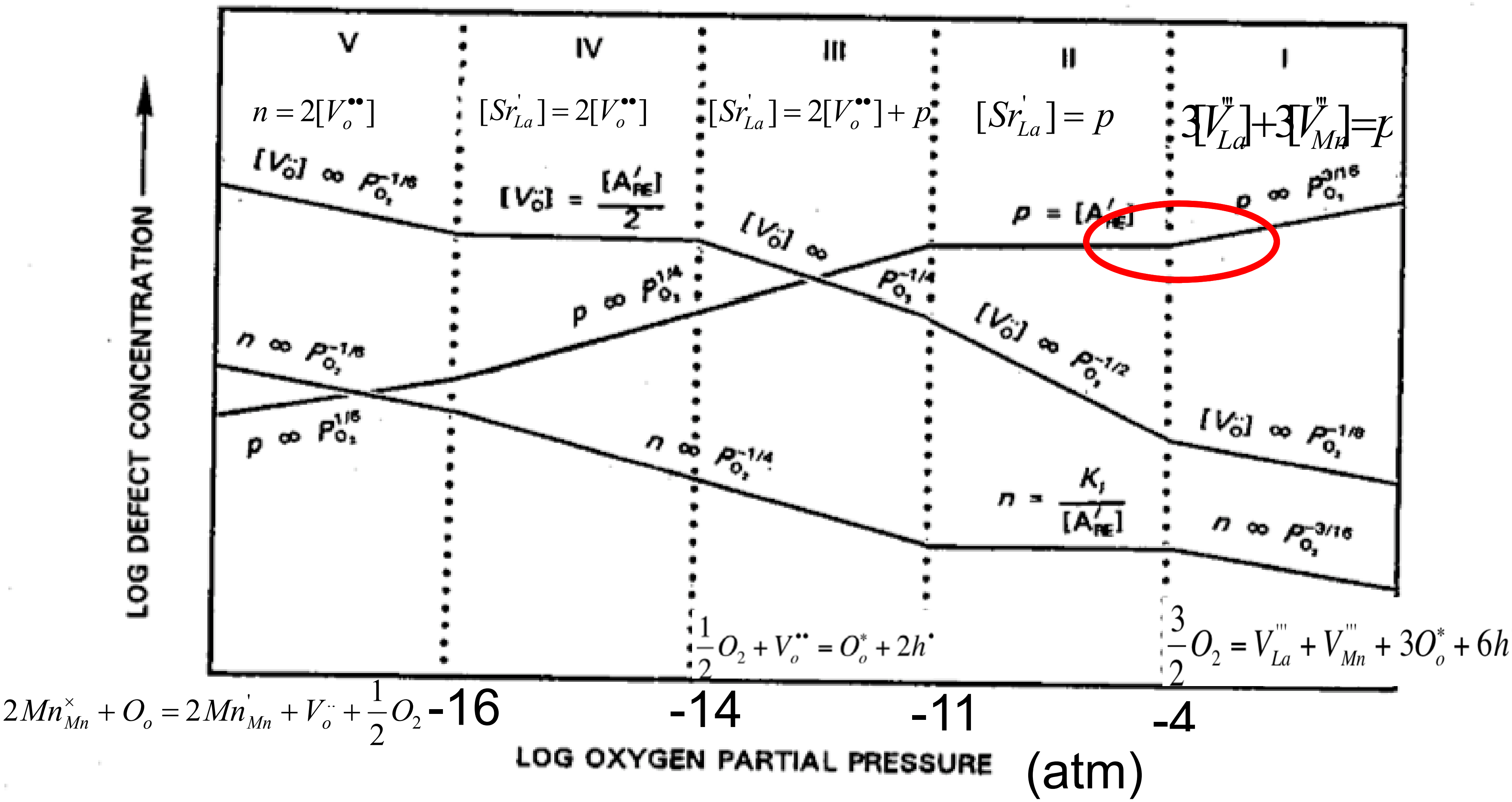
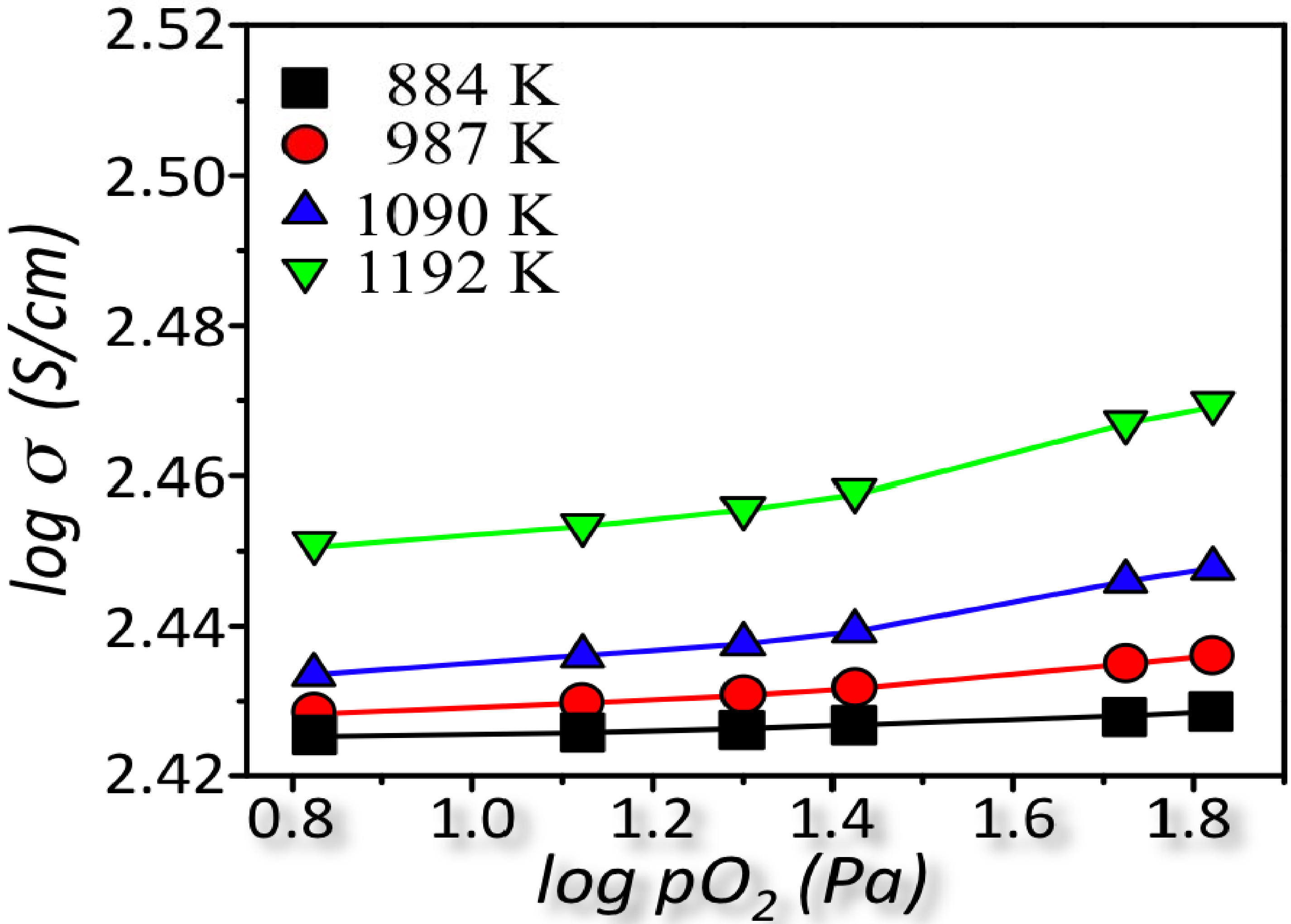


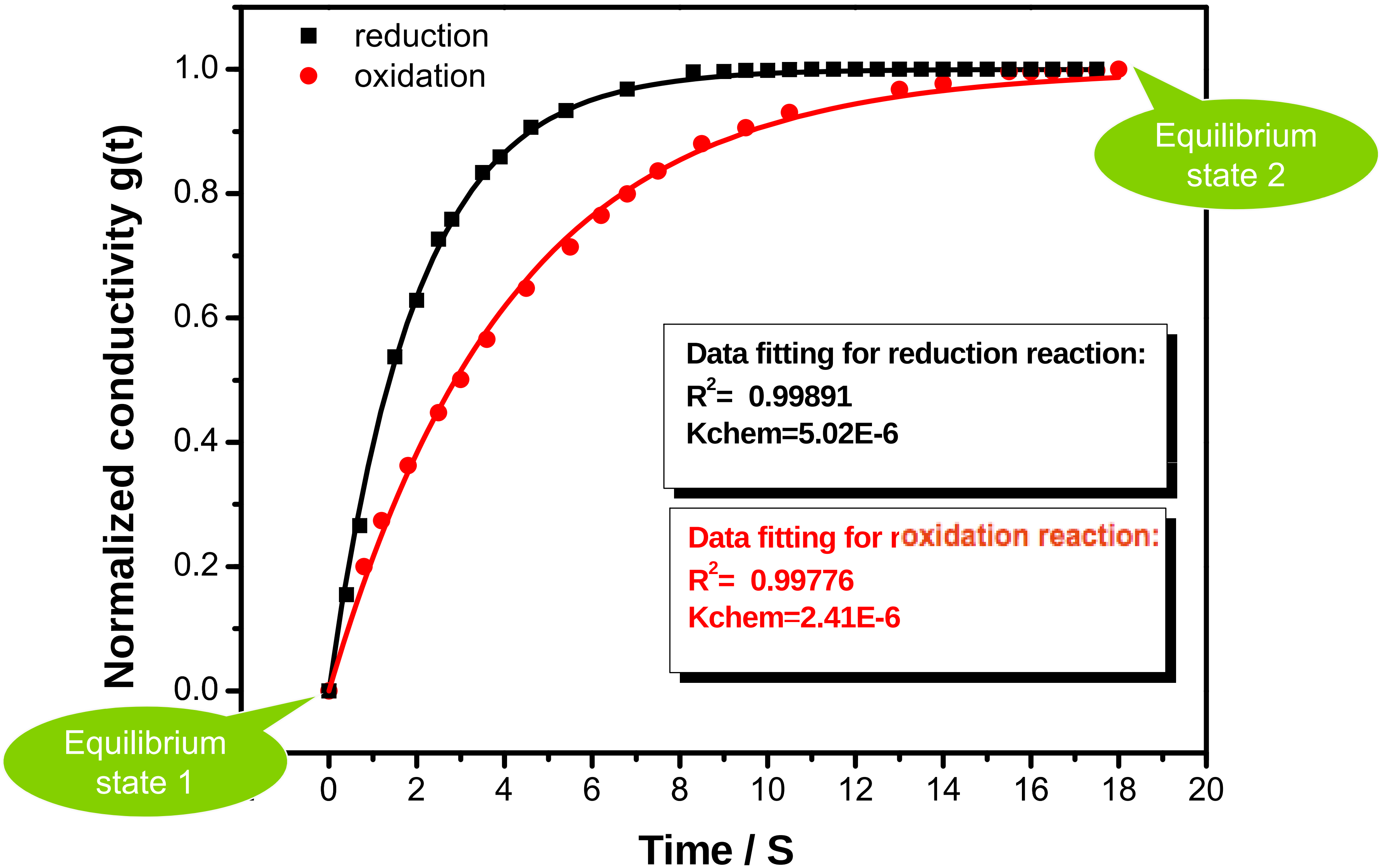
Figure 3.7. *Defect concentration as a function of oxygen partial pressure for a rare-earth perovskite oxide*

LSMO (111) film conductivity dependency on PO_2



Transition region, slope gradually increases which coincide with theory and the slopes lie between 3/16 to 0 according to theoretical calculation.

ECR data fitting for fast and slow surface exchange processes



Diffusion models for surface exchange controlled reaction

J_{in} :flux into the sample

K_{chem} :surface exchange coefficient

Linear flux-force relationship:

$$J_{in} = -K_{chem}(c_t - c_{final}) \quad \text{Eq.(1)}$$

C_{final} :concentration at the final equilibrium state.

C_t : nonstoichiometric species' concentration at time t

According to Fick's 2nd law with $J_{out}=0$:

$$\frac{\partial c}{\partial t} = \frac{\partial J}{\partial x} = -\frac{K_{chem}}{L}\left(c_t - c_{final}\right) \quad \text{Eq.(2)}$$

L: sample thickness

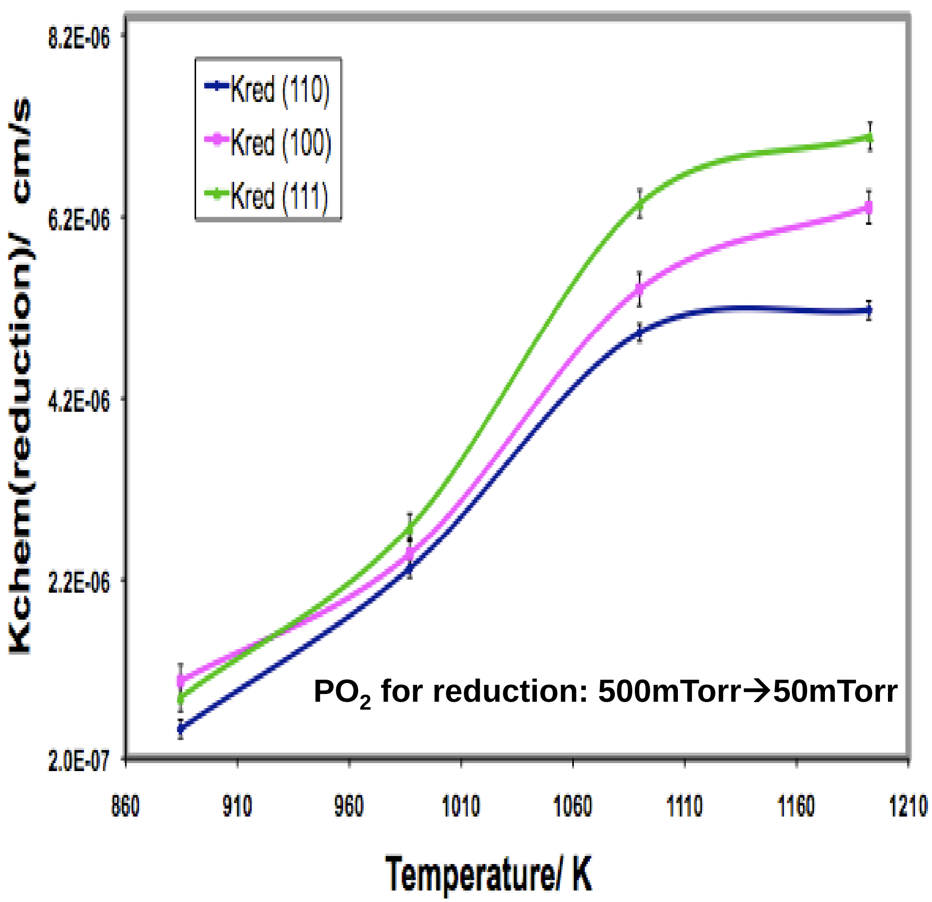
Integration gives:

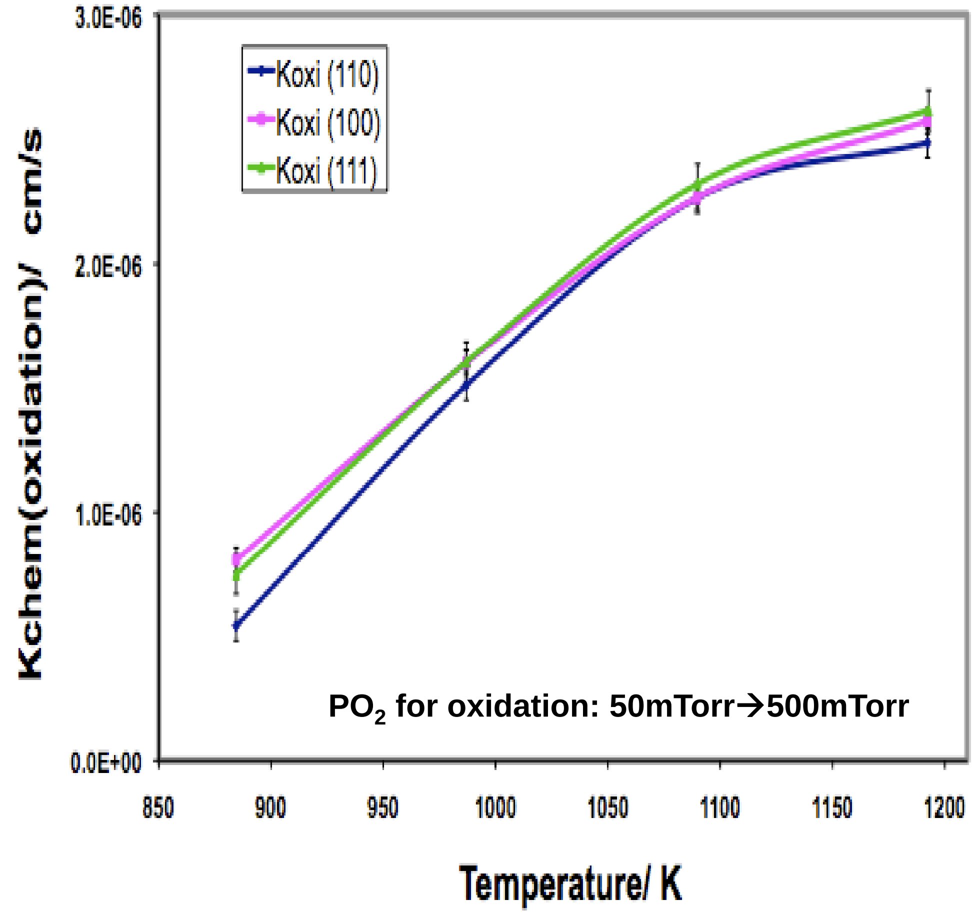
$$\frac{c_t - c_{inital}}{c_{final} - c_{initial}} = 1 - \exp\left(-\frac{K_{chem}t}{L}\right) = 1 - \exp\left(-\frac{t}{\tau}\right) \quad \text{Eq.(3)}$$

C_{final} :concentration at the final equilibrium state.

τ: time constant

K_{chem} dependency on film orientation





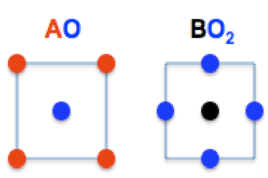
K_{chem} dependency on film orientation data sheet

	T1(K)		T2(K)		T3(K)		T4(K)	
K_{chem} (reduction)	1192 K	$\frac{K_i - K_{max}}{K_{max}}$	1090 K	$\frac{K_i - K_{max}}{K_{max}}$	987 K	$\frac{K_i - K_{max}}{K_{max}}$	885 K	$\frac{K_i - K_{max}}{K_{max}}$
111	7.09E-06	0%	6.35E-06	0%	2.78E-06	0%	0.91E-06	17%
100	6.31E-06	11%	5.41E-06	15%	2.49E-06	11%	1.09E-06	0%
110	5.18E-06	27%	4.93E-06	22%	2.33E-06	16%	0.56E-06	48%
K_{chem} (oxidation)								
111	2.62E-06	0%	2.32E-06	0%	1.61E-06	0%	0.75E-06	7%
100	2.57E-06	2%	2.27E-06	2%	1.60E-06	0%	0.81E-06	0%
110	2.49E-06	5%	2.26E-06	2%	1.51E-06	6%	0.54E-06	33%

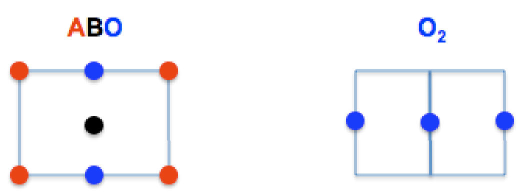
Revisiting Anisotropy

Surface anisotropy of cathode materials → oxygen surface exchange process.
Different orientations → Different K_{chem}

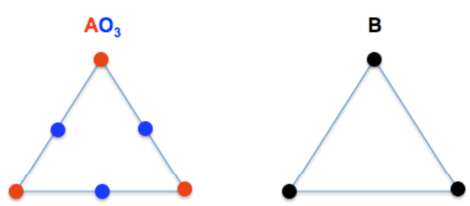
- *Total broken bond density. If true, then*
  $K_{chem}(100) \approx K_{chem}(110) > K_{chem}(111)$.
- *Broken MnO bond density. If true, then*
  $K_{chem}(111) > K_{chem}(110) > K_{chem}(100)$.
- ***50-50 coverage of 2 terminations, and broken MnO bond***
  $\boldsymbol{K_{chem}(111) > K_{chem}(100) > K_{chem}(110)}$.



(100)



(110)

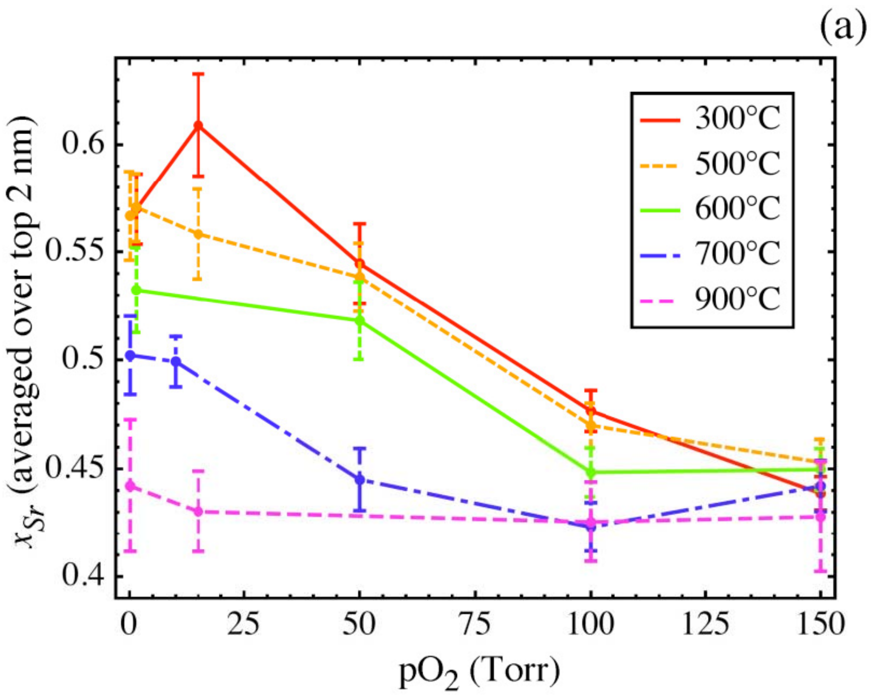


(111)

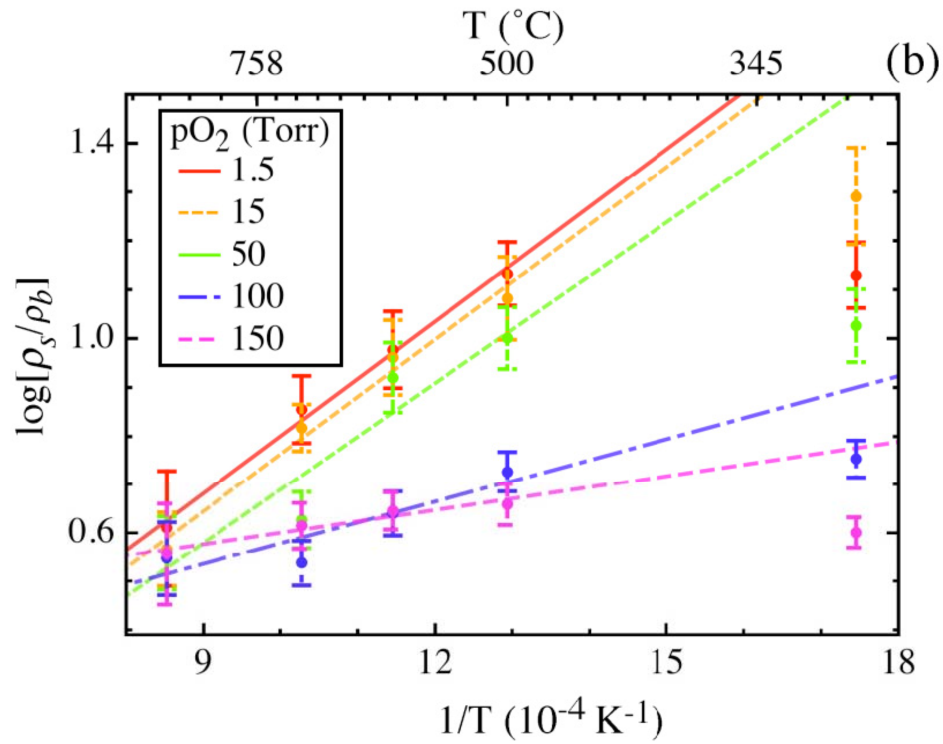
Strontium Segregation vs T an P

16 nm LSMO on DyScO3,

700°C, pO2 = 150 Torr



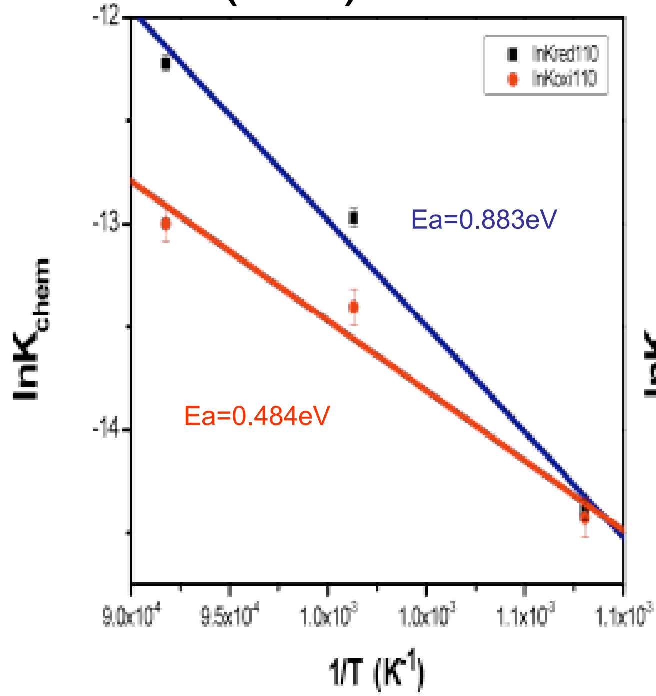
16 nm LSMO on DyScO3,



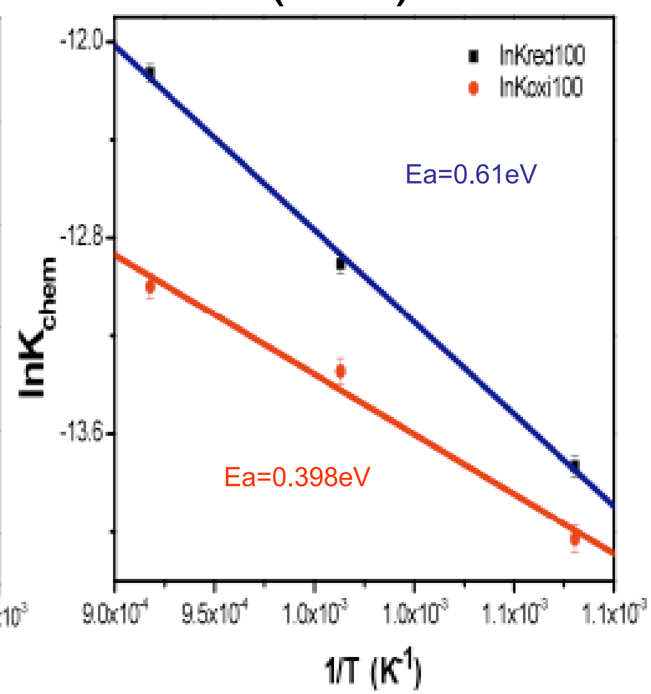
- **Observe that Sr segregation depends on both T and pO_2**
  - plot shows average Sr composition in ~3 nm surface region (bulk composition = 0.3)

K_{chem} dependency on temperature for LSMO films

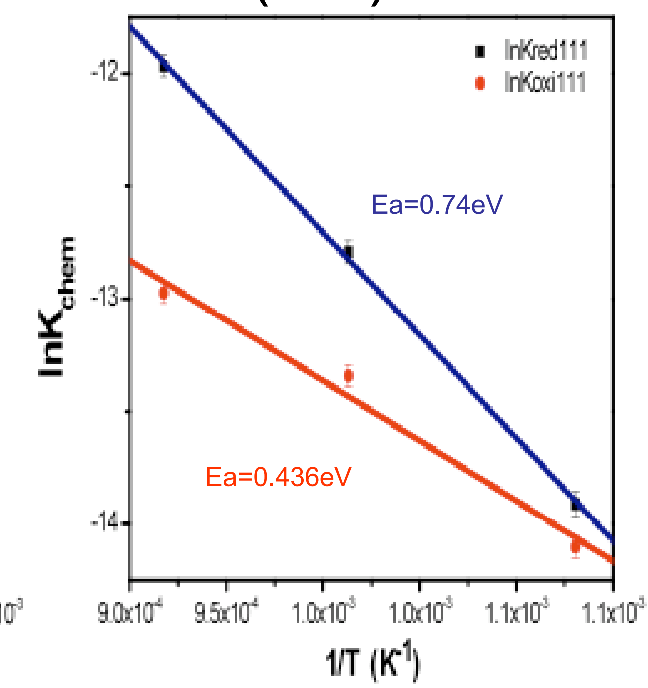
(110) surface



(100) surface



(111) surface



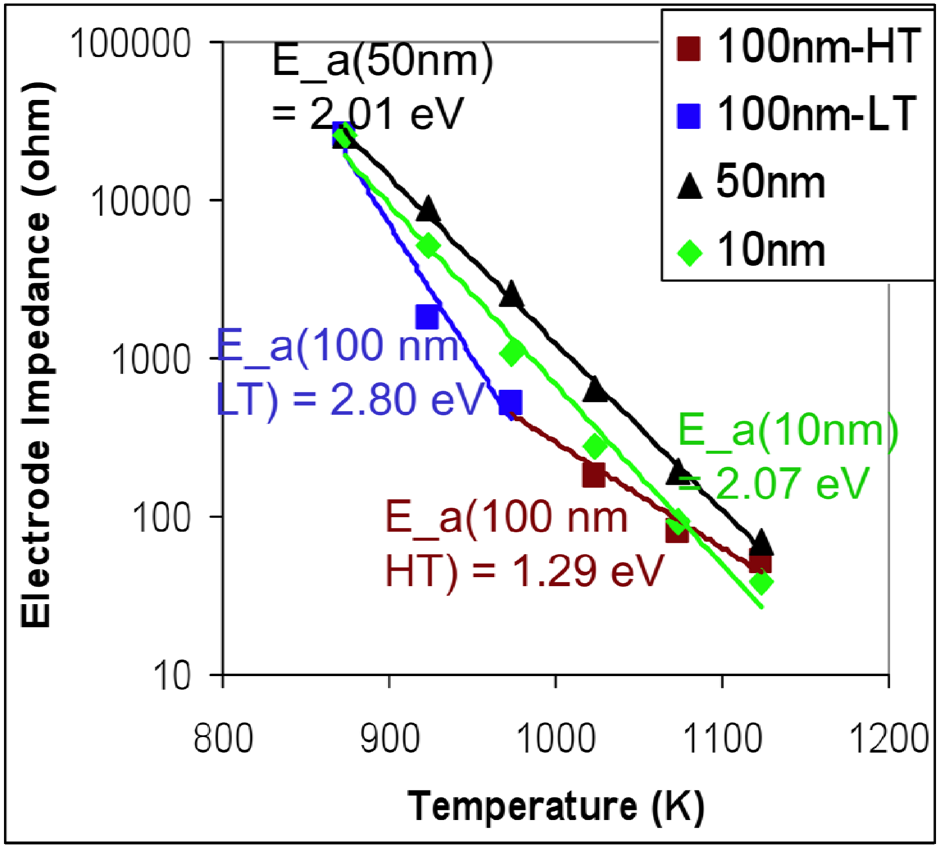
: 100<111<110

K_{chem} reduction > K_{chem} oxidation.

Physical adsorption/desorption might be the rate limiting steps for oxygen exchange.

Impedance vs Thickness and Temperature

IS at MIT of Films prepared at CMU
B. Kavaipatti, P. Salvador, B. Yildiz



2eV of effective activation energy indicates surface-limited oxygen reduction [1,2]

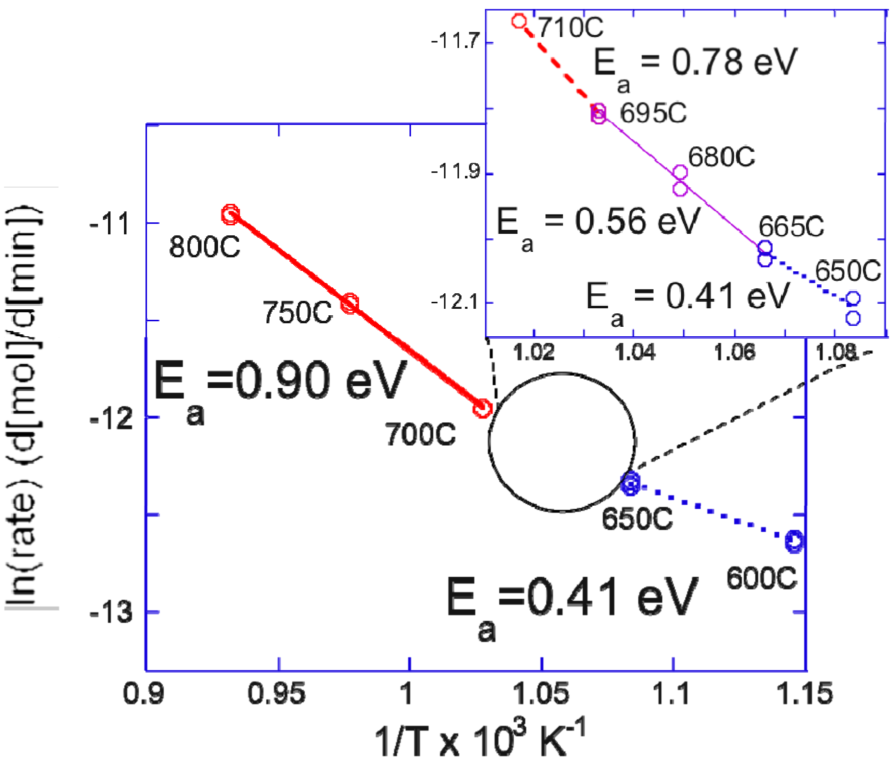
HT region for 100nm thick film indicates a change in the mechanism

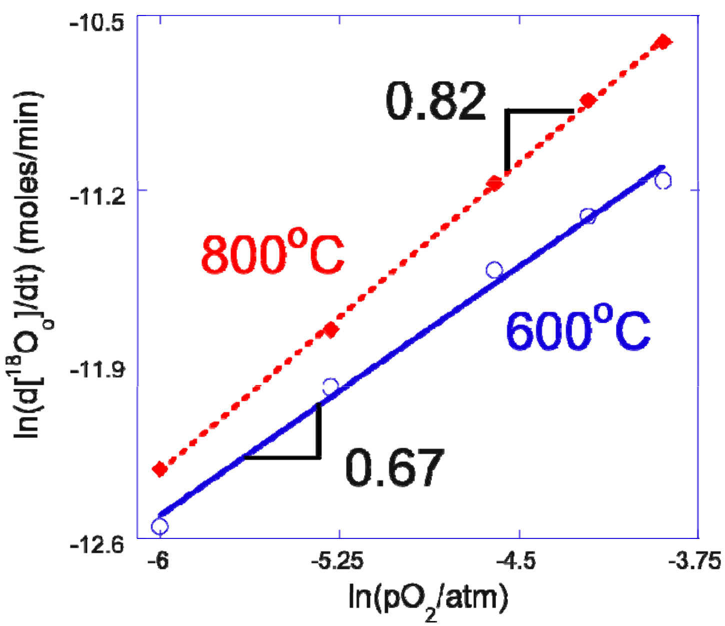
Surface Limited Mechanism is Consistent with Fermi Level Conduction Mechanism

*[1] E. P. Murray, T. Tsai, S. A. Barnett, Solid State Ionics **110**, 235 (1998).*
*[2] S. P. Jiang, J. G. Love, Y. Ramprakash, J. Power Sources **110**, 201 (2002).*

Electronic Structure and Impedance are Correlated

Similar activation Energy for $^{18}O_2$ exchange for LSMO powder

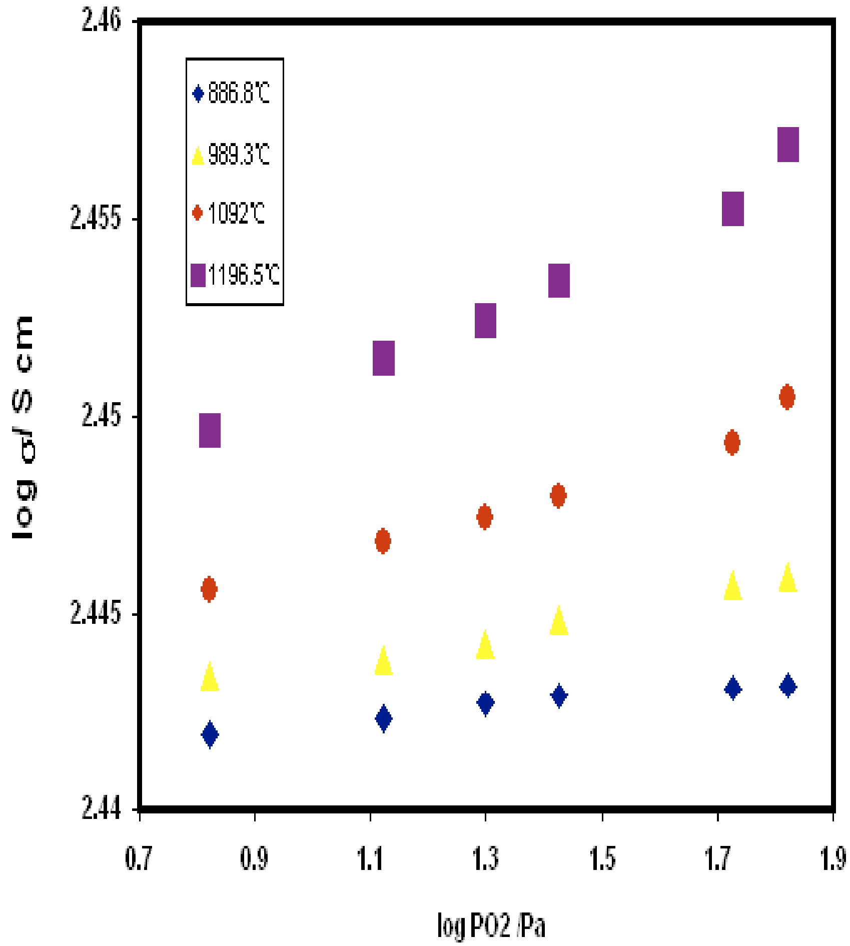




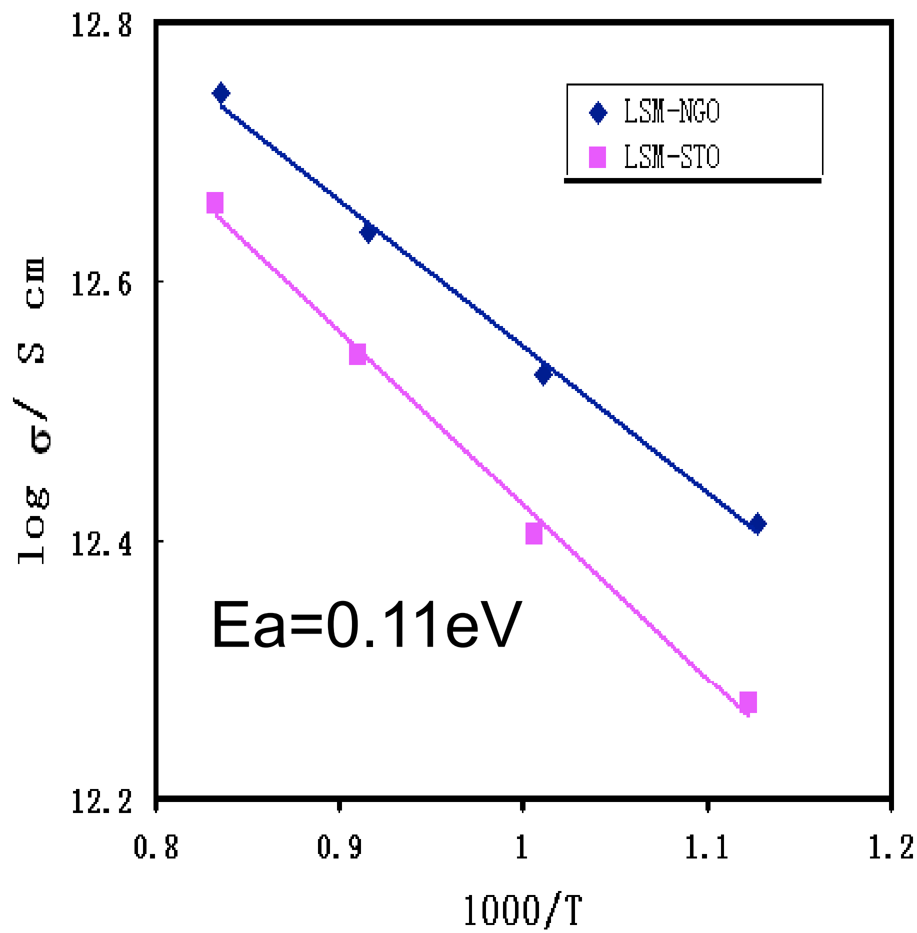
*C. C Kan, H. H Kan, F. M Van Assche, E. N Armstrong, E. D Wachsman, Journal of The Electrochemical Society, **155** B985-B993 (2008).*

Affect of Substrate on Conductivity

150nm LSM(100) on NGO(100)

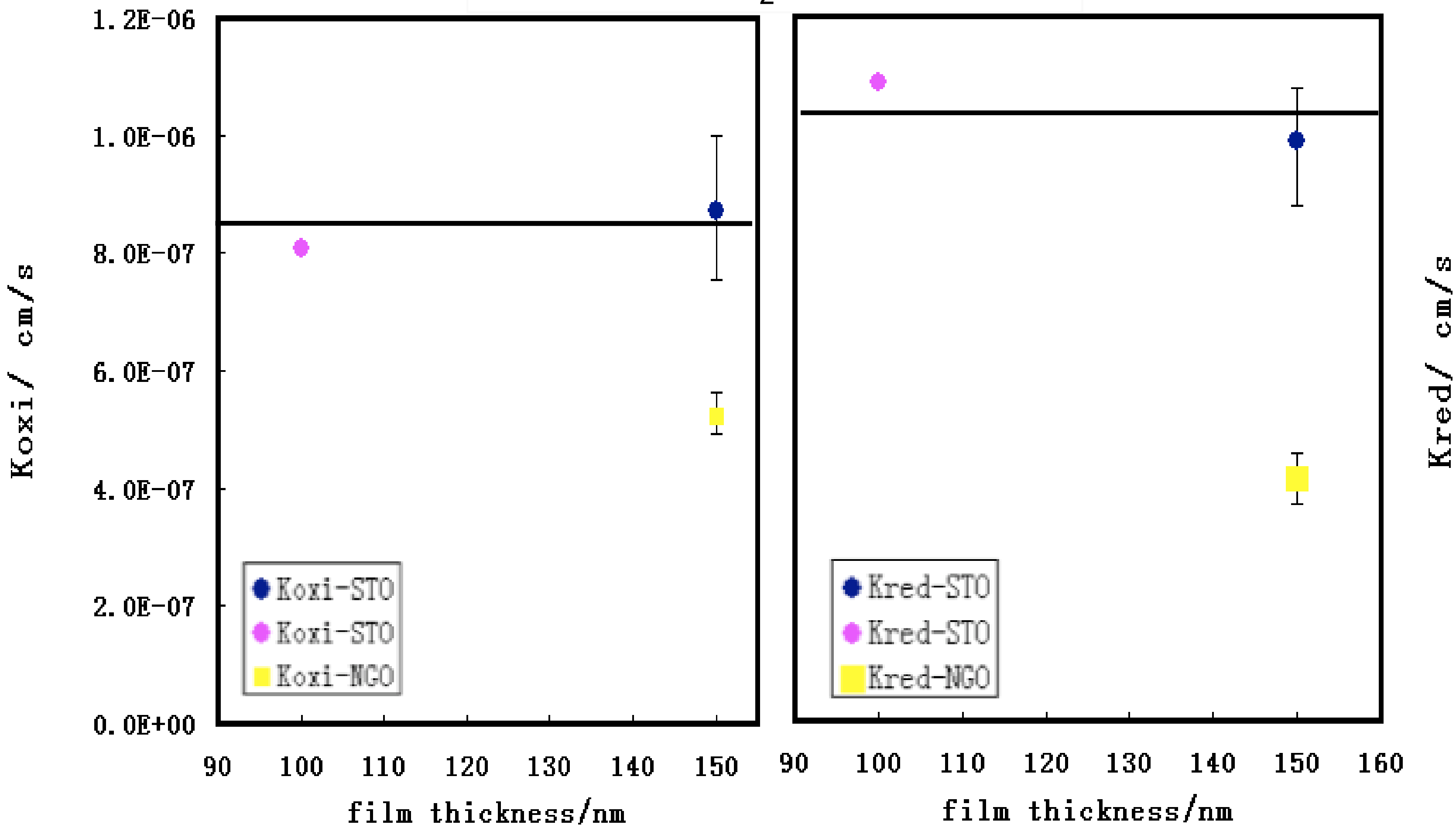


150nm LSM(100) in 500 mTorr



Thickness and Substrate Dependence

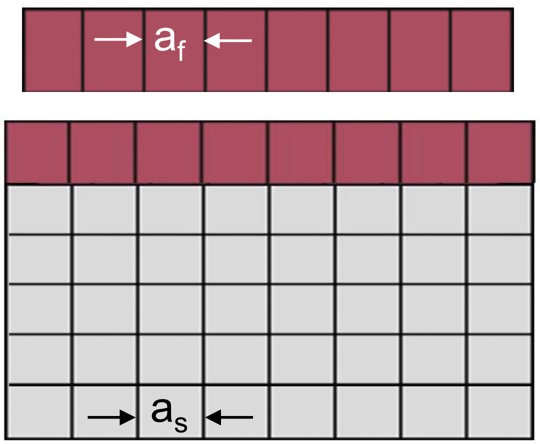
T = 600 ℃, PO_2 : 500mT-50mT



Cathode thin film growth – Substrate choice and orientation

Mismatch Strain

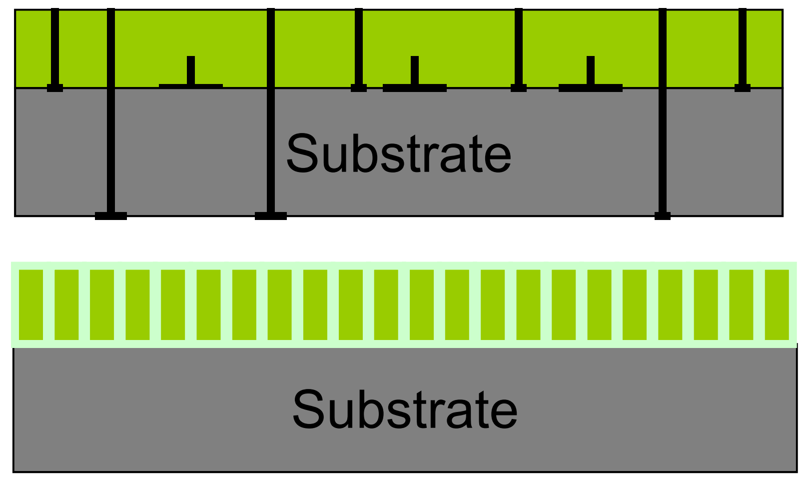
$$f = \frac{(a_s - a_f)}{a_f}$$



$$w_{strain}^{max} = \frac{2\mu(1+\nu)f^2}{(1-\nu)}$$

Dislocations

Misfit
Threading (relaxation)
Threading (inherited)



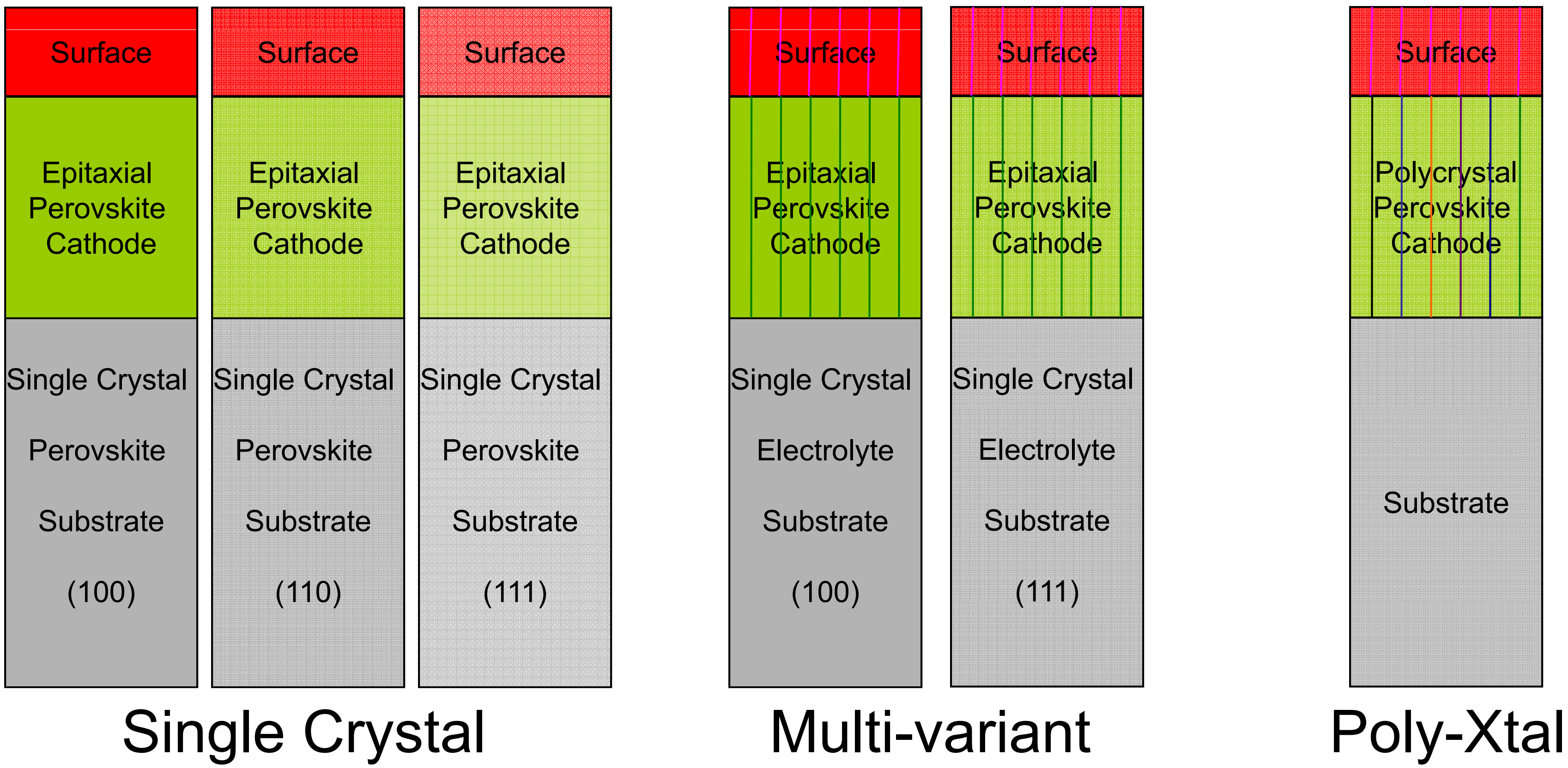
Substrates have different lattice mismatches and
Different dislocation densities

Thin Film Samples Driving Surface Science

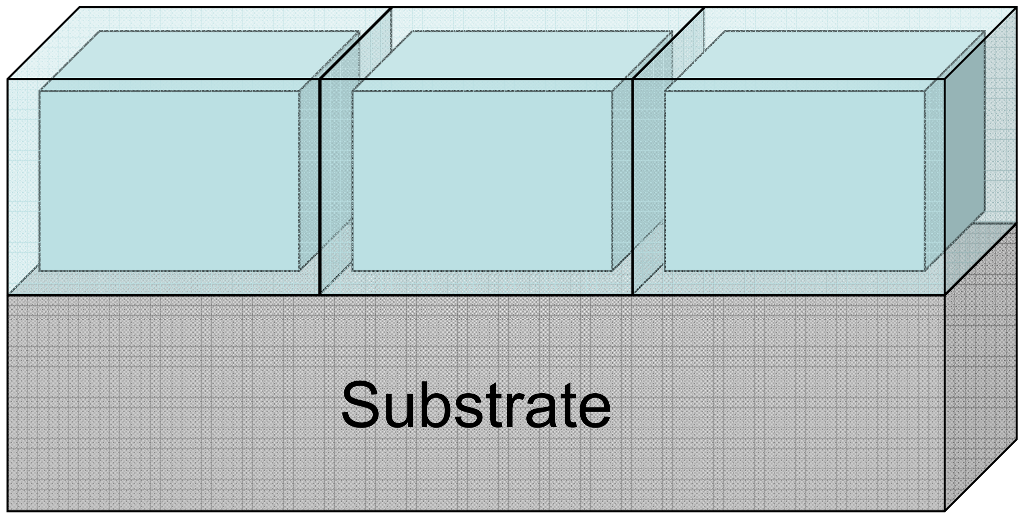
Reaction Occurs at Surface:

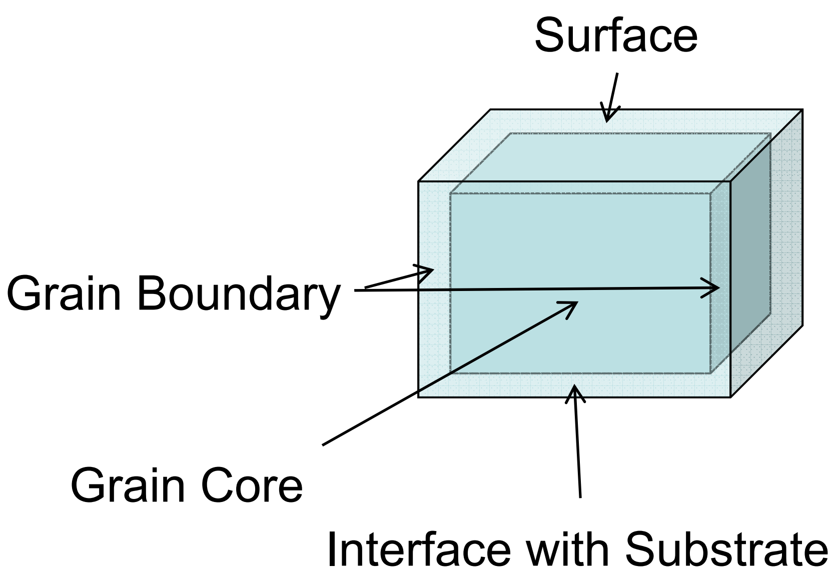
$1/2\ O_2(g)$	**$+\ 2e^-$**	$\rightarrow$	**O^{2-}**
pore	*conductor*		*ion conductor*

Films Allow for Surface / Microstructural Control



Brick-Layer Type Model of Interaction



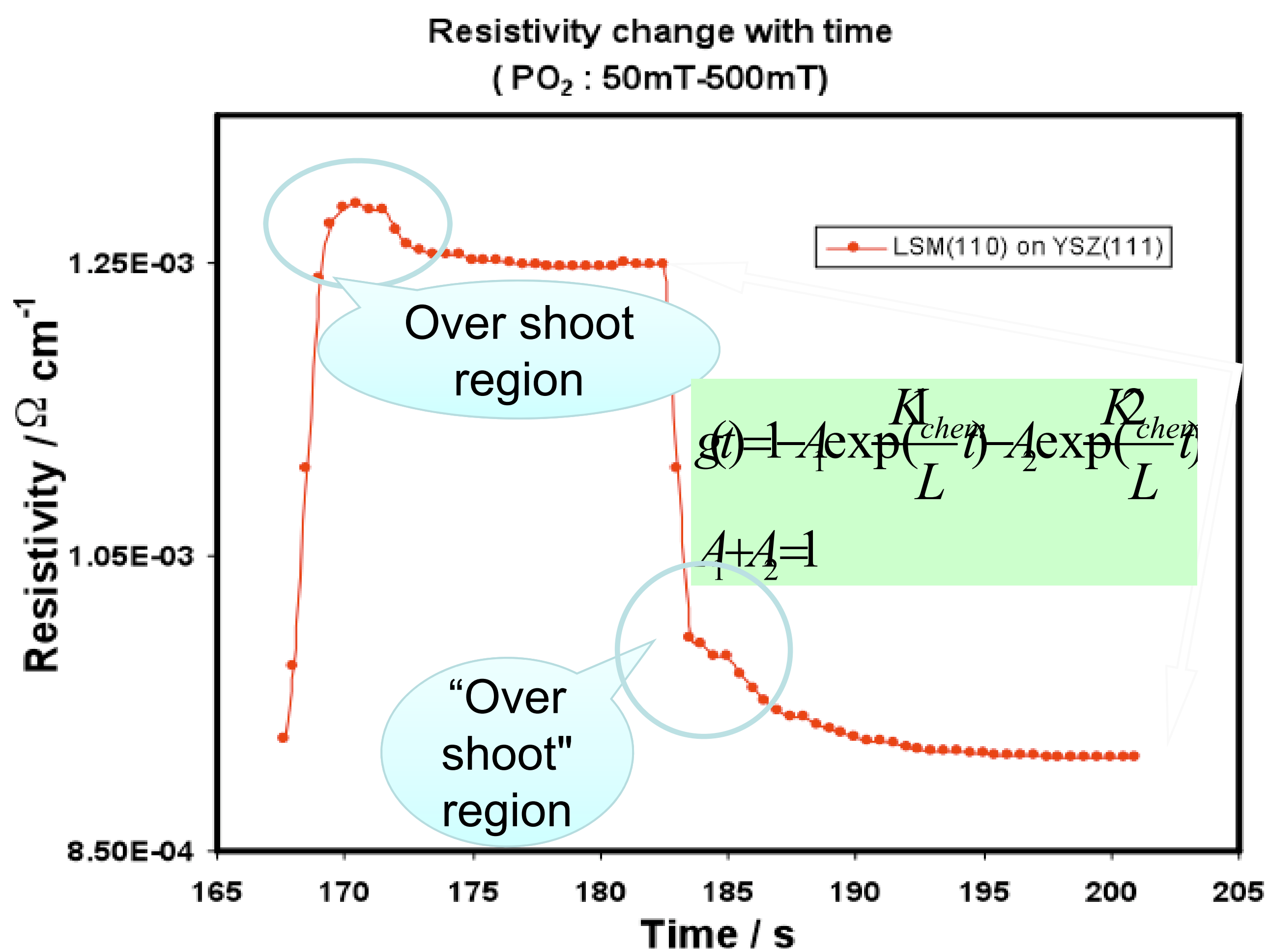


All Films have some level of Defects

How does the nature of the interfacial features affect performance?

- ***Surface***
- ***Grain Boundary***
- ***Interface***

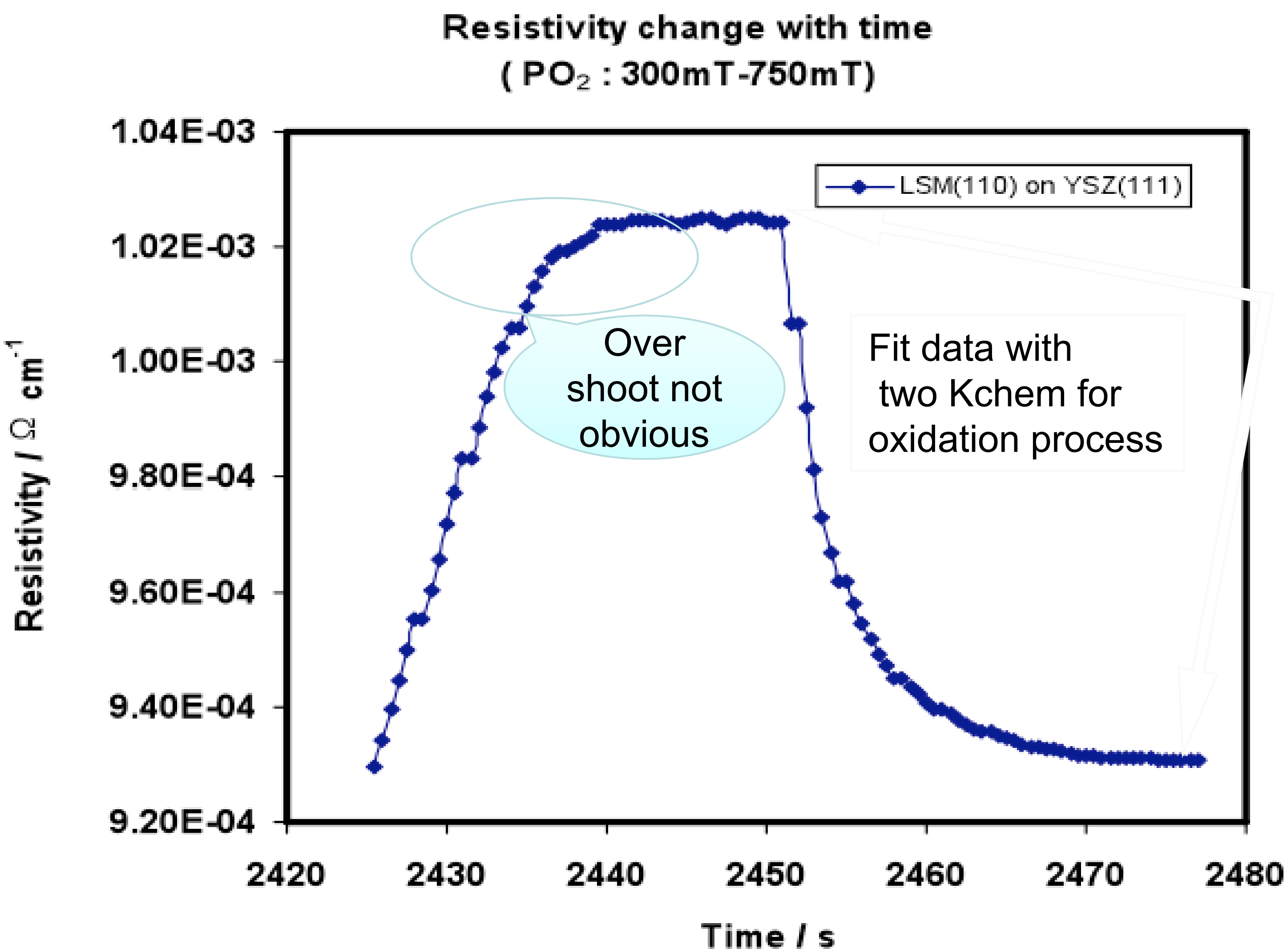
ECR data fitting for Large Pressure Change: (110) LSM on YSZ(111)



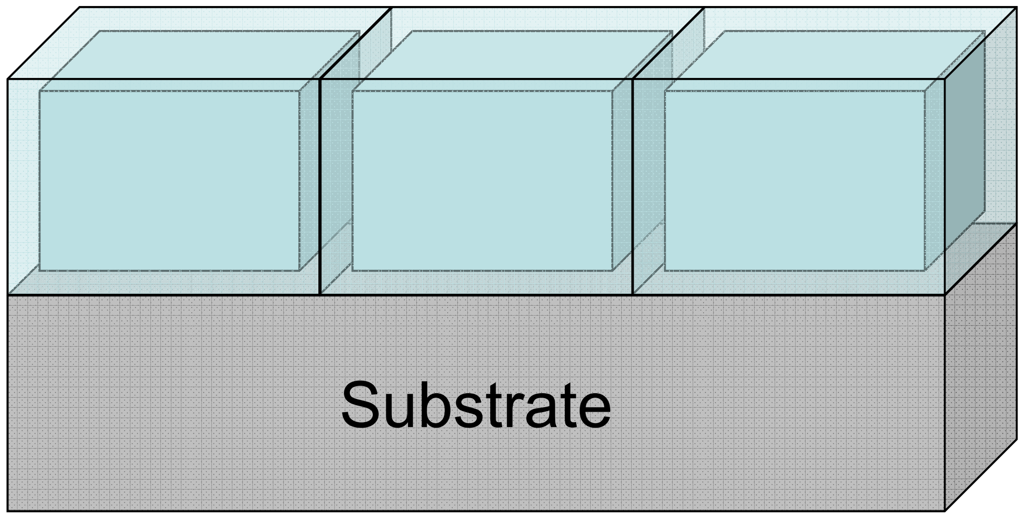
$$g(t) = 1 - A_1 \exp\left(-\frac{K1_{chem}}{L} t\right) - A_2 \exp\left(-\frac{K2_{chem}}{L} t\right)$$

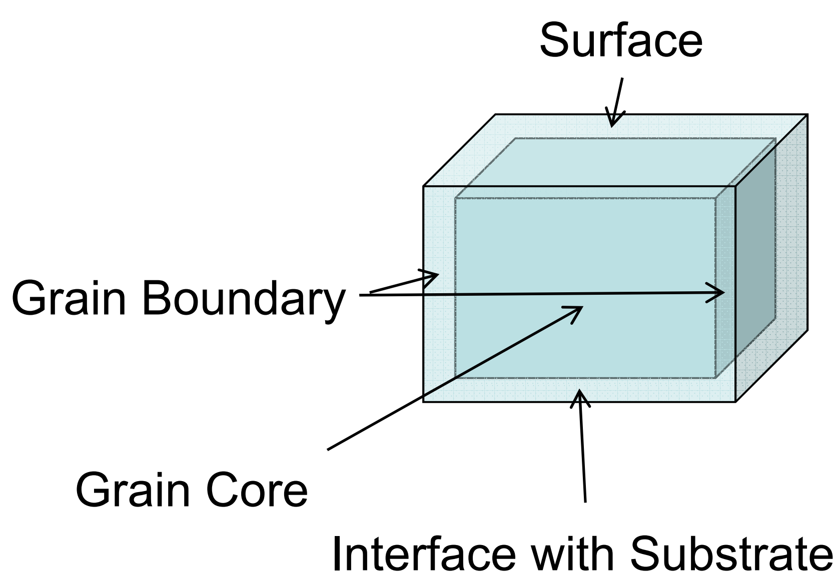
$$A_1 + A_2 = 1$$

ECR data fitting for Small Pressure Change: (110) LSM on YSZ(111)



Brick-Layer Type Model of Interaction

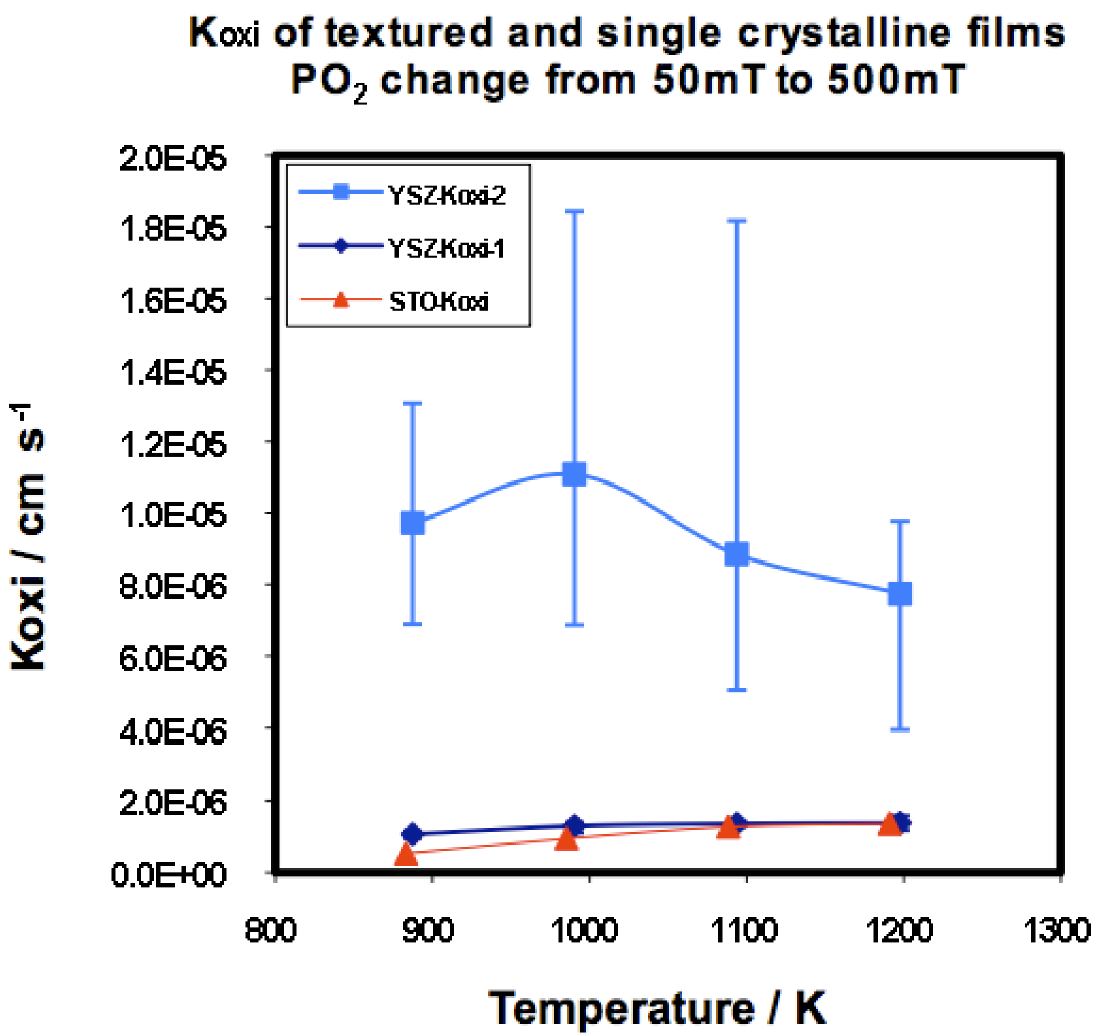


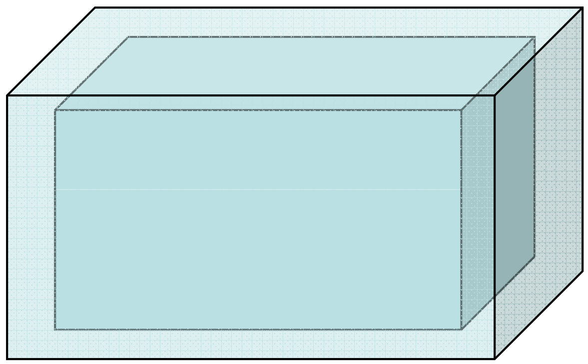


All Films have some level of Defects

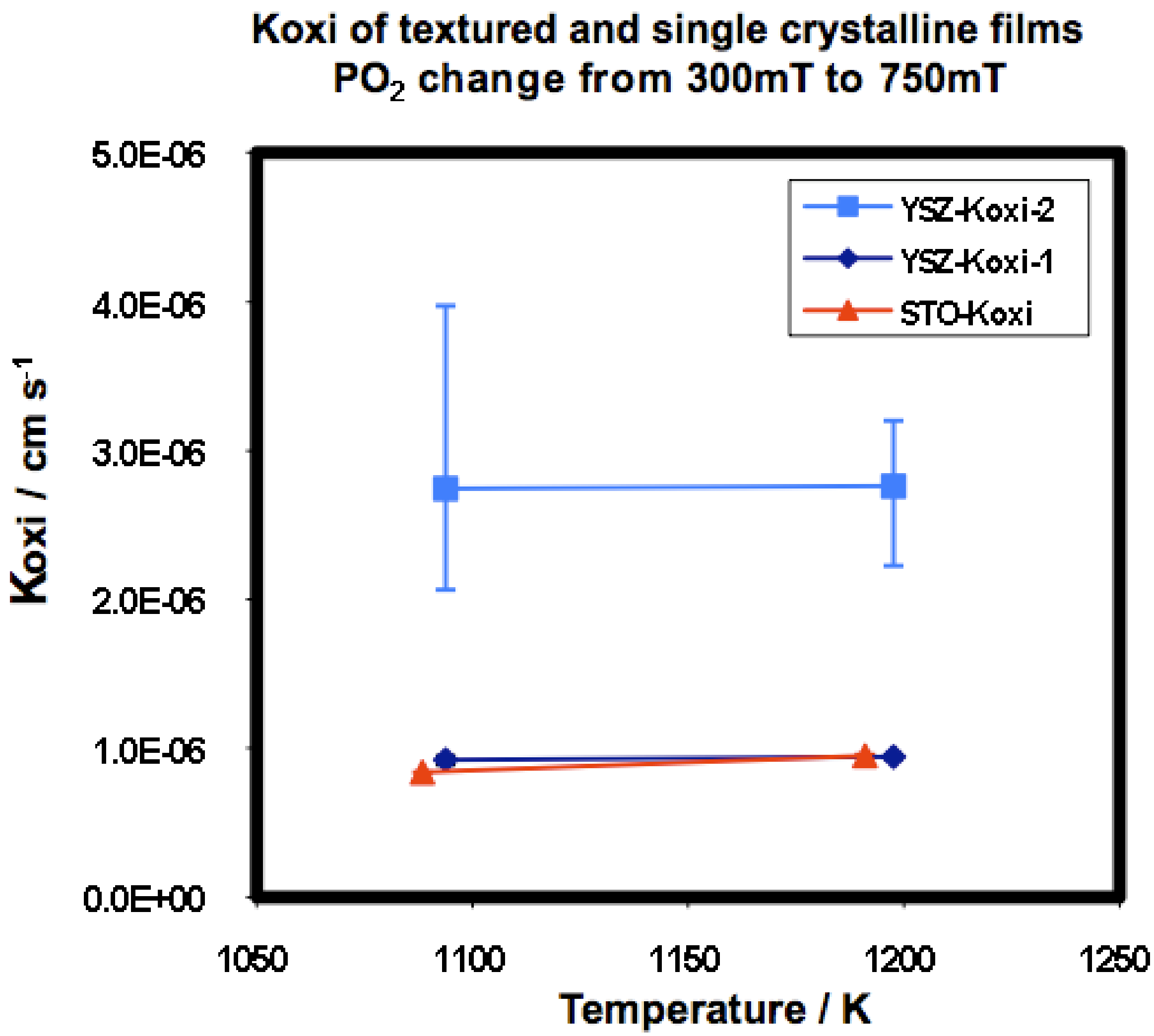
How does the nature of the interfacial features affect performance?
- ***Surface***
- ***Grain Boundary***
- ***Interface***

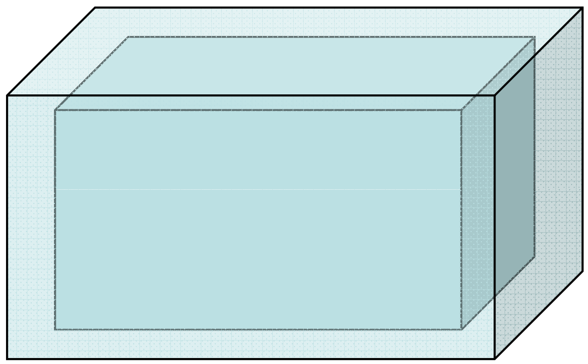
Typical Values for Two Activation Energies
Typical Explanation





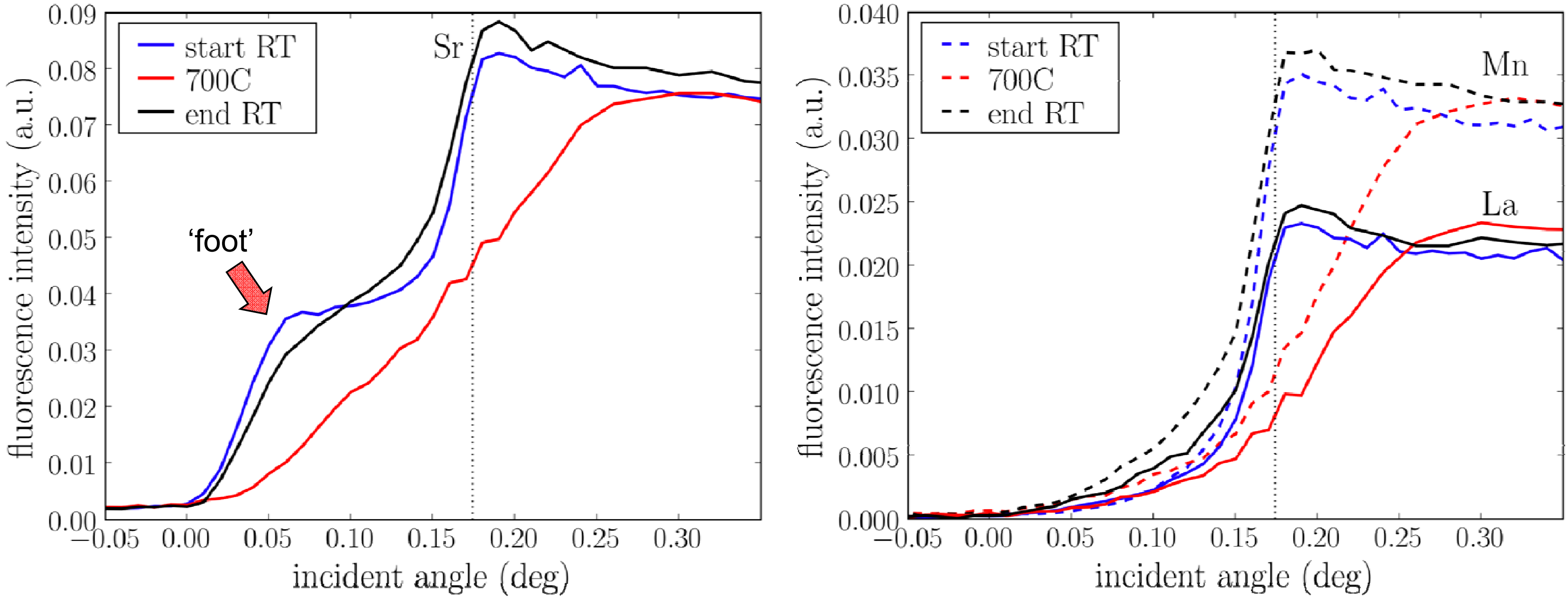
Typical Values for Two Activation Energies
Typical Explanation





Temperature Dependent TXRF of LSM(110)

60 nm $La_{0.7}Sr_{0.3}MnO_3$ on YSZ



- At room temperature, there is a 'foot' in the Sr fluorescence but not in Mn and La
- This is evidence of Sr rich particles at the LSM surface due to Sr segregation.
- This 'foot' gradually disappears at high temperature implying particles are re-incorporated.
- Process is reversible, 'foot' reappears at room temperature despite rapid cooling (700°C to room temperature in 30 minutes)

LSMO Experimental Summary

1. Single oriented, epitaxial, smooth LSMO (100), (110) and (111) films were fabricated on STO and LSMO (100) on NGO.

1. Multivariant epitaxial LSMO (100) and (110) were fabricated on YSZ(100)/GDC(100) and YSZ(111)

3. Steady-state conductivity measurements on LSMO films exhibit consistent results as reported in literatures.

4. Transient conductivity measurements proved that surface anisotropy plays a role in the oxygen exchange process:

   at high T: K_{chem} (111)> K_{chem} (100)> K_{chem} (110)

   at low T: K_{chem} (100)> K_{chem} (111)> K_{chem} (110)

   K_{chem}(reduction)>≈ K_{chem}(oxidation).

5. Values on NGO are slightly lower than on STO.

6. Microstructure is observed to play a role on thin films…

CMU Work for Cathode Surface Science Project

- ***Growth of High-Quality Thin Film Samples***
  - ***Perovskite / Perovskite Epitaxy and Surface Control***
  - ***Perovskite / Fluorite Epitaxy and Surface Control***
  - *Generation of Surface-Modified Samples*

- ***Surface Kinetics for Oxygen Uptake***
  - ***Electrical Conductivity Relaxation***
  - ***Piezoelectric Crystal Microbalance Gravimetry***
  - ***Kelvin Probe Spectroscopy***

- *Surface Thermodynamics of Oxygen Uptake*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

- *Electronic Structure*
  - *Kelvin Probe Spectroscopy*
  - *STM (MIT)*

- *Ex-situ Surface Characterization for Correlations*
  - *Scanning Auger / XPS*