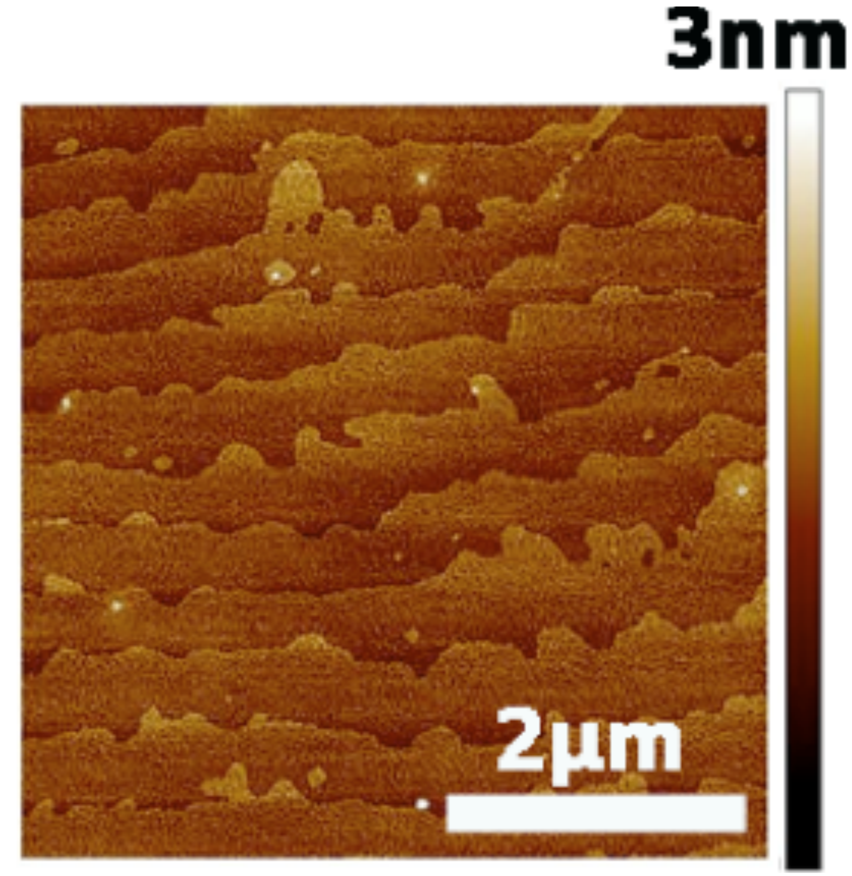
SOFC Cathode Surface Chemistry and Optimization



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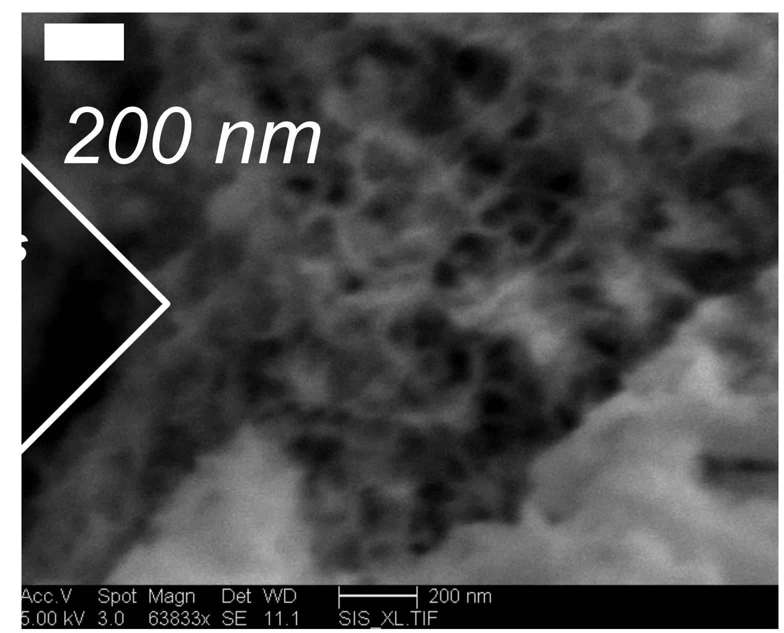


Funded by DOE - SECA, Thanks to L. Wilson, W. Surdoval, B. White, P. Burke, Shailesh Vora

Program Goals and Collaborations

- Improve the Performance of Solid Oxide Fuel Cell Cathodes
  - Reduce Cathodes Losses (increased power) (CMU / NETL)
  - Understand Degradation Mechanisms (CMU / ANL / Delphi / SECA)

- Understand and Optimize Cathode Surfaces
  - Determine what surfaces exist in SOFCs (CMU / NETL)
  - Develop methods to prepare optimal/engineered surfaces. (CMU / NETL)
  - Determine the surface properties of SOFC cathodes (CMU / ANL / MIT / UNLV)
  - *Understand size / support effects on infiltrate surfaces (CMU / ANL / MIT / UNLV / NETL)*
  - Model Electrochemical Performance (CMU / NETL / WVU)

K. Gerdes, C. Matranga, R. Gemmen (NETL);
P. Fuoss, J. Eastman, H. You, M. Krumpelt, B. Ingram (ANL)
B. Yildiz (MIT);

I. Celik and Z. Xu (WVU)

C. Heske and S. Krause (UNLV)

Solid Oxide Fuel Cell Cathodes

- Performance of SOFCs depend on microstructure of electrochemically active regions

multi-phase composite

interpenetrating and 3D-connected

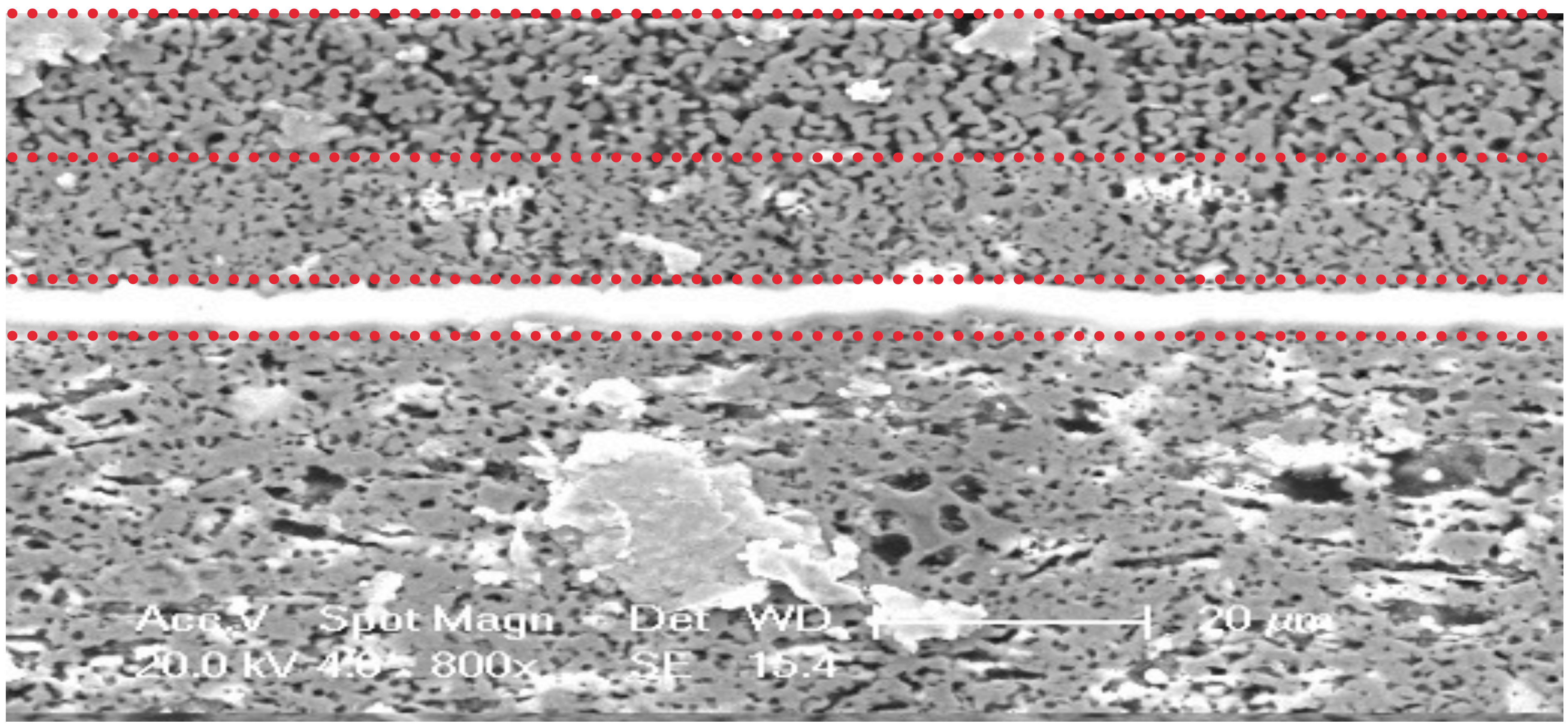
electrochemical reactions occur at or near triple points / surfaces

Current Collector
Pores + $(La,Sr)MnO_3$

Active Cathode
P + LSM + YSZ

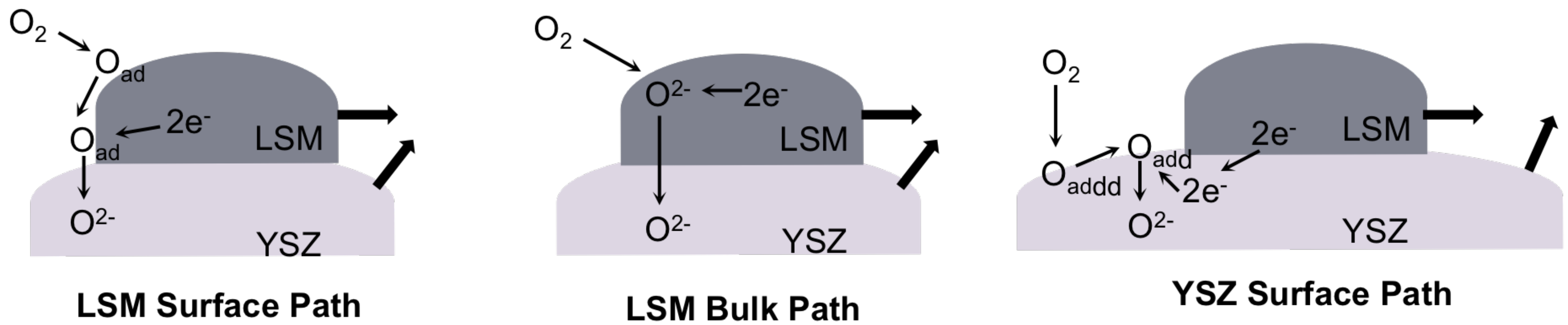
Electrolyte (YSZ)

Anode
P + YSZ + Ni

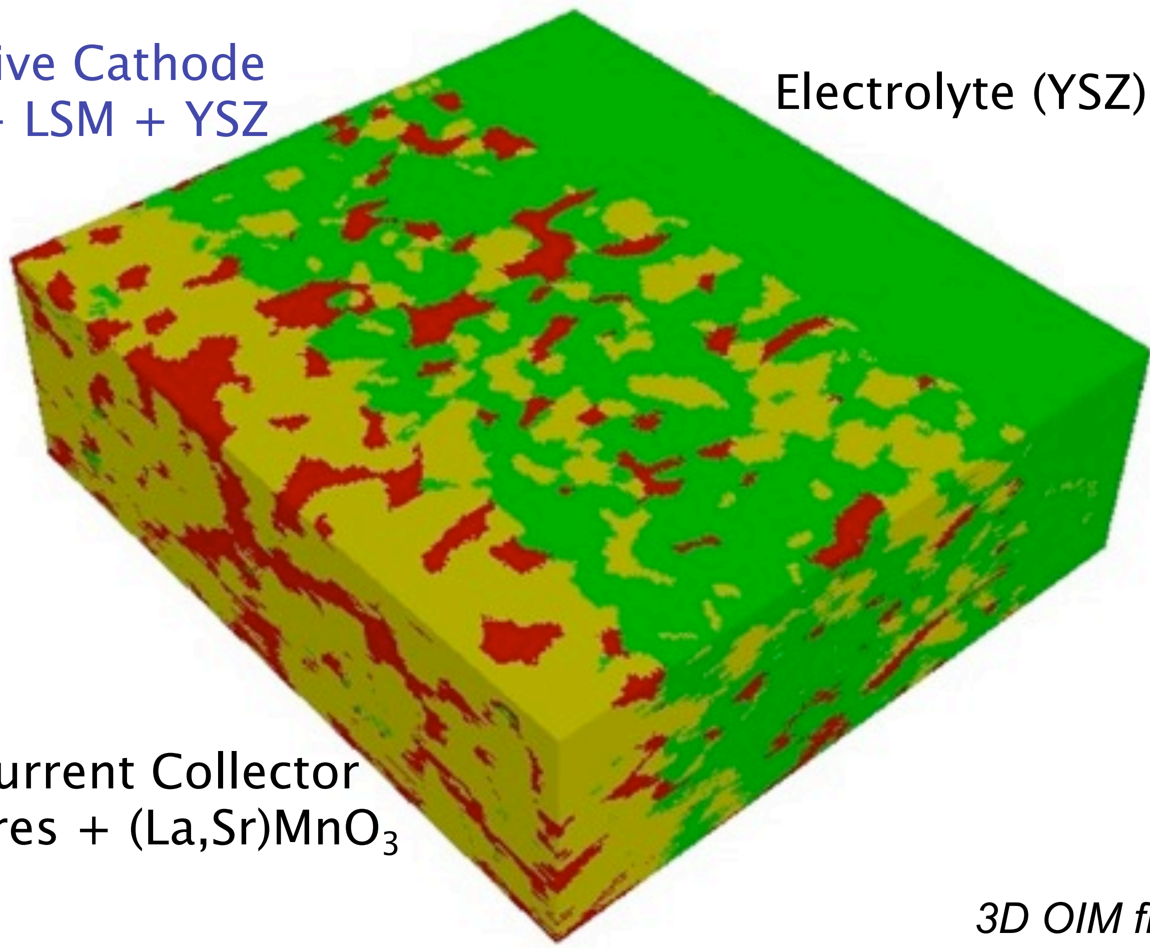


SEM from CMU of NETL prepared SOFC

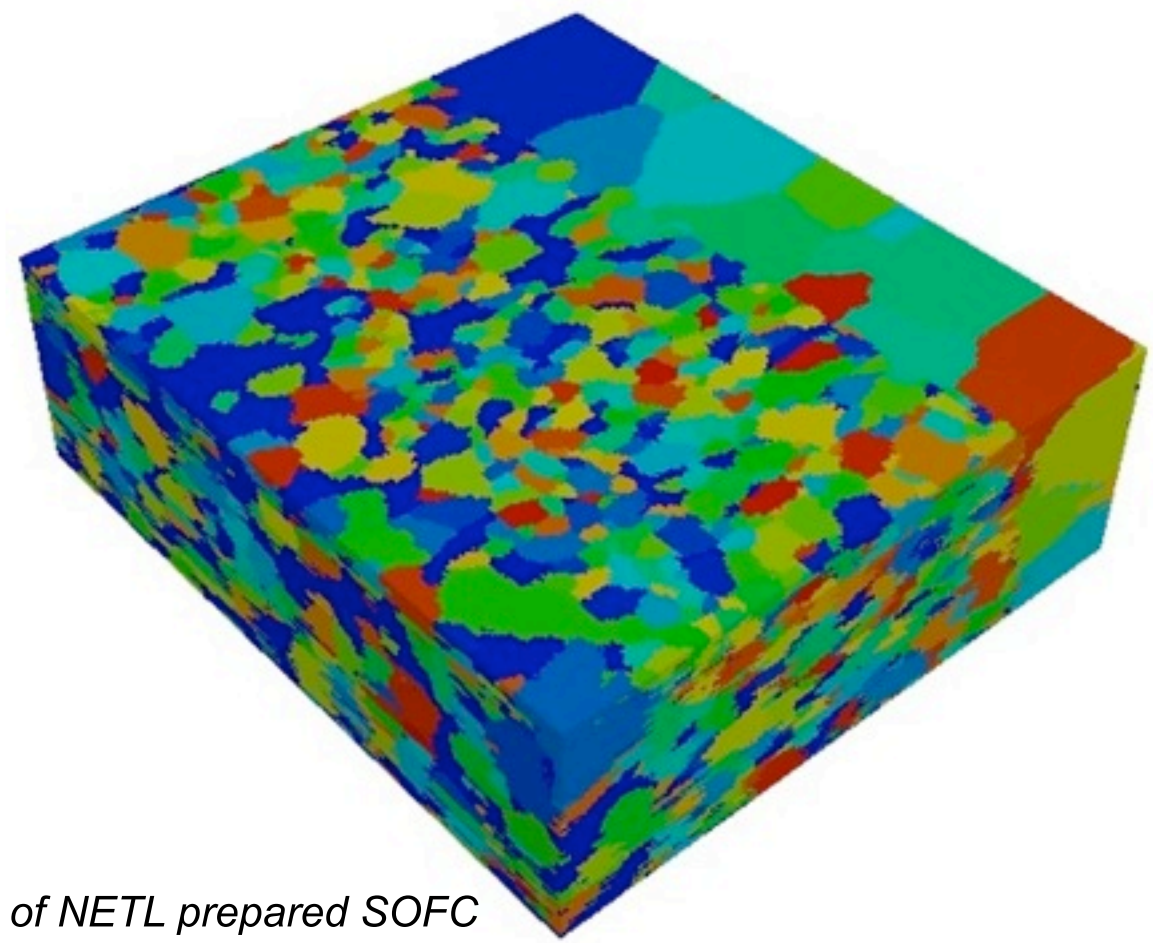
Surfaces and Oxygen Uptake: What is Important?



Phase Distributions



Crystallographic Information



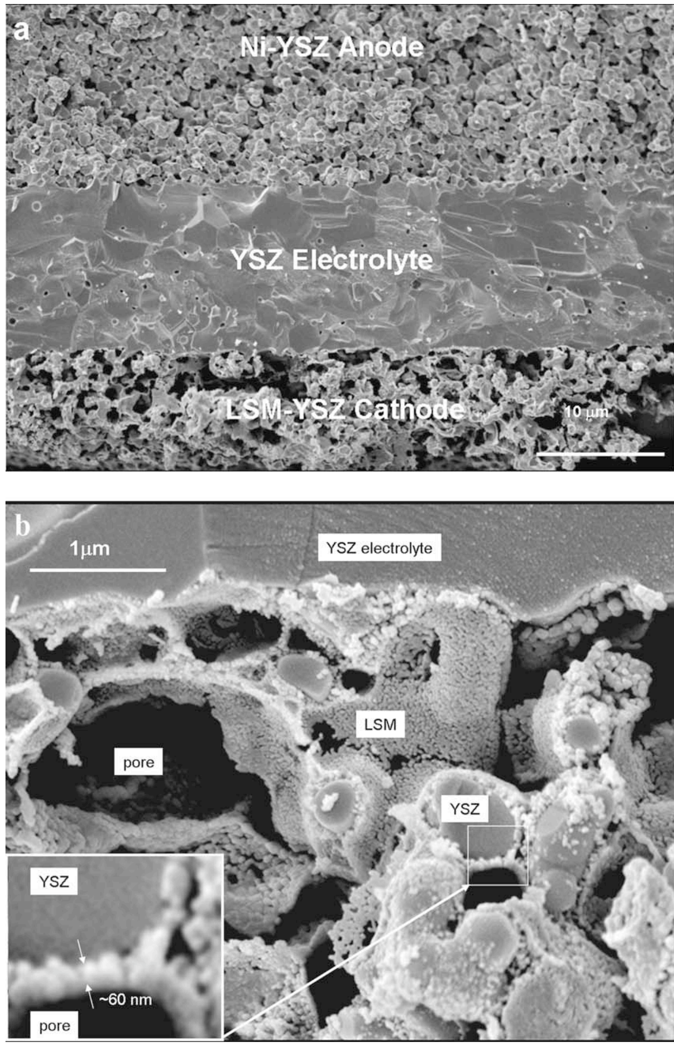
3D OIM from CMU of NETL prepared SOFC

S. Dillon, L. Helmick, G. Rohrer, P. Salvador, R. Gemman, C. Johnson, L. Wilson

All Orientations Exist in a Nearly Random Fashion

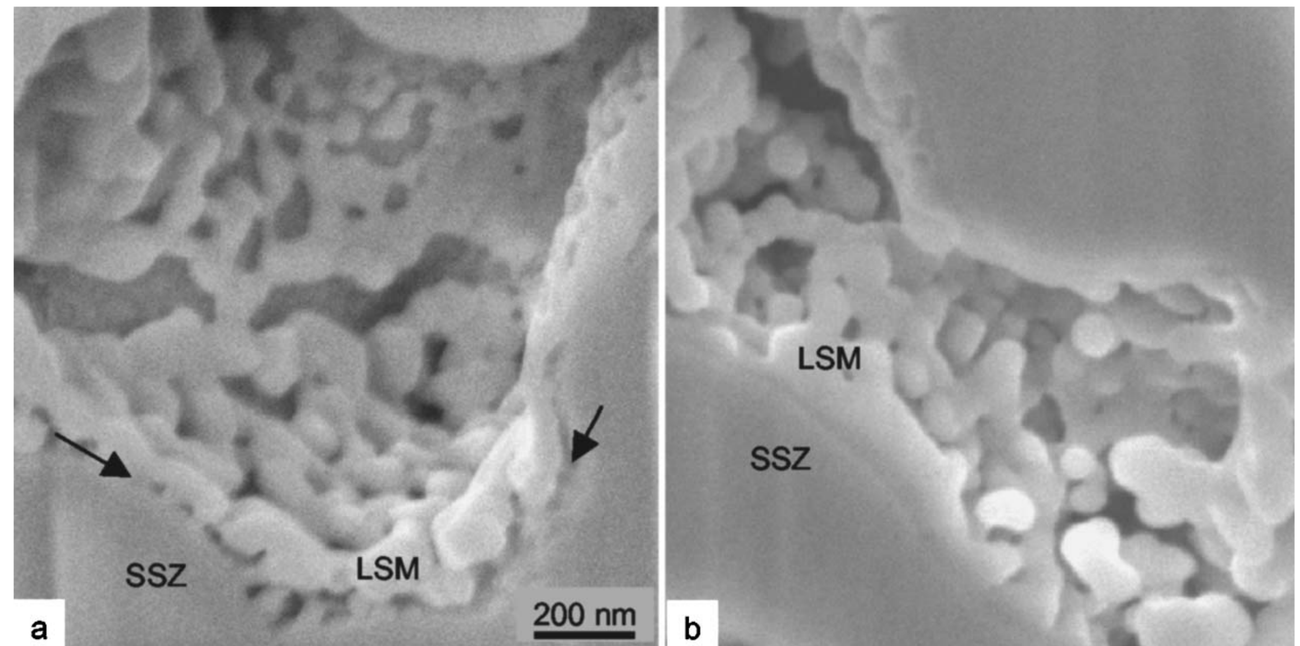
Infiltration: Stable nanoparticles for SOFC activation

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 optimal materials to use for infiltration?

What are the mechanisms of enhanced performance / degradation?

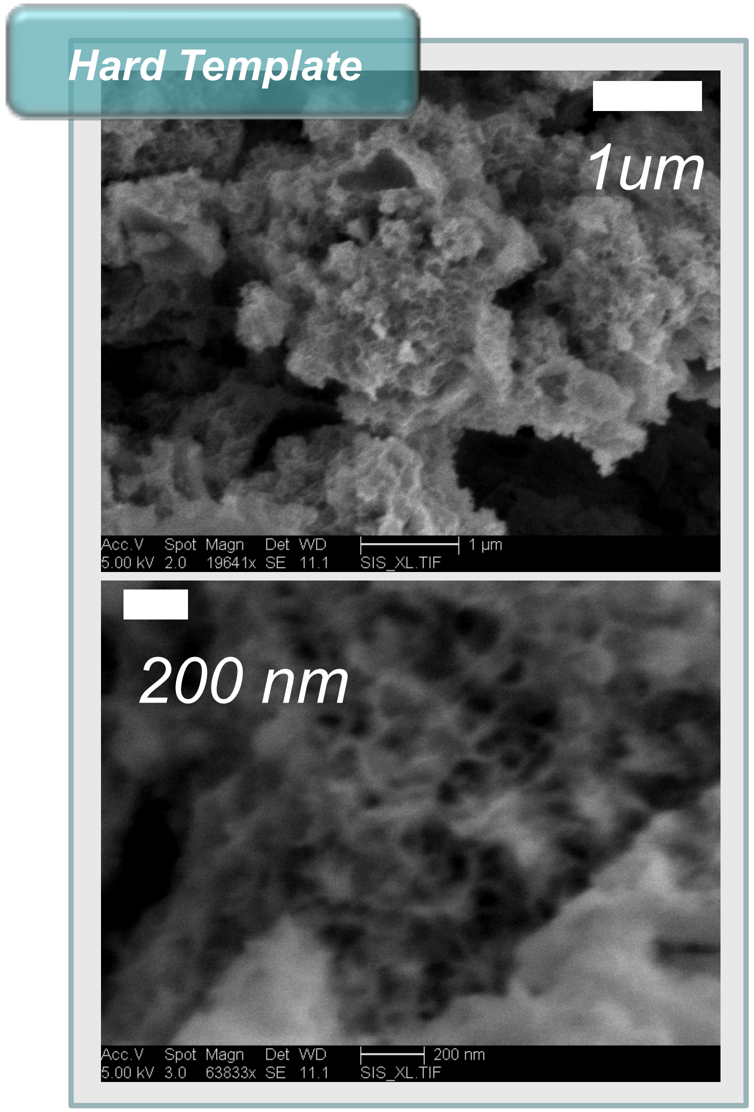
What are the properties of nanosized particles?

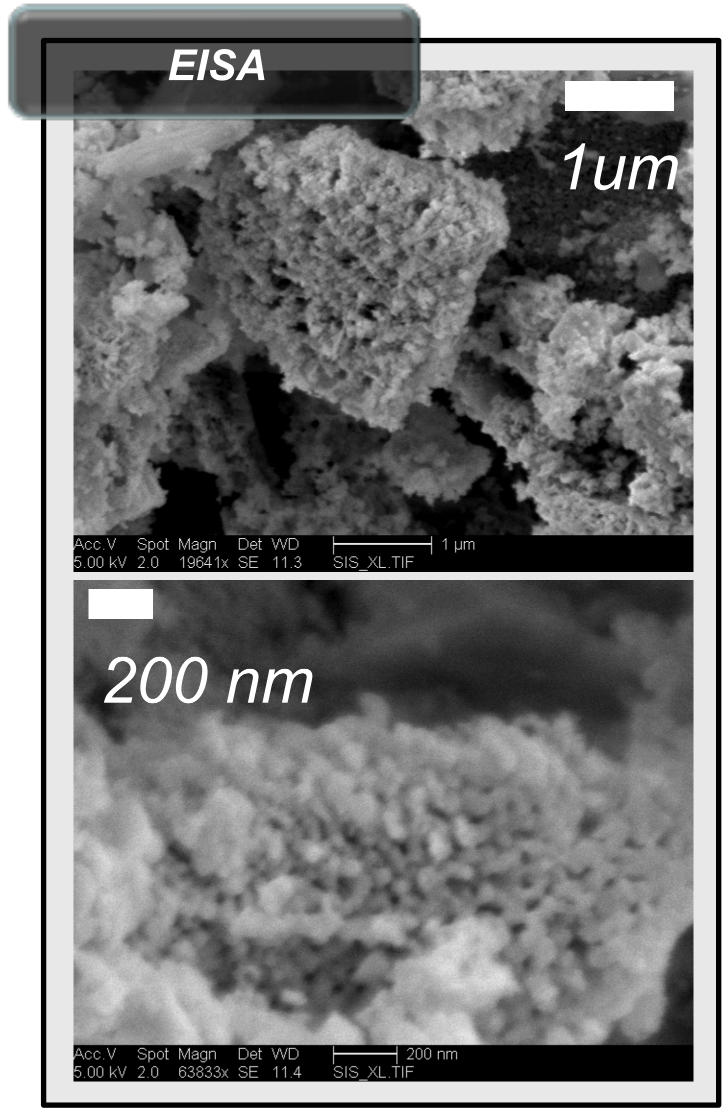
What are the effects of the support on the properties of cathodes?

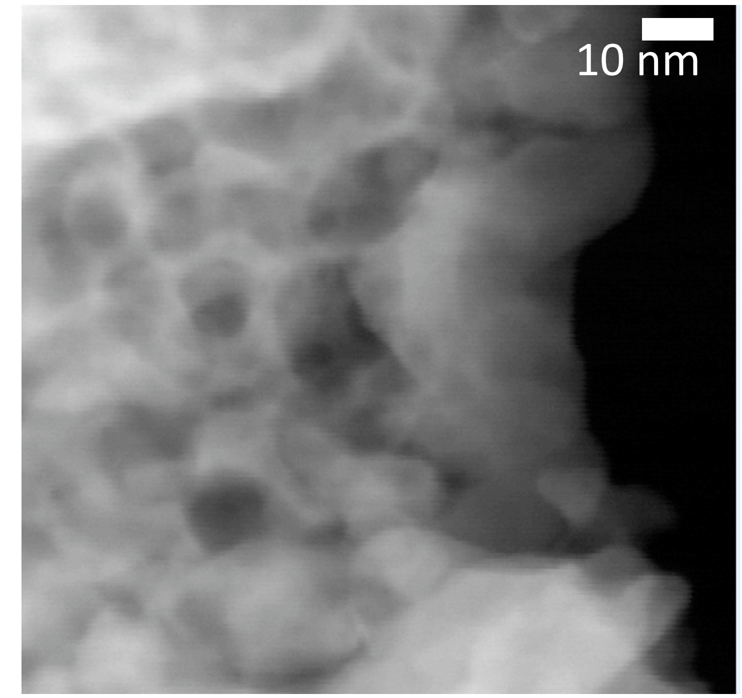
What are the surface properties of cathode materials?

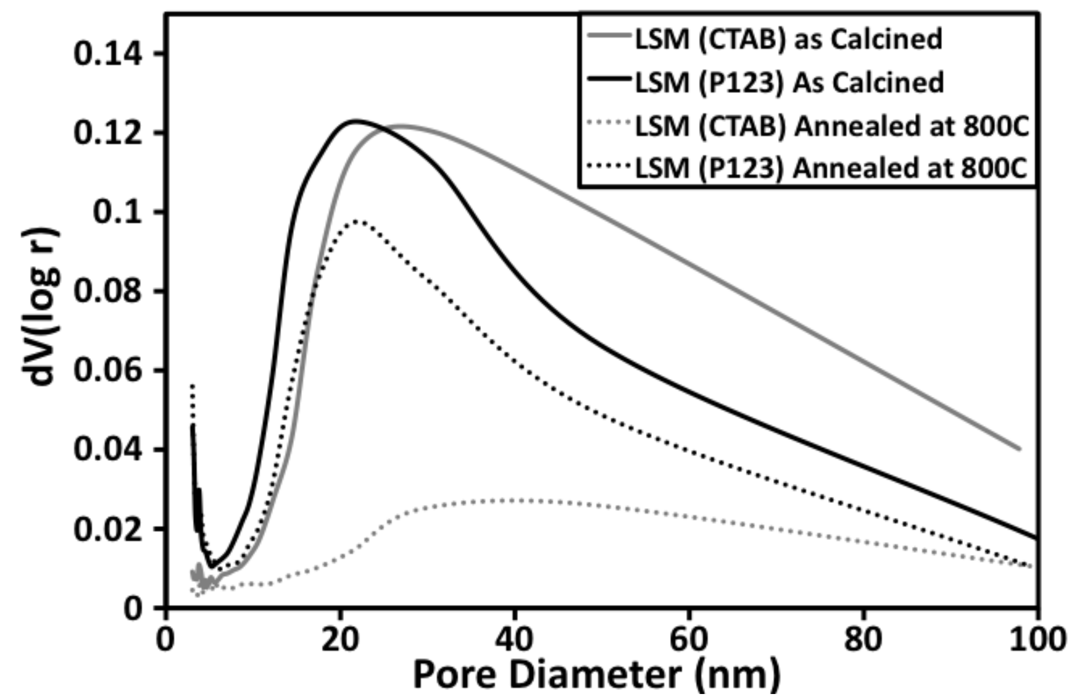
High Surface Area $(La,Sr)MnO_3$ Powders for Surface

> 100 m^2/gm ≈50 m^2/gm





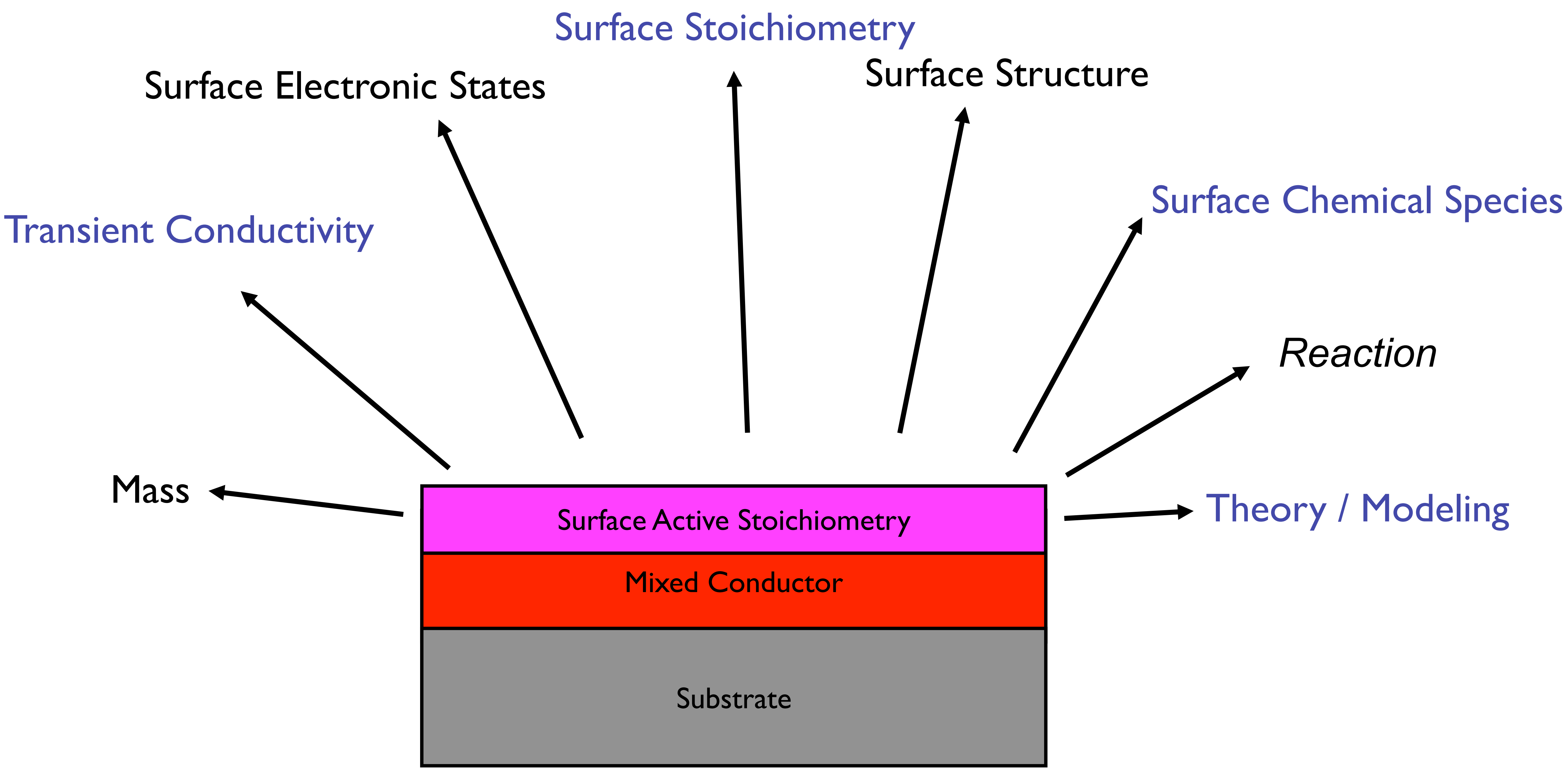




Thermally-stable, mesoporous, high surface area nanoparticles

Conceptual Thin Film Sample: Proxy to Crystals

Probe the nature of atomic scale surface chemistry or interface



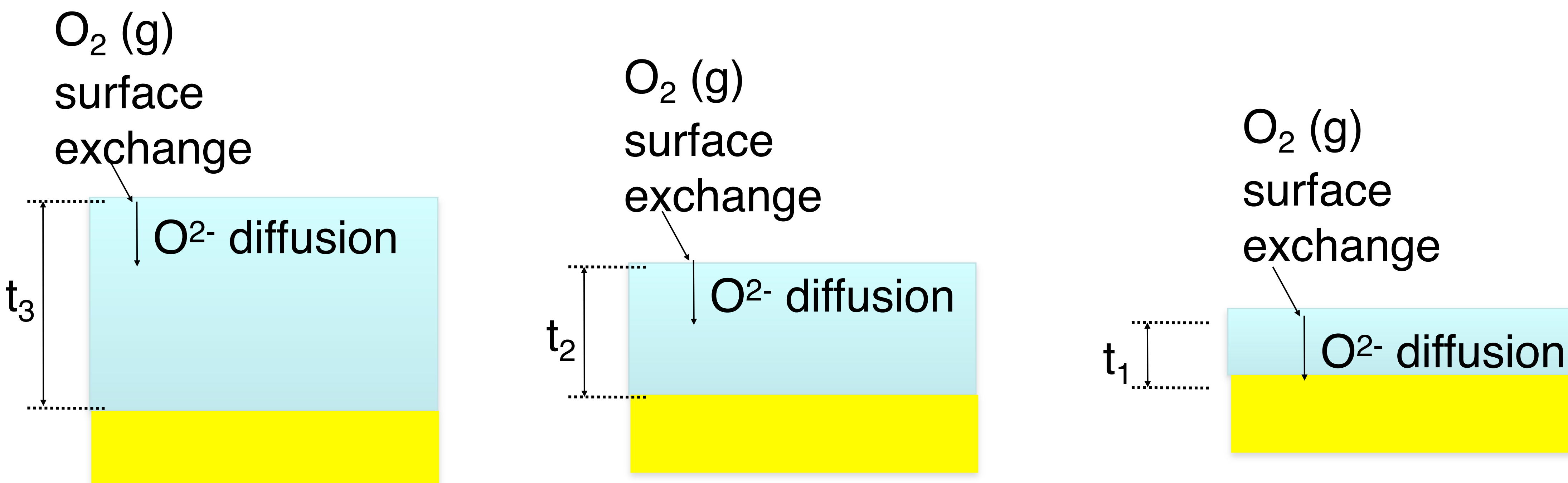
Need High Quality Samples with Controlled Microstructural Features: Thin Films

Thin film geometry selection

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

$\widetilde{D}$:chemical diffusion coefficient

k :surface exchange coefficient



$t_3 \gg l_d$	$t_2 \approx l_d$	$t_1 \ll l_d$
$\widetilde{D}$	$\widetilde{D}, k$	k

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

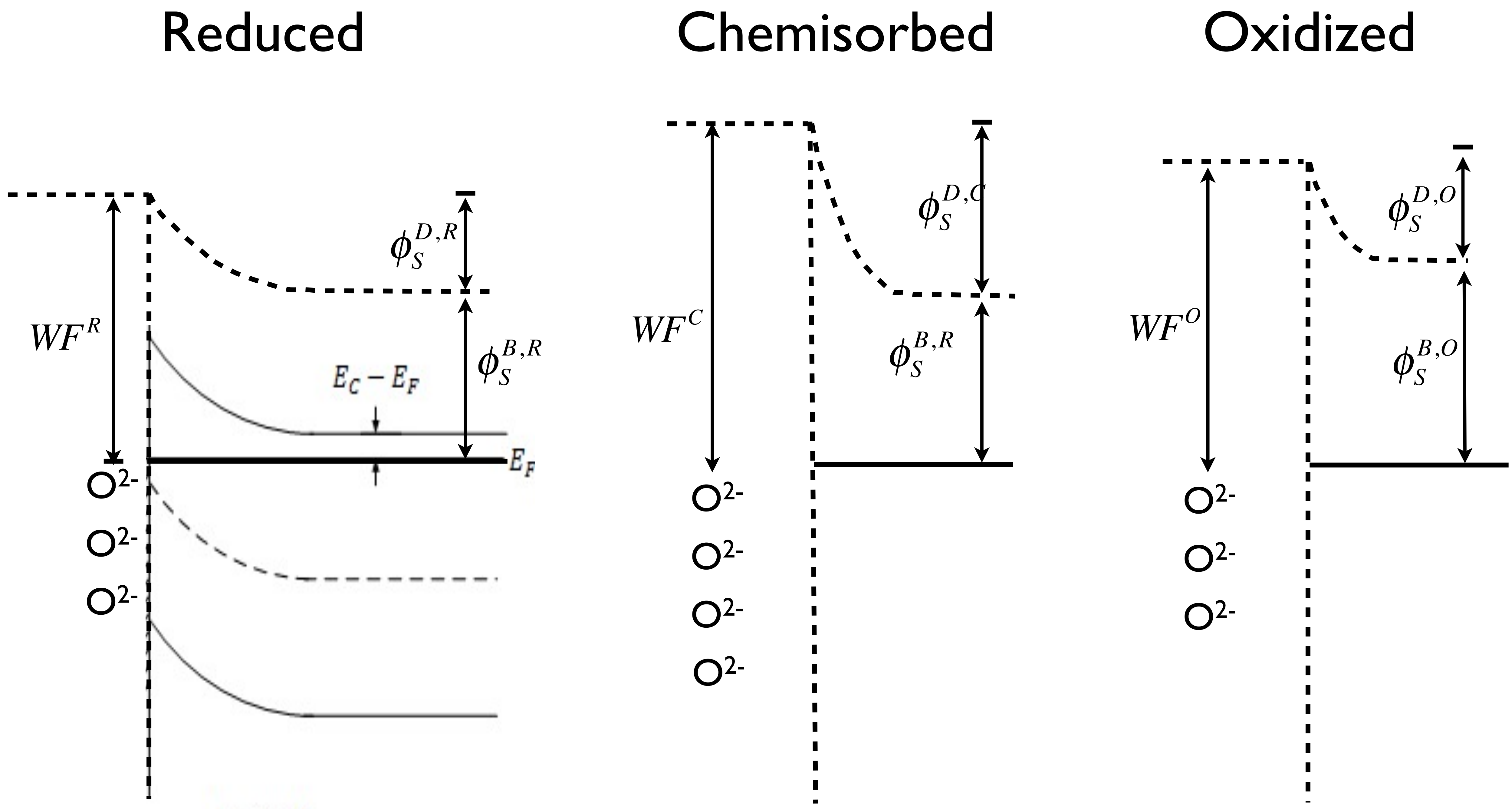
Strategy for Probing Surface Activity

- Prepare Ultra-Flat, Epitaxial Thin Films of Controlled Thickness
  - Expose Specific Surface Orientations: 100, 110, 111
  - Generate Many Thicknesses : Infiltrates to Bulk
  - Use Different Supports: Control Microstructural / Crystal Quality

- Determine Physical Properties
  - ***Electrical Conductivity Relaxation:*** ***Measure of effective time constant and*** k_{chem}
  - Transient Kelvin Probe Spectroscopy: Measure of work function and surface dipoles

- Generate Samples for Colleagues
  - Surface Composition
  - Surface Electronic Structure
  - Surface Charge States

Kelvin Probe Spectroscopy and Surfaces



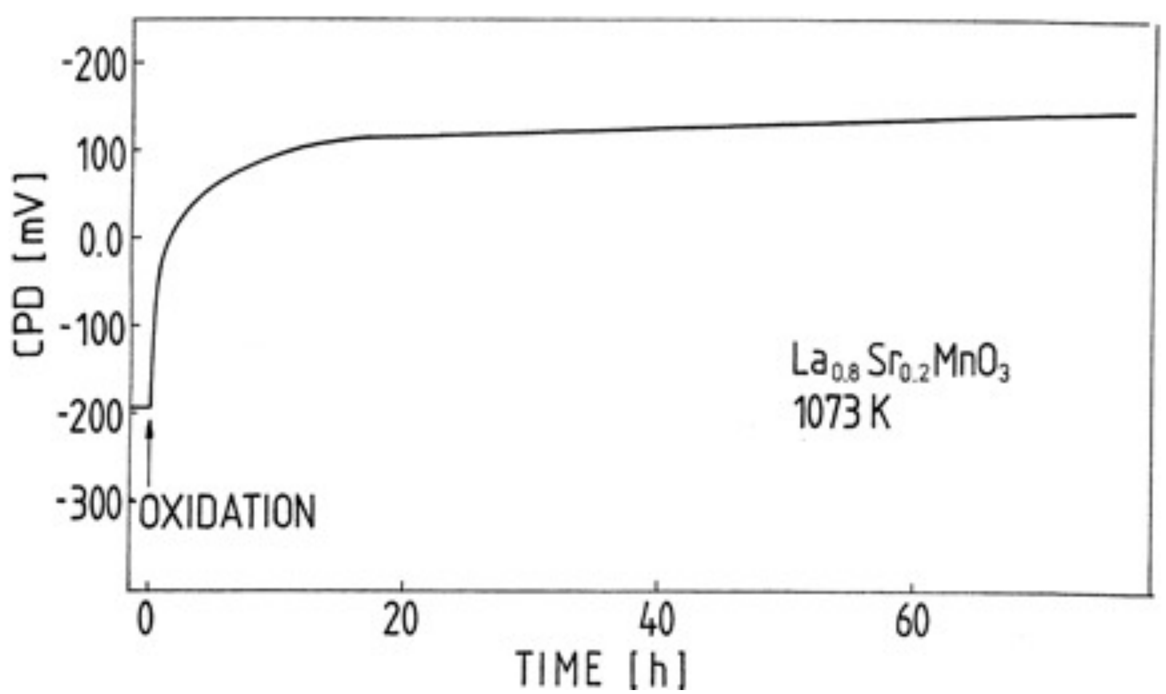
Work Function of Semiconductor has as least Two Terms that vary with pO_2

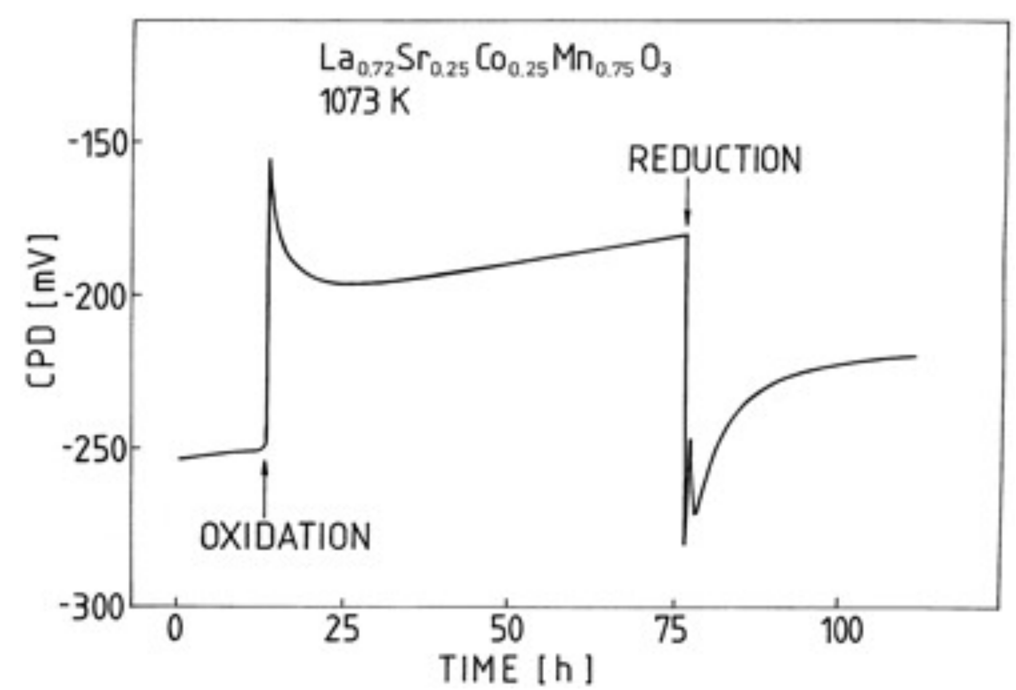
Kelvin Probe Spectroscopy: Bulk Samples

Several Different Regimes Observed on PolyXtal Ceramics

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

Requires Consistent surface engineered samples



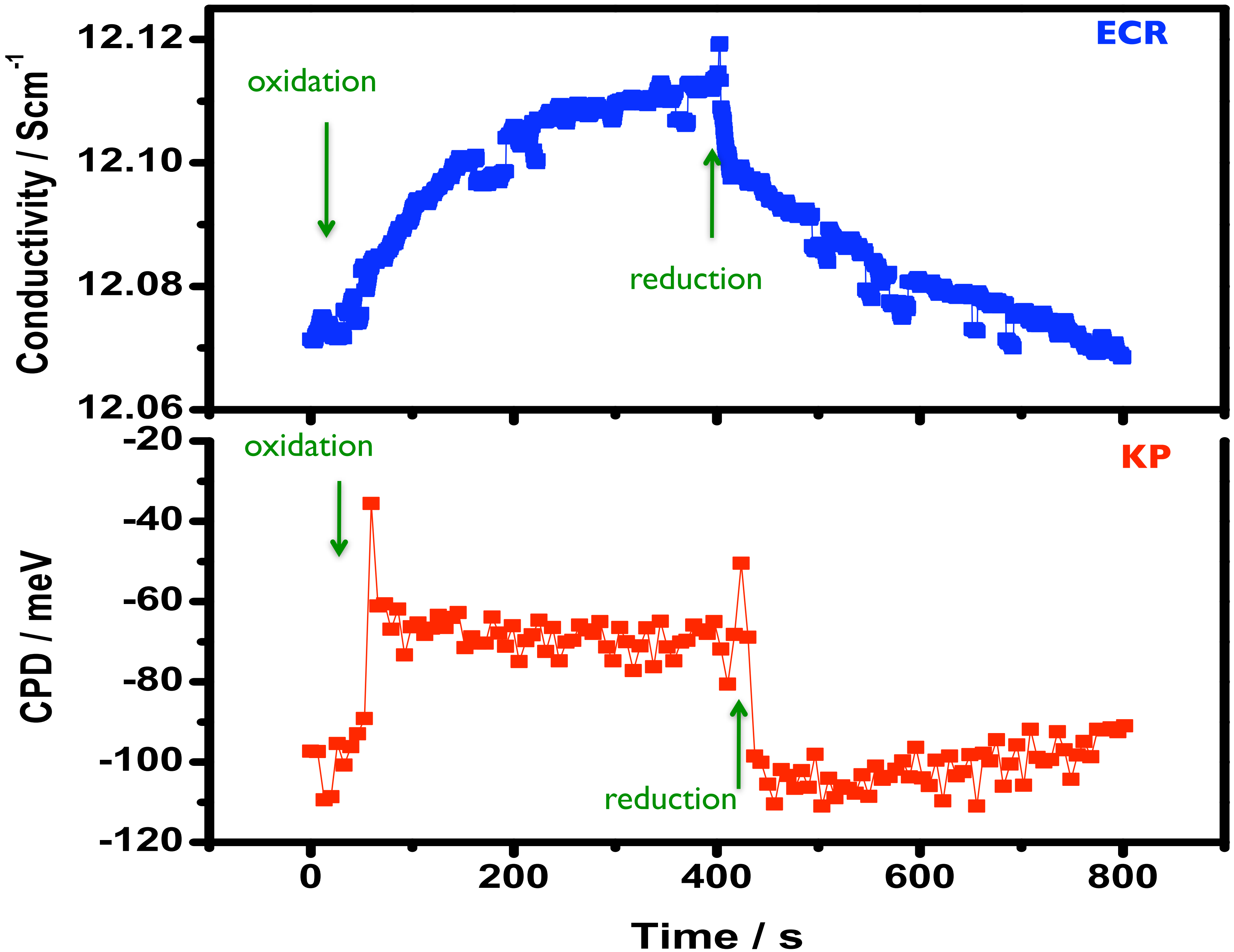


Badwal et al. J. Phys. Chem. Sol. ***62****, 723 (2001)*

Comparison of ECR and KPS Measurements

$La_{0.7}Sr_{0.3}MnO_3(100)$ on $SrTiO_3(100)$
T = 600 °C, t = 600 nm

$$pO_2^{OX} = 0.2 \quad atm$$
$$pO_2^{RED} = 0.02 \; atm$$



KPS and ECR complement one another

KPS Results for $La_{0.7}Sr_{0.3}MnO_3$(100), 600 nm

T (°C)	Delta Pt Surf[*,a]	Delta E_F Sample*	Delta Surf Chemisorb	Delta CPD
600	24	37	62	10
700	27	44	0?	16
800	30	45	0?	-230

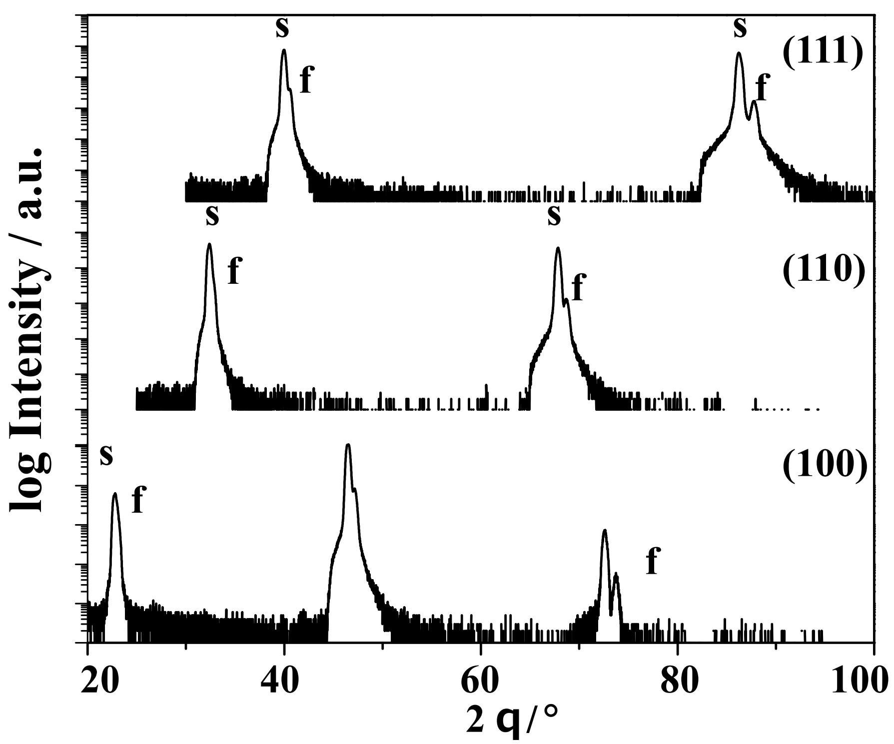
[a] all potential differences in meV
* From references of Nowotny et al.

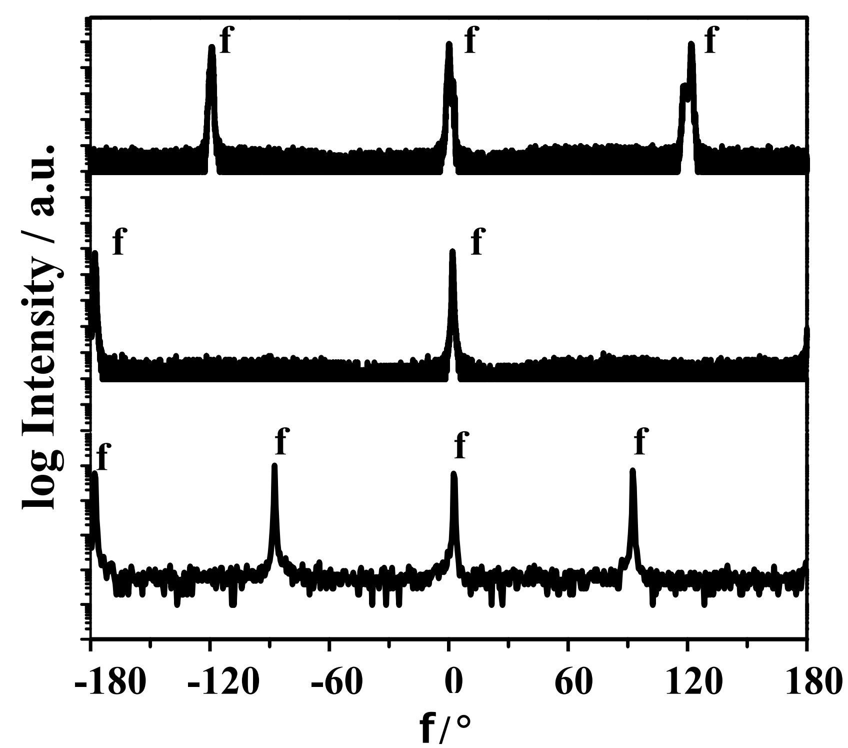
Prior Work on ECR

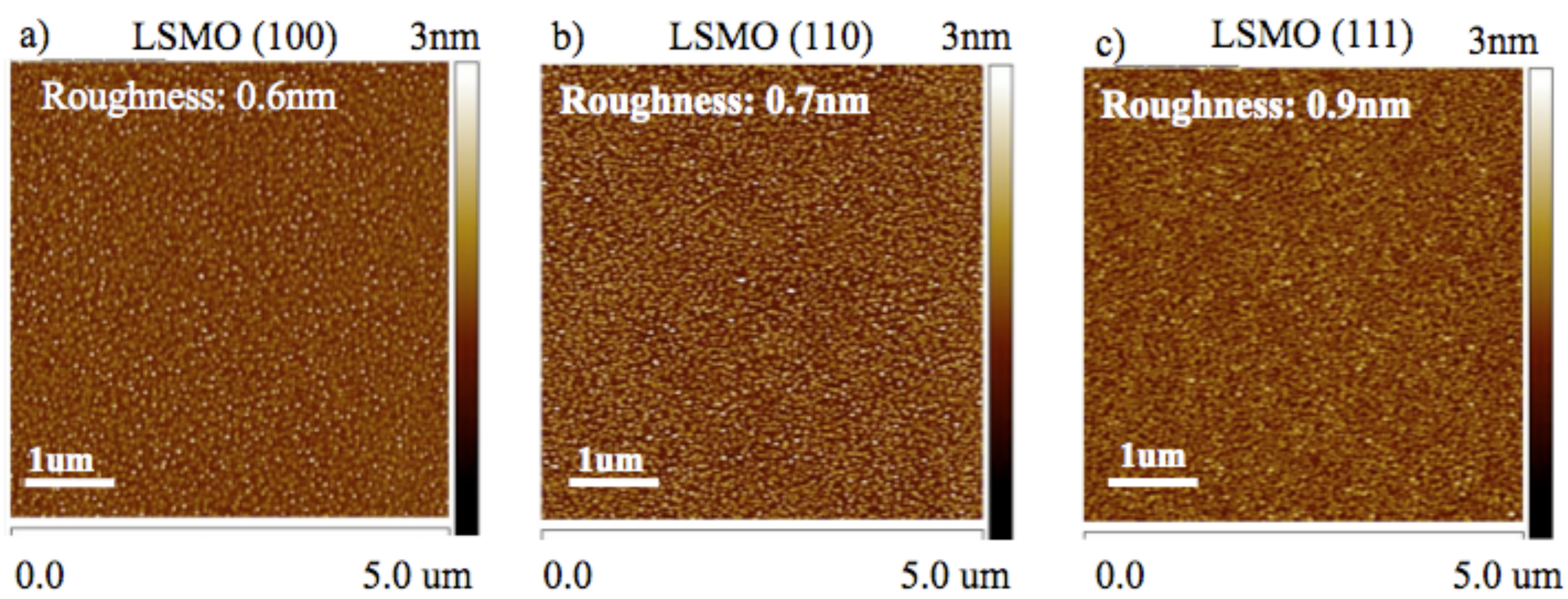
	This study	Chen *et al.*[1]	*Kim et al.*[2]	*Wang et al.*[3]	*Yasuda et al.*[4]
Film/bulk composition	$La_{0.8}Sr_{0.2}MnO_3$	$La_{0.5}Sr_{0.5}CoO_3$	La_2NiO_4	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$	$La_{0.8}Sr_{0.2}MnO_3$
Substrate	STO(100) (LSMO 100)	$LaAlO_3$(100) (LSCO 100)	$LaAlO_3$(100) (LNO 110)	BULK	BULK
Pressure range	50 to 500 mTorr	380 to760 Torr	15 to 76 Torr	7.6 to 76 Torr	10^{-11} to10^{-8} mTorr
K_{oxi} At 900°C		≈ 1.00×10^{-4} cm/s	≈3.00×10^{-5} cm/s	≈1.06×10^{-3} cm/s	≈5.00×10^{-5} cm/s

- X. Chen *et al.*/Solid State Ionics 146(2002)
- G. Kim *et al.*/solid State Ionics 177 (2006)
- S. Wang *et al.*/solid State Ionics 156 (2003)
- I. Yasuda *et al.*/Journal of Solid State Chemistry, 123 (1996)

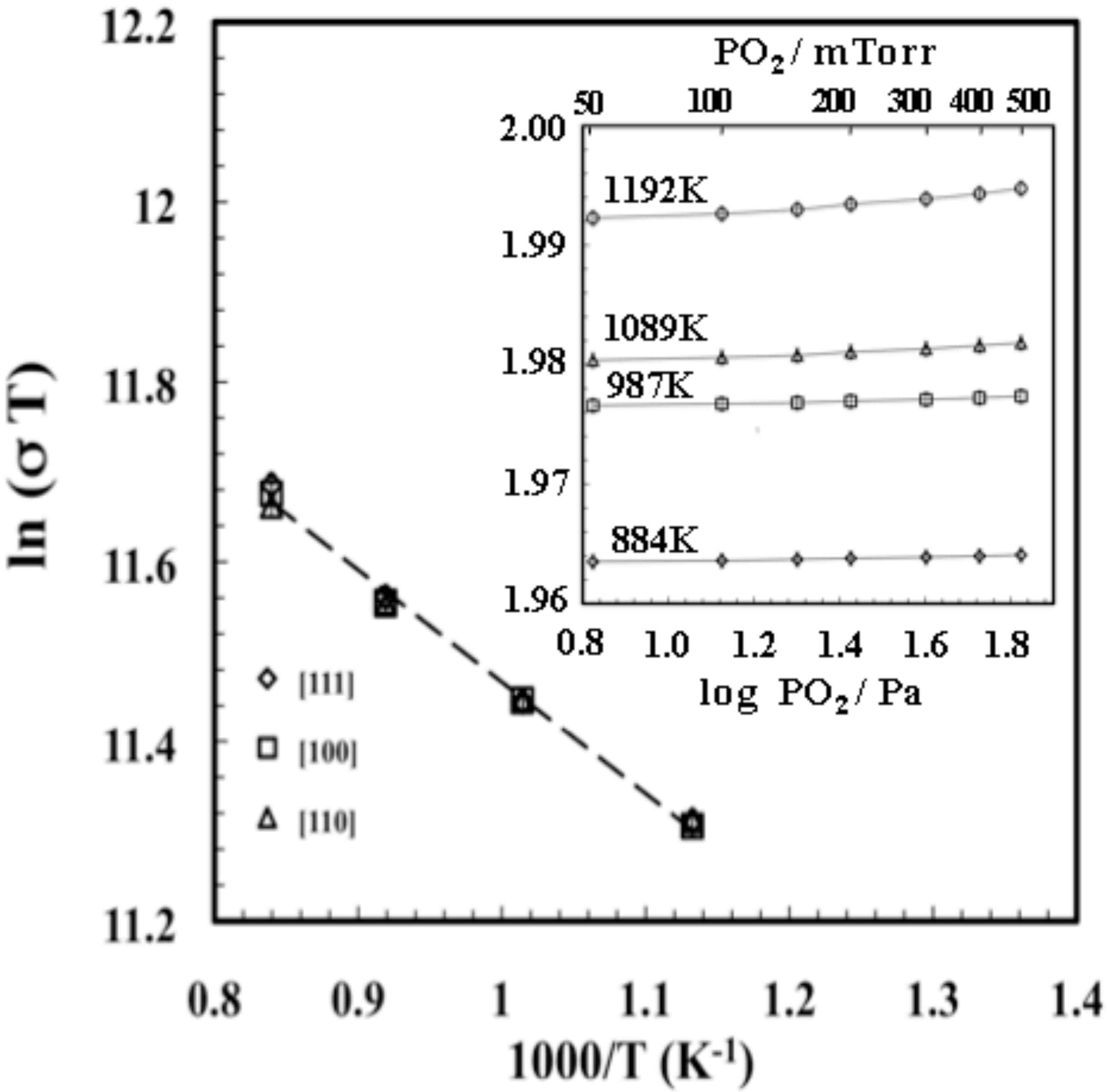
Preparation of Flat, Oriented, Single Crystal Films







600 nm-thick films have bulk-like properties



All Orientations have similar conductivity

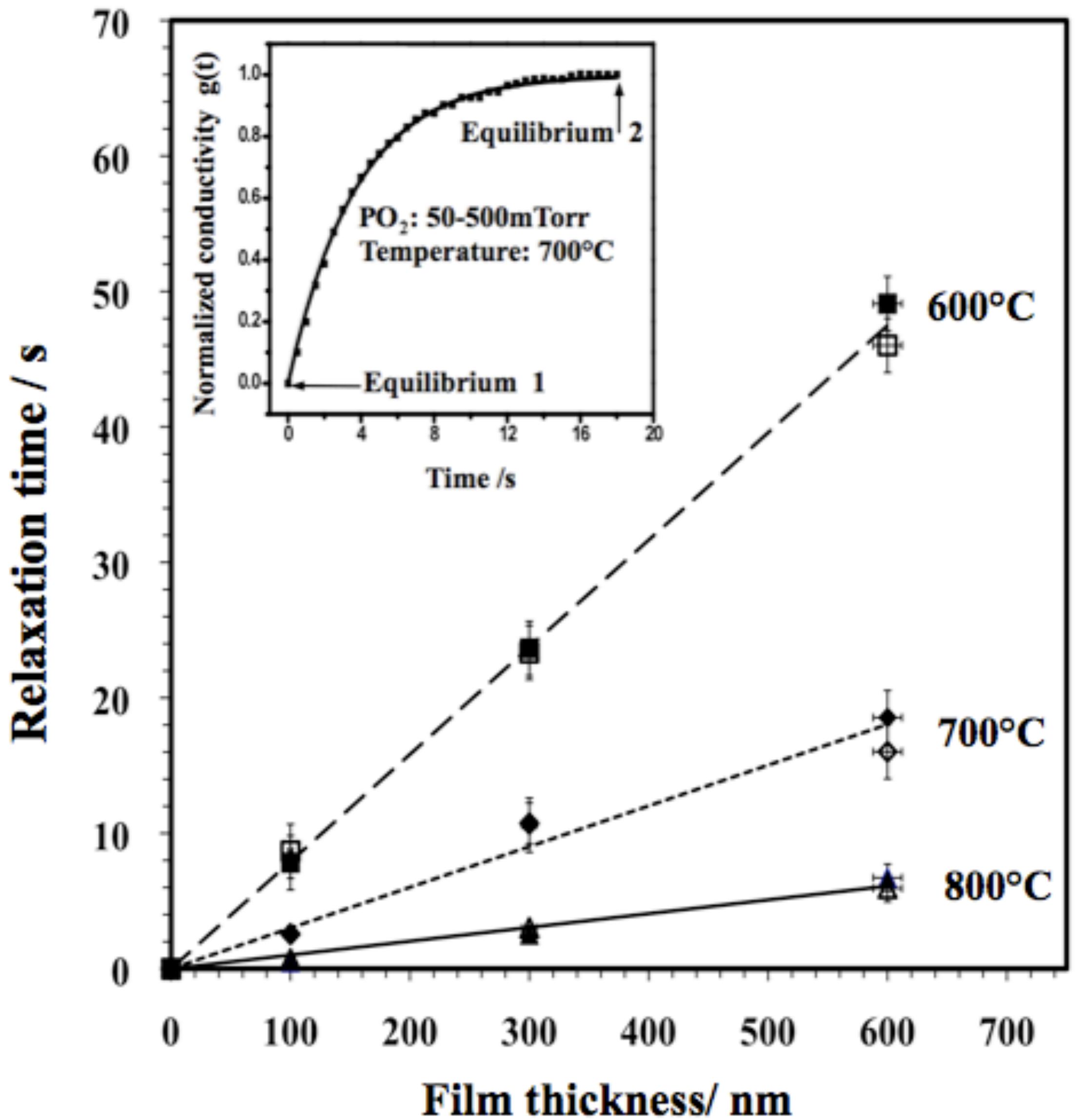
All orientations have similar activation energy of conductivity

Activation energy is similar to literature (0.1 eV/atom)

Oxygen pressure dependence of conductivity is similar to bulk.

FILMS ARE GOOD PROXIES FOR BULK CERAMICS

Films have surface activated response to ECR



Linear relationship of Relaxation and Thickness indicates the response is Surface Limited.

Reduction

Temperature / K	Kr (100) $\times 10^{-6}$/cm•s^{-1}	Kr (110) $\times 10^{-6}$/cm•s^{-1}	Kr (111) $\times 10^{-6}$/cm•s^{-1}
883	1.22	2.31	2.84
986	3.24	14.2	5.92
1088	8.93	40.7	23.2
1191	*57.9*	*79.1*	*63.9*

Oxidation

Temperature / K	Ko (100) $\times 10^{-6}$/cm•s^{-1}	Ko (110) $\times 10^{-6}$/cm•s^{-1}	Ko (111) $\times 10^{-6}$/cm•s^{-1}
883	1.30	2.18	2.83
986	3.74	17.2	6.40
1088	10.1	64.3	16.9
1191	*29.8*	*118*	*80.3*

Oxidation and Reduction are Similar

Crystalographic Anisotropy Exists by ≈ 75 %

ECR Comparison to Literature

	This study	Chen *et al.*[1]	*Kim et al.*[2]	*Wang et al.*[3]	*Yasuda et al.*[4]
Film/bulk composition	$La_{0.8}Sr_{0.2}MnO_3$	$La_{0.5}Sr_{0.5}CoO_3$	La_2NiO_4	$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$	$La_{0.8}Sr_{0.2}MnO_3$
Substrate	STO(100) (LSMO 100)	$LaAlO_3$(100) (LSCO 100)	$LaAlO_3$(100) (LNO 110)	BULK	BULK
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K_{oxi} At 900°C	$\approx 3\times10^{-5}$ cm/s	$\approx 1.00\times10^{-4}$ cm/s	$\approx 3.00\times10^{-5}$ cm/s	$\approx 1.06\times10^{-3}$ cm/s	$\approx 5.00\times10^{-5}$ cm/s

- X. Chen *et al.*/Solid State Ionics 146(2002)
- G. Kim *et al.*/solid State Ionics 177 (2006)
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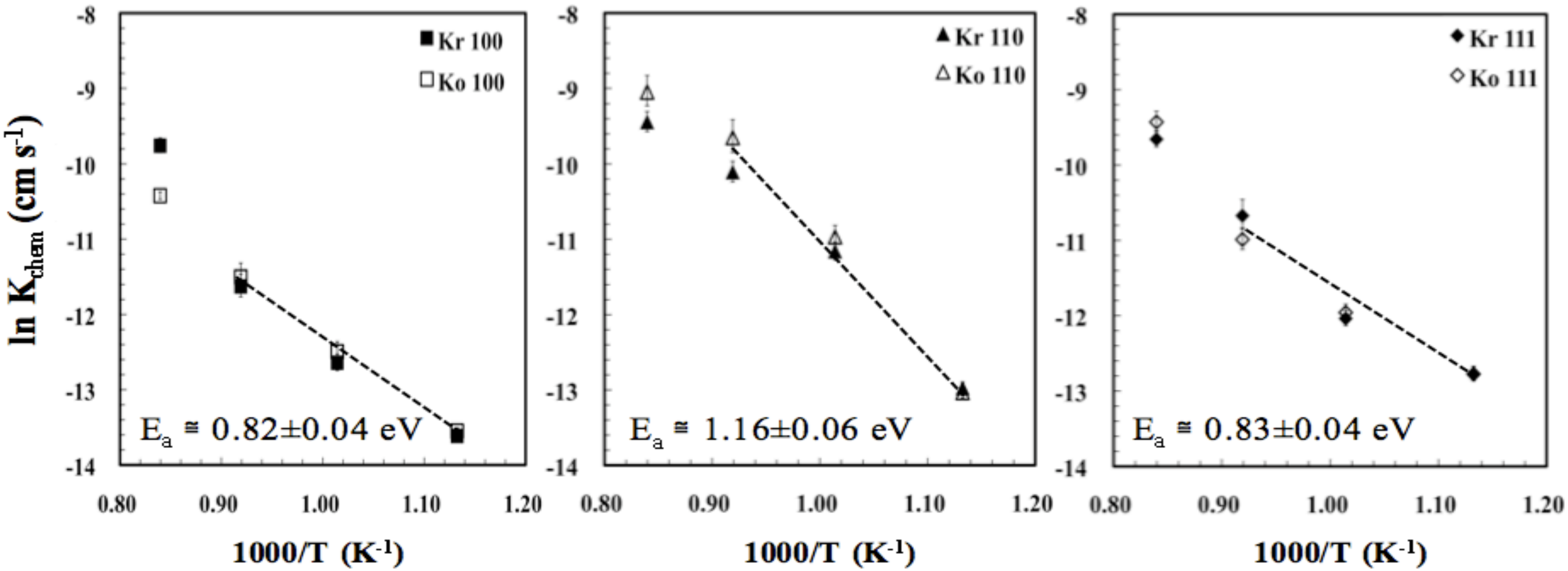
- I. Yasuda *et al.*/Journal of Solid State Chemistry, 123 (1996)

Crystallographic Anisotropy in Apparent E_A

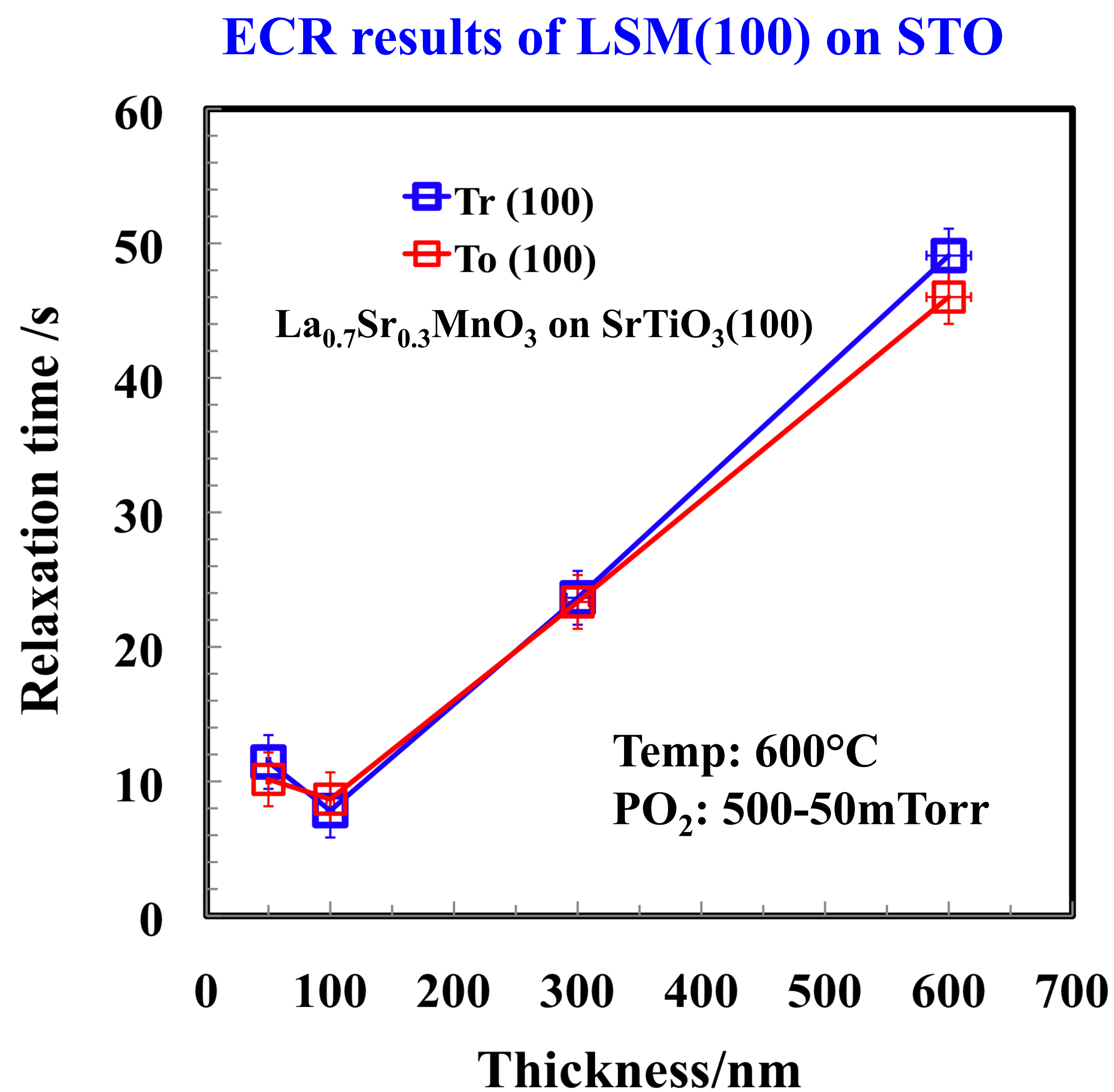


Different Orientation have different activation energies and k_{chem}'s

Activation Energies are on the order of Literature Values

Activation Energies are Orientation Dependant

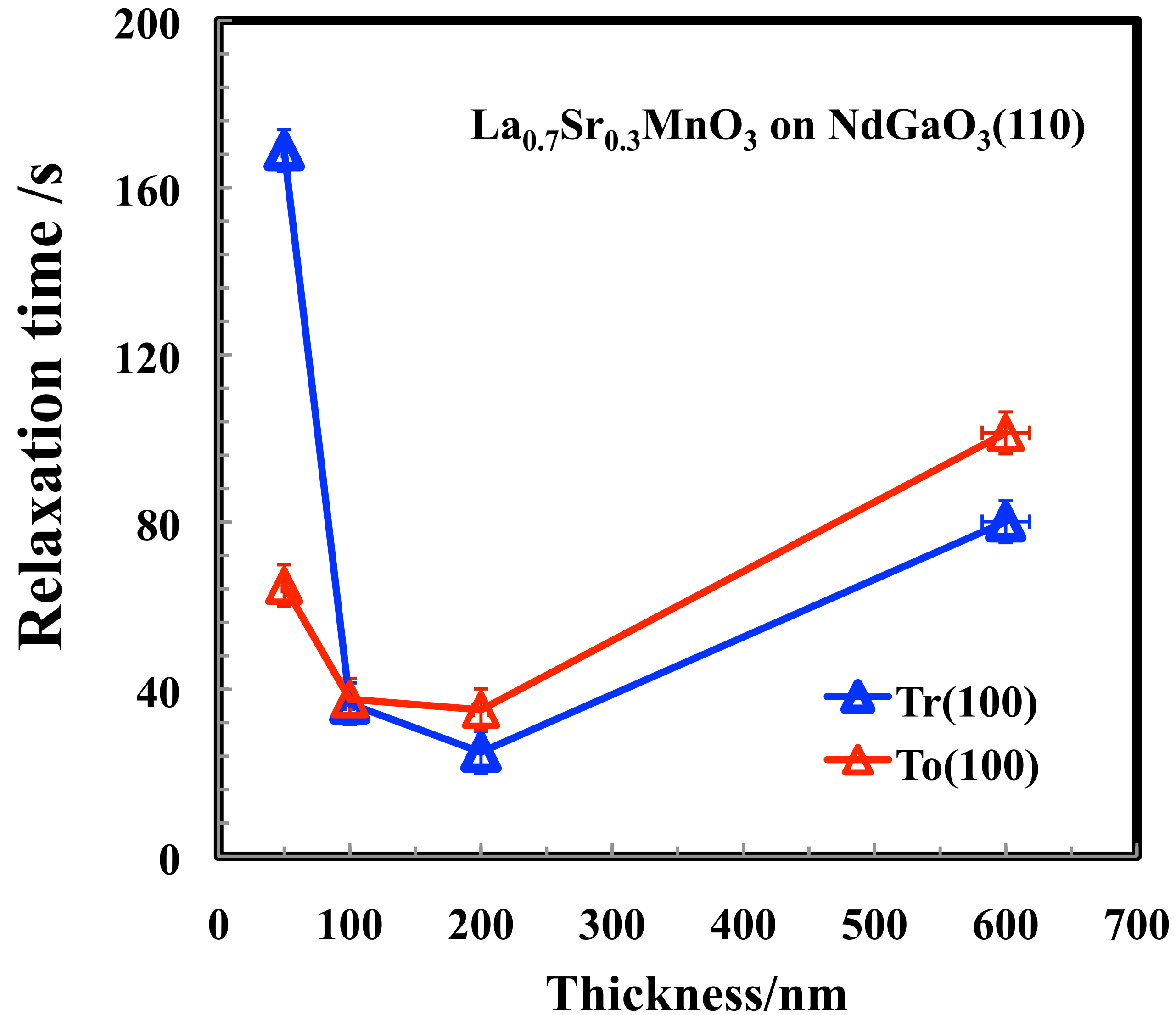
Size Effects on $SrTiO_3$: In-Plane Tension



$La_{0.7}Sr_{0.3}MnO_3$/nm on $SrTiO_3$	c-perpendicular/Å	a-in plane/Å	Strain State
20	3.855	3.905	full tensile
50	3.848	3.905	full tensile
100	3.848	3.899	partial tensile
300	3.862	3.870	relaxed
600	3.867	3.873	fully relaxed

❖ bulk $SrTiO_3$: a=3.905Å   bulk $La_{0.7}Sr_{0.3}MnO_3$: a=3.873Å

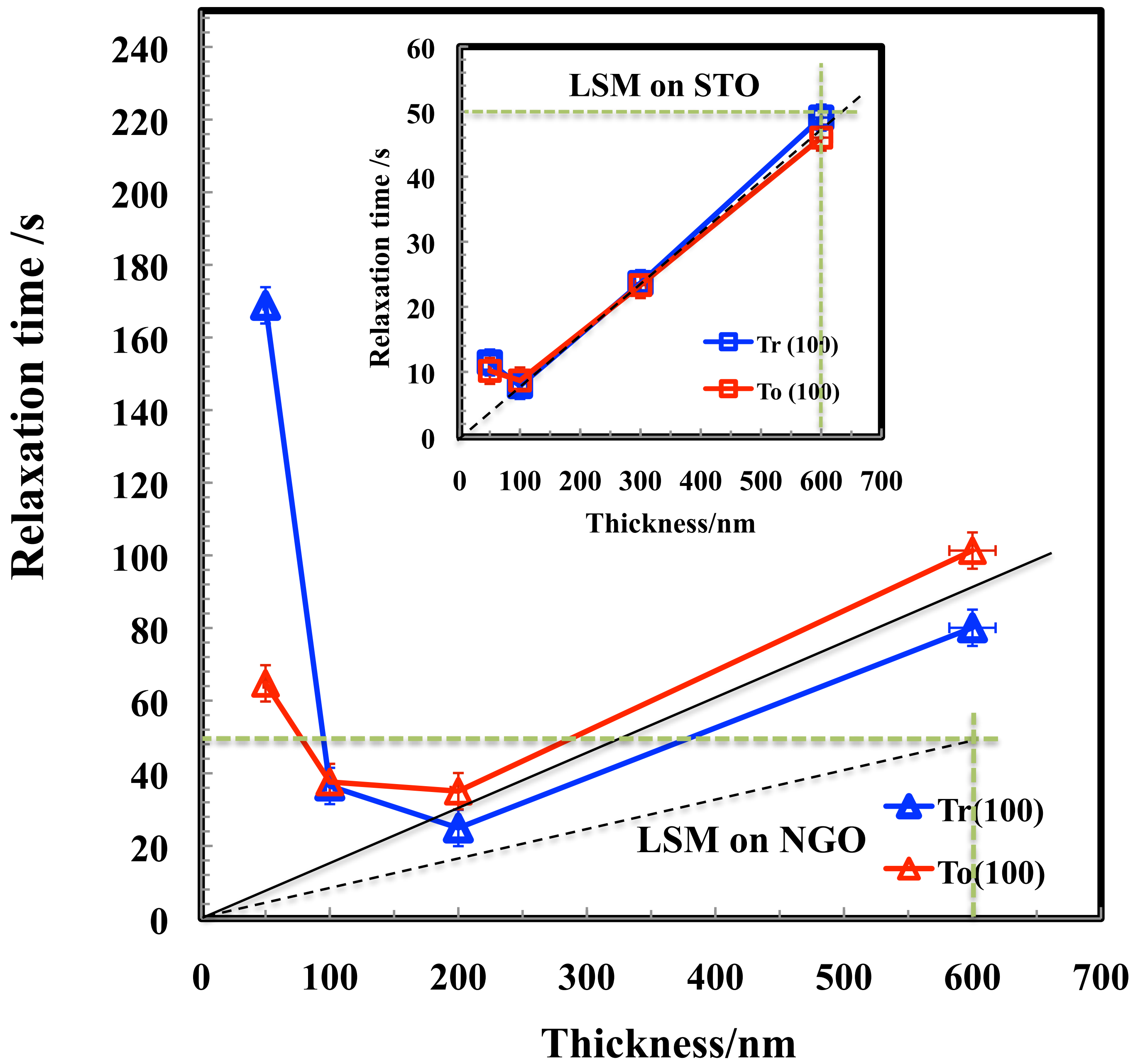
Size Effects on $NdGaO_3$: In-Plane Compression



$La_{0.7}Sr_{0.3}MnO_3$/nm on $NdGaO_3$	c-perpendicular/Å	a-in plane/Å	b-in plane/Å	Strain State
50	**3.904**	**3.855**	**3.864**	**fully compressive**
100	**3.902**	**3.859**	**3.870**	**partial compressive**
200	**3.900**	**3.862**	**3.873**	**partial relaxed**
600	**3.885**	**3.868**	**3.875**	**relaxed**

❖Bulk $NdGaO_3$: a=5.43Å, b=5.5Å, c=7.71Å (a-in plane =3.864Å, b-in plane =3.855Å)
❖Bulk $La_{0.7}Sr_{0.3}MnO_3$: a=3.873Å

What is the difference for Supports?



K_{chem} Reduction

600nm	7.49E-07
STO 600nm	1.22E-06

K_{chem} Oxidation

NGO 600nm	5.92E-07
STO 600nm	1.30E-06

Reduction

Temperature / K	Kr (100) $\times 10^{-6}$/cm•s^{-1}	Kr (110) $\times 10^{-6}$/cm•s^{-1}	Kr (111) $\times 10^{-6}$/cm•s^{-1}
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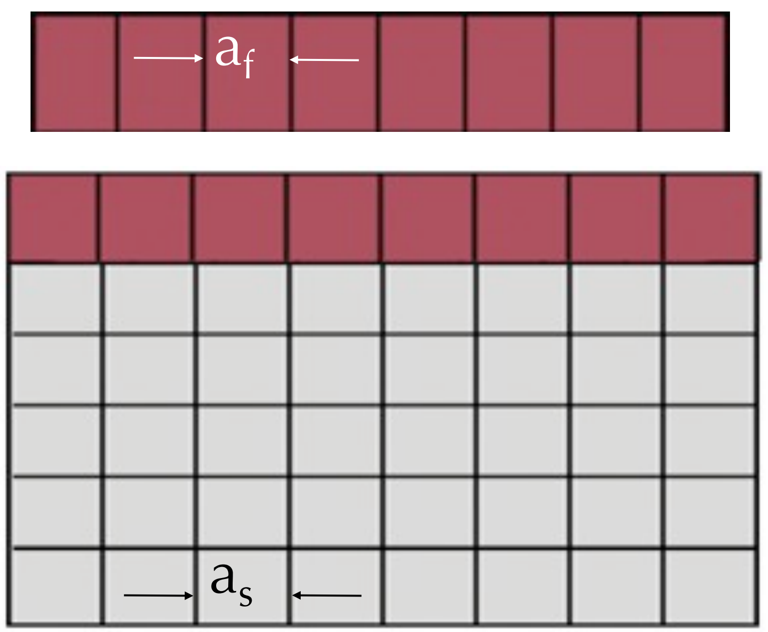
Cathode thin film growth – Substrate choice and orientation

Mismatch Strain

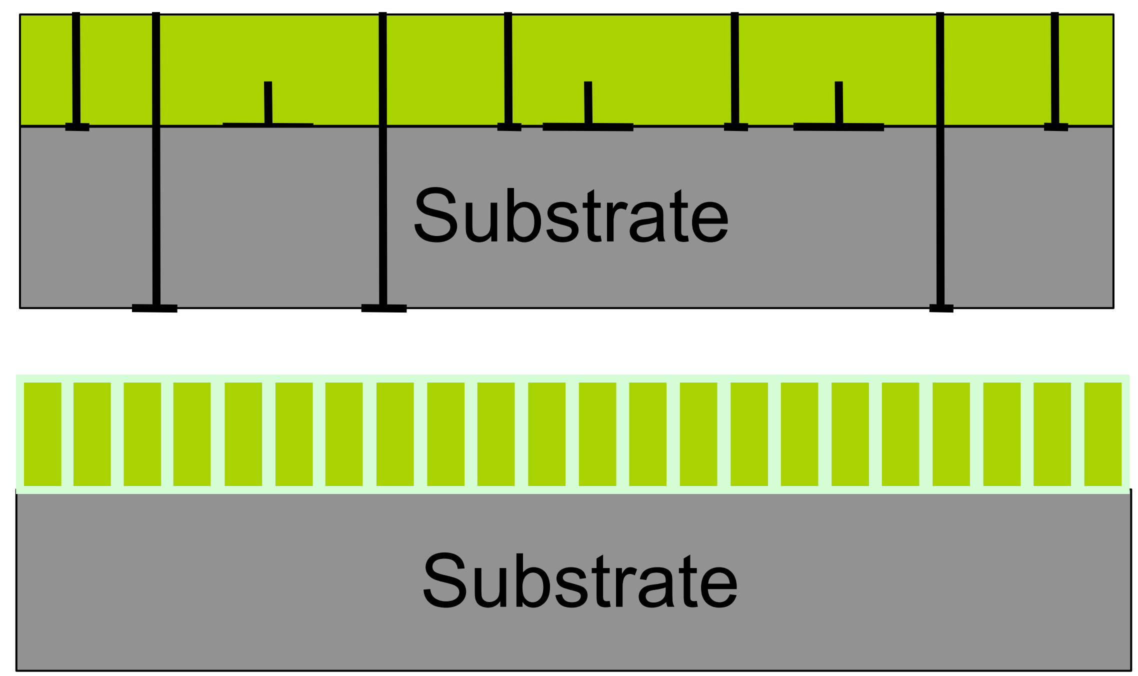
$$f = \frac{(a_s - a_f)}{a_f}$$



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

Dislocations

Misfit
Threading (relaxation)
Threading (inherited)



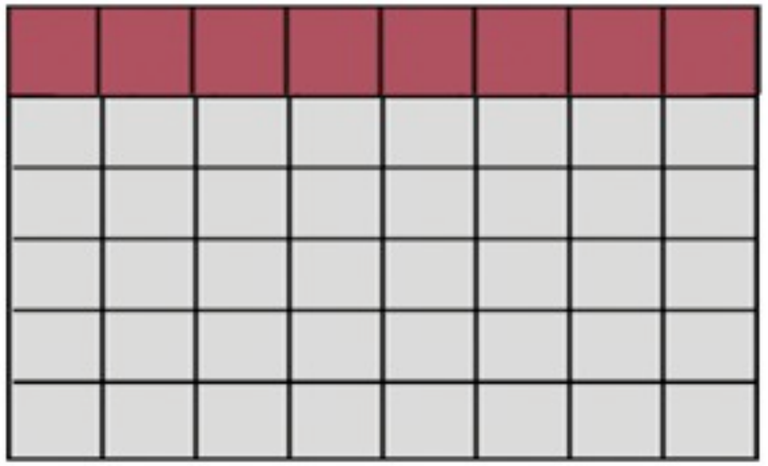
Substrates have different lattice mismatches and Different dislocation densities

Cathode thin film growth – Substrate choice and orientation

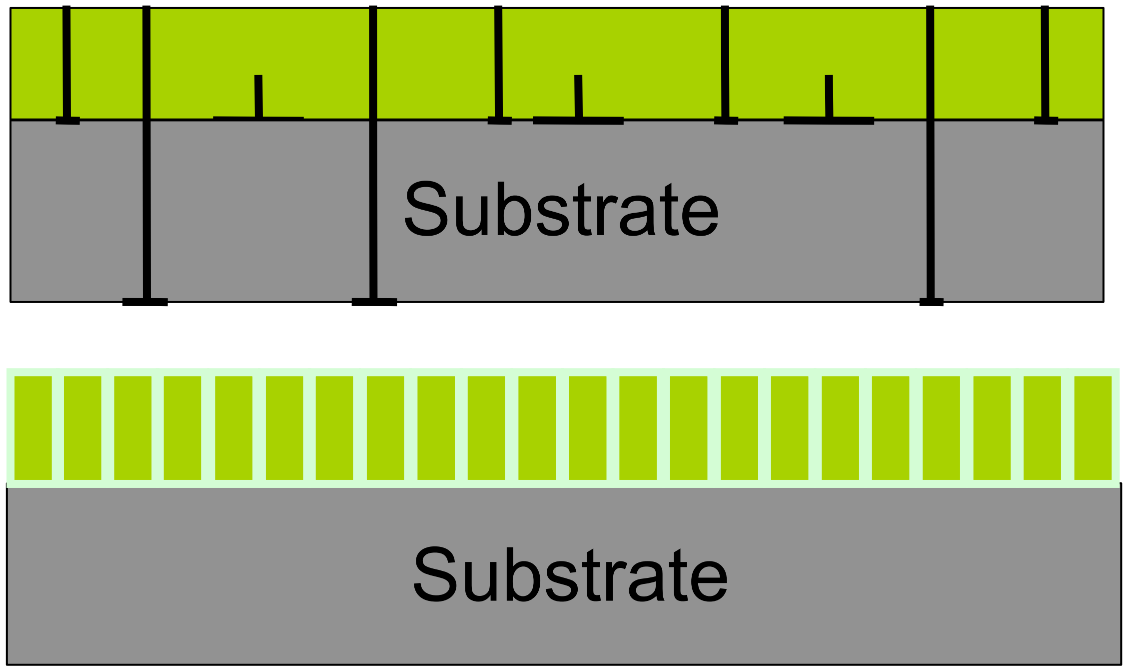
Mismatch Strain

Dislocations

Misfit
Threading (relaxation)
Threading (inherited)



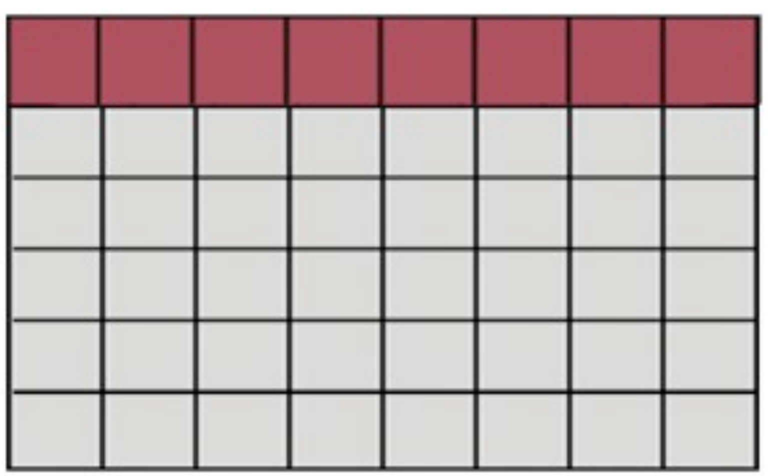
$$w_{strain}^{max} = \frac{2\mu(1+\nu)f^2}{(1-\nu)}$$



Substrates have different lattice mismatches and Different dislocation densities

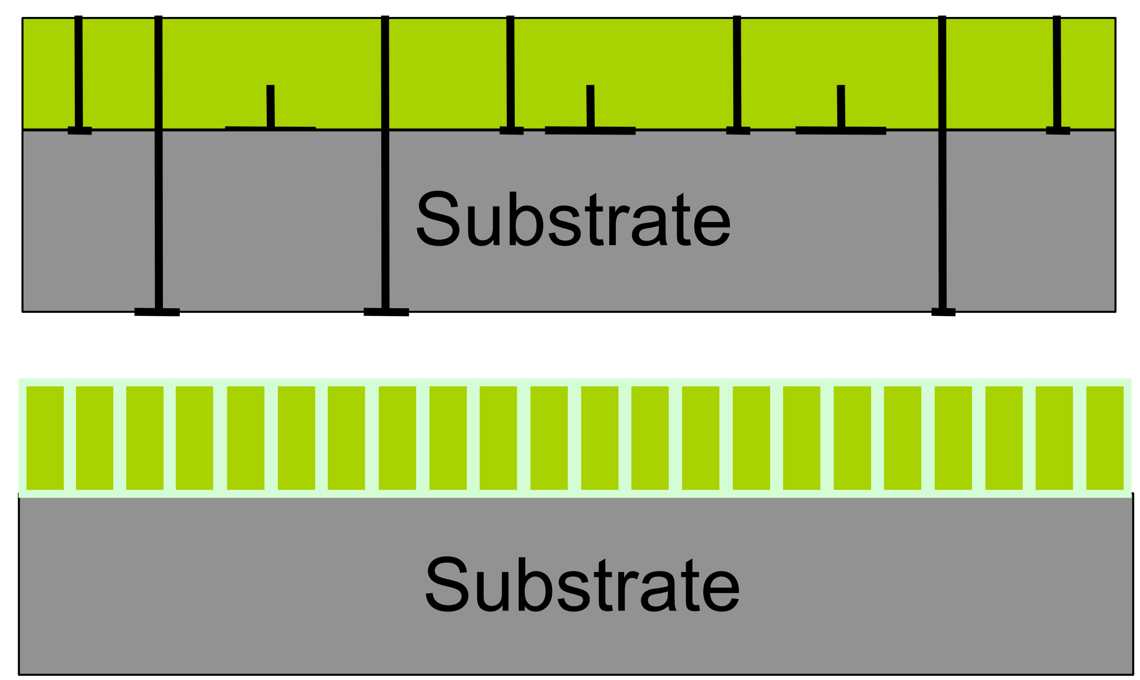
Cathode thin film growth – Substrate choice and orientation

Mismatch Strain



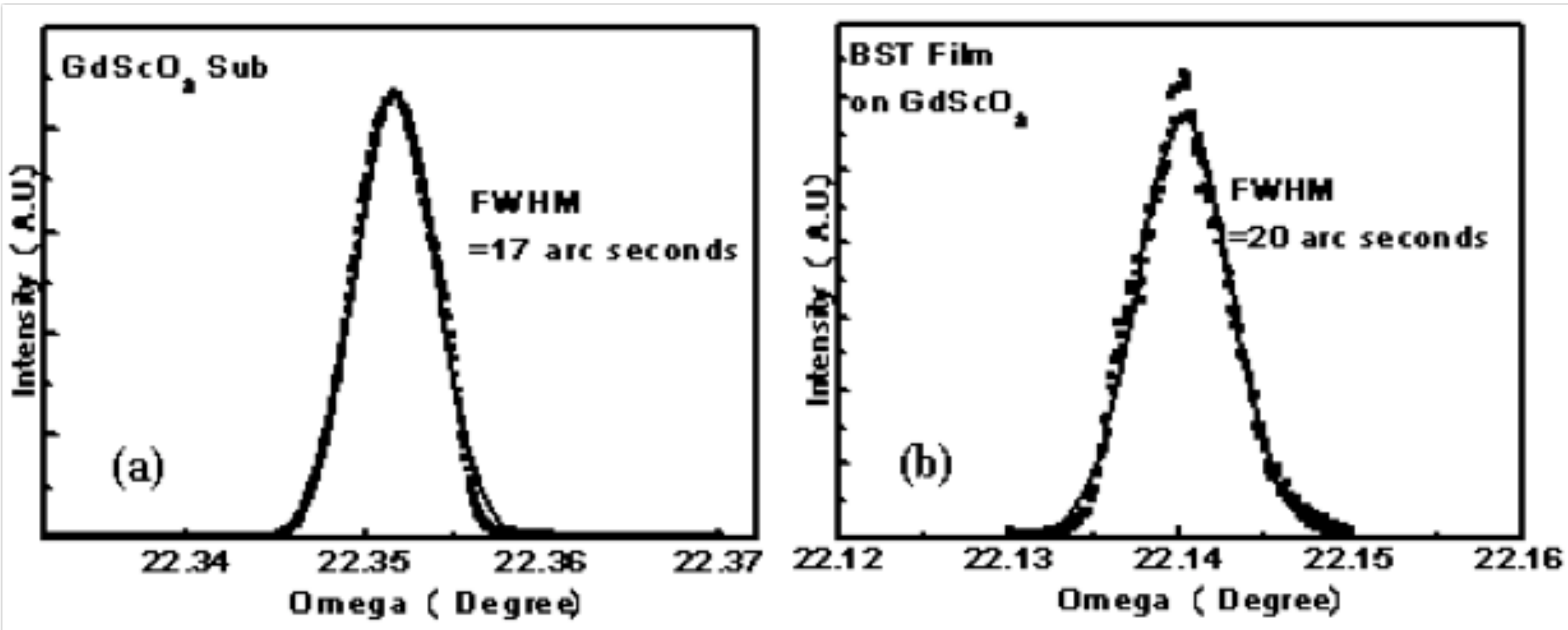
Dislocations

Misfit
Threading (relaxation)
Threading (inherited)

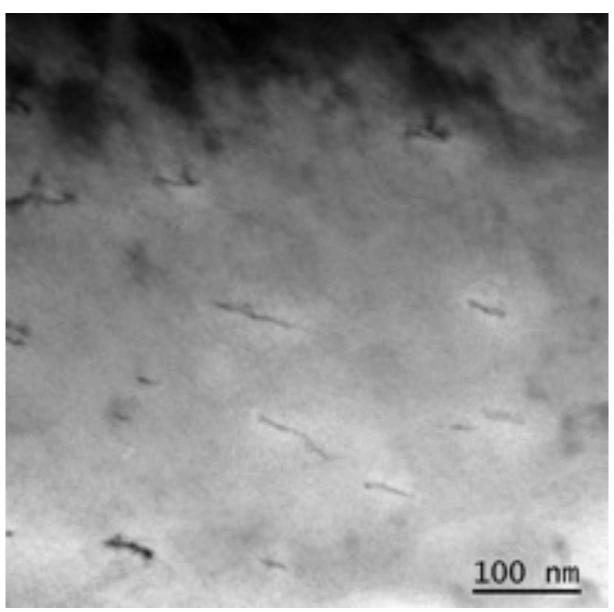


Substrates have different lattice mismatches and Different dislocation densities

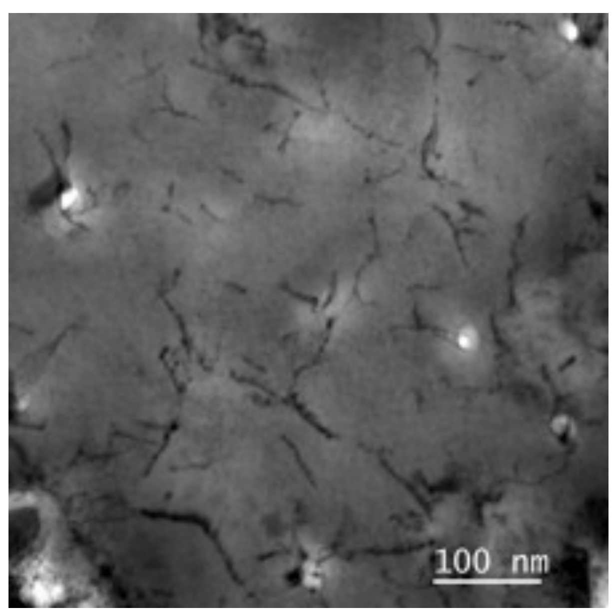
Film Dislocation Densities: (Ba,Sr)TiO_3 Example



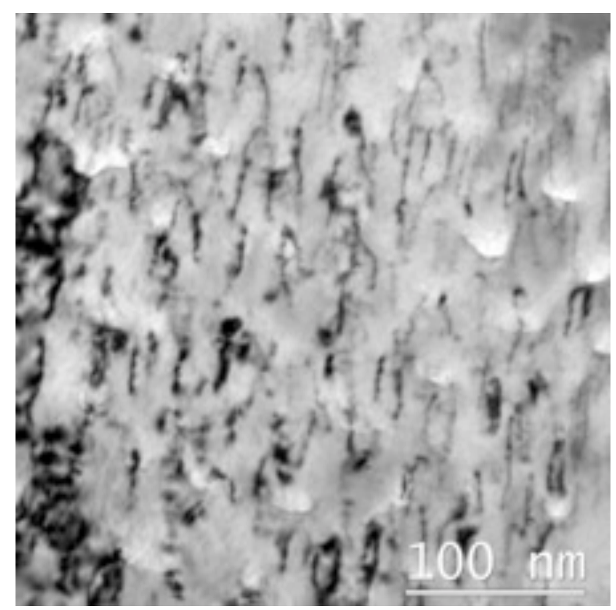
Substrate Material	FWHM of Film Rocking Curve (°)
MgO (100)	0.153
$GdScO_3$(110)	0.008
$DyScO_3$(110)	0.009
LSAT (100)	0.016
$LaAlO_3$(100)	0.183



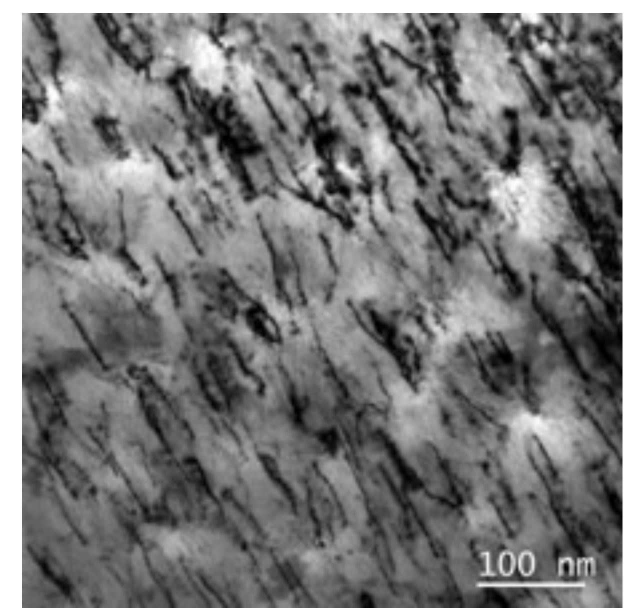
BST/$GdScO_3$
$6x10^9$/cm2



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



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

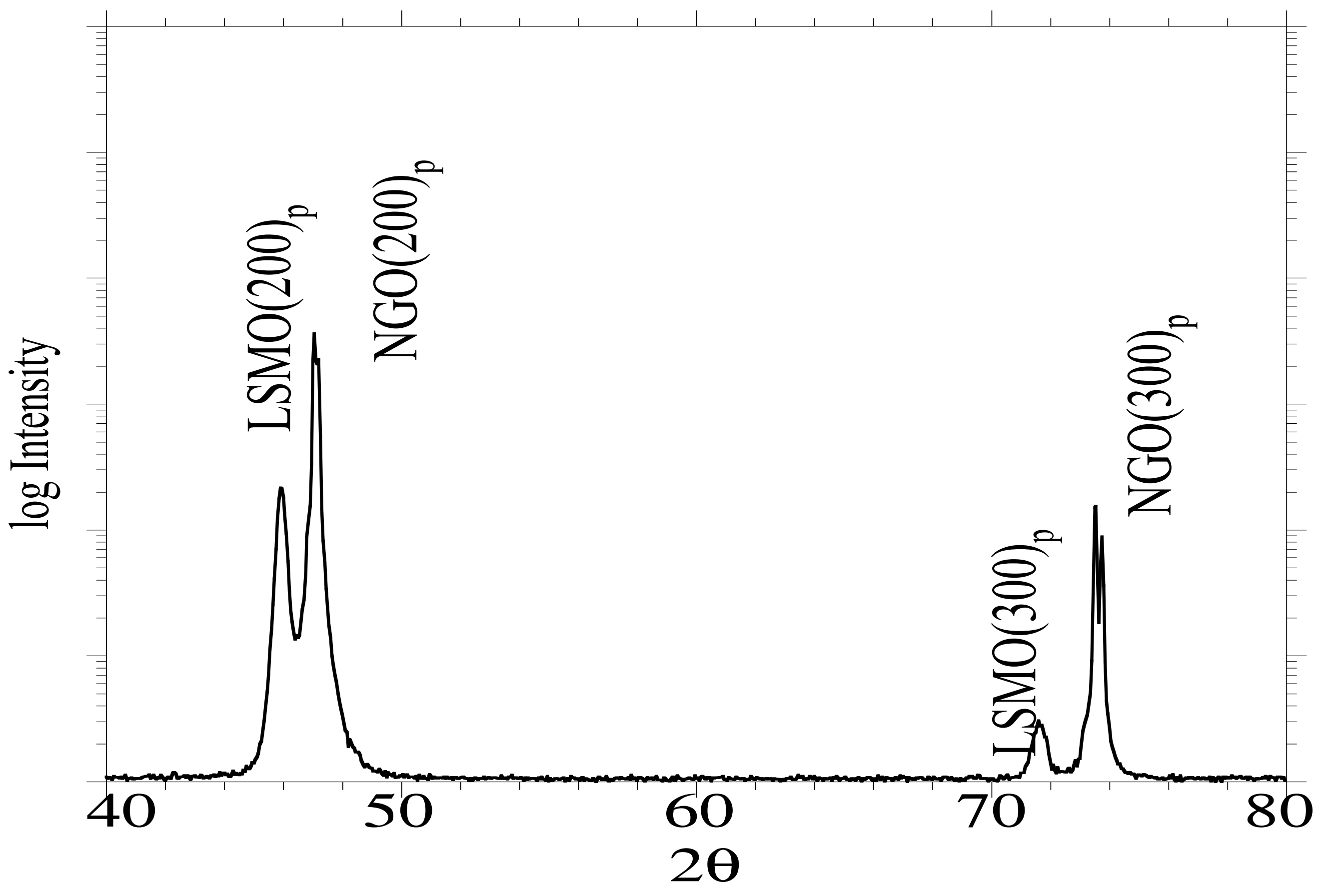


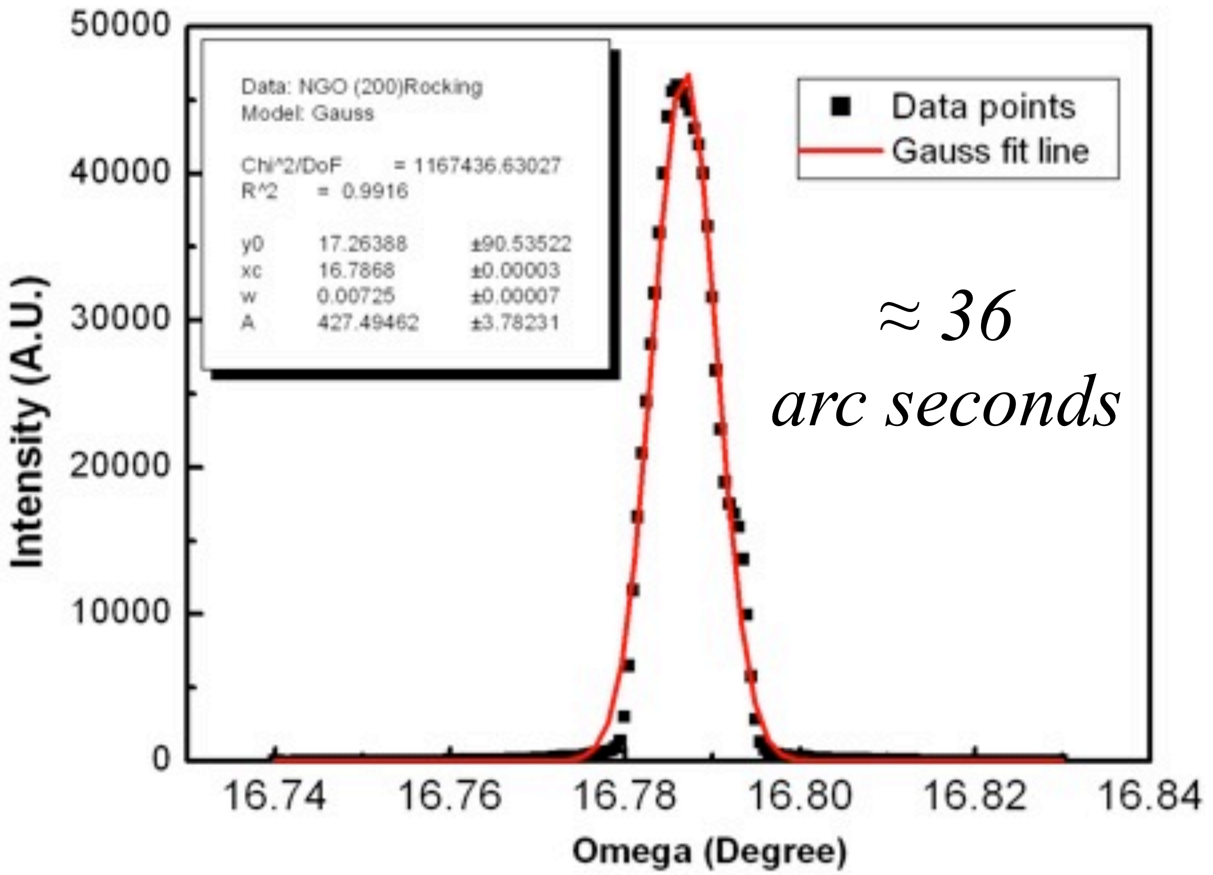
BST/LAO
$2.7x10^{11}$/cm2

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

Progress and Conclusions

- Complex Microstructures can be Quantitatively Characterized
- Mesoporous Nanoparticles of Cathodes were prepared
- High Quality Thin Films of Cathodes Prepared

- Kelvin Probe Spectroscopy on Films
  - Decouple Surface Dipoles and Conductivity
  - Mechanisms for LSM are varying with Temperature

- ECR on LSM Films
  - Anisotropy Exists for Various Orientations on Same Substrate
  - ECR is SURFACE LIMITED: Scales with Thickness
  - Value varies greatly with thickness and substrate orientation
  - Incorporation sites likely vary with substrate