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NETL

Electrode Optimization Studies and Cathode Surface Chemistry:

Determination of Key Correlations between Surface Features and Electrochemical Performance

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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Multifunctional Electronic Materials Center

MEMC

Outline for Cathode Surface Chemistry

- ***Overview of Program (Started May 2007)***
  - ***Background***
  - ***Goals***
  - ***Approach***
  - ***Team***

- *Initial Thin Film Work at CMU*
  - *Growth Systems*
  - *Thin Film Characteristics*
  - *Demonstrations of Control*

- *Initial In-situ X-ray Characterization at ANL*
  - *Environmental Chamber*
  - *Initial Results*

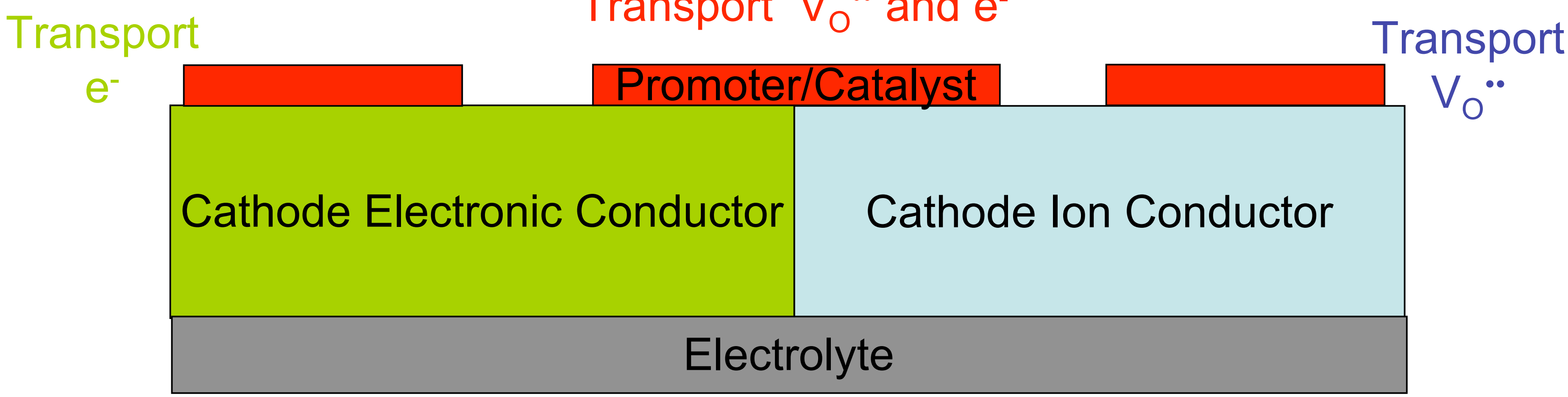
- *Summary / Future*

Ideal Cathode Materials

$$\frac{1}{2} O_2(g) \quad + 2e^- \quad \rightarrow \quad O^{2-}$$

pore *conductor* *ion conductor*

Actively Reduces O_2 and Transport $V_O^{\bullet\bullet}$ and e^-



There is <u>no reason</u> to believe that the ideal backbone will have the ideal <u>surface kinetics</u>.

There <u>is</u> reason to believe that the <u>surface structure</u> of known backbones is <u>dynamic under load</u>.

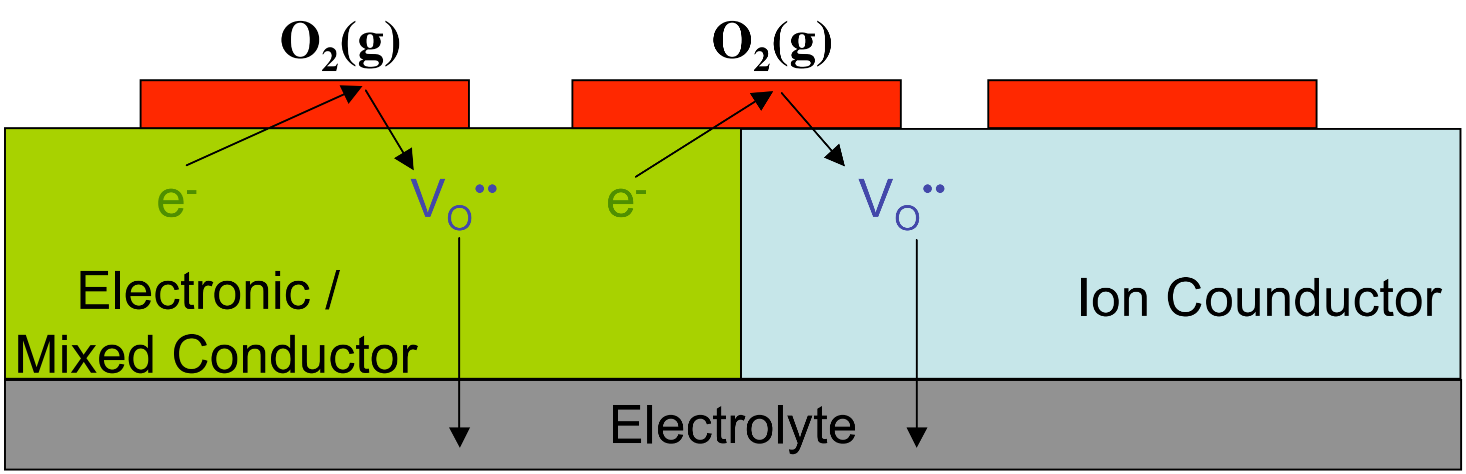
Can we understand / engineer highly-active and stable surfaces?

Ideal Surface Active Cathode Materials

Dynamic Surface / Promoter / Catalyst

- Actively Reduces O_2:
- Has high O_2 catalyst site density:
- Has sufficient population of $V_O^{\bullet\bullet}$:
- Has low interfacial resistance:
- Has long term surface stability:
- Actively conducts $V_O^{\bullet\bullet}$, e^-:

Overlays both electronic and ionic conductor



Experimental Philosophy / Goals

The basic lack of direct correlations between surface/interface chemistry/structure and performance hinders the design of optimized (active/stable) SOFC Cathodes.

- *Probe the nature of atomic scale surface chemistry or interface crystallography rather than the device scale micro-structural perturbations.*

- *Determine key correlations between:*
  solid state atomic, electronic, and chemical structure parameters and
  kinetic electrochemical (mass and charge transfer) performance parameters.

- *Correlations will be used to develop and employ:*
  a high throughput chemical screening methodology that
  does not require cell optimization and that
  will provide a sensitive measure of activity/stability in operational conditions.

Conceptual Sample

General Schematic

1 - 2 Atomic or Unit Cell Monolayers

≈ 20 - 50
Unit Cells of Epitaxial Perovskite

Macroscopic, Single Crystal
Perovskite Substrate
of specific orientation / termination

Example

$SrMnO_3$

(100)-terminated
$(La,Sr)MnO_3$

(100)-terminated
$SrTiO_3$

Concept

Gate

Reservoir

Support /

Electrolyte

Reservoir Remains the Same while the Surface layer is Varied
In this case:
$LaMnO_3$, $SrMnO_3$, SrO, MnO_2, or Metal (Pt, Ag,…)

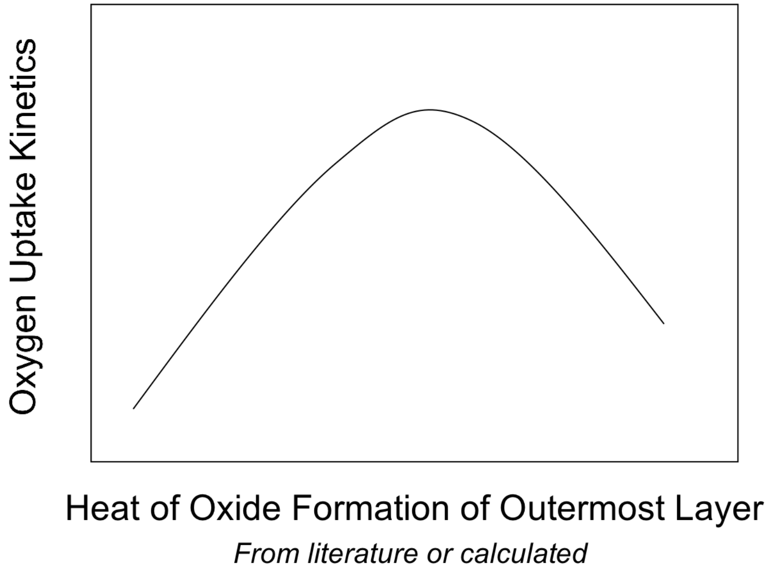
Surface Activity

Guiding ideas that will lead to generation of testable hypotheses:

1. A parameter can be identified that dictates the performance of perovskite cathodes

2. This parameter is surface sensitive and is related to: cation-gas bonding, vacancy population, electronic character, etc…

3. Noble metals can be used to change landscape of oxygen surface adsorption

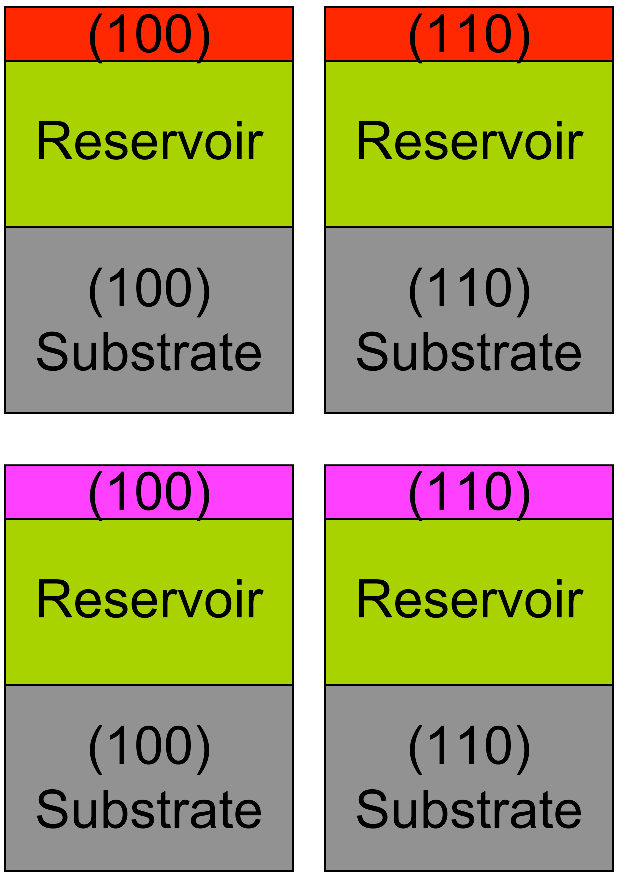


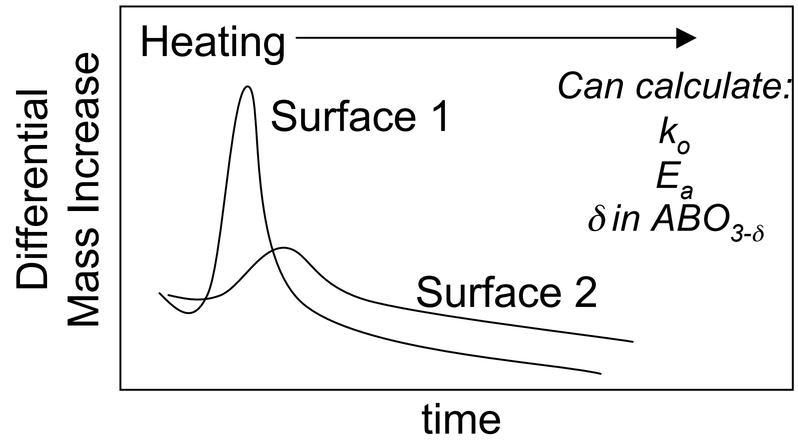
NEED NEW SAMPLE GEOMETRIES AND CHARACTERIZATION METHODS

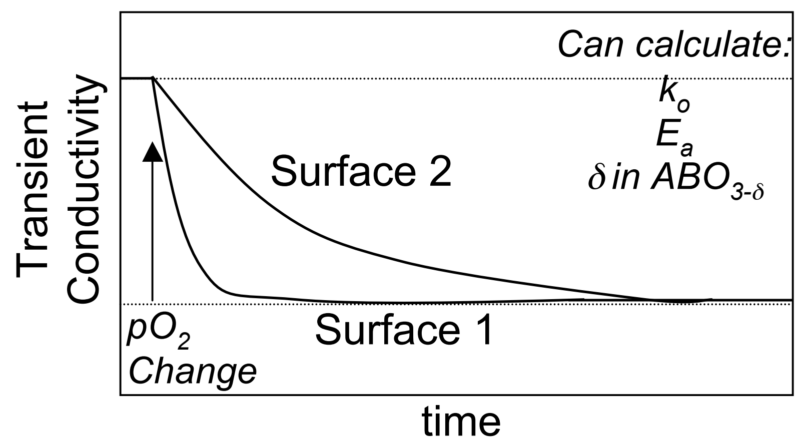
REAL TIME, IN-SITU MEASUREMENTS OF SURFACE!

Schematic Approach

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



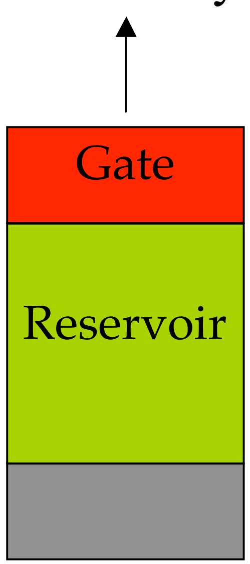




Other techniques: Electrical and mass-uptake conductivity relaxation, IS …

Experimental Values of Interest that are in Dynamic Equilibrium

Need Surface Sensitivity



1. Oxygen uptake kinetics
   (CMU / NETL / ANL)
2. Surface reduction state / surface vacancy concentration
   (CMU / NETL / ANL)
3. Adsorbed oxygen species
   (CMU / NETL)
4. Cation segregation / dopant distribution
   (CMU / ANL)
5. Nanostructural surface defects
   step density, surface reconstruction, correlated vacancies
   (CMU / ANL)
6. Surface band structure / electronic species
   (ANL)
7. Surface Species
   (NETL / CMU)

Collaborators

Surface Engineering / Characterization / TEM
B. Kavaipatti, S. Wang, R. Petrova
Carnegie Mellon

O. Maksimov, CMU/Penn State

Detailed Structure and Surface Segregation vs Oxygen Activity
J. Eastman, D. Fong, P. Fuoss
APS, Argonne National Laboratories

Surface Stability / Interface Stability
L. Helmick, S. Seetharaman
Carnegie Mellon

R. Gemman, C. Johnson
National Energy Technology Laboratories

Detailed Structure and Surface Segregation vs Electrochemical Activity
K.-C. Chang, D. J. Myers, J. D. Carter, H. You
APS, Argonne National Laboratories

B. Yildiz, MIT

Surface Chemistry
J. Kitchin
Carnegie Mellon

C. Matranga
National Energy Technology Laboratories

Electrochemical Activity and Cr-Poisoning
B. Ingram, T. Cruse, M. Krumpelt
Argonne National Laboratories

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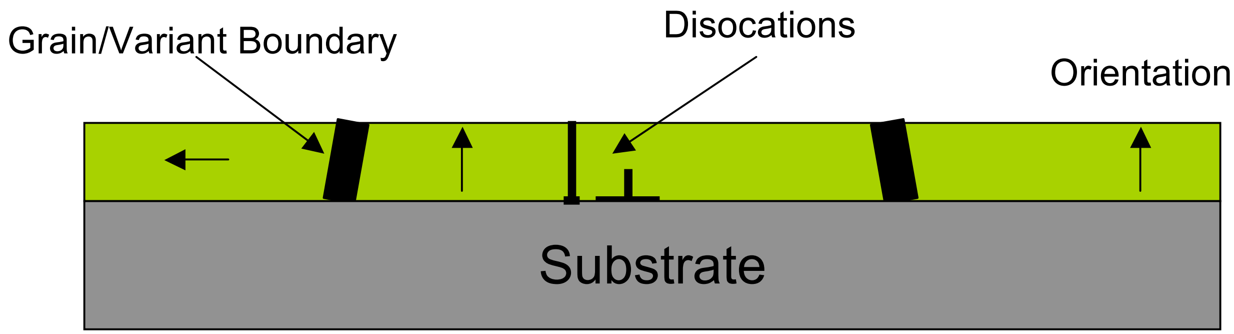
Thin film approach



Characteristics of thin film growth that affect the oxygen uptake kinetics:

- Film thickness
- Film Morphology
- Orientation/Epitaxy
- Strain
- Dislocation networks
- Growth on electrolytic substrates
- Grain/Variant boundary
- Interdiffusion

Gate Materials:

- $LaMnO_3$
- $SrMnO_3$

Reservoir Materials:

- $(La,Sr)MnO_3$
- $NdNiO_3$

Substrate Materials

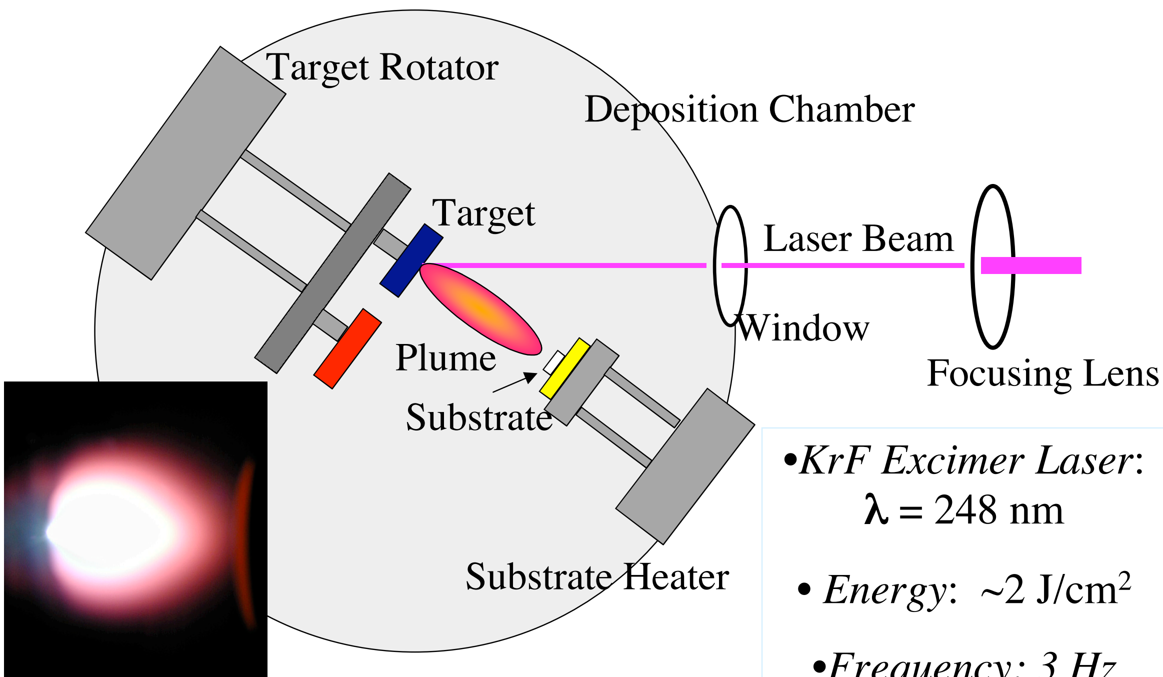
- $SrTiO_3$
- $NdGaO_3$
- *YSZ*

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

Pulsed Laser Deposition



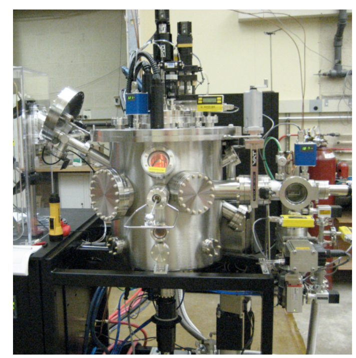
•*KrF Excimer Laser*:
λ = 248 nm

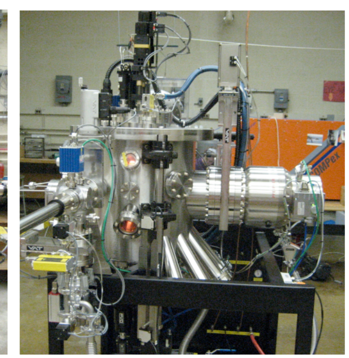
• *Energy*: ~2 J/cm^2

•*Frequency: 3 Hz*

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



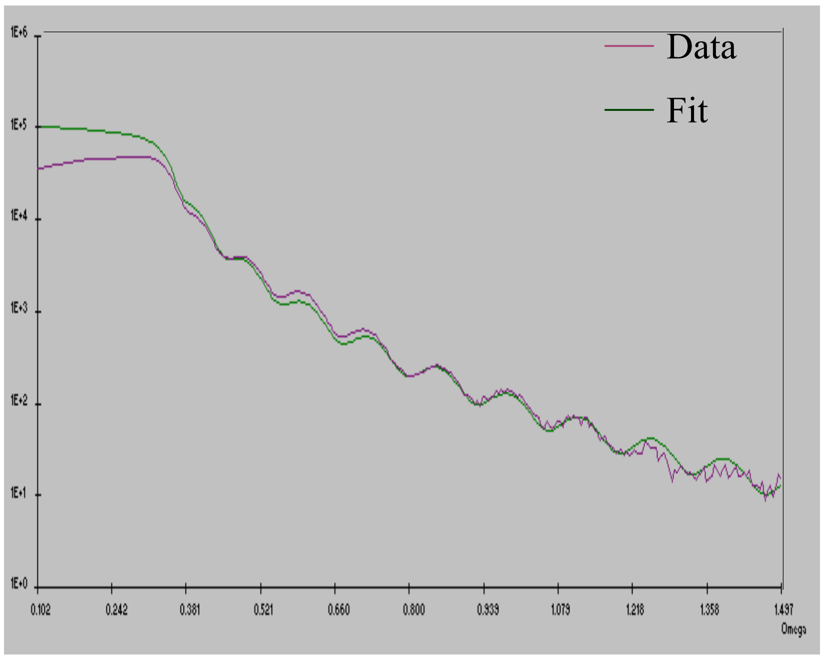


Growth rate / Surface Morphology

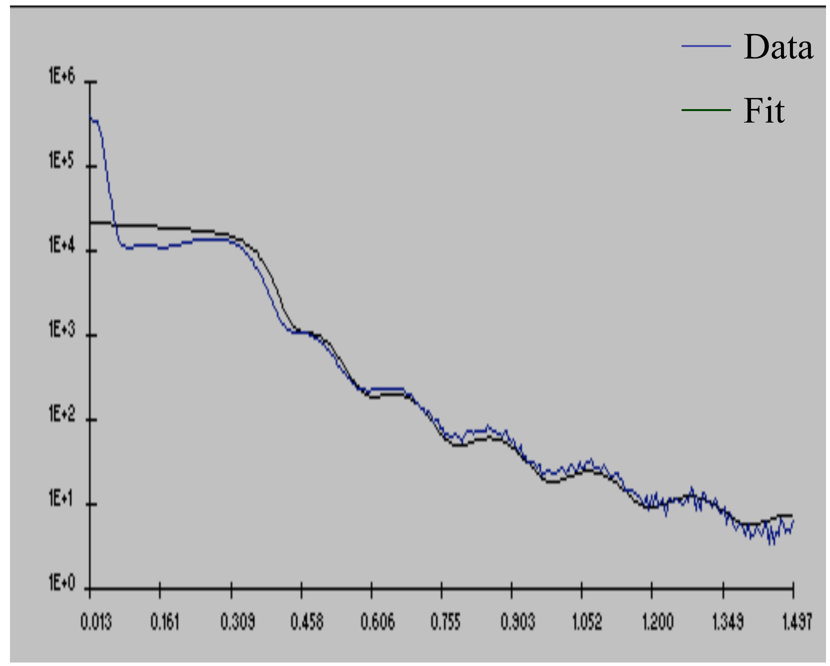
Oscillations in the X-ray reflectivity scan measure thickness

Determine growth rate of Reservoir and Gate

$(La,Sr)MnO_3$ - 0.11 Å/pulse



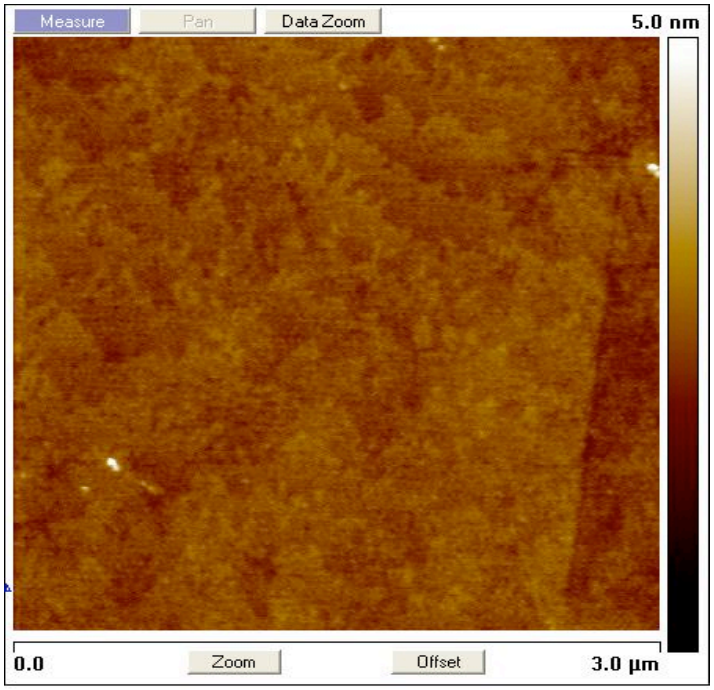
$LaMnO_3$ - 0.10 Å/pulse



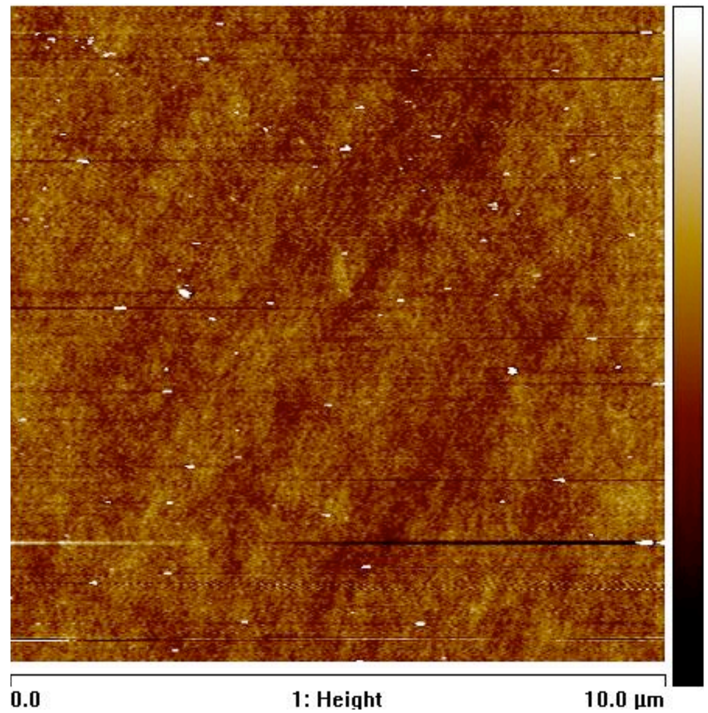
PLD Produces High Quality Surface Engineered Films with Controlled Thickness / Roughnes

Surface Morphology

$LaMnO_3$ and (La,Sr)MnO_3 films (~ 54 nm thick) with low roughnesses obtained on $SrTiO_3$(100) substrates



rms = 5.5 Å
Peak-to-Valley = 50 Å

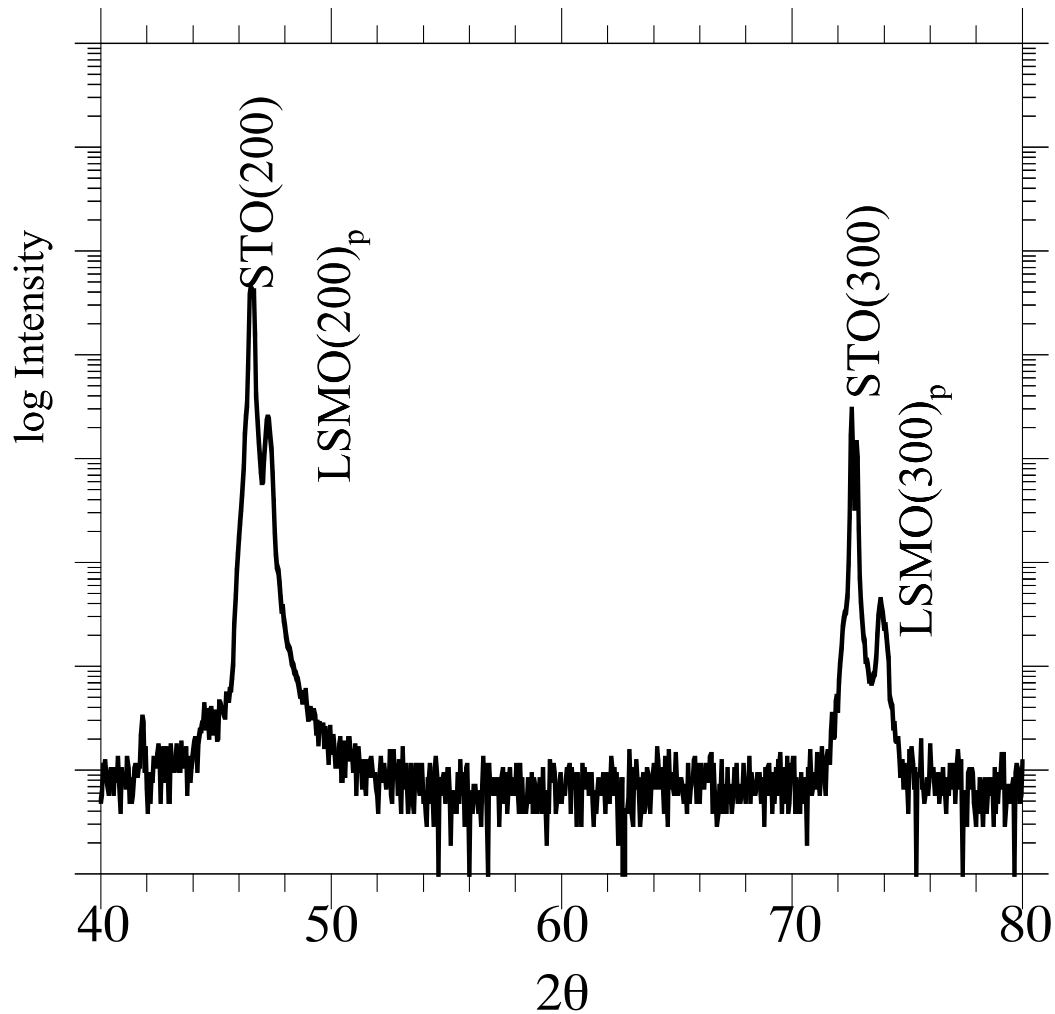


rms = 4.41 Å
Peak-to-Valley = 30 Å

PLD Produces High Quality Surface Engineered Films with Controlled Thickness / Roughnes

(La,Sr)MnO$_3$ thin films on SrTiO$_3$(100)

Standard X-ray Diffraction Scans of Films 54 nm thick

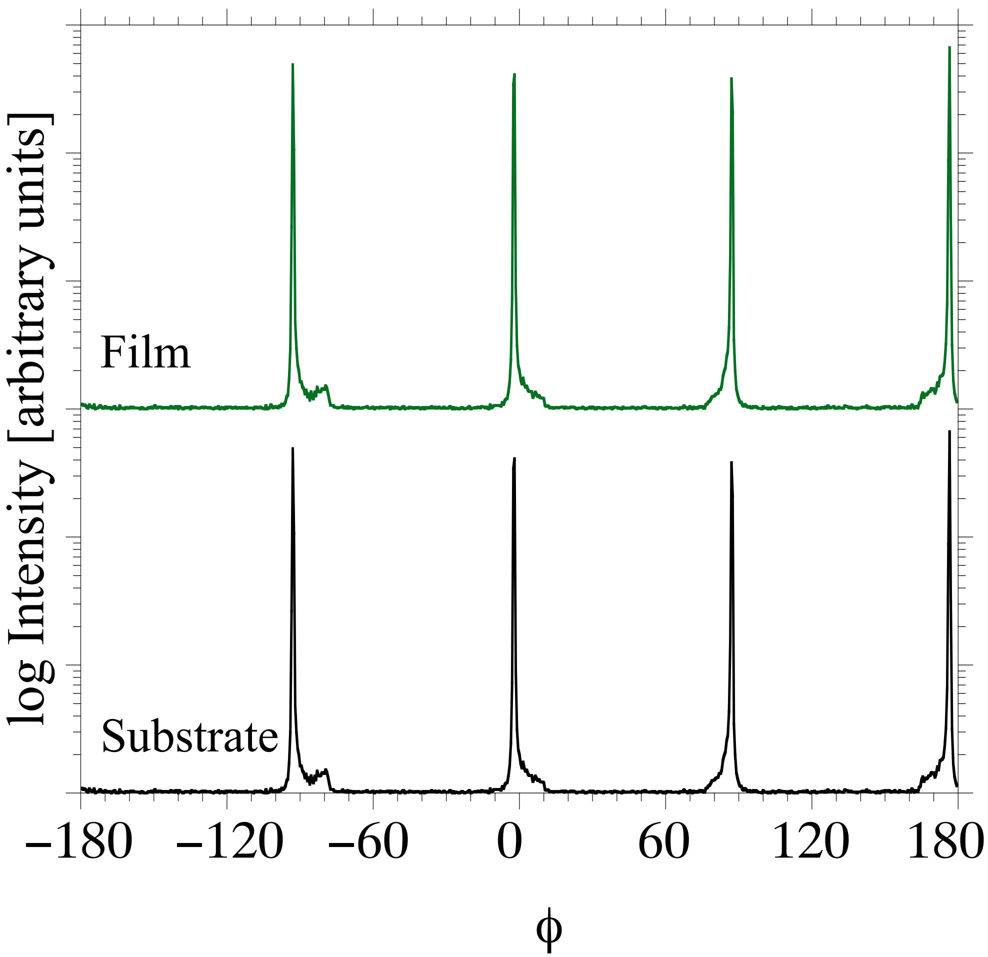


- *(100)$_p$-oriented*
- *Out-of-plane compression*
- *In-plane tension*
- *Below critical thickness*

All films routinely characterized for XRD

In-plane orientation / Epitaxy

Phi Scan of in-plane X-ray Diffraction Scans of Films 54 nm thick



(402) Peak

Peaks are well aligned

Films is strained to substrate

Orientation relationship is:

$$\{100\}_{p_{Film}} \| \{100\}_{Substrate}; \langle 001 \rangle_{p_{Film}} \| \langle 001 \rangle_{Substrate}$$

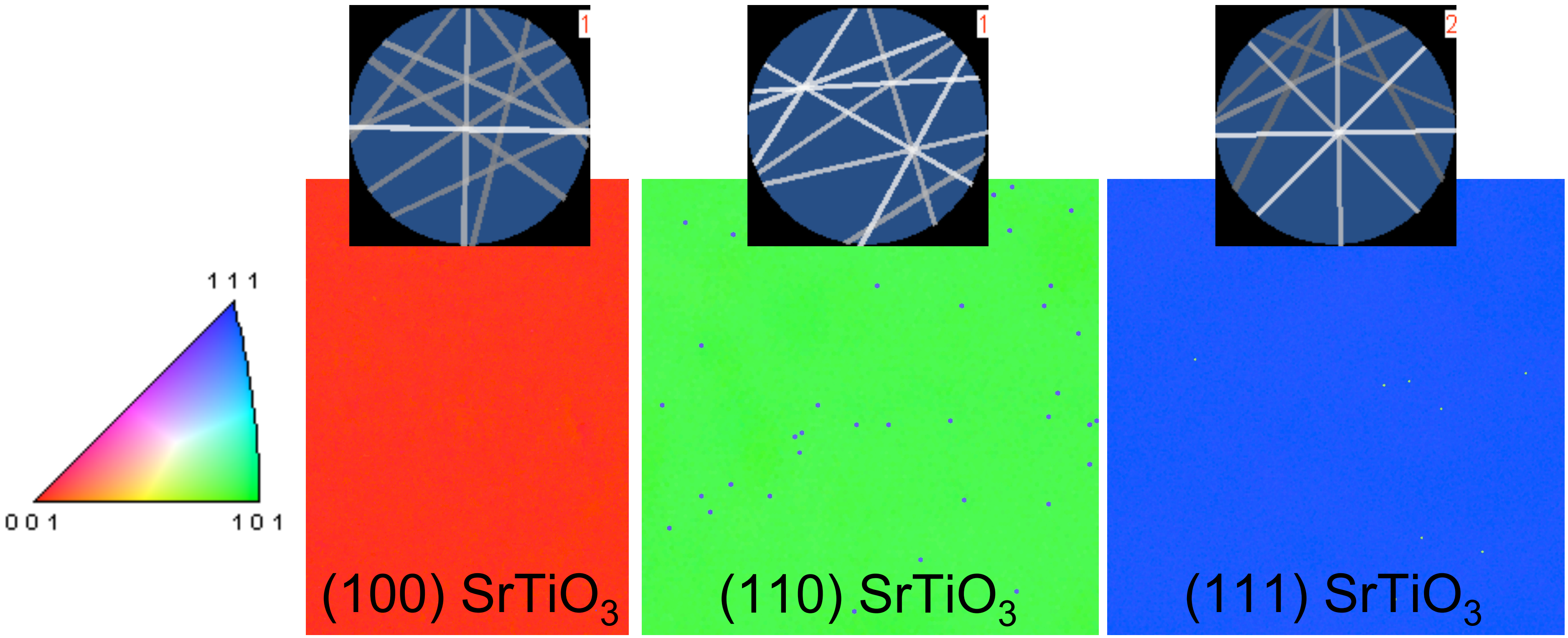
Standard Characterization Method to Ensure Quality Prior to Other Characterization

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



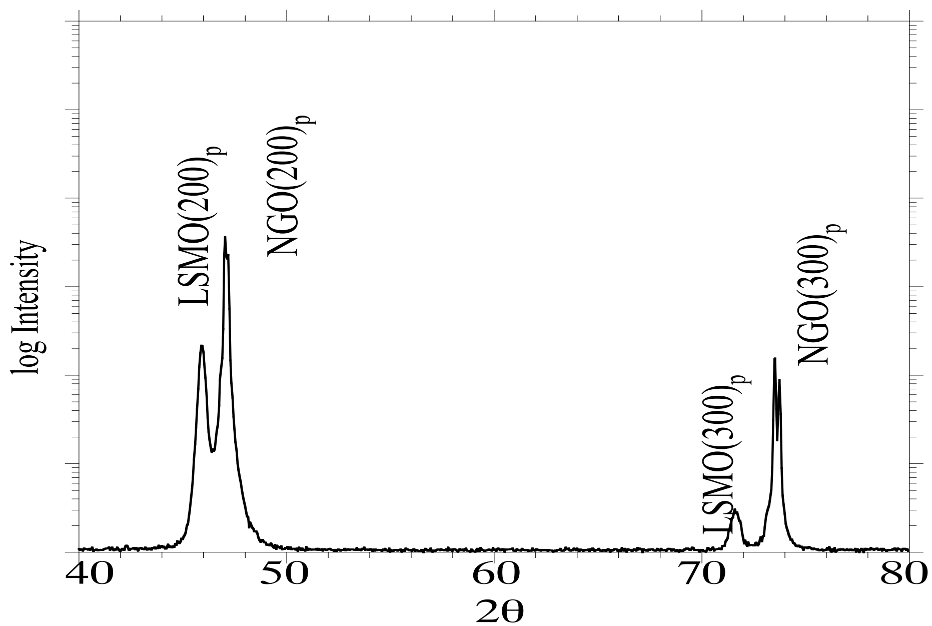
All three low-index surfaces are obtained as epitaxial films

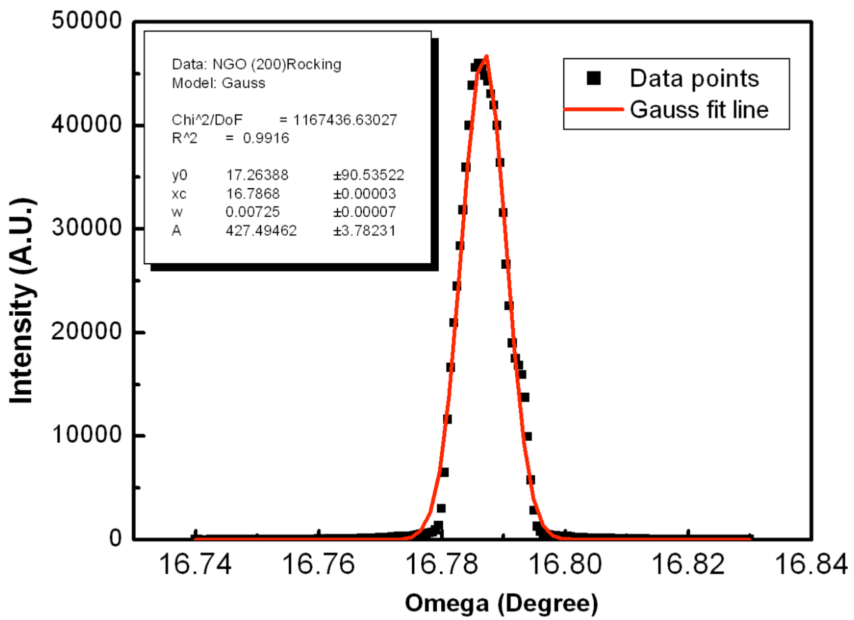
$(La,Sr)MnO_3$ thin films on High Quality Insulators

Control Strain State

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

Minimize Dislocations

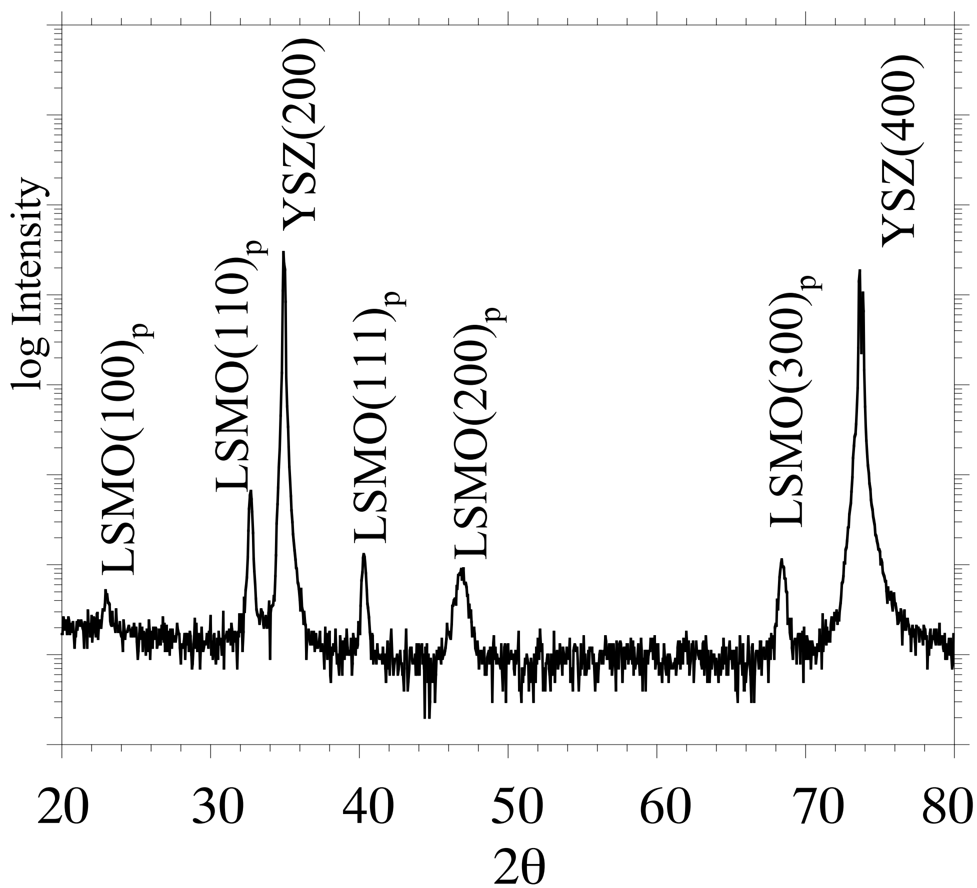




Need Reasonable Perovskite Electrolyte(s) for Electrochemistry

$(La,Sr)MnO_3$ thin films on YSZ(100)

Perovskite / Fluorite Interface in ESSENTIAL in final ION TRANSFER



Film prefers to grows in a polycrystalline fashion on YSZ(100)

Can obtain textured (110) films

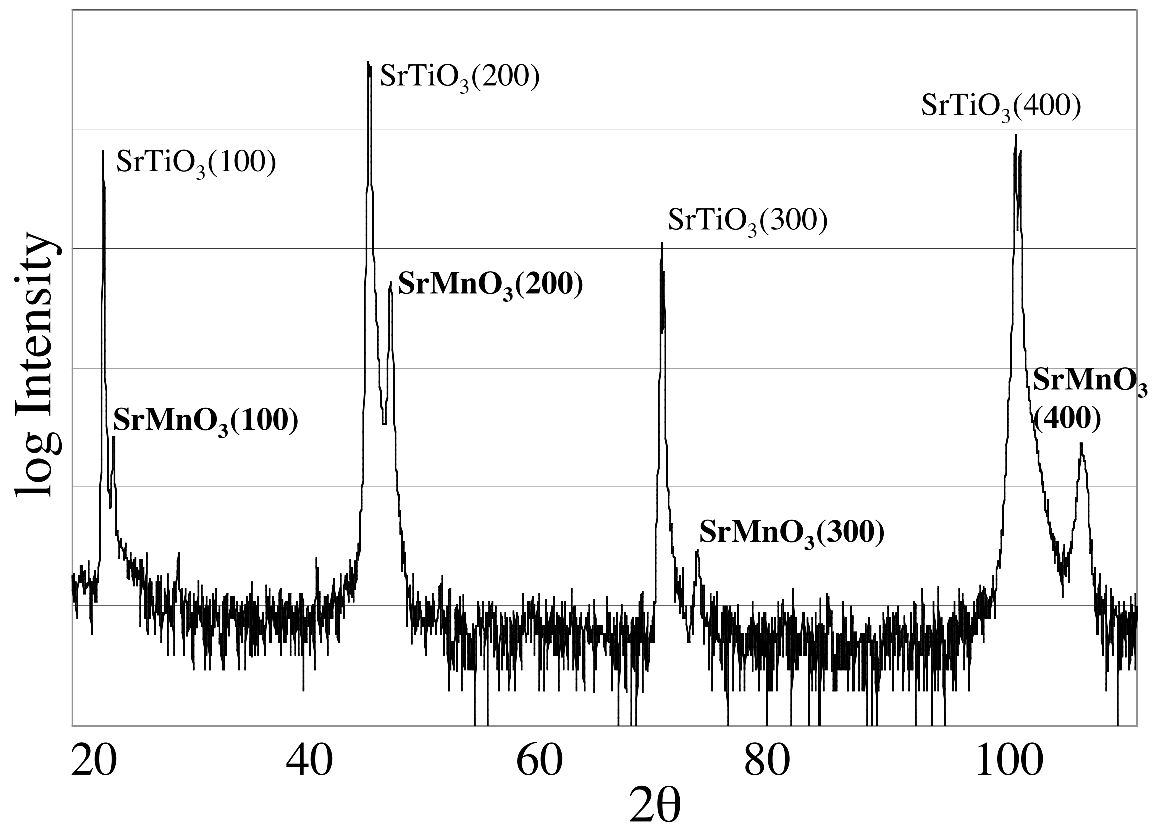
Good for comparison to real SOFC

Poor for Surface Engineering

Will study both Fluorite and Perovskite Electrolytes using Electrochemical Methods
Includes Synchrotron In-situ experiments

$SrMnO_3$ thin films on $SrTiO_3(100)$
Alternate "native perovskite" gate for LSM

Highly-oriented (h00) *perovskite-like films attained on the perovskite $SrTiO_3(100)$ substrates*



Have made surface engineered samples with different gates: starting to measure Intermixing?

Artificial $(LaMnO_3)_{15.5}(SrMnO_3)_{5.5}$ structures

Artificial Structures Stable

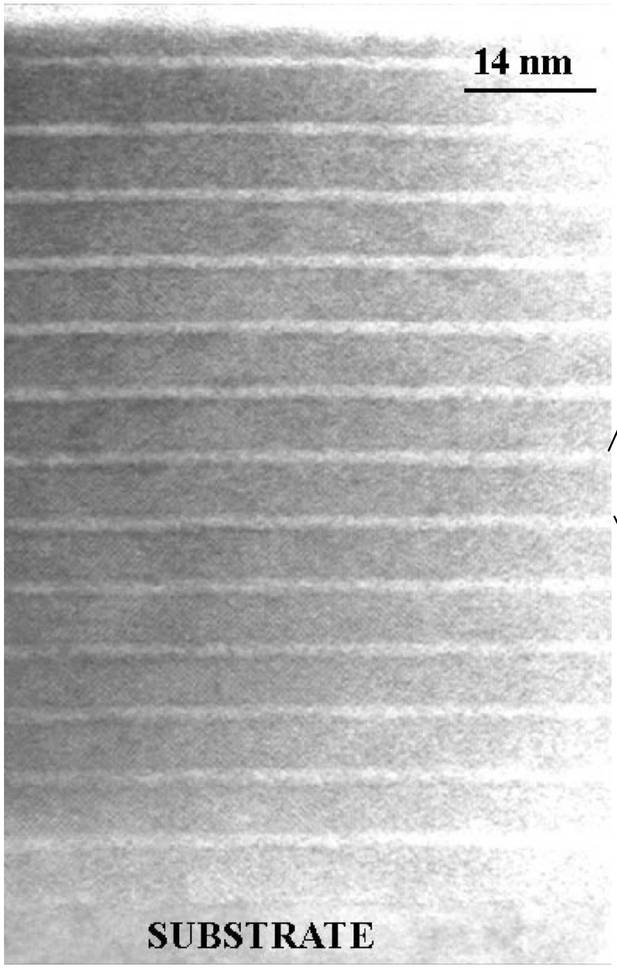
Mixing driving force small

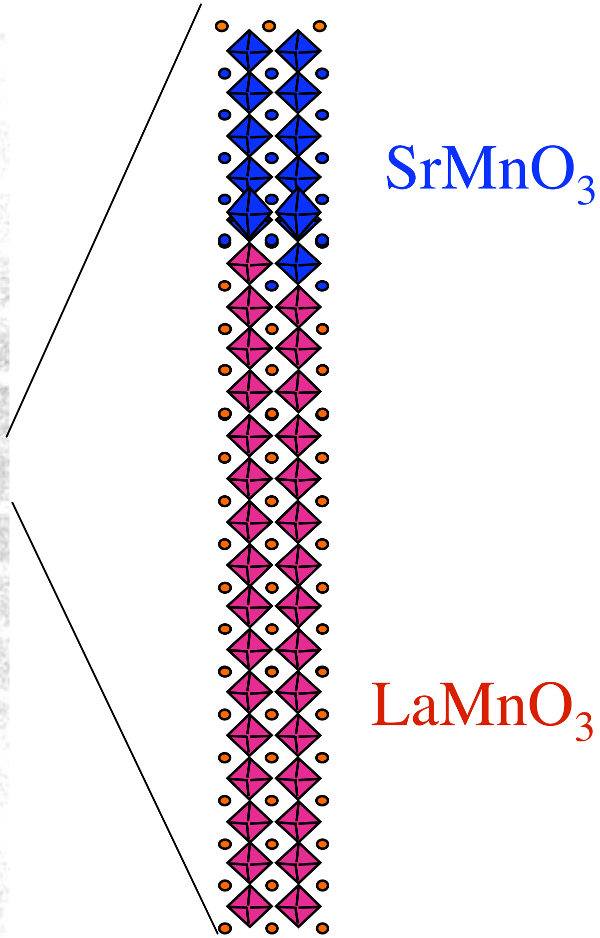
Inner / Outer Layers Same

Surface can be engineered

Samples can be measured

Long term stability???





Samples are easy to grow once calibrated; several can be grown simulaneously

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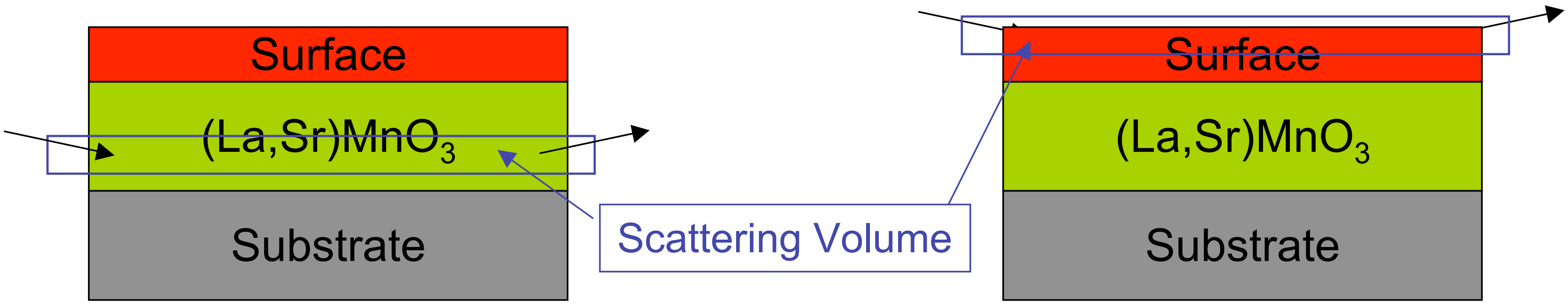
Synchrotron Glancing Angle X-Ray

GOAL: Understand HOW (La,Sr)MnO_3 and (La,Sr)(Co,Fe)O_3 Behave

APPROACH: Use IDEAL Samples and Sensitive *In-Situ* Probe



- Environmetal Cell
- Good Samples
- Surface Morphology
- Grain/Variant boundary
- Segregation / Interdiffusion

- Beam Line / Time
- Structure
- Strain
- Temperature (Quenching?)
- Electrochemistry

Preliminary Investigation Using Synchrotron XRD

<u>Environmental Chamber</u>
Allows to Investigate in appropriate cathode conditions

Temperature: RT - 800°C

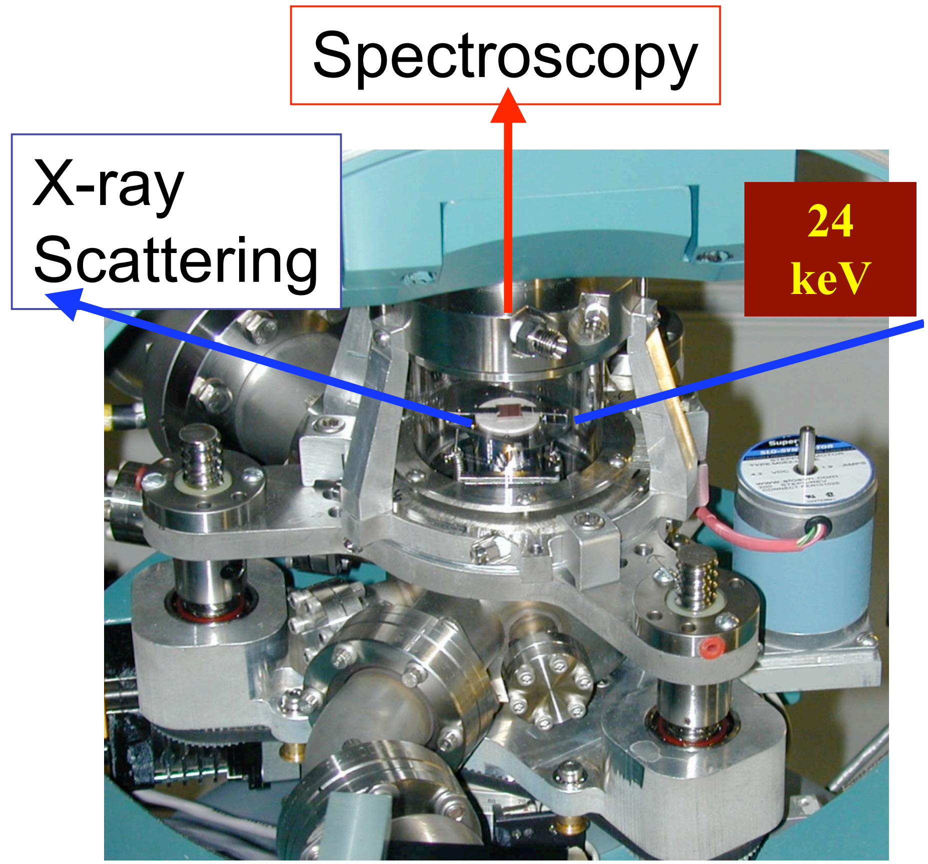
Pressure: 10^{-3} - $7x10^{2}$ Torr

Process Gas: O_2 - Argon

Flow Rate: 1 - 10^{3} sccm

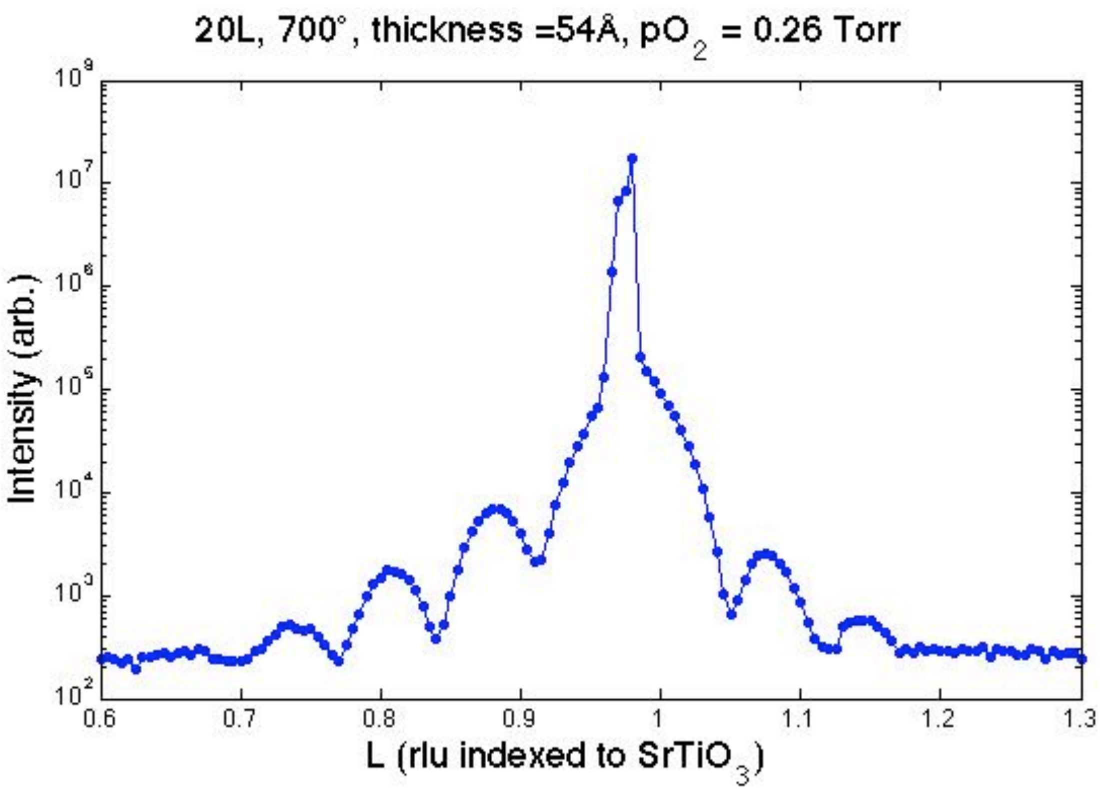
Ideal thin film samples:
atomically FLAT
no wafer curvature
Low dislocation content

<u>Grazing Incidence X-ray</u>
Provides Surface Sensitivity



$La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3(100)$

Glancing Angle Measurements on thick"Capping Layers" (14 Unit Cells)



- Films Ultrathin and Ultraflat

  at temperature

- Thickness = 54 Å

  from fringes

- Film lattice-matched to the substrate

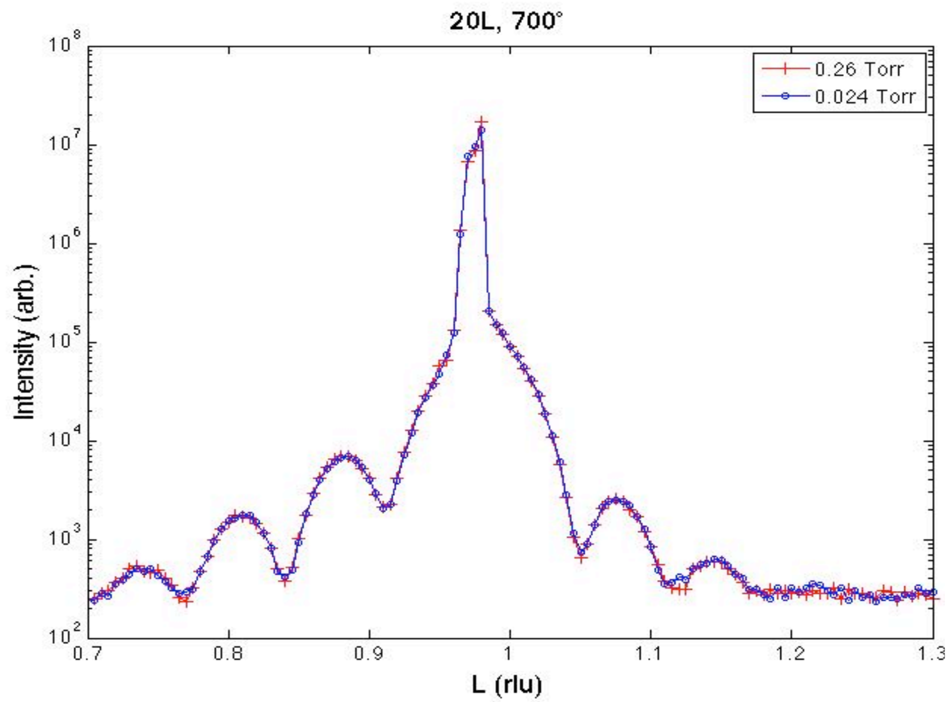
  in-plane scan (not shown)

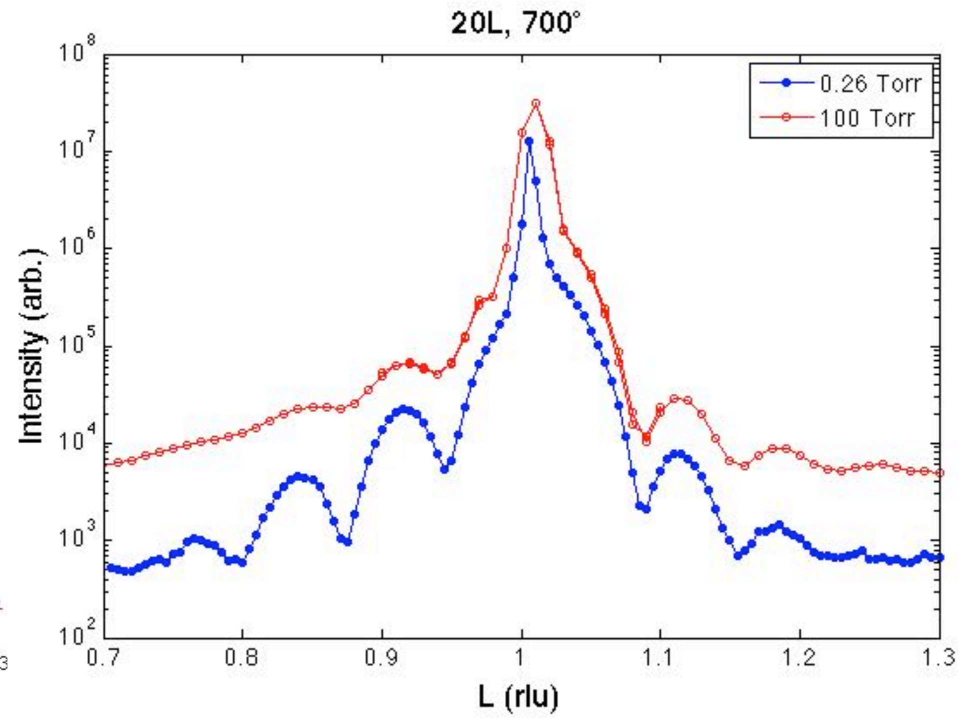
  0.77% tensile strain

PLD Produces
High Quality Surface Engineered Films that are Flat, Stable, and Measurable

Oxygen Pressure Effects
In-situ Surface Morphology

Glancing Angle Measurements on Roughness of Thick Capping Layer





Low pO_2

0.26 Torr to 0.024 Torr

no measurable effect

High pO_2

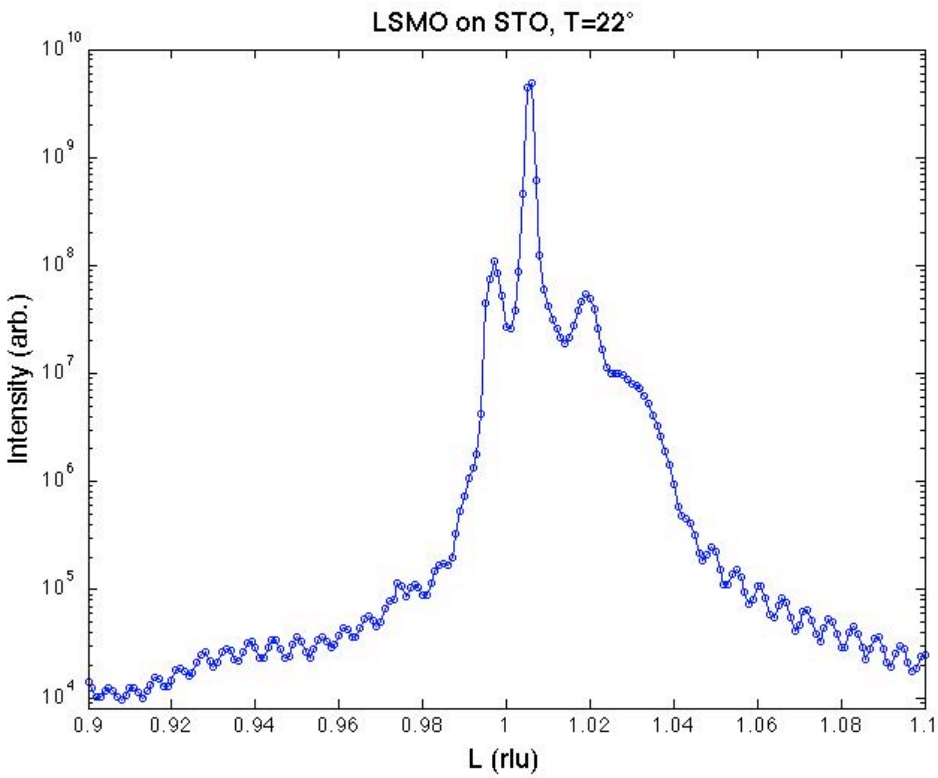
0.26 Torr to 100 Torr

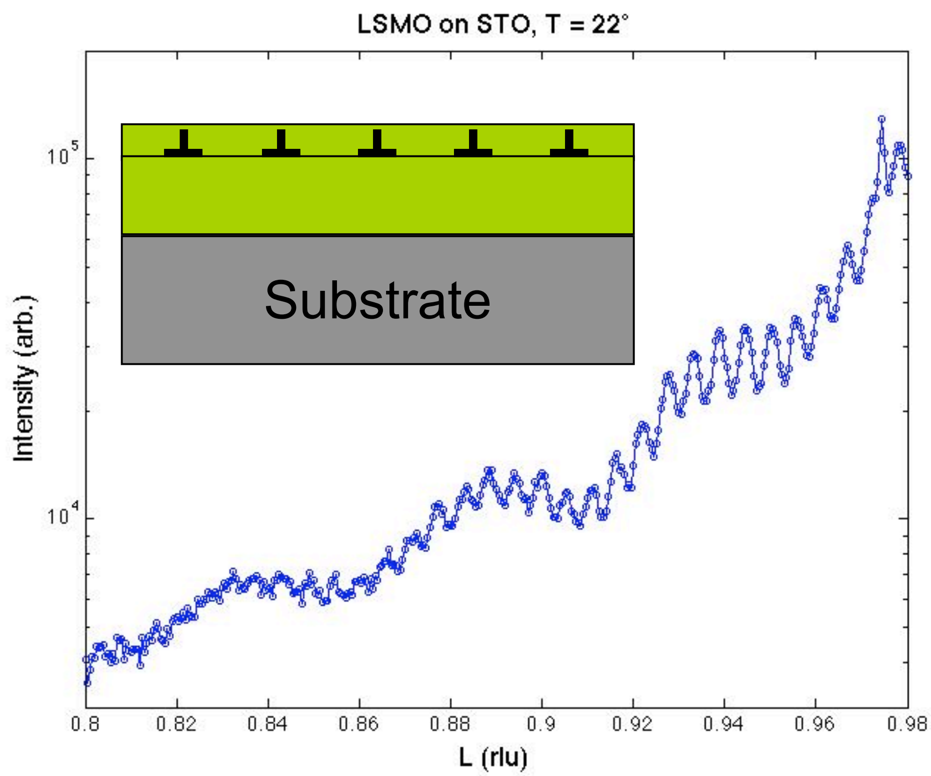
roughness increased

Real-time measure on affect of P / pO_2 on surface structure

Effects og Increasing Thickness

Glancing Angle Measurements on thin "Reservoirs" (200 Unit Cells)





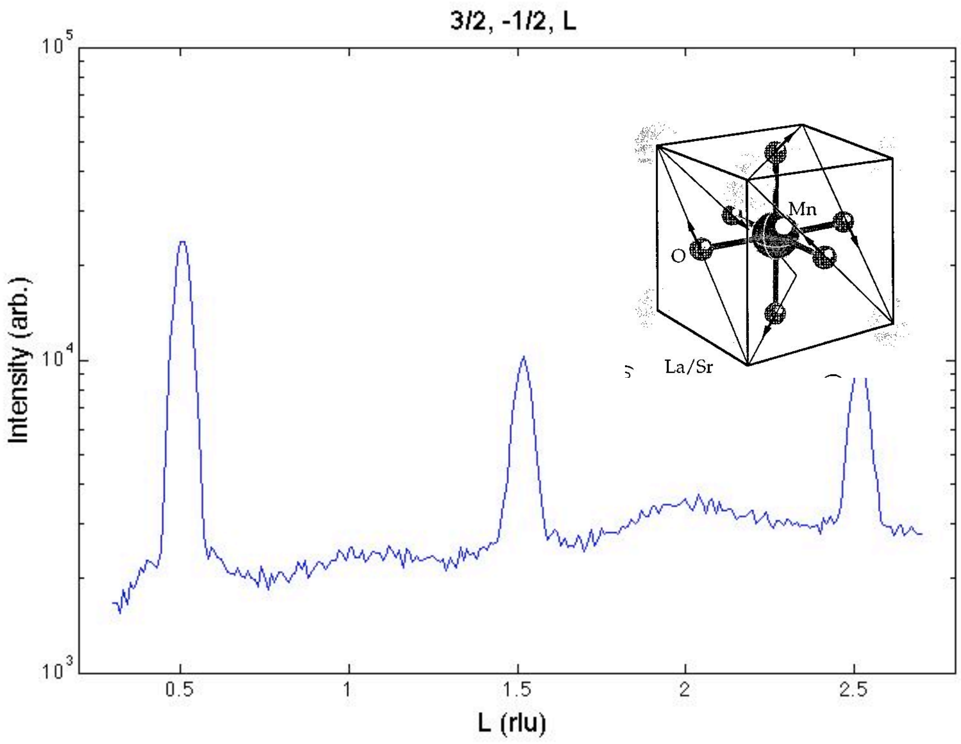
- Thickness fringes with two characteristic lengths are observed (~68 nm and ~7.5 nm)
- Consistent with previous TEM observations of partially relaxed films
  - ➜ Wiedenhurst et al. (J. Mag. Mag. Mater., **211**, 16, 2000)

    misfit dislocations localized to ~60 nm from the $(La_{.7},Sr_{.3})MnO_3$ / STO interface

Can observe relaxations in films / Determine Strain State In-situ

Bulk Structure of Strained $La_{0.7}Sr_{0.3}MnO_3$

Scattering Measurements on thin "Reservoirs" (200 Unit Cells)



- Observe 1/2-order reflections;

  likely related to octahedral tilts

- Not typical for films at 700°C

  (not typical to observe this)

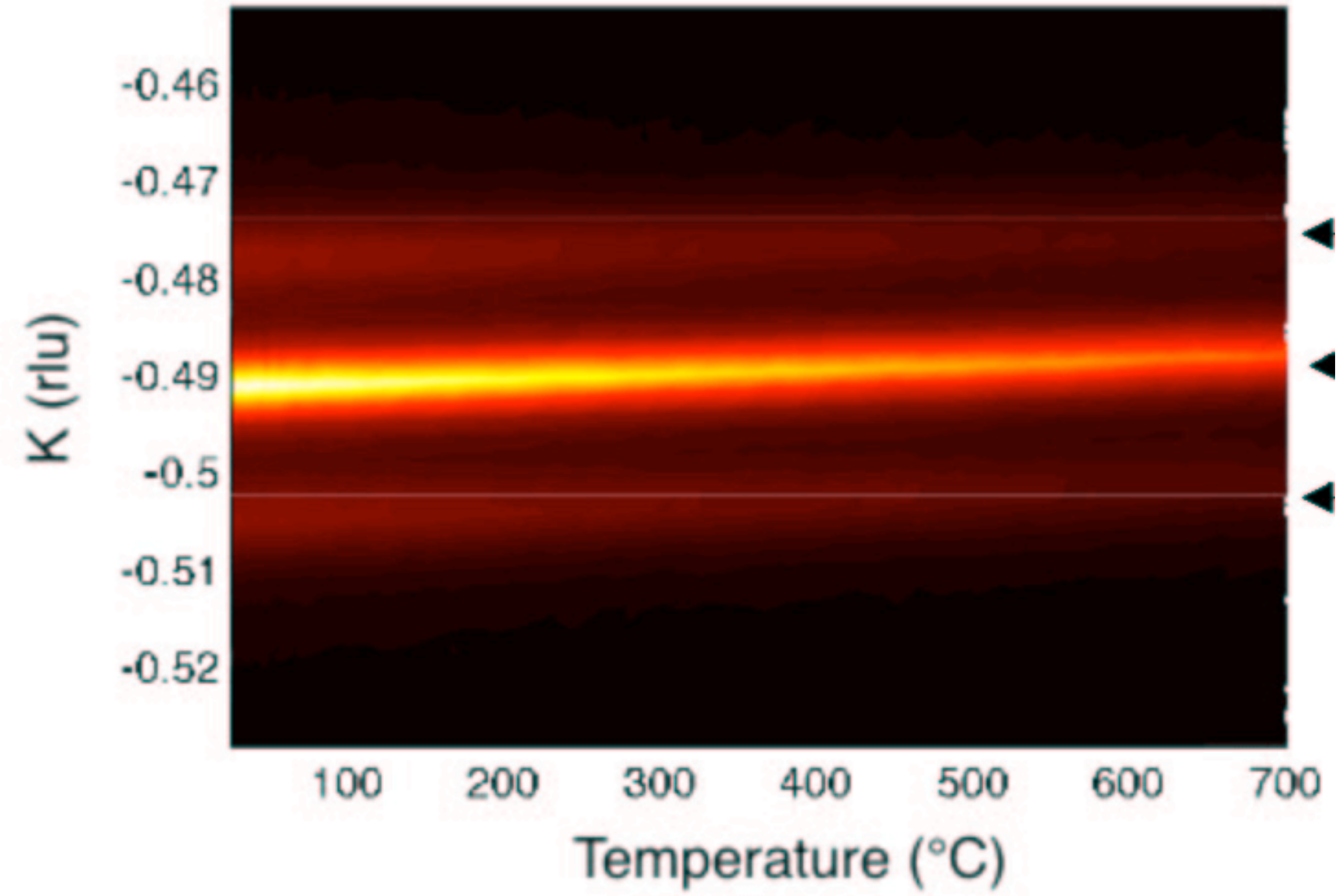
- Observed in polycrystalline LSMO;
  Martin et al. *(PRB*, **53**,14285,1996*)*
  antiferrodistortive structure

- *Need to Determine Origin*

Bulk Reservoir Structure Determination In-situ

Temperature DependentStructure Investigations

Scattering Measurements on thin"Reservoirs" (200 Unit Cells)



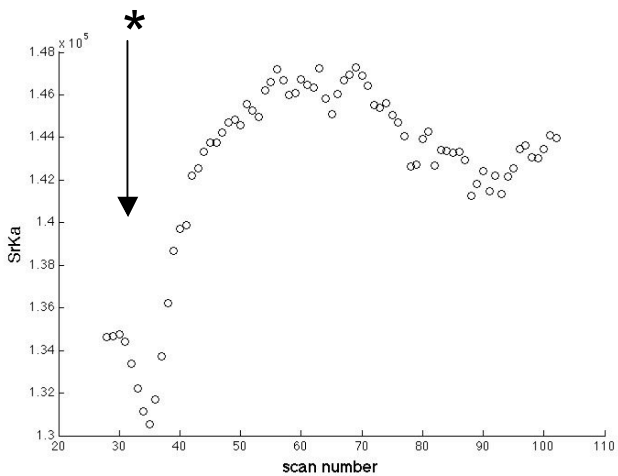
Superstructure Persists from Room-Temperature to 700°C

Can determine structure that is "quenched"

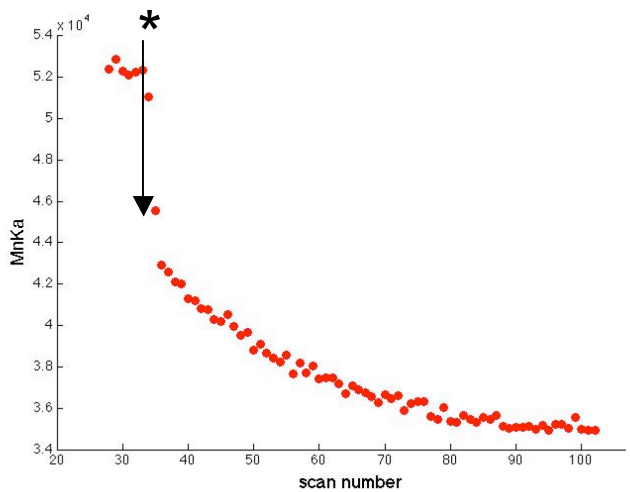
Surface Sensitive Fluorescence

*Pressure Changed (at *) from 100 Torr to 0.01 Torr*

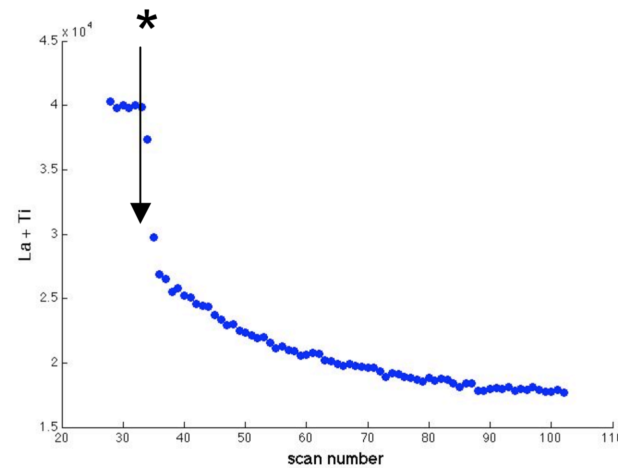
Sr Signal



Mn Signal



(La+Ti) Signal



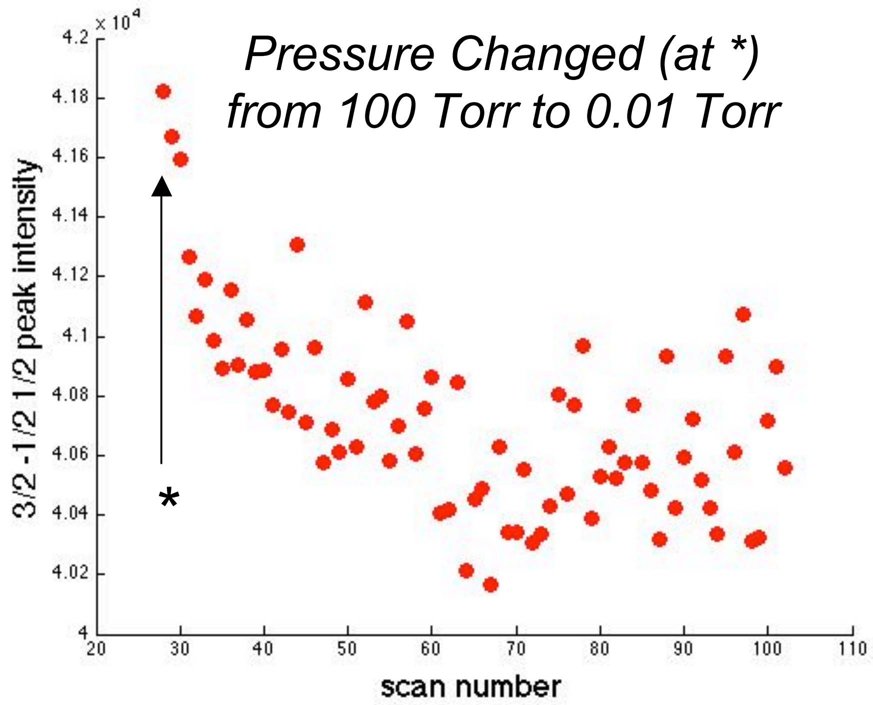
1. Careful analysis is required to correct for absorption:
PRELIMINARY OBSERVATIONS

2. Sr-signal increases on decrease of pO_2, while Mn and La(+Ti) decreases

3. Consistent with few literature reports that surface segregation occurs

Surface Structure

Surface Sensitive Scattering Measurements on thin"Reservoirs" (200 Unit Cells)



1/2-order reflections Persist

Only weak drop in intensity

Surface STRUCTURE weakly changed

implies no clear phase separation

Need to combine fluoresence and XRD…

Both Structure and Composition of Surface Have been measured: being analyzed

Summary / Future Directions

- ***Kicked Off Large-Scale Effort to Understand / Engineer Cathodes Surfaces for Improved Performance***
  Assembled Large Group with Appropriate Expertise
  All Groups Have Launched Initial Studies

- ***Effort focused on Thin Film / Engineered Surfaces***
  CMU Generating Samples for Wide Ranging Efforts
  Characterize In-House Samples Prior to Sending
  Implement ECR / XPS / Auger In-House
  Develop / Implement High-T Crystal Microbalance
  Develop HIGH-THROUGHPUT Method to identify KEY CORRELATIONS

- ***Initial In-situ X-ray Characterization at ANL***
  Environmental Chamber Analyze Results
  Investigate Surface Engineered Samples
  Use other Beams: Surface Electronic Structure / Electrochemical