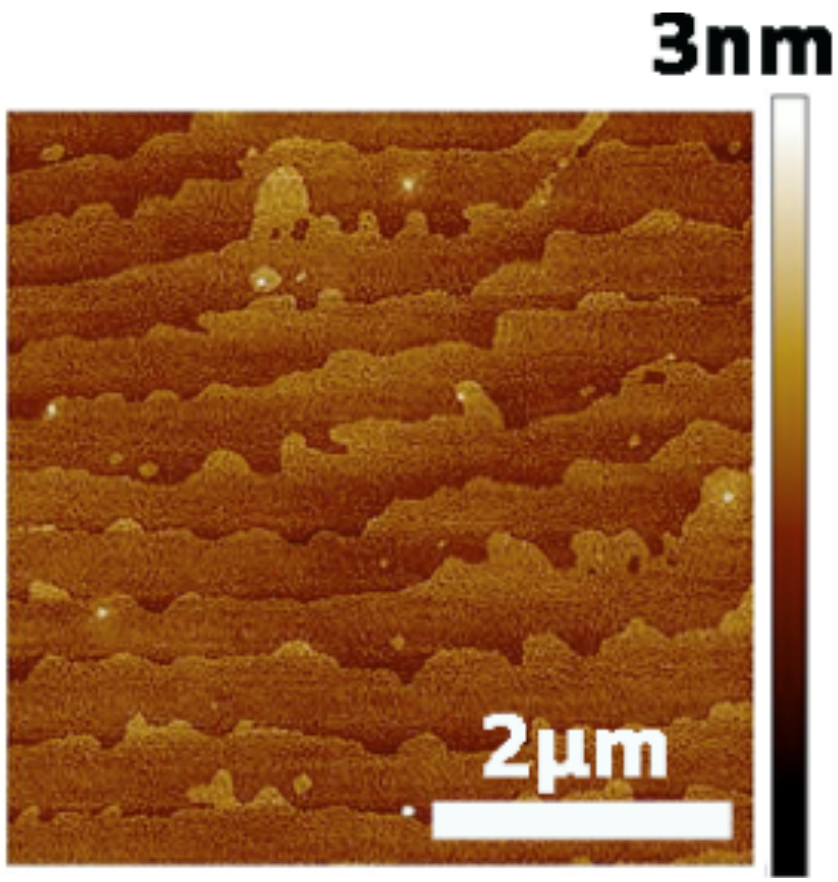
Oxygen Exchange in Thin Layers of SOFC Cathode



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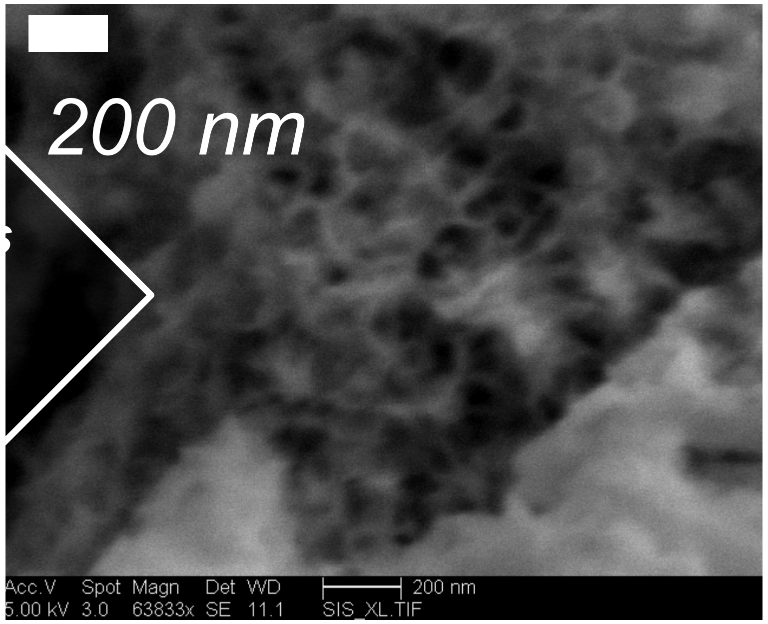


Funded by DOE - SECA, Thanks to L. Wilson, W. Surdoval, B. White, P. Burke, Shailesh Vora

Outline

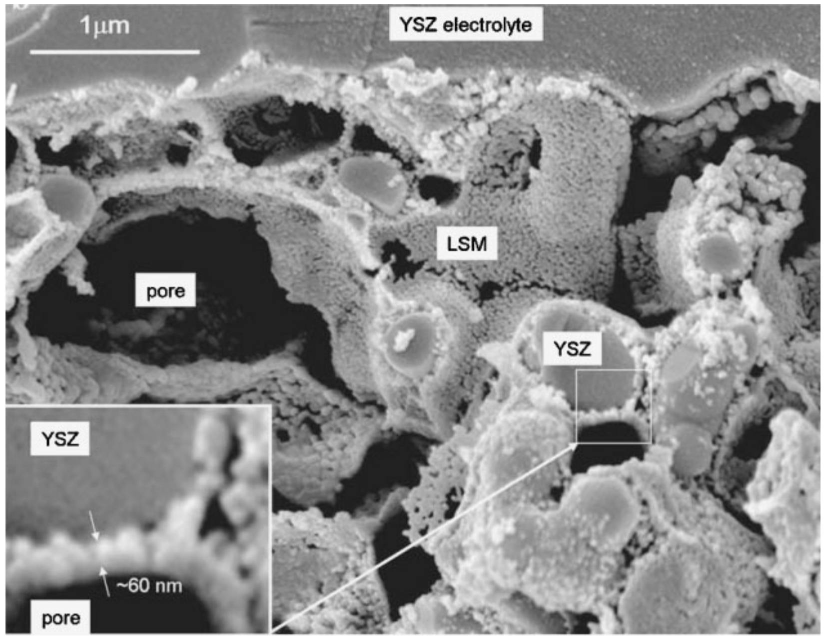
- **Utility of thin layers**
  - Functioning SOFCs
  - Basic science
  - Fuel cell collaboration

- **Microstructure and oxygen exchange**
  - Orientation of relaxed layers
  - Dislocations and strain
  - Extended boundaries in polycrystalline layers
  - Free surfaces

- **Conclusions**

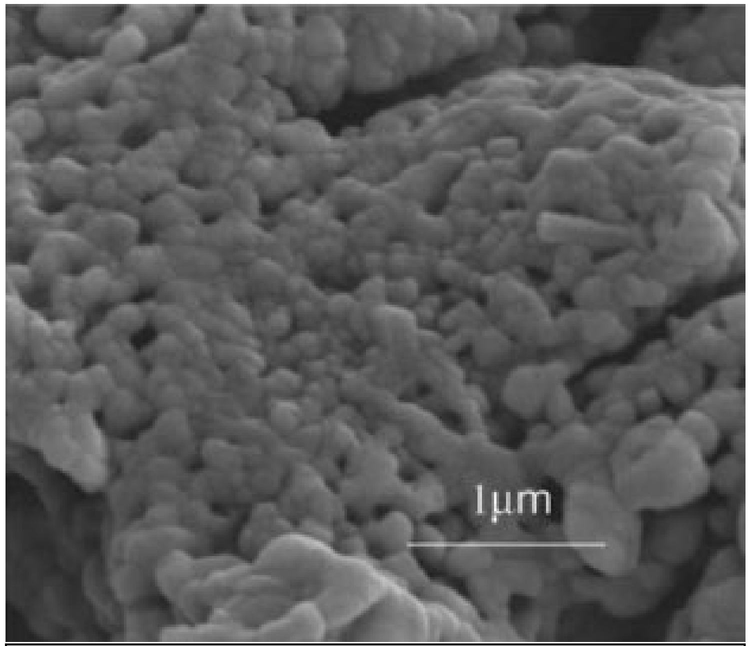
Infiltration: Surface Active nanoparticles for SOFCs

LSM on YSZ
LBL



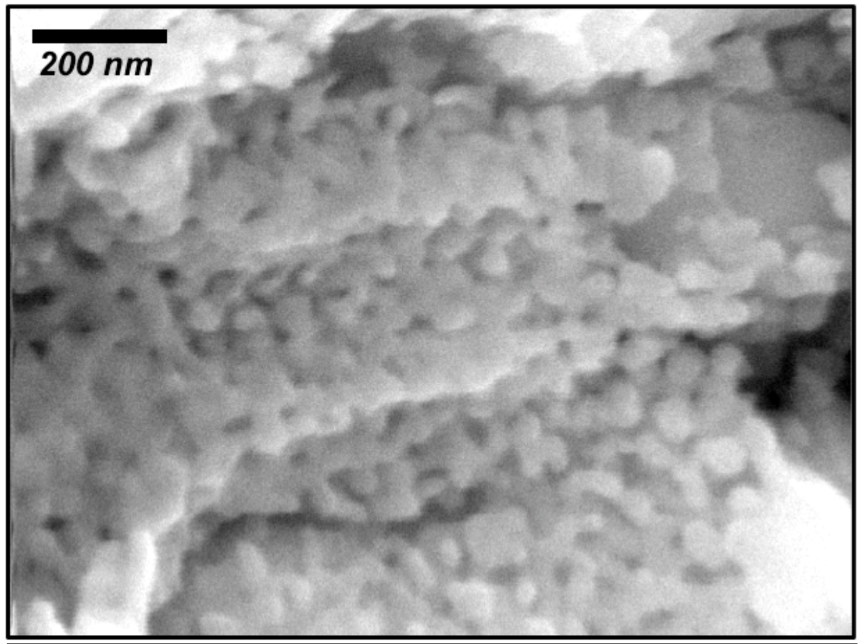
Scholklapper et al. (LBL),
Electrochem. Solid-State Lett., **9**, A376 (2006)

LSCF on YSZ
Penn



W. Wang et al. (Penn)
J. Electrochemical Society, **154**, B439-B445 (2007).

LSM on LSCF
CMU



Chao, Gerdes, Kitchin, Salvador (CMU)
Electrochemical Society Trans, **35,** 2387-2399, (2011).

What are the optimal materials to use for infiltration?

What are the surface properties of cathode materials?

What are the mechanisms of enhanced performance / degradation?

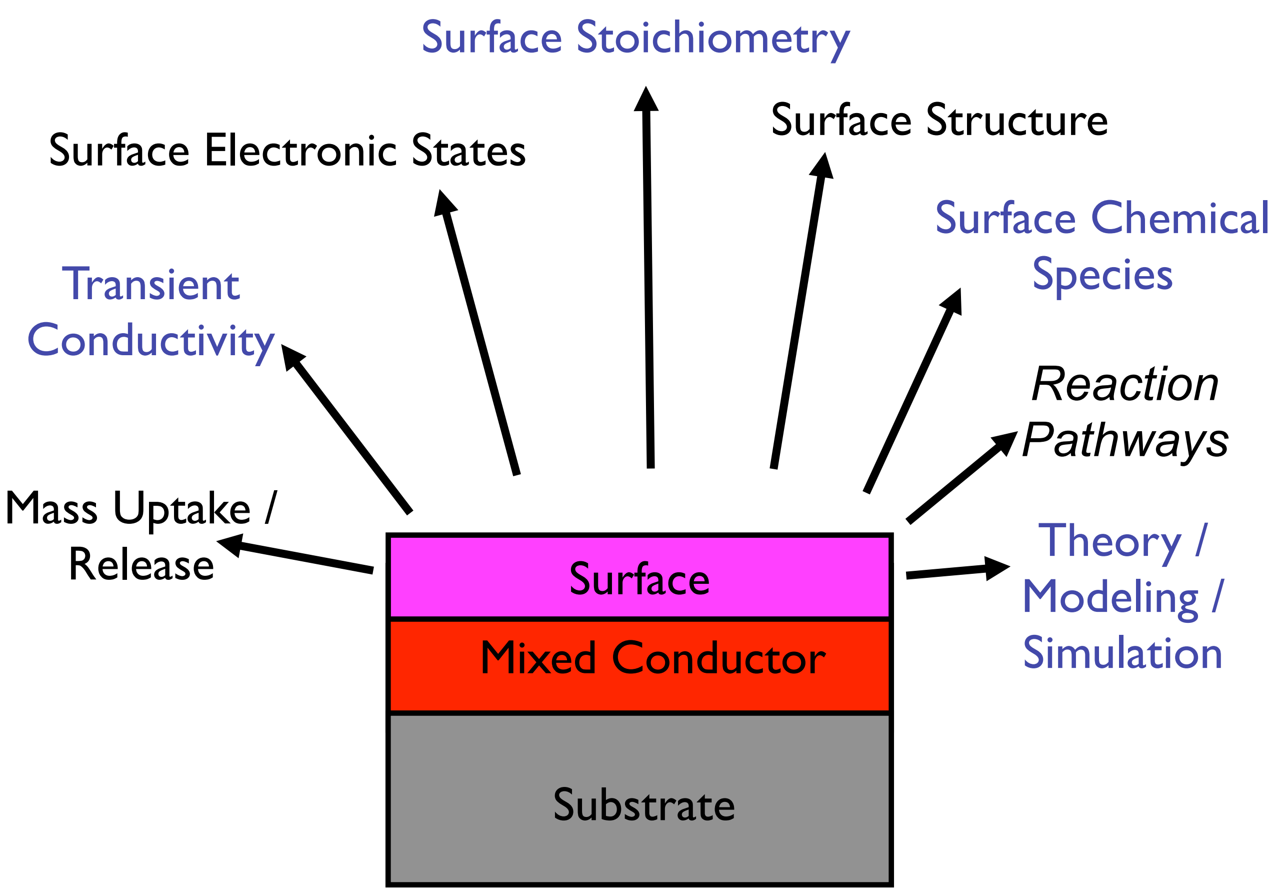
What are the properties of nanosized particles?

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

Conceptual Thin Film Sample: Proxy to Crystals

Probe the nature of atomic scale surface chemistry or interface crystallography rather than the device scale micro-structural perturbations in SOFC conditions:

T = 500 - 900 °C, $PO_2 \approx 10^{-5}$ - 1 atm, Overpotential ≈ 0 - 0.4 V



- thickness < D / k
- surface sensitive : k
- characterization of film quality / microstructural states
- compare properties to bulk / films

FILMS ARE GOOD PROXIES FOR BULK CERAMICS

Need High Quality Samples with Controlled Microstructural Features:

Single Crystals or Thin Films

SOFC Fuel Cell Collaborators

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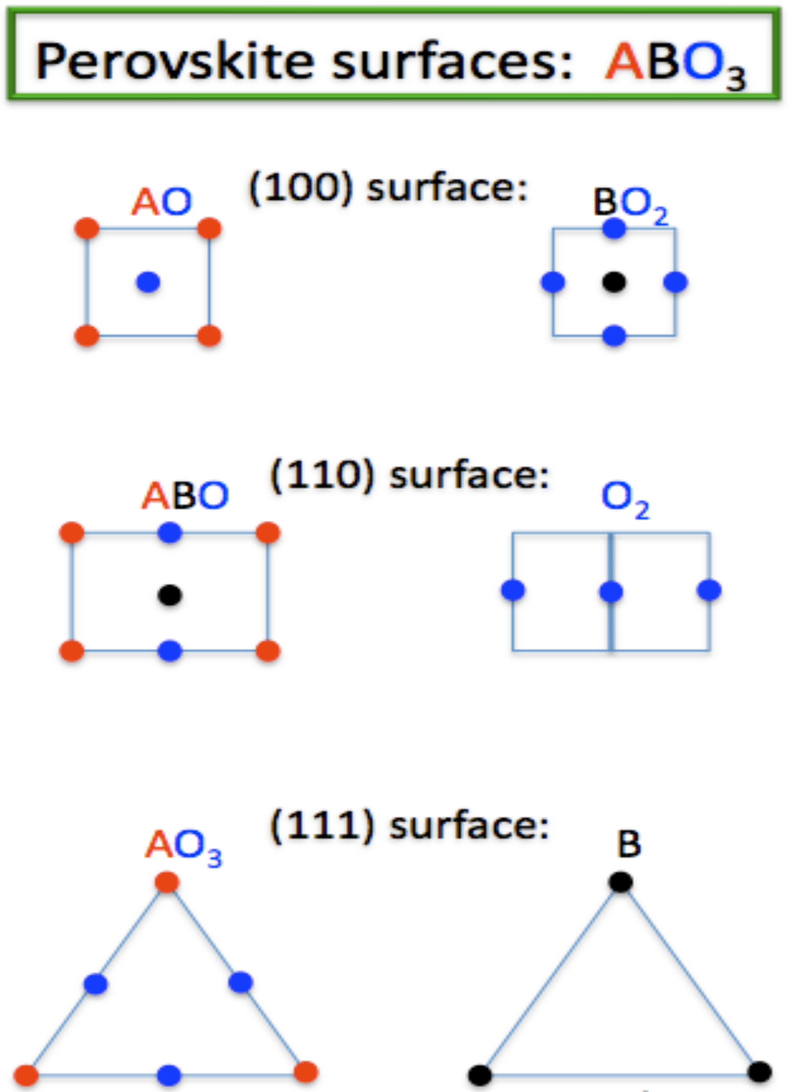
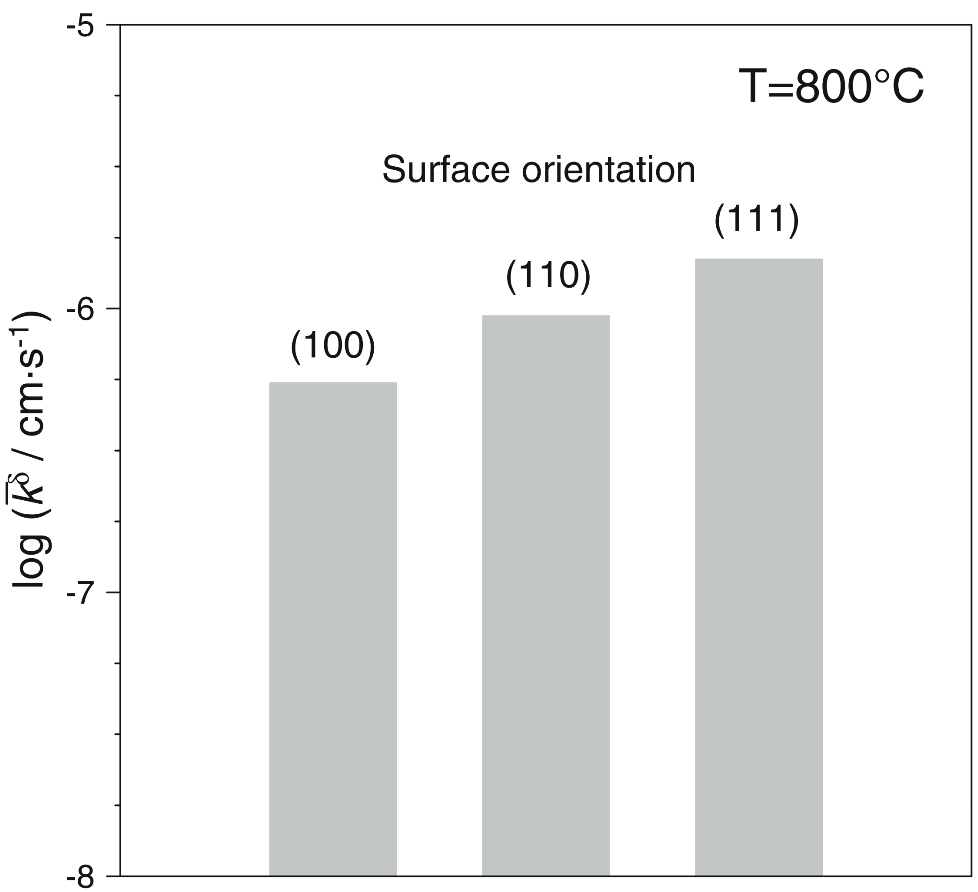
Orientation Dependence

LSM Films



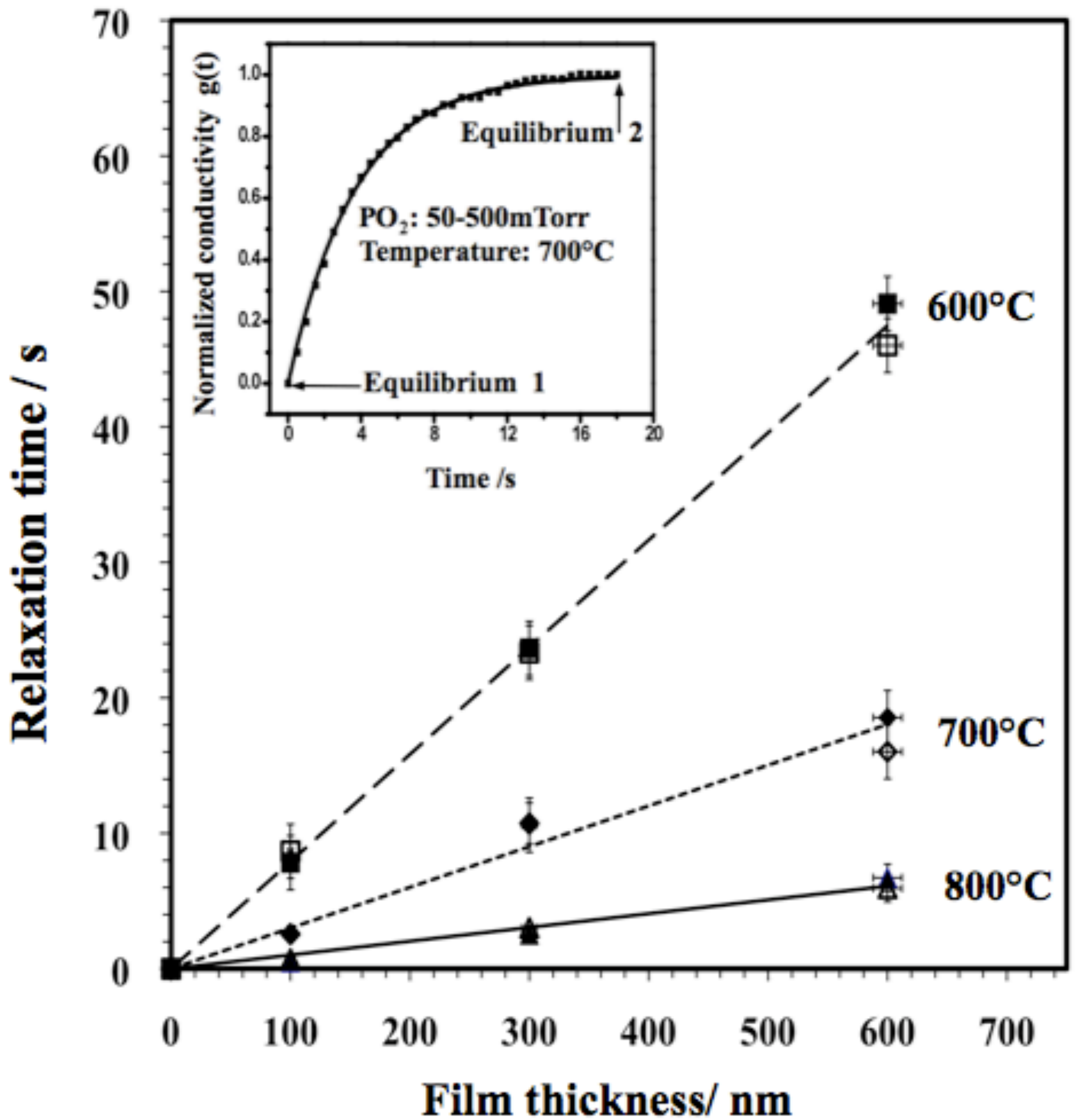
YSZ Single Crystals



K_{chem} (111) > K_{chem} (110) > K_{chem} (100)

Sasaki et al. Solid State Ionics. 161: 145-154 (2003)

Films have surface activated response to ECR



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

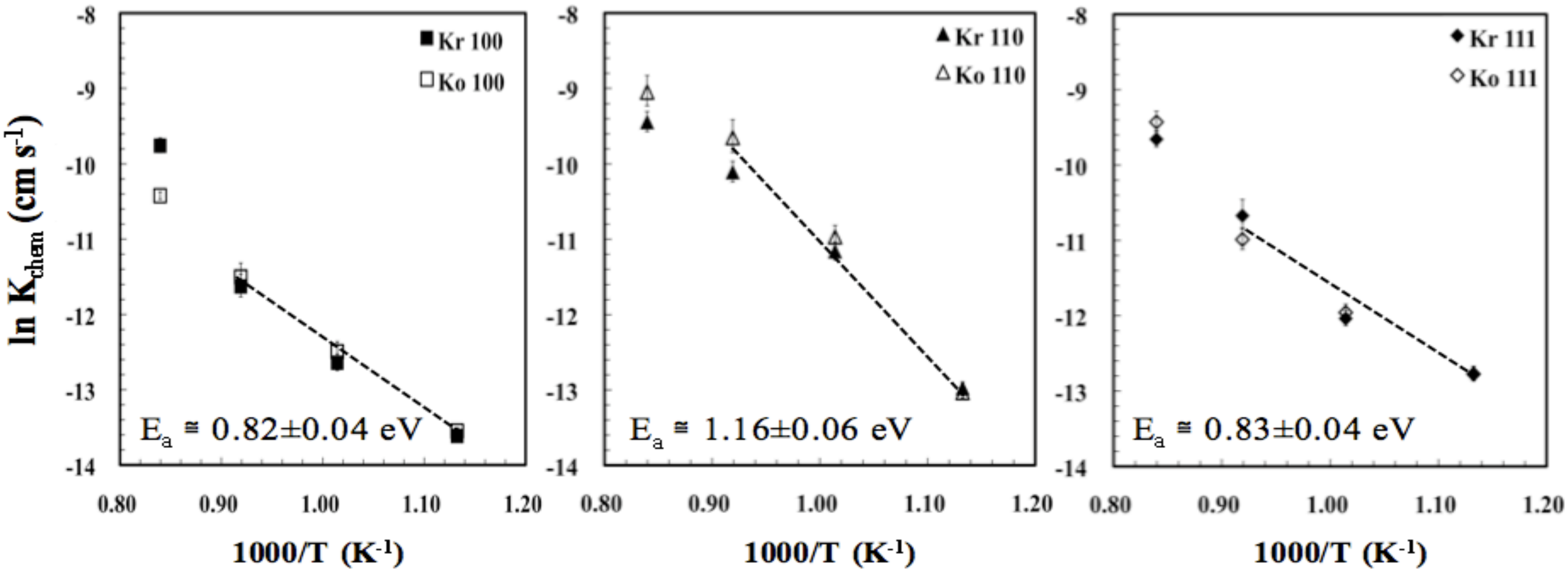
Temperature / K	Ko (100) $\times 10^{-6}$/cm•s^{-1}	Ko (110) $\times 10^{-6}$/cm•s^{-1}	Ko (111) $\times 10^{-6}$/cm•s^{-1}
883	1.30	2.18	2.83
986	3.74	17.2	6.40
1088	10.1	64.3	16.9
1191	*29.8*	*118*	*80.3*

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

Oxidation and Reduction are Similar

Crystallographic Anisotropy Exists by ≈ 75 %

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

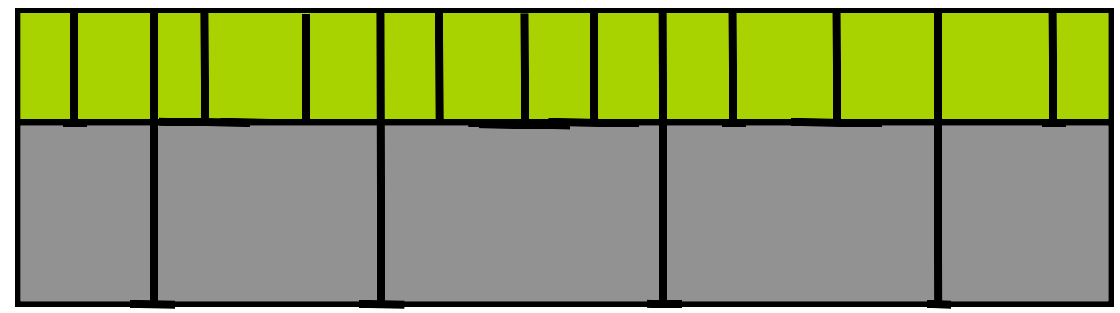
Activation Energies are Orientation Dependant

Controlling Dislocations in Films

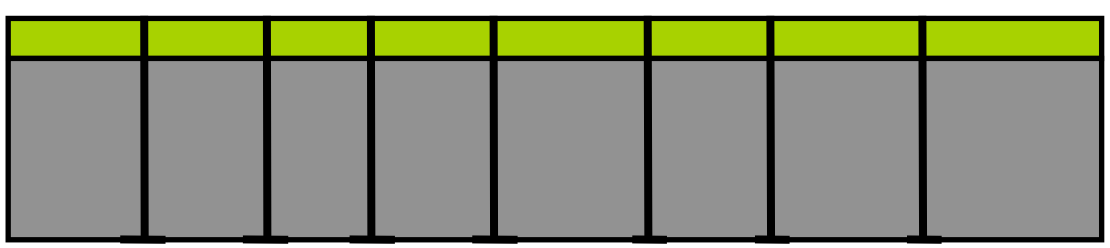
Strained Films:
Inherited Dislocations

Relaxed Films:
Misfit Dislocations from Surface

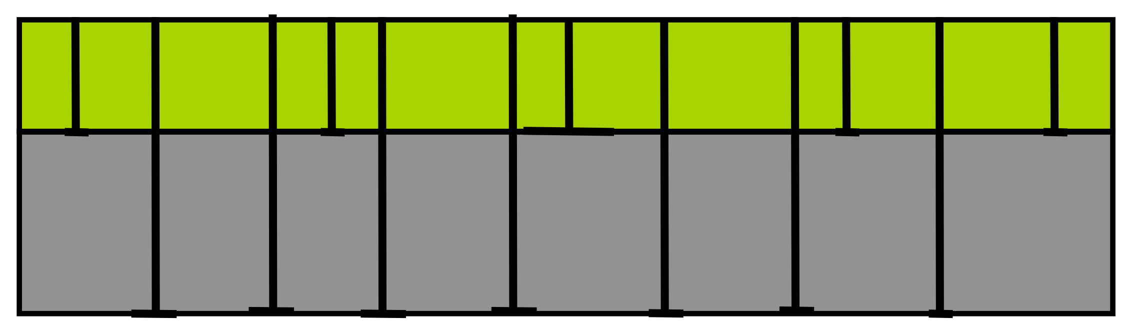
Low Dislocation (LD) Substrate



High Mismatch (HM) Substrate



High Dislocation (HD) Substrate

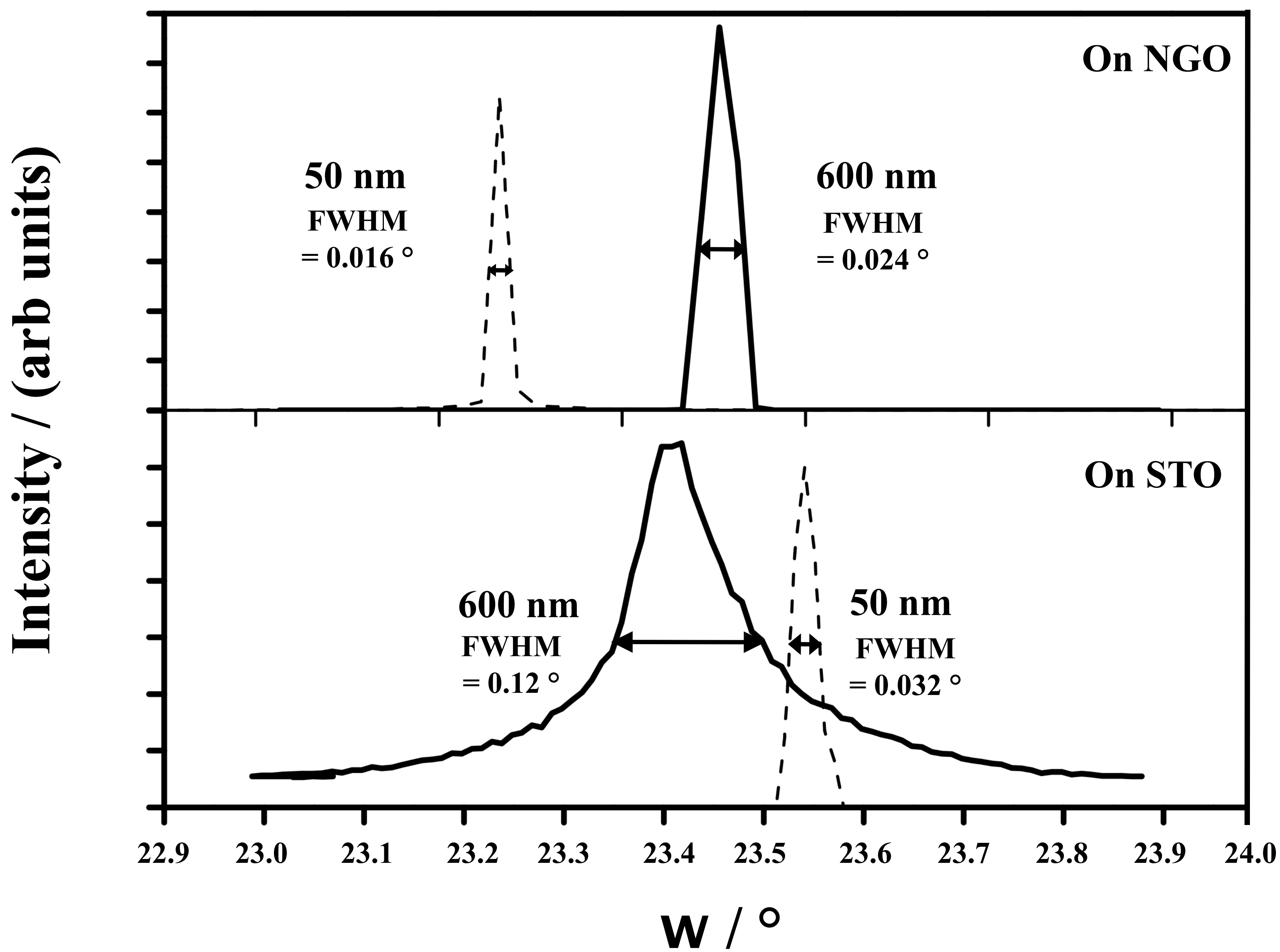


Low Mismatch (LM) Substrate

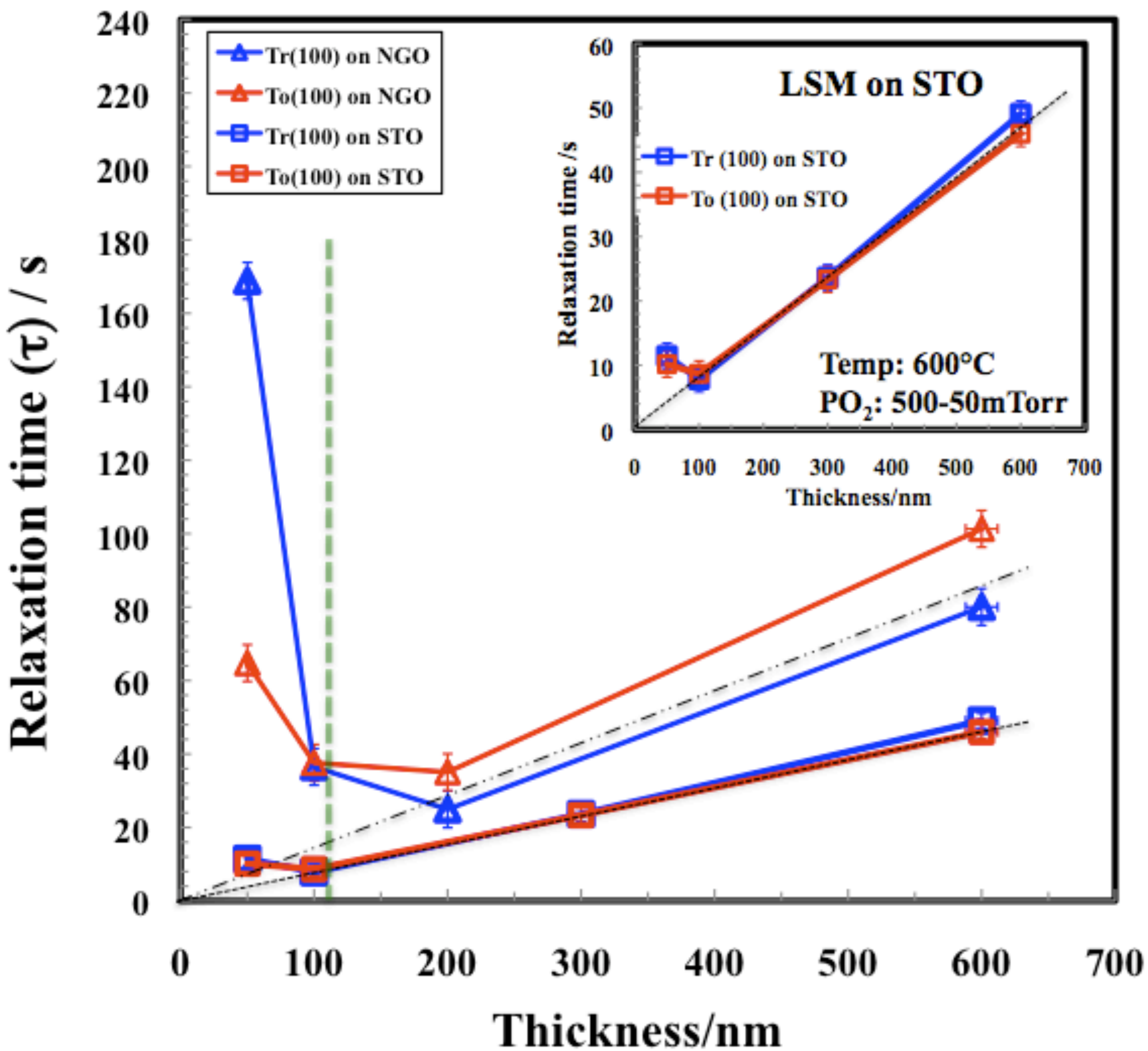
Thickness →

How do Dislocations Impact Surface Properties?

Rocking Curve Widths and Dislocation Content



Anomalous Relaxation Behaviors



$$g(t) = 1 - \exp(-\frac{K_{chem}t}{L})$$

$$K_{chem} = \frac{L_{thickness}}{\tau_{relaxation\ time}}$$

significant substrate effect:

STRAIN (<100 nm).

significant substrate effect:

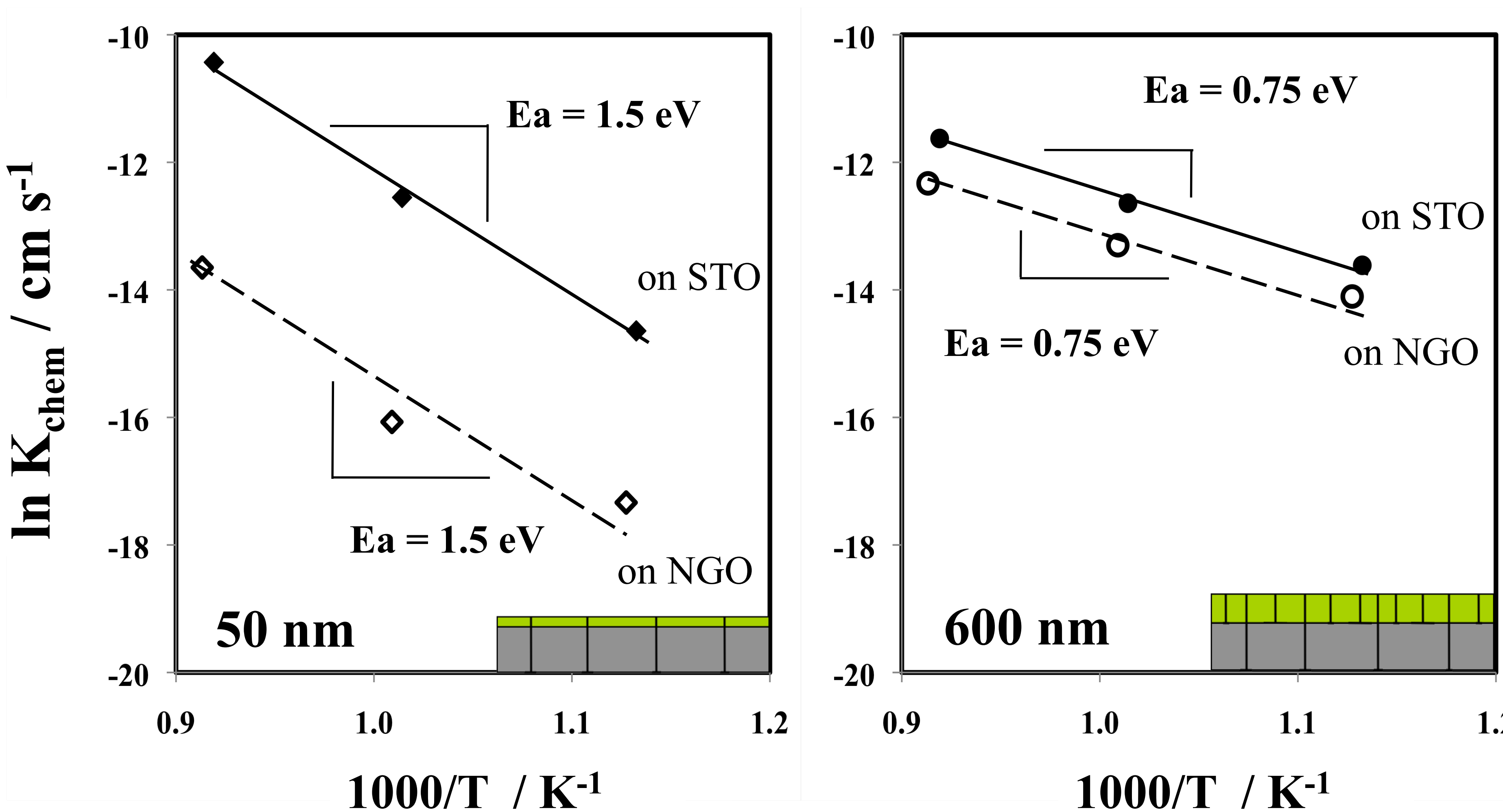
DISLOCATION (>100 nm).

- **surface exchange :**

on STO > on NGO

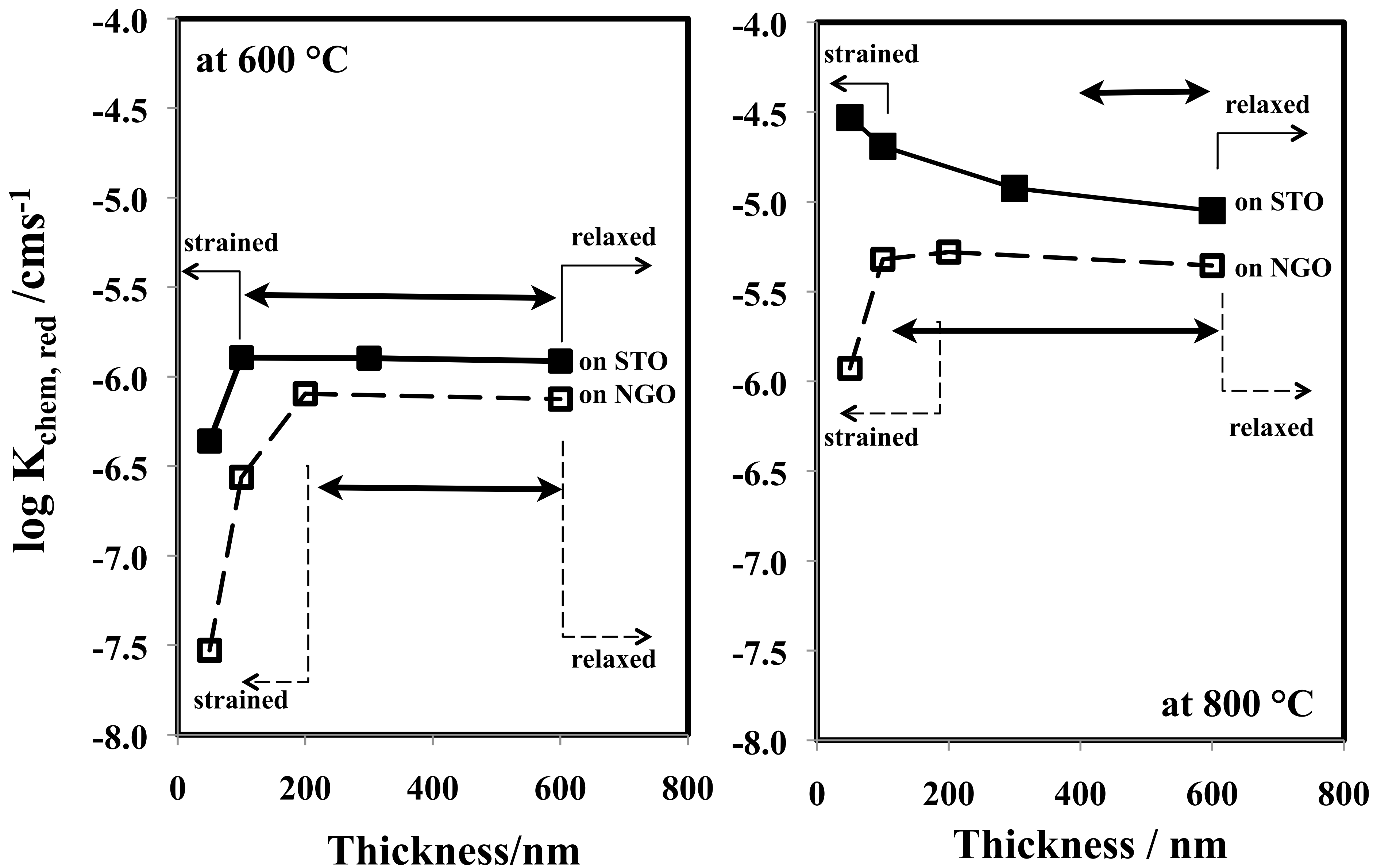
Activation energy vs thickness and substrate

Thin Films on Different Substrates | **Thick Films on Different Substrates**



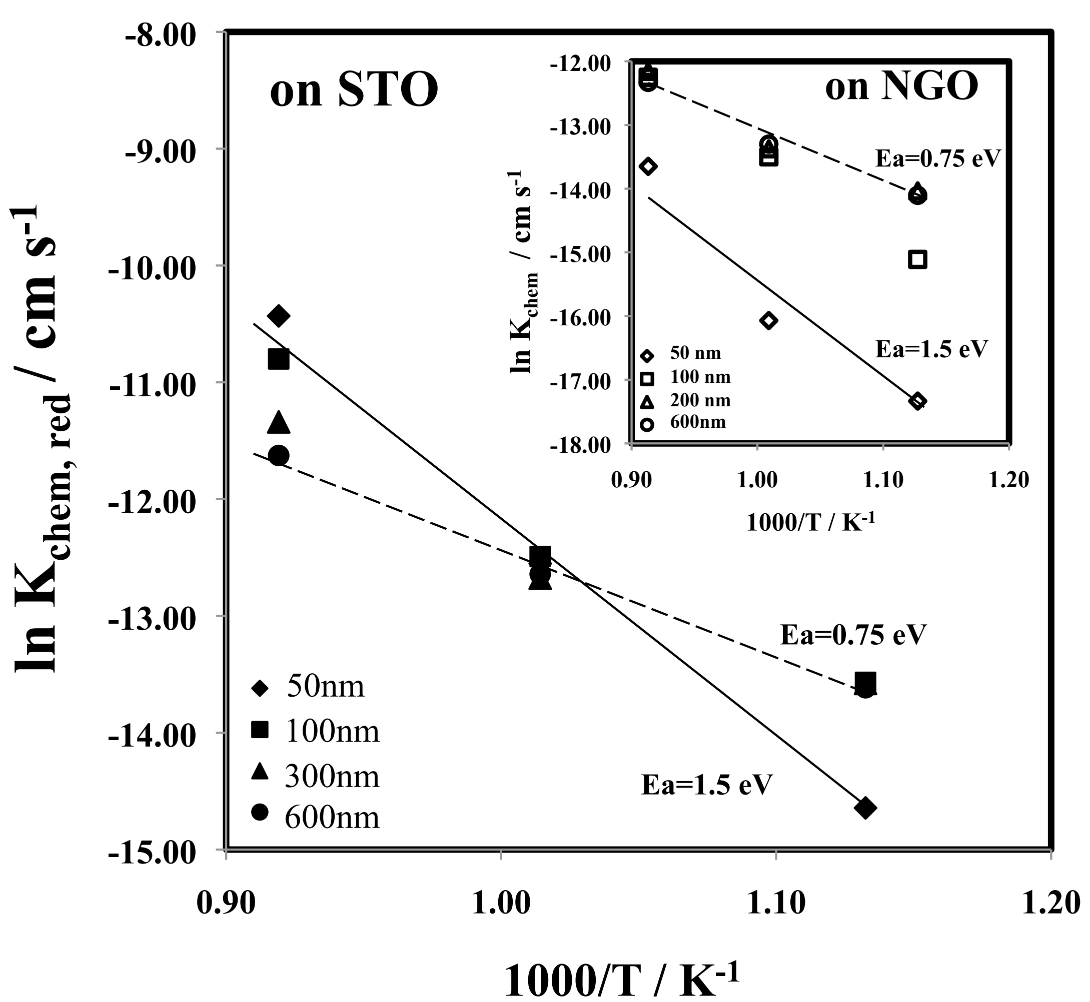
- *Two different activation Energies: two different processes*
- *Thick Films are more similar to one another and are generally more active*
- *at higher temperature, thinnest film on STO is most active*
- *for thin films, values are almost and order of magnitude different*

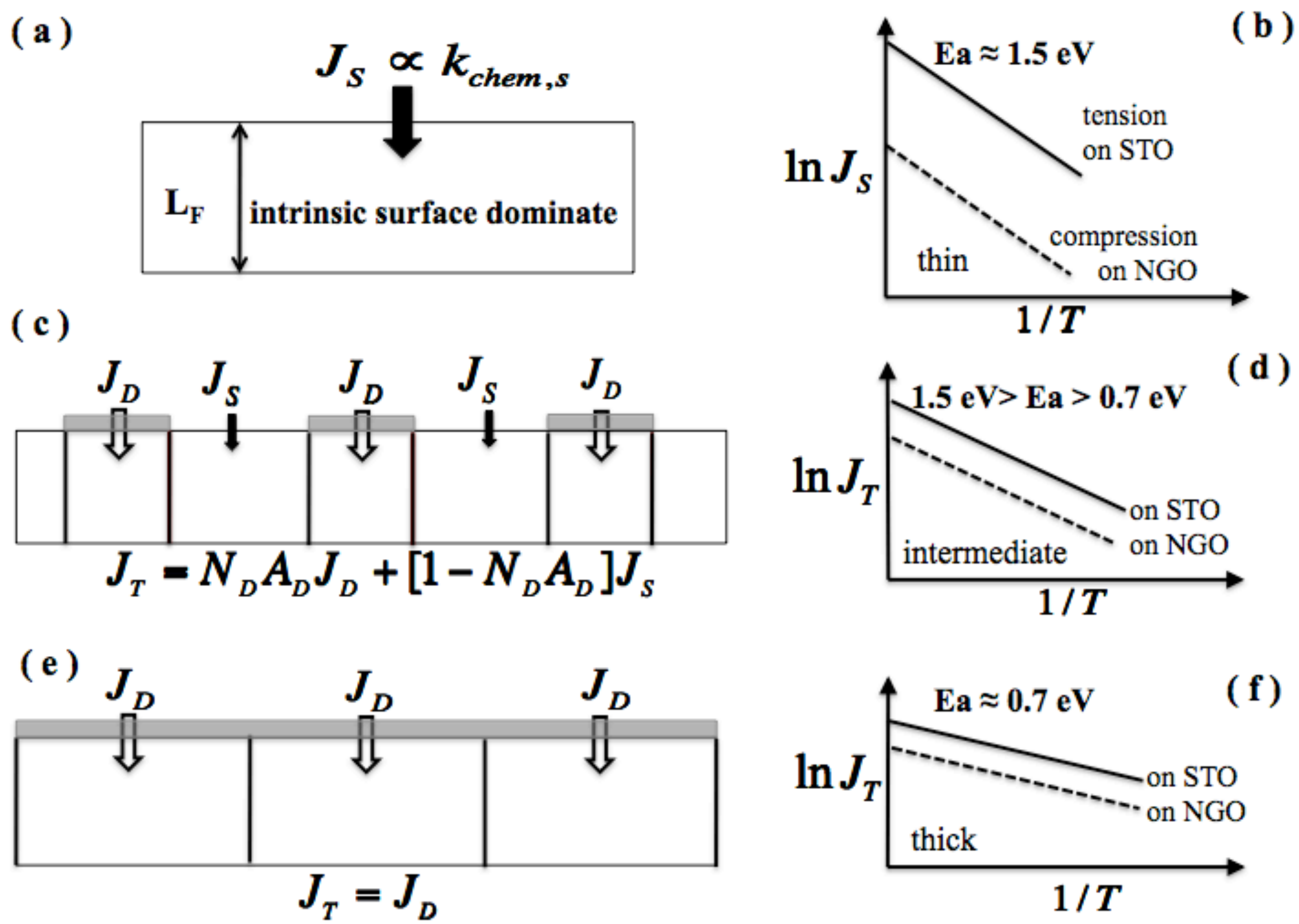
Dependence on thickness and temperature



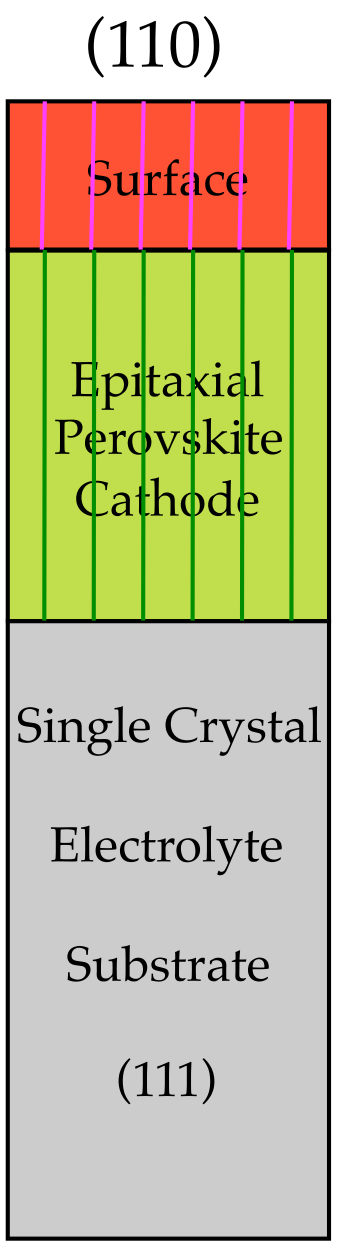
- *Solid horizontal arrows represent thickness independent regimes*
- *Locations of coherent strain a full relaxation are marked*
- *Behaviors are somewhat complex...*

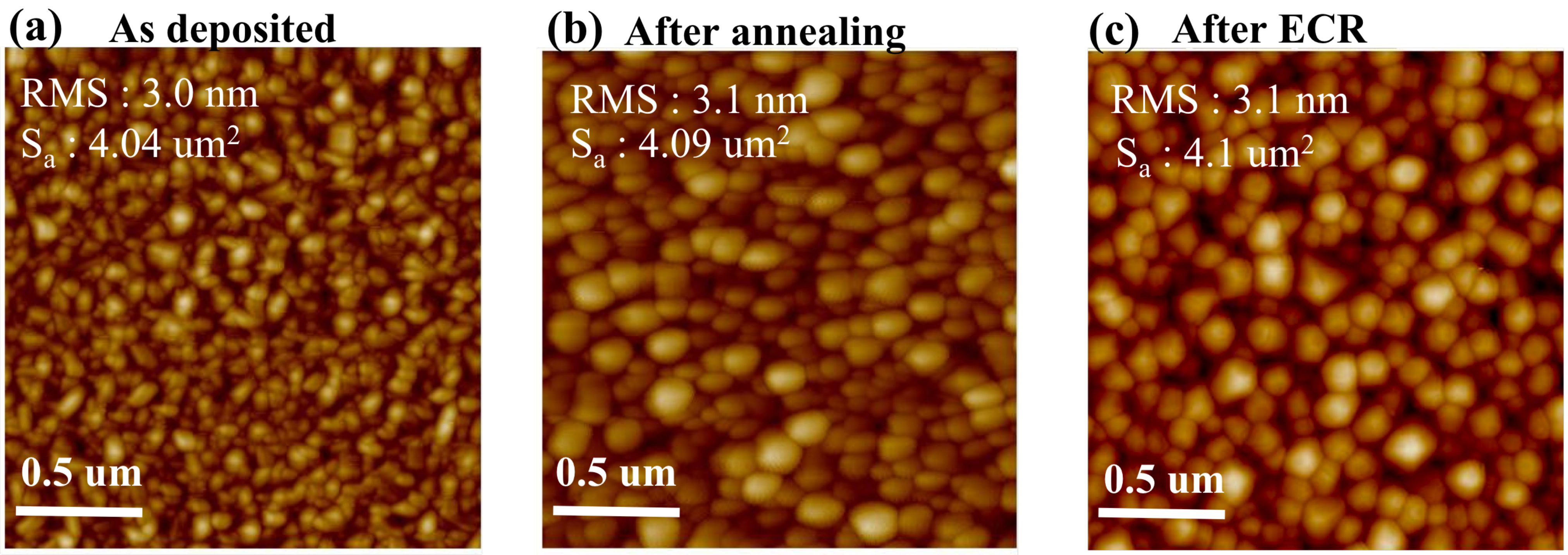
Explanation of Epitaxial Film Observations

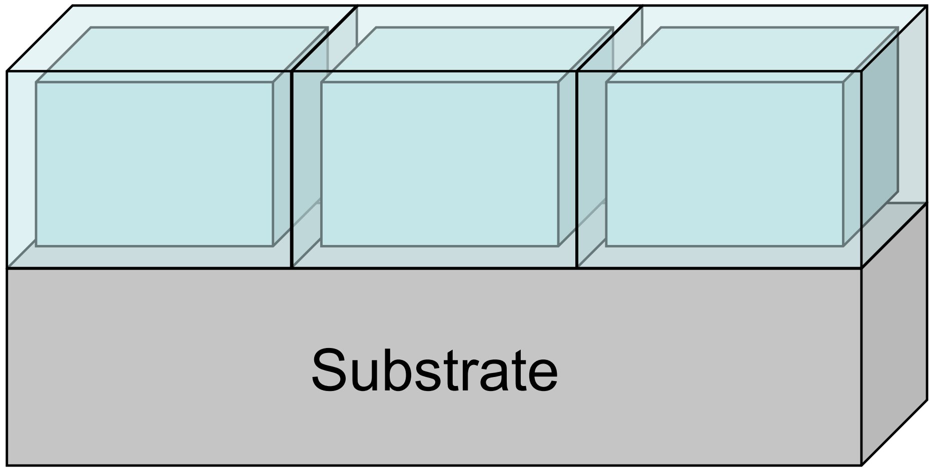




Textured Film Surfaces

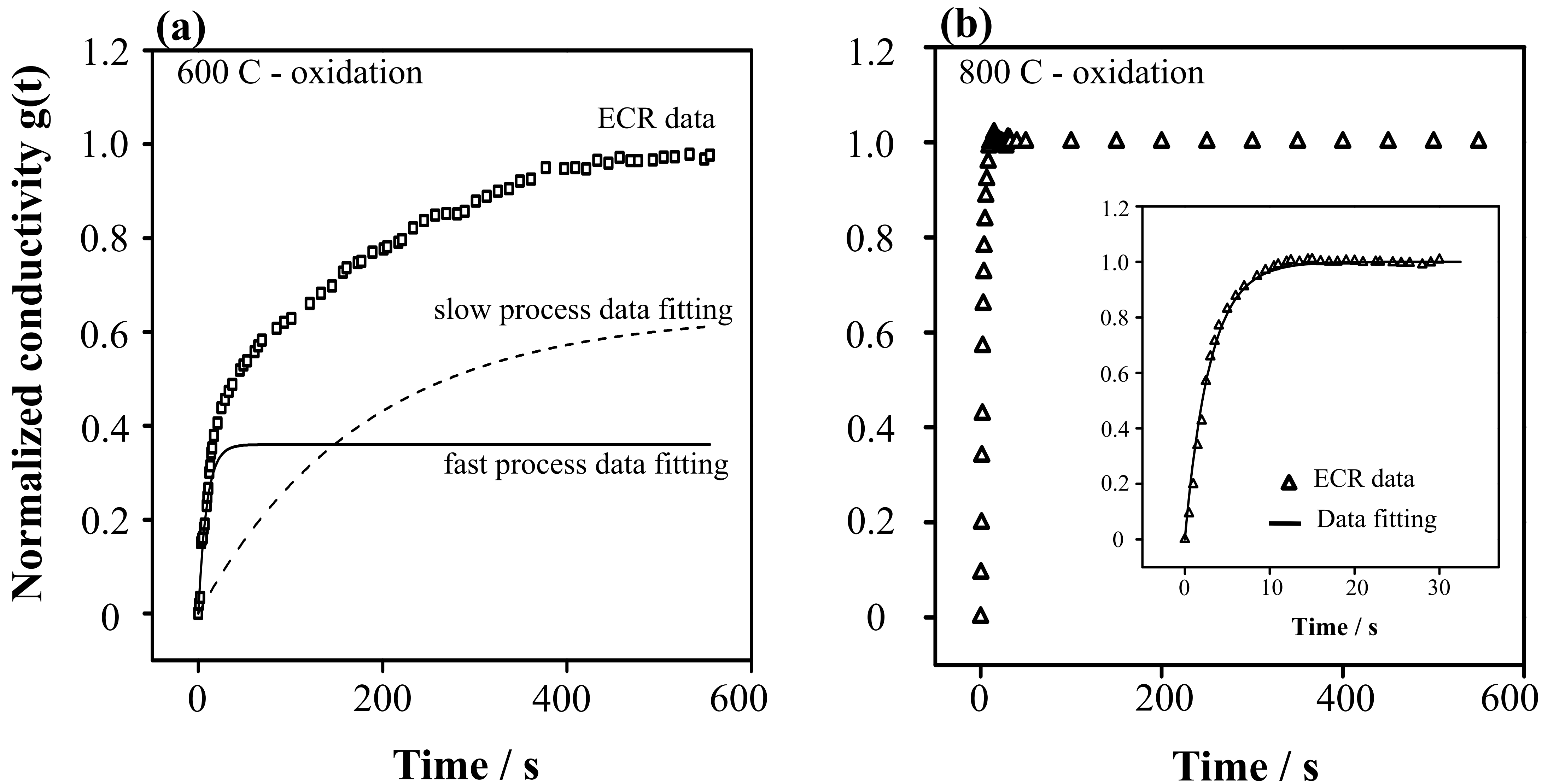






Can the Strain Free Surface and Grain Boundaries be Separated?

ECR Properties fit to 2 Separate Processes

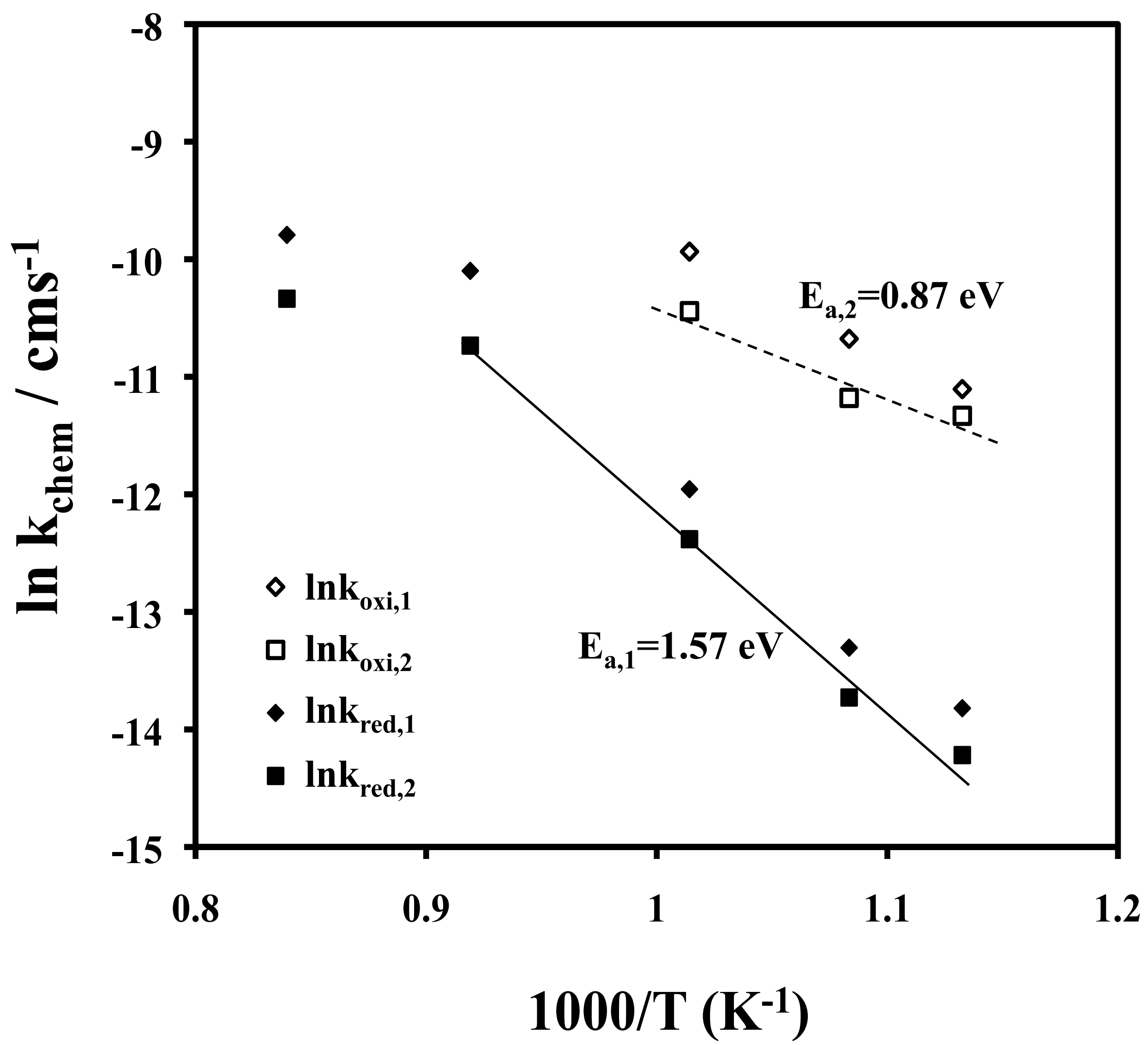


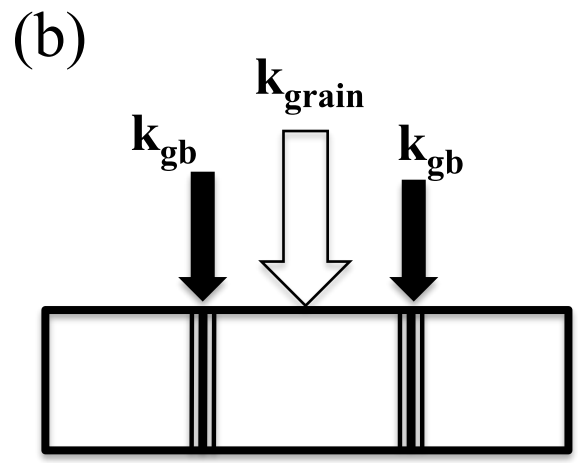
$$g(t) = \frac{\sigma_t - \sigma_{final}}{\sigma_{final} - \sigma_{initial}} = 1 - A\exp(-\frac{K_{1,chem}t}{L}) - (1-A)\exp(-\frac{K_{2,chem}t}{L})$$

< 800 °C, A≠1, two K_{chem} : a fast and a slow processes.

≥ 800 °C, A=1, one K_{chem} : faster response at 600 °C diminishes with ↑ temperature.

Temperature dependence of two mechanisms



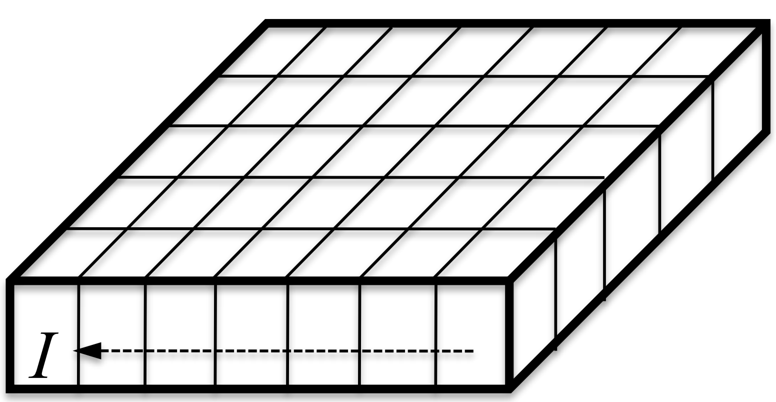


Our data agree with literature:

K_{chem} is on the order of 10^{-5}cm/s.[1-5]

Ea1: 1.48 eV for microelectrode[1],
1.32 eV dense pellet[2],

Ea2: 0.8 eV (100) and (111) on STO[3],
0.07-0.8 eV powder[4].

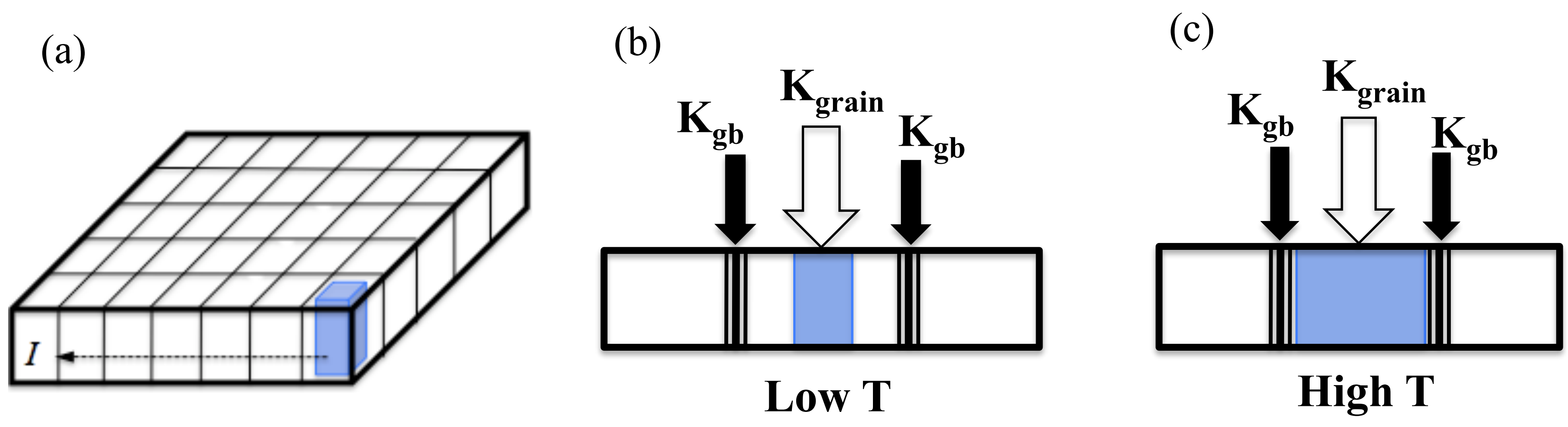


1. la O' et al, J. Electrochem sec. (2009).
2. De Souza et al, Mater. lett. (2000).
3. Yan et al, Solid state ionics. (2011).
4. Kan et al, Solid state ionics. (2010).
5. Yasuda et al, J Solid State Chem. (1996).

Relative Contribution to Responses

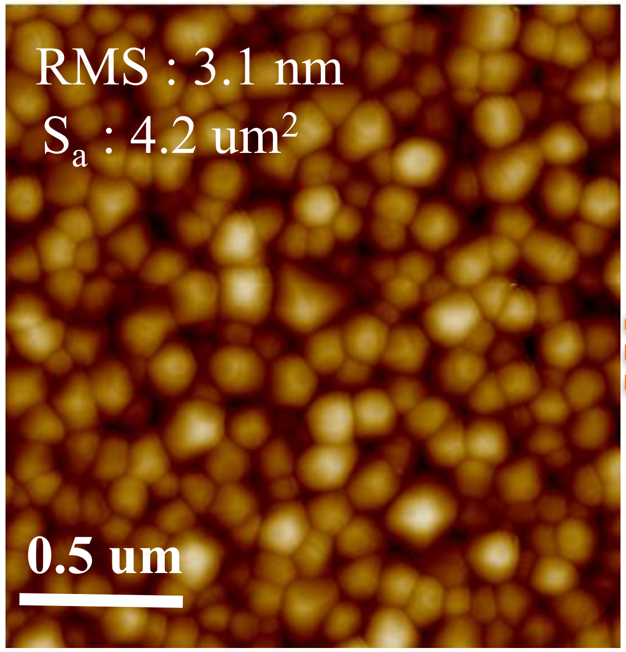
$$g(t) = \frac{\sigma_t - \sigma_{final}}{\sigma_{final} - \sigma_{initial}} = 1 - A\exp(-\frac{k_{1,chem}t}{L}) - (1-A)\exp(-\frac{k_{2,chem}t}{L})$$

Temp / K	883	923	986	1088	1191
A	0.6	0.7	0.8	1	1
$k_{oxi,1}$ $\times 10^{-6}$ / cms^{-1}	0.668	1.09	4.20	21.8	32.4
$k_{oxi,2}$ $\times 10^{-6}$ / cms^{-1}	12.0	14.0	29.2	N/A	N/A
$k_{red,1}$ $\times 10^{-6}$ / cms^{-1}	0.996	1.67	6.42	41.1	55.8
$k_{red,2}$ $\times 10^{-6}$ / cms^{-1}	15.0	23.1	48.4	N/A	N/A



600 nm LSM on YSZ (111) with different grain size

850°C annealed 24 hr

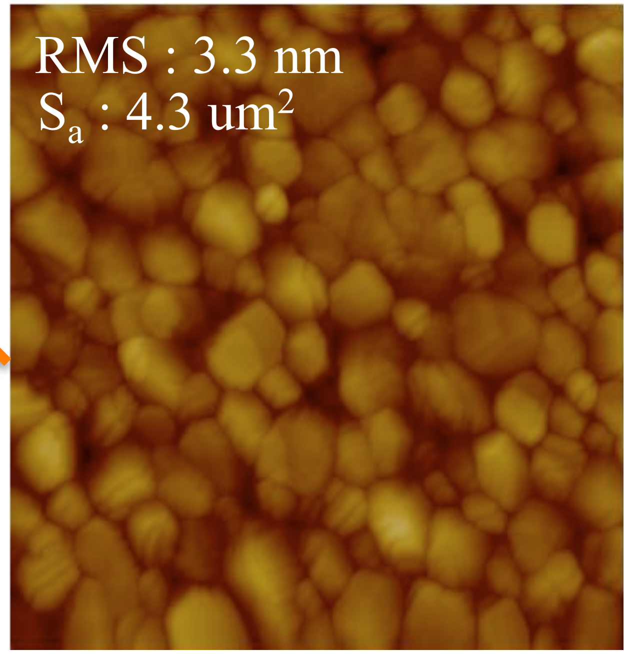


Grain size: ≈ 100 nm

Post-annealing after 750°C deposition

Grain size increases

900°C annealed 24 hr

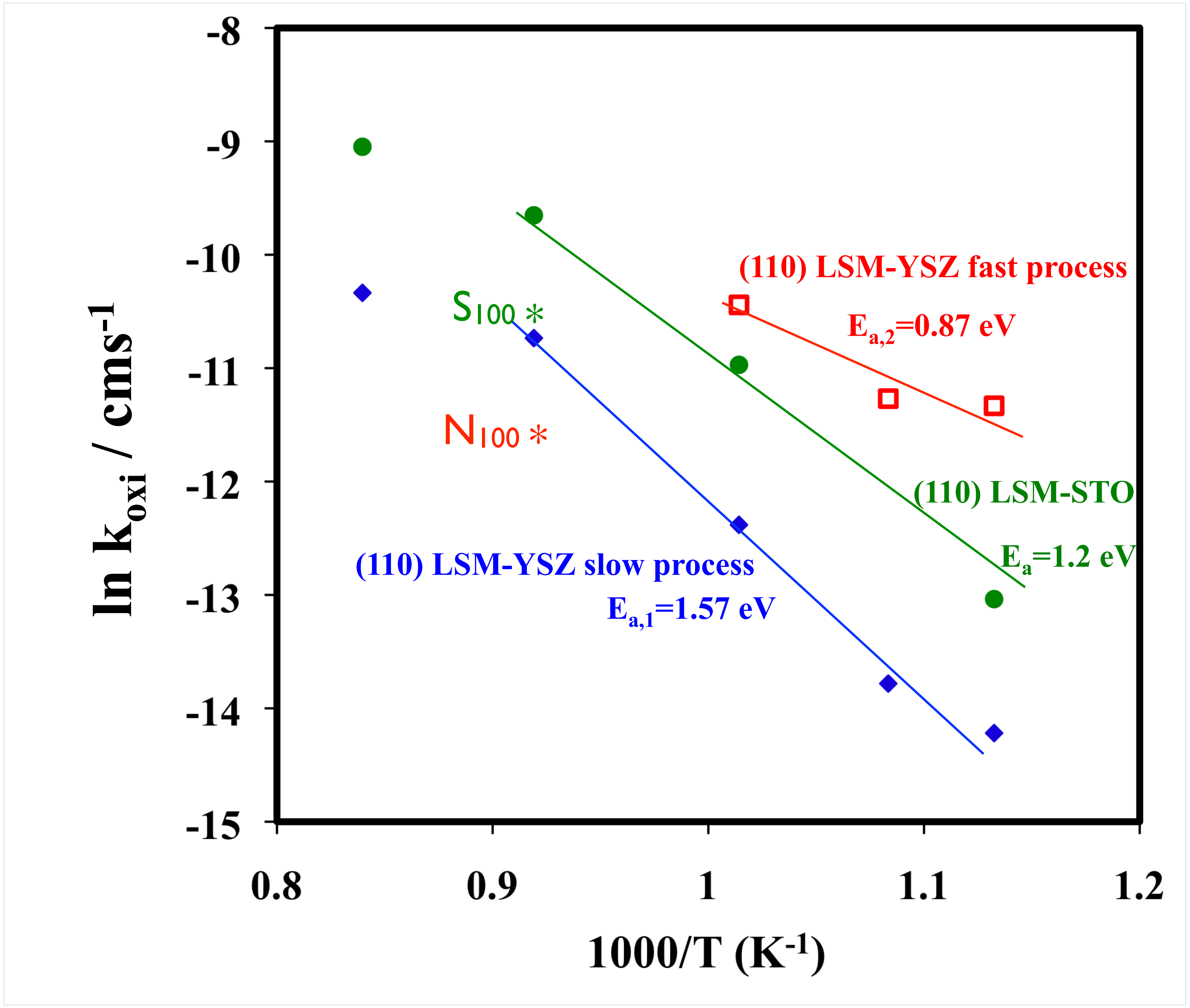


Grain size: ≈ 150 nm

Temp / K	883	923	986	1088	1191
$A_{small\ grain}$	0.6	0.7	0.8	1	1
$A_{big\ grain}$	0.7	0.75	0.84	1	1

K_{chem} values for the fast process and the slow process are the same for both grain sizes.

Comparison of Textured and Epitaxial (110)



Summary

Two apparent processes occuring on the surface (E_a) for K_{chem} .

These were interpreted as belonging to:
(1) the native surface response of individual grains/variants and
(2) the variants boundaries / grain boundaries of the textured films.

The first (native surface) process : $E_{A,1} \approx 1.5$ eV,
the second (extended defect) process $E_{A,2} \approx 0.75$ eV.

The $K_{chem,2}$ values are almost 3 orders of magnitude higher than the $K_{chem,1}$ values at low temperatures (< 700°C)
Depends on the density of the defects.

At higher temperatures, the data can be fit with one K_{chem}
Intermediate value of E_A indicate that both processes contribute to overall exchange
The native surface, higher activation energy process is competitive with

The native surface processes are
Strain dependent
Orientation Dependent
Substrate dependent