Oxygen incorporation and diffusion in SOFC electrode materials:

FOXSI Functional Oxide Surfaces and Interfaces

TU WIEN

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✓the role of defects

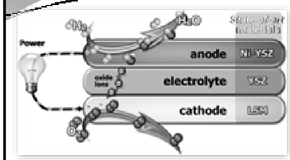
✓strain

✓bias and

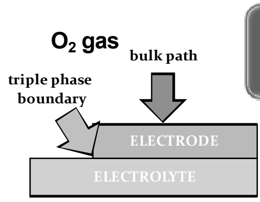
✓ambient humidity

5th Annual SFB FOXSI PhD Workshop 2016

Motivation



- •Strain
- •Defects like dislocations, twin boundaries, grain boundaries
- •Space charge layer
- •Ambient humidity



Electrical measurements
or
Isotope exchange depth profiling

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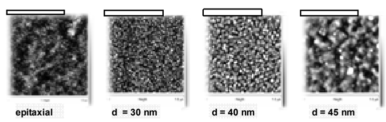
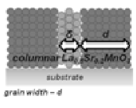
Oxygen incorporation in columnar LSM thin films

LSM layers with varied microstructure





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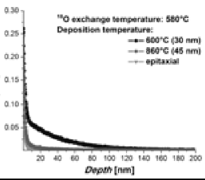
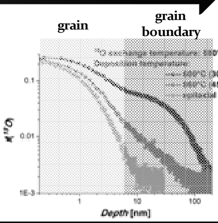
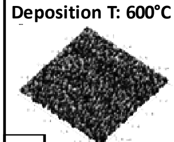


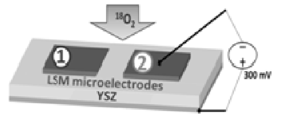


✓Bias effect

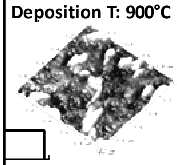
oxygen isotope exchange

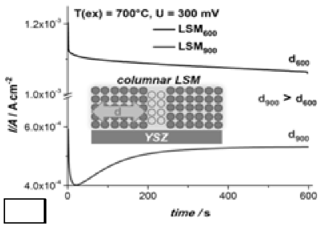
Deposition T: 600°C





Deposition T: 900°C





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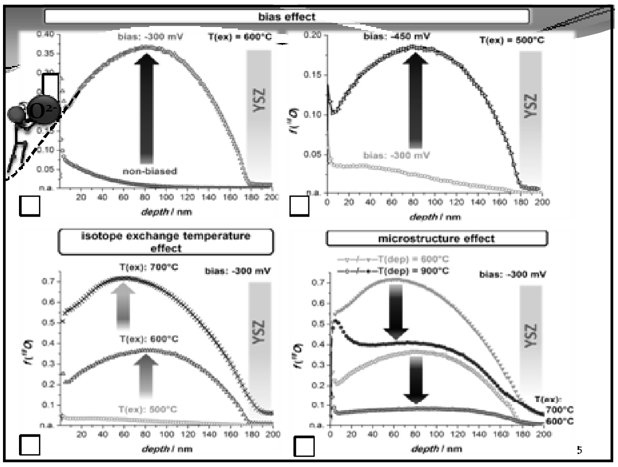

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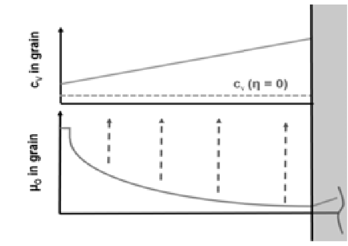

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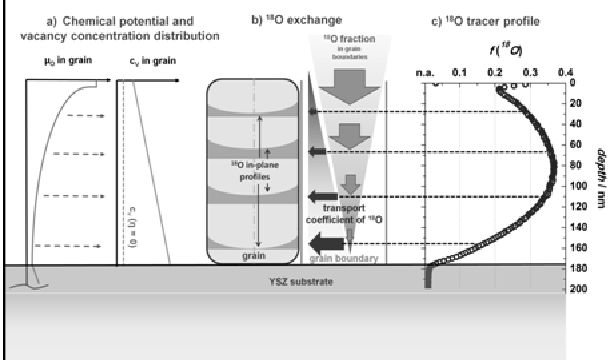
Diffusion model



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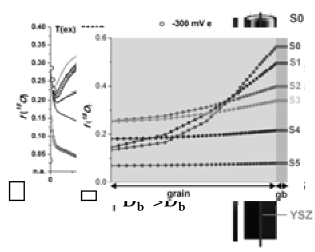

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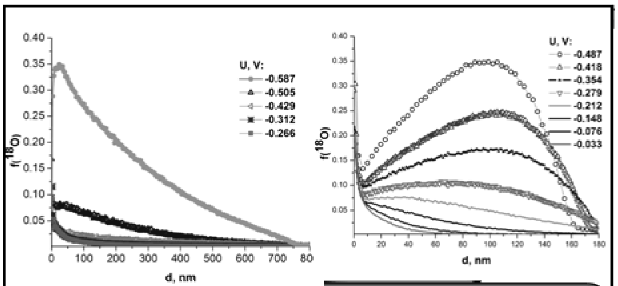
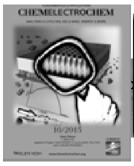
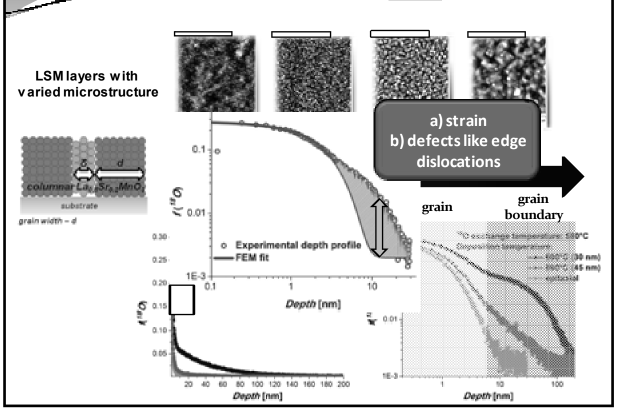


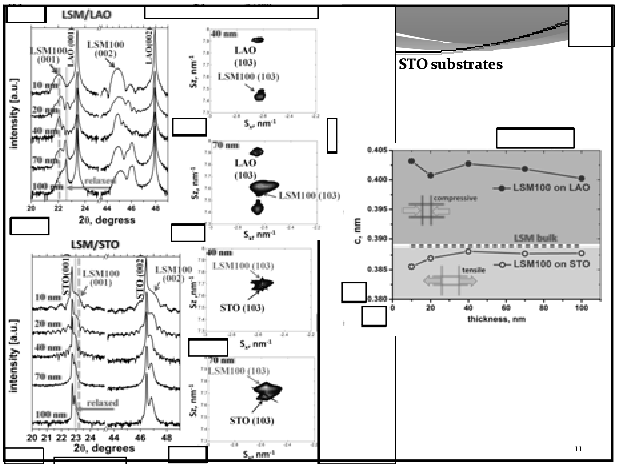


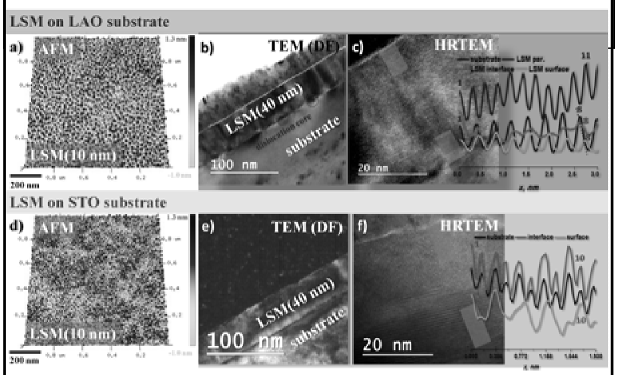
Conclusions

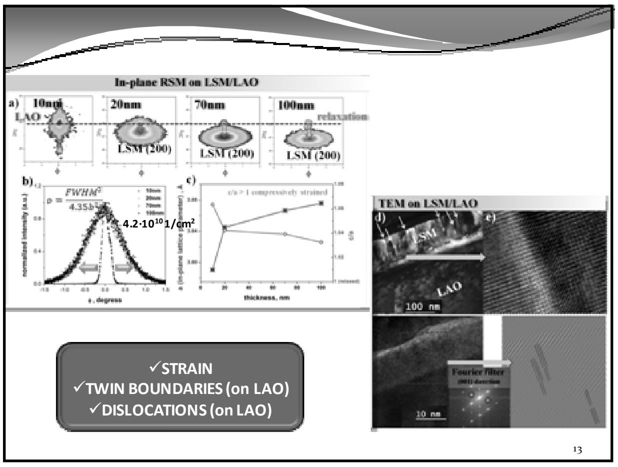
The uncommon uphill-like diffusion with an oxygen tracer maximaximum in the center of the LSM film is caused by the interplay of fast oxide ion diffusion along grain boundaries and stoichiometry polarization of LSM upon application of a voltage, which led to a vacancy concentration gradient in the LSM grains.

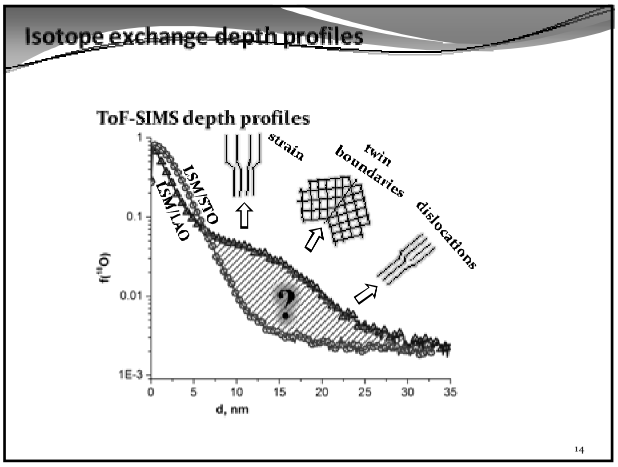
Oxygen incorporation in columnar LSM thin films

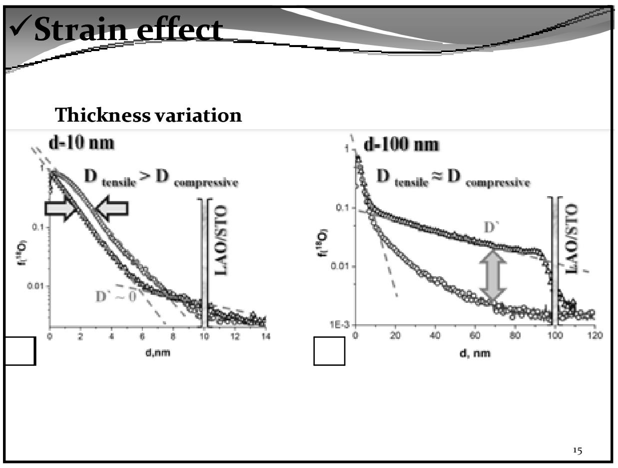


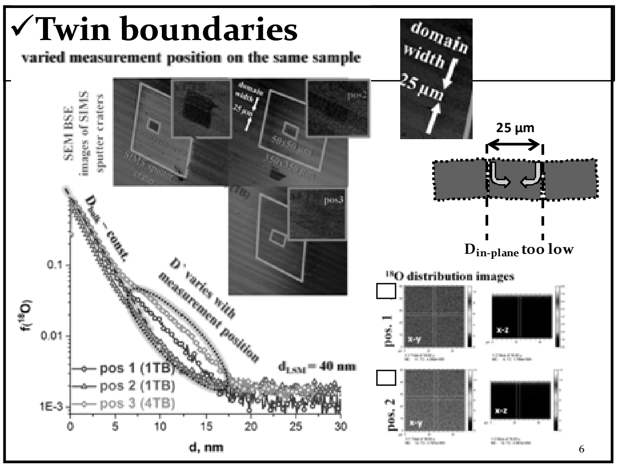




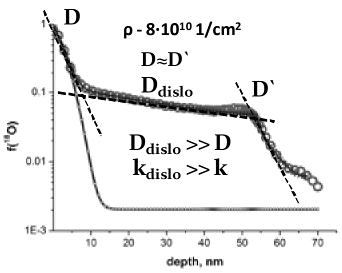

In-plane RSM on LSM/LAO
a) 10nm
LAO
20nm
70nm
100nm
relaxation
LSM (200)
LSM (200)
LSM (200)
b)
c)
4.2·10^10 1/cm^2
TEM on LSM/LAO
LSM
LAO
100 nm
10 nm
Fourier filter
✓STRAIN
✓TWIN BOUNDARIES (on LAO)
✓DISLOCATIONS (on LAO)
13


Isotope exchange depth profiles
ToF-SIMS depth profiles
strain
twin boundaries
dislocations
LSM/STO
LSM/LAO
?
f(18O)
d, nm
14


✓Strain effect
Thickness variation
d-10 nm
D tensile > D compressive
D` ~ 0
LAO/STO
f(18O)
d,nm
d-100 nm
D tensile ≈ D compressive
D`
LAO/STO
f(18O)
d, nm
15


✓Twin boundaries
varied measurement position on the same sample
domain width 25 µm
SEM BSE images of SIMS sputter craters
pos3
25 µm
D in-plane too low
18O distribution images
pos. 1
pos. 2
D bulk - const
D` varies with measurement position
d LSM = 40 nm
pos 1 (1TB)
pos 2 (1TB)
pos 3 (4TB)
f(18O)
d, nm
6

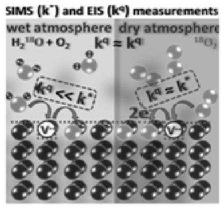
Model



✓Ambient humidity

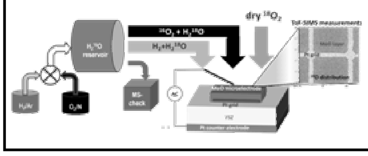
Motivation $k^* = k^q$ in dry atmosphere

Oxygen exchange via water dissociation requires no electron transfer, therefore in humid atmosphere $k^* >> k^q$



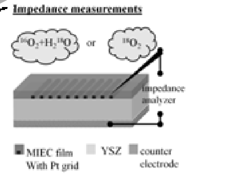
There is no direct proof of water dissociation mechanism

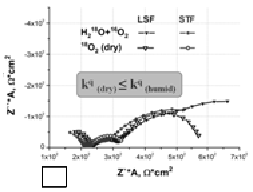
Experimental



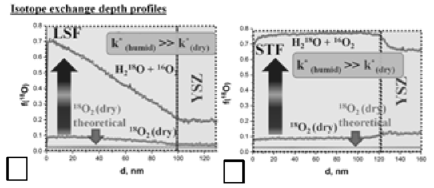
- humid-oxidizing: 200 mbar $^{16}O_2$ + 15-25 mbar $H_2{}^{18}O$ in Ar
- dry-oxidizing: 200 mbar of dry $^{18}O_2$, dried with a zeolite filter
- usual: 200 mbar of $^{18}O_2$ without zeolite filter.

Impedance measurements

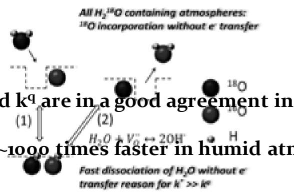




Isotope exchange depth profiles

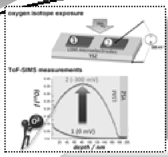


Material	$^{18}O_2$ + zeolite 418°C	$^{18}O_2$ no zeolite 420°C	$^{16}O_2 + H_2{}^{18}O$ 418°C
STF	$k^* = 3.0\cdot10^{-8}$ cms^{-1} $k^q = 9\cdot10^{-9}$ cms^{-1} $k^*/k^q = 3.3$	$k^* = 3.5\cdot10^{-8}$ cms^{-1} $k^q = 5.9\cdot10^{-9}$ cms^{-1} $k^*/k^q = 5.9$	$k^* = 5\cdot10^{-6}$ cms^{-1} $k^q = 5\cdot10^{-9}$ cms^{-1} $k^*/k^q = 1000$
LSF	$k^* = 1.4\cdot10^{-8}$ cms^{-1} $k^q = 7.5\cdot10^{-9}$ cms^{-1} $k^*/k^q = 1.9$	$k^* = 1.5\cdot10^{-8}$ cms^{-1} $k^q = 3.1\cdot10^{-9}$ cms^{-1} $k^*/k^q = 4.8$	$k^* = 1.5\cdot10^{-6}$ cms^{-1} $k^q = 9\cdot10^{-9}$ cms^{-1} $k^*/k^q = 167$

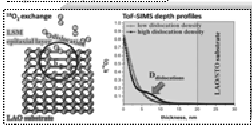


- k^* and k^q are in a good agreement in dry $^{18}O_2$
- k^* is ~1000 times faster in humid atmosphere

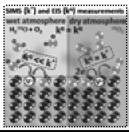
Conclusions



The uncommon uphill-like diffusion with a oxygen tracer maximaximum in the center of the LSM film is caused by the interplay of fast oxide ion diffusion along grain boundaries and stoichiometry polarization of LSM



- Thin films on LAO show a highly pronounced second diffusion process. Variation of the measurement location highly influences second diffusion part which suggests variation of the defect density.
- Variation of twin boundary density



- k^* and k^q are in a good agreement in dry $^{18}O_2$
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Acknowledgements

Thank you for your attention!

Prof. B. Yildiz group @ MIT

USTEM

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FWF Der Wissenschaftsfonds.