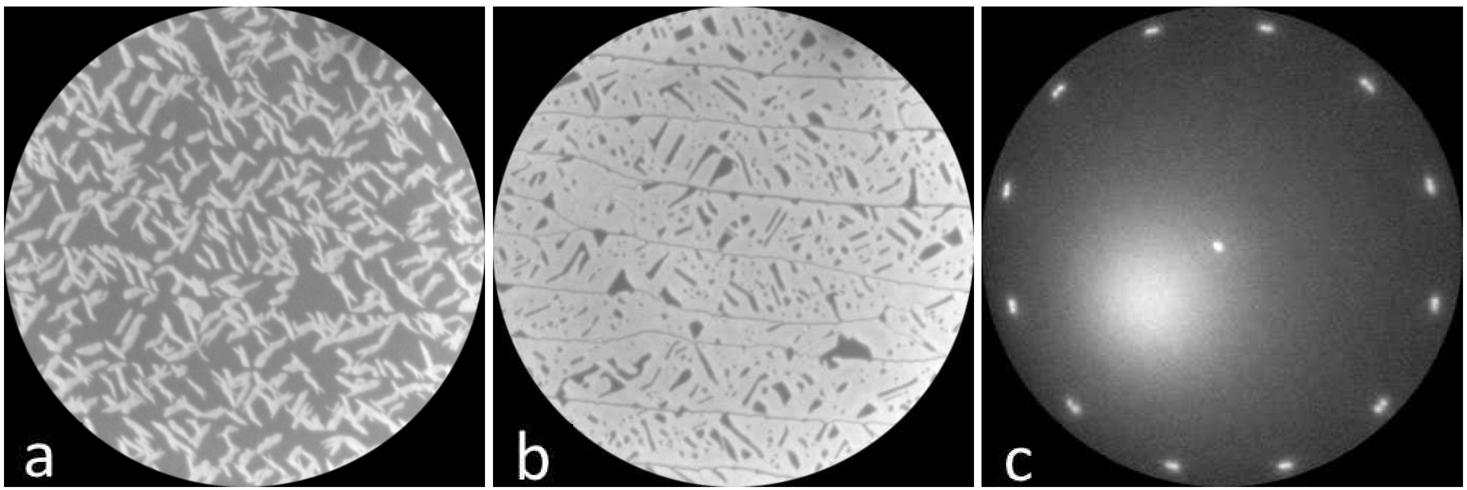
SAND2011-1871C

Ultrathin film growth of iron oxides on YSZ(001)

Ivan Ermanoski and G. L. Kellogg

Sandia National Laboratories*, Albuquerque, New Mexico 87185



*This work was supported the LDRD program at Sandia National Laboratories, in the form of a Grand Challenge project entitled Reimagining Liquid Transportation Fuels: Sunshine to Petrol. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Motivation: The Sunshine-to-Petrol Grand Challenge

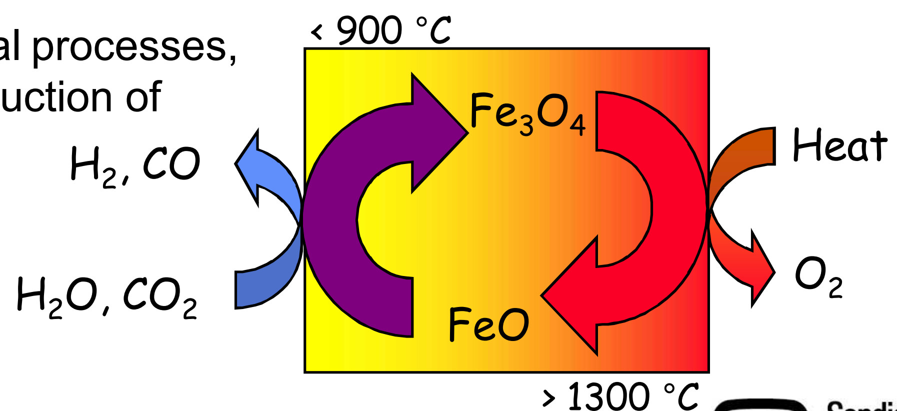
Goal: To produce liquid hydrocarbon fuels from carbon dioxide and water using concentrated solar power as the energy source. The conversion is based on the following formula:

$$\text{Sunlight} + CO_2 + H_2O = \text{Fuel} + O_2$$

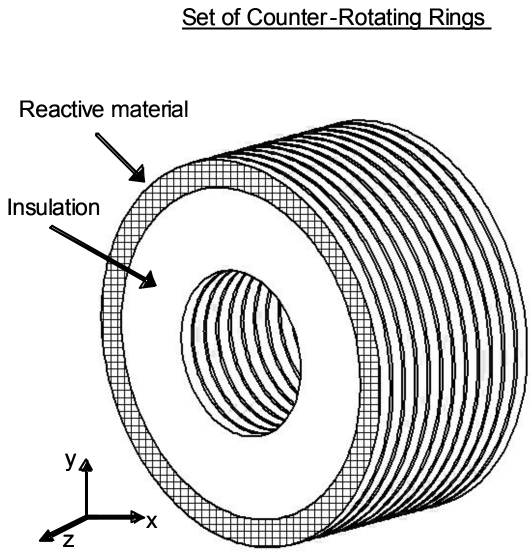
Actual stoichiometry: $xCO_2 + (x+1)\, H_2O \rightarrow C_xH_{2x+2} + (1.5x+.5)\, O_2$

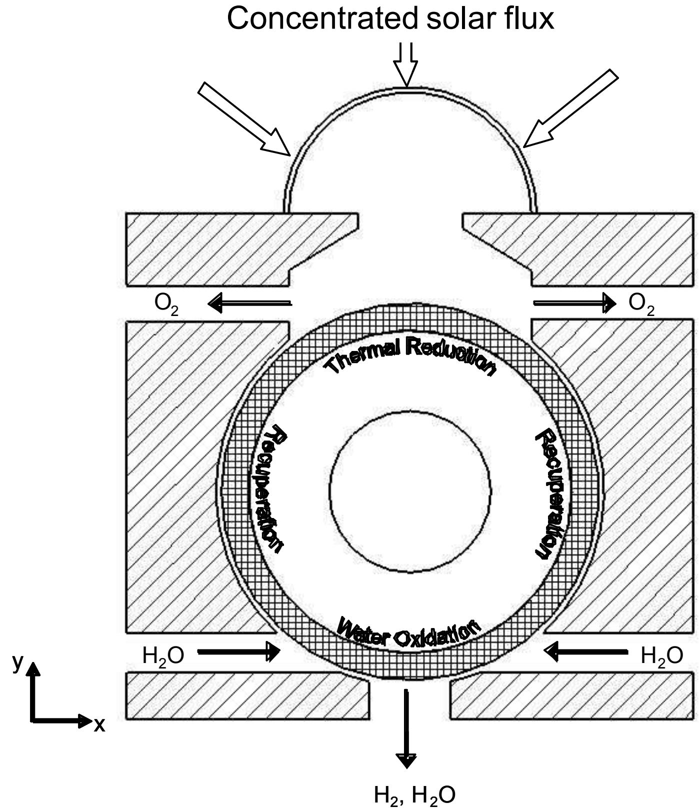
There are many ways to produce liquid fuels from sunlight including biological, thermochemical, and electrochemical pathways

This project focuses on thermochemical processes, specifically the cyclic oxidation and reduction of a metal oxide to produce H_2 and CO (syngas) from water and CO_2.



The Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5) recaptures heat during cycling



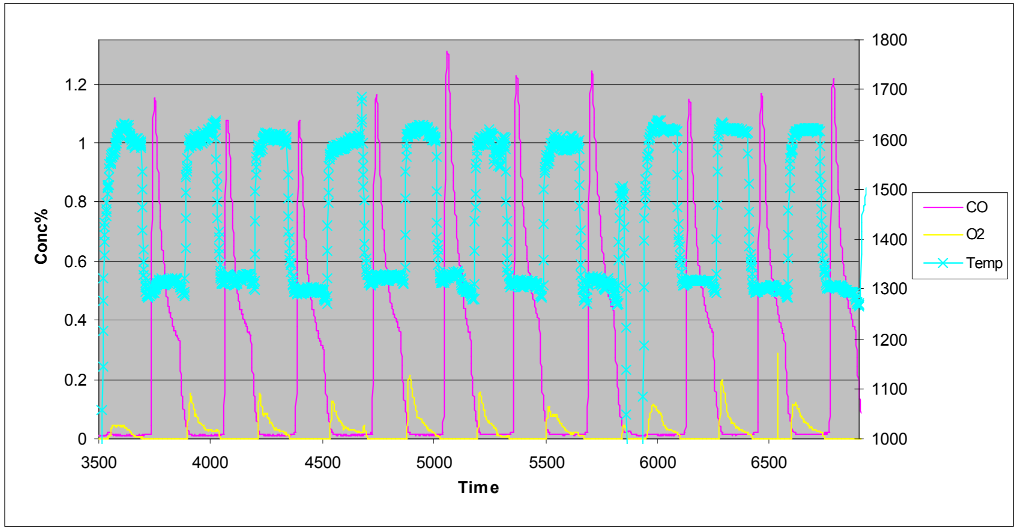


- *Countercurrent recuperation* of sensible heat.
- Intrinsic separation of H_2 (or CO) and O_2.
- Initial CR5 concept designed for a dish platform.

Sandia National Laboratories

What Works? Transition metal ferrites in/on Yttria Stabilized Zirconia (YSZ) supports

A candidate working oxide for the CR5 is a mixture of iron oxide and YSZ. A fundamental understanding why this mixture works (can be cycled) when pure iron oxide alone does not is still in its infancy. We are developing capabilities to investigate to characterize inter-diffusion processes between iron oxide and YSZ on model single-crystal surfaces using LEEM-based techniques.



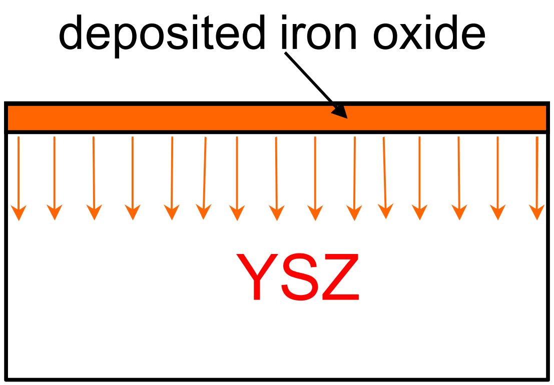
Solar furnace test data (Nate Siegal)

Sample: 10% Fe_2O_3 in YSZ, 3% Y_2O_3

Test Conditions: Oxidation Temp – 1300 C, Reduction Temp – 1600 C

Sandia National Laboratories

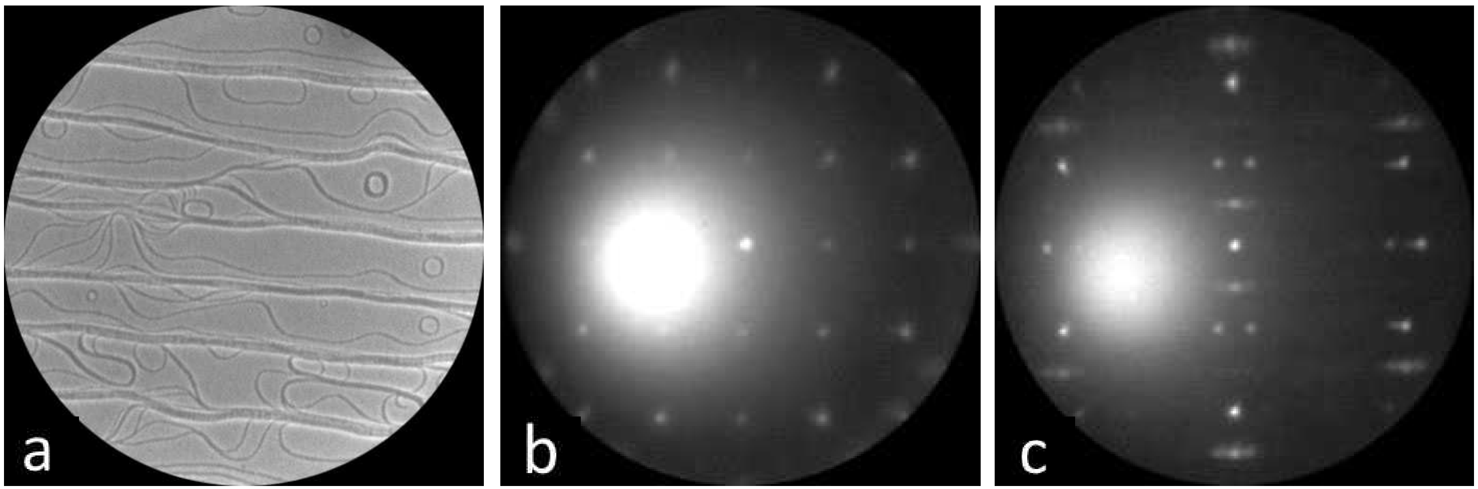
First step: Grow and characterize iron oxide films on YSZ(001)



- Characterize YSZ single-crystal surfaces by LEEM and LEED
- Deposit iron oxide films while watching with LEEM or LEED
- Determine the growth morphology, domain structure and stoichiometry as a function of deposition conditions
- Investigate film dissolution into the bulk

LEEM images and LEED patterns of YSZ(001) are obtained by imaging at temperatures above 200°C

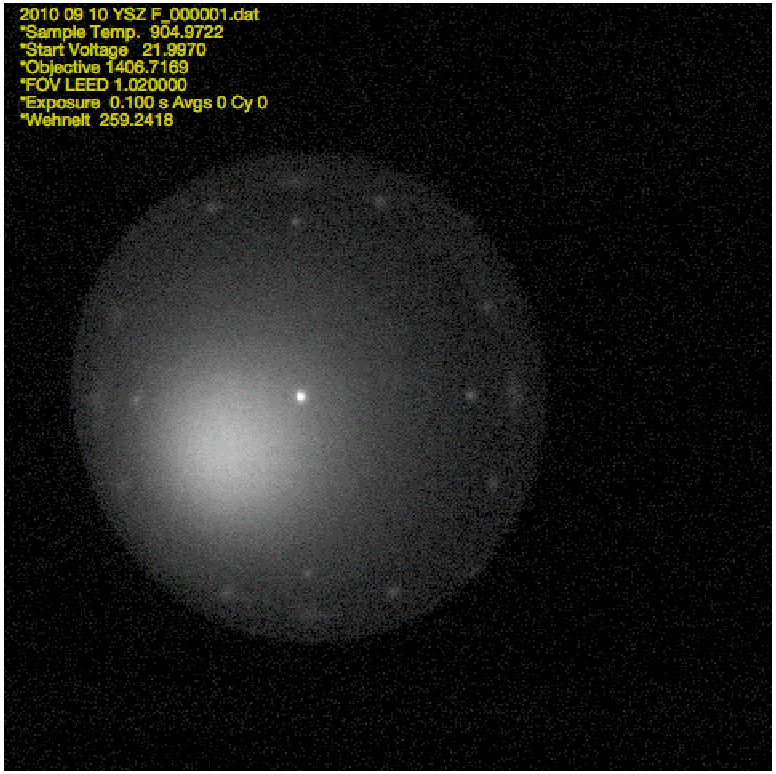
Surfaces are prepared by heating bulk crystals to 1375°C in air and subsequent heating in the vacuum chamber at 300-350°C in $5x10^{-7}$ Torr O_2



(a) LEEM image from YSZ(001) showing step bunches (thick horizontal lines) and single steps (thin meandering lines on terraces). FOV=20 μm (b) (2x2) LEED pattern from YSZ(001) at 350°C. (c) Above 800°C it converts to a "hex" pattern.

Sandia National Laboratories

Iron oxide films are grown on YSZ by depositing Fe in $3x10^{-6}$ Torr oxygen at 900°C



5 frames/sec

30 min total deposition time

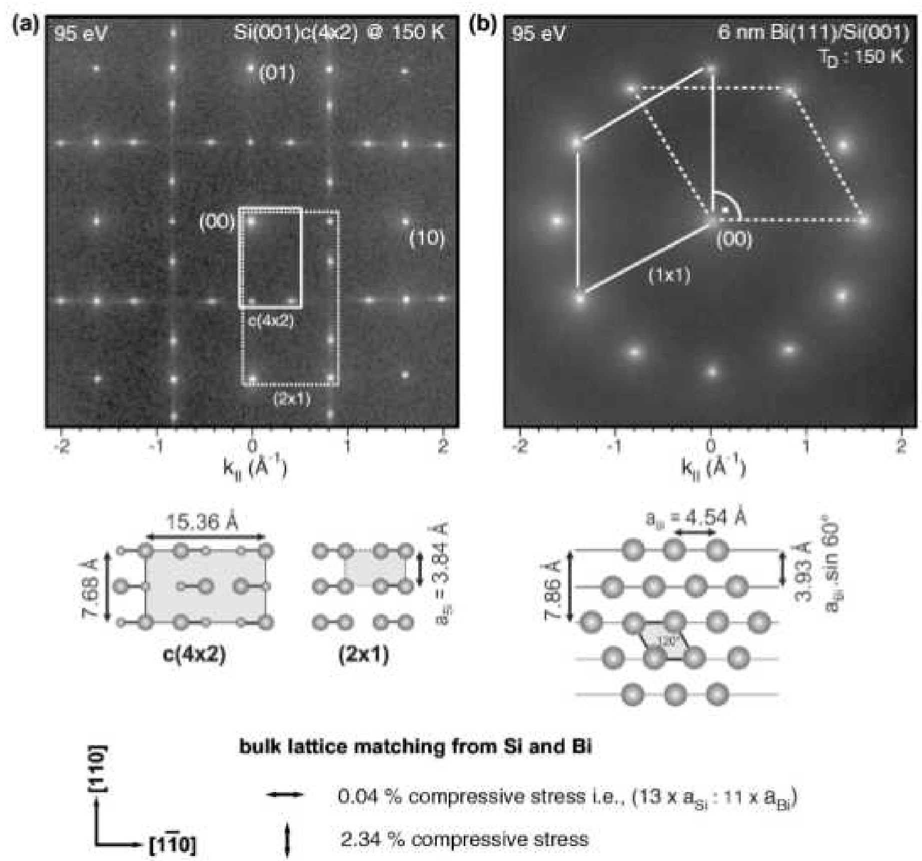
Hex reconstruction disappears

12-fold “clock” pattern appears

12-fold LEED patterns have been seen previously

Two domains of 6-fold patterns superimposed on each other. (111)-oriented cubic lattice on (100)-oriented cubic lattice

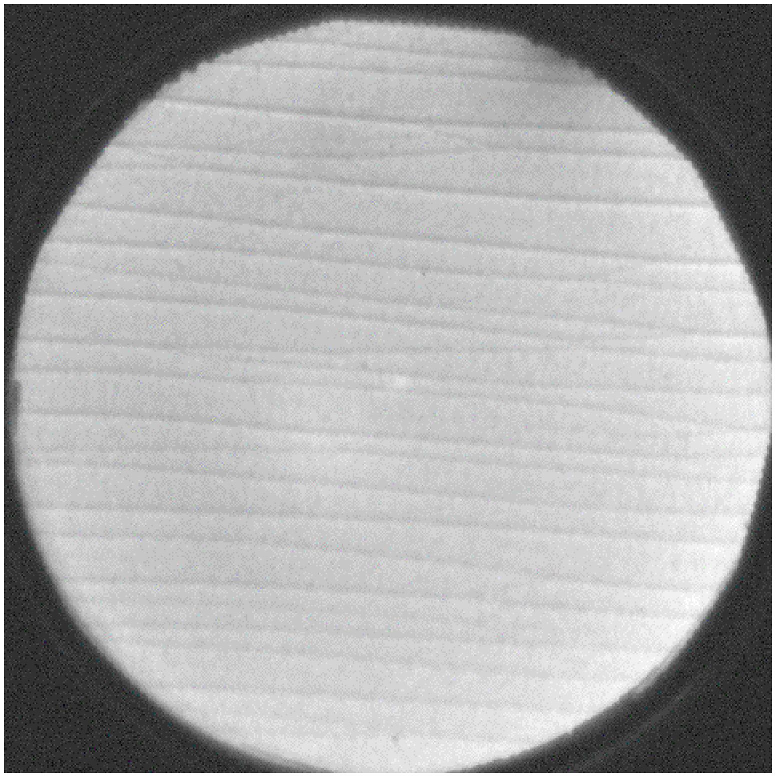
JNAWALI *et al.* PHYSICAL REVIEW B **74**, 195340 (2006)



Sandia National Laboratories

FeO film growth depends on oxygen pressure and sample temperature

2010 09 10 YSZ_A

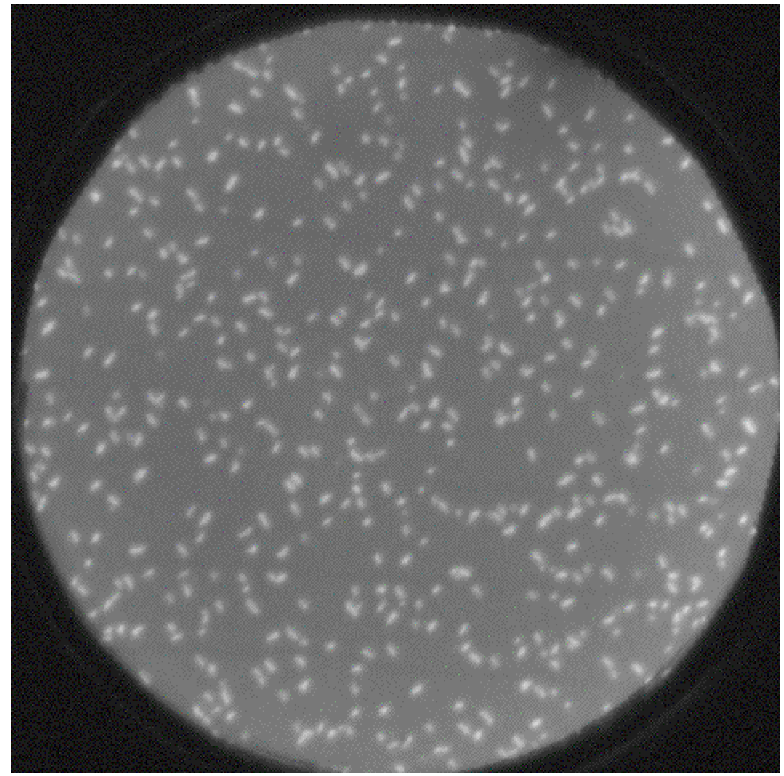


Grow at 900°C (15 min)

2.0×10^{-6} Torr O_2

Field of view = 20 μm

2010 10 06 YSZ_C



Initiate at 870°C (16 min)

Grow at 920°C (12 min)

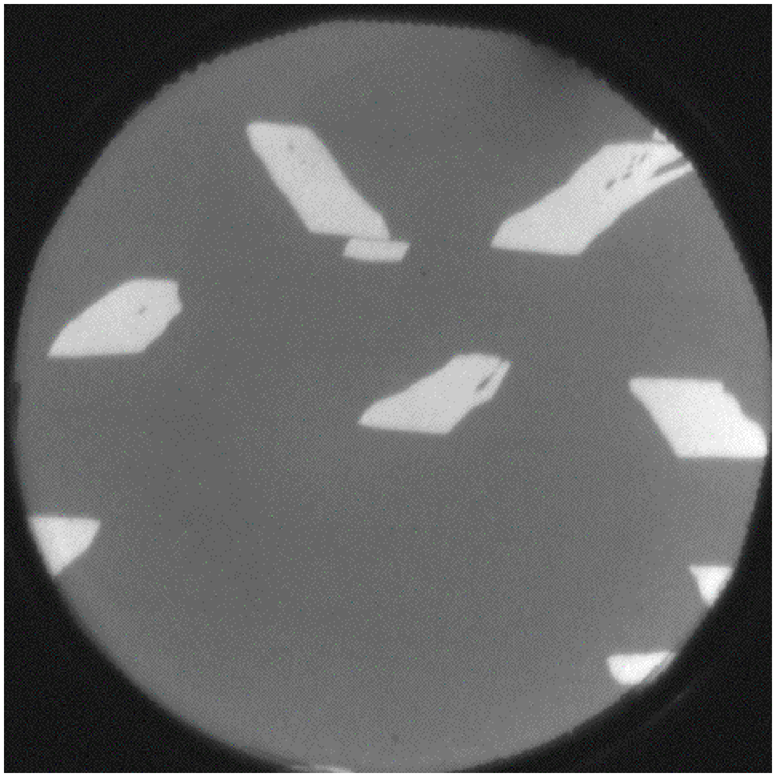
5.0×10^{-6} Torr O_2

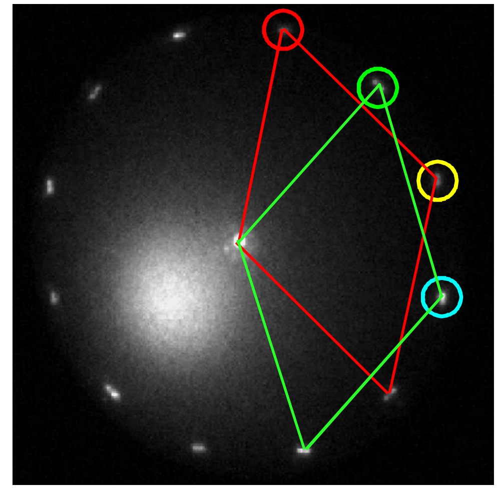
Field of view = 20 μm

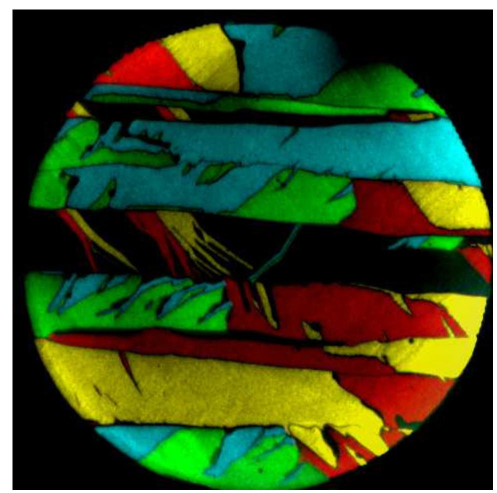
Sandia National Laboratories

Dark-field imaging shows <u>four</u> non-equivalent domains of FeO on YSZ(001)

2010 09 27 YSZ-Fe_9







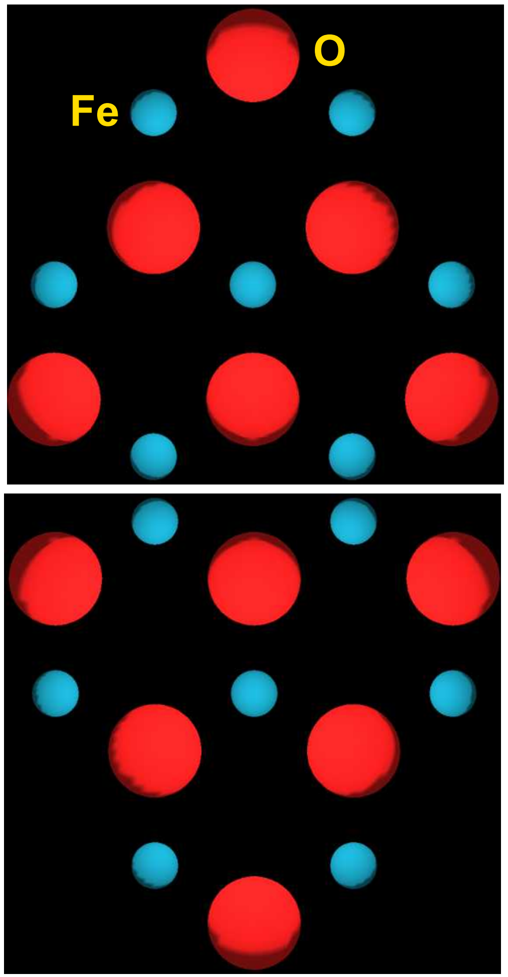
Initiate at 893°C (7 min) (not shown)

Grow at 1052°C (14 min)

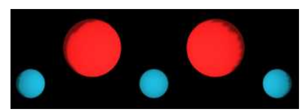
8.6×10^{-6} Torr O_2

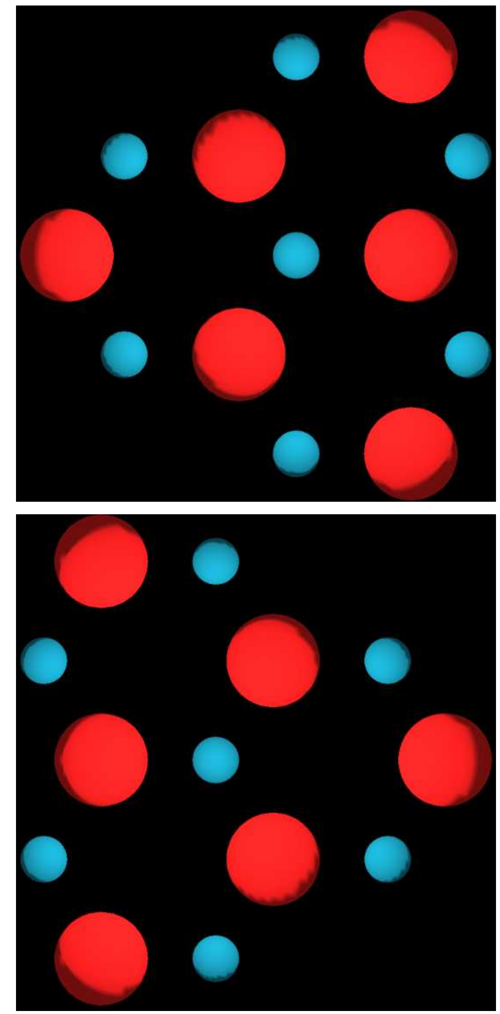
Field of view = 20 μm

Each rotated domain has a "twin" depending on the bi-layer stacking

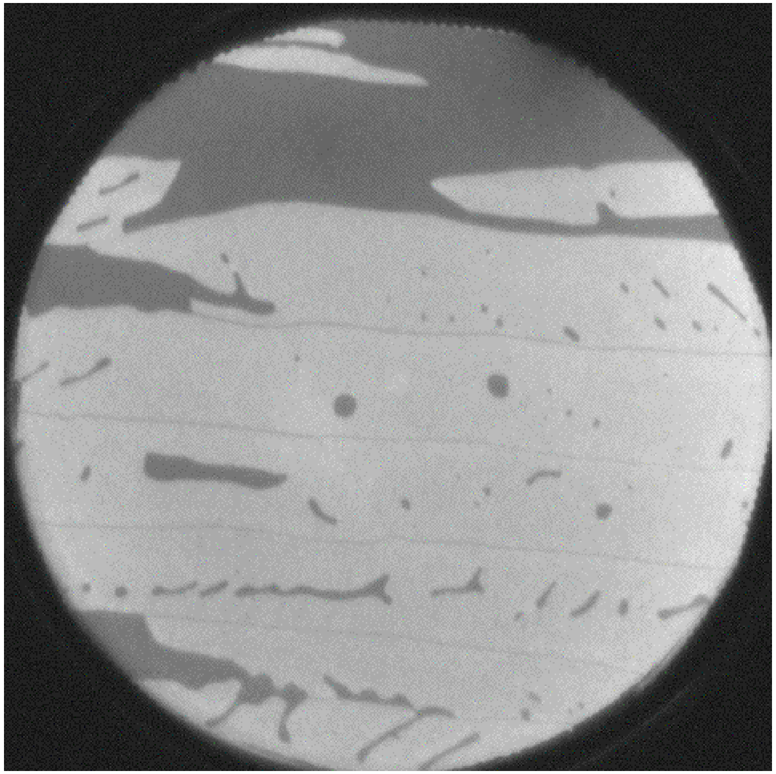


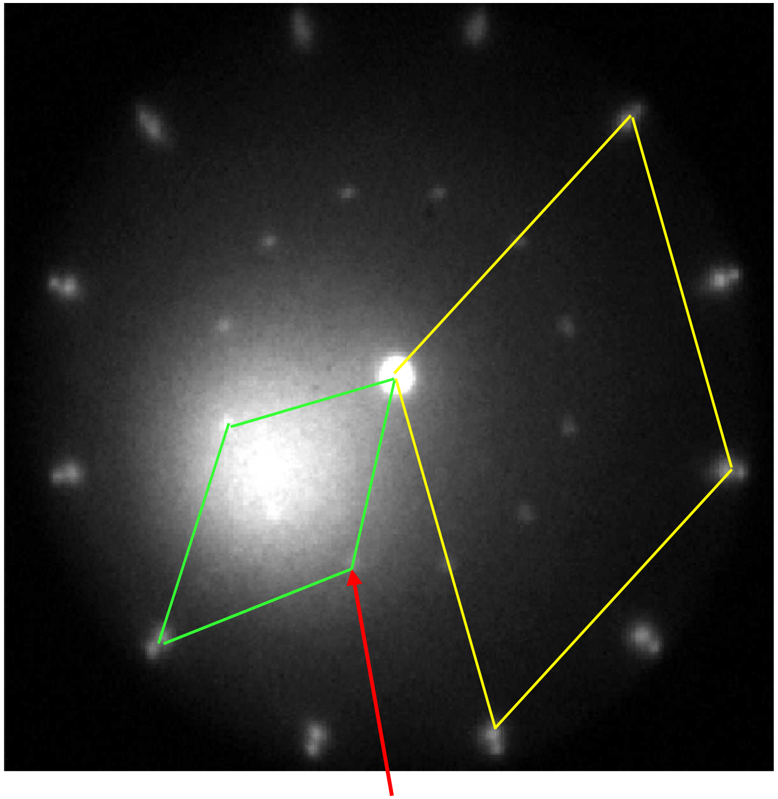
Side view?





Second-layer growth starts only after first is completed (temperature must be lowered): Fe_2O_3





$Fe_2O_3(0001)$: 0.503nm

Sandia National Laboratories

Summary

- Iron oxides can be grown on YSZ(001) while observing in LEEM or LEED in real time
- The first layer is FeO and grows in four non-equivalent structures (two rotations plus twins)
- FeO growth is anisotropic (hexagonal film growth on square substrate)
- Uniform FeO growth is achieved by Fe seeding at ~900°C and growing at ~1050 °C at O_2 pressures above $5x10^{-6}$ Torr
- Coarsening of small FeO islands (or annealing FeO films) produces a “rotated” 12-fold LEED pattern with higher thermal stability
- Second layer does not grow until first is complete – stoichiometry is Fe_2O_3
- First and second layers have unique LEEM IV fingerprints

Sandia National Laboratories