Iron Oxide Growth on YSZ(001)

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Sandia National Laboratories

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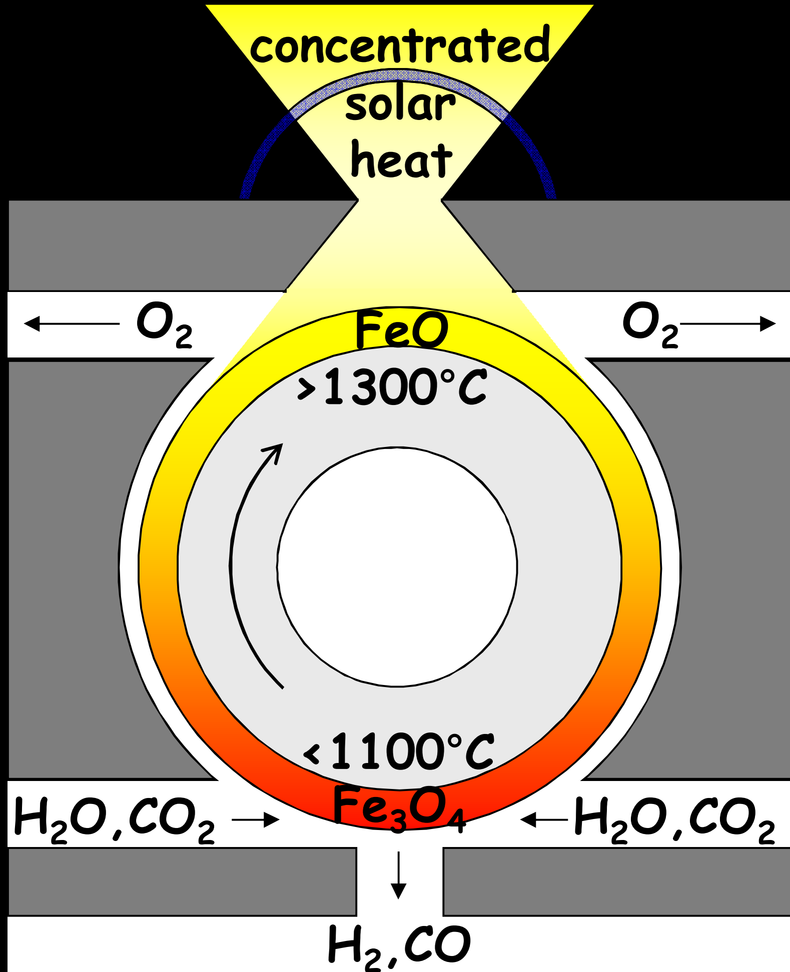
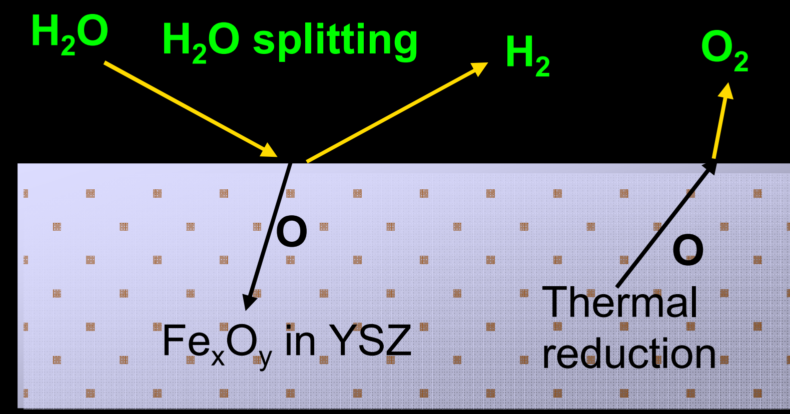
The Sunshine-to-Petrol Grand Challenge (S2P)

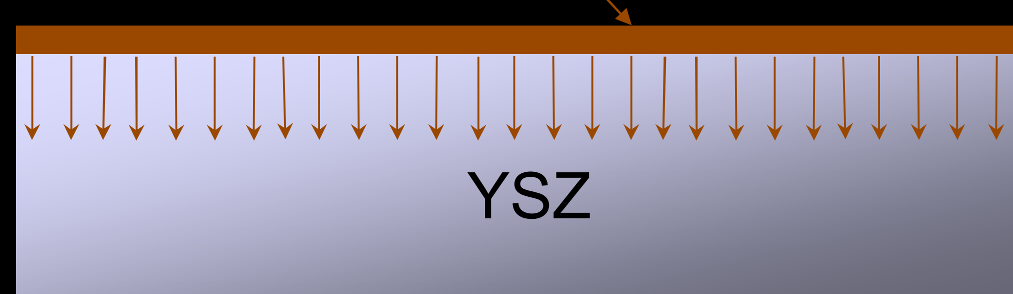
Goal: To produce liquid hydrocarbon fuels from CO_2 and H_2O using concentrated solar power.

Sunlight + CO_2 + H_2O = Fuel + O_2



Counter-Rotating-Ring Receiver/Reactor/Recuperator (CR5) increases efficiency by recapturing heat





Diver et al., J. Solar Ener. Eng. 130 (2008) 041001

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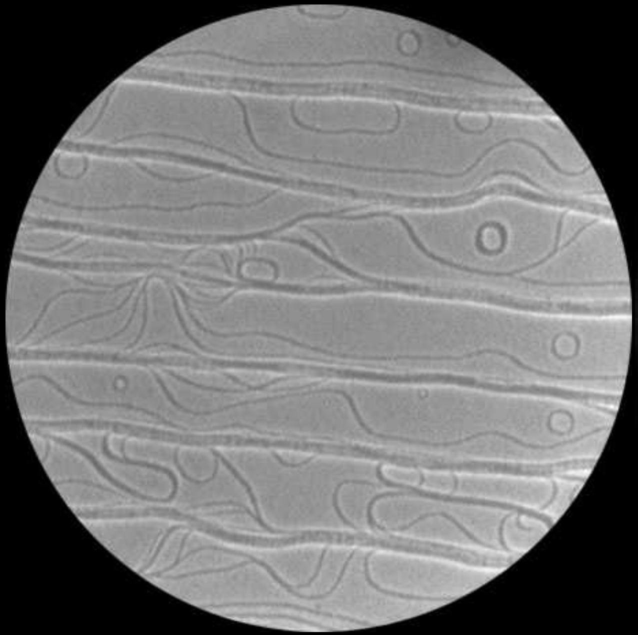
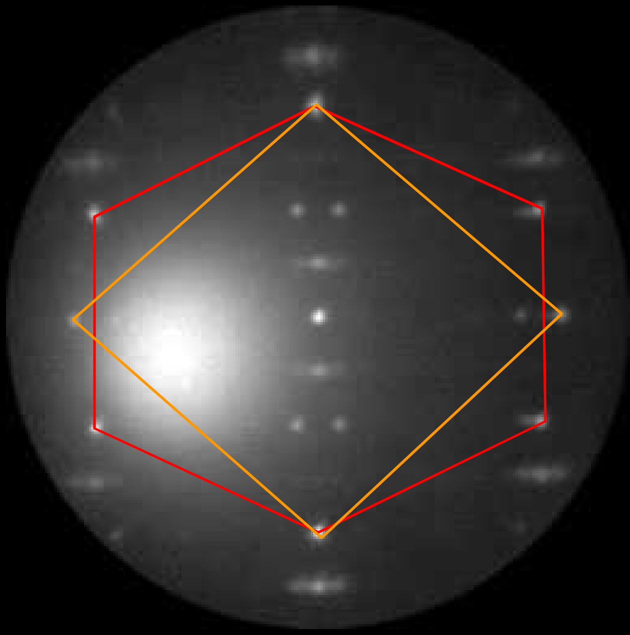
Clean YSZ(001): Imaging Above 300°C

YSZ prepared by heating to 1375°C in air
and subsequent heating in 5×10^{-7} Torr O_2 at 300-350°C



LEEM image
Step bunches: thick horizontal lines
Single steps: thin meandering lines
field of view = 20 μm

(2x2) LEED pattern at 350°C
sample is transparent/white



"hex" LEED pattern: above 1200°C
sample is opaque/black

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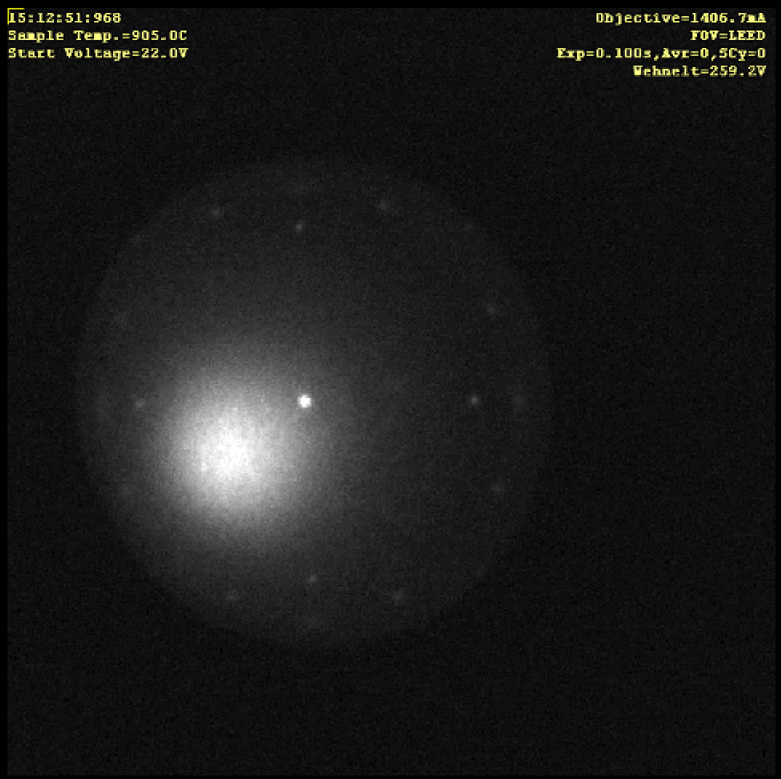
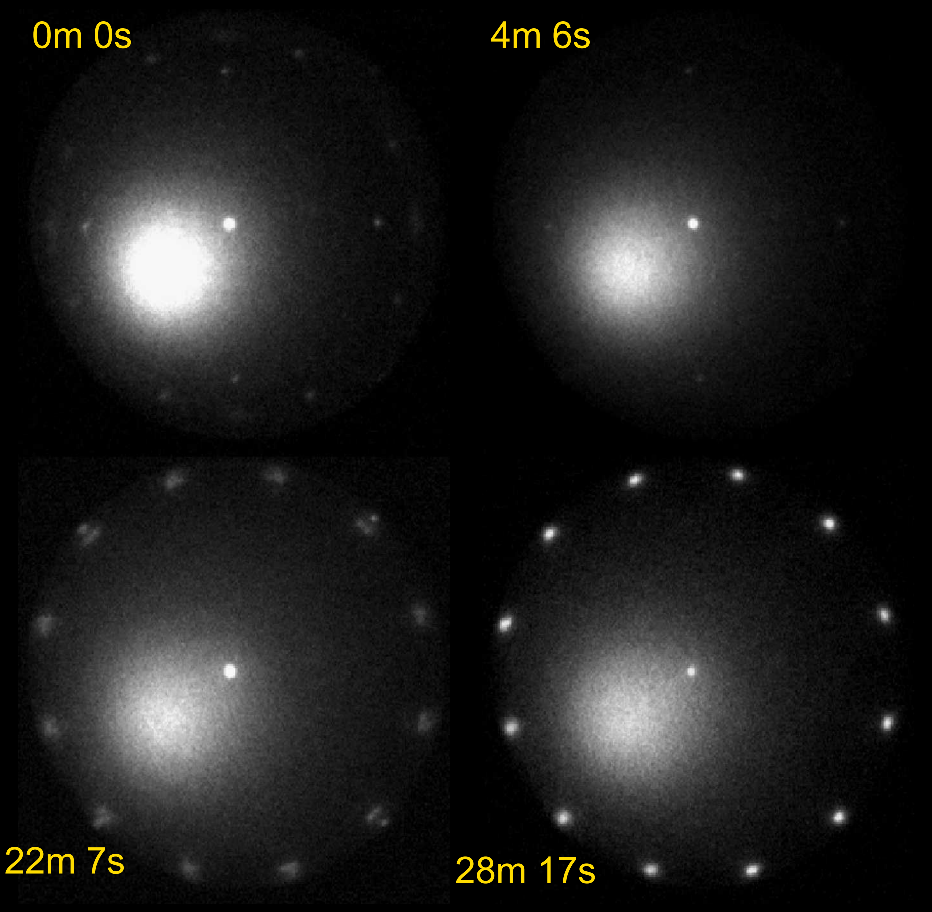
“Hex” Substrate: Oxide Growth by Fe Dosing in ~5x10^{-6} Torr O_2

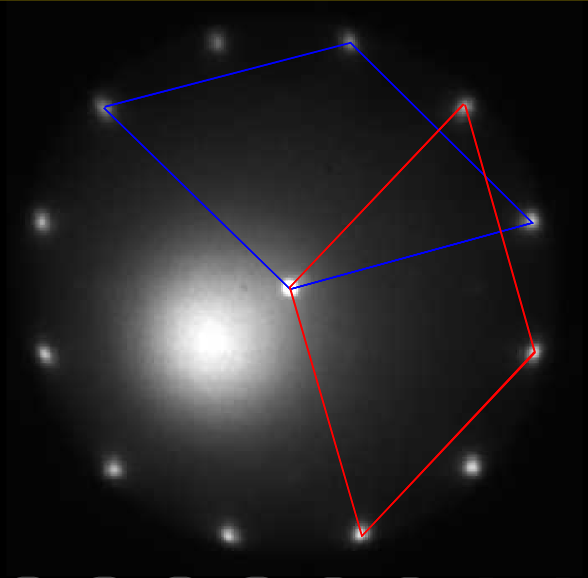


LEED pattern of Fe deposition on YSZ(001)
T ~1000°C, p_{O2}=3x10^{-6} Torr
total time ~30 min

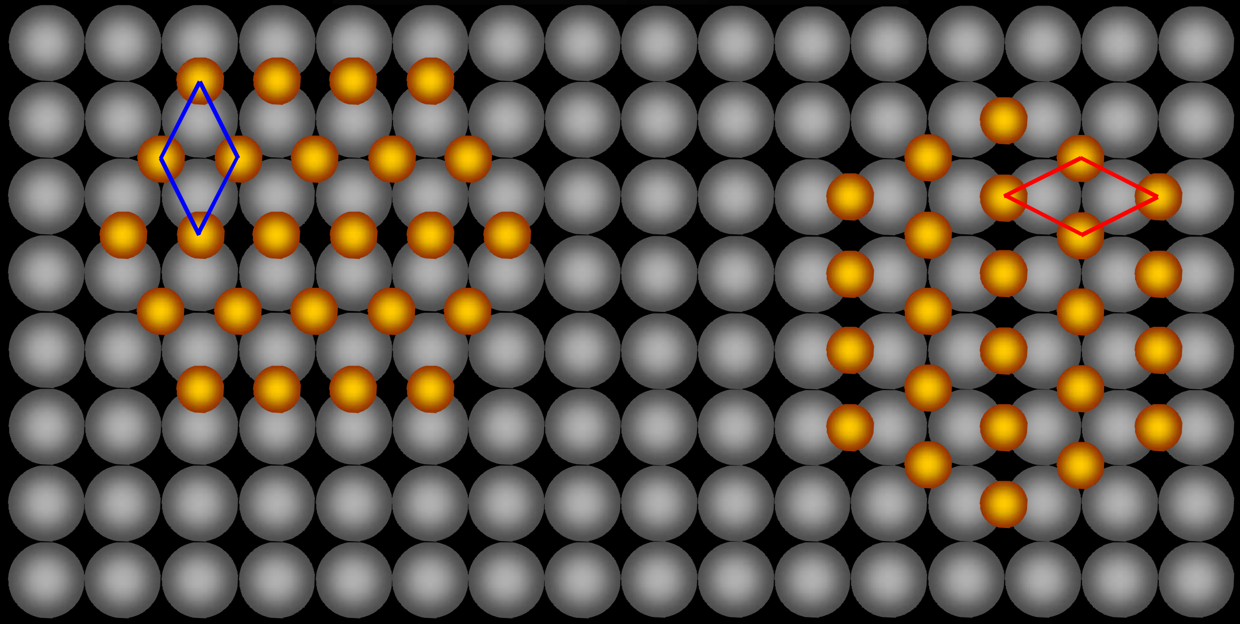


- “Hex” reconstruction disappears after only a few minutes
- A 12-fold pattern appears and converges

LEED: Two Rotational Domains of FeO



Measured lattice constant: 0.316 nm
FeO(111) lattice constant: 0.304 nm
Not Fe_2O_3: 0.503 nm
Not Fe_3O_4: 0.592 nm



Oxide films grown at ~1000°C are FeO(111) with 2 rotational domains

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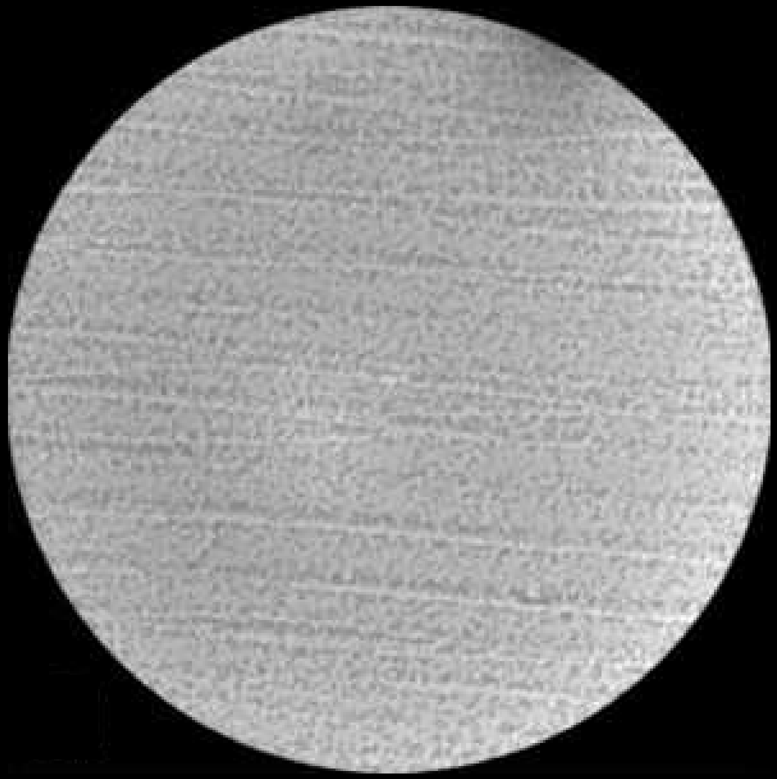
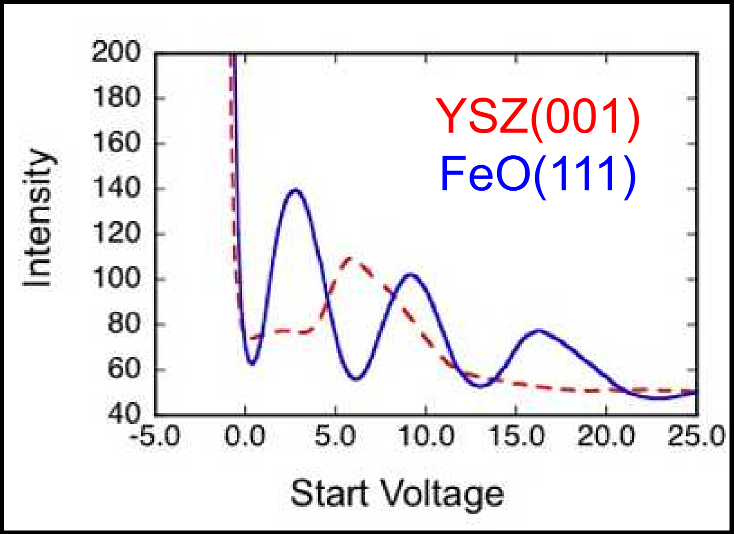
LEEM: Non-uniform Growth and IV Surface Fingerprinting

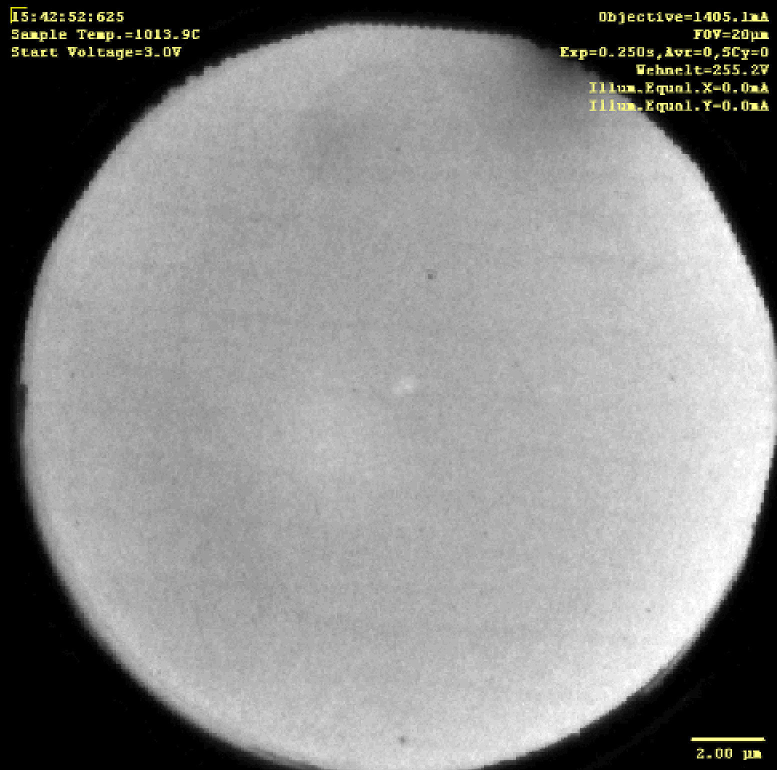


LEEM image of FeO(111)/YSZ(001) film
deposition T ~1000°C
field of view = 20 µm

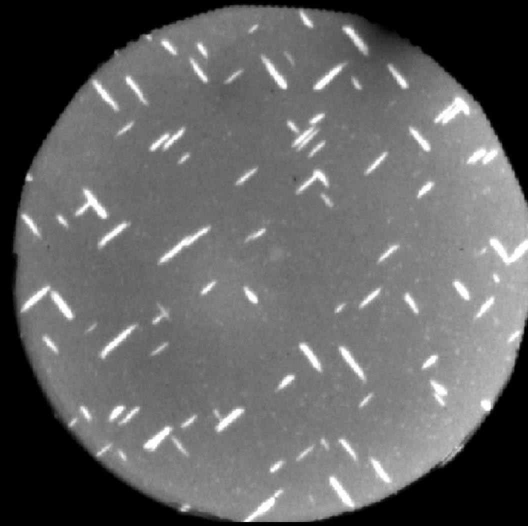


LEEM IV curves for the clean YSZ(001) surface and following FeO deposition

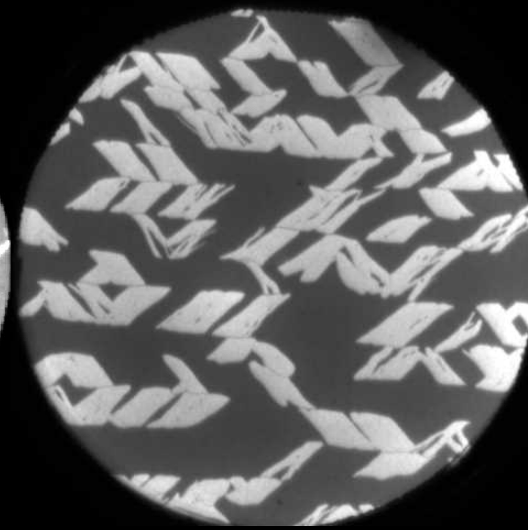
Higher T: More Uniform FeO Film Growth



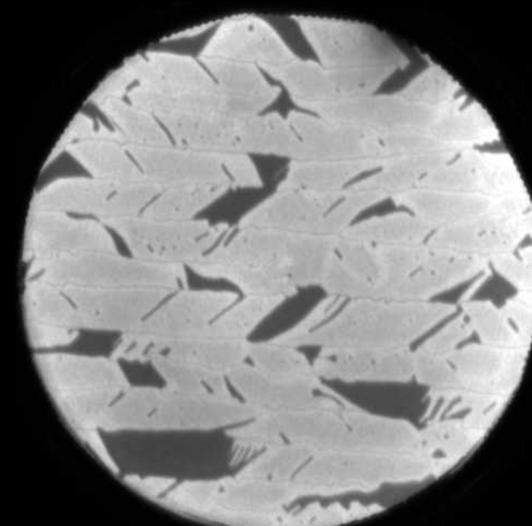
LEEM: Fe/YSZ(001) deposition sequence
T~1110°C, p_{O2} = 3x10^{-6} Torr
total time ~15 min, FOV=20µm



14m 9s



19m 9s



28m 4s

- No growth at 1100°C
- Must "seed" at 1000°C
- Fast growth in 2 perpendicular directions:
  - Initially high aspect ratio islands
  - Terminates at step bunches
- Slow growth causes island widening

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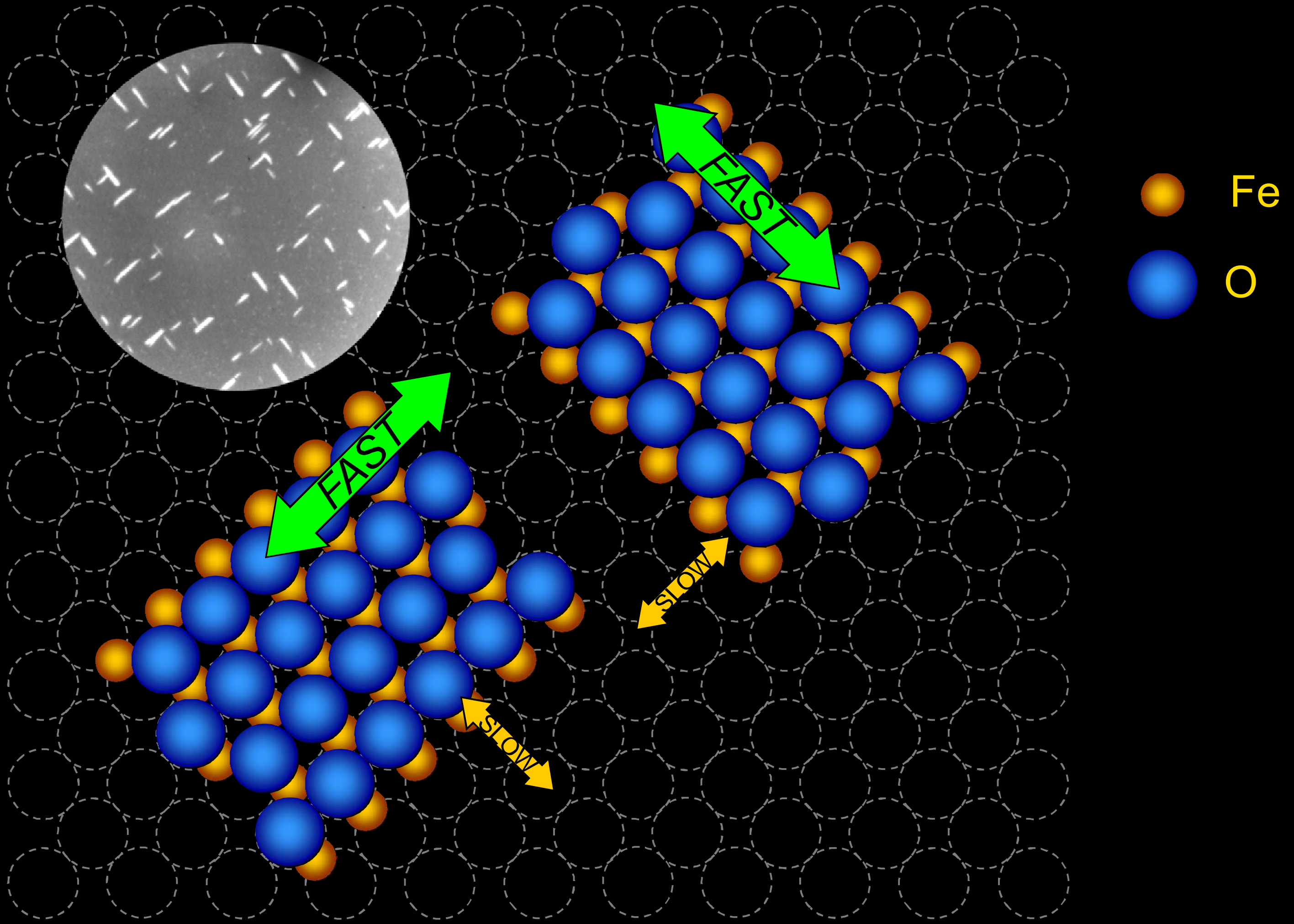
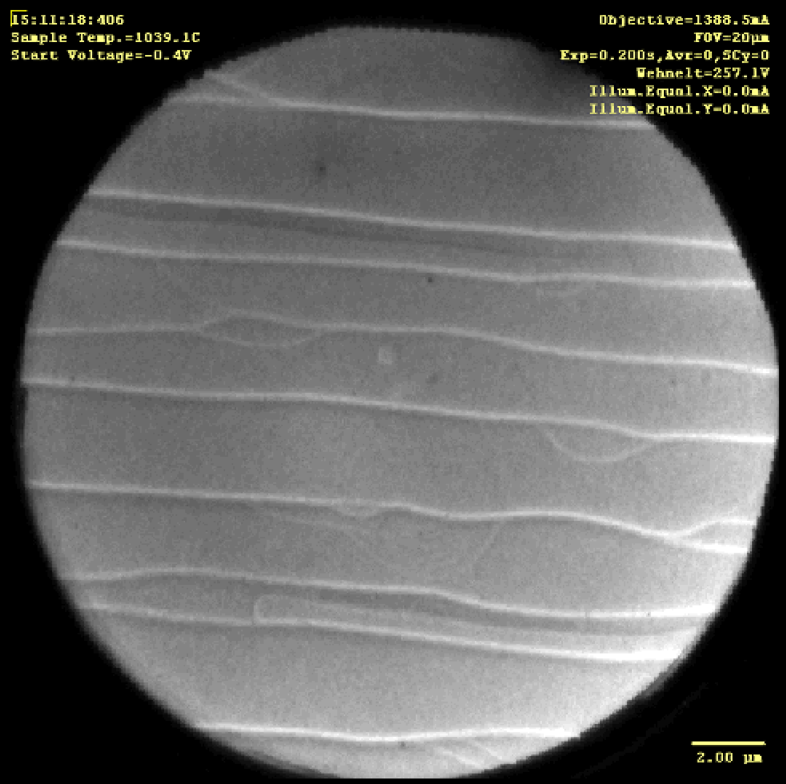
2 Rotational Domains – 2 Fast Growth Directions



Different atomic configurations at edges leads to different growth speeds

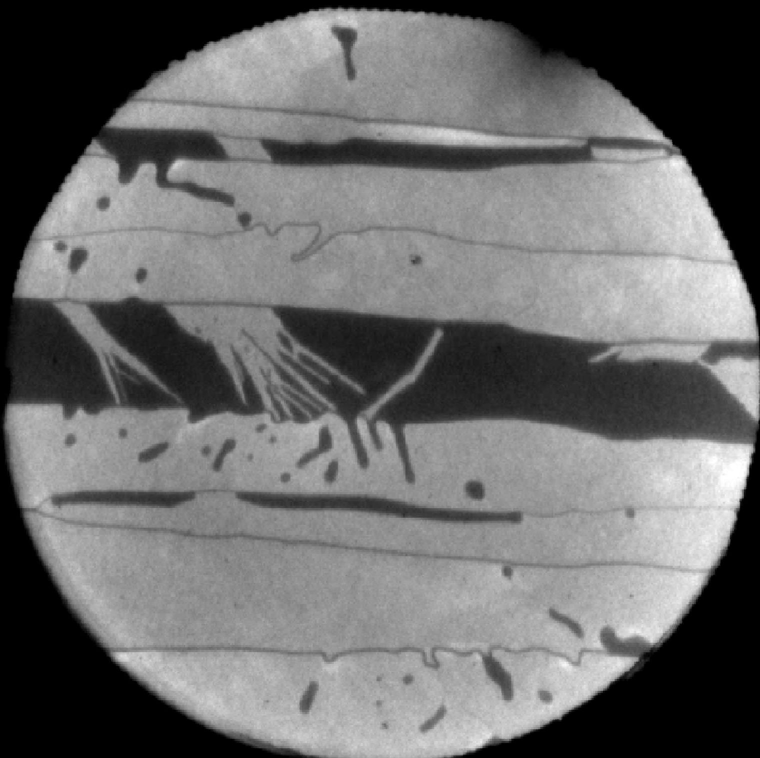
- Preferential attachment
- Anisotropic diffusion
- Preferential oxygen dissociation

Higher T → Larger Domains → Probe Domain Structure

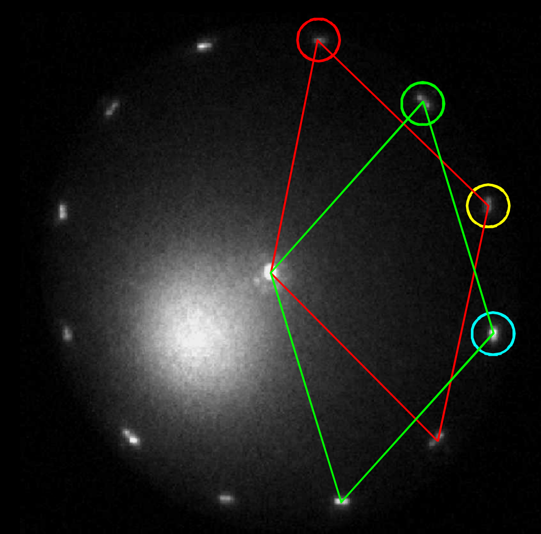


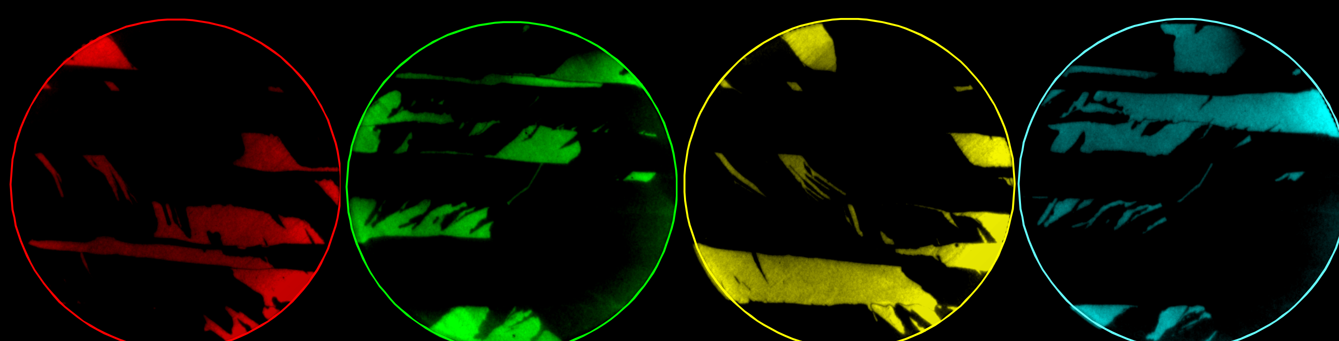
Fe/YSZ(001) deposition sequence
T~1110°C, p_{O2} = 3x10^{-6} Torr
total time ~23 min, FOV=20μm

Higher T → Larger Domains → Probe Domain Structure



LEEM image of FeO(111)/YSZ(001) film
FOV=20μm





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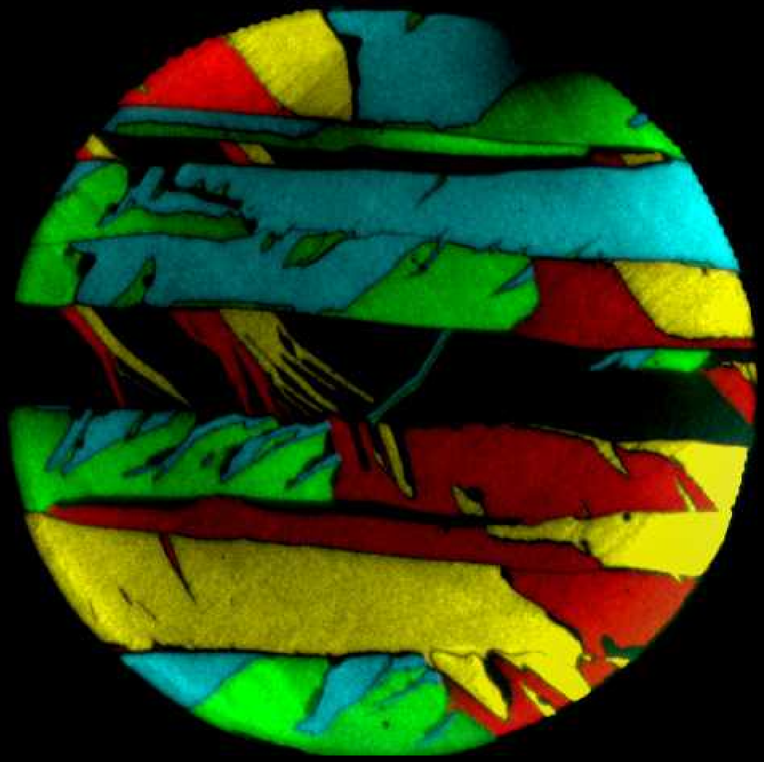
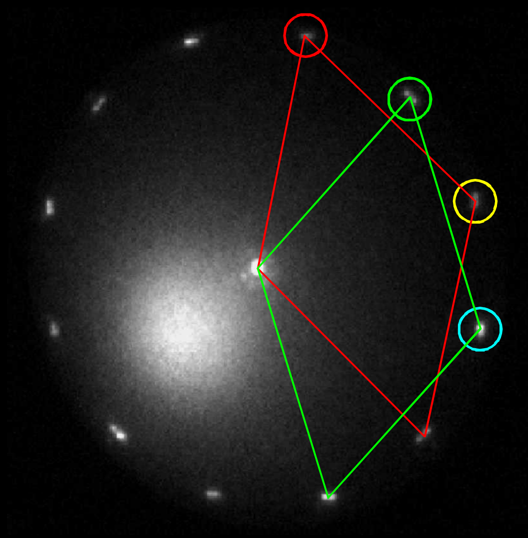
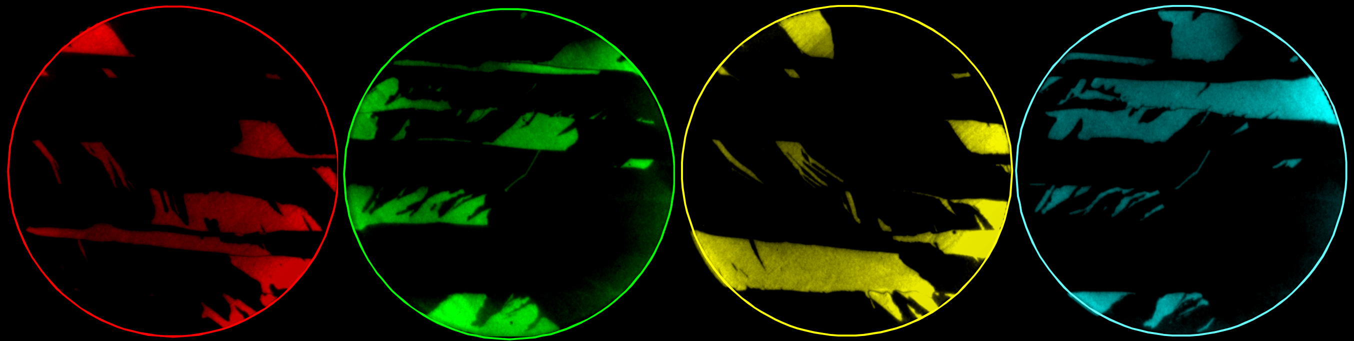
Dark field LEEM Reveals Double the Domains

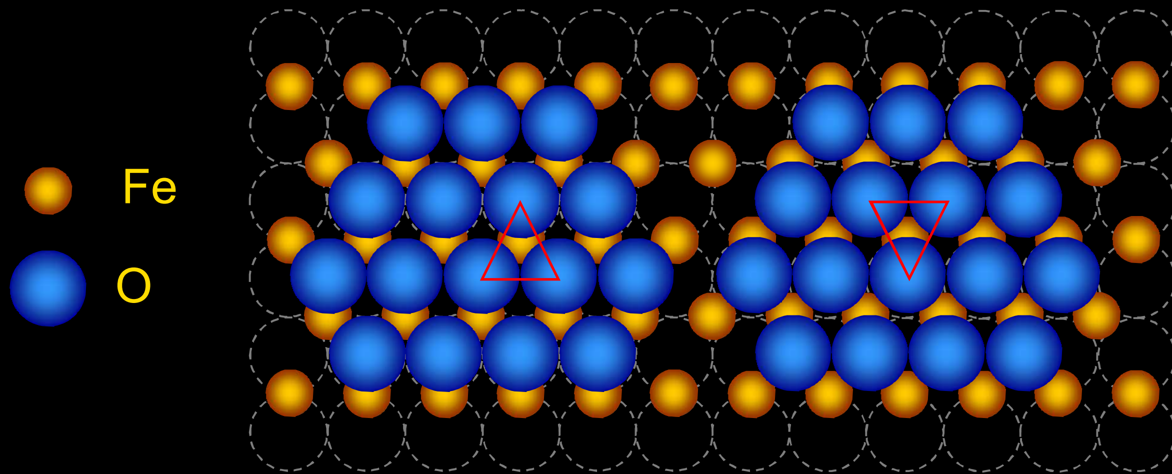


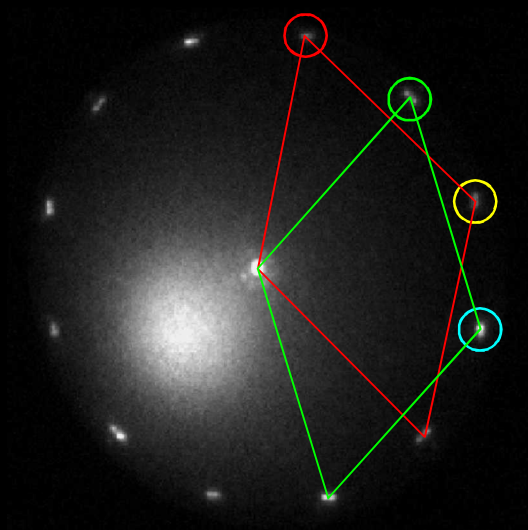
Composite LEEM image of
FeO(111)/YSZ(001) film domains
FOV=20μm





Origin of 4 Domains: 2 Stackings for Each Rotation



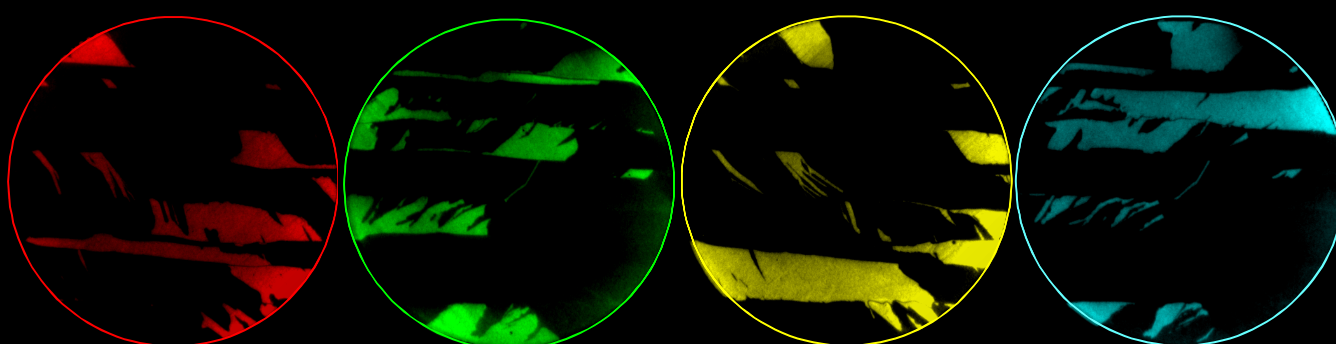


Rotation A Stacking X

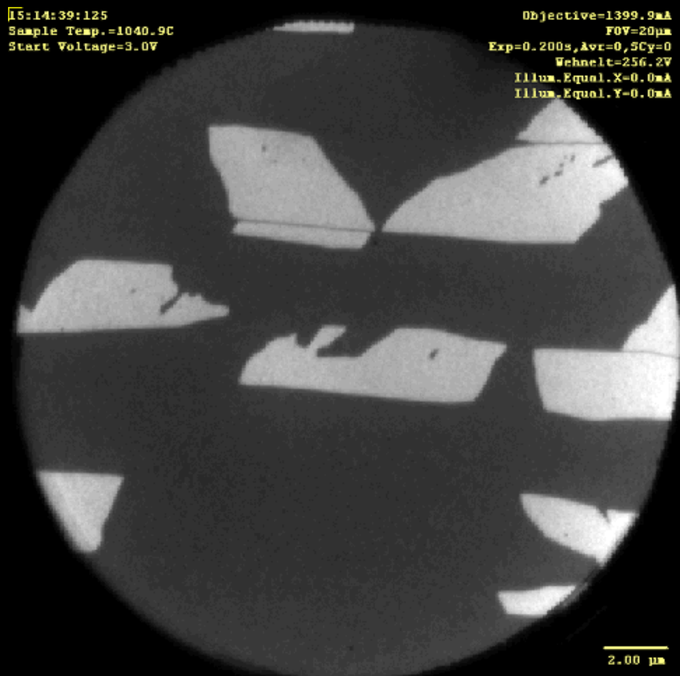
Rotation B Stacking X

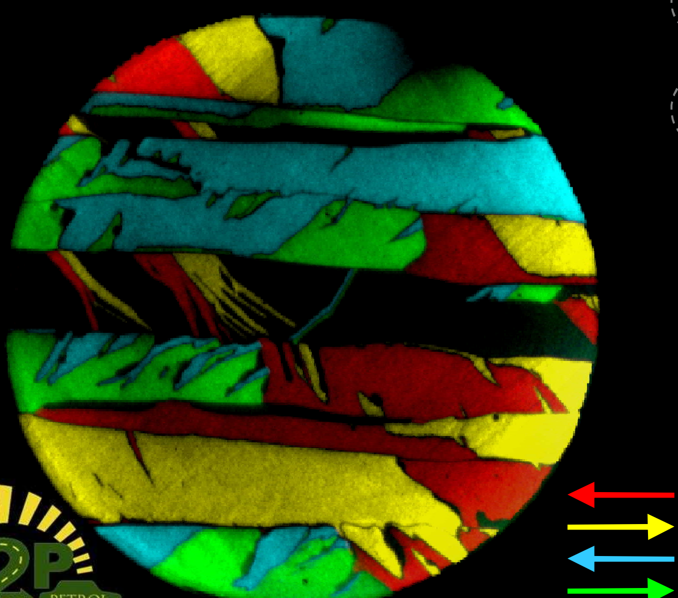
Rotation A Stacking Y

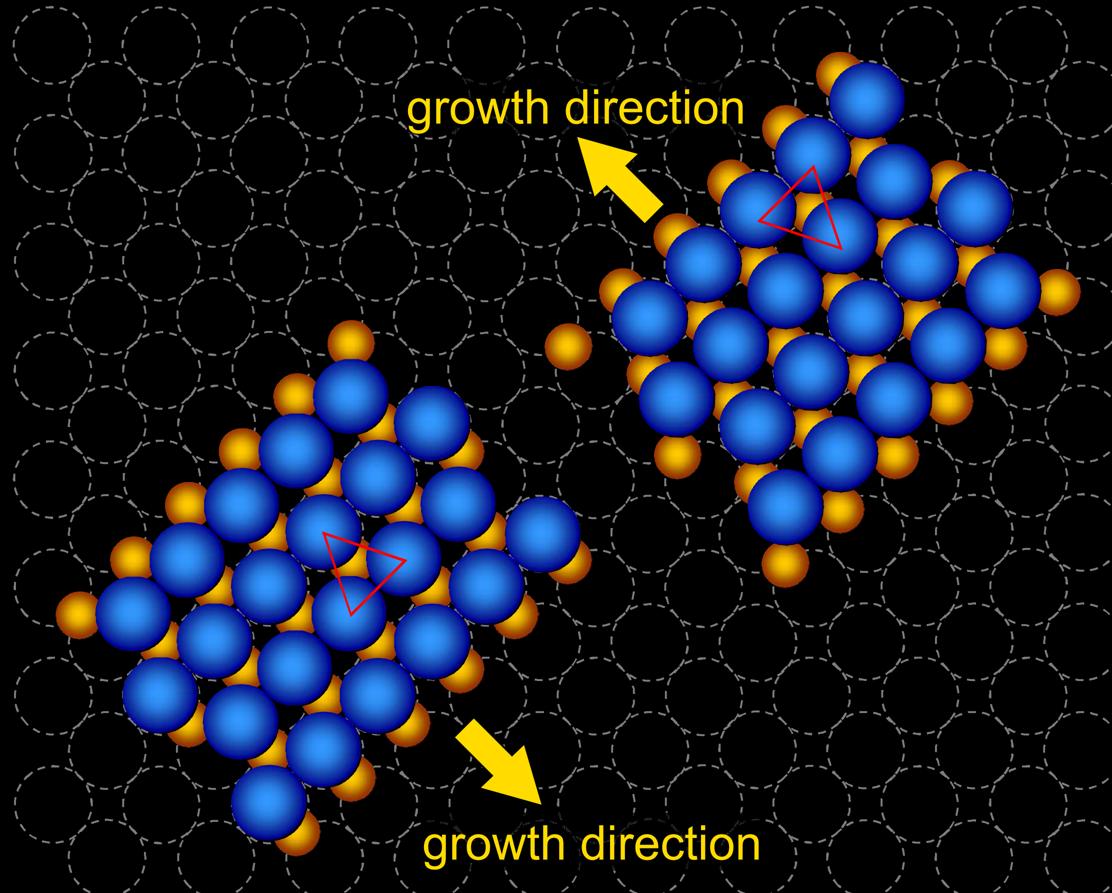
Rotation B Stacking Y



Bilayer Stacking Order Determines Slow Growth Direction



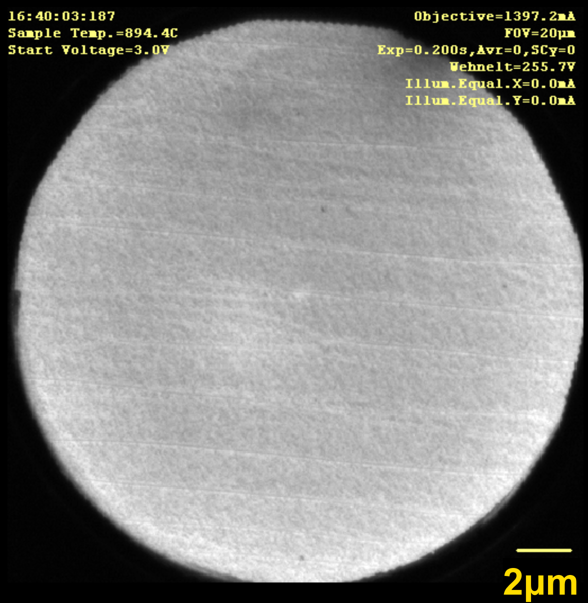




Probable cause: preferential oxygen dissociation:

- Growth rate increases and is more uniform with increase in oxygen pressure

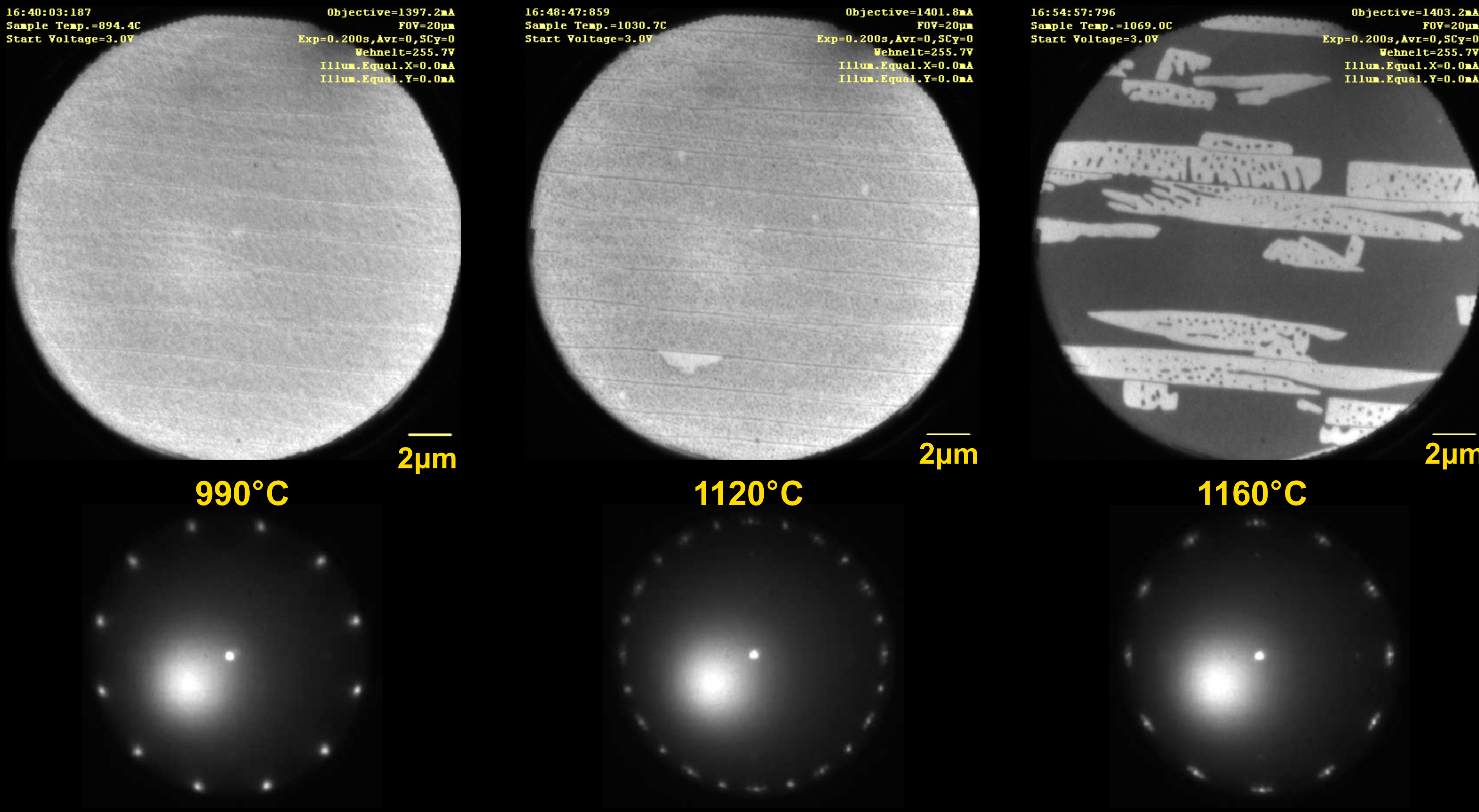
FeO(111): High Temperature Morphological Transformation



990°C

FeO/YSZ(001) annealing sequence
T~1090-1160°C, p_{O2} = 5x10^{-6} Torr
total time ~8 min, FOV=20μm

FeO(111): High Temperature Morphological Transformation



- Lattice is (still) consistent with FeO(111)
- Triplet spots caused by rotated domains
- Rotated structure is stable to higher T
- Double bilayer formation (surface dewetting)?

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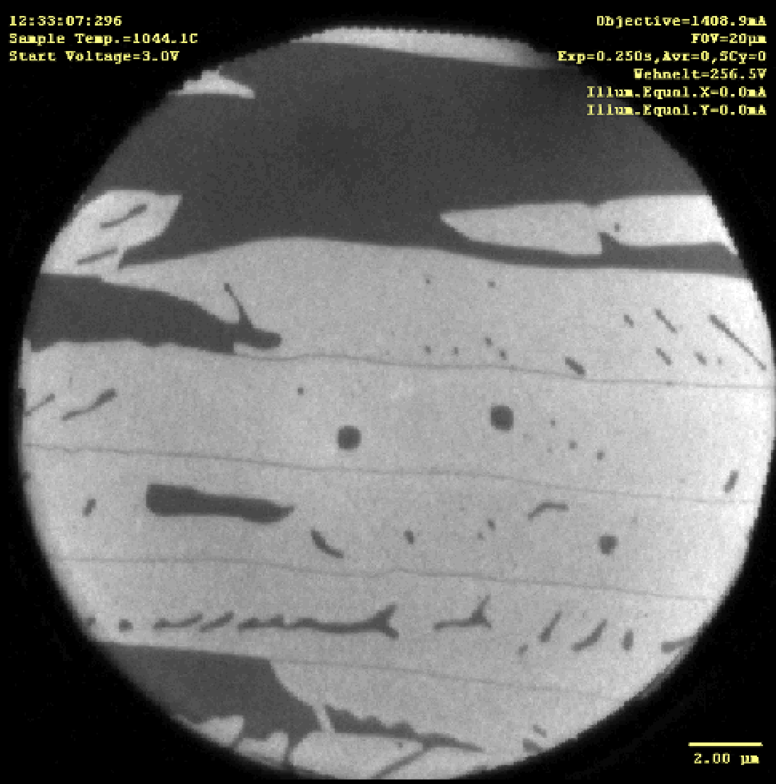
Second Layer Growth Only When First Complete



Fe/YSZ(001) deposition sequence
T~1130°C→1110°C→1000°C,
p_{O2} = 5x10^{-6} Torr
total time ~180 min, FOV=20μm

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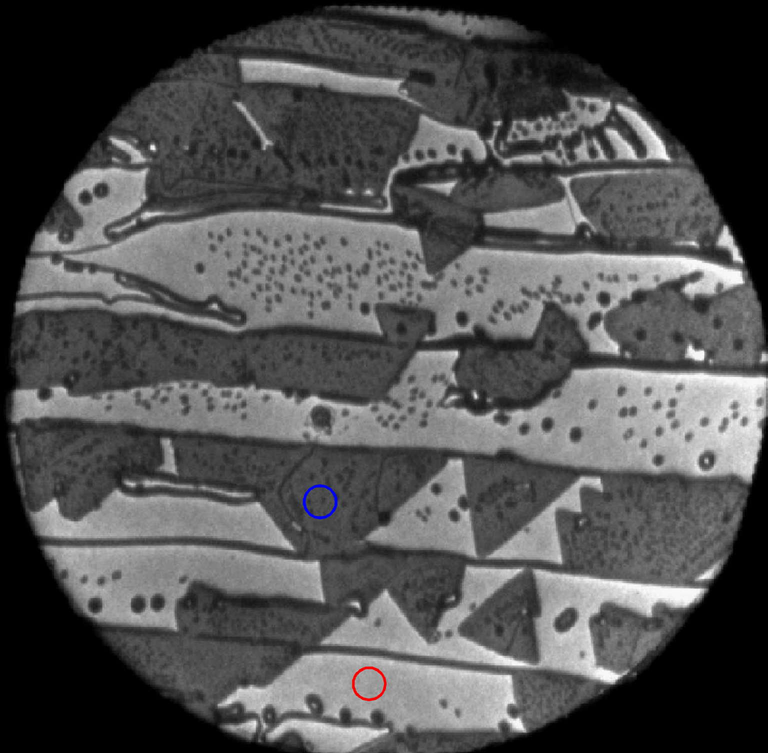
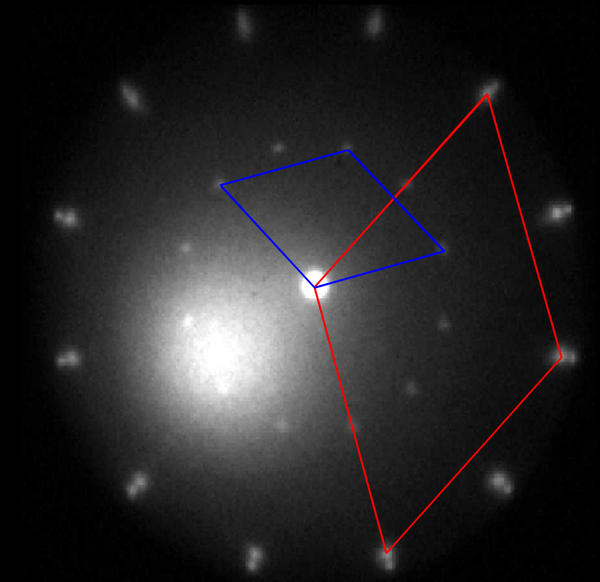
Second Layer Growth: Fe_3O_4

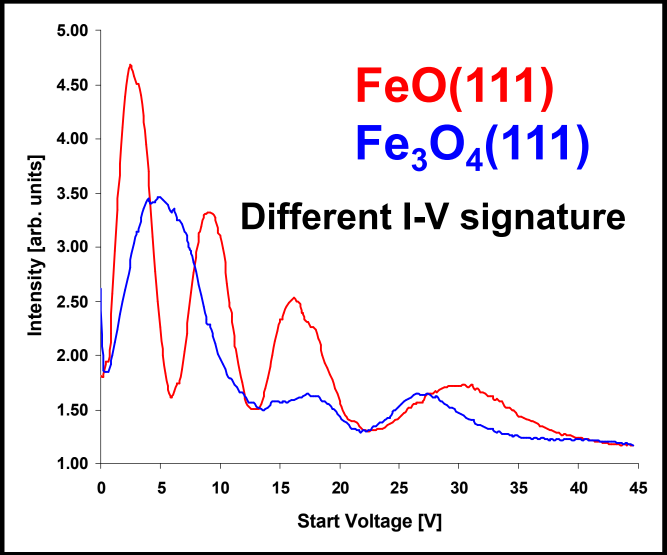


LEEM image of FeO(111) and Fe_3O_4(111)/YSZ(001)
FOV=20μm, start voltage 2.8V

Same area at 5.8V

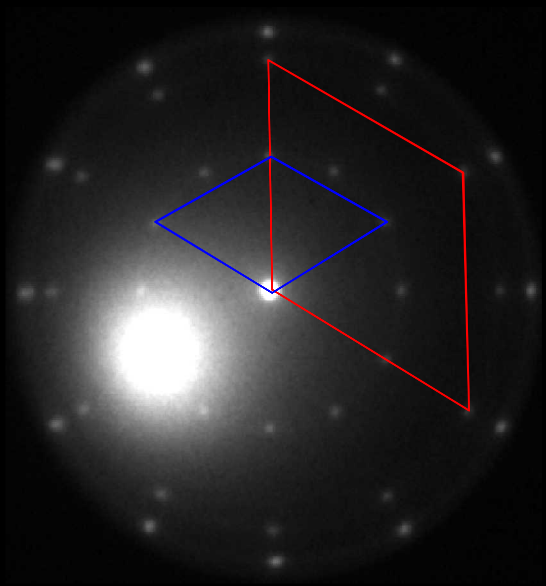


Fe_3O_4(111)/FeO(111) lattice constant ratio: 1.947
Measured in LEED: 1.92



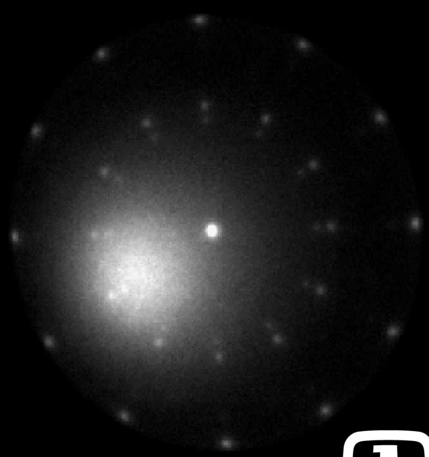
Oxide Growth on Fully Oxidized YSZ(001)

Fe/YSZ(001)
T~795°C, p_{O2} = 6x10^{-6} Torr
t~42 min



Fe_2O_3(0001)/FeO(111) lattice constant ratio: 1.655
Measured in LEED: 1.67-1.70

- Simultaneous oxide growth
- Lattice constant consistent with Fe_2O_3
- All 3 oxides can be grown in more elaborate experiments



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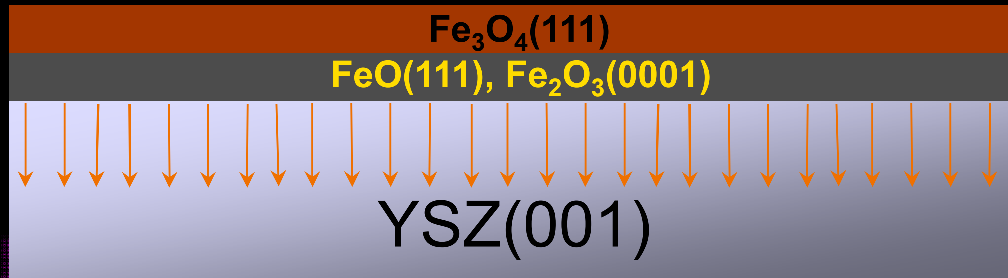
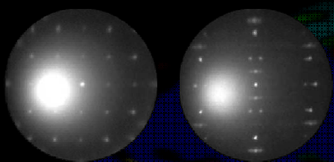
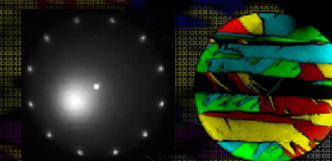
Summary… So far

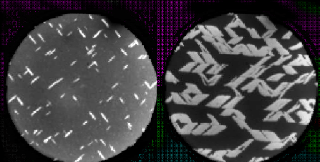




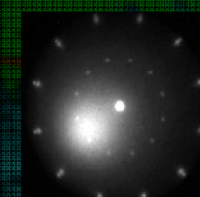
- Different surface reconstructions for fully oxidized and partially reduced YSZ(001)



- On partially reduced YSZ(001), FeO(111) grows with 2 rotational and 2 stacking domains

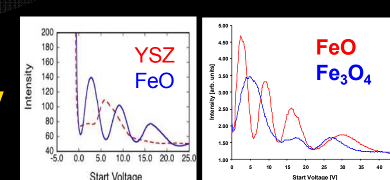


- Domain rotation and stacking affect the oxide growth rate. Temperature affects domain size



- 2nd oxide layer on partially reduced YSZ(001) grows as $Fe_3O_4(111)$

- On fully oxidized YSZ(001), FeO(111) and $Fe_2O_3(0001)$ grow simultaneously
- Surfaces easily distinguishable in LEED and LEEM I-V



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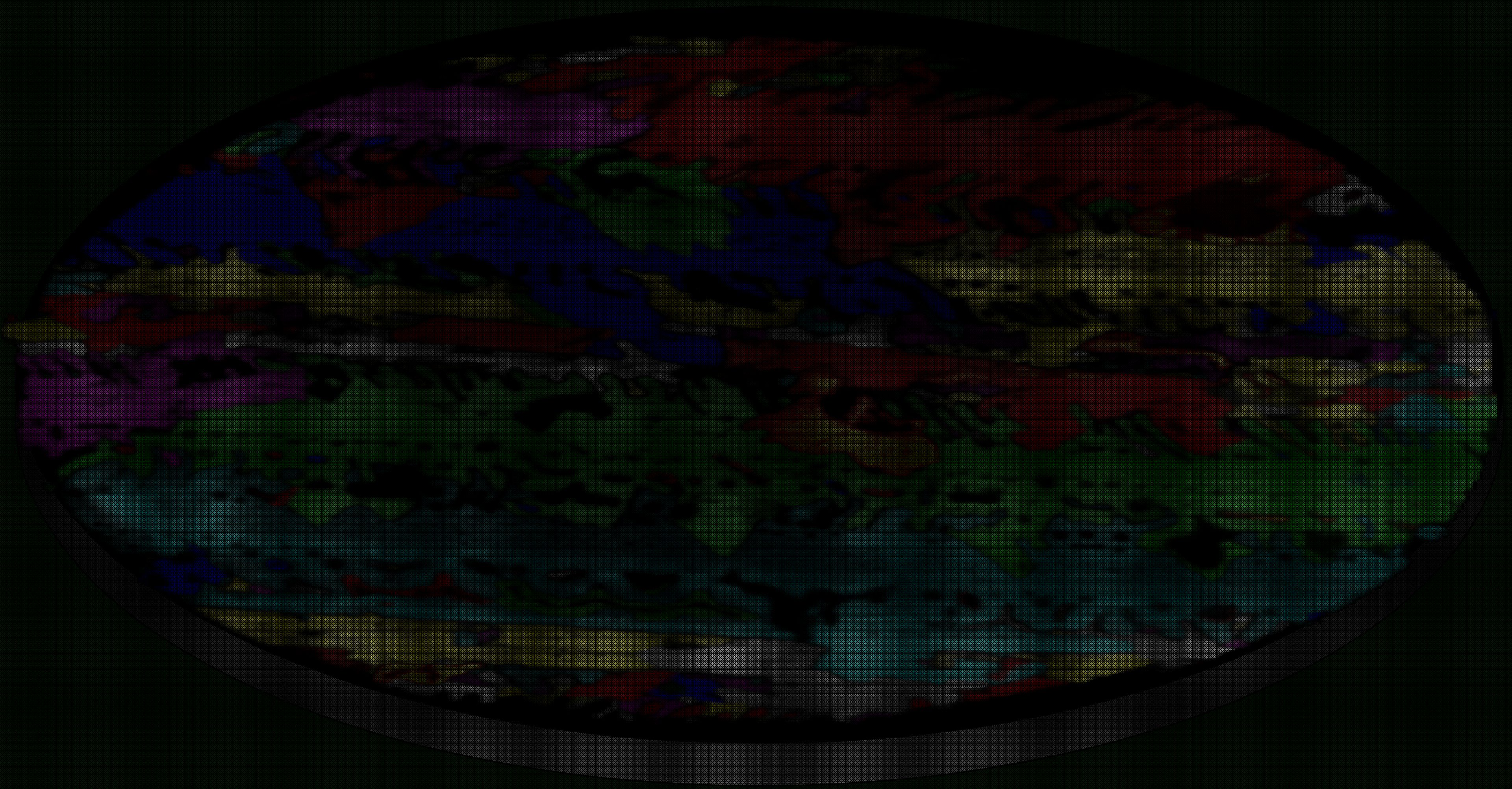
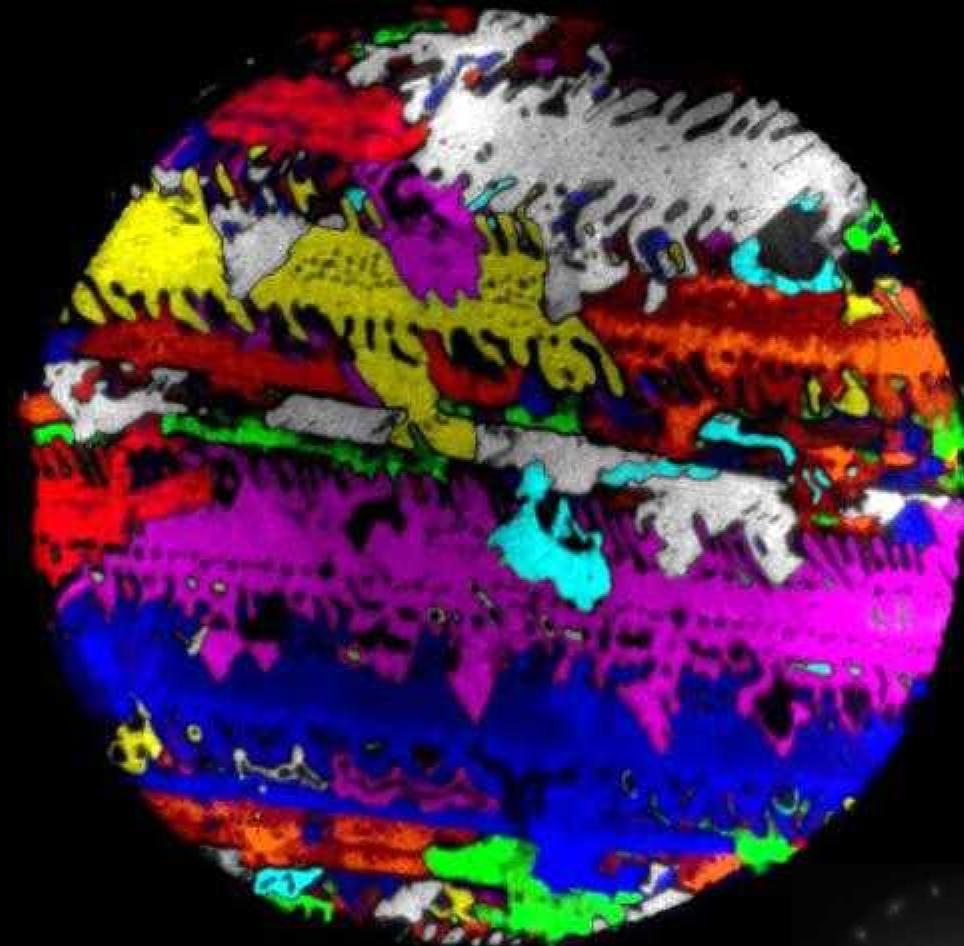
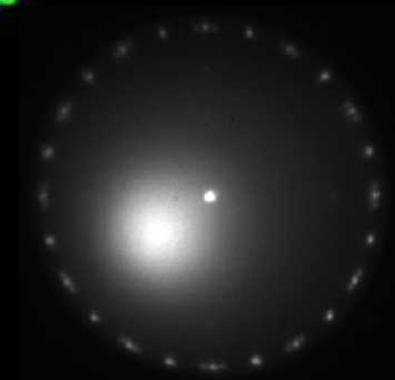




FOV=20μm



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