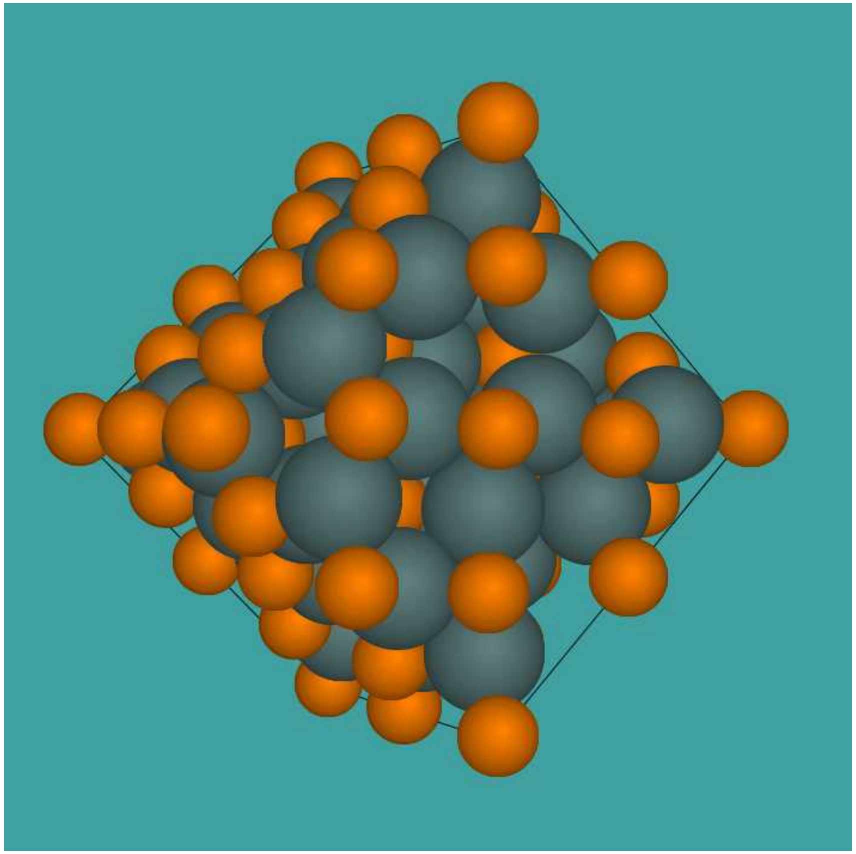
SAND2008-0754P

TEM investigation of oxygen incorporation in ErH_2 films



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Acknowledgements:
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National Nuclear Security Administration

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Erbium hydrides are susceptible to oxide contamination

Erbium hydrides (ErH_2, ErD_2, ErT_2) are of interest for neutron sciences

Driving force for oxidation is very high

$Er(H,D,T)_2$ films may be easily contaminated with erbium oxide Er_2O_3

Here, we will present investigations into how oxygen is incorporated in ErD_2 thin films

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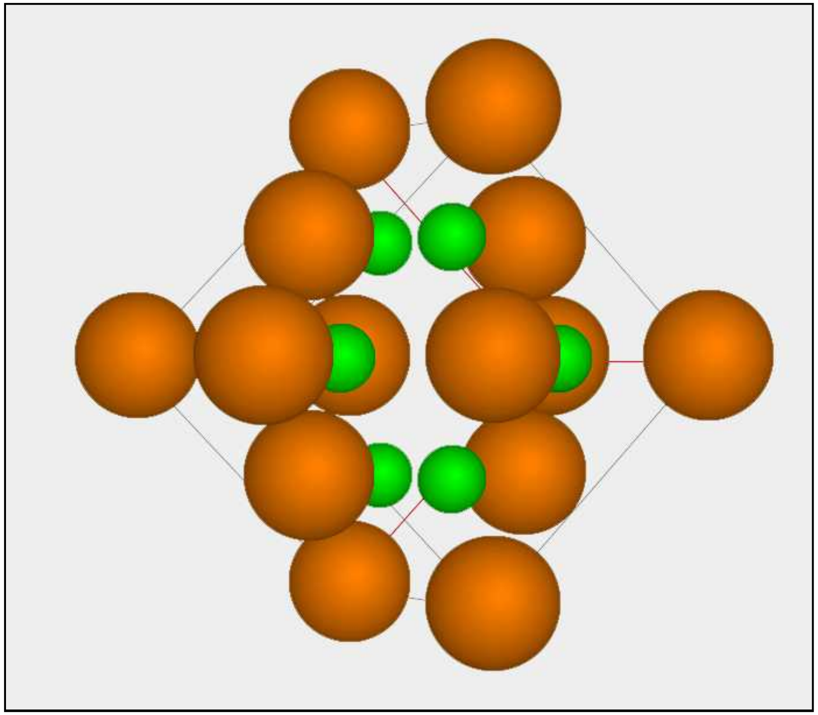
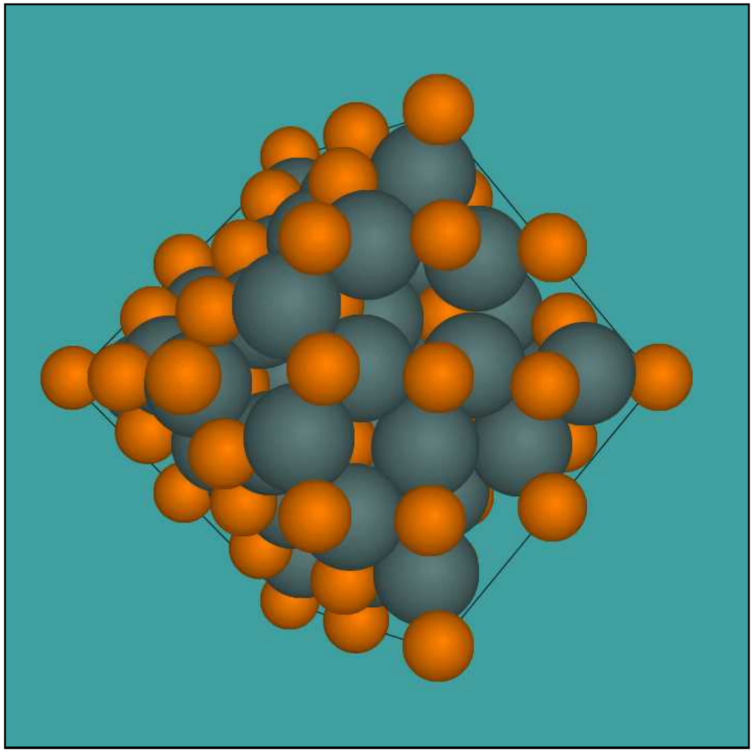
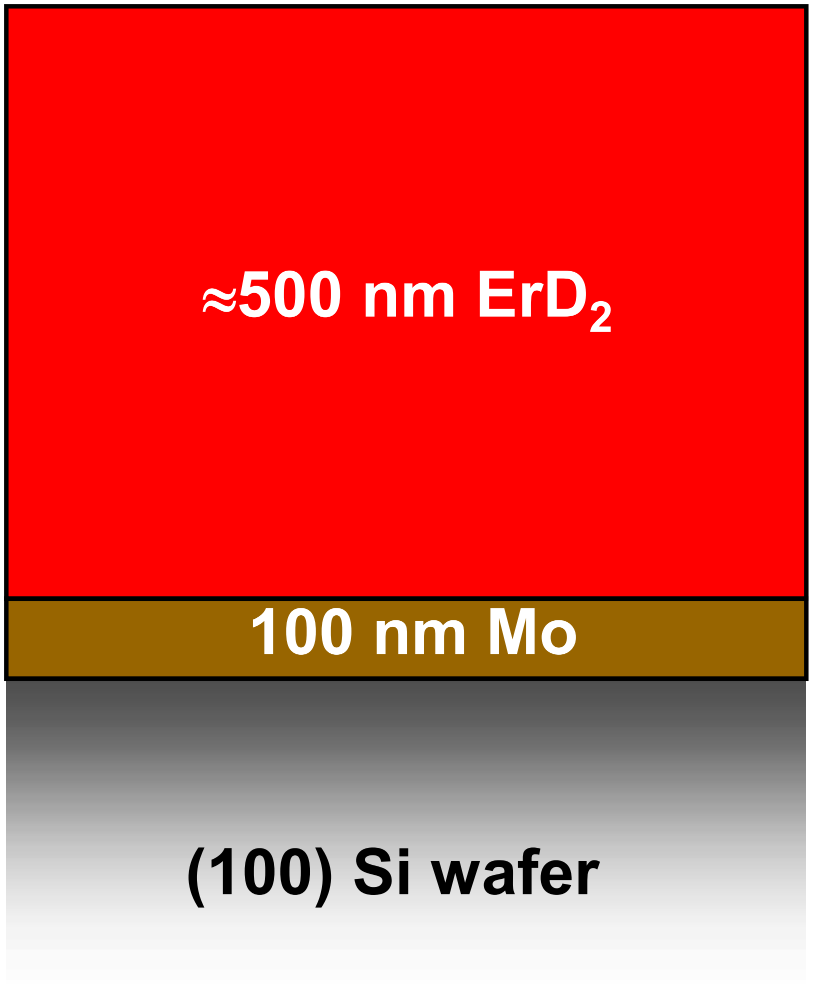
ErH_2: fluorite structured
Er_2O_3: bixbyite structured

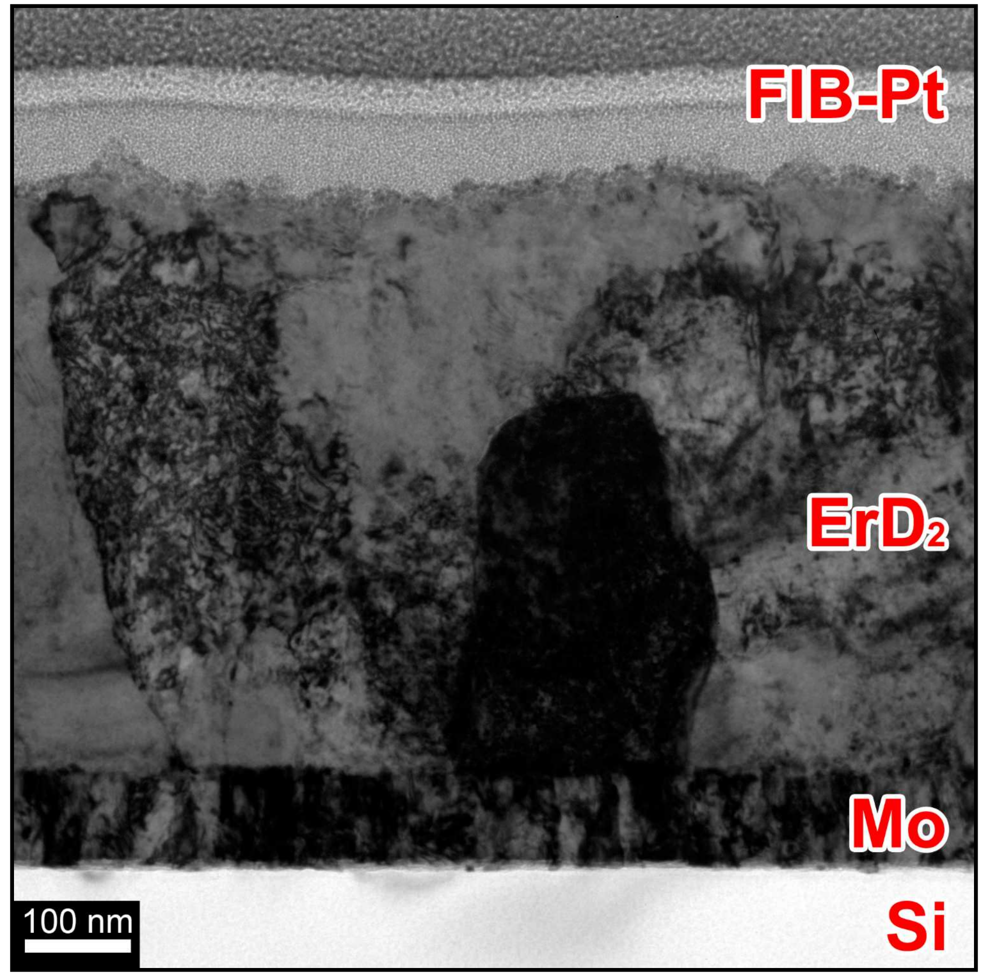
ErD_2	Er_2O_3
	
a_{ErD2}=0.512 nm	a_{Er2O3}=1.054 nm

$a_{Er2O3} / a_{ErD2} \approx 2.06$

Samples are ErD_2 thin films on Mo // Si

Films grown on Mo // Si





TEM samples cut by focused ion beam (FIB)

TEM provides complimentary techniques to examine the ErD_2-Er_2O_3 system

Transmission electron microscopy (TEM) allows:

- **Chemical microanalysis & imaging**
- **Structural imaging**
- **Electron diffraction and crystallography**

…all at nanometer resolution

We will examine oxygen incorporation in ErD_2 films with these techniques

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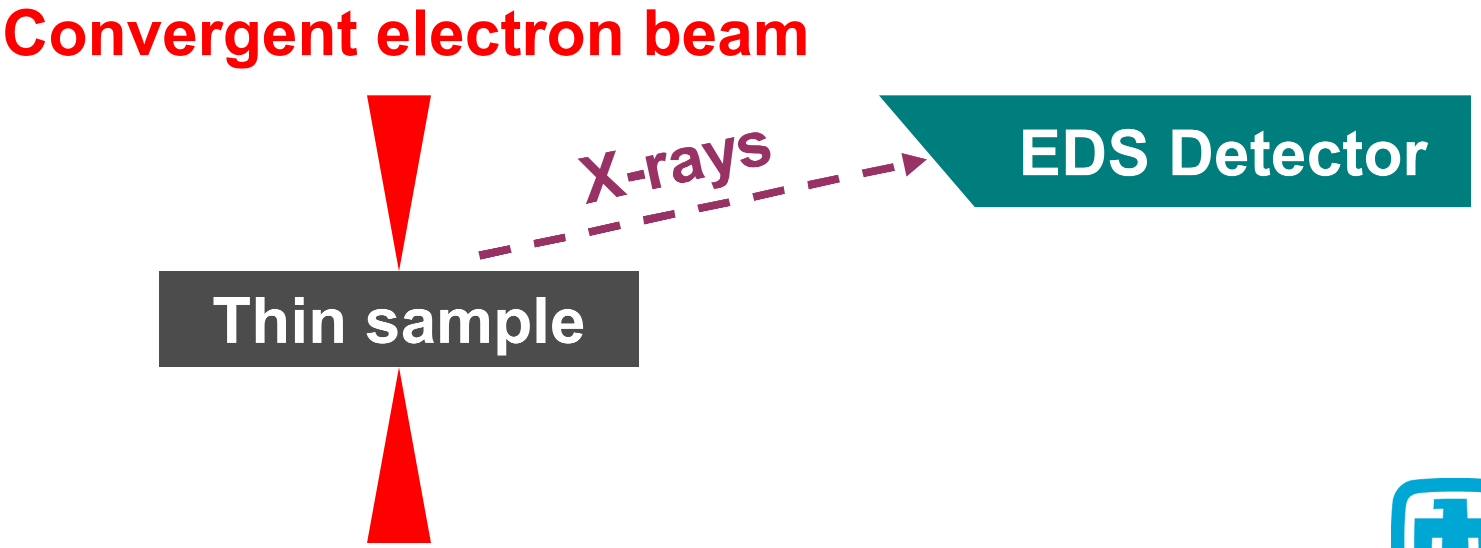
EDS and EFTEM analytical techniques were used

Energy dispersive spectroscopy (EDS) measures X-rays produced when a small electron probe excites the sample

- Oxygen X-ray yield is ≈1 per 1000 ionizations
- Low energy (525 eV) oxygen X-ray easily absorbed

→Poor signal-to-noise achieved for oxygen via EDS



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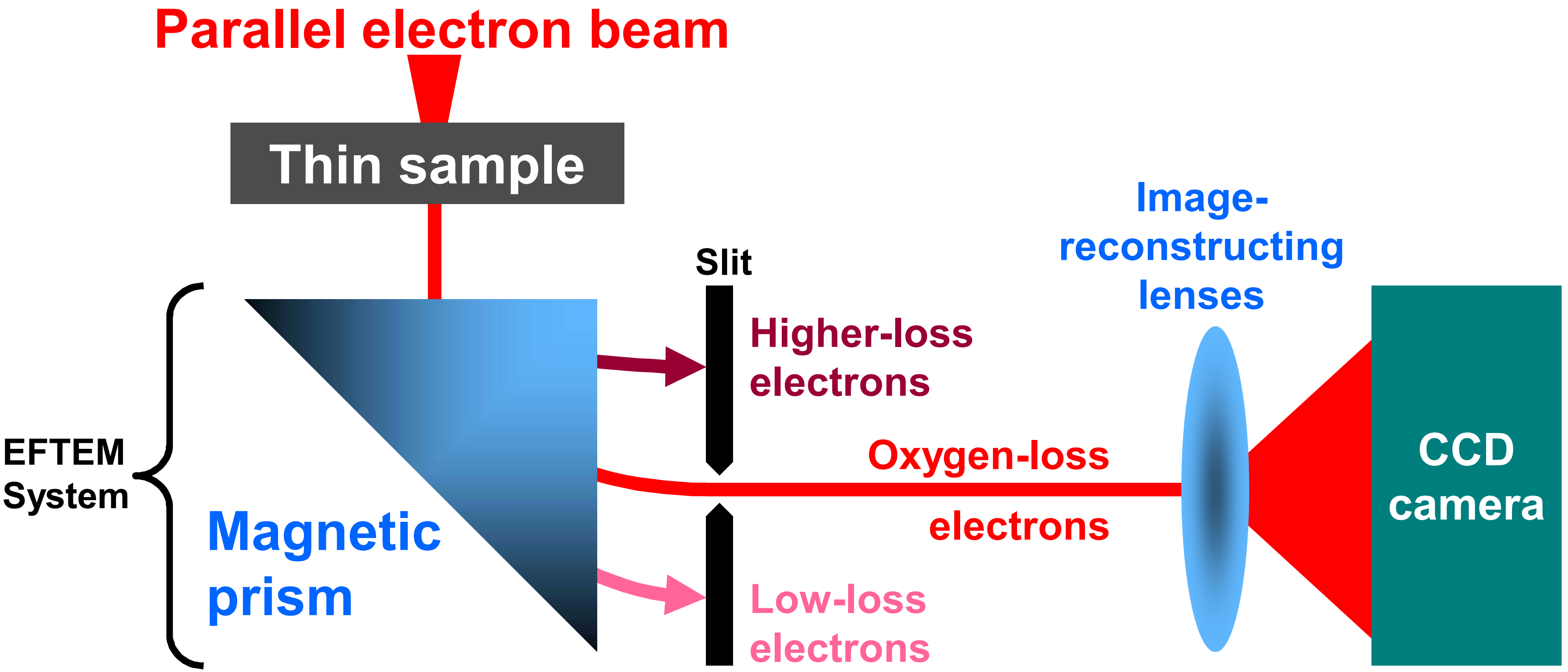
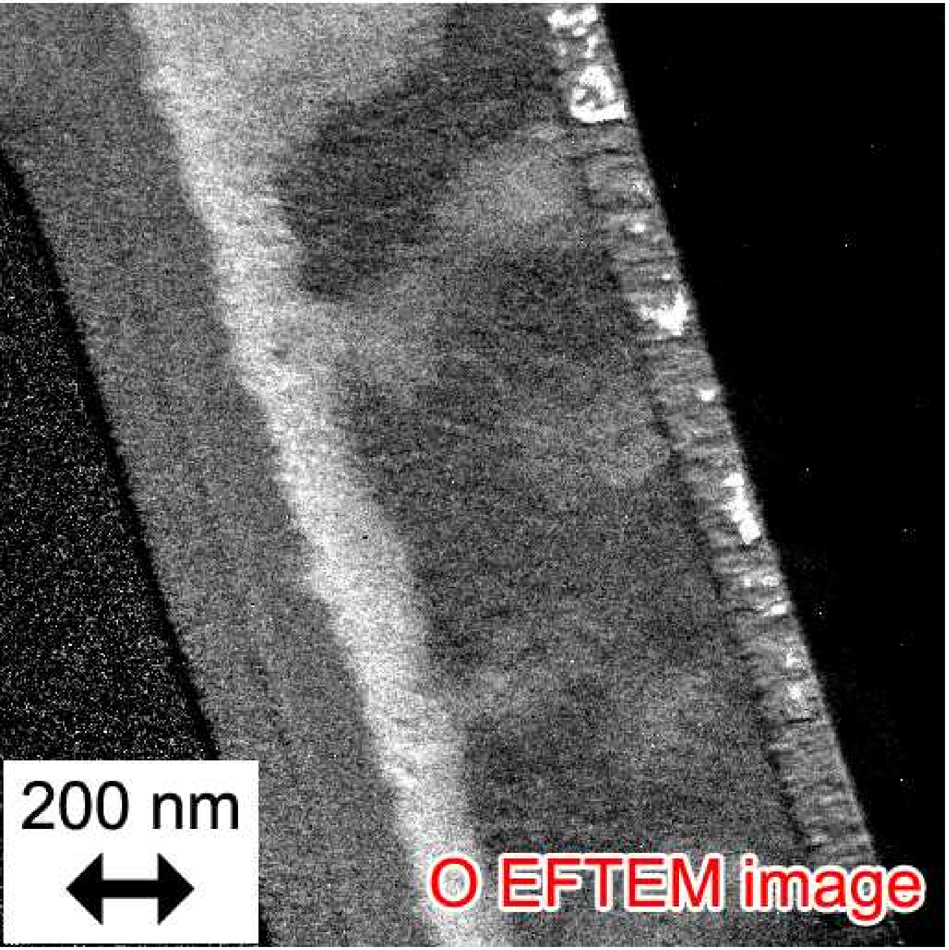
EDS and EFTEM analytical techniques were used

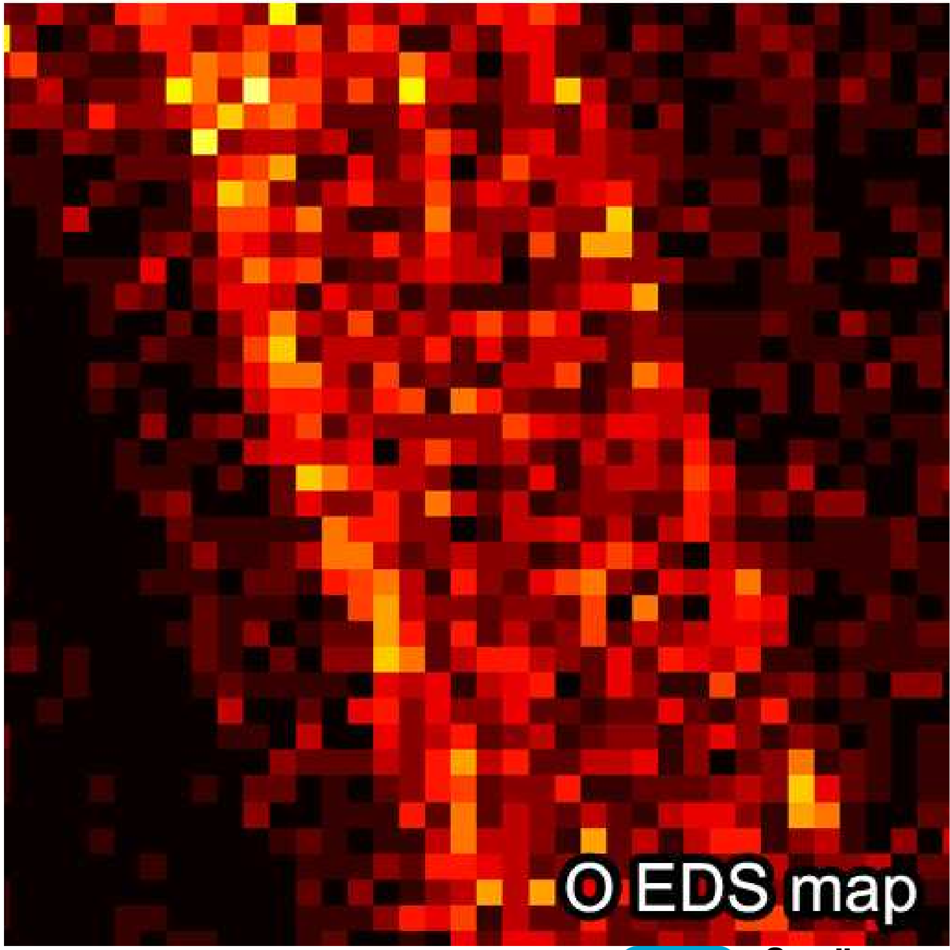
Energy-filtered TEM (EFTEM) maps areas where electrons loose energy by ionizing oxygen atoms

→EFTEM is the method of choice for mapping low-Z elements in TEM

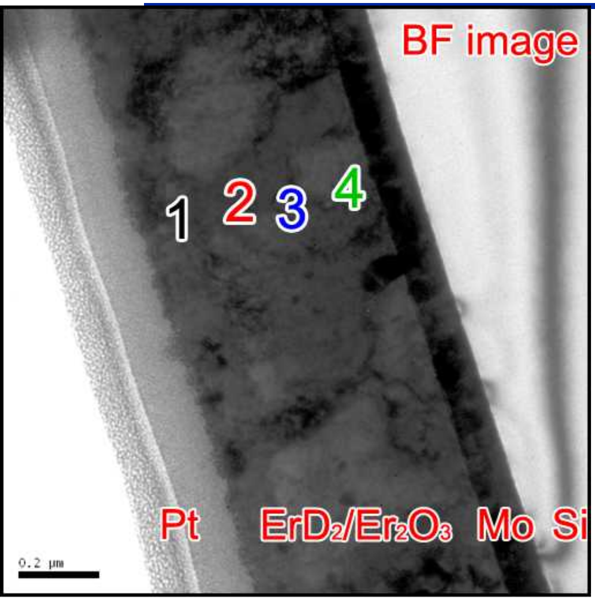


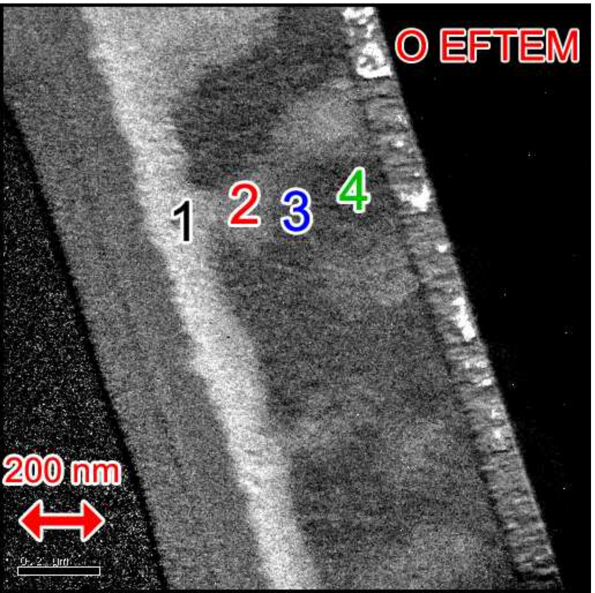
EFTEM delineates oxides more clearly than EDS

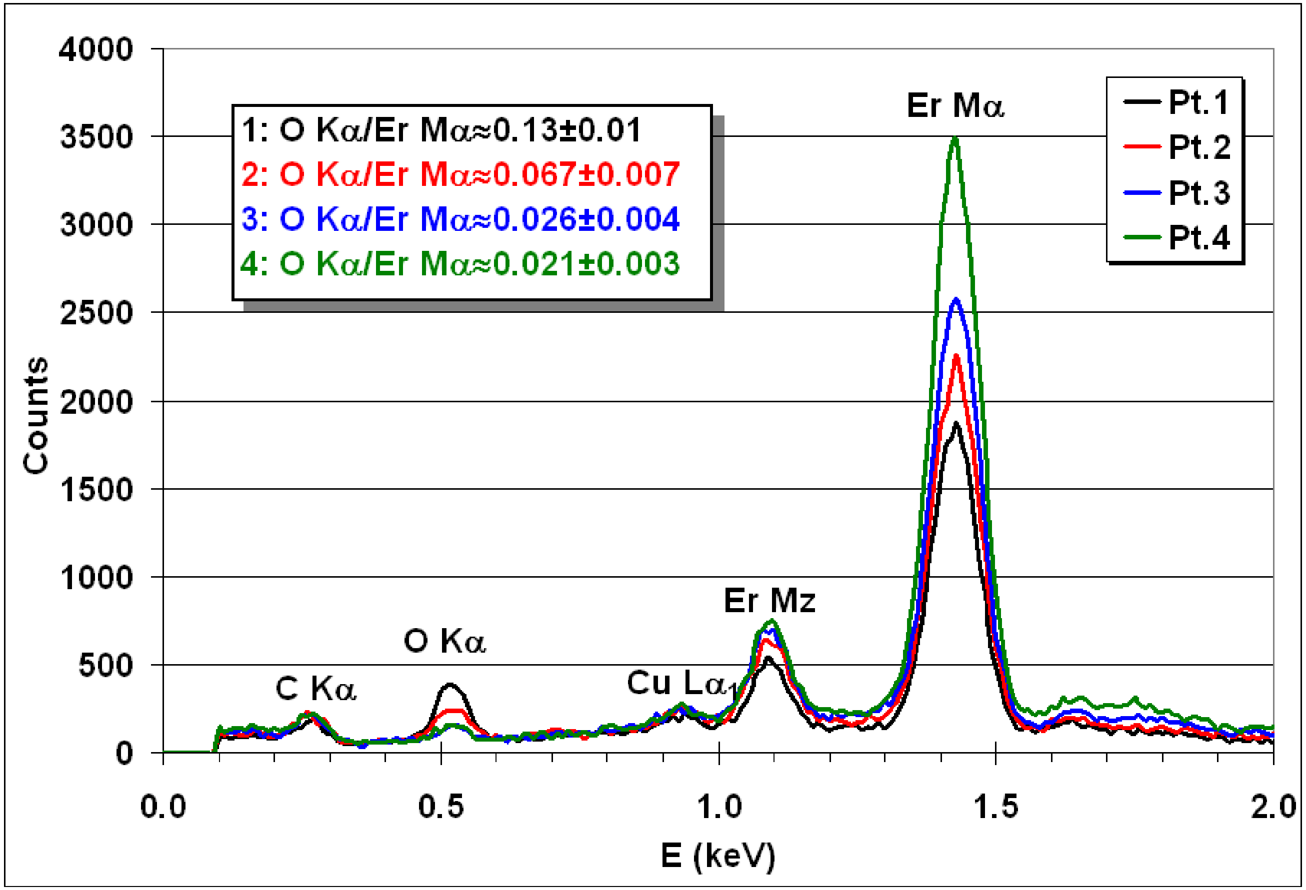




However, EDS point spectra can confirm the identity of an area chosen by EFTEM







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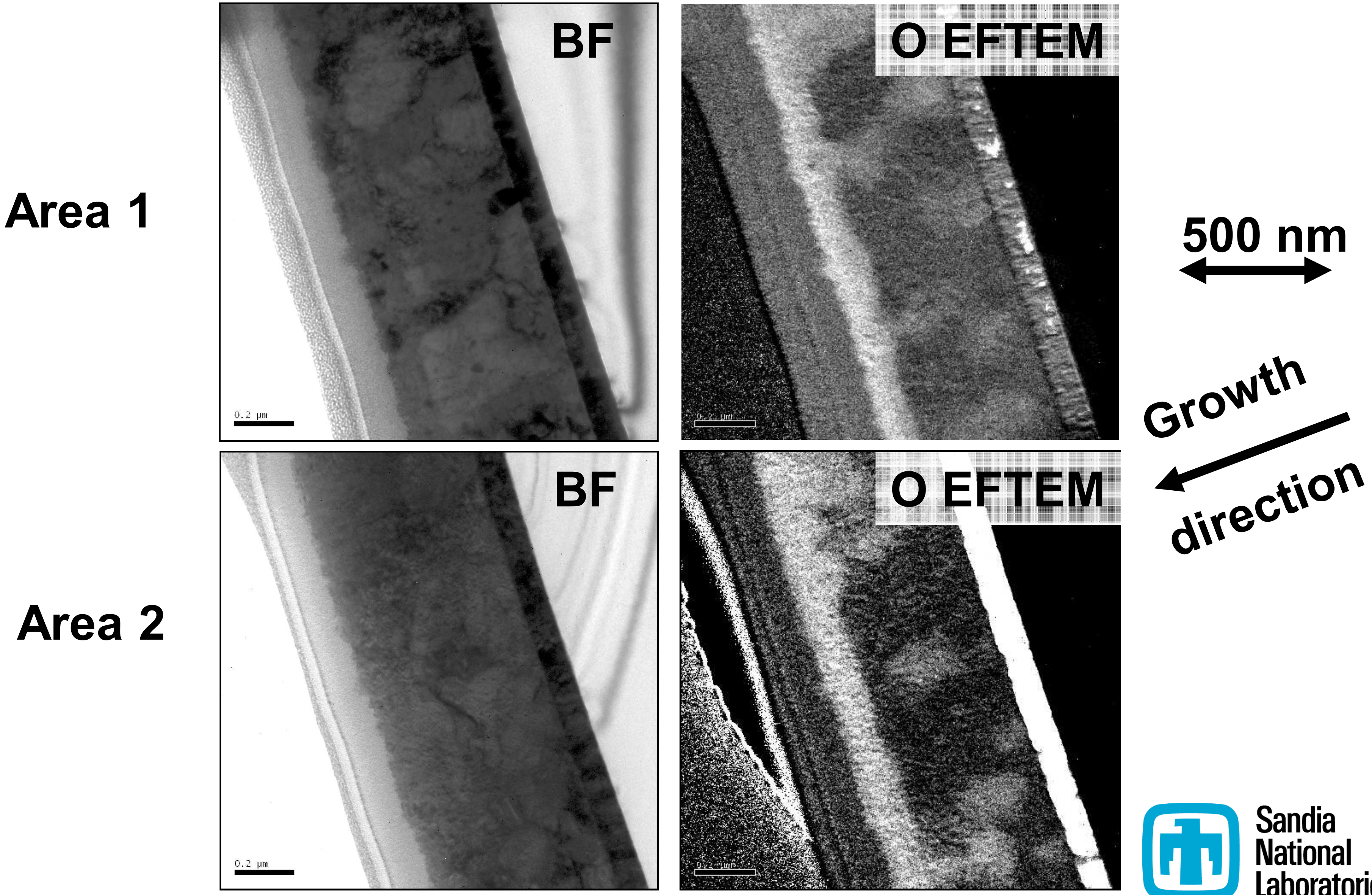
EFTEM indicates surface oxides and penetration into the film



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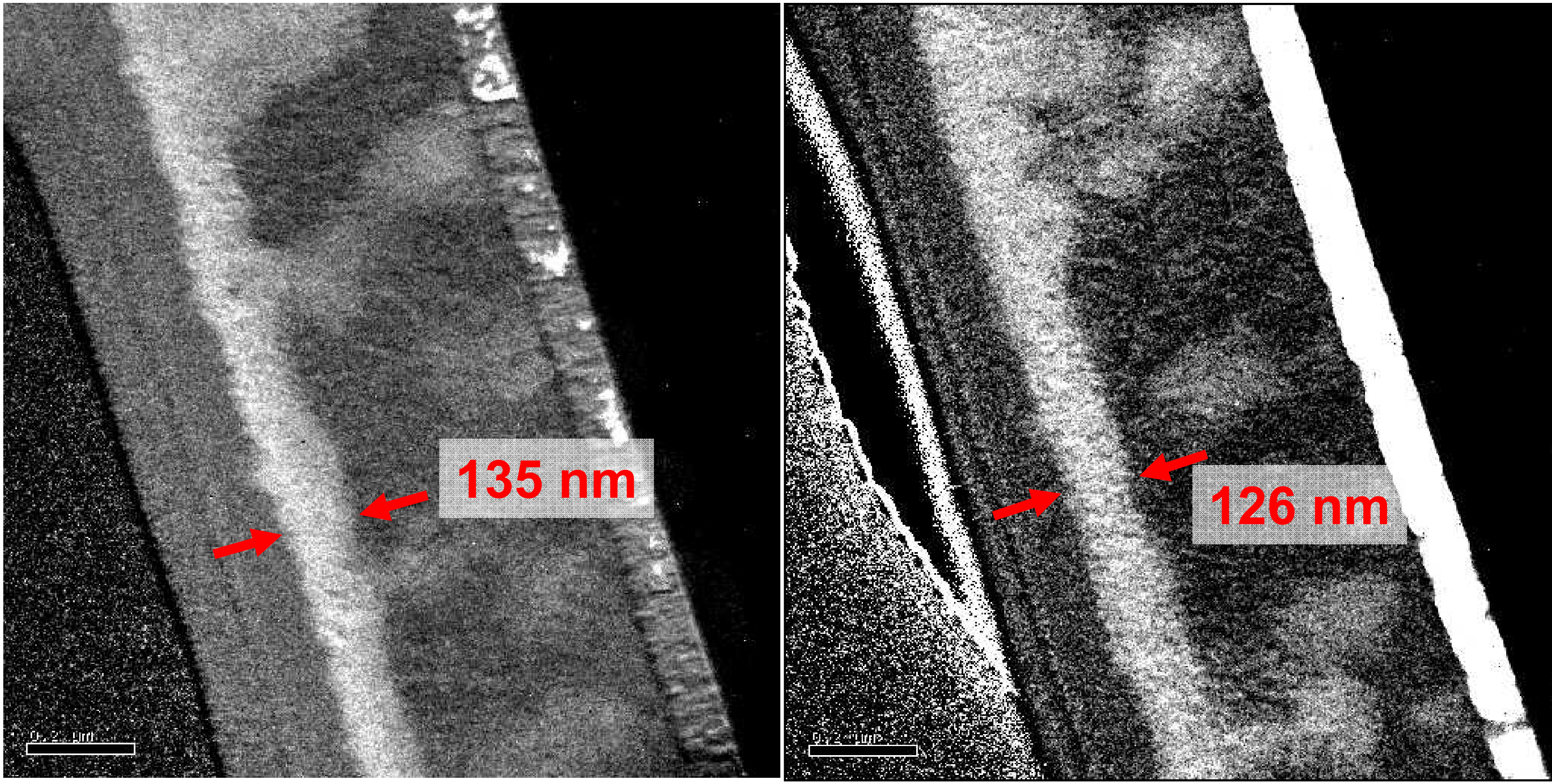
In this sample, surface oxides appear to be ≈100 nm thick



200 nm

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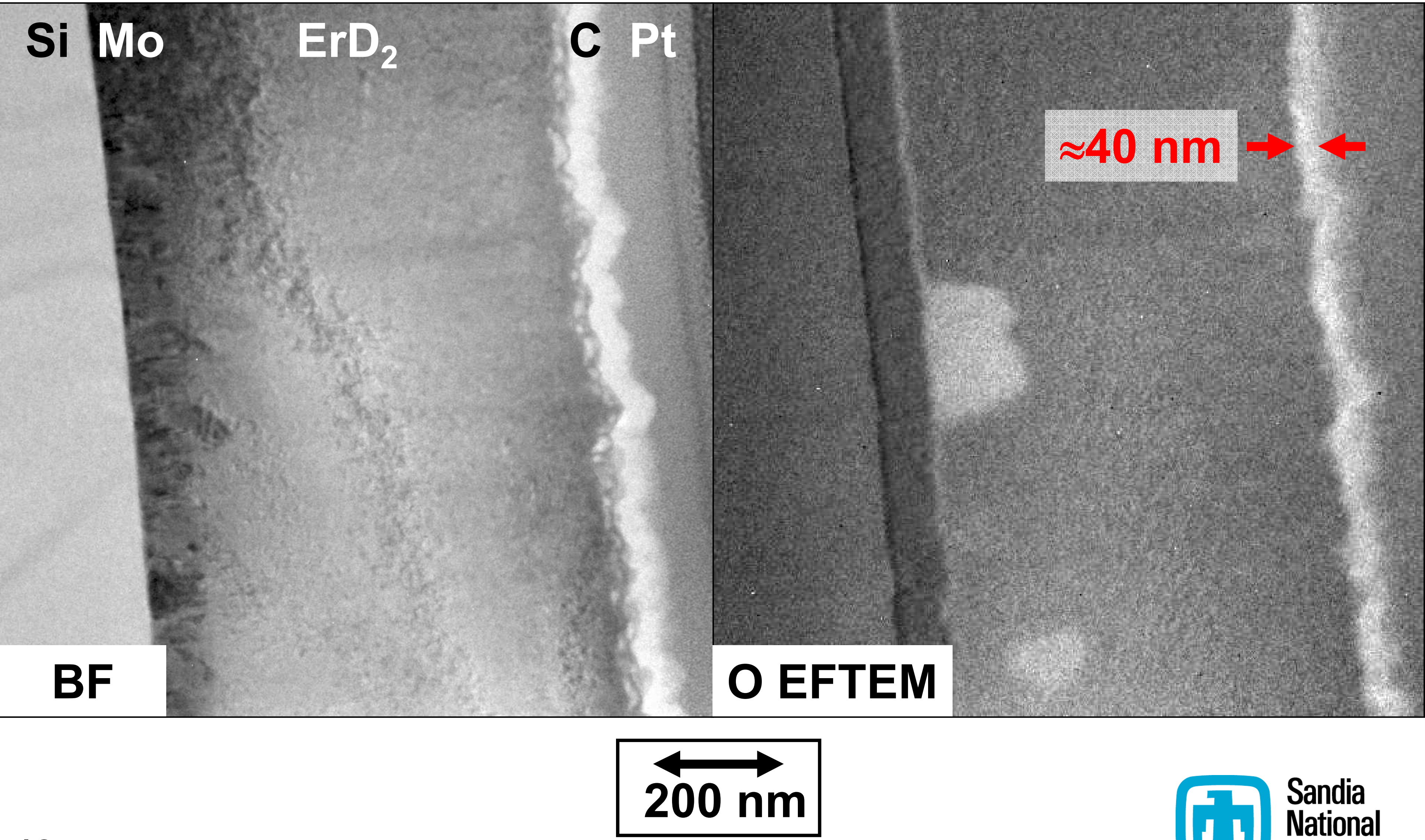
In other samples, fewer large oxides and 30-40nm surface oxide



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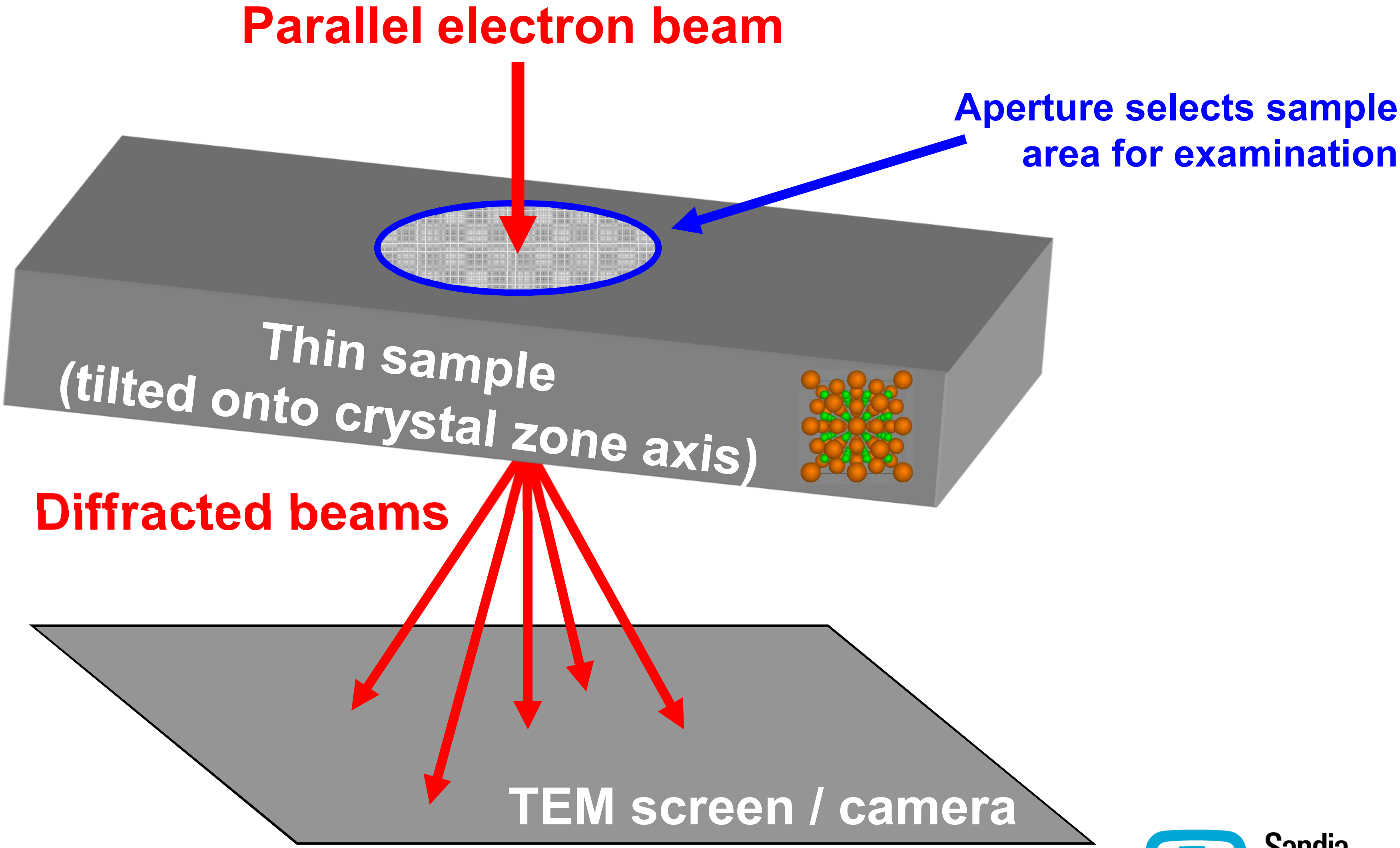
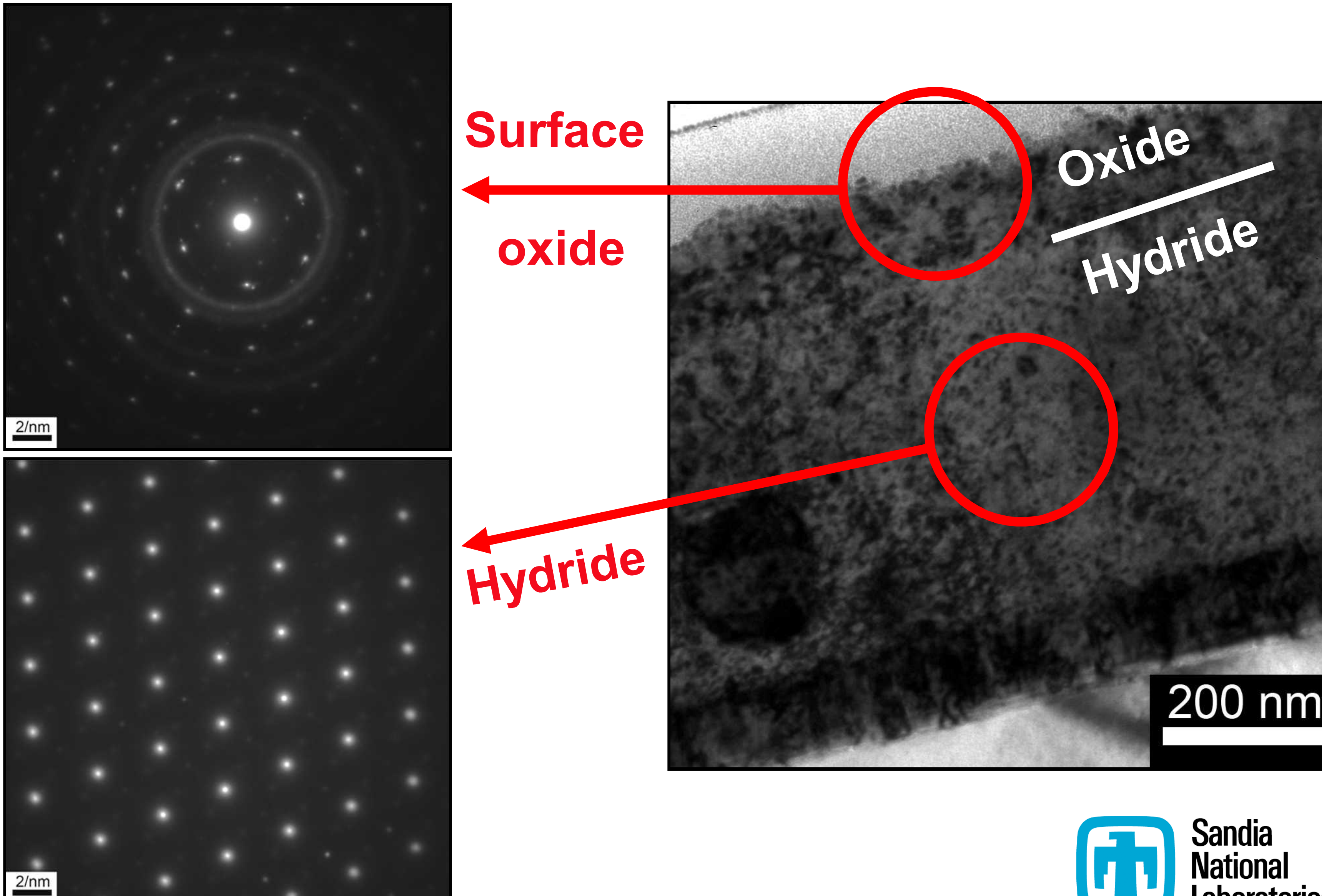
Selected-area electron diffraction (SAD) allows us to examine crystallography



We can use diffraction to verify crystallography of the layers



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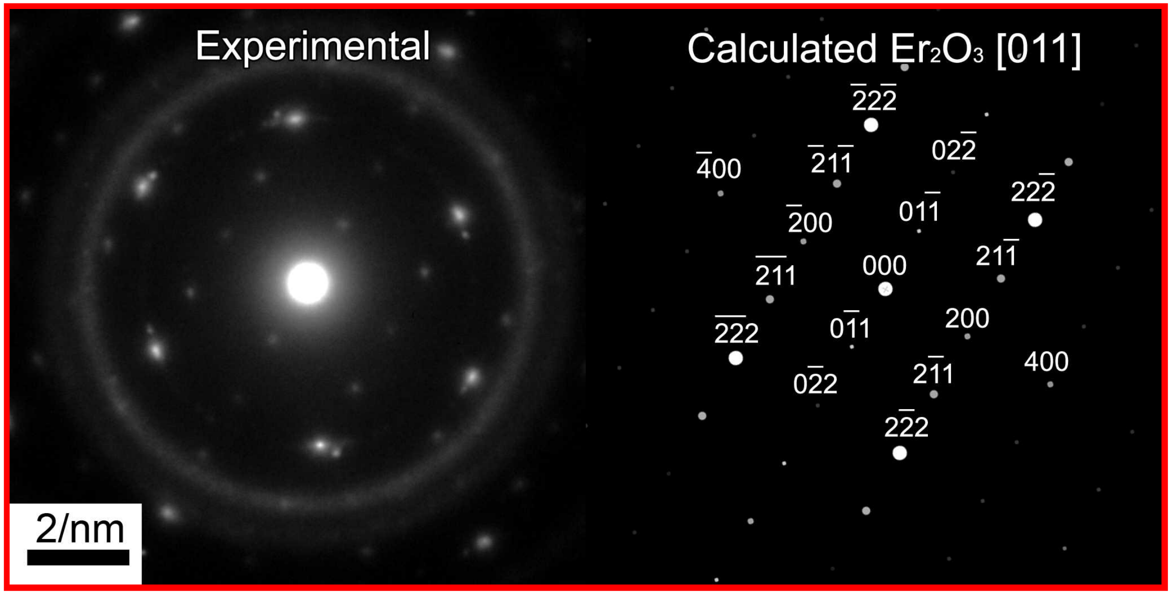
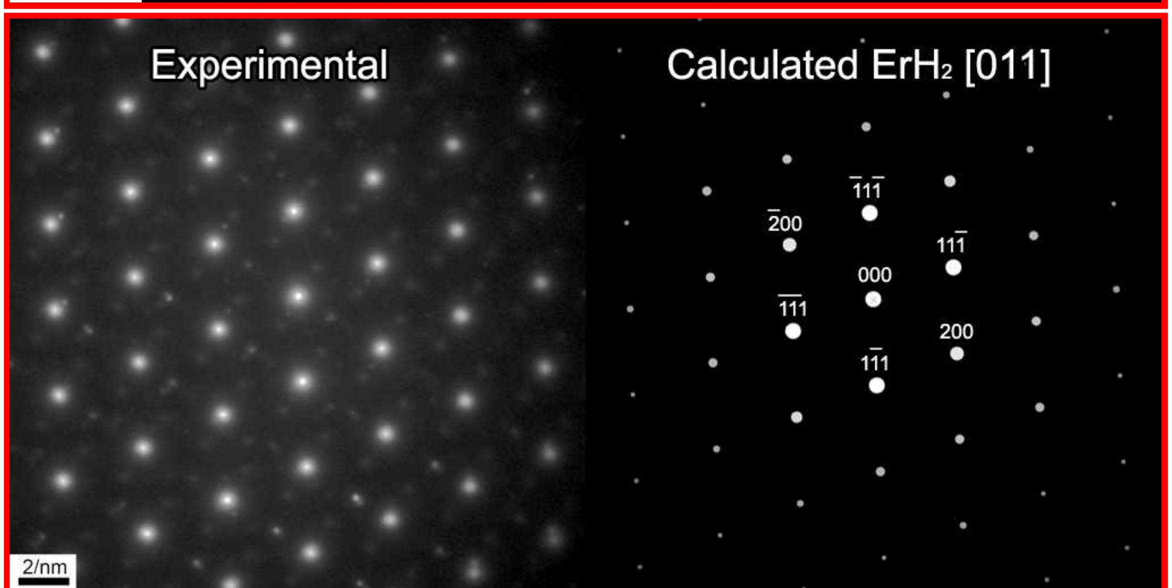
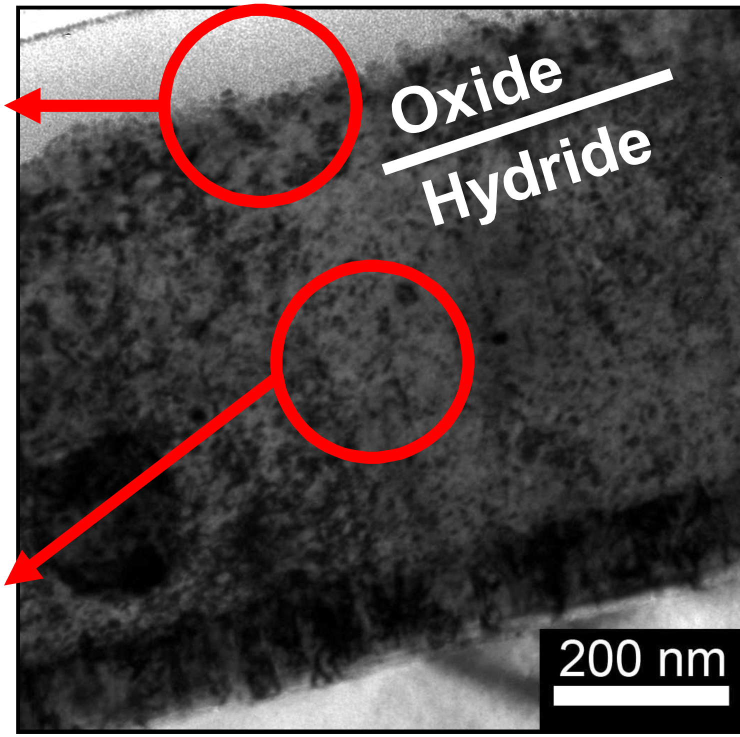
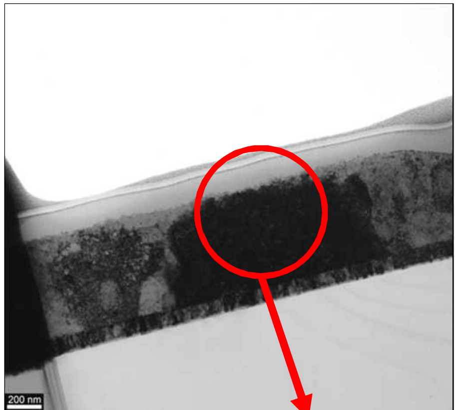
Diffraction patterns confirm EFTEM phase identification

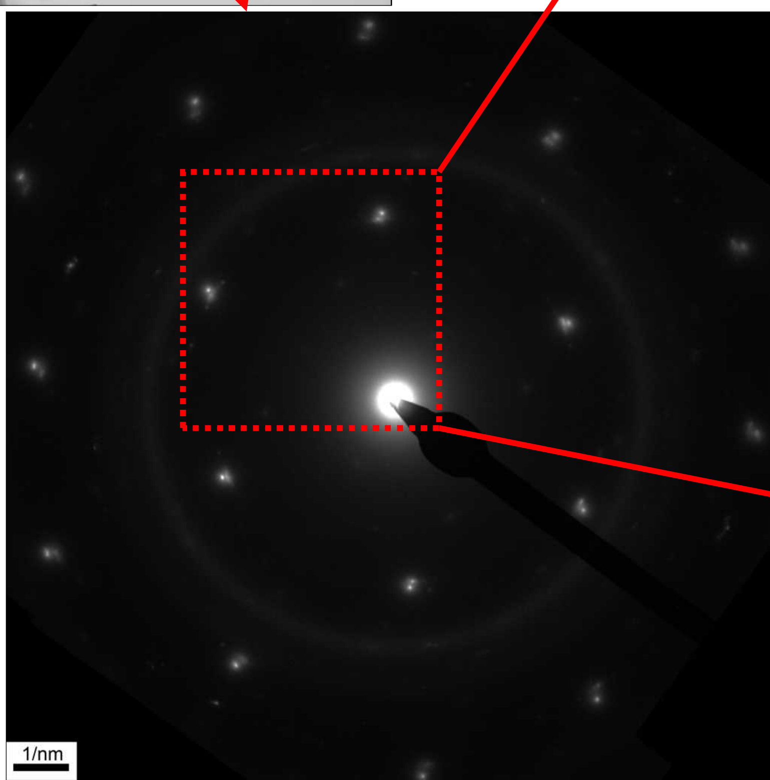


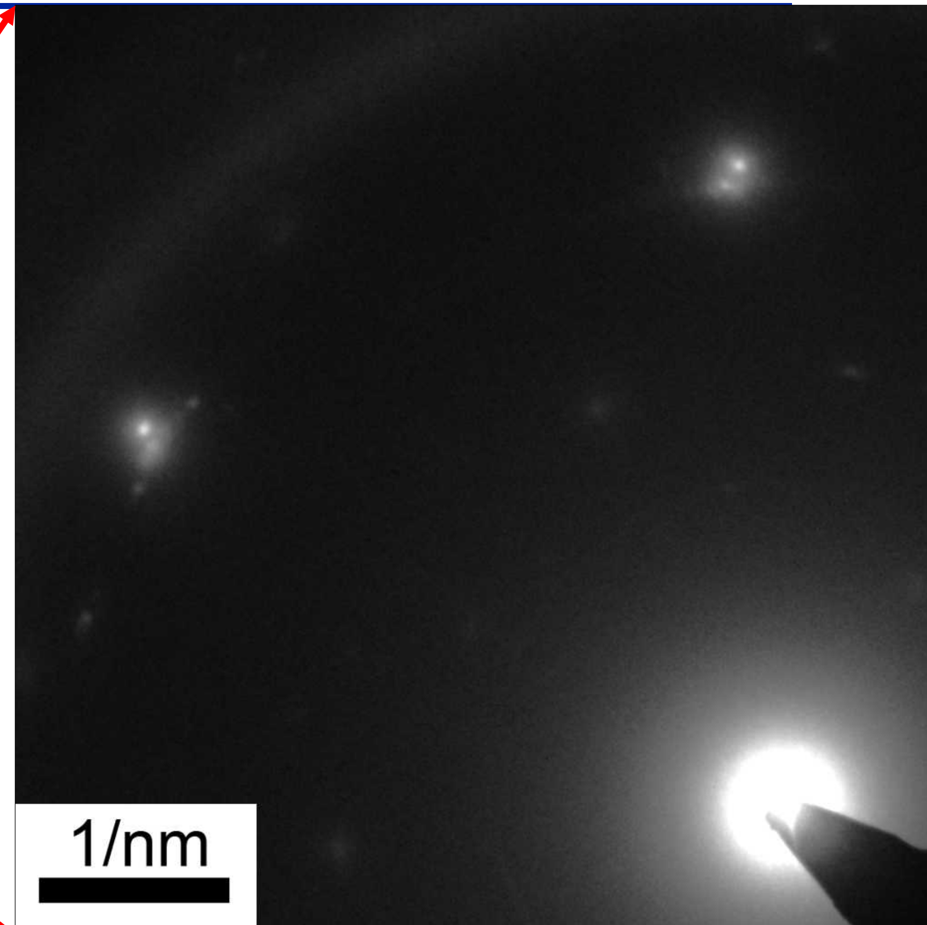




Diffraction shows hydride and oxide have epitaxial orientation







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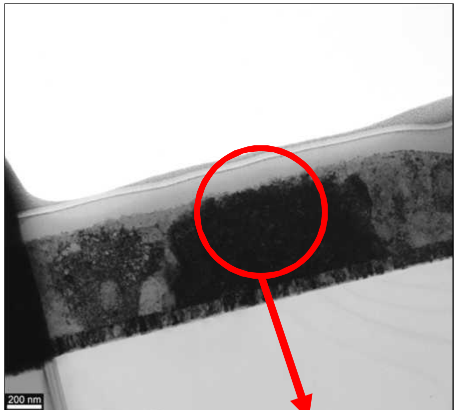
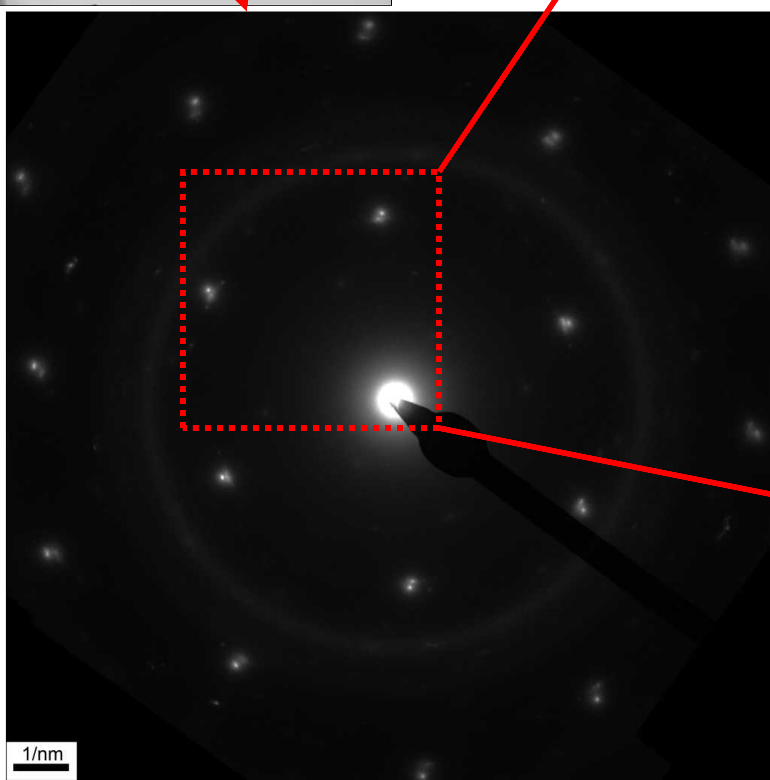
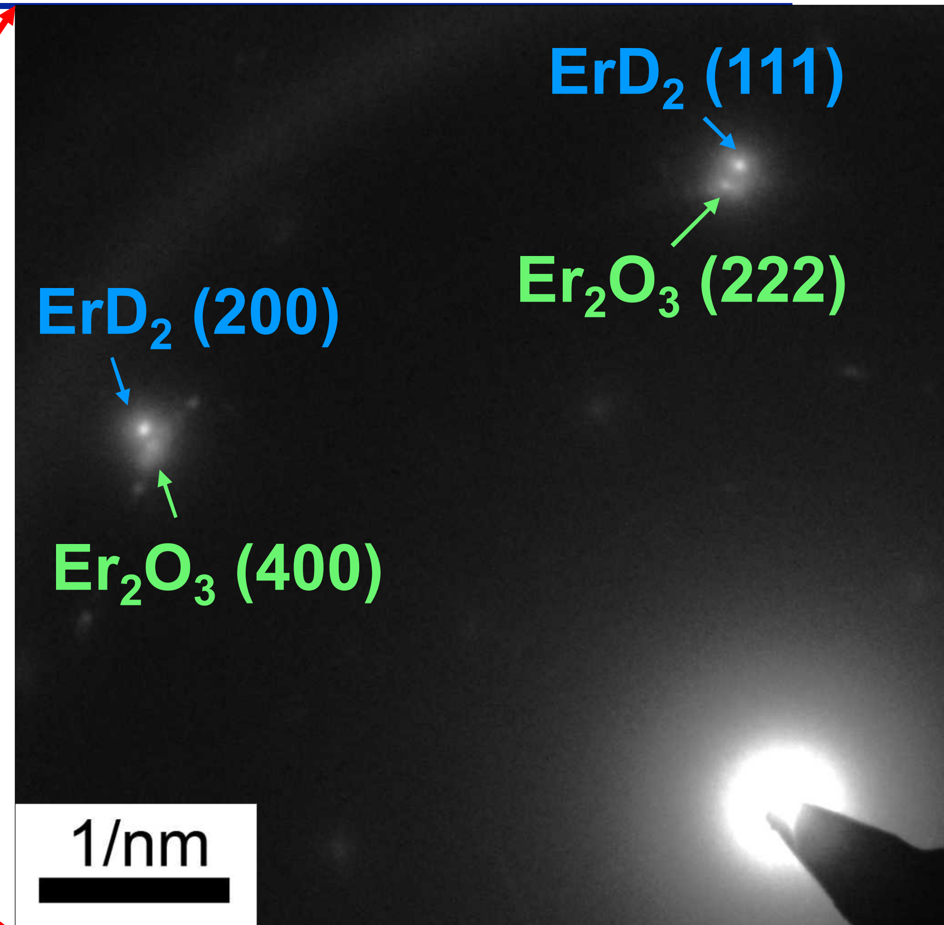
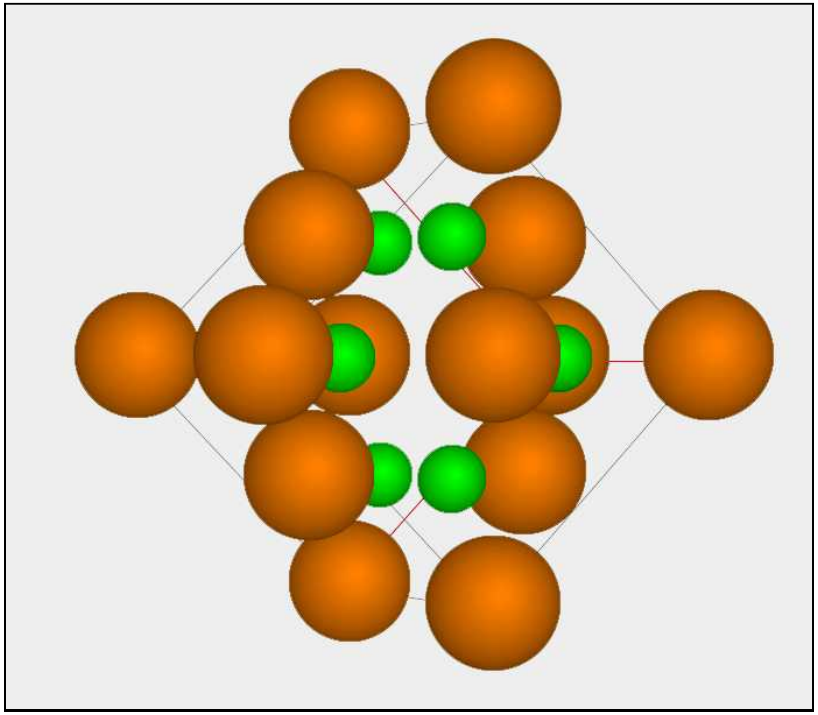
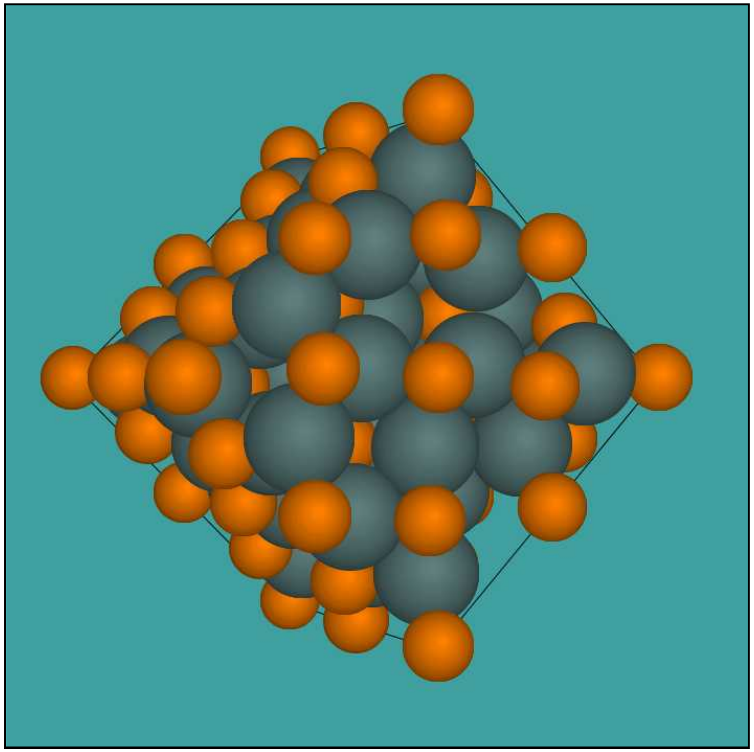






Near-integral lattice mismatch probable cause for epitaxy

ErD_2	Er_2O_3
	
a_{ErD2}=0.512 nm	a_{Er2O3}=1.054 nm

$a_{Er2O3}/a_{ErD2} \approx 2.06$

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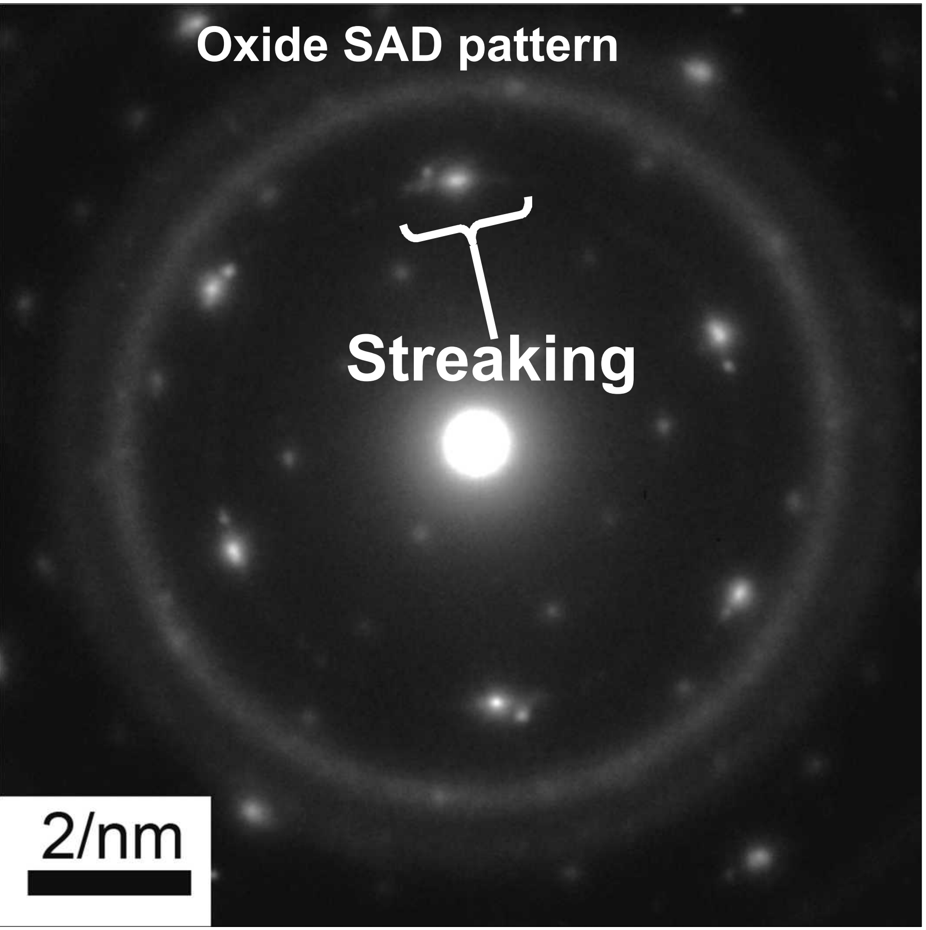
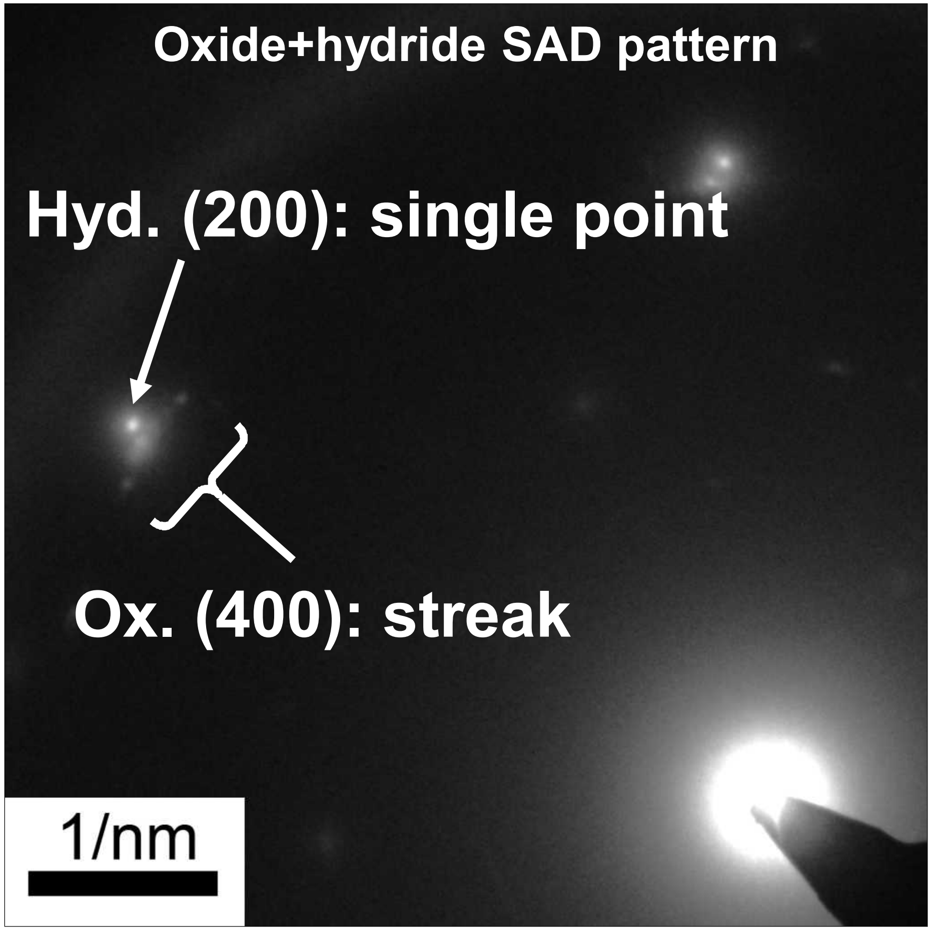
Streaking in oxide SADP indicates highly textured subgrains, not a single crystal





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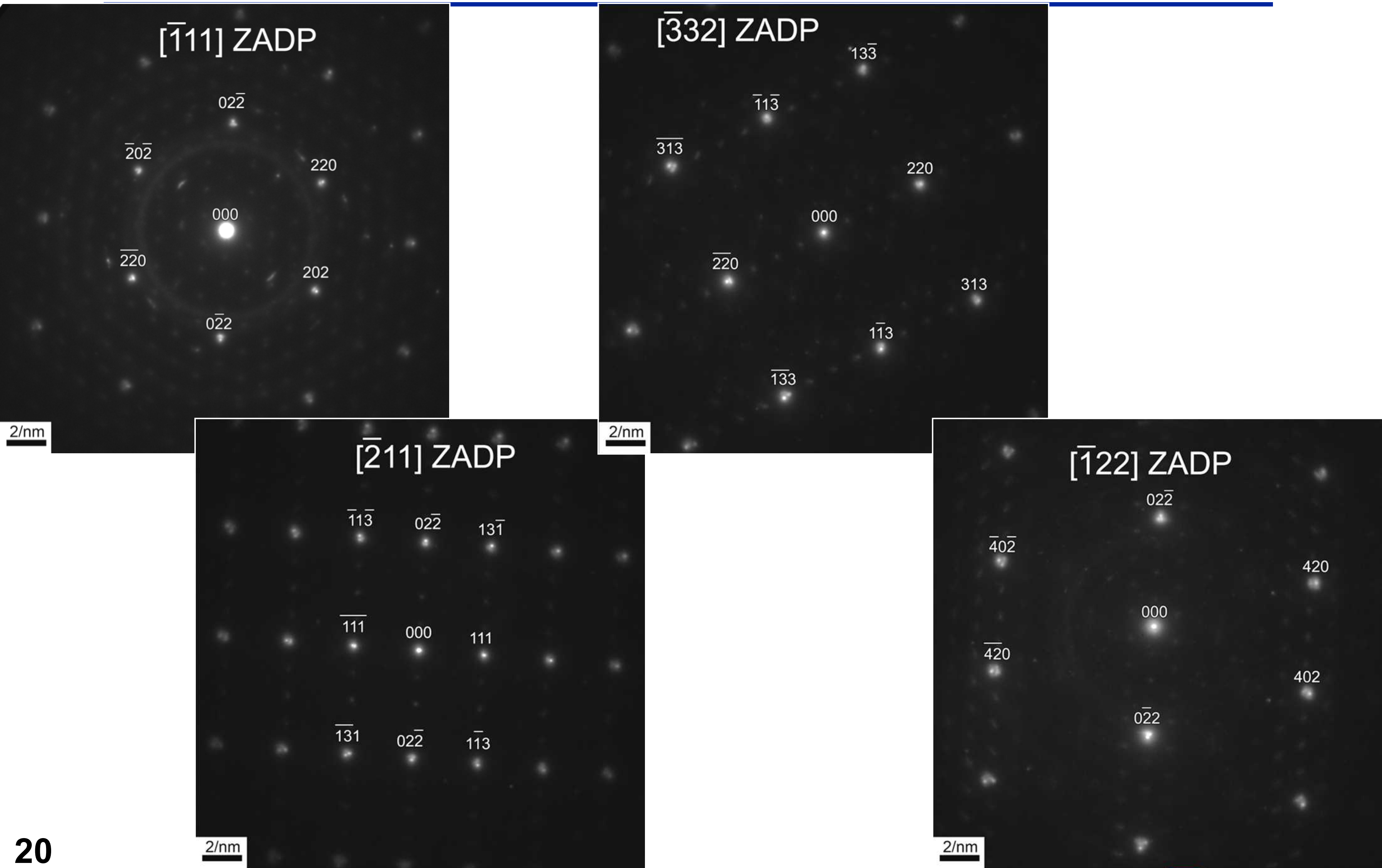
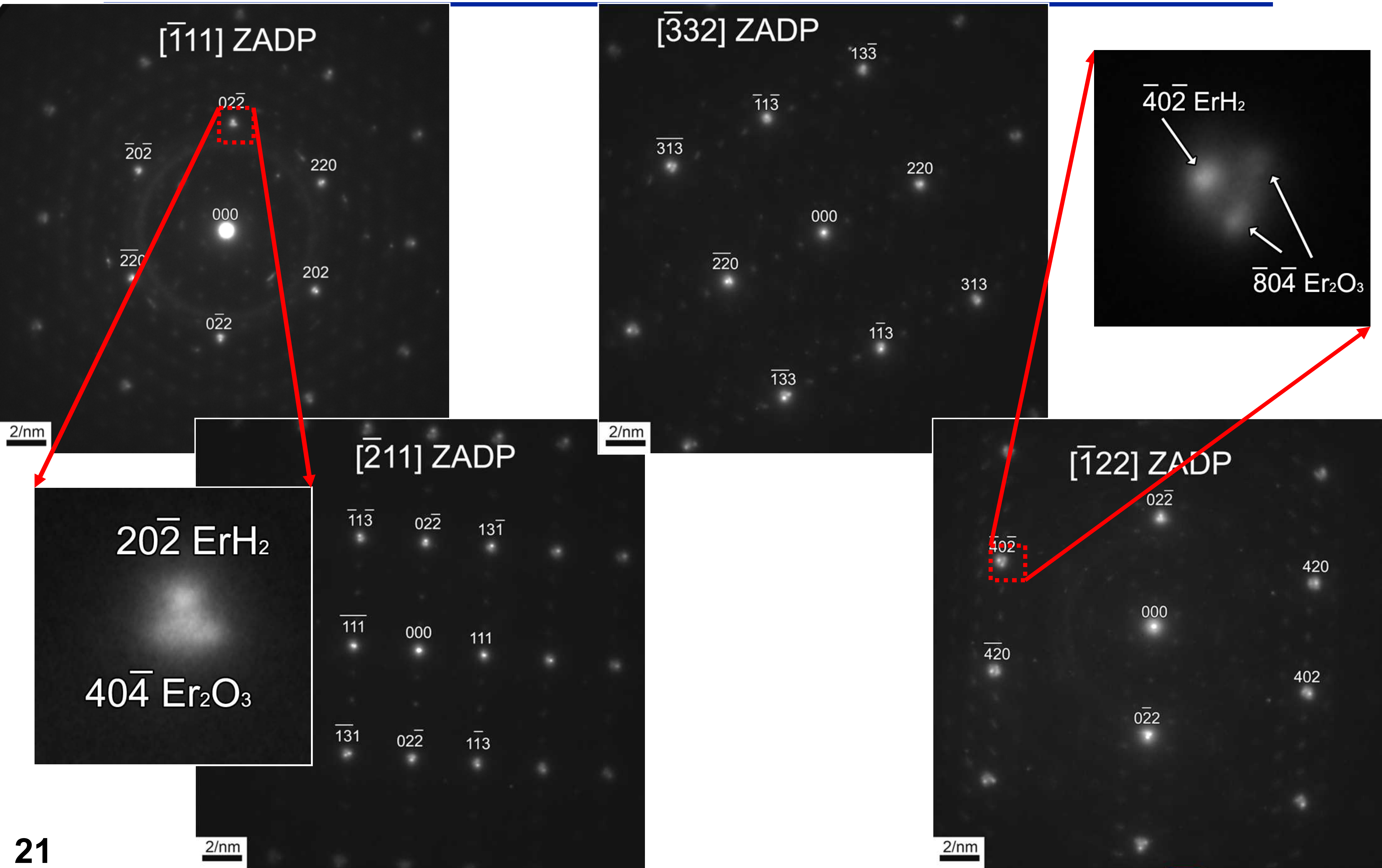
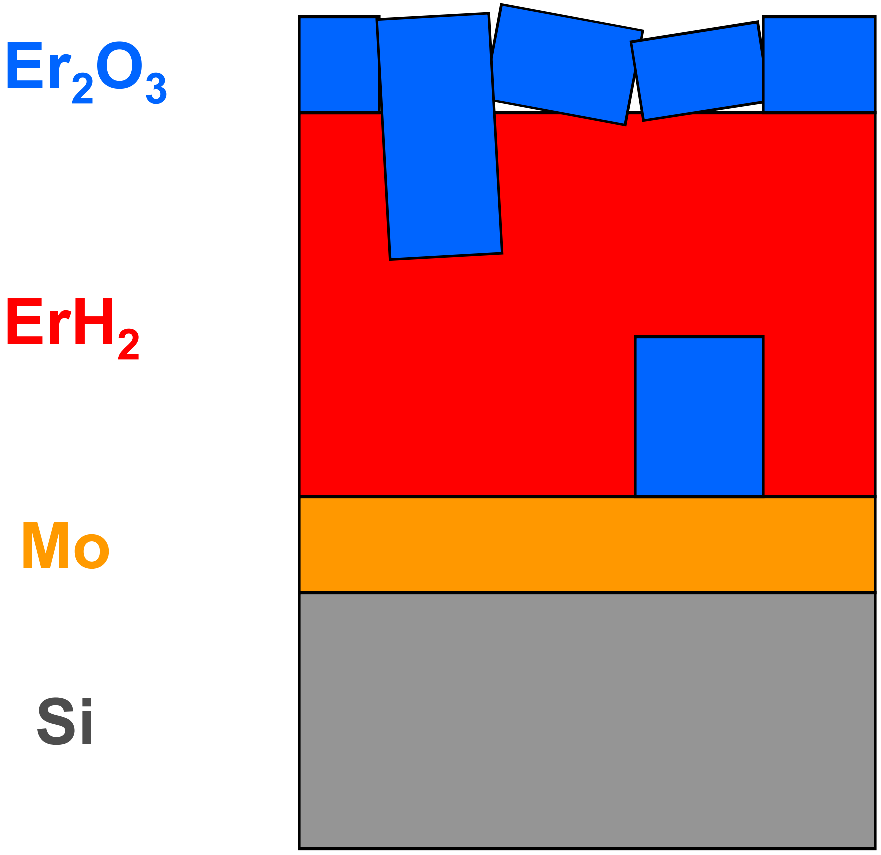
Different zone axes indicate a cube-on-cube orientation



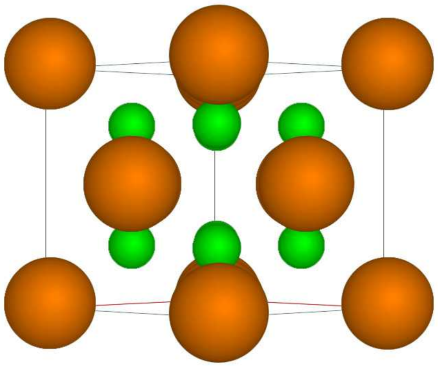
Different zone axes indicate a cube-on-cube orientation

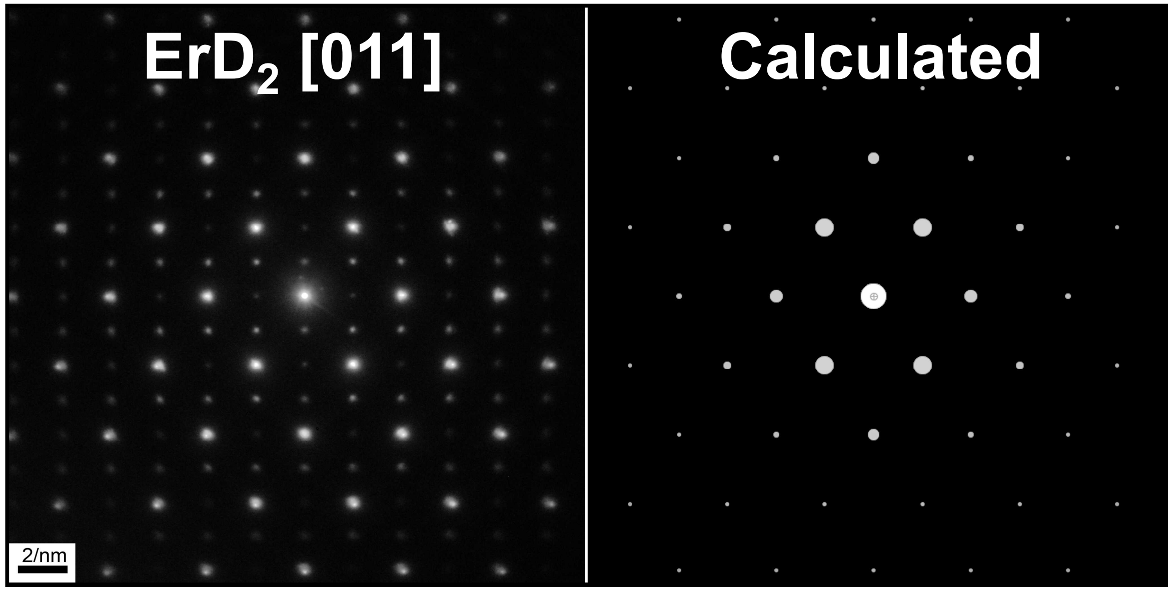


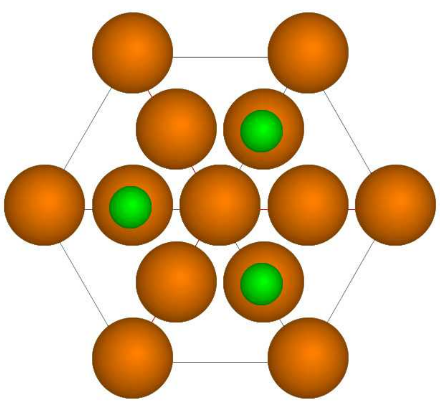
Oxides seen at the surface and penetrating within the film

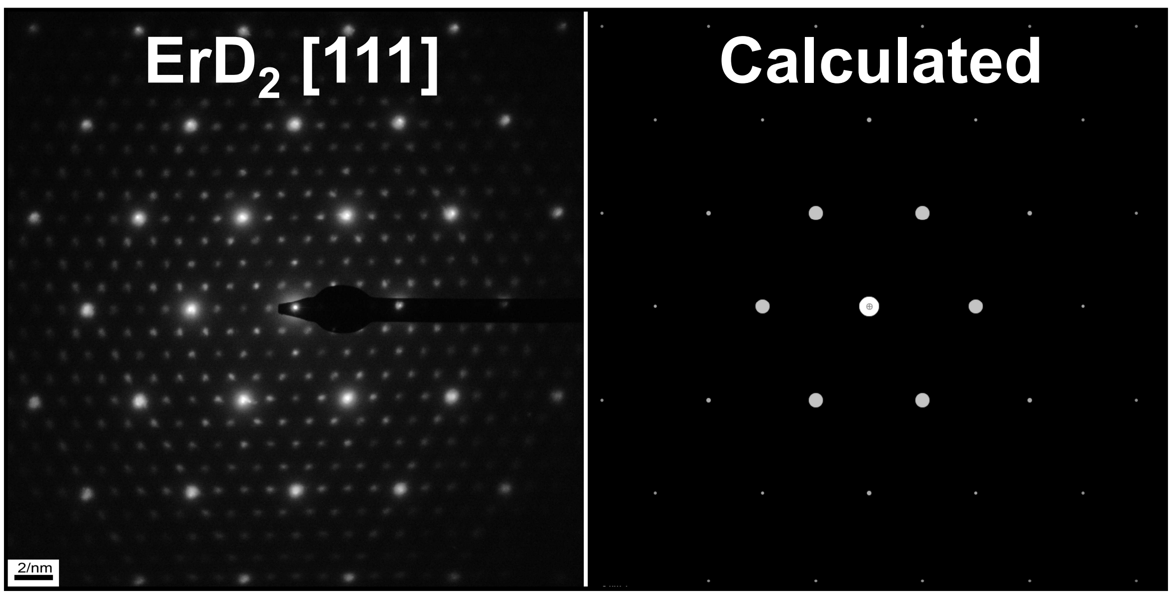


We observe satellite spots that are not predicted from the ErD_2 structure



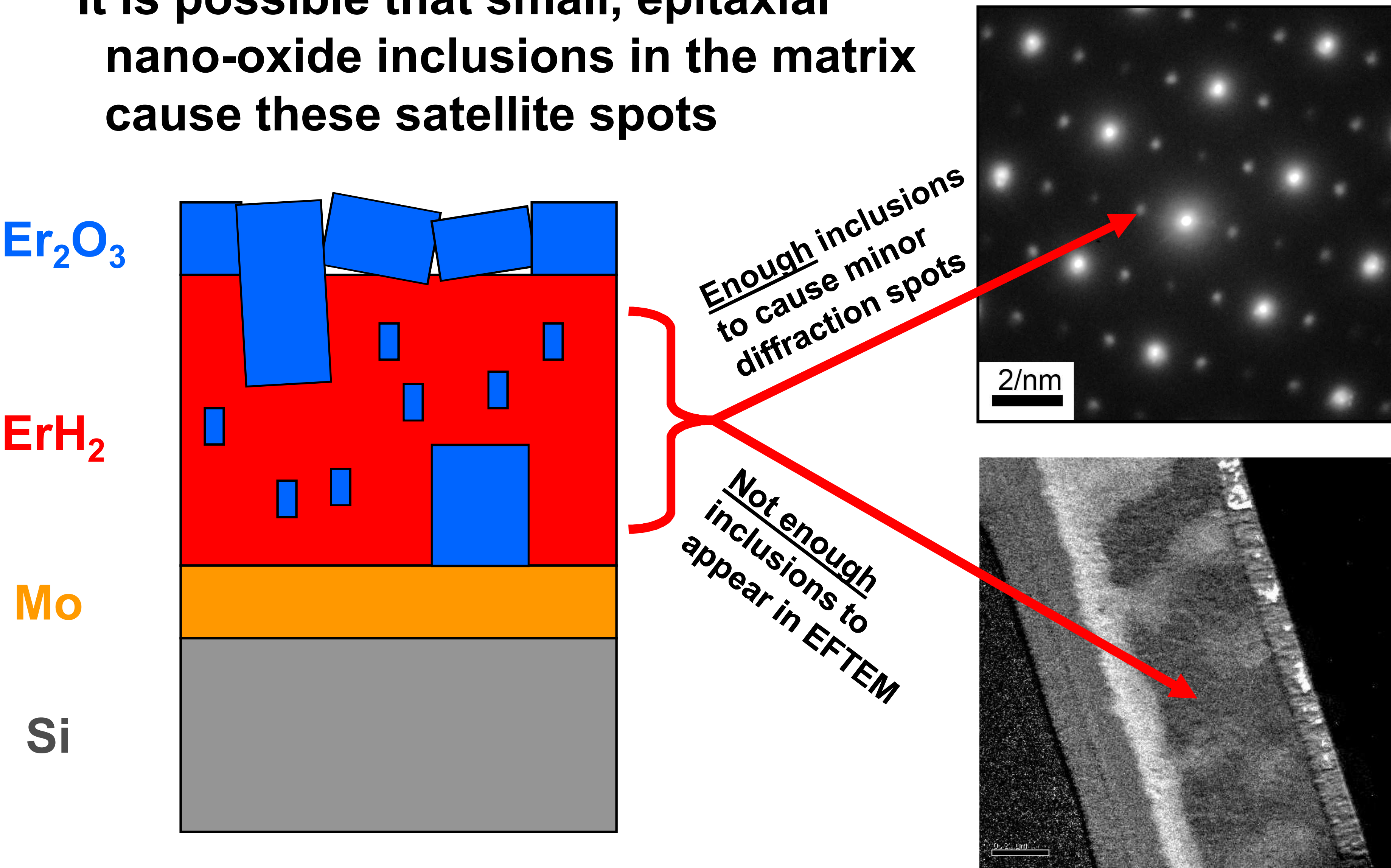






We have previously hypothesized these spots are due to double diffraction

- It is possible that small, epitaxial nano-oxide inclusions in the matrix cause these satellite spots



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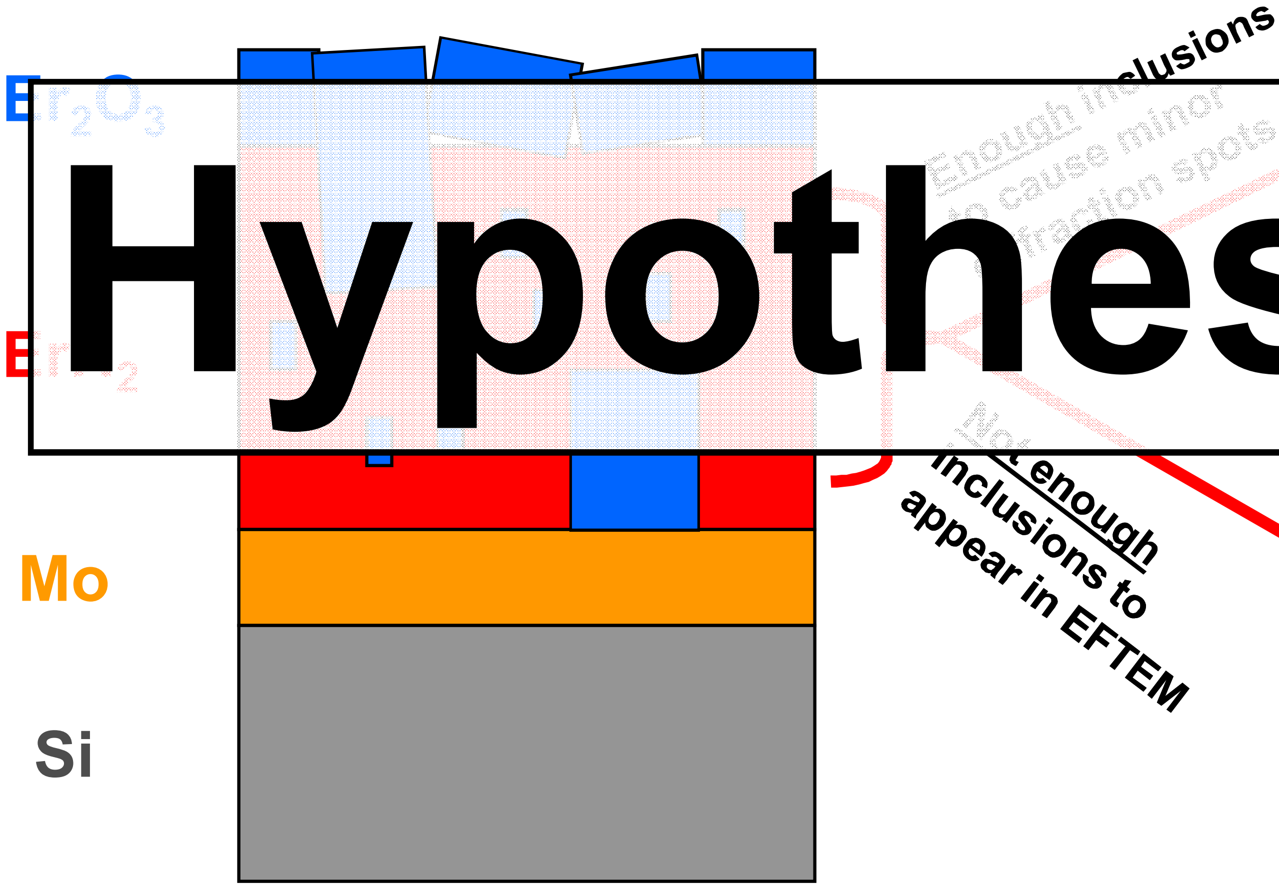
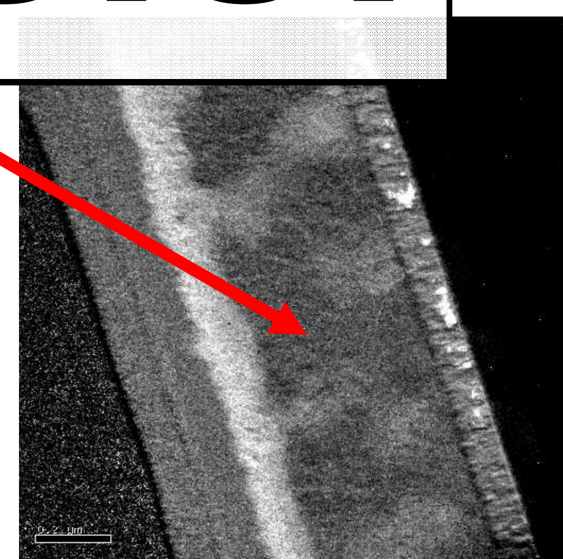
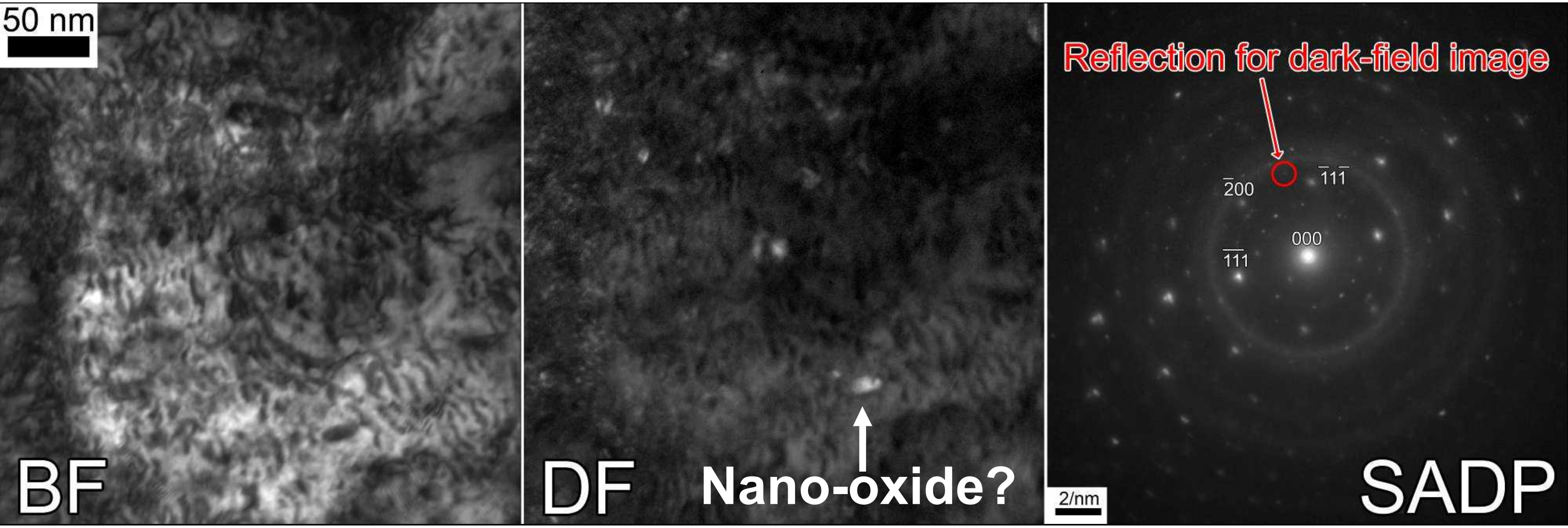




Hypothesis!

We have previously hypothesized these spots are due to double diffraction

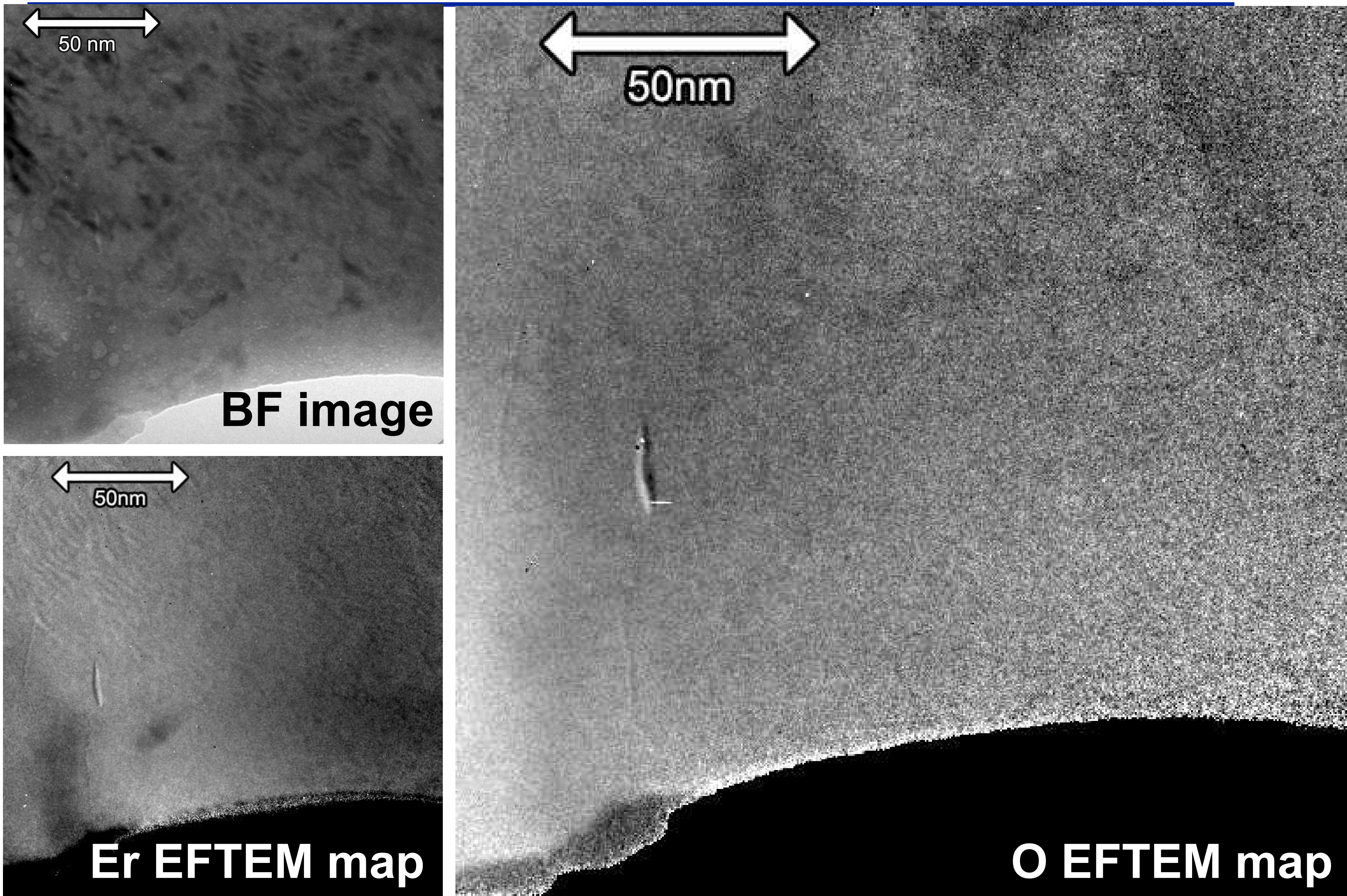
Due to low intensity of satellite spots, imaging of supposed oxide is ambiguous:



Other possibilities:

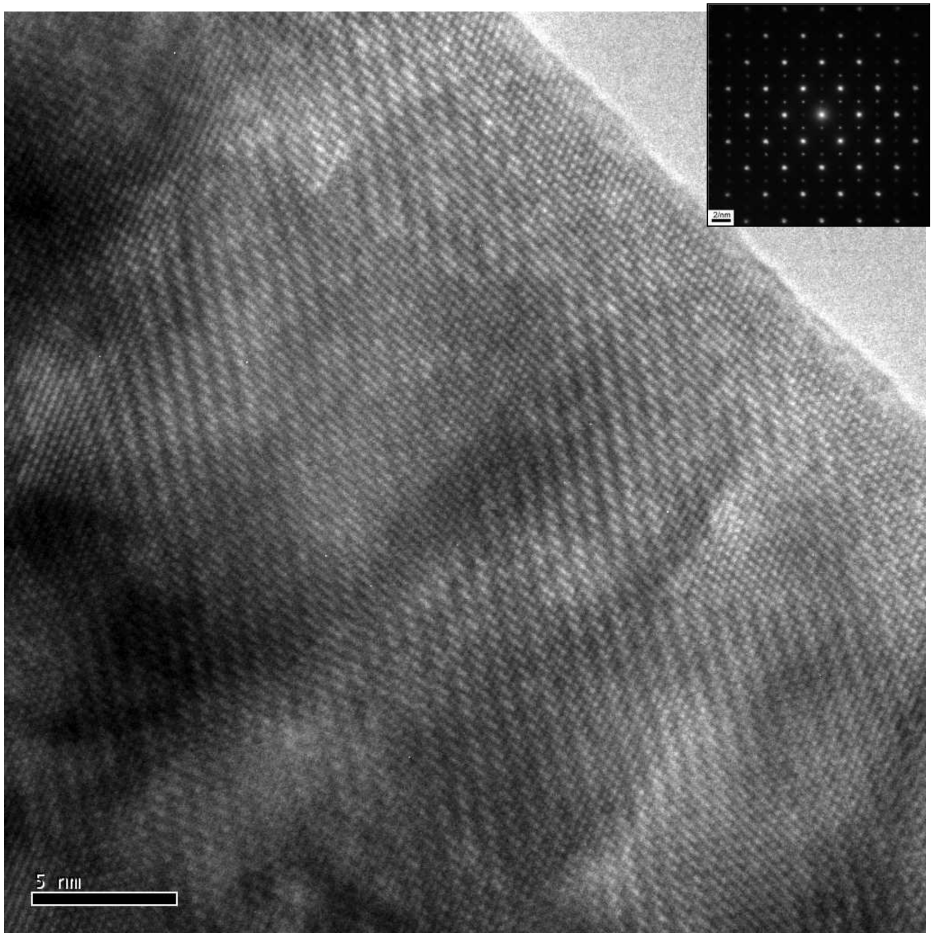
- **Use higher-resolution EFTEM**
- **Use lattice-imaging high-resolution TEM (HREM)**
- **Use electron-energy-loss spectroscopy (EELS)**

Higher-resolution EFTEM shows no obvious oxide particles

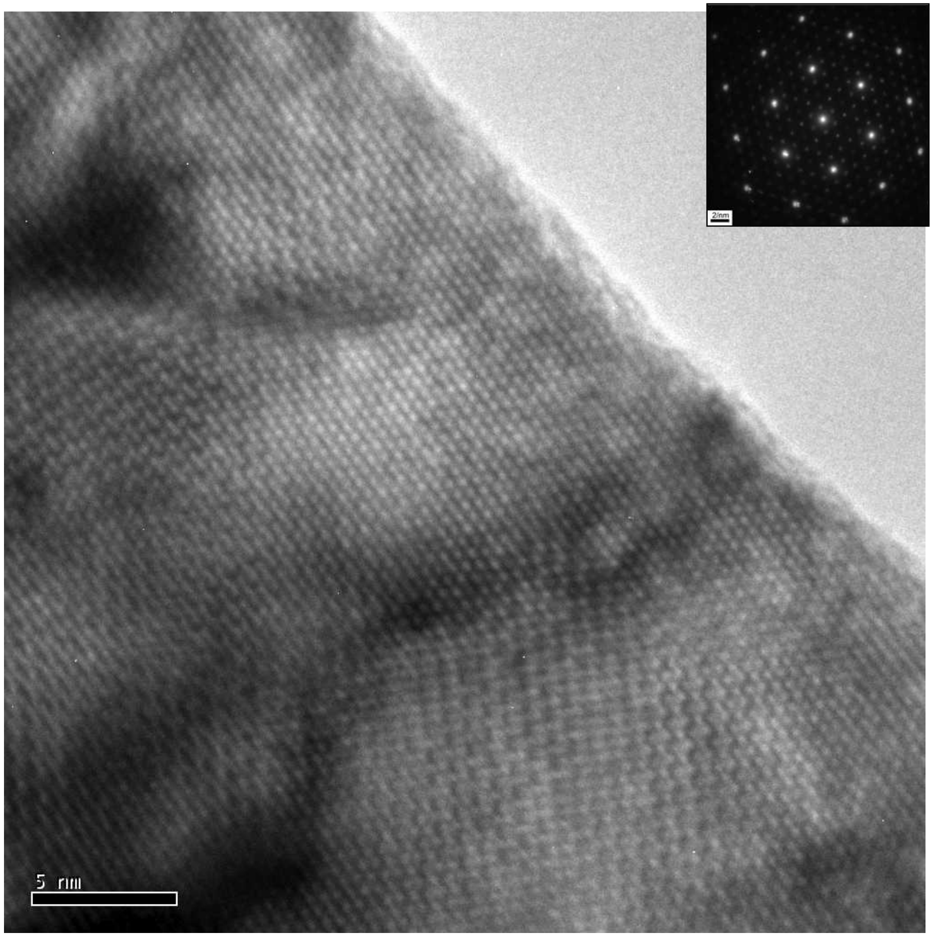


HREM shows details of structure

011 zone



111 zone



5 nm

Micrographs are not the same area
Sample prepared by conventional ion milling, not FIB

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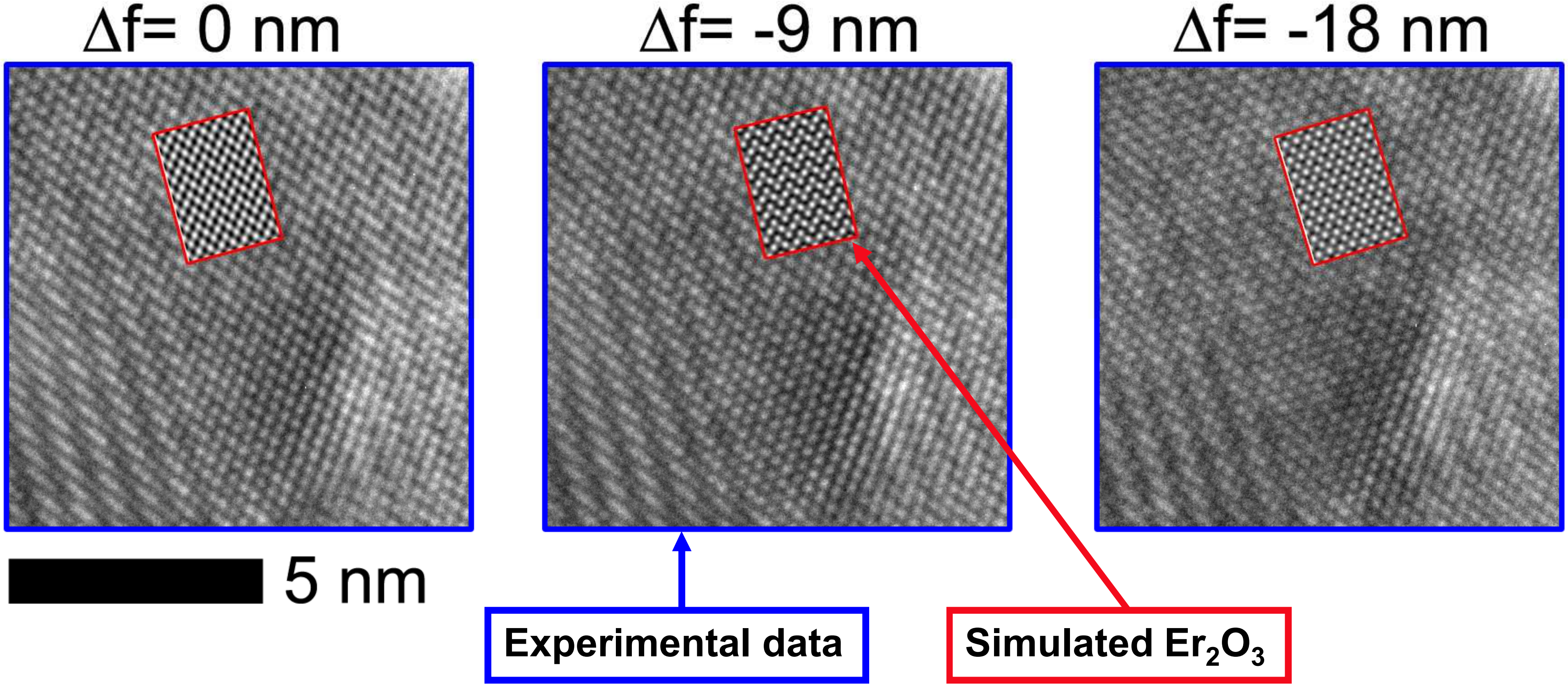
HREM lattice images at different defocus values Δf must be compared to simulations



Calculated images match some sample areas, but not others

→Continuing to explore in more detail

→Not conclusive yet

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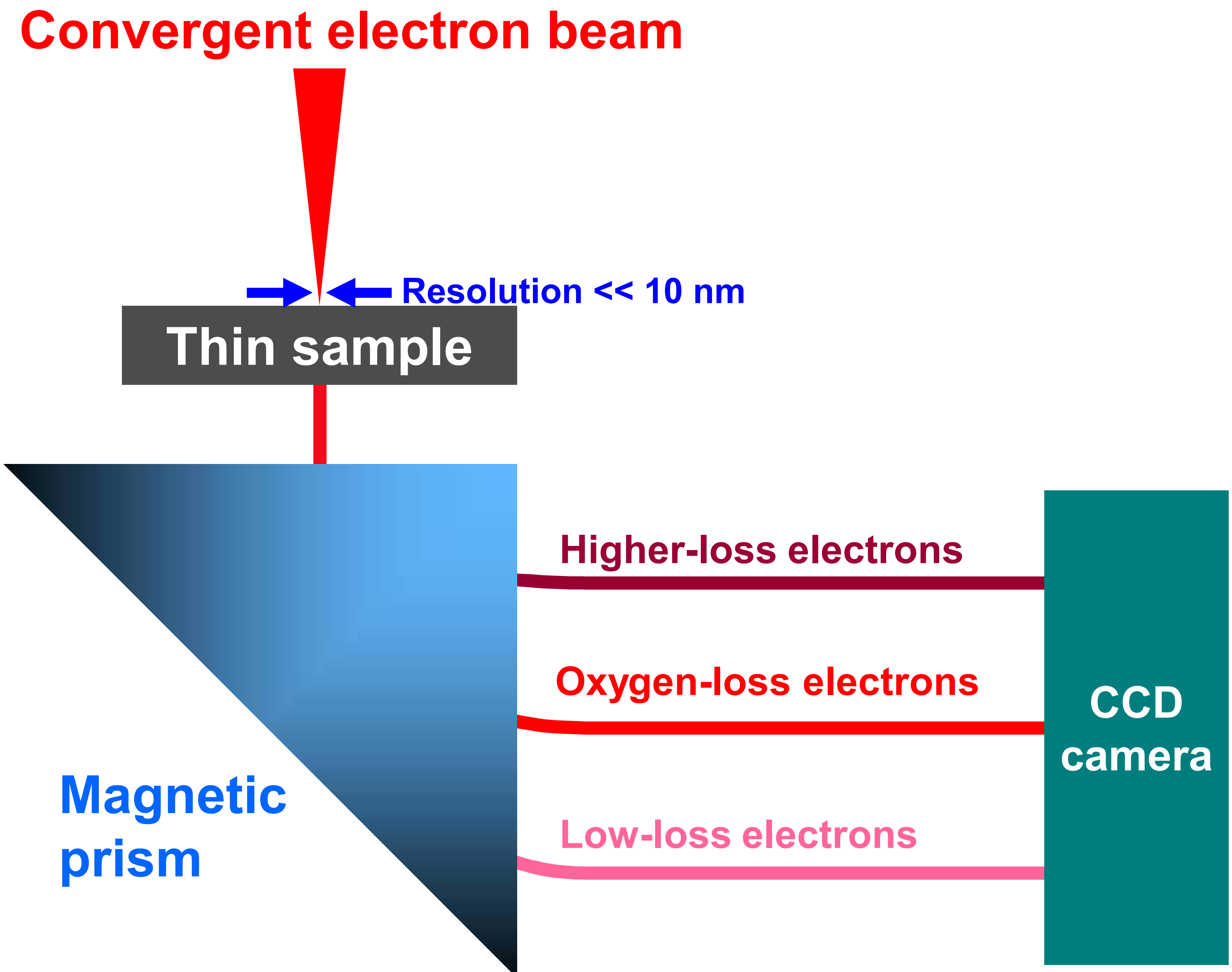
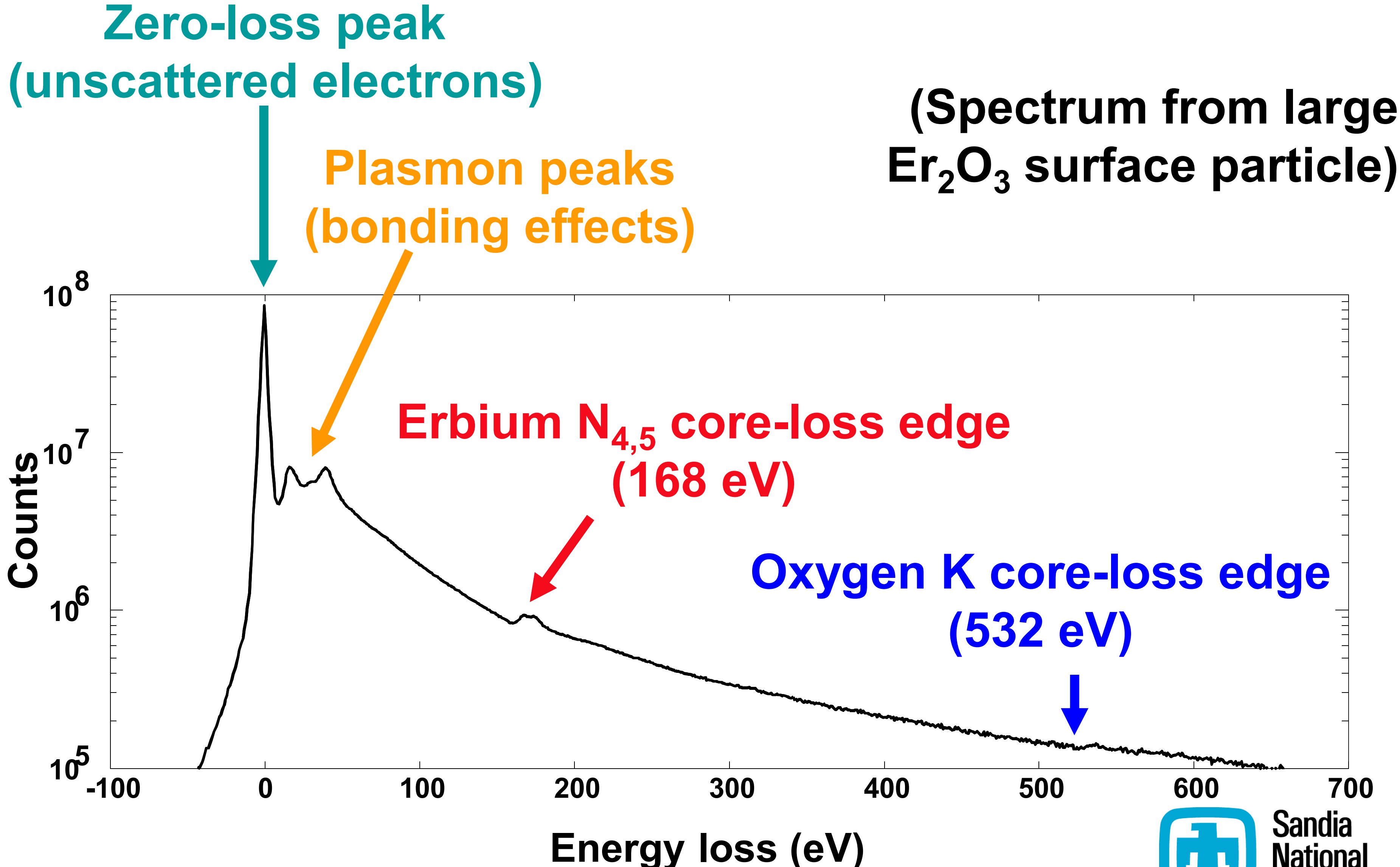
EELS can be used to look for oxygen at the nanometer scale



EELS spectra show erbium and oxygen



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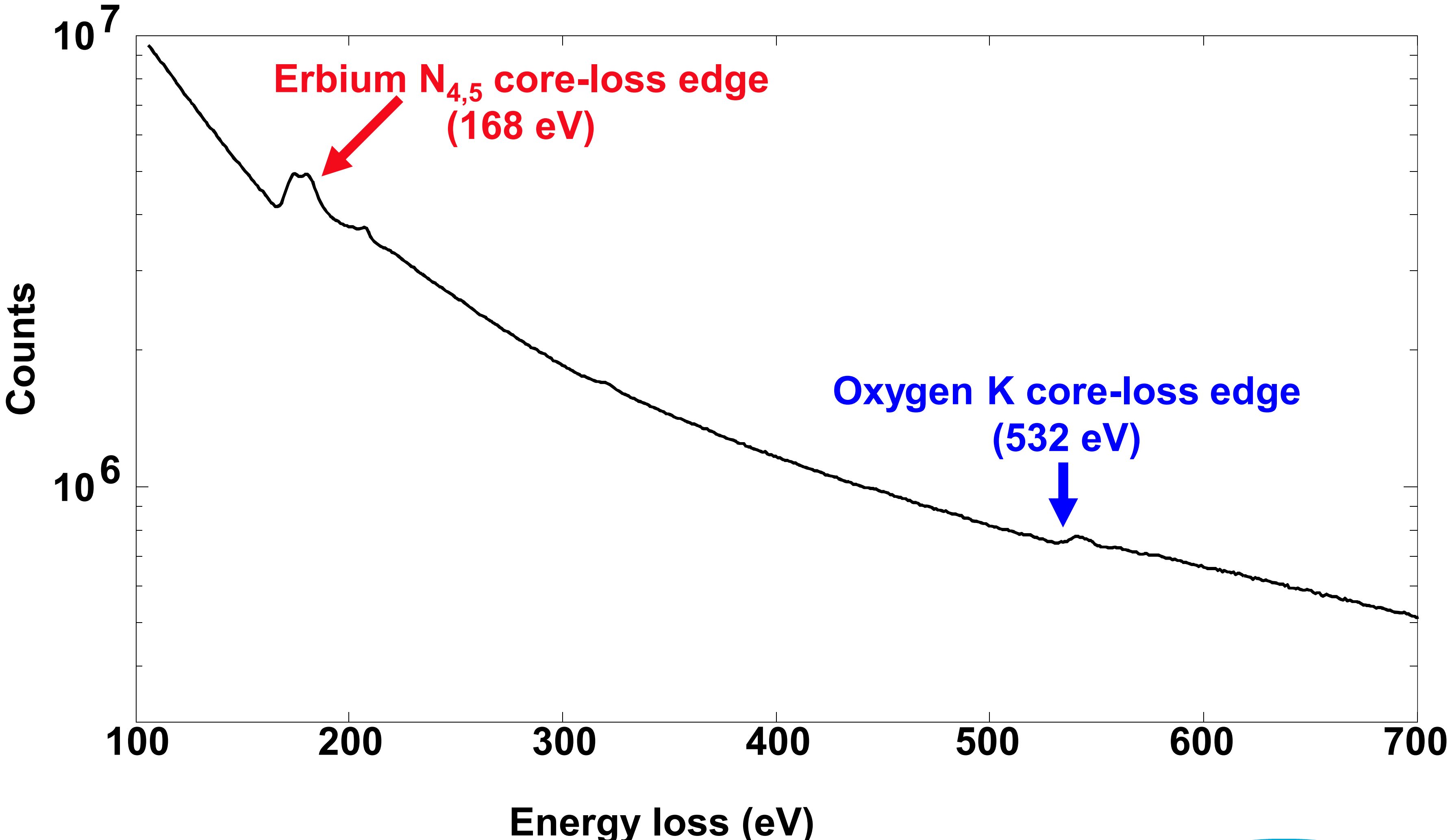

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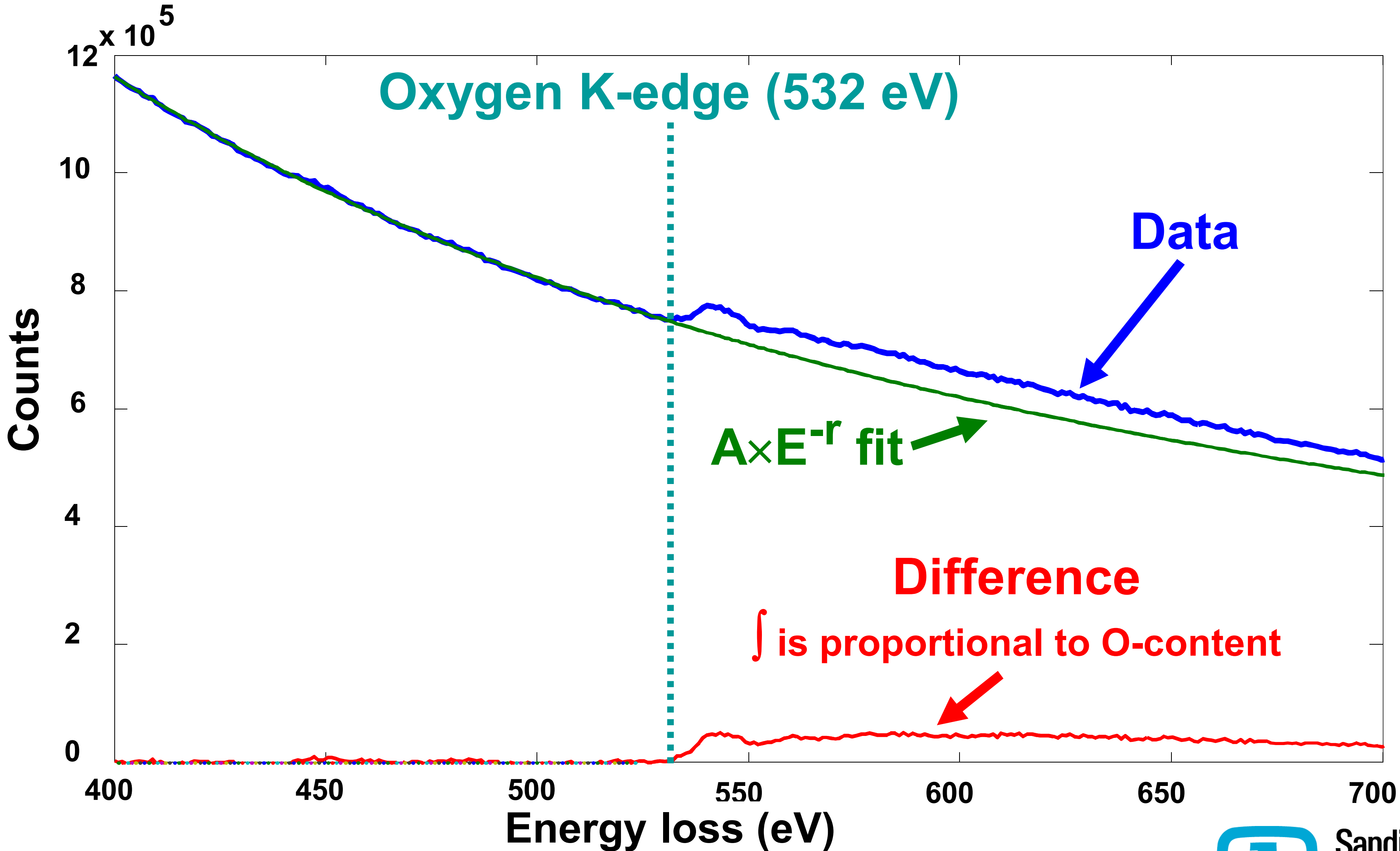
Curve fitting allows semi-quantitative analysis of oxygen content



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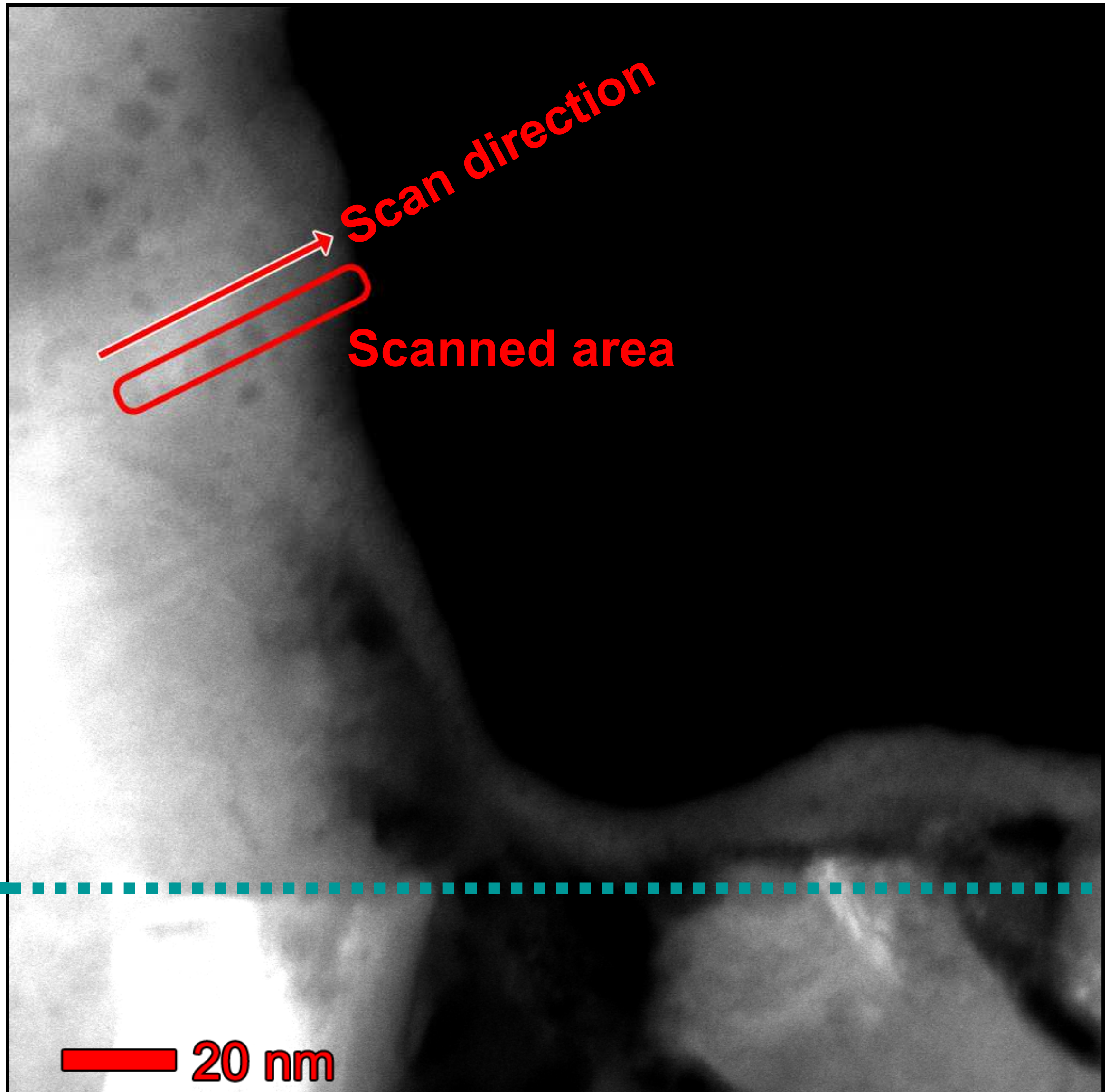
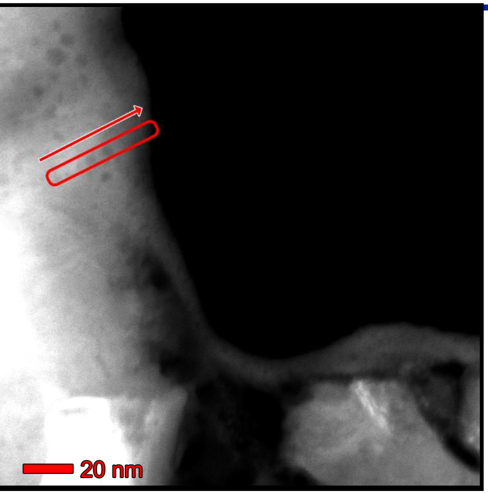
EELS data taken across dark features

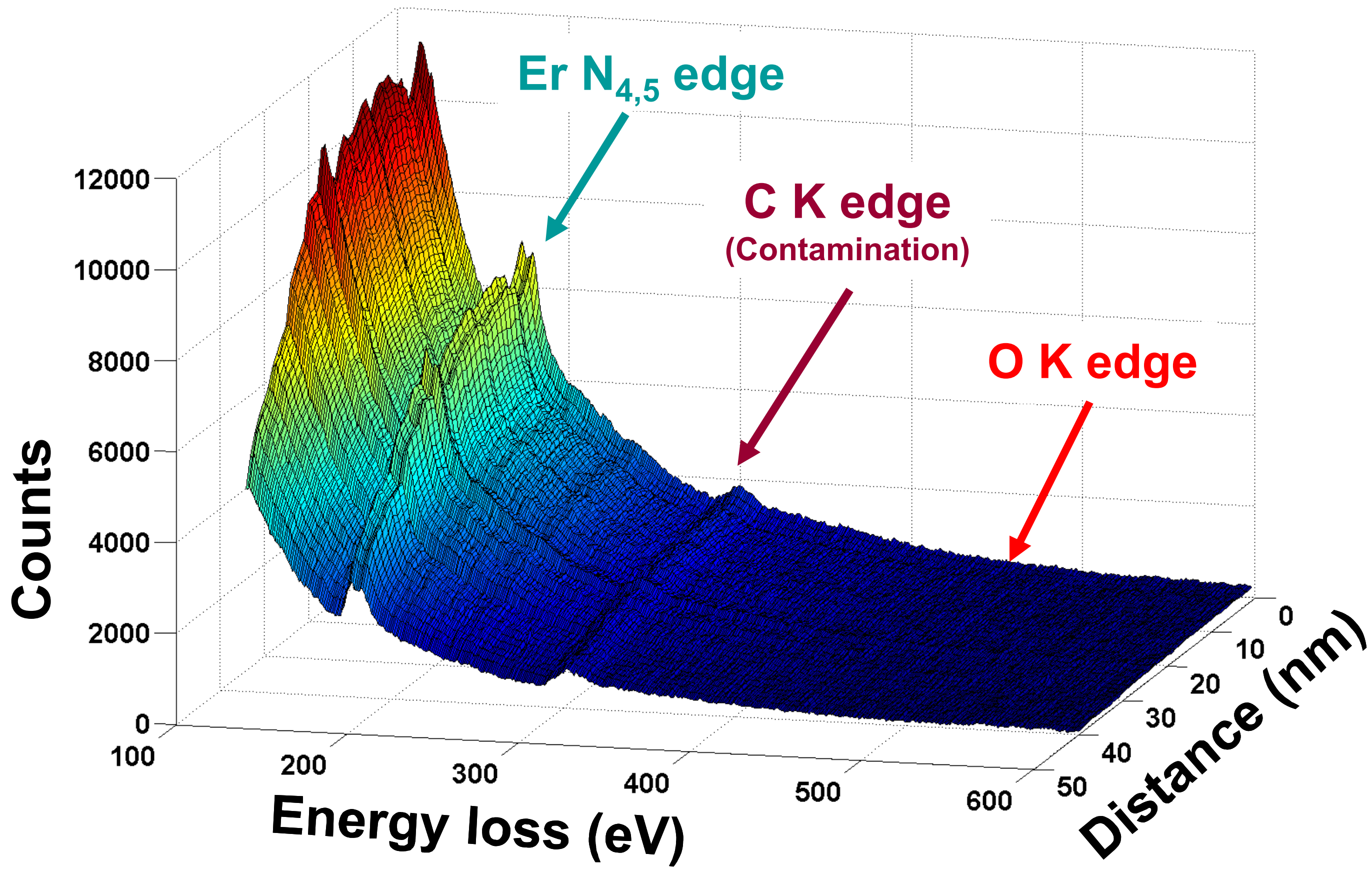


ErD_2

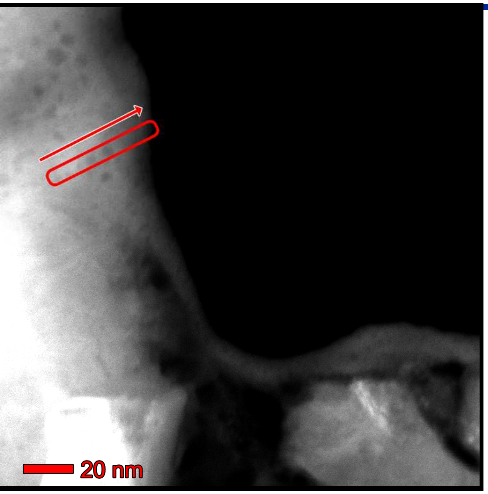
Mo

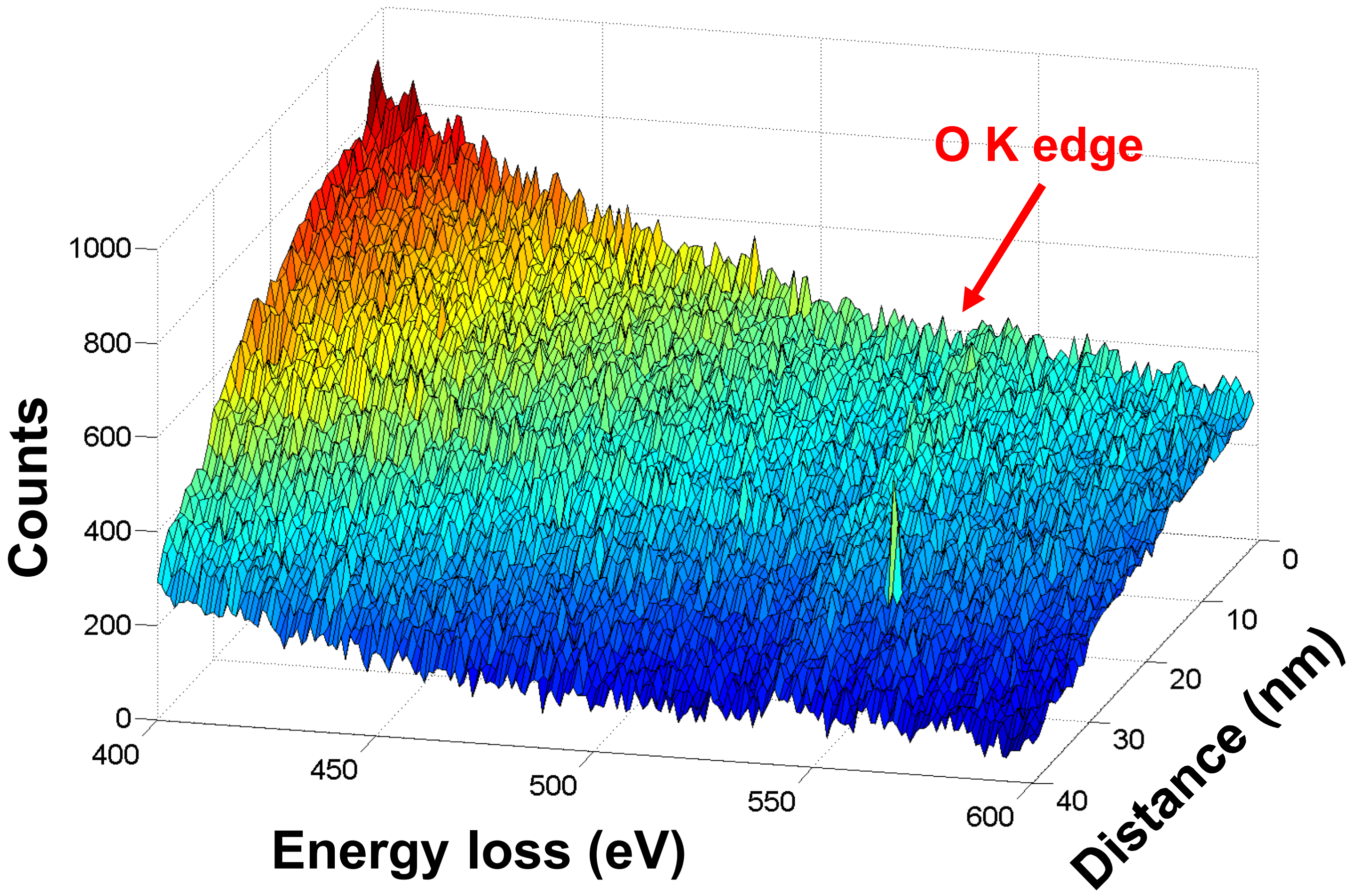
EELS data taken across dark features





EELS data taken across dark features





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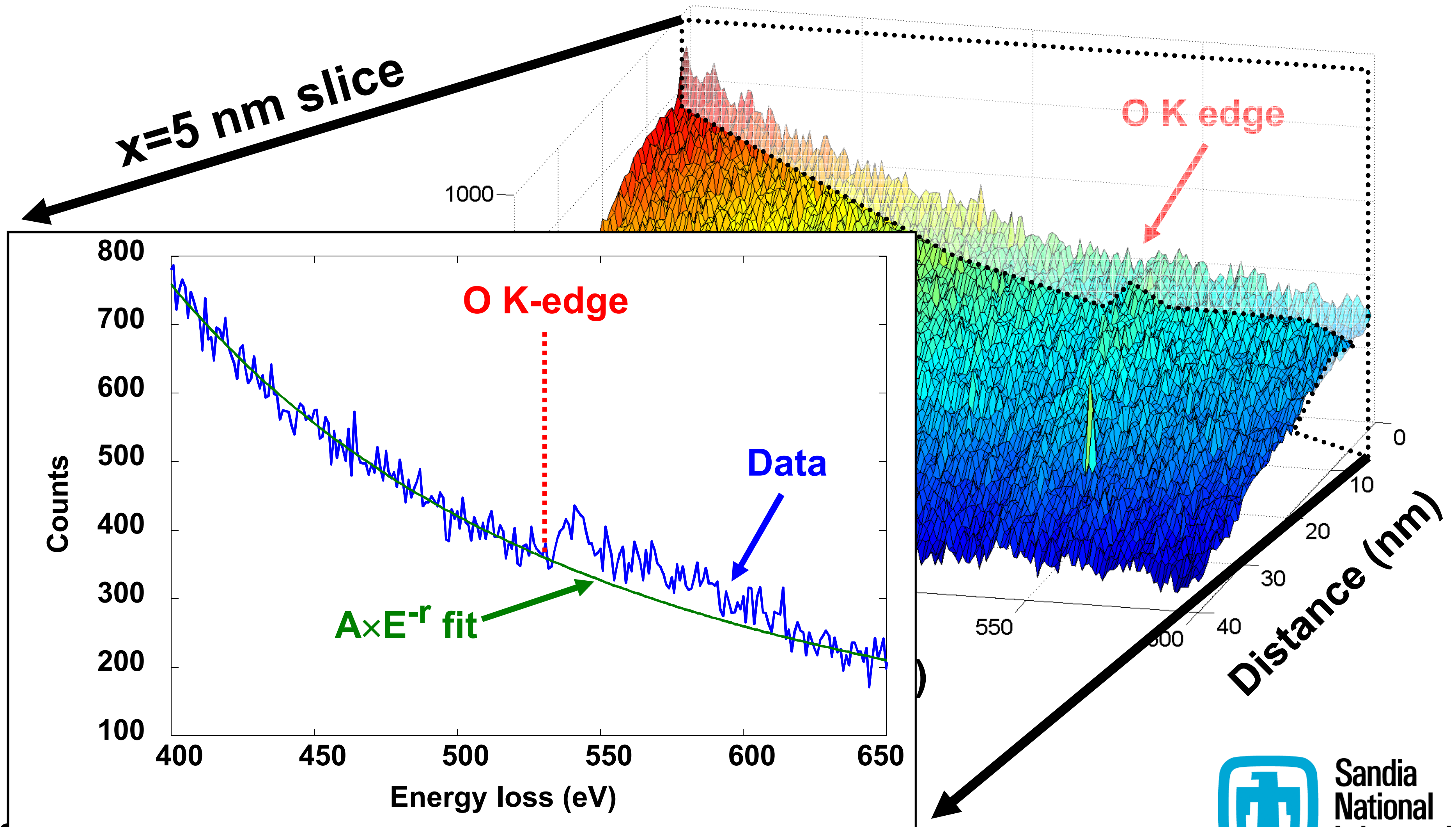

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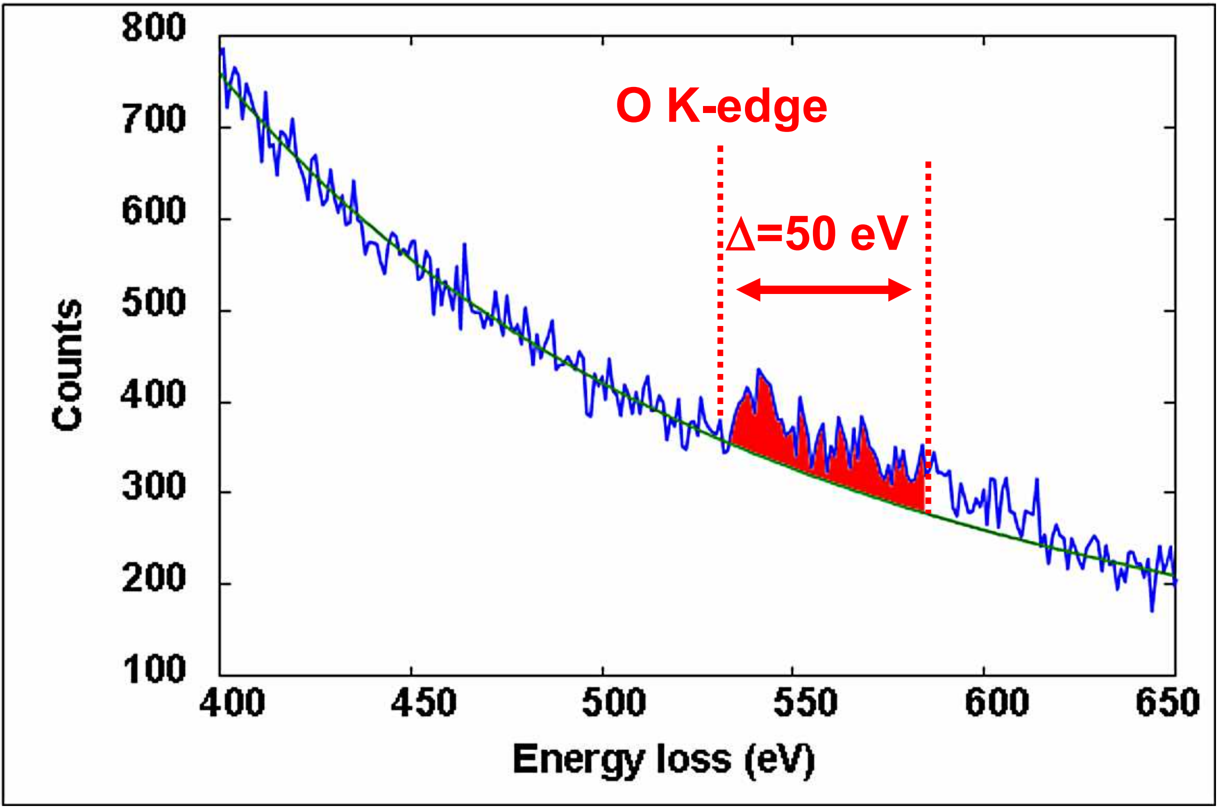
Can oxygen content be correlated to image features?

Relative oxygen content can be found from summing the area above fit:



$$\textbf{Oxygen} \propto \int_{E=532\ eV}^{E=582\ eV} \left(Data - Fit \right) dE$$

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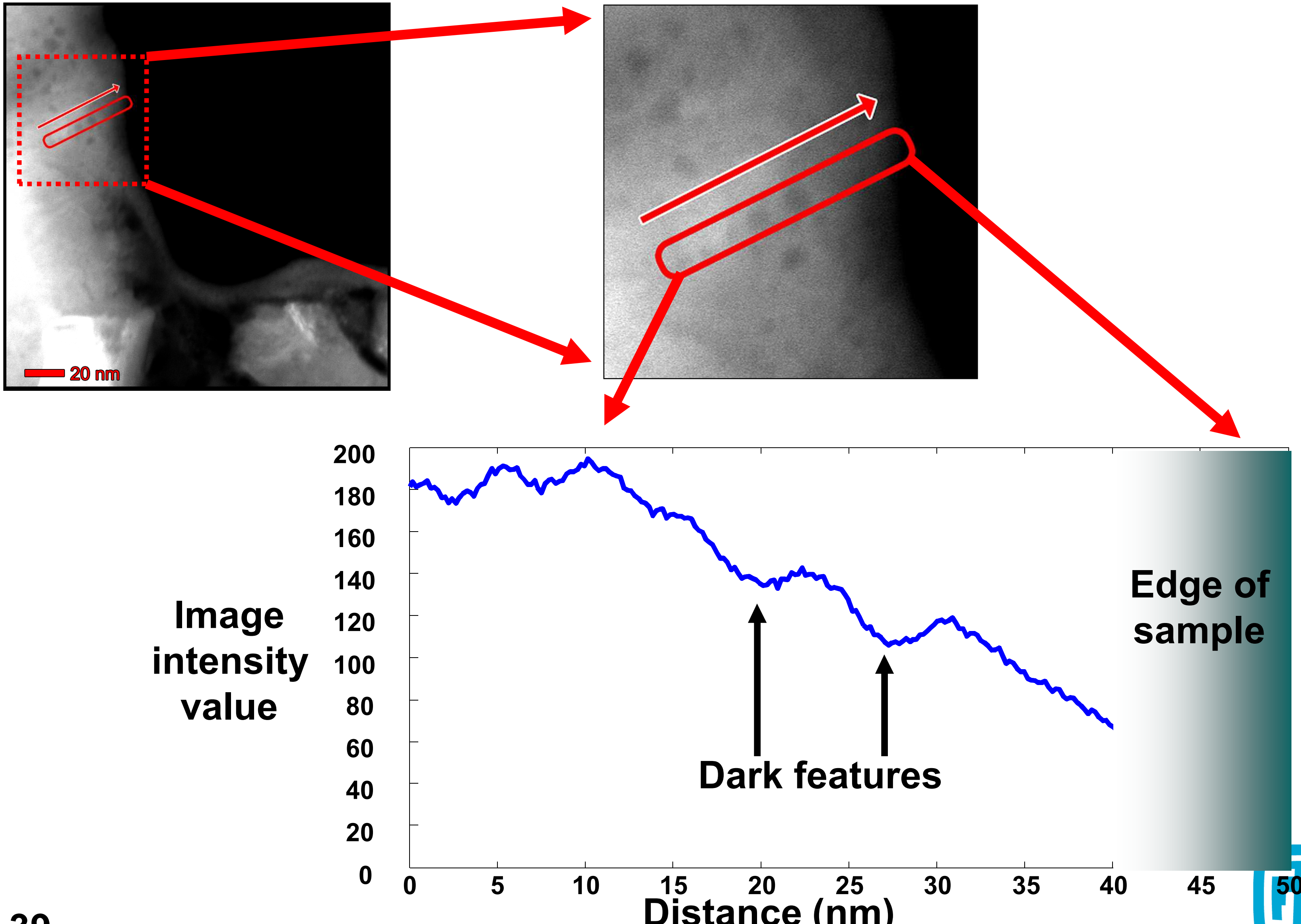
Can oxygen content be correlated to image features?



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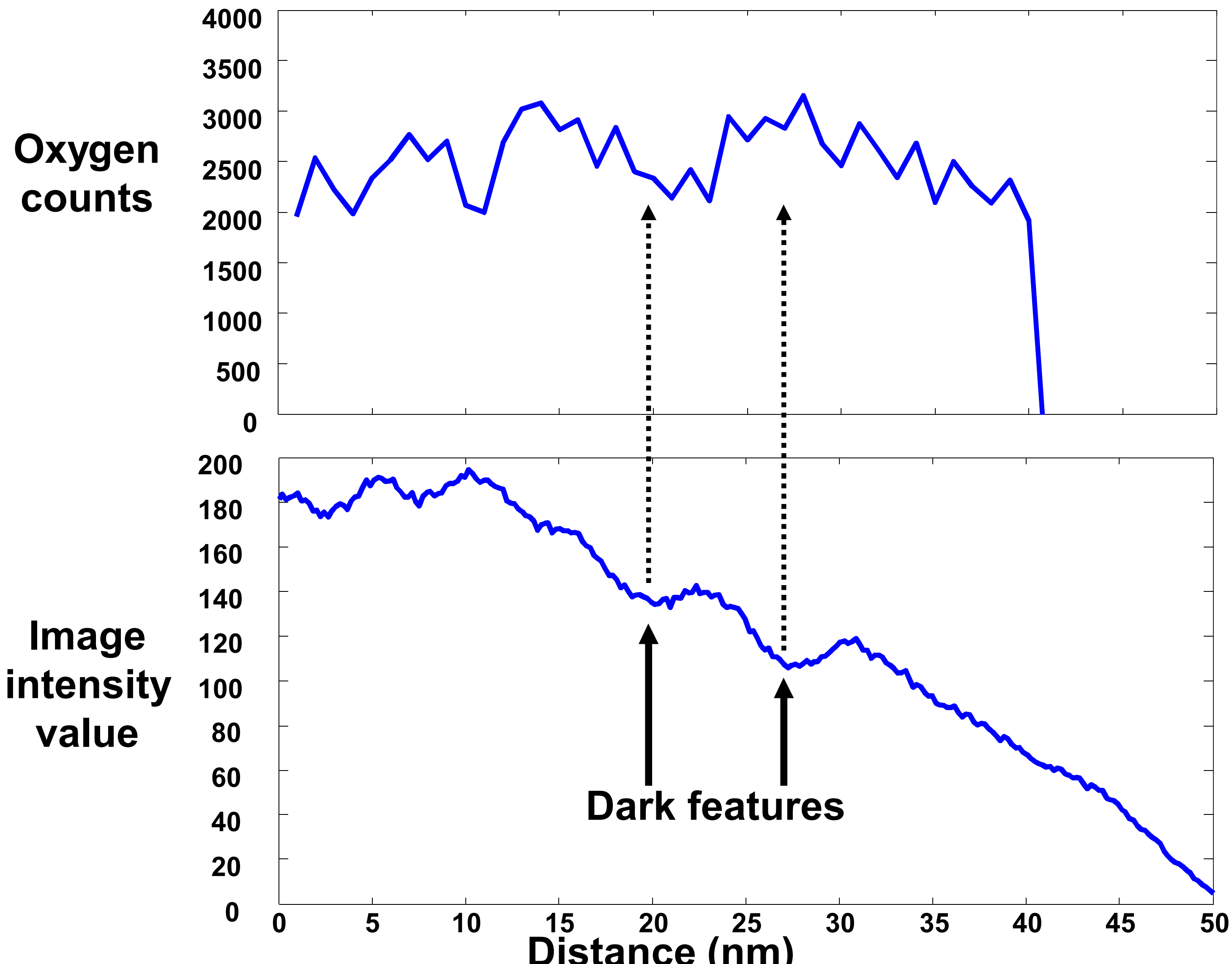
Oxygen counts correlate poorly to image contrast



No obvious nano-oxide inclusions found via EFTEM, lattice-imaging, or EELS

Satellite spots seen in diffraction hypothesized to arise from nano-oxide inclusions

EFTEM did not show nano-oxides

Lattice imaging of ErD_2 difficult to interpret – experiments are continuing, but no conclusive nano-oxides to date

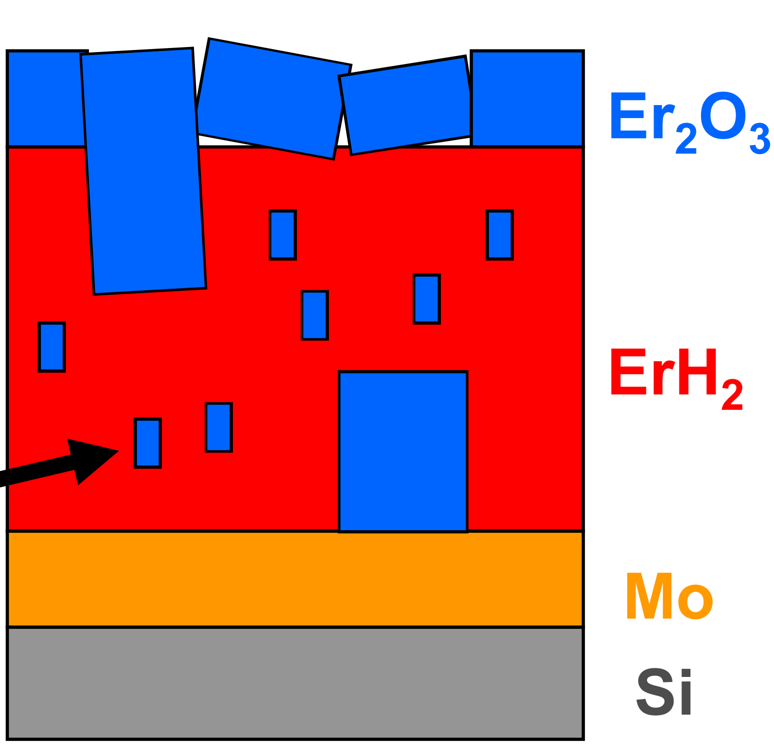
EELS showed ≈constant oxygen, possibly due to surface oxides

→Continuing to refine EELS techniques

→More conclusive data soon

Oxides in ErD_2 grow epitaxially on the surface, and nano-oxides may exist in the matrix

- Imaging, EFTEM, and diffraction indicate oxide films formed on the sample surface ✓
- Satellite diffraction spots could be due to nano-oxides within the ErD_2 matrix ?



- EELS and lattice-imaging experiments are underway to confirm or refute this nano-oxide hypothesis