Activation of Erbium Films for Hydrogen Storage

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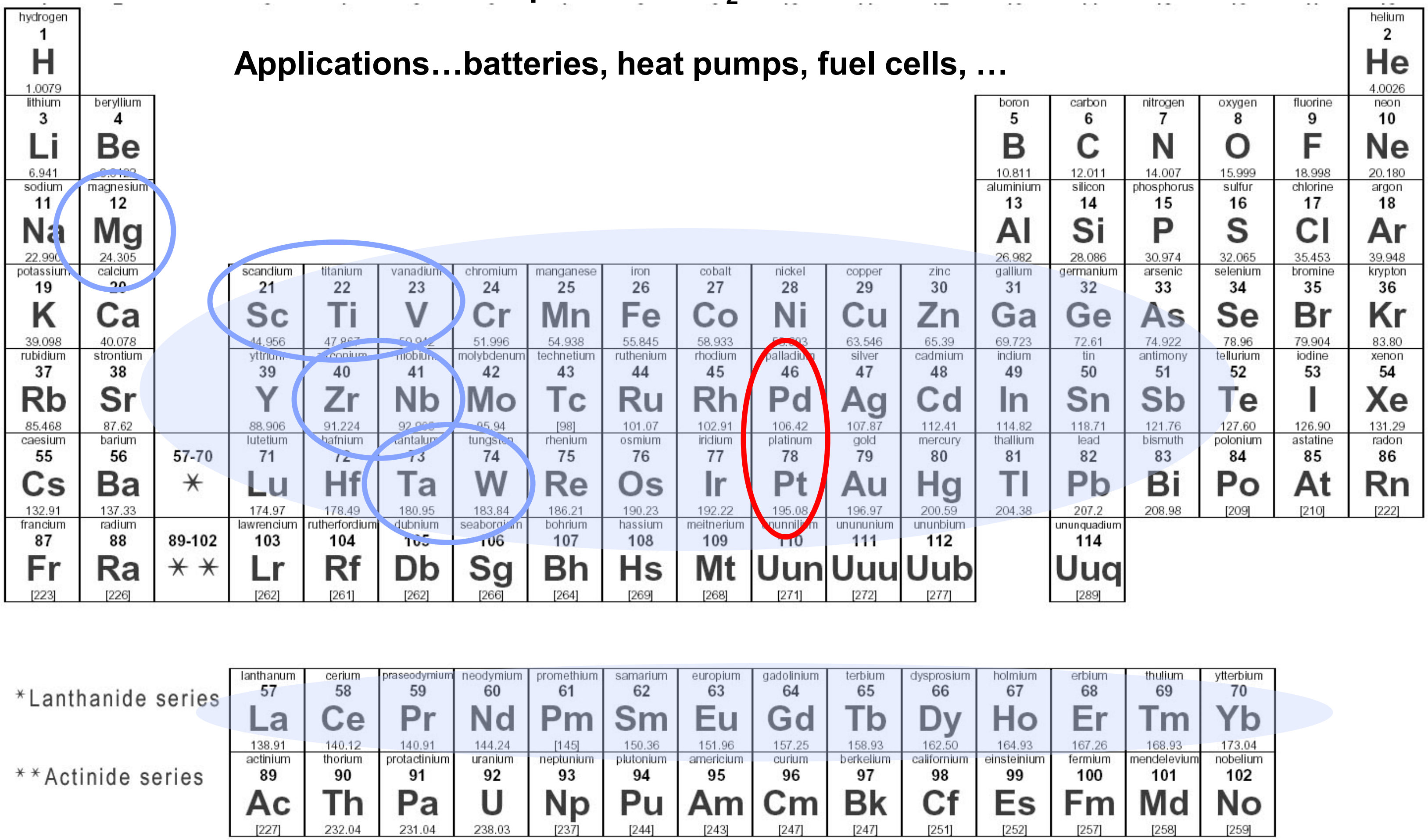
Hydrogen storage

>50 elements are known to form stable metal hydrides – transition metals and lanthanides

Mg, Sc, Ti, Nb, Ta, etc.

Pt and Pd – important for H_2 dissociation

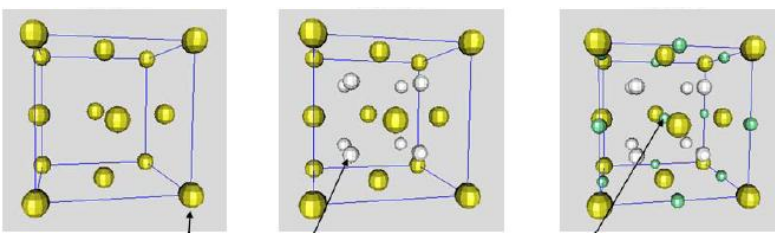
Applications…batteries, heat pumps, fuel cells, …

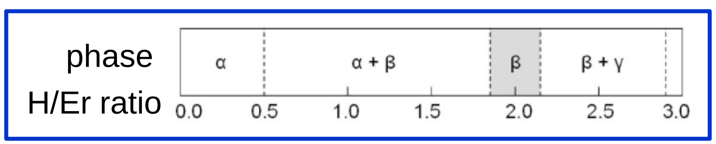


Erbium

~43rd most abundant element in earth's crust
Melting point ~1530°C
[Xe]$6s^2 4f^{12}$

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]





__Three known hydride phases__

Alpha – solid solution

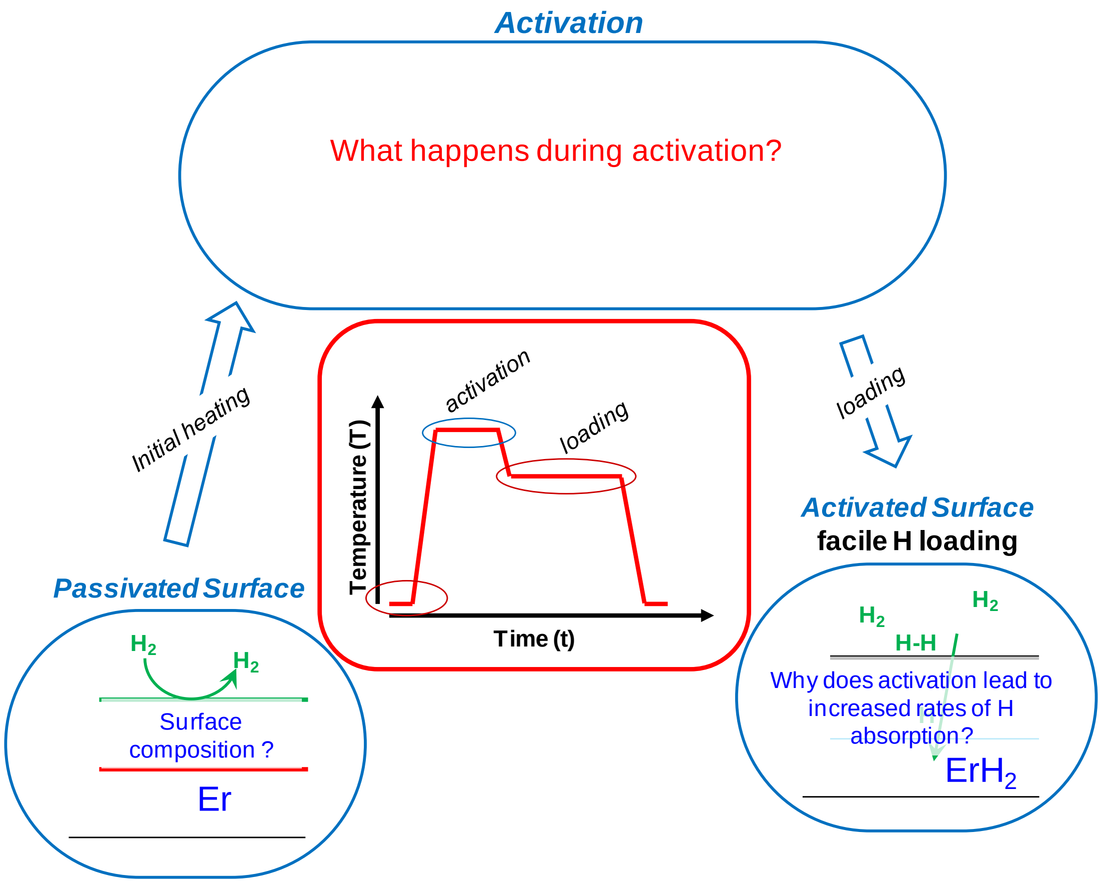
Beta – FCC – ErH_2

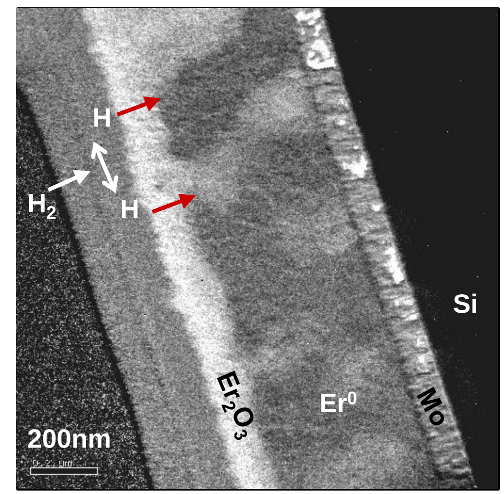
Gamma – "unstable ErH_3" (decomposes to ErH_2 without overpressure of H_2)

Commonly used as optical dopant in IR absorbing glasses

Activation?

Hydriding of metals (erbium and others) requires a thermal activation step in order to load the metals with hydrogen in a manageable timeframe.





Parish, Snow, Brewer. *J. Mater. Res.* **24** (2009) 1868-79.

Tewell, King. *App. Surf. Sci.* **253** (2006) 2597-602.

Characterization of the Activation Process

1. in situ

XPS
Chemistry

Quantification

Depth-profiling

Photoelectron Spectroscopy (XPS/UPS)
Kratos Axis Ultra DLD

VKE-XPS
Chemistry

Non destructive depth-profiling

Variable kinetic energy XPS at X24A
National Synchrotron Light Source at Brookhaven National Labs

2. ex situ

LEIS
Sensitivity

Quantification

Depth-profiling

Low Energy Ion Scattering
ION-TOF qtac^{100}

3. ex situ

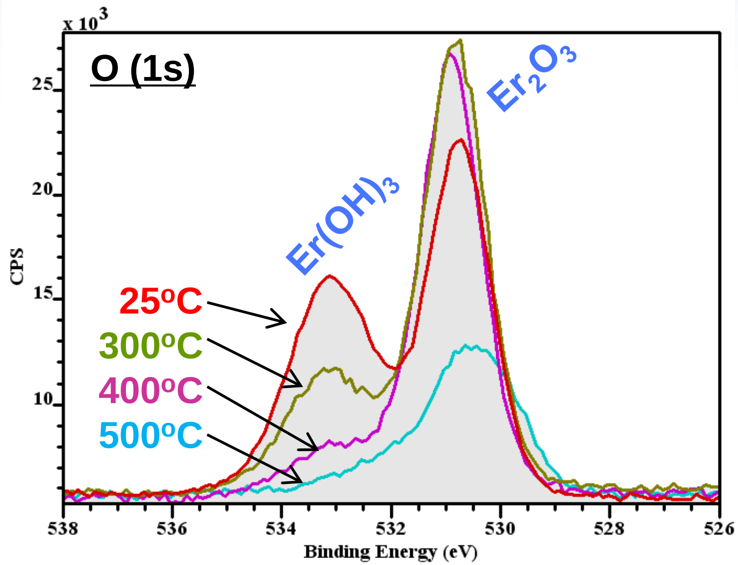
ToF-SIMS
Sensitivity (ppm-ppb)

H can be observed

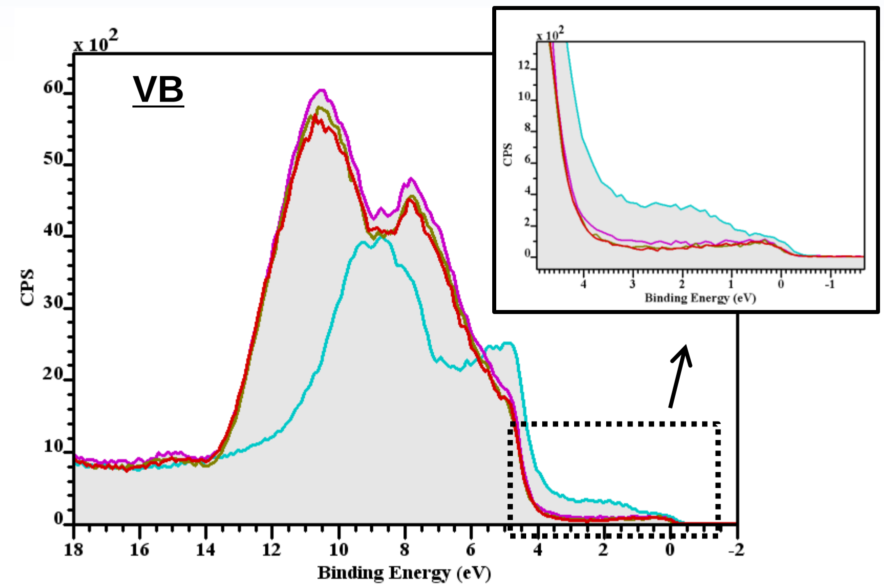
Depth-profiling

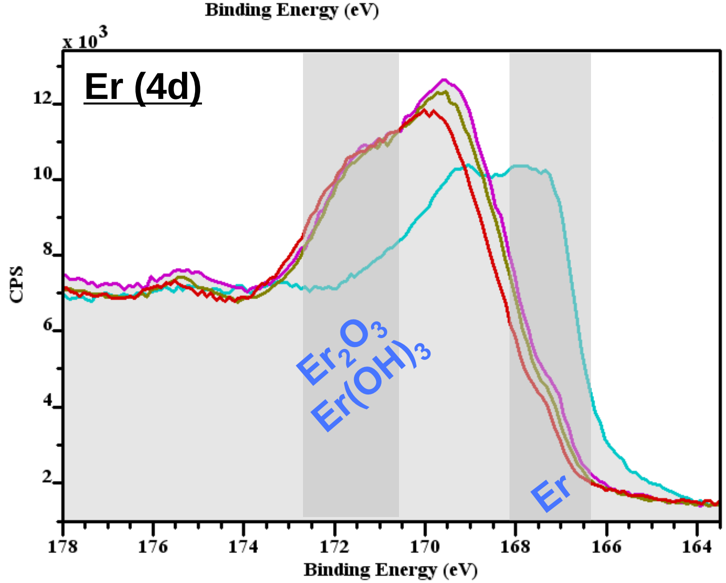
Time-of-Flight Secondary Ion Mass Spectrometry
(ToF-SIMS) Ion-TOF.SIMS 5

Identifying the threshold temperature



hv = 2.2 keV





1. Initial heating leads to decrease in hydroxide concentration

2. < 400°C - slight changes in the Er (4d) lineshape and valence band spectra

3. > 400°C - substantial decrease in the O (1s) intensity and the Er (4d) shifts
   - photoemission in the band gap

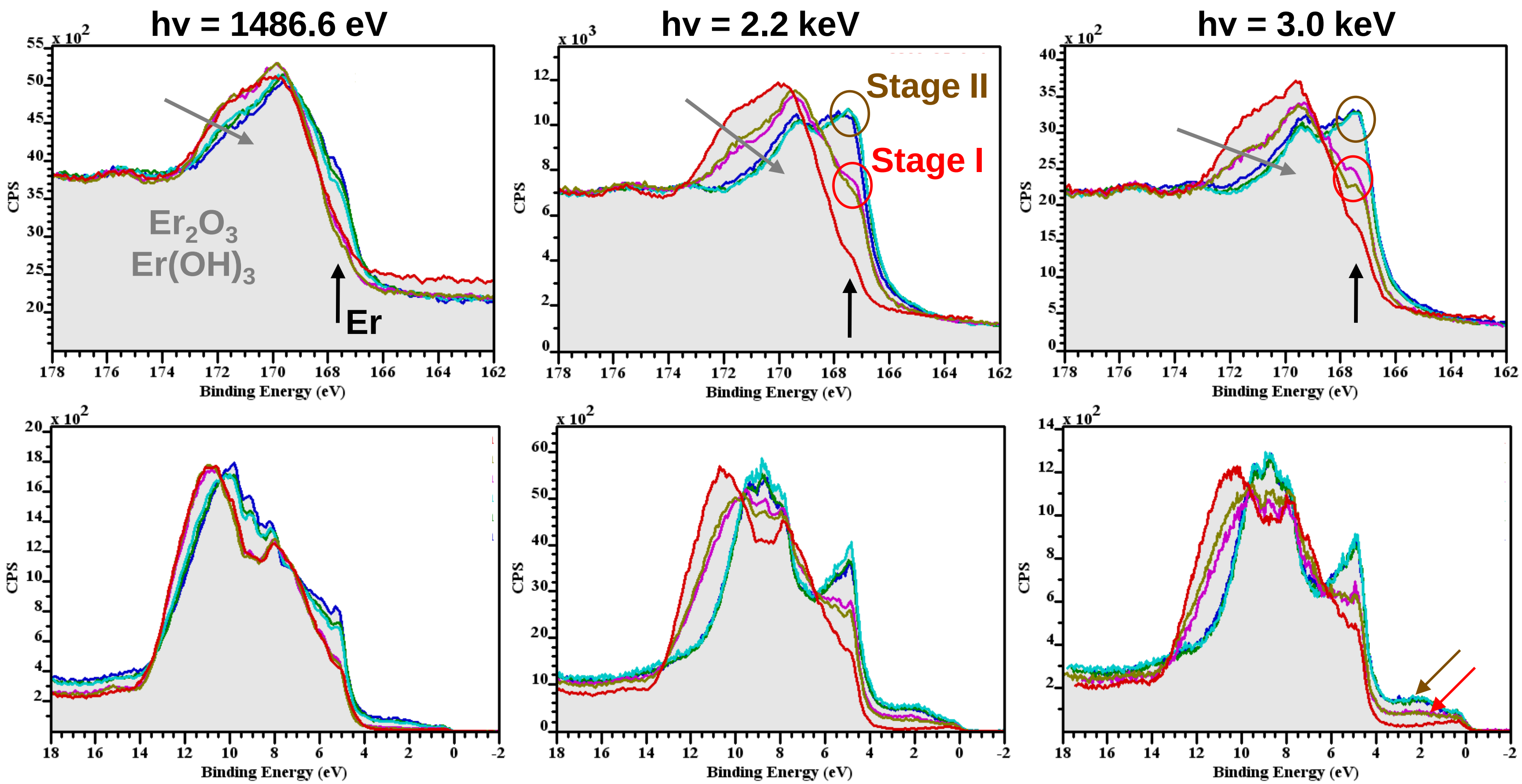
Time evolution at the threshold temperature

Two stages are evident.

400^{o}C for 0, (5, 10), [20, 30, 50] minutes

Er 4d

Valence band



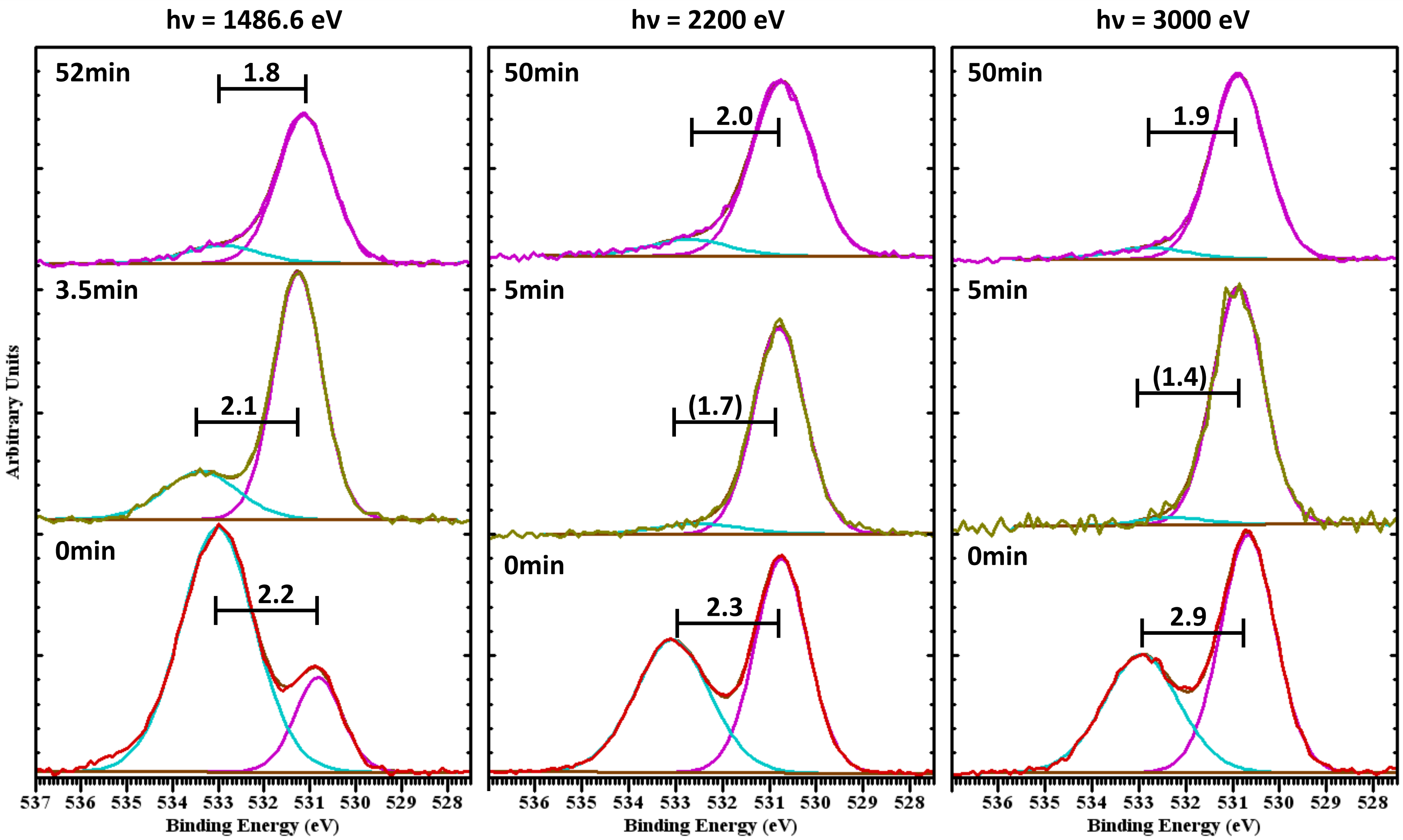
Shallowest analysis:
Mostly erbium oxide

Two stage transition from oxide to metal is evident
1st stage – 5 min.
2nd stage – 20 min.

Deepest analysis:
more metallic-like erbium
(evaluation through the oxide)

Evolution of the oxide

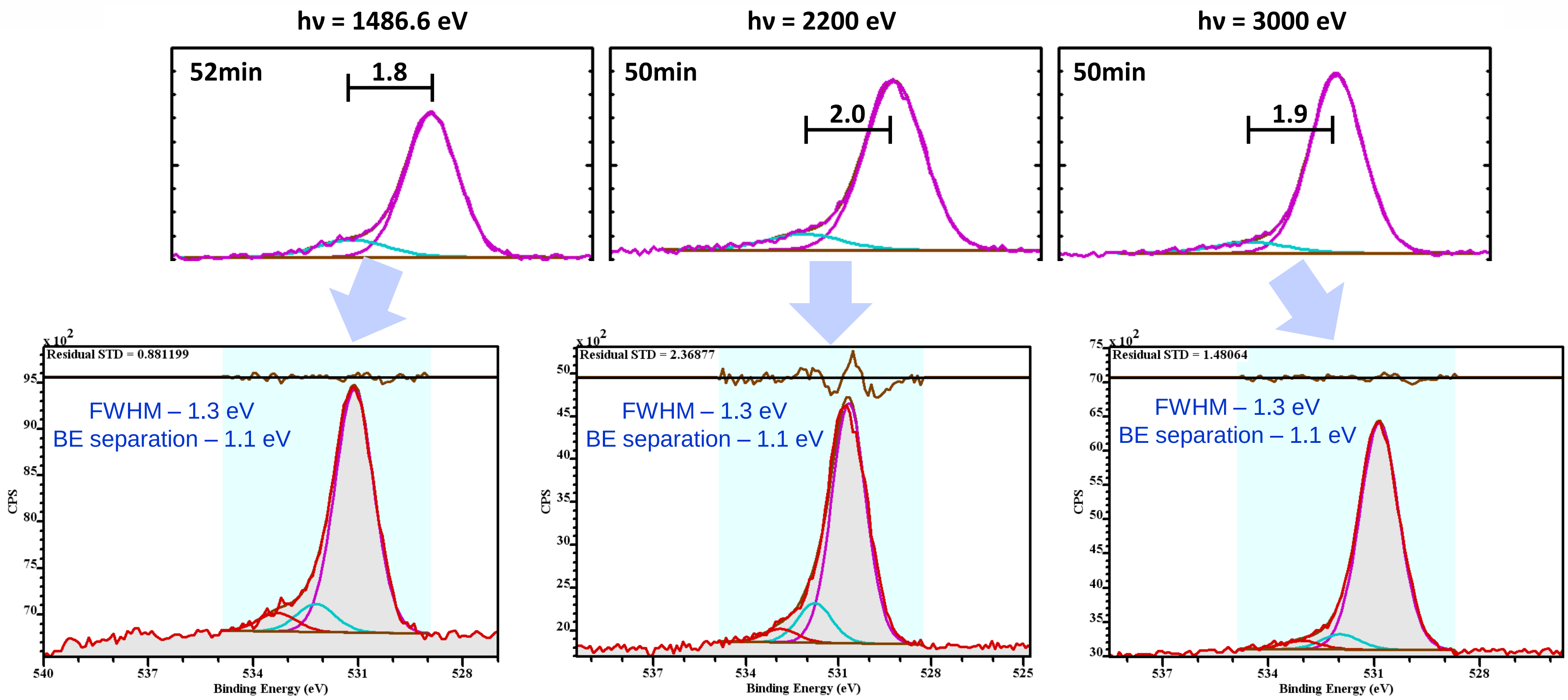
Stage I - Initial heating substantially decreases hydroxyl content.
Stage II - Additional heating leads to re-emergence of a high BE component.



→ BE separations change. FWHM change.
Simplest fitting strategy (2 peaks – oxide and hydroxide) – doesn't work.

Peak shape change of the O 1s

<u>Activated</u> films show an O 1s lineshape that can be fit with three identical components.



PHYSICAL REVIEW B 73, 245312 (2006)

Surface states, surface potentials, and segregation at surfaces of tin-doped In_2O_3

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Darmstadt University of Technology, Institute of Materials Science, Petersenstrasse 23, D-64287 Darmstadt, Germany

S. Zafeiratos, M. Hävecker, A. Knop-Gericke, and R. Schlögl
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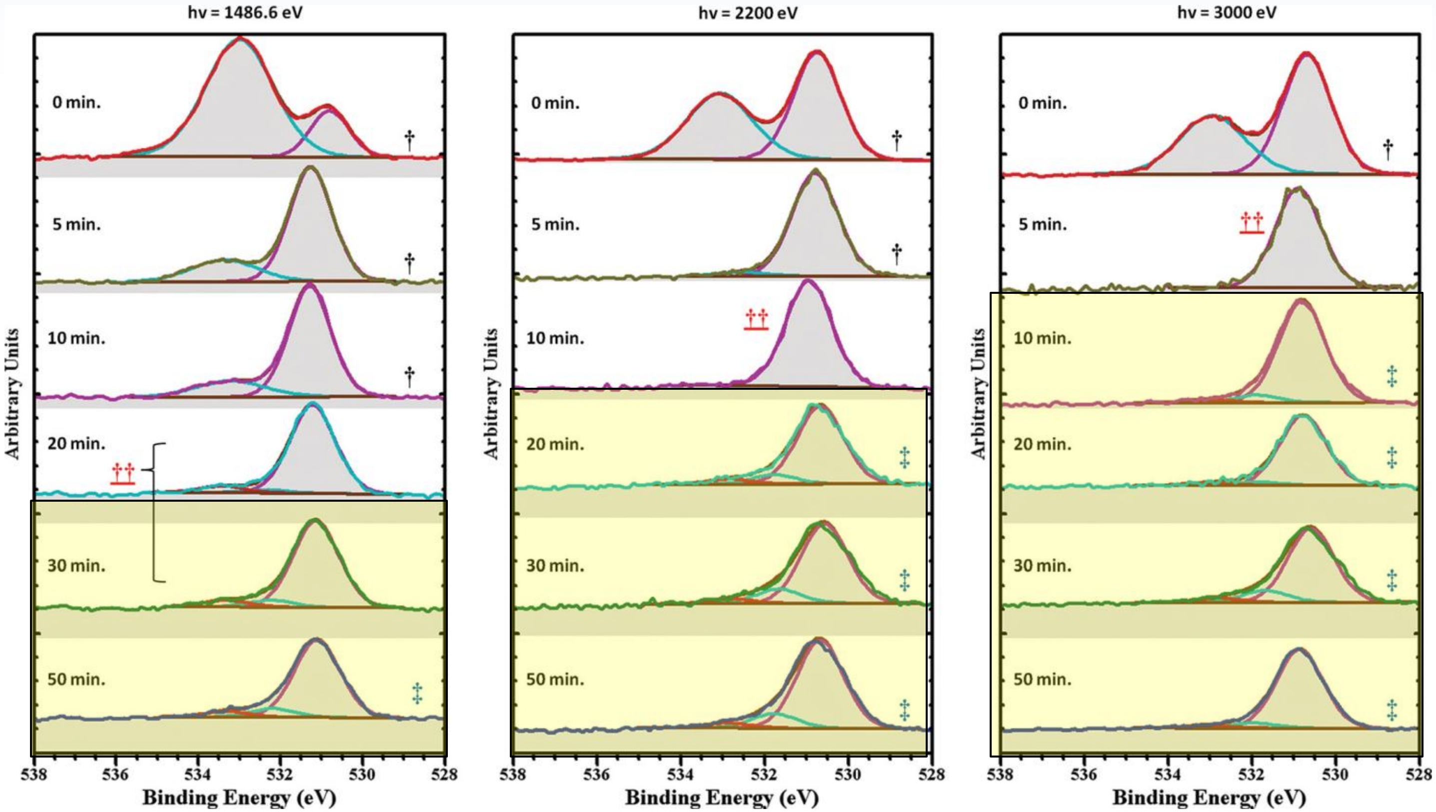
Used this peak fitting for O 1s and In 3d in Sn:In_2O_3 – surface plasmon losses

New lineshape emerges from subsurface boundary



Change in lineshape occurs earliest in deepest analysis
(high BE shoulder shows greater intensity with continued annealing – oxygen defect at the oxide/metal interface)

Stage II - Subsurface boundary moves nearer to surface with continued annealing

Low Energy Ion Scattering (LEIS)

(matrix independent quantification of elemental surface coverage)

<u>Principles</u>

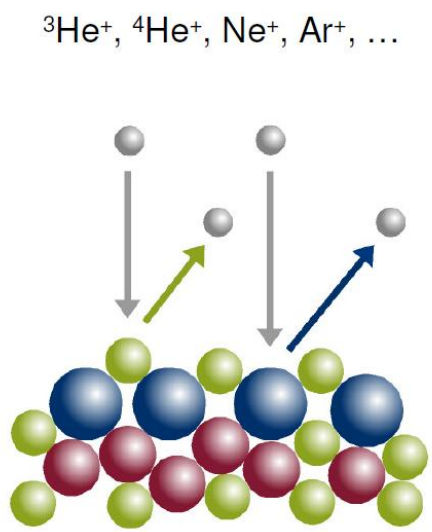
Bombard surface with noble gas ions at low energy (few keV)

Ions are scattered by surface atoms according to conservation laws of energy and momentum

Measure energy of the scattered ions → determine mass of surface atom

→ Intensity is proportional to surface coverage

Low Energy Ion Scattering
ION-TOF qtac^{100}

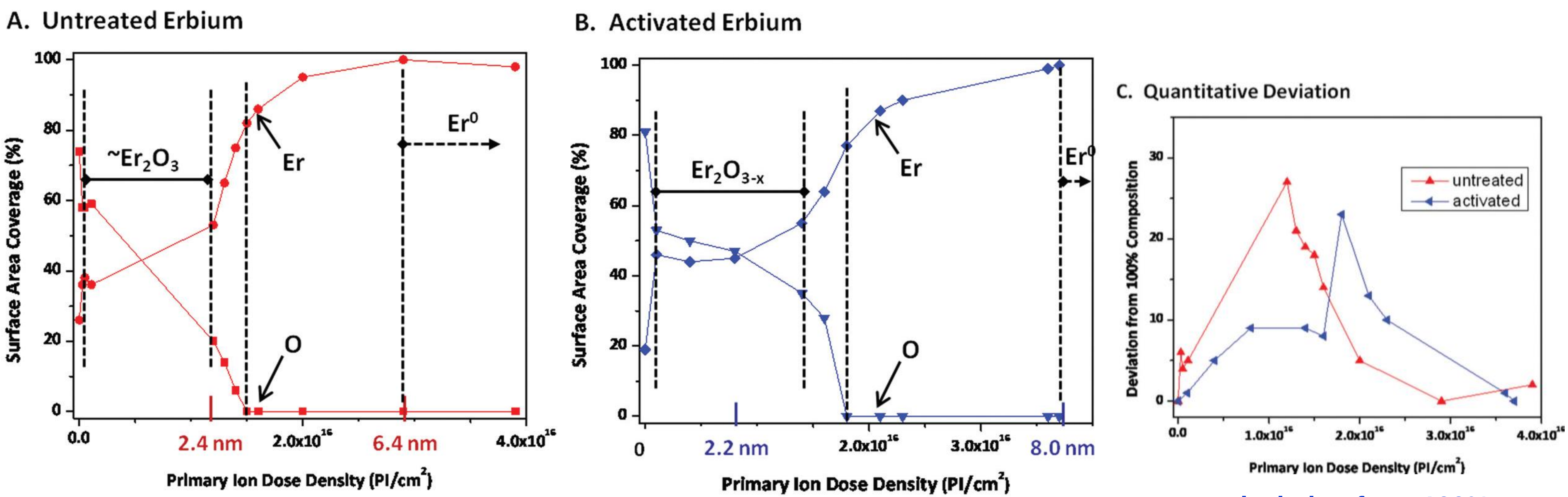


LEIS Features

- Reliable and straight-forward quantification
- Ultra-high surface sensitivity – top atomic layer analysis
- Detection of all elements > He
- Non-destructive in-depth analysis
- Sensitive to isotopes
- Detection limits:
  Li - O ≥ 1 %
  F - Cl 1 % - 0.05 %
  K - U 500 ppm - 10 ppm

LEIS (ion scattering) depth profile

Annealing/Activation leads to deeper penetration of Oxygen and a sub-stoichiometric surface oxide.



As-Received

- nearly stoichiometric Er_2O_3 surface layer
- O content goes to 0%, but Er does not go to 100%

(other components not identified in XPS, TOF-SIMS)

After Activation

- sub-stoichiometric oxide surface layer
- Surface layer approx. twice as thick
- erbium content does not reach 100% until 1.6 nm deeper than in the as-received film

- deviation from 100% quantification shifts further from the surface after annealing

iONTOF

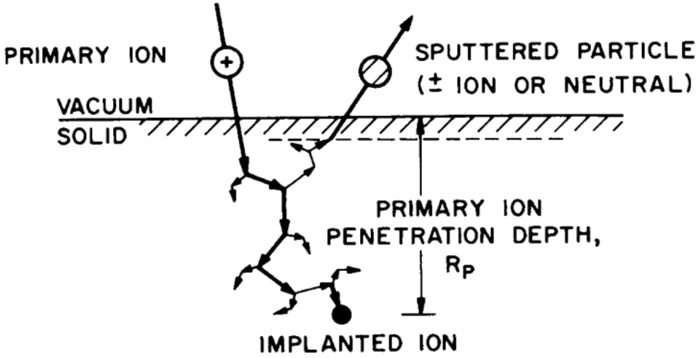
Nathan Havercroft,
Michael Fartmann,
Daniel Breitenstein

Sensitivity and Hydrogen: ToF-SIMS depth profile

Principles

Bombard surface primary ion beam
Secondary ions are extracted and injected into time-of-flight analyzer
ToF analyzer separates ions over time according to mass to charge ratio

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) Ion-TOF.SIMS 5



ToF-SIMS features

Sensitivity (ppm-ppb)

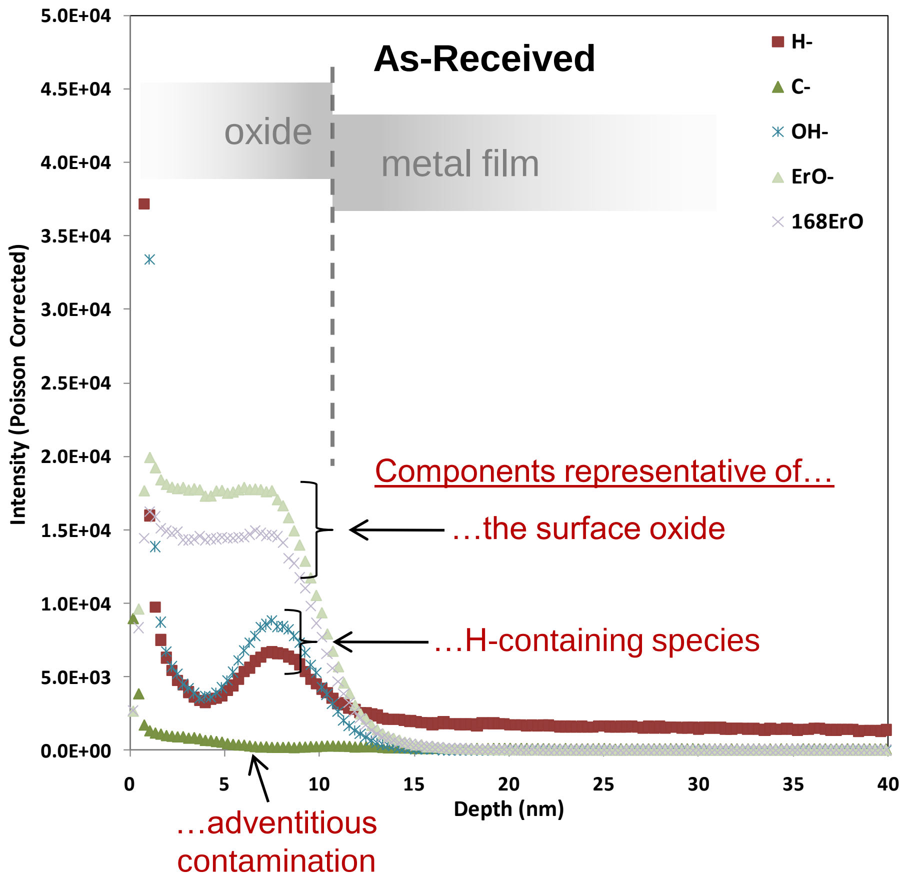
All elements can be observed (including H)

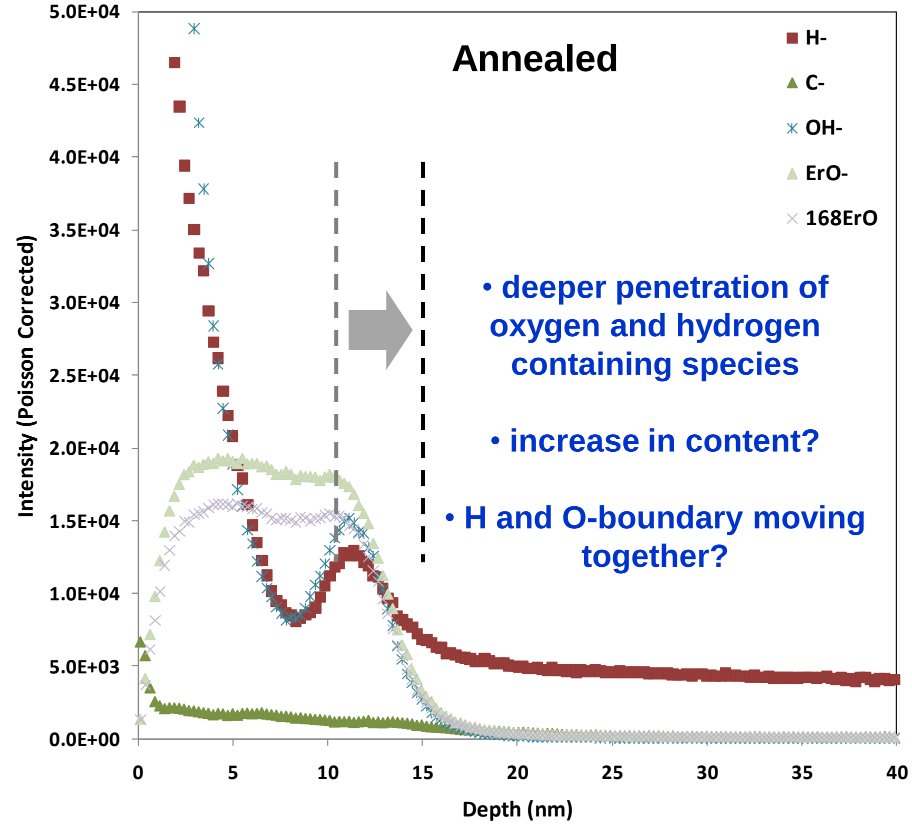
High mass resolution

Depth-profiling

Hydrogen Containing Species in Near Surface Region

Annealing leads to deeper penetration of Oxygen into the bulk along with a larger peak in Hydrogen concentration at the metal/oxide interface.



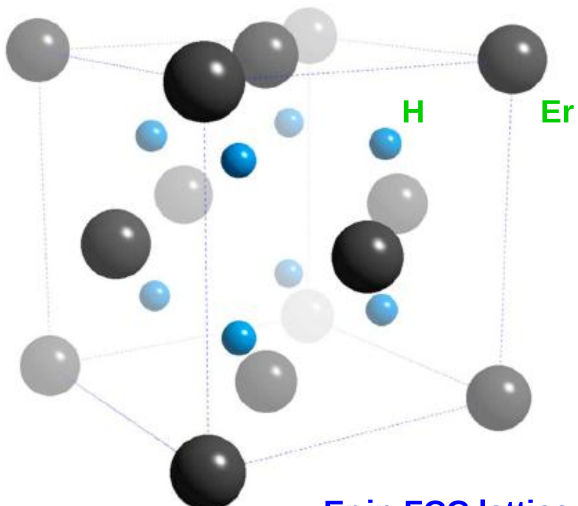


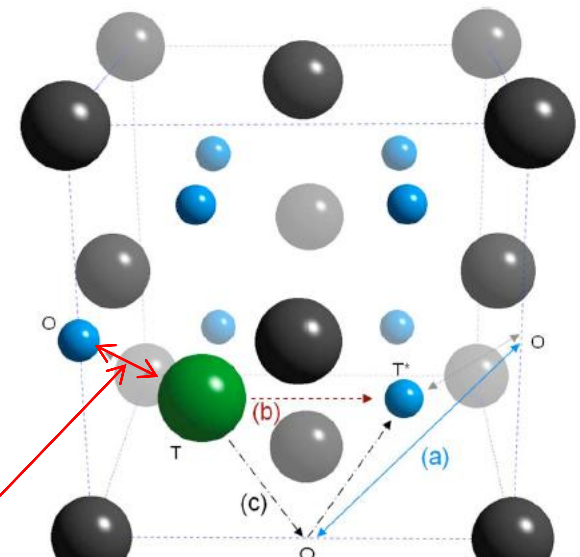
• other species (Sc, Ti, …) not identified at any significant level

Wixom, Browning, Snow, Schultz, Jennison,
J. App. Phys. 103, 123708 (2008).

O and H in ErH_2

Annealing leads to O diffusion into the bulk with concerted motion of H.

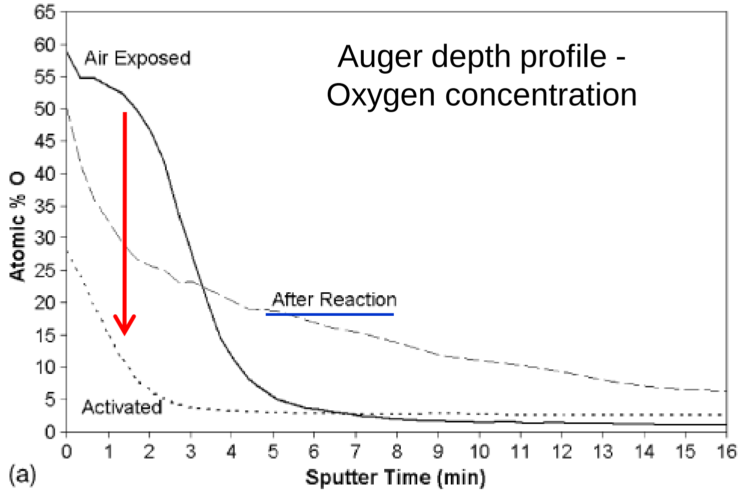




- Er in FCC lattice
- H prefers tetrahedral sites in unit cell
- O also prefers tetrahedral sites and will displace H to occupy tetrahedral site
- H is displaced to octahedral sites (along edges of unit cell)
  (each O potentially creates an $H_{oct.}$ occupancy)
- rate-limiting barrier for $H_{oct.}$ transport is significantly less than for $H_{tet.}$
- O movement proceeds via $O_{tet.} \rightarrow O_{oct.} \rightarrow O_{tet.}$ displacing H to $H_{oct.}$ with each step

Previous work

→ Surface oxide prevents H absorption and desorption
→ Hydrided films have shown a thick "oxide" layer



Tewell, King. *App. Surf. Sci.* **253** (2006) 2597-602.

Activation shows a decrease in oxygen at the surface,

but hydrogen reaction shows a large increase in total oxygen.

The manifestation of oxygen contamination in ErD_2 thin films

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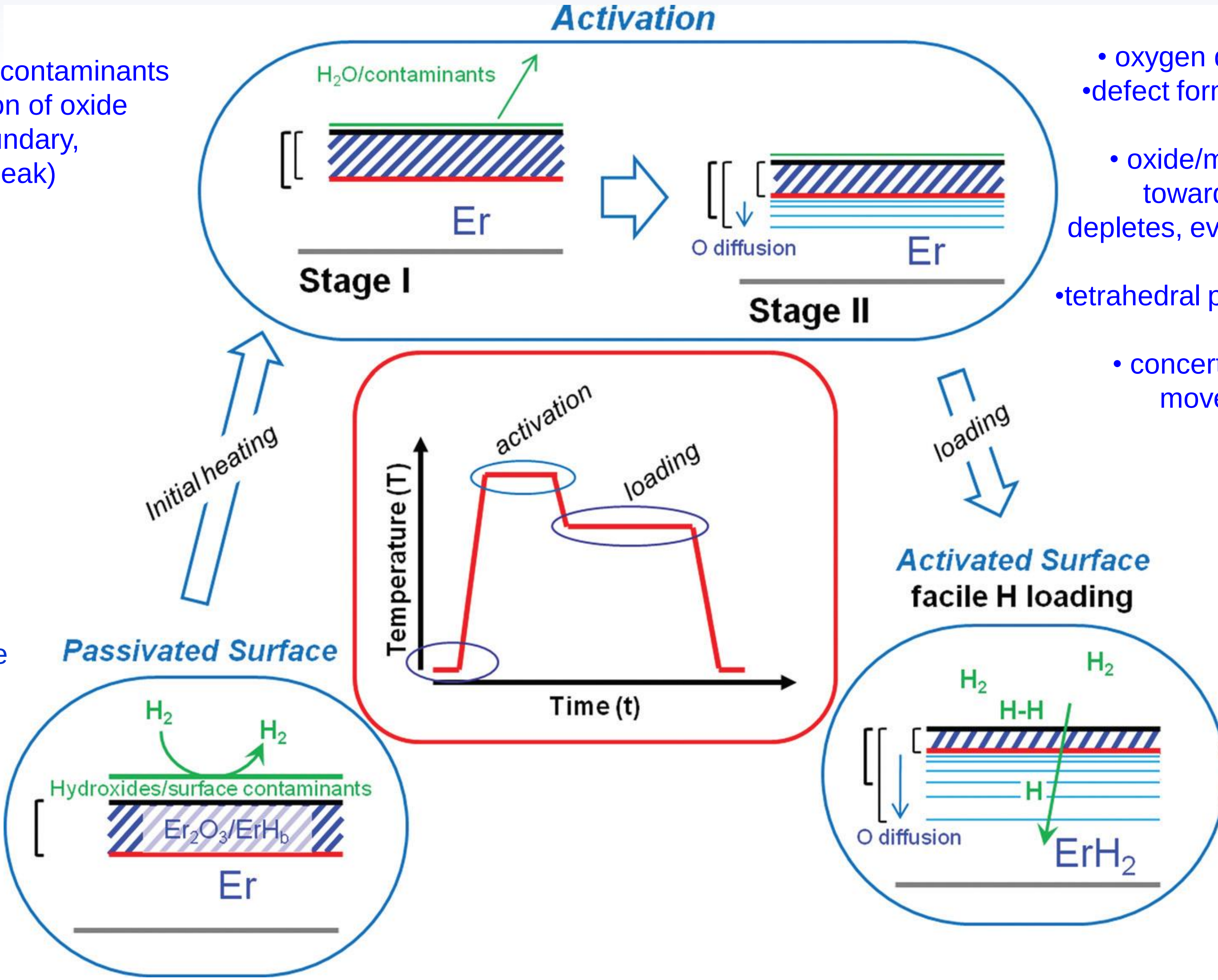
J. Mater. Res., Vol. 24, No. 5, May 2009

Erbium dihydride $Er(H,D,T)_2$ is a fluorite structure rare-earth dihydride useful for the storage of hydrogen isotopes in the solid state. However, thermodynamic predictions indicate that erbium oxide formation will proceed readily during processing, which may detrimentally contaminate $Er(H,D,T)_2$ films. In this work, transmission electron microscopy (TEM) techniques including energy-dispersive x-ray spectroscopy, energy-filtered TEM, selected area electron diffraction, and high-resolution TEM are used to examine the manifestation of oxygen contamination in ErD_2 thin films. An oxide layer ~30–130 nm thick was found on top of the underlying ErD_2 film, and showed a cube-on-cube epitaxial orientation to the underlying ErD_2. Electron diffraction confirmed the oxide layer to be Er_2O_3. While the majority of the film was observed to have the expected

Thermal Activation Description

Stage I
- elimination of contaminants
- recrystallization of oxide (thinning of boundary, uniform oxide peak)



Stage II
- oxygen diffusion into the bulk
- defect formation at metal/oxide interface
- oxide/metal interface moves towards surface as oxygen depletes, eventually Er^0 exposed at surface
- tetrahedral positions available for H occupation
- concerted hydrogen/oxygen movement with interfacial boundary

Passive
Passive surface oxide prevents hydrogen adsorption and dissociation.

Activated
High electron density from metallic species exposed at the surface, H_2 dissociation is enhanced.

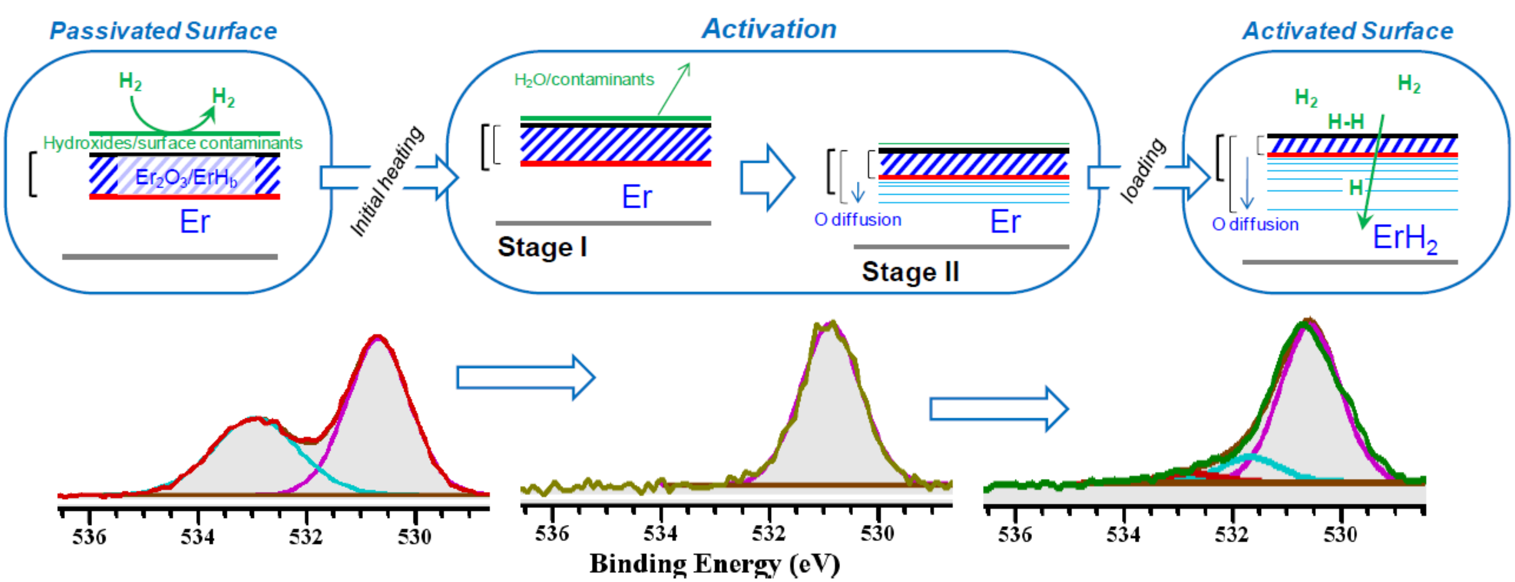
Conclusions

The passive surface oxide prevents H loading, but can be degraded by thermal treatment.

"Activation" is degradation of the surface oxide by diffusion of oxygen into the bulk.

Oxygen occupies tetrahedral sites that H would prefer to occupy.

Reformation of the surface oxide after hydriding probably stabilizes the hydride over the long term.
Oxygen is incorporated during hydriding and thereby reduces H loading level.



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Daniel Breitenstein

More details can be found at…
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