SAND2022-12935C

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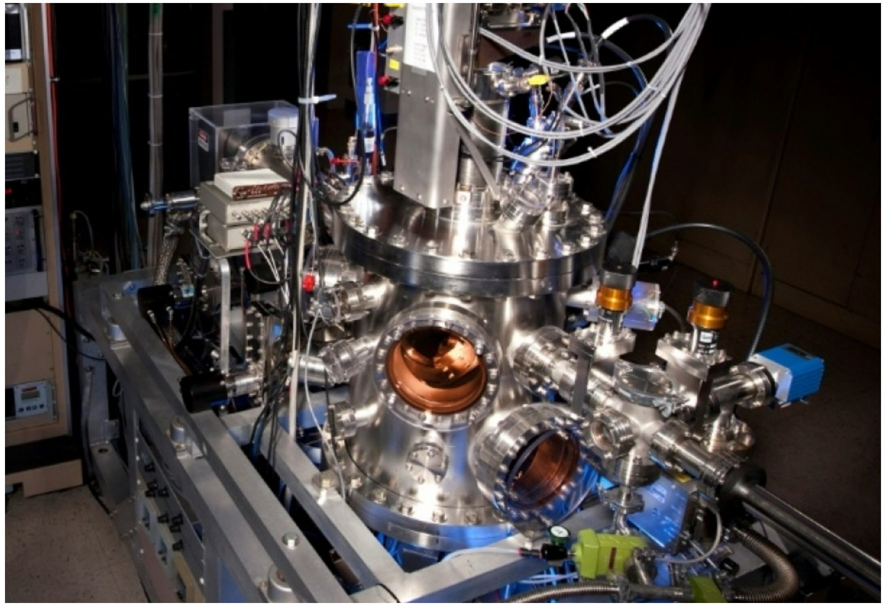
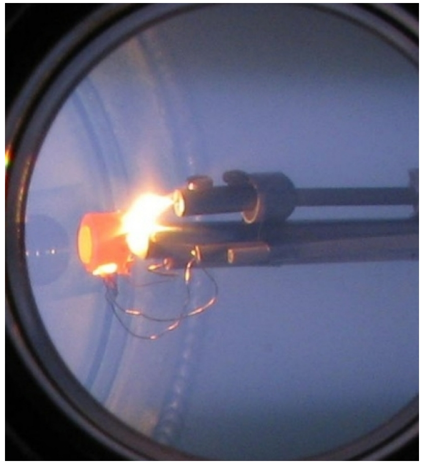
Mechanisms of iron aluminide surface passivation against D, D_2, and D_2O exposure

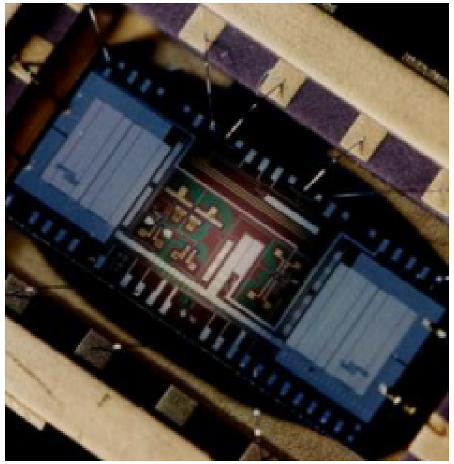


Robert Kolasinski and Tim Wong

PLASMA & REACTING FLOW SCIENCE DEPARTMENT

SANDIA NATIONAL LABORATORIES – LIVERMORE





Mid-year update meeting (May 24, 2022)

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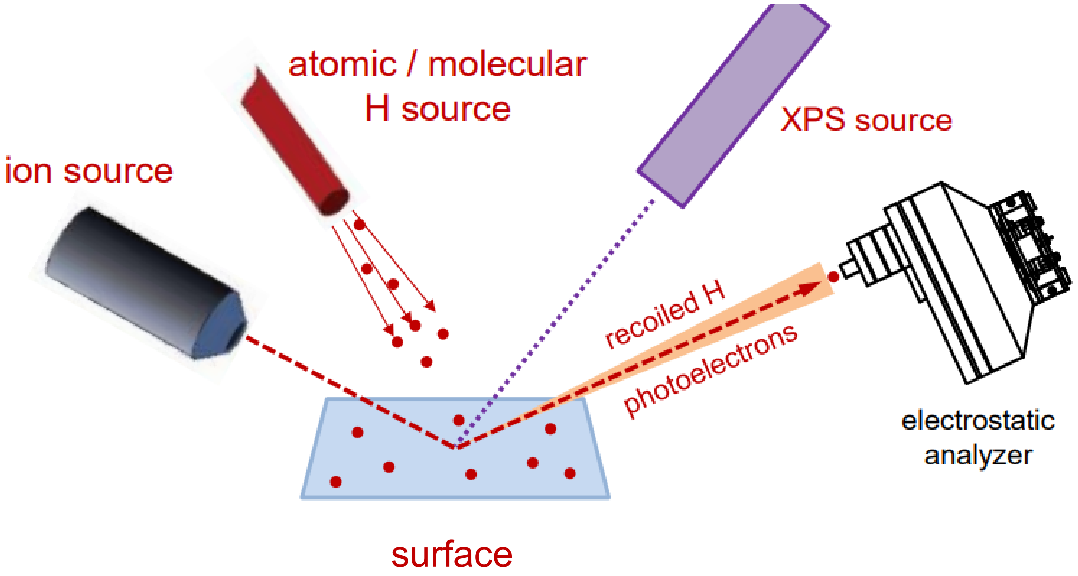
Mechanisms of iron aluminide surface passivation against D, D_2, and D_2O exposure

- TPBARs include an iron aluminide (Fe-Al) coating on 316 stainless steel cladding, serving as a tritium permeation barrier.
- Surface is exposed to T_2 and T_2O at elevated temperatures.
- Goal of this work is to decipher surface phenomena that may play a role in hydrogen chemisorption and uptake.

Key science questions:

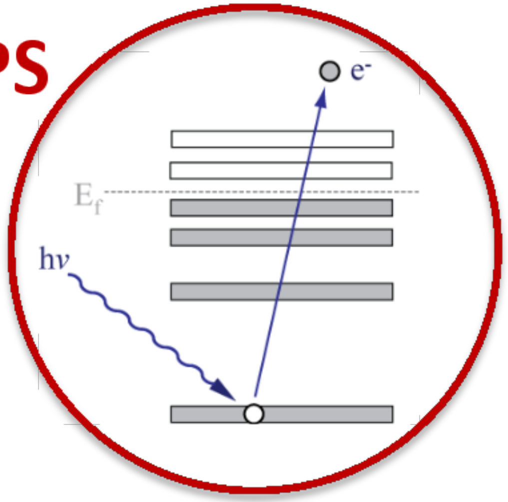
- Is adsorption of atomic D different from molecular D on Fe-Al surfaces?
- What is the nature of the surface composition and oxide thickness on technical Fe-Al surfaces?
- How do water molecules adsorb and dissociate on the surface? What effect does this have on H chemisorption?



Overview of Experimental Approach

We use a combination of techniques to understand the H behavior on surfaces

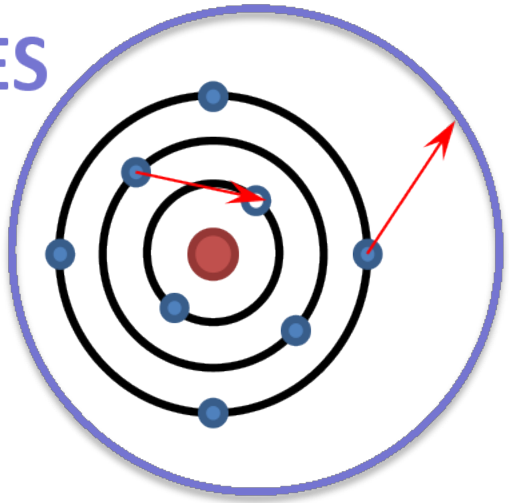
XPS



X-ray Photoelectron Spectroscopy

Surface chemistry & bonding information Analysis depth: 5 nm

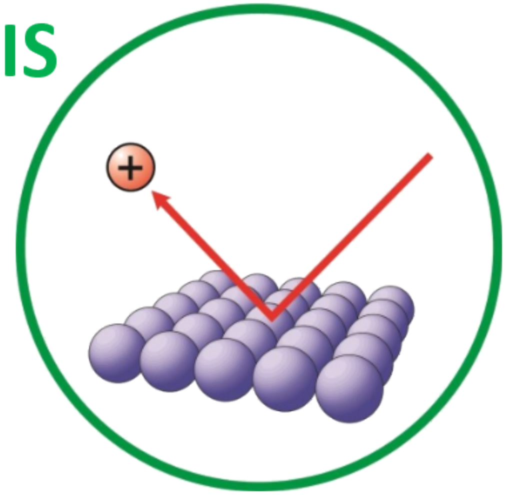
AES



Auger Electron Spectroscopy

Surface composition & imaging Analysis depth: 5 nm

LEIS



Low Energy Ion Scattering

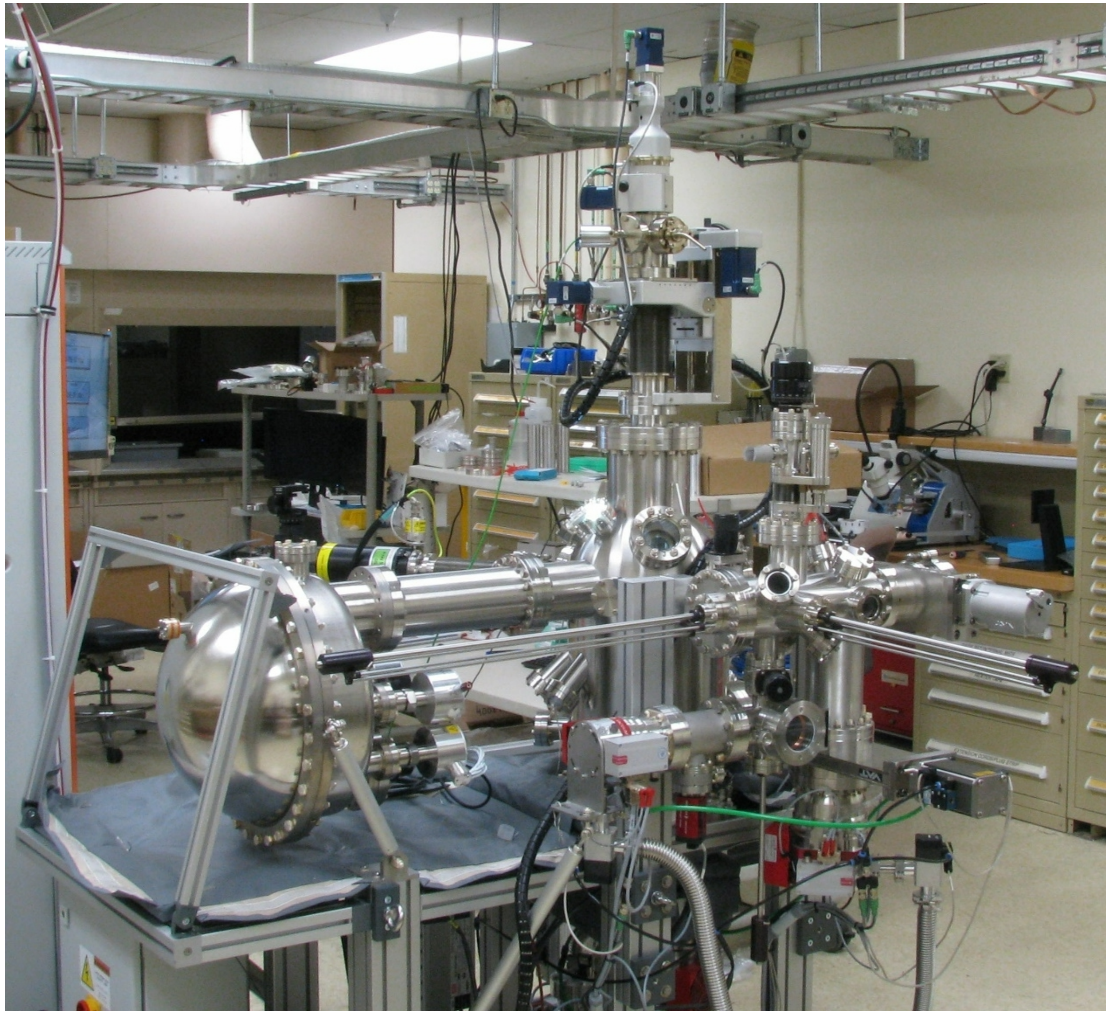
Hydrogen coverage Analysis depth: 1 ML

New instrument for XPS / low energy ion beam analysis

Intended for studies of hydrogen interactions with surfaces

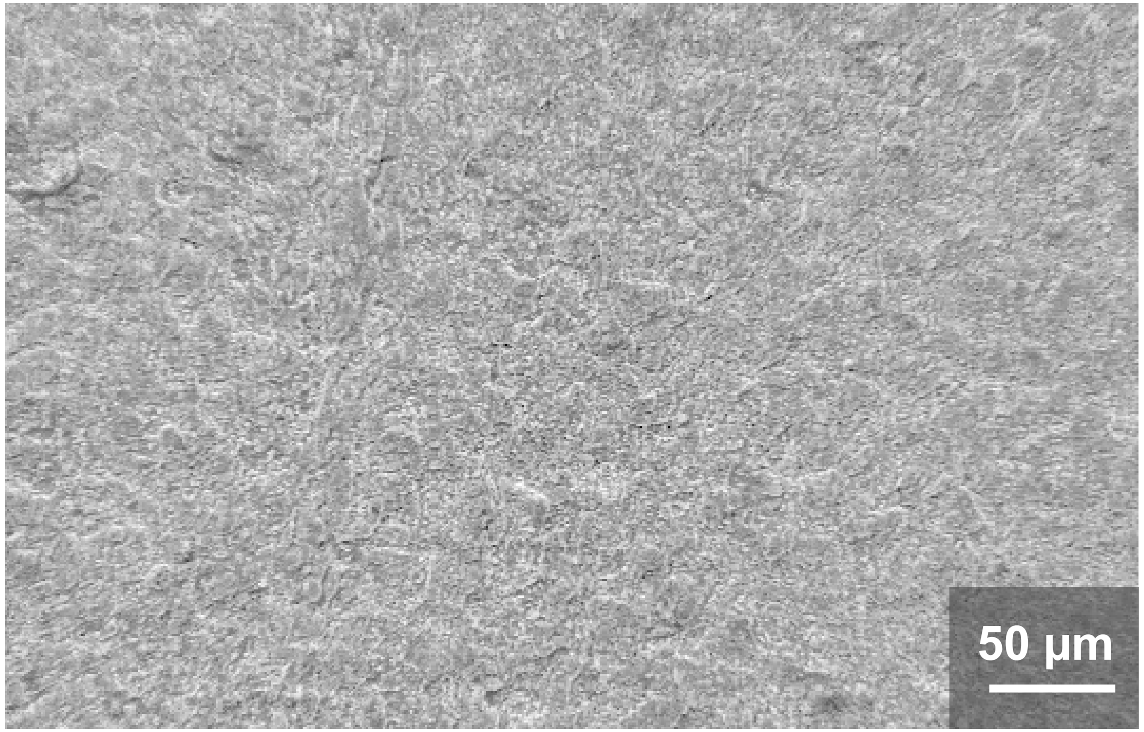
Optimized for:
- X-ray photoelectron spectroscopy
  - Local chemical environment
- Ion scattering / direct recoil spectroscopy
  - Detection of H isotopes
- In-situ annealing of samples up to 1900 °C in UHV

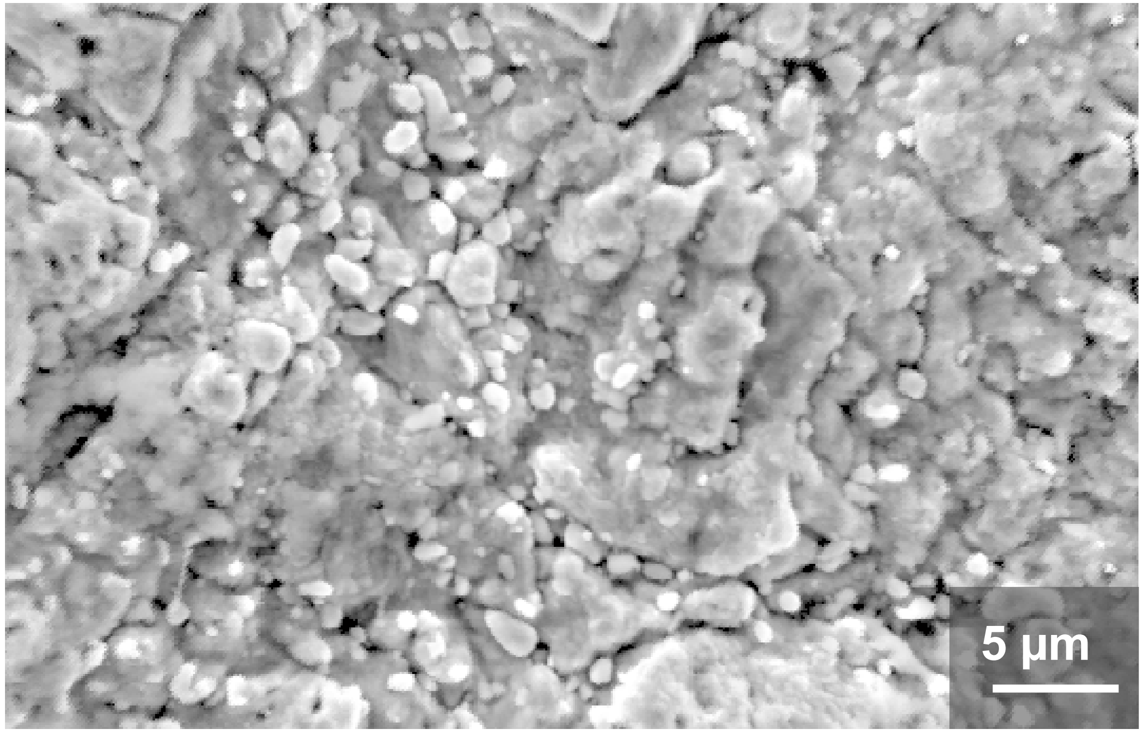
Instrumentation:
- 135 mm radius hemispherical analyzer
- Two ion sources to be added in Fall 2022 for ion scattering and depth profiling studies
- Precision manipulator for structural studies



LEIS / XPS instrument at SNL-Livermore

SEM imaging of Fe-Al coatings

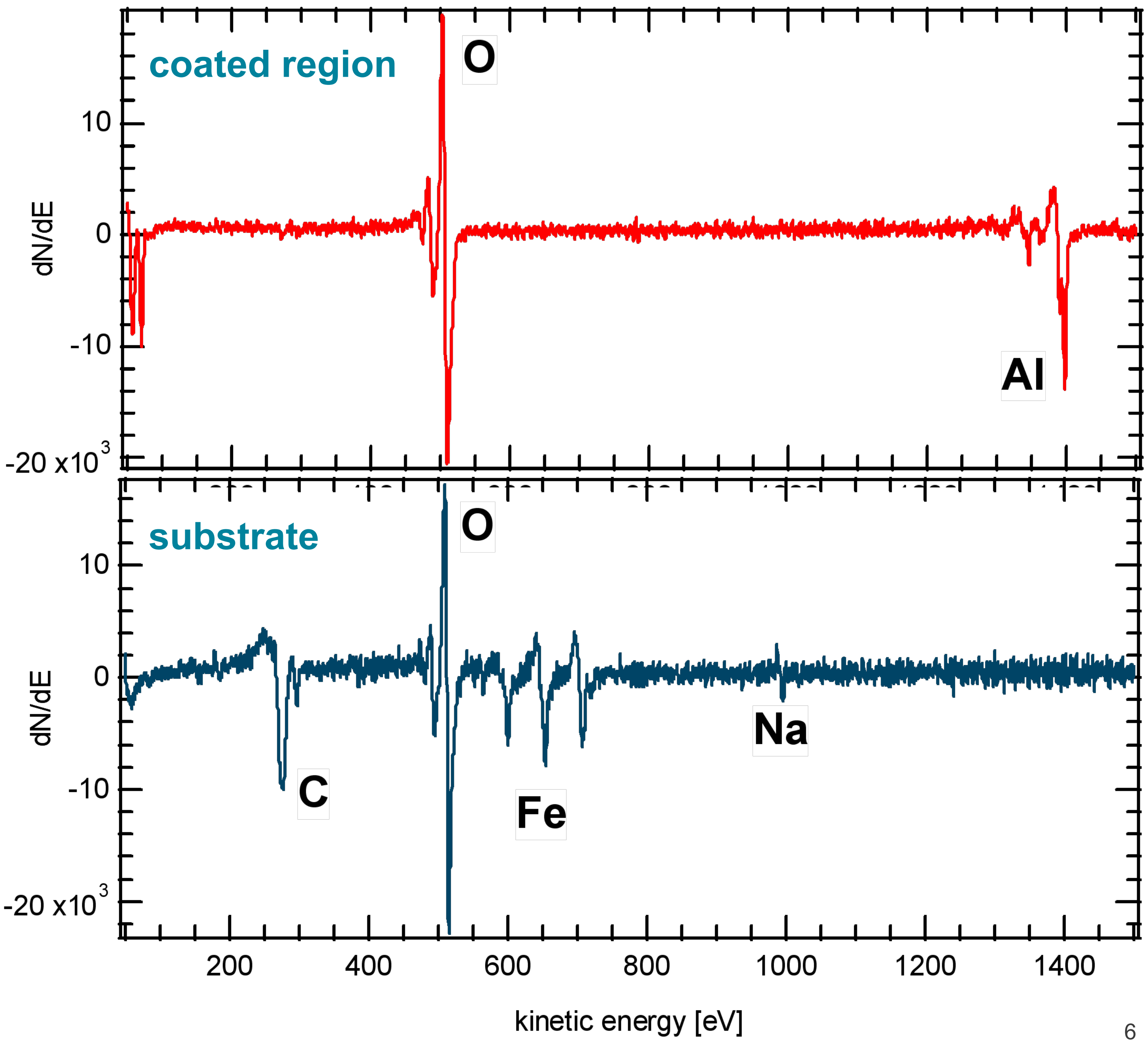




- We cut apart a Fe-Al specimen provided by PNNL using a diamond saw
- Sample imaged using scanning Auger for baseline analysis of surface composition / structure
- Coated surface has highly textured morphology. Coverage was continuous aside from some small gaps created by mechanical abrasion during handling / surface preparation

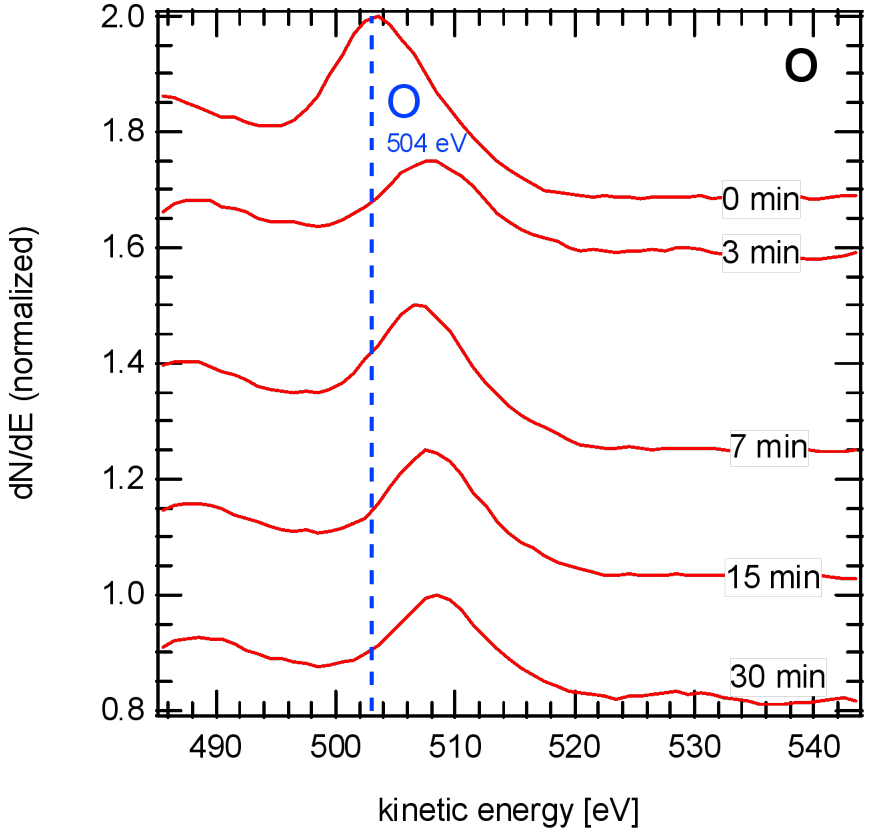
AES analysis

- Coating is enriched with Al, consistent with findings of prior work. The aluminum appears heavily covered by O.
- As received composition:
  - **48 % O**
  - **43 % Al**
  - **4 % C**
  - **3 % Fe**
- Almost no signs of Fe, except in regions that had been scratched (removing part of the coating)
- Other species absent, with the exception of typical contaminants (including C and Na)



AES depth profiling results

- Depth profiling attempted using 2 keV Ar^+ ion with 1 μA current
- After continuous sputtering over 30 min., only a modest change in composition observed
- Slight shift in O KLL peak after 3 min. sputtering consistent with removal of chemisorbed O layer covering oxide beneath



Evolution of O KLL peaks as a function of sputter depth profiling.

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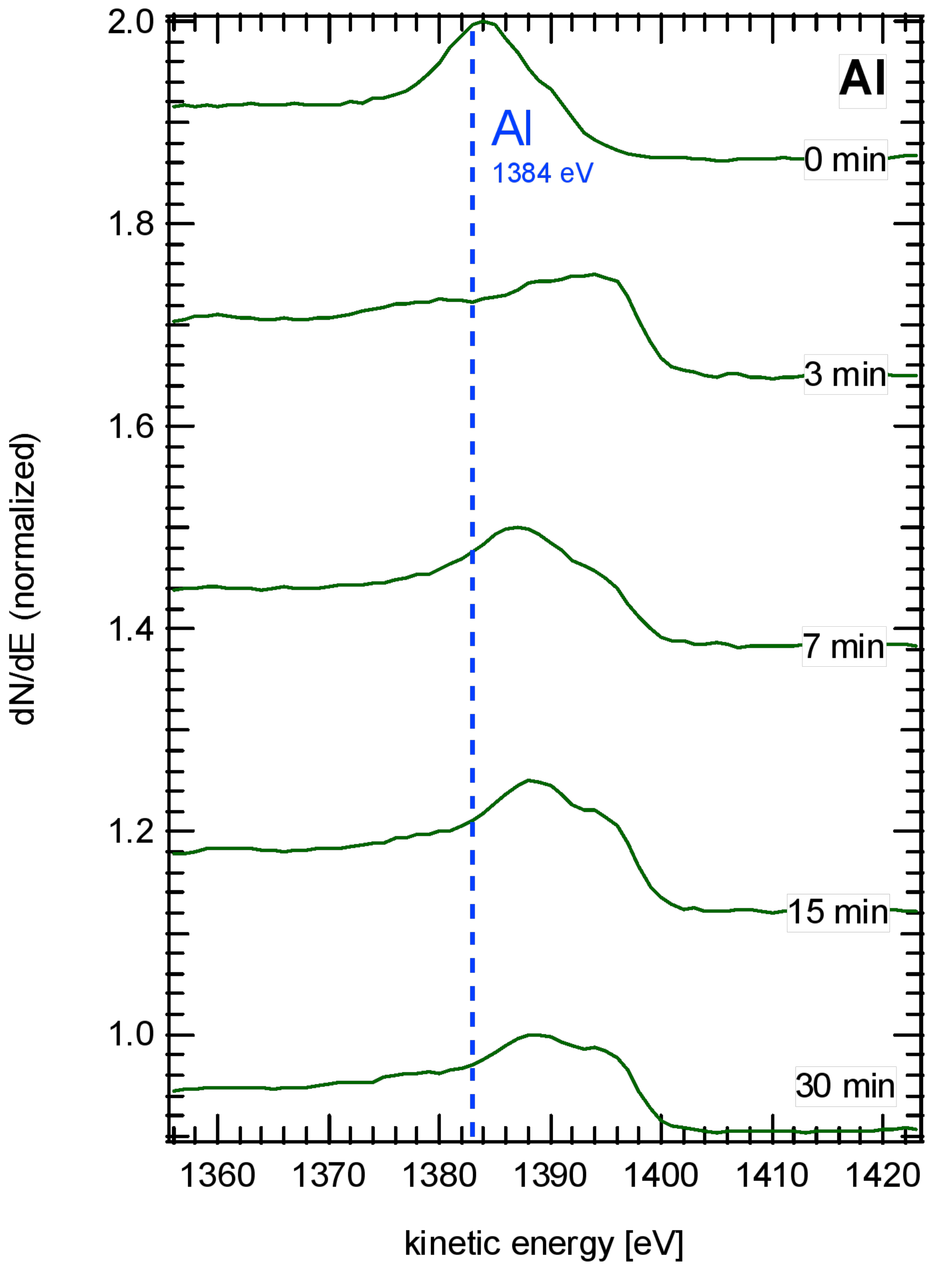
- A similar evolution of the AL KLL peaks to higher energy is observed, suggesting outer layer of metallic Al covered with O.



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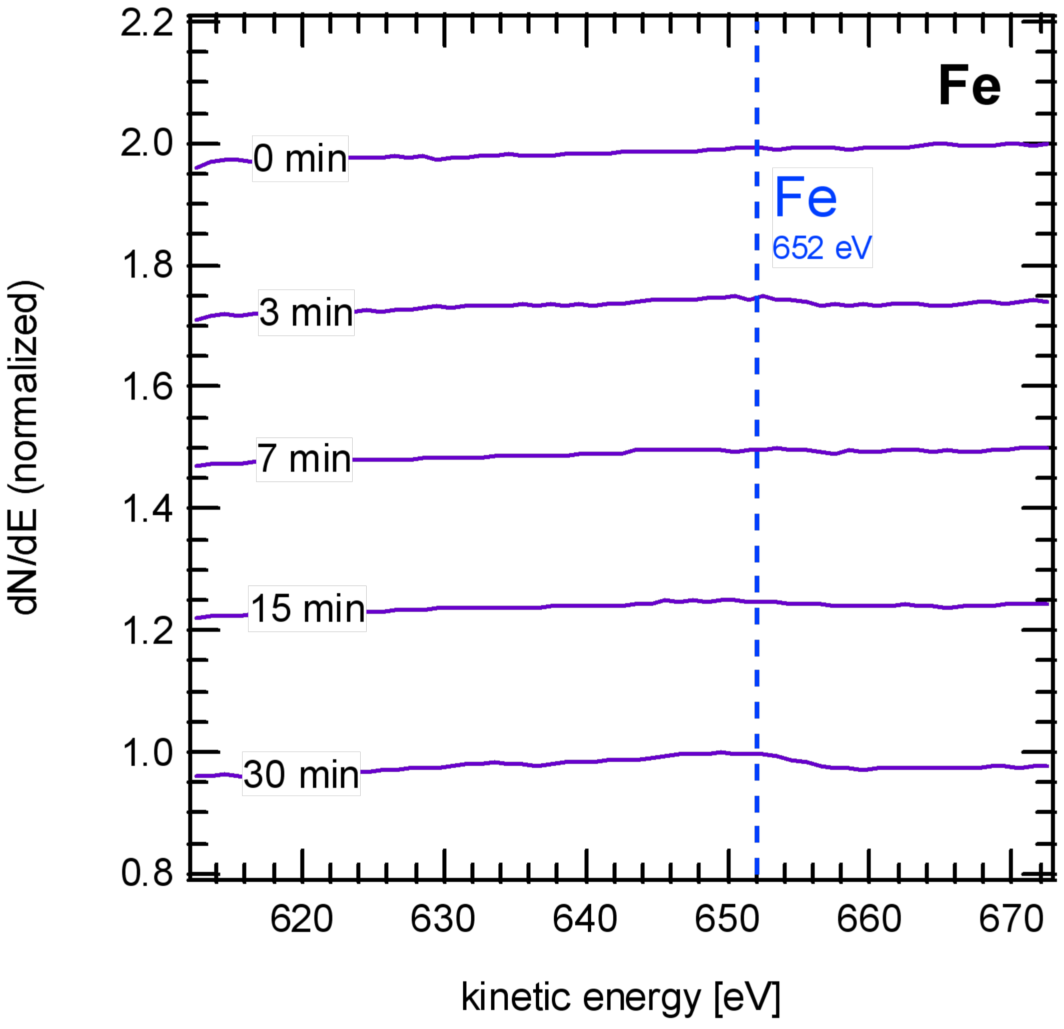
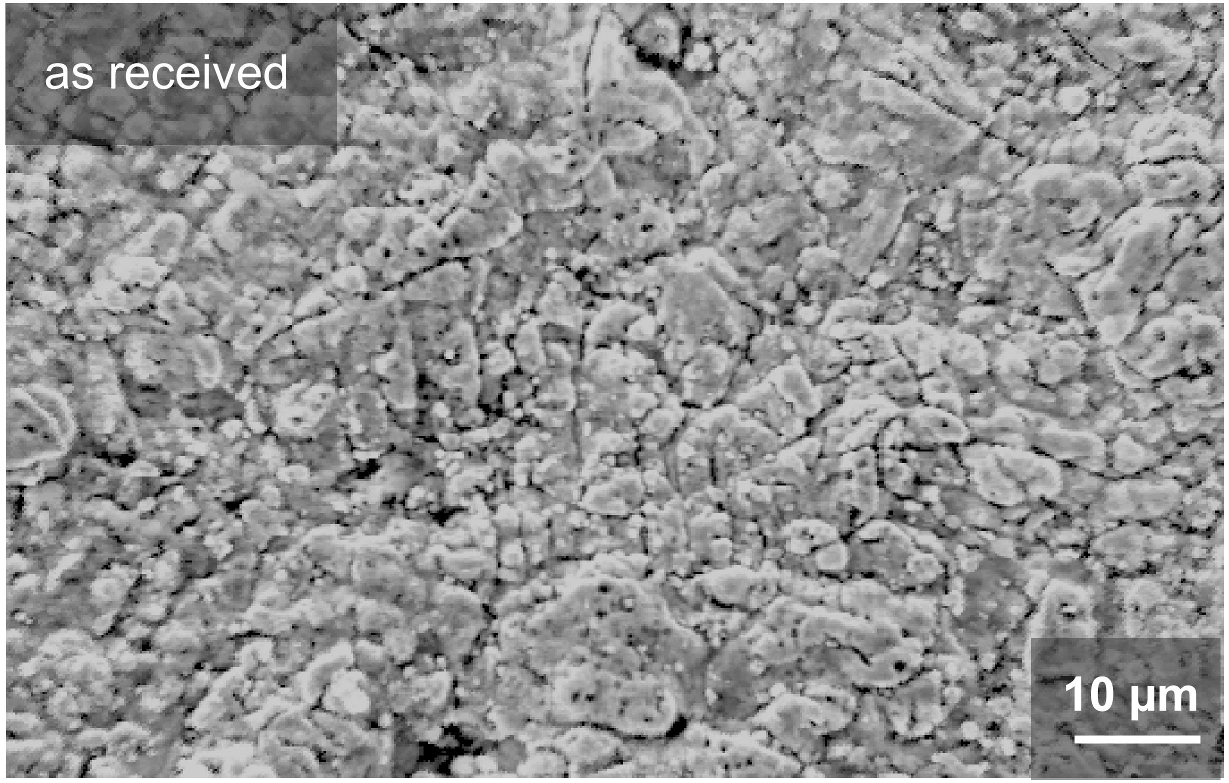
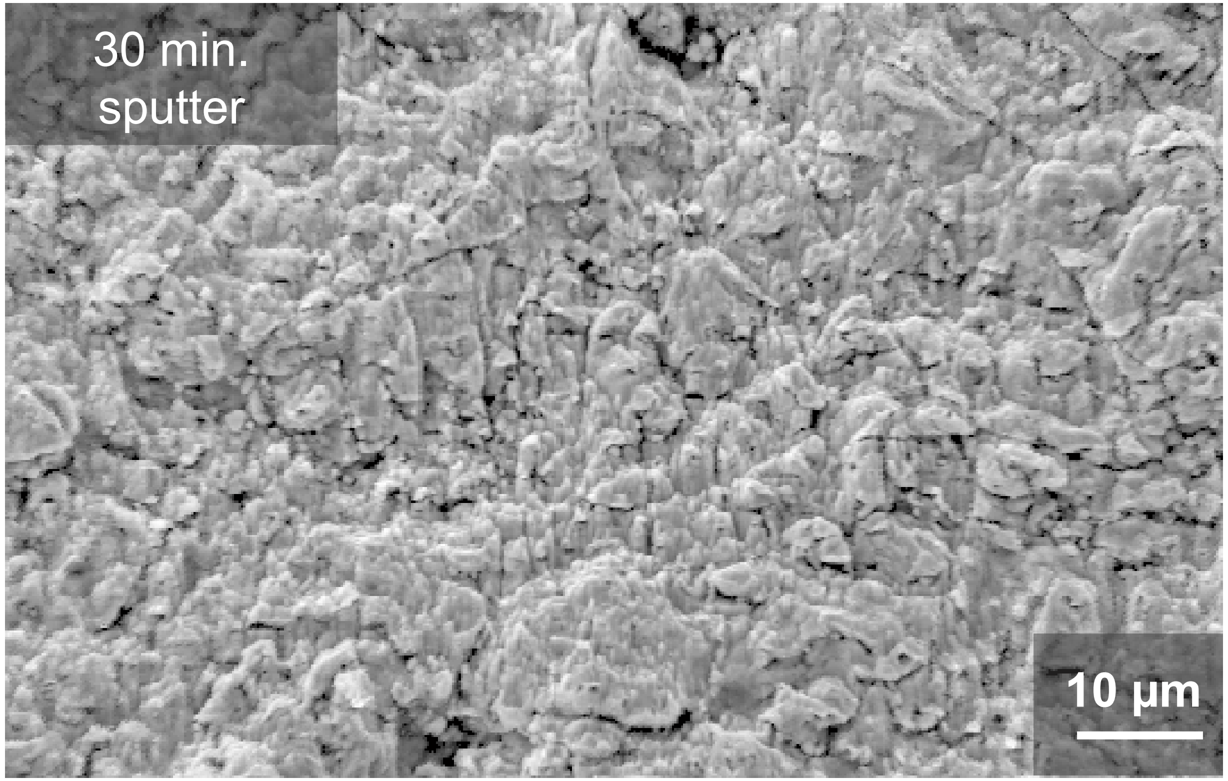
- Trace amounts of Fe only apparent after 30 min. of sputtering, suggesting it is buried well beneath the surface



Minimal evidence of Fe during sputtering

Appearance of Fe-Al coating before and after sputtering

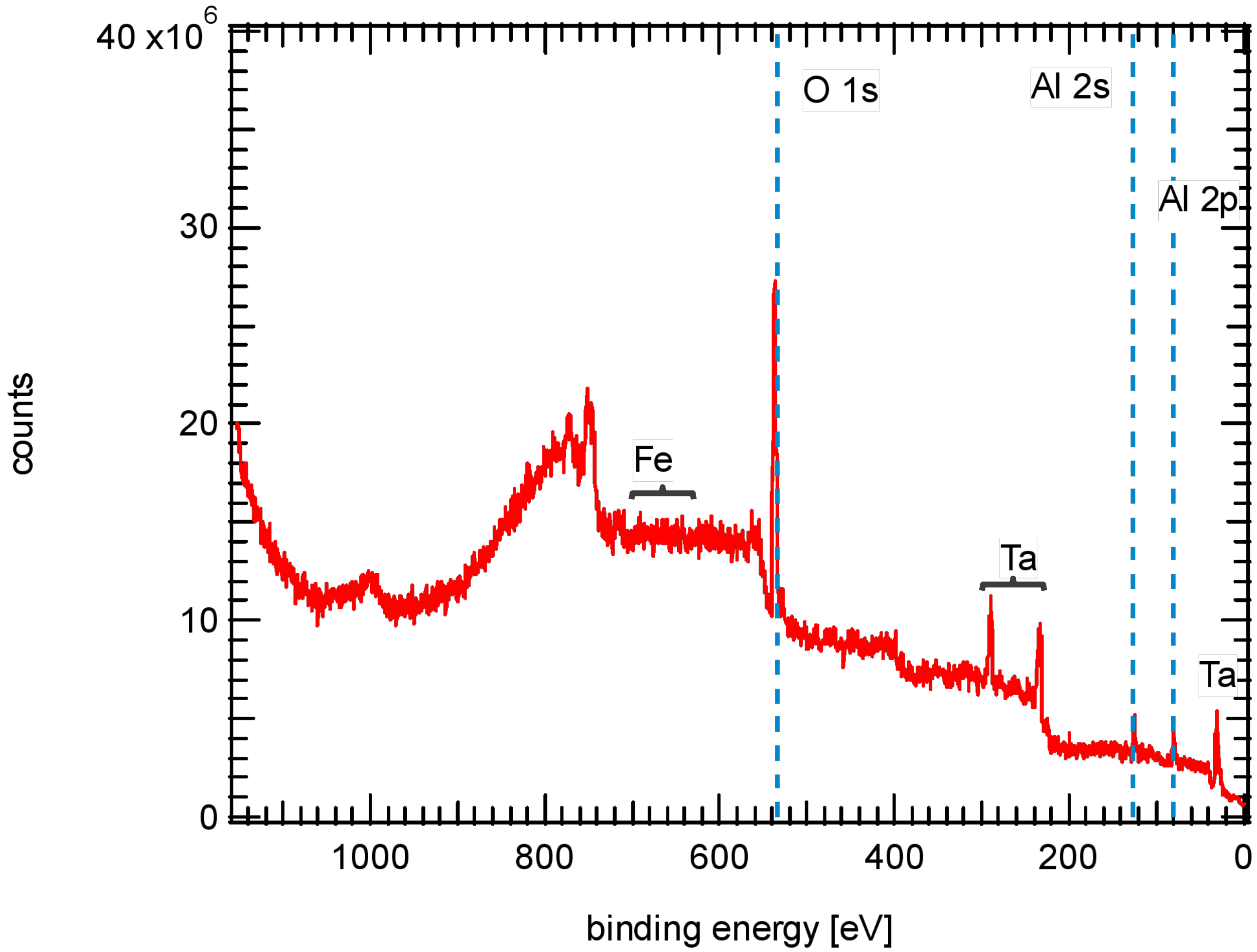




- We observed minimal changes to surface morphology after sputtering for 30 min. The observed surface morphology may be largely due to oxide growth.

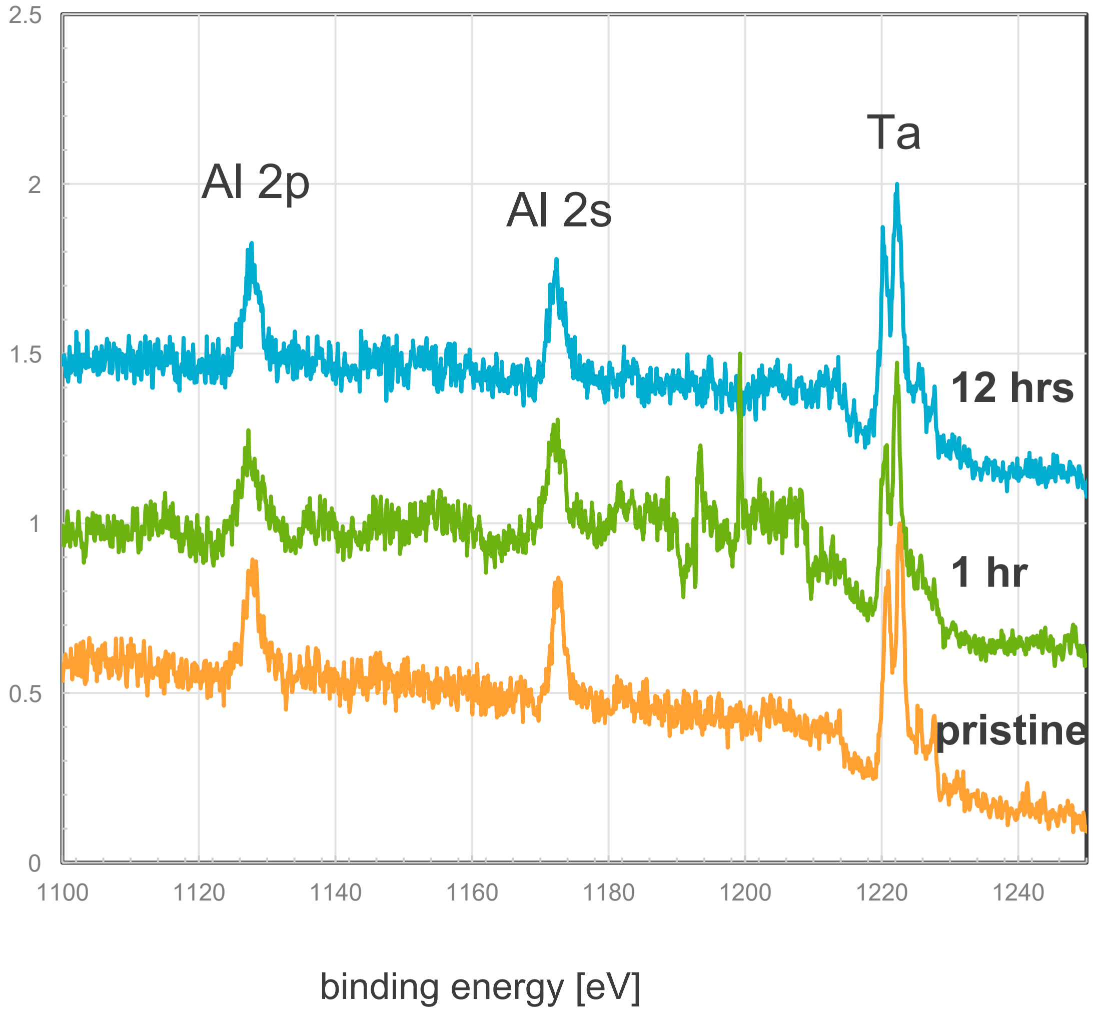
XPS analysis

- Initial survey scan revealed similar information as the AES analysis, with the surface primarily covered with Al and O.
- No evidence of Fe at the surface was observed. XPS samples to a depth of ~5 nm.
- Specimens were inserted into a high temperature annealing stage and were heated to 300 °C for different durations up to 12 hours. Samples were transferred in-vacuum to an analysis chamber.
- Detailed scans of the regions containing Al, Fe, O and C photoelectron peaks were acquired afterward.



XPS survey spectrum of Fe-Al technical surface

XPS analysis indicates that heating to 300 °C for long duration does not drastically alter composition



XPS spectra showing Al peaks

Observations

- Al present within the surface as predominantly Al_2O_3 oxide phase
- Annealing at 300 °C does not drastically alter the peak intensities, suggesting that the overall surface composition remains roughly the same, even after long duration heating.
- No Fe present at the surface, even after 12 hr annealing cycle.

Why is only Al present at the surface?

Potential mechanisms underlying segregation of Al to Fe surfaces

Components that lower surface energy tend to segregate to surfaces.

For binary materials, the Gibbs segregation rule is:

$$\gamma_A + \frac{RT}{\sigma_A}\ln(\frac{x_s}{x_b}) = \gamma_B + \frac{RT}{\sigma_B}\ln(\frac{1-x_s}{1-x_b})$$

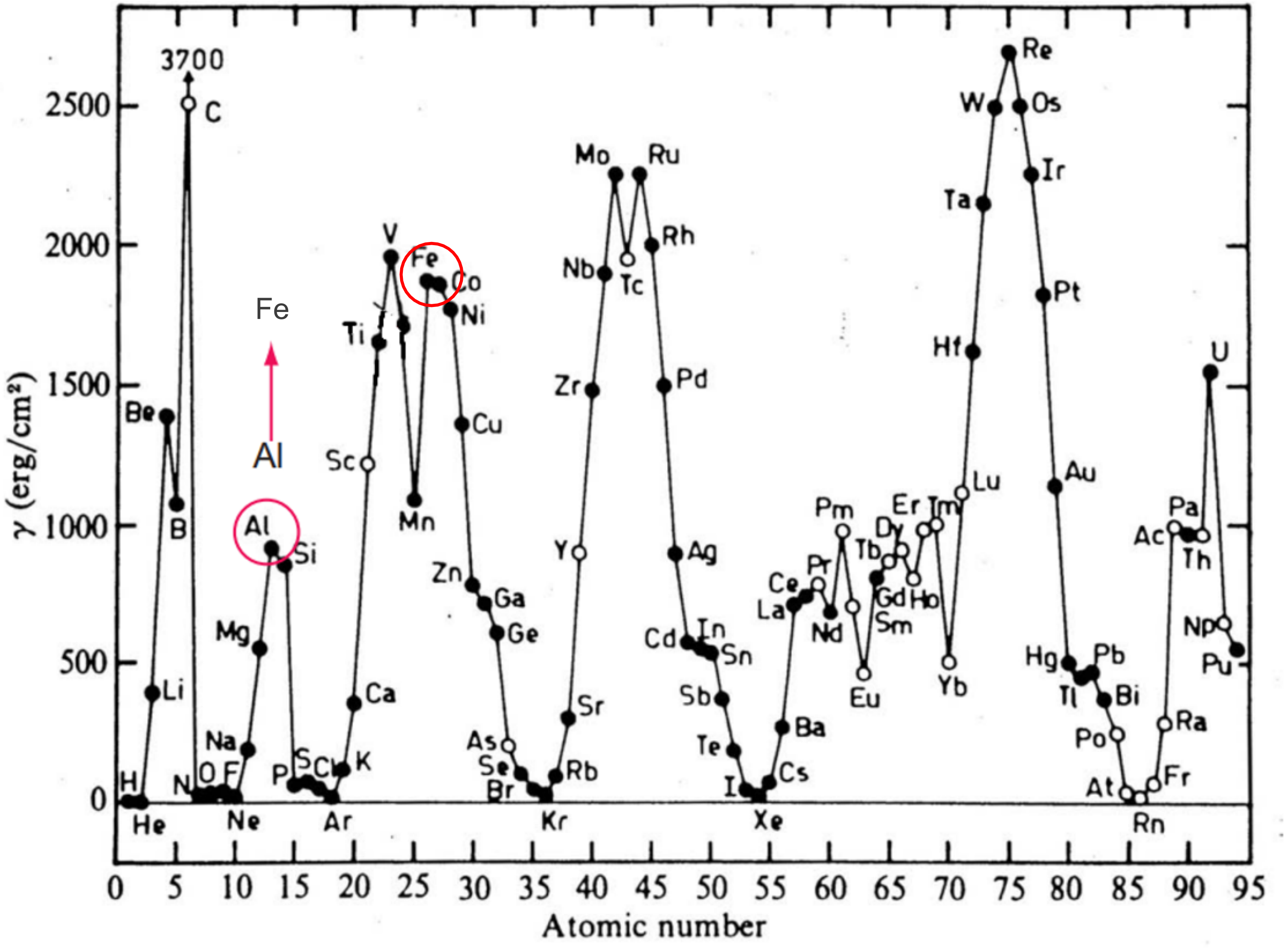
where:

γ_i is the surface tension and

σ_i is the surface area for species i

Since $\gamma_{Fe} > \gamma_{Al}$

Al should segregate to Fe surfaces.

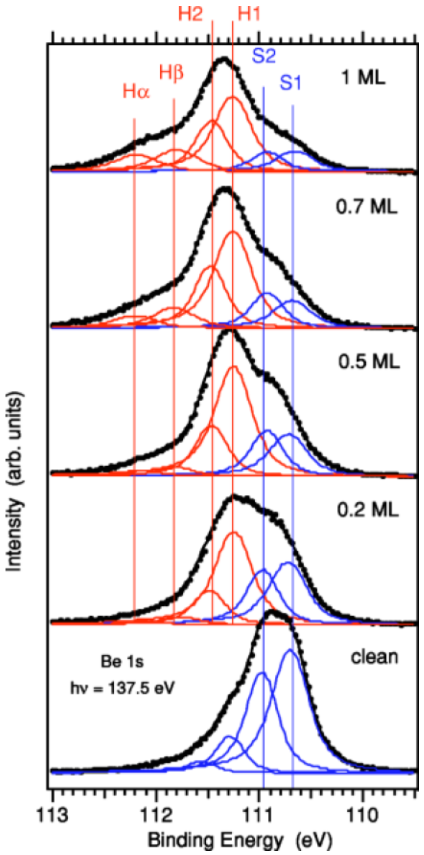


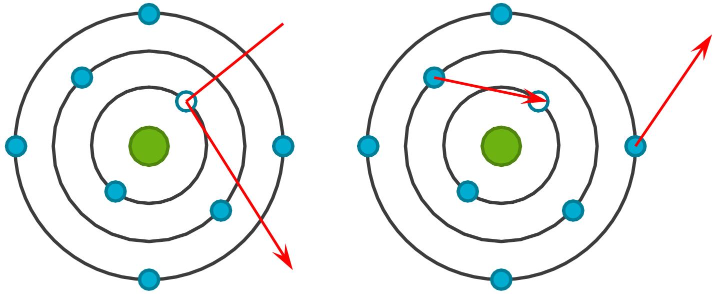
Surface tensions of the elements as liquids
A. Zangwill, Physics at Surfaces (Cambridge Press, 1988), p 11.

courtesy of Robert Bastasz

Detection of hydrogen on surface presents considerable challenges for many conventional surface techniques

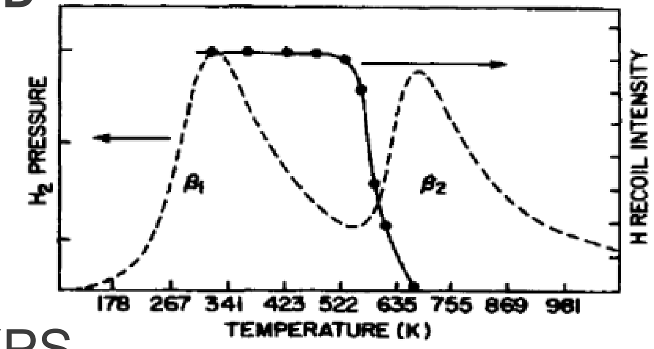
XPS





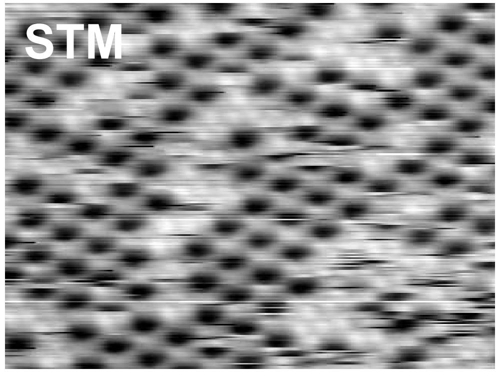
AES

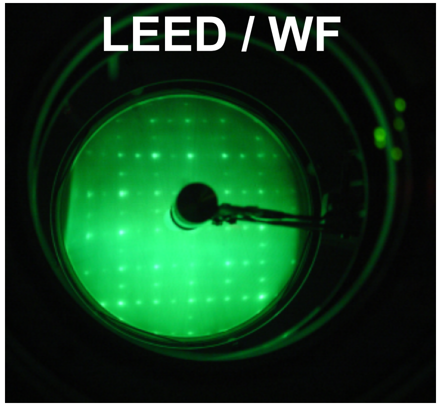
TPD



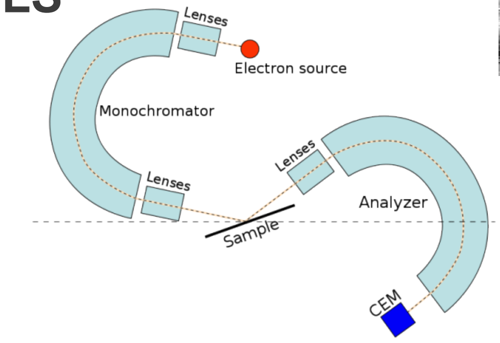
Technical challenges:

- Detection impossible with AES, fitting possible with XPS
- Detectable signal may be overwhelmed by substrate (LEED, STM, HREELS)
- Ambiguous/difficult to interpret. (TDS)



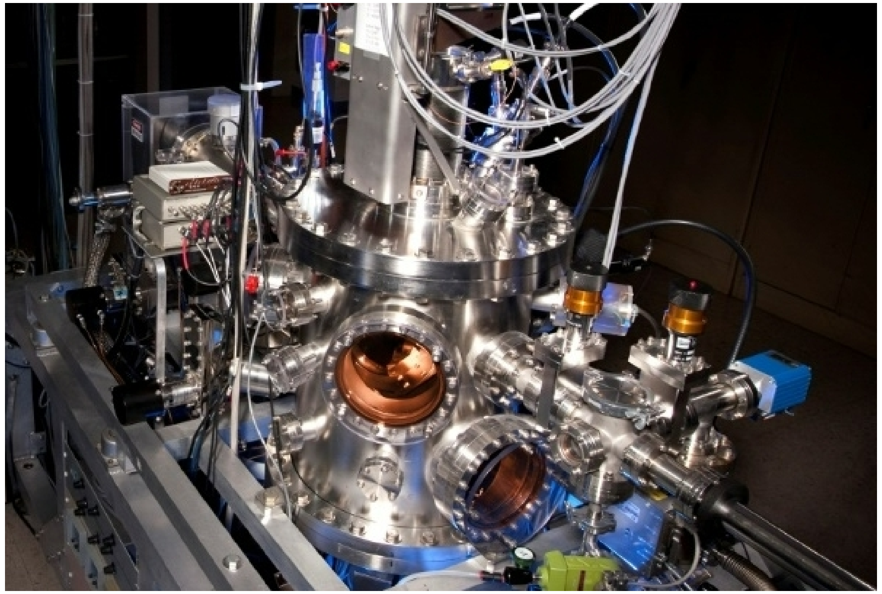


HREELS

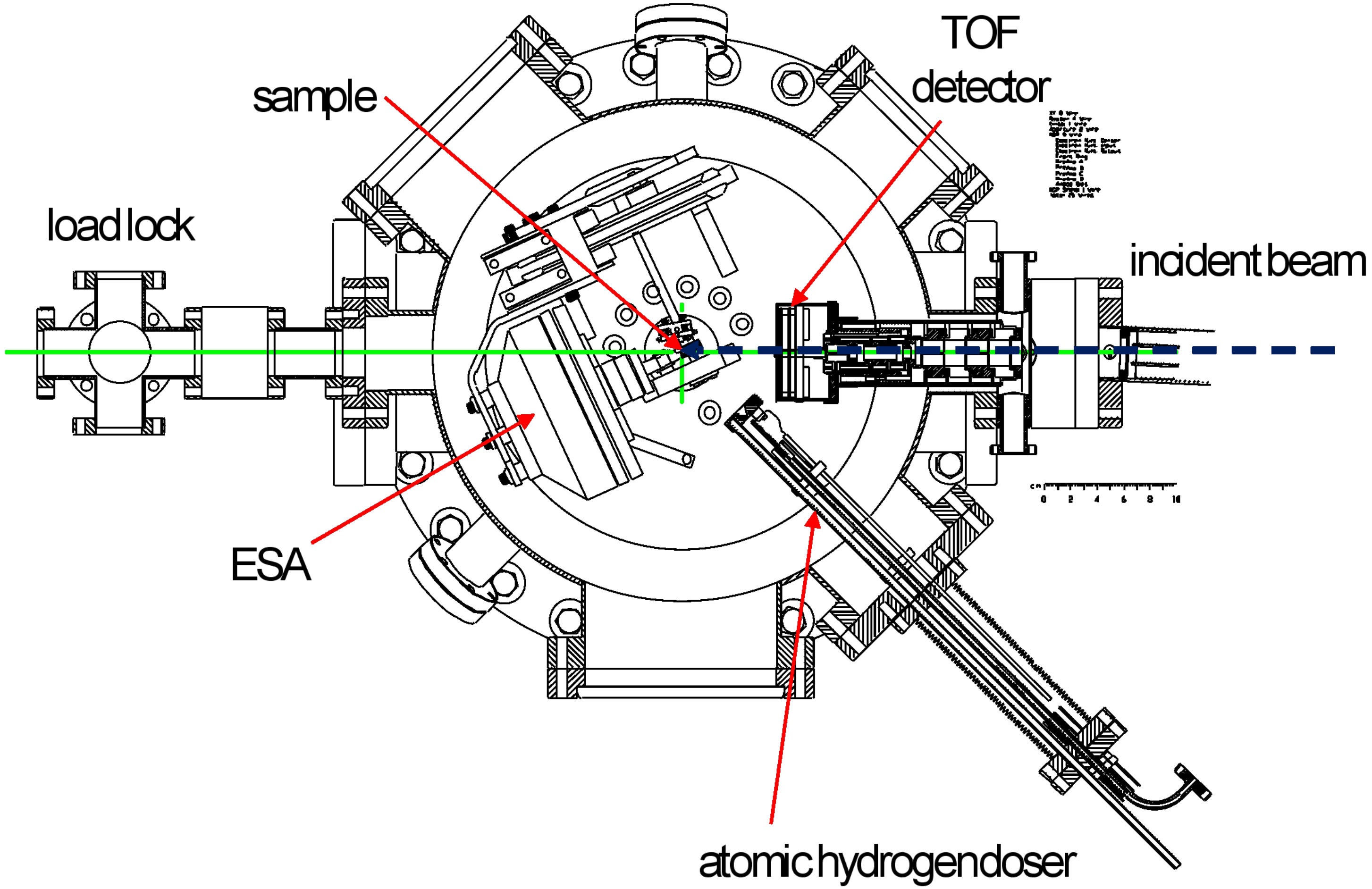


Low energy ion scattering can be used to answer questions about the behavior of chemisorbed H

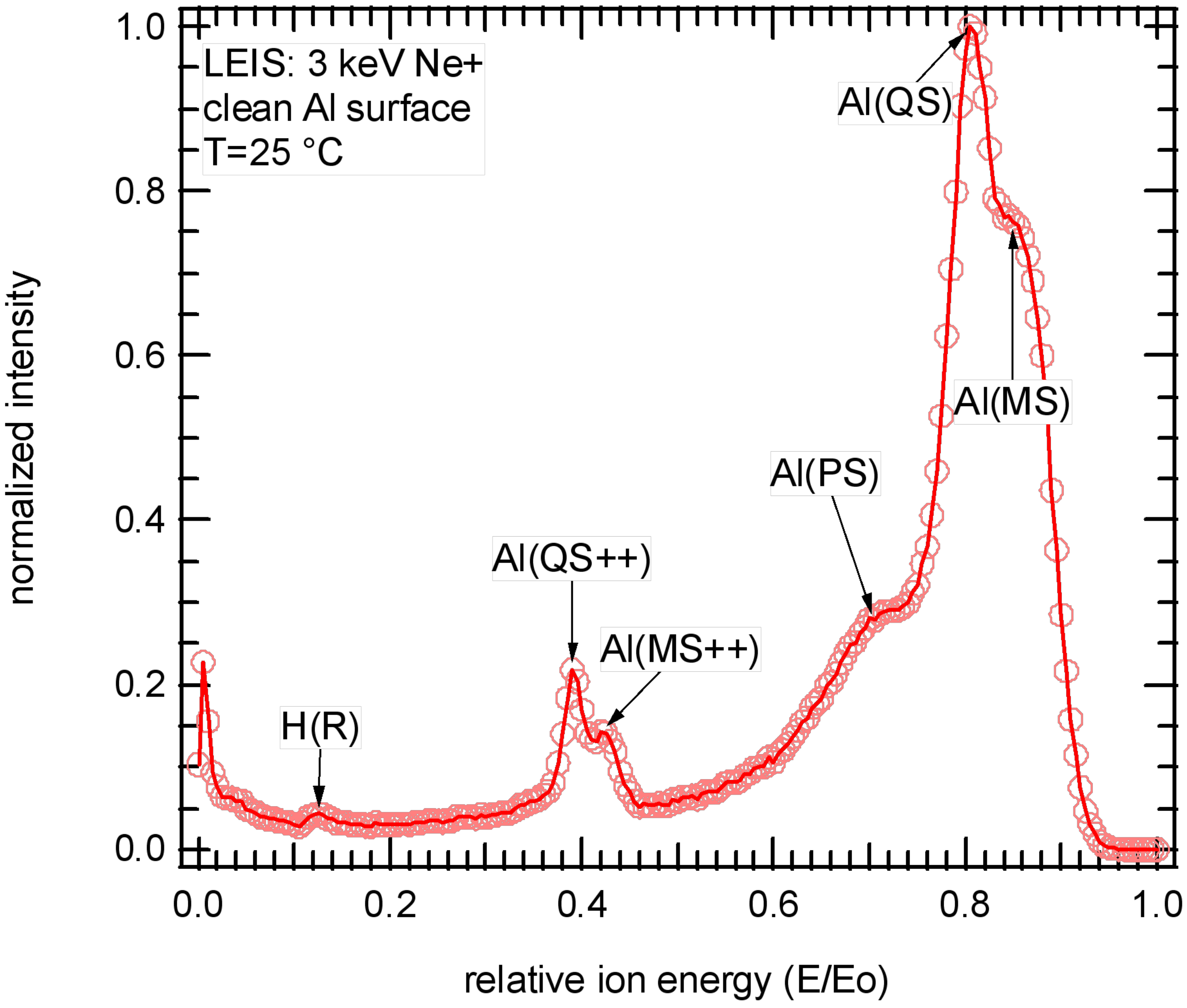
- Low energy ions: **< 3 keV He^+, Ne^+**
- Oblique incidence: **70° < α < 85°**
- Detection in far-forward direction
  - Scattering angle **θ < 45°**
- Atomic **H / D** dosing



Above: Angle-resolved ion energy spectrometer

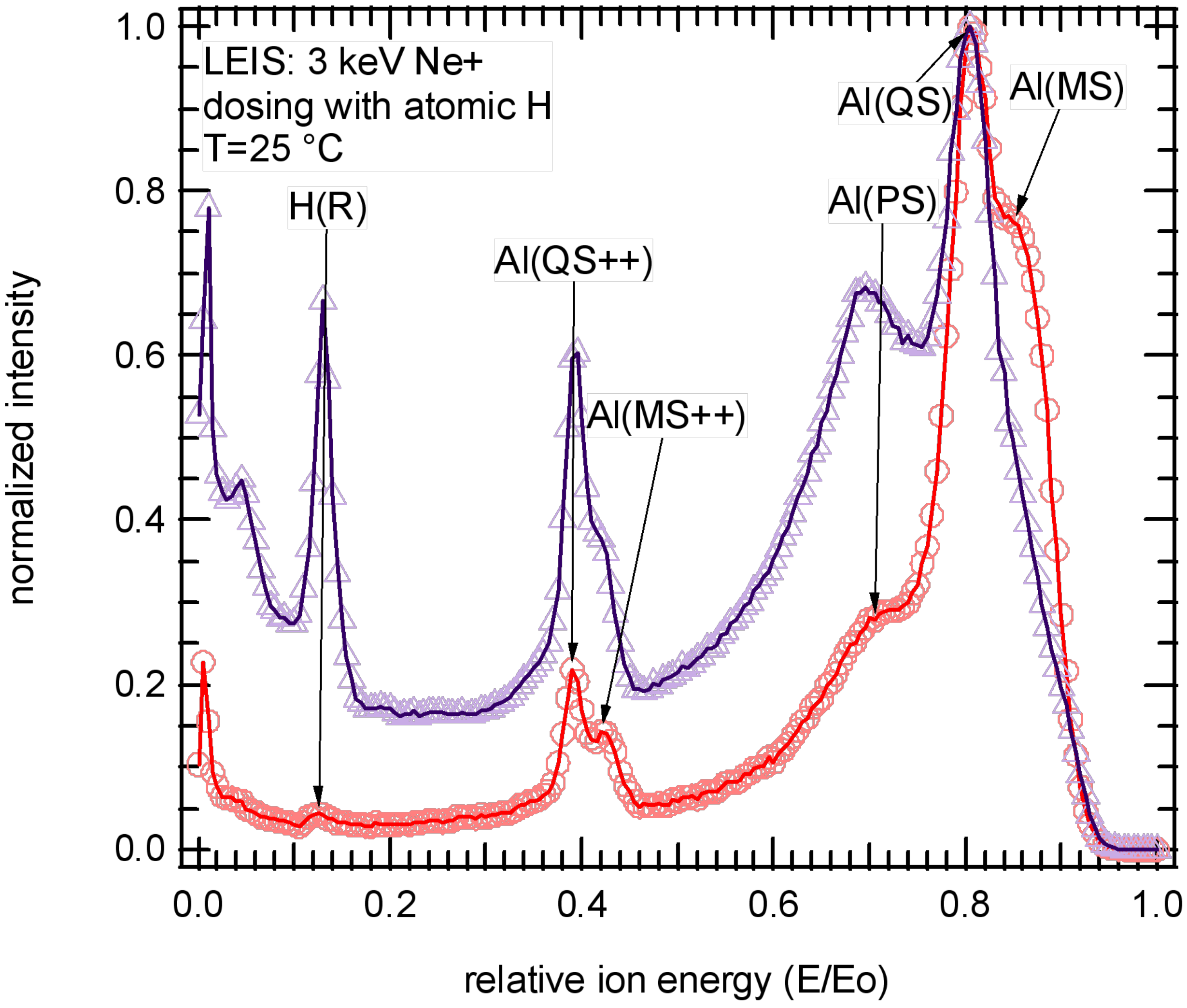


Ion scattering analysis of Al specimen during dosing with atomic and molecular hydrogen & deuterium



- A polycrystalline Al specimen was prepared by sputter cleaning with 3 keV Ne^+ at oblique incidence, followed by cycles of annealing to 500 °C.
- Residual hydrogen is detected at room temperature, even when not dosing the surface.
- Some hydrogen is dissociated by the filaments in our vacuum chamber. When these are deactivated, the hydrogen disappears.

Ion scattering analysis of Al specimen during dosing with atomic and molecular hydrogen



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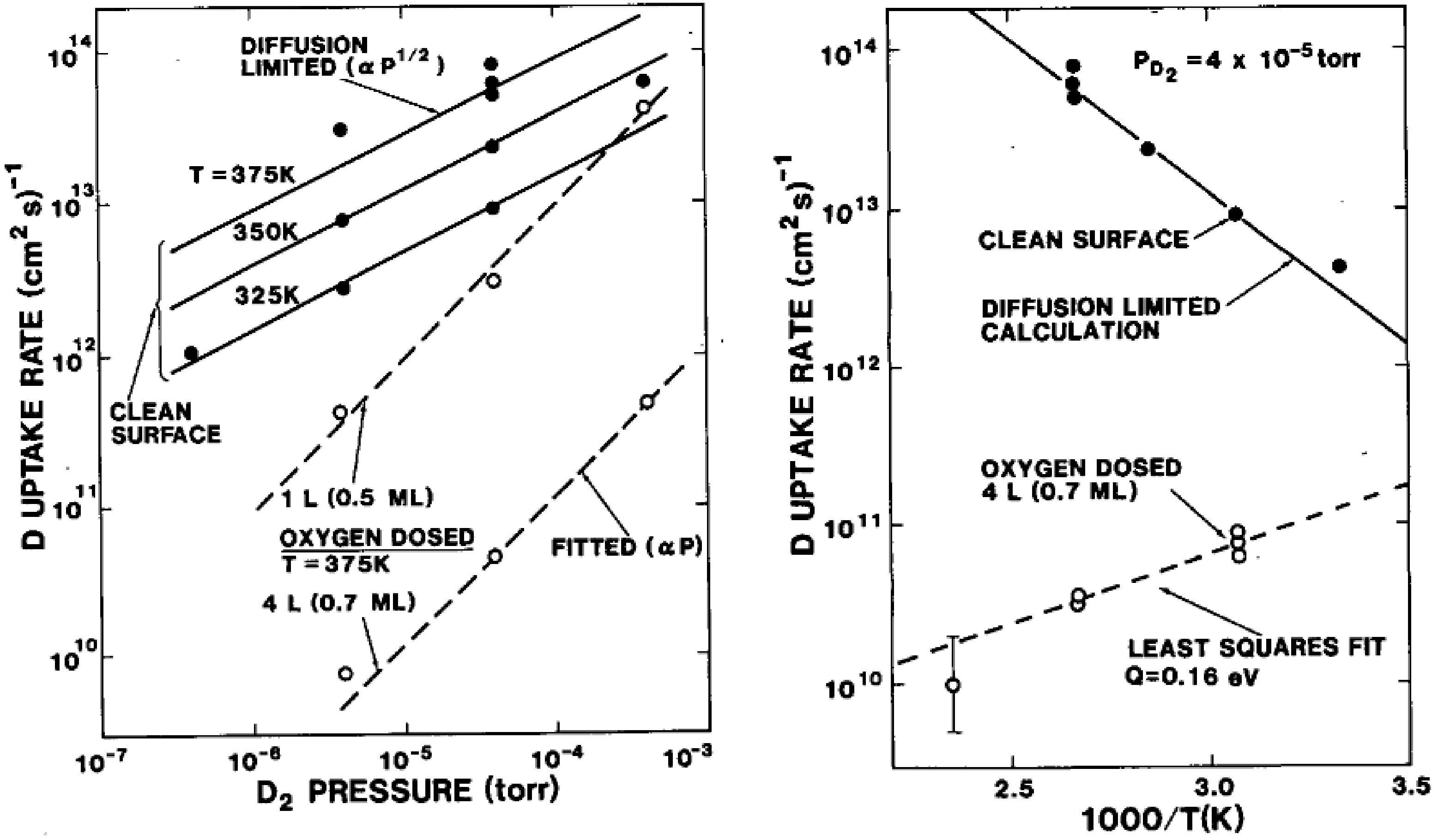
- Residual hydrogen is detected at room temperature, even when not dosing the surface.
- Some hydrogen is dissociated by the filaments in our vacuum chamber. When these are deactivated, the hydrogen disappears.
- Dosing with molecular H2(g) produces no effect on the H(R) signal. Atomic H readily sticks to the surface.

Previous work demonstrates how hydrogen permeates into iron



D uptake rate and recombination coefficients for Fe surfaces

- Prior work by Wampler [J. Appl. Phys. **65** (1989) 4040.] illustrates that H uptake by clean Fe surfaces is diffusion limited. However, contamination with < 0.5 ML O can cause uptake to be surface limited.
- < 1 ML dosing with O can reduce recombination by several orders of magnitude.
- Freshly exposed areas of Fe underneath a Fe-Al coating could dominate hydrogen permeation into the material.

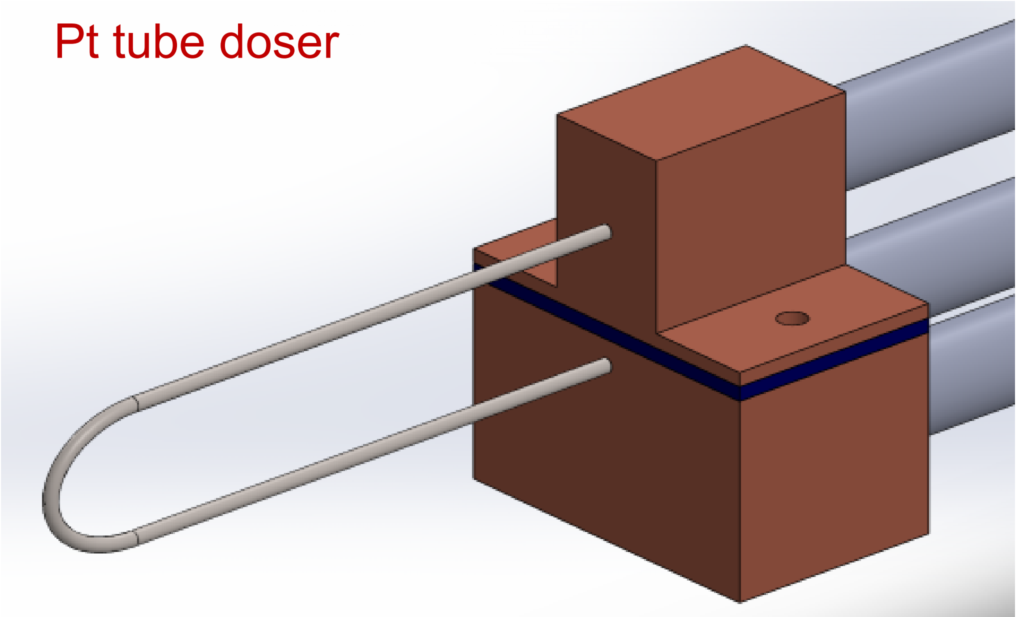
Concluding remarks

Summary:

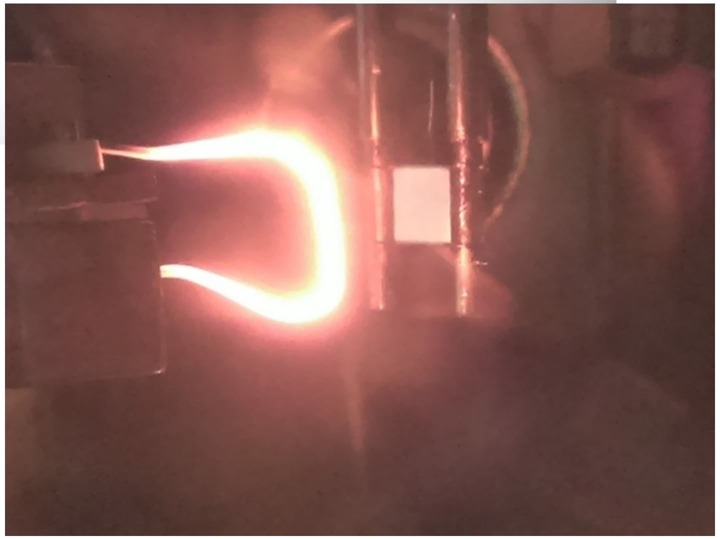
- Auger and XPS spectroscopy reveal that the Fe-Al technical surfaces, as prepared, consist primarily of Al_2O_3.
- Sputter depth profiling was performed:
  - Outer-most layer may include metallic Al with a chemisorbed layer of O.
  - Below this, the Auger spectra appears consistent with Al_2O_3. The surface has a rough morphology, with surface features on the order of ~10 μm.
  - Only trace amounts of Fe revealed after 30 min. of sputtering, indicating that it is deeply buried beneath the Al_2O_3 layer at the surface.
- Long-duration heating does not alter the surface composition appreciably.
- Ion scattering reveals that molecular H does not chemisorb on sputter-cleaned Al surfaces, whereas atomic hydrogen does chemisorb with high initial sticking coefficient.
- Any hydrogen permeation through the Fe-Al coating may dominated by regions of the surface where the coating has been compromised (mechanical abrasions, etc.)

Possible follow-on work: Pt-tube dosers for cleaner exposure of the surface to atomic D

- Conventional technique involves using a Bertel -type doser, which relies on an electron-beam heated W capillary. These systems have been shown to be effective at providing a large flux of atomic H, but can contaminate the surface.
- New design, developed at Princeton / PPPL, uses a resistively heated Pt tube.
- The heated Pt is more reactive than the W, and allows it to be operated at a lower temperature
- This results in lower desorption of impurities



Images courtesy of B. Koel (Princeton / PPPL)



Fabrication of D_2O dosing system

- Basic design based on prior work by Konrad Thuermer (SNL)
- Small quartz thimble is filled with water, attached a leak valve.
- Water is frozen with LN2, remaining gas is pumped away through gas manifold and valves.
- Several purge / pump cycles repeated, then valve above water is closed.
- Water vapor then admitted through leak valve into analysis chamber (can potentially be directed toward the sample using a capillary).