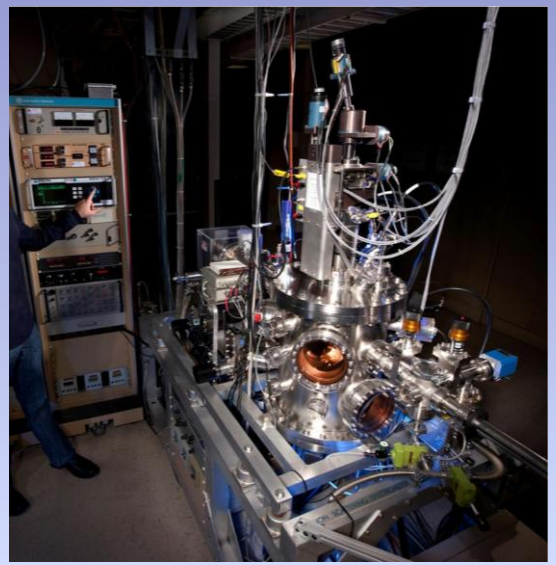
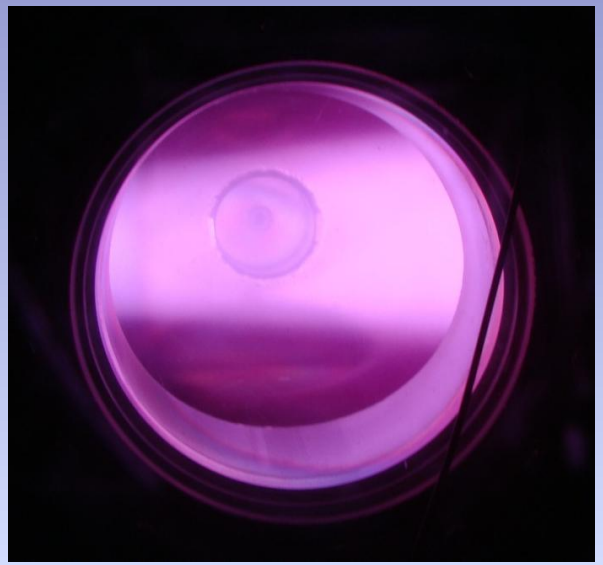
EXPERIMENTAL ANALYSIS AND MODELING OF HYDROGEN ADSORPTION AND PRECIPITATION IN TUNGSTEN





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PSI Science Center

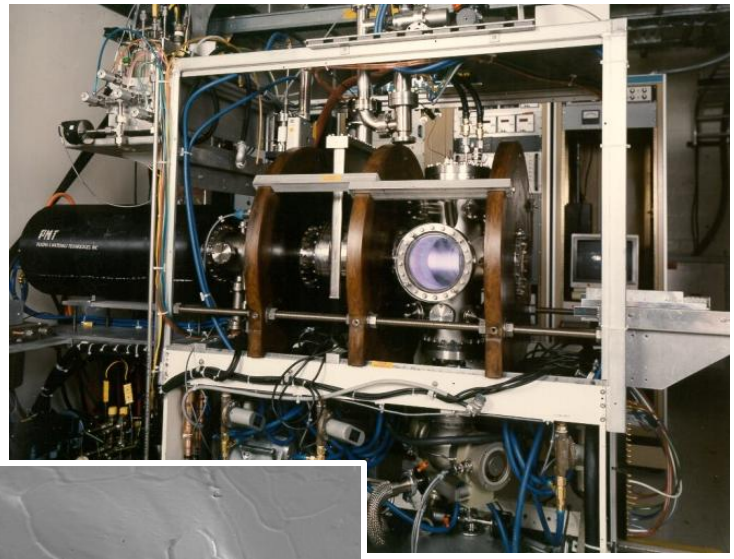
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

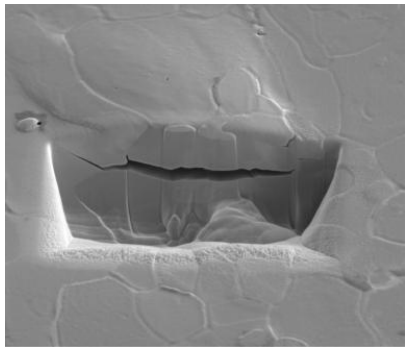
Overview

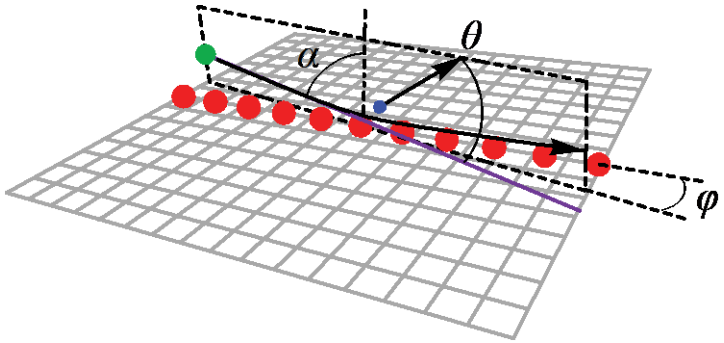
Summary of three projects with tungsten emphasis:

- Hydrogen precipitate model
  - continuum-scale bubble growth
- Tritium plasma experiment (TPE)
  - plasma-driven permeation system
  - surface morphology characterization
- Surface studies (ARIES)
  - molecular-dynamics (MD) models of surface channeling
  - instrument upgrades (time of flight, Auger)

Scope ranges from applied experiments to fundamental studies.







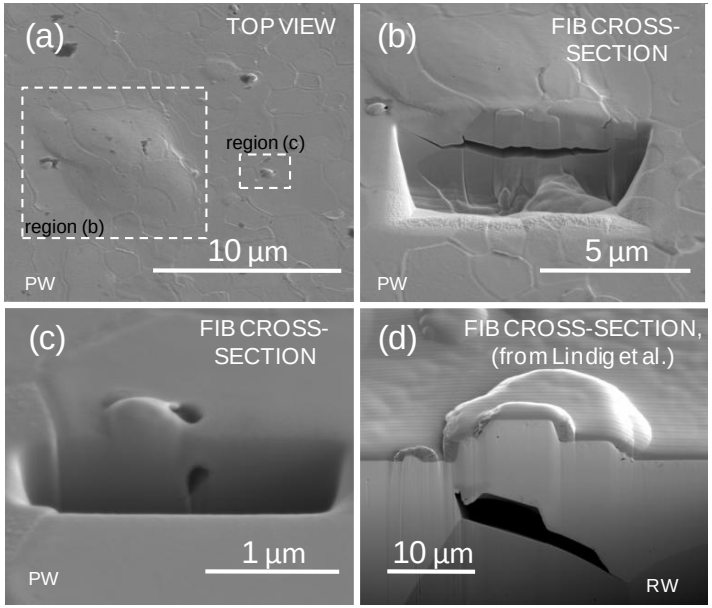
Part 1: hydrogen precipitate model

Continuum-scale finite difference model enables simulations of bubble growth

Precipitation affects hydrogen diffusion in metals [W.R. Wampler, *Nucl. Fusion* (2009)]

How do hydrogen bubbles grow?

- DFT, MD, and Kinetic Monte Carlo reveal key nucleation and growth mechanisms.
- Incorporate insight into continuum approach to model practical environment
- Existing models (TMAP, DIFFUSE) exclude important physics (e.g. precipitation)



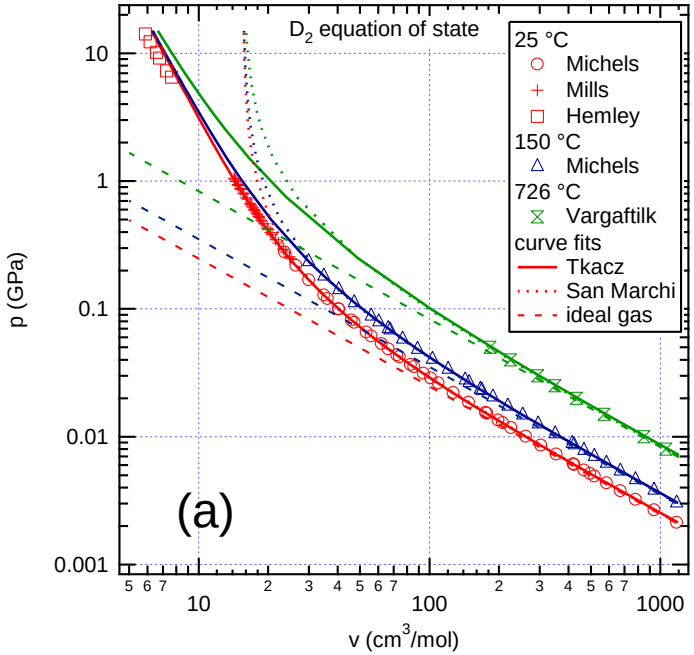
(a-c) contributed by John Smugeresky, (d) from S. Lindig et al., *Phys. Scr.* (2009).

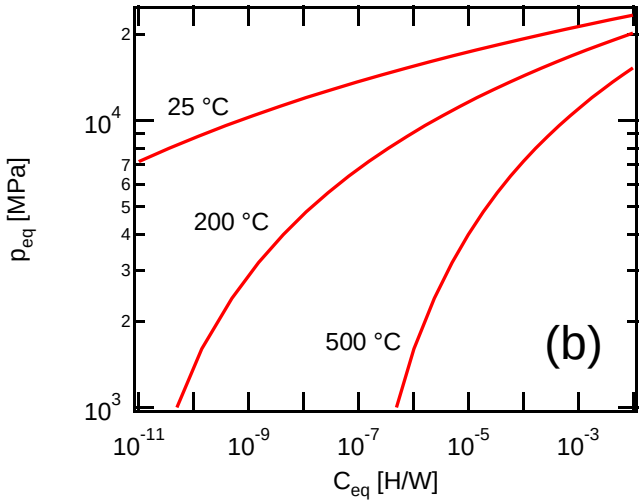
- ❑ We leverage metal tritides expertise at Sandia from ^{3}**He bubble** growth models [D.F. Cowgill, *Fusion Sci. & Technol.* (2005)]
- ❑ Altered to simulate hydrogen bubbles:
  - Different nucleation process [Henricksson *Appl. Phys. Lett.* (2008).]
- ❑ Use experiments to refine model.

Previous work identified conditions necessary for bubble growth

How much hydrogen can we force into the bubbles?

- ❑ Bubbles fill until **chemical equilibrium** is reached.
- ❑ Equilibrium determines whether precipitation is favored:
  - At RT, bubbles grow even at low H conc.
  - At high temperature, need high H conc. for growth.
- Findings consistent with experiments.





R.D. Kolasinski, D.F. Cowgill, R.A. Causey, *J. Nucl. Mater.* (2010).

Continuum-scale approach enables rapid solution of diffusion equation

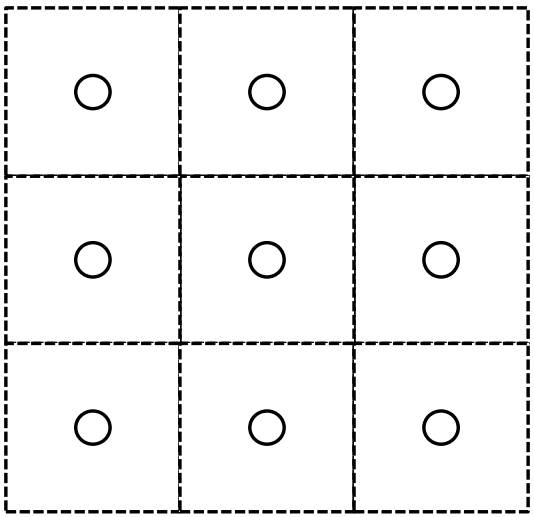
Assume:

(a) Point defects saturable, do not behave as bubble nucleation sites.

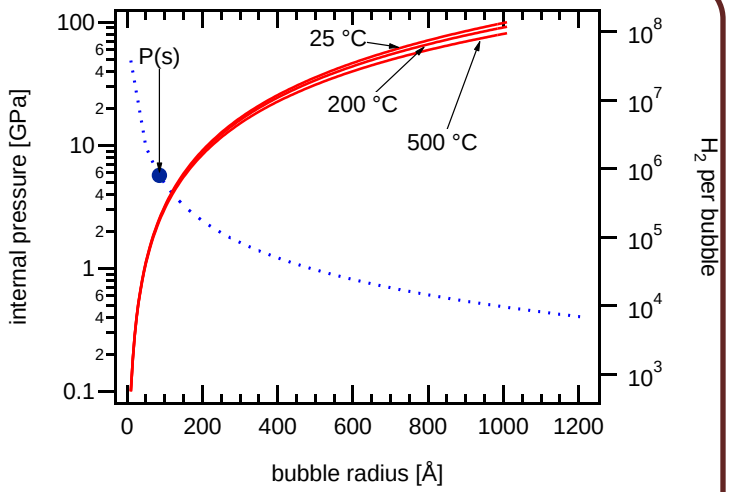
(b) Array of evenly-spaced sperhical bubbles.

(c) Bubble diameter smaller than inter-bubble spacings

(d) Slow thermal ramp (quasi-equilibrium is satisfied.)



Array of evenly-spaced spherical bubbles.



Bubble growth by loop punching

Simple loop punching condition:

$$p_{LP} \geq 2\gamma/r_b + \mu b/r_b$$

γ = surface energy

r_b = bubble radius

b = Burgers vector

μ = shear stress

Basis for finite difference model: need to integrate three coupled PDE's

Governing equation (1-D diffusion w / 2 sink terms):

$$q_T = \partial u_T(x,t)/\partial t$$

$$\partial u(x,t)/\partial t = D(t)\,\partial^2 u(x,t)/\partial x^2 - q_T(x,t) - q_B(x,t)$$

Flow into or out of the bubbles determined by local eq. conc.

$$q_B = \partial u_B(x,t)/\partial t = 4\pi D(t) r_B(x,t) N_B(x)\left[u(x,t) - u_{eq}(x,t)\right]$$

Concentration at bubble surface determined by Sievert's Law:

$$u_{eq}(x,t) = \sqrt{f}\,S_0 \exp(-E_s/RT)$$

Fugacity (requires aforementioned EOS):

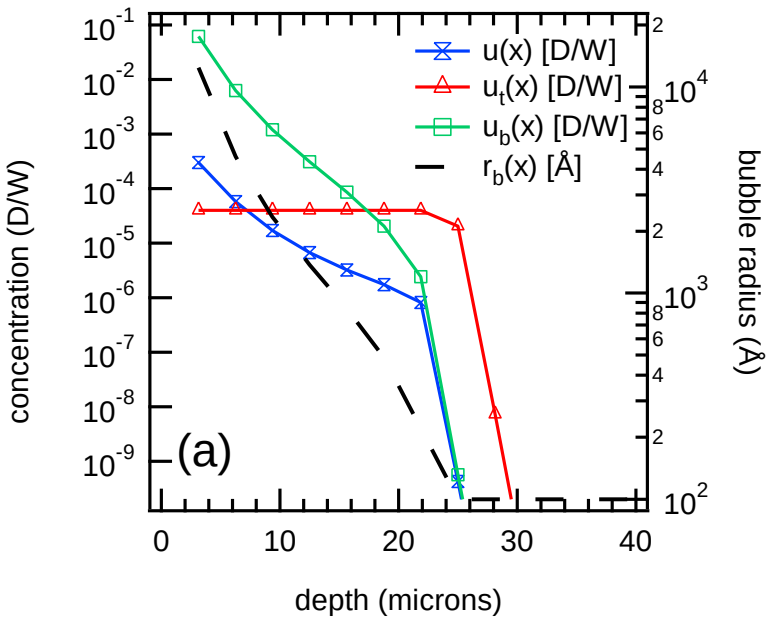
$$\ln(f/p) = \int_0^p (v(p,T)/RT - 1/p)\,dp$$

Simulated bubble sizes consistent with experimental findings

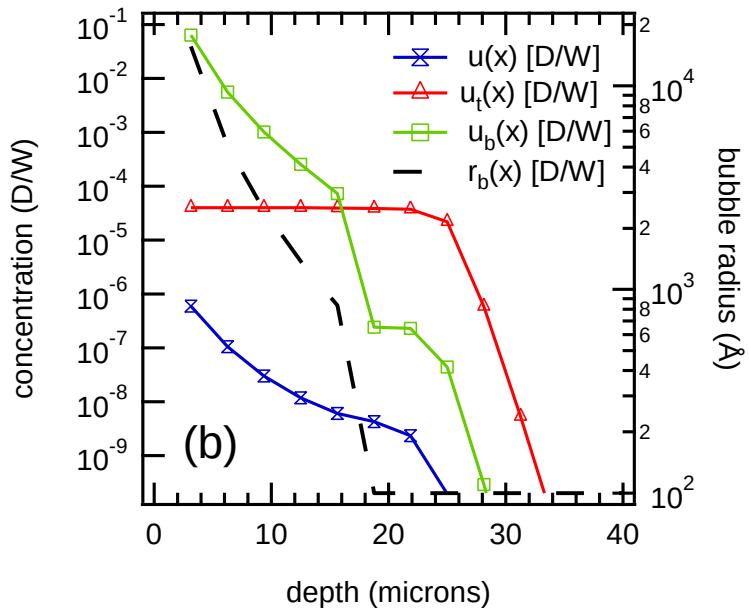
- Assumed a pre-existing concentration of nucleation sites (eventually growing into bubbles.)
- Traps fill first, followed by bubble growth.
- Using realistic input conditions, depth profiles consistent with experimental findings.

N_t=4×10^{-5} W^{-1}
N_b=10^{-12} W^{-1}
F=10^{18} D/cm^2-s, calculated near-surface conc. at the end of range from $F=Du/r$.
r=2.5 nm for 100 eV D$^+$ ions

300 K



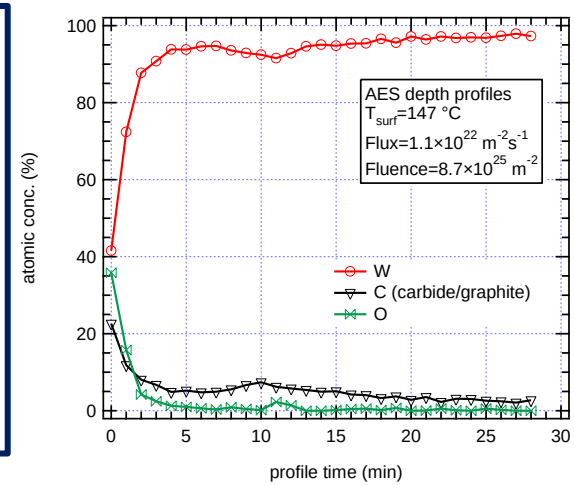
500 K

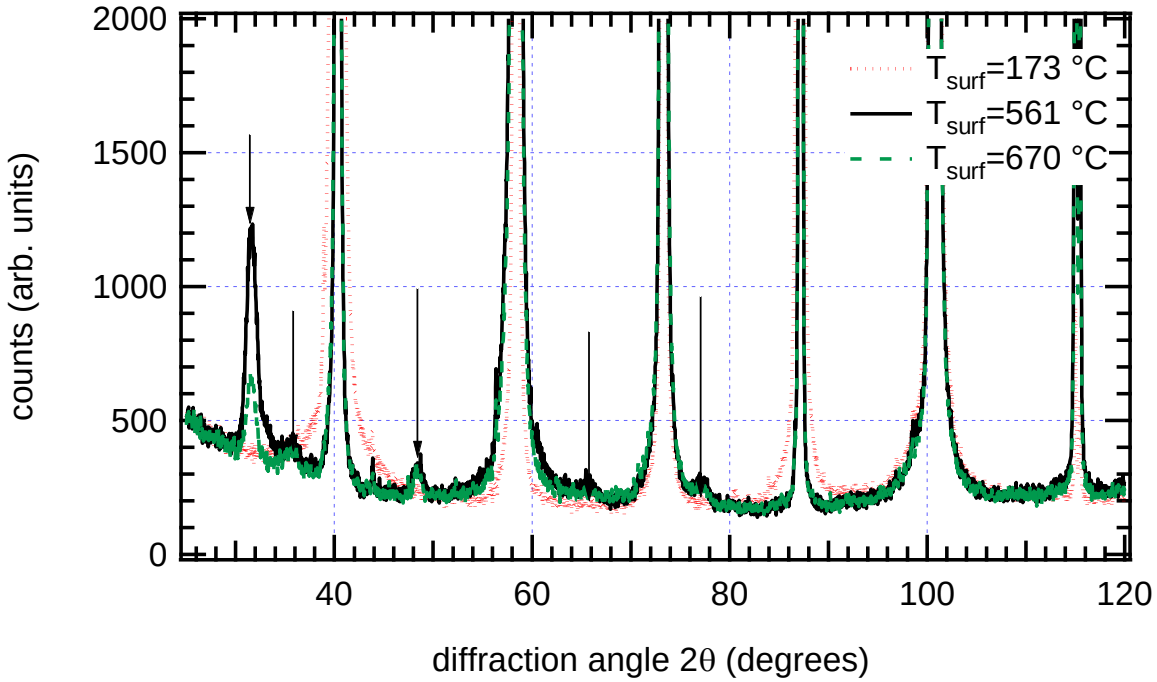


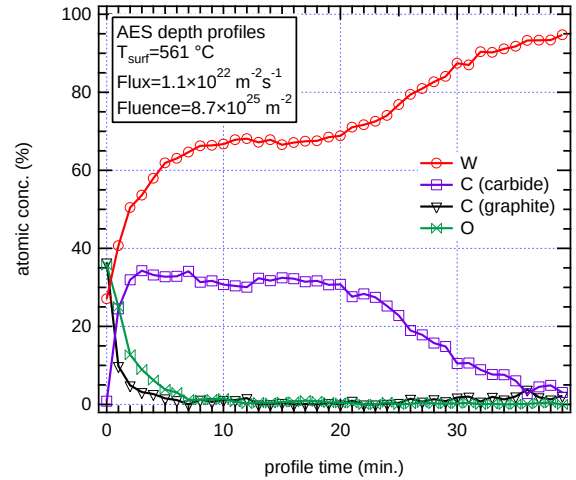
Part 2: tritium plasma experiment

Planned TPE studies will focus on understanding microstructure effects

- Objective for upcoming work: perform experiments to examine microstructure effects.
- Present work aimed at eliminating uncertainties in the instrument:
  - Eliminating C components in TPE
  - Better thermal control of the target

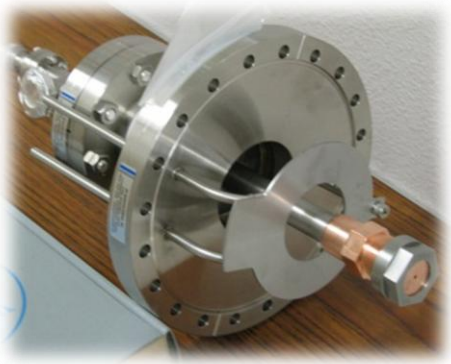






AES depth profiles

Development of plasma-driven permeation experiments underway



- Plasma-driven tritium permeation using "realistic" samples.
- Experiments part of the PSI-Science Center and collaboration with INL
- Leverages unique capabilities of the tritium plasma experiment (TPE)
- **See subsequent talk (Shimada, Session 1)**

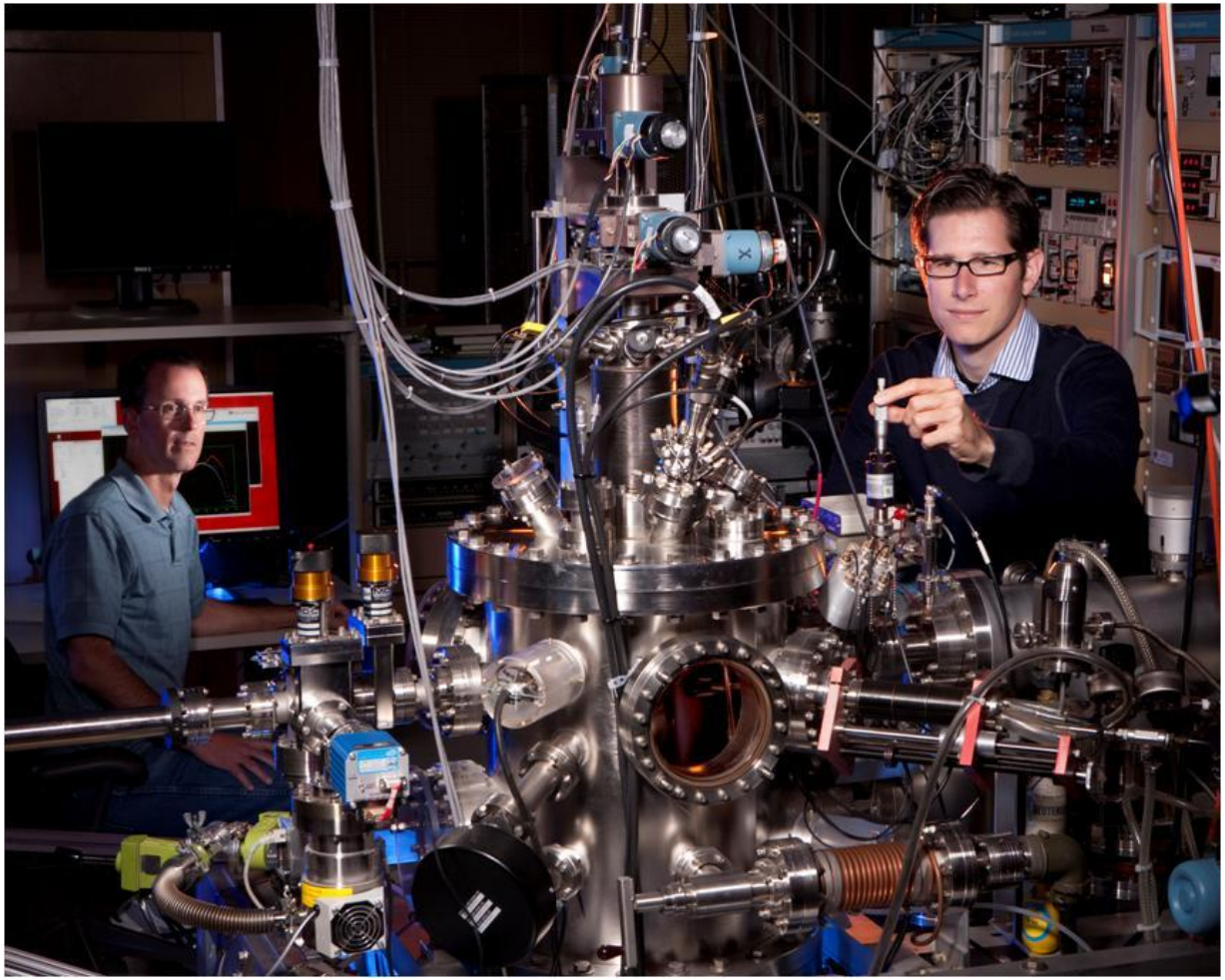
Low-flux ion beam studies:

- Anderl (1992) (initial measurements, measured recombination rate)
- Ueda (2011) compared different material structures
- Early high-flux attempts using TPE unsuccessful (~1995) due to temperature control difficulties

Progress to date:

- First generation design completed; demonstrated superior temperature control.
- Gas-cooled design fabricated ready for testing.

Part 3: surface analysis & hydrogen adsorption studies

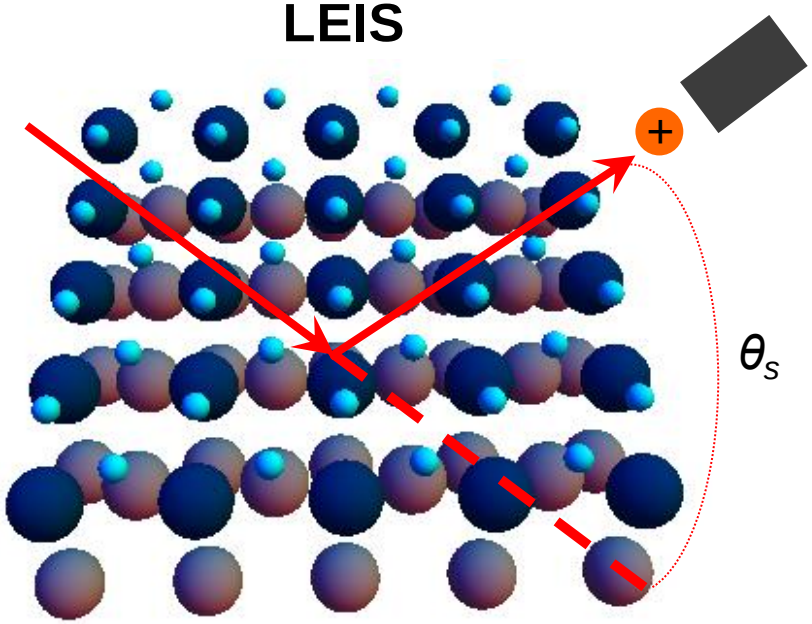


Ion scattering enables advanced studies of surface effects relevant to fusion materials

Objective: improve understanding of hydrogen-surface interactions.

- **How does H adsorb bind to surfaces?**
- *Important for understanding:*
  - recycling
  - adsorption/desorption
  - dissociation/recombination
  - validation of fundamental models (DFT)
- *ARIES:* Angle-resolved ion energy spectrometer
- *Low energy ion scattering (LEIS):*
  - Unique for high sensitivity to hydrogen
- *Systems under examination:*
  - W(100)+H
  - Be(0001)+H
  - Al(111)+H

LEIS



Determine surface composition based upon:

E_o= initial incident particle energy

E_s= particle energy after scattering

ϑ_s= scattering angle

$$2\cos\theta_s = (1+A)\sqrt{E_s} + (1-A)/\sqrt{E_s}$$

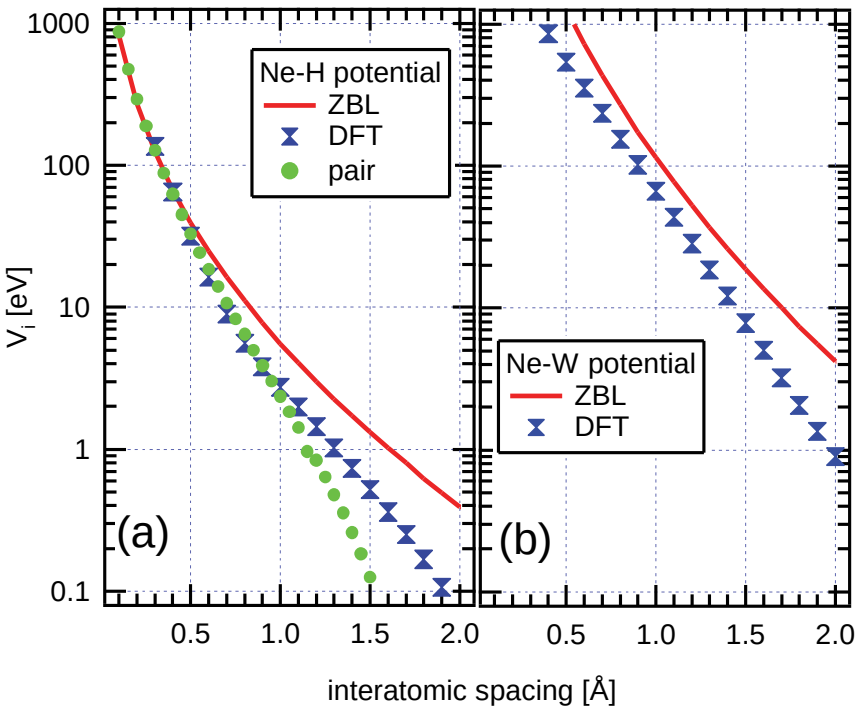
Calculate:

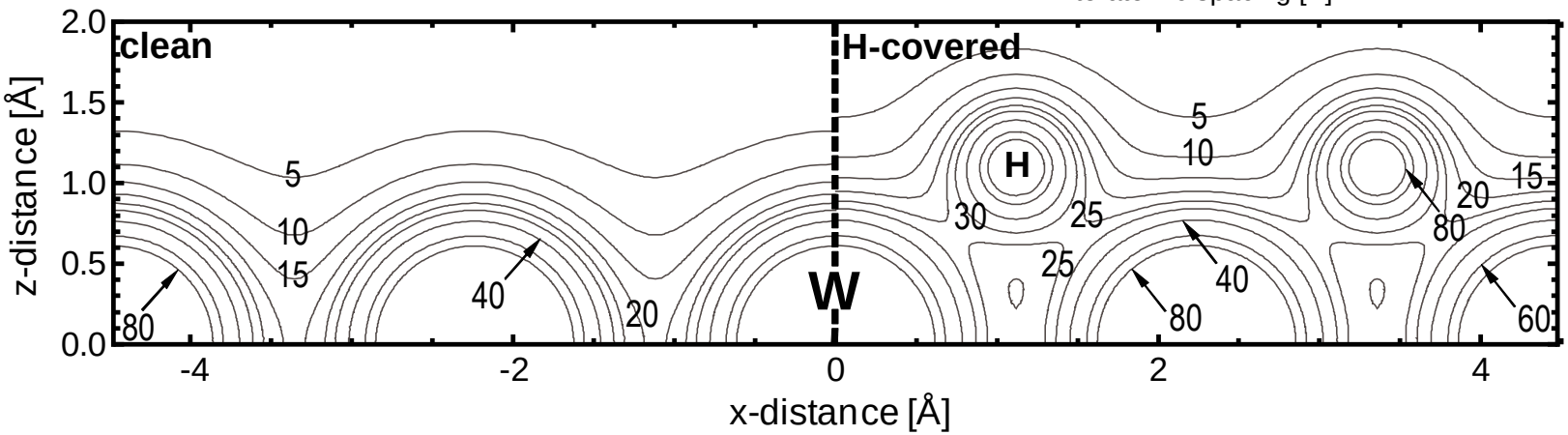
Mass ratio, $A=m_2/m_1$

Refinement of interatomic potentials needed for accurate modeling of scattering

Calculation of pair potentials

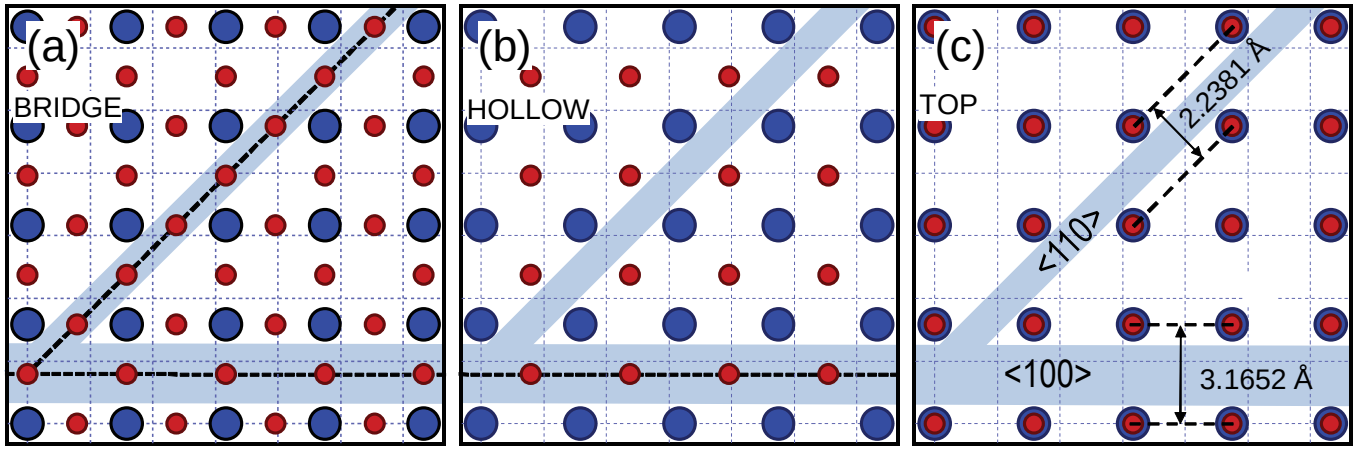
- Only repulsive portion is needed.
- "Universal" potentials (ZBL) too repulsive at large impact parameters.
- We calculate interaction based on superposition of electron shells of Hartree-Fock atoms.
- Result compares well with DFT.
- Potentials incorporated into the molecular dynamics code *Kaylpso*.

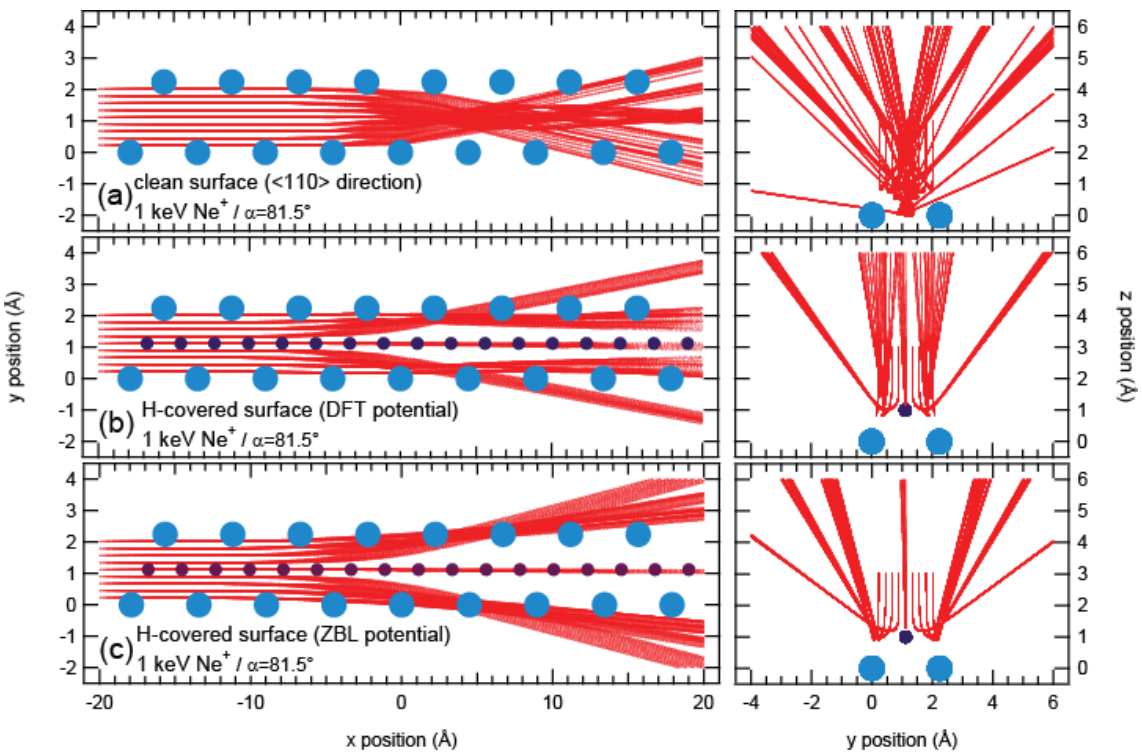




Equi-potential contours for the W(100) surface (<110> channel.) Potential strength in eV.

Surface channeling strongly affected by the hydrogen location

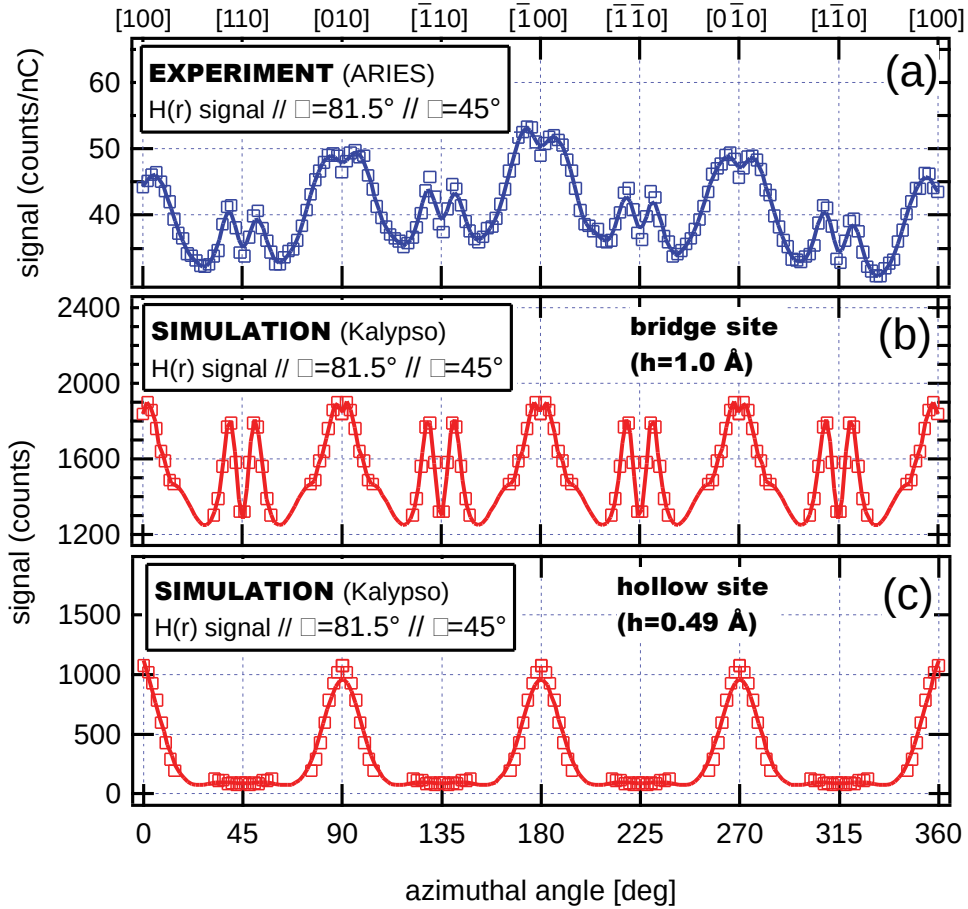




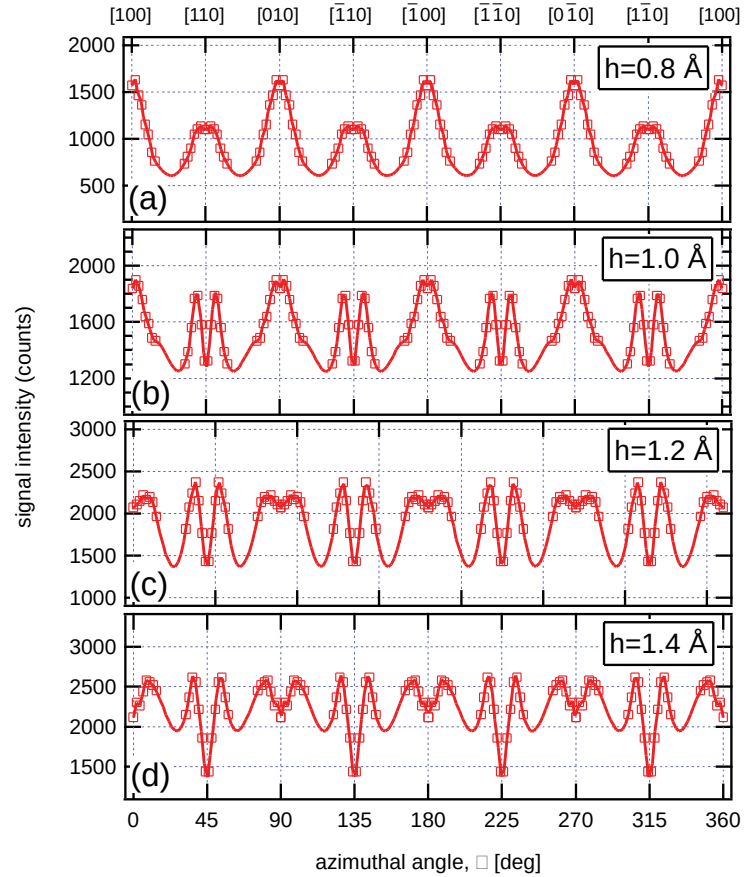
- **MD simulations**
  - Use **grazing incidence** to access adsorbated hydrogen high above the surface.
  - Perpendicular energy $E_{perp}=E_o\cos^2(\alpha)$ is small at grazing incidence (binary collision approximation invalid.)
  - Presence of hydrogen atoms in surface channels strongly influences ion focusing.

MD calculations reproduce experiments for correct adsorbate height

We can simulate experimental results for different binding sites.



Signal depends on where H resides

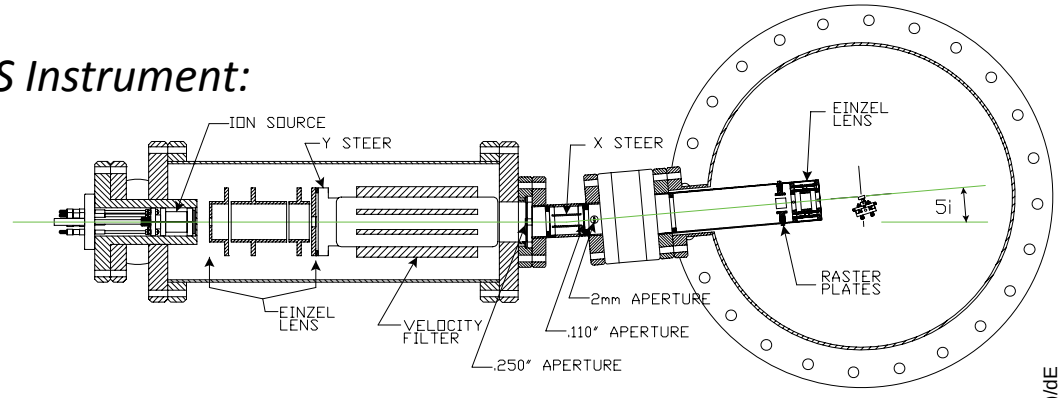


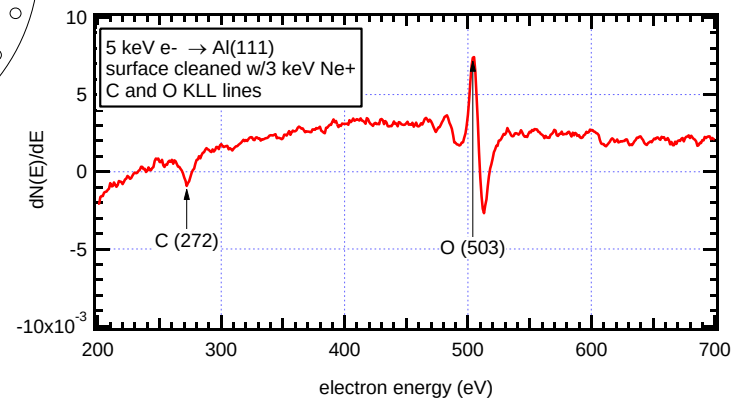
- Blocking depends on H height.
- Best agreement consistent with DFT (VASP).

R. Kolasinski, N. Bartelt, J. Whaley, T. Felter, *Phys. Rev. B* (submitted.)

New time of flight capability enhances sensitivity by 10^4

ARIES Instrument:

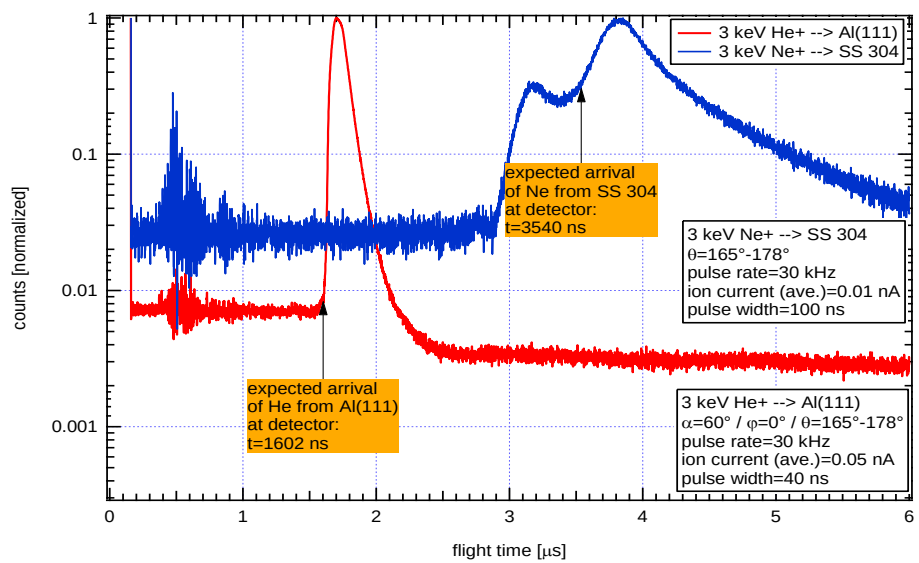




AES enables quantification of surface-adsorbed impurities (e.g. C and O).

Time of flight detector improves sensitivity dramatically:

- ❑ Eliminates need for neutralization model
- ❑ Non-destructive analyses of delicate surfaces
- ❑ Opens up a wealth of surface chemistry experiments.



Concluding Remarks

We have studied….

- *Hydrogen bubble growth*
  - Successfully adapted Sandia ^{3}He bubble growth code
  - Model accurately predicts conditions for bubble growth, produces realistic bubble size distributions.
- *Tritium plasma experiment*
  - Future retention experiments to examine microstructure effects.
  - Plasma-driven permeation testing system under development.
- *Hydrogen adsorption on surfaces*
  - Determined H binding site on W surface, extensive modeling with DFT / MD
  - New detector makes analysis non-destructive, opens up a wealth of surface chemistry experiments.

Acknowledgements

- It is a pleasure to thank Rion Causey and Robert Bastaz (formerly of SNL) for many helpful suggestions regarding this work.
- We express our appreciation to our collaborators at UC-San Diego, MIT, Univ. of Tennessee, and INL.
- Funding:
  - Office of Fusion Energy Science
  - Sandia Early Career Laboratory Directed Research and Development (LDRD) program
  - Plasma-Surface Interactions Science Center
- Sandia is a multi-program 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.