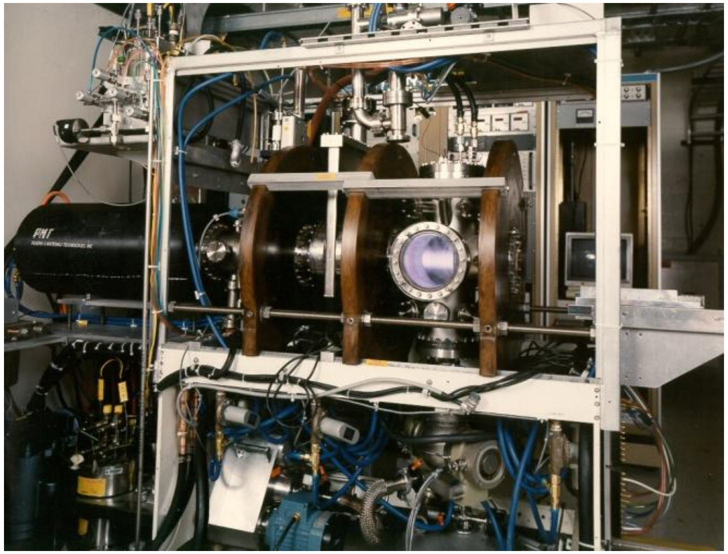
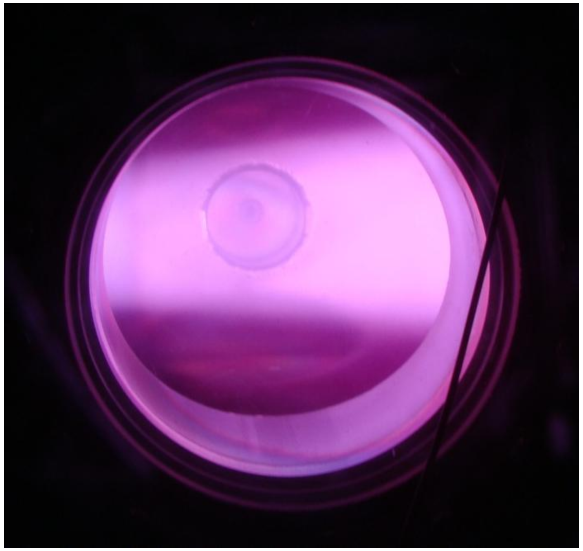
SAND2011-6164C

Hydrogen retention studies in TPE and modeling of precipitate growth





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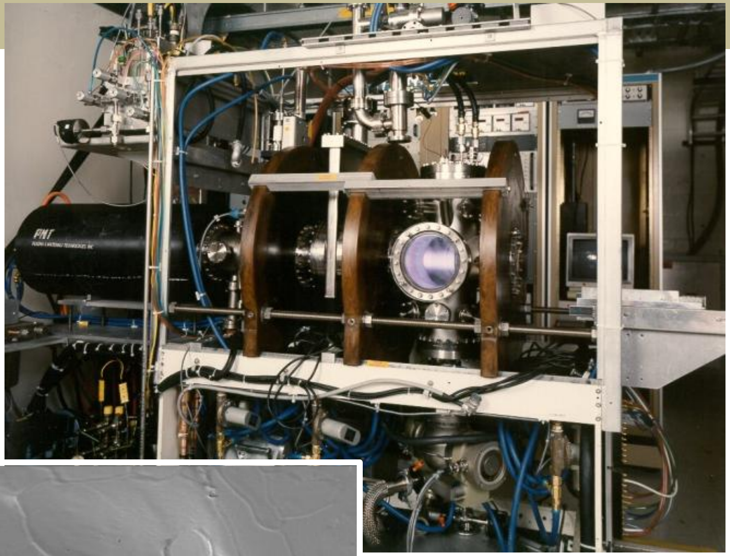
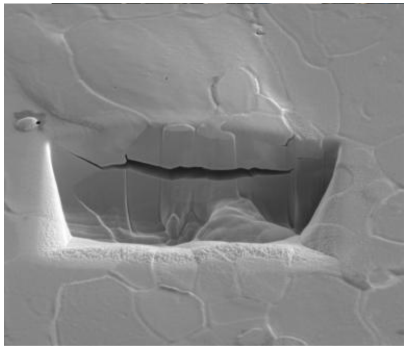
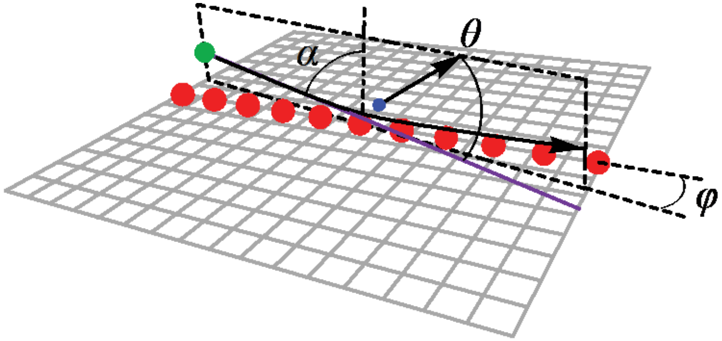
Overview







Summary of two closely-related projects with tungsten emphasis:

- Hydrogen precipitate model
  - continuum-scale bubble growth
- Tritium plasma experiment (TPE)
  - plasma-driven permeation system
  - surface morphology characterization

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)]

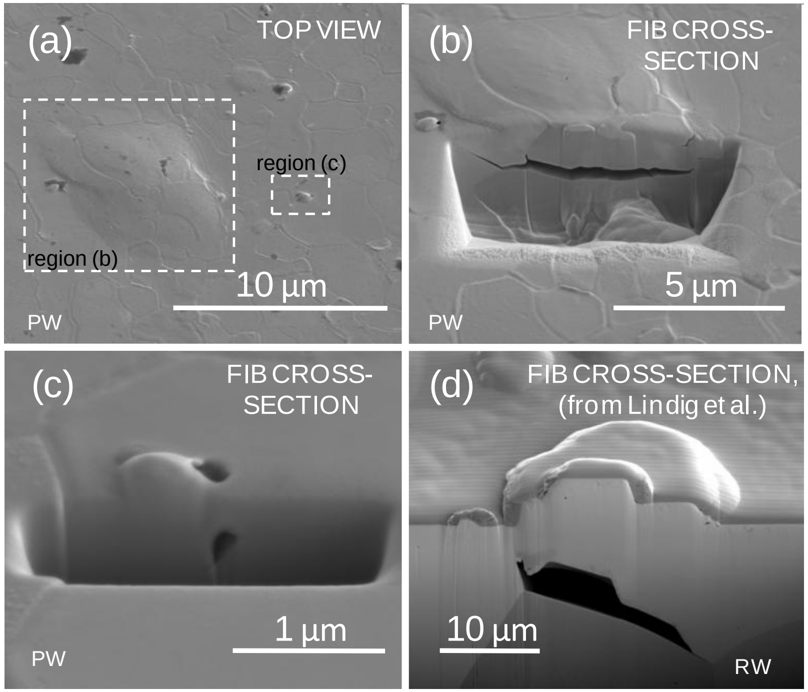
Motivation for further model development:

- 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)

- ❑ 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.

Hydrogen precipitate growth in tungsten: experimental findings

- Motivation: **Development a continuum scale model of hydrogen diffusion and precipitation in tungsten.**
- Previous work: Our approach leverages previous model of He bubble in metal tritides [Cowgill, *Fusion Sci & Technol.*, 2005].



Focused ion beam (FIB) results:

- Profiled PLANSEE tungsten materials which had been previously exposed in TPE: 70 eV D^+ ions, $\Phi=1.1\times10^{18}$ $cm^{-2}s^{-1}$, $F=8.7\times10^{21}$ cm^{-2}, $T=385$ ° C. [Details in J.P. Sharpe et al., *J. Nucl. Mater.*(2009).]
- Large blister in Fig. 1(b) has enlarged by crack growth.
- Small blister in Fig. 1(c) has grown by dislocation loop punching.
- For comparison, a FIB profile of re-crystallized tungsten exposed under similar conditions is shown in Fig. (d). Image from [Lindig et al., *Phys. Scr.* (2009).] Growth mechanism also appear to be due to dislocation loop punching.

Bubble growth mechanisms:

- Crack propagation
- Dislocation loop punching
- Vacancy clustering

Diffusion and trapping were modeled using a continuum-scale approach

Diffusion:

Basic 1-D diffusion equation assuming uniform temperature.

Point defects:

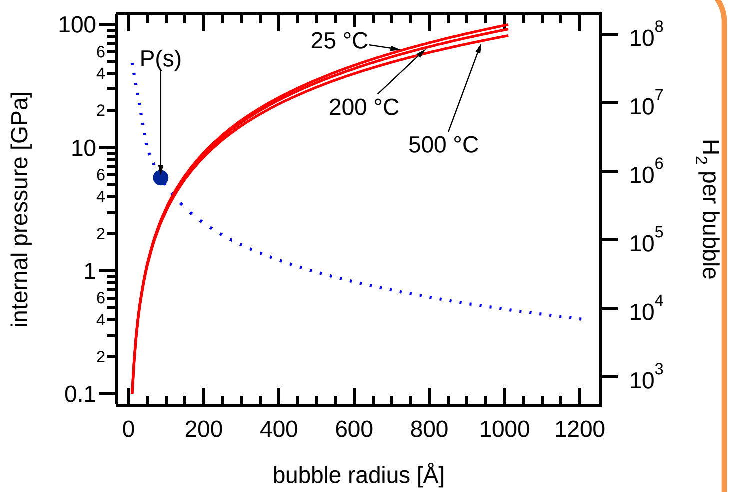
Point defects modeled as 1.4 eV saturable traps (not permitted to serve as nucleation sites for bubbles.) Used approach of Ogorodnikova [*J. Nucl. Mater.* 2009] to address trapping and release:

$$\partial C_t(x,t)/\partial t = (2Da/3)[C_m(N_t - \delta C_t) - (12\delta C_t / a^3)\exp(-E_t / kT)]$$

δ = inverse trap saturability; N_t = trap density; C_t = H concentration in traps.

Trapping by bubbles:

Modeled using a simple approach developed by Mills [J. Appl. Phys. (1959)].



Bubble growth by loop punching

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

Plot above shows the p_{LP} for W. For small bubbles, p_{LP} is >10 GPa. Need equation of state to calculate H_2 per bubble from loop punching stress.

Internal pressure within bubbles can exceed 1 GPa

H_2 equation of state (EOS):

Very high pressures (>1 Gpa) expected within small hydrogen bubbles.

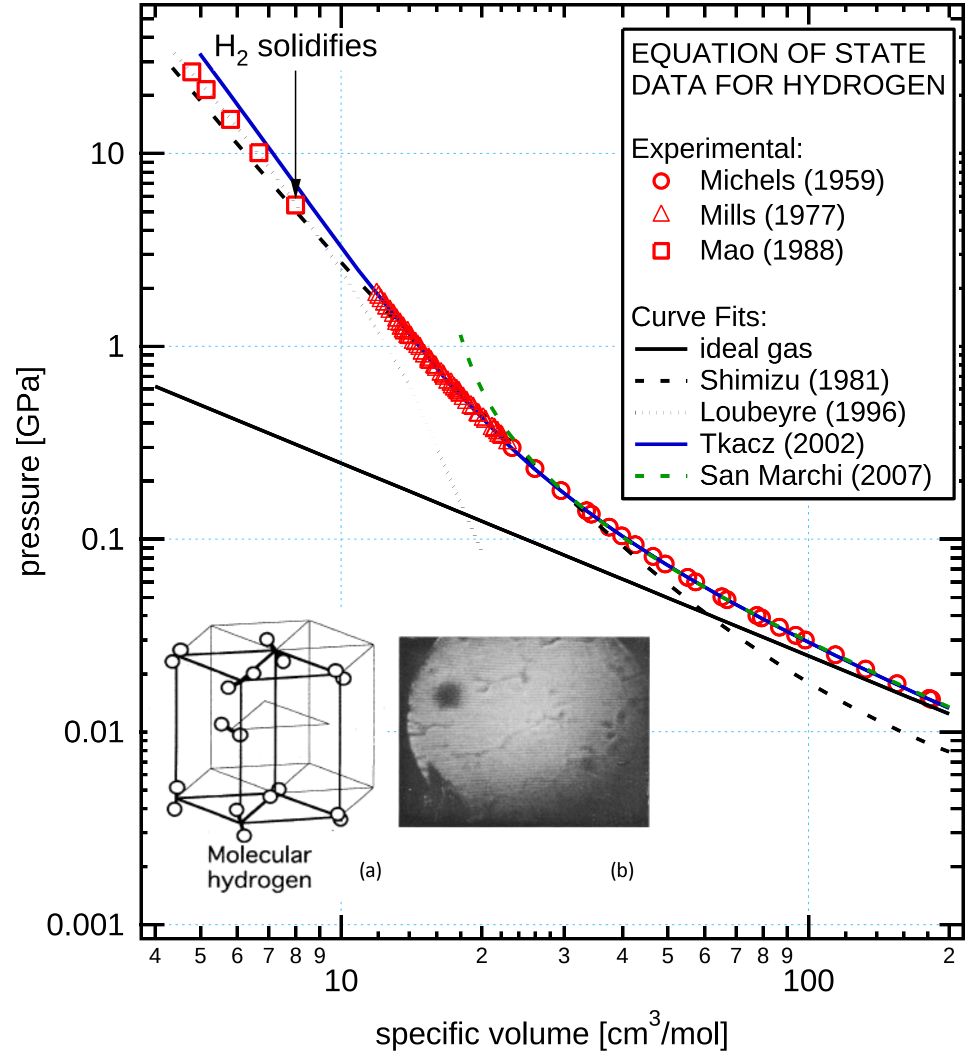
At **25 ° C**, H_2 solidifies at ***p*=5.7 GPa**, forming an hexagonal close-packed molecular solid.

- Over the range of pressures of interest for this work, we found Tkacz's [J. Alloys & Compounds (2002)] EOS to provide the best fit:

$$v = Ap^{-1/3} + Bp^{-2/3} + Cp^{-4/3} + (D + ET)p^{-1}$$

- San Marchi's simplified EOS is also quite accurate at lower pressures:

$$v = \frac{RT}{p} + b$$



Equilibrium conditions dictate the when bubbles will grow

Calculation of equilibrium pressure:

When will the precipitate gas be in equilibrium with the hydrogen in solution?

- Equate the **chemical potentials** of the gas phase and solution.
- Account the non-ideal behavior of the gas in bubbles by incorporating hydrogen **fugacity**:

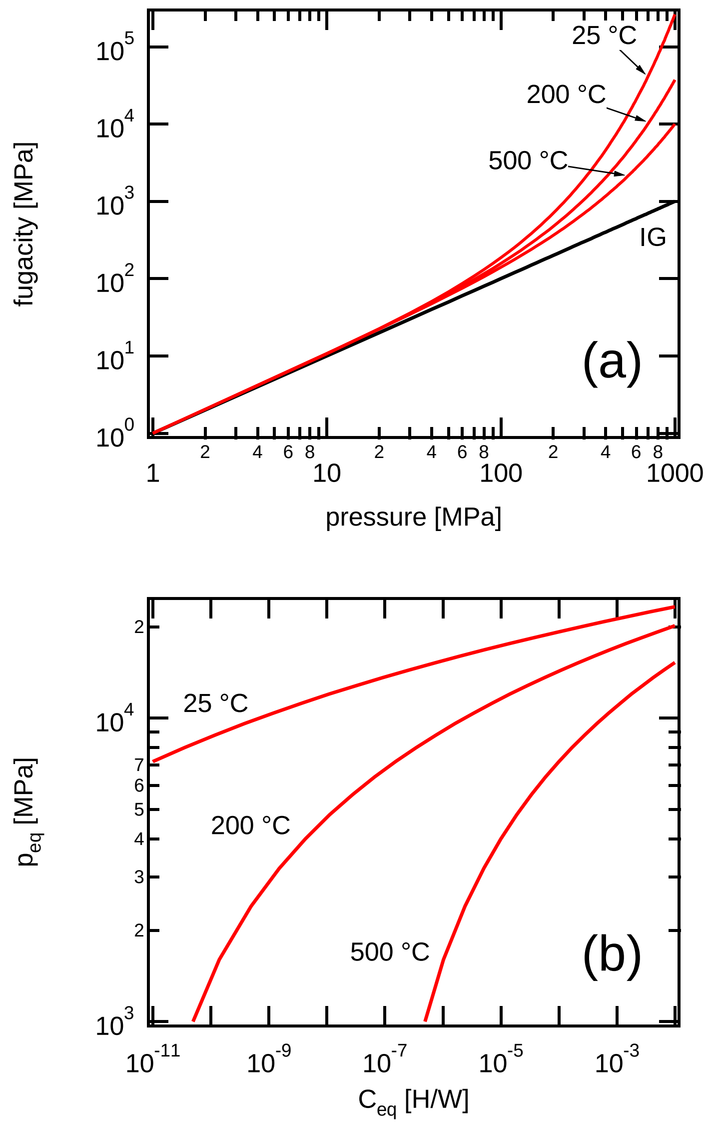
$$\ln(f/p) = \int_0^p (v(p,T)/RT - 1/p)\,dp$$

- The **equilibrium concentration** is then given by the following expression:

$$C_{eq} = \sqrt{f}\,S_0 \exp(-H_S/RT)$$

S_o and H_s are solubility parameters from Frauenfelder [*J. Vac. Sci. & Tech.*, 1969].

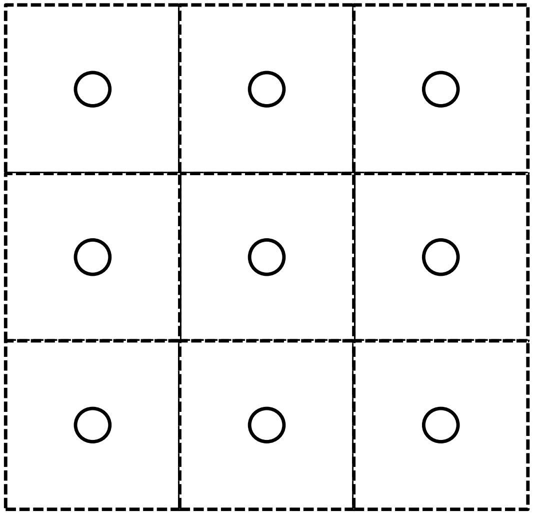
Equilibrium conditions predict when precipitation is favorable.



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.

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:

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

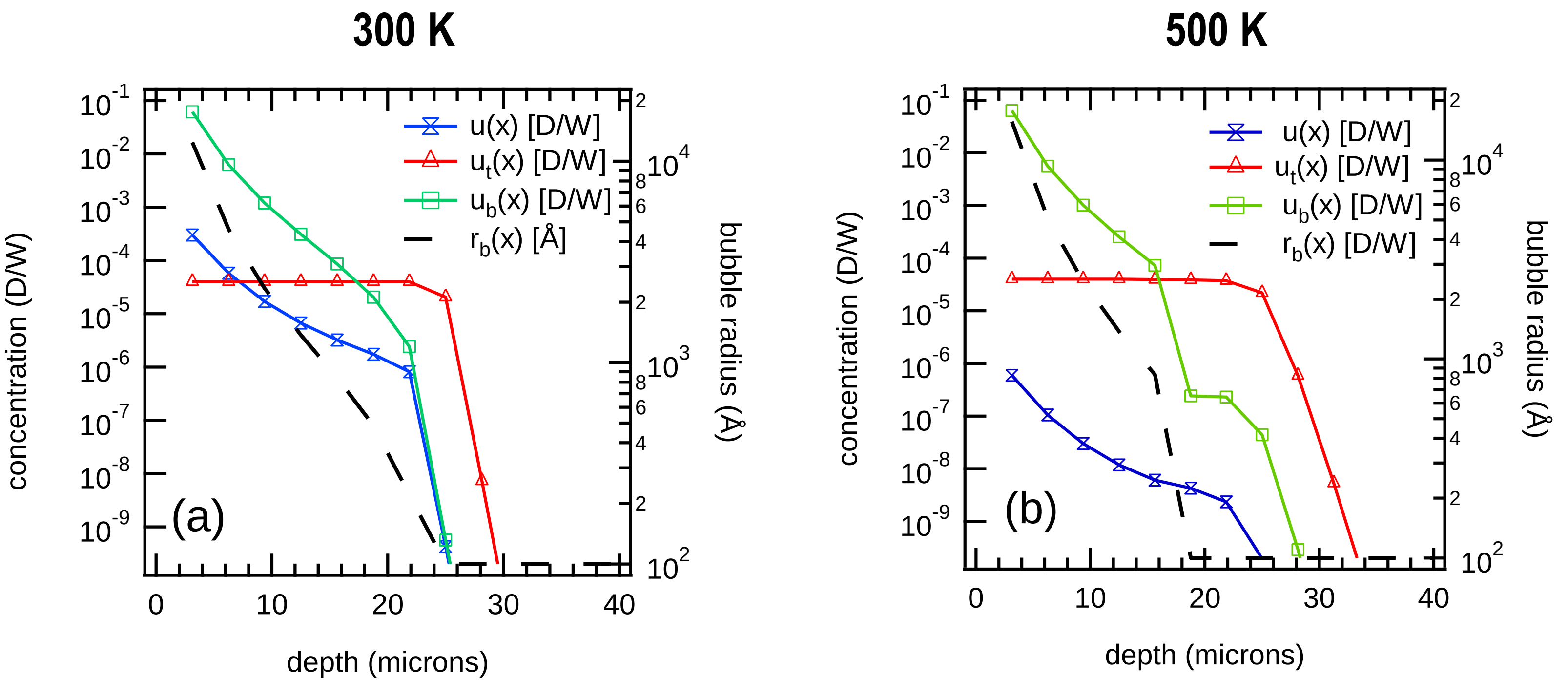
Fugacity (requires aforementioned EOS):

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

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.

$N_t = 4 \times 10^{-5}\ W^{-1}$
$N_b = 10^{-12}\ W^{-1}$
$F = 10^{18}$ 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



Part 2: tritium plasma experiment

Tritium plasma experiment overview

Tritium retention and plasma driven permeation studies in fusion reactor materials.

Primary objective: Understanding tritium inventory issues in reactor first walls.

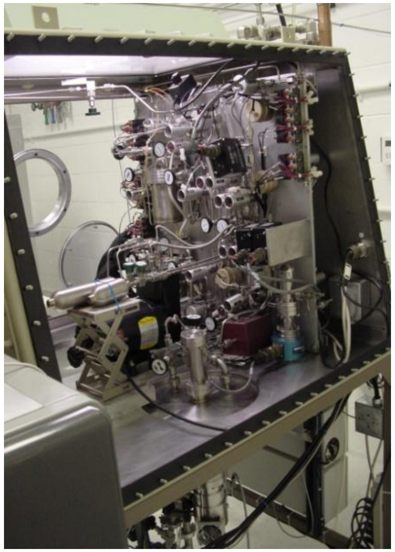
- Joint effort between Sandia Livermore and **Idaho National Laboratory** (INL).
- **Unique** capability to subject materials to intense fluxes of T ions.
- Handling of neutron irradiated samples.
- Tritium permeation measurements.
- Tritium surface/depth profiling using imaging plate scanner.
- INL collaborators: M. Shimada, J. P. Sharpe

Experiment History:

- Originally developed at SNL as TPX (1982), later moved to LANL (1993) and INL (2002).
- System presently located at the Safety and Tritium Applied Research (STAR) facility.
- Restarted plasma operations in August 2007.

15000 Ci limit

500 Ci typical source



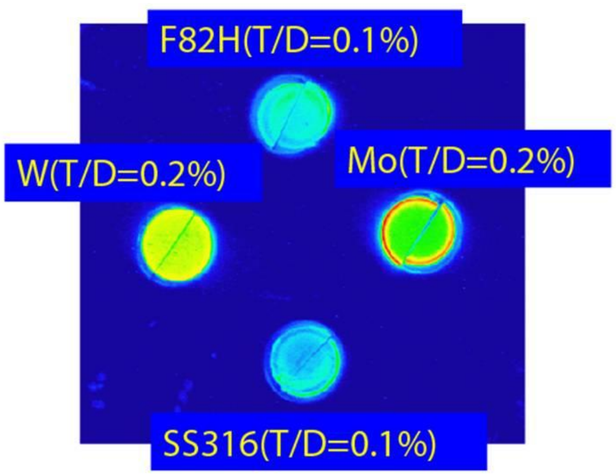
Operating with Tritium

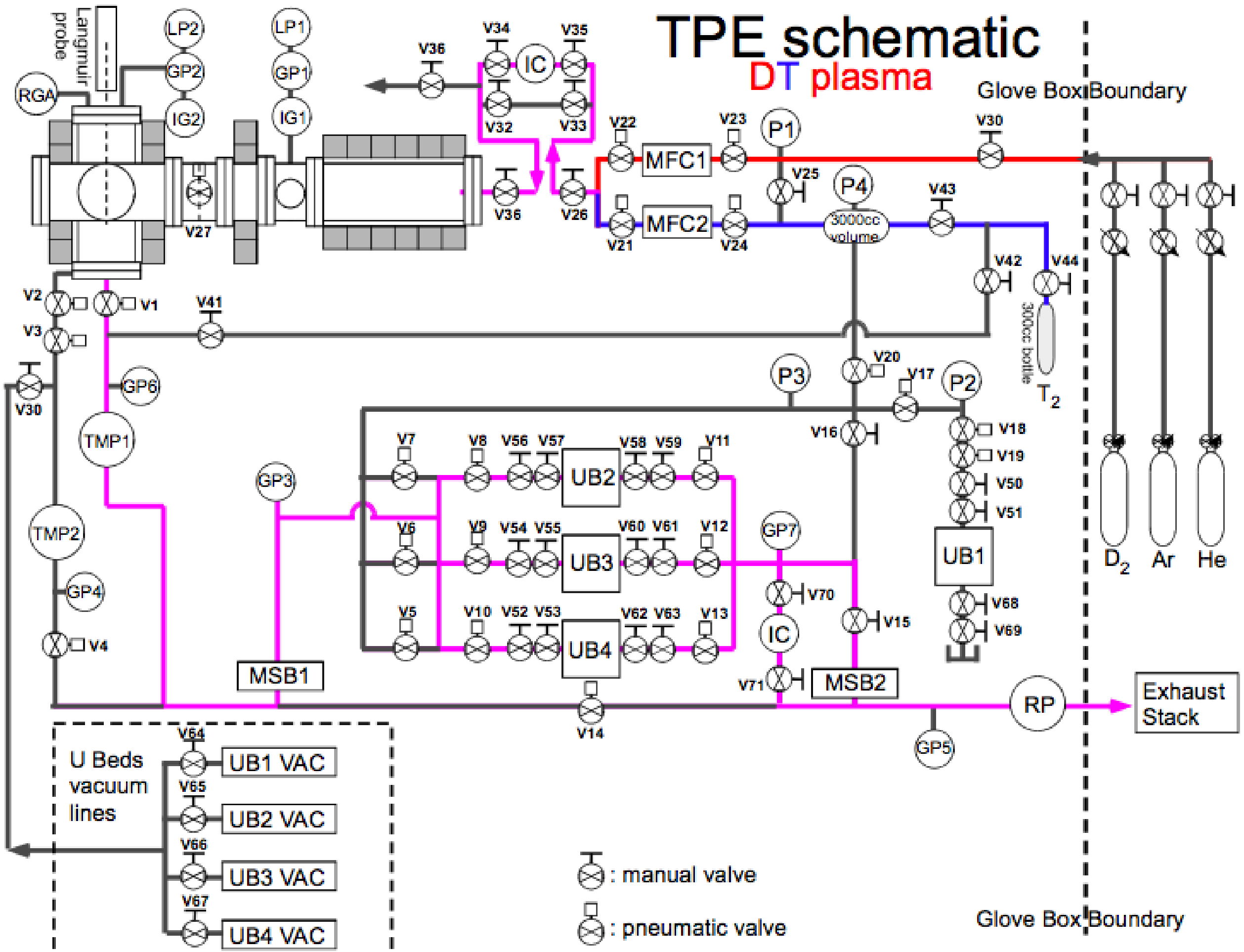
Use of tritium (even in trace amount <1 %)

- Enhance the detection sensitivity significantly (by ion chamber or LSC)
- Trace the surface profile easily (by IP)

Sensitivity: ~10^{-12}= ppt (part per trillion)

Initial testing with tritium completed March 2009.



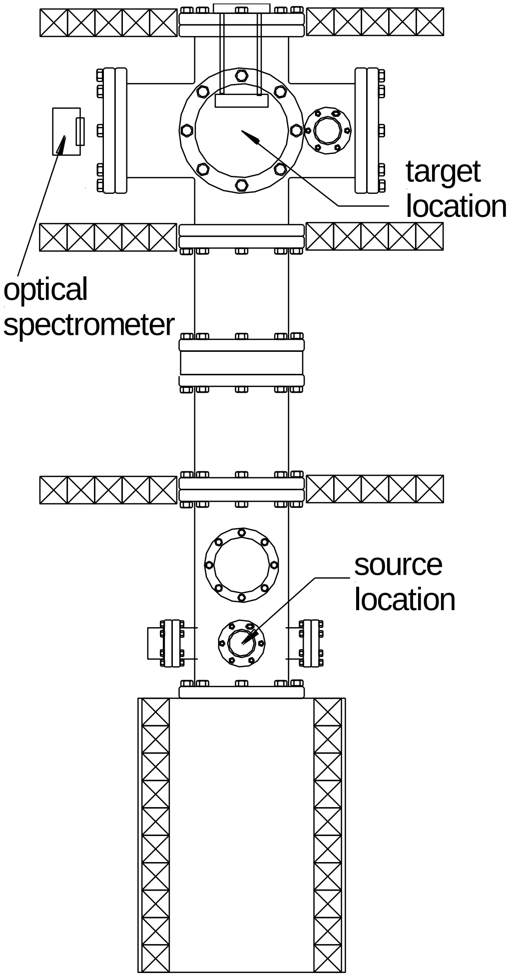


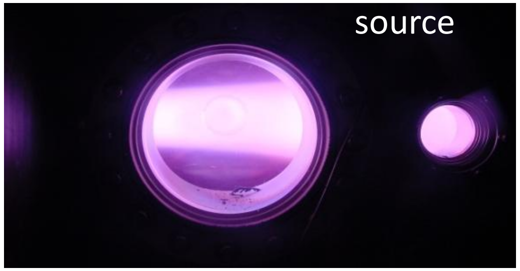
Schematic courtesy of M. Shimada.

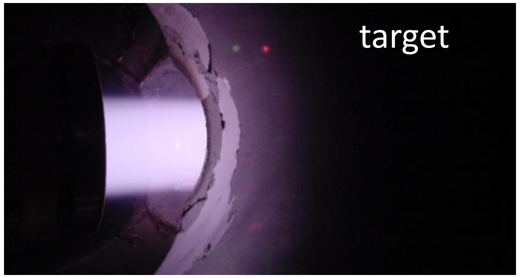
TPE plasma discharge characteristics

Diagnostics:

- Langmuir probe measurements at locations near both the source and target ends of the plasma chamber.
- Optical spectrometer available at target end (λ=585-685 nm.)
- Retention obtained by thermal desorption spectroscopy (TDS).





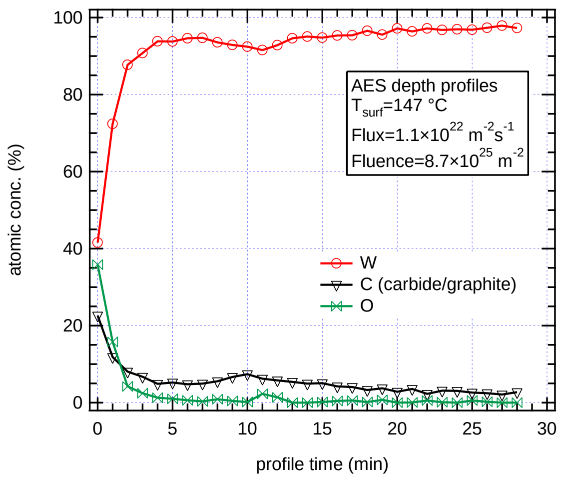


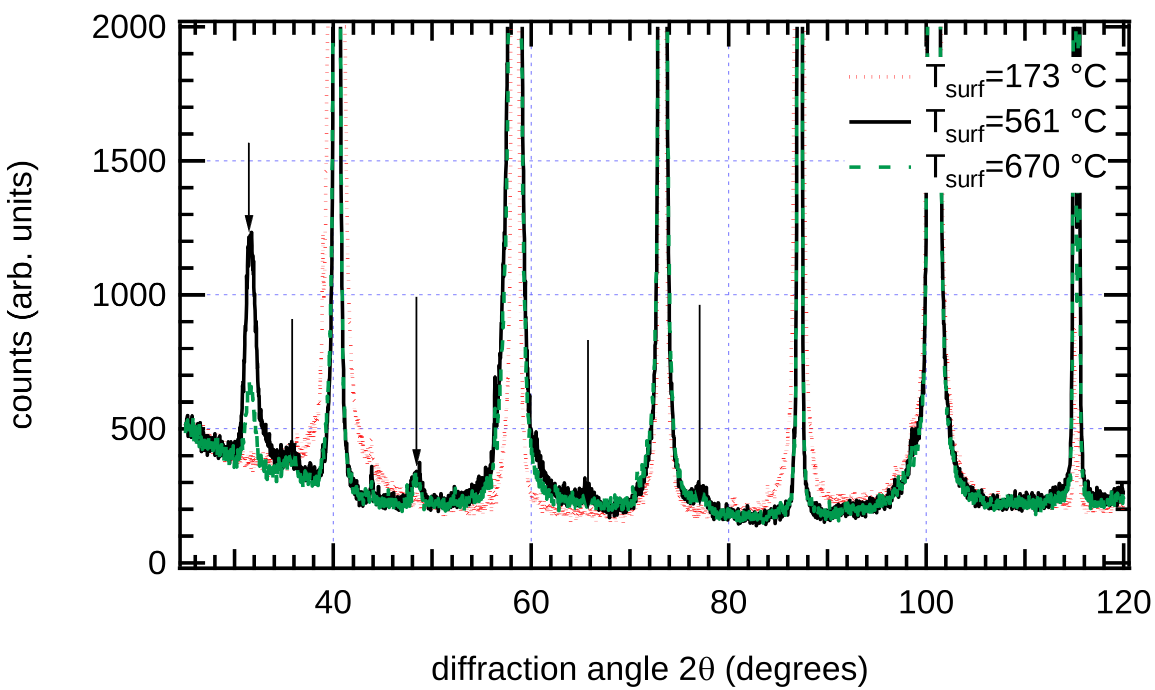
Discharge Properties:

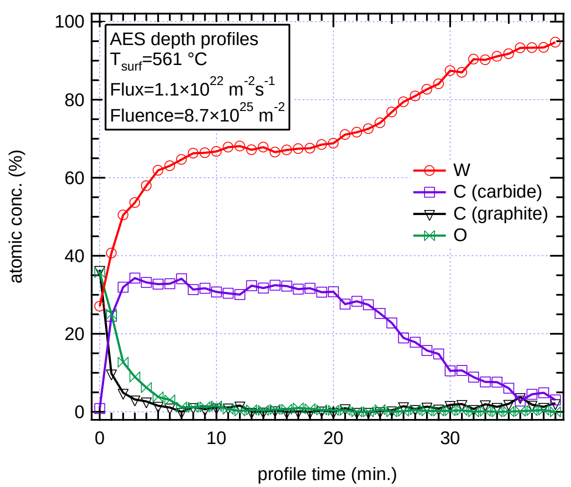
- Electron temperature = 8 - 15 eV
- Electron density = $10^{16} – 10^{18}$ m^{-3}
- Ion Flux = $10^{20} – 10^{22}$ $m^{-2}s^{-1}$
- Ion Fluence = $10^{23} – 10^{26}$ m^{-2}
- Plasma column FWHM = 5 cm

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

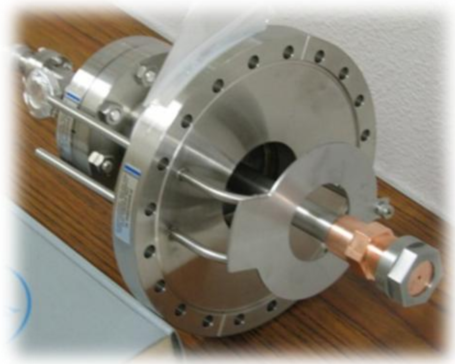






AES depth profiles

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)

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.

Concluding Remarks

- Successful development of a continuum-scale model of hydrogen precipitate growth in tungsten, useful for predicting conditions where bubble growth will occur.
- Present work focuses on converting this to a finite difference model of hydrogen precipitate growth.
- Development of plasma-driven permeation target holder for TPE is now underway; testing of first-generation device anticipated in August.

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