Parameter dependence of dynamic D retention in W

-- Based on D. Nishijima et al., Nuclear Fusion 61 (2021) 116028.

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In-operando surface measurements during plasma exposure are required to explore dynamic retention.

- **Dynamic retention**, including both solute (un-trapped) and “weakly” trapped D atoms, is quickly released after the termination of the incident plasma flux.
  - Ex-situ analysis (e.g. TDS) is not appropriate.

- In-operando ion beam analysis (IBA), such as NRA, has been used to study dynamic retention in a couple of experiments so far.

- We have applied **LIBS (laser-induced breakdown spectroscopy)** for conducting in-operando surface measurements.
  - In comparison with IBA, an LIBS system is much simpler, and quicker measurements are possible.

- Example of NRA measurements during D plasma exposure of Mo in DIONISOS.
- Measurement depth ~ 5 µm.

![Diagram](image-url)

Fig. 1. A schematic of the DIONISOS experiment

Fig. 4. NRA measured retained D fluence in the Mo plate in real-time; before, during, and after a deuterium plasma exposure with flux density of \(1.8 \times 10^{21} \text{ D/m}^2 \text{s}\) and \(V_{\text{bias}} = 100 \text{ V}\). \(T_s \sim 300 \text{ K}\)

_G.W. Wright et al., JNM 2007_
An in-operando/in-situ LIBS system has been developed and upgraded in PISCES-A.

- Q-switched Nd:YAG laser ($\lambda = 1064$ nm, $\Delta t_L \sim 5$ ns, $E_L \sim 115$ mJ)
- A remote-controlled motorized mirror mount enables to quickly and accurately control the laser spot location.
- Echelle type spectrometer (Andor ME5000) + ICCD camera (Andor iStar DH334T): $t_{\text{delay}} \sim 10$ ns & $t_{\text{width}} = 2 \mu$s
- Ablation depth: $\sim 350$ nm/shot & Spot diameter: $\sim 150$ $\mu$m
- The laser spot location was moved between each laser shot.
- 20 shots were accumulated to produce an emission spectrum for better statistics.
- Around 5 spectra were typically collected for each condition.
  - Mean value and uncertainty
- D I 656.1 nm/W I 429.4 nm intensity ratio is used to study dynamic D retention behavior in W.
How can we extract the dynamic retention component from in-operando LIBS $\text{D}_\alpha$ signal during steady-state plasma exposure?

The $\text{D}_\alpha$ line emission of in-operando LIBS measurements during steady-state plasma exposure can contain the following multiple components:

- **Background D/D$_2$ gas excited by steady-state plasma**
  - $\text{D}_\alpha$ line emission was not detected due to the short $t_{\text{width}} = 2 \mu s$.

- **Ejected D atoms (dynamic and static retention) excited by steady-state plasma**
  - Laser-induced plasma $\text{D}_\alpha$ emission is localized right on the W surface.
  - The steady-state plasma $n_e \sim 0.1 \times 10^{18} \text{ m}^{-3}$ is several orders of magnitude lower than that of typical laser-induced W plasmas.

  Negligible.

- **Dynamic retention excited by laser-induced plasma**

- **Static retention excited by laser-induced plasma**

- **Background D/D$_2$ gas excited by laser-induced plasma**
The $P_{D2}$ dependence reveals that there is no contribution of Bg gas to the LIBS signal during plasma exposure at $P_{D2} \leq 1.0$ mTorr.

- St was taken under vacuum, and is consistent.
- StBg linearly increases with $P_{D2}$.
- On the other hand, DyStBg is nearly constant at $P_{D2} \leq 1.0$ mTorr, and increases with $P_{D2}$ at $> 1.0$ mTorr.
- There is no contribution of Bg gas to in-operando LIBS $D_\alpha$ signal during plasma exposure at $P_{D2} \leq 1.0$ mTorr.
- Hard to quantify the Bg component at $P_{D2} > 1.0$ mTorr. → Not used in further studies.
- Note that no steady-state background plasma emission was detected even at $P_{D2} > 1.0$ mTorr.
The dynamic retention component can be extracted from
\[ \text{Dy} = \text{DySt} \left( P_{D2} \leq 1 \text{ mTorr} \right) - \text{St} \ (\text{vacuum}). \]

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Ambient background gas</th>
<th>LIBS signal can contain contributions from</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>During</td>
<td>( P_{D2} \leq 1 \text{ mTorr} )</td>
<td>Dynamic + Static</td>
<td>DySt</td>
</tr>
<tr>
<td>After</td>
<td>( P_{D2} &lt; 5 \times 10^{-7} \text{ Torr} )</td>
<td>Static</td>
<td>St</td>
</tr>
</tbody>
</table>

Dynamic retention: \( \text{Dy} = \text{DySt} \left( P_{D2} \leq 1 \text{ mTorr} \right) - \text{St} \ (\text{vacuum}) \)
D/W atomic fraction can roughly be converted from D I/W I line ratio.

- Laser ablation depth: \(\sim 350 \text{ nm}\)
- Static \(\frac{D}{W}_{\text{SSL}}(0-10\text{nm}) \sim 0.1\) in the near-surface layer at \(T_s \sim 300 \text{ K}\) [1].
- Static \(\frac{D}{W}_{\text{PL}}(10-350\text{nm}) \sim 10^{-4}\) in a plateau region [2].

\[
\int_{0 \text{nm}}^{350 \text{nm}} \frac{D}{W_{\text{St}}} dz \\
= \frac{D}{W}_{\text{SSL}}(0-10\text{nm}) \times 10 \text{ nm} + \frac{D}{W}_{\text{PL}}(10-350\text{nm}) \times 340 \text{ nm} \\
= 0.1 \times 10 \times 10^{-9} + 10^{-4} \times 340 \times 10^{-9} \sim 1 \times 10^{-9} \text{ (dominated by D/W in SSL)}
\]

- Dynamic retention is assumed to be localized in the near-surface layer.
  - Dynamic retention can be negligible in the deeper region because of the low solubility of W.
- D I/W I intensity ratio: \(Dy \approx St\) at \(T_s \sim 350 \text{ K}\) (and \(\Gamma_i \sim 0.9 \times 10^{21} \text{ m}^{-2} \text{s}^{-1}\))

\[
\int_{0 \text{nm}}^{10 \text{nm}} \frac{D}{W_{\text{Dy}}} dz = \int_{0 \text{nm}}^{350 \text{nm}} \frac{D}{W_{\text{St}}} dz \\
\rightarrow \frac{D}{W_{\text{Dy}}}(0-10 \text{ nm}) \times 10 \text{ nm} \approx 1 \times 10^{-9} \rightarrow \frac{D}{W_{\text{Dy}}}(0-10 \text{ nm}) \sim 0.1
\]

[1] L. Gao et al., NF2017
[2] V.Kh. Alimov et al., JNM2005
The behavior of dynamic retention of D in W is systematically explored, while varying the plasma exposure parameters.

- Apply the conversion factor \( \frac{D}{W} \sim 0.70 \times \frac{D}{I/W I} \) to the following parameter dependence study.

- **Incident ion energy, \( E_i \), dependence**: \( E_i \sim 45 – 175 \text{ eV} \)

- **Sample temperature, \( T_s \), dependence**: \( T_s \sim 348 – 573 \text{ K} \)

- **Incident ion flux, \( \Gamma_i \), dependence**: \( \Gamma_i \sim 0.26 \times 10^{21} – 2.9 \times 10^{21} \text{ m}^{-2}\text{s}^{-1} \)
  - A low flux range because of \( P_{D_2} \leq 1 \text{ mTorr} \)

- **Effect of He bubbles**
  - Sequential plasma exposure from pure He to pure D

In each parameter scan, the other parameters were kept as constant as possible.
Measured dynamic D retention in W depends on $T_s$ and $\Gamma_i$, while no/little $E_i$ dependence is observed.

- No clear $E_i$ dependence of all three components is seen in the range of $E_i \sim 45 - 175$ eV.
- All three components monotonously decrease with increasing $T_s$.
- The $T_s$ dependence of Dy is stronger than that of St.
- Dy linearly increases with increasing $\Gamma_i$ and saturates at $\Gamma_i \geq 0.75 \times 10^{21}$ m$^{-2}$s$^{-1}$.
- DySt (St) only slightly increases (decreases) or both are nearly constant with increasing $\Gamma_i$.

- Measured dynamic D retention in W depends on $T_s$ and $\Gamma_i$, while no/little $E_i$ dependence is observed.
Observed trends on $E_i$ and $T_s$ are qualitatively consistent with a global model prediction (E.A. Hodille et al., PRM 2018).

- The global model assumes two kinds of “trapping” sites: interstitial sites and single vacancies (with various $VH_x$).
- The global model predicts that H atoms trapped in single vacancies are dominant over solute H in the total retention, when an SSL is formed.
- In our experiments, the amount of dynamic retention is comparable to that of static retention.
  - In addition to solute H, “weakly” trapped H atoms in vacancies ($E_t < 1$ eV?) should/may also be treated as dynamic retention.
  - LIBS cannot distinguish solute and weakly trapped D atoms.

- The $T_s$ dependence of Dy is observed to be stronger than that of St.
  - De-trapping energies of solute & weakly trapped D (dynamic retention) are lower than those of strongly trapped D (static retention).

- The model prediction is qualitatively consistent with our observed trends on $E_i$ and $T_s$ for both dynamic (Dy) and total (DySt) retention.
  - The very weak or no $E_i$ dependence and the decreasing retention with increasing $T_s$.
There is a discrepancy between our measurement and the global model prediction in the $\Gamma_i$ dependence.

- DySt (St) only slightly increases (decreases) or both are nearly constant with increasing $\Gamma_i$.
- Dy saturates.
  - May interstitial & trapping sites saturate with D?
  - May diffusion/recombination/reflection properties effectively change with the high fraction of D?
- The model predicts a strong increase of the total retention with an increase in $\Gamma_i$.
- Does the total retention saturate?

![Graph showing the relationship between D/W atomic fraction and $\Gamma_i$](image)

**E.A. Hodille et al., PRM 2018**

**FIG. 4.** Total solubility of hydrogen (bold lines) implanted at $R_p$ for various incident fluxes ranging from $\Phi_{inc} = 10^{22}$ to $10^{24} \text{m}^{-2}\text{s}^{-1}$ plotted as a function of the temperature of implantation and for an incident energy of $E_{inc} = 500 \text{eV/ia}$. The fraction of hydrogen trapped at interstitial sites is also plotted in dotted lines for comparison.

- Initially perfect bcc W lattice is assumed.
- No change in W lattice and H behavior at interstitial H/W ≤ 1 at.%. 
- At interstitial H/W = 10 at.%, H atoms quickly start to agglomerate into multiple platelets.
- H self-trapping phenomenon leads to the spontaneous formation of platelets.

- With a pre-existing dislocation, lower interstitial H/W = 0.3-1 at.% are enough to form self-trapped H structures (platelet).
- De-trapping energy of H atoms from a platelet.

**Figure 3.** Platelet-like structures of self-trapped hydrogen atoms (purple dots) forming at 10 at.% hydrogen density in the initially perfect bcc tungsten lattice at 0.5 ns (a), 5 ns (b), and 50 ns (c) simulated time. The black lines represent edges of the simulation box. The vector tripod indicates principal directions of the initial bcc tungsten lattice. Color in this figure is available on-line. 

**Figure 4.** Top and front views of spatial distribution of hydrogen atoms (purple dots) near the edge dislocation (green line) in tungsten sample with 1 at.% hydrogen at 5 ns (a) and 80 ns (b) simulated time. The vector tripod shows coordinate system used in the simulations. Color in this figure is available on-line.

**Figure 12.** The evaluated hydrogen atom de-trapping energy from the platelet-like structure formed near the edge-dislocation as function of the number of hydrogen atoms in the structure for the different system temperatures. Color in this figure is available online.

- This stress-induced H self-trapping mechanism can also contribute to the surface super-saturation.
Dynamic D retention in W is not strongly affected by He bubbles in the near-surface region.

- First, a W target was exposed to pure He plasma at $T_s \sim 773$ K to produce He bubbles in the near-surface region.
- Then, the W target was exposed to pure D plasma at $T_s \sim 423$ K.

- Dynamic retention is not strongly affected by He bubbles in the near-surface region.

- Static retention in the near-surface region slightly increases with increasing He fluence.
  - D atoms can be trapped around He bubbles [e.g. S. Markelj et al., NF2020].
D retention properties of W during plasma exposure have been investigated in PISCES-A using the in-operando LIBS system.

- $E_i$ dependence
  - No clear dependence of Dy, St, and DySt in the range of $E_i \sim 45 – 175$ eV.
  - Qualitatively consistent with the global model prediction and the MD simulation.

- $T_s$ dependence
  - Dy, St, and DySt monotonously decrease with increasing $T_s$ at $\sim 348 – 573$ K.
  - Qualitatively consistent with the global model prediction.
  - $T_s$ dependence of Dy is stronger than that of St.
    → Lower de-trapping energies of solute and weakly trapped D atoms (Dy).

- $\Gamma_i$ dependence
  - Dy linearly increases with increasing $\Gamma_i$, and saturates at $\Gamma_i \geq 0.75 \times 10^{21}$ m$^{-2}$s$^{-1}$.
  - DySt (St) only slightly increases (decreases) or both are nearly constant with increasing $\Gamma_i$.
  - Inconsistent with the global model prediction.

- Effect of He bubbles
  - Dy (St) only slightly decreases (increases).
Ex-situ analyses of supersaturated layer will be performed using FIB/TEM and GDOES.

- Layer thickness and (relative) D amounts vs. $E_i$, $T_s$, and $\Gamma_i$.
- GDOES depth profiling of RAFM steel samples was done.
  - Depth resolution: $\sim 0.125$ nm.
  - D signal ($\text{Ly}_\alpha$ at 2nd order) was successfully detected in a Cr-rich surface layer.

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D. Nishijima et al., NME 2021

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