Isolating the Detrapping of Deuterium in Heavy Ion Damaged Tungsten via Partial Thermal Desorption

M. J. Simmonds^a, T. Schwarz-Selinger^b, J. H. Yu^a, M. J. Baldwin^a, R. P. Doerner^a, G. R. Tynan^{a,c}

^a*Center for Energy Research, UC San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0417, USA*

^b*Max-Planck-Institut für Plasmaphysik, Boltzmannstrasse 2, D-85748 Garching, Germany*

^c*Department of Mechanical and Aerospace Engineering (MAE), UC San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0411, USA*

Abstract

Partial Thermal Desorption Spectrometry (pTDS) progressively depopulated trapped deuterium (D) from heavy-ion damaged tungsten (W) to determine spatial location and detrapping energies. W samples were prepared identically: 5 MeV Cu²⁺ damaging ions (0.12 peak dpa dose) before D₂ plasma loading (10²⁴ D/m² fluence) held at 373 K. Each sample reached one of six pTDS peak-and-hold temperatures. Nuclear Reaction Analysis (NRA) measured the D spatial profile remaining after pTDS, before final TDS.

NRA and TDS measured total D retention were in good agreement. NRA displayed three zones of D-populated defects: (I) near-surface (below 0.1 μm), (II) heavy-ion damage (peaked $\sim 1 \mu\text{m}$), and (III) uniform intrinsic (bulk). D concentration in zone I reduced by $\sim 97\%$ in samples with pTDS at 597 K and higher, indicating near-surface traps have low detrapping energy. The Stopping and Range of Ions in Matter (SRIM) predicts a displacement profile

Email address: msimmonds@eng.ucsd.edu (M. J. Simmonds)

for zone II that coincided with measured D profile for samples with pTDS at 597 K and higher. Samples prepared with pTDS below 597 K display a distinctly different D profile in zone II. The complete cycle of D₂ plasma loading, pTDS, NRA, and final TDS was modeled with Tritium Migration Analysis Program (TMAP) using a recently developed Pseudo Trap and Temperature Partition (PTTP) scheme. Differences in TDS profiles isolated traps that release between consecutive pTDS temperatures, demonstrating 6 distinct release peaks. The best fit was found with detrapping energies near 1.0, 1.2, 1.4, 1.6, 1.8, and 1.9 eV. These results show that heating at 762 K for 2.5 hours released $\sim 99\%$ of retained D in heavy-ion damaged W.

Keywords: Tungsten, Deuterium, Retention, Heavy ion damage, Partial Thermal Desorption, Peak-and-hold, NRA, TDS

1. Introduction

The retention of tritium in Plasma Facing Materials (PFMs) is an important issue due to both safety concerns as well as maintaining the fuel cycle in fusion devices [1]. The production of fusion neutrons will lead to the degradation of PFMs throughout the bulk of the material. In order to study the effects of neutron damage and tritium exposure, heavy ion damage and deuterium are used as proxies, respectively. The guidelines for the use of heavy ions to simulate neutron damage are outlined in [2].

Experiments conducted to study displacement damaged W typically use NRA and TDS to quantify D retention. NRA probes the D distribution across the near-surface region up to depths of $\sim 10 \mu\text{m}$, whereas TDS measures the released D from throughout the bulk. NRA can not differentiate between trapped and solute D atoms located between W lattice sites, nor can it directly determine detrapping energy or trap type. Among other factors such as surface recombination, the release peaks for thermally desorbed D from W are correlated to both the spatial position and detrapping energy of a particular type of defect. The measured release rate from the surface is the result of the escape of D from multiple types of defects, each having a particular detrapping energy, followed by subsequent diffusion through the material to reach the surface where recombination occurs. The resulting TDS data may display one or more effective release peaks, due to nearby detrapping energies from multiple defects as well as multiple D fill levels for a single defect type.

Comparing the activation energies calculated with Density Functional Theory (DFT) and attained by modeling thermal desorption data, various

defect types in W have been associated with a particular dominant detrapping energy [3]. Inferred detrapping energies range for dislocations and grain boundaries from 0.8 to 1.0 eV, vacancies from 1.3 to 1.7 eV, and vacancy clusters from 1.8 to 2.4 eV. Detrapping energies may also overlap. Scanning transmission electron microscopy [4] suggests dislocation loops span 0.4 to 1.8 eV [5]. Though DFT predicts multiple D filling of some defects (e.g. mono-vacancies [6, 7]) the individual release peaks may not be directly resolvable in TDS data if the detrapping energies are too close together. Note that the values determined from TDS data are dependent on both the attempt frequency, generally assumed to be 10^{13} s^{-1} [7], as well as the value used to model surface recombination.

Previous studies [3, 8, 9] have used varied sample temperatures during plasma exposure to selectively populate defects. At higher sample temperature, defects with lower detrapping energies can not be effectively filled with D if the release rate is large relative to the trapping rate. The increased temperature may significantly influence the evolution of defects to be populated, complicating the interpretation of such experiments. For instance, mono-vacancies may be partially annealed as they recombine with mobile interstitials, and between 523-573 K the vacancies become mobile and can further annihilate or agglomerate into clusters [10, 11]. Positron annihilation spectroscopy shows that the clusters grow in samples heated to 650 K in under 5 minutes [12]. Thus, at high sample temperatures, the assumption of a static population of defects during plasma exposure may no longer be valid. In addition, the increased diffusivity of D at higher temperature may increase retention as deeper intrinsic traps become filled. This results in the

51 broadening of each release peak. Therefore the direct comparison of samples
52 prepared with various sample temperatures during plasma exposure is not
53 straightforward.

54 To better quantify the spatial location and detrapping energies associated
55 with various defects, we devised an experimental approach to sequentially
56 depopulate each defect according to detrapping energy. Whereas previous
57 experimental studies that attempted to model NRA and TDS data have as-
58 sumed specific detrapping energies and spatial concentrations, this approach
59 aims to constrain both quantities and test if a discrete detrapping energy
60 model can reproduce the experimental data. Similar to the approach by Efi-
61 mov *et al.* [13], all damaged and D decorated samples have the same initial
62 conditions prior to pTDS. Unlike Efimov, by holding the sample at a fixed
63 elevated temperature (peak-and-hold) after the pTDS linear ramp, defects
64 with appreciable release rates at that temperature will further depopulate.
65 The released D then either travels further into the material, filling traps with
66 higher detrapping energy, or reaches the surface to escape the sample. NRA
67 is carried out after each pTDS procedure to provide a spatial profile of the
68 remaining D atom concentration. The resulting data allows us to then in-
69 fer the spatial profile with respect to detrapping energies and densities from
70 each spatial zone attributed to plasma-induced, heavy ion beam induced, and
71 intrinsic trap sites.

72 Typically the TDS temperature ramp is assumed fast enough to ne-
73 glect defect evolution, while the pTDS peak-and-hold may change the defect
74 population. Since pTDS temperatures in this experiment span 467-762 K,
75 mono-vacancies may become mobile but vacancy clusters would not dissoci-

76 ate (~ 1200 K [14]). Additionally, traps may agglomerate migrating defects
77 that can result in an increase to the detrapping energy.

78 In a similar experiment, Zhao *et al.* [15] performed pTDS on W samples
79 with 0.01 and 1 displacements per atom (dpa). The resulting full TDS profiles
80 show that the initial release for the 0.01 dpa sample starts at a temperature
81 well above the peak-and-hold and slightly above initial release for the 1 dpa
82 sample. Here it is worth noting that the full TDS of the 0.01 dpa sample does
83 not exhibit obvious defect evolution due to the pTDS. On the other hand,
84 the 1 dpa does show that the highest temperature release peak significantly
85 grew, likely due to vacancy agglomeration during the peak-and-hold.

86 In some previous experiments, within the heavy ion damage region there
87 is a discrepancy between some experimental NRA data and SRIM predicted
88 damage profiles. NRA data from plasma exposure at elevated sample tem-
89 peratures (~ 600 K and above) [8, 9, 12, 16] do not display a significant
90 near-surface peak and are spatially commensurate with the SRIM calculated
91 dpa profile. Yet lower sample temperature during plasma exposure yields
92 a D concentration in the near-surface that can not be explained by plasma
93 induced defects alone. The deviation in trap profile and consequently D con-
94 centration measurements is likely due to a different spatial profile for low
95 detrapping energy defects.

96 **2. Experiment**

97 *2.1. Sample Preparation*

98 W samples originated from a certified 99.95 wt.% powder metallurgy
99 polycrystalline rod, 6 mm in diameter and cut into disks 1.5 mm thick.

100 The plasma facing surface received a mirror-like finish by successive polish
 101 treatments ending with a 3 μm grit. Arithmetic mean surface roughness,
 102 measured with a confocal microscope, resulted in 28 ± 5 nm after polish.
 103 Contaminants from polishing were removed in successive ultrasonic baths of
 104 acetone followed by ethanol. Next, the samples were annealed at 1173 K for
 105 1 hour in a vacuum chamber below 10^{-4} Pa. As noted in [17], a broken W
 106 sample displayed elongated grains perpendicular to the surface with dimen-
 107 sion on the order of 10 μm parallel to the surface, as viewed by a scanning
 108 electron microscope. The maximum annealing temperature is well below
 109 the recrystallization temperature, leaving an intrinsic level of various defects
 110 throughout the bulk of the sample.

111 2.2. Heavy Ion Damage

112 The previously prepared W samples were irradiated with 5.0 MeV Cu^{2+}
 113 ions at the TOF beamline of the tandem accelerator laboratory at Max-
 114 Planck-Institut für Plasmaphysik in Garching (IPP) while under a low vac-
 115 uum of 10^{-6} Pa and held at 295 K with a water-cooled sample holder. Details
 116 of the setup can be found in [18]. The beam had a full width at half maximum
 117 of 2 mm, and was rastered over the samples to achieve lateral homogeneity.
 118 The implanted Cu dose was 1.215×10^{18} ions/ m^2 with an average flux of
 119 2.4×10^{15} ions/ m^2/s , which maintained an impurity level below the intrinsic
 120 Cu level [19]. In accordance with Stoller *et al.* [20], the “Quick” Kinchin-
 121 Pease option and a displacement damage threshold of 90 eV were used to
 122 calculate the displacement profile in SRIM shown in Fig. 1 with a peak dpa
 123 of 0.12. According to the simulation, on average each energetic Cu ion is
 124 estimated to produce a collision cascade with over 5,600 W lattice displace-

125 ments. This sample temperature during plasma exposure was low enough
126 to avoid the annealing of displacement damage that we have reported in
127 previous work [17].

128 *2.3. D₂ Plasma Exposure*

129 One undamaged sample, as well as the identically prepared Cu ion irra-
130 diated samples, were exposed to D₂ plasma with a neutral pressure of 0.7 Pa
131 in the PISCES-E device, a plasma etcher with a 13.56 MHz RF source [21].
132 The air-cooled sample holder was negatively biased to implant D with an ion
133 impact energy of 110 eV and maintained the sample at 373 K as measured by
134 a thermocouple in contact with the rear of the sample. An RF compensated
135 Langmuir probe inferred an average flux ($\Gamma_{incident}$) of 1.8×10^{20} ions/m²/s
136 uniformly across the surface of the sample holder as detailed in [22]. Each
137 sample received a total fluence of 10^{24} D/m² after ~ 1.5 hours.

138 *2.4. Partial TDS*

139 The plasma-exposed samples were kept at room temperature for 25 days
140 before being subjected to pTDS. Samples were mounted on the tip of a
141 thermocouple within a vacuum below 10^{-6} Pa. Parabolic mirrors focused the
142 heat from infrared lamps on the sample surface. A programmable controller
143 was set to heat the samples at a constant rate of 0.5 K/s before plateauing
144 for 2.5 hours at a particular peak-and-hold temperature. That is, instead
145 of completely desorbing the sample as in a typical TDS run by heating the
146 samples to a peak temperature near 1300 K, temperatures well below that
147 were chosen to selectively depopulate the corresponding lower energy traps.
148 In what follows, the label for each pTDS sample refers to this peak-and-hold

149 temperature (e.g. “pTDS at 467 K”). It should be noted that two control
150 samples were not thermally desorbed at this stage, one without pTDS labeled
151 “No pTDS” and one without heavy ion damage, “No Cu”.

152 2.5. NRA

153 NRA was performed on each sample at IPP Garching 20 days after the
154 pTDS procedure. The $D(^3\text{He},p)^4\text{He}$ nuclear reaction measured the depth
155 profiles of the remaining D concentration as prescribed by Mayer with a
156 detector positioned at a scattering angle of 135° [23]. A ^3He ion beam was
157 used to probe the first $\sim 6\ \mu\text{m}$ of D implanted in W with decreasing energies
158 of 3.5, 2.5, 2.0, 1.65, 1.5, 1.3, 1.1, 0.8, and 0.6 MeV. Both the energy spectra
159 of the resultant protons and alphas were captured in solid state detectors to
160 determine the depth distribution of the retained D. Relative to the protons,
161 the resulting alpha particles are only detectable for low ^3He beam energies
162 since the energy of reflected ^3He ions overlap with the alpha energy. Probing
163 with a ^3He energy slightly below and above the cross section peak (i.e. 0.6
164 and 0.8 MeV) enhances the near-surface resolution of D concentration. In
165 addition to detecting both product ions, the various sources of straggle are
166 minimized with relatively low probing energies. As a result, we can resolve D
167 trapped within the near-surface ($\sim 100\ \text{nm}$) region; deeper NRA results have
168 poorer spatial resolution. Using the NRA data, both SimNRA and NRADC
169 were then employed to determine the most probable D concentration as a
170 function of depth [23, 24].

171 2.6. *Final TDS*

172 A further 18 days elapsed between NRA and the final TDS run where all
173 samples were heated with a constant 0.5 K/s ramp rate up to a peak temper-
174 ature above 1300 K to ensure full desorption of D. The partial pressures of
175 H₂, HD, and D₂ were measured with a quadrupole mass spectrometer (QMS).
176 The thermally desorbed particle flux was calculated by converting the QMS
177 measured partial pressure via a calibrated D₂ leak. The total D flux was
178 calculated as described in further detail by Yu [25], as the sum of the HD
179 and twice the D₂ flux. Note that the HD flux was calibrated to the D₂ leak,
180 without any further correction for ionization efficiency. Since the detection
181 efficiency is expected to increase for ions of lighter mass this procedure leads
182 to a small overestimation of the total D flux. However, as HD contributed
183 only an average of 28% to the total D flux this is of minor importance. As
184 described previously [17], variable ambient laboratory humidity, tempera-
185 ture, and length of vacuum break influence the water content adsorbed to
186 the TDS chamber walls. This leads to a significant H₂ background signal
187 that was scaled to and subtracted from the raw HD and D₂ signals.

188 3. Results

189 After the pTDS procedure was applied to each sample, and prior to final
190 TDS, the spatial profile of D concentration in each sample was measured
191 with NRA. In Fig. 1, the experimental data displays a monotonic decrease in
192 D concentration as the pTDS peak-and-hold temperature is increased. The
193 estimated error determined by NRADC as a concentration range is indicated
194 as the corresponding transparent colored region in the figure. The NRA pro-

195 files have distinct spatial zones, labeled I-III respectively: zone I composed
 196 of the near-surface ($\sim 0.1 \mu\text{m}$) region, zone II composed of the Cu damage
 197 ($\sim 1 \mu\text{m}$) region, and zone III composed of the bulk of the samples depth.
 198 Within zone I, the control sample without heavy ion beam damage (solid
 199 black) displays a peak D concentration near 1.5 at. % that decays exponen-
 200 tially with a characteristic length of $0.05 \mu\text{m}$. The intrinsic defects left after
 201 sample preparation annealing (below the recrystallization temperature) are
 202 assumed to have a uniform distribution throughout the bulk, zone III. For Cu
 203 ion beam damaged samples, the dominant contribution to total D retention
 204 is seen in zone II. The D concentrations for pTDS temperatures of 525 K and
 205 higher largely coincide with the SRIM predicted damage profile (dot-dashed
 206 orange). The “No pTDS” and the 467 K pTDS samples have profiles that
 207 are more heavily weighted closer to the surface. The small, but measurable,
 208 D level near $2 \mu\text{m}$ suggests the D diffusion front reached beyond the SRIM
 209 profile, which was confirmed by subsequent TMAP modeling that predicted
 210 the front reached $\sim 20 \mu\text{m}$.

211 In Fig. 2, the surface flux of D atoms released from the W samples during
 212 each pTDS and final TDS are shown as dashed and solid lines respectively.
 213 The 700 K pTDS sample is not shown due to an experimental error with
 214 the initial temperature ramp. The pTDS profiles (dashed lines) display the
 215 sequential removal of D from traps with increasing pTDS temperature, and
 216 exhibit a sharp drop in released D flux when fixed at their peak-and-hold
 217 temperature. This D flux plotted against time instead of temperature dis-
 218 plays an exponential decay during the pTDS peak-and-hold (not shown here
 219 but similar to [15]), indicating the depopulation of traps that exhibit a signif-

Figure 1: The D concentration measured through NRA decreases with increasing pTDS temperature. The SRIM predicted trap profile (dot-dashed orange) for 5 MeV Cu^{2+} displays a peak near $\sim 0.9 \mu\text{m}$ and shown here scaled to 1. Note that the experimental dose resulted in a calculated peak dpa of 0.12. A two Gaussian fit to the SRIM profile is defined by the normalized function. Dashed silver vertical lines indicate the approximate transition between zones I-III.

220 icant release probability at the pTDS peak-and-hold temperature. The first
 221 and weakest D filled traps are highly sensitive to surface conditions and stor-
 222 age time in between D implantation and TDS [26, 27]. Whereas the pTDS
 223 samples were thermally desorbed after ~ 1 month, the control samples waited
 224 ~ 2 months. That extra storage time likely led to the “No pTDS” control
 225 (dark blue) having a lower first peak than in the other Cu damaged samples.
 226 The “No pTDS” control sample shows a significant increase in the amount
 227 of released D as compared to the “No Cu” control sample (black) for all tem-
 228 peratures below 1000 K. The initial release of the “No pTDS” control sample

229 begins near the 373 K plasma exposure sample temperature. For all cases,
 230 it appears that the pTDS peak-and-hold temperature is at least 40 K lower
 231 than the leading edge of the initial release temperature during the subsequent
 232 final TDS. For example, the sample with a pTDS peak-and-hold temperature
 233 of 467 K (dashed gold) only begins to appreciably release D when the tem-
 234 perature exceeds 510 K during the subsequent final TDS (solid gold). This
 235 separation indicates that the underlying assumptions of the PTTP scheme
 236 [28] can be used to distinguish and isolate traps with progressively higher
 237 release energies. As a result, taken together the NRA and TDS data can be
 238 used to quantify the location and concentration of D residing in each trap,
 as illustrated in the following discussion.

Figure 2: The D surface flux during pTDS (dashed) and the final TDS (solid) are plotted with respect to a 0.5 K/s linear heating ramp. Once pTDS samples reached a specific peak-and-hold temperature, the flux during the 2.5 hr peak-and-hold decays exponentially in time and approaches zero at this fixed temperature.

239

240 Note that in Fig. 1, the NRA profiles for the control samples labeled

241 “No Cu” and “No pTDS” have a high D concentration located in zone I.
 242 In the “No Cu” case this zone I population forms the majority of retained
 243 D inventory, while for the “No pTDS” case (which did suffer Cu ion beam
 244 damage) the zone I retained population sits on top of a significant retained
 245 D inventory located deeper in zone II. Comparing the “No pTDS” and the
 246 467 K and 525 K pTDS cases in Fig. 1, we observe that the zone I retained
 247 D inventory is largely reduced, and is undetectable for the 597 K pTDS case
 248 shown in red in Fig. 1. Furthermore, the “No Cu” (solid black) and 597 K
 249 (solid red) final TDS curves in Fig. 2 display a crossing near 700 K. These ob-
 250 servations show that the majority of the “No Cu” sample D inventory that
 251 was trapped in zone I has been completely released at 700 K whereas the
 252 ion beam damaged sample that underwent a 597 K pTDS treatment is just
 253 beginning to release D at this temperature. Considering Fig. 1 and Fig. 2 re-
 254 sults together, we can then conclude that the zone I traps are induced by the
 255 plasma and have relatively low detrapping energies that release at tempera-
 256 tures below 700 K. Furthermore, we can conclude that most of the increased
 257 inventory in ion beam damaged samples is located in zone II and releases at
 258 higher temperatures. These two experimental observations suggest that the
 259 NRA, pTDS, and final TDS approach used here may permit the inference of
 260 both spatial distribution of traps with differing trapping energies. We take
 261 up a deeper examination of the utility of the combined NRA, pTDS, and final
 262 TDS data sets after examining the self-consistency of the overall retention
 263 data emerging from these combined techniques.

264 By integrating the NRA profile over the depth into the material we can
 265 determine the remaining retained D inventory for each pTDS case. The

266 result of this analysis is shown by the black circle symbols in Fig. 3, and
 267 shows a gradual reduction in the retained D as the pTDS peak-and-hold
 268 temperature is increased. Likewise, by integrating the pTDS release histories
 269 shown by the dashed curves in Fig. 2, we can determine how much D was
 270 released for each pTDS case. The result of this analysis is shown by the filled
 271 blue upright triangle data points in Fig. 3, and shows a gradual increase in
 272 the amount of released D with increasing pTDS peak-and-hold temperature.
 273 Finally, integrating the final TDS release curves shown by the solid curves
 274 in Fig. 2, we can determine the remaining D inventory throughout the bulk
 275 of the material. The result, shown as the inverted red triangles in Fig. 3
 276 shows a gradual decrease in retained D inventory as the pTDS peak-and-
 277 hold temperature is increased, and is in good quantitative agreement with
 278 the NRA results. The sum of the pTDS and TDS data (purple diamonds)
 279 provides an independent measurement of retained inventory and shows a
 280 nearly constant value of $(12 \pm 1) \times 10^{20}$ D/m², consistent with the data point
 281 obtained from the damaged control sample (“No pTDS” in Fig. 1 and 2)
 282 which is plotted at 373 K on the x-axis in Fig. 3. Thus the independent
 283 NRA, pTDS, and final TDS techniques give consistent retained inventory
 284 measurements.

285 **4. Isolating Detrapping Energies**

286 The simulation of the pTDS, NRA, and final TDS stages are well con-
 287 strained by both the identical initial conditions and the controlled depop-
 288 ulation of each trap. Here we assume each trap concentration and spatial
 289 profile as well as the filling thereof during D implantation are the same for

Figure 3: The sum total D retention measured in the first 5.5 μm through NRA and the bulk through TDS. Plotted at the plasma exposure sample temperature of 373 K, the “No pTDS” sample shows the largest deviation from NRA. The sum of D retention measured from pTDS and TDS is consistent as seen by the average (orange shaded region). Dashed lines are only shown to guide the eye.

290 all samples prior to the application of the pTDS procedure. In what follows,
 291 we exploit the selective depopulation of traps with lower detrapping energies
 292 in order to isolate the spatial location and detrapping energy of the desorbed
 293 D. In order to do this, for a given NRA profile or pTDS release dataset, we
 294 subtract the next highest pTDS temperature dataset (i.e. consecutive pTDS
 295 temperatures). The difference then can be used to determine spatial location
 296 (from differential NRA data) or release temperatures (from differential final
 297 TDS data). Furthermore, the spatial location of a given trap energy will be
 298 described by a spatial profile function ($f_k^j(x)$) that corresponds to the spatial
 299 distribution of the D that was released during consecutive pTDS exposures;

we will find that this function will be zone (j) and trap type (k) dependent.

4.1. NRA Subtraction

The NRA D profiles shown in Fig. 1 display a distinctly different shape for pTDS samples subjected to peak-and-hold temperatures of 525 K and above. Fig. 2 shows the remaining D in these higher temperature pTDS samples are trapped in defects with increasing detrapping energy. Fig. 4 displays the concentration difference profiles (ΔC) computed as the difference between consecutive NRA D profiles and labeled by the two pTDS temperatures used to produce a given profile. The difference profiles for these higher temperature pTDS samples and the 762 K pTDS sample display a peak at a depth of 0.7-1.0 μm , in agreement with the SRIM predicted dpa profile (dot-dashed orange), showing that the computed dpa distribution at a given depth is correlated to the difference concentration at that location. We therefore use the SRIM predicted spatial profile to define the spatial profile function $f_{high}^{II}(x)$ for zone II, where the trap type ($k = high$) refers to high detrapping energies associated with higher temperature release.

In Fig. 5, the D concentration profile for the “No Cu” sample (black) displays a large near-surface component in zone I due to D₂ plasma exposure (note the much larger concentration scale compared to Fig. 4). The profile exponentially decays into the bulk as seen in previous work [29, 30]. A fit (dot-dashed red) to the “No Cu” is shown as an intrinsic concentration plus an exponential decay with characteristic length of 0.05 μm . The exponential fit to the plasma induced trap distribution in zone I is then chosen to define the spatial distribution $f_{low}^I(x)$, where “low” refers to low detrapping energy traps (i.e. Fig. 4 shows $f_{high}^I(x)$ equals zero).

Figure 4: The difference in D concentration between consecutive pTDS samples are shown as solid lines. The damage profile of zone II is further defined and fit well by the SRIM dpa profile scaled to 0.3 for ease of comparison (dot-dashed orange).

325 In order to isolate and determine the spatial location of low energy traps
 326 in zone II, both the “No Cu” and 597 K pTDS profiles are subtracted from
 327 the “No pTDS” profile (solid blue). First, noting the similarity in D profile
 328 for zone I between the “No Cu” and “No pTDS” NRA data shown in Fig. 1,
 329 we assume the plasma induced traps are represented by the “No Cu” profile.
 330 Second, the samples with pTDS peak-and-hold temperature at 597 K and
 331 above display no additional zone I component. Lastly, as shown in Fig. 4,
 332 these higher temperature pTDS samples display a D concentration coinci-
 333 dent with heavy ion induced traps located in zone II. Thus the remaining
 334 D found after subtracting both the “No Cu” and 525 K pTDS reveals the
 335 profile for heavy ion induced traps associated with lower detrapping energies.

Figure 5: The ‘No Cu’ sample is shown as solid black with an exponential decay function (dot-dashed red). The solid blue line representing “No pTDS,” subtracting both the “No Cu” and 597 K pTDS NRA profiles, isolates the low energy traps due to heavy ion damage. An empirical fit (dot-dashed magenta) to this D profile is significantly shallower than the SRIM profile (dot-dashed orange).

336 An empirical fit to this difference ($f_{low}^{II}(x)$) is shown in Fig.5 as the sum of
 337 two Gaussians (dot-dashed magenta), though the two distinct features may
 338 simply be an artifact of the NRA resolution. This difference-concentration
 339 distribution is quite distinct from both the near-surface zone I concentration
 340 profile, and the trapped D located within higher detrapping energy traps
 341 found in Fig. 4.

342 4.2. TDS Subtraction

343 Similarly, the differences between the final TDS data obtained from con-
 344 secutive pTDS peak-and-hold temperature runs are shown in Fig. 6. Using

345 the difference-flux ($\Delta\Gamma$) TDS profiles, we can infer the minimum number of
 346 distinct traps in damaged W. The first difference (dark blue) is too broad
 347 to be due to a single trap but would appear to have at least two detrapping
 348 energies. The separation and width of each additional difference suggest at
 349 least four more individual detrapping energies. Note that the overlapping
 350 initial release of the last two differences (turquoise and green) is likely due to
 351 the same detrapping energy. Lastly, the highest pTDS temperature at 762 K
 352 (purple) may have a unique detrapping energy of its own as further evidenced
 353 by the corresponding NRA profile in Fig. 4. Thus, there are likely at least 6
 354 or 7 unique detrapping energies needed to model this data set obtained with
 355 a sample temperature of 373 K during plasma exposure, as seen in previous
 work [28, 13, 31].

Figure 6: The difference in D flux during final TDS ($\Delta\Gamma$) for each consecutive pTDS sample pair are shown. The first dark blue line displays a broader primary peak than the other differences. Each of the remaining differences can be modeled with a single detrapping energy. All of the differences, except for the green line, begin to escape the sample at a unique temperature.

356 These difference datasets obtained from NRA and final TDS measure-
 357 ments can be used to constrain a reaction-diffusion model of the D in dam-
 358 aged W to determine the spatial distribution and trapping energy that best
 359 reproduces these observations. We take up this modeling effort in the follow-
 360 ing.

361 5. TMAP Simulation with PTTP

362 In order to use the verified and validated reaction-diffusion code TMAP7
 363 [32, 33, 34] to model these results that require more than three types of traps
 364 with distinct detrapping energies, we employed a Pseudo Trap and Temper-
 365 ature Partitioning (PTTP) scheme as outlined and applied to TMAP7 [28].
 366 In brief, for a particular temperature range this scheme utilizes a pseudo trap
 367 that accounts for multiple traps with deep energy wells that do not appre-
 368 ciably release but may act to trap mobile D from solute. When applied to
 369 TMAP7, only three traps are modeled at a time: the two lowest detrapping
 370 energy traps are included and can act to both trap and detrap D atoms, and
 371 a pseudo trap (which models all traps with higher detrapping energies) is
 372 included and primarily acts to trap D atoms.

373 Reaction-diffusion parameters as outlined in [28, 26] were used and de-
 374 tailed in Table 1. During the D₂ plasma exposure phase, the implanted D
 375 flux was simulated as a Gaussian with mean depth (r_{implant}) and standard
 376 deviation (σ_{implant}) with a reflection coefficient (R).

377 The heavy ion damage, together with the intrinsic defects leftover after
 378 sample preparation and annealing act as the initial trap concentrations for

Table 1: Summary of fixed parameters and activation energies (E_a) used in the TMAP simulation.

Ref.	Parameter			E_a [eV]
[6]	D_s	1.6×10^{-7}	$[\text{m}^2/\text{s}]$	0.25
[35]	K_r	$3 \times 10^{-25} T^{-1/2}$	$[\text{m}^4/\text{s}]$	-2.06
[7]	ν_0	10^{13}	$[1/\text{s}]$	
[36]	R	0.65		
[36]	r_{implant}	4	$[\text{nm}]$	
	σ_{implant}	2	$[\text{nm}]$	

379 zone II and III respectively. Since TMAP7 uses a static trap concentration,
 380 here we also take the plasma induced trap profile in zone I as an initial con-
 381 dition. The formation of plasma induced defects is postulated to be due to
 382 a solute D saturated region stressing the near-surface zone I [29]. As de-
 383 tailed in [37], equation 1 estimates the diffusion limited D solute maximum
 384 concentration during D implantation. Using the parameters from Table 1
 385 and sample temperature (T) during plasma exposure gives a D saturation
 386 level that approaches 2×10^{-4} at. %. TMAP simulations show that within
 387 1 % of total exposure time (< 1 min), the solute concentration has reached
 388 this saturation value. Compared to the total plasma exposure time of over
 389 an hour, the time required for plasma to induce these traps through satura-
 390 tion of zone I is relatively short and simply approximated as an initial trap
 391 concentration.

$$C_{s,max} \approx \frac{(1 - R) \cdot \Gamma_{\text{incident}} \cdot r_{\text{implant}}}{n_W \cdot D_s(T)} \quad (1)$$

Equation 2 defines the total initial trap concentration ($C^o(x)$) as a sum-
 mation over trap type and spatial zone. Each trap type (k) is identified by a
 distinct detrapping energy (E_k). Note that the traps are ordered according
 to increasing detrapping energy. Each spatial zone ($j = \text{I, II, or III}$) has an
 associated profile function ($f_k^j(x)$), that is chosen according to the inferred
 trap distributions found from experimental data and shown in Fig. 4 and 5.
 All the profile functions are normalized to a peak value of unity. The profile
 function is multiplied by the peak concentration (C_k^j) for each trap and zone.
 For $j = \text{I}$, the exponential fit detailed in Fig. 5 defines the profile function.
 For $j = \text{III}$, the profile function is simply a constant. We also differentiate
 the particular trap profile in zone II for low and high energy traps as seen
 in Fig. 4 and 5. For $j = \text{II}$, the lower detrapping energies use the empirical
 fit shown in Fig. 5 for zone II, while the higher detrapping energies use the
 SRIM profile. As a result of constraining the profile functions by experiment,
 the peak concentration (C_k^j) for each trap (k) in each zone (j) and the detrap-
 ping energies (E_k) become the free parameters that can be adjusted within
 TMAP7 in order to fit the experimental NRA and TDS data. Note that the
 sample preparation and D implantation phase are assumed identical for all
 samples in this dataset, thus we need only model this part of the experiment
 once for a given set of free parameters.

$$\begin{aligned}
 C^o(x) &= \sum_k C_k^o(x) \\
 &= \sum_k [C_k^I f_k^I(x) + C_k^{II} f_k^{II}(x) + C_k^{III} f_k^{III}(x)]
 \end{aligned} \tag{2}$$

412 5.1. Annealing Defects

413 While the assumption of a static trap concentration is likely valid for a
414 relatively fast temperature ramp (e.g. 0.5 K/s), the peak-and-hold during
415 pTDS may allow for significant trap evolution. Sakurada *et al.* [38] presents
416 D retention data from post damage (6 MeV Fe, 0.1 dpa) annealed W. Noting
417 the similarity of damaging species, energy, and dpa level as well as the clear
418 TDS release peaks, we inferred the reduced trap fraction (δ_k) with respect
419 to each TDS release peak. Table 2 summarizes the reduction values at sev-
420 eral anneal temperatures (T_{anneal}) and a linear interpolation determined the
421 reduction value at each pTDS temperature. In this simplified model, traps
422 are removed (e.g. Frenkel pair recombination), while defect agglomeration is
423 neglected. Once again, since TMAP7 uses a static trap concentration, the
424 removal of defects may be modeled incrementally. The first 30 minutes of
425 the peak-and-hold duration was broken into 100 equal time increments and
426 at the end of each increment a hundredth of the estimated reduced fraction
427 ($0.01\delta_k$) was removed from the trap population. D was conserved as filled
428 traps were removed by moving the excess D to solute concentration. Includ-
429 ing trap removal provides the best agreement with experimental data and
430 are the parameters presented in Table 2.

431 5.2. Fitting Results

432 The complete cycle of D₂ plasma exposure, pTDS, and final TDS was
433 simulated for each sample and all free parameters were optimized utilizing
434 the technique of simulated annealing [39]. During the simulated annealing,
435 the free parameters were constrained according to the differences in consecu-
436 tive TDS and NRA data previously outlined. The simulation of a particular

Table 2: Summary of the best fit parameters for each trap (k). The peak concentrations (C_k^j) in each zone (j) and the detrapping energies (E_k) modeled using the PTTP scheme. Reduced trap fraction ($\delta_k(T_{anneal}) = 1 - C_k(T_{anneal})/C_k(300)$) for each annealing temperature in Kelvin estimated from [38].

k	C_k^I	C_k^{II}	$f_k^{II}(x)$	C_k^{III}	E_k	$\delta_k(300)$	$\delta_k(573)$	$\delta_k(873)$
1	0.80	0.26	Empirical	0.0001	1.01	0	1	36
2	1.18	0.28	Empirical	0.0022	1.19	0	44	63
3	0.45	0.43	Empirical	0.0020	1.39	0	32	51
4	0.34	0.15	SRIM	0.0019	1.57	0	44	61
5	0.00	0.48	SRIM	0.0008	1.76	0	8	50
6	0.00	0.23	SRIM	0.0000	1.93	0	0	2
	[at.%]	[at.%]	Profile	[at.%]	[eV]	[%]	[%]	[%]

437 set of trap parameters results in unique NRA and TDS profiles. Both the
 438 experimental and simulation data were interpolated to a finely spaced grid to
 439 directly compare the “goodness of fit.” The Normalized Root Mean Square
 440 Error (NRMSE) as well as the Normalized Mean Absolute Error (NMAE), de-
 441 fined by the absolute difference between experiment and simulation, were the
 442 metrics used to determine the optimal fit. In addition, the resulting NRMSE
 443 and NMAE were weighted with respect to their total D retention and added
 444 together to determine a single fit metric. For instance, the “No pTDS” sam-
 445 ple had the highest D retention and had the largest weight while the highest
 446 temperature pTDS at 762 K contributed the least weight when determining
 447 the best fit parameters.

448 The number of traps used to simulate the experiment was varied from 5
 449 to 9. As outlined in the section on TDS subtraction, the best fit was found
 450 with 6 traps with detrapping energies near 1.0, 1.2, 1.4, 1.6, 1.8, and 1.9 eV.
 451 Using 7 traps, nearly the same energies were found and one additional energy
 452 of 2.4 eV produced nearly the same fit metric. The highest pTDS sample at
 453 762 K may either be due to a partially released 1.9 eV trap or a filled 2.4 eV
 454 trap. The experimental TDS release temperature appears significantly higher
 455 than a 1.9 eV trap. By 762 K, an appreciable amount of vacancy agglomer-
 456 ation may have occurred during the peak-and-hold that is not modeled but
 457 may account for the higher temperature release. We also note that the results
 458 shown are based on the PTTP scheme that assumes a minimal separation in
 459 detrapping energies. For instance, a difference below 0.1 eV for consecutive
 460 detrapping energies leads to a significant error as outlined in [28]. Table 2
 461 provides a summary of the resulting trap concentrations and energies found
 462 to give the best fit to the NRA and pTDS data with the least number of
 463 traps. The total trap concentration, $C^o(x)$, is shown in Fig. 7 (solid black)
 464 together with the k^{th} trap concentration profiles, $C_k^o(x)$, given as the dot-
 465 dashed lines. The measured NRA profile from the “No pTDS” sample is also
 466 shown and has a shape that overlays with the $C^o(x)$ total trap concentration
 467 profile.

468 The simulated NRA profiles and final TDS release histories (dashed lines)
 469 are compared to the experimental data (solid lines) in Fig. 8 and 9 respec-
 470 tively. The simulated NRA and TDS produced reasonable fits with normal-
 471 ized fit metric values of ~ 0.7 for both. A possible reason for the discrepancy
 472 may be due to using detrapping energies separated by at least 0.1 eV. For

Figure 7: The total trap concentration (black) compared to the “No pTDS” NRA data (blue). The individual trap concentrations for $k = 1-6$ are shown as dot-dashed lines.

instance, what appears as a single peak in Fig. 9 can be made of several nearby detrapping energies. If three detrapping energies made the peak near 620 K, the lowest energy may be completely released, the middle partially, and the highest remained filled for a pTDS at 467 K (gold). As pointed out by Efimov *et al.* [13], several more intermediate pTDS peak-and-hold temperatures would be needed to discern if this was indeed the case.

6. Discussion

The detrapping energies found here are similar to values observed in previous studies as described in the Introduction. Some defects associated with the two lowest energies near 1.0 and 1.2 eV are likely grain boundaries and dislocations as seen in the control sample without heavy ion damage. In ad-

Figure 8: The comparison of the NRA data (solid) and the simulation result (dashed) using the optimized fit parameters, summarized in Table 2. For clarity, only 4 samples are shown.

dition, the spatial segregation of defects observed for the lowest three detrapping energies of 1.0, 1.2, and 1.4 eV are consistent with the multiple fill levels for mono-vacancies. The highest three detrapping energies of 1.6, 1.8, and 1.9 eV are likely related to vacancy clusters. The various overlapping values do not contradict, but demonstrates that nearby detrapping energies are not fully resolved.

Recent work done with x-ray spectroscopy [40] has quantified the number of defects due to dislocation loops. For a single crystalline W sample damaged to 0.2 dpa with Cu ions at 5 MeV, the vacancy-type dislocation loop concentration was near 0.1 at.%. The scattering experiment was not spatially resolved but averaged over the first few microns of the W sur-

Figure 9: The comparison of the TDS data (solid) and the simulation result (dashed) using the optimized fit parameters, summarized in Table 2.

face, and could not resolve vacancy defects with radii below 5 Å. Thus that
 quoted vacancy concentration is for larger vacancy complexes averaged over
 the near-surface region and primarily includes large vacancy complexes. The
 x-ray scattering results indicated that the average size of a vacancy complex
 was (6.76 ± 0.16) Å, which would correspond to a dislocation loop incorpo-
 rating ~ 30 W atoms. Traps 4-6 inferred in our work here have energies that
 are consistent with such larger vacancy complexes and have atomic concen-
 trations of the same order of magnitude as these x-ray scattering results.
 Note that due to multiple occupancy, the concentration of D and traps are
 not likely one-to-one. The x-ray data also yields the size distribution, where
 the largest complexes are nearly two orders of magnitude lower in concentra-
 tion than the smallest (5 Å) observable dislocation loop. Having the largest
 detrapping energy, the possible 7th is likely due to a large vacancy complex
 and has a concentration nearly two order of magnitude lower than traps 4-

509 6. This initial necessarily brief comparison between our inferred results and
510 the x-ray scattering results thus shows a similar order-of-magnitude defect
511 density and similar inferred defect size. Clearly additional work focused on
512 direct measurement of defects, determination of the corresponding trapping
513 energies from computational modeling and D atom capacity is needed in or-
514 der to determine if the observed D retention and release is self-consistent
515 with actual defect structures produced in the W material.

516 The spatial segregation of ion damage-induced defects shown in Fig. 5
517 suggest insights into how to compare D retention from ion beam damage
518 with what might be expected to occur from neutron damage. While the
519 neutron only interacts with the nuclei of lattice W, the electronic stopping
520 loss of heavy ions produces a distinctly unique profile for various defects. The
521 significantly higher Primary Knock-on Atom (PKA) energy for heavy ions
522 will create larger and denser collision cascades as well as overlapping sub-
523 cascades [41]. Molecular dynamic modeling by Sand *et al.* [42] predicts no
524 subcascade break-up below 150 keV. A threshold energy for break-up near
525 150 keV is predicted in [8] by comparing the similarity of D retention in
526 neutron and heavy ion damaged W. Though the maximum heavy ion PKA
527 energy ($\sim$ MeV) significantly exceeds the neutron PKA energy ($\sim$ 300 keV),
528 the threshold energy makes the sub-cascades comparable. Yet for heavy ions,
529 the overlap of sub-cascades will increase and allow for more defect evolution
530 (e.g. cluster formation) to occur as the cascades approach the Bragg peak.
531 Our results show evidence for a significant deviation in the spatial location
532 of high and low detrapping energies. The defects with higher detrapping
533 energies (traps $k = 4-6$) correlate to the SRIM predicted Bragg peak while

534 defects with low detrapping energies (e.g. mono-vacancies and small vacancy
535 clusters) are located between the surface and the Bragg peak location. Noting
536 that the neutron damage profile in PFMs should yield similar mono-vacancy
537 and small vacancy clusters, we are then led to speculate that retention and
538 release from such neutron-induced damage might appear similar to what we
539 observe in the intermediate spatial region of our experiments.

540 Finally we note that SRIM is a kinetic Monte-Carlo code that does not
541 simulate the accumulation or agglomeration of defects [43]. Each simulated
542 energetic ion interacts with a new, undisturbed amorphous target that does
543 not retain the induced damage from previous ions and thus has no memory.
544 The formation of defect structures such as loops or clusters is not accounted
545 for as only displacements are counted when collisions impart enough energy
546 to a lattice atom (i.e. above the displacement threshold). Qualitatively,
547 SRIM predicts that the density of collision cascades increases as the heavy
548 ion projectile loses energy to recoils and the highest density occurs at the
549 peak dpa depth. Closer to the surface, the initially highly energetic heavy
550 ions impart less energy to lattice atoms and are more likely to form smaller
551 collision cascades nearer to the surface. The result may then be a segregation
552 of defects, with more lower-order vacancies produced towards the surface and
553 larger vacancy clusters closer to the peak dpa zone.

554 7. Summary

555 Trapped D in Cu ion damaged W was sequentially depopulated with
556 increasing temperature to determine the spatial profile and detrapping en-
557 ergies. The total D retention measured through pTDS, NRA, and TDS are

558 shown to be in excellent agreement as well as demonstrating the repeatability
559 of sample preparation. Comparing the NRA data from the control sample,
560 without pTDS, and the lowest pTDS temperatures demonstrates that all of
561 the plasma induced defects in the near-surface were depopulated by holding
562 the sample at 597 K. In addition, the majority of retained D is depopulated
563 by a pTDS temperature of 762 K. For pTDS peak-and-hold temperatures
564 between 525 and 762 K, the D profiles measured via NRA are similar to the
565 displacement damage profile predicted by SRIM. The full cycle of D₂ plasma
566 loading, to pTDS, and finally a final TDS cycle was modeled with TMAP7
567 utilizing a Pseudo Trap and Temperature Partition (PTTP) scheme. De-
568 trapping energies near 1.0, 1.2, 1.4, 1.6, 1.8, and 1.9 eV were found to fit the
569 experimental data.

570 **8. Acknowledgments**

571 This work was supported by U.S. Department of Energy under DE-FG02-
572 07ER54912 and DE-SC0001999 as well as the University of California Office
573 of Presidential Research Fund under 12-LR-237801. Part of this work has
574 been carried out within the framework of the EUROfusion Consortium within
575 the work project PFC and has received funding from the Euratom research
576 and training programme 2014-2018 under grant agreement No 633053. The
577 views and opinions expressed herein do not necessarily reflect those of the
578 European Commission.

579 **9. Data Availability**

580 The raw/processed data required to reproduce these findings cannot be
581 shared at this time as the data also forms part of an ongoing study. Data
582 requests and inquiries may be sent to the primary author.

10. References

- [1] V. Philipps, Tungsten as material for plasma-facing components in fusion devices, *Journal of Nuclear Materials* 415 (2011) S2 – S9. Proceedings of the 19th International Conference on Plasma-Surface Interactions in Controlled Fusion.
- [2] A. E521, Standard Practice for Neutron Radiation Damage Simulation by Charged-Particle Irradiation (1996). Reapproved 2009.
- [3] O. V. Ogorodnikova, Fundamental aspects of deuterium retention in tungsten at high flux plasma exposure, *Journal of Applied Physics* 118 (2015) 074902.
- [4] E. A. Hodille, A. Zalonik, S. Markelj, T. Schwarz-Selinger, C. S. Becquart, R. Bisson, C. Grisolia, Simulations of atomic deuterium exposure in self-damaged tungsten, *Nuclear Fusion* 57 (2017) 056002.
- [5] W. Xiao, W. Geng, Role of grain boundary and dislocation loop in h blistering in w: A density functional theory assessment, *Journal of Nuclear Materials* 430 (2012) 132 – 136.
- [6] K. Heinola, T. Ahlgren, K. Nordlund, J. Keinonen, Hydrogen interaction with point defects in tungsten, *Phys. Rev. B* 82 (2010) 094102.
- [7] N. Fernandez, Y. Ferro, D. Kato, Hydrogen diffusion and vacancies formation in tungsten: Density functional theory calculations and statistical models, *Acta Materialia* 94 (2015) 307 – 318.

- [8] O. V. Ogorodnikova, V. Gann, Simulation of neutron-induced damage in tungsten by irradiation with energetic self-ions, *Journal of Nuclear Materials* 460 (2015) 60 – 71.
- [9] V. K. Alimov, B. Tyburska-Pschel, Y. Hatano, J. Roth, K. Isobe, M. Matsuyama, T. Yamanishi, The effect of displacement damage on deuterium retention in iter-grade tungsten exposed to low-energy, high-flux pure and helium-seeded deuterium plasmas, *Journal of Nuclear Materials* 420 (2012) 370 – 373.
- [10] A. Debelle, M. F. Barthe, T. Sauvage, First temperature stage evolution of irradiation-induced defects in tungsten studied by positron annihilation spectroscopy, *Journal of Nuclear Materials* 376 (2008) 216 – 221.
- [11] S. Ryabtsev, Y. Gasparyan, M. Zibrov, A. Shubina, A. Pisarev, Deuterium thermal desorption from vacancy clusters in tungsten, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 382 (2016) 101 – 104. The 21st International workshop on Inelastic Ion Surface Collisions (IISC-21).
- [12] M. H. J. 't Hoen, M. Mayer, A. W. Kleyn, H. Schut, P. A. Z. van Emmichoven, Reduced deuterium retention in self-damaged tungsten exposed to high-flux plasmas at high surface temperatures, *Nuclear Fusion* 53 (2013) 043003.
- [13] V. S. Efimov, Y. M. Gasparyan, A. A. Pisarev, Investigation of a fine structure of deuterium thermal desorption spectra from tungsten, *Jour-*

- nal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques 7 (2013) 472–478.
- [14] F. Ferroni, X. Yi, K. Arakawa, S. P. Fitzgerald, P. D. Edmondson, S. G. Roberts, High temperature annealing of ion irradiated tungsten, *Acta Materialia* 90 (2015) 380 – 393.
 - [15] M. Zhao, Q. Zhou, M. Nakata, A. Togari, F. Sun, Y. Hatano, N. Yoshida, Y. Oya, Deuterium removal efficiency in tungsten as a function of hydrogen ion beam fluence and temperature, in: G. Laukaitis (Ed.), *Recent Advances in Technology Research and Education*, Springer International Publishing, Cham, 2019, pp. 20–27.
 - [16] A. Zalonik, S. Markelj, T. Schwarz-Selinger, K. Schmid, Deuterium atom loading of self-damaged tungsten at different sample temperatures, *Journal of Nuclear Materials* 496 (2017) 1 – 8.
 - [17] M. J. Simmonds, Y. Q. Wang, J. L. Barton, M. J. Baldwin, J. H. Yu, R. P. Doerner, G. R. Tynan, Reduced deuterium retention in simultaneously damaged and annealed tungsten, *Journal of Nuclear Materials* 494 (2017) 67 – 71.
 - [18] T. Schwarz-Selinger, Deuterium retention in mev self-implanted tungsten: Influence of damaging dose rate, *Nuclear Materials and Energy* 12 (2017) 683 – 688. *Proceedings of the 22nd International Conference on Plasma Surface Interactions 2016, 22nd PSI.*
 - [19] J. L. Barton, Y. Q. Wang, T. Dittmar, R. P. Doerner, G. R. Tynan, Deuterium retention in tungsten after heavy ion damage and hydro-

- gen isotope exchange in {PISCES}, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 332 (2014) 275 – 279.
- [20] R. E. Stoller, M. B. Toloczko, G. S. Was, A. G. Certain, S. Dwaraknath, F. A. Garner, On the use of {SRIM} for computing radiation damage exposure, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 310 (2013) 75 – 80.
- [21] G. R. Tynan, A. D. B. III, G. A. Campbell, R. Charatan, A. de Chambrier, G. Gibson, D. J. Hemker, K. Jones, A. Kuthi, C. Lee, T. Shoji, M. Wilcoxson, Characterization of an azimuthally symmetric helicon wave high density plasma source, Journal of Vacuum Science & Technology A 15 (1997) 2885–2892.
- [22] K. J. Taylor, S. Yun, G. R. Tynan, Control of plasma parameters by using noble gas admixtures, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 22 (2004) 2131–2138.
- [23] M. Mayer, E. Gauthier, K. Sugiyama, U. von Toussaint, Quantitative depth profiling of deuterium up to very large depths, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 267 (2009) 506 – 512.
- [24] K. Schmid, U. von Toussaint, Statistically sound evaluation of trace element depth profiles by ion beam analysis, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 281 (2012) 64 – 71.

- [25] J. H. Yu, M. J. Simmonds, M. J. Baldwin, R. P. Doerner, Deuterium desorption from tungsten using laser heating, *Nuclear Materials and Energy* (In Press) (2016).
- [26] O. V. Ogorodnikova, J. Roth, M. Mayer, Deuterium retention in tungsten in dependence of the surface conditions, *Journal of Nuclear Materials* 313-316 (2003) 469 – 477. *Plasma-Surface Interactions in Controlled Fusion Devices* 15.
- [27] R. Bisson, S. Markelj, O. Mourey, F. Ghiorghiu, K. Achkasov, J.-M. Layet, P. Roubin, G. Cartry, C. Grisolia, T. Angot, Dynamic fuel retention in tokamak wall materials: An in situ laboratory study of deuterium release from polycrystalline tungsten at room temperature, *Journal of Nuclear Materials* 467, Part 1 (2015) 432 – 438.
- [28] M. J. Simmonds, J. H. Yu, Y. Q. Wang, M. J. Baldwin, R. P. Doerner, G. R. Tynan, Expanding the capability of reaction-diffusion codes using pseudo traps and temperature partitioning: Applied to hydrogen uptake and release from tungsten, *Journal of Nuclear Materials* 508 (2018) 472 – 480.
- [29] O. V. Ogorodnikova, J. Roth, M. Mayer, Ion-driven deuterium retention in tungsten, *Journal of Applied Physics* 103 (2008) 034902.
- [30] M. Poon, A. A. Haasz, J. W. Davis, Modeling deuterium release during thermal desorption of d⁺-irradiated tungsten, *Journal of Nuclear Materials* 374 (2008) 390 – 402.

- [31] A. Rusinov, Y. Gasparyan, N. Trifonov, A. Pisarev, S. Lindig, M. Sakamoto, Investigation of hydrogen-defect interaction in tungsten by the probe fluence method, *Journal of Nuclear Materials* 415 (2011) S645 – S648. Proceedings of the 19th International Conference on Plasma-Surface Interactions in Controlled Fusion.
- [32] B. Merrill, J. Jones, D. Holland, Tmap/mod 1: Tritium migration analysis program code description and user’s manual, Idaho National Engineering Laboratory EGG-EP-7407, EG and G (1986).
- [33] G. Longhurst, Tmap7 user manual, Idaho National Engineering and Environment Laboratory INEEL/EXT-04-02352(Rev. 2) (2008).
- [34] J. Ambrosek, G. R. Longhurst, Verification and validation of tmap7, Idaho National Engineering and Environment Laboratory INEEL/EXT-04-01657 (Rev. 2) (2008).
- [35] M. A. Pick, K. Sonnenberg, A model for atomic hydrogen-metal interactions application to recycling, recombination and permeation, *Journal of Nuclear Materials* 131 (1985) 208 – 220.
- [36] W. Eckstein, Calculated sputtering, reflection and range values, IPP-Report IPP 9/132 (2002).
- [37] L. Gao, W. Jacob, U. von Toussaint, A. Manhard, M. Balden, K. Schmid, T. Schwarz-Selinger, Deuterium supersaturation in low-energy plasma-loaded tungsten surfaces, *Nuclear Fusion* 57 (2017) 016026.

- [38] S. Sakurada, K. Yuyama, Y. Uemura, H. Fujita, C. Hu, T. Toyama, N. Yoshida, T. Hinoki, S. Kondo, M. Shimada, D. Buchenauer, T. Chikada, Y. Oya, Annealing effects on deuterium retention behavior in damaged tungsten, *Nuclear Materials and Energy* 9 (2016) 141 – 144.
- [39] S. Kirkpatrick, C. D. Gelatt, M. P. Vecchi, Optimization by Simulated Annealing, *Science* 220 (1983) 671–680.
- [40] P. Sun, Y. Wang, M. Frost, C. Schnwlder, A. L. Levitan, M. Mo, Z. Chen, J. B. Hastings, G. R. Tynan, S. H. Glenzer, P. Heimann, Characterization of defect clusters in ion-irradiated tungsten by x-ray diffuse scattering, *Journal of Nuclear Materials* (2018).
- [41] P. Vladimirov, S. Bouffard, Displacement damage and transmutations in metals under neutron and proton irradiation, *Comptes Rendus Physique* 9 (2008) 303 – 322. Materials subjected to fast neutron irradiation.
- [42] A. E. Sand, S. L. Dudarev, K. Nordlund, High-energy collision cascades in tungsten: Dislocation loops structure and clustering scaling laws, *EPL (Europhysics Letters)* 103 (2013) 46003.
- [43] J. Ziegler, J. Biersack, U. Littmark, The stopping and range of ions in matter, Pergamon Press (1985).