

Hydrogen and helium trapping in tungsten under simultaneous irradiations

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Abstract

Hydrogen and helium trapping in polycrystalline tungsten under simultaneous He⁺-H⁺ and He⁺-D⁺ irradiation was measured by thermal desorption spectroscopy. At 300 K: He retention and release are affected very little by the presence of H, closely following He⁺-only irradiations; He is trapped within ~30 nm of the surface. D retention is similar to D⁺-only levels but the presence of He enhances D trapping in the near surface, while limiting D diffusion into the bulk; D is trapped within ~30–35 nm of the surface possibly at interstitial sites surrounding He-vacancy defects. At 700 K: He retention and release are again similar to He⁺-only cases; He is trapped within ~30 nm of the surface while no D is observed.

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1. Introduction

Tungsten is a candidate plasma-facing material for the ITER divertor. One concern with tungsten is its hydrogen transport and trapping properties. Irradiation from the He⁺ ash further complicates the picture as it creates blisters and bubbles in tungsten [1,2]. Such He damage is expected to affect the hydrogen trapping properties in tungsten. Some sequential D⁺ and He⁺ irradiation studies aimed at understanding the interaction between hydrogen

and helium in tungsten are available [3–6]. However, no experimental data are available for D and He trapping in tungsten during simultaneous D⁺ and He⁺ irradiations. Here we present results for D and He trapping in polycrystalline tungsten (PCW) for simultaneous irradiations by combined He⁺-H⁺ and He⁺-D⁺ ions at 300 and 700 K.

2. Experiments

Specimens of 8 × 10 mm² size were cut from the same 25 μm thick foil of PCW obtained from Rembar Corp. The quoted purity was 99.96 wt%, with the main impurities being Mo (<100 ppm), C

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(<30 ppm), and O (<30 ppm). The grain size of this PCW material, based on scanning electron microscopy (SEM) surface analysis, was seen to be about 5–10 μm [7]. All specimens were annealed at 1500 K for 30 min prior to irradiation in a separate facility. A dual-beam ion accelerator was used to implant 500 eV He^+ and D^+ (H^+) ions with fluxes of 10^{18} – 10^{19} $\text{He}^+/\text{m}^2\text{s}$ and $\sim 10^{19}$ $\text{D}^+(\text{H}^+)/\text{m}^2\text{s}$; fluences were 10^{21} – 10^{23} He^+/m^2 and 0.5 – 2×10^{23} $\text{D}^+(\text{H}^+)/\text{m}^2$. A ceramic heater clamped to the back of the specimens was used for 700 K irradiations and the temperature was measured with a chromel–alumel thermocouple. Some specimens were held at 700 K for 1 h following irradiation and then cooled at ~ 100 K/min; they are marked by (τ) in the figures.

He and D retention was measured using thermal desorption spectroscopy (TDS) with a quadrupole mass spectrometer (QMS) in a separate TDS facility. Following irradiation, the specimens were held in air, typically for ~ 7 days, and then they were transferred to the TDS facility. The air exposure does not significantly affect He retention, but the D retention levels in this study are about 50% lower than those obtained from in situ desorption [8] without air exposure. This loss of retained D arises from the combined effects of hydrogen adsorption during air exposure and the time delay before TDS [8], but the relative contribution of these effects is not known.

In order to ensure that our comparisons of single species and simultaneous irradiations are made for similar experimental procedures (including post-irradiation air exposure), in addition to the simultaneous irradiation cases, we have also performed both He^+ -only and D^+ -only irradiations in the present study. (We note that in some previous experiments, e.g. [6,8,11], the TDS chamber – with the specimen in it – was baked at about 380–410 K prior to performing thermal desorption. However, for the present experiments, no such chamber baking was performed.)

During TDS, the specimens were heated linearly (temperature-wise) at 2.1–2.8 K/s to ~ 1500 K and held there for 2 min. Since the small mass difference between He and D_2 (^4He : $m = 4.0026$ amu and D_2 : $m = 4.0282$) could not be distinguished by our QMS, experiments were performed with combinations of He^+ – H^+ and He^+ – D^+ – assuming similar trapping behaviour for H and D in W. He retention and desorption spectra were obtained from He^+ – H^+ irradiations, where the mass-4 QMS signal was entirely He. D retention and desorption spectra

were derived by taking the sum of the following two components: (i) The directly measured HD molecules (mass-3 QMS signal) formed by the released D from the specimen and the H in the desorption chamber; and (ii) the amount of D_2 molecules obtained by taking the difference in mass-4 QMS signals between He^+ – H^+ and He^+ – D^+ irradiations. Typically, HD accounted for 10–20% and D_2 for 80–90% of the total D retention. QMS signals for He and D_2 were calibrated with He and D_2 leak bottles, respectively.

3. Results and discussion

3.1. Simultaneous He^+ – H^+ irradiations at 300 K

The helium release spectra for simultaneous (SIM) He^+ – H^+ irradiations reveal the three primary peaks (near ~ 500 , ~ 1000 , and ~ 1100 – 1200 K) characteristic of He^+ -only irradiations [6]; see Fig. 1. The He release profiles at ~ 500 and ~ 1000 K for SIM irradiations closely follow the He^+ -only profiles. Although a third peak at ~ 1100 – 1200 K has been observed for some He^+ -only irradiations [6], it appears more frequently for the SIM cases, possibly due to the presence of implanted H^+ . (This peak is also present for simultaneous He^+ – D^+ irradiations; see below.) Overall, the presence of H^+ does not appear to have a significant effect on the He release profiles. Furthermore, the total He retained closely follows the He^+ -only values and fluence-dependence trend; compare data (1) and (2) in Fig. 2. This is further evidence of the negligible effect of H^+ on He trapping during simultaneous irradiations.

During sequential irradiations, D and He were observed to de-trap each other from their original trapping configurations in the near surface, resulting in different TDS profiles [6]. The effect of He de-trapping by H^+ during SIM irradiations is very small, since He traps as if implanted alone. Implanted low-energy He rapidly diffuses interstitially until it traps at vacancies, impurities or grain boundaries to form He clusters [9]. The He clusters eject self-interstitial W atoms creating He–vacancy complexes (He_nV_m) that grow into platelets and bubbles, producing secondary defects like interstitial loops [10]. The ~ 1000 K peak is postulated to be He release from such He–vacancy complexes [6]. He release at < 700 K is thought to be from He clusters at grain boundaries and secondary defects like dislocation loops surrounding He_nV_m [6]. In

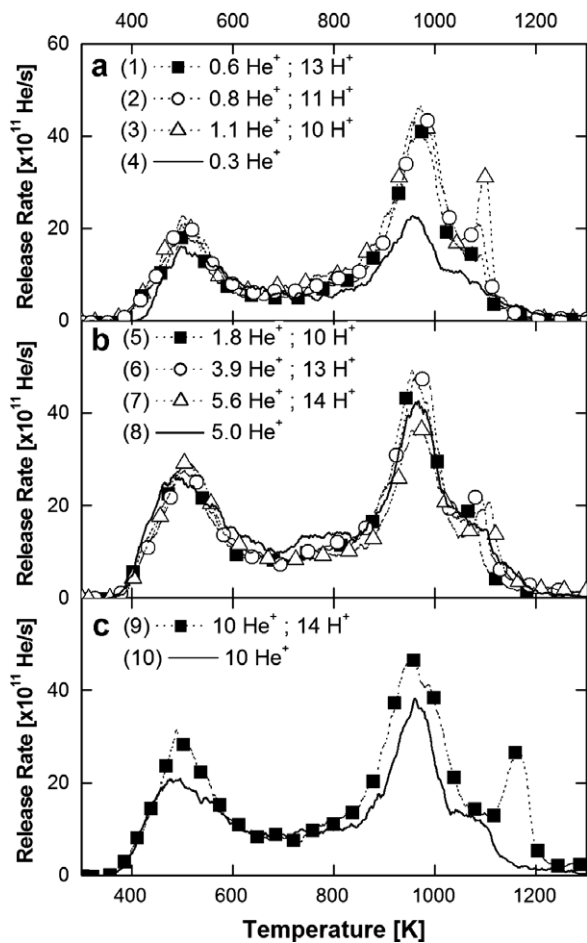


Fig. 1. TDS profiles for different fluence combinations of SIM $\text{He}^+ - \text{H}^+$ irradiations at 300 K. Temperature ramping rates were 2.1–2.8 K/s. He^+ -only irradiations at 300 K are shown for comparison. (Legend: fluences in units of $\times 10^{22}/\text{m}^2$).

the present study, the observed saturation of He retention with increasing He^+ fluence (Fig. 2) might be due to the creation of a dense array of He–vacancy complexes within ~ 30 – 35 nm of the surface that can no longer expand due to the stress fields of adjacent complexes. Expansion to He bubbles is expected to occur for implantation temperatures > 700 K, as was observed by Nishijima et al. [5].

3.2. Simultaneous $\text{He}^+ - \text{D}^+$ irradiations at 300 K

Thermal desorption spectra for SIM $\text{He}^+ - \text{D}^+$ irradiations at 300 K also show three prominent release peaks centered at ~ 500 , ~ 1000 , and ~ 1100 – 1200 K; see Fig. 3. The most revealing difference between the SIM $\text{He}^+ - \text{D}^+$ and SIM $\text{He}^+ - \text{H}^+$ profiles occurs in the temperature range 400–

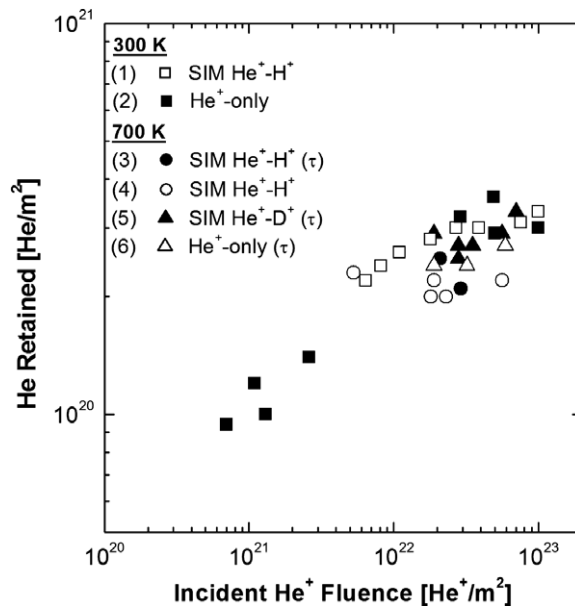


Fig. 2. He retention as a function of incident He^+ fluence. Profiles labeled with (τ) correspond to specimens held at 700 K for 1 h following irradiations at 700 K. The temperature ramping rates varied between 2.0 and 2.8 K/s. The relative uncertainty in the amount of retained He is estimated to be $< 10\%$.

800 K, indicating significant contributions of D_2 to the total mass-4 release in the SIM $\text{He}^+ - \text{D}^+$ cases; e.g., compare profiles (2) and (3) in Fig. 3(a). This is the temperature range where D release is observed for D^+ -only irradiations at 300 K [11]. The D and He contributions to the spectra can be separated by taking the difference between SIM $\text{He}^+ - \text{D}^+$ and SIM $\text{He}^+ - \text{H}^+$ profiles in the range 400–800 K. This difference, together with a D^+ -only profile, is plotted for four $\text{He}^+ - \text{D}^+$ fluence combinations in Fig. 4. (The D^+ -only TDS profile was obtained as part of the current study.) Only one desorption peak, centered at ~ 520 K, is observed; the ~ 650 K peak characteristic of D^+ -only is significantly reduced. This indicates that He has modified the nature of some D trapping sites and examination of the D depth profiles (Fig. 5) further indicates differences in D trapping; see below. The total D retention (based on D_2 and HD contributions) for SIM $\text{He}^+ - \text{D}^+$ was ~ 2 – 3×10^{20} D/ m^2 , which is roughly equal to the amount measured for D^+ -only (2.2×10^{20} D/ m^2) in the current study.

The release peaks at temperatures > 800 K, which are associated with He release, show some differences both in magnitudes and the peak temperatures for SIM $\text{He}^+ - \text{D}^+$ and SIM $\text{He}^+ - \text{H}^+$;

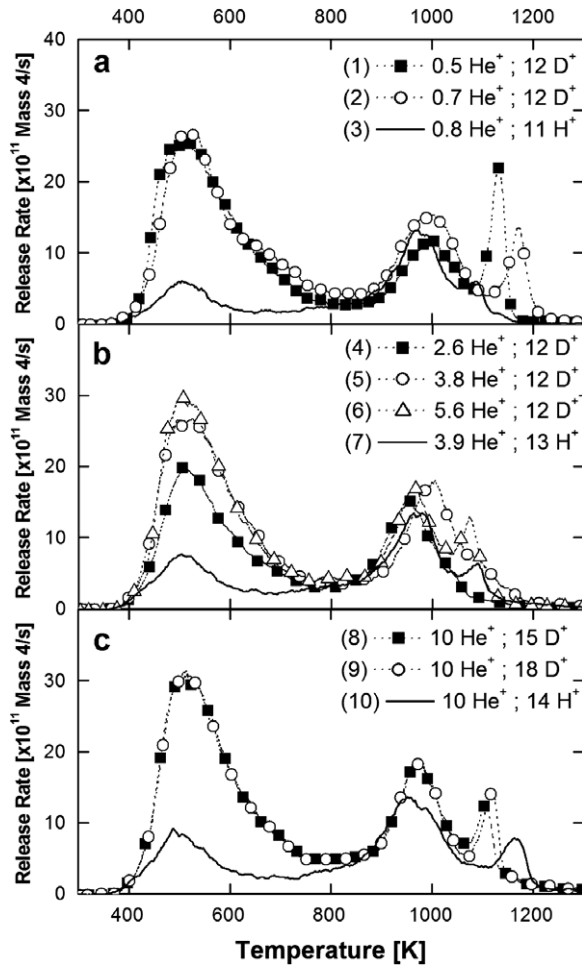


Fig. 3. TDS profiles for different fluence combinations of SIM He⁺-D⁺ irradiations at 300 K. Temperature ramping rates were 2.0–2.7 K/s. SIM He⁺-H⁺ irradiations at 300 K are shown for comparison. (Legend: fluences in units of $\times 10^{22}/\text{m}^2$).

e.g., compare profiles (8) and (10) in Fig. 3(c). The magnitudes of the ~ 1000 K and ~ 1100 – 1200 K peaks are greater for SIM He⁺-D⁺, but it is unclear whether this arises from D to H isotopic effects or due to experimental variations. Contribution from D release is ruled out since this effect was also seen for 700 K irradiations where no D was trapped; see Section 3.3. The shift in temperature of the third peak (range 1100–1200 K) is real and is not caused by experimental jumps in the ramping rate. The origin of this third peak – and the effect D or H may have on it – has not been identified. We note that van Veen [10] has observed He–vacancy dissociation from various different configurations in this regime, albeit at much lower implanted He fluences.

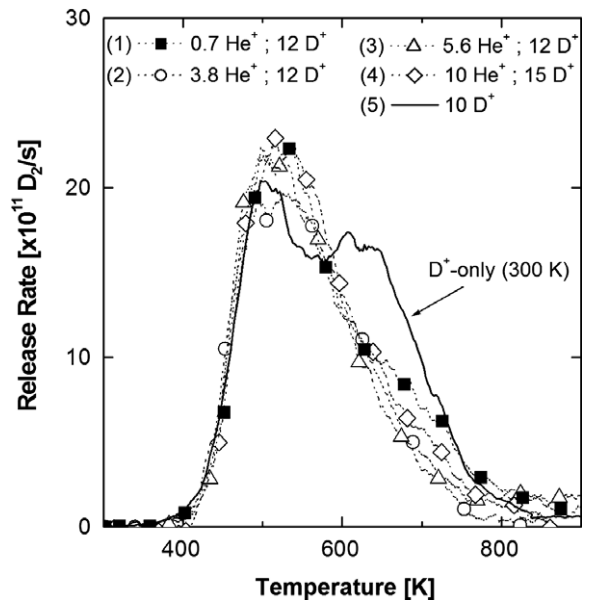


Fig. 4. Derived desorption profiles of D release from SIM He⁺-D⁺ irradiations at 300 K were obtained by subtracting SIM He⁺-H⁺ profiles (Fig. 1) from SIM He⁺-D⁺ profiles (Fig. 3). A TDS profile of a D⁺-only case at 300 K obtained in the present study is shown for comparison. (Legend: fluences in units of $\times 10^{22}/\text{m}^2$).

The trapped D and He depth profiles were obtained using elastic recoil detection (ERD) for SIM He⁺-D⁺ irradiations at 300 and 700 K; see Figs. 5(a) and (b), respectively. D trapping is confined to a depth of ~ 30 – 35 nm, similar to previous results from sequential He⁺-D⁺ irradiations in PCW [6]. Deuterium, when implanted alone into PCW at 300 K, normally diffuses deep into the bulk (>500 nm) [12]. Hence, the shallower D range observed from the present simultaneous and previous sequential He⁺-D⁺ [6] irradiations indicates that the presence of He in tungsten limits D diffusion into the bulk. For D⁺-only irradiations, the D trapped in the bulk accounts for $\sim 30\%$ of the total D retention [6]. Since the amount of D retained for SIM He⁺-D⁺ and D⁺-only irradiations is nearly equal, and D is confined to within ~ 30 – 35 nm of the surface for the SIM case, there must be a corresponding increase of $\sim 30\%$ in D retention at the near surface. Enhanced D trapping due to He has also been observed by Iwakiri et al. [3] from secondary defects surrounding He bubbles. The overlapping depth profiles of trapped D and He, as seen in Fig. 5(a), is consistent with such a trapping mechanism.

The exact mechanism of D trapping in W is still unclear, with microcavities [13] and vacancy sites [14] being proposed. In the near surface, the D

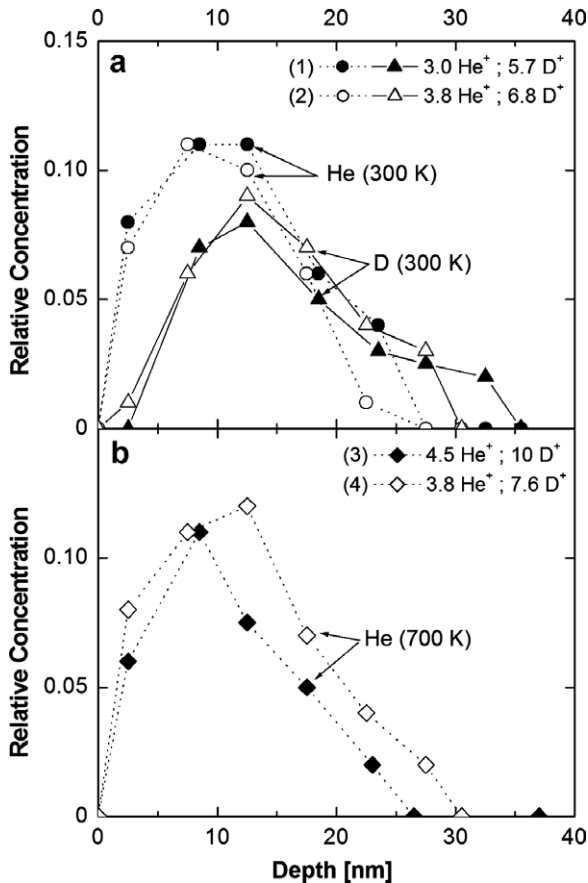


Fig. 5. ERD depth profiles for SIM He^+-D^+ irradiations at (a) 300 and (b) 700 K. No D was observed for the 700 K irradiation. (Legend: fluences in units of $\times 10^{22}/\text{m}^2$).

desorption spectra were found to be similar for both D^+-He^+ and He^+-D^+ sequential irradiations [6], despite the fact that in the first case He–vacancy complexes are formed while in the latter case they are reduced by D^+ . The fact that D trapping does not depend on the existence of He–vacancy complexes suggests that D is not trapped either by chemisorption on the inner surfaces of the He–vacancy complex, or by molecule formation within the He–vacancy complex. Rather, the crystal defects created by the high stress fields of the He–vacancy complexes appear more likely to be the trapping sites for D.

3.3. Simultaneous He^+-H^+ and He^+-D^+ irradiations at 700 K

As with the 300 K irradiations, the desorption profiles for SIM He^+-H^+ and He^+-D^+ irradiations

at 700 K occur in the vicinity of ~ 500 , ~ 1000 , and ~ 1100 – 1200 K; see Fig. 6. He release at < 1100 K for SIM He^+-H^+ closely follows the He^+ -only case; compare profiles (3) and (4) in Fig. 6(a). He retention values also closely follow within experimental error; compare data (3) and (4) with (6) in Fig. 2. A slight increase in He release at ~ 1000 K for SIM He^+-D^+ compared to He^+ -only is observed; compare profiles (5) and (8) in Fig. 6(b). A corresponding increase in He retention is expected but its magnitude is within experimental error; compare data (5) and (6) in Fig. 2. Thus, the He trapping behavior appears to be largely unaffected by D and H presence at 700 K. In the range ~ 1100 – 1200 K a third peak is present in some cases for both He^+-H^+ and He^+-D^+ irradiations. The

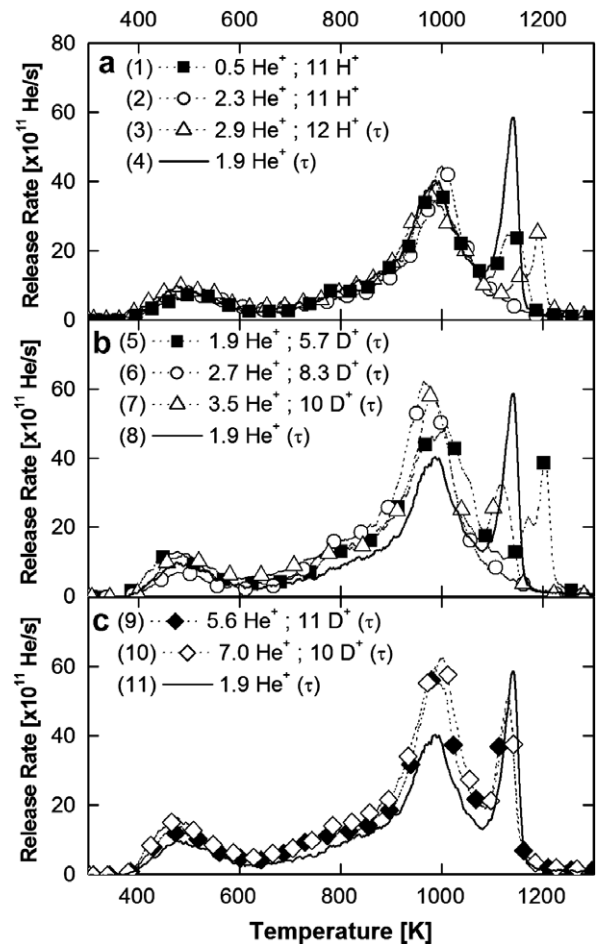


Fig. 6. TDS profiles of the D release for different fluence combinations of SIM He^+-H^+ and He^+-D^+ irradiations at 700 K. Temperature ramping rates were 2.4–2.7 K/s. He^+ -only irradiations at 700 K are shown for comparison. (Legend: fluences in units of $\times 10^{22}/\text{m}^2$).

random appearance of this third peak has also been observed for SIM He⁺–H⁺ (Fig. 1) and SIM He⁺–D⁺ (Fig. 3) irradiations at 300 K and He⁺-only irradiations at 700 K [6]. As noted previously in Section 3.2, the origin of this peak and the cause of the observed temperature shifts have not been identified.

The ERD depth profiles for SIM He⁺–D⁺ irradiations at 700 K (see Fig. 5(b)) show that He trapping is confined to ~30 nm of the surface and there is no D trapping. Therefore, the mass-4 release for the SIM He⁺–D⁺ irradiations in Fig. 6(b) and (c) is entirely attributed to He release. Interestingly, He release at 500 K is observed in both the SIM and He⁺-only [6] cases despite the fact that irradiations were performed at 700 K. It appears that He⁺ irradiation at elevated temperatures involves some mechanism whereby He atoms in higher-energy traps are transferred to low-energy traps – possibly when the specimen cools.

4. Conclusions

There is no observable effect of the presence of H or D on the trapping of He in W during simultaneous He⁺–D⁺(H⁺) irradiations at 300 and 700 K; ERD shows He trapping being confined to ~30 nm of the surface. The He retention levels and release spectra closely follow He⁺-only irradiations. It is postulated that the incident He⁺ forms He–vacancy complexes that produce secondary defects surrounding them.

The D release spectrum for the simultaneous He⁺–D⁺ irradiations at 300 K differs from the D⁺-only case by the reduction of the peak at ~650 K; the primary peak at 500 K was similar in both cases. Furthermore, D diffusion was observed to be limited by the presence of He. The total D retention was largely independent of the incident He⁺ fluence and was equal to the retained amount for the D⁺-

only case. However, with D being trapped within ~30–35 nm of the surface for SIM He⁺–D⁺ irradiations, a 30% enhancement is attributed to D retention in the near surface – possibly trapped in secondary defects produced by He–vacancy complexes. No D was observed at 700 K.

Acknowledgements

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