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Journal of Nuclear Materials 266–269 (1999) 520–525

journal of nuclear materials

The effect of ion damage on deuterium trapping in tungsten

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Abstract

A systematic study investigating the effect of ion-induced damage, due to prior ion implantation, on deuterium retention in tungsten has been performed. Implantations with 1.5 keV D_3^+ ions (500 eV/D^+) to 10^{23} D/m^2 at 500 K show a factor of 3–4 increase in retention for specimens previously exposed to a fluence of 10^{24} D/m^2 and a factor of 6–7 increase for specimens previously exposed to a fluence of 3×10^{24} D/m^2 over specimens exposed only to an incident fluence of 10^{23} D/m^2. However, implantations with 1.5 keV D_3^+ (500 eV/D^+) ions to 10^{23} D/m^2 at 500 K on specimens previously exposed to a fluence of 10^{25} D/m^2 show no increase in retention. Implantations with 3 keV D_3^+ ions (1 keV/D^+) at the above conditions give retention results which do not depend on prior implantation treatments; only a slight increase in retention values with cumulative fluence is observed. Possible mechanisms are suggested to explain the observed effects. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Deuterium inventory; Ion implantation; Hydrogen retention; Hydrogen trapping; Tungsten

1. Introduction

The low divertor plasma temperatures currently envisioned for the next generation of fusion reactors, such as ITER, mean that escaping fuel and light impurity ions will have energies below the threshold for physical sputtering of heavy metals like tungsten. Thus, there has been renewed interest in determining some of the fusion-relevant properties of these materials. Of special interest for ITER are the hydrogen transport and trapping properties, as they may have a significant impact on tritium inventory. In a previous paper [1], inconsistencies arose in the retention values at elevated temperatures. Specifically, we found that implantations on the same specimen at the same temperature and flux to the same fluence gave retention values with up to a factor of 5 difference. The only difference between these data points was the implantation history of the specimen prior to implantation. The lowest retention value was always associated with the first implantation on a virgin specimen, with retention values generally increasing with higher cumulative fluence. It was suggested [1] that the increases in retention may be due to ion-induced damage which is not removed during thermal desorption. This would lead to a greater number of trapping sites for the subsequent implantations resulting in greater deuterium retention.

The purpose of the present experiments is to perform a controlled set of implantations with intermediate desorptions to establish the implantation history of the specimen, thus performing a systematic investigation on the effect of cumulative ion damage at elevated temperatures. In the previous investigation on deuterium retention in tungsten [1], we were unable to precisely align the specimens to implant the same spot each time, and in addition, the specimens were implanted to random fluences at random temperatures. In the present set of experiments, alignment of beam spots is possible and different specimens are used to trace the effect of different incident fluences and energies.

2. Experiment

2.1. Tungsten specimens

All the results have been obtained for a polycrystalline W foil, 25 μm thick and 99.96 wt% pure (Rembar

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PII: S0022-3115(98)00586-8

Corp.). A total of eight specimens, ~8 × 10 mm^2, were cut from the same sheet of foil. In fact, these specimens were cut from the same W foil sheet as those used in the previous investigation [1]. In all cases, the specimens were heated to >1473 K for 1 h prior to first implantation.

2.2. D implantation

All implantations were performed in an ultrahigh vacuum accelerator facility using D_3^+ ions at normal incidence to the test specimen. The test specimen was set up in an unbaked vacuum chamber, where the background pressure was typically 10^{-6} Pa with the D_3^+ beam off, and ~10^{-5} Pa (mainly D_2) during implantation. In order to reduce the spatial beam flux variations, only the central part of the beam was allowed to impact on the specimen. This was achieved by clamping a W foil mask, with a 1.4 mm diameter aperture, in front of the specimens. A 25 μm thick strip of mica, with a 2 mm diameter aperture was inserted between the specimen and the mask to allow the implanted ion current to be measured directly. Another set of mica strips were fixed around the specimen to provide an edge for specimen alignment, thus ensuring that the specimens are implanted on exactly the same spot each time. A ceramic heater clamped behind the specimen was capable of heating it to >700 K. A chromel–alumel thermocouple positioned between the specimen and the mica insulator was used to measure the specimen temperature.

Implantations were performed for ion energies of 3 keV D_3^+ (1 keV/D^+) and 1.5 keV D_3^+ (500 eV/D^+) with associated fluxes of ~2×10^{20} D^+/m^2s and ~1×10^{20} D^+/m^2s, respectively. During implantation, the specimen was biased at +40 V for the 3 keV D_3^+ case to suppress secondary electrons. The large flux densities during implantations with 1.5 keV D_3^+ ions were achieved by utilizing a 2.5 keV D_3^+ beam with the specimen biased at +1000 V to decelerate the beam. To investigate the effect of previous implantations on D retention, different damage conditions were created using implantation fluences of 10^{23} D/m^2, 9×10^{23} D/m^2, 3×10^{24} D/m^2, 10^{25} D/m^2 and 3×10^{25} D/m^2 on different specimens. Following the implantation to create damage, the specimens were then implanted to a fluence of 10^{23} D/m^2 which served as a "probe" fluence for comparison. Thermal desorption of the specimen followed each *damage* and *probe* implantation. Thus, one complete cycle consisted of (i) an implantation to a given *damage fluence*, (ii) a *thermal desorption*, (iii) an implantation to the *probe* fluence (10^{23} D/m^2), and, (iv) another *thermal desorption*. To trace the effect of cumulative fluence on D retention, the same cycle was applied a number of times to the same specimen. All implantations were performed at 500 K. This temperature was chosen since it was at 500 K that the largest inconsistencies were observed in our previous experiments [1].

2.3. Thermal desorption spectroscopy (TDS)

To ensure that the mask did not interfere with the desorption phase of the experiments, TDS was performed in a separate vacuum system, with delays of 16–72 h between implantation and desorption. Thus, *only trapped D concentrations* (*no solute concentration*) were measured [2]. The vacuum system used for TDS was not baked, and had base pressures ~10^{-6} Pa, which was dominated by D_2 from the calibration leak bottle. During TDS, the D-implanted specimens were heated by placing them in a W foil cradle. The cradle was heated resistively to give specimen temperatures reaching 2100 K but held for only a couple seconds. The temperature of the specimen was measured directly by an optical pyrometer. Temperature ramping rates during thermal desorption were ~10 K/s. The amount of D retained in the specimens was determined by integrating the quadrupole mass spectrometer (QMS) signals for D_2 and HD during thermal desorption; during TDS, negligible amount of water was observed [1]. The QMS was calibrated in situ using H_2 and D_2 calibrated leak bottles. The sensitivity to HD was assumed to be the average of the H_2 and D_2 sensitivities.

3. Results

3.1. Using 1 keV/D^+ (3 keV D_3^+ ions)

Three specimens were used to study the effect of 3 keV D_3^+ (1 keV/D^+) ion damage. Each specimen was subjected to a different damage history by varying the incident fluence. In order to compare the effects of the different damage conditions, a subsequent implantation fluence of 10^{23} D/m^2 was used as the probe case. The reference specimen, W2, was exposed to a series of runs, each with the 10^{23} D/m^2 probe fluence. The retained D for these runs was found to be ~5.5×10^{20} D/m^2 ± 20%. The specimen W1 was subjected to a damage creation fluence of 9×10^{23} D/m^2, and thermal desorption, prior to implantation at the probe fluence of 10^{23} D/m^2. Thus, at the end of each complete cycle (damage-fluence and probe-fluence implantations), W1 has seen a cumulative incident fluence of 10^{24} D/m^2. Specimen W3 was damaged with a fluence of 10^{25} D/m^2 prior to implantation at the 10^{23} D/m^2 probe fluence.

By comparing the retention values obtained from thermal desorption of the probe-fluence implantation, the effect of implantation history on deuterium trapping can be seen. The effect of cumulative fluence on deuterium trapping is seen on the retention vs. cumulative fluence plot in Fig. 1. The retention values from the W1 damage-fluence implantations of 9×10^{23} D/m^2 do increase with cumulative fluence, but the values appear to level off after 8 cycles (8×10^{24} D/m^2 cumulative),

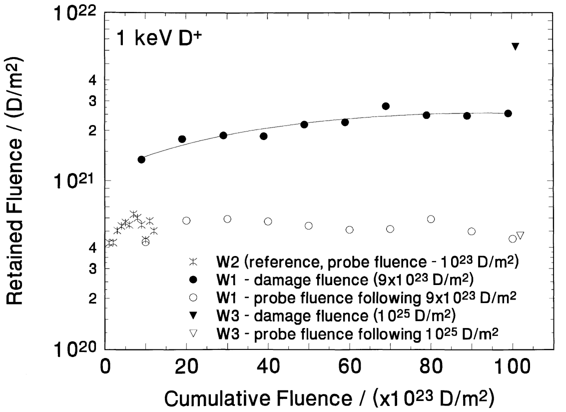


Fig. 1. Retained vs. cumulative fluence for 1 keV/D$^+$ implantations at 500 K. Data are shown for specimens W2 (10^{23} D/m^2 probe fluence only), W1 (9×10^{23} D/m^2 damage fluence and probe fluence), and W3 (10^{25} D/m^2 damage fluence and probe fluence). The 'open' symbols correspond to 'probe-fluence' implantations subsequent to 'damage-fluence' implantations represented by filled symbols of the same shape.

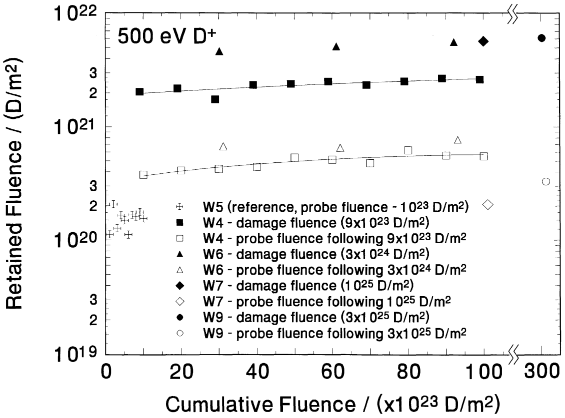


Fig. 2. Retained vs. cumulative fluence for 500 eV/D$^+$ implantations at 500 K. Data are shown for specimens W5 (10^{23} D/m^2 probe fluence only), W4 (9×10^{23} D/m^2 damage fluence and probe fluence), W6 (3×10^{24} D/m^2 damage fluence and probe fluence), W7 (10^{25} D/m^2 damage fluence and probe fluence), and W9 (3×10^{25} D/m^2 damage fluence and probe fluence). The 'open' symbols correspond to 'probe-fluence' implantations subsequent to 'damage-fluence' implantations represented by filled symbols of the same shape.

approximately a factor of 2 above the virgin damage implantation value.

Also, we found that the amount of D retained in W1 after implantation at the probe fluence of 10^{23} D/m^2 is essentially the same regardless of implantation history. The difference in the amount of D retained from probe-fluence implantations is less than a factor of 1.5 between the highest and lowest retention values; the latter corresponding to the initial probe-fluence implantation. These levels are also similar to the probe-fluence implantations with the W2 reference specimen. Based on these results, we conclude that above 10^{23} D/m^2, previous ion-induced damage at 500 K does not significantly affect D retention at *subsequent implantations* with 3 keV D_3^+ ions. This is further evidenced by the probe-fluence implantation subsequent to a damage-fluence run at 10^{25} D/m^2 with specimen W3; see Fig. 1. These observations appear to contradict our previous results [1] which gave increasing retention values as a function of cumulative fluence, during implantations with 3 keV D_3^+ ions at 500 K to a fluence of 10^{23} D/m^2; we attempt to provide an explanation in Section 4.2.

3.2. Using 500 eV/D$^+$ (1.5 keV D_3^+ ions)

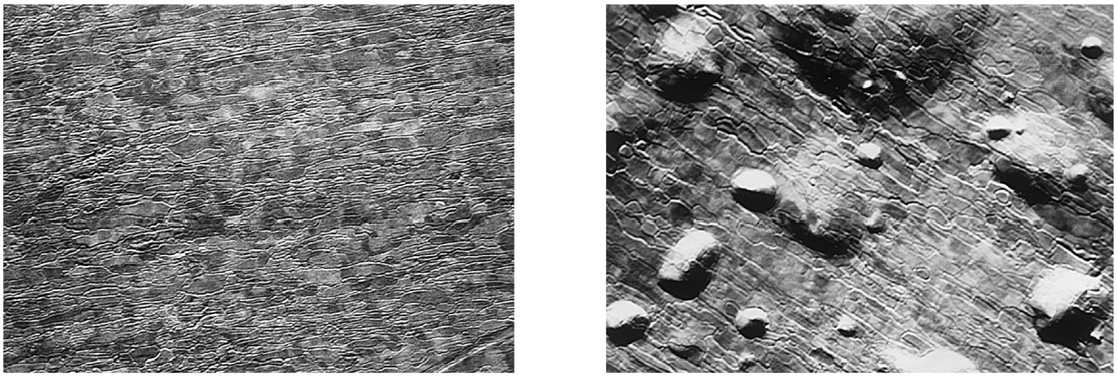
The *damage* and *probe* fluences used for the 500 eV/D$^+$ ion implantations were identical to those used for the 1 keV/D$^+$ case, with the addition of 3×10^{24} D/m^2 and 3×10^{25} D/m^2 damage-fluence runs. The results from these specimens are shown in Fig. 2. Retention values for a particular set of *damage-fluence* runs are seen to increase as a function of cumulative fluence, but the dependence appears to be weak. (A similar trend was seen for the 1 keV/D$^+$ case in Section 3.1) We note that the retention values corresponding to the 3×10^{24} D/m^2 damage-fluence runs (W6) are about twice the values obtained for the 9×10^{23} D/m^2 runs (W4), but going from 3×10^{24} D/m^2 (W6) to 10^{25} D/m^2 (W7) to 3×10^{25} D/m^2 (W9) damage fluences, no further increase is seen in the D retention levels. This indicates that for 500 eV implantation at 500 K, the amount of D trapped in the 25 μm thick foil saturates for incident fluences $>3 \times 10^{24}$ D/m^2.

Comparing the amount of D retained for the *probe-fluence* (10^{23} D/m^2) implantation following the above *damage-fluence* runs, one sees significantly different results for different specimens corresponding to different damage conditions. In particular, the amount retained from the probe-fluence implantation increases on specimens previously exposed to higher damage fluences; the largest increase is about a factor of 5 observed for W6, in comparison with the reference case. The retention in the reference specimen (W5) was about 1.5×10^{20} D/m^2 ± 20%. An exception to this trend is seen in specimens W7 and W9 which have been implanted at the highest damage fluences (W7: 10^{25} D/m^2 and W9: 3×10^{25} D/m^2) prior to implantation at the probe fluence. The amount of D retained from the probe-fluence implantation on W7 is at the same level as the reference case, while the probe fluence on W9 gives a retention value which is about double the reference case. These two results are similar in nature to the 1 keV/D$^+$ results which yielded similar retention values from the probe implantation regardless of the previous damage implantations.

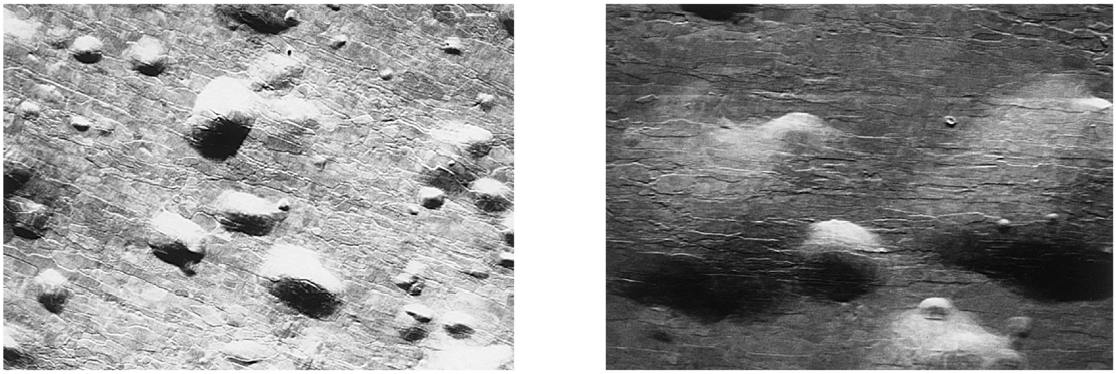
4. Discussion

4.1. Behaviour of 500 eV/D$^+$ ion damage

When implanting 500 eV/D$^+$ ions into W at 500 K, one observes an increase in D retention on specimens implanted to the same incident fluence (10^{23} D/m^2), but which have previously been damaged at the higher fluences of 9×10^{23} and 3×10^{24} D/m^2. We suggest two possible explanations for the increase. One possibility is the formation of D_2 bubbles within the tungsten. There is evidence of the formation of hydrogen bubbles during high energy (8 keV H$^+$) irradiation of polycrystalline tungsten [3]. Although no microstructural evolution was observed for irradiation to 10^{22} H/m^2 with H$^+$ ion energies below 2 keV, it was found that at lower ion energies, defect clusters appeared only at higher fluences [3]. In our experiments, the damage cycle fluence of $\sim 10^{24}$ D/m^2 may be sufficient to produce defects even with low energy 500 eV D$^+$ ions. Evidence of blister formation at the surface can be seen in Fig. 3(b)–(d); SEM photographs of the W9 surface (not shown) appear similar to specimen W7 (Fig. 3(d)). At the high fluences, bubbles may form and swell, producing stresses within the material. These stresses may lead to a higher concentration of dislocations or they may produce grain cracking. In effect, the swelling due to D_2 bubble formation is cold working the material. However, the amount of cold working by internal swelling is probably too small to be annealed, so the damage produced during the high-fluence implantations is retained even after thermal desorption. Even though the recrystallization temperature for W is 1273 K [4], annealing the specimen at 2073 K for 30 min did not reduce the retention levels to those seen in the low-fluence specimen. Thus, when the specimen is subsequently implanted at a



(a) W5, 10^{23} D/m^2 — 10 μm (b) W4, 10^{24} D/m^2 — 10 μm



(c) W6, 3×10^{24} D/m^2 — 10 μm (d) W7, 10^{25} D/m^2 — 10 μm

Fig. 3. SEM photographs of 500 eV/D$^+$ implanted specimens: (a) specimen W5 (reference, probe fluence – 10^{23} D/m^2) after a cumulative fluence of 10^{24} D/m^2; (b) specimen W4 (damage fluence – 9×10^{23} D/m^2) after a cumulative fluence of 1.0×10^{25} D/m^2; (c) specimen W6 (damage fluence – 3×10^{24} D/m^2) after a cumulative fluence of 9.3×10^{24} D/m^2; (d) specimen W7 (damage fluence – 10^{25} D/m^2).

lower fluence (in our case, the 10^{23} D/m^2 probe fluence), more D is retained because of the additional traps created from the high-fluence implantation, but the swelling-induced stress produced at the low fluence is not strong enough to create additional damage. Fig. 3(a) shows the beam spot surface of the reference specimen, W5, which was subject to the low-(probe) fluence implantation only; it is indistinguishable from an off-beam surface (not shown in the figure). When the specimen is implanted at the high fluence again, the trapped deuterium is divided among a greater number of traps, due to a higher trap concentration, so slightly more D is retained, however, the stresses produced are much less, leading to a smaller amount of retained damage creation with each high-fluence implantation. Eventually, the number of created traps will reduce the stress levels so that no new damage will be created for the same high-fluence implantation. Thus, for a given incident fluence, there will be a maximum trap concentration, above which no stress-induced damage will occur.

Alternatively, dislocation damage and grain cracking could be a result of the stresses induced by precipitation forming W hydrides. Thus, hydride precipitation may also lead to increased D retention of 500 eV D^+ ions. One could also have a combination of the two effects since bubble formation would most likely occur along the grain boundaries, while precipitation of W hydrides would be intergranular. Also, dislocation of impurities cannot be ruled out.

An exception to this behaviour was seen in specimens W7 and W9 which were implanted to a damage fluence of 10^{25} D/m^2 and 3×10^{25} D/m^2, respectively, prior to implantation at the probe fluence. We expected the retention measurement from the probe-fluence implantation of W7 to be even higher than the probe-fluence implantation for W6 (damage fluence of 3×10^{24} D/m^2), given the above hypothesis. However, the amount retained from the probe-fluence implantation of W7 was only slightly higher than the retention values for the reference specimen, W5. It is possible that the decrease in D retention may be a result of surface modifications which inhibit deuterium retention. From Fig. 3(d) and Fig. 4, we see large blisters on the damaged area. We suspect that small cracks or fissures not visible on the photographs are present on the larger blisters which allow the deuterium to escape the material. Opening of the blister would allow a mechanism for the implanted D to escape the created traps, thus reducing the amount of D retained. It would appear that the amount of damage done by a low-energy, high-fluence implantation reaches a saturation level. Formation of the blister causes plastic deformation of the W metal so that the blisters are still present even after stress relief. Even with a damage-fluence implantation 3 times higher (3×10^{25} D/m^2) on W9, the amount retained from the subsequent probe-fluence implantation is only about twice that seen for the reference case. It is postulated that the heavily damaged surface created by the high-fluence implantation creates a network of open porosity which enhances the release of implanted hydrogen before it can diffuse into the bulk. This hypothesis was proposed by Causey [5] who also observed a similar effect during high flux ($\sim 10^{22}$ D + T/m^2 s) hydrogen exposure of tungsten in the Tritium Plasma Experiment.

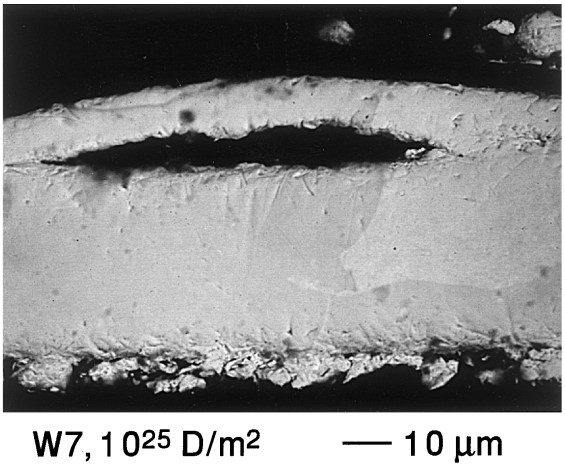


Fig. 4. Cross-sectional SEM photograph of specimen W7 (damage fluence – 10^{25} D/m^2) showing a large blister.

4.2. Behaviour of 1 keV/D^+ ions

One would expect the same swelling/precipitation effect as seen in the 500 eV/D^+ ion case, but for 1 keV/D^+ ions, one does not see a significant effect of implantation history on D retention. It cannot be assumed that bubble formation and precipitation occur only with the 500 eV/D^+ ions, but rather, one must assume an additional mechanism not present with the 500 eV/D^+ ions which dominates the increased D retention due to retained damage creation. The main difference associated with different ion energies is displacement damage. From TRVMC calculations for 1 keV D^+ ions impacting on W, using a dislocation energy of 38 eV [6], one finds that some displacement damage occurs within the first 5 nm, whereas no displacement damage occurs with the 500 eV D^+ ions. It is noted, however, that significant displacement damage is predicted by the TRVMC code [6] for both 1 keV and 500 eV D^+ when light impurities such as carbon and oxygen are present in the W lattice. This is true, even using the higher dislocation energy of 44 eV used by Sakamoto et al. [3]. Because of this additional trap producing mechanism, it is possible that with 1 keV/D^+ ions, an incident fluence of 10^{23} D/m^2 may already be saturating the near-surface trap concentration. Thus, additional traps created as a result of the swelling and/or precipitation induced by the high-fluence (damage) implantation do not add significantly to the amount retained during probe (10^{23} D/m^2) implantations. It is also possible that the displacement damage may modify the surface in some way which inhibits deuterium retention. In experiments using 9 keV He$^+$ ions (9×10^{23} He/m^2) to produce high levels of displacement damage, we found that with subsequent 1 keV/D$^+$ implantations to a fluence of 10^{23} D/m^2 (probe fluence), the retention values are 30% of those for a specimen implanted using 1 keV/D$^+$ only (10^{23} D/m^2).

In our previous paper [1], the effect of implantation history was more noticeable in specimens implanted with 1 keV/D$^+$ ions than with 500 eV/D$^+$ ions. Our present results show the opposite to be true. However, our present results with the 500 eV/D$^+$ ions are consistent with the previous paper in terms of retention values and changes in retention as a result of implantation history. It is difficult to account for the differences in our 1 keV/D$^+$ results because the specimens used in the previous investigation [1] were exposed to a large variety of different implantation temperatures and incident fluences, any one of which may alter subsequent retention amounts. It is possible that displacement damage created at lower or higher temperatures is able to diffuse into the material, leading to an increased volume of trapping sites. Preliminary tests with a 1 keV/D$^+$ damage implantation at room temperature (300 K), followed by a probe-fluence implantation at 500 K, shows that the 300 K damage implantation significantly increases the amount retained in the subsequent probe implantation, supporting this hypothesis.

5. Conclusions

From our experiments with 500 eV/D$^+$ ions, we see increased D retention on specimens which have previously been exposed to high fluences as compared to specimens which have only seen low-incident-fluence implantations. We suggest that this increased retention may be due to swelling-induced stresses and/or precipitation of W hydrides leading to dislocation creation and grain cracking. Evidence of surface blisters due to high fluences is seen. Such effects appear to be dependent on both ion energy and incident fluence. This damage is not removed during TDS so that more trapping sites are present in subsequent implantations. An exception to this trend is the drastically reduced level of D retention at the 10^{23} D/m^2 probe fluence subsequent to the 10^{25} and 3×10^{25} D/m^2 damage-fluence runs. The effect is consistent with blister formation and hydrogen recycling through fissures in the blisters.

Identical experiments using 1 keV/D$^+$ ions do not show any significant change in retention due to prior implantations. For this higher energy, the probe fluence of 10^{23} D/m^2 may be sufficient to saturate trap sites in the near surface, so that higher fluence implantations do not affect the trapping. To explain the difference between the strong dependence on implantation history found in our previous experiments [1] and the lack of such dependence in the present work, it is thought that implantations (damage creation) at lower (or higher) temperatures could lead to the diffusion of trapping sites into the bulk, providing a greater volume for subsequent trapping.

Acknowledgements

This work was supported by the Canadian Fusion Fuels Technology Project and the Natural Sciences and Engineering Research Council of Canada. We wish to thank Dr. W. Eckstein of the Max-Plank-Institut für Plasmaphysik, Garching, for making the TRVMC code available for our D displacement damage calculations.

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