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Deuterium retention in tungsten for fusion use

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Abstract

The retention of deuterium in polycrystalline W foils has been measured as a function of ion fluence and implantation temperature. At temperatures in the range 350–550 K, retention levels were found to be above the 300 K value. This retention enhancement is attributed to an increase in the D diffusion coefficient, which allows a greater diffusion depth. Furthermore, while retention at room temperature saturates as a function of fluence, at 500 K no saturation is observed. D(^{3}He,^{4}He)p nuclear reaction analysis measurements show that at room temperature most of the D is trapped in the near-surface region of the specimen, but significantly beyond the implantation range. At higher temperatures, much lower levels are observed in the near-surface, and diffusion through to the back of thin specimens is observed; the front and back surface D concentrations are similar. While the D retention in a proposed W alloy for ITER applications (W–1%La_2O_3) is similar to that measured in the pure W foils over most of the range of the experiments, two important differences are noted: a trend to saturation of the amount retained is observed at fluences $>10^{24}$ D/m^2 and 500 K, and the D concentration at the back of the W–1%La_2O_3 alloy is about 1% of that at the implanted surface. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The low divertor plasma temperatures currently envisioned for the next generation of fusion reactors, such as ITER, mean that escaping fuel 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], a saturation trend for the retained D was observed with increasing D^+ fluence when 1 keV D^+ was implanted into a 25 μm thick W foil at 300 K. For discussion purposes, it was assumed that the D was trapped in the implantation zone, ~40 nm; however, the diffusion of D in W at room temperature [2] would allow significant motion of D beyond the implantation zone. In fact, diffusion through the 25 μm foil thickness could not be ruled out. For exposure times of $\sim 10^5$ s (corresponding to fluences of $\sim 10^{25}$ D^+/m^2 at fluxes of 10^{20} D^+/m^2s), using Frauenfelder's diffusion coefficients [2], diffusion lengths in W range from ~0.3 mm at 300 K to ~6 mm at 500 K.

In the present experiments, we seek to gain a greater understanding of the trapping characteristics of the W foils, through the use of a greater range of implantation conditions. In addition to TDS, D(^{3}He,^{4}He)p Nuclear Reaction Analysis (NRA) has been utilized to determine the trapping distributions. As the experiments progressed, it became apparent that ion-induced damage by 1 keV D^+ might have affected the retention properties, and thus the incident ion energy was also altered.

In order to reduce both material and machining costs, a W alloy, containing 1% La_2O_3 is being considered for ITER [3]. The D retention properties of this material have also been studied, and the results are compared with pure W.

2. Experiment

2.1. Tungsten specimens

Most of the results have been obtained for a polycrystalline W foil, 25 μm thick and 99.95 wt% pure

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(Rembar Corp.). Twelve specimens, ~8 × 9 mm^2, were cut from the same sheet of foil. In addition, a specimen of 250 μm thick polycrystalline foil (99.95% pure, Johnson Matthey) was used for some measurements. Specimens of the ITER W alloy, W–1%La_2O_3 (Plansee Aktiengesellschaft), were 100 μm thick and ~10 × 8 mm^2 area. In all cases, prior to the first implantation, specimens were heated to >1473 K for 1 h.

2.2. D implantation

The experimental procedure for the present TDS experiments is similar to that followed in our previous retention measurements in metals [1] and doped graphites [4]. All implantations were performed in an ultra-high vacuum accelerator facility using D_3^+ ions at normal incidence to the test specimen. 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 pyrolytic graphite or W mask, with a 2 mm diameter aperture, in front of the specimens. A 25 μm thick strip of mica, with a 3 mm diameter aperture, was inserted between the specimen and the mask to allow the implanted ion current to be measured directly. A ceramic heater clamped behind the specimen was capable of heating it to >700 K. A chromel–alumel thermocouple was used to measure the specimen temperature.

Implantations were performed at three ion energies with the indicated flux densities: 3 keV D_3^+ (1 keV/D^+; ~10^{20} D^+/m^{2}s), 1.5 keV D_3^+ (500 eV/D^+; ~8 × 10^{19} D^+/m^{2}s) and 900 eV D_3^+ (300 eV/D^+; ~1.3 × 10^{19} D^+/m^{2}s). (In referring to energy, particle fluxes and fluences, we use the notation D^+ even though not all of the D in the D_3^+ molecular ion are charged.) During implantations, the specimen was biased at +30 V for the 3 keV D_3^+ and 900 eV D_3^+ cases in order to suppress secondary electrons. In order to maintain large flux densities during implantations with 1.5 keV D_3^+ ions, a 2.5 keV D_3^+ beam was utilized, with the specimen biased to +1000 V to decelerate the beam.

2.3. Thermal desorption spectroscopy (TDS)

To ensure that the mask did not interfere in 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 [5]. During TDS, the D-implanted foils were heated by placing them in a W foil boat, which was resistively heated to >2000 K; specimen temperatures reached 1700–1900 K. The temperature of the specimen could be measured directly by an optical pyrometer. Temperature ramping rates during TDS were ~10 K/s and reasonably uniform for the 25 μm W foils, but varied from ~10 to ~20 K/s for the thicker foils. 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. 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. No significant signals at $m/e = 20$ (D_2O or CD_4) were observed during desorptions (<1% of the $m/e = 4$ signal).

2.4. Nuclear reaction analysis (NRA)

The near-surface D concentrations in the specimens were measured via D(^{3}He,^{4}He)p nuclear reaction analysis with the McMaster University KN van de Graaff accelerator. ^{3}He beams of energy 0.9–1.7 MeV, 0.5 mm in diameter, were incident at 60° from the sample normal. Deuterium profiles on both the front and back surfaces were obtained. The analysis depth in the W foils was ~800 nm, with a resolution of ±25 nm at the surface, degrading to ±100 nm at 800 nm. Uncertainty in the surface location is ±30–40 nm.

3. Results and discussion

3.1. Where is the deuterium at room temperature?

One of the objectives of the current work is to determine where the D is trapped in the specimens. If the D is trapped primarily in the implantation zone, then a reduction in the thickness of the implantation zone, i.e., by reducing the D^+ energy, should reduce the trapped amount. Alternately, if diffusion is fast enough, such that D is trapped through the bulk of the specimens, then increasing the specimen thickness will lead to increased retention. In Fig. 1(a), we compare the results of 1 keV D^+ and 300 eV D^+. Clearly, for fluences >10^{22} D^+/m^2, the reduction in energy, and thus the implantation range, does not lead to a reduction in the amount retained. In fact, the amount retained for 300 eV D^+ (at 2 × 10^{23} D^+/m^2) incident on a spot used for prior 1 keV D^+ implantation actually is about two times higher than the 1 keV D^+ retention. Similarly, implanting a foil 10 times thicker than the first set of specimens (250 μm compared to 25 μm) resulted in somewhat lower retention, see Fig. 1(a).

For 1 keV D^+-implanted specimens of the 25 μm foil at 300 K, NRA depth profiles (Fig. 2(a)) show the peak of the distribution at ~80 nm, well beyond the limit of the implantation range (~40 nm, calculated by TRVMC [6]), and a long tail extending beyond 500 nm. Integration of this near-surface peak gives ~3 × 10^{20} D/m^2, about half of the amount measured by TDS. It must be assumed that about an equal amount has diffused

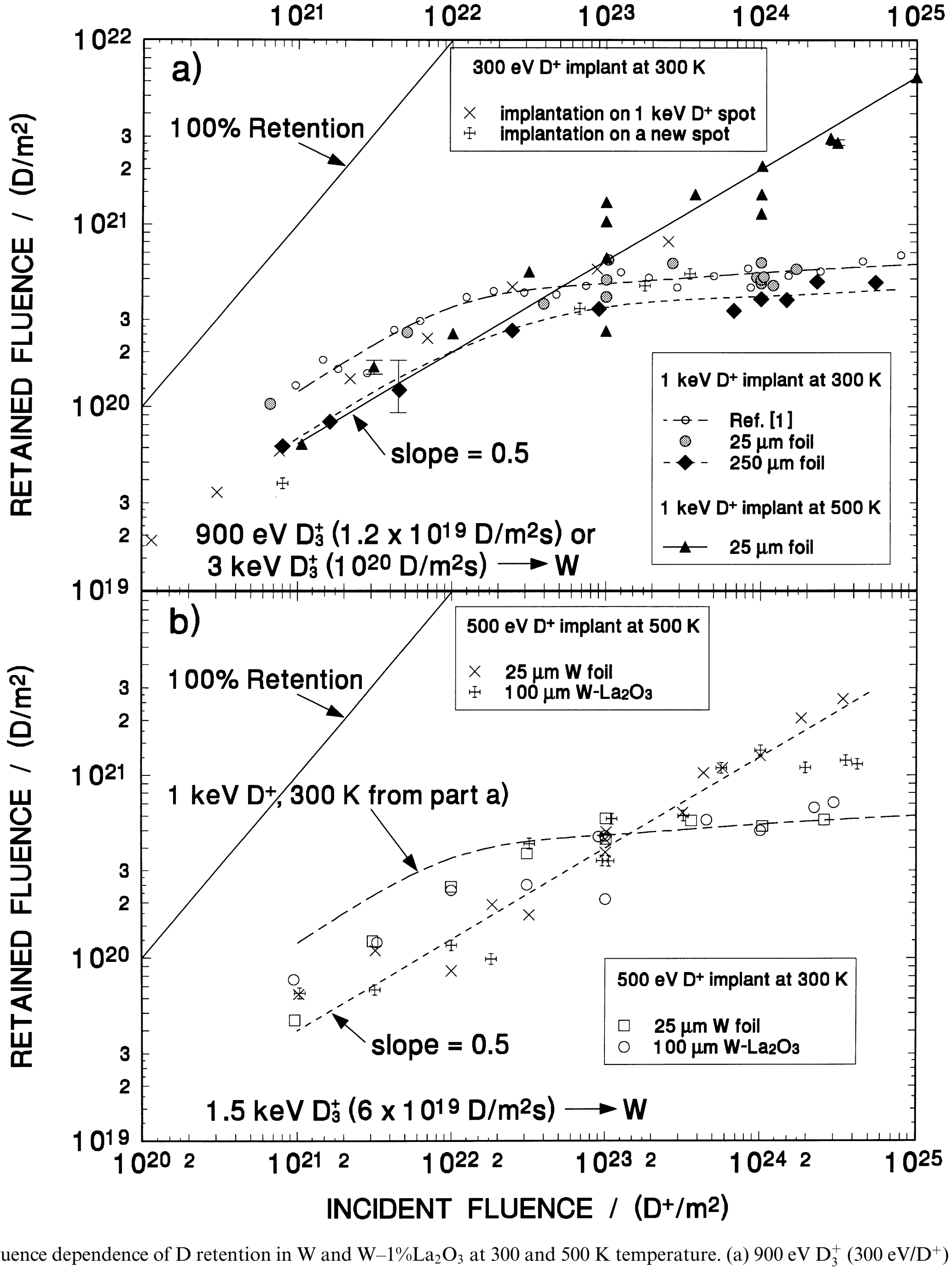

Fig. 1. Fluence dependence of D retention in W and W–1%La$_2$O$_3$ at 300 and 500 K temperature. (a) 900 eV D$_3^+$ (300 eV/D$^+$) and 3 keV D$_3^+$ (1 keV/D$^+$), (b) 1.5 keV D$_3^+$ (500 eV/D$^+$).

beyond 500 nm. This is somewhat consistent with the modelling of Franzen et al. [5], whose calculations show D trapping within a depth which could be up to 100 times the implantation range. NRA measurements taken of the back of a similarly implanted foil (1 keV D$^+$, 25 μm, 300 K), however, show no D on the back surface. The absence of a trapped D peak corresponding to the implantation zone is consistent with the results of Sakamoto et al. [7], which indicate that 1 keV D$^+$ ions do not have sufficient energy to create traps in tungsten.

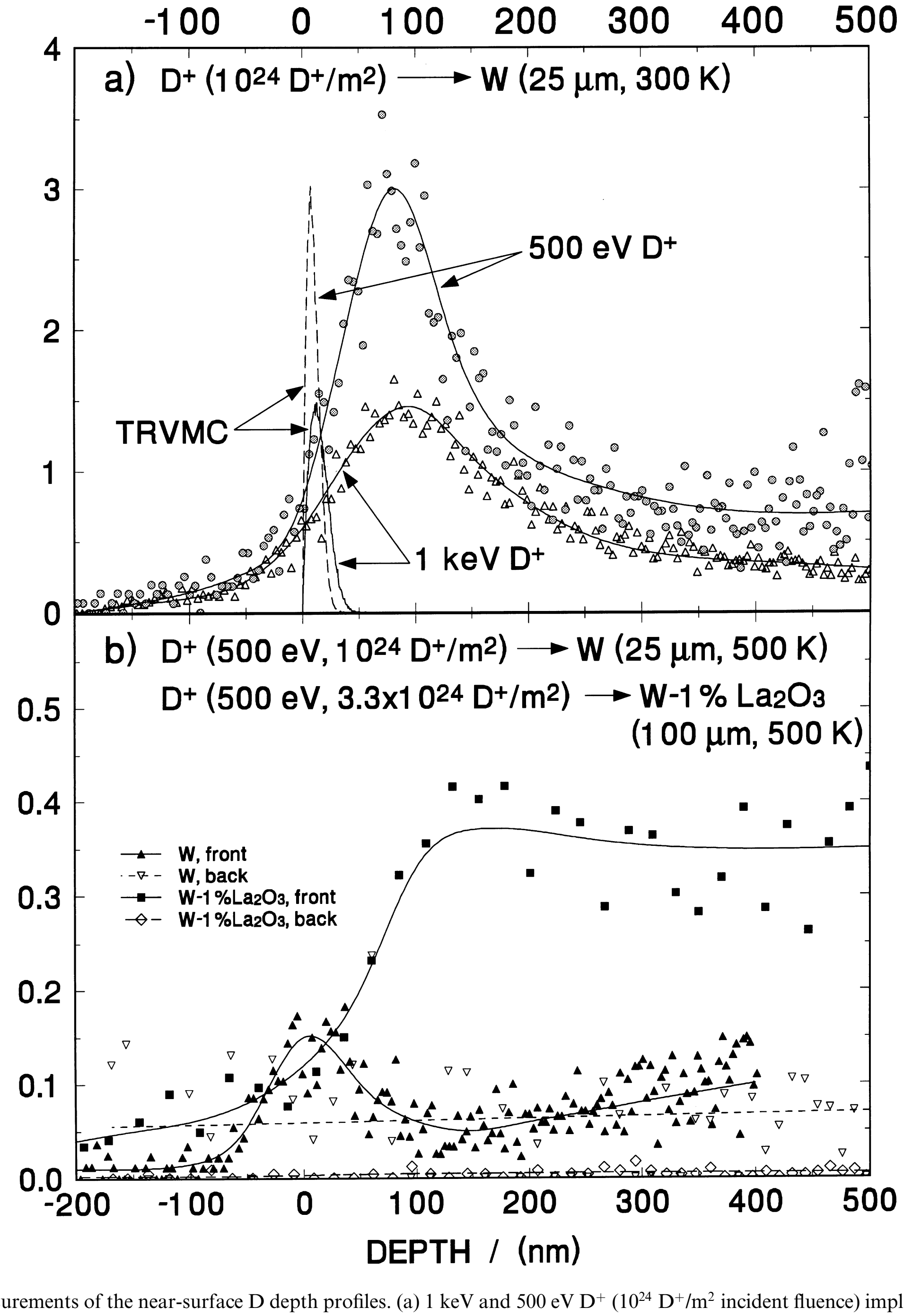

Fig. 2. NRA measurements of the near-surface D depth profiles. (a) 1 keV and 500 eV D^+ (10^{24} D^+/m^2 incident fluence) implanted into W at 300 K. Implantation profiles for 1 keV D^+ and 500 eV D^+ as calculated by TRVMC [6] are shown for comparison (normalized to the peak height of the measured profiles). (b) 500 eV D^+ implanted at 500 K into W (10^{24} D^+/m^2) and W–1% La_2O_3 (3.3×10^{24} D^+/m^2). Lines through the data are drawn as a guide to the eye.

It is noted, however, that 300 eV D^+ retention is consistently 1.5–2 times higher on spots previously exposed to 1 keV D^+ than on spots not previously exposed, see Fig. 1(a), implying that 1 keV D^+ ions generate trapping sites leading to enhanced retention during subsequent 300 eV D^+ exposure.

3.2. Where is the deuterium above room temperature?

It is clear from the above 300 K results that diffusion is playing some role in the retention of D in W. At elevated temperatures, diffusion is expected to take on even greater importance. In Fig. 3(a), we show the amount of 1 keV D^+ retained as a function of temperature, for various implantation conditions. An enhancement of the amount retained (in comparison with the 300 K cases) is found for temperatures up to ~550 K, although a very large scatter is observed in the data.

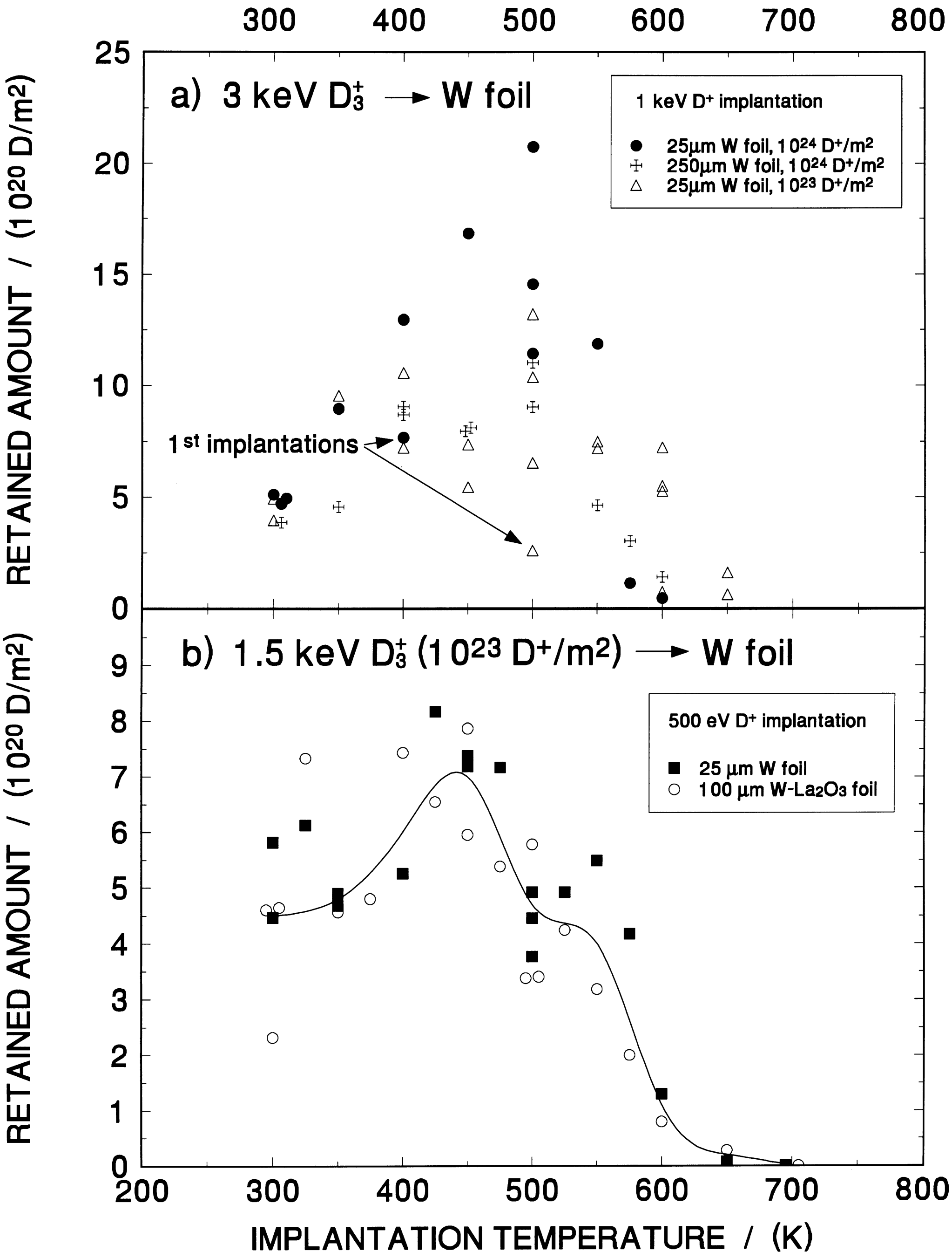

Fig. 3. Temperature dependence of D retention in W and W–1%La_2O_3. (a) 1 keV D^+ at fluences of 10^{23} and 10^{24} D^+/m^2, (b) 500 eV D^+ at a fluence of 10^{23} D^+/m^2.

TDS measurements at 500 K and fluences of 10^{23} D/m^2 on two different specimens reveal a factor of 5 difference in the amount retained (Fig. 3(a)). This may be related to the implantation history of the specimens. The lowest value was recorded on the first measurement on a *new specimen*, while the highest was on a specimen which had seen a cumulative fluence in excess of 10^{25} D^+/m^2, but with multiple intermediate desorptions. Even though it was not possible to line up the beam-exposed region on the specimens with the aperture in the mask, the specimens were generally placed in nearly the same position. This apparent increase in the number of "trapping sites" with cumulative fluence leads to differences in the TDS spectra for the 4 cases (see Fig. 4). Two trap energies are evident on all but the virgin specimen which has only seen a total fluence of 10^{23} D/m^2. The higher trap energy dominates for the highest cumulative fluences. It is difficult to say that one trap is inherent in the material, while the other is due to ion damage as proposed by Franzen et al. [5].

The fluence dependence of 1 keV D^+ trapping in W at 500 K is shown in Fig. 1(a). At low fluences, the amount retained is less than the room temperature case, but at the highest fluences measured, the amount is 10 times larger, and there is no evidence of saturation. Given the scatter in the data, the results are consistent with a diffusion-limited trapping mechanism (slope = 0.5).

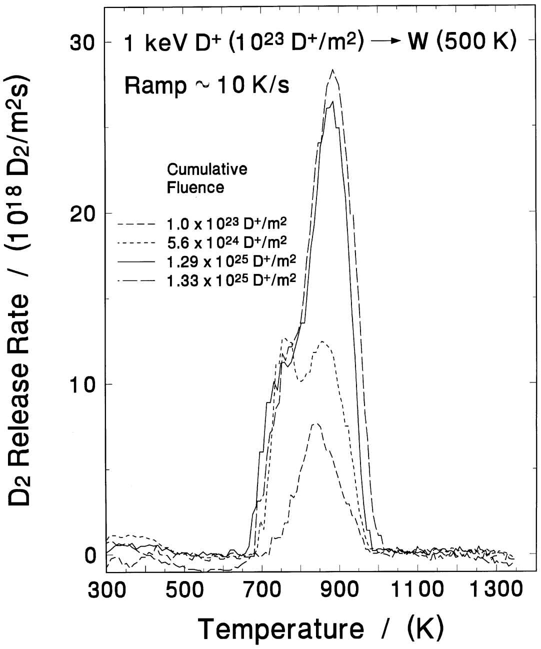

Fig. 4. TDS spectra for 1 keV D^+ (10^{23} D^+/m^2) implantation in W for different fluence histories.

3.3. 500 eV D^+ retention

The above evidence that the possible accumulation of trapping sites (perhaps due to an accumulation of ion damage) might be affecting the amount retained for 1 keV D^+ implantation has led us to perform retention measurements with 500 eV D^+ ions. This energy is well below the energy required for defect creation in pure W [7]. It is noted, however, that there is a small impurity component in the material (~0.05 wt%), and it is possible that defect creation at impurity (e.g. C, O, etc.) sites may take place at much lower ion energies. In Fig. 1(b), results are presented for the fluence dependence of 500 eV D^+ trapping at 300 and 500 K.

For fluences $\lesssim 10^{22}$ D^+/m^2, the amount retained at 300 K is a factor of 1.5–2 lower than for 1 keV D^+. This may be due in part to a higher reflection coefficient, and, because the time for diffusion is small, a shallower implantation zone may also have some effect. At higher fluences, the amount retained at 300 K approaches saturation at the same level observed for 1 keV D^+. The NRA depth profile of 500 eV D^+ in W (Fig. 2(a)) is similar in shape to that of 1 keV D^+, however, the trapped concentration is a factor of two larger. At present, we have no explanation for this difference.

For pure W, the fluence dependence of 500 eV D^+ retention at 500 K (Fig. 1(b)) is also similar to that observed for 1 keV D^+ at 500 K (Fig. 1(a)); with increasing incident fluence the trapped amount continues to rise with *no sign of saturation*. Again, the results appear to correspond to a diffusion-limited process. The NRA profiles of a specimen implanted at 500 K by 500 eV D^+ (10^{24} D^+/m^2) show (see Fig. 2(b)) that a nearly uniform concentration of D exists through the specimen: ~0.1 at.% on both front and back surfaces. Integration of this concentration gives excellent agreement with TDS measurements. The nearly uniform D concentration implies that nearly all of the traps in the bulk have been filled by diffusing D (i.e., via trapping controlled diffusion), and thus one would expect that additional increases in the incident fluence would not contribute significantly to the D retention level. Yet, for a fluence of 3×10^{24} D^+/m^2 (see Fig. 1(b)) no sign of saturation is evident. Perhaps one must go to higher fluences to reach bulk saturation, or there is a source of traps associated with the implantation process.

The temperature dependence of 500 eV D^+ retention is shown in Fig. 3(b), for a fluence of 10^{23} D^+/m^2. While there is some indication of increased retention at ~450 K over the 300 K case, the large increases in retention found for 1 keV D^+ (Fig. 3(a)) are not seen.

3.4. D retention in ITER alloy W–1%La_2O_3

Because of the lower mass of the La and O atoms, damage creation by incident ions could occur at lower ion energies. Thus some differences were expected between the ITER W alloy and the pure W foil. As seen in Figs. 1(b) and 3(b), however, there were no significant differences over most of the parameter range of the experiments. The exception is the observed tendency to saturation at high fluences and 500 K. NRA measurements of ~0.35 at.% on the front surface, and ~0.004 at.% on the back (Fig. 2(b)) indicate a higher near-surface (on the front) trap concentration, and possibly suggest a diffusion-limited permeation of D through the foil. However, the assumption of a triangular D concentration leads to an integrated retained amount an order of magnitude larger than the TDS measurements. Therefore, it appears to be more likely that most of the D is trapped in the front surface region; if we assume that the 0.35 at.% level extends deeper in the bulk, consistency with TDS implies ~6 μm depth.

4. Conclusions

For D^+ implantation of polycrystalline W foils at 300 K, the amount of D trapped in the material approaches saturation at $\sim 6 \times 10^{20}$ D/m^2 for incident fluences $\gtrsim 10^{23}$ D^+/m^2. Such room temperature measurements are very consistent, independent of specimen history or ion energy. For temperatures between 300 and 550 K, higher retention levels are observed, but the levels depend on ion energy, fluence and implantation history. *Fluence-dependence measurements at 500 K, in contrast to the 300 K results, show no sign of saturation*; the amount retained appears to be diffusion limited. For 500 eV D^+ (10^{24} D^+/m^2), 500 K implantation into W, NRA depth profiles on both the front and back surfaces show ~0.1 at.% D, without peaks, indicating a uniform D concentration throughout.

While the D retention in a proposed W alloy for ITER applications (W–1%La_2O_3) is similar to that measured in the pure W foils over most of the range of the experiments, two important differences are noted: a trend to saturation of the amount retained is observed at fluences $>10^{24}$ D/m^2 and 500 K, and the D concentration at the back of the W–1%La_2O_3 alloy is about 1% of that at the implanted surface.

For temperatures above 300 K, higher cumulative fluences lead to higher retention levels for 1 keV D^+ implantation. It is not evident, however, how previous implantations are affecting subsequent ones. TDS profiles do not give a clear indication of trap generation, although differences are seen as the cumulative fluence increases. NRA depth profiles do not show a high concentration of D in the implantation zone, which might be associated with ion-induced trap generation. This leads us to speculate that ion-induced trapping sites may be diffusing into the bulk, even at temperatures as low as 300 K.

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