Deuterium retention in single-crystal tungsten irradiated with 10-500 eV/ D^+

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Deuterium retention in single-crystal tungsten was measured by thermal desorption spectroscopy as a function of D^+ energy, fluence and specimen temperature. At 300 K, D retention increased significantly with increasing ion energy but at 500 K the energy dependence was weak. For both 300 and 500 K implantations, the retention was significantly lower for10 eV/D^+ than for 500 eV/D^+ over the fluence range ~10^{22}-10^{24} D/m^2. Depth profiles in D-implanted SCW show D retention at 300 K extending beyond 7 μm while at 500 K retention concentration is detectable at the surface <60 nm. By comparison, D retention of 10 eV/D^+ at both 300 and 500 K is detectable in the very near surface. Similar TDS release peaks for both 10 and 500 eV/D^+ indicate that trapping mechanisms are independent of incident ion energy, and the reduced D retention is likely to be due to the shallower trapping depth.

PSI 20 Keywords: Deuterium Depth Profiling, Deuterium inventory, Tungsten, Ion-surface Interactions

PACS: 28.52 Fa, 79.20 Rf, 61.80 Jh

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1. Introduction

Due to its importance for ITER, deuterium retention in tungsten has been studied extensively in both polycrystalline (PCW) and single-crystal tungsten (SCW), and retention data are primarily available for energies ≥200 eV e.g. [1-5]. However, only limited retention data exist for low energy D^+ (10 eV [6] and 38 eV [7]) characteristic of Franck-Condon energies in the ITER divertor. Previous low-energy D retention studies used plasma devices [8-11]. Here, we have used a mass-analysed ion beam with energies down to ~10 eV/D^+. The fluxes achievable with this system are about 3-4 orders of magnitude lower than those obtained in plasma devices, making direct comparisons and projections to ITER fluxes/fluences difficult. Comparisons of D retention data obtained with ion guns, accelerators, and plasma devices [1,3,7,8] show little effect of flux on D retention at fluences $>10^{24}$ D^+/m^2 (for fluxes between 10^{18}-10^{22} D^+/m^2s). Unless unforeseen D retention mechanisms will occur at the higher ITER relevant fluxes, the available data (produced with ion guns, accelerators and plasma devices) provide a good guideline for deuterium retention estimates in ITER. In the present experiments single-crystal tungsten was used to avoid D diffusion and retention at grain boundaries, and to provide insight into the role of grain boundaries through comparison with previous results on PCW [6].

2. Experiment

The single-crystal tungsten was grown along the [001] direction by double electron beam zone melting by the Rare Metals Institute in Moscow. The material was 99.98% pure W (with the main impurities being 460 appm C, 460 appm O and 130 appm N) and was provided to us as thin disks. For the present experiments, specimens were cut from these disks into 5×5 mm^2 and 5×8 mm^2 pieces, each ~500 μm thick. Each specimen was mechanically and electrochemically polished between implantations removing ~20 μm to ensure the removal of memory effects caused by the previous implantation. Furthermore, specimens were annealed to 1700 K for 5 minutes between mechanical and electrical polishing to remove surface impurities that cause pitting and uneven electropolishing. After polishing, the specimens were annealed at 1500 K for 2 h.

Implantation was performed at the University of Toronto Institute for Aerospace Studies (UTIAS) using a mass-analysed D_2^+ ion beam with fluxes in the range 1–8×10^{18} D^+/m^2s, depending on energy. A mass-analysed ion gun system was selected for the low contamination content and single ion species (D_2^+ in this case) in the ion beam. For more details on the ion gun see [12]. The beam spot size, controlled with a tungsten mask, was ~2 mm diameter. The specimen was electrically and thermally isolated from the mask allowing for direct measurement of current on both the mask and specimen. A ceramic heater held directly against the back of the specimen was used for heating and the temperature was measured with a K-type thermocouple attached on the irradiated side. After ion implantation, thermal desorption spectroscopy (TDS) was performed in a separate vacuum system at UTIAS. Prior to TDS measurements, the chamber was baked at ~400 K for 2 h to release hydrogen adsorbed on the chamber walls following atmospheric exposure. The specimens were heated from room temperature to 1473 K at a rate of ~4 K/s with temperature monitored by a C-type thermocouple spot welded at least 5 mm from the irradiation spot, while released D_2 and HD were monitored using a Hyden quadrupole mass spectrometer (QMS). The QMS signals were calibrated using a D_2 leak bottle with a known leak rate. Due to the difficulty of separating specimen-specific HD signals from the background, all reported retention values are for D contained in D_2 only, with the HD contribution used as an upper limit of uncertainty (see uncertainty spread in Figs. 1, 3 and 4).

Nuclear reaction analysis (NRA) was performed at the Max-Planck-Institut für Plasmaphysik in Garching, Germany using the $D(^3He,p)^4He$ reaction; depth profiles were produced to a depth of 7 μm [13]. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) depth profiling was performed by Surface Interface Ontario at the University of Toronto using an ION-TOF IV from ION-TOF Gmbh (Munster, Germany). A 3 keV Cs^+ beam was used to sputter away a 200×200 μm surface layer and a 25 keV Bi^+ beam was used to analyze a 50×50 μm area at the centre of the sputter crater. The analysis beam was optimized to produce negative ions. SIMS depth profiles were measured to a depth of ~100 nm.

3. Results and Discussion

3.1 Energy Dependence

The energy dependence of deuterium retention in SCW was measured and compared with previous PCW results [6] to assess the effect of grain boundaries on retention. SCW specimens were irradiated to a fluence of 10^{24} D^+/m^2 at 300 and 500 K for energies of 10–500 eV/D^+; see Figure 1. Deuterium retention in 300 K SCW increased significantly as the energy was increased from 10 to 500 eV; see Fig. 1a. Retention for 10 and 25 eV/D^+ was ~1–3×10^{18} D/m^2, which is about 2 orders of magnitude lower than the ~3×10^{20} D/m^2 retention in PCW under similar conditions [6]. However, D retention for 100-500 eV/D^+ in SCW was found to be ~4–5×10^{20} D/m^2, in good agreement with PCW.

For implantations of SCW at 500 K, D retention for 10 eV/D^+ is similar to that of PCW; see Fig. 1b. Over the range 10–500 eV/D^+, SCW retention showed little dependence on energy (possibly a slight increase for 500 eV implantations), differing from the PCW trend where the increase is ~ 2 orders of magnitude. The weak energy dependence for SCW at 500 K is thought to be due to the reduction of flux of inwardly diffusing D atoms. The results of a related study on D retention in SCW [14] indicated the presence of a diffusion barrier due to the formation of nanobubbles in the near surface that limits D trapping to the first 60 nm for 500 eV/D^+ implantation at 500 K.

To further investigate the reduction of D retention in SCW at low ion energies, the TDS spectra were compared across the energy range 10-500 eV/D^+ for implantations at both 300 and 500 K; see Figure 2. As ion energy decreases from 500 to 10 eV no significant changes in the peak locations of the TDS spectra are seen at both temperatures. For the 300 K implantations (Fig. 2a), the main release peak for 500 eV/D^+ is centred on ~650 K while for the 10, 25 and 100 eV/D^+ the peaks are centred on ~700 K, indicating trapping of one D atom at a vacancy [15]. The slight difference in peak temperature is within the uncertainty of the temperature measurement; the only major difference in the spectra is the peak height, which results from reduced D retention at the lower energies.

For 500 K implantations (Fig. 2b) the spectra for both 10 and 500 eV/D^+ show a similar peak location at ~900 K, indicating deuterium adsorbed onto the interior surface of nano-sized cavities [16], with the only difference being the significantly reduced peak height in the 10

eV/D^+ spectrum. The consistent peak locations in the TDS spectra across the ion energy range studied indicate that the trapping mechanism is the same for 10 and 500 eV/D^+ ions.

3.2 Fluence Dependence

For 500 eV/D^+ implantations performed at 300 K over the fluence range 10^{22}–3×10^{24} D^+/m^2 the present retention measurements agree well with previous SCW [3] and PCW [6] results; in all three cases retention tends to saturate at ~5–6×10^{20} D/m^2 for incident D^+ fluences above ~5×10^{23} D^+/m^2 as the near-surface traps are filled and diffusion to the bulk does not occur in significant amounts. However, the present SCW retention data for 10 eV/D^+ show only a weak dependence on fluence and are about one order of magnitude lower than retention for 500 eV/D^+; see Fig. 3. This is in contrast to the case of 10 eV/D^+ implantation in PCW [6] where a significant increase with increasing fluence is seen between 10^{23} and 10^{25} D^+/m^2. Moreover, for the present10 eV/D^+ implantations to a fluence of 10^{24} D^+/m^2 a wide spread of nearly 50 × was observed; see Sec 3.4 for a proposed explanation.

For 500 K 500 eV/D^+ implantations in SCW, the present retention results (Fig.4) are in good agreement with previously published results by Poon et al. [3]; however, they are approximately an order of magnitude lower than 500 eV/D^+ retention in PCW [6]; see Sec. 4 for proposed explanation. Retention of 10 eV/D^+ in SCW at 500 K (Fig. 4) was generally lower than that observed for 500 eV/D^+, however the difference is difficult to quantify due to a significant spread in the 10 eV/D^+ retention measurements.

3.3 Deuterium Depth Profiles

NRA and SIMS deuterium depth profiles in SCW are shown in Fig. 5 for 10 and 500 eV implantations. NRA for 500 eV/D^+ implantations at 300 K shows D extending beyond 7 μm, while at 500 K D is detectable (NRA detection threshold: 10^{-3} at.%) at the surface to the first ~60 nm; Fig. 5a. In contrast, NRA depth profiles for 10 eV/D^+ implantations at both 300 and 500 K show detectable retention only at the very near surface; Fig. 5a. This finding is confirmed by SIMS on the same SCW specimens; Fig. 5b. SIMS shows retention of 500 eV/D^+ extending ~20 nm into the bulk, while deuterium from 10 eV implantations is only detected within ~0.7 nm.

TRIM was used to estimate the penetration depth of D^+ in tungsten [17]. The predicted mean depth for 500 eV is ~20 nm with standard deviation σ=8 nm, while for 10 eV the mean depth was ~0.8 nm with σ=0.5 nm. (Although TRIM is strictly not applicable for 10 eV, it does provide a comparative trend as the energy decreases from 500 to 10 eV.) Accordingly, a significant fraction of 10 eV D^+ will not penetrate beyond the first few monolayers of tungsten. This is fully consistent with the SIMS depth profiles in Fig. 5a. Comparison of the NRA profiles with TDS retention measurements shows that the NRA retention is consistently lower by ~2-5×10^{19} D/m^2; this is within a factor of 2 of the TDS amount for 500 eV/D^+ implantations. However, for 10 eV/D^+ experiments the NRA-measured retention was an order of magnitude lower than the TDS-measured amount. The difference between NRA and TDS measurements can be attributed to uncertainties in the detection methods or possibly bulk trapping at concentrations below the NRA detection limit (10^{-3} at%); 40 μm of tungsten with a D concentration of 10^{-3} at% will contain 2.5×10^{19} D/m^2.

3.4 Mechanism for trapping of 10 eV/D^+ in SCW

As was seen in Figure 2, reducing the implantation energy from 500 to 10 eV/D^+ does not affect the TDS peak locations for implantations at both 300 and 500 K. This finding suggests that there is no change in the trapping mechanism but rather only a reduction in the amount of deuterium being trapped as the energy is reduced from 500 to 10 eV. It is proposed that the shallow implantation depth of the 10 eV/D^+ ions is the primary reason for the reduced retention. Based on the mean penetration depth of ~0.8 nm for 10 eV/D^+ (as predicted by TRIM [17]), we estimate that 50% of the implanted D will be within the first three monolayers and nearly 20% will not penetrate beyond the first monolayer. For a tungsten surface with monolayer coverage of hydrogen, the penetration will be even shallower. Furthermore, the shallow implantation depth of 10 eV deuterium also reduces the volume of tungsten in the near surface that may undergo trap creation due to the lattice stresses involved in deuterium implantation. This will result in fewer near surface trapping sites created thus lowering retention in the near surface region. When considering diffusion as Brownian motion steps between lattice points in the tungsten crystal structure, ~50% of the implanted atoms would be three steps away from the surface where they can recombine and desorb. It is hypothesized that atoms implanted in the first few monolayers are more likely to diffuse to the surface before being trapped than those implanted

deeper into the specimen, thus reducing deuterium retention compared to higher energy implantations.

When comparing D retention in SCW for implantations at 300 and 500 K, we note a weaker energy dependence and lower retention at 500 K. This observation is consistent with the hypothesis that shallow implantation depth will increase the probability of diffusion to the surface resulting in lower retention. NRA and SIMS depth profiles for 500 eV/D^+ implantations at 500 K show that D is detectable at a depth of about 20–60 nm with the concentration below the detection limit in the bulk due to the formation of a diffusion barrier in the near surface (mechanism discussed in detail in [14]), whereas for 300 K implantations D was detected over 7 μm into the bulk. The same process that reduces deuterium diffusion into the bulk at 500 K increases the probability of deuterium diffusing to the surface before being trapped, thus reducing retention of 500 eV/D^+ and narrowing the gap in retention between 10 and 500 eV implantations at 500 K resulting in the observed weaker energy dependence of D retention seen in Fig.1.

Due to the shallow implantation depth of the 10 eV/D^+, nanoscale surface structures may have a large effect on retention. Clusters of surface defects such as a Beilby layer produced during mechanical polishing or pitting during electropolishing will increase the probability of trapping as well as provide a pathway for diffusion into the bulk, thus increasing retention. Thus, minor inconsistencies during specimen preparation could result in differences in surface structure from specimen to specimen leading to the wide spread in the observed retention; see retention for 10 eV/D^+ at fluence $10^{24}D^+/m^2$ in Fig. 3. The effect of diffusion pathways into the bulk on deuterium retention is most clearly seen in comparisons with PCW experiments. Previous studies of 10 eV/D^+ on PCW [6] show significantly higher retention at 300 K and 500 K than is observed here for the SCW. Although the difference of NRA and TDS indicates some fraction of retained D is trapped in the bulk in SCW, the concentration is very small and below the detection thresholds of NRA and SIMS. Furthermore, according to Alimov et al. [7] retention of 38 eV/D^+ shows higher D concentration extending over 7 μm into the bulk in PCW at 320 and 505 K. Comparing the present SCW results with [6,7] clearly shows the increase in low-energy D retention and deep D diffusion and trapping along grain boundaries in PCW.

4. Conclusions

Energy and fluence dependence of retention: Retention of 10 eV/D^+ in SCW is lower than that of 500 eV/D^+ at both 300 and 500 K. As ion energy decreases from 500 to 10 eV, D retention also decreases. The weak fluence dependence of D retention for 10 eV/D^+ in SCW at 300 and 500 K contrasts previous PCW results [6] where a strong increase in retention is seen for increasing fluence. This finding highlights the importance grain boundaries play in deuterium retention.

Comparing retention in SCW and PCW: Retention in 300 K SCW increased significantly with increasing D^+ energy. Retention for 10 and 25 eV/D^+ was about 2 orders of magnitude lower than retention in PCW under similar conditions [6]; however, D retention for 100-500 eV/D^+ in SCW was similar to that in PCW. For implantations of SCW at 500 K, D retention for 10 eV/D^+ is similar to that of PCW; however, over the range 10–500 eV/D^+, D retention in SCW showed a weak energy dependence, which differs from the significantly increasing trend in PCW [6]. The weak energy dependence for SCW is thought to be due to the reduction of D diffusion into the bulk during implantation at 500 K. More details on the SCW-PCW comparisons are available in [14].

TDS spectra: Comparison of TDS spectra show that peak locations do not change with decreasing ion energy, only the peak height changes, indicating that the same trapping mechanism is occurring for both 500 and 10 eV/D^+ implantations. NRA and SIMS depth profiles in SCW for 10 eV/D^+ implantations at both 300 and 500 K show retention being detectable only at the near-surface. The difference in NRA and TDS could indicate low concentration D trapping in the bulk of SCW for both 10 and 500 eV implantations, but the trapping concentration is much lower than in PCW [7] which shows detectable D concentration extending over 7 μm into the bulk. By comparison, profiles for 500 eV/D^+ implantations at 500 K show D within 20–60 nm, while at 300 K deuterium was detected by NRA as deep as 7 μm. It is proposed that the shallow implantation depth of 10 eV deuterium ions results in increased probability of diffusion to the surface where it can recombine and desorb before being trapped in the tungsten lattice compared to higher energy implantations.

Acknowledgements

We gratefully acknowledge the funding from the Natural Sciences and Engineering Research Council of Canada. We thank Charles Perez for his continual technical assistance in ensuring the smooth operation of the experimental facility. Finally we thank Peter Brodersen of Surface Interface Ontario at the University of Toronto for his expertise and analysis of SIMS depth profiles.

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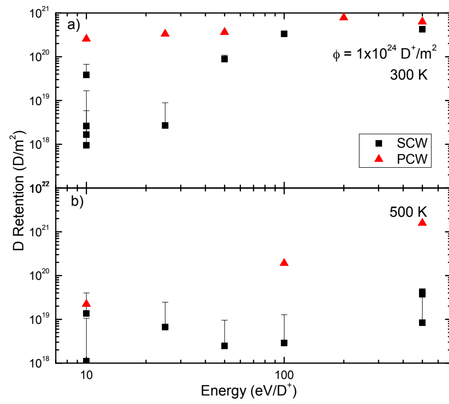

Figure 1 Energy dependence of D retention in SCW at (a) 300 K and (b) 500 K; data for PCW [6] are shown for comparison. D from HD molecules is not counted in the total D retained but is included as an uncertainty; the error bars in Figs 1, 3 and 4 indicate an upper bound of this uncertainty. Fluence: $\Phi=1\times10^{24}$ D^+/m^2.

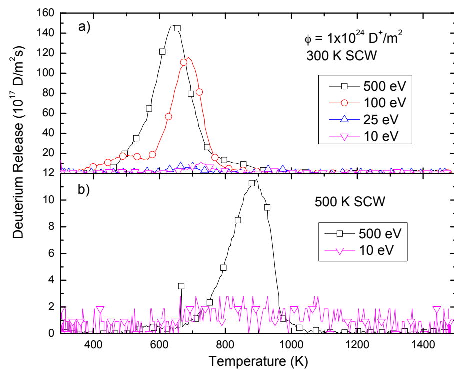

Figure 2 Energy dependence of TDS spectra at (a) 300 and (b) 500 K. Note: the spectra for 10 and 25 eV have been magnified 10 times. Fluence: $\Phi=1\times10^{24}$ D^+/m^2.

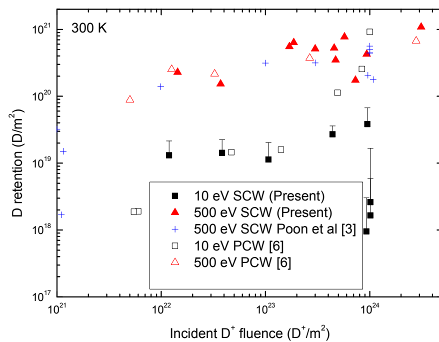

Figure 3 Fluence dependence of 10 and 500 eV/D^+ in 300 K SCW. Previous results from [3,6] are also shown. (The uncertainties represented by the HD components for the 500 eV data are not discernible since they are smaller than the actual data point markers.)

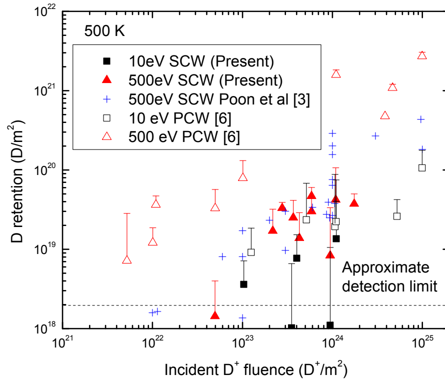

Figure 4 Fluence dependence of 10 and 500 eV/D^+ implantations at 500 K. Previous results from [3,6] are also shown.

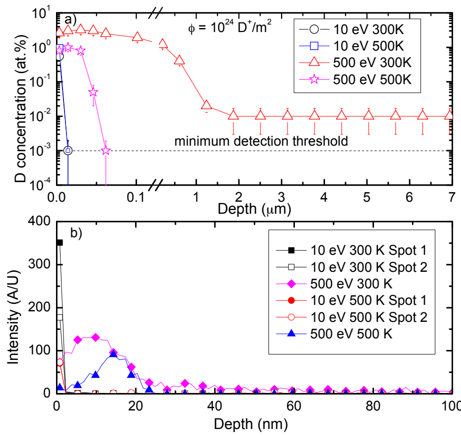

Figure 5 (a) NRA and (b) SIMS depth profiles of 10 and 500 eV/D^+ implanted in SCW at 300 and 500 K. Fluence: $\Phi=1\times10^{24}$ D^+/m^2.