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Deuterium retention in single crystal tungsten

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Abstract

The retention of deuterium in single crystal tungsten (SCW) has been measured at 300 and 500 K, as a function of incident ion fluence over the range 10^{21}–10^{24} D^+/m^2. Irradiation of SCW with 1.5 keV D_3^+ ions at 300 K leads to saturation at a much lower incident fluence than seen in polycrystalline tungsten (PCW), but with the same levels of D retention at saturation, $\approx 5 \times 10^{20}$ D/m^2. Implantations at 500 K reached saturation at a very low incident fluence, below 10^{21} D^+/m^2, with the amount of D retained at saturation $\approx 1.5 \times 10^{20}$ D/m^2. This level is 3–4 times lower than the saturation value for 300 K implantation of the same single crystal of tungsten. Deuterium depth profile analysis by secondary ion mass spectrometry (SIMS) shows D trapping primarily within the 500 eV D^+ ion implantation range for both 300 and 500 K profiles. SIMS also revealed that the depth profiles for oxygen and deuterium were similar. When the tungsten was annealed at 500 K for 1 h after implantation at 500 K, SIMS indicated that the deuterium retention decreased by an order of magnitude. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Deuterium inventory; Hydrogen retention; Thermal desorption; Ion implantation; Tungsten

1. Introduction

The database for hydrogen interactions with tungsten [1–20] has been growing steadily since tungsten was proposed as a plasma-facing material in next-generation fusion reactors (e.g. ITER). However, the transport and retention of hydrogen in tungsten is largely controlled by the concentration and nature of trapping sites in the bulk, which in turn are sensitive to both the impurity levels in the tungsten and the manufacturing process of the specimens [1–3]. The ability to predict the behaviour of hydrogen in tungsten thus becomes clouded by the variations in composition and fabrication of tungsten specimens used by different researchers. Therefore, a basis for comparison is required. In order to achieve the most control, the ideal choice for a reference material would be high purity single crystal tungsten (SCW). SCW will obviously not be used in a fusion reactor, but the study of SCW may allow us to determine the role of grain boundaries, impurities, vacancies, porosity and other material characteristics on hydrogen retention, recycling and permeation.

Due to the limited amount of experimental data on hydrogen retention in SCW [2–6], we have undertaken this study with the objective of investigating deuterium retention in SCW as a function of incident ion fluence and implantation temperature. The incident D^+ energy was selected to be 500 eV, considerably below the threshold energy for elastic collision damage formation in tungsten [7,19]. Relative deuterium and impurity depth profiles have been obtained from secondary ion mass spectrometry (SIMS) measurements. The D retention results from SCW are compared with previous polycrystalline tungsten (PCW) results.

2. Experiment

2.1. Specimen

A SCW (bcc) specimen, 9 mm diameter and 1 mm thickness was used for all experiments. The manufacturer, Johnson Matthey, quoted the purity as 99.9 wt% with the main impurities H ($\approx$ 0.1 at.%), C ($\approx$ 0.5 at.%) and O ($\approx$ 0.5 at.%). The specimen was mechanically

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polished and electropolished prior to any heat treatment or implantation. The orientation of the single crystal surface, deduced from a reflection electron diffraction pattern, was 8.5° from the [0 0 1] plane. Prior to initial implantation, the specimen underwent six rapid thermal anneal cycles in ultra-high vacuum, where it was held at 1400 K for 2 min.

2.2. D^+ implantation

All implantations were performed in an ultra-high vacuum accelerator facility using D_3^+ ions at normal incidence to the test specimen. However, the implantation experiments were performed without prior system bakeout. The background pressure was typically $\approx 10^{-5}$ Pa with the D_3^+ beam off, and $\approx 5 \times 10^{-5}$ 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 1.0 mm diameter aperture in front of the specimen. A 25 μm thick strip of mica with a 1.3 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 was fixed around the specimen to provide an edge for specimen alignment, thus ensuring that the specimen could be implanted on the same spot each time. A ceramic heater clamped behind the specimen was capable of heating the specimen to >700 K. A chromel–alumel thermocouple positioned between the specimen and the mica insulator, within 0.5 mm of the beam spot, was used to measure the specimen temperature.

Implantations were performed using 1.5 keV D_3^+ ions (500 eV/D^+) with a flux of $\approx 5 \times 10^{19}$ $D^+/m^2/s$. In order to maintain large flux densities during implantation, a 2.5 keV D_3^+ beam was utilized, with the specimen biased to +1000 V to decelerate the beam. Here we designate the incident particles as D^+ although not all of the deuterium atoms are ionized in the D_3^+ molecular ion.

2.3. Thermal desorption spectroscopy (TDS)

To minimize the background and 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 more than 12 h between implantation and desorption. We note that for the 500 K implantation cases, specimen heating is discontinued within seconds of the beam turn off. The specimen is then allowed to cool down to room temperature in the implantation vacuum chamber for ≈ 30 min, before being moved to the TDS chamber. Since the diffusion coefficient at 300 K is $\approx 10^{-13}$ m^2/s [10], only trapped D concentrations (no solute concentrations) were measured [8]. The vacuum system used for TDS was not baked and had base pressures $\approx 10^{-6}$ Pa. During TDS, the D-implanted specimen was heated in a W foil cradle. The cradle was heated resistively such that the specimen temperature was ramped up to 1400 K and held at high temperature for 2–5 min during each TDS heating cycle. The temperature of the specimen was measured directly by an optical pyrometer. Temperature ramping rates during thermal desorption were ≈ 6 K/s. The amount of D retained in the specimen 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.

3. Results and discussion

3.1. D retention at 300 K

The fluence dependence results for SCW at 300 K are shown in Fig. 1. For comparison, the retention trends for PCW are also plotted [9]. While the saturation levels in both SCW and PCW are very similar, differences are noted at low fluences. For fluences $<10^{22}$ D^+/m^2, the amount of D retained in SCW is 3–4 times higher than that measured in the PCW. The differences in saturation rates between the SCW and PCW may be due to differences in the *effective* diffusion rates, which control recycling on the sample surfaces and thereby control the volume of material in which trapping may occur. Thermal diffusion in W is quite rapid: the diffusion length at 300 K is ≈ 80 μm in 12 h using Frauenfelder's diffusion coefficient [10]. However, the effective diffusion rate, which includes both enhancements and barriers to diffusion, may be much faster or slower than thermal

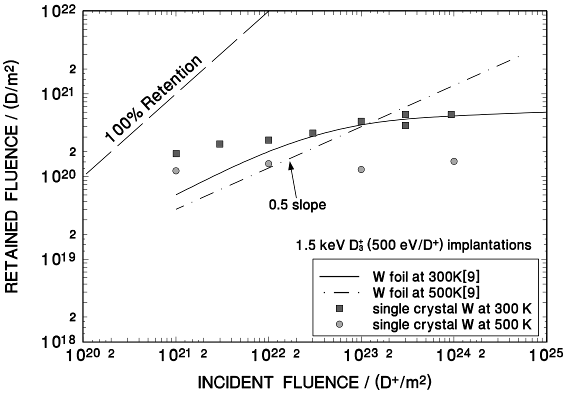

Fig. 1. D-retention as a function of incident D^+ fluence for 1.5 keV D_3^+ irradiation of SCW at 300 and 500 K. D^+ flux was $\approx 5 \times 10^{19}$ $D^+/m^2/s$ for all experiments. Trends for PCW foil are shown for comparison [9].

diffusion, depending upon which diffusion mechanisms are dominant. For example, trapping can slow diffusion dramatically, and grain boundaries can enhance diffusion. If one assumes the *effective* diffusion in PCW to be enhanced by grain boundary diffusion, then the deuterium concentration in the implantation zone will be lower than in SCW: more D atoms diffuse beyond the implantation zone or recombine and desorb from the surface, thus delaying the onset of saturation until much higher fluences. Evidence of this mechanism can be seen in the PCW foil at 300 K which shows diffusion-controlled trapping (slope of 0.5) at low incident fluences ($< 2 \times 10^{22}$ D^+/m^2) [9].

Based on sputter SIMS analysis (see Fig. 2), it appears that the trapped D in SCW is mainly confined to the 500 eV D^+ implantation zone, which is ≈ 20 nm according to a TRVMC [21] calculation. In PCW, D trapping at 300 K extends beyond the implant zone [9] to depths of > 500 nm. However, from surface analysis (SIMS for SCW and nuclear reaction analysis (NRA) for PCW) of both the upstream and downstream surfaces, there does not appear to be D trapping throughout the bulk nor on the downstream surface in either form of W at 300 K.

At higher fluences ($> 10^{23}$ D^+/m^2), D retention in SCW reaches the same saturation level as the PCW, $\approx 5 \times 10^{20}$ D/m^2, implying that D retention in SCW at 300 K is trap limited, with a similar trap concentration to that of PCW. It is surprising that SCW and cold-rolled PCW foil would have about the same number of trapping sites at 300 K, even with similar impurity levels, since the PCW foil will have grain boundaries and dislocations which may also act as trap sites. However, similar saturation levels of D retention at 300 K have been found in single crystal W, chemical vapour deposited W, inert gas plasma-sprayed W and vacuum plasma-sprayed W measured by NRA, despite orders of magnitude differences in porosity, impurity content and surface roughness [3]. D retention levels in W–1% La_2O_3 following 1.5 keV D_3^+ implantations to saturation at 300 K were also found to be the same as pure PCW foil levels [9]. Although 4 keV D^+ ion irradiation is known to produce dislocations in tungsten [7], a study by Sakamoto et al. [2], comparing 8 keV and 0.5 keV D_2^+ irradiation at room temperature, indicated that radiation-induced defects do not strongly influence D retention. This would suggest that dislocations and vacancies are not the dominant traps at 300 K. Furthermore, if impurity trapping were dominant, the impurity concentration in the implantation region would have to be ≈ 25 at.%, which is much greater than the 0.5 at.% indicated by the manufacturer. It would appear that D retention saturation levels at 300 K are dictated by self-trapping, as in the formation of interstitial clusters and possibly nano-bubbles. Since the SIMS profiles in Fig. 2 for D and oxygen are very similar, it is possible that oxygen impurities act as nucleation sites for self-trapping.

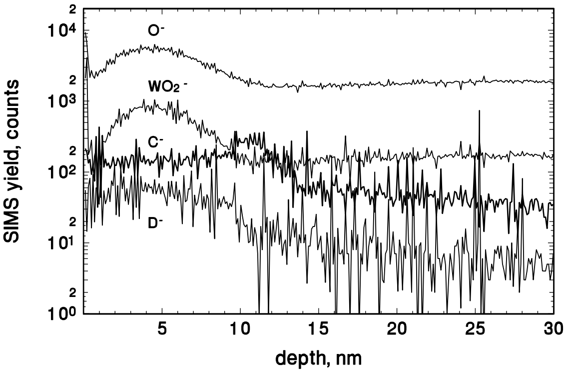

Fig. 2. SIMS profiles for SCW implanted with 1.5 keV D_3^+ at 300 K to a fluence of 10^{24} D^+/m^2. Sputter rate estimated to be 0.03 nm/s.

3.2. D retention at 500 K

The fluence dependence of retention in SCW at 500 K is quite different from the PCW case [9]. For incident fluences in the range 10^{21}–10^{24} D^+/m^2, the amount of D retained in SCW at 500 K is approximately constant, while for the PCW, the retained D was seen to increase with fluence with a slope of 0.5, indicating diffusion-controlled trapping in the bulk [9]; see Fig. 1. This implies that D retention in SCW is still trap limited and saturation at 500 K is also trap limited and saturation is reached even earlier than at 300 K, at incident fluences $< 10^{21}$ D^+/m^2. This is consistent with the results of Alimov and Scherzer [3] who also found that the incident fluence required for single crystal W to saturate at 600 K was much less than that required for saturation at 300 K [3]. This is in sharp contrast to the behaviour in PCW, which exhibits diffusion-limited retention with no signs of saturation for incident fluences below 3×10^{24} D^+/m^2.

The saturation level for SCW at 500 K, 1.5×10^{20} D/m^2, is a factor of 3 lower than at 300 K. Re-emission measurements on SCW at 300 and 600 K by Alimov and Scherzer [3] also show D saturation levels at the higher temperature to be about a third of the room temperature levels. The lower saturation level is probably due to partial de-population of the traps at elevated temperatures. SIMS measurements on a specimen implanted at 500 K, cooled to 300 K, and then annealed at 500 K for 1 h, indicate that retention near the surface is reduced by an order of magnitude. (Since the SIMS analysis was performed after the TDS experiments were completed, confirmation by TDS of the deuterium loss in an annealed specimen has yet to be performed.) The lower retention is thought to be due to de-trapping at 500 K, indicating traps of about 0.7–1.0 eV [1,14,18]. SIMS D profiles in SCW at 500 K were similar to those at 300 K, i.e. the deuterium is trapped primarily within the implantation zone in both cases. By contrast, the NRA measured D profile in PCW at 500 K was found to be more or less constant throughout the 25 μm thick W foil [9].

The difference in trapping behaviour at 500 K between the SCW (trap limited) and the PCW (diffusion limited) suggests that another mechanism is active in the PCW. Enhanced diffusion along grain boundaries and dislocations may increase the number of trap sites accessible in the PCW.

4. Conclusions

Single crystal W implanted with 1.5 keV D_3^+ ions at 300 K shows deuterium saturation at a lower incident fluence than that observed with polycrystalline W, however the amount of D retained at saturation remains the same. At 500 K, D retention in SCW shows no fluence dependence over the fluence range studied (10^{21}–10^{24} D^+/m^2). D retention at 500 K appears to be trap-limited but the D retention levels at saturation are about 3-4 times lower than the amount seen at 300 K. This is in sharp contrast with the fluence dependence of D retention in PCW at 500 K, where the retained fluence increases with incident D^+ fluence, indicating diffusion-controlled trapping [9]. Deuterium depth profiles for SCW from SIMS show D trapping primarily within the ion implantation region at both 300 and 500 K. These differences are attributed to large differences in the effective diffusion rates of deuterium in the two materials. Deuterium retention appears to be dominated by ion-induced self-trapping, with a small contribution from impurity sites.

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