Deuterium removal from radiation damage in tungsten by isotopic exchange with hydrogen atomic beam

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Abstract. The tungsten samples were pre-irradiated with self-ions to create radiation-induced defects and then exposed to the deuterium atomic beam. The deuterium removal was studied by isotopic exchange with atomic hydrogen beam. Modification of the deuterium depth profile in self-ion irradiated tungsten under isotopic exchange up to a depth of 6 μm was measured in-situ by nuclear reaction analysis. The total deuterium retention after isotopic exchange was measured by thermal desorption spectroscopy. It is shown that the efficiency of the deuterium removal increases with increasing of the hydrogen incident flux, incident energy and temperature of the tungsten sample.

1. Introduction

Due to its physical properties such as low coefficient of physical sputtering and high melting temperature, tungsten (W) is considered as a priority plasma-facing material for fusion reactors [1-5]. In the burning fusion plasmas, plasma-facing components will be exposed to intense fluxes of deuterium (D), tritium (T) and helium (He) particles and neutrons (n) with energy of 14 MeV arising in the course of the D-T reaction. The decrease of tritium in fusion reactor materials is today one of the main requirements for materials that come into contact with the fusion plasma because of both the safety limitation of total tritium retention in fusion reactors and tritium self-sufficiency [3-5]. In order to stay below the safety limit, the fuel removal methods from the wall materials need to be developed. One possible method is the isotope exchange [6-8]. In the present paper, the isotope exchange technique is examined to be used as tritium removal method from radiation damage in W.

Tungsten (W) samples were first pre-irradiated with self-ions up to a fluence of 1.6x10¹⁸ W/m² to create radiation damage (0.5 dpa) [9] and then exposed to atomic D beam at sample temperature of either 600 K or 700 K. After it, the H atomic beam was used to remove D at the sample temperature of either 600 K or 500 K. The atomic H or D beam is created by thermal dissociation of H or D molecules in a hot capillary of the atomic beam source, HABS [10]. The capillary was heated with the same power of 195 W for all exposures providing capillary temperature of 2150 K. H₂ dissociation is typically from 80 to 98% depending on operation conditions. The source produces only neutral atoms without any high-energy particles and ions. The translation kinetic energy of hydrogen atoms can be estimated as $E_{kin}=(3/2)kT$ that is about 0.28 eV for the present operational temperature of the W capillary. The H₂ or D₂ gas pressure in the gas supply side was controlled by an all-metal leak valve, Baratron by MKS. The average driving pressure
during the atom exposures of tungsten sample was 250 ± 10 mbar for D₂ and 190±10 mbar for H₂. The distance between the sample surface and the capillary exit was 80 mm and the angle between the atom beam and the surface normal was 51°.

The atomic beam is distributed inhomogeneously over loaded surface with a maximum flux in the middle of sample. The maximum D and H atomic flux densities at the sample were 5.2 × 10¹⁸D/m²s and 6.7x10¹⁸ H/m²s, respectively. The beam spot size and position was determined by observing the burn trace after short exposure of a millimetre paper mounted at the location of the sample. The average flux densities at the probing beam position were (4.5±0.3)x10¹⁹D/m²s for D atoms and (5.6±0.1)x10¹⁹H/m²s for H atoms [12]. Modification of the deuterium depth profile in self-ion irradiated tungsten during isotopic exchange up to a depth of 6 μm was measured in-situ by nuclear reaction analysis (NRA) using ³He⁺ as the analysing beam as described in [11,12]. Kinetics of the D release from radiation-induced defects of specimens after isotopic exchange was studied by thermal desorption spectroscopy (TDS). The samples were heated resistively up to 1500 K with a linear ramp of 2 K/s.

2. Results and discussion

The D depth profile obtained after the D atomic exposure at sample temperature of 700 K up to a fluence of 7.8x10²³ D/m² is shown in figure 1. Modification of the D depth profile after the H atomic beam loading at 500 K at different fluences is also shown in figure 1. More efficient isotopic exchange occurs near the surface up to 1 μm, however, the D concentration only slightly decreases after the H atomic flux of ~1x10²³ H/m² and significant removal of the D up to 1 μm takes place at H atomic fluence of ~2x10²⁴ H/m². The noticeable change of the D concentration at a peak damage was observed only at the highest fluence of the present experiment of 5.7x10²⁴ H/m² (284.5 h). This is in an agreement with diffusion model with trapping of hydrogen at radiation defects reported in [13]. As it was found in [13], the D atoms reach the peak damage of ~1.3 μm at a fluence of about 6x10²⁴ D/m² at 500 K. The isotopic exchange at the same depth also starts at ~5.7x10²⁴ H/m² at 500 K as one can see in figure 1. This means that diffusion of H is the limiting process that defines the efficiency of isotopic exchange.

![Figure 1.](image-url)

**Figure 1.** The D depth profile after the D atomic exposure at sample temperature of 700 K up to a fluence of ~7.8x10²³ D/m² (48 h) and sequentially after the H atomic exposure at sample temperature of 500 K at different fluences up to a fluence of ~5.7x10²⁴ H/m² (284.5 h). Dashed line shows the damage profile calculated by SRIM [9]. The D atomic flux density was 4.5x10¹⁸ D/m²s and H atomic flux density was 5.6x10¹⁸ H/m²s.
After the isotope exchange of D by H at 500 K and NRA measurements of the D concentration up to 6 μm, total D concentration in W was measured by TDS. TDS analysis has been performed several months after atomic exposure. A quadrupole mass spectrometer (QMS) was used to monitor the desorbed hydrogen molecules: mass 2(H2), mass 3 (HD) and mass 4 (D2), and D-related water: mass 19 (HDO) and mass 20 (D2O). The absolute sensitivity of QMS to D2 was routinely measured after every experiment using a system including two leak valves and a baratron (see details in [14]). The relative sensitivity to H2 was determined once in a separate experiment with the same procedure. The relative sensitivity for HD was taken as an average between H2 and D2 values. Figure 2 shows total D release from self-ion damaged W after the only D exposure at 700 K up to a fluence of 3.78x1023 D/m2 (see details in [13,15]) and after the isotopic exchange experiment. Total D retention was defined as 2signal(D2)+0.5signal(HD)/2. TDS of D from the sample without H exposure shows higher D retention (6.4x1019 D/m2) compared to D in the sample after H exposure (4.7x1019 D/m2) (figure 2). The total D retention measured by TDS many months after atomic exposure is much lower compared to the D retention measured by NRA up to 6 μm. TDS of D from sample without H exposure is narrower than that from sample after isotopic exchange. The comparison of release of D in the form of D2 and HD is shown in figure 3. For the experiment of only D atomic beam exposure, mass 4 (D2) was dominating the release spectrum. Obviously, more D is desorbed in the form of HD (mass 3) than in the form of D2 (mass 4) after H exposure as shown in figure 3 because of high density of hydrogen in the sample.

An increase of the sample temperature results in an increase of diffusion of hydrogen isotopes [13] and, consequently, the rate of replacing of D atoms by H atoms increases. Therefore, the efficiency of isotopic exchange increases. Figure 4 shows the D depth profile after the D atomic exposure at sample temperature of 600 K and modification of this profile after sequential H atomic exposure at the same temperature. Between the end of the D exposure and start of H exposure the sample was kept at 600 K during 20 hours to study the effect of the D release under the annealing in vacuum and exclude the impact of this effect on the isotopic exchange. The annealing in a vacuum only slightly reduces the D...
concentration at a peak damage (~1.3 μm) by a factor of ~1.5. While the isotopic exchange during 20 hours reduces the D concentration at a peak damage by a factor of ~3.3. Therefore, the efficiency of isotopic exchange for D removal from self-ion irradiated W is 2 times higher than annealing in vacuum as it was also stated in [11]. The increase of the D release from radiation-induced defects in W by exposure to H plasma and by heating in H₂ atmosphere compared to annealing in vacuum was also reported in [16,17] and [18], respectively. Increasing of the H fluence results in further removal of D from damaged zone by replacing with H and diffusion of D both to the surface to be desorbed and into the bulk to be re-trapped. At H atomic fluence of ~2x10²⁴ H/m², the D is removed not only from radiation-induced defects in damaged zone but also from bulk intrinsic defects which are out of the damaged zone.

Figure 4. The D depth profile after the D atomic exposure at sample temperature of 600 K up to a fluence of ~4.3x10²³ D/m² and modification of this profile after sequential H atomic exposure at sample temperature of 600 K at different fluences up to a fluence of ~2x10²⁴ H/m² (100 h). Dashed line shows the damage profile calculated by SRIM [9]. The H atomic flux is ~5.6x10¹⁸ H/m².s.

According to the analytical expression derived in [14], the time to decorate radiation-induced defects up to a depth x decreases with ion flux and ion energy

\[ t = \left( \frac{x^2}{2I_0R_p} \right) \sum_{i=1}^{m} W_i(T), \]  

(1)

where \( I_0 \) is the ion flux, \( \xi \) is the penetration probability, \( R_p \) is the mean ion range and \( W_i = \sum_{k=1}^{m} W_{ik} \) is the total density of defects (\( m \) is the number of defects), which can be occupied by D at certain temperature \( T \). The D diffuses deeper at higher temperatures or in the case of small trap density. In the case of the exposure of W to D atoms at 700 K, only the defects with high binding energy (deep traps) are populated with D. Whereas H populates both kinds of defects with low and high binding energies under exposure of W to H atoms at 500 K. Because the rate of D and H diffusion is different only by a factor of \( \sqrt{2} \) at the same sample temperature [19], the fact that the isotopic exchange at certain depth x starts approximately at the same fluence when the H atom reaches this depth confirms that H atom replaces D atom from deep traps. In the case of the exposure of W to D atomic beam at 600 K and sequentially to H atomic beam at 600 K, the D from both shallow and deep defects is exchanged with H. The rate of this exchange depends mainly on the diffusion of H atoms, namely, on the sample
temperature in the present experiments, but it seems that this rate does not depend on the initial concentration of deuterium. To confirm or reject this suggestion and define probabilities of the D depopulation from deep and shallow defects by exchange with H, we will populate only deep defects with D using the D atomic exposure at 700 K (in contrast with the present experiment shown in figure 4 where we populated with D both kinds of defects with low and high binding energies using the D atomic exposure at 600 K) and sequential exposure to H atoms at 600 K in the future experiment. The efficiency of isotopic exchange increases with increasing the sample temperature, incident ion/atomic flux and incident H energy, as it was derived analytically in [19], that is consistent with the present experimental data and experimental data at different ion fluxes and energies reported in [16-18].

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