The Effect of Displacement Damage on Deuterium Retention in Tungsten Exposed to D Neutrals and D_2 Gas

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Abstract

Samples of polycrystalline ITER-grade W and recrystallized W were irradiated at room temperature with 20 MeV W ions to displacement damage up to 0.5 dpa. The damaged W samples were then exposed to (i) D neutrals at 403–573 K and (ii) D2 gas at 673–1073 K and pressures of 1.2 and 100 kPa. Trapping of deuterium in the damage zone was examined by the D(^{3}He, p)^{4}He nuclear reaction with ^{3}He energies between 0.69 and 4.0 MeV allowing determination of the D concentration up to a depth of 6 lm. It has been found that generation of the W-ion-induced displacement damage leads to accumulation of deuterium in the damage zone up to concentration depending on the exposure temperature and, at temperatures ≥ 673 K, on the D_2 gas pressure. Thermal desorption spectra allowed a conclusion that deuterium is mainly accumulated in the form of D atoms bound to inner walls of vacancy clusters.

PACS: 52.40.Hf, 61.72.Qq, 61.80.Jh

PSI-20 Keywords: Deuterium inventory, Tungsten

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1. Introduction

As a material for plasma-facing components in future fusion reactors, tungsten (W) will be subjected to intensive fluxes of energetic deuterium (D) and tritium (T) as well as 14 MeV neutrons (n). Neutron irradiation generates displacements in the bulk of W and creates thus defects at which hydrogen isotopes can be trapped [1,2]. These processes lead to concerns about tritium inventory in the n-irradiated W after long-term deuterium–tritium plasma exposure. One of the ways to investigate the influence of n-produced defects on the hydrogen isotope inventory is to simulate displacement damage in tungsten using irradiation with energetic ions. Radiation damage generated by fusion neutrons and by MeV W ions is to some extent comparable [3]. For both neutrons and heavy ions, the energy distribution of primary knock-on atoms peaks at high energies, and they both create dense collision cascades [4]. However, damage created by heavy ions is concentrated in a narrow region below the surface, while neutron-induced damage extends to larger depths.

It has been shown that defects produced by irradiation with light (H, Si) and heavy (W) ions enhance deuterium retention in W materials after subsequent irradiation with D ions or exposure to D and D–He plasmas [5–13]. However, exposure to high flux plasmas interferes with the modification of the near-surface by heavy-ion-induced defects. If such modification takes place, the effects of displacement damage on the bulk retention of diffusing D atoms cannot be simulated properly by D plasma exposures. The objective of this work is to study D retention at displacement damage in W after exposure to low-flux beam of D neutrals and D_2 gas at temperatures up to 1073 K.

2. Experimental

Two types of tungsten with a purity of 99.99 wt.% were used in this work: (i) a polycrystalline ITER-grade tungsten and (ii) the polycrystalline W fully recrystallized at 2073 K for 1 h after cutting and polishing.

The ITER-grade W is deformed (rolled, swaged and/or forged) followed by appropriate heat-treatments to obtain better mechanical properties after the sintering process [14]. The microstructure of the Japanese ITER-grade W produced by A.L.M.T. Corp., Japan, consists of grains elongated along the deformation axis. The grain size is 1–3 μm in section and up to 5 μm in length. Individual elongated cracks observed between grains are due to the deformation treatment [15] Square-shaped samples, 10 × 10 × 2 mm in size, were prepared by the manufacturer such that the plasma-facing surfaces were perpendicular to the deformation axis.

The samples were mechanically polished, cleaned in an acetone ultrasonic bath, and then annealed in vacuum at 1473 K for 30 min for stress relief.

Recrystallized W samples were prepared from powder-metallurgy W by A.L.M.T. Corp., Japan. After hot-rolling samples of 10 × 10 × 2 mm in size were cut and followed by dry-hydrogen annealing at 2073 K for 1 h. In consequence of this, the W grain size is 20-200 μm.

In an implantation chamber connected to the 3 MV tandem accelerator at IPP, Garching, the W samples were irradiated with 20 MeV W ions to a fluence of 8×10^{17} W/m^2 at room temperature. As a result, the near-surface layer of the samples was damaged to 0.5 displacements per atom (dpa) at the damage peak situated at a depth of 1.35 μm. The damage profile was calculated using the program SRIM 2008.03 [16] with a displacement threshold energy of E_d = 90 eV [17].

The damaged W samples as well as undamaged ones were exposed to D particles at elevated temperatures in the range from 473 to 693 K in DC glow discharge. The sample on a holder equipped with an ohmic heater and a thermocouple served as anode, whereas a tungsten disc located at a distance of about 10 cm from the sample holder was used as a cathode. Deuterium pressure in the chamber was maintained at 1 Pa, DC discharge voltage was around 400 V, and discharge current averaged about 0.18 A. As a result, the W sample placed on the sample holder was exposed to uncharged D particles (neutrals) and negatively charged deuterium ions originated in the glow discharge and also to D atoms reflected from the W cathode. An implantation flux of the D neutrals and negatively charged ions was estimated to be about 2×10^{18} D/m^{2}s with the use of Ti probe exposed in the DC glow discharge at room temperature for 10 and 60 min, while the D retention in the Ti probe was determined by thermal desorption spectroscopy (TDS). It seems plausible that a fraction of negatively charged D ions in the implantation flux was negligibly small [18], therefore below we can talk about D neutrals with energies in the range from few eV (atoms originated in the glow discharge) to ~ 150 eV (atoms reflected from the cathode [19]).

The undamaged and damaged W samples were also exposed to D_2 gas at pressures of 1.2 and 100 kPa and temperatures in the range from 673 to 1073 K in a quartz tube connected to the high-vacuum pumping system. The sample was placed inside the quartz tube and heated in a vacuum with the use of an external ohmic heater. The temperature was monitored using a type K thermocouple contacted directly to the sample inside the tube. As the sample temperature reached the required value, a valve between the tube and the pumping system was

closed and the tube was filled with D_2 gas. The background pressure inside the tube was measured with an ionization gauge, whereas the D_2 gas pressure was controlled with a Baratron capacitance manometer. The samples were exposed to D_2 gas at 673 K for 10 h, at 773 and 873 K for 3 h, at 973 and 1073 K for 1 h.

The deuterium depth profiles in the W samples were determined by nuclear reaction analysis (NRA). The $D(^3He,p)^4He$ reaction was utilized, and both the α particles and protons were analyzed. The α-spectrum was transformed into a D depth profile at depths up to ~0.5 μm using the program SIMNRA [20]. To determine the D concentration at larger depths, the energy of the analyzing beam of ^3He ions was varied from 0.69 to 4.0 MeV. The proton yields measured at twelve different ^3He ion energies allow D depth profiles to be measured to depths of up to 6 μm [21,22] with acceptable depth resolution [22].

After the NRA measurements, the samples were analyzed ex-situ by thermal desorption spectrometry (TDS). A controlled ohmic heater was used to heat the sample placed inside a quartz tube at a ramp rate of 0.5 K/s and the sample temperature was raised to 1300 K. H_2, HD and D_2 molecules released during TDS measurement were monitored by a quadrupole mass spectrometer. It was observed that kinetics of HD and D_2 thermal desorption were different. In most TDS measurements, the HD spectrum was correlated rather with the H_2 spectrum. Just to avoid influence of H_2 pressure variation on a shape of the deuterium TDS spectrum, we examined D_2 signal only. Whereas deuterium was mainly accumulated in the damaged zone at depths of up to 2 μm (Figs. 1 and 2), for each TDS experiment the TDS D_2 signal integral was intentionally equated to the amount of deuterium determined by NRA.

3. Results and Discussion

After exposure of undamaged W samples to D neutrals at temperatures of 403 and 473 K, deuterium is detected in the near-surface layer solely, at depths less than 0.1 μm (the depth profiles are not shown).

Generation of displacement damage in the W materials and subsequent exposure to D neutrals at temperatures from 403 to 573 K leads to accumulation of deuterium at depths up to 2 μm (i.e., in the damage zone) to a concentration of 0.4–1.1 at.%, depending on the exposure temperature (Fig. 1). Note that after exposure to D_2 gas a pressure of 1 Pa (the same deuterium pressure was maintained under DC discharge) and temperatures of 403 and 573 K for 12 h (i.e., for time period of highest D neutral fluence), the D concentration in the damage zone does not exceed 10^{-2} at.%. During D neutral exposure, the W-ion-induced defects

become fully occupied to a depth depending on implantation fluence (or time) and are empty at greater depths (Fig. 1b). Thus, the D depth profiles are consistent with saturable strong traps[1] being filled by D atoms diffusing from the surface. Accumulation of deuterium in the damage zone is observed also after D_2 gas exposure at pressures of 1.2 and 100 kPa and temperatures of 673-1093 K (Fig. 2). It should be noted that in undamaged W exposed to the D neutrals and D_2 gas, the D concentration at depths ≥ 0.1 μm is below the NRA detection limit of 5×10^{-4} at.%.

For both W materials exposed both to D neutrals and D_2 gas at the same conditions, values of the D concentration (given in D/W) at the depth of the damage peak are comparable (Fig. 3). However, after gas exposure at 673 K and 100 kPa, the D concentration in the ITER-grade W beyond the damage zone (at depths ≥ 2.5 μm) is noticeably higher than that in the recrystallized W (Fig. 2). Obviously, the intrinsic intergranular cracks inside the ITER-grade W serve as traps for diffusing D atoms.

After D loading near room temperature, saturation concentration of D trapped in the damage zone, ${}^{tr}C_D$, is about 0.01 D/W and, as the exposure temperature increases up to 573 K, decreases to about 4×10^{-3} D/W (Fig. 3). In the case of D_2 gas exposure at ≥ 673 K, the concentration ${}^{tr}C_D$ depends strongly on the exposure temperature and gas pressure (Fig. 3).

Deuterium atoms injected into damaged W settle into interstitial solution sites, diffuse through the metal lattice, and become trapped at defects like vacancies and vacancy clusters [23, 24] generated from the displacement damage. The results show that the saturation D concentration in the damage zone depends not only on an exposure temperature but also on a concentration of deuterium atoms in solute state [25, 26] (Fig. 3).

TDS spectra of D_2 molecules released from the damaged W materials exposed to D neutrals at 423 K demonstrate dominating peak at 930-950 K and a shoulder at ~820 K. However, after exposure at 573 K, the ~820 K shoulder disappears and the spectra are characterized by the dominating peak at 950 K (Fig. 4a). After exposure to D_2 gas, the TDS spectra can be described by a single peak at 940-1000 K and high-temperature (1100-1270 K) desorption tail (Fig. 4b).

According to van Veen et al. [26] and modeling deuterium thermal release by Poon et al. [27], a TDS peak at ~900 K can be ascribed to detrapping of atomic deuterium from walls of voids or large vacancy clusters. Formation of large vacancy clusters comprising 300-600

[1] Saturable traps are traps having finite capacity. Traps where D in solution becomes trapped when it encounters unoccupied traps are denoted as strong traps [4].

vacancies in W after irradiation with 50 keV W ions at 300 K to damage levels from 0.01 to 5.5 dpa was observed with the use of field ion microscopy [24]. Thus, it is safe to assume that in the W-ion-damaged W, deuterium is mainly accumulated in the form of D atoms bound to inner walls of large vacancy clusters.

After exposure of damaged W to low-energy (several tens of eV) D plasmas with high incident ion fluxes (10^{22} – 10^{24} D/m^{2}s) at temperatures below 600 K [9, 11-13], the D concentration in the damaged zone is nearly twice as high as that for D neutral exposure with low implanted flux of ~2 × 10^{18} D/m^{2}s (Fig. 3). This difference can be explained by accumulation of molecular deuterium inside small voids due to high concentration of D atoms in solution maintained in the near-surface layer under high-flux D plasma exposure. However, under D plasma exposures at temperatures above 650 K, D_2 molecules are released from the voids [26] and D is accumulated mainly as D atoms.

4. Summary

In W materials damaged by irradiation with 20 MeV W ions at room temperature to 0.5 dpa at the damage peak and subsequently exposed to D neutrals and D_2 gas at elevated temperatures, deuterium accumulates in the damage zone to a saturation concentration depending on the exposure temperature (e.g., ~10^{-2} D/W at 403 K and ~4 × 10^{-5} D/W at 1073 K) and D concentration in solute state. The high temperature (930-1000 K) single TDS peaks obtained after exposure of the damaged W materials both to the D neutrals and D_2 gas allow a speculation that deuterium is mainly accumulated in the form of D atoms bound to inner walls of vacancy clusters.

Acknowledgement

The authors thank S. Lindig and M. Balden (IPP Garching) for the SEM/FIB analysis of the W materials and M. Fußeder (IPP Garching) for irradiation of the W samples with W ions and technical assistance with the ^{3}He beam analyses. This work was supported by Kakenhi on Priority Areas, 476, Tritium for Fusion, from MEXT, Japan.

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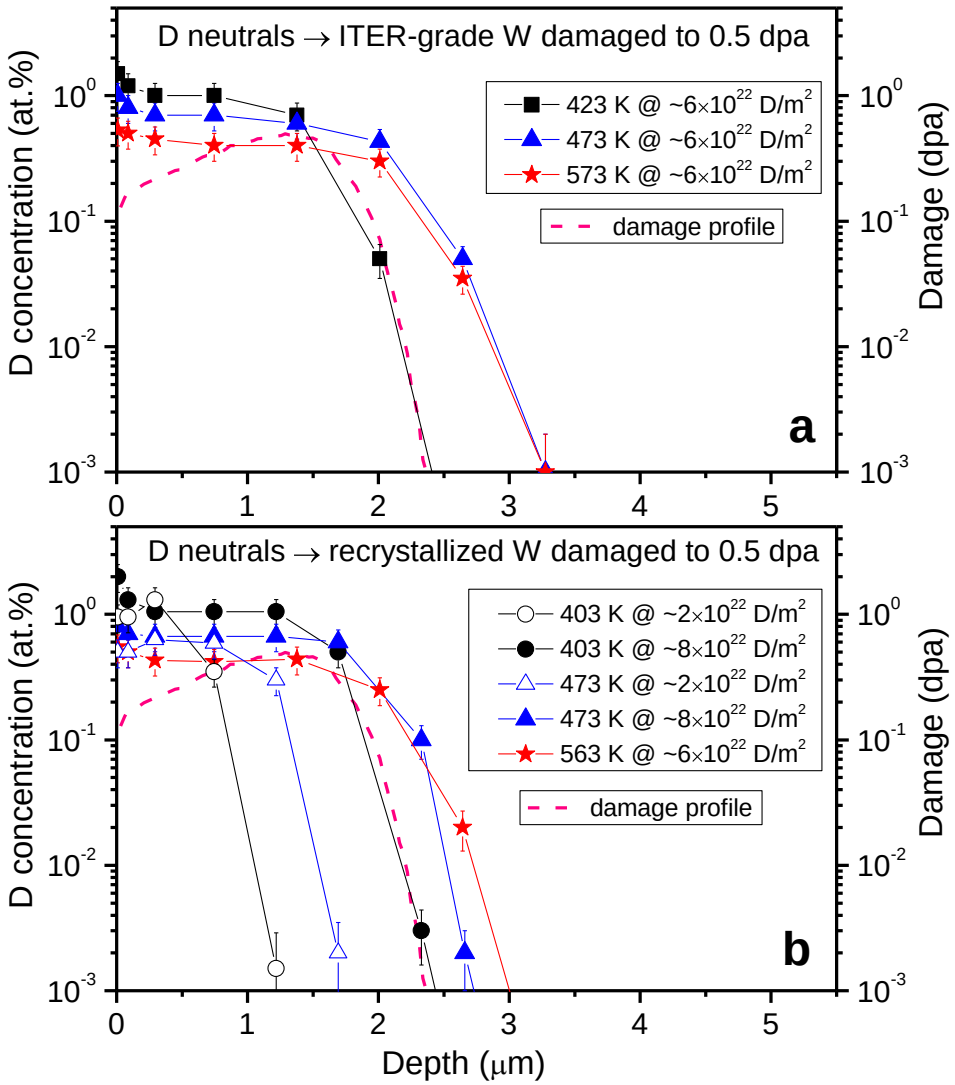
Figure captions

Figure 1. Depth profiles of deuterium retained in damaged ITER-grade W (a) and recrystallized W (b) after exposure to D neutrals. Exposure temperatures and D implantation fluences are indicated in the legends. In both panels, damage depth profiles as calculated by SRIM 2008.03 [16] are also shown.

Figure 2. Depth profiles of deuterium retained in damaged ITER-grade W (a) and recrystallized W (b) after exposure to D_2 gas. Exposure temperatures, gas pressures and exposure durations are indicated in the legends. In both panels, damage depth profiles as calculated by SRIM 2008.03 [16] are also shown.

Figure 3. Saturation concentration of deuterium (D/W) in the damage zone of ITER-grade W and recrystallized W exposed (i) to D neutrals and (ii) to D_2 gas at pressures of 1.2 and 100 kPa, as a function of exposure temperature. Additionally, D concentrations in the damage zone of W-ion-damaged W materials exposed to low-energy, high-flux D plasmas [9,11–13] are shown for a comparison. The W materials were damaged by irradiation with 5.5–20 MeV W ions at room temperature. Types of W materials and displacement damage levels are indicated in the legends.

Figure 4. Thermal desorption spectra of D_2 molecules for damaged ITER-grade W exposed to D neutrals (a) and recrystallized W exposed to D_2 gas (b). Exposure temperatures, D implantation fluences, gas pressures and exposure durations are indicated in the legends. The TDS heating rate was 0.5 K/s. In both panels, the deuterium release rate is shown on a logarithmic scale.



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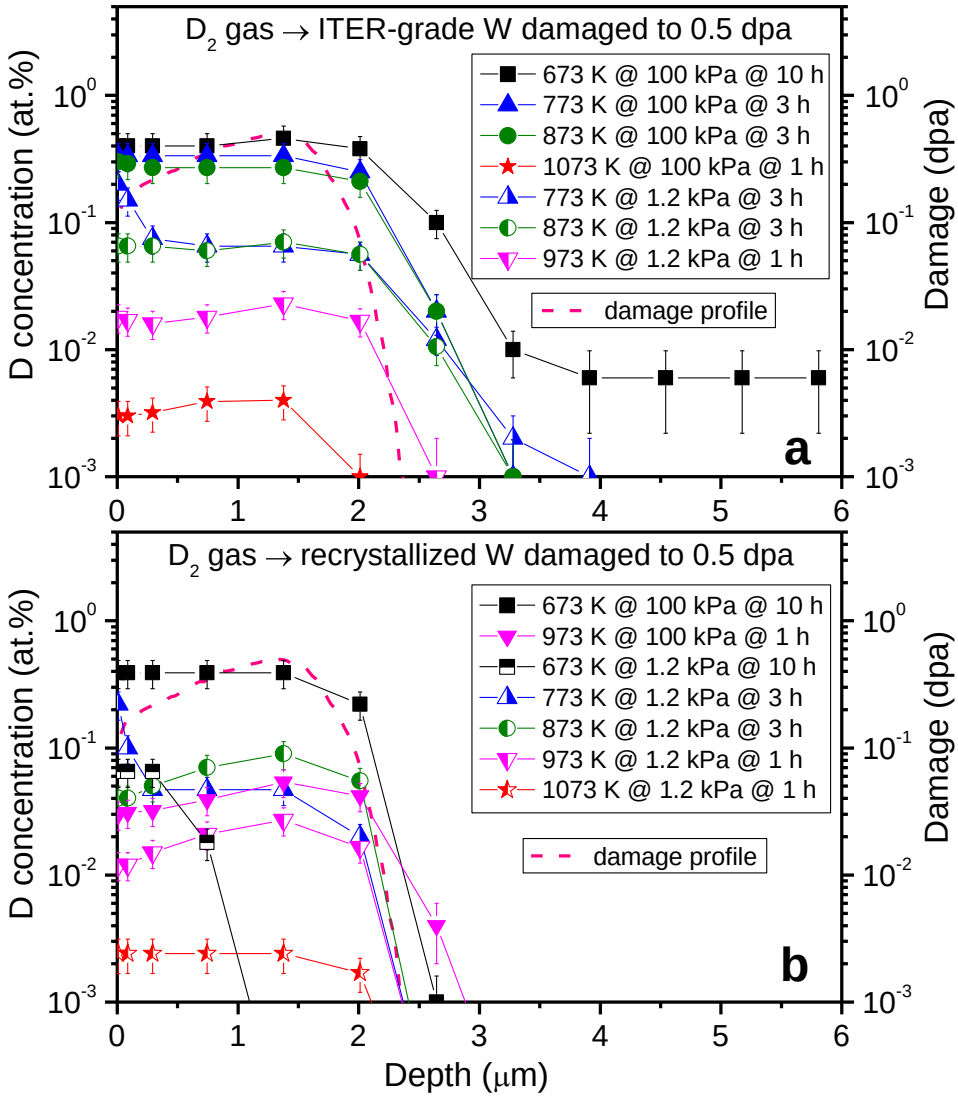

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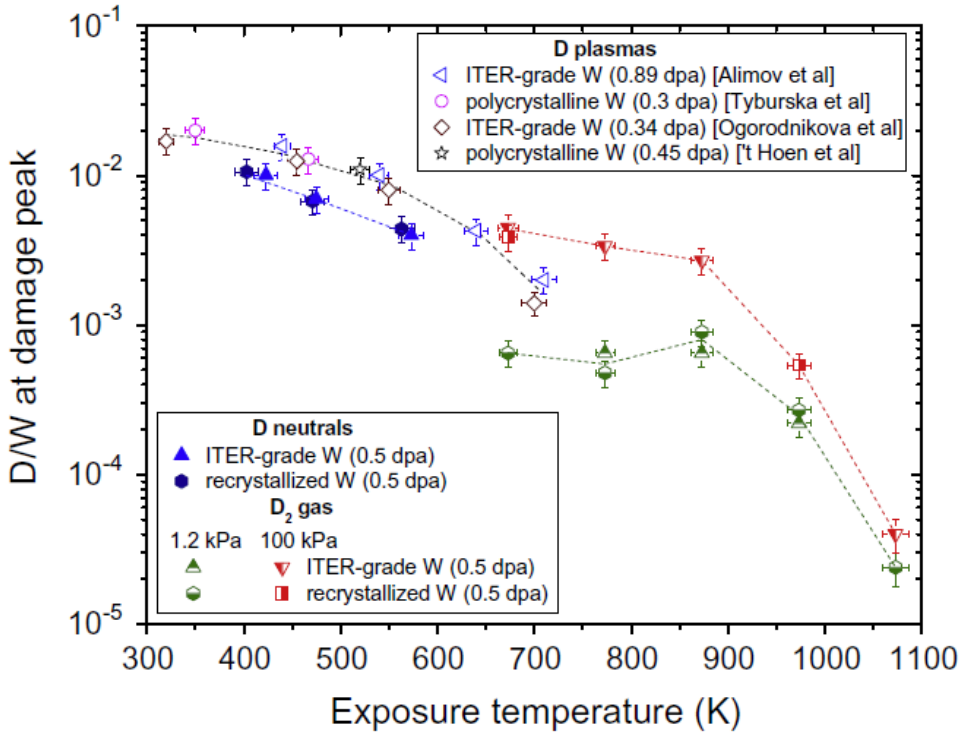

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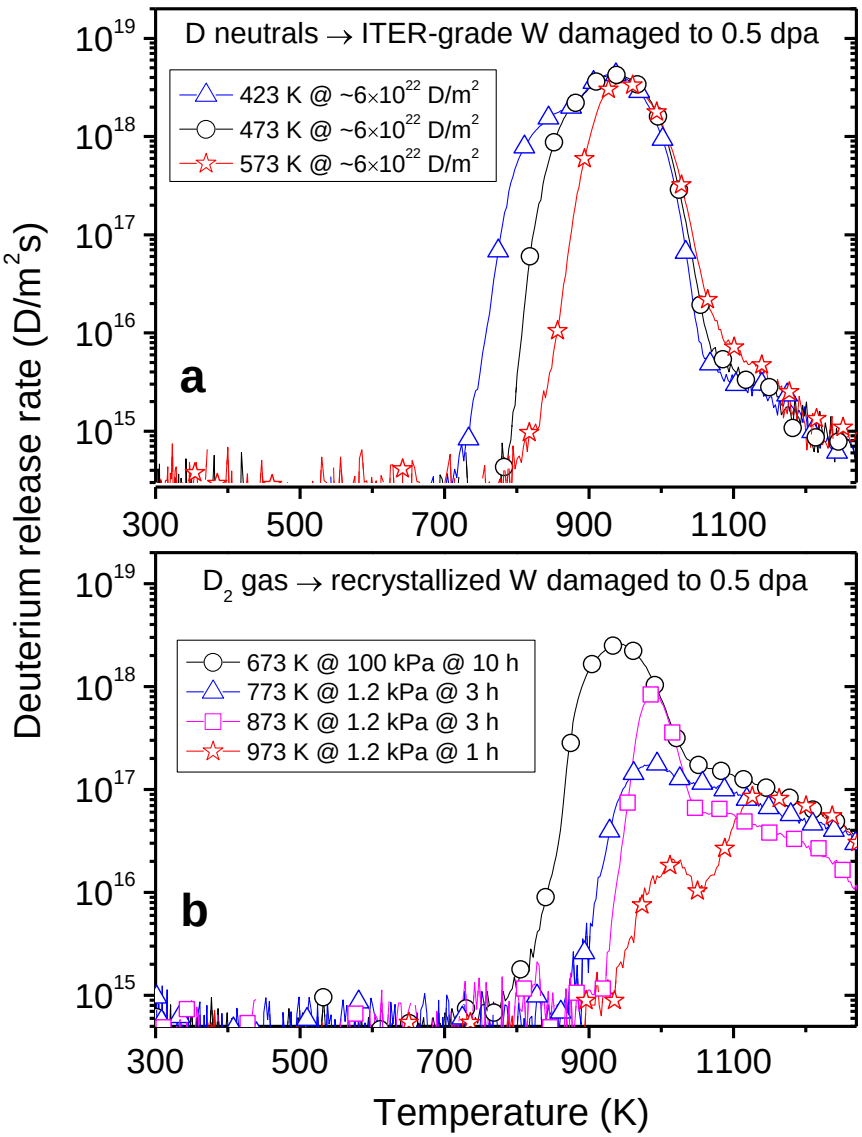

Figure 4. Thermal desorption spectra of D_2 molecules for damaged ITER-grade W exposed to D neutrals (a) and recrystallized W exposed to D_2 gas (b). Exposure temperatures, D implantation fluences, gas pressures and exposure durations are indicated in the legends. The TDS heating rate was 0.5 K/s. In both panels, the deuterium release rate is shown on a logarithmic scale.