# Reduced deuterium retention in simultaneously damaged and annealed tungsten

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## ARTICLE INFO

## ABSTRACT

Deuterium (D) retention in polycrystalline tungsten (W) with copper (Cu) ion damage concurrently produced at elevated surface temperature is investigated. An in situ heated stage held W samples at a controlled temperature up to 1243 K, which were subjected to displacement damage produced by 3.4 MeV Cu ions. D retention is subsequently explored by exposure of the W samples held at 383 K to a $D_2$ plasma ion fluence of $10^{24}$ $D^+/m^2$. Nuclear reaction analysis (NRA), utilizing the $D(^3He,p)^4He$ nuclear reaction, is used to probe the D concentration in the near surface up to 6 $\mu$m. Thermal desorption spectroscopy (TDS) is used to measure outgassed HD and $D_2$ molecules to determine the bulk D concentration. Both NRA and TDS measure a significant reduction in D retention for samples damaged at elevated temperature. TDS quantitatively shows that the lowest energy trap remains largely unaffected while higher energy traps, induced by Cu ions, are annealed and approach intrinsic concentrations as the temperature during ion damage approaches 1243 K. Analysis of TDS data yields an activation energy of $(0.10 \pm 0.02)$ eV for recovery of ion-damage induced traps at elevated temperature.

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## 1. Introduction

The trapping and retention of tritium fuel within neutron damaged plasma facing components (PFC) is of primary concern for next step fusion devices such as ITER and DEMO [1]. However, the direct study of neutron damaged material is difficult due to the time needed for activated samples to decay back to safe levels and the lack of high flux neutron sources to produce a fusion relevant fluence in a short period of time [2]. As such, the use of heavy ion damage and deuterium as a proxy for neutrons and tritium, respectively, allow for more timely experimental studies of fundamental aspects of this important problem. The reader is referred to ASTM E521 [3] for the key differences between neutron and heavy ion displacement damage.

Currently, W is the primary PFC candidate for first wall and divertor armor due to its high melting point, low H isotope retention, and resistance to sputtering [1]. Relevant PFC temperatures span 373—1273 K for tokamak devices such as ITER and DEMO [4]. Previous studies that induced ion damage near room temperature followed by subsequent annealing steps before or during plasma exposure have shown a reduction in D retention [5,6]. In order to further isolate and investigate fusion relevant damage production and recovery, heavy ion damage was performed while simultaneously heating/annealing W samples. In accordance with similar experiments [7,8], the concurrent heavy ion irradiation at elevated temperature will be referred to as dynamic annealing. In this experiment, further recovery of defects during plasma exposure is limited by holding the sample at a low temperature of 383 K. This sample temperature still allows rapid D diffusion in W [9] while limiting the release rate, thus allowing D to occupy near-surface ion induced traps. These considerations allow D to act as an effective marker for trap sites that can be probed by NRA and TDS techniques.

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## 2. Experiment

### 2.1. W sample preparation

Supplied by Midwest Tungsten, samples were cut from certified 99.95 wt% powder metallurgy polycrystalline W rod, 6 mm in diameter and 1.5 mm thick. The surfaces to be exposed to plasma were mechanically polished down to 3 $\mu$m grit, producing a mirror finish. Afterwards, the samples were cleaned in ultrasonic baths, first in acetone and then ethanol. To further relieve mechanical stress and reduce intrinsic defects, the samples were then annealed *in vacuo* below $10^{-4}$ Pa at 1173 K for 1 h. Under a scanning electron microscope, an annealed sample broken in half was observed to display elongated grains perpendicular to the surface with dimension on the order of 10 $\mu$m parallel to the surface.

### 2.2. Heavy-ion displacement damage in W

In the Ion Beam Materials Laboratory (IBML) at Los Alamos National Laboratory (LANL), a tandem ion accelerator irradiated the polished W samples with 3.4 MeV $Cu^{2+}$ ions. Cu was chosen over W, since the lighter Cu ions penetrate deeper for comparable energies. SRIM-2012 [10] was used to estimate the displacements per atom (dpa) profile as a function of the beam parameters. Per Stoller et al. [11], the "Quick" Kinchin-Pease option and a displacement damage threshold of 90 eV for W were used. A peak dpa of 0.2, achieved by a dose of $1.82 \times 10^{18}$ ions/m$^2$ with an average flux of $\sim 10^{15}$ ions/m$^2$/s, ensured the implanted Cu remained below intrinsic Cu impurity levels [12].

In general, the ion beam community follows the practice recommended by ASTM [3] when performing ion irradiations. Specifically, it recommends to use a defocussed ion beam to avoid periodic local flux variations artificially introduced when rastering a beam. However, it is also a common challenge to produce a uniform irradiated sample with the defocussed beam. We chose the rastering beam to produce a relatively large damaged sample size with excellent lateral uniformity.

### 2.3. Concurrent heating during damage

A vacuum chamber at IBML with a heated stage was used to hold W samples at 300, 573, 873, 1023, or 1243 K during Cu ion irradiation, inducing dynamic annealing. The samples were affixed to a Ni slab that housed heating elements as well as a thermocouple used to measure the sample temperature. Before Cu ion implantation, the sample holder was heated to the desired plateau temperature. To ensure damage uniformity, the ion implantation was then performed by raster scanning across an area larger than the sample. Prior to reaching the sample, the ion beam was masked to allow the center of the scan to reach the sample while indirectly measuring the current by four corner positioned Faraday cups. Once the desired Cu ion dose was reached, the beam and heating elements were shut off. The sample holder was then actively cooled with pressurized air to decrease the temperature by half the plateau/room temperature difference within a minute, limiting additional post irradiation annealing of defects.

### 2.4. $D_2$ plasma exposure

One undamaged sample, as well as the Cu ion irradiated samples, were exposed to D2 plasma with a neutral pressure of $\sim$ 0.7 Pa at UCSD in the PISCES-E device, a plasma etcher with a 13.56 MHz RF source [13]. An RF compensated Langmuir probe measured a flux of $\sim 10^{20}$ ions/m$^2$/s uniformly across the surface of the sample holder. The probe was positioned near the sample

holder and the voltage was swept as described in Ref. [14]. A total fluence of $10^{24}$ D/m$^2$ was chosen to decorate the defects throughout the damage region. During plasma exposure the sample holder was negatively biased to achieve an ion energy of 110 eV and air cooled to 383 K as measured by a thermocouple in contact with the rear of the sample. As noted by Yu [15], the molecular ion concentrations were calculated to be 0.72, 0.06, and 0.22 for $D^+$, $D2^+$, and $D3^+$ respectively.

### 2.5. Nuclear reaction analysis (NRA)

After the plasma exposure, the $D(^3He,p)^4He$ nuclear reaction was used to measure depth profiles of D concentration through NRA as prescribed by Mayer [16]. At IBML, a $^3He$ ion beam was used to probe the D implanted W samples. Increasing $^3He$ energies of 0.6, 0.8, 1.1, 1.5, 2.0, 2.5 and 3.5 MeV probed the first 6 $\mu$m. The energy spectrum of protons captured in a solid state detector was used to determine the depth distribution of the nuclear reactions. The 2 mm thick Si detector was protected from elastically scattered $^3He$ and reactant $^4He$ by a 24 $\mu$m thick Al foil. Proton counts were binned according to the detector energy resolution of 22 keV. Two software programs were employed to extract D depth profiles. SIMNRA was used to calibrate and simulate the proton energy spectrum produced from a given D depth profile [16,17]. To fit the proton energy spectra associated with each $^3He$ energy, the software requires the user to input and adjust both a D concentration and associated W layer thickness. NRADC calls upon multiple instances of SIMNRA and utilizes a Markov Chain Monte Carlo scheme to optimize fits for concentration and thickness, producing the most probable D depth profile [18].

### 2.6. Thermal desorption spectroscopy (TDS)

The thermal desorption of D from the samples' surface and total D retention throughout the bulk were measured with TDS. Samples were mounted with a thermocouple pressed against the rear surface, pumped down to a vacuum below $10^{-6}$ Pa, and heated by infrared lamps at a constant rate of 0.5 K/s before plateauing near 1300 K. D trapped in lattice defects acquires thermal energy to escape, diffuse, trap, and repeat many times before reaching the surface. In order to leave the surface, recombination to form a free molecule must occur. The partial pressures of $H_2$, HD, and $D_2$ were measured with a quadrupole mass spectrometer (QMS). A calibrated $D_2$ leak was used to convert the partial pressure from the QMS to a thermally desorbed particle flux from the sample. The total D flux was calculated as described by Yu [15], as the sum of the HD and twice the $D_2$ flux. Note that the HD flux was calibrated to the $D_2$ leak, without any further correction for ionization efficiency, and contributed an average of 25% of the total D flux.

Depending on ambient laboratory humidity, temperature, and the length of vacuum break, the installation of a sample allows water to be adsorbed on the vacuum chamber walls when exposed to atmosphere. These walls were indirectly heated while performing TDS on a sample, creating $H_2$, HD, and $D_2$ signals due to degassing water. The isotopic partial pressure is typically small for HD and $D_2$ relative to $H_2$, with a natural abundance below $10^{-3}$ and $10^{-4}$ respectively. With increasing temperature this water vapor contribution becomes large enough that it must be corrected. In order to remove this background signal, the dominant $H_2$ is scaled separately to the HD and $D_2$ signals. After the initial 0.5 K/s temperature ramp, Fig. 2 demonstrates the use of several additional temperature ramps to aid in the linear scaling and offset of $H_2$ to HD and $D_2$.