

# Depth distribution of deuterium in single- and polycrystalline tungsten up to depths of several micrometers

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## Abstract

Depth profiles of deuterium trapped in W single crystals and polycrystalline W irradiated with 200 eV D ions at 300–323 K have been measured up to a depth of 7  $\mu\text{m}$  using the  $\text{D}(\text{}^3\text{He}, \text{p})\text{}^4\text{He}$  nuclear reaction in a resonance-like technique. The proton yield as a function of incident  $\text{}^3\text{He}$  energy was measured and the D depth profile was obtained by deconvolution of the measured proton yields using the program SIMNRA. The depth at which deuterium is retained can be tentatively divided into three zones: (i) the near-surface layer (up to a depth of  $\sim 0.2\ \mu\text{m}$ ), (ii) the sub-surface layer (from  $\sim 0.5$  to  $\sim 2\ \mu\text{m}$ ), and (iii) the bulk ( $> 5\ \mu\text{m}$ ). Low-energy D ion irradiation modifies the W structure to depths of up to about 5  $\mu\text{m}$ , both for W single crystals and polycrystalline W. Up to this depth trapping sites are created at a fluence of  $5 \times 10^{22}/\text{m}^2$  for the retention of deuterium at about 0.1 at.%.  
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## 1. Introduction

Due to its favorable physical properties, like low erosion yield and high melting temperature, tungsten is foreseen as plasma-facing material in fusion devices, such as ITER [1]. Of special interest are the hydrogen transport and trapping properties, as they may have a significant impact on tritium inventory. Available data indicate that hydrogen retention in tungsten depends on both the type of tungsten structure and implantation conditions [2–18]. Information about the total amount of hydrogen retained in W materials and about hydrogen detrapping

energies can be obtained from thermal desorption measurements. Measurements of hydrogen depth profiles can give detailed information about the depth distribution of defects which are responsible for hydrogen trapping and, therefore, can help to understand the mechanisms of hydrogen–material inter-actions.

In this work we report measurements of depth profiles of deuterium trapped within the 7  $\mu\text{m}$  thick sub-surface layers of different tungsten materials irradiated with 200 eV D ions. The  $\text{D}(\text{}^3\text{He}, \text{p})\text{}^4\text{He}$  nuclear reaction at different  $\text{}^3\text{He}$  energies was used for quantitative depth profiling.

## 2. Experimental

Two types of W specimens with dimensions of  $12 \times 14\ \text{mm}^2$  and different thicknesses were investigated:

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- (i) Single crystal tungsten specimens with a purity of 99.99 wt% produced by double electron-beam zone melting (State Institute of Rare Metals, Moscow). The macro-crystallite sizes were in the range of 10–20 μm. The specimens were cut from a W rod by spark cutting and were 0.8–0.9 mm thick.
- (ii) High purity (99.6 at.%) polycrystalline tungsten foils, 0.3–0.4 mm thick, produced by Plansee AG (Reutte, Austria), a reduced-rolled, powder-metallurgy product. The grain sizes were estimated to be in the range of 1–20 μm.

The irradiated surfaces of the single crystals and polycrystalline specimens were mechanically and electrochemically polished. After polishing the samples were annealed at 1573 K for 3.5 h in a vacuum chamber with a background pressure of  $\sim 2 \times 10^{-4}$  Pa during annealing.

The irradiation with 600 eV  $D_3^+$  (200 eV/D) was performed in a vacuum chamber connected to a high-current ion source [19] at normal ion incidence. For better ion source performance, a 3600 eV  $D_3^+$  ion beam was extracted from the ion source, magnetically analyzed, and decelerated in front of the samples by a positive target bias of 3000 V to achieve 600 eV  $D_3^+$ . The ion flux was  $(3.6 \pm 1.1) \times 10^{19}$  D/m<sup>2</sup>s. This ion beam was applied for the D ion irradiation of polycrystalline specimens. During irradiation, the polycrystalline specimens were heated by the ion beam up to 323 K.

A small fraction of neutral particles ( $\sim 1.5\%$ ) was present in the 3600 eV  $D_3^+$  beam after passing the magnet [19]. These neutrals were not decelerated by the target bias. Just to be sure that the W single crystals were implanted with D ions at energies below the threshold for displacement, an extracted 1000 eV  $D_3^+$  ion beam and a deceleration bias of 400 V were used for the D ion irradiation. In this case the ion flux was  $(1.9 \pm 0.2) \times 10^{18}$  D/m<sup>2</sup>s and the irradiation temperature was 300 K.

The D concentration within the near-surface layer (at depths up to  $\sim 0.6$  μm) was measured by means of the  $D(^3\text{He},\alpha)H$  reaction at a  $^3\text{He}$  energy of 0.69 MeV, and the  $\alpha$  particles were energy-analyzed with a small-angle surface barrier detector at the laboratory scattering angle of 102°. The  $\alpha$  spectrum was transformed into a D depth profile using the program SIMNRA [20].

To determine the D concentration at larger depths, an analyzing beam of  $^3\text{He}$  ions with energies varied from 0.69 to 4 MeV was used. The protons from the  $D(^3\text{He},p)^4\text{He}$  nuclear reaction were counted using a wide-angle proton detector placed at an angle of 135°. The  $D(^3\text{He},p)^4\text{He}$  nuclear reaction has a broad maximum at around 0.63 MeV, which can be used for resonant depth profiling. In order to determine the D concentration profile in deeper layers, the computer program SIMNRA was used for the deconvolution of the proton yields measured at different  $^3\text{He}$  ion energies. A

deuterium depth distribution was assumed taking into account the near-surface depth profile obtained from the  $\alpha$  particles spectrum, and the proton yield as a function of incident  $^3\text{He}$  energy was calculated. The form of the D depth profile was then varied using an iterative technique until the calculated curve matched the measured proton yields [21].

Deuterium profiling at depths larger than 7 μm was performed by removing the surface layer on the irradiated side by electrochemical etching in 2 wt% NaOH aqueous solution. The etching was performed through a mask pressed to the tungsten surface, and the crater depth was measured with a profiler.

The surface morphology was investigated by scanning electron microscope (SEM).

### 3. Results and discussion

Depth distributions of deuterium retained in W single crystals and polycrystalline W irradiated with 200 eV D ions to different fluences are shown in Figs. 1 and 2, respectively. The depth at which deuterium is retained can be tentatively divided into three zones: (i) the near-surface layer (up to a depth of  $\sim 0.2$  μm), (ii) a

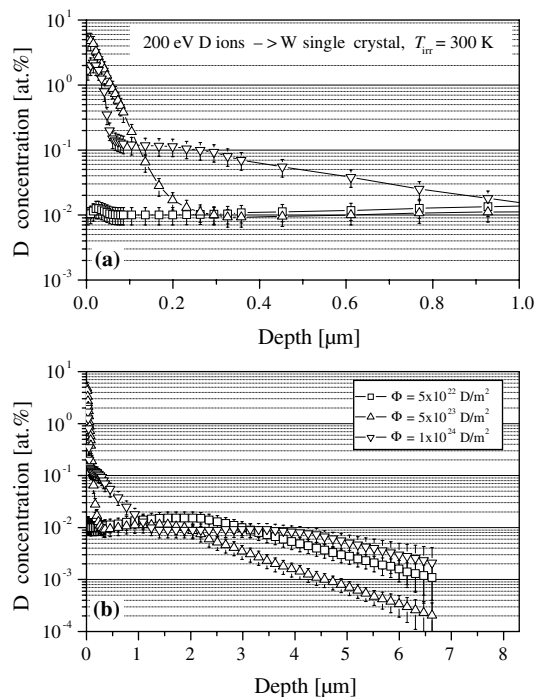


Fig. 1. Depth profiles of deuterium trapped in the near-surface layer (a) and in the bulk (b) of W single crystals irradiated at 300 K with 200 eV D ions to different fluences. Note the different depth and concentration scales in parts (a) and (b).

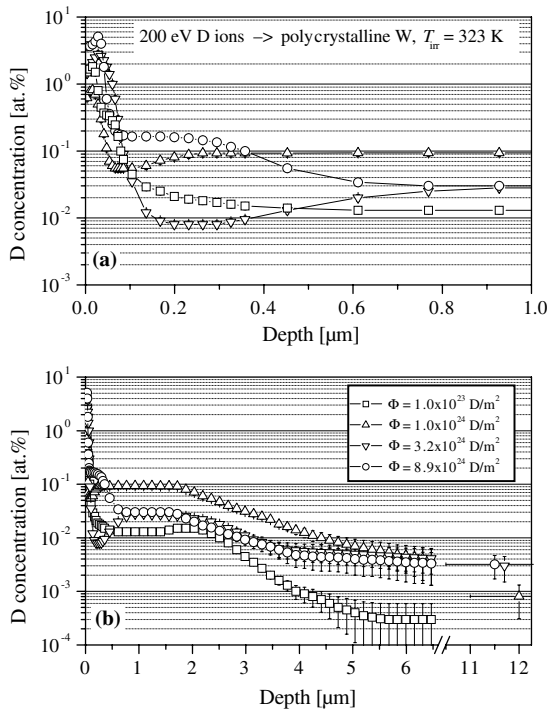


Fig. 2. Depth profiles of deuterium trapped in the near-surface layer (a) and in the bulk (b) of polycrystalline W irradiated at 323 K with 200 eV D ions to different fluences. Note the different depth and concentration scales in parts (a) and (b).

sub-surface layer (from  $\sim 0.5$  to  $\sim 2 \mu\text{m}$ ), and (iii) the bulk ( $> 5 \mu\text{m}$ ).

In W single crystals, an increase of the ion fluence from  $5 \times 10^{22}$  to  $5 \times 10^{23} \text{ D/m}^2$  leads to an increase of the near-surface concentration  ${}^{\text{near}}C_{\text{D}}$  by a factor of more than 100, from 0.01 to 2 at.% (Fig. 1(a)). The drastic increase of the D concentration can only be explained by a sudden structural change during the low-energy D ion irradiation. At a fluence of  $1 \times 10^{24} \text{ D/m}^2$ , the concentration  ${}^{\text{near}}C_{\text{D}}$  reaches 6 at.%. The concentration within the sub-surface layer is about 0.01 at.% for all ion fluences used (Fig. 1(b)), whereas the D concentration in the bulk is below  $10^{-4}$  at.%.

In polycrystalline W specimens, the D concentration in the near-surface layer is in the range 1–5 at.% for fluences increasing from  $1 \times 10^{23}$  to  $8.9 \times 10^{24} \text{ D/m}^2$  (Fig. 2(a)). Within the sub-surface layer, as the fluence is increased to  $1 \times 10^{24} \text{ D/m}^2$ , the D concentration  ${}^{\text{sub}}C_{\text{D}}$  reaches its maximum value of 0.1 at.%. A further fluence increase leads to a decrease in the D concentration, and at high ion fluences ( $\geq 3.2 \times 10^{24} \text{ D/m}^2$ ) the value  ${}^{\text{sub}}C_{\text{D}}$  is  $\sim 0.03$  at.% (Fig. 2(b)). Blisters were observed on the surface of the polycrystalline W specimens at ion fluences above  $1 \times 10^{24} \text{ D/m}^2$  (Fig. 3). The D concentration in the bulk increases with the ion fluence and reaches a

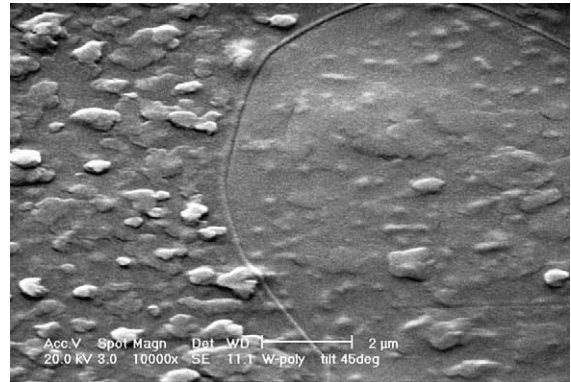


Fig. 3. SEM images of polycrystalline W surfaces irradiated with 200 eV D ions at 323 K to a fluence of  $8.9 \times 10^{24} \text{ D/m}^2$ .

steady state value of  $\sim 0.003$  at.% at a fluence of  $1 \times 10^{24} \text{ D/m}^2$  (Fig. 2(b)).

The release of deuterium from the sub-surface layer of polycrystalline W may be connected with the appearance of blisters and accompanying porosity development. Note that blisters were not observed on W single crystal surfaces, and the D concentration did not show the effect of decreasing with increasing fluence.

The high deuterium concentration in the sub-surface layer and the formation of blisters allows the conclusion that irradiation with 200 eV D ions at 300–323 K modifies the surface to depths of up to about  $5 \mu\text{m}$ , both for W single crystals and polycrystalline W. This range is much larger than the deuterium implantation range. It has been shown recently that on the surface of a W foil exposed to a low energy ( $\sim 200 \text{ eV}$ ) and high-flux ( $> 10^{21} \text{ m}^{-2} \text{ s}^{-1}$ ) D plasma, blisters were formed [17]. In the bulk of the blister lids deuterium was accumulated in the form of  $\text{D}_2$  molecules, as could be shown by Alimov et al. [10] using a sputter-RGA technique. Vacancy clusters and voids were formed by the low-energy ion irradiation [18]. In our case, blisters are also observed on the surface of the polycrystalline specimens. However, the energy of the D ions of 200 eV, is well below the energy threshold for displacement of W atoms. A review of hydrogen bubbles in metals by Condon and Schober [22] outlines some possible cavity formation mechanisms. The mechanism of near-surface plastic deformation caused by deuterium supersaturation within the near-surface layer was considered by Poon [23] for the explanation of TDS spectra for W single crystals irradiated with 500 eV D ions.

This mechanism is also proposed for the interpretation of the present results. During irradiation the D concentration in the implantation zone greatly exceeds the solubility limit and stresses the matrix lattice until plastic deformation with formation of voids and vacancy clusters occurs to alleviate these tensions. This deformation

is assumed to be responsible for the sudden increase in trapping sites for deuterium and the concurrent accumulation of deuterium, both in the form of  $D_2$  molecules and D atoms. According to van Veen et al. [24], the  $D_2$  gas inside the voids is expected to be released during annealing at 400–600 K (dissociation energy  $\sim 1.4$  eV), whereas the D atoms bound on the inner surface of voids (binding energy  $\sim 2.1$  eV) is expected to be released at 700–900 K [24]. From depth profiling it can be concluded that the concentration of  $D_2$  filled voids within the sub-surface layer of polycrystalline W specimen is at least one order of magnitude higher than in W single crystals (compare Figs. 1 and 2). The initial structure of the W materials plays a major role in the stress-induced void formation. Possibly, the grain boundaries serve as preferential sites for void nucleation and growth.

Changes in the D concentration at high ion fluences result from W structure modifications caused by the low energy ion irradiation. As the ion fluence increases, the concentration of gas-filled voids within the sub-surface polycrystalline layer (1–5  $\mu\text{m}$ ) increases, and after certain fluence interconnected porosity starts develop. This leads to the release of a fraction of the molecular deuterium. This is demonstrated by the decrease of the D concentration at  $\Phi > 1 \times 10^{24}$  D/m<sup>2</sup> (Fig. 2). Deuterium retaining in the bulk (at depths above 6  $\mu\text{m}$ ) is thought to be in form of D atoms trapped at intrinsic defects.

The modification of the W single crystal structure happens at an ion fluence below  $5 \times 10^{22}$  D/m<sup>2</sup>. At higher fluences the structure of the sub-surface layer remains unaltered. Only the structure of the near-surface layer (up to 1  $\mu\text{m}$ ) varies abruptly with increasing fluence (Fig. 1(a)). It has been recently suggested by Poon [23] that in W single crystal irradiated with 500 eV D ions at 300 K, deuterium is trapped at vacancies with trap energies of 1.4 and 1.2 eV for the first and second D atoms, respectively. The trap energy of 1.4 eV agrees well with the dissociation energy for  $D_2$  molecules accumulated inside voids [24]. For further identification of the type of defects (vacancies or voids) responsible for D trapping, additional measurements able to profile D atoms and  $D_2$  molecules [10,18] are required.

#### 4. Summary

Depth profiles of deuterium trapped in W single crystals and polycrystalline W samples irradiated with 200 eV D ions at 300–323 K have been determined up to a depth of 7  $\mu\text{m}$  using the  $D(^3\text{He},p)^4\text{He}$  reaction in a resonance-like technique. The proton yield as a function of incident  $^3\text{He}$  energy was measured and the D depth profile was obtained from the measured proton yields by deconvolution with the program SIMNRA.

The depth at which deuterium is retained can be tentatively divided into three zones: (i) the near-surface layer (up to a depth of  $\sim 0.2$   $\mu\text{m}$ ), (ii) the sub-surface layer (from  $\sim 0.5$  to  $\sim 2$   $\mu\text{m}$ ), and (iii) the bulk ( $> 5$   $\mu\text{m}$ ). The D concentration at high ion fluences  $\geq 1 \times 10^{24}$  D/m<sup>2</sup> decreases from several at.% in the near-surface layer to below  $10^{-4}$  at.% for W single crystal and  $3 \times 10^{-3}$  at.% for polycrystalline W in the bulk. Blister formation at high fluences is observed for polycrystalline W, but not for W single crystals.

D ion irradiation with ion energies well below the displacement threshold modifies the W structure to depths of up to about 5  $\mu\text{m}$ , both in W single crystals and polycrystalline W. Plastic deformation of the W matrix caused by deuterium supersaturation within the near-surface layer is proposed as explanation of the present results.

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