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Letter

Suppression of hydrogen-induced blistering of tungsten by pre-irradiation at low temperature

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Abstract

Blistering of tungsten (W) surfaces due to deuterium (D) implantation was investigated by a sequence of exposures at two different temperatures—230 and 450 K—and by the reversed sequence. A single exposure at 230 K leads to a high areal density of small dome-shaped blisters (up to 3 μm in diameter) together with much smaller flat-topped structures, while a single 450-K exposure produces large dome-shaped blisters up to 40 μm in diameter without the flat-topped structures. Most of the small dome-shaped blisters from 230 K exposure disappeared after annealing at 450 K for 17 h, but survived and even grew in size if the surface was exposed to D plasma during annealing. Sequential exposure at the two temperatures reveals a non-commutative behaviour: after a first exposure at 450 K the second exposure at 230 K leads to superposition of the observed blister structures without changing the large blisters from the first exposure. By contrast, a first exposure at 230 K almost completely suppresses the formation of large blisters during a second exposure at 450 K. Obviously, the presence of the small blisters strongly influences the penetration of D into the W bulk.

Keywords: Plasma-surface interaction, hydrogen blistering, tungsten, low temperature

Tungsten (W) is presently the most promising plasma-facing material foreseen for the ITER divertor. Here, the intense bombardment with energetic particles will induce strong surface modifications caused by the implantation of hydrogen isotopes from the plasma. One such effect is the formation of gas-filled bubbles and cavities [1], which are often visible as blisters on the material surface. W blistering could lead to instability of the plasma if blisters burst and eject large amounts of gas and/or material from the blister cap [2]. In addition, an increasing inventory of hydrogen isotopes in the near-surface region of the plasma-facing components, particularly of the radioactive fusion fuel tritium, will result in great concerns with respect to safety and cost efficiency [3]. Found not only very often on W surfaces exposed to laboratory deuterium (D) plasmas under different conditions [4–11], blisters on W have also been observed on material samples exposed in fusion experiments [12, 13]. Up to now, most experiments were carried out at sample temperatures of 300 K or higher. This article reports first measurement of W samples exposed to D plasma at low temperature, i.e. 230 K, the lower limit temperature for the present experimental set-up. Exposure at 230 K shows previously unseen morphological features that were so far not observed on W surfaces exposed to low D fluxes at temperatures higher than 300 K. However, at high-flux exposure similar features have been observed even at temperature of 500 K and higher [10, 11]. Another new aspect is the interaction of blister populations nucleated at different temperatures. We exposed W samples to D plasma at sample temperatures of 230 and 450 K, and investigated the effect of exposing W samples to D plasma sequentially at these two temperatures. We will show that the blistering of the W surface depends not only strongly on temperature, but also on the order in which a sample is exposed at different temperatures.

Polycrystalline, hot-rolled W samples ($15 \times 12 \times 0.8$ mm^3, 99.97 wt% purity, Plansee SE, Austria), with sub-grain sizes of the order of 1 μm [14], were mechanically polished to a mirror-like finish and annealed in vacuum at 1200 K for 2 h. D implantations were performed in a quantified plasma source [15] delivering primarily D_3^+ ions (94%) with minor contributions of D_2^+ (3 %) and D^+ (3 %). The applied ion

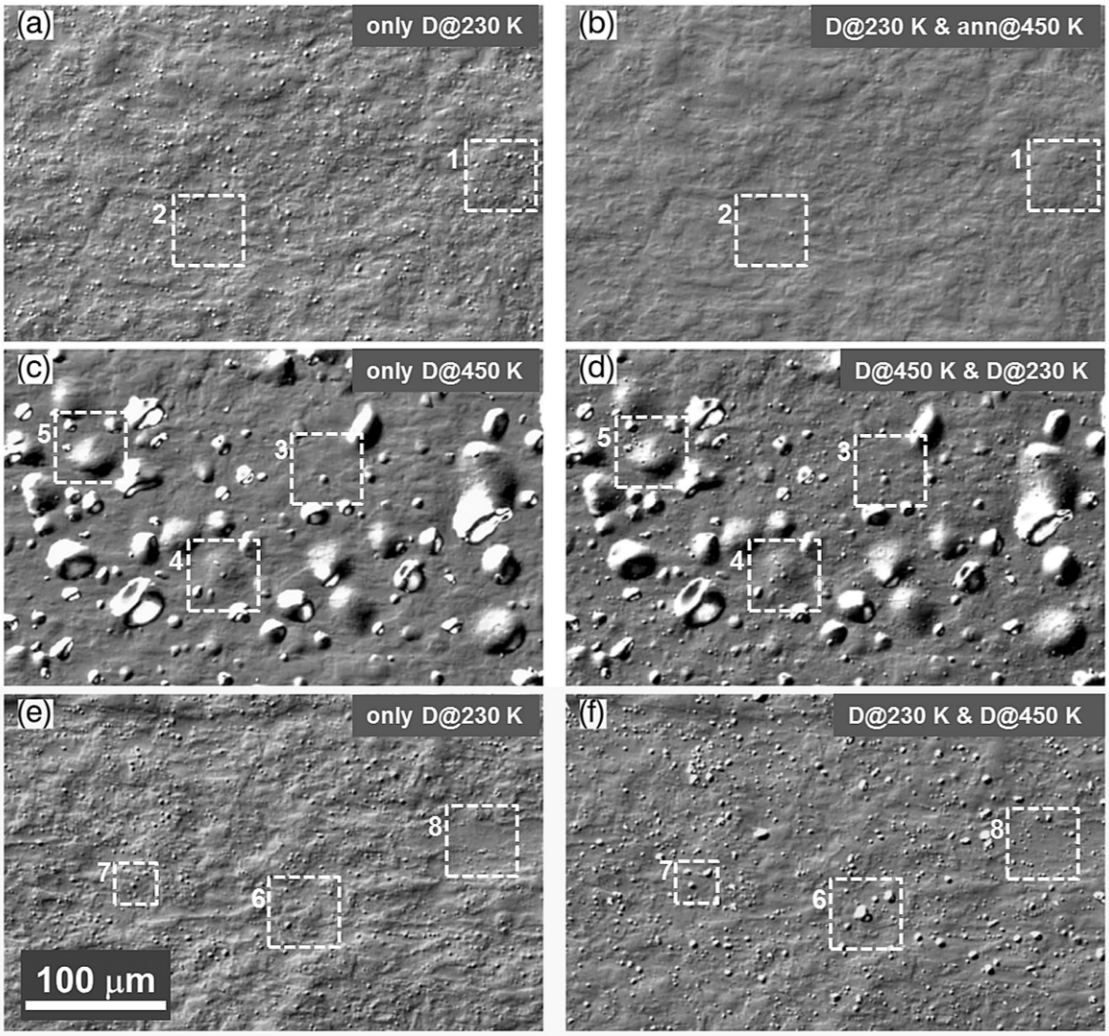

Figure 1. Surface morphology (CLSM) of blistered polycrystalline W after D plasma exposure with a fluence of $6 \times 10^{24}\,\mathrm{D\,m^{-2}}$ (*a*), (*c*) and (*e*) and the identical area with additional treatment (*b*), (*d*) and (*f*): (*a*) at 230 K only; (*b*) the identical area as in (*a*) after annealing at 450 K for about 17 h; (*c*) at 450 K only; (*d*) the identical area as in (*c*) with additional exposure at 230 K; (*e*) at 230 K only; (*f*) the identical area as in (*e*) with additional exposure at 450 K. All the CLSM sub-figures share the same scale bar shown in figure 1(*e*). Small blisters shown in (*a*), (*d*), (*e*) and (*f*) have diameters up to 3 μm and heights up to 100 nm, and medium ones in (*c*), (*d*) and (*f*) have 4–10 μm in diameter and up to a few hundreds nanometres in height. The large blisters shown in (*c*) and (*d*) have 30–40 μm in diameter and up to 2 μm in height.

bombardment energy of ∼215 eV corresponds to a mean energy of 72 eV per D for the dominant ion species D_3^+. The used D flux was $9.9 \times 10^{19}\,\mathrm{D\,m^{-2}\,s^{-1}}$. All individual D exposure steps were carried out with the identical D fluence of $6 \times 10^{24}\,\mathrm{m^{-2}}$. The accumulation of this D fluence took ∼17 h. The two investigated sample temperatures (230 K and 450 K) were controlled using a thermocouple integrated in the substrate holder just underneath the samples and two independent cooling circuits (ethanol for 230 K and silicon oil for 450 K).

The sequentially loaded W samples were first exposed to D plasma at T_1 (being either 230 or 450 K) and then exposed additionally applying the same fluence at T_2 (being the other temperature than T1) with one half of the sample surface covered by a thin W foil. By this method, one sample with two different surface areas was produced: the covered half was loaded with a fluence of $6 \times 10^{24}\,\mathrm{D\,m^{-2}}$ at T_1 and held at T_2 for the same duration as the exposure; the uncovered half was exposed to twice the fluence from the two exposures. The surface morphology of the samples before and after each step of D exposure was investigated by a confocal laser scanning microscope (CLSM, Olympus LEXT OSL 4000) and scanning electron microscopy (SEM) assisted by focused-ion-beam (FIB) cross-sectioning (Helios NanoLab 600, FEI), by which the three-dimensional information as well as the cross-section of the blisters can be provided.

Images taken by CLSM from blistered surfaces are compiled in figure 1. Figures 1(*a*), (*c*) and (*e*) show areas after a single exposure and the corresponding figures 1(*b*), (*d*) and (*f*) are the identical areas after additional treatments. The background structures visible in each CLSM picture are the surface morphologies produced by the chemo-mechanical polishing processes with heights always below 100 nm. Special regions of interest (ROI) are marked by the dashed rectangles. The ROI's in corresponding figures (left to right in figure 1) mark the identical locations.

Figures 1(*a*) and (*b*) show the identical area from the surface exposed first to D plasma at 230 K (figure 1(*a*)) and

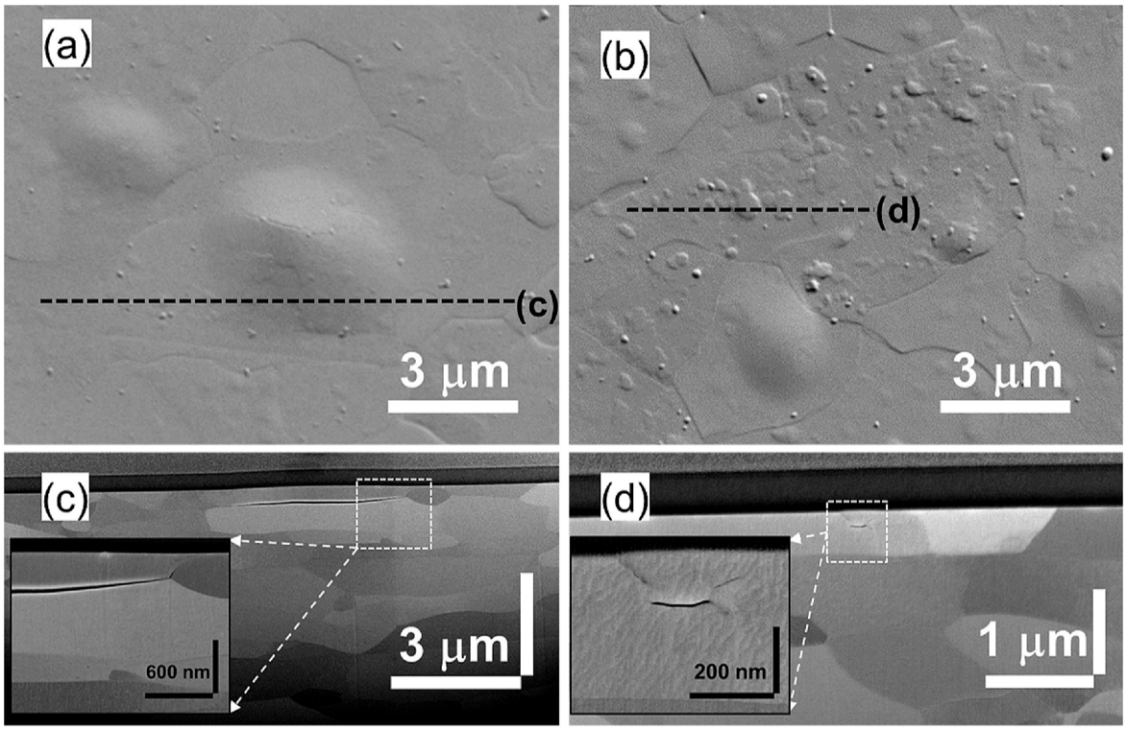

Figure 2. Polycrystalline W exposed to D plasma with a fluence of 6×10^{24} D m^{-2} at 230 K: (*a*) surface topography (SEM) of small dome-shaped blisters; (*b*) surface topography of protrusions; (*c*) cross-section at the position indicated by the dashed line in (*a*); (*d*) cross-section at the position indicated by the dashed line in (*b*). Both dome-shaped blisters with cavities at grain boundaries and sharp-edged protrusions with in-grain cracks were found. The surfaces in (*c*) and (*d*) were protected by an amorphous Pt : C layer before cutting.

then annealed at 450 K for about 17 h (figure 1(*b*)). D plasma exposure at 230 K results in a large areal density of small, dome-shaped blisters with diameters up to 3 μm (figure 1(*a*)) and heights up to 200 nm (figure 2(*a*)). Cross-sectioning of these small dome-shaped blisters (figure 2(*c*)) shows that the corresponding cavities are located at grain boundaries in depths of less than 1 μm. Furthermore, it was confirmed by the same technique as in [6] that these cavities are gas-filled: drilling a hole with the focused ion beam into the blister cap leads to a sudden elastic relaxation of the blister. SEM images taken at higher magnification reveal a lot of small flat-topped and partially irregular-shaped structures (<300 nm) with sharp edges formed within some but not all grains (figure 2(*b*)) with heights up to a few tens nm (figure 2(*d*)). These flat-topped structures will in the following be called *protrusions*, while the dome-shaped features will be called *blisters*. Noteworthy is the fact that most blisters are only found in grains without such protrusions. Unlike for the blisters, cross-sectioning of protrusions shows that the underneath cracks are within isolated grains in depths of about 200 nm (figure 2(*d*)). Similar structures have been observed in W surfaces under high-flux exposures [10, 11], but we have not found such in-grain cracks in W surfaces after exposure under comparable bombardment conditions at higher (>290 K) sample temperatures [6–9]. After annealing (figure 1(*b*)), most of the small blisters have disappeared, a few of them got smaller (see, e.g. lower and upper right corner in ROI-1), and very few remained unchanged (see, e.g. the right one in ROI-2). Interestingly, SEM imaging shows no detectable change for the protrusions. The disappearance or shrinking of blisters indicates that the corresponding deformations were elastic and can relax after D release due to annealing. The unchanged blisters and the protrusions are due to plastic deformation. Because D_2molecules cannot diffuse through bulk W [6, 8, 16], the release of D_2 from the blister cavity requires either presence of cracks open to the surface or dissociation of D_2 at the inner surface followed by diffusion as atoms to the surface, and desorption as molecule. Our results clearly show that 450 K is high enough for the D_2 release from the blister cavities.

Figures 1(*c*) and (*d*) show the same area from a W surface which was first exposed to D plasma at 450 K (figure 1(*c*)) and then exposed additionally at 230 K (figure 1(*d*)). Most of the blisters in figure 1(*c*), with typical diameters of 30–40 μm and heights up to 2 μm, are almost ten times larger than those from exposure at 230 K (figure 1(*a*)). In addition to the large blisters we also find a few small (up to 3 μm in diameter) and some medium-sized (4–10 μm in diameter, see, e.g. ROI-3) blisters. Some of the small blisters are observed on top of large ones (see, e.g. ROI-4). However, no protrusions are found anywhere on the surface after exposure at 450 K only. The subsequent exposure at 230 K results in the appearance of many additional small blisters (figure 1(*d*)) together with the flat-topped protrusions (not shown). Interestingly, the blisters from the first exposure are unchanged in both lateral dimensions and heights as confirmed by evaluating the three-dimentional CLSM images. However, a comparable experiment with two consecutive exposures at 450 K (not shown) clearly shows growth of the large blisters from the first exposure due to the second exposure at 450 K. The newly emerged small blisters and protrusions after the second exposure at 230 K

(figure 1(*d*)) are found not only in flat areas (e.g. ROI-3), but also on top of large blisters from the first exposure (e.g. ROI-4&5). They are in both size and density similar to those from the 230 K exposure only (figure 1(*a*)). From this apparent superposition of both blister distributions we conclude that the nucleation depth for the small blisters from the 230 K exposure is much smaller than that of the large ones from the 450 K exposure. Cross-sectioning of several blisters with typical sizes showed that the blister cavities for the large blister are ~3 μm in depth and less than 1 μm for the small ones (figure 2(*c*)). Actually, our data regarding the depth of blister cavities are in good agreement with those after D implantation at 300 K [6, 7], 370 K [8] and 500 K [9]. A calculation of the diffusion length for D in W at 230 K according to a one-dimensional-diffusion model without trapping influence based on Fraunfelder's [16] diffusion coefficient yields a value of about 12 μm within ~17 h, which is much larger than the blister nucleation depth at 450 K (3–4 μm). Accordingly, the D implanted during the second exposure should be able to reach the nucleation depth of the large blisters and inflate them. This is obviously not the case because the blisters do not grow during the second exposure at 230 K while they grow if the second exposure is also performed at 450 K. These findings indicate that a simple one-dimensional-diffusion model is insufficient for describing the present case and that the influence of traps on the D diffusion has to be taken into account. The interaction of diffusing D with traps leads to a reduction of the effective diffusion coefficient [17, 18], but the details are too complicated to be discussed here. Another noteworthy point is the similar blister population from the second 230 K exposure compared with that from the single 230 K exposure only (figure 1(*a*)). It seems that the first 450 K exposure has little influence on the blister formation during the second exposure at 230 K, although the pre-existing trap sites in the topmost 3 μm have already been partially decorated by D during the first exposure. Obviously, the decoration of such defects, namely the trapped D does not affect the following blister formation at 230 K. It is often hypothesized [1, 11, 17] that a relatively high local hydrogen concentration (higher than a critical value) is required for blister nucleation. From this, we conclude that for blister nucleation the solute D concentration during D loading plays a much more important role than the trapped D.

Figures 1(*e*) and (*f*) show an area which was first exposed at 230 K (figure 1(*e*)) and then additionally at 450 K (figure 1(*f*)). Comparable to figures 1(*a*), (*e*) shows a high areal density of small blisters after the first exposure. After the second exposure at 450 K (figure 1(*f*)) the number of small blisters remains largely unchanged, but most of them increased in size and some new medium-sized blisters (5–8 μm in diameter) did appear (several in ROI-6). In ROI-7 one of the blisters has even disappeared while three other small blisters have increased in size. In some areas, small blisters with sizes comparable to those from the first exposure show up after the second exposure, preferably in areas without previous blistering (ROI-8). The growth of the small blisters from the first exposure is attributed to further uptake of D in the cavities during the second exposure at 450 K. Unlike the case from figures 1(*c*) to (*d*), here the deuterons implanted during the second exposure are able to reach the nucleation depth of the small blisters from the first exposure and accumulate in the cavities due to a 4 orders of magnitude higher diffusivity at 450 K than at 230 K. Only a few blisters disappeared (e.g. one in ROI-7) or remained unchanged after the second exposure. Disappearance could be explained by cracking and full relaxation while unchanged blisters might be due to plastically deformed and cracked blisters from the first exposure.

Another interesting phenomenon is the survival of the small blisters from the first exposure if we compare figures 1(*b*) and (*f*). In principle, the surface shown in figure 1(*f*) should experience the same annealing effect as the surface in figure 1(*b*). However, most of the small blisters survived and some of them even grew in size if the surface is exposed to D plasma during annealing. Obviously, the plasma loading is either able to compensate the loss from cavities due to annealing or it can refill blisters which were depleted during annealing (heating up of the sample to 450 K prior to starting the plasma takes about 30 min). In agreement with the annealing induced disappearance of blisters, we suggest that the dominating mechanism for D release is dissociation and diffusion to the topmost surface instead of cracking.

Most interesting is the comparison of figure 1(*f*) with figure 1(*d*). Both of these shown surfaces have experienced one exposure at 230 K and one at 450 K, but with the reversed temperature sequence. It is evident that in figure 1(*f*) the number and size of newly formed large blisters are significantly reduced compared to figure 1(*d*). Pre-exposure at 450 K generates blisters with diameters of ~40 μm and no change has been found for these large blisters after the second exposure at 230 K; while small blisters from the first exposure at 230 K grew to medium size after the second exposure at 450 K. But these medium-sized blisters are still far smaller than the large ones formed by the 450 K only exposure. Obviously, pre-exposure at 230 K has significantly suppressed the formation of large blisters in the following exposure at 450 K. As mentioned above, it is assumed that a relatively high local solute D concentration near the nucleation points is required to form blisters. However, it appears that the blistered layer at smaller depth from the first exposure at 230 K can strongly reduce D penetration to larger depth, either by uptake of diffusing D (e.g. by the growth of blisters or protrusions) or by enhanced reemission of the D, e.g. by cracks open to the surface. Without a sufficiently high D diffusion flux penetrating beyond the blistered layer, the solute D concentration near the nucleation points responsible for the large blisters cannot reach the critical value and thus cannot nucleate or inflate the large blisters. Unfortunately, from the present results we are not able to distinguish between the two mechanisms.

In summary, we have shown a strongly temperature-dependent blistering on W surfaces and a non-commutative behaviour of blister populations sequentially exposed to D plasma at different temperatures. Surface features on a W surface after a single exposure at 230 K are very different in population, distribution, sizes and shapes from those at 450 K. Most of the small dome-shaped blisters produced at 230 K disappeared during annealing at 450 K for 17 h, but survived or even grew in size if exposed to D plasma at this temperature. The significant suppression of the formation of large blisters at 450 K by pre-exposure at 230 K is attributed to a strongly

reduced D penetration beyond the blistered layer from the first exposure. From the observed superposition of the blister structures from the low-T exposure without changing the large blisters from the preceding high-T exposure we conclude that the trapped D concentration is not the dominant factor for blister nucleation.

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