Letter to the editor, Journal of Nuclear Materials

D_2 gas-filled blisters on deuterium-bombarded tungsten

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Submission date: 3rd Dec. 2010

Most of spherical blisters formed by deuterium (D) bombardment (33 eV/D) up to 3×10^{24} D/m^2 at 300 K on polycrystalline tungsten are fully elastic deformations. This has been proven by opening individual blisters with a focused ion beam and in-situ observation of their complete relaxation by scanning electron microscopy. The D_2 gas filling is confirmed by observing simultaneously the D_2 puff. The gas pressure is causal for the stability of such spherical blisters after implantation and the gas release leads to sudden relaxation. The dilatation of the blister cap by trapped D can be excluded as cause for the blisters.

PACS: Refractory Materials **81.05.Je**, Irradiation effects in solids **61.80.-x**, Diffusion of protons in solids **66.30.jp**, Mechanical properties of solid surfaces and interfaces **68.35.Gy**

Bombardment of materials with gaseous projectiles was intensively investigated in the past due to its importance, e.g., for plasma wall interaction in nuclear fusion devices [1,2] and for semiconductor technology [3]. In many studies, formation of bubbles beneath and of blisters on the surface was observed for various materials with limited solubility of gaseous projectiles. Several articles review the requirements for the formation of blisters [4,5] and the retention of projectiles [6-10]. Two possible mechanisms for blister formation are discussed since decades: i) stress due to implanted projectiles and ii) gas filling of cavities with extremely high gas pressures [4].

In recent years blistering of tungsten (W) by hydrogen impact attracted new attention, leading to many publications in 2009-2010 [10-22]. Depending on bombardment conditions (ion energy, species distribution, fluence, flux, implantation temperature) and material grade (grain structure, microstructure, impurity content, specimen pre-treatment), different appearances of blisters and other surface protrusions were observed. The reported surface features vary from spherical, “classical” blisters [4,20] to stepped, high domed structures [13,18,19]. Furthermore in the subsurface, a spectrum of different crack and cavity features was observed [13,18,19].

In this study spherical blisters were investigated which were formed by deuterium (D) bombardment between 300 K and 500 K on polycrystalline rolled tungsten (Plansee 99.97 wt.% purity, thickness 0.8 mm). The specimens were mechanically polished to a mirror finish and thereafter stress-relieved and out-gassed at 1200 K for 1 h. For comparison, one sample was also investigated which was neither sufficiently polished nor stress relieved. A deuterium flux of 10^{20} D/m^{2}s, which contains ~95% D_3^+ ions extracted from a remote ECR plasma [23], was applied to obtain fluences of up to several 10^{24} D/m^2. The impact energy was adjusted by biasing the specimen.

The surface morphology was observed by scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM) and atomic force microscopy (AFM). With the two latter methods, the absolute height of blisters was determined. SEM combined with a focused ion beam (FIB) was used for preparing and imaging cross-sections. Nuclear reaction analysis (NRA, reaction D(^{3}He,p)^{4}He) using different ion energies [24] was applied to examine the depth profile of the retained D. Thermal desorption spectroscopy (TDS) was performed to study the behavior of thermal D release.

Figure 1(a) presents an overview over the strongly blistered surface with an areal density of 3×10^9 blister/m^2, covering ~30% of the surface. The blisters are circular and their size ranges from below 1 µm up to ~20 µm in diameter. The ratio height to diameter is usually about 0.02 and below. Total D retention of this specimen is 2×10^{20} D/m^2, which is in the range of reported values [8-10,25,26]. The D concentration is above 1% in the surface layer (<20 nm) and decreases strongly with distance from the surface. The D concentration is about 0.1% in 1 µm depth [26].

A single blister of medium size is shown in figure 2(a). By sequentially sputtering a hole with FIB into this individual blister and observing with SEM, i.e., alternating sputtering and imaging, the elastic relaxation of the blister was detected. The relaxation took place from one image to the next without any hint of the impending collapse in any of the previous images [Fig. 2(b)]. No further sputtering was performed after observing the relaxation. The figures 2(b) and 2(c) show the surface and cross-section of the collapsed blister, respectively. Only a crack system at about 1 µm below the surface remains of the blister cavity, which is often closer to the surface at the border of the blister. The crack system follows the grain boundaries of several grains, and the hole sputtered by FIB intersects this crack system. The deformation of the blister cap was fully elastic. Such a collapse was observed for many blisters. It was independent of the position of the hole on the blister cap, i.e., at the center or at the border. The ratio of the area of the hole to the blister size also does not have any influence on the collapsing behavior, even when the complete area of the blister was eroded. A continuous relaxation was never observed. Collapsing promotes the interpretation that the blister is stabilized by the over-pressured D_2 gas inside, which is released by opening a hole with FIB. If the blisters were stabilized by a dilatation of the cap due to the trapped deuterium, the removal of a small part of the cap would not lead to their relaxation. Furthermore, it can be excluded that a surface layer with a very high D concentration is responsible for any stress stabilizing the blister because removing this layer with FIB had no effect on the blister.

About ~75% of all blisters collapsed during the deuterium release by annealing up to 1200 K [Fig. 1(b)], i.e., in the view of the above presented results, they are all fully elastic. Note that in the literature blistering is normally described as plastic deformation [5,12,18] and a possible vanishing of blisters during desorption experiments is not taken into account.

Simultaneously to FIB sputtering, the D_2 partial pressure was monitored by residual gas analysis with a quadrupole mass spectrometer (QMS). Unfortunately, for blisters of the size shown in figure 2(a), the sensitivity was not sufficient to unambiguously detect the D_2 burst. However, much larger blisters (with a more than 1000 times larger volume) were created by exposure to a deuterium fluence of 8×10^{24} D/m^2 with an energy of 200 eV/D at a specimen temperature of 500 K. The investigated specimen was not stress-relieved. When one of these large blisters was opened by FIB, the D_2 burst was observed coincidentally with a partial relaxation of the blister cap. The remaining shape of the blister is due to plastic deformation. In figure 3, the time evolution of the D_2 signal together with markers for the sequential sputtering and imaging and for the observation of the partial relaxation of the large blister with ~150 µm diameter is given. This clearly shows the D_2 gas filling of blisters, which was suggested decades ago [4,5] and which is supported by recent experiments, e.g., by D_2 bursts during TDS of implanted W or D_2 molecule observation in depth profiles of secondary ion mass spectrometry [10,11,18,19]. Such D_2 bursts were observed for many blisters of different sizes when they were individually opened by FIB. The value of the gas pressure inside the blister is strongly discussed [4,11,12,18]. By quantifying the D_2 content in the spike of an individual blister with a calibrated QMS (not yet done) and measuring the blister volume by, e.g., CLSM, the gas pressure of at least large blister could be determined in the future.

A first estimate for the gas pressure inside a fully elastic blister can be gained by applying the Kirchhoff's plate theory [27] for a thin circular plate clamped on all sides and deformed by a uniform pressure. The geometry of blisters as shown in Figs. 1 and 2 was obtained by three-dimensional profile measurements (AFM, CLSM). Typical values for a medium-sized blister are a height of ~150 nm and a diameter of ~10 µm. The thickness of the blister cap, the plate, is assumed to be 1 µm, based on the cross-section images of blisters [see Fig. 2(c)]. With a Young's modulus of 411 GPa and a Poisson ratio of 0.28 for bulk W and with the assumption of similar values for the D loaded W, the pressure necessary for this elastic deformation is calculated by Kirchhoff's plate theory [27] to be ~0.7 GPa.

More precise finite element (FE) calculations based on continuum mechanics in the elastic assumption were performed on a circular W plate (20 µm diameter, 10 µm thick), which has a circular planar defect (diameter 10 µm) at a depth of 1 µm. From these calculations it can be concluded that a gas pressure of the order of 0.1 GPa is sufficient to cause the observed elastic deformation. This first calculations show also that the von Mises stress reaches values far above the yield strength of W (0.5 – 1 GPa) for pressures above 0.1 GPa, implying that calculations beyond the elastic assumption are necessary. Furthermore, it results that the radial strain component is strongly inhomogeneous ranging from tensile to compressive in the blister center across the cap thickness from top to bottom (strain from +0.27% to – 0.24% and stress from +1.6 GPa to – 1.5 GPa for 0.1 GPa gas pressure leading to bulge height of 50 nm). In addition to simulate the effect of dilatation by trapped D, such FE calculations with a 1% volumetric dilatation of the cap (with a gas pressure of 10 MPa as an initial distortion) leads to a far too low blister height while the von Mises stress already reaches values far above 1 GPa, i.e., far above the yield strength of W. Therefore, gas pressure is necessary to reach observed blister heights.

Both assessments of the D_2 gas pressure in the blisters, i.e., FE calculations and Kirchhoff's plate theory [27], lead pressure to values framing the discussed range [4,11,12,18]. If the gas pressure is determined for a well-characterized individual blister, the mechanical properties of the W cap could probably be derived.

The following picture can be drawn from the presented results: The implanted deuterons in W can be sorted into four classes: i) D dissolved as an interstitial in the W lattice up to only a very low concentration ($<<10^{-7}$ [28]). ii) A large transient dynamical D inventory, which is only present during the D bombardment and which will be reemitted quickly after stopping the D implantation (vanishs <1 h after the exposure stopped). This transient inventory is assumed to be orders of magnitude higher than the normal solubility of H in W due to the non-equilibrium loading conditions. iii) D trapped at lattice defects of W (e.g., vacancies, dislocations, grain boundaries). iv) D recombined to D_2 molecules in cavities leading to high gas pressure.

The transient dynamic D inventory can be ruled out as the exclusive reason for the existence of the blisters discussed here. If solely the stress caused by this inventory during the exposure pushes out the blisters, then they must be plastically deformed, otherwise they would vanish after the ion bombardment stopped. The D inventory trapped inside the W lattice would not be released by opening the blister with FIB and, therefore, the blister would not collapse. Thus, only the D_2 gas pressure in the cavities can be causal for the existence of these blisters after the D bombardment. It cannot be excluded that the dynamic D inventory during D bombardment initiates the blister with accompanied mechanical stress and by D decoration of the grain boundaries, which would weaken their bonding. But at least the successive filling of the cavity with D_2 gas stabilizes the blister beyond the D plasma exposure. In addition, it can be assumed that even gas pressures exceeding the yield strength of W are reached, leading to plastic deformation (Fig. 3) up to the reported bursting of the blisters during exposure [19] and to blister growing in size with fluence.

Based on the observation that the blister cavity is always located at the grain boundary, it can be assumed that the nucleation of blisters takes place at the grain boundary itself or precipitates there. Furthermore, after the nucleation the cavity widens along the weak grain boundaries, which could be even further weakened by D decoration. Nevertheless, other nucleation mechanisms such as vacancy clustering and dislocation loop punching [4,5] can not be fully excluded by the current data as cause for the blister types presented here.

Acknowledgment

The authors would like to thank C. Adelhelm for his technical assistance with the mass spectrometer, O.V. Ogorodnikova for providing one specimen and V.Kh. Alimov, H. Maier, J. Roth, K. Schmid and U. von Toussaint for fruitful discussions.

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Vitae

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Figure Captions

Fig. 1: (a) Optical micrograph of polycrystalline tungsten after plasma exposure (33 eV/D, 3×10^{24} D/m^2, 300 K) and (b) the same area after additional degassing at 1200 K. The "T"-shaped markers were cut by FIB prior to the degassing. This allows the identification of the identical position before and after D implantation.

Fig. 2: (a) SEM image of an individual blister on polycrystalline tungsten after plasma exposure (33 eV/D, 3×10^{24} D/m^2, 300 K); (b) same surface area after sputtering a hole with FIB into the blister cap and its elastic collapse after degassing; (c) cross-section through the cap of the collapsed blister at the position of the hole sputtered to degas the blister. Arrows indicate the remaining crack system of the former blister.

Fig. 3: (color online) Time trace of the mass 4 signal, i.e., D_2 signal with markers for sequential FIB sputtering and SEM observation of an individual blister on polycrystalline tungsten after plasma exposure (200 eV/D, 8×10^{24} D/m^2, 500 K). Insert: SEM image before FIB opening, which leads to a partial elastic relaxation and reduces the blister height by ~100 nm to ~2.7 µm.

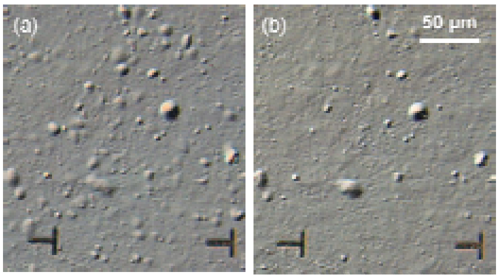

Fig. 1.

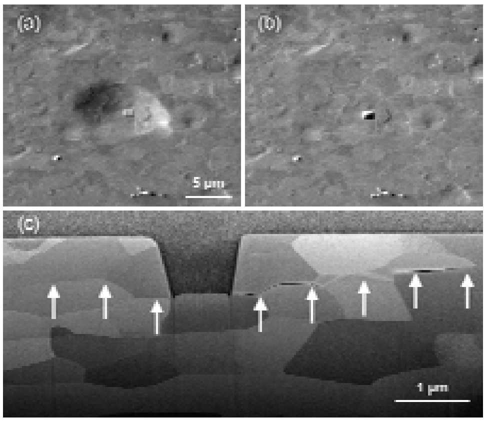

Fig. 2.

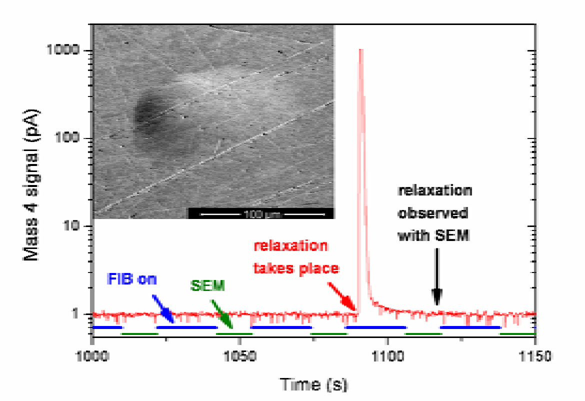

Fig. 3.