Statistical analysis of blister bursts during Temperature Programmed Desorption of deuterium-implanted polycrystalline tungsten

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Abstract. During Temperature Programmed Desorption of stress-relieved polycrystalline tungsten samples exposed to a deuterium plasma, short, intense bursts of D_2 were observed on the low–temperature flank of the main desorption peak. These bursts are attributed to the rupturing of blisters filled with high–pressure D_2 gas. A statistical analysis of the size distribution and temporal correlation of the bursts is presented. The influence of different measurement intervals and TPD heating rates on the observed bursts is simulated based on these statistics and compared to experimental results. The contribution of bursts to the total D inventory in the sample is also estimated.

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1. Introduction

Temperature Programmed Desorption (TPD) measurements with different heating rates were performed on hot-rolled polycrystalline tunsten samples exposed to a deuterium plasma. The D_2 desorption spectrum (mass 4) showed significant excursions for temperatures from 300 K up to the desorption maximum at approximately 600–700 K. These excursions were not visible in any of the other observed masses. Also, they became more pronounced for slower heating rates and were clearly separable into short individual bursts for heating rates of 3 K/min or slower. Because all samples showed strong blistering due to the deuterium plasma exposure, the bursting of these blisters is an obvious explanation for the observed D_2 gas bursts. Such bursting events during TPD that were associated to blisters were already reported several times for deuterium implanted into tungsten [1, 2, 3]. Similar phenomena were also observed during TPD analysis of other systems, e.g., for silicon co-implanted by helium and deuterium [4].

This paper presents a detailed statistical analysis of the D_2 bursts during the TPD experiments described above. The size distribution, temporal correlation and the contribution of blister bursts to the total D release from the samples will be derived from measurements acquired with high time resolution at a slow heating rate. Also, the effect of overlapping blister bursts for fast heating rates and slow acquisition is discussed.

2. Experimental

16 hot-rolled polycrystalline tungsten samples (purity: 99.97 wt.%, manufacturer: PLANSEE) were mechanically polished until no distorted surface layer was present

anymore. After ultrasonic cleaning, they were degassed and stress-relieved at 1200 K for 60 minutes in a high-vacuum furnace. The microstructure of these samples, i.e., grain structure and dislocation density, was already described in [5]. All samples were subsequently implanted with low-energy deuterium ions in a fully quantified remote ECR plasma source [6] under identical conditions. The ion flux was 10^{22} D m^{-2} s^{-1} at an energy of 38 eV/D. The samples were irradiated to a fluence of 6×10^{24} D m^{-2} at a temperature of 370 K. These implantation conditions lead to a strong blister formation on the surface of the samples. An example is shown in Figure 1.

After 2 months of resting time in a vacuum exsiccator, TPD measurements with various temperature ramps between 0.3 K/min and 600 K/min were performed on these samples. The TPD measurements were performed in the quartz tube of the TESS set-up [7] at a base vacuum of the order of 10^{-9} Pa. The typical integration time for mass 4 (corresponding to D_2) was 1 second, with a total cycle time of approximately 5 s for the monitoring of masses 1–4, 12, 17–20, 28, 32 and 44. For very fast ramps, only masses 3 and 4 were observed with an integration time of 100 ms and a cycle time of ≈ 0.35 s. For high time resolution measurements, only mass 4 was observed with an integration time of 50 ms and a cycle time of 90 ms. The quadrupole mass spectrometer was operated with the secondary electron multiplier in single ion counting mode for all measurements. The temperature response of the samples to the linear oven temperature ramp was calibrated by a thermocouple spot-welded to a sample prior to the actual TPD measurements.

3. Observations

The signal of mass 4, corresponding to D_2 molecules, always showed noticeable excursions in the low-temperature part of the desorption spectrum. They did not occur for any other observed mass. The excursions started already at very little above 300 K, more or less at the same time as the D_2 release from the sample. For faster heating rates, e.g. 15 K/min, these excursions could be mistaken for unusually strong noise. However, this apparent "noise" was only present in the low-temperature part of the desorption spectrum. In the high-temperature part at comparable or even lower count rates, the signal was much smoother. For slow ramps, i.e., 3 K/min and slower, many individual spikes in the mass 4 signal were visible up to the release maximum at about 600–700 K, with the position of the maximum depending on the heating ramp. Such spikes were not observed significantly beyond the release maximum. Examples of TPD spectra with heating rates of 1, 15 and 600 K/min are shown in Figure 2. The sampling interval was 5 s for both slower heating rates and 0.35 s for the fast one.

Due to the long cycle time of typically ≈ 5 seconds, each burst consisted only of a single measurement point even for the slowest ramps. Therefore, a measurement was performed where only mass 4 was recorded with a cycle time of 90 ms, at a temperature ramp of 1 K/min. Due to limitations of the data acquisition system, only about one third of the low-temperature part of the desorption spectrum could be observed with this high time resolution. Now most bursts could be resolved individually and with several measurement points in the decaying flank, as it is shown in Figure 3. One burst typically contains of the order of 10^{11} D_2 molecules. This is in reasonable agreement with observations by [8]: In this paper the internal D_2 gas pressure of blisters is estimated to be of the order of 0.1 GPa. For a typical blister volume of the order of 10 μm^3, this corresponds to about 2×10^{11} D_2 molecules per blister. It is clear that the peak shape observed in our experiment is dominated by the pumping time constant $\tau \approx 100$ ms of the TESS set-up. The actual blister bursting event probably happens on an even shorter timescale.

4. Statistical analysis

The statistical analysis of the blister burst events requires a separation of the blister burst signal contribution from the remaining TPD signal. This task is complicated by the unknown — but in any case non-Gaussian — distribution of the burst size. For this signal–background separation problem elaborate approaches based on Bayesian probability theory are known [9, 10, 11], which also allow the estimation of the higher order moments. For the present paper the use of the simple but efficient median filtering approach turned out to be adequate. A sliding median window spanning roughly 30 consecutive data points was used to estimate the TPD signal without burst contributions. The subtraction of the median signal from the measured signal yielded the blister burst signal. The low signal part of the extracted blister burst signal was fluctuating around zero with no visible signs of a trend which substantiates that the median filtering process did not convey contributions from the slowly varying TPD signal into the blister burst data.

The blister bursts were analysed with respect to intensity (size) distribution, temporal correlations and total contribution to the TPD signal. The time integral over the separated burst signals turned out to be independent of the heating rate of the sample. Within the experimental uncertainties the integral was the same for 0.3 K/min, 1 K/min and 3 K/min and was about 3–5% of the total TPD signal. For the measurement of the size distribution of the blister events the mass 4 bursts taken with a high time resolution of the mass spectrometer (90 ms) were used. For this data set the bursts are well separated from each other. This allows performing a statistical analysis on the magnitude of the individual events without too much influence of data from simultaneously recorded blister burst events. Figure 4 shows the histogram of all deviations from the median of the measured mass 4 signal. In order to avoid multiple counting of a burst spanning more than one acquisition cycle (see Figure 3), only local maxima respectively minima are considered in the histogram. Since a typical burst consists of a (nearly) vertical rising flank followed by an exponential decay with the pumping time constant τ, the relation between burst height A and burst integral I is given by

$$I(t_0) = \int_{t_0}^{\infty} A e^{t/\tau}\, dt = A\tau e^{-t_0/\tau}. \tag{1}$$

Taking $t_0 = 0$ as the time when the peak maximum is observed, this yields $I(0) = A\tau$. Therefore, considering only the burst maxima in the histogram still yields the correct size distribution of the blister bursts. Equation 1 can also be used to estimate an upper bound for the observation error of the total amount of D_2 molecules released in a single burst: Typically, the rising flank of a burst contains no other datapoint besides the maximum. Considering the cycle time of 90 ms and the integration time of 50 ms per datapoint, the actual burst event cannot have happened more than $\Delta t = 40$ ms before the observed maximum. In the worst case, the amount of D_2 molecules released in a burst could accordingly be underestimated by a factor $I(-\Delta t)/I(0) = \exp(\Delta t/\tau) \approx 1.5$.

Centred around zero deviation from the median is a Gaussian distribution of excursions corresponding to the noise of the measured signal. This part of the distribution is indicated by the dashed line. Towards larger excursions, a significant tail of the distribution is visible. As the continuous line shows, the dominant part of the size distribution can well be described by an exponential function. The contributions at even larger sizes can be partly assigned to pile-up: the simultaneous recording of two or more burst events, resulting in an apparently very large burst. Please note the peak in the histogram exactly at zero, which is due to the median filter but does not harm the further analysis. The time gaps between individual burst events $\Delta t_i = t_{i+1} - t_i$ followed over most of the disruptive phase (excluding the initial and final phases) a *heating rate* dependent exponential distribution

$$p(\Delta t) \sim c \exp(-ct), \tag{2}$$

where c is proportional to the heating rate. The results of a subsequent analysis of the time lag distribution $f(\Delta t_i, \Delta t_{i+1})$ of consecutive burst events as well as of the size distribution of neighboured peaks were also compliant with the assumption of independent burst events. These results favour a Poisson process [12] as probabilistic model for the observations: The blister size distribution is a sample property and the rate distribution of the burst events follows a Poisson distribution with a temperature heating rate dependent burst rate. This model does not incorporate correlation effects (e.g. a large burst event triggers immediate subsequent bursts) since no experimental indications have been found for this. As a test if this simplified model captures the essential features of the burst events a synthetic data series has been simulated based on the burst rate coefficient and the size histogram derived from the TPD data as the only input data. A comparison of the measured and simulated time series is given in Fig. 5. The two spectra with high time resolution of the acquisition are virtually indistinguishable in a statistical sense, thus providing some support that the introduced Poisson model captures the essential features. It can also be clearly seen that at higher heating rates and longer integration times individual spikes in the signal start to overlap and an average signal is being recorded — which may even be mistaken as an (additional) peak at low temperatures. With the present model these effects can be simulated and subsequently taken into account or eventually deconvoluted.

5. Summary

It was shown that blisters formed on hot-rolled polycrystalline tungsten due to deuterium plasma exposure produce bursts of D_2 gas during TPD due to the rupturing of these blisters. The size distribution of the bursts is exponential. The cumulative amount of deuterium released in such bursts is approximately 3–5% of the total released amount. The bursts occur independently from each other. Comparing the same temperature region at different heating rates, the burst frequency per temperature increase is constant. Faster heating rates and slower measurement intervals lead to a less pronounced burst signature and this effect can be reproduced by simulation based on the proposed Poisson model. The rupturing of blisters still produces a detectable signature in the TPD spectrum even for very fast heating rates, both in the simulation and in the present experiments but may be blurred significantly or even masked by lower pumping speeds or low time resolution. This might, in the worst case, lead to misinterpretation of TPD spectra. Binding energies of deuterium are usually derived assuming an Arrhenius-like desorption process from traps. However, the D_2 release due to rupturing of blisters is certainly a different process. Accordingly, if there is a significant contribution from blister bursts to the D_2 release spectrum, it should be treated separately from thermally activated release.

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Figure captions

Figure 1. Differential interference contrast micrograph of blisters on the sample surface after deuterium plasma exposure.

Figure 2. TPD spectra of deuterium plasma exposed samples for heating ramps of 1, 15 and 600 K/min. The sampling interval was 5 s for 1 and 15 K/min and 0.35 s for 600 K/min. The count rate of the mass 4 signal is scaled to the heating rate. Excursions in the low-temperature part of the spectra are due to rupturing blisters and become more pronounced as the heating rate decreases.

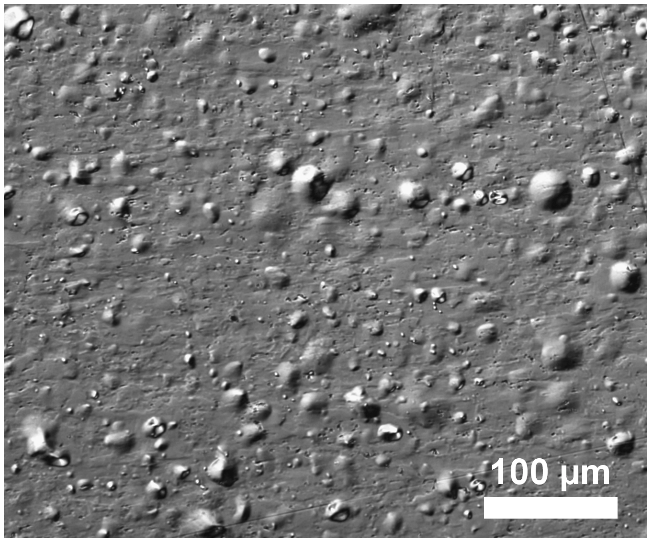
Figure 3. Mass 4 bursts recorded with high time resolution of the mass spectrometer (cycle time 90 ms). They were observed at a heating rate of 1 K/min at a temperature of approximately 390 K.

Figure 4. Histogram of excursions from the median value of the measured mass 4 signal for a heating rate of 1 K/min. Besides the Gaussian noise (dashed line), a heavy tail of the distribution towards larger excursions, i.e., blister bursts, is visible. The dominant contribution can be described by an exponential distribution (continuous line). Very large events can be attributed to pile-up.

Figure 5. Simulation of the mass spectrometer response to blisters with an exponential size distribution bursting at a fixed rate per temperature interval. The

simulation is compared to the TPD signal of the measurement with 90 ms time resolution. A simulation with 15 K/min, integration time of 1 s and cycle time of 5 s shows the effect of overlapping bursts.

Figures



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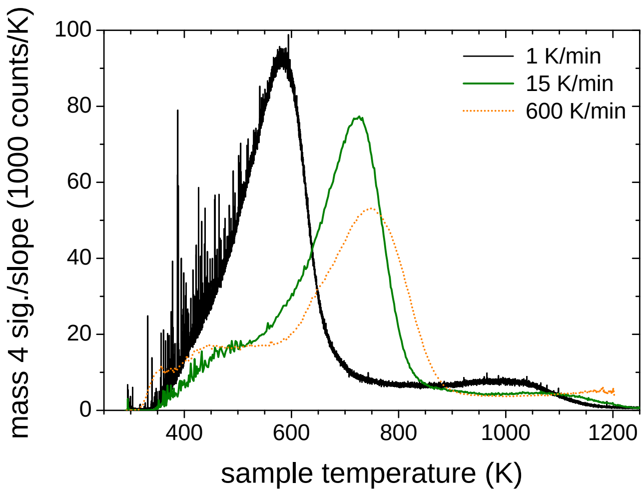

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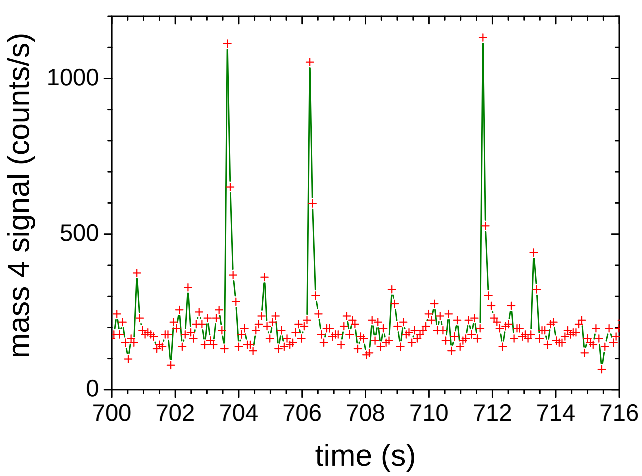

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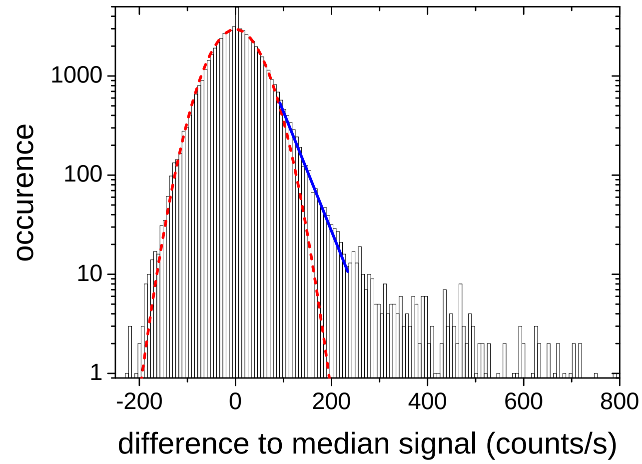

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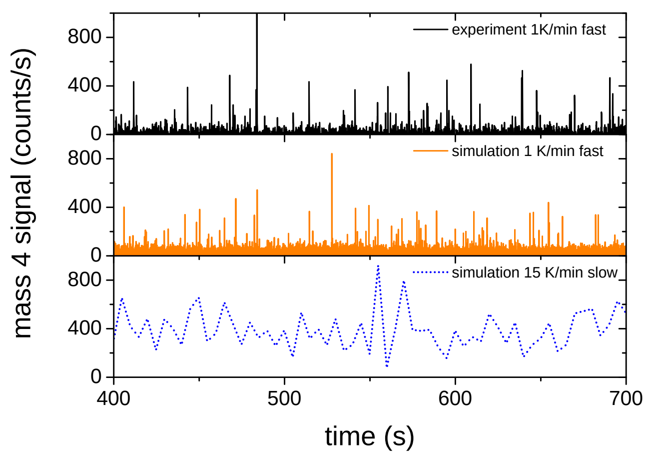

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