Deuterium retention in radiation damaged tungsten exposed to high-flux plasma

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Deuterium retention and surface modifications of thin tungsten films exposed to high-flux plasmas

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Abstract

Deuterium retention studies will be presented for nanostructured tungsten films exposed to high-flux deuterium plasmas. The thin tungsten films of ~1 µm thickness were deposited with pulsed laser deposition on bulk tungsten. Surface modifications were studied with scanning electron microscopy and deuterium retention with thermal desorption spectroscopy.

Three different types of pulsed laser deposition films were studied, columnar (density ~18×10³ kg m⁻³, crystallite size ~15 nm), nanocrystalline (density ~15×10³ kg m⁻³, crystallite size ~12 nm) and amorphous-like (density ~12×10³ kg m⁻³, crystallite size ~2 nm). The targets were exposed to deuterium plasmas while being biased at -40 V. Exposures are carried out either at low temperature, where the surface temperature ranged from about 460 K at the periphery to about 520 K at the centre of the targets or at high surface temperature (Tₘₐₓ = 1000 K). Generally, the films withstand the intense plasma exposure maintaining overall integrity. An increase of deuterium retention was observed with decreasing tungsten density. At the same time, the deuterium desorbed at lower temperatures. We found formation of micrometer-sized blisters as well as structures on the nanometer scale depending on the layer type. The relation between the density of the film and the plasma-induced modifications and amount of retained deuterium will be discussed.

in preparation for publication
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8.1 Introduction

Tungsten is foreseen as divertor material in future magnetic fusion devices such as ITER [13]. The divertor tiles of ITER are predicted to handle high particle fluxes \(10^{24} \text{m}^{-2} \text{s}^{-1}\) and heat fluxes \(10 \text{ MW m}^{-2}\) [8]. Apart from the extreme conditions that these tiles need to survive, the tritium inventory and surface modifications are important criteria for the specific material choice. The tritium inventory in ITER should be kept low \((<700 \text{ g})\) for safety and efficiency reasons. Surface modifications might be problematic, because they can lead to degradation of heat conductivity. These modifications may enhance erosion, which could be problematic because tungsten cannot be tolerated in the core plasma.

Pulsed laser deposition (PLD) makes it possible to grow films of any composition and with very different morphology and structure [160]. The micrometer thick PLD layers were exposed to high-flux deuterium plasmas to investigate surface modifications and deuterium retention. Besides the fundamental interest in these phenomena, there is also a practical motivation for this work. Present-day tokamaks like JET make use of thin tungsten films, while the retention properties are largely unknown. Furthermore, redeposition of thin films of tungsten may occur during operation of ITER.

In this chapter, experiments are described in which thin PLD tungsten layers with different compositions are tested in high-flux plasmas. Materials are tested both at low surface temperature \((<520 \text{ K})\) and at high surface temperature \((<1000 \text{ K})\) conditions. For the film with the highest density (columnar tungsten), the layer thickness was varied as well. Targets with thin films show a considerably larger fraction of deuterium retained in the material than bulk polycrystalline tungsten, even after pre-damaging the latter with MeV tungsten ions.

8.2 Experiment

Polycrystalline tungsten targets (PLANSEE, 99.96% purity, \(\Phi 20 \text{ mm}, 1 \text{ mm thick}\)) consisting of micrometer-sized grains were mechanically polished until mirror finish and coated with thin films by PLD. Different background pressures were chosen during deposition in order to create three different PLD structures [160]. The most dense is the ‘columnar’ structure with a density that is 7% less than bulk tungsten: \(\sim 18 \times 10^3 \text{ kg m}^{-3}\) and consists of typical crystallite sizes of \(\sim 15 \text{ nm}\). The tungsten coating with a density of \(\sim 15 \times 10^3 \text{ kg m}^{-3}\) and a crystallite size of around 12 nm is referred to as ‘nanocrystalline’ structure. The most open layer type is the ‘amorphous-like’ structure, with crystalline domains of only \(\sim 2 \text{ nm}\). Its density is only 60% of the polycrystalline bulk tungsten: \(\sim 12 \times 10^3 \text{ kg m}^{-3}\). Before the amorphous-like layer was deposited on tungsten, first a 150 nm thick layer of the columnar structure was coated, in order to improve adhesion.

The targets were exposed to high-flux deuterium plasmas in the linear plasma generator Pilot-PSI at FOM-DIFFER [10]. Two types of deuterium plasma exposures were used resulting in a low surface temperature \((T_{\text{max}} = 520 \text{ K})\) and a high surface temperature \((T_{\text{max}} = 1000 \text{ K})\). The electron density and temperature of the plasma were measured with Thomson scattering [96]. They were used to calculate the particle flux shown in fig-
8.3 Results

8.3.1 Blister formation

The surfaces of the thin films showed blister formation on micrometer scale upon plasma bombardment at low surface temperature. Optical microscope images of the centre of the targets, where the flux is typically \( \sim 1.4 \times 10^{24} \text{ m}^{-2}\text{s}^{-1} \), are shown in figure 8.2. Polycrystalline bulk tungsten shows only a few small blisters (figure 8.2a). These blisters are similar to the ones described in chapter 7 and probably caused by plastic deformation. On columnar coatings many more and larger blisters than on polycrystalline tungsten are found (figure 8.2b). These blisters are uniformly distributed over the sample and have a typical size of 20 – 30 \( \mu \text{m} \). The nanocrystalline coating shows similar blisters (figure 8.2c). However, the blister formation on nanocrystalline tungsten is less frequent than on columnar and concentrated at the periphery of the sample. Amorphous-like tungsten exhibits a large number of blisters (average size 20 – 60\( \mu \text{m} \)), which are concentrated at
Figure 8.2: Blister formation on the samples. a) Polycrystalline bulk tungsten, b) 1 µm columnar tungsten, c) 1 µm nanocrystalline tungsten and d) 1 µm amorphous-like tungsten.

Figure 8.3: Nanostructure formation in the centre of the thin tungsten layers, where the plasma flux was typically $\sim 1.4 \times 10^{24} \text{ m}^{-2} \text{s}^{-1}$. a) Polycrystalline bulk tungsten, b) 1 µm columnar tungsten, c) 1 µm nanocrystalline tungsten and d) 1 µm amorphous-like tungsten.
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the periphery of the film (figure 8.2d). The black circles indicate blisters that were burst and delaminated. Delaminated blisters lost their blister caps. These blisters are larger than the normal blisters as if the latter is still developing until a critical size is reached. The critical size of the delaminated blisters is strongly dependent on the radial position. On the other PLD structures, generally, no delaminated blisters were found.

8.3.2 Nanostructure formation

SEM analysis revealed the formation of structures on the nanometer scale after high-flux plasma exposure (figure 8.3). On the polycrystalline tungsten substrate, grains are clearly distinguishable. These grains show different nanostructures (figure 8.3a). The grain in the top of the image shows a lamellae structure, the grain in the lower part, a triangular-like morphology. These nanostructures resemble the formations of chapter 7. Xu et al. characterized such structures and found that their appearance is dependent on the grain orientation [146]. The nanostructures formed on the columnar tungsten (figure 8.3b) seems to reflect the grain orientations of the substrate. It seems therefore likely that the columnar structures grow according to the orientation of the substrate. This results in a sharp interface between the triangular-like and the lamellae structures. On the nanocrystalline tungsten (figure 8.3c) the different nanoscale structures are still distinguishable: on the top left lamellae are observed and the bottom left shows a triangular-like nanostructure. There is no sharp interface between the nanostructures. The amorphous-like layer exhibits a mixture of randomly orientated lamellae (figure 8.3d). Thus, for decreasing density and crystallite size, the coupling with the substrate becomes less evident.

8.3.3 Deuterium retention

The deuterium retention of the samples was measured by thermal desorption spectroscopy (figure 8.4). The polycrystalline tungsten, the bulk material on which the layers are deposited, retains only a very small amount of deuterium (\( \sim 0.9 \times 10^{20} \text{m}^{-2} \)). The target with a columnar PLD structure, the layer with the highest density of the thin films, retained much more deuterium and revealed two desorption peaks, one at 500 K and one at 700 K. A decrease of the layer density, increased the total retention (nanocrystalline sample). The amorphous-like tungsten, finally, shows a large increase of the retention. The 500 K peak strongly increases, while the 700 K desorption peak disappears. In conclusion, the total retention increases with decreasing density. The fraction of deuterium retained in the polycrystalline sample is very low compared to the retention in the layers. Thus, the polycrystalline bulk tungsten underneath the coated PLD hardly contributes to the total retention.

As a comparison, a polycrystalline sample that was pre-irradiated with W\(^{4+}\) ions to a damage level of 0.45 dpa was exposed in the same measurement series to similar plasma conditions. In chapter 5 is described that the created damage consists of mono-vacancies and small vacancy clusters and extends to a depth of 1.5 \(\mu\text{m}\), which is comparable to the thickness of the PLD layers. The blister formation was found to be somewhat less than
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Figure 8.4: Thermal desorption spectra of the samples with PLD layers. The low temperature plasma exposures ($T_{\text{max}} = 520$ K) are shown in the left graph, at the right the TDS spectra after high temperature plasma exposure are plotted. The heating rate was 1 K/s.

for the polycrystalline tungsten, which agrees with our findings of chapter 7. The nanostructures did not differ. The deuterium retention measured by TDS was $5.4 \times 10^{20}$ m$^{-2}$, which is almost a factor two lower than the retention in the columnar layer. Thus, the retained fraction in the nanostructured layers is larger than in the pre-damaged sample. The low temperature desorption peak is found at the same temperature of 500 K. The high temperature desorption peak is however different and was found to appear at 900 K.

8.3.4 Film thickness

Three different layer thicknesses of the columnar structure were deposited on polycrystalline samples. These thicknesses were 0.15, 0.5 and 1.0 µm. Subsequently, the samples were exposed to high-flux deuterium plasma at low surface temperature ($T_{\text{max}} = 520$ K). The thermal desorption spectra are shown in figure 8.5. The shape of the spectra hardly change with thickness, only the absolute level. The small shift of the low temperature peak may be a result of differences in depth where the deuterium is retained. In figure 8.5b the integrated retention is plotted as function of thickness. A fit through the data shows a linear dependence of the deuterium retention, $D_{\text{tot}}$, as function of thickness $d$: $D_{\text{tot}} = 2 \times 10^{20} + 7.4 \times 10^{26} \cdot d$. When we assume that the columnar layer is homogeneously filled with deuterium, the interpretation of this fit is as follows: The constant value $2 \times 10^{20}$ m$^{-2}$ is the surface coverage, similar for all thicknesses. The linear term $7.4 \times 10^{26}$ m$^{-3}$ indicates the volumetric retention of the columnar structure and corresponds to 1.2 at.%.

SEM analysis of the columnar 0.15 and 0.5 µm layers revealed similar nanostructure formation as on the 1 µm thick layer (figure 8.5b). The blister formation, on the contrary, is dependent on the layer thickness. The typical size of the blisters found on the 0.5 µm columnar layer was typically smaller than for the 1.0 µm columnar layer. The 0.15 nm columnar layer did not show any blisters at all.
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Figure 8.5: Deuterium retention in columnar PLD layers. a) Desorption of three different layer thicknesses: 0.15, 0.5 and 1 µm (1K/s). b) Total deuterium retained in these layers averaged over the plasma exposed area. The fit through the measurement data is shown.

8.3.5 High temperature

The PLD structures were also exposed to plasma at high surface temperature ($T_{\text{max}} = 1000$ K). The thickness of the nanocrystalline and columnar tungsten was 0.5 µm. The amorphous-like sample was deposited with a coating of 1 µm. High temperature exposure enhances the formation of blisters on the amorphous-like sample. Typically, large blisters (up to 70 µm) were observed, of which a large fraction was burst. On columnar and nanocrystalline tungsten films blisters of 5 – 20 µm arose, uniformly distributed over the sample surface. Close inspection by SEM (figure 8.6) revealed micrometer-sized cracks in the columnar films and cracked blisters on the nanocrystalline films.

SEM analysis revealed nano-droplet formation (30 – 50 nm) on all inspected samples, both on polycrystalline tungsten as on the PLD layers. In figure 8.7, the SEM images of these droplets are shown in the centre and halfway between the centre and edge for the amorphous-like tungsten. A radial dependence of the droplet size and density is observed.

Figure 8.6: a) High temperature plasma exposure induced micrometer-sized cracks on the columnar film. b) Cracked blisters appeared on the nanocrystalline sample.
Figure 8.7: SEM analysis of amorphous-like tungsten. On the left image the surface morphology in the centre of the sample and on the right image, the half-radius is shown. Small droplet-like features were found on all samples, they decreased in size further from the centre.

Towards the edge of the sample the plasma flux is lower, just as the surface temperature. These differences resulted in the formation of smaller droplets. EDS analysis of the amorphous-like sample did not show any impurities apart from the standard oxygen and carbon concentrations. However, EDS is averaged over hundreds of nm depth. Therefore, the possibility remains that very small surface quantities are below the detection limit.

In figure 8.4b the desorption spectra after high surface temperature exposure are shown. Note that the scale on the vertical axis differs from the low temperature desorption spectra. Furthermore, the nanocrystalline and columnar sample correspond to a layer of only 0.5 µm thick. These samples exposed at high temperature retained respectively 62% and 51% of the deuterium found in the equivalent layer of 1 µm thick films exposed at low surface temperature. In the TDS spectra of the columnar tungsten in figure 8.5a it is indeed clear that the total retention of the 0.5 µm layer exposed to low and high temperature is very similar. There ratio between the low temperature and high temperature desorption changes are result of the differences in surface temperature. The deuterium retention of the amorphous-like sample, did change considerably: for the same thickness films, the total retention increased with a factor of two and a desorption peak at a temperature of 800 K appeared.

8.4 Discussion

An overview of the layer structure (material density and crystallite size), the blister formation, nanostructure formation and deuterium retention is shown in table 8.1. Generally, the PLD layers withstand the plasma interaction maintaining the overall integrity. Nevertheless, abundant blister formation was found on the PLD layers. The amount, distribution and shape depend on the PLD structure and layer thickness. The nanostructures increase in disorder with decreasing layer density. The deuterium retention strongly increased for PLD layers with respect to the polycrystalline tungsten. Decrease of the layer density resulted in an increase of the deuterium retention.
8.5 Conclusions

An experimental study is presented in which the properties of tungsten films, deposited by PLD, are analysed after high-flux deuterium plasma exposure (T\(_{\text{max}}\) = 520 K). Generally speaking, all the coatings withstand the high-flux plasma interaction. Nevertheless, the thin films showed abundant formation of micrometer-sized blisters. The nanostructures that were formed on the tungsten films, were more disordered with decreasing film density.

### Table 8.1: Overview of the blister formation, nanostructure and deuterium retention on the different type of layers after low temperature exposure.

<table>
<thead>
<tr>
<th></th>
<th>polycrystalline</th>
<th>columnar</th>
<th>nanocrystalline</th>
<th>amorphous-like</th>
</tr>
</thead>
<tbody>
<tr>
<td>density (kg m(^{-3}))</td>
<td>19.3 \times 10^3</td>
<td>\sim 18 \times 10^3</td>
<td>\sim 15 \times 10^3</td>
<td>\sim 12 \times 10^3</td>
</tr>
<tr>
<td>crystallite size (\mu\text{m})</td>
<td>\sim 15 nm</td>
<td>12 nm</td>
<td>2 nm</td>
<td></td>
</tr>
<tr>
<td>blisters</td>
<td>few</td>
<td>uniform</td>
<td>periphery</td>
<td>periphery</td>
</tr>
<tr>
<td></td>
<td>none burst</td>
<td>none burst</td>
<td>none burst</td>
<td>often burst</td>
</tr>
<tr>
<td>nanostructure</td>
<td>grain dependent</td>
<td>grain dependent</td>
<td>partly mixed</td>
<td>mixture</td>
</tr>
<tr>
<td>D retention</td>
<td>8.6 \times 10^{19} m(^{-2})</td>
<td>9.6 \times 10^{20} m(^{-2})</td>
<td>1.3 \times 10^{21} m(^{-2})</td>
<td>2.1 \times 10^{21} m(^{-2})</td>
</tr>
</tbody>
</table>

The volumetric deuterium retention was found to be 7.4 \times 10^{26} m\(^{-3}\) in columnar tungsten (section 8.3.4). The deuterium retention of the 0.5 \mu m columnar layers exposed at low surface temperature and high surface temperature is comparable (figure 8.5). This suggests that in both cases the PLD layer is completely filled with deuterium. Thus, the nano-droplets found on the tungsten surfaces are not likely to have affected the deuterium retention. The volumetric deuterium retention (7.4 \times 10^{26} m\(^{-3}\)) of the columnar layer is comparable to the saturation of deuterium retention in pre-damaged polycrystalline tungsten at 0.45 dpa (1.4 at.\% \approx 8.8 \times 10^{26} m\(^{-3}\), chapter 4). However, the retained fraction in D/m\(^2\) of the pre-damaged tungsten is a factor two lower. It seems that the penetration of deuterium into columnar tungsten is quicker than penetration into pre-damaged tungsten. It provides insight to compare the volumetric retention in columnar tungsten to its density. Although 7\% of the tungsten lattice is empty, the concentration of deuterium is only 1.25 at.\%.

The TDS spectrum of the amorphous-like tungsten film shows a large retention peak at around 500 K. The total retention is much higher than in the other films. This low temperature desorption peak is usually assigned to grain boundaries and dislocations [52]. The crystallite size is typically \sim 2 nm and the density is only 60\% of polycrystalline tungsten. Thus, the amorphous-like sample indeed contains many grain boundaries that presumably trap the deuterium. Comparison of the volumetric retention of the amorphous-like layer with its density amounts to 5.4 at.\%. 
The retained fraction of deuterium in all thin films was found to be higher than in polycrystalline tungsten, even after pre-damaging with W⁴⁺ ions to 0.45 dpa. Thermal desorption measurements showed that the retention properties are highly affected by the film density. A low film density led to very high deuterium retention with a low trapping energy. Variation in layer thickness of the columnar film allowed us to estimate the deuterium retention in the layer to be $7.4 \times 10^{26} \text{ m}^{-3}$.

During high temperature plasma exposure ($T_{\text{max}} = 1000 \text{ K}$) very small droplets (30 – 50 nm) were formed on all films. The amorphous-like film showed delaminated blisters at the periphery, the blisters on the nanocrystalline layers are cracked and also on the columnar films micrometer-sized cracks are observed.

**Acknowledgements**

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