Deuterium retention and surface modifications of nanocrystalline tungsten films exposed to high-flux plasma

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1. Introduction

Tungsten is foreseen as divertor material in future magnetic fusion devices such as ITER [1]. These divertor tiles are predicted to handle high particle fluxes (10^{24} m^{-2} s^{-1}) and heat fluxes (10 MW m^{-2}) [2]. In addition, both tritium inventory and surface modifications are important criteria for the specific material choice. The tritium inventory in ITER should be kept low (<700 g [3]) for safety and efficiency reasons. Surface modifications might be problematic, because they can lead to degradation of heat conductivity. These modifications may further enhance erosion, which could be problematic because tungsten cannot be tolerated in the core plasma. Furthermore, redeposition of thin films of tungsten may occur during operation of ITER. The retention properties of thin films are largely unknown and are therefore important to study, for ITER as well as for present-day tokamaks like JET that make use of thin tungsten films.

In this paper, experiments are described in which thin tungsten layers with different morphology and structure are tested in high-flux plasmas. Pulsed laser deposition (PLD) is exploited for W film production, since PLD makes it possible to grow films with very different morphology and structure [4]. The PLD layers were exposed, at low surface temperature (<520 K), to high-flux deuterium plasmas to investigate surface modifications and deuterium retention. It is shown that targets with thin films exhibit a considerably larger fraction of deuterium retained in the material than bulk polycrystalline tungsten, even after pre-damaging the latter with MeV tungsten ions.

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2. Experiment

Polycrystalline tungsten targets (PLANSEE, 99.96% purity, ∅ 20 mm, 1 mm thick) containing micrometer-sized grains were mechanically polished until mirror finish and coated with thin films by PLD. Different helium background pressures were chosen during deposition in order to create W coatings with three different structures. Details about experimental procedure, morphology characterization, crystal structure and related discussion are reported elsewhere [4]. The most dense one is the 'columnar' structure with a density, measured using a quartz crystal microbalance, that is only 7% less than bulk tungsten: $\sim 18 \times 10^3$ kg m^{-3} and consisting of columns 100–150 nm wide, made of crystallites with typical sizes of ∼ 15 nm (calculated using the Scherrer formula). The next dense tungsten coating, with a density of $\sim 15 \times 10^3$ kg m^{-3}, an irregular columnar growth and a crystallite size of around 12 nm is referred to as 'nanocrystalline' structure. At the highest He pres-sure the 'amorphous-like' structure, with a featureless morphology and crystalline domains of only ∼2 nm is obtained. Its density is only 60% of the polycrystalline bulk tungsten: $\sim 12 \times 10^3$ kg m^{-3}. Before the amorphous-like layer was deposited on tungsten, first a 150 nm thick layer of the columnar structure was deposited in order to improve coating adhesion.

The targets were exposed to high-flux deuterium plasmas in the linear plasma generator Pilot-PSI at FOM-DIFFER [5] at a low surface temperature (T_{max} = 520 K). The electron density and temperature of the plasma were measured with Thomson scattering [6]. The targets were subject to 4 plasma shots of 80 s, which leads to an average plasma fluence of typically 2.5×10^{26} m^{-2}. During exposure, the targets were kept at a bias of −40 V.

3. Results

3.1. Blister formation

Optical microscope images of the centre of the targets, where the flux is typically $\sim 1.4 \times 10^{24}$ m^{-2} s^{-1}, are shown in Fig. 1. Polycrystalline bulk tungsten shows only a few small blisters (Fig. 1a). These blisters are similar to the ones described in Ref. [7], and probably originate from plastic deformation. On columnar coatings many more and larger blisters are observed (Fig. 1b). These blisters are uniformly distributed over the sample and have a typical size of 20–30 μm. The nanocrystalline coating shows similar blister formation (Fig. 1c), although the amount of blisters and their size seems to be smaller and concentrated at the periphery of the sample. Amorphous-like tungsten exhibits large numbers of blisters (average size 20–60 μm), which are concentrated at the periphery of the film (Fig. 1d). The black circles indicate blisters that were burst and delaminated, meaning that they lost their caps. The delaminated blisters are larger than the regular ones as if the latter are still developing until a critical size is reached. The critical size of the delaminated blisters is strongly dependent on the radial posi-tion. On the other PLD coatings, no delaminated blisters were found.

3.2. Nanostructure formation

SEM analysis revealed the formation of structures on the nanometer scale after high-flux plasma exposure (Fig. 2). On the polycrystalline tungsten substrate, separate grains with dif-ferent nanostructures are clearly distinguishable (Fig. 2a). The grain in the top of the image shows a lamellae structure, while the grain in the lower part, a triangular-like morphology. These nanostructures resemble the formations discussed in Ref. [7]. Xu et al. characterized such structures and found that their appearance is dependent on the grain orientation [8]. The nano-structures formed on the columnar tungsten (Fig. 2b) clearly reflect the underlying grain structure of the substrate as well. It therefore seems that growth of the columnar structure preserves the orientation of the substrate. This results in a sharp interface between the triangular-like and the lamellae structures. On the nanocrystalline tungsten (Fig. 2c), different nanoscale structures are still distinguishable: in the top left part of the image lamellae are observed, in the bottom left triangular-like nanostructures. There is however no sharp interface anymore between the nano-structures. The amorphous-like layer, finally, exhibits a mixture of randomly orientated lamellae (Fig. 2d) indicating that the ori-entation of the substrate is completely lost in growth of the layer.

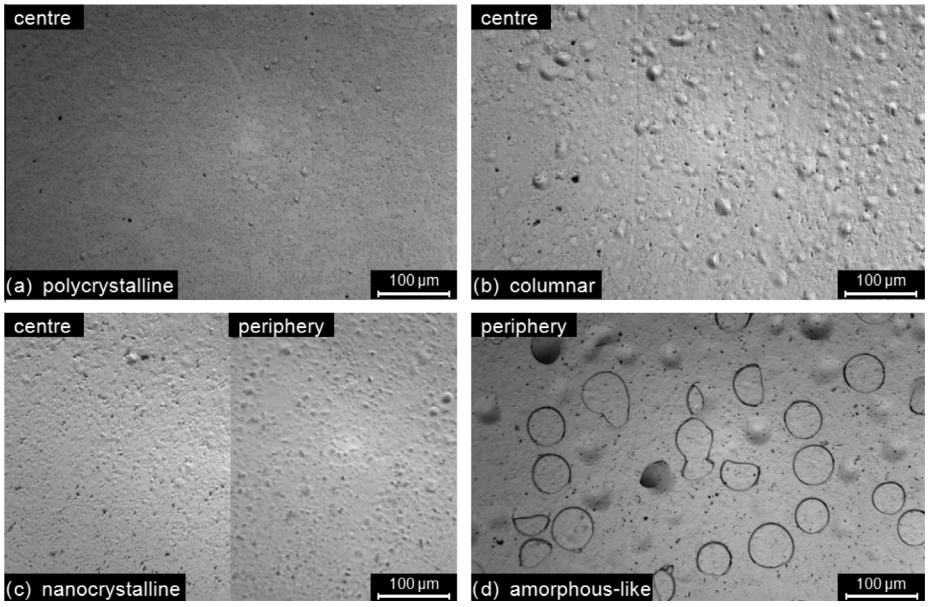

Fig. 1. Blister formation on the samples. (a) Polycrystalline bulk tungsten, (b) 1 μm columnar tungsten, (c) 1 μm nanocrystalline tungsten and (d) 1 μm amorphous-like tungsten.

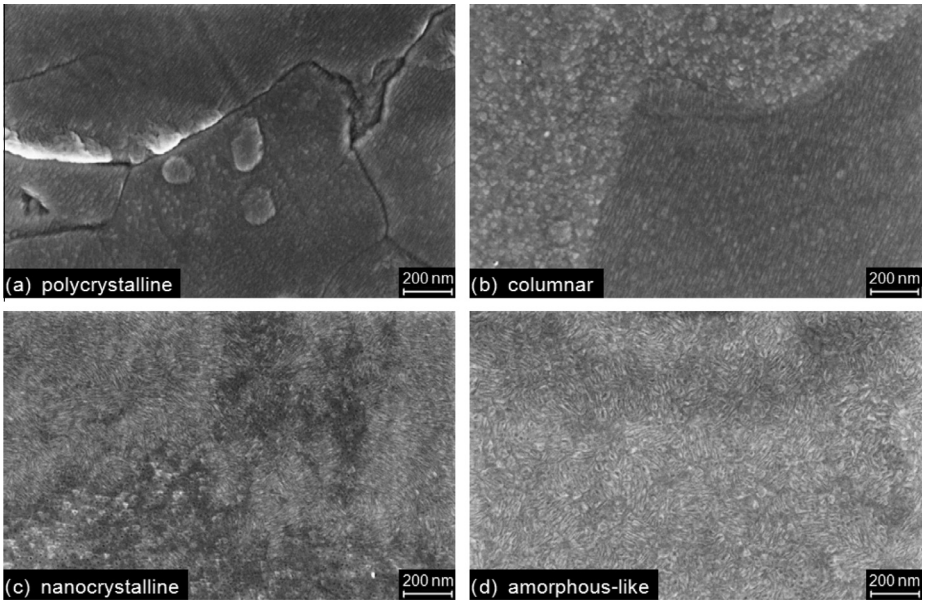

Fig. 2. Nanostructure formation in the centre of the thin tungsten layers, where the plasma flux was typically ~1.4×10^{24} m^{-2} s^{-1}. (a) Polycrystalline bulk tungsten, (b) 1 μm columnar tungsten, (c) 1 μm nanocrystalline tungsten and (d) 1 μm amorphous-like tungsten.

3.3. Deuterium retention

The deuterium retention of the samples was studied by thermal desorption spectroscopy (TDS) (Fig. 3a). Polycrystalline tungsten retains only a very small amount of deuterium (~0.9×10^{20} m^{-2}). The target with the columnar PLD structure, the layer with the highest density of the thin films, retained significantly more deuterium and revealed two desorption peaks, one at 550 K and one at 700 K. Decrease of the layer density increases the total retention (nanocrystalline and amorphous-like samples). For the amorphous-like tungsten, the 700 K desorption peak has completely disappeared. The fraction of deuterium retained in the polycrystalline sample is very low compared to the retention in the layers, which means that the polycrystalline bulk tungsten underneath the films will hardly contribute 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 to similar plasma conditions in the same measurement series. In Ref. [7] it has been discussed that the created damage consists of mono-vacancies and small vacancy clusters and extends to a depth of 1.5 μm, which is comparable to the thickness of the PLD layers. It is clear that the retained fraction in the pre-damaged sample is significantly smaller than in the nanostructured layers. The low temperature desorption peak is found at a similar temperature of 500–550 K. The high temperature desorption peak is at a significantly different position at 900 K.

In a second series of experiments, 3 targets with columnar films with different thicknesses were exposed to plasma at low surface temperature (T_{max} = 520 K). The thicknesses of the films were 0.15, 0.5 and 1.0 μm. The thermal desorption spectra are shown in Fig. 3a. The shape of the spectra hardly changes with thickness, only the absolute level. The small shift of the low tem-perature peak may be the result of the difference in depth where the deuterium is retained. In Fig. 3b, the integrated retention is plotted as function of thickness. A fit through the data shows a linear dependence of the deuterium retention D_{tot} as function of thickness d: $D_{tot}(d) = 2 \times 10^{20} + 7.4 \times 10^{26}\, d$. The linear depen-dence indicates that all 3 columnar films are homogeneously filled with deuterium. The constant value of 2×10^{20} m^{-2} corre-sponds to the surface coverage. The term 7.4×10^{26} m^{-3} indicates the volumetric retention of the columnar structure and corre-sponds to 1.2 at.%.

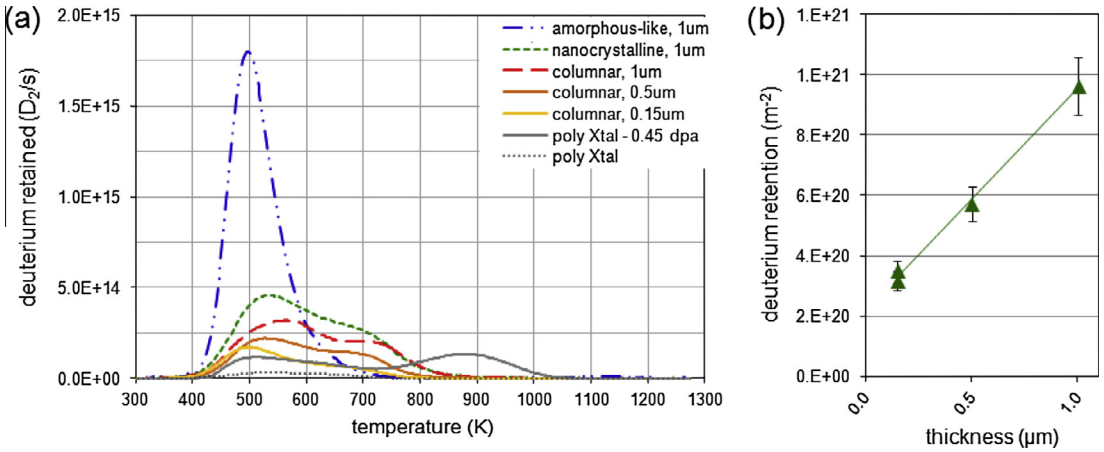

Fig. 3. (a) Thermal desorption spectra of the samples with PLD layers. The heating rate was 1 K/s. (b) Total deuterium retained in the columnar layers as function of thickness averaged over the plasma exposed area. The fit through the measurement data is shown.

Table 1
The main experimental findings for the four different phases studied, as listed at the top row. Four properties of the phases are listed as indicated in the first column.

	Polycrystalline	Columnar	Nanocrystalline	Amorphous-like
Density (kg m^{-3})	19.3×10^3	$\sim 18 \times 10^3$	$\sim 15 \times 10^3$	$\sim 12 \times 10^3$
Crystallite size	$\sim$μm	15 nm	12 nm	2 nm
Layer thickness	–	1 μm	1 μm	1 μm
Blisters	Few	Uniform	Periphery	Periphery
	None burst	None burst	None burst	Often burst
Nanostructure	Grain dependent	Grain dependent	Partly mixed	Mixture
D retention	8.6×10^{19} m^{-2}	9.6×10^{20} m^{-2}	1.3×10^{21} m^{-2}	2.1×10^{21} m^{-2}

SEM analysis of the columnar 0.15 and 0.5 μm layers revealed similar nanostructure formations as on the 1 μm thick layer (Fig. 2b). The blister formation, on the other hand, strongly depends on the layer thickness. The typical size of the blisters found on the 0.5 μm columnar layer was typically smaller than on the 1.0 μm columnar layer. The 0.15 nm columnar layer did not show any blisters at all.

4. Discussion

An overview of the structure of the layers, blister and nanostructure formation, and deuterium retention is shown in Table 1. The PLD layers withstand the plasma interaction maintaining their overall integrity. Nevertheless, abundant blister formation was observed on the PLD layers. The amount, distribution and shape depend on the W structure and layer thickness. For the high-density films, the growth seems to have preserved the grain structure as indicated by the observation of areas with clearly distinct nanostructures. The interfaces between these areas become fainter with decreasing film crystallinity and are completely gone for the amorphous-like films. The deuterium retention has strongly increased for the PLD layers with respect to polycrystalline tungsten. Decrease of the layer density and crystalline order results in an increase in deuterium retention.

The volumetric deuterium retention in columnar tungsten was found to be 7.4×10^{26} m^{-3} which corresponds to 1.25 at.% This is comparable to saturated values of deuterium retention in pre-damaged polycrystalline tungsten (at 0.45 dpa; 1.4 at.% $\approx$ 8.8×10^{26} m^{-3} [9]). The total retention in the pre-damaged sample was found to be 5.4×10^{20} m^{-2}, the deuterium penetrated only 0.6 μm into the material. Thus, the penetration of deuterium into columnar tungsten is significantly quicker than penetration into pre-damaged tungsten. The TDS spectrum of the amorphous-like tungsten film shows a large retention peak at around 500 K and the total retention is much higher than in the other films. This low temperature desorption peak is usually assigned to grain boundaries and dislocations [10]. This makes sense since the crystallite size is typically ~ 2 nm and the amorphous-like sample therefore contains many grain boundaries that presumably trap deuterium. Comparison of the volumetric retention of the amorphous-like layer with its density (only 60% of polycrystalline tungsten) amounts to 5.4 at.%.

5. Conclusion

An experimental study has been presented in which the properties of nanostructured tungsten films, deposited by PLD, are analysed after high-flux deuterium plasma exposure (T_{max} = 520 K). All coatings withstand the high-flux plasma interaction. Nevertheless, the thin films show abundant formation of micrometer sized blisters. The nanostructures are more disordered with decreasing film crystallinity.

The retained fraction of deuterium in all thin films was found to be higher than in polycrystalline tungsten, even after pre-damaging with W^{4+} ions to 0.45 dpa. Thermal desorption measurements showed that the retention properties are highly affected by the film density and crystalline order. The low film density of the amorphous-like film led to very high deuterium retention with low trapping energies. Variation in layer thickness of the columnar film allowed us to estimate the deuterium retention in the layer to be 7.4×10^{26} m^{-3}.

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