



Deuterium retention and release in tungsten co-deposited layers

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ABSTRACT

A systematic study of the influence of the deposition conditions on the deuterium retention in co-deposited tungsten layers formed both by magnetron sputtering and in the PISCES-B linear device has been carried out. Experimental parameters such as the tungsten deposition rate, the incident particle energy and the substrate temperature are shown to affect the level of deuterium retention in the layers. A decreased retention for increased substrate temperature and deposition rates, and an increased retention for increasing incident deuterium particle energy are observed. A scaling equation is proposed to describe the influence of the conditions during the co-deposition process (surface temperature, incident particle energy and deposition flux) on the deuterium retention. In addition, the desorption kinetics of deuterium has been studied by TDS. Two desorption stages at 473–573 K and at 1073 K have been observed.

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1. Introduction

Co-deposition of tritium, with material eroded from the plasma-facing components (PFC), in deposition-dominated areas will be the main source of tritium accumulation in ITER [1,2]. Co-deposition with carbon and beryllium will be the main contributors to the global tritium retention due to their higher sputtering rate and thus co-deposition rate. ITER will use tungsten in the divertor baffle and septum regions and may use a full tungsten divertor at a later stage of operations, which will be subject to high fluxes of energetic particles. Although, eroded tungsten atoms are usually promptly re-deposited close to their original location [3], the possible co-deposition of tritium with tungsten needs to be assessed. In addition, the thermal release properties of such layers, will define the amount of fuel released during a bake-out of the vacuum vessel. Furthermore, it is important to understand the co-deposition process with the single elements used for PFCs, in order to try and understand the retention in real ITER co-deposited layers which will very likely be made of mixed materials [4].

Co-deposition of hydrogen with carbon is known to lead to significant retention, as was observed in the TFTR [5] and JET [6] tokamaks, and has been extensively investigated. A systematic study of the deuterium retention in co-deposited beryllium layers has recently [7] shown that the surface temperature during the deposition, the beryllium deposition rate and the energy of the incident particles can be used to predict the amount of deuterium trapped in the layer. To date, deuterium retention in tungsten layers has been scarcely studied. Although the solubility of deute-

rium into tungsten is low [8], large amounts of hydrogen isotopes can be loaded into the near surface region by implantation. Indeed, after implantation with 1 keV deuterium ions, a concentration of $D/W \sim 0.24$ was measured within the implantation depth [9]. On the other hand, it was reported in [10], that although not measurable, the deuterium content in co-deposited tungsten layers should be below a few percents. This contrasts with more recent data [11] where H/W values of about 0.15 have been observed for tungsten layers formed in a pure hydrogen plasma. It should also be noted that as the carbon plasma facing components of ASDEX-Upgrade were progressively replaced by tungsten-coated tiles, a significant reduction in the global deuterium retention has been observed [12], and co-deposition of deuterium with tungsten contributes only partially to the global retention. In the case of ITER, however, the longer pulse and higher duty cycle will lead to increased erosion (and thus re-deposition) of the tungsten PFCs and an assessment of the possible retention in such layers is of importance for the predictions of the tritium retention in ITER.

This paper describes a first attempt to conduct a systematic study of the influence of the deposition conditions on the retention in co-deposited tungsten layers. Experimental parameters such as the tungsten deposition rate, the incident particle energy, and the substrate temperature are explored and are all shown to affect the level of hydrogen isotope retention in co-deposited tungsten layers. From these results, an empirical relation is established and is shown to be able to account for the combined influence of the conditions during the co-deposition process. In addition, the thermal release behavior of deuterium has been studied in order to evaluate the efficiency of fuel removal techniques based on bake-out of the ITER vessel.

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2. Experimental

Co-deposited tungsten layers were produced by magnetron sputtering in a high vacuum chamber pumped down to a typical base pressure better than 10^{-6} Pa. A high purity circular tungsten target (99.9%) mounted on a water-cooled magnetron was used. The target was driven by a DC power supply, with a typical applied power of 150 W (400 V, 0.38 A). A mixture of argon and deuterium, introduced through mass flow controllers, was used as process gas. The fraction of argon (c_{Ar}) in the gas mixture was determined from the measurement of its partial pressure. Different mixtures were used in the present study, c_{Ar} from 0% to 50%. During deposition, the working gas pressure was typically 1.2 Pa.

Co-deposited layers were formed on polished copper substrates mounted on a heatable sample holder (up to 600 K) facing the target at a distance of about 10 cm. Copper was chosen as a substrate material because it does not form an alloy with tungsten and thus avoids any potential mixing at the film/substrate interface. During deposition, the sample temperature is monitored by a thermocouple installed at the sample back. For deposition at low temperature, water cooling was used to maintain a stable temperature and avoid any heating by the plasma radiations.

During deposition, the tungsten deposition rate was monitored by using a quartz crystal installed in the vicinity of the substrate. The deposition rate was also cross-checked by weighing the samples before and after deposition. In the present study the layer thickness is in the range 100–200 nm.

One co-deposited layer was also formed in the PISCES-B linear device, where a tungsten target was bombarded by a high flux deuterium plasma with about 15% of Ar. The copper substrate was installed on the witness plate manipulator which is described in more details in [13]. A negative bias of -100 V was applied on the target to control the impinging ion energy.

Deuterium retention in the co-deposited layers as well as the deuterium desorption kinetics was studied using thermal desorption mass spectrometry (TDS). Each sample was separately desorbed in a TDS chamber of typical pressure better than 10^{-6} Pa.

An infrared heat source is programmed to linearly increase the sample temperature at a rate of 18 K/min up to 1100 K and then held at that temperature for a further period of 10 min before cooling, also at 18 K/min. Prior to deposition, the samples are ultrasonically cleaned using acetone then alcohol, and then outgassed using the same procedure used for TDS measurements. This ensures there is no residual mass 4 inventory in the samples prior to deposition. To check the level of retention in the copper substrate, a sample was installed at the witness plate location in PISCES-B using a pure deuterium plasma bombarding the biased tungsten target (-100 V). The ion energy was lower than the physical sputtering threshold for deuterium on tungsten thus preventing the tungsten co-deposition on the substrate, which was bombarded by deuterium neutrals reflected from the target. The exposure time was similar to the D_2/Ar case. Retention in the copper substrate was found to be negligible compared to the amount of deuterium retained in the co-deposited layer.

Surface morphology of the layers was studied by means of a JEOL-JSM 6830 scanning electron microscope (SEM), whilst the layer composition was studied by Energy Dispersive X-Ray analysis (EDX).

3. Results and discussion

3.1. Morphology of the layers

To investigate the influence of the deposition conditions on the layer morphology, experiments were made with different fractions of argon in the gas mixture and with different substrate temperatures. Fig. 1 shows the layer morphology obtained at room temperature under different deposition conditions. Under those conditions the layers contained only a small amount of impurities (oxygen, carbon) with a concentration lower than 5%. Evidently, the argon fraction has a strong influence on the layer morphology. For $c_{Ar} = 15\%$ (Fig. 1(a)), the layers appear pretty smooth and no specific features can be observed at the magnification used here. For substrate temperatures during deposition up to 300 °C, no

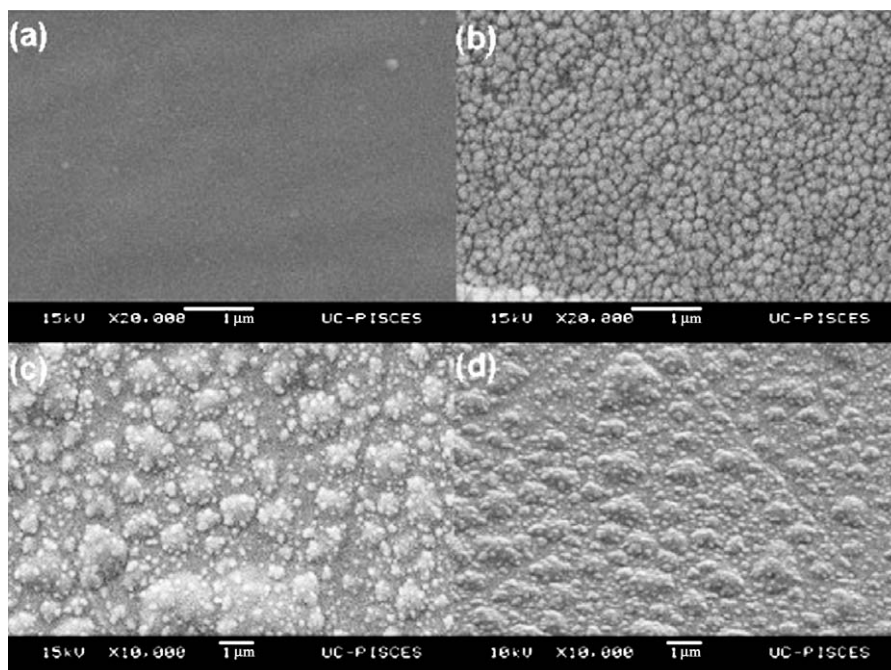


Fig. 1. Surface morphology of co-deposited tungsten layers formed with different fractions of argon in the gas mixture at room temperature, (a) $c_{Ar} = 15\%$, (b) $c_{Ar} = 50\%$, (c) and (d) $c_{Ar} = 5\%$. In (d) the sample has been tilted to 45°.

change of the surface morphology has been observed. For higher argon fraction, $c_{Ar} = 50\%$ (Fig. 1(b)), the layers become porous. This is consistent with the structure zone model, presented in [14], describing the evolution of the morphology of a sputter deposited layer as a function of the pressure and temperature during deposition. Porous layers are known to be formed at high neutral pressure because of the associated reduced mobility of the atoms on the surface. Moreover, the minimum pressure to observe a porous structure decreases with increasing gas to target mass ratio. In the present case, for $c_{Ar} = 50\%$, the argon pressure during deposition is sufficient to significantly reduce the mobility of the atoms and create a porous structure. At lower argon fractions, $c_{Ar} = 5\%$ (Fig. 1(c) and (d)), the formation of blisters is observed at the surface of the film, with diameter of about 1–5 μm . Formation of blisters has been observed for tungsten surfaces exposed to deuterium ion bombardment [15,16], as well as on tungsten layers formed by hydrogen RF plasma [17]. In the present case, the blister formation may be explained by the continuous bombardment of the growing layer by energetic deuterium atoms reflected from the target.

3.2. Deuterium retention and influence of the deposition conditions

Fig. 2 shows the evolution of the D/W ratio as a function of the substrate temperature during deposition. In this case, the power applied to the magnetron was 150 W which corresponds to a voltage of about 400 V, and the argon fraction in the gas mixture was $c_{Ar} = 15\%$. For these experiments, the deposition rate was $r_d = 0.06 \text{ nm s}^{-1}$ and was found to be constant over the different runs. Deuterium retention in the co-deposited tungsten layers is almost constant up to 373 K with $D/W = 0.03$ and then decreases with increasing temperatures. At 573 K, D/W has decreased by almost one order of magnitude ($D/W \sim 5 \times 10^{-3}$), compared to the values measured below 373 K. Also shown in Fig. 2, is the D/W ratio measured on a co-deposited layer formed in PISCES-B. For a similar substrate temperature during deposition (473 K), the retention in the codeposit formed in PISCES-B is much lower than that in the magnetron case although the Ar fraction in the gas mixture was about 15% in both cases. However, both the negative bias on the tungsten target (-100 V) and the tungsten deposition rate (0.01 nm s^{-1}) on the substrate were much lower in PISCES-B than in the magnetron sputtering device. It therefore appears that those 2 variables may have an effect on the deuterium retention.

The effect of the tungsten deposition rate on the deuterium retention was investigated in 2 different ways. First, codeposits were formed with different values of the power applied to the magnetron. Indeed when increasing the applied power from 50

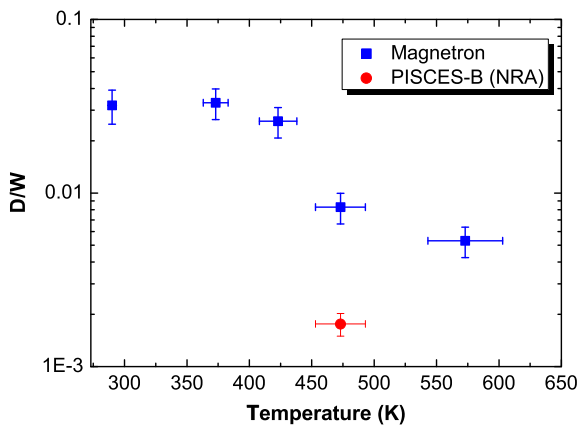


Fig. 2. D/W ratios measured on co-deposited tungsten layers formed under similar deposition conditions but with different substrate temperatures. Also shown is the D/W ratio measured on a co-deposited layer formed in PISCES-B.

to 200 W, the applied voltage increased by only 10% while the applied current increased by a factor of 3. Thus, the energy of the impinging ions on the target is roughly constant while the ion flux increases. An factor of 2 increase of the deposition rate is measured for a factor of 4 increase in the applied power to the magnetron. Secondly, since the sputtering yield of tungsten by argon is much higher than that by deuterium ions [19], varying the fraction of Ar in the gas mixture changes the tungsten deposition rate. Four different D_2/Ar mixtures were used with $c_{Ar} = 0\%, 5\%, 10\%$, and 50% . The power applied to the magnetron was kept constant at 150 W, which corresponds to an applied voltage of about 400 V. A clear decrease of the deuterium retention is observed for increasing Ar fractions (Fig. 3(a)). Fig. 3(b) shows both the data obtained when varying the Ar fraction and the power to the magnetron. A clear decrease of the D/W ratio for increasing tungsten deposition rate is observed. From the fit to these data, it is found that $(D/W) \sim r_d^{-0.39}$. The fact that the deuterium retention decreases for increasing deposition rates is not surprising, as it is usually observed in vacuum deposition techniques that the impurity content in the deposited layer decreases with increased deposition rate. In addition a similar trend has been observed for beryllium co-deposited layers [7].

Since the deposition conditions (temperature and deposition rates) appear to influence the deuterium retention in tungsten layers in the same way as for beryllium codeposits [7], a similar empirical scaling is proposed to describe the evolution of the D/W ratio with the deposition conditions. Hence it is proposed that:

$$\frac{D}{W} = C \cdot r_d^\alpha \cdot E_n^\beta \cdot \exp\left(\frac{\gamma}{T}\right), \quad (1)$$

where, C is a constant, r_d is the tungsten deposition rate, E_n is the average energy of the incoming particles on the substrate and T the substrate temperature during deposition. E_n is determined using the following formula [19]:

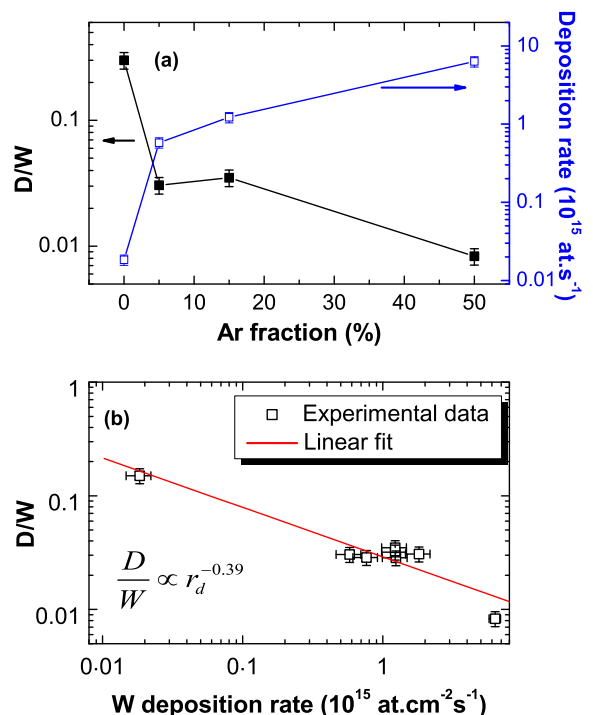


Fig. 3. D/W ratio dependence on the Ar fraction in the gas mixture (a) and tungsten deposition rate (b). All results have been obtained for a fixed substrate temperature (293 K) and a similar voltage applied on the tungsten target. The lines between the data points in (a) are only guides to the eye.

$$E_n(E_0) = E_0 \frac{R_E(E_0)}{R_N(E_0)}, \quad (2)$$

where E_0 is the energy of the ions impinging on the target, R_N is the fraction of backscattered particles and R_E the energy reflection coefficient. Through the use of this expression, and the variation of the applied voltage on the magnetron as well as the value of the negative bias on the target in the case of the sample prepared in PISCES-B the average energy of target reflected (and thus co-deposited) deuterium particles is in the range 60–280 eV. In order to determine, the different coefficients in Eq. (1), a regression analysis is performed on all of the data, allowing the dependence on each parameter to be taken into account. The full scaling expression determined from fitting all of the data is then:

$$\frac{D}{W} = 5.7 \cdot 10^{-8} \cdot r_d^{-0.41 \pm 0.1} \cdot E_n^{1.88 \pm 0.4} \cdot \exp\left(\frac{779 \pm 220}{T}\right), \quad (3)$$

where r_d is in units of $10^{15} \text{ at} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, E_n in eV and T in K, and with $293 \text{ K} \leq T \leq 600 \text{ K}$ and $60 \text{ eV} \leq E_n \leq 280 \text{ eV}$.

However, in order to ease possible extrapolation for future devices like ITER, for which the deposition rates of impurities are not known, it is proposed to use the ratio of the flux of deuterium to tungsten atoms arriving at the substrate (Γ_D/Γ_W), which can be estimated for the ITER case from numerical modelling [18].

The arrival rate of deuterium atoms impinging on the substrate has been estimated by using the measured current on the target and the reflection coefficient of deuterium ions on tungsten. The arrival rate of tungsten atoms is estimated from ion flux and the sputtering yield of tungsten by argon and deuterium. For the data shown in Fig. 3, the flux of deuterium atoms impinging on the substrate surface is between 2 and 500 times higher than the flux of tungsten atoms. The deposition rate varies with the relative arrival rate of deuterium and tungsten atoms: the higher Γ_D/Γ_W , the lower the deposition rate. The full scaling expression determined from fitting all of the data is then:

$$\frac{D}{W} = 5.13 \cdot 10^{-8} \cdot \left(\frac{\Gamma_D}{\Gamma_W}\right)^{0.4 \pm 0.1} \cdot E_n^{1.85 \pm 0.4} \cdot \exp\left(\frac{736 \pm 228}{T}\right), \quad (4)$$

where $2 \leq \Gamma_D/\Gamma_W \leq 500$, E_n in eV and T in K, and with $293 \text{ K} \leq T \leq 600 \text{ K}$ and $60 \text{ eV} \leq E_n \leq 280 \text{ eV}$. It is interesting to note that the exponents of the temperature and energy terms do not vary much between both scalings, and in addition the exponent of the flux ratio term in Eq. (4) appears to be the opposite of the deposition rate exponent in Eq. (3).

A comparison of the experimentally measured D/W ratios with the ratio predicted by Eq. (4) is shown in Fig. 4. There is evidently a relatively good agreement between both values.

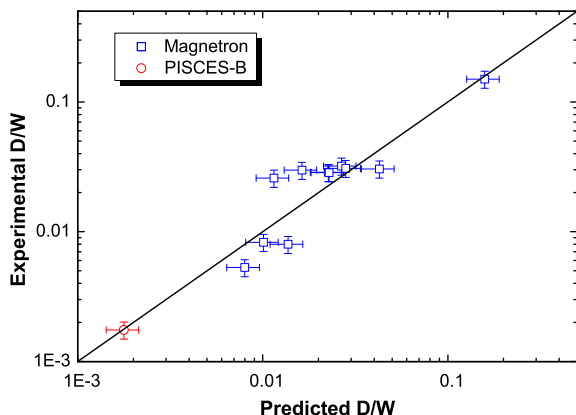


Fig. 4. Comparison between experimentally measured D/W ratios with values predicted by Eq. (4).

Although the deposition conditions have an influence on the layer morphology, no clear influence of the morphology on the deuterium retention could be evidenced since the deposition rate was also changed at the same time.

It therefore appears that the retention in tungsten co-deposited layers can be described by an empirical relation of the same form to that proposed for beryllium co-deposited layers. It is worth noting, however, that for a similar set of deposition conditions, the retention in tungsten layers is significantly lower than in beryllium layers. Indeed, if we consider the case $\Gamma_D/\Gamma_{Be} = \Gamma_D/\Gamma_W = 100$, $E = 60 \text{ eV}$, and $T = 500 \text{ K}$, one obtains $D/W \approx 0.003$ and $D/Be \approx 0.28$; i.e. the retention in tungsten co-deposited layers is 2 orders of magnitude lower than that in beryllium layers.

3.3. Thermal desorption of retained deuterium

Fig. 5 shows the TDS spectra of tungsten layers prepared at different temperatures but with otherwise similar deposition conditions (deposition rate, applied power to the magnetron). The TDS spectra are characterized by 2 main desorption peaks; one at 473–573 K and the second around 1073 K. It is interesting to note that for the 3 layers presented here, the level of the 2nd peak is constant. This observation is also valid for all the layers produced here for which no noticeable difference in the intensity of the high temperature desorption stage has been observed, it should be kept in mind however that given the very low signal associated with this peak, the signal to noise ratio is correspondingly low, hence a low accuracy. The intensity of the low temperature peak strongly decreases for increasing substrate temperatures during deposition. Those desorption stages have also been observed for tungsten target exposed to 100 eV deuterium ions from a deuterium plasma [20].

According to [21], the high temperature desorption peak may be attributed to deuterium detrapping from voids, while 2 desorption stages are reported at low temperatures (640 K and 520 K) corresponding to detrapping from vacancies and desorption of the second deuterium atom trapped at a vacancy (in the form of a D_2V complex). While a clear distinction between those 2 peaks is not observed here, it should be mentioned that the desorption spectrum obtained for the sample deposited at 373 K is broader than that obtained for the sample deposited at room temperature which may indicate the presence of the second peak which is not well resolved. More details about the desorption kinetics of deuterium from tungsten co-deposited layers and implications for ITER can be found in [22].

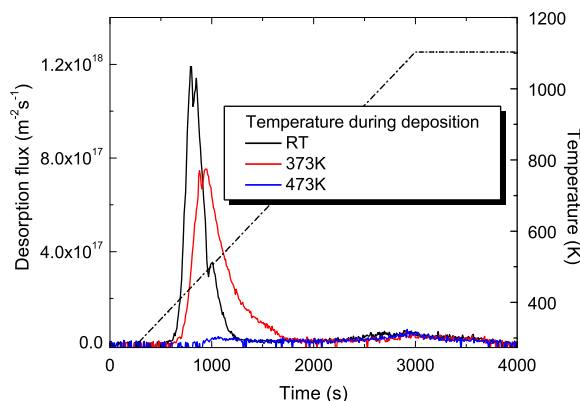


Fig. 5. Thermal desorption behavior of deuterium from co-deposited tungsten layers formed at different temperatures but with a similar deposition rate.

4. Conclusion

The deuterium retention in tungsten co-deposited layers formed both by magnetron sputtering of a tungsten target and in the PISCES-B linear device, was found to strongly depend on the layer formation conditions: tungsten deposition rate, substrate temperature and energy of incident deuterium particles. The deuterium retention decreases with increasing deposition rates and temperatures, and increases for increasing energy of the impinging particles. Those observations are similar to what was previously observed for beryllium co-deposited layers, for which the co-deposition mechanism appeared to be a combination of co-deposition and implantation.

Following these observations, an empirical equation has been proposed to account for the influence of the substrate temperature, the energy of the incident deuterium particles and the ratio of the flux of deuterium to beryllium atoms arriving at the substrate surface on the D/W ratio. It is found that for similar deposition conditions, the deuterium retention in co-deposited tungsten layers is about 2 orders of magnitude lower than in co-deposited beryllium layers.

The desorption kinetics of deuterium has been studied by TDS. 2 desorption stages have been observed at 473–573 K and 1073 K respectively. No influence of the layer morphology (presence of blisters) has been found on the thermal release behavior of deuterium.

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