



Deuterium plasma sputtering of mixed Be-W layers

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ABSTRACT

In ITER, the first mirrors would be vulnerable to deposition from the first wall materials, namely beryllium (Be) and tungsten (W) in mixed compositions. In this study we investigate the capacitively coupled RF plasma sputtering of such mixed Be-W deposits on rhodium-coated substrates, using deuterium as the process gas, and track the enrichment of W during the sputtering process. Experiments were conducted on Be-W deposits with W concentration varying from 2 to 8.3 at.%, and maximal deuterium ion energies in the plasma of 70 and 220 eV. The evolution of the W concentration in the deposits during the plasma sputtering depended considerably on both deuterium ion energy as well as the initial concentration of W in the films. With 220 eV sputtering, a rapid enrichment of W was observed, with all the W changing from Be_xW before sputtering to metallic W and its oxides after sputtering. With 70 eV sputtering, there was no net change in the W concentration, as long as the initial concentration of W in the film was below 4 at.%. Moreover, the W remained considerably in the state of Be_xW after the sputtering as well. However, a W enrichment was also observed with 70 eV sputtering, when the W concentration in the films was higher (8.3 at.%). The rate of W enrichment was also observed to increase monotonically with the increase in the initial concentration of W in the deposits. SDTrimSP simulations performed with experimental parameters indicate that sputtering yield of Be increases with W concentrations in the Be-W layers due to backscattering of D projectiles off W atoms. These studies show that low energy deuterium sputtering of mixed Be-W layers with low W concentrations, allows for removal of Be without rapidly enriching W in the films, making it a promising option for ITER.

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1. Introduction

Nearly 40 optical diagnostic systems in ITER are equipped with metallic first mirrors (FMs) with the objective of directing the light from the fusion plasma towards the diagnostics through an optical labyrinth in order to prevent neutron leakage. However, the FMs being the initial elements in the optical diagnostics, would be subject to constant erosion from charge exchange neutrals as well as deposition of the first wall materials: beryllium (Be), tungsten (W) and their oxides, that would significantly degrade their optical properties [1,2]. The FMs would hence require a regular cleaning to restore their optical properties, currently foreseen to be achieved by an *in-situ* capacitively coupled radio-frequency (CCRF) plasma cleaning technique [3].

CCRF plasma cleaning technique and its application for removal of ITER relevant deposits from FMs has been a subject of numerous studies [4–8]. However, due to toxicity of Be, majority of the plasma cleaning studies make use of aluminium (Al) which acts as a Be proxy due to similarity in their chemical properties [9]. Experimentation with Be instead of a proxy requires special handling facilities such as the Beryllium Laboratory at the National Institute of Laser, Plasma and Radiation Physics (NILPRP), Romania or the previously operational JET Be handling facility installed in the Culham Science Centre, England (JET-BeHF).

There have been a few studies exploring the plasma cleaning of Be deposits making use of controlled environments in the facilities mentioned above. Moser et al. performed plasma cleaning experiments on both lab made deposits (Be and W) [10] as well as tokamak deposits grown in JET-ILW mirrors on molybdenum (Mo) and rhodium (Rh) coated mirrors [11]. Using helium (He), argon (Ar) or a mix of both in the RF discharge, it was shown that the thickness of the deposits could be reduced followed by a cor-

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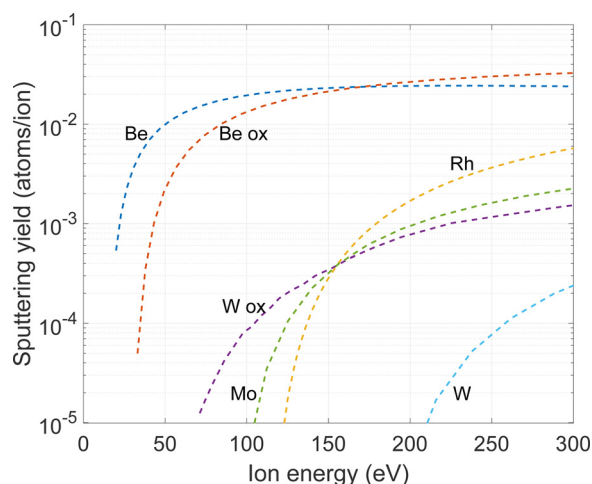


Fig. 1. Sputtering yield (Y) of ITER relevant deposits, Be, W and their oxides as well as FM materials, Rh and Mo, with D^+ projectile reported in literature. Y of Be, Be oxide, W and Mo is a fit of the experimental data points and is taken from [13]. Y of W oxide is also a fit of experimental data points and is taken from [14]. Y of Rh is numerically derived for lack of experimental data in literature and is taken from [15]. ox in the legend refers to the oxide of the corresponding metal.

responding increase in mirror reflectivity. Helium, due to its low sputtering yield (Y) on Mo and Rh, offered gentler cleaning preserving the mirror surfaces while removing Be contaminants as efficiently as Ar. Ben Yaala et al. performed plasma cleaning experiments with 60 eV and 220 eV deuterium (D_2) on lab coatings of Be as well as on mirrors exposed in JET-ILW containing upto 1.5 at.% W [12]. While they were able to completely sputter lab grown Be deposits with D_2 , the deposits from JET-ILW mirrors could not be completely cleaned. It was also shown that at low energies (60 eV), the small fraction of W present in the deposits remains unsputtered and leads to a W enrichment of the surface, which in turn acts as a protective layer against sputtering.

D_2 is an interesting choice of process gas for plasma cleaning of FMs for its high Y on Be while having a negligible impact on FM material (Rh and Mo) at low energies, as can be observed in Fig. 1. D_2 is also beneficial for operation in ITER as it is known to prevent polluting the neutral beam injection system [16]. One of the most interesting properties of D_2 is its ability to sputter Be at low ion energies via chemically-assisted physical sputtering, and the same has been a subject of multiple studies [17–22]. Brezinsek et al. reported that at medium D impact energies (~ 75 eV), about one third of the sputtered Be came from chemically-assisted physical sputtering, with the mechanism being the formation of BeD molecules [17]. Björkas et al. showed experimentally, that the chemical sputtering via formation of BeD molecules was promoted at low D energies [18]. They observed that the fraction of Be sputtered as BeD molecules was as high as 80% at 9 eV, while this fraction dropped to 40% at 90 eV. Ballauf et al investigated the sputtering of Be as BeD as a function of ion energy (20 to 500 eV) and temperature (300 to 700 K) [19]. They found that the ratio BeD^+/Be^+ increased both with an increase in ion energy and temperature. All the studies agree on the fact that as the D ion energies increase over 100 eV, the contribution of chemically-assisted physical sputtering of Be diminishes and physical sputtering becomes the main mechanism of Be removal.

In ITER, however, the contaminants on FMs would also include W in addition to Be, although in minor amounts. Experimental campaigns in ITER like wall of the JET tokamak have indicated W is deposited on the FMs in small amounts ($< 5\%$) particularly in the divertor region, while Be makes up majority of the surface co-deposition [23–25]. There are also other elements in the co-

deposits, such as carbon, nitrogen, oxygen as well as deuterium. However, deposition of W even in small amounts is concerning due to its high sputtering energy threshold in comparison to other co-deposits. Furthermore, the composition of W in the co-deposits in ITER could also increase beyond that measured in JET campaigns, depending on the location of FM in the tokamak as well as the duration of the hot plasma pulse. Hence for D_2 plasma cleaning of ITER relevant contaminants, it is important to understand its interaction with mixed Be-W deposits. There have been very few studies to date dealing with sputtering of mixed Be-W layers with D projectiles [26–30]. Björkas et al. studied the sputtering of Be and Be_2W by D bombardments in the energy range of 7–200 eV via molecular dynamics (MD) simulations [26]. They found that both surfaces led to formation of BeD molecules as a result of swift chemical sputtering, and that physical sputtering yield was more efficient than swift chemical sputtering as the energies became larger. They explained that at lower ion energies (10–20 eV), the D surface concentration is higher making it more likely for any Be atom to have many D neighbours, compared to at higher energies where the D penetration depth is larger. This D bonding on the surface Be, lowers the binding energy of Be atoms, making it more easily sputtered at lower energies. Lasa et al. presented an atomistic study on D irradiation on Be-W mixtures via MD simulations, and reported chemical effects on sputtering at low energies, and a purely physical sputtering at higher energies (100–200 eV) [27]. Mutzke et al. showed via simulations with H and He projectile, that the Y of Be in mixed Be-W targets can get even larger than Y of pure Be targets and explained the additional Be sputtering caused by reflection of impinging ions by W atoms in the mixed layers [28]. The proposed effect, however, was only observed at ion energies greater than 1000 eV.

However as Be is removed from the mixed Be-W surfaces, either via chemically assisted physical sputtering at low energies or physical sputtering at higher energies, an enrichment of W on the surface which is particularly problematic for FM cleaning can be observed. The enriched W layer, which has a larger sputtering energy threshold, could block the removal of the Be beneath it and become a major obstacle towards low energy deuterium cleaning of FMs, calling for a thorough investigation on the topic. In this work we study the influence of ion energy in D_2 plasma and the resulting regime of sputtering (physical or chemically-assisted physical sputtering) in the removal of lab grown mixed Be-W deposits with CCRF plasma sputtering. We also investigate the role of the initial concentration of W in the mixed Be-W deposits, in the removal of Be and enrichment of W.

2. Experimental

Owing to the toxicity of Be, the experiments were conducted in a controlled environment at the Beryllium Handling Facility at the National Institute for Laser, Plasma and Radiation Physics (NILPRP) in Măgurele, Romania. Seven mirror substrates with 25 mm diameter and 8 mm thickness were used for the experiments. Five of the mirror substrates were made of stainless steel (SS) while two were made of Mo. Prior to the experiments, all the mirror substrates were polished (with silicon carbide (SiC) paper, diamond paste and alumina powder of $0.05 \mu\text{m}$) and coated with 500 nm of Rh using magnetron sputtering at University of Basel to mimic ITER first mirrors. The corresponding deposition procedure is described elsewhere [31].

2.1. Be-W deposition

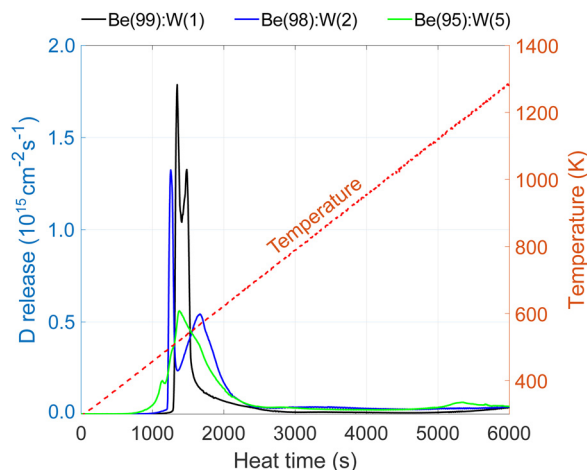
In ITER, co-deposition would be one of the main mechanisms that leads to D retention in the wall materials [32,33]. Studies in JET tokamak [34] as well as lab experiments [35] have indicated

Table 1Discharge voltage (U_{disc}) and current (I_{disc}), rates of deposition (R.D.) for Be and W, as well as gas flows for Ar and D_2 and gas pressure.

Be:W atomic ratio	Be			W			Flow (sccm)		P (Pa)
	U_{disc} (V)	I_{disc} (A)	R.D. (\AA s^{-1})	U_{disc} (V)	I_{disc} (A)	R.D. (\AA s^{-1})	Ar	D_2	
99:1	450	0.36	3.2	312	0.06	0.03	20	6	1
98:2	410	0.36	2.8	335	0.09	0.05			
95:5	490	0.36	2.5	325	0.2	0.25			

that D retention in co-deposited layers is large. Hence, in order to imitate the contaminants that would be obtained in the environment of fusion reactor, we produced Be-W films with deuterium seeding. The D seeded Be-W coatings were performed by using the Direct Current Magnetron Sputtering (DCMS) technique in a circular chamber used exclusively for Be containing thin films within the Beryllium Handling Facility at NILPRP. The details of this set-up are described in a previous paper [36]. The Be and W sputtering sources consisted in two water-cooled magnetron cathodes provided with high purity Be (99.95%) and W (99.95%) circular (50 mm diameter and 3 mm thickness) targets operated in DCMS regime. Prior to the deposition process, starting from a base pressure of 3×10^{-4} Pa, Ar and D_2 were inducted into the deposition chamber until the stable pressure of 1 Pa was achieved. The Ar : D_2 flow ratio was kept constant at 10:3. Deposition rate values were between 0.03 and 0.25 \AA s^{-1} for W, and between 2.5 and 3.2 \AA s^{-1} for Be, depending on the required Be/W atomic ratio. These values for gas flows, pressure and coating speeds were carefully selected, based on previous experience and calibrations performed especially for this experiment. The thickness of the deposited Be-W films was targeted at 150 nm. All the relevant parameters for the plasma depositions are presented in Table 1.

Additionally, during each mirror deposition, two silicon (Si) samples were placed next to the substrate to be used as witness samples. One set of witness samples S1, S2 and S3 deposited with Be:W coatings of 99:1, 98:2 and 95:5, respectively were chemically characterized using X-ray photoelectron spectroscopy. It is important to note that the Be:W ratios mentioned are that of the target material used for deposition. As will be discussed later, the actual composition of Be and W obtained on the samples after the deposition can differ from the Be:W ratios of the target material. The second set of Si samples were used to perform thermal desorption spectroscopy (TDS) (method described in [36]) in order to assess the deuterium content added during the deposition process. The samples were heated up to 1275 K with a ramp of 10 K min^{-1} , measuring the amount of HD and D_2 molecules released in the process. The release of D through HDO and D_2O was carefully monitored during TDS measurements and it was found that it was below the detection level of the spectrometer. The quantification of HD and D_2 was performed based on spectrometer calibrations with known amounts of H_2 and D_2 gas. The total D release was calculated by summing the contribution of HD and D_2 . The D desorption profiles as a function of temperature for the investigated samples are presented in Fig. 2. The TDS spectrum of the Be (99):W (1) shows that the largest part of the D in sample is released in a narrow temperature range of just 50 K. In this range the spectrum exhibits two sharp desorption peaks, the first one appears at 510 K and the second smaller peak at ~ 550 K. For higher W concentration (2%), the first peak has a minor shift towards lower temperatures and its intensity decreases compared to the first sample (1%). Moreover, as the W content increase, it transforms the peak at 550 K into a wide peak in the TDS spectrum. Compared with the above-mentioned samples, the D release profile of the layer with the highest W content (5%) exhibits a broad desorption peak at 520 K, a very small low temperature peak at 478 K and a shoulder at 1150 K which indicates the presence of an additional desorption

**Fig. 2.** The TDS spectra of the Be-W coatings deposited on silicon witness samples.

peak. One can observe that with the increase of the W concentration in layers the D is released over a wider temperature range which can imply that additional trapping states in the layer are created or the W trapping states are substituting the Be trapping states.

The total D amount introduced inside of the coated layers was calculated by integrating the desorption curves presented in Fig. 2. The amount retained was approximately 20 at.% with a small increase (22.5 at.%) observed for layers with higher W content compared to Be (99%):W (1%) where D retained was 18.5 at.%. This variation can occur due to different plasma parameters used in order to achieve the desired atomic ratios. In this case the input power on the W cathode is raised, which increases the plasma density leading also to an increase of the ion flux towards the substrates.

2.2. Plasma sputtering

The substrates deposited with Be-W films were sputtered with CCRF plasma discharges in a high vacuum (HV) chamber at NILPRP (Fig. 1 of reference [12]). The HV chamber is evacuated to a background pressure of 10^{-4} Pa. In the plasma generation process, the RF power is directly fed to the mirror thus acting as the powered electrode, while the entire vacuum chamber serves as the grounded electrode. The asymmetry of the areas between the powered and grounded electrode leads to development of a negative self-bias V_{DC} on the electrode. This causes the positively charged ions to accelerate towards the electrode surface with an energy of $e(V_p - V_{\text{DC}})$, where V_p is the plasma potential. A 60 MHz RF generator (Comet cito) coupled with a matchbox was used to generate a 1 Pa D_2 plasma inside the vacuum chamber. The typical V_p of the generated plasma is approximately 20 V [12]. The RF power was adjusted to have either -50 V or -200 V self bias (SB) on the sample, leading to a corresponding maximum ion impact energy of 70 eV or 220 eV, respectively. The self-bias voltage as well as the sputtering duration of the samples are detailed in Table 2. It is

Table 2
Details of the deposition, sputtering parameters and the W concentration obtained via XPS measurements (before and after sputtering) of the mirror samples.

Sample	Substrate + coating	Be:W deposition	Total sputtering time (h)	Self Bias (-V)	W conc. (at.%)	
					Before sputtering	After sputtering
Rh1	SS+Rh	99:1	11.7 (5 + 6.7)	200	2.0	5.2
Rh2	SS+Rh	99:1	10.0	50	2.0	1.3
Rh3	Mo+Rh	99:1	17.8	50	2.0	2.1
Rh4	SS+Rh	98:2	5.0	200	2.9	6.8
Rh5	SS+Rh	98:2	13.0	50	2.9	2.3
Rh6	SS+Rh	95:5	11.3 (5 + 6.3)	200	8.3	36.3
Rh7	Mo+Rh	95:5	17.8	50	8.3	24.2

worth noting that this HV chamber used for sputtering is separate from the chamber used for deposition. Hence the samples were exposed to air between transfer from the deposition chamber to the sputtering chamber.

A low temperature deuterium plasma is known to generate multiple ion species, particularly D^+ , D_2^+ and D_3^+ [37]. This significantly affects the evaluation of the incident energy and flux, as D_2^+ and D_3^+ impact the surface as two D atoms with one half and three D atoms with one third of the energy of D^+ , respectively [26]. Furthermore, the ratio of the different ion species in the plasma can vary considerably depending on the discharge conditions [37–41]. Unfortunately, we do not have quantitative information on the different ion species present in our plasma, but we estimate a majority ion flux (over 75%) carried by D^+ and D_2^+ with a minor flux of D_3^+ . Relevant to our study, maximal ion impact energies of 70 and 220 eV would correspond to 70 and 220 eV per D for the D^+ ions, 35 and 110 eV per D for the D_2^+ ions, and 23 and 73 eV per D for the D_3^+ ions, respectively. Further in this manuscript, ion energies are referred to as 70 and 220 eV for the sake of convenience. However, it must be taken into account that these are only the maximal ion energies corresponding to the self-bias, and that ions with lower energies would also be a part of the total flux. As can be inferred, the penetration depth of deuterium ions in Be-W coatings increases with an increasing ion energy. For instance, in pure Be the penetration depth of 70 eV and 220 eV D^+ is 20 and 60 Å, respectively [42].

2.3. Characterization techniques

After the D_2 plasma sputtering experiments, the samples were characterized with X-ray Photo-electron Spectroscopy (XPS) to analyse their surface chemical composition. The electron spectrometer is equipped with a hemispherical analyzer (Leybold EA10/100 MCD) and a non-monochromatized Mg $K\alpha$ X-ray source ($h\nu = 1253.6$ eV) was used for core level spectroscopy. The binding energy (BE) scale was calibrated using the Au $4f_{7/2}$ line of a cleaned gold sample at 84.0 eV. The fitting procedure of core level line is described in [43]. The measurement depth of XPS is ~ 5 nm. It is worth noting that the samples were exposed to air before transferring them to the XPS chamber for analysis.

3. SDTrimSP simulations

In order to understand some of our experimental results, we also performed Monte-Carlo-based SDTrimSP simulations [44] with experimental variables. This code uses the binary collision approximation to model transport of energetic particles through amorphous targets of arbitrary composition, and has been shown to be valid for impinging particle energies in the eV - keV range [44]. The code can yield the fluence-dependent sputter yields, implantation depths, reflection yields, etc. for all projectile-target combinations. Particle trajectories are calculated in three dimensions, while the target is one-dimensional, computed as a series of smooth

slabs or arbitrary thicknesses and compositions. SDTrimSP is capable of both static (the target composition is fixed) and dynamic simulations (the target composition changes as a function of fluence). We performed static calculations, where 8×10^4 particles were simulated. The depth discretization was set to 1 nm.

4. Results and discussion

The XPS measurements on the witness samples revealed a W concentration of 2 at.% on S1, 2.9 at.% on S2 and 8.3 at.% on S3. These are used as the starting concentrations of W (or 0 h of sputtering time) on the samples deposited with Be:W coatings of 99:1, 98:2 and 95:5, respectively. The W4f core level spectra were deconvoluted in different components and are presented in Table 3. Only W and Be concentrations are considered (i.e. their sum totalizes 100 at.%) for the calculation of the relative atomic concentration of W in this manuscript. While not included in calculations, XPS measurements also revealed C and O, owing to the exposure of samples in air. The deconvolution of C1s core level spectra indicated that C was present as C-C, C-O and C=O, but not carbide.

After coating with corresponding Be-W deposits, the mirror samples were subjected to deuterium plasma sputtering with an ion energy of either 220 eV or 70 eV. As described in Section 1, 220 eV deuterium ions have a higher penetration depth and lead to pre-dominant physical sputtering of Be. However at 70 eV, the ions have a lower penetration depth and the D concentration on the surface is higher allowing for swift chemical sputtering via formation of BeD/BeD₂ molecules [26] in addition to physical sputtering. Deuterium ions with these energies have negligible or no impact on W as can be observed in Fig. 1. Hence, any impact on W concentration after the plasma sputtering is a result of the change in the concentration of Be, caused by its removal with deuterium sputtering. Furthermore, exposure to air before XPS measurements, also led to formation of oxides (BeO, WO₃, WO₂ and BeWO₃) on the surface of samples. The sputtering yield of the oxides varies from their metallic counterparts as can be observed in Fig. 1. At 70 eV, the sputtering yield of BeO is almost half of Be, while at 220 eV the sputtering yield of BeO is ~ 1.2 times higher than that of Be. Moreover, while W itself cannot be removed, W oxide can be sputtered considerably at 220 eV. The removal of W oxide would also contribute to change in W concentration after plasma sputtering. This would however be a minor contribution, as there were only traces of W oxide on the mirror surface before plasma sputtering as can be observed in Table 3.

On the samples coated with 99:1 Be:W deposits (Rh1, Rh2 and Rh3), the deconvolution of the W4f spectrum indicated that all the W was bonded to Be in the form of Be_xW. Similar deconvolution was also done for the Be1s spectra to verify the presence of Be_xW. The binding energies (BE) of the different pure Be-W compounds are quite identical. For instance, in the Be1s spectra the BE of Be₂W is 111.1 eV and that of Be₁₂W is 111.4 eV [45], while we measure a BE of 111.2 eV. Since we cannot confidently resolve the BE of different pure Be-W compounds in our XPS system, they are collec-

Table 3

Chemical compounds identified after deconvolution of the XPS measurement for the W4f core level spectra. The atomic concentrations are calculated taking into account that Be+W corresponds to 100%.

Sample	Be:W deposition	Ion energy (eV)	Atomic concentration (at. %)				
			W4f				
			Be _x W	W	BeWO ₃	WO ₂	WO ₃
S1	99:1		2.0				
Rh1 (1/2)	99:1	220	2.1		0.2		1.5
Rh1 (2/2)	99:1	220		1.5		0.5	3.1
Rh2	99:1	70	0.8		0.5		
Rh3	99:1	70	0.8		0.9	0.1	0.3
S2	98:2		2.4			0.3	0.2
Rh4	98:2	220		1.9	0.7	0.9	3.3
Rh5	98:2	70	1.6		0.7		
S3	95:5		7.4			0.9	
Rh6 (1/2)	95:5	220		4.0		4.0	28.6
Rh6 (2/2)	95:5	220		6.3		3.2	26.7
Rh7	95:5	70	5.0		5.1	0.9	13.2

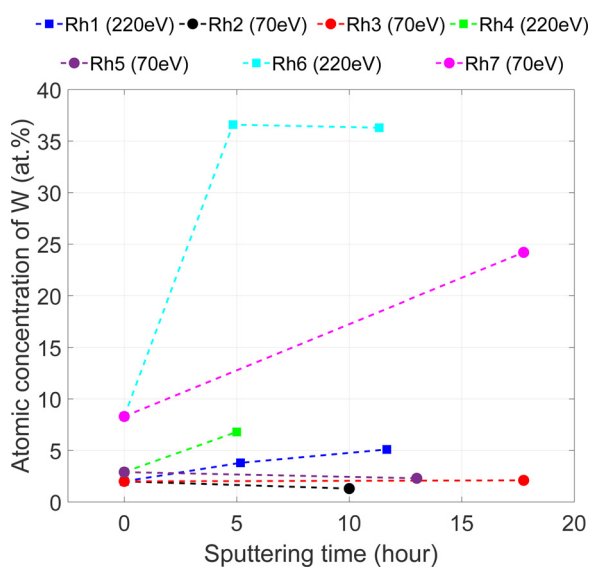


Fig. 3. Time evolution of the atomic concentration of W with respect to Be during the plasma sputtering process.

tively referred to as Be_xW in this manuscript. However, Be atoms are most stable in Be₂W systems than the rest [30]. Furthermore, the deuterium sputtering yield of Be in Be₂W is lower than that of metallic Be [26]. Rh1 was sputtered with 220 eV in two steps of 5 h and 6.7 h, respectively. The evolution of total W concentration during plasma sputtering can be observed in Fig. 3. After the 5 h sputtering, the total W concentration on its surface increased from 2 to 3.8 at.%. The state of W also changed from purely Be_xW to a mix of Be_xW, BeWO₃ and WO₃ after the sputtering. It is worth noting that difference in the BE of Be_xW, BeWO₃ and WO₃ in the Wf4 spectrum is sufficiently large (> 1 eV) to be resolved confidently. The emergence of BeWO₃ and WO₃ was most likely due to oxidation of enriched W when the sample was exposed to atmosphere before XPS measurement. The oxidation of enriched W could also occur during sputtering, most likely by residual H₂O in the vacuum chamber. With an additional sputtering of 6.7 h, the total W concentration further increased to 5.2 at.%, with the state of W changing to a mix of W and its oxides. This indicates a change of W chemical state from pure Be_xW towards pure W during the plasma sputtering process. On Rh2 and Rh3, which were sputtered with 70 eV ions, the concentration of W remained roughly the same after sputtering. The amount of W in Be_xW reduced from 2 to 0.8 at.% in both the samples, with emergence of BeWO₃ and W

oxides, indicating a change of W chemical state after the process. The transition from Be_xW to W was however considerably lower than Rh1.

Similar trends were obtained on samples coated with 98:2 Be:W deposits (Rh4 and Rh5). After sputtering of Rh4 with 220 eV ions for 5 h, the concentration of W almost doubled from 2.9 to 6.7 at.%, with the chemical state of W changing from predominantly Be_xW to metallic W and its oxides. There were also W oxides in minor concentration (0.5 at.%) at the beginning, which most likely also got sputtered as evident from Fig. 1. As mentioned earlier, a major part of W oxides obtained after the sputtering is very likely due to atmospheric oxidation of the metallic W on the surface after the sample removal from vacuum. On the other hand, after the sputtering of Rh5 with 70 eV ions for 13 h, the total concentration of W roughly remained unchanged. Furthermore, while all of the W was in the form of Be_xW and W oxides before sputtering, it modified to a mix of Be_xW and BeWO₃ after sputtering without any W metallization.

On the samples coated with 95:5 Be:W deposits (Rh6 and Rh7), however, a strong W enrichment was observed after sputtering with both 70 eV and 220 eV ions. Rh6 was sputtered with 220 eV in two steps of 5 h and 6.3 h respectively. The concentration of W increased significantly from 8.3 to 36.3 at.% after the first sputtering step. Furthermore, all of the W changed from predominantly Be_xW before sputtering to metallic state and oxides after sputtering. After the second sputtering step, the net W concentration remained the same. The state of W also remained identical to that obtained after first sputtering step, indicating a saturation of W composition on the surface. Rh7, which was sputtered with 70 eV ions for 17.8 h also displayed an increase in the total concentration of W from 8.3 to 24.2 at.%. However, the W measured was still in the state of Be_xW with presence of BeWO₃ and W oxides, indicating a lower metallization of W.

The results clearly indicate that the evolution of W depends considerably on the ion energy used for sputtering of the Be-W films. With all the samples sputtered with 220 eV ions, a net increase of W concentration was obtained, with all detected W changing from Be_xW to metallic W and its oxides, indicating an overall enrichment of W. For the samples sputtered with 70 eV ions, however, no net increase in W concentration was measured (with the exception of Rh7). Furthermore, in all the cases, the W remained mostly in the state of Be_xW after the sputtering as well. The W enrichment in Rh7 suggests that the evolution of W depends as well on the starting concentrations of W. This can be observed well by comparing the results of Rh1, Rh4 and Rh6, which were all sputtered with 220 eV ions but having different starting concentrations of W. We can calculate the percentage of increase in

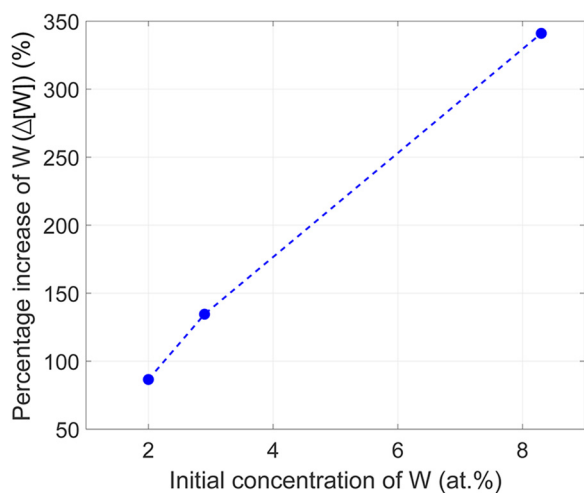


Fig. 4. Percentage increase in the atomic concentration of W versus initial concentration of W after 5 h plasma sputtering with 220 eV deuterium ions.

the atomic concentration of W after the plasma sputtering ($\Delta[W]$) via the following relation,

$$\Delta[W] = \frac{[W_f] - [W_i]}{[W_i]} \times 100 \quad (1)$$

where $[W_f]$ and $[W_i]$ are the final and initial atomic concentrations of W, respectively. After the uniform sputtering time of 5 h, Rh1, Rh4 and Rh6 recorded $\Delta[W]$ of 85%, 134% and 341%, respectively. As can be observed from Fig. 4, $\Delta[W]$ increases almost linearly with the increase in initial concentration of W from 2 to 8.3 at.%. This indicates that a relatively higher amount of Be is sputtered from the deposits at the same energy when the initial concentration of W is higher. One way to explain the increase in Be sputtering (leading to W enrichment) with the increase in initial concentration of W could be the increased reflection of deuterium ions from W atoms in the Be-W deposited layer as discussed in [28]. The deuterium ions can enter inside the Be-W layer and get reflected back to surface upon impact with W atoms, leading to additional sputtering of surface Be atoms. As the initial concentration of W increases in the Be-W films, the reflection of deuterium ions from W atoms would increase as well. The increase of reflected deuterium ions could enhance the sputtering of surface Be and hence the W enrichment rate.

In [28] however, they discussed this behavior only at energies greater than 2800 eV, and hence cannot be extrapolated to our results directly. In order to understand the enhancement of Be sputtering yield in mixed Be-W layers at low energy deuterium sputtering as observed in Fig. 4, we performed static SDTrimSP simulations with 220 eV D particles impinging under normal incidence on Be-W layers of varying initial W content. The simulations reveal an increase in the sputter yield of Be as a function of the W surface content (shown in Fig. 5), until roughly 20 at.%. Due to the larger atomic mass of W relative to Be, backscattering recoils are more likely when a D projectile recoils off a W atom in the target. In addition to this, a larger fraction of the initial energy is conserved after a W recoil than after a Be recoil. Up to 20 at.% W, despite the surface being partly covered in W, which does not sputter at this impinging particle energy, a larger fraction of impinging D particles can reflect off the atoms in the subsurface layers towards the surface with sufficient energy to sputter Be, leading to a larger sputter yield than if the target were exclusively Be. This behavior is consistent with the experimental results (Fig. 4), which show a greater relative and absolute level of enrichment (i.e., more Be sputtered) after equal exposure for higher initial concentrations of

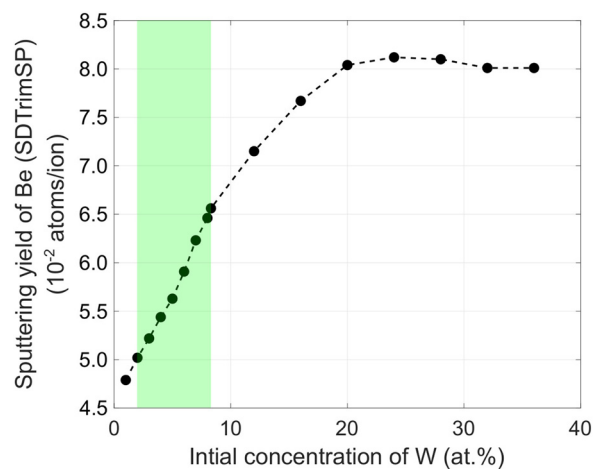


Fig. 5. Sputtering yield of Be in Be-W layer obtained by static SDTrimSP simulations for different initial concentrations of W in the layer. 220 eV D^+ ions are used as the projectile. The highlighted portion in the plot corresponds to the initial concentrations of W in Be-W layers used in the experiments, i.e., 2 to 8.3 at.% (Fig. 4).

W. At roughly 20 at.% W, the sputter yield plateaus and starts to slowly decrease. From this concentration onward, the increase in D recoils with sufficient energy to sputter Be does not offset the depletion of Be at the surface.

5. Conclusion and outlook

In this study, we investigated the enrichment of W during deuterium plasma sputtering of samples deposited with mixed Be-W layers. The evolution of the W concentration in the deposits during the process depended considerably on the deuterium ion energy. At 220 eV, where the sputtering is predominantly physical, a net increase of W concentration was obtained. Furthermore, all of the W in the film changed from Be_xW before sputtering to metallic W and its oxides after sputtering, indicating an overall surface metallization of W. At 70 eV, where deuterium is known to sputter Be via chemically-assisted physical sputtering, there was no net change in the W concentration, as long as the initial concentration of W in the film was below 4 at.%. Moreover, in all the cases of sputtering with 70 eV, W remained mostly in the state of Be_xW after the sputtering as well. Hence, the enrichment of W was considerably lower when sputtered with 70 eV compared to 220 eV at the same conditions. The enrichment of W also depended on the initial concentration of W in the deposits. With 220 eV ions, the percentage rise of W in the film after sputtering for the same duration increased almost linearly with the increase in the initial concentration of W from 2 to 8.3 at.%. In other words, at the same ion energy and sputtering parameters, the enrichment of W during the plasma sputtering was faster when the initial concentration of W in the deposits was higher. Static SDTrimSP simulations were also performed with 220 eV D projectiles on Be-W layers with varied W compositions. Simulation results indicated that the sputtering yield of Be increase with increasing W concentration in the Be-W layers upto 20 at.%, due to backscattering recoils of the D projectiles off W atoms in the layers.

The results shed considerable light on the viability of deuterium as a process gas for plasma cleaning of FMs in ITER. As can be inferred, the ideal case scenario for cleaning of mixed Be-W deposits with deuterium plasma would be to keep the rate of W enrichment minimal so as to maximise the removal of Be from the deposits. As long as the W concentration in the deposits is low (< 4 at.%), the Be can be sufficiently removed with 70 eV deuterium ions without considerably enriching the W in the deposits. With 220 eV however, where the physical sputtering of Be dominates, the W

enrichment rate increases considerably. This leads to formation of a metallic W layer, slowing down and eventually stopping the removal of Be from the deposits. Hence, 70 eV deuterium cleaning is optimum for removal of Be deposits when the concentration of W in the film is below 4 at.%. However, if the W concentration in the deposits is high (> 8 at.%), the W enrichment rate increases even at lower ion energy (70 eV), making deuterium cleaning undesirable.

The results call for further work in deuterium cleaning of Be-W deposits in scope of FMs in ITER. Additional measurements can be performed with deuterium plasma to identify suitable ion energies to have a sustained cleaning of Be in mixed Be-W deposits when the W concentration is high (> 8 at.%). Our results suggest saturation of W enrichment along the cleaning process, possibly due to formation of a metallic W layer. This trend can be verified by characterising the surface of mirrors in shorter intervals during their cleaning process. More investigation is also necessary to understand the impact of W concentration in the deposits in its evolution during the sputtering process, by having controlled experiments with varied W concentrations. Furthermore, plasma cleaning of FMs in ITER is foreseen to be conducted in presence of a notch filter [46], which leads to a considerable increase of plasma potential [47] and wall sputtering [48]. Hence, it is important to investigate the Be-W sputtering on FM surfaces in presence of notch filter, as the sputtering of Be/W deposits from the walls adjacent to the FMs and ensuing deposition onto the FMs could impact the overall Be removal.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kunal Soni: Writing – original draft, Investigation, Formal analysis, Visualization. **Lucas Moser:** Conceptualization, Methodology, Investigation. **Corneliu Porosnicu:** Resources, Investigation, Writing – review & editing. **Rodrigo Antunes:** Writing – review & editing, Visualization, Formal analysis, Resources. **Rodrigo Arredondo:** Software, Formal analysis, Writing – review & editing. **Paul Dinca:** Resources. **Roland Steiner:** Methodology. **Laurent Marot:** Supervision, Project administration, Funding acquisition, Formal analysis. **Ernst Meyer:** Project administration.

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