Plasma cleaning of beryllium coated mirrors

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Abstract.

Cleaning systems of metallic first mirrors are needed in more than 20 optical diagnostic systems from ITER to avoid reflectivity losses. Currently, plasma sputtering is considered as one of the most promising techniques to remove deposits coming from the main wall (mainly beryllium and tungsten). This work presents the results of plasma cleaning of rhodium and molybdenum mirrors exposed in JET-ILW and contaminated with typical tokamak elements (including beryllium and tungsten). Using radio frequency (13.56 MHz) argon or helium plasma, the removal of mixed layers was demonstrated and mirror reflectivity improved towards initial values. The cleaning was evaluated by performing reflectivity measurements, Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy and ion beam analysis.

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1. Introduction

Several optical diagnostics foreseen in ITER will rely on metallic First Mirrors (FMs) enabling light originating from the plasma or from probing light sources to travel through the neutron shielding towards detectors. Because these FMs are in such a close proximity to the fusion plasma, they will experience high particle fluxes (from charge-exchange neutrals and neutrons to ultraviolet, X-ray and gamma radiations) and inevitably suffer from erosion and/or deposition. Studies showed that the main concern for FMs reflectivity was the deposition of material sputtered from the main wall, i.e. mainly beryllium (Be) and tungsten (W) [1,2]. Along with laser cleaning [3–6] in situ plasma sputtering is currently considered as one of the most promising cleaning techniques to remove deposits from FMs [7,8]. For the latter, several studies conducted worldwide have shown successful plasma cleaning on molybdenum (Mo) or stainless steel mirrors (up to a size of 90 mm diameter) contaminated with aluminium (Al), alumina (Al_2O_3), W or mixture of them [9–13]. Various gases (argon (Ar), neon (Ne), helium (He) or deuterium (D_2)) were employed and the discharges were sustained using different techniques (capacitively coupled radio-frequency (RF), penning discharge or RF magnetron sputtering).

Nevertheless, all the previous mentioned experiments were accomplished by using a Be proxy with similar chemical properties, i.e. aluminium [14]. Indeed due to the toxicity of Be, deposition or sputtering experiments can only be performed in dedicated environment such as the JET Be handling facility installed in the Culham Science Centre in England (JET-BeHF). So far, no experiments on plasma sputtering of tokamak-like films containing Be have been performed. The aim of this experimental campaign was to confirm the removal efficiency of plasma cleaning on 8 tokamak deposits grown in JET-ILW [15] on Mo and rhodium (Rh) coated mirrors (both considered as candidates for FM [16]). For this purpose a vacuum chamber (see figure 1) was mounted in the JET-BeHF to perform plasma cleaning with different gas composition (helium (He), Ar or a mix of both) and ion energy (from 200 to 600 eV). The effects of such cleanings on the mirror's optical properties were investigated.

2. Experimental conditions

The 8 mirror samples were $10\times10\times10$ mm^3 cubes of polycrystalline Mo with one polished face. Among those 8 mirrors, 4 were coated with 1 μm of Rh at the University of Basel using magnetron sputtering [17]. The mirrors were exposed in JET-ILW in various locations of the tokamak including the divertor base, the outer and inner divertor and the outer wall as described in [15, 18]. More information can be found in table 1. All mirrors used in this study were characterized before and after the exposure in JET-ILW. Due to the toxicity of the JET-ILW mirrors (contaminated with Be and tritium and activated), a vacuum chamber was built and installed in the JET-BeHF where a pressure of about 1×10^{-6} mbar was achieved with a conventional pumping system.

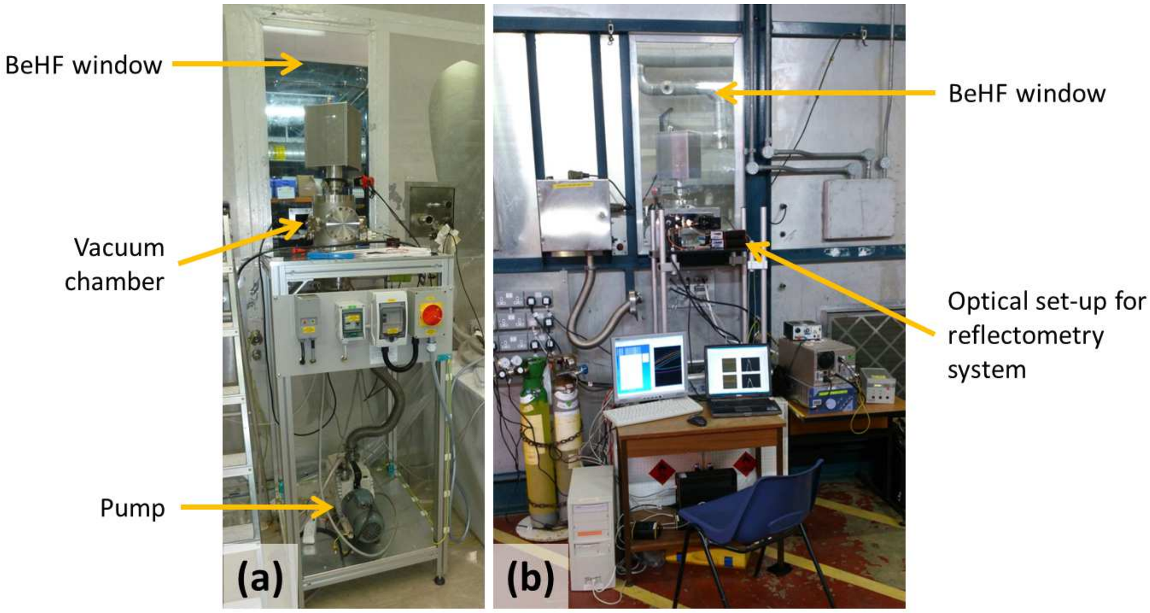

Figure 1: (a) Picture of the vacuum chamber installed inside the JET-BeHF in front of a window and of (b) the equipment needed to control the experiments located outside of the JET-BeHF.

The plasma was generated by applying 13.56 MHz RF directly to the electrode where the mirror is mounted (RF capacitively coupled discharge). Due to the asymmetry of the powered to grounded areas, a negative DC component (called self-bias) is created on the electrode/mirror, accelerating the plasma ions towards the mirror's surface (Ar^+ and/or He^+). In addition to the negative self-bias on the mirror, the plasma is positively charged (plasma potential measured by Langmuir Probe in the range of 25 to 40 V) and therefore the ion energy (in eV) is equal to the sum of self-bias and plasma potential. The discharge conditions (gas, pressure, ion energy) can be found in table 2. All the electronic devices to control the experiment were located outside and connected to the chamber via a feedthrough panel mounted on the JET-BeHF wall. The chamber was mounted on a frame in front of a JET-BeHF window in order to monitor the change of specular R of the mirror during the cleaning process: a reflectometry system developed in Basel [19] was adapted outside of the JET-BeHF for measurements from 400 to 800 nm. The informations obtained were guiding the cleaning times (estimated from calculation using Be sputtering yield and ion flux from Langmuir probe measurements done in Basel) as no surface characterisation techniques were available directly on-site. The cleanings were confirmed by ex situ measurements of the total R of each mirror between 400 and 1600 nm by using a spectrophotometer. In addition, total and diffuse R for cleaned mirrors with low Be content was measured with a Varian Cary 5 apparatus (250–2500 nm). The total reflectivity recovery (see table 2) was calculated by using the measurements performed before exposure, before cleaning and after cleaning at two wavelengths, namely in the visible (400 nm) and in the infra-red (1600 nm) according

Table 1: List of mirrors from JET-ILW and their location during exposure.

Mirror	Material	Location	Position in the channel
61	Rh	Outer wall	1.5 cm
69	Rh	Inner divertor	2.5 cm
77	Rh	Outer divertor	1.5 cm
80	Rh	Divertor base	0.0 cm
96	Mo	Outer wall (unit 4B)	0.0 cm
98	Mo	Outer wall (unit 4B)	1.5 cm
99	Mo	Outer wall (unit 4B)	3.0 cm
100	Mo	Outer wall (unit 4B)	4.5 cm

to equation 1:

$$\text{Reflectivity recovery (\%)} = \frac{R_a - R_b}{R_i - R_b} \times 100 \tag{1}$$

where R_i, R_b and R_a correspond to the total reflectivity of the mirror before JET-ILW exposure (pristine mirror), after JET-ILW exposure (before cleaning) and after cleaning, respectively. A complete recovery of the total reflectivity would give a value of 100 % while a degradation of the total reflectivity through cleaning would lead to a negative value. In the case were this value is greater than 100 %, the mirror has a higher total reflectivity after cleaning than before exposure in JET-ILW. Surface analysis of all test mirrors was performed with nuclear reaction analysis (NRA) using a 2.5 MeV ^{3}He^{+} beam for light elements and time of flight elastic recoil detection analysis (ToF-ERDA) using a 36 MeV ^{127}I^{8+} beam for heavy elements and compared with the values obtained after the exposure in JET-ILW. X-ray photoelectron spectroscopy (XPS) was added for samples with low Be content (setup and fitting procedure described in [20]). Surface images were done using a Field Emission Scanning Electron Microscope (SEM) from ZEISS (MERLIN) equipped with an Oxford Instruments Energy Dispersive X-Ray (EDX) analyser for surface composition measurements. After the first cleaning in JET-BeHF, some Mo mirrors were Be free but still oxidized. A second RF plasma cleaning was therefore performed in Basel in a vacuum chamber with a base pressure of 1×10^{-7} mbar with conditions listed in table 2.

3. Results and Discussion

3.1. Rhodium mirrors

All 4 mirrors were heavily coated with typical JET elements (Be, inconels (Inc), nitrogen (N), carbon (C), oxygen (O), ...) and mirror 77, close to a Be coater has the highest Be content of all. The inconels group denotes a sum of nickel, iron and chromium which cannot be separated. The mirrors optical properties were strongly degraded after the exposure as can be seen in [15] and that the reflectivities are well below those of Be from the handbook of Palik [21] (see mirror 77 in figure 2). This confirms that even

Table 2: List of experimental conditions applied for each mirror in the JET-BeHF (A) and in Basel (B). When a gas mixture is used, the partial pressure ratio are expressed in brackets.

Mirror	Conditions (pressure in mbar)	Cleaning time	Total R recovery (%)	
			400 nm	1600 nm
61 (Rh)	5×10^{-3} Ar; 225 eV	4h30	87.2	81.1
69 (Rh)	2×10^{-2} He; 630 eV	15h	85.6	96.5
77 (Rh)	2×10^{-2} He; 630 eV	7h	− 3.8	− 7.2
80 (Rh)	1×10^{-2} He + Ar (90/10); 340 eV	11h	92.2	94.3
96 (Mo)	2×10^{-2} He; 340 eV	6h30	67.6	45.5
98 (Mo)	A) 2×10^{-2} He; 630 eV	1h30	− 91.1	44.1
	B) 1.5×10^{-2} H_2 + Ar (50/50); 175 eV	5h	134.2	126.8
99 (Mo)	A) 2×10^{-2} He; 240 eV	3h30	35.6	41.0
	B) 1.5×10^{-2} H_2; 100 eV	5h	73.9	38.6
100 (Mo)	A) 5×10^{-3} Ar; 225 eV	1h30	22.1	97.5
	B) 1.5×10^{-2} H_2 + Ar (50/50); 175 eV	5h	104.5	120.8

if material from the vessel can theoretically be highly reflective (Be, W), it will not necessarily be the case for the redeposited films [15, 22]. The deposits on mirror 61, 69 and 80 were reduced and for some entirely removed (see table 3). Special attention has to be paid to W which was fully removed from mirror 69 and 80 by using either pure He at high energies (630 eV) or mixture of He and Ar with lower energies (340 eV). This is of prime interest for ITER has W will be used for the divertor and might end up on FMs. The three previous mentioned mirrors exhibited similar post-cleaning behaviour: partial recovery of the total R, increase of the diffuse R (see example of mirror 69 in figure 2) and metallic Rh surface after cleaning (measured by XPS). The largest changes in diffuse reflectivity before JET-ILW exposure and after cleaning were observed at 675 nm for mirror 61 and at 250 nm for mirror 69 and 80. For mirror 61, 69 and 80 those values went from 1%, 2% and 2% to 7%, 11% and 17%, respectively. From that result, one could deduce that the use of He and Ar at 340 eV damages mostly the mirror's surface while using Ar at 225 eV is the least harmful. Still due to unknown damage coming from the exposure in JET-ILW and different deposits and cleaning times, it is difficult to conclude on the most appropriate cleaning condition to use. For mirror 77, the Be content decreased by more than 90% although not fully removed due to lack of experimental time in the JET-BeHF. Using ion flux determined by Langmuir probe and sputtering yield for BeO corresponding to the used ion energy [23], the time needed to remove 400 nm of oxidized Be is equal to 6 h and is in very good agreement to the 7 h applied experimentally. Because Be was still present the reflectivity did not change and did even slightly decrease. After cleaning in the JET-BEHF, the mirror 77 exhibited buckling observed by SEM in figure 3. EDX measurements performed on position A

Table 3: NRA and ToF-ERDA characterisations after exposure in JET-ILW and after cleaning in the JET-BeHF. Units are 10^{15} atoms per cm^2. The equivalent Be thickness was calculated using the standard Be density of 1.848 g.cm^{-3}.

Mirror	D	Be	Equivalent Be thickness	C	N	O	Inc	W
61(Rh) before	0	94	8 nm	14	2.1	52	89	0
61(Rh) after	0	20	2 nm	4.5	0.6	8.9	20	0
69(Rh) before	180	710	58 nm	120	150	190	11	9.1
69(Rh) after	0	0.7	$<$ 1 nm	5.6	0.9	4.1	4	0
77(Rh) before	520	5400	437 nm	51	130	590	57	0
77(Rh) after	130	460	37 nm	35	94	590	55	0
80(Rh) before	18	390	32 nm	87	22	420	20	33
80(Rh) after	0	2.2	$<$ 1 nm	13	0.7	6.4	8.9	0
96(Mo) before	6	400.4	32 nm	44	4.4	100	3.8	0
96(Mo) after	1.4	86	7 nm	17	1	23	1.1	0
98(Mo) before	1.2	12	1 nm	38	1.6	17	2.8	0
98(Mo) after	0	0.1	$<$ 1 nm	8.6	0.3	9.6	0.8	0
99(Mo) before	1.6	3.2	$<$ 1 nm	32	1.2	11	2	0
99(Mo) after	0	0.3	$<$ 1 nm	12	0.8	5.9	0.9	0
100(Mo) before	1.8	0.8	$<$ 1 nm	30	0.8	5.4	1.6	0
100(Mo) after	0	0	$<$ 1 nm	2.8	0.3	3.2	0.5	0

and B have shown that the dark grey surface is corresponding to the contaminants layer (mainly Be) while the light grey circles are Rh film. On the surface, formation of bubbles of different sizes can be seen and for some of them the top layer is already delaminated. It is not yet known if the delaminated film is only composed of contaminants or if a fraction of the Rh film **is** delaminated too.

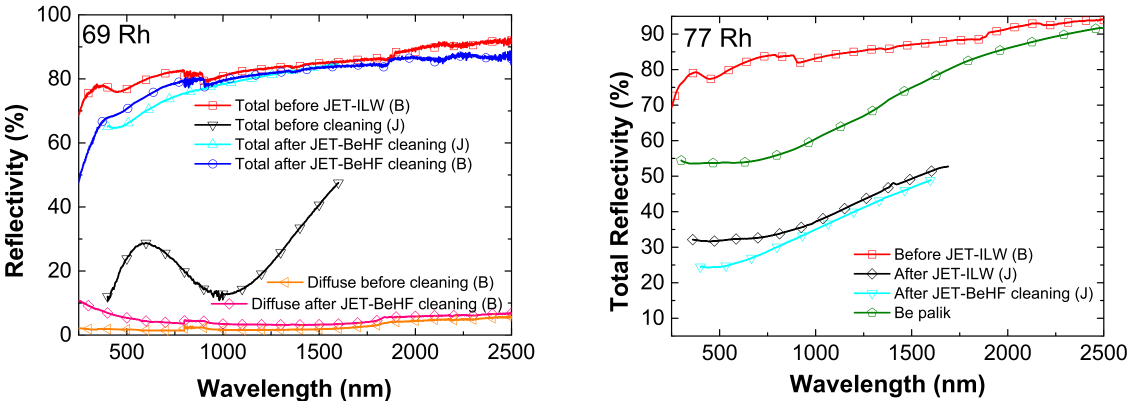

Figure 2: Total and diffuse reflectivity measured in JET (J) and/or Basel (B) before exposure in JET-ILW (denoted before JET-ILW), before cleaning and after cleaning in the JET-BeHF for mirror 69 and 77.

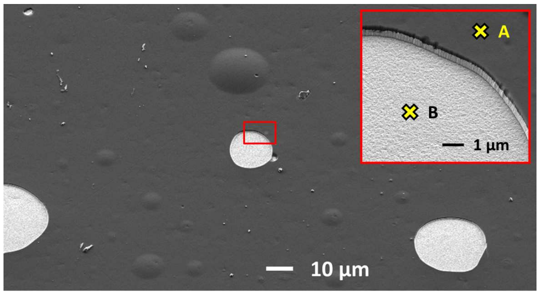

Figure 3: SEM image of mirror 77 after cleaning in the JET-BeHF with two different magnifications. EDX measurements were performed on point A and B.

3.2. Mo mirrors

The 4 polycrystalline mirrors exposed in JET-ILW did not experience the same balance between deposition and erosion in JET-ILW. As can be seen in table 3, mirror 96 suffered from high quantity of contaminants while mirror 98, 99 and 100 only had low deposition and probably experienced more erosion through plasma: the total reflectivity increased after plasma exposure compared to the reflectivity measured just before installation in JET probably due to the removal of the Mo surface oxide layer (see figure 12 of [15]). Nevertheless, due to air storage for a few months between the retrieval of mirrors from JET and the plasma cleaning, the mirrors 98, 99 and 100 got oxidized again (see total reflectivity "After JET-ILW (J)" and "Before cleaning (J)", figure 4 (a)). All cleanings performed in the JET-BeHF were effective as the contaminants were almost fully removed for mirror 98, 99 and 100, and strongly decreased for mirror 96 as displayed in table 3. Mirror 96 whose reflectivity was low after JET exposure experienced a consequent increase of its total reflectivity (see table 2) while the diffuse reflectivity did not change. Similar evolution of reflectivity was observed for mirror 98, 99 and 100, namely a small or non-existent increase in the total reflectivity as seen in figure 4 (a) by taking a closer look to the black curve "Before cleaning (J)" and the blue curve "After JET-BeHF cleaning (B)" while no increase was observed for the diffuse component (see figure 4 (b)). As the contaminants were almost fully removed, the main explanation is the presence of a oxidized Mo surface: the reflectivity was similar to calculated reflectivity of a Mo mirror oxidized over 15 nm and was confirmed by XPS measurements.

As the samples were Be free, a second cleaning in Basel was carried out using either pure H_2 for mirror 99 or a mixture of H_2 and Ar for mirror 98 and 100 (see table 2). Using only H_2 it was not possible to fully remove the oxide layer: after 5 h, the surface was still oxidized (35% MoO_2 measured by XPS) and the total reflectivity was not completely recovered. By adding Ar and increasing the ion energy (98 and 100 Mo), the oxide was completely removed (Mo metallic state measured by XPS) and the total reflectivity was restored and even slightly enhanced compared to original values. Comparing the two methods, the one using only H_2 at low energies seems to be the less damaging as the diffuse reflectivity did not change while the cleaning with H_2 and Ar at higher energies led to an increase (1.5 to 2 times more than before cleaning in Basel). Such effects are expected when using polycrystalline material and should disappear for single or nano crystalline mirrors.

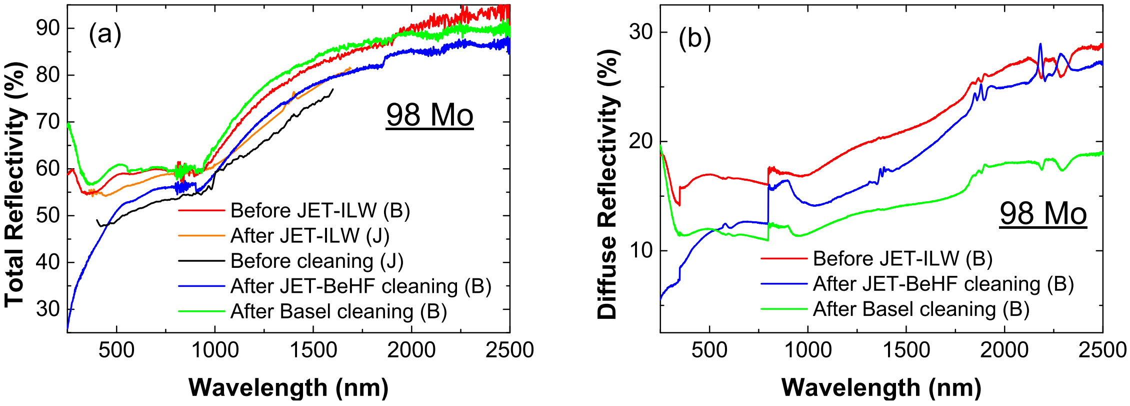

Figure 4: (a) Total reflectivity and (b) diffuse reflectivity measured in JET (J) and/or Basel (B) before exposure in JET-ILW (denoted before JET-ILW), before and after cleaning in the JET-BeHF and after additional cleaning in Basel.

4. Conclusion and Outlook

The cleaning of JET-ILW mirrors (Rh and Mo) deposited with Be, W and other tokamak impurities using RF plasma with He and/or Ar was performed. For all mirrors, the co-deposit thickness was significantly reduced and the reflectivity was improved though not fully recovered in most of the cases. Mo mirrors were oxidized after the cleaning in the JET-BeHF but the oxide was removed by adding a cleaning step in Basel. In contrary to Mo, Rh mirrors which are interesting for ITER due to their high initial reflectivity [17] were fully metallic after cleaning and did not delaminate.

New cleaning experiments on films deposited in tokamak and especially similar in composition to ITER shall be performed by varying the plasma conditions to optimize the cleaning. Up-stream investigations should also be done on the material resilience to plasma sputtering with various gas composition and ion energy. A special effort has to be undertaken regarding the use of low energy deuterons to remove Be deposits as BeD might be formed on the surface, weakening the surface binding energy of Be atoms hence increasing their sputtering yield [24]. In addition, low energy deuterons have low sputtering yields on Mo and Rh, thus preserving the mirrors integrity. Still for mixed layers containing heavy material e.g. W, the efficiency of D_2 could be questionable and should be investigated.

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