Post-mortem analysis of tungsten plasma facing components in tokamaks: Raman microscopy measurements on compact, porous oxide and nitride films and nanoparticles

C. Pardanaud, D. Dellasega, M. Passoni, C. Martin, P. Roubin, Y. Addab, C. Arnas, L. Couèdel, M. Minissale, E. Salomon, G. Giacometti, A. Merlen, E. Bernard, R. Mateus, E. Alves, Z. Siketic, I. Bogdanovic Radovic, and A. Hakola

1 Aix Marseille Univ, CNRS, PIM, Marseille, France
2 Dipartimento di Energia, Politecnico di Milano, Milano, Italy
3 Istituto per la Scienza e Tecnologia dei Plasmi, CNR, Milano, Italy
4 Phys. and Eng. Phys. department, University of Saskatchewan, Saskatoon, SK, S7N 5E2, Canada
5 Aix Marseille Univ, Universite´ de Toulon, CNRS, IM2NP, Marseille, France
6 CEA, IRFM, F-13108, Saint Paul lez Durance, France
7 Instituto Superior Tecnico, Universidade de Lisboa, Bobadela, Portugal
8 Rudjer Boskovic Institute, P. O. Box 180, 10002, Zagreb, Croatia
9 VTT, P. O. Box 1000, 02044 VTT, Finland

Received 2 December 2019, revised 27 April 2020
Accepted for publication 14 May 2020
Published 3 July 2020

Abstract

Raman microscopy is one of the methods that could be used for future post-mortem analyses of samples extracted from ITER plasma facing components. This study shows that this technique is useful for studying tungsten-based materials containing impurities including oxides and nitrides. Here, we apply pulsed laser deposition and DC argon glow discharges to produce tungsten-containing synthetic films (compact, and porous), and nanoparticles, and investigate the influence of their morphology on the measured Raman spectra. The amounts of oxygen and/or nitrogen in the films are also investigated. Comparative data are obtained via x-ray Photoelectron Spectroscopy, Atomic Force Microscopy, Electron Microscopies (Scanning and Transmission), Energy Dispersive x-ray spectroscopy, and Time-of-Flight Elastic Recoil Detection Analysis. The power density of the laser beam used to perform the Raman microscopy is varied by up to 4 orders of magnitude (0.01–20 mW µm−2) so as to investigate the thermal stability of films and nanoparticles. As a first result, we give evidence that Raman microscopy is sensitive enough to detect surface native oxides. Secondly, more tungsten oxides are detected in porous materials and nanoparticles than in compact films, and the intensities of the Raman band correlate to their oxygen content. Thirdly, the thermal stability of these films (i.e. structural and chemical modification under laser heating) is poor when compact films contain a sufficiently large amount of nitrogen. This finding suggests that nitrogen can be substituted by oxygen during Raman laser induced heating occurring in ambient air. Finally, our

See Brezinsek et al 2017 (https://doi.org/10.1088/1741-4326/ab9347) for the EUROfusion WP PFC contributors team.
methodology can be used to rapidly characterize the morphology and chemistry of the samples analyzed, and also to create oxides at the micrometer scale.

Keywords: PLD, Raman spectroscopy, tungsten oxide, tungsten nitride, plasma wall interaction, laser heating, post-mortem analysis

(Some figures may appear in colour only in the online journal)

1. Introduction

Tungsten is one of the elements to be used in the fabrication of plasma facing components (PFC) for the ITER tokamak. It has been chosen due to its good thermomechanical properties, and its low affinity with hydrogen isotopes, in order to face the high heat due to nuclear fusion reactions between hydrogen isotope nuclei [1, 2]. Heat fluxes, in the range 10 to 20 MW m$^{-2}$ in steady state operations, and even higher (in the GW m$^{-2}$) for edge localized modes or other transients, will have to be radiated off [3, 4], mainly on the divertor [5]. However, due to plasma wall interactions [6], PFC characteristics will be modified during the lifetime of the machine [7]. This is due to the many simultaneous processes (erosion, morphological changes, melting, defect formation, etc.), involving high heat fluxes, impinging ions and neutrals [8] formed by hydrogen isotopes (which fuel the reaction), helium (ashes from the reaction), and neutron bombardment, all of which will potentially modify the PFCs. The presence of impurities such as oxygen or nitrogen, and eroded species capable of migration or redepositing [9, 10] should also be taken into account. As a result, PFCs will react chemically, for example forming oxide layers in specific conditions [11, 12], with seeding gas [13, 14], with the possibility of melting enhancing these chemical effects. As a consequence, the safety conditions of ITER may be compromised, mainly due to the formation of dusts [15–17] and the retention of radioactive tritium used to fuel the plasma [18–20]. Predicting how these modifications will alter long term operations is thus a keystone in the field. To this end, two complementary strategies are generally used. The first involves testing scenarios in existing tokamaks, e.g. in the JET tokamak with an ITER-like wall (ILW) configuration [21] or in the WEST tokamak [22, 23], and then using scaling laws to predict what could happen under ITER conditions. The second strategy involves testing for PFC and/or laboratory materials for one specific or several synergetic effects together, in facilities [24, 25] allowing controlled parameters (surface temperature, morphology, composition, ion flux and energy, etc.) [26–29]. In this article, synthesized materials are produced to mimic deposits or modified surfaces [6].

Here, post-mortem analyses are undertaken for all samples, to obtain a before/after comparison. Traditional techniques include ion beam analyses [30] and thermal desorption spectroscopy to obtain the concentrations and depth distributions of the various elements, electron microscopy to obtain information relating to morphology/porosity, and x-ray diffraction (XRD), which reveals the structure of and nature of traps in the material [31, 32]. In addition, we use Raman microscopy. This technique is based on an inelastic light scattering process, and is highly sensitive to chemical composition, structure and morphology. Depending on the optical constants of the probed material, Raman microscopy can be sensitive to the near surface (a few tens of nanometers in the case of metals), with a micrometer lateral resolution which enables the monitoring of spatial inhomogeneities [11, 12]. The Raman microscopy method provides information about atomic vibrations, and is thus able to distinguish chemical bonds in solids, and to reveal how hydrogen isotopes and impurities are bonded, either to metal atoms or to each other’s [33, 34]. It is particularly sensitive in its capacity to detect tungsten oxides, and the modifications of their characteristic structure and composition after He or D implantation [35–37], as well as to detect the presence of H in oxides [38]. It is also sensitive to crystalline structures, and to the presence of defects [39].

In this work, we focus on both the detection of impurities in tungsten by means of Raman microscopy, and the influence of material surface roughness on the measured spectra. We use a large variety of laboratory samples: pulsed laser deposition (PLD) grown W films with different morphologies (porous or compact), and different chemical compositions (with different O and N contents), W nanoparticles, and a W bulk ITER-grade sample with thick WO$_3$ layers. This is a continuation of our previous research [40], which demonstrated that Raman microscopy achieves reliable detection of oxides for Be based samples [11, 12], and for W based samples. It is therefore an appropriate technique for post-mortem analyses of ILW PFCs. In addition, in this study, by varying the power of the incident laser by up to 4 orders of magnitude, we can study the fingerprint of laser irradiation on the Raman spectra. This allows the rapid retrieval of information about the morphologies of O and N containing W films. This is due to structural changes induced by laser heating where thermal dissipation is inefficient, which is the case with porous samples.

2. Methods

2.1. Sample preparation

For this study, we synthesized and analyzed 11 W based samples, containing various amounts of O and N. We compared them to a polycrystalline tungsten sample with a mirror-like polishing, provided by the A.L.M.T. Corp (Japan), and a set of WO$_3$ tungsten oxide layers obtained by the thermal oxidation of W under O$_2$ pressure (see [35] for details), with thicknesses varying from 20 to 200 nm. From the batch of 11 samples, 1 was composed of agglomerated nanoparticles, deposited by magnetron DC sputtering (see [41] for details), while the other 10 were produced by Pulsed Laser Deposition
The morphology of the 10 PLD samples was assessed by a Zeiss Supra 40 scanning electron microscope (SEM) using an acceleration voltage of 5–7 kV, presented in more detail in section 3. Nanoparticles were examined using transmission electron microscopy (TEM). A Cs corrected FEI 80–300 device was used to acquire high resolution electron micrographs (HR TEM) [41]. The bulk elemental composition of the 10 PLD films was obtained via time-of-flight elastic recoil detection analysis (TOF ERDA) and/or energy dispersive x-ray spectroscopy (EDX). The EDX system used is an Oxford Instruments Si(Li) detector, in combination with a SEM microscope. The TOF-ERDA measurements were performed using a 6 MV Tandem Van de Graaff accelerator located at the Rudjer Bošković Institute, Zagreb. For the analysis, 20 MeV $^{127}$I$^{5+}$ ions at a 20° incidence angle toward the sample surface were used, enabling measurement down to 300 nm in the bulk. The TOF-ERDA spectrometer was positioned at an angle of 37.5° toward the beam direction. Further details regarding the experimental setup may be found in ([44, 45]). Note that samples cWO(25.2) and pWO(60,2.5) were previously analyzed in [46]. Atomic force microscopy (AFM) was used to study the roughness of the samples. Here, the tapping mode of an NTMDT solver was deployed, with a tip radius of $\approx$10 nm, and with vertical and horizontal resolutions of $\approx$1 and $\approx$10 nm, respectively. X-ray photoelectron spectroscopy (XPS) analyses were performed at the PIIM laboratory. The experimental setup is composed of a high-intensity twin (Mg/Al) anode x-ray Source (provided by PREVAC), emitting at 1253.6, and 1486.6 eV, respectively. The analyzed samples were placed in a movable sample holder inside a mu-metal ultra-high vacuum chamber (at a base pressure of $1 \times 10^{-10}$ mbar). Photoelectrons were detected via a high-resolution electron energy analyzer (Scienta Omicron R3000) composed of a high transmission electron lens with an acceptance angle of $30^\circ$, and a 40 mm MCP detector monitored by a FireWire CCD-Camera. The resolution of the XPS spectrometer, determined from the full width at half maximum of the Ag 3d core levels of a clean Ag single crystal, was 0.9 eV.

Raman spectra were recorded in the back-scattering geometry using a Horiba-Jobin-Yvon HR LabRAM HR800 Raman microspectrometer, with one laser wavelength $\lambda_L = 514.5$ nm. The objectives were set at $\times 100$ magnification, with a numerical aperture (N.A.) of 0.9 and $\times 50$ magnification, and a numerical aperture of 0.5. The radius of the laser spot with N.A. = 0.9 is $R \approx 0.6 \times \lambda_L / \text{N.A.} \approx 0.34$ µm. To study possible heating effects, the laser power density was tuned from 0.01 to $\approx 17$ mW µm$^{-2}$, using the mapping mode for low power density in order to avoid any oxidation due to the probe beam, as measurements were performed in air. The selected grating (600 lines mm$^{-1}$) gave a spectral resolution of $\approx 1$ cm$^{-1}$.

### 2.2. Sample characterization

The morphology of the 10 PLD samples was assessed by a Zeiss Supra 40 scanning electron microscope (SEM) using an accelerating voltage of 5–7 kV, presented in more detail in section 3. Nanoparticles were examined using transmission electron microscopy (TEM). A Cs corrected FEI 80–300 device was used to acquire high resolution electron micrographs (HR TEM) [41]. The bulk elemental composition of the 10 PLD films was obtained via time-of-flight elastic recoil detection analysis (TOF ERDA) and/or energy dispersive x-ray spectroscopy (EDX). The EDX system used is an Oxford Instruments Si(Li) detector, in combination with a SEM microscope. The TOF-ERDA measurements were performed using a 6 MV Tandem Van de Graaff accelerator located at the Rudjer Bošković Institute, Zagreb. For the analysis, 20 MeV $^{127}$I$^{5+}$ ions at a 20° incidence angle toward the sample surface were used, enabling measurement down to 300 nm in the bulk. The TOF-ERDA spectrometer was positioned at an angle of 37.5° toward the beam direction. Further details regarding the experimental setup may be found in ([44, 45]). Note that samples cWO(25.2) and pWO(60,2.5) were previously analyzed in [46]. Atomic force microscopy (AFM) was used to study the roughness of the samples. Here, the tapping mode of an NTMDT solver was deployed, with a tip radius of $\approx 10$ nm, and with vertical and horizontal resolutions of $\approx 1$ and $\approx 10$ nm, respectively. X-ray photoelectron spectroscopy (XPS) analyses were performed at the PIIM laboratory. The experimental setup is composed of a high-intensity twin (Mg/Al) anode x-ray Source (provided by PREVAC), emitting at 1253.6, and 1486.6 eV, respectively. The analyzed samples were placed in a movable sample holder inside a mu-metal ultra-high vacuum chamber (at a base pressure of $1 \times 10^{-10}$ mbar). Photoelectrons were detected via a high-resolution electron energy analyzer (Scienta Omicron R3000) composed of a high transmission electron lens with an acceptance angle of $30^\circ$, and a 40 mm MCP detector monitored by a FireWire CCD-Camera. The resolution of the XPS spectrometer, determined from the full width at half maximum of the Ag 3d core levels of a clean Ag single crystal, was 0.9 eV.

Raman spectra were recorded in the back-scattering geometry using a Horiba-Jobin-Yvon HR LabRAM HR800 Raman microspectrometer, with one laser wavelength $\lambda_L = 514.5$ nm. The objectives were set at $\times 100$ magnification, with a numerical aperture (N.A.) of 0.9 and $\times 50$ magnification, and a numerical aperture of 0.5. The radius of the laser spot with N.A. = 0.9 is $R \approx 0.6 \times \lambda_L / \text{N.A.} \approx 0.34$ µm. To study possible heating effects, the laser power density was tuned from 0.01 to $\approx 17$ mW µm$^{-2}$, using the mapping mode for low power density in order to avoid any oxidation due to the probe beam, as measurements were performed in air. The selected grating (600 lines mm$^{-1}$) gave a spectral resolution of $\approx 1$ cm$^{-1}$.

### 2.3. Sensitivity and capability of Raman spectroscopy for studying oxides and nitrides

Since only acoustic phonon branches occur in tungsten, and given that, due to the spectroscopic configuration used in

### Table 1. Sample description. Sample designations beginning with c (p) correspond to a compact (porous) morphology, as observed by electron microscopy. The first number in parenthesis is the O content, and the second is the N content, expressed as an atomic percentage.

| Sample | Synthesis method | Elemental composition |
|--------|------------------|-----------------------|
| cW bulk | From A.L.M.T | O 0%, N 0% (purity: 99.9999 wt%) |
| cWO(25,2) | PLD (He, P = 2 Pa) | O 25%, N 2%, H 2% (TOF ERDA) |
| cWN(0,20) | PLD (N, P = 2.5 Pa) | O 0%, N 0% (EDX) |
| cWON(37,16) | PLD (He 90% + N 10%, P = 55 Pa) | O 37%, N 16%, H 8% (TOF ERDA) |
| cWON(20,35) | PLD (N, P = 20 Pa) | O 20%, N 35% (EDX) |
| pWO(60,2.5) | PLD (Ar; P = 50 Pa) | O 60%, N 2.5%, H 15% (TOF ERDA) |
| pWO(52,4) | PLD (Ar 97% + D 3%, P = 50 Pa) | O 52%, N 4% H 19% (TOF ERDA) |
| pWON(53,12) | PLD (Ar 97% + N 3%, P = 50 Pa) | O 53%, N 12%, H 19% (TOF ERDA) |
| pWON(47,9) | PLD (Ar 94% + N 3% + D 3%, P = 50 Pa) | O 47%, N 9%, H 24% (TOF ERDA) |
| pWON(20,35) | PLD (N, P = 40 Pa) | O 20%, N 35% (EDX) |
| NP-W | DC argon glow discharge | – |
| WO$_3$ on W (20–200 nm) | Thermal oxidation at 400 °C [35] (O$_2$ partial pressure: from 0.7 to 79 kPa) | – |
In this study, no Raman bands are expected to be detected, one might infer that this spectroscopic technique is not adequate for probing pure W. However, oxides, even if not wanted, will generally be present in tokamaks [12, 47]. Moreover, the Raman spectroscopy signal is expected to be very rich for oxides and bronzes (i.e. hydrogen in oxides), as the numerous structures listed in the literature lead to optical phonon branches. In figure 1, some typical oxide spectra are shown, together with the phonon density of states (PDOS) of pure W, which can be observed due to relaxing quantum selection rules when defects are introduced [48]. Whatever the O/W stoichiometry, the spectra are mainly composed of bands related to the bending and stretching modes of W-O-W bonds, in addition to a band related to the vicinity of the surface [49–51]. To better understand the spectra, we need to go deeper into the structural details of tungsten oxide. The building blocks of tungsten oxide are WO₆ octahedra: 1 W and 4 surrounding O form a basal plane, and 2 out of plane O, above and below that plane, form the octahedra. This local arrangement governs the main trends observed in the Raman spectra, particularly those bands lying at 270, 714 and 805 cm⁻¹. However, these octahedra are corner- or edge-sharing to form the numerous tungsten oxide polymorphs observed in nature; this can affect the Raman spectra as symmetry, stoichiometry, and interatomic distances change. Depending on the tilting angle and rotation direction of an octahedra relative to others [52], several WO₃ phases can exist. For example, for bulk WO₃, triclinic δ-WO₃ is the existing phase at low temperatures. From 17 °C up to 330 °C, the monoclinic phase γ-WO₃ dominates, followed by the orthorhombic β-WO₃ phase, which occurs at temperatures up to 740 °C, where tetragonal α-WO₃ starts to form. The transition temperatures can decrease when nanostructures appear [39, 49], and/or when the stoichiometry changes slightly from that of a trioxide [53]. Magneli phases with stoichiometries close to trioxide, from 2.625 to 2.92, have previously been reported [54]. The aim of figure 1 is thus to give a brief overview of the main spectroscopic features and differences characterising tungsten oxides. The vertical dashed lines give the band positions (270, 714 and 805 cm⁻¹) of the three main Raman active modes of bulk monoclinic WO₃. Subtle changes in the spectra (mainly relating to band position) can occur, depending on the WO₃ phase, but these are considered negligible at this stage, in comparison to the differences introduced by other kinds of oxides in the spectra, as illustrated by a quick view in this figure. Introducing defects which diminish the crystallite size at which the octahedral periodic pattern is perfectly repeated results in broadening the peaks and increasing the intensity levels of the low frequency bands centered at 270 cm⁻¹. This can be seen on the spectrum labeled d-WO₃, where d denotes `defective’. Details of this sample synthesis can be found in [35]. For nano trioxide (labelled n-WO₃, with a crystallite size of 4 nm only [39]), broadening increases further, resulting in the merging of the 714 and 805 cm⁻¹ bands, and the intensity of the low wavenumber bands diminishes. For samples labelled WOₓ [55], where oxygen content is low compared to that of a trioxide, the stretching mode bands are distinguishable, but are overlapping and shifted. The 275 cm⁻¹ band, superimposed to a broad weak band, is sharp, and close to the value recorded for monoclinic WO₃, a phenomenon for which there is to date no real explanation. For d-WO₃, a-WO₃ and WOₓ, a band close to 950–960 cm⁻¹ becomes visible. This is interpreted as a W = O bond, due to electronic reorganization where neighbors are missing at the surface or at the limits of crystallites. A sub trioxide labelled WO₃-x (possibly WO₂.₉ according to [56]) but it could also be WO₂.₇₂ and WO₂ (formed by heating the d-WO₃ up to 800 °C in vacuum), are also shown, for comparison. The literature on tungsten nitride is not as plentiful as that relating to oxides, which may be due to there being comparatively fewer applications for nitrides. However, cubic W₂ N, which is considered to be the most stable phase under normal conditions, is not considered Raman active. When the stoichiometry is not preserved, the W phonon density of states has been observed to rise close to 200 cm⁻¹, with the corresponding bands being roughly ten times more intense than other bands involving W-N bonds, and lying at 471 cm⁻¹, in the range 700–800 cm⁻¹ [48]. Therefore, for an unknown sample possibly containing both N and O, if bands are observed close to 800 cm⁻¹, they could in principle involve both W-N and W-O bonds. Depending on the relative amounts of N and O, it can be difficult to disentangle the chemical origin of this band. Fortunately, the shape and intensity of bands below 300 cm⁻¹ behaves differently for oxides and nitrides. For example, the W PDOS is very intense, compared to other bands, in the presence of nitridies; this is not the case for oxides.

3. Results

The content of impurities (O and N) was one of the main parameters varied in this study (see table 1). For O, this ranged from trace levels, where only surface native oxides are formed (as is the case for the cW sample), up to 75 at. % in the bulk.
for WO$_3$ reference layers, with intermediate concentrations varying from 25 to 60 at. % for the PLD samples. Another parameter to be altered was the morphology of the samples. Raman band intensities have also to be considered in order to obtain information on O and N content. Note that this aspect is in general not addressed in the literature, as optical properties and electromagnetic wave propagation in the materials need to be precisely known [58], and roughness can play an important role which is difficult to take into account. We present morphology and chemical composition analysis in section 3.1, information retrieved from absolute intensities of oxide related bands in section 3.2, and the effect of the laser beam power in Raman excitations in section 3.3.

### 3.1. Morphology and chemical composition

Figure 2 shows SEM and AFM images of the PLD films, and TEM images of the nanoparticles (NP). Top views of PLD films, cWO(25,2), pWO(60,2.5), pWO(52,4), pWON(53,12), and pWON(47,9) can be seen in figures 1(a)–(e), respectively. Typical porous and compact film SEM cross sections (obtained after cleaving the samples) are displayed in figures 1(f) and (g), respectively. A 30 × 30 µm$^2$ AFM image of a typical porous film is displayed in figure 1(h), and typical height profiles of porous and compact films are given in figure 1(i). A TEM image of nanoparticles is shown in figure 1(j), which reveals a core–shell structure. From figures 1(a) to (e), one can observe that the morphology of the cW film is different from that of porous films: the pWO(60,2.5), pWO(52,4), pWON(53,12) and pWON(47,9) films show a cauliflower-like feature, whereas the surface of the cWO(25,2) film is flat and smooth. This morphology is directly related to growth mechanisms [59] governed by the expansion dynamics of the plasma plume during deposition, as discussed elsewhere [42, 43]. Some cracks are present on the porous films. Cross sections are shown in figures 1(f) and (g), illustrating the 1 µm thickness of the films. Columnar structures are better visible, at the origin of the porous label of the pWO(60,2.5), pWO(52,4), pWON(53,12) and pWON(47,9) films. AFM measurements confirm the rough morphology of the porous films (≈25 nm amplitude obtained on profiles by measuring the peak to peak height) as compared to that of the compact samples (≈7 nm). Some columns higher than the mean surface by as much as ≈200–300 nm can be seen in figure 1(b) (top right), (f), and (h) (white spots are not due to dust). Raman spectra were not acquired on these columns, so as to avoid probing non-representative locations. As reported in [42, 46], both cWO and the different pWO and pWON films exhibit a nanocrystalline structure, where the crystallite domains range between 4 and 7 nm. Nanoparticles (figure 1(j)) display a polyhedral form, in some cases nearly spherical, with diameters ≈14–20 nm, a core composed of W in the β phase [41], and an oxide shell with a thickness of ≈4–5 nm.

XPS spectra of selected W, WN, compact WO, and porous WO samples are shown in figures 3(a) and (b) (XPS was not possible for NP as there was not enough material). Their Raman spectra are given in figure 3(c). XPS spectra recorded in the 4 f region are displayed in figure 3(a) for bulk oxide samples (d-WO$_3$, pWO(60,2.5) and cW(25,2)), and in figure 3(b) for surface oxides (cW) and nitrides (cW(N(0,20))). According to the 2012 update of the NIST database [60] 4f$_{5/2}$ and 4f$_{7/2}$ lie at 31 eV and 33 eV, respectively for W [61], whereas they lie at around 36 and 37.5 eV for WO$_3$ [61, 62]. An additional shift of roughly 0.5 eV has been reported in the literature [53], possibly due to nano structuration and phase changes; we do not discuss this in this publication. The XPS spectrum of d-WO$_3$, extracted from [37], is composed of two peaks related to WO$_3$ but slightly shifted (this may be due to a variation of the work function between the different samples, or to setup calibration). The XPS spectra of pWO samples mainly display two peaks, at 36 and 37.5 eV, originating from oxide formation, but these are broader and more overlapped compared to those of d-WO$_3$. A weak peak observed at 30.8 eV for pWO is due to bulk W. Such measurements are consistent with the stoichiometry measured by TOF-ERDA. The XPS spectra of the cWO samples shows a combination of oxide and W components, indicating the coexistence of an oxide phase and a W phase, in different proportions than for the pWO samples, but still consistent with TOF-ERDA measurements. For samples supposed to contain no oxide in the bulk, XPS spectra are shown in figure 3(b). The XPS spectrum of the cW sample is composed of 2 intense peaks lying at 31 and 33 eV, plus two weaker peaks at 35 and 37.5 eV. These indicate a low quantity of oxide at the surface of the film (here, XPS probes to a depth of approximately 1.5 nm). The XPS spectrum of the cWN(0,20) sample is composed of 4 broad overlapping peaks, situated approximately where WO and W signals are expected. Some studies suggest that WN signals are in the range 31.5–31.7 eV [63], whereas others mention 32.6 and 34.7 eV [64]. One must note that the most intense peaks in figure 3(b) are those at 35.7 and 33.7 eV, close to where WN should fall, according to [64]. In any case, the WN signal overlaps with W and WN signals, and the spectrum shown corresponds to a mixture of W, WN and WO. This reveals that the cW film is oxidized within the probed XPS depth range, to a much greater extent than the cW film. Note that the oxidation levels can also affect the global shape of the XPS spectra: for example, those present in W$^{4+}$ are close to 4f$_{5/2}$ and 4f$_{7/2}$ related to W, and W$^{5+}$ are in between 4f$_{5/2}$ and 4f$_{7/2}$ related to WO$_3$ [37], and given the resolution used, will not allow quantitative results.

In figure 3(c), the Raman spectrum recorded for the cW sample display bands lies in the bending (300 cm$^{-1}$) and stretching (700–800 cm$^{-1}$) spectral regions, confirming the presence of oxide. There is also an additional surface band (950 cm$^{-1}$) which is very intense, proving the presence of defective W = O bonds. In W crystals, the penetration depth of visible light is expected to be only a few tens of nm, due to the metallic nature of W [66]. Therefore, this band originates from W-O bonds close to the surface, formed due to exposure to air. A comparison with other materials (pWO(60,2.5), cW(25,2), cW(N(0,20), NP, and defective WO$_3$) is also shown in this figure. Both pWO and NP display an intense 950 cm$^{-1}$ band, indicating the existence of a large amount of surface area in these samples, in agreement with what is revealed.
Figure 2. Morphology of PLD films and nanoparticles. (a)–(e) PLD films, top view; the dashed white circle represents the size of the laser beam used in the Raman experiments when using an objective with N.A. = 0.9. From (a) to (e): cWO(25,2), pWO(60,2.5), pWO(52,4), pWON(53,12), and pWON(47,9). (f) and (g) Typical SEM cross section views of PLD films, porous (f) and compact (g). (h) Typical AFM top view of porous films. (i) Typical AFM profiles of porous and compact films. (j) Nanoparticles.

by electron microscopy in figure 2 for pWO (figure 2(f)) and NP (figure 2(j)) samples. Regarding the cW sample, the 950 cm\(^{-1}\) band is also observedhere, also demonstrating the presence of a large surface. Moreover, for the cW sample, extra well-defined bands are observed close to 400 and 650 cm\(^{-1}\). According to ultra-high vacuum experiments, vibrational modes of O, adsorbed on top of W(110) for high surface coverage (750 ml) [67], lie at 428 and 657 cm\(^{-1}\). These observations suggest that two contributions leading to WO bonds exist for the cW sample: O adsorbed on the W surface, and WO bonds organized as small WO\(_3\) crystals, leading to a large quantity of crystallite surface sites. Note that the features appearing in the dashed rectangle of figure 3(c) are attributed, not to the samples, but to experimental conditions, taking into account the nature of the lens employed, time acquisition and incident angle [65].

Figure 4 shows normalized Raman spectra for different WON samples, either compact or porous. An initial observation is that porous and compact samples behave differently, and that the weight of the W PDOS (below 300 cm\(^{-1}\)) compared to the O- or N-related bands at higher wavenumbers is much higher for compact samples than for porous samples. A second observation concerns the surface W = O band at 950 cm\(^{-1}\). The pWON(47,9) spectrum is similar to that of WO\(_x\) with a strong contribution at this band; the quantity of O is far more important than the quantity of N, and in addition nitrides are not expected to be Raman active. Thus, for low N concentrations, oxygen governs the overall Raman spectral shape in the 300–1000 cm\(^{-1}\) spectral region. However, the shape of the bands below 300 cm\(^{-1}\) differs to those of WO\(_x\); this could be due to the presence of N (activating W PDOS), as discussed in section 2.3. When the N/O ratio increases, the behavior changes. For example, pWON(20,35) is composed of three broad overlapping gaussian profiles in the range 300–1000 cm\(^{-1}\). The main one is centered at 833 cm\(^{-1}\), whereas the others are centered at 417 and 573 cm\(^{-1}\). The first band is interpreted as being partly due to W-N and W-O bonds, because of its position close to both W-N and W-O stretching mode bands, according to figure 1, whereas the two other bands are due to W-N bonds. For the compact cWON(20,35) sample, the 300–1000 cm\(^{-1}\) spectral range is also composed of three broad overlapping bands attributed to W-N. But this is not the case for allN/O ratios. Pure nitrogen-doped tungsten, the cWN sample, displays bands at 813 and 950 cm\(^{-1}\),


Figure 3. XPS and Raman spectra of d-WO₃, NP, pWO, cWO, cW and cWN samples. XPS spectra of (a) pWO(60, 2.5), cWO(25, 2) and d-WO₃ (the latter from [37]) and (b) cWN(0, 20) and cW. (c) Raman spectra. The dashed rectangle of figure 3(c) is attributed not to the samples, but to the experimental conditions, taking into account the nature of the lens employed, time acquisition, and incident angle [65].

Figure 4. Comparison of the Raman spectra of N containing films. in addition to weaker features around 400 cm⁻¹ (with broad features occurring between 300 and 550 cm⁻¹). The 813 and 950 cm⁻¹ bands are interpreted as originating from octahedra, and from surface W = O bonds, respectively. W-N bonds could be related to the very weak signal around 400 cm⁻¹. The spectrum from the cWON(37, 16) sample is totally flat in the same spectral region. In this case, the absence of bands, given that W-N bonds are present in cWON(37, 16), may be due to some quantum-selection rules relating to structure during the Raman scattering process, whereas the presence of defects (such as oxygen and nitrogen, grain boundaries due to small crystallite size, etc.) can break the related quantum selection rules, leading to the presence of these bands. The lack of signal intensity corresponding to W-O bonds is different here, possibly due to the stability of the W-N bonds hindering the formation of W-O bonds during the deposition process of the film. This point will be addressed in section 3.2.

To briefly summarize the findings reported above, concerning Raman spectroscopy measurements:

- Oxides have been detected on a compact W sample, likely due to native oxides (see section 3.2 for sensitivity discussion)
- Compact and porous PLD films exhibit distinct Raman spectra
- Spectra of porous films and oxides found on nanoparticles are similar, displaying a mode related to surface bonds, lying at 960 cm⁻¹
- N content does not lead to strong specific bands, but to low frequency modes related to the PDOS of W, as was found for mixed W:Be deposits [68].
- For some concentrations, oxides are no longer observed on W/O/N samples, which could indicate the presence of substituting N.

[423x129]
[68]
3.2. Information retrieved from Raman absolute band intensities

Whereas we have discussed information retrieved from the spectral shape, band positions and relative intensities, and methods of distinguishing the presence of N where a sample also contains also oxygen, we now discuss the information retrieved from absolute band intensities, and its relation to sample composition. Absolute band intensities refer here to the height of the band, normalized by the height of the band at 520 cm$^{-1}$, H$_{Si}$, of a silicon crystal measured under the same experimental conditions, as this intense band is often used as a reference [40].

In figure 5, the height of the band at 800 cm$^{-1}$, H$_{800}$, is taken on the rough spectra, i.e. without band fitting, and after base line subtraction. The height ratio, H$_{800}$/H$_{Si}$, is shown in figure 5(a) as a function of the oxygen atomic fraction. A general tendency is that the more oxygen a material contains, the more intense the 800 cm$^{-1}$ band, approximately following an exponential law (the dashed line is a guide for the eyes). This trend is certainly followed for samples with a similar porous morphology: pWO(60,2.5), pWO(52,4), pWON(47,9), and pWON(53,12), and for which nitrogen is not the dominant impurity element. For nanoparticles, the H$_{800}$/H$_{Si}$ ratio is 0.12, the highest value recorded in this study. The intersection between the dashed line and this value occurs at 63% of oxygen. This value is close to the fraction of oxides that can be estimated from TEM images for an average nanoparticle. This indicates that the empirical exponential behavior mentioned above also works well, qualitatively, for this sample. When the nitrogen content increases a little, as with, e.g. the pWON(53,12) sample, data are still close to the dashed line, although slightly up-shifted. The shift becomes far greater for the high N/O ratio of the pWON(20,35) data. Note that this data point could be moved a little closer to the dashed line if one replaces the x-axis, which is the fraction of oxygen O(%), by O(%) $\times$ 100/(100-N(%)), which represents the fraction of O bonded to W, excluding the overall tungsten content of that bonded to N. This transformation is shown in figure 5(b). This approach assumes that W-N bonds do not contribute significantly to the intensity of the band close to 800 cm$^{-1}$. Another hypothesis is that O and N are not bonded together, but only to W. If this were not the case, it would shift the experimental point in figure 5(b) horizontally. However, the operation that permits a jump from figures 5(a) to (b) is not 100% satisfactory, as all the corresponding data do not align well on the dashed line. Other parameters, which are difficult to take into account (and which fall outside of the scope of this study), can also influence band intensities, and explain some behaviors. Firstly, the optical constants of the sample (real and imaginary parts of the refractive index, $n$ and $k$, respectively) which depend on chemical composition, drive light propagation. According to [69], tungsten oxides with an O content higher than $\approx$73% behave as dielectrics, whereas for concentrations lower than 73%, the sample behaves as a metal. According to [70], tungsten nitrides are good absorbers, but with $k$ values which can be $\approx$60% lower than the corresponding value for tungsten. To the best of our knowledge, no documentation currently exists regarding the optical constants of mixed WON samples. However, one can imagine that if the $k$ value is lower for pWON(20,35) than for the samples aligned...
on the dashed line, light is then able to probe deeper into the sample, thus increasing the intensity of the 800 cm$^{-1}$ band, which could explain part of the deviation from the empirical relation. Another parameter that influences band intensities is surface roughness. For conducting media such as W, light penetrates only to a few tens of nm. The scattering process is then very sensitive to surface structure, and an increase of Raman intensities is expected in the case of roughness. Here, the roughness is in the range from a few nm to a few tens of nm, as shown in figure 2(i), which is a likely explanation of the H$_{800}/$H$_3$ ratio increase (one order of magnitude) from compact cWON(20,35) to porous pWON(20,35), given that both share the same chemical composition.

Focusing now on the compact samples, one can observe that, with the exception of cWON(25,2), all display a lower band intensity than that shown by porous samples. For cW, the tungsten oxide comes from native oxide, and the H$_{800}/$H$_3$ value is representative of WO bonds close to the surface. XPS measurements conducted after heating the sample to 700 °C under UHV conditions allowed us to obtain the atomic composition from relative intensities of W and WO peaks: the results showed 21.9% oxygen content in the surface layer, this being close to a W$_2$O stoichiometry [71]. The oxygen content was estimated by performing Angle-resolved XPS experiments. The emission angle at which the electrons were collected was varied from 0 to 30° (with respect to the normal), thereby enabling electron detection at different material depths. Raman data were recorded in air only a couple of hours after the XPS measurement. The Raman spectrum (see figure 3(a)) suggests a W$_6$O$_5$ octahedral symmetry, as discussed above, and gives a value of H$_{800}/$H$_3 = 0.0027$, which may indicate a low oxide thickness. Some comments relating to oxide thickness are given later in this article, in connection with figure 5(c). The cWN(0,20) sample contains no oxygen in the bulk. The 800 cm$^{-1}$ band of its Raman spectra, originating from W-O bonds, is then related to the surface. Its intensity is lower than that of cW because not all tungsten atoms close to the surface are free to bond with surface oxygen, but are instead involved in W-N bonds. This is even more pronounced in regard to cWON(37,16) where no band at 800 cm$^{-1}$ was detected. According to the empirical law, H$_{800}/$H$_3$ should be close to 0.01, whereas our analyses reveal it to be lower than 0.0001. This discrepancy could be due to a crystallographic structure which differs from the other samples, leading to an absence of Raman active modes in that spectral region, and highlighting the fact that atomic structure can play a huge role.

As shown in the previous section, compact or porous characteristics can play an important role in determining the amount of oxides in a material. We address here the question of whether or not oxidation can be induced by local heating via Raman laser beam, as with measurements performed under ambient atmosphere. We propose below a methodology involving a power variation of laser intensity of up to four orders of magnitude.

3.3. Laser heating as complementary diagnostic: O/N substitution

As shown in the previous section, compact or porous characteristics can play an important role in determining the amount of oxides in a material. We address here the question of whether or not oxidation can be induced by local heating via Raman laser beam, as with measurements performed under ambient atmosphere. We propose below a methodology involving a power variation of laser intensity of up to four orders of magnitude.

Figure 6 shows the evolution of Raman spectra of the pWON(60,2.5) sample under different power laser conditions. The spectra in figures 6(a) and (c) are normalized to a height...
of 800 cm\(^{-1}\), and shifted vertically for clarity. The spectra 1 to 5 (6 to 13) of figures 6(a)–6(c) correspond to power densities varying from 0.3 to 3 (4 to 10) mW,\(\mu\text{m}^{-2}\). In figure 3(a), in the range 500–1100 cm\(^{-1}\), the spectral shape does not evolve, and is composed of three overlapping bands, demonstrating the presence of oxides in octahedral forms, as discussed in figure 3. For power densities higher than 1.5 mW,\(\mu\text{m}^{-2}\), the band at 800 cm\(^{-1}\) becomes slightly weaker with respect to the band at 800 cm\(^{-1}\), showing that the surface to volume ratio starts to be somewhat modified under the beam. There is a new signature at 205 cm\(^{-1}\), and its relative intensity diminishes when the laser power increases. This signature will be discussed in figure 7. The 800 cm\(^{-1}\) band intensity variation with power density is given in figure 6(b), where \(H_{800}\) evolves linearly as expected, since the Raman signal is proportional to the number of incoming photons. When the power is increased beyond 4 mW,\(\mu\text{m}^{-2}\), changes in the 500–1100 cm\(^{-1}\) region become important (see figure 6(c)); the 950 cm\(^{-1}\) band significantly diminishes compared to the other bands, and the overlap between the bands close to 700 and 800 cm\(^{-1}\) decreases, behaving more and more as an organized phase, resembling WO\(_3\) (see figure 1). In figure 6(d), the \(H_{800}\) versus power density curve increases its slope drastically for power densities higher than a threshold of 4 mW,\(\mu\text{m}^{-2}\). Figure 6(e), in semilogarithmic plot on the vertical axis, shows the existence of a saturation regime reached for this sample of close to 12 mW,\(\mu\text{m}^{-2}\). These observations indicate that a well-organized WO\(_3\) layer is formed under the laser beam, and therefore that the temperature is sufficiently high to activate oxidation mechanisms in the presence of \(=0.2\) bar of O\(_2\) and traces of water (a few hundreds of kelvins according to [35] and references therein. See also the discussion on the last figure of this paper). This is possible only if heat cannot be evaporated by the sample, which principally occurs when the morphology is not optimal for heat dissipation. In such a case, reaching the laser power density threshold allows atoms to reorganize and change structure. To prove this qualitative argument, we show in figure 7 the same kind of graph for the three studied morphologies: compact (figure 7(a)), porous (figure 7(b)) and nanoparticles (figure 7(c)). Compact sample spectra do not evolve across the whole range of power densities tested here (up to 24.15 mW,\(\mu\text{m}^{-2}\)), whereas for the porous sample and nanoparticles, the shapes in the 500–1100 cm\(^{-1}\) region (which are similar but with a higher 950 cm\(^{-1}\) band for nanoparticles) change from disordered to a more organized oxide at 4, and 1 mW,\(\mu\text{m}^{-2}\), respectively. The power

---

**Figure 6.** Influence of laser power density on the pWO(60,2.5) sample. (a) Normalized spectra (vertically shifted for clarity) and (b) 800 cm\(^{-1}\) band height (\(H_{800}\)) as a function of power density (from 0.3 to 4 mW,\(\mu\text{m}^{-2}\)). (c)–(e) Normalized spectra and \(H_{800}\) as a function of power density for power densities higher than 4 mW,\(\mu\text{m}^{-2}\). Dashed square of (d) is the range of (b). The density at which the spectra plotted in figures (a) and (c) were recorded are given in figures (b), (d), and (e).
level at which new oxide is created is higher for the porous sample than for nanoparticles, indicating that the porous film dissipates heat more efficiently than nanoparticles (which are agglomerated). The Raman spectral shape corresponding to the more organized samples differs in the two cases: it is similar to what would be expected for well-organized WO₃ in the porous sample, whereas for nanoparticles the main signal comes from the band at 950 cm⁻¹. This reveals a phase which has a large surface/volume ratio (with no coalescence of nanoparticles when the power increases). The band observed at 205 cm⁻¹ has been observed previously, and tentatively attributed to the presence of small domains and stoichiometric defects [55]. This is not often reported in the literature, and its interpretation is still under debate. We show here that the band disappears when the applied laser power density is too high. Note that this band is not observed for compact samples, but is observed, although down-shifted by 65 cm⁻¹, for nanoparticles: this indicates that it is related to surface vibrators, confirming the previous interpretation relating to small domains and/or defects.

In order to systematically investigate the power density at which the laser beam creates oxide, the intensity of the oxide band at 800 cm⁻¹ is compared to that of silicon at 520 cm⁻¹, recorded under the same experimental conditions. If no evolution with power density is expected, then as the band intensities of oxide and silicon are both proportional to the number of incoming photons (and thus to the power density of the used laser beam), Hₒ₈₀₀/Hₛ₁₀ should remain constant. On the other hand, if oxides are created, as shown in figure 6, Hₒ₈₀₀/Hₛ₁₀ will evolve with the laser power density. In figure 8, we plot this ratio for a selection of compact and porous samples, as a function of laser power density, for samples without nitrogen in figure 8(a), and for samples with both oxygen and nitrogen in figure 8(b). Figure 8(a) shows that, as expected for compact samples, for cW and cWO (25, 2), the ratio remains constant within the entire range of investigated power densities (dispersion around this value comes from the size of the spot, which could change a little from one measurement to another), indicating that the oxides probed by Raman spectroscopy are not created, but are inherent to the pristine samples. On the other hand, for porous samples and nanoparticles,
there is a clear threshold (close to 4 for pWO(52,4), and pWO(60,2,5), and 1 mW·µm⁻² for NP) after which the ratio starts to increase drastically, up to H_{800}/H_{850} \approx 5. According to the model presented in figure 5(c), this value corresponds to a thickness of approximately 50 nm. This is of course a very approximate thickness estimation, as the model is based on a simple slab geometry. In reality, samples are porous, and the oxide created by the laser beam is almost circular in the x, y plane, with a radius close to that of the laser spot, indicating that the oxide created is surrounded by porous tungsten containing various amounts of O, depending on the sample. On the contrary, figure 8(b) shows that, for compact samples, except in the case of cWN(0,20) which behaves similarly to cW, cWON(20,35) and cWON(37,16) starts to evolve at a threshold of \approx10 and 8 mW·µm⁻², respectively (with no detectable oxide for the latter below this threshold). These results show that the presence of N potentially favors the creation of oxides in compact layers. On the other hand, the three porous samples (pWON(53,12), pWON(47,9) and pWON(20,35)) behave more or less similarly to each other and to that without N: the H_{800}/H_{850} ratio is constant until a threshold is reached, and then increases. The thresholds range from 2 to 5 mW·µm⁻² and, contrary to the compact samples, there is no evidence for the role of nitrogen.

3.4. Qualitative information on the sample temperature during oxide formation

When increasing the power density of the laser beam under atmospheric conditions, we have seen previously that sample chemistry can evolve, due to local heating creating bulk oxides. However, since the laser beam which locally heats the sample is also the beam that probes the sample on the exact same spot, the retrieved spectrum is recorded at a sample temperature, which can in principle be higher than room temperature. Figure 9(a) shows two spectra taken from the cWON(37,16) sample: one recorded when the power density was 17 mW·µm⁻², the other recorded after this measurement, at a lower power density of 1 mW·µm⁻², for which the sample is expected to be close to room temperature. The two spectra are different: at low laser power densities, the 800 cm⁻¹ band slightly upshifts (4 cm⁻¹) and narrows, while the band at 700 cm⁻¹ becomes more intense and better defined. To obtain hints on the sample temperature due to laser heating, we studied a reference WO₃ sample, heated in a furnace (1 bar argon atmosphere, temperatures varied from 20 to 1050 °C) equipped with a window, allowing in-situ Raman spectroscopy to be performed. Figure 9(b) shows the evolution of the Raman spectrum of this WO₃ sample as a function of temperatures. The laser power was kept low enough to avoid local heating. When the temperature increases, the 800 cm⁻¹ band downshifts and broadens, and the band at 700 cm⁻¹ starts to disappear. The effect is reversible (not shown here). Note that WO₃ is polymorphic and presents a series of transitions between 17 °C and 740 °C, from δ-WO₃ to γ-WO₃ to β-WO₃ to α-WO₃ (see section 2.3). The 1050 °C spectrum then corresponds to a spectrum of the α-WO₃ phase. This spectrum being similar to that observed for the sample heated at 17 mW·µm⁻² and recorded at 17 mW·µm⁻² (figure 9(a)), one can conclude that it corresponds to α-WO₃, whereas the subsequent 1 mW·µm⁻² corresponds to γ-WO₃ (with defects, as widths are larger than the reference well-crystallized sample). However, one cannot form exact conclusions as to the value of the temperature attained due to laser heating, because Raman spectra of WO₃ are sensitive to the crystal order and to the presence of defects (here for example, the two spectra at room temperature of figures 9(a) and (b) are not strictly similar). However, one can conclude the sample reached an elevated temperature.

4. Discussion and concluding remarks

We have investigated the sensitivity of Raman spectroscopy to tungsten oxide and nitride that could occurring in compact, porous, and nanoparticle forms. In the perspective of a tokamak post-mortem campaign, this technique has the advantage of rapid provision of a large amount of data based on semi-qualitative spectroscopic observations. This could be used to select samples requiring quantitative analysis with more time-consuming techniques, like TOF-ERDA or electron microscopies. The main spectroscopic findings observed based on relevant laboratory samples are:

(1) Raman spectroscopy is sensitive enough to detect surface native oxides, and the optimal experimental conditions to perform such measurements were derived.
(2) More tungsten oxides are detected for porous materials and nanoparticles than for compact materials, due to the high degree of roughness of the former class of materials.
(3) Raman band intensity varies and increases qualitatively with O content
(4) Crystallographic structure has an influence on band intensities
(5) Long-term storage of a sample between production and analysis can affect the results, due to the growth of native oxide in the interim
(6) Porous materials are less thermally stable than compact materials
(7) The relative thermal stability of compact materials deteriorates with increasing nitrogen content
(8) Oxides and nitrides can be detected and distinguished (directly by the presence of additional broad bands in the range 300–600 cm⁻¹, and indirectly by the W PDOS activation close to 200 cm⁻¹, for nitrides), even if sensitivity to N is lower than that of O
(9) An oxygen/nitrogen substitution occurs when the temperature is high, and oxide is created under the laser beam

We believe this work will also be useful for Laser cleaning activities [75], mirror activities [76–79], tungsten oxide engineering activities [54, 80–83], N/O substitution in W, and the characterization of new tungsten nitride phases [84] involved, for example, in water splitting [85]. Two natural continuations of this work could be: to study the kinetics of growth after exposure to air, and the detection/quantification of hydrogen isotopes introduced in these materials.

Note that to obtain more quantitative results, details of light propagation inside these complex materials should be considered. Stoichiometry, as well as roughness and porosity can alter optical properties, and thus Raman band intensities. For example, oxides with a O/W atomic ratio of 2.7 occur at the edge of a metallic/insulator transition [69], and thus exhibit totally different optical properties.

Regarding the phenomenological points evidenced in this paper, Raman spectroscopy, used as an initial post-mortem technique, could be of importance for systematic measurements conduced in the framework of post-mortem campaigns, as these measurements could be accomplished rapidly for many samples. Moreover, statistics could be achieved in a reasonable time frame, even for a single sample, due to the lateral micrometric resolution of this method.

Acknowledgments

This work has been carried out within the framework of the EUROrfusion Consortium, and has received funding from the Euratom research and training programme 2014-2018, and 2019-2020, under Grant Agreement No. 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. Work performed under EUROrfusion WP PFC.

M. M. has received funding from the Excellence Initiative of Aix-Marseille University—A*Midex, a French ‘Investissements d’Avenir’ programme, as well as from the ANR under grant ANR-18-CE05-12

ORCID IDs

C. Pardanaud https://orcid.org/0000-0001-8974-4396
D. Dellasega https://orcid.org/0000-0002-7389-9307
M. Passoni https://orcid.org/0000-0002-7844-3691
C. Martin https://orcid.org/0000-0002-4704-3273
L. Couëdel https://orcid.org/0000-0003-0749-9273
M. Minissale https://orcid.org/0000-0001-6331-1402
E. Alves https://orcid.org/0000-0003-0633-8937
Z. Siketic https://orcid.org/0000-0002-7358-8090
I. Bogdanovic Radovic https://orcid.org/0000-0002-4100-736X

References

[1] Vassallo E., Angella G., Caniello R., Deambrosis S., Inzoli F., Miorin E. and Pedroni M. 2015 Effects of nitrogen concentration on microstructure of tungsten coatings synthesized by plasma sputtering method J. Fusion Energy 34 1246–51
[2] Linke J., Du J., Loewenhoff T., Pintsuk G., Spilker B., Steudel I. and Wirtz M. 2019 Challenges for plasma-facing components in nuclear fusion Mater. Radiat. Extremes 4 056201
[3] Hill D.N. 1997 A review of ELMs in divertor tokamaks J. Corros. Sci. Eng. 241 182–98
[4] Huang Y., Sun J.Z., Sang C.F. and Wang D.Z. 2016 Two-dimensional numerical study of ELMs-induced erosion of tungsten divertor target tiles with different edge shapes Fusion Eng. Des. 102 28–35
[5] Pitts R.A. et al 2013 A full tungsten divertor for ITER: physics issues and design status J. Nucl. Mater. 438 S48–56
[6] Brezinsek S. et al 2017 Contributors, Plasma-wall interaction studies within the EUROfusion consortium: progress on plasma-facing components development and qualification J. Nucl. Mater. 57 116041
[7] Mayer M., Krat S., Baron-Wiechec A., Gasparyan Y., Heinola K., Koirananta S., Likonen J., Ruset C., de Saint-aubin G., Widdowson A. and JET Contributors 2017 Erosion and deposition in the JET divertor during the second ITER-like wall campaign Phys. Scr. 014058
[8] Greuner H., Maier H., Balden M., Linsmeier C., Boswirth B., Lindig S., Norajitra P., Antusch S. and Rieth M. 2013 Investigation of European tungsten materials exposed to high heat flux H/He neutral beams J. Corros. Sci. Eng. 442 S256–60
[9] Brezinsek S. et al J.E.T. Contributors 2015 Beryllium migration in JET ITER-like wall plasmas Nucl. Fusion 55 063021
[10] Bykov I., Bergsaker H., Possnert G., Zhou Y., Heinola K., Pettersson J., Conroy S., Likonen J., Petersson P., Widdowson A. and JET contributors 2016 Studies of Be migration in the JET tokamak using AMS with Be-10 marker Nucl. Instrum. Methods Phys. Res. B 371 370–5
[11] Kumar M. et al 2018 Identification of BeO and BeOxSy in melted zones of the JET Be limiter tiles: raman study using comparison with laboratory samples Nucl. Mater. Energy 17 295–301
[12] Makepeace C. et al 2019 The effect of beryllium oxide on retention in JET ITER-like wall tiles Nucl. Mater. Energy 19 346–51
[13] Oberkofler M. et al 2015 Plasma-wall interactions with nitrogen seeding in all-metal fusion devices: formation of nitrides and ammonia Fusion Eng. Des. 98–99 1371–4
[14] Markelj S., Založnik A. and Cadez I. 2017 Interaction of ammonia and hydrogen with tungsten at elevated
temperature studied by gas flow through a capillary. J. Vac. Sci. Technol. A 35 061602

[15] Fortuna-Zalesna E., Grzonka J., Moon S., Rubeł M., Petersson P., Widdowson A. and JET Contributors 2017 Fine metal dust particles on the wall probes from JET-ILW Phys. Scr. T170 014038

[16] Fortuna-Zalesna E., Grzonka J., Rubeł M., Garcia-Carrasco A., Widdowson A., Baron-Wiecheck A., Ciupinski L. and JET Contributors 2017 Studies of dust from JET with the ITER-Like Wall: composition and internal structure Nucl. Mater. Energy 12 582–7

[17] Masuzaki S. et al 2017 Analyses of microstructure, composition and retention of hydrogen isotopes in diverter tiles of JET with the ITER-like wall Phys. Scr. T170 014031

[18] Heinola K., Widdowson A., Likonen J., Alves E., Baron-Wiecheck A., Barradas N., Brezinski S., Catarino N., Coad P. and Koivuranta S. 2016 Long-term fuel retention in JET ITER-like wall Phys. Scr. T167 014075

[19] Likonen J. et al. 2016 Deuterium trapping and release in JET ITER-like wall diverter tiles Phys. Scr. T167 014074

[20] Bernard E. et al. 2019 Tritium retention in W plasma-facing materials: impact of the material structure and helium irradiation Nucl. Mater. Energy 19 403–10

[21] Matthews G.F. et al 2011 JET ITER-like wall-overview and experimental programme Phys. Scr. T145 014001

[22] Bucalossi J. et al 2014 The WEST project: testing ITER divertor high heat flux component technology in a steady state tokamak environment Fusion Eng. Des. 89 907–12

[23] Richou M. et al 2015 Design and preliminary thermal validation of the WEST actively cooled upper divertor Fusion Eng. Des. 96–99 1394–8

[24] Kreter A., Brandt C., Huber A., Kraus S., Moller S., Reinhart M., Schweer B., Sergentino G. and Unterberg B. 2015 Linear plasma device PSI-2 for plasma-material interaction studies Fusion Sci. Technol. 68 8–14

[25] Linsmeier C., Unterberg B., Coenen J.W., Doerper R.P., Greuner H., Kreter A., Linke J. and Maier H. 2017 Material testing facilities and programs for plasma-facing component testing Nucl. Fusion 57 092012

[26] Alimov V.K., Tyburska B., Balden M., Lindig S., Roth J., Isobe K. and Yamanishi T. 2011 Surface morphology and deuterium retention in tungsten oxide layers exposed to low-energy, high flux D plasma J. Nucl. Mater. 409 27–32 (https://www.sciencedirect.com/science/article/pii/S0023154710008500)

[27] Coenen J.W., Philipp V., Brezinski S., Pintsuk G., Tanabe T., Ueda Y. and TEXTOR team 2011 Analysis of structural changes and high-heat-flux tests on pre-damaged tungsten from tokamak melt experiments Phys. Scr. T145 014066

[28] Richou M. et al. 2016 The WEST project: validation program for WEST tungsten coated plasma facing components Phys. Scr. T167 014029

[29] Schoof F. and Gorlie M. 2019 A route to standardised high heat flux testing: an example for tungsten Fusion Eng. Des. 139 132–6

[30] Alves L.C., Alves E., Barradas N.P., Mateus R., Carvalho P., Coad J.P., Widdowson A.M., Likonen J. and Koivuranta S. 2010 Erosion and re-deposition processes in JET tiles studied with ion beams Nucl. Instrum. Methods Phys. Res. B 268 1991–6

[31] Guterl J., Smirnov R.D., Krasheninnikov S.I., Zibrov M. and Pisarev A.A. 2015 Theoretical analysis of deuterium retention in tungsten plasma-facing components induced by various traps via thermal desorption spectroscopy Nucl. Fusion 55 093017

[32] Hodille E.A., Ferro Y., Fernandez N., Becquat C.S., Angot T., Layet J.M., Bisson R. and Grisolia C. 2016 Study of hydrogen isotopes behavior in tungsten by a multi trapping macroscopic rate equation model Phys. Scr. T167 014011

[33] Hodille E.A. et al. 2017 Retention and release of hydrogen isotopes in tungsten plasma-facing components: the role of grain boundaries and the native oxide layer from a joint experiment-simulation integrated approach Nucl. Fusion 57 076019

[34] Hodille E.A., Ferro Y., Piazza Z.A. and Pardanaud C. 2018 Hydrogen in beryllium oxide investigated by DFT: on the relative stability of charged-state atomic versus molecular hydrogen J. Phys.: Condens. Matter. 30 305301

[35] Addab Y. et al. 2016 Formation of thin tungsten oxide layers: characterization and exposure to deuterium Phys. Scr. T167 014036

[36] Hijazi H., Addab Y., Maan A., Duran J., Donovan D., Pardanaud C., Ibrahim M., Cabie M., Roubin P. and Martin C. 2017 Tungsten oxide thin film exposed to low energy He plasma: evidence for a thermal enhancement of the erosion yield J. Corros. Sci. Eng. 48 91–97

[37] Martin C., Hijazi H., Addab Y., Domenichini B., Bannister M.E., Meyer F.W., Pardanaud C., Giacometti G., Cabie M. and Roubin P. 2017 Tungsten oxide thin film bombarded with a low energy He Ion beam: evidence for a reduced erosion and W enrichment Phys. Scr. T170 014019

[38] Ahmadi M., Sahoo S., Younesi R., Gaur A.P.S., Katryš R.S. and Guinel M.J.F. 2014 WO3 nano-ribbons: their phase transformation from tungstite (WO3 center dot H2O) to tungsten oxide (WO3) J. Mater. Sci. 49 5899–909

[39] Pagnier T., Boulova M., Sergent N., Bouvier P. and Luczaeau G. 2007 Nanopowders and nanostructured oxides: phase transitions and surface reactivity J. Raman Spectrosc. 38 756–61

[40] Rusu M.I. et al. 2017 Preparing the future post-mortem analysis of beryllium-based JET and ITER samples by multi-wavelengths Raman spectroscopy on implanted Be, and co-deposited Be Nucl. Fusion 57 076035

[41] Arnas C., Chami A., Couedel L., Ascente T., Cabie M. and Neisius T. 2019 Thermal balance of tungsten monocrystalline nanoparticles in high pressure magnetron discharges Phys. Plasmas 26 085706

[42] Dellasde A., Merlo G., Conti C., Bottani C.E. and Passoni M. 2012 Nanostructured and amorphous-like tungsten films grown by pulsed laser deposition J. Appl. Phys. 112 084328

[43] Pezzoli A., Dellasde A., Russo V., Gallo A., van Emmichoven P.A.Z. and Passoni M. 2015 Thermal annealing and exposure to divertor-like deuterium plasma of tailored tungsten oxide coatings J. Corros. Sci. Eng. 463 1041–4

[44] Siketic Z., Radovic I.B. and Jaksic M. 2008 Development of a time-of-flight spectrometer at the Ruder Boskovic Institute in Zagreb Nucl. Instrum. Methods Phys. Res. B 266 1328–32

[45] Siketic Z., Skukan N. and Radovic I.B. 2015 A gas ionisation detector in the axial (Bragg) geometry used for the time-of-flight elastic recoil detection analysis Rev. Sci. Instrum. 86 083301

[46] Mateus R., Dellasde A., Passoni M., Siketic Z., Radovic I.B., Hakola A. and Alves E. 2018 Helium load on W-O coatings grown by pulsed laser deposition Surf. Coat. Technol. 355 215–21

[47] Yan R. et al. 2018 Plasma cleaning of ITER edge Thomson scattering mock-up mirror in the EAST tokamak Nucl. Fusion 58 026008

[48] Addonizio M.L., Castaldo A., Antonia A., Gambale E. and Iemmo L. 2012 Influence of process parameters on properties of reactively sputtered tungsten nitride thin films J. Vac. Sci. Technol. A 30 031506

[49] Boulova M. and Luczaeau G. 2002 Crystallite nanosize effect on the structural transitions of WO3 studied by Raman spectroscopy J. Solid State Chem. 167 425–34
