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CHAPTER 1

Raman Microscopy: A Suitable Tool for Characterizing Surfaces in Interaction with Plasmas in the Field of Nuclear Fusion

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Additional information is available at the end of the chapter

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Abstract

Raman microscopy, which is sensitive to chemical bonds, defects, structure, is a suitable tool that can give information on how a material can be modified by interacting with ions. We will first give concrete examples on how it can be used to characterize with a micrometric resolution samples extracted from tokamaks. We will then give concrete examples on what information can be obtained by doing a study on laboratory synthesized materials, benchmarking Raman microscopy with quantitative techniques. The first part of the chapter is focused on carbon-based material analysis. We will show how Raman spectra are sensitive to the presence of hydrogen, a major safety issue in the field. The second part of the chapter will be focused on beryllium- and tungsten-based material analysis. We will show that hydrogen can be stored as an hydride after ion implantation and that it can be released easily in tungsten oxide.

Keywords: plasma wall interaction, hydrogen isotope implantation, carbon, beryllium, tungsten

1. Introduction

Raman microscopy, which is sensitive to chemical bonds, defects, and structure, is a suitable tool that can give information on how a material can be modified by interacting with ions. We first gave concrete examples on how it can be used to characterize with a micrometric resolution samples extracted from tokamaks. We then gave concrete examples on what information can be obtained by doing a study on laboratory-synthesized materials, comparing
Raman microscopy with quantitative techniques. The first part of the chapter is focused on carbon-based material analysis. We showed how Raman spectra are sensitive to the presence of hydrogen, a major safety issue in the field. The second part of the chapter is focused on beryllium- and tungsten-based material analysis. We showed that hydrogen can be stored as a hydride after ion implantation and that it can be released easily in tungsten oxide.

1.1. Plasma-wall interactions in tokamaks

Tokamaks are machines made to study the possibility to make energy from nuclear fusion reactions by confining hot plasma (1–100 keV ions) magnetically. The future international reactor ITER\(^1\) (International Thermonuclear Experimental Reactor), now in construction at Cadarache (south of France), is one of them. One of its aims is to produce, with the help of the D+T nuclear reaction, 500 MW by injecting 50 MW. The D+T nuclear reaction has been chosen because it has the highest cross section in the relevant domain of energy (one to two orders of magnitudes higher than the D+D reactions). The D+T reaction will produce 14-MeV neutrons and 3.52-MeV He nuclei, which will maintain the temperature of the D+T reacting plasma to an equilibrium state. Magnetic field lines are however connected to the inner walls of the ITER torus, which leads to the existence of cold edge plasma (composed of He, D, T, impurities such as oxygen or eroded metals) interacting with them. The heat produced by the hot plasma is received mainly on a part of the wall called a divertor. The material that will compose this part will have to work with heat loads in the range 10–20 MW/m\(^2\).

Then, in tokamaks, understanding and being able to predict the evolution of the plasma-facing components (PFCs) that interact with both heat loads and the cold edge plasma is one of the keystones to make nuclear fusion a way of producing energy in the future \[2\]. The material chosen for the divertor is tungsten as it drives well the heat to the underlying cooling loops present in the PFCs, it is difficult to erode, and its melting/fusion temperatures are very high, and hence creating bonding with hydrogen isotope is supposed to be difficult. The other parts of the PFCs are composed of beryllium \[3\]. Some tokamaks are already working nowadays in an ITER-like wall (ILW) configuration to prepare the ITER project, such as the Joint European Torus/JET tokamak, with some PFCs composed of tungsten-coated carbon tiles \[4–6\], carbon tiles, mounted on limiters and/or neutralizers, being used in the ancient carbon area of tokamaks, now abandoned, because of tritium retention (tritium being radioactive and being easily trapped in carbon) \[7, 8\]. In that framework, the surface composition and morphology modifications under operation will lead to changes in the material properties that can address safety issues. These changes will have to be measured and then understood. In more details, the migration \[9\] and/or melting of elements in the machine \[10, 11\], the production of dust, the hydrogen isotope retention \[12, 13\], the impurity contamination (traces of carbon and/or oxygen, nitrogen seeding \[14\], etc.) leading to formation of new mixed materials/phases (such as oxides or alloys) and the complex surface erosion will all influence the lifetime of these PFCs and their fuel retention properties. Surface characterization techniques are then necessary to measure the elemental changes in JET and in ITER PFCs erosion zones and deposits.

\(^{1}\)To give an idea of the size of the project and the machine: the tokamak alone will stay in a room which is 60 m high, all the site will be sprayed on a surface which is 420,000 m\(^2\) and the machine itself weighed 23,000 tons \[1\].
1.2. Raman microscopy as a technique to probe the top of deposits

In this field of research, due to their isotope selectivity, ion beam analyses (IBA) play a prominent role in this characterization, as discussed in Refs. [15, 16]. Thermal desorption spectroscopy (TDS) also plays a key role as it can give access to the characterization of D or T trap energies in metals such as Be [17–19] or W [20]. However, even if TDS and IBA techniques give quantitative information about hydrogen isotope concentration, they only give indirect information about chemical bonding. A direct way to probe that chemical bondings is to probe them spectroscopically by means of their vibrational spectrum using Raman microscopy.

Moreover, the in-depth resolution reached by IBA is not enough to describe properly the top layer of deposits called the hydrogen isotope supersaturated layer, which sizes in the range of tens of nanometers, and is composed of few atomic percent to few tens of atomic percent of hydrogen isotopes [13]. Depending on the material, Raman microscopy can be a well-suited technique adapted to that depth, as can be seen in Figure 1. In that figure, the transmittance coding the effectiveness of a material in transmitting incident light is plotted for $\lambda_L = 514$ nm and for Be, W, C (graphite and amorphous form). The depth at which the transmitted energy reaches 10% of the initial incident energy is 30, 35, 70 and 310 nm for, respectively, Be, W, C\ graphite and amorphous carbon. The last value depends on the local organization of the amorphous structure, as detailed in Refs. [21–23]. Note that as the Raman measurements are generally done in back scattering geometry, one as to take into account an additional factor 2 in the argument of the exponential, as mentioned in [21, 22].

![Figure 1. Transmittance in function of the depth for Be, W, C.](image-url)
The aim of this chapter is to give concrete examples on how Raman microscopy can be used to characterize samples extracted from tokamaks, from the micrometric to the macroscopic scale of the machine. We then gave concrete examples on what information can be obtained by doing a study on laboratory-synthesized materials, benchmarking Raman microscopy with quantitative techniques such as TDS or IBA. The first part of the chapter is focused on carbon-based material analysis as all the previous tokamaks were using this element in the past. We showed how Raman spectra are sensitive to the presence of hydrogen, a major safety issue in the field. The second part of the chapter is focused on beryllium and tungsten based material analysis. We showed that hydrogen can be stored as a hydride after ion implantation, and that it can be released easily in tungsten oxide.

2. Carbon materials

2.1. Context

The Tore Supra tokamak had the ability to perform long plasma discharges with actively cooled PFC, which was a good opportunity to study fuel retention, a major concern in the plasma-wall interaction community. The study devoted to that was the Deuterium Inventory in Tore Supra (DITS) campaign. It was aimed at studying and linking the erosion of carbon PFCs and the fuel retention. The in-vessel D inventory was followed after the D loading campaign through particle balance [24], a part of the toroidal pump limiter (TPL), which was actively cooled during discharges, was dismantled for an extensive postmortem analysis of a few tens of carbon fiber composite tiles (CFC). The TPL was situated on top of a part of the machine called the neutralizer (NTR), which was also composed of CFC, but which was not actively cooled during discharges.

The post-mortem analyses used techniques devoted to the estimation of the D inventory [25, 26] and to structural and chemical characterizations [27], Raman microscopy being one of them [26, 28, 29]. Due to the different rates of erosion/deposition associated to the plasma footprint, the TPL surface exhibited a pattern which combined deposition-dominated zones (labeled thick and thin depending on the amount of matter found) and erosion-dominated zones. The shapes of these patterns were reproduced by simulating plasma wall interactions from the micrometric to the metric scale [30, 31].

Temperatures of the TPL were determined (with the help of thermographic measurements [24]) to be 500°C for gap surfaces of both thick deposit tiles and eroded tiles, 200°C for top surfaces of eroded tiles and 120°C for both gap and top surfaces of CFC tiles situated in the so-called thin deposit region. Temperature was estimated to vary in the range 500–900°C for the top surface of thick deposit tiles.

In Figure 6, we display Raman spectroscopic parameters of several samples, but before detailing the figure, we need to remember some well-known facts about the Raman
spectroscopy of disordered and amorphous carbons. They are briefly given below but are not detailed.

Raman microscopy is routinely used to characterize rapidly C-based materials, from nanocrystalline graphite (nc-G) to amorphous carbons, hydrogenated or not (a-C:H or a-C). It probes the structure [32] and is highly sensitive to bonding properties by interpreting the 1000–1800 cm$^{-1}$ region, dominated by the G and D bands due to C(sp$^2$) hybridization of carbon atoms [33]. The G band, close to $\sigma_G=1600$ cm$^{-1}$, is assigned to the bond stretching of both aromatic and aliphatic C-C pairs, whereas the D band, close to 1350 cm$^{-1}$ with a 514-nm laser (associated with a D’ band close to 1620 cm$^{-1}$) is assigned to the breathing mode of aromatic rings. The Raman analysis of graphite and nc-G clearly shows that this D band exists only when there is disorder [32]. Implanted graphite also displays this D band [34]. For a-C and a-C:H, the G bandwidth is related to disorder (sp$^2$ cluster size, cluster size distribution, chemical bonding) or stress [35] and presence of C(sp$^3$). For disordered multilayer graphene, the G bandwidth evolution can also be related to disorder [36].

Spectra of a-C and nc-G are clearly distinct [37] (spectrum 1 from Figure 8(a) belongs to a-C, whereas spectrum 3 belongs to nc-G, whereas spectrum 2 is in between): for example, G and D bands are much broader for a-C (width $\Gamma_G \sim$80–200 cm$^{-1}$) than for nc-G (width $\sim$15 to 40 cm$^{-1}$). Moreover, the intensity ratio (D over G band intensity) depends on the amount of disorder. Generally, to reproduce experimental nc-G spectra, bands at $\sim$1500 cm$^{-1}$ and at $\sim$1200 cm$^{-1}$ are very often needed, interpreted as sp$^3$ or out-of-plane defects, or as an additional amorphous contribution [38–43], see the discussions in Refs. [29, 43]. Raman spectra thus contain information on disorder [35] such as the size clusters, $L_a$ [32, 44], the C(sp$^2$)/C(sp$^3$) ratio, the hydrogen content [45–47], etc. All these information will help trying to understand the complex thermo/chemistry story of samples extracted from tokamaks.

2.2. Laboratory experiments

2.2.1. H-content determination in a-C:H layers

The Raman parameters generally used to probe the structure are the peak wavenumber and the width of the G and D bands, respectively, and the peak height ratio of these two bands, $H_B/H_G$ [48]. An additional spectral feature has to be taken into account: a photoluminescence background which is superimposed to the Raman spectrum and is correlated to the H content [46]. The slope of this background, $m$, is calculated between 800 and 2000 cm$^{-1}$. The higher $m$, the higher is the photoluminescence intensity. Figure 2 displays ultra-high vacuum heating effect on a 220-nm thick hard amorphous, hydrogenated carbon thin films (a-C:H) that were deposited on a Si [49]. The mass density of such typical hard a-C:H layers, with H/H+C $\sim$ 30 at.% is $\sim$1.9 g cm$^{-3}$ are formed [50].

Figure 2 displays the thermal evolution of $m/H_G$ and $H_B/H_G$ compared to the H content determined by IBA and the $H_2$ release determined by TPD. $\sigma_G$ is not shown here but it reaches a plateau for $T > 600°C$, meaning that the number of C(sp$^3$) neighboring C(sp$^2$) no longer changes.
We see that m/H$_G$ increases by $\sim$40% between room temperature and 300°C, decreasing between 300 and 600°C (at that point, m/H$_c$ $\sim$0.05). For $T > 600^\circ$C, the slope is close to zero. If we compare to the H content, between RT and 300°C, it is constant (H/H+C $\sim$ 30 at.%). Then, the increase of the m/H$_c$ spectroscopic parameter is due to aromatization (and defect passivation) that leads to an increase of the photoluminescence background. As a consequence, m/H$_G$ cannot be related easily to H/H+C in this thermal range. For higher temperatures, the H content decreases from 30 down to approximately 2%, without reaching a plateau.

The bottom part of Figure 2 shows that H$_D$/H$_G$ and H/H+C evolve in a remarkably symmetrical way. This suggests that the two parameters are correlated and that H$_D$/H$_c$ could be used to probe the hydrogen content. The relation obtained that works with a 514 nm laser is (H/H+C = 0.54−0.53 H$_D$/H$_G$) in the range H/H+C = 2−30 at.%. Such a linear law, with the same slope, can be obtained for other wavelengths (407–633 nm has been tested), but with a different value at the origin.

**Figure 2.** TDS, IBA and Raman microscopy measurements of a heated a-C:H sample.
2.2.2. Long-term hydrogen release revealed by in situ Raman spectroscopy

The thermal stability of six 200-nm-thick plasma enhanced chemical vapor deposited a-C, a-C:H and a-C:D layers ranging from soft to hard layers has been studied. The imaginary part of the refractive index at 633 nm and the corresponding H or D contents have been displayed together and compared to results from the literature [50], showing a good agreement with what is known: when the H content increases, the sample becomes more transparent, because of the diminution of aromatic C(sp²) bonds. Figure 3(b) displays the thermal evolution of H_D/H_G for these six samples heated with a linear ramp (3°C min⁻¹) under a 1-bar argon atmosphere from room temperature to 600°C. Without entering into details, that can be found in [23], let us only focus on H data. One can see that the more hydrogen there is on the as deposited sample, at a lower temperature, the H_D/H_G ratio starts to increase. Because the evolution of H_D/H_G for a H-free amorphous carbon is small and because of what was shown in the previous part, most of the evolution in that thermal range is due to hydrogen release from C(sp³). This is consistent with what is known in the literature about the bad thermal stability of hydrogen-rich a-C [51–55].

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**Figure 3.** Thermal evolution of HD/HG for six a-C samples. (a) Optical constant in function of H content. (b) Comparative linear ramp study. Green stars in the top figure are from Ref. [50].
Figure 4 displays an example of isothermal evolution in function of time. This evolution cannot be due to the effect of the laser on the sample, accumulating heat with long times, as we compared two sets of data: one by switching off the laser between acquisitions and one with a continuous flux of heat. The position of the G band (not shown) no more evolves after 50 min, meaning there is no order increase due to an overestimated heat load by the probe laser. In Ref. [56], we studied that we had no power dependence in the range 0.01–1 mW/μm². Then, this technique allows to probe long-term hydrogen release. We will use it on tokamak samples in Section 2.3.

Then, to resume, we have shown that

- The $m/H_G$ parameter, often used to estimate the H content in the literature, should be used with care, first because it is sensitive to various photoluminescence-quenching processes and second because it is not sensitive to H bonded to C(sp²).
- The $H_D/H_G$ parameter is quasi-linear in the full range of H content and can thus be used to estimate the H content.
- $H_D/H_G$ can be used in situ to retrieve the H content evolution under heating.

2.2.3. H, D and He implantation in graphite: Starting the amorphization regime

The modification by ion impact of graphite has been studied both theoretically and experimentally ([57–67] and references therein). Inside the sample, collision cascades are created by ions that knock on the surface and penetrate. It creates defects and vacancies, ions being implanted...
after they slow down [68]. Protusions (height lower than 1 nm), called hillocks, are observed for low fluencies (<10^{14} ions cm^{-2}) [57, 58]. They are due to stress created by the first collision under the near surface region. More precisely, interstitial carbon clusters or coalescence of interstitials and vacancies are at the origin of these hillocks. At fluencies >10^{15} ions cm^{-2} [61, 62] and in the 400–800 K range, domes with a height one order of magnitude higher were observed.

We have exposed graphite to hydrogen deuterium and helium plasma (from 10^{16} to 10^{18} cm^{-2}) [43]. The energies were tuned from 40 to 800 eV. The ion incidence was parallel to the basal plane for CFC (carbon/carbon composite) and perpendicular for HOPG (highly oriented pyrolitic graphite). The changes of the material were studied by means of both Raman and atomic force microscopies.

We display the 400 eV/D implantation Raman spectra in Figure 5 as an illustration. The main differences or common points between HOPG and CFC are

- Pristine HOPG contains less defects than CFC (D band at 1350 cm^{-1} is close to zero for HOPG, whereas H_D/H_G is close to 2 for CFC, indicating nanometric crystal size domains)
- Implantation produces an amorphization for both materials (broad bands at 1500–1300 cm^{-1} appearing in the spectra, looking like the spectrum 1 in Figure 8(a))
○ The underlying pristine sample is visible can be seen in both cases. This is because the ions penetrate only 15–20 nm and the penetration depth of light is few tens of nanometer (see Figure 1).

○ Both bombarded Raman spectra display two kind of environment: in-plane defects and out of plane defects (see Ref. [43] for details).

○ No laser probe polarization effect of IPD and OPD on the HOPG sample, whereas there is one for IPD of the CFC.

When increasing the impinging ion energy, the growth of nanometric domes at the surface has been observed by atomic force microscopy (AFM) and the incident kinetic energy has been found as the parameter determining their height. The Raman study has also revealed that both the defect-defect distance in the IPD and OPD are typically 1 nm. When the number of vacancies created in the material increases, the number of in-plane defects decreases to the benefit of the out-of-plane defects.

2.3. Information retrieved from tokamak samples

2.3.1. Raman measurements inside the tokamak Tore Supra

Figure 6 displays the G band position, $\sigma_G$, in function of its width, $\Gamma_G$, for many samples collected in the Tokamak Tore Supra (deposition zones and erosion zones of the TPL, and on the NTR) and compared to pristine CFC and to heated laboratory deposited a-C:H (see Sect. 2.2 of this chapter for more information). The data points form a wide range of carbon materials from nc-G to a-C, all described in more details in [28, 69, 70]. Pristine CFC data points are all situated at $\Gamma_G\sim 25$ cm$^{-1}$ and $\sigma_G\sim 1580$ cm$^{-1}$. NTR deposits form a data point cloud continuously spread either along the positive slope straight line ($\Gamma_G$ in the range 20–80 cm$^{-1}$, $\sigma_G$ in the range 1580–1600 cm$^{-1}$) or along the negative slope straight line for the TPL deposited and eroded samples ($\Gamma_G$ in the range 80–180 cm$^{-1}$, $\sigma_G$ in the range 1600–1520 cm$^{-1}$). The deposited TPL points are very close to a-C:H data points, at slightly lower frequency. Note that the shift between heated a-C:H and the TPL deposits can be attributed to an isotopic effect as TS samples are deuterated samples, which downshifts the G band position. A proof of that can be found in Ref. [23] where both synthetic a-C:H and a-C:D were heated and compared. The a-C:H data were heated under vacuum from room temperature (right down corner up to 1000°C, left up corner). Then this line from right to left means that the carbons locally organize under heating. This is in agreement with the temperature measured in situ by thermography. The NTR deposits display lower $\Gamma_G$ values, meaning they are more structured. This is in agreement with the fact that the NTR was not actively cooled, being able to reach temperatures higher than 1000°C. As it is know that the deuterium is released at these temperatures (see Section 2.2 of this chapter, below), one can say that the D is mainly trapped in deposits found on the TPL and not on the NTR. The eroded TPL samples are less spread than the others, meaning the structure of the implanted carbons is more homogeneous and more amorphous. It can retain more deuterium, relatively. However, the thickness of that layer was found to be few nanometers only [69], which is low compared to the hundreds of microns found for Tore Supra deposits, meaning the D is essentially trapped in these deposits or deeper in the porosities of the initial pristine CFC. These points are investigated in a next subpart.
2.3.2. Micrometric inhomogeneities and long-term release of H

In Ref. [23], we compared with Raman microscopy the thermal evolution of reference samples to samples extracted from the Tore Supra tokamak, as it was shown that a long-term mechanism [71] occurred even at low temperature (low means here 120°C, which correspond to the thermostat temperature of the PFC cooling loop, staying at this values for days and weeks even when the plasma is off) and as we wanted to distinguish the Raman signature of this heating. Figure 7 displays the Raman data of the Tore Supra samples. Figure 7(a) and (b) is mappings of \( m/H_G \) and \( s_G \), respectively, for an as received sample. One can see that the deposit is inhomogeneous, the sample being more organized in the upper right part. The high value of \( m/H_G \) does not mean here that there is more hydrogen there, as mentioned by discussing Figure 2. In fact, this is the opposite. The value of \( H_{\text{D}}/H_{\text{G}} \) in the blue and red regions (not shown here) give typically values of 28 down to 17%, using the linear relation mentioned in Sect. 2.1. The zone where hydrogen has been outgassed displays a higher value of \( \sigma_G \) which is in agreement with what we know about the thermal stability of a-C:H [23, 49, 56]. The histograms of a TS deposit heated isothermally at 120°C for three times (120, 300 and 640 h) and at 250°C allows to show that the sample still evolve under long time scales (the average value of \( m/H_G \) increases slightly with time). The problem is that we need to average spectra on large zones because of large inhomogeneities found at the micrometric scale. However, using the mapping mode allows to identify different kind of defects of chemical environments which is needed to better characterize the sample. The average value of \( H_{\text{D}}/H_{\text{G}} \) (not shown here) leads to a value of H close to 20 %.

Figure 6. Carbon deposits spectroscopic parameters: G band position in function of its full width at half maximum.
2.3.3. Hydrogen depth concentration and history of Tore Supra deposits

In Ref. [72], lock-in thermography, scanning electron microscopy and confocal microscopy were used to study the erosion and depositions on the TPL of the Tore Supra tokamak. Taking into account, all the methods allowed the authors to perform a complete mapping of the mass of carbon that has been eroded and deposited. The findings were 520 g of deposits and 920 g of eroded carbon. It shows that more than a half of the carbon that is eroded is redeposited on the TPL. It was also found that the zones containing the highest deposits were found close to erosion zones.

Such things were simulated recently [31]. The gap deposition contribution is estimated at 23%, mostly from the erosion zones and with a main contribution from the low field side of the tile toroidal gap surfaces. This deuterium impoverishment in the deep layer has also been investigated more systematically in Ref. [73] where IBA and cross-section electron microscopy were done on 15 samples. The mean in-depth hydrogen isotope content is plotted in Figure 8(b) and scaled to the 120 μm of the deposit shown. The surface content has been divided by 2 in less than 20 μm. In parallel, $\sigma_G$ is displayed for three lines of sight. Then on top of this deposit, the H content is close to 20%, whereas it decreases close to zero at the interface between the deposit and the top of the CFC. The diminution is rapid in the 20 first microns. Same trends are seen with the structure probed with Raman spectroscopy: carbon close to the surface is less organized ($\sigma_G$ close to 1520 cm$^{-1}$), whereas $\sigma_G$ increases (meaning an increase of order) and then reaches a plateau 20 μm deep in the deposit, at the value of $\sigma_G = 1580$ cm$^{-1}$. This deuterium impoverishment of the deep layers may be caused by long-term release mechanisms, as discussed in the previous part.

Figure 7. Raman spectroscopy imaging of a unheated Tore Supra (TS) deposit. (a) m/H$_G$ mapping of this TS sample. (b) $\sigma_G$ mapping. (c) Histograms of heated TS samples (120°C during 120, 300 and 630 h, and 250°C).
3. Beryllium- and tungsten-based materials

3.1. Context

Tritium retention, occurring in a magnetically confined deuterium plus tritium plasma, can be obtained by erosion, retention, material modification, dust formation (and more generally plasma wall interactions). This is a big safety issue because of tritium radioactivity [7, 74].

Figure 8. H-content impoverishment in deep deposits compared to ordering of the carbon. H content is extracted from Ref. [73].
Hydrogen isotope retention in beryllium can also play a role in the lifetime estimation of the ≈700 m² ITER’s beryllium inner walls because of erosion [75]. This explains why several studies based on ion irradiation of Be samples have been devoted to D behavior to ensure that tritium retention will not be a limiting issue in ITER operations. Previous studies found D/Be ratio in the range 0.1–0.7 using energies in the range 0.6–20 keV/D and fluence in the range 10¹⁶–10¹⁹ cm⁻² [76–82].

At fluencies close to 2 × 10¹⁷ cm⁻² (in the range 0.6–1 keV/D), the existence of the D-content saturation (D/Be close to 0.25) has been shown [13, 83–84]. For fluencies lower than 0.7 × 10¹⁷ cm⁻² TDS display only one peak at 900 K, whereas for fluencies between 0.7 and 1 × 10¹⁷ cm⁻², a second peak lies at 750 K. For fluencies higher than 1.2 × 10¹⁷ cm⁻², two extra peak rise close to 500 K. These last peaks were explained by structural modification of the sample. Moreover, the role of crystal orientation and D diffusion along grain boundaries was investigated in [85]. The existence of BeH₂ was suggested in [17] but never observed before.

Raman microscopy is a nondestructive, noncontact and local (=1 μm² lateral resolution [86]) technique that has been proved to be sensitive to Be stretching modes [87], beryllium oxide modes [88], bending and stretching tungsten oxide modes [89], Be,Wₓ-mixed samples density of states [90], BeCW-irradiated samples [91] and give information when a pristine material is implanted by hydrogen ions [90, 92, 93]. First Raman analyses in ILW-tokamaks were performed on some molybdenum JET mirrors [90], showing that the technique is sensitive to thin ≈10 nm deposited layer composed of ≈33% Be, ≈33% C and ≈33% O and the underlying molybdenum oxidized mirror. C-O and C=O modes have been detected in that layer and defective or beryllium mixed with O and/or C have been found without possibility to identify the phases rigorously up to now, because of a poor benchmarking of the technique for these materials. Raman microscopy can also be able to give information about the hydrogen isotope behavior by combining IBA, Raman microscopy, atomic force microscopy (AFM) and with the help of DFT modeling. As an illustration of this complementarity, in Ref. [94], we identified on laboratory experiments the growth of BeD₂ with dendritic forms appearing subsequently to 2 keV ion implantation when the Be layer is saturated by implanted D ions. The width of the bands recorded by Raman microscopy suggested that this hydride has grown in a crystalline form which seems to be close to a body-centered orthorhombic structure with Ibam symmetry as the spectra look like to the ones reported in [95], who determined recently the structure by using additionally synchrotron X-ray diffraction. In [94], we showed that these dendrites appear when the amount of deuterium in the material is higher than ≈2 × 10¹⁷ D.cm⁻², when the ≈40 nm under surface layer is saturated by D.

3.2. Laboratory experiments

3.2.1. Defect-induced bands in beryllium

Below, we compare defective Be samples that have been produced by Be deposits in an impurity atmosphere or by D implantation. In more details, the defective deposit sample has been produced by the thermionic vacuum (TVA) method (more details can be found in Ref. [96] and references therein). To introduce disorder, a partial pressure of N₂ (in the range from 10⁻² to 10⁻³ Pa partial pressure) has been used during the deposit. The amount of N being ≈5 atomic %.
The D-implanted Be sample have been prepared with two impinging ion geometries, with 2 keV/D: normal incidence (90°) and 45° incidence. More details about the implantation of the 90° geometry can be found in [94].

**Figure 9** displays Raman spectra of a deposited Be sample with a high content of defects for four laser wavelengths. Data were acquired with 633, 514, 488 and 325 nm lasers. The band associated to the \( E_{2G} \) Raman active mode is downshifted for the defective sample, but the shift depends on the wavelength. \( I_{E2G} \) for the reference sample is close to 8 cm\(^{-1}\). For the defective sample, it is higher (27 cm\(^{-1}\)). The logarithmic scale used here allows to distinguish several additional broad bands (413, 544 and 616 cm\(^{-1}\)) that were first evidenced in Ref. [90] and called defect-induced bands. These bands are attributed to the phonon density of states (PDOS), as can be seen by comparing the Raman spectrum (where the \( E_{2G} \) band has been removed) to the PDOS of Be measured in the literature. Their intensity reaches values as high as 23% of the Raman active \( E_{2G} \) mode heights and they are related to the defect content, defect being a term which can be impurity, vacancy or other kind of defects.

![Raman spectra](image_url)

**Figure 9.** Normalized Raman spectra of a pristine (a) and defective (b) Be deposited sample, using four laser wavelength. (c) The 633 nm spectrum of the defective sample is displayed after removing the \( E_{2G} \) Raman active mode and is compared to the PDOS measured by INS and by PCEPI [97]. The bands marked by stars are due to other laser electronic transitions.
Changing the wavelength does not change the qualitative trends: the band related to the $E_{2G}$ mode is more downshifted to low frequencies and broader. However, quantitative differences can also be seen, with some information. For example, the height of the PDOS diminishes monotonically with the decrease of the laser wavelength (from 23% with 633 nm down to 4% with 325 nm for the defective sample). $\sigma_{E_{2G}}$ does not display a monotonic evolution with the laser wavelength for the defective sample. The reference sample, oppositely, does not disperse in the range 325–633 nm. Shifts observed may then be due to stress [86] in the deposited layer, the nonmonotonic behavior being caused by two effects: stress gradients existing in the deposited layers and the penetration depth of the laser that is wavelength dependent.

In Figure 10, we compare 514 nm spectra of a pristine Be, a Be sample containing $2 \times 10^{17}$ D cm$^{-2}$ in the 90° geometry and 514 nm spectrum of Be sample in the 45° geometry. D implantation (Figure 10(b)) and vacancy creation profiles were evaluated for the 90° and 45° geometries.

![Figure 10](image-url)

**Figure 10.** Varying the in-depth defects. (a) Normalized Raman spectra of D implanted Be samples. Geometry implantation (90° and 45°) are compared with the 514 nm laser wavelength.
using the stopping and range of ions in matter (SRIM) code\textsuperscript{2} \cite{srims}. If we believe in SRIM calculations (which gives trends as many mechanisms and effects are not included), we can then estimate that 16\% of the implanted deuterium atoms are implanted in the range 0–19 nm, 31\% in the range 0–28 nm and 37\% in the range 0–31 nm. For the corresponding ranges, the total amount of vacancies created are, respectively, 37, 59 and 65\% of the total vacancies created. The lineal density of vacancies is the higher in the range 0–28 nm, being lower by 7.6\% in the 0–19 nm range and by 0.4\% in the 0–31 nm range.

We see that the Be implanted by D in the 90° geometry displays a Raman spectrum with a $E_{2G}$ mode downshifted by 5 cm\textsuperscript{-1} and with an additional broadening of 6.5 cm\textsuperscript{-1} compared to the pristine sample. The PDOS is present, with a relative height ratio of $H_{PDOS}/H_{Be}=3\%$. If we compare with the Be implanted by D in the 45° geometry, we see that the band corresponding to the $E_{2G}$ mode is downshifted by 5 cm\textsuperscript{-1}, with an additional broadening of 30 cm\textsuperscript{-1} compared to the pristine sample. The PDOS is rising, with a relative height ratio $H_{PDOS}/H_{Be}$ of 24\%. The band position is the same in the two implantation geometries. However, the bandwidth $\Gamma_{Be}$ is increased by a factor 2.7 and the PDOS relative height $H_{PDOS}/H_{Be}$ is increased by a factor 11 from the 90° to the 45° geometry. How these differences can be interpreted? According to SRIMS calculations in the subsurface slab going from 0 down to 31 nm, there are more defects (implanted D and vacancy) created in the 45° geometry than in the 90° geometry. Then, it explains why $H_{PDOS}/H_{Be}$ and $\Gamma_{Be}$ are higher in the first case than in the second.

3.2.2. Characterization of Be nanometric hydrides

By using energetic ions, and with the help of nuclear reaction analysis (NRA), AFM, optical microscopy and quantum calculations compared to Raman spectroscopy, we were able to evidence the formation of crystalline BeD\textsubscript{2} \cite{crystalline}. The spectra are typically close to the one found for BeH\textsubscript{2} in Ref. \cite{beh2} using high pressure to form them. It was shown previously that this latter technique is sensitive to the way hydrogen isotopes are bonded and organized in materials and thus that it can be relevant for fusion \cite{fusion} and might be of interest for hydrogen storage by forming hydrides \cite{storage}.

Figure 11 shows Raman imaging in the vicinity of a dendrite. In Figure 11(c), the intensities of the band at 1397 cm\textsuperscript{-1} due to a Be-D mode are displayed. It is more intense on the dendrite and less intense off the dendrite. The corresponding spectra are displayed in Figure 11(d). Details on how were obtained the spectra can be obtained in \cite{crystalline}. The bands marked by stars are due to Be-D bonds in BeD\textsubscript{2}. The fact that their corresponding intensity are higher are more intense on dendrite allows to conclude that the dendrites are made of BeD\textsubscript{2}. If the formation of such dendrites occurs in tokamaks, it could become a high fuel reservoir.

Figure 11(d) display the intensity of a mode found close to 1580 cm\textsuperscript{-1} and due to carbon contamination of the sample before it was bombarded (D and G bands in Figure 11(e)), and that has nothing to do with the experimental conditions.

\textsuperscript{2}This code is widely used to investigate ion-surface interaction phenomena. It is a free access Monte-Carlo computer program based on the binary collision approximation that do not take into account crystal structure or vacancy diffusion (i.e. each single collision event is treated independently between two steps).
3.2.3. Hydrogen behavior in tungsten oxide

Tungsten alone cannot be seen using standard Raman microscopy because there are no optical phonons that can be probed close to the center of the Brillouin zone. However, as oxygen is one of the impurities that can be found in tokamaks, and as the inner walls will be at temperatures ranging from few hundreds to 1000°C because of heat loads, it could be possible
that some oxide will be formed [99]. Then it would be of interest for the plasma-wall interaction community to take care of D and T behavior in tungsten oxides. Without entering into details, tungsten oxides can exist in various forms (dioxiﬁd, trioxide, in between stoichiometry), with many phase transitions that can be affected by nanosize effects [100] so that a systematic D implantation study could be helpful for the future. Today, only a few studies exist on the subject. In [93], we report on the formation of thin tungsten oxide layers that have been grown on W surfaces by thermal oxidation (thicknesses up to ~250 nm) and that have been exposed to low energy deuterium plasma (11 eV/D\textsuperscript{+}). Raman microscopy and X-ray diffraction show a nanocrystalline WO\textsubscript{3} monoclinic structure. We observed that the low-energy deuterium plasma exposure has induced a phase transition, a change in the sample color and the formation of tungsten bronze (D\textsubscript{x}WO\textsubscript{3}). After exposure under ambient conditions, a reversible deuterium retention, due to oxidation of the D\textsubscript{x}WO\textsubscript{3} layer, has been observed.

Figure 12 displays the effect of D implantation. The spectral range of tungsten trioxides can be roughly distributed in two kind of spectral regions: the bending modes region, lower than 500 cm\textsuperscript{-1} and the stretching modes region at higher wavenumbers. Before exposure, we can see the characteristic peaks of the monoclinic structure at 703 and 805 cm\textsuperscript{-1} which are attributed to symmetric and antisymmetric (O-W-O) stretching modes, respectively (see references in Ref. [93]). The wing in the range 920–970 cm\textsuperscript{-1} is attributed to terminal oxygen bonding in case of nanocrystalline structures, but other interpretations can be found in the literature that we do not review here. Due to implantation, all the peaks are broadened, the bending modes display bands that are more intense than stretching modes, which can be the sign of some disorder, and two new bands appeared: one at 950 and the other at 388 cm\textsuperscript{-1}. These bands disappeared with time once put in air due to reoxydation.

Figure 12. Raman spectra of bombarded WO\textsubscript{3}.
4. Discussion/conclusion

Because of safety issue, it is important to understand how and where tritium will be stored in tokamaks due to plasma-wall interaction. In this chapter, we have demonstrated the ability of Rama microscopy to detect and characterize material changes subsequently to interaction with hydrogen, for both carbon-based tokamaks and for ITER-like wall materials (tungsten that is oxidized and beryllium). The comparison between well-controlled samples and sample extracted from tokamak has been used to better characterize some of the tokamaks’ properties.

Among other findings, we report that by changing temperature on various carbon samples, extracted from tokamak (Tore Supra) or comparative reference laboratory samples (a-C:H) synthesized in controlled conditions, we have shown how Raman spectroscopic parameters can be used to characterize structural and H-content evolution/changes.

We also report that beryllium hydrides that can form high tritium reservoir in tokamaks can be formed and detected under ion implantation.

To conclude, next studies will have to use different laser wavelengths as they can be used to probe gradients of properties in the beryllium’s depth due to the fact the depth probed is in the range of few tens of nanometer. This is the typical depth at which a high content of hydrogen isotope is found in modern tokamak samples like JET. Future studies have to be driven with this technique to better characterize the so-called supersaturated layer.

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