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# Hydrogen storage in beryllium enhanced by nanocrystalline growth of BeD<sub>2</sub> under D implantation: Raman microscopy detection

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## Abstract

We report on a way to form nanometric height  $\text{BeD}_2$  crystal by means of beryllium sample exposed to energetic deuterium ions, which has a high potential of storing hydrogen isotopes. We focus on polycrystalline beryllium exposed to D ions at 2 keV/atom leading to laterally averaged deuterium areal densities up to  $3.5 \times 10^{17} \text{ D cm}^{-2}$ , determined by the  $\text{D}(^3\text{He,p})\text{He}$  nuclear reaction, Raman microscopy, atomic force microscopy, optical microscopy, and a vibrational mode analysis deduced from quantum calculations. For deuterium concentrations lower than  $1.5 \times 10^{17} \text{ D cm}^{-2}$ , we observe that incorporating D in the beryllium generates a tensile stress that reaches a plateau at  $1.5 \times 10^{17} \text{ D cm}^{-2}$ . For higher values than  $2.0 \times 10^{17} \text{ cm}^{-2}$ , we observe the growth of  $\approx 90 \text{ nm}$  high dendrites which can cover up to 10 % of the sample surface when the deuterium concentrations is  $3 \times 10^{17} \text{ D cm}^{-2}$ . These dendrites display the Raman spectrum of a  $\text{BeD}_2$  crystal. These structures are candidates to explain low temperature Thermal Desorption Spectroscopy peaks observed when bombarding Be samples with D ions with fluencies higher than  $1.2 \times 10^{17} \text{ D cm}^{-2}$ . This crystal growth observed on top of a bulk material can be used to produce nanometric powders that could be used in principle for storing hydrogen efficiently.

## 1. Introduction

Hydrogen isotope behavior in beryllium can concern plasma wall interactions in tokamaks [1] together with hydrogen storage in metallic hydrides [2].

Plasma wall interactions (erosion, retention, material modification, dust formation,...) occurring in tokamaks like the future ITER reactor (devoted to demonstrate the feasibility of obtaining energy from a magnetically confined D+T plasma) can lead to tritium retention, which is a major safety issue, due to its radioactivity [3, 4]. Hydrogen isotope retention in beryllium can also play a role in the life time estimation of the  $\approx 700 \text{ m}^2$  ITER's beryllium inner walls because of erosion [5]. This explains why several studies, based on technologies using ion beams, have been devoted to the study of the D behavior in beryllium. This was done to be predictive and ensure that hydrogen isotope retention will not be a limiting issue in ITER operations. For deuterium kinetic energies in the range 15-60 eV, a D/Be ratio up to 0.7 has been reached in forming co-deposited Be layers and by varying substrate temperature and deposition rate [6, 7]. Older data also focusing on co-deposits reported values in the range D/Be=0.1-0.4 [8-10]. Values in the range D/Be=0.2-0.4 have been measured under ion implantation of 20 keV/D with  $10^{19} \text{ D cm}^{-2}$  [11]. For 9 keV/D implantation, a storage of D as  $\text{D}_2$  molecules has been reported in bubbles tending to interconnect in the material [12]. Studies of 0.6 and 1 keV/D ions impinging on polycrystalline beryllium samples have shown that at fluencies  $\approx 2 \cdot 10^{17} \text{ cm}^{-2}$ , saturation of D content was shown to occur [13, 14], with a D/Be ratio in the range 0.2-0.3, close to values reported in [15]. The thermal desorption spectroscopy of such samples only displayed one  $\text{D}_2$  peak at 900 K for fluences lower than  $0.7 \cdot 10^{17} \text{ cm}^{-2}$ . A second peak was shown to appear at 750 K at a fluence of  $\approx 1 \cdot 10^{17} \text{ cm}^{-2}$ . Two additional peaks appeared between 450 and 500 K for fluences higher than  $1.2 \cdot 10^{17} \text{ cm}^{-2}$ , a structural modification being involved to explain their existence. A comparative study of thermal desorption of D implanted in Be samples with two different crystalline orientation and in a polycrystalline Be sample has been done, revealing the role

of both crystal orientation and D diffusion along grain boundaries under thermal annealing [16]. Except in [14] where it was suggested, it should be noted that none of all these studies reported the formation of beryllium hydride in the form  $\text{BeH}_2$ .

As shown above, many studies (mainly experimental) have been done mimicking future ITER materials to check hydrogen isotope retention issues. However, the presence of hydrogen in beryllium is a serious concern not only for safety issue reasons in ITER, but also in mobility purposes for hydrogen storage. To act efficiently as an energy carrier, hydrogen should be absorbed and desorbed easily in specific materials. Many of them are expected to fit more or less these two constraints [17, 18].  $\text{MgH}_2$  is the prototype of the metallic hydrides having an interesting gravimetric capacity (7.6 wt.%), but its decomposition temperature is too high compared to others [19]. Beryllium hydride,  $\text{BeH}_2$  being one of them, has been envisaged very recently, from a theoretical point of view, as a promising and more efficient hydrogen storage media than  $\text{MgH}_2$  [20]. It has been synthesized in the past in a crystalline form [21, 22], in an amorphous form [23], and transitions between crystalline and amorphous forms have been studied [24].

In this study we propose a way to form a  $\text{BeD}_2$  crystal (i.e.  $\text{D}/\text{Be}=2$ ) by using plasma irradiation, and a way to characterize it, by using nuclear reaction analysis (NRA), atomic force microscopy (AFM), optical microscopy, and quantum calculations compared to Raman microscopy. It was shown previously that this latter technique, as it is sensitive to the way atoms are bonded and organized in the material, can be able to detect and characterize the way hydrogen isotopes are bonded in materials relevant for both fusion applications [25] and for hydrogen storage [26]. This work is organized as follows: experimental and computational details are given in Section 2. Results obtained from the computational study are presented in Section 3. Results obtained from experimental measurements are presented in Section 4. A discussion highlighting the consistency of all our results is presented in Section 5. Conclusions are given in Section 6.

## 2. Experimental and computational details

### 2.1 Ion implantation and sample characterization

The experimental study focuses on a 1.5 cm diameter polycrystalline beryllium sample that has been bombarded by a relatively homogeneous beam of 6 keV  $D^{3+}$  (2 keV per deuterium) at a fluence of  $1.9 \cdot 10^{17} \text{ D cm}^{-2}$ . At the center of the sample, roughly 30% of the samples surface contains  $1.0 \cdot 10^{17}$  deuterium atoms. On the other parts of the sample, the number of implanted deuterium atoms decreases rapidly down to  $\approx 0$  at the edges. Sample implantation and in situ ion-beam analysis are performed in the ultra high vacuum experiment ARTOSS [27]. Detailed information on experimental setup, sample and procedure are published elsewhere [28]. In brief, a polycrystalline Be sample is cleaned by cyclic sputtering with  $Ar^+$  ions and subsequent annealing to 1000 K. This sample is exposed to a mass separated beam of  $D_3^+$  ions at 2 keV/D with a fluence of  $1.9 \cdot 10^{17} \text{ D cm}^{-2}$  in the central area of  $5 \cdot 8 \text{ mm}^2$ . The amount of deuterium trapped is measured on several locations of the sample surface by means of the  $D(^3\text{He},p)\text{He}$  nuclear reaction with a lateral resolution on the order of 1 mm. Raman spectra were also recorded in the vicinity of some of these regions and some spectra are given in Figure 5. The numbers given in that figure, and referred to as  $N_D$  later in the text and figures, are the absolute numbers of implanted D atoms measured by means of this nuclear reaction. For comparison with results from the literature we give  $N_D$  in deuterium per  $\text{cm}^2$ .

Raman spectra were recorded on several locations of the sample, using a Horiba-Jobin-Yvon HR LabRAM apparatus (with x100 objective, with a numerical aperture of 0.9) in the backscattering geometry.  $\lambda_L = 514.5$  and  $632.8 \text{ nm}$  were used. The laser power was kept at  $\sim 1 \text{ mW } \mu\text{m}^{-2}$  to prevent damages. Spectra were recorded with various exposure times to check that samples do not evolve under laser irradiation. We also used, when indicated in the text, the Raman imaging mode. It consists in moving the sample under the laser beam by  $0.5 \mu\text{m}$  steps, and recording spectra at all the locations probed. Optical images obtained with the 100x objective used for making Raman spectra

were recorded on several locations and some images were thresholded and binarized to determine the surface coverage of structures detailed below. Atomic force microscopy (AFM) was performed on some zones of the sample using the tapping mode of an AFM-NTMDT solver. The tip radius was smaller than 10 nm, the vertical and horizontal resolutions were  $\approx 1$  nm and  $\approx 10$  nm, respectively.

## 2.2 Computational details

The calculations were performed within the framework of the spin-polarized gradient-corrected density functional theory (DFT) using the Perdew-Burke-Ernzerhof functionals (PBE [29]) and including a semi-empirical pairwise London damped dispersion correction (PBE-D2 [30, 31]). A plane-wave basis set was used with kinetic energy cutoff for wavefunctions of 70 Rydberg (952 eV). The calculations were carried on using the *Quantum-Espresso* suite [32]. The Vanderbilt ultrasoft pseudo potentials are taken from the GBRV database [33], all the electrons are included in the DFT calculation i.e. one  $e^-$  for H and 4  $e^-$  for Be, this justifies the large energy cutoff. Using this parameterization for linear  $\text{BeH}_2$  molecule placed in a cubic box yields the Be-H bond of 1.340 Å, that is in good agreement with the experimental data (1.332 to 1.342 Å [34]). The associated vibrational frequencies are 707.8, 1990.6 and 2225.9  $\text{cm}^{-1}$ , in very good agreement with the Spectroscopic constants determined using the potential energy surfaces calculated at various many body Coupled Cluster quantum methods and extended Gaussian basis sets of orbitals [CCSD(T) / *ccpVnZ*] [35], 713.41, 1984.77 (Raman active) and 2170.62  $\text{cm}^{-1}$ . Note that the calculated vibrational frequencies in figures 1, top of figure 2 and figure 4, are only a representation of the calculated vibrational modes dressed with Gaussian functions of 20  $\text{cm}^{-1}$  half-width, the height of the peak being proportional to the number of frequencies in this interval. They cannot be compared directly to Raman spectrum because of selection rules that can extinguish some modes and have not been taken into account here (except for the bottom of figure 2).

The calculated lattice parameter for the hexagonal beryllium crystal (two atoms per cell)  $a$  is 2.275 Å in very good agreement with the experimental value 2.29 Å and better than other GGA published ones 2.26 Å [36] and also our previous results [37]. The difference is that in [37] the London correction was not taken into account, this interaction is responsible for the shorter distance calculated between the metal basal planes. This inconvenient is counterbalanced by a better representation of the elasticity of the material. The elastic properties are tested calculating the bulk modulus and it was found that the full electron calculation yields more accurate results than in [37],  $B^0 = 120$  GPa (Exp: 110 ~127 GPa), this indicates that the crystal response to the stress produced by an increase of pressure will be well represented by the PBE-D2 model. The photon spectrum at the (0,0,0) point of the Brillouin zone gives 469.15, 469.17 and 723.85  $\text{cm}^{-1}$ , the discrepancy with experiment is no more than 7 % [38].

However, studying trapping of deuterium atoms in beryllium requires a larger working system, the 2x2x2 multiple cell (2 Be atoms per cell, i. e. 16 Be atoms in total) proved adapted to this task, we use this cell in the next part.

### 3. Computational studies

In this section we obtain phonon spectra of a linear molecule trapped in a Be crystal. We then do the same with a bent molecule and continue by increasing the number of trapped deuterium atoms up to the  $\text{BeD}_2$  stoichiometry ( $\text{D}/\text{Be}=2$ ). Position of Be atoms are not relaxed and phonon spectra are calculated under this assumption. We finally investigate the influence of taking into account relaxation (volume increase) on the phonon spectra, on two selected examples.

First, we start by trapping a linear  $\text{BeD}_2$  molecule in the Be crystal, which will mimic low D concentrations in the material, and in order to highlight environmental effects on vibrational frequencies. The substrate structure being hexagonal, all the interstitial sites are not equivalent and the linear  $\text{BeD}_2$  molecule orients itself such that one deuterium is close to a hcp site and the other

one to the fcc site. Therefore, the molecule is not anymore strictly linear, but makes an angle of  $169^\circ$  whereas the Be-D distances are markedly longer than in the isolated molecule, with respectively 1.44 and 1.51 Å. As a result the phonon spectrum of the molecule in the crystal is significantly modified compared to the molecule in gas phase, as shown in Figure 1. The most remarkable effect of the beryllium crystal field on the trapped linear molecule is the downward shift of the stretching modes from 1408.1 and 1711.6  $\text{cm}^{-1}$  to 1210 and 1060  $\text{cm}^{-1}$ , respectively. The bending mode is split into two components, both shifted towards the higher frequency domain, 755 and 850  $\text{cm}^{-1}$ , instead of 540  $\text{cm}^{-1}$  for the gas phase linear molecule.

Second, we continue by trapping a bent molecule, which is slightly less stable than the quasi linear molecule (0.1 eV, see [37]). The D-Be-D angle is now  $70.7^\circ$  and the bond distances being 1.51 and 1.61 Å. The phonon spectrum is different than in the case of the trapped quasi linear molecule. Compared to it, one of the two components (the higher in frequency in figure 1) is hardly affected, it corresponds to the shorter Be-D distance. The main components of the bending modes are unaffected, but a new doublet appears at 627 and 653  $\text{cm}^{-1}$ . Distinguishing low amounts of hydrogen in beryllium crystal and the way hydrogen is bonded can in principle be done by measuring frequency shifts.

Third, we continue trapping the deuterium atoms by increasing progressively the D/Be ratio, up to 2 ( $\text{BeD}_2$ ). Increasing D concentration produces the progressive enlargement of the interval spectrum and the shift of the higher peak from 1200  $\text{cm}^{-1}$  for the trapped quasi-linear  $\text{BeD}_2$  molecule to 1580  $\text{cm}^{-1}$  (D/Be = 1), as can be seen in figure 2. This wavenumber is similar in magnitude to that of the free molecule, although smaller. The lower part of the frequency distribution is also analogous to that of the gas phase, 590  $\text{cm}^{-1}$  compared to 546  $\text{cm}^{-1}$ .

Finally, while increasing the deuterium concentration it becomes harder to discriminate between linear or bent  $\text{BeD}_2$ . From the already published paper [37] it is known that the  $\text{BeD}_n$  groups tends to adopt a tetrahedral-like structure, as expected from a second-row element such as beryllium. In fact the tetrahedral organization is detectable in the crystal structure of beryllium

dihydride [39, 40] and the corresponding frequency distribution (taking into account the Raman activity) is shown in the lower part of Figure 2. The progression towards the pyramidal structure is revealed in Fig.3-a: the mono-hydride structure ( $D/Be = 1$ ) is obviously completely disordered, whereas the amorphous dihydride ( $D/Be = 2$ ) displays two main peaks where only two types of D-Be-D angles are observed, at  $96^\circ$  and  $116^\circ$  (the perfect tetrahedral angle being  $109.5^\circ$ ). Nevertheless, the Be-D distances show a broader range of distribution (Fig.3-b). Amorphous  $BeD_2$  should tend towards the crystal with a unique Be-D distance of  $1.41 \text{ \AA}$ . The reason it does not occur is that the cell parameters are kept unchanged for all the models of deuterium trapping in amorphous solids presented above. Actually, the beryllium Bravais lattice is hexagonal and the beryllium dihydride one is orthorhombic; for a high deuterium concentration, the internal constraints must induce a great stress inside the crystal cell and then the probability of a phase transition must be considered. For this purpose the working cell parameters have been relaxed for some deuterium concentrations and at normal pressure (1 bar). The resulting swelling is shown on phonon spectrum, displayed for two  $D/Be$  ratios in figure 4. The cell relaxation produces the enlargement of the spectral window, with emergence of new low frequencies. Note that the largest frequencies disappear. Therefore high frequencies without low frequencies in spectra must be considered as the signature of highly constrained structures.

#### 4. Experimental studies

The influence of the number of implanted D atoms on the pristine material can be seen in Figure 5-a, which displays the spectral window where the beryllium stretching mode lies. The band, at  $459 \text{ cm}^{-1}$  for the pristine sample, downshifts and broadens when  $N_D$  increases. This is usually interpreted as due to the creation of defects in the material induced by ion implantation. However, as it is known that Be-D bonds can be formed easily when D is implanted into a beryllium crystal, and that this results in a volume increase per beryllium atom [37], one can conclude, according to [41],

that this downshift is induced by tensile stress in the material, exactly what is expected theoretically (see part III of this work). Note that a study of the effect of external compressive stress on a beryllium crystal has reported the upshift and the broadening of the band related to the beryllium stretching mode with the pressure increase [42]. Figure 5-b displays the 200-1800  $\text{cm}^{-1}$  spectral window, with a zoom on the vertical axis. Contrary to what is expected by the Raman selection rules of a perfect Be crystal, which predict only the beryllium stretching mode to be active (found at 459  $\text{cm}^{-1}$  in our study), the spectrum of the pristine sample is not flat elsewhere, especially in the 750-1100  $\text{cm}^{-1}$  region where large bumps are clearly seen. We do not want to interpret in details their origin here but we can notice that it is not related to the presence of D in the material, as they are also displayed in the D free spectrum, nor to the presence of a surface oxide layer because it does not fit with the 338, 684, 1082  $\text{cm}^{-1}$  frequencies reported for BeO [43]. When increasing  $N_D$ , several bands appear at 255, 278, 617, 907, 1397,  $\approx 1420$ , 1696, 1724  $\text{cm}^{-1}$ . Most of these bands have their wavenumbers close to the one calculated for the  $\text{BeD}_2$  crystal. It proves first that these bands are due to a Be-D bond, second: the D/Be ratio should be close to 2, and third: the material probed is crystalline, as the experimental and calculated spectra are very similar. Another argument suggests that it is crystalline: the full-widths-at-half-maximum (FWHM) of the Raman bands are close to 10  $\text{cm}^{-1}$ , contrary to what is generally measured for amorphous beryllium hydride (generally hundreds of  $\text{cm}^{-1}$ ) [44]. The intensities of these bands seem to be related to the amount of D trapped in the material as they increase with  $N_D$ .

Having a crystalline structure subsequently to a high fluence implantation is counterintuitive and needs to have a closer insight. Figure 6 shows a survey of the surface morphology at different locations of the sample, obtained by means of optical microscopy. In that figure we display some images showing that in zones where  $N_D < 1.5 \cdot 10^{17} \text{ D cm}^{-2}$ , some dark spots can be evidenced, their concentration depending on  $N_D$ . In zones where  $N_D > 1.5 \cdot 10^{17} \text{ D cm}^{-2}$  dendrites appear together with the already existing dark spots. The dendrite shape, contrast, size and concentration vary depending

on  $N_D$ , too. For example, low contrast dendrites in Figure 6-d seems to be composed of disconnected 1-2  $\mu\text{m}$  size branches, whereas high contrast dendrites in Figure 6-g are composed of 5 (or more)  $\mu\text{m}$  size interconnected branches. Figures 7-a and 7-b show height measurements of these structures, such as those found in Figures 6-d and 6-g, by means of AFM. It appears more clearly than in the optical microscope images that the dendrites coexist with circular domes, the latter being the dark spots visible in Figure 6. From that we can conclude that domes appear at lower deuterium  $N_D$  than dendrites. Dendrite heights are in the range 50-200 nm, whereas domes are smaller. These two kinds of structures are clearly distinguishable in Figure 7-a, where dendrites appear dense and bulky and domes are regularly distributed on the surface. These two kinds of structures are not so clearly distinguishable in Figure 7-b where dendrites appear sparsely connected, and domes are not distributed regularly, as if they were constituting units of the nascent dendrites.

Figure 8 shows a closer look on the domes (Figure 8-a) and dendrites (Figure 8-b) by means of AFM. The domes are smoother than the dendrites, the latter can even be composed of two collinear branches. This observation suggests that dendrites are more complex objects than domes. Figure 8-c and 8-d display some dome and dendrite profiles, respectively. The larger heights can be as high as 75 and 160 nm for domes and dendrites, respectively. The dome average profiles exhibit a parabolic average shape with a 50 nm height and 600 nm base. The average profiles of the dendrites are more rectangular with a 90 nm height and a 1  $\mu\text{m}$  base. The rectangularity is just the consequence of summing up single and double dendrite branches, and do not reflect the shape of single dendrite profiles, but it is useful for mean height estimation on all the sample.

Figure 9 shows Raman imaging in the vicinity of a dendrite, in the zone of the sample where  $N_D=3 \cdot 10^{17} \text{ D cm}^{-2}$ . In Figures 9-c and 9-d the intensities of the band close to  $459 \text{ cm}^{-1}$  due to the Be stretching mode, and the band at  $1397 \text{ cm}^{-1}$  due to a Be-D mode are displayed, respectively. These two bands are more intense on the dendrite than off the dendrite. In Figure 9-e, we compare the spectra on and off dendrite. These two spectra have been obtained by summing all the spectra over the two areas and normalizing to the band at  $459 \text{ cm}^{-1}$ , the threshold distinguishing between on and

off dendrite being fixed at a value of 100 in the Figure 9-c map. The 5 bands identified in Figure 5-b (and pointed by a star in Figure 9) as due to Be-D modes in a BeD<sub>2</sub> crystal are much more intense on dendrites than off dendrites. The spatial correlation between the dendrites and the BeD<sub>2</sub> Raman signature allows us to conclude that the dendrites, formed under ion bombardment, are a high reservoir of trapped deuterium.

Figure 10 displays the evolution with  $N_D$  of two spectroscopic parameters related to the Be stretching mode (wavenumber,  $\nu$ , and FWHM) and compared to the dendrite surface coverage (obtained by thresholding + binarizing  $\approx 4500 \mu\text{m}^2$  optical images, as shown in the Figure 10-c insert). From 0 to  $1.5 \cdot 10^{17} \text{ D cm}^{-2}$ ,  $\nu$  decreases linearly by  $\approx 3 \text{ cm}^{-1}$  and the FWHM increases linearly by  $\approx 6 \text{ cm}^{-1}$ , for both laser wavelengths used. In this interval, the dendrite coverage is close to zero, meaning that most of D atoms are implanted in a  $\approx 50 \text{ nm}$  depth layer, according to the implantation depth profile calculated using SRIM [45] (given in the insert of Figure 10), a free access Monte Carlo computer program based on the binary collision approximation. For  $N_D = 1.5 \cdot 10^{17} \text{ D cm}^{-2}$ , and taking into account the  $\approx 50 \text{ nm}$  of implantation depth, it gives a value  $D/\text{Be} \approx 0.24$ , which is compatible with what was previously measured [14]. For  $N_D > 1.5 \cdot 10^{17} \text{ D cm}^{-2}$ ,  $\nu$  and FWHM both reach a plateau. The dendrite coverage starts to increase linearly from  $\approx 0$  at  $N_D \approx 2 \cdot 10^{17} \text{ D cm}^{-2}$  and reaches up to 10% close to  $3 \cdot 10^{17} \text{ D cm}^{-2}$ , without tendency for saturation in our experimental conditions. Note that the values of  $\nu$  and FWHM recorded using the 632.8 nm laser are slightly lower than the one recorded using the 514.5 nm laser. This may be due to a resonance effect, as suggested previously in [42] and references therein, to explain the slight discrepancies found in the literature.

## 5. Discussion

The comparison of vibrational spectra obtained from quantum calculations of amorphous and crystalline Be containing D, and Raman spectra obtained for the dendrites formed on the D implanted Be sample indicates that the D/Be ratio in dendrites is close to 2 and the structure is

probably crystalline and not amorphous. On the zone of the sample where 10% of the surface is covered by dendrites, the number of D retained in such structures is  $N = (3 \cdot 10^{17} - 2 \cdot 10^{17} \text{D cm}^{-2}) = 1 \cdot 10^{17} \text{D cm}^{-2}$ . Knowing that dendrites are 90 nm in height and cover 10 % of the surface, the density, expressed in  $\text{g cm}^{-3}$ , is:

$$\rho = (N \times (2 + 9/x)) / (5.4 \times 10^{15})$$

where  $x = \text{D/Be}$ . Assuming a density of  $1.23 \text{ g cm}^{-3}$ , obtained from quantum calculations for the  $\text{BeD}_2$  crystal (see Table 1),  $x$  is found equal to 2.1, confirming in very good agreement the assumption of the crystalline structure suggested by the comparison of calculated and measured spectra.

Knowing first that dendrites appear when  $N_D$  is higher than  $2 \cdot 10^{17} \text{D cm}^{-2}$ , and second that the 450 and 500 K TDS peaks of [13, 14] (with samples implanted in similar conditions than ours) which appear for fluences higher than  $1.2 \cdot 10^{17} \text{D cm}^{-2}$ , we propose that the two peaks result from the thermal degradation of dendrites.

The formation of circular domes and dendrites is reported here, but not fully explained. We only suggest that increasing tensile stress in the material (suggested by both Raman measurements and quantum calculations) due to volume increase subsequently to Be-D bond creation may play a role in the formation of the  $\text{BeD}_2$  crystal. It is also evident that the impinging ion kinetic energy, tuning the implantation depth in the material, is a key parameter in creating this stress, similarly to what was found on bombarded graphite: the height of nanometer sized domes was observed to increase when a higher amount of underlying amorphous carbon (generating stress) was created, using higher implantation energies [46]. In the literature, other structures have been obtained on Be samples after irradiation: cone-like shapes under plasma exposures in the PISCES-B plasma facility [47], interconnected labyrinths with hydrogen bubbles at higher energies [48]. In ITER, only taking into account the charge exchange process leads to anticipate at least a homogeneous  $4 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$  flux bombarding the Be walls [49]. Extrapolating our result to this flux, we guess that the initial Be surface state in ITER will be completely transformed in a rough surface in only few seconds.

These surface modifications under bombardment can significantly influence the local sputtering yield [50], which is of importance for extrapolating the lifetime of the future ITER reactor beryllium walls, future work should focus on the understanding of formation mechanisms leading to these structures (and for example explaining the route leading from dome formation to dendrite formation). However, to our knowledge the observation of such dendrites was not yet reported in the JET tokamak with ITER-like wall configuration where such fluences can be found.

The eventual role of particle (sputtered Be, hydrogen,...) mobility on the surface may also be considered for explaining these dendrites formation in the framework of the diffusion limited aggregation model [51]. Stability of the sample after being placed in air for several months (time spent between the different analyses) should also be addressed.

In parallel, but for hydrogen storage purposes, ion assisted techniques should be used, systematically varying the relevant parameters, to optimize the volume of BeD<sub>2</sub> formed, to increase the possibility of storing hydrogen isotope in beryllium.

## 6. Conclusion

After deuterium ion irradiation of a polycrystalline beryllium target (2 keV/D), we have shown that deuterium is trapped up to a saturation value of  $D/Be \approx 0.24$  when  $N_D = 1.5 \cdot 10^{17} \text{ D cm}^{-2}$ , with an increasing tensile stress developing inside the material, and saturating at this  $N_D$  value. For higher  $N_D$  values, we have observed that a higher amount of D can be trapped in dendritic structures that start to grow at  $N_D = 2.0 \cdot 10^{17} \text{ D cm}^{-2}$  and cover for example 10% of the surface when  $N_D = 3 \cdot 10^{17} \text{ D cm}^{-2}$ . By using a multi-technique approach (nuclear reaction analysis, atomic force microscopy, optical microscopy, and quantum calculations compared together with Raman microscopy), we conclude that these dendrites are crystalline and composed of BeD<sub>2</sub>. These structures can be suitable

for storing hydrogen. As they might play a role in hydrogen isotope retention, future experiments should be devoted to search for such dendrites in the JET tokamak, or in the future ITER tokamak.

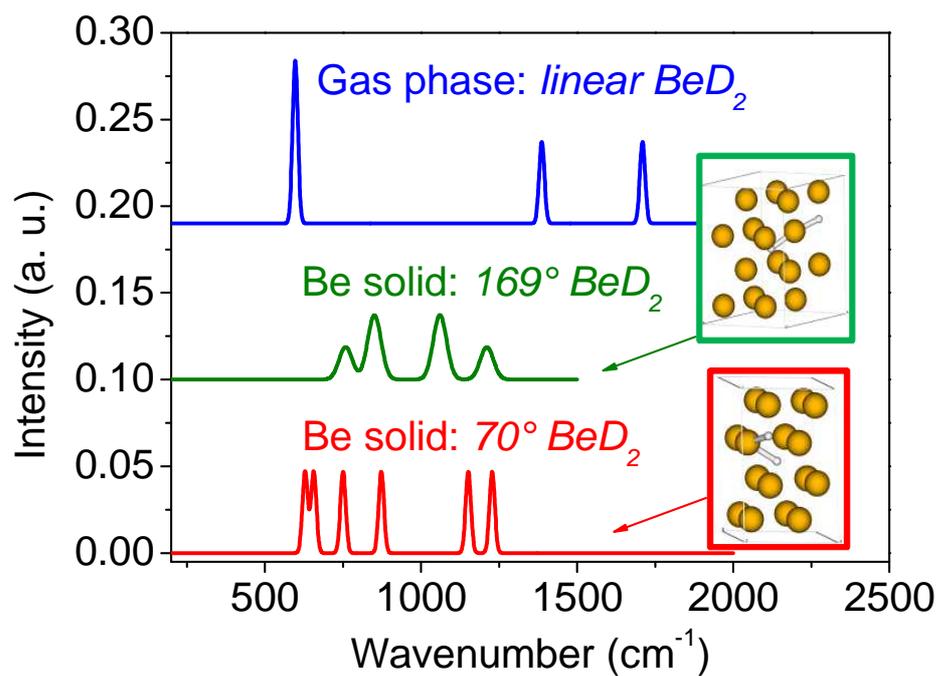


Figure 1. Calculated vibrational frequencies obtained in dressing the numerical values by a Gaussian function of the BeD<sub>2</sub> molecule in beryllium and in gas phase (same convention in Figures 2 and 4).

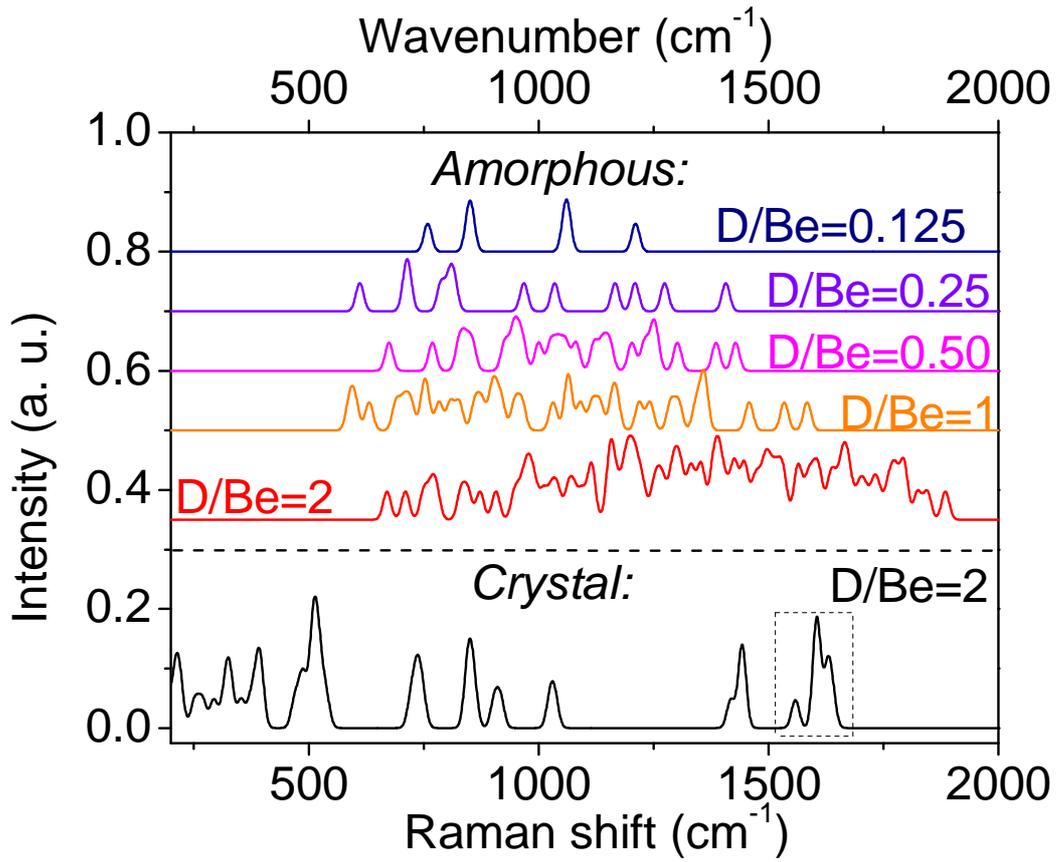


Figure 2. Vibrational frequencies associated to deuterium trapping in the beryllium crystal as a function of the deuterium concentration (D/Be atomic ratio), only the modes involving D are represented. In the lower part of the figure the calculated full beryllium hydride crystal Raman active frequencies are shown.

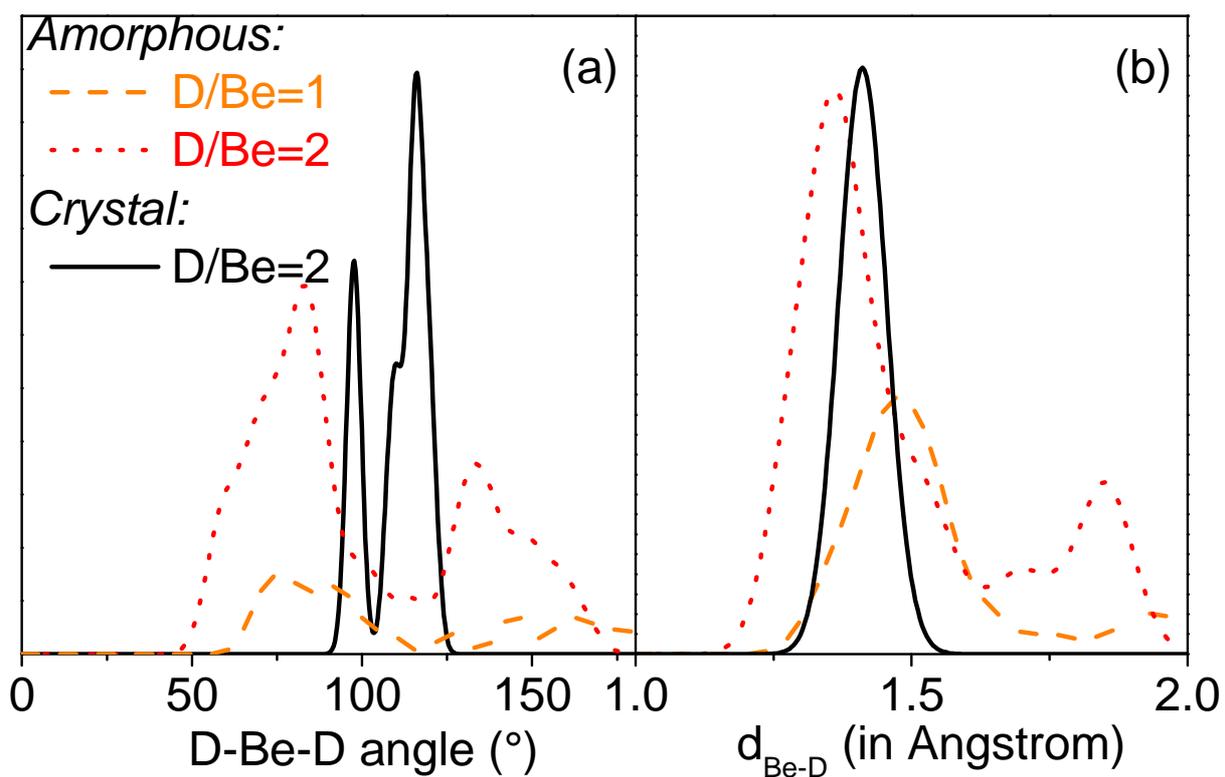


Figure 3. Beryllium hydride structure evolution towards a tetrahedral beryllium one, comparison with the beryllium hydride crystal. (a) Angular distribution in amorphous and ordered beryllium hydrides. (b) Be-D length distribution in amorphous and organized beryllium hydrides. Only the Be-D distances shorter than 2 Å are considered.

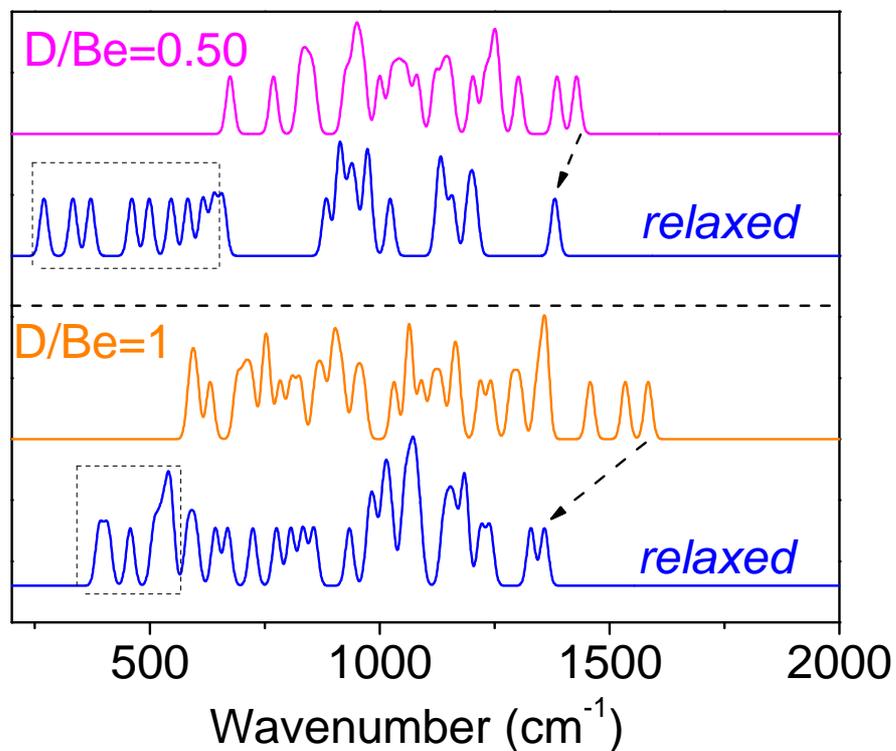


Figure 4. Vibrational frequencies for the ratio D/Be= 0.5 (a) and 1.0 (b) after cell parameter relaxation, compared to the original beryllium cell.

D/Be		Density (g.cm <sup>-3</sup> )
Amorphous	0	1.95
	0.5	1.77
	1	1.58
	2	1.33
Crystal	2	1.23

Table 1. Volume and density evolution as a function of deuterium concentration at the pressure of 1 atmosphere.

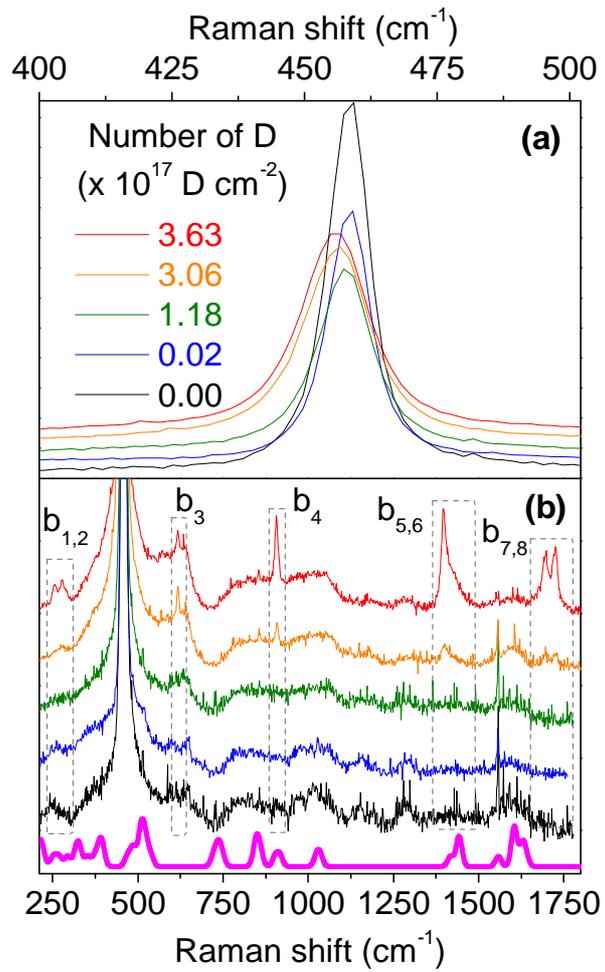


Figure 5. Raman spectra of deuterium implanted beryllium. (a) Beryllium stretching mode spectral window. (b) Beryllium deuteride spectral window. The lowest Raman spectrum is the calculated BeH<sub>2</sub> crystal BeH. For each spectrum, the colors indicate the D areal densities.

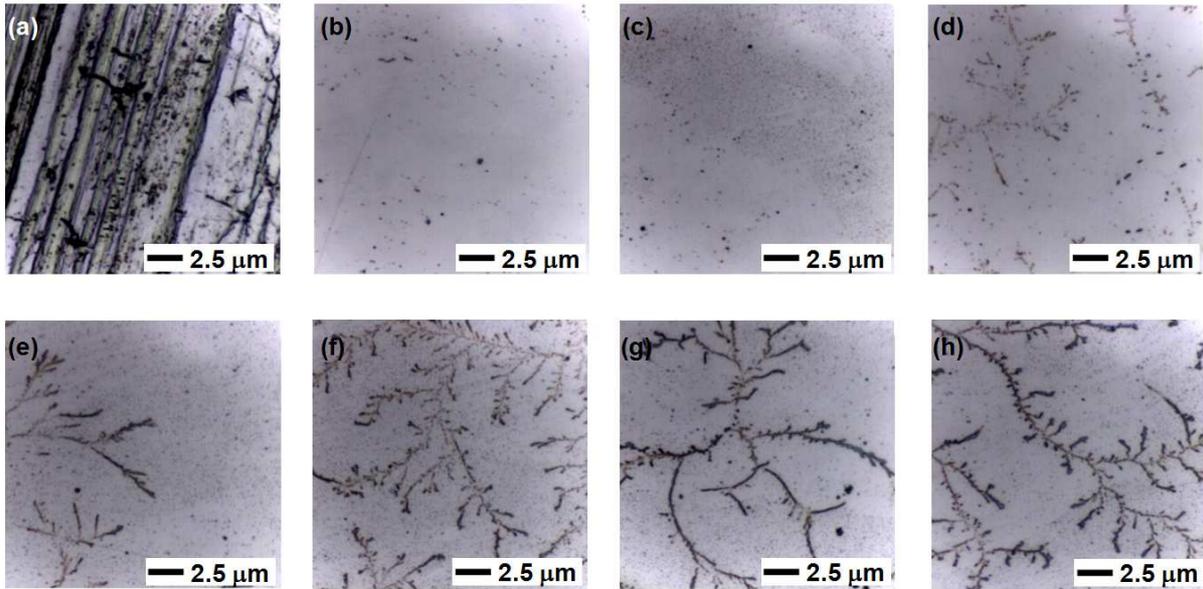


Figure 6. Optical microscope images of various regions on a deuterium-implanted beryllium sample.

(a) Pristine. (b) and (c) In zones of the sample where  $N_D < 2.0 \cdot 10^{17} \text{ D cm}^{-2}$ . (d) to (g) In zones of the sample where  $N_D > 2.0 \cdot 10^{17} \text{ D cm}^{-2}$ .

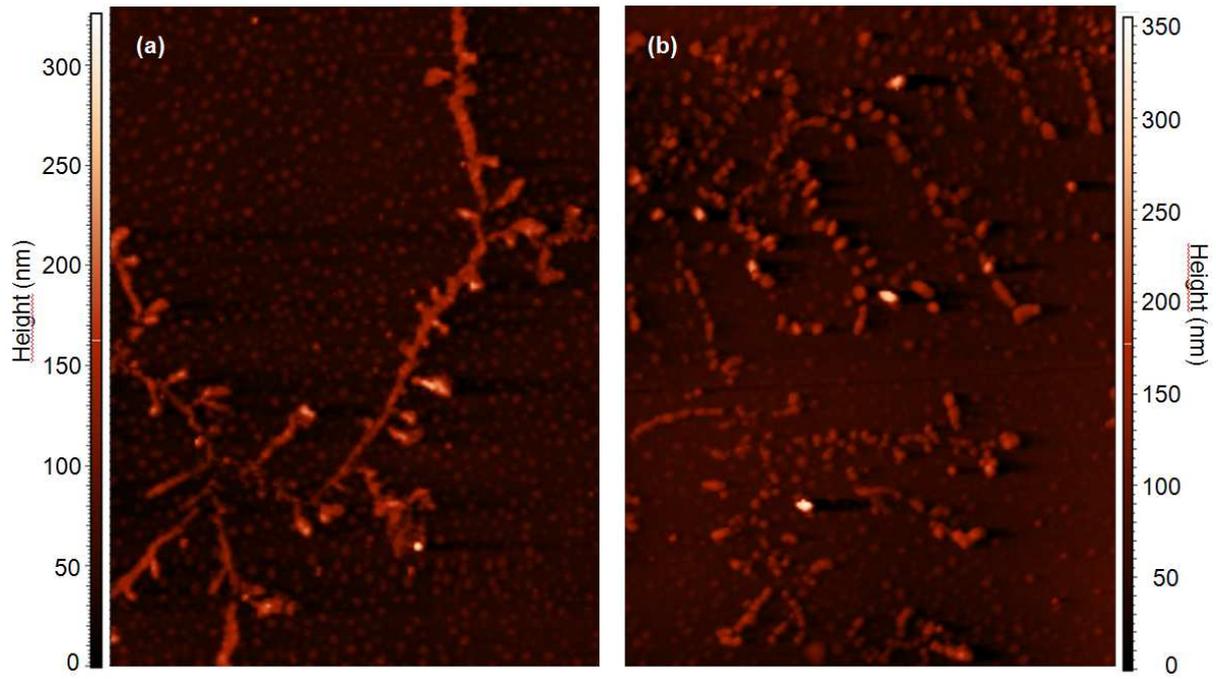


Figure 7. Height of the deuterium implanted sample in zones containing  $N_D > 2.0 \cdot 10^{17} \text{ cm}^{-2}$ , obtained by AFM. (a) and (b) represent typical morphologies found in that zone.

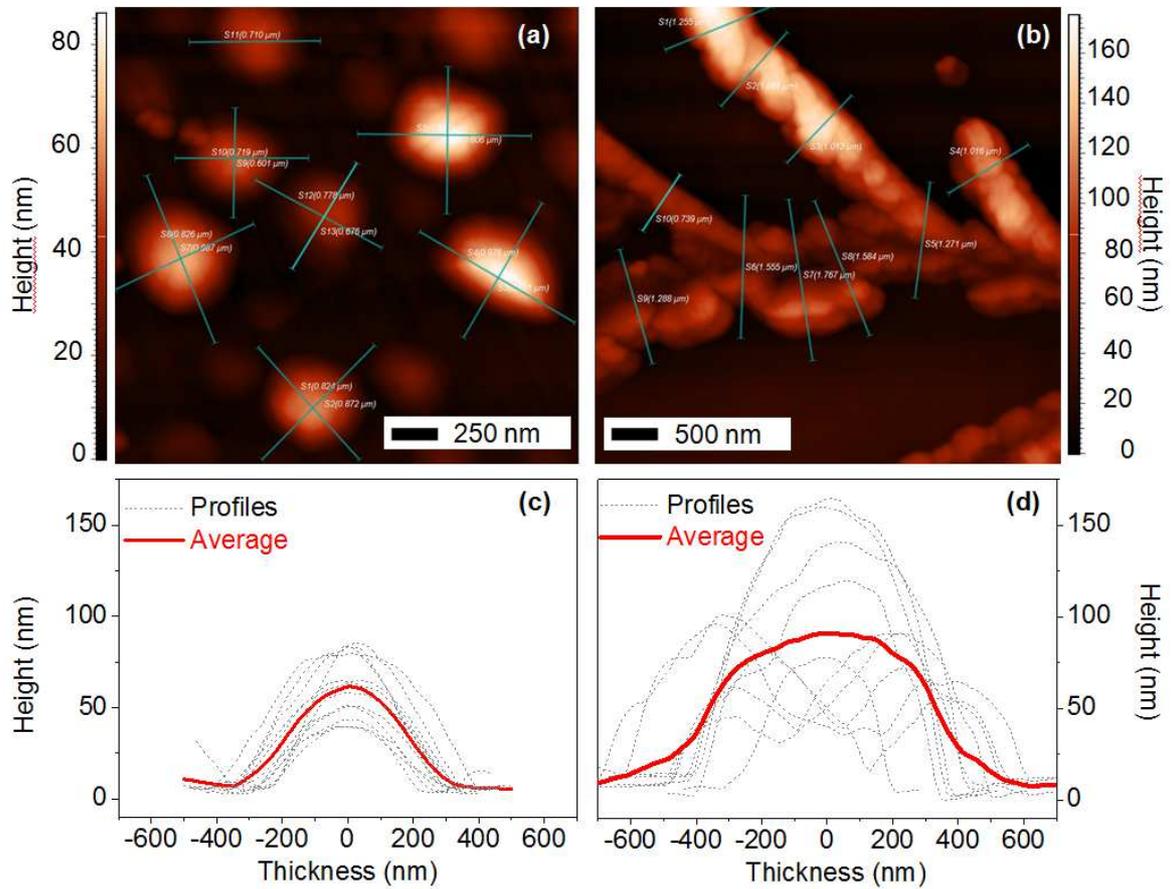


Figure 8. Height profile analysis of the domes and dendrites. (a) and (b) are AFM images representing the height of domes and dendrites. (c) and (d) show profiles extracted from (a) and (b) respectively.

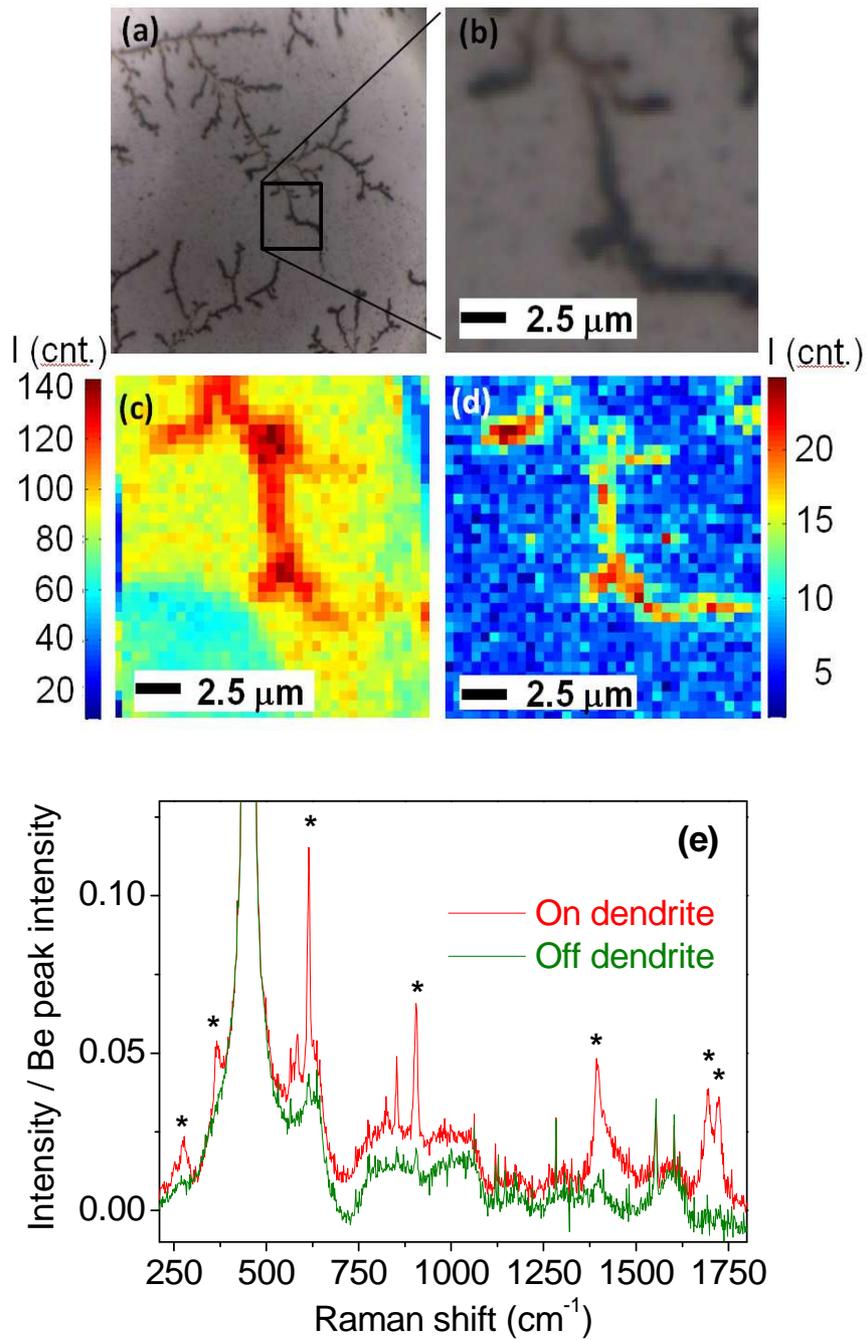


Figure 9. Raman imaging in the vicinity of a dendrite. (a, b) optical microscope images. (c) Intensity of the band corresponding to the Be stretching mode. (d) Intensity of the band corresponding to the mode lying at  $1397\text{ cm}^{-1}$ , in the same intensity unit as in (c). The zone on the sample corresponds to  $N_D=3 \cdot 10^{17}\text{ D cm}^{-2}$ . (e) Comparison of on-dendrite and off-dendrite Raman spectra. Spectra were summed over the two areas and are then normalized to the beryllium band, fixed at a value of 1. The threshold for distinguishing if a zone is on or off dendrite was fixed at a value of 100 in Figure 9-c.

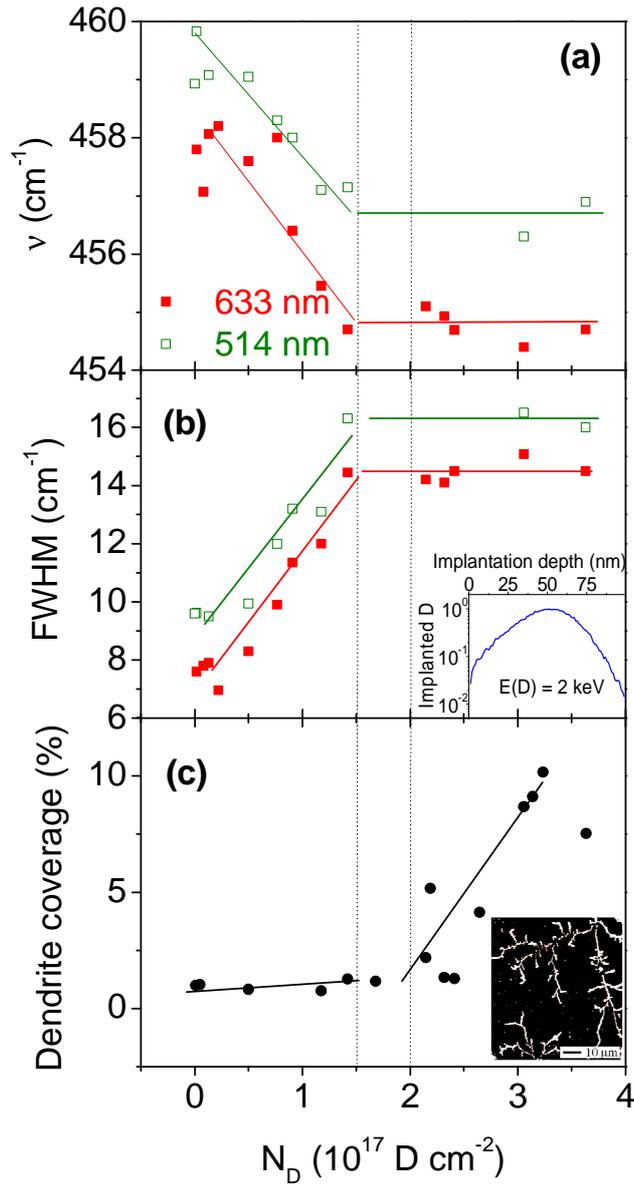


Figure 10. Evolution of Raman parameters and dendrite surface coverage versus the quantity of implanted deuterium. (a) and (b) Be stretching mode band center and full-width-at-half-maximum, respectively. (c) Surface coverage of the dendrites retrieved by optical microscopy.

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