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Tritium retention: Synthesis of beryllium hydrides in chemical sputtering by deuterium from 20 to 420 eV

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Keywords

beryllium hydride, tritium retention, low energy sputtering, chemical sputtering, BeD, thermonuclear fusion, co-deposition

Contents

1 Abstract

This work describes the formation of beryllium hydrides in collisions of deuterium ions with a beryllium surface. These chemical sputtering products have been experimentally resolved by mass spectrometry. In the manifold of products, beryllium hydride is of special interest as a candidate for tritium retention in thermonuclear fusion devices. Our experiments show, that it can be synthesized in nearly all conditions comparable to plasma and wall temperature, with two mechanisms involved: First, BeD^+ is formed directly in a reaction of the D_2^+ molecules with the bulk beryllium surface, which is the main aspect of this work. Focusing on Be^+, BeH^+ and BeD^+ products, their dependence on different parameters is measured: Scanning the impact energy from 20 to 426 eV reveals that the molecular BeD^+ is preferably produced at low energies. Surprisingly its yield is three times higher than that of pure Be^+ at 20 eV. When the surface temperature is raises from 298 to 673 K, sputtering yields increase two orders of magnitude for both, Be^+ and BeD^+. The second reaction pathway produces BeH^+. It is efficiently synthesized from water vapor adsorbed on the surface, much less abundant from hexane and hydrogen adsorbates. In general, such surface experiments are very challenging and great care has been taken to rule out experimental concerns systematically, using the measurements above in combination with an element composition profile of the beryllium sample.

2 Introduction

Hydrogen and its isotopes can be trapped in bulk material. In the context of fusion devices like ITER, JET or many more, this is commonly called “tritium retention”. The radioactivity of tritium then poses a security threat, as in an accident this tritium might be released into the environment. As an example, for ITER, the maximum tritium inventory may not exceed 0.7 kg [1]. Therefore, operating intervals between cleaning interruptions are limited. Estimates are between two months [2] and only one week [3], they still have “extremely large uncertainties” [2]. In this sense tritium retention could make thermonuclear fusion unfeasible in a commercial implementation.

There is strong evidence that most of the tritium is retained in the divertor region of fusion devices [1], [2], [4]. Above the bulk tungsten, a thin film (e.g. 40 µm in JET ILW [1]) of co-deposition between tritium and beryllium was found. So the beryllium starts in the upper parts

of the vessel (PFC in the blanket), in a region of net-erosion by the plasma wall interaction and forms some sort of compound with tritium as it migrates towards the divertor. This happens in a series of deposition and re-emission cycles, until it finally ends up in the vacuum pumping system, or in a "cold" region of net-growth in the divertor. It is not clear, where this compound is formed (gas phase / surface), nor, if it is a rather physical or chemical process.

Our measurements show, that, at least partly, this compound consists of molecules, directly formed in the sputter process on the surface. We cannot provide a quantitative analysis of their relevance for fusion devices. This is the domain of tailored simulations that make use of our data. Experimentally, we find BeD^+ and BeH^+, pointing towards charged and neutral BeT. Indeed, BeD was found in the co-deposition layer in question [5] in the PISCES-B experiment [6]. There, the source of the BeD molecules remains quite unclear and is argued to be a gas-phase reaction. By assuming a much lower kinetic energy of BeD relative to the surface in comparison with Be, their intensity profiles at a given target distance should be different when BeD is produced on the surface [7], but this is not the case. At least for the ionic fraction, however, we have measured that the kinetic energy of BeD^+ and Be^+ is the same (at a given projectile energy), simply by varying the surface potential. Thus, the gas phase justification described above does not hold for at least the ionic fraction. Additionally, an ion-surface interaction is conceptually more likely for the pressures present in fusion devices.

At first glance, molecule formation seems not to be important for a plasma device, as any molecule that is emitted deep into the plasma will immediately fragment. But the same is true for any process that could create the co-deposited material in question, so today molecules are seen as a substantial challenge for plasma wall interactions [8]. Additionally, the charged species discussed here will follow the magnetic field lines towards the divertor, being guided away from the hot core, in contrast to neutrals. For a stable chemical species, the relevant re-emission cycles are obviously those where the particle energy or plasma temperature is low. We show below that the relative yield for BeD^+ is strongly increasing with lowering the projectile energy, which would lead to a hydride-enrichment during the re-emission cycles. It is not just this qualitative fit to the analysis from JET ILW surface samples that makes our approach valuable. Data on molecules have been requested [2], but there are only few experiments that can access the low-energy sputtering regime [9]–[11]. These studies on the beryllium-deuterium ion surface system often suggest the low-energy sputtering threshold energy to be lower than expected from fitting the Bohdansky formula, due to a lowering of the Be surface binding energy by surface roughness [9]. However, they usually lack the chemical analysis in situ and suffer from larger errors [9]. Our studies show that these results

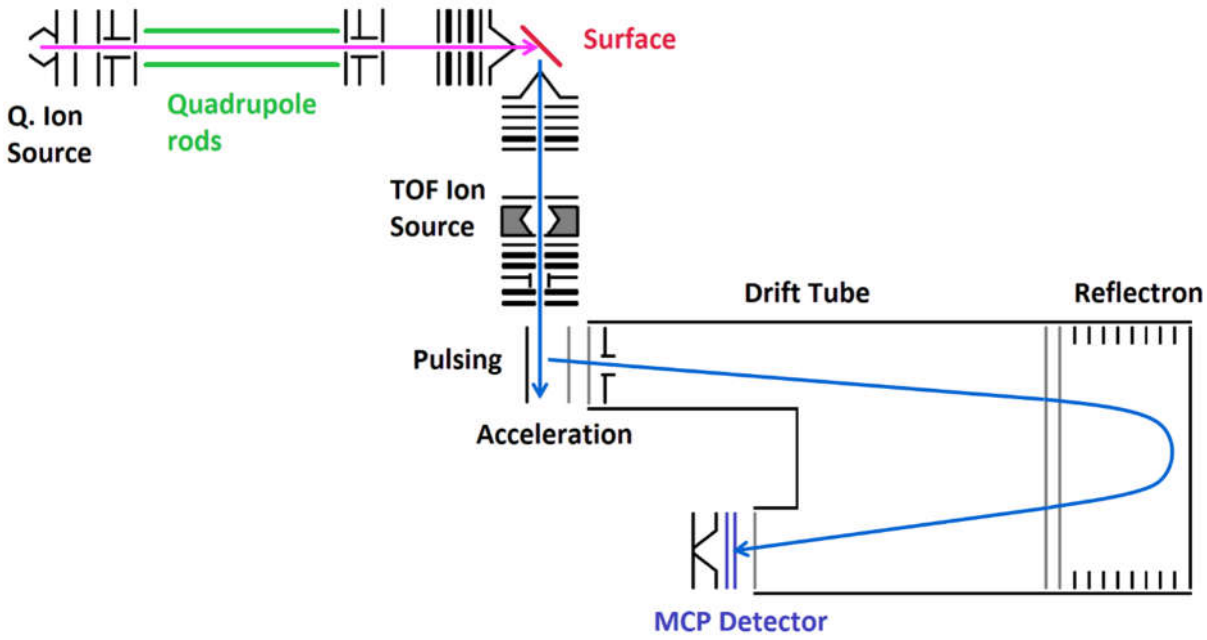
may be altered by the increased BeD^+ chemical sputtering yield not being distinguished from the pure Be yield.

To our knowledge, there are currently no experimental setups that can analyze the chemical composition of sputter products in situ providing good data quality, sensitivity and permanently clean surface conditions. Conceptually similar experiments suffered from surface hydrocarbon films on top of the surface [12]–[18], generated by pump oil adsorption (also with turbopumps). The newly constructed apparatus (SurfTOF, Surface Time-of-Flight), achieves a hydrocarbon free surface by in situ sputter cleaning via a high projectile ion flux. Besides causing repeatable measurements, this also opens the way to proper measurements of how neutral molecules, intentionally adsorbed to the surface, influence sputter products. As a simple example, water will adsorb much less on a surface if there are hydrocarbons present [19]. This work includes first data on adsorption as well. With only minor relevance to fusion devices (reactions of cooling water impurities in a tokamak), the purpose here is to understand and evaluate the ion beam method itself more deeply.

Pressures are mutually comparable to SurfTOF (ITER: 10^{-8} mbar background [20], up to 0,1 mbar in the neutral pumping section [21]). Other experimental conditions, like surface temperature and particle energy can be adjusted to resemble different parts of a fusion device. The surface ion flux of particles per area and per time is much lower in an ion beam device. However, measurements with variable flux could be performed for the first time, indicating whether a certain process discovered depends on the flux or not.

3 Experimental setup

The idea of this experiment is an MS-MS technique or tandem mass spectrometer with a surface placed between the two mass spectrometers.



1: Sketch of the SurfTOF experiment. Arrows indicate the ion flightpath, Electrostatic lenses drawn schematically. The vacuum system encloses the whole experiment, with differential pumping across the quadrupole, in order to maintain a low pressure in the chamber containing the surface.

Projectile ions are generated in an electron ionization source, with the ionization potential kept at 100 V, except for the He^+ measurements it is raised to 200 V. Ions are then focused into a quadrupole mass filter. This “m/z selected ion gun” is a highly modified Pfeiffer QMA 400 quadrupole, delivering up to 80 nA ion current to the surface, depending on the projectile and resolution settings. The mean impact energy results from the potential difference between the ionization region and the surface itself (between 5 and 500 V) which gives good energy resolution (smaller than 1 eV) for the projectiles used in this study.

The impact and analysis is kept at 45° to the surface. This collision region is field-free, only the charged sputtering products that make it past the conical lens can be transported towards the analysis section of the experiment. The filaments of the TOF ion source are usually switched off, only its lenses are used to focus product ions into the acceleration region of the home built, orthogonal pulsing, reflectron time-of-flight (TOF) mass spectrometer.

Although this looks similar to a SIMS (secondary ion mass spectrometer), it is entirely different. The aim utilizing SurfTOF is to observe chemical reactions and low energy sputtering behavior, whereas SIMS analyzes the surface content trying not to trigger reactions. Hence, the projectile energy differs by several orders of magnitude. Moreover, the

surface region is not field free in a SIMS experiment and the equilibrium conditions described in the experimental procedure are not met.

The instrument can also be used as a high precision residual gas analyzer. By switching on the TOF ion source, the residual gas in the surface vacuum chamber can be monitored, handy for impurity-sensitive surface experiments. Additional checks are possible: When a repulsive potential is applied to the surface, one can bend the ion beam towards the TOF, without a surface collision. This allows monitoring the quadrupole mass selection and therefore the purity of the projectile beam. Furthermore, the residual gas in the quadrupole ion source can be analyzed, when the quadrupole is switched to the ion guide mode.

The surface can be heated, up to 730 K, the temperature is measured by a Type-K thermocouple. The surface current is measured with a pA-meter (rbd instruments 9103).

The vacuum is generated by turbomolecular pumps (Pfeiffer) that are oil-free on the high vacuum side. The base pressure is 1.5×10^{-8} mbar, which is sufficient as shown later. The neutral gas can be introduced in a very controlled way: in collaboration with pressurecontrolsolutions.nl a PID controller was developed, that uses the analog signal from the cold cathode vacuum gauges to control a proportional valve. This ensures stable pressures (relative standard deviation typically 0.003) and ion currents. Additionally, it is designed to be leak tight and allows to start and stop gas flow safely via the measurement PC. A gas barrier allows for differential pumping of the quadrupole ion source and surface chamber, creating pressure differences of up to two orders of magnitude.

4 Experimental procedure

Surface experiments in general, low-energy ones especially, are difficult with respect to repeatability and stability. The new experiment allows us to monitor and reach, what we call equilibrium condition. The idea is the following: The peaks in mass-spectra obtained from a surface, may not be constant over time, if the underlying processes are slow. As an example, if the sputter yield of a certain product relies on projectile implantation and re-emission by projectiles coming later, it will increase over time until it reaches a steady state. Those are rather slow processes and influence the yields measured over hours or even days. There are two ways to monitor, if the investigated process has reached its equilibrium. First, the intensity of many peaks is high enough to trace temporal behavior and thus stability. For peaks close to the detection limit, the equilibrium conditions are checked in the following

way: Usually, one parameter (e.g. projectile energy), is scanned between single mass spectra taken. Such a scan is not performed one-after the other (e.g. 20, 30, 40 eV…), but in a random order (e.g. 30, 320, 50 eV…). Later the plot of the scan (e.g. figure 4) is checked for extensive scatter. If this was not done, one cannot attribute a change in yield to a parameter change. It might simply be a slow diffusion, whose variation in time would be interpreted wrongly as a dependence on the parameter investigated. Only if these checks are passed, we refer to a process as having reached equilibrium conditions. Thereby, results are reproducible, even if the measurements are months apart or the sample was exposed to the atmosphere. We attribute this exceptional stability also to the high surface currents in general.

Scatter in random parameter scans is also the best estimate for systematic error. As can be seen from the data (figure 3 to 8), it is very low for most products. Statistical errors are: The counting error, slight instabilities of the surface temperature (max. +/- 4 K), the pressure error, estimated as the standard deviation of all the samples in one measurement. The correction factor for each gas measured in the cold cathode gauges is obtained from the electron ionization cross section at 100 eV [22].

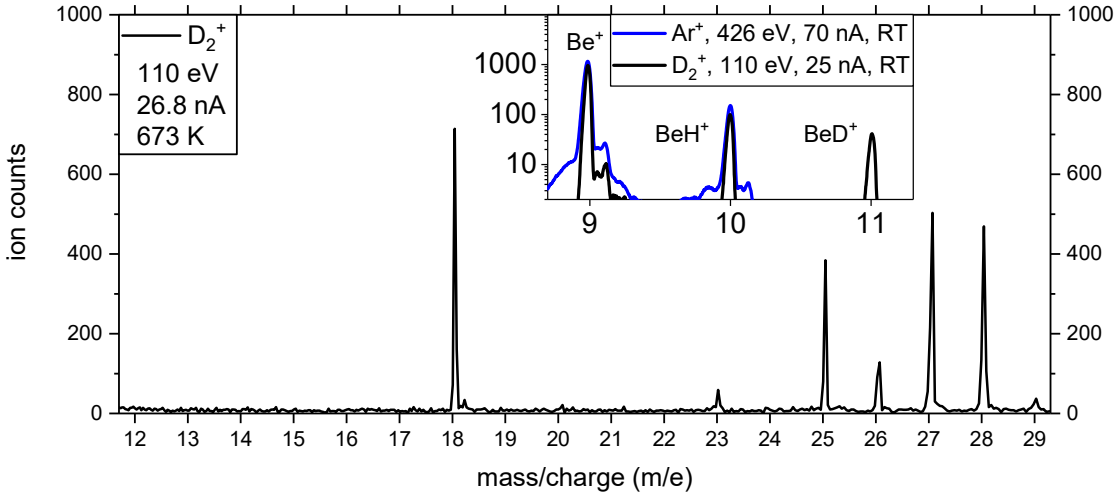
The surface current is sampled before and after a measurement and their difference is denoted as the error bar. The error of the impact energy is smaller than the symbols in the graphs. Straight lines between single measurement points are drawn as a guide to the eye, having no physical meaning.

Data analysis is straightforward, as a mass-peak of interest is summed up in the raw TOF data and a constant background correction subtracted, estimated from signal free parts in the spectra. This noise is low, for example 0.3 % of the BeD^+ peak area in figure 2. Throughout this work, absolute yield refers to this number of ions divided by the number of TOF scans and divided by the surface current in Ampere, leading to units of $\frac{ion\ counts}{N_{scans} \times A} = A^{-1}$. The normalization factor ($N_{scans} \times I_{Surf}$) is around 10 for an overnight and typically 1 for a two-hour measurement. The so-called relative yield is obtained, when the number of ions in the peak of interest is divided by the number of Be^+ ions in that measurement. This efficiently cancels many instabilities, being small they influence the Be^+ yield linearly, so the latter becomes an in situ probe for instabilities. Additionally, the relative yield is essentially an ion yield ratio, for example the BeD^+/Be^+ yield. This can be compared well to other results from the literature and theory.

Preliminary results were compared among different bulk beryllium samples, with little differences between them. All data shown in this publication was obtained using the same

rolled amorphous beryllium sample (obtained from alfa aesar), in order to lower the number of possible error sources in mutual comparisons.

5 Results and discussion



2: Examples of mass spectra obtained. m/e 9 is Be^+, m/e 10 is BeH^+, m/e 11 is BeD^+, only produced when using D-containing projectiles (other products discussed in the text). There is a peak shape issue with ghost peaks on the right of the parent, caused by faulty beam focusing, but it does not alter analysis, as it repeats on every peak.

We can attribute the following mass to charge ratios from figure 2:

- m/e 9 is Be^+, m/e 10 is BeH^+, m/e 11 is BeD^+, only produced when using D-containing projectiles. BeD_2^+ and BeD_3^+ were not observed.
- Hydrocarbon residues, for example C, …, CH_3^+, m/e 12 – 15 are absent.
- m/e 18 is mostly Be_2^+, with only little H_2O^+ contribution as the OH^+ fragment is missing, which was observed when water adsorbed to the surface on purpose ($H_2O^+/OH^+ \approx 3$).
- m/e 23 is Na^+, an impurity that has a low neutral content, but its charged yield is large due to a high (surface) ionization probability [23].
- m/e 25 is BeO^+, m/e 26 is $BeOH^+$, m/e 34 (not shown) is abundant as well, associated with Be_2O^+.

- m/e 27 could be Be_3^+, but Be_4^+ was not observed.
- m/e 28 is Si^+ (compare figure 9), an impurity in the sample, originating from the ore. N_2^+ is not expected, the N^+ fragment is missing.

5.1 In situ sputter cleaning

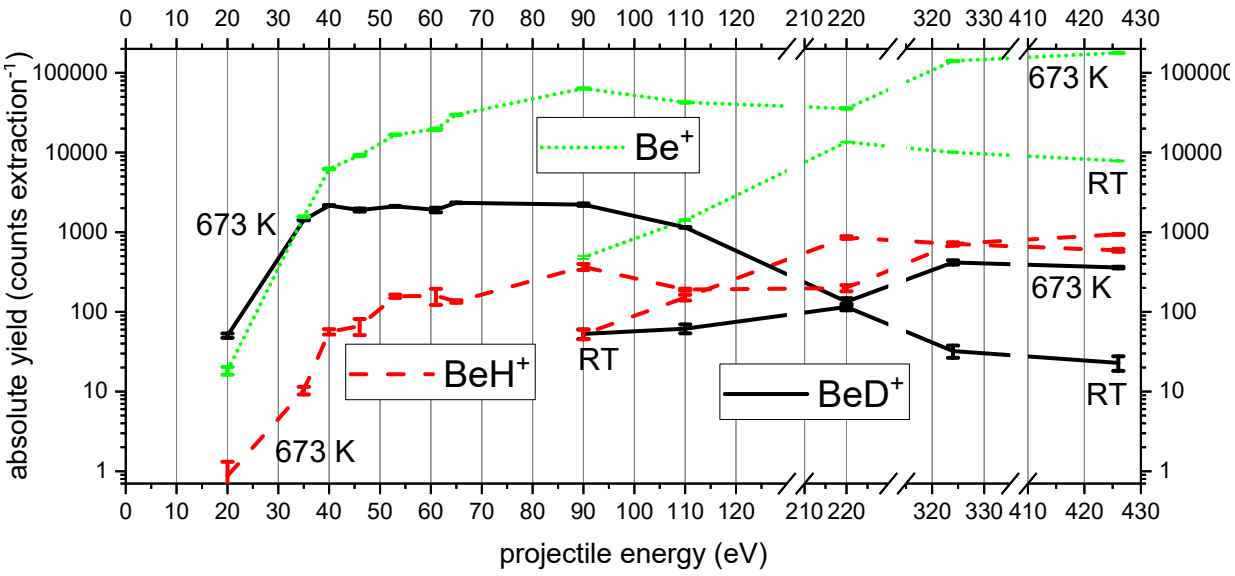
As can be seen, the typical mass peaks resulting from hydrocarbon impurities (C, CH^+, …, CH_3^+ compare figure 2) obtained in similar experiments [24], [25] are completely absent for the first time. This is achieved via in situ sputter cleaning, simply by the very intense projectile ions flux. Typically, those products are very intense when a measurement is started, and decrease over a few hours into a steady state [26]. Its value is determined by the incoming rate from the background gas, versus the sputter cleaning rate. As the SurfTOF experiment has a higher projectile flux by 2 to 4 orders of magnitude, the steady state value of hydrocarbon products is below the detection limit. Consistently, hydrocarbon peaks can only be seen for a few minutes when a new sample has been put into the setup. To our knowledge, there is no comparable experiment that has reached this in situ cleaning regime yet.

5.2 Formation of BeD^+: the projectile reaction

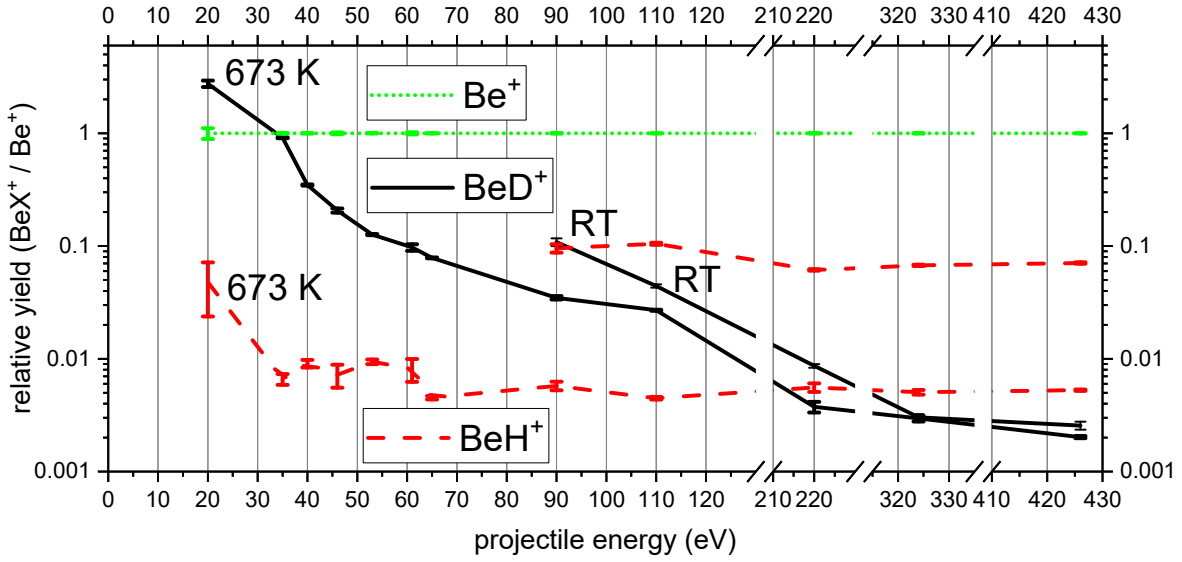
5.2.1 Energy scan

The product ion BeD^+ is formed in a surface reaction between the incident ions D_2^+ and Be sample. The absolute yield of BeD^+ (figure 3) increases from the value at 20 eV to a maximum at 40 eV and then it decreases at 90 eV and above. Be^+ increased from the value at 20 eV over the entire energy region. The yield of BeH^+ followed approximately the yield of Be^+ at a given T_{Surf} and its origin will be discussed later on. The low energy behavior of all these major product ions indicates a sputtering threshold below 20 eV.

The very high relative yield of BeD^+ (figure 4, 673 K), already above 10 % below 60 eV and reaching 275 % at only 20 eV, is remarkable. As this curve has no maximum, one may extrapolate that the relative content of BeD^+ is the highest at the sputtering threshold.



3: Absolute yield for the main products Be^+, BeH^+ and BeD^+. The range covers the transition from very low energy chemical and potential sputtering to high energy kinetic sputtering. T_{Surf} is 673 K and 298 K (RT), D_2^+ projectiles. The surface current is 8.0(1) nA for 20 eV, then it increases from 14.4(2) nA at 35 eV to 23.2(2) nA at 426 eV.



4: Relative yield for the same energy scan. The outstanding feature is that at 20 eV projectile energy, the BeD^+ yield is nearly 3 times higher than Be^+. BeH^+ is constant at a given T_{Surf}, except at 20 eV, due to the low 8.0(1) nA I_{Surf} leading to inefficient sputter cleaning of H_2O.

As stated in the introduction, the quantitative relevance for fusion devices are difficult to derive. This experiment serves for the discovery and qualitative understanding of reactions taking place on a surface bombarded with ions. Quantitative analysis has to be done later by tailored simulation or specific analysis in tokamaks where possible.

Thus, the implication towards tokamak experiments is not straightforward. Allover we find good qualitative agreement with tokamak data, although there, D_2^+ is very rare, D^+ is the main projectile. But as the different experimental techniques show the same key features, we expect that D^+ is at least as reactive as D_2^+ in the BeD^+ synthesis. The bare D^+ was not chosen in this work, as this would have made access to the ultra-low energy sputtering regime impossible, due to much lower projectile current. Their difference will be examined in our future work.

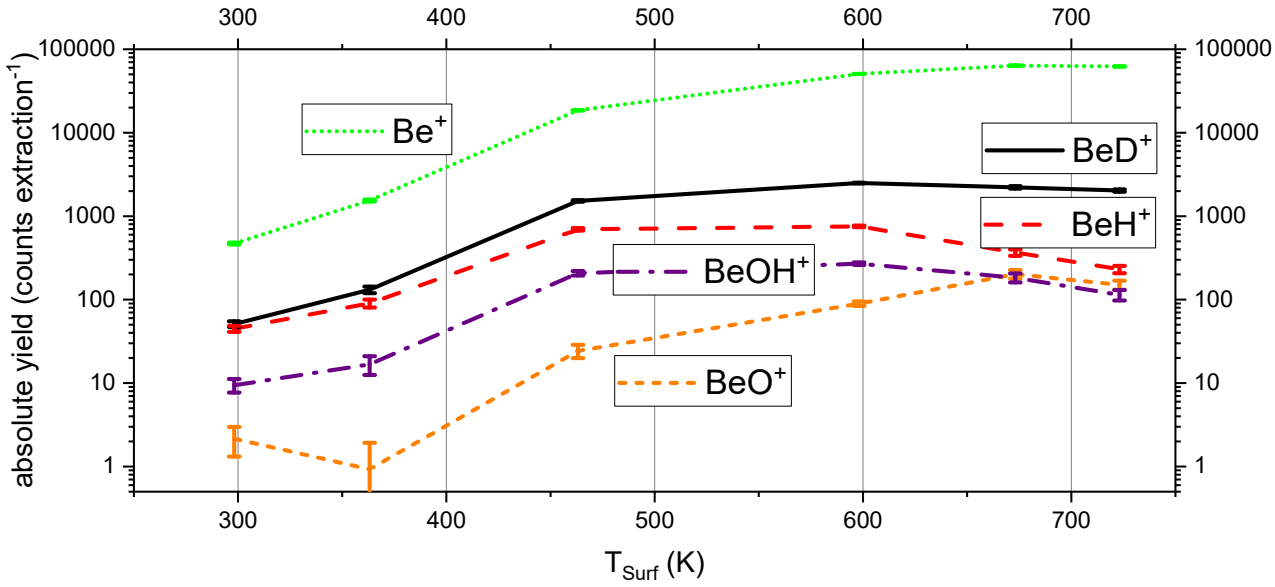
For the energy scan, we like to compare our data to JET experiments [27]. There, the projectile energy can only be controlled via the ion temperature, if the surface is directly exposed to the plasma, i.e. as a beryllium limiter tile. Then, the ion temperature is calculated from the electron temperature, thus it is less well defined. Also the limited control of projectile species in a tokamak overlays the beryllium hydride chemical sputtering with Be self-sputtering above 150 eV. In JET, the neutral BeD/Be ratio is measured as 1/3, determined at ~ 75 eV impact energy (similar T_{Surf}) [27]. On the one hand, this offset between the ratios might be attributed to the experimental differences: at JET neutral products are analyzed by spectroscopy, in contrast to charged products analyzed by mass spectrometry. Also, ionization probabilities in the sputtering process of Be and BeD might be different, resulting in quantitative mismatch between neutral and ionized BeD/Be ratios. Nevertheless, the qualitative trends between different experimental methods and theory should still be comparable (see also the temperature scan, figure 5). Hence, ion beam experiments can extend the parameter range down to the dilute plasma, low-energy conditions where co-deposits are formed. These regions could not be monitored in the JET experiment [27], but are responsible for T retention, as they are the regions of net-deposition. This step in the parameter range is also the step where BeD^+ molecules can become stable, due to their standard free energy for dissociation being above 2 eV, even at 1000 K, as derived by theory [28]. With the ratio of $T_{ion} = 5 \times T_{electron}$ [27], it is sure that these molecules are stable at cold regions in the divertor of typically $T_{ion} = 5$ eV as the electron energy is below the dissociation threshold.

The BeD^+ projectile reaction channel may be regarded as equivalent to a BeT^+ channel, which is one of many potential ways in which tritium can be retained in the reactor wall. The idea of forming stable molecules, especially at low energies, also agrees well with the experimental finding, that the removal of T from T-Be co-deposits in tokamaks only by heating might not be sufficient [1]. It also might offer an answer to the question, why the retention at various incident particle energies behaves opposite to what is expected from Be co-deposit density [29], pointing towards the re-emission cycles that enrich hydrides, as discussed in section 1.

The high energy part of BeD^+ dependence in figure 3 and 4 shows a decrease, due presumably to the fragmentation of highly internally excited BeD^+. However, the absolute yield for BeD^+ is still high towards increasing energies, it is also the increasing Be^+ physical sputtering yield that lowers the relative BeD^+ content – so, even at 426 eV, BeD^+ is still synthesized on the surface.

An energy scan was also performed at room temperature (RT, figure 3 and 4). It shows little difference in the qualitative behavior, but the absolute yield for BeD^+ and Be^+ is substantially lower. This behavior was investigated in a temperature scan at fixed impact energy (90 eV, figure 5 and 12, supplement).

5.2.2 Temperature scan



5: Absolute yields at different T_{Surf}. There are two orders of magnitude increase in the Be^+ yield towards a hot surface, which cannot simply be attributed to BeO on the surface. BeD^+ can be formed on a very hot surface, adsorbate products (BeH^+, $BeOH^+$) go down. D_2^+ impacting Be with 90 eV and 16.1(2) nA.

The temperature behavior (figure 5) gives another qualitative match between diverse experimental techniques (ion beam, linear plasma and tokamak devices). Not only the SurfTOF and JET experiment [27], but also MD simulations [28], [30] find a linear decrease of BeD/Be ratio (BeD^+/Be^+ respectively, figure 12) with increasing surface temperature. The

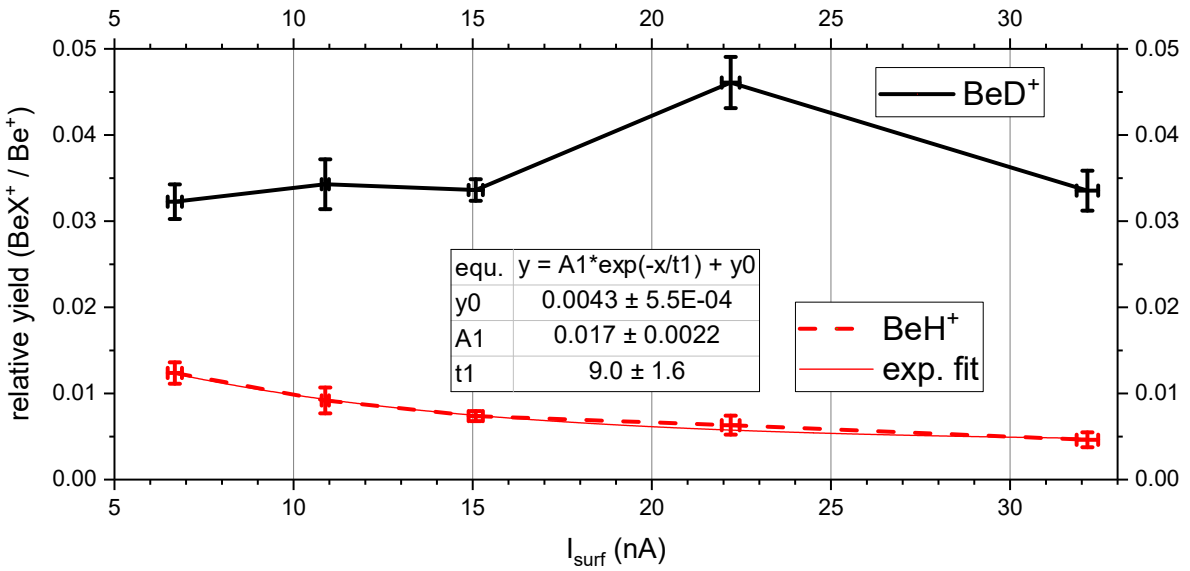
resulting slopes are comparable within one order of magnitude. This underlines again the expectation that the more fusion relevant projectile D^+ is at least as reactive as D_2^+.

There is a pronounced increase in the Be^+ yield for elevated surface temperatures (figure 5). As we did not observe this for other metals, we doubt that this is only due to the high energy tail of the thermal distribution approaching the surface binding energy. In the literature, one finds this attributed to Be starting to diffuse through the oxide layer at higher temperatures, and BeO has a higher surface binding energy resulting in less sputtering at low temperatures [10]. If this explanation would also apply to the situation in our experiment, then the BeO^+/Be^+ ratio should drop at elevated temperatures, but it remains constant (rel. yield in figure 12, supplement). This disagreement should not be an experimental artefact, again due to the high projectile current. The initial BeO layer on the sample formed in atmosphere (figure 9) is later removed in the experiment (figure 14, supplement). This is similar to the in situ sputter cleaning, but on a much longer timescale than for hydrocarbon impurities (days compared to minutes). Another possible artefact would be creating BeO from surface water, but when BeO^+ and $BeOH^+$ yields are compared in any figure, one sees that their behavior for various temperatures is very different. The BeO^+ yield even decreases by higher H_2O partial pressures (in the relevant regime, figure 8), as discussed in the next section.

The BeD^+ temperature dependent yield follows the Be^+ trend, with the relative yield BeD^+/Be^+ falling linearly from 0.108(8) at room temperature to 0.032(1) at 723 K (figure 5 and figure 12, supplement). The influence of the 540 K BeD_2 decomposition from temperature-programmed desorption (TPD) measurements [5] seems to be small, as well as the desorption of implanted D around 460 K [31], [32]. Still, both are possible explanations of the BeD^+ yield not rising further in that range. As mentioned above, this decrease is consistently found throughout various experiments [27] and in theory [28], [30].

5.2.3 Projectile current scan

The surface current was scanned, in order to see ion-flux dependencies. The beam diameter varies with projectile energy and cannot be measured in situ. An ex situ estimate (figure 14) suggests at least 10^{17} ions m^{-2} s^{-1} for 20 nA surface current, likely more.



6: Relative yield for BeH^+ and BeD^+ depending on the surface current. The BeD^+ value at 24 nA is considered an artefact, caused by the process not being in equilibrium in that particular mass spectrum. The absolue Be^+ yield (figure 13, supplement) and interestingly also BeD^+ increase linearly with surface current, indicating a direct, one-particle process. Exponential behavior of BeH^+ agrees with sputter cleaning. D_2^+ impacting Be at 673 K with 90 eV.

The absolute Be^+ yield (figure 13, supplement) increases linearly with the surface current, as expected for a direct knockout. A linear fit of $ion\ yield\ [counts\ extraction^{-1}] = s \times I_{Surf}\ [nA]$, results in a slope $s = 7.3\ (1)\ [counts\ extraction^{-1}\ nA^{-1}]$ for the Be^+ yield. For BeD^+ a quadratic behavior is anticipated, for an expected two-step, e.g. a two-particle process: The first D_2^+ projectile forms a BeD (or BeD_2) on the surface, and then the second projectile sputters it away as BeD^+.

However, we find a clearly linear behavior. Thus, it is either a one-particle process as well, or more likely one of the steps involved strongly assisted by the beryllium surface. A surprising result, as it points towards a direct process, or a quasi-direct process at least.

The linear rise with no measured onset of saturation also implies a high relevance of the projectile reaction channel when the flux is scaled from an ion beam experiment to a tokamak. The BeD^+ absolute yield increases over flux with a slope of $s = 2.53\ (2)\ [counts\ extraction^{-1}\ nA^{-1}]$, which shows as a constant relative yield in figure 6.

There was a certain concern that the BeD^+ may have been formed from the D_2 gas leaking from the ion source through the gas barrier into the vacuum chamber of the surface. In the supplementary material, there are two measurements reported, which clearly show that the

small amounts of neutral D_2 in the surface chamber do not play a role in the measurements above. For very high D_2 partial pressures, it is possible to form BeD^+ from adsorbates as well, analogous to the next section.

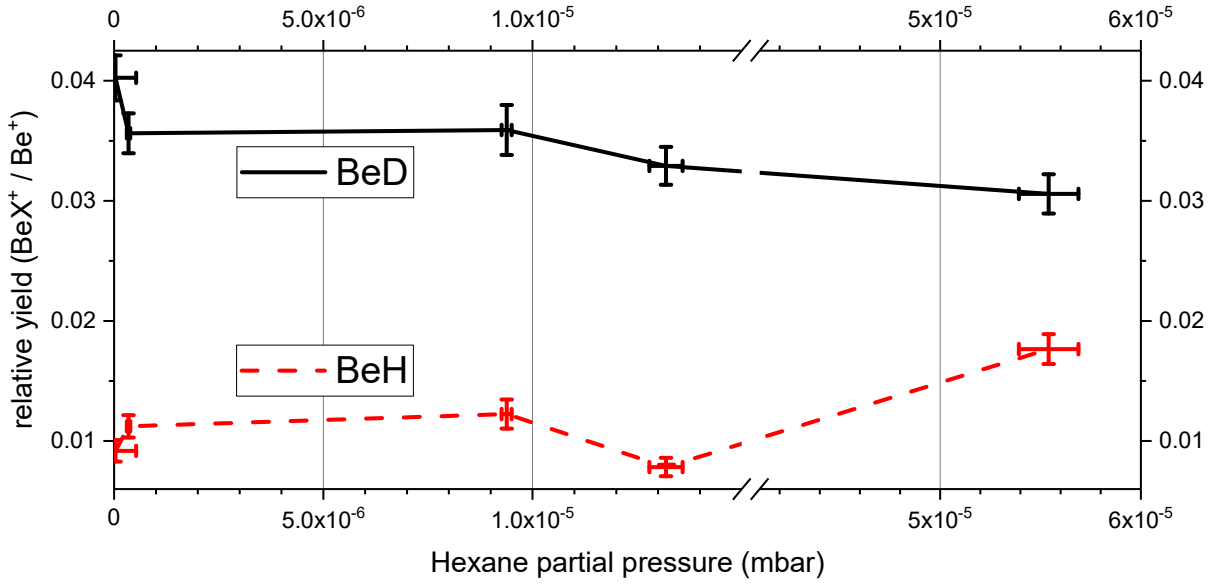
5.3 Formation of BeH^+: the surface adsorbate channel

This channel has only minor relevance to fusion reactors allover, but it will occur in the context of cooling water impurities. However, it is important for ion beam experiments. The information helps to understand impurities in ion beam experiments and demonstrate, that they do not influence the projectile reaction (yielding BeD^+), if sufficiently high surface currents and temperatures are used.

Indeed, the beryllium hydride synthesis was discovered in our experiment via impurities. BeH^+ was produced, when a Be surface was bombarded with Ar^+ ions (inset in figure 2): Without intentionally providing hydrogen, a very low reactant concentration in other words, BeH^+ is produced. This points towards an efficient mechanism producing a stable species. Consistent with the sputter cleaning, high currents lead to a lower relative BeH^+ yield (figure 6). Therefore, possible impurity candidates are tested by introducing them into the surface collision chamber and varying their partial pressure.

5.3.1 C_6H_{14} pressure scan

First, to serve as a model system for long hydrocarbons, hexane (C_6H_{14}) vapor was introduced into the surface chamber (figure 7). Hydrocarbons from diffused pump oils were so far the dominant impurity in similar setups.

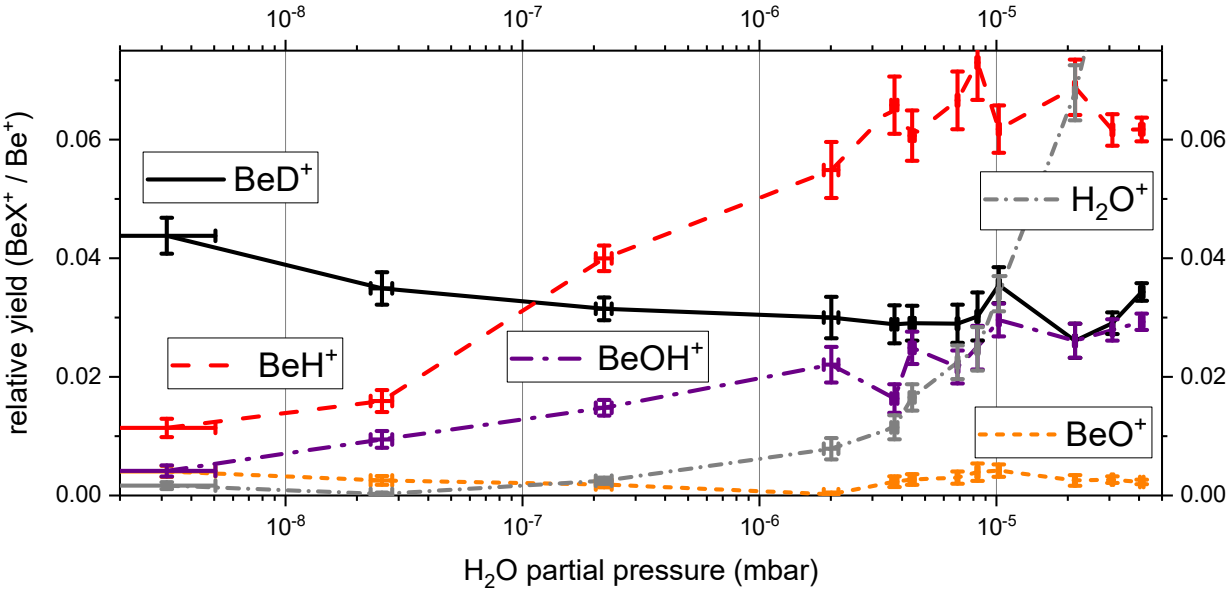


7: Relative yield with different hexane partial pressures. Hexane adsorbate is not a good source for hydrogen in BeH^+. D_2^+ projectiles impacting Be at 673 K with 90 eV and 16.0(2) nA. D_2 partial pressure 1.0(1) × 10^{-6} mbar.

It increases the BeH^+ yield only by a factor of about two, when the hexane partial pressure is above 5.5 × 10^{-5} mbar. That is at least a factor 4000 more than the absolute residual gas pressure. This excludes hydrocarbons as a possible hydrogen source. Hexane also suppresses the BeD^+ production slightly, it likely starts to form a layer on top of the metal.

5.3.2 H_2O pressure scan

Water vapor, the natural residual gas component, was tested next:



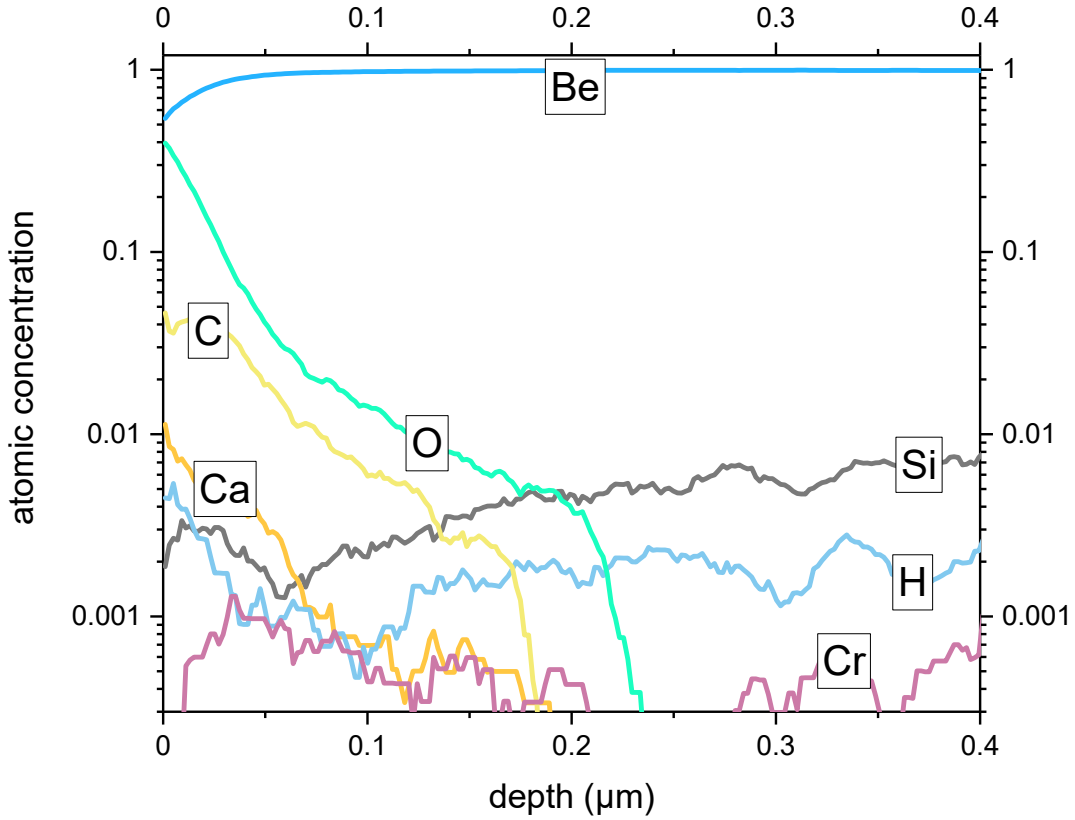
8: Relative yield using different H_2O partial pressures. Strong BeH^+ synthesis already with little H_2O adsorption. D_2^+ projectiles impacting Be at 673 K with 90 eV and 16.1(4) nA. D_2 partial pressure 1.0(1) × 10^{-6} mbar.

Already small amounts of water vapor in the surface chamber (figure 8) lead to a sharp increase in the BeH^+ yield, which even crosses the BeD^+ yield at about 3 × 10^{-7} mbar. The attenuation of the BeD^+ production by the water being present is also more pronounced than with hexane, which points towards longer sticking time due to its polar nature.

The less abundant $BeOH^+$ product shows the same energy and temperature behavior as BeH^+, indicating the formation from absorbed water.

5.4 TOF-ERDA: elemental composition profile

This section shows that a possible third channel for beryllium hydride synthesis connected with the bulk hydrogen in the beryllium sample only plays a minor role. Therefore, an elemental composition profile was recorded using TOF-ERDA in Uppsala ([33], results figure 9), after the surface was used in the SurfTOF experiment.



9: TOF-ERDA [33] elemental profile analysis: Atom number concentration, 15 points adjacent average smoothing, I^{8+} projectiles with 36 MeV. Consistent with SurfTOF data. On the surface: Oxides attributed to the transport in air, C and H result from hydrocarbon impurities. In the bulk, Si, H and Cr are remnants of the production process.

The hydrogen number concentration in the bulk material is around 0.002 (figure 9). In order to clarify ratios: Assuming exactly $\frac{2\,H}{1000\,Be} = 0.002$, the maximum BeH/Be yield to be obtained is $\frac{2\,BeH}{998\,Be} \approx 0.002004$, if all hydrogen is sputtered as BeH. The ionized ratio may still be different, but for a basic investigation, the H/Be ratio serves as an upper boundary for BeH^+/Be^+ obtained from the bulk.

However, we consistently measure a BeH^+/Be^+ ratio of 0.008 at a given surface current and temperature (figure 4, 6, 10, and 11). This confirms, that the bulk hydrogen can only be a

small source for hydrogen in BeH^+. Nevertheless, one can estimate the bulk hydrogen contribution also from the SurfTOF data alone. As sputter cleaning is a rate model, the BeH^+/Be^+ ratio (Y) will follow an exponential behavior with the surface current:

$$Y = A\, e^{\frac{-I_{Surf}}{t}} + y_0$$

The exponential part contains the idea of sputter cleaning a surface adsorbate. A is the amplitude specific for BeH^+ products, t describes how sensitive they are to differences in ion current. It contains the assumption $I_{Surf} \gg 0$, meaning there is sufficient projectile flux, removing all hydrogen that is adsorbed. The constant term, y_0, is the underlying contribution from bulk hydrogen. It has to be current-independent.

We obtain y_0 = 0.0043(6) by a fit to the current scan (figure 6). As this is still about twice the H/Be = 0.002, we conclude:

- There is only a minor contribution from bulk hydrogen to the overall BeH^+/Be^+ ratio.
- The exponential curve fits the data very well, prooving sputter cleaning as a valid concept.
- The largest uncertainty remaining is the ion-to-neutral ratio, which we will address in future experiments.

The hydrogen impurities come from the industrial production process in a hydrogen atmosphere. Together with Si from the ore and Cr they are the only impurities contained in the bulk material.

On top of the surface, there is a thick oxide layer found (more than 1 % O along the top 0.1 µm). It mostly originates from the sample being transferred in atmosphere for a couple of days between the experiments. But even this thick oxide layer is removed in the SurfTOF experiment in the timespan of a few weeks. Creating an optical 3D model of the surface before and after bombardment of the surface, we estimate that 1.0(5) µm of material was removed perpendicular to the surface, with a FWHM beam cross section of about 1.5 mm² in about 4 months. (figure 14, supplement, using an “infinite focus microscope” [34]).

This also gives information about the much thinner oxygen layer, that could form from residual gas in the UHV apparatus. During measurements, it cannot be formed, as the ion flux is at least in the same order of magnitude than the neutral gas flux to the surface. If it formed between the measurements, beryllium oxide yields would decrease during long measurements, which they do not. This means, in total, in-situ sample oxidation is very little.

The reason for calcium found on the surface in low concentration remains unclear, but it is seen in the mass spectra from SurfTOF as well, mainly due to its high ionization probability.

There was no implantation of deuterium observed, consistent with experiments and MD simulations at elevated temperatures [5], [31], [32], [35]. This supports the idea, that BeD^+ is formed in a (quasi-)direct reaction with the projectile and not from implantation.

6 Conclusion and outlook

A new type of research apparatus was built that enables efficient in situ sputter cleaning by a very high projectile current. This also allows to reach equilibrium conditions for all processes described here. Both are responsible for outstanding data quality and repeatability. The unique measurements describe chemical sputtering in detail, down to a molecular picture.

The beryllium surface plays a much bigger role than only providing the reactant for the beryllium hydride formation: In the synthesis from the impacting ion, it assists the presumed multi-step reaction, leading to a direct process (linear surface flux dependency). Its many degrees of freedom also take away excess energy in a reaction, as it is still possible to form BeD^+ at an impact energy of 426 eV. We observe that all hydride products do not require more energy to form than is needed to sputter them towards the detector. In fact, the maximum relative yield of BeD^+/Be^+ of 2.75 is reached at 20 eV, the lowest impact energy measured.

Comparing the BeD^+ yield to findings from experimental fusion reactors, the qualitative image fits very well. Its quantitative relevance should be further clarified using tailored simulations. Also the higher fluxes in a tokamak device will impact the BeD^+/Be^+ ratio obtained. However, flux dependencies measured in this work point towards an effective mechanism also at higher fluxes. Allover it offers substantial evidence for molecular tritium retention in beryllium co-deposits, which we did not find discussed in the literature. It is an alarming fact, that we could produce at least some BeD^+ using any projectile energy and surface temperature accessible.

The second reaction channel, forming beryllium hydrides from surface adsorbates was clearly identified. The product ion yield does not depend on projectile properties (species, kinetic energy), but on the surface condition (temperature, surface ion flux).

Surface adsorbates will not play a decisive role for thermonuclear fusion, nevertheless we showed that adsorbate surface chemistry is still efficient at high temperatures. Even at 723 K, molecules remain on the surface for a long enough time to react with impacting ions. This should be kept in mind, as fusion devices deal with seeding gases and impurities, especially cooling water.

Experimental concerns were carefully ruled out, discovering a possible third reaction channel. BeH^+ might also be formed from impurities in the bulk, similar to the adsorbate mechanism.

In general, beryllium is not as reactive as the previously used carbon (CFC), but metal surfaces bombarded with ions pose ideal conditions for a rich chemistry. In future, neutral products, as well as D^+ and N^+ projectiles will be examined. The latter is motivated by the fact of nitrogen seeding causing more tritium retention [36], pointing towards chemistry as well. Also, reactions of high-Z materials, such as tungsten hydrides, are of interest for the proposed all-tungsten design of a commercial reactor [37].

7 Acknowledgments

We kindly like to thank Daniel Primetzhofer, the Swedish Research Council and the Swedish Foundation for Strategic Research for making the TOF-ERDA measurements possible. Our work is supported by Friedrich Schiedel Foundation for Energy Technology 259564, “Reaktive Ionen-Oberflächenstöße”. Austrian Science Fund (FWF) W1259-N27 „DK-ALM“. This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

8 References

[1] X. Litaudon *et al.*, “Overview of the JET results in support to ITER,” *Nucl. Fusion*, vol. 57, no. 10, p. 102001, 2017.

[2] M. Shimada *et al.*, “In-vessel dust and tritium control strategy in ITER,” *J. Nucl. Mater.*, vol. 438, Supplement, pp. S996–S1000, Jul. 2013.

[3] G. Federici *et al.*, “In-vessel tritium retention and removal in ITER,” *J. Nucl. Mater.*, vol. 266–269, pp. 14–29, Mar. 1999.

[4] G. De Temmerman *et al.*, "Efficiency of thermal outgassing for tritium retention measurement and removal in ITER," *Nucl. Mater. Energy*, 2017.

[5] R. P. Doerner, M. J. Baldwin, D. Buchenauer, G. De Temmerman, and D. Nishijima, "The role of beryllium deuteride in plasma-beryllium interactions," *J. Nucl. Mater.*, vol. 390–391, pp. 681–684, Jun. 2009.

[6] Y. Hirooka *et al.*, "A new plasma-surface interactions research facility: PISCES-B and first materials erosion experiments on bulk-boronized graphite," *J. Vac. Sci. Technol. Vac. Surf. Films*, vol. 8, no. 3, pp. 1790–1797, May 1990.

[7] D. Nishijima, R. P. Doerner, M. J. Baldwin, G. D. Temmerman, and E. M. Hollmann, "Properties of BeD molecules in edge plasma relevant conditions," *Plasma Phys. Control. Fusion*, vol. 50, no. 12, p. 125007, 2008.

[8] G. Federici *et al.*, "Plasma-material interactions in current tokamaks and their implications for next step fusion reactors," *Nucl. Fusion*, vol. 41, no. 12, p. 1967, 2001.

[9] P. C. Smith and D. N. Ruzic, "Low energy (10 to 700 eV) angularly resolved sputtering yields for D + on beryllium," *Nucl. Fusion*, vol. 38, no. 5, p. 673, 1998.

[10] J. Bohdansky and J. Roth, "Light ion sputtering of low Z materials in the temperature range 20–1100°C," *J. Nucl. Mater.*, vol. 123, no. 1, pp. 1417–1424, May 1984.

[11] J. Roth, J. Bohdansky, R. S. Blewer, W. Ottenberger, and J. Borders, "Sputtering of Be and BeO by light ions," *J. Nucl. Mater.*, vol. 85–86, pp. 1077–1079, Dec. 1979.

[12] A. Keim, M. Harnisch, P. Scheier, and Z. Herman, "Collisions of low-energy ions Ar+ and N2+ with room-temperature and heated surfaces of tungsten, beryllium, and a mixed beryllium–tungsten thin film," *Int. J. Mass Spectrom.*, vol. 354–355, pp. 78–86, Nov. 2013.

[13] M. Harnisch, A. Keim, P. Scheier, and Z. Herman, "Formation of HCN+ in Heterogeneous Reactions of N2+ and N+ with Surface Hydrocarbons," *J. Phys. Chem. A*, vol. 117, no. 39, pp. 9653–9660, Oct. 2013.

[14] M. Harnisch, A. Keim, P. Scheier, and Z. Herman, "Collisions of low-energy Ar+, N2+, and D2+ ions with room-temperature and heated surfaces of mixed beryllium–tungsten thin films of different composition," *Int. J. Mass Spectrom.*, vol. 365–366, pp. 316–323, May 2014.

[15] V. Grill, R. Wörgötter, J. H. Futrell, and T. D. Märk, "Surface induced reactions of cluster ions," *Z. Für Phys. AtomsMolecules Clust.*, vol. 40, no. 1, pp. 111–114, Mar. 1997.

[16] J. Žabka, Z. Dolejšek, J. Roithová, V. Grill, T. D. Märk, and Z. Herman, "Energy partitioning in collisions of slow polyatomic ions with carbon surfaces," *Int. J. Mass Spectrom.*, vol. 213, no. 2, pp. 145–156, Feb. 2002.

[17] M. A. Mabud, M. J. Dekrey, and R. Graham Cooks, "Surface-induced dissociation of molecular ions," *Int. J. Mass Spectrom. Ion Process.*, vol. 67, no. 3, pp. 285–294, Nov. 1985.

[18] V. H. Wysocki, J.-M. Ding, J. L. Jones, J. H. Callahan, and F. L. King, "Surface-induced dissociation in tandem quadrupole mass spectrometers: A comparison of three designs," *J. Am. Soc. Mass Spectrom.*, vol. 3, no. 1, pp. 27–32, Jan. 1992.

[19] E. N. Rudisill, J. J. Hacskaylo, and M. D. LeVan, "Coadsorption of hydrocarbons and water on BPL activated carbon," *Ind. Eng. Chem. Res.*, vol. 31, no. 4, pp. 1122–1130, Apr. 1992.

[20] R. J. Pearce *et al.*, “The ITER divertor pumping system, design evolution, simplification and performance,” *Fusion Eng. Des.*, vol. 88, no. 6, pp. 809–813, Oct. 2013.

[21] R. A. Pitts *et al.*, “Status and physics basis of the ITER divertor,” *Phys. Scr.*, vol. 2009, no. T138, p. 014001, 2009.

[22] J. H. Leck, *Total and Partial Pressure Measurement in Vacuum Systems*. Springer US, 1989.

[23] B. Wolf, *Handbook of Ion Sources*. CRC Press, 1995.

[24] M. Harnisch, P. Scheier, and Z. Herman, “Heterogeneous reactions between ions NH3+ and NH+ and hydrocarbons adsorbed on a tungsten surface. Formation of HCN+ in NH+-surface hydrocarbon collisions,” *Int. J. Mass Spectrom.*, vol. 392, pp. 139–144, Dec. 2015.

[25] J. Kubišta, Z. Dolejšek, and Z. Herman, “Energy Partitioning in Collisions of Slow Polyatomic Ions with Surfaces: Ethanol Molecular Ions on Stainless Steel Surfaces,” *Eur. Mass Spectrom.*, vol. 4, no. 5, pp. 311–319, Oct. 1998.

[26] M. Harnisch, “Ion-surface collisions of slow ions with fusion-relevant surfaces,” Phd, University of Innsbruck, 2015.

[27] S. Brezinsek *et al.*, “Study of physical and chemical assisted physical sputtering of beryllium in the JET ITER-like wall,” *Nucl. Fusion*, vol. 54, no. 10, p. 103001, 2014.

[28] I. Sukuba, A. Kaiser, S. E. Huber, J. Urban, and M. Probst, “Energetics and reactivity of small beryllium deuterides,” *J. Mol. Model.*, vol. 23, no. 7, p. 203, Jul. 2017.

[29] R. P. Doerner *et al.*, “Codeposition of deuterium with ITER materials,” *Nucl. Fusion*, vol. 49, no. 3, p. 035002, 2009.

[30] E. Safi, G. Valles, A. Lasa, and K. Nordlund, “Multi-scale modelling to relate beryllium surface temperature, deuterium concentration and erosion in fusion reactor environment,” *J. Phys. Appl. Phys.*, vol. 50, no. 20, p. 204003, 2017.

[31] M. Oberkofler, M. Reinelt, A. Allouche, S. Lindig, and C. Linsmeier, “Towards a detailed understanding of the mechanisms of hydrogen retention in beryllium,” *Phys. Scr.*, vol. 2009, no. T138, p. 014036, 2009.

[32] M. Oberkofler and C. Linsmeier, “Deuterium release from implanted beryllium and beryllium oxide,” *J. Nucl. Mater.*, vol. 415, no. 1, Supplement, pp. S724–S727, Aug. 2011.

[33] Y. Zhang *et al.*, “Detection efficiency of time-of-flight energy elastic recoil detection analysis systems,” *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 149, no. 4, pp. 477–489, Mar. 1999.

[34] “InfiniteFocus,” *Alicona – That’s metrology*, 09-Feb-2018. [Online]. Available: http://www.alicona.com/products/infinitefocus/. [Accessed: 23-Apr-2018].

[35] E. Safi, C. Björkas, A. Lasa, K. Nordlund, I. Sukuba, and M. Probst, “Atomistic simulations of the effect of reactor-relevant parameters on be sputtering,” *J. Nucl. Mater.*, vol. 463, pp. 805–809, Aug. 2015.

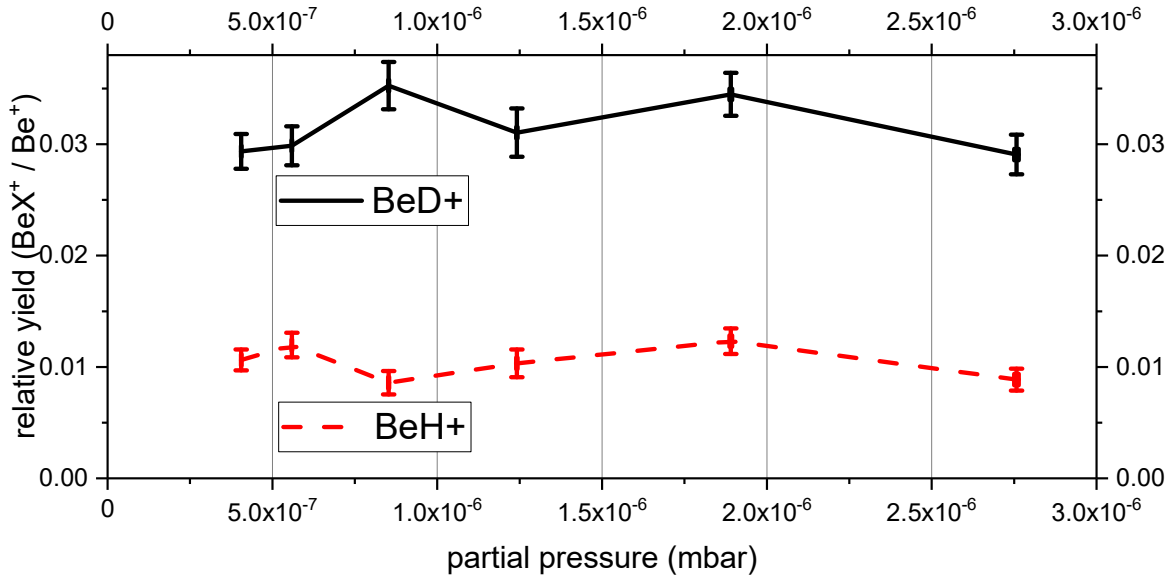
[36] M. Oberkofler *et al.*, “First nitrogen-seeding experiments in JET with the ITER-like Wall,” *J. Nucl. Mater.*, vol. 438, pp. S258–S261, Jul. 2013.

[37] G. Janeschitz, “Plasma–wall interaction issues in ITER,” *J. Nucl. Mater.*, vol. 290–293, pp. 1–11, Mar. 2001.

9 Supplementary material

9.1.1 D_2 pressure scan, D_2^+ projectile

There was a certain concern that the BeD^+ may have been formed from the D_2 gas leaking from the ion source through the gas barrier into the vacuum chamber of the surface. Though the low sticking probability of D_2 (a non-polar, light molecule) on a 673 K surface contradicts this idea already, as well as the surface current scan does (figure 6), we ran experiments showing that this is not the case.



10: The relative BeD^+ yield does not depend on the D_2 partial pressure in the surface chamber. D_2^+ projectiles impacting Be at 673 K with 90 eV and 5.6(2) nA.

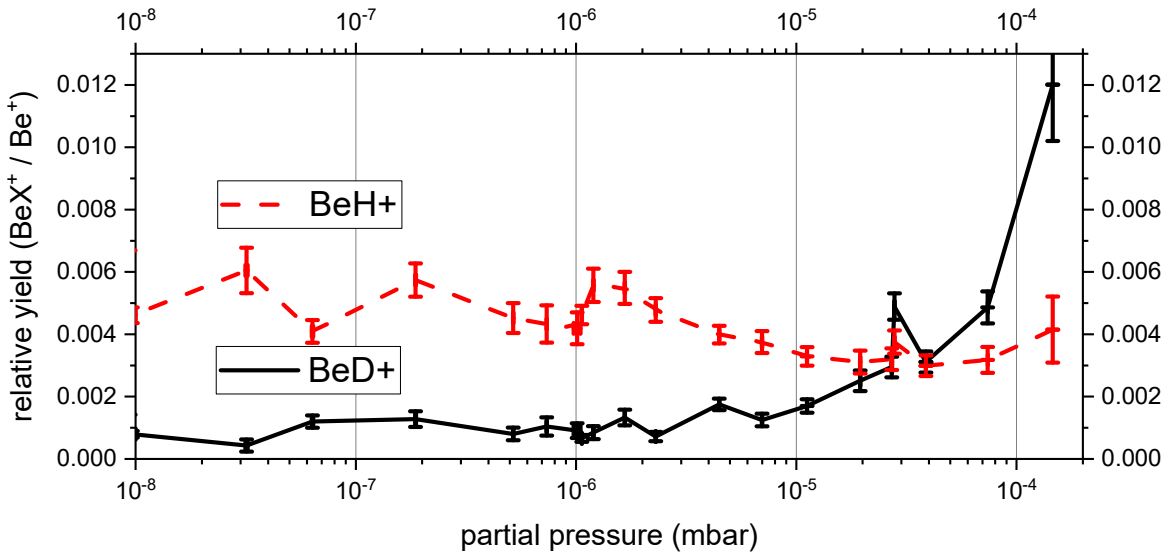
By changing the D_2 pressure in the quadrupole chamber and adjusting the ion source, a constant surface current of 5.6(2) nA was achieved at different D_2 partial pressures in the surface chamber. This is about 4 times lower current than in the other measurements reported here, but it should increase the relative yields from surface adsorbates (inverse sputter cleaning). As can be seen in figure 10, neither BeD^+ nor BeH^+ depend on the neutral D_2 partial pressure.

This already shows that the neutral D_2 does not influence the measurements in the relevant regime, but to be sure we are not measuring a saturated adsorption process, an exchange of the projectile to He^+ allows to remove any neutral D_2 from the surface chamber.

644

645 9.1.2 D_2 pressure scan, He^+ projectile

646 The following graph was obtained using He^+ projectiles and different D_2 partial pressures in
647 the surface chamber. While the BeH^+ relative yield remains unchanged, BeD^+ is far below its
648 usual level and increases only at very high partial pressures.



649

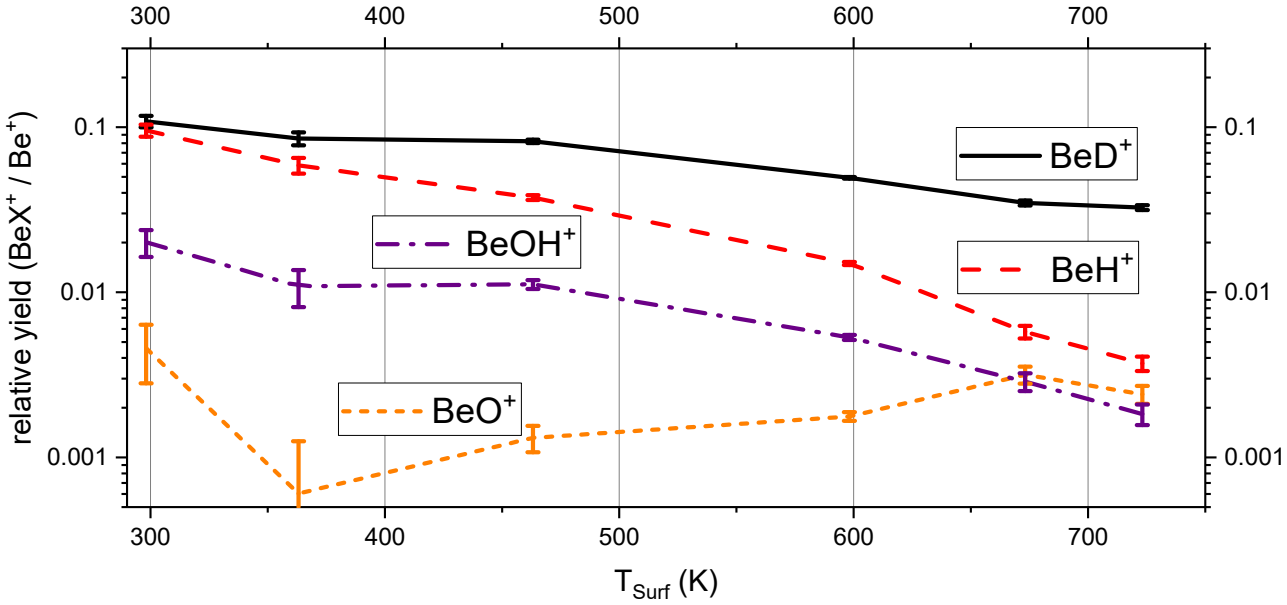
650 *11: He^+ projectiles impacting Be at 673 K with 90 eV and 5.7(2) nA. Relative yield with*
651 *different D_2 partial pressures in the surface chamber. BeH^+ yield remains unchanged, albeit*
652 *the different projectile. BeD^+ forms from adsorbates only at very high partial pressures. He*
653 *partial pressure 1.1(2) × 10^{-7} mbar.*

654 Despite He^+ and D_2^+ having the same nominal mass, exchanging the projectile should alter the
655 sputter yields as they are products of a chemical reaction. This indeed is the case when the
656 projectile reacts; but for the surface adsorbate channel, the projectile seems to provide the
657 activation energy only. This can easily be seen, as the BeH^+/Be^+ ratio is constant (around
658 0.008 at 673 K, compare figure 4, 6, and 10 with figure 11), and is very close to this value
659 when the projectile is changed from D_2^+ to He^+. As BeH^+ and BeD^+ are chemically identical,
660 the BeD^+ relative yield would not depend on the type of projectile, if BeD^+ was formed from
661 surface adsorbates as well. Instead, it drops by a factor of 30 down to the background level (at
662 relevant D_2 pressure 1.0(1) × 10^{-6} mbar, compare again figure 4, 6, and 10 with figure 11).
663 This confirms the D_2^+ projectile and clearly excludes the D_2 neutral adsorbate being
664 responsible for the BeD^+ production.

665 Additionally, figure 11 shows the onset of the surface adsorbate channel, which also exists for
666 BeD^+, but only for D_2 partial pressures of much more than 10^{-5} mbar – D_2 adsorption to the

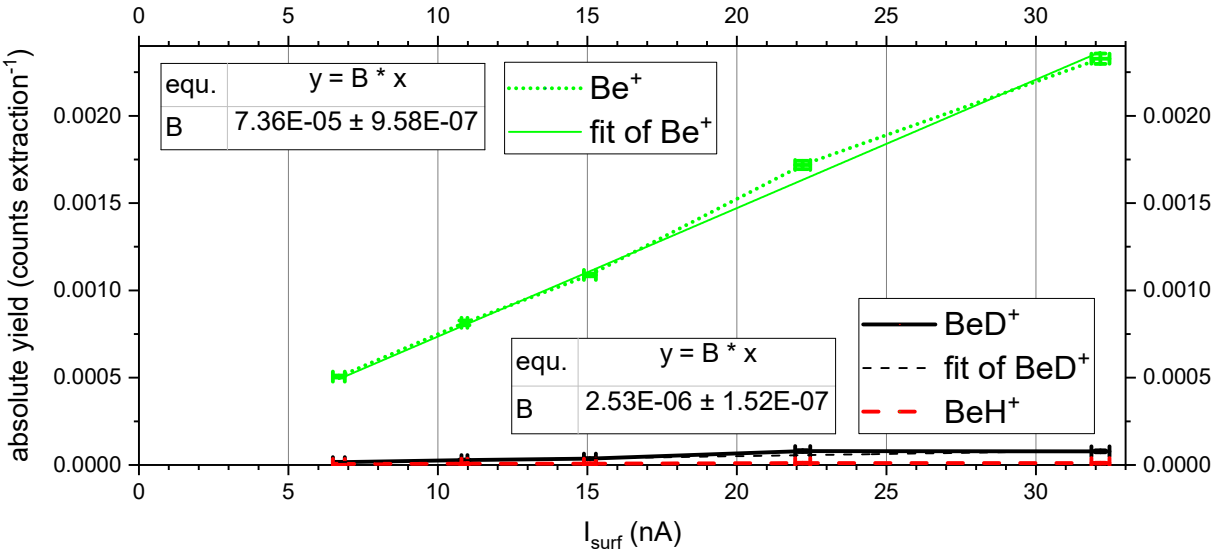
surface is irrelevant for the SurfTOF experiment, but might be a concern in fusion devices in regions of high neutral density, for example the divertor [8].

9.2 Temperature scan, relative yield



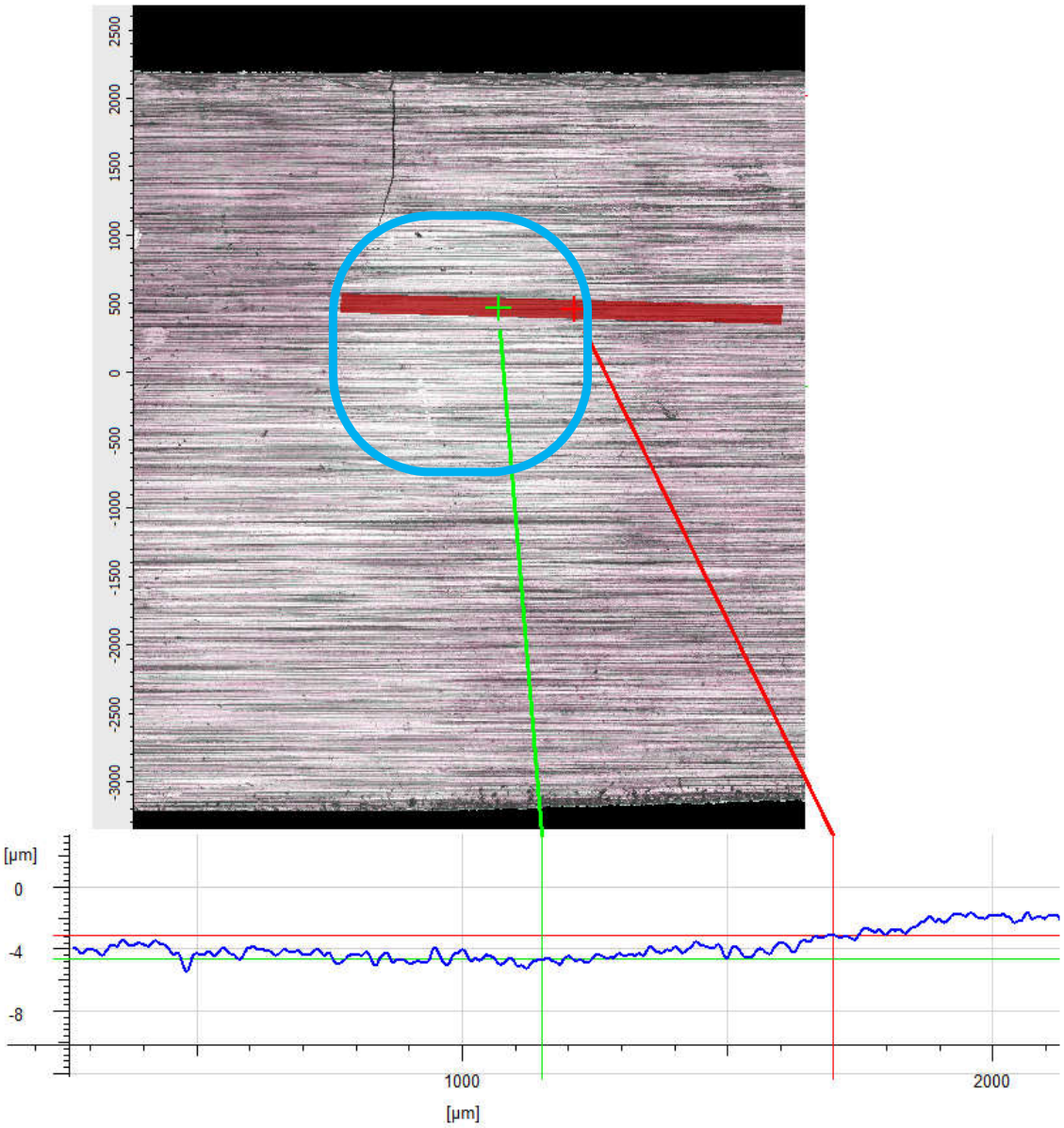
12:Temperature dependence of the relative yield. The linear decrease of the BeD^+/Be^+ ratio (BeD/Be respectively) with increasing T_{Surf} is found throughout different experiments [27], theory and MD simulations [28], [30]. D_2^+ impacting Be with 90 eV and 16.1(2) nA.

9.3 Current scan, absolute yield



13: Absolute yield depending on the Surface current. Be^+ and BeD^+ yields are linear through the origin, which identifies both as direct or a quasi-direct process. BeH^+ behaves differently (also figure 6) identifying the Surface adsorbate channel. D_2^+ impacting Be with 90 eV, T_{Surf} is 673 K.

9.4 3D surface profile



14: Optical 3D profile scan of the rolled beryllium sample obtained using an Alicona IFM [34]. The area marked in light blue (XY-plane) has been hit by the projectile, resulting in a clearly different color of the beryllium. The Z-profile at the bottom shows, that this area has lost approximately 1,0(5) µm of material (compare green and red cross).