

Temperature programmed desorption of 1 keV deuterium implanted into clean beryllium

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Beryllium is planned as a plasma-facing material for ITER covering most of the inner wall of the plasma vessel. It is thus subject to intense fluxes of escaping hydrogen ions from the plasma, which are implanted and retained in the plasma-facing material. As beryllium reacts very quickly with oxygen and especially with water, forming a surface oxide layer even under good vacuum conditions, previous studies of the interaction of deuterium and beryllium had to deal with oxygen contamination as a factor of uncertainty. To rule out the influence of a BeO-covered surface, the retention and release of 1 keV deuterium ions implanted in clean beryllium at room temperature are investigated by temperature programmed desorption (TPD). The surface composition is measured by X-ray photoelectron spectroscopy (XPS). The outline of a retention mechanism is developed by discussing the thermal release behaviour as a function of increasing deuterium fluence.

Introduction

Although a large number of earlier studies have been dedicated to the retention behaviour of hydrogen in beryllium [1], the details of the mechanism are still unclear. Moreover, there is a large scatter in the experimentally evaluated parameters such as detrapping energies, diffusivity, solubility and recombination rates. These values are especially important for ITER to estimate the tritium accumulation in the first wall material, which is an important safety issue. This raises two questions: What are reliable characteristic values that describe the interaction between D and Be and why is there such a poor agreement between different experiments? In this context, the retention and desorption behaviours of D implanted into Be are investigated and conclusions about a retention mechanism are drawn from the results. Special emphasis is put on the control of the elemental surface composition to exclude an influence of contaminated surface layers.

Experimental

The sample under investigation is a polished beryllium disc with a diameter of 14 mm and a thickness of less than 1 mm. One sample was used for all experiments described here. Laue diffraction measurements at various positions on the sample indicate full single crystallinity with an orientation of $(11\bar{2}0)$ and a miss-cut of less than 1° . The surface is cleaned by cycles of 3 keV Ar^+ bombardment under 45° incidence and annealing. The surface composition is monitored by X-ray photoelectron spectroscopy (XPS). The cleaning cycles are repeated until less than 0.2 monolayers (ML) of residual oxygen as only remaining impurity are detected by XPS. Even though the preparation is performed under UHV conditions with a base pressure better than $3 \cdot 10^{-11}$ mbar, an oxygen contamination of 1 ML is accumulated over a period of a few hours demanding further cleaning and annealing prior to each experiment. A fluence of $1 \cdot 10^{17}$ Ar cm^{-2} is needed to regain sub-monolayer oxygen coverage. Annealing the sample at 1000 K removes implanted Ar. The background pressure in the experimental chamber stays below $4 \cdot 10^{-10}$ mbar at this sample temperature. The cleaned sample is implanted at room temperature with a 3 keV monoenergetic and mass-selected D_3^+ ion beam under normal incidence. This corresponds to a kinetic energy of 1 keV per D atom. The beam is not masked by an aperture to prevent contamination of the surface by sputter deposition of aperture material. The beam is scanned over the target by deflection plates (100 V) flattening the implantation profile from the Gaussian-shaped beam over a width of 5 mm. From the measured ion current onto the target, the incoming absolute amount of deuterium ions is determined. The fluence profile is measured by scanning the beam with a Faraday cup with a 0.5 mm opening mounted on the sample manipulator. The increased background pressure of $2 \cdot 10^{-9}$ mbar during implantation is due to molecular deuterium. Temperature programmed desorption (TPD) is performed by positioning the target in front of a differentially pumped funnel that shields both a quadrupole mass spectrometer (QMS) in line-of-sight geometry and the target. The target is heated by electron impact from the backside, increasing the

temperature linearly from room temperature to 1000 K at 0.5, 1 or 4 K/s. The temperature ramps are pre-programmed and optimised for linearity. The sample temperature is measured by a thermocouple spot-welded to the surface. XPS measurements show that one implantation and subsequent TPD up to 1000 K do not increase the oxygen contents of the cleaned Be surface. The absolute retained amount of deuterium and retained fluence in the maximum of the implantation spot are measured by nuclear reaction analysis (NRA) using the $D(^3\text{He,p})^4\text{He}$ reaction at 800 keV. This amount is used to calibrate the deuterium desorption rate measured by TPD. All experiments are performed in situ in a setup described elsewhere in detail [2].

Results

1) Retention

Fig. 1 shows the retained deuterium fluence measured by TPD plotted versus the implanted fluence (in the maximum of the ion beam profile). The order in which the fluence steps were implanted was chosen randomly to exclude an influence of the sample history. Below fluences of $1.5 \cdot 10^{17} \text{ D cm}^{-2}$, a linear fit to the data shows that $78 \pm 3 \%$ of the implanted deuterium is retained in the sample. As expected, the retention tends to saturate at higher fluences. In the steady state, the amount of deuterium lost by erosion from the D-enriched Be region is in equilibrium with the retained amount. The data points are in good agreement with earlier retention measurements [3, 4], although the surface in those experiments was not free of BeO.

2) Desorption characteristics

The thermally activated deuterium release of a saturated sample occurs mainly in two stages: a broad structured stage at a temperature above 700 K and a sharp double peak around 480 K (Fig. 2). The high temperature stage consists of at least two peaks (1 and 2). The low temperature stage is composed of a sharp peak (4) with a shoulder at a higher temperature (3). More than 99% of deuterium is released as D_2 , the rest ($<1 \%$) as HD molecules due to low water and H_2 background pressures. Release of atomic D, D_2O and HDO was not observed. Heating the sample up to 950 K is enough to remove all retained deuterium. This was

confirmed by NRA of a degassed sample. Additionally, no further deuterium is released in subsequent TPD experiments. Such TPD measurements without prior deuterium implantation also indicate that a background correction of the spectra is not necessary, because in that case the signals for D₂ and HD are near the detection limit of the QMS. Fig. 3 shows a series of TPD spectra with D fluences between $4.7 \cdot 10^{16}$ and $1.44 \cdot 10^{17}$ D cm⁻². All fluences in Fig. 3 are below the saturation of the sample. At low fluences (up to $1 \cdot 10^{17}$ D cm⁻²), only the high temperature states (1) and (2) are populated with maxima of the release rate at 800 and 880 K, respectively. The deuterium inventory in these states increases with the fluence. Above $1 \cdot 10^{17}$ D cm⁻², an additional low temperature release stage appears, consisting of peaks 3 and 4. Initially, state 3 is populated. The retention in state 4 increases rapidly and finally retains more deuterium than state 3. The fraction of deuterium in states 3 plus 4 is plotted in Fig. 4 versus the implanted fluence. The low temperature stage appears after the threshold fluence of $1 \cdot 10^{17}$ D cm⁻². The retention behaviour can therefore be divided into three phases. In phase A, only the high temperature states are occupied. In phase B, retention in the low temperature states increases rapidly. The system is in steady state in phase C.

Discussion

The TPD spectra of implanted hydrogen show a superposition of the temperature (and therefore energy) dependence of all release-determining processes. Activation energies for the release-determining processes can thus be obtained from the temperature of release stages. This, however, implies knowledge of the character of the processes and therefore the mechanisms that govern the trapping and release of deuterium. Without prior qualitative assignment of the observed release stages to corresponding release-determining processes, quantification is not possible.

Three principle processes can provide energy barriers for the release of implanted deuterium into the vacuum: diffusion, surface recombination and detrapping from defects. The diffusion

barrier for deuterium in beryllium is very low (0.29 eV [5]) and deuterium diffuses very fast even at room temperature. For this reason, diffusion is no release-determining effect for the experimental conditions discussed here. Deuterium has to form D₂ molecules in order to desorb into vacuum within this temperature range. The recombination rate depends on surface diffusivity and surface binding energies and is therefore directly influenced by the surface chemical composition. TPD spectra (not shown here) demonstrate that none of the observed release stages is directly influenced by changing the chemical surface composition of the sample from Be to more than 1 ML BeO. This indicates that recombination is no limiting effect either. The third and remaining process is detrapping. Therefore, one can suggest that the peaks measured by TPD are caused by the thermally activated detrapping from sites in the Be bulk.

At fluences far below $1 \cdot 10^{17}$ D cm⁻², deuterium is implanted into an undisturbed bulk lattice. This assumption is justified, because the sample is single crystalline and annealed before each implantation at a temperature above half of the melting point [6]. An implantation profile with a maximum at a depth of 30 nm results from calculations by SDTRIM [7]. Two explanations for the high temperature states are possible. They can be due to either intrinsic trap sites or sites created by the collision cascade. If both types of trap sites are intrinsic in the Be lattice, they would be abundant throughout the bulk and their ratio of concentration would be constant. Trapping of stopped deuterium at the end of its collision cascade would occur in the nearest possible trap site (which is accessible by diffusion) leading in average to a constant occupation ratio between state 1 and 2 with increasing fluence. The increase of the temperature up to 800 K during a TPD experiment mobilizes D bound in state 2, enables diffusion through the bulk, and finally trapping again in an unoccupied state 1. If this state is intrinsic, there are always unoccupied sites available. This means that state 2 would never be observed in a TPD experiment. Because it is observed and the ratio of occupation between the two states changes with fluence, at least site 1 is ion induced and must be limited in its

concentration. Increasing the fluence means that the D concentration is locally increased, which leads to a saturation of the trap sites available within the implantation zone. Unoccupied states with the highest binding energy being locally accessible are occupied by diffusion. This explains the behaviour of the system shown in Fig. 3, where at first state 1 and subsequently increasing amounts of state 2 are occupied.

If all possible trap sites are occupied, the local oversaturation enforces a structural modification in the bulk. This occurs at $1 \cdot 10^{17}$ D cm⁻² and explains the sharp threshold fluence observed for the appearance of release states 3 and 4. Lossev et al [9] performed thermal desorption spectroscopy (TDS) of adsorbed atomic deuterium on clean Be surfaces and found a dominant desorption peak at 425 K, which was assigned to surface recombination. Although the low temperature release stage observed in our experiments has almost the same temperature, it is not identical. First of all, the measured release peaks are much sharper than the peaks observed for surface desorption [9]. Under the assumption of a saturated Be surface, the amount released from the low temperature states must be correlated to the sample surface. The fraction of low temperature desorption presented in Fig. 4 is determined from the ratio of the desorbed absolute amounts from high and low temperature stages measured by TPD. Due to the implantation method, the lateral deuterium concentration in the sample is not homogeneous. Instead, the concentration is smaller in the outer regions of the implantation spot. If the low temperature states are created in the center of the irradiation spot, they are not yet created in the outer regions. This means that the fractions shown in Fig. 4 underestimate the amount released from the low temperature stage above $1 \cdot 10^{17}$ D cm⁻². Accordingly, earlier TPD experiments [10] show a higher peak at low temperature. Hence, a lower limit of $6 \cdot 10^{16}$ D cm⁻² can be given for the release from the low temperature stage in steady state, which is more than 30% of the overall retained amount. The D areal density of a saturated Be surface is $1 \cdot 10^{15}$ D cm⁻² [9]. If the low temperature release stage originates from a surface, this surface would accordingly be 60 times larger than the projected (flat) sample surface. Ex-situ atomic

force microscopy (AFM) measurements, however, indicate that the true surface area of the sample is in the range of 1.1 to 1.2 times the projected surface area. This means that release stages 3 and 4 are energetically similar to surface desorption but are not related to the actual sample surface.

There is agreement in the literature that the maximum concentration of D in Be is roughly 0.4 [7], which would equal a formal stoichiometry of $\text{Be}_{2.5}\text{D}$. The inventory of $2 \cdot 10^{17} \text{ D cm}^{-2}$ observed here in steady state, together with an implantation profile calculated by SDTRIM leads a maximum stoichiometry of $\text{Be}_{2.85}\text{D}$. Such a high D concentration cannot be realized by evenly distributed point defects. Assuming only intrinsic traps like interstitial sites, those lattice positions would correspond to e.g. 1/5 of all tetrahedral holes or 2/5 of all octahedral holes within the hcp Be lattice, which had to be occupied by D. Another possibility is that D is not evenly distributed but the concentration of 0.4 is realized by bulk areas of a much higher D concentration (>0.4) and areas of saturated Be grains. The saturation of the Be grains (with a D concentration < 0.4) is reached at $1 \cdot 10^{17} \text{ D cm}^{-2}$. Regarding these considerations and the above discussions of the TPD results, we suggest that D is bound primarily in ion induced defect sites.

Conclusion

The retention of 1 keV deuterium implanted into clean, single crystalline beryllium at room temperature is investigated by TPD up to saturation of the sample. The chemical composition of the near surface region is controlled by XPS and kept below 1 ML residual BeO coverage. About 78% of the implanted deuterium is retained below a fluence of $2 \cdot 10^{17} \text{ D cm}^{-2}$. Above, the sample saturates retaining a D areal density of $2 \cdot 10^{17} \text{ D cm}^{-2}$. The release is not surface-recombination limited. It is suggested that the release-determining processes are detrapping from bulk sites. Four different trap sites are proposed. The two high temperature traps have a release temperature of 800 and 880 K, respectively. At least one of them is created by ion

implantation. Two additional trap sites are supposed to be formed due to structural modifications provoked by local oversaturation of the bulk above a fluence of $1 \cdot 10^{17}$ D cm⁻². The respective release temperatures are 450 and 470 K. They are energetically similar to surface desorption states, but are not related to the sample surface.

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Fig. 1: Retention of 1 keV deuterium implanted into clean beryllium at room temperature. The dashed line is a linear fit to the data points at low fluence and indicates a retention of $78\pm 3\%$. The steady state fluence is above $2\cdot 10^{17}$ D cm⁻². The data points are obtained from TPD measurements calibrated in situ by NRA.

Fig. 2: Typical TPD spectrum ($m/z=4$) of $2.6\cdot 10^{16}$ deuterium ions (fluence in maximum $2.04\cdot 10^{17}$ D cm⁻² at 1 keV) implanted into single crystalline beryllium at room temperature with 0.1 ML residual BeO surface coverage. The heating ramp is 1 K/s. Four release peaks are apparent (labelled 1—4), separated into a high temperature stage (peaks 1 and 2) and a low temperature stage (peaks 3 and 4).

Fig. 3: Series of TPD spectra with increasing deuterium fluences below saturation. The release states are occupied sequentially from the highest to lower temperatures. The low temperature states are absent at low fluences. The spectra are measured at random order.

Fig. 4: The fraction of deuterium released from the low temperature states (3) and (4) as a function of implanted fluence. These states are not occupied at fluences below $1\cdot 10^{17}$ D cm⁻² (region A). The deuterium retention of the sample and accordingly the retention in the low temperature states saturate in region C.

Fig 1:

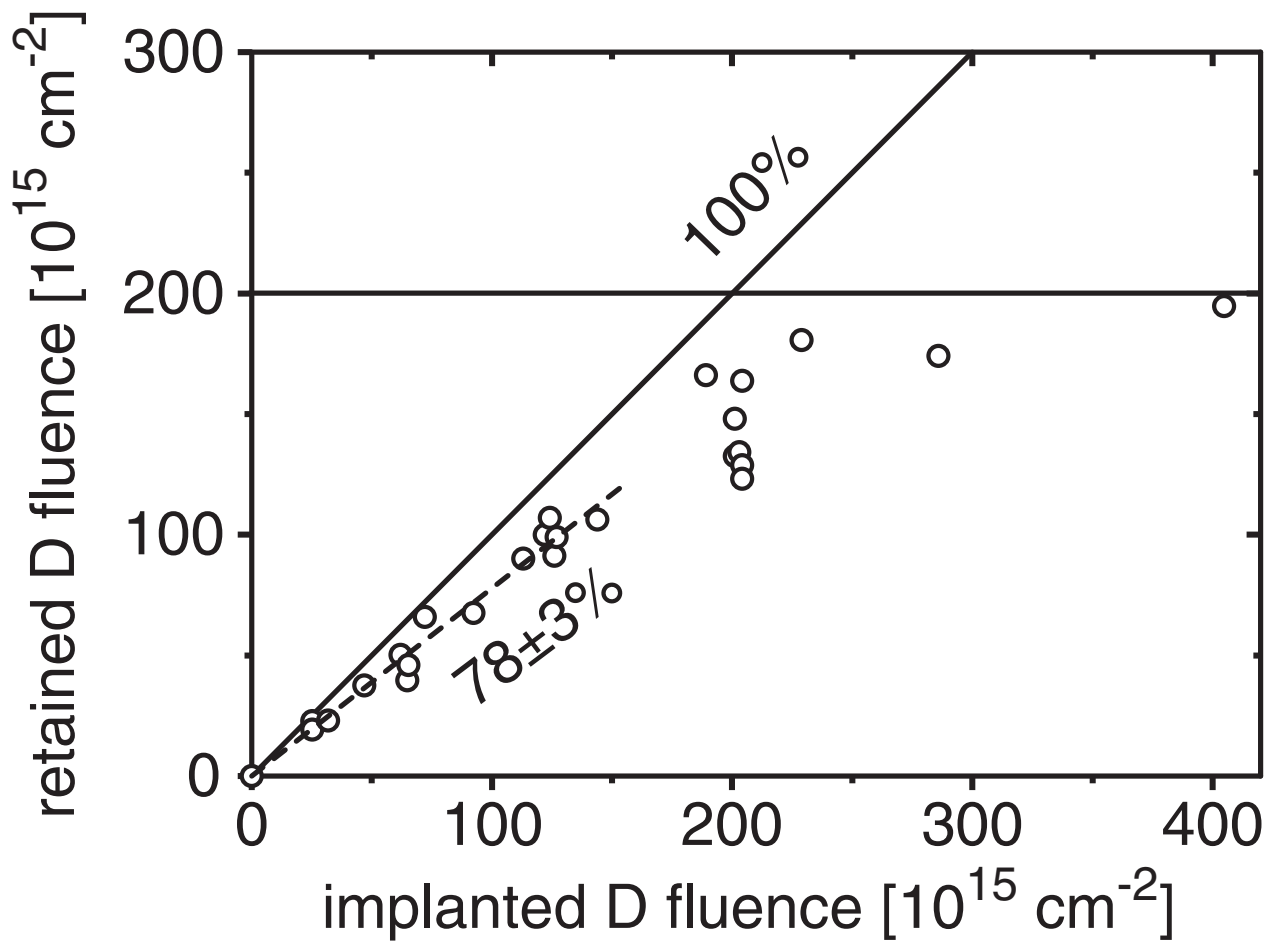


Fig 2:

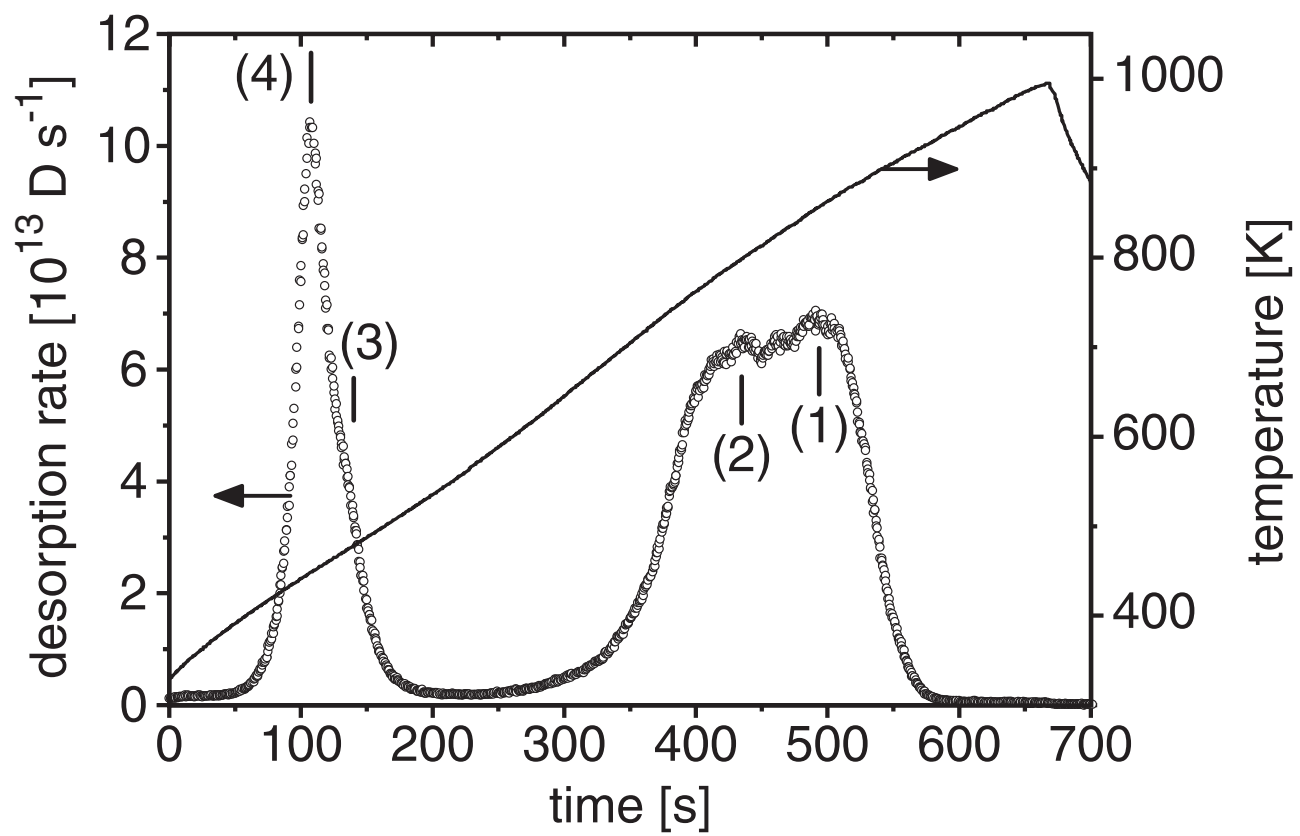


Fig 3:

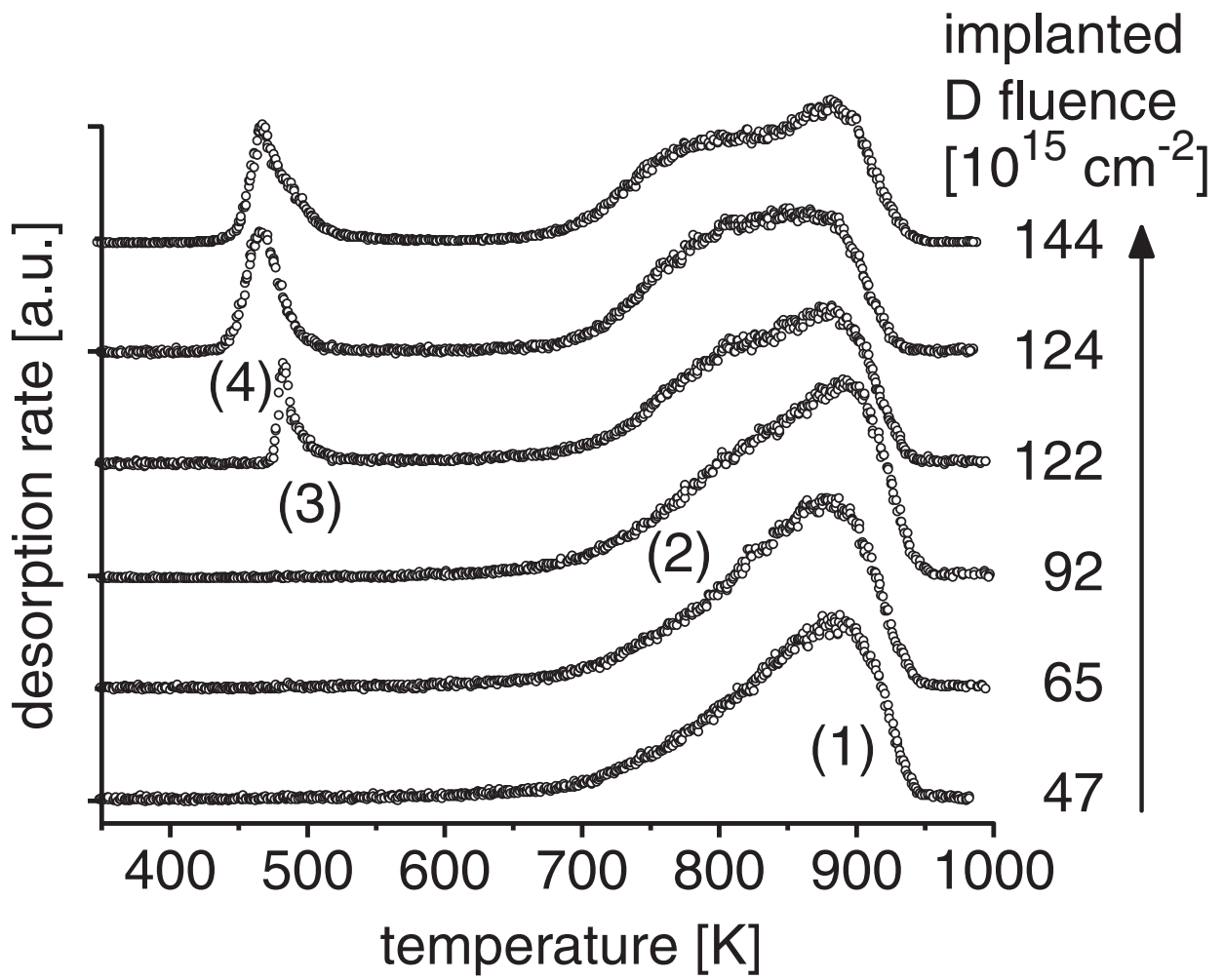


Fig 4:

