Thermal release of D₂ from new Be-D co-deposits on previously baked co-deposits

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Abstract

Past experiments and modeling with the TMAP code in [1, 2] indicated that Be-D co-deposited layers are less (time-wise) efficiently desorbed of retained D in a fixed low-temperature bake, as the layer grows in thickness. In ITER, beryllium rich co-deposited layers will grow in thickness over the life of the machine. Although, compared with the analyses in [1, 2], ITER presents a slightly different bake efficiency problem because of instances of prior tritium recover/control baking. More relevant to ITER, is the thermal release from a new and saturated co-deposit layer in contact with a thickness of previously-baked, less-saturated, co-deposit.

Experiments that examine the desorption of saturated co-deposited over-layers in contact with previously baked under-layers are reported and comparison is made to layers of the same combined thickness. Deposition temperatures of ~ 323 K and ~ 373 K are explored. It is found that an instance of prior bake leads to a subtle effect on the under-layer. The effect causes the thermal desorption of the new saturated over-layer to deviate from the prediction of the validated TMAP model in [2]. Instead of the D thermal release reflecting the combined thickness and levels of D saturation in the over and under layer, experiment differs in that, i) the desorption is a fractional superposition of desorption from the saturated over-layer, with ii) that of the combined over and under -layer thickness. The result is not easily modeled by TMAP without the incorporation of a thin BeO inter-layer which is confirmed experimentally on baked Be-D co-deposits using x-ray micro-analysis.

Keywords: Beryllium, Co-deposits, Desorption, ITER, TMAP, PISCES

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1. Introduction

In non-erosion dominated locale in ITER, beryllium (Be) rich layers, formed by the co-deposition of eroded first wall Be and incident plasma species, are projected to be a driver [3, 4] of the in-vessel tritium (T) inventory. According to simulations [5, 6], the layers are expected to be up to ~ 1 μm thick per ITER shot, and high retained total T levels of potentially grams per shot [6] are possible depending on co-deposition conditions. In laboratory plasma-material interaction (PMI) studies [7, 8, 9, 10, 11, 12, 13, 14], it has been shown that the isotope deuterium (D) readily traps with co-deposited Be and compositional fractions of D/Be > 0.1 can occur, particularly if the substrate temperature is low (< 500 K) and energetic species bombardment is present. The high level of D inventory in Be co-deposits is accommodated by the action of two types of trap, separated by ~ 0.2 eV, and reported to be in the energy range $0.6 - 1.3$ eV [1, 2, 7, 9, 15, 16]. While, a clear physical picture of these trap mechanisms remains elusive, the ~ 1 eV trap release energy means that low temperature baking, such as will be employed in ITER, provides a means of recovery for some fraction of the trapped inventory [1].

The current ITER strategy to keep T accumulation below the 700 g in-vessel administrative limit [4], involves baking of the first wall and divertor, at 513 K and 623 K respectively. Past laboratory work has focused on the study of the efficacy of hydrogen isotope removal from Be-D co-deposits [1, 2] through the systematic study of co-deposit thermal desorption combined with modeling with the Tritium Migration and Analysis Program (TMAP-7). In Ref. [2], it was shown in both experiment and model, that increasingly time inefficient hydrogen removal is evident as a co-deposited layer grows in thickness; a consequence of the increased random walk time for hydrogen in relatively thicker layers before escape from a surface boundary, coupled with the re-capture action of depleted traps. The prior work, however, did not consider the potential influence of baking the thickness of under-layer co-deposit. So, the question naturally arises: In that case, does the combined thickness of the co-deposit dictate the thermal release, as in [2], or does the new relatively more thin co-deposit over-layer desorb in a manner reminiscent of its own intrinsic thickness? In terms of bake efficiency, the worse case is the situation that the over and under layer act as a single combined and thicker layer. Conversely, the better scenario is that the over-layer

desorbs in a manner that reflects its relative 'thinness' with respect to the overall layer thickness. The experiments reported here investigate this issue.

2. Methods

The majority of methods and procedures employed in the current work are described in detail in [1, 2] and so are only briefly covered here.

2.1. Multi-layered repeat baked co-deposited layers

Multi-layered Be-D co-deposits are formed at controlled temperature on 2 mm diameter tungsten (W) substrate spheres using a sputter magnetron coating method [1]. Thermal release of deuterium from the multi-layered spheres is measured using the technique of thermal desorption mass spectrometry (TDS). TDS involves heating a sphere in-vacuo so that its temperature varies linearly in time, while the evolution of the partial pressure corresponding to a relevant hydrogen isotope species, is recorded; in this case D_2 . The same method is used for the baking of a layer at fixed temperature.

To examine the influence of a prior bake on subsequent over-layer thermal desorption, different types of Be-D co-deposited multi-layer systems are explored. The process starts with batches of W spheres, and figure 1 illustrates the steps in producing the various Be-D multi-layered sphere systems, labeled ①-③:

Figure 1: Schematic depiction of types of baked and built up multi-layered Be-D co-deposited sphere samples used in this study. (Note: In general, under and over -layers are not necessarily the same thickness, but for meaningful comparison the combined thickness of the multi-layered systems must be consistent.)

- 55 ① A batch of W spheres is coated, at fixed temperature, in a layer of Be-D
 56 co-deposit. Layer thickness is determined by batch mass gain. A se-
 57 lected sphere is desorbed using TDS to measure the layer (or equivalent
 58 to under-layer) thermal release properties.
- 59 ② A fraction of the spheres from the batch ① are further coated, at same
 60 fixed temperature, with additional Be-D co-deposit, to build up a
 61 thicker overall multi-layer consisting of an under and over-layer. Again,
 62 batch mass gain gives the over-layer thickness. The thermal release of
 63 the combined layer is then also measured with TDS. Steps ① and ②
 64 provide the basis for understanding the co-deposit thermal release as a
 65 function of layer thickness, as was demonstrated in [2].
- 66 ③ A separate single layered sphere batch, of the type produced by step ①,
 67 is fully, or partially, baked using TDS to deplete all or a fraction of the
 68 layer inventory. An over-layer of Be-D co-deposit is then applied. The
 69 TDS thermal release from this combined multi-layer system reveals the
 70 influence of a prior full, or partially, baked under-layer in contact with
 71 an over-layer of new saturated co-deposit. For the purpose of compar-
 72 ison, the over-layer of sphere type ③ is made identical in thickness to
 73 the under-layer of sphere type ②, and care taken to ensure that the
 74 overall multi-layer thickness is identical to sphere type ②.

75 2.2. TMAP modeling

76 The thermal release from the multi-layered co-deposit systems in sim-
 77 ulated as described in [1, 2] using the TMAP-7 hydrogen transport code
 78 [17, 18]. The TMAP computes the time varying solution for hydrogen isotope
 79 concentration and flows in a system of enclosures and structures given the
 80 presence of hydrogen. The simulation provides for full interaction between
 81 gaseous hydrogen species in enclosures and, dissolved and trapped hydrogen
 82 species in structures. Boundary conditions include time dependent hydrogen
 83 sources and sinks, enclosure and structure physical properties and thermal
 84 history, and the initial distributions of hydrogen in the system.

85 A single layer TMAP model for Be-D co-deposits is described in detail in
 86 [1, 2]. Here, that same model is extended to accommodate additional Be-D
 87 co-deposited layers, in a multi-layer arrangement, utilizing the same known
 88 trap types, and recombinative surface release at the uppermost top layer. To
 89 be certain of the reliability of the multi-layered model, effort was invested

in validating it against the single layered model of [1, 2]. This was done by ensuring that a multi-layer TMAP solution was degenerate with a single layer computation for the same overall thickness.

A further consideration is given as to how the hydrogen distribution in the multi-layered systems is accommodated. In the TMAP simulations of [1, 2], a uniform distribution of D in a saturated co-deposited layer is assumed, and good agreement is found between the simulated thermal release, and that of experiment. The uniformity of the hydrogen distribution in such layers is confirmed experimentally in the recent work of Kogut *et al.* [19]. In the current work, the same assumptions are made, but, in the case of baked under-layers, the baked layer D distribution is established from TMAP simulation of the experimental thermal history of the layer, as was described previously in [1, 2], and shown, also, to be in good agreement with experiment.

2.3. Layer analysis

Where necessary, surface analysis methods are used to examine specific co-deposited Be-D layer properties. These methods included scanning electron microscopy (SEM), energy and wavelength dispersive x-ray micro-analysis (EDX) and (WDX), and glancing angle x-ray diffraction (GAXRD). SEM and EDX-WDX were undertaken using a JEOL-JSM 6360 electron microscope with an on-board Inca x-ray micro-analysis system from Oxford Instruments. XRD was undertaken by Evans Analytical Group, Inc. using a PANalytical XPert Pro MRD diffractometer set to an incidence angle of 0.7° .

3. Results

Multi-layered sphere types (refer to figure 1) were formed under two different deposition temperature regimes, ~ 323 K and ~ 373 K. The different temperatures result in different levels of trapping and desorptive behavior from Be-D co-deposited layers, characterized by activity from one or both of the observed ~ 1 eV trap types. It is therefore necessary to detract from the results of multi-layer desorption, briefly, and examine the basic desorption properties of co-deposits as a function of the deposition temperature.

122 3.1. Co-deposit thermal release with deposition temperature

123 In figure 2, TDS data from single Be-D co-deposited layers are shown
 124 for four different deposition temperatures. The layer deposited at 330 K¹
 125 shows desorption features reminiscent of the activity of the two ~ 1 eV traps
 126 (labeled P1 and P2). Layers formed at a higher deposition temperature of 373
 127 K and above show desorption due mostly to release from the higher energy
 128 trap P2, but with decreased magnitude as the deposition temperature is
 129 increased to 450 K. The dashed lines are TMAP modeling, and the simulations
 130 indicate that the three higher temperature cases are best accommodated by
 131 fully removing the effect of trap P1.

132 The inset of figure 2 shows the Be-D fraction in the layer according to
 133 the results of the respective TMAP models, the trap parameters for which
 134 are given for completeness in Table 1². The results (symbols) agree with the
 135 full line, which is the De Temmerman *et al.* empirical scaling [13] calculated
 136 for the deposition conditions of the current magnetron set-up [1]. The ITER
 137 bake temperatures, $T_{b1} = 513$ K and $T_{b2} = 623$ K are also shown in figure
 138 2. In general, the placement of these reference temperatures relative to a
 139 release peak temperature serves as a rough indicator of the effectiveness of
 140 that temperature for inventory removal during a fixed temperature bake. For
 141 instance, in [1], for layers deposited at ~ 330 K, it is shown that the wall
 142 bake temperature T_{b1} is effective for bake removal of the inventory in trap P1,
 143 but almost ineffective for inventory removal from trap P2, while the divertor
 144 bake temperature, T_{b2} thermally accesses both trap types.

Table 1: TMAP trap parameters for simulations in figure 2. Variable definitions are given in [1] and Appendix A.

T_{dep} (K)	L (μm)	C_0^{t1}/N	f_{t1}	C_0^{t2}/N	f_{t2}
330	1.0	0.098	0.7	0.032	0.3
373	0.8	-	-	0.083	0.7
403	0.8	-	-	0.092	0.7
450	0.8	-	-	0.050	0.7

In all, $E_m = 0.364$ eV, $E_{r1} = 0.743$ eV, $E_{r2} = 0.940$ eV, $\alpha_{ti} = \alpha_{ri} = 4 \times 10^{12} \text{ s}^{-1}$.

¹TDS data (330 K) and simulation reproduced from [1].

²Other TMAP model details are given in [1, 2].

Figure 2: TDS data from Be-D co-deposited layers formed at 330 K (reproduced from [1]), 373 K, 403 K, and 450 K. Dashed lines are TMAP simulations. The heating rate was 0.3 Ks^{-1} . Labels, P1 and P2, refer to desorption peaks associated with different trap energies [1]. Dotted lines indicate the ITER bake temperatures, $T_{b1} = 513 \text{ K}$ and $T_{b2} = 623 \text{ K}$. The ordinate minor tick increment is $4 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$. The inset is a plot of the D:Be ratio (symbols) in TMAP simulations ($\Sigma_t C_0^t f_t / N$) against T_{dep} , and agrees with the De Temmerman *et al.* scaling [13] (line).

145 3.2. Multi-layered co-deposit release

146 With reference to the influence of deposition temperature on Be-D co-
 147 deposit thermal release, shown in figure 2, the results of multi-layered, re-
 148 peated bake desorption can be interpreted, and two different deposition tem-
 149 perature regimes (~ 323 K and 373 K) are explored. Figure 3 shows D_2
 150 TDS data (symbols) from layered spheres created using the steps outlined
 151 in figure 1. These layers are produced at the low deposition temperature of
 152 ~ 323 K and consequently show desorption activity from both trap types, as
 153 is the case also in figure 2. For this set of data the under-layer was $0.22 \mu\text{m}$
 154 in thickness and the over-layer $0.44 \mu\text{m}$, giving a combined $0.66 \mu\text{m}$ thick
 155 layer system. The thermal desorption of spheres of type ① and ② reflect the
 156 release behavior of layers of varied thickness³, as described in [2]. The dashed
 157 lines through TDS data ① and ② are single and double layer TMAP models
 158 and agree with experiment. In the double layer TMAP model, ideal contact
 159 and homogeneity across the under and over -layer interface is assumed. Thus,
 160 by the agreement between the simulations, ①, ②, and the TDS data ①, ②,
 161 it is the case that multi-layers produced in-vacuo at low temperature, are
 162 not far from this assumption in practice. The dotted line shows, again for
 163 reference, the ITER wall bake temperature $T_{b1} = 513$ K, and highlights the
 164 fact that thicker layers are relatively more difficult to desorb, time-wise, by
 165 the subtle shifting of the desorption peaks (① $\rightarrow$ ②) to higher temperature.

166 The situation becomes interesting however, when examining the TDS
 167 data from the combined over and under -layer system formed on sphere ③,
 168 whereby the under-layer was baked to full D inventory removal at 923 K for
 169 6 minutes following a 0.3 Ks^{-1} ramp from room temperature. For sphere
 170 ③, the baked under-layer was $0.44 \mu\text{m}$ in thickness and the over-layer 0.22
 171 μm , giving the same $0.66 \mu\text{m}$ total thickness as sphere ②. The correspond-
 172 ing TDS data reveals the degree to which the over-layer interacts with the
 173 under-layer during desorption. A complete lack of layer interaction could
 174 only give rise to desorption similar to TDS data set ①, since the single layer
 175 of ① and the over-layer of ③ are both $0.22 \mu\text{m}$ thick. On the other hand,
 176 full interaction sees the inventory of the over-layer in transport through the
 177 under-layer as TDS progresses, in accordance with the total thickness of the
 178 superimposed under and over-layer system. The TMAP simulation ③, is a
 179 description of such layer interaction but does not describe experiment to the

³TDS data and simulations for cases ① and ② are reproduced from [2].

Figure 3: TDS data from sphere types ① and ② (reproduced from Ref. [2]), and ③ for Be-D co-deposited layers formed at 323 K. Dashed lines are TMAP simulations of the TDS data using input to be found in Table 2 and [1, 2]. The rate of heating was 0.3 Ks^{-1} . For reference, $T_{b1} = 513 \text{ K}$ indicates the ITER wall bake temperature.

180 usual level of agreement. In the TMAP simulation ③, when compared to ①,
 181 the initial D_2 release to vacuum from lower temperature traps (P1) in the
 182 over-layer is considerably reduced and the simulation, more or less, takes on
 183 the thermal release nature of the thicker overall layer system, ②. Figure 4,
 184 which shows the corresponding TMAP simulated deuterium fluxes across both
 185 boundaries of the over-layer as TDS progresses, demonstrates why. Well be-
 186 fore any release flux of deuterium to vacuum ③, there is a significant internal
 187 deuterium flux from the over-layer into the under-layer. However, this trend
 188 is reversed at high temperature, owing to the Arrhenius increase of surface
 189 recombination (D_2 release) at the vacuum side. Comparison of the two flux
 190 trends reveals the issue at hand regarding the expected loss of bake efficiency
 191 for a newly deposited saturated over-layer on a previously baked under-layer

192 system. In this example, there is a larger over-layer flux of deuterium into
 193 the under-layer than into vacuum at the ITER wall bake reference T_{b1} . A
 194 considerably longer fixed temperature bake, or higher temperature, is thus
 195 necessary to return to the prior level of time-wise bake efficiency.

Figure 4: TMAP simulated over-layer (o) boundary fluxes for sphere type ③ in figure 3. The under-layer (u) was baked to complete inventory removal. Simulation parameters are given in Table 2. The rate of heating is 0.3 Ks^{-1} . $T_{b1} = 513 \text{ K}$ indicates the ITER wall bake temperature.

196 In practice however, the actual TDS desorption from sphere type ③ in
 197 figure 3, resembles a fractional superposition of TMAP simulations ① and
 198 ③; the implication being, that there is an influence at play that affects
 199 the transport from the over-layer to the under-layer during TDS, but this
 200 influence is only active when the under-layer is baked. Note that it does not
 201 manifest with sphere ②, which is also a built up multi-layer, and for which
 202 both TDS data and TMAP agree.

203 A similar situation is found with the 373 K deposited layer experiments

Figure 5: TDS data from sphere types ①, ② and ③ for Be-D co-deposited layers formed at 373 K. Dashed lines are TMAP simulations of the TDS data using input to be found in Table 2 and [1, 2]. The rate of heating was 0.3 K s^{-1} . For reference, $T_{b2} = 623 \text{ K}$ indicates the ITER divertor bake temperature.

204 and TMAP simulations in figure 5, where an identical set of results to figure
 205 3 is displayed, but due to the higher deposition temperature, only desorption
 206 from the higher temperature trap (P2) is apparent (see figure 2). Again, the
 207 TDS desorption data of spheres ①, and ② reflect the characteristic shifting
 208 of the peak as the layer doubles in thickness from $0.8 \mu\text{m}$ to $1.6 \mu\text{m}$, and
 209 TMAP simulations agree with the TDS data for sphere types ① and ②. In
 210 producing sphere ③, the under-layer was baked for 2 h at 623 K to imitate a
 211 short ITER like divertor bake, resulting in an under-layer inventory reduction
 212 by 67 %, prior to depositing the over-layer. Again, the results for ③ are
 213 interesting, and the TMAP simulation displays similar behavior to the prior
 214 lower temperature deposited example of figure 3. That is, the simulation
 215 suggests that the over-layer inventory is rapidly re-distributed throughout

the combined layer thickness as TDS progresses, and that recapture action by combined layer traps, shifts the overall release to higher temperature, more consistent with layer ②. Yet, just as with the TDS data set ③ of figure 3, the actual thermal release of sphere ③ appears to be a fractional superposition of TMAP simulations ① and ③. This is the influence of the prior bake. To reiterate, the nature of this effect is to preserve some fraction of the D₂ release from the over-layer in a manner that reflects only the over-layer thickness, while the remaining fraction reflects the total multi-layer thickness. The TMAP layer parameters used to generate the curves in figures 3, 4 and 5 are given in Table 2.

Table 2: TMAP trap parameters for built up layer simulations in figures 3, 4, 5 and 9.

T_{dep} (K)	Sphere (Fig. 1)	Layer	L (μm)	$C_0^{t_1}/N$	f_{t_1}	$C_0^{t_2}/N$	f_{t_2}	T_{bake} (K)	t_{bake} (h)
323 [†]	①	single	0.22	0.076	0.7	0.016	0.3	923	0.1
		under	0.22	0.076	0.7	0.016	0.3		
		over	0.44	0.076	0.7	0.016	0.3		
	③	under	0.44	0.076	0.0	0.016	0.0		
		over	0.22	0.076	0.7	0.016	0.3		
373 [‡]	①	single	0.80			0.083	0.7	623	2.0
		under	0.80			0.083	0.7		
		over	0.80			0.083	0.7		
	③	under	0.80			0.083	0.2		
		over	0.80			0.083	0.7		

In all, $E_m = 0.364$ eV and $\alpha_{t_i} = \alpha_{r_i} = 4 \times 10^{12} \text{ s}^{-1}$.

[†] $E_{r_1} = 0.805$ eV, $E_{r_2} = 0.980$ eV. [‡] $E_{r_1} = 0.743$ eV, $E_{r_2} = 0.940$ eV.

3.3. EDX-WDX and GXRD analysis of unbaked and baked co-deposits

Figure 6 shows scanning electron micro-graphs of a selection of the Be-D coated sphere targets of figure 2 under high magnification. The images (a)-(c), taken immediately following deposition, show little difference between layers deposited at the different temperatures of 373, 403 and 450 K. All of the layers are well adhered and free of any obvious irregularity. However, in contrast, a sphere similar to that shown in (a), but further baked to 623 K in-vacuo for 2 h (d) shows clear differences in surface morphology. Contrast is enhanced and the surface takes on a visually speckled appearance.

The baked layer of figure 6(d), was further examined using EDX-WDX, and revealed a slightly better than fourfold enhancement in x-ray fluorescence

Figure 6: Electron micro-graphs of (a)-(c) W spheres coated with $0.8 \mu\text{m}$ thick Be-D layers formed at 373 K, 403 K, and 450 K, and (d) a sphere such as in (a) further baked at 623 K in-vacuo for 2 h.

237 associated with oxygen (O), compared to a freshly deposited un-baked case.
 238 EDX, which detects, but is insensitive to Be for compositional quantification,
 239 did not show evidence of any elements other than Be, O, and W. Quantitative
 240 analysis of these elements was therefore pursued with WDX, that does allow
 241 quantification. To perform WDX analysis, the electron beam energy was set
 242 to 15 keV, so that a small and closely comparable level of x-ray fluorescence
 243 could be detected from the underlying W substrate sphere in both the baked
 244 and unbaked co-deposited layers. This ensured that the volume of material
 245 probed by the electron beam was consistent in both samples, and sufficient
 246 such that the entire co-deposited layer is probed depth-wise, and contributes
 247 detected x-rays. Determination of the composition is facilitated by compar-
 248 ison to x-rays detected from calibration samples of Be, W, and SiO_2 , taken
 249 under the same beam parameters. The unbaked sample revealed an O con-
 250 tent of 0.6 at.% while the baked layer was measured at 2.7 at.%, with an
 251 uncertainty being ± 0.1 at.%. Given the thickness of the each co-deposited
 252 layer as $0.8 \mu\text{m}$, and assuming the localization of the O at the surface, as in
 253 [20], this corresponds to surface oxidation thicknesses of $\sim 9 \text{ nm}$ and ~ 43
 254 nm respectively when taking stoichiometry into account. A thin oxide layer
 255 must also be present on the W substrate; WDX analysis shows considerably
 256 less O count from a W sphere without a Be layer, but rather than neglect

257 this contribution it is assumed that at most, the W oxide layer is of similar
 258 thickness to that of an unbaked Be-D co-deposit layer. Therefore, we infer
 259 an unbaked layer to have an oxide layer of thickness ~ 4 nm and a baked
 260 layer close to ~ 40 nm.

261 Another influence on the co-deposited Be-D layers, that may potentially
 262 affect desorptive behavior, could be due to the elevated temperature during
 263 baking causing structural change in the material. GAXRD was used to look
 264 for such structural changes, if any, as bake temperature is varied. Because
 265 the multi-layered sphere samples are of incompatible size and geometry for
 266 GAXRD, four separate co-deposited Be-D layers were produced on flat 20
 267 mm diameter W disc samples at 360 K for this analysis. Each co-deposited
 268 layer was $7\text{ }\mu\text{m}$ thick, and produced using the same methods and practices
 269 described in [1] and/or step ①. Three layers were separately baked for 2 h
 270 at 513 K, 623 K and 923 K respectively, whilst one layer was left unbaked,
 271 for comparison as a control case. A pure bulk Be target supplied by Brush-
 272 Wellman was also examined.

Table 3: Glancing angle x-ray diffraction determined crystallite properties for un-baked and baked Be-D co-deposited layers, and bulk Be

Material	T_{dep} (K)	T_{bake} (K)	t_{bake} (h)	Avg. crystallite size	
				Be (nm)	W (nm)
Be-D (control)	360			40 ± 8	19 ± 4
Be-D	360	513 (T_{b1})	2	40 ± 17	18 ± 5
Be-D	360	623 (T_{b2})	2	67 ± 26	23 ± 6
Be-D	360	923	2	200 ± 50	32 ± 6
Be (bulk)				172 ± 50	

273 The results of the GAXRD analysis are summarized in table 3. Bragg
 274 reflections were observed for both Be and W crystal phases. No convincing
 275 evidence for BeO structure was found, but this is not expected due to the
 276 thinness of any BeO layer ($\sim$ a few tens of nm at best). Further, the av-
 277 erage crystallite size, determined by analysis of Be and W x-ray signatures
 278 indicated little change in the structural properties (within error) of the co-
 279 deposited layers as a result of baking in vacuo up to 623 K, but a change in
 280 the average crystallite grain size is found for bake at the much higher tem-
 281 perature of 923 K. Crystallite size increased from $\sim 40 - 60$ nm, typical for

co-deposit, to ~ 200 nm for the 923 K baked layer; a value close to that of the bulk Be sample.

4. Discussion

The TDS data of figure 2, as with prior work [1, 2, 9, 7, 12] show that Be co-deposited layers are highly efficient at trapping levels of hydrogen isotopes far in excess of that soluble in crystalline Be [21]. In agreement, the inventory fraction follows the prior established Be-D co-deposit PMI scaling of De Temmerman *et al.* [13, 14]. The high level of inventory is accommodated by the action of two trap types separated by ~ 0.2 eV, that lie in the energy range $0.6 - 1.3$ eV [1, 2, 7, 9, 15, 16]. It is interesting to note, in figure 2, that the thermal release activity by the lower temperature trap is not observed for deposition temperatures of 373 K and above. However, evidence of release from this trap state was apparent at 373 K in [14], which means that the impact of this trapping mechanism on ITER inventory can not be ignored in spite of the expected ambient wall temperature being close to 373 K.

The current experiments suggest a subtle, if not positive influence on subsequent bake efficiency, that manifests because of an instance of prior baking. Although, this effect is difficult to properly quantify without further systematic study. The described influence is evidenced by figures 3 and 5, which depict TDS data of layer systems ③ that have some characteristics of layer ① desorption. That is, new saturated co-deposited layers (overlayers) release some inventory at a lower temperature, that reflects its own 'thinness', relative to the higher temperature release seen with the combined thickness of it and prior layers. Prior work [2] demonstrated in both experiment and in modeling, that such relatively thicker co-deposited layers incur a loss of time-wise bake efficiency as co-deposits gain thickness over time. Based on that work, an instance of prior baking was expected to be such that baked (depleted) under-layer traps capture some fraction of the inventory from the newly deposited and saturated over-layer on the next instance of baking. And, according to TMAP simulations, both under and over -layers act as a single comparatively thicker layer, which nevertheless, requires increased bake time to give up a similar fractional level of inventory [2]. This is what is shown by TMAP simulations ③; but such simulations do not fully agree with TDS data ③. The disagreement lies with an influence that affects Be-D co-deposited layers when baked in-vacuo, in such a way as to inhibit the 'usual' D transport from a newer over-layer, into under-layers, when next baked;

318 with ‘usual’ implying what is seen with TDS data and TMAP simulation ②,
 319 that do in fact agree, and where the under-layer is not baked. To re-iterate,
 320 the TDS data ③ reveal thermal release characteristics that are a fractional
 321 superposition of a singular over-layer release ① and the expected release ③
 322 predicted by TMAP. If applied to an ITER scenario, a better understanding,
 323 and control of this influence, could potentially lead to optimal time-wise bake
 324 removal efficiency for trapped Be co-deposit inventory in newly deposited
 325 over-layers in multi-layer systems.

326 Comparative surface analysis of unbaked and baked Be-D co-deposits
 327 using EDX-WDX reveals the presence of oxidation of respective thicknesses
 328 ~ 4 nm and ~ 40 nm. Both values are in good agreement with recent work by
 329 Roth *et al.* [20], where the oxidation of bulk Be samples by atmospheric gases
 330 as a function of temperature was studied. Although not directly comparable
 331 to the current work, their work showed that an oxide layer $\sim 10 - 60$ nm
 332 thick can form in 6 h of exposure to air at ~ 600 K, similar to the baked
 333 co-deposit, and below 450 K the thickness of the oxide was better than an
 334 order of magnitude less, comparable to the unbaked case. In view of this, it
 335 is not unreasonable to argue that in-vacuo bake results in an O rich surface
 336 layer due to uptake from residual gas in the TDS vacuum. The TDS system
 337 base pressure is $\sim 1.3 \times 10^{-5}$ Pa and residual gas analysis shows the dominant
 338 gaseous contributors to correspond to the masses of N_2 , O_2 and H_2O .

339 GAXRD measurements show that baked Be-D co-deposits undergo struc-
 340 tural change in terms of crystal growth at high temperature 923 K but little
 341 change is noted at 623 K. It is interesting to note that even at 923 K, a
 342 significant fraction of any empty traps must have been preserved in spite of
 343 the physical change in crystallite dimensions. This is because, in the case of
 344 TDS data ③ in figure 3, a broad release profile is found following the 923
 345 K bake. Had the depleted trap concentration been annealed or diminished,
 346 due to the high temperature bake and accompanying crystallization growth,
 347 the TDS desorption of ③ would have reverted to a ① style release according
 348 to TMAP simulation of such an effect. One could, however, take the view
 349 that that is what TDS data ③ may in fact show. But, in that sense the ③
 350 TDS profile in figure 3 would not be consistent with TDS data ③ in figure
 351 5, which showed the same behavior, but for which the bake temperature was
 352 only 623 K, and crystallite size was not increased.

353 Thus, taken together, the EDX-WDX and GAXRD results suggest that it
 354 is less likely that bake induced structural changes or trap depletion affects
 355 baked multi-layer desorption, and more likely that surface O uptake plays a

356 role.

357 4.1. The influence of a bake induced surface-oxide diffusion barrier

358 In this section additional evidence, argument and TMAP modeling is
359 shown, that is consistent with the surface oxidation of Be-D co-deposited
360 layers, when baked, acting as a diffusion barrier to the D inventory. It is
361 shown that TMAP simulations of similarity to type ③ TDS data are obtained
362 when this is taken into account. However, to study this conclusively requires
363 systematic experimentation, and for this reason the following is presented as
364 discussion, rather than in the main body of results.

365 In view of evidence given by EDX-WDX analysis, a BeO inter-layer TMAP
366 model was developed in an attempt to achieve better agreement with TDS
367 data ③. Model results are presented that compare to the TDS data ③ of
368 figure 5, but a similar level of agreement was also found with the TDS data
369 ③ of figure 3. The BeO inter-layer model, is an extension of the double
370 layer version described in Table 2, and differs only by the inclusion of a thin
371 ($\sim$ nm scale) BeO diffusion barrier⁴, or inter-layer, between the under and
372 over -layers. However, it is found that such a BeO inter-layer model is highly
373 sensitive to the BeO diffusivity in spite of the thinness of the BeO inter-layer,
374 and that the widely accepted literature value for D in BeO of Fowler *et al.*
375 [23] did not account for the TDS observations ③ of figures 3 and 5. The
376 quoted result of Fowler *et al.* is simply too low. The natural question that
377 follows is how applicable the BeO diffusivity of Fowler *et al.* is to the current
378 experiments, given the considerably different nature of co-deposits compared
379 to bulk Be. Based on smaller crystallite size, as indicated in table 3, and
380 hence increased opportunity for fast grain boundary diffusion, a more rapid
381 diffusivity is arguable.

382 The influence of passivating oxide layers on thermal D release from ion
383 implanted Be has recently been studied [24, 25]. Both studies note the need
384 for a moderate increase in temperature to fully desorb D from the implanted
385 BeO layer compared to pure Be, but it is also noted that a thin oxide layer
386 does not act as strong diffusion barrier to D trapped in an underlying Be
387 substrate. The BeO inter-layer TMAP simulations implied the same: the D
388 in BeO diffusivity of Fowler *et al.* [23] being too small to give agreement with

⁴The D in BeO solubility was taken from [22] and the diffusivity from Fowler *et al.* [23].

Figure 7: TDS data from a deuterium plasma exposed oxidized Be sample. Full details about this sample are given in Fig. 6(a) in Ref. [20] and accompanying text. The rate of heating was 0.3 Ks^{-1} . The dashed lines are TMAP models for different D in BeO diffusivities, D_i , and D_{ii} . D_i is taken from [23], D_{ii} is discussed in the text.

389 TDS data sets ③, but the diffusivity of D in Be (i.e. no barrier) being to
 390 high.

391 To address this, a stored sample from prior experiments [20] was further
 392 analyzed using TDS. This sample had a history that included oxidation in
 393 atmosphere and subsequent exposure at $\sim 300 \text{ K}$ to $\sim 30 \text{ eV}$ deuterium ions
 394 in the periphery of a PISCES-B plasma. In [20] the D depth profile for the
 395 target was measured using nuclear reaction analysis (NRA) (Refer to Fig. 6a
 396 in [20]), making TMAP modeling of the TDS thermal release possible. Figure
 397 7 shows the resulting TDS thermal desorption profile. Also shown are two
 398 TMAP simulations of the expected thermal release for this sample based on
 399 the specified NRA D depth profile. In simulations the surface recombination
 400 rate for D release is taken as the Arrhenius rate for a Be surface [1] and only

401 the D in BeO diffusivity is varied. The simulation labeled D_i is based on
 402 the best fit diffusivity for D in BeO given by Fowler *et al.* [23]. Notably,
 403 the simulated release occurs at much higher temperature ~ 800 K and does
 404 not reflect the actual TDS data set. That is, the diffusivity is too low to
 405 explain the observed TDS release. On the other hand, using the diffusivity
 406 as a free parameter can give better agreement with the TDS data. The
 407 diffusivity $D_{ii} = 4.0 \times 10^{-12} \exp(-0.67[\text{eV}]/kT)$ $[\text{m}^2\text{s}^{-1}]$ better describes the
 408 experimental TDS data, and is consistent with the observations of [24, 25],
 409 which report a weak diffusion barrier effect for D through Be surface oxide.
 410 In this case, weak to the extent that D_{ii} lies more or less intermediate to
 411 that commonly accepted for Be [26] and BeO [23].

Figure 8: D in BeO diffusivities used in TMAP models compared to available literature. Full lines correspond to hydrogen isotopes in Be, dashed lines to BeO. Refs: 1.) [23], 2.) [27], 3.) [28], 4.) [26], 5.) [29], 6.) [30], 7.) [31], 8.) Ref. [5] in [32], 9.) Ref. [15] in [32], 10.) [33], 11.) [34], 12.) [35].

412 A survey of the literature emphasizes widespread variation of the diffu-

413 sivities for D in Be and BeO, as shown by figure 8, which is a plot of reported
 414 diffusivities for D in Be (full lines) and BeO (dashed lines). In general, re-
 415 ported diffusivities associated with Be are higher than that for BeO, but the
 416 spread in values extends over many orders of magnitude for both. The dot-
 417 ted line labeled ' D_{ii} ' shows the diffusivity used to describe the experimental
 418 TDS result of figure 7. For interest, D_i in figure 7 corresponds to a best fit
 419 of lines marked 1. in figure 8, which comes from Fowler *et al.* [23].

420 Using the diffusivity D_{ii} and the inferred thickness of an oxide layer as
 421 ~ 40 nm, yet a further attempt was made to match the TMAP BeO inter-layer
 422 model with the experimental TDS data ③ of figure 5. However, for TMAP
 423 simulation to agree, a moderately higher D in BeO (inter-layer) diffusivity,
 424 $D_{iii} = 2.2 \times 10^{-9} \exp(-0.62[\text{eV}]/kT)$ [m^2s^{-1}], was found to be necessary for
 425 co-deposits compared to the bulk target for which D_{ii} was determined. This
 426 is also plotted as a dotted line in figure 8 and is not considered unreason-
 427 able given the vast differences between bulk and co-deposited layers and the
 428 spread in literature diffusivities. It is pointed out however, that both D_{ii} and
 429 D_{iii} , and the low temperature diffusivities of Fowler *et al.* (1. in figure 8,
 430 $1.5 < 1/T < 2$) display similar activation energies, also close to that for the
 431 diffusivities of Be; but with vastly differing pre-factors.

432 The results of the BeO inter-layer TMAP model are given in figure 9,
 433 which reproduces the TDS data set ③ from figure 5. The dashed lines show
 434 various TMAP BeO inter-layer simulations as a function of the BeO inter-layer
 435 thickness. The interpretation, from a variation of the oxide layer thickness
 436 reflects the diffusion barrier effect. For thickness below ~ 1 nm the BeO
 437 inter-layer does not act as a diffusion barrier; the simulation is degenerate
 438 with the TMAP simulation ③ of figure 5. Similarly, a layer of ~ 4 nm (an
 439 unbaked layer) does not show much of an influence. A 40 nm BeO inter-layer
 440 resembles the observed TDS data ③, but it is made clear that the diffusivity
 441 D_{iii} is chosen to achieve this result. Emphasis is placed more on the fact
 442 that the BeO inter-layer model, which is supported by x-ray micro-analysis,
 443 reasonably matches TDS data of type ③. At 100 nm thick and above, more
 444 inventory is released at low temperature than higher temperature, and the
 445 diffusion barrier effect becomes apparent. That is, the desorptive release
 446 begins to show an increased level of release features that reflect a single over-
 447 layer (sphere type ① release), rather than the superimposed thickness. In
 448 light of this, BeO formation on the baked co-deposit under-layer, induced
 449 from the action of baking, can explain the nature of TDS layer systems ③.
 450 It is arguable that such an effect is beneficial, particularly when considered

Figure 9: TMAP-7 simulations (dashed lines) of TDS data ③ (symbols) in figure 5 using a BeO inter-layer model that includes a BeO diffusion barrier between the under and over-layer of varied thicknesses: 1 nm, 2 nm, 4 nm (similar to the unbaked case), 10 nm, 20 nm, 40 nm (similar to the baked case), 100 nm and 200 nm. For thicknesses of BeO less than ~ 1 nm, simulations are redundant with simulations ② that do not include the inter-layer.

451 in an ITER scenario. An ITER bake is likely to last hundreds of hours.
 452 Consequently, co-deposit surfaces could be affected by oxidation much in
 453 excess of that in this study. If this is the case, figure 9 would suggest that
 454 newly co-deposited over-layers will have thermal release properties that may
 455 not be heavily influenced by the overall multi-layer thickness. In terms of
 456 ongoing bake efficiency [2], this is a desirable result.

457 5. Conclusions

458 Fixed temperature baking of Be-D co-deposits leads to thermal desorption
 459 of some fraction of the retained, or trapped, D inventory. The influence

460 of the depleted under-layer, on the desorption properties of a subsequently
461 formed co-deposited Be-D over-layer is studied. Prior TMAP simulation of the
462 thermal release from the a combined under and over -layer system suggests
463 that a fraction of the more D saturated over-layer inventory is re-distributed
464 throughout the under-layer where it participates in trap capture and release
465 and thereby reflects the desorptive behavior of the overall layer thickness
466 . Such a tendency implies that an ITER bake will become more time-wise
467 inefficient with ongoing machine operation. However, in practice, it is found
468 that low temperature baking in vacuum leads to an influence on the under-
469 layer that affects hydrogen transport. The release from the multi-layered
470 co-deposit becomes a fractional superposition of release from the singular
471 over-layer, and the combined over and under -layer system. This result is
472 not easily modeled by the TMAP model of [1], that has been successful in the
473 simulation of D₂ desorption from unbaked multi-layer Be-D co-deposits in
474 the past. Analysis of baked co-deposits using EDX-WDX indicates O uptake
475 during baking, that can potentially act as a diffusion barrier at inter-layer
476 locale. With the inclusion of a BeO inter-layer, TMAP simulations are found
477 to be in better agreement with baked under-layer desorption trends, but the
478 value of D in BeO diffusivity required by TMAP lies closer to that for Be
479 than previously reported results for BeO.

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482

483 **Appendix A. Parameter definitions**

484 T_{dep} [K]: co-deposit layer formation (deposition) temperature.

485 L [μm]: co-deposited layer thickness.

486 E_{m} [eV]: migration energy for mobile D in Be; equivalent also to energy for
487 trap entry.

488 α_{t_i} [s^{-1}]: attempt frequency for D to enter a trap of type i .

489 α_{r_i} [s^{-1}]: attempt frequency for D to escape a trap of type i .

490 E_{r_i} [eV]: release energy for D to escape trap of type i .

491 $C_0^{\text{t}_i}$ [m^{-3}]: initial concentration of D in traps of type i .

492 N [m^{-3}]: number of Be atoms per unit volume.

493 f_{t_i} : initial fraction of traps of type i that are occupied.

494 D [m^2s^{-1}]: diffusivity

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