Deuterium Thermal Desorption From Mixed Layers Relevant for ITER

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ABSTRACT

Thermal desorption of deuterium from mixed C:W and C:W:Al layers was studied in situ by Nuclear Reaction Analysis (NRA) and mass spectrometry during linear sample heating. The deuterium thermal desorption was correlated by decrease of the proton signal at single $^3$He probing beam energy (2.5 MeV) and increase of the masses 3 and 4 in the mass spectrum. Main deuterium desorption in C:W mixed layer takes place at relatively high temperature, around 1000 K, what is higher than typical desorption temperatures for W and amorphous deuterated carbon films. The deuterium depth profile in the layer was measured before and after heating and some deuterium was found to remain after the experiment. Deuterium atom absorption in multilayer film (200 nm of C on top of 500 nm W on graphite substrate) exposed to deuterium atom beam for one day was also studied by the same procedure.

1 INTRODUCTION

Mixed material deposits are formed on various surfaces during operation of fusion devices [1]. Fuel retention in these deposits during their formation and also later after subsequent exposure to discharges is important for predicting the overall fuel retention. The materials that will be used in the largest fusion device ITER are beryllium for the inner wall and tungsten in the divertor area so that the mixed material deposits will mostly consist of these two metals and possibly of seeding (e.g. nitrogen) and intrinsic (e.g. carbon) impurities. The formation of mixed material deposits and deuterium co-deposition is extensively studied by in situ and post mortem analyses in tokamaks but also by depositing such layers using laboratory plasmas (e.g. magnetron sputtering) with addition of deuterium. In this work we have studied deuterium thermal desorption from mixed materials C:W and C:W:Al (Al used as Be substitute) and from multilayer film 200 nm of C on 500 nm of W on C substrate by in situ NRA and mass spectrometry.
2 EXPERIMENT

2.1 Sample production

The layers deposited on silicon and carbon surfaces were obtained using Thermionic Vacuum Arc (TVA) method [1]. The deposition process takes place in high vacuum in the presence of ions generated from the depositing materials. In the deposition chamber all three TVA guns (W, C and Al) were mounted. The lack of any gaseous inclusion inside the deposition layer due to extremely high vacuum conditions is another advantage offered by the TVA deposition method [3]. All these aspects are essential for high quality depositions. One positive aspect offered by this deposition technique consists of using punctual evaporation sources which allow for a large variety of elemental concentration of the materials simultaneously deposited [4]. According to the requirement of the film composition, two or three plasmas were ignited simultaneously. The film thickness and deposition rates were monitored for each of the deposited materials during the deposition process using three Q-pod micro-quartz balances. For composite layers, by controlling the electrical parameters of the discharges the deposition rate was monitored and controlled in real time in order to achieve the desired relative concentration. The final thickness of the deposited layer was given by summarization of corresponding thickness for each element. For deuterium containing samples a special designed gas inlet was used during the deposition. It has 12 small holes (200-300µm in diameter) in order to achieve a uniform D flux. Each aperture of these holes was directed straight to one sample that was subjected to a D flux of 7.5 ml/min.

2.2 Sample analysis

Deuterium thermal desorption during linear sample heating was monitored in situ by Nuclear Reaction Analysis (NRA) and mass spectrometry. The depth profile was measured before and after the thermal desorption. For this purpose a \(^{3}\text{He}\) ion beam was used inducing nuclear reaction \(\text{D}(^{3}\text{He},p)^{4}\text{He}\). The deuterium depth profile is obtained by analyzing the energy distribution of protons created by this nuclear reaction [5]. For the detection of protons a 1500 µm thick proton detector (NRA detector) was mounted at 135° in the vacuum chamber with 24 µm Al absorber placed in front of it in order to stop the backscattered \(^{3}\text{He}\) and reduce the energy of protons from the reaction. Second detector was placed at 170° for detecting the backscattered projectile particles (RBS detector), giving the information about species in the material that are heavier than \(^{3}\text{He}\). By this detector information about mixed material content was obtained. The probing He beam is impacting perpendicular to the sample surface. The configuration of the set up is shown in Fig. 1. An additional detector is shown in Fig. 1 (α-particle detector), but was not used in this experiment. A thin aluminum foil (0.8 µm) was placed in front of the α-particle and RBS detector in order to avoid the noise which would be created by radiation from the hydrogen atom beam source. In order to obtain the D concentration profile in the layer, five different \(^{3}\text{He}\) ion beam energies from 760 keV to 4.3 MeV are used. During the linear sample heating the NRA signal was measured at single \(^{3}\text{He}\) energy 2.5 MeV. This energy was chosen due to several reasons: i) the beam goes through the layer, obtaining the whole signal from D, ii) proton peaks from nuclear reaction between \(^{3}\text{He}\) and \(^{12}\text{C}\) are also visible in the NRA spectrum, giving the information about C content in the layer and iii) the Rutherford Backscattering signal is well resolved. The sample was heated by a heater (Boralectric heater) and its temperature was computer controlled and monitored by a thermocouple attached to the sample surface by a sample holding clamp.

Mass species, desorbed from the sample, were measured by a mass spectrometer (PRIZMA Pfeiffer, 1 to 100 m/q) during linear sample heating. During the heating several
masses were followed including masses 2, 3 and 4 which correspond to $\text{H}_2/\text{D}$, HD and $\text{D}_2$ ions, respectively. The base vacuum pressure in the vacuum chamber was $1 \times 10^{-7}$ mbar. We need to stress that the chamber used for this experiment is basically meant for ion beam analysis and not for thermal desorption studies; therefore the data obtained by the mass spectrometer are qualitative and complementary to the NRA. Moreover the mass spectrometer was in line of sight of the sample not having any preference for the species desorbing from the sample.

![Figure 1: The set up for the present in situ NRA measurements. Incident $^3\text{He}$ beam is perpendicular to the sample surface. The mass spectrometer (RGA) and the hydrogen atom beam source (HABS) are also shown.](image)

The atomic hydrogen (H or D) beam was also used in the case of multilayer sample. Atoms are created by thermal dissociation of hydrogen molecules in a hot capillary of a hydrogen atom beam source, HABS [6]. The 2D atomic flux density map was determined by exposing a heated (600 K), dense, amorphous-hydrogenated carbon (a-C:H) thin film to hydrogen atom beam [7]. The experimental configuration is shown in Fig. 1, with distance between the sample surface and capillary exit being 80 mm and atom beam angle to the surface normal being 51°. For given conditions the central D atom flux density at the sample was $5.2 \times 10^{18}$ D/m$^2$.s. The ion beam spot size and position were determined by observing the burn trace after short exposure of a millimetre paper mounted at the location of the sample. The average D flux density at the probing ion beam position was $(4.5 \pm 0.1) \times 10^{18}$ D/m$^2$.s.

3 RESULTS

3.1 C:W ($\text{D}_2$) mixed layers

First sample that was studied was C:W mixed layer, 1.5 μm thick on Si substrate, with deuterium co-deposited during sample preparation. Such type of mixed material would be formed in the initial option of the ITER’s divertor with CFC and W tiles [1]. It was decided in 2012 that full W divertor will be build and used in ITER from the beginning. Still, there will be carbon in the device as impurity therefore it is interesting to see how it can influence the deuterium retention. We made two experiments with two almost identical samples #1 and #2. The mixed layer in both samples had approximately 6 atomic % of W and 93 atomic % of C as measured by RBS, yielding approximately 1:1 mass ratio. The concentrations of C, W and D are not homogeneous over the depth in layer. The deuterium depth profile was measured by NRA before and after the sample heating. The comparison of the deuterium concentration in samples #1 and #2 before the heating is shown in Fig. 2, having almost identical deuterium
concentrations depth profiles. Mean deuterium concentration in the pristine layer is about 1 atomic %. This is not typical for W where deuterium concentrations below 1 at. % are usually obtained in different tungsten grades exposed to plasma [8]. On the other hand the hydrogen (deuterium) content in plasma-deposited amorphous hydrogenated carbon layers, can be 30 at. % or even higher, even up to 50 at. %, depending whether the layer is hard or soft [10].

Figure 2: Deuterium depth profile measured in C:W mixed layer for samples #1 and #2 before and after the linear heating.

After the depth profile analysis the sample #1 was heated linearly with constant heating rate of 23 K/min. During the heating several masses were followed with the mass spectrometer. Ion current at M/q equal 2, 3 and 4, attributed to H₂/D, HD and D₂ ions and the sample temperature are shown in Fig. 3 as a function of time. The main desorbing specie was mass 3, followed by mass 4 and 2 all having one main desorption peak at 970 K. Since desorption is similar for all three masses one could doubt that the signal is coming from the sample. Mass 3 (HD) had the highest desorption peak, meaning that there is beside deuterium also hydrogen in the layer. After the heating, the deuterium depth profile was measured again, shown in Fig. 2. About half of deuterium still remained in the layer, being distributed over the whole layer.

We have repeated the experiment on sample C:W #2, that had the same properties as the first sample. The experimental procedure was somehow modified with respect to the first sample and during the sample heating the NRA signal was recorded at single ³He ion energy, 2.5 MeV. The integral of the proton peak from the nuclear reaction gives information about the total content of the deuterium in the layer. At first the sample was heated to 970 K very fast, heating rate 120 K/min, and then again with slower heating rate of 15 K/min up to 1170 K, as can be seen in Fig. 4. There were two main NRA signal decreases, which can be also correlated to the desorption peaks measured by the mass spectrometer. First decrease was during the first ramp, where maximum of desorption was at 930 K, and the second one was during the second ramp with peak maximum at 1040 K. The temperature of the desorption peaks for samples #1 and #2 are in good agreement, where the difference in temperature could be due to the different heating rates. The NRA signal decrease is 32% of the initial signal during the first ramp and during the second ramp the remained signal drop is 60%. After the second NRA signal decrease, desorption of masses 2, 3 and 4 starts to increase, which is attributed to degassing of the sample holder and heating of the surrounding. The depth profile for C:W sample #2 after the thermal desorption is shown in Fig. 2. The deuterium concentration is approximately half smaller than in the case of sample #1, but still about 0.25 at. % of
deuterium remained in the sample. We have obtained similar results on both samples and with both techniques used during the linear heating. Both measurement methods were correlated when deuterium desorption took place, what is optimistic for the experiment especially since our thermal desorption spectroscopy is more of quantitative nature due to the non-ideal properties of the vacuum chamber for thermal desorption spectroscopy.

Figure 4: Heating of the sample C:W #2 by two heating rates: 120 K/min and 15 K/min. a) Integrated NRA signal at 2.5 MeV $^3$He energy and b) ion signals of masses 2, 3 and 4 measured by the mass spectrometer are shown as a function of time, together with the sample temperature.

3.2 C:W:Al ($D_2$) mixed layer

The other most relevant element for material mix in ITER is Be. For this purpose a second material mix layer was produced: 1.5 μm thick C:W:Al layer deposited on Si substrate with $D_2$ present in the vacuum chamber. Here Al is used as the proxy element for Be due to many similar properties on one side and the toxicity of Be on another. Even though a frequent opinion is that Al cannot be used as proxy element for retention studies, we preformed such study with Al to see how inclusion of different element can influence deuterium desorption and the total retention. The deuterium concentration depth profile obtained by NRA is shown in Fig. 5, obtaining approximately 0.6 atomic % of deuterium in the layer. As in the case of C:W mixed layer the distribution is also inhomogeneous. Mean concentrations of the other elements in the pristine layer were: 42 at. % of C, 6 at. % of W and 51 at. % of Al. The deuterium depth profile was measured by NRA after the heating of the sample up to 1080 K by a linear ramp 13 K/min. Most of the deuterium diffused out, only deep inside the layer the concentration remained almost unchanged.

The analysis of deuterium content in the layer by NRA at 2.5 MeV $^3$He ion energy is shown in Fig. 6a during the heating. The deuterium started to decrease at 750 K and the middle of the NRA signal decrease is at 940 K, marked as vertical line. There is no prominent desorption peak observed in masses 2, 3 and 4 recorded by the mass spectrometer, Fig. 6b. The dominating desorbing masses were 2 and 3 but masses 3 and 4 had similar behaviour starting to increase when the NRA signal started to drop. It could be that due to slower heating rate as compared to C:W sample, the surroundings becomes hotter and the species desorbing from it start to become dominant. Therefore faster heating rate would be better,
since in that case the heating is more locally on the sample and also desorption peaks are narrower.

![Graph showing deuterium depth profile measured by NRA in C:W:Al mixed layer before and after the linear heating.](image)

**Figure 5:** Deuterium depth profile measured by NRA in C:W:Al mixed layer before and after the linear heating.

![Graph showing heating of the C:W:Al mixed layer.](image)

**Figure 6:** Heating of the C:W:Al mixed layer. a) Integrated NRA signal at 2.5 MeV $^3$He energy and b) ion signals of masses 2, 3 and 4 are shown as a function of time. On both graphs sample temperature is also shown, heating rate 13 K/min.

### 3.3 C:W multi layer

The third variant of the material mix is multilayered film. For this purpose a sample with 200 nm of carbon deposited on 500 nm of tungsten, on carbon substrate, was prepared. There was no deuterium in the pristine sample. The sample was exposed to a deuterium atom beam at 490 K for 25 h in the same chamber as the NRA is made. The deuterium concentration in the layer was measured by NRA *in situ* 2.5 h and 22 h after the start of deuterium atom exposure, corresponding to $4 \times 10^{22}$ D/m² and $3.6 \times 10^{23}$ D/m² deuterium fluence, respectively. The deuterium concentration in top C layer was 0.48 at. % after 2.5 h and 0.87 at. % after 22 h and in W layer it was under detection limit after 2.5 h and 0.025 at. % after 22 h. Therefore deuterium atoms were absorbed in both layers. The real thickness of layers measured by RBS after 2.5 h was 180 nm of C on 600 nm of W. The thickness of top carbon layer was reduced during the atom exposure to 140 nm, observed by decrease of the
proton peaks due to nuclear reaction between $^3$He and C and also by the shift of W RBS edge [7]. This decrease is presumably due to carbon chemical erosion by deuterium atoms [7].

Figure 7: Heating of the multilayer sample C on W by constant heating rate of 12 K/min. a) Integrated NRA signal at 2.5 MeV $^3$He energy and b) ion signals of masses 2, 3 and 4 are shown as a function of time. On both graphs sample temperature versus time is also shown.

After stop of sample exposure to deuterium atoms, the sample was heated with linear ramp of 12 K/min. During the heating the NRA signal was recorded and again masses 2, 3 and 4 were followed by the mass spectrometer, shown in Fig. 7. Before the heating started, several NRA spectra were recorded in order to see if there is any thermal deuterium desorption, since sample temperature was still at 490 K, as during the exposure. The deuterium decrease was observed only when the sample was heated above the exposure temperature. The deuterium signal decrease starts at 700 K. The half of NRA signal decrease is positioned at about 770 K, marked by a vertical line in Fig. 7, what is lower as compared to the mixed C:W layer. The NRA signal decreases almost to zero, meaning that most of deuterium was desorbed. Desorption of masses is not directly correlated to the decrease of the NRA signal, having large desorption peak after the main deuterium signal drop. The decrease of masses 4 and 3 before the temperature ramp is due to pumping of the gas that was closed after the stop of deuterium atom exposure.

4 DISCUSSION AND CONCLUSIONS

Different mixed materials were studied by NRA and mass spectrometry during linear heating of the samples. The two methods gave complementary information at which temperature deuterium concentration decreased in the layer. Moreover, the depth profile analysis after the heat treatment gave information how much of deuterium remained in the layer. This is the first time that such experiment was performed without any sample transport through air. For the first time the NRA signal was also recorded during the heating of the mixed layer. It was observed that in all cases of mixed layers some deuterium still remained in the layer. Moreover, the desorption temperature for C:W mixed layer was quite high, having desorption maximum at around 1000 K. This temperature is higher than typical desorption temperatures for polycrystalline W, from 400 K to 800 K [9], and amorphous deuterated carbon films, 870 K for hard and 740 K for soft layers [12]. The above mentioned maximum desorption temperatures were obtained for 15 K/min heating rate, similar to our heating rates. Besides, such high desorption temperatures were observed for deposited W
layers [8], meaning that tungsten substantially influences the release of deuterium. However, the maximum of deuterium desorption for multilayered sample C on W is close to the amorphous deuterated carbon films [12]. The C:W:Al mixed layer has also high desorption temperature, close to the C:W mixed layer.

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