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Laser annealing in combination with mass spectroscopy, a technique to study deuterium on tokamak carbon samples, a tool for detritiation

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Abstract

In this study, a method is presented based on mass spectroscopy to measure the areal density of deuterium on a graphite surface exposed to tokamak discharges. The studied sample was cut from a bumper limiter exposed in the TEXTOR tokamak and annealed by a 1 J Excimer laser (KrF). The energy used was 400 mJ cm^{-2}, which is below the threshold for ablation, 1 J cm^{-2}. The release of HD and D_2 was measured by a mass spectroscopy set-up and no other species released from the sample were detected in this experiment. The amount of D released from the sample after 20 laser pulses was measured to 7×10^{16} D atoms per cm^{-2} (for this particular sample) and most of the hydrogen at the surface was released in the first pulse, as checked by nuclear reaction analysis (NRA) techniques, which gave changes of the amount of deuterium before and after laser annealing. The sensitivity in this experiment was 5×10^{14} atoms per cm^{-2} for HD and 5×10^{13} atoms per cm^{-2} for D_2.

1. Introduction

Tritium related problems of the International Thermonuclear Experimental Reactor (ITER) necessitate the investigation of tritium behaviour in plasma facing materials (PFM). One of the tasks is detritiation of PFMs after ITER operation with tritium [1]. Among other techniques [2–4], laser desorption is considered and there are two principal modes that can be used. The energy in the laser pulse can be so high that the surface of the sample is evaporated, i.e. ablation mode. The ablation mode can be used to remove the films deposited by the plasma. A lower energy of the laser pulse can also be used and in this case the surface is annealed at elevated temperatures. Increasing the temperature can additionally result in reactions of the surface with the surrounding atmosphere. CO and CO_2 are probably formed when the PFM is made out of carbon, so the surface could be chemically etched. The addition of oxygen can have both a positive or a negative effect on the detritiation process by the formation of carbon oxides or water. In order to avoid that the carbon and carbohydrates are re-deposited elsewhere in the reactor the

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formation of carbon oxides is probably a positive effect. The formation of water could become an effective way of releasing hydrogen from the wall materials, but on the other hand heavy water, containing Tritium is an unpleasant component for safety reasons.

Shu et al. [5] and Shibara et al. [6] have published data on MS analyses of the release of hydrogen from carbon films during laser irradiation in vacuum. The samples in Ref. [5] were taken from the tokamak JT-60 and the samples in Ref. [6] were prepared by ion implantation. The hydrogen adsorption and transport has also been studied in graphite [7]. In both cases the main component detected by the quadruple mass spectrometer was molecular hydrogen H_2. One of the main problems with hydrogen analysis is that air is an effective source of hydrogen in the form of hydrocarbons and water. Using samples charged with deuterium minimised this problem. Kéroack et al. [8] and Schiettekatte et al. [9] have studied the laser induced release of deuterium from graphite. In these experiments the deuterium was introduced into graphite by ion implantation.

In this paper we describe the results of mass spectrometric measurements of gaseous species released from laser irradiation of a deuterium loaded sample (from bumper limiter graphite tiles of TEXTOR) in an oxygen atmosphere. The atmosphere where the laser annealing takes place can be arbitary choosen. In this study we have used 2 mbar O_2 as atmosphere. The reason of choosing oxygen was to study the effect of oxygen on annealing conditions. Possibly oxygen could increase the detritiation kinetics. This could happen by either the formation of water or the oxidation of the carbon matrix and surface hydrocarbons. The formation of water (T_2O) could become a severe problem in a future tokamak reactor. Experimentally there is also an advantage in having a process gas as this will give an internal calibration of the measurements. In addition, as this is an instrumental paper, we would like to show that the method can be used not only under vacuum condition but also under conditions more close to ambient pressures. This type of experimental equipment has previously been used to study the oxidation kinetics for different materials [10–12], the oxygen exchange reactions [13,14], and outgassing of different metals [15].

2. Experimental

A sample was cut from a tile taken from the stock of used bumper limiter graphite tiles of TEXTOR (the tile was marked 2002-05-05). The tile exposure time was over 100 000 plasma seconds and the tile was stored in air for 2.5 years before being analysed. The sample showed visable interference colors. The tile was investigated by scanning electron microscopy (SEM) [16] and a film thickness between 0.1 and 0.3 μm was measured. The film was inhomogeneous over the tile, which is typical for tokamak‘s plasma facing components. The carbon film was investigated by rutherford backscattering spectrometry (RBS) and the main metal impurities were Ni, Cr, and Fe – the components of the TEXTOR liner made of Inconel. The total amount of metal atoms in the film was estimated to 10^{16} at/cm^2. The oxygen concentration in the film was measured with RBS to 10^{17} at/cm^2.

The mass spectrometer system used in this study is shown in Fig. 1. The system consist of a gas handling system, a reaction chamber (enclosed volume) and a mass spectrometer in UHV. The different parts are separated by valves. Between the enclosed volume and the mass spectrometer there is a leak valve, by which an inlet to the MS is regulated. The composition of the enclosed volume is probed by the inlet to the MS. The base pressure of the MS is 10^{-10} mbar and the vacuum is maintained by an ion pump. In addition, the pumping speed of the MS, and thereby the pressure in the MS, can be regulated by opening and closing a valve between the ion pump and the mass spectrometer. The reaction chamber is evacuated with a turbo pump, so the admissible pressure of the reaction chamber ranges from low vacuum ($\sim 10^{-6}$ mbar) up to ambient pressure (1000 mbar). The pressure in the reaction chamber is continuously measured with a MKS Baratron Capacitance manometer (0–100 torr). The gases in the enclosed volume can

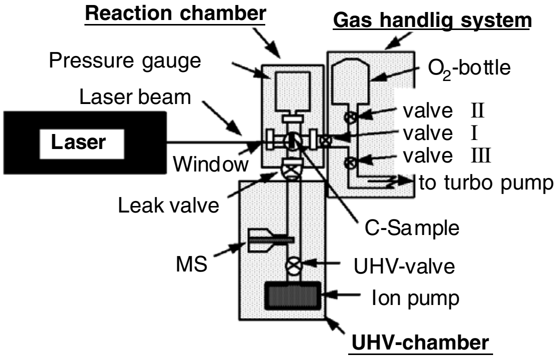

Fig. 1. Schematic figure of the mass spectrometer set-up.

be chosen arbitrarily. The volume of the reaction chamber was measured to be 550 cm^3 and was made of standard UHV-parts.

A 1 J KrF excimer laser (Lamda Physics) with an area of the outgoing beam size of 1 × 2 cm was used and the laser beam was admitted through a quartz window. In this study, the energy of the outgoing beam was 900 mJ with a pulse length of 25 ns. An aperture of 4 × 5 mm was used and the laser beam gave a visual 4 × 5 mm mark on the sample. The energy losses of the system has been measured with a energy meter to approximately 10%. The laser intensity was 400 mJ cm^{-2} on to the sample, which is below the ablation threshold [18]. The repetition frequency of the laser pulses was variable. In this study, we used two types of time intervals between the laser pulses. The first 5 pulses were made with a time interval of 8 min. The pulses 6–20 were made in series of 5 with 10 seconds between the individual pulses and 8 min between each series. After the 1–5, 10, 15, and 20 pulses the gas composition in the reaction chamber was measured with the MS.

3. Measuring scheme

The experimental scheme used in this study is shown in Fig. 2 and mass spectra from four different points in Fig. 2 are shown in Fig. 3. The first spectrum in Fig. 3 is the background spectrum of the UHV chamber and the main residual gases in the vacuum are 2 (hydrogen), and 28 (CO, fractioning of CO gives peaks at masses 12 and 16). The inlet to the MS can be regulated by a leak valve and at $t = 0$ in Fig. 2 the leak valve is set to a fixed opening. Two (2) mbar O_2 was let in to the reaction chamber at A in Fig. 2. As seen by the increase of mass number 32 in the MS, after $t = 1.5$ min the pressure of O_2 in the reaction chamber was constant. The characteristic mass spectrum for times between 1.5 min and 4.3 min is shown in Fig. 3(b). The main difference from Fig. 3(a) is the presence of mass 32 (O_2) in the spectrum. The sensitivity of the measurements can be increased (by 2 orders of magnitude) by closing the UHV-valve (between the mass spectrometer and ion pump) so that the pressure in the MS increases. In Fig. 2(a) cycle is twice closing (in cycle 1 at B_1 and B_2, and in cycle 2 at LP_1 and B_4) and opening (in cycle 1 at C_1 and C_2, and in cycle 2 at C_3 and C_4) the UHV-valve in each measurement. The valve was closed during 3 minutes and then opened for 1 min, so the system was evacuated by the ion pump. Each cycle thereby takes 8 min. The first cycle is for pure O_2 (blank measurement) and the characteristic mass spectrum is shown in Fig. 3(c). In Fig. 3(a) and (b) the increase in the masses 2 (H_2), 3 (HD), 18 (H_2O), 28 (CO) and 44 (CO_2) come from the MS part of the vacuum chamber. To confirm this, we have made experiments without any inlet (closed leak valve) to the MS (response of the vacuum system) and with inert gases (N_2 and Ar). These experiments gave the same increase in masses 2, 3, 18, 28 (not in the case of N_2 since $28 = CO + N_2$) and 44 was seen as mention above. The HD is from the natural abundance of D in hydrogen as the ratio between 3 (HD) and 2 (H_2) is $\sim 3 \times 10^{-4}$, in good agreement with the natural abundance of HD ($2 \times 1.5 \times 10^{-4}$) [17]. The increase in mass 32 (O_2) is due to the inlet from the reaction chamber, and agrees well with O_2 being the only component in the reaction chamber. The responses in the MS are within 5% for the two consecutive closings and openings of the UHV-valve in the first cycle. The reproducibility was tested by measuring the response in the MS to 5 consecutive closing/opening and the responses in the MS were within 10%. At LP_1 the carbon sample was irradiated with one laser pulse after which one cycle was made. The increase of mass number 32 is the same as in cycles 1, but there is a clear increase of the masses, 3 and 4. The mass spectra in 3c and 3d are before and after the laser pulse and all masses, except 3 and 4, are the same; the only measurable effect of the laser pulse is an increase of HD

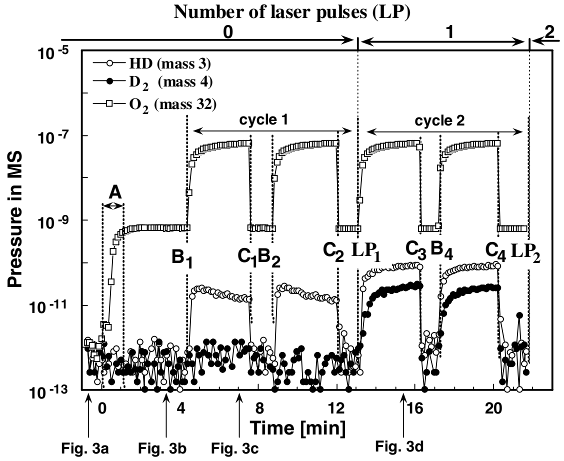

Fig. 2. Measuring scheme, A is when 2 mbar O_2 is let in to the reaction chamber, B is when the UHV-valve in this is closed, C is when the UHV-valve in this figure is opened, and LP is when the sample is hit by 1 laser pulse. Number of laser pulses used is also indicated at the top of the figure.

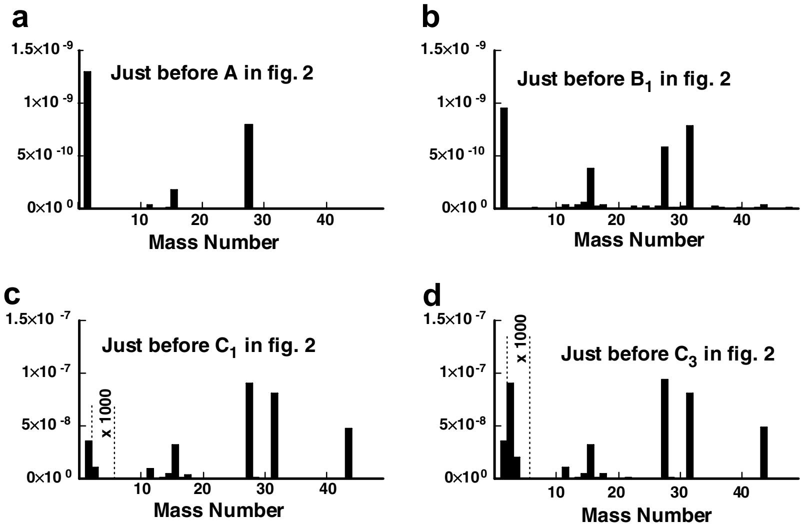

Fig. 3. Mass spectrum for different times in Fig. 2, (a) mass spectrum from $t = 0$, (b) mass spectrum taken between $t = 1.5$–4.3 min., (c) mass spectrum taken just before C_1 in Fig. 2, and (d) mass spectrum taken just before C_3 in Fig. 2.

and D_2 in the reaction chamber. In LP_2 in Fig. 2 the sample is again irradiated with one laser pulse, and a new cycle is made (cycle 3). The increase in masses 3 and 4 is higher in cycle 3 than in cycle 2. The procedure of irradiating the sample with one laser pulse and measurement cycles was repeated until the sample was exposed to 4 laser pulses (cycles 2, 3, 4 and 5). The concentrations of HD and D_2 in the reaction chamber increase after each laser pulse and after the 4th pulse the amount released was much smaller than the amount in the reaction chamber. The reaction chamber was, therefore, evacuated and new O_2 containing no HD and D_2 was let into the reaction chamber. A new blank experiment was made (cycle 6) and the result was the same as in cycle 1. The sample was then again irradiated with one laser pulse (5th pulse and cycle 7) and there was only a slight increase of masses 3 and 4. In order to get a higher release of HD and D_2 from the sample we changed the number of laser pulses (from 1–5) in between each MS measurements (cycle 8 after a total of 10 laser pulses). The time between the 5 laser pulses were 10 s. The same procedure was repeated twice (cycles 9 and 10) so the sample was exposed to a total of 20 laser pulses. After the 20 pulses the reactor was evacuated and new O_2 with a pressure of 2 mbar was introduced. A new blank measurement (cycle 11) was made and the result was the same as for the cycle 1 in Fig. 2. The response in the MS was the same in all cases when fresh O_2 was used (cycles 1, 7 and 11) so the reproducibility of the measurement was good.

The experimental data obtained is pressure in the MS, but the aim is to determine the amount HD and D_2 that has been released from the sample. The partial pressures in the MS can be converted to concentration in the reaction chamber, but this conversion depends on parameters, such as the sensitivity to the gases in the MS itself (ionisation yield), the size of the species, velocity of the species, etc. Fortunately by calibrations, all these parameters can be put in to a single conversion factor. The calibrations were made by introducing different amounts (pressures) of D_2 and O_2 into the reaction chamber and using the same type of measuring cycles as in Fig. 2. As in Fig. 2 the partial pressure of 4 and 32 continuously increases, but after approximately 1 minute the fraction between mass 4 and 32 is constant. The partial pressure in the MS is measured just before opening the valve to the ion pump. In Fig. 4 these data are plotted versus the measured partial pressure in the reaction chamber. The sensitivity factor of D_2 in Fig. 4 is measured to 6.7 (sensitivity factor of $O_2 = 1$). Using different mixtures of D_2 and O_2 also shows that there are no synergistic effects between D_2 and O_2.

4. Calculating procedure

The volume of the reaction chamber (V), the total pressure in the reaction chamber (P), and the temperature (T) are known and using the ideal gas law:

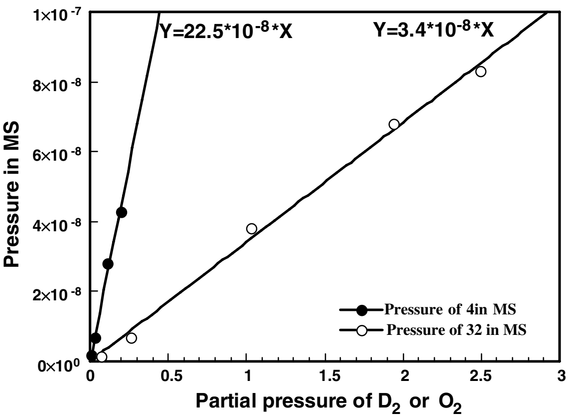

Fig. 4. Calibration curves for D_2 and O_2. The MS response to different pressures in the reaction chamber. The relative sensitivity for D_2 is 6.7 ($22.5 \times 10^{-8}/3.4 \times 10^{-8}$).

$$PV = nRT \tag{1}$$

gives that 1 mbar of gas corresponds to 1.4×10^{19} molecules ($P = 1 \times 10^{-3}$ bar, $V = 550\ \mathrm{cm}^{-3}$, $R = 8.31 \times 10^{-5}\ \mathrm{m}^3\ \mathrm{bar}\ \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$, and $T = 293$ K). The use of the ideal gas law will only give a small error in the total amount released. Most real gases have a molar volume of 22.2–22.4 L/mol (table 5.1 page 175 in Ref. [19]) compered to the ideal molar volume of 22.4 L/mol. The error if using the ideal gas theory to calculate the amount will thereby be negligible. Fig. 2 shows the response of masses 3, 4, and 32. The blank experiments gives the background for the measurements, which has to be subtracted from the measurements after the laser exposure. The amount of D released (as HD and D_2 in the reaction chamber) can thereby be calculated. The spot size of the laser beam on the sample is easy to measure as there are structural changes, visual to the naked eye, where the laser hit the sample [16]. We know thereby the change in the areal density of D in each cycle.

5. Results

Using the quantification method described above, the amount of D released can be calculated and the areal density of released D is shown in Fig. 5. Fig. 5 shows that a major part (more than 50%) of the deuterium is released in the first laser pulse and most of the deuterium (~90%) is released in the first 5 pulses. The amount of D in the sample was measured with nuclear reaction analysis NRA before and after the 20 laser pulses, and 90% of the deuterium has been released from the sample. The amount released was measured to 10^{17} D atoms per cm^{-2} and this number agrees well with the 0.7×10^{17} D atoms per cm^2 measured from Fig. 5. The laser annealing can thereby be used as a method to determinate the deuterium content in carbon samples even in an non ablation mode for the thin films. In order to evaluate the release kinetics the data in Fig. 5 have been plotted on linear, parabolic, logarithmic, or log–log scale, but neither of these plots gave a straight forward answer. There are several reasons why the kinetics is difficult to evaluate. A major part of the deuterium is released after the first pulse, so there are no kinetic data for the major part of the release. As this is the case, the original depth profile would be needed for an evaluation. The sample surface was rough with an inhomogeneous film thickness. The surface roughness, apart from making the kinetic evaluation difficult, also makes it difficult to determine the original depth profile of D. The measurement, therefore, gives the kinetics of the release, but in order to evaluate the mechanisms of the release a complete different type of samples would be needed.

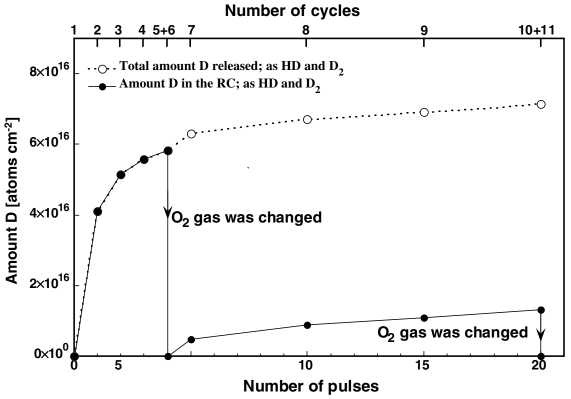

Fig. 5. The release of deuterium versus number of laser pulses.

As can be seen in Fig. 3(c) the background of H is very high, so the release of H cannot be directly measured. A relation between H and D can however be calculated from the released HD and D_2. The relative concentration of deuterium in the walls can be calculated to 40%, assuming that the relative sensitivity is the same for HD and D_2 and that the D and H will be statistically distributed in the hydrogen molecules [20]. This number is lower than the deuterium content in the plasma of TEXTOR. So hydrogen from the atmosphere has been introduced to the sample and this can be expected when considering that the tile has been stored for ~2.5 years in air. The hydrogen can have many sources. Part of it is probably from a hydrogen uptake from hydrocarbons and from water in the atmosphere. Part of it can be an exchange with hydrogen containing species in the air. There is also only a small change of this number with number of laser pulses. One could expect that the surface concentration of H could be higher (due to the adsorption of hydrocarbons and water). An increase of D/H ratio with number of laser pulses could have been expected.

The detection limit of the experiment is different for different species and depends mainly on two factors, the sensitivity factor and the background level. The background level can be converted to an amount in the MS using the sensitivity factor. The variation in the background level corresponds to $\pm 2 \times 10^{14}$ HD molecules per cm^2, resulting in a detection limit of 5×10^{14} D atoms per cm^2 in HD. This amount corresponds to approximately 1/2 of a monolayer. The background level for D_2 is a factor 10 lower than for HD, see Fig. 2, and assuming the same sensitivity factor the detection limits of D_2 is 5×10^{13} atoms per cm^2. The detection limit, measured as atoms per cm^2 released, in the method can be increased in two other ways. The first is to decrease the volume of the reaction chamber (as $n = PV/RT$). The second is to increase the area exposed to the laser, Realistically, these two ways could increase the sensitivity with a factor 1000.

The detection limit of the technique is very good for species like HD and D_2. These species have a low background in the MS and adsorb very little on the walls of the reactor. The detection limit of H_2 (mass 2) is much worse, since there is a large background level in the MS (H_2 coming from the vacuum system), see Fig. 3(c). The large background of H_2 also effects the HD background as the natural abundance of D is 0.015%. The background level of H_2O (mass 18) in the MS is also high, but with water (H_2O, HDO, and D_2O) there exists also another problem, the adsorption on the walls of the reactor. In general, a thin water film will form on all surfaces exposed to air and the first monolayer of water is quite strongly bonded to the wall. The desorption of this first monolayer is very slow and up to 15% of the monolayer will remain after 120 h of pumping in vacuum[21]. One monolayer is approximately 10^{15} atoms per cm^2 and the walls of the reactor has a surface area in the order of $\geqslant 1000\,cm^2$. More than 10^{18} water molecules can be adsorbed on the walls without any significant increase of the pressure in the reaction chamber. The conclusion of this is that the deuterium released as water can be very difficult to analyse as the water is adsorbed on the walls of the reactor. The same problem as for water exists for hydrocarbon, carbon oxide and carbon dioxide. So even though we do not measure any change in these species after the laser pulses, there can be a relative high release of these species from the sample.

6. Conclusions

We have measured the deuterium release in situ during laser annealing of graphite sample from TEXTOR. The measurements were made with an MS set-up and the following conclusions can be drawn.

- Laser annealing below the threshold for ablation is a possible method to remove deuterium from plasma deposited layers in tokamaks. The major part (more than 50%) of the deuterium was released in the first pulse and almost all (~90%) was released in the first 5 pulses.
- The deuterium release was 0.7×10^{17} D atoms per cm^{-2} and was mainly in the form of molecular hydrogen. No other species (water or hydrocarbons) were detected.
- Mass spectrometry can be used to study the kinetics of the release, but in order to evaluate the mechanisms for the release, the experiment made in this study was not suitable.
- The sensitivity of the technique is 5×10^{14} atoms per cm^{-2} for HD and 5×10^{13} atoms per cm^{-2} for D_2 using a laser spot size of 0.4×0.5 cm, 2 mbar O_2 pressure, and a $550\,cm^3$ volume of reaction chamber.
- The deuterium to hydrogen ratio can be calculated to ~0.4.
- The methods contain information on the release of water, but this is more complicated to study as water adsorbs on the walls of the reactor. One monolayer of water can be adsorbed on the walls with a very low partial pressure of water. The wall area is $\geqslant 1000\,cm^2$, so 10^{18} water molecules can be easily expected to adsorb on the walls without any noticeable effect on the pressure in the reaction chamber.

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