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Oxidation and hydrogen isotope exchange in amorphous, deuterated carbon films

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Abstract

The hydrogen desorption and air oxidation of amorphous deuterated carbon (a-C:D) films deposited on Si are investigated. The results are compared with a hydrogenated carbon layer deposited on a silicon collector sample mounted on the wall of tokamak ASDEX Upgrade during 6 months' plasma operation. The a-C:D films, deposited on a silicon substrate by the RF glow-discharge method, are exposed to air at room temperature and between 500 and 800 K. The total amounts and depth profiles of both deuterium and carbon are measured by ERD (elastic recoil detection) and PES (proton enhanced scattering). It is found that the surface deuterium loss is accompanied by oxygen uptake and hydrogen isotope exchange in the film until deuterium is completely released. Further annealing leads to the removal of the whole carbon layer. In accordance with previous oxygen implantation studies the erosion is modeled to be due to the chemical reaction of carbon and deuterium with oxygen from air. The removal of the codeposited layer from the ASDEX-Upgrade sample proceeds much faster than that found for a-C:D films under identical treatment conditions. The removal rate strongly depends on film structure.

1. Introduction

Graphite was used for limiters and protective tiles in almost all fusion devices, and was selected as the reference material for plasma-facing components in the future fusion experiment ITER. However, a problem emerges because of its erosion and hydrogen retention behavior when exposed to high fluxes of plasma particles. The eroded carbon atoms are redeposited on less exposed surfaces together with hydrogen isotopes to form an amorphous hydrogenated carbon (a-C:H) layer with an atomic ratio of hydrogen isotopes to carbon of about 0.4. The trapping of large amounts of hydrogen isotopes in graphite tiles may result in accidental recycling of the fuel and problems of density control. Furthermore, significant amounts of tritium will be retained in the codeposited layer on the wall surface during D–T operation, resulting in a potential environmental risk during accidental vacuum loss because the codeposited films are not stable in air at elevated temperatures. It is, therefore, important to know the release rate of the trapped hydrogen isotopes from the codeposited layer when it is exposed to air. In order to keep the total tritium inventory below an acceptable level it is desirable to find an effective method of removing the codeposited layer during the intervals between every two plasma campaigns. Therefore, it is necessary to study the hydrogen release from samples of graphite implanted with deuterium or amorphous carbonized layers (a-C:D films) in laboratory.

The removal of hydrogen isotopes from hydrogenated carbon layers was investigated by different methods [1–4]. The chemical release of implanted deuterium in graphite was investigated by Chiu and Haasz applying laser thermal desorption [1]. They found that oxygen exposure is most effective in removing the implanted deuterium from graphite. An amorphous, deuterated carbon (a-C:D) film was studied by Haasz et al. [2]. D_2O, CO_2 and CO were found to be the predominantly released reaction products

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when the films were exposed to oxygen. The stability of tritium/carbon films was studied by Causey et al. [3]. They found that for a 20 nm thick film annealing to 573 K in air leads to a complete release of the tritium. Thiele and Oelhafen investigated the interaction of energetic oxygen ions with a-C:H films by photoelectron spectroscopy indicating the chemical state of oxygen in the films [4]. Thermal desorption spectroscopy was widely used in these studies to detect the released gases, and XPS (X-ray photoelectron spectroscopy) was applied to measure the change of the chemical state of the film components. In the present work, the oxidation and hydrogen isotope exchange in a-C:D films due to air exposure are studied by ion beam analysis. The total amounts and depth profiles of C, D, O and H in the layer are quantitatively measured during air exposure in order to get a quantitative understanding of the deuterium removal process.

2. Experimental

The investigated a-C:D films, 350–770 nm in thickness and with D/C ratios of about 0.45, were deposited in 1988 on silicon substrates by plasma chemical vapor deposition (PCVD) in an RF glow-discharge [5]. The feed gas was deuterated methane CD_4 with a pressure of about 3 Pa. The RF frequency was 20.7 MHz. An RF power of 40 W was applied, resulting in a dc bias of 350–400 V. The details of the sample preparation are described in Ref. [5]. The samples were stored in ambient atmosphere since 1988. The deuterium release of these samples is compared with a long term sample from a collection probe, where a deuterated carbon layer was deposited onto a silicon sample mounted on the wall of tokamak ASDEX Upgrade during the campaign of December 1994 till June 1995. The thickness of the codeposited layer is about 750 nm. Besides carbon and deuterium, this ASDEX-Upgrade sample also contains hydrogen with a H/D ratio of 0.3 and boron because of frequent neutral injection with hydrogen and wall boronization using B_2H_6 during the 6 months' plasma campaign [6].

The a-C:D samples were exposed to ambient atmosphere at ambient pressure for 1 h at temperatures of 500 to 800 K. For each temperature step a fresh sample was used. For comparison, a-C:D films were annealed in a vacuum chamber with a residual gas pressure of 10^{-8} Pa for 1 h at temperatures between 600 and 900 K in order to distinguish the deuterium release due to thermal desorption from that due to a chemical reaction with reactive gases in air. The time dependence of the air exposure was measured at 650 K. The a-C:D films were annealed for varying periods from 1 to 16 h.

The oxidation and hydrogen isotope exchange in the films due to air exposure were investigated by ion beam analysis. The total amount and the depth profile of retained deuterium and hydrogen in the films were determined by ERD (elastic recoil detection) with 2.6 MeV He^+. The cross-section data for the $H(^4He, p)^4He$ and the $D(^4He, d)^4He$ reactions were taken from Refs. [7–9], respectively. Carbon and oxygen were detected by PES (proton enhanced scattering) with 1.5 MeV H^+. For the C(p, p)C reaction the cross-section data of Amirikas et al. were used [10]. The areal density of the film was determined by ion beam analysis in units of atoms/cm^2, and the total film thickness measured in units of nanometers by means of profilometry. These two measurements served to calculate the film density.

3. Results and discussion

3.1. Long air exposure at room temperature

Fig. 1 compares the long term stability of the a-C:D films and the ASDEX-Upgrade deposit at room temperature. D/C measurements taken soon after deposition by Boutard et al. [5], which yielded D/C ratios between 0.40 and 0.43, used somewhat larger C(p, p)C cross-sections [11] and have been corrected to the more recent data [10] to allow a comparison with our results. While in both measurements the amount of deuterium was closely the same, the carbon areal density was determined to different values, but remaining within the estimated errors between 5 and 10% due to solid angle and background subtraction uncertainties [12]. Within this error margin, the D/C ratio of the a-C:D film is very stable and the decrease from 0.45 to 0.4 during 8 year's air exposure at room temperature may partially be balanced by a small concentration of hydrogen (see Fig. 4a). The data are taken from four

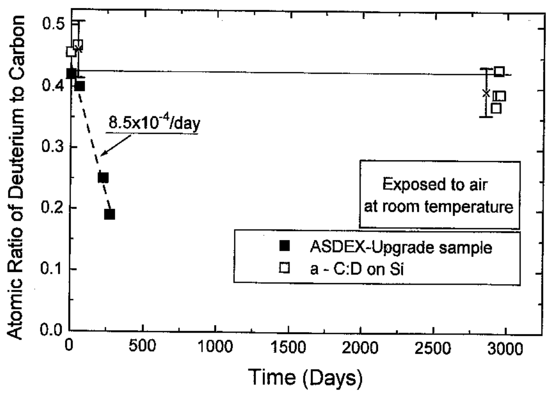

Fig. 1. Dependence of the D/C and (D+H)/C ratio on time for exposure to the ambient atmosphere for a-C:D films and the ASDEX-Upgrade sample, respectively. The estimated experimental uncertainties of 10% are shown as error bars together with the mean values of all measurements for the a-C:D films (×). While the D/C ratio of the a-C:D films is within these error margins compatible with a constant D/C value (solid line), the ASDEX-Upgrade sample shows a drastic decrease.

samples with different thicknesses between 350 and 770 nm. In contrast, a significant release of hydrogen isotopes from the ASDEX-Upgrade sample was found. The ratio of $(H + D)/C$ decreases from 0.42, measured 2 days after the sample was removed from ASDEX-Upgrade, to 0.19 measured 272 days later. The decrease rate of $(H + D)/C$ is 8.5×10^{-4}/day. A very similar deuterium loss rate as for the ASDEX-Upgrade sample was found by Causey et al. in a long air exposure of a codeposited carbon layer with the thickness of 200 nm prepared by laser plasma deposition in deuterium [3]. Compared with a very quick release of deuterium from a thin film prepared by RF plasma deposition in deuterium and methane, he suggested that the properties of the different codeposited films depend on the deposition conditions, such as substrate temperature and sample bias voltage, and suggested that the thick C:D layer may be partially self-protecting. In this work, the ASDEX-Upgrade coating has a similar thickness to one of the a-C:D films, but the behavior of deuterium release is quite different from each other. Besides, we found that the release rate of deuterium from different a-C:D films is independent of thickness. This result strongly suggests that different film structures resulting from different deposition conditions are the dominant factor for the deuterium release. It should be noticed that the atomic ratio of H/D for the ASDEX-Upgrade sample increases from 0.3 to 0.7 during 272 days of air exposure. It implies that D–H exchange for this sample occurs already at room temperature.

3.2. Exposure at elevated temperatures

Fig. 2 shows the temperature induced changes for a-C:D samples annealed for 1 h in air and in vacuum, respectively. The atomic ratio of D/C is about 0.37 before annealing for the two groups of experiments. For the samples annealed in vacuum no decrease of both carbon and deuterium is observed at temperatures below 700 K, i.e., no thermal desorption of deuterium occurs in this temperature range. For temperatures higher than 700 K both carbon and deuterium decrease with temperature. 7.4% of carbon and 42.5% of deuterium are lost at 900 K due to the thermal release of D_2 and hydrocarbons, similar to the thermal desorption from graphite implanted with deuterium [13,14]. The atomic ratio of D/C decreases gradually from 0.37 at room temperature to 0.23 at 900 K. For the sample exposed to air both carbon and deuterium are released at temperatures below 700 K, where thermal desorption does not yet occur. This result suggests that the removal of deuterium and carbon is due to a chemical reaction of the sample with reactive gases in air. The amounts of deuterium and carbon in the film are quickly decreasing with increasing temperature. Almost all deuterium and 70% of carbon are removed at 700 K, while the incorporated hydrogen and oxygen amounts increase with temperature and reach a maximum of 2.8×10^{17} at/cm^2 for oxygen and 1.5×10^{17} at/cm^2 for hydrogen at 700 K. At 725 K and higher temperatures — we measured up to 800 K — the deposited layers are completely removed. Compared with the deuterium release at room temperature, shown in Fig. 1, it is obvious that the release rate is significantly increased by annealing. A previous work from Chiu and Haasz [1] showed three orders of magnitude reductions of the deuterium content in less than one hour of oxygen or air exposure at 770 K for graphite implanted with 1 keV D^+, which agrees well with the present results. Causey et al. [3] observed that tritium could be completely released from a codeposited carbon layer due to air exposure at 573 K. The sample used in Causey's experiment is a very soft C:(D + T) film with a $(D + T)/C$ ratio of 1 formed in a plasma discharge and is very thin (20 nm), leading to a quick release of hydrogen isotopes at a lower temperature than that in our experiment. The different removal temperatures suggest that the release of the hydrogen isotopes from the codeposited layer is strongly dependent on the film structure.

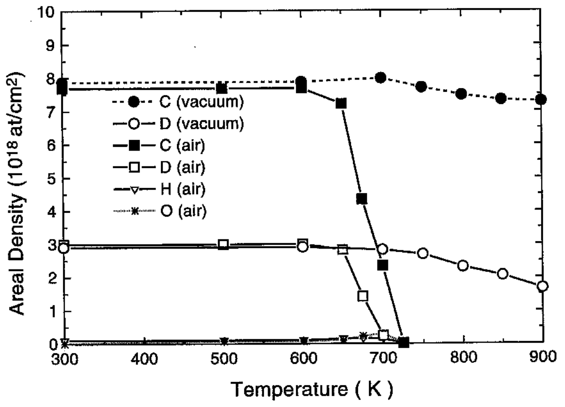

Fig. 2. Temperature dependence of a-C:D film erosion due to 1 h annealing in air and in vacuum. The samples were 730 nm thick. For each temperature step a fresh sample was used.

Fig. 3 shows the effect of annealing time on the erosion of a-C:D films exposed to air at the temperature of 650 K. Both deuterium and carbon in the film decrease with annealing time. Almost all deuterium and 73% of the carbon are removed after 8 h. In contrast, oxygen and hydrogen increase with time and reach a maximum, 5.5×10^{17} at/cm^2 for oxygen and 2.3×10^{17} at/cm^2 for hydrogen, after 8 h. Further annealing leads to a continued carbon erosion with a removal rate of 1.4×10^{17} at/cm^{2}h. Only 10% of the carbon remain when the sample is annealed for 16 h. It is estimated that all the carbon will be eroded when the annealing lasts 21 h. Simultaneously, the amount of oxygen and hydrogen decreases with time due to the layer removal.

A better understanding of the atomic processes is obtained by analyzing the depth profiles of C, D, O and H in the a-C:D films exposed to air before and after 2, 4 and 8 h annealing at 650 K (Fig. 4a–d). In the virgin film a homogeneous deuterium concentration in the a-C:D film with a thickness of 730 nm is found. The atomic ratio of D to C is about 0.43. Very few hydrogen is adsorbed on the surface layer. After annealing for 2 h the layer thickness decreased to 710 nm. 11% of carbon and 12% of deuterium are removed. The average atomic ratio of D/C in the whole layer is still 0.43, but a pronounced change occurs in a surface layer of about 100 nm. Deuterium is depleted in this layer in exchange to 1.0×10^{17} at/cm^2 of hydrogen and 2.4×10^{17} at/cm^2 of oxygen. In addition, the amount of carbon in the oxidized surface layer is about 15% lower than the bulk value. After annealing for 4 h the total layer thickness decreased to 580 nm. 35% carbon and 50% of deuterium are removed. The average atomic ratio of D/C in the whole layer decreased to 0.34, but the local ratio in deep layers stayed constant at about 0.43. Deuterium is depleted to a depth of about 200 nm. Oxygen and hydrogen uptake extends to the same depth. After annealing for 8 h the layer thickness decreased to 280 nm. Almost all deuterium and 73% of carbon are eroded. Oxygen and hydrogen are incorporated throughout the whole layer, corresponding to the maximal amounts shown in Fig. 3, and homogeneously distributed. Further annealing only leads to a decrease in thickness until the whole layer is removed. The atomic ratios of O/C and H/C in the oxidation layer reach constant values of 0.30 O/C and 0.11 H/C in Fig. 4b, c and d. The saturation concentration of 0.30 O/C is comparable to the values of 0.24 O/C reported in Ref. [15] and 0.25 O/C reported in Ref. [16] for oxygen implantation in graphite at saturation condition. But, the value 0.11 H/C is much lower than the saturation concentration of 0.4 H/C for hydrogen implantation in graphite. The atomic ratios of 0.30 O/C and 0.11 H/C are equivalent to an oxygen concentration of about 21 at.%, which is substantially higher than the oxygen saturation value of 12 at.% in a pure a-C:H film implanted with 0.1–1 keV oxygen ions [4].

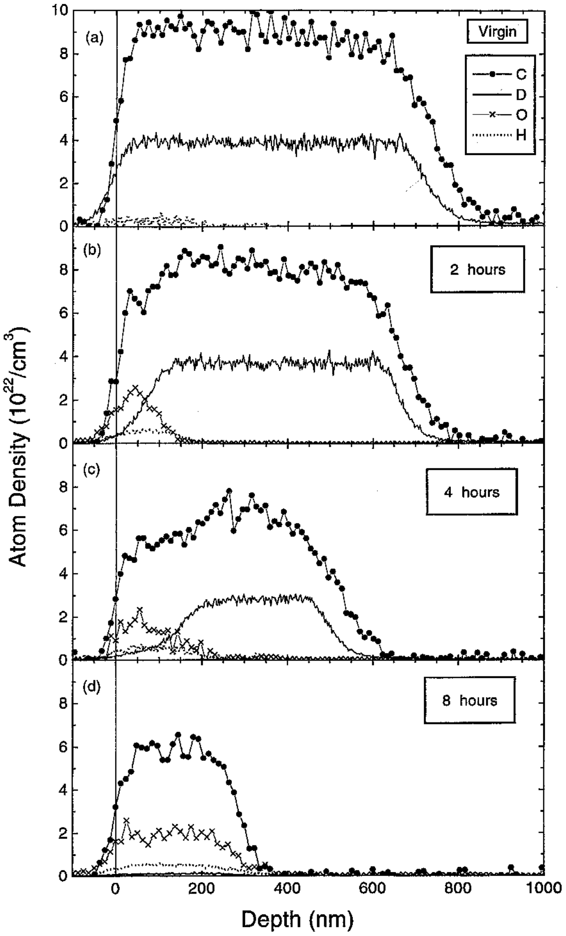

Fig. 4. Depth profile changes of carbon, deuterium, oxygen, and hydrogen in a-C:D films due to air exposure at 650 K. (a) before annealing, (b) after annealing for 2 h, (c) after annealing for 4 h, and (d) after annealing for 8 h. The original film thickness was 730 nm. For each temperature step a fresh sample was used.

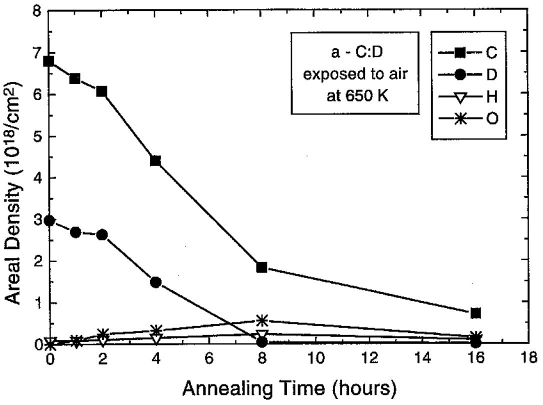

Fig. 3. Annealing time dependence of total amounts of carbon, deuterium, hydrogen, and oxygen in a-C:D film due to air exposure at 650 K. The samples were 730 nm thick. For each temperature step a fresh sample was used.

The results from Figs. 2–4 suggest that the removal of a-C:D layers due to air exposure is dominated by the chemical reactions between oxygen from air and the film components. During ion implantation of graphite with oxygen [17] it was shown that oxygen accumulates within the ion penetration depth and volatile molecule desorption, such as CO and CO_2, only starts when saturation is reached. The erosion of the a-C:D film can be modeled in a similar way. The depth profiles show that oxygen diffusing into the film is trapped until saturation is reached. Further oxygen uptake increases the thickness of the saturated layer. Assuming that volatile erosion products, such as CO, CO_2, are produced throughout the whole oxidized layer, the dependence of the thickness of the oxidized layer, D_o, on the annealing time, t, can be written as

$$D_o(t) = A/R(1 - e^{-Rt}), \qquad (1)$$

where A is the growth velocity of the oxidized layer (nm/h) and R the erosion coefficient (1/h). The total layer thickness, D_{tot}, is derived from

$$\frac{\mathrm{d}D_{\text{tot}}(t)}{\mathrm{d}t} = -RD_0(t),$$

$$D_{\text{tot}}(t) = D_{\text{tot}}(0) - A\left(t + 1/Re^{-Rt}\right) + A/R. \tag{2}$$

The model predicts that with increasing oxidation layer thickness also the erosion increases until the oxygen uptake equals the oxygen release in products such as D_2O, CO and CO_2. At this time the maximum erosion rate of the total layer is reached being equal to the growth velocity of the oxidized layer, A. When the total layer thickness is reduced to the thickness of the oxidized layer further erosion proceeds as

$$D_{\text{tot}}(t) = A/Re^{-Rt}. \tag{3}$$

A good fit of the model to the present data is obtained for the parameters $A = 100$ nm/h and $R = 1/3\ \text{h}^{-1}$ (Fig. 5). It is evident that the maximum possible erosion of 100 nm/h is not reached for the present conditions, i.e., film thickness and temperature. An increase in a-C:D film thickness by a factor of three to 2.5 μm increases the total erosion time only from 16 to 24 h. Also, a small increase in temperature by 25 K increases the erosion rate drastically (Fig. 2).

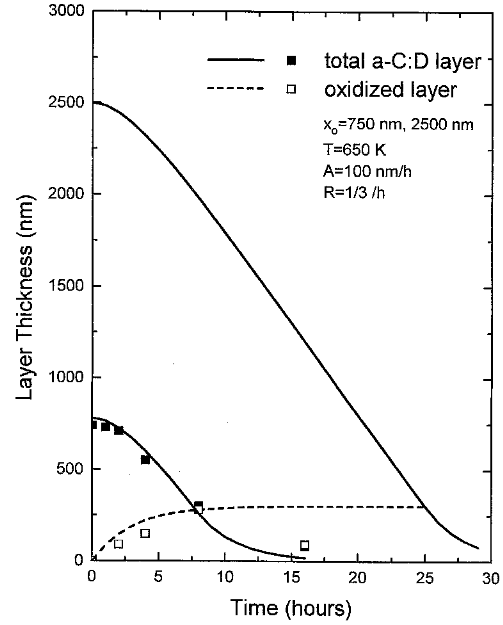

Fig. 5. Time dependence of the oxidation and erosion of a 750 nm a-C:D film during air exposure at 650 K. Experimental results are shown as data points, model calculations assuming a growth rate of the oxidized layer of 100 nm/h and an erosion coefficient of $1/3\ \text{h}^{-1}$ (see text) are shown as curves. The calculated erosion for a 2.5 μm layer is also shown.

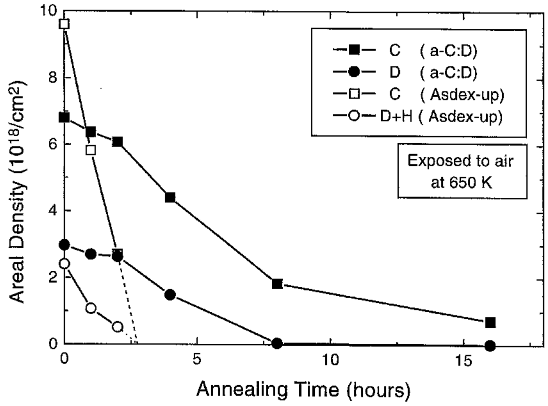

Fig. 6. Comparison of the erosion rate between the ASDEX-Upgrade sample and an a-C:D film for air exposure at 650 K.

The details of the oxygen trapping and the formation of volatile erosion products are still unresolved. Based on a general accepted scheme for simple thermal oxidation of hydrocarbon polymers [18,19], Haasz et al. proposed a plausible reaction mechanism for the polymerlike C:D film $(CD_2)_n$ with oxygen by a series of chain reactions leading to releases of D_2O, CO_2 and CO [2]. However, the reaction mechanism for a hard a-C:D film with oxygen and the chemical state of the large amount of oxygen in a deuterium depleted carbon layer are not very clear. In addition, water vapor in air is another possible source for the exchange reaction of $H_2O + D \Rightarrow H + HDO$, which can explain the exchange of D by H in the oxidized layer as shown in Figs. 2–4. Further work will study the dependence of hydrogen isotope exchange on the water vapor content.

3.3. Comparison with the ASDEX-Upgrade sample

Fig. 6 shows the difference of the erosion rate between an a-C:D film and the ASDEX-Upgrade sample during air exposure at 650 K. The two samples have similar layer thickness and similar hydrogen/carbon ratios. However, the removal rates of both carbon and deuterium for the ASDEX-Upgrade deposit are much higher than for the a-C:D film. About 72% of carbon and 83% of deuterium are lost already after 2 h annealing from the ASDEX-Upgrade sample, while only 11% of carbon and 12% of deuterium are removed during the same period from the a-C:D film. The ASDEX-Upgrade sample has a very rough surface with bubbles, cracks and, of course, many impurities. Some hydrogen isotopes may only be trapped in defects instead of a strong bonding to carbon chains as in a-C:D films deposited in controlled discharge conditions in the laboratory. Furthermore, the hydrogenated carbon layer deposited during plasma operation on the wall of tokamaks is very complex and depends on a large number of parameters, such as the flux ratio of hydrogen ions to carbon ions, contribution of thermal atomic hydrogen, simultaneous irradiation with high energetic charge-exchange neutrals. Therefore, further simulation experiments have to be performed using a variety of a-C:D films deposited under different plasma discharge conditions to achieve a better understanding of the film oxidation mechanism.

4. Conclusion

The erosion of a-C:D films during annealing in air was investigated. The films were between 350 and 770 nm thick. Annealing in air leads to a significant release of deuterium and an erosion of carbon. The release rate is significantly increased by annealing. For 1 h air exposure deuterium release is observed at temperatures above 600 K, and almost all deuterium is released at 700 K. During the exposure carbon is also eroded, and the whole codeposited layer is removed at 725 K.

At a fixed temperature of 650 K the erosion of a-C:D film depends on the annealing time in air. Annealing for 8 h leads to a complete release of deuterium, and further annealing results in the removal of the whole 750 nm carbon layer.

The a-C:D films are eroded due to surface oxidation in contrast to vacuum annealing which results in thermal desorption of deuterium and hydrocarbons at temperatures higher than the range in our experiments. Oxygen reacts with carbon and deuterium leading to the release of volatile products, such as D_2O, CO and C_2O. Another part of the oxygen is trapped in the film leading to further reactions in the bulk and forming a saturated oxidation layer in which deuterium is depleted. The thickness of the deuterium depleted and oxygen saturated layer increases with annealing time until it finally extends throughout the whole remaining carbon layer. Further annealing leads to a thickness decrease until the complete layer is removed. Hydrogen isotope exchange occurs simultaneously, probably due to the reaction of film components with water vapor from the air.

The release rate of deuterium strongly depends on the film structure. It is found that the erosion of a hydrogenated carbon layer codeposited during 6 months' plasma operation in ASDEX Upgrade is much faster than the erosion of an a-C:D film which is attributed to their different deposition conditions. It is expected that the ASDEX-Upgrade deposit could be removed by annealing in air at a temperature below 600 K within one day. Further experiments will be performed using a variety of a-C:D films to simulate the hydrogenated carbon layer codeposited on the wall in tokamak devices. The dependence of the deuterium release rate on exposure conditions, such as water vapor pressure, oxygen and hydrogen pressure will be studied.

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