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Erosion of a-C:H in the afterglow of ammonia plasma

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Abstract Amorphous hydrogenated carbon (a-C:H) deposits were eroded in the afterglow of NH_3 plasma, created with an inductively coupled RF generator in pure NH_3 at the gas pressure of 50 Pa. The plasma system was characterized by optical emission spectroscopy and mass spectrometry, the erosion process was monitored in-situ with a laser interferometry system. In the plasma, NH_3 molecules were dissociated to a varying degree, depending on forward generator power. The resulting NH_x radicals recombined back into $NH₃$ molecules, whereas N and H atoms were more likely to form N_2 and H_2 molecules. The erosion rates were found to increase with surface temperature and forward generator power. The dependence on the forward generator power, linked to the estimated degree of dissociation of the NH_3 molecules, and the mass spectrum of reaction products suggest that the dominant process in the a-C:H removal was erosion by neutral nitrogen atoms.

1. Introduction

In the recent years, a lot of research efforts were invested in the problem of removal of amorphous hydrogenated carbon (a-C:H) layers[1-6]. The formation of these layers occur when carbon-based plasma facing materials are eroded by H species from the plasma. The resulting C_xH_y complexes are re-attached to the surface, forming a-C:H deposits[7-10].

As ITER was planned to operate with carbon based divertor components, the formation of a-C:H layers would lead to in-vessel tritium retention, a serious concern from the legal, safety and operational point of view[7]. Ultimately, a decision has been reached to start ITER without carbon based components, owing to the high susceptibility of carbon to chemical erosion by hydrogen species and subsequent growth of a-C:H. However, thanks to their excellent power handling capabilities, and the low Z of carbon, many fusion devices still operate, or will be starting to, with carbon (graphite or carbon fibre composite) plasma facing components. Moreover, while the carbon content in the plasma has been significantly diminished after switching to full metal inner wall configuration in AUG an JET, it has nonetheless not been removed completely[11, 12]. As another campaign of D-T operation is foreseen for JET, the problem of tritium retention in carbon codeposits could still persist on a small scale.

Even without D-T operation, coverage of surfaces with a-C:H could lead to several problems. As a-C:H deposits are easily eroded by the plasma, a change in the plasma configuration could erode deposits accumulated on previously non-wetted areas. This could result in rapid release both of impurities and hydrogen species into the plasma, causing problems with impurity and density control.

Coverage of inner vessel surfaces with a-C:H affects the low-energy end of their plasma-wall interaction properties, as it alters the probability of heterogeneous recombination of neutral atoms[13, 14] which in turn affects the fuel recycling properties. The accumulation of a-C:H also impedes optical spectroscopic diagnostics when the a-C:H deposits cover the surfaces of the mirrors^[15].

The research of chemical methods of a-C:H removal has approached the problem from two sides. The conventional approach was based on using chemically active species to remove the a-C:H deposits from reactor vessel walls. The chemically active species would either be formed in the vessel, as was demonstrated with glow discharge cleaning in oxygen[3, 4], or produced externally (in a remote plasma system) and puffed into the reactor vessel[16]. The drawback of using oxidative species is the risk of damage to plasma-facing and structural components. The other approach was to use chemically active species to prevent the formation of a-C:H deposits by binding to the precursors, i.e. the scavenger effect[17]. The effectiveness of the scavenger effect has been demonstrated with nitrogen species (molecular and atomic nitrogen, ammonia), both in Pilot PSI-2[18] as well as in TEXTOR[19]. While nitrogen species were shown to be effective scavengers (and thus inhibit the growth of a-C:H layers) in separate laboratory experiments, the final, in-situ result is most likely a combined effect of the inhibited deposition and the erosion by active nitrogen species.

Our previous study demonstrated that the ionic species of a NH3 plasma can erode a-C:H deposits[20]. In this work, we focused on the neutral radicals that are formed in a NH₃ discharge.

2. Experimental

The main vacuum vessel of the plasma reactor, shown in Fig. 1, was a borosilicate glass tube with the inner diameter of 36 mm, and two side arms which allowed for mounting of the sample holder and the optical view-port for the laser interferometry system. The distance between the side arms and the discharge coil of 35 cm allowed for a negligible density of charged particles at the position of the sample. The vacuum system was pumped with a two stage rotary pump with the pumping speed of 80 $m³/h$, which could be attenuated with a butterfly valve. Ammonia was leaked into the system through a mass-flow controller at the flow rate of 183 sccm, and the butterfly valve was set so that the pressure in the reactor

chamber was 50 Pa. The effective pumping speed was thus $16.6 \text{ m}^3/\text{h}$ (4.6 $\cdot 10^{-3} \text{ m}^3/\text{s}$). The average drift velocity of gas through the glass tube was 4.6 m/s and the gas required about 0.08 s for drifting from the coil to the sample.

The plasma was created with an inductively coupled radiofrequency (RF) generator. The generator was operating at the frequency of 13.56 MHz with the maximum available output power of 1000 W. The generator was coupled to the plasma system though a matching network and six turn, water-cooled coil, wound around the glass tube, which defined the discharge region in the reactor. The discharge region was actively cooled by compressed air.

Prior to measuring the erosion of a-C:H, the plasma system was characterised by optical emission spectroscopy and residual gas analysis. Optical emission spectroscopy (OES) was performed with an Avantes AvaSpec 3648 optical emission spectrometer. The spectrometer was linked to the system with an optical fibre which was mounted very near (less than 1 cm away) to the inductive winding, as indicated in Figure 1. A differentially pumped Pfeifer PrismaPlus QMG 220 Residual Gas Analyser (RGA) was mounted downstream of the discharge. It was used to record continuous mass spectra of the ammonia discharge, in the $0 -$ 35 Atomic Mass Unit (AMU) range. Because the pressure in the reactor chamber was considerably higher than the maximum allowed operating pressure of the RGA, it was connected to the reactor through a glass-tube flow restrictor which kept the pressure in the RGA chamber below 5·10⁻³ Pa. This pressure drop of 5 orders of magnitude unfortunately made it impossible to calibrate the RGA against partial pressures in the reactor chamber, or to carry out any gas-balance analysis.

Samples of approximately 250 nm thick a-C:H thin films with an approximately 40 at % hydrogen content were produced by a previously described procedure[14], and deposited on polished stainless steel substrates.

In the erosion experiments, the samples were mounted on a temperature controlled holder, positioned 35 cm away from the discharge region as shown in Figure 1. Flash-dry silver paint (SPI Supplies) was used to ensure a good thermal contact between the samples and the sample holders. The erosion of the amorphous hydrogenated carbon deposits was monitored with a laser interferometry system. The system consisted of a laser module that produced laser light with the wavelength of 635 nm and the intensity of 3 mW. The light was passed through a quartz window to the sample. The intensity of the reflected light was measured with a Hawkeye ® laser detector. The details of such in-situ erosion monitoring are described elsewhere[6].

3. Results and discussion

3.1. Characteristics of the plasma system

The characterisation of the NH₃ discharge by RGA is shown in Figures 2a and 2b. Mass spectra were acquired without plasma operation, and during plasma operation at generator forward owers ranging from 100 to 1000 W. Spectra recorded without plasma operation (0 W), at 200 W and at 700 W forward power are shown in Figure 2a, and peak intensities at 2, 16, 17 and 28 AMU/ e_0 are shown in Figure 2b versus generator forward power. At powers up to 350 W, the plasma system operates in the E-mode, characterized by incomplete coupling to the power supply and generally lower values of plasma parameters (electron density, degree of source gas dissociation). At powers above 600 W, it is in the H-mode, where the coupling is more efficient and the plasma parameter values increase. At powers between 400 and 650 W, the system is in a transitory mode in which prolonged operation is not possible, therefore no measurements were made in this power range. As Zaplotnik *et al*[21] have shown, the power at which the mode transition occurs is pressure dependent. In the presented system, it was not possible to achieve the H-mode at significantly higher pressures than 50 Pa.

Without plasma operation, the most prominent features in the spectrum are peaks at 16 and 17 AMU, corresponding to ammonia, while the intensities of peaks related to nitrogen, hydrogen and water (background atmosphere) are orders of magnitude lower (Figure 2). Additionally, a faint peak is found at 8.5 AMU, most likely corresponding to NH_3^{++} . In the E-mode, the intensity at 17 and 16 AMU as shown in Figure 2 decreases very slightly due to logarithmic scale while the intensity at 1, 2, 14 and 28 AMU increases by orders of magnitude, indicating the conversion of NH_3 to N_2 and H_2 . The relative intensities of ammonia related peaks does not change, which means that only the NH₃ molecule contributes to the peaks. The NH and $NH₂$ radicals that are produced in the plasma must recombine into $NH₃$ or $N₂$, $H₂$ on the way to the mass spectrometer. In the H-mode, the conversion is saturated throughout the range of generator powers (from 700 to 1000 W). The intensity of NH3 related peaks is reduced by approximately a factor of 10 in regard to their original (no plasma) value. The saturation of the conversion indicates an almost complete dissociation of the $NH₃$ molecule in the plasma phase, resulting in a population of N and H radicals. The persistence of a small amount of NH3 in the recorded mass spectra even at high powers, however, indicates that while the

recombination into N_2 and H_2 molecules is a far more probable process, a small part of the N and H radicals still recombine into the NH₃ molecule.

In the case of full dissociation of the NH_3 molecule at 50 Pa, the resulting density of N and H atoms is $1.21 \cdot 10^{22}/m^3$ and $3.46 \cdot 10^{22}/m^3$ respectively. The density of atomic species at the location of the sample holder is expected to be a combined result of the gas flow through the experimental system, diffusion and recombination on the walls of the vessel. Experiments and simulations of oxygen atom density in a very similar system have shown that the reduction in density from the source to the approximate location of the sample holder would range between a factor of 3 and 4[22].

Values of the recombination coefficient for nitrogen and hydrogen atoms on borosilicate glass at room temperature are between $5 \cdot 10^{-8}$ and $2 \cdot 10^{-4}$, and $1.05 \cdot 10^{-5}$ and 5.8·10[−]³ respectively[23-25]. As these values are similar to the recombination coefficient of oxygen atoms, we estimate the neutral atomic species density near the samples is around 25 % of their density in the discharge region, i.e. $3.0 \cdot 10^{21} / m^3$ and $8.6 \cdot 10^{21} / m^3$ for nitrogen and hydrogen atoms respectively. In contrast, the probability of neutralization of ionic species upon contact with solid surfaces is 100 %, so their density declines much more rapidly and is negligible at the location of the sample holder. The difference between the E mode and H mode is further illustrated in the OES measurements. The spectrum of the E mode plasma, in Figure 3a, shows a prominent peak attributed to the NH radical and a band which is attributed to the NH2 radical. In the H mode, the NH2 band is not present and the NH peak is strongly reduced as compared to H lines of Balmer series. This is even more evident in Figure 3b which shows the emission intensities of some relevant spectral features $(H_{\alpha}, N_2, NH, NH_2)$ versus forward generator power. Coherently with the findings of the RGA measurements, this implies that there is a significant reduction of the density of NH_x species in the H-mode. The resulting gas in the late afterglow becomes mixed nitrogen-hydrogen molecules, rather than ammonia.

3.2. Erosion of thin a-C:H films

The erosion of a-C:H samples was performed at the forward power of 200 W, 350 W (E mode) and 700 W (H mode). The measured erosion rates plotted against temperature, for different forward powers, are shown in Figure 4. They increase both with temperature as well as forward generator power. The highest recorded erosion rate was 10 ± 1 nm/s, at the forward power of 700 W and the surface temperature of 623 K. Similar to the degree of

dissociation of NH₃, the most striking difference occurs between the results obtained in the Emode and the H-mode. The fast increase of the erosion rates with the surface temperature clearly indicate that the observed erosion is a predominantly chemical process, i.e. the contribution of neutral species is vastly stronger than that of ionic species.

Since the rates of erosion of a-C:H with neutral O or H atoms are proportional to the atom density[26-28]we expect that the differences in the erosion rates at a given temperature, obtained at different forward powers, are due to the density of active species. As the degree of the dissociation of $NH₃$ increases drastically in the E- to H-mode transition, the increase in the erosion rate is likely due to the increase of the density of N and H atoms. At the same time, it should be noted that while the intensity at 2 and 28 AMU/ e_0 in the mass spectra, and accordingly the density of N and H atoms, increases by a factor of 3 between the forward powers of 200 and 350 W, this increase is not reflected in the erosion rates. This suggests that in the E-mode, the key species that drive the erosion process are NH_x radicals, where the variation in density is probably smaller. In contrast, the increase of erosion rates in the E- to H-mode transition matches the increase in the H and N atom related intensities in the mass spectra, suggesting that at these densities, H and N atoms take on the dominant role in the erosion process.

Due to the small surface area of the samples, partial pressures of the volatile reaction products were in general too small to be detected with the mass spectrometer. Accordingly, a detailed RGA characterisation of the process was not attempted. Instead, the spectra were recorded only at the conditions that yielded the highest erosion rate – H-mode plasma operation and the surface temperature of 623 K. The recorded spectra are shown in Figure 5. Small increases are found at 12 AMU, 24, 25, 26 and 27 AMU, which can be explained by the expected reaction products: the C atom (12 AMU), C_2H_2 (24 – 26 AMU) and HCN (26 and 27 AMU). The masses corresponding to CH4 (14 – 16 AMU) are populated by NH_3 and N_2 related peaks with far greater intensities, so it is not possible to verify their presence. Among the detected reaction products related peaks, the highest increase is observed at 27 AMU, which suggests that HCN is the most prominent reaction product, which in turn indicates that the nitrogen atoms are taking part in the erosion process. Hydrogen is present both in the gas phase as well as in the deposits, so the role of the hydrogen atoms cannot be identified with these results. Erradi *et al*[27]*.* have reported significantly lower a-C:H erosion rates by atomic hydrogen alone, whereas other studies have shown synergistic effects of H and N species in the removal of a-C:H[29, 30], as well as other surface processing applications[31]. The noted

increase at 19 and 20 AMU could be attributed to the release of impurities from the silver paint, used to affix the samples to the sample holder.

The erosion rates, recorded in the H-mode, are approximately 4 times lower than those obtained with atomic oxygen, at the same surface temperatures and similar densities of active species. This suggests that the erosion yield of atomic nitrogen is considerably lower than that of atomic oxygen, however the present experimental setup does not allow for the determination of the atomic nitrogen density beyond the order of magnitude estimate. Contrary to the erosion by oxygen, the erosion by N, H and NH_x species does not produce water. This is favourable both from the point of view of general vacuum conditions, as well as of implications of potential tritium operation.

4. Conclusions

Experiments of a-C:H erosion were performed in the afterglow of $NH₃$ plasma. The temperature controlled sample holder was located downstream of the region of plasma generation. The erosion process was monitored *in situ* with a laser interferometry system. The operation of the plasma system was characterised by OES and RGA.

After being dissociated in the plasma, part of the NH₃ molecules were being converted into N_2 and H_2 molecules. While the intermediary reaction products could not be detected with the RGA, the most likely precursors to N_2 and H_2 are N and H atoms, suggesting that the afterglow of the NH₃ plasma is populated not only by NH and NH₂ radicals but by N and H atoms as well.

In the H-mode, the degree of NH_3 conversion saturated at a very high value of about 90%, indicating that it was mostly N and H atoms that comprised the afterglow of the plasma. Because of the high efficiency of dissociation combined with the low atom loss coefficient of the borosilicate glass, the NH₃ plasma was a very efficient source of atomic nitrogen and hydrogen.

Taking into account the wall neutralization and recombination coefficients, the area around the sample holder is populated by neutral active species, while the density of charged species is negligible. Thus, the erosion of the a-C:H is predominantly due to the interaction of neutral radicals. In the E-mode, the neutral radical population is comprised of NH, NH2, N and H species whereas in the H-mode, N and H atoms prevail. The erosion rates in the Hmode were found to be an order of magnitude higher than in the E-mode, corresponding to an

approximately equal increase in the density of N atoms. The mass spectrum of the exhaust during erosion of the a-C:H sample indicates that the most prominent reaction product is HCN. These results underline the key role of the nitrogen atoms in the erosion process.

Moreover, these results show that erosion of already existing a-C:H deposits is likely an important component of the scavenger effect. Active species that are created when ammonia or nitrogen is injected into the tokamak edge plasma will serve also to remove a-C:H layers from nearby surfaces, especially plasma-shadowed surfaces which are not accessible to ionic species, such as castellation gaps. The same areas could be cleaned during wall conditioning with ICRH plasmas in nitrogen or ammonia containing gas mixtures. In fusion devices which operate with heated walls, the erosion rates in the remote surfaces would thus be significantly increased. As nitrogen seeding is routinely used to lessen the heat loads on divertor surfaces in metal-walled fusion devices, the interaction of nitrogen species with surface contaminants will no doubt make up a part of the complex mosaic of plasma-wall interaction.

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7. Figure captions

Figure 1: experimental set-up. 1 – temperature controlled sample holder, 2 – sample, 3 – laser interferometry system, 4 – optical viewport, 5 – glass tube, 6 – discharge region, 7 – inductive winding, coupled to the RF generator.

Figure 2: a) Mass spectra recorded without plasma operation and with plasma operation at the forward power of 200 and 700 W, b) intensities in mass spectra at 2, 16, 17 and 28 AMU shown versus generator forward power.

Figure 3: a) Optical emmision spectra at 200 and 700 W forward power, b) and the evolution of relevant emission lines versus forward generator power.

Figure 4: Erosion rate of a-C:H vs. surface temperature, at different forward generator powers

Figure 5: Mass spectrum in the $1 - 28$ AMU range with no plasma operation, and during erosion at 700 W forward generator power. The sample surface temperature in both cases was 673 K.

8. Figures

Figure 1

Figure 2a

Figure 2b

Figure 3

Figure 4

Figure 5

