



## Erosion of a-C:H films under interaction with nitrous oxide afterglow discharge

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### ABSTRACT

Hydrocarbon film removal using chemically active oxygen formed in a direct current glow discharge with a hollow cathode in nitrous oxide was investigated. In the afterglow region sufficiently fast removal of a-C:H films about 500 nm thick during about 8 h was achieved at N<sub>2</sub>O pressure of 12 Pa and 370 K. The erosion rate in the afterglow region was directly proportional to the initial pressure and increased two orders of magnitude at temperature rising from 300 to 500 K. The products of a-C:H film plasmolysis were CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>. After removal of a-C:H films previously deposited on stainless steel, molybdenum or tungsten 3–30 nm thick oxide films were formed on the substrates. Reactions of oxygen ion neutralization and atomic oxygen recombination suppressed further oxidation of the materials.

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### 1. Introduction

In most modern tokamaks the possibility is stipulated of glow discharge usage in various gases for preparation of inner surfaces of a main chamber and divertor for the experiments with the hot plasma [1]. By now numerous attempts were made to use different types of gas discharges in hydrogen, oxygen or in oxygen/inert gas mixture [2] for hydrocarbon film removal. As a result of ion-induced oxidation, hydrocarbon films are gasified more effectively in oxygen plasma than in hydrogen plasma [1].

Experiments in tokamaks have shown that due to low recombination coefficients of methyl and some other hydrocarbon radicals hydrocarbon films can form on the surfaces which are not in contact with plasma [3]. In [4] the removal of a-C:H film by oxidation in molecular oxygen atmosphere was investigated by heating the whole vacuum chamber covered with a-C:H films up to 473 K.

In this connection the problem arises of enhanced a-C:H film removal using chemically active neutral particles (e.g., atomic oxygen) capable to be transferred over significant distances from a particle generation source.

In this article the removal of a-C:H films is investigated using chemically active oxygen formed in a direct current glow discharge with a hollow cathode in nitrous oxide. We focus on the film gasification in the afterglow region and the formation of oxide layers on molybdenum, tungsten and stainless steel after a-C:H film removal.

### 2. Experimental

Direct current glow discharge (DCGD) with a hollow cathode in nitrous oxide was used as source of atomic oxygen. As a chemical reactor we used a quartz tube 110 cm long (inner diameter of 1.9 cm) with two soldered quartz tubes of the same diameter and each 25 cm in length both located in a horizontal plane (Fig. 1). The N<sub>2</sub>O flow was set by a controller (1) in the range 3–10 sccm. After the controller the flow entered the discharge zone through the hollow cathode made from stainless steel (SS). A connection circuit between the hollow cathode and the grounded anode permitted to achieve a stable discharge at pressures of 3–24 Pa and currents of 5–50 mA. A part of the afterglow region of the 50 cm long could be heated by an external cylindrical furnace with a length of 15 cm. In the gap between the furnace and tube a thermocouple was placed. The pressure in the reactor was regulated by means of a valve (5) located at the tube outlet. A Pirani gauge (PG3) was placed at the pumping tube end. A small part of gas mixture was extracted for analysis in a differentially pumped quadrupole mass-spectrometer connected to the reactor by a leak valve (4). The reactor was pumped down to a pressure of 0.1 Pa before starting the experiment. A rate of inleakage of air did not exceed  $3 \times 10^{-3}$  sccm at limiting background better 0.1 Pa.

The discharge was limited by a special anode arrangement in the lateral quartz tube from the main tube (anode 1) or a hollow SS anode (anode 2) in the main tube (Fig. 1). The average energy of ions impinging the cathode did not exceed 100 eV [5] at cathode drop of 350 V. The plasma column consisted as a rule of the set of the immobile strata (laminated discharge) formed in the gas moved with a velocity 1–5 m/s. The average energy of ions impinging the tube wall in the positive column region did not exceed 10 eV [5].

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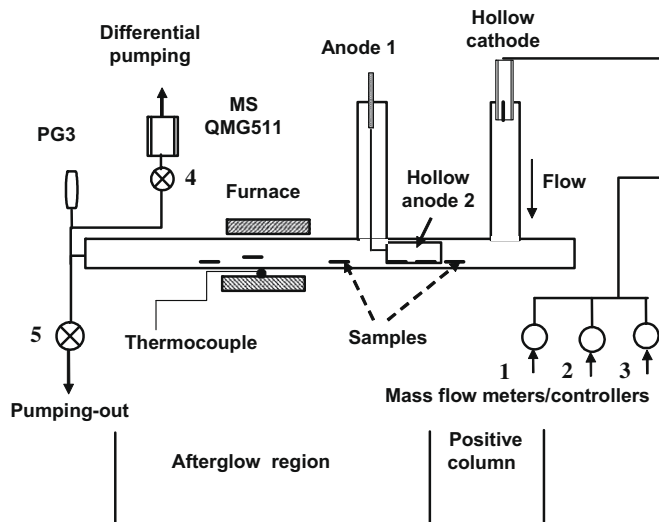


Fig. 1. Scheme of setup for studying of a-C:H film deposition and gasification.

We assumed that in the afterglow region the ions were absent and only the neutral atoms and excited molecules were chemically active since the a-C:H film erosion rate decreased sharply. The investigation of carbon gasification and metal oxidation in the afterglow region is especially urgent in connection with the necessity of the hydrocarbon film removal from the regions which have no direct contact with plasma.

To study carbon erosion different a-C:H films were chosen that were deposited either directly in the tube on the cathode surface and tube wall in hydrogen/methane mixture DCGD (soft a-C:H films) or in a separate setup on Si, Mo, W, and substrates of a sheet stainless steel (hard a-C:H films) [6]. Some film properties are given in Table 1. The film erosion process was studied by mass-spectrometry (MS) in the interval 0–100 amu and by electron probe microanalysis (EPMA).

Before and after the experiments the C, O and N areal densities ( $\mu\text{g}/\text{cm}^2$ ) in the a-C:H films were measured by EPMA using the radiation intensities of  $\text{CK}_\alpha$ ,  $\text{OK}_\alpha$  and  $\text{NK}_\alpha$  lines with  $\gamma$ -quantum energies 283, 523 and 392 eV, respectively. In most experiments the film weight with an accuracy of  $5 \times 10^{-7}$  g were measured too.

### 3. A-C:H film erosion initiated by glow discharge in nitrous oxide

For MS analysis of gasification the soft a-C:H films (Table 1) were chosen. The films were deposited on the walls of the hollow cathode and tube filled with positive column plasma in DCGD using  $\text{H}_2/\text{CH}_4$  mixture or pure  $\text{CH}_4$  that entered through the controllers (2) and (3) (Fig. 1). After the a-C:H film deposition nitrous oxide was introduced to the tube and a discharge was started. During the discharge (current 30 mA, voltage 0.8 kV, wall temperature 293–310 K, initial pressure 15 Pa) the entering mass flow in the tube was maintained strictly constant (7 sccm).

The  $\text{N}_2\text{O}$  mass-spectrum (without DCGD) consisted of lines of atomic nitrogen N (14 amu), molecular nitrogen  $\text{N}_2$  (28 amu), nitric

oxide NO (30 amu), and nitrous oxide  $\text{N}_2\text{O}$  (44 amu). In DCGD the  $\text{N}_2\text{O}$  linear molecule decomposed into  $\text{N}_2$  and O. The degree of  $\text{N}_2\text{O}$  decomposition increased with increasing discharge current and 100% decomposition of  $\text{N}_2\text{O}$  occurred at current 30 mA. From the MS data we supposed that during the transport along the tube the atomic oxygen transformed into molecular oxygen in result of the recombination reaction on tube surface.

In the spectrum of erosion products we detected lines of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and CO line coinciding with  $\text{N}_2$  one, and  $\text{CO}_2$  line coinciding with  $\text{N}_2\text{O}$  one. As in DCGD the  $\text{N}_2\text{O}$  decomposed completely the line  $\text{CO}_2$  was well identified and it permitted to follow the gasification rate of hydrocarbon deposits in the tube (Fig. 2). When the discharge was switched on the pressure in the tube increased from 15 to 18 Pa due to decomposition of  $\text{N}_2\text{O}$  and then up to 22 Pa in the process of carbon gasification. After 100 s exposure in the  $\text{N}_2\text{O}$  discharge the MS signal (44 amu) began to decrease. Simultaneously a cathode potential decreased also indicating on the film removal from the cathode inner surface. The total pressure diminished gradually as well approaching the pressure value established in the tube with clean walls. In this experiment 3 mg of carbon were removed.

The experiments described below were performed with hard a-C:H films (Table 1). The weight and EPMA measurements showed that the a-C:H film erosion rate ( $G$ ) was maximal in the hollow cathode. In the positive column it was 2–3 $\times$  lower than in the cathode but higher than in the afterglow region (Fig. 3).  $G$  decreased for the samples located in the afterglow region as  $\exp(-x/L)$ , where  $L = 8.9$  cm is a transport length for transport of oxygen atoms in the flow of  $\text{N}_2$  and  $\text{O}_2$  (Fig. 3). Such character of the erosion rate changing in the afterglow region indicates that oxygen atom recombination on quartz wall occurs according to the first order and is proportional to oxygen atom concentration in gas phase.

In the afterglow region (downstream at distance of 11 cm from plasma column)  $G$  increased linearly with increasing  $\text{N}_2\text{O}$  pressure in the temperature range 300–500 K (Fig. 4). The  $\text{H}_2$ , CO and  $\text{CO}_2$  molecules were recorded by MS. If the a-C:H film was heated in  $\text{N}_2\text{O}$  without discharge (24 Pa, 500 K)  $G$  was lower than  $0.3 \times 10^{14}$  at.C/cm<sup>2</sup> s.

In some experiments the oxygen erosion process was interrupted and O and N contents in the film was measured by EPMA. As a rule the oxygen content was higher than in the initial film and its increase was equal to  $(1-2) \times 10^{16}$  at.O/cm<sup>2</sup> at all stages of the a-C:H film thinning from 400 to 100 nm. Nitrogen in partly gasified films was not detected.

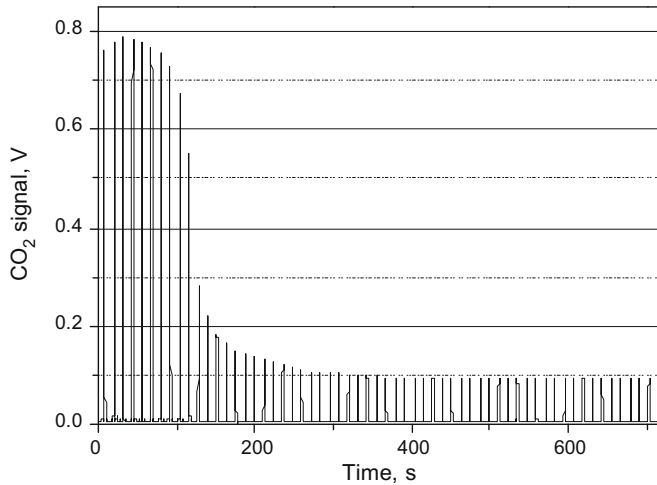
In Arrhenius co-ordinates the a-C:H film erosion rate in dependence on inverse temperature was described by straight lines. The activation energies of the film gasification were  $0.45 \pm 0.05$  and  $0.1 \pm 0.03$  eV in the temperature ranges 370–500 and 270–370 K, respectively (Fig. 5). Very low energies of the graphite gasification activation in air plasma ( $\approx 0.1$  eV) were reported in the literature [8]. The obtained effective activation energies turned out to be much lower than the activation desorption energies of molecules CO (3.3 eV) and  $\text{CO}_2$  (about 1 eV) [9]. The erosion rate in air was lower than in  $\text{N}_2\text{O}$  at pressure of 12 Pa. In these experiments gas flowing out of the plasma moved along the quartz tube.

Table 1  
Some properties of the hard and soft a-C:H films.

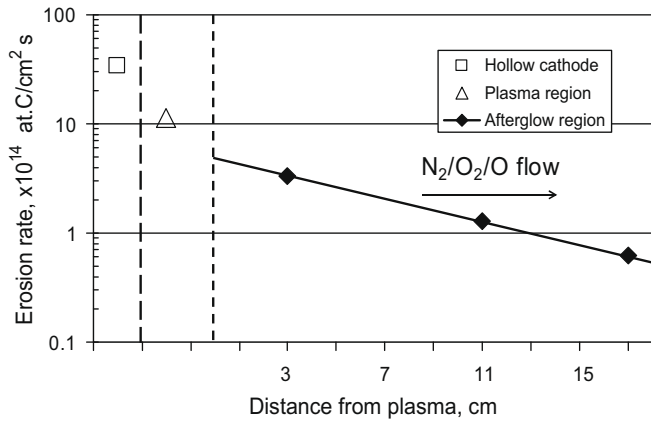
a-C:H film	Areal density (EPMA), $\mu\text{g}/\text{cm}^2/\text{at.C}/\text{cm}^2$	Thickness (TEM*) (nm)	Density** ( $\text{g}/\text{cm}^3$ )	Ratio H/C (SIMS, RGA [7], EPMA)	Ratio O/C (EPMA)
Hard	60–100/(3–5) $\times 10^{18}$	330–540	1.83	0.3–0.4	0.005–0.01
Soft	80–100/(5–6) $\times 10^{18}$	700–800	1–1.4	1–1.5	0.01–0.03

\* TEM - transmission electron microscopy.

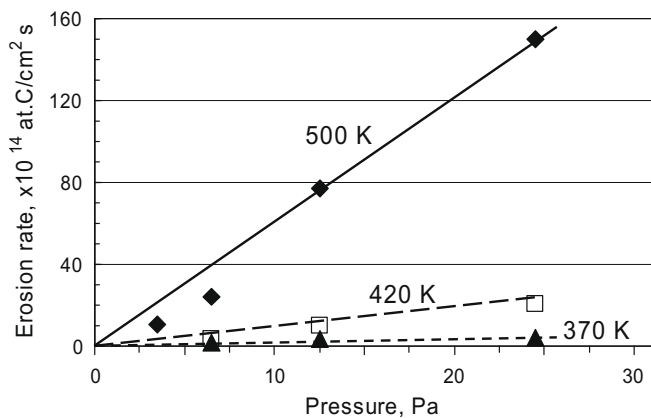
\*\* Density was determined from EPMA and TEM data and weighing as well.



**Fig. 2.** Changing of amplitude  $\text{CO}_2$  signal (44 amu) in time after discharge switching on (mass flow rate  $Q = 7$  sccm,  $P(\text{N}_2\text{O}) = 22$  Pa, flow velocity  $V = 1.7$  m/s,  $T = 320$  K, discharge parameters  $J \times U = 30$  mA  $\times$  0.8 kV).

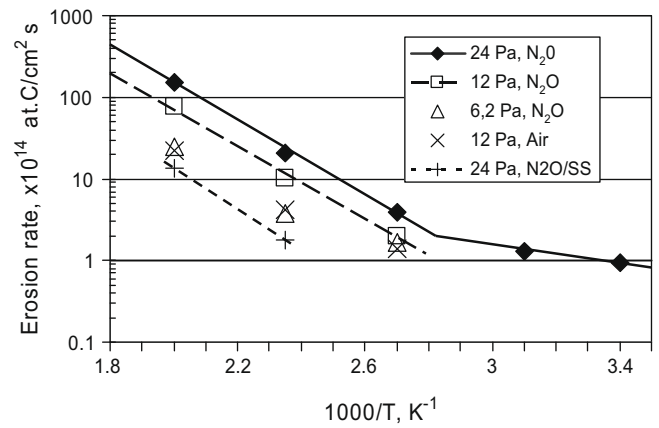


**Fig. 3.** Hard a-C:H film erosion rate in different DCGD regions (on the  $\text{N}_2\text{O}$  base) and in afterglow ( $Q = 8.8$  sccm,  $P(\text{N}_2\text{O}) = 24$  Pa,  $V = 1.95$  m/s,  $T = 320$  K,  $J \times U = 30$  mA  $\times$  0.8 kV).



**Fig. 4.** Hard a-C:H film erosion rate change in afterglow at 11 cm distance from plasma depending on initial  $\text{N}_2\text{O}$  pressure at different temperatures ( $Q = 8$  sccm,  $J \times U = 30$  mA  $\times$  0.8 kV).

In special series of experiments in the afterglow region there was placed a SS hollow cylinder with 7 cm length and inner diameter 1.7 cm. The a-C:H film samples were located inside the cylin-



**Fig. 5.** Hard a-C:H film erosion rate change in afterglow at 11 cm distance from plasma depending on inverse temperature at different initial  $\text{N}_2\text{O}$  pressures.

der end at distance of 11 cm from plasma. After leaving the plasma the neutral flow of plasmolysis products moved 4 cm along the tube and 7 cm inside the cylinder (Fig. 5,  $\text{N}_2\text{O}/\text{SS}$  line). In these experiments the activation energy of the film erosion was also 0.45 eV. At the same time the absolute values of erosion rate decreased an order of magnitude (Fig. 5).

Apparently, there exist several reaction pathways of the interaction of O atom with a-C:H film: i) oxygen atom can replace one or two hydrogen atoms from the film with formation of hydrogen or water molecules; ii) O atom is capable to penetrate into surface complex through the C–H bond with C–OH complex formation; iii) O atom can break off the single C–C bond or penetrate through double C=C bond with formation of C=O or C–O–C fragments. The final gaseous products CO and  $\text{CO}_2$  are the result of the successive reaction of surface CO groups with two or more O atoms.

Such reaction scheme of carbon gasification assumes an increased oxygen content in the surface layer of eroded film compared with the oxygen content of a film oxidised in molecular oxygen only. We assume that this leads to a lowering of the film gasification activation energy.

After the hydrocarbon film removal from the metal materials and subsequent one hour exposure in the plasmolysis products at 11 cm distance from plasma (initial nitrous oxide pressure 24 Pa, 420 K) the oxygen content in the surface layers of polycrystalline Mo and W substrates was less than  $3 \times 10^{16}$  at.O/cm<sup>2</sup> and in SS substrate was equal to  $3 \times 10^{16}$  at.O/cm<sup>2</sup>. On the SS substrate at 500 K a relatively thin layer of chromium oxides was formed with oxygen content  $6 \times 10^{16}$  at.O/cm<sup>2</sup>. If we assume that the chromium oxide density is 5.2 g/cm<sup>3</sup> the indicated oxygen content corresponds to oxide thickness of 9.6 nm.

Directly in the discharge region the oxide film thicknesses on SS reached 30 nm (420 K). The relatively low oxide film thicknesses on the metal materials which were in contact with oxygen atoms may be explained by enhanced recombination of oxygen atoms on the metal oxide surface.

**4. Summary**

1. In afterglow region we found a relatively fast removal of about 500 nm thick a-C:H films during 8 h (12 Pa, 370 K, 11 cm from plasma). The films erosion rate depended on their location with regard to the plasma and decreased in a row: hollow cathode, positive column, afterglow region.
2. The carbon gasification rate in afterglow region at 11 cm from plasma was directly proportional to the nitrous oxide pressure and increased two orders of magnitude with increasing process temperature from 300 up to 500 K.

3. CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub> were the a-C:H plasmolysis products.
4. After removal of hydrocarbon films previously deposited on SS, Mo and W, oxide films of the thickness 3–30 nm were formed on the substrates. The oxide layer thickness depended on the sample location and decreased from the cathode, through the positive column to the afterglow region.
5. On the substrates of SS, Mo and W the reactions of oxygen ion neutralization and atomic oxygen recombination suppressed the further oxidation of the materials.

#### Acknowledgements

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