A–C:H Film Removal from and Oxidation of W and Mo in H_2/Air Glow and Afterglow Discharge

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Abstract. A direct current glow discharge in H_2/air mixture with a hollow cathode was used as source of chemically active oxygen and nitrogen for selective removal of soft and hard amorphous hydrogenated carbon (a–C:H) films deposited on W and Mo. Additionally oxidation of W and Mo surfaces was studied by different techniques. The film erosion experiments have shown that erosion rates of soft a–C:H films increased about 6 times at 300 K as compared to pure H_2 discharge and were about 43, 6 and 1.5 nm/min in the cathode, positive column and afterglow regions, respectively. For hard a–C:H films the erosion rates were several times lower than for the soft films. After complete removal of a-C:H films the carbon traces on the W and Mo substrates were not observed by EPMA. At the same time in the cathode region the nitrogen and oxygen areal densities in the surface layers were about 2 and 4.5 $\mu g/cm^2$, respectively. In the positive column region the nitrogen and oxygen areal densities were about 2 $\mu g/cm^2$. It has been shown that after removal of the a-C:H films a primary (~1 nm thick) continuous amorphous oxide film transformed into secondary (up to 4 nm thick) island-like oxide films. The polycrystalline island-like oxide films were generated due to recrystallization of the primary oxide film. Metal oxidation suppression was caused by reactions of oxygen ion neutralization and atomic oxygen recombination on metals. Air presence in low-temperature hydrogen plasma results in formation of stationary thin oxide films. In products of a-C:H film erosion CO, CO_2, H_2O, NH_3, and HCN have been found by a quadrupole mass-spectrometer. The technique suggested is one of possible variants of an effective gas-discharge technology for a-C:H film removal from metal surfaces.

1. Introduction

In tokamaks, such as ITER, where carbon fiber components are proposed as divertor targets for exhaust D/T plasma, chemical erosion of carbon materials by hydrogen fuel can lead to formation of hydrocarbon molecules and radicals. Experiments on current tokamaks have shown that deposited hydrocarbon films contain a large amount of D and T [1]. Retention limit of tritium has not to exceed 700 g. Therefore, development both methods for decreasing of chemical erosion of carbon materials and techniques for T-C film removal is necessary.

On the other hand, a problem of hydrocarbon film deposition is connected with plasma diagnostics using mirrors and the necessity of constant monitoring of their condition [2]. Under deposition-dominated conditions the mirrors can be contaminated with deposits formed due to plasma-induced erosion of divertor tiles and first-wall components. The interference of reflected beams on thin and transparent carbon films may change the shape of reflectance spectra of reflective mirrors (e.g., W or Mo) that are located over the periphery of the plasma volume [3]. The reflective optical characteristics of the mirrors are to be invariable during tokamak pulses and after cleaning. In this respect, it is also necessary to have methods for removal of carbon deposits from mirrors.

In modern tokamaks, including ITER, the possibility is stipulated of glow discharge usage in various gases for treatment of inner surfaces of a main chamber and divertor for the experiments with the hot plasma. By now numerous attempts were made for soft and hard hydrocarbon film removal by means of gas discharges (H_2, H_2/N_2, N_2O, He/O_2, O_2, air) [4–8] and by oxidation in O_2 during heating at elevated temperatures [9]. In an oxygen plasma the amorphous hydrogenated carbon (a–C:H) films are volatilized more effectively than in a

hydrogen plasma due to ion-induced oxidation. In the case of oxygen-containing plasmas the oxide layers may be formed on the surface of metal materials. Metal oxides could be a source of oxygen ions polluting the plasma and could change also the optical reflective characteristics of mirrors. During removal of a–C:H films some parts of metal surface can be cleaned, but other parts may still be covered by the films. Therefore, in this paper oxidation of W and Mo surfaces is investigated after complete removal of a–C:H films from the surfaces using chemically active oxygen formed in H_2/air direct current glow discharge.

The goal of the work is to develop an effective oxygen-containing gas discharge technology for removal of hydrocarbon deposits from metallic substrates and minimal oxidation of their surfaces.

2. Experimental

A direct current glow discharge (DCGD) in H_2/air mixture with a hollow cathode was used as a source of atomic hydrogen and chemically active species (oxygen and nitrogen) capable to form gaseous carbon compounds. In a stream technique 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 H_2 and air flows were set by controllers (1) and (2) at 7 and 1.38 sccm, respectively, with an accuracy of 0.01 sccm. After the controllers the flows entered the discharge zone through the hollow cathode (15 cm length, 1 cm radius) made from stainless steel (SS) and cooled by piped water. A connection circuit between the hollow cathode and a grounded hollow anode permitted to achieve a stable discharge at pressures of 10-200 Pa and currents of 5-50 mA. The lengths of positive column and afterglow regions were 42 and 70 cm, respectively. 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). Before starting the experiment the reactor was pumped down to a pressure of 0.1 Pa. An air inleakage rate did not exceed 3×10^{-3} sccm at limiting background better 0.1 Pa.

The average energy of ions impinging the cathode did not exceed 100 eV 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 of 1-5 m/s. The average energy of ions impinging the tube wall in the positive column region did not exceed 10 eV.

Deposition of soft a-C:H films (up to 800 nm thick) has been performed in an H_2/CH_4 (7 and 4.8 sccm) DCGD before erosion experiments. The films were deposited on the hollow cathode, quartz tube walls, and W and Mo samples at 320 K. After the a-C:H film formation the CH_4 flow entered through controller (3) was switched off and an air flow instead of the methane one was introduced in the setup.

Hard diamond-like a-C:H films (600-800 nm thick) have been deposited in an asymmetrical capacitance methane discharge at frequency of 200 kHz on Mo at temperatures of 300-320 K [10] and than they have been used for carbon erosion study.

Before and after the experiments, C, N, and O areal densities ($\mu g/cm^2$) in the samples were measured by electron probe microanalysis (EPMA) using diamond, BN, and SiO_2 standards and the radiation intensities of CK_α, NK_α, and OK_α lines with γ-quantum energies 283, 392,

and 523 eV, respectively. In most experiments the film weights with an accuracy of 10^{-7} g were measured too. A film thickness has been measured by transmission electron microscopy. Knowing the film thickness and areal density, one can determine a film density. Average densities of the hard and soft a-C:H films were equal to about 1.8 and 1 g/cm^3, respectively. Oxygen content in the a-C:H film deposited on W and Mo was 2-3 at.%.

Products of a-C:H film erosion have been studied by the differentially pumped quadrupole mass-spectrometer. The chemical composition and structures of W thin (~5 nm thick) surface layers after a–C:H film removal were analyzed by X-ray photoelectron spectroscopy (XPS) and reflected high-energy electron diffraction (RHEED), respectively.
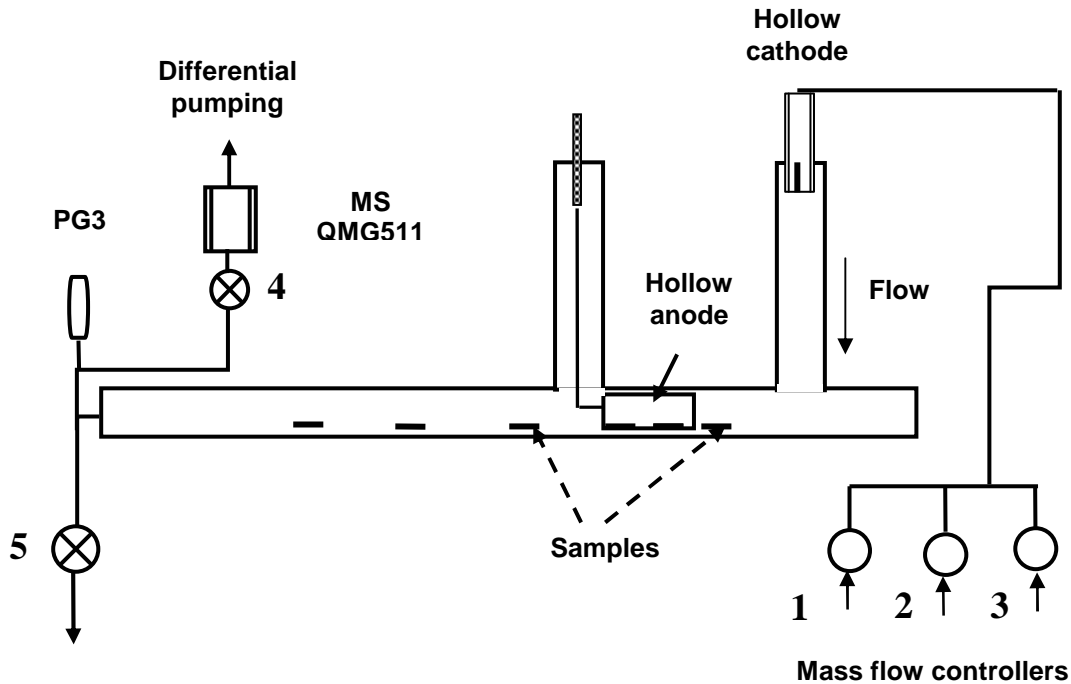

FIG. 1. Scheme of setup for studying of a-C:H film erosion. 1, 2, 3, - controllers. 4, 5 - valves.

3. Results and discussion

For efficiency enhancement of removal of a-C:H films preliminary deposited on the hollow cathode and quartz tube walls (area ~300 cm^2) at room temperature it was decided to add air to molecular hydrogen. The reasons were the following: i) to use atomic oxygen formed in DCGD for increasing of a-C:H film erosion rate, especially in places shadowed from plasma; ii) to prevent oxide film formation on divertor metallic units; iii) to simulate accidental ingress of air into a lower part of tokamak main chamber and its influence on structural transformations in the surface layers of divertor materials.

An H$_2$/air mass-spectrum (without DCGD) consisted of the following peaks: molecular hydrogen H$_2$ (2 amu), atomic nitrogen N (14 amu), atomic oxygen O (16 amu), molecular nitrogen N$_2$ (28 amu), and molecular oxygen O$_2$ (32 amu). For the primary mixture, the hydrogen peak (2 amu) is one order of magnitude higher than the nitrogen (28 amu) one and an amplitude ratio of the nitrogen peak (28 amu) to oxygen one (32 amu) is close to 5 (*FIG. 2a*) instead of assumed ratio of 3.7 (N$_2$ and O$_2$ concentrations in the air are 78 and 21 mol.%). One of possible reasons of reduced oxygen signal may be connected with the reactions of water formation from hydrogen and oxygen adsorbed on a vacuum chamber surface.

At discharge switching on (50 mA) the essential changes took place (*FIG. 2b*). The O_2 (32 amu) amplitude decreased from 0.69 down to 0.05 V because the most part of O_2 was expended on water formation. The water (18 amu) amplitude increased by 1.2 V (*FIG. 3a, b*). Simultaneously the amplitude of the peak (17 amu) connected with appearing of ammonia (NH_3) and coincided with water peak (OH) increased (*FIG. 3b*). In a water mass-spectrum an amplitude ratio of the H_2O (18 amu) peak to OH (17 amu) one is usually close to 4.3 (*FIG. 3a*). In the discharge illustrated in *FIG. 3b* the ratio decreased down to 2.78. An additional increment in regard to the OH signal was equal to 0.7 V and ascribed to the ammonia formation. In a pure hydrogen discharge (the same conditions) the ratio was equal to 4.2 (*FIG. 3c*). The calibration measurements for H_2/NH_3 mixtures allowed to conclude that 0.08 sccm of the inlet nitrogen turned into ammonia.
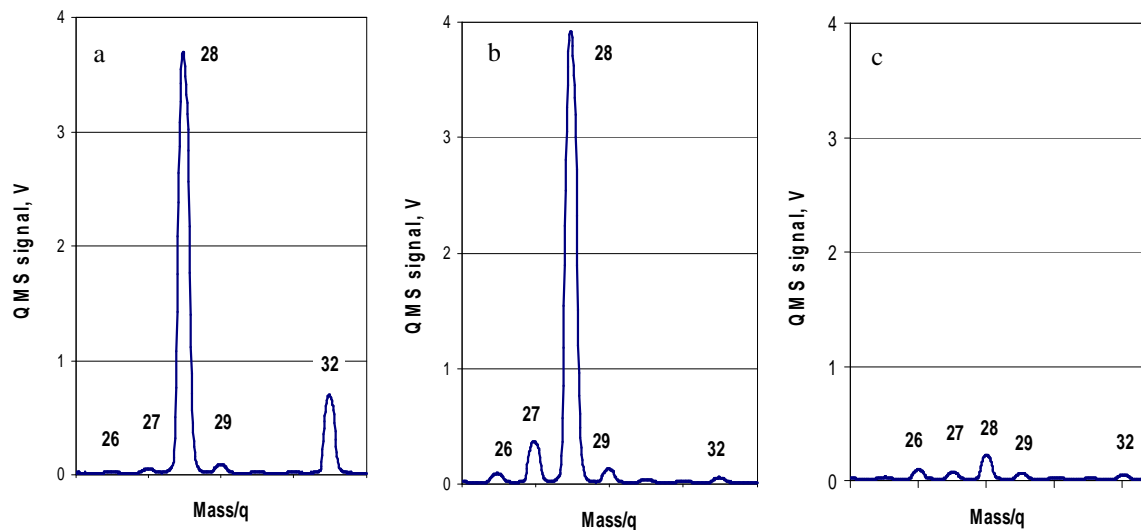

FIG. 2. Mass-spectra in the 26-32 amu range: (a) H_2/air mixture without discharge; (b) plasmolysis products in H_2/air mixture (Q_{H2} = 7 sccm, Q_{air} = 1.38 sccm, $J \times U$ = 50 mA $\times$ 0.6 kV). Pressure was 10 Pa; (c) plasmolysis products in pure H_2 (Q_{H2} = 7 sccm, $J \times U$ = 50 mA $\times$ 1 kV). Pressure was 7 Pa.
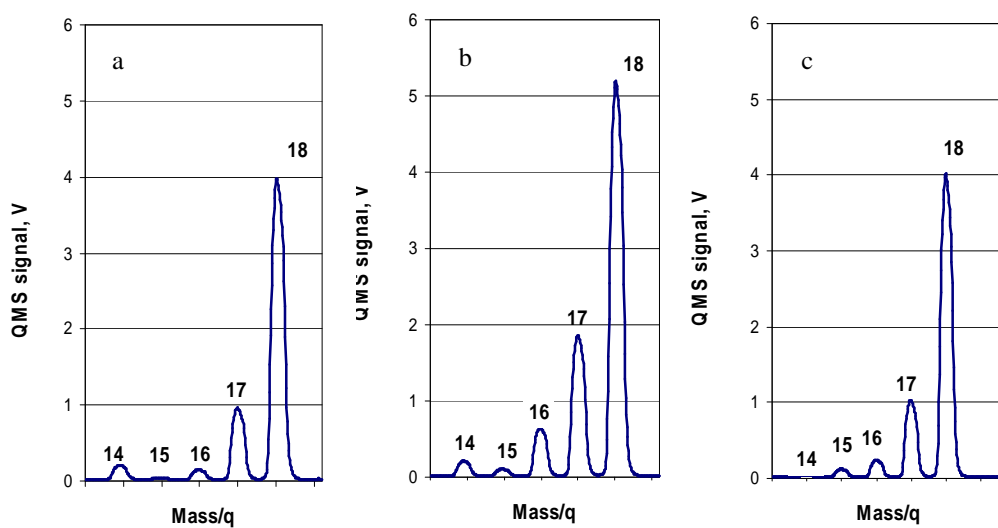

FIG. 3. Mass-spectra in the 14-18 amu range: (a) H_2/air mixture without discharge; (b) plasmolysis products in H_2/air mixture (Q_{H2} = 7 sccm, Q_{air} = 1.38 sccm, $J \times U$ = 50 mA $\times$ 0.6 kV). Pressure was 10 Pa; (c) plasmolysis products in pure H_2 (Q_{H2} = 7 sccm, $J \times U$ = 50 mA $\times$ 1 kV). Pressure was 7 Pa.

Here should be noted one peculiarity of ammonia behavior at interaction with hydrocarbon films deposited on tube walls. The ammonia molecules adsorbed easily on hydrocarbon film surface but they more difficult and slower desorbed into gas phase. Therefore, to achieve a steady concentration of ammonia in the gas flow passing through the discharge with fixed current a considerable time was required (up to 30 min).

In the discharge the amplitude of the peak (28 amu), which included N_2 and CO, increased from 3.69 up to 3.91 V (*FIG. 2a, b*) at nitrogen concentration decreasing due to NH_3 and HCN (hydrocyanic acid) formation. The latter had to lower the amplitude approximately 0.3 V. At the same time the formation of CO molecules on the other hand led to an amplitude increment of 0.4-0.5 V.

The calibration measurements for an $H_2/O_2/CO$ mixture (at the same concentrations of O_2 and CO) have shown that O_2 and CO amplitudes were equal to each other. This fact allowed to conclude that about 0.1 sccm of the inlet oxygen was transformed into CO and CO_2.

In the mass-spectrum of erosion products the signal (27 amu) is responsible for HCN formation. HCN flow rate was equal to 0.1-0.12 sccm. To our estimates the HCN formation (*FIG. 2b*) required about 0.06 sccm of the inlet nitrogen. It should be noted that at current decreasing from 50 down to 10 mA the HCN line amplitude also decreased, but the CO_2 line amplitude increased. In pure H_2 discharge the line (27 amu) was also present (*FIG. 2c*), but in the last case it was connected with C_2H_x and C_3H_x hydrocarbon formation. The amplitude of the peak (27 amu) was lower than in the H_2/air discharge. In pure H_2 discharge the peak (26 amu) amplitude exceeded the peak (27 amu) one.

The film erosion experiments in the H_2/air DCGD (30 mA) have shown that the erosion rates of the soft a-C:H films deposited on Mo and W increased about 6 times as compared to pure H_2 discharge and were about 43, 6 and 1.5 nm/min in the cathode, positive column and afterglow regions, respectively. For the hard a–C:H films the erosion rates were 30, 3 and 0.24 nm/min in the same places. After removal of the a-C:H films the carbon traces on the W and Mo substrates were not observed by EPMA. At the same time in the cathode region the nitrogen and oxygen areal densities in the surface layers were about 2 and 4.5 $\mu g/cm^2$, respectively. In the positive column region the nitrogen and oxygen areal densities were about 0.2 $\mu g/cm^2$.

After removal of the a-C:H films the thin (~5 nm thick) surface layers of W sample, which was located in the H_2/air plasma, has been analyzed by XPS (ex-situ). Besides tungsten (22.46 at%) carbon (39.72 at%) and oxygen (34.69 at%) were found to be the main impurities. There was also nitrogen (3.13 at%) with minor content.

O1s XPS spectrum (*FIG. 4*) was a sum of two Lorentz's functions with binding energy maxima at 530.7 and 532.4 eV. Such shape of the spectrum was connected with presence of oxygen in tungsten oxides and adsorbed water. W4f XPS spectrum (*FIG. 5*) could be represented as a sum of three duplets: i) the duplet with minimal binding energy is connected with metallic tungsten; ii) the duplet with maximal binding energy is responsible for tungsten trioxide (WO_3); iii) the weakly duplet with middle binding energy belonged to tungsten dioxide (WO_2) in which W is four-valence metal.
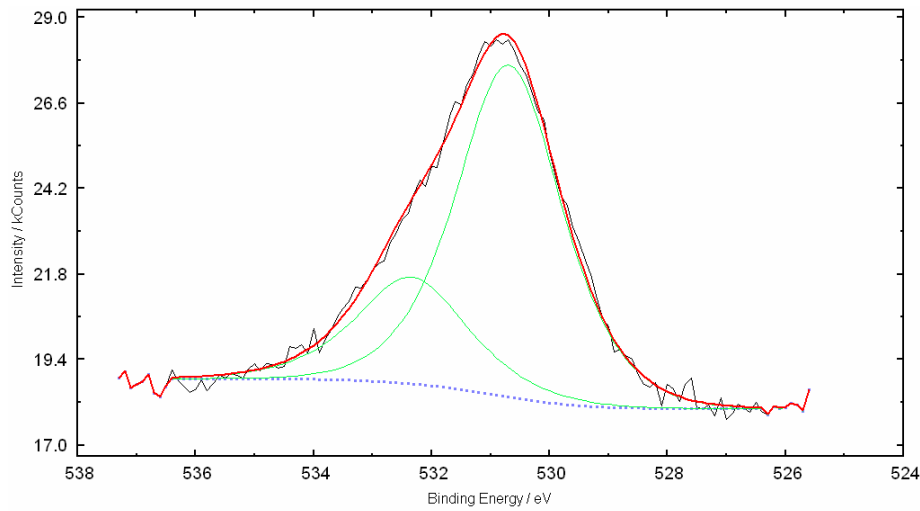
FIG. 4. O1s XPS spectrum for the W sample located in plasma (H$_2$/air mixture, 21 cm) after removal of the a-C:H film. The black curve is experimental data. The red curve is a sum of two Lorentz's functions (green). The blue curve is background.
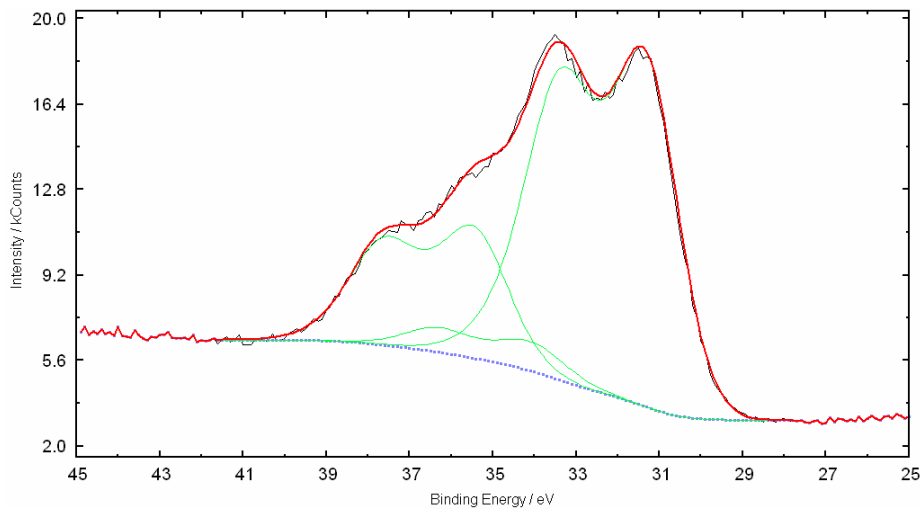

FIG. 5. W4f XPS spectrum for the W sample located in plasma (H$_2$/air mixture, 21 cm) after removal of the a-C:H film.

Ar ions (0.1 mA, 6 kV) have been used for etching of the near surface layers of the W sample for 3 min. After the ion etching the XPS spectrum changed significantly. A ratio of the metallic W peak to the oxidized W one increased indicating practically full removing of WO$_2$ and remarkable decreasing of WO$_3$ (*FIG. 6*).
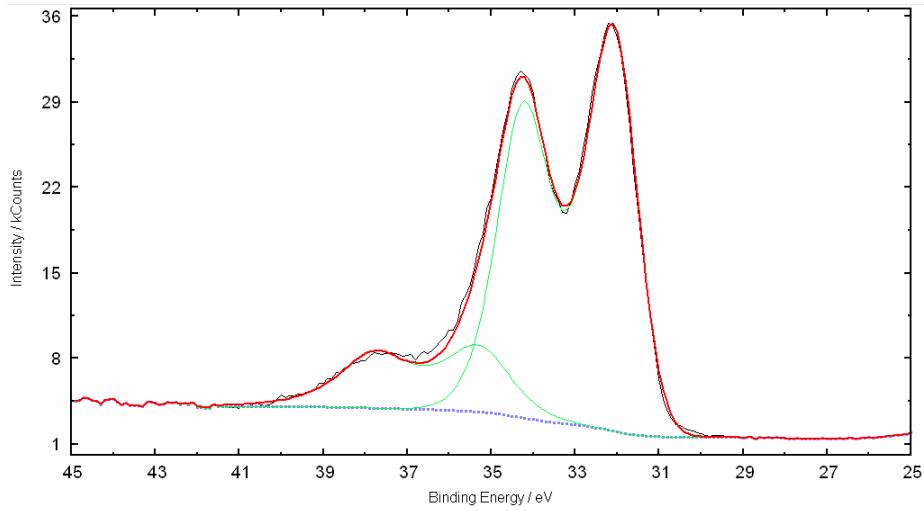
FIG. 6. W4f XPS spectrum for the W sample located in plasma (H_2/air mixture, 21 cm) after removal of the a-C:H film and Ar ion etching (0.1 mA, 6 kV, 3 min).

Special analysis of the N1s XPS spectra showed that nitrogen concentration in the surface layer was about 3 at.% and after the Ar ion etching (~10 nm) the nitrogen was not detected by XPS and carbon (31.21 at%) and oxygen (9.71 at%) concentrations decreased.

Estimations of thicknesses of homogeneous layers (contamination, hydroxides or water, tungsten trioxide) on the metallic W were calculated on the base of corresponding electron mean free paths (Table I).

TABLE I: ESTIMATIONS OF THICKNESSES OF HOMOGENEOUS LAYERS (CONTAMINATION, HYDROXIDES OR WATER, TUNGSTEN TRIOXIDE) ON THE METALLIC TUNGSTEN (NM).

Treatment	CH_x	OH or H_2O	WO_3
Sample after removal of the a-C:H film	1.28	2.08	1.80
Sample after removal of the a-C:H film and Ar ion etching	1.04	0.01	0.66

The above mentioned spectra were obtained after 1.5 h plasma exposure (300 K) of the W sample from which surface the a-C:H film was removed preliminarily in the plasma (H_2/air mixture, 21 cm). They clearly indicate an insignificant oxidation rate of tungsten in the plasma. The appearing of WO_2 could be attributed to the reduction reaction of tungsten trioxide.

Simultaneously after removal of the a-C:H films deposited on W and Mo, the oxidation of the metals has been studied by EPMA and RHEED. It has been shown that primary (~1 nm thick) continuous amorphous and secondary (up to 4 nm thick) island-like oxide films were formed on the metal surfaces. Polycrystalline island-like oxide films were generated due to recrystallization of the primary oxide films. Metal oxidation suppression was caused by reactions of oxygen ion neutralization and atomic oxygen recombination on metals.

4. Conclusions

1. The a–C:H film erosion rate depended on the sample location in relation to the plasma and decreased by two orders of magnitude in the row: hollow cathode, positive column, afterglow region. It was possible to remove 100 nm thick hard a–C:H films from W and Mo in the afterglow region for about 7 h at 300 K.

2. Primary (~1 nm thick) continuous amorphous and secondary (up to 4 nm thick) island-like oxide films were formed on the W and Mo surfaces after removal of the a–C:H films. Polycrystalline island-like oxide films were generated due to recrystallization of the primary films. Material oxidation suppression was caused by reactions of oxygen ion neutralization and atomic oxygen recombination on the metals.

3. The main plasmolysis products during interaction of a-C:H films with H_2/air direct current glow discharge were CO, CO_2, and H_2O. The hydrocyanic acid (HCN) and ammonia (NH_3) also have been found in plasmolysis products.

4. The XPS spectra obtained after 1.5 h plasma exposure (300 K) of the W sample, from which surface the a-C:H film was removed preliminarily in the plasma, clearly indicated an insignificant oxidation rate of tungsten in the plasma. The appearing of WO_2 could be attributed to the reduction reaction of tungsten trioxide.

5. For cleaning of fusion devices from carbon deposits by means of oxygen-containing plasmas it is necessary to carry out a systematic investigation of possible effects connected with oxidizing of divertor material surface layers (especially stainless steel and beryllium).

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