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Removal of codeposited layers by ECR discharge cleaning

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Abstract

Redeposition of eroded carbon on the walls of fusion devices together with the D–T plasma forms amorphous, hydrogenated carbon films with D–T concentrations ranging for deposition at a surface temperature of 300 K from 0.3 up to 0.6, depending on the deposition conditions. The trapping of large amounts of hydrogen isotopes in these so-called codeposited layers may represent a potential safety hazard during D–T operation because large amounts of tritium will be retained in these layers. To erode carbon films and deplete the T concentration an experimental investigation was performed using O_2, D_2, H_2, H_2O, and O_2/H_2, electron cyclotron resonance low-pressure discharges. Real-time in-situ ellipsometry was applied to measure the optical response of the layers during deposition and erosion. This allows a precise determination of the optical constants and the film thickness. From these data the deposition and erosion rates are calculated. The dependence of the erosion rates on substrate temperature, applied ion energy, gas composition and discharge pressure for two different types of a-C:H films was measured. In the investigated parameter range oxygen discharges showed the highest erosion rates of all investigated source gases. The highest rates achieved at 300 K with the substrate at floating potential are 3.6 μm/h for polymer-like, soft C:H films (H/C about 1) and 1.7 μm/h for hard a-C:H films (H/C about 0.5). The erosion rates increase with increasing substrate temperature (roughly by a factor of 3–4, 300–650 K) and with increasing ion energy (by about a factor of 6–8, 0–200 eV). The paper presents the experimental results and a discussion of the parameter dependencies and the consequences for the removal of codeposited layers by low-pressure discharge cleaning in ITER. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

All present day fusion experiments use carbon as a part of the first wall, limiter or divertor target plate material. In particular for the planed International Thermonuclear Experimental Reactor (ITER), the use of carbon-fiber-reinforced carbon appears, due to its superior thermal properties, to be indispensable to withstand the high thermal loads expected during plasma transients or disruptions [1]. During hydrogen plasma interaction with carbonaceous surfaces carbon is eroded and redeposited together with the available hydrogen isotopes. This leads finally to the growth of so-called codeposited layers [1]. In the case of ITER, which will be operated with a deuterium/tritium mixture (D/T), such codeposited layers will contribute significantly to the in-vessel tritium inventory. The tritium in surface layers represents a potential safety hazard because it can form volatile species with the ambient atmosphere and thus be set free in the event of an accident. On the other hand, net growth of thick codeposited layers as found recently on the cooled louvers in the shadowed regions of the inner divertor of the Joint European Torus (JET) [2], may contribute to a considerable consumption of the tritium fuel. Therefore, the primary concern for ITER with respect to the tritium inventory remains codeposition of tritium and carbon in areas, mainly in the divertor, not directly exposed to the plasma (shaded regions).Thus, techniques are required to efficiently remove tritium from

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these layers. Removal of T from thick codeposited layers – more than 40 μm thick films have been found in JET [1,2] – requires to remove the layers themselves. This can be achieved by oxidizing the layers in an oxygen-containing atmosphere to form volatile species such as CO, CO_2, and H_2O at increased surface temperature above about 600–650 K [3,4] (see also review in Ref. [1]) or by the application of low-pressure gas discharges using reactive gases as suggested by Hsu already 10 years ago [5]. Some laboratory studies with respect to erosion of codeposited layers using low-pressure gas discharges were conducted in the past [5–7], but until recently [8–11] no systematic measurements investigating the different parameter dependencies aiming at an basic understanding of the erosion process and an optimization of the achievable erosion rates were performed. In addition, the fusion community has not yet started to make use of the wealth of knowledge gathered in the field of plasma technology about the deposition and erosion of amorphous hydrogenated carbon films using low-pressure plasmas [10,12, and references therein]. From this work it is well known that a wide variety of a-C:H films with a broad range of physical and chemical properties can be deposited from low-pressure plasmas. In particular, the hydrogen content (H/(H+C)) of films deposited at room temperature may vary between about 0.3 and 0.6. This corresponds to H/C ratios, which are more often used in the fusion community, between 0.4 and 1.5. It turned out that the H/C ratio (which will be used in the remainder of this article to classify the films) permits a reasonable first estimate of the general film properties [10] due to a high correlation between various film properties. Soft, polymer-like C:H films with a high degree of sp^3 hybridization are characterized by a high H/C ratio (around 1) and hard, dense a-C:H films with a substantial degree of sp^2 hybridization (typically around 50–60%) by a low H/C ratio (0.4–0.5). It should be emphasized that these two kinds of films represent the extreme cases and anything in between can be produced. Hard a-C:H films are deposited if the growing film surface is bombarded with energetic ions with at least about 50–100 eV ion energy. If no energetic ion bombardment is present during deposition (ion energy below about 20–30 eV) soft films will grow [9,10].

The purpose of this paper is to communicate results of a systematic study of the parameter dependencies of the erosion of a-C:H films, which can be considered as a model system for the codeposited layers in fusion research, using low-pressure gas discharges. Particular emphasis is put on oxygen and hydrogen isotope containing plasmas. The erosion rates are determined in situ using real-time ellipsometry. Erosion is measured as a function of precursor gas composition and pressure, ion energy, and substrate temperature for two different sets of plasma-deposited a-C:H layers.

2. Experiment

Deposition and erosion of hydrocarbon films is investigated in an electron cyclotron resonance (ECR) plasma. Details of the experimental setup and the data collection and processing are published elsewhere [9,11,13]. In short, the plasma chamber consists of a stainless steel vessel (6-way cross, 150 cm inner diameter) and is pumped to a base pressure in the 10^{-4} Pa range by a turbomolecular pump. The microwave power at 2.45 GHz is coupled into the chamber from top through a ceramic window. The absorbed microwave power is determined by directional couplers measuring the incoming and reflected power. The resonance magnetic field of 87.5 mT is generated by external water-cooled copper solenoids.

To achieve a certain decoupling of the production of reactive species such as ions and radicals in the bulk plasma from the applied experimental conditions at the substrate, the plasma is confined in a metallic cage inside the vacuum chamber. This cage has cylindrical shape with an inner diameter of 15 cm and a length of 15.3 cm yielding a volume of 2700 cm^3. The lateral area of the cylinder is made of a stainless steel mesh, so that the plasma is confined in it, but neutral species can pass easily through it. The bottom plate of the cage is made of a solid stainless steel plate with a central aperture 3.5 cm in diameter. Through this aperture a diverging plasma beam is extracted and impinges perpendicularly onto the substrate electrode. Another set of experiments was conducted without this plasma-confining cage. This setup permits a direct interaction of the plasma with the substrate surface and leads to substantially higher erosion rates than with the cage in place, however, this results in a less efficient decoupling between the bulk plasma and the surface so that the conditions at the surface, in particular the application of a bias voltage, may have an influence on the plasma. The motivation to perform the experiments without cage is that this enables us to measure the erosion rates in a significantly shorter time. This is of particular importance if very low erosion rates have to be measured.

The substrate electrode is electrically isolated from the rest of the chamber. The potential at the electrode can be varied by application of an RF bias at 2 MHz from floating potential up to about −260 V DC self-bias. In the following the amount of the applied DC self-bias ($U_{SB} = |U_{SB}|$) is used as experimental parameter, where $U_{SB} = 0$ corresponds to floating potential. The ion energy is about 10–20 eV higher than the applied DC self-bias. The temperature of the electrode can be increased from room temperature up to about 650 K by resistive heating. The substrate temperature is measured by a thermocouple in the electrode and calibrated with the substrate temperature derived from ellipsometry as described by von Keudell and Jacob [9].

The deposition and erosion rates and the variation of the optical constants of the investigated thin films are measured in situ by real-time ellipsometry at a fixed wavelength of 600 nm. In ellipsometry the change in the state of polarization upon reflection of a polarized light beam from the sample is measured, yielding the two ellipsometric angles Ψ and Δ, which are connected to the Fresnel coefficients for reflection parallel to the plane of incidence r_p and perpendicular to the plane of incidence r_s by $r_p/r_s = \tan \Psi \exp(i\Delta)$. r_p and r_s are determined by the film thickness and the optical constants n (refractive index) and k (extinction coefficient). Details of the ellipsometry set-up and the data evaluation are presented elsewhere [9,11,13].

Precursor gases of standard purity (hydrogen and oxygen: 5.0, deuterium: 2.8, and methane: 2.5) are introduced from the side of the chamber and the gas flow is controlled by commercial mass flow controllers. a-C:H films are deposited at a pressure of 0.2 Pa, a methane gas flow of 20 sccm, an absorbed power of 50 W (100 W in the experiments without cage due to the larger plasma volume) and a substrate temperature of 300 K. Soft, polymer-like, mainly sp^3 hybridized films are deposited without additional substrate bias ($U_{SB} = 0$ V). This yields optical constants of $n = 1.6$ and $k = 0.002$ and an H/C ratio of 1.2. Hard a-C:H films with a high degree of sp^2 hybridization are deposited applying an additional bias of $U_{SB} = 100$ V. This yields optical constants of $n = 2.05$ and $k = 0.06$ and a H/C ratio of 0.54. The H/C ratio is determined ex situ by ion-beam analysis [8,9]. The optical constants and the stoichiometry of these films are in good agreement with data published previously from our group [10] and with other data from literature [12].

The films are eroded in the same chamber using oxygen, hydrogen, deuterium, hydrogen/oxygen mixtures, or water plasmas. Even though identical plasma parameters such as pressure, power and residence time are applied, the ion and neutral gas fluxes may differ because of the different masses and ionization energies of the plasma gases. The following plasma parameters are applied during erosion (if not stated otherwise) $p = 0.25$ Pa, $\Gamma = 20$ sccm and absorbed microwave power is 50 and 100 W with and without cage, respectively. Since the actual erosion rate is influenced by a partial consumption of reactive species due to interaction with the a-C:H coated chamber walls, the plasma reactor is cleaned from the deposited a-C:H films by an oxygen plasma prior to the erosion measurement. During this cleaning cycle the samples are protected by a shutter which completely covers the film surface. The complete removal of coated wall material was detected by the change in the plasma emission spectrum. Afterwards, the shutter is removed and the erosion rate is measured.

3. Results and discussion

In a recent publication [11] we have shown that hydrogenated carbon films can be efficiently removed in oxygen-containing low-pressure gas discharges. The results are shortly summarized here. As working gases O_2, H_2O, and O_2/H_2 mixtures were used. Standard erosion plasma parameters were: $p = 0.25$ Pa and applied microwave power = 50 W. These experiments were performed with the above-mentioned plasma-confining cage in place. Among the investigated gases and gas mixtures pure oxygen discharges turned out to be most efficient. At 300 K the erosion rate increases linearly with increasing ion energy showing no saturation up to $U_{SB} = 260$ V. The yield of eroded carbon atoms to incoming ions increases from about 0.5 at $U_{SB} = 0$ V to 4 at $U_{SB} = 260$ V. The yield bigger than one for the ions clearly indicates that neutral reactive species from the plasma contribute to the erosion process. At lower discharge pressure the erosion rate increases notably. This was explained with the increase of the ion flux with decreasing pressure which will be discussed in more detail in a forthcoming publication [14].

At floating potential ($U_{SB} = 0$ V) the erosion rates for the different source gases increase also with substrate temperature roughly by a factor of 2–4 if T is increased from 300 to 650 K. The following erosion rates R for a hard a-C:H layer with H/C = 0.54 in pure O_2 plasmas were reported: at $T = 300$ K and $U_{SB} = 0$ V, $R = 0.04$ nm/s = 0.14 μm/h corresponding to about 0.33×10^{15} C atoms cm^{-2} s^{-1} increasing to $R = 0.47$ nm/s (= 1.7 μm/h or 3.9×10^{15} C atoms cm^{-2} s^{-1}) at $U_{SB} = 260$ V ($T = 300$ K), respectively to $R = 0.15$ nm/s (= 0.54 μm/h or 1.3×10^{15} C atoms cm^{-2} s^{-1}) at $T = 650$ K ($U_{SB} = 0$ V). This means an increase of about a factor of 10 with U_{SB} and a factor of about 4 with T. As mentioned before, the erosion rates depend strongly on the structure of the material to be eroded. The numbers cited above are valid for a hard a-C:H film with H/C = 0.54. The measured rates for a soft C:H layer with H/C = 1.2 are about a factor of 2 higher if expressed in nm/s, but due the lower density of the material [10] the number of eroded carbon atoms per area per second is for the investigated soft films only about 25–30% higher.

In the experiments reported in the following, the plasma-confining cage is removed. Fig. 1 shows a comparison of the erosion rates R measured for a hard a-C:H film (H/C = 0.54) as a function of U_{SB} and substrate temperature for O_2, D_2, and H_2. All rates increase with increasing substrate temperature (at $U_{SB} = 0$) and with increasing U_{SB} (at $T = 300$ K). In all investigated cases oxygen shows always the highest rate. At $T = 300$ K the relative rates behave as O_2:D_2:H_2 = 10:2:1. We explicitly emphasize that a clear isotope effect between deuterium and hydrogen is observed in these measurements which is especially distinct at $T = 300$ K and $U_{SB} = 0$ V. The

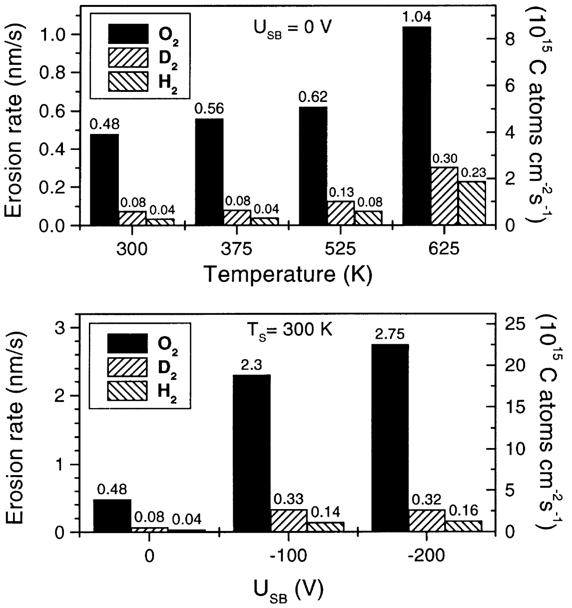

Fig. 1. Erosion rates in low-pressure O_2, D_2, and H_2 ECR glow discharges for hard a-C:H films (H/C = 0.54) as a function of temperature at $U_{SB} = 0$ V (top) and as a function of U_{SB} at $T = 300$ K (bottom). The erosion rates are given in nm/s on the left-hand scale and in 1015 C atoms cm^{-2} s^{-1} on the right-hand scale. The following plasma parameters are applied: $p = 0.25$ Pa, $\Gamma = 20$ sccm, $P = 100$ W.

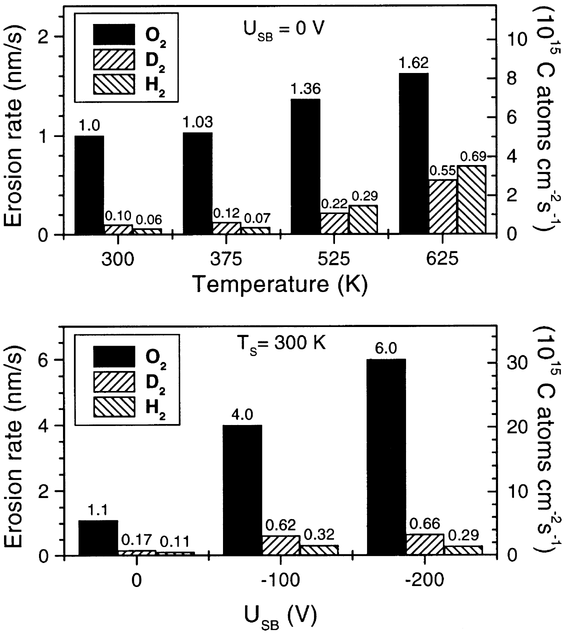

Fig. 2. Same as Fig. 1, but for a soft C:H film (H/C = 1.2).

rates for O_2 can be compared to the values of the experiment with the plasma-confining cage, cited above. Indeed, due to the changed setup and may be also plasma conditions, the observed erosion rates are about a factor of 10 higher. At $T = 300$ K and $U_{SB} = 0$ V the erosion rate in oxygen is 0.48 nm/s (4.0×10^{15} C atoms cm^{-2} s^{-1}). This increases to 1.04 nm/s (8.6×10^{15} C atoms cm^{-2} s^{-1}) at $T_s = 625$ K. The increase of R with U_{SB} in the interval from 0 to 200 V is not as pronounced as in the experiment with cage (factor of 8 instead of 10) this might simply be caused by the scatter of the experimental data or by an influence of the RF bias to the bulk plasma due to a less efficient decoupling of surface and plasma.

Fig. 2 shows identical measurement as Fig. 1, but now for a soft, polymer-like a-C:H film with an H/C ratio of 1.2. The general behavior is almost identical to that of the hard films with the only difference that all rates are roughly a factor of 2 higher than for the hard films. Similar to the experiments with cage this difference in the rates reduces to about 30% if the erosion rates are expressed as the number of eroded carbon atoms per area and second instead of nm/s.

It stands to reason that all erosion rates given above depend critically on the particle fluxes arriving at the surface and thus on the particular discharge conditions. The absolute magnitude of the given erosion rates is, therefore, only an indication of what can be achieved. The more important results of this study are the observed parameter dependencies, namely the strong increase of the erosion rates with T_S and U_{SB}. It is worth noting that for both types of C:H films the difference in R between the three investigated gases increases with increasing U_{SB}, but it decreases with increasing temperature. This can be understood on the basis of the anti-synergistic interaction of hydrogen ions and atomic hydrogen [9,10]. This complicated interplay of hydrogen ion bombardment and thermally-induced chemical erosion by atomic hydrogen was thoroughly reviewed recently [10]. The precursor state for thermally-induced chemical erosion by atomic hydrogen is a high density of sp^3 hybridized carbon atoms at the surface [10,15]. Ion bombardment tends, however, to increase the number of sp^2 hybridized carbon atoms, thus decreasing at increased substrate temperatures the erosion rate under simultaneous interaction of atoms and ions at the surface [9,10]. This leads to the surprising result that the plasma erosion rate at higher temperatures (above about 400 K) decreases if the ion energy is increased [9,10]. Obviously, such an counteracting interaction does not occur during plasma erosion using oxygen, but much more work is necessary to study the microscopic processes to a similar extent as in the C–H system [10]. At present, we perform quantitative measurements of the particle fluxes impinging on the substrate [14]. This will allow us to calculate the erosion yields from the measured rates.

X-Ray Photoelectron Spectroscopy (XPS) using a Perkin Elmer 5600 ESCA system with monochromatized Al K radiation was applied to investigate the incorporation of oxygen into the film surface. For this analysis, the plasma treated samples had to be carried through air. Therefore, a sample without any oxygen plasma treatment was analyzed for reference. Because of the short exposure to atmosphere during transfer of the samples, an oxygen concentration of about 15% was found already for the untreated sample. This is probably due to adsorbed water. This oxygen contamination could not be removed through heating to 400 K. The surface concentration of a sample treated in an oxygen plasma at floating potential increased to about 18% and for a sample treated at $U_{SB} = 200$ V to about 23%. A depth profile, recorded using sputtering by 1 keV helium atoms, revealed that oxygen is incorporated in a thin surface layer with a thickness of about 10 nm only and no significant diffusion into deeper layers occurs.

4. Conclusions

The erosion of hydrocarbon films in an ECR glow discharge was investigated as a function of substrate temperature, substrate bias (= ion energy), and precursor gas composition for soft and hard films. These a-C:H layers are a model system for the so-called codeposited layers observed in fusion experiments and the two investigated types are typical examples for films deposited with simultaneous bombardment of energetic particles (typically >50–100 eV kinetic energy) and without bombardment of energetic particles (<20–30 eV kinetic energy).

The erosion rates increase with increasing ion energy (at $T = 300$ K) and with increasing substrate temperature (at $U_{SB} = 0$ V). However, at $U_{SB} = 100$ V no increase of the rate with T was found. This indicates that the simultaneous increase of T and U_{SB} does not lead to a simple multiplication of the enhancement factors observed when only one parameter is changed. The following gases and gas mixtures were investigated using identical external plasma parameters: O_2, D_2, H_2, H_2O, and O_2/H_2 (1:2). In all investigated cases oxygen shows always the highest rate. At $T = 300$ K the relative rates behave as $O_2{:}D_2{:}H_2 = 10{:}2{:}1$.

Summarizing the results, the best conditions for a fast and effective removal of tritium from codeposited layers are an oxygen plasma at a low pressure to achieve high ion fluxes and at increased wall temperature. At components with a high codeposition rate, for example in shaded regions of the divertor, the application of a DC self-bias to increase the ion energy, if technically feasible, could generate locally higher erosion rates. At a bias voltage of 200 V, corresponding to ion energies slightly above 200 V, we measured in our setup erosion rates of 2.75 nm/s (9.9 μm/h) and 6.0 nm/s (21.6 μm/h) for hard and soft a-C:H films, respectively. We anticipate that a hydrogen plasma applied after an oxygen cleaning discharge will efficiently decrease the oxygen content in the first monolayers. But this is a process that has to be investigated in more detail.

Increased wall temperatures (e.g. 600 K) offer the possibility to remove codeposited layers by thermally-induced chemical erosion with atomic hydrogen. This process relies only on the efficient production of atomic hydrogen in the plasma and does not require direct line-of-sight with the cleaning plasma. It is only about a factor of 3 slower than oxygen at these high temperatures and low ion energy. It offers the advantage that no detrimental effects on other than carbon materials have to be anticipated. However, much more work has to be done to allow a finally assessment of the possibilities and shortcomings of each option.

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