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Erosion of thin hydrogenated carbon films in oxygen, oxygen/hydrogen and water plasmas

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Abstract

The erosion of amorphous hydrogenated carbon films in oxygen, oxygen/hydrogen and water electron cyclotron resonance plasmas was investigated by in situ ellipsometry. The erosion was measured as a function of the energy of the impinging ions and the substrate temperature. Erosion is most effective in pure oxygen plasmas. The erosion rate rises with increasing ion energy and substrate temperature, in the latter case however only at low ion energies. The reaction layer at the surface of the eroded film is further analyzed by X-ray photoelectron spectroscopy (XPS). The C 1s peak of the XPS spectra shows, that oxygen is implanted in the films and forms double and single bonds to the carbon atoms. This modification, however, is limited to a few atomic layers. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Large areas of the first wall in present days as well as in planned fusion experiments consists of graphite. During hydrogen plasma exposure of this material an amorphous hydrogenated carbon film (a-C:H) builds up due to H implantation or due to codeposition of eroded wall material. Naturally, depending on the hydrogen isotope composition of the plasma, these films will reflect this isotope composition and contain certain amounts of hydrogen and deuterium. In future fusion experiments such as International Thermonuclear Experimental Reactor (ITER) the plasma will also contain tritium which leads to the formation of tritium containing films at the walls and thereby to an in-vessel tritium inventory. This tritium inventory has to be reduced in order to minimize potential safety hazards and to use the fuel tritium efficiently. This might be achieved by a D–T exchange reaction using a D_2 plasma for the production of atomic deuterium. However, this D–T exchange reaches only a thin surface layer, about 1 nm thick, whereas codeposited layers can have thicknesses up to several 10 μm [1]. Therefore, it was proposed already ten years ago by Hsu [2] to remove the codeposited films by means of low-pressure cleaning discharges. Very efficient removal of a-C:H films can be achieved by low-temperature plasmas containing atomic oxygen [2].

The purpose of this paper is to quantify the erosion efficiency of oxygen containing low-pressure glow discharges as a function of source gas composition, ion energy, and substrate temperature, and to establish a data basis for an assessment of the applicability of a glow discharge cleaning technique for the removal of codeposited layers in fusion experiments. An important question for operating a fusion device is whether large inventories of oxygen will build up in carbon films exposed to oxygen containing plasmas. To investigate this point, we analyzed the surface composition of untreated a-C:H samples and of samples exposed to oxygen glow discharges using X-ray photoelectron spectroscopy (XPS).

2. Experiment

Deposition and erosion of hydrocarbon films are investigated in an electron cyclotron resonance plasma.

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A sketch of the experimental setup is shown in Fig. 1. The chamber consists of a stainless steel 6-way cross made of three perpendicularly intersecting tubes with an inner diameter of 15 cm and a length of 33 cm each. The chamber is pumped to a base pressure in the 10^{-4} Pa range by a combination of a turbomolecular pump and a mechanical forepump via another 6-way cross of identical size. The total volume of the vacuum chamber is 27 000 cm^3.

The plasma is heated by microwaves at a frequency of 2.45 GHz. The microwave power is coupled to the chamber from top through a ceramic window. The absorbed microwave power is determined by directional couplers measuring the incoming and reflected power. The magnetic field is generated by external water-cooled copper solenoids. The diverging magnetic field has its maximum of about 105 mT at the position of the coupling window. It decreases continuously going away from the window and reaches a value of about 20 mT at the substrate position. The position of the resonance zone with a resonance field of 87.5 mT is about 4 cm below the coupling window. 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 wire-lattice with a mesh width of about 1 mm being considerably larger than the Debye length of the plasma ($\lambda_{Debye} \approx 160$ μm at an estimated plasma density of 10^{10} cm^{-3}). Although the plasma can leak through the mesh because λ_{Debye} is much smaller than the mesh width, it is actually confined by the cage because the microwaves (vacuum wavelength 12.2 cm) are efficiently confined. Only at absorbed microwave powers markedly higher than those used in the experiments, we observed a weak plasma glow outside the cage. In spite of the plasma confinement neutral species can easily pass through the wire-lattice. 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 on the substrate electrode.

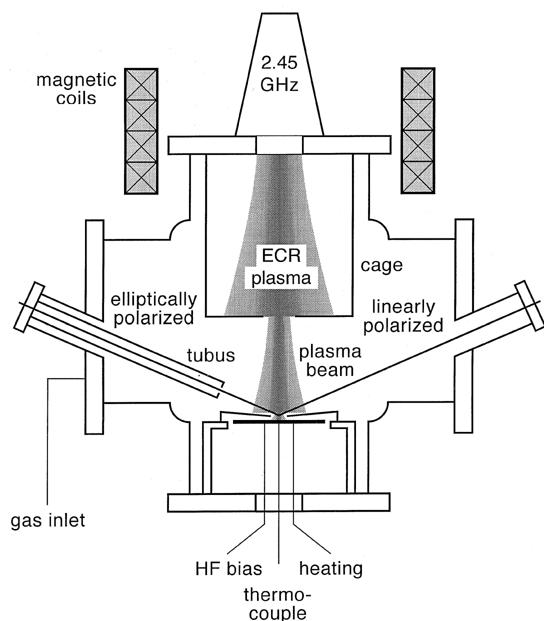

Fig. 1. Vacuum chamber used for deposition and erosion.

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. To generate the maximal applied dc self-bias voltage an rf power of about 25 W is required. This corresponds to an average power density of 0.39 W cm^{-2} on the electrode with an area of 64 cm^2. It should be noted that a notable fraction (estimated 50% or more) of this rf power is consumed in the feed through and the substrate holder and does not couple to the plasma. The application of a dc bias instead of an rf bias is not practical because the deposited films are insulating and charging of the film surface during plasma operation will continuously change the effective sheath potential. Measurements of the ion flux energy distributions in this setup yielded ion fluxes in the range of some 10^{15} cm^{-2} s^{-1} and a mean ion energy at floating potential of about 15 eV at the operating conditions used in the experiments reported here [3]. Therefore, the energy of the ions impinging on the substrate can be varied between 15 (at floating potential) and 275 eV (at −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 and we assume that the energy of the impinging ions is about 15 eV higher than eU_{SB}.

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. To obtain good thermal contact between the thermocouple and the substrate, as well as between the electrode and substrate, colloidal carbon is used as bonding substance. The substrate temperature measured by the thermocouple is calibrated with the substrate temperature derived from ellipsometry as described by von Keudell and Jacob [4].

Precursor gases of standard purity (H_2 5.0, O_2 5.0, CH_4 2.5, H_2O two-times distilled) are introduced from the side of the chamber and the gas flow is controlled by commercial mass flow controllers. For the deposition of the a-C:H films pure methane is used as precursor gas

and the following experimental parameters are applied: pressure $p = 0.2$ Pa, methane gas flow $\Gamma = 20$ cm^3 min^{-1} STP (cm^3 min^{-1} STP = sccm), applied microwave power = 50 W (yielding an average power density of 18 mW cm^{-3}, if spatially homogeneous absorption within the plasma-confining cage is assumed), and substrate temperature = 300 K. From the pressure p and the gas flow Γ we calculate the particle residence time τ (for non-reactive species) within the cage ($\tau = pV/(kT\Gamma)$ with V = volume, T = gas temperature) to be $\tau = 15$ ms. For comparison, the residence time in the whole vacuum chamber is 150 ms, due to the larger volume.

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. 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 of light with a polarisation parallel to the plane of incidence r_p and perpendicular to the plane of incidence r_s by $r_p/r_s = \tan\Psi \exp(i\Delta)$. The ellipsometer is a rotating analyzer ellipsometer (RAE) with a short arc xenon lamp as a light source. The collimated light beam is monochromatized by an acousto-optical tunable filter and polarized by a Glan–Thomson prism. After reflection from the sample, the light beam passes through the rotating analyzer mounted on a computer-driven stepper motor and is detected by a window-free photodiode. The whole setup is controlled by a personal computer, which generates the trigger pulses for the stepping motor and the analog-to-digital converter. The setup is calibrated by 'residuum' calibration [5] and statistical errors of about 0.0038° in Ψ and 0.009° in Δ for $\Psi = 12.2°$ and $\Delta = 112.7°$ at a wavelength of 600 nm are obtained. Details of the ellipsometry setup are presented elsewhere [6,7]. All ellipsometric measurements reported in this article were performed at a wavelength of 600 nm, an incident angle of 70° and a polarizer angle of 55°.

Fig. 2 shows a Ψ–Δ trajectory of a hard film during the erosion in an O_2 plasma. Each data point in Fig. 2, recorded with a constant step time of 3.1 s represents a Ψ–Δ value for a fixed thickness. The thickness is determined through comparison of the data points with a representative model, calculated from Fresnel's equations with the assumption of a homogeneous layer. The solid line in Fig. 2 shows the results of such a model calculation for a complex refractive index $\tilde{n} = n - ik$, with n (refractive index) = 2.015 and k (extinction coefficient) = 0.06. Evaluation of an experimental Ψ–Δ trajectory is done in an iterative procedure by adjusting the optical constants n and k in the model to match the experimental values. Since different parts of the Ψ–Δ trajectory are sensitive to n and k (high sensitivity with respect to n for $\Delta \leqslant 45°$, high sensitivity with respect to k for Δ around 180°), this procedure converges quickly

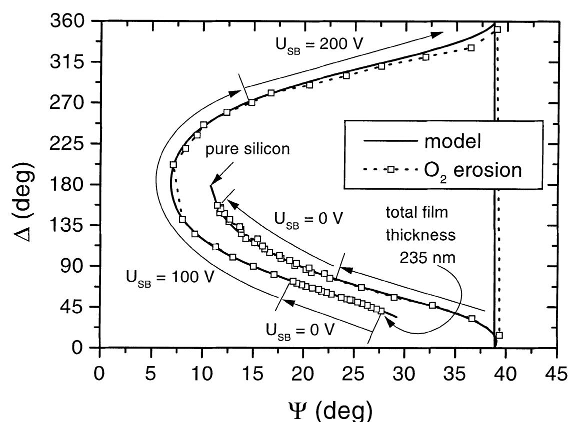

Fig. 2. The Ψ–Δ map. Shown are a modeling result (solid line) in the Ψ–Δ plane for a homogeneous hard a-C:H film on silicon with the optical constants $\tilde{n} = n - ik = 2.015 - i0.06$ at an angle of incidence of 70.17° and a corresponding oxygen erosion measurement (open squares) with varied dc self-bias voltage U_{SB}. The starting point for the model is the silicon single-crystal surface ($\Psi \approx 11°$, $\Delta \approx 180°$) with an 8 nm thick SiO_2 adlayer.

and in general high precision for the determination of n, k, and the film thickness is achieved. Dividing the thickness change during some (usually averaged over about 5) measurement points through the elapsed time yields directly the erosion rate for the corresponding plasma conditions. The larger point-to-point distance in the parts of Fig. 2 with $U_{SB} = 200$ V is a consequence of the much higher erosion rate.

Soft, polymer-like, mainly sp^3-hybridized films are deposited without additional substrate bias (substrate at floating potential, i.e. $U_{SB} = 0$ 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 $n = 2.015$ and $k = 0.06$ and an H/C ratio of 0.54. The H/C ratio was determined ex situ by ion-beam analysis. Rutherford backscattering (RBS) using 1.5 MeV hydrogen ions and elastic recoil detection (ERD) measurements using 2.6 MeV helium ions are applied to measure the carbon and hydrogen content, respectively. The optical constants and the stoichiometry of these films are in good agreement with data published previously from our group [4,8–11], and other data from literature [12].

These films are eroded in the same chamber using oxygen, hydrogen/oxygen mixtures or water plasmas. The following external parameters are applied if not stated otherwise: pressure $p = 0.25$ Pa, microwave power 50 W and total gas flow 20 cm^3 min^{-1} STP. From these parameters only the pressure p was varied in one set of experiments. Even if the macroscopic plasma parameters as pressure, power or residence time are identical, the ion and neutral gas fluxes may differ because of the

different masses and ionization energies of the plasma gases. Since the actual erosion rate is, furthermore, 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 the material deposited at the chamber walls is detected by the change in the plasma emission spectrum. Afterwards, the shutter is removed and the erosion rate is measured.

X-ray photoelectron spectroscopy (XPS) using a Perkin Elmer 5600 ESCA system with monochromatized Al K_α radiation was applied to investigate the incorporation of oxygen into the film surface.

3. Results and discussion

The dependence of the erosion rate on the ion energy in pure oxygen, water, and in a mixture of oxygen and hydrogen (O:H = 1:2) at a pressure of $p = 0.25$ Pa was investigated. Fig. 3 shows the dependence of the erosion rate on the applied self-bias voltage for hard a-C:H films with an H/C ratio of 0.54 (a) and polymer-like a-C:H films with an H/C ratio of 1.2 (b). The erosion rate of the hard a-C:H films increases linearly with the bias voltage for all source gases and no saturation effect occurs up to a dc self-bias of 260 V. The total increase amounts to a factor of 10 in this bias interval. This result cannot be explained by increasing ion energy since a constant erosion yield of nearly 1 for oxygen ions impinging on graphite with energies above 50 eV has been measured, as compiled by Vietzke et al. [13]. In our experiment, only the ion energy is varied through the applied dc self-bias, but not the ion or the atomic oxygen flux. Therefore, we conclude that the variation of the erosion rate with the applied bias is caused by the synergistic interaction between energetic oxygen ions and atomic or molecular oxygen neutrals.

The erosion rate in a pure oxygen plasma is largest compared with water and the mixture of oxygen/hydrogen plasmas. This holds for the hard and the soft a-C:H films as shown in Fig. 3(a) and (b). Only at 25 and 50 eV ion energy in the case of a hard film in the oxygen/hydrogen plasma the erosion rate appears to be higher than in pure oxygen. But this is within the error margins and therefore not significant. The erosion rate for the polymer-like a-C:H film in an oxygen plasma increases by a factor of 5 from floating potential to 50 V, whereas it increases only by a factor of 2 between 50 and 260 V. The same is true for the oxygen/hydrogen and the water plasma, although the absolute erosion rates are smaller compared to pure oxygen discharges.

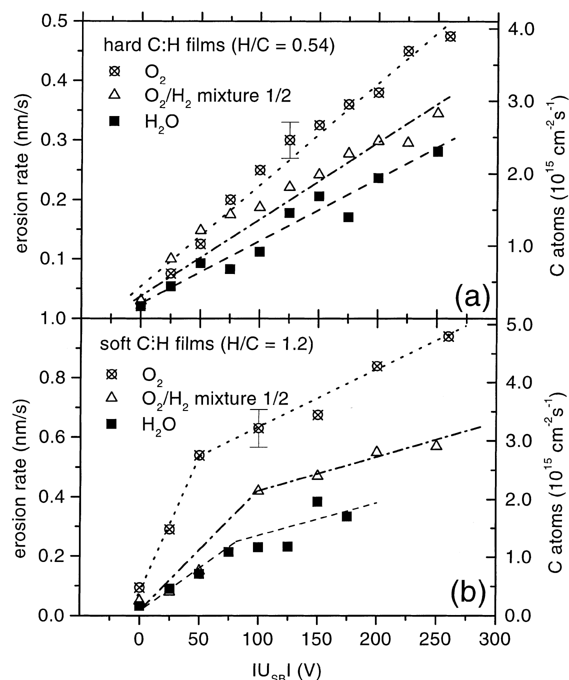

Fig. 3. Erosion rates at 300 K substrate temperature as a function of the dc self-bias voltage for hard (a) and soft (b) a-C:H films in ECR plasmas at a pressure of 0.25 Pa and an applied microwave power of 50 W using O_2, H_2O, and an O_2/H_2 mixture. The left-hand scale gives the erosion rate in nm/s as measured by ellipsometry, the right-hand scale in carbon atoms per cm^2 and s as calculated from the thickness change and the carbon density determined by ion-beam analyses.

One possibility to explain the increase of the erosion rates is that the decoupling of ion generation in the cage and the application of a substrate bias is not perfect. First measurements with a retarding field analyzer showed a small increase of the ion flux with an applied dc bias especially at low energy [3]. This measured increase of the ion flux is, however, too small to account for an increase of the erosion rate by a factor of 10. Another reason could be, that in soft films higher ion energies (>50 eV) lead to stronger film modification than in hard films, but this needs further investigations.

The comparison of the erosion rates between polymer-like and hard a-C:H films shows only a small difference if quantified in terms of eroded carbon atoms, which is shown on the right-hand scale of Fig. 3(a) and (b). This indicates that the main erosion reaction at high ion energies (>50 eV) does not strongly depend on the structural difference between hard and polymer-like a-C:H films.

The ion flux in pure oxygen plasma was measured at floating potential and at a dc bias of 260 V with a retarding field analyzer [3]. From this ion flux and the measured erosion rates we calculate an erosion yield of

about 0.5 removed carbon atoms per impinging ion at floating potential and a yield up to 4 at a dc self-bias of 260 V for both types of films at 300 K.

The variation of the erosion rate with the substrate temperature, is shown in Fig. 4. For substrate temperatures below 500 K the erosion rate increases slightly. Above 500 K we find a steep increase for all investigated gas mixtures for both, polymer-like and hard films. The thermally induced increase of the erosion rate is for the polymer-like films higher than for the hard a-C:H films. This can at least partially be explained by the fact that hydrogenated polymer-like carbon films thermally decompose at temperatures higher than 600 K in an O_2 containing atmosphere [14,15]. This is illustrated by the dotted line in Fig. 4(b) showing the erosion due to heating of a soft film at a pressure of 400 Pa molecular O_2 (no plasma!); above 550 K thermally induced chemical erosion sets in [15]. Heating the film at a background pressure of 10^{-4} Pa causes also a slight erosion (not shown), but this is not as effective as in an oxygen atmosphere. An identical experiment was performed with the hard film, but below 700 K no reaction

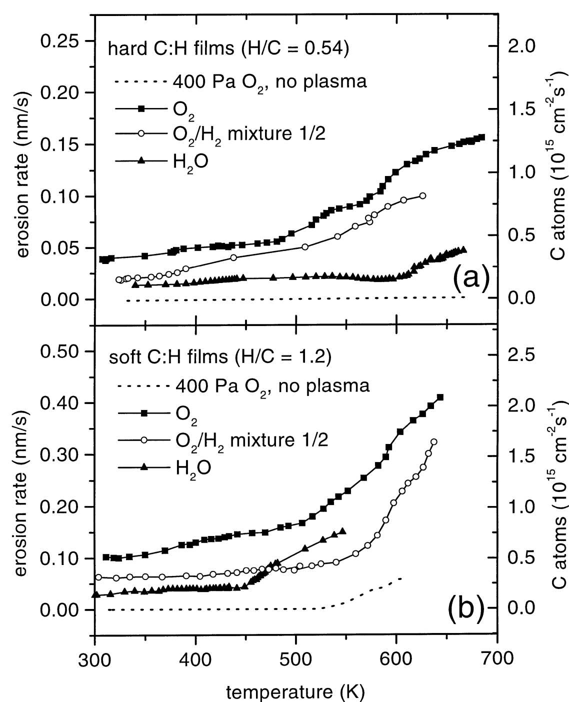

Fig. 4. Erosion rates at $U_{SB} = 0$ V (mean ion energy 15 eV) as a function of the temperature for hard (a) and soft (b) a-C:H films in ECR plasmas at the pressure 0.25 Pa and an applied microwave power of 50 W using O_2, H_2O, and a O_2/H_2 mixture. The thermally induced erosion in an oxygen atmosphere at 400 Pa without plasma is also shown. For the right- and left-hand scales the same as in Fig. 3 applies.

with molecular oxygen could be detected (see dotted line in Fig. 4(a)). The results of these two thermally induced erosion experiments are in excellent agreement with recent results for the erosion of hard and soft hydrocarbon films due to annealing in air by Wang et al. [14] and Maruyama et al. [15], respectively.

If the thermally induced chemical erosion of a-C:H films in oxygen exhibits Arrhenius-like behavior, i.e. the erosion rate is proportional to $\exp(-E_a/kT)$ with an activation energy E_a (k represents the Boltzmann constant, T the sample temperature), then a logarithmic plot of the erosion rate versus $1/T$ should give a straight line with a slope proportional to the activation energy E_a. Such an analysis of the erosion rates of soft and hard films in an oxygen plasma yields, however, for both types of films not a single, but two distinctly different activation energies. Up to about 500 K we find an apparent activation energy E_a of 0.027 eV for the hard film and 0.037 eV for the soft film. Above 500 K the apparent activation energies are 0.14 and 0.19 eV for soft and hard films, respectively. Both the notable differences below and above 500 K and between soft and hard films indicate that not a single microscopic process is responsible for the observed behavior. The reason for these differences as well as the underlying processes are presently not understood, but investigations by Wang et al. [14] and Maruyama et al. [15] have shown that the onset of structural changes in a-C:H layers occurs at these temperatures and that at higher temperatures these layers decompose in ambient or oxygen-containing (see also Fig. 4(b), erosion without plasma) atmosphere, most probably by forming CO, CO_2, and H_2O. We therefore conclude that the difference below and above 500 K is due to this onset of structural changes in the films. The determined apparent activation energies below 500 K are surprisingly low. This could mean, that the volatile species, such as C≡O, have a very low binding energy to the a-C:H film or the whole desorption process is assisted by ion-induced desorption as shown by Refke et al. [17].

Summarizing the results from Figs. 3 and 4 we note that the highest rates can be achieved in pure oxygen plasmas. Dilution with hydrogen reduces the erosion rate. The erosion rates increase with increasing substrate temperature and with increasing ion energy (= increasing self-bias voltage). However, the increase with ion energy is much stronger (about a factor of 10) than with substrate temperature (about a factor of 3–4) in the investigated parameter range. A certain complication arises from the fact, that the bonding structure of the films, in particular for soft films, changes due to an increase of the substrate temperature, so that the erosion rate depends simultaneously on structural changes and thermally activated chemical erosion processes. It is rather difficult to separate these processes experimentally.

Since the erosion rates of hard and polymer-like films are very similar, if expressed as the number of eroded carbon atoms, we discuss in the following only the erosion of hard a-C:H films, prepared from a methane plasma at a dc self-bias voltage $U_{SB} = 100$ V. Because the erosion rates are highest in pure oxygen plasmas we concentrated our further investigations on that gas. The increase of substrate temperature at $U_{SB} = 0$ V as well as the increase of U_{SB} at 300 K causes an significant increase of the erosion rate. One might therefore conclude that even higher rates could be achieved if both, temperature and U_{SB}, are increased simultaneously. To check this assumption, the following experiment is conducted: The variation of the erosion rate with substrate temperature is investigated in a pure oxygen plasma at $U_{SB} = 100$ V. The results are shown by the cross-filled circles in Fig. 5(a). In contrast to our anticipation, the temperature increase has no influence on the erosion yield, if the films are eroded at an additional dc self-bias of 100 V. At floating potential the same temperature rise causes an increase of the erosion rate by about a factor of 4. However, the erosion rate at a bias voltage of 100 V is already a factor of 1.7 higher ($=0.26$ nm/s) than the rate measured at the highest T_S at $U_{SB} = 0$ V ($=0.15$ nm/s). Fig. 5(a) also shows, that the erosion rate is higher at lower pressures. At 0.03 Pa the rate is about two times higher than at 0.25 Pa. This fact can be explained by an increase of the ion flux with decreasing pressure [3]. At 0.74 Pa the measured erosion rate is even lower than at 0.25 Pa.

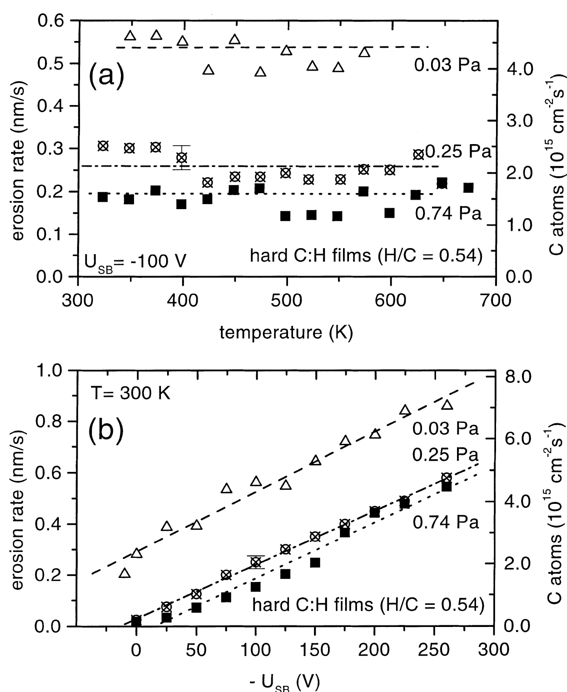

Fig. 5. Influence of the pressure on the erosion rate in an oxygen ECR plasma during variation of the temperature (a) at a constant ion energy of 100 eV and the variation of ion energy (b) at a constant temperature of 300 K. For the right- and left-hand scales the same as in Fig. 3 applies.

Fig. 5(b) shows the erosion rate as a function of U_{SB} for three different pressures at room temperature: the erosion rate increases linearly with bias voltage and has the same slope at all pressures. The highest difference of the rates is seen at floating potential: at 0.03 Pa it is about a factor of 4 higher than at 0.25 Pa. This increase is not only caused by a higher ion flux at lower pressures but also by shift in plasma potential from about 15 eV at $p = 0.25$ Pa to about 30 eV at 0.03 Pa [3]. This different potential offset has to be added to the applied dc self-bias voltage to calculate the ion energy for a quantitative comparison.

The production of volatile species such as CO and CO_2 which are responsible for the erosion of a-C:H films requires the break-up of several C–C and C–H bonds. It is hard to imagine that this happens in a one-step process. It is more reasonable to assume that at first oxygen atoms are incorporated at the surface of the film, then volatile precursors are formed, and finally the volatile species are desorbed. The desorption step may be either thermally activated or ion-induced. As a consequence of such a multi-step process, we expect a steady-state oxygen coverage on the surface or in the near-surface layer. This is in agreement with ion-beam experiments which show the build-up of an oxygen saturated layer with an O/C ratio of 0.25 [16,17]. The formation of a modified layer at the surface should become visible in the real-time in situ ellipsometry measurement provided the optical constants of this modified layer differ from those of the underlying material. In principle, our ellipsometric setup has a sub-monolayer sensitivity for thickness changes and a detection limit for surface modifications in the range of about 1 nm [9], so that also minute changes should be detectable. For the erosion of a-C:H films in hydrogen plasmas a modified layer with a thickness from 1 to 4 nm depending on ion energy has been reported [4,9]. Our experiment shows, however, no clear indication of such a modified layer during erosion in an oxygen plasma. This could have two reasons: the first is that no such modified layer exists, and the second is that the optical constants of the modified layer are very close to those of the underlying material and are thus invisible for ellipsometry. Therefore, we investigated plasma-treated samples ex situ by XPS. The problem with such an ex situ analysis is that the films have to be transported through air. The short air exposure during transport causes the adsorption of an oxygen-containing layer already on the samples not treated in an oxygen plasma, which leads to a measured oxygen concentration of about 10% averaged over the information depth of about 3–5 nm for the XPS

measurement. This adsorbed layer sticks relatively well to the surface since it cannot be desorbed in vacuum at temperatures up to about 400 K. At higher temperature thermally induced changes in the film structure occur, so that thermal desorption cannot be applied to remove the adsorbed layer. All samples were, therefore, analyzed without any cleaning procedure. The oxygen concentration of various untreated samples varied between 10% and 15%. Consequently, all analyses of oxygen-plasma-treated samples have to be analyzed relative to this unavoidable adsorbed layer.

The results of the XPS analyses are shown in Fig. 6. The oxygen content, determined from the peak area, increases by 8.4% for the plasma treatment without self-bias and by 12.4% for an erosion at $U_{SB} = 100$ V or 200 V. No chemical shift of the binding energy is found for the O 1s-peak (Fig. 6(a)) which is in good agreement with the literature data on the oxygen treatment of polymer-like and diamond-like a-C:H films [18,19]. However, a considerable broadening of the C 1s peak (Fig. 6(b)) is visible in the spectra of the plasma-treated samples. This broadening is attributed to the formation of oxygen-containing functional groups due to the plasma treatment. The single C–O bond corresponds to a binding energy of 286.5 eV and the double C=O bond (carbonyl groups) to 288 eV [18,19].

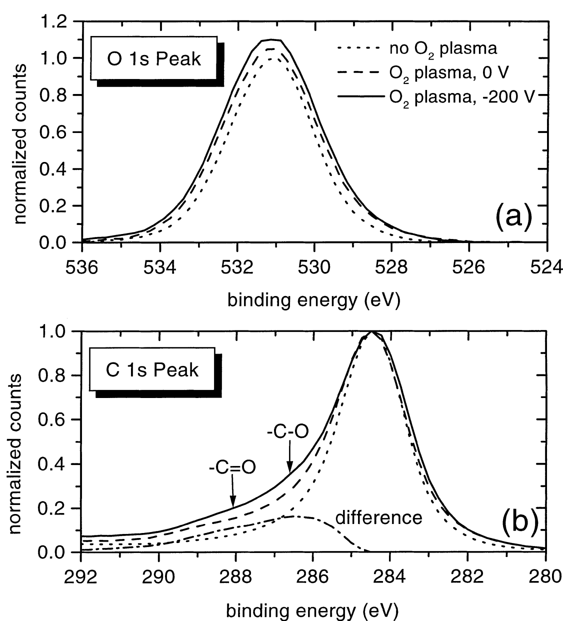

Fig. 6. The treatment of soft a-C:H films in an oxygen ECR plasma leads to a chemical shift (broadening) in the C 1s peak (b) of the XPS spectra, but no equivalent shift in the O 1s peak (a). Also shown in (b) is the difference between the sample treated in an oxygen plasma at a DC self-bias voltage of 200 V and an untreated sample. The position of published values of the binding energy of C–O and C=O groups is marked in (b).

Unlike the total amount, the relative contribution of C=O and C–O groups does not change markedly with ion energy (estimated from the peak shape). Sputtering with 1 keV helium ions was applied to measure a depth profile of the oxygen distribution. The results are shown in Fig. 7. Oxygen is only incorporated into the first 10–15 monolayers, and apparently no diffusion into deeper layers occurred during plasma exposure. This is consistent with ion-beam measurements of Wampler et al. [16] or Refke et al. [17], who found a saturation of the retained oxygen in graphite of about 10^{16} O/cm^2 by implanting 1.5 keV oxygen ions. Since we are dealing with much lower ion energies, we anticipate to find a much lower oxygen incorporation. 10% of oxygen in thicknesses of 10–15 monolayers corresponds to about 10^{15} O atoms cm^{-2}.

4. Conclusions

We have shown that hydrogenated carbon films, which represent a model system for codeposited layers in fusion experiments, can be efficiently removed in oxygen-containing low-pressure gas discharges. 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. This clearly indicates that neutral reactive species from the plasma contribute to the erosion process. At lower discharge pressure the erosion rate increases notably. This is explained with the increase of the ion flux with decreasing pressure which will be discussed in more detail in a forthcoming publication [3].

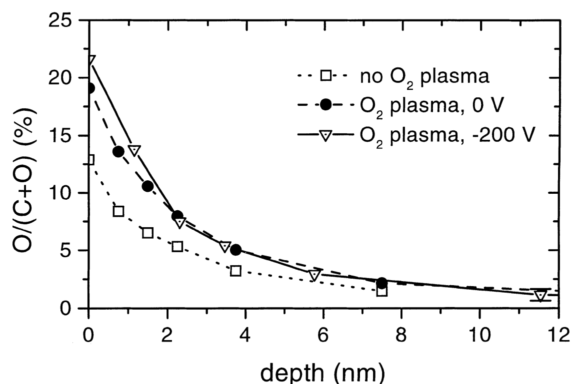

Fig. 7. XPS depth profiles of soft a-C:H films using 1 keV helium ions, treated in oxygen plasmas at $U_{SB} = 0$ and 200 V and without plasma treatment.

At floating potential ($U_{SB} = 0$ V) the erosion rate increases also with substrate temperature by about a factor of 3–4 if T is increased from 300 to 650 K. An exponential fit of the temperature dependence at $U_{SB} = 0$ V and below 500 K yields apparent activation energies of 0.027 and 0.037 eV for the hard and soft film, respectively. XPS analyses revealed that oxygen is incorporated in a thin surface layer with a thickness of about 5 nm only and no significant diffusion into deeper layers occurs.

In summary, the best conditions for an effective removal of codeposited layers are pure oxygen plasmas at a low pressure to generate high ion fluxes. If it is technically feasible to apply a bias voltage to increase the flux and energy of impinging ions (this could also be done locally), then significantly higher rates can be achieved. A second possibility to generate locally higher erosion rates is an increase of the surface temperature.

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