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Near-surface generation of negative ions in low-pressure discharges*

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Formation processes of negative ions in low-pressure plasmas are not yet fully understood: as a rule experiments reveal higher negative ion density than predicted by the models. In this work we report near-surface generation of negative ions. This hitherto neglected formation mechanism appears to be important in low-pressure discharges and can have large impacts on the bulk plasma chemistry. We monitor energy-resolved positive and negative ion fluxes arriving at the electrodes in an oxygen parallel-plate radio-frequency (rf, 13.56 MHz) and dc glow plasmas by means of a quadrupole mass spectrometer. Negative ions formed in the plasma volume are observed by extracting them through an orifice in the anode of a dc glow discharge. Unexpectedly, we record large negative ion signals at the cathode of a dc discharge and at the grounded electrode of an rf discharge. These ions are formed in the plasma sheath, in collision processes involving high-energy species. We propose an efficient mechanism of negative ion generation due to ion pair formation in the sheath. © 2001 American Vacuum Society. [DOI: 10.1116/1.1374617]

I. INTRODUCTION

Numerous applications of low-pressure plasmas require thorough studies of neutral species as well as ions. There are many situations in which the role of negative ions is essential. For example, electronegative gases are widely used in the technology of plasma-surface processing. In deposition plasmas silane, hydrocarbons, and ammonia are involved, while in sputtering and etching applications oxygen, halogens, fluorocarbons, and related gases are popular. These electronegative species readily attach electrons in the discharge: $XY + e \rightarrow (XY^-)^*$. Under low-pressure conditions the above process is often followed by dissociation of the excited complex: $(XY^-)^* \rightarrow X + Y^-$. This dissociative attachment (DA) process is accepted as the major formation mechanism of negative ions in low-pressure plasmas. Its efficiency depends on the individual molecule; the cross sections can be as high as 10^{-18} m^2 . DA may be strongly enhanced by vibrational/electronic excitation of the parent gas. In electronegative plasmas for surface processing negative ions can reach relatively high densities as a result of electron attachment to ground state and excited species. For example, in oxygen and CF_4 plasmas negative ion density is about 10^{16} m^{-3} , which exceeds the electron density by one order of magnitude. The presence of negative ions completely alters the discharge operation and opens a new field in plasma chemistry. Essential issues are the mechanisms of the negative ion generation and destruction, the influence of negative ions on transport properties of charged species (ambipolar diffusion), the structure of the plasma sheath (Bohm velocity), and finally the chemical interactions between neutrals and negative ions.¹

Electronegative low-pressure media are also commonly used for the generation of negative ion beams,² e.g., for thermonuclear fusion applications. One can distinguish between volume sources and surface converters. Volume sources are usually realized by means of low-pressure plasmas, and negative ion production proceeds by DA to (excited) molecules. Surface sources are also often plasma assisted; negative ions are formed by surface conversion of positive ions or by ion-induced sputtering of surface-adsorbed atoms. The mechanism involves electron transfer from the conduction band of the solid state. Usually, materials with low work function, like caesium or barium are applied, but recently many authors have considered stainless steel³ or diamond surfaces.⁴ In the latter case, the conduction band of the (111) surface lies even above the vacuum level. For insulating surfaces, like LiF, up to 60% surface conversion of O^+ to O^- has been reported.⁵ In most surface sources positive ions are accelerated perpendicularly to the surface and the resulting negative ions are backscattered. However, electron transfer is more efficient at grazing incidence of the positive ion, due to the longer interaction time with the surface.⁵

It is believed that in electronegative radio-frequency (rf) discharges used for surface processing negative ions are not involved in surface interactions. Unlike positive ions, which are accelerated in the plasma sheath towards the electrode, negative ions remain confined in the positive plasma glow. Normally, their behavior is governed by volume production (DA) and destruction (recombination, detachment) processes. Extraction of negative ions from radio-frequency sources is generally a troublesome task. Negative ion fluxes cannot be recorded at the surface during normal rf plasma operation. Mass spectrometric detection of negative ions is achieved either by pulsing the plasma and collecting signals in the afterglow phase, or by applying a positively biased

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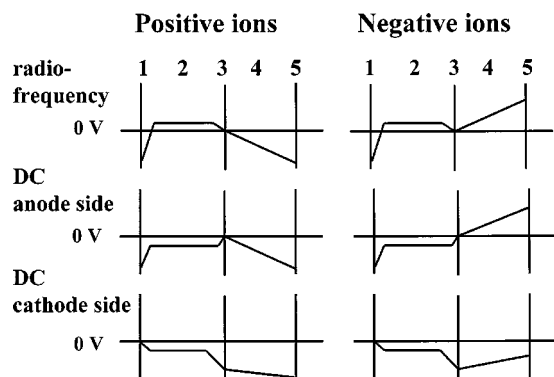


FIG. 1. Scheme of the potential distribution inside the radio frequency (top) and dc plasmas, while measuring on the anode (middle) and cathode sides (bottom), including the first ion lens of the mass spectrometer for both positive (left) and negative (right) ion flux measurements. The numbers indicate: (1) counter electrode, (2) plasma region (about 5 cm), (3) extraction electrode, with an extraction orifice of 150 μm , (4) differentially pumped acceleration region inside the quadrupole mass spectrometer, and (5) first ion lens, typically at an acceleration voltage of 100 V with respect to the extraction orifice. The horizontal lines indicate ground potential. In the radio frequency and anode measurements the extraction electrode (3) is at ground potential, while in the cathode measurements the counter electrode (1) is grounded.

extraction orifice. However, in this work we report direct mass spectrometric measurements of negative ion fluxes during rf plasma operation, using an unbiased orifice. Since these ions cannot originate from the plasma volume, we consider several possibilities of near-surface ion generation. These effects have been observed in oxygen and CF_4 gases, using rf as well as dc excitation. The latter case has been studied to obtain insight in bulk plasma and sheath/surface ion production. Negative ions in dc glow discharges can be directly extracted from the volume on the anode side, but we have also observed large signals at the cathode side, presumably from ions formed in the cathode fall region.

II. EXPERIMENT

Measurements have been performed in a low pressure parallel-plate reactor with electrodes of 10 cm diameter, made of stainless steel. Two kinds of plasmas have been generated: a capacitively coupled 13.56 MHz and a dc glow discharge. The pressure ranges between 0.05 and 0.2 mbar. Low oxygen flows have been used. The measured ion count rates are found to be independent of the gas flow; the data shown in this work are collected at a standard flow rate of 10 sccm oxygen. Positive and negative ion fluxes arriving at the upper electrode have been monitored by a HIDEN quadrupole mass spectrometer (QMS) with an energy selector. Species have been extracted through a 150 μm orifice in the upper electrode. In Figure 1 the local potentials for the various cases are shown schematically, including the potential on the first ion lens in the QMS. The extraction electrode is grounded during the measurements in the rf discharge, and in the dc discharge when it acts as the anode. For the measurements at the cathode side, a high negative dc bias (up to -900 V) is applied and the whole QMS frame is set at this

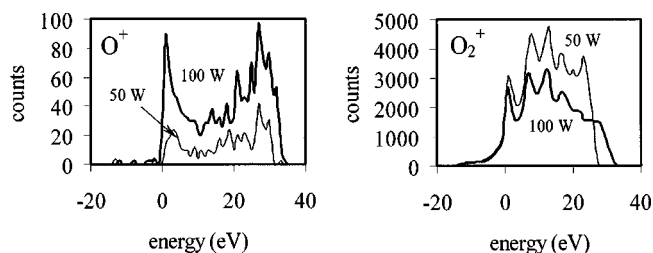


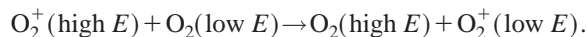
FIG. 2. Energy-resolved positive ion spectra of O_2^+ and O^+ in an rf plasma at 0.150 mbar, for two power levels: 50 and 100 W.

reference potential. In this case the counter electrode is grounded. After passing the extraction orifice the ions are focused by an ion lens into the energy and mass selection units of the QMS. The ion lens has an accelerating voltage of about 100 V with respect to the extraction orifice. Thus it is positive when detecting negative ions and negative when detecting positive ions. In practice the energy spectra are obtained by recording ion fluxes at zero energy in the energy selector, while varying the reference potential of the complete QMS unit. In this way, the potential range available to scan is largest (from -1000 to 1000 V), and in case the electrode is biased with a high voltage, ion energies with respect to the bias potential are obtained. Consequently, the ion energy, measured by the QMS, reflects the kinetic energy of ions at the extraction orifice.

III. ION ENERGY SPECTRA

A. Positive ions in a radio-frequency oxygen plasma

First, we would like to discuss some features of energy spectra of positive ions extracted from 13.56 MHz oxygen plasma. Energy-resolved signals of O^+ and the dominant ion O_2^+ are shown in Fig. 2. At the applied excitation frequency, energy distributions of positive ions accelerated in the plasma sheath often display a typical double-peak (saddle) structure, with the high-energy peak corresponding roughly to the maximum sheath voltage during the rf cycle. However, in the considered pressure range various collision processes lead to a loss of high-energy ions, and to the creation of new ions on arbitrary position in the sheath. As a result, the saddle-like features are lost and many low-energy ions are observed in the energy spectra. This is especially valid for O_2^+ ions, which can undergo charge transfer with O_2 molecules while passing through the sheath:



Cross sections are typically in the order of 10^{-19} m^{-2} for resonant charge transfer processes.⁶ Charge transfer is predominantly responsible for the deformation of the O_2^+ energy distribution, and additionally it leads to near-electrode formation of neutral species with high kinetic and/or internal energies. In the spectrum it is visible that some O_2^+ ions have apparently negative energies. This effect can also be explained by collision processes. After positive ions pass through the orifice, they are subject to ion focusing optics. First they are accelerated by the lens with a standard setting

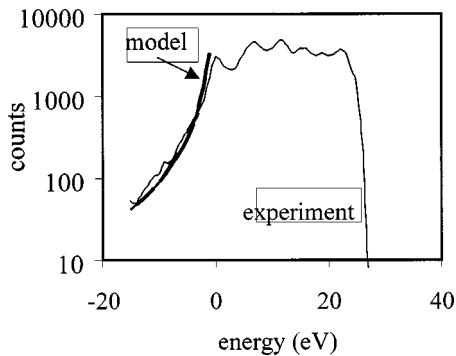


FIG. 3. Measured “negative energy” tail of the O_2^+ spectrum in an rf plasma (at 0.150 mbar, 50 W power). Thick line corresponds to the charge transfer model. The experimental counts of incoming O_2^+ at energies > 0 eV are used as input to predict the count rates at negative energies.

of -100 V, and subsequently decelerated before they enter the energy analyzer (see Fig. 1). In the first sector of about 1 cm length, between the orifice and the lens, some background gas can still be present. Charge transfer collisions between O_2^+ and background O_2 molecules lead to the creation of ions with zero kinetic energy, at a local potential which is negative with respect to the electrode (orifice). In terms of the QMS settings, these ions are collected when the QMS frame is set at a negative potential. The “negative energy” tail can be modeled taking a gas density profile between the orifice and the ion-focusing lens and a charge transfer cross section. The former can be approximated by an adiabatic expansion profile with a density decaying as $n(\mathbf{x}) \sim \mathbf{x}^{-2}$, where \mathbf{x} is the penetration depth into the QMS. The cross section can be reasonably estimated from semiempirical formulas, e.g., using a hydrogen-like model and scaling laws of Firsov and Demkov.⁶ The cross section varies slowly with ion energy as $\sigma_{CT} \sim 10^{-19} [3 - \log(E)] \text{ m}^{-2}$, for E in the range of tens to hundreds of eV. The amount of ions created at position \mathbf{x} within the QMS is thus $n(\mathbf{x}) < n_+(E) \sigma_{CT} [E + eV(\mathbf{x})] > \Delta \mathbf{x}$, where $n_+(E)$ represents the positive ions from the plasma. The counts taken from energy spectra at $E > 0$ are a good measure for $n_+(E)$, allowing to scale the “negative tail” to the bulk plasma spectrum. Ions created by charge transfer at \mathbf{x} are eventually detected when the reference is set to the local potential $V(\mathbf{x}) \sim -10^4 \mathbf{x} [\text{V}]$, and $\Delta \mathbf{x} \sim 10^{-4}$ m corresponds to the energy resolution (1 eV). In Fig. 3 it can be seen that this simple approach allows modeling the count rates of ions with a “negative energy” with a reasonable accuracy. Naturally, the “negative energy” tail is absent in the energy spectra of O^+ . In our conditions the possibilities of a symmetric charge transfer of O^+ with O are limited due to overall low density of oxygen atoms. Therefore, despite relatively high pressures, the O^+ energy distribution still resembles the saddle-like one expected in absence of collisions.

B. Negative ions in a radio-frequency oxygen plasma

In oxygen rf plasma, direct signals of O^- ions extracted through an orifice in the grounded electrode have been re-

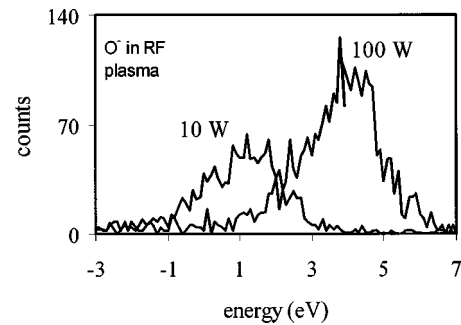


FIG. 4. Typical energy-resolved spectrum of the O^- flux arriving at the grounded electrode of an rf plasma at 0.150 mbar oxygen pressure for 10 and 100 W power.

corded in the pressure range of 0.050–0.200 mbar. Typical energy spectra at two power levels are shown in Fig. 4. Ions arrive at the electrode with low kinetic energies, of at most a few eV. The dependencies of total (energy-integrated) count rates on power and pressure are displayed in Fig. 5. Ion energy increases somewhat with increasing rf power and pressure. These dependencies indicate that O^- ions are created in a genuine plasma process, possibly with the assistance of energetic plasma particles. Negative ions from the plasma glow cannot reach the electrode. With their typical velocities of a few hundreds m/s they cannot pass the distance of the sheath (about 1 cm) in the short time (about 10 ns) when the sheath voltage collapses during the rf cycle. No realistic ion formation process in the glow can provide ions with kinetic energies sufficient to cross the potential barrier of the sheath (30–40 eV, as can be seen from positive ion spectra in Fig. 2). It is therefore plausible to conclude that detected negative ions do not originate from the glow, but are produced in the near-electrode region. We are aware that the fraction of sheath-produced ions that eventually reaches the QMS is small; the majority is most likely directed into the plasma. Thus this sheath process opens a new, potentially important formation channel, which may have large implications for understanding the negative ion chemistry in low-pressure discharges.

C. Negative ions in an oxygen dc glow

Before proposing actual sheath/surface formation mechanisms, it is interesting to compare the negative ion behavior in rf and dc discharges. In the latter case, negative ions can

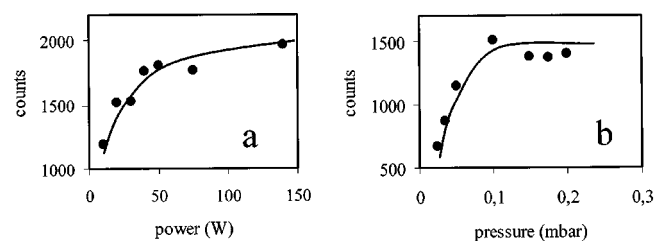


FIG. 5. Energy-integrated count rates of O^- measured at the grounded electrode of an rf plasma as a function of rf power at 0.150 mbar (a) and pressure at 30 W (b).

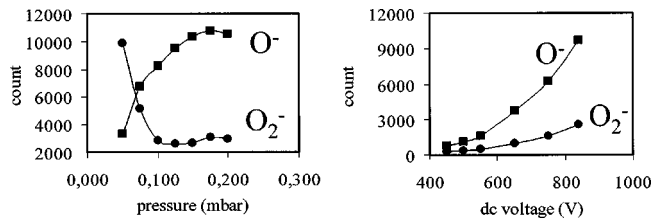


FIG. 6. Energy-integrated negative ion fluxes of O_2^- and O^- arriving at the anode side of a dc plasma glow as a function of pressure at 840 V cathode voltage and as a function of cathode voltage at 0.150 mbar O_2 pressure.

be extracted directly through an orifice in the anode. Therefore one can use the same mass spectrometric diagnostics for bulk ions as for near-surface created ions. This yields information on the negative ion densities in the plasma and helps to decide on the importance of bulk plasma and sheath/surface formation processes.

In an oxygen dc discharge, fluxes of both O_2^- and O^- ions have been detected. The total counts are shown in Fig. 6 as a function of discharge pressure and voltage. As expected, under most of the studied conditions O^- is the dominant negative ion. This is consistent with previous measurements by laser-induced photodetachment.⁷ In low-pressure discharges, O^- is readily produced by DA, while O_2^- cannot be efficiently formed by nondissociative, three-body attachment to O_2 molecules. Some O_2^- can result from charge transfer between O^- and excited O_2 molecules [$O_2(a)$, $O_2(b)$], but these processes do not provide high densities of molecular ions.

Typical energy spectra are shown in Fig. 7. Ions arrive at the electrode with a kinetic energy of about 5 eV, corresponding to the anode fall voltage. A remarkable difference between the energy distributions of O^- and O_2^- is that the former displays a high-energy and the latter a low-energy tail. O^- ions, when produced by DA in the plasma glow, can carry some kinetic energy (of the order of 1 eV). Moreover, ions are created over the whole length of the plasma. Since there is a small potential gradient in the positive column, negative ions arriving at the anode can have higher energies (10–20 eV) than the mere 5 eV gained in the anode fall. A high-energy tail is not observed for O_2^- ions. These species, in analogy to O_2^+ , can undergo symmetric charge transfer collisions with O_2 molecules, which provides very efficient

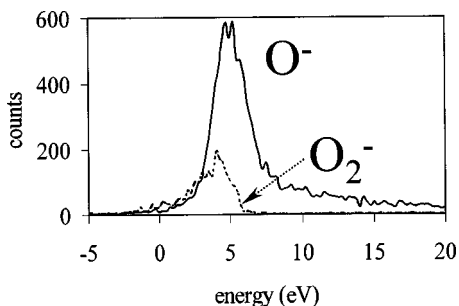


FIG. 7. Typical energy spectra of O_2^- and O^- arriving at the anode side of a dc plasma glow at 840 V cathode voltage and 0.150 mbar pressure.

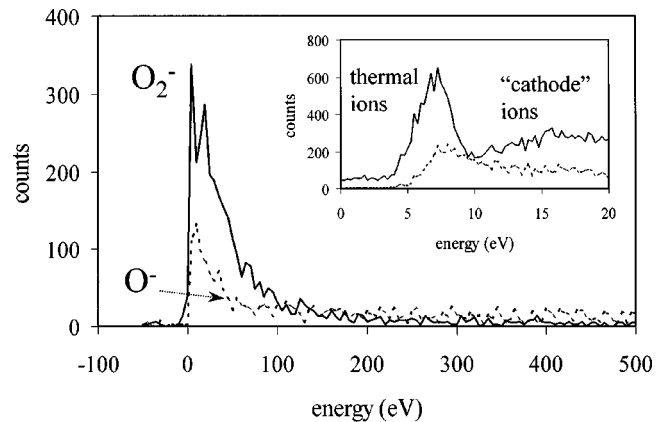


FIG. 8. Energy spectra of O_2^- and O^- arriving at the anode side of a dc plasma glow at 840 V cathode voltage and 0.050 mbar pressure. The inset shows the detailed structure of the spectrum at the low-energy side. Negative ions from the plasma bulk (thermal ions) are present, as in Fig. 7. In addition, high-energy ions formed in the cathode region and accelerated through the plasma are visible at low pressures.

thermalization with the background gas. Charge transfer also occurs while O_2^- ions pass through the anode fall. This is the reason for the low-energy tail in the O_2^- energy distribution from Fig. 7.

So far one cannot distinguish between “ordinary” negative ions, produced by DA in the plasma column, and ions created by near-surface processes, as suggested above in the case of rf plasma. At the considered pressures, thermalization and detachment in the glow are very efficient, so no special features can be observed in the energy spectra. However, measurements at lower pressures bring more insight. In Fig. 8 energy distributions of O^- and O_2^- at 0.05 mbar are shown. The spectrum still displays the “thermal” peak at about 5 eV, as in Fig. 7, but the abundance of high-energy negative ions is striking. The total counts from the high-energy tail exceed the counts of thermal ions by a factor of 10 for O^- and 5 for O_2^- . Note also that under these conditions O_2^- is the dominant negative ion: the abundance ratio of O_2^-/O^- is about 2.5 for thermal ions (0–20 eV, see Fig. 6) and 1.2 for high-energy ions (higher than 20 eV). The high-energy tail extends to high values, especially for the O^- ion. Naturally, collisions in the plasma column result in energy loss, but still some ions arrive at the anode with very high energies, of about 800 eV. This is a clear indication that some ion production must take place close to the cathode surface. Ions created in the cathode fall region are accelerated towards the anode by the cathode voltage, which is only slightly lower than the total discharge voltage (850 eV). Only in this way can the ions gain energies of several hundreds of eV. Similar observations were made by Zeuner *et al.*⁸ who studied hydrogen rf plasmas at very low pressures. Some negative ions were produced at the powered electrode and accelerated by the rf sheath. Under low-pressure conditions, these species traveled as “projectiles” through the whole plasma glow. Since the sheath voltage at the grounded electrode is substantially lower than the rf sheath voltage, fast ions had enough energy to cross the sheath, so they could be detected at the

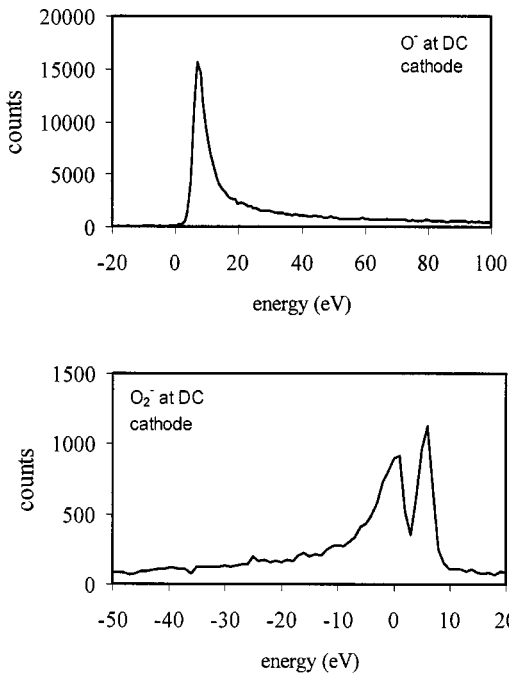


FIG. 9. Energy-resolved negative ion fluxes of O^- and O_2^- arriving at the cathode side of a dc plasma glow at 0.150 mbar pressure, 850 V cathode voltage. Note the typical double peak structure and the “negative energy” tail in the energy distribution of O_2^- .

grounded electrode. Note that in our oxygen rf plasma, described in the previous section, we do not observe ions created at the opposite (powered) electrode, since the pressure is too high. Since the signal detected at the grounded electrode increases with pressure [Fig. 5(b)], it can be only due to ions created near the extraction place, otherwise it would rapidly decrease with pressure, as in case of Zeuner *et al.*⁸ Note, however, that the measurements of the latter authors also indicate negative ion production inside the sheath region of a radio-frequency plasma.

The described arrival of high-energy ions at the anode of a dc glow, or at the grounded electrode of an rf discharge is an indication of negative ion formation near the surface of the opposite electrode. Next, we have checked whether negative ions can be also detected close to their formation place in a dc glow, i.e., at the cathode side. The conditions at the cathode are comparable with the previously described rf case, except that the cathode fall voltage is higher than the sheath voltage at the grounded electrode (see Fig. 2). Indeed, also at the cathode side large signals of O^- and O_2^- ions have been recorded. Typical energy spectra are shown in Fig. 9. In Fig. 10 it can be seen that the height of the signals increases exponentially with increasing dc voltage. Moreover, a considerable increase of ion fluxes with pressure has been observed, as shown in Fig. 11. The energy spectra from Figs. 9 and 10 are remarkable and they can yield some clues about the ion formation mechanism. Generally, most ions detected at the cathode side have low energies. The energy distribution of O^- peaks at zero eV, with a width at half height of about 5 eV. However, in the case of O^- a significant high-energy tail can be observed, which extends to

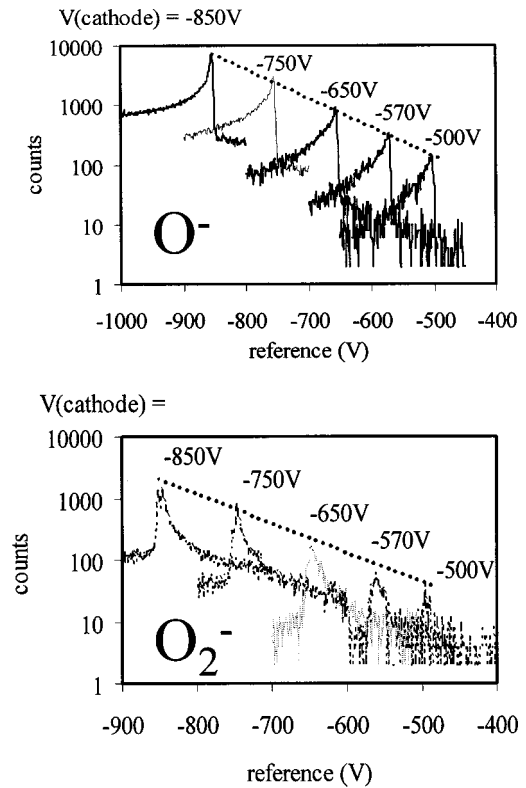


FIG. 10. Energy-resolved negative ion fluxes of O^- and O_2^- arriving at the cathode side of a dc plasma glow at 0.150 mbar pressure for various cathode voltages. The ion energies are measured with respect to ground (reference voltage). Thus, at a given cathode voltage $V(\text{cathode})$, the ions collected at reference equal to $V(\text{cathode})$ are zero-energy ions. Ions with velocity towards the cathode (kinetic energy larger than zero) are measured at reference voltage more negative than $V(\text{cathode})$. Therefore O^- displays a high-energy tail, while O_2^- has apparently negative kinetic energy.

about 50 eV. This implies that some negative ions created near the cathode surface have high velocities towards the surface. The amount of detected ions and their high kinetic energies are surprising, considering the presence of a large cathode voltage, which repels negative ions from the extraction place.

Unlike O^- , the energy distribution of O_2^- does not display a high-energy tail. It has a typical double peak structure at energies around 0 eV, and it extends towards negative

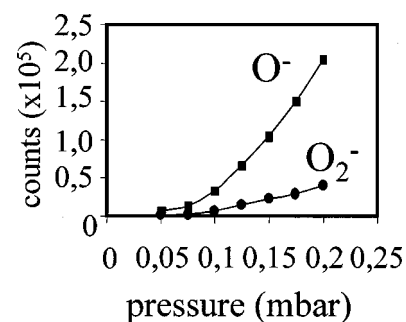


FIG. 11. Energy-integrated negative ion fluxes of O_2^- and O^- arriving at the anode side of a dc plasma glow as a function of pressure, at 850 V cathode voltage.

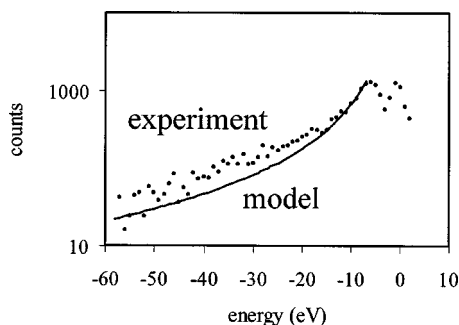


FIG. 12. Measured “negative energy” tail of the O_2^- energy spectrum at 0.2 mbar pressure and 850 V cathode voltage. The thick line indicates the model, used to predict the count rates of ions created behind the extraction orifice due to charge transfer reactions (similar to O_2^+ from Fig. 3).

energies. The latter feature has already been mentioned for O_2^+ ions (see Fig. 3), and it can be modeled in a similar way by assuming a symmetric charge exchange process in the region immediately behind the extraction orifice. However, in the case of O_2^- ions taking part in symmetric charge transfer, they have rather low energies. The semiempirical approximation for the charge transfer cross section predicts 10^{-18} m^2 in the limit of low energy, but it may significantly underestimate the real value. For most ions, charge transfer cross sections are largest at zero energy. Therefore in the model we have used a somewhat larger value of $2 \times 10^{-18} \text{ m}^2$. As shown in Fig. 12, a good fit to the experimental data has been obtained.

D. Positive ions in an oxygen dc glow

Finally, some energy spectra of positive ions arriving at the cathode are given for comparison. In Fig. 13 energy distributions of O_2^+ (the dominant ion) and O^+ are shown. High-energy ions accelerated by the cathode fall are visible, but most of the ions have lower energies due to collisions. A striking feature of the O_2^+ spectrum is a characteristic double peak at nearly zero energy. This resembles a structure in the O_2^- spectrum (Fig. 9). Charge transfer or collisional energy loss of bulk ions cannot explain the peak in the O_2^+ signal at zero energy, as these processes result only in broadening of the energy distribution. Therefore we conclude that the zero energy positive ions are created in the sheath very close to the electrode surface, in an ionization process which is essentially different from bulk processes.

IV. POSSIBLE NEGATIVE ION FORMATION MECHANISMS

The above observations indicate that the chemistry of the plasma sheath is very rich. A variety of electron transfer or ionization processes can occur, but so far their nature and influence on the bulk chemistry is poorly understood. In any case one can expect that high-energy species arriving at the surface (positive ions accelerated in the sheath, and hot neutrals created by charge transfer) take part in the generation of negative ions. This follows from the dependence of the signals on plasma power in rf [Fig. 5(a)], and voltage in the dc

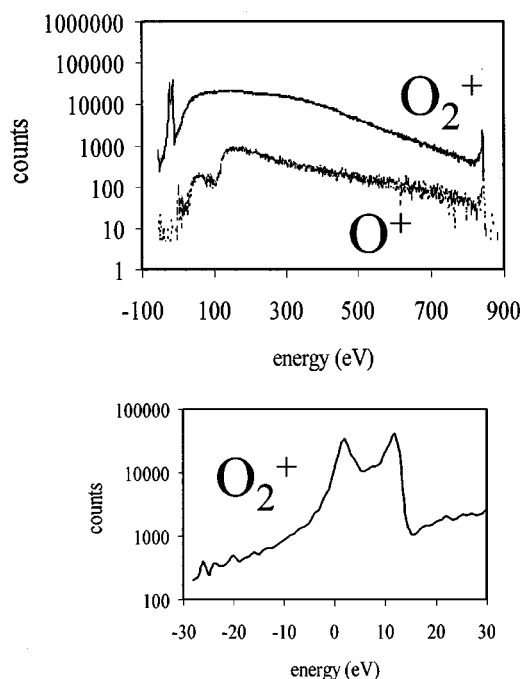
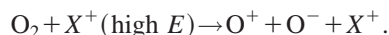


FIG. 13. Energy spectra of O^+ and O_2^+ arriving at the cathode of a dc glow discharge at 0.150 mbar pressure and 850 V cathode voltage. A detailed low-energy structure in the O_2^+ spectrum is shown separately.

case (Fig. 10). In both cases, negative ion fluxes are clearly enhanced at high voltages/power levels, which correlates with the amount and energy of positive ions and neutral species. Next, the increase of the signals with pressure [Figs. 5(b) and 11] does not necessarily indicate a genuine surface process, but rather a near-surface collision process with the background gas. Another remarkable feature is the high-energy tail of O^- ions, especially at the cathode in the dc case (Fig. 9). For O^- , a possible mechanism could be ion pair formation from O_2 upon impact of high-energy positive ions:



The proposed process explains why we are able to detect any negative ions by the QMS. The momentum transfer from a high-energy positive ion will result in a certain velocity component of O^- towards the electrode, so that the produced negative ion can be extracted through the orifice. For high incident X^+ energies, one can also expect the existence of high-energy tail in the energy distribution of negative ions, in agreement with observations at the cathode of a dc discharge (Fig. 9).

Ion pair formation in oxygen upon electron impact is a well-known process: its cross section is about $5 \times 10^{-23} \text{ m}^2$ for electron energies higher than 30 eV. It is expected that energetic heavy particles, like positive ions or fast neutrals, are more efficient in dissociating and ionizing molecules, due to a large momentum transfer in a collision. Some data are available for high-energy hydrogen ion beams in the keV range. For example, ion pair formation: $H^+ (\text{high } E) + H_2 \rightarrow H^+ + H^+ + H^-$ has a cross section of 10^{-21} m^2 at 10–20

keV. This is in the same order of magnitude as cross sections for other proton-induced ionization processes of H_2 [e.g., H^+ (high E) + $\text{H}_2 \rightarrow 2\text{H}^+ + \text{H} + e$]. Interactions of H^+ (high E) with oxygen lead to the production of secondary O^+ ions with a total cross section of $2 \times 10^{-20} \text{ m}^{-2}$. Considering the large contribution of H^+/H^- formation process to the total ionization in the case of hydrogen, one can expect also in O_2 that O^+/O^- formation will occur with a reasonable probability. The cross sections are weakly dependent on the incident ion energy. The trends in the high-energy range indicate that also for ion energies in the sub-keV range (e.g., 0.5–0.9 keV, as in our dc cathode fall) the cross section for ion pair formation is still quite large. Moreover, heavier positive ions, like O_2^+ and O^+ are expected to be more efficient than H^+ . Concluding, although to our knowledge there is no specific data on ion pair formation in O_2 upon O_2^+ impact, one can anticipate a cross section σ_{ip} in the order of 10^{-20} m^{-2} for this process.

Formation of negative ions in the above process occurs most likely in the closest vicinity of the electrode, where the positive ions have their highest energies. At 0.2 mbar, the mean free path for O^+/O^- formation would be about 3 cm. Assuming that O^- is created close to the electrode in a slab with thickness Δx of about 1 mm, the detected count rate of O^- should be at most 3% of the detected count rate of high-energy positive ions. Of course, it is not expected that all the generated negative ions will reach the QMS; most of them will be scattered and reflected to the plasma glow. We observe O^- signals of 0.1%–1% of the O_2^+ count rates, which is in a reasonable range. Furthermore, it is interesting to estimate to what extent ion pair formation in the sheath can contribute to the total negative ion production in the discharge. For this purpose, one has to compare the volume production by DA, given by $n_0 n_e k_{\text{att}} V_{\text{pl}}$, where n_0 is the background gas density, n_e the electron density, k_{att} the DA cross section for oxygen, and V_{pl} the plasma volume, with sheath production $n_0 \sigma_{ip} \Phi_+ V_{\text{sh}}$ where V_{sh} is the volume of the slab with thickness Δx . The positive ion flux Φ_+ can be approximated by the Bohm flux $n_+ v_B$, with typical ion densities $n_+ \approx 10^{16} \text{ m}^{-3}$ and Bohm velocities $v_B \approx 10^3 \text{ m/s}$. Further, the electron density in the considered discharge is in the order of 10^{15} m^{-3} and $k_{\text{att}} \approx 10^{-17} \text{ m}^3/\text{s}$. By filling in the above values one can estimate the ratio of surface to volume production rates:

$$\frac{P_{\text{sh}}}{P_{\text{pl}}} = \frac{\sigma_{ip} \Phi_+}{n_e k_{\text{att}}} \cdot \frac{\Delta x}{L} \approx 10 \frac{\Delta x}{L}.$$

Since the length of the plasma glow in most parallel plate configurations does not exceed a few centimeters, one can see that the sheath production rate is in the same order of magnitude as the volume rate. In other words, ion pair formation in the sheath forms potentially an important channel for negative ion generation in low-pressure discharges.

For molecular ions, near-surface production processes are expected to play an even more important role than for O^- . As stated before, volume production of O_2^- is not efficient under low pressures. In contrast to O^- , O_2^- production by

ion pair formation is not likely. On the other hand, the energy density in the vicinity of the electrode is so high that there are many processes that can occur only there. One could consider conversion of high-energy positive ions arriving at the surface, or charge transfer between ground state and highly excited O_2 molecules (the reverse of commonly known ion–ion recombination: $\text{O}_2^* + \text{O}_2 \rightarrow \text{O}_2^+ + \text{O}_2^-$). The latter process would explain the similarity in the low-energy structures present both in O_2^+ and O_2^- spectra (Figs. 9 and 13). However, there is little known about the abundance of O_2^* in the sheath, so no conclusive answer can be given at present.

V. CONCLUSIONS

We have measured the positive and negative ion fluxes arriving at the electrodes in an oxygen radio frequency and dc plasma by means of energy-resolved mass spectrometry. Surprisingly, negative ions have been found arriving at the electrode of a radio-frequency plasma and at the cathode of a dc plasma. These ions cannot come from the plasma glow. They are also unlikely to result from the conversion of positive ions upon impact on the electrode surface, since any negative ion formed in this process would be accelerated into the plasma and not towards the mass spectrometer. Therefore, the detected negative ions must be formed inside the plasma sheath, close to the surface. Apparently, the sheath chemistry is very rich and various processes involving high-energy species can lead to negative ion generation. Ion pair formation from O_2 by positive ion impact is proposed as an efficient sheath production channel of O^- . The results indicate that sheath and surface can be important sources of negative ions. So far, such formation processes have not been considered in plasma models, which deal only with electron attachment in the plasma glow. On the other hand, most experiments show that negative ion densities in the glow of low-pressure plasmas are higher than the ones predicted by the models. In order to overcome this inconsistency in modeling, and to obtain the full view of plasma chemistry, near-surface as well as volume processes must be taken into account.

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