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Polymerization of fluorocarbons in reactive ion etching plasmas

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Polymerization reactions in radio frequency fluorocarbon plasmas of CF_4 , C_2F_6 , and C_4F_8 have been studied by electron attachment mass spectrometry (EAMS). In these plasmas polymerization occurs readily and molecules containing up to ten carbon atoms (the mass limit of the mass spectrometer) have been found. The densities of large polymers increase with increasing size of the parent gas. In a fluorine-rich environment like a CF_4 plasma the detected polymers are mainly fully saturated with F ($\text{C}_n\text{F}_{2n+2}$). As the amount of fluorine in the parent gas decreases, also the degree of saturation of the polymers decreases, which is clearly seen in C_2F_6 and C_4F_8 plasmas. The unsaturated polymers are more reactive, so they can stick more easily to surfaces and possibly create thick polymer films, which are often observed after discharge operation. The polymerization rate depends on the chemical activity of the plasma, which can be easily enhanced by increasing the radio frequency power. The positive ions, extracted from the plasma, are generally somewhat smaller than the neutral polymers and their fluorine content is lower. This is probably due to dissociation of neutrals during their ionization by plasma electrons and to ion collisions in the sheath region. Finally, we have shown that EAMS has considerable advantages in the study of electronegative plasmas and polymerization processes in comparison with traditional mass spectrometry. Unlike the traditional mass spectrometry, employing ionization by high energy electrons, EAMS much better preserves the structure of high polymers, allowing us to detect them as large negative ions. © 1998 American Vacuum Society. [S0734-2101(98)03601-X]

I. INTRODUCTION

Reactive ion etching of semiconductor materials using fluorocarbon gases is one of the most important surface processing methods in the semiconductor industry. In spite of the widespread usage of this technique and extensive research effort invested in understanding plasma-surface interactions, the exact etching mechanisms are still under discussion. In order to improve performance in technologically important areas like selective etching of SiO_2 over Si or high-aspect ratio etching, one needs still more insight in the complex plasma chemistry and its impact on the surface.¹ Numerous experimental studies of these chemical processes have been performed, involving *in situ* plasma diagnostics such as infrared spectroscopy, mass spectrometry and laser induced fluorescence, and surface diagnostics like ellipsometry, x-ray photoelectron spectroscopy, and attenuated total reflection Fourier transform infrared spectroscopy (see Refs. 2 and 3 and the references therein). Moreover, elaborate models for plasma chemistry and plasma surface interactions have been developed.^{4,5} Especially in reactive media like fluorocarbon plasmas, the combined action of high energy ions and active species is essential for a successful etching process. Therefore most emphasis has been put on understanding the ion and radical kinetics, while relatively little attention has been paid to plasma polymerization. Nevertheless it is clear that the latter process can drastically alter the plasma chemistry. The plasma-produced polymers have a

lower ionization threshold and a higher electron attachment cross section than the parent gas, so both positive and negative ion formation are enhanced in the presence of these species. Furthermore, polymerization reactions form a sink for radicals and can lead to formation of macroscopic structures. These dust grains have been found in many reactive etching and deposition plasmas and they are responsible for surface damage. Many studies have revealed that large grains can be produced by gas-phase polymerization in low pressure plasmas.⁶

Next to gas phase polymerization, formation of polymer films on the surface is an important issue in etching plasmas. A clear example of this effect is side wall passivation in deep trench etching.^{7,8} Elaborate studies by Oehrlein *et al.*⁷ revealed that the presence of such films has a major impact on the etching performance of the plasma. It influences the resistivity of the coated surface, which will be reflected by an altered plasma impedance and consequently the effective power input. Charging of a deposited layer influences the positive ion flux towards the surface.⁹ This leads to undesired effects in high aspect ratio etching, where charging of the layer deposited on a side wall of a trench reduces the etch rate at the bottom and deteriorates the quality of the fabricated structure. Moreover, large dust grains which can contaminate the substrate surface, are often formed during plasma processing by flaking or sputtering of the polymer layer.⁶ Finally, the presence of a polymer layer changes the surface conditions, which in many cases seriously affects the plasma chemistry by changing the sticking probabilities of plasma species and by introducing new surface reactions.

The deposition mechanisms of these polymer films are at

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present poorly understood. Polymer layers on the surface are easily formed in fluorocarbon discharges with high concentrations of radical species, like CF , CF_2 , and CF_3 .¹⁰⁻¹² However, generally these radicals themselves do not contribute to the polymer film formation. Contrariwise, in many cases a net radical flux *from* the surface *into* the plasma glow has been observed.^{10,11,13} This together with the observation, that small radicals stick poorly on a polymer-coated surface, gives a strong indication that they are not the building stones of the polyfluorocarbon films, the deposition mechanism remaining thus an open question. It has been established that small radicals are predominantly formed close to or at the surface and several production mechanisms have been considered: surface conversion of radicals, ion-induced sputtering of the polymer layer, reactions with high energy positive ions in the sheath, etc. Chemical conversion of radicals from the plasma has been excluded, as all these species appear to be produced at the surface.¹⁰ Purely physical sputtering by energetic ions has also been ruled out, based on the absence of radical fluxes from a polymer film, exposed to ion bombardment in an argon plasma. However, the importance of positive ions in the radical production process is clear: the outflux of radicals from the surface is correlated to the flux and energy of the ions, reaching the electrode. A quantitative analysis reveals that the net outflux of radicals away from the surface exceeds the influx of positive ions.¹⁰ Therefore, a single ion must create several (up to ten) radicals. It has been suggested that a positive ion gains enough energy in the sheath region to produce many radical species by collisions with neutrals. Indeed, energy-resolved mass spectrometry shows that positive ions undergo many collisions in the sheath under the same conditions in which a high radical outflux is observed.¹⁴ This mechanism certainly can contribute to radical production, yet it requires a considerable efficiency of the ion-induced process in order to explain the effect quantitatively. At present, knowledge of such collision processes and their cross sections is very limited. Another way to produce several small radicals from a single positive ion involves fragmentation of ions containing several carbon atoms. Although mass spectrometric measurements show that in most fluorocarbon plasmas CF_3^+ is the dominant positive ion,¹⁴ also high polymeric ions are present in these plasmas, as discussed further in this work. Finally, complex chemical sputtering of the polymer film has been considered, in which both positive ions and radicals (e.g., fluorine) are involved. In this kind of process the yield of radicals per ion can be much larger than unity.¹⁵ Thus, this scheme can provide an explanation for ion-induced radical production.

The remaining problem is the actual deposition mechanism of the polymer layer. Recently, Booth *et al.*¹⁶ have suggested that this process is related to gas phase polymerization. The growth of a fluorocarbon film on the surface proceeds by sticking of large polyfluorocarbons, formed in the discharge and diffusing towards the surface. This mechanism can be verified by checking the presence of polymeric species in the discharge.

As discussed above, a study of gas phase polymerization

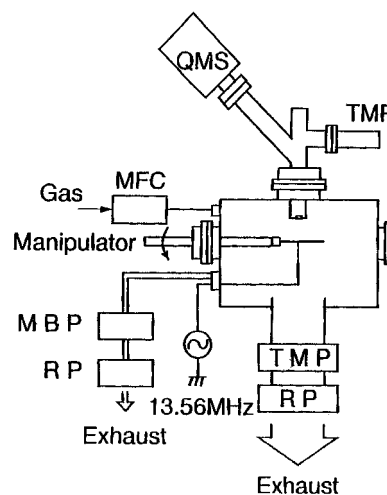


FIG. 1. Schematic view of the experimental setup; TMP, RP, and MBP indicate turbo molecular, roots, and mechanical booster pumps, MFC is a mass flow controller.

processes can provide valuable insights in the plasma chemistry. Many important aspects of etching plasmas are covered: understanding of deposition processes leading to side wall passivation and surface radical production; clarifying formation mechanisms of dust particles; and testing the plasma chemical models. In this work we present a study of polymer formation in CF_4 , C_2F_6 , and C_4F_8 low-pressure radio frequency discharges. The polymeric neutral species are detected by means of a newly implemented technique: electron attachment mass spectrometry (EAMS). While the traditional mass spectrometry uses electron impact ionization to transform neutrals to positive ions, EAMS uses low-energy electrons, which attach to neutrals and yield negative ions. The EAMS technique, when applied to electronegative molecules, has been recently proven to have many advantages over ionization mass spectrometry, one of them is its clearly less destructive character.¹⁷ The traditional electron impact ionization mass spectrometry applied to heavy molecules results in a very complicated fragmentation pattern, in which heavy ions are rather scarce. In contrast, only a few different negative ions are produced from a given neutral parent, the fragmentation is limited and consequently heavy negative ions are readily visualized in EAMS. This structure-preserving feature of EAMS facilitates detection of large, fragile molecules, like polymers.

II. EXPERIMENTAL SETUP

A detailed description of the experimental setup as well as of the electron attachment mass spectrometry technique has been published previously.^{17,18} In summary, a capacitively coupled low-pressure 13.56 MHz plasma is generated in an open configuration, as shown in Fig. 1. The plasma reactor is evacuated by a roots blower and a turbo molecular pump. The powered electrode is a square (7×7 cm) aluminum plate, separated from a grounded aluminum shield underneath by 5 mm ceramic spacers in the upper part of the

reactor, where the diagnostic system is mounted. The electrode is connected to a vacuum manipulator, which allows us to adjust the position of the electrode. The plasma is generated using a RF Power Products RF10S-type generator and a homebuilt π -type matching network. The power levels reported in this work are the nominal values, not corrected for the losses in the matching network and cables. The stainless steel walls of the reactor and the quadrupole mass spectrometer (QMS) head act as the grounded electrode. Process gas is supplied by a Tylan mass flow controller and a typical flow rate is 2–4 sccm. In this open configuration the residence times can be relatively long (about 10 s at the lowest applied flow rate), which is optimal for plasma polymerization, as it allows the produced species to accumulate in the discharge. The gas pressure, measured by a Baratron manometer, is typically 15–30 mTorr. The measurements are performed using a Hiden EQP500-type QMS with an ion energy selector. In our setup the grounded QMS orifice (150 mm diameter) is situated about 5 cm away from the powered electrode. The electron filament in the QMS, normally used as an ionization source, is now operated at low electron energies to allow for electron attachment to sampled plasma species. The pressure in the attachment (or ionization) chamber is kept below 10^{-6} Torr. The design of the Hiden ionization cage allows for an electron energy resolution of about 0.1 eV. Negative ions, formed from plasma species by attachment of filament electrons, are detected by the QMS. In case of F^- detection, a background signal must be subtracted from the data. This signal, emerging at electron energies higher than 8 eV, is ascribed to sputtered material of the heated electron filaments. For other ions no background signal has been observed. The maximum mass, detectable by the QMS is 510 amu and the sensitivity of the system decreases substantially with increasing ion mass. Mass dependent transmission can be accounted for by calibration with some known source gases and according to the Hiden specifications it decreases approximately as $10^{-M/100}$, where M is the mass in amu. This correction has not been incorporated in the data presented below, which means that the relative densities of large polymers are substantially higher than indicated by their count rates. The differences in the attachment efficiencies of the various ions have not been taken into account, mainly due to the absence of quantitative cross-section data for the polymeric species. In this work we consider large polymers, typically attaching at low electron energies (0–2 eV). For these species it can be assumed that the absolute values of the attachment cross sections increase slightly with increasing number of carbon atoms.¹⁹ The EAMS data are collected by making an electron energy scan from 0 to 10 eV. When the resonances from different species are well pronounced, the count rates of ions produced from the corresponding molecules are separated. For example, in case of a CF_4 plasma, the contributions of CF_4 , C_2F_6 , and C_3F_8 can be distinguished in the electron energy dependent signals of F^- or CF_3^- ions. However, when no fine structure

is visible in the resonances, the count rates presented here are integrated over the electron energy. This is the case for most heavy ions detected.

Alternatively, neutral polymeric species have been detected by the traditional mass spectrometry, using electron impact ionization. The system is tuned for maximum detection and an electron energy of 50–70 eV is used. In this range the corresponding ionization cross sections are high. On the other hand, the polymers are easily dissociated at these high energies and consequently only few heavy molecules can be detected. The detection of large polymers by ionization mass spectrometry cannot be improved by using lower energy electrons, as in this case the ionization cross sections are also low.

Finally, the study is completed with measurements of positive ion fluxes from the plasma. To determine the count rate of positive ions, the Hiden QMS settings are optimized for each mass. The ions are collected at an energy of 20 eV, which is close to the plasma potential under the considered conditions.

III. RESULTS AND DISCUSSION

A. Dissociative attachment processes

Before discussing polymerization processes, we shall show some features of electron attachment mass spectrometry. The method is based on electron attachment to electronegative species. In contrast to electron impact ionization, attachment is a resonant process, which requires a well-defined electron energy. The negative parent ion, formed in this process often carries a substantial internal energy. In the absence of collisions with a third particle, small negative ions can stabilize by dissociation, yielding a lighter ion and a neutral. The fragments carry away the excess kinetic energy, which is the sum of the kinetic energies of the neutral and electron before attachment and the electron affinity of the neutral minus the dissociation energy. For example, attachment to CF_4 with maximum cross sections at electron energies between 6–8 eV, results in the formation of $F^- + CF_3$, $F^- + CF_2 + F$, or $F + CF_3^-$. In the first case ($F^- + CF_3$) the F^- ion has a significant kinetic energy (1–2 eV), which influences its detection.¹⁷ For larger molecules, attaching only low-energy electrons such energy effects are not present. Moreover, large molecules have many internal degrees of freedom, into which the excess energy can be distributed, so the parent ion may stabilize without dissociation. In such cases the parent neutral can be also observed as a negative ion, like, e.g., SF_6^- , resulting from nondissociative attachment to SF_6 . For fluorocarbon polymers, however, we have no evidence of nondissociative attachment. At least, parent negative ions of fully saturated fluorocarbons ($C_nF_{2n+2}^-$) have not been observed, most likely due to their unfavorable electronic configuration.

The resonant character of the attachment process is a great advantage of EAMS. Even if several species in a mixture produce the same negative ion, their contributions can often be separated, as each component yields a rather

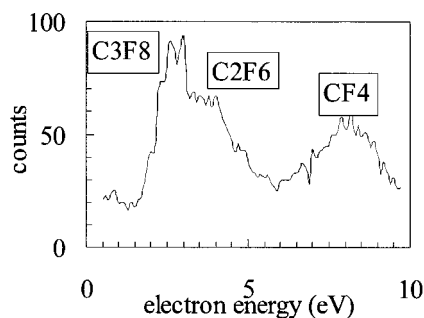


FIG. 2. EAMS of F^- observed in a 20 W CF_4 plasma at 15 mTorr pressure and 2 sccm flow rate. The peak at 8 eV is due to dissociative attachment to CF_4 , while the peaks at 3 and 4 eV result from dissociative attachment to C_3F_8 and C_2F_6 formed in the plasma.

peaked, distinct resonance at his own electron energy. Such separation is much more troublesome in ionization mass spectrometry, where the cross sections are broad and overlapping is inevitable. In Fig. 2, the EAMS count rate of F^- in a CF_4 plasma is shown. The resonance at 8 eV is due to dissociative electron attachment to CF_4 . The signal at lower energies is observed only in the presence of the plasma, and based on the electron energy it is attributed to dissociative attachment to C_2F_6 at 4 eV and to C_3F_8 at 3 eV.¹⁹ A similar resonance due to plasma-produced C_2F_6 is identified in the CF_3^- signal, but the C_3F_8 contribution is absent. Separation and detection of species present in a plasma is only one example, demonstrating the advantage of EAMS. Another important application is the study of the negative ion chemistry in a plasma. The same negative ions, detected during the EAMS measurements are also abundantly present in the plasma. In the considered CF_4 discharge F^- and CF_3^- are formed by dissociative attachment from the same neutrals, as in the QMS system; F^- is the dominant plasma anion. Negative ions are the major negative charge carriers in low pressure fluorocarbon plasmas, with densities exceeding the electron density by more than an order of magnitude.²⁰ Naturally, such high negative ion densities influence many plasma properties and clarifying the ion formation mechanisms is essential for a good understanding of the discharge. The negative ion signal, shown in Fig. 2 represents the effective cross section for F^- formation by dissociative attachment in a discharge. In combination with the electron energy distribution function in the plasma, this allows us to determine the negative ion formation rate, without knowing the density of the various contributing species and/or their attachment cross sections. It can be easily seen in Fig. 2 that in this CF_4 plasma, with a typical electron temperature of about 3 eV, dissociative attachment to the parent gas is not the dominant process for negative ion formation. Instead, the conversion products C_2F_6 and C_3F_8 , with their higher cross sections for dissociative attachment and lower electron energy thresholds provide the bulk of the negative ions, even though the C_2F_6 and C_3F_8 densities are at most a few percent of the CF_4 density.¹⁷ This directly confirms previous indirect measurements, relating infrared absorption data of C_2F_6 with

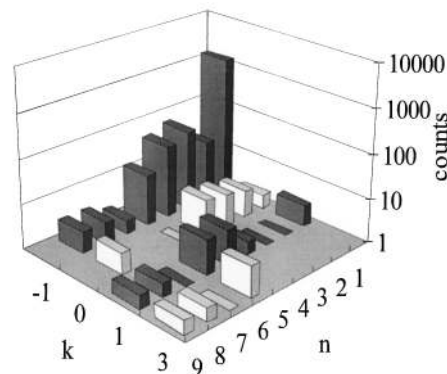


FIG. 3. EAMS count rates of polymers, formed in a 9 W, 30 mTorr, 4 sccm CF_4 plasma. The data are arranged in series C_nF_{2n-k} . Thus a large n implies a larger polymer, while a large k denotes relatively little fluorine. The EAMS counts for each species are integrated over an energy scan of the attaching electrons.

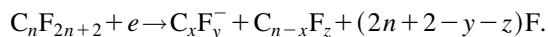
negative ion densities and their formation rates, determined by laser-induced photodetachment.²⁰ In future studies the EAMS data will be compared with mass spectrometric measurements of negative ion fluxes from the plasma. Generally, extraction of negative ions from a discharge is difficult, as these species cannot pass the potential barrier, created by the plasma. Many successful attempts have been made to collect the negative ions in the afterglow.²¹ However, the major drawback is that this is not an *in situ* method and the acquired data may be influenced by some afterglow effects.

After this introduction to the EAMS technique we proceed with the discussion on neutral and ionic polymers formed in CF_4 discharge, followed by a comparison with C_2F_6 and C_4F_8 plasmas.

B. The CF_4 plasma

Figure 3 shows the polymers, extracted from a CF_4 plasma at 30 mTorr, 4 sccm, and 9 W, and detected using the EAMS technique. The counts of C_nF_{2n-k} are integrated over an electron energy scan of the QMS and the results are presented as a function of n and k . Thus n denotes the number C atoms and a higher k corresponds to species with less fluorine than the fully saturated fluorocarbon (C_nF_{2n+2} , $k = -2$). In our case C_nF_{2n+1} ($k = -1$) is the largest detected anion for a given n ; parent ions of fluoroalkanes have not been observed. Figure 3 shows clearly that polymer formation readily occurs, as molecules with up to nine carbon atoms are observed. Nevertheless, the dominant fluorocarbon anion is CF_3^- , which has more than an order of magnitude more counts than $C_3F_7^-$, the next most abundant anion. Note that mainly anions with an odd number of fluorine atoms have been detected. Species like $C_nF_{2m+1}^-$ have no unpaired electrons, so their formation is energetically preferred. As can be seen, saturated anions ($k = -1$) are relatively abundant in a CF_4 plasma. The resonances of $C_nF_{2n+1}^-$ for $n > 2$ appear at low electron energies (0–2 eV). The fact that little energy is needed to form a heavy polymeric ion suggests that no extensive fragmentation of the parent molecule occurs

during dissociative attachment. This gives some clues in the identification of the parent neutral species in the complicated mixture, which is formed in the plasma. Thus, it is likely that the observed ions originate from fluoroalkanes (C_nF_{2n+2}). The ions with $k=0$, although energetically less favorable than series with an odd k , are still visible, especially for lower n values. At higher n values also some fluorine-stripped negative ions emerge ($k=1,3$), although their count rates are considerably lower. In contrast to the $C_nF_{2n+1}^-$ ions, more electron energy is needed to form the unsaturated ions. This indicates that these unsaturated anions are mainly formed from saturated parent molecules in an attachment process, followed by multiple bond breaking, e.g.,



Of course, some unsaturated ions may also be formed from unsaturated parent neutrals. However, in a fluorine-rich environment like a CF_4 plasma unsaturated species, containing relatively little F, are not expected to be abundant. For the same reason polymerization is not very efficient, as all dangling bonds are readily saturated by the excessively present fluorine and consequently the growth of the carbon chain is terminated. Thus, in comparison with less fluorine-rich C_2F_6 and C_4F_8 chemistries, discussed below, the count rates of large polymers and especially unsaturated species in a CF_4 plasma are relatively low. In a CF_4 chemistry only limited deposition of polymer layers has been observed. Therefore, the above measurements support the idea of film deposition by sticking of polymers to the surface.

It is remarkable that $C_2F_5^-$ has a significantly lower count rate than the next higher anion $C_3F_7^-$. This feature, which is observed also in C_2F_6 and C_4F_8 discharges, must be related to the specific formation process of $C_2F_5^-$. Its major production channel is dissociative attachment to C_2F_6 . This reaction has indeed a low cross section and the preferred dissociative attachment channels of C_2F_6 yield F^- (see Fig. 2) and CF_3^- with cross sections about 1000 and 300 times higher, respectively.¹⁹ Of course, most fluorocarbon species, including large polymers, can form F^- by dissociative attachment and consequently many resonances contribute to the EAMS signal of F^- . These numerous resonances overlap, which makes the analysis of the F^- signal less convenient for the study of polymer formation in plasmas. On the other hand, the F^- signal is the most interesting one in the study of negative ion formation in the discharge, where F^- is the dominant negative ion.

Figure 4 shows the radio frequency power dependence of the count rates of saturated polymeric anions ($C_nF_{2n+1}^-$) in a CF_4 plasma. The electron density increases with increasing power level,²² resulting in an increased chemical activity of the plasma. This leads to enhanced dissociation and polymerization, which is reflected by an increase of polymeric anion signals with power. In Fig. 4(a) the total electron energy integrated count rates are displayed, so count rates of heavy ions increase faster with power than the CF_3^- and F^- signals. The increase of the latter signals is due to resonances, emerging at low electron energies. The signals resulting from dis-

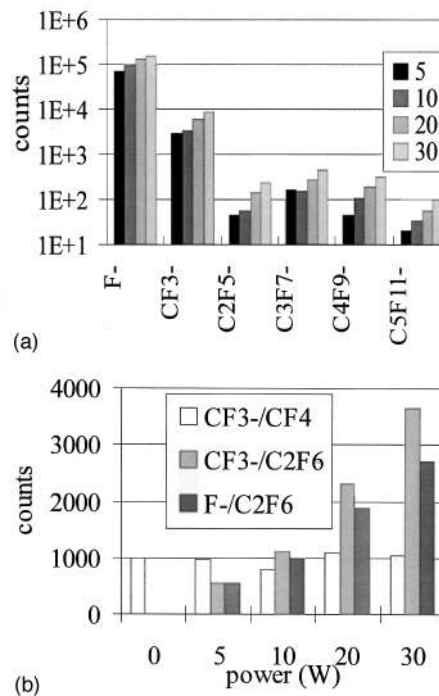


Fig. 4. (a) EAMS count rates of some selected polymers, formed in a CF_4 plasma at 30 mTorr pressure and 4 sccm flow rate for 5, 10, 20, and 30 W radio frequency power inputs. (b) The count rate of CF_3^- formed by dissociative attachment to CF_4 in gas (0 W) and plasma, and CF_3^- and F^- formed by dissociative attachment to plasma produced C_2F_6 as a function of power.

sociative attachment to CF_4 stay roughly constant, as there is no significant depletion of the parent gas under these conditions. This can be seen in Fig. 4(b), where the major low-energy resonances in the CF_3^- and F^- signals, attributed to C_2F_6 , and the CF_4 resonance are shown separately. Another contribution to the F^- count rate is dissociative attachment to F_2 at 0–1 eV. The latter is readily formed in the fluorine-rich CF_4 discharge and can be easily monitored by EAMS.

The polymerization reactions in low pressure plasmas are relatively slow. In a CF_4 plasma, the saturated polymeric products are removed from the discharge region by the gas flow rather than transformed into even larger species or destroyed at the surface. This is visualized in Fig. 5, where the gas flow dependence of some polymer signals is shown for a 20 W, 30 mTorr CF_4 plasma. The polymer density decreases with increasing gas flow, indicating that flow is the major destruction process for these species. Note that in industrial reactors the residence times at the applied high flow rates are shorter, but also the power densities are substantially higher. Thus efficient gas phase polymer formation is expected to occur during industrial surface processing.

In order to compare the neutral chemistry with the ion chemistry, we have collected the positive ions, arriving at the QMS head. This is representative for the ion flux, reaching the grounded electrode. The measured $C_nF_{2n-k}^+$ ion count rates in a 30 mTorr, 30 W, and 4 sccm CF_4 plasma are shown in Fig. 6. These results should be compared with the EAMS data shown in Fig. 3. The most striking difference is the

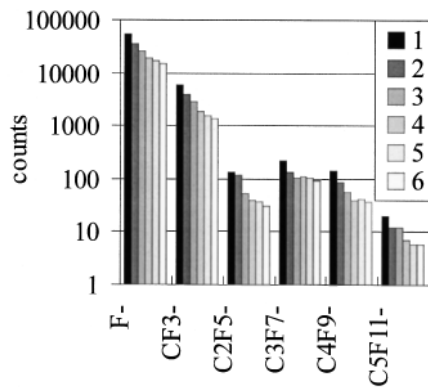


FIG. 5. EAMS count rates of some selected polymers, formed in a CF_4 plasma at 30 mTorr pressure and 20 W radio frequency power input for a gas flow rate from 1 to 6 sccm.

large amount of unsaturated positive ions. The dominant negative ions, observed by EAMS are saturated species like CF_3^- , C_2F_5^- , and C_3F_7^- , whereas in the positive ion mass spectrum small ions like CF_2^+ and CF^+ are abundant. Moreover, larger ions with a high k value, like C_3F_3^+ are readily observed. Possibly, these ions are created in a dissociative ionization process or fluorine is stripped from saturated ions as they collide in the sheath region. Another difference is the much faster, monotonous decrease of the ion count rate with increasing number of carbon atoms. Even though the positive ion data is collected at a higher power level than the EAMS data (Fig. 3), conditions in which polymerization is more efficient (see Fig. 4), large positive ions ($n > 5$) are not present in the plasma. Presumably, this is also due to fragmentation during the ionization step and dissociative collisions with neutrals in the sheath region. Note that ion fragmentation due to collisions will be more efficient in the sheath at the powered electrode, due to a higher sheath voltage. Thus, the positive ions, arriving at the powered electrode are expected to be smaller. Polymeric ions and neutrals have been investigated by Howling *et al.*²³ in a SiH_4 deposition plasma and similar observations have been made. These authors have performed an extensive study of plasma chemistry and dust particle formation, by means of mass spectrometry of positive ions and neutrals. Large negative ions

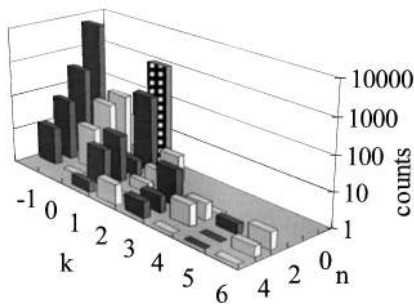


FIG. 6. Polymeric positive ions formed in a CF_4 plasma at 30 mTorr pressure, 30 W radio frequency power, and 4 sccm gas flow rate. The ions are arranged in $\text{C}_n\text{F}_{2n-k}^+$ series. The fluorine ion F^+ is cross hatched at $n=0$, $k=1$.

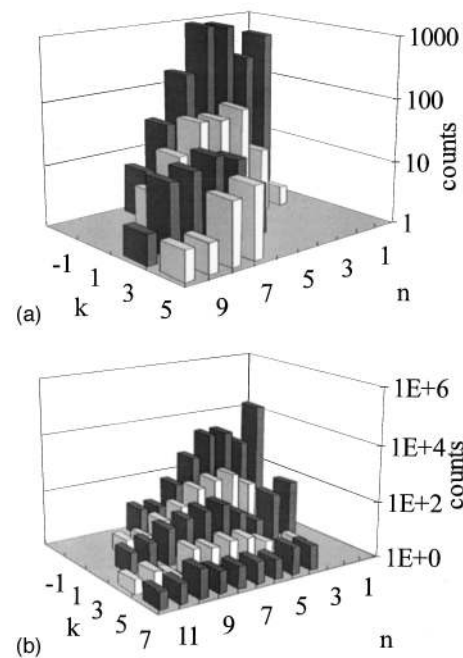


FIG. 7. Polymer formation, studied by EAMS in a C_2F_6 plasma at 20 mTorr pressure, 2 sccm flow rate, and (a) 7 W and (b) 20 W radio frequency power. The polymers are arranged in $\text{C}_n\text{F}_{2n-k}$ series. The series with an even k number have very low count rates, so they are not displayed here.

and negatively charged dust particles have been detected in this radio frequency silane plasma, while no large positive ions nor neutrals have been visualized. The lack of heavy neutrals may be due to the detection method by electron impact ionization mass spectrometry, in which polymeric molecules easily fragmentize.

C. The C_2F_6 and C_4F_8 plasmas

Figure 7 shows the EAMS data in a C_2F_6 plasma at radio frequency power levels of 7 and 20 W, respectively. As in a CF_4 plasma (Fig. 3), the species belonging to the series $\text{C}_n\text{F}_{2n+1}^-$ are most abundant for low n values. In the low power case [Fig. 7(a)] C_3F_7^- and C_4F_9^- have higher count rates than CF_3^- . This indicates that the first polymerization step $\text{C}_2\text{F}_5 + \text{C}_2\text{F}_5 \rightarrow \text{C}_4\text{F}_x + \dots$ is quite efficient. Furthermore, it can be easily seen that the degree of saturation with fluorine is lower than in the CF_4 plasma, especially in the high power case [Fig. 7(b)]. Larger saturated species ($k = -1$, $n > 7$) are not observed, while in comparison to CF_4 there are many more unsaturated polymers, also with high n values. This result is not an artifact of the EAMS method, but a fundamental difference between the CF_4 and C_2F_6 plasma chemistries. Saturated species are present in both plasmas, but in a C_2F_6 plasma, with a lower fluorine content, unsaturated neutrals are also expected to be well represented. In addition, the resonances of the unsaturated negative ions appear at low electron energies, which suggests limited fragmentation of parent species (see discussion above). It is thus plausible to assume, that the negative ions with high k values, detected in the C_2F_6 case, originate from unsaturated

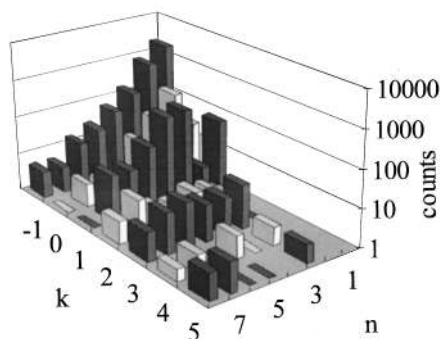


FIG. 8. Polymeric positive ions formed in a C_2F_6 plasma at 20 mTorr pressure, 4 sccm gas flow rate, and 7 W radio frequency power. The ions are arranged in $C_nF_{2n-k}^+$ series.

molecules/radicals. Note that in a C_2F_6 plasma large polymers (regardless of k) are more abundant than in CF_4 . This is again the consequence of a lower fluorine content of C_2F_6 , which enhances polymerization, as the number of termination reactions with fluorine atoms is lower. Abundant film deposition on the surface has been observed in a C_2F_6 plasma, which is an evidence of correlation between gas phase polymer formation and film deposition.

The count rates of positive ions arriving from the C_2F_6 plasma, collected by the QMS, are shown in Fig. 8. The extracted positive ions are slightly smaller than the neutrals, detected by EAMS in C_2F_6 (Fig. 7). This is similar to the CF_4 case (see Figs. 3 and 6). As in CF_4 , positive ions contain less fluorine than neutrals. Again the dominant positive ion is CF_3^+ , but also $C_2F_5^+$, $C_2F_4^+$, and $C_2F_3^+$, which are directly formed from the C_2F_6 parent gas, are abundant. Note that there is a clear preference to form ions with paired electrons ($C_nF_{2m+1}^+$), as these are more stable. For the negative ions, formed in the EAMS method, this effect is even more pronounced, as ions with an unpaired electron are not observed (see Figs. 3 and 7), with an exception of $k=0$ series in a CF_4 plasma. This agrees well with the negative ion formation reactions, reported by Spyrou *et al.*²⁴

Figures 9 and 10 show the neutral and positive ion data obtained in a C_4F_8 plasma. The ratio of F to C for the parent molecule is lower than in the case of C_2F_6 and CF_4 . This is reflected by an even lower fluorine content of the polymers

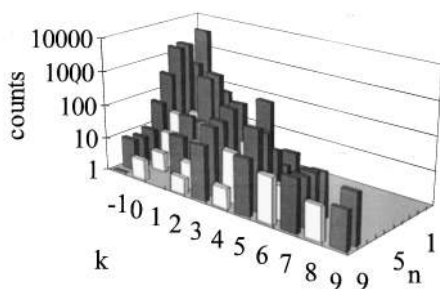


FIG. 9. Polymer formation, studied by EAMS in a C_4F_8 plasma at 15 mTorr pressure, 4 sccm flow rate, and 8 W radio frequency power. The polymers are arranged in C_nF_{2n-k} series.

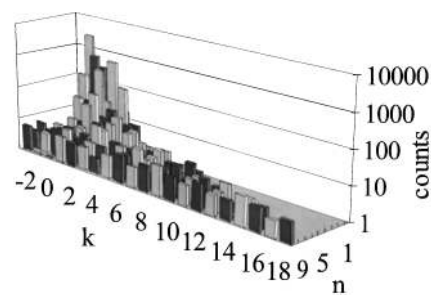


FIG. 10. Polymeric positive ions formed in a C_4F_8 plasma at 15 mTorr pressure, 4 sccm gas flow rate, and 8 W radio frequency power. The ions are arranged in $C_nF_{2n-k}^+$ series.

than in the previously discussed plasmas. It is especially clear for the positive ions, reaching the surface (Fig. 10). Positive ion chemistry in this plasma is very complicated and the presence of cations of fully saturated fluorocarbons ($C_nF_{2n+2}^+$, $k=-2$) is striking. As the parent gas is already a large molecule, significantly larger polymers can be formed in this system. Unfortunately the mass limit of our system is 510 amu, so we cannot detect species with more than eight or nine carbon atoms. The presence of even larger structures can nevertheless be expected, based on the comparison of the count rates in a C_4F_8 plasma with those observed in C_2F_6 and CF_4 . In the latter cases a fast decrease of the count rates of neutrals and ions with increasing number of carbon atoms is observed, while in a C_4F_8 plasma the count rate distribution is flat and high polymeric species still yield considerable signals. Note that as the transmission of the QMS system significantly decreases with increasing ion mass, the actual densities of the high polymers are even higher than indicated here. In C_4F_8 formation of polymer layers on the surface is more efficient than in the chemistries discussed above, again supporting the proposed film deposition mechanism by polymer sticking. Unlike CF_4 and C_2F_6 , in C_4F_8 also some polymers with an unpaired electron (even k) are detected, though their count rates are much lower than those of the species with paired electrons. Nevertheless, this interesting feature can be a consequence of a high radical density in a C_4F_8 plasma. As the fluorine content in this plasma is low, neutral species with dangling bonds (C_nF_{2m+1}) are expected to be relatively abundant. These species are very reactive and they readily form negative ions. Even though $C_nF_{2m}^-$ are not the most favorable negative ions, attachment to radicals can result in formation of detectable amounts of these species.

Finally, we want to demonstrate the advantage of EAMS over the traditional detection method by electron impact ionization of neutrals. Figure 11 shows the data collected using electrons of 50 eV to transform the neutral polymers formed in a C_4F_8 plasma into positive ions. This figure should be compared with Fig. 9, which shows the neutral species extracted from the discharge under identical conditions and detected by means of EAMS. It is obvious that in ionization mass spectrometry the high energy electrons cause fragmentation of the polymers and consequently the maximal detectable size is only about half of that for EAMS. Moreover,

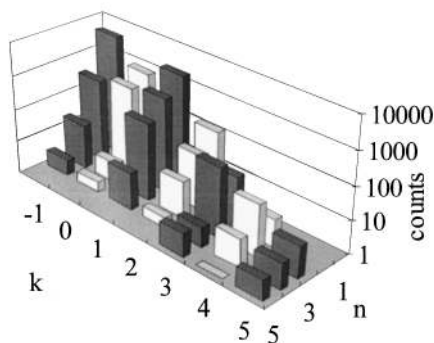


FIG. 11. Polymer formation in a C_4F_8 plasma at 15 mTorr pressure, 4 sccm flow rate, and 8 W radio frequency power, studied by ionization mass spectrometry. The polymers are arranged in C_nF_{2n-k} series. These data are obtained using 50 eV electrons to ionize the neutral polymeric species and detect the resulting positive ions, which in contrast to the data obtained by EAMS under the same conditions (Fig. 9) results in a much poorer detection of polymeric species.

large amounts of fluorine are stripped during ionization and consequently all possible combinations of C and F are present in the mass spectrum. As a result, there is virtually no structure left in these data and the only information one can obtain is that there are some polymers present in the plasma, but no conclusions can be drawn about their size distribution and degree of saturation with fluorine. Anyway, the high polymers, which are most interesting from the point of view of polymer deposition or dust particle formation, remain hidden. Similar data sets to the one presented in Fig. 11 have been also collected in CF_4 and C_2F_6 plasmas. However, in contrast to the EAMS method, no significant differences in the polymer chemistry of the considered fluorocarbon gases have been found using ionization mass spectrometry. Applying lower energy electrons to perform the ionization might be a way to limit the undesired fragmentation. This is clear from the comparison of the data from Fig. 11 with the positive ion count rates from the plasma (Fig. 10). Positive ions are produced in the plasma, where the electron temperature is a few eV. Ionization is performed by the electrons from the tail of the energy distribution function, with energies just above the threshold of the ionization. Consequently, there is significantly less fragmentation and large positive ions are present in the plasma. However, for the detection of neutrals by ionization mass spectrometry lowering the electron energy is not a practical solution, as the ionization cross sections at the threshold are extremely low.

IV. CONCLUDING REMARKS

We have shown that fluorocarbon gases easily polymerize in low pressure discharges. Both polymeric neutrals and positive ions have been detected; heavy neutrals appear to be relatively abundant. The study has been performed by means of a new technique: electron attachment mass spectrometry, which is proven to be extremely efficient for the detection of electronegative polymers.

We have found that the polymerization proceeds more rapidly in fluorine-poor conditions. It has been established

before that the presence of silicon in the plasma drastically lowers the fluorine content, mainly due to efficient formation of the etching product SiF_4 .²² Therefore, it is expected that polymer formation will be especially efficient in an etching environment, in which a silicon substrate is inserted. Moreover, the polymers formed in a fluorine-poor environment are less saturated and they may contain dangling bonds. This makes the gas phase formed polymers especially reactive, which will enhance the deposition of fluorocarbon films on areas, which are not exposed to a heavy ion bombardment, such as reactor walls, grounded electrodes, and side walls of trenches on a processed wafer.

For the formation channels of the observed polymers several processes can be considered. In all cases small radicals play a crucial role, either as building blocks or in terminating reactions. This means that apart from the question of the radical formation process at the surface, discussed in the introduction, the density of radicals and polymers are anyway strongly linked. As gas phase polymerization under plasma conditions has many important implications for surface processing, it cannot be neglected in a study of plasma chemistry of processing discharges. More research effort should be put in clarifying the polymerization mechanisms and understanding the influence of polymers on the plasma and surface.

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- ¹J. W. Coburn, *J. Vac. Sci. Technol. A* **12**, 617 (1994).
- ²G. M. W. Kroesen and F. J. de Hoog, *Appl. Phys. A: Solids Surf.* **56**, 479 (1993).
- ³*Plasma Diagnostics*, edited by D. Auciello and D. L. Flamm (Academic, New York, 1989).
- ⁴M. J. Kushner, W. Z. Collison, M. J. Grapperhaus, J. P. Holland, and M. S. Barney, *J. Appl. Phys.* **80**, 1337 (1996).
- ⁵D. Edelson and D. L. Flamm, *J. Appl. Phys.* **56**, 1522 (1984).
- ⁶Various contributions in *Plasma Sources Sci. Technol.* **3**, (1994), and *J. Vac. Sci. Technol. A* **14**, (1996).
- ⁷G. S. Oehrlein, J. F. Rembetski, and E. H. Payne, *J. Vac. Sci. Technol. B* **8**, 1199 (1990).
- ⁸V. A. Yunkin, I. W. Rangelow, J. A. Schaefer, D. Fischer, E. Voges, and S. Sloboshanin, *Microelectron. Eng.* **23**, 361 (1994).
- ⁹K. Kurihara and M. Sekine, *Plasma Sources Sci. Technol.* **5**, 121 (1996).
- ¹⁰M. Haverlag, W. W. Stoffels, E. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **14**, 384 (1996).
- ¹¹M. Haverlag, E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **12**, 3102 (1994).
- ¹²M. Kitamura, H. Akiya, and T. Urisu, *J. Vac. Sci. Technol. B* **7**, 14 (1989).
- ¹³J. P. Booth, G. Hancock, N. D. Perry, and M. J. Toogood, *J. Appl. Phys.* **66**, 5251 (1989); N. St. Braithwaite, J. P. Booth, and G. Cunge, *Plasma Sources Sci. Technol.* **5**, 677 (1996).
- ¹⁴R. J. M. M. Snijders, Ph.D. thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1993.
- ¹⁵D. C. Gray, I. Tepermeister, and H. H. Sawin, *Proceedings of the Second International Symposium on Reactive Plasmas and 11th Symposium on Plasma Processing*, edited by T. Goto, Yokohama, Japan, published by Organizing Committee of ICRP-2/SPP-11, 1994, p. 751.

- ¹⁶J. P. Booth, G. Cunge, P. Chabert, F. Neuilly, J. Derouard, and N. Sadeghi, Proceedings of the Third International Conference on Reactive Plasmas and 14th Symposium on Plasma Processing, edited by K. Tachibana and Y. Watanabe, Nara, Japan published by Organizing Committee of IRCP-3/SPP-14, 1997, p. 75.
- ¹⁷E. Stoffels, W. W. Stoffels, K. Tachibana, *Rev. Sci. Instrum.* (in press).
- ¹⁸W. W. Stoffels, E. Stoffels, and K. Tachibana, *Jpn. J. Appl. Phys., Part 1* **36**, 4638 (1997).
- ¹⁹S. R. Hunter and L. G. Christophorou, *J. Chem. Phys.* **80**, 6150 (1984).
- ²⁰E. Stoffels, W. W. Stoffels, D. Vender, M. Haverlag, G. M. W. Kroesen, and F. J. de Hoog, *Contrib. Plasma Phys.* **35**, 331 (1995).
- ²¹L. J. Overzet, Y. Lin, and L. Lou, *J. Appl. Phys.* **72**, 5579 (1992).
- ²²E. Stoffels and W. W. Stoffels, Ph.D. thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1994.
- ²³A. A. Howling, L. Sansonnens, J.-L. Dorier, and Ch. Hollenstein, *J. Appl. Phys.* **75**, 1340 (1994).
- ²⁴S. M. Spyrou, I. Sauers, and L. G. Christophorou, *J. Chem. Phys.* **78**, 7200 (1983).