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Decomposition of gaseous dielectrics (CF_4, SF_6) by a non-equilibrium plasma. Mechanisms, kinetics, mass spectrometric studies and interactions with polymeric targets

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Fluorinated monomers such as sulfur hexafluoride SF_6 and carbon tetrafluoride CF_4 are widely used, at low gas pressures in plasma etching of silicon and insulating substates for microelectronic applications, and at high pressures in high voltage insulation systems. This paper reports on the decomposition of SF_6, CF_4 and their mixtures by a non-equilibrium plasma and their interaction with polyethylene films. The presence of oxygen and water vapor as trace contaminants and their role in the decomposition mechanisms were pointed out both by mass spectrometry and optical emission spectroscopy. The comparison of the results obtained by kinetic calculations and those measured by surface and plasma diagnostic techniques brought evidence on the participation of the fluorine atoms in the heterogeneous mechanisms. Finally, the effect of the addition of a fluorine containing molecule such as CF_4 to SF_6 discharges on the energetic aspect of the discharge, the decomposition mechanisms and the fluorination processes will be discussed. The excitation efficiency of the electrons was correlated to the fluorine concentration as measured by actinometry and to surface fluorination as shown by the XPS analysis.

I. INTRODUCTION

Over the past twenty years, the use of compressed gaseous SF_6 as an insulating medium in HV power systems has increased significantly due to its high dielectric strength, chemical inertness and extremely low toxicity. The fact that SF_6 has a very good dielectric strength is due to its relatively large cross section for attaching low-energy electrons [1-4]. This leads to the removal of the electrons from the gas under electrical stress by formation of negative ions and constitute an important process in inhibiting the initiation and the growth of the electrical discharges. Total electron scattering cross sections, dissociative and nondissociative electron attachment cross sections have been measured by Christophorou et al [5] and Van Brunt et al [6] for SF_6 as well as for the by-products, such as SOF_2, SO_2F_2, SF_4 and SO_2, that can be formed in the electrical discharge of SF_6 in the presence of contaminants such as water vapor and oxygen [7-9].

The role of these contaminants on the decomposition mechanisms of SF_6 to form various reactive and stable by-products has been extensively studied by Van Brunt et al [10,11]. A theoretical chemical kinetic model has been proposed in this case [11]. It included reactions of SF_6 dissociation products among themselves and with O_2 or H_2O leading to the formation of products such as S_2F_{10}, SOF_4, HF, SO_2F_2, and SOF_2. These fundamental decomposition and oxidation processes have been investigated in glow and corona discharges at atmospheric pressure as a function of the gas temperature and / or the electric field to gas density ratio (E/N) [11,12]. As a result of these fundamental reactions taking place in the presence of such contaminants (H_2O and O_2), the electrical breakdown voltage measured by Berger et al in HV power systems and in the presence of insulators such as PP and PET, was reduced [13]. The presence of impurities modified the discharge mode in corona discharges. The role of water was to enforce the decrease of the breakdown voltage at high pressures. Negative ions such as $OH^-(H_2O)_n$ have been identified by mass spectrometry [13] and accounted with other ions such as $O_2^-(H_2O)_n$, $H_2O^-(H_2O)_n$ for the discharge mode modification. The effect of coronas on insulating surfaces such as epoxy resins leads to the formation of a surface water layer both by transport phenomena or polymer etching and accelerates polymer ageing [14,15].

A large interest has also been shown concerning low pressure discharges in either pure SF_6, pure CF_4, or mixed with other gases, in particular oxygen, for etching different materials in VLSI circuit fabrication [16-21]. The plasma chemistry of SF_6- O_2 and CF_4- O_2 mixtures has been investigated extensively by different research groups. A model, which considers only gas-phase neutral reactions has been developed by Ryan and Plumb for both cases to describe the chemistry which occurs [22-24]. A large number of possible reactions has been proposed; kinetic constants were calculated for reactions giving products such as SF_4, SOF_4, SOF_2 and SO_2F_2 in the case of SF_6/O_2 mixtures [22] and CO, COF_2, CO_2 in those of CF_4/O_2.[23] These reactions were correlated with the mass spectrometric results found by Turban et al who also proposed several reaction schemes on the basis of their results [20]. In this case the analysis of gaseous effluents by mass spectrometry indicated that both atomic fluorine and atomic oxygen are the main etchants of polymers such as Kapton H polyimide [16]. The relative concentration profiles of these species have been determined by d'Agostino et al [25,26]. Argon was utilized as an actinometer for both fluorine and oxygen atoms [27]. The analysis of the treated surfaces by complementary analytical techniques showed that the physical and chemical properties of the surface are modified [28-30]. Fluorinated groups were identified in CF_4 and SF_6 discharges changing thereby the surface wettability [31,32]. Sulfur residues were observed on treated photoresists during the reactive ion etching of consumable cathodes (W, Si) in SF_6 plasmas, as well as on resins in microlithography [33,34]. For this reason, the question about the possible participation of S and S_2 to the etching action has been brought up .

II. EXPERIMENTAL

Figure 1 shows the drawing of the low-pressure plasma reactor used for the surface treatment of polyethylene films with a nonsymmetrical-configuration of electrodes. The power is coupled to the reactor from an rf generator (13.56 MHz) via a suitable impedance matching network. Full details on the operating conditions are given elsewhere [32].

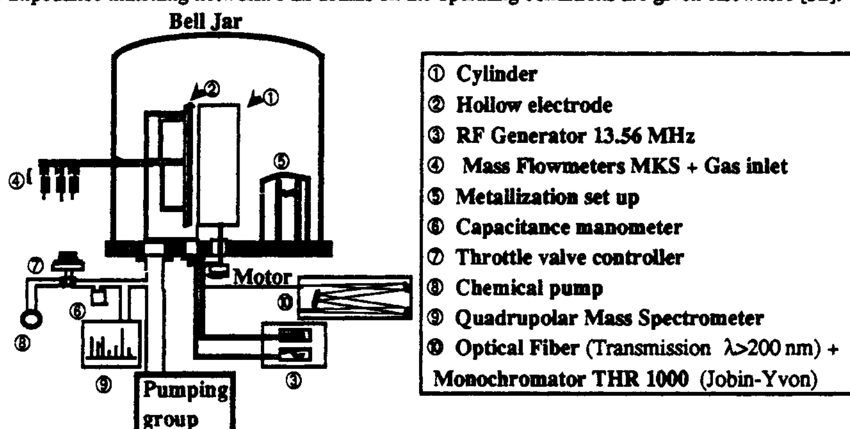


Figure 1. Schematic drawing of the bell jar reactor with the non-symmetrical configuration of electrodes used for the surface treatment of polyethylene films by a low-pressure plasma.

Discharge charcterization by Optical emission spectroscopy: Plasma emission was collected by an optical fiber inserted into the plasma. The emission signal was selected by a Jobin-Yvon spectrometer having a 1 m focal length and a 3600 grooves/mm grating for the UV range and by a Jobin Yvon HRS 2 spectrometer having a 0.6 m focal length and a 1200 grooves/mm grating for the wavelength ranging between 450 and 850 nm.

Analysis of the neutral effluents by mass spectrometry. Effluents were pumped through a capillary tube from the interelectrode space up to a leak valve installed on line with a Balzers QMG 420 quadrupole mass spectrometer. Neutral species were ionized by using the electron impact ionizer of the mass spectrometer set at 70 eV for comparison with published fragmentation patterns. If a peak results from several compounds, mass interference corrections were made, based on these patterns. Transmission coefficients calculations were not included in the measurements, however, in our case, for a given gas mixture the ratio of the parent peaks was about the same as that of the corresponding molecules in the gas feed. The pressure in the ionization chamber was held at 3. 10^{-4} Pa by varying the leak rate through the sampling valve.

III. RESULTS AND DISCUSSION

III.1. Interaction of pure SF_6 discharge with polyethylene films

III.1.1. Discharge characterization by optical emission spectroscopy

The emission spectra resulting from the interaction of the SF_6 plasma with polyethylene are shown in figure 2 for two different treatment times (t<10 min and t > 10 min) after the plasma ignition. These spectra correspond to a shift of the discharge color from pink (①) to blue (②) due to the emission of the third positive system of B $^1\Sigma \rightarrow$ A $^1\Pi$ transition of CO bands. This is an indication of the polymer surface degradation since CO is not a by-product of the input gases, and consequently results only from the surface etching of the PE film. The H_α and H_β lines of the Balmer serie were also observed and is witness to the polymer surface degradation.

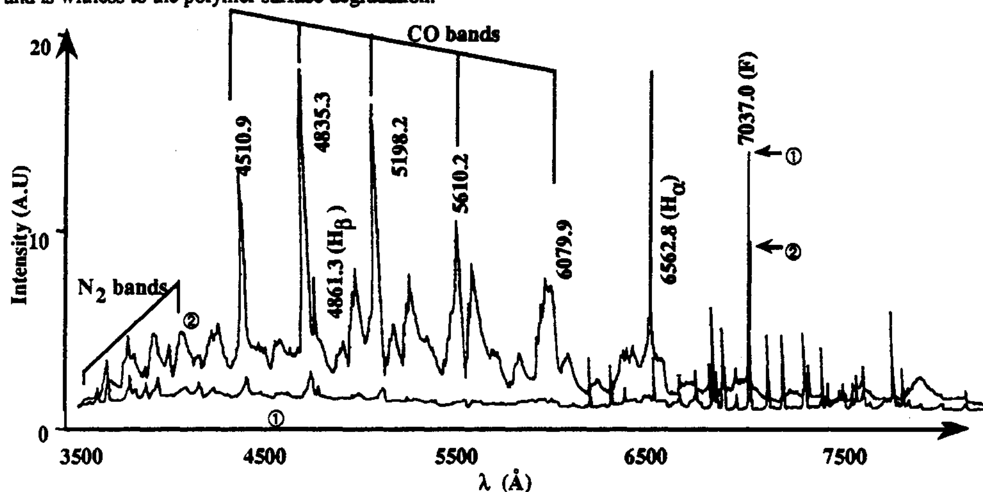


Figure 2. Emission spectra in the range of 3500 - 8000 Å of a pure SF_6 discharge with O_2, N_2 and H_2O as contaminants. ① : 0 to 10 minutes after plasma ignition. ② : t > 10 minutes after the plasma ignition. (P= 10^2 Pa, Q = 100 sccm, P_w = 30 W, f = 13.56 MHz).

The intensity of the fluorine line observed at 7037 Å shows that it decreases with the treatment duration. This can be related to its consumption both through homogeneous and heterogeneous mechanisms as it will be shown in next sections.
No emission bands pertaining to CH, CS or S_2 were observed as it has been shown by Gilbert et al [35] who have detected these bands on SF_6 treated polymers such as teflon and epoxy resin. However, in the case of PE only CH and CS bands were detected. The latter was due to the presence of CS_2 in significant quantity among the degradation products whereas the absence of S_2 was suggested to be due to its quenching by species other than hydrogen present in the discharge. S_2 has also been identified by Greenberg et al [36] and by Sadeghi et al [37]. In the latter case, the emission of S_2 bands was enhanced in the presence of etched material due to the consumption of the fluorine atoms by the consumable substrate. In order to obtain CS_2 or S_2 molecules in SF_6 discharges, an important process for the decomposition of this gas is the stripping of all the fluorine atoms. The lower value of the injected power in our case as compared to that used by Gilbert et al and Sadeghi et al (100 W) can explain why the above sulfur containing molecules have not been detected.

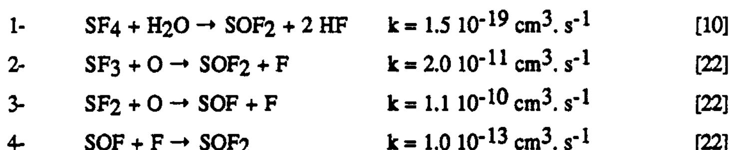
Some of the bands observed correspond to the emission of the nitrogen and were used to characterize the energetic aspect of the discharge. The ratio of first negative system of N_2^+ at 391.4 nm and that of the second positive system of N_2 at 394.3 nm has been used to estimate the mean electron temperature of the plasma [38]. Under these operating conditions Te was estimated to be around to 5 eV.

III.1.2. Analysis of the stable effluents of a pure SF_6 discharge

Figure 3 shows the evolution of the etch products as a function of the treatment time before and after the plasma ignition. It can be clearly seen that the ion mass intensity at m/e = 28 attributed to CO increases significantly 10 minutes after

the plasma ignition, which is in agreement with the optical emission spectroscopy results. Note that residual nitrogen can entirely account for the peak intensity at m/e = 28 before the plasma is put on. One can also note the increase after the plasma ignition of the ion mass signal at m/e = 69 assigned to CF_4 molecule. This has also been shown by Turban et al [16] i.e: CF_4 was the main gaseous product resulting from etching of polyimide with pure SF_6 or with SF_6/O_2 mixtures containing up to 20% oxygen. Furthermore, the ion mass signal at m/e = 18 corresponding to H_2O also increases. This can be due either to water desorption from the polymer and the walls of the apparatus, or to the polymer etching. Comparison with experiments that we performed on polytetrafluoroethylene, a non-hydrogen containing substrate, showed that both desorption and oxidation phenomena are responsible for the water peak increase.

The observation of the ion mass signal at m/e = 67 assigned to SOF_2 shows that its intensity increases rapidly after the plasma ignition. A reaction scheme involving atomic oxygen and water vapor has been proposed by differents authors in order to explain the SOF_2 formation.



1- $SF_4 + H_2O \rightarrow SOF_2 + 2\,HF$ $k = 1.5\ 10^{-19}\ cm^3.\ s^{-1}$ [10]

2- $SF_3 + O \rightarrow SOF_2 + F$ $k = 2.0\ 10^{-11}\ cm^3.\ s^{-1}$ [22]

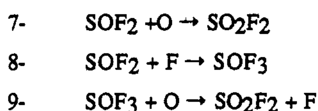
3- $SF_2 + O \rightarrow SOF + F$ $k = 1.1\ 10^{-10}\ cm^3.\ s^{-1}$ [22]

4- $SOF + F \rightarrow SOF_2$ $k = 1.0\ 10^{-13}\ cm^3.\ s^{-1}$ [22]

SOF_4 at m/e = 105 has been observed but to a less extent than SOF_2 whileas SO_2F_2 at m/e = 83 was not detected. Siddagangappa and Van Brunt have suggested that, under conditions where SF_6 is used as an insulator, SO_2F_2 is formed via

5- $SF_2 + O_2 \rightarrow SO_2F_2$ $k < 5.10^{-16}\ cm^3.\ s^{-1}$ [10] and 6- $SF_3 + O_2 \rightarrow SO_2F_2 + F$ [10]

whereas d'Agostino and Flamm [17] proposed the following reactions :



7- $SOF_2 + O \rightarrow SO_2F_2$

8- $SOF_2 + F \rightarrow SOF_3$

9- $SOF_3 + O \rightarrow SO_2F_2 + F$

are the major sources of SO_2F_2 formation in low-pressure SF_6/O_2 plasmas. The absence of SO_2F_2 in our case can be explained by the fact that molecular oxygen is only present as traces (reactions 5 and 6 can thus be excluded) and is completely dissociated to atomic oxygen (as measured by mass spectrometry). However, the concentration of the latter remains very low to let reactions 7, 8 and 9 occur assuming SOF_2 as a precursor for SO_2F_2.

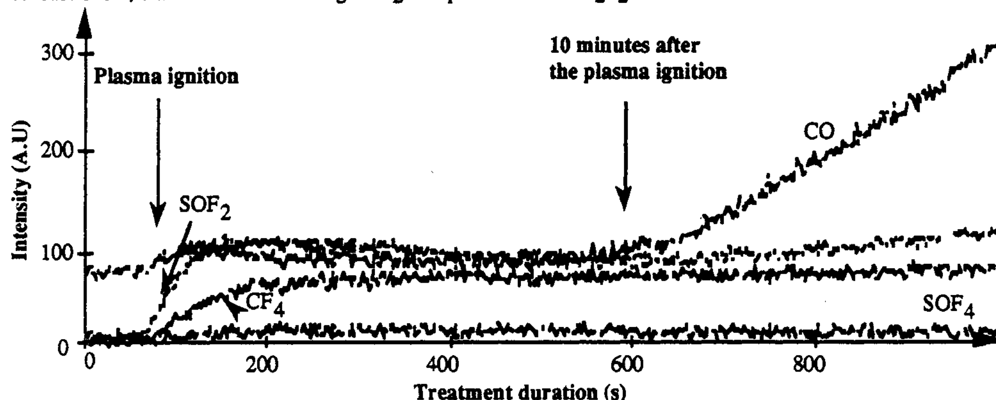


Figure 3. Evolution of the etch products resulting from the surface degradation of polyethylene treated by pure SF_6 discharge ($P = 10^2$ Pa, P_w = 30 W, Q = 100 sccm, f = 13.56 MHz).

III.1.3. Chemical characterization of the surface by XPS

X-ray photoelectron spectroscopy measurements (XPS) were performed both on pure SF_6 treated films and untreated polymers. Full details about the operating conditions have been given elsewhere [32]. The results confirmed the above observations i.e for short treatment times (t< 10 min) highly fluorinated groups (CF_2 and CF_3) were detected at the surface.

The mass of the polymer increased after the treatment due to the substitution of H atoms by fluorine. On the contrary, for treatment times exceeding 10 minutes, although fluorine was observed at the surface, the polymer mass decreased confirming thereby the important etching of the fluorinated layer.

III.2. Analysis of the SF_6/O_2 mixtures

SF_6/O_2 plasmas are extensively used in the semiconductor industry to etch a wide variety of materials. Stable effluents were identified by performing mass spectrometric analysis of these mixtures. Results were then compared with those calculated by a kinetic model which account only for reactions occuring in the gas phase in order to obtain a better understanding of the processes that occur both in the gas phase and in the gas-solid interface.

III.2.1. Mass spectrometric analysis of the stable effluents

Figures 4 to 7 show the variation of the relative concentration of various gaseous products as a function of the gas mixture in O_2-SF_6 plasmas. These curves clearly demonstrate that for low percentages of O_2 (input O_2 < 10%) SOF_2 (figure 5) and CF_4 (figure 7) are the most dominant gaseous products whereas for higher contents in O_2, the etching of PE gives rise to effluents such as CO, CO_2 SO_2, SO_2F_2, SOF_4 and HF with a greater contribution of the latter (figure 4) due to the reaction of atomic fluorine with water vapor i.e : $F + H_2O \rightarrow HF + OH$ $k = 1.1.\ 10^{-11}\ cm^3.s^{-1}$ [39] and with hydrogen resulting from the polymer degradation.

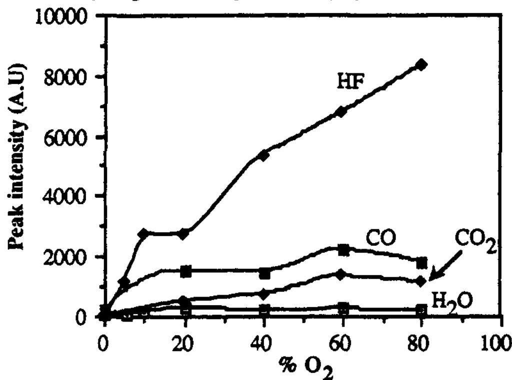


Figure 4. Variation of CO, CO_2, HF and H_2O peak intensities measured by mass spectrometry as a function of the gas composition. (P= 10^2 Pa, Q= 40 sccm; P_w=10 W)

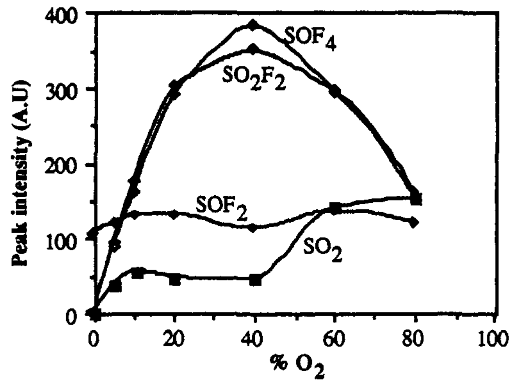


Figure 5. Variation of SOF_4, SO_2F_2, SO_2, and SOF_2 peak intensities measured by mass spectrometry as a function of the gas composition. (P= 10^2 Pa, Q= 40 sccm; P_w=10 W)

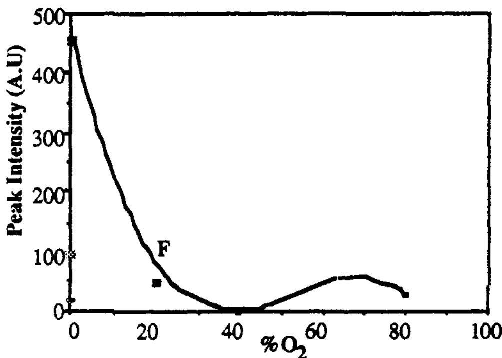


Figure 6. Variation of F peak intensity measured by mass spectrometry as a function of the gas composition. (P= 10^2 Pa, Q= 40 sccm; P_w=10 W)

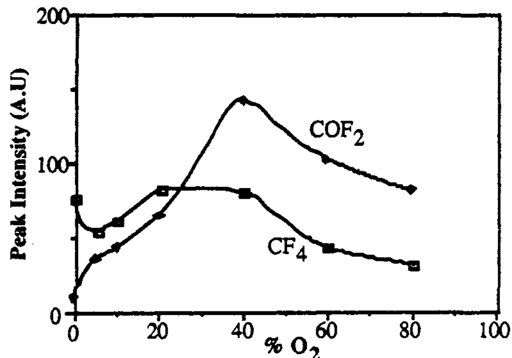


Figure 7. Variation of CF_4 and COF_2 peak intensities measured by mass spectrometry as a function of the gas composition. (P= 10^2 Pa, Q= 40 sccm; P_w=10 W)

As one can point out from figure 6, the fluorine concentration presents a minimum at 40% O_2 which corresponds to the maxima observed for SOF_4, SO_2F_2 as well as for products that result from the polymer surface degradation such as CF_4, and COF_2 (figures 5,7). The fluorine consumption increases the formation rate of all the secondary products which is a further indication of the F atoms participation both in homogeneous and heterogeneous mechanisms such as surface fluorination and etching. Different reactions involving atomic oxygen and fluorine [22] and leading to the formation of these products have been proposed. Reactions with H_2O and O_2 [11] can also contribute to the formation rate of species such as SO_2, SO_2F_2 and SOF_4.

III.2.2. Comparison of computer simulations results of SF_6/O_2 plasmas with experimental data.

The broad features of the stable products analysis in SF_6/O_2 plasmas are described by a kinetic model, developped in our laboratory [40]. It is based on an implicit calculation method and allows to take into account reactions with rate constants varying several orders of magnitude. In order to see to what extent the neutral chemistry alone is able to explain the products observed by mass spectrometry, only gas-phase reactions involving neutral species have been introduced in the reaction scheme assuming a constant temperature of 298 K and a pressure of 133.3 Pa. Reactions of electronically and vibrationally excited molecules have not been considered. The subset of reactions used by Ryan and Plumb [22] has been included as well as reactions involving the reactivity of water vapor [11,39] to simulate the presence of water as traces in the reactor.

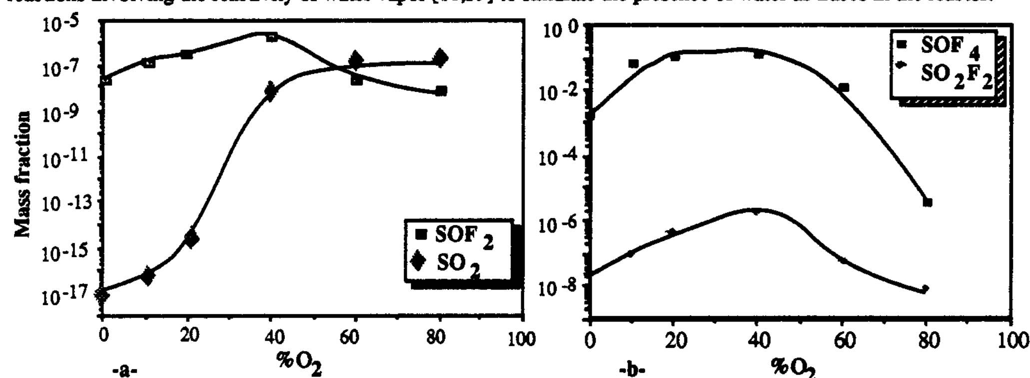


Figure 8. Computed mass fractions for a x% O2/ (99-x %) SF6/ 1 %H2O mixture. (P=133.3 Pa, T= 298 K).

It can be pointed out that the trends of the calculated (figures 8a, 8b) and the measured concentrations (figure 6) are similar for the oxyfluorinated species such as SOF_2, SOF_4 and SO_2F_2. On the contrary, the trend of the fluorine concentration exhibits a completely different behaviour as compared with that of the experimental data (figure 9).

However, the relative concentrations of the oxyfluorinated species are different i.e: the measured concentration of SO_2F_2 as compared to that of SOF_2 and SOF_4 is higher than that predicted by the model. As reported by Van Brunt et al, the formation of SO_2F_2 seems to require a reaction of SF_2 with molecular oxygen rather than water vapor. This could be explained by the acid-base properties of the above reactants. Indeed, excited singlet O_2 ($^1\Delta_g$) has a lifetime of 45 minutes and presents a vacancy in its configuration. This confers to it acidic properties according to Lewis and can account for its reaction with SF_2 which can consequently react only as a base.

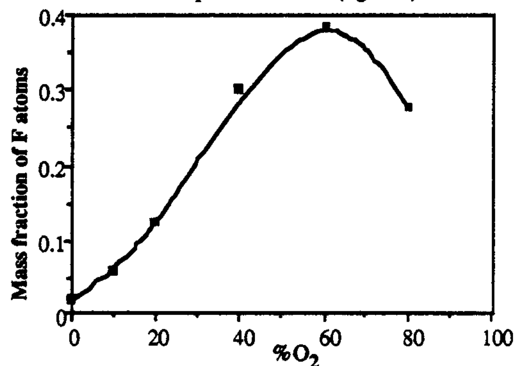


Figure 9. Variation of the calculated mass fraction of F atoms as a function of oxygen percentage in the gas feed.

As the reaction of SF_2 with O_2 ($^1\Delta_g$) has not been taken into account in the kinetic model, it could explain the discrepencies which exist between the relative concentrations measured and those calculated.

III.2.3. Surface characterization of treated PE by x-ray photoelectron spectroscopy

Figure 10 displays the evolution of the F1s/C1s ratio as a function of the treatment time as measured by XPS. One can clearly see that the F1s/C1s ratio increases with treatment time and remains constant (over the analyzed depth) after a few seconds. The C1s spectrum revealed various fluorine containing moities such as CF, CF_2 and CF_3 which proves the fluorination of the carbon network and confirms our previous assumption on the fluorine participation in the gas-polymer interactions. The intensity of the highly fluorinated groups increased with treatment time. Sulfur concentration did not exceed 2%. The molecular modelling of CF_2, SF_2, F and their interactions with a very simplified polymeric model that is propane has been undertaken in order to understand the above phenomena [42].

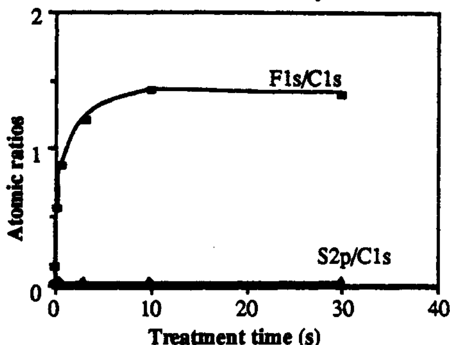


Figure 10. F1s/C1s ratio versus treatment time, as measured by XPS.

Ab-initio calculations were made based on the functional density method, and using the DMol software developed by Biosym Society. Preliminary results showed no interaction between CF_2 in its fundamental state with propane whileas orbital overlapping of F and SF_2 radicals with those of propane was more likely to occur when approaching these species to the polymeric model. Further studies are needed in order to know more about the reactivity of these species under a given electric field and their interaction with the polymer targets.

III.3. Analysis of the SF_6 / CF_4 plasmas and their interactions with polyethylene films.

The SF_6/ CF_4 mixtures have been studied because CF_4 is always present as traces in SF_6 (the requirements prescribed for the SF_6 use in electrical insulation material specifies that CF_4 should not exceed a mximum of 830 ppm) and is also a product resulting from the interaction of the low-pressure SF_6 discharges with polymer targets as shown by mass spectromery. Moreover, for electrical insulation material operating at very low temperatures, additives (up to 15 %) such as N_2 and CF_4 are added to SF_6. SF_6/CF_4 mixtures were analyzed by means of optical emission spectroscopy and mass spectrometry in order to have a better knowledge on the effect of these additives on the discharge characteristics.

III.3.1. Discharge characterization of SF_6/CF_4 mixtures by OES

Figure 11 reports on the evolution of the mean electron temperature T_e versus the SF_6 concentration in the gas feed. One can clearly see that the estimated mean electron temperature increases with the addition of small amounts of SF_6 to CF_4 and then remains constant for higher SF_6 contents.

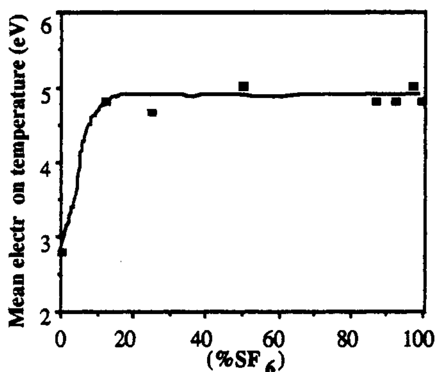


Figure 11 . Electron temperature versus %SF_6 in the gas mixture. ($P=10^2$ Pa, Q= 40 sccm, P_w =10 W, f= 13.56 MHz).

The broad continuum centered at 290 nm which has been assigned to the emission of CF_2^+ [41] has been observed in CF_4 containing mixtures. Its intensity was maximum when approximatively 10% of SF_6 was added to CF_4 plasmas. This is a further indication for the increase of the energetic aspect of the discharge because of the high energy threshold of CF_2^+ formation (16.4 eV). Furthermore argon was used as an actinometer for the tracing of fluorine atoms [25,26]. Its intensity is correlated to the electronic excitation efficiency of the plasma [27]. The decrease of Ar intensity can be a result of either the variation of the electron temperature or to that of

the electron density. Since the electron temperature remained constant for these mixtures, the decrease of the excitation efficiency can thus only be explained by the decrease of the electron density. This is well explained by the electron attachment and dissociative electron attachment processes which are known to be important in SF_6 discharges. The electron energy distribution is consequently shifted to higher mean electron energies.

Fluorine concentration as measured by actinometry is plotted versus the composition of the gas feed (figure 13). It exhibits two maxima one in CF_4 dominant mixtures, the other in SF_6 dominant mixtures. In fact, this figure can be divided in three domains. The first one corresponds to an SF_6 percentage less than 10% where an increase, then a maximum for the fluorine concentration is observed. The second domain is for SF_6 percentages varying from 20% to 80% where fluorine atoms concentration decreases. In both cases, the results are well correlated with the variation of the Ar line intensity observed by actinometry. The third domain is for SF_6 rich mixtures (> 80%) where once again another maximum is observed for F atoms concentration. Since the argon intensity line decreases and the mean electron temperature remains constant, the dissociation mechanism of SF_6 or CF_4 by direct electron impact cannot explain the second maximum observed. Therefore, the increase of [F], in this case, may be due to other reactions taking place in the discharge leading to the formation of fluorine atoms.

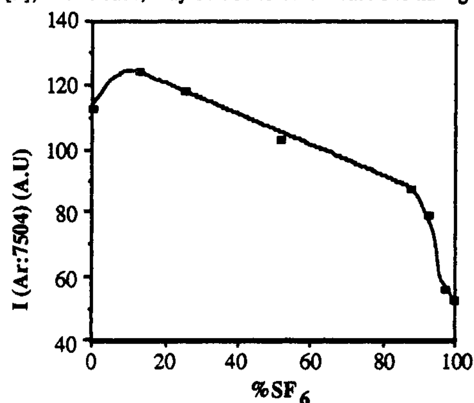


Figure 12. Variation of the argon line intensity at 750.4 nm as a function of the SF_6/CF_4 gas composition. ($P=10^2$ Pa, Q= 40 sccm, P_w =10 W, f= 13.56 MHz).

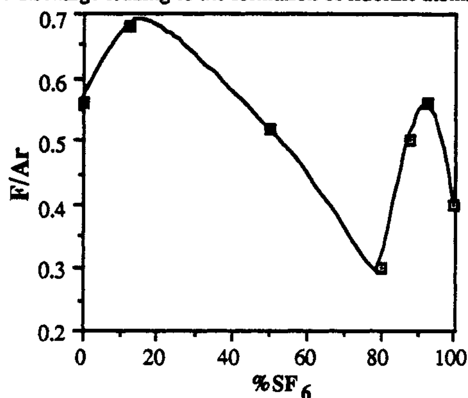


Figure 13. Variation of the [F] measured by actinometry as a function of the SF_6/CF_4 gas composition. ($P=10^2$ Pa, Q= 40 sccm, P_w =10 W, f= 13.56 MHz).

III.3.2. Mass spectrometric analysis of the SF_6/CF_4 mixtures

SF_6/CF_4 mixtures were analyzed by mass spectrometry over the complete range of the gas composition. Only dissociation rate of SF_6 calculated from the parent peak (SF_5^+ at m/e = 127) will be discussed (figure 14). It can be seen that the addition of small percentages of CF_4 to SF_6 (less than 20%) lead to a decrease of the SF_6 decomposition rate. This is in agreement with the lower fluorine concentration observed by actinometry. Indeed CF_4 can act as a source of fluorine atoms which can recombine with SFx radicals regenerating SF_6. Further experiments are needed in order to have a better understanding of the mechanisms which take place.

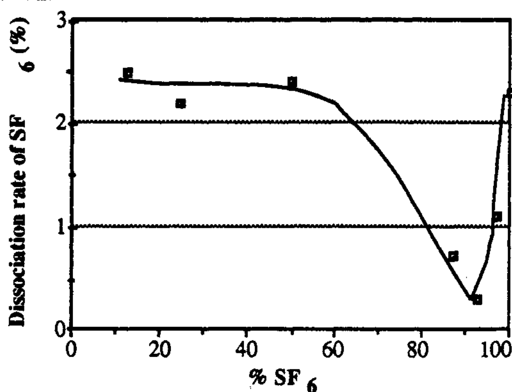


Figure 14. Variation of the dissociation rate of SF_6 in SF_6/CF_4 plasmas as a function of the gas composition.

III.3.3. Chemical characterization of the treated surface by XPS

The variation of the F1s/C1s ratio, measured by XPS, as a function of the % SF_6 is displayed in figure 15.

It can be clearly seen that this ratio follows the same trend as that obtained from actinometry (figure 13). This leads to the conclusion that a close correlation exists between the fluorine density measured in the plasma and the surface fluorination process. One should mention that actinometric measurements were carried out after the surface saturation with fluorine (within ≈10s) . Introducing low % of SF_6 in the CF_4 discharges seems to enhance the surface fluorination by increasing the mean electron temperature, the electron excitation efficiency and consequently the fluorine concentration in the discharge. On the contrary, for small amounts of CF_4 added to SF_6 the dissociation rate of the latter decreases as shown by mass spectrometry.

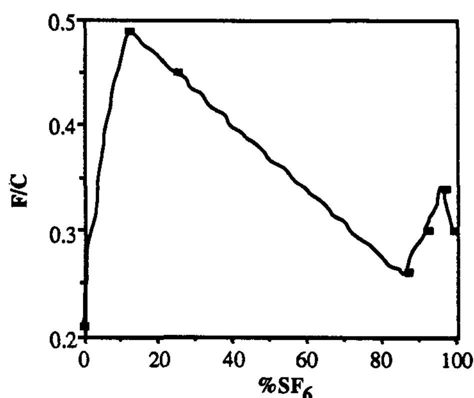


Figure 15. F1s/C1s atmic ratio measured by XPS over the complete range of the SF_6/CF_4 gas mixture composition.

IV. CONCLUSIONS

The decomposition mechanisms of SF_6 plasmas have been studied in the presence of contaminants such as oxygen and water vapor during the surface treatment of polyethylene films. Optical emission spectroscopy, actinometry and mass spectrometry techniques have been used to characterize the discharge. The results show that the surface degradation products depend tightly on the applied power i.e high powers lead to the formation of sulfur containing molecules such as CS and S_2 by the stripping of all the fluorine atoms from the SF_6 molecules [36], whileas at low powers the main species detected by OES were CO and H atoms. In SF_6/O_2 mixtures, the experimental data were compared with a kinetic model offering the possibility to consider different reactions with rate constants varying several orders of magnitude. The comparison brought evidence on the fluorine atoms participation both in homogeneous and heterogeneous reactions. The lower concentration of SO_2F_2 predicted by the model as compared with that measured by mass spectrometry can been explained by the role of excited O_2 ($^1\Delta_g$) molecules in terms of acid-base reactivity with respect to SF_2. The atomic percentage of the sulfur detected at the surface of the SF_6 treated polyethylene films was less than 2%. An attempt has been undertaken by molecular modelling in order to predict the interactions of SF_2, CF_2 and F radicals with respect to a simplified polymeric model that is propane.

The mixtures of SF_6 and another fluorine containing molecule such as CF_4 seem to offer new possibilities in the surface treatments. Depending on the relative percentage of SF_6 in CF_4, the fluorine concentration in the discharge measured by actinometry changes. for CF_4 rich mixtures (in our experimental conditions 10% SF_6 in CF_4) a high fluorine atomic concentration has been observed leading to a considerable fluorination of the polymeric surface. Whileas, by introducing a few percentages of CF_4 in SF_6 (up to 20% CF_4), i.e in SF_6 rich mixtures the dissociation rate of SF_6 can be decreased which offers an interesting application in high voltage insulating systems.

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