STUDY OF THE PLASMA-POLYETHYLENE INTERACTIONS IN THE CASE OF SF_6 AND SF_6 - CF_4 NON-EQUILIBRIUM DISCHARGES.

Y. Khairallah-Abdelnour[1], F. Arefi-Khonsari[1], J. Amouroux[1], D. Leonard[2], P. Bertrand[2].

1- Laboratoire de Génie des Procédés Plasmas. ENSCP - 11 rue P. & M. Curie - 75005 Paris - France. 2- U.P.C.P.M, Université Catholique de Louvain, Bâtiment Boltzmann, 1, Place Croix du Sud, 1348 Louvain-la-Neuve.

ABSTRACT : Low-density polyethylene (LDPE) films are treated in a low-pressure plasma reactor using SF_6 and SF_6-CF_4 mixtures. The characterization of the SF_6 plasma gave evidence both on the gas and the polymer surface degradation. Surface analysis pointed out the formation of C_xF_y structures as well as the incorporation of SF_x species at the surface. The intensities of the different species were dependent on the treatment time. SF_6-CF_4 mixtures revealed interesting features concerning the chemical stability of the gas mixture and the modifications of the polymer surface properties.

I- INTRODUCTION

The use of compressed gaseous SF_6 as an insulating medium in high voltage power systems has increased significantly over the past twenty years 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 [1-3]. The role of contaminants such as O_2 and H_2O on the decomposition mechanisms of SF_6 has been extensively studied and theoretical chemical kinetic models have been proposed [4,6]. 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 [7-10]. The analysis of the polymer treated surfaces by complementary analytical techniques showed that the physical and chemical properties of the surface are modified [11-13]. Fluorinated groups were identified in CF_4 and SF_6 discharges changing thereby the surface wettability [14,15]. 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 [16,17]. For this reason, the question about the participation of S and S_2 to the etching action has been brought up .

II- EXPERIMENTAL

The low-pressure plasma reactor used for the surface treatment of LDPE films has a nonsymmetrical configuration of electrodes [15]. The power is coupled to the reactor from an rf generator (13.56 MHz) via a suitable impedance matching network. The reactor chamber was pumped to a background pressure of 10^{-3} Pa and the gas flow monitored by MKS flowmeters. Plasma emission was collected by an optical fiber inserted into the plasma and the emission signal was selected by a Jobin-Yvon spectrometer. 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. Full details on the operating conditions are given elsewhere [15].

III- RESULTS AND DISCUSSION

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

III.1.1. Discharge characterization by optical emission spectroscopy

The emission spectra resulting from the interaction of the SF_6 plasma with LDPE films are shown in figure 1 for two different 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. The H_α and H_β lines of the Balmer serie were also observed and witness of the polymer surface degradation.

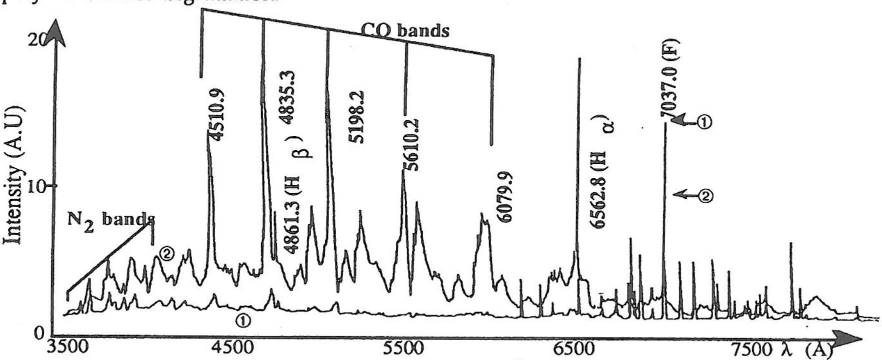

Figure 1. Emission spectra in the range of 3500 - 8000 Å of a pure SF_6 discharge with O_2, N_2 and H_2O as contaminants. ① : 0 to 10 min after plasma ignition. ② : t > 10 min after the plasma ignition. P= 10^2 Pa, Q = 100 sccm, P_w = 30 W, f = 13.56 MHz.

The intensity of the fluorine line observed at 7037 Å decreases with the treatment duration. This can be related to its consumption both through homogeneous and heterogeneous mechanisms. 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 [18].

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

Figure 2 shows the evolution of the stable 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 [6] 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.

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 whileas that of SOF_4 at m/e = 105 is observed but to a less extent than SOF_2. A reaction scheme involving atomic oxygen and water vapor has been proposed by differents authors in order to explain the SOF_2 formation :

This is confirmed by the increase of the peak intensity at mass 30.99 amu corresponding to CF^+ after treatment. More information can be obtained if we use the high resolution capabilities, as illustrated by magnifying the 69.6-70.4 amu and the 88.5-90.5 amu mass ranges of the same spectrum (figure 4). The normalized intensities of SF_2^+ and SF_3^+ ions are small but not negligible. S^+, SF^+, and SF_5^+ ions were also detected. The absence of SF_4^+ ion is explained by the preferential reaction of the SF_4 species with O_2, H_2O and/or F in the gas phase.

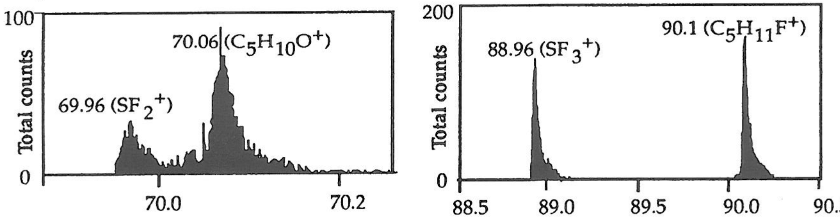

Figure 4. Positive ToF-SIMS spectrum in the mass ranges of 69.8-70.2 amu and 88.5-90.5 amu for SF_6 treated LDPE, t= 0.23 s.

Effect of treatment time

The role of treatment time on the surface functionalization has been studied especially in the case of SF_x^+ ions (figure 5). The main feature in the variation of the normalized intensities is the decrease for treatment times exceeding 2 seconds. This has been attributed to the ablation of these species under ion bombardment of the surface. On the contrary the intensities of $C_xF_y^+$ ions increased with increasing treatment time up to 30 seconds [19]. These discrepancies can be explained by the fact that the S-C bondings (259 $kJ.mol^{-1}$) are weaker than the C-F (427 $kJ.mol^{-1}$) and the C-C (335 $kJ.mol^{-1}$) bondings.

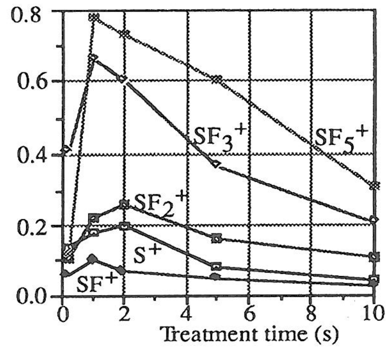

Figure 5. Normalized ToF-SIMS SF_x^+ ion intensities as a function of the SF_6 plasma treatment time

III.2. Analysis of the SF_6/CF_4 plasmas and their interactions with LDPE 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 materials operating at very low temperatures, additives (up to 15 %) such as N_2 and CF_4 are added to SF_6.

III.2.1. Discharge characterization of SF_6/CF_4 mixtures

The ratio N_2^+/N_2 has been calculated for different SF_6 concentrations in the gas feed and showed an increase with the addition of small amounts of SF_6 (10%) to CF_4. This implies an increase of the energetic aspect of the discharge. N_2^+/N_2 and, consequently T_e, remained

1-	$SF_4 + H_2O \rightarrow SOF_2 + 2\,HF$	$k = 1.5\;10^{-19}\,cm^3.\,s^{-1}$	[4]
2-	$SF_3 + O \rightarrow SOF_2 + F$	$k = 2.0\;10^{-11}\,cm^3.\,s^{-1}$	[5]
3-	$SF_2 + O \rightarrow SOF + F$	$k = 1.1\;10^{-10}\,cm^3.\,s^{-1}$	[5]
4-	$SOF + F \rightarrow SOF_2$	$k = 1.0\;10^{-13}\,cm^3.\,s^{-1}$	[5]

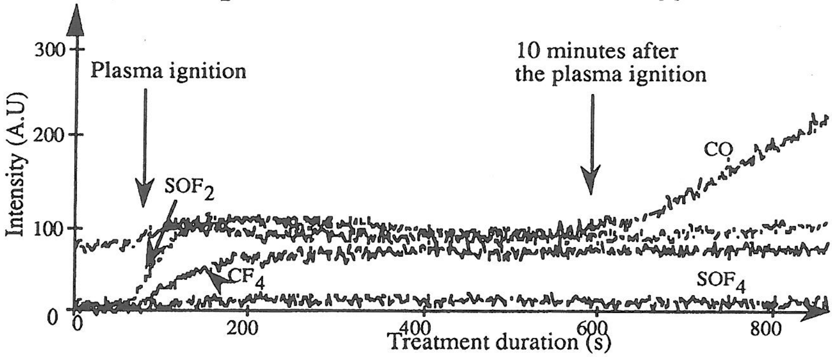

Figure 2. Etch products resulting from the surface degradation of polyethylene treated by pure SF_6 discharge ($P= 10^2$ Pa, $P_w = 30$ W, Q= 100 sccm, f= 13.56 MHz).

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 [15]. 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.1.4. Analysis of the surface by ToF-SIMS

ToF-SIMS measurements were performed a few weeks after the treatment using a ToF-SIMS trift spectrometer from Charles Evans & Associates. The experimental conditions are given elsewhere [19]. The comparison of the spectra of untreated PE and that of SF_6 plasma treated LDPE (0.23 s) reveals interesting results (figures 3a and 3b). It can be pointed out that there is a clear difference in the relative intensities of peaks in cluster C1. The C^+ ion relative intensity increases after treatment. This is generally related to unsaturation, but in our case, it is due to the substitution effect of H by F.

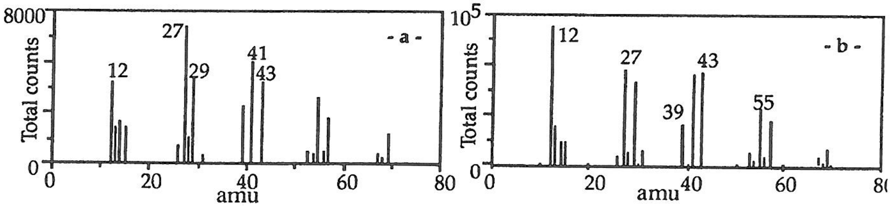

Figure 3. Positive ToF-SIMS spectra of (a) untreated LDPE and (b) SF_6 plasma treated LDPE, t= 0.23 s, $P= 10^2$ Pa, Q= 40 sccm, P_w= 10 W, f= 13.56 MHz.

constant for higher SF_6 contents. Furthermore argon was used as an actinometer for the tracing of F atoms [20]. Its intensity decreased with increasing SF_6 percentage over the complete range in the SF_6 - CF_4 mixture. This was explained by the decrease of the electron density due to the electron attachment processes which are known to be important in SF_6 discharges.

Fluorine concentration as measured by actinometry is plotted versus the composition of the gas feed (figure 6). 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 [19]. 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.

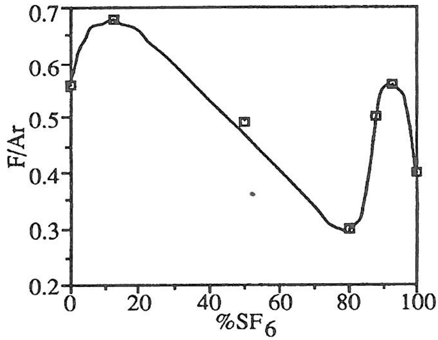

Figure 6. Variation of the [F] measured by actinometry as a function of the SF_6/CF_4 gas composition. $P=10^2$ Pa, Q= 40 sccm, P_w =10 W.

SF_6/CF_4 mixtures were analyzed by mass spectrometry over the complete range of the gas composition [19]. The addition of small percentages of CF_4 to SF_6 (less than 20%) led to a decrease of the SF_6 decomposition rate. This explains the lower fluorine concentration observed by actinometry at 20% of CF_4 in the mixture (figure 6). Indeed CF_4 can act as a source of fluorine atoms which can recombine with SF_x radicals regenerating SF_6. Further experiments are needed in order to have a better understanding of the mechanisms which take place.

III.2.3. Chemical characterization of the treated surface by XPS

The variation of the F_{1s}/C_{1s} ratio, measured by XPS, as a function of the SF_6 % is displayed in figure 7. It can be clearly seen that this ratio follows the same trend as that obtained from actinometry (figure 5). This leads to the conclusion that a close correlation exists between the fluorine density measured in the plasma and the surface fluorination process. 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 and, consequently, F atoms concentration in the gas and at the surface decrease.

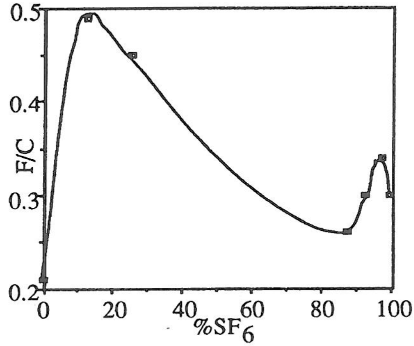

Figure 7. F1s/C1s atmic ratio measured by XPS over the complete range of the SF_6/CF_4 gas mixture composition.

IV- CONCLUSION

The decomposition mechanisms of SF_6 plasmas have been studied during the surface treatment of LDPE films. The results brought evidence on the gas and the surface degradation giving products such as SOF_2, CF_4 and CO. The atomic percentage of the sulfur detected at the surface of the SF_6 treated polyethylene films was less than 2%.

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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