STUDY OF THE DECOMPOSITION MECHANISMS OF SF_6/N_2 MIXTURES AND THEIR INTERACTIONS WITH A HIGH DENSITY POLYETHYLENE TARGET.

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ABSTRACT : The aim of this work was to study the interactions of SF_6/N_2 mixtures and LDPE target knowing that N_2 addition could lead to an increase of etching. In this aim, plasma (OES, MS) and surface diagnostic methods (XPS, SEM) were coupled in order to find the optimum mixture for the etching of LDPE. The results bring evidence on the particularity of the SF_6 80%/ N_2 20% mixture i.e. an increase of the polymer degradation and SF_6 decomposition rate but also an increase of the specific species resulting from the interaction of N_2 and SF_6.

1- INTRODUCTION

Different kinds of mixtures such as SF_6/O_2, SF_6/N_2 have been studied for etching of Si, SiO_2 and refractory metals.The SF_6/N_2 mixtures have been used to increase the etching rate of metals such as tungsten by increasing the ion energy as well as the fluorine atom concentration upon addition of N_2 in the SF_6. Reactive ion etching is of current interest because of its importance for use in the fabrication of very large scale integration circuits (VLSI) [1] and for the fabrication of microstructure semiconductor devices [2]. Since we are interested in the interactions between the low density polyethylene (LDPE) and the gaseous mixture, we have studied the effect of N_2 addition to SF_6 discharge, knowing that SF_6 rich mixtures are used for fluorination and etching purposes and N_2 rich mixtures for environmental problems in application to high voltage power systems.

2- EXPERIMENTAL

This study is performed in a low pressure discharge with a nonsymmetrical-configuration of electrodes (high voltage hollow electrode-grounded cylinder) with an excitation frequency of 70 kHz. The details of the experimental set-up has been given elsewhere [6].
The operating pressure was 100 Pa. The polymer used was the polyethylene (LDPE), 70 µm thick with no additives except 100 ppm of an antiblocking agent SiO_2 has been added. The power used was about 30 W and the total flow rate is 40 sccm. The treatment time studied varied between 0.7 seconds up to 1 min. The OES has been investigated using an optical fiber to collect the plasma emission and the signals were selected 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 stable effluents was made by mass spectrometry. The species 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. The electron impact ionizer was set at 70 eV to allow comparison with published fragmentation patterns. The intensity of each fragment was normalized with respect to the total intensity of all of the peaks. If a peak resulted from several compounds, mass interference corrections were made. Transmission coefficient calculations are not included in the measurements. The pressure in the ionization chamber was held at 1.6×10^{-4} Pa.

3- RESULTS AND DISCUSSION

3-1- Characterization of the SF_6/N_2 mixture.

- **The optical emission spectroscopy (OES)** : argon has been used as an actinometer in order to estimate the atomic fluorine concentration in the fundamental state.
It has been shown that IF/IAr ratio (Ar : 750.4 nm, F : 703.7 nm) versus the percentage of N_2 in the mixture, is maximum for around 20 % N_2 in SF_6. At the same time, the Ar actinometer which represents the excitation efficiency of the electrons is maximum for the same mixture.
Besides, it has been shown [4] that N_2 increases the energy of the ions which has been demonstrated by the measure of the bias voltage. Therefore, knowing that fluorine atoms are excellent etching agents [8], [9] in particularly for an excitation frequency of 70 kHz [7] and that N_2 increases the ionic energy of such mixtures, the polymer etching rate can be optimized for SF_6/N_2 mixtures.

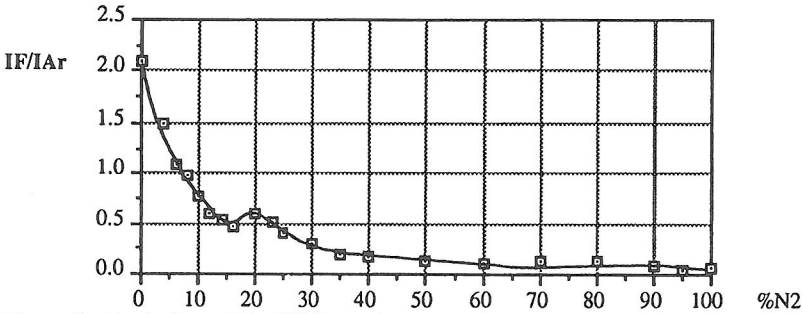


Figure 1- Evolution of the IF/IAr ratio versus the percentage of N_2 in the mixture.

As far as the excited species are concerned, no characteristic species of SF_6/N_2 mixtures such as NS, NSF have been detected since these species are very difficult to detect by OES [5]. However, species corresponding to the polymer degradation such as H_α (λ = 656.2 Å)and H_β (λ = 434.0 Å) and CO lines (λ = 451.1; 483.5; 519.8; 561.0; 607.9 Å) have been detected in pure SF6 and in the mixture.
- **Mass spectrometry** : has been used to analyze the neutral stable species resulting from the gas and polymer decomposition .
First, the calculation of the SF_6 dissociation rate by the variation of the parent peak SF_5^+ with or without plasma points out a maximum for about 20 to 30% N_2 in SF_6.

This result is in agreement with the calculated evolution of the intensity of formation of the species such as SF_4^+, SF_3^+ which present also a maximum for 20-30% N_2 in SF_6. The formation of SF_2^+ ion (m/e = 70) from the decomposition of SF_6 is negligeable in our case after all mass interference corrections. This can be explained by a reaction such as SF_2 + O ---> SOF + F which is correleted to the importance of SOF^+ (figure 5).

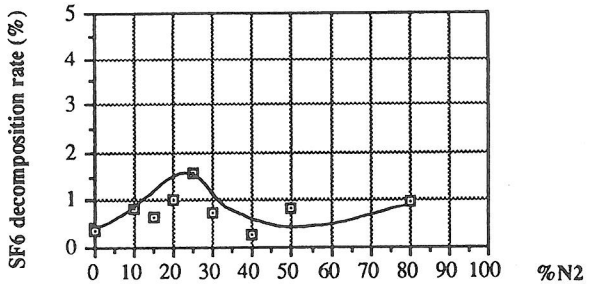


Figure 2- SF_6 decomposition rate versus the percentage of N_2 in the mixture.

Secondly, the species resulting from the polymer decomposition are observed : m/e = 69 (CF_3^+), 50 (CF_2^+), 31 (CF^+) which point out the formation of CF_4, but also 26 (CN^+), 20 (HF^+), 34 (H_2S^+). The two last hydrogenated species could be formed either by the interaction of sulfur or fluorine atoms with hydrogen coming from the reactor walls mainly (in the form of water vapor) or from the decomposition of the polymer as confirmed by OES.

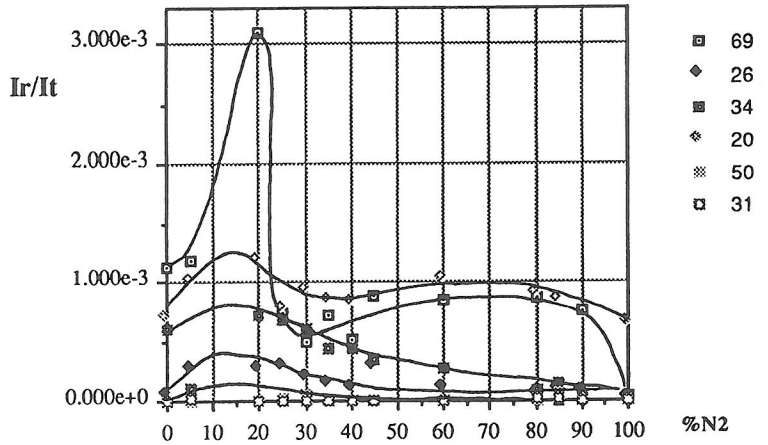


Figure 3- Decomposition products versus the percentage of N_2 in the mixture.

Moreover the intensities of the species resulting from the reaction of SF_6 with N_2, i.e. NF_3^+ (parent molecule NF_3,m/e = 71), NF_2^+ (NF_3, m/e = 52), NS^+ (unknown fragmentation pattern, m/e = 46) present each a certain maximum for 20-30% N_2.

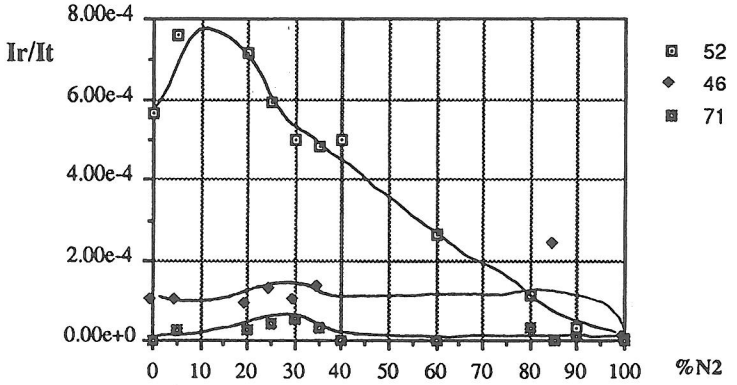


Figure 4- Principal products resulting from the interaction SF_6/N_2 versus the percentage of N_2.

The figure 5 shows the evolution of these species with or without plasma and confirm the other results and the particularity of the SF_6 80%/ N_2 20% mixture in application to etching of LDPE.

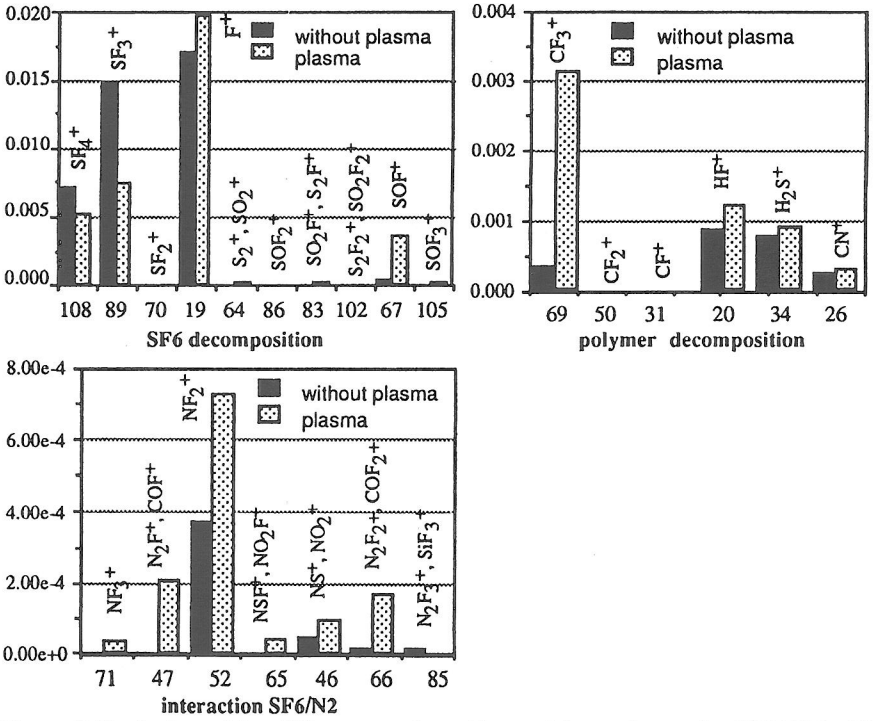


Figure 5-Evolution of the different species with or without plasma for 20%N2 in SF6.

3-2- Polymer surface characterization

- **XPS Analysis** has been carried out on LDPE films treated with different SF6/N2 percentages. The results show that the F/C ratio passes through a minimum around 15-20% N_2 in the discharge. We can point out that as soon as N2 is added to SF6 the nitrogen is incorporated in the polymer surface. However, for percentages varying between 10 to 20% the N/C ratio remains constant and increases only above 20% suggesting that in this region, the polymer nitridation is slowed down by polymer etching. The latter is confirmed by mass spectrometry results which have shown that CN intensity (m/e = 26) presents a maximum for 20% N_2 in the mixture.

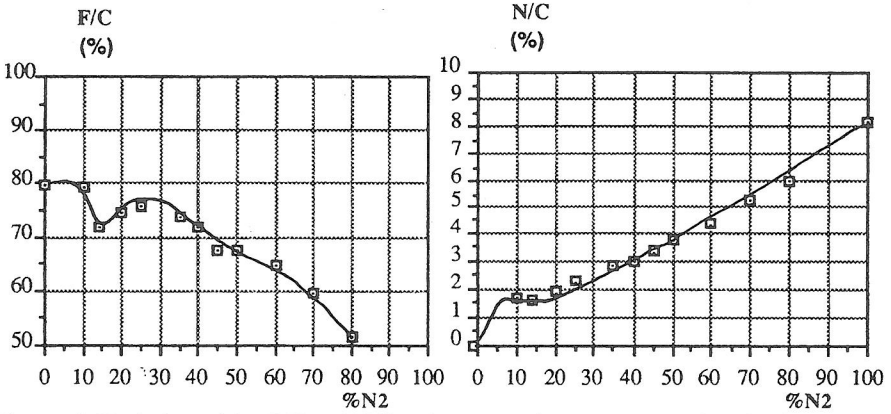
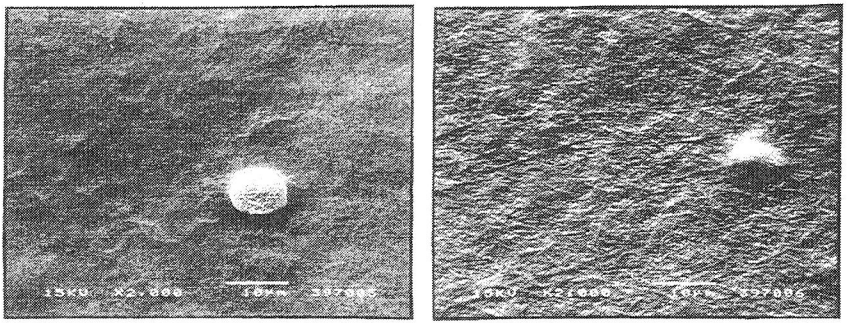


Figure 6- Variation of the F/C and N/C ratio versus the percentage of N_2 in the mixture.

- **SEM Observations :**

This study has been carried out for different treatment times and for different percentages of N_2. The evolution versus the percentage of N_2 in the mixture shows that for 20% N_2, the surface roughness is different and shows a nodular structure. This structure increases in length with the treatment time.

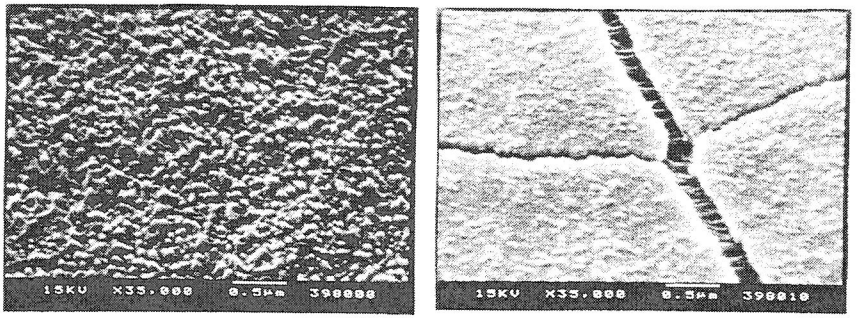


10 % N2 20% N2

Figure 7- SEM analysis of the LDPE surface for 10% N_2 and 20 % N_2 in SF_6.

The change of the morphology versus the time shows that for long treatment time, cracks are formed on the polymer, leading to a lamination of the polymer layer. At this

stage of the treatment, the polymer becomes opaque and its mechanical properties are drastically weakened which explains its lamination.



10 s 30 s

Figure 8- SEM analysis of the LDPE surface for long treatment time (10 and 30 s)

4- CONCLUSION

The results obtained from plasma diagnostic techniques (OES and MS) allows us to present a preliminary reaction scheme occuring in our plasma knowing that atomic fluorine concentration is maximum for the 20% N_2 / 80% SF_6 mixture.

* SF_6 decomposition ---> SF + F
* SF + N --> NS + F
* F + N --> NF
* F + NF --> NF_2
* F + NF_2 --> NF_3

The reactions characteristic of the mixture i.e.

$$SF + N \text{ ---> } NS + F$$
$$SF_n + N \text{ ---> } NSF_{n-1} + F$$

Surface analysis (XPS, SEM) put forward the polymer degradation and the resulting etching in particularly for the mixture containing 20-25 % N_2 in SF_6 which seems to be the optimum mixture for this purpose.

References :

[1] S. Adachi, N.Susa, J. Electrochem. Soc., vol.132, n°12, (1985), p.2980.
[2] M.C. Peignon, Ch. Cardinaud, G. Turban, J. Electrochem. Soc., vol.140, n°2, (1993), p.505.
[3] N. Mutsukura, G. Turban, J. Electrochem. Soc., vol.137, n°1, (1990), p.225.
[4] G. Turban, J.F. Coulon, N. Mutsukura, Thin Solid Films, 176, (1989), p. 289
[5] Thèse Coulon, Oct. 1992, Université de Nantes.
[6] Y. Khairallah, F. Arefi and J. Amouroux, Pure and Applied Chem. 66, p.1353, (1994)
[7] P. Montazer-Rahmati, F. Arefi, J. Amouroux, Proc. of ISPC 10 (IUPAC)
[8] F.D. Egitto, V. Vukanovic and G.N. Taylor, Plasma Deposition Teatment and Etching of Polymers, edited by R. d'Agostino, Academic Press, New York, 1990.
[9] R. d'Agostino, F. Cramarossa, F. Fracassi and F. Illuzzi, Plasma Deposition Teatment and Etching of Polymers, edited by R. d'Agostino, Academic Press, New York, 1990.
[10] G. Turban, B. Grolleau, P. Launay, P. Briaud, Revue Phys. Appl. 20, p.609, 1985.
[11] M. Strobel, S. Corn, C.S. Lyons, G.A. Korba, J. Polym. Science : Polym. Chem. vol.23, 1125-1135, 12985.