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## **ABSTRACT**

The gas phase species produced in RF plasmas of hexamethyldisiloxane (HMDSO),  $Si_2O(CH_3)_6$ , diluted with oxygen have been investigated. The complementarity of Fourier transform infrared absorption spectroscopy (FTIR) and mass spectrometry (QMS) allows the determination of the most abundant neutral components present in the discharge. The measurements reveal that methyl groups ( $CH_3$ ), abundantly formed by the dissociation of the HMDSO molecule, are the precursor for the most abundant species which stem from two kinds of reaction: 1) Combustion of the  $CH_3$  by oxygen producing formaldehyde ( $COH_2$ ), formic acid ( $CO_2H_2$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ) and water. It is shown that high mass carbonated radicals such as  $Si_xO_yC_zH_t$  first diffuse to the surface and then the carbon is removed by oxygen etching to form  $CO_2$ . 2) Hydrocarbon chemistry promoted by  $CH_3$  producing mainly hydrogen ( $H_2$ ), methane ( $CH_4$ ) and acetylene ( $C_2H_2$ ).

# 1. INTRODUCTION

Plasma enhanced chemical vapour deposition (PECVD) of silicon dioxide finds many important applications in industry. Plasma assisted processes are commonly used in the semiconductor industry for the production of insulating layers or in the packaging industry to deposit an ecological oxygen barrier on polymers<sup>1</sup>. Recently, organosilicons began to replace the often used, but dangerous, monomers such as silane<sup>2</sup>. HMDSO plasmas (hexamethyldisiloxane), diluted in oxygen and noble gases such as helium and argon, have taken over in SiO<sub>x</sub> deposition processes.

At present, the chemistry and the plasma-substrate interaction in these plasmas are almost unknown. Many ex-situ investigations (ellipsometry, EELS, XPS, IR,...) have been carried out to characterise silicon dioxide-like films but only few reports<sup>3,4</sup> are dedicated to the mechanisms and the chemical reactions in these deposition plasmas. The fragmentation of the organosilicon into neutrals and ions in the plasma, and their reactions with other reactive species present such as oxygen have not been studied in detail up to now. The powder formation<sup>5,6,7</sup> and its influence on the plasma and the deposited film are other topics which have not yet been clarified.

An understanding of the basics of these reactive plasmas is of importance for optimising the functionality of the coating and for process and quality control. Recently it has been shown that the stoichiometry of the  $SiO_x$  film is strongly related to the plasma composition. The functionality such as the oxygen permeation is strongly influenced by the carbon content in the film<sup>8</sup>.

In recent years, considerable progress has been made in the development of new in-situ plasma diagnostic methods<sup>5,9</sup>. In particular, infrared absorption spectroscopy using FTIR spectrometers is a powerful technique for the investigation of the on-going chemistry in complex plasma systems<sup>9</sup>. Complemented by additional diagnostic methods such as optical emission spectroscopy and mass spectrometry, a rather detailed picture of the reactive plasma and its chemistry can be obtained, as recent studies in hydrocarbon plasmas have shown<sup>10</sup>.

The first part of this paper is dedicated to mass spectrometry measurements which exhibit the precursive character of the methyl group in the formation of the dominant gas phase species in HMDSO/oxygen plasmas. In the second part, FTIR absorption spectroscopy is used to confirm the abundant production of oxygenated and hydrocarbon species.

# 2. EXPERIMENT

The experiments were performed in a capacitively-coupled rf plasma reactor (Fig.1) with 13 cm diameter electrodes placed 2.5 cm apart and operated at an excitation frequency of 13.56 MHz. The reactor is described in more detail in reference [11]. The experiments were performed at room temperature at 0.1 mbar, with a RF power of 100 W (0.75 W/cm²). The flow rates of HMDSO in oxygen were set in a range of 0 to 20 sccm, maintaining a total flow rate of 20 sccm.

In order to reduce the influence of carbon contamination from the reactor walls, the reactor was cleaned by a helium/oxygen discharge before each experiment. Infrared absorption spectroscopy of the diluted HMDSO plasma was performed by means of a commercial FTIR instrument (Bruker Equinox). The schematic arrangement of the in-situ infrared absorption spectroscopy is shown in Figure 1. The infrared beam leaving the spectrometer is directed through the plasma (single pass) via ZnSe windows. After the exit window, the beam is focused by an off-axis paraboloid gold coated mirror onto an external liquid nitrogen cooled mercurycadmium-telluride (MCT) detector. Transmission spectra in the range between 700-4000 cm<sup>-1</sup> with a spectral resolution of 1 cm<sup>-1</sup> were usually recorded. To ensure reasonable signal-to-noise ratio, averaging of up to five hundred spectra was usually performed. To avoid the influence of water vapour and atmospheric CO<sub>2</sub> absorption bands, the infrared light path, including the detection systems, were enclosed and continuously flushed with pure nitrogen gas. Transmission spectra with the reactor under vacuum were acquired before and after each measurement to check for possible influences of deposited layers on the windows, variations in the sensitivity of the detector and as reference spectra for calculation of absorbance spectra. In addition to the infrared absorption measurements, quadrupole mass spectrometry was simultaneously employed. A Balzers PPM 421 mass spectrometer with a mass range up to 512 amu was used to measure the composition of the neutral gas and of the positive ion population.

The probe head of the mass spectrometer was positioned adjacent to the electrode gap at 1 cm from the plasma boundary.

# 3. RESULTS AND DISCUSSION

Mass spectrometry and infrared absorption spectroscopy each give quantitative information on the species present in the plasma. Simultaneous application of these diagnostic methods can circumvent many of their intrinsic limitations and drawbacks and permits to identify precisely the most abundant neutral species and their precursors in reactive plasmas such as the diluted HMDSO/oxygen plasmas investigated here.

# 3.1 Mass spectroscopy of HMDSO/oxygen plasmas.

Single ionization of molecules is generally the main process used for the measurement of neutrals by mass spectrometry <sup>12,13</sup>. According to Basner et al [14], for the complex molecule HMDSO, dissociative ionization was found to be the dominant process, where the dominant channel is the removal of a methyl group CH<sub>3</sub> from the HMDSO molecule to produce the ion Si<sub>2</sub>O(CH<sub>3</sub>)<sub>5</sub><sup>+</sup> with a cross section of 1.7x10<sup>-15</sup> cm<sup>2</sup> at 70 eV. Figure 2 shows the mass spectra of pure HMDSO at a pressure of 0.1 mbar without plasma measured as a function of the applied electron energy in the ionization source. In the present experiments, the electron energy was varied from 11 to 70 eV. With the present experimental arrangement, lower electron energies could not be attained due to space charge limitations in the ionisation source of the mass spectrometer.

At 20 eV and 70 eV, the two main dissociative ionization events are the dissociation of the HMDSO molecule into the ion  $Si_2O(CH_3)_5^+$  (m=147 amu) and the neutral radical  $CH_3$  (m=15 amu) and into the ion  $Si(CH_3)_3^+$  (m=73 amu) and the neutral radical  $SiO(CH_3)_3$  (m=89 amu). In our case, except for the ion  $CH_3^+$ , the relative intensities of the species shown in figure 2 corresponds to the relative intensities predicted by Basner et al. The difference in the relative intensity of the ion  $CH_3^+$  could be explained by the fact that our spectrometer is not equipped for a efficient detection of ions with an excess kinetic energy<sup>13,14</sup>. Besides, the masses 52 and 66  $(Si_2OC_4H_{12}^{++})$  (m=104 amu) and  $Si_2OC_2H_8^{++}$  (m=132 amu)) no longer appear in

figure 2 at 20 eV due to their high appearance energy, which proves that the masses apparent at 70 eV are not due to secondary ion-radical reactions in the mass spectrometer but rather to the cracking pattern of the HMDSO molecule. At  $11 \,\text{eV}$ , only the fragment ions  $\text{Si}_2\text{O}(\text{CH}_3)_5^+$  (m=147 amu) and  $\text{Si}_2\text{O}(\text{CH}_3)_6^+$  (m=162 amu) should appear because they have an appearance energy (AE) lower than  $11 \,\text{eV}$ , 9.6 and 8.8 eV respectively. It can be considered that the most abundant produced neutrals are the radicals  $\text{CH}_3$  and  $\text{SiO}(\text{CH}_3)_3$ . Moreover, as a function of decreasing electron beam energy from 70 to  $11 \,\text{eV}$ , the positive ion  $\text{Si}_2\text{O}(\text{CH}_3)_5^+$  remains the most abundant charged species produced by dissociative ionization.

The discussion about most abundant species can be carried over to a HMDSO plasma with an average electron temperature of a few eV. Below 8.8 eV, the dissociation of the HMDSO molecule by electron impact is the dominant process. Since the bonding energy of the Si-O bond (8.31 eV) is two times higher than the Si-C bond (4.53 eV), the dissociation process also induces a dominant production of the neutral radicals CH<sub>3</sub> and Si<sub>2</sub>O(CH<sub>3</sub>)<sub>3</sub>. Therefore this indicates that further reactions will be dominantly initiated from these most abundant species produced in the plasma, in particular in HMDSO/oxygen plasma where oxygen can strongly react with the deposit and the gas phase species<sup>15</sup>.

Figure 3 shows mass spectra of neutrals in HMDSO/oxygen with and without plasma for two oxygen to HMDSO flow ratios. A small amount (1 sccm) of argon and helium was added for actinometry. Since the added partial pressures of argon and helium are very low, we supposed their influence on the plasma behaviour to be negligible. A strong increase in masses 2 (H<sub>2</sub>), 12 (C), 28 (CO and/or C<sub>2</sub>H<sub>4</sub>), 44 (CO<sub>2</sub> and/or radical SiO), 46 (CO<sub>2</sub>H<sub>2</sub>)) and a clear consumption of molecular oxygen is observed which indicates strong combustion reactions in the presence of oxygen for both dilution conditions. In figure 3b, we also note a significant appearance of masses 15 (CH<sub>3</sub>), 16 (CH<sub>4</sub>,O), 17 (OH), 18 (H<sub>2</sub>O), 26 (C<sub>2</sub>H<sub>2</sub>), 29 (COH, C<sub>2</sub>H<sub>5</sub>), 30 (COH<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>). The presence of a large amount of molecular hydrogen might result from the high fragmentation of the many C-H bonds in the HMDSO molecule. Hydrocarbon chemistry is clearly revealed by the presence of acetylene (C<sub>2</sub>H<sub>2</sub>) determined by mass spectrometry.

No new species appear in the range of masses from 50 to 162 amu. On the contrary we observe that the intensity of some species decrease in the plasma phase, indicating a

consumption. The change in the low mass intensities (< 50 amu) with plasma shows that the produced species are the results of oxidation reactions or hydrocarbon chemistry. We demonstrated above that the most abundant masses in a HMDSO plasma are the neutral radicals CH<sub>3</sub> and SiO(CH<sub>3</sub>)<sub>3</sub>. Since no new masses above 50 amu appear in the HMDSO/oxygen plasma, the neutral radical CH<sub>3</sub> undergoes combustion reactions with oxygen and may also lead to hydrocarbon chemistry in the plasma. The consumption of complex radicals such as  $Si_xO_yC_zH_t$  is mainly due to their diffusion to the surface and their consequent contribution to the growing layer.

Figure 4 shows the positive ion spectra as a function of the dilution of HMDSO in oxygen. These spectra were recorded for the same plasma conditions as the previously shown neutral mass spectra (0.1 mbar, 0.75 W/m²). At high dilution conditions (flow ratios:  $[O_2]/[HMDSO]=31$  and 10), the positive ion spectra show that the most abundant ions are  $O_2^+$ ,  $CH_3^+$ ,  $H_3O^+$ ,  $H_2O^+$ ,  $CO_2^+$  and  $HSiOSi(CH_3)_5^+$  (m=148),  $SiOSi(CH_3)_6^+$  (m=162) and the mass 176 attributed to the ion  $HSi_3O_2(CH_3)_2(CH_2)_2^+$ . The presence of dominant oxygenated species indicates that the oxygen chemistry is more efficient under these conditions than the hydrocarbon chemistry.

Similar to the neutral spectra, the positive ion mass spectra do not show strong intensities in the mass range from 50 to 147 amu. The main difference compared to neutral spectra is the appearance of masses up to 300 amu. Alexander<sup>18</sup> also observed masses up to 300 amu, but in pure HMDSO plasmas. Positive ions between the masses 59 amu and 162 amu come from of the dissociative ionisation of the HMDSO molecule. Above the mass 162 amu and up to 300 amu, the masses are are due to ion-neutral reactions which lead to the formation of higher mass positive ions. These species contain three silicon bonded to two oxygen atoms. Contrary to Alexander we did not detect masses in the range from 300 to 400 amu, probably due to a shorter residence time of the species in the plasma, which limits the ion-neutral reactions.

Figure 5 a) and b) show the behaviour of the most abundant neutral species as a function of the flow ratio  $[O_2]/[HMDSO]$ . The intensities are normalised with respect to the argon mass intensity. In addition to the mass spectrometer measurements, the ratio  $[HMDSO]/[HMDSO+O_2]$ , which corresponds to the partial pressure of HMDSO in the

chamber without plasma, is also plotted. The trends of  $H_2$ , CO,  $H_2O$ , OH and  $CO_2H_2$  in Fig 5a) follow closely the behaviour of the HMDSO partial pressure, which means that the source of the carbon for these radicals originates from the HMDSO molecule dissociated in the plasma. The only exception is the level of  $CO_2$  which stays constant for all dilutions. Consequently there must exist an additional source of carbon which can most probably only come from the reactor surfaces. The carbon containing species are first deposited on the reactor's surfaces and then removed by oxygen etching thereby producing  $CO_2$ . Consequently, the deposition of a:SiO<sub>x</sub> with1 $\leq$ x $\leq$ 2 and a carbon to silicon ratio <<1 obtained in similar dilution conditions (flow ratio of  $[O_2]/[HMDSO] \geq 30)^{19}$  is not due to the deposition of species such as SiO radicals but mainly by removing the carbon from previously deposited  $Si_xO_yC_zH_t$  radicals. Since the main species, which are contributing to the deposition, are carbonated due to an incomplete fragmentation of the HMDSO molecule (fig 3), the oxygen content in the plasma will determine the stoichiometry of the deposited film.

In Fig 5b) the mass 30 could be attributed to C<sub>2</sub>H<sub>6</sub> and/or COH<sub>2</sub> and the mass 29 to C<sub>2</sub>H<sub>5</sub> and/or COH (cracking pattern of CO<sub>2</sub>H<sub>2</sub> and COH<sub>2</sub>) respectively. The mass 26 clearly corresponds to acetylene and presents the same behaviour as the masses 29 and 30. For these masses it was found that the intensities decrease faster than the HMDSO partial pressure. The trend of C<sub>2</sub>H<sub>2</sub> seems to indicate that the other species are hydrocarbons, thus C<sub>2</sub>H<sub>5</sub> and C<sub>2</sub>H<sub>6</sub>. The intensities of acetylene compared to oxygenated species, presented in figure 5a, indicates that hydrocarbon chemistry is not promoted in HMDSO/oxygen plasmas. It is due to the fact that dominating combustion products such as CO, CO<sub>2</sub>, CO<sub>2</sub>H<sub>2</sub>, water and the hydrocarbons have the same precursor: the CH<sub>3</sub> radical. Thus, the combustion of CH<sub>3</sub> by oxygen shortcuts the hydrocarbon chemistry as already demonstrated by Pedrazzini<sup>20</sup>.

## 3.2 Infrared absorption spectroscopy of HMDSO/oxygen plasmas.

Infrared absorption spectroscopy gives complementary information for determining the nature of the dominant neutral species in the plasma. Figure 6 shows the measured absorbances of HMDSO/oxygen plasmas for different oxygen flux ratios. Besides the characteristic

absorption peaks of the HMDSO molecule (see table I), additional absorption features reveal the production of gas phase species within the plasma.

Table I. Frequencies of absorption bands related to the HMDSO molecule

Bond	Vibration type	Frequency (cm <sup>-1</sup> )	
Si-O-Si	bending	830	
Si-O-Si	asym. stretch.	1072 (TO) mode	
Si-(CH <sub>3</sub> ) <sub>1-2</sub>	bending	830	
Si-(CH <sub>3</sub> ) <sub>1-2</sub>	symm. stretch	1263	
Si-(CH <sub>3</sub> ) <sub>3</sub>	rocking	844	
CH <sub>3</sub>	asym. stretch	2913	
CH <sub>3</sub>	symm. stretch	2966	

The absorbance spectra show the production of methane  $(CH_4)$ , acetylene  $(C_2H_2)$ ,  $CO_2$ , water, formaldehyde  $(COH_2)$  and formic acid  $(CO_2H_2)$ . The characteristic absorption peaks of these molecules are listed in Table II. The attribution of the peaks at 2140 cm<sup>-1</sup> to the CO stretching mode and of the absorption peaks at 667 and 2340 cm<sup>-1</sup> to the bending and asymmetric stretching of  $CO_2$  respectively, have already been made in previous work<sup>4,8,21</sup>. The absorption features in the range between 1400-1800 cm<sup>-1</sup> are attributed to the production of  $H_2O$  within the plasma.

**Table II**. Frequencies of absorption bands for the different species created in an oxygen diluted HMDSO plasma.

Species	Vibration type	Frequency (cm <sup>-1</sup> )	
CH <sub>4</sub>	CH3 stretch.	3018	
$C_2H_2$	CH deform.	670	
$\mathrm{CH_{2}O}$	C=O stretch.	1725	
$CH_2O_2$	C=O stretch.	1783	
CO	stretching	2140	
$CO_2$	bending	667	
$CO_2$	asymm. stretch.	2340	
$H_2O$	OH bending	1400-1800	

The absorption peak at 3018 cm<sup>-1</sup> has been attributed to the Q branch of the stretching of the methyl group in the methane molecule. At 2966 cm<sup>-1</sup>, the R branch overlaps the stretching band of the methyl group from the HMDSO molecule. The difference between the two absorption frequencies is due to the different neighbours involved in the bonding with the methyl group. The absorption peak at 730 cm<sup>-1</sup> is attributed to the vibration of the C-H bond inside the acetylene ( $C_2H_2$ ) molecule.

The broad absorption band centred at  $1745 \text{ cm}^{-1}$  is interpreted as the convolution between two bands<sup>22</sup>. The range from  $1715 \text{ cm}^{-1}$  to  $1790 \text{ cm}^{-1}$  is characteristic of the infrared absorption of the double bond in C=O containing molecules. The neutral mass spectra do not show any production of masses beyond 50 amu, but possible molecules containing a C=O structure more complex than  $COH_2$  (formaldehyde) and  $CO_2H_2$  (formic acid) would inevitably be heavier than 50 amu. Therefore it is speculated that the C=O stretching vibration centred at  $1745 \text{ cm}^{-1}$  and centred at  $1783 \text{ cm}^{-1}$  are the fingerprint of the simplest possible structures: formaldehyde ( $COH_2$ ) and formic acid ( $CO_2H_2$ ) respectively. Since there is no evidence of the  $C_2H_6$  molecule in the infrared spectra ( $2900-3100 \text{ cm}^{-1}$ ), the ambiguity, discussed in section 3.1, between the  $C_2H_6$  and the  $COH_2$  molecule can be resolved.

Figure 7 a), b), c) and d) shows the infrared spectra of HMDSO/oxygen/helium, helium/oxygen, pure oxygen and pure helium plasmas respectively. Infrared spectra for helium/oxygen, pure oxygen and pure helium plasmas were performed just after a HMDSO/oxygen/helium diluted plasma. In the oxygen and helium/oxygen plasmas, the CO<sub>2</sub> is produced by oxygen reactions with the carbon previously deposited on the surface, whereas CO and the species described as formaldehyde (COH<sub>2</sub>) and formic acid (CO<sub>2</sub>H<sub>2</sub>) are not present, in the limit of detection of the infrared absorption measuement. In figure 8, the integrated intensities of formaldehyde, formic acid, CO, CO<sub>2</sub> and CH<sub>4</sub> centered at 3018 cm<sup>-1</sup> are plotted as a function of the oxygen dilution. The integrated intensity of the whole absorption band from 1730 to 1780 cm<sup>-1</sup> corresponding to the sum of the formaldehyde and the formic acid contributions is as well plotted. It is found that the CO<sub>2</sub> intensity remains constant while varying the oxygen dilution, whereas all the other species decrease with increasing oxygen content. In figure 8 the integrated intensity of the Si-O-Si absorption band of the HMDSO molecule

without discharge is also shown. This intensity is proportional to the partial pressure of HMDSO molecules in the reactor. The decrease of the infrared absorption of CO, formaldehyde and CH<sub>4</sub> with increasing dilution follows the trend of the HMDSO partial pressure in the plasma, indicating their origin from homogeneous reactions.

The origin of the carbon present in CO<sub>2</sub>, CO, COH<sub>2</sub> and CO<sub>2</sub>H<sub>2</sub> molecules is expected to come from the radical CH<sub>3</sub> by homogeneous reaction in the bulk of the plasma and the carbon deposited on the surface is etched off and leaves it in the form of CO<sub>2</sub>. These infrared spectra (fig 6) confirm and complete the results observed from mass spectra and are summarised as follows (see figure 9):

- 1) The radical  $CH_3$  is found to be the precursor for two reaction pathways. In a first case the presence of methane leads to acetylene production. In a second case if oxygen is present it reacts with carbon present in the radical  $CH_x$ ,  $0 \le x \le 3$  to form formaldehyde, formic acid, carbon oxide, carbon dioxide and water. In addition the  $CO_2$  is also the result of heterogeneous reaction of oxygen with the carbon from deposition on the surfaces. It is difficult to determine the dominant mechanism because it depends strongly on the oxygen dilution and the history surface. It was found that, in high dilution conditions (flow ratio  $[O_2]/[HMDSO] >> 10$ , cf fig 8), heterogeneous reaction is dominating. The presence of oxidation products and hydrocarbon detected by means of FTIR spectroscopy indicates that these species are abundant in the plasma. For example, the partial pressure calibrated by means of infrared spectra in pure CO,  $CO_2$  and methane atmosphere give an average of 10% for CO,  $CO_2$  and 1% for  $CH_4$  of total pressure (0.1 mbar) in low dilution conditions (flux ratio  $[O_2]/[HMDSO] = 3$ ).
- 2) The partial fragmentation of the HMDSO molecule in the plasma implies that carbonated radicals contribute to a growing film on the electrodes. The carbon is etched by oxygen and it explains the heterogeneous production of the CO<sub>2</sub> molecule in the plasma. Consequently, the addition of oxygen and its concentration can be used to control the carbon content of the deposition.
- 3) Besides the oxidation and hydrocarbon chemistry pathways, a third pathway leading to powder has to be mentioned. A characterisation of the particles formed in the plasma is

described in ref[8]. Details of the chemistry leading to powder formation in these HMDSO plasmas are presently under investigation.

## 4. CONCLUSIONS

The complementarity of in situ infrared absorption spectroscopy and mass spectrometry allows a clear description of the most abundant neutral species produced in oxygen diluted hexamethyldisiloxane (HMDSO) rf plasmas. In oxygen dilution conditions, the infrared spectra reveal the presence of oxidation steps of the methyl-groups: formaldehyde (COH<sub>2</sub>), formic acid (CO<sub>2</sub>H<sub>2</sub>), CO and CO<sub>2</sub> and water as combustion products. The presence of methane (CH<sub>4</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>) indicates the presence of hydrocarbon chemistry. The methyl radical (CH<sub>3</sub>) is shown to be the most important precursor for the formation of the species mentioned above. Infrared spectra clearly show that all the species produced under different dilution conditions (O<sub>2</sub>/HMDSO), except CO<sub>2</sub>, are mainly the result of homogeneous reactions between oxygen and CH<sub>x</sub> for  $1 \le x \le 3$ . It is shown that CO<sub>2</sub> also comes from the reaction between oxygen and the carbon present on the surface of the reactor (heterogeneous reaction). This effect dominates at high dilution conditions (flow ratio [O<sub>2</sub>]/[HMDSO]>>10). The partial fragmentation of the HMDSO molecule and the heterogeneous contribution of the CO<sub>2</sub> in the plasma imply that carbonated radicals contribute to the growing film and confirms that oxygen concentration strongly influences the carbon concentration in the deposit.

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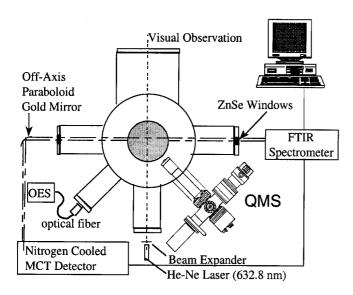


Figure 1: Schematic top view of the experimental arrangement. Quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES) were implemented to complement the Fourier transform infrared (FTIR) absorption spectroscopy. A He-Ne laser was used for visual observation of Rayleigh-Mie scattering of particles produced in the plasma.

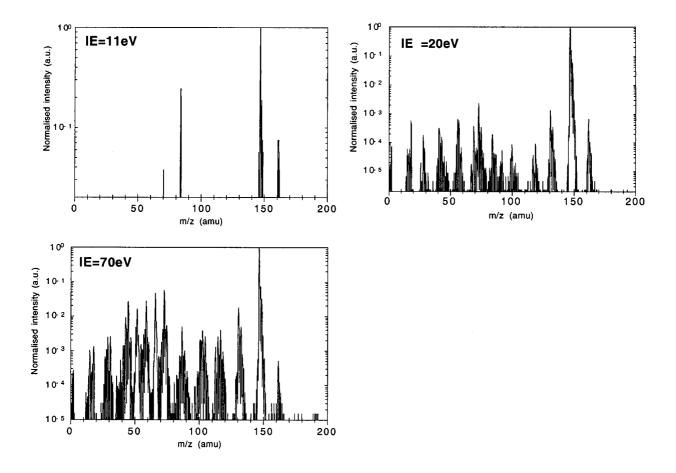


Figure 2: Mass spectra of neutrals without plasma for pure HMDSO at electron energies (IE) of 11, 20 and 70 eV.

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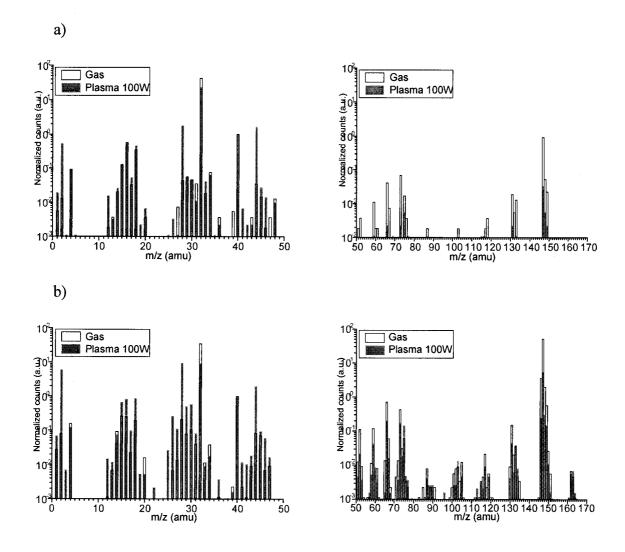


Figure 3: Neutral mass spectra at 70 eV of  $O_2$ /HMDSO plasmas for two oxygen flow ratios: a) 31 and b) 3.5. The spectra are normalized to the amplitude of the mass 40 (argon), whose partial pressure is equal to 0.5% of the total pressure (0.1mbar). The abcsissae are separated for better visualization.

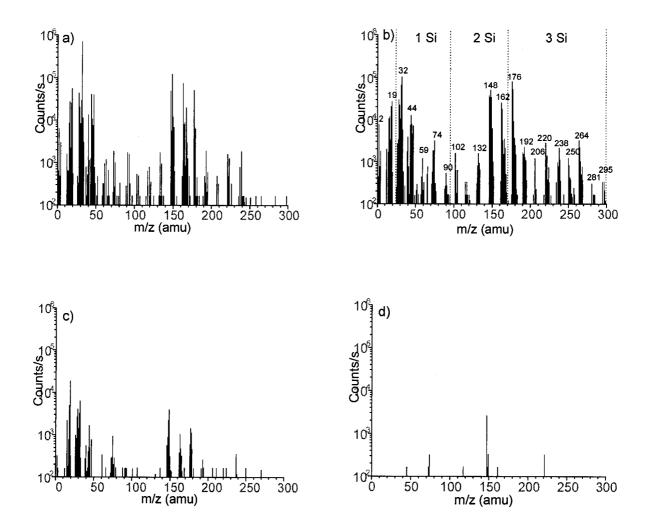


Figure 4: Mass spectra of positive ions generated by HMDSO/oxygen plasmas at four oxygen to HMDSO flow ratios: a) 31, b) 10, c) 3.5, d) pure HMDSO. The dotted lines separate the ranges of masses whose structures contain one, two or three silicon atoms.

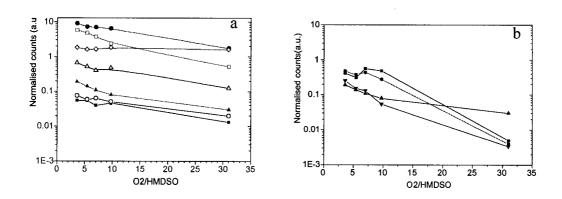


Figure 5: Intensity of neutral masses normalized to  $Ar^+$  as a function of the dilution: a) o:OH, •:CO,  $\Diamond$ :CO<sub>2</sub>,  $\Delta$ :H<sub>2</sub>O,  $\blacktriangle$ :HMDSO,  $\blacksquare$ :CO<sub>2</sub>H<sub>2</sub>,  $\square$ :H<sub>2</sub>. b)  $\blacktriangle$ :HMDSO, •:C<sub>2</sub>H<sub>6</sub> or COH<sub>2</sub>,  $\blacksquare$ :C<sub>2</sub>H<sub>5</sub> or COH,  $\blacktriangledown$ :C<sub>2</sub>H<sub>2</sub>.

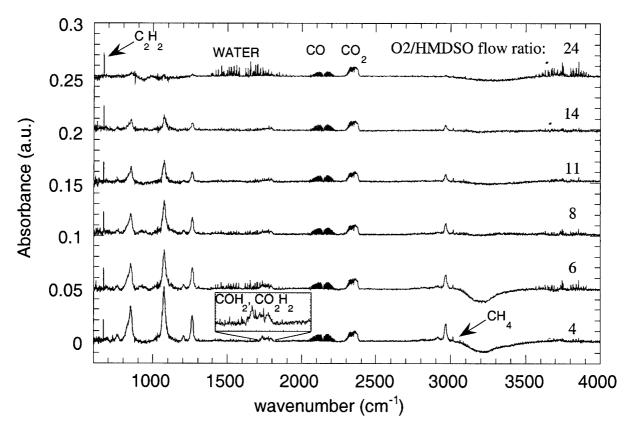


Figure 6: Infrared absorption spectra of HMDSO plasmas diluted with oxygen as a function of the flow ratio O<sub>2</sub>/HMDSO. The spectra have been shifted vertically for clarity. The infrared bands of these radicals are listed in Table II.

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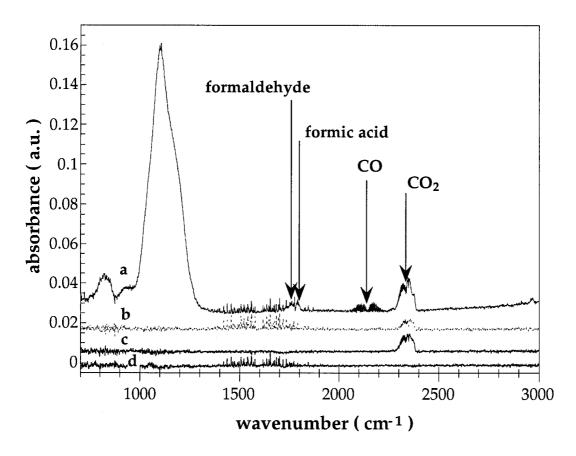


Figure 7: Infrared spectra of a) HMDSO/oxygen/helium plasma, b) helium/oxygen plasma, c) pure oxygen plasma, d) pure helium plasma, at 0.8mbar, 40W. In figure 7 a), the large absorption band from 1000 to 1300 cm<sup>-1</sup> represents particles trapped in the plasma.

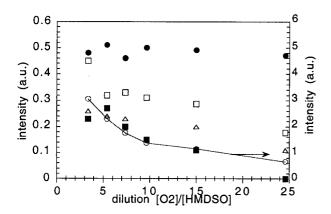
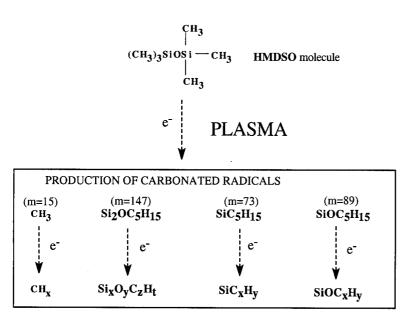
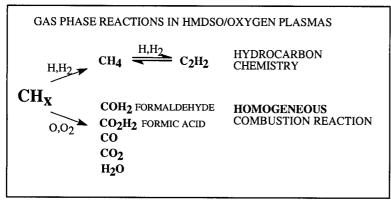


Figure 8: Integrated intensity of absorption bands related to  $CO_2$ , CO, formaldehyde  $(COH_2)$ , formic acid  $(CO_2H_2)$  and methane  $(CH_4)$ . The curve corresponds to the partial pressure of HMDSO for each dilution.  $\square$ :  $CH_4$ ,  $\blacksquare$ : aldehydes and formic acid,  $\Delta$ : CO,  $\bullet$ :  $CO_2$ , O: HMDSO partial pressure.





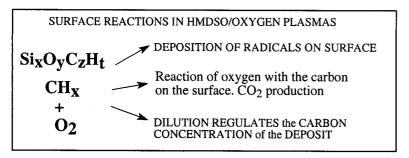


Figure 9: Schematic of the reactions of the most abundant species in HMDSO plasma diluted in oxygen.