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## **GC-MS Investigation of Hexamethyldisiloxane-Oxygen Fed Cold Plasmas:**

### **Low Pressure vs. Atmospheric Pressure Operation**

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## Summary

This study deals with the investigation by means of gas chromatography-mass spectrometry of the exhaust gas of a rf low pressure glow discharge and of an atmospheric pressure filamentary DBD fed with HMDSO, O<sub>2</sub> and Ar.

The influence of feed composition on monomer depletion and on the quali-quantitative distribution of stable by-products formed by recombination of plasma intermediates is investigated. Without O<sub>2</sub> addition to the feed almost comparable values of HMDSO depletion are observed both at low and atmospheric pressure. Oxygen addition does not influence the monomer depletion at low pressure while it induces a slight decrease of the depletion at atmospheric pressure. Whatever the working pressure, O<sub>2</sub> controls the overall chemistry of the plasma, since it influences the concentration of by-products (e.g. silanes, silanols, linear and cyclic methylsiloxanes). At atmospheric pressure evidences of the importance of methyl abstraction from HMDSO molecule have been obtained, while at low pressure the prevalence of Si-O bond rupture, of fragmentation and oligomerization reactions is observed. The comparison of results from the GC-MS investigation of the exhaust gas with FT-IR spectra of the deposited coatings allows to enhance hypotheses on the formation of silanols in the gas phase and in the deposit.

## Introduction

Organosilicon compounds, such as hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS) in mixture with oxidants (i.e. O<sub>2</sub> and N<sub>2</sub>O) and/or noble gases (i. e. Ar and He), are widely used both in low pressure (LP) and in atmospheric pressure (AP) plasma-enhanced chemical vapor deposition (PE-CVD) of silicon-based thin films. In particular, the extensive investigations performed during the last decades on low pressure organosilicon-containing plasmas<sup>[1-20]</sup> have clearly shown the versatility of these reactive systems due to the tunability of the chemical composition of the deposited coatings from silicone-like to SiO<sub>2</sub>-like<sup>[1,11,12,16,19]</sup> for applications in several technological fields.<sup>[16,21-25]</sup> The general deposition mechanism proposed for low pressure plasmas rationalizes the published experimental evidences, i.e. the effect of process parameters, such as feed composition, power density, substrate temperature, substrate bias voltage, etc.. According to this overall mechanism,<sup>[11-16,18,19]</sup> the organosilicon monomer is activated (i.e. transformed into reactive fragments) by electron collision and/or reaction with oxygen and/or reactions with excited Ar or He. The fragments can undergo either heterogeneous gas-surface reactions, which contribute to film growth, and homogeneous reactions such as oligomerization (that can ultimately lead to powder formation), or oxidation (with production of partially or totally oxidized species). The heterogeneous reactions involve fragments, also oxidized, which react on the substrate surface where they can experience ion bombardment as well as oxidation with release of water and other oxidized compounds. As a function of the experimental conditions, it is possible to influence these reactions and, therefore, to change the chemical composition and the properties of the coating.

Several diagnostic techniques such as Fourier transform infrared absorption spectroscopy (FT-IRAS),<sup>[15,16,18,19]</sup> optical emission spectroscopy (OES),<sup>[12,16,19]</sup> mass spectrometry (MS),<sup>[9-11,15,17,19]</sup> etc., have been utilized to investigate the plasma chemistry. These diagnostics provide complementary information, e.g.: OES allows the detection of low molecular weight

emitting radicals/molecules (O, H, SiO, CH, OH, CO, CO<sub>2</sub>, etc.), while high mass-species (hydrocarbons, carboxylic acids, siloxanes, etc.) can be monitored by means of MS and FT-IRAS. Besides these “*direct*” diagnostics, which are performed in situ and do not require discrete sampling, gas chromatography with mass spectrometric detection (GC-MS) has shown to be a very powerful gas phase “*indirect*” diagnostic technique.<sup>[2-6,8,12]</sup> When coupled with direct diagnostics, GC-MS can improve the understanding of plasma chemistry since it allows the qualitative and quantitative determination of stable by-products formed by plasma activation, provided that a suitable discrete exhaust sampling system is available such as, for instance, a cold trap located between the plasma chamber and the pump.<sup>[2-6,8,12]</sup>

GC-MS has been extensively utilized by several authors to investigate the low pressure PE-CVD and remote plasma chemical vapour deposition processes carried out with different organosilicon monomers (e.g. alkylsilanes, alkoxysilanes, alkylsiloxanes, alkylsilazanes).<sup>[2-6,8,12]</sup> The results were exploited to raise hypotheses on the possible reaction paths and film precursors. Sarmadi et al.<sup>[8]</sup> utilized GC-MS to analyze the condensable products collected from rf low pressure plasmas fed with HMDSO. The qualitative investigation of the gaseous and liquid fraction of the sampled mixture allowed the detection of the unreacted monomer, of Si<sub>x</sub>O<sub>y</sub>(CH<sub>3</sub>)<sub>z</sub> derivatives even heavier than HMDSO, as well as of C<sub>2</sub> and C<sub>3</sub> hydrocarbons. Fracassi et al.<sup>[13]</sup> performed an extensive GC-MS investigation of the effluent gas of low pressure plasmas fed with HMDSO, oxygen, and Ar and reported the effect of the feed composition, of the input power and of the pressure. The results indicated that, under the experimental conditions investigated, the monomer is not activated by reactions with oxygen but mainly by electron collisions. However, oxygen controls the overall chemistry of the plasma since it influences the quali-quantitative distribution of by-products.

Presently a significant interest is directed to the study of atmospheric pressure PE-CVD of silicon-containing films because of the possibility of cost reduction due to the dismissal of

vacuum systems and of the easy on-line integration. In particular, the researches have been devoted to the PE-CVD from organosilicon precursors with atmospheric pressure dielectric barrier discharges (DBDs) both in homogeneous and filamentary regime.<sup>[26-50]</sup> Published studies deal mainly with the performances of the deposition process in terms of deposition rate, homogeneity of the deposited layer, chemical composition and final properties of the coatings. Despite the intense efforts, only few published papers deal with the diagnostic investigation of the plasma chemistry<sup>[28,29,46,48-50]</sup> and the deposition mechanism is not definitively known. Vinogradov et al. utilized the FT-IRAS to investigate the gas phase of HMDSO-fed DBDs;<sup>[46]</sup> they suggested that monomer fragmentation mainly results in the production of four radicals:  $(\text{CH}_3)_3\text{SiO}$ ,  $\text{Si}(\text{CH}_3)_3$ ,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2$  and  $\text{CH}_3$ . These reactive fragments can be responsible of the formation of pentamethyldisiloxane, trimethylsilane and methane. The concentration of these species decreases with oxygen addition, when oxidation processes are dominant and  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{O}_3$  and  $\text{HCOOH}$  are produced.

Sonnenfeld et al.<sup>[28]</sup> performed the GC-MS investigation of an Ar-HMDSO- $\text{O}_2$  ferroelectric barrier discharge; the only identified by-products were pentamethyldisiloxane, trimethylsilane, tetramethylsilane, and some low molecular weight hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ). Oxygen addition did not result in the appearance of oxidation products. Since only small amounts of unidentified oligomerization products (i.e. species heavier than HMDSO) were detected, and in particular neither octamethyltrisiloxane nor heptamethyltrisiloxane were observed, the authors assumed that the polymerization processes mainly take place at the surface of the growing polymer.

Recently Fanelli et al.<sup>[48-50]</sup> reported the GC-MS investigation of the exhaust gas of filamentary DBDs (FDBDs) fed by Ar in mixture with oxygen and different methyldisiloxanes, such as hexamethyldisiloxane, pentamethyldisiloxane and 1,1,3,3-tetramethyldisiloxane. In particular in the case of HMDSO-containing DBDs<sup>[48]</sup> without  $\text{O}_2$

addition the exhaust contains several by-products such as silanes, silanols, linear and cyclic siloxanes, most of which were detected also in low pressure plasmas.<sup>[12]</sup>

In this work we report results on the GC-MS investigation of low pressure rf glow discharges and atmospheric pressure DBDs fed with HMDSO-O<sub>2</sub>-Ar gas mixtures. The effect of feed composition on monomer depletion and on the quali-quantitative distribution of by-products was investigated in order to draw a comparison between these two processes optimized for thin film deposition in order to obtain powder free coatings with different carbon contents.

## **Experimental part**

The rf low pressure plasma was generated in a stainless steel capacitively coupled asymmetric parallel plate reactor pumped by a turbomolecular-rotary pumping system (**Figure 1a**). The upper electrode was connected to a 13.56 MHz power supply (RF Power Products, model RF5) through a LC matching network. The gas flow rates were controlled with MKS mass flow controllers, while the HMDSO vapour flow rate was set by means of a MKS vapour source controller. Glow discharges were fed with HMDSO-O<sub>2</sub>-Ar at the total flow rate of 78 sccm. HMDSO (Fluka, 98.5 % purity) flow rate was kept constant at 3 sccm, while O<sub>2</sub>/HMDSO feed ratio was varied in the range 0 – 25 (O<sub>2</sub> and Ar flow rates were varied in the range 0 – 75 sccm). Experiments were performed at 100 W and 200 mTorr.

The atmospheric plasma was generated between two parallel plate electrodes (2 mm gap, 25 cm<sup>2</sup> electrode area), both covered with an Al<sub>2</sub>O<sub>3</sub> plate (CoorsTek, 96% purity, thickness of 2.54 mm), by applying an AC high voltage (7 kV<sub>p-p</sub>) at 30 kHz by means of a STT power supply (model SG2). The electrode system was located into an airtight Plexiglas box slightly pumped with a dry diaphragm pump (Pfeiffer) to avoid overpressure (Figure 1b). The voltage applied to the electrodes was measured by means of a high voltage (HV) probe (Tektronix

P6015A, 75 MHz bandwidth, 1000 attenuation factor); the current (I) and the charge (Q) were evaluated by measuring with a Tektronix P2200 probe the voltage drop across a 50  $\Omega$  resistor and a 4.7 nF capacitor connected in series with the grounded electrode, respectively. The data were recorded by means of a digital oscilloscope (Tektronix TDS2014B). The power dissipated in the discharge was evaluated employing the Manley method and in particular the voltage-charge (V-Q) Lissajous figure.<sup>[48,51]</sup> The discharge was fed with 4 slm of Ar in mixture with 1 sccm of HMDSO and oxygen at flow rate ranging between 0 and 25 sccm ( $O_2/HMDSO$  feed ratio = 0 – 25). The gas flow rates were controlled with MKS mass flow controllers; HMDSO vapours were introduced into the reactor by an Ar stream bubbling through a liquid HMDSO reservoir kept at 30°C. The effective amount of precursor admitted into the reactor was evaluated by reservoir weight variation per unit time and, assuming an ideal gas behaviour, it was converted to flow rate expressed in sccm.

In both apparatuses a stainless steel liquid nitrogen ( $LN_2$ ) trap, located between the reactor and the pumping system (Figure 1), allowed the sampling of the compounds contained in the plasma exhaust: namely unreacted HMDSO and stable products derived from the recombination of plasma intermediates. The sampling was performed for 20 min and 30 min at low pressure and atmospheric pressure, respectively. The trap was then isolated from the system, the condensate was dissolved in acetone (Aldrich, 99.8 % purity) and analyzed by means of gaschromatography (GC) with mass spectrometric (MS) detection. The GC apparatus (GC 8000Top Thermoquest Corporation) was equipped with the capillary column Alltech AT<sup>TM</sup>-5MS (5% phenyl-95% methylpolysiloxane 0.25  $\mu m$  thick stationary phase, length of 30 m, internal diameter of 0.25 mm). The analyses were performed with 1 sccm of He as carrier gas, at 200°C injector temperature and a column temperature programmed from 30 to 200°C (temperature program: 1 min at 30°C, linear heating rate of 10°C·min<sup>-1</sup>, 1 min at 200°). Separated products were analyzed with a quadrupole mass spectrometer (Voyager, Finnigan, Thermoquest Corporation) at the interface and source temperature of 250 and

200°C, respectively. Mass spectra at 70 eV were recorded in full-scan (FS) mode in the m/z range 15–500. The products were identified by means of available libraries,<sup>[52]</sup> some species were tentatively identified through the interpretation of their mass spectra according to the typical fragmentations pattern of organosilicon compounds. The identification of some products was confirmed by the comparison of retention time and mass spectrum with standard compounds.

The quantitative analysis of identified products was performed utilizing nonane (Sigma Aldrich, 99% purity) as internal standard (IS) and considering the area of the corresponding peaks in the chromatogram acquired in FS mode. Absolute quantification was possible for by-products available as standards through calibration curves in the linear range; otherwise relative quantification was obtained. The amounts of quantified compounds is then expressed as a flow rate ( $\Phi$ ) determined by equation (1) under the assumption of ideal gas behaviour:

$$\Phi = \frac{m}{MM} \cdot V_m \cdot \frac{1}{t_{\text{sampling}}} \quad (1)$$

where  $m$  is the mass of a selected species collected with the cold trap,  $MM$  is the molecular mass,  $V_m$  is the molar volume at normal temperature and pressure conditions (22400 mL·mol<sup>-1</sup> at 273 K and 1 atm) and  $t_{\text{sampling}}$  is the exhaust sampling duration. In this work the by-products flow rates are represented after division by the monomer flow rate introduced in the reactor, i.e. 1 and 3 sccm at atmospheric and low pressure, respectively.

The extent of HMDSO utilized by the plasma process, namely the HMDSO depletion ( $\text{HMDSO}_{\text{depletion}}$ ), is calculated according to equation (2):

$$\text{HMDSO}_{\text{depletion}} = \frac{\Phi_{\text{HMDSO OFF}} - \Phi_{\text{HMDSO ON}}}{\Phi_{\text{HMDSO OFF}}} \cdot 100 \quad (2)$$

where  $\Phi_{\text{HMDSO OFF}}$  and  $\Phi_{\text{HMDSO ON}}$  are the monomer flow rates in the gaseous effluent in plasma off and plasma on conditions, respectively.



Considering the overall procedure utilized (sampling procedure, GC-MS analysis conditions, etc.) the limit of quantification (LOQ) of by-products in the exhaust was approximately  $10^{-4}$  sccm.

Deposition processes for coatings characterization were carried out for 5 min both at low and atmospheric pressure. At low pressure substrates were placed in the middle of the ground bottom electrode; while at atmospheric pressure samples were positioned on the alumina plate that covers the ground electrode both in the middle of the discharge zone (20-30 mm from the gas entrance) and downstream of the electrode area (50-60 from the gas entrance).<sup>[48]</sup>

Film chemical composition and structure were investigated by Fourier Transform Infrared (FT-IR) spectroscopy with a Bruker Equinox 55 FT-IR spectrometer. Spectra of coatings deposited on c-Si(100) substrates were recorded from 400 to 4000  $\text{cm}^{-1}$  in absorbance mode at 4  $\text{cm}^{-1}$  resolution. In order to minimize effects of water vapor and carbon dioxide, the spectrometer was purged with nitrogen for 10 min between each measurement. Baseline correction was applied to the spectra and they were then normalized to the most intense absorption band. Deposition rate was evaluated by measuring film thicknesses with a profilometer (TENCOR  $\alpha$ -step 500).

## **Results and Discussion**

### ***GC-MS investigation of the exhaust gas: qualitative analysis***

This comparative study takes into consideration two processes optimized for the deposition of  $\text{SiO}_x\text{C}_y\text{H}_z$  thin films in order to obtain powder free coatings with different carbon contents. The deposition processes were performed in a rf capacitively coupled low pressure plasma and in an atmospheric pressure filamentary DBD, both in a parallel plate electrode configuration and fed with HMDSO.

The identified by-products formed in both cases are reported in Table 1. It can be appreciated that HMDSO generates many different linear and cyclic compounds containing up to five silicon atoms. These stable species could be produced inside or outside the discharge zone from the recombination of neutral and charged reactive species formed by plasma activation. Heavier compounds (containing more than five Si atoms) are not detected since, for their low volatility, they are not collected by the LN<sub>2</sub> trap but condensate in the pipelines, while light volatile species (e.g., CO, CO<sub>2</sub>, CH<sub>4</sub>, SiH<sub>4</sub> etc.) are lost during manipulation of the condensate. Trimethylsilane is the lightest identified compound (74 amu) with boiling point of 7°C.

The species reported in Table 1 give evidence of the dissociation of Si-C, Si-O and C-H bonds in the monomer molecule, but also of the formation of new bonds: Si-H (e.g. in trimethylsilane), Si-C (e.g. in tetramethylsilane), Si-O (e.g. in trisiloxanes), C-C (e.g. ethyl groups), C-O/C=O (e.g. in trimethylsilylformiate) and Si-Si (i.e. in 2,2,4,4,5,5,7,7-octamethyl-3,6-dioxa-2,4,5,7-tetrasilaoctane). For instance, the two disiloxanes, pentamethyldisiloxane and 1,1,3,3-tetramethyldisiloxane, are reasonably formed directly from the rupture of one and two Si-C bonds of the monomer, respectively. On the other hand trimethylsilyl fragments, formed from the Si-O bond rupture in HMDSO molecules, could lead to trimethylsilane and tetramethylsilane for the formation of new Si-H or Si-C bonds, respectively. It is important to emphasize that due to the different bond energy, the cleavage of Si-O (799 kJ·mol<sup>-1</sup>) bond is more difficult than that of Si-C (318 kJ·mol<sup>-1</sup>).

The presence of species containing the dimethylsiloxane (-Me<sub>2</sub>SiO-) repeating unit confirms the occurrence of chain propagation and ring formation processes, which lead to linear and cyclic compounds with general formulas Me-(Me<sub>2</sub>SiO)<sub>n</sub>-SiMe<sub>3</sub> (n = 1 – 4) and (Me<sub>2</sub>SiO)<sub>n</sub> (n = 3 – 4), respectively. Other authors<sup>[9,10]</sup> obtained similar results by means of direct mass spectrometric characterization of low pressure RF plasmas fed with HMDSO, revealing the presence of neutral and cationic species analogous to those reported in Table 1. They detected

only linear compounds among neutral species, while positively charged fragments were found to have both linear and cyclic structures. Secondary ion mass spectrometry analysis of coatings obtained in low pressure RF plasmas fed with HMDSO showed some fragments with chemical structure similar to those detected in this work in the exhaust of HMDSO containing plasmas.<sup>[8]</sup>

The presence of trimethylsilanol and hydroxypentamethyldisiloxane (Table 1) is in agreement with what found in the gas phase by Creatore et al. by means of FT-IRAS.<sup>[16]</sup> The formation of these species is interesting in particular if the presence of silanol groups in the deposit is considered.<sup>[16,32,33,39,43]</sup>

As evident from Table 1, most of the identified species are formed both at low and at atmospheric pressure. As far as the qualitative investigation is concerned, the main differences between the two pressure conditions are:

- (i) the species with Si-H bonds are mainly present at atmospheric pressure; at low pressure only pentamethyldisiloxane is detected;
- (ii) trimethylsilylformiate ( $\text{HCOOSiMe}_3$ ), an evident oxidation product, is present only in oxygen containing feeds at LP and not at AP.

### ***GC-MS investigation of the exhaust gas: quantitative analysis***

The most abundant species under all the experimental conditions explored was the unreacted monomer. At low pressure the HMDSO depletion does not depend significantly on the feed composition (**Figure 2**), even if the  $\text{O}_2/\text{HMDSO}$  flow rate ratio is varied in a wide range (0 – 25); this indicates that under the process conditions explored, oxygen does not play a fundamental role in the activation of the monomer, which reasonably occurs mainly through electron impact.

At atmospheric pressure oxygen addition has a negative effect on the monomer depletion which decreases from 76% to 50% when the  $\text{O}_2/\text{HMDSO}$  feed ratio varies from 0 to 25. Since

a contemporaneous increase of the average power delivered to the DBD is measured (from 5.0 W to 8.2 W for O<sub>2</sub>/HMDSO feed ratio of 0 and 25, respectively), the depletion reduction is not due to a reduction of the input power.

The electrical characterization of the discharge can help to clarify the trend of monomer depletion at atmospheric pressure in Figure 2. Without O<sub>2</sub> the discharge current signal is formed by few peaks (i.e. quasi-periodical multipeak signal), the discharge is characterized by a quasi-homogeneous appearance ascribed to stochastically distributed microdischarges and only few filaments<sup>[53]</sup> are observed (poor filamentary character). At O<sub>2</sub>/HMDSO ratio of 25 the current signal is composed by many peaks and the DBD exhibits a marked filamentary behaviour characterized by numerous, intense and well-distinguished filaments.<sup>[48,51,53]</sup> This variation of the discharge character could be responsible for the reduction of monomer depletion in Figure 2. When the O<sub>2</sub>/HMDSO feed ratio is increased, for the higher filamentary character of the discharge, the plasma is less homogeneous, more concentrated in the filaments and the effective plasma volume, wherein electron impact and most chemical reactions occur, is smaller, with a consequent reduction of the overall monomer activation.

Another possibility that could explain the decrease of monomer depletion at AP is connected to the possible important role played by Ar metastables in the HMDSO activation, due to the high flow rate of Ar (4 slm) and low flow rate of reactive compounds (maximum 26 sccm). Ar metastables could be also responsible of oxygen activation and therefore when the O<sub>2</sub> content of the feed increases, Ar metastables could be mainly involved in the activation of oxygen rather than in that of HMDSO, with a consequent decrease of the HMDSO depletion.

The quantitative distribution of by-products formed by plasma activation is affected by the feed composition. For instance **Figure 3** shows a steep decrease of tetramethylsilane, pentamethyldisiloxane and octamethyltrisiloxane flow rates as a function of the O<sub>2</sub> content in the feed both at low and at atmospheric pressure. Similar trends were observed for all the

other silanes, disiloxanes as well as for linear trisiloxanes and tetrasiloxanes (i.e. oligomerization products).

As evident from Figure 3, the by-products flow rate is lower at atmospheric pressure and their distributions are different at the two pressures. For instance, at AP the most abundant product is pentamethyldisiloxane, i.e. a species with a molecular structure close to that of the starting monomer, deriving from methyl abstraction (Si-C bond rupture) from the HMDSO molecule, while at LP tetramethylsilane and octamethyltrisiloxane are more abundant than pentamethyldisiloxane, indicating the relevance of the fragmentation of Si-O bond in the HMDSO molecule and the occurrence of oligomerization reactions.

At atmospheric pressure the concentration of siloxanes with the same number of Si atoms increases with the number of methyl groups as shown for methyltrisiloxanes in **Figure 4**. Analogous considerations can not be made for LP plasmas because, as already discussed, the only specie containing the Si-H bond is pentamethyldisiloxane.

Another difference between LP and AP operation is shown by the two cyclic oligomers detected, i.e. hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane; while at AP they are present in traces (below the limit of quantification), at LP they can be quantified and show a maximum at  $O_2$ /HMDSO feed ratio of about 7. It can be also observed that the concentration of cyclic compounds at low  $O_2$ /HMDSO is lower than the correspondent linear oligomer as evident for octamethyltrisiloxane and hexamethylcyclotrisiloxane in **Figure 5**.

Also the trends of silanols are different at low and atmospheric pressure (**Figure 6**). At low pressure the trimethylsilanol and hydroxypentamethyldisiloxane exhibit a maximum as a function of the  $O_2$ /HMDSO feed ratio. At atmospheric pressure their flow rates are much lower, steeply decrease with oxygen addition and they are above the quantification limit also at  $O_2$ /HMDSO feed ratio of 25, when the other by-products are not detected. Hydroxymethhyldisiloxane, along with pentamethyldisiloxane, is the most abundant by-products in the exhaust of DBDs at low  $O_2$ /HMDSO feed ratios.

Trimethylsilylformate ( $\text{HCOOSiMe}_3$ ), has been detected only at low pressure for  $\text{O}_2/\text{HMDSO}$  feed ratio higher than 4 (Figure 6). Since its relative concentration increases with oxygen addition it is reasonable to consider this product related to oxidation reactions.

### *Thin film deposition*

**Figure 7** shows the FT-IR spectra of film deposited at LP and AP under the same experimental conditions utilized for GC-MS investigation. As expected, in both cases the film deposited without oxygen shows the typical features of silicone-like films: the intense Si-O-Si asymmetric stretching band at  $1042\text{ cm}^{-1}$ , the  $\text{Si}(\text{CH}_3)_x$  symmetric bending at  $1258\text{ cm}^{-1}$ , and the  $\text{CH}_x$  absorptions in the  $2850 - 3000\text{ cm}^{-1}$ .<sup>[1,11,14,16,18,22,48]</sup> The absorptions in the  $750 - 900\text{ cm}^{-1}$  region suggest the presence of di- and tri-substituted  $\text{Si}(\text{CH}_3)_x$  moieties.<sup>[1,11,14,16,18,22,48]</sup> The significant presence of  $\text{Si}(\text{CH}_3)_2$ , i.e. chain-propagating units, and  $\text{Si}(\text{CH}_3)_3$ , i.e. chain-terminating units, is further confirmed by the position of  $\text{Si}(\text{CH}_3)_x$  absorption at  $1261\text{ cm}^{-1}$  and  $1258\text{ cm}^{-1}$  at LP and AP, respectively. The intensity of absorption bands due to carbon-containing moieties appears to be higher at AP than at LP. This indicates that the carbon content is higher for the coatings produced at atmospheric pressure, as also confirmed by the fact that at  $\text{O}_2/\text{HMDSO}$  feed ratio of 0 an oily film is obtained for AP DBDs.

At low pressure the intensity of the IR absorptions due to carbon-containing groups (e.g.  $\text{CH}_x$  and  $\text{Si}(\text{CH}_3)_x$  at  $2850\text{-}3000\text{ cm}^{-1}$  and about  $1258\text{ cm}^{-1}$ , respectively) steeply decrease with oxygen addition and almost completely disappear at  $\text{O}_2/\text{HMDSO}$  feed ratio of 6. At atmospheric pressure the reduction of the absorptions of the carbon-containing groups with  $\text{O}_2$  addition is less important, in fact these absorptions are still visible at an  $\text{O}_2/\text{HMDSO}$  feed ratio of 25. The increase of the  $\text{O}_2$  content in the feed also results in the appearance of silanol absorptions (the broad OH absorption at  $3200 - 3600\text{ cm}^{-1}$  and the Si-OH stretching at  $930\text{ cm}^{-1}$ ) as well as in the shift of the intense Si-O-Si asymmetric stretching band to higher

wavenumbers.<sup>[1,11,14,16,18,22,48]</sup> At the O<sub>2</sub>/HMDSO feed ratio of 25 in LP plasmas, the Si-O-Si asymmetric stretching shifts to 1070 cm<sup>-1</sup> as reported for inorganic SiO<sub>2</sub>-like coatings;<sup>[1,11,14,16,18,22]</sup> while it falls at to 1050 cm<sup>-1</sup> in the case of AP DBD, due to the presence of carbon-containing groups in the films.

At atmospheric pressure the FT-IR spectra of the downstream deposits were also registered.<sup>[48]</sup> Without oxygen addition, no significant differences with respect to the film deposited inside the discharge zone are detected, while at O<sub>2</sub>-to-HMDSO ratio of 25 the deposit consists of powders with higher absorptions of CH<sub>x</sub> and Si(CH<sub>3</sub>)<sub>x</sub> groups. Also a different shape of the Si-O-Si asymmetric stretching signal is evident indicating a less dense and ordered network with respect to the coating deposited in the discharge zone.<sup>[48]</sup>

Under the experimental conditions explored in this study the deposition rate varies between 150 to 120 nm min<sup>-1</sup> at atmospheric pressure (oily coating are obtained at O<sub>2</sub>/HMDSO feed ratio of 0) and between 45 and 61 nm min<sup>-1</sup> at low pressure.

## ***Discussion***

The above results allow to make some considerations on cold plasmas containing HMDSO generated both at low and atmospheric pressure. In spite of the completely different experimental conditions in which the processes are carried out (e.g. pressure, dissipated power, excitation frequency, gas residence time in the discharge, etc.), the quali-quantitative investigation of the exhaust gas as a function of O<sub>2</sub>/monomer feed ratio allows to outline similarities and differences concerning the overall reaction mechanism for the two approaches both optimized for thin film deposition.

Considering the results on monomer depletion it seems that oxygen is not significantly involved in HMDSO activation; in fact at LP, O<sub>2</sub> addition does not enhance significantly the monomer activation, while at AP it has a negative effect on HMDSO depletion likely due to the change in discharge regime as well as to the reduction of monomer activation by

metastable Ar. Results show that in spite of the completely different experimental conditions in which the processes are carried out at low O<sub>2</sub>/HMDSO feed ratio LP plasmas and AP DBDs are characterized by the same monomer depletion. This could be due to a combination of effects related to the residence time and power density: while at atmospheric pressure the discharge residence time is lower than at low pressure (0.08 s at AP vs. 0.4 s at LP), the power density is much higher (1.0 – 1.6 W cm<sup>-3</sup> at AP vs 0.05 W cm<sup>-3</sup> at LP).

Table 1 shows that in both cases almost the same by-products are formed; most of them exhibit the –(SiO)– backbone, and, in particular, the –Me<sub>2</sub>SiO– and/or the –MeHSiO– repeating units. The main differences between the two pressure conditions are the formation of species with Si-H bonds mainly at atmospheric pressure (at low pressure only pentamethyldisiloxane is present) and of trimethylsilylformate detected only at LP in oxygen containing feed.

Despite the comparable values of monomer depletion (in particular at low O<sub>2</sub>/HMDSO feed ratios), the flow rate of by-products is higher at LP than at AP and the relative distribution of by-products is different, highlighting the importance of different reaction pathways under the two pressure conditions.

The GC-MS results allow to draw the following conclusions:

### **Low pressure operation**

- (i) The major content of tetramethylsilane and octamethyltrisiloxane in the exhaust indicates that the Si-O bond cleavage in HMDSO is important (trimethylsilane formation) as well as oligomerization reactions (e.g. formation of octamethyltrisiloxane).
- (ii) The decrease of the flow rates of silanes and linear siloxanes as well as the appearance of the trimethylsilylformate with oxygen addition are due to oxidation reactions.



- (iii) The appearance of silanols in the coatings with increasing the O<sub>2</sub>/HMDSO feed ratios correlates with the fact that silanols are the most abundant quantified by-products at high O<sub>2</sub>/HMDSO feed ratios. This evidence can be explained in different ways, for instance: a) the oxygen favours the formation of silanols both in the gas phase (homogeneous reactions) and in the coatings (heterogeneous reactions); b) the silanols formed in the plasma phase can contribute to film growth; c) some silanols formed at the coating surface can be released in the gas phase by energetic ion bombardment.

### **Atmospheric pressure operation**

- (i) Since at low oxygen content the most abundant species are pentamethyldisiloxane and hydroxypentamethyldisiloxane, the Si-C bond dissociation can be considered the most important monomer activation pathway, leading to the formation of pentamethyldisiloxanyl fragments (i.e. Me<sub>3</sub>SiOSiMe<sub>2</sub>). The dangling bond left after methyl loss can be saturated by H atoms or OH radicals, resulting in Si-H and Si-OH bond formation and, therefore, to pentamethyldisiloxane or hydroxypentamethyldisiloxane, respectively.
- (ii) Also in this case the concentration decrease of by-products with oxygen addition is due to oxidation reactions.
- (iii) The fact that any Si-OH absorption can not be detected in the FT-IR spectra of the coatings when the silanol concentration in the exhaust is maximum (i.e. without oxygen addition to the feed) indicates that the Si-OH content in the coating is not correlated to that in the exhaust. This suggests that the silanols formed in the plasma phase are not incorporated in the deposit and that the Si-OH groups in the deposits are generated mainly through heterogeneous reactions on the film surface during the growth process.
- (iv) Since a mass balance of the overall monomer utilization can not be performed because, for instance, it is not possible to estimate the overall fraction of HMDSO converted into deposit (specially outside the electrode region) and into powders downstream and in the

pipeline, the justification of the lower by-products flow rates observed at AP despite the similar values of HMDSO depletion at LP and AP is not straightforward. However the following points should be taken into consideration: the different monomer flow rate at low and atmospheric pressure (3 and 1 sccm, respectively), the higher deposition rates observed at AP and the formation of powders downstream the atmospheric pressure plasma.

## Conclusion

In this paper we have reported on the GC-MS investigation of the exhaust gas of both low pressure and atmospheric pressure cold plasmas fed with HMDSO, O<sub>2</sub> and Ar utilized for the deposition of SiO<sub>x</sub>C<sub>y</sub>H<sub>z</sub> thin films without powders and with variable chemical composition.

At low O<sub>2</sub>/HMDSO feed ratio similar monomer depletion was observed at low and atmospheric pressure and oxygen addition did not seem significantly involved in HMDSO activation.

At low and atmospheric pressure, HMDSO generates many different linear and cyclic compounds. The analytical approach utilized allowed the detection in the exhaust of by-products containing up to five silicon atoms, with quantitative distribution highly affected by feed composition and pressure conditions (the concentrations are lower at atmospheric pressure). For all the silanes, siloxanes, linear disiloxanes and trisiloxanes a concentration decrease with oxygen addition to the feed was revealed.

At atmospheric pressure methyl abstraction from a HMDSO molecule seems to be an important route for monomer activation, while at low pressure Si-O bond cleavage appears to be more important. Silanols are the most abundant quantified by-products at high O<sub>2</sub>/HMDSO feed ratios both at low and atmospheric pressure. While at low pressure there is a correlation between the amount of silanols in the exhaust and in the coatings, at atmospheric pressure the two quantities are not connected. At atmospheric pressure the silanols formed in the plasma

phase are not incorporated in the deposit; heterogeneous reactions on the film surface during the growth process are reasonably responsible of silanol formation in the film.

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**Keywords:** hexamethyldisiloxane (HMDSO), plasma-enhanced chemical vapor deposition (PE-CVD), low-pressure discharges, dielectric barrier discharges (DBD), gaschromatography-mass spectrometry (GC-MS)

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## Figure captions

*Figure 1.* Schematic representation of the plasma reactors and of the sampling system: (a) low pressure and (b) atmospheric pressure DBD apparatuses.

*Figure 2.* HMDSO depletion as a function of the O<sub>2</sub>/HMDSO feed ratio for low pressure and atmospheric pressure plasma processes.

*Figure 3.* Trends of the flow rate of tetramethylsilane, pentamethyldisiloxane and octamethyltrisiloxane as a function of the O<sub>2</sub>/HMDSO feed ratio at LP and AP.

*Figure 4.* Atmospheric pressure operation: flow rate of octamethyltrisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane and 1,1,3,3,5,5-hexamethyltrisiloxane as a function of the O<sub>2</sub>/HMDSO feed ratio.

*Figure 5.* Low pressure operation: octamethyltrisiloxane and hexamethylcyclotrisiloxane flow rates as a function of the O<sub>2</sub>/HMDSO feed ratio.

*Figure 6.* Flow rates of trimethylsilanol and hydroxypentamethyldisiloxane as a function of the O<sub>2</sub>/HMDSO feed ratio at LP and AP, and relative concentration of trimethylsilylformiate at LP.

*Figure 7.* FT-IR spectra of thin film deposited at LP and AP (HMDSO/O<sub>2</sub> feed ratios of 0, 6 and 25).

Table 1. Identified species detected in the exhaust gas of low pressure and atmospheric pressure HMDSO-containing plasmas (Compound identified by mass spectra in the available libraries (<sup>L</sup>),<sup>[52]</sup> mass spectrum interpretation (MS) and standard analysis (S)).

	<b>Compound</b>	<b>Formula</b>	<b>LP</b>	<b>AP</b>
	Hexamethyldisiloxane <sup>L,S</sup>	Me <sub>3</sub> Si-O-SiMe <sub>3</sub>	✓	✓
1	Trimethylsilane <sup>L</sup>	SiMe <sub>3</sub> H		✓
2	Tetramethylsilane <sup>L,S</sup>	SiMe <sub>4</sub>	✓	✓
3	Ethyltrimethylsilane <sup>L</sup>	SiEtMe <sub>3</sub>	✓	✓
4	Trimethylsilanol <sup>L</sup>	SiMe <sub>3</sub> OH	✓	✓
5	Trimethylsilylformiate <sup>L</sup>	HCOOSiMe <sub>3</sub>	✓	
6	1,1,3,3-Tetramethyldisiloxane <sup>L,S</sup>	Me <sub>2</sub> HSi-O-SiMe <sub>2</sub> H		✓
7	Pentamethyldisiloxane <sup>L,S</sup>	Me <sub>3</sub> Si-O-SiMe <sub>2</sub> H	✓	✓
8	Ethylpentamethyldisiloxane <sup>L</sup>	Me <sub>3</sub> Si-O-SiEtMe <sub>2</sub>	✓	✓
9	Hydroxypentamethyldisiloxane <sup>MS</sup>	Me <sub>3</sub> Si-O-SiMe <sub>2</sub> OH	✓	✓
10	1,1,3,3,5,5-Hexamethyltrisiloxane <sup>L</sup>	H-(Me <sub>2</sub> SiO) <sub>2</sub> -SiMe <sub>2</sub> H		✓
11	Hexamethylcyclotrisiloxane <sup>L,S</sup>	(Me <sub>2</sub> SiO) <sub>3</sub>	✓	✓
12	1,1,1,3,5,5,5-Heptamethyltrisiloxane <sup>L,S</sup>	Me <sub>3</sub> Si-O-SiMeH-O-SiMe <sub>3</sub>		✓
13	1,1,1,3,3,5,5-Heptamethyltrisiloxane <sup>L</sup>	Me-(Me <sub>2</sub> SiO) <sub>2</sub> -SiMe <sub>2</sub> H		✓
14	Octamethyltrisiloxane <sup>L,S</sup>	Me-(Me <sub>2</sub> SiO) <sub>2</sub> -SiMe <sub>3</sub>	✓	✓
15	1-Ethyl-1,1,3,3,5,5,5-heptamethyltrisiloxane <sup>MS</sup>	Et-(Me <sub>2</sub> SiO) <sub>2</sub> -SiMe <sub>3</sub>	✓	✓
16	3-Ethyl-1,1,1,3,5,5,5-heptamethyltrisiloxane <sup>MS</sup>	Me <sub>3</sub> Si-O-SiEtMe-O-SiMe <sub>3</sub>	✓	✓
17	Octamethylcyclotetrasiloxane <sup>L,S</sup>	(Me <sub>2</sub> SiO) <sub>4</sub>	✓	✓
18	1,1,1,3,3,5,7,7,7-Nonamethyltetrasiloxanes <sup>MS</sup>	Me-(Me <sub>2</sub> SiO) <sub>2</sub> -SiMeH-O-SiMe <sub>3</sub>		✓
19	1,1,1,3,3,5,5,7,7-Nonamethyltetrasiloxanes <sup>MS</sup>	Me-(Me <sub>2</sub> SiO) <sub>3</sub> -SiMe <sub>2</sub> H		✓
20	Decamethyltetrasiloxane <sup>L,S</sup>	Me-(Me <sub>2</sub> SiO) <sub>3</sub> -SiMe <sub>3</sub>	✓	✓
21	2,2,4,4,5,5,7,7-octamethyl-3,6-dioxa-2,4,5,7-tetrasilaoctane <sup>L</sup>	Me <sub>3</sub> Si-O-SiMe <sub>2</sub> -SiMe <sub>2</sub> -O-SiMe <sub>3</sub>	✓	✓
22	Dodecamethylpentasiloxane <sup>L</sup>	Me-(Me <sub>2</sub> SiO) <sub>4</sub> -SiMe <sub>3</sub>	✓	✓



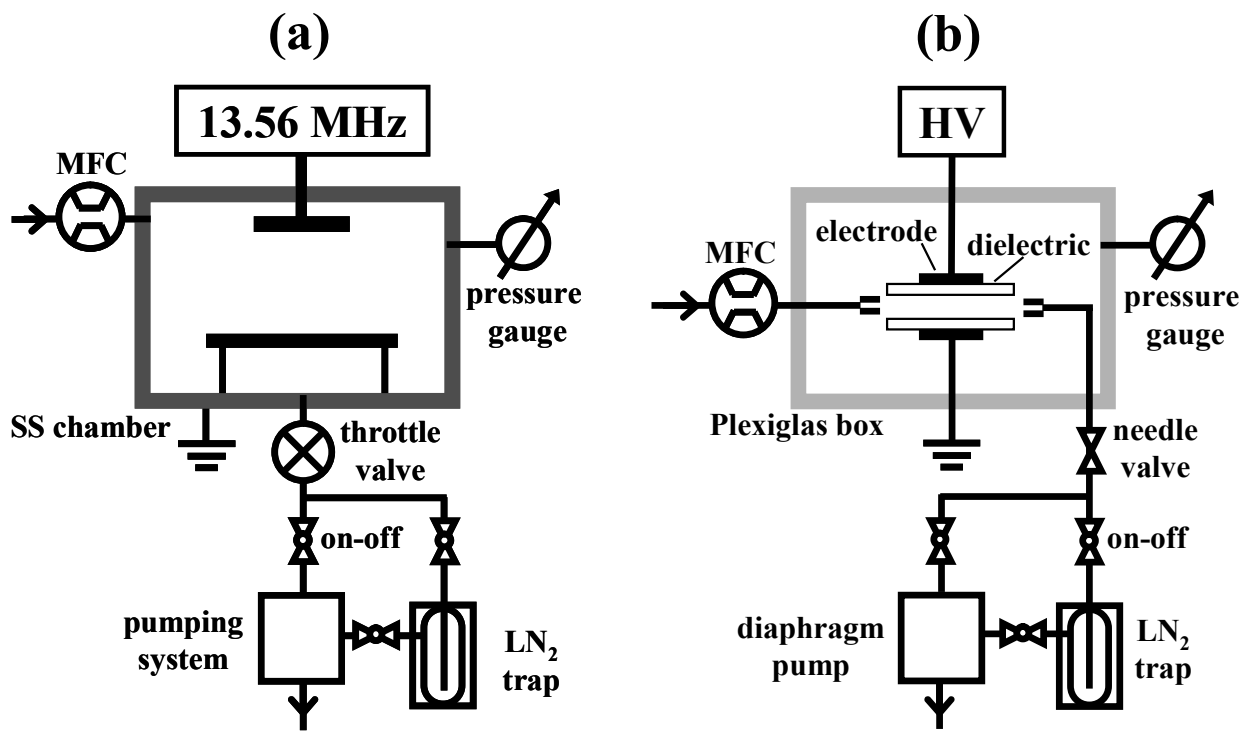


Figure 1

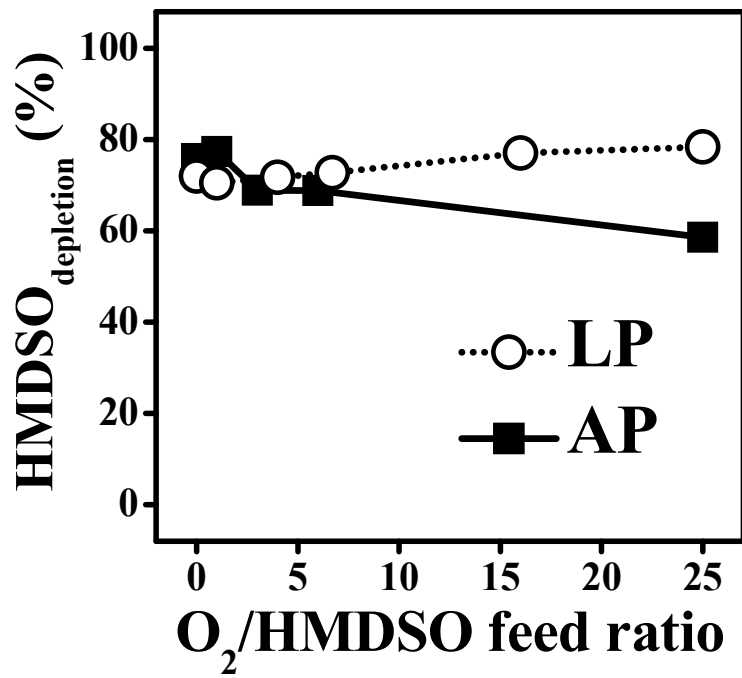


Figure 2

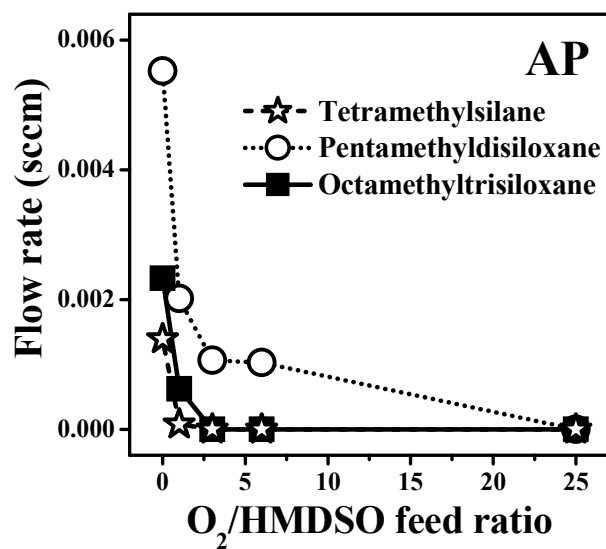
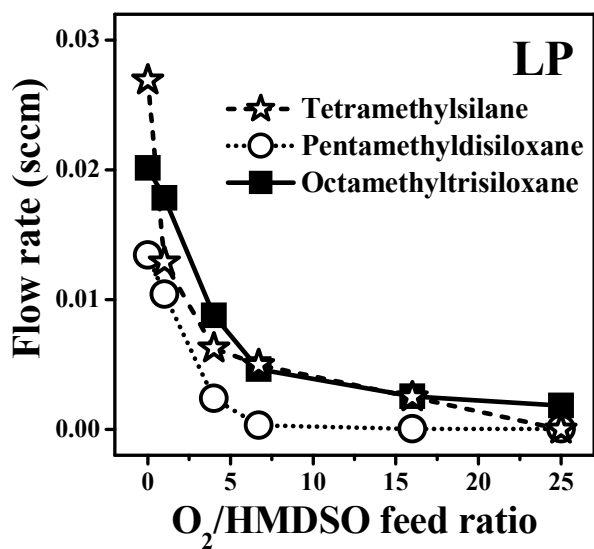


Figure 3

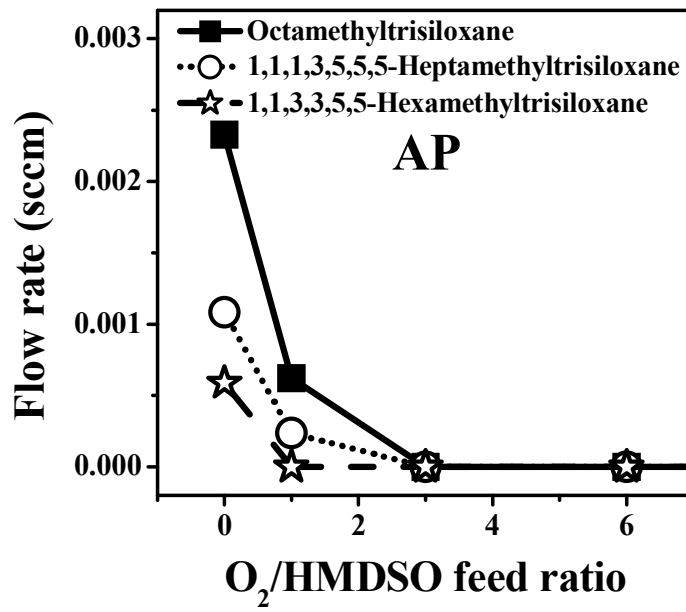


Figure 4

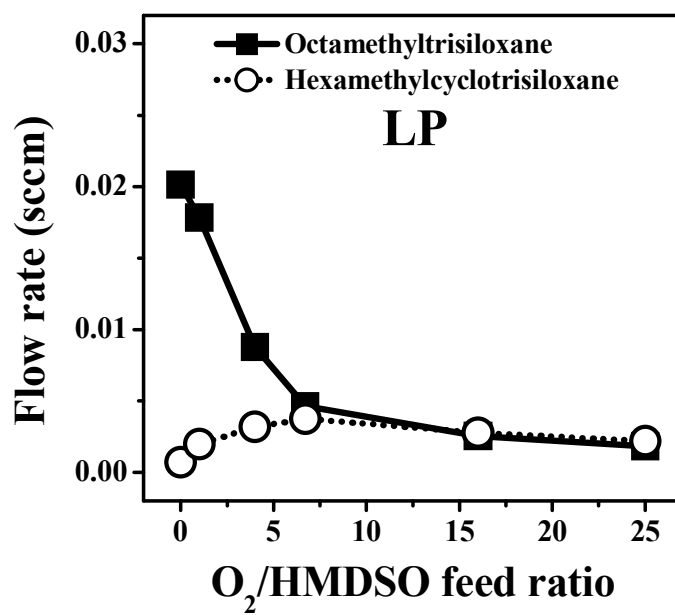


Figure 5

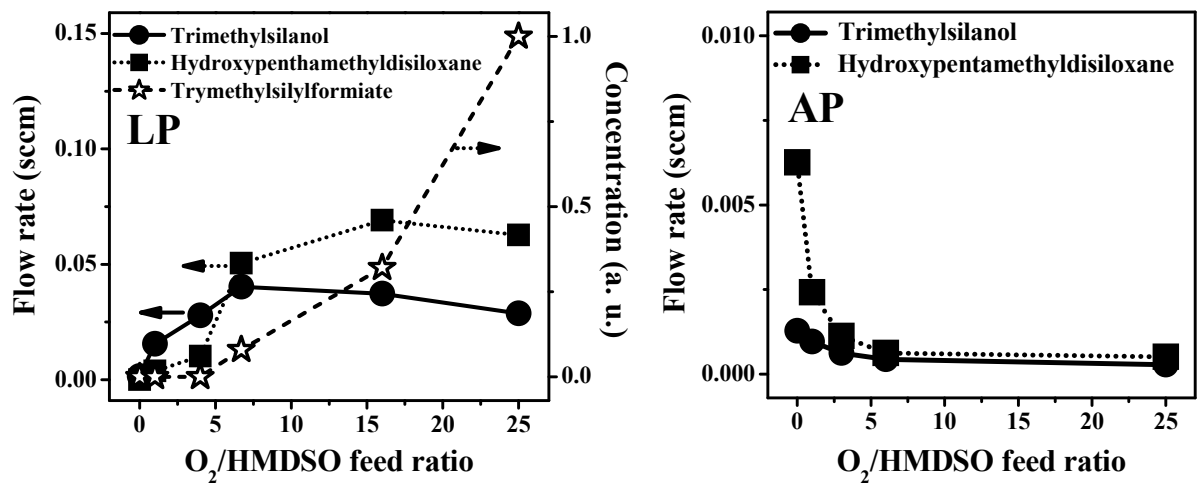


Figure 6

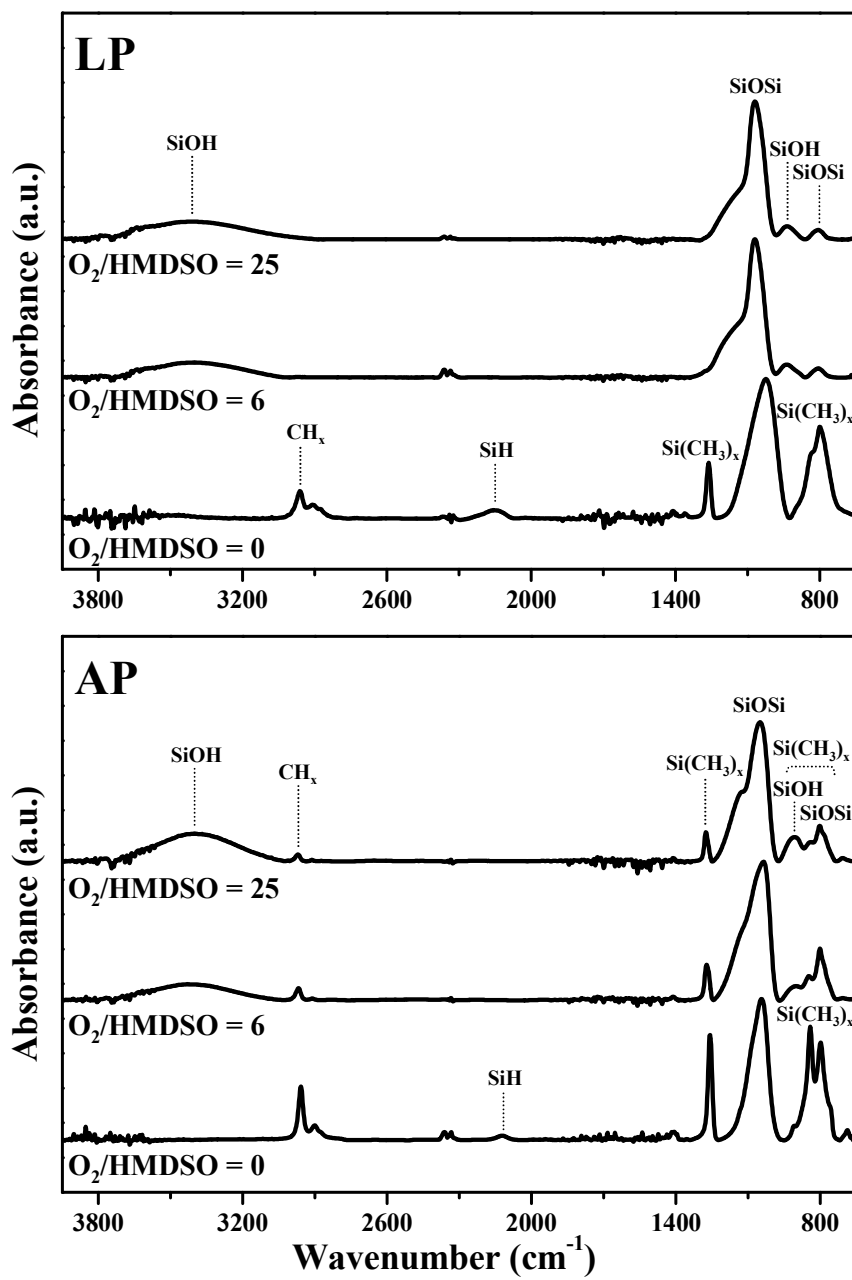


Figure 7

## Text and Figure for the Table of Contents

In this work we report results on the GC-MS investigation of low pressure rf glow discharges and atmospheric pressure DBDs fed with HMDSO-O<sub>2</sub>-Ar gas mixtures. The effect of feed composition on monomer depletion and on the quali-quantitative distribution of by-products (e.g. silanes, silanols, linear and cyclic siloxanes) was investigated in order to draw a comparison between these two processes utilized for the PE-CVD of SiO<sub>x</sub>C<sub>y</sub>H<sub>z</sub> thin films.

