

OES and FTIR diagnostics of HMDSO/O₂ gas mixtures for SiO_x deposition assisted by RF plasma

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Abstract

A capacitively coupled radiofrequency PACVD process for SiO_x deposition using oxygen-hexamethyldisiloxane (HMDSO) gas mixtures is characterised under a pressure of 1 Torr. Optical emission spectroscopy and FTIR absorption spectroscopy analyses are performed for different values of the dilution ratio X_{hm} of HMDSO in oxygen. The power delivered to the plasma is set high enough (5 W/cm²) to have a strong fragmentation of the monomer by electron impact. Two different regimes are then observed depending whether X_{hm} exceeds or not 20 vol.%. Below this critical value, the monomer fragments are strongly oxidised. Above, densities of CO and CH₄ molecules strongly decrease. Trends observed in the evolution of the species concentrations as a function of X_{hm} better agree the results by Aumaille et al. [K. Aumaille, C. Vallée, A. Granier, A. Goulet, F. Gaboriau, G. Turban, Thin Solid Films 359 (2000) 188] than those by Lamendola et al. [R. Lamendola, R. d'Agostino, F. Fracassi, Plasmas Polym. 2 (1997) 147] despite the pressure set in this work is closer to that used by the latter.

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1. Introduction

Capacitively coupled radiofrequency glow discharges (CCRF) are widely used in surface treatment processes. Plasmas of that kind, created in the vapor of a metallorganic compound mixed with oxygen, are studied to improve the deposition of plasma polymers or oxide thin films depending on the ratio of the partial pressures of gases. For example, SiO_x thin films can be deposited in an O₂/HMDSO CCRF plasma. The O₂/HMDSO ratio can be varied from 0 to 30, leading to different properties and characteristics of the SiO_x layers [1–4]. Although such processes have been studied for many years, they are not completely understood and the scaling up of the reactors still remains difficult to achieve. Indeed, most of the studies dealing with O₂/HMDSO CCRF plasmas are performed in

laboratory-scale devices and the complexity of such plasmas does not allow an easy up scaling. Resorting to the process modeling is often the cheapest way to overcome this problem [5]. However, the complete modeling of such complex processes cannot be achieved without the help of an experimental approach to get reliable data about the species that govern the discharge behavior.

Moreover, plasmas containing organic molecules are not easy to analyze, owing to the poor knowledge of the dissociation processes of such molecules. In DECR plasmas, at low pressure, it was shown that the organic precursor is totally broken into its constituent atoms [6–8]. However, the dissociation of the parent molecule may be not complete whether the pressure is increased or electron density and temperature are lower, as this is the case in RF discharges. Moreover, the chemistry of HMDSO plasmas is complex and the polymerization of the organic precursor may arise creating thus macromolecules [9].

In the case of O₂/HMDSO plasmas, previous works [1,10] have shown comparable trends on the behavior of

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carbon- and oxygen-containing species observed by optical emission spectroscopy (OES) and Fourier-transform infrared absorption spectroscopy (FTIRAS). Both of them observe a transition of regime close to 20% of HDMSO in O₂. Nevertheless, some discrepancies in the results obtained by these authors can be noticed. Lamendola et al. [1] have found that the densities of OH, CO and H were almost constant for O₂/HDMSO ratios greater than 5 (i.e., below 20% of HDMSO in O₂), whereas Aumaille et al. [10] have observed a strong decrease in these densities. On the contrary, the density of SiO was found to be high by the former whereas the latter could not measure it below 20% of HDMSO in O₂. The influence of the total pressure on those results is probably the main reason why these discrepancies exist (50–100 mTorr in Ref. [1] and only 2 mTorr in Ref. [10]).

The results reported in this paper attempt to better understand the kinetic processes in these plasmas, especially at high dilution of the monomer. The comparative study by OES and FTIRAS when varying the HDMSO dilution rate allows us to shed light on some kinetic processes leading to the dissociation of the monomer and to link the behavior of the observed species to the film composition. This paper is thus organised as follows. The experimental arrangement and the observed transitions and absorption bands are first presented. The results obtained from OES and FTIRAS measurements are reported and discussed in the next section.

2. Experimental

2.1. Plasma source

Experiments were carried out in a capacitively coupled radiofrequency (13.56 MHz) plasma device. The cylindrical vacuum chamber (Fig. 1) is 300 mm in diameter and 350 mm in height. The two electrodes are 50-mm-diameter stainless-steel discs that face one other at a distance of 40 mm. One of the electrodes is grounded while a RF generator powers the other one through an RF matching network. The experiments are performed using a power ranging from 50 to 150 W. Most of the results are given at 100 W (i.e., 5 W/cm²). It is high enough to ensure a strong dissociation of the monomer and it is similar to power densities used by Refs. [1,10]. Oxygen gas is introduced in the chamber through a mass flow controller. The HDMSO liquid monomer is placed in a temperature-controlled container. The amount of HDMSO injected in the close vicinity of the grounded electrode is set by a needle valve previously calibrated to control the monomer flow rate in the reactor. The working pressure is kept constant at 1 Torr (133 Pa).

2.2. Plasma diagnostics

For the purpose of plasma diagnostics, the chamber is equipped with different view-ports allowing the plasma analysis by means of optical emission spectroscopy (quartz windows) and Fourier transform infrared absorption spectroscopy (CaF₂ windows).

The light emitted by the plasma is collected by an optical fibre and directed towards a 550-mm focal length monochromator equipped with a 1200 groves/mm holographic grating and a CCD detector. This apparatus allows us to study emission lines in the range 300–900 nm. The main transitions that are observed in an O₂/HDMSO plasma are reported in Table 1 with the corresponding wavelengths. A typical spectrum of an O₂/HDMSO plasma is presented in Fig. 2. It must be noted that our experimental tool does not permit us to observe wavelengths below 300 nm. The main emissions of SiO radical, C and Si atoms occurring at 241.3, 247.8 and 251.6 nm, respectively, could not be measured. On the other hand, whatever the HDMSO dilution rate, no CH line has ever been observed. In particular, the strong emission due to the transition $A^2\Delta-X^2\Pi$ (0–0 band head at 431.4 nm), which is characteristic of the presence of CH radicals [11], could not be detected under our pressure conditions.

For absorption measurements, we use a standard FTIR spectrometer with a remote MCT detector located on the opposite side of the plasma chamber. The spectral resolution is 2 cm⁻¹ and each absorption spectrum is acquired over 40 scans to improve the signal to noise ratio. No purging of the optical path was carried out. Therefore, it is assumed that the composition of the surrounding atmosphere does not change over the measurement duration. Thus, the reference spec-

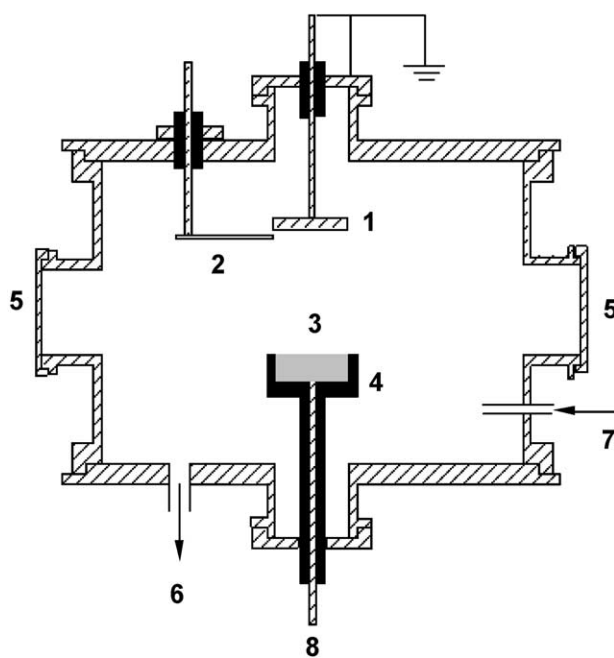


Fig. 1. Schematic drawing of the plasma chamber. 1=grounded electrode; 2=HMDSO inlet; 3=powered electrode; 4=insulated electrode mount; 5=windows; 6=pumping unit; 7=O₂ gas inlet; 8=RF power.

Table 1
Main transitions observed by optical emission spectroscopy

Species	Transition	Wavelength (nm)
CO	$B^1\Sigma^- - A^1\Pi(v, v')$ (0,0)	451.1
	-id- (0,1)	483.5
	-id- (0,2)	519.8
	-id- (0,3)	561.0
	-id- (0,4)	608.0
	-id- (0,5)	662.0
OH	$A^2\Sigma^+(v=0) - X^2\Pi(v'=0)$	306.4
O	$^5P - ^5S_o$	777
	$^3P - ^3S_o$	844
H	$H_\beta: H(n=4) \rightarrow H(n=2)$	486.1
	$H_\alpha: H(n=3) \rightarrow H(n=2)$	656.3
H ₂	Fulcher $\alpha: H_2(d^3\Pi_u - a^3\Sigma_g^+)$	570–650

trum (plasma chamber pumped down to 10^{-3} Torr) and the gas phase spectra (plasma on or off) are acquired with the same surrounding contamination. This last remark implies that the observation of absorption bands of CO₂ and OH, which are usually known as impurities, really indicates something that occurs inside the plasma chamber.

Owing to the CaF₂ windows, no absorption of the plasma species can be investigated below 1000 cm^{-1} (above 10^4 nm). The observed absorption bands and corresponding chemical bonds are presented in Table 2 with their wave numbers and vibration modes.

3. Results and discussion

3.1. Optical emission spectroscopy of the plasma

The variations of the line intensities corresponding to the optical transitions reported in Table 1 with the monomer dilution ratio ($X_{\text{hm}}=100$ [HMDSO]/([O₂]+[HMDSO])), are reported in Fig. 3. The RF power is 100 W. At this point, we

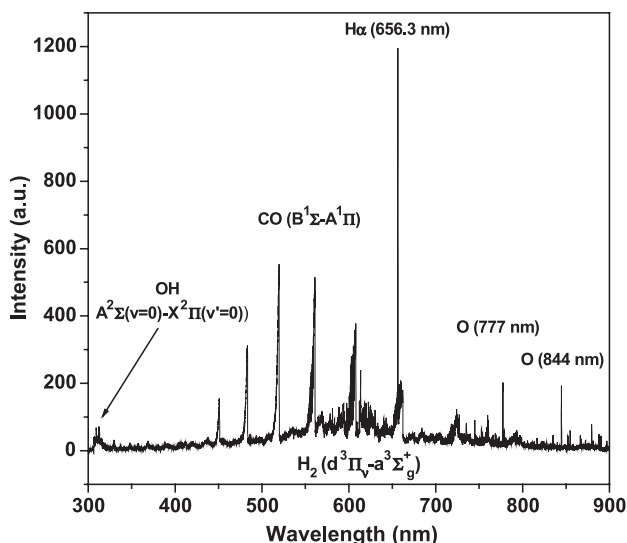


Fig. 2. OES spectrum of an O₂-10% HMDSO plasma; RF power=100 W.

Table 2
Vibration modes investigated by FTIR absorption spectroscopy

Species	Vibrating mode	Wave number (cm ⁻¹)
H ₂ O	OH stretching	3800–3400
		3250
CH ₄	CH ₃ stretching	3018
CH ₃	C–H: asym. stretching	2966
CH ₃	C–H: sym. stretching	2913
CO ₂	Asym. stretching	2340
CO	Stretching	2140
CO ₂ H ₂	C=O stretching	1783
COH ₂	C=O stretching	1745
H ₂ O	OH bending	1800–1400
Si(CH ₃) _x	Sym. stretching	1263
Si–O–Si	Asym. stretching	1072

must note that the line intensity can be directly connected to the density of the radiating species only if both the electron density and temperature are assumed unchanged when changing the gas feed composition. This is likely the case as reported by other authors [1,4]. Similar works performed in O₂/TEOS plasmas [12] reported a variation in electron density from $1.6 \times 10^{10}\text{ cm}^{-3}$ down to $3.5 \times 10^{10}\text{ cm}^{-3}$ and an electron temperature in the range 3–5.5 eV for a concentration of TEOS ranging from 14% to 0%, respectively. Moreover, probe measurements carried out in our experimental device for two different values of X_{hm} showed that the electron density remains nearly unchanged and the electron temperature varies by a factor 1.1 when changing X_{hm} from 5% to 11%. Consequently, the results presented below are discussed with the reasonable assumption of rather constant electron density and temperature.

The behaviour of CO, OH and H is similar to that already reported by Aumaille et al. [10]. The increase with X_{hm} for high dilution ratios is followed by a decrease at low dilution ratios. The value of X_{hm} corresponding to the maximum in density is almost the same than that reported by the previous

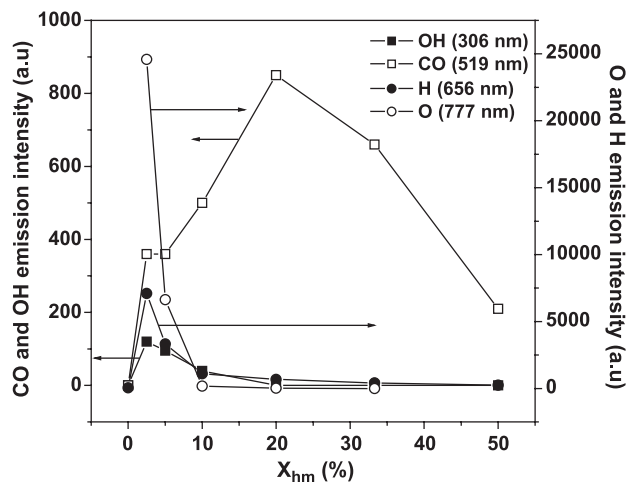


Fig. 3. Variation of O, OH, CO and H line intensity as a function of the amount X_{hm} of HMDSO in the gas mixture.

authors. The behaviour depicted in Fig. 3 exhibits two different regimes.

- For $X_{\text{hm}} < 20\%$, the intensity of the transition at 777 nm of atomic oxygen decreases sharply as soon as the organic precursor is introduced in the plasma chamber while the transition at 519 nm of carbon monoxide increases with X_{hm} . As it will be confirmed later by FTIR measurements, oxygen atoms, which are produced by electron impact in the discharge, react quickly with carbon containing species issued from the dissociation of HMDSO. They mainly form CO radicals. Consequently, the emission line intensity of O-atoms decreases to reach zero for X_{hm} close to 10%, as already reported by other authors [1,10,13].

- For $X_{\text{hm}} \geq 20\%$, the dilution of HMDSO in oxygen is low and the only species observed by OES, among those under study, are mainly CO radicals and H-atoms that decrease with increasing X_{hm} . This may be due to two effects that probably occur simultaneously. On the one hand, the atomic species (H, C, O) are consumed to synthesize bigger molecules such as formic acid (CO_2H_2) or formaldehyde (COH_2). In fact, as already mentioned, oxygen atoms are consumed by C containing species (especially CH_x) to mainly create CO and CO_2 . Then, the loss in O atom density induces a lower production of carbon oxide species, this latter being involved in the creation of large molecules. On the other hand, the dissociation of the monomer and of O_2 is certainly lower at high values of X_{hm} .

3.2. FTIR absorption analyses of the gas phase

FTIR absorption analyses of a pure HMDSO gas, with the plasma off and on for two different RF powers (100 and 150 W) were first performed. The respective spectra are

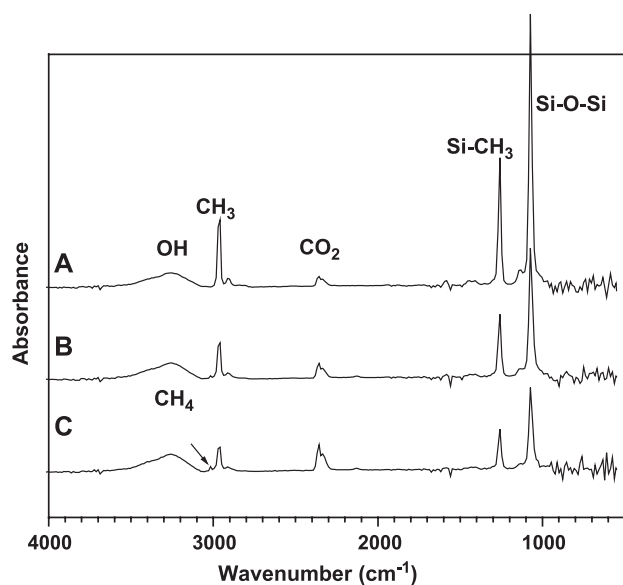


Fig. 4. FTIR absorption spectra of pure HMDSO. (A) plasma off; (B) plasma 100 W; (C) 150 W.

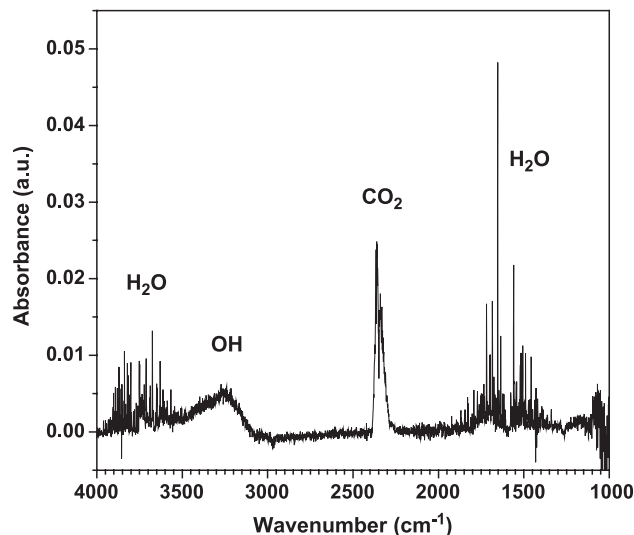


Fig. 5. FTIR absorption spectra of pure oxygen plasma. RF power=100 W.

reported in Fig. 4. The first comment concern the presence of CO_2 and OH absorption bands in the plasma-off spectrum (Fig. 4A) Taking into account the above-mentioned remark (see Section 2.2), this indicates that these species may be introduced inside the reactor as impurities within the oxygen and HMDSO gases. Moreover, the broad shape of the OH band is more characteristic of OH group in solid than free OH radical. This may be due to the hydrolysis of HMDSO molecule, thus leading to large polymeric molecules in the chamber atmosphere.

As one could expect it, the absorption bands that are the fingerprint of CH_3 , $\text{Si}(\text{CH}_3)_x$, SiOSi in the HMDSO molecule decrease when the plasma is set on and the RF power is increased. A higher dissociation of the precursor and of its by-products occurs. Indeed, from these spectra, the amount

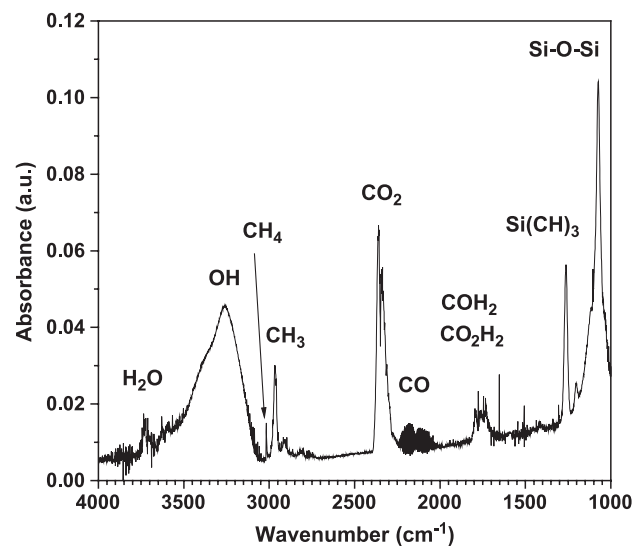


Fig. 6. FTIR absorption spectra of O_2 -10% HMDSO plasma. RF power=50 W.

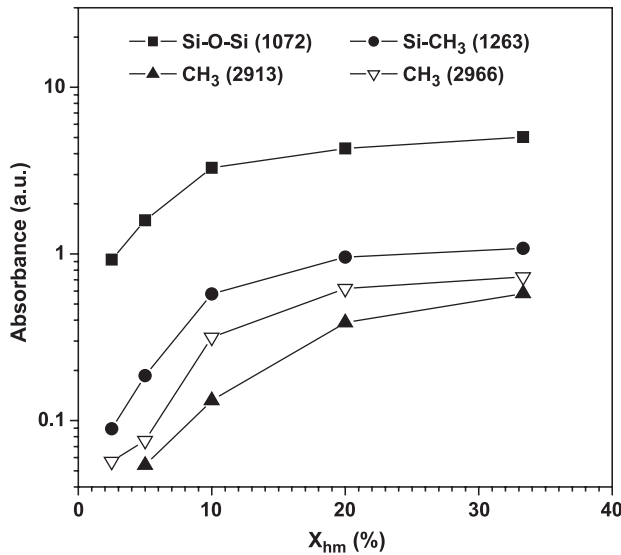


Fig. 7. Variation of the area of different absorption bands (CH_3 , $\text{Si}(\text{CH}_3)$, SiOSi) as a function of the amount X_{hm} of HMDSO in the gas mixture. RF power=100 W.

of HMDSO that is dissociated may be estimated from the ratio of the absorption peaks with and without plasma:

$$\text{HMDSO}_{\text{diss}} = (A_o - A)/A_o$$

where A_o stands for the area of the absorption peak when the plasma is off and A is the area of the same peak with the

plasma on. Applying the above formula to the absorbance peak of Si-O-Si at 1072 cm^{-1} or that of $\text{Si}(\text{CH}_3)_x$ at 1263 cm^{-1} leads to $\text{HMDSO}_{\text{diss}} = (45 \pm 3)\%$ at a power of 100 W, increasing to $(66 \pm 4)\%$ at 150 W.

The absorption bands of OH , CO_2 and H_2O are more intense in plasma on than in plasma off. In fact, these molecules are synthesised by the recombination of the species created by the dissociation of the monomer.

In a pure oxygen plasma, only H_2O , OH and CO_2 are observed (Fig. 5). These species are issued from residual impurities on the reactor walls, which are removed as soon as the plasma is powered on.

A typical FTIR absorption spectrum of an O_2/HMDSO plasma is represented in Fig. 6 for a dilution ratio $X_{hm} = 10\%$ and a RF power equal to 50 W. When the HMDSO content increases, the absorbance due to the bonds belonging to the precursor increases too as depicted in Fig. 7. Nevertheless, the variation of the different bands is not proportional to X_{hm} but is limited by a saturation level. It means that either the plasma parameters (electron density and temperature) are affected by the HMDSO content or that oxygen plays a role in the kinetics of dissociation of the monomer. The bonds of species that are not issued directly from the HMDSO dissociation such as CH_4 , CO and OH (Fig. 8) behave differently and exhibit a maximum value for X_{hm} close to 10–20% while CO_2 reaches a constant level for $X_{hm} > 20\%$. It results from a lower efficiency of the HMDSO dissociation processes that involve electron collision and is

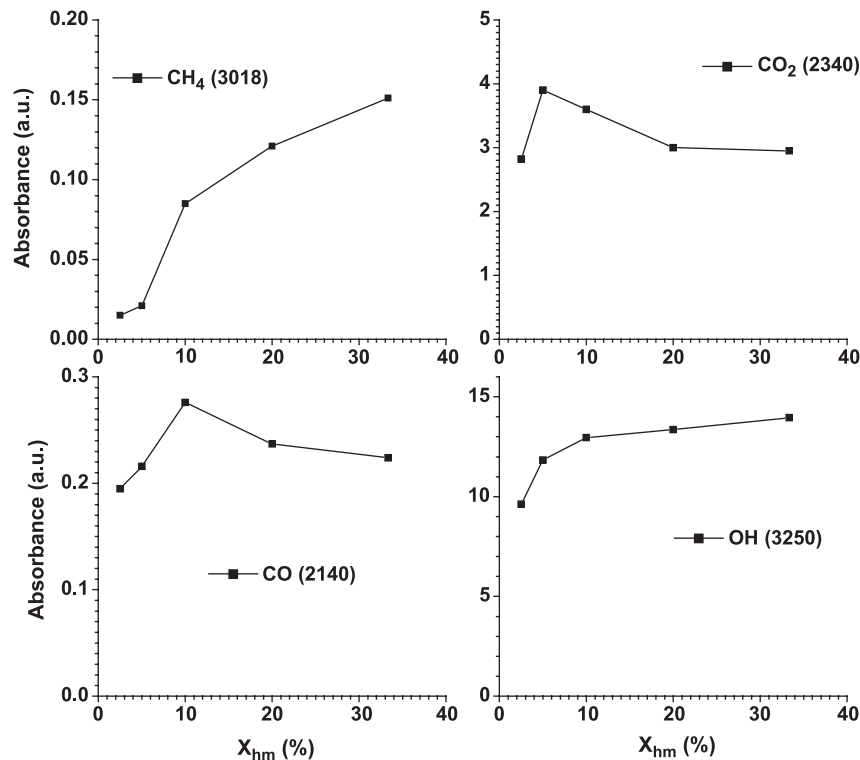
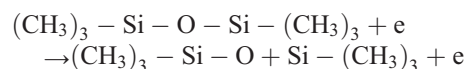


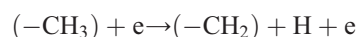
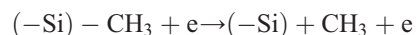
Fig. 8. Variation of the area of different absorption bands (OH , CO_2 , CH_4 , CO) as a function of the amount X_{hm} of HMDSO in the gas mixture. RF power=100 W.

dependant on the O₂/HMDSO ratio. Note that the behaviour of CO₂ and OH that do not increase linearly with X_{hm} indicates that these species are issued from plasma processes and not only from impurities coming from outside with the plasma gases.

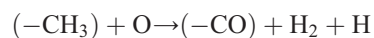
From the previous observation, it is possible to suggest the following steps in the fragmentation of the monomer. The Si–O bond (8.3 eV) is broken by high-energy electron collisions:



while Si–C (4.5 eV) and C–H (3.5 eV) bonds are broken by lower energy electrons:



However, at high dilution of HMDSO, H atoms are preferentially created through the dominant oxidation kinetics of CH₃ to create CO and H:



($k=5.6 \times 10^{-5}$ cm³/s [14]). This also explains the decrease in CO and OH with increasing X_{hm} because of the strong decrease in O atom density.

Concerning CH₄, its behaviour is consistent with that of CH₃ radical. Indeed, CH₄ is formed by recombination of CH₃ and H. When increasing X_{hm}, CH₃ increases and so does CH₄ at high value of X_{hm}.

It appears clearly that the dissociation processes are strongly dependant of the dilution ratio of HMDSO in O₂. In particular, at low dilution (X_{hm}>20%), CH₃ density is high, the dissociation of HMDSO mainly occurs by electron impact when the power regime is of strong fragmentation and atomic oxygen is lost in oxidation processes.

4. Conclusion

A capacitive RF O₂/HMDSO plasma for SiO_x thin film deposition is characterised. OES and FTIRAS experimental diagnostics are used to determine the variation of the species density with the HMDSO dilution rate. The presented

results have pointed out that the deposition process may occur with two different regimes, depending on whether the amount of HMDSO in the gas mixture (X_{hm}) is greater or lower than 20%. Trends observed in the evolution of the species concentrations as a function of X_{hm} better agree with the results by Aumaille et al. [10], although the pressure set in this work is closer to that used by Lamendola et al. [1].

The amount of broken HMDSO has been estimated and was shown to increase with the input power.

From the obtained results, steps for the fragmentation of the organic precursor have been proposed.

Further work is presently on the way to investigate the variation of the dissociation rate as a function of the process parameter such as input power and HMDSO dilution rate.

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