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Optical emission spectra of TEOS and HMDSO derived plasmas used for thin film deposition

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Abstract

This paper is devoted to the optical emission spectra (OES) of low pressure (1 mTorr–1 Torr) plasmas created in tetraethoxysilane (TEOS) and hexamethyldisiloxane (HMDSO) used pure or mixed with oxygen. The UV-visible emission spectra are recorded at low resolution (0.3 nm) using a 46 cm focal length monochromator and at high resolution (0.3 cm⁻¹) using a Fourier transform spectrometer. Since almost all the atomic and molecular emissions have been identified, the spectra displayed here can be used as reference emission spectra for TEOS, HMDSO and O₂/TEOS(HMDSO) plasmas. The OES of O₂/TEOS and O₂/HMDSO plasmas are very close and are dominated by CO, OH, H₂ and H emissions. In contrast, the OES of TEOS and HMDSO plasmas are quite different: the emissions of excited Si, SiO and SiH are characteristics of HMDSO plasma, while those of OH, CO, CO⁺, C₂O⁺ are characteristics of TEOS plasmas. On the basis of these spectra and the data reported in the literature, it is finally concluded that the CO and OH molecules detected in TEOS plasmas are very likely created at the reactor walls by desorption from the growing film.

1. Introduction

Tetraethoxysilane (TEOS) and hexamethyldisiloxane (HMDSO) are widely used for the deposition of silicon oxide or organosilicon films which are used as insulating, optical or barrier films. Although the properties of the deposited film have been extensively investigated in the literature [1], fewer studies have been devoted to the plasma itself. The most complete studies of the O₂/TEOS and O₂/HMDSO plasmas have been achieved using mass spectrometry (MS) [2–7] and infrared absorption spectroscopy (IRAS) [8]. MS and IRAS allows us to evidence the ionic and neutral stable species in the plasma, provided their concentration is higher than the detection limit. In contrast, optical emission spectroscopy allows us to evidence the radiative excited states of stable and radical species. Since it allows the detection of short life radicals which are difficult to

detect by MS or IRAS because of their low concentration, the optical emission spectroscopy appears to be a diagnostic technique which is complementary to MS and IRAS and has the advantage of being easy to implement. To our knowledge, only very few detailed analyses of the optical emission spectra (OES) of O₂/TEOS and O₂/HMDSO plasmas have been published [7–11]. Most of the OES reported in the literature only refer to a very limited spectral range and only the strongest lines are identified. Nevertheless, it can be expected that much more information can be extracted from the detailed analysis of the emission spectra recorded in the UV-visible-near infrared spectral range. This paper is devoted to such a detailed study of the OES of TEOS and HMDSO plasmas, either pure or mixed with oxygen with the following aims: (i) to present a complete identification of the spectra recorded from the UV to the near infrared, namely from 180 to 850 nm; (ii) to compare the OES obtained from TEOS and HMDSO; (iii) to try to deduce from these OES information relative to the fragmentation of TEOS and HMDSO molecules, which are still far from being understood.

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Therefore, two kinds of investigations have been carried out. First of all, a monochromator equipped with gratings is used to record the emission spectra of a low pressure plasma created in a radio-frequency (rf) helicon reactor, under deposition conditions. The second approach consists in using a high resolution Fourier transform (FT) spectrometer to record the OES of pure TEOS and HMDSO plasmas created in a quartz tube under different excitation conditions. Since the OES of organosilicon plasmas are very rich, the high resolution FT will allow us to get better insight into the identification of the emitting species.

2. Experimental

2.1. OES recorded with a monochromator on the low pressure rf plasma

The low pressure rf (13.56 MHz) helicon reactor used to create plasmas in TEOS ($\text{Si}-(\text{O}-\text{C}_2\text{H}_5)_4$) and HMDSO ($\text{O}-(\text{Si}(\text{CH}_3)_3)_2$) is described in detail in [12]. Briefly, it is made of two parts: the plasma source where the rf power is inductively coupled via the external helicon antenna, and the diffusion chamber where the plasma diffuses and where the organosilicon vapour is introduced via a dispersal ring. The plasma is operated at 2 mTorr, 300 W with a fixed total gas flow rate of 16 sccm. The light emitted by the plasma is transmitted to a 46 cm focal length monochromator (JY HR460) by an optical fibre positioned at mid-height of the diffusion chamber, which probes the plasma located between the dispersal ring and the substrate. The monochromator is equipped with two gratings (a 2400 grooves mm^{-1} grating used in the 180–420 nm spectral bandwidth and a 1200 grooves mm^{-1} used in the 420–850 nm spectral range), and a 928S Hamamatsu photomultiplier. The acquisition of spectra is monitored by a PC and the spectramax software. Under standard acquisition conditions the resolution is fixed at 0.3 nm, but a higher resolution of 0.1 nm is achieved in order to identify unambiguously the multiple structures present in the emission spectrum.

2.2. OES recorded with a FT spectrometer on microwave and rf discharges

Emission spectra were recorded by flowing successively TEOS and HMDSO at low pressure through a microwave (2.45 GHz) and a rf (27 MHz) discharge. The pressure in the cell (length = 30 cm, diameter = 1 cm) was maintained at about 0.1 and 0.5 Torr for microwave and rf discharges, respectively. The light of the discharge was focused onto the entrance iris of a Bruker IFS 120 FT spectrometer. The spectra were recorded between 18 000 and 36 000 cm^{-1} (277–555 nm) using photomultipliers (Hamamatsu, model 1P28 and solar blind) and appropriate coloured glass optical filters. Spectra were obtained after co-addition of 50 scans with a maximum optical path difference restricted to 3.3 cm giving an apodized resolution of 0.3 cm^{-1} .

3. OES of pure TEOS and HMDSO plasmas

3.1. HMDSO plasmas

3.1.1. Low resolution spectra. A typical UV and visible emission spectrum of a low pressure rf HMDSO plasma is

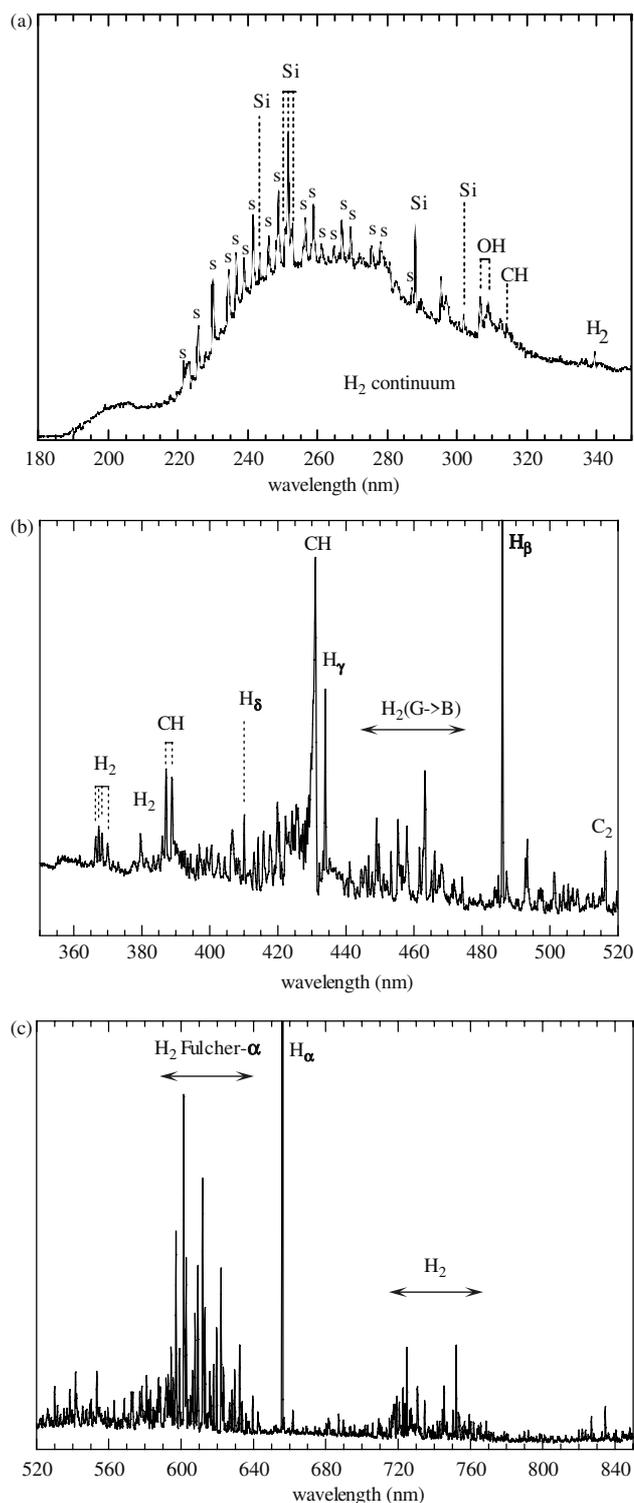


Figure 1. Low resolution spectra of the low pressure rf HMDSO plasma (2 mTorr—300 W) (a) 180–350 nm; (b) 350–520 nm; (c) 520–850 nm. The letter s refers to SiO systems.

shown in figure 1. For the sake of clarity, it has been divided into three spectral ranges: 180–350, 350–520 and 520–850 nm. Although these spectra are very rich in emission features, most of the atomic lines or molecular systems can be unambiguously identified, using reference books for atomic lines [13] and molecular structures [14]. The detailed assignments are given

Table 1. Radiative species identified in HMDSO plasmas.

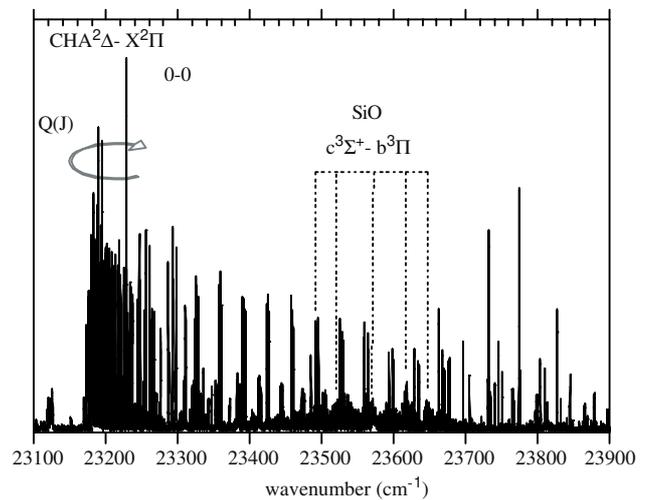
Species	Symbol used in figures 1 and 6	Transition	System name	Wavelength (line) or spectral range (system) (nm)
Si	Si	4s → 3p		243.5, 251.6, 288.2, 302.0
H	H _α , H _β , H _γ , H _δ	n(>2) → n = 2	Balmer lines	656.3, 486.1, 434.0, 410.0
SiO	s	A ¹ Π-X ¹ Σ	Main system	216–293
SiH	SiH	A ² Δ-X ² Π	4142 Å system	414.2
H ₂	H ₂	³ Σ _g ⁻ - ³ Σ _u	Primary system	200–320
		G ¹ Σ _g ⁺ -B ¹ Σ _u ⁺	G → B	453–464
		d ³ Π _u -a ³ Σ _g ⁺	Fulcher-α	580–650
CH	CH	A ² Δ-X ² Π	4300 Å system	431.4 (0, 0)
		B ² Σ-X ² Π	3900 Å system	388.9, 387.1 (0, 0)
C ₂	C ₂	A ³ Π _g -X ³ Π _u	Swan system	512.9 (1, 1)–516.5 (0, 0)

in table 1. The main conclusion is that emission from excited Si, SiO, H, H₂, CH and C₂ species are clearly seen. The 200–360 nm UV part of the OES is dominated by the emission of Si and SiO, which are superimposed to a continuum emission due to H₂ (primary system) [15]. On the other hand, the 360–850 nm spectral range is dominated by the emissions of H, CH, C₂ and the complex secondary spectrum of H₂ [16]. In addition, the emission of SiH at 413.4 nm could be established using a higher resolution, but is weak. In the 520–850 nm range, H₂ is the only emitting species, so that the corresponding spectrum is similar to the one recorded in a hydrogen discharge. A very weak emission from the OH 3060 Å system can be seen. But, since OH emission is very weak, it is more likely to come from traces of water vapour in the reactor rather than from the HMDSO plasma itself. Finally, no emission from ionic species was detected under these plasma conditions.

3.1.2. High resolution spectra. Although they have been recorded under different plasma conditions (microwave and rf excitation at higher pressure), the same neutral radiative species are evidenced by high resolution FT spectra, except OH which is completely absent from the FT spectra. Almost all the intense lines have been identified, as emitted by one of the atom or molecules quoted above. The FT spectra do not evidence any system emitted by any other atom or molecule than Si, SiO, SiH, H₂, CH or C₂. The presence of the Si line at 288 nm is confirmed. Since the spectral range below 270 nm could not be recorded, the presence or absence of the SiO main system can not be established but a weaker system of SiO, the c³Σ⁺-b³Π system centred around 23 550 cm⁻¹ (424 nm) was clearly seen in some of the HMDSO plasma emission spectra recorded by FT spectroscopy. Figure 2 displays the c³Σ⁺-b³Π SiO system overlapped by CH 4300 Å system. In addition, a very weak emission of the A²Δ-X²Π system of SiH centred around 24 130 cm⁻¹ (414.2 nm) was detected in the microwave plasma.

3.2. TEOS plasmas

3.2.1. Low resolution spectra. The UV and visible emission spectra of the helicon TEOS plasma are plotted in figures 3(a)–(c), using the same spectral ranges as for the HMDSO plasma spectra. A survey of figures 1 and 3, shows

**Figure 2.** High resolution FT spectrum of a HMDSO microwave plasmas (0.5 Torr) between 23 100 and 23 900 cm⁻¹ (418–433 nm).

that the OES recorded in pure HMDSO and TEOS completely differ. The OES of the TEOS plasma are even more dense in emission features, so that the identification of the different structures is a much harder task. It appears in different spectral bandwidths that several systems overlap, so that FT spectroscopy is required to confirm the identification of some radiative species. From the precise analysis of the OES of TEOS low pressure plasmas the main conclusions are the following: (i) no emission from Si atoms or any silicon containing molecules (namely SiO and SiH) previously observed in HMDSO plasmas could be detected, (ii) at least ten systems of CO, CO⁺, CO₂⁺, which were totally absent from the OES of HMDSO plasmas, are identified [14, 17] and listed in table 2, (iii) the emissions from H, H₂, CH and C₂, in the 350–850 nm part of the OES, superimpose to the different systems of CO, (iv) in addition, an intense emission of the OH 3064 Å system is now observed. Thus, the OES of the TEOS plasma is dominated by the strong emission of the different systems of CO, which are likely to hide emission from other weaker systems. As an example, the 4300 Å system of CH can be masked by the triplet system of CO and the comet tail system of CO⁺, or the 288 nm line of Si could be embedded in the CO₂⁺ emission, which emphasises the interest in high resolution FT spectroscopy.

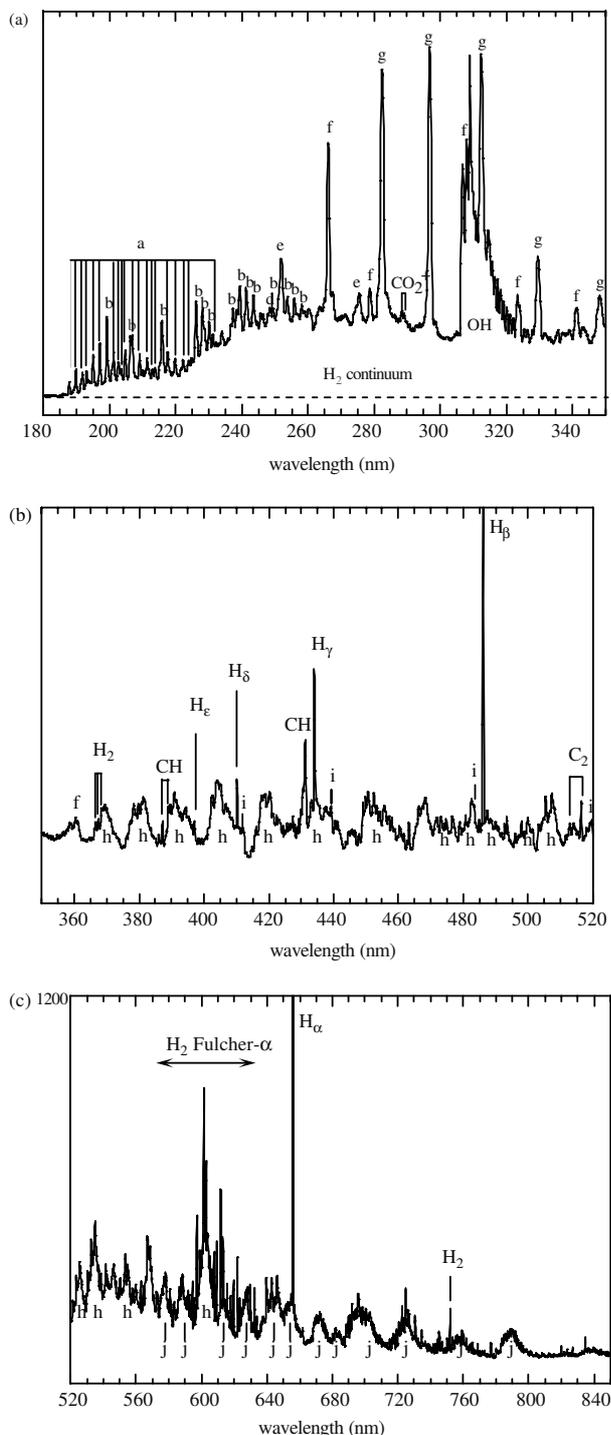


Figure 3. Low resolution spectra of the low pressure rf TEOS plasma (2 mTorr—300 W) (a) 180–350 nm; (b) 350–520 nm; (c) 520–850 nm. The letters a, b, d, e, f, g, h, i and j refer to different systems of CO (see table 2).

3.2.2. High resolution spectra. The high resolution FT spectra of rf and microwave TEOS plasmas clearly show strong emissions of OH, CO, CO⁺, CO₂⁺, CH, H and H₂, while the 288 nm Si line, the 414.2 nm system of SiH and the SiO c³Σ⁺–b³Π system are totally absent from the FT spectra. The only difference between FT and low resolution emission spectra stands in C₂ Swan system, which was identified in the low

resolution spectrum (cf figure 3(b)) but is absent from all FT spectra.

To illustrate the differences between HMDSO and TEOS plasmas, the FT spectra recorded in the 34 200–35 600 cm⁻¹ (282–292 nm) and 23 050–23 550 cm⁻¹ (430–434 nm) spectral ranges for both organosilicons have been plotted in figures 4 and 5, respectively. In the 282–292 nm range, the HMDSO plasma spectrum only presents the atomic emission of Si at 288.2 nm, while the spectrum of the TEOS plasma is very rich, with the emissions of CO₂⁺ (λλ2883 and 2896), CO (third positive system (0, 0)) and OH (3064 Å system (1, 0)) but without any emission at the Si line wavelength. The 430–434 nm spectrum clearly demonstrates that the CO⁺ comet tail system (2, 0) emission superimposes to the CH 4300 Å system only in the case of TEOS plasmas.

4. Oxygen/organosilicon plasmas

The addition of oxygen to a TEOS plasma does not drastically change the general aspect of the plasma OES. The main trends observed as the oxygen fraction is increased, are the appearance of the oxygen atomic lines (mainly, the 844.6, 777.3 and 463.8 nm lines), and the progressive disappearance of the CH, C₂ and H₂ systems. As the TEOS fraction is less than 25%, which will be denoted hereafter an oxygen-rich mixture, the emissions from CH, C₂ and H₂ are totally absent and the OES mainly consists in the atomic lines of O, H and the molecular structures of OH, CO, CO⁺ and CO₂⁺.

In contrast, the addition of oxygen to a HMDSO plasma immediately modifies its OES with the appearance of the emission of the numerous systems of CO, CO⁺, CO₂⁺ and OH. As the oxygen fraction increases, the CH, C₂ and H₂ systems decrease, as previously observed in O₂/TEOS plasmas. In addition, the Si, SiO and SiH emissions decrease and become hidden by the CO structures. Finally, the OES of oxygen-rich O₂/HMDSO and O₂/TEOS are very similar, without any evidence of Si containing species. This is illustrated by the figures 6(a) and (b) which represent the OES between 250 and 500 nm recorded in oxygen-rich plasmas containing 20% HMDSO and 20% TEOS, respectively.

5. Discussion

The detailed analysis of the OES of different low pressure (≤0.5 Torr) plasmas of pure TEOS and HMDSO, using either a monochromator or a high resolution FT spectrometer leads us to the conclusion that the radiative species are strongly linked to the nature of the organosilicon molecule but only weakly depend on the kind of plasma excitation. The OES of HMDSO and TEOS plasmas have only in common the emissions of excited H, CH, H₂ and the absence of any emission from O*. The emissions of excited Si, SiO and SiH are shown to be characteristics of HMDSO, while those of OH, CO, CO⁺, CO₂⁺ are characteristics of TEOS. The presence or absence of emission from C₂ is more sensitive to the plasma conditions.

In order to interpret these results, we will successively compare our spectra to those previously reported in the literature and to the spectra obtained by controlled electron impact on HMDSO and TEOS molecules. Then the mechanisms yielding the creation of these radiative species in a plasma will be discussed.

Table 2. Emission systems of OH, CO, CO⁺ CO₂⁺ identified in TEOS plasmas.

Species	Symbols used in figures 3 and 6	Transition	System name	Spectral range (nm)
OH		A ² Σ ⁺ -X ² Π	3064 Å system	281 (1, 0)-309 (0, 0)
CO	a	A ¹ Π-X ¹ Σ	Fourth positive system	180-255
	b	a ³ Π-X ¹ Σ	Cameron bands	206-258
	d	c ³ Π-a ³ Π	3A bands	230-271
	e		Kaplan bands	252, 275
	f	b ³ Σ-a ³ Π	5B bands	266-383
	g	b ³ Σ-a ³ Π	Third positive system	283-370
	h	d ³ Δ-a ³ Π	Triplet bands	401-647
	i	B ¹ Σ-A ¹ Π	Angström system	451-608
	j	a' ³ Σ-a ³ Π	Asundi bands	575-800
	CO ⁺		B ² Σ-X ² Σ	First negative system
CO ₂ ⁺	CO ₂ ⁺	A ² Π-X ² Σ	Comet-tail system	309-640
		A ² Σ ⁺ -X ² Π	λλ2883 and 2896	288.3, 289.6

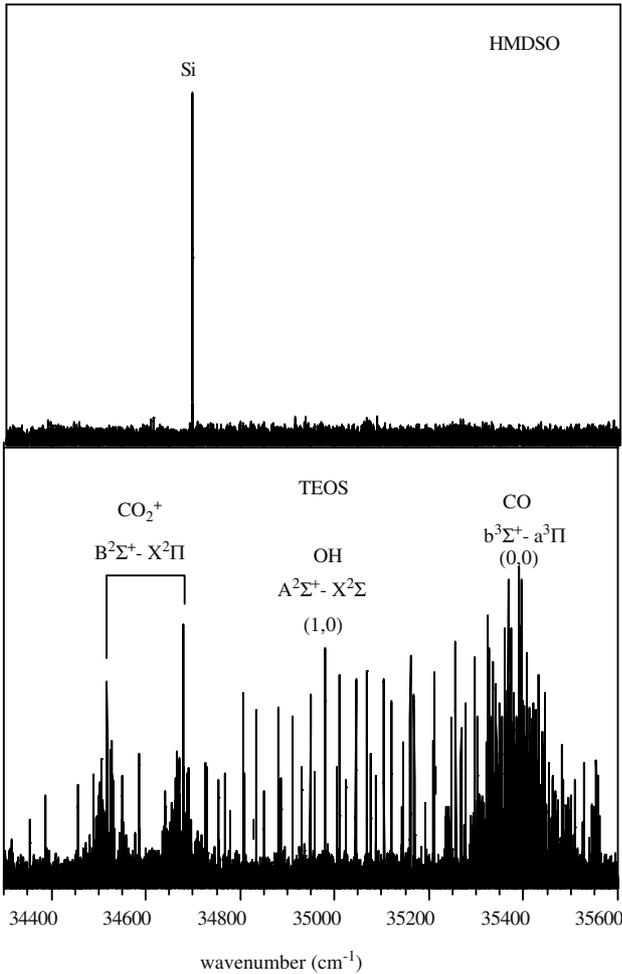


Figure 4. High resolution FT spectra of HMDSO and TEOS microwave plasmas (0.1 mTorr—40 W) between 34 200 and 35 600 cm⁻¹ (282–292 nm).

5.1. Comparison with the literature

In the case of HMDSO plasmas, the emission of excited Si, CH, H, H₂ and the absence of any emission of excited O, CO, CO⁺, and CO₂⁺ have been mentioned by all the authors reporting OES of pure HMDSO plasmas [4, 8, 11, 18]. Moreover, these results are consistent with the results of MS and IRAS investigations,

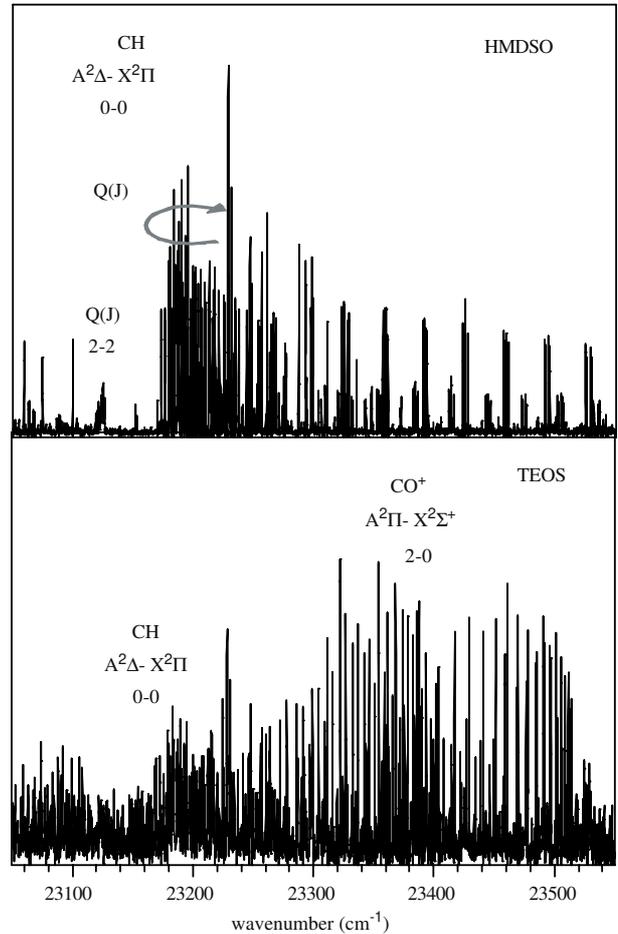


Figure 5. High resolution FT spectra of HMDSO and TEOS microwave plasmas (0.1 mTorr—40 W) between 23 050 and 23 550 cm⁻¹ (430–434 nm).

which have shown that H₂, CH₄, C₂H₂ and C₂H₄ are detected but not CO, nor CO₂ [6–8]. The information relative to SiH and SiO are much more divided. SiH and SiO emissions were clearly observed in a surface wave microwave discharge [9–11], but not detected in a microwave distributed electron cyclotron resonance (DECR) plasma [8]. In this latter case, this absence might be due to the further dissociation of these species in the case of the dense DECR plasmas [8].

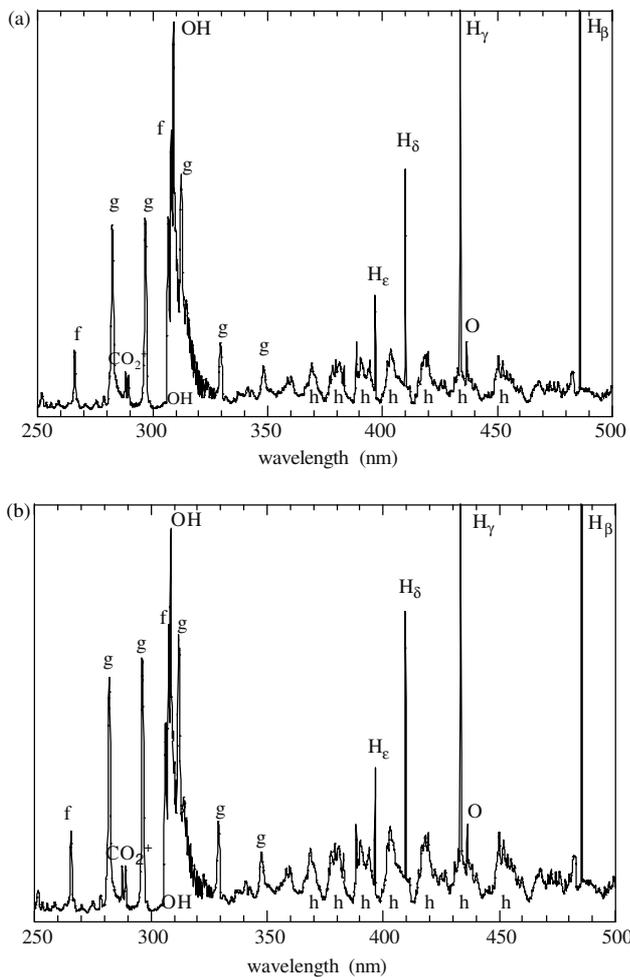


Figure 6. Low resolution spectra of the low pressure rf O_2 /HMDSO and O_2 /TEOS plasmas (2 mTorr—30 W, 80% O_2 –20% organosilicon) between 250 and 500 nm.

In the case of TEOS or O_2 /TEOS plasmas, the emissions of H, CO, OH and the absence of emission from Si, SiO and SiH were clearly indicated in the case of a rf diode plasma [4], and a DECR plasma [7, 8]. The absence of any emission from excited Si and SiO is consistent with the very low concentrations (10^{-5} – 10^{-4} times the neutral density) which were measured in a low pressure ECR O_2 /TEOS plasma by Augustyniak [19] and Chew [20]. The emission from CO^+ and CO_2^+ depends on the plasma conditions, and appears, in addition to CO emission, only if the electron temperature and density are high enough [7, 8]. There is again a pretty good agreement between the appearance of emission from CO, CO^+ and CO_2^+ and the detection of CO and CO_2 by MS and IRAS [2, 7, 8]. The conclusions relative to the correlation between the emission of excited OH radicals and the concentration of the ground-state OH radical are less obvious. Indeed, the fairly strong emission of the 3060 Å of OH which has been observed in different TEOS plasmas, is expected to be correlated to the presence of hydroxyl radicals. Nevertheless, this is not consistent with the recent measurements of OH achieved by Bogart *et al* [21] by laser induced fluorescence (LIF). These later established that OH could only be the product of a reaction between TEOS and O_2 , and could not be created in pure

TEOS. In the low pressure rf plasma, it was shown that OH emission was strongly increasing as O_2 was added to TEOS, but its intensity in pure TEOS is too high to be only due to traces of water vapour as observed in the case of HMDSO plasmas.

5.2. Comparison with the OES obtained by electron impact on the molecules

The VUV, UV and visible emissions obtained by controlled electron impact on HMDSO and TEOS molecules have been studied by Ducrepin *et al* and Kurunczi *et al* [22–25]. They have shown that these spectra were different with the appearance of emissions from Si, H (Balmer and Lyman lines) and CH in the case of HMDSO but only from H and CH in the case of TEOS. They have shown that even at an electron energy of 100 eV, no emission from Si could be detected [23, 24], which shows how difficult it is to break the four Si–O bonds of the TEOS molecule. These results are consistent with what is observed in the HMDSO and TEOS plasmas. These authors have also determined the thresholds and cross sections for these dissociative excitations, which are reported in table 3. As can be seen, the excitation thresholds are high and the excitation cross sections weak, so that the dissociative excitation of HMDSO or TEOS is not expected to be an important process for the creation of CH^* , H^* or Si^* in an organosilicon plasma, where the electron temperature is less than 4 eV [12]. Additional information can be deduced in the case of TEOS: upon electron impact on TEOS there is no emission from either OH 3060 Å system, or any excited level of CO [24]. Thus, the OH^* and CO^* emissions, which were shown to be characteristics of TEOS plasmas, cannot be created by dissociative excitation of TEOS. In addition, Basner *et al* [26] have shown that neither CO^+ nor OH^+ were created upon the dissociative ionization of TEOS. Hence, it seems very unlikely that CO and OH are created upon TEOS dissociation by electron impact, and we suggest that CO and OH desorb from the film surface, for instance under the positive ion bombardment. This is supported by the analysis of the films deposited in HMDSO and TEOS plasmas which has shown that TEOS derived films contain C–O and O–H bonds but not the HMDSO derived films [27]. In order to further investigate whether CO and OH can be formed by desorption from the reactor walls, these later were covered by an organosilicon film in a TEOS plasma and then, submitted to an argon plasma, created at the same pressure and power as the usual deposition plasmas (2 mTorr, 300 W). The optical emission spectrum recorded during the argon plasma is shown in figure 7. It shows the emissions of excited CO, and OH species, which confirms that CO and OH molecules are efficiently created by desorption from the reactor walls. Under these argon plasmas conditions, it is likely that CO and OH are desorbed upon bombardment by Ar^+ ions, which the energy is about 20–25 eV. Then, the same experiment was performed in a reactor covered with a HMDSO derived film. The optical emission of the argon plasma obtained in this case, which is also plotted in figure 7, is completely different from the one obtained when the argon plasma was created in a reactor covered with a TEOS derived film: CO and OH emissions are almost undetected while a weak emission from Si is clearly identified. Hence,

Table 3. Data relative to H_{β} , CH (430 nm) and Si (288 nm) emissions upon electron impact on HMDSO and TEOS molecules from Kurunczi *et al* [23–25].

	HMDSO [23]	TEOS [23–25]
H_{β} first emission threshold	22.7 eV	17 ± 1.5 eV
H_{β} second emission threshold	35 eV	27 ± 1.5 eV
H_{β} emission cross section at 100 eV	4×10^{-19} cm ²	3.4×10^{-19} cm ²
CH ($A^2\Delta \rightarrow X^2\Pi$) emission threshold	33.1 eV	30.7 ± 2 eV
CH ($A^2\Delta \rightarrow X^2\Pi$) emission cross section at 100 eV	6.1×10^{-19} cm ²	2.4×10^{-20} cm ²
Si 288 nm emission threshold	44.6 eV	No emission

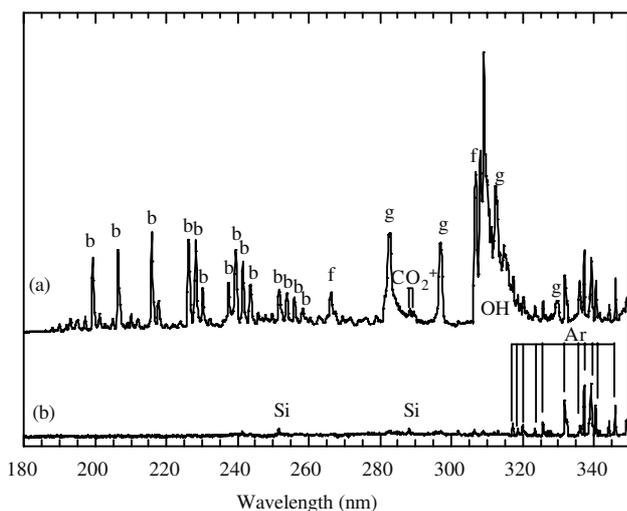


Figure 7. Low resolution spectra of the low pressure Ar plasmas (2 mTorr—300 W) recorded between 180 and 350 nm in a reactor covered with: (a): TEOS derived film; (b): HMDSO derived film. The letters b, f, g, refer to different systems of CO (see table 2).

in the case of TEOS plasmas, these additional experimental data relative to heterogeneous reactions on the walls confirm the hypotheses derived from the data relative to homogeneous dissociative reactions involving TEOS. It can be concluded that, in a pure TEOS plasma, CO and OH are very likely created upon desorption from the surface of the film which is growing on the reactor walls.

6. Conclusion

The low resolution and high resolution UV–visible OES of low pressure (1 mTorr–1 Torr) TEOS, HMDSO plasmas have been studied in detail. The high resolution FT spectra were shown to be essential to assign without any doubt some structures of the low resolution spectra and to prove the presence of the weakly emissive species whose emission is superimposed to the strong emission of other species. The low resolution (0.3 nm) spectra in the 180–850 nm spectral range displayed in this paper can be used as reference spectra to facilitate the interpretation of the optical emission spectra of TEOS and HMDSO containing plasma.

This study has first shown that TEOS and HMDSO had different emission signatures: Si and SiO emissions are characteristics of HMDSO plasmas while CO, CO⁺ and OH emissions are characteristics of TEOS plasmas. Since Si, SiO, CO, CO⁺ and OH species, are mainly emitting in the

180–360 nm range, the UV spectral range is by far the best adapted for the study of organosilicon containing plasmas by optical emission spectroscopy. These different optical emission signatures of TEOS and HMDSO plasmas have to be related to the structure of the organosilicon molecule. The CO and CO⁺ emissions are related to the presence (TEOS) or absence (HMDSO) of C–O bond in the organosilicon precursor. In the case of Si and SiO emission, the Si environment has to be considered: Si and SiO emissions are observed in the case of HMDSO (3 Si–C bonds and one Si–O bond), since Si–C bonds are easily broken upon electron impact and only one strong Si–O bond has to be broken to create Si. In contrast, in the case of TEOS (4 strong Si–O bonds) the creation of Si and SiO requires to break at least three strong Si–O bonds and appears to be almost impossible. On the other hand, the excited CO and OH species detected in TEOS plasmas are very likely to be created by electron impact on CO and OH molecules which desorb from the growing film at the reactor walls.

Acknowledgments

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