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Characterization of an Ar-TMS microwave discharge using mass spectrometry: effect of the reactor design on free-radical contents

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Abstract

A microwave plasma (2.45 GHz) containing Ar-TMS (TMS = tetramethyl silane) gas mixture is investigated by means of a quadrupole mass spectrometer, equipped with a two-stage differential pumping under deposition condition of silicon carbide. An ionization threshold method is used in order to detect and to determine the various species created within the plasma, which are species like SiC_xH_y or lighter ones like H_2, CH_x, and SiH_y. The mass spectrometer signal intensity measured for each ion is corrected in order to suppress the contribution of the TMS dissociative ionization in the total signal intensity. We show that contributions due to dissociative ionization of others species SiC_xH_y can be neglected in comparison with the contribution of the TMS. The effect of the incident microwave power on the plasma composition has also been investigated. The microwave plasma is very efficient for dissociating TMS (80% of TMS is dissociated at 100 W). At a power lower than 40 W, TMS dissociates mainly via Si–C bond breaking; the main species produced in the plasma are $Si(Me)_x$ radicals. At a higher power it dissociates via C–H bond breaking and mostly SiH_x or CH_x radicals are produced. The plasma composition is investigated in four different reactor configurations corresponding to various TMS injectors and analyzer positions within the reactor. The design parameters and the gas mixture (TMS content in Ar-TMS), change the plasma composition and can promote the dissociation of TMS and of the secondary species (SiC_xH_y) via Si–C bond breaking or C–H bond breaking. (Int J Mass Spectrom 189 (1999) 63–77) © 1999 Elsevier Science B.V.

Keywords: Tetramethyl silane; Microwave discharge; Plasma composition

1. Introduction

Plasma discharges are widely employed as a basic technology for thin film deposition, used, for instance, in electronic devices. Reactive species are generated by striking the plasma discharge in an appropriate gas mixture where the electrons and the ions cause dissociation and subsequent chemical reactions. Numerous free radicals are produced and their concentration depends on experimental conditions. Control of the free radicals generated is essential for the efficiency of such a plasma device.

Organosilicon compounds are of particular interest for many deposition applications [1,2] and tetramethyl silane (TMS) is one of the simplest organosilicon compounds. Mixed with a carrier gas (N_2, Ar, . . .), it is used in plasma discharges in order to produce silicon nitride or silicon carbide films [3]. Understanding of the reaction processes produced in such a discharge requires a good knowledge of gas phase composition (atoms, molecules or free radicals).

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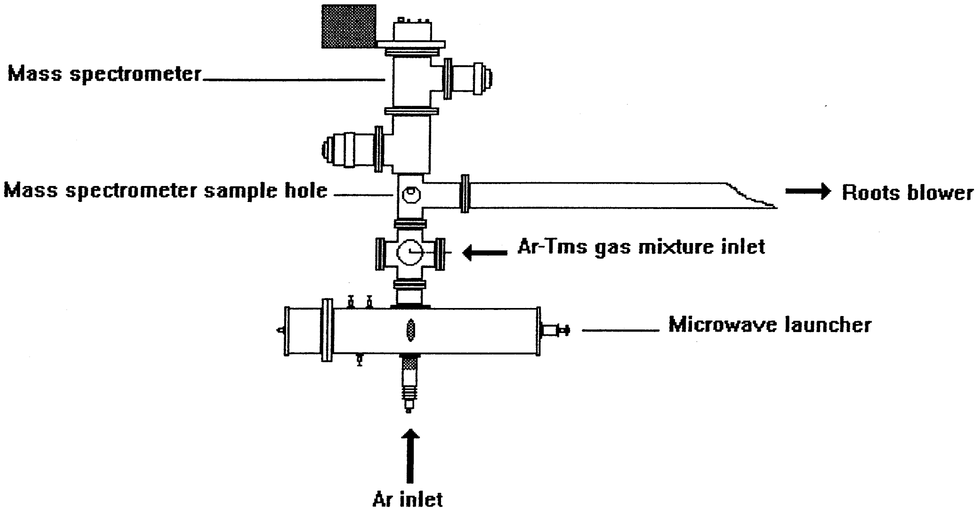

Fig. 1. Experimental setup.

The purpose of this work is to investigate the neutral species generated in the plasma in various Ar-TMS gas mixtures by means of mass spectrometry. The mass spectrometer is equipped with a two stage differential pumping system in order to sample from a process chamber with a relatively high pressure corresponding to the deposition conditions of thin silicon carbon film, i.e. 66 Pa.

The effect of the reactor design on the gas composition is also investigated. This study is performed in four different configurations corresponding to four different TMS injector positions or observation regions within the reactor.

2. Experimental setup

The experimental setup is shown in Fig. 1. It consists of a microwave discharge containing an Ar-TMS gas mixture created in a quartz tube (outer diameter 19 mm, inner diameter 16 mm) and used to dissociate molecular species. In order to maintain a constant wall temperature, the outside of the quartz tube is refreshed by means of air cooling. The total pressure in the vessel is kept constant using a Roots blower pump (70–700 m^3/h) that allows a constant gas flow velocity in the postdischarge (stainless tube with an inner diameter of 50 mm) located above the microwave discharge. The total pressure is maintained at 66.5 Pa. According to the reactor design, the mixture of Ar-TMS can be injected into the discharge, before or after the discharge. Analysis is performed using a quadrupole mass spectrometer (QMG 421 Balzers) equipped with a secondary electron multiplier amplifier. Because the mass spectrometer cannot operate at pressures lower than 10^{-3} Pa, a differential pumping is required. We use a two-stage differential pumping unit, with a turbomolecular pump at all stages; the pumping speed (in N_2) in the first stage is 210 L/s and in the second stage 56 L/s. During the gas sampling, the pressure is 10^{-2}–10^{-3} Pa for the first stage and 10^{-4} Pa for the second. The extraction hole diameter is 100 μm whereas the diameter of the hole located between the two stages is 500 μm. The distance between the mass spectrometer sample hole and the discharge center can be changed in order to analyze the gas phase in different parts of the reactor.

The TMS sample is contained in a stainless steel vessel and it is carried along the reactor with argon. The TMS partial pressure within the reactor is measured using the following method: When the discharge is turned off, there are only two species in the gas mixture: Ar and TMS; thus the total pressure P_T is the sum of the two partial pressures $P_T = P_{\mathrm{Ar}} +$

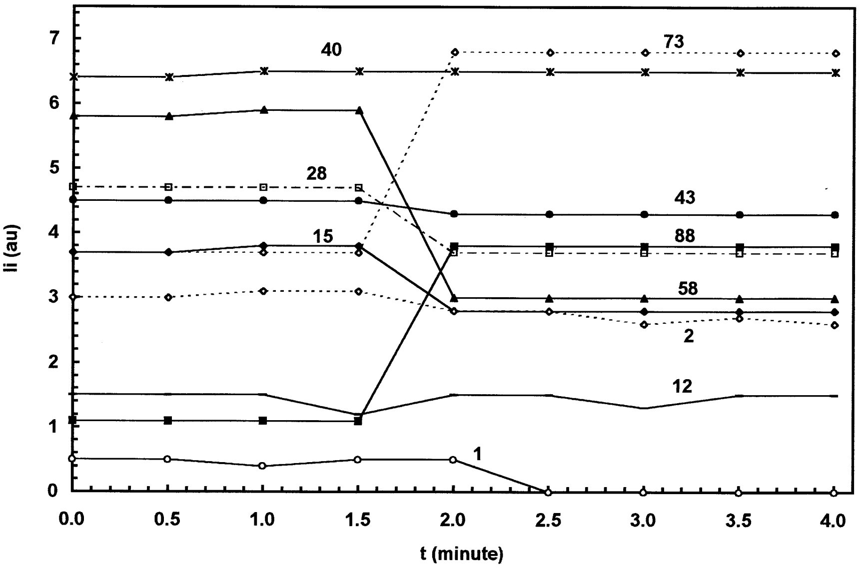

Fig. 2. Mass spectrometric intensity measured for *m/z* = 88, 73, 58, 43, 40, 28, 15, 12, 2, 1 versus time.

P_{TMS}. The mass spectrometer signal I_i measured for a species *i* is given by [4],

$$I_i = n_i \cdot \sigma(\varepsilon_e) \cdot T(m_i, n_i) \tag{1}$$

In this relation n_i is the density of the species, $\sigma(\varepsilon_e)$ is the ionization cross section at an electron energy ε_e, and $T(m_i, n_i)$ (unity $A \cdot m$) is the transmission factor of the species, depending on the mass and the density of the species. We will see later that this factor also depends on the quadrupole mass spectrometer characteristics.

The partial pressure of TMS is given by

$$P_{TMS} = P_T + P_{Ar0} \cdot I_{Ar}/I_{Ar0} \tag{2}$$

where P_T is the total pressure, I_{Ar0} is the signal intensity measured (discharge off) in a pure argon flow corresponding to the argon pressure $P_{Aro} = P_T$, and I_{Ar} is the signal intensity measured in the gas mixture (discharge off) containing the TMS partial pressure P_{TMS} for the same total pressure.

3. Threshold ionization of the different species

Electron ionization of the monomer is one of the most fundamental collision processes in a nonequilibrium and low temperature microwave plasma. So, we have studied the dissociation of TMS by electron collision versus the electron energy. The mass spectrum of TMS shows abundant parent ions resulting in dissociative ionization processes occurring even at low ionization electron energy.

Fig. 2 displays the mass spectrometer signal intensity measured in the plasma containing Ar-TMS for the species corresponding to *m/z* = 88, 73, 58, 43, 40, 28, 15, 12, 2, and 1 versus the time. The gas mixture is Ar-5% TMS, total pressure is 66.6 Pa, microwave power is 150 W, and electron energy is 18 eV. In this case the plasma is suddenly stopped after 1.5 min. It can be seen in Fig. 2 that when the discharge is stopped, the intensity of the species of *m/z* = 88 or 73 increases and the intensity of the species of *m/z* = 58, 28, 15, 2, and 1 is decreasing. For *m/z* = 43, the signal intensity slightly decreases when the discharge is switched off and for *m/z* = 12 or 40, the intensities remain constant. These results show that the species of *m/z* = 73 and 88 are mainly produced by TMS ionization in the mass spectrometer ionization chamber and the species corresponding to *m/z* = 58, 43, 28, 15, 2, and 1 are produced by ionization of species previously created in the Ar-TMS plasma. The behav-

Table 1
The different ions (*m/z*) observed when the TMS monomer is ionized in the ionization chamber, and the appearance energy measured for each ion and the corresponding fragment ion

m/z	**88**	**74**	**73**	**72**	**71**	**70**	**58**	**45**
E_a (eV)	9.5–10	10	10	10	10	10	10–10.5	10.5
Ion	$SiMe_4^+$	$HSiMe_3^+$	$SiMe_3^+$	$SiMe_2CH_2^+$	$SiMe_2CH^+$	$SiMe_2C^+$	$SiMe_2^+$	H_2SiMe^+
m/z	**44**	**43**	**40**	**28**	**15**	**12**	**2**	**1**
E_a (eV)	10.5	10.5	15.75	9.5–10	10	11	15–16	>15
Ion	$HSiMe^+$	$SiMe^+$	Ar^+, SiC^+	Si^+, $C_2H_4^+$	CH_3^+	C^+	H_2^+	H^+

ior observed in the case of the signal intensity of $m/z = 43$ can be explained by the fact that when the discharge is switched off, the specy of $m/z = 43$ is produced via dissociative ionization of the TMS in the ionization chamber of the mass spectrometer analyser. However, when the discharge is switched on, this specy can also be produced via dissociative ionization processes of other species produced in the discharge when the TMS is dissociated.

This first qualitative analysis shows the difficulties encountered in the study of such a system. The fragment ions caused by electron impact in the ionizer can potentially mask the signals generated by direct ionization of radicals. For each specy, it is necessary to take into account the various contributions due to different species during the signal acquisition, i.e. it is necessary to identify the part due to direct ionization of the detected species and parts due to dissociative ionization of other species present in the gas mixture that produce the same ion. We will describe in detail how one can overcome this difficulty.

The identification of the different species is achieved using a threshold ionization method [5,6]. We compare the ionization threshold measured for each *m/z* value to data given in the literature. In Table 1, different ions are given when the TMS monomer is ionized in the ionization chamber. In this table we have compiled the different *m/z* ratios observed in the mass spectrum and we report on the appearance energy measured (ionization threshold). We also give the fragment ion corresponding to each *m/z* ratio.

For *m/z* = 88: This ion corresponds to the $SiMe_4^+$ parent ion (where Me designates a methyl group CH_3). The ion is mainly produced via direct ionization of the TMS molecule,

$$e + SiMe_4 \rightarrow SiMe_4^+ + 2e$$

$$E_a = 9.74\text{–}9.9 \text{ eV [7]}$$

The appearance energy measured ranges between 9.5 and 10 eV. It corresponds to the ionization threshold value given in the literature.

For *m/z* = 73: This ratio corresponds to $SiMe_3^+$; the ionization threshold that we measure is about 10 eV and corresponds to the value given in the literature [7] in the case of the dissociative ionization of TMS,

$$e + SiMe_4 \rightarrow SiMe_3^+ + 2e + Me$$

$$E_a = 10.09\text{–}10.6 \text{ eV}$$

As shown in Fig. 2, the signal measured for this species increases when the discharge is switched off. This behavior can be ascribed to the sudden increase of the TMS content.

For *m/z* = 58: This ratio corresponds to the ion $SiMe_2^+$. The ionization threshold measured is about 10–10.5 eV.

Fig. 2 shows that when the discharge is switched off, the signal measured for $m/z = 58$ decreases. Thus, these ions are probably created with species produced in the plasma and not from the dissociative ionization of TMS in the ionization chamber. The formation of this fragment ion can proceed via three different reaction processes,

$$HSiMe_2 + e \rightarrow SiMe_2^+ + 2e + H$$

$$E_a = 10.3\text{–}10.5 \text{ eV}$$

$$HSiMe_3 + e \rightarrow SiMe_2^+ + 2e + H + Me$$

$$E_a = 10.5 \text{ eV}$$

$$H_2SiMe_2 + e \rightarrow SiMe_2^+ + 2e + H_2$$

$$E_a = 10.7 \text{ eV}$$

The appearance energy measured for this ion agrees with the value given in the literature [7] and corresponds to the two first processes. These ions seem to proceed via the dissociative ionization of $HSiMe_2$ or $HSiMe_3$ radicals created within the discharge. However, only species corresponding to $m/z = 74$ ($HSiMe_3$) have been detected. Thus, this ion seems to proceed via the dissociative ionization of $HSiMe_3$.

For m/z = 45, 44, 43, and 28: The first three species correspond to H_2SiMe, HSiMe, and SiMe radicals. For the sake of clarity, $m/z = 45$ and 44 signals that have been detected (see Table 1) are not reported in Fig. 2. The appearance energies measured for these species are about 10.5 eV. They could not proceed via the dissociative ionization of the TMS molecule, because in that case the ionization threshold should be larger (17.1–17.3 eV [7]). The formation of these ions can be explained as rearrangement ions produced in an ionization process with intermediate metastable species [7–9]. van der Kelen et al. [9] explain the formation of these rearrangement ions via metastable ion transition (mainly $SiMe_3^+$) with cleavage processes and elimination of stable molecules like C_2H_4. According to Distefano et al. [8], the formation of species like H_2SiMe^+, $HSiMe_2^+$, $HSiMe^+$, or SiH^+ can be explained only if we consider the consequence of rearrangement on metastable ions like $SiMe_3^+$. We believe the metastable ions could contribute up to 21.6% of the total ionization. The most important metastable ion in such a plasma is expected to be $SiMe_3^+$ and the main transitions are:

$$SiMe_3^+ \rightarrow H_2SiMe^+ + C_2H_4$$

$$H_2SiMe^+ \rightarrow SiMe^+ + H_2$$

Starting from $SiMe_2^+$, the process is

$$SiMe_2^+ \rightarrow SiMe^+ + Me$$

When the rearrangement proceeds via the cleavage of $SiMe_3^+$, the reaction produces H_2SiMe^+ ($m/z = 45$) and C_2H_4. The ionization threshold of C_2H_4 is 10.5 eV [7]. It is of the order of the value that we have measured for the appearance energy of the ion corresponding to $m/z = 28$ (9.5–10.5 eV). The species detected for $m/z = 28$ cannot be the silicium ion because the ionization threshold of Si^+ is equal to 8.15 eV [7]. It is lower than the appearance energy measured for $m/z = 28$. The species detected for $m/z = 28$ is probably $C_2H_4^+$ produced after ionization of C_2H_4 which is created when the rearrangement process of $SiMe_3^+$ [9] occurs.

For m/z = 15: The appearance energy measured for this ion corresponds to the value given in the literature for the direct ionization of the methyl group ($E_a = 9.82$–9.87 eV) [7].

For m/z = 2: The ionization threshold measured corresponds to the direct ionization of H_2 ($E_a =$ 15–16 eV) [7].

For m/z = 1: This ratio corresponds to the H^+ ion. However, the appearance energy measured (about 15 eV) is too large. It cannot proceed via direct ionization of the H atom (13.56 eV). Other processes like the dissociative ionization of organic compounds are more probable. For instance, in the case of C_3H_6, the ionization threshold corresponding to the dissociative ionization producing H^+ is 19.5 eV.

4. Contribution of the dissociative ionization of TMS to the signal intensity

Fig. 3 displays the signal intensity measured for the species $m/z = 88$, 73, 43, 58, and 15, versus the electron energy, when the discharge is off and on. In both cases the various species are detected even at low electron energy. This phenomena can be explained by considering (1) the contribution due to species desorbed by the wall of the reactor (which also occurs when the discharge is off) and (2) the contribution due to dissociative ionization of TMS. In the case of species like $SiMe_3^+$ ($m/z = 73$), the contribution of the dissociative ionization of TMS is very important even at low electron energy (typically 10 eV), whereas in the case of a species like CH_3^+ ($m/z = 15$) this contribution can be neglected at low electron energy because of the large ionization threshold value

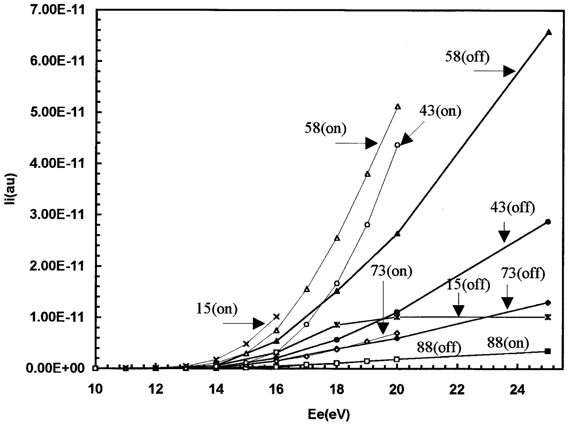

Fig. 3. Mass spectrometric signal intensity measured for the species corresponding to *m/z* = 88, 73, 43, 58, and 15 versus electron energy in the ionization chamber. The figure compares the intensities measured when the discharge is off to the intensities measured when it is on.

that ranges between 23 and 24 eV [10]. For each species it is necessary to correct the signal measured when the discharge is on and to suppress these two contributions. The first one (due to wall desorption) is expected to remain low and constant regardless of the TMS content in the gas mixture. Thus, it can be corrected with a simple subtraction of the signal measured discharge off from the signal measured discharge on. However, the second one can be very important and increases with the TMS partial pressure increasing. For each species, the intensity must be corrected, taking into account the part corresponding to the dissociative ionization of TMS into the ionization chamber of the mass spectrometer. This contribution is deduced from the signal measured when the discharge is switched off. As is shown in Fig. 3, the signal intensity is larger when the discharge is on than when it is off and the difference between the two signals increases with decreasing *m/z* ratio. At an electron energy of 20 eV, the signal measured for *m/z* = 43 when the discharge is off is about 27% of the signal measured when the discharge is on. It is 50% for *m/z* = 58 and 88% for *m/z* = 73. Thus, the contribution due to dissociative ionization of TMS increases as the *m/z* ratio increases.

Considering the ion $SiMe_4^+$ (*m/z* = 88), we measure an intensity I_{88} corresponding to the density n_{88}. However, taking into account the part of TMS that is dissociated when ionized, the real abundance of TMS should be n_{88r} and corresponds to the real signal I_{88r}.

The relation between the densities is given by

$$n_{88r} = n_{88} + \Delta n_{88} \tag{3}$$

where Δn_{88} is the part of TMS that is dissociated when ionized in the mass spectrometer. Thus, we arrive at the following expression

$$I_{88r} = I_{88}/(1 - \alpha) \tag{4}$$

with

$$\alpha = \Delta n_{88}/n_{88r} \tag{5}$$

If we consider the case of the species *i* created within the plasma, i.e. when the discharge is switched on, the signal measured for this specy is I_{iad}. It contains an ion due to ionization of the species *i* as well as ions due to dissociative ionization of the TMS that can be estimated using the signal measured for the species *i* when the discharge is switched off I_{isd}.

The real signal I_{iadr} corresponding to the direct ionization of the species *i* when the discharge is switched on, is given by the following expression that is obtained using Eq. (4)

$$\begin{aligned} I_{\mathrm{iadr}} &= I_{\mathrm{iad}} - [I_{\mathrm{isd}}/(I_{88\mathrm{sd}}/(1 - \alpha))(I_{88\mathrm{ad}}/(1 - \alpha))] \\ &= I_{\mathrm{iad}} - (I_{\mathrm{isd}}\, I_{88\mathrm{ad}}/I_{88\mathrm{sd}}) \qquad (6) \end{aligned}$$

where $I_{88\mathrm{sd}}$ and $I_{88\mathrm{ad}}$ are the signal measured for the TMS when the discharge is switched off and switched on, respectively.

This expression can be used in order to correct the signal measured for each species *i* when the discharge is on. However, only the part due to dissociative ionization of TMS is considered. Thus, in a more rigorous expression it should be necessary to take into account the part due to dissociative ionization of each species created within the discharge and to also consider the dissociative ionization of the species *i* itself. So, we have to check the effect of $Si(Me)_3$, $Si(Me)_2$, and Si(Me) dissociative ionization on the signal intensity measured when the discharge is on.

These radicals are created within the discharge and they are ionized in the ionization chamber. It can be a direct ionization, for instance $Si(Me)_2 + e \rightarrow Si(Me)_2^+ + 2e$, but also a dissociative ionization, like for instance, $Si(Me)_3 + e \rightarrow Si(Me)_2^+ + CH_3 + 2e$ or $SiMe_3 + e \rightarrow SiMe_2 + CH_3^+ + 2e$.

The contribution of the dissociative ionization of these species to the signal can be roughly estimated by considering the case of the CH_3^+ ion. Because the Si–C and C–H binding energies are equal to 76 kcal/mol and 99 kcal/mol, respectively, the dissociative ionization of the $Si(CH_3)_x$ radical is expected to arise mainly from the Si–C bond breaking. In a first approximation we assume that the density of CH_3^+ created in the ionization chamber is representative of the dissociative ionization processes of these species. This supposes that the dissociative ionization process is efficient enough at the electron energy value that we use in the ionization chamber.

The $m/z = 15$ signal intensity versus the electron energy, when the discharge is off and when it is on, is shown in Fig. 3. The measurements are performed at a partial pressure PArTMS of 40 Pa, a total pressure of 66 Pa, and a microwave power of 100 W. In order to estimate the part due to direct ionization of CH_3^+ in the signal intensity measured, we have calculated this signal intensity assuming only the direct ionization process ($CH_3 + e \rightarrow CH_3^+ + 2e$). For each species i, the mass spectrometer output current I_i is given by relation (1). According to Toyoda et al. [11], the transmission factor $T(m_i, n_i)$ is related to the electron beam current I_b by

$$T(m_i, n_i) = A_i(m_i, n_i) \cdot I_b \tag{7}$$

where $A_i(m_i, n_i)$ is a proportional parameter depending on both the sensitivity of the mass spectrometer and the vacuum conductance in the extractor. It also depends on the mass and on the concentration of the species i.

Before calculating the signal resulting from the direct ionization of CH_3 it is necessary to measure the product $A_i \cdot I_b$ for each electron energy value. It increases with increasing electron energy and it can be achieved from the mass spectrometer signal measured for $m/z = 88$ (TMS) when the discharge is off, using the TMS ionization cross section values given by Basner et al. [10]. After this, it is possible to calculate the signal measured in the case of $m/z = 15$ considering only the direct ionization of methyl radicals. The direct ionization cross section value is calculated using the binary–encounter–dipole–Bethe method (BEB method) given by Hwang et al. [12]. The threshold behavior of the ionization cross section is sensitive to the lowest value of the binding energy. Thus, we use a value given in the case of the molecular $3a_1$ orbital, corresponding to the lowest binding energy (9.84 eV).

Fig. 4 shows the mass spectrometer signal intensity measured for $m/z = 15$ (CH_3^+) versus the electron energy in the range 10–16 eV. The intensity is measured when the discharge is on (I_{15ad}) and when it is off (I_{15sd}). In the same figure we have plotted the signal intensity corrected using [Eq. (6)] I_{15adc}. Then, we compare this last curve to the signal intensity calculated assuming only a direct ionization of CH_3 with the previous method (I_{15cal}). This last curve has been normalized using the signal intensity I_{15adc} measured for an electron energy of 16 eV. There is a good agreement between I_{15adc} and I_{15cal}. The calculated intensity remains in the error value range estimated for I_{15adc}. These results show that the intensity value measured for $m/z = 15$ when the discharge is on and after correction [Eq. (6)], is mainly due to ionization of the neutral radical CH_3 produced in the discharge. Thus the contribution in the ionization chamber due to dissociative ionization (producing CH_3^+) of $Si(CH_3)_{x<4}$ can be neglected.

So, in this work we correct the signal measured for the different species using the previous relation (6) corresponding to the case where only the dissociative ionization of TMS is efficient. We consider that the contribution due to other species remains low compared with the contribution due to dissociative ionization of the TMS.

According to Wrobel et al. [13,14] the initial stage of dissociation of the TMS molecule arises from bond breaking after collisions with the electrons of the plasma. Mainly, Si–Me bond breaking or C–H bond breaking occur. In the first case the main radical produced is $SiMe_3$ and in the second case it is $SiMe_3CH_2$. Because of the strong difference in bond

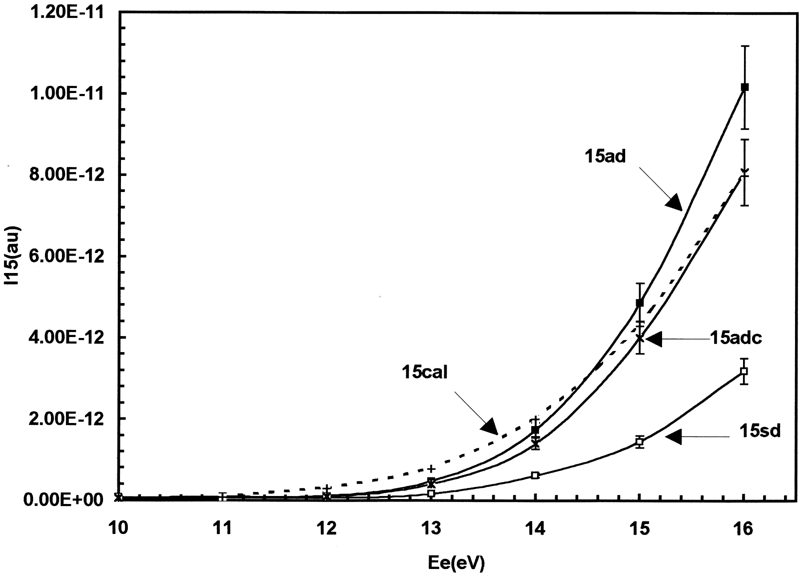

Fig. 4. Mass spectrometric signal intensity measured for $m/z = 15$ (CH_3) versus the electron energy in the range from 10–16 eV. The intensity is measured with discharge I_{15ad} and without discharge I_{15sd}.

energy between the Si–C bond at 76 kcal/mol and the C–H bond at 99 kcal/mol, the first dissociation process is more probable.

Thus, the density of the methyl radical accounts for dissociation processes by Si–C bond breaking and the density of H_2 accounts for dissociation processes by C–H bond breaking. In order to check the dominant dissociative reactive process (Si–C or C–H bond breaking), mass spectrometer measurements given in the next part of this article are compared to the intensity measured for the Me radical ($m/z = 15$) and H_2 molecule ($m/z = 2$).

The signal intensity measured for CH_3^+ when the discharge is on is mainly due to direct ionization of the CH_3 radical produced in the discharge and ionized in the ionization chamber. Therefore, this signal intensity is consistent with the CH_3 density contained in the discharge.

5. Effect of the microwave power on the plasma composition

Mass spectrometric analysis has been performed for different microwave powers $P\mu$ within the plasma discharge containing an Ar-TMS gas mixture. The TMS is diluted in argon and is carried along the reactor at 30 m/s from an injector located below the discharge. The total pressure is equal to 26.6 Pa and the distance between the discharge center and the mass spectrometer sample hole is fixed at 380 mm.

The mass spectrometry measurements obtained for $m/z = 73$, 58, 43, 28, 15 (or 2) divided by the signal intensity measured for $m/z = 15$ and $m/z = 2$, versus the incident microwave power are shown in Figs. 5 and 6, respectively. Fig. 5 also gives the TMS decay in the plasma versus the microwave power. It can be seen that when the microwave power is lower than 40 W the main specy produced is $SiMe_3$ ($m/z = 73$). In that case the dominant dissociation process arises from Si–C bond breaking. As the power increases, the lighter species like $m/z = 58$ ($SiMe_2$) and 43 (SiMe) prevail. The ratio I_{Me}/I_{H2} decreases with increasing incident power (see Fig. 6). This shows that at higher power the C–H bond breaking process prevails in comparison to the Si–C bond breaking process. Thus, the normalized signal measured for $m/z = 28$ (C_2H_4) decreases with increasing power because of the decrease of the $SiMe_3^+$ content. In this plasma device the

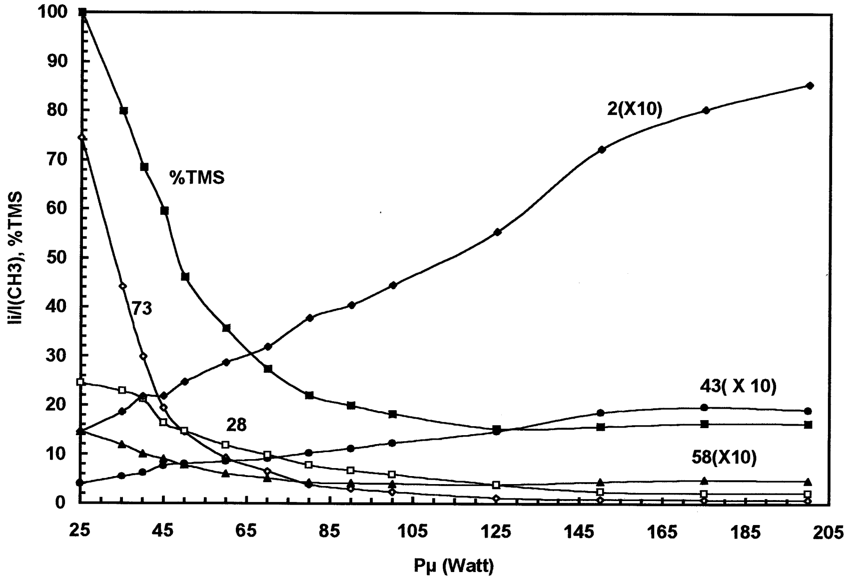

Fig. 5. Mass spectrometric signal intensity measured for *m/z* = 73, 58, 43, 28, 15 (or 2) divided by signal intensity measured for *m/z* = 15 versus the microwave power $P\mu$. In this figure the percentage of TMS remaining in the plasma versus the microwave power is also displayed.

dissociation of TMS is very efficient; at 40 W, 30% of the initial TMS is dissociated and at powers higher than 100 W, more than 80% is dissociated. These results show that it is not necessary to work with a microwave power larger than 100 W in order to efficiently dissociate the TMS contained in the gas mixture.

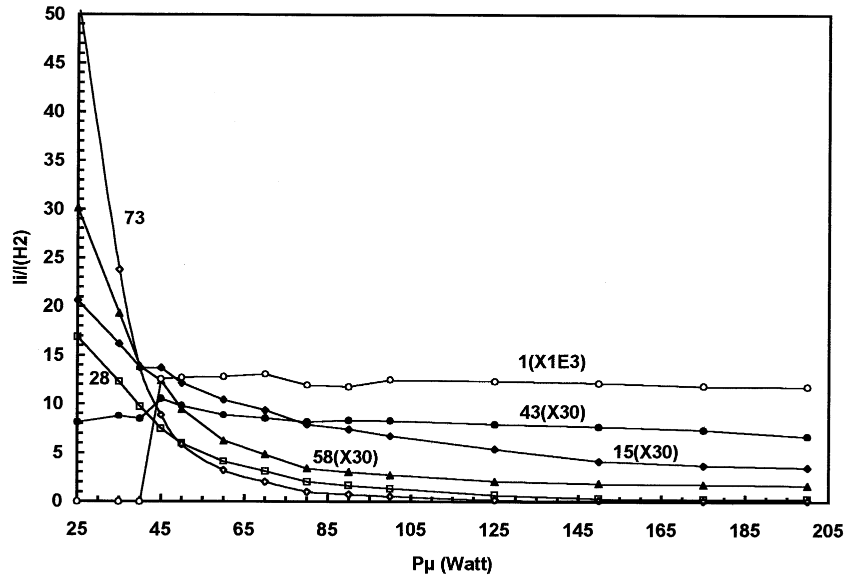

Fig. 6. Mass spectrometric signal intensity measured for *m/z* = 73, 58, 43, 28, 15 (or 2) divided by the signal measured for *m/z* = 2 versus the incident microwave power $P\mu$.

Table 2
Values of the reactor parameters, d, d', and D, in the four different reactor configurations a, b, c, and d

Configurations	a	b	c	d
d (mm)	−8	35	10–20	−8
d' (mm)	55	20	28–38	48
D (mm)	55	55	48	48

At low power, typically 40 W, the dissociation proceeds via Si–C bond breaking and the main radicals produced within the plasma are heavy radicals like $SiMe_3$. By increasing the power, high densities of $SiMe_2$ and SiMe are produced. Moreover, the ratio I_{H2}/I_{Me} also increases with increasing power due to C–H bond breaking.

The signal intensity measured for Me ($m/z = 15$) first increases with increasing power from 6×10^{-9} A at $P\mu = 25$ W to 1.29×10^{-8} A at 85 W. It then decreases for higher power values (9×1.10^{-9} A at 175 W). All of these results show that at low power, the density of the methyl radical increases with increasing power. At a higher power the methyl radical density decreases with increasing power. Thus, the CH_3 radical is probably dissociated, producing simple radicals $CH_{x<3}$ and H atoms. The H_2 density increases with the power due to C–H bond breaking, producing H atoms that recombine in H_2.

6. Effect of the dilution of TMS in argon on the plasma composition: study in various configurations

We have changed the design parameters of the reactor in order to selectively convert TMS to useful radicals and to control the reactions involving radicals and other reactive species generated within the plasma. Investigations have been performed using the mass spectrometer in four different reactor designs. A list of the parameters concerning the reactor design are reported in Table 2, where d corresponds (see Fig. 1) to the length between the exit of the microwave launcher and the TMS injector, d' is the length between the mass spectrometer sample hole and the TMS injector, and D is the length between the microwave launcher exit and the mass spectrometer sample hole. In each configuration of the reactor, we study the effect of the TMS fraction mixed in the Ar-TMS gas mixture on the plasma composition.

In these four different configurations the TMS can be injected into the discharge (case a and d), close to the discharge (case c) or far away from the discharge (case b). As previously reported, the signal intensity measured for each specy is divided by the signal intensity measured for the methyl radical and for the hydrogen molecule. The resulting ratio allows one to show the main dissociative process involved in each reactor design (Si–C or C–H bond breaking).

These measurements have been performed at a total pressure of 66 Pa with an incident microwave power of 100 W. For each reactor design, the signal intensity corresponds to $m/z = 73$ ($SiMe_3^+$), 58 ($SiMe_2^+$), 28 ($C_2H_4^+$), 14 (CH_2^+), 15 (CH_3^+), 2 (H_2^+), and 1 (H^+). This signal is divided with the signal intensity measured for CH_3^+ and H_2^+ versus the TMS partial pressure. The signal measured for $m/z = 43$ is very small at this power. Therefore, in the remaining figures we have not reported measurements corresponding to this specy.

In configuration a, the TMS is injected into the discharge and the mass spectrometer is located outside of the discharge. For each specy i the ratios Ii/I_{CH3} and Ii/I_{H2} versus the TMS partial pressure are displayed in Figs. 7 and 8, respectively. For the heavier radicals like $SiMe_{2,3}$, the ratio Ii/I_{CH3} remains constant when the TMS content increases, whereas for the lighter radicals like CH_2, H_2, or H, the ratio decreases suddenly with increasing TMS contents. Only for C_2H_4 does the ratio Ii/I_{H2} increase with increasing TMS contents. It remains constant for the other heavy radicals and decreases for the light species. This configuration mainly produces heavy species $SiMe_{2,3}$ by Si–C bond breaking with a quite good TMS dissociation efficiency that is closed to 100%.

In configuration b, the TMS is injected far away from the microwave launcher and the detection is performed downstream and outside of the discharge. In this case the TMS dissociation is low (10–20%). The Ii/I_{CH3} and Ii/I_{H2} ratios versus the TMS partial

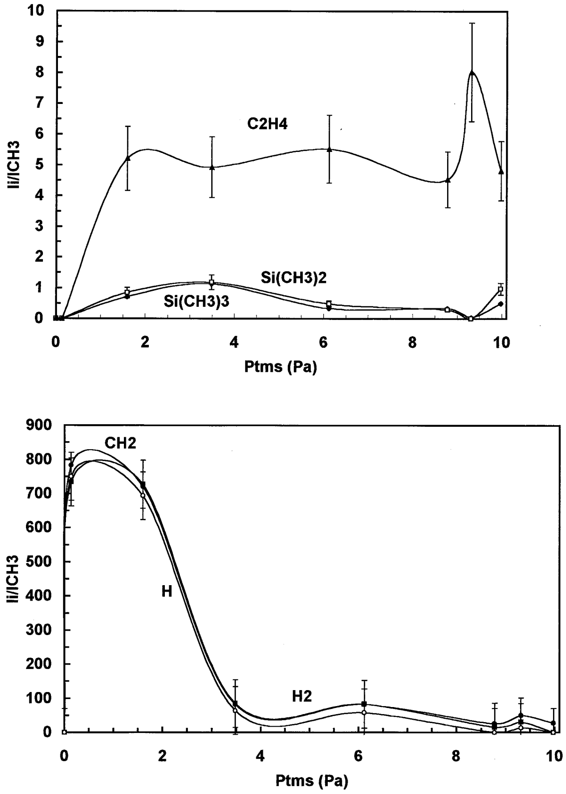

Fig. 7. Configuration a: ratios Ii/I_{CH3} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

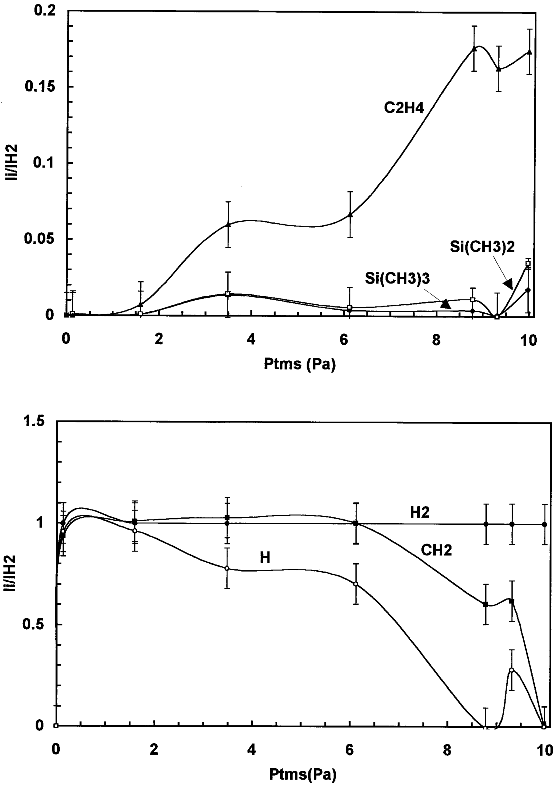

Fig. 8. Configuration a: ratios Ii/I_{H2} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

pressure are displayed in Figs. 9 and 10, respectively. The relative change in $SiMe_{2,3}$ or C_2H_4 is difficult to estimate. Whereas for the lighter species CH_2, H_2, or H, the Ii/I_{CH3} ratio decreases with increasing TMS content and the ratio Ii/I_{H2} remains nearly constant over all the TMS partial pressure ranges investigated. This behavior can be explained by considering the strong reactivity of the simple radicals like CH_2 or H in such a plasma [14]. These species are quickly recombined in the area located between the discharge and the mass spectrometer sample hole. The heavy species are probably less reactive than the former so they are more easily detected. In configuration c, the TMS is injected outside of the microwave launcher and measurements are performed in a part corresponding to the expanding plasma outside of the microwave launcher. In that case the TMS dissociation is less efficient than when the TMS is injected in the launcher (more than 60%). The TMS is mainly converted into heavy radicals like $SiMe_{2,3}$. The relative change of Ii/I_{CH3} and Ii/I_{H2} versus the TMS partial pressure is displayed in Figs. 11 and 12, respectively. For the heavy radicals, the ratio Ii/I_{CH3} first increases with increasing TMS partial pressure until 3.5–4 Pa and then remains constant for higher TMS partial pressure, and the ratio Ii/I_{H2} also increases with increasing TMS pressure until at least a partial pressure equal to 10 Pa. For the light species, the Ii/I_{H2} ratio remains quite constant with increasing TMS pressure and the Ii/I_{CH3} ratio increases until 2 Pa and then decreases with increasing TMS partial pressure because of the simple radical recombination process, as in the previous reactor design. This configuration seems to be more convenient for producing

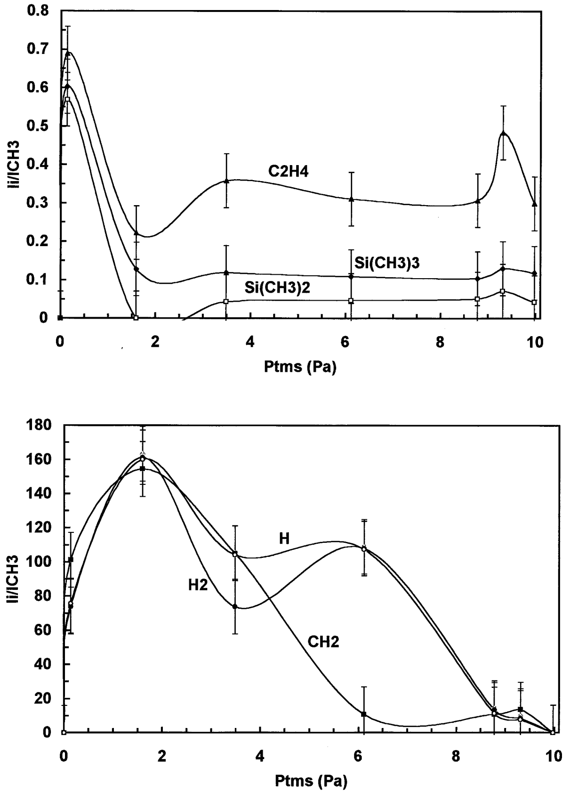

Fig. 9. Configuration b: ratios Ii/I_{CH3} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

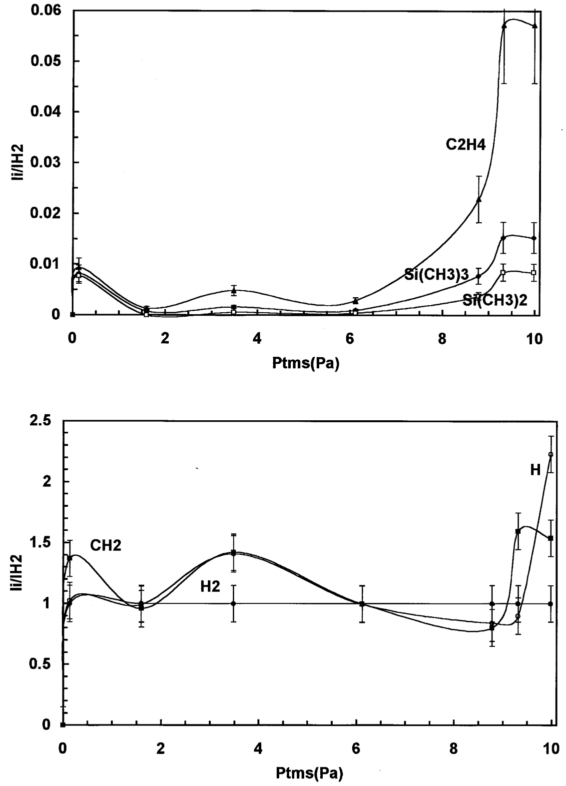

Fig. 10. Configuration b: ratios Ii/I_{H2} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

heavy species via the Si–C bond breaking processes. Nevertheless, the dissociation yield of TMS seems to be more important than in the former case.

In the last configuration (d), the TMS is injected into the microwave launcher and measurements are performed in the expanding plasma out of the launcher. Results are shown in Figs. 13 and 14. In that case the dissociation yield of the TMS is very efficient (close to 100%). The ratio Ii/I_{CH3} and Ii/I_{H2} decrease with TMS partial pressure increasing for the heavy species and increase with increasing TMS content for the light species. This reactor design is the most convenient for producing simple species like CH_3 (or CH_2), H or H_2.

This study concerning the plasma composition in different reactor configurations shows that the position of the TMS injector (into or outside of the microwave launcher) has a large effect on the TMS dissociation yield. This TMS dissociation yield is more important when the TMS injector is placed into the launcher. However, the composition of the gas phase in the vicinity of the analyzer (or substrate in the case of a layer deposition) strongly depends on the length between the microwave launcher and the mass spectrometer sample hole. When this length is short, the plasma expands until the sample hole and the measurements are inside the discharge. Thus, the simple radical does not have enough time to recombine efficiently, so its density is important. When the distance between the TMS injector and the mass spectrometer sample hole is large, measurements are performed outside of the discharge. Thus, the light reactive species are recombined strongly and the gas mixture contains mainly stable species like, for example, the heavy radicals SiMe2,3.

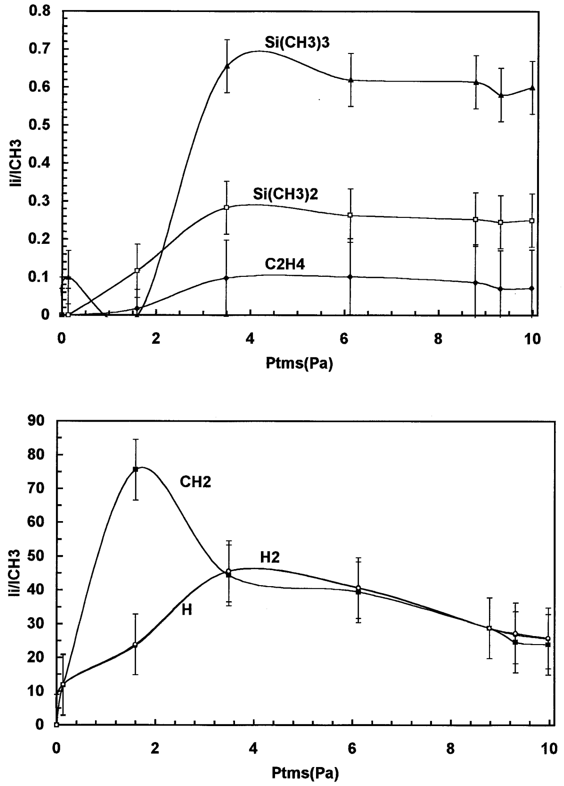

Fig. 11. Configuration c: ratios Ii/I_{CH3} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

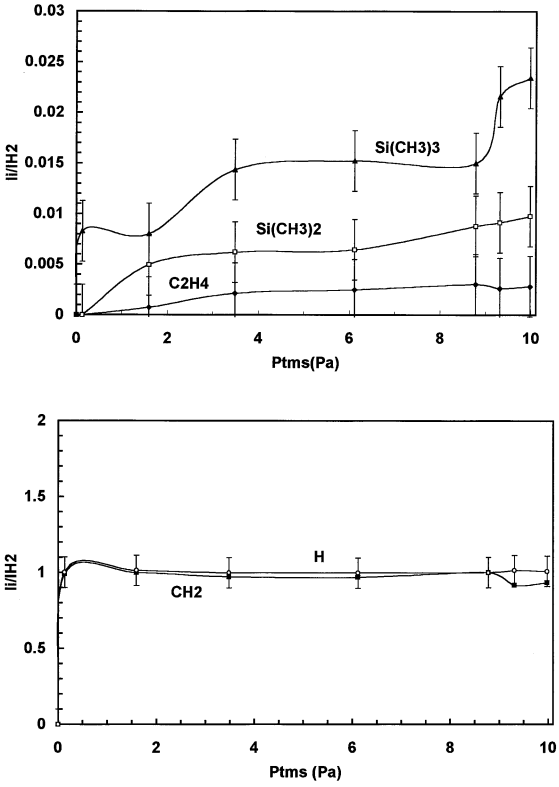

Fig. 12. Configuration c: ratios Ii/I_{H2} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

7. Conclusions

This work is devoted to the study of a microwave plasma containing Ar-TMS. Investigations on the plasma composition are performed by means of a mass spectrometer equipped with a two-stage differential pumping in order to work under SiC deposition layer conditions. We use an ionization threshold method in order to identify the different species produced within the plasma. We compare the appearance energy of the species to the value given in the literature. Particularly, we show that $m/z = 28$ corresponds to $C_2H_4^+$, resulting mainly from metastable ion transition (mostly $SiMe_3^+$) with cleavage processes and elimination of stable molecules like C_2H_4.

We then give the method that we use in this work to correct the signal intensity measured for each specy. This method takes into account the part due to dissociative ionization of the TMS. The contribution of other species ($SiMe_3^+$, $SiMe_2^+$, $SiMe^+$) produced within the discharge seems to be very low.

Using the previous correction method, we have studied the effect of the incident microwave power on the plasma composition. We show that dissociation of the TMS molecule is very efficient. At 100 W, more than 80% of TMS is dissociated. Therefore, it is not necessary to work with a higher power in order to dissociate the TMS. At low power, typically 40 W, the main dissociative processes are Si–C bond breaking and the main radicals produced within the plasma are heavy radicals like $SiMe_3$. Then with increasing power the light radicals like $SiMe_2$ and SiMe are produced. The ratio I_{H2}/I_{Me} also increases because of the numerous C–H bonds that break with increasing power.

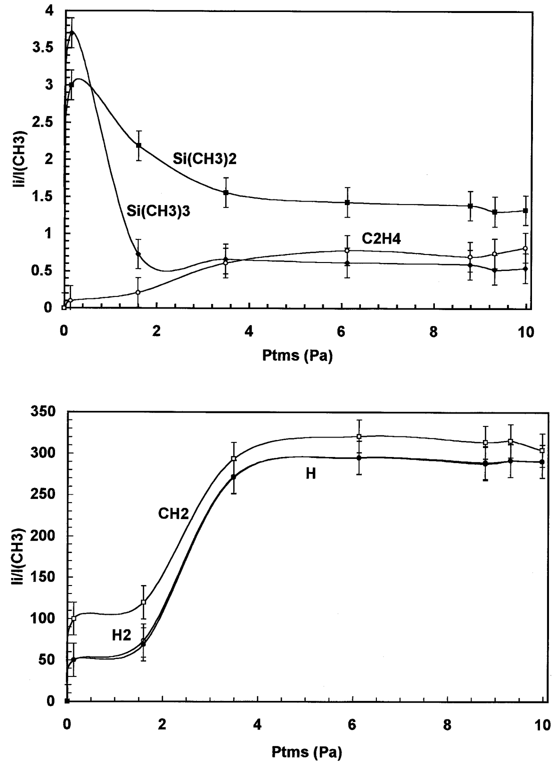

Fig. 13. Configuration d: ratios Ii/I_{CH3} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

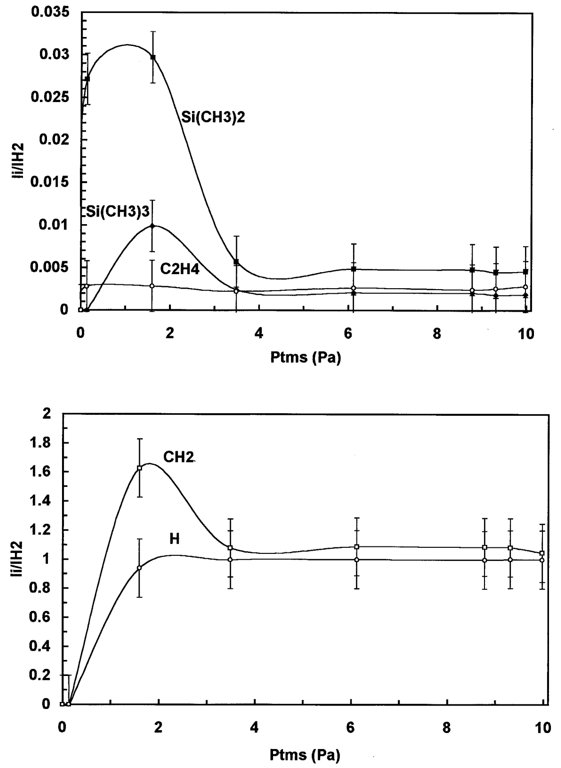

Fig. 14. Configuration d: ratios Ii/I_{H2} for the main species (heavy species top and light species bottom) versus the TMS partial pressure.

Investigations are also performed on the gas composition in different reactor designs. The results obtained in different reactor designs show that the position of the TMS injector (inside or outside of the microwave launcher) has a large effect on the TMS dissociation yield. This one is more important when the TMS injector is placed inside the launcher. However, the composition of the gas phase in the vicinity of the analyser (or substrate in the case of a layer deposition) strongly depends on the length between the microwave launcher and the mass spectrometer sample hole. When this length is short, the plasma expands until the sample hole so the measurements are performed in the discharge. In that case simple radical densities are more important.

Each specy produced within the plasma depends on the reactor design and on the gas mixture injected into the reactor. Both parameters are important and act on the discharge gas composition. Thus, it is necessary to adjust the gas mixture from one configuration to another in order to obtain similar gas composition at the exit of the discharge.

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