NATURE AND ROLE OF THE VARIOUS NEUTRAL AND CHARGED SPECIES CREATED IN LOW PRESSURE ORGANOSILICON PLASMAS

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Abstract

The neutral and charged species created in in organosilicon containing plasmas are probed by mass spectrometry, optical emission spectroscopy and Langmuir probe. On the basis of these analyses, the organosilicon cracking pattern and the neutral or ionic nature of the precursors to the film growth are discussed.

5. Introduction

Low pressure organosilicon-based plasmas are widely used for PECVD deposition of organic and inorganic SiO₂-like films. This paper is focused on the analysis of the low pressure (a few mTorr) plasmas created from hexamethyldisiloxane (HMDSO) mixed with argon or oxygen by mass spectrometry (SM), optical emission spectroscopy (OES) and Langmuir probe (LP). After a brief description of the experimental setup, the results concerning the neutral and charged species measured in Ar/HMDSO and O₂/HMDSO plasmas will be successively presented. At last, these results will be discussed with the aim of getting better insight in the organosilicon cracking pattern and in the neutral or ionic nature of the precursors responsible for the film growth.

4. Experimental setup and diagnostics

The low pressure rf (13.56 MHz) inductively coupled plasma reactor used to create the plasma is described in detail in [1]. In brief, it consists of a diffusion stainless-steel chamber (30 cm in diameter and height) and a plasma source made of a glass tube surrounded by a helicon antenna (15 cm in diameter and 30 cm in height). The reactor is pumped by a turbo/rotary device and the residual pressure measured by an ionization gauge at the diffusion chamber outlet is a few 10⁻⁶ Torr. The oxygen gas is introduced at the top of the plasma source while the organosilicon vapor is injected into the diffusion chamber via a dispersal ring. Argon is used as an actinometer. The experimental conditions are as follows: a 2.5 mTorr pressure before plasma, a magnetic field equal to 60 G at the center of the plasma source. The organosilicon flow rate is mixed to either oxygen or Argon and its fraction as deduced from the organosilicon to oxygen partial pressures, is varied from zero to 100 %. The rf power and total gas flow rate are fixed at 300 W and 16 sccm, respectively.

Three in situ diagnostics are used to characterize the O₂/organosilicon plasma created in the diffusion chamber: mass spectrometry, optical emission spectroscopy and Langmuir probes.

Mass spectrometry: the neutral species and positive ions extracted from the plasma through a sampling orifice (100 μm in diameter) are analyzed by a Balzers Plasma Process Monitor (PPM 421), which offers an energy range of -500 to +500 eV. Experimental mass spectra are recorded in the mass range 1-512 amu with a resolution of 0.5 amu. For the neutral species analysis, ions are created upon electron impact and the electron energy can be varied from 8
to 120 eV with an estimated energy spread of about 0.5 eV. during the experiments. The sampling orifice used to sample neutral species emanating from the plasma is located between the ring and the substrate holder, at about 5 cm from the reactor wall. The mass dependent response of the mass spectrometer was measured in the 4-209 amu range using calibrated He/N\textsubscript{2}/Ar/Kr/Xe/TEOS neutral mixtures. It was shown to be only weakly mass depending in the 40-200 amu range [2]. Mass spectra for neutral species were recorded at a 18 eV electron energy in order to limit the organosilicon cracking in the ionization chamber.

Optical emission spectroscopy: the light emitted by the plasma is analyzed in the 180-850 nm spectral range by a Jobin-Yvon monochromator (HR 460). The light emitted by the discharge is sampled through a quartz window located at mid height of the diffusion chamber, between the ring and the substrate holder.

Langmuir Probes: Ar/HMDSO plasmas have been investigated by LP, using the rf compensated Smart Probe from Scientific Systems. The 50\mu m-diam and 5mm-long probe was introduced at the centre of the plasma, between the dispersal ring and the substrate. The tungsten probe tip was heated by electron bombardment before and during the measurement of the probe I/V characteristics. I/V characteristics were measured in argon, before and after each measurement in Ar/HMDSO plasma in order to check that there was no significant insulating deposition on the probe tip during the I/V acquisition.

12. HMDSO and Ar/HMDSO plasmas

3.1 Neutral species

Complementary information on neutral species are derived from plasma analysis by mass spectrometry and optical emission spectroscopy.

Mass spectrometry (MS):

MS allows the detection of all the stable molecules. Nevertheless, in organosilicon plasmas which contain many different neutral species, additional investigations using the ionization threshold technique are necessary to obtain a reliable analysis of the spectra [3]. The mass spectra measured in HMDSO and Ar/HMDSO plasmas are very similar. The spectra recorded in HMDSO plasma-off and plasma-on (300 W) conditions are plotted in Fig.1.

In addition to HMDSO ion fragments (m/z = 73, 147, 148, 149 [4]), the plasma off spectrum exhibits peaks at 18 (due to residual water) and 28 amu. The intensity of the m/z 28 peak was recorded versus the electron energy and exhibits only one threshold energy at about 10.5 eV, which indicates that the 28 amu ion can be assigned to C\textsubscript{2}H\textsubscript{4}-, and not CO\textsuperscript{+} (CO ionization energy = 14 eV). C\textsubscript{2}H\textsubscript{4} is likely to be created by pyrolysis of HMDSO on the hot filament in the ionization chamber. The most likely molecular formulae and possible structural assignments for the ions detected in plasma-off and plasma-on conditions are given in Table I, together with the parent neutral molecules (as far as it can be predicted).

The comparison of the plasma off and plasma on spectra yields the following information:
- the intensity of the main HMDSO fragment ion (m/z 147) decreases by a factor of about 4 when the plasma is ignited, which means that the dissociation rate HMDSO is about 75 %
- H\textsubscript{2} (m/z 2), CH\textsubscript{4} (m/z 16), C\textsubscript{2}H\textsubscript{2} (m/z 26) and C\textsubscript{2}H\textsubscript{4} (m/z 28) are detected,
- the signal at m/z 18, is almost unchanged as the plasma is switched on, which means that there is almost no production of water in the HMDSO plasma,
Fig 1: Mass spectra recorded in HMDSO plasma-off and plasma-on (300W) conditions

- the analysis of the peak at m/z 28 and the absence of any peak at m/z 44 indicates that CO and CO₂ are almost absent,
- the intensity of the m/z 73 ion, assigned to Si(CH₃)_3⁺, increases whereas the intensity of the main HMDSO ion fragment at m/z 147 decreases. In addition, new peaks appear at m/z 58, 59, 119, 133. The possible molecular formulae for these ions are given in Table I and they might be formed upon dissociative ionization of Si(CH₃)₃ (for m/z 58, 59, 73) and (CH₃)₃SiOSi(CH₃)₂ (for m/z 119 and 133).
- a new peak is observed at m/z 221, which is likely to correspond to (CH₃)₃SiOSi(CH₃)₂OSi(CH₃)₂⁺. The formation of this molecule, containing 3 Si atoms, is the first step towards homogeneous oligomerization in the plasma phase.

<table>
<thead>
<tr>
<th>M/z</th>
<th>Ion formula</th>
<th>Plasma off</th>
<th>Plasma on (300 W)</th>
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<tr>
<td>2</td>
<td>H₂⁺</td>
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<td>H₂</td>
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<tr>
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<td>147</td>
<td>(CH₃)₃SiOSi(CH₃)₂⁺</td>
<td>HMDSO</td>
<td>HMDSO</td>
</tr>
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</table>

Table 1: Ions and related neutral species detected by MS in HMDSO plasma
It is worth noting that the mass spectra of the neutral portion of the plasma are very similar to those reported by Alexander et al [5] at a slightly higher pressure (60 mTorr).

Optical Emission Spectroscopy (OES):

Further information stem from the plasma analysis by OES. The emission spectra of HMDSO and Ar/HMDSO plasmas are almost the same (except Ar emission) and yield the following information:
- the emissions of H, H2, CH and C2 are consistent with the presence of H2, CH4, C2H2 and C2H4 detected by MS,
- there is no emission from CO and OH: this is in very good agreement with MS analysis which has shown that neither CO nor H2O was formed in the plasma,
- Si and SiO emissions are clearly detected in the UV spectral range (200-300 nm).

The presence of Si and SiO radicals, which is demonstrated by OES, is consistent with the following cracking pattern of HMDSO: one of the two strong Si-O bonds is broken, yielding the formation of Si-(CH3)3 (detected by MS) and O-Si(CH3)3. Then the less strong Si-C bonds are easily broken, yielding the creation of Si and SiO. These results, obtained in a low pressure HMDSO plasma, are in perfect agreement with those obtained by controlled electron impact on HMDSO by Kurunczi et al [6]

3.2 Charged species

Information on charged particles, namely electrons, positive and negative ions can be derived from Langmuir probe and mass spectrometry, respectively. Although negative ions have been shown to be formed in HMDSO based plasmas in the 100 mTorr - 1 Torr pressure range [7], their density is expected to be weak in low pressure conditions and only results concerning positive ions and electrons will be reported hereafter.

Langmuir Probes (LP):

Figs. 2 and 3 display a typical I/V characteristics obtained in a 67%Ar-33%HMDSO plasma (300W) and the variations of the electron density ($n_e$) and electron temperature ($T_e$) with the HMDSO fraction (equal to the HMDSO pressure to total pressure ratio), respectively.

![First derivative of probe curve](image1.png)

![Variations of Te and ne](image2.png)

**Fig 2 :** probe curve and its first derivative in Ar/HMDSO-300W plasma. **Fig 3 :** variations of $T_e$ and $n_e$ versus the HMDSO fraction in Ar/HMDSO-300W plasma.
plasmas

$T_e$ is shown to decrease from 4.5 eV in a pure argon plasma to 1.5 eV in a pure HMDSO plasma, whereas the electron density only slightly depends on the HMDSO fraction and is always between 5 and 9 $10^9$ cm$^{-3}$. The decrease in $T_e$ may be explained as follows: since the HMDSO ionization threshold is about 8 eV, against 15.78 eV for Ar, the addition of HMDSO to Ar favours the gas ionization and the mean electron energy required to maintain the plasma significantly decreases. In addition, the measurement of $V_p$ and $V_f$ allows to determine the energy of the positive ions impinging upon a substrate at the floating potential. In the 300W 67%Ar-33%HMDSO plasma, this energy ($E_{ion}=e(V_p-V_f)$) is found to be equal to 13 eV.

Mass Spectrometry:

The mass spectra of the positive ions extracted from HMDSO and Ar/HMDSO plasmas are very similar. The spectrum recorded in a 67%Ar-33%HMDSO-300W plasma is displayed in Fig. 4. The most intense peaks are detected at m/z 3 ($\text{H}_3^+$), 15 ($\text{CH}_3^+$), 27 ($\text{C}_2\text{H}_5^+$), 26 ($\text{C}_2\text{H}_2^-$), 41 (ArH$^+$), 2 ($\text{H}_2^-$). The HMDSO fragment ions at m/z 147, 133, 73, 59 are detected, but their intensity is one to two orders of magnitude smaller than the one of $\text{H}_3^+$ and $\text{CH}_3^+$.

![Mass spectra of the positive ions extracted from a HMDSO plasma (300W)](image.png)

Fig. 4: Mass spectra of the positive ions extracted from a HMDSO plasma (300W)

13. Oxygen/HMDSO plasmas

4.1 Neutral species:

The neutral mass spectrum measured in a 67% O$_2$-33% HMDSO plasma is shown in Fig. 5

![Mass spectra in a 67%O$_2$-33%HMDSO plasma (300W)](image.png)

Fig. 5: Mass spectra in a 67%O$_2$-33%HMDSO plasma (300W).
As can be seen, they are completely different from those obtained in HMDSO and Ar/HMDSO plasmas. In addition to the peaks related to H₂ and hydrocarbons (m/z 2,16,26), intense peaks appear at m/z 18, 28 and 44, which can be assigned to H₂O, CO and CO₂, respectively. The presence of H₂O, CO and CO₂, which is also clearly demonstrated by OES, is typical of homogeneous and heterogeneous reactions oxidation reactions and is currently observed in oxygen/organosilicon plasmas [3,7]. The intensity of O₂⁻ (m/z 32) and the main HMDSO fragment ions (m/z 147) strongly decrease as the plasma is switched on, and the O₂ and HMDSO dissociation degrees are measured to be 90 % and 81 %, respectively.

4.2 Charged species
The positive ion mass spectrum is now dominated by H₃O⁺ (m/z 19). Peaks at m/z 29 (COH⁺), 31 (CHO⁺), 32 (O₂⁺), 15(CH₃⁺), 2 (H₄⁺) and 45 (COH⁺) are also detected with an intensity of 20 to 5% of the one of H₃O⁺. The HMDSO fragment ions at m/z 147, 133 are completely absent from the mass spectrum, and the only Si containing ion is detected at m/z 73 peak with an intensity of only 1% of the m/z 19 peak.

14. Discussion and Conclusion
The measurement of both the positive ion mass spectra and the ion density (namely, nₑ by LP) allows to estimate the flux of positive ions containing one (m/z : 59, 73, 74, 75) or two Si atoms (m/z : 133, 147, 148), with the following assumptions:
- the ion transmission is independent of the ion mass,
- the m/z peak intensity is proportional to the ion Bohm velocity and ion density,
- the sum of all the m/z intensities is proportional to the ion density measured by LP.

Then, the deposition rate corresponding to the sticking of the Si-containing ions may be estimated, provided the film density and molecular formula are known. In the case of a 67%Ar-33%HMDSO-300W plasma, it is finally estimated to 10 nm/min, namely the third of the measured deposition rate (30 nm/min). Although such approximations are very rough, it is likely that the ion sticking can significantly contribute to the film growth in the Ar-HMDSO plasmas, as previously suggested by Alexander et al [5].

In contrary, in the case of oxygen/HMDSO plasmas, the deposition rate corresponding to the sticking of the Si-containing ions is estimated to be ten times less than the measured deposition rate. Hence, in the case of oxygen-rich O₂/HMDSO plasmas, it appears that not the ions but the neutral radicals are likely to have the dominant role in the film growth.

References