Effects of cross field diffusion in a low pressure high density oxygen/silane plasma

C. Charles

Citation: Journal of Vacuum Science & Technology A 20, 1275 (2002); doi: 10.1116/1.1481042
View online: http://dx.doi.org/10.1116/1.1481042
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvsta/20/4?ver=pdforcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in
Ion flux and ion distribution function measurements in synchronously pulsed inductively coupled plasmas
J. Vac. Sci. Technol. A 31, 020604 (2013); 10.1116/1.4790364

Effect of bulk electric field reversal on the bounce resonance heating in dual-frequency capacitively coupled electronegative plasmas

Ion distribution measurements to probe target and plasma processes in electronegative magnetron discharges. II. Positive ions
J. Appl. Phys. 109, 073303 (2011); 10.1063/1.3553847

Surface radicals in silane/hydrogen discharges

Density of CH 3 radicals and the ionic composition in a low pressure methane plasma beam
J. Appl. Phys. 84, 6923 (1998); 10.1063/1.368990
Effects of cross field diffusion in a low pressure high density oxygen/silane plasma

C. Charles

Plasma Research Laboratory, Research School of Physical Sciences and Engineering, The Australian National University, Acton, ACT 0200, Australia

(Received 29 October 2001; accepted 2 April 2002)

A low pressure high density oxygen/silane radio frequency (13.56 MHz) plasma coupled in a helicon reactor used for silicon dioxide deposition is characterized by using an energy selective mass spectrometer situated at the wall of the processing chamber: measurements of positive and negative ion energy distribution functions and mass spectra (1≤amu≤150) are obtained for various flow-rate ratios (R=O₂/SiH₄=1 to 10 but constant total flow rate of 30 sccm), and for a constant radio frequency power and magnetic field of 800 W and 70 G, respectively. Plasma potentials between 35 (R=10) and 60 V (R=1) are measured depending on the silane and oxygen flows showing charging of the silico-covered diffusion chamber wall. The magnitude of the wall charging most likely depends on the effective capacitance formed by the silica layer (which results from months of deposition) and on the imbalance between the positively and negatively charged particles which impinge onto the sidewalls at the discharge initiation until equilibrium of fluxes is reached.

This imbalance is a result of the magnetic field configuration generated by the four coils surrounding the reactor and of the subsequent cross-field diffusion of the positively and negatively charged particles to the sidewalls. Maximum wall charging is observed when the silane flow is maximum (R<=2), a situation where polymerization is observed in the mass spectrum of the positive ions, and where a minimum density of negative ions (O⁻, OH⁻, and H⁻) are detected close to the walls. Although the polymerization appeared to be a primary candidate for the increase of the plasma potential to ~60 V, its presence does not significantly change the total positive ion density at equilibrium but is accompanied by a dramatic decrease (two orders of magnitude for the O⁻ ions) in the negative ion density close to the walls when R is increased from 1 to 10. The change in the degree of electronegativity close to the walls affects the global plasma equilibrium and appears as an indirect factor in the magnitude of the wall charging. © 2002 American Vacuum Society. [DOI: 10.1116/1.1481042]

I. INTRODUCTION

The use of the helicon radio frequency (rf) source for plasma processing has been widely demonstrated over the past decade. Silicon dioxide deposition from oxygen/silane plasmas has been successfully carried out in continuous and pulsed modes and the results show great promise for the production of silicon-based optical waveguide devices (couplers, splitters, . . .). As there is no driven electrode, the substrate, which is placed at the bottom of the diffusion chamber attached to the helicon source, can be either independently biased or allowed to float. It has been shown that the positive ion flux impinging onto the substrate during the deposition process is an important parameter which should be monitored during the deposition process. In addition, the ions can contribute up to 50% of the oxide growth itself in our high density system in a situation where the substrate is “floating.” Lately, it has also been shown that the presence of insulating walls can strongly affect the plasma potential (Vₚ) in an oxygen plasma as a result of wall charging to positive voltages at the initiation of the discharge. In plasma deposition or etching systems, it is common to increase the effect of the ion bombardment by biasing the substrate (Vₚ) to increase the energy of the ions impinging onto the wafer during the deposition, hence reducing the film porosity, or during etching to improve the anisotropy. The charging of the walls will have to be considered when evaluating the impact energy from the potential difference Vₚ−Vₚ and controlling the ion flux during the deposition presents many difficulties associated with the plasma equilibrium and the plasma–surface interaction on the substrate and at the walls.

It is well recognized that the energy of the positive ions impinging on the film during the deposition will affect its properties. It is much less known and understood whether negative ions may affect this process. Primarily this is because negative ions are not directly incorporated in the film but are trapped in the plasma by the sheath created by the plasma potential (and which accelerates the positive ions to the surface). As previously reported for a pure oxygen plasma, the spatial balance between the positive and negative ions across the processing chamber results in a positive wall potential which subsequently increases the plasma potential and the impact energy of the positive ions which finally find their way to the depositing substrate. Hence we believe that this indirect effect of the negative ions on the
global plasma equilibrium can be an important factor though not obvious when investigating the structure of the film. Here results are presented which show a correlation between negative ions near the walls of a helicon reactor and the charge state of the wall for oxygen/silane plasmas. The wall potential increases with the silane flow and the polymerization of the positive ions. Initially, this polymerization appeared to be a primary candidate for explaining the change of $V_p$ and the enhanced charging of the wall. However, the results suggest that the diffusive equilibrium of the negative ions across the magnetic field to the walls is more likely responsible. The conclusion was arrived at after observing that the positive ion flux was quasi-constant in both magnitude and species (polymerization of less than 4%) whereas the negative ion flux changed dramatically (two orders of magnitude) with the gas flow-rate ratio and this correlated well with the measured change of $V_p$. Although the positive ions get to the walls first, the radial plasma potential profile thereby set up is such as to insure an equal flux of positively charged particles to reach each part of the wall at steady state. This diffusion characteristic will be strongly affected by the density and the mass of the negative ions. Although the negative ions presumably do not flow to the wall while the discharge is on, their presence near the wall manifested by my results must affect the plasma equilibrium via their recombination with the positive ions and this may well be the determining factor in the charging of the walls. I have not attempted to model this complicated situation, and I present the experimental results showing this effect.

I present results on wall charging (via plasma potential measurements at the wall) and electronegativity (via positive and negative ion extraction) in a low pressure high density oxygen/silane plasma excited in the helicon deposition reactor for constant rf source power (800 W) and magnetic field (70 G in the middle of the diffusion chamber). A detailed analysis in pure oxygen has been previously reported and the results are summarized here and used as a reference for the more complex oxygen/silane case. The main parameter is the flow-rate ratio $R$ between oxygen and silane which varies from 1 (15 sccm/15 sccm) to 10 (27.3 sccm/2.7 sccm) while keeping a constant total gas flow rate of 30 sccm. The main diagnostic for detecting the positive and negative ions in the processing chamber is an energy selective mass spectrometer.

II. PLASMA DEPOSITION REACTOR

The reactor has been described in previous publications, its schematic is shown in Fig. 1(a) and briefly, it consists of a 15-cm-diam, 30-cm-long glass tube (the source) surrounded by a helicon antenna and two solenoids, which are contiguous with a 35-cm-diam, 30-cm-long aluminum diffusion chamber surrounded by two solenoids. The metallic chamber walls, covered with silica on the inside from multiple operation cycles with oxygen/silane plasmas, are water-cooled and maintained at a temperature of about 15 °C. The reactor (source and chamber attached) is pumped down to a base pressure of a few $10^{-5}$ Torr (1 Torr = 133 Pa) by using a turbomolecular pump placed on top of the source. The silane and oxygen gas inlets are situated on top of the chamber and gas flows of 10–100 sccm lead to pressures of a few mTorr, measured by a baratron gauge mounted at the back of the chamber. Radio frequency power at 13.56 MHz is coupled to the plasma in the source area via a matching network including the helicon antenna. When operating in its resonant regime, this type of reactor produces high plasma densities; the matching network configuration used for the experiments presented in this article consists of a high impedance (two loops in series) silver plated copper antenna connected to variable vacuum capacitors to form an L resonant circuit. In pulsed operation (a condition necessary for the negative ion extraction), the rf generator/matchbox system has rise and fall times of about 80 and 60 μs, respectively. The magnetic field configuration (field lines, radial and axial components) used for all the experiments is detailed in Ref. 9 and corresponds to 70 G in the middle of the diffusion chamber.

III. DIAGNOSTICS

The main diagnostic used when coupling oxygen/silane plasmas is an energy selective mass spectrometer (Hiden...
Analytical Limited Plasma Monitor type HAL EQP for masses 1–300 amu; the spectrometer, which is differentially pumped to a pressure of $2 \times 10^{-7}$ Torr, is mounted directly on the chamber wall—via the side port situated 12 cm from the bottom of the chamber—so as to provide the closest extraction possible [Fig. 1(a)]. The spectrometer can be used either to analyze the ions (positive or negative) or the neutrals escaping radially from the plasma [Fig. 1(b)]. In the experiments presented here, only the ions extracted directly from the plasma are analyzed. The spectrometer consists of an ion extractor with a 300-μm-diam aperture followed by an electrostatic energy analyzer matched to a quadrupole mass filter and a channeltron detector. The internal radius of the chamber and the thickness of the chamber wall are 17.2 and 1.5 cm, respectively, and the ion extractor is positioned at a radius of 19.2 cm (x axis) from the main vertical axis (z axis) of the reactor. In pulsed operation, the dwell time of the spectrometer is chosen so as to average the ion collection over many pulses.

IV. EXPERIMENTAL RESULTS

A. Pure oxygen plasma

1. Positive ion detection at the wall

The diffusion of the plasma from the helicon source to the chamber wall has been previously studied for a pure oxygen plasma\(^9\) by using a Langmuir probe (LP) and the main results are summarized in Figs. 2(a) and 2(b). Figure 2(a) shows the plasma ($V_p$) and floating ($V_f$) potential profiles across the diffusion chamber as well as the negative/positive saturation current ratio $I(-100\, \text{V})/[I(V_p) - I(-100\, \text{V})]$ profile obtained with the LP for 800 W, 2 mTorr, and 30 sccm rf power, pressure, and total gas flow, respectively. Figure 2(b) shows the ion energy distribution function (IEDF) of the O$^+$ ions measured at the chamber wall using the Hiden spectrometer. The distribution exhibits a single peak at an energy corresponding to the height of the sheath in front of the earthed spectrometer extractor (Fig. 1b) which we take to be the local plasma potential. The value of 32 V agrees quite well with the LP measurement of $V_p$ close to the wall (~35 V). For the oxygen/silane mixtures, the plasma potential in the diffusion chamber will be determined from the IEDFs measured by the Hiden spectrometer since a LP cannot be used (deposition of an insulator on the probe tip).

For pure oxygen, the value of the plasma potential in the diffusion chamber (30–40 V) is rather large compared to previous measurements obtained in equivalent systems for various plasmas\(^10,11\) which showed values around 15 V in argon for similar rf power and pressure conditions but with conducting walls (including the substrate table). This suggests the importance of the wall state on our plasma potential.

The wall state can be monitored by measuring the floating potential very close to the chamber sidewall as shown by Fig. 2(a). The floating potential is high (25–30 V) close to the wall and decreases to about −12 V in the center of the chamber, over a diameter of about 10 cm. The transition in $V_f$ occurs at a radius of about 8 cm, which corresponds to the last magnetized field line connected to the source\(^8\) and which creates two regions in the diffusion chamber: the inner electropositive region corresponding to the source "image" (0 $\leq r \leq 8$ cm) and the outer electronegative region ($r \geq 8$ cm). The hot electrons ($T_e = 6–8$ eV), heated in the source by the radio frequency field, have been confined by the magnetic field lines and move freely from the source to the bottom of the chamber. As a result of the confinement along the vertical axis of the reactor, the radial diffusion of the electrons to the wall is strongly limited and only results from elastic collisions. This limitation of the radial electron flux allows a large change in the floating potential across the field lines (6 $\leq r \leq 9$ cm) up to a value of about 30 V. Outside the source "image," the floating potential does not vary much (25–30 V) and is much closer to the plasma potential (32–38 V).

The sheath voltage $V_{p-f}$ at the chamber wall represents 10%–20% of the floating potential or wall charging magnitude and for the present study we will assume that the mea-

![Fig. 2. (a) Radial profile of the (C) plasma potential $V_p$, (●) floating potential $V_f$, and (╳) negative/positive current ratio $[I(-100\, \text{V})/I(V_p) - I(-100\, \text{V})]$ across the diffusion chamber obtained with the Langmuir probe at 800 W and 2 mTorr rf power and pressure "off" conditions, respectively (from Ref. 9). Error bars on $V_p$ and $V_f$ are to be read from left to right. The pressure with the plasma "on" is 2.3 mTorr. (b) Ion energy distribution function of the O$^+$ ions escaping radially from the diffusion chamber to the wall obtained with the spectrometer (from Ref. 9); the internal chamber radius is 17.2 cm and the spectrometer ion extractor plate is situated at a radial position of 19 cm [same plasma conditions as (a)].](https://example.com/fig2.png)
measurement of the plasma potential at the wall will reflect the wall charging.

2. Negative ion detection at the wall

Though negative ions have been extracted from continuous plasmas in very electronegative discharges, pulsing the oxygen plasma with a square signal at 1 kHz was necessary in order to extract the negative ions during the postdischarge. Detection of the negative ions occurs in the postdischarge, when the positive sheath in front of the earthed analyzer has collapsed and when the plasma and floating potentials have also collapsed. The main negative ions are O$_2^-$ and OH$^-$ and their respective IEDFs are shown in Fig. 3. For both ions a single peak at 22 V is detected.

Figures 2 and 3 show that for pure oxygen, O$_2^+$ and O$^-$ are the main positive and negative ions, respectively, and the negative/positive saturation current ratio measured with the LP is minimum (1.4–2.4) close to the chamber walls [Fig. 2(a)]. In the absence of any electrons, the saturation current ratio would be similar to the square root of the O$_2^+$ to O$^-$ mass ratio (the main positive and negative ions, i.e., 0.7. Consequently, near the chamber edge, the small difference between $V_p$ and $V_f$ is due to the high percentage of negative ions (mostly O$^-$), to the low percentage of electrons, and to a lower electron temperature.

B. Oxygen/silane plasma

1. Positive ion detection at the wall

Measurements of the positive IEDFs and mass spectra have been performed for all ratios $R$ and the results have been previously correlated to the quality of the deposited films of silica. The thickness of the silica covering the reactor walls after months of deposition is of the order of a few millimeters. Slight changes in the wall conditions (about a few volts) are observed since the reactor is continuously used for processing wafers for various applications. To minimize the effect of the long term drift of the reactor, the oxygen/silane plasma is maintained “on” during the time necessary to collect all the data.

Although the ratio of 1 does not lead to the best film quality, it corresponds to the maximum wall charging effect which is presently investigated. The IEDF of the H$_2$O$^+$ ions measured with the Hiden spectrometer for an oxygen/silane ratio of 1 (15/15) is shown in Fig. 4(a). It exhibits a single peak at an energy of 58.5 V. Similar results are obtained for all masses showing that no major change in the wall state occurs during the time required to collect the data. The corresponding spectrum of the positive ions obtained with the spectrometer is measured at an energy of 58.5 V and is shown in Fig. 4(b). H$_3$O$^+$ is the predominant positive ion. Polymerization is observed with the detection of high mass ions (up to 120 amu) and masses above 52 amu represent about 3% of the total ion flux. The heavy ions are probably of Si$_x$O$_y$H$_z$ type. The main silicon-containing ions are SiOH$^+$, SiOH$_2^+$, Si$^+$, SiH$_2^+$, and SiH$_3^+$. Their respective densities are similar and close to that of the O$_2^+$ ions.

The results of the gas flow conditions, the total positive
ion flux \( (j^+) \) and polymerization fraction \( (j_{525}^+ / j^+) \) are summarized in Table I. To limit the deposition on the spectrometer extractor, measurements were performed for \( R = 2 \) to 10 (low silane flow), then from \( R = 2 \) to 1 (large silane flow). The changes in the total ion flux \( j^+ \) \( (6 \times 10^5 \) to \( 2 \times 10^6 \) cts s\(^{-1}\) measured with the spectrometer) are small and mostly result from some deposition on the orifice plate of the spectrometer rather than changes in the plasma equilibrium.\(^8\) for \( R = 2 \), two measurements are performed which correspond to the beginning and the near end of the data collection, showing a decrease by a factor of 2.3 in the total positive ion flux (Table I).

Figure 5(a) and 5(b) show the signal intensity of the \( O_2^+ \) and \( H_2O^+ \) and of the \( O^- \) and \( H^+ \) ions as a function of the oxygen and silane flows, respectively. Figure 5(a) shows that when the oxygen flow is increased from 15 to 27.3 sccm, the predominant positive ion changes from \( H_2O^+ \) to \( O_2^+ \) for 20 sccm \( (R = 2) \), where the polymerization fraction becomes negligible (<0.1% in Table I). The sum of the \( H_2O^+ \) and \( O_2^+ \) fluxes represent 60% of the total ion flux for \( R = 1 \) and 80% for \( R = 1.5 \). As reported below, the negative ions presently detected are of \( O^- \), \( OH^- \), and \( H^+ \) type and it is of interest to analyze the corresponding positive ions as shown in Fig. 5(b). The \( H^+ \) signal is constant (although the silane flow is varied from 15 to 27.7 sccm) and the \( O^- \) signal increases by a few orders of magnitude when the oxygen flow is increased from 15 \( (R = 1) \) to 27.3 sccm \( (R = 10) \). The low \( O^+ \) intensities correspond to the spectra where the \( H_2O^+ \) ions are predominant and where polymerization is observed \( (Si_2O_3H_4^+) \) ions. Although not plotted for better clarity of the graph, the variation of the \( OH^+ \) ions is similar to that of the \( H^+ \) ions. The jump by a factor of \( ~1000 \) observed for the \( O^+ \) signal intensity when \( R \) is increased from 1 to 10 cannot be fully accounted for by the oxygen flow increase (factor of 2) or by the change in the extractor collection area (factor of 2.3).

Coupling an oxygen/silane plasma induces a pressure increase as a result of the oxygen and silane dissociation rates. For a pure oxygen plasma with a total flow of 30 sccm giving a pressure “off” of 2 mTorr, the pressure increase is about 0.3 mTorr and the silane dissociation\(^9\) is consequently mostly responsible for the large pressure increase measured when changing \( R \). Figure 6 shows the pressure “on” (using the baratron gauge) as a function of the silane and oxygen flows and the plasma potential derived from the IEDF measurements. The pressure “on” increases linearly with the silane flow and the plasma potential is constant \((\sim 35 \text{ V})\) for a flow ranging from 2.7 \( (R = 10) \) to 10 sccm \( (R = 2) \) and strongly increases to \( \sim 60 \text{ V} \) at a flow of 15 sccm \( (R = 1) \).

### Table I

<table>
<thead>
<tr>
<th>Collection order</th>
<th>( R = O_2/SiH_4 )</th>
<th>( O_2 ) flow (sccm)</th>
<th>( SiH_4 ) flow (sccm)</th>
<th>( j^+ \times 10^6 ) cts s(^{-1})</th>
<th>( j_{525}^+ / j^+ ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>15</td>
<td>15</td>
<td>2</td>
<td>3.4</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>18</td>
<td>12</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>20</td>
<td>10</td>
<td>0.6</td>
<td>0.07</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>20</td>
<td>10</td>
<td>1.4</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>22.5</td>
<td>7.5</td>
<td>1.2</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>24</td>
<td>6</td>
<td>1.1</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>25</td>
<td>5</td>
<td>1.2</td>
<td>0.04</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>26.7</td>
<td>3.3</td>
<td>1.3</td>
<td>0.03</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>27.3</td>
<td>2.7</td>
<td>1.2</td>
<td>0.02</td>
</tr>
</tbody>
</table>

2. Negative ion detection at the wall

Pulsing the oxygen/silane plasma with a square signal at 2 kHz was necessary in order to extract the negative ions during the postdischarge. Increasing the pulsing frequency from 1 to 2 kHz was necessary when changing from pure oxygen to the oxygen/silane plasmas to obtain an enhanced signal (increase by a factor of \( \sim 3 \)) and signal/noise ratio. Figure 7(a) shows the IEDF of the \( H^- \) ions for \( R = 1 \). It exhibits a single peak at about 25 V. The corresponding spectrum of the negative ions obtained with the spectrometer set at 25 V is shown in Fig. 7(b). The main negative ions are \( H^- \) and \( OH^- \) and no \( O^- \) ions are detected for \( R = 1 \). No heavy negative ions, precursors for powder formation,\(^15\) are detected in our high density plasma despite the polymerization observed in the positive ion spectrum [Fig. 4(b)].

Although no \( O^- \) ions were detected for \( R = 1 \), they appeared as the predominant negative ion for pure oxygen and for oxygen rich plasmas. The IEDFs of the \( O^- \) ions are shown in Fig. 8 for \( R = 3 \) and \( R = 10 \) and the main results on the \( H^+ \), \( O^+ \), and \( OH^- \) ion fluxes as well as the plasma potential and total positive ion flux are summarized in Table II for oxygen/silane ratios of 1, 3, and 10 and for pure oxygen. The variation in the \( H^- \) and \( OH^- \) ion fluxes are significantly smaller than that of the \( O^- \) ions which is maximum for a pure oxygen plasma (the estimated \( O^- \) ions count at 2 kHz would be \( \sim 10^5 \) cts s\(^{-1}\) for pure oxygen) and decreases by a few orders of magnitude when \( R \) is decreased from 10 to 1. Figure 5(b) and Table II show that the \( O^+ \) and \( O^- \) ion fluxes exhibit similar relative evolution when changing from a pure oxygen plasma to an oxygen/silane plasma of decreases.
ing flow-rate ratio, while the H\textsuperscript{+}, OH\textsuperscript{+}, H\textsuperscript{-} and OH\textsuperscript{-} variations can be neglected to the first order.

V. DISCUSSION

A pure oxygen plasma has been diagnosed\textsuperscript{9} and used as a reference for the more complex oxygen/silane case. Spatial measurements of the main plasma parameters are performed across the chamber using a Langmuir probe [Fig. 2(a)] and the O\textsubscript{2}\textsuperscript{+} IEDF is measured using the mass spectrometer with the extractor plate placed on the chamber sideport [Fig. 2(b)]. The IEDF exhibits a single peak around $V_p$ (which corresponds to the plasma potential with reference to the ground) and the value of 32 V is in good agreement with that measured by the LP at the wall ($\sim$35 V). The spectrometer is subsequently used to determine $V_p$ in the reactive oxygen/silane plasma where a LP cannot be used (deposition of an insulator on the probe).

The floating potential profile measured with the LP across the chamber shows the presence of two regions within the discharge: a center electropositive region, the extension of the helicon source and main area for gas phase reactions (dissociation, ionization, excitation, ...), with a large density ($\approx$ a few $10^{11}$ cm$^{-3}$) of hot electrons ($\approx$6–8 eV) and an outer electronegative region with a lower density of cold electrons, the main area for negative ion formation by attachment. Although the chamber wall is externally connected to the ground, a large floating potential is measured at the wall ($r \approx 17$ cm): a thick layer of insulating silica (which results from months of deposition) covers all the interior of the deposition chamber and acts as a capacitor. Our magnetic field configuration (and the corresponding cross-field diffusion mechanisms) is such that the positive ions reach the insulating sidewall before the negatively charged particles at the initiation of the discharge and a temporal study previously reported\textsuperscript{8} has shown that a capacitive charging is observed for the first 150 $\mu$s of an oxygen discharge until equilibrium between the positive and negative fluxes is reached. Consequently, the magnitude of the wall charging will depend on two main parameters, the effective capacitance of the insulating layer covering the wall and the positive charge accumulation due to the imbalance between positively and negatively charged particles at the initiation of the discharge.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5a.png}
\caption{(a) Signal intensity of the (●) O\textsubscript{2}\textsuperscript{+} and (□) H\textsubscript{3}O\textsuperscript{+} ions measured with the spectrometer (at an energy corresponding to $V_p$) as function of the oxygen flow in an oxygen/silane plasma of variable gas flow-rate ratio ($R = 1$–10) for 800 W, 2 mTorr, and 30 sccm rf power, pressure “off,” and total gas flow-rate conditions, respectively. For an oxygen flow of 20 sccm ($R = 20/10 = 2$), two measurements were taken which correspond to the beginning and near end of the data collection to monitor any deposition on the spectrometer extractor (Ref. 8) (Table I). (b) Signal intensity of the (●) O\textsuperscript{-} and (□) H\textsuperscript{+} ions measured with the spectrometer (same conditions as (a)).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5b.png}
\caption{Signal intensity of the (●) O\textsuperscript{-} and (□) H\textsuperscript{+} ions measured with the spectrometer (same conditions as Fig. 5(a)).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{(+) pressure $p$ with the plasma “on” and (●) plasma potential $V_p$ measured at the wall as a function of silane flow rate in an oxygen/silane plasma of variable gas flow-rate ratio ($R = 1$–10) for 800 W, 2 mTorr, and 30 sccm rf power, pressure “off,” and total gas flow-rate conditions, respectively.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6.png}
\caption{Pressure $p$ with the plasma “on” and (●) plasma potential $V_p$ measured at the wall as a function of silane flow rate in an oxygen/silane plasma of variable gas flow-rate ratio ($R = 1$–10) for 800 W, 2 mTorr, and 30 sccm rf power, pressure “off,” and total gas flow-rate conditions, respectively.}
\end{figure}
The magnitude of the wall charging at equilibrium can be directly related to the floating potential value of 30 V measured with the LP placed close to the sidewall, and to the plasma potential value at the wall, since the corresponding sheath potential is a few volts only. We assume that the two regions will be qualitatively similar for all values of $R$ when studying the oxygen/silane mixtures. The wall charging does not affect plasma parameters such as the ion density or electron temperature at equilibrium but affects the potential reference seen by the plasma. For this reason, a higher value for $V_p$ (32 V) is measured for oxygen in our deposition reactor compared to a standard value of about 15 V for argon in an identical reactor with “clean” walls.\textsuperscript{11}

For oxygen/silane plasmas of varying flow rate ratio ($R = 1 – 10$ with a constant total flow rate of 30 sccm), plasma potential values between 34 and 58.5 V are obtained with the spectrometer showing enhanced charging compared to the pure oxygen case (Fig. 6). The maximum plasma potential value is obtained for an oxygen/silane ratio of 1 where polymerization is observed in the positive ion spectrum [Fig. 4(b)], and the fraction of silicon-containing positive ions of masses greater than 52 amu is maximum (3.4% in Table I). The presence of a transition at $R = 2$ also observed for other plasma parameters such as the nature of the predominant ion, the $O^+$ and $O^–$ ion density, and the total negative ion density suggests changes in the global plasma equilibrium at that ratio.

For oxygen/silane plasmas of varying flow rate ratio ($R = 1 – 10$ with a constant total flow rate of 30 sccm), plasma potential values between 34 and 58.5 V are obtained with the spectrometer showing enhanced charging compared to the pure oxygen case (Fig. 6). The maximum plasma potential value is obtained for an oxygen/silane ratio of 1 where polymerization is observed in the positive ion spectrum [Fig. 4(b)], and the fraction of silicon-containing positive ions of masses greater than 52 amu is maximum (3.4% in Table I). The presence of a transition at $R = 2$ also observed for other plasma parameters such as the nature of the predominant ion, the $O^+$ and $O^–$ ion density, and the total negative ion density suggests changes in the global plasma equilibrium at that ratio.

A plasma potential increase can result from an increase in the floating potential in a situation where insulating walls are present (wall charging) as previously observed for pure oxygen. It could also result from an increase in the electron temperature. This is unlikely in our case since we observe a pressure increase, hence a collision frequency increase and an electron temperature decrease, due to the silane and oxy-

![Figure 7](image7.png)  
Fig. 7. (a) Ion energy distribution function of the $H^–$ ions escaping radially from the diffusion chamber to the wall and (b) mass spectrum of the negative ions (at an energy of 25 V) obtained with the spectrometer for a pulsed (square signal at 2 kHz) $R = 1$ oxygen/silane plasma at 800 W, 2 mTorr, and 30 sccm rf power, pressure “off,” and total gas flow-rate conditions, respectively. The extractor voltage is set at 65 V.

![Figure 8](image8.png)  
Fig. 8. Ion energy distribution function of the $O^–$ ions escaping radially from the diffusion chamber to the wall obtained with the spectrometer for a pulsed (square signal at 2 kHz) oxygen/silane plasma with $\bullet R = 10$ (extractor voltage of 65 V) and $\times R = 3$ (extractor voltage of 60 V). Operating conditions are 800 W, 2 mTorr, and 30 sccm rf power, pressure “off,” and total gas flow-rate conditions, respectively.

\begin{table}
\centering
\caption{Plasma potential ($V_p$), total positive ion flux ($j^+$), and flux of the $H^–$, $O^–$, and OH$^–$ ions for various gas mixtures but constant total flow rate, rf power, and magnetic field of 30 sccm, 800 W, and 70 G, respectively. For the negative ion extraction, the pulsing frequency is 1 kHz for pure oxygen (Ref. 9) and 2 kHz for the oxygen/silane mixtures. The noise ($\approx 250$ cts s$^{-1}$) has been subtracted for all fluxes.}
\begin{tabular}{cccccc}
\hline
Gas mixture & $V_p$ (V) & $j^+$ (cts s$^{-1}$) & $H^–$ (cts s$^{-1}$) & $O^–$ (cts s$^{-1}$) & OH$^–$ (cts s$^{-1}$) \\
\hline
$R = O_2/\text{SiH}_4$ & & & & & \\
$R = 1$ & 58.5 & $2 \times 10^6$ & $1.1 \times 10^3$ & 0 & $2.7 \times 10^2$ \\
$R = 3$ & 36.8 & $1.2 \times 10^6$ & $4.5 \times 10^2$ & $7.5 \times 10^2$ & $2.9 \times 10^2$ \\
$R = 10$ & 36 & $1.2 \times 10^6$ & $1.5 \times 10^3$ & $2 \times 10^4$ & $1.8 \times 10^3$ \\
pure oxygen & 32 & $3 \times 10^6$ & $1 \times 10^2$ & $2.3 \times 10^9$ & $1.7 \times 10^3$ \\
\hline
\end{tabular}
\end{table}
gen dissociation (Fig. 6): the pressure with the plasma “on” is about 2.3 mTorr in pure oxygen plasma and 9.6 mTorr for $R = 1$. Although the main external parameters are kept constant, the pressure increase will be a determinant factor in the cross-field diffusion of the particles and in their subsequent fluxes onto the sidewall. The thickness deposited on the sidewall during the charging time (less than a few hundreds of $\mu$s) is certainly negligible compared to the thickness deposited over many months of deposition and the effective capacitance is assumed constant. Hence the increase in $V_p$ for $R < 2$ (Fig. 6) probably results from an increase in the imbalance between the positive ions and the negatively charged particle at the discharge initiation. Our measurements correspond to a situation where the wall charging is completed and characterizing the positively and negatively charged particles fluxes to the wall during the early stage of an oxygen/silane discharge is a complex task well beyond the scope of this article.

Initially it appeared that the polymerization observed for $R < 2$ [Fig. 4(b) and Table I] and the corresponding increase in the measured $V_p$ (Fig. 6) were directly connected. Still, the polymerization is very small for all $R$’s ($< 4\%$) and the total positive flux $j^+$ mostly results from one predominant ion ($> 60\%$), H$_2$O$^+$ for low values of $R$ and O$_2^+$ for large values of $R$. At equilibrium, the total density of positive ions measured at the wall is maintained in the $(0.6– 2) \times 10^6$ cts s$^{-1}$ range (Table I), with most of the variation resulting from some deposition on the spectrometer extractor. Hence the total positive ion flux $j^+$ can be considered constant to the first order.

The total density of negative ions has not been measured at equilibrium since pulsing the plasma was necessary to extract the negative ions during the postdischarge. Negative ions are formed by attachment with low energy electrons and Fig. 2(a) shows that the negative ions are present in the outer region of the diffusion chamber (close to the wall). Their higher mass compared to that of the electrons will affect the cross-field diffusion and the plasma equilibrium at the walls. For a pure oxygen plasma, and for $R = 10$ and $R = 3$, the O$^-$ ions are the predominant negative ions (Figs. 3 and 8). The negative ion spectrum measured for $R = 1$ in the pulsed mode [Fig. 7(b)] exhibits only H$^-$ and OH$^-$ ions. No O$^-$ ions are detected and H$^-$ is the predominant negative ion. Table II shows that the H$^-$ and OH$^-$ ion intensity variations are much smaller than that of the O$^-$ ions and can be neglected to the first order. The total negative flux $j^-$ corresponds to the sum of the H$^-$, O$^-$, and OH$^-$ ion fluxes and any variation in $j^-$ is essentially caused by the change in the O$^-$ ion flux. The latter changes from $\sim 10^5$ cts s$^{-1}$ for pure oxygen to $\sim 0$ cts s$^{-1}$ for $R = 1$ and this depletion results in a change in the degree of electronegativity of the discharge close to the wall (since $j^+$ is constant for all $R$’s). No estimation of the degree of the electronegativity is made since the time span for the negative ion collection is not known when pulsing.

It is likely that the similar variation in the O$^+$ and O$^-$ ion intensities when changing $R$ are correlated to the same changes in the physicochemistry of the discharge. Figure 5(b) shows that while the H$^+$ signal is constant (a few $10^5$ cts s$^{-1}$) for all oxygen flows, we observe a dramatic drop (three orders of magnitude) in the O$^+$ signal intensity as the oxygen flow is decreased from 27.3 to 15 sccm. For $R = 1$, the O$^+$ ion signal intensity ($\sim 7 \times 10^3$ cts s$^{-1}$) is two orders of magnitude lower than the predominant H$_2$O$^+$ ions ($\sim 10^6$ cts s$^{-1}$) and for $R = 10$, the O$^+$ ion intensity ($\sim 10^5$ cts s$^{-1}$) is one order of magnitude lower than the predominant O$_2^+$ ions ($\sim 10^6$ cts s$^{-1}$). This dramatic decrease in the O$^+$ ion intensity could be related to some consumption of the oxygen atoms by the H$_2$O$^+$ and the Si$_2$O$_2$H$_4^+$ ions resulting in a depletion in the density of oxygen atoms in the discharge or to a decrease in the oxygen dissociation and dissociative ionization rates (pressure increase).

Although polymerization appeared to be a primary candidate for explaining the change of $V_p$ and the enhanced charging of the wall, the diffusive equilibrium of the negative ions across the magnetic field to the walls is more likely responsible: the positive ion flux is quasi-constant in both magnitude and species (polymerization of less than 4%) whereas the negative ion flux changed dramatically (two orders of magnitude) with the gas flow-rate ratio and this also correlates well with the measured change of $V_p$. Although the positive ions get to the walls first, the radial plasma potential profile thereby set up is such as to insure an equal flux of positively (positive ions) and negatively (negative ions and electrons) charged particles to reach each part of the wall at steady state. This diffusion characteristic will be strongly affected by the density and the mass of the negative ions. Although the negative ions presumably do not flow to the wall while the discharge is on, their presence near the wall manifested by our results must affect the plasma equilibrium via their recombination with the positive ions and this may well be the determining factor in the charging of the walls.

Our measurements show that the degree of electronegativity in the outer region decreases when the silane content is increased, and this is accompanied by a decrease in wall charging. However, these measurements are not representative of the early stage of the discharge and we can only assume that the measurements at equilibrium and during breakdown would show similar evolutions when changing $R$. The charging occurs during the discharge breakdown phase and the time constants involved in the respective production of the positive and negative ions, as well as the cross-field diffusion of each species, are not known. Extensive work on plasma breakdown in argon has been previously reported which shows that breakdown can be divided into three consecutive phases, a prebreakdown phase (first few $\mu$s), a breakdown phase (next 70 $\mu$s in argon), and a postbreakdown phase (hundreds of $\mu$s). During prebreakdown, electron heating is mostly efficient during the first microseconds when the skin depth is larger than the size of the helicon source tube allowing the plasma potential to oscillate at rf frequency with an amplitude of hundreds of volts (for injected power of a few hundred watts) and leading to a high ionization rate and density increase. The subsequent ap-

approach to equilibrium is characterized by a plasma potential decrease (and an electron temperature decrease) and a density increase which I have measured in the center of the diffusion chamber with “clean walls” using an energy analyzer. Most of the charging occurs during this second phase. The high values of the plasma potential creates a large electric field between the center of the chamber and the earthed chamber walls and the positive ions are accelerated by this field from the center of the discharge where they are created to the sidewalls. Since negative ions are formed by attachment with low energy electrons, their creation rate will be subsequent to the electron temperature drop. Hence for similar positive ion density at equilibrium, it is reasonable that for discharges with similar $V_p$ and $V_f$ profiles across the diffusion chamber, the dynamics for the negative ion formation could have a direct effect on the plasma equilibrium and wall charging: a decrease in the negative ion density close to the walls (hence a decrease in the degree of electronegativity) has been correlated to an increase of the positive wall charging.

VI. CONCLUSION

Wall charging has been measured for a low pressure high density oxygen/silane plasma of various flow-rate ratios ($R = 1-10$). As previously reported for a pure oxygen plasma, the magnitude of the charging depends on the wall capacitance (constant) and on the inbalance between positively and negatively charged particles at the discharge initiation. The latter results from two successive processes, the large values of $V_p$ during breakdown and the positively and negatively charged particles’ creation rates and diffusion rates across the magnetic field. Our experimental results suggest that the degree of electronegativity of the discharge close to the wall (given by the O$^-$ ion flux since $j^+$ and the H$^-$ and OH$^-$ ion fluxes are quasi-constant) is the main varying parameter when changing $R$. A major transition in the physicochemistry of the discharge is observed for $R = 2$. For $R < 2$, polymerization is observed in the positive ion spectrum which is accompanied by a depletion in the O$^+$ (which does not affect the total positive ion flux) and O$^-$ ions (which drastically affects the total negative ion flux). The decrease in the degree of electronegativity close to the walls for $R < 2$ could be related to an increased inbalance between positively and negatively charged particles at the discharge initiation, hence to the observed enhanced wall charging to positive values.