

Transient plasma-induced emission analysis of laser-desorbed species during Cl_2 plasma etching of Si

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The surface during the etching of Si in a Cl_2 inductively-coupled plasma (ICP) was analyzed by laser desorption (LD), followed by detection of the desorbed species by monitoring the transient changes by plasma-induced emission (PIE). Optical emission from Si, SiCl , SiCl_2 , and possibly other species was detected *in situ* using this LD-PIE method as a function of rf power, substrate bias, and pressure. The surface coverage of chlorine was determined by normalizing the LD-PIE signal by either of two ways: by the electron density, as measured by microwave interferometry, or by using the background PIE signal. Little change in surface coverage was observed as the ion density was changed by varying the rf power supplied to the ICP, confirming the observation made using laser-induced fluorescence (LIF) detection (LD-LIF). The LD-PIE signal is related to the density of species desorbed from the surface and subsequently excited by electrons. LD-PIE analysis of the surface is more versatile than LD-LIF—sometimes it can detect the desorbed species while LD-LIF cannot. Still, it requires calibration to account for the electron collision-induced excitation of the laser-desorbed species. © 2000 American Vacuum Society. [S0734-2101(00)00506-6]

I. INTRODUCTION

Probing the surface during plasma etching can provide valuable information needed to understand the etching mechanism, especially when the information obtained about the surface is combined with the etching rate and diagnostics of the plasma. Laser-induced thermal desorption (LITD) has been used to probe the surface during the etching of Si and Ge in high density plasmas in a series of studies.^{1–4} In each case, laser desorbed (LD) species were detected by laser-induced fluorescence (LIF). In the etching of Si by Cl_2 , Si by HBr , and Ge by Cl_2 , respectively, SiCl , SiBr , and GeCl were both desorbed from the surface and optically excited by a XeCl laser (308 nm) to give an LD-LIF signal that is proportional to the halogen coverage on the surface. However, LD-LIF has limitations. A desorbed species of interest may not be in resonance with the laser wavelength chosen for desorption, so one laser LD-LIF cannot be used and a second laser has to be used to excite LIF. Even if a given species is resonant with this second laser, others are likely not. Also, species which can only fluoresce from levels that cannot be excited by electric-dipole allowed absorption from the ground state are not easily detected by LD-LIF, and if the emitting levels are very high in energy very short wavelength lasers may be needed to excite LIF. Furthermore, if only one

species can be detected by LD-LIF, it may not be the dominant desorbing species and may not necessarily represent the surface conditions during plasma etching.

An alternative detection method entails monitoring the transient change in plasma-induced emission due to the electron excitation of the transiently altered densities of desorbed species. This technique is termed laser desorption-plasma induced emission (LD-PIE). The principles of this method were demonstrated in Ref. 1 and will be systematically examined in this article. In the current study, LD-PIE from various atomic and molecular species is monitored during Si etching in a Cl_2 inductively coupled plasma (ICP) reactor and analyzed to see if this method can accurately examine the surface adlayer composition and thickness, and consequently serve as a useful alternative to LD-LIF. Energetic processes that are associated with LD-PIE, such as electron impact excitation and dissociation, other collisions, and radiative decay of the excited species, are analyzed to interpret these emission signals. The versatility of LD-PIE stems from its ability to probe many desorbed species with only the one-fixed-frequency laser used for desorption. The ability of high energy electrons to excite high energy levels and the ability of electrons to excite levels that are not accessible by single photon absorption are other advantages of LD-PIE over LD-LIF. A limitation of both LD-PIE and LD-LIF detection is that larger species are either difficult or impossible to detect because of fast nonradiative decay.

Several different types of silicon chlorides are formed on the surface and are sputtered from the surface during Si etch-

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ing in Cl_2 plasmas.^{2,5,6} Even though the mono-silicon chloride appears to be the dominant component of the adlayer,^{2,5} monitoring desorbing species other than SiCl may give a more accurate assessment of the surface etching process. There is no one-to-one correspondence between surface species and the laser-desorbed species; it is not clear whether SiCl_x on the surface always or often desorbs as SiCl_x . It is difficult (or impossible) to detect these other species by LIF. In Ref. 1, LD-LIF of SiCl was observed but none from SiCl_2 was seen, due either to the lower sensitivity of detecting SiCl_2 by LIF or the small amount of desorbing SiCl_2 . The LD-PIE measurements presented here provide direct evidence of the desorption of higher chlorides SiCl_2 and/or SiCl_3 , as well as that of SiCl . While LD-PIE is more universal than LD-LIF, it requires more calibration because the probability of detecting desorbed species depends on plasma conditions. Furthermore, there may not be one-to-one relationship between laser-desorbed species and emitting species.

II. EXPERIMENTAL METHODS

The ICP reactor, excimer laser, and signal detection optics and electronics were described in detail in Refs. 3 and 4. This ICP reactor operates in the inductive or bright mode for net rf power delivered to the ICP coil ≥ 300 W and in the capacitive or dim mode for rf powers ≤ 300 W for a pure Cl_2 discharge. (Herein, the net rf power delivered to the coil will be referred to as the rf power.) A Si (100) wafer (n type, 8–10 Ω cm) was bonded to the sample holder using indium and smaller samples of Si were mounted on top of this wafer. Pulses from a XeCl excimer laser (Questek 2440, 308 nm, ~ 60 mJ/pulse, ~ 20 ns long pulses) were focused by a 50 cm focal length quartz lens, and directed onto the sample at normal incidence. The laser pulse heated the sample to induce thermal desorption of surface adsorbates and the subsequent increase in the PIE intensity due to desorbing species that are

excited by plasma was monitored. Emission was collected by a 6 in. focal length lens and focused into a monochromator, and detected by a GaAs photomultiplier. This transient signal was captured by a boxcar integrator which was triggered synchronously by the laser pulse. The signal was averaged in the boxcar integrator and recorded on a computer. The delay and gated times were first adjusted to obtain the optimum signal at the wavelength of each species that was monitored. At this optimum setting, the LD-PIE signal was measured as a function of plasma parameters such as rf power, substrate bias voltage, and pressure. Transmission filters were used to reject scattered laser light.

Measurements of the electron density, n_e , were needed to interpret the LD-PIE signal. A microwave interferometer operating at a frequency of 94.8 GHz was used to measure the line-integrated electron density of the plasma. The microwave waveguide and horns were placed on either side of the quartz windows on opposing sides of the reactor. As the plasma was turned on and off, the phase change introduced by the plasma was compared to that of the reference waveguide and the difference was recorded. This phase difference was converted to the line-integrated electron density. An approximate form for the spatial dependence of the electron density can be determined from this line-integrated value by using the positive ion density profile from Ref. 3, assuming charge neutrality in the bulk of the plasma and either a relatively low density of Cl^- or the same spatial variation of n_e and n_{Cl^-} .

III. EXPERIMENTAL RESULTS

A. Laser desorption

A PIE spectrum during Si etching by the Cl_2 plasma is shown in Fig. 1. Strong, sharp emission features from atomic Si and Cl, and SiCl $B' {}^2\Delta \rightarrow X {}^2\Sigma_r$ are seen. Broad emission band heads from SiCl_2 $\tilde{A} {}^1B_1 \rightarrow \tilde{X} {}^1A_1$ near 330 nm,^{7–12} and

TABLE I. Types of species monitored during Si etching by a Cl_2 plasma. PIE, but no LD-PIE, was seen from Cl^* , Cl_2^* , and $\text{Cl}_2^+{}^*$.

Species	λ (nm)	Transition	Lifetime	Upper level energy eV	Detection
Si	251.4	$4s {}^3P_1^0 \rightarrow 3p {}^2 {}^3P_0$	16.7 ns ^a	4.93 ^b	LD-PIE
Si	288.2	$4s {}^1P_1^0 \rightarrow 3p {}^2 {}^1S_0$	5.3 ns ^a	5.08 ^b	LD-PIE
SiCl	280.9	$B' {}^2\Delta \rightarrow X {}^2\Pi_r$	1 μs^c	4.4 ^d	LD-PIE
SiCl	292.4	$B {}^2\Sigma^+ \rightarrow X {}^2\Pi_r$	10 ns ^e	4.2 ^d	LD-LIF
SiCl ₂	330	$\tilde{A} {}^1B_1 \rightarrow \tilde{X} {}^1A_1$	77 ns ^f	3.76 ^f	LD-PIE
SiCl ₂ or Si ₂ or SiCl ₃	385.4	$\tilde{A} {}^1B_1 \rightarrow \tilde{X} {}^1A_1$ or $H {}^3\Sigma_u^- \rightarrow X {}^3\Sigma_g^-$	77 ns ^f	3.22 ^f	LD-PIE
Cl	837.6	$4p {}^4D_{3/2} \rightarrow 4s {}^4P_{2/2}$	36 ns ^g	10.4 ^b	LD-PIE
Cl ₂	257.0	$2({}^3\Pi_g) \rightarrow 1({}^3\Pi_u)$	120 ns ^h	7.1 eV ⁱ	LD-PIE
Cl ₂ ⁺	450.5	$A_1 \rightarrow X_1$	$\sim 1 \mu\text{s}^j$	2.75 eV ^d	LD-PIE

^aReference 17.

^bReference 23.

^cReference 18.

^dReference 24.

^eReference 19.

^fReference 8.

^gReference 20.

^hReference 21.

ⁱReference 25.

^jReference 22.

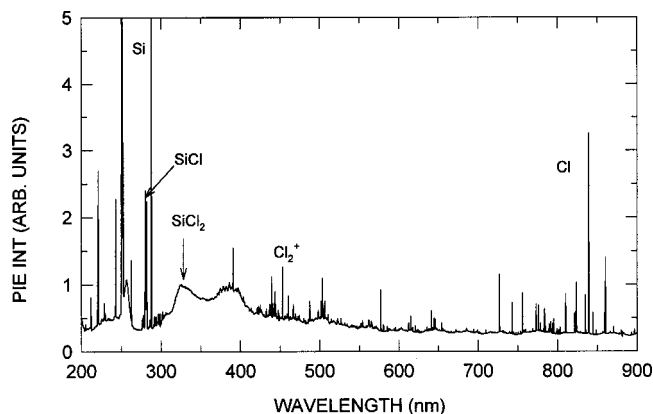


FIG. 1. PIE spectrum during Si etching by the Cl_2 plasma (18 mTorr Cl_2 , 500 W rf power, -40 V substrate bias).

Cl_2 $2(^3\Pi_g) \rightarrow 1(^3\Pi_u)$ near 256.7 nm can be observed. The emission band around 380 nm has been identified as being due to Si_2 $H^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$,^{7,13,14} the SiCl_2 $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ transition,^{8,9,15} an unidentified band in SiCl_3 , or to bands in both SiCl_2 and SiCl_3 .¹⁶ Weak emission lines from Cl_2^+ around 450 nm and SiCl $A^2\Sigma \rightarrow X^2\Pi$ around 500 nm are also observed. Table I lists these features, along with upper level radiative lifetimes^{8,17–22} and upper level energies of each.^{8,17–25}

Figure 2 shows the trace of the intensity of the SiCl_2 $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ LD-PIE feature near 330 nm as the ICP was repetitively turned on and off (with different rf power delivered to the coil). During the plasma on period, the background steady state PIE level was first measured by setting the boxcar delay time to ~ 1 – 2 ms. Then, the total emission signal (LD-PIE plus steady-state PIE plus background laser scatter) was measured by setting the boxcar delay time to the optimized time (usually in the several μs range, and equal to $2 \mu\text{s}$ in Fig. 2) while the plasma was still on and laser pulses were striking the surface. Finally, the background steady-state PIE was measured again by switching the boxcar setting to 1 – 2 ms for several laser pulses before turning off the

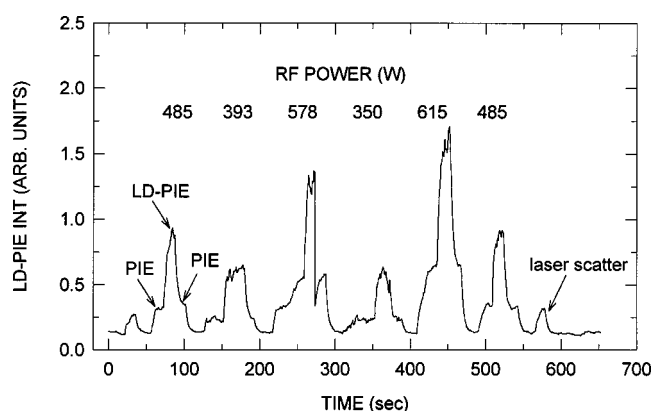


FIG. 2. Trace of the intensity of the SiCl_2 $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ LD-PIE feature near 330 nm as the ICP was repetitively turned on and off (with different rf power delivered to the coil) (18 mTorr Cl_2 , -20 V substrate bias).

plasma. For this measurement cycle, the overall trace has a “head and shoulders”-type profile. Similar measurements were made in which the substrate bias voltage and pressure were varied during the run.

To make sure that the PIE measured with 1 – 2 ms delay is the true steady-state background PIE, this signal (measured while the laser pulses were striking the surface) was compared to that measured with the laser blocked [but still triggering the boxcar that was set at the optimized delay time (μs range)]. In both cases, the plasma was on with the same rf power, substrate bias, and pressure. The intensities of the two cases were almost exactly the same. This is reasonable since desorbing species diffuse ~ 15 mm in ~ 1 ms and out of the ~ 1.6 -mm-wide imaging region; the LD-PIE signal clearly decays to the background steady-state PIE level in several milliseconds. At the beginning and end of each run, the laser scattering background level was measured by changing the boxcar delay time to the same 1 – $2 \mu\text{s}$ setting as during the LD-PIE measurement with the chlorine gas still flowing but the plasma off. Since the “background PIE” was measured with a ~ 1 – 2 ms delay, this background signal did not include a contribution from laser scatter. The net LD-PIE signal, as plotted in Fig. 3, was obtained by subtracting the PIE background and laser scattering background from the total “LD-PIE” peak. The typical run-to-run error is shown in the lowest panel of Fig. 4.

These measurements were conducted for each of species listed in Table I by setting the monochromator at the corresponding PIE wavelength and the boxcar at the optimized delay and gate width for that species. The optimized delay and gate width varied for each species and were typically ~ 2 and ~ 5 – $9 \mu\text{s}$, respectively. LD-PIE signals for the smaller molecular or atomic species (Si or SiCl) were large for $\sim 5 \mu\text{s}$, while for the heavier molecular species (SiCl_2) these were large for $\sim 9 \mu\text{s}$. This indicates the mass-dependent speed of species desorbing with similar kinetic energies during the LITD, as is typically observed during time-of-flight/mass spectrometry measurements of desorbing species.

LD-PIE was detected for Si, SiCl, and SiCl_2 , and possibly Si_2 or SiCl_3 (the 385.4 nm transition). Within the limit of detection, LD-PIE signals from Cl (837.6 nm), Cl_2 (257 nm) and Cl_2^+ (450.5 nm) were not observed. LD-PIE could not be seen at the SiCl 292.4 nm line used for LD-LIF in Refs. 1–3 (after the LIF signal had decayed). Reference 1 suggested that either the nearly isoenergetic, stronger optical transition $B^2\Sigma^+ \leftarrow X^2\Pi_r$ is not strongly favored in electron-impact excitation, or that $B'^2\Delta$ emission is a result of the electron-impact dissociation of SiCl_2 . LD-PIE was, however, observed at the SiCl $B'^2\Delta \rightarrow X^2\Sigma_r$ transition at 280.9 nm.

The open circles and dashed line fits to the eye in Figs. 3, 4, and 5 respectively show the rf power (bright mode only), substrate bias, and pressure dependencies of the net LD-PIE signals from Si^* (251.4 nm), Si^* (288.2 nm), SiCl^* (280.9 nm), SiCl_2^* (330 nm), and $\text{Si}_2^*/\text{SiCl}_2^*/\text{SiCl}_3^*$ (385.4 nm). The variations with rf power and pressure are roughly the same for most species, but the variations with bias are somewhat

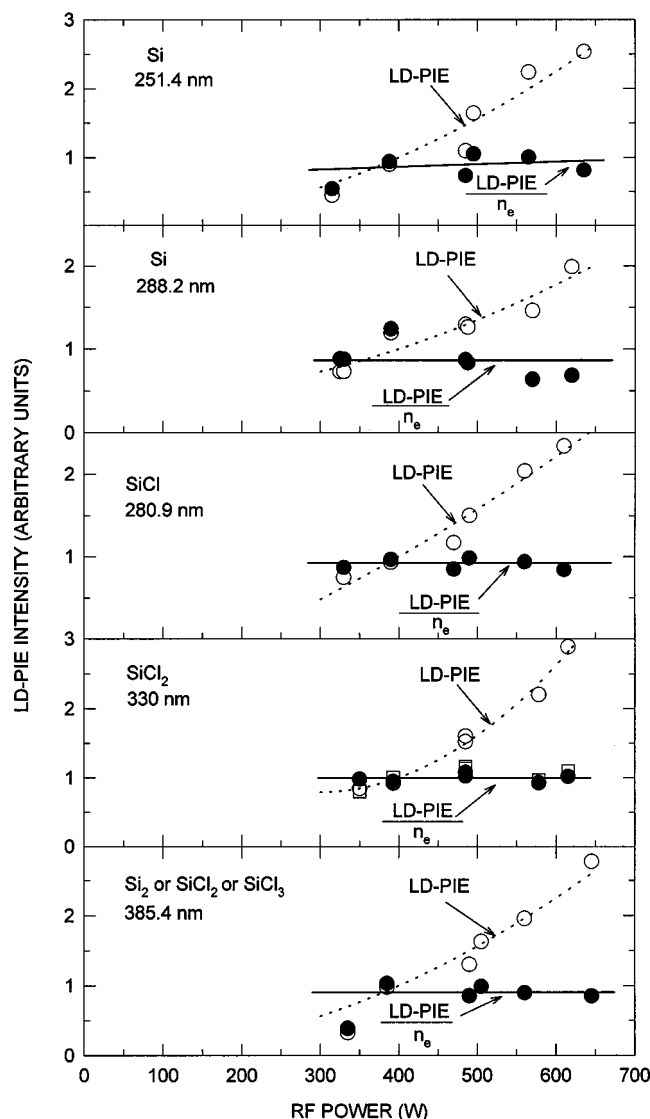


FIG. 3. Variation of the net LD-PIE signal (open circles) at five wavelengths vs rf power (bright mode only) (18 mTorr Cl₂, -20 V substrate bias). Also shown is the LD-PIE signal normalized by the electron density n_e (normalization approach No. 1, closed circles) and, for the 330 nm signal only (SiCl₂⁺), the LD-PIE signal normalized by the ratio of the background SiCl₂⁺ PIE signal to the etch rate (normalization approach No. 2, open squares).

different. The LD-PIE signals of most species are relatively independent of pressure. Note that each LD-PIE signal increases rapidly with rf power, whereas the SiCl LD-LIF signal was seen to vary little (if at all) with rf power in Refs. 2 and 3.

B. Electron density measurement

The line-integrated electron density measured by microwave interferometry was divided by the chamber length 19.5 cm to give the average electron density $\langle n_e \rangle$. Figure 6 shows that $\langle n_e \rangle$ increases with rf power. The positive ion density in the center of the wafer n_i , measured by a Langmuir probe as reported in Ref. 3, is also plotted for comparison. Assuming that the lateral spatial variation of the electron density is the same as that measured for the ion density with the Langmuir

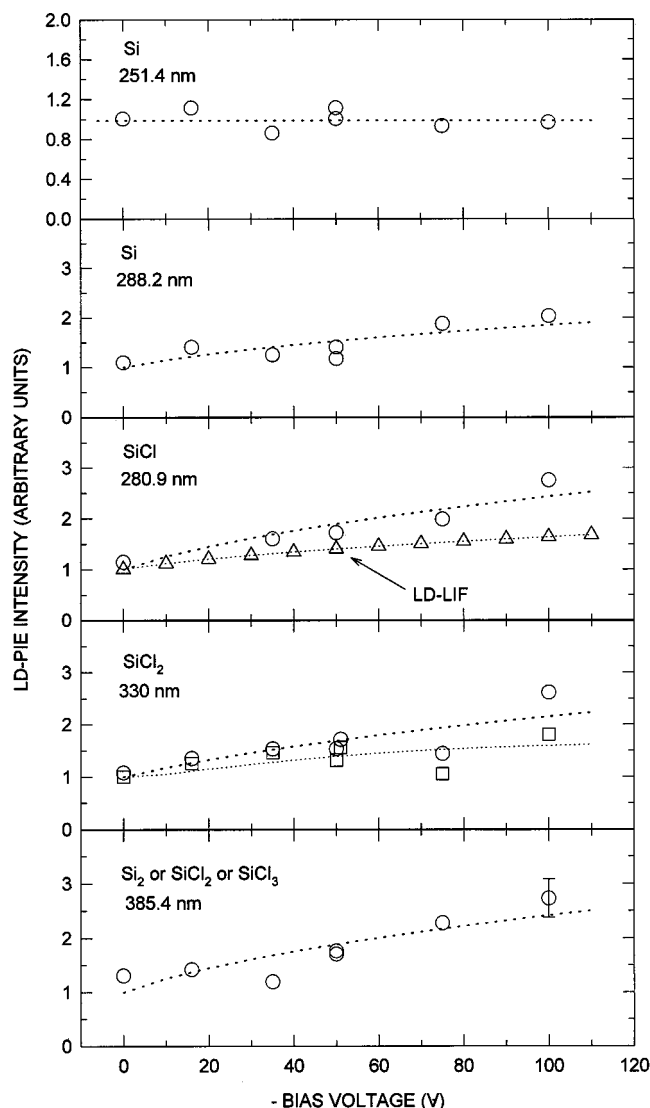


FIG. 4. Variation of the net LD-PIE signal (open circles) at five wavelengths vs substrate bias (bright mode only) (18 mTorr Cl₂, 500 W rf power). Also shown for the 330 nm signal only (SiCl₂⁺) is the LD-PIE signal normalized by the ratio of the background SiCl₂⁺ PIE signal to the etch rate (normalization approach No. 2, open squares). For reference, a fit to the variation of SiCl LIF at 292.4 nm vs bias from Ref. 3 is also plotted.

fast probe in Ref. 3, the peak electron density, n_e , in the center of the wafer is $2\langle n_e \rangle$; this is also plotted in Fig. 6. While the Langmuir probe was 1.8 in. below the top window above the center of the wafer, the microwave horns were placed 1.5 or 2.5 in. below the window. (In Figs. 6–8, only data with the horns 1.5 in. below the window are plotted.) The substrate was placed 1 in. below the height of the microwave horns. In the bright mode, the ion density increased nearly linearly with rf power. In contrast, the electron density measured 1.5 in. below the window seems to increase linearly at lower power and quadratically at higher power. The electron density is seen to be almost independent of substrate bias (Fig. 7). Figure 8 shows the variation of $\langle n_e \rangle$ with pressure. At low pressure (below ≤ 15 mTorr), it seems that $\langle n_e \rangle$ decreases with pressure and is nearly independent of pressure at higher pressure when it was measured 1.5 in. below the

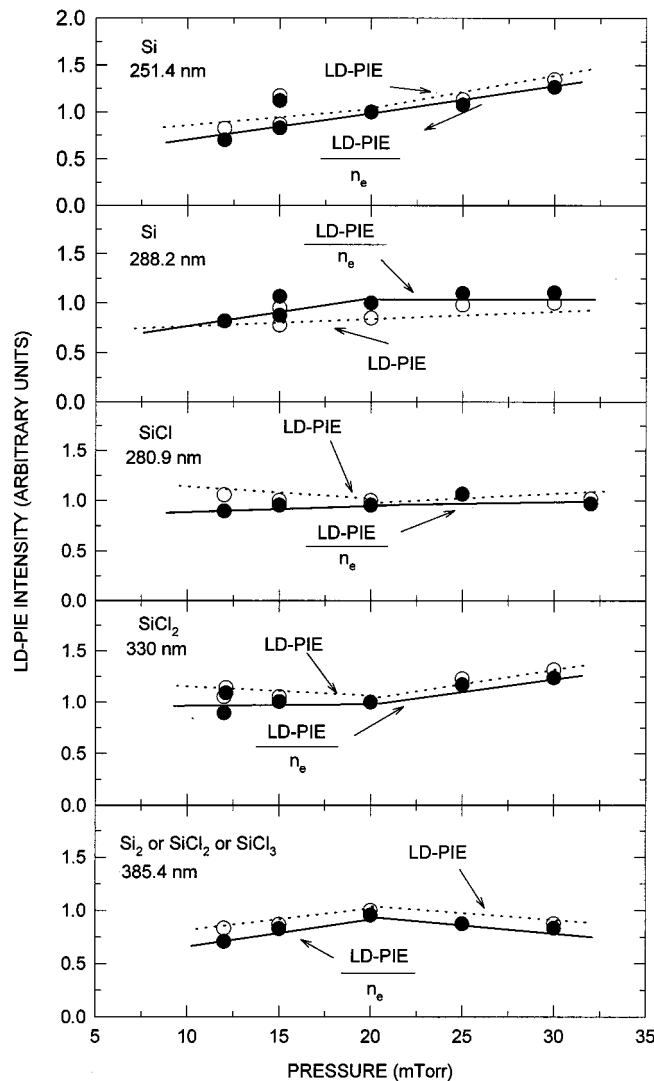


FIG. 5. Variation of the net LD-PIE signal (open circles) at five wavelengths vs pressure (bright mode only) (500 W rf power, -20 V substrate bias). Also shown is the LD-PIE signal normalized by the electron density n_e (normalization approach No. 1, closed circles).

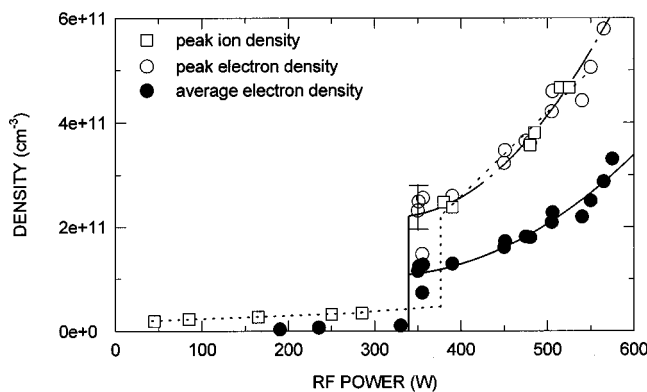


FIG. 6. Line-integrated electron density measured by microwave interferometry divided by the chamber length, the average electron density $\langle n_e \rangle$, vs rf power (18 mTorr Cl₂, 0 V substrate bias). The ion density n_i , measured by a Langmuir probe over the middle of the wafer,³ is also plotted along with the peak electron density n_e , from $\langle n_e \rangle$ and the spatial profile of n_i .

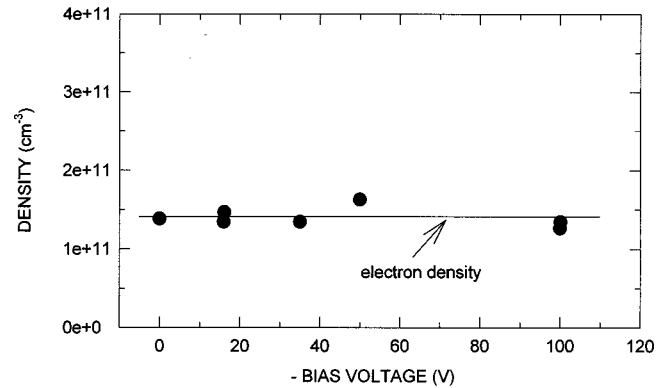


FIG. 7. Average electron density $\langle n_e \rangle$ vs substrate bias (18 mTorr Cl₂, 500 W rf power).

window. However, $\langle n_e \rangle$ seems to decrease slightly with pressure over the entire range when it was measured 2.5 in. below the top window (which is not shown in Fig. 8).

IV. DISCUSSION

A. Differences between LD-PIE and LD-LIF detection

The LD-LIF signal intensity of SiCl_y during Cl₂ etching of Si is given by

$$S_{\text{LD-LIF, SiCl}_y} = A \sum_x \theta_{\text{SiCl}_x} (Q_{\text{plasma}}) \bar{P}_{\text{SiCl}_x \rightarrow \text{SiCl}_y} (I_{\text{laser}}) \times \tilde{P}_{\text{SiCl}_y} (I_{\text{laser}}), \quad (1)$$

where A is a proportionality constant and θ_{SiCl_x} is the surface coverage of SiCl_x, which is a function of plasma conditions—rf power, bias, and pressure (collectively designated as Q_{plasma}). $\bar{P}_{\text{SiCl}_x \rightarrow \text{SiCl}_y}$ is the probability of getting laser-desorbed SiCl_y from SiCl_x on the surface (which is also a function of laser intensity) and $\tilde{P}_{\text{SiCl}_y}$ is the probability of exciting the desorbed SiCl_y to emit LIF (which is a function of laser intensity I_{laser}).

The LD-PIE signal intensity of SiCl₂ during Cl₂ etching of Si is

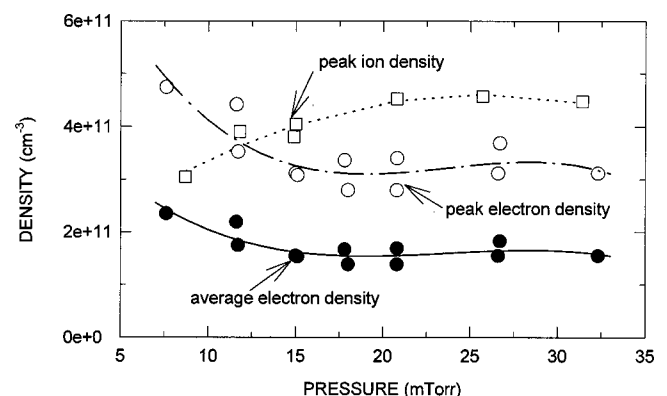


FIG. 8. Average electron density $\langle n_e \rangle$ vs Cl₂ pressure (500 W rf power, 0 V substrate bias).

TABLE II. Reactions of possible interest in LD-PIE for laser-desorbed SiCl, SiCl₂ and SiCl₃. * denotes electronically excited species. Multiple excitation routes are not listed.

Reaction	Required energy (eV)	No.
SiCl + e ⁻ → SiCl* + e ⁻	4.4	1
→ Si + Cl + e ⁻	3.86	2
→ Si* + Cl + e ⁻	8.9	3
→ Si + Cl* + e ⁻	14.2	4
SiCl ₂ + e ⁻ → SiCl ₂ * + e ⁻	3.8	5
→ SiCl + Cl + e ⁻	5.06	6
→ SiCl* + Cl + e ⁻	9.46	7
→ SiCl + Cl* + e ⁻	15.4	8
→ Si + Cl + Cl + e ⁻	8.92	9
→ Si* + Cl + Cl + e ⁻	13.9	10
→ Si + Cl* + Cl + e ⁻	19.3	11
→ Si + Cl ₂ + e ⁻	6.41	12
→ Si* + Cl ₂ + e ⁻	11.4	13
→ Si + Cl ₂ * + e ⁻	13.5	14
SiCl ₃ + e ⁻ → SiCl ₃ * + e ⁻ (?)	3.2	15
→ SiCl ₂ + Cl + e ⁻	3.56	16
→ SiCl ₂ * + Cl + e ⁻	7.32	17
→ SiCl ₂ + Cl* + e ⁻	14.0	18
→ SiCl + Cl ₂ + e ⁻	6.1	19
→ SiCl* + Cl ₂ + e ⁻	10.5	20
→ SiCl + Cl ₂ * + e ⁻	13.2	21
→ SiCl + 2Cl + e ⁻	8.61	22
→ SiCl* + 2Cl + e ⁻	13.0	23
→ SiCl + Cl + Cl* + e ⁻	19.0	24
→ Si + Cl ₂ + Cl + e ⁻	9.96	25
→ Si* + Cl ₂ + Cl + e ⁻	15.0	26
→ Si + Cl ₂ * + Cl + e ⁻	17.1	27
→ Si + Cl ₂ + Cl* + e ⁻	20.4	28

$$S_{\text{LD-PIE, SiCl}_2} = A' \sum_{x,y} \theta_{\text{SiCl}_x} (Q_{\text{plasma}}) \bar{P}_{\text{SiCl}_x \rightarrow \text{SiCl}_y} (I_{\text{laser}}) \times \tilde{P}'_{\text{SiCl}_y \rightarrow \text{SiCl}_z^*} (Q_{\text{plasma}}), \quad (2)$$

where A' is a proportionality constant and $\tilde{P}'_{\text{SiCl}_y \rightarrow \text{SiCl}_z^*}$ is the probability that collisions with electrons excite SiCl_y to produce SiCl_z* (which is a function of plasma conditions). The latter is normalized here to become the probability of such collisions in a time τ .

There are two fundamental differences in these two detection schemes. First, for example, a SiCl LD-LIF signal comes only from SiCl, while a SiCl LD-PIE signal could come from electron excitation of SiCl, electron-induced dissociation of SiCl₂ leading to excited SiCl, and possibly also from other species, as seen in reactions 1, 7, 20, and 23 in Table II. Given the time scales, only a single collision between SiCl_y and an electron is expected to occur before diffusion of the desorbed species out of the field of view, as is shown later. Second, for fixed laser parameters, the surface coverage of SiCl_x, θ_{SiCl_x} , varies exactly as does $S_{\text{LD-LIF}}$ as plasma parameters are changed, so when plasma conditions are varied, the measured variation in $S_{\text{LD-LIF}}$ is exactly the same as that for θ_{SiCl_x} . However, for LD-PIE analysis, θ_{SiCl_x} varies as does $S_{\text{LD-PIE}}/\tilde{P}'$, so the LD-PIE signal must be

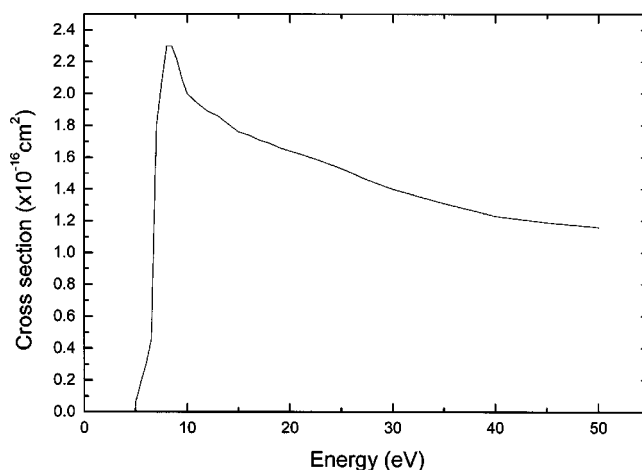


FIG. 9. Excitation cross section for SiCl₂ $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ calculated in Ref. 26. It is used here with E_{act} linearly shifted in energy to E_{excite} for the reactions listed in Table II.

normalized by $\tilde{P}'$ —which varies with plasma conditions—to determine how θ_{SiCl_x} varies with plasma conditions.

B. Electron excitation and signal normalization

Table II lists reactions that can lead to LD-PIE from desorbed SiCl, SiCl₂, and SiCl₃. (Desorption of Si is assumed to be less important.) There are very little data for the cross sections of the processes listed in Table II. Estimates of excitation probabilities are made here using the calculated cross section for electron excitation of SiCl₂ $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ from Ref. 26, shown in Fig. 9. This cross section is linearly shifted in energy so the apparent activation energy E_{act} (defined here as the energy at which the cross section increases from zero) equals the minimum energy barrier E_{excite} for each reaction listed in Table II. These estimates provide some insight; still, they do involve two major assumptions: (1) all of these processes have the same maximum cross section (even if some have more than one channel), and (2) $E_{\text{act}} = E_{\text{excite}}$. This latter assumption leads to overestimates of the excitation rates because E_{act} can be much higher than E_{excite} for several reasons. The lowest energy of states that can be reached without nuclear motion (Franck–Condon principle) can exceed this minimum value by several electron volts. Also, the density of final states factor can only become large much above this minimum energy barrier. For electron excitation of SiCl₂ $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$, E_{act} is ≈ 5.0 eV, which is higher than $E_{\text{excite}} \approx 3.8$ eV for the associated Reaction 5.

Reference 26 also gives the calculated SiCl ($B^2\Sigma^+ + B'^2\Delta$) $\leftarrow X^2\Pi_r$ electron excitation cross section, for which E_{act} is ~ 5.6 eV, which is higher than $E_{\text{excite}} \approx 4.4$ eV for the associated Reaction 1 in Table II. The cited cross section is the average of that to these two states, and gives rates of excitation that are about half those to the SiCl₂ $\tilde{A}$ state. Since PIE is seen from the B' and not from the B state,

most of the electron excitation is to the B' state, and the excitation rates of $\text{SiCl } B'^2\Delta \leftarrow X^2\Pi_r$ and $\text{SiCl}_2 \tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ would then be roughly equal.

The probability of a collision in a time τ is $\tilde{P}' = n_e k \tau$ where k is the rate constant for excitation. A high value of the measured electron density, ($n_e = 2\langle n_e \rangle$), $\sim 5 \times 10^{11}/\text{cm}^3$, is used along with $\tau = 10 \mu\text{s}$, which is the upper limit of the LD-PIE time delay plus gate window. With $T_e = 2.8 \text{ eV}$, as measured in Ref. 3, $k = 11.6, 7.3, 1.9$, and $0.4 \times 10^{-9} \text{ cm}^3/\text{s}$ for $E_{\text{act}} = 3, 5, 10$, and 15 eV respectively using the energy-shifted cross sections, leading to $\tilde{P}' = 0.058, 0.037, 0.0095$, and 0.0022 collisions during the measurement time, respectively. The collision probability for the (actual, unshifted) cross section for $\text{SiCl}_2 \tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ is 0.037 and that for $\text{SiCl } (B^2\Sigma^+ + B'^2\Delta) \leftarrow X^2\Pi_r$ is 0.020 (using the average $B + B'$ cross section). Ref. 26 also gives the summed cross section for the five lowest energy routes for electron-induced dissociation of SiCl_2 ; using this, there are 0.045 dissociative collisions during the time window. This compares to a total of 0.092 collisions for the lowest five dissociation channels for SiCl_2 listed in Table II, obtained using the cross section in Fig. 9 shifted in energy for each reaction.

Therefore, these energy-shifted cross sections suggest that it is unlikely that more than one electron collision occurs during the LD-PIE measurement. Therefore, $\tilde{P}'(Q_{\text{plasma}})$ would be expected to be proportional to $n_e(Q_{\text{plasma}})$. If T_e does not change, then θ_{SiCl_x} should vary as $S_{\text{LD-PIE}}/n_e$ as plasma conditions are varied. (This is normalization approach No. 1.) If excitation cross sections were a factor of five larger, $\tilde{P}'$ could be as large as 0.3 and the possibility of two-step excitation processes would have to be considered.

This analysis assumes that the electron energy distribution function is a Maxwellian. There is some evidence that this may not be true and that there is, in fact, a depleted high-energy tail.²⁷ It would then be better to normalize the LD-PIE signal by the density of high-energy electrons, which may not vary with plasma conditions as does the line-integrated value $\langle n_e \rangle$ determined by microwave interferometry. One way to do this is to use the background PIE intensity for normalization, which would include variations of this high-energy tail. The excitation mechanism for the background PIE signal is similar to that for LD-PIE,

$$S_{\text{PIE, SiCl}_z} = B' \sum_y n_{\text{SiCl}_y}(Q_{\text{plasma}}) \tilde{P}'_{\text{SiCl}_y \rightarrow \text{SiCl}_z^*}(Q_{\text{plasma}}), \quad (3)$$

where n_{SiCl_y} is the steady-state density of SiCl_y . If it is assumed that the etch rate ER varies as the average of the various n_{SiCl_y} , then

$$S_{\text{PIE, SiCl}_z} = B'' ER(Q_{\text{plasma}}) \tilde{P}'_{\text{SiCl}_y \rightarrow \text{SiCl}_z^*}(Q_{\text{plasma}}). \quad (4)$$

Then, $\tilde{P}' \propto S_{\text{PIE}}/ER$ and θ_{SiCl_x} in Eq. (2) would vary as $S_{\text{LD-PIE}}/(S_{\text{PIE}}/ER)$. (This is normalization approach No. 2.)

C. Desorption detected by LD-PIE

Layadi *et al.*⁵ used x-ray photoelectron spectroscopy (XPS) to show that the relative coverages of near-surface SiCl_x integrated over depth on Si exposed to a helical resonator Cl_2 plasma is $[\text{SiCl}]:[\text{SiCl}_2]:[\text{SiCl}_3] = 1:0.34:0.087$ at 40 eV ion energy and $1:0.33:0.13$ at 280 eV energy. The simulation of Si etching by Cl^+ by Hanson *et al.*²⁸ predicts the relative abundance of near-surface $[\text{SiCl}]:[\text{SiCl}_2]:[\text{SiCl}_3]$ to be $1:0.29:0.03$ at 50 eV ion energy. It also predicts that SiCl_2 is the major etch product at 50 and 100 eV , with lesser amounts of SiCl and SiCl_3 , and even lesser amounts of Si. Somewhat different interatomic potentials lead to different predictions about the dominant etch products.^{29,30} The simulation of chlorinated Si etching by Ar^+ by Kubota *et al.*³¹ found SiCl to be the major product, and lesser amounts of Si and SiCl_2 . Using single-photon ionization time-of-flight mass spectrometry Goodman *et al.*³² probed the products of Ar^+ -enhanced ($275\text{--}975 \text{ eV}$) etching of room temperature $\text{Si}(100)$ exposed to Cl_2 . They found Si and SiCl to be the main products, with SiCl having a much larger yield, and they also saw smaller amounts of SiCl_2 . Using the same method, Materer *et al.* found SiCl and SiCl_2 to be the major products of thermal etching of $\text{Si}(100)$ by Cl_2 in the range of $1023\text{--}1373 \text{ K}$.³³ The SiCl yield was larger than that of SiCl_2 and it became increasingly more important as temperature increased above 1200 K .³³ SiCl_3 could have been seen in both Refs. 32 and 33 and it was not; also, it was not possible to observe SiCl_4 in those studies. Laser thermal desorption of SiCl from a thermally³⁴ and plasma¹ chlorinated Si surface has been directly observed by LIF. Mass spectrometry detected Cl, SiCl , and SiCl_2 as the major products of LITD of thermally chlorinated silicon, with the SiCl yield being much larger than that of SiCl_2 .^{35,36} Reference 36 concluded that the SiCl was due to SiCl_2 fragmentation in the mass spectrometer. On the basis of all of these studies, it would be reasonable to expect that during plasma etching of Si by Cl_2 , SiCl and SiCl_2 could be LITD products and that SiCl_3 is not likely a LITD product. It is also less than likely that Si or clustered Si desorbs directly.³⁷

There is no strict one-to-one correspondence between desorbing species SiCl_y and emitting species SiCl_z^* . For example, the LD-PIE signal from SiCl_2^* can come from desorbed SiCl_2 or from a more chlorinated desorbed species. Previous LD-LIF measurements confirm the direct desorption of SiCl .¹ The observation of SiCl_2^* LD-PIE suggests that it is likely that there is some SiCl_2 desorbing from the surface by LITD or, in a less likely scenario, desorbed SiCl_3 or SiCl_4 is dissociated to form SiCl_2^* . SiCl_4 might form on the surface just prior to the desorption process.

The excitation and dissociation of desorbed species by electrons lead to the processes listed in Table II. Next to each reaction is the minimum energy needed for the process E_{excite} , which is the energy of the upper level of (any) excited states (from Table I) plus the bond breaking energies (if any). In general, the reactions with both electron-induced dissociation and excitation have higher energy barriers than those with solely excitation. The bond breaking energies in

reactions 2, 6, 9, 12, 16, 19, 22, and 25 for unexcited products are 3.86, 5.06, 8.92, 6.41, 3.56, 6.1, 8.61, and 9.96 eV, respectively.³⁸ The upper level energy of Si* is taken as 5.0 eV, since that of the 251.4 nm (4.93 eV) and 288.2 nm (5.05 eV) are roughly this value. For SiCl₂*, only the upper level of the 330 nm transition is considered. The activation energies E_{act} for most of these reactions are not known and, as stated earlier, they may be several electron volts above E_{excite} .

Unravelling the exact pathways relating desorbing SiCl_y and emitting SiCl_z* requires better cross sections for the processes listed in Table II than exist at present. Still, the rate constants determined using the data in Fig. 9—with the stated assumptions—do give some insight. All desorbing species suffer much less than one collision with electrons before leaving the optical field of view. This is also true for those collisions in Table II that do not lead to excitation. Consequently, it can be assumed that electrons collide only with species that have directly desorbed from the surface. Appropriately shifting in energy the cross section in Fig. 9, desorbed SiCl is excited to produce SiCl* (0.0425 SiCl* produced per desorbed SiCl during 10 μs, with $T_e = 2.8$ eV and $n_e = 5 \times 10^{11}/\text{cm}^3$), Si* (0.0130) and Cl* (0.0028); desorbed SiCl₂ produces SiCl₂* (0.0488), SiCl* (0.0111), Si* (0.0094), Cl₂* (0.0034), and Cl* (0.0025); and desorbed SiCl₃ produces SiCl₃* (0.0558, if the 385.4 nm emission is actually due to SiCl₃*), SiCl₂* (0.0201), SiCl* (0.0122), Cl₂* (0.0049), Cl* (0.0039), and Si* (0.0022). This means that it is likely that desorbing SiCl forms mostly SiCl*, SiCl₂ forms mostly SiCl₂*, and SiCl₃ forms mostly SiCl₂* (unless the 385.4 nm emission is actually due to SiCl₃*, in which case SiCl₃ forms mostly SiCl₃*); when available, the path of excitation without dissociation dominates over the others. The validity of these conclusions rests on the two stated assumptions at the beginning of Sec. IV B. The first assumption automatically assumes that there is only one effective exit channel each for Si* and Cl*. Likely, more than one exists for each.

The observed LD-PIE signal for each excited state is proportional to the density of the excited state $\times$ the probability or radiative decay during the observation time $\times$ the detection probability. The second term is $\sim \tau_{\text{spont}}^{-1}/(\tau_{\text{spont}}^{-1} + \tau_{\text{gate}}^{-1})$, where τ_{spont} is the spontaneous emission lifetime (Table I) and $\tau_{\text{gate}} \sim 5\text{--}9\ \mu\text{s}$ is the gate width. It is unity for Si*, SiCl₂*, the 385.4 nm emitter (Si*/SiCl₂*/SiCl₃*), Cl* and Cl₂*; and ~ 0.8 for SiCl* (at 280.9 nm). The detection probability includes the usual spectral sensitivity of the collection optics and the fraction of the emission from the excited state that is detected. This detected fraction is the product of the emission branching fraction and fraction of the spectral emission profile detected by the spectrometer. This can be larger for atomic emission than for molecular emission, so larger LD-PIE signals can come from excited species with smaller densities.

Conversely, the emission from a given SiCl_z* (which can come from several processes in Table II) can be related to densities of each desorbing SiCl_y. $S_{\text{LD-PIE, Si}} \propto n_{\text{SiCl}}$

$+ 0.73n_{\text{SiCl}_2} + 0.17n_{\text{SiCl}_3}$, $S_{\text{LD-PIE, SiCl}} \propto n_{\text{SiCl}} + 0.26n_{\text{SiCl}_2} + 0.29n_{\text{SiCl}_3}$, and $S_{\text{LD-PIE, SiCl}_2} \propto n_{\text{SiCl}_2} + 0.41n_{\text{SiCl}_3}$, each normalized to the density of the dominant density term (which has the smallest E_{excite}). This means that Si*, SiCl*, and SiCl₂* emissions are weighted toward detecting desorbed SiCl, SiCl, and SiCl₂, respectively. (This is true for Si* if there is no directly desorbing Si.) The dominant terms become even more so at lower T_e . Other measurements of T_e in ICP reactors that may be more sensitive to the high energy tail²⁷ suggest that T_e might be a bit smaller than the 2.8 eV used here, and nearer to 2 eV. If $T_e = 2.0$ eV, then, for example, $S_{\text{LD-PIE, Si}} \propto n_{\text{SiCl}} + 0.46n_{\text{SiCl}_2} + 0.07n_{\text{SiCl}_3}$. If E_{act} were several electron volts higher than E_{excite} for each of these routes, then the dominant route is slightly even more favored. If, for example, all E_{act} exceed their respective E_{excite} by 2 eV, then for $T_e = 2.8$ eV $S_{\text{LD-PIE, Si}} \propto n_{\text{SiCl}} + 0.70n_{\text{SiCl}_2} + 0.16n_{\text{SiCl}_3}$. These distributions for $S_{\text{LD-PIE, Si}}$ will likely change when the different routes of producing various Si* states are included.

It is possible that some of the Si* LD-PIE could come from electron excitation of desorbed Si, which is thought by some to be a product of plasma etching and LITD of Si. Also, approximately 3×10^8 Si atoms/cm² (5×10^{-7} monolayers) evaporate from a Si surface at the melting temperature (which is the temperature during LITD here) during the laser pulse. During LITD, the laser may heat regions of the Si surface with no SiCl_x overlayer and some evaporation of Si could occur. While the amount of desorbing Si per unit area is much less than the $\sim 1 \times 10^{15}$ SiCl_x/cm² that desorbs per laser pulse (i.e., roughly half¹ of the $\sim 2 \times 10^{15}$ Cl/cm² on a Si surface exposed to a Cl₂ plasma⁵), excitation and detection of this Si* could be relatively efficient.

The detected SiCl* 280.9 nm LD-PIE signals were typically twice the SiCl₂* 330 nm emissions for similar conditions; given the transmission of the filters the SiCl* emission from the reactor is ~ 6.7 times stronger. However, this does not imply that the desorbed density of SiCl is much larger than that of SiCl₂, or even that it is larger. Determination of the relative densities of desorbing species (much less the absolute densities) requires reliable cross sections for each excitation pathway. The (actual, unshifted) calculations in Ref. 26 suggest that for $T_e = 2.8$ eV the rate of exciting ground state SiCl to the $B' \ ^2\Delta$ state is about 1.08 times that for exciting SiCl₂ to $\tilde{A} \ ^1B_1$ (assuming that excitation to the SiCl B state is negligible). If these direct non-dissociative pathways for exciting SiCl and SiCl₂ were the only important ones, given these rates and the relatively smaller detected fraction of SiCl₂ emission (it is 16 times spectrally broader than the SiCl emission band), one could conclude that more (and perhaps twice as much) SiCl₂ desorbs than SiCl. Since other excitation routes are possible, and given the uncertainties in the cross sections and the fraction of detected emitted light, and other experimental uncertainties, this calibration of relative densities is still very uncertain at present.

No LD-PIE is observed here from Cl, Cl₂, and Cl₂⁺, suggesting that steady-state physisorption of chlorine is negligible during Cl₂ plasma etching of Si and that observable excited states of these species are not formed in any electron-induced dissociation of desorbed SiCl_y. If these species were

present on the surface and were directly desorbed by LITD, a transient increase of PIE from these species should have been observed. Gupta *et al.*³⁷ attributed the observed LITD signal of Cl during laser desorption of a thermally chlorinated silicon surface to electron impact fragmentation of SiCl_2 by the ionizer in the mass spectrometer. They did not notice a Cl_2 LITD signal either. This may seem to be inconsistent with the observation of LD-PIE from Si^* because it is known that during the LITD of a chlorinated Si surface, desorbing species apparently do not include atomic or clustered Si.³⁷ Table I shows that the upper levels populated in the Si^* emission transitions are 5 eV above the ground state, while the upper level of the Cl^* line examined (and of other similar lines) is much higher (10 eV) and therefore much harder to excite in this discharge. Using the aforementioned estimates of collision probabilities, the rate of production of Cl^* from SiCl is much smaller than those for SiCl^* and Si^* ; those of Cl^* and Cl_2^* from SiCl_2 are much smaller than those for SiCl_2^* , SiCl^* and Si^* ; and those of Cl^* and Cl_2^* from SiCl_3 are much smaller than those for SiCl_2^* and SiCl^* , but somewhat larger than those for Si^* . Energetically, it is very unlikely that Cl_2^{+*} would form. (14.25 eV is needed to form it from Cl_2 ; 11.5 eV ionization energy + 2.75 eV excitation energy.)

D. Dependence of the LD-PIE signal on plasma conditions

One goal is to see whether monitoring LD-PIE of Si^* , SiCl^* , and SiCl_2^* each gives the same degree of surface chlorination, as well as one that is the same as was determined by LD-LIF in Ref. 3. The LD-PIE at the five wavelengths measured track almost the same way as plasma conditions are varied (exceptions are noted later), which means that they imply similar chlorine contents of the surface adlayer. Consequently, the total chlorination of the surface from all surface SiCl_x $\theta_{\text{Cl}} \propto \theta_{\text{SiCl}}$, θ_{SiCl_2} . Note that the 330 nm emission from SiCl_2 and the 385.4 nm emission attributed to Si_2 , SiCl_2 , or SiCl_3 track fairly the same with substrate bias and other plasma parameters.

Figure 3 (open circles) shows that $S_{\text{LD-PIE}}$ increases rapidly with increasing rf power at constant pressure (18 mTorr) and dc bias (−20 V) [36 eV ion energy] for Si^* , SiCl^* , and SiCl_2^* . Of interest is the SiCl_x coverage of the surface θ_{SiCl_x} , which varies as $S_{\text{LD-PIE}}/\tilde{P}'$.

Using the collision cross section in Fig. 9 and the assumption that $E_{\text{act}} = E_{\text{excite}}$, the dependence of the collision probability $\tilde{P}'$ on the electron density n_e and temperature T_e can be determined (it is roughly $n_e e^{-E_{\text{excite}}/kT_e}$). Figure 6 shows that the electron density increases by an order of magnitude as the rf power is increased. Langmuir probe analysis in Ref. 3 showed no change of T_e with rf power changes (2.8 eV at 18 mTorr); recent optical actinometry work²⁷ suggests that there may be some small change increase in T_e with increasing rf power, probably less than 0.4 eV. The collision probability calculated using Fig. 9, increases by 33%, 67%, and 109% as T_e increases from 2.4 to 2.8 eV for $E_{\text{excite}} = 4, 8,$

and 12 eV, respectively. If there is any change in T_e its effect is small, especially for the dominant, low-energy processes. While it is not negligible, it likely affects $\tilde{P}'$ much less than the concomitant changes of n_e with rf power, and will not be considered here.

Since $\tilde{P}'$ is expected to be proportional to n_e for constant T_e , Fig. 3 also plots the normalized $S_{\text{LD-PIE}, \text{SiCl}_x}$ data divided by n_e , which is $\propto \theta_{\text{SiCl}_x}$, as filled circles, with straight line fits to the eye. (Normalization approach No. 1.) Each normalized LD-PIE signal has the same variation and is essentially independent of rf power. The most reasonable conclusion is that the adlayer content θ_{SiCl_x} is essentially independent of rf power. This is consistent with the LD-LIF study, in which $S_{\text{LD-LIF}, \text{SiCl}}$ and, therefore, θ_{SiCl_x} were seen not to change with rf power (or at most they increased only slightly with power within the bright mode); this was corroborated by XPS measurements.² That observation suggested that increasing ion flux equally increases the rates of adlayer formation (chlorination) and adlayer removal (etching).³ Alternative conclusions can be drawn, but they are less likely. For example, the LD-PIE data are also consistent with an interpretation with $\tilde{P}' \propto n_e^2$ and $\theta_{\text{SiCl}_x} \propto n_e^{-1}$; however, the probability of two collisions during the observation time is negligible. If any of the emitting species were predominantly produced by two collisions, normalization would have required dividing $S_{\text{LD-PIE}}$ by n_e^2 ; this is not seen.

The results using the second calibration approach are also provided in Fig. 3 for SiCl_2^* , for which the assumption that the etch rate ER and n_{SiCl_2} vary with plasma conditions in the same way seems reasonable. This normalization approach also suggests that θ_{SiCl_x} is essentially independent of rf power.

The unnormalized dependence of LD-PIE on substrate bias is plotted in Fig. 4 (0 to ~ -100 V, corresponding to ~ 16 to 116 eV average ion energy). The LD-LIF study of Si etching in Ref. 3 showed that the level of adlayer chlorination increases with increasing substrate bias voltage due to the deeper penetration of chlorine into subsurface. XPS of Si surfaces etched in a helical resonator chlorine plasma showed that much of increase in chlorine coverage can be attributed to subsurface Cl, which is up to ~ 20 Å deep into the surface when the incident chlorine ion has ~ 116 eV kinetic energy.⁵ Microwave interferometry (Fig. 7) shows that the electron density in the bulk of the plasma is nearly constant as the substrate bias voltage is changed. Therefore, no calibration by the n_e term in $\tilde{P}'$ is required. T_e was seen not to vary with bias at all,³ and so any variation in $\tilde{P}'$ with T_e is not expected to be important either. LD-PIE from most of the individual emission features increased with bias voltage, as did the LD-LIF signal. However, there are different variations with bias at each spectral feature (Fig. 4), most of which are larger than that seen with LD-LIF. Over this bias range, the LD-LIF signal increases by ~ 1.6 . The LD-PIE increase is about $\sim 1.0, 1.8, 2.2, 2.5,$ and 2.5 for the Si^* 251.4 nm, Si^* 288.2 nm, SiCl_2^* 330 nm, SiCl^* 280.9 nm,

and 385.4 nm $\text{Si}_2^*/\text{SiCl}_2^*/\text{SiCl}_3^*$ features, respectively. The reason for these differences in the LD-PIE signals is not clear.

The voltage drop across the sheath increases with the rf bias applied to the substrate. The desorbed species diffuse over a distance of ~ 1.0 mm during the $\sim 5\text{--}10\ \mu\text{s}$ LD-PIE signal, which is much larger than the sheath thickness ($\sim 0.2\text{--}0.4$ mm). Also, there are relatively few electrons in the sheath and the energies of these electrons are lower than those in the bulk plasma because of the retarding potential. Therefore, most of the excitation by electrons comes from outside of the sheath. Even though the plasma density does not change with bias, the etch rate increases with bias and therefore the composition of the gas in the plasma is altered. This could influence the electron temperature and density. The second calibration approach, which may include some of these changes, is shown in Fig. 4 for the SiCl_2^* LD-PIE bias dependence; the increase of the normalized signal ($\propto \theta_{\text{SiCl}_x}$) over this range is by ~ 1.5 , and is closer to that of the SiCl LD-LIF signal.

The unnormalized LD-PIE signal intensity either is nearly constant or may increase slightly with pressure (Fig. 5). Microwave interferometry measurements show that the electron density decreases slightly with increasing pressure, when measured either 2.5 and 1.5 in. below the top window. Electron density decreases with increasing pressure since dissociative electron attachment increases with increasing chlorine density.³⁹ The LD-LIF study of Si etching showed that the adlayer remains almost unchanged with pressure when the Si wafer is 1.5 in. below the window, but that it decreases slightly (and linearly) with pressure when the wafer is 2.5 in. below the window. Figure 5 shows that the net LD-PIE signal normalized by n_e , filled circles, is nearly independent of pressure, which is consistent with the results of the LD-LIF study. The Langmuir probe analysis in Ref. 3 showed that T_e decreases with pressure change from ~ 3.0 to 2.4 eV in the 12–30 mTorr range in Fig. 5. Using the cross sections in Fig. 9, this decrease corresponds to 33%, 51%, and 64% decreases in the collision probability over this pressure range for $E_{\text{act}} = 4, 8, \text{ and } 12$ eV, respectively.

Note that the bias and pressure dependences of the Si^* 251.4 nm feature are very different from those of the four other emission features. In fact, it shows no variation with substrate bias. The energy of the upper level of this Si^* emission line is about the same as that for the Si^* 288.2 nm line (Table I), but it is a triplet (that emits to the ground state of the Si atom), while the latter is singlet. It is possible that the 288.2 nm Si emission is a result of dissociative excitation of desorbing SiCl_y , since the LD-PIE signal of this feature varies with bias as do the SiCl_2^* emissions, and that the 251.4 nm feature comes from the triplet ground state of Si atoms that are desorbed directly from exposed regions of the Si surface (that are initially under the SiCl_x layer), since this would be minimally affected by substrate bias.

V. CONCLUSIONS

The etching of silicon by a chlorine ICP was studied using LD-PIE analysis to determine the surface coverage of chlorine during steady-state etching in this high density plasma reactor. Laser-induced thermal desorption followed by the transient increase in plasma-induced emission of the desorbing species can be used to analyze surface adlayer compositions *in situ* and in real time during plasma etching. In contrast to LD-LIF, LD-PIE can be used to monitor almost all the species that desorb and are subsequently excited by electrons in the plasma. The time resolution of the detection method is limited by the laser repetition rate.

To obtain the relative chlorine content of the adlayer, the LD-PIE signal was normalized by the electron density to compensate for the change in the collisional excitation rate due to electron density variations. The chlorine content of the surface adlayer changed slightly when rf power was changed. This is consistent with the SiCl LD-LIF study conducted in the same ICP reactor. Most of the LD-PIE signals increased monotonically as the ion energy was increased from 16 to 116 eV by increasing the rf substrate bias voltage. There was somewhat better agreement with the LD-LIF measurements for the bias dependence of the SiCl_2 LD-PIE signal when the alternative normalization approach was used, which assumes that the excitation rate is $\propto \text{SiCl}_2$ PIE signal/etch rate. The LD-PIE signal suggested a nearly constant adlayer content with changing pressure. This agreed with the LD-LIF results.

LD-PIE and LD-LIF have their own strengths. LD-LIF is specific to a particular species that resonantly absorbs the laser radiation and therefore, typically produces a strong emission signal. Also, LD-LIF does not rely on electrons in the plasma to excite the species. Therefore, it can be used to compare the adlayer content during laser-induced etching by non-ionized chlorine gas or during plasma etching in the dim mode (where the electron density is very low). However, LD-LIF is usually limited to only one type of desorbing species that may not necessarily represent the surface composition during plasma etching. Each desorbed species amenable to LIF, must be probed by a separate laser, except for fortuitous resonances. On the other hand, LD-PIE can usually be seen due to the excitation of many different species and therefore it is more universal. While there is a one-to-one correspondence between desorbed and detected species in LD-LIF, this is not necessarily true in LD-PIE.

Future studies of the LD-PIE method could consider including the use of a rare gas actinometer, such as Ar^* or Xe^* , to help determine the rate of electron excitation of excited states and normalize the LD-PIE signals better; this is a variation of the normalization approach No. 2. Better absolute measurements of the LD-PIE signals and excitation cross sections would result in an improved absolute determination of desorbed species densities. An LD-PIE comparison between chlorine-gas exposed and chlorine-plasma exposed surfaces by the “wait and probe” measurement described in Ref. 1 could be developed by using a low mass, relatively nonsputtering plasma such as hydrogen or helium. More de-

tailed investigations of how LD-PIE is affected by collisional excitation of desorbed species with electron temperature variations, electron density variations, and quenching could be of interest. The variation with electron density could be tested by: (1) varying conditions to enhance the probability of collecting light from regions where two collisions are more likely, (2) looking over a large range of rf power, and therefore n_e , and, (3) examining the temporal dependence of the LD-PIE signal to distinguish between one- and two-step processes.

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