# Analysis of the etching of silicon in an inductively coupled chlorine plasma using laser thermal desorption

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The etching of silicon by a chlorine inductively coupled plasma (ICP) was studied using laser desorption laser-induced fluorescence (LD-LIF) analysis to determine the surface coverage of chlorine during steady-state etching. Laser interferometry was used to measure etch rates, and optical emission actinometry and Langmuir probe analysis were used to characterize the plasma. The ICP operated in the dim mode for radio frequency (rf) powers $\lesssim$ 350 W and in the bright mode for higher powers. Under typical operating conditions in the ICP bright mode, the ion density was about $4\times 10^{11}/\mathrm{cm}^3$, the electron temperature was 2.8 eV, and about 90% of the $Cl_2$ was dissociated. The chlorine surface coverage in the dim and bright modes was $\sim 2.0\times$ that with chlorine flow and the plasma off, and increased slowly with power. This coverage ratio monotonically increased from $\sim 1.6\times$ to $2.5\times$ that with the plasma off as the ion energy was increased from 16 to 116 eV by increasing the rf substrate bias voltage during bright mode operation. Since roughly equivalent adlayer chlorine contents were measured by LD-LIF under high ion current/fast etch conditions (ICP bright mode), and low ion current/slow etch conditions [ICP dim mode and reactive ion etching mode (substrate stage powered and no ICP power)], both the adlayer chlorine content and the etch rate seem be controlled by the ion current to the wafer. © *1997 American Vacuum Society.* [S0734-2101(97)01806-X]

## I. INTRODUCTION

High charge density plasmas are being used increasingly in etching Si and other semiconductors. Such etching reactors use one of several types of high-charge density sources, such as helical resonators (HRs), electron cyclotron resonance (ECR) plasmas, and inductively coupled plasmas (ICPs). These sources share a defining characteristic: independent control of the ion density and the energy with which ions strike the wafer. Consequently, in some ways thin film processes induced by these different sources are thought to be interchangeable; however, the details of the mechanism of plasma-assisted etching may be different for these sources. In this article we present a study of the etching of Si(100) by $Cl_2$ in an inductively coupled plasma in which several *in situ* diagnostic methods are used. The goal of this work is to understand the processes at the surface by probing the surface layer that forms during steady-state etching, using laser-induced thermal desorption (LITD) with detection of the desorbed species by laser-induced fluorescence (LIF). This technique has been termed laser desorption-laser-induced fluorescence (LD-LIF) analysis. Optical interferometry, optical emission (OE) actinometry, and Langmuir probe analysis are also used to help characterize the plasma and the etching process. The comparison of the Si etching process in the ICP with previous LITD studies of etching in a HR is of particular interest here.[1–3]

Inductively coupled plasmas are known to operate in one of two modes: a low power mode called the dim mode or *E*-mode, from which there is relatively dim optical emission, and a high power mode called the bright mode or the *H*-mode, with relatively bright optical emission. The dim mode is dominated by capacitive coupling, while the bright mode is dominated by inductive coupling. Another motivation of this study is to better understand the differences in the plasma and the etching process, when the ICP is operated in these two modes.[4,5]

The LD-LIF detection method has been described in Refs. 1–3. This technique was previously used to parameterize the surface during Si etching in a HR $Cl_2$ plasma as the rf power, substrate bias, discharge pressure, and laser repetition rate were varied. The surface adlayer was also examined during exposure of Si to plasmas with mixtures of $Cl_2$ with $O_2$ (Ref. 2) and HBr.[3]

The LD-LIF method used to probe the surface during plasma etching of Si by $Cl_2$ employs 308-nm radiation both for surface desorption and LIF excitation, and is sensitive only to desorbed SiCl. The chlorinated species on the surface includes SiCl, $SiCl_2$, and $SiCl_3$ (Ref. 6), and the species desorbed during laser desorption can include these three species,[7] although not likely in the same proportion as that on the surface. Furthermore, there is evidence for nanofissure formation at the surface and subsurface chlorine during $Cl_2$ plasma etching.[8,9] The x-ray photoelectron spectroscopy (XPS) studies in Refs. 1 and 2 have shown that the LIF intensity of laser-desorbed SiCl at 308 nm is proportional to the concentration of chlorine adsorbed on the surface, so the

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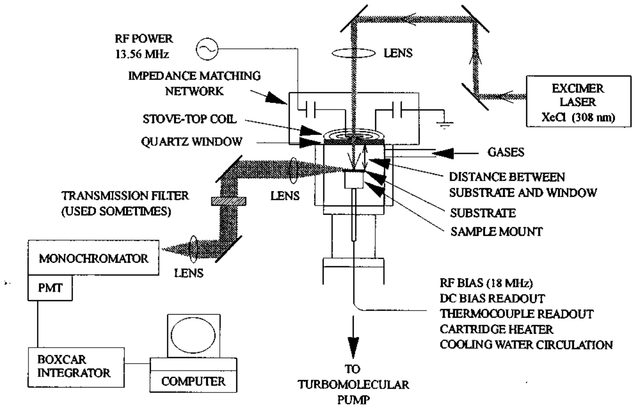

FIG. 1. Experimental apparatus used for laser desorption experiments, excluding the laser interferometry and Langmuir probe components.

LD-LIF intensity is a reliable semiquantitative measure of surface chlorine (even if SiCl is not the dominant desorbed species). The surface during steady-state etching is being probed with this technique because every laser pulse interrogates the surface after many monolayers have been etched since the last laser pulse, for sufficiently low laser repetition rates.

## II. EXPERIMENTAL METHODS

The ICP chamber was constructed from a 6-in. stainless steel cube with six ports, as shown in Fig. 1. The four side-facing viewports were used for light collection and for mounting the Langmuir probe (Fastprobe, PMT, Inc.). The sample was placed on a 2-in. diam wafer holder that was mounted on a support that extended through the bottom port. A 2-in. diam Si wafer was bonded to the wafer holder using indium and smaller Si samples were mounted on top of this wafer. For optical emission and laser desorption measurements, these samples were cleaved from a Si wafer (⟨100⟩, *n*-type, 8–12 Ω cm), while for the laser interferometry experiments, samples were cleaved from a wafer with a 5000-Å-thick polysilicon layer deposited on top of 1000 Å SiO$_2$ upon a Si substrate. Samples were cleaned with hydrofluoric acid before insertion into the chamber through a side optical port door; nitrogen was flowed into the chamber during this procedure to lessen contamination. The temperature of the sample mount was monitored with a thermocouple. To avoid wafer heating by the plasma, the mount was cooled with water to maintain the substrate near 22 °C. In the laser desorption and etch rate measurements, the sample was placed either 3.8 or 6.3 cm below the window at the top port of the chamber. In the optical actinometry and Langmuir probe measurements, the wafer was set at 6.4 and 5.5 cm below the probed volume, respectively.

Gas flow was controlled with mass flow controllers, and entered the chamber from four inlets symmetrically placed near the top port. A turbomolecular pump evacuated the system through the bottom port. Capacitance manometers monitored pressure at two points in the vacuum system, leading to an accurate value of the pressure within the plasma chamber. Chlorine flow rates of 10–50 sccm led to chamber pressures ranging from 8.5 to 30 mTorr. ICP operation was unstable below ∼10 mTorr.

Radio frequency (rf) power at 13.56 MHz was coupled to a water-cooled 3.5 in. diam stove-top coil (constructed from 1/8 in. diam copper tube) mounted ∼1 mm above the quartz window (4.5 in.-diam, 0.5 in.-thick), which served as the top port of the plasma chamber. This window also transmitted the lasers used for laser desorption (XeCl laser) and laser interferometry (He–Ne laser). The forward and reflected rf powers were measured with in-line Bird watt meters. Only the net rf power is cited here (0–∼550 W). The substrate holder was biased using a second rf source (at 18.0 MHz). The direct current (dc) bias of the substrate was monitored (0–∼−100 V). Separate rf matching networks were used to couple power to the ICP coil and the substrate stage. In one series of experiments, the discharge was operated in the reactive ion etching (RIE) mode, with the main ICP rf power at 13.56 MHz turned off and only the ''bias'' rf power to the substrate stage at 18.0 MHz on.

Discharge characteristics were analyzed by Langmuir probe measurements 4.6 cm below the window and 5.5 cm above the Si wafer. Etch rates were monitored *in situ* using laser interferometry. A He–Ne laser (632.8 nm) was directed through the top window (not shown in Fig. 1) to the sample at near normal incidence, and the reflected beam was detected by a Si photodiode outside the chamber. OE was collected by a 15 cm focal length lens and monitored with a 0.45-m spectrometer and GaAs photomultiplier. The same collection system was used to monitor LIF in the laser desorption-laser-induced fluorescence measurements to image a region ∼1.5 mm above the wafer; however, in LD-LIF measurements the photomultiplier output was directed to a boxcar integrator, which was gated to detect this transient LIF signal.

In the LD-LIF experiments, radiation from a XeCl excimer laser (Questek 2440, 308 nm, ∼20-ns-long pulses) was focused by a 50 cm focal length quartz lens, and was directed onto the Si wafer at normal incidence. Typically, the pulse energy was $\gtrsim$20 mJ, the spot size was 2.5 mm×1.4 mm (3.5 mm$^2$), and therefore the fluence was $\gtrsim$0.6 J/cm$^2$. Earlier work[1] showed that this fluence led to a saturated LD-LIF signal. The pulse energy was attenuated to this desired value using quartz flats and the distance from the lens to the wafer was varied with a translation stage to obtain the desired spot size. In LD-LIF measurements, the 292.4-nm band in the SiCl $B\ ^2\Sigma^+ - X\ ^2\Pi_r$ transition was monitored with the spectrometer, sometimes through an interference filter centered at 290 nm to minimize the collection of scattered laser light. With the measured etch rate of ∼2000–10 000 Å/min during bright mode operation, 5–25 monolayers are etched between laser pulses when a 5 Hz laser repetition rate is used in the bright mode studies; therefore, each laser pulse probes a surface representative of steady-state etching during bright mode operation. Studies conducted in Ref. 2 also suggest that during ICP bright mode operation the surface is completely rechlorinated in the 200 ms between laser pulses (5

Hz rate); this was confirmed here. The laser repetition rate was decreased when the reactor was operated in the ICP dim mode and the RIE mode to allow complete chlorination between pulses.

## III. RESULTS

### A. Characterization of the ICP

The ICP was first operated using one- and two-turn rf coupling coils. Dim mode operation was observed with Ar plasmas for rf powers up to ~200 W, and bright mode operation at higher powers. Bright mode operation was attainable with $Cl_2$/Ar mixtures with $Cl_2$ fractions up to 8% (above 550 W), but not for $Cl_2$ plasmas. Use of a Faraday shield between the rf coil and the coupling window had little effect on the discharge. Bright mode operation in $Cl_2$ plasmas was obtained when these rf coupling coils were replaced by a four-turn coil. Increasing the number of turns in the coil, and therefore its inductance, apparently improved inductive coupling to the discharge. With this four-turn coil, bright mode operation began near 400 W when rf power was increased. When rf power was subsequently decreased, bright mode operation persisted for powers down to about 260–300 W. (This method was used in some of the reported experiments to obtain bright mode operation at these lower rf powers.) Such hysteresis has been observed in other ICP reactors.[4,5] Unless otherwise specified, all of the reported experiments were conducted with this four-turn coil and a pure chlorine discharge. In the bright mode, the bright glow region of the plasma generally extended from the coupling window down to ~8 cm below it at 18 mTorr. This distance decreased with increasing pressure, with the bright glow region extending down ~6 cm at 25 mTorr and ~4 cm at 30 mTorr.

The color of the discharge was usually blue-tinged white. The slight blue coloring was probably due to emission from $Cl_2^+$, which suggests incomplete dissociation of $Cl_2$—even in bright mode operation. When the discharge was operated for an extended time after sample insertion, the region near the dielectric window turned pink and that further away was whiter than before. This suggests that with continued use of the chamber in the bright mode, the dissociation of $Cl_2$ becomes more nearly complete, probably because of wall passivation (see below). Unless otherwise stated, the experiments reported here were conducted in the former mode, with a blue-tinged white discharge.

Langmuir probe measurements in the chlorine plasma indicated that the electron temperature was ~2.8 eV and the plasma potential was ~16 V at 18 mTorr in the bright mode for rf powers in the range of 390–525 W. The electron temperature decreased with increasing pressure from 3.1 eV at 10 mTorr to 2.4 eV at 31 mTorr for bright mode operation with 450 W, and the plasma potential decreased from 17 to 15 V over this pressure range. The ion density was typically $\approx 4.3\times10^{11}/cm^3$ with 480 W rf power, no applied dc bias, and a pressure of 18 mTorr. [This is calculated assuming that $Cl^+$ (and not $Cl_2^+$) was the dominant ion, using the 2.8 eV electron temperature.] This density varied little with pressure at constant rf power, increasing by 25% from 8 to 32 mTorr, and little with substrate dc bias. In the dim mode, the density was an order of magnitude smaller, varying from $1.9\times10^{10}/cm^3$ at 45 W to $3.4\times10^{10}/cm^3$ at 285 W (with $Cl_2^+$ the dominant ionic species, see below). In the bright mode, the density increased from $2.4\times10^{11}/cm^3$ at 390 W to $4.7\times10^{11}/cm^3$ at 525 W [with $Cl^+$ the dominant ion] (18 mTorr). With extended operation the ion density increased slowly from $3.6\times10^{11}/cm^3$ to $6.6\times10^{11}/cm^3$, with the concomitant change in the color of the discharge that was mentioned earlier (450 W, 0 V bias, 18 mTorr). After the transfer port was reopened and closed (and the system was pumped down), the same initial ion density was measured, and the same slow increase in ion density was observed again. This suggests that the walls passivate after extended plasma operation in a manner that decreases wall recombination processes. It is well known that Cl-based plasma processing is affected by the condition of the chamber walls, since Cl loss by surface recombination can be significant.[10]

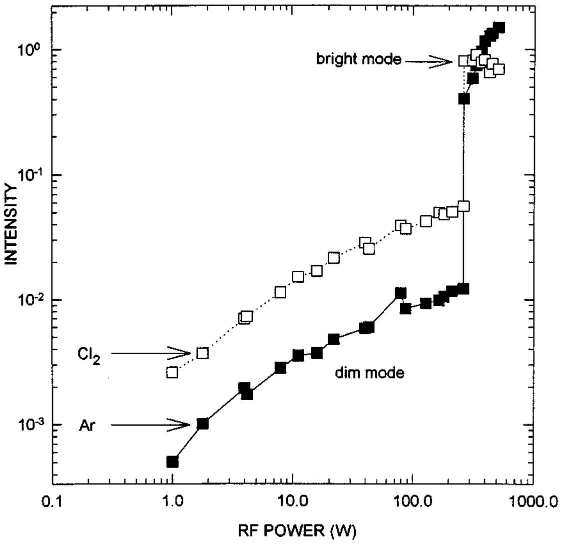

FIG. 2. Optical emission intensities of $Cl_2$ (306 nm) and Ar (750.4 nm) as a function of rf power.

Optical emission actinometry[11] was used to estimate the fractional dissociation of $Cl_2$ in a $Cl_2$ discharge with 3.8% Ar added as the actinometer (18 mTorr total pressure). Light was collected 3.8 cm below the coupling window, with the unbiased Si substrate set 6.4 cm below this collection region. Emission from the 306-nm $Cl_2$ $4s\sigma_g\ {}^1\Pi_g\rightarrow{}^1\Pi_u$ molecular band and the 750.4 nm Ar line were monitored as a function of rf power, as is shown in Fig. 2. Both emissions increased monotonically with rf power, and increased quite abruptly near 260 W, at the dim-to-bright mode transition. There was much stronger emission in the bright mode than in the dim mode, by a factor of ~50, for both pure chlorine and argon discharges (see also Ref. 5). Figure 3 shows the ratio the $Cl_2$ and Ar OE intensities as a function of rf power. In the dim mode the ratio was fairly constant as power was increased. It decreased abruptly at the dim-to-bright mode tran-

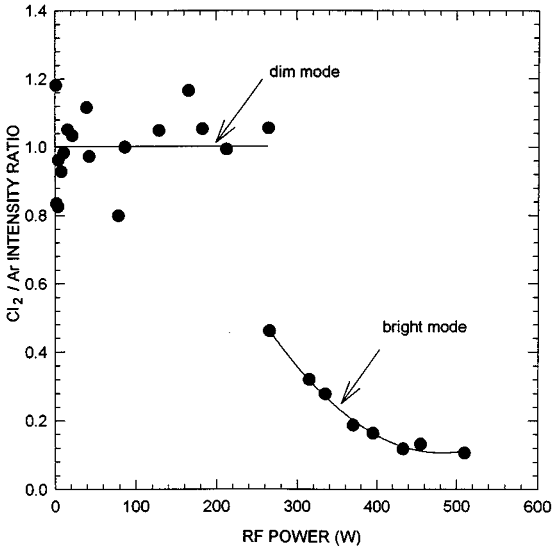

FIG. 3. The ratio of the $Cl_2$ (306 nm) and Ar (750.4 nm) optical emission intensities from Fig. 2, as a function of rf power.

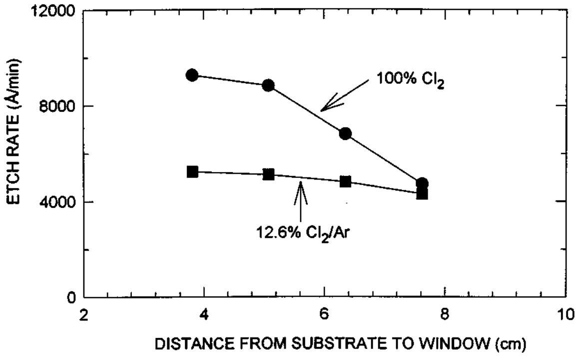

FIG. 4. The etch rate as a function of the separation between the rf coupling window and the Si wafer, for 100% $Cl_2$ (filled circles) and 12.6% $Cl_2$/Ar (filled squares) mixtures (16 mTorr, 350 W, bright mode, −30 V dc substrate bias).

sition, and monotonically decreased with increasing rf power in the bright mode. Since very little $Cl_2$ was dissociated as the rf power approached zero, it appears that 90% of the $Cl_2$ was dissociated at 500 W (assuming that Ar is a good actinometer). Corrections for changes in gas temperature with rf power have relatively little effect on this conclusion.[11]

Compared to the HR reactor used in the LD-LIF studies of Refs. 1–3, this ICP reactor has a higher ion density, a lower plasma potential, and a similar percent dissociation of $Cl_2$. It etches Si at a faster rate, but leaves a somewhat rougher surface.

## B. Optical analysis of etching

The etching of Si by $Cl_2$/Ar mixtures was briefly examined with the one-turn coil (bright mode, 510 W rf, −42 V dc bias, 19 mTorr total pressure). The etch rate increased monotonically from ~100 Å/min in a pure argon discharge (due to sputtering) to 2200 Å/min with 5.5% $Cl_2$, and showed no sign of saturating. A similar increase, with no sign of saturation, was observed in optical emission from the 2823 Å line of SiCl. All other experiments reported here were conducted with the four-turn coil.

The etch rate was measured as a function of plasma conditions using laser interferometry. Figure 4 shows the etch rate as the distance between the coupling window and the Si wafer was varied. With bright mode operation (350 W rf, −30 V dc bias of the substrate, 16 mTorr total pressure) the etch rate decreased monotonically with sample distance. A similar decrease was observed with 12.6% $Cl_2$/Ar mixtures. Etch rates exceeding 1 $\mu$m/min have been measured in this reactor with chlorine discharges. All subsequent reported work was performed with pure chlorine discharges.

Figure 5 shows a slow increase in the Si etch rate in a chlorine discharge as the rf power was increased from 300 W in bright mode operation, at fixed pressure (18 mTorr) and substrate bias (−40 V) with the wafer in the higher position (3.8 cm below the window). In the dim mode, very slow etching was observed in this run. Similar results were seen with the wafer in the lower position (6.3 cm below the window). Figure 6 shows a steady increase in etch rate with

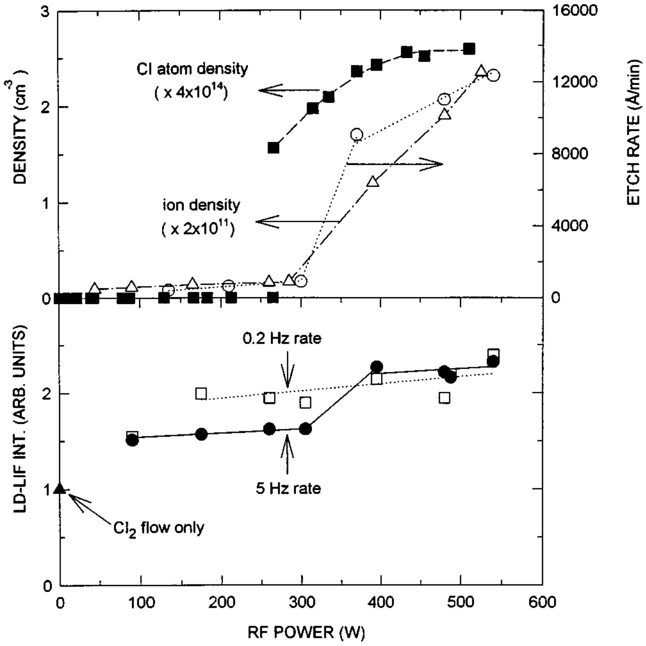

FIG. 5. The LD-LIF intensity and etch rate (open circles) versus net rf power (18 mTorr $Cl_2$, −40 V dc substrate bias, wafer 3.8 cm below the window). The LD-LIF intensities, of the 292.4 nm SiCl $B\rightarrow X$ transition, were obtained with laser repetition rates of 0.2 Hz (open squares) and 5 Hz (filled circles). Notice the nearly overlapping points for the two repetition rates at 90, 490, and 540 W. (The lines through the points are drawn for reference only, and are not curve fits.) The filled triangle denotes chlorine exposure with the plasma off. Also plotted are the Cl atom density (filled squares) plotted using the actinometry data from Fig. 3 (with the Cl density in the dim mode plotted as zero) and the ion density (open triangles) from Langmuir probe measurements. The ICP operated in the bright mode above 300 W and in the dim mode at 300 W and lower, except for the two points of the Cl atom density at 260 W, for which the larger (smaller) value was obtained during bright (dim) mode operation.

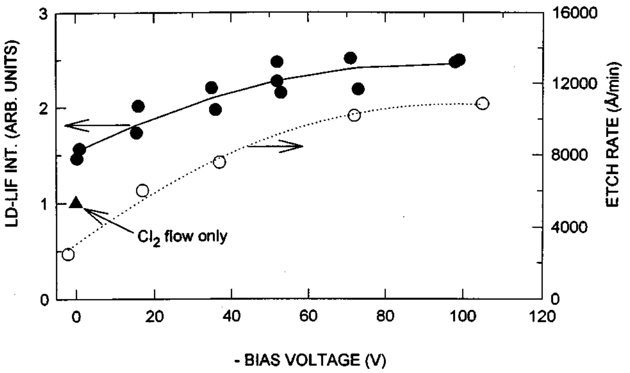

FIG. 6. The LD-LIF intensity (filled circles) and etch rate (open circles) vs dc substrate bias (18 mTorr $Cl_2$, 480 W rf, bright mode, wafer 6.3 cm below the window).

increasing magnitude of the dc bias on the Si wafer, increasing from ~2000 Å/min with no applied bias to ~11 000 Å/min with −105 V bias (18 mTorr, 480 W) with the wafer in the lower position. Since the plasma potential is 16 V, the ions were bombarding the surface with an average energy ranging from 16 to 121 eV. With the wafer in the higher position (not shown), the etch rate increased from ~4000 Å/min with no applied bias to ~13 000 Å/min with −90 V bias (18 mTorr, 480 W). Figure 7 shows that the etch rate increased somewhat as the chlorine pressure was varied from 8 to 30 mTorr, for both wafer positions. Since pressure was varied by changing the flow rate, these data suggest some ''starving'' of the discharge for chlorine at the lower operating pressures.

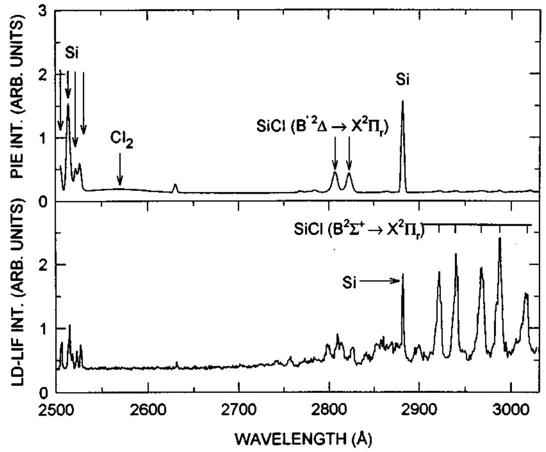

FIG. 8. The steady-state plasma-induced emission (PIE) [top] and transient LD-LIF spectra [bottom] (18 mTorr $Cl_2$, 480 W rf, bright mode, −40 V dc bias for PIE; −20 V dc bias for LD-LIF). While the LD-LIF spectrum is dominated by the SiCl $B \rightarrow X$ transition, there is a background of Si transitions due to a transient enhancement in the PIE signal from the laser desorption (called LD-PIE in Ref. 1).

The measured LD-LIF spectrum was similar to that reported earlier,[1,2] showing several bands in the $B\ ^2\Sigma^+ - X\ ^2\Pi_r$ transition (Fig. 8). Also, as reported earlier, LD-LIF analysis showed that the level of surface chlorination did not change after the plasma was turned off and subsequent pumpdown after the chlorine flow stopped. This stability of the chlorinated layer was indicated by the equally large LD-LIF signal during steady-state plasma etching (or nonplasma chlorination), and the first laser pulse in the series of pulses irradiating the sample after pumpdown.

LD-LIF was used to measure the chlorine content of the $SiCl_x$ adlayer as a function of rf power, dc bias, and pressure, by monitoring the 292.4 nm line through a transmission filter centered at 290 nm, placed before the monochromator to reduce collected laser scatter. Figure 9 shows a representative run in which the LD-LIF signal per pulse is plotted, with no signal averaging, versus time as the ICP was repetitively turned on (with different substrate biases) and then off. All data were obtained using similar comparative procedures. LD-LIF signal intensities have been normalized to the value measured with $Cl_2$ flow with the plasma turned off. Most measurements were conducted with the wafer both at the higher and lower positions, respectively, 3.8 and 6.3 cm below the dielectric window. The dependences of LD-LIF in-

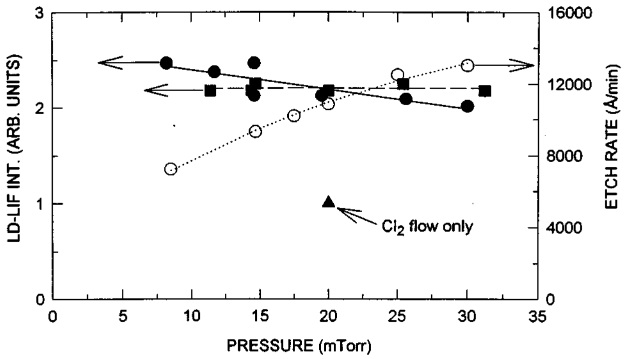

FIG. 7. The LD-LIF intensity (filled squares and filled circles for the wafer 3.8 and 6.3 cm below the window, respectively) and etch rate (open circles, wafer 6.3 cm below the window) vs $Cl_2$ pressure (480 W rf, bright mode, −40 V dc substrate bias).

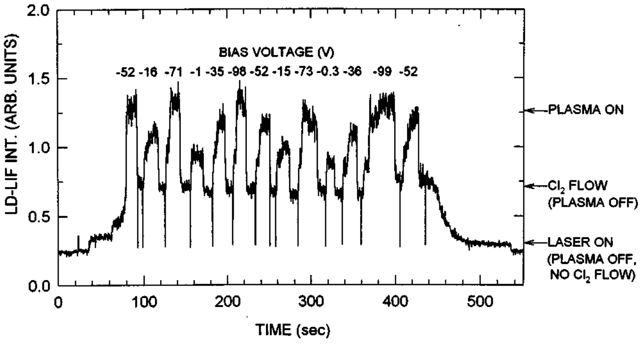

FIG. 9. Trace of the LD-LIF SiCl intensity at 292.4 nm as the plasma was turned on and off, vs time, with the different biases during each on-cycle, with the given values (18 mTorr, $Cl_2$, 470 W rf, bright mode, wafer 6.3 cm below the window). [Note the momentary glitches when the plasma was turned on (and sometimes off) due to electronic noise.]

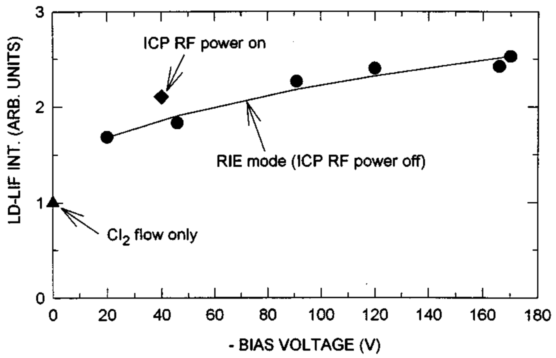

FIG. 10. LD-LIF intensity (0.2 Hz) vs dc bias with RIE operation (18 mTorr $Cl_2$), with the reference value given for ICP operation (480 W, bright mode, $-40$ V dc substrate bias) obtained during this run.

tensity on rf power and substrate dc bias were nearly the same for both wafer positions; small differences were seen for the pressure dependence.

Figure 5 plots the signal for different rf powers at constant pressure (18 mTorr) and dc bias ($-40$ V) [56 eV ion energy]. Using a 5 Hz laser repetition rate, in the dim mode the LD-LIF intensity was $\sim 1.5\times$ that with the plasma off and perhaps increased slightly with rf power, and in the bright mode it was $\sim 2.0\times$ that with the plasma off and again perhaps increased slightly with power within this range (both wafer heights). However, with a 0.2 Hz repetition rate, the LD-LIF signal during dim mode operation increased to approximately the value for the bright mode (for powers above 100 W). Figure 6 shows that, with the wafer in lower position, the LD-LIF intensity during bright mode operation increased from 1.6 to $2.5\times$ that with the plasma off as the bias was changed from 0 to $-100$ V, corresponding to an increase in average ion energy from 16 to 116 eV. With the wafer in the upper wafer position, LD-LIF increased from 1.7 to $3.0\times$ that with the plasma off as the ion energy was increased from 16 to 120 eV. Figure 7 shows a very slow decrease in LD-LIF intensity with increasing pressure with the substrate 6.3 cm below the dielectric window, and essentially no change with pressure with the substrate 3.8 cm below the window.

The LD-LIF intensity was measured as a function of substrate bias voltage with the reactor operating in the RIE mode, with no rf power applied to the ICP coil, using either 0.2, 1, or 5 Hz laser repetition rates. Figure 10 plots the results for the 0.2 Hz rate, along with the datum point for ICP operation with $-40$ V substrate bias for reference. For each of the three repetition rates, the LD-LIF signal was significantly larger than the value with $Cl_2$ flow and the plasma turned off, and it monotonically increased with substrate bias. However, the ratio of the LD-LIF intensities measured during RIE and bright mode ICP operation, both with $\sim -40$ V substrate bias, increased with increasing time between laser pulses from $\sim 0.65$ for 200 ms (5 Hz) to $\sim 0.85$ for 5 s (0.2 Hz), so the LD-LIF intensity was almost as large in the RIE mode as during ICP operation for sufficiently slow repetition rates.

## IV. DISCUSSION

As monitored by the LD-LIF intensity, the chlorine content in the adlayer is larger with the plasma on than off (with $Cl_2$ flow), and it increases slightly with rf power and somewhat more markedly with dc substrate bias. The etch rate increases proportionately faster with increasing rf power and dc bias than does the LD-LIF signal. Using Fig. 5 and the measured variation of ion density with rf power, the etch rate is seen to nearly linearly track the ion density (and current) as rf power is varied, while the LD-LIF intensity increases much more slowly.

References 1 and 2 reported that the chlorinated layer on the surface during plasma etching of Si(100) in a HR reactor contains $1.0\times 10^{15}$ Cl/cm$^2$. This was determined using the concentration of Cl on the surface during the exposure of Si(100) to a $Cl_2$ beam, as previously measured by XPS, $0.5\times 10^{15}$ Cl/cm$^2$, and the two-fold higher surface concentration of Cl during plasma etching, as measured by LD-LIF. Recent measurements of this surface layer during $Cl_2$ HR plasma etching of Si(100) using angle-resolved XPS by Layadi *et al.*,[9] suggest that this areal density is actually higher, increasing from $1.8\times 10^{15}$ Cl/cm$^2$ for 40 eV ions to $3.5\times 10^{15}$ Cl/cm$^2$ for 280 eV ions. Since the fractional increase in the LD-LIF signal when the plasma is first turned on and when the substrate bias is increased are nearly the same in this ICP study and the HR study in Ref. 2, the areal concentrations of Cl are likely the same. Consequently, the surface concentration is $\sim 2\times 10^{15}$ Cl/cm$^2$ for typical bright mode conditions.

Layadi *et al.*[9] also found that the relative coverages of $SiCl_x$ integrated over depth was $[SiCl]:[SiCl_2]:[SiCl_3] = 1:0.34:0.087$ at 40 eV ion energy and 1:0.33:0.13 at 280 eV ion energy. In the heavily chlorinated 1–2 monolayers near the surface $[SiCl] \sim [SiCl_2] > [SiCl_3]$. Chlorine was observed even deeper below the surface, to ~13 Å for 40 eV ion energy and ~25 Å for 280 eV, predominantly as SiCl, which is consistent with the simulation by Barone and Graves.[8] Much of the increase in ''surface'' chlorine density when the plasma is turned on (with $Cl_2$ flow) and with increasing substrate bias may be due to increased subsurface bound chlorine. On the basis of these studies, one would expect that during bright mode ICP operation the surface has roughly equal concentrations of SiCl and $SiCl_2$, and that SiCl is present down to a depth of ~15 Å.

LD-LIF probing of the plasma-treated surface with a series of laser pulses, after the ICP was extinguished and the flow was stopped, showed that about half of the surface chlorine that can be removed by LD-LIF is removed by the first pulse. It is not clear whether subsurface Cl buried ~15 Å beneath the surface is observed as part of the signal from the first pulse, as the main part of the signal in subsequent pulses, or is buried so deeply that it is never observed by LD-LIF probing. Reference 12 showed that if the laser desorption pulse melts the surface layer, as is expected for the fluences used here and in Refs. 1 and 2, there is recrystallization from below that leads to mixing of subsurface species, and that chlorine should come to the surface. Consequently, subsurface chlorine is likely detected. Furthermore, since

XPS measurements have shown that subsurface chlorine increases with increasing substrate bias,[9] it is likely that the LD-LIF signal increases with increasing bias precisely for this reason.

The differences in plasma characteristics and etching in the ICP dim and bright modes are, not unexpectedly, striking. Compared to the bright mode, in the dim mode optical emission is much weaker, the ion density is much smaller, the fractional dissociation of $Cl_2$ is much smaller, and the etch rate is much slower. With 200 ms between laser pulses (5 Hz) the coverage with dim mode operation, while significantly larger than that with $Cl_2$ flow and the plasma off, is still significantly smaller than that in the bright mode. However, with 5 s elapsing between pulses (0.2 Hz), the coverages for the dim and bright modes are roughly the same.

In the dim mode, $>\sim 90\%$ of all chlorine is $Cl_{2,}$ and therefore the dominant ion is expected to be $Cl_2^+$ (Fig. 3). The density of $Cl_2^+$ is $\sim 2\times 10^{10}/\mathrm{cm}^3$, which increases slowly with rf power. As rf power is increased and bright mode operation is achieved, the fractional dissociation of $Cl_2$ suddenly increases (to 80%–90% for 370–510 W), meaning that Cl is the major species impinging the surface (90%–95% of all neutrals) and $Cl^+$ is probably the major ionic species hitting the surface. The ion current increases by an order of magnitude.

The contributions of $Cl_{2,}$ Cl, and $Cl^+$ (or $Cl_2^+$) to creating and removing the chlorinated adlayer can be analyzed building upon the mechanism given in Ref. 2. With the plasma off, the surface is chlorinated only by $Cl_2$. With the plasma on, the surface is chlorinated by $Cl_2$, Cl, and by chlorine ions. The ions chlorinate the surface and subsurface regions directly by implantation, and indirectly by creating additional surface/subsurface sites where Cl and $Cl_2$ can react. The etch rate is controlled by the ion flux; for constant adlayer chlorination it is proportional to the ion flux. In the HR studies of Ref. 2, the LD-LIF signal increased as rf power was increased to 100 W and then saturated, while the etch rate increased at approximately the same rate as the ion flux up to 300 W, where they both saturated. Reference 11 showed that virtually all of neutral chlorine exists as Cl atoms at 100 W and higher powers in this HR, suggesting that the increased chlorination of the surface layer by the plasma may be due to Cl atoms. However, it is possible that this extra chlorination by Cl atoms occurs only at ion-produced sites. Since the adlayer thickness in the HR studies did not change above 100 W, while the etch rate and ion flux continued to increase with rf power from 100 to 300 W, in this higher power range the increasing ion flux apparently equally increased the rates of adlayer formation (chlorination) and adlayer removal (etching).

The roughly equivalent adlayer chlorine content for high ion current and fast etch rate operation (ICP bright mode) and low ion current and slow etch rate operation (ICP dim mode and RIE mode), suggest that the chlorine content of the adlayer and etch rate are both limited by the ion flux to the surface. With an order of magnitude larger ion current to the wafer in the bright mode *vis à vis* the dim mode, there is an order of magnitude increase in both the rate of surface and subsurface chlorination (due to the rate-limiting direct or indirect effects of ions, or other processes that happen to scale with ion current) and the rate of adlayer removal, i.e., etching (which scales with ion current). With the dim-to-bright mode transition also comes a large increase in Cl atom density and a switchover of incident ions from being predominantly $Cl_2^+$ to $Cl^+$ (with their smaller size and smaller momentum at equal energy). Neither change seems to have a large effect on the chlorine content of the adlayer.

The increase in adlayer chlorine content with increasing substrate dc bias in bright mode operation is likely due to the increased penetration of (neutralized) $Cl^+$ into the subsurface region. The small decrease in the LD-LIF signal, and therefore adlayer chlorine content, with increasing pressure when the substrate is in the lower position was not seen with the substrate nearer the dielectric window. Since at 18 mTorr the brightest part of the discharge extends down only to approximately that lower position, this observation is not surprising.

The SiCl LD-LIF signal increased by a factor of 2 when the plasma was turned on (during the flow of $Cl_2$) in both the present study, conducted in the ICP, and the HR study presented in Ref. 2. The LD-LIF signal increased faster with bias voltage in this study, by a factor of 1.75 as the bias voltage was increased in magnitude from 0 to 100 V, than in the HR study, in which it increased by a factor of 1.25 over the same range. Furthermore, in the ICP study the LD-LIF intensity began to saturate at higher biases, and the slope of the LD-LIF intensity versus bias plot was approximately that measured in the HR. These observations are explained by the different plasma potentials in the two plasma reactors, 16 V in the ICP (as reported here) and 40 V in the HR (which is slightly revised from the 50 V value reported in Ref. 2). The LD-LIF intensity variation with substrate biasing in the two studies look much more similar when the data are plotted versus mean ion energy (plasma potential + the magnitude of the bias voltage). If the ICP and HR LD-LIF signals are normalized to the same value at 40 eV, the difference in the LD-LIF intensity is $\leqslant\sim$ 20% for both wafer positions, up to 120 eV ion energy (the maximum in the current study), as is seen in Fig. 11. Moreover, both studies show the same monotonic increase in LD-LIF intensity with ion density (rf power), with saturation at higher ion densities.

With equal dc biasing and with sufficient time between laser pulses, the surface appears to be almost as chlorinated during RIE operation as during ICP bright mode operation. (Perhaps it is less chlorinated by $\sim$15%.) Even though there are much lower densities of ions and Cl atoms during RIE (and ICP dim mode) operation than during ICP bright mode operation, the chlorination of the adlayer is roughly the same because the ion density controls both the chlorination and etching processes. The XPS measurements in Ref. 9 also suggested equivalent chlorination during HR and RIE operation at equal substrate biases.

The rate of chlorination is important in conducting and interpreting LD-LIF measurements. Surface chlorination has three major components: (1) that due to $Cl_2$, which occurs

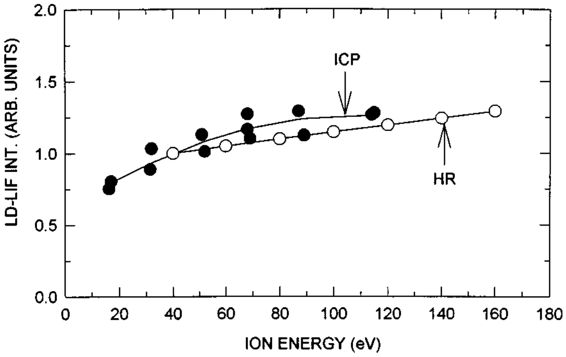

FIG. 11. Comparison of LD-LIF intensity vs ion energy for ICP bright mode operation (from Fig. 6) and helical resonator (HR) (Ref. 2) studies, using the substrate bias voltages and plasma potentials (16 and 40 V) from the respective studies [with the LD-LIF intensity normalized to the same value at 40 eV].

even with the plasma off, (2) that due to Cl, which occurs only with the plasma on, and (3) that due to ions (either directly or indirectly), which leads to the extra surface/subsurface chlorination seen during plasma operation. In Ref. 2, the LD-LIF signal in the HR decreased with laser repetition rate only for rates exceeding ~10–20 Hz (at several mTorr $Cl_2$). Since the densities of Cl and $Cl^+$ are much larger in the ICP (bright mode) than in the HR, the surface is expected to rechlorinate as fast as in the HR, and certainly within 200 ms (5 Hz). This is observed here. In ICP dim mode operation, chlorination due to neutrals is still very fast; however, the ion current is lower by an order of magnitude and the rate of ion-induced chlorination is likely slower by an order of magnitude. (Similar arguments are valid for operation in the RIE mode.) This explains the relative increase in LD-LIF signals during dim (and RIE) mode operation when the laser repetition rate was decreased by a factor of 25 (from 5 to 0.2 Hz). While the LD-LIF intensity is a good measure of the chlorine content in the adlayer, it is a good measure of the steady-state adlayer chlorine content only if the time between laser pulses is long enough to permit steady-state chlorination.

## V. CONCLUSIONS

The etching of silicon by a chlorine ICP was studied using LD-LIF analysis to determine the surface coverage of chlorine during steady-state etching. Under typical operating conditions in the ICP bright mode, the ion density was $\sim 4 \times 10^{11}/\text{cm}^3$, the electron temperature was 2.8 eV, and ~90% of the $Cl_2$ was dissociated. The chlorine surface coverage in the dim and bright modes was ~2.0× that with chlorine flow and the plasma off, and increased slowly with power. This coverage ratio monotonically increased from 1.6× to 2.5× as the ion energy was increased from 16 to 116 eV by increasing the rf substrate bias voltage during bright mode operation. The chlorine coverage was roughly the same when the plasma was operated in the ICP mode and in a reactive ion etching mode (substrate stage powered and no ICP power). Since roughly equivalent adlayer chlorine contents were measured by LD-LIF under high ion current/fast etch conditions (ICP bright mode) and low ion current/slow etch conditions (ICP dim mode and RIE mode), the chlorine content of the adlayer and the etch rate seem to be controlled by the ion current to the wafer. The laser repetition rate must be decreased to allow complete chlorination between laser pulses to measure the chlorine content of the steady-state adlayer.

The relative chlorine content in the adlayer measured in this study for a stove-top coil ICP plasma is the same as that previously measured for a helical resonator plasma, and the dependences of the chlorine content of this adlayer on ion energy (moderately strong) and pressure (weak) are the same for these two types of reactors. This suggests that the etching mechanism is the same for these two high density sources.

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