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Time-resolved measurements of Cl₂ density in high-density plasmas and application

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Absorption at 355 nm, with a pulsed frequency tripled yttrium-aluminum-garnet laser as light source, is used to monitor the time evolution of the Cl₂ density in high-density inductively coupled plasmas. The detection limit over a 0.1 s acquisition time is about 0.2 mTorr of Cl₂. This technique is well suited for monitoring chlorine density when studying elementary processes in Cl₂ containing plasmas. Furthermore, it can be applied to control the process drift in industrial etch reactors resulting from the modification of the chamber walls conditions: by measuring the Cl₂ density in a reference Cl₂ plasma before etching a wafer, it can be determined if the chamber wall conditions are kept identical from one wafer to another. © 2006 American Institute of Physics.

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Cl₂ based plasmas are widely used to etch silicon,¹ metals, and high-*k* dielectric² materials in the semiconductor industry, or other emerging materials for application in the field of UV light emitting diodes³ and spintronics.⁴ Measuring the Cl₂ density in high-density plasmas is important to get a better understanding of their physicochemistry⁵ and to improve plasma models that are widely used for the maturation of plasma reactors.⁶ However, it is difficult to measure the absolute density of Cl₂ molecules⁵ in low pressure high-density plasmas, in which the gas is highly dissociated. Broadband UV absorption spectroscopy (BBAS) has been used⁷ to probe Cl₂ from its weak absorption continuum between 250 and 400 nm. However, the small absorption cross section,⁸ combined with the issue of base-line fluctuations (inherent to the xenon lamp light source of the technique) have limited the detection sensitivity to about 20 mTorr of Cl₂. Furthermore, in BBAS a few minutes acquisition time is necessary to record an absorption spectrum with a good signal to noise ratio. Also, the plasma must be stopped to acquire the lamp spectrum. These preclude both time-resolved measurements and industrial applications. In this letter, we will show that laser absorption at 355 nm can be used to detect below 0.5 mTorr of Cl₂ with a time resolution of about 0.1 s, allowing the real time monitor of the Cl₂ density in low pressure high-density plasmas. This technique can be used in pure Cl₂ plasmas as well as in gas mixtures such as Cl₂/HBr, Cl₂/O₂, Cl₂/SF₆, and Cl₂/CF₄ plasmas, because the absorption coefficient of these molecules at 355 nm is negligible.^{9,10}

Experiments are carried out in a LAM 9400 industrial plasma source (designed to etch 200 mm diameter silicon wafers) described elsewhere.^{10,11} As shown in Fig. 1, the laser beam from a pulsed triple yttrium-aluminum-garnet (YAG) laser (Nanolase, subnanosecond pulses of ~0.5 μJ at 10 kHz) is divided in two parts by a beam splitter (BS). One beam is directed to the photodiode (PD1) to measure the unabsorbed $I_o(t)$ laser intensity. The second beam crosses the

reactor chamber, through two sapphire windows, 1 cm above the electrostatic chuck holding the wafers and is detected by photodiode PD2. 30 nm full width at half maximum band-pass filters centered at 350 nm are placed in front of photodiodes. Two 1 mm diameter diaphragms (*D*) are positioned in front of PD2 to minimize the intensity of the plasma emission reaching it. "Slow" time response operational amplifiers rectify the 10 kHz laser signals from the photodiodes into almost continuous voltages that are digitalized by analog digital converters at 100 kHz sampling rate. Each signal is averaged over 10 000 sampling and then recorded in a personal computer at 10 Hz, providing a time resolution of 0.1 s. Since signals $I(t)$, from PD2 and $I_o(t)$, from PD1, are recorded simultaneously, the absolute density of Cl₂ at time t , $[Cl_2](t)$, is given by $\ln[I_o(t)/I(t)] = \sigma L [Cl_2](t)$, where σ is the absorption cross section at 355 nm ($1.61 \times 10^{-3} \text{ A}^2$) (Ref. 8) and L the beam path length through the plasma (50 cm). It follows that 1 mTorr of Cl₂ at room temperature corresponds to an absorbance ($1-I/I_o$) of about 2.6×10^{-4} . Figure 2 shows the variation over 4 min of I, I_o , and the corresponding ratio I/I_o in an empty reactor. We observe that both the base line fluctuation and the long-term base line drift of I/I_o are below 5×10^{-5} , leading to a sensitivity limit of about 0.2 mTorr of Cl₂ with a 100 ms time resolution and without any long-term drifts. In the range 1–70 mTorr, we have verified that without a discharge in the reactor the measured Cl₂ density by laser absorption predicts perfectly the gas pressure measured with

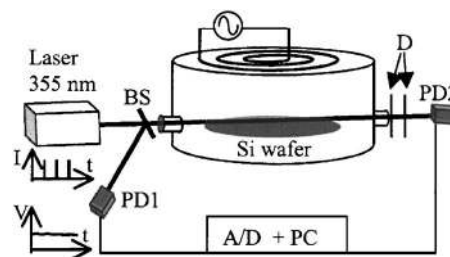


FIG. 1. Schematic of the experimental setup.

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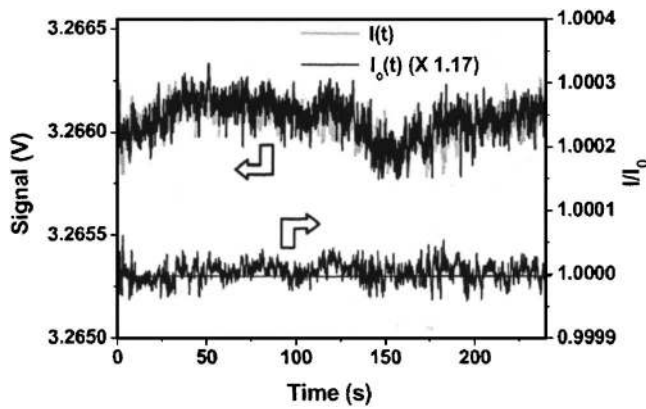


FIG. 2. Time variation of signals I and I_0 (in volts) and the ratio I/I_0 in an empty reactor.

the baratron gauge. Figure 3 shows the time variation of the Cl_2 density in a 68 mTorr Cl_2 plasma without any wafer on the chuck. During this experiment, the pressure regulation valve is held at a fixed position, allowing pressure variation in the chamber. A relatively high pressure is chosen in this example because it allows to observe particular features in the time evolution of the Cl_2 density. At $t=0$ starts the injection of Cl_2 gas into the chamber with a rate of 50 sccm and after 15 s the steady-state pressure is achieved. The Cl_2 density variation during the reactor filling obeys a simple differential equation, which solution is $[\text{Cl}_2](t) = Q/S[1 - \exp(-t/\tau)]$, where Q is the gas flow rate in molecules s^{-1} , S the pumping speed in $\text{cm}^3 \text{s}^{-1}$ and the gas residence time, $\tau=2.9$ s, is deduced from $Q, V=27$ l reactor volume and $p=68$ mTorr. As shown in Fig. 3, this solution fits correctly the Cl_2 density variations during the reactor filling. At time $t=20$ s [point (1)] the plasma is ignited and the Cl_2 density decreases between points (1) and (2) due to electron impact dissociation and gas heating to approximately 400 K.¹² Between points (2) and (3), the Cl_2 density continues to decrease with a much slower characteristic time constant until it reaches a new steady state value. This slow density variation corresponds to the time necessary to reach an equilibrium between Cl_2 and Cl densities (driven by

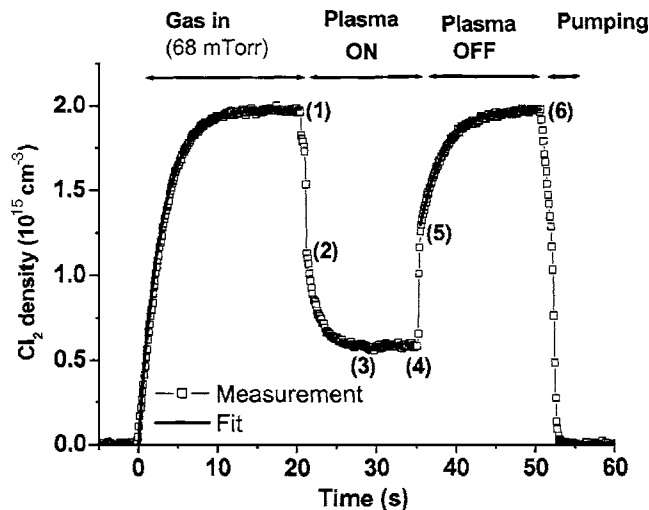


FIG. 3. Time evolution of the Cl_2 density in a pure Cl_2 plasma without wafer. Plasma conditions are 50 sccm Cl_2 flow rate, 68 mTorr pressure, and 700 W source power. Solid lines before point (1) and between points (5) and (6) are the calculation results for the reactor filling with Cl_2 .

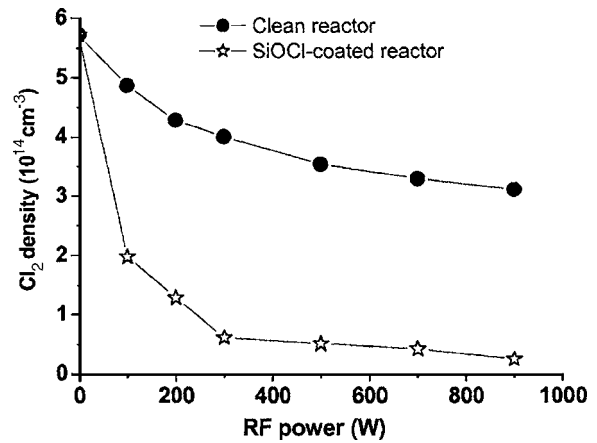


FIG. 4. Source rf power dependence of the Cl_2 density in both clean reactor and in a SiOCl -coated reactor. Plasma conditions: 50 sccm Cl_2 flow rate, 20 mTorr pressure, no bias power, and no wafer.

pumping, Cl_2 dissociation by electron impact and diffusion followed by recombination of Cl atoms at the chamber wall surfaces, all of which are slow processes at a few tens of mTorr). At time $t=35$ s [point (4)] the plasma is switched OFF and the Cl_2 density increases with two different time scales. The fast initial increase of the Cl_2 density is attributed to Cl atoms recombination on the reactor walls, which occurs on a timescale of about $\Lambda^2/D \approx 6$ ms, where Λ is the characteristic diffusion length and D the diffusion coefficient of Cl atoms. Since recombination and gas cooling are fast compared to the gas residence time (2.9 s), it follows that the Cl atoms density in the steady state plasma can be estimated to be about $1.4 \times 10^{15} \text{ cm}^{-3}$ [twice the Cl_2 density rise between points (4) and (5)]. Added to the Cl_2 density, this leads to a total pressure in the reactor at point (4) of about 82 mTorr (at 400 K). Finally, at point (5), when all the Cl atoms have recombined into Cl_2 , the reactor contains $1.37 \times 10^{15} \text{ Cl}_2$ molecules/ cm^3 at 320 K (the chamber wall temperature), corresponding to a pressure of 44 mTorr. As this value is below the steady state pressure (68 mTorr) thus between points (5) and (6) the reactor is refilled with Cl_2 , which density increases with a time constant identical to that observed before point (1) during the reactor filling.

Beside the possibility of measuring the degree of dissociation, one of the most important parameters of Cl_2 plasma, one particularly attractive application of the technique is the monitoring of industrial reactors in real time. One major issue in etching processes is to maintain reproducible plasma reactor wall conditions to avoid process drifts.^{11,13} When a drift occurs, expensive wafers are destroyed and the chamber must be opened for a wet clean operation. To minimize this issue, the best known strategy is to clean and/or to condition the chamber before each wafer.¹³ However, up to now, there was no simple way to determine whether the reactor has been correctly conditioned (or cleaned) before the etching process starts again with a new wafer. This can be readily achieved by measuring the Cl_2 density (without wafer) in a *reference* Cl_2 -based plasma. In fact, the Cl_2 density in a given plasma is extremely sensitive to the chamber wall chemical nature because the recombination probability of Cl atoms on a surface greatly depends on its chemical nature.¹⁴ This is illustrated in Fig. 4, which shows the variation of the Cl_2 density as a function of the radiofrequency (rf) inductive power both in a clean reactor and in a reactor coated with an SiOCl layer

(following the etching of a silicon wafer in a Cl_2/O_2 plasma).¹⁵ Since the electron density increases linearly with the rf power, in both cases the Cl_2 density decreases accordingly. But Fig. 4 shows that under otherwise identical plasma conditions, the Cl_2 density could be up to seven times higher in the clean reactor. Hence, by measuring the Cl_2 density in a *reference* Cl_2 plasma it is possible to deduce within a few seconds the precise state of the plasma reactor walls. This procedure can be applied just before processing the wafer (typically after the waferless chamber dry clean), and thus allows to prevent process drifts due to changes in the chamber wall conditions.

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