Probing radical kinetics in the afterglow of pulsed discharges by absorption spectroscopy with light emitting diodes: Application to BCI radical

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Measuring decay rates of radical densities in the afterglow of pulsed plasmas is a powerful approach to determine their gas phase and surface loss kinetics. We show that this measurement can be achieved by absorption spectroscopy with low cost and simple apparatus by using light emitting diodes as a light source. The feasibility is demonstrated by monitoring BCI radicals in pulsed low pressure high-density BCl3 plasmas. It is shown that BCI is lost both in the gas phase by reacting with Cl2 with a cross section of 9 Å2 and in the chamber walls with a sticking coefficient of about 0.3. © 2009 American Institute of Physics. [DOI: 10.1063/1.3067996]

Small polyatomic radicals often play a major role in plasma processes because they are the precursor to etching and deposition reactions at the wafer and reactor wall surfaces. It is thus important to determine their surface sticking coefficient as well as their chemical reaction rates in the gas phase. A technique based on time-resolved laser induced fluorescence (LIF) has been developed for this purpose; it consists of measuring the decay of the radical density in the afterglow of pulsed discharges. When the rf power is switched off, there is no more radical production by electron impact collisions and the radicals diffuse toward the reactor walls. When radicals are lost in the reactor walls, a fundamental diffusion mode (cosine spatial distribution) is rapidly reached, and the radical density decays exponentially in time at a rate that is related to their averaged sticking probability on the reactor walls and to their volume average loss rate by chemical reactions. LIF is one diagnostic that has proven to be able to be sensitive enough to probe the density decay of small polyatomic radicals in the afterglow of low pressure discharge, but this is a sophisticated and expensive diagnostic technique. Furthermore, the LIF intensity is dependent on the population of a given rotational level of the ground state, which for a given radical density is dependent on the gas temperature. Since the gas temperature decreases in the afterglow, this must be accounted for when treating the LIF signal from a single rotational line. As a result, only a few experimental measurements in fluorocarbon plasma have been reported with this technique.

In contrast to LIF, broadband UV absorption spectroscopy (BBUVAS) is quantitative, and the density deduced from the measurement does not depend on the species’ temperature provided that the absorption is integrated over a vibronic transition. In an BBUVAS experiment, the incident and transmitted spectra [I0(λ) and I(λ), respectively] of a beam crossing an absorbing medium of length l are acquired with a monochromator backed by a photodiode array, as shown in Fig. 1. In the UV range, the light source is typically a Xe arc and I0 is measured with the plasma off. The absorption spectrum of the medium is then deduced from the Beer–Lambert law, \[ \frac{I}{I_0}(\lambda) = \exp[-A(\lambda)], \]

where \[ A(\lambda) = N \sigma(\lambda) \]

is the absorbance, \( N \) is the density of absorbing species, \( l \) is the absorption length, and \( \sigma \) is the absorption cross section. The density \( N \) is determined by integrating \( \ln(I/I_0) \) over the associated absorption domain of \( \lambda \). However, this technique suffers from a lack of sensitivity that is due to the temporal fluctuations in the light source intensity \( I_0(t) \). As a result, time-resolved measurements are not feasible unless the absorbance is much larger than the variations in the intensity of the light source. This is rarely the case. One exception is the resonant absorption of some atoms using microhollow cathode lamp as light source in which the absorbance is often very large (10%). In contrast to atomic species, the broadband absorbance of polyatomic radicals in reactive plasmas is typically smaller than 1%, which precludes time-resolved measurements. Nevertheless, we have shown recently that the sensitivity of BBUVAS could be considerably improved by using light emitting diodes (LEDs) as light source because their spectral intensity distribution is very stable. As a result, the sensitivity of the absorption technique has gained one order of magnitude, and it was reported that absorbance of 10−4 can be detected within 10 ms. In this letter, we show that it is

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**FIG. 1.** Schematic of the experimental setup.
possible to use BBUVAS with a LED to probe the decay of the density of radicals in the afterglow of pulsed discharges with a few microsecond time resolution, providing a low cost and simple technique to determine their surface and gas phase reactivity.

Experiments are carried out in an industrial inductively coupled etching tool from Applied Materials designed to etch 300 mm wafers. The reactor body is in Al₂O₃ and its temperature is kept at 65 °C. The experimental setup is shown in Fig. 1. The reactor has been modified by adding several optical ports-facing each other on the top of the chamber. The oxide windows on the optical ports are separated from the plasma by high aspect ratio holes dug in the reactor body and whose role is to prevent polymer buildup on the windows. A 10 s long plasma at 5 mTorr, pulsed periodically at 150 Hz with a duty cycle of 2% (133 μs on-period for a period of 6.67 ms). The reactor has been modified by adding several optical ports-facing each other on the top of the chamber. The oxide windows on the optical ports are separated from the plasma by high aspect ratio holes dug in the reactor body and whose role is to prevent polymer buildup on the windows. A 10 s long plasma at 5 mTorr, pulsed periodically at 150 Hz with a duty cycle of 2% (133 μs on-period for a period of 6.67 ms). The reactor has been modified by adding several optical ports-facing each other on the top of the chamber. The oxide windows on the optical ports are separated from the plasma by high aspect ratio holes dug in the reactor body and whose role is to prevent polymer buildup on the windows. A 10 s long plasma at 5 mTorr, pulsed periodically at 150 Hz with a duty cycle of 2% (133 μs on-period for a period of 6.67 ms).

Measurements are carried out in an 800 W BCl₃/Cl₂ plasma at 5 mTorr, pulsed periodically at 150 Hz with a duty cycle of 5% (133 μs on-period for a period of 6.67 ms). The output of the PM is amplified by a transimpedance amplifier having a gain of 10³ (which provides a bandwidth of 10⁷ s⁻¹) and recorded by a 1 bit analog/digital converter (A/D) triggered by the plasma pulse generator. The A/D converter samples 1300 points/period at 200 kHz (5 μs per point). As shown in Fig. 2, absorbance of 10⁻³ can be measured with this system with a signal to noise (S/N) ratio of 5 by averaging over 1500 plasma periods only (a 10 s long experiment). The S/N ratio can be further improved by increasing the accumulation time. Furthermore, since there is no plasma emission in the afterglow, the time variation of the density of radicals in the afterglow of pulsed discharges with a few microsecond time resolution, providing a low cost and simple technique to determine their surface and gas phase reactivity.

Figure 2 shows the time variations of the BCl absorbance in the afterglow of a BCl₁₋₃ plasma for various BCl₁ and Cl₂ flow rates. The density variations observed during the first 500 μs of the afterglow can be due to the relaxation of high order diffusion modes and are not considered here. However, after 1 ms the density profile of BCl in the reactor has collapsed into the first order diffusion mode, and the BCl density decays exponentially at a rate $k_{loss}$, which depends strongly on the initial gas mixture. The decay rate $k_{loss}$ is the sum of the three possible loss paths for BCl: loss by reacting in the chamber walls (at rate $k_{wall}$), loss by chemical reactions in the gas phase (at rate $k_{gas}[R]$), where [R] is the reactant density and loss by pumping (at rate $k_{pump}$),

$$\frac{d[BCl]}{dt} = -k_{loss}[BCl] = -\left( k_{wall} + \sum_{R} k_{gas}[R] + k_{pump} \right) \times [BCl],$$

where the sum $\Sigma$ is all the other possible chemical reactions of BCl with other radicals R. The density decay is exponential only if $[R]$ is time independent, i.e., $[R] \gg [BCl]$. Under our conditions $k_{pump}$ is about 8 s⁻¹ only and can be neglected. In a cylindrical geometry, the decay rate $k_{wall}$ of a radical’s density due to its gas phase diffusion and effective sticking on the vessel walls with probability $\alpha$ is given by $^{2}$

$$\frac{1}{k_{wall}} = \frac{p\Lambda^2}{D} + \frac{V(2-\alpha)}{A} v_{th}\alpha,$$

where $p$ is the gas pressure in Torr, $D$ is the diffusion coefficient that is estimated to be about 200 Torr cm² s⁻¹, $\Lambda$ is the characteristic diffusion length, $1/\Lambda^2 = (\pi/L)^2 + (2.405/R) - 6$ with $L$ the reactor height (17 cm) and $R$, its radius (27 cm), $v_{th}$ the thermal speed of the radicals (4.3 × 10³ cm s⁻¹ at 400 K), and $V/A$, the volume to surface ratio of the reactor. By using Eq. (2) with $\alpha=1$, we find that the upper limit for the BCl loss rate on the reactor walls is $k_{wall}=680$ s⁻¹ at 5 mTorr. This value is much smaller than the decay rates deduced from Fig. 2, which range between $10 s^{-1} < k_{loss} < 6600 s^{-1}$ (see Fig. 3). Therefore, $\sum k_{gas}[R] \gg k_{wall}$ and the dominant loss mechanism of BCl in the after-
In conclusion, we have developed a simple technique to measure the time variation of radical densities in pulsed discharges, which allows measuring their gas phase reaction rates and surface sticking probability, thus providing considerable insight on the plasma chemistry and useful data for plasma modeling. The technique can be applied to a wide variety of plasma chemistry and operating conditions.