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Doppler spectroscopic measurements of sheath ion velocities in radio-frequency plasmas

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We have measured the distributions of N_2^+ ion velocity components parallel and perpendicular to the electrode in the sheath of a radio-frequency nitrogen reactive ion etching discharge, using pulsed laser-induced fluorescence. Parallel to the electrode, the ions have throughout a thermal distribution that is found to be consistent with the rotational temperature of 355 K. In the perpendicular direction, we see clearly the acceleration of the ions towards the electrode, and our results agree well with theoretical predictions although an unexpected peak of unaccelerated ions persists. We have also determined the absolute ion concentrations in the sheath, which we have calibrated by analyzing the decay in laser-induced fluorescence in the plasma bulk after discharge extinction. At 20 mTorr, the bulk concentration of 1.0×10^{10} cm^{-3} falls to around 2×10^{8} cm^{-3} at 2 mm from the electrode. © *1997 American Institute of Physics.* [S0021-8979(97)05703-4]

I. INTRODUCTION

The accelerating field of the sheath surrounding an object in a rf plasma results in a uniform, fast, directed flux of positive ions that may be used to etch semiconductor wafers or to implant surface-hardening species. In both cases the ion velocity distributions, which depend upon the reactor geometry, pressure, rf power and gas mixture, determine the processing effectiveness and the nature and extent of detrimental, secondary effects; for semiconductor etching, the flux collimation defines the sharpness of the etched edge, and hence the achievable device density.

Many studies have been made of such systems using retarding field analysis and mass spectrometry to determine the distributions and fluxes.[1] Such methods are well developed but tend to perturb the plasma and can only measure at the electrode surfaces. Optical emission spectroscopy allows a noninvasive one-dimensional measurement of the velocity distribution,[2] but suffers from poor spatial localization. If a laser is used to excite the fluorescing population, however, the sample is spatially defined by the overlap of the laser beam and imaged area, and the correlation between excitation and fluorescence provides useful discrimination against plasma excitation. Laser-induced fluorescence (LIF) is therefore a powerful technique for measuring species concentrations and lifetimes, velocity distributions, gas temperatures and electric field strengths.[3–9] Spatially resolved velocity distributions have also been measured using Raman spectroscopy.[10]

In this article we report measurements of ground state N_2^+ ion velocity distributions within the sheath of a capacitatively coupled nitrogen plasma using the technique of Doppler-resolved LIF. Such experiments have previously measured profiles for metastable species in plasmas of argon,[1,7] and similar techniques have been applied in electron cyclotron resonance[5,6,11–14] and helicon[15,16] plasma chambers for velocity distribution measurements of ground state N_2^+ ions[5,6] as well as metastable Ar^+ and Cl^+ ions.[11–16] In contrast, our measurements are on the dominant (ground-state) ionic species in the sheath of a radio frequency plasma, at concentrations down to a few times 10^8 cm^{-3}.

II. EXPERIMENT

Our experimental arrangement is shown in Figure 1. We use a capacitatively coupled discharge in a Plasmatech RIE80 parallel-plate chamber that we drive at 13.56 MHz and through which we maintain a constant flow of nitrogen. The chamber is composed of a grounded upper electrode 28 cm in diameter and a driven lower electrode of 24 cm that is surrounded by a base plate thus increasing the effective area of the grounded electrode to 2.5 times that of the driven electrode. The upper and lower electrodes are 55 mm apart and separated by a borosilicate glass cylinder, to which we have added several fused silica windows for horizontal optical access. The electrode parts are all of anodized aluminium, and are water cooled to around 15 °C; a narrow port in the center of the upper electrode allows a laser beam to be sent perpendicularly to the driven electrode. Radio frequency power is supplied through a dc blocking capacitor, and may be switched with rise and fall times below 30 μs. Nitrogen gas enters through an array of small holes in the ground electrode, and the residence time at 20 mTorr is some 60 ms; a wire mesh ''dark space shield'' around the pump orifice confines the plasma to the reaction vessel.

Our light source is a Lambda Physik LPD3002E dye laser, pumped by an EMG201MSC XeCl excimer laser and frequency doubled in a crystal of KDP to give 200 μJ pulses of around 10 ns at 330 nm and 20 Hz. The linewidth of the ultraviolet radiation may be reduced from 0.4 cm^{-1} to about 0.08 cm^{-1} by the inclusion of an intracavity étalon which lowers the pulse energy by a factor of 2. The 4×6 mm laser beam is directed into the plasma chamber through either the vertical port or one of the horizontal ports, depending upon the velocity component to be

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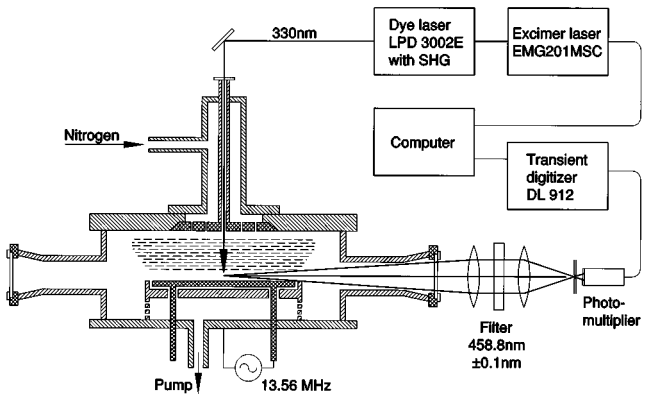

FIG. 1. Schematic diagram showing the experimental arrangement. The laser beam is shown entering vertically, perpendicular to the driven electrode.

measured, and excites the R(6) component of the $B^2\Sigma_u^+(v'=2)\leftarrow X^2\Sigma_g^+(v''=0)$ transition in N_2^+. Perpendicular fluorescence at 458.8 nm to the $v''=4$ level is recorded by a photomultiplier through a horizontal port. A narrow-band filter, transmitting 458.8 ± 0.1 nm, restricts detection to around the R(6) line, and our imaging system selects a region approximately 2 mm high, which is a compromise between spatial resolution and signal strength. The photomultiplier signal is then processed by a Datalab DL912 transient digitizer that acts as a gated detector to remove the strong plasma emission background signal. The pulse energy is monitored by a photodiode and shot-to-shot variations are corrected assuming a linear relation between pulse energy and signal. Correction is also made for the experimentally measured position-dependent collection efficiency.

The experimental arrangement therefore resembles that of Goeckner *et al.*,[7] and suffers from a similarly poor signal-to-noise ratio. Within the sheath region, we expect to detect only one fluorescence photon per laser pulse against the bright plasma emission background, and we therefore average several thousand shots per data point.

At our intensities, a monochromatic laser would saturate the electronic transition, exciting the ion in a period shorter than both its natural lifetime and the laser pulse length and leaving the ion population equally distributed between the ground and excited states, thus yielding a constant fluorescence rate of half a photon per ion per pulse. Because the spectral and spatial extents for saturation increase with intensity, however, the total signal would still be intensity dependent. The effective intensity of a nonmonochromatic laser seen by a given ion is that which lies within the power-broadened interaction line shape, which itself depends upon the effective intensity, and the experimental resolution and signal saturation thus depend upon the coherence properties of the laser. Goeckner and Goree[17] have modelled the saturation of pulsed laser-induced fluorescence assuming a fixed Gaussian laser line shape, but our laser spectrum is unfortunately observed to be composed of a few sharp modes, and is Gaussian only when averaged over a number of pulses. Since our measurements show no broadening with increasing laser energy, however, we conclude empirically that our resolution is dominated by the time-averaged laser linewidths of around 0.4 cm^{-1} and 0.08 cm^{-1} respectively without and with the intracavity étalon, and that saturation does not have a significant effect.

III. ION CONCENTRATION MEASUREMENTS

Although laser induced fluorescence provides an excellent noninvasive method for the relative measurement of ion concentrations within a plasma, it must be calibrated if absolute values are required. In order to determine the absolute N_2^+ ion concentration, we study the fall in LIF signal after the rf power sustaining the discharge has been switched off. Three processes determine the evolution of the ion concentration in the afterglow, and in the absence of well-determined rate constants, we have carried out an extensive study[18] to establish a good calibration point.

For our typical experimental conditions, the loss of N_2^+ ions shows approximately second-order kinetic behavior, corresponding to dissociative recombination

$$N_2^+ + e^- \xrightarrow{k_r} N_2^* \rightarrow N + N, \tag{1}$$

where reported values of the rate constant k_r are in the range $1-4\times10^{-7}$ cm^3s^{-1}; we assume a value[19] of 2.3×10^{-7} cm^3s^{-1}. N_2^+ is the dominant ion in a plasma of N_2 under our conditions[20] and thus its concentration is close to that of the electrons. If the loss of N_2^+ after plasma extinction is dominated by process (1), then providing that the rate constant k_r is known, the decay can be analyzed to yield the initial N_2^+ concentration.[8,21,22]

At high pressures, the loss of N_2^+ ions is modified by association of the ion with neutral N_2 according to the reaction

$$N_2^+ + N_2 \underset{k_d}{\overset{k_a}{\rightleftharpoons}} (N_4^+)^* \xrightarrow{k_s[N_2]} N_4^+ . \tag{2}$$

Below a few Torr where $k_d \gg k_s[N_2]$, and for a constant concentration of neutral molecular nitrogen and with the transition complex $(N_4^+)^*$ in equilibrium, the rate of loss of N_2^+ may be described by a pseudo-first-order rate coefficient $k_1=(k_ak_s/k_d)[N_2]^2=k_3[N_2]^2$ where k_3 is the termolecular rate coefficient. N_4^+ also provides a route for the loss of electrons from the plasma

$$N_4^+ + e^- \xrightarrow{k_l} N_4^* \rightarrow N_2 + N_2 \tag{3}$$

and the rate constant[20] k_l is around 2×10^{-6} $cm^3\ s^{-1}$.

At low pressures, and particularly in the large ion concentration gradients in the plasma sheath region, diffusion to the walls and electrodes is significant and may be described by

$$\partial[N_2^+]/\partial t = D_a\nabla^2[N_2^+], \tag{4}$$

where the ambipolar diffusion coefficient D_a has been given[21] as 220 $cm^2\ s^{-1}$Torr. Electrons and N_4^+ ions are assumed to behave similarly.

To calibrate our LIF measurements, we have therefore measured the loss of N_2^+ in the plasma bulk after extinction

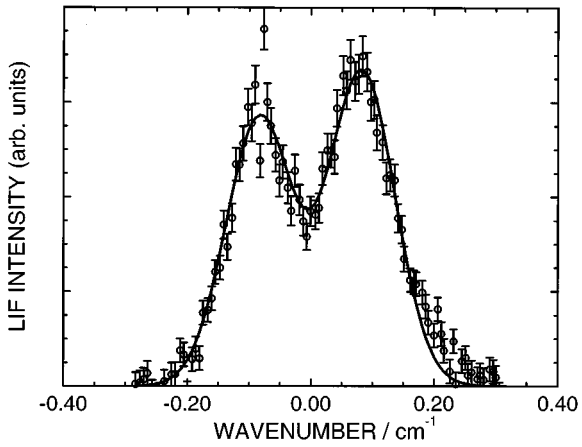

FIG. 2. Doppler profile measured parallel to and 10 mm above the driven electrode at a pressure of 20 mTorr. A Doppler shift of 0.1 cm^{-1} corresponds to a velocity component of 1000 $m\,s^{-1}$. The data were fitted to a double Gaussian distribution with the separation expected for the two spin components of the R(6) line. The total ion concentration is 7×10^{8} cm^{-3}.

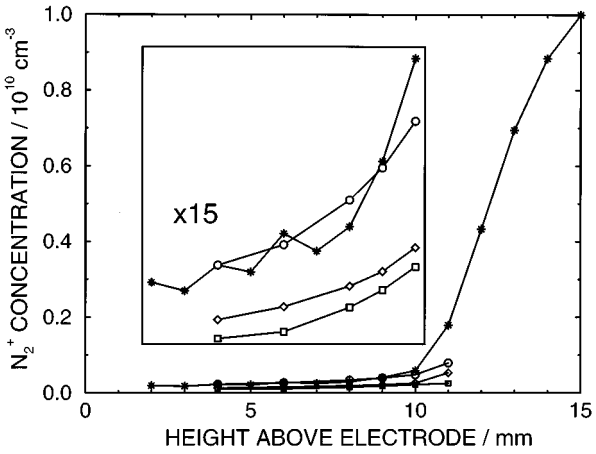

FIG. 3. Variation in N_2^+ ion concentration with height above the driven electrode, derived from measurements of the total LIF intensity. Points are measured (*) parallel and (○) perpendicular to the electrode, and the latter were broken into (□) slow and (◇) fast components by fitting a Gaussian line shape to the zero velocity peak. Parallel measurements were calibrated absolutely by measuring the decay in LIF signal after switching off the discharge; perpendicular measurements are normalized to give the same signal 15 mm above the electrode.

at pressures of 20, 100 and 500 mTorr (with a supplied power of 200 W but an effective electrode area ratio of 5) and have compared these results with computer simulations. In each case, we have allowed the various rate coefficients to float within the range of reported values, and we derive a self-consistent set of data which agrees well with the observed variation in LIF signal between the three pressures. At 500 mTorr, ion-neutral association (2) is significant and indicates a termolecular rate coefficient $k_3=1.1\times10^{-29}$ $cm^6\ s^{-1}$, in reasonable agreement with that found by Bohme *et al.*[23] At 20 mTorr, diffusion is important and we find that a value of $D_a=310$ $cm^2\ s^{-1}$Torr must be assumed. At 100 mTorr, both processes are apparent although dissociative recombination (1) dominates. For 20, 100 and 500 mTorr, we derive initial N_2^+ ion concentrations of 1.0×10^{10}, $2.7\pm0.5\times10^{10}$ and $1.2\pm0.2\times10^{11}$ cm^{-3}, which are in the ratio 1:2.7:12. The corresponding LIF signals were in the ratio 1:2.7:10, and we thus have confidence in our measurement of an ion concentration of $2.0\pm0.4\times10^{10}$ cm^{-3} at 100 mTorr with the smaller electrode area ratio of 2.5. The LIF data presented in this article are calibrated using this value, which corresponds to an ionization ratio of 6×10^{-6}.

IV. RESULTS

Our experiments were carried out at a pressure of 20 mTorr, flow rate of 50 sccm and nominal rf power of 200 W. The N_2^+ ion density in the plasma bulk is 1.0×10^{10} cm^{-3}, and such conditions provide the thickest and most collision-free sheath for which the LIF signal is adequate.

Figure 2 shows the Doppler-broadened line shape measured parallel to the electrode just inside the sheath using the étalon-narrowed laser. The 0.17 cm^{-1} spin splitting of the R(6) $v'=2\leftarrow v''=0$ line is clearly resolved, and the underlying linewidth of 0.13 cm^{-1} represents roughly equal contributions from the laser bandwidth and the ion velocity distribution. Similar profiles are measured in the plasma bulk and at other positions within the sheath, showing only a fall in overall intensity, and thus signal-to-noise ratio, as the electrode is approached. Variations in laser bandwidth during the experiment make a precise determination of the parallel velocity distribution impossible, but all our Doppler profiles measured parallel to the electrode are consistent with our measured rotational temperature in the plasma bulk of 355 ± 15 K, suggesting that, although the plasma is never equilibrated overall, the translational and rotational degrees of freedom in N_2^+ achieve local thermal equilibrium at least in the plasma bulk. The ion concentration derived from these parallel measurements is shown as a function of height above the driven electrode by the (*) symbols in Figure 3; as can be seen, the LIF intensity drops by a factor of 50 in the sheath.

Measurements of the velocity components perpendicular to the electrode are shown in Figure 4 for various heights above the electrode, and there is a clear change in the ion velocity distribution as the electrode is approached. In the plasma bulk, 15 mm from the electrode, the distribution is symmetric, with a width of a few hundred $m\,s^{-1}$, consistent with the rotational temperature of 355 K and the parallel velocity distribution of Figure 2. By 9 mm from the electrode we see a definite asymmetry and, as the electrode is approached, the broadening distribution shows the ions accelerating towards the electrode, although a strong component remains unexpectedly around zero velocity. The variation in the total (perpendicular) signal with height above the electrode is shown by the (○) symbols in Figure 3, and to aid the following analysis, we have separated this into fast (◇) and slow (□) components by fitting a Gaussian line shape to the zero velocity component.

V. MODELING

For comparison, we have modelled the ion velocity distribution using a Monte-Carlo simulation of the sheath.[24] The

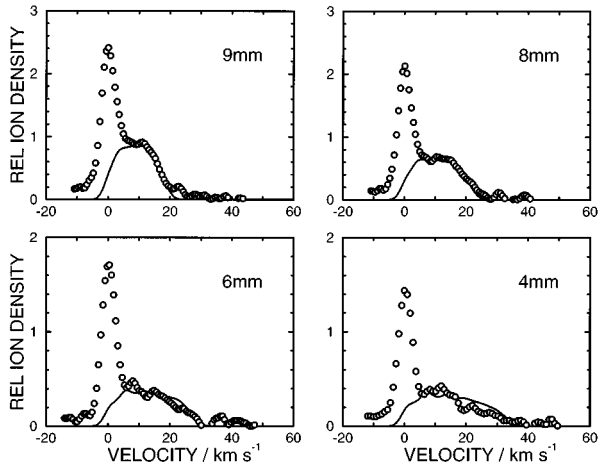

FIG. 4. Measured (points) and predicted (lines) relative ion densities as a function of velocity component perpendicular to the electrode surface at 9, 8, 6 and 4 mm above the driven electrode and at a pressure of 20 mTorr. The total ion concentrations are respectively 4.6, 3.9, 3.0 and 2.6×10^{8} cm^{-3} and the curves are plotted in the same relative units. The laser was used without the étalon for these measurements, and hence the spin splitting is no longer resolved.

model derives the plasma potential and hence the time-varying sheath voltage from the driven-to-grounded electrode area ratio, the measured dc bias and the electron temperature, which we assume[22] to be 2 eV and upon which the model is not strongly dependent. The measured dc bias under the conditions of Figure 4 was 255 V. We should also define the sheath thickness, which in practice we leave as a free parameter and adjust to achieve the best agreement between the predicted and observed velocity distributions. The fitted velocity profiles yielded a sheath thickness of 14 mm; under roughly similar conditions, we estimated the sheath thickness both visually and from the measured variation in ion concentration to be 12.5 ± 0.5mm.

Our simulation begins by calculating the time-varying sheath electric field, using the analysis of Song *et al.*[25] and assuming steady-state solutions at each (time-varying) sheath voltage and a collisionless form of the Child-Langmuir potential. Ions are then introduced with thermal velocities into the sheath at random phases of the rf cycle, and their progress through the sheath is calculated at time steps of 1 ns. The model takes account of symmetric charge exchange and elastic scattering between N_2 and N_2^+ using reported energy-dependent cross sections[26–29] down to 20 eV; extrapolated values are used for lower energies.

The structured distributions thus produced are then integrated over a range of frequencies and positions to match the limited experimental spatial and spectral resolution. The results are shown as the lines in Figure 4. In order to compare the forms of the experimental and computed curves, we have scaled the data vertically by a factor within the experimental precision; in no case was this greater than 20%.

VI. INTERPRETATION

As is evident from Figure 4, there remains throughout a strong peak of slow ions that we are unable to explain properly. Gerassimou *et al.*[4] have considered, and dismissed, a number of effects that might reduce the lifetime of excited N_2^+ near the electrode surface, some of which might create a real population of slow ions. We have also considered the possibility of formation by charge exchange, but for an effect of this magnitude we require cross sections that are considerably larger at low energies than our extrapolated values would suggest. If such processes in fact occur, then the flux to the surface of fast neutral nitrogen molecules will be considerable and will need to be considered in any models of materials processing.

From the variation of signal strength with laser intensity, which we find to be roughly linear, we can exclude nonlinear processes such as the multiphoton generation of N_2^+ ions by the laser pulse itself. We are unable, however, to dismiss completely the possibility that laser-induced fluorescence from the plasma bulk, through which the vertical laser beam must of course pass, enters our detector at a level comparable with the real signal from the more rarified plasma sheath, and we note that the cylindrical glass surround to our plasma chamber will image such fluorescence back onto the same axis. Nonetheless, tests of the imaging selectivity would appear to eliminate such a mechanism.

A convincing indication that such slow ions indeed exist in the sheath is given by the curves of Figure 3, which show the total LIF signal as a function of height above the electrode for measurements both parallel and perpendicular to the electrode, normalized to their values at 15 mm. The total LIF signal should simply be proportional to the ion concentration at that position, and we see good agreement between the two curves provided that the full measured perpendicular velocity distribution, including the slow ions, is considered. If these data are converted into fluxes, then we find that to within experimental precision the ion flux is the same at each height. Our measurements of concentration are more sensitive to slow species than are measurements of flux, but we have no method of further diagnosing the origin of the low velocity peak.

The most plausible physical explanation for such a distribution is the ionization of slow neutrals by impact with electrons produced at the electrode by secondary emission, as has been suggested by Goeckner *et al.*[30] The perturbation of plasma processes by effects related to the electrode has been considered by Gerassimo *et al.*[4] and Olthoff *et al.*[31] The further investigation of these processes is beyond our present apparatus, but should shortly be possible with new equipment currently being constructed.

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