Time- and Space-Resolved Electron-Impact Excitation Rates in an rf Glow Discharge

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Electron-impact excitation rates in a capacitively coupled 13.6-MHz rf argon discharge were derived from optical emission measurements with high time and space resolution. A propagating excitation wave form is shown to exist at gas pressures as high as 1.0 Torr. The observed features—including temporal broadening of the wave form—are in agreement with recent simulation results, and can explain apparent transitions in electron energy distributions previously reported.

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Optical emission spectroscopy has been a standard diagnostic tool in the study of glow discharges.[1] Plasma-induced-emission (PIE) measurements can probe excited discharge species with no perturbation of the discharge. An additional advantage is the excellent space and time resolution possible with this technique. Several time-resolved PIE studies of discharges driven at or near 13.56 MHz have been reported in recent years.[2-6] de Rosny *et al.*[2] observed time-dependent excitation of Si with a temporal full width at half maximum (FWHM) of about 10 ns in a capacitively coupled silane discharge. They also found that the excitation propagated away from the electrodes by measuring PIE at different spatial positions. Bletzinger and DeJoseph[3] reported similar results for a nitrogen discharge. Time-dependent PIE data have also been published for oxygen,[4] chlorine,[5] and argon[6] discharges for a limited number of spatial positions, showing evidence of a similar phenomenon.

A time- and space-dependent excitation or ionization wave form resulting from electron heating in the sheaths of rf discharges has also been observed in recent computer simulations[7-11] for a wide range of discharge parameters. There is general agreement between the published simulation results and experimentally observed features of the excitation wave forms. However, detailed experimental studies of the evolution of the excitation wave form have been limited to pressures below 0.3 Torr (Refs. 2 and 3) and observation of the temporal broadening of the wave form predicted by Graves[7] has not yet been reported. In this Letter, we describe optical emission measurements with improved space and time resolution. Data are presented for a 13.6-MHz argon discharge detailing the evolution of the excitation wave form at pressures of 1.0 and 0.2 Torr. Our measurements at both pressures reveal an excitation wave form which propagates and broadens in time.

A schematic of the experimental arrangement is shown in Fig. 1. This configuration is similar to that used by de Rosny *et al.*,[2] with the exception of the collection optics. The discharge is maintained between parallel aluminum electrodes having a diameter of 7.6 cm and spaced 2.2 cm apart. The rf generator supplies the 13.6-MHz signal which is amplified and applied to the electrodes in a push-pull mode[2] with a transformer-coupled matching network. Voltage and current wave forms are recorded with a 350-MHz digital oscilloscope. A discharge current of 71 mA rms was maintained for these experiments. The voltage lagged the current by about 76° at 1.0 Torr, in reasonable agreement with simulation results.[6,8,11] At 0.2 Torr, the voltage phase delay increased to about 87°.

The discharge is imaged at the entrance slit of a 0.3-m monochromator by lenses L1 (25-cm focal length) and L2 (30-cm focal length). The separation between the lenses is 60 cm. The monochromator is mounted so that the entrance slit is parallel to the electrode surfaces. The entrance and exit slits are 60 μm wide and the entrance slit is 1.2 cm long, allowing wavelength resolution of less than 2 Å. The optical axis defined by L2 and the entrance slit is parallel to the electrode surfaces and lies 6 mm above the electrode to which all measurements are referenced. L1 is mounted on a micrometer to allow scanning along the discharge axis. Offsetting the optical axes of L1 and L2 introduces a systematic error with an upper limit of 10 μm (measured along the discharge axis) at 6-mm separation.[12] The total error in scanning from the reference electrode to the midplane of the discharge is less than 20 μm. This error has not been

FIG. 1. Schematic of experimental arrangement. See text for description.

compensated for, since the position of the reference electrode can only be determined to within 50 μm. The electrode position is determined by imaging scattered light from a He-Ne laser marking the center of the electrode.

Observation of the actual time dependence of the excitation wave form depends on the spatial resolution of these measurements. The spatial resolution becomes critical at higher gas pressures where the amplitude of the excitation wave form varies rapidly with position. For this reason, a 2-mm-wide slit oriented parallel to the electrode surfaces was installed near lens L1 to limit the solid angle collected. With this modification, a spatial resolution of about 80 μm is achieved.[13] As shown below, the slit installation is critical for the observation of temporal broadening of the excitation wave form and for accurate determinations of the average speed of propagation.

Time-dependent emission spectra were obtained using the time-to-amplitude conversion method. In this method, a histogram of time delay per photon with respect to a fixed phase of the rf voltage wave form is collected. The time delay is represented by the amplitude of a pulse generated by the time-to-amplitude converter (TAC). Single-photon pulses from the photomultiplier tube (PMT) were amplified and then detected by a constant-fraction timing discriminator which triggered the TAC start signal. Peak count rates were approximately 20000 counts/s and counts were accumulated for 300 s per data set. The TAC stop signal was triggered every fourth period by the rf generator. A PC-based multichannel analyzer generated time-dependent spectra from the TAC output pulses with a resolution of 0.49 ns per channel. The overall time resolution of the system was approximately 2 ns. The rf phase calibration of the data was determined by the delay between photon emission and a trigger at the TAC start (including time of flight, PMT transit time, and electronic delays) and the delay between a positive zero crossing of the electrode voltage and a trigger at the TAC stop. The estimated uncertainty in the phase determination is about 5% of the rf period.

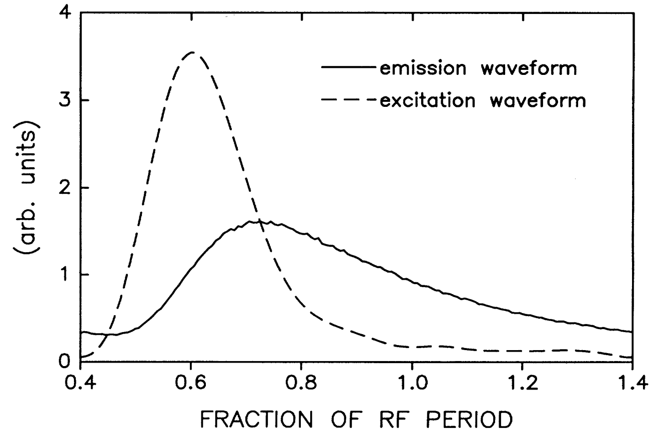

FIG. 2. Emission wave form at 750.4 nm ($2p_1$-$1s_2$). The excitation rate is obtained by deconvolution of the emission wave form following background subtraction and smoothing. The fraction of the rf period is relative to the positive zero crossing of the voltage at the reference electrode. Gas pressure: 1.0 Torr. Position: 2.0 mm from reference electrode.

Data are presented here for the $2p_1$-$1s_2$ transition at 750.4 nm. One period of a typical spatially resolved emission wave form is shown in Fig. 2 (solid line). We have assumed that radiative decay is the dominant loss mechanism for the $2p_1$ population.[14] The excitation rate (dashed line in Fig. 2) can then be found from the relation[2]

$$E(t)=I(t)+\tau dI(t)/dt\,.$$

$E(t)$ is the electron impact excitation rate, $I(t)$ is the observed emission intensity, and τ is the radiative lifetime of 22.5 ns.[15] The data are corrected for background and smoothed with a Savitsky-Golay routine before the excitation rates are derived.

Excitation rates from seven positions in a 1.0-Torr discharge are shown in Fig. 3. Several features are evi-

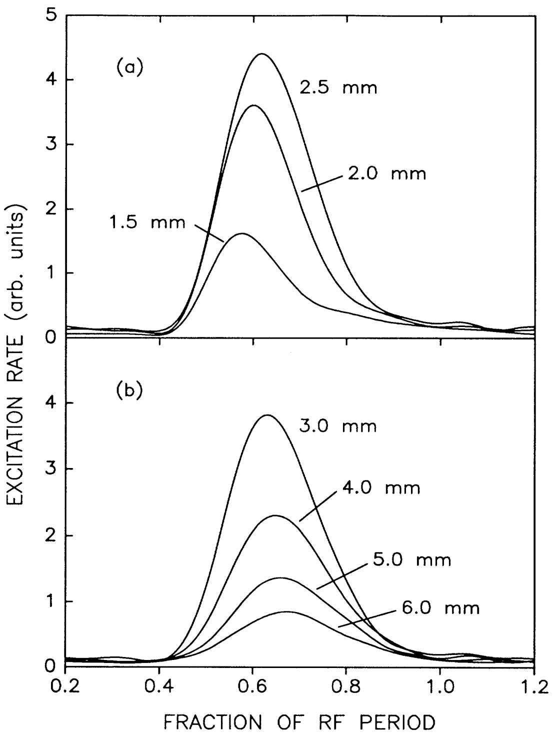

FIG. 3. Excitation wave forms at 1.0 Torr. Wave forms from several positions are shown. The amplitude of the excitation (a) rapidly increases with distance from the electrode to a maximum at about 2.7 mm, and then (b) decreases as the excitation moves with greater speed toward the center of the discharge. Also note the temporal broadening of the wave form as it moves away from the electrode.

dent in the data. The amplitude of the excitation pulse increases rapidly with distance from the electrode to a maximum at about 2.7 mm, and then decreases more slowly toward the center of the discharge. The temporal FWHM is 14 ns at 1.5 mm and gradually increases to 20 ns at 6.0 mm. The average speed of the peak of the excitation pulse prior to reaching maximum amplitude [Fig. 3(a)] is approximately 3×10^7 $\mathrm{cm\,s^{-1}}$. The average speed following this point [Fig. 3(b)] is approximately 1×10^8 $\mathrm{cm\,s^{-1}}$. Finally, the peak excitation occurs during the negative half of the rf voltage cycle, as expected for an electropositive discharge.[7,8,11]

To demonstrate the importance of limiting the solid angle collected, emission wave forms were also recorded without the slit at L1 (Fig. 1) for the same discharge conditions. The discrimination level for the amplified PMT pulses was adjusted to maintain a peak count rate of about 20000 counts/s. The apparent temporal FWHM only varied from 16.5 ns at 1.5 mm to 19 ns at 6.0 mm from the electrode, because of the influence of the strong emission near 2.7 mm on data from less intense regions a few mm away. The apparent average speed of peak propagation was also affected, increasing by as much as a factor of 3.

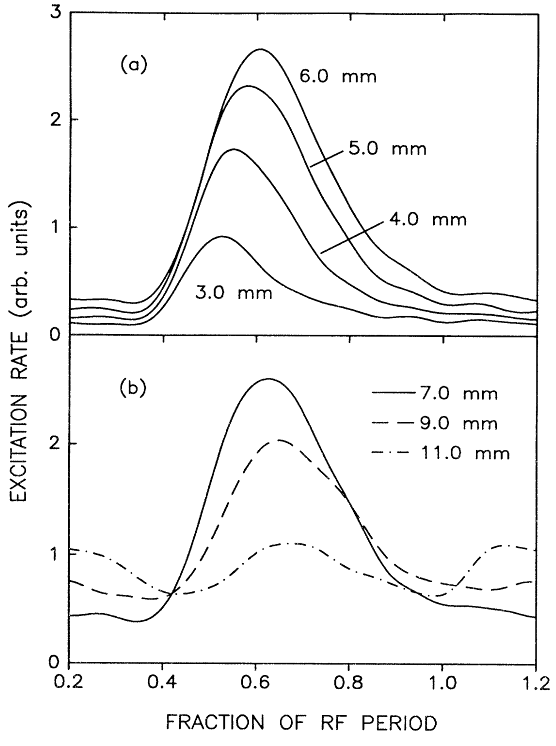

FIG. 4. Excitation wave forms at 0.2 Torr. The features are similar to those at 1.0 Torr: The amplitude (a) increases, and then (b) decreases with distance from the electrode. Temporal broadening is also evident. The position of maximum amplitude, however, is now roughly 6.5 mm from the electrode, and the excitation reaches the center of the discharge (11.0 mm).

The excitation-wave-form features described above are in agreement with the results of a fluid model simulation by Graves[7] of an argonlike discharge at 0.8 Torr. Graves found that the excitation wave form was the result of electron heating which peaked at the plasma-sheath boundary, and the wave-form properties were determined by the combined variations in electron temperature and density. Despite the differences in electrode spacing, rf power, etc., between Graves's simulation[7] and our experiment, most of the features predicted by the fluid model have been observed. However, we did not observe the large plasma continuum excitation toward the center of the discharge which appears in Graves's results. This difference will be discussed later.

The excitation wave forms at 0.2 Torr (Fig. 4) are qualitatively very similar to those at 1.0 Torr. However, the position of maximum amplitude is now between 6.0 and 7.0 mm from the electrode and the excitation propagates past the center of the discharge. These observations are consistent with previous PIE measurements[2] in which the range of the excitation increased as the gas pressure was lowered. The dependence of the spatial extent of an excitation or ionization "pulse" on pressure is also apparent in recent simulations.[8-11] This pressure dependence may explain the observation by Ingram and Braithwaite[16] of an apparent threshold for a high-energy tail in measured electron energy distributions. In that case, the high-energy electrons appeared at the grounded electrode in an argon discharge at pL values less than about 0.2 Torr cm. Here, p is the gas pressure and L is the electrode spacing which ranged from 5.5 to 13.5 cm. These electrons were assumed to be secondary electrons accelerated by large sheath fields near the powered electrode.

An apparent threshold dependence of the electron energy distribution on p was also observed in a recent probe study[17] at the *center* of an argon discharge for $L=2.0$ cm. This result was attributed to a change from collisional electron heating at high pressures to stochastic electron heating at lower pressures, with the threshold value $p\simeq0.35$ Torr ($pL\simeq0.7$ Torr cm). Our data at 0.2 Torr show an excitation wave form propagating past the center of the discharge but not reaching the opposite electrode. These data correspond to $pL=0.44$ Torr cm, which is between the two observed "threshold" values. No abrupt changes in the excitation wave forms were observed at pressures between 0.2 and 1.0 Torr. We therefore suggest that the abrupt transitions in measured electron energy distributions are due to the dependence of the range of the high-energy electron "pulse" on pressure.

The excitation rates calculated in simulations of argon or argonlike discharges[7,8,11] are typically for excitation to the 1s levels with a threshold energy of about 11.6 eV. Time-averaged rates of excitation to these levels may be deduced from absolute level densities determined by laser absorption.[18] The time dependence of the excitation, however, cannot be observed in experiments probing the 1s levels because of the long decay times associated with metastable diffusion and resonance radiation trapping. There are considerable differences between the ionization rates and 1s excitation rates calculated in these simulations, due to a higher threshold energy (15.7–17.7 eV) for ionization. The $2p_1$ level probed in this work has a threshold energy of about 13.5 eV; therefore, a quantitative comparison with either calculation is not warranted.

Electron excitation beyond the argon 1s levels has been treated in a recent simulation;[8] however, only time-averaged densities were reported in that case. The variation in spatial distributions of different excited states in that work nevertheless illustrates the effect of excitation thresholds on excitation rates. This effect may explain the absence of the large plasma continuum excitation in our measurements at 1.0 Torr (Fig. 3), as compared with fluid model predictions.[7] The presence of a large continuum excitation observed at 0.2 Torr (Fig. 4) again reveals a strong dependence of the electron energy distribution on gas pressure. Discharge simulations calculating excitation rates to various levels with p and L as parameters should therefore be quite useful.

In summary, we have presented new results on electron excitation wave forms obtained from high time and space resolution PIE studies of an argon discharge. The wave forms are qualitatively similar at pressures of 1.0 and 0.2 Torr, and the observed features are in agreement with the results of a recent fluid model simulation.[7] This work, coupled with discharge simulations[7-11] and previous PIE studies,[2,3] indicates that excitation and ionization rate pulses due to sheath heating are a general feature of rf discharges for a wide range of operating conditions.

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