Time-resolved Balmer-alpha emission from fast hydrogen atoms in low pressure, radio-frequency discharges in hydrogen

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Doppler-broadened H_α emission (656.28 nm) detected from a 13.56 MHz, parallel-plate, radio-frequency discharge in hydrogen indicates the presence of fast excited H atoms throughout the discharge volume. Time and spatially resolved measurements of the Doppler-broadened emission indicate that the fast H atoms are formed primarily at the surface of the powered electrode with kinetic energies exceeding 120 eV.

Energetic neutrals produced in radio-frequency (rf) discharges used in the production of microelectronic devices can influence etching rates, the quality of diamond deposition, and plasma cleaning mechanisms. While the anticipated energies of these neutrals have been calculated,[1] almost no experimental data exist. In this paper we present a new technique that allows the determination of fast atom velocities parallel to the electrode axis in a parallel-plate rf reactor by measuring the time-resolved Doppler-shifted optical emission perpendicular to the electrode axis. We apply the technique to the detection of fast H atoms in a 13.56-MHz hydrogen discharge because of the interest[2–4] in the production and transport of fast H.

Doppler-broadened Balmer-alpha (H_α) emission from excited fast hydrogen atoms has been previously observed from dc and low frequency rf discharges ($\leqslant$300 kHz) in pure hydrogen.[2,3,5] The fast atoms observed in dc and low frequency discharges have kinetic energies of hundreds of electron volts, far in excess of the kinetic energies (up to approximately 8 eV) that have been reported due to electron-impact dissociative ionization of hydrogen.[6] Recent work[2] suggests that there are two sources of these fast atoms in dc discharges. The first is charge-exchange collisions between fast ions and the background H_2 gas, producing fast atoms moving towards the cathode. The second is the formation of fast H atoms at the cathode surface due to bombardment by fast ions and neutrals formed in the discharge. This produces fast atoms moving away from the cathode. The fast H atoms may be excited to the $n=3$ state either when they are formed or at some later time and place in the discharge by collisions with the H_2 background gas.[7] Emission from H($n=3$) atoms with energies approaching those in dc discharges has been hypothesized[2,4] but not previously reported.[3] Measurements presented here indicate the presence of fast H atoms with kinetic energies exceeding 120 eV.

The rf discharges investigated here were generated in a Gaseous Electronics Conference rf reference cell[8] with two 10-cm diameter, parallel-plate, aluminum electrodes separated by 2.5 cm. The lower electrode is capacitively driven at 13.56 MHz, while the upper electrode is grounded to the vacuum chamber. Electrical measurements are analyzed to determine the voltage and current waveforms at the surface of the powered electrode.[8]

Spectral scans from the discharge were obtained at 90° to the central axis of the electrodes (i.e., parallel to the electrode surface) by using a scanning monochromator with spectral resolution of 0.03 and 0.06 nm for slit widths of 50 μm or 100 μm, respectively. The spatial resolution of the optical system was 5 mm horizontally and 0.1 mm vertically when using 50 μm slits (0.2 mm vertically for 100 μm slits). Time-resolved measurements of H_α emission were obtained by utilizing a time-to-amplitude converter and multichannel analyzer with a time resolution of 0.78 ns/channel. Details of the optical apparatus, including the determination of the instrumental signal delays, are presented elsewhere.[9] Data were obtained at 25 locations along the interelectrode axis, and converted into the surface and contour plots presented here.

Analysis of the observed Doppler shift of the detected emission determines the magnitude of the velocity component perpendicular to the electrode axis ($v_\perp$). The approximate magnitude of the fast H-atom velocity component parallel to the electrode axis ($v_\parallel$) can be derived from correlations between the time and location of the Doppler-broadened emission in the discharge, as determined from temporally and spatially resolved measurements.

The measured H_α spectral profile from a hydrogen rf discharge with an applied peak-to-peak voltage (V_{pp}) of 350 V and a pressure (p) of 33.3 Pa is presented in Fig. 1 with both a linear (lower curve) and logarithmic (upper curve) y axis. The Doppler-broadened emission is evident as symmetric ''wings'' that are barely observable on the linear scale (a), but are clearly evident on the semi-log plot (b). The spectral profile exhibits three distinct features that result from different H_α excitation processes. The ''slow'' component of the profile is due to dissociative electron-impact excitation of thermal H_2, while the ''intermediate'' component is due to electron-impact dissociative ionization of H_2. These two components represent emission from atoms with relatively low kinetic energies ($\leqslant$10 eV), and were previously observed by Baravian *et al.*[6] in rf discharges. The extensive ''fast'' component (0.8 nm spectral width) has not been previously reported for rf discharges in pure hydrogen with driving frequencies exceeding 300 kHz, although it has been observed for 13.56 MHz discharges in Ar-H_2

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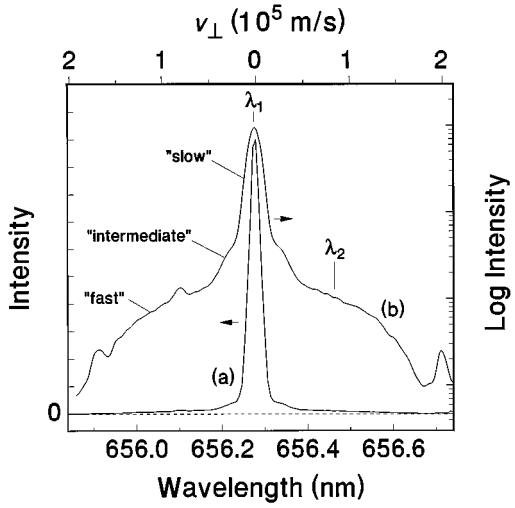

FIG. 1. Linear (a) and semi-log (b) plots of the spectral profile of Balmer-alpha (H_α) emission from a rf discharge in hydrogen at 22.5 mm from the grounded electrode with $p=33.3$ Pa, $V_{pp}=350$ V, power = 7.7 W, and a slit width of 50 μm. Points λ_1 and λ_2 indicate the wavelengths at which the time-resolved data in Figs. 2 and 3 were obtained. The upper scale is the perpendicular velocity component corresponding to the Doppler shift ($\Delta\lambda$) from 656.28 nm.

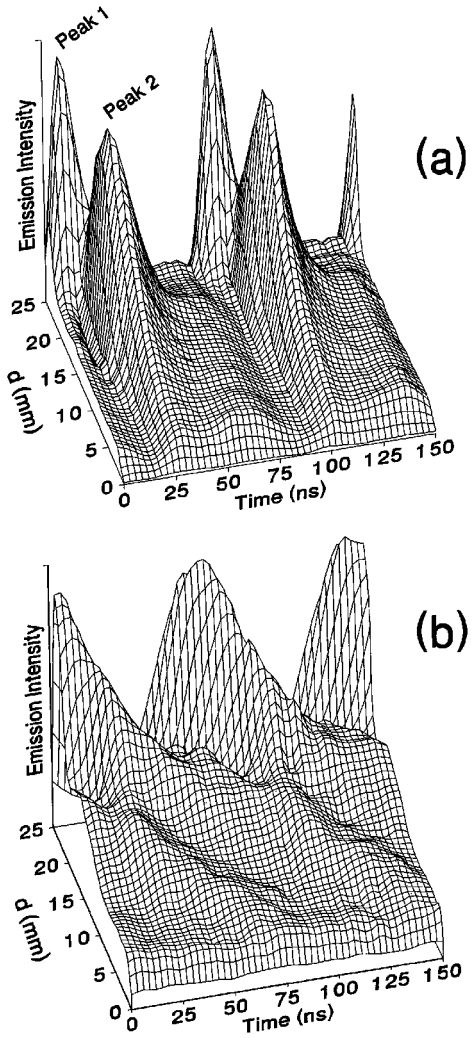

FIG. 2. Surface plots of H_α emission as a function of time and distance (d) from the grounded electrode at wavelengths λ_1 (a) and λ_2 (b). Plasma conditions are the same as in Fig. 1, and monochromator slit widths were (a) 50 μm and (b) 100 μm. Each plot is normalized to its maximum intensity.

mixtures.[10] In our experiments, the fast component was detected throughout the volume of the H_2 discharge, but could not be observed for $V_{pp}<300$ V.

The perpendicular velocity component of the fast H atoms derived from the observed Doppler shift ($\Delta\lambda$) is shown on the upper axis of Fig. 1. The two indicated wavelengths (λ_1 and λ_2) correspond, respectively, to the peak in the spectral profile, where the emission is primarily from thermal H($n=3$) atoms formed by electron impact processes, and to the approximate mean of the observed Doppler-shift ($\Delta\lambda=0.18$ nm), where emission is only from fast H($n=3$) atoms. The magnitude of $v_\perp$ corresponding to λ_2 is 8.2×10^4 m/s.

Three-dimensional surface plots representing time and spatially resolved H_α emission at wavelengths λ_1 and λ_2 are presented in Figs. 2(a) and 2(b), respectively, for a time interval of approximately two rf periods. To help in observing the time and space dependence of the optical emission, and the correlation between the emission and the electrical waveforms, the data from Fig. 2 are also presented as two-dimensional contour plots in Fig. 3, along with the voltage and current waveforms at the surface of the powered electrode. Time $t=0$ corresponds to the maximum of the applied voltage waveform, and d is the distance from the grounded electrode.

Figures 2(a) and 3(a) show two peaks in the emission that are primarily from thermal H($n=3$) atoms in the discharge. Peak 1 is located 1 mm from the surface of the powered electrode, and occurs 15 ns prior to the second peak which is located further inside the discharge volume. These two peaks are the source of the ''double-sheath'' observed by Mutsukura *et al.*[11] in time-averaged optical studies, and are similar to the peaks observed by Tochikubo *et al.*[4] in time-resolved studies. Makabe and co-workers[4] hypothesize that Peak 1 is due to the formation of a weak electric field produced in front of the powered electrode during the positive portion of the voltage waveform. Peak 2, similar to the emission observed in argon,[9] shows the development of the glow during the negative portion of the applied rf voltage.

The profiles in Figs. 2(b) and 3(b) of the Doppler-shifted emission at λ_2 exhibit a maximum 1.5 mm from the powered electrode at $t\cong0$. The fact that the Doppler-broadened emission peaks near the powered electrode and extends throughout the low-field (bulk) region of the plasma suggests that the fast H atoms are formed at the surface of the powered electrode and then travel into the discharge, away from the powered electrode. This is similar to observations in dc discharges,[2] and suggests that the fast H atoms are formed primarily by bombardment of the electrode surface by high velocity ions. The short radiative lifetime (<15 ns) of the H($n=3$) state implies that the observed H_α emission occurs near the point of excitation. This suggests that the emission observed in the bulk is most likely due to excitation of fast ground-state H atoms by collisions with the background H_2 gas, i.e.,

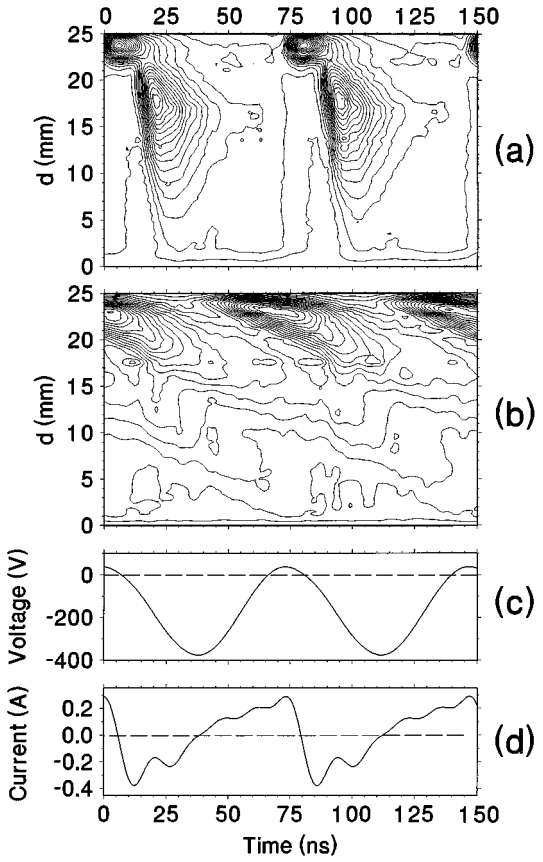

FIG. 3. Contour plots of constant intensity for the data presented in Fig. 2, along with corresponding voltage (c) and current (d) waveforms at the surface of the powered electrode.

$$H + H_2 \rightarrow H(n=3) + H_2, \tag{1}$$

since this process has an excitation threshold of approximately 30 eV,[7] and the density of H_2 exceeds that of any other species in the discharge by many orders of magnitude.

It is possible that some Doppler-broadened emission observed near the powered electrode is due to fast excited H atoms produced in the plasma sheath by gas-phase ion-molecule collisions. However, these fast H($n=3$) atoms move toward the electrode surface, and are localized in the sheath region (approximately $d=18-25$ mm), implying that they cannot be the source of the Doppler-broadened emission observed throughout the bulk of the discharge.

The profile in Fig. 2(b) clearly exhibits a correlation between the time and position that fast H atoms are produced at the surface, and the distance the atoms travel into the discharge before being excited by collisions with H_2. This is evident from the diagonal ''ridge'' in the emission profile that runs from the maximum near the point $t=0$ ns, $d=25$ mm to the point near $t=150$ ns, $d=5$ mm. This is in contrast to the peak shapes in Fig. 2(a) that extend directly into the bulk of the discharge with little corresponding time delay.

The fact that time-varying, Doppler-broadened H_α emission is observed at all locations between the electrodes [see Fig. 2(b)] indicates that a portion of the fast H atoms travel through the discharge without experiencing collisions that significantly effect their initial trajectories parallel to the electrode axis. This results in a velocity distribution of fast H atoms that is not isotropic, i.e., on average $v_\parallel > v_\perp$. If the fast H atoms experience significant scattering, then the velocity distribution would tend to become isotropic, resulting in Doppler-broadened H_α emission throughout the discharge volume with no observable time dependence.

The diagonal ''ridge'' that is apparent in Fig. 2(b) provides a means to estimate the magnitude of $v_\parallel$ for the fast H atoms. By using Fig. 3(b), it can be estimated from the nearly linear correlation between position and time of the fast H($n=3$) emission in the bulk of the discharge, that the H atoms observed here travel a distance parallel to the electrode axis of approximately 20 mm in 150 ns. This implies an average value of $v_\parallel \cong 1.3\times 10^5$ m/s. The combination of the values of $v_\perp$ and $v_\parallel$ derived here implies the presence of fast H atoms throughout the discharge volume with a kinetic energy of 123 eV.

The mean free path of H atoms in hydrogen is calculated to be approximately 8 cm at 33.3 Pa for atoms with kinetic energies comparable to those measured here, assuming the dominate loss mechanism is momentum transfer.[7] This mean free path is comparable to but longer than that implied by the fall-off of the optical signal observed in Fig. 2(b), because of additional inelastic collision processes, such as vibrational and electronic excitation.

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