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Neon excimer emission from pulsed high-pressure microhollow cathode discharge plasmas

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Abstract

Microhollow cathode discharge (MHCD) plasmas in high-pressure Ne (up to and exceeding atmospheric pressure) are known to be efficient sources of Ne_2^* excimer radiation in the vacuum ultraviolet spectral region between 75 and 90 nm. By operating the MHCD plasma in a pulsed direct current (dc) mode, we were able to increase the Ne_2^* excimer emission by up to 1 order of magnitude compared to the emission intensity obtained from the same MHCD plasma excited by a constant dc current. Time-resolved emission spectroscopic studies of the Ne_2^* excimer emission following pulsed dc excitation of an MHCD plasma in high-pressure Ne were carried out to elucidate the microscopic details of the excimer formation and destruction processes. Our studies provide direct evidence that quenching of the $Ne_2^*(^3\Sigma_u)$ excimer molecules and other loss processes of the excimer molecules are important processes in high-pressure MHCD plasmas and represent, in fact, the dominant destruction channel of the $Ne_2^*(^3\Sigma_u)$ excimer molecules in the MHCD plasma under a wide range of operating conditions. (Int J Mass Spectrom 223–224 (2003) 37–43)

Keywords: Hollow cathode discharges; High-pressure plasmas; Excimers

1. Introduction

Excimers are molecules with a weakly bound excited state and a repulsive ground state. Excimer molecules decay radiatively emitting intense ultraviolet (UV) and vacuum ultraviolet (VUV) radiation. High-pressure, self-sustained or externally sustained discharge plasmas in the rare gases He, Ne, Ar, Kr, and Xe are prominent sources of the rare gas excimer emissions. The emission spectra of pure rare gas excimers are dominated by the so-called second excimer continua [1,2] with peak emissions at wavelengths of 170 nm (Xe), 145 nm (Kr), 130 nm (Ar), 84 nm (Ne), and 75 nm (He). Hollow cathode (HC) discharges with hole dimensions in the range of 100–500 μm (so-called microhollow cathode discharges (MHCDs)) have been used extensively for the generation of noncoherent UV and VUV excimer radiations, in particular, in the pure rare gases [3–9]. The MHCD device exploits the inverse scaling of the hole diameter of an HC discharge with the operation pressure [3,4] which means that atmospheric pressure operation in N_2 and the rare gases is possible for hole sizes of around 100 μm.

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HC discharges have been widely used since the early days of discharge physics and gaseous electronics, primarily as low-pressure discharge devices that can achieve a high-electron density which is desirable in a variety of applications [10–12]. An HC discharge device consists of a metallic cathode with a hole in the center and an arbitrarily shaped metallic anode. The two electrodes are separated by an insulator with a hole in it that is similar in size and shape to the hole in the cathode. When a discharge is ignited in such a configuration, the negative glow is spatially confined in the cathode cavity. The electric field in this region creates a trough which is responsible for the strong acceleration of the electrons and may cause an oscillatory motion of the electron in the trough ("pendulum electrons" [11,13,14]). These "pendulum electrons" can undergo many ionizing collisions with the background gas, thus, creating a high-density plasma which emits intense radiation.

We have studied VUV emissions from MHCD plasmas in high-pressure pure Ne and He and in gas mixture containing high-pressure Ne or He admixed with trace amounts (1% or less) of H_2, O_2, and N_2 [7,9]. We observed intense VUV helium and neon excimer emissions from the pure rare gases as well as intense, near-monochromatic atomic line radiation, in particular H Lyman-α at 121.6 nm from Ne and H_2 admixtures, superimposed on the excimer emission from the gas mixtures containing the molecular gases. These atomic line emissions were attributed to near-resonant energy-transfer reactions between the Ne_2^* and He_2^* excimers and the molecular gases. In all our previous studies, the MHCD plasma was excited by a dc voltage. Recently, Schoenbach and coworkers [15] reported a significant increase in the xenon excimer emission intensity following pulsed dc excitation of an MHCD plasma in pure Xe. In this paper, we report the result of time-resolved emission spectroscopic studies of the Ne_2^* excimer emission following pulsed excitation of an MHCD plasma in pure Ne. A detailed analysis of the time-resolved fluorescence spectra allows insight into the microscopic processes that govern the Ne_2^* excimer formation and decay processes.

2. Excimer formation and emission

All rare gas atoms have an $^1S_0$ electronic ground state associated with a completely filled p-shell (except for He, which has a $(1s)^2$ ground state electron configuration). The lowest excited states in Ne, Ar, Kr, and Xe result from the promotion of a (np) valence electron to the $(n+1)$s level ($n = 2$, 3, 4, 5 for Ne, Ar, Kr, Xe) leading to four "P-states". Two of these P-states are metastable, while the other two states decay to the ground state via dipole-allowed transitions [16]. In He, the lowest-lying excited states result from the promotion of one of the two 1s electrons to 2s or 2p level which leads to metastable S-states and radiatively decaying P-states [16]. The most common routes to rare gas excimer formation are either via electron-impact ionization

$$e^- + X \rightarrow X^+ + 2e^- \quad (1a)$$

$$X^+ + 2X \rightarrow {X_2}^+ + X \quad (1b)$$

$${X_2}^+ + e^- \rightarrow X^* + X \quad (1c)$$

$$X^* + 2X \rightarrow {X_2}^* + X \quad (1d)$$

where X = He, Ne, Ar, Kr, or Xe and the asterisk denotes a metastable rare gas atom, or alternatively directly via excitation of metastable rare gas atoms by electrons

$$e^- + X \rightarrow X^* + e^- \quad (2a)$$

$$X^* + 2X \rightarrow {X_2}^* + X \quad (2b)$$

In either case, the excimer molecules are formed in three-body collisions involving a metastable rare gas atom and two ground state atoms. Efficient excimer formation requires (i) a sufficiently large number of electrons with energies above the threshold for the metastable formation (or ionization), and (ii) a pressure that is high enough to have a sufficiently high rate of three-body collisions. In the ionization route, reaction (1c) is usually the rate-limiting process, as this recombination process has a cross-section as a function of electron energy which exhibits a narrow peak at energies close to zero. Minimum electron energies

required for excimer formation range from 11–14 eV in Xe to 20–24 eV in He.

Rare gas excimer emission spectra are dominated by transitions from the lowest-lying bound $^3\Sigma_u$ excimer state to the repulsive ground state (second continuum) [1,2] with peak emissions at 170 nm (Xe), 145 nm (Kr), 130 nm (Ar), 84 nm (Ne), and 75 nm (He). The so-called first excimer continua in the rare gases are observed on the short-wavelength side of the second continua and are attributed to the radiative decay of vibrationally excited levels of the $^1\Sigma_u$ excimer state. Most work to date has been carried out in Xe, Kr, and Ar, where the high-pressure MHCD can be "sealed off" with a window (LiF or MgF_2) for VUV spectroscopic investigations of the excimer emissions in the 130–170 nm region. Spectroscopic investigations of the Ne_2^* and He_2^* excimers, on the other hand, require a specially designed "open" MHCD source [7,9] connected directly to a VUV monochromator, since no material is transparent below 105 nm.

3. Experimental details

In the present studies, we used the same MHCD device that was described in detailed in earlier publications [8,10]. Briefly, the electrodes of our MHCD device are made of 0.1-mm thick molybdenum foils separated by a 0.25-mm spacer of mica with a hole of typically 0.1–0.2-mm diameter in the cathode, the dielectric, and in the anode. We operate the MHCD in a pulsed dc mode with pulses of peak voltages of several hundreds volts and up to 25 mA, pulse-width from 50 ns to 20 μs, and repetition rates in the kilo-Hertz range. The MHCD is mounted directly on to the entrance slit of a Minuteman 302-V 0.2 m VUV monochromator (wavelength range 50–250 nm, reciprocal linear dispersion of 4 nm/mm). Neon excimer radiation from the MHCD enters the VUV monochromator through a 0.2-mm pinhole between the discharge region and the monochromator, which is differentially pumped to provide an operating pressure in the 10^{-5} Torr range in the detector chamber. The VUV photons are detected by a channel electron multiplier connected to a standard pulse counting system. Time-resolved fluorescence spectra of the Ne_2^* excimer emission are recorded with an SR400 gated photon counting system controlled by a PC.

4. Results and discussion

Fig. 1 shows the time-resolved emission of the Ne_2^* excimer from an MHCD plasma in 420 Torr Ne following pulsed dc excitation (dashed line). The diagram also depicts the discharge current pulse (solid line) that ignites the MHCD plasma. The point $t = 0$ in Fig. 1 was chosen arbitrarily in a way that the figure conveniently displays the entire timing sequence of the experiment. As the discharge current rises to its maximum value of about 4 mA on a time scale of 5 μs, the excimer emission slowly increases and reaches a steady-state intensity after about 8 μs indicating that the excimer formation increases with increasing discharge current as one would expect. After both the discharge current and the excimer emission intensity reach their steady-state values, the current pulse is turned off. Almost immediately, the excimer emission intensity begins to rise sharply and reaches a peak value that is about a factor of 2.5 higher than the steady-state value during the time the current pulse was applied. We attribute this increase to a rapid cooling of the plasma electrons as the input power to the MHCD plasma is terminated. As the plasma electrons approach zero energy, the recombination step (1c), which is usually the "bottleneck" in the ionization route becomes temporarily a very efficient channel for excimer formation. Thus, the increase in the excimer formation when the exciting current is terminated, can be attributed to a temporary enhancement in the ionization route to excimer formation. Eventually, all excimer formation processes cease and the excimer emission decays exponentially as one would expect (see the following discussion). This behavior indicates that excimer light sources based on MHCD plasmas are much more efficiently excited by pulsed dc power sources.

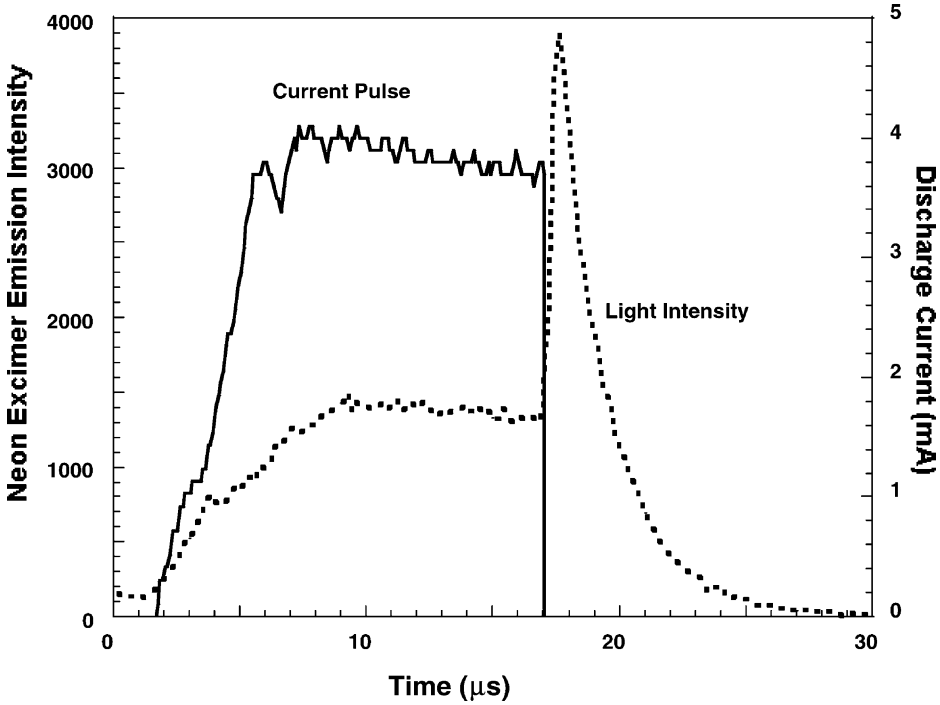

Fig. 1. Time dependence of the current pulse (solid line) and Ne_2^* excimer emission (dashed line) following pulsed dc excitation of an MHCD plasma in Ne at 420 Torr.

Fig. 2 shows the Ne_2^* excimer emission and the exciting discharge current pulse for the case of a much shorter, but more intense current pulse (pulse-width of less than 0.5 μs, peak current close to 20 mA) and a slightly higher Ne pressure of about 500 Torr. As before, the excimer emission intensity begins to rise slowly after the current pulse is applied. However, in this case the current pulse is turned off before the excimer emission intensity can reach a steady-state value. Nonetheless, the excimer emission intensity continues to rise dramatically for almost 2 μs after the end of the current pulse before decaying exponentially. In fact, the increase in peak excimer emission by a factor of 8 over the intensity at the time the current pulse is turned off, is even more dramatic than before. This indicates that the most efficient way to excite MHCD excimer light sources for maximum light output is by short (less than 1 μs) dc pulses.

In Figs. 3 and 4, we show a more detailed analysis of the time-resolved excimer emission spectra in the two previous cases after the exciting current pulse is turned off. In both figures, the time $t = 0$ was chosen to coincide with the falling edge of the exciting dc current pulse. The rate equation describing the destruction of $Ne_2^*(^3\Sigma_u)$ excimers which give rise to the emission of the second continuum following pulsed excitation has the form

$$\frac{d[Ne_2^*]}{dt} = -[Ne_2^*](A_{ik} + k_q[Q]) \quad (3)$$

where $[Ne_2^*]$ is the density of the Ne_2^* excimers, A_{ik} the inverse spontaneous emission life time of the $Ne_2^*(^3\Sigma_u)$ excimer molecules (which has a value of $1/8.9\,\mu s^{-1}$ [17][3]), $k_q[Q]$ is the sum of all quenching rates (collisional quenching by impurities, other losses due to, e.g., wall processes, etc.) that contribute

[3] As discussed in this article, the radiative lifetime of the $Ne_2^*(^3\Sigma_u)$ excimer state has been measured by several authors who report values ranging from 5.1 to 12 μs with an average value of 8.9 μs which has an estimated uncertainty of no less than about 30%.

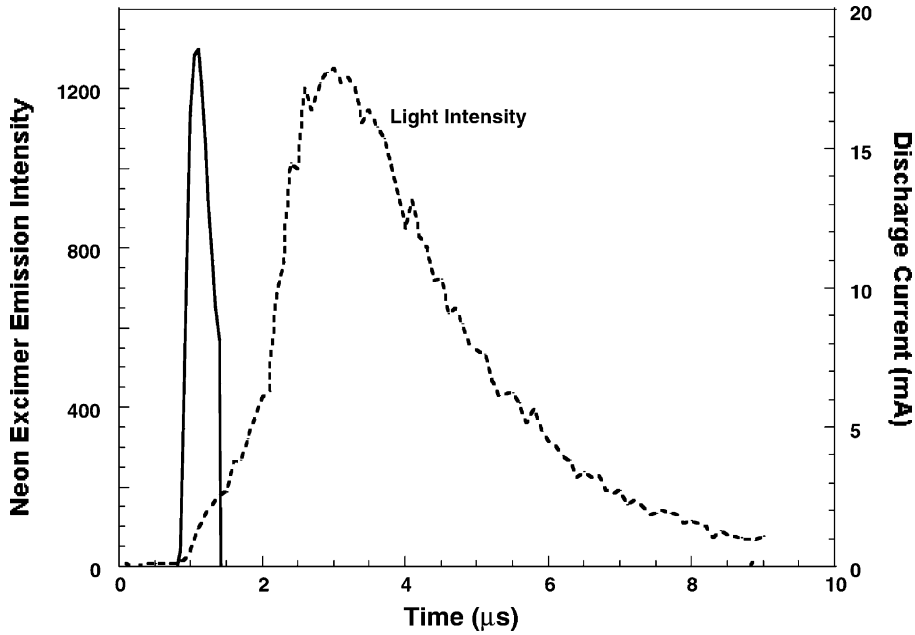

Fig. 2. Time dependence of the current pulse (solid line) and Ne_2^* excimer emission (dashed line) following pulsed dc excitation of an MHCD plasma in Ne at 500 Torr.

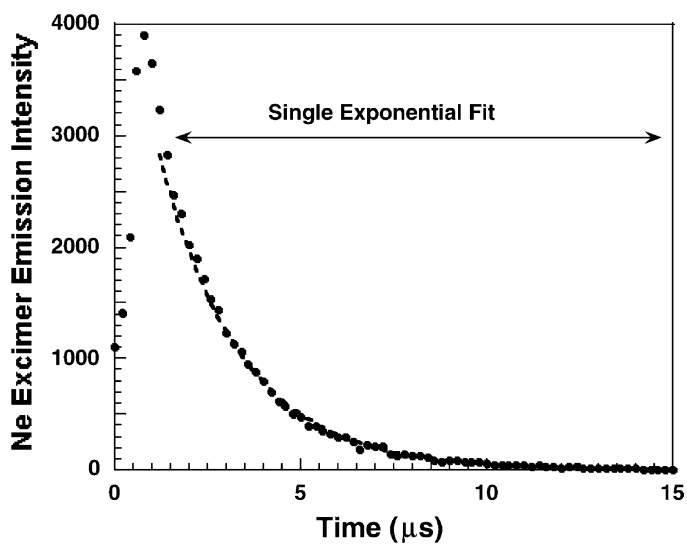

Fig. 3. Time dependence Ne_2^* excimer emission following pulsed dc excitation of an MHCD plasma in Ne at 420 Torr. The time $t = 0$ corresponds to the end of the exciting dc current pulse. The dashed line represents a single-exponential fit to the decaying part of the recorded time-resolved emission spectrum.

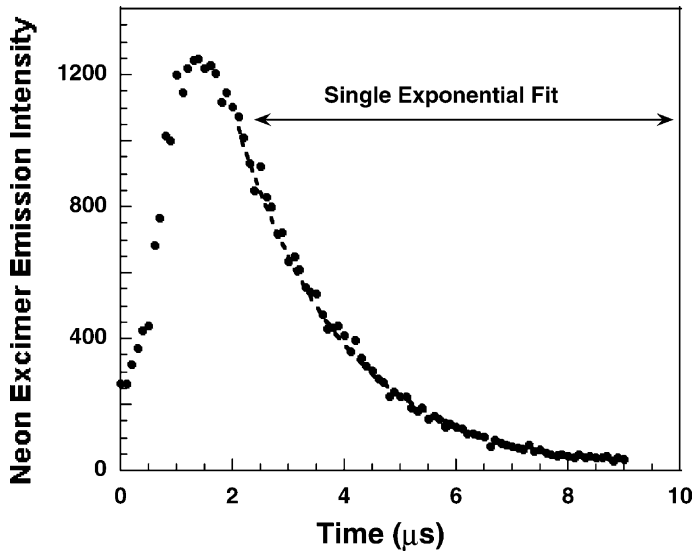

Fig. 4. Time dependence Ne_2^* excimer emission following pulsed dc excitation of an MHCD plasma in Ne at 500 Torr. The time $t = 0$ corresponds to the end of the exciting dc current pulse. The dashed line represents a single-exponential fit to the decaying part of the recorded time-resolved emission spectrum.

to the nonradiative decay of the $Ne_2^*(^3\Sigma_u)$ excimer molecules. Eq. (3) results in a simple exponential decay of the Ne_2^* emission intensity with a decay constant $1/\tau$ given by

$$\frac{1}{\tau} = A_{ik} + \frac{1}{k_q[Q]} \tag{4}$$

Fig. 3 shows the decay of the Ne_2^* excimer emission from an MHCD in 420 Torr Ne following long-pulse dc excitation (see Fig. 1). The rapid rise of the recorded emission intensity is followed by a decay that is well represented by a single-exponential fit. We obtain a decay constant of the Ne_2^* excimer emission which corresponds to an apparent lifetime of about 2.2 μs, which is shorter than the natural lifetime of the $Ne_2^*(^3\Sigma_u)$ excimer state by more than a factor 3. According to Eq. (4), this indicates that quenching processes expressed by the second term in Eq. (4) are very important in MHCD plasma under these operating conditions and, in fact, represent the dominant channel of Ne_2^* excimer destruction. This notion is reinforced by the results depicted in Fig. 4 which shows a similar time-resolved emission spectrum following short-pulse excitation (see Fig. 2) of the same MHCD in 500 Torr Ne. The decay time of the excimer emission shown in Fig. 4 yields an apparent lifetime of the Ne_2^* excimer molecules of 2.0 μs under these conditions. This is even shorter than the 2.2 μs determined before for the MHCD plasma at 420 Torr. In fact, we found a systematic decrease in the apparent lifetime of the Ne_2^* excimer molecules in MHCD from about 2.4 to 1.9 μs as the pressure is increased from 250 to 700 Torr. This indicates that (i) quenching rather than the radiative decay is the dominant destruction channel for the Ne_2^* excimer molecules in an MHCD plasma and that (ii) quenching and other nonradiative loss processes become more important as the pressure in the MHCD plasma increases. This makes it imperative to ensure a very high gas purity in VUV light sources that are based on MHCD plasmas in Ne (and other rare gases) and to select materials with low sputtering yields to minimize contamination of the operating gas.

The rise time of the excimer emission shown in Fig. 4 to its peak value after the exciting current pulse has been turned off is similar to the rise time of the

spectrum shown in Fig. 3 (and similar to rise times observed in spectra obtained at gas pressures from 250 to 700 Torr). This indicates that the time scale of the excimer formation processes is essentially independent of the gas pressure in the MHCD plasma in that pressure range.

5. Conclusions

We carried out time-resolved emission spectroscopic studies of Ne_2^* excimer radiation from MHCD plasmas in high-pressure Ne following pulsed dc excitation. It was found that pulsed excitation results in drastically enhanced excimer emission after the termination of the exciting pulse (by almost 1 order of magnitude) and that the highest efficiency in terms of emitted light intensity per unit input power is obtained for dc pulses that are shorter than about 1 μs. The analysis of the decaying part of the time-resolved Ne_2^* excimer emission reveals that the destruction of the $Ne_2^*(^3\Sigma_u)$ excimer that give rise to the second excimer continuum emission in high-pressure MHCD plasmas in Ne is dominated by quenching processes and other nonradiative losses which are about three times as efficient in destroying the Ne_2^* excimers compared to the radiative decay and which need to be minimized in order to increase the overall efficiency of an Ne MHCD plasma-based VUV light source.

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