Basic Principles and Applications of Atmospheric-Pressure Discharge Plasmas

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ABSTRACT

This presentation summarizes the principles that govern the generation and maintenance of atmospheric-pressure discharge plasmas. The properties and operating parameters of various high-pressure discharge plasmas such as dielectric barrier discharge plasmas, corona discharge plasmas, microhollow cathode discharge plasmas, and dielectric capillary electrode discharge plasmas are introduced. Several applications where atmospheric-pressure plasmas have gained prominence recently such as UV and VUV light sources, remediation of pollutants and waste streams, and surface cleaning will be discussed.

1. Introduction

Discharge plasmas at high pressures (up to and exceeding atmospheric pressure), where single collision conditions do no longer prevail, provide a fertile environment for the experimental study of collisions and radiative processes dominated by (i) step-wise processes, i.e. the excitation of an already excited atomic/molecular state and by (ii) three-body collisions leading e.g., to the formation of excimers. The dominance of collisional and radiative processes beyond binary collisions involving ground-state atoms and molecules in such environments allows for many interesting applications of high-pressure plasmas such as high power lasers, opening switches, novel plasma processing applications and sputtering, EM absorbers and reflectors, remediation of gaseous pollutants, and excimer lamps and other non-coherent vacuum-ultraviolet (VUV) light sources. A recent summary of various types of atmospheric-pressure discharge plasmas and their applications was given by Kunhardt [1].

2. Basic Principles of High-Pressure Discharges

Dielectric barrier discharges (DBDs), corona discharges (CDs), dielectric capillary electrode discharges (CDEDs), and microhollow cathode discharges (MHCDs) are all self-sustained, non-equilibrium gas discharges that can be operated at atmospheric pressure. CDs and DBDs represent very similar types of discharges. While DBDs are characterized by insulating layers on one or both electrodes, CDs depend on inhomogeneous electric fields at least in some parts of the electrode configuration to restrict the primary ionization processes to a small fraction of the inter-electrode region. At atmospheric pressure, the physical processes in both types of discharges are similar and resemble those in transient high-pressure glow discharges. In addition to pure CDs and DBDs, there are certain hybrid discharges, which are a mixture between a DBD and CD.

Usually, DBDs at atmospheric pressure consist of many tiny current filaments which are referred to as microdischarges. Homogeneous (i.e. diffuse, non-filamentary) discharges can be obtained under very special circumstances with plasma parameters that are quite different from filamentary DBDs. At atmospheric pressure, the discharge in a conventional DBD device starts with local gas breakdown at many points in the discharge volume. The gas breakdown in a DBD and the formation of microdischarges has been thoroughly studied and is fairly well-understood [2]. The discharge sequence encompasses four phases. The initial

gas breakdown at sufficiently high electric fields is called the Townsend phase. Subsequently, the streamer or ionization phase leads to the formation of a highly conducting channel, a so-called filament with a diameter of about 0.1 mm and a current density of up to 100 A/cm^2. Charges are transferred through this channel and accumulate on the dielectric surface (phase 3) until the voltage across the filament is compensated and the discharge dies out (phase 4). The time scale for the completion of a full 4-cycle discharge development is of the order of 10^{-8} s. Typical conditions in a filament are as follows: electron densities up to 10^{14} cm^{-3}; average electron energies of up 20 eV, particularly in the narrow streamer head; gas temperatures only slightly above room temperature, 300 – 400 K. However, these conditions exist only in a filament, i.e. on the ns time scale and in very small spatial volumes.

Common CDs geometries have at least one electrode which favors the generation of highly non-uniform, locally high electric fields, e.g. point-to-plate, wire in a cylinder, knife-edge shapes electrodes, etc.). When the voltage is raised, current starts to flow at the corona onset and increases until the potential for spark breakdown is reached. This range of corona activity is called partial breakdown. The corona discharge is characterized by a faint glow in the region of high electric field accompanied by streamers propagating towards the other electrode. Even with dc pulses the appearance is that of a burst corona with regular current pulses. The physical mechanism of these current pulses is a regular build-up and removal of space charge that modulates the ionization in the high-field region. High concentration of radicals can be generated by using fast-rising high-voltage pulses which lead to the formation of streamers to bridge the gap between the electrodes. The properties of these streamers are similar to the streamers in DBDs (diameter of 0.1 – 0.2 mm, duration of a few nanoseconds, peak average electron energy of up to 20 eV at gas temperature near room temperature near the streamer head. Highest efficiency is achieved when the length of the exciting HV pulse equals the streamer transit time. Thus, the properties of a corona discharge are similar to those of a DBD in the filamentary mode.

The basis for the atmospheric-pressure operation of the CDED is a novel electrode design which uses dielectric capillaries that cover one or both electrodes. The capillaries, with diameters in the range from 0.01 to 1 mm and length-to-diameter ratios of the order of 10:1, serve as plasma sources which produce jets of high-intensity plasma at atmospheric pressure under the right operating conditions. The plasma jets emerge from the end of the capillary and form a "plasma electrode" for the main discharge plasma. The field inside the capillary does not collapse after the formation of the streamer discharge due to the fact that the high electron-ion recombination at the wall of the capillary requires a large ion production rate along the axis of the capillary in order to sustain the current. Under the right combination of capillary geometry, dielectric material, and exciting electric field, a steady state can be achieved. Run-away into the arc is prevented by the fact that the current through the capillaries is self-limiting, i.e. the gas density inside the capillary decreases with time due to gas heating which puts an upper limit to the conductivity as a result of gas starvation. Compared to other atmospheric-pressure discharge plasmas, the CDED plasma requires a lower sustaining voltage, lower energy input per cm^3 of plasma generated. CDEDs achieve plasma parameters (electron densities and average electron energies) in the bulk plasma that are much higher than the corresponding parameters in DBDs and CDs. In fact., the bulk plasma parameters in a CDED plasma are closer to the plasma parameters that are realized in the filaments of DBDs and CDs, average energy of the plasma electrons of up to 6 eV at gas temperature in the 350 - 400 K range and electron densities of up to 10^{14} cm^{-3}.

Another approach towards the generation and maintenance of a high-pressure discharge plasma is based on the hollow cathode (HC) discharge concept and exploits the inverse scaling of the hole diameter with the operating pressure which makes atmospheric-pressure operation possible, if the hole diameter is of the order of about 0.1 – 0.5 mm (microhollow cathode discharge, MHCD). HC discharges have been widely used since the early days of

discharge physics and gaseous electronics as high-density, low-pressure discharge devices for a variety of applications [3-5]. A HC discharge device consists of a metallic cathode with a hole in the center and an arbitrarily shaped metallic anode. A HC discharge is created by confining the negative glow of the discharge to the cathode cavity. This is accomplished by an externally applied dc or a time-varying voltage applied to the electrodes which a potential trough in the cathode cavity that results in a strong acceleration of the electrons and a possible oscillatory motion (pendulum electrons). The trapped "pendulum electrons" [4,6,7], can undergo many ionizing collisions with the background gas thus creating a high-density plasma which emits intense radiation and is characterized by a very high current density (hollow cathode effect).

3. Selected Applications of High-Pressure Discharge Plasmas

Among the various applications of high-pressure discharge plasmas, novel light sources in the ultraviolet (UV) and vacuum ultraviolet (VUV) spectral region have gained prominence recently. MHCD plasmas have been used extensively for the generation of non-coherent UV and VUV excimer radiation using either pure rare gases, rare gas - halide mixtures, or gas mixtures of rare gases and molecular gases such as H_2, O_2, and N_2. Schoenbach and co-workers were the first to report excimer emissions from MHCD plasmas in Xe and Ar [8-13]. Subsequently, excimer emissions were also reported from MHCD plasmas in Ne and He [14,15]. Rare gas atoms have a $^1S_0$ electronic ground state. The lowest excited-states result from the promotion of a (np) valance electron to the (n+1)s-level (n=2,3,4,5 for Ne, Ar, Kr, Xe) leading to four "P-states", two of which are metastable, while the other two states decay to the ground state via dipole-allowed transitions . The most common routes to rare gas excimer formation are either via electron-impact ionization

(1a) $e^- + X \rightarrow X^+ + 2\,e^-$
(1b) $X^+ + 2\,X \rightarrow X_2^+ + X$
(1c) $X_2^+ + e^- \rightarrow X^* + X$
(1d) $X^* + 2\,X \rightarrow X_2^* + X$

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

(2a) $e^- + X \rightarrow X^* + e^-$
(2b) $X^* + 2\,X \rightarrow X_2^* + X$

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. 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 $^1\Sigma_u$ excimer state to the repulsive ground state (second continuum) [16,17] 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 spectroscopic

investigations of the excimer emissions in the 130 - 170 nm region. Studies of the Ne_2^* and He_2^* excimers, on the other hand, require an "open" MHCD source [14,15] connected directly to a VUV monochromator, since no material is transparent below 105 nm.

Kurunczi et al. [14] reported the emission of intense H Lyman-α emissions from MHCD plasmas in gas mixtures of high-pressure Ne with trace amounts of H_2. Kurunczi et al. [14] *monitored simultaneously the* Ne_2^* *excimer emission and the Lyman-α emission and* observed a dramatic decline in the Ne_2^* excimer emission when H_2 was added to the gas mixture. This provided direct experimental evidence that the near-resonant energy transfer reaction involving Ne_2^* excimers and H_2 molecules is the source of this intense atomic H emission. Ne_2^* excimers in the bound $^3\Sigma_u$ state have enough energy to dissociate H_2 and excite one of the H atoms to the n = 2 state. The subsequent decay of the excited H atom results in the emission of the 121.6 nm H Lyman-α line. Earlier, Wieser et al. [18] had observed a similar emission of intense, monochromatic H Lyman-α radiation from high-pressure gas mixtures of Ne with trace amounts of H_2 bombarded by high energy electrons and ions and first suggested the above near-resonant energy transfer process as the most likely mechanism leading to the emission of the H Lyman-α line [18] solely on the basis of spectroscopic studies of the Lyman-α emission. Further details of excimer light sources based on high-pressure discharge plasmas are given in the oral presentation.

Other applications of high-pressure plasmas that will be addressed in the conference talk include the remediation of gaseous pollutants from effluent gases and waste streams, the cleaning of conducting and non-conducting surfaces, and the decontamination of chemical and biological agents.

Acknowledgments

This work was supported by the NSF, DOE, and by DARPA/ARO. I gratefully acknowledge the contributions of Peter Kurunczi and Karl Schoenbach to the material presented in this article.

References

[1] E.E. Kunhardt, *IEEE Trans. Plasma Sci* **28**, 189 (2000)
[2] U.Kogelschatz, B. Eliasson, and W. Egli, *J. Phys. IV (France)* **7**, C4-47 (1997)
[3] F. Paschen, *Ann. Phys.* **50**, 901 (1916)
[4] A. Güntherschulze, *Z. Tech. Phys.* **19**, 49 (1923)
[5] A. Walsh, *Spectrochim. Acta* **7**, 108 (1956)
[6] H. Helm, *Z. Naturforg.* **27a**, 1712 (1972)
[7] G. Stockhausen and M. Kock, *J. Phys. D* **34**, 1683 (2001)
[8] A. El Habachi and K.H. Schoenbach, *Appl. Phys. Lett.* **72**, 22 (1998)
[9] K.H. Schoenbach, A. El-Habachi, W. Shi, M. and Ciocca M, *Plasma Sources Sci. Technol.* **6**, 468 (1997)
[10] K. H. Schoenbach, A. El-Habachi, M. M. Moselhy, W. Shi, and R. H. Stark, *Physics of Plasmas* **7**, 2186 (2000)
[11] M. Moselhy, W. Shi, R.H. Stark, and K.H. Schoenbach, *IEEE Trans. Plasma Science* (2001), submitted.
[12] A. El-Habachi and K.H. Schoenbach, *Appl. Phys. Lett.* **72**, 22 (1998)
[13] M. Moselhy, A. El-Habachi, K.H. Schoenbach, and U. Kogelschatz, *Appl. Phys. Lett.* **78**, 880 (2001)
[14] P. Kurunczi, H. Shah, and K. Becker, *J. Phys. B* **32**, L651 (1999)
[15] P. Kurunczi, J. Lopez, H. Shah, and K. Becker, *Int. J. Mass Spectrom.* 205, 277 (2001)
[16] W. Waller, U. Schaller, and H. Langhoff, *J. Chem. Phys.* **83**, 1667 (1985)
[17] D.C. Lorents, *Physics C* **82**, 19 (1976)
[18] J. Wieser, M. Salvermoser, L.H. Shah, A. Ulrich, D.E. Murnick, and H. Dahl, *J. Phys. B* **31**, 4589 (1998)