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Fused hollow cathode cold atmospheric plasma source for gas treatment

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Abstract

A new type of the cold atmospheric plasma source for catalytic plasma treatment of gas is presented. The fused hollow cathode (FHC) source is based on simultaneous radio frequency (rf) generation of hollow cathode discharges in an integrated, open structure, with flowing gas. The resulting FHC discharge is very stable, homogeneous, luminous, volume filling, without streamers. The power consumption is very low, of the order of tenths of Watt per cm^2 of the electrode structure area. Experiments for the hollow electrode integrated open structure up to $20\,cm^2$ were performed. The concept of the source is extremely suitable for scaling up for different gas throughputs. The FHC source represents a new non-equilibrium atmospheric plasma source suitable for transformation of gas. Moreover, its design offers both catalytic reactions in the bulk of plasma and at solid surfaces composing the open structure.

Keywords: Cold atmospheric plasma; Fused hollow cathode; Radio frequency

1. Introduction

In a non-equilibrium plasma individual temperatures characterizing gas, inner states of molecules (rotational, vibrational and electronic temperatures) and electrons are not equal. It is possible especially for electrons to attain high energy, while the gas temperature remains relatively low. This occurs typically at low collision frequency, corresponding to pressures below 100 Torr. Atmospheric plasma, however, is typically in equilibrium. To ensure the features of non-equilibrium at atmospheric pressure, it is necessary to pump the energy mainly into electrons. Pulsed corona discharge, dielectric barrier discharge, microwave discharge and radio frequency (rf) plasma jet are examples of such plasma sources.

The hollow cathode is a non-equilibrium source from its principle. So called "electron exchange", pendulum motion of fast electrons between opposite space charge sheaths or cathode falls at the cathode walls not only enhances excitation and ionization, but it is also responsible for forming the high energy population of electrons.

There were already reported dc hollow cathode microdischarge devices operating at high, even at atmospheric pressure [1–3]. Those microdischarges were mostly performed in a static gas environment, with microcavities evacuated and backfilled with gas. The arrangement with an additional electrode [3] enabled extending microdischarge in the longitudinal direction to 2 mm, but the plasma volume was only several cubic milimeters. However, a limiting factor of power density did not enable generation of plasma over larger area through parallel operation of the microhollow discharges.

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In this paper, we present two novel plasma sources based on rf hollow cathodes, operating at atmospheric pressure. Both sources operate with flowing gas, in open chamber, and over the areas of 7 and 20 cm^2, respectively.

2. Single hollow cathodes at reduced and atmospheric pressures

Fig. 1 shows a schematic diagram of the cylindrical rf hollow cathode, the concept of which was patented already in 1985 [4]. The cylindrical nozzle is connected to the rf generator (13.56 MHz) through an impedance matching unit.

The "electron exchange" occurs only at certain combinations of dimensions of the hollow cathode and pressures. The higher the pressure, the thinner the space charge sheath at the cathode wall which means that the dimension of the inner diameter must be correspondingly reduced. The single rf hollow cathode (inner diameter of 400 μm) generation and operation were successfully tested at atmospheric pressure, with gas flowing through the device [5], see the configuration in Fig. 1.

We found out that the *V–I* characteristics of the atmospheric pressure rf hollow cathode indicates a similar sequence of regimes as those for the reduced pressure operating rf generated hollow cathode [6]. At low levels of delivered rf power there exists only an rf discharge acting as a predischarge. Increasing the power, a breakdown of the sheath–plasma boundary occurs, accompanied by a drop of the self-bias voltage across the space charge sheath and a hollow cathode discharge is developed. When the power is increased further and the temperature at the cathode surface is high enough to supply high currents by thermionic emission, the hollow cathode discharge is transferred into the hollow cathode arc. At this point, a decrease of the self-bias voltage takes place again. Both transitions depend on the discharge parameters. At a definite geometry of the hollow cathode and at a definite (reduced) pressure the major parameters influencing the generation and performance of the hollow cathode are the type of the gas and the cathode material [6].

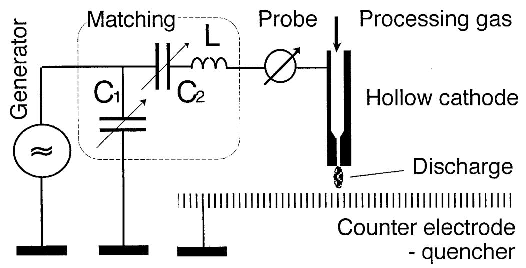

Fig. 1. Schematic diagram of the cylindrical rf hollow cathode.

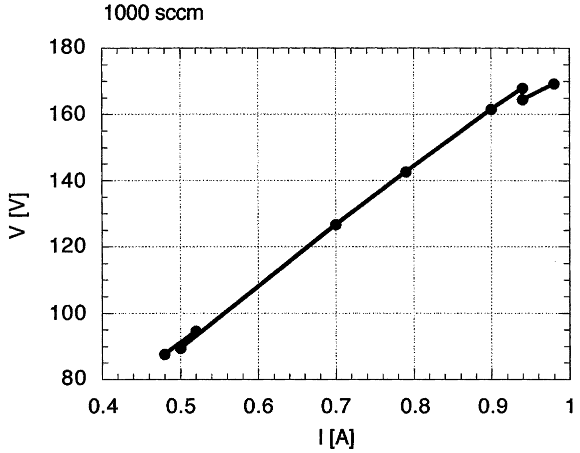

Fig. 2. *V–I* characteristics of the single atmospheric pressure rf hollow cathode, 400 μm in diameter. The chamber is open to air. Neon flow of 1000 sccm.

The *V–I* characteristics of the rf powered single hollow cathode is shown in Fig. 2. At atmospheric pressure, two marked discontinuities at the *V–I* characteristics indicate again the transition from predischarge into the hollow cathode discharge and from the hollow cathode discharge into the regime resembling the hollow cathode arc column. The latter transition is accompanied by an abrupt increase of the $N_2(C^3\Pi_u)$ vibrational temperature, by 500 K.

3. Fused hollow cathodes with integrated open structure

For large area application, two new systems that integrate atmospheric rf hollow cathodes, were developed [7]. Fig. 3 shows the schematic diagram of the system with hollow electrode with integrated open structure (HEIOS), the structure being placed

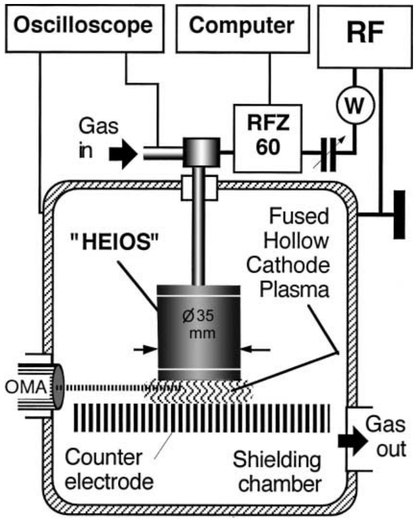

Fig. 3. The schematic sketch of the FHC cold atmospheric plasma system with the cylindrical electrode cartridge.

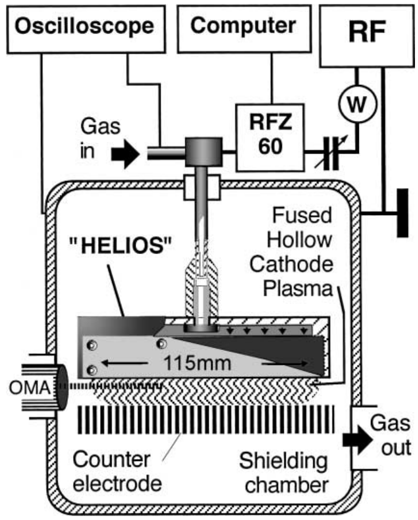

Fig. 4. The schematic sketch of the FHC cold atmospheric plasma system with the rectangular electrode cartridge.

into the cylindrical cartridge with the diameter of 35 mm. The electrode comprises an integrated open structure which generates about 900 hollow cathode discharges simultaneously and unifies them into one fused hollow cathode (FHC) discharge over an area of 30 mm in diameter. Inner diameters of individual hollow cathodes are in the range between 200 and 400 μm. The electrode is connected through an impedance matching unit to the 13.56 MHz power supply. The delivered power, discharge voltage *V*, current *I* and impedance data were acquired by the AE RFZ 60 rf impedance probe. The average dc voltage and peak-to-peak voltage were measured using a 100 MHz digitizing oscilloscope. The optical emission was analyzed by an EG&G Princeton Applied Research OMA 333 1460 multichannel analyzer.

The system with rectangular electrode cartridge, hollow electrode with linear integrated open structure (HELIOS) is shown in Fig. 4. A uniform FHC discharge is excited over the area of 20 cm^2.

The carrier gas, neon, argon or nitrogen, flows through the electrode. The operational stability of both HEIOS and HELIOS sources is very good, substantially better than for the single rf hollow cathode. The shielding chamber can be open to air or closed. However, all experiments referred to were performed with chamber completely open, with side ports removed. Thus, optical emission spectra can be measured directly from the discharge and special windows or feed throughs are not needed. The discharge is homogeneous, does not exhibit filamentary structure or streamers and fills the volume between the FHC electrode and the counter electrode. As the system is open to air, the optical emission spectra

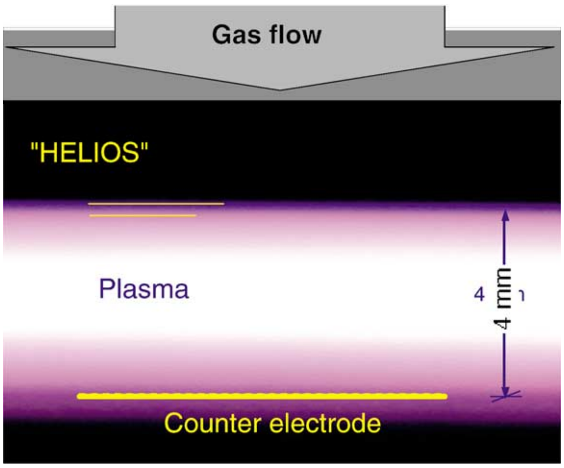

Fig. 5. Photograph from the FHC cold atmospheric plasma discharge. System with the rectangular electrode cartridge (HELIOS). Forward rf power of 40 W, Ne flow of 1000 sccm. The chamber is open to air.

exhibit a strong emission from nitrogen in the ultraviolet and visible ranges of the spectra. The second positive system $C^3{}_u - B^3{}_g$ is favored by the presence of oxygen [8]. The Ne and Ar lines of carrier gases are usually weak in the presence of the air. The forward rf power to sustain the discharge can be as low as 2 and 4 W for circular and rectangular arrangements, respectively.

A typical character of the atmospheric pressure discharge in the FHC is shown in Fig. 5, for the system with the rectangular electrode cartridge HELIOS facing the counter electrode at a distance of 4 mm. The forward rf power was 40 W and the carrier gas (Ne) flow rate was 1000 sccm. The chamber was open to air. The $N_2(C^3{}_u)$ vibrational temperature corresponding to these parameters is 4706 K.

4. Gas transformation applications

The FHC is a non-equilibrium plasma source operating at atmospheric pressure, providing a high activation degree of species. Tests on surface activation of plastics and on cleaning of metal surfaces confirm very high efficiency of the source [9]. Treatment of polyethylene in the FHC Ne + air atmospheric plasma at forward rf power 10–30 W increases the surface tension from the value of 34 to 56 mN/m after the exposition time as low as 1 s. The FTIR spectra from the polyethylene surface layer reveal formation of alkene groups and formation of C=C bonds.

Treatment of the In–Sn–O (ITO) surface by the FHC discharge affects the content of oxygen in the ITO film. The change in the film stoichiometry was reflected by the change of film resistivity. The ITO films spin-coated from nanoparticle dispersion exhibited 1 order increase in the sheet resistance after 10 min treatment, at the rf power of 30 W. A similar effect was observed after annealing of dc sputtered ITO in air at elevated temperature of 450 °C [10]. The oxygen diffusion into oxides during FHC treatment could be possibly applied for recovery of oxygen deficient targets in rf sputtering of transparent conductive oxides.

The geometry of the source, the gas volume being surrounded by the cathode walls is extremely beneficial for conversion of gases. The concept of the integrated open structure enables to employ the catalytic process together with plasma chemistry processes. Instead or besides the separate plasma–catalyst configuration it is possible to utilize the "inner catalysis" in the FHC discharge. Both the electrode inner structure surfaces and quencher surfaces can be coated by suitable catalyst. The catalytic reaction can then take place both in the glow and afterglow parts of the plasma. The intense ultraviolet radiation, typical for hollow cathodes can contribute also to photocatalytical processes. Provided that the source is operated at elevated powers and a release of the material from the cathode occurs, the catalyst particles can be dispersed into the plasma, thereby extending the catalytic reaction into the volume.

5. Conclusions

The FHC cold atmospheric plasma source based on the rf hollow cathode discharges generated simultaneously in the integrated open structure represents an efficient and very promising source for gas transformation. Two configurations, HEIOS and HELIOS, both working with flowing gas in the open screening chamber are presented. The FHC discharge is very stable and uniform over the whole active area of the source.

The source power consumption is very low, the minimum power density at the electrode active area is 0.2 W/cm^2, and the operational power density is below 1 W/cm^2. The power consumption is about 1–3 orders lower than for other non-equilibrium atmospheric plasma sources, e.g. corona, dielectric barrier discharge, microwave discharge or rf atmospheric plasma jet. It is also substantially lower (5 orders) than for atmospheric hollow cathode microdischarges.

The FHC integrated open structure makes the source extremely suitable for scale-up and flexible for different applications. The option of "inner catalysis" given by the concept of the FHC cold atmospheric plasma source extends its utilization offering combination of plasma technology and catalysis.

Acknowledgements

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