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Characterization of atmospheric pressure discharges

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Abstract

The interest towards atmospheric pressure discharges for plasma processing of materials is continuosly growing because of their technological advanteges respect to low pressure discharges. The development of new plasma source design and their application to processes of surface modification and functionalization of materials is actively pursued also in the plasma physics community. On the contrary, research aimed to the development of suitable diagnostics and process control tools is not so advanced and investigated. Indeed diagnostics of atmospheric pressure plasmas are very demanding because of the short temporal and the small spatial scales involved in the plasma state and in the different discharge regimes. Indeed such plasmas are often made up of intermittent and higly localized structures like stremers or microdischarges. We will presents results concerning the diagnostics of dielectric barrier discharges (DBD) operated in a streamer regime in a controlled high pressure gas mixture. We presents experimental results concerning the characteristics of the stremer regime, the influence of the discharge operating parameters and some interesting features observed in the statistical properties by such intermittent discharges.

1. Introduction

Atmospheric pressure discharges can be operated to obtain a cold plasma state, aimed to avoid a strong thermal transfer to the substrates which are exposed to the plasma [1]. This prompted the opening of new and wide sectors for the technological application of atmospheric pressure plasmas including lighting, plasma display panels and material functionalization [2]. Applied research readily entered the new field, attracted by the capability of avoiding costly vacuum technology, which is implied by the use of plasmas from low pressure discharges.

However the mechanisms involved in gaseous discharges at atmospheric pressure make most of the diagnostics developed for the characterization of low pressure, steady state plasmas unfit. Indeed suitable diagnostics for atmospheric pressure discharges is a great challenge for plasma experimental researchers. Applications of electrical and optical tecniques to such low temperature, spatially small and fast varying and intermittent in time environment poses serious problems that deserve attention and dedicated effort. However the benefits of the capability in the characterization of the plasma state are considerable. Discharge parameters directly affects the nature of the prevailing plasma surface interactions and so the results of plasma processing. On the other hand discharge control is mandatory whether the process has to be engineered in a technological application.

Here we present results obtained in a dedicated plasma source developed to study atmospheric pressure plasmas, which are produced in a dielectric barrier discharge (DBD). The device was equipped with the implementation of suitable diagnostics tools. Interesting features have been obtained in the characterization of the plasma state and of the discharge regimes. Results can be linked to the applicative findings in plasma processing of materials, in order to unveil the mechanism involved in the plasma-surface interaction.

2. Experimental setup

DBDs are one of the typical plasma discharges operating at high pressure [3]. The main feature of a DBD device consist in the insertion of a dielectric layer within the discharge gap insulating at least one of the electrodes. Steady operation is normally sustained by applying an oscillating voltage to one of the electrodes at kHz frequencies. At high pressure, in small gap, the discharge operates in the so called streamer regime characterized by narrow discharge filaments [3,4]. In particular plane electrode DBDs in streamer regime at atmospheric pressure show current filaments with high electron density (10^{12}-10^{17} cm^{-3}) and very short lifetimes (few tens of ns) [5]. Filaments appears through the gap at seemingly random locations and not exactly at the same time during each voltage cycle. When the voltage is reversed a new streamer directed in the opposite direction could develop at the same location on the surface [3].

In our experimental set-up the electrodes for DBD have been inserted into a vacuum chamber in order to perform experiments under controlled atmosphere and gas flow. A layout of the set-up is sketched in fig.1. We used a cubic vacuum chamber (Copra Cube by CCR Technologies Gmbh), 40 cm in size, which could be evacuated up to a residual pressure of 30 Pa by a double-stage rotary pump (SD-301 by Varian). Then the desired gas mixture at a fixed pressure is injected through a micrometer valve. Pressure is monitored by a piezoelectric gauge (PiezoVac by Leybold). When stationary flow operating conditions are needed, for instance during plasma polymerization processes, the flowrates of the component of the gas mixture are controlled by an automated system of flowmeters (EL-Flow E06 by Bronkhorst) and the flow is driven by a 60 l/min dry pump (ZA60 by Rial). Vapours can be introduced in the vacuum chamber too, through a mass flowmeter (μ-Flow by Bronkhorst) coupled to an evaporator mixer using a nitrogen flow as carrier. The electrical system is componed by two rod electrodes (220 mm long, 8 mm diamter) coated with pure (>99.7%) Al2O3 synterized ceramic dielectric (thickness 2 mm). The two electrodes are displaced by 20 mm and between them it was inserted a rectangular shower in polycarbonate where the incoming gas mixture is injected in the discharge region. The two rod are connected through an HV cable to the secondary coil of a transformer, whose primary circuit is connected to a tunable power generator, providing the driving high voltage for the discharge. Alternating voltage frequency is varied automatedly between 18 and 50 kHz or it can be fixed depending on the operating choices. The two rod system is aligned and maintained at a fixed distance (variable between 0 and 8 mm, but in the reported experiments was set to 2 mm) from a stainless steel cylinder (diameter 150 mm) coated by the same dielectric material (thickness 5 mm). The cylinder is grounded and it can rotate around its axis at a fixed rate. Materials in sheet form can be treated rolling on the cylinder and wrapping outside. Small samples of materials can be treated fixing them on the cylinder surface. Exposure time is determined by the rotating speed of the cylinder and by the number of rotations.

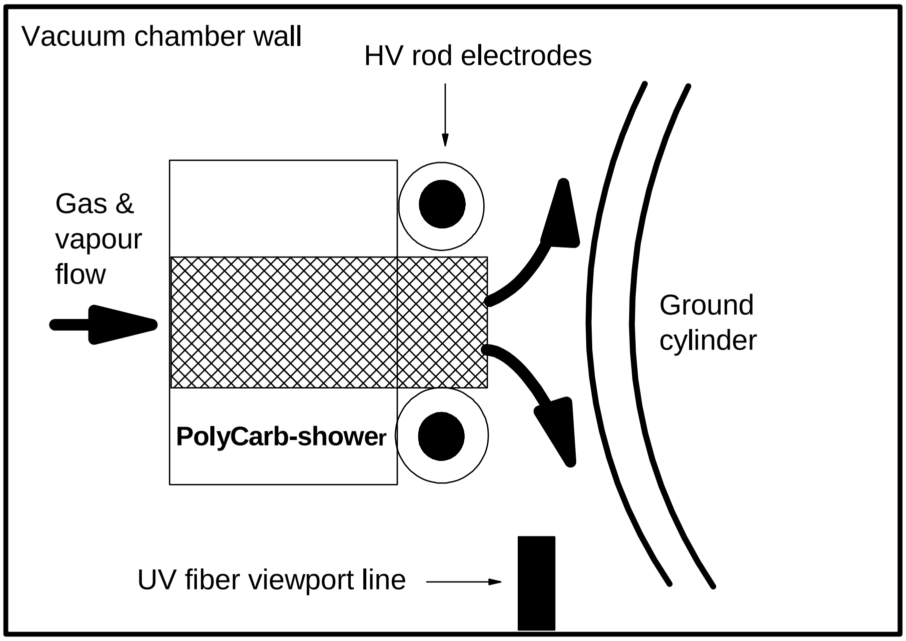

Fig. 1 - Lay-out of a section of the discharge region. The electrode system was mounted inside a vacuum chamber for the study of dielectric barrier discharge in a controlled atmosphere

3. Diagnostics

High voltage probes can be used to monitor the voltage on the two rod electrodes system. The actual voltage drop in the discharge gap can be estimated experimentally by measuring the capacitance of the dielectric coatings. We employ a P6015A HV probe by Tektronix which is granted for a bandwidth of 75 MHz, which is sufficient for assessing the effects on the circuitry voltage of the dynamics of streamers.

However the most interesting signal is that of the discharge current. In order to measure fast current pulses due to microdischarges superimposed to the low frequency oscillation of the in a DBD, it is necessary to employ a diagnostics with both a high sensitivity and a wide bandwidth. Large bandwidth and sensible current probes are more difficult to be obtained. A current trasducer like a Rogowski coil matches these characteristics [6]. The addition of a suitable magnetic core allows to obtain a wider bandwidth and to avoid waveform oscillations [7]. By tuning the geometrical and electrical parameters of the measuring circuitry it is possible to work in the self-integrating regime, which allows to measure on a scope a voltage signal directly proportional to the current over a wide bandwidth. The transducer was calibrated with a tunable frequency waveform generator feeding a 50 Ω high power (50 W) resistance through a impedance matched 50 Ω BNC wire. Results for two of our home-made probes are shown in Fig. 2. Then the total discharge current have been investigated together with the electrodes voltage and during experiments we have acquired data sets of $3x10^5$ points time series which have been recorded with a 200 MHz scope and subsequently analyzed.

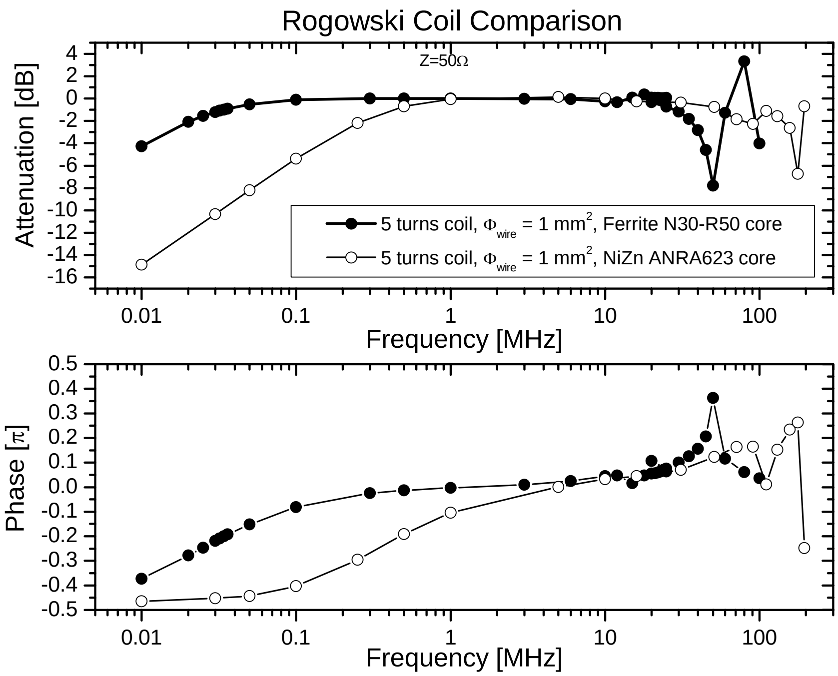

Fig. 2 - Amplitude and phase response characteristics of the current transducer measured over the frequency range

Optical emission spectroscopy can be employed to reveal the light emitted by the de-excitation of electronically excited energy levels of atoms, molecules, ions and radicals which are present in the discharge gas-phase. From the wavelength and the intensity of the emission lines it is possible to identify specific chemical species and to gain insight about their abundances [8]. However only after a detailed modeling of the excitation and non radiative quenching processes it is possible to determine the absolute concentrations of each emitting species and this reduce the utility of such diagnostics..

We have measured emission spectra of the discharges by means of a wide band, low resolution spectrometer (PS2000 by Ocean Optics). The spectrometer, equipped with a 10 μm slit, a holographic grating (600 lines/mm, blazed at 400 nm) and a 1024 pixels CCD, has a resolution of 1.02 nm and a spectral band extending from 200 to 850 nm. Emission spectra of the discharges have been recorded through an UV enhanced optical fiber, connected to the device by a vacuum feed-through.

Discharge spectra with an exposure time of 10 s have been acquired and averaged (60 spectra) to reduce noise. Dark spectra are subtracted too. The brightest feature in the spectra is the 2nd positive system of nitrogen, from which it is possible to estimate the vibrational temperature T_{vibr} of the excited energy level N2(C), according to the formula [9]:

$$n_{N2(C,v)} = \sum_{v'} \frac{I_{N2(C,v)\to N2(B,v')}}{\nu^4_{N2(C,v)\to N2(B,v')}} \propto e^{-\frac{E_{N2(C,v)}}{kT_{vibr}}}$$

Where v and v’ are the vibrational level index, I is the intensity and ν the frequency of the electronic transition between N2(C) and N2(B) levels of nitrogen.

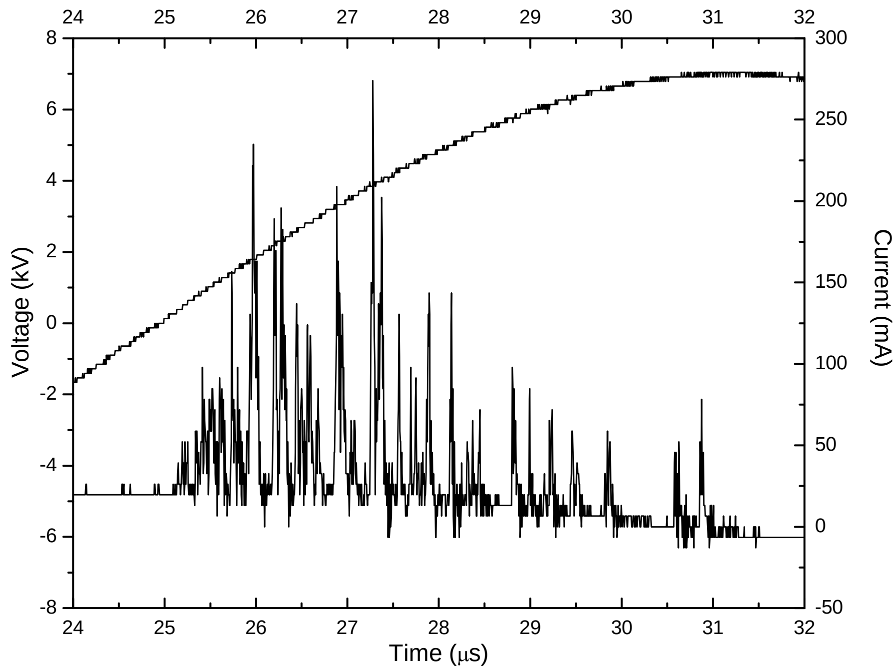

Fig. 3 - Voltage and current measured during a cycle of the discharge.

4. Plasma characterization

The current signal was analysed after subtraction of the displacement current oscillations (see Fig.3). The signal is composed of burst of activity, each composed of several current peak, a few tens of ns in duration, corresponding to single microdischarges. We have studied the dependance of the number and duration of the bursts as a function of the power supplied. This parameters turns out to be linearly correlated to the peak voltage that is applied to the two rod electrodes. DBD frequency is automatedly tuned and decreases slightly with the power level ranging between 36 and 32 kHz in this configuration.

Burst number increases linearly with power, after breakdown threshold, up to 200 W. At larger power burst number increases at a lesser pace, probably because bursts tend to overlap and their average number gets underestimated. This is displayed in Fig.4. The time duration of current burst was studied. A complete probability distribution function can be calculated for each power value. In fig.5 it is displayed the dependance from the DBD power of the first four moments of the PDF. Again the trend is a linear increase with the power level from 5 to 30 ns for the presented experimental conditions. On a semi-log plot it is possible to see a change in the variance, which is possibly due to Skewness and Kurtosis have been calculated showing large positive values for power greater than 100 W (Sk~2, Ku~10) indicating the presence of an excess of long burst activity respect to a Gaussian distribution. This is in agreement with observations of an intermittent character in this systems [10,11].

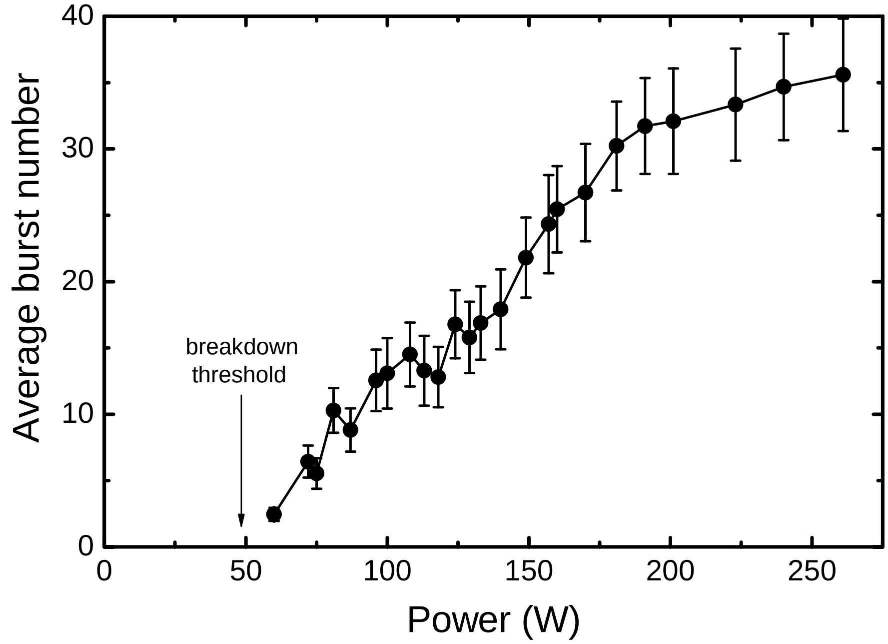

Fig. 4 - Average number of bursts measured as a function of the DBD total power. Error bars are the variance measured from the whole time series over about 500 cycles.

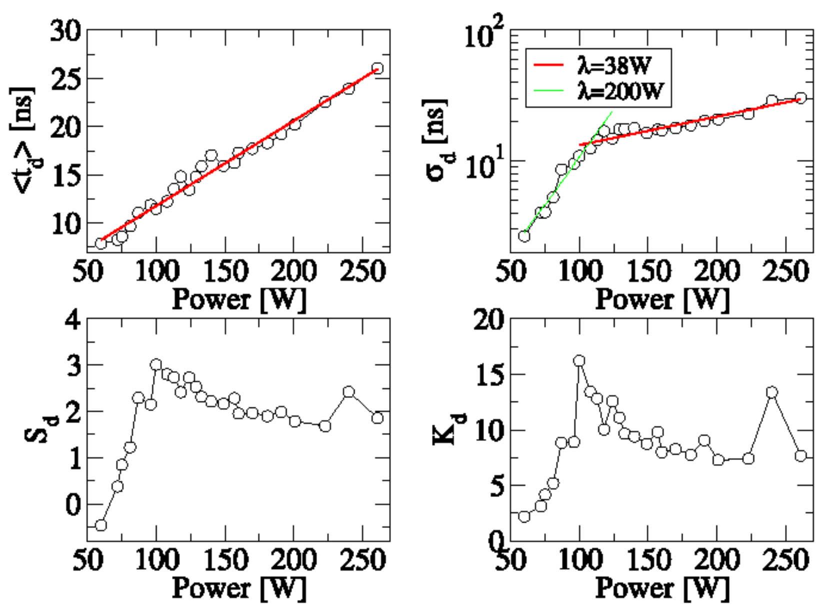

Fig. 5 - Moments of the PDF of the time duration of bursts measured as a function of the DBD total power.

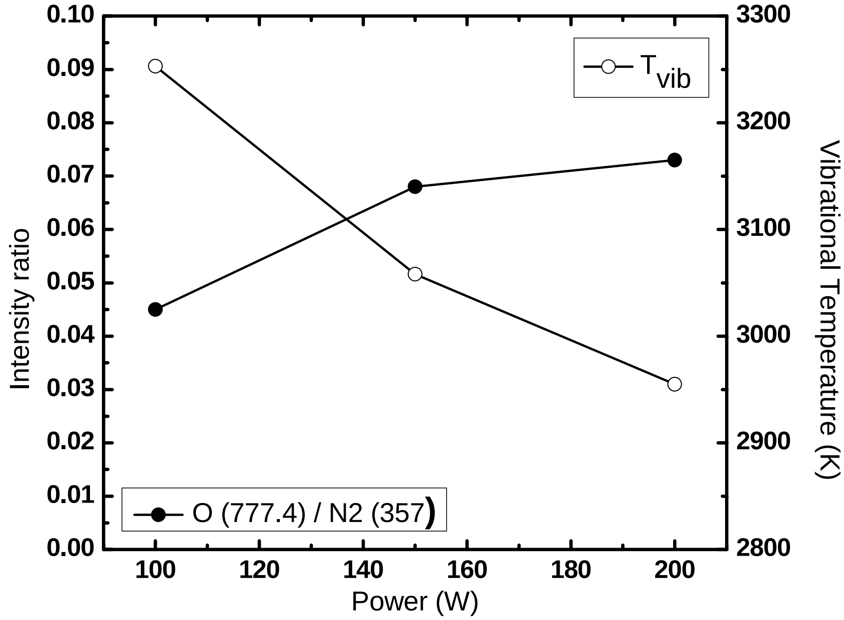

Fig. 6 - Vibrational temperature of the N2(C) excited energy level molecules (open). Intensity ratio of the emission line of atomic oxygen (777.4 nm) and one band of the 2^{nd} positive system of nitrogen at 357 nm (full).

Results of the OES spectroscopy are displayed in Fig. 6. It can be noted that the vibrational temperature is of the order of 3000 K, which means that in such discharges also the neutral molecules have thermal energy sufficient to influence directly the chemical kinetics evolution of the gas-phase [12]. Vibrational temperature decreases slightly with the power level, possibly because of the longer duration of discharges which allows for a more pronounced quenching of the excited vibrational levels respect to its ground state.

As stated before, an evaluation of the concentration of active chemical species,. ions or radicals from OES diagnostics requires a detailed modeling of the excitation and quenching processes for each light emitting energy level observed in the spectra. However relative information could be inferred by normalizing the emission intensities of different emitting molecules. As an example, we discuss the production of atomic oxygen in our experiments, since we easily detected the emission line at 777.4 nm. The line intensity was normalized to that of one of the brightest band of the 2^{nd} positive system of nitrogen at 357 nm. In this way the contribution arising from direct excitation from high energy electrons in the discharge region, which is proportional to the local electron density is factored out. Since also the energy of the two excited levels is similar, we could expect that the coefficient depending on the electron energy distribution is factored out. Moreover, since dissociation level is usually very low, the absolute density of nitrogen is constant and the intensity ratio should be proportional to the relative concentration of atomic oxygen during the discharge (actinometry [13]). The reported increase of oxygen production with the power level connected with the increase of burst activity in number and duration is indeed in rough ageement with such expectations.

5. Conclusions

We have presented preliminary results concerning the use of diagnostics tools developed for the characterization of gaseous discharges at atmospheric pressure. Electrical and optical diagnostics have been implemented on a isolated from atmosphere high pressure dielectric barrier discharge setup, in order to make experiements easily repeteable and controlled. Different kind of discharge parameters, including number and durations of discharge bursts, vibrational temperature and abundances of active radicals can be evaluated and could be used to investigate the nature of the prevailing plasma surface interactions and so the results of plasma processing. In our view, such an approach would be of great benefit also for the research activity focused on the engineering of plasma processing in technological applications.

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