MICRO-STRUCTURED ELECTRODE ARRAYS: A NEW DISCHARGE DEVICE FOR POLLUTION CONTROL?

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Abstract

Micro-structured electrode (MSE) arrays allow to generate large-area glow discharges over a wide pressure range up to atmospheric pressure applying only moderate voltages. Electrode distances in the micron-range are realized by means of modern micromachining technologies. Direct current (DC) or radio frequency (RF, 13.56 MHz) power is applied to the arrays. Typical power densities needed to generate a RF discharge plasma in noble gases at atmospheric pressure are about 3-6 W/cm^2. Possible important areas of application of the MSE arrays are pollution control, surface modification of materials, plasma chemistry and the use as light sources. For a performance test, serving to evaluate the applicability of the arrays to the field of non-thermal plasma processing of gaseous emission, an available experimental setup for the detection of nitrogen oxide (NO) via laser induced fluorescence (LIF) spectroscopy and via online quadrupole mass spectrometry (QMS) was used.

1. Introduction

Non-thermal plasma processing techniques [1] are well established in pollution control [2]. The applied weakly ionized plasmas are highly non-equilibrium, i.e. the electrons have large mean kinetic energies equivalent to several 10000 K whereas the gas remains at ambient temperature. The technically most common method to generate a non-thermal plasma is by high electric field (electrical discharge). For that, direct current (DC), alternating current (AC), or radio frequency (RF) can be applied. Since the basic electrical discharge creation process in gases proceeds via electron impact ionization, electrons must be accelerated by the applied field E over the mean free path λ to gain a minimum kinetic energy

$$E_{kin} = e \cdot E \cdot \lambda > E_{ex} \tag{1}$$

where E_{ex} is the threshold energy necessary for electronic excitation, dissociation, fragmentation or ionization of the gas. Therefore, operation of electrical discharge devices requires either a low gas pressure, i.e. large λ, or a very strong electric field E. For example, if an electron should gain a mean kinetic energy of 10 eV at atmospheric pressure, where λ is about 10^{-5} cm, E must exceed 10^6 V/cm. Electrode arrays fabricated by means of modern micromachining technologies can provide distances on a micron-scale between the electrode elements. Here, even at moderate voltages, the electrostatic field can exceed the threshold value required to initiate the electrical breakdown process. The field between the electrodes easily exceeds 10^5 V/cm and can approach 10^6 V/cm and even higher values at the edges of the electrodes. In this regard it is possible to produce electrical gas discharges up to atmospheric pressure by means of MSE arrays with very moderate voltages so that a wide area of plasma applications becomes feasible under reasonable conditions. MSE arrays are being considered for possible applications to pollution control, surface modification of materials, plasma chemistry and the use as light sources. A series of measurements has been performed, serving to evaluate their applicability to pollution control. For these investigations an experimental setup was realized for the detection of NO via laser induced fluorescence technique and quadrupole mass spectrometry.

2. Experiment

The MSE arrays consist of parallel metal strips with a width ranging from 160 to 350 µm and with a length of about 25 mm, which are attached to a dielectric substrate. Areas, where the electrical contact is established, link the electrodes together, so that two matching comb-like structures originate (figure 1). The electrode gap was varied from 50 to 250 µm. Using lithography technology the arrays were manufactured of 36 x 36 mm^2 or 36 x 18 mm^2 glass or ceramic substrates on which a metal layer of copper, chromium or gold was evaporated. Because of the area needed for the electrical contact the maximal size of the discharge was about 25 x 30 mm^2 and 25 x 15 mm^2, respectively. For the usage with RF power some of the electrode arrays were additionally coated with a dielectric layer consisting of Al_2O_3, which serves as a protection for the electrodes against corrosive gases and inhibits sputtering effects.

Fig.1 schematically shows the experimental setup for the online detection of NO with QMS. Uniform electrical discharge plasmas were generated up to atmospheric pressure using a RF power supply at 13.56 MHz (ENI ACG 3B) equipped with a matching network for automatic impedance matching (ENI MW-5D). The measurements were performed in a plasma reactor made of stainless steel with a total volume of about 0.1 litres. The reactor was evacuated to a pressure $p \leq 10^{-3}$ mbar before each measurement. A gas flow rate between 50 and 200 sccm was set up by means of mass flow controller (MFC). The pressure was maintained constant with an automatic flow control valve. Measurements were carried out in a gas mixture of helium with 500 ppm NO. For the online detection of the NO at the outlet of the plasma reactor a quadrupole mass spectrometer (Pfeiffer Vacuum QMS 200) with a capillary inlet was used.

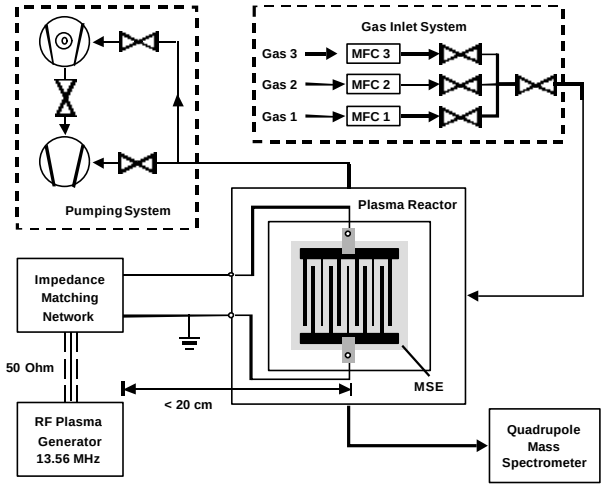

FIG. 1: *Experimental setup for quadrupole mass spectroscopy with RF powered MSE arrays.*

For the operation with direct current a high voltage supply was used, which can provide voltages up to 5 kV (max. 5 mA). In order to limit the discharge current a ballast resistor was employed in series. A cubical chamber made of stainless steel with a total volume of about 1.5 litres was used as a reactor. It was evacuated to a pressure $p \leq 10^{-3}$ mbar before each measurement. The experimental setup was outlined for the detection of NO via LIF technique. Tunable laser light with a wavelength around 226 nm probed the discharge volume a few millimeters above the array surface. The reemitted fluorescence light was detected under 90° by a photomultiplier. For an absolute determination of the NO concentrations the system was calibrated with a pure NO gas filling at low pressure. The LIF measurements were performed under static conditions. The experimental setup is described in detail elsewhere [3].

3. Results and Discussion

Fig. 2 shows a glow-like uniform RF discharge in helium at atmospheric pressure generated with a MSE array with an electrode gap of 100 µm and 160 µm wide copper electrodes. The area of the discharge amounts to 25 x 15 mm^2. For the performance tests presented in this paper helium was chosen as carrier gas, because of its low breakdown voltage compared with other gases. Therefore, a stable discharge can be generated up to atmospheric pressure with low RF power densities between 3 and 6 W/cm^2. Neon was also used as an alternative to helium. The sustaining voltage of the helium discharge amounts to about 200 V.

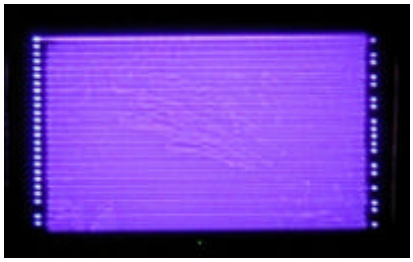

FIG. 2: *Electrical discharge plasma in helium at atmospheric pressure. Area of the discharge: 25x15 mm^2.*

In other noble gases like argon or in molecular gases like nitrogen a much higher RF power density is necessary to generate the discharge, which heats up the electrode systems and, therefore, decreases their lifetime. At present, work is in progress to overcome this issue, so that other carrier gases can be tested in the future, which are of higher relevance with respect to the application to pollution control.

Fig. 3 presents a Multiple Ion Detection (MID) measurement demonstrating the removal of NO in a MSE generated discharge in a gas mixture of helium with 500 ppm NO. A MSE array with copper electrodes (width: 160 µm, gap: 100 µm) on a glass substrate was used. The following seven ion currents were detected: He^+ (m/z = 4), H_2O^+ (18), N_2^+ (28), NO^+ (30), O_2^+ (32), Ar^+ (40) and NO_2^+ (46). The detection time for one cycle is about 8 s, thus the figure shows a period of about 1 h.

The pressure in the reactor was maintained at 700 mbar and a constant mass flow of 72.5 sccm of the He/NO mixture was adjusted. The sampling pressure in the QMS amounted to $2.9 \cdot 10^{-6}$ mbar. The area of the discharge was 25 x 30 mm^2 and a RF power of 29 W was applied to the electrode array, thus resulting in a power density of about 3.9 W/cm^2.

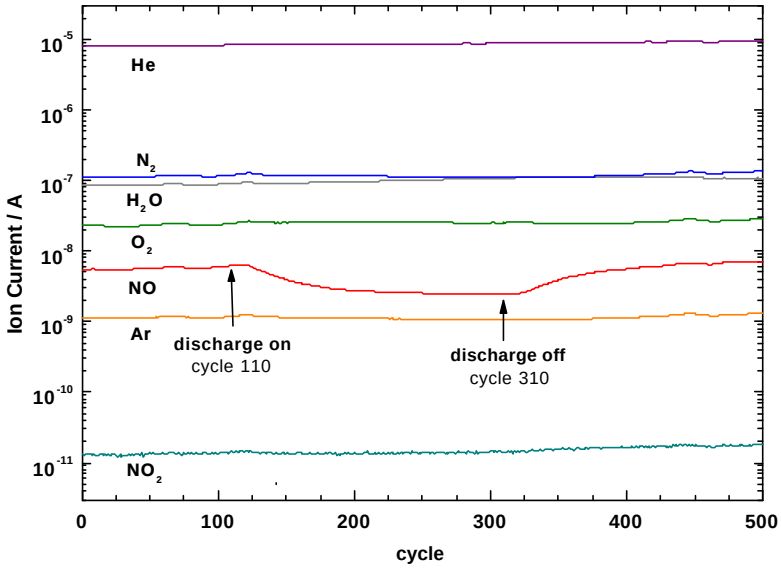

FIG. 3: *MID measurement demonstrating the removal of NO in a MSE generated discharge plasma in helium at a pressure of 700 mbar and a mass flow of 72.5 sccm of a mixture of He with 500 ppm NO. RF power density: 3.9 W/cm^2.*

The cycles 1-109 show the ion currents for the species without the discharge. The ion current measured for NO^+ is about $6 \cdot 10^{-9}$ A. At the beginning of cycle 110 the discharge plasma was

generated. One can observe a slight increase (cycle 110-117) of all ion currents immediately after the ignition of the discharge. This is due to a temporary increase of the chamber pressure induced by gas heating by the discharge. After that, the currents of He^+, N_2^+, O_2^+ Ar^+ and NO_2^+ remain almost constant, whereas the H_2O^+ current shows a small continuous rise until the discharge is switched off (cycle 310). It is reasonable that this increase is due to residuals of water on the reactor walls and on the electrode surfaces, which begin to evaporate, when the discharge plasma is running.

Beginning with cycle 118, i.e. about 1 min after the discharge was ignited, a continuous decrease of the NO^+ ion current is observed. After 135 cycles (cycle 253) the current has already decreased to $2.5 \cdot 10^{-9}$ A. In the next 65 cycles measured with the running discharge the decrease is only small. When the discharge was switched off (cycle 310) the value of the NO^+ current was $2.45 \cdot 10^{-9}$ A. As a result, the removal of the NO in this measurement is about 60 %. Further measurements have shown a reduction of NO between 50 and 70 % in a flow of 50-150 sccm of the He/NO gas mixture. The applied RF power in all experiments was about 30 W (4 W/cm^2).

The decomposition of dinitrogen monoxide (N_2O) into NO and N_2 in N_2/N_2O mixtures was investigated at low pressures with DC powered MSE arrays. Fig. 4 shows an example. The reactor was filled with a mixture of 0.15 mbar N_2O and 7.5 mbar N_2. The time dependent decomposition of N_2O is detected by the formation of NO molecules, which are excited by laser light from the $X\,^2\Pi$ ground state to the $A^2\Sigma^+$ excited electronic state at wavelengths around 226 nm. The NO concentration was then determined from the intensity of the fluorescence light. We have chosen a comparatively low pressure for this basic measurements, because the LIF diagnosis technique works quantitatively only for gas pressures in the few mbar regime, due to the large absorption cross section of the fluorescence light resulting in self absorption at higher pressures. The measurements were performed under static conditions, and, therefore, the gas exchange in the reactor proceeded by diffusion only.

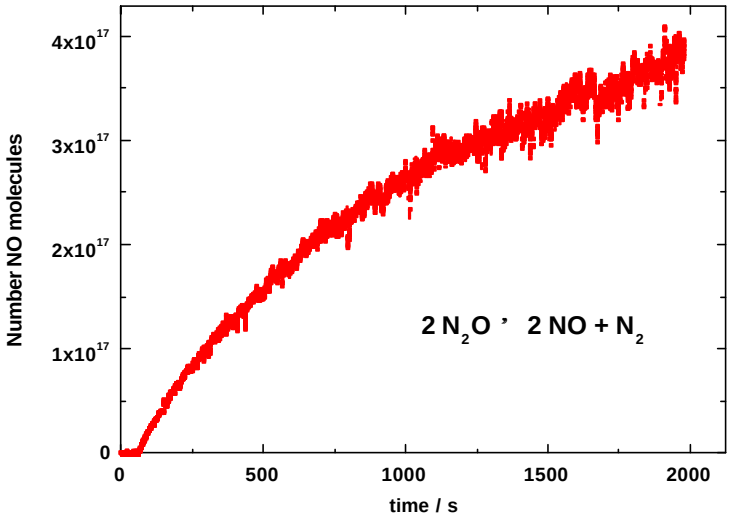

FIG. 4: *LIF measurement demonstrating the removal of N_2O in a MSE generated discharge plasma in a mixture of 7.5 mbar N_2 and 0.15 mbar N_2O. Applied voltage: 570 VDC.*

As the discharge started the LIF signal immediately began to increase due to the decomposition of the N_2O molecules and the formation of NO. The initial NO formation rate (equivalent to the N_2O removal rate) is about 6.3 x 10^{14} molecules/s. A DC voltage of 570 V was applied to a 36 x 36 mm^2 MSE array with chromium electrodes on a glass substrate.

4. Conclusion

The measurements presented were performed in order to allow a first evaluation of the capability of MSE arrays for an application in the field of pollution control. Exemplary, the decomposition of two nitrogen oxides (NO, N_2O) was investigated. This was a priori advantageous with regard to the available LIF and QMS diagnosis techniques. At present, measurements at atmospheric pressure are limited to helium, neon and argon as carrier gas for the reasons mentioned and the plasma reactor design is not yet optimized, e.g. with respect to the gas flow. Therefore, statements about the efficiency of the discharge, i.e. about the specific energy consumption, are not useful at the moment. Detailed investigations are in progress.

Although the results are of preliminary character it is shown that a removal of NO and N_2O from gaseous emissions is possible with DC and RF discharge plasmas generated with MSE arrays. QMS measurements show a NO reduction up to 70 %. Much higher efficiencies will be achieved by optimizing the relevant experimental parameters. The high application potential of MSE arrays in pollution control is clearly demonstrated.

References

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