Micro-structured electrode arrays:
Atmospheric pressure plasma processes and applications

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Abstract

Micro-structured electrode (MSE) arrays allow to generate large-area uniform glow discharges over a wide pressure range up to atmospheric pressure. The electrode dimensions in the micro-range realized by means of modern micro machining and galvanic techniques are small enough to generate sufficiently high electric field strengths to ignite gas discharges applying only moderate radio frequency (13.56 MHz) voltages (80 V to 390 V in Ne, He, Ar and N_2). The non-thermal plasma system is characterized by a special probe measuring the electric parameters. Possible industrial applications of the MSE arrays are plasma chemistry (e. g. waste gas decomposition) and surface modification of materials. Using an MSE based micro-reactor the abatement of the greenhouse gas CF_4 was performed with decomposition rates of over 90 % at a pressure of 100 mbar in He and N_2. The decomposition of waste gases in the plasma was monitored online with quadrupole mass spectrometry. At atmospheric pressure in He the abatement rate of CF_4 is still over 70 %. Other applications realized in our lab are thin film deposition of diamond-like carbon layers and SiO_2 layers on various substrates and sterilization of food packaging materials.

1. Introduction

Non-thermal plasma processing techniques optimized for atmospheric pressure applications are the subject of recent growing interest due to their significant advantages. At atmospheric pressure thin film deposition with very high rates is possible and cost-intensive vacuum technology is avoided. There are many approaches published recently [see 1, 2, 3 and references therein] to overcome the problems of generating and sustaining a stable uniform non-thermal atmospheric pressure plasma.

A useful method to generate atmospheric plasmas (glow discharges) is to scale down the electrode dimensions by applying the Paschen similarity law *(p · d) = const.*, where *p* is the pressure and *d* is the electrode gap width [3, 4, 5]. This is realized using a system of planar and parallel electrodes arranged on an insulating substrate called micro-structured electrode arrays (MSE) because of the micro-system dimensions in the 100 μm-range. These dimensions are necessary to operate the discharge in the minimum of the Paschen curve corresponding to He, Ne, Ar or N_2 applying only moderate voltages [6, 7].

The MSE arrays are suitable plasma sources for various applications using the advantages of small dimensions and the possibility of a modular scale up. With the MSE array incorporated into a micro-reactor it is possible to decompose perfluorocompounds (PFCs). PFCs have considerable atmospheric lifetimes and are very efficient absorbers of infrared radiation resulting in a large global warming potential. CF_4 in particular is extensively used for semiconductor manufacturing processes, and as an exhaust gas of the processing tools it has proven to be particularly difficult to destroy and remove [8, 9].

We will demonstrate that an MSE based micro-reactor is a suitable scalable alternative tool to the presently used inefficient thermal incineration process tools for the CF_4 abatement. Additionally, we will characterize the MSE plasma and present other successful applications of the MSE arrays as coating and sterilization tools.

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2. Experimental

The plasma micro-reactor consists of the MSE plasma source and a glass structure forming a reaction chamber. The base dimensions are 15 mm x 15 mm with a height of 2.5 mm. The chamber size is 8.4 mm x 7.2 mm with a height of 1 mm resulting in a reactor volume of 60.5 mm^3.

The electrode arrays are micromachined nickel structures on an alumina substrate. The electrode gap design is shown in Fig. 1. In order to achieve high-pressure ranges a thickness up to 100 µm is necessary. Therefore, a 150 µm thick layer of SU8 photoresin [10] is spun on a ceramic wafer being already covered with a thin copper layer. The SU8 is prebaked by heating at 100°C. UV-exposure with a chrome mask initiates crosslinking that is continued on a hotplate. The nonpolymerized resin is resolved leaving a complementary geometry to the desired electrode design.

Fig. 2. Scheme of a reaction chamber cut atop the micro-structured electrode array showing the gas flow.

during plasma operation. A gas flow rate between 1 and 200 sccm was set up by means of mass flow controllers. For online detection of the plasma product gases a differentially pumped quadrupole mass spectrometer (Pfeiffer Vacuum QMS 200) was used. The discharges were generated using an RF power supply at 13.56 MHz (ENI ACG-3B) equipped with a matching network (ENI MW-5D). Between the matching network and the micro-reactor a special probe (ENI VI-Probe) is inserted in order to measure voltage, current and phase angle of the system.
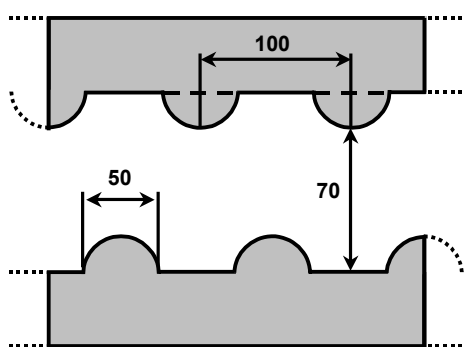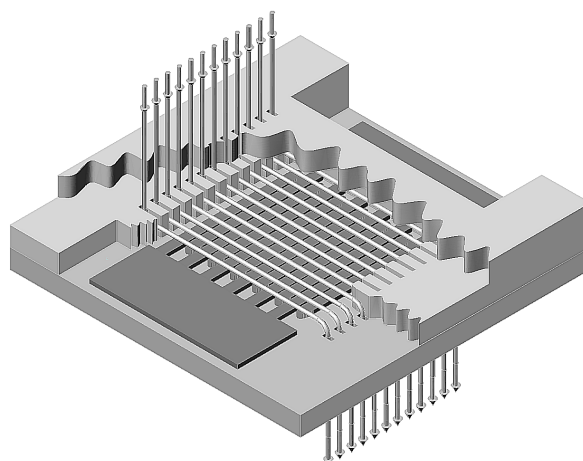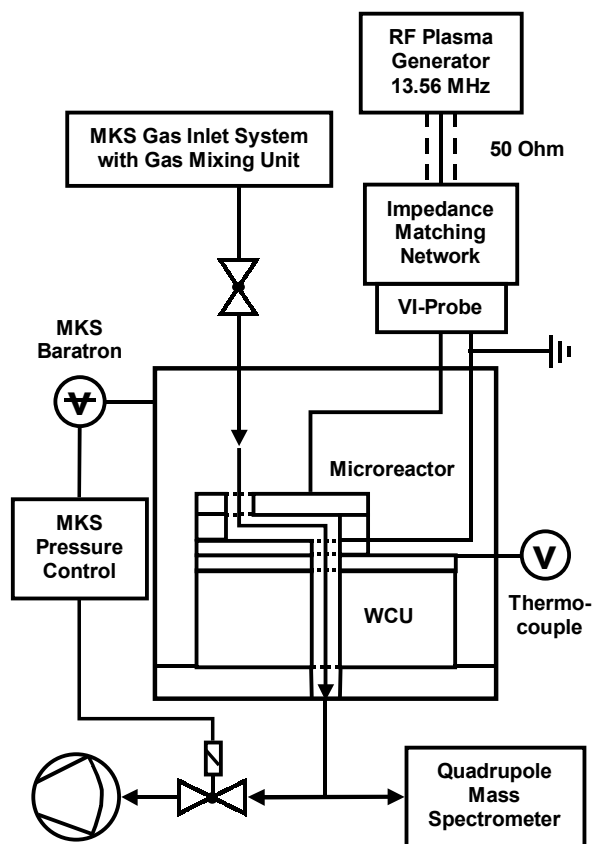

Fig. 1. Geometry of the electrode gap (dimensions in µm).

After plating with nickel most of the SU8 is removed by a long exposure to acetone, and the remaining resin and also the start layer are etched away by a short exposure to hot sulphuric acid. After cleaning a 0.5 µm alumina layer is deposited on the structures to form a protective barrier. Completing the MSE the outlet of the reactor is cut with an Nd:YAG-laser. The MSE is fixed below the glass part. Both parts are bonded by a silicone glue interlayer.

The reaction chamber has inlet and outlet channels and provides the micro-structured electrode array with a constant gas flow. The photosensitive glass Foturan [11] allowing direct view of the plasma is used because of its good structurability that is needed for the inlets and chamber design. The external pressure difference between inlet and outlet necessitate the special chamber and gas channel geometry leading to a constant mean residence time in the micro-reactor. The gas flow inside the reactor is shown in Fig. 2. Also shown are the contact pads that provide radio frequency power supply and mechanical fixing of the device in the experimental setup.

The micro-reactor is installed onto a complex gas flow and water-cooling unit (WCU) system inside a vacuum chamber shown in Fig. 3. The entire experimental setup is described in detail elsewhere [1, 2, 4]. A Chromel-Alumel thermocouple of K-type is directly placed under the micro-reactor measuring the temperature rise of the micro-reactor

Fig. 3. Schematic view of the experimental setup.

3. Characterization of the MSE plasma

MSE arrays allow to generate large-area uniform glow discharges in He and Ne at pressures up to 1500 mbar and in Ar and N_2 up to 1200 mbar. The non-thermal discharges [4] are generated at the gaps between electrodes, up to 500 mbar the plasma covers the whole electrode system.

In Fig. 4 the breakdown voltages (ignition potentials U_{IP}) of the gases Ne, He, Ar and N_2 of the pressure range 100 to 1000 mbar are shown. The right-hand branches of the Paschen curves of Ar and N_2 and the left-hand branches of Ne and He at $p \cdot d$ values higher than 5.0 mbar $\cdot$ cm obey the Paschen formula [6, 7] derived from the Townsend breakdown theory:

$$U_{IP} = \frac{B \cdot (p \cdot d)}{C + \ln(p \cdot d)}.$$

The mentioned $p \cdot d$ regions are fitted with the Paschen formula shown in Fig. 4, the fitted constants are listed in Table 1.

Table 1. Fitted constants of the Paschen formula and regions of applicability (B and E / p in V mbar^{-1} cm^{-1}).

Gas	Experiment (RF)			Lit. [6] (DC)	
	B	C	E_{eff} / p	B	E / p
Ne	6.72 ± 0.43	-1.38 ± 0.03	$11 - 115$	75	$75 - 300$
He	15.73 ± 0.23	-1.02 ± 0.01	$17 - 135$	26	$15 - 100$
Ar	66.2 ± 1.4	-0.15 ± 0.03	$37 - 230$	135	$75 - 450$
N_2	237.8 ± 5.2	$+0.98 \pm 0.04$	$109 - 335$	256	$75 - 450$

The determined B values of the RF field are lower than the B values of the DC field [6], because the voltages required to initiate and maintain the alternating current discharge decrease strongly in comparison to a DC glow discharge [7].
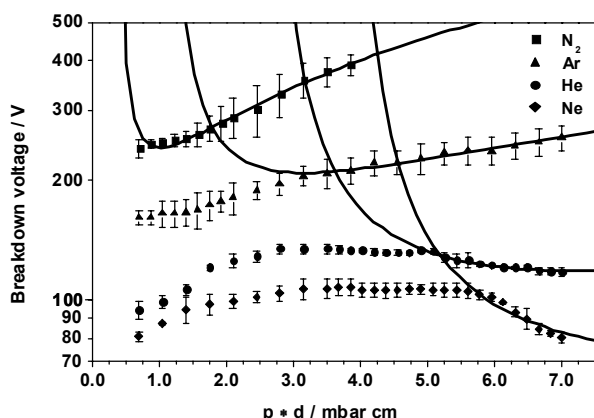

Fig. 4. Experimental breakdown voltages and fitted Paschen curves in Ne, He, Ar and N_2 (RF 13.56 MHz; electrode gap width 70 μm, 100 mbar – 1000 mbar).

While the Paschen curves fit very well the experimental data at high $p \cdot d$ values, the curves for Ar, He and Ne deviate at low $p \cdot d$ values significantly. Theoretically, higher breakdown voltages are expected due to the growing lack of impact partners with decreasing $p \cdot d$ values. Hartherz *et al.* [12] have shown that with d values in the μm-range the breakdown voltages are increasingly dominated by field electron emission with decreasing pressure, although the used electric field strengths are less than one magnitude below 10^6 V cm^{-1} [6]. Further investigation is needed in order to give a definitive explanation of the pressure dependent behavior of Ne, He and Ar at pressures lower than 300 mbar. Nevertheless, Fig. 4 clearly demonstrates the different behavior of MSE driven plasmas and conventional discharge plasmas.

4. Applications

4.1 Decomposition of CF_4 and NO

The decomposition rates of CF_4 are summarized for three different gas mixtures introduced to the micro-reactor at pressures of 100 and 1000 mbar in Table 2. The measured power densities vary in He between 14 and 35 Wcm^{-2} and in N_2 between 23 and 40 Wcm^{-2}. The $CF_4 : H_2$ ratio of 1:7 gives maximum CF_4 decomposition rates at a pressure of 100 mbar. The rates at atmospheric pressure are low, because the plasma is destabilized by the high concentration of the H_2 molecules (only 2 of 5 possible electrode gaps are burning). A decrease of the H_2 portion to 1 sccm increases the rate up to 70.5 % (35 W, 26 Wcm^{-2}).

Table 2. Decomposition rates (%) of CF_4 (3 different gas mixtures at pressures of 100 and 1000 mbar) dependent on the RF generator power.

Gas mixture	2 sccm CF_4 14 sccm H_2 50 sccm He	2.5 sccm CF_4 14 sccm H_2 50 sccm N_2	1 sccm CF_4 7 sccm H_2 50 sccm He
RF generator power	100 mbar	100 mbar	1000 mbar
25 W	32.7	39.6	33.4
30 W	54.9	58.3	34.0
35 W	78.8	93.9	37.2
40 W	80.2	90.0	42.2

During plasma operation an abatement of the fragments, radicals and molecules H (1), H_2 (2), H_2O (18), F (19), CF (31), O_2 (32), CF_2 (50) and CF_3 (69) is observed with the exception of the 1000 mbar He gas mixture where H_2O is produced. O_2 and H_2O are residual gases probably coming from the vacuum chamber walls. The both gases support the decomposition of CF_4, but an excess of O_2 or H_2O destabilizes the plasma and does not increase the rate.

The product distribution is shown in the following three unbalanced equations where the products are listed by relative concentrations based on the HF occurrence:

100 mbar He: $2 CF_4 + 14 H_2 + 50 He \longrightarrow HF (20) + HCN (27) + CN (26) + COF (47) + CO_2 (44) + COF_2 (66)$

100 mbar N_2: $2.5 CF_4 + 14 H_2 + 50 N_2 \longrightarrow NF (33) + HF + NF_2 (52) + HCN + CN + COF + NO_2 (46) + COF_2$

1000 mbar He: $CF_4 + H_2 + 50 He \longrightarrow COF + CO_2 + COF_2 + CO (28) + HF + H_2O + HCN + CN$

As expected [8, 9] only small product molecule ions are detected. The production of NF_3 (71), NO (30), N_2O_3 (76), N_2O_5 (108) and C_2F_6 (138) is not observed.

The gas flow between 52 sccm and 66 sccm results in mean residence times between 55 ms and 70 ms. The maximum measured temperature rises of the MSE are 80°C for He and 125°C for N_2.

In order to evaluate the potential of the micro-reactor the decomposition of NO (500 ppm in 50 sccm He) has been investigated in comparison with the CF_4 abatement. At atmospheric pressure the decomposition rates already pass through a maximum at a RF generator power of 15 W (69.4 %, 5 Wcm^{-2}). Thus, the two processes are controllable by the applied generator power.

4.2 Thin film deposition and sterilization

The MSE plasma source is an ideal device to treat surfaces of various sizes, because it may be individually adapted to the substrate size by a modular scale-up [3].

Thin diamond-like carbon (DLC) film layers have been deposited from mixtures of 5 % methane or 2 % acetylene in helium [2, 5] and silicon dioxide layers have been produced by bubbling a mixture of 1 % oxygen in helium through tetraethoxysilane (TEOS) at pressures up to 100 mbar.

The gap width between the MSE array and the substrate was 9 mm (Fig. 5), and the substrate was biased with a voltage of 550 Vpp to 1000 Vpp at 9.5 kHz. The deposition time varied between 10 and 30 minutes at RF generator powers of 20 W to 30 W.

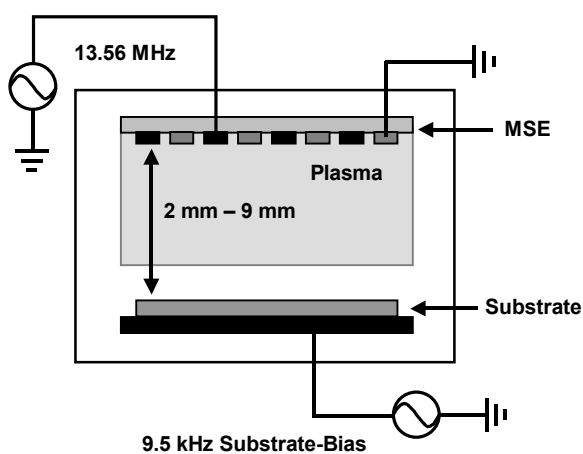The 1 – 10 μm thick films have been deposited on various substrates (silicon, copper, aluminum and plastic film). The film layers have been characterized by glow discharge optical emission spectroscopy, micro-hardness indentation, ellipsometry and raster electron microscopy. The non-optimized DLC films already possess a hardness of 9000 MPa. Currently, efforts are made to deposit high quality layers at pressures up to 1 atm by varying the gap width and other parameters.

The attempt to sterilize plastic films at atmospheric pressure has already been successful. In order to provide plastic films being suitable materials for food packaging it is necessary to inactivate thermoresistent bacterial spores, which survive the pasteurization process (10 min. at 80°C). 10^6 spores of Bacillus cereus are terminated by a plasma exposure of four minutes (35 W, 1000 Vpp, 3 sccm O_2, 300 sccm He, gap width 2 mm).

Conclusions

In this paper, we presented MSE arrays as powerful alternative atmospheric pressure plasma sources (e. g. inside a micro-reactor). Additionally, we showed the potential of MSE arrays being used as coating and sterilization tools.

Acknowledgements

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Fig. 5. Scheme of the deposition and sterilization setup.