Micro-structured electrode arrays: Plasma based sterilization and coating over a wide pressure range

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Abstract

Micro-structured electrode (MSE) arrays consist of an interlocked comb like electrode system with µm-gap widths. These arrays are capable to generate large area uniform glow discharges up to atmospheric pressure. In order to ignite discharges at atmospheric pressure this approach using the Paschen similarity law (pd = const.) is established beneath dielectric barrier arrays and plasma jets. The generated electric field strengths to ignite gas discharges apply only moderate radio frequency (RF, 13.56 MHz) voltages. The electric parameters of the non-thermal plasma system are characterized by a special probe and the generated excited species of the plasma are observed by optical emission spectroscopy.

Keywords: Atmospheric pressure plasma; Micro-structured electrodes; Sterilization; Functional coating; Food packaging materials

1. Introduction

Non-thermal plasma processing at atmospheric pressure is the subject of growing interest due to the suitability of plasma chemistry and excitation. There are many approaches published in the last 15 years to overcome the problems to generate and sustain stable uniform and homogenous non-thermal atmospheric plasma.

Massines et al. [1], Okazaki et al. [2], Trunec et al. [3] and Roth et al. [4] successfully generated atmospheric pressure glow discharges with a dielectric barrier array, and Selwyn et al. [5] developed an atmospheric pressure plasma jet producing a stable and homogenous plasma. There are two approaches based on the Paschen similarity law (p·d=const.), which scale down the electrode dimensions to the µm range in order to ignite discharges at atmospheric pressure at moderate voltages working in the Paschen minima of the different gases.

Schoenbach et al. [6], Schmidt-Böcking et al. [7] and Eden et al. [8] use a micro hollow cathode array. We introduced micro-structured electrode arrays (MSE) consisting of an interlocked comb like electrode system with µm gap widths [9-12]. The electrodes are arranged on an insulating substrate and are manufactured by means of modern micro machining and galvanic techniques.

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With the MSE array it is possible to decompose perfluorocompounds (PFCs) [13]. 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 [14].

Another application of the MSE plasma source is the synergetic result of sterilisation and coating of food packaging materials. The reactive species of the plasma lead to a physical destruction of the spores´ cell walls and the deposition of thin films as a diffusion barrier results in a refinement of the packaging materials. In our sterilization experiments the thermo resistant spores of the vegetative bacteria Bacillus cereus (B.cereus) and the UV resistant spores of the fungus Aspergillus niger (A. niger) were chosen. Both types use a mechanism to protect their DNA against radiation below 300 nm. The endospores of B.cereus are protected by the spore specific substance 2,6-pyridine-dicarboxylic acid. This substance has absorption maxima at 275 nm and 220 nm with absorption coefficients of $5.0 \cdot 10^5$ l/mol·m and $8.5 \cdot 10^5$ l/mol·m respectively. The A.niger konidiospores are protected by the black pigment coating.

This publication presents the deposition results in various gas mixtures and pressure ranges, compares the ignition pathways in a RF and DC driven plasma and excludes radiation as the dominant sterilising agent down to 130 nm.

2. Experimental

Figure 1 shows a MSE array and the electrode gap design to support the ignition of the plasma. The processing of the MSE arrays is already published [14]. The characteristic MSE dimensions are electrode width (1350 µm), electrode thickness (70 µm) and electrode gap width (70 µm) in order to achieve high pressure ranges.

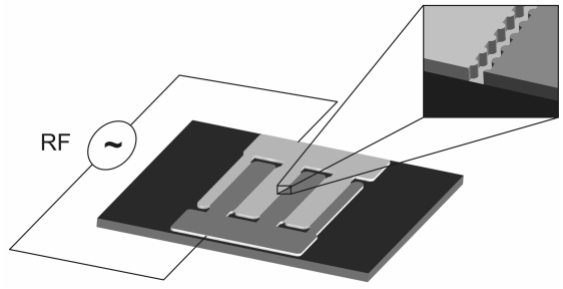

Fig. 1: Scheme of a Microstructured Electrode array

The sterilization and deposition setup consists of the MSE plasma source and an additional coplanar installed movable electrode plate at a variable distance of 2 mm - 9 mm. This electrode serves as a carrier for the substrates and is also biased with variable acceleration potentials (i.e. AC and pulsed DC voltages with various frequencies) to bridge the gap between the MSE and the substrate for the reactive species formed in the plasma. The acceleration potential signal is produced in a waveform generator (Stanford Research Systems, DS 345), afterwards amplified and finally transformed with a coil as shown in figure 2.

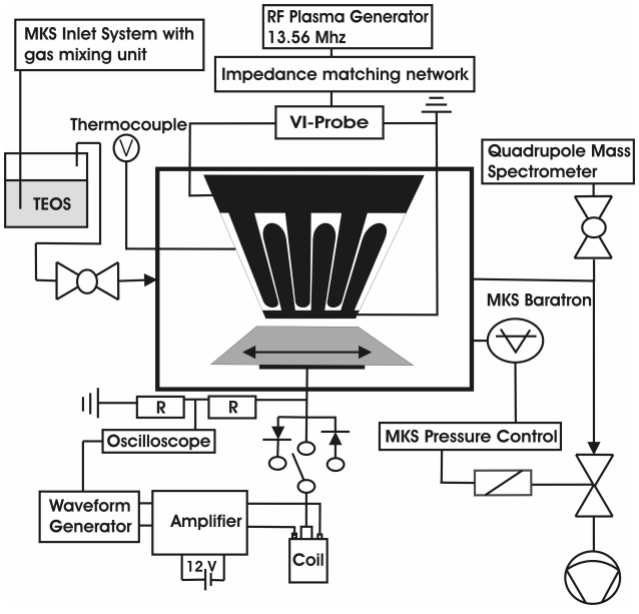

Fig. 2: Schematic view of the experimental setup

The output signal can also be rectified with a high voltage diode in order to investigate AC and pulsed DC with both polarities. A gas flow rate between 1 sccm and 200 sccm is set up by means of mass flow controllers. The discharges are generated using a RF power supply at 13.56 MHz (ENI, ACG-3B) equipped with a matching network (ENI, MW-5D). Between the matching network and the plasma source a special probe is inserted in order to measure voltage, current and phase angle of the system. Other plasma characterising devices are the optical emission spectrometer consisting of a CCD camera system (La Vision, Flame Star 2F) and a VUV photomultiplier (Hamamatsu R7639).

3. Deposition Results

To deposit SiO_2 layers on various substrates the precursor molecule tetraethoxysilane (TEOS) was used. This substance was added into the buffer gases (He, Ne, Ar and N_2) with a bubbler as shown in figure 2. The feed gas with the precursor and 1% of oxygen was conducted into the plasma reactor with a fixed flow rate (200 sccm) by a gas mixing unit. The deposition experiments were tested on various substrates like PET, PP, PS, copper and silicon with a similar deposition period of 300 s. The acceleration potential on the coplanar installed electrode in a distance of 6 mm to the plasma source was performed by a sine potential with f = 9.5 kHz leading to a maximum voltage of 1800 Vpp. The applied RF power ranged from 22 W to 32 W in Ar and from 30 W to 35 W in nitrogen.

The results showed no thermal damage of the substrates independent of the substrate material and the buffer gas. The deposition experiments led to adhesive layers on PET, PS, copper and silicon with the buffer gas nitrogen up to 300 hPa and the buffer gas argon up to 1000 hPa, respectively. The deposited layers are apparent by iridescence effects on the surface of the substrates. These effects are primarily visible at the boundaries of the area exposed to the plasma.

The usage of helium and neon led to non-adhesive amorphous powders. Polypropylene was not a suitable substrate for deposition experiments. The deposition experiments with polypropylene (PP) as substrate showed non adhesive layers obtained in all applied buffer gases and pressures removable with 70 % ethanol solution. Confirming this observations IR spectra have been made approving the complete removal.

Characterization of the deposited layer by profilometry and ellipsometry

To determine the thickness of the SiO_2 layer a trench was etched into the SiO_2 layer. Therefore a photoresist was spun on the layer and photolithographically structured. Afterwards the trench was etched into the SiO_2 layer with a buffered hydrofluoric acid (20 %).

Figure 3 shows the result of a 3D-scan of the trench. The measurement has been carried out with a Tencor P10 Profilometer. The scanned field is 5mm in depth and 2 mm in width. The resulting thickness of the SiO_2 layer ranges from 350 nm to 700 nm. This results in an average coating rate of 1,6 nm/s.

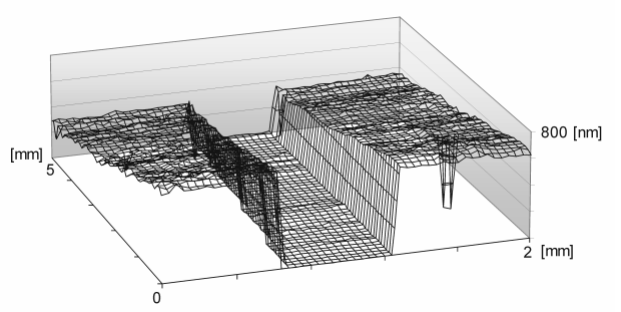

Fig. 3: 3D-scan of a trench in the SiO_2 layer recorded with a profilometer

Additionally the measured values of the 3D-scan made it possible to calculate the RMS (Root-Mean-Square)-roughness of the surface of the deposited SiO_2-layer. The RMS-roughness of the SiO_2-surface is 14,09 nm. This corresponds approximately 2-4 % of the SiO_2-layer thickness. The refractive index of SiO_2 has been determined by ellipsometry with 1,476 showing a good accordance with the literature value of 1,460 for thin films [15].

Characterization of the deposited layers with IR-spectroscopy

In order to obtain IR transmission spectra of the deposited layers roughly independent from the substrate a graising incidence reflection (GIR) unit was applied.

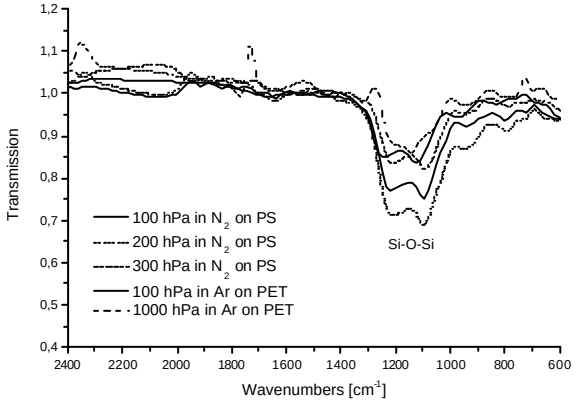

Fig 4. Infrared spectroscopy results with a graising incidence reflection (GIR) unit

To obtain the transmission spectrum the absorption spectra of the bare and coated substrate were measured. Each absorption spectrum of the deposited substrate was divided by the bare one leading to the characteristic spectra shown in figure 6 with the Si-O-Si specific peak at 1100 cm^{-1}. The spectrum also shows a pressure and buffer gas dependent growth. Apparently the ratio between oxygen and tetraethoxysilane and also the applied buffer gas play a significant role in the deposition mechanisms.

4. Comparison between DC and RF driven plasmas

With optical emission spectroscopy we tried to approve the theoretical interpretation of the remarkable difference between the breakdown voltages required to ignite a RF or a DC plasma at atmospheric pressure published in [16]. In the case of DC plasma in helium voltages around 351 V are necessary instead of the RF case where only 248 V are sufficient to ignite the plasma with our MSE. This difference cannot only be described with lowering effects of the high frequency regime or field electron emission. The reason is the main difference between AC (RF) and DC. For AC the voltage passes through a sinusoidal curve with the two extreme values $\pm U_0$ and two nodes during each period, whereas for DC the voltage is constant. The ionization energy of He (24.6 eV) is significantly higher than the ionization energies of N_2 (15.6 eV). Additionally, N_2 has much more electronic and vibrational states lower than the ionization energy of He. These excited states cause an additional loss of electron kinetic energy missing for the ionization process of He. The lowest excited state of He ($^3S_1$, 19.8 eV) possess energy, which is still higher than the ionization energy of N_2. Therefore, electrons with kinetic energies lower than 19.8 eV cannot excite He in contrast to N_2.

The measured RF breakdown voltages are effective voltages (rms values) which periodically increase to a value of $U_0 = 2^{1/2} \cdot U_{IP}$. The voltages higher than U_{IP} provide a much higher ionization probability for He. Concurrently, the voltages significantly lower than U_{IP} are not high enough to excite He. The electrons accelerated in an electric field with a strength of $E < E_{IP}$ (ignition field strength) are still able to excite rotational and vibrational states of N_2.

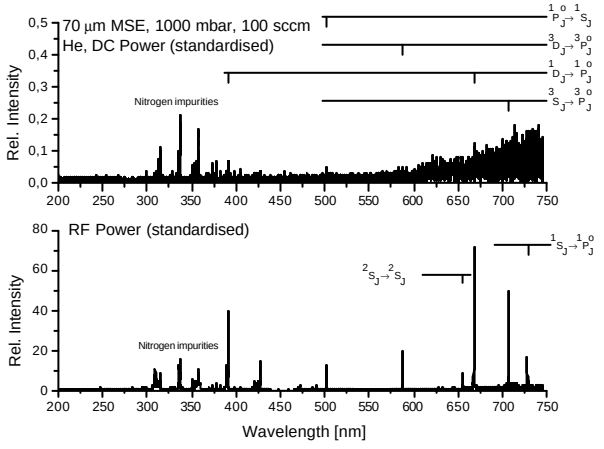

Fig. 5: Emission characteristics at 1000 mbar (DC/RF) in helium

If we compare the emission characteristics in figure 5 we see a remarkable difference between the signals´ relative intensities in the RF and the DC case. About two orders of magnitude difference are observable. Confirming the theory the DC setup was not capable to excite helium to electronic states in contradiction to the RF setup.

5. Sterilisation experiment

We successfully sterilized 10^6 spores of both mentioned types of microorganisms inoculated in 50 µl spore suspension. Therefore the spore suspension was placed on the polymer foils and exposed to the noble gas plasmas in He and Ar at atmospheric pressure. The effective power amounted 15 W and 13 W respectively. After a treatment period of 240 s the spores were pressed on the spore specific ager medium to detect viable spores. With this method it was only possible to detect the total deactivation.

In order to investigate radiation as sterilizing agent emission characteristics between 130 nm and 800 nm have been measured and showed no influent transitions leading to deactivation mechanisms of the spores.

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