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Characterization of stationary and pulsed inductively coupled RF discharges for plasma sterilization

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Abstract

Sterilization of bio-medical materials using radio frequency (RF) excited inductively coupled plasmas (ICPs) has been investigated. A double ICP has been developed and studied for homogenous treatment of three-dimensional objects. Sterilization is achieved through a combination of ultraviolet light, ion bombardment and radical treatment. For temperature sensitive materials, the process temperature is a crucial parameter. Pulsing of the plasma reduces the time average heat strain and also provides additional control of the various sterilization mechanisms. Certain aspects of pulsed plasmas are, however, not yet fully understood. Phase resolved optical emission spectroscopy and time resolved ion energy analysis illustrate that a pulsed ICP ignites capacitively before reaching a stable inductive mode. Time resolved investigations of the post-discharge, after switching off the RF power, show that the plasma boundary sheath in front of a substrate does not fully collapse for the case of hydrogen discharges. This is explained by electron heating through super-elastic collisions with vibrationally excited hydrogen molecules.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Inductively coupled plasmas (ICPs) using radio frequency (RF) excitation have considerable potential for technological applications. Recently, plasma sterilization [1], in particular, the treatment of food packaging [2, 6], and bio-medical materials has been investigated [3, 5].

Common sterilization methods like autoclaves, ovens or different chemical processes such as treatment with ethylene oxide (ETO) and hydrogen peroxide (HPO) have various disadvantages. Medical implants are made of, e.g. polylactide, ultra-high molecular weight

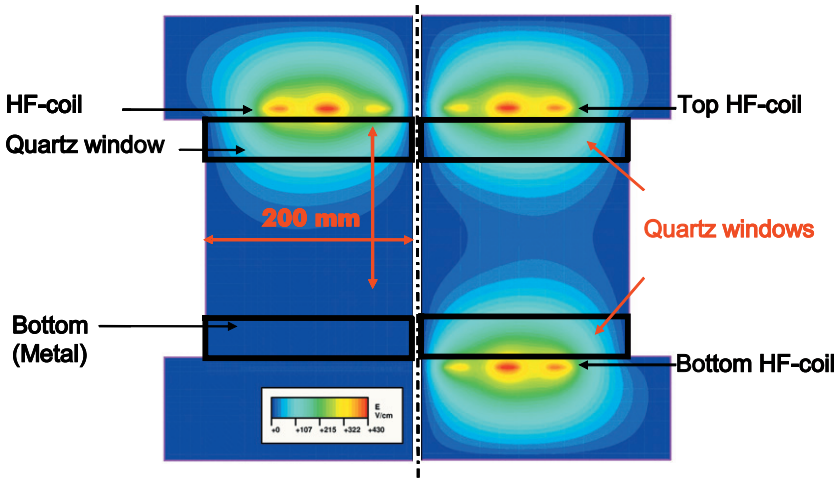

Figure 1. Comparison of the induced electric field of the DICP (right) and a common ICP (left).

polyethylene (UHMWPE), titan and combinations of them. Depending on the material the implant should not be exposed to water, HPO or high temperatures. In the case of ETO, especially, there are toxic residues which can take days to diffuse out of the implant.

The advantages of plasma sterilization are: dry treatment at low temperatures, short treatment times and absence of toxic matter. Gas mixtures of argon with oxygen, hydrogen or nitrogen are used. Depending on the mixture the dominant sterilization mechanisms are UV radiation, etching or ion bombardment.

The homogenous treatment of three-dimensional objects, such as bio-medical materials, demands high plasma uniformity. Common ICPs, however, exhibit inhomogeneities particularly pronounced in the axial direction [10], as can be seen along the vertical axis in figure 1. A double ICP (DICP) has, therefore, been developed to improve axial uniformity of the plasma, providing homogenous reduction of germs and spores [3].

The DICP source can also be operated in pulsed mode. To the knowledge of the authors the effects of pulsing on sterilization has not been investigated in detail. Fundamental investigations have to be, therefore, correlated to sterilization efficiency. Initially, we try to explore basic mechanisms effecting sterilization. Afterwards, micro-biological characterization and correlation to these effects will be investigated. Pulsing provides additional control of various plasma parameters. It also reduces the time average heat strain on the substrate. The process temperature is a crucial parameter for treatment of temperature sensitive objects, such as bio-medical materials.

A pulsed inductively coupled hydrogen plasma, in particular the post-discharge phase, is investigated by means of various diagnostic techniques: time and mass resolved ion energy analysis, phase resolved optical emission spectroscopy (PROES), molecular optical emission spectroscopy (OES), Langmuir-probe measurements and numerical simulations. These investigations provide insight into the additional control of different plasma parameters, in particular electron heating and the corresponding ion bombardment of the substrate.

2. Experimental set-up

Plasma sterilization experiments have been carried out in the above mentioned DICP. The DICP has a planar coil at both the top and bottom of the reactor, each separated from the

chamber by a quartz plate (at each side). The chamber is 40 cm in diameter and 20 cm in height, which is sufficient volume for a hip joint. A matching unit distributes the power (max. 5 kW @ 13.56 MHz) equally between the top and bottom coils. The discharge can be operated using various gases, e.g. mixtures of argon with oxygen, hydrogen or nitrogen (typically: 1.3 kW, 10 Pa, 100 sccm Ar, 20 sccm H_2). For micro-biological investigations flat substrates of glass have been contaminated with different germs and endospores (*B. subtilis*, *B. stearothermophilus*, *A. niger* and others). Here, only reduction of *B. subtilis* endospores is shown. The substrates have been contaminated by spraying a mono-layer of 10^6–10^7 spores, or by a cyto-centrifuge applying ten dots around 10^5 spores.

In figure 1 the induced electric field simulated by a hydro-electrodynamic model is shown [10]. On the left-hand side the inhomogeneity of the induced electric field in the axial direction of a common ICP is clearly visible. The right-hand side shows the improved uniformity in the case of the DICP. In the case of the single ICP mode the electron density decreases in the axial direction, by more than two orders of magnitude in the plasma bulk, whereas, in the DICP mode the decrease is less than an order of magnitude.

A second experimental set-up, providing better diagnostic access, has been used for investigations of the fundamental physics of pulsed ICPs. The discharge chamber is a modified GEC reference cell. Several modifications have been made to the original GEC reference design in order to improve performance for inductive coupling. A bifilar (double spiral) antenna, 12 cm in diameter, is used and the stainless steel housing around the antenna is replaced with a quartz cylinder. In comparison to common single spiral antennae, the bifilar antenna induces a similar electric field with a factor of two smaller voltage drop across the antenna. The residual capacitive coupling is, therefore, strongly reduced. The bifilar antenna also shows an improved homogeneity of the induced electric field. At a distance of 5 cm below the antenna a grounded aluminium electrode limits the discharge region in the vertical direction.

A mass resolved ion energy analyser (Balzers PPM 422) is incorporated into the grounded electrode. The PPM consists of an energy analyser and a quadrupole mass spectrometer. The energy resolution is approximately 0.5 eV and results were taken in 0.3 eV steps. For accurate measurements of ion energy distribution functions (IEDFs) a procedure based on simulations of ion trajectories and extensive experimental checks has been applied [4]. Charge exchange collisions of H_2^+ ions are exploited for accurate energy calibration. The ion fluxes measured with the PPM can be absolutely calibrated using a retarding field analyser (RFA) at the grounded electrode.

The ICP is driven with an excitation frequency of 13.56 MHz. The RF power supply can be pulsed at variable frequencies and duty cycles. To perform time resolved measurements, the detector of the PPM is connected to a multi-channel scaler (MCS) card synchronized with the pulsing of the power supply.

A 2 m spectrograph (Jenoptik PGS 2, 1302 grooves mm^{-1}) is installed for molecular OES. The discharge light is imaged with fibre optics onto the entrance slit of the spectrograph. Spectra are sampled using a diode array, synchronized with the pulsed RF power supply for time resolved measurements. Additionally, a gated ICCD camera (Roper Scientific) is synchronized with the RF power supply for PROES measurements. A commercial Langmuir-probe system (Scientific Systems, Smart Probe) allowing time resolved measurements is also installed.

3. Results

The reduction of germs is defined as the difference between the number of living cells, cell forming units (CFUs) of an untreated assay and the number of CFUs of a treated assay. For bio-medical applications a reduction of 10^6 CFU is desired.

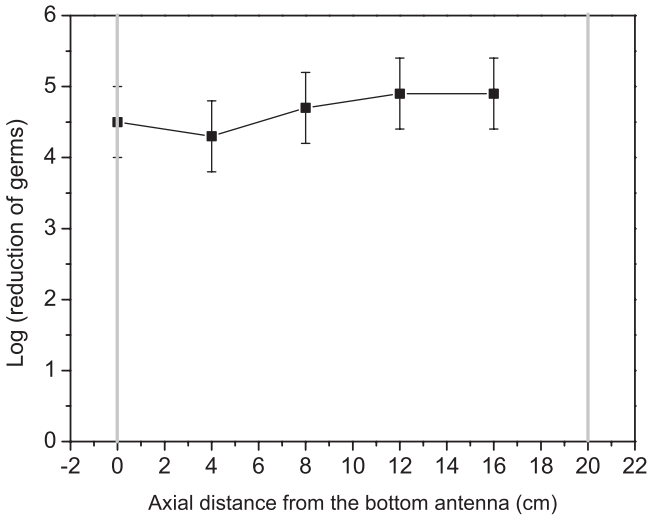

Figure 2. Axial dependence of germ reduction in the DICP. The grey lines in the vertical direction indicate the positions of the quartz windows in front of the two RF-antennae.

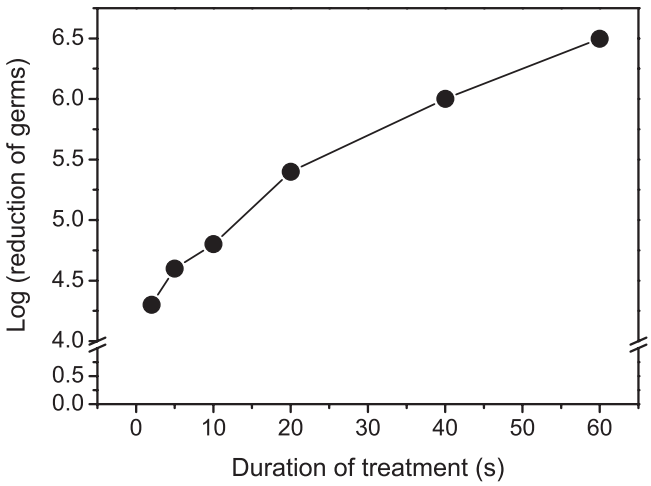

Figure 3. Reduction of germs as a function of the duration of treatment.

As figure 2 shows, sterilization is perfectly uniform within the measurement accuracy of half an order of magnitude, at treatment durations shorter than the saturation time of sterilization.

Depending on the substrate geometry and material sterilization saturation is achieved at durations of 60 s or longer. Figure 3 shows the time resolved sterilization of *B. subtilis* spores on a glass sample. In this case saturation is achieved after around 2 min. The required duration of treatment is shorter than in commonly used sterilization processes with the additional advantage of no toxic residua using argon or oxygen discharges, which has been proved by so-called migration tests. The process parameters were chosen so that sterilization of *A. niger* or *B. stearothermophilus* requires comparable duration of treatment. Different germs and spores are not necessarily reduced in similar times.

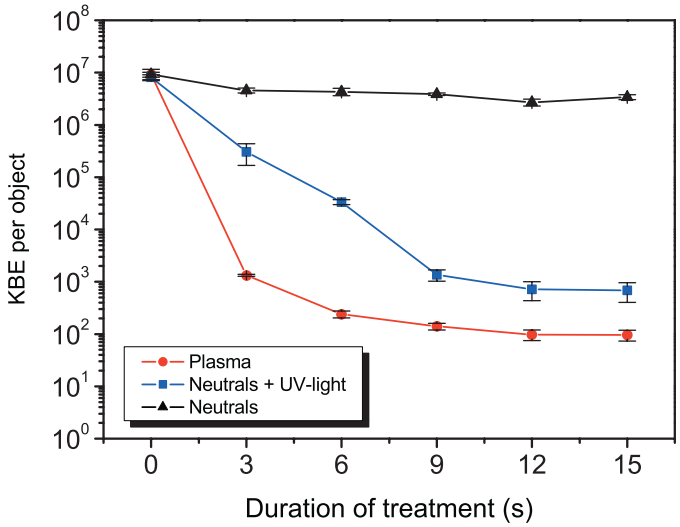

Figure 4. Separate influence on germ reduction of neutral radicals and UV-light in comparison to plasma treatment.

In order to distinguish the effects of different plasma sterilization mechanisms, a contaminated assay can be screened from the plasma by a UV-filter or a metal grid. This allows us to determine the sterilization efficiency of neutral radicals in combination with UV-light and radicals only (figure 4). Treatment by radicals only results in relatively slow reduction of CFU. For longer sterilization durations the combination of radicals and UV-radiation shows an asymptotic behaviour of the efficiency, where the differences between the various mechanisms still remain. Depending on the chemical potential of the radicals the long term differences may even vanish. For short treatment durations, however, exposure to total plasma is around two orders of magnitude more efficient. This difference at short times cannot be compensated by highly toxic radicals such as flourine. The results indicate UV-radiation to be the most efficient individual sterilization mechanism on a short time scale. The temporal behaviour of sterilization, with all mechanisms simultaneously, seems to be initially dominated by a synergy of all three mechanisms. This is in contrast to the proposed sequence of individual mechanisms where UV-sterilization is continued by a combination of etching and deactivation through UV-radiation [5, 6].

Control of the various sterilization mechanisms may be achieved by pulsing of the plasma. Pulsing also reduces the time average heat strain, providing a broader application potential of plasma sterilization for temperature sensitive materials. Detailed investigations of a pulsed ICP have been carried out in the modified GEC reference cell to obtain a better understanding of the fundamental physics of pulsed ICPs. Figure 5 shows PROES measurements in the ignition phase of a pulsed hydrogen ICP operated at 10 Pa with 300 W RF power in the plasma on-phase. Two RF cycles are resolved, with a 2 ns gate width, at various times of the ignition phase in steps of 1 s. The absolute intensity of the measured H_α emission varies over orders of magnitude while the discharge transits from capacitive to inductive power coupling. The plotted modulation, however, is normalized to the time averaged intensity at each time of the ignition. The normalized modulation clearly illustrates the capacitive ignition and the transition to inductive mode. The capacitive coupling is characterized by a pronounced modulation, with one emission maximum per RF cycle, while the inductive mode exhibits a smaller modulation

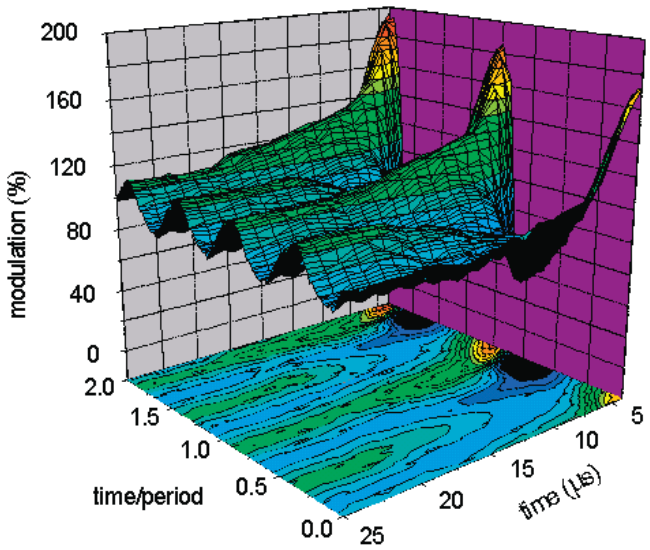

Figure 5. PROES in the ignition phase of a pulsed hydrogen ICP.

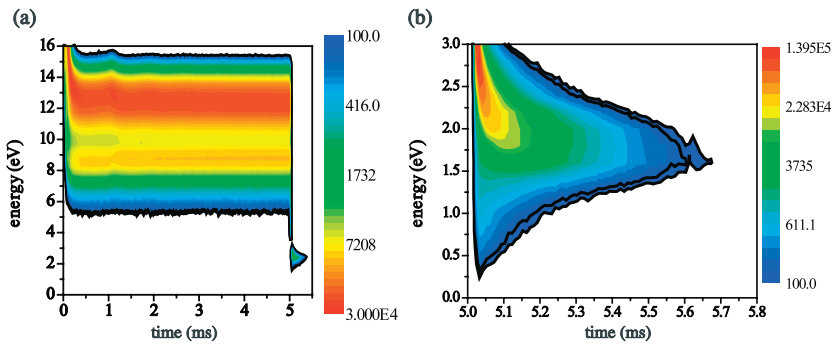

Figure 6. Time resolved IEDFs of H_3^+ in a pulsed hydrogen ICP: (*a*) plasma on-phase + afterglow; (*b*) afterglow in detail.

amplitude with twice the RF frequency. The capacitive ignition is related to comparatively high ion energies during the ignition phase.

The relatively high ion energies are confirmed in time resolved measurements of IEDFs. Figure 6(*a*) shows time resolved H_3^+ IEDFs under the same conditions as for the PROES measurements (300 W, 10 Pa) with a pulsing frequency of 100 Hz and a 1 : 1 duty cycle. The discharge ignites capacitively, with relatively high ion energies exceeding the used energy scale, reaching a stable inductive mode within the order of a hundred microseconds. The mean ion energy, in inductive mode, is around 13 eV. In the afterglow, the ion energy drops rapidly after the RF power is switched off. However, a constant ion energy of a few electronvolts is observed for several hundred microseconds. The H_3^+ IEDF in the afterglow is shown in detail in figure 6(*b*). After a transient phase between the plasma on-phase and the afterglow, a constant ion energy of about 2 eV is observed. Accordingly, time averaged measurements with the RFA also show a peak at 2 eV. The energy of the peak depends on the modulation frequency of the plasma, the duty cycle, the RF power and the gas pressure [7].

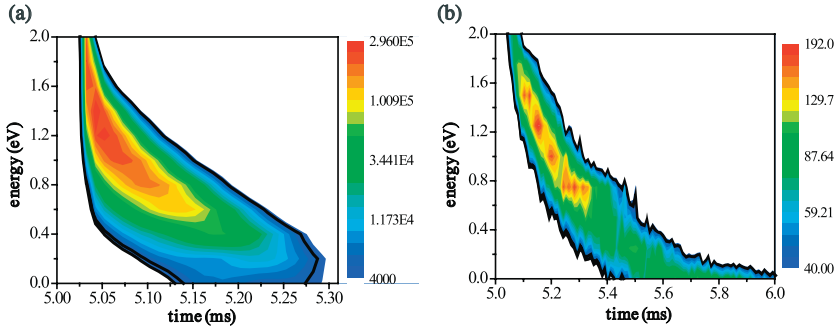

Figure 7. Time resolved IEDFs in the afterglow of a pulsed helium discharge: (*a*) He^+; (*b*) H_3^+.

The IEDF of He^+ in the afterglow of a helium discharge exhibits a different time behaviour. Figure 7(*a*) clearly shows that the ion energy relaxes to zero—the plasma boundary sheath collapses completely. The IEDF of H_3^+ as a small impurity (H_2 diffusing out of the chamber walls) in the helium plasma is shown in figure 7(*b*). The ion energy also relaxes to zero in this case.

There is obviously a difference in the temporal behaviour of the plasma boundary sheath in the afterglow of hydrogen and helium discharges. An ion energy E_{ion} of approximately 2 eV, in the case of hydrogen, corresponds to a boundary sheath potential caused by electrons of $k_{\mathrm{B}}T_{\mathrm{e}} = 0.5\,\mathrm{eV}$, as confirmed by Langmuir-probe measurements.

$$E_{\mathrm{ion}} = k_{\mathrm{B}}T_{\mathrm{e}}\frac{1}{2}\left(1 + \ln\left(\frac{M_{\mathrm{ion}}}{2\pi m_{\mathrm{e}}}\right)\right). \tag{1}$$

Here, m_{e} is the electron mass and M_{ion} the ion mass—in this case, the mass of H_3^+. The finite electron temperature can be explained by an energy transfer from vibrationally excited hydrogen molecules to electrons in the afterglow of the hydrogen discharge [7]. Vibrationally excited hydrogen molecules have a lifetime of several hundred microseconds or longer [8]. They can, therefore, act as an energy reservoir for electrons between the plasma on-phase and the post-discharge. The observed dependence of the ion energy in the afterglow on various plasma parameters is in full agreement with the measured vibrational excitation of molecular hydrogen [7]. The vibrational excitation is measured by molecular OES. Analysis of the diagonal Fulcher-bands allows us to determine the relative populations in the electronic ground state of hydrogen molecules up to $v = 4$ [9]. Langmuir-probe measurements and numerical simulations of the hydrogen post-discharge also confirm the electron heating through super-elastic collisions with vibrationally excited molecules [7].

4. Conclusions

A DICP for homogenous plasma sterilization has been developed and investigated. Efficient germ reduction of more than six orders of magnitude within 1 min has been achieved. The sterilization is perfectly uniform within the measurement accuracy of half an order of magnitude. Various sterilization mechanisms, such as UV-light, neutral radical treatment and ion bombardment were separated. Sterilization through UV-light seems to be most efficient under the conditions investigated. An indication of synergistic effects is also observed. Pulsed plasmas can be used for the treatment of temperature sensitive materials with lower heat strain. There is, however, a lack of fundamental understanding of the physics of pulsed plasmas. A pulsed ICP, in particular the post-discharge phase, has been investigated by means of various

diagnostic techniques: time and mass resolved ion energy analysis, PROES, molecular OES, Langmuir-probe measurements and numerical simulations. PROES measurements show that a pulsed ICP ignites capacitively with comparatively high ion energies and turns inductive after a hybrid transition phase. Time resolved measurements of IEDFs confirm the capacitive ignition. The measurements also show a surprising finite ion energy in the afterglow of a hydrogen discharge. The plasma boundary sheath does not fully collapse due to electron heating through super-elastic collisions with vibrationally excited hydrogen molecules in the afterglow. The finite post-discharge boundary sheath, in front of the substrate, might limit the desired process control through separation of various processes by pulsing; e.g. the separation of neutral radical treatment and ion bombardment in the post-discharge phase can be hindered.

Acknowledgment

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