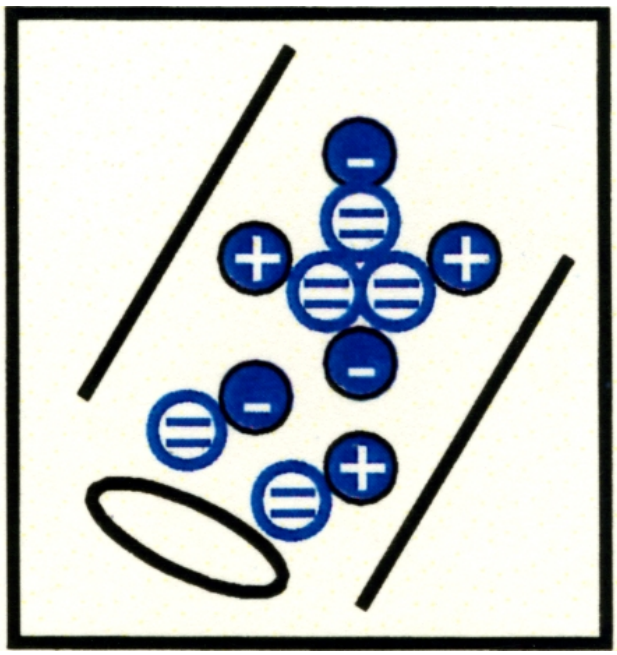
Frontiers in Low Temperature Plasma Diagnostics 8



19th - 23th April 2009
Blansko, Czech Republic

Book of abstracts

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Invited lectures

Atmospheric pressure plasma diagnostics by OES, CRDS and TALIF

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Nanosecond repetitively pulsed discharges were used to generate atmospheric pressure plasma in preheated air or nitrogen. In order to understand the physico-chemical mechanisms that control the concentrations of active species, *in situ* optical diagnostic techniques were developed. The ground state of atomic oxygen was measured by Two-Photon Absorption Laser Induced Fluorescence (TALIF), the $N_2(A)$ was measured by Cavity Ring Down Spectroscopy (CRDS), and the $N_2(B)$ and $N_2(C)$ were measured by optical emission spectroscopy (OES). The challenges of these plasma diagnostics and the approaches to solve them are presented.

Atmospheric pressure air plasmas are increasingly used for surface treatment and activation, exhaust gas control, aerodynamic flow control, plasma assisted combustion, and destruction of toxic compounds [1]. The efficiency of these processes strongly depends on the energy requirements of the plasma sources employed. Here, we use a nanosecond repetitively pulsed (NRP) discharge generated in a pin-to-pin electrode configuration (gap distance 5 mm), in preheated atmospheric pressure air or nitrogen at 1000 K, (flow rate 1-17 m/s), by 10-ns short high voltage pulses (5-8 kV) at a pulse repetition frequency of 10 kHz. These discharges are non-thermal plasma characterized by low energy requirements, a few W/cm^3, for production of electron densities of about 10^{12} cm^{-3}, with electron temperature of the order of 20000 – 50000 K, well above the gas temperature [2].

Plasma-assisted combustion is one of the current applications of NRP discharges. These discharges have been successfully employed for flame ignition and flame stabilization [3]. For understanding the plasma physics and chemistry there is a strong need to investigate the channels of production and to obtain quantitative measurements of the concentrations of the key species of interest. These can be either the reactive species used for a specific application, or those that control the production of such reactive species. However the small plasma volume (1-5 mm^3) and the short lifetime of plasma species (tens to hundreds of nanoseconds) limit the available diagnostic methods.

The atomic oxygen is a key species in the plasma assisted combustion process. The formation of O in NRP plasma was suggested to be via a fast two-step mechanism. Excited molecular nitrogen, such as $N_2(A,B,C)$, are formed by electron impact excitation. Next, they produce atomic oxygen by dissociative quenching in reaction with O_2, with heat release. In order to validate this prediction, time-resolved measurements of these species have been performed.

The ground state of atomic oxygen was measured by Two-Photon Absorption Laser Induced Fluorescence (TALIF) [3]. Several challenges have to be addressed using this diagnostic. These include the necessity of performing a fluorescence calibration using Xe gas, working in the non-saturation regime (no depletion of fundamental level), measurements/calculation of quenching rates and (the dominant processes at atmospheric pressure), ionization rates, and measurements of the second order correlation function (a laser characteristic: photon bunching). These issues will be addressed in the talk. Time resolved measurements down to 6-ns (limited by the laser pulse length) were performed.

The metastable $N_2(A)$ was measured by Cavity Ring Down Spectroscopy (CRDS) [4]. Because its radiative lifetime is on the order of seconds, $N_2(A)$ can constitute a reservoir of energy for many chemical reactions of nitrogen-containing plasmas. Its detection by CRDS has the advantage of no calibration requirements. However many difficulties are present. High temperature gradients in the discharge region result in laser beam-steering inside the optical cavity. This problem is solved by a proper design of the cavity. Spatial, spectral filtering and mode matching optics were used for adequate coupling of the laser beam inside the cavity. Another important issue was the concentration variation of the species during the CRDS decay time. Time resolved measurements down to 100-ns were performed using a time-dependent data analysis. The plasma temperatures were determined from the spectrally resolved rotation-vibration-electronic absorption transitions.

Furthermore, the densities of $N_2(B)$ and $N_2(C)$ were measured by fast optical emission spectroscopy (OES). Absolute densities were determined by

calibration using a tungsten lamp and based on the spectral simulation software SPECAIR [2]. Rotational, vibrational and electronic temperatures were obtained from spectral fits. Measurements with a time resolution down to 2 ns were obtained.

Space-resolved measurements were also performed. An Abel inversion was used to obtain the radial distribution of the species from the integrated lateral intensities (emission or absorption experiments), which were measured perpendicular to the axis of the axisymmetric discharge. Prior to the Abel inversion, the lateral spatial profiles were corrected for the instrumental convolution.

The obtained results are valuable for the understanding of discharge behaviour and induced plasma chemistry.

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Diagnostics of Negative Hydrogen Ion Sources for ITER: A Comparative Study

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Different diagnostics techniques are used to measure spatially and temporal resolved negative hydrogen ion densities and electron densities in low pressure RF plasmas operating at high power. Advantages and disadvantages of the methods are discussed and the results are compared.

1. Introduction

Large high power RF sources operating at low pressure in hydrogen and deuterium are the basis for the powerful neutral beam injection system for ITER [1]. A negative deuterium ion current density of 200 A/m^2 uniform over an area of 1.9×0.9 m^2 for one hour must be provided from a low temperature plasma. The negative ion source development at IPP is carried out at prototype sources of the size of 1/8 and 1/2 of the ITER source [2]. At the required low pressure of 0.3 Pa negative hydrogen ions are produced by the surface mechanism, i.e. the interaction of hydrogen particles with a cesiated surface with low work function. In order to optimize the source parameters suitable techniques for measuring absolute densities of negative hydrogen ions and electrons resolved in space and time are mandatory.

2. Diagnostic methods

The techniques have to deal with the difficult environmental conditions of high-power RF-driven sources (100 kW power at 1 MHz frequency). In order to take advantage of their specific strengths different methods have been applied.

For measurements of negative hydrogen ions cavity ringdown spectroscopy (CRDS) [3], laser photodetachment (LD) [4] and optical emission spectroscopy (OES) [5] have been used. CRDS as a purely optical approach is insensitive to RF-interference and yields very reliably the absolute line-of-sight integrated density, however, it requires proper and stable alignment. The LD technique allows spatially resolved measurements of the negative ion to electron density ratio and is very sensitive on RF-interference since it utilizes a Langmuir probe system. Using the OES line-of-sight averaged results are obtained from the Balmer line ratio H_α/H_β and data analysis with a collisional radiative model. OES offers the most stable and simple setup with a good time resolution.

Electron densities are measured with a Langmuir probe system using the conventional setup [6] and by utilizing the Boyd-Twiddy setup [7]. The spatial resolved measurements are complemented by line-of-sight averaged results from OES using the Balmer line ratio H_β/H_γ.

3. Results

Measurements of negative ion densities are in clear correlation with the extracted ion current densities. Depending on input power and caesium conditioning of the source, i.e. optimisation of the negative ion production, the densities range typically between 10^{16}–10^{17} m^{-3}. Density ratios of negative ions to electrons of 0.2–1.5 are obtained near the cesiated surface showing that negative ions can not be treated as a minority in these plasmas any longer. Taking into account that all three diagnostics measure at different locations a good agreement is observed.

The electron density increases with pressure and slightly with RF power, and varies with the amount of negative ions which indicates that the electrons are pushed away in order to keep quasineutrality. Thus high currents of negative ions are accompanied by a reduced amount of electrons. Temporally resolved measurements show clearly the influence of the beam extraction. The agreement between Langmuir probe measurements and OES results is satisfying keeping in particular in mind the experimental effort.

OES has been benchmarked with the other techniques and is now used as simple-to-use monitor.

In conclusion, valuable information about the negative ion density and the electron density in the source close to the extraction area has been obtained by applying the diagnostic techniques which complement each other.

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Optical diagnostic studies of non-equilibrium plasmas and high speed flows

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A series of optical diagnostic studies of plasma assisted combustion employing single and two photon LIF as well as pure rotational CARS are presented, along with recent advanced in ultra-high frame rate (up to 1 MHz) Planar Doppler Velocimetry and NO and OH PLIF.

Several recent applications of optical diagnostics to non-equilibrium plasmas and high speed flows will be presented. The first part of the talk will focus on diagnostic studies of hydrocarbon oxidation mechanisms under conditions of extreme thermal non-equilibrium. Large non-equilibrium, initial pools of important hydrocarbon combustion intermediate and electronically excited air species are created in a short pulsed fuel-air plasmas, created using ~10-20 nsec duration – high (~20 kV) voltage pulsers, capable of operation at repetition rates as high as 40-50 kHz. This part of the talk will particularly focus on recent measurements of absolute atomic oxygen and NO measurements, by two photon and single photon laser induced fluorescence, respectively, and pure rotational CARS thermometry. As an example Fig. 1 shows absolute atomic oxygen mole fraction in air and in a Φ = 0.5 ethylene-air mixture at 60 torr and approximately 300 K as a function of time after initiation of a single, 20 nsec discharge pulse, along with predictions from a fuel oxidation plasma kinetic modeling code which has been assembled over the last several years at OSU [1]. Relative intensity data was put on an absolute scale using the Xe calibration method described by Nieme, et al [2]. It can be seen that in air oxygen atoms peak on a time scale of ~10-100 μsec after discharge initiation due to collisions with nitrogen metastable molecules $N_2(A^3\Sigma) + O_2 \rightarrow N_2(X^1\Sigma) + O + O$. It can also be seen that O atom decay in the presence of ethylene is faster, by approximately three order of magnitude, due to processes such as $O + C_2H_4 \rightarrow CH_3 + HCO$ which is relatively rapid ($k \sim 4.9 \cdot 10^{-13}$ cm^3/s) at ~300 K. Modeling results will be presented which predict that the observed rapid reaction of O atoms with ethylene initiates a series of exothermic low temperature oxidation processes, resulting in substantial heating (~500-700 ^{o}C) and, in some cases, ignition.

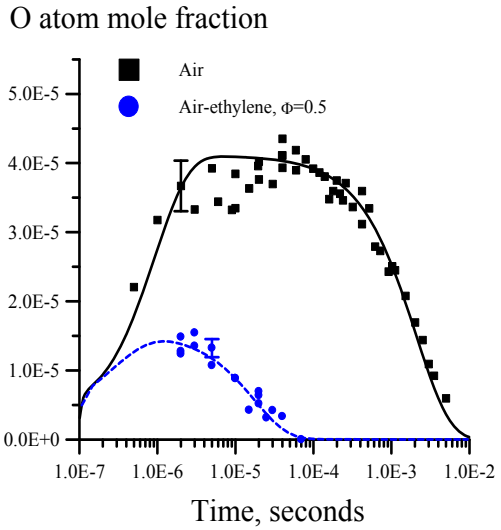

Fig. 1: *Absolute O atom mole fraction in air and Φ = 0.5 ethylene-air at 60 torr and 300K as a function of time after initiation of a single, 20 nsec, 20 kV discharge pulse, along with OSU PAC modeling code predictions.*

The second part will focus on recent advances in ultra high (up to one MHz) frame rate imaging, in particular quantitative Planar Doppler Velocimetry studies in Mach 2 shear layers, and demonstration of NO and OH PLIF at 500 kHz and 40 kHz, respectively.

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Plasma diagnostics using electron paramagnetic resonance

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Using absorption spectroscopy in microwave region, one is able to determine absolute densities of many atoms, molecules and excited states. This paper gives overview of the electron paramagnetic resonance (EPR) technique and several examples of measurements done with this method.

1. Introduction

One of the tasks of low temperature plasma diagnostics is to detect all important species present in the plasma. When not only their presence but also the absolute concentrations are requested, the choice of suitable methods is reduced.

In molecular gas plasmas the atoms play quite substantial role and obviously, their density is needed. The relatively high energy of first excitation level of many atoms practically excludes direct optical absorption spectroscopy. Mass spectroscopy of reactive atoms has also some problems, mainly due to the high (and rather unknown) recombination coefficient of these atoms on metallic walls of extraction orifice.

Currently the obvious choice is to use two photon absorption laser induced fluorescence (TALIF). It is well established, gives reliable results and is commercially available. However, due to nonlinearity of the absorption process, indirect nature of fluorescence and certain assumptions about quenching, it can advantageous to use some other absolute method, e.g. for verification.

2. Principle of EPR

The phenomenon of resonant absorption of high-frequency energy in paramagnetic samples placed in magnetic field was first described by Zavoyiskyi [1].

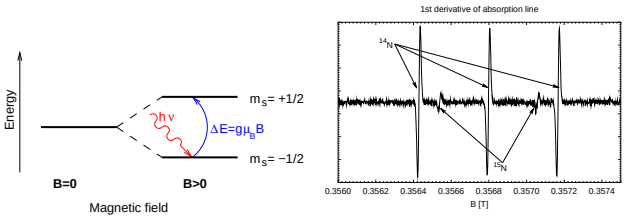

Fig. 1: *Principle of resonant absorption (left) and typical EPR spectrum of N atom (right).*

The EPR method is based on resonant absorption of microwave photons (see Fig.1) by transitions between Zeeman-split [2] energy levels. Necessary condition is thus the existence of non-zero magnetic momentum and the presence of external magnetic field.

3. Plasma diagnostic method

Although the EPR technique is suitable for measurement of absolute densities of many atoms [3], in our works [4, 5, 6, 8, 7, 9] we concentrated on the most prominent (H,N,O). Presence of strong magnetic field can influence the active discharge and therefore the main use is in the afterglow. Typical arrangement for measuring the influence of admixture on the dissociation degree in the afterglow is in Fig. 2.

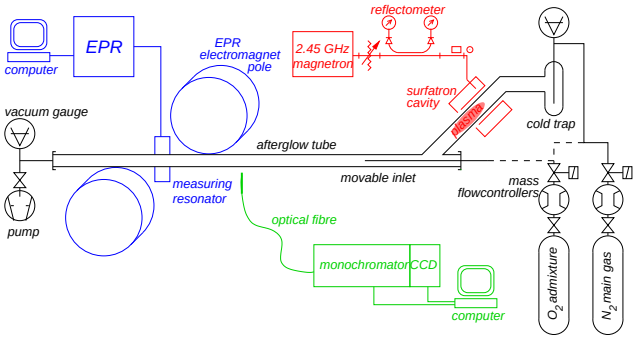

Fig. 2: *Typical arrangement for plasma diagnostics: EPR and OES in afterglow.*

5. Acknowledgements

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Laser-heated emissive probes for the diagnostics of the plasma potential

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While cold probes can only deliver an indirect measure of the plasma potential, emissive probes offer the possibility for a direct determination of this particularly important plasma parameter by their floating potential. This is due to the fact that an electron emission current can flow from the probe into the plasma as long as the probe voltage lies below the plasma potential. In this way the emission current compensates the plasma electron current, thereby shifting the floating potential towards the plasma potential. Eventually the floating potential of the emissive probe presents an acceptable measure of the plasma potential. It is important to note that this method also works if there are electron drifts and beams in the plasma. This is in contrast to other the cold probe method and other methods for a direct determination of the plasma potential.

Recently arrays of emissive probes were also used in fusion experiments to detect plasma potential fluctuations and electric fields to derive the radial fluctuation-induced particle flux and other essential parameters of edge turbulence in magnetized toroidal hot plasmas.[i]

A conventional emissive probe consists of a loop of refractory wire such as tungsten or thoriated tungsten, heated electrically by an external power supply or battery. We have developed various types of emissive probes which consist of just a pin of graphite or LaB_6 of 1,5 mm diameter and 3 mm length, heated by a focused infrared laser beam of 808 nm wavelength delivered by a diode laser with a maximum output power of 50 W.[ii]

Our most recent type of laser-heated probe can also be shifted radially through a plasma column. The laser light is coupled to an optical fibre cable of 0,6 mm diameter and 3 m length. The emerging beam from the fibre cable is transformed into a parallel beam by a lens mounted on a quartz window of the VINETA helicon plasma machine at the IPP in Greifswald. Inside the vacuum chamber the parallel laser beam is focused by a lens with a focal length of 10 cm onto the probe pin. Both, the probe pin, carried by a ceramic tube, and the lens are mounted on a radially movable system so that the focus of the infrared light always stays on the probe pin. In this way the probe can be shifted through more than one half of the VINETA plasma column without perturbation of the plasma by the lens. With this heating system the LaB_6 pin can be heated to more than 1800°C.

The VINETA plasma is produced by a helicon discharge with an RF power of 2 kW creating central plasma densities up to about 10^{19} m^{-3} and an electron temperature between 3 and 5 eV.

In this type of plasma, with graphite pins at a laser power of 50 W we could produce a maximum emission current of 250 mA which was sufficient to compensate the plasma electron current. At the same heating power the LaB_6 pin probe could deliver an emission current of more than 2 A, which makes it suitable for even denser and hotter plasmas. We found slight positive and negative deviations of the emissive probe floating potential from the plasma potential determined from the inflection point of the current-voltage characteristic.

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Kinetics of metal atoms produced in magnetron sputtering plasmas

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We investigated kinetics of metal atoms in magnetron sputtering plasmas by laser-induced fluorescence imaging spectroscopy. We have obtained a lot of knowledge on the two-dimensional distributions of metal atom density, metal ion density, and velocity distribution function of metal atoms. However, we still have open questions on the kinetics of metal atoms in magnetron sputtering plasmas from the fundamental point of view.

1. Introduction

Magnetron sputtering deposition is a well-developed technology used in various industrial fields such as surface coating of mechanical parts and thin film formation in electronics devices. Because of the fact that it is better-developed than plasma-based dry etching and plasma-enhanced chemical vapor deposition, advanced investigation for obtaining deep understanding on magnetron sputtering is rather insufficient to date. In this talk, we will show kinetics of metal atoms produced from metal targets installed in a magnetron sputtering source. We have obtained a lot of fundamental knowledge via the research processes, but we still have open questions on the kinetics of metal atoms in magnetron sputtering plasmas.

2. Diagnostics

We used laser-induced fluorescence imaging spectroscopy, in which the discharge space in front of the target was illuminated by a tunable planar laser beam. The image of laser-induced fluorescence, which was formed on the planar laser beam having a resonance wavelength with an atom or an ion in the plasma, was taken by an charge-coupled device camera with a gated image intensifier (ICCD camera). The picture taken by the ICCD camera represented the two-dimensional distribution of the density of the atom or the ion when the laser intensity was high enough for the saturated excitation. We also obtained the two-dimensional distribution of the velocity distribution function by reducing the laser intensity below the saturation level and by scanning the laser wavelength over the Doppler broadening of the excitation line.

3. Knowledge on the kinetics of metal atoms

We measured distributions of Ti and Ti^+ densities in high-pressure magnetron sputtering plasmas employing a Ti target [1], and examined the sticking probability of Ti atoms [2] and the contribution of Ti^+ ions to the deposition inside narrow trenches [3]. We also investigated the production of metastable Ar in the afterglow of pulsed high-pressure magnetron sputtering discharges [4]. In addition, we measured the distributions of Y, Ba, Cu, YO, BaO, and O densities [5, 6] and Si and H densities [7] in magnetron sputtering deposition of superconductive YBaCuO films and hydrogenated microcrystalline Si films, respectively. The spatial distribution of the velocity distribution function of Fe atoms ejected from the target [8] was valuable knowledge for us to understand the distributions of radical densities in magnetron sputtering plasmas.

4. Open questions on the kinetics of metal atoms

We have obtained better understanding on the magnetron sputtering plasmas by using laser-induced fluorescence imaging spectroscopy. However, we still have open questions on the kinetics of metal atoms ejected from the target. In this talk, we will discuss 1) the production mechanism of Ti^+ in high-pressure magnetron sputtering plasmas and 2) the production process of metal atoms [9].

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Oral presentations

Measuring plasma boundaries via observations of DNA damage

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We used the damage induced by a plasma on DNA samples as an indication of the presence of an atmospheric pressure plasma jet. While plasma emission was observed up to 60 mm from the jet orifice, DNA damage could be detected at distances of up to 200 mm from the jet. This opens up the possibility of a novel method for determining the extent of discharges operated in the open atmosphere.

1. Introduction

Plasmas operated in open atmospheres usually have a clearly visible component, in which high energy electrons induce light emission but the effect of the plasma may extend much further than this, as plasma species diffuse into the surrounding atmosphere. The extent of this open boundary is difficult to quantify as conventional plasma measurement techniques rely on detecting particle species, such as electrons, ions and energetic neutrals, which may exist only at very low density in this extended plasma region..

In this study, we investigated the extent of an atmospheric pressure jet by exposing plasmid DNA in regions close to the jet. The plasmid DNA is very sensitive to impact of low energy electrons, ionic and neutral species. By analysing the damage caused by the plasma to the DNA, the extent of the open plasma boundary surrounding the jet may be determined.

2. Experimental setup

The low frequency atmospheric pressure plasma jet used in this study is made from a 4 mm inner diameter dielectric tube with two ring electrodes around the outside of the tube. Helium is flowed through the tube and a plasma excited inside the tube by a low frequency (3.2 kHz) rf voltage applied to the ring electrodes. This produces a plume of plasma outside the tube. Depending on the discharge conditions, visible plasma emission from the plume extends to up to 60 mm from the tube orifice. Electrical and optical measurements are used to characterise the discharge.

Plasmid DNA (pBR322), extracted from E coli bacteria, was used to detect the presence of species generated by the discharge. The DNA was deposited onto mica substrates that were then exposed to the plasma. Upon exposure, the DNA molecule changes from its natural supercoiled form into two types of damaged forms. The change may be induced by charged particle impact, radical impact and/or the impact of UV photons. The change in DNA structure was determined by analysing exposed samples with a gel electrophoresis measurement.

3. Results and discussion

Measurements of DNA damage were made for varying distance between the DNA sample and the jet orifice. When the DNA sample was placed close to the visible plasma, approximately 70% of the DNA was damaged by plasma exposure. The extent of the damage reduced as the sample was placed further and further from the visible plasma. Although light emission is visible for only 60 mm from the jet orifice, DNA damage was observed at distances of up to 200 mm.

Subsequent measurements have shown that the observed damage is not due to UV photon generated in the plasmas. At present, we believe that the damage must be due to species (electrons, ions or neutrals) generated in the high energy part of the plasma and carried downstream to the DNA sample by the He flow. Further measurements are needed to confirm this hypothesis and to identify the species responsible for the DNA damage.

These measurements indicate the extent of the plasma jet is much larger than the visible plasma, and this conclusion is only possible due to the extreme sensitivity of the DNA samples to plasma species. This method of determining the extent of the plasma should be applicable to a wide range of discharges operated in open air.

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Optical high space and time resolved plasma investigations and application to LIBS in gas/liquids

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In this work single pulse (SP)- and double pulse (DP)- LIBS in collinear configuration on different sets of metallic targets, in air and water, have been studied by spectrally resolved Imaging and theoretical models to find out the fundamental differences in terms of fluidynamic and chemical aspects.

An assessment of the various mechanisms proposed in literature to explain the DP-LIBS signal enhancement is carried out. Results indicate that the substantial difference between SP and DP-LIPs is connected to the different environment where the expansion occurs and that the differences in the spatial and temporal behavior of the plasma expansion can explain the main features of DP-LIPs including signal enhancement and plasma stability. The effect of the interaction of the expanding plasma with the air within the shockwave contact wall is examined in details from both experimental and theoretical point of view [1]. The analysis of data suggests, as a general result, that the SP-LIP can be considered as an "open system" exchanging work (air compression), internal energy (heating and ionization of nitrogen and oxygen) and matter (formation of chemical products from LIP and air particles) with the environment while the DP-LIP is more akin to a "closed system", because it expands in a hot environment and it loses small energy in re-exciting the surrounding particles. Additionally DP-LIBS does not exchange matter via chemical reactions and remains confined inside the contact wall. These peculiarities determine a different recombination route for SP- and DP-LIPs demonstrating higher stability and thermodynamic conditions closer to LTE when DP-technique is performed. This same interpretation also explains what has been observed with DP- and SP-LIBS under water, where this effect is much more marked as a consequence of the higher density and reactivity of water with respect to air. In fact, in case of under water measurements the improvement of the emission signal obtained by the DP-technique represents a unique feature with respect to SP-LIBS, allowing to induce the expanding plasma in a hot water vapor bubble instead of in the liquid water environment[2]. Therefore, DP-technique allows to extend LIP applications in submerged environment where the possibility of obtaining fast elemental analysis in situ is extremely attracting for many applications including under liquid elemental chemical analysis and nanoparticles production.

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Optical emission spectroscopy as a diagnostic for gas temperatures and electron densities in 'liquid plasmas': opportunities and pitfalls.

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In this contribution, the use of optical emission spectroscopy as a diagnostic for plasma temperatures and electron densities in plasmas in and in contact with liquids is evaluated and thoroughly analyzed. Possible pitfalls in interpretation of obtained temperatures and electron densities are discussed.

1. Introduction

Optical emission spectroscopy is often used as a diagnostic tool to investigate atmospheric pressure plasmas in and in contact with liquids but mostly only to identify excited species in application oriented studies [1]. Accurate and reliable diagnostics of plasma temperatures and species densities (such as electron densities) are necessary for a better understanding of the physics and chemistry of liquid plasmas. The typical strong emission of OH(A-X) and hydrogen Balmer lines in liquid plasmas provide a means for obtaining these plasma properties.

2. Results

2.1. Gas temperatures

Although the rotational temperature (T_{rot}) of OH(A-X) is often assumed to be equal to the gas temperature in atmospheric pressure discharges (e.g.[2]), it is observed in liquid plasmas that the rotational population distribution is non-Boltzmann [3, 4]. Even when in some cases a Boltzmann distribution is observed the rotational temperature of OH(A-X) is significantly larger than the one of N_2(C-B) and N_2^+(B-X). This phenomenon occurs not only in direct streamer discharges in liquids and streamer discharges in gas bubbles but also in the diffuse positive column of an atmospheric pressure glow discharge with liquid electrodes.

The non-Boltzman behaviour occurs due to the significant electronic quenching of OH(A-X) by water which inhibits thermalization of the rotational states by rotational energy transfer (RET) in the case of large concentrations of water vapour in the gas phase. This is because the RET rate is of the same order of magnitude as the quenching rate for the typical plasma properties of non-thermal liquid plasmas. As a consequence the rotational population distribution of OH(A) does not reveal a kinetic temperature but rather the OH(A) formation process, similar as in low pressure discharges where the inter-collision time is of the same order of magnitude as the radiative life time of OH(A-X) [5].

Nonetheless, only taking into account the rotational levels smaller than J = 6-12 (depending on the background gas), the T_{rot} of OH is in correspondence with the T_{rot} of N_2 within experimental accuracy.

2.2. Electron densities

Electron densities in direct liquid plasmas and discharges in vapour bubbles are derived from the Stark broadening of the H_α, H_β, and H_γ-lines by comparing the calculated and experimental obtained full line profiles [6]. The obtained electron densities are of the order of 10^{20}-10^{21}m^{-3}. If in the case of H_α fine structure effects are taken into account the differences of the electron densities obtained from these three lines are smaller than 10%[4]. For gas temperatures of the order of 1000-2000 K obtained from the rotational temperatures of N_2, inclusion of the van der Waals broadening improves the comparison of the modelled and experimentally obtained line profile.

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Mid-infrared laser spectroscopy using pulsed and cw quantum cascade lasers

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The application of quantum cascade lasers (QCLs), both pulsed and cw, to absorption spectroscopy will be shown. We will show that accurate densities and rotational temperatures of species in low-pressure plasmas can be obtained using pulsed QCLs even where the measurements are affected by the rapid passage effect occuring in low-pressure conditions. We will also show the potential of external cavity cw QCLs for use in high resolution spectroscopy and sensing applications.

1. General

High power sources of narrow bandwidth coherent mid-infrared (MIR) radiation are highly desirable for research of fundamental and applied science. In the MIR region many molecules have their fundamental vibrations with a high degree of ro-vibrational structure with large absorption cross sections. Pulsed and cw distributed feedback (DFB) quantum cascade lasers (QCLs) are becoming increasingly popular sources for high resolution molecular spectroscopy in the midinfrared region (4 - 10 μm) given their increasingly high output powers and near room temperature operation [1]. These sources are limited however, by their tuning range which is typically of the order of 5 - 10 cm^{-1}. Such a range is suitable for many specific applications involving small molecules with well-defined rovibrational spectra, but is a clear limitation, both for studying complex spectra in the gas phase and in the condensed phase. There has therefore been great interest in the development of external cavity quantum cascade lasers (EC-QCLs) with wide tunability.

2. Results

In particular, the intra-pulse operation mode of pulsed QCLs provides a promising technique for $in situ$ study of fast chemical processes [2, 3]. This is because a complete absorption spectrum may be obtained during a single current pulse of tens up to hundreds of nanoseconds utilizing the frequency down chirp due to resistive Joule heating of the laser. As a result of the chirping, rapid passage (RP) structures will be observed in the absorption spectra of low-pressure gases as the intense rapidly swept radiation passes through a molecular resonance on a timescale that is much shorter than the relaxation time [4], rendering the determined densities inaccurate. QCLs have previously been applied to study plasma processes [2, 5], but mainly outside the pressure regime where the rapid passage effect is observed. However, their widespread application to the study of low-pressure plasmas, which are used extensively in industrial plasma processing, is hampered by the occurrence of this rapid passage effect.

In this contribution, we show that accurate densities and rotational temperatures of species in low-pressure plasmas can be obtained using QCLs even where the measurements are affected by the rapid passage effect [6]. We focus on measuring the CH_4 density in a rf-CCP CH_4 plasma. We demonstrate that by characterizing the density of CH_4 under controlled gas phase conditions with and without rapid passage effects, the latter achieved through buffering the system with Ar and N_2 gas, the measurements in the plasma can be calibrated on an absolute scale. Furthermore, we show that the ratio of the integrated absorptions of two transitions in the obtained CH_4 spectra, which are a measure of the rotational temperature, are not affected by the rapid passage effect.

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Tunable diode laser induced fluorescence on Al and Ti atoms in low pressure magnetron discharges

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Two different blue light laser diodes were used to investigate two type of atoms, namely Ti with resonance transition centred at λ_0 = 398.289 nm and Al with transition centred at λ_0 = 394.512 nm. Tunable Diode Laser Induced Fluorescence (TD-LIF) offers local information and the possibility to follow non-themalized and anisotropic velocity distribution functions (*vdf)* of sputtered particles, in two directions: parallel to the target, v_r, and perpendicular to it, v_Z.

1. Introduction

Magnetron sputtering is a widely used technique for deposition of metallic and compound thin films. Despite of the important progress made in the understanding of elementary processes, a detailed description of the sputtered species, especially in the intermediate and low pressure regime, is still challenging, for both fundamental and applicative reasons. Laser diode systems permitted now to obtain experimental results concerning space resolved *vdf* of metallic species [1,2].

2. Experimental results

The space resolved TD-LIF measurements were performed in two different planar circular magnetron discharges, using two schemes of excitation for the atoms in ground state. The resolution achievable with our systems permitted to investigate the spatial evolution of *vdf* in the plasma. In the low pressure regime a two population distribution can be extracted from the *vdf* [1], showing the presence of both thermalized and energetic atoms.

The measurements on velocity component parallel to the target surface shows a symmetrical profile corresponding to symmetry axes, and a pronounced asymmetrical profile in the other cases [1]. As for the component perpendicular to the target (Fig.1), the *vdf* measurements show a convolution between thermalized particles (centred at v_z=0 km/s on Fig.1) and energetic ones ejected perpendicular to the target (v_Z negative on Fig.1). The energetic component of the distribution decreases drastically when moving away from the target, Fig.1(a), and increases when increasing the discharge current, Fig.1(b). Close to the target, and for a high enough discharge current intensity, the energetic component overcomes the thermalized one (background of atoms), showing a pronounced directional movement.

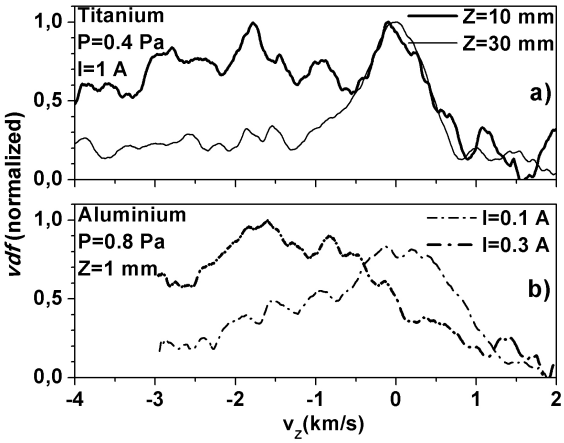

Fig. 1. *Vdf* perpendicular to the target of (a) Titanium atoms, at P=0.4 Pa, I=1A, for two distances from target surface; and (b) Al atoms, at P=0.8 Pa, Z=1 mm, for two discharge current intensities.

2. Conclusions

The experimental results offer a complete view on the evolution of the both *vdf* and flux distribution functions of the sputtered metallic species. The effect of the discharge parameters on these evolutions is made obvious in this contribution.

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Negative ion surface production in hydrogen plasma

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A graphite sample is negatively biased in hydrogen plasma. Upon positive ion bombardment some negative ions are created on the surface and accelerated toward plasma. These negative ions are detected according to their energy by a mass spectrometer facing the sample. Surface production mechanisms are investigated.

1. Introduction

Negative ions in plasmas can be formed through electron attachment on molecules or through positive ion bombardment of surfaces. While the first mechanism is largely studied, few works deal with the second one. However this process can produce a large number of negative ions and could largely improve negative ion sources efficiency if well characterised, understood, and optimized. We have developed a special design of experiment allowing us to detect negative ion formation on various surfaces with the aim of improving hydrogen negative ion sources used in the context of magnetically confined fusion.

2. Experimental results

2.1. Experiment

We measure H^- negative ions by means of a mass spectrometer in a helicon plasma reactor. The H_2 plasma operates between 50 and 1000 W, under low pressure conditions (between 0.2 and 1 Pa). A highly oriented pyrolytic graphite (HOPG) sample centred in the expanding chamber and facing the mass spectrometer nozzle placed 40 mm away is negatively biased. Negative ions formed on the graphite surface upon positive ion bombardment are accelerated toward plasma and are detected according to their energy by the mass spectrometer. We obtain the H^- ion distribution function (IDF) [1]. Special attention has been paid to mass spectrometer tuning and two sets of lens values have been used. One set ensures a constant negative ion transmission function inside the mass spectrometer and constant negative ion extraction from plasma to mass spectrometer whatever negative ion energy. This tuning is used for measuring negative ion relative flux versus surface bias. However, IDF shape is slightly distorted. Therefore a second tuning saving IDF shape has also been used. Positive ion composition is measured by mass spectrometry while electron density and temperature are measured by Langmuir probe.

2.2. Results

An example of negative ion distribution function is shown on figure 1. On this graph is indicated the energy E_0 of a negative ion created at rest on surface and accelerated by the sheath in front of the sample: $E_0 = e(V_p-V_s)$ where V_p and V_s are the plasma and surface potentials respectively. One can see that most ions have energy higher than E_0 indicating they are not created at rest. By studying shape and intensity of these ion distribution functions, we establish the different negative ion production mechanisms. We showed for instance that two electron capture by an incident positive ion is one of these mechanisms. By varying surface temperature we demonstrated sputtering of an adsorbed hydrogen atom as a negative ion is the second mechanism involved under our experimental conditions. While the first mechanism is not strongly dependent on positive ion energy, the second one is producing no ion below threshold for sputtering (20 eV), and is responsive for more than 75 % of negative ion production at positive ion energy equal to 60 eV.

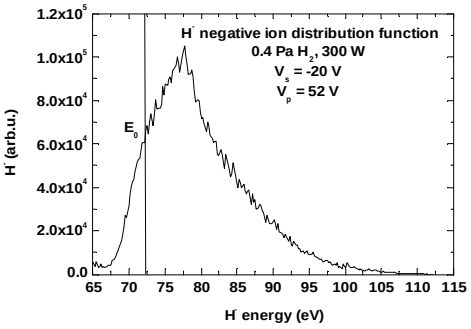

Fig. 1: *Surface produced H- negative ion distribution function in hydrogen plasma.*

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Time resolved studies on pulsed fluorocarbon plasmas using pulsed QCL

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Absorption spectroscopy based on pulsed quantum cascade lasers (QCL) was applied in the mid-IR spectral range of 1269-1275 cm^{-1} (7.86 µm) to measure absolute densities of the precursor molecule CF_4 and of the stable product C_3F_8 formed in pulsed CF_4/H_2 asymmetrical cc-rf (13.56 MHz) discharges with a time resolution of up to 1 ms.

1. Introduction

Fluorocarbon plasmas are of high interest as a model system for plasma chemical investigations and are widely used in technical applications. Their increasing importance and plasma surface interactions which are still not entirely understood motivate fundamental studies of these complex plasmas.

Absorption spectroscopy (AS) in the mid-infrared molecular fingerprint region (3 - 20 µm) has been successfully applied as a versatile plasma diagnostic tool for years. In particular tunable diode lasers (TDL) have been employed for time resolved studies of key transient and stable species, among them the CF and CF_2 radical [1], and the time resolved determination of the rotational temperature of the CF_2 within a single pulse in capacitively coupled radio frequency (cc-rf) CF_4/H_2 pulsed plasmas [2]. Recently, quantum cascade lasers (QCL) have become available as alternative light sources and are increasingly used for plasma diagnostics[3,4] and process monitoring[6].

2. Experimental

The QCLAS measurements of the precursor molecule CF_4 and the stable product C_3F_8 were carried out on pulsed cc-rf CF_4/H_2 plasmas in the spectral range of 1269 - 1275 cm^{-1} using a pulsed thermoelectrically (TE) cooled QCL and a fast TE cooled detector. Laser pulses of 300 ns provided spectral scans of ~ 1 cm^{-1}. The application of QCLAS to low pressure conditions is typically hampered by non-linear effects [5] and requires a careful calibration, especially in the case of complex spectra where single line parameters are not available. Furthermore the measurements were carried out under identical plasma conditions at two spectral positions centred around 1271 and 1274 cm^{-1} respectively to enable a separation of the overlapping spectral contributions of the target molecules.

3. Results

First, effective absorption cross sections of CF_4 and C_3F_8 in the target spectral range were determined and their temperature dependence was studied in the relevant range up to 400 K and found to be non-negligible. Thus, the absorption cross section of CF_4 rises by up to 50 % for a 100 K temperature increase above 296 K whereas the absorption cross section of C_3F_8 decreases by not more than 20 % in the same temperature range. Next, the gas temperature in the plasma was found to be around 390 K which agrees with earlier results based on the simultaneous monitoring of selected absorption lines of the CF_2 radical. During a 1 s plasma pulse a total consumption of ~ 12 % of the precursor gas CF_4 was observed, whereas C_3F_8 appeared to be produced mainly during the plasma "on-phase" and immediately followed the discharge pulse, i.e. with a decay time of < 50 ms. Even under the assumption that C_3F_8 is formed in the plasma from amorphous fluorocarbon layers at the chamber walls, the observed rapid decrease of C_3F_8 in the "off-phase" was not expected for a stable molecule. Very efficient chemical reactions in the "off-phase" or not yet considered spectral contributions (e.g. CF_4 hotbands) could explain this behaviour.

Acknowledgement

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Kinetic processes in nitrogen-argon post-discharge

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This study extends our recent experimental works of the changes in nitrogen-argon post-discharge kinetics. The optical emission spectroscopy was used for monitoring of the influence of different gas pressure and argon concentration on kinetic processes during the nitrogen-argon afterglow.

1. Introduction

Nitrogen-argon mixture is widely used in the various plasma-chemical technologies [1, 2]. The observation of visible light emission up to one second after switching off an active discharge strongly depends on the experimental conditions, e.g. gas pressure and argon concentration and thus the kinetic processes are changed. The kinetic modeling of pure nitrogen was given in [3].

2. Experimental set up

The flowing discharge in nitrogen argon mixture was created in a Pyrex discharge tube with 140 mm electrode distance at constant discharge power of 300 W. Nitrogen purity was 99.999 % and it was further cleaned by impurity traps. Argon concentration was varied in the range of 0% - 83%. The system was pumped continuously by a rotary oil pump and allowed the observations up to the decay time of 140 ms. The total gas pressure (measured by capacitance gauge) was varied in the range of 500 – 5000 Pa. The optical spectra in the range of 300 – 850 nm were measured by Jobin Yvon TRIAX 550 spectrometer. The emitted light was collected by the quartz optical fiber, movable along the discharge tube. The reactor wall temperature was of 300 K.

3. Results

The bands of the nitrogen 1st and 2nd positive and 1st negative systems were recorded in all spectra. Besides them, the weak NO^{β} bands were observed. It was visible, that intensity of these bands increase with the increase of pressure and decay time. The maximum intensity of visible effect – pink afterglow emission was at the decay time of 20 ms – 25 ms. Presented figures show the dependencies of nitrogen 1st positive system 11-7 and 2-0 band head intensities at the decay time of 23 ms. When argon concentration increases the reactions between excited nitrogen atoms and metastable argon are more probable and they lead to the creation of atomic nitrogen that consequently populates the levels $N_2(B\,^3\Pi_g,\ v = 10 - 12)$ by three body recombination. The $N_2(B\,^3\Pi_g,\ v = 2)$ level is dominantly populated by the pooling.

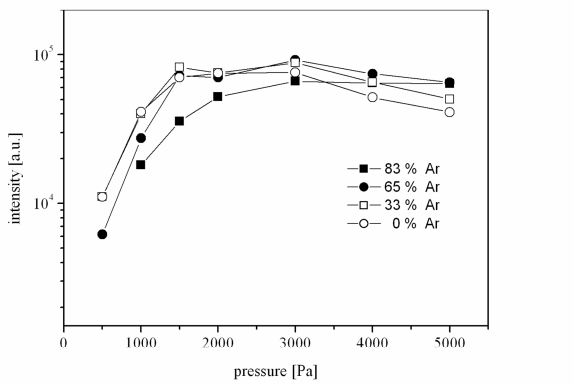

Fig. 1: D*ependence of the nitrogen 1st positive system 11-7 band head intensity on gas pressure for different argon concentration.*

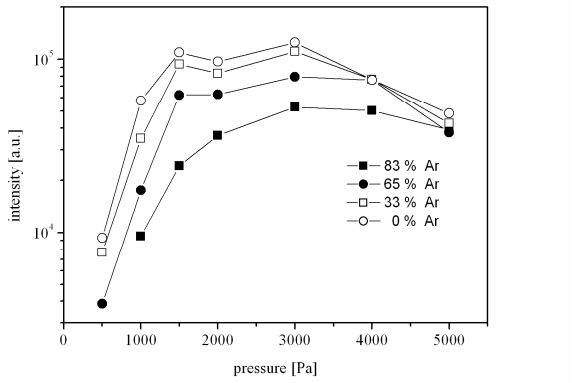

Fig. 2: D*ependence of the nitrogen 1st positive system 2-0 band head intensity on gas pressure for different argon concentration.*

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Acoustic diagnostics of dusty plasma

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Analysis of experimental and theoretical works on the propagation of acoustic waves in heterophase plasma shown that usage of acoustic diagnostics in dusty plasma is advisable. The peculiarities of such systems and their influence on the corresponding dispersion relations are investigated. The gain-phase characteristics of acoustic – type vibrations for acoustic diagnostics are estimated.
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It is known that acoustic diagnostics was applicable to the investigation of nucleation process in PECVD reactor [1]. This and other works deal with such parameters of dusty plasma: phase velocity and damping constant of a definite type of acoustic wave. Within framework of ITER the presence of dust grains in fusion devices has received enhanced attention [2]. It is interesting that special conditions in the edge plasma make some origins of dust with unusual features: high radioactivity, very large chemical activity and so on. Some of these particles can have a significant magnetic moment.

On the one hand we have a regular method of investigations, but on the other hand it demands a specific knowledge about these parameters. Firstly, the comparison between hydrodynamic and kinetic approaches in dusty plasma with dust size distribution is well - handled. Also we evaluated a contribution of the magnetic dipole moment of granules in the tensor of magnetic permeability of dusty plasmas. The interaction of rotating dipole moments with plasma waves result in the Landau damping that does not depend on a wave vector.

According to the results, which are obtained at International Space Station dust-acoustic waves are considered for dusty plasmas containing, besides the electrons and ions, dust particles with continuous mass (size) distributions. For broad size spectra, self-gravitational effects cannot be neglected anymore because in the competition between electromagnetic and gravitational forces, the scale tips over towards gravitation for the heavier dust grains. Self-gravitational effects are clearly interwoven with the grain size distribution and here the effects of different power-law size distributions on the propagation, damping, and instability of low-frequency waves are discussed.

Also fine dust particles (diameter less than 500 nm) can be used as test grains for visualisation of the plasma potential distribution. Larger dust particles can be used as specific probes to determine the sheath structure. The equilibrium position of such grains is determined mainly by gravity and electrostatic forces in the sheath region. This means that the equilibrium position and motion of the grains is strongly dependent on plasma and sheath conditions. Analysis of grain behaviour can provide information on the spatial profile of electric field and the sheath edge location. So, we can use Acoustic Diagnostic and other Transient Motion Technique methods for determination:

1. Size distribution function of dusty particles;
2. Spatial profile of electric field and sheath conditions of edge dusty plasma.

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Influence of a levitating microparticle cloud on metastable density in an Argon discharge

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Spectroscopic evaluation of influence of microparticles on parallel plate RF plasma is presented. Spatial distribution of the emitted spectra is recorded in pristine plasma and plasma with microparticle cloud under same discharge conditions. DIfference in spatial distribution and intensity of Argon spectra lines due to the presence of particle cloud are presented for different pressures. Combining selfabsorption of Ar lines on metastables and transparency of the dust cloud, changes in metastables density due to the presence of dust cloud in plasma is evaluated.

Optical emission spectroscopy (OES) is a standard tool for monitoring end evaluating plasma. There are many suggested models for extracting data such as electron temperature and density and information about other neutral species of plasma. As undestructive method OES is very interesting in complex plasma groups. In this paper we used OES to evaluate density of metastables and resonant levels in pristine plasma and with presents of microparticles.

Experiment was done in PK3+ chamber, in detail described in [1]. Measurements were done on 15, 30 and 60 Pa with melamine-forlamdehyde micronsize particles of 1.55 μm in diameter. Average density of particles in plasma was about 10^5 particle per cm^3. Emitted light from discharge was measured in 8 points with 3 mm resolution so spatial profile of the discharge was reconstructed. For this analysis we used 6 spectral lines: 826.4 nm, 738.3 nm, 706.7 nm, 763.5 nm and 794.8 nm. There is clear evidence of changing of light intensity due to the injection of particles. This change is shown in Figure 1.

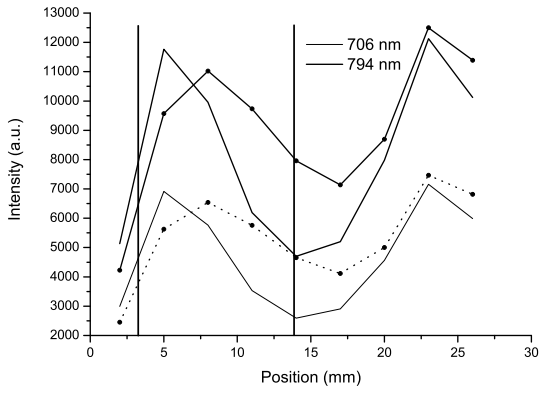

Fig 1: *Example of intensity profile of two observed lines in pristine plasma (without symbols) and in dusty plasma (with symbols) for 30 Pa. Vertical solid lines on* 3 *mm and* 14 *mm indicates the position of particle cloud.*

Here we used method which allows to extract metastables and resonant levels density with least assumption necessary concerning type of discharge. This method does not assume any specific type of plasma mechanisms and don't care about excitation from the ground state. Here we used a well known method with the mirror to evaluate selfabsorption of the plasma light [2]. This method allows to obtain number density of two metastables $1s_3$ and $1s_5$ and two resonant levels $1s_2$ and $1s_4$ connecting selfabsorption and number density by equation from [3].

With small modification and some additional measurements this method can be used in complex plasma. Additional information needed for this model to be used in complex plasma is transparency of the particle cloud. Due to the size of particles in the system, any estimation of mie scattering for observed lines will be not precise enough so we used Ar calibration lamp for measuring transparency of the cloud in Neon background plasma. In this case measured extinction of Ar lines is only caused by presents of particles and not by metastables in the plasma. With this information model could be applied so metastables density could be evaluated with the presence of particles.

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Manipulation of microparticles in complex plasmas by means of high-voltage nanosecond pulses

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It is demonstrated, that repetitive high-voltage pulses of nanosecond duration, superimposed onto the steady-state radiofrequency discharge, sustaining the complex plasmas, produce significant influence on the dynamics of microparticles. Mechanisms of energy transfer from the pulses to the microparticles are discussed.

Influence of high-voltage nanosecond pulses [1-3] on the dynamics of dust particles levitating in a plasma of a rf discharge is studied. The experiments were performed in a modified GEC cell. High-voltage pulses (20 ns duration, 1-11 kV amplitude, up to 1 kHz repetition rate), were superimposed with a steady-state capacitively coupled rf-discharge. RF voltage 50-100 V peak to peak was applied to the large bottom disc electrode, whereas for the pulses additional ring-shaped electrode placed 30 mm above the rf-electrode was used. A confinement ring was installed on the rf-electrode coaxially with the high-voltage electrode to provide the radial confinement of the microparticles. Pulse generator was loaded with its characteristic impedance of 50 Ω in parallel to the plasma. Pulse and rf-generators were protected against mutual action by filters.

Melamineformaldehyde spheres of 7.17 μm levitated between the rf-electrode and the high-voltage ring and were highlighted with a laser sheet in order to be observed with a high-speed CMOS videocamera either from top or from side.

Experiments were performed in argon at pressure of 0.3 Pa, which is low enough to observe the undamped dynamics of the microparticles.

The influence of these pulses on the plasma was monitored by measuring the voltage on the bottom electrode. It was found that after the pulse the voltage on the bottom electrode becomes more negative. The relaxation lasts several hundreds μs and increases with the pulse amplitude, whereas the amplitude of the voltage variation saturates around the pulse amplitude of 3 kV. Therefore pulse produces significant non-stationary influence on the steady-state rf plasma.

Following the plasma, microparticles were also affected by the repetitive pulses. They started to oscillate as the repetitive pulses were applied. They exhibited resonance curves, known from low voltage excitation. The amplitude of the microparticle oscillations increased with the increase of pulse amplitude. Clusters of microparticles exhibited parametric instabilities when the repetition frequency of the pulses equalled doubled the frequency of one of the cluster modes and was close to the resonance of the vertical oscillations.

A simple model of the plasma response to the high voltage pulse supports the observation. Due to the low background gas pressure electrons may be considered collisionless within the pulse duration. The energetic electron beam may charge the microparticles up to 15% more negatively with respect to their steady-state charge. The relaxation time of the plasma is then long enough to produce the resonance of the oscillations with the amplitude, of the order of that is experimentally observed.

However, the quantitative details of the influence of the nanopulses on steady-state RF plasma and, consequently, on the nanoparticles, are not understood. This requires extensive work on time-resolved diagnostics of the plasma as well as simulations. More advanced configurations of the experiment are in development, i.e. application of RF and high-voltage signals to the same plane electrode.

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$N_2(A)$ behaviour in N_2 –NO surface dielectric barrier discharge under modulated AC regime at atmospheric pressure

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Optical, electrical and discharge products measurements were performed in order to reveal behaviour of $N_2(A)$ metastables in a surface dielectric barrier discharge driven in N_2 with small NO admixtures under modulated AC regime. Basically, $N_2(A)$ species observed in a thin plasma surface layer follow the discharge current while in the space afterglow evolve in millisecond time-scale.

1. General

Behavior of $N_2(A)$ metastables produced by atmospheric-pressure surface Dielectric Barrier Discharge (DBD) [1] driven under modulated AC regime fed with N_2+NO mixtures (total flow 1-5 slm, NO=0-200 ppm) was investigated by time- and space-resolved Optical Emission Spectroscopy (OES) and by Optical-Optical Double Resonance Laser Induced Fluorescence (OODR-LIF) techniques. The study follows a previous one carried out recently in continuous AC regime in pure nitrogen [2].

In this work, the AC high voltage (5 kHz) was amplitude modulated (variable duty cycle: T_{ON}= 1-10 ms and T_{OFF}=20 ms). Voltage-charge/voltage-current discharge characteristics were determined through a non-inductive resistor/capacitor connected in series with the DBD. Photon-counting measurements tracked indirectly free electrons, $N_2(A)$ and NO(X) produced in a thin surface plasma layer through emissions of N_2^+ first negative (1.NG), N_2 second positive (2.PG), N_2 Herman infrared (HIR) and NO-γ systems [3]. Direct measurements of $N_2(A)$ and NO(X) in the space afterglow were performed at a fixed distance from the discharge surface (1 mm) by the OODR-LIF and LIF, respectively [2,4]. Finally, the NO/NO_X and N_2O analyzers were used to quantify stable discharge products.

2. Experiments and Results

After switching the discharge ON, all observed emissions closely follow the discharge current for both polarities during an AC cycle. As soon as the discharge stops to develop (during either positive or negative half-cycle), a fast decay of 1.NG emission indicates beginning of plasma decay. During early afterglow, both HIR and 2.PG emissions decay exponentially with $\tau \approx 20$ μs while NO-γ decays with $\tau \approx 40$ μs, all independently of the initial NO concentration. This evidences that all three emissions are controlled by $N_2(A)$ species.

$N_2(A)$ observed through the OODR-LIF signal in the space afterglow builds up with a delay (≈2 ms) [4] and remains almost unchanged for T_{ON} duration confirming our observation under continuous AC regime [1]. During T_{OFF}, $N_2(A)$ decays in the volume as a single exponential in millisecond time scale. There is a weak dependence of the decay on T_{ON} increase. In addition, the admixture of 1-60 ppm of NO does not change appreciably the $N_2(A)$ decay in the space afterglow though its quenching by NO would be effective in milisecond time-scale. However, NO density measured by LIF at the same position decreases significantly when the discharge is switched ON suggesting the NO conversion products do not contribute to the quenching of $N_2(A)$. A former observation is consistent with results of the DBD products analysis. Depending on the duty cycle and nitric oxide admixture, we observed up to 50 % reduction of initial NO concentration followed with measurable production of N_2O.

Acknowledgments

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On electric field measurements in surface DBD discharge with nanosecond triggering

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Emission spectra of DBD discharge with a nanosecond triggering have been obtained for 300-400 nm wavelength range. Value of reduced electric field was estimated and compared with data available in the literature.

1. Introduction

Surface dielectric barrier discharges (DBD) have been studied in connection with their application in flow control. Previous papers of our group [1,2] are devoted to ICCD imaging and measure-ments of electrical parameters of surface DBDs for different configuration of electrode system. Here, a detailed analysis of technique used to measure the electric field and preliminary results are presented.

2. Description of experiments

Electrode system consisted of two electrodes separated by a 4 mm glass plate. The high voltage electrode was 1x3 cm, and the grounded electrode was 8x8 cm. High-voltage electrode was connected to a 50 Hz 20 kV peak-to-peak sinusoidal power supply (A2E Technology). A nanosecond voltage pulse with a 1.5 ns rise time and 8 ns duration has been superimposed on the sinusoidal voltage so that it was in the first quarter of period of the sinusoid. This allowed controllable triggering of the discharge. The experiments were carried out in ambient air. Discharge spectra were recorded with Andor Star 734 CCD camera connected to SHAMROCK spectrometer. The discharge image was focused onto the entrance slit of spectrometer. Bands of molecular nitrogen were clearly identified. To estimate electric field value, we measured relative intensity of second positive (N_2, $C^3\Pi_u$, v'=0 – $B^3\Pi_g$, v''=0, λ=337.1 nm) and first negative (N_2^+, $B^2\Sigma_u^+$, v'=0 – $X^2\Sigma_g^+$, v''=0, λ=391.4 nm) systems of nitrogen. Relative calibration of spectral sensitivity of the system at 337.1 and 391.4 nm was made using deuterium lamp (ORIEL 63163).

As far as in the future we plan to perform time-resolved measurements of electric field, different gates, from 2 ns up to 100 ns, were used in the experiments. Up to 2000 accumulations of the signal were used to reduce signal-to-noise ratio.

3. Results

Fig.2 represents typical spectra obtained for the region of 391.4 nm. It is clearly seen that emission of first negative system is rather intensive. N_2 band (389.5 nm) corresponding to second positive system is significantly lower in amplitude. Electric field value estimated according to [3] was found to be equal to 650 Td. This value is rather high in comparison with DBDs in gas gap, but it correlates reasonably with value obtained for surface DBD initiated by high voltage nanosecond pulses [4].

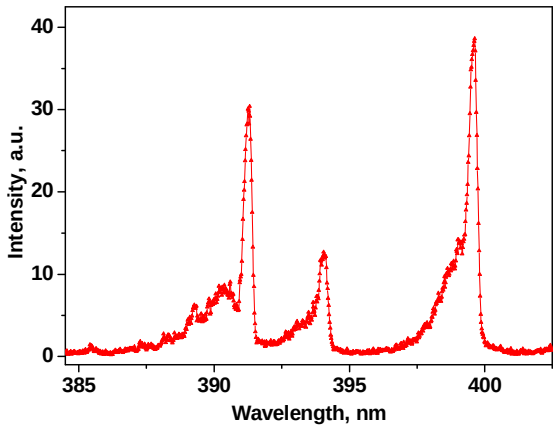

Fig. 2: *Typical spectra of the discharge in air, Δt=100 ns*

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Population inversion in a magnetized expanding thermal plasma investigated by photo-detachment and emission spectroscopy

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A weakly magnetized expanding hydrogen plasma is investigated by means of photo-detachment and optical emission spectroscopy. The atomic state distribution of hydrogen atoms shows an overpopulation between the electronic states p = 5, 4 and 3. Mutual recombination of hydrogen ions is suggested to be responsible for this overpopulation.

1. Introduction

When an expanding hydrogen plasma jet, produced from a cascaded arc source, is weakly magnetized, the emission of the expanding plasma jet is dominated by the red H_α emission in the first centimetres from the exit of the source, but changes to blue at larger distances from the exit due to higher Balmer lines (n > 4). Moreover, higher electronic states (n > 4) of H atoms become stronger populated than the lower states [1]. The reaction pathway proposed for the formation of these highly excited hydrogen atoms is via mutual recombination of positive (H_2^+) and negative ions (H^-). The latter are formed by dissociative attachment of electrons with ro-vibrationally excited hydrogen molecules.

The emission of the magnetized hydrogen plasma jet is dominated by red H_α light in the beginning of the jet. Since electron energies in the jet are too low (1 eV and less) to excite atomic hydrogen to the state p = 3, a possible formation route is via mutual recombination of atomic ions: $H^+ + H^- \rightarrow H + H(p = 2, 3)$. After 20 to 30 cm a transition occurs from a red to a blue emission. This is due to a population inversion between higher excited atomic states of p = 4, 5 and 6 in respect to p = 3 [1]. The reaction proposed to be responsible for this overpopulation is the mutual ion-ion recombination reaction: $H_2^+ + H^- \rightarrow H_2 + H(p \geq 2)$, in which highly excited hydrogen atoms can be formed. However, this reaction is still under some debate, e. g., it can also produce electronically excited H_2 molecules instead of excited hydrogen atoms.

2. Results

We have recorded the densities per statistical weight of the atomic hydrogen levels p = 3 to 6 as a function of the axial position z, i. e., the distance from the exit of the source. The first 22 centimeters of the jet is dominated by H_α light. After that, H_β to H_δ light becomes dominant and the corresponding weighted densities n_p/g_p become higher than the one for p = 3.

To study the role of H^- on the population of the excited hydrogen atoms, the photo-detachment technique is used. Laser radiation with a wavelength of 1064 nm, a pulse duration of 5 ns and a beam diameter of 10 mm is directed into the jet perpendicular to the flow direction. The photon energy of the laser light is sufficiently high to remove the extra electron of the H^- ion that is attached to the atom with a binding energy of 0.75 eV [2]. If we assume that the population into the excited H-atom states is partly due to mutual ion-ion recombination, the destruction of H^- ions, through the laser-induced photo-detachment process, will disturb the plasma chemistry and thus the emission originating from the excited states. The change in emission of the Balmer-α line is recorded at the center of the crossing of the plasma jet and the laser beam.

The emission of the Balmer-α line is measured to be constant during steady state operation. When pulsed laser radiation is directed into the plasma jet, the emission of the Balmer-α line decreases temporally. This decrease is up to 50 % of the steady-state intensity. It will be argued that the laser induces a decrease in the H^- ion density, which results in a decease in population of excited hydrogen atoms via the mutual ion-ion recombination process (as is discussed above).

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Poster presentations

Low Pressure Gas Breakdown in Combined Fields

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The aim of our paper is to study the longitudinal combined discharge ignition in low pressure gases. We distinguish the ignition of the combined discharges in three possible modes: 1) RF breakdown perturbed by a DC electric field, 2) breakdown in the combined field, 3) DC breakdown perturbed by a RF electric field.

Gas discharges in the combined (RF+DC) electric field are applied in a number of technological devices for spectral-chemical analysis, plasma oxidation of silicon, etc. The aim of our paper is to study the longitudinal combined discharge ignition in low pressure gases. Experiments were performed at the nitrogen in the pressures range $p = 0.01 – 10$ Torr with the amplitude values of the RF voltage $U_{rf} \le 2000$ V, $U_{dc} \le 600$ V and the RF field frequency $f = 13.56$ MHz. The distance between stainless steel electrodes was $L = 10$ mm. The RF voltage was applied to one of the electrodes whereas another one was grounded. The RF electrode also served as a "cathode", because a negative DC potential was applied to it.

Under the breakdown curve of the combined discharge we mean the dependence of the RF voltage U_{rf}, at which the discharge ignites, at the fixed value of the applied DC voltage U_{dc} or the dependence of the DC voltage U_{dc}, at the fixed value of the applied RF voltage U_{rf} on gas pressure.

By analogy to the three modes of the combined (RF+DC) discharges existence [1], we distinguish the ignition of the combined discharges also in three modes: 1) RF breakdown perturbed by a DC electric field, 2) breakdown in the combined field, 3) DC breakdown perturbed by a RF electric field.

The DC breakdown curve, influenced by the RF voltages higher than the minimum RF breakdown voltage $U_{rf.min}$, consists of two parts (see Fig.1). The lower part of this combined curve possesses the shape of an arc approaching zero at two values of the gas pressure at which a self-sustained RF discharge (unperturbed by the DC field) is ignited at the RF voltage given. An upper part of the plot corresponds to the ignition of the discharge in the third mode (DC discharge perturbed by the RF field). Critical pressure value, where the breakdown curve splits into two parts, corresponds to the pressure of the turning point in the RF breakdown curve.

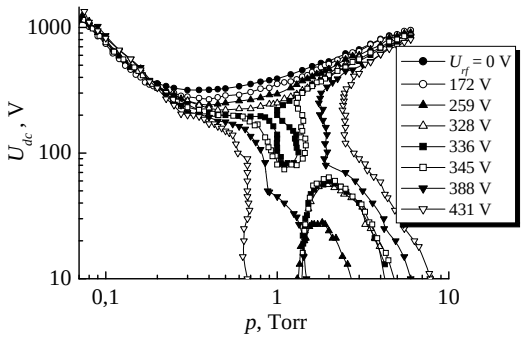

Fig.1. *DC breakdown curves at various fixed values of the RF voltage.*

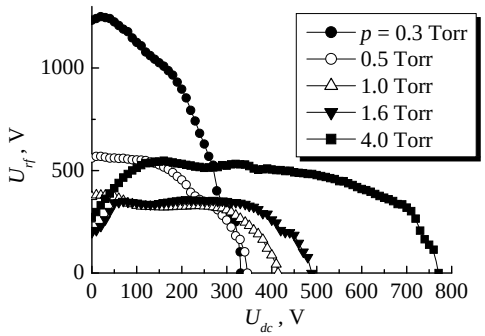

Fig.2. *RF breakdown voltage against the DC voltage at fixed values of nitrogen pressure.*

According to Fig.2 applying of DC voltage first increases the RF breakdown voltage compared to the breakdown voltage of self-sustained RF discharge. However at sufficiently high DC voltages the DC field starts to contribute to the ionization of gas molecules, the ion-electron emission from the electrode surface playing a substantial role. Under these conditions the RF breakdown voltage decreases with the DC voltage increasing and it vanishes when a self-sustained DC discharge ignites.

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Emission Spectra of Plasmas Generated by Discharges on Solar Array Surfaces

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Emission spectra of arc plasmas contain valuable information regarding arc sites, plasma parameters and composition, and temporal dynamics of plasma expansion. Emission spectra within the range of 200-800 nm were measured for trigger arcs on triple junctions and sustained arcs between solar array strings. Spectra were recorded from arcs on several different brands of conventionally designed solar array samples immersed in simulated Low Earth Orbit plasma.

Physical mechanisms of differential charging and electrostatic discharges (ESD) on spacecraft surfaces have been investigated for over thirty years. ESDs are located on areas of triple junctions (interconnector-coverglass-plasma) and are accompanied by bright flashes of light. our The first-ever study of correlations between electrical and optical emission properties of ESD on a solar array sample was conducted in 1992, and it was shown that both light intensity and arc current temporal behaviors were practically identical, and emissive spectral lines of cathode material (silver) were clearly resolved and measured. ESD on triple junctions has many common features with vacuum arcs such as cold emission of electrons due to the high electric field in the cathode area, arc initiation on a small spot on the cathode surface, and traces of melted cathode material observed on its surface after the arc is extinguished. This commonality between vacuum arcs and ESD on triple junctions was confirmed by measurements of emission spectra of ESDs initiated on surfaces of dummy samples and real solar cells. However, there are essential differences between vacuum arcs and ESD on triple junctions in discharge initiation and development. In particular, emission spectra contain spectral lines that certainly do not belong to the corresponding metal atoms (or ions), for example atomic hydrogen H_α line. It is known that the spectra of vacuum arcs consist of cathode metal lines only but adding air into the vacuum chamber (0.1 mTorr) results in the appearance of hydrogen and hydroxyl lines. However, the presence of air could not be considered as an explanation for the observations where the nitrogen partial pressure was below 1 uTorr.

The main stimulus for a further thorough investigation of arc emission spectra was to understand the important correlations between the electrical and optical properties of these discharges. The presence of dielectrics with specific physical and chemical properties in the area of ESD on triple junctions makes these discharges different from pure vacuum arcs, and if the electrical characteristics of arcs are different, one can expect the emission spectra to be different as well. The expectations were confirmed by measuring the emission spectra of arcs located on solar array sample interconnects, dummy sample electrodes, and in the gap between separate strings in cases of sustained arcs.

Observations of spectral lines belonging to metal ions confirmed the presence of a flux of energetic electrons emitted by a protrusion on the interconnect surface.

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Plasma etch process monitoring and control using quantum cascade laser absorption spectroscopy

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Quantum cascade laser absorption spectroscopy (QCLAS) was applied for the monitoring of the etch product SiF_4 in silicon plasma etch processes. It is demonstrated how the measured concentration can be used for the dynamical control of mass flow controllers (MFC).

1. Introduction

In plasma etch processes the gas composition in the plasma bulk is a key parameter determining process stability and process results. It depends on various factors, like (i) controllable feed gas flows, determined by MFC and pump speed, (ii) not controllable gas flows caused by, e.g. adsorption and desorption at the reactor chamber walls, (iii) chemical reactions at the wafer surface often leading to significant amounts of etch products and (iv) total gas pressure and temperature.

In plasma etch chambers the quantitative measurement of gas concentrations is still an unsolved issue. In situ QCLAS has the potential to solve this general problem [1]. It will be demonstrated, that using quantum cascade lasers (QCL) not only the concentration of molecular etch products can be monitored during the etch process, but also it is possible to control MFC because of measured species concentrations in the plasma bulk.

2. Experimental

The QCLAS measurements of the etch product SiF_4 were carried out at an industrial MERIE plasma etch chamber at typical pressures of 20 Pa [2]. The gas composition fed to the chamber for the silicon etch process consisted of NF_3, HBr, O_2 and $SiCl_4$. The IR radiation of the QCL in the spectral range of 1030 cm^{-1} was transmitted via an optical fiber to the reactor. Using a mirror inside the plasma chamber the IR radiation was reflected back to the detector unit outside of the chamber. The QCLAS measurement system (Q-MACS) was synchronized with the etch chamber via software communication enabling the monitoring during automated processing of wafer batches.

3. Results

For a set of 25 processed wafers to create deep holes into crystalline silicon the SiF_4 concentration during each process was measured. The comparison between the time developments of the etch product SiF_4 allows to draw conclusions from the etch process itself. Within the first 2 minutes the production of the SiF_4 molecules increases to a maximum followed by a slower decrease because of a lower etch rate with increasing depth in the holes. The data for the first wafers varies significantly indicating seasoning effects in the chamber. In subsequent following clean cycles the SiF_4 concentration was more reproducible. The comparison with *ex situ* inspection data of the wafers showed first correlations with the SiF_4 concentrations, in particular when a clean cycle process failed.

Besides the monitoring of etch species the measured molecular concentration was fed back to a MFC via a PID loop in a demonstration setup. In addition this setup was extended for two QCL using the same fiber allowing the measurement of two species simultaneously. In a first step a gas composition of SiF_4, C_4F_6 and N_2 was investigated keeping the total pressure constant. With the help of a PID control loop the concentrations of SiF_4 and C_4F_6 as well were kept constant independently but simultaneously even in case of changing the admixture of N_2. Furthermore the concentration of the SiF_4 could be kept constant even when fragmentation due to the plasma starts. In this case the PID control loop enforced more than a doubling of the SiF_4 flow when the plasma is switched on.

Acknowledgements

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Dielectric Barrier Discharge in air: Optimising for Biomedical Application

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Dielectric barrier discharge (DBD) for therapeutic application in dermatology is characterized using optical emission spectroscopy, current-voltage measurements, microphotography, and plasma chemical simulation. Plasma parameters like electron distribution function, electron density, gas temperature, and ignition voltage and discharge current are determined. Material and geometry of opposite electrode, and the inter-electrode distance influence plasma conditions.

1. Introduction

Our DBD source comprises of only one ring shaped copper electrode (ϕ = 10mm), covered with ceramic [1]. Any material of high capacitance can be used as the counter electrode and discharge can be produced in air present between the electrodes. In medical applications, the human body itself can serve as the counter electrode. Despite high ignition voltage, the averaged current is low and hence human skin can be treated without causing any acute pain. Human body is a complex system and the characterization of the discharge produced will have greater degrees of freedom. So, for characterization purpose and to study the influence of the opposite electrode properties on plasma conditions, simple electrode materials (like metal, water and glass) are used as the opposite electrode and plasma conditions are studied for different inter-electrode distances (d).

2. Methodology and Simulation

Low voltage 300 Hz pulses are transformed into high voltage 100 kHz pulses with damped amplitude. They are used to ignite air present between the electrodes. The emission in the discharge is observed using Echelle Spectrometer with resolution 0.02 - 0.03nm. The voltage and current pulses are measured using a capacitive voltage divider and a current monitor respectively. A high speed PCO SensiCam with 5µm spatial resolution is used to determine discharge channel dimensions. In the emission spectrum, bands of neutral nitrogen molecule (2^{nd} positive system, 280 - 450 nm), molecular ion (1^{st} negative system, 390 nm), and γ-system of nitrogen oxide (200-300 nm) are seen. Gas temperature (T_g) in plasma channel is determined by fitting procedure, using emission at 337.1 nm and simulated spectra. The electron distribution function - *f*(E), for different reduced electric fields (E/N) is determined by solving Boltzmann equation numerically, in local approximation using the program code EEDF [2]. Using these values and functions, the emission intensities of nitrogen molecule are calculated, considering the quenching of excited states in air at gas temperature. By comparing the simulated with measured values, *f*(E) and E/N are determined. Electron density is determined using known *f*(E), plasma volume and measured intensity of nitrogen.

3. Results

DBD in air shows narrow discharge channels of 50 µm diameter. Duration of microdischarge increases linearly with *d*; 10 ns, 13 ns and 25 ns for d = 0.5 mm, 1.0 mm and 2.0 mm correspondingly. Gas temperature in the micro discharge channel ranges from 390 K to 820 K. Electron density and electron distribution depend strongly on *d* values, as shown in Fig. 1

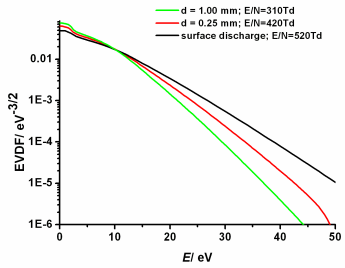

Fig. 1*: EVDF in DBD at different inter electrode distances and on the surface of dielectric.*

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Ozone generation by surface dielectric barrier discharge under modulated AC regime

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Electrical discharge characteristics were studied and O_3 concentration measurements were performed in order to reveal influence of duty cycle on ozone production efficiency of a surface dielectric barrier discharge driven under modulated AC regime. Basically, the highest observed ozone production yield well exceeds 100 g/kWh in synthetic air and 200 g/kWh in pure oxygen.

1. General

Ozone is a powerful disinfecting and oxidizing agent, which is used in water treatment, food processing, medicine etc. Basically, ozone for these applications is produced by various atmospheric pressure electrical discharges [1-3] frequently in combination with other secondary agents such as catalysts [4]. Performance of ozone generating system is usually evaluated on the base of O_3 energy cost or O_3 production yield. Efficiency of plasma-chemical O_3 synthesis generally depends on the nature of the working gas (air or oxygen), on the humidity, on the amount of contaminants and, namely, on the way, how the energy is delivered to the discharge. With the aim to clarify the role of the discharge energization we investigated dependence of ozone production yield on AC power modulation in the case of the Surface Dielectric Barrier Discharge (SDBD).

2. Experiment

Ozone production by atmospheric-pressure Surface Dielectric Barrier Discharge [1] fed either with synthetic air or with pure oxygen (at fixed flow 5 slm) was investigated under modulated AC regime. Newly designed SDBD reactor consists of high-purity Al_2O_3 ceramic plate with deposited electrodes (a nickel-based discharge electrode and a silver-based induction electrode) and a Plexiglas chamber. Applied AC high voltage (1-10 kHz, <16 kV peak-to-peak) was amplitude modulated using a rectangular modulation waveform with a variable duty cycle (D=0.001-0.8). Experimental voltage-charge and voltage-current SDBD characteristics were determined through the non-inductive capacitor and resistor connected, respectively, in series with the DBD. Two independent ozone monitors were used to determine ozone concentrations in discharge products.

3. Results and conclusions

The O_3 concentrations were monitored outside the SDBD chamber by a non-dispersive UV absorption technique. For each single measurement (*i.e.,* for a given combination of the AC frequency&amplitude and modulation duty cycle D), the discharge ran continuously unless steady-state ozone levels were indicated by both O_3 analyzers. The highest observed ozone concentrations were ~900 ppm and ~2300 ppm in synthetic air and in pure oxygen, respectively. Averaged voltage-charge and voltage-current SDBD waveforms obtained by a fast digitizing oscilloscope were analyzed to determine mean energy dissipated during one discharge cycle and, consequently, mean discharge power and ozone production yield. Calculated ozone yield reached as much as 120 g/kWh and 290 g/kWh in synthetic air and in pure oxygen, respectively.

In conclusion, the highest ozone production efficiency was achieved when combining low duty cycle $D<10^{-1}$ with the lowest AC high voltage amplitude sufficient to produce micro-discharges homogeneously over all SDBD electrode surface.

Acknowledgments

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UV detector made from CVD diamond for electric discharges in liquid research.

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Characteristics of diamond detector for short-wave part of electric discharge in submerged liquid stream pulse radiation registration are given.

Interest to investigations in electric discharges in liquid is mostly connected with their practical application for currents commutation [1], decontamination and cleaning liquid (particularly, water) from pollutions [2] and also for nanomaterials production [3]. In our paper [4] was for the first time shown, that electric discharge in flowing water is considerably lighten without a qualitative changes of the process of its development in rather wide interval of electrical conduction in liquid values. Abnormal features of electric discharge, initiated and formed in submerged stream appears both at initiation stage and during steady-state combustion [5]. It was shown, that the discharges are good electric energy transducers in radiation energy and can be used for water decontamination. The high-current electric arc, initiated during the opening of cylindrical contacts and deformed by intensive liquid flow was also studied.

In energy balance in such a case the radiation played a main role. Radiation spectral distribution determines just qualitatively with a help of high-speed photography and light filters. But for liquid decontamination should be known both radiation spectral distribution and provide its optimal exposure. For this, the UV-radiation detector should be placed in immediate proximity to electric discharge. Now, the most studied interval for germs destruction is 225 – 280 nm with maximum 254 nm. Although, it is interesting to investigate bactericidal effects of UV-radiation in the area of shorter wavelengths (less than 225 nm). In such a case it is possible to use the discharge as a source of ultraviolet in this spectral distribution and control the short-wave radiation composition with a help of diamond detector. The advantage of diamond detectors over detectors based on the others semiconductors (e.g. silicon) is that they insensitive to a visible light and can effectively register only UV-radiation.

Detector, based on artificial diamond is proposed to be used for electric discharge in liquid UV-radiation analysis.

The photoresponse spectrum of this detector has expressed sharp growth of photocurrent under 225 nm, which is stipulated by forbidden zone of the diamond.

The spectral response maximum of the detector is significantly shifted in short-wave area (λ = 210 nm). The detector spectral response has no peculiarities, typical for impurity photosensitivity of natural diamond samples in interval between 240 – 280 nm. Also, diamond detectors have high time resolution (better 1ns).

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Standing Wave Phenomena in Helicon and Neutral Loop Discharges

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The field structure and the heating mechanism in a Helicon and in a Neutral Loop Discharge (NLD) in Argon are investigated. In the Helicon mode Landau damping turns out to be the main damping mechanism. We demonstrate that the NLD is closely related to the Helicon discharge and that the heating mechanism in inductive NLDs is in fact given by the formation of an azimuthally isotropic m = 0 Helicon wave. The key diagnostics is measurement of the spatial structure of the induced magnetic field by B-Dot probes. This is supplemented by emission spectroscopic observations.

The discharge can be operated either in the Helicon mode or the NLD mode. A flat coil antenna excites a Helicon wave in the azimuthally isotropic m = 0 mode [1]. Radial B-Dot measurements in the Helicon mode confirm that the azimuthal B field component is proportional to the derivative of the axial component as can be seen in Fig. 1. Operation is only possible at certain ratios of power to static magnetic field strength [2]. These ratios are identified as modes of standing waves by axial B-Dot probe measurements. In modes showing a strong damping of the wave, the inferred phase velocity is close to the electron thermal velocity. The electron density and temperature are obtained by Langmuir probe measurements. An analytical standing wave model including Landau damping and Coulomb collisions reproduces very well the experimental results. From this comparison it can be clearly concluded that Landau damping of electrons traveling along the field lines at speeds close to the helicon phase velocity is the main damping mechanism.

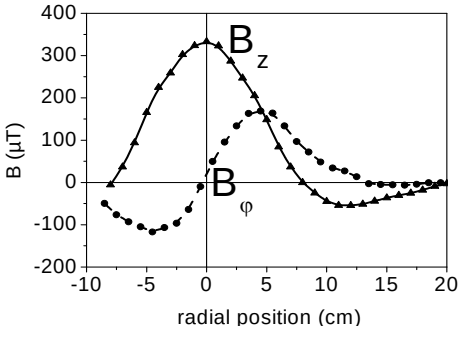

Fig. 1: *Magnetic field distribution in the Helicon discharge (0.1 Pa, 1kW) measured by a B-Dot probe.*

In the NLD mode a Helicon wave is identified (Fig. 2). The current induced in the vicinity of the X-point modifies the Helicon field structure compared to the standard case observed in homogeneous fields. This leads to a beating of different longitudinal modes. In addition, standing wave patterns by reflection from the chamber bottom are observed. The parallel occurrence of different longitudinal modes stabilizes the discharge and operation is less critical to phase and refractive index matching than in a standard Helicon discharge. The above picture is the result of intensive measurements using Langmuir and B-Dot probes as well as phase resolved optical emission spectroscopy (RF-MOS) [3]. The measured wave field structures agree well with a simple model including the diamagnetic current induced close to the X-point.

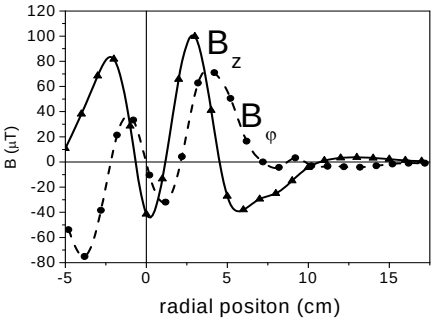

Fig. 2: *Magnetic field distribution in the NLD (0.5 Pa, 1kW) measured by a B-Dot probe*

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Etch process control with a deposition-tolerant planar electrostatic probe

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A deposition-tolerant electrostatic probe has been implemented as an in-situ sensor for process control during plasma etching during semiconductor device manufacture. The probe measures ion flux, electron temperature, floating potential and deposited film thickness and resistivity. This paper will explore how this information can be used to improve reactor yield, throughput and cost of ownership.

1. Introduction

Etching of nanometre-scale features in conducting and insulating materials is one of the most critical steps in the fabrication of integrated circuits for logic and memory applications. The move to 300mm wafers and to smaller critical dimensions (currently 45nm in production), accompanied by increasing pressure on cost control has brought us to the point where open-loop control of the plasma conditions is no longer adequate. Therefore there is a need for advanced sensors which can directly monitor the plasma environment to which the processed wafer is exposed. Combined with Advanced Process Control (APC) methodologies these can improve the etch tool's productivity in three key areas: improved product yield (chamber matching, fault detection and prediction, drift correction, chamber wall state characterization), throughput (reducing unnecessary process time and tool down-time) and lowering cost-of-ownership (minimizing unnecessary plasma exposure of consumable reactor parts). However, to be successful such sensors must satisfy stringent requirements, including:

-Sensitivity to wafer-level etch performance, particularly critical dimension variance

-Accuracy and repeatability: the sensor must remain accurate throughout the wet clean cycle without requiring any external calibration. Absolute measurements of plasma parameters (densities, fluxes, temperatures) are therefore highly preferred over relative techniques such as conventional optical emission spectroscopy.

-Process transparency and absence of maintenance: the sensor must not significantly perturb the etch process in terms of etch uniformity and critical dimensions, particle generation or other contamination. Any exposed sensor components must last at least as long as other consumable parts of the reactor such as counter-electrodes.

We have implemented the deposition-tolerant ion flux probe described by Braithwaite et al. [1] as an in-situ process monitoring sensor on a commercial dielectric etch tool. The probe head is integrated into the upper (grounded) electrode and is made of the same material, and has been shown to have negligible process impact. With the use of an embedded digital signal processor to analyze the current-voltage characteristics in real-time, this sensor delivers high-precision time-resolved measurements (at 10 Hz) of the ion flux, electron temperature and probe floating potential. In addition, if there are thin films deposited on the probe, the film thickness and conductivity can be determined. This gives unprecedented insight into the power delivery, gas composition and surface state of the reactor during wafer processing. This talk will explore how this information can be used to improve the yield, throughput and cost-of-ownership of production etch tools.

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Sterilization using helium and air plasma

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The effect of the plasma irradiation on the capability of bacteria to form colonies (growth) was studied. Air and helium plasma were generated using home made Dc source. Bacteria samples were treated using Air and helium plasma at different irradiation times (10 to 180 seconds). Sterilization (No growth of bacteria) was observed to occur only at irradiation time of 180 second and at a different plasma power while using oxygen plasma.

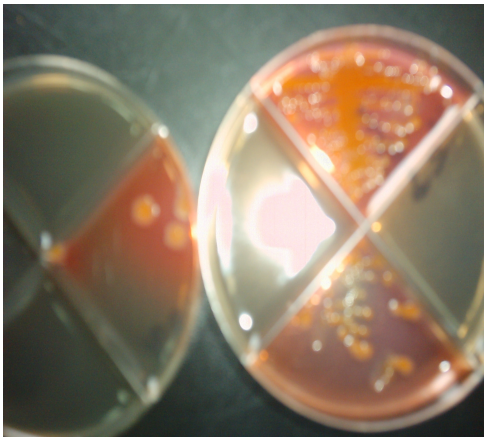

Fig. 1: *300 colonies after treatment 3 colonies*

Diagnostic of low-temperature air plasma at atmospheric pressure by electrical characteristics

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Low temperature plasmas have had a very broad range of applications ever since their discovery. The technological electrical barrier discharge at normal atmospheric pressure is applied ever more into the practice of plasma-chemical technologies as an alternative to the electric glow and RF discharges.

The present work investigates theoretically and experimentally the electrical characteristics of the technological barrier discharge. The electrical characteristics of this discharge are studied on the basis of its experimentally measured external static volt-ampere characteristic.

The determination of the following basic electric discharge characteristics is substantiated: the active power, the specific surface power density, and the average value of the electric current density as a function of the voltage.

The experimental investigations have been realized under no-load conditions of the plasma technological system, i. e. without taking into account the influence of the treated material upon the electrical characteristics of the discharge.

The technological electric barrier discharge at a normal atmospheric pressure finds application into the practice of plasma-chemical technologies as a successful alternative to the electric glow and RF discharges in vacuum. The elimination of the expensive and diffi-cult-to-operate vacuum system is one of the great ad-vantages of the barrier discharge.

At low active power the barrier discharge produces technological cold plasma containing ozone and chemically active products from its destruction. At high value of the active power the nitrogen oxides pre-vail and induce another character to the plasma-chemical process. This requires searching for a more reliable control of this process by using electrical characteristics of the barrier discharge.

Effect of filament position on plasma parameters in a double plasma device

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A transverse magnetic field (TMF) separates the source and target region of a double plasma device. Two sets of tungsten, placed at different distances from the TMF, are then used to produce plasma alternately and the plasma parameters in the source and target regions for different discharge voltages and discharge currents are measured using Langmuir probes. The plasma parameters are found to be considerably influenced by the position of the filaments.

1. Introduction

Researchers have conducted studies in plasmas, produced by different ways, having a filtering magnetic field and explored ways to control the plasma parameters by using different methods [1,2]. We present our observations on the dependence of the plasma parameters on the position of the filaments with respect to a transverse magnetic field.

2. Experimental procedure

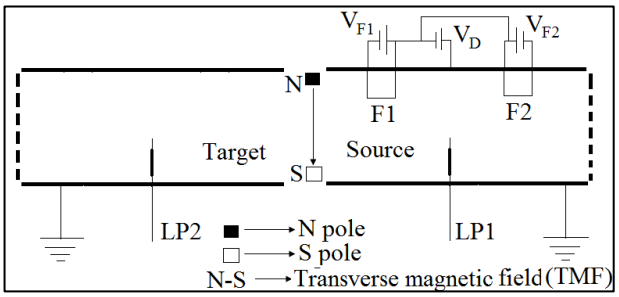

Fig. 1: *Sketch of the experimental setup.*

In Fig. 1, the distance between the N-S poles of the magnetic field (and the corresponding magnetic field strength at the centre) are 15 cms (81 Gauss), 11.5 cms (130 Gauss) and 8cms (230 Gauss) respectively. F1 and F2, at 12.5 cms and 23.5 cms away from the TMF respectively, are two sets of tungsten filaments, each set consisting of five filaments of length 3 cms. Plasma is produced in the source region and diffuses to the target region through the TMF produced by permanent magnets. V_d and V_f are the discharge voltage and filament voltage power supplies. Hydrogen plasma at a pressure of $5x10^{-4}$ Torr is created by striking a discharge between the incandescent filaments treated as cathode and the grounded magnetic cage which functions as anode. F1 and F2 are used alternately to produce plasma. Plasma parameters in the source and the target regions for different discharge voltages (V_d) from 60 V to 100 V and discharge currents (I_d) from 0.5 A to 2 A are measured using Langmuir probes LP1 and LP2 placed radially at the centre of the source and target regions.

3. Results

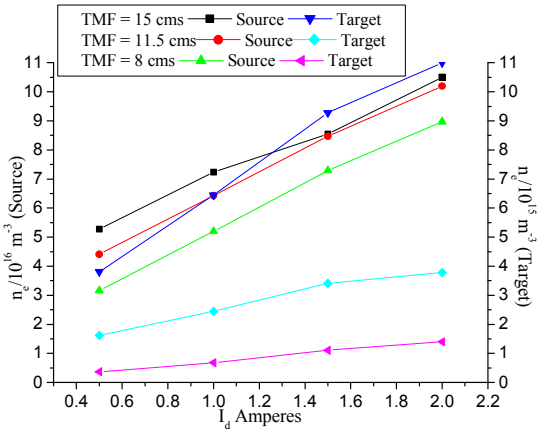

Fig. 2: *Change of n_e with I_d at V_d = 80 V (F2 filaments).*

From plots such as in Fig. 2, it is found that plasma density (n_e) for both filaments F1 and F2 are lower in the target than in the source. In the source region, better uniformity in change of n_e with V_d and I_d occurs in the case of the F2 filaments. In the target region, variation in n_e with I_d and V_d is found to be more uniform for F2 filaments than F1 filaments for all the TMF separations. Electron temperature (T_e) for both F1 and F2 filaments are found to be lower in the target region than in the source region. Change of T_e with I_d and V_d is not as uniform for the F1 filaments as in the case of the F2 filaments.

4. Conclusions

In order to have better control of change in the plasma parameters with discharge parameters, the location of the filaments has been found to be important with F2 filaments giving better uniformity and control of plasma parameters with discharge parameters than the F1 filaments.

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Diagnostics of a DC–Energized Hollow-Cathode Plasma Jet System for TiO_2 Thin Films Deposition in Continuous and Pulse Operation

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We present time- and space-resolved Langmuir probe measurements of plasma parameters in a DC and RF plasma jet systems used for deposition of TiO_2. The pulse generator consists of a standard DC power supply (Advanced Energy MDX 500) followed by a home-made switch with IGBT power transistors and it yields several tens of amps of discharge current during the pulse.

1. Introduction

The use of pulsed power in plasma-aided technologies is known for many years. Apart from that it prevents arcing when sputtering non-conductive layers [1], the pulsing of the discharge controls the heat load onto the substrate, controls the ion/neutral flux to the substrate, limits the substrate ion bombardment (which reduces the compressive stress in the film) and controls the dissociation of the precursor [2].

The hollow cathode plasma jet (HCPJ) systems that exploit for technological purposes the low-pressure hollow cathode discharge have been developed some two decades ago [3]. The hollow cathode discharges are excited by RF or DC continuous or pulsed power. This system requires a relatively low pressure of the working gas inside the reactor vessel; typically tens of Pa. The advantage of the system with plasma jet is that it is able to deposit thin films inside the cavities and bores and on substrates with the complex shapes with high deposition rate.

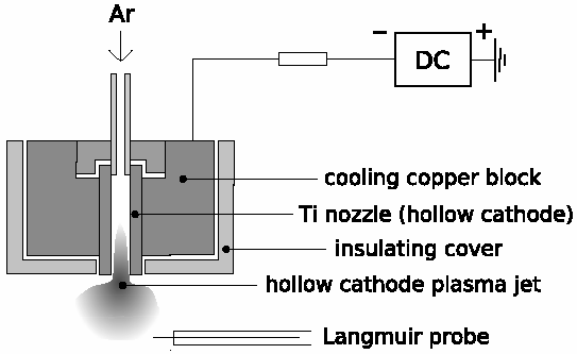

Fig. 1 Schematic drawing of the plasma jet system.

The main part of the HCPJ is a nozzle made from titanium and placed in a continuously pumped UHV chamber; see Fig. 1. The nozzle is flown through with argon and is connected to a pulsed DC power source. A plasma jet is created at the outlet of the nozzle and interacts with the deposition substrate placed downstream. Molecular oxygen is added sideways to the chamber and reacts with sputtered Ti particles creating a TiO_2 layer on the substrate.

The discharge voltage in pulse regime ranged from 600 to 1000 V with the duty cycle 10 to 20% and the repetition period of 1 ms. For creation of power pulses the maximum output peak current of the used DC power supply was reinforced by battery of 3×3 500 μF capacitors and connected to the nozzle-hollow cathode via the IGBT switch which was controlled by the TTL generator.

2. Experiments

Space-resolved measurements were performed using the cylindrical Langmuir probe mounted on radially movable feedthrough and positioned at 20 or 40 mm downstream of the nozzle end. Time-resolved Langmuir probe technique was simultaneously used to observe the temporal changes of bulk plasma parameters. Electron density, electron temperature, and plasma potential in the plasma jet were determined. The dependence of the measured parameters on the discharge conditions such as discharge current or duty cycle was studied and discussed.

Acknowledgments

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Plasma electron temperature of Cu alloy caused by N_2 laser

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A nitrogen laser beam (337 nm, 6 ns (FWHM), (3,2 ± 0.2) mJ was focused with a quartz lens onto Cu-Sn Zn-Pb alloy target in air at normal pressure. The laser irradiation and plasma explosion were generated. The electron temperature of the plasma cloud was determined by the standard method of plasma spectroscopy. The result of this experiment was compared with electron temperature estimated with the theoretical formula known from literature [1], which was modified for the Cu-Sn-Zn-Pb alloy ($T_{e\ Cu\text{-}Sn}$ = 13600 K).

Measurements and calculations

Intense laser radiation from nitrogen laser was focused on the copper (Cu-Sn-Zn-Pb) alloy surface. (Zn 5.75%, Ni 0.52%, Fe 0.31 % Pb 6.12% Cu rest).The target was placed in air at normal pressure. The produced plasma 0.1 mm above the target surface was analysed (in the spectral range between 250 nm and 510 nm) by a 220 mm grating Spex monochromator.

Relative Cu line intensities provided data for the derivation of electron temperature under the assumption of LTE and it was assumed to be equal, i.e. $T_e = T_{e\ Plasma}$. The Cu I and Cu II line pairs were analysed. The transition probabilities for Cu-spectral lines were taken from Ref. [2].

The mean value of the derived electron temperature is 14000 K ± 10%. In vacuum temperature is about 13 % lower [3], e.g. 11900 K ± 10%.

The plasma electron temperature for an element can be verified by means of the theoretical formula known from literature [1]:

$$Te = 2.98\times10^4 A^{1/8}(Z+1)^{-5/8} Z^{3/4} (I\lambda)^{1/2}\tau^{1/4}; \quad [Te] = K, \qquad (1)$$

where A is atomic weight of an ion, Z is the average charge of ions in the plasma cloud, I is the laser radiation intensity, λ is radiation wavelength, and τ is laser pulse duration. The experiment has shown that the atoms in plasma were singly ionised (Z = 1).

This formula was modified for the Cu-Sn-Zn-Pb alloy case in order to take into consideration the target structure. We suggest the following formula for the alloy $T_{e\ Cu\text{-}Sn}$:

$$Te_{Cu-Sn} = Te_{Cu}a_{Cu} + Te_{Sn}b_{Sn} + Te_{Zn}c_{Zn} + Te_{Pb}d_{Pb} + Te_{Ni}e_{Ni} + Te_{Fe}f_{Fe}, \qquad (2)$$

where *a, b, c, d, e*, and *f* are values of an element participation. The proposed Equation (2) observes the alloy plasma like an ideal gas. The total internal energy is proportional to the mixed electron temperature $T_{e\ Cu\text{-}Sn}$. It is equal to the sum of particular energies of participants. For example: $T_{e\ Cu}$ = 13500 K from Eq. (1) for pure (100%) Cu, and the contribution in alloy $T_{e\ Cu}\ a_{Cu}$ = 13500 K *x0*.8424 = 11400 K, from Eg. (2), because in alloy it is 84.24 % Cu *(Table 1*). The last value (11400 K) is in good agreement with the measurement done by the spectral Cu lines (e.g. with 11900K). The result of our calculation by means of formula (1) and (2) is $Te_{Cu\text{-}Sn}$ = 13600 K with contributions from all participants.

Conclusion

Our measurement of the electron temperature of the Cu alloy plasma was performed with the Cu spectral lines only. This temperature (11900 K) is comparable with the calculated value from Eq. 2 in case of 84.24% Cu (11400 K). The total electron temperature of Cu alloy from Eq. 2 is about $T_{eCu\text{-}Sn}$ = 13600 K. From literature (4) a similar behaviour observed with Al alloy is known.

Acknowledgement

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Laser ablation time-of-flight mass spectrometry (LA-TOF-MS) of silicon doped diamond-like carbon (DLC-Si)

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Silicon-doped diamond-like carbon (DLC-Si) was prepared by plasma-enhanced chemical vapor deposition (PECVD) technique from a mixture of hexamethyldisiloxane (HMDSO) and oxygen using dual frequency capacitive discharge. Time of flight mass spectrometer equipped with nitrogen laser (337 nm) was used to characterize its structure via laser ablation. Stoichiometry of positively or negatively charged species was confirmed via isotopic pattern simulation. DLC-Si material shows typical spectral patterns similar to those diamond-like carbon. In addition, chemical bound of Si-C in this material was proved and many positively or negatively charged $O_mSi_nC_oH_p$ species were identified in plasma plume.

1. Introduction

Low temperature plasma PECVD is used to produce different materials and/or surface modification. One of the most known is diamond-like carbon due to its high hardness and elasticity modulus, low friction, chemically inert etc. Properties like stress[1], thermal stability[2] can be upgraded by doping with silicon. Diamond-like carbon (DLC) doped with silicon is important for solar technology[3], surface modification etc.

Information about chemical structure of such deposits can be the way how to better understand processes in plasma plume and moreover how to design material with desired properties. As it was previously shown on DLC doped by nitrogen, the laser ablation mass spectrometry (LA MS) can provide such information.[4]

In this work via diagnostic of plasma formed by laser ablation, chemical composition of DLC doped with silicon was studied.

2. Experimental

Silicon-doped diamond-like carbon (DLC-Si) material was prepared by plasma-enhanced chemical vapor deposition (PECVD) technique, using dual frequency capacitive discharge (100 kHz and 13,56 MHz) at low pressure (10 Pa) from a mixture of hexamethyldisiloxane (HMDSO) and oxygen. DLC-Si layer was grown on single-crystalline silicon wafer. Time of flight mass spectrometer AXIMA CFR (Kratos Analytical, Manchester, UK) equipped with nitrogen laser was used to characterize its structure via laser ablation. The stoichiometry of observed species was also confirmed by isotopic pattern simulation.

2. Results and discussion

DLC-Si material was ablated using 337 nm pulsed laser under vacuum less then 10^{-4} Pa and spectra measured in positive and negative ion modes were analyzed. The mass spectra show typical properties for diamond-like carbon polymers. In negative mode the species SiC_n^- (n = 2-10), $Si_2C_n^-$ (n = 0-2) and C_n^- (n = 2-15) were found. Some of them were also partially hydrogenated with H_n (n = 1-3). Positively charged species C_n^+ (n = 9-18), SiC_2H^+, $SiC_2H_3^+$ were unambiguously identified. However, several undistinguishable isobaric compounds: Si_2H^+ (isobars $OSiCH^+$, $SiC_2H_5^+$, $C_4H_9^+$), O_2Si^+ (isobars C_5^+, SiH_4^+, $SiC_2H_8^+$), OSi_2^+ (isobars O_2SiC^+, $SiC_3H_7^+$, $Si_2CH_4^+$, C_6^+), SiC_4H^+ (isobars $C_6H_5^+$, OC_5H^+, $O_2SiCH_5^+$, $Si_2CH_9^+$), $Si_2C_2^+$ (isobars $OSiC_3^+$, $C_6H_8^+$), $Si_2C_2H^+$ (isobars $SiC_4H_5^+$, $C_6H_9^+$), $Si_2C_2H_3^+$ (isobars $C_6H_{11}^+$, $SiC_4H_7^+$, $Si_2C_2H_3^+$), Si_3^+ (isobars $O_2Si_2H_4^+$, C_7^+, OSi_2C^+), Si_3H^+ (isobars C_7H^+, $OSiCH^+$, $Si_2C_2H^+$, $C_6H_{13}^+$), C_5HSi^+ (isobars $OSiC_3H_9^+$, $Si_3H_5^+$, $O_2Si_2H^+$), were observed. For example, series Si_2C, Si_2C_2, etc. has mass equivalent to $OSiC_2$, $OSiC_3$, etc. compounds.

3. Conclusion

The studied material is most probably DLC doped (modified) with silicon, silicon oxide and partially also with HMDSO fragments. Silicon is bound chemically to carbon, so the material can be called as DLC doped with silicon and/or silicon oxo-carbide when -SiC- is incorporated in DLC structure.

Acknowledgements

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Quantum Cascade Laser Absorption Spectroscopy Study on the Influence of Plasma Stimulated Surface Adsorptions to the NO Destruction Kinetics

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Two quantum cascade laser absorption spectroscopy (QCLAS) systems were applied to measure absolute densities of NO and NO_2 in the mid-IR spectral range of 1896cm^{-1} (5.3µm) and 1612cm^{-1} (6.2µm). The influence of (i) surface treatment and (ii) direct impact of a pulsed cc-rf plasma was studied with a time resolution of 200µs.

1. Introduction

Recent concerns about pollution of the atmosphere, including NO_x emission, have led to increasing research in the field of exhaust gas cleaning technologies. Beside conventional techniques, such as catalysis or adsorption on active carbon, plasma technology offers promising techniques for toxic gas removal.

Based on the previous work of Welzel et al. [1] the plasma surface interaction has been investigated by means of a rf plasma. The focus of this study is two-fold (i) to understand the deposition of atomic species on surfaces during a rf plasma, (ii) to measure the influence of rf plasma treated surfaces during a series of rf plasma pulses. A double quantum cascade laser measurement and control system (Q-MACS) has been used to measure absolute densities of NO and NO_2.

2. Experimental

Quantum cascade laser absorption spectroscopy (QCLAS) has been applied as a new approach for fast in situ plasma diagnostics which is, in this case, capable of realising a time resolution of 350ns. The archived time resolution was finally about 200µs, after the post-measurement data treatment. Each QCL was working in the intra pulse mode with a pulse length of 150ns. A beam splitter was used to combine both laser signals through the reactor and guide them on the same detector. To avoid an overlapping of the spectra a delay generator was employed to establish a sufficient time delay between them, which was about 50ns. The system was calibrated (for all measurements) using reference gas mixtures at different pressures.

The experiments were carried out in a cylindrical plasma reactor made of Pyrex. The inner surface of the tube was pre-treated by capacitive coupled rf plasma for 1h at 0.53mbar. The plasma was driven with different precursors, namely O_2, N_2, Ar, and synthetic air (80 % N_2 , 20 % O_2). The input power was 30W. Thereafter, a gas mixture of 1% NO in N_2 was filled into the tube and used as a probe.

The time dependent concentrations of NO and NO_2 in the tube were monitored employing two systems (Q-MACS). NO was observed at 1896cm^{-1} and NO_2 at 1612cm^{-1}. Two kinds of experiments have been performed.

First, NO and NO_2 were measured over 2h in a pre-treated tube without plasma to study potential adsorption phenomena.

Second, the behaviour of both molecules was measured during a 500ms rf plasma pulse.

3. Results

For the adsorption experiment, it could be shown, that after O_2 or air pre-treatment, the concentration of NO decreased whereas the NO_2 concentration increased simultaneously. The NO concentration remains constant after N_2 or Ar pre-treatment. The time scale for the measurement is in the range of several tens of minutes, up to 2h after plasma. For O_2 containing precursors (O_2 and air) the NO_2 concentration showed saturation at 5.3x 10^{14}cm^{-3} for O_2 and 1.2x 10^{14}cm^{-3} for air pre-treatment. This drop corresponds to the reduced O_2 concentration in air.

As a first result an initial oxygen deposition rate on the surface of 1.7x 10^{12} O/cm^2 can be calculated for the pre-treated tube assuming that all oxygen from the surface is used to oxidise NO ($NO + O \rightarrow NO_2$).

Acknowledgements

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Application of infrared absorption techniques to study VOC destruction in a multi stage dielectric pellet bed plasma reactor

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The destruction of VOCs in a pellet bed plasma reactor has been investigated ex situ using a Fourier Transform Infrared Spectrometer (FTIR) combined with an optical long path cell. The destruction of the test VOC ethylene (C_2H_4) could be monitored down to 100ppm.

1. Introduction

Over the last decades the pollution of the environment has become more and more into human minds. One group of these pollutants are chemical substances which have a high vapour pressure. They are called volatile organic compounds (VOCs). These substances are easy to vaporise and therefore, when exhausted, are present in the gas phase at room temperature and ambient pressure. Accordingly, they are easy to breath. Some VOCs are toxic to humans or under suspicion to cause cancer. For example the VOC ethylene has narcotic properties. Overall, VOCs must not be accumulated in the atmosphere or in the ground water. Therefore, contaminated industrial exhaust gases have to be cleaned before they are released. Conventional methods for VOC removal like flaring or adsorption on active carbon are extensive to handle. On the other hand, plasma technology provides promising tools for a simplified removal of VOCs. Based on a new approach by Whitehead and co-workers a new multi-stage packed-bed dielectric barrier discharge reactor working at atmospheric pressure has been designed and tested. It has been reported, that such a reactor working in series has a much higher VOC destruction rate compared to a parallel arrangement [1]. This synergistic effect is in the center of interest.

2. Experimantal

The new reactor consists of five stages. Each stage is made of two stainless steel meshes which serves as electrodes. The space between them is filled with glass beads. The dimension of one electrode is 109mm x 109mm x 1.1mm. They are approximately 15mm apart from each other. The ac voltage applied to the electrodes is in the kV and kHz range. Gas samples can be taken via tube connections between each stage. Additionally, IR transparent windows (KBr) are placed between each stage for absorption spectroscopy (AS) purposes.

For overview spectra Fourier Transform Infrared Spectroscopy (FTIR) is used. The spectrometer was combined with an optical long path cell of 32.5 m path length. For higher sensitivity and absolute concentration measurements including time dependent studies Tuneable Diode Laser Absorption Spectroscopy (TDLAS) and Quantum Cascade Laser Absorption Spectroscopy (QCLAS) will be applied, either combined with an optical long path cell or for in-situ monitoring. These techniques have been successfully established for studying molecular phenomena in plasmas and gases, especially in the field of kinetic and chemical processing [2]. In the present work the VOC ethylene has been used as a test pollutant. Ethylene is gaseous at ambient conditions with a melting point of -169°C and a boiling point of -103°C and. The concentration has been 0.1% ethylene in air.

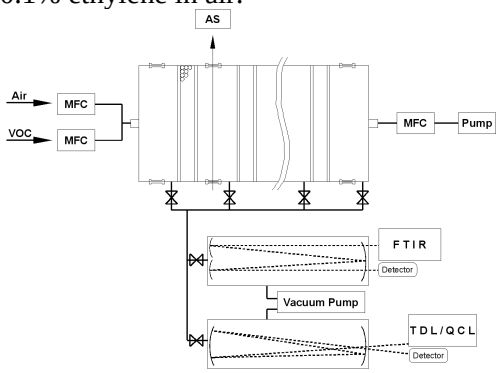

Fig. 1: *Sketch of the experimental setup. For in-situ measurements, the side walls are equipped with windows.*

3. Results

First results show, that the initial concentration of 0.1% ethylene in air was almost removed from the gas stream. Only three stages were working with a power of P=8W each. Typical products of the plasma treatment were found to be CO, CO_2, N_2O, O_3, H_2CO and H_2CO_2.

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Design of a system of electrostatic probes for the RF negative ion source of the SPIDER experiment

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A test facility (SPIDER) is foreseen to be built in Padova, Italy, in order to test and optimize the RF source of negative ions to be used in the ITER neutral beam injectors. In this contribution the Langmuir probe system designed for monitoring the region, where most of negative ions are expected to be produced, will be presented.

1. Introduction

The realization of the Neutral Beam Injector (NBI) for ITER represents a technology challenge. ITER will be equipped with at least two NBI systems providing an effective power to the plasma of about 16 MW each of accelerated particles at 1MV [1]. The required initial current is of 40A of negatively charged deuterium for each system will be provided by an RF ion source.

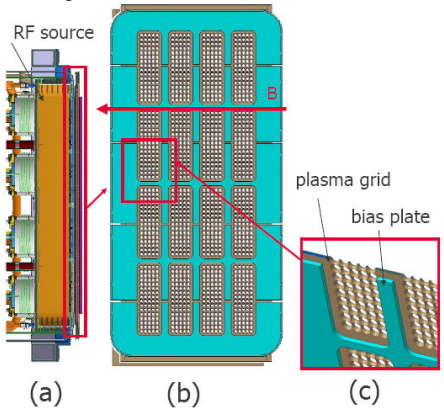

Fig. 1*: section of the RF ion source of SPIDER an of the extraction region(a), the bias plate and the plasma grid are evidenced (b,c)*

In order to test, commission and optimize the ion source and all the beam line components of the NBI system for ITER a facility is foreseen to be built in Padova (Italy). Within this project a specific facility, SPIDER (Source for the Production of Ions of Deuterium Extracted from Rf plasma), will be devoted to the ion source test and optimization. The negative ions extracted in this case will be accelerated up to 100 kV. In SPIDER, a system of electrostatic probes will measure the plasma parameters and monitor their homogeneity in the region facing the plasma grid, where most of the negative ions are expected to be produced and extracted.

2. Design of the Langmuir probe system

The functioning principle of the above mentioned RF negative ion source can be found in [2].

The SPIDER source will be equipped with 2x4 RF drivers. In figure 1a the vertical section of the SPIDER source is shown, some details of the plasma facing components before the acceleration step are also given in fig. 1b and 1c: the plasma grid is characterized by the presence of 4x4 modules of 16x5 apertures through which the ion beam will be extracted; the bias plate plays the role of favouring the extraction of the negative ions.

The plasma grid and the bias plate will support the electrostatic probe system. Sensors will be installed on the plasma-facing surface of plasma grid and bias plate, as well as on the sides of the bias plate perpendicular to the local magnetic field. The global system involves 72 probes and will allow the spatial characterization of plasma parameters in the extraction region.

This contribution will present the design criteria and the adopted solutions. The presence of RF and magnetic fields, deposition of conducting materials (es. Cu, Cs) during the operations, robustness and easy maintenance are some of the aspects guiding the design work, as well as the constraints related to the integration of the probes in the source design. As an example fig 2 shows the components constituting a probe designed for the plasma grid and its integration in the grid itself.

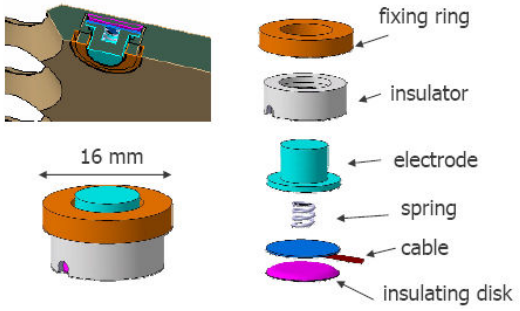

Fig 2. *Details of the Langmuir probe assembly, the section upper right show how one of the probe is embedded in the plasma grid*

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A numerical procedure for the evaluation of data with local, close-to-coherent noise

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A numerical procedure able to effectively eliminate close-to-coherent noise from measured data is presented. Previous standard techniques try to identify the signal in order to remove the noise. Conversely, the current procedure identifies the disturbance itself. As a result, it additionally provides all the information required for the reconstruction of data that may have become distorted due to the superimposed noise in case of non-liner systems, *e.g.* in Langmuir probe measurements.

1. Introduction

Data processing of noisy signals is probably the most delicate phase in an experimental work and its complexity increases as the *a priori* information on what the signal and the noise actually are is missing. Indeed, what common filtering procedures do is to eliminate the spectral region where the noise content is supposed to be, which obviously will distort data as much as their spectra are merged.

Manufacturers of instrumentation dedicated to measurements under noisy conditions, *e.g. data averagers*, *boxcar integrators*, *lock-in amplifiers*, etc., use to "sell" the idea that such equipments solve whatever noise problems users may have. Yet, the above equipments are really effective under rather peculiar conditions, namely in case of *white noise*, periodic signals, etc.

As a result, filtering at data processing-time may be a soundest filtering alternative as compared to trying to do so while data is being acquired and may be the only effective solution. Yet, the most common procedures for the numerical filtering of data rely on (or are equivalent to) Fourier transforms, which typically suffer from a drawback: they require huge acquisition-times in order to be effective whenever the acquisition-time is not an exact integer multiple of the characteristic period of either the signal or the noise. The reader must keep in mind that increasing the data acquisition-time, though being a last resource, should be avoided as much as possible because experimental conditions inevitably change along time and also long-time correlated noise will have a chance to become a main concern.

If the disturbances in plasma measurements were always of a coherent type, *e.g.* the noise due to mains and due to the generator excitation frequency (HF and MW discharges) and their harmonics, they could be readily filtered. In such a case and even if data had been distorted due to a plasma non-linearity, also the information required for data reconstruction would be readily available. Unfortunately, plasma instabilities and data acquisition procedures based on common operating system of PCs are sources of non-coherent disturbances.

2. An adaptive, self-tuning numerical procedure

The current numerical procedure is intended to identify what we call locally, close-to-coherent noise, *i.e.*, whatever is not what the user intends to measure but that can be acceptably described by a slow-varying (along the whole set of data), time- and frequency-modulated function.

Once launched the procedure starts by identifying any characteristic period by cross-correlating two half-sets of data, whose value is used as a seed for a precise identification of the disturbing frequencies. Next, it identifies the local values of the amplitudes and of the amplitude- and frequency-modulations. As a result, not only the so evaluated noise can be readily eliminated, because it as been well identified, as all its characteristics are kept, which means that deconvolution procedures have the basic information required for carrying out data reconstruction.

The correctness of the current procedure was proven using model tests, whose results will be presented.

This work is a logical continuation of previous ones on the filtering of Langmuir probe data and their reconstruction, which have been presented in previous editions of the FLTPD series [1-2].

Acknowledgment

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On the plasma properties of diffuse coplanar surface barrier discharge in humid nitrogen and humid air studied by optical emission spectroscopy

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In this work we investigated the influence of working gas humidity on the plasma properties of diffuse coplanar surface barrier discharge. As working gases pure nitrogen and technical air admixed with the vapours of distilled water were used. The intensities of second positive system of nitrogen and OH radical together with ignition and extinction voltages were measured.

1. Introduction

The plasma technology based applications have important role in industrial processing of materials [1] especially in case of surface modification. There is great demand on the generation of highly non-equilibrium homogeneous plasma with as high as possible power density.

The diffuse coplanar surface barrier discharge (DCSBD) [2], compared with other atmospheric pressure barrier discharge systems, has advantages in its simplicity, robustness and capability to process in a wide range of working gases [3].

Extensive research of DCSBD has been started in order to better utilize the discharge parameters for industrial applications. Among others the influence of electrode temperature and applied voltage [4] or discharge geometry [5] on the plasma parameters of DCSBD have been investigated and published.

2. Experimental

In this work the influence of working gas humidity on plasma parameters of DCSBD was investigated. The commercial DCSBD reactor [2] was used. As the working gases pure nitrogen and technical air at atmospheric pressure were used. The humidity of working gas was controlled in the range of 3 to 80 g_{H2O}/kg_{GAS} by mixing of dry gas with gas flowing through thermostatic heated bubbler filled with distilled water.

The following plasma parameters were studied: the discharge pattern of DCSBD, intensities of second positive system of nitrogen and OH radical band. Oxygen and NO system intensities were also measured. The vibrational temperature of second positive system of nitrogen and rotational temperature of OH were also estimated, where possible.

Gas humidity and temperature were measured by Extech Instruments RH520 chart recorder. Discharge spectra were recorded by Jobin-Yvon Triax 550 spectrometer equipped by CCD detector cooled with liquid nitrogen. Discharge patterns were taken by digital camera.

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Surface nanosecond discharge at elevated pressures as a tool for initiation of combustion

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Surface nanosecond discharge at elevated pressures has been proposed as a tool to initiate combustion assisted by nonequilibrium plasma at elevated pressures. Preliminary experiments have been carried out; ICCD imaging of the discharge has been obtained for 1-5 atm ambient air.

1. Introduction

Typically, plasma assisted combustion (PAC) experiments are carried out at atmospheric or at decreased gas pressure [1]. Here we propose a system which can lead to ignition under conditions of automotive engines, including HCCI, gas turbines and other high-pressure devices. It is proposed to use surface nanosecond discharge [2] developed for aerodynamic applications in combination with rapid compression machine [3] for quantitative study of PAC initiation at elevated pressures.

2. RCM applications for plasma assisted ignition and combustion

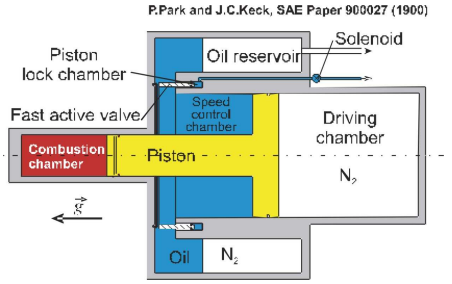

Fig. 1: *Scheme of RCM machine [3]*.

Rapid compression machines (RCM, Fig.1) are designed to study the ignition delay time at low temperatures (about 1000 K) and high pressures (tens and hundreds of atm), at the conditions similar to those in internal combustion engine. The only RCM application for artificial (laser stimulated) ignition is known in the literature [4]. If we manage to organize the nonequilibrium plasma between the end plate of the combustion chamber and the piston, or, at least, near the end plate, we will be able do decrease the ignition delay time and to investigate kinetics of plasma assisted ignition at high pressures.

3. High-voltage pulsed discharge at elevated pressure: preliminary experiments

Nanosecond DBD discharge in a special coaxial geometry of electrodes was used to produce a thin layer of quasi-uniform plasma in the vicinity of low-voltage electrode. High voltage pulses of 10-20 kV amplitude, 25 ns duration, 3 ns rise time, positive or negative polarity, and repetitive frequency 40 Hz were used to ignite the discharge in ambient air at pressures 1-5 atm. Emission was registered by LaVision PicoStar ICCD camera (200-800 nm) in nanosecond time scale. ICCD images of nanosecond DBD discharge in ambient air are given by Fig. 1. Gas pressure, voltage amplitude in the cable, and ICCD gate are indicated for each picture. The total energy input in the discharge did not exceed approximately 10 mJ, or 10 % of the energy stored in incident nanosecond pulse.

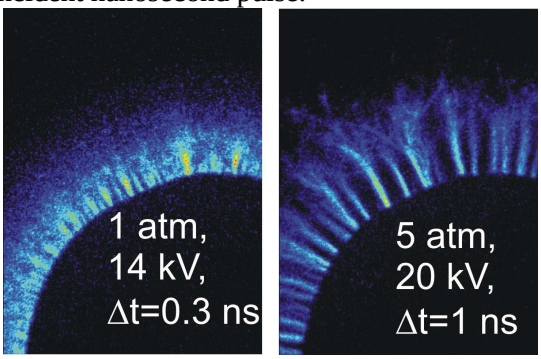

Fig. 2: *ICCD images of nanosecond surface discharge*

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Influence of mineral vapour compounds on metal plasma temperature

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This paper focus on complex gas-metal vapour influence on plasma arc. The measurement set-up and calculation techniques are described. Calculated plasma compositions are presented. Experimental results for various metal contaminants in plasma are discussed.

The electric arc in gas-metal atmosphere appears in many applications. Determining of metal vapour density in plasma is essential for mathematical modelling of plasma behaviour as a conducting medium. The circuit breakers are an excellent example of influence of metals on plasma conductivity due to contamination of evaporating electrodes. Low value of the ionization potential of metallic contacts leads to the ac arc reignition at the current zero that in turn cause higher erosion of contacts.

Another example of metal contaminated electric arc is the plasma waste destruction with no residues. Wastes are composed mostly of metal oxides such as SiO2, Al2O3, CaO, MgO, Na2O, K2O. They are over 95% of ash composition. During plasma waste treatment the electric arc is mostly initiated in neutral working gas e.g. argon. The arc plasma high temperature leads to vaporization and decomposition of wastes. Gaseous metals enter the arc channel changing its parameters such as conductivity, temperature, electron density etc.

Metal-gas atmosphere also appears in metallurgical processes involving plasmas. Welding and cutting arc contains significant quantities of metal vapour that considerably decrease the effective ionization potential of the mixture of gases being the plasma medium.

This paper deals with investigations of arc plasma in complex gas – metal vapour mixtures. Experimental techniques in the diagnostics were presented. Various detecting materials were analyzed and advantages of using copper have been shown. Spectroscopic measurements of electric arc temperature profiles are discussed. Plasma composition has been calculated and compared to the measured results.

Acknowledgement

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The challenge of CH spectroscopic measurement in a He(N_2)-CH_4 atmospheric pressure dielectric barrier discharge

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In this contribution we report the most recent progress in our attempts to determine CH density and time evolution in a He(N_2) DBD with small CH_4 additions at atmospheric pressure, by Laser Induced Fluorescence and by Optical Emission Spectroscopy.

1. LIF detection of CH(X, v=0)

Laser Induced Fluorescence detection of CH in a Dielectric Barrier Discharge (DBD) at atmospheric pressure is almost an archetype of all the difficulties that can be encountered in the application of this spectroscopic technique. These difficulties are relevant to:

a) *the discharge kinetics* - low average CH densities are expected, due to its high reactivity and to the pulsed and spatially inhomogeneous nature of the discharge.

b) *the CH molecular structure* – all available electronic transitions (CH(A-X), CH(B-X) and CH(C-X)) are strongly diagonal, limiting the choice of an efficient excitation-detection scheme in which the detected fluorescence band is different from that chosen for laser absorption.

c) *the CH electronic states kinetics* – the collision quenching due to the high discharge pressure, and the pre-dissociative nature of the CH electronic states strongly lower the fluorescence yield.

d) *the discharge hardware structure* – the small dimensions, of the order of the laser beam ones, and the fluorescing nature of the materials employed, are a big concern in a LIF experiment, due to the resulting strong diffused light that is superimposed to the true LIF signal.

We have applied the following excitation-detection scheme:

$$CH(X,v=0)+h\nu_L \rightarrow CH(B, v=1) \rightarrow CH(X,v=1)+ h\nu_F$$

that gives the best combination of diagonal/off-diagonal absorption/emission coefficients, to a He-CH_4 discharge, getting a low but measurable signal. In this contribution we will show these results and discuss a special design of the discharge apparatus aimed at the improvement of the LIF outcomes.

2. OES detection: a possible route to CH(X) density calibration

Quantitative comparison of CH(A) and N_2(C) (second positive system) emissions can give a chance to infer the absolute CH concentration in a discharge containing a known N_2 quantity. The N_2(C) kinetics is in fact actually well known, and the use of SPS emission as an electron temperature monitor is quite well established [1]. Furthermore, a significant progress has been achieved very recently in the knowledge of CH(A, B, C) states electron impact excitation [2].

The possibility of a quantitative CH density determination from OES is linked to the following conditions:

a) *electron impact excitation of CH(A,B,C) states* – discharge conditions in which such occurrence can be ascertained must be selected.

b) *a maxwellian EEDF* – due to the quite different excitation threshold of CH(A,B,C) states and N_2(C) state, the electron energy distribution function (EEDF) must be well characterized.

c) *knowledge of the CH(A,B,C) yield* – the collision quenching and pre-dissociation rates of CH electronic states must be well known, as it is the case for N_2(C) state.

d) The discharge must be homogeneous (glow type), in order to compare OES results to LIF ones, that are volume averaged. In the case of a filamentary discharge OES density estimates would be relevant to a density inside the filaments, that fill only a small part of the discharge volume. CH radicals in fact are not able to escape the filaments volume, due to their low lifetime.

In this contribution we discuss the applicability of an OES method for CH density estimation to selected discharge conditions.

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Absorption spectroscopy with an UHP-backlight system – an innovative and simple concept for particle density diagnostics in HID-lamps

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Aim of the presented work is the optimization of electrodes in high intensity discharge (HID) lamps by investigating the gas-phase emitter-effect. An innovative, simple and cheap absorption diagnostic setup will be presented consisting mainly of a strong UHP-backlight source. The new concept can replace the complex conventional laser absorption systems in special applications like HID diagnostic. Results are given exemplarily for particle density measurements in HID lamps.

1. Introduction/ Motivation

Due to their small size and high efficiency, high intensity discharge (HID) lamps are recently installed within several modern lighting applications like car headlights and video projectors. However, fundamental research on the electrodes of HID-lamps is still needed to increase their efficiency and lifetime. One optimization concept is the reduction of the electrode temperature by use of the so called "gas-phase emitter effect" [1]. Previous investigations are based on emission spectroscopy measurements of the densities of emitter materials (Dy, Na, Ba and Ce) in correlation with electrode temperature measurements [2].

Within this work a new absorption spectroscopy setup was developed and applied to HID lamps to become more flexible in lamp diagnostics.

2. The UHP-absorption measurement

2.1. Absorption spectroscopy

To determine the density of specific atoms within a plasma, the spectral absorption of an artificial light source behind the plasma can be measured. This absorption measuring method has several advantages compared to the emission measurement of excited state atoms: At first, the ground state atom densities can be calculated directly from the spectral absorption without any information about the plasma temperature or their partition function. Additionally, the backlight can be positioned independently of the plasma discharge, so that atom densities can also be measured at positions where no emission from excited states is present.

2.2. The measuring setup

As the backlight source of an absorption spectroscopy system should offer more spectral power than the plasma itself, conventional setups consist mostly of complex and expensive laser systems. In contrast, the absorption setup within this work is realized by means of a powerful and filtered ultra high pressure light source. This UHP solution is simple and can measure the absorption profile during one single measurement while avoiding any spectral-sweep process as being needed in case of a laser absorption measurement. The original light intensity without absorption can be determined by fitting a polynomial line to the measurement (fig. 1).

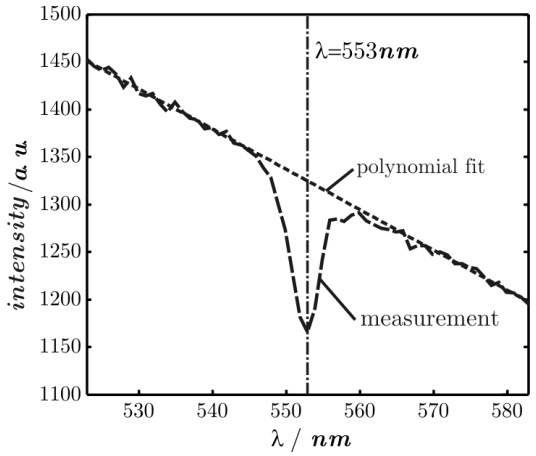

Fig. 1: *Example of a Ba absorption peak measured at λ=553nm and the corresponding polynomial fit*

3. Results

By means of the presented absorption diagnostic setup it was possible to measure and investigate the transport process of barium emitter material around the electrode shaft in a high pressure sodium lamp. Ba densities and the diffusion optimization will be presented leading to a significant extension of the lifetime of the HID lamp.

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Characterization of a low-pressure microwave plasma for sterilization of polyethylene terephthalate bottles using optical emission spectroscopy and Langmuir probe diagnostic

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The goal of this work is to get a space and time resolved characterization of a plasma process and to optimize radiation in the desired wavelength range for the development of a sterilization process for polyethylene terephthalate (PET)bottles. For that purpose optical emission spectroscopy (OES) and Langmuir probe diagnostics are performed.

1. Introduction

Modern packaging materials such as polyethylene terephthalate (PET) offer various advantages over glass or metal containers and are gaining in importance for food and beverage packaging. PET bottles are nonbreakable and lightweight compared to established materials, but they only offer a reduced heat resistance. Therefore, the sterilization of polyethylene terephtalate (PET) bottles in aseptic filling machines is based on toxic sterilants such as hydrogen peroxide.

As an alternative, a low-pressure microwave plasma process is developed where a plasma is ignited inside a PET bottle to reach a sterilization by applying non-toxic gases argon, hydrogen and nitrogen. Radiation in the wavelength range from 160 to 300 nm is known to be very efficient in sterilizing spores such as *B. atrophaeus* and *A. niger*. The goal of this work is to get a space and time resolved characterization of the plasma process and to optimize radiation in the desired wavelength range for sterilization. For that purpose optical emission spectroscopy (OES) and Langmuir probe diagnostics are performed and results are discussed.

2. Experimental setup

The experimental setup as described in previous works consists of a vacuum chamber with a volume of 6 liter being capable to treat various bottle sizes up to 1.5 liter. A coaxial wave guide combined with a gas-inlet, called Plasmaline, is used for injecting microwave power and gas mixture into the bottle [1].

The plasma is investigated by means of optical emission spectroscopy (OES). Two absolute calibrated spectrometers are used for revealing spectra in the wavelength range from 110 to 800 nm. Additionally, Langmuir probe measurements are performed to yield plasma parameters, like electron density ($\mathrm{n_e}$), average electron energy ($\mathrm{E_{mean}}$) and electron energy distribution function of the electrons (EEDF). The plasma parameters are determined with time ($\Delta t = 20\,\mu\mathrm{s}$) and spatial ($\Delta x = 1\,\mathrm{mm}$) resolution.

Plasmas with various gas mixtures like Ar, Ar:$\mathrm{H_2}$ and Ar:$\mathrm{N_2}$, a set of process pressures from 20 to 50 Pa, various duty-cycles and generator powers up to 2000 W are examinated.

3. Results and discussion

OES spectra and spatial and time resolved profiles of $\mathrm{n_e}$ and $\mathrm{E_{mean}}$ are discussed by means of parameter variation. Typical electron densities can be specified in the range of $5 \cdot 10^{-16}$ to $8 \cdot 10^{-17}\ \mathrm{m^{-3}}$ depending on spatial position. Average electron energies remain almost constant at 2 eV with a strong increase close to Plasmaline. A hydrogen continuum emitted by a Ar:$\mathrm{H_2}$ plasma yield a maximum of radiation in the desired wavelength range.

Sterilization tests are performed to document the capability of this optimized gas mixture. After a treatment time of 4 s the sterilization results satisfy the requirements for aseptic packaging machines as defined by the U.S. Food and Drug Administration and the German Engineering Federation.

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Higher harmonics of plasma potential in capacitively coupled discharges

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Measurement of the waveform of the plasma potential and its harmonic frequencies was made by means of an uncompensated probe. The analysis of the measured data requires a model of the sheath around the probe.

Due to the nonlinearity of sheaths of capacitively coupled discharges, plasma potential waveform contains not only DC component and fundamental frequency but a number of higher harmonic frequencies as well [1, 2]. Higher harmonic frequencies influence the plasma [3] and can be used for plasma diagnostics and process monitoring [4, 5, 6, 7]. The harmonics can be measured by means of an uncompensated probe [8], a segment of the reactor wall that collects a part of the discharge current [6] or by means of measurement of the RF voltage and current on the cable between the power generator and the powered electrode [4]. The uncompensated probe, which is immersed directly into the plasma, is a very sensitive sensor of higher harmonics [5]. Moreover, it is the only method which enables to do space-resolved measurements of harmonics of the plasma potential. However, the interpretation of the measured data is not straightforward, since the measured probe voltage is influenced by a thin nonlinear sheath around the probe and by electric parameters of the probe. Due to these effects the measured waveform differs strongly from the plasma potential waveform.

Consequently, an effort is made to calculate the waveform of the plasma potential by means of data measured by the uncompensated probe. For this purpose a simple model of the thin sheath around the probe was made which suppose a homogeneous concentration of positive ions in the sheath, constant ion current and time-varying electron and displacement currents flowing through the sheath. If the waveforms of the probe tip voltage and of the total current flowing to the probe tip are known, the model enables to calculate the waveform of the plasma potential. In order to get reliable results the calculation requires knowledge of parameters measured by the RF compensated Langmuir probe, especially the mean (DC) value of the plasma potential. At present, the highest problem of the presented method is the error-prone calibration of the electric parameters of the probe itself, i.e. the relationship between waveforms at the probe tip and waveform measured at the output of the probe by an oscilloscope.

The probe, which consisted from a thin conductive wire connected to a 50 Ω coaxial cable, was used to measure the waveform of plasma potential in low-pressure capacitive discharge in hydrogen. The measured data were analyzed by the described model. In the Fig. 1 examples of amplitudes of the harmonics are shown, which were calculated by Fourier transformation of the plasma potential waveform. High amount of higher harmonic frequencies, especially at low pressure, is evident.

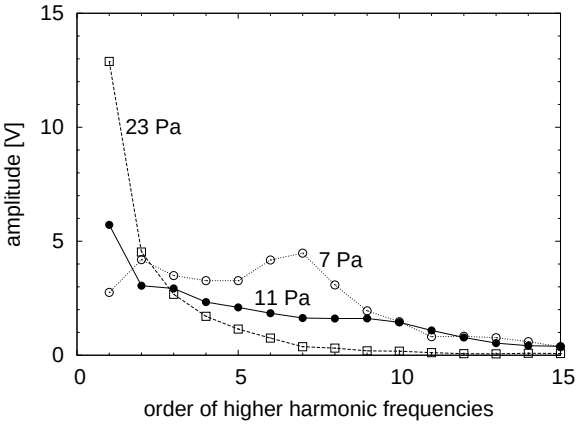

Fig. 1: *Amplitudes of fundamental and higher harmonic frequencies of plasma potential in capacitive discharge in hydrogen. Measured for pressures 7, 11 and 23 Pa.*

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Analysis of optical emission spectra in supersonic thermal plasma jet

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We present optical emission spectroscopy investigation of thermal plasma jet generated by the torch with hybrid stabilization. The results include different temperature distributions obtained from spectra of atoms and molecules.

1. Introduction

Operating of the plasma jets at low-pressure conditions brings advantages especially from the point of view of application in deposition of different coatings. Lower amount of oxygen is appreciated because of increased quality of the deposited layer. This work presents investigation of plasma jet, which is located in the chamber with pressures from 1 kPa to 10 kPa. Plasma jet is generated by the DC torch, which is stabilized by gas and liquid. The jet is studied by means of optical emission spectroscopy, which is straightforward and useful method to obtain temperatures, densities and composition of the plasma.

2. Experimental Setup

Our plasma jet is generated by the plasma torch with hybrid water-argon stabilization, where the argon is supplied along the cathode and the water vortex is created around the plasma column in the second part of arc chamber. The water-cooled anode is located outside the arc chamber, while the nozzle is not used as an electrode because of very high thermal load. The plasma jet is expanding into the chamber, where the pressure can be kept between 1 kPa and atmospheric pressure. Commonly the plasma at the nozzle exit is composed from the atoms and ions of argon, oxygen and hydrogen and possibly some admixture of chemically active radical OH. It is possible to add small admixture of some other gas into the argon or some chemical substance dissolved in water. Optical emission spectroscopy diagnostics is made by means of monochromator Jobin Yvon – Spex Triax 550 equipped with gratings 300, 1200 and 3600 grooves/mm. The output spectrum is detected with MTE CCD 1024x256 detector connected to the CCD 3000 controller and to the PC.

3. Results

From the lines of neutral argon and oxygen, assuming Boltzmann distribution of population of excited levels, it is possible to obtain excitation temperature. Similarly, using Saha equation characterising number densities of ionised species, we have ionisation temperature. The rotational and vibrational temperatures are derived by fitting experimental UV OH band $A^2\Sigma$, $v = 0 \rightarrow X^2\Pi$, $v' = 0$, to the simulated spectrum using LIFBASE software. In case of nitrogen addition we are able to detect also molecular spectra of NH and N_2, from which temperatures are calculated using the software SPECAIR.

Close to the nozzle exit of the plasma torch, the jet is characterized by high temperature and intensity of radiation. Results in this region are independent from the chamber pressure. It is caused by the fact that the pressure at the nozzle exit is higher than the chamber pressure, which creates expansion of high pressure plasma to the low pressure chamber. This type of jet is called underexpanded. High pressure region with its high particle density is dominated by collisions of the particles, which creates local thermodynamic equilibrium. It means that the processes of excitation and ionisation are in equilibrium and temperature is unambiguously defined. Measurements of excitation and ionisation temperatures in this region confirm this assumption.

Rotational and vibrational temperatures are studied especially in the colder parts of the jet, i.e. downstream from the hot core and in the fringes of the jet, where atomic emissions were too weak. These results give information about prevailing processes in plasma and reveal non-thermal mechanisms populating excited levels of molecules.

Argon ion velocity distributions in a helicon discharge measured by laser induced fluorescence

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In an argon Helicon discharge, generated with a flat coil at a frequency of 13.56 MHz, the radial and axial velocity of the ions is measured spatially resolved by laser induced fluorescence. The results show a drift outwards the discharge centre with velocities of several 100 m/s.

1. Introduction

Helicon discharges allow the generation of high density plasmas although operated at low pressure around 0.1 Pa. Here the ion velocity distribution in an argon discharge is studied experimentally. The Helicon discharge is generated by a flat coil antenna operated at 13.56 MHz in an azimuthally isotropic m = 0 mode. The Helicon wave develops as a standing wave confined along the static magnetic field lines between the antenna and the chamber bottom (distance 50 cm). Ion velocity distributions along and perpendicular to the static magnetic field are measured by laser induced fluorescence spectroscopy of metastable argon ions. The velocity distribution measurements are supplemented by probe measurements of the ion density, the electron energy distribution, and the floating and plasma potentials. Possible heating mechanisms for the ions are discussed. Candidates are wave heating, temperature and density gradients, and a double-layer in the divergent magnetic field.

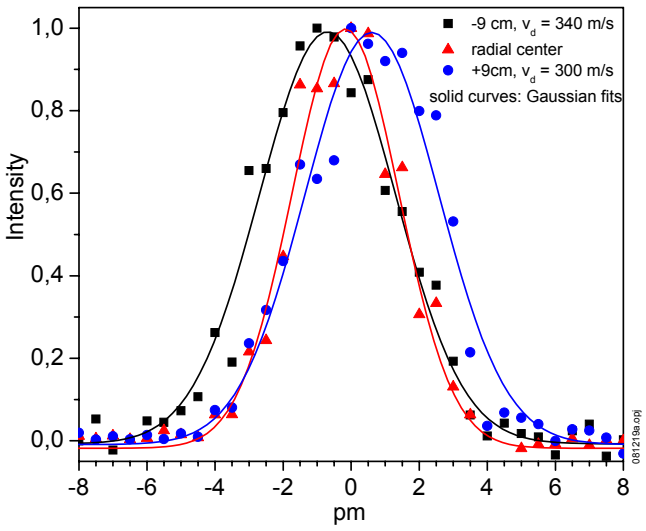

Fig. 1: *Doppler profiles taken 10 cm below the axial chamber center at three different radial positions.*

2. Experimental results

The discharge for the measurements shown here has been operated in argon at a pressure of 0.1 Pa, an RF power of 1 kW. Pulsed radiation ($\Delta t \approx 5$ ns) from a dye laser with a spectral bandwidth of 0.03 cm^{-1} and a power density below 1 kW/cm^2 is aligned parallel as well as perpendicular to the static magnetic field. Perpendicular to the laser beam an intensified CCD camera measures the induced fluorescence spatially and temporally resolved.

Figure 1 shows the Doppler profiles taken in the axial center of the discharge at different radial positions. Clearly a drift of the ions outwards the center of the helicon with a velocity in the order of 300 m/s can be observed.

The measurements with the laser in the axial direction along the magnetic field lines show an increasing drift away from the axial center. In parallel also the ion temperature determined from the width of the spectra increases (fig. 2).

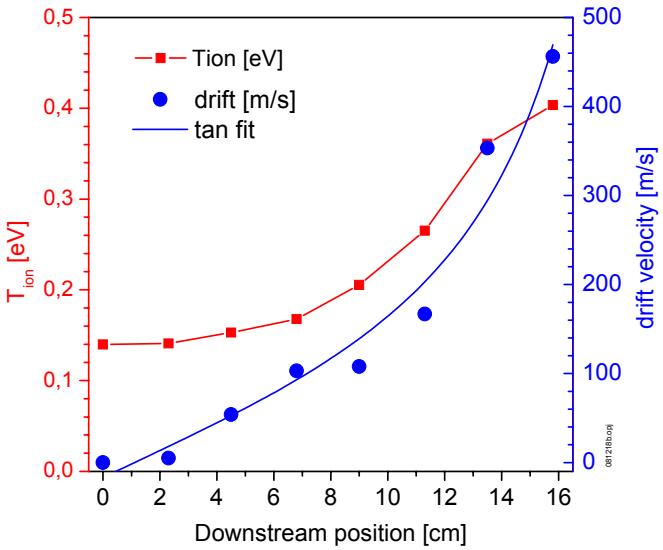

Fig. 2: *Axial temperature and drift velocity measured in the radial center. A tangent function is fitted tentatively to the drift velocity as a simple approximation for acceleration by the ambipolar field.*

Investigation on the sterilization mechanisms of a double inductively coupled plasma

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Gentile plastic materials used for medical implants are a challenge for common sterilization processes, which are either too hot or toxic. Plasma sterilization is a method to achieve cold, gentile and fast sterilisation of medical objects. This contribution focuses on sterilization caused by radiation in the range of 110 - 450 nm . Two absolute calibrated optical emission spectrometers are used to characterize different gas mixtures and filters used for sterilization experiments. Sterilization results are presented to show the efficiency of optical emission as an important sterilization mechanism in plasmas.

1. Introduction

Nowadays a broad range of different materials are used for medical implants. Especially plastics need gentile sterilization methods in order to endure the sterilization process. Common sterilization methods have disadvantages concerning thermolabile or biodegradable materials. An approach developed at the Institute for Plasma Technology in Bochum is sterilization with a low temperature plasma. With this it is possible to sterilize medical surfaces with non-toxic gases such as argon, oxygen or nitrogen. Different sterilization mechanisms inside a plasma are known: radicals, ion bombardment and radiation. Radicals etch the spore coat, ions with enough energy break bonds, UV and VUV photodesorbtion can produce volatile species in the spore coat. This can lead to cell death during proliferation. Additionally radiation below 275nm can cause strand breaks in the DNA.

2. Experimental setup and results

A double inductively coupled plasma reactor (DICP) [1] is used for the investigation of the specific sterilization mechanisms. The stainless steel vessel has a volume of 25 l. The thin copper coils at the top and bottom are divided by quartz glass from the chamber. A power between 500 and 5000 W and a pressure between 1 and 20 Pa is used.

In order to investigate the optical radiation, two optical emission spectrometers are available. An Echelle- and a VUV-spectrometer. These spectrometers are absolute calibrated as described by Bibinov et al. in [2, 3]. This setup is capable to meassure from 110 to 800 nm. A variation in power, pressure and gas mixture allow a characterization of the plasma discharge. Differnt filters used for sterilization experiments are characterized by the Echelle-spectrometer and a deuterium-lamp.

Samples of different bacterial and fungal spores such as *B. atrophaeus* or *A. niger* are prepared by the Fraunhofer Institute for Process Engineering and Packaging. These spore are treated at different plasma parameters as well as the spores are covered by different cut-off filters in order to determine the radiation dependency of these spores in the UV range. Differnt gas mixtures are found, which allow to confine the sensitivity in the VUV range.

It can be shown that *B. atrophaeus* spores are sensitive to radiation between 235 and 300 nm. In contrast to this, *A. niger* spores are resistant to radiation above 235 nm. VUV radiation is needed to sterilize *A. niger* spores. With an optimized gasmixture it is possible to sterilize *B. atrophaeus* spores in 20 s at a intensity of $1.4 \cdot 10^{20}\ \mathrm{photons/(m^3\,s)}$.

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SPATIAL DISTRIBUTION OF PLASMA PARAMETERS IN DC-ENERGIZED HOLLOW CATHODE PLASMA JET: SYSTEM STABILITY

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Spatial distribution of electron concentration, plasma potential and mean electron energy were obtained in the hollow cathode plasma jet system by Langmuir probe diagnostics. The plasma jet was energized by a current-stabilized DC source. TiOx thin films were deposited onto silicon and glass substrates and examined by AFM. Temporal system stability was investigated by measurement of time dependences of main plasma parameters in argon and argon-oxygen mixture.

1. Introduction

DC energized plasma jet systems which utilize hollow cathode effect are well known as deposition sources [1]. The system with cylindrical symmetry, which used in our experiments, works at low pressure of several Pa. The UHV technology provides good cleanliness and hence the studied processes are well reproducible. The used DC power supply in current stabilizing mode was chosen since it offers stable conditions of the plasma under study.

The principle of the plasma jet system with hollow cathode is presented in Fig.1. The depicted hollow cathode is positioned at the axis of cylindrical continuously pumped reactor chamber of 30 cm in diameter. Water cooled pure Ti nozzle serves as hollow cathode and sputtering target and is connected to the negative pole of the DC power supply. The system with Ti nozzle permits deposition of pure Ti as well as its compounds with active working gas admixtures such as O_2, N_2, etc. [2]. The used buffer gas was argon.

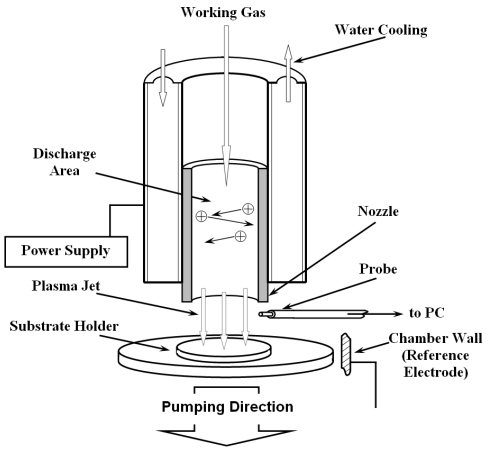

Fig 1. The principle of hollow cathode plasma jet.

Working gas can be introduced in the reactor chamber in two gas flow modes. In the first mode the argon-oxygen admixture is fed directly into the hollow cathode. In the second mode argon is fed into the hollow cathode and oxygen is fed into the chamber volume. The Ar flow was 50 sccm, the oxygen flow 5 sccm. For both measurement modes the experiments were performed at similar power, pressure and gas proportion conditions. The discharge voltages for clean argon and argon-oxygen mixture were in the limits 260-370V.

2. Experiment

The Langmuir probe method is capable of determining the fundamental plasma parameters [3]. We have used cylindrical tungsten probe 30 μm in diameter and 3 mm in length oriented parallel with the system axis. The radial dependence of plasma parameters was measured for distances from the system axis 0-116 mm.

Before each measurement the probe surface was cleaned by argon positive ion bombardment, i.e. with the oxygen flow stopped. From current-voltage probe characteristics we estimated the electron concentration, plasma potential and the mean electron energy.

System stability was assessed from probe measurements in periodic time intervals with the probe being positioned at a fixed radial position 20 mm from system axis for discharges running in clean argon and in argon-oxygen mixture.

Acknowledgment

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Electric and Spectroscopic Characterization of Magnetized Hydrogen and Helium Hot Cathode Discharge Plasma

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In this contribution we present the characteristic properties of magnetized hydrogen and helium plasma measured with probes and optical emission spectroscopy, i.e., by diagnostic techniques which are readily available in divertor plasma simulators and in smaller experimental fusion devices.

Intensive research efforts are currently devoted to the role of hydrogen atoms and molecules as well as helium atoms in fusion edge plasmas [1]. For such investigations linear magnetized plasma machines have recently gained importance for simulating edge or divertor plasmas in fusion experiments. In such devices basic plasma-wall interaction mechanisms and turbulent transport across the magnetic field can be studied conveniently. One great advantage is that simple plasma and neutral gas diagnostic techniques can be applied and improved or new methods developed and tested. We have investigated novel probe and spectroscopic techniques under complex edge-like plasma conditions. Here we present the results of investigations on the characteristic properties of magnetized hydrogen and helium plasmas with diagnostic techniques readily available in divertor plasma simulators [2] and smaller experimental fusion devices [3].

The linear magnetized plasma machine (LMPM) at Jožef Stefan Institute in Ljubljana consists of a source chamber and an experimental chamber. The source chamber is embedded in a weak converging magnetic field. The experimental chamber has a diameter of 17 cm, is 1,5 m long and is situated inside 14 magnetic coils producing a linear magnetic field from 0,01 T to 0,4 T. The pressure ranges from about 0,05 Pa to 0,6 Pa. Plasma is generated by a hot cathode discharge between ten heated thoriated tungsten wires and the source wall. The thoriated W-wires are 0,2 mm thick and 10 cm long, connected in parallel and heated with 40 A current to the emitting temperature. The discharge voltage is 50 V. The plasma column in the experimental region has a diameter of 2,5 cm and is terminated by a floating or biased end plate. The length of the plasma column is 1 m.

A cylindrical Langmuir probe (CLP) is inserted from top of LMPM. It consists of thoriated W-wire with 0,2 mm diameter and 5 mm length. The probe serves for the evaluation of electron temperature, plasma potential and floating potential. The second method is applied by using an optical spectrometer, and its probe is inserted form the side of LMPM at a distance of 20 cm from the CLP. A new diagnostic system for Fulcher band spectroscopy was installed at the machine. In parallel we introduce a seldom used method for measuring the electron temperature with a floating emissive probe. In this case, the bi-Maxwellian nature of the electron distribution function has to be carefully taken into account.

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Experimental and modelling study of the nitrogen kinetics in active-discharge and post-discharge

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The nitrogen afterglow of a DC discharge was studied by optical emission spectroscopy and the experimental data was compared with modelling results. At p=1000 Pa, experiment exhibits the appearance of the raise in optical emissions characteristic of the pink afterglow when the discharge current increases from 50 to 70 mA. There is indication that the gas temperature may play an important role in a more detailed understanding of the phenomenon.

1. Introduction

The study of nitrogen discharges and afterglows is a rather complex problem, as a consequence of the strong interplay between different kinetics. In spite of the many experimental and theoretical investigations carried out along the years, these discharges keep challenging scientists. As a matter of fact, the application of relatively well-established models to new experimental conditions often leads to surprises. In order to refine the kinetic description of nitrogen plasmas, the available models should be continuously put to test in different conditions. In this way, new mechanisms can be identified and the description of others can be improved. Hence, it is desirable to obtain consistent sets of experimental data in well-defined conditions and to confront them with simulations undertaken for the same conditions.

2. Results and discussion

In this work we studied the afterglow of a DC discharge in pure nitrogen at a fixed pressure of 1000 Pa, and discharge currents of 50, 60 and 70 mA. Optical emission spectroscopy was used to measure the 1st positive, 2nd positive and 1st negative systems of nitrogen.

The emission from the 1st positive system obtained experimentally for the (2-0) transition is shown in figure 1, as a function of afterglow time. There is an important difference in behaviour when the discharge current increases from 60 to 70 mA. In the latter case the emission intensity increases during the post-discharge, which is a characteristics of the pink afterglow [1]. This phenomenon is not visible for lower discharge currents.

Preliminary simulations do not reflect this difference, as it can be seen in figure 2. The calculations were performed for a fixed gas temperature both in the discharge (500 K) and in the afterglow (300 K). Notice that the gas temperature is a key parameter, as it controls the V-V up-pumping rate, which is in the origin of the pink afterglow [1]. However, exploratory measurements of the gas temperature indicate these values may be somewhat underestimated. The rough estimations of the gas temperature used in the model for now probably justify the differences between the simulation results and experiment. Work is now in progress to clarify this issue.

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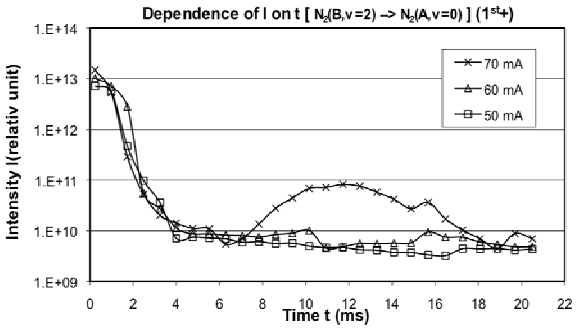

Fig. 1: *1st positive system of nitrogen from experiment.*

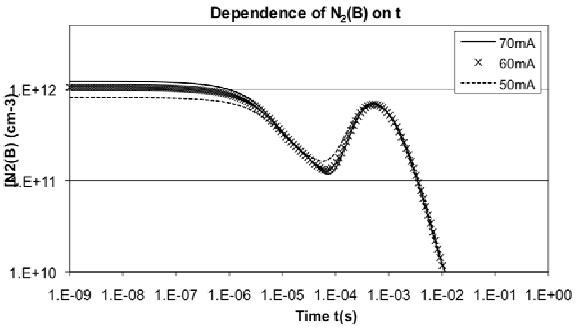

Fig. 2: *1st positive system of nitrogen from model.*

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An electromagnetic model of the multipole resonance probe

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An electromagnetic model of the "multipole resonance probe" (MRP) is presented. The MRP is a new diagnostic concept which enables the simultaneous determination of plasma density, electron temperature, and collision rate in low-pressure gas discharges. In this work, the influence of electromagnetic effects on the probe behavior and its influence on the data interpretation is investigated.

1. Introduction

Plasmas have the natural ability to resonate on or near the electron plasma frequency; once ω_{pe} is known, one can calculate the electron density as $n_{\mathrm{e}} = \omega_{\mathrm{pe}}^2 \epsilon_0 m_{\mathrm{e}}/e^2 = 1.24\, f_{\mathrm{GHz}}^2 \times 10^{10}\,\mathrm{cm}^{-3}$. The idea of the so-called "plasma resonance spectroscopy" methods has found renewed interest as a basis for industry-compatible diagnostic methods. A review of these specific methods was recently given [1]. This contribution concentrates on a particular realization of one of these methods, the MRP [2].

2. Electromagnetic model

We will outline the principle of the MRP on the basis of an idealized geometry, where the holder (containing the RF supply) is neglected and the analysis can be carried out largely by analytical means. The geometry properties are depicted in Fig. 1.

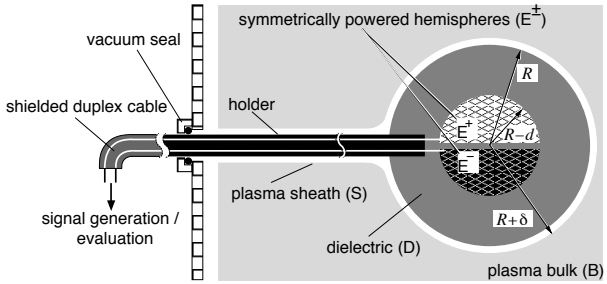

Fig. 1: *Schematic of the MRP. The geometry parameters are the probe radius R, the coating thickness d, and the sheath thickness δ. For idealization the holder is neglected.*

Since it is intended to employ an electromagnetic model, the full set of Maxwell's equations has to be taken into account. For each of the media (D,S and P) restrictions concerning the influence of charges ($\rho, \vec{j}$) and permitivities (ϵ_r) have to be considered.

$$\frac{1}{\mu_0}\nabla\times\vec{B} - \epsilon_0\epsilon_r\frac{\partial\vec{E}}{\partial t} = \vec{j} \qquad \nabla\times\vec{E} + \frac{\partial\vec{B}}{\partial t} = 0$$

$$\nabla\cdot\vec{B} = 0 \qquad \epsilon_0\epsilon_r\nabla\cdot\vec{E} = \rho$$

Concentrating on the RF behavior, the ions are too heavy to follow the electric field ($\omega_{\mathrm{pi}} \ll \omega_{rf} \lesssim \omega_{\mathrm{pe}}$), thus current is carried by displacement and electron conduction alone. In our plasma regime the so-called cold plasma approximation can be adopted .

$$\frac{\partial\vec{j}}{\partial t} = \epsilon_0\omega_{\mathrm{pe}}^2\vec{E} - \nu\vec{j}$$

Expanding the field variables into spherical harmonics in each medium (D, S and P), the problem can be solved analytically.

3. Results

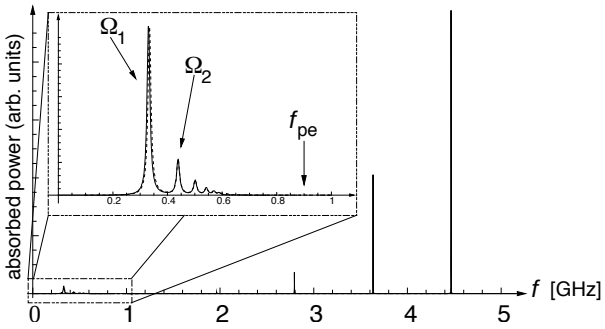

Fig. 2: *Resonance behavior of the MRP (solid - full EM treatment, dashed - electrostatic treatment)*

Fig 2. shows a resonance spectrum for typical probe and plasma conditions. Obviously, **above** f_{pe} only the full treatment of Maxwell's equation is capable to capture the resonances. The restriction on the electrostatic approximation to characterize the resonance behavior of the MRP is well justified **below** f_{pe}. Following these insights, one can find analytic descriptions for the resonance frequencies Ω_i [2].

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Acknowledgement

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X-ray diagnostics of high-current discharge in a high-pressure gas

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Results are presented from experimental studies of self-constricted discharge in dense hydrogen at initial pressure of hydrogen up to $10MPa$ and current amplitude up to $1.6MA$ with current raise rate $dJ/dt \sim 10^9 - 5 \cdot 10^{10} A/s$. An experimental complex for flash x-ray radiography diagnostic and self-SXR detecting is described.

The aim of these studies was to increase the energy density in the discharge channel, to investigate mechanisms for energy transfer from the discharge to the ambient gas, and to determine the parameters of the plasma [1]. The main diagnostic problem for such conditions is high density of the discharge channel. Only x-ray methods can manage direct diagnostic of inner channel plasma.

The experiments were performed in axial geometry. The diameters of steel electrodes were $20mm$ and the discharge gap was $5 - 20mm$. Detail description of the experimental setup can be found in [2].

1. Flash radiography

The X-ray diagnostic system for determination of metal vapour concentration, based on pulsed X-ray source with hardness of $20 - 50keV$ and X-ray CCD camera, was designed. Two samples of nanosecond generators (with duration of pulses $10 - 20ns$ and $50ns$) and two types of X-ray tubes (through-target and anticathode) were designed and used.

Experimental data on spatial metal vapour distribution in discharge gap, provided by electrode erosion, were obtained (fig. 1). The result of experiments show that main part of metal vapours concentrates to the axis of discharge channel.

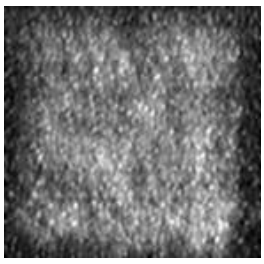

Fig. 1: *Radiography image of discharge gap at* $20\mu s$ *after initiating discharge with current amplitude* $600kA$

2. X-ray self-radiation

Designed complex for detecting SXR from the discharge channel and difficulties with its development are described in [3]. Typical signal of SXR from channel is shown on fig. 2.

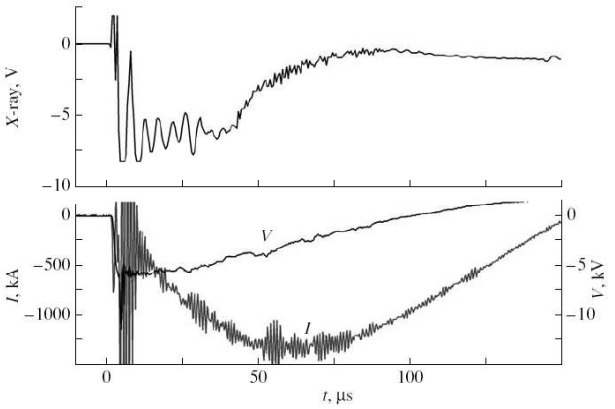

Fig. 2: *Typical oscillograms of current, voltage and x-ray signal*

The brightness temperature of external hydrogen shell surrounding the discharge channel was $1 - 9eV$. It was measured by two monochromatic pyrometers with effective wavelengths 694 and $550nm$. The SXR intensity was measured with $SPD - 8UVHS$ photodiodes. Temperature of the central zone, from which SXR is registered, achieves several hundreds eV. SXR hardness was increased with current raise rate but visible brightness was decreased.

The constricted discharge channel surrounded by hydrogen shell can be used for producing pure photoionized hydrogen plasma, for modelling various astrophysical phenomena.

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Probing the ion flux in an hydrogen plasma jet

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The ion flux in an hydrogen plasma is determined by a novel electrostatic probe. The pressure dependence of the ion flux shows a maximum in the low background pressure regime

1. Introduction

The present-day chip industry is one of many examples that relies heavily on the plasma processing of surfaces. This surface treatment is done primarily by radicals produced by the plasma and ions from the plasma impinging on the surface (or substrate). To influence the surface processing itself, the ion energy is often controlled through substrate biasing with high voltages (> 50 V).

The ion flux can be determined by standard (double) Langmuir probes. However, such probes do not function when coated with an insulating layer. Therefore, they can not be used in depositing plasmas or etching plasmas, in which etch products can re-deposit on the probe itself. Also, most of the time the position of the probe does not coincide with the position of the substrate. This will give an ion flux for the plasma, but not directly at the place of interest, i.e. the substate. The ion flux probe, discussed in the next section, will solve these two problems.

The ion flux probe is applied in an hydrogen plasma jet. Such a plasma jet is used for etching of amorphous hydrogenated carbon (a-C:H) samples.

2. Ion flux probe

The ion flux probe (based on the work of [1]) is a planar probe embedded in an substrate holder. The collecting area (area A) is made from tungsten (W), but can be replaced by a thin layer of insulating material (hereafter coated probe head), e.g. a-C:H deposited on a silicon carrier wafer. With the tungsten collection area, the probe can be used as a standard planar Langmuir probe.

The electronics of the ion flux probe consists of a capacitor (of known size C) that connects the collecting area with a function generator. The coated probe head acts as a second capacitor in the circuit. A square puls from the function generator will charge and discharge the capacitors.

By measuring the voltage difference over the capacitor as a function of time, the current (eq. 1) can be calculated. Since the measured current equals the plasma current, the ion flux can be determined (eq. 2).

$$I = C_p \frac{dV}{dt} = I_p = eA\Gamma_i \qquad (1)$$

$$\Gamma_i = C_p \frac{dV}{dt} \frac{1}{eA} \qquad (2)$$

Applying a (squared) puls to the circuit for measuring the ion flux, also implies that the substrate will be biased (ranging from close to floating potential, up to 20 V). However, due to collection of electrons or ions at the surface, the bias voltage will not remain constant in time. To compensate for this effect, the applied signal will not be squared, but rather sloped.

The actual bias voltage depends on the capacitor size of the probe head. For W, the bias voltage will equal the amplitude of the applied voltage. For a coated probe head however, this will depend on the thickness and dielectric constant of the coating material, since both capacitors in series will act as a voltage divider. During etching or depositing of e.g. amorphous hydrogenated carbon, the thickness of the material can be determined from *in situ* spectroscopic ellipsometry.

3. Hydrogen ion flux

With this probe, the influence of the background pressure (20 - 200 Pa) on the ion flux is determined for an hydrogen plasma jet. Here, two competing mechanisms will determine the ion flux at the surface. By increasing the background pressure, the plasma beam diameter will decrease. This has a focusing effect for the ion flux. However, by increasing the pressure, the likelihood for collisions will also increase, resulting in a loss of ions. The maximum ion flux is in the low background pressure regime (25 - 40 Pa).

4. conclusion

The ion flux probe can simultaneously measure the ion flux and bias the surface. The ion flux is thus directly determined for the position of the substrate. The highest ion flux in an hydrogen plasma jet, as measured with the ion flux probe, falls in the low background pressure regime (25 - 40 Pa).

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Positive ion mass spectrometry studies of the atmospheric pressure plasma treatment of polymers

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A low power atmospheric pressure helium plasma torch was used to modify the surface chemistry of substituted polythylenes grouped in aromatic (Poly(α-methylstyrene) (PαMS) and polystyrene (PS)) and hydrocarbon polymers (poly(propylene) (PP) and poly(ethylene)(PE)). Mass spectra of the positive ions present in the plasma during the treatment revealed dominant ions with structures that reflected the structure of the polymer. A series of hydrocarbons of the structure $C_nH_{2n\pm1}$ up to n = 14 were observed in PP whereas a series of ions containing aromatic groups and having a structure related to the PαMS were observed for that polymer.

1. Introduction

One of the main characteristics of Polymers is their unreactive surface, which makes it difficult to join them together using adhesive or to apply coatings which impart a useful functionality to the surface of the material. Plasma treatments to alter the nature of the polymer surface in terms of chemistry have great utility in surface modification of polymers. There are a range of types and regimes of low temperature discharges that operate around atmospheric pressure that can be applied to modifying the surface of polymers [1].

To understand the mechanisms of the surface activation of the polymer under plasma treatment it is desirable to relate the resultant species in the plasma during the treatment with an analysis of the modified surface. A nonthermal atmospheric plasma jet [2] is used to treat the polymers. Plasma phase Positive ions created from desorption and ionization processes at the polymer surface were sampled directly and analysed using a mass spectrometer. The treated surface was studied by XPS analysis

2. Experiment

A series of substituted polyethylenes grouped in aromatic (Poly(α-methylstyrene) (PαMS) and polystyrene (PS)) and hydrocarbon polymers (poly(propylene) (PP) and poly(ethylene)(PE)) where chosen for this study. The polymer pieces were fixed to a glass rod and held in the plasma plume during acquisition of the mass spectrum. Positive ions from the plasma and the sample were analysed by the HPR60 molecular beam mass spectrometer (MBMS) (Hiden Analytical Ltd., Warrington, U.K.) which consists of a single-stage quadrupole energy mass spectrometer with a differentially pumped three-stage inlet system.

3. Results

The plasma treatment etched some material became the polymer surface and a portion of this becomes mixed into the plasma as neutral and ionic species. The PαMS had a series of dominant peaks at m/z 77, 91, 105 and 119 which are likely to be due largely to structures containing an aromatic group, Fig1. XPS analysis revealed significant oxygen and some nitrogen content in the surface of the treated polymers.

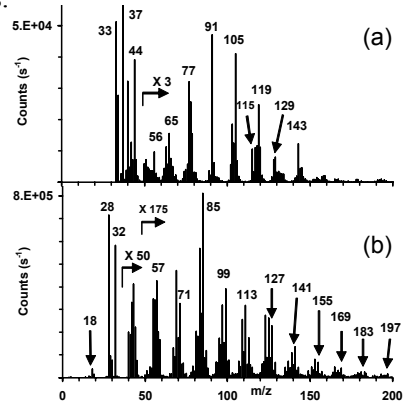

Fig.1 Positive ion mass spectra of plasma during the treatment of (a) PαMS and (b) PP.

4. Conclusions

Mass spectrometry was used successfully to sample the positive ions present in atmospheric pressure plasmas during treatment of polymers. The technique was able to differentiate between ions produced during the atmospheric plasma treatment of aromatic and hydrocarbon polymers.

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Electric field measurements in near-atmospheric pressure nitrogen and air based on a four-wave mixing scheme

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An important parameter for understanding the physics of discharges is the electric field strength. Knowledge of the spatial and temporal distribution of the field strength can provide information about the distribution of charged particles, current density, and dissipated power. A novel method based on nonlinear laserspectroscopy was applied for determination of the electric field strength in nitrogen and open air environment.

1. Introduction

Various non-invasive optical methods based on the Stark effect have been developed for low pressure environment (1-100 Pa). Due to quenching effects, however, these techniques are not suitable for experiments in the high-pressure region, where many novel plasma applications are reported. In this work, we therefore employ a different field measurement technique, i.e. a field-induced coherent Raman scattering (CRS) method [1] for determining the electric field strength locally in nitrogen and air environments at higher pressures.

This method has been successfully applied to measure electric fields in high-pressure hydrogen environments. To our knowledge, the work presented here is the first successful measurement in nitrogen and air environments.

2. Method

The basic principle follows a four-wave mixing scheme. By a static electric field a dipolmoment is induced in the diatomic molecules of a medium which then becomes anisotropic. Thereby frequency mixing becomes possible. Combining the first and second order effects a third order non-linearity arises similar to a CARS scheme where the frequency of the third wave is set to zero [2]. The intensity of the generated infrared radiation (I_{IR}) scales with the square of the electric field, the square of the nonlinear susceptibility, and the product of the incident laser intensities. Therefore it is a direct measure of the squared field strength.

3. Experimental apparatus

The measurements are carried out by a frequency doubled Nd:YAG-Laser at 532 nm and a dye laser tuned to 607 nm. The field-dependent radiation I_{IR} (at ~4 µm) is detected by an InSb-detector, the field-independent anti-Stokes radiation I_{CARS} (at ~473 nm) by a photo-diode.
Measurements are performed between two stainless steel electrodes with a gap length of 3.2 mm and applied fields up to 1 kV/mm. The working medium is pure nitrogen at pressures of 1 atm up to 2.5 atm or an open air environment.

4. Results

Figure 1 shows the square root of the normalized field dependent signal (I_{IR} / I_{CARS}) as a function of the electric field at 1 atm pressure. The linear relation agrees perfectly with the theoretical expectation. Similar results are also obtained at higher pressures. It should be emphasized that the normalized representation shown here is independent of the particular vibrational population in the molecules.

Further details of the measurement technique will be shown. Application of the technique to discharges is presently in progress.

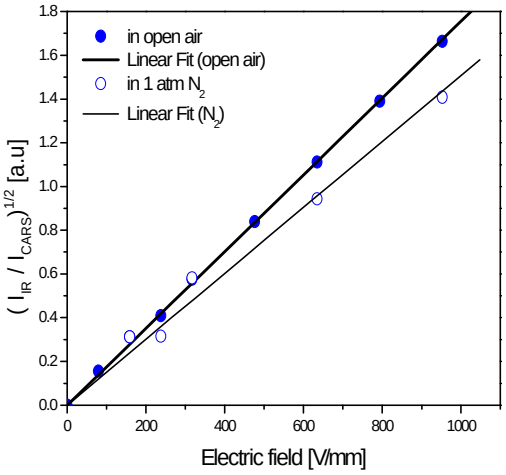

Fig. 1 Normalized signal intensity as a function of the electric field strength. The difference between two slopes is most likely caused by difference in the laser setup made between the two independent measurements.

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Silver deposition on polypropylene nonwoven fabric modified by atmospheric pressure diffuse coplanar surface barrier discharge

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The present work focuses on the preparation of biomedical materials by deposition of silver ions on nonwoven polypropylene fabric. The textile surface modification is done by diffuse coplanar surface barrier discharge at atmospheric pressure. This method brings new opportunities and new challenges in the field of surface activation of different materials.

1. Introduction

Polypropylene (PP) is a plastic material widely used in many engineering and biomedical applications. By appropriate surface treatments PP can be rendered biocompatible and can acquire antimicrobial properties. For polymer surface modifications it is possible to attempt different methods such as plasma treatment techniques.

The aim of this work is application of antimicrobial agents on textile substrates. The present study is focused on the absorption of silver ions on nonwoven PP surface after plasma treatment.

2. Experiment and results

For the surface modification of nonwoven PP fabric we used a planar source of the atmospheric pressure low temperature plasma worked in ambient air. The plasma was produced in Diffuse Coplanar Surface Barrier Discharge (DCSBD) generating a thin plasma layer in good contact with the fabric fibers [1].

The surface properties of both treated and untreated fabrics were characterized by measurements of wettability. Samples of dimension 12 x 14 cm were fixed on the metal web, immersed in water for 60 s and then drained for 120 s.

Mass of each sample was measured before and after the absorption of water and this values were used for determination of liquid absorption capacity (LAC) in %. The LAC measured immediately after plasma treatment was higher than the value for unmodified fabric.

Silver ions were incorporated into previously plasma treated and untreated nonwoven polypropylene by conditions described in Ref [2]. The amount of absorbed silver was measured by atomic mass spectrometry using UNICAM 939 AA spectrometer. The solutions were vaporized in graphite coated furnace. The untreated samples and samples treated with plasma for 3 s, 6 s, and 12 s were used for the measurements. The effect of plasma exposure time on the silver ions uptake is presented in Fig 1.

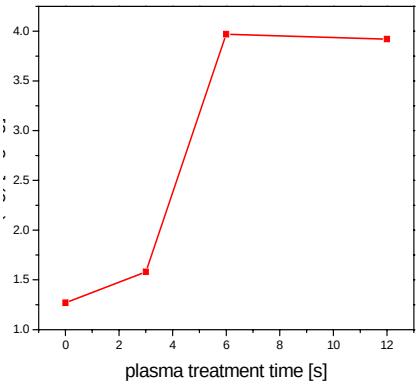

Fig. 1: *The effects of plasma exposure time on the Silver ions uptake by plasma activated nonwoven PP fabric*

An agar diffusion plate test was used to assess the antimicrobial activity of the silver loaded PP nonwoven fabrics. Two test organisms were used: gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae*. Samples obtained by silver ion sorption show antimicrobial activity against tested pathogens.

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Electrical and emission spectroscopic characterization of a self-pulsing micro hollow cathode discharge

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In recent years atmospheric pressure micro plasmas have become a strongly emerging field in plasma research and application. A particularly interesting micro plasma is the so called micro hollow cathode discharge (MHCD) [1, 2]. One of the unique features of this discharge is the occurrence of self-pulsing [3]. We characterize a MHCD operated in argon (1000 Pa to atmospheric pressures) electrically and by use of emission spectroscopic techniques in order to determine plasma densities and temperatures.

1. Introduction

Micro hollow cathode discharges (MHCD) consist of two electrodes separated by a thin dielectric (here: 100 µm). The discharge develops in a hole penetrating all three foils (here: 200 µm diameter) (Fig. 1). When powered by a DC voltage of several 100 V, the discharge shows self-pulsing operation (Fig. 2). The emission in the discharge in argon at pressures up to atmospheric pressure is investigated. Mixing small amounts of hydrogen (less then 1%) electron densities can be obtained from the Stark broadening of the H_β-line (486.13 nm).

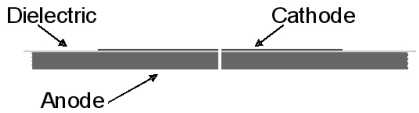

Fig. 1: *A schematic of a micro hollow cathode discharge*

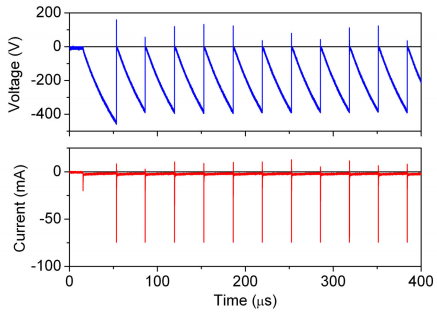

Fig. 2: *Time resolved discharge voltage and current of the MHCD in argon at p = 900 mbar*

2. Experimental setup

The micro hollow cathode charge is generated by pulsed DC voltage with 10 Hz frequency and 1 ms duration in argon. Optical emission of the discharge is recorded by gated ICCD camera equipped with a microscope lens. To determine electron density from the Stark broadening of the H_β-line, 1% hydrogen is mixed with argon (1 sccm H_2 + 100 sccm Ar). An optical fiber collects the emission from the discharge and guides the light to a 2m-spectrograph which has a solution of 0.01 nm. The H_β-line is detected by the 2m-spectrograph. Interpretation of the electrical measurements requires a careful analysis of stray capacitances and inductances.

3. Results

The ICCD image shows that the discharge pulses constrict within the hole. This makes current densities in the kA/cm^2 range likely. Stark broadening of the H_β-line with a Lorentzian profile is observed at high pressures (Fig. 3) with a FWHM ($\Delta\lambda$) of 1.7 nm. Further results and a detailed discussion will be presented.

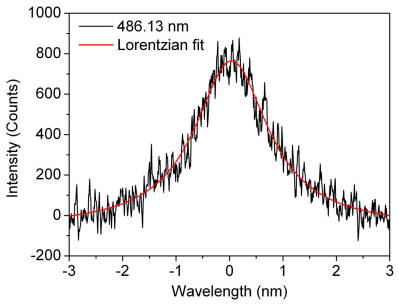

Fig. 3: *Stark broadening of H_β-line at pressure of 950 mbar and voltage supply of 1.2 kV.*

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Phase Resolved Optical Emission Spectroscopy – A non-intrusive diagnostic to study electron dynamics in capacitive RF discharges

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In capacitive RF discharges Phase Resolved Optical Emission Spectroscopy (PROES) is used to investigate the generation and dynamics of electron beams, field reversals, the Plasma Series Resonance (PSR) and Non-Linear Electron Resonance Heating (NERH), frequency coupling in dual-frequency discharges as well as the Electrical Asymmetry Effect (EAE). Using a collisional-radiative model PROES can provide access to various plasma parameters space and time resolved. A PIC simulation demonstrates limitations of PROES.

1. Introduction

Using a fast-gateable ICCD camera synchronised with the RF voltage and an optical filter the emission from specifically chosen rare gas levels is measured space and time resolved. From the emission the excitation is calculated with one dimensional spatial resolution along the discharge axis and temporal resolution within the RF period [1]. PROES is only sensitive to electrons with energies above the threshold for excitation (typically E > 12 eV). It is assumed that the measured excitation probes the ionisation so that mechanisms of plasma generation can be investigated non-intrusively via PROES. Various plasma parameters can be determined using a collisional radiative (CR) model of the population dynamics of the observed level.

2. Results

In a geometrically strongly asymmetric capacitive discharge the generation of beams of highly energetic electrons by the expanding sheath and their reflection at the plasma boundaries is studied by PROES (Fig. 1, [2,3]). Model calculations show that these electron beams lead to an enhanced high energy tail of the Electron Energy Distribution Function (EEDF) and are, therefore, closely related to stochastic heating [2,3]. The PSR leads to non sinusoidal RF current waveforms and a faster sheath expansion. Consequently, it enhances the generation of electron beams and stochastic heating (NERH) [3,4]. Similar to dual-frequency discharges the PSR causes high frequency oscillations of the sheath that cause additional excitation monitored by PROES.

In a symmetric dual-frequency discharge operated at 2 MHz and 27 MHz the frequency coupling [5-7] and electric field reversals during sheath collapse [8] are studied by PROES. Results are compared to a PIC simulation [8]. A CR model yields information about the electron temperature, -propagation velocity, density of highly energetic electrons, and the EEDF space and time resolved [5].

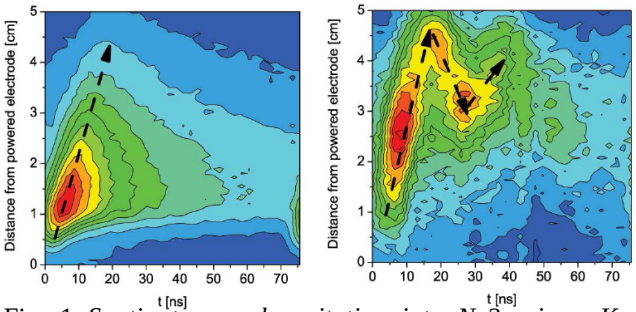

Fig. 1 *Spatio temporal excitation into Ne2p$_1$ in a Kr discharge with 10% Ne admixture at 8 W (left: 5 Pa, right: 0,2 Pa). Electron beams are indicated by arrows.*

In a dual-frequency discharge operated at a fundamental frequency and its even harmonic (e.g. 13.56 MHz and 27.12 MHz) with variable phase shift in between the EAE allows efficient separate control of ion energy and flux [9-11]. PROES is used to verify the EAE.

A PIC simulation reveals a fundamental limitation of PROES: The excitation does not necessarily probe the ionisation as it is usually assumed [7].

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Plasma series resonance and E to H mode transitions in low-pressure rf inductively coupled plasmas

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The E mode of radiofrequency inductively coupled plasmas is characterized by dominating capacitive coupling which includes the occurrance of the so-called plasma series resonance effect. This phenomenon is investigated and used as a means to distinguish between capacitive and inductive coupling during E to H mode transitions.

Abstract

Radiofrequency (rf) inductively coupled plasmas (ICPs) exhibit two distinct modes of operation. At low input power, the plasma is mainly capacitively driven through the voltage drop across the induction antenna (E mode). Consequently, the discharge shows characteristics of a capacitively coupled plasma (CCP) in this regime. With increasing power, a sudden transition to the inductive regime (H mode) occurs, which is more or less abrupt and typically accompanied by quite drastic changes in the plasma properties. With this contribution we present an investigation of the power coupling in the E mode together with a detailed characterization of the dynamics of the E to H mode transition.

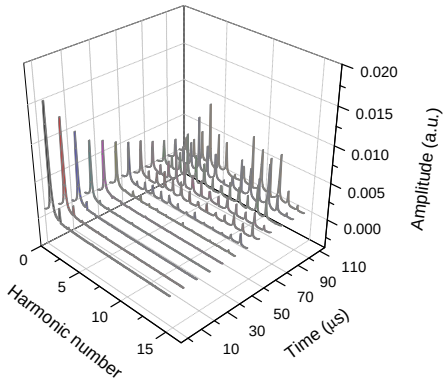

Fig. 1: *temporal evolution of the rf current spectrum during the H to E mode transition, Ar, 0.8 Pa.*

The capacitive nature of the power coupling in the E mode of rf ICPs leads to the occurrence of certain phenomena, known from capacitive discharges. One of these is the so-called plasma series resonance effect, the generation of high harmonics of the driving rf in the discharge current, caused by the nonlinear charge-voltage relation of the plasma sheath. In this work, the effect is investigated experimentally and described by means of a lumped element circuit model which is an extension of existing models for capacitively coupled plasmas [1].

The results of this investigation are used to determine the change from capacitive to inductive power coupling during the E to H mode transition. Further the transition dynamics are investigated experimentally and the results are compared to a simple time-resolved global model. An example of the temporal evolution of the rf current spectrum during the H to E mode transition is shown in figure 1. It shows an oscillation almost only at the fundamental frequency in the H mode which evolves into a very broad spectrum as capacitive coupling becomes more and more dominant. Figure 2 shows the corresponding evolution of the electron energy distribution. It shows a small bump structure which occurs with the broadening of the current spectrum and is probably related to high frequency interference or anisotropy effects [2].

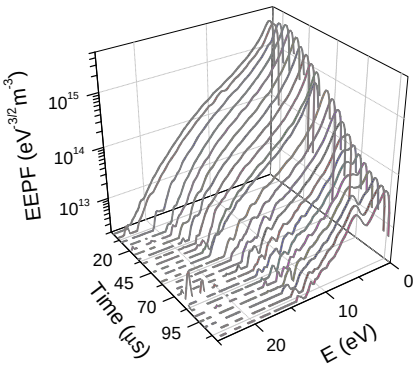

Fig. 2: *temporal evolution of the electron energy distribution during the H to E mode transition, Ar, 0.8 Pa.*

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Study of Underwater Diaphragm Discharge Method for Silver Coating of Polypropylene Fabrics

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Underwater plasma discharge is used for surface activation of polypropylene fabrics with subsequent immobilisation of silver. Results of optical emission spectroscopy as well as characterization of treated material are presented.

1. Introduction

An application of plasma discharge in medicine has been intensively studied [1]. The plasma generated at atmospheric pressure is preferred as this is a low cost and environmental considerate technique in comparison with other techniques. On the other hand, the antibacterial properties of silver are well known. The underwater discharge [2 - 4] makes possible immobilisation of silver on surface textiles such as polypropylene (PP) textile. Moreover, in the liquid solution, during the discharge, it is required keeping the nanoparticles [5] of silver separately, and the subsequent treatment in one step, too.

One of the advantages of underwater plasma is the possibility to combine plasma chemical activity with the selectivity of processes in solutions. Investigations of underwater discharges generated in water solutions at atmospheric pressure have shown effective production of OH radicals, solvated electrons and a number of other active species.

2. Experiment and discussion

In contrast to other types of underwater discharges (reactive OH radicals are generated), in our diaphragm discharge arrangement, the plasma is not in direct contact with the metallic electrodes.

The discharge was generated in a narrow slit of 0.1×1 mm positioned between two metallic electrodes at 2 cm mutual distance. Both electrodes and the slit (diaphragm) were immersed in the water solution of $AgNO_3$.

Polypropylene nonwoven fabrics of 50 gsm and 30 mm width was fed trough the slit with an adjustable speed. The electrodes were connected to a pulsed HV power supply based on the double rotating spark gap. The maximum peak voltage was 40 kV DC. The maximum repetitive rate of pulses was 60 Hz.

The discharge manifests itself as thin plasma filaments propagating along the textile surface up to the distance where the metallic electrodes are positioned. The length of propagation is given by the conductivity of water solution and amplitude of the applied voltage.

Beside the plasma parameters (electron number density, temperature of electrons, excitation temperature) voltage and current were measured.

After treatment we washed the sample in a detergent solution in Ultrasonic Bath for 15 minutes to see how much of silver remains attached to the textile material.

Size and distribution of dispersed silver nano-particles were measured by SEM.

3. Conclusion

By performing diaphragm plasma in the water solution of silver salt we were able to immobilize silver crystals on the PP surface which potentially could be used in biomedical applications.

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Is it possible to control degree of target poisoning during RF reactive magnetron sputtering by higher harmonic frequencies of discharge voltage?

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Reactive sputtering controlled by flow of the reactive gas suffers from problems in processing stability caused by an abrupt transition between the metallic and the compound mode. During this transition many important parameters including target composition and gas composition change dramatically. A sensitive monitoring method is proposed which is based on the measurement of amplitudes of fundamental or higher harmonic frequencies of discharge voltages. Voltage waveforms recorded from the cathode and from an uncompensated probe were analyzed. Uncompensated probe exhibited higher sensitivity significantly better than sensitivity of any other known electrical method used for the control of magnetron sputtering process. Moreover, some particular experiments show that the changes in amplitudes of the harmonics by the transition are due to the changes of the target composition rather than due the change of the gas composition.

1. Introduction

Deposition of thin films by reactive magnetron sputtering is nowadays largely used process to prepare wide range of compound thin films. Adding a reactive gas to the deposition chamber may result in processing stability problems and the process shows a hysteresis. Since for certain range of reactive gas supply there exists two different conditions in the deposition chamber, to distinguish them the process monitoring is desirable.

2. Results and discussions

In this work, we propose very sensitive method to control whether a radio-frequency (RF) sputtering deposition processes runs in a pre-adjusted experimental conditions. Due to the non-linearity of sheaths, RF discharges are sources of higher harmonic frequencies of electric voltage and current. Since the amplitudes of the harmonics are sensitive functions of plasma parameters, they can be used as a simple diagnostic tool for RF plasma processes. Therefore, one may expect that the abrupt change of all processing parameters during the transition from the metallic to the compound regime (such as formation of compound layer on the target, changes of plasma composition followed by change in plasma conductivity etc.) should affect the sensitive amplitudes of the harmonics.

The proposed method includes identification of sensitive harmonics by harmonic analyses of discharge voltages and regulation of reactive gas flow according to variation of amplitude of selected harmonic frequency.

The frequency spectrum of the cathode voltage and of the voltage on an uncompensated probe immersed in the plasma was measured in order to test the performance of the proposed method. The experiment was performed sputtering titanium target in argon gas with small admixture of nitrogen or oxygen. The outputs were compared to other quantities usually used for process monitoring. It has been proved, that some of the harmonics are extremely sensitive markers of the transition between two regimes of interest.

To distinguish whether the observed changes in amplitudes are caused by changes in the composition of the target surface or by other phenomena, the following experiment was performed. The target was poisoned on purpose and then, the discharge and reactive gas was stopped simultaneously. After evacuating all the reactive gas from the chamber, the discharge was turned on again and the cleaning procedure of the target was resolved in time. Similar changes in the amplitudes of the harmonics as during the transition were observed. Since in this particular experiment, the composition of the gas did not change as by the transition, we concluded that the observed changes in amplitudes of harmonics by the transition are caused mainly by the changes of the target composition.

3. Conclusion

We described a very sensitive method to control the state of the RF magnetron sputtering deposition process based on measurement of the higher harmonic frequencies of discharge voltages. It was proved that observed changes in amplitudes are correlated with the degree of the target poisoning.

This research has been supported by the MSM contract 0021622411 and by GACR contract 202/08/P038.

Modelling of surface processes taking place during reactive magnetron sputtering deposition process with simultaneous adding of O_2 and H_2

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Hydrogen adding into magnetron sputtering deposition process used for preparation of TiO_2 thin films influences the structure of the deposited films and changes the behaviour of the whole deposition process. A model of reactive magnetron sputtering is developed in order to accomodate simultaneous oxidation and reduction processes taking place at the target and at the substrate as well as H_2 contribution to the target poisoning. These processes were integrated into the model in order to explain the changes in hysteresis behaviour observed by Ondok, et al [3]. Moreover, the model enables us to determine the aproximative rates of assumed processes.

1. Introduction

Magnetron sputtering deposition processes controlled by the reactive gas flow exhibit a hysteresis behaviour. There is well known Berg's model [1] which describes the behaviour of such process. Recently, we extended this model in order to accommodate the non-uniform discharge current density because in the real experiment the presence of the magnetic field causes a high density plasma to form in front of a cathode in a shape of toroid and thus the discharge current density is very non-uniform [2].

Hydrogen addition into magnetron sputtering deposition process used for preparation of TiO_2 thin films reduces the arcing, influences the structure of the deposited films and changes the behaviour of the whole deposition process [3]. We assumed simultaneous oxidation and reduction processes taking place at the target and at the substrate and we integrated them into the model in order to explain the changes in hysteresis behaviour observed by Ondok, et al [3].

2. Model specifications

Model is based on the assumption that O_2 and H_2 both react with the target surface. We presumed only TiH, TiO and TiO_2 to be created. For each part of the target the balance equations were written. The Gaussian discharge current density profile with FWHM = 0.03 m with center at half radius of the target was used. By analogy to the target we received the situation on the substrate. We used some known parameters from real experiment [3]: I = 3 A, A_T = 0.008 m^2. Sputtering yiels were chosen as follows $Y_{Ti} = Y_{TiH}$ = 0.65, Y_{TiO} = 0.035, Y_{TiO_2} = 0.025.

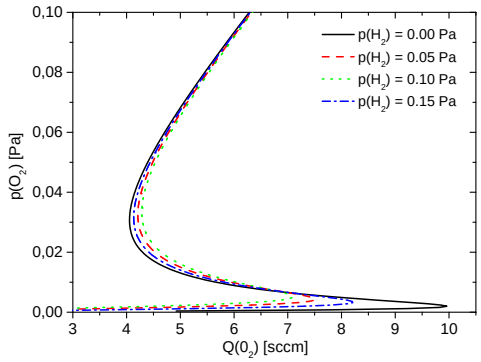

Fig. 1: *O_2 pressure dependency on the consumption of O_2 for different values of presure of H_2.*

3. Conclusions

We have modelled process of the magnetron sputtering for the situation of two reactive gases and we have compared the results to the experimental data [3]. The model predicts that the reduction of oxides on the target surface is insignificant and the oxidation of TiH should be described by higher rate than the creation of TiH in order to get agreement between model and experiment. The target gets poissoned by both O_2 and H_2 so the system transits from the mettalic to the compound mode for smaller amount of O_2 than is needed in the situation without H_2, see Fig.1.

4. Acknowledgement

This research has been supported by the MSM contract 0021622411 and by GACR contract 202/08/P038.

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Time resolved Ha emission in pure hydrogen discharge

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Time dependent Hα excitation is studied by Monte Carlo technique for the conditions of very high *E/N* (E-electric field, N-gas density). Calculating the excitations in the whole volume, originating from electrons, H^+, H_2^+ and H_3^+ ions, fast H and fast H_2 we obtained that only fast H atoms are source of the emission in the microsecond time scale.

1. Introduction

The first interpretations of unusually high Doppler broadening of hydrogen lines in non-equilibrium plasmas were based on possible dissociative processes, recombination and excitation [1]. The experiments, especially the experiments performed at DC fields revealed a large asymmetric component with energies exceeding the energy available from the repulsive potentials of the dissociating molecules [2, 3]. The explanation of such results was found in a specially designed high *E/N* swarm experiment [4, 5] which gave a proof that, to the largest degree the excitation is due to collisions of fast neutrals formed in charge transfer collisions of the feed gas with fast ions. At high *E/N*, which can only be achieved under breakdown conditions at the left branch of the Paschen curve, the mean free paths are sufficiently high to allow large energy gain by ions and consequently formation of very fast neutrals with comparable energies. In addition it is possible to have reflection and neutralization of ions with reflection as fast neutrals, which leads to different components in blue and red wings of the Doppler profile [4].

High, DC, *E/N* swarm experiment (self sustained discharge operating in the Townsend regime) may be modeled directly and exactly as it does not require self consistent calculation of the electric field and is thus open to a simple Monte Carlo simulation (MCS) that may include maximum complexity in the representation of collisions.

2. Monte Carlo simulation

The Monte Carlo code [6] based on null collision technique was used to follow electrons and heavy particles (H^+, H_2^+, H_3^+, fast H and fast H_2) between collisions with H_2 or with the cathode surface for the conditions of high electric field (*E*) to gas density (*N*) ratios *E/N*. 10^6 electrons released at the cathode were followed up to the anode as well as trajectories of all reaction fragments until they neutralized or thermalized below the Hα excitation energy.

Conditions of simulation are appropriate for very high *E/N* (*E*/*N*=10 kTd, *p*=145 mTorr, interelectrode distance is *d*=4 cm) and are selected from experimental Townsend discharges in pure H_2 [4].

From MCS results (Fig. 1) comes out that fast H atoms are only source of Hα emission in the microsecond time scale.

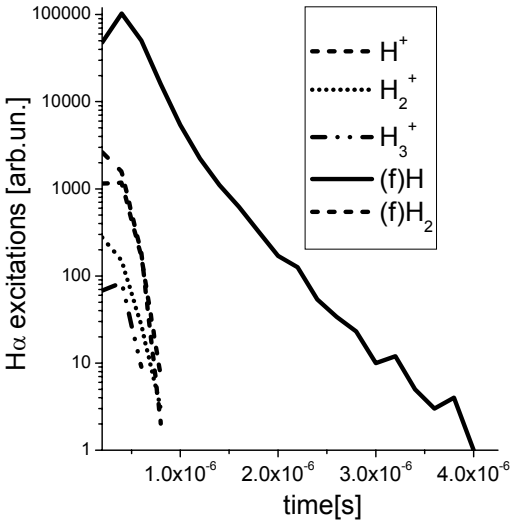

Fig. 1: *The total emission from discharge volume as a function of time for10^6 initial electrons.*

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Measuring and interpreting rf harmonics from a pulsed discharge

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A current sensor placed between the power supply and the electrode in an rf plasma discharge can measure signals at the fundamental rf frequency and at harmonics of this frequency. In this research, we measured rf harmonic signals from a low pressure pulsed discharge, with the aim of correlating the harmonic content with bulk plasma properties.

1. Introduction

When rf power is applied to generate a plasma, harmonics of the rf frequency arise due to the non-linear response of the plasma to the applied rf power. The harmonic signals arise in response to the properties of the discharge, and if there is a correlation between signal magnitudes and specific discharge properties, this could provide a valuable non-intrusive plasma diagnostic method. This possibility has led to various attempts to interpret this information, in a new measurement area often called rf spectroscopy [1,2]

In this research, we applied rf spectroscopy to pulsed rf discharges, correlating harmonic signals with measurements of electron density, temperature and plasma emission.

2. Experimental setup

The research was conducted in a capacitively coupled discharge, operated with rf power at 13.56 MHz. Measurements were made in Ar, SF_6 and Ar/SF_6 discharges, with pressures in the range 50~500 mTorr.

Plasma properties were measured with a hairpin probe and a Langmuir probe, to determine electron density and temperature, and an ICCD camera, which was used to image the total plasma emission.

RF harmonic signals were measured using an *Octiv* current sensor, placed between the rf power source and the matching box. The sensor, manufactured by Impedans [3], was modified to enable measurements to be made in pulsed discharges.

3. Preliminary results

Initial measurements were made in a capacitively coupled discharge. Clear differences were observed in the time dependence of the harmonic signals between discharges operated in argon and discharges operated in SF_6. Fig. 1 shows example data from the sensor. Further measurements will be presented at the conference.

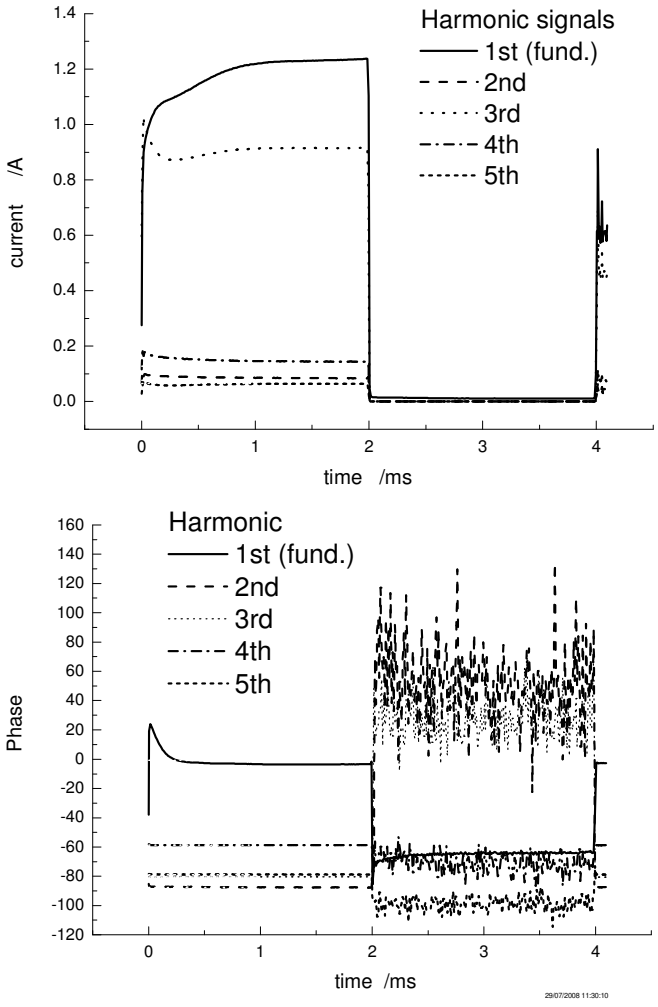

Figure 1: Amplitude and phase of the current signal measured from a pulled SF6 discharge.

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Determination of electron density in RF discharge in neon by emission spectroscopy complemented with C-R model and PIC/MC simulation

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The aim of this work was to determine the electron density in the RF discharge in neon from the absolute intensity measurement of neon spectra. The measured optical emission spectra were compared with the spectra calculated by the collisional-radiative model. The electron distribution function, needed for these calculations, was determined from 1D Particle-in-Cell / Monte Carlo model. The electron density was determined with spatial resolution over the discharge gap, reaching peak value of about 1.7×10^{10} cm^{-3} in the middle.

1. Introduction

Emission of radiation from excited states in coronal equilibrium is directly proportional to electron density. Thus, absolute intensity measurement of optical transitions originating from the excited states can serve, with the knowledge of excitation rate, for the determination of this density. However, the population of excited state is in general influenced by number of other processes induced by electron impact, heavy particles or radiation. Therefore, collisional-radiative model [1] is used for correct calculation of intensities of optical transitions.

The determination of rates of processes involving electrons is in the studied low pressure (10 Pa) capacitively-coupled RF (13.56 MHz) discharge in neon quite complicated. Due to mean free path comparable with the discharge gap (4 cm) and low ionization degree the electron distribution function is nonlocal and generally non-Maxwellian. Thus, Monte Carlo approach (in Particle in Cell method) is used for determination of electron distribution function.

2. Experimental set-up

The capacitively-coupled RF discharge was generated in a grounded stainless-steel vacuum chamber with inner diameter of 33 cm between parallel plate circular electrodes with diameter of 8 cm, placed 4 cm far from each other. The chamber was filled with neon up to pressure of 10 Pa. The light coming only from narrow discharge region parallel to electrodes was taken out with two iris diaphragms, mounted on movable table 25 cm in front of the optical fibre. The spectra were recorded with Jobin Yvon FHR 1000 spectrometer with CCD detector. Oriel Tungsten halogen lamp calibrated by NIST was used for measurement of fibre irradiance. Uniform radial intensity profile was assumed for region between the electrodes to derive the plasma emission coefficient from the fibre irradiance.

3. Results

The electron density profile across the discharge gap determined from the optical spectra is presented, together with electron kinetic energy calculated with PIC/MC model in Fig. 1. Spatial intensity development of neon line at 585 nm is also shown (in relative scale). Obviously, the density profile is different from the intensity one due to the varying mean electron energy from place to place. Going into the bulk plasma, mean energy of electrons decreases, which results in decrease of excitation rates. However, substantially higher electron density in the bulk plasma maintains the emission of radiation at considerable high level.

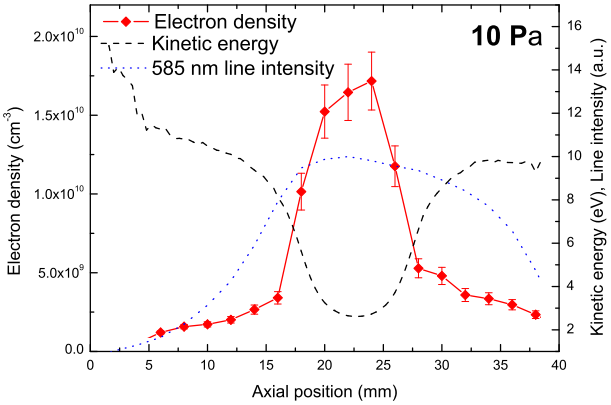

Fig. 1: *Electron density, electron kinetic energy and intensity of the most prominent 585 nm line accross the discharge gap.*

Acknowledgment

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Gold carbides laser ablation synthesis and mass spectrometry

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Formation of gold carbides from various carbon forms like nanodiamonds, graphite, fullerene, carbon nanotubes and nanogold was studied.

1. Introduction

Gold belongs to the group of precious metals and it was for a long time considered as chemically quite resistant. In last decades it was shown that gold chemistry is quite rich and that nanogold (NG) is very reactive. Nice review about gold chemistry is that of Pyykkö [1].

It was believed for a long time that gold is not forming carbides. In spite of the first paper proving the formation of gold carbides via gaseous phase reactions seems to be that of Gibson [2] and Ticknor et al., 2008 [3], the very first reference about the formation of gold carbide is that of Mathews and Watters (1900) [4] published more than 100 years ago. However this compound called as gold-carbide is gold acetylide Au(C≡C). Recently, we have proved and preliminary reported that gold carbides can also be synthesised via laser ablation synthesis using NG and nanodiamonds (ND) as precursors of carbon [5, 6].

Laser desorption-ionization (LDI) time of flight (TOF) mass spectrometric study of various carbon materials (CNT, synthetic diamond, graphite, and glassy carbon) [7] is showing that laser ablation hyphenated with TOF MS is a powerful tool in analysing various carbon materials. In this work, we are extending our previous studies [5, 6] where the formation of gold carbides was reported and we have been examining also reactivity of NG with the other sources of carbon.

2. Experimental

2.1 Preparation of nanogold

NG was synthesised from $HAuCl_4$ (auric acid) using various reducing agents like hydrogen peroxide, hydrazine, azide, gallic or citric acids.

2.2 Diagnostics by TOF mass spectrometry

Plasma was created using 337 nm nitrogen laser pulses with frequency of 10 Hz. Diagnostics of plasma plume reactions in plasma was done on a commercial MALDI instrumentation (Kratos, Shimadzu, UK) with TOF detector and/or using a MALDI-TOF Auto-flex mass spectrometer (Bruker Daltonics, Bremen, Germany).

Laser ablation synthesis was performed from a mixture of NG and sources of carbon (ND, graphite, CNT or C_{60}). An aqueous suspension of NG mixed with carbon material at different ratio was dried in a stream of air, then ablated by laser and TOF mass spectra were analyzed using linear positive mode.

3. Results

Formation of gold carbides $Au_mC_n^+$ and their adducts with sodium was detected in mass spectra from a mixture of ND with NG. The yield of production from CNT and C_{60} is limited and no carbides were detected using graphite.

4. Conclusions

Nanogold and ND are forming in plasma Au_m^+ and C_n^+ clusters which react together and produce various gold carbides $Au_mC_n^+$, where m = 1-3, n = 1-31. Highest intensity was observed for AuC_{18}^+ cluster.

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Controlling plasma properties by voltage pulse shaping

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We have investigated the effect of tailored voltage pulses on the properties of a low pressure pulsed rf discharge. Three different types of pulses were investigated: a plain square wave pulse, a pulse with a slowly rising amplitude and a pulse with a slowly falling amplitude. Electrical probes and optical emission methods were used to characterise the plasma properties.

1. Introduction

For plasma applications it is often advantageous to be able to control different plasma properties independently. For example, in low temperature plasma processing of silicon wafers, it is desirable to alter ion flux and ion energy. However, in many cases, plasma properties are coupled strongly and independent control is difficult. Simple methods of control include changing input electrical power and gas pressure, while more complicated methods such as using dual-frequency excitation have been developed.

In this research we investigated a novel method of plasma control, tailoring the magnitude of the applied power. By using a pulsed discharge and altering the shape of the applied voltage pulse, we aimed to selectively control different discharge properties. Pulsed plasmas are particularly interesting for production of negative ions in electronegative plasmas because electron attachment has a maximum at low energies, which are easy accessible in the afterglow[1].

2. Experimental setup

The research was conducted in a GEC cell[2]. The capacitively coupled discharge was maintained between planar stainless steel electrodes with diameter of 100 mm were separated 25 mm. Measurements were made in argon discharges, at pressures in the range 50~500 mTorr and rf power in the range 1 - 100 W. The rf frequency was 13.56 MHz.

Initial measurements were made when the discharge was pulsed with square pulses, with varying duty cycles. Subsequent measurements were made with specially shaped asymmetric pulses.

Plasma properties were measured with a hairpin probe and a Langmuir probe, to determine electron density and temperature, and an ICCD camera, which was used to image the total plasma emission.

3. Results and discussion

When the discharge was operated with square-shaped pulses, the main observed features was a sharp peak in light emission and electron temperature in the first few microseconds of the pulse. This period of low electron density and high electron energy, observed by many others[3], could be controlled to some extent by varying the duty cycle and pulse frequency.

Different combinations of plasma and afterglow durations were investigated, such as changing the afterglow duration (1 μs to 100 ms) while keeping plasma period short (50 μs). In particular, we observed that, for afterglow time shorter than 100 μs, changing the afterglow duration had huge impact on ignition of the next plasma pulse.

In second stage measurements, we used specially tailored pulses, with tailored rise-times and fall-times. With these pulses, we found that we could obtain the same variation in plasma properties, such as electron density and temperature, while keeping the pulse duty cycle and pulse frequency constant. This behaviour can be explained by considering the effect of rising and falling voltage amplitudes on the electron behaviour.

In the afterglow, electron temperature falls rapidly, electron production stops, and electrons diffuse to the walls. Ignition at the next voltage pulse depends strongly on the density of electrons remaining at the end of afterglow. If the voltage pulse rises steeply, as in a square wave, the rf pwer is absorbed by small number of electrons and the electron energy rises rapidly. If the voltage pulse rises slowly, as in our tailored pulse, the electron energy will also rise slowly. Similar control can be achieved by varying the rate at which the rf power turns off at the end of the voltage pulse.

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Comparative study of different types of barrier discharges by cross-correlation spectroscopy

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High-speed optical techniques with fine spatial resolution were applied to the investigation of several barrier discharge types: one-sided and two-sided volume barrier discharge and coplanar barrier discharge, respectively. Spectrally resolved results then allowed determination of plasma parameters and described mechanisms of these discharges operating at atmospheric pressure air.

1. Introduction

The techniques of cross-correlation spectroscopy (CCS) and intensified high-speed CCD camera are already well established optical techniques for investigation of highly transient discharge events. The prephase, ionizing wave propagation and 2D structure of two-sided barrier discharge were already reported in [1]. 3D results on coplanar barrier discharge are introduced in [2]. In this contribution, results on one-sided volume barrier discharge are presented and compared to results on above mentioned barrier discharges.

2. Experimental setup and procedure

The microdischarges operated in flowing air, driven by means of sinusoidal high-voltage between two semi-spherical electrodes (volume discharges) or electrodes in coplanar configuration, both placed in a discharge chamber. Used dielectric was alumina in all cases. CCS enables the recording of the spatio-temporally resolved development for a selected spectral lines. Therefore, a monochromator and a time-correlated single photon counting technique (with two photomultipliers) were used. The temporal resolution of presented measurements reached the order of tens of picoseconds. The emission of the molecular bands of the first negative (at 391.5 nm) and second positive (at 337.1 nm) system of nitrogen were recorded in order to determine the E/n spatio-temporal distribution according to calibration results based on [3]. All microdischarges were scanned along their length with submillimeter resolution.

3. Results and conclusions

The mechanisms of all above mentioned barrier discharge types show common characteristics. Indeed, the starting Townsend phase, the phase of cathode-directed ionizing wave propagation and the decay phase with on-dielectric (surface) discharges were recognized. The velocities of cathode-directed ionizing waves in all discharges are of the same order of magnitude. However, there are several differences caused by the geometry or by the used electrode's material.

From our results follows, that the only difference in discharge development between volume and coplanar discharge is the presence of well pronounced second ionizing wave in the case of the coplanar discharge. The possible mechanisms of the second ionizing wave (also denoted as an anode-directed streamer) are two: a fast electron drift towards anode or truly streamer based discharge event. Partially, the second wave was detected already for two-sided volume discharge as well. However, the geometry of coplanar discharge cell allowed full development of this phenomenon.

In the case of one-sided volume discharge the main differences from two-sided volume discharge are caused by the presence of metal electrode. There are various durations of the Townsend phase, depending on the fact whether the anode is metal or dielectric, and the presence of the transient cathode layer in the discharge, when the metal electrode is cathode. It is recognized by long lasting emission at 391.5 nm (high E/n value) at the cathode edge. This led to the description of one-sided volume discharge with metal cathode as an atmospheric pressure transient glow discharge.

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Micro hollow cathode discharge experiment in argon

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In present work we have studied Micro hollow cathode discharge (MHCD) in pure Argon. The MHCD was generated in a structure with a single hole (diameter of 1.2 mm) in a ceramic insulator (thickness of 600μm) between two Cu electrodes. The breakdown voltage and volt-ampere characteristic of MHCD were measured as a function of the gas pressure.

Experiment

We have used home made MHCD structure prepared by deposition of Cu electrodes on both sides of the ceramic (Al2O3 96%) film. The ceramic was chosen due to suitable thermal and electric properties and a low sputtering coefficient that enables a longer lifetime. The hole was drilled mechanically with diameter of 1,2 mm. The Cu electrodes have been made by vacuum evaporation technique. The discharge current of the MHCD was limited to 0,2 mA and discharge current was measured by a 1 kΩ resistor.

In the present experiments we have measured the breakdown voltage of the MHCD structure as a function of the Ar pressure in a limited pressure range 3-200 mbar due to technical problems to create thick electrodes which would have longer life time at higher pressures. The measured curve is presented in a form of a Paschen curve in the Fig. 1. Present data are compared with Paschen-curve of Ar of ordinary planar discharge tube published in Reizer [1]. The minima of the Paschen curves are mutually shifted due to a different mechanism of ignition and different shapes of electrodes used in the experiments.

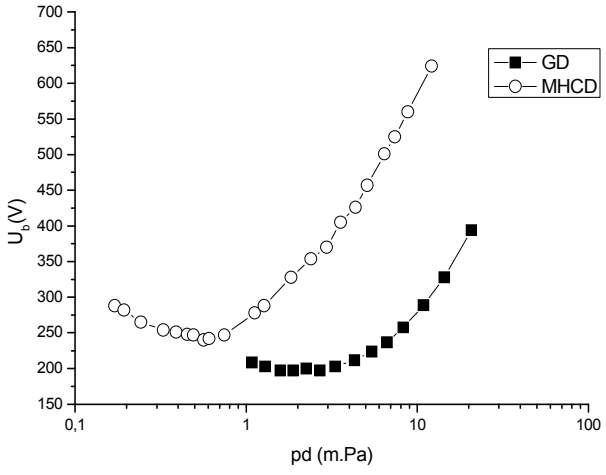

Fig. 1. *Paschen curve for MHCD in Ar and Paschen curve of Ar from Reizer [1].*

In the Fig. 2 the time dependence of the discharge voltage and discharge current of the MHCD is presented. We have observed a self-pulsing character of the MHDC-type DC discharge. This self-pulsing regime (according to [2]) occurs between the abnormal glow regime where the plasma is confined in side of the hole (low current) and the normal glow regime where the plasma expand (high current).

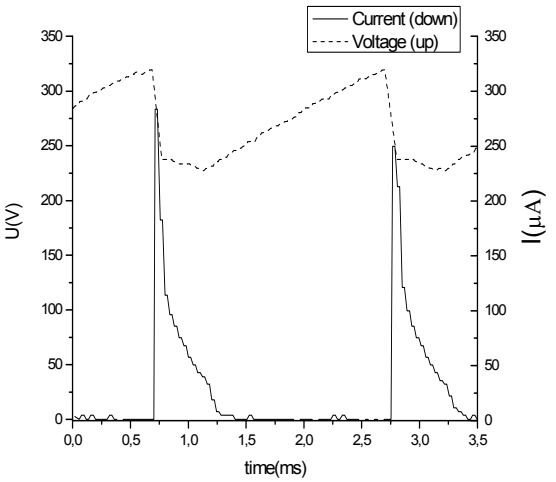

Fig. 2 *Discharge course for time, p=30mbar*

Acknowledgements

This work was supported by the Slovak grant agency VEGA project Nr. VEGA-1/0051/08 and Comenius University Grant GUK_407

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Positive corona discharge experiment in admixtures of N_2 and CH_4 - A simulation of Titan's atmosphere

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A discharge simulation of processes in Titan's atmosphere has been carried out using coaxial wire-to-cylinder corona discharge reactor in stationary regime at constant voltage of 6.6 kV. An analysis of gaseous and solid products was also performed using FTIR and SEM-EDX methods.

Experiment

Titan is considered as one of the few places in Solar system, where atmospheric and surface conditions could have produced organic molecules as precursors of higher hydrocarbons, nitriles or amino acids. Most of laboratory simulations of Titan's atmosphere were carried out at lower pressures presenting stratospheric conditions but there is poor knowledge about simulated reactions of Titan's troposphere [1, 2]. In our work an experimental investigation of products in positive coaxial corona discharge fed by mixture of N_2 and CH_4 with ratio of N_2:CH_4=98:2 in stationary regime has been made using FTIR spectroscopy. The measurements have been carried out at pressure of 1 bar and ambient temperature. The discharge reactor used for the treatment of the gas mixture consisted of a brass cylinder with diameter of 16 mm and length of 70 mm. A stainless steel of diameter of 0.125 mm was centred inside the metal cylinder and was connected to the high voltage power supply. Coaxial corona discharge was generated by a Glassman high voltage power supply. The mixing

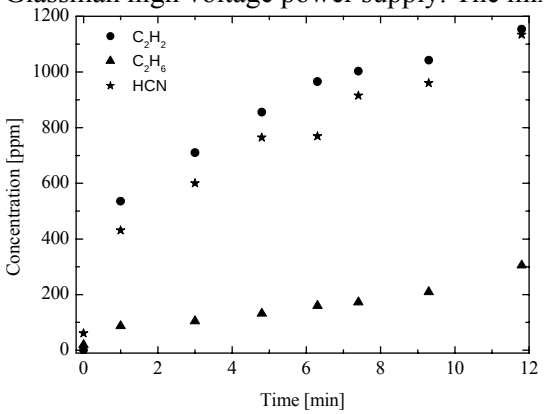

Fig. 1: *Evolution of concentration of C_2H_2, C_2H_6 and HCN produced in a positive corona discharge fed by a static CH_4-N_2 gas mixture operating at atmospheric pressure driven by a constant voltage U=6.6 kV.*

ratio of methane and nitrogen was regulated by a MKS flow controllers. The reactor was placed in a Nicolet FTIR spectrometer for the in-situ measurements of absorbance of synthesized compounds. The measurements were focused on the time evolution of C_2H_2, C_2H_6, CH_4 and HCN concentrations (Figure 1) and SEM-EDX study of the deposited compounds on discharge electrode. After a certain time a yellow-orange layer was formed on the active discharge electrode causing sparks and forming a dense rose-like spots on the covered electrode surface (Figure 2). FTIR studies of gaseous products show increase with time. After 10-12 minutes the C_2H_2 concentrations show an effort to reach saturated values.

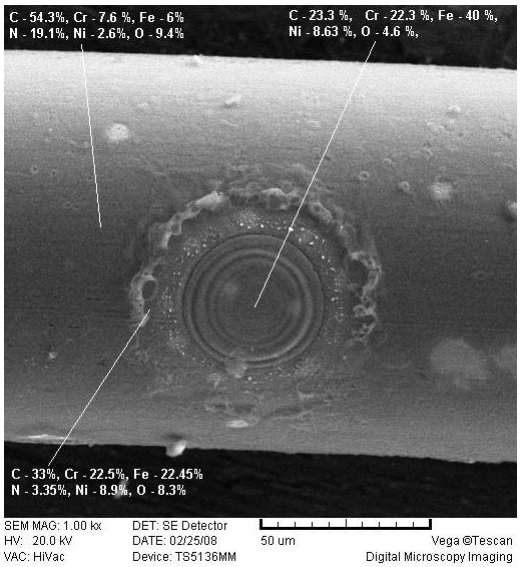

Fig. 2: *SEM-EDX study of electrode surface.*

Acknowledgment: This project was supported by the Slovak grant agency VEGA project Nr. VEGA-1/0051/08.

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Atomic oxygen distributions along the discharge channel and guided effluent of a micro scaled atmospheric pressure plasma jet

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We report on absolutely calibrated atomic oxygen measurements along the discharge channel of a micro scaled atmospheric pressure plasma jet with special emphasis on the transition between plasma core discharge channel and it's elongated guided effluent. Challenges regarding the discharge design and the used two photon absorption laser induced fluorescence technique will be discussed.

The recently more and more increasing field of micro plasmas offers a great potential for low temperature surface treatment on atmospheric pressure [1]. One of the major reactive species is the generated atomic oxygen.

To understand the creation and destruction processes, it is of great importance to understand the atomic density decay especially inside the transition region between core plasma and effluent.

The co-planar capacitively coupled radio frequency discharge is operated under a helium gas flux of about 1.5 slm and a molecular admixture of about 1% of oxygen. Electrode length is 40 mm and the discharge cross-section is 1x1 mm^2. The device was specially developed for optical access.

The diagnostics used here is the latterly established xenon calibrated two-photon absorption laser induced fluorescence spectroscopy, revealing spatially highly resolved density maps [2].

For the oxygen atoms produced in the discharge, there still is a discrepancy between the densities inside the plasma core of up to $10^{16}cm^{-3}$ [3] and the highest measured values in the effluent of some $10^{14}cm^{-3}$ decaying with distance. It could be shown for this micro scaled atmospheric pressure plasma jet (µ-APPJ) that up to $10^{13}cm^{-3}$ can be measured even several centimetres down the effluent [4].

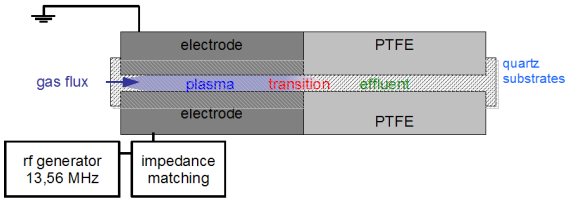

Fig. 1: Schematic sketch of the improved µ-APPJ

For common micro jet devices, the important values inside the transition region between plasma and effluent have to be estimated due to the lack of optical access (e.g. quartz and electrode edges).

However, since this transition region is of special interest, a set-up with an elongated discharge channel of the same cross section suppresses gradients in gas pressure, speed, and mixture with ambient atmosphere as well as the formation of vortexes (Fig. 1), and supplies excellent optical access to each region.

This allows continuous density scans from the discharge core along the effluent at equal geometric parameters (Fig. 2).

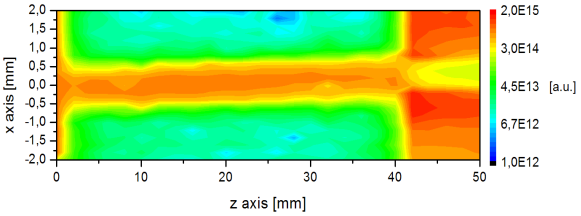

Fig. 2: Continuous relative TALIF signal profile from discharge to guided effluent

For absolute calibration, apart from the local heavy particle densities (collisional de-excitation) also the local gas temperature is of major importance. Whereas the gas temperature can easily be measured via thermocouples in an open effluent configuration, the plasma core and elongated effluent requires optical methods due to the small dimensions.

This project is supported by the DFG in the framework of "Graduiertenkolleg 1051", project "SCHU-2353/1", and the "Research School der Ruhr-Universität Bochum".

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Excitation dynamics of micro-structured atmospheric pressure plasma arrays

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We report on phase, space and spectrally resolved optical emission spectroscopic measurements on micro-structured atmospheric pressure plasma arrays. Ignition and sustaining mechanisms as well as energy transport and wave-phenomena are investigated..

Atmospheric pressure micro-plasmas recently enjoy great interest due to their huge application potential especially in the technological and biomedical sector. Their small confining structures allow localized treatment and reduce working gas consumption while the absence of vacuum equipment additionally reduces processing costs compared to low pressure plasmas.

Micro-structured atmospheric pressure plasma arrays [1] are very efficient UV light sources whereas they exceed commercial plasma display panels (PDP) in the VIS by a factor of 2. Moreover, the photosensitivity of such devices excels that of conventional Si-based detectors by an order of magnitude [2]. As such plasma arrays are available in various sizes and also in form of transparent or flexible devices they are well suited for numerous applications such as wound sterilization or optoelectronics.

Nevertheless, the fundamental knowledge of such plasmas particularly with regard to ignition and sustaining mechanisms is only rudimentary.

We report on simultaneously phase, space and spectrally resolved optical emission spectroscopic measurements on such micro-structured atmospheric pressure plasma arrays. An intensified CCD camera with attached telescope allows to resolve small sections of the array without interfering with the discharge.

The arrays investigated here have typical dimensions of 5x5 mm and each consists of 50x50 pixels, where each pixel measures 50x50 µm². One pixel consists of an inverted pyramidal Si electrode where a Ni grid serves as counter electrode. The electrodes are covered with SiO2-Si3N4 polymers.

The discharges are operated in helium, argon or neon and in mixtures of those at different mixing ratios. Excitation frequencies are in the order of several kHz and voltages in the range of a few 100 $V_{p\text{-}p}$.

Species distributions on array structures are investigated in order to get information on local excitation processes and characteristics.

Former measurements [3] using triangular driving voltages show that the ignition behavior of such plasma arrays is similar to that of a Townsend discharge whereas self-pulsing similar to that of dielectric barrier discharges (DBD) is observed (see fig. 1). We study the influence of the excitation function shape and frequency on the development of the pulse bursts. This determines the on-time and hence the emission efficiency of the devices.

Furthermore, wave-like excitation features running across the arrays are observed, indicating cross-talk between individual pixels. First measurements on the basic energy transport systems and excitation dynamics leading to this phenomenon have been performed.

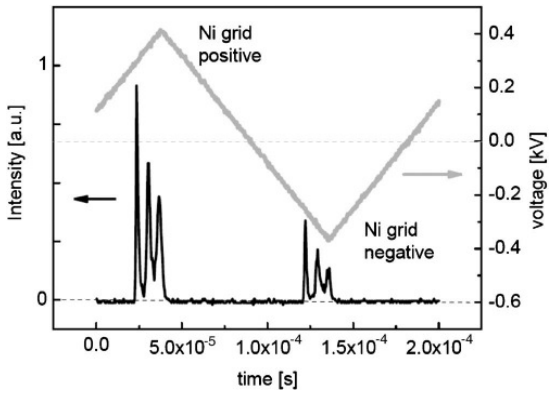

Fig. 1: *PMT intensity signal (black) and driving voltage (gray) over one AC cycle at f=5 kHz, p=1 bar, Vp-p=780 V, and Ne/Ar-mixture 4:1 [3]..*

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Spectroscopic investigation of high power pulsed microwave discharge

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Using a spectrometer equipped with ICCD we carried out a time resolved diagnostics of high power pulsed microwave plasma operating in neon at reduced pressure. The temporal evolution of intensities of selected spectral lines was then compared to a theoretical model, giving the estimation of electron energy distribution function.

1. Introduction

Although there are many studies of pulsed discharges, they have mostly used common supplies (dc, radiofrequency, microwave), with relatively low peak power (10^2 – 10^3 W). However, this work deals with pulse peak powers of the order of 10^5 W. The conditions in this type of plasma are substantially different from the common case. Comparison between the experiments and the results of current model can reveal some discrepancies and therefore point to processes which are significant only at extreme conditions.

As our previous works [1, 2, 3, 4] focused mainly on nitrogen plasma, in this paper we use neon as the working gas. This opens the possibility of testing a collision-radiative model of neon [5] under these conditions.

2. Experimental

We have developed the apparatus with suppressed plasma–wall interaction. Plasma is produced in spherical glass vessel with inner diameter of 0.5 m, on one side covered by reflection foil, which reflects and focuses the microwaves radiated on another side by horn antenna. Microwaves with 3 cm wavelength (X-band) are generated by radar magnetron (peak power reaches 100 kW). The pulses have duration 2.5 μs and are repeated 400 times per second.

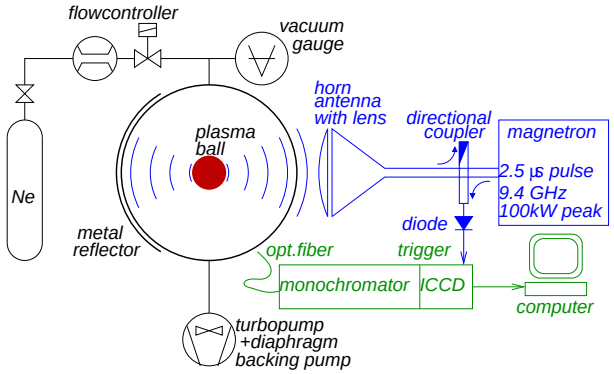

Fig. 1: *Experimental setup.*

The horn antenna is designed to spread the power over a larger surface in order to be under a breakdown limit. Only when focussed by dielectric lens into the centre of the glass vessel, the electric field has sufficient intensity there and a plasma ball is formed. The pressure of working gas (neon) is measured by a capacitance absolute gauge and controlled by a gas flow meter and by varying rotation speed of the turbo pump. The operating pressure is in the range 20–2000 Pa.

The spectra were measured with Jobin Yvon FHR 1000 monochromator with ICCD detector, which was calibrated with Oriel Tungsten filament lamp.

3. Model

The collisional-radiative model [5] was used to calculate the optical emission spectra of the neon discharge. Number of elementary processes was taken into account (electron excitation, de-excitation and ionization of ground-state or excited atoms, excitation transfer, emission and absorption of radiation, metastable-metastable collisions, two-body and three-body collisions with neon ground state atoms etc. The measured and calculated spectra were compared on the basis of sum of squared intensity differences and the plasma parameter determining the electron energy distribution function was found from the best fit. Maxwellian electron distribution function with electron temperature as parameter was assumed as the first step.

5. Acknowledgements

This work was financially supported by project of Czech Ministry of Education MSMT 0021622411.

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Hybrid PVD-PECVD sputtering deposition process – from properties of deposited films to process characteristics

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In this paper we derived process characteristics of hybrid PVD-PECVD sputter deposition process only from properties of deposited thin films. We found three probable sources of carbon atoms incorporating into the growing film – methane partially or fully dissociated in magnetised plasma near the target, methane partially or fully dissociated in the non-magnetised plasma near the substrate and carbon atoms sputtered from the carbon layer formed on the boron target.

1. Introduction

Standard procedure for plasma diagnostics and description of plasma processes is to directly measure significant discharge parameters and from obtained results predict the process behaviour and optimal conditions for thin film deposition. We performed an uncommon approach. The goal was to estimate relevant processes taking place in hybrid PVD-PECVD process using nitrogen and methane gasses added to the reactor while boron target was being sputtered only from properties of deposited films. From the trends in the deposition rate and FTIR spectroscopy of the deposits concerning carbon incorporation to the growing films some interesting statements about behaviour of this hybrid PVD-PECVD are derived.

2. Experimental

Industrial system Alcatel SCM 650 was used. Boron target was mounted on a well balanced magnetron cathode 20 cm in diameter which was driven by a 1 kW RF source at industrial frequency of 13.56 MHz. The distance between the target and substrate holder was 7 cm. Constant Ar flow of 20 sccm was maintained. The experiment was performed in two steps – with and without biasing the substrate. Thin film properties were determined using UV/VIS reflectometry and FTIR spectroscopy.

3. Results

While no bias was applied, addition of nitrogen gas leads to an increase in deposition rate followed by a decrease. This behaviour is typical for reactive magnetron sputtering process. When methane was added simultaneously with nitrogen, no significant changes in the deposition rate are observed.

Applying RF power of 500 W on the substrate holder leads to DC self bias approx. -100 V. When no reactive gas was added, no film was acquired, so the outsputter rate of boron atoms exceeded their deposition rate. When only nitrogen is added, similar behaviour as reported for the case without RF biasing the substrate is observed. Keeping the same conditions which lead to no deposition and adding only methane without nitrogen leads to deposition.

Adding small amount of methane to certain amount of nitrogen leads firstly to a significant increase of deposition rate followed by a decrease.

4. Discussion

When no RF power is applied to the substrate, carbon can originate from methane partially or fully dissociated in the magnetized plasma or from carbon layer probably formed on the target. From IR spectroscopy it can be seen, that carbon peaks rise in favour of boron peaks while deposition rate is not really affected. This indicates that boron atoms are partially replaced in the film by carbon atoms. Since sputtering rate of carbon is twice lower comparing to boron and the deposition rate is kept rather constant, there must be another source of carbon atoms, probably from the methane partially dissociated in the magnetised plasma.

Applying of 500 W of RF power to the substrate leads to formation of an additional plasma region near the substrate. Also argon ions with high enough energies to resputter the growing film are present. Important processes are now flux of boron and carbon atoms from the target, flux of carbon atoms from both plasma regions and the loss of carbon and boron atoms from the growing film.

Deposition process with both nitrogen and methane added simultaneously behaves similarly to reactive magnetron sputtering with two reactive gasses.

Acknowledgment

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Optical diagnostics of transversal gas discharges under atmospheric pressure

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Plasma parameters of the transversal gas discharges were studied by optical emission spectroscopy. Excitation temperatures (electronic T^*_e, vibration T^*_v, rotation T^*_r) were determined. Method of determining relative concentrations of radiating plasma species by using SPECAIR program was suggested. Codes SPEC-ELEMENTS for simulation emission spectra of some elements with taking into account the apparatus function of used spectrometer were developed.

1. Introduction

Generators of non-thermal atmospheric pressure plasma, such as: gliding arc *GA*, gliding arc in tornado *GAT,* transverse atmospheric glow discharge, arc in the transverse blowing gas flow (transverse arc *TA*) [1] and discharge in the gas channel with liquid walls *DGCLW* [2] provide simultaneously high plasma density and operating pressure with high level of non-equilibrium. Transverse gas flows in these discharges increases efficiency of heat- and mass- exchange between plasma and environment. It makes these dynamic plasma systems attractive for different plasmachemistry applications. The main researching results of the *TA* and *DGCLW* plasma parameters are presented in this work.

2. Experiment

Design of the *TA* discharge and schema of optical diagnostics are thoroughly described in [1]. The atmospheric airflow was directed from the nozzle across two horizontal opposite copper electrodes and formed a bright crescent-shaped electric arc. The discharge was powered by the DC source at the ballast resistance in the circuit. The gas flow rates G=0-110 cm^3/s and discharge current I_d (330-660 mA) were kept constant.

Research of the *DGCLW* was carried out in the reactor, which scema is described in [2] in detail. Reactor consists of quartz cylinder filled by working liquid– distilled water. Cylindrical copper electrodes were placed inside glass tubes narrowed on the end. Flows of air directed into these glass tubes along to the top and to the bottom electrodes were colliding and forming stable gas channel, in which the discharge burns. DC source was used to supply the *DGCLW*. Different regimes of the discharge were realized: a- both solid (copper) electrodes, b – one solid and one liquid electrodes with different polarities („liquid" anode and „liquid" cathode). Airflow rate G=55 cm^3/s was maintained and the discharge current I_d was changed from 60 to400 mA.

Diagnostics of plasma parameters of both discharges was made by optical emission spectroscopy. CCD-based spectrometer Plasma-Spec with spectral resolution ~0,7 nm was used for spectra registration in the range of 210-1100 nm.

3. Results and conclusions

Emission spectra of plasma of both discharges are muticomponent and simultaneously contain a lot of spectral lines (electrode material, blowing gas atoms, etc) and overlapping bands that complicates their diagnostics. SPEC-ELEMENTS codes were developed for simulation of metals (electrode material) emission spectra.

T^*_e≈4600K of H atoms was determined from Boltzmann plots. T^*_v≈4000-4600K and T^*_r≈2000-2800K in *TA* plasma were estimated from 2nd positive system of N_2 by fitting the experimental spectra with the simulated ones. The excitation temperatures were estimated for plasma of the investigated regimes. It was shown that level of non-isothermality of the *DGCLW* plasma is lower than for the *TA* discharge ($T^*_e(H)$≈5000-5500K, $O^*_v(N_2)$≈4500-5000K and $T^*_r(N_2)$≈4200-4500K). The comparative analysis of plasma parameters investigated discharges with other transverse discharges known from the literature was made.

The relative concentrations of radiating plasma species in both discharges were estimated with SPECAIR by using method suggested in [3].

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Time of Flight Mass Spectrometry as a tool for plasma diagnostics

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1. Introduction

Time of Flight Mass Spectrometry (TOF MS) belongs to one of the most powerful modern spectrometric techniques. TOF MS is often used in connection with Matrix Assisted Laser Desorption Ionisation (MALDI) for analysis of bio molecules like peptides and proteins. MALDI is using a suitable organic compound (matrix) absorbing the laser pulse and while the matrix is decomposed, the analyte is ionized mostly without any fragmentation. MALDI is therefore called "soft" ionization technique; the scheme is given in FIGURE 1.

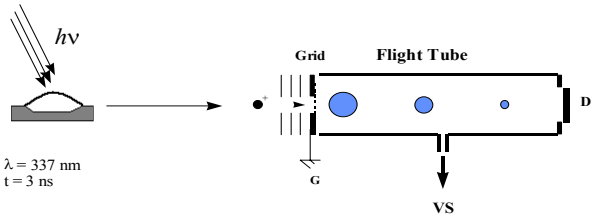

FIGURE 1: Scheme of MALDI TOF MS (G ground, VS vacuum source, D detector).

MALDI TOF MS instrumentation can also be used for Laser Desorption Ionisation (LDI) or Laser Ablation (LA) TOF MS of various materials including inorganic compounds, nano materials and even for Laser Ablation Synthesis [1-4]. In these cases no matrix is used. Formation of ions in plasma can be followed by TOF MS. In this paper we will review the principals and analyze possibilities and limitations of this technique to low temperature plasma diagnostics. Several examples will be demonstrated and discussed.

2. Experimental

Nitrogen laser 337 nm and MALDI instrumentation of Kratos Shimadzu (Manchester, UK) and/or a MALDI-TOF Auto-flex mass spectrometer of Bruker Daltonics (Bremen, Germany) were used.

3. Results

TOF MS analysis of plasma plume was applied to analysis of carbon clusters, diamonds, gold clusters and recently also to elucidate the structure of nanodiamonds, chalcogenides glasses, pulsed laser deposited materials like $AgSbS_2$, etc. [4, 5]. The examples of TOF MS plasma diagnostics will be demonstrated and discussed.

4. Conclusions

TOF MS is a suitable technique which can be applied to a low temperature plasma diagnostics, analysis of chemical processes in plasma, identification of chemical species formed in plasma and can also contribute to understand chemical structure of ablated materials.

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Fast time resolved imaging of the fast positive mode and slow negative mode of a plasma discharge in water

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Time resolved imaging of a plasma discharge in water has been performed. A pulsed filamentary plasma discharge is generated in water by a high voltage pulse. The initiation and the propagation of the discharge through the dense medium has been studied for several experimental parameters. Fast modes and slow propagation modes are reported.

Plasma discharges in water can be used as a source of chemical radicals (OH) for pollution control applications [1]. Such filamentary discharges are able to non selectively oxidize any toxic organic molecules dissolved in the liquid into harmless components. However, the initiation and propagation mechanisms of a plasma discharge inside a dense media are still intensively discussed. It is not clear if there is a streamer-like mechanism or a "bubble mechanism" [2]. The main question for plasma discharge in liquids is if there are electron avalanches in the dense media.

1. Experimental setup

In the present study, time resolved imaging of the discharge is performed in a point to plane configuration with cm gap range powered by a Marx generator. Two iCCD and a streak camera have been used for time resolved imaging and were triggered on the electrical diagnostics. Several experimental parameters have been investigated: voltage amplitude, voltage pulse duration, voltage polarity, gap, liquid ionic conductivity, presence of gas injection, presence of a dielectric barrier, etc.

2. initiation and propagation

A statistical study (laue plot) of the time delay of the discharge initiation was performed. Its experimental behaviour is consistent with a microbubble nucleation with local joule heating at the tip electrode.

The propagation velocity was also measured as a function of those experimental parameters. Two different plasma modes have been observed in the positive polarity: a slow mode(10m/s) and a fast mode(30-35km/s). Only one slow mode has been observed at negative polarity (400-500m/s). In both polarities the slow modes are weakly luminous and consist of a heavily structured gas cavity. The discharge current is a succession of 20ns peaks of typically 1A amplitude. Transient bright spots can be observed at filaments tips. The fast positive mode has a more filamentary morphology with branching. The number of filaments is related to the discharge current. The emission intensity is uniform along the filament and the propagation is continuous without steps.

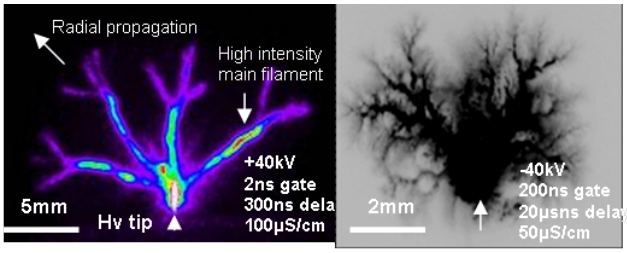

Fig. 1: fast positive mode and slow negative mode of the filamentary plasma discharge in water.

The discharge stops to propagate when applied voltage reaches a threshold value or after some electric field screening at low ionic conductivity. Ultrafast reillumination of a previously extinguished filament can occur at low ionic conductivity and lead to a step propagation [3]. The propagation velocity of the fast mode has been found to be constant during the propagation whatever the experimental parameters, and in particular as a function of the Laplacian electric field and the water ionic conductivity. Measuring the propagation velocity gives an insight on the propagation mechanism. The fact that the measured propagation velocity remains constant indicates some limiting mechanism such as voltage drop inside the plasma filament or density lowering by local energy deposition at the plasma channel tip.

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Coupling of imaging and emission spectroscopy for micro hollow cathode discharges study.

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A microsplasma is generated in the microhole of a molybdenum-alumina-molybdenum sandwich (MHCD type) [1]. Imaging and emission spectroscopy give indications on the electronic density in the microhole and allow indentifying the different zones of the micro discharge in which different mechanisms of atoms excitation are involved. To confirm the experimental interpretations we use a simple 1D model to obtain the radial evolution of the densities.

1. Experimental set-up

Experiments are run in stable discharge conditions at constant argon flow rate of 100 sccm. Argon pressure ranges from 30 to 300 Torr and discharge current between 0.5 and 2.5 mA.
The image of the MHCD, viewed from the anode side, is formed on the entrance slit of a 2m spectrograph. A CCD camera placed on the exit plane of the spectrograph captures the horizontally dispersed images at different spectral lines.

2. Emission spectroscopy

2.1. Radial profile of the emission intensities

We study an atomic line (427.217nm) and an ionic line (427.752nm) of argon. The intensity of Ar^+ emission has an annular shape with its maximum near the cathode surface, whereas the intensity of Ar line shows a pronounced maximum at the centre of the MHCD hole.
We plot the radial profile of the emission intensity of Ar and Ar^+ line at different pressures. The 'peaks' observed near the edge at high pressure (P≥100 Torr) for the two lines may correspond to the position of the cathode sheath edge where electron excitation occurs. At lower pressure (30 Torr), the sheath length is no more smaller than the hole radius and thus maxima from both side approach the centre and form a single maximum. We plot the evolution of the sheath thickness with the pressure. The atomic line shows a second component in the centre of the MHCD, probably due to electron-ion recombination.

2.2. Electron density

The spectral profile of the H_β-line at 486.1 nm and particularly the Stark broadening of this line, gives information about the radial profile of the electron density inside the hole [2]. We plot the radial evolution of the Stark broadening for four different pressures. In the bulk, ω_{Stark} is relatively constant along the MHCD diameter which corresponds to $n_e=2.10^{13}cm^3$. In the sheath region, the increase of ω_{Stark} corresponds either to a contribution of the electric field or to a real drop of n_e in the centre due to the electron-ion recombination.

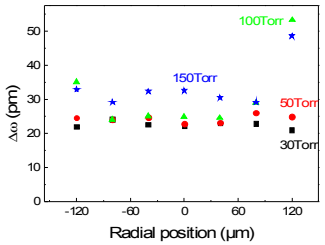

Fig. 1: *Radial evolution of the Stark broadening at different pressures in the 400 μm diameter.*

3. Numerical prediction

To try to confirm the n_e decrease in the centre we use a simple model with only 3 species, which gives the radial evolution of n_e. With increasing the pressure, electron density is flatter but there is no drop in the centre.

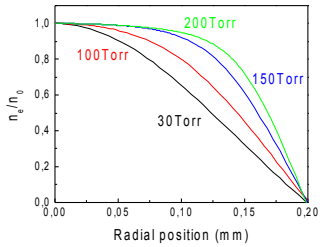

Fig. 2: *Radial evolution of the electron density at different pressures in the 400 μm diameter.*

This result let us think that a drop of n_e in the centre is not possible and that we only observe experimentally the electric field effect.

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Dielectric Barrier Discharge (DBD) and Zeolite Coupling Butane case

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The combination of Dielectric Barrier Discharges (DBDs) and adsorbent catalytic material was investigated for butane case. Several additional experiments were tested, to distinguish different phenomenon's: chemical desorption (temperature effect), molecular adsorption competition (water vapor effect), etc.

1. Introduction

The majority of studies have examined ozonation/zeolite coupling; relatively few have focused on plasma/Zeolite coupling [1-3]. Zeolite catalytic reactions are broadly classified as acid-base reactions, and these reactions depend on the nature of adsorption sites. In this study, zeolite was used for this catalyst/adsorbent property association.

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2. Experimental procedure

The power supply used is a pulsed-bipolar one with 1µs pulse duration at 1 kHz. The air flow was fixed at 2l/min and the voltage was 6 kV. FTIR measurement in the post discharge was used to observe chemistry dynamics. Butane was used like molecular model at low concentration. This concentration inlet is 40 ppm during all experiment with relative humidity 50%. The plasma was turned on and off periodically.

3. Results

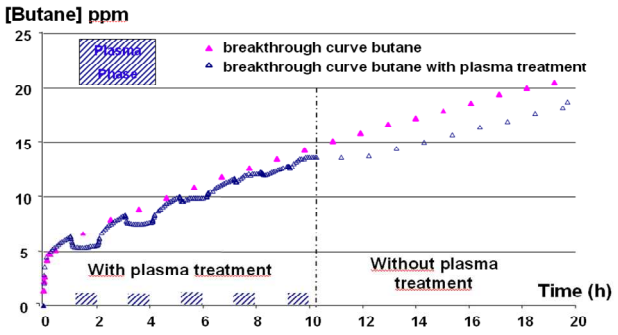

Fig 1. Butane breakthrough curve with (open symbols) and without (closed symbols) plasma treatment

For the first hour, the breakthrough curve follows the same evolution as plasma OFF. Butane concentration at the outlet decreases when the plasma is turned ON. On the contrary, when the plasma is turned OFF butane concentrations increase. After several plasma treatment phases the same evolution is observed. During the plasma ON phase and also from one cycle to the next one, by-product (CO, CO2) concentrations increase. At the same time, ozone concentration decreases. Efficiency of plasma treatment increases as a function of the saturation rate of zeolite. Catalytic activity continues (CO2 outlet) even during post discharge (plasma OFF phase).

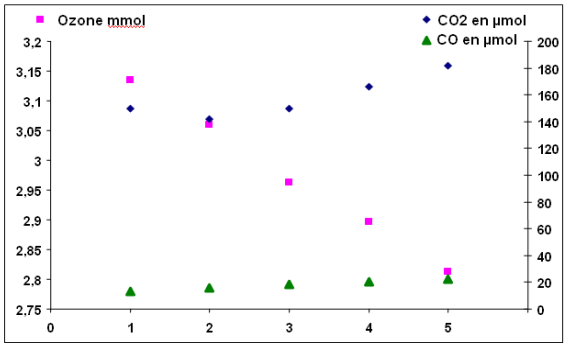

Fig 2. By-products CO, CO2 and ozone concentration

4. Discussion

Zeolite is located downstream of the plasma treatment zone. As a consequence, only stable molecules present during post-discharge. Te reason for this is that the diffusion delay time is longer than the lifetime of ions and radicals. Nevertheless, ozone was adsorbed on zeolite. Ozone decomposition produces the oxygen radical; which is adsorbed on the zeolite structure. Affinity between zeolite and the butane is weak because for example the physico-chemical properties of butane. Zeolite permits first the adsorption of pollutants and plasma by-products on the surface. Surface treatment by plasma (plasma ON) is more efficient than catalytic activity (Plasma OFF). The oxygen radical from ozone dissociation in structure of zeolite can oxidize pollutant.

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Study of the Mechanical Properties of Diamond-like Carbon Coatings on Polymer Substrates

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Plastics have become important materials because they can be produced in large scale and are cheaper and lighter than many other materials. Among them, polycarbonate (PC) is well-known, commercially available material. Owing to its excellent breakage resistance, PC has replaced glasses in many applications. Another polymer, the Bulk Molding Compound offers properties that are requisite for engineering applications.

BMC has traditionally been molded into components requiring significant structural, corrosion resistant and heat resistant properties. BMC applications have generally been restricted to the non-visual or "working" areas of appliances.

The third type of polymer we used in our study was the glass reinforced polyphenylene sulfide (PPS) which is one of the most important high temperature polymers because it exhibits a number of desirable properties such as resistance to heat, acids and alkalies, to aging, sunlight, and abrasion. It absorbs only small amounts of solvents and resists dyeing.

Despite all these properties, PC, BMC and PPS have their limitations. In order to improve the poor mechanical properties low hardness and the low scratch resistance, the materials can be coated by hydrogenated amorphous carbon films (a-C:H). They have very attractive properties such as high hardness, infrared transparency, chemical inertness, low friction coefficients, and biocompatibility. However, weak adhesion and delamination from polymer substrates, arising from high tangential stress and high internal compressive stress of a-C:H films, are main factors that limit the film thickness and their durability over time.

We focused our work on optimizing the deposition parameters to improve the coatings adhesion to the polymer surface. Hydrogenated amorphous carbon (a-C:H) and nitrogen incorporated hydrogenated amorphous carbon (a-C:H:N) films were deposited on polycarbonate, glass reinforced PPS, and BMC substrates by r.f. plasma enhanced chemical vapor deposition (PECVD). A mixture of hexamethyldisiloxane (HMDSO) and $CH_4/N_2/H_2$ gases was utilized to reduce the internal compressive stress of the deposited films. The reactor was a glass cylinder with two, inner parallel plate graphite electrodes. The bottom electrode was coupled to the r.f. generator via a blocking capacitor. The depositions were performed at the applied power of 50 W. The Depth Sensing Indentation (DSI) technique allowed us to determine the hardness and the elastic modulus of studied samples. The carbon layers deposited on the polymer samples presented high values of hardness up to 20 GPa and elastic modulus up to 120 MPa. The optimum coatings on PPS and BMC samples withstood a one hour long thermal treatment at 200 °C, the ones on polycarbonate at 100 °C and also withstood boiling in concentrated NaCl solution. After these tests it was observed that the coatings resist in severe conditions such as high temperatures and corrosive environment without delamination.

This work has been supported by the Science Foundation of the Czech Republic, contract 202/07/1669 and by Ministry of Education, Youth and Sports of the Czech Republic, contract MSM 0021622411411 and by Ministry of Industry and Trade, contract FTTA5114.

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Thermal Desorption Spectroscopy Study on Diamond-like Carbon Coatings

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The thermomechanical stability of diamond-like protective (DLC) films play a crucial role for their technological application and its study is of great importance. The main disadvantages of amorphous hydrogenated carbon (a-C:H) films prepared using PECVD are their low thermomechanical stability (due to hydrogen loss and graphitisation at temperatures exceeding 300°C) and high compressive intrinsic stress (due to intense ion bombardment). It was generally observed that the DLC films presented stable properties up to about 300 °C. After achieving this temperature the thermal degradation process starts due to the graphitization caused by hydrogen losses. The objective of the present work was to modify DLC films with the aim to decrease their high internal compressive stresses and to increase their low thermal stability.

The modified DLC films were prepared using low pressure RF capacitive discharges from mixtures of CH_4 and H_2 or N_2 with a small admixture of hexamethyldisiloxane ($Si_2OC_6H_{18}$). The thermal stability of the films was studied using thermal desorption spectroscopy (TDS). The films on silicon substrates were annealed in the laboratory furnace Classic Clare 4.0. The furnace chamber was evacuated by turbomolecular pump down to minimum pressure of about 10-5 Pa. The studied samples were subjected to heating with constant heating rate in the range from 2 20K/min. The mass spectrometer Pfeiffer Vacuum Prisma 80 was set in order to follow the evolution in time of 15 specific masses.

In case of modified coatings the desorption of hydrogen was minimal until 450 °C. Interesting is the fact, that the hardness and elastic modulus had an increasing tendency in temperature range from 450 to 1000 °C. Achieving the temperature of 450 °C, the hydrogen started rapidly to leave the film. The first desorption peak is associated to the loss of hydrocarbon groups. In case of DLC film the loss of bonded hydrogen resulted in decrease of sp3-bonded carbon content and in creation and growth of islands with prevalence of sp2-bonded carbon. This process leads in complete graphitisation of the DLC film. The rapid graphitisation is often accompanied with cracking and delamination of the film due to rapid change in the film structure. On the other hand, the desorption of hydrogen and hydrocarbon fragments (CH+, CH_2+, CH_3+, CH_4+, etc.) did not lead to deterioration of the DLC:SiOx film. Moreover, its hardness and elastic modulus increased. This effect may be explained by nanostructure character of the film.

Summarizing the results nanostructured silicon-oxide containing diamond-like coatings were prepared with low compressive stress, high fracture toughness, low roughness, low friction coefficient and good adhesion to different substrates. The coatings were stable up to minimum 400°C. The hydrogen and hydrocarbon desorption did not cause deterioration of the films. The hardness and elastic modulus of films increased. The films could withstand temperatures up to 1000 °C without delamination. These coatings, because of their high fracture toughness, low friction coefficient and thermal stability have prospect for application in particular in automobile industry.

This work has been supported by the Science Foundation of the Czech Republic, contract 202/07/1669 and by Ministry of Education, Youth and Sports of the Czech Republic, contract MSM 0021622411411 and by Ministry of Industry and Trade, contract FTTA5114.

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Plasma flow measurements in the processing chamber of an inductive plasma source

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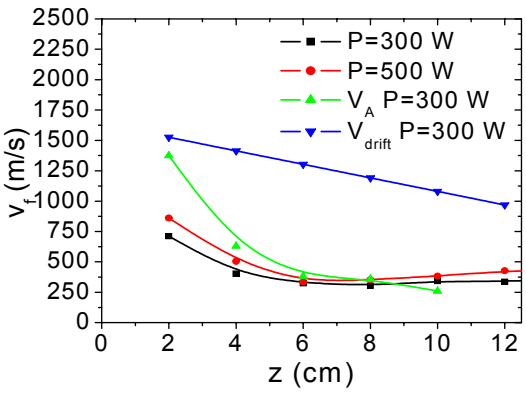
The study presents results from measurements of the plasma flow velocity by Mach probe technique in the processing chamber of an inductive plasma source. The passive compensations for each plate of the Mach probe are used to avoid the rf distortions of the probe characteristics. The flow velocity decreases with the distance from the discharge and it has week dependence on the RF power.

1. Introduction

Plasma technologies in the semiconductor industry widely use inductive discharges for plasma etching, deposition of films or implantation. The plasma created in the cylindrical dielectric tube expands in a second metallic processing chamber. The control of the directed velocity of ions and their flux increases the effectiveness of plasma etching and deposition process. At low pressure helicon discharges the existing current-free double layers accelerate ions to supersonic velocities. The simple construction and possibility for local measurements of ion velocity by Mach probe determines its applications in plasmas with strong magnetic field [1, 2] and recently in weakly ionized plasmas without magnetic field [3, 4]. The study presents results from measurements of the plasma flow velocity by Mach probe technique in the processing chamber of an inductively-driven plasma source. The input power up to 500 W at frequency 27 MHz is used in the experiments. The working gas is argon at pressure p = (0.5-15) Pa.

2. Results and discussions

For the investigated pressure range the body of the EEDF obtained from the second derivative of the cylindrical probe current at p=5 Pa, P=500 W is close to Maxwellian. The disk plates of the Mach probe can be used as single probes and they act as a retarding potential analyzer for the electrons. The first derivatives of their electron currents are related to the distribution of the electron velocities projected onto the normal to the probe surface. The slopes of these curves are the same for the upstream and the downstream Mach probe plates. This allows using the same electron temperature for both ion saturation currents and ensures the validity of the flow velocity formula. The electron temperature, plasma density and plasma potential decrease with distance from the driver (z=0) because of expansion of the plasma from the driver to the processing chamber. This process leads to electron cooling in the first region z<6 cm and almost constant Te at the second region z>6 cm. The changes of the electron temperature with the applied rf power are below 10%. With decreasing of the gas pressure in the processing chamber Te increases weakly. The density increases with the increase of the rf power and of the pressure for the investigated region of the processing chamber. The plasma potential smoothly decreases with the distance z and at the higher pressures its gradient is steeper. Potential jumps are not observed in the investigated pressure range 0.5-15 Pa.



The measured flow velocity v_f by Mach probe varies from 300 to 900 m/s. For all gas pressures vf decreases with the distance z from the driver for both input powers P=300 W and 500 W. The fast decrease in the flow velocity for z<6 cm, followed by weak dependence on z most likely is determined by axial profiles of n and Te. The estimations for the ambipolar ion flow velocity V_A from gradients of the plasma parameters and ion drift velocity V_{drift} (from the gradient of plasma potential) show higher values at 0.5 Pa and much lower values for 15 Pa in comparison to the experimental values.

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Chemistry of organic compounds in atmospheric air plasmas

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Atmospheric (or non-thermal) plasmas produced by means of electrical discharges in air at atmospheric pressure and ambient temperature are gaining increasing importance for advanced oxidation processes (AOPs) in environmental pollution control [1, 2]. Following an initial phase devoted largely to prove the non-thermal plasma process feasibility and competitiveness in terms of energy and cost efficiency, research is currently focussed on the products being released and on the chemical reactions leading to them. Due to the very complex nature and composition of these plasmas, comprising numerous highly reactive neutral and charged species, the characterization and quantification of all products (volatile and not) formed in the oxidation of volatile organic compounds (VOCs) and the study of the underlying chemical mechanisms is all but a trivial task. Such knowledge is perceived as a uniquely powerful tool for developing more efficient and cleaner processes. Our research aims at characterizing the chemistry underlying the oxidation of volatile organic compounds (VOCs) within plasmas produced by corona discharges in air at room temperature and atmospheric pressure.

Our contribution toward this goal is based on studies carried out with a large bench-top wire/cylinder corona reactor (38.5 mm i.d. x 600 mm), which can be powered by DC or pulsed voltage of either polarity, and on ion studies performed with an APCI (*Atmospheric Pressure Chemical Ionization*) - mass spectrometer [2-4]. Different corona regimes are compared and characterized by means of chemical, spectroscopic and electric analysis by monitoring the reactivity of selected VOCs which are used as chemical probes within the complex environment of in research is currently focussed on the products being released and on the chemical reactions leading to them. Such knowledge is perceived as a uniquely powerful tool for developing more efficient and cleaner processes. Due to the complex nature of atmospheric air plasmas which comprise numerous highly reactive neutral and charged species, Experiments run on the corona reactor rely on chemical diagnostics for the analysis of stable products and oxidation intermediates as well as that of short lived reactive neutral species and on the application of mechanistic probes (effect of humidity in the air, structure/reactivity relationships, effect of VOC concentration). Qualitative and quantitative determination of volatile products and intermediates (CO_2, CO plus trace amounts of organic byproducts) is performed by gas chromatographic separation coupled to different detectors (GC/FID, GC/TCD, GC/MS) and by on-line FT/IR analysis. In addition, the most important neutral reactive species, O(3P) for dry air and •OH for humid air, are investigated using specific chemical probes (ozone formation and CO oxidation, respectively). Finally, emission spectroscopy measurements are used to assay excited atomic oxygen and to derive the electronic, vibrational and rotational temperatures for the different plasma regimes investigated. As for the ionized component of the plasma, the mass spectrometric analysis provides a unique clue for the interpretation of current/voltage characteristics measured for DC corona. Specifically, we compare the ion spectra and the corona current/voltage curves obtained in pure air with those obtained, under otherwise identical conditions, in air doped with trace amounts of VOC (typical VOC concentrations range around a few hundred ppm). Depending on the specific VOC and the energization conditions used one finds that the presence of the organic pollutant can produce significant effects both on the ion population within the plasma and on the corona current/voltage characteristic. Thus, we have shown that in the case of hydrocarbon pollutants (hexane, i-octane, toluene), there is no detectable effect either in the corona current or in the ions produced by –DC corona discharge, whereas important differences are observed in the case of +DC corona discharge The APCI-mass spectra show that when the hydrocarbon is present, the characteristic positive ions of the discharge in air are substituted by many hydrocarbon-derived positive ions, thus accounting for the observed different discharge currents and average ion mobility.

The situation is quite different with halogen-containing VOCs, compounds which have significant electron affinities: in this case the

presence of the VOC produces evident effects on the current/voltage characteristic of –DC corona discharge, consistent with the observation of prevailing VOC-derived negative ions.

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Diagnostic based modelling of radio-frequency driven microplasmas

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N Knake[2], H Böttner[2], V Schulz-von der Gathen[2]

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The dynamics of a radio frequency driven atmospheric pressure plasma jet is investigated using various advanced optical diagnostic techniques and numerical simulations. The obtained insight is subsequently used in diagnostic based modelling for determining absolute number densities of atomic radicals. Diagnostic based modelling exploits the synergy of actively coupling easy to employ measurements and comparatively simple simulations.

1. Introduction

Radio-frequency driven atmospheric pressure plasma jets (APPJ) can provide high radical concentrations at low gas temperatures, e.g. for modification of sensitive surfaces in biomedicine [1]. The plasma dynamics is a complex multi-scale problem with pronounced electron dynamics within the radio-frequency cycle governing plasma ionization and initiating non-equilibrium plasma chemistry. Of particular interest are power coupling and energy transport processes from the plasma core region into the chemically reactive effluent region which is targeted for technological exploitations.

2. Plasma design

Investigations of the plasma dynamics are carried out in the so-called µ-APPJ. The µ-APPJ is an especially designed micro-scale version of the APPJ providing excellent access for optical diagnostics, in particular to the core plasma. Details of the plasma design and various results can be found in references [2], [3], and [4].

3. Employed techniques

Diagnostics of atmospheric pressure plasmas are extremely challenging due to small confining structures and the collision dominated high pressure environment demanding exceptionally high spatial and temporal resolution down to microns and picoseconds. The most promising approach is active combination of advanced optical techniques and numerical simulations. Employed techniques include: classical optical emission spectroscopy (OES), phase resolved OES (PROES), laser spectroscopy, finite-element numerical simulations, and diagnostic based modelling.

Diagnostic based modelling exploits the synergy of actively coupling easy to employ measurements and comparatively simple numerical simulations.

4. Selected results

Plasma ionization and sustainment are governed by electrons energized through the dynamics of the plasma boundary sheath. Excellent agreement between PROES measurements and numerical simulations reveals mode transitions between different ionization mechanisms during sheath expansion, sheath collapse, and electron acceleration in the high voltage sheath region – see fig. 1.

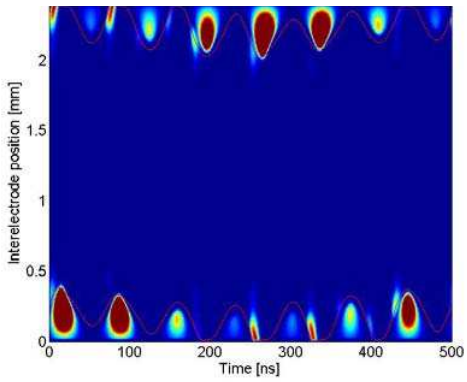

Fig. 1: Ionization dynamics in a dual frequency driven atmospheric pressure plasma jet.

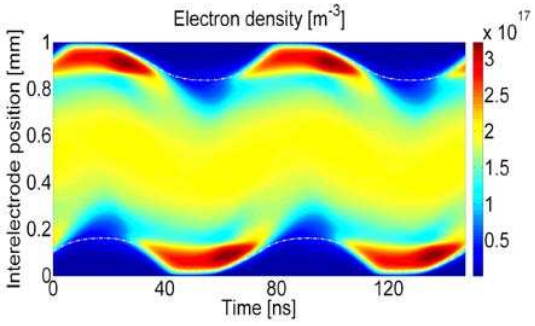

Fig. 2: Dynamics of the electron density in an electronegative radio-frequency driven atmospheric pressure plasma jet.

Under certain conditions the operation in He/O_2 gas mixture indicates an electronegative character. Fig. 2 illustrates possible consequences in a space and time resolved contour plot of the electron density. Maximum density is observed in close vicinity of the electrodes during sheath collapse where quasi neutrality cannot be satisfied through negative ions confined to the time averaged plasma bulk region.

The determination of absolute atomic oxygen densities is of particular interest for the dynamics of plasma chemistry, energy transport mechanisms, and technological applications. Spatial profiles along the plasma channel towards the effluent region are obtained using diagnostic based modelling – see fig. 3. The results show very good quantitative agreement with independent TALIF measurements.

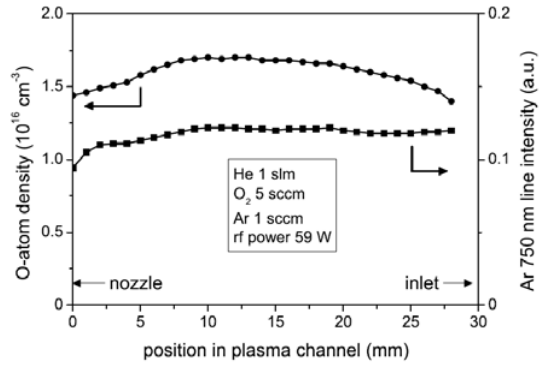

Fig. 3: Spatial profile of absolute atomic oxygen densities.

5. Acknowledgement

The numerical simulations have been generously supported by Y Sakiyama and DB Graves from the University California Berkeley. We would also like to greatly acknowledge very helpful discussions with F Iza and MG Kong from Loughborough University.

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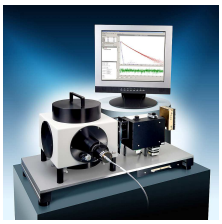
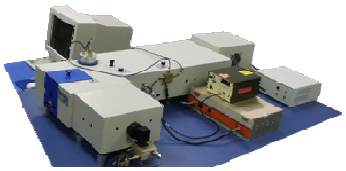


Time domain, TCSPC



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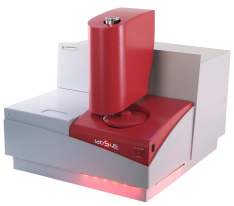

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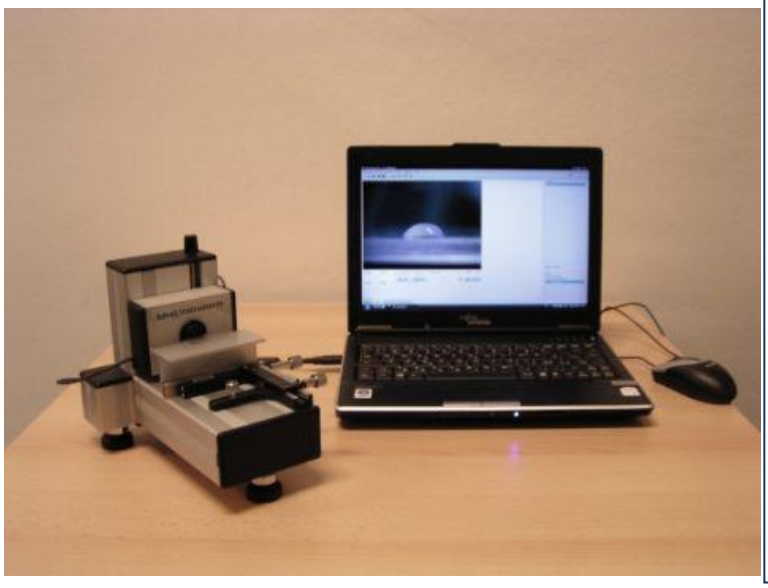

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FINAL PROGRAM

Sunday April 19	Monday April 20	Tuesday April 21	Wednesday April 22	Thursday April 23
	8:45 opening ceremony			
	9:00-9:50 S. Kassi	excursion	9:00-9:50 T. Gans	9:00-9:50 C. Ionita
	9:50-10:40 G. D. Stancu		9:50-10:40 M. Kong	9:50-10:40 K. Sasaki
	10:40-11:00 coffeebreak		10:40-11:00 coffeebreak	10:40-11:05 R. Engeln
	11:00-11:25 M. Bowden		11:00-11:25 Y. Martysh	11:05 closing ceremony
	11:25-11:50 A. De Giacomo		11:25-11:50 S. Mitic	11:30 lunch
	11:50-12:15 P. Bruggeman		11:50-12:15 M. Pustylnik	
			12:15 FLTPD 9 announcement	departures
	12:30 lunch	13:30 lunch	12:30 lunch	
	informal discussions	15:00-15:15 sponsor's time	informal discussions	
		15:15-16:05 U. Fantz		
15:00-19:30		16:05-16:30 G. Cartry		
registration	16:30-17:00 coffeebreak	16:30-17:00 coffeebreak	16:30-17:00 coffeebreak	
	17:00-17:50 C. Paradisi	17:00-17:50 W. Lempert	17:00-17:50 V. Kudrle	
	17:50-18:15 J.-P. van Helden	17:50-18:15 J. Roepcke	17:50-18:15 M. Simek	
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welcome party	18:45 dinner	conference dinner	18:45 dinner	
	20:00-22:00 poster session I		20:00-22:00 poster session II	