

CHARACTERISATION OF A NOVEL MICRO-STRUCTURED PLASMA SOURCE VIA OPTICAL EMISSION AND LASER INDUCED FLUORESCENCE SPECTROSCOPY

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1. Abstract

Electrode arrays fabricated on a micro-structure scale have electrode dimensions small enough to generate sufficiently high electric field strengths to ignite uniform gas discharges at wide pressure ranges up to atmospheric pressure, applying only moderate dc or rf voltages. This new plasma source is characterised via optical emission spectroscopy (OES) for various species, e.g. noble gases. In He and Ne discharges characteristic emission spectra of the neutral atoms can be observed, whereas in Ar, Kr and Xe plasmas in addition transitions of singly positive ions are detected. Electron energies of up to 20.6 eV are derived from these spectra. The number densities of electrons with energies above 20.6 eV is low, and thus ionisation of neon or helium with their high ionisation energies of 21.6 eV or 24.6 eV, respectively, becomes unlikely. Optical emission spectroscopy only allows the observation of electronically excited species. Species in their electronic ground state can be characterised via laser induced fluorescence spectroscopy (LIF) by state selective excitation to an excited electronic state and observation of the total fluorescence light. Temperatures of neutral species in the discharge are obtained by analysis of the population of rotational states. NO LIF spectra ($A^2\sigma^+$ $X^2\sigma_{1/2}$) indicate that the gas temperature of the plasma is only a few ten degrees above room temperature. Thus, a variety of typical plasma-chemical processes (exhaust gas cleaning [1], plasma enhanced synthesis, surface treatment) can be performed in a rather cold gas-phase.

2. Introduction

Plasma enhanced processes grow more and more important in many industrial applications, including surface treatment (e.g. etching, film deposition, coating), exhaust gas cleaning and plasma chemistry. Many of these processes are carried out under low pressure conditions with the restraint of costly vacuum equipment. To minimise these costs and to facilitate plasma processes, it is desirable to achieve stable operation of plasma sources at atmospheric pressure. To this aid, a novel plasma source has been developed, consisting of micro-structured electrode systems (MSE). These electrode systems form arrays of electrodes on micrometer scale, meshed together in a comblike manner, possessing electrode distances of 10 to 300 μ m. According to the minimised cathode-anode distances d , high electric field strength E of about 10^7 V/m are obtained, following the $E = U/d$ law, while applying only moderate voltages of a few hundred Volts. High electric fields are essential to initialise electric breakdown in gases via an electron avalanche. The avalanche process starts with seed electrons, that have to be accelerated in their mean free path gaining enough energy to ionise gas molecules via impact ionisation.

3. Experiment

Micro-structured electrode arrays (MSE) made of chromium, copper or gold are fixed on silica glass or ceramic substrates. Typical geometry parameters are electrode width of 10 to 400 μm and an electrode gap of 10 to 300 μm . Non-symmetric MSE with smaller anodes and broader cathodes as shown in FIG. 1 are optimised for dc-operation, while Si_3N_4 , SiO_2 and Al_2O_3 coated symmetric MSE are employed in rf-discharges. The coating material protects the electrodes sufficiently against corrosive gases and prevents sputtering of electrode material.

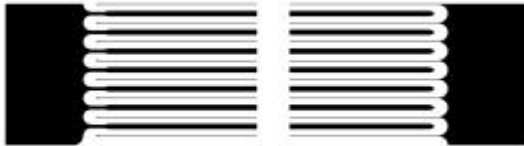


FIG. 1 Schematic presentation of micro-structured electrode arrays (MSE)

Uniform discharges are ignited over a wide range of pressures, using dc and rf-voltages. Discharges in a low pressure regime (≈ 80 mbar He, Ne) are powered by dc-voltages of 200 to 400 V at currents ≈ 2 mA. Mean dc power densities are 0.03 W/cm^2 . Variation of the geometry parameters quoted above has no significant influence on the maximum discharge pressure.

To raise the operating pressure in helium to about 200 mbar, a mesh electrode (mesh 20 - mesh 500) is employed. The mesh is positioned in a definite distance of 3.5 mm in front of the micro-structured electrode system. The MSE is powered by a dc voltage of 400 V, while a negative dc voltage of 500 V is applied to the mesh electrode.

Discharges at pressures up to 1500 mbar in helium and neon are obtained by rf-powered MSE. The electrode systems are connected to a 13.56 MHz generator (ACG-3B ENI), equipped with an automatic matching network (MW-5D ENI). A power of ≈ 15 to 30 W is forwarded to the discharge, thus, typical rf power densities are 3 W/cm^2 , where the sustaining voltage amounts to about 200 V.

3.1 Characterisation of discharges via optical emission spectroscopy (OES)

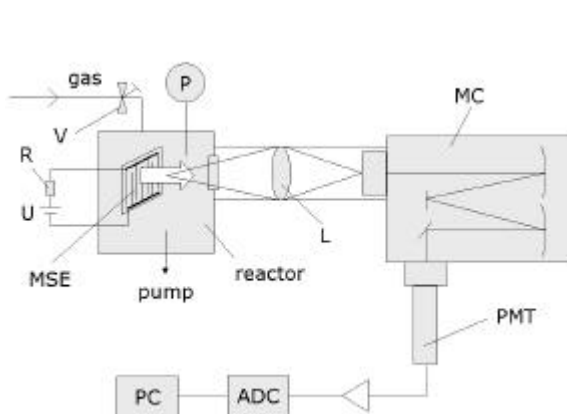


FIG. 2. Schematic presentation of the OES apparatus

To obtain optical emission spectra of noble gas discharges the apparatus in FIG. 2 is employed. The spectra were monitored in the low pressure regime (≈ 10 mbar) using dc-operated MSE.

The light emitted by excited species in the plasma is focused onto the entrance slit of a Czerny-Turner monochromator (Minuteman 305 M, 1200 g/mm grating, focus = 500mm, resolution = 0.03 nm) and detected by a photomultiplier tube. The photomultiplier output is amplified and registered via PC.

3.2 Characterisation of discharges via laser induced fluorescence spectroscopy (LIF)

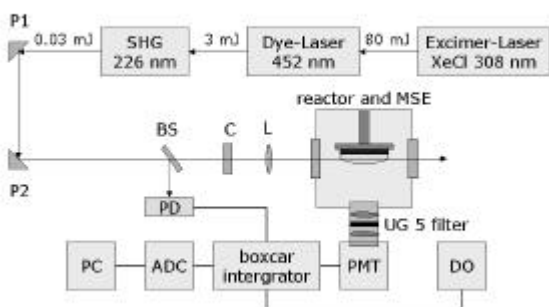


FIG. 3 Presentation of the LIF apparatus

Analysis of rotational resolved LIF spectra yields information on species in their electronic ground state. NO was chosen as a well characterised test molecule. LIF spectra of NO are monitored by scanning the laser excitation wavelength over the (0,0) band of the $A^2\sigma^+ - X^2\sigma_{1/2}$ transition at an excitation range of 225.5 to 226.4 nm. The ultraviolet laser radiation is obtained by second harmonic generation via autotracker (Scantrack, Radiant Dyes) of the radiation emitted by a tuneable pulsed dye laser (NARROWscan, Radiant Dyes), pumped by a XeCl excimer laser (LPX605iMC, Lambda Physics). The laser beam is expanded using a combination of cylindrical and converging

lenses to form a laser sheet which is conducted throughout the plasma just above the MSE-surface. Thus, molecules within a defined plane are selectively excited. The fluorescence signal is detected by a photomultiplier tube, sampled by a boxcar integrator and registered via PC. The experimental set-up is presented in FIG. 3.

4. Results and Discussion

OES spectra allow determination of electron energies, whereas LIF spectra yield information on the temperature of neutral species in the discharge.

The helium emission spectrum in FIG. 4 proves the existence of electrons with energies up to

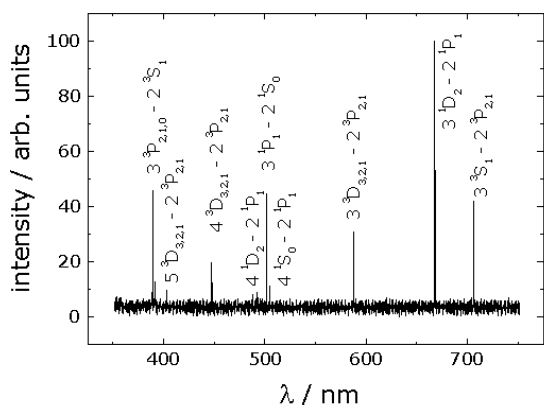


FIG.4 Helium emission spectrum, indicating transitions of the neutral helium atom

20 eV. The highest excited states of helium atoms observed in this spectrum are $5^3D_{3,2,1}$, 4^1D_2 and 4^1S_0 with energies between 23.5 and 24 eV. These states can be populated sequentially via the lowest excited states of the helium atom $1S_0$ and $3S_1$, with energies of 20.6 and 18.8 eV. Therefore, electrons with energies of up to 20 eV are present in the discharge, causing the transitions $5^3D_{3,2,1} - 2^3P_{2,1}$, $4^1D_2 - 2^1P_1$ and $4^1S_0 - 2^1P_1$ indicated in FIG.4.

Whereas helium and neon spectra only show transitions of highly excited rare gas atoms, argon, krypton and xenon spectra indicate additionally to the atomic transitions between highly excited electronic states $(np^5 [n+1]s^1 - np^5 [n+1]p^1, n = 3,4,5 \text{ for Ar, Kr, Xe})$

transitions of the singly positive ions Ar^+ , Kr^+ and Xe^+ . As an example, FIG. 5 presents a krypton emission spectrum. The ionic lines are enlarged. Considering that only argon, krypton and xenon exhibit ionisation energies lower than 20 eV, the expected electron energy according to the emission spectrum of helium, this observation can be rationalised. The

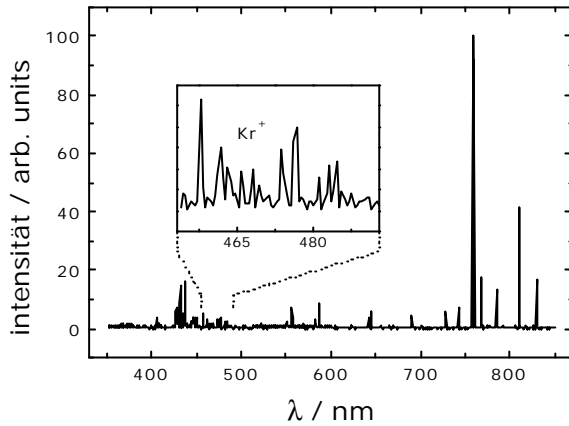


FIG.5 Krypton emission spectrum, indicating atomic and ionic transitions

number density of electrons above 20 eV is low, and thus, ionisation of neon or helium with their high ionisation energies of 21.6 eV or 24.6 eV respectively becomes unlikely. Ionic krypton and xenon lines decrease in intensity with increasing pressure. A possible explanation for this observation is the reduction of the density of high-energy electrons in the discharge, resulting from the decrease of the mean free path with increasing gas pressure. Thus, especially the electrons necessary to ionise krypton or xenon atoms are removed from the discharge.

Besides the optical emission spectra, laser induced fluorescence spectra of NO were obtained as presented in FIG.6. These spectra were measured twice, first with the plasma "switched off", second with the plasma ignited, in order to determine the change of the plasma temperature, when operating the plasma. All observed lines can be assigned to the rotational transitions belonging to the R_1 , R_{21} and Q_1 branches of the $v' = 0 \quad v'' = 0$ band of the $A^2\sigma^+ \quad X^2\delta_{1/2}$ electronic transition.

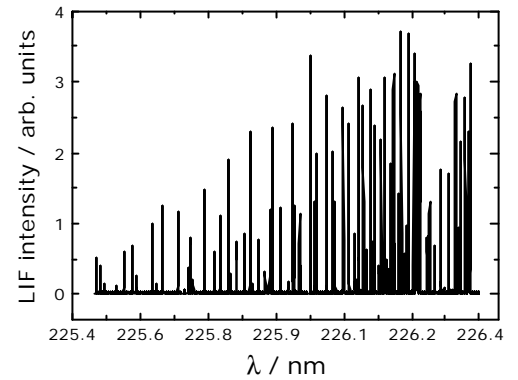


FIG.6 NO LIF spectrum of the $v' = 0 \quad v'' = 0$ band of the $A^2\sigma^+ \quad X^2\delta_{1/2}$ transition, $p = 15$ mbar (500 ppm NO in He)

The rotational lines of the R_1 branch are well resolved and are used to determine the plasma temperature T according to

$$I \propto S_{J'J''} (2J+1) \exp(-E_{rot}/kT)$$

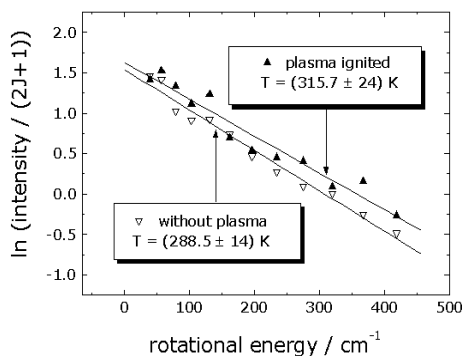


FIG. 7 Boltzmann plot for the R_1 branch of the $(0-0)$ band of the $A^2\sigma^+ \quad X^2\delta_{1/2}$ transition in the NO molecule.

where I is the intensity of lines belonging to the R_1 branch and E_{rot} the rotational energy of the lower J'' state. Plotting $\ln(I/(2J+1))$ versus the rotational energy E_{rot} , the temperature T can be determined from the slope of the resulting line, as shown in the Boltzmann plot in FIG.7. The temperature obtained without plasma ignition $T = 289 \pm 14$ K corresponds to the room temperature, the second one with the plasma ignited $T = 316 \pm 24$ K is only a few ten degrees higher.

A new micro-structured plasma source is characterised via optical emission and laser induced fluorescence spectroscopy. Uniform discharges ignited at these electrode arrays over a wide range of pressure up to 1500 mbar, applying only moderate dc or rf voltages of a few hundred volts, provide a two-temperature system, containing hot electrons with energies up to 20 eV and neutral species with temperatures of about 316 K. The high energy electrons provide sufficient energy to ionise or fragment molecules, without raising the gas temperature of the discharge significantly above room temperature. Thus a variety of plasma-chemical reactions (e.g. exhaust gas cleaning processes, plasma enhanced chemical synthesis or surface treatment) can be carried out in a rather cold gas phase.

6. References

- [1] P. Scheffler, C. Geßner, K.-H. Gericke "*Micro-structured electrode 2D-arrays as a new discharge device for pollution control*", contributed to Hakone VII, conference topic 5: Environmental Applications