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Comparative diagnostics of Ar and He surfatron generated plasma by means of optical emission spectroscopy and probe measurements

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Abstract

The article is focused on comparative diagnostics of microwave plasmas, generated by surfatron, where Ar and He are used as carrier gases N₂ is used as reactive gas. The diagnosed microwave-driven plasma source consists of a surfatron powered by a microwave magnetron generator, working at frequency 2.45 GHz in the output power range 0-300 W, which creates plasma from the flowing working gas in a quartz nozzle. The gas flow rate is kept typically constant at 600 sccm but ratio of carrier gas and reactive gas is varied. We present some results of diagnostics of generated plasma at nozzle exit as well as in the nozzle at different experimental conditions: variable absorbed power, total chamber pressure etc. The diagnostics of plasma column was performed by means of double probe measurement (mainly electron temperature is calculated from measured data) and by optical emission spectroscopy (rotational and vibrational temperatures, estimation of plasma composition from overview spectra).

Introduction

The plasma application are quickly broadening in the technological processes at present. Due to its unique reactivity and chemical interaction with materials plasma is capable to treat the surface i.e. to be used for material deposition, surface cleaning or surface activation etc. Recently plasma has begun to spread in the area of medicine and biology where it is most often used for sterilisation [1], increasing of biocompatibility [2] and occasionally, but nevertheless, for direct application on living tissues [3]. In our case we have diagnosed the microwave plasma generated by surfatron with the purpose to be used for sterilisation in the next step.

Generally sterilisation means the process, physical or chemical, that destroys or eliminates all forms of life, especially micro organisms. Plasma sterilisation operates differentially from the common ways of sterilisation (high temperature in autoclaves or ovens and using of toxic gases, ethylene oxide, or liquids). Plasma specific sterilisations agents are mainly UV photons and radicals (atoms or assembly of atoms with unpaired electrons, therefore chemically reactive, e.g. O and OH) [4]. The efficiency of the sterilisation processes is viewed by so-called survival curves; a plot of the logarithm of the number of surviving micro organism as a function of exposure time to the plasma [5,6]. The composition of working gas, used power and exposure time of the discharges mainly determinate the shape of

survival curves. Some of survival curves for microwave discharges burning at differential experimental conditions and for different kinds of spores can be compared [1,7,8].

We have investigated the main parameters of plasma discharges where different mixtures of working gases were used: Ar and He as carrier gas (major component of the mixture) and N₂ as a reactive gas (minor component of the mixture). The rotational temperature and consistence of atomic spectra were determined by means of optical emission spectroscopy. The rotational temperature approximates the temperature of neutral particles with good agreement [9]. Therefore knowledge of the rotational temperature gives a good idea about range of application possibility, e.g. application on polymer-based materials/instruments without their degradation. The attendance of a considered active species N, O atoms and NO molecules [8], occurred in the discharge as added gas or as impurities, was discovered from overview spectra. The dependences of electron temperature, computed from the data acquired by double probe measurement, show the energetic proportion of investigated plasma discharge.

Experimental apparatus and data acquisition systems

Our experiments were carried out with plasma generated by the surfatron fed by microwave power. We have used commercial (Sairem) surfatron (1) and microwave generator 300 W (GMP 03) in configuration, which can be seen in Fig. 1. A quartz tube (2), 6 mm in inner diameter, is inserted into a surfatron cavity and working gas flows through that tube. The microwave power is coupled from the resonator to the plasma via thin slit and cause ionization of flowing gas in the quartz tube. Plasma created in this manner is sustained further downstream by a surface wave, which propagates along the plasma column [10,11].

Experimental arrangement consists of a vacuum vessel (3) made from stainless steel. The upper flange (5) of the vessel is made of plastic in order to enable the propagation of the surface wave into the vessel. Four quartz windows (6) are provided in the vessel for the observation of the discharge and as diagnostic ports for the probe feed-through and optical diagnostics. The outlet of the quartz tube protrudes into the vessel using silicon O-ring sealed PTFE feed-through (4). The tube is designed as two coaxial quartz cylinders at the bottom part; the space between both tubes is cooled by compressed air. The working gas flow rate is controlled by MKS flow-controller. The flow rate of working gas was kept constant at 600 sccm of mixture of technical Ar or He and N₂ with technical purity grade 4.6 was used. The volume of the vessel is pumped out by a large rotary vacuum pump down to ultimate pressure of the order units of Pascal. The butterfly VAT valve between the vessel and the pump controls the pumping speed and thus allows setting the desired pressure independently of the working gas flow rate. Pressure in the vessel is measured by MKS Baratron. The body of the surfatron is cooled by water and compressed air.

The plasma exiting from the nozzle outlet was studied by probe measurements and optical emission spectroscopy. Besides, by means of optical spectroscopy we investigated also the plasma burning in the quartz nozzle. The double probe technique was used for probe diagnostics. The probes (9) were made from tungsten wire with diameter 50 μm and length 4 mm. The probes were bent in the right angle and positioned by movable probe holder (10) from the axis of the stream (axis of the nozzle) to its edge. The shape of probe arrangement allowed achieving sufficient space resolution. One window of the vessel served as a port for probe holder. The probe data were sampled by PC-controlled system AD-96 [12]. The probe circuit was opto-isolated from the control part of the system. Optical emission spectroscopy of the plasma was realised by means of Jobin Yvon Horiba Triax 550 spectrometer equipped with CCD detector Spectrum One with 2000 x 800 pixels cooled by liquid nitrogen. The end of the optical fibre (8) was situated outside of the vessel close to the quartz window (6). The

movable holder of the fibre allowed the adjustment in three dimensions. Anyhow this arrangement was used only for investigation in axial direction. The distance between plasma light source and the fibre was about 18 cm which caused that emission spectrum was averaged almost over the whole radial cross section (6 mm in the tube). The axial dependences were investigated in the plasma burning in the tube (axial positions $x = 26 - 50$ mm in the plots) as well as in plasma plume spreading out of the tube (axial positions $x = 0 - 26$ mm in the plots). Langmuir probes were used for diagnostics in radial direction.

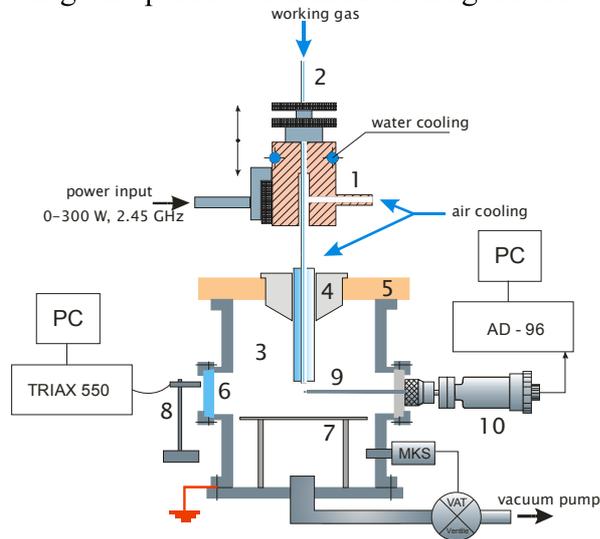


Fig. 1. Scheme of the experimental set-up.

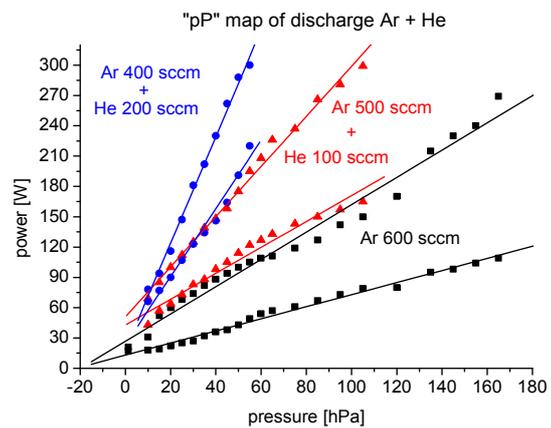


Fig. 2. „pP“ map of surfatron discharge.

At a certain microwave power it was impossible to cover the whole range of pressures. As a rule, at lower pressure only low microwave power was needed to sustain the plasma plume downstream of the nozzle end and vice versa. The stable working conditions were therefore determined mainly by pressure in the vessel and supplied microwave power. The range of stable working conditions is displayed as an area between two lines in so called "pP map" in Fig. 2. Under the lower line of the chart the plasma is burning only in the tube; above the upper line there is created a standing wave pattern and plasma is burning around the tube. One can see different surfaces and positions of the working areas for plasma burning only in Ar and mixtures of Ar and He at different ratios (Ar 500, 400 sccm and He 100, 200 sccm). These pP maps for Ar-He mixtures are roughly similar for Ar-N₂ mixtures but with another ratio: Ar 500 + He 100 sccm \approx Ar 595 + N₂ 5 sccm, Ar 400 + He 200 sccm \approx Ar 590 + N₂ 10 sccm. But on the other hand a discharge burning only in He does not create a pP map. The plasma burns only in the tube and very weak yellow afterglow can be observed in the vessel. At such conditions the probe diagnostics is almost impossible. Plasma plume is visible only if another reactive gas is added (N₂, O₂) in proportion to carrier gas in the order of tens percent. These differences are probably caused by different ionisation potential and ratio of the carrier gas versus reactive gas mixture.

Experimental results and discussion

The electron temperature was calculated from double probe VA characteristics [13]. A program written in Matlab software has been used for the double probe data processing. The program also enabled to test the sensitivity of the computed temperature T_e to the choice of the fitted intervals and fitting functions. The measurement was focused on determination of the radial dependences of electron temperature of surfatron plasma. The distance between the nozzle outlet and probes was 4 mm in radial distance. The mixture of He+N₂ and Ar+He in

large range of different ratios were used as working gas for different incoming powers and vessel pressures. The total flow rate was kept constant at 600 sccm (the optimal flow rate for experiment running [14]), incoming power 100 W and pressure in the vessel 50 hPa. The courses of electron temperature in the mixture He+N₂, see Fig. 3, have two local maxima: around the axis of the tube, $r = 0$ mm in the plot, and at the edge of plasma plume, $r = 5$ mm in the plot. This profile probably corresponds to azimuthally symmetric $m = 0$ mode of TM surface wave generated in the surfatron. Generally the electron temperature decreases and profiles became flatter when bigger amount of N₂ is added into working gas mixture. These values and courses are similar to electron temperatures in Ar+N₂ discharge burning at equivalent experimental conditions. Differences between these specific mixtures are in the order of units percent [14]. However, the radial courses of He discharges are flatter and electron temperatures lower in comparison with measurements in pure argon [15].

The results of probe measurement in Ar+He mixture are presented in Fig. 4. As it was mentioned above the amount of Ar in He must be comparatively higher in order to achieve reasonable working area in the pP map. Also, bigger amount of He in Ar caused decrease of electron temperature in spite of higher incoming power to the discharge and different shape of radial electron temperature profiles. The local maxima at $r \cong 3$ mm in the Ar:He mixture 5:1 are more pronounced than in 4:2 mixture. Generally, the electron temperature in discharges burning in rare gases (Ar, Ar+He) is several times higher than in cases when N₂ is added.

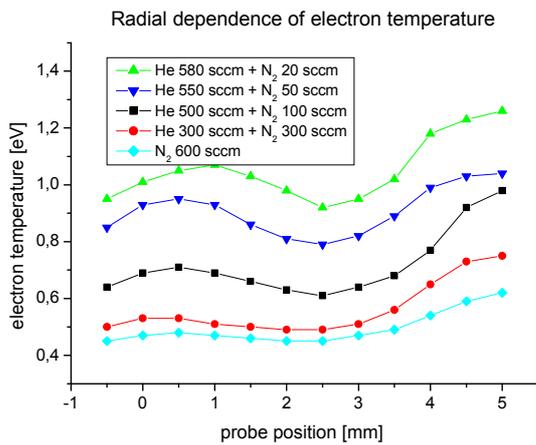


Fig. 3. Radial dependences of electron temperature in He+N₂ mixture.

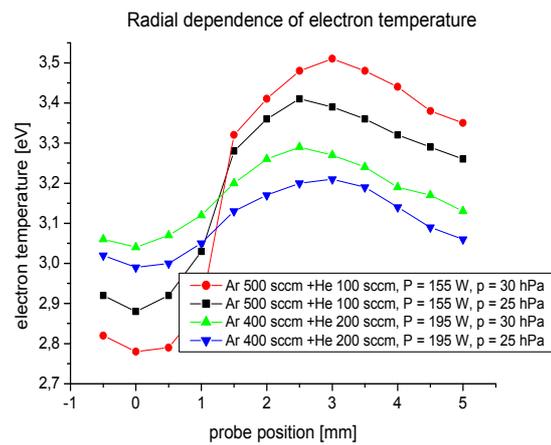


Fig. 4. Radial dependences of electron temperature in Ar+He mixture.

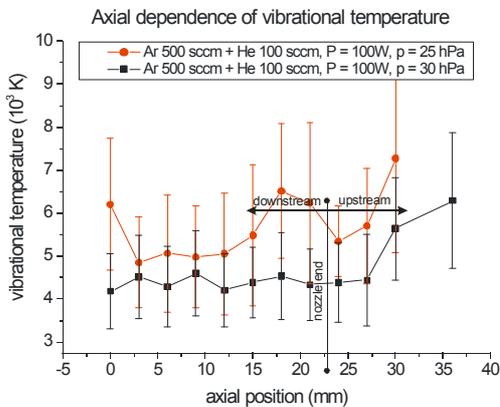


Fig. 5. Axial dependences of nitrogen vibrational temperature in Ar+He mixture.

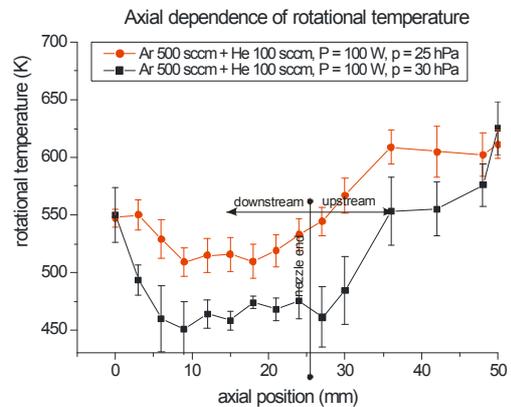


Fig. 6. Axial dependences of OH rotational temperature in Ar+He mixture.

The results of optical emission spectroscopy are displayed in Figs. 5-10. Spectra measured in Ar-He mixtures revealed the presence of OH and N₂ representing gas impurities. Their relative large intensities allowed us to determine the rotational and vibrational temperature. For vibrational temperature estimation the bands of second positive system of nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$) with $\Delta v = -2$ were used, see Fig. 5. The rotational temperature was calculated from 0-0 band of OH system ($A^2\Sigma^+ \rightarrow X^2\Pi$), see Fig. 6. We see that while the vibrational temperature remains constant along the nozzle axis within the measurement error, the rotational one increases towards the nozzle since the carrier gas heats up in the hot nozzle.

The emission spectra of the discharge in Ar+N₂ and He+N₂ mixtures are shown in Figs. 7 and 8. They consisted mainly of NO γ -system ($A^2\Sigma^+ \rightarrow X^2\Pi$), NO β -system ($B^2\Pi \rightarrow X^2\Pi$) and the N₂ first positive system ($B^3\Pi_g \rightarrow A^3\Sigma^+_u$). The spectra in these figures were measured in position 26 mm below the nozzle exit, where recombination predominates. Helium and argon have larger excitation energies (compare 21 and 11 eV) in comparison with NO (5.5 eV of NO $A^2\Sigma^+$) and they need to be excited in collisions with electrons. That is the reason why helium and argon atomic lines are not present.

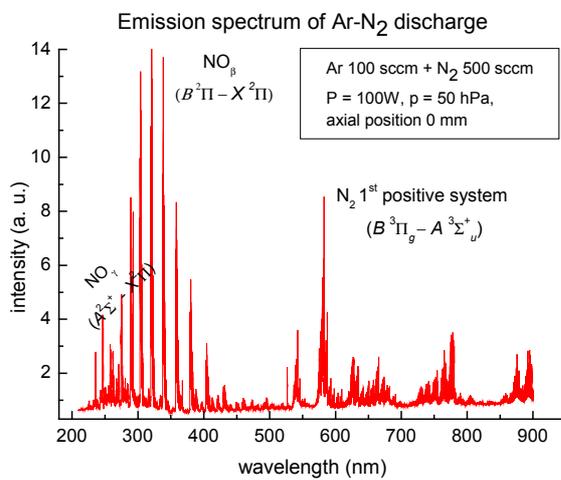


Fig. 7. Optical emission spectrum of Ar+N₂ discharge measured 26 mm below the nozzle exit.

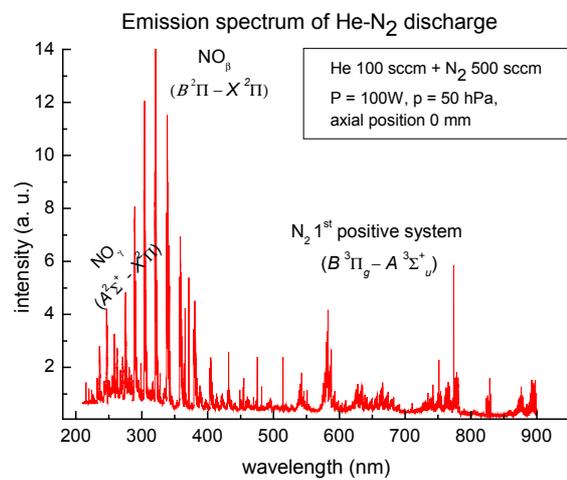


Fig. 8. Optical emission spectrum of He+N₂ discharge measured 26 mm below the nozzle exit.

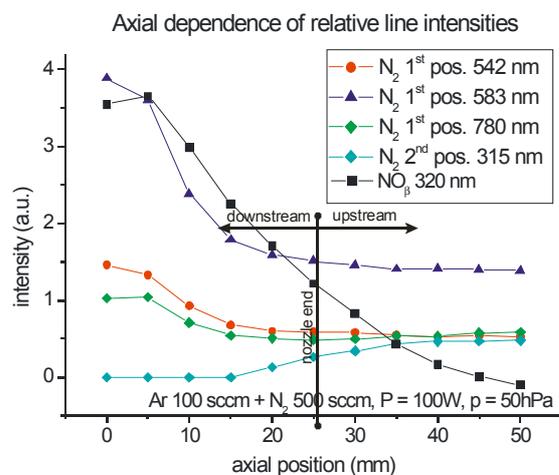


Fig. 9. Axial dependences of light intensities emitted by Ar +N₂ discharge.

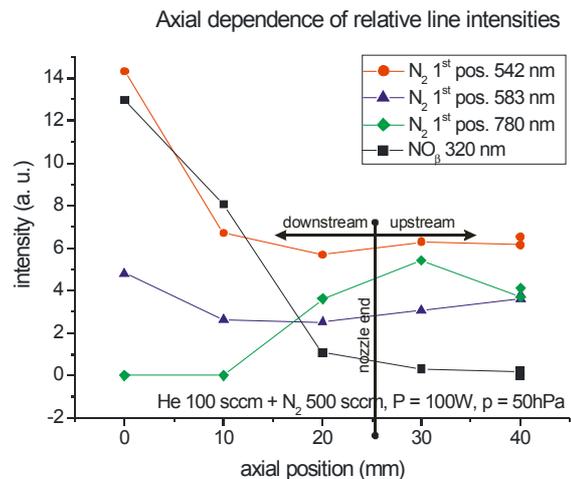
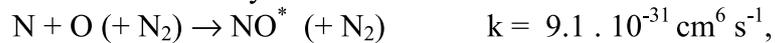


Fig. 10. Axial dependences of light intensities emitted by He + N₂ discharge.

Also the intensities of N₂ and NO molecular systems depend on the axial position (see Figs. 9 and 10). Particularly, intensity of NO_β system decreases with increasing position coordinate (i.e. towards the surfatron). This behaviour can be explained regarding the production of NO* radiative states by reaction



which produces NO* according to the amount of oxygen coming into the vessel and into the nozzle from the vessel leaks. The N₂ first positive system is more intensive outside the nozzle, too. To explain this, the mechanism of N₂ B³Π_g population must be considered. According to [16], upper N₂ B³Π_g vibrational states of electronic transitions with the wavelength of about 540 nm or 580 nm are populated predominantly by three-body atomic N(⁴S) recombination than by electron impact. Therefore their intensity should increase with decreasing position more substantially than the intensity of bands at 780 nm with a small contribution of recombination. Indeed, such behaviour can be observed in Ar+N₂ mixture in Fig. 9. Besides, 780 nm band in He+N₂ mixture even increases with increasing position (i.e. inside the nozzle). This can mean, that upper states of 780 nm bands are populated substantially by electron impact, which is again in agreement with [16]. Such intensity increase in the nozzle was also observed in Ar+N₂ mixture in case of the second positive system of nitrogen (see Fig. 9). In He+N₂ mixture the second positive system was not observed.

Conclusion

The comparative diagnostics of surfatron Ar+He, Ar+N₂ and He+N₂ plasma has been done by means of optical emission spectroscopy and double Langmuir probe measurement. Various plasma parameters have been determined (vibrational, rotational and electron temperature, consistence of emission spectra and axial intensity dependences of particular molecular systems). The results presented above predestinate that surfatron plasma source can be potentially used for plasma sterilisation processes.

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