16. ENVIRONMENTAL ENGINEERING PLASMA LABORATORY

C. M. Ferreira (Head), F. M. Dias (Deputy Head), E. Tatarova, J. Henriques

16. 1. INTRODUCTION

The research work carried out by this team in 2005 falls into the following main fields of investigation:

- Spatial structure and radiation of microwave plasma sources;
- Surface wave induced N2 – Ar plasma torch;
- Flowing N2 and N2-O2 discharges and post-discharges;
- Improved Langmuir Probe Techniques for Plasma Diagnostics.

16.2. SPATIAL STRUCTURE OF MICROWAVE N_2-AR PLASMA SOURCE[1]

A theoretical model for *a large-scale, slot-antenna excited surface wave plasma source operating in N_2-Ar mixtures* was developed. The model incorporates the description of both the discharge plasma, sustained by a pure TM_{140} surface mode, and the remote "electric field free" plasma. Maxwell's equations and the rate balance equations for the most important species – vibrationally

$$N_2(X^1\Sigma_g^+, v), \tag{16.1}$$

electronically excited molecules

$$N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a'^1\Sigma_u^-, a^1\Pi_g, w\,'\Delta\,u), \tag{16.2}$$

Ar($3p^5 4s$) and Ar($3p^5 4p$) atomic states,

$$N^+, N_2^+, N_4^+, Ar^+, Ar_2^+ \tag{16.3}$$

ions, and nitrogen atoms $N(^4S, ^2P, ^2D)$ are consistently solved to yield the species spatial distributions. The model further determines the three-dimensional discharge structure, i.e., the radial, azimuthal and axial variations of the main plasma quantities. Strong correlation is shown to exist between the density distributions of plasma electrons and electronically excited states of molecules and atoms and the electric field intensity distribution in the discharge zone of the source. This indicates that electron driven processes play a dominant role in the discharge workings.

The transition from the source discharge to the remote plasma was analysed in detail. The pumping of the higher vth levels as a result of near-resonant V-V energy-exchanges between vibrationally excited $N_2(X^1\Sigma_g^+, v)$ was shown to be very effective, and to influence strongly the remote plasma kinetics. In fact, the pumping of the vibrational distribution function "tail" strongly influences the axial evolution of the EEDF and the number density of electrons and electronically excited states of molecules in the remote plasma zone. Collisions of

$$N_2(X^1\Sigma_g^+, v) \tag{16.4}$$

molecules in highly vibrational levels with ground $N(^4S)$ atoms are responsible for the formation of

$$N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a'^1\Sigma_u^-) \tag{16.5}$$

electronically excited states. As a result, the number densities of electrons and electronically excited states

$$N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a'^1\Sigma_u^-) \tag{16.6}$$

increase in the "late" remote plasma zone, at axial distances $\Delta z > 35$ cm (Figure 16.1).

An *experimental validation of the model* predictions was achieved *using optical emission spectroscopy.* The spatial variations of the emission intensities of the lines belonging to the 1st negative and 2nd positive systems of nitrogen have been detected and compared with the theoretical results. The agreement obtained between experimental and theoretical results is satisfactory, taking into account the numerous uncertainties in collisional data still existing.

The results obtained clearly demonstrate that the remote "electric field free" plasma zone of the present source is a big reservoir of excited species in metastable and vibrational states and of charged particles. By changing the mixture composition, and thus the dissociation degree of N_2 molecules, it is possible to control the processes of excited species production in the remote plasma zone of this microwave source.

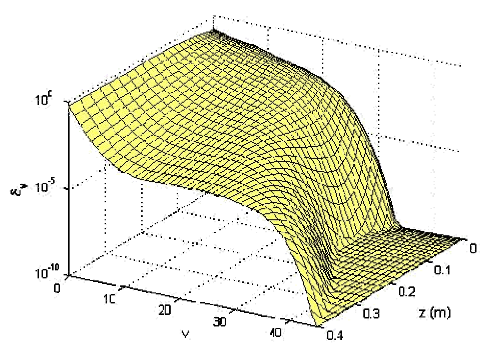

Figure 16.1 - Axial variation of the vibrational distribution function (80%N_2 – 20% Ar, p = 0.9 mbar, r = cm, φ = 162).

[1] Colaborators: Prof. H. Sugai and Dr. I. Ganachev (Nagoya University, Japan)

16.3. HYDROGEN BALMER LINE BROADENIBNG IN A MICROWAVE PLASMA SOURCE[2]

Emission spectroscopy (Doppler broadening technique and molecular rotational bands measurements) was used *for the diagnostic of gas particle temperatures in a large-scale,* slot-antenna excited *microwave plasma source* operating in pure hydrogen, helium-hydrogen and argon-hydrogen mixtures at low-pressures (p = 0.3 Torr). The measured profiles of H_α and H_β lines are well fitted by a Gaussian profile, (Figure 16.4 (a,b)). For the purposes of comparison, the normalized profiles of the 6678.8 Aº helium line [transition $3^1D \rightarrow 2^1P$] (shifted along the scale of wavelengths) are also shown (Figure 16.2). The helium line profiles are also well fitted by a Gaussian one. The emission profile of the Balmer-α line shows larger broadening than that of the Balmer-β and helium singlet line at 6678.8 Aº [transition $3^1D \rightarrow 2^1P$]. The line profiles do not present wings and we could not find any evidence of fast hydrogen atoms in the discharge zone of the plasma source. The Doppler temperatures corresponding to the helium singlet line at 6678.8 Aº (400 – 900 K) are close to the rotational temperatures (300 – 800 K) calculated from the Q-branch of the Fulcher-α band [$d^3\Pi_u$ (v=0) → $a^3\Sigma_g^+$ (v=0)] under the same conditions. Therefore these temperatures can be assumed to be indicative of the gas temperature. The measured Doppler temperatures of hydrogen atoms range from 3100 K to 3700 K (Figure 16.5b) in a 95% He-5% H_2 mixture (P = 900 W) and from 2700 K to 3600 K in a 95% Ar- 5% H_2 mixture (P = 600 W) while in pure hydrogen (P = 600 W) the minimum and maximum temperatures are 2500 K and 3400 K, respectively. Thus, there is a "separation" of the excited hydrogen atom temperature from the gas temperature. The reason for such "separation" are connected to the processes leading to the creation of excited atoms such as electron impact dissociation and ion conversion.

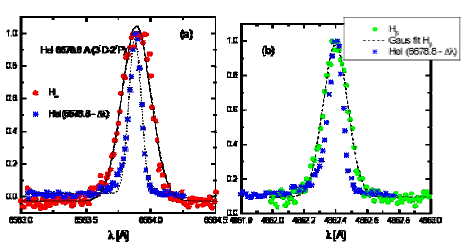

Figure 16.2 - H_α (a) and H_β (b) profiles compared with 6678 A He line profile.

16.4. SURFACE WAVE INDUCED N_2 – AR PLASMA TORCH[3]

Theoretical investigation on surface wave driven N_2-Ar microwave plasma torch at atmospheric pressure conditions is presented. The main plasma and wave characteristics are obtained in the framework of self-consistent 1D theoretical model which describes the axial structure, including overdense discharge plasma sustained by an azimuthally symmetric TM surface mode and post-discharge plasma arising due to the axial gas transport.

The system of equations (in the framework of fluid approach) considered to describe the plasma source includes: Maxwell´s equations; The rate balance equations for the vibrationally excited states of electronic ground state molecules

$N_2(X^1\Sigma_g^+, v)$; $N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a'^1\Sigma_u^-, a^1\Pi_g, w\,'\Delta u)$

and Ar($3p^54s$), Ar($3p^54p$) excited states of molecules and atoms, positive

$N_2^+, N_4^+, N^+, Ar^+, Ar_2^+$

ions and electrons, ground state N(^4S) and excited N(^2P, ^2D) atoms. Further on, the gas thermal balance equation and the equation of mass conservation for the fluid as a whole are incorporated in the model.

The results show high values of the gas temperature (up to 12 000 and very strong population in vibrational levels of the electronic ground state

$N_2(X^1\Sigma_g^+, v)$

molecules in the discharge part of the, close to the microwave source (Figure 16.3).

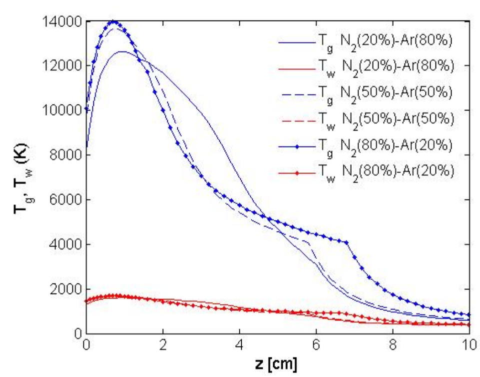

Figure 16.3 - Axial variation of T_g at different Ar percentages (P=2000 W, Q=1000 sccm).

16.5. EXPERIMENTAL AND THEORETICAL STUDY OF FLOWING N_2 AND N_2-O_2 DISCHARGES AND POST-DISCHARGES[4]

A complex experimental and theoretical investigation on a strong afterglow formed in the post-discharge region of a microwave plasma source is performed (Figure 16.4). The objective of this work was to investigate the concentration of various active species, such as O and N – atoms, N_2^+ ions, and $N_2(A^3S_u^+)$ and $NO(A^2S_u^+)$ molecules, as a function of the spatial position and the mixture composition. Emission spectroscopy was used to measure

[2] Work carried out in collaboration with Dr. N. Puac (Belgrade University, Serbia) and Dr. A. Ricard (CPAT, Université Paul Sabatier, France)

[3] Work performed in collaboration with Prof. Dr. B. Gordiets (Institute of Physics, Academy of Sciencies, Russia).

[4] Work carried out in collaboration with André Ricard (CPAT, Université Paul Sabatier, France)

the $N_2(1^+,2^+,1)$ and NO(g,b) band intensities in the discharge and in early post-discharge (see pictures below). The densities of N and O – atoms were measured using an actinometry method in the plasma region and NO titration in the post-discharge. The titration technique that provides absolute densities was used to calibrate the actinometry method in the early post-discharge, close to the discharge end. The experimental results are interpreted using kinetic theory in the discharge and in the late afterglow. The post-discharge region is of particular interest due to the formation of a strong afterglow and this extended “field free region” is rich in active species such as nitrogen and oxygen atoms, vibrationally and electronically excited nitrogen molecules and ions as the results show. The obtained results have *direct application for cold plasma sterilization of surgical material and other medical devices.*

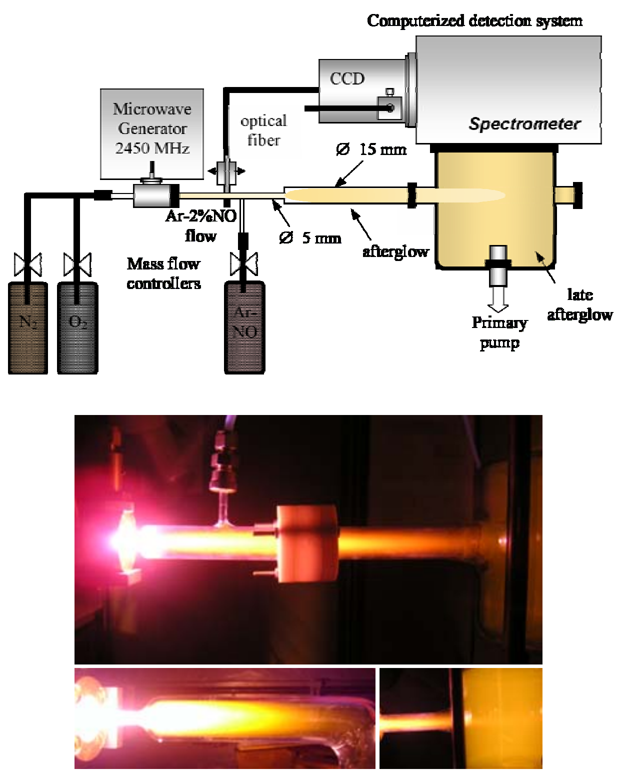

Figure 16.4 - Experimental setup showing the discharge and post-discharge reactor.

16.6. IMPROVED LANGMUIR PROBE TECHNIQUES FOR PLASMA DIAGNOSTICS[5]

16.6.1. Restoration of Time-averaged Probe Characteristics

We developed three simple methods that enable restoring time-averaged Langmuir probe characteristics measured under time-varying plasmas, in the sense that plasma parameters, *i.e.*, electron density and average energy, electron energy distribution function (EEDF), and plasma potential, are deduced more accurately than what otherwise could be retrieved from averaged data.

The first method (SAM) is based on analytic expressions of the first and second derivatives of the probe characteristic, and only requires the standard deviation of the measured current, *i.e.*, the probe characteristic itself is not needed. The other two methods assume that the probe characteristic experiences either an anamorphic deformation (ADM) or a linear deformation of the low-energy part of the EEDF (BDM), which from our experience are the most simple, acceptable assumptions (Figure 16.5).

Although our motivation were probe diagnostics, the above techniques are of general interest since all kinds of data acquisition have to deal with the problem of a finite integration time, and the output is always the result of some kind of average.

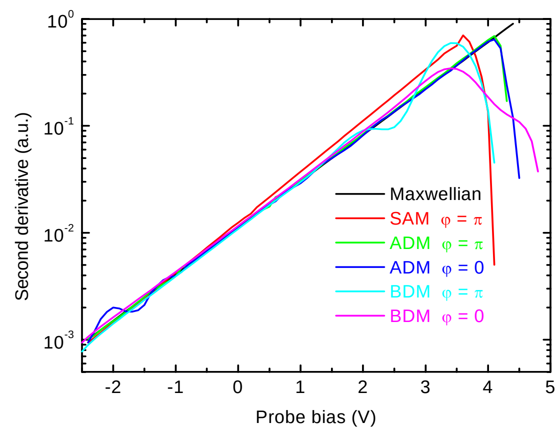

Figure 16.5 - Model test of the three restoration methods (Maxwellian EEDF)

16.6.2 Improved Probe Differentiation Techniques

A combination of the *harmonic and numerical differentiation techniques* is being developed *in order to measure the electron energy distribution function* (EEDF) with an error of the order of the 8th derivative instead of the order of the 4th derivative, which is typical in standard methods. In addition to the increased accuracy, instrument functions are adaptively adjusted in such a way that the error and the noise levels are continuously kept at similar levels, which is possible because the overall system has the ability to evaluate the noise as well as the error levels of the differentiators at measuring time.

The superior differentiation performance is achieved using a redundant approach, which enables keeping the noise from individual differentiators uncorrelated, and signals are combined in such a way that the resulting signal-to-noise ratio is the maximum possible.

[5] Work carried out in collaboration with Tsv. Popov, and M. Dimitrova (St. Kliment Ohridski University of Sofia, Faculty of Physics, Bulgaria)