IONIZATION AND EXCITATION PROCESSES IN ANALYTICAL PLASMA OF GDOES AND GDMS SYSTEMS WORKING IN PULSED RF REGIME*

A. SURMEIAN[1], C. DIPLASU[1], A. GROZA[1], P. CHAPON[3], A. TEMPEZ[3], M. GANCIU[1,2]

1. National Institute of Lasers, Plasma and Radiation Physics, 077125 Bucharest- Magurele, Romania
2. Laboratoire de Physique des Gaz et des Plasmas, UMR CNRS-UPS 8578, Université Paris-Sud, Bat 210, 91405 Orsay, France
3. Horiba Jobin Yvon, 91665 Longjumeau, France

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The GDOES and GDMS analytical systems working in Pulsed RF regime have some distinct advantages compared to non-pulsed glow discharge analytical systems. In this paper we report a rise in MS ionic signals, and in emission atomic lines of analysts in the beginning of the afterglow of RF pulsed GD sources. Making experimental studies with Langmuir probe we demonstrate that the ionization and excitation processes in the early afterglow of the RF pulsed GD involve the metastable atoms of the working gas.

INTRODUCTION

The commercial glow discharge source for GDMS and GDOES analytical systems is of Grimm type with a plasma chamber having an inner diameter of 4 mm and operating in RF regime using argon as carrier gas in a pressure range of typical 5 to 9 kPa. A more detailed description of the Grimm type source can be found in the literature [1-3]. Glow discharges operating in a pulsed power mode have been explored as an effective approach to enhance sputtering, excitation, and ionization while avoiding problems related to sample overheating and thermal degradation. In such pulsed operation, a relatively brief ''power-on'' period followed by a much longer ''power-off'' period allows for efficient sample cooling. This advantage includes also the creation of three distinct time regimes, the prepeak, plateau, and afterpeak, during which the signal to noise ratio is enhanced. Of these three regimes, the period immediately following the discharge power termination, the afterpeak, has been the focus of recent attention because it affords the ability to study the unique plasma chemistry of metastable argon species. Starting from the observation that in GDMS and GDOES analytical systems, working in RF pulsed regime the MS and OES signals present a peak in the so called afterglow, *i.e.*, when the voltage pulse is turned off, we made systematic measurements trying to give a plausible explanation of this effect. Thus,

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besides the MS and OES measurements, using an adapted Langmuir probe we identify the existence in the early afterglow of reactive processes involving argon metastable atoms.

2. RESULTS AND DISCUSSIONS

2.1. MS MEASUREMENTS

The instrument used in the MS measurements was widely described in [4]. It comprises a modified Grimm GD source and a very fast orthogonal TOFMS. RF power is applied to the back side of a flat sample that seals the 4 mm diameter anode chamber. The distance between the cathode/sample surface and the 0.3 mm diameter sampler is 17 mm while the sampler and the 0.1 mm diameter skimmer are separated by 7 mm. A 2.5 mm inner diameter flow tube directs the 0.5 l/min Ar flow toward the sample surface. The source Ar pressure is 1.5 Torr. Pure copper (CP4) standards were used as samples. The duty cycle was either 10% (pulse 1 ms long at 100 Hz).In the measurements reported below, ion extraction rate is 20 kHz (giving a mass range of several hundreds Thompsons). One GD pulse period is thus monitored by fifty or a hundred 50 µs-long TOF spectra. Figure 1 shows the temporal profiles of Cu and Ar ion signals from a pure copper standard sample for the RF pulse length discharge of 1 ms operated at 60 W and in argon at 550–850 Pa. It can be seen that the profiles are strongly dependent on the gas pressure of the working gas.

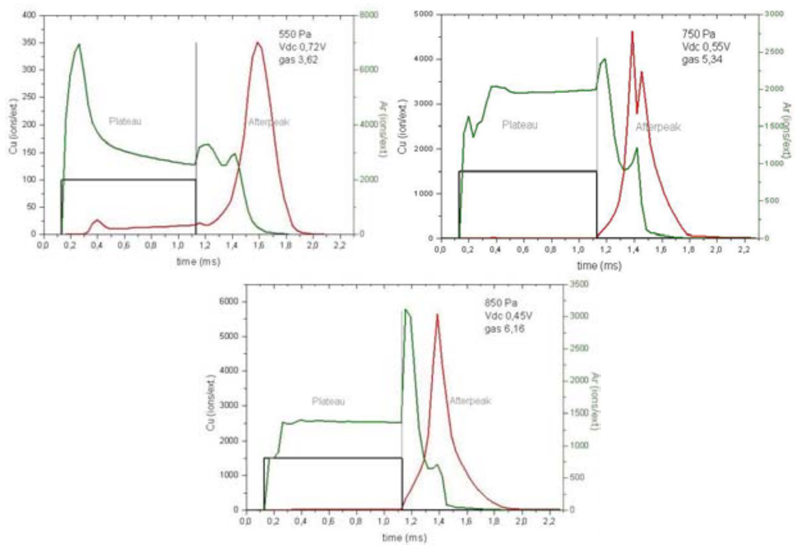

Fig. 1 – The dependence of $^{65}Cu^+$ and $^{36}Ar^+$ temporal profiles for RF pulse duration 1 ms on the working gas pressure.

We assume that the afterpeak $^{65}Cu^{+}$ MS signal is due to Penning ionization by Argon metastables and $^{36}Ar^{+}$ increase in the afterpeak is due to $\mathrm{Ar}^{m} + \mathrm{Ar}^{m} \rightarrow \mathrm{Ar}^{0} + \mathrm{Ar}^{+} + \mathrm{e}^{-} + \Delta E$.
The next results presented below, obtained in the same experimental conditions by Langmuir probe measurements and atomic emission measurements, prove the truthfulness of these assumption.

2.2. LANGMUIR PROBE MEASUREMENTS

The parameters of the 1ms pulsed RF plasma (plateau) and afterglow pulsed RF plasma (afterpeak) were measured using a Langmuir probe technique considering the plasma is quasistationary on both, the plateau and afterpeak. The probe's metal tip, which is exposed to the plasma, is made from nickel-chromium (Ni-Cr) alloy and it has a diameter of 0.2 mm and the length of 3.5 mm. The part of the Ni-Cr wire which is not exposed to the plasma is covered by glass tube. The probe tip is centered on the anode axis at 3 mm from the cathode. Temporal shape of Langmuir probe current (I_p) and probe bias voltage (V_p) for plateau and afterpeak of 20 different bias voltages in the range between −30 V and +30 V were averaged on 128 pulses and recorded on a Tektronics digital oscilloscope. The Figure 2 presents the variation of the temporal profiles of the Langmuir probe current when the pressure is increased from 600 to 900 Pa, biased at +30V voltage. It can be seen in the figure the same pressure dependence of the afterpeak probe current as Cu and Ar ions afterpeak MS signal in Figure 1.

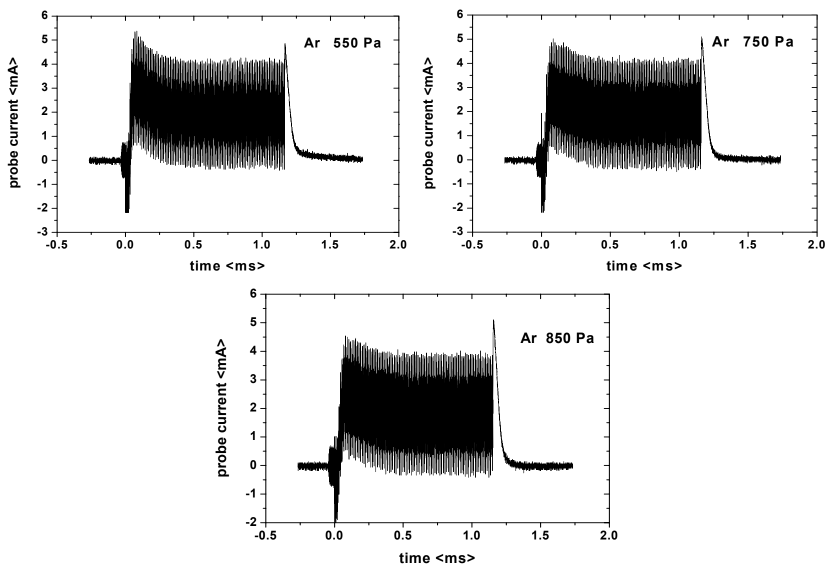

Fig. 2 – The temporal profiles of the Langmuir probe current biased at +30V.

Sweeping the voltage at the tip from -30V to +30V and using the averaged Langmuir probe signals, discrete point characteristics (20 points) were raised for plateau and afterpeak temporal range, Figure 3.

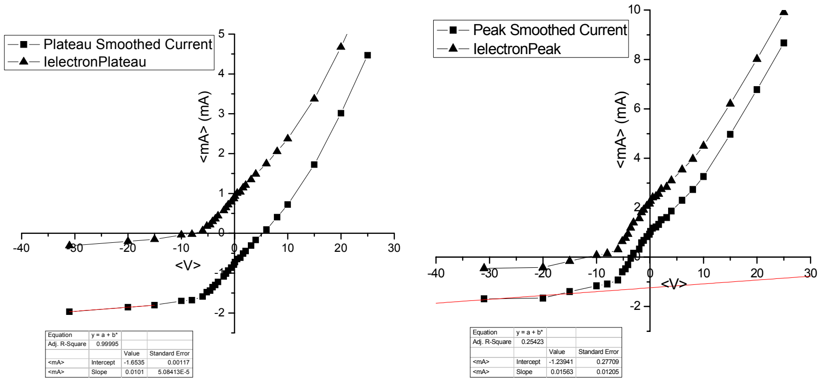

Fig. 3 – I-V plot for the Langmuir probe inside the pulsed RF GD cell; (a) plateau plasma (b) afterpeak plasma.

To derive the value of electron temperature in our plateau and afterpeak GD plasma, a linear fit is conducted of the ion saturation portion of the I-V curve. The linear fit of such portion is extrapolated to obtain the ion saturation current, I_{is}. The electron current, I_e, is then obtained by subtracting out the ion current, I_{is}, from the plasma current, I_p. Typically, the electron current, I_e, for any Maxwellian plasma can be expressed by $I_e \propto \exp\left(-\frac{eV_p}{kT_e}\right)$. Therefore, one can find the electron temperature by fitting I_e versus V_p on a semi-log plot as shown in Figure 4.

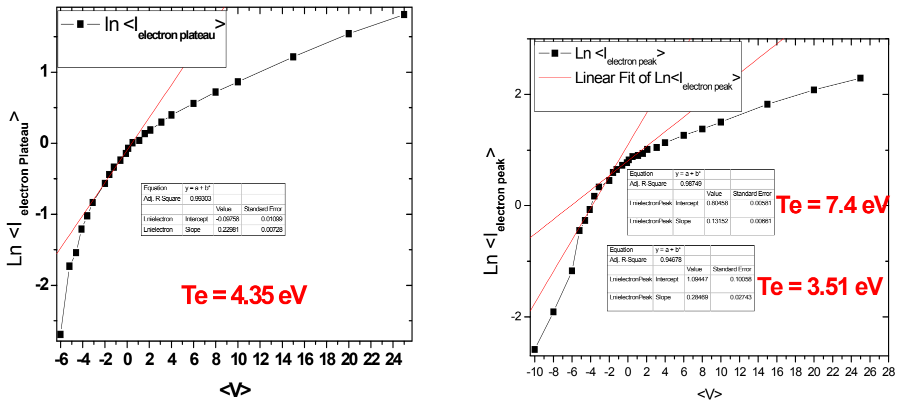

Fig. 4 – Electron temperature is extracted from ln (I_e) versus V_p (a) plateau of the RF pulsed plasma; (b) afterpeak RF pulsed.

The logarithmic representation of the probe characteristics, Figure 4 (a) illustrates the existence of one electronic group with 4.35 ± 10% eV energy. Unlike the RF plateau plasma, the logarithmic representation of RF afterpeak plasma illustrates the presence of two groups of electrons with different energy in the afterpeak plasma (3.51 ± 10%eV and 7.4 ± 10%eV energy groups). The electrons in the second group, with high energy, (7.4 eV) produced by the reaction $\mathrm{Ar}^m + \mathrm{Ar}^m \rightarrow \mathrm{Ar}^0 + \mathrm{Ar}^+ + \mathrm{e}^- + \Delta E$ where ΔE = 7.48 eV represents the main process in the local excitation and ion production.

We estimated the electron density of plateau and afterpeak plasma being about 10^{12} cm^{-3} and the Debye length of about $\lambda_D \cong 9$ μ. Thus, the measurements and the results obtained are consistent with the hypothesis of the Langmuir probe theory: the requirement probe radius $r_p >> \lambda_D$, which insures that edge effects may be neglected and the electron and ionic mean path $\lambda_{e,i} >> \lambda_D$ which insures that the collisions may be neglected in the space charge of the probe.

2.3. ATOMIC EMISSION MEASUREMENTS

Atomic emission was used to determine the population mechanism of various excited states of atomic Cu in the RF afterpeak plasma. The emission light was focused at the entrance of a Jarrell Ash monochromator. A photomultiplier tube (EMI) detected the emission output of the monochromator. The signals were fed into oscilloscope (TEKTRONIX) that provides the temporal emission profiles. The Copper transitions explored were 515.3 nm line ($^2D_{3/2}$ – $^2P_{1/2}$) the upper level situated at 6,19eV and 465.1 nm line ($^4D_{7/2}$ - $^4F_{9/2}$) with the upper level at 7,74eV. The temporal profiles of the two transitions are presented in Figure 5. We presume that in the RF pulsed plateau plasma the Copper atoms energy levels are populated by electronic collisions and remain relatively stable during the pulse period because of the slow diffusion processes. The afterpeak intensity of the transition at 515.3 nm of Cu can be attributed to corresponding excitation mechanism of copper.

$\mathrm{Ar}^m + \mathrm{Ar}^m \rightarrow \mathrm{Ar}^0 + \mathrm{Ar}^+ + \mathrm{e}^- + \Delta E$ where $\Delta E = 7.48$ eV and $\mathrm{e}^-(fast) + \mathrm{Cu}^0(ground) \rightarrow \mathrm{Cu}^*\left(excited\right)$.

The energy pooling of a pair of argon metastable atoms yields an electron carrying the extra energy of 7.48 eV. The energetic electrons generated can subsequently excite copper atoms.

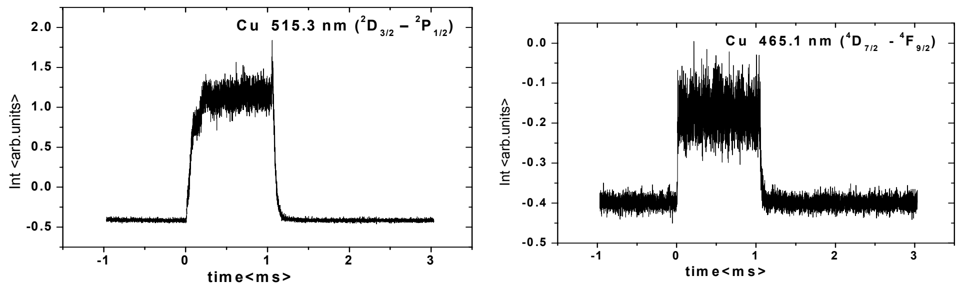

Fig. 5 – The temporal distribution of 515.3 nm and 465.1 nm Copper emission lines.

This excitation mechanism can be sustain by the fact that the Copper level at 7.74 eV (7.74 > 7.48) may not be populated by the fast electrons produced by the mentioned mechanism. As it can be seen in the Figure 5, the temporal distribution of the emission line 456.1 nm ($^4D_{7/2}$ - $^4F_{9/2}$) from $^4D_{7/2}$ positioned at 7.74 eV do not present any increase in the afterpeak region.

CONCLUSIONS

The experiments presented in this paper clearly revealed that in the afterglow of the analytical Pulsed RF GD plasma, the high concentration of argon metastable favorites the reaction metastable – metastable which provides high energy electrons which assure the excitation and ionization of analyte atoms.

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