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IONIZATION MECHANISM OF SPUTTERED ATOMS IN ANALYTICAL GDMS SYSTEM OPERATION

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Abstract: The role of neon metastables in ionization processes of sputtered titanium atoms in like GDMS analytical plasma was demonstrated.

Key words: analytical plasma, ionization mechanism, metastables.

1. INTRODUCTION

Glow Discharge Mass Spectrometry (GDMS) is an extremely powerful technique for direct elemental analysis of solid materials. Its principle involves the atomization of samples by sputtering in low-pressure plasma, the ionization of sputtered atoms in the plasma, and the extraction of ions into the mass analyzer for separation and detection.

The processes of atomization and ionization being separated in GDMS, the ion yields are mostly based on collision processes occurring in the flow gas plasma and so, in order to fully optimize GDMS analysis, a better understanding of plasma ionization processes is needed.

In order to investigate the plasma processes with characteristic times in the range from microseconds to milliseconds (ionization, recombination, etc.) as accurately as possible, we used a pulsed discharge with the duration much shorter (at least one order of magnitude shorter) than characteristic times.

Using a dedicated experimental set up, we have been looking with an optical diagnostic system at a specific plasma configuration, namely the afterglow of a pulsed Grimm discharge and we demonstrated the existence of a large amount of sputtered atoms and atomic metastables, which are involved in many excitation and ionization processes, one of them leading to the ionization of sputtered atoms.

2. EXPERIMENTAL SETUP

The experimental set up shown in Figure 1 was specially designed to investigate the excitation and ionization processes occurring in the afterglow plasma of a high voltage pulsed discharge in a Grimm cell configuration.

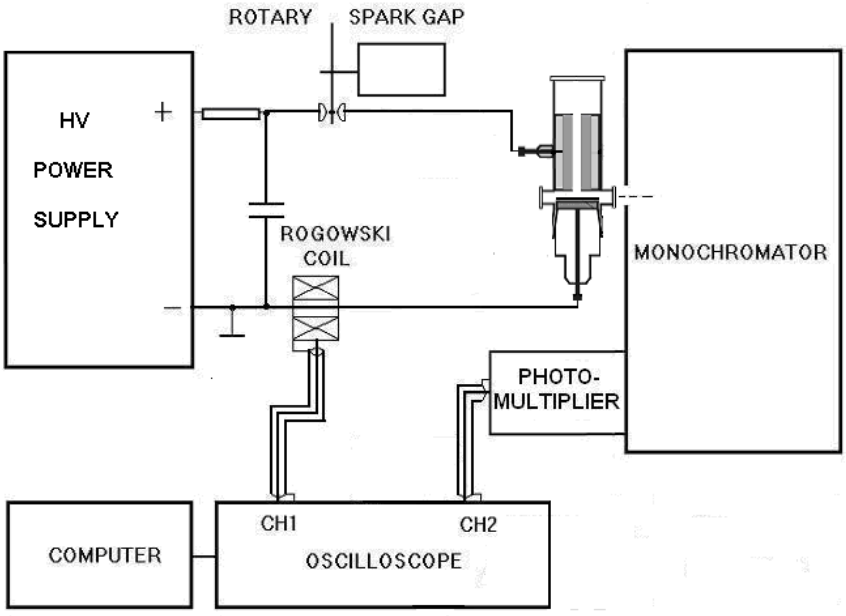

Fig.1 - Experimental setup.

The discharge tube, made of glass, contains a cylindrical hollow anode of Copper (15 mm length and 4 mm diameter). The cathode, a stainless steel disk (10 mm diameter) is positioned 2 mm apart from anode and sustains the samples, metallic and non metallic layers. The cathode is welded to a glass stopper, which may be handled in the glass vacuum system, and in this way the samples could be easily changed. The sample a titanium disk, 10 mm diameter and 1 mm thickness is stuck on the cathode.

Short high current pulses were produced by discharging a storage capacitor C through a rotary spark gap with a commutation time below 10 ns [1]. At 1-10 torr filling gas pressure, peak current pulses ranged between 20 and 100 A with a duration of 400 ns (at half-width) depending on the charging voltage of the main capacitor. Pulses of high current provide a large amount of multiple ionized atoms, which produce atomic and ionic metastables by electron recombination. The light emission of the afterglow plasma was filtered with 1-m Jarrell-Ash grating monochromator and detected with an EMI photomultiplier tube. The signals were averaged over 128 discharge pulses and recorded with a TEKTRONIX DPO 4032.

1. RESULTS AND DISCUSSIONS

One of the issues of the GDMS analytical plasma is the increasing of the ionization rate of the sputtered atoms from the samples. This requirement may be

achieved by a good knowledge and a good control of the ionization processes occurring in plasma.

Using the dedicated experimental setup we raised the temporal profile of emission lines of Ne, Ne^+ and Ti^+ which are presented in the Figure 2. It can be seen in the figure the long afterglow of Ne, Ti^+ by comparison with the Ne^+ which has no afterglow. As we have already mentioned in our previous papers [2], in contrast to the pulsed discharge period, when the ionization and excitation is caused mainly by impact with energetic electrons, during the GDMS analytical afterglow plasma the only source of ionization and excitation are the atomic and ionic metastables which are generated in a large amount by the recombination of the ions produced during the discharge pulse, and lost mainly by diffusion [3]. Skrzypkowski et al.[4] reported a yield of about 35% for Ar metastable formation by electron ion recombination.

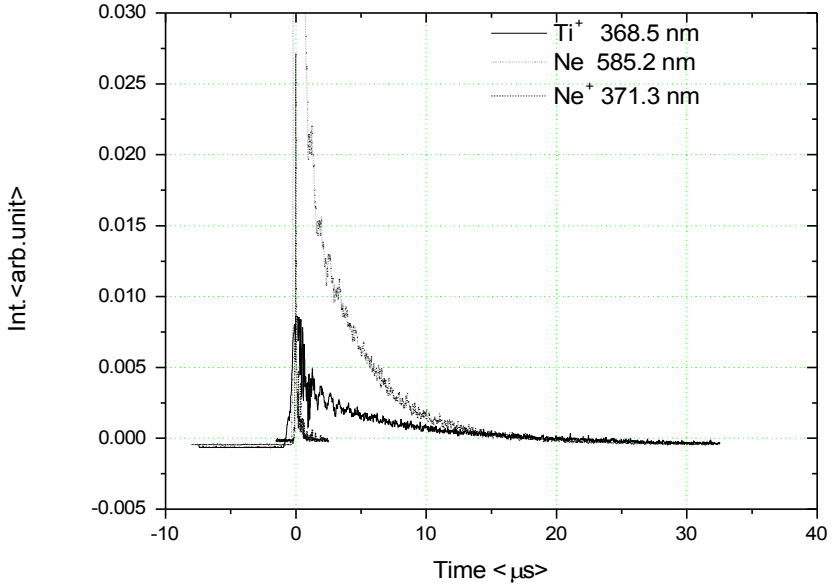

Fig. 2 - The emission profile of Ne, Ne^+ and Ti^+ spectral lines.

The purpose of this paper is to elucidate the ionization mechanism of the sputtered titanium atoms in a neon Grimm configuration pulsed plasma. Therefore, we investigated the temporal evolution of Ti^+ and H_α. The hydrogen present as an impurity of about $8.6*10^{-2}$ torr in the neon comes out during repeated pulsed discharges from the cathode and the surrounding glass wall. The temporal profiles of the both lines and their fitting exponential functions are presented in the Figure 3. As it can be seen, the time constant for the both fitting functions is about the same, suggesting that the n=3 hydrogen level (H_α line) and Ti^+ energetic levels in the afterglow are populated by similar processes.

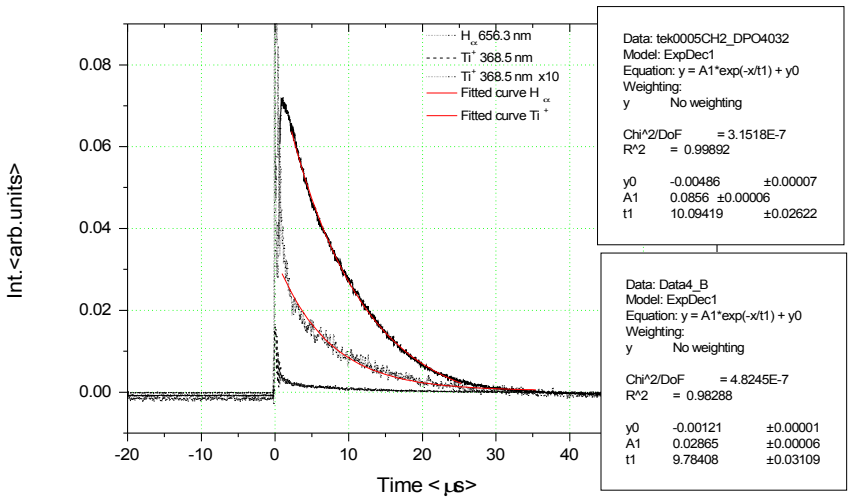

Fig. 3 - The emission lines of Ti+ and H_α and the corresponding fitting curves.

The n= 3 level of hydrogen (H_α line) is populated by a process proposed by Marshall[5] and confirm by Ricard [6] which reveals another application of the neon metastables in low pressure discharges; the dissociation of molecules.

$$Ne^m + H_2 \rightarrow Ne + H(n=3) + H(n=1)$$

with a cross section $\sigma_m = 7.10^{-16}$ cm^2.

As the neon metastables are responsible for the long afterglow H_α line, we may suggest that the neon metastables are also involved in the Ti^+ energy levels population, so that it is quit possible that a Penning ionization effect occurs between neon metastable and sputtered titanium atoms.

$$Ne^m + Ti \rightarrow Ne + Ti^+$$

We may assume that the exponential decaying function follows (reveals) the temporal decay of the metastables during the afterglow. In the frame of the model presented in our previous papers [7], we demonstrated that, after the discharge pulse comes to the end, the large amount of metastables produced by electron-ion recombination decreases during the afterglow because of the loss processes as diffusion and deactivation by collisions with noble gas atoms and molecular hydrogen impurities. The rate equation for metastables concentration is given by the differentiate equation:

$$\frac{\partial M}{\partial t} = D_m \nabla^2 M - \nu_d M - \nu_i M - \alpha_1 M^2 \qquad (*)$$

This linear equation in M which can be solved using ordinary techniques.
Neglecting the last term we shall assume that the metastable concentration, M, has an exponential decay

$$M = M_o \exp(-t / \tau_m),$$

with the initial concentration M_o and the time constant τ_m. According to the (*) equation the time constant τ_m is given by

$$1/\tau_m = (D_m / \Lambda^2) + \nu_d + \nu_i$$

with $D_m / \Lambda^2 = \frac{kT_{gas}}{p_{Ne}\sigma\Lambda^2}\sqrt{\frac{\pi kT_{gas}}{8m_{Ne}}}$, where k=1.38 10^{-23} J/K is Boltzmann constant , $\sigma = 10^{-19}$ m^2 is the elastic collision cross section and $m_{Ne} = 20* 1.67*10^{-27}$ kg is the atomic relative mass of neon. Also, the quenching frequency of metastables due to the collision with neutral neon atoms is given by

$$\nu_d = \sigma_d \sqrt{\frac{8kT_{gas}}{\pi m_{Ne}}}\frac{p_{Ne}}{kT_{gas}}$$

where $\sigma_d = 8.9\ 10^{-24}$ m^2 is quenching cross section [8], and the frequency of the Penning transfer on the hydrogen molecule is

$$\nu_i = \frac{\sigma_i p_{H_2}}{kT_{gas}}\sqrt{\frac{8kT_{gas}}{\pi m_{H_2}}}$$

where $\sigma_I = 4.10^{-20}$ ±28%m^2 [9] is the cross section of the Penning transfer Ne-H_2.

For our experimental conditions p_{Ne} *=10 Torr* , T_{gas}*=2100 K* [10] and Λ= *2 mm*, the time constant for the metastable resulted from the fitting of H_α is 10.09419 ± 0.02622 μs and from the fitting of Ti^+ 368.5 nm is 9.78408 ± 0.03109 μs as it can be seen in the Figure 3.
The calculated time constant value of about 8.57μs ± 20% are consistent with those obtained by fitting method and represents a further argument for the ionization mechanism given in the present paper.

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