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APPLICATION OF RELATIVE SENSITIVITY FACTORS FOR INVESTIGATION OF PROCESSES IN PULSED GLOW DISCHARGE PLASMA WITH TOFMS ION DETECTION

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Abstract. Relative sensitivity factors (RSF's) for different matrices (copper, steel, nickel, lead, silicon) in pulse-GD MS are determined. The possibilities of time-of-flight mass spectrometry with pulse glow discharge ionization in semi-quantitative analysis without using of standards samples are discussed. Dispersal of RSF's is appreciably low in comparison with RSF dispersal for DC discharge. Different types of correlation between RSF of the element and its ionization potential were obtained. According to this fact assumptions about different plasma processes in glow discharges were made.

1. LOW TEMPERATURE PLASMAS

1. 1. PLASMA APPLICATIONS AND DEVICES

It is known that sensitivities for different elements in Glow Discharges (GD) are to lesser degree depend on matrix than ones for spark, laser ablation and ICP MS. This feature connects with two factors – sputtering rates for the elements in GD are equal and differences of rates of ionization (it is determined in high degree by nonselective Penning process) aren't very high. Relative Sensitive Factor (RSF) is used for description of matrix influence on measured concentrations:

$$RSF(x/y)_z = \frac{I_x \cdot C_y}{I_y \cdot C_x}, \tag{1}$$

where I_x and I_y – intensities of determined element and element used as internal standard (main component of the sample), C_y and C_x – appropriate concentrations. RSF describes dependence of sensitivity of element X from matrix Z.

Due to that processes of atomization and ionization in glow discharge are divided in space and in time, the disorder of sensitivities for different elements is not so great. This case the analysis possible without strict conformity of a standard and analyzed samples. Besides at values of RSF close to unit, carrying out the semi-quantitative analysis without use of the standard is possible.

There are numerous measurements RSF for various elements and matrixes at ionization in the glow discharge. Values RSF of elements for the given matrix at ionization in the glow discharge make sizes of one order, as against again secondary ionic and laser sources where distinction can achieve three orders. Besides spread in values of RSF in GD MS doesn't exceed 30% for one element in different matrix. These features make GD by attractive source for sample ionization, therefore many investigations carried out in this field. However all of this works relate to DC and RF discharges, while RSF for pulsed discharges don't investigate practically. Taking into account that processes in afterglow play primary role in pulsed discharges, which can essentially differ from the processes in DC or RF discharges, than one can expect of rather another situation with RSF.

Experiments were carried out on TOFMS with pulsed ionization in combined hollow cathode. The cathode consisted of flat sample and cathode wall produced from pure Aluminum (99.9999%). The sample press oneself to the wall. This technique allowing analyze as conductive as semiconductive and dielectric samples. RSF were measured for different samples – Copper, Nickel, Lead, Steel and Silicon (see Table 1).

RSF for the most part of the elements close to 1 (moderate differences can be explained by the differences of cross sections of Penning ionization for different elements) while distinction is appreciable greater for few elements. The distinction can be connects with selective process (for example asymmetric charge transfer). However this dispersal is appreciably low in comparison with RSF dispersal for DC discharge. Apparently efficiency of different selective processes of ionization (for example asymmetric charge transfer) in afterglow is appreciably lower than efficiency of Penning ionization, while in DC or RF discharge selective processes of ionization play significant role.

For two matrices in the case of pulsed GD (cooper and silicon) influence of ionization potential on RSF was investigated (see Figure 1). Also such investigations were made for the DC GD using experimental data from literature (see Figure 2).

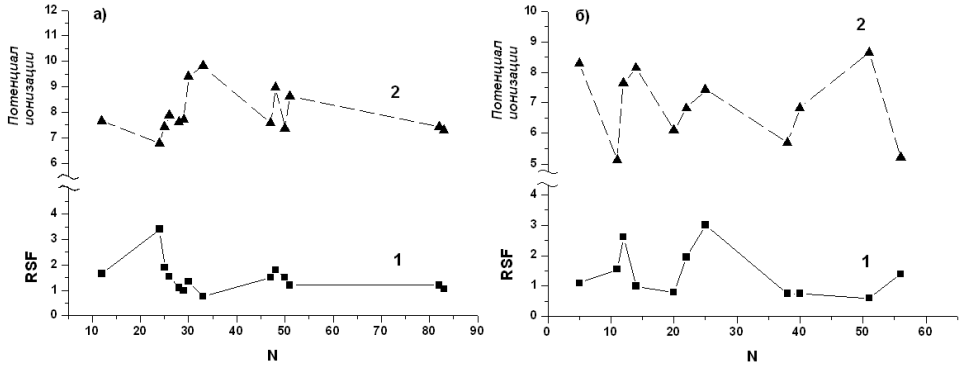

Figure 1: Correlation between RSF (1) of an element and its ionization potential (2). Pulsed GD. a) – cooper matrix b) – silicon matrix.

In the case of DC GD slight positive correlation between RSF of an element and its ionization potential was found. Meanwhile for pulsed GD there was no such correlation. Correlation coefficients are presented in Table 2. These facts confirm our previous assumption that in pulsed GD Penning ionization is dominating ionization process, while in DC GD selective processes such asymmetric charge transfer play significant role.

Table 1: Determined relative sensitivity factors

Sample	Element RSF	
Copper	Mg	1.65
	Cr	3.4
	Mn	1.9
	Fe	1.55
	Ni	1.1
	Zn	1.35
	As	0.76
	Ag	1.5
	Cd	1.8
	Sb	1.2
	Sn	1.50
	Pb	1.2
	Bi	1.05
	Cu	1.0
Nickel	Ag	2,10
	Pt	1,45
	Pd	2,30
	Rh	2,0
	Ni	1,0
Lead	Ag	2.1
	Se	0.65
	Te	0.65
	Sb	1.45
	Pb	1,0
Steel	Cr	1.4
	Mn	1,2
	Ni	1.5
	Fe	1.0
Silicon	Sr	0.75
	Mn	3.0
	Ti	1.95
	Ca	0.80
	Mg	2.6
	Ba	1.4
	Na	1.55
	B	1.1
	Zr	0.75
	Sb	0.6
	Si	1.0

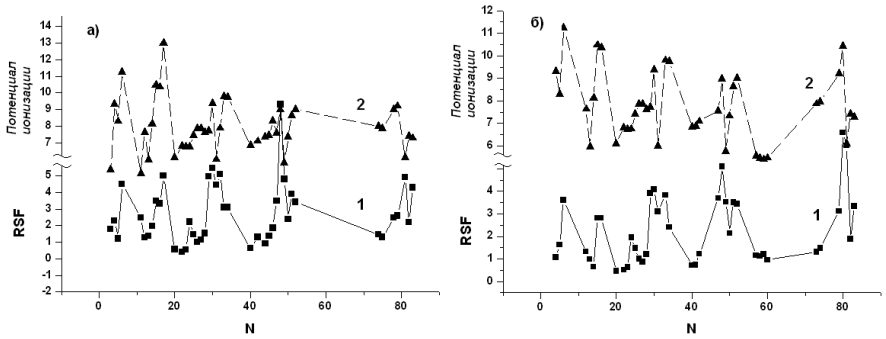

Figure 2: Correlation between RSF (1) of an element and its ionization potential (2). DC GD. Steel matrix.a) – Bogaerts and Gijbels 1996 b) – Saka and Inoue 2000

Table 2: Correlation coefficients
* - different literature sources were used for DC GD.

Matrix. Discharge type.	r
Cooper. Pulsed GD	-0,45
Silicon. Pulsed GD	0,03
Steal. DC GD [1]*	0,35
Steal. DC GD [2]*	0,52

Indeed according to computer simulation results for used pulsed GD concentration of argon ions in the discharge cell decreases sharply after pulse, whereas concentration of argon metastables decreases in significantly lesser degree. Such situation determines dominate role of Penning ionization mechanism and nearly absence of asymmetric charge transfer from argon ions for pulsed GD.

For cooper matrix in pulsed GD was found slightly negative correlation between RSF of an element and its ionization potential. Possible explanation of this fact is the presence of asymmetric charge transfer with cooper ions. Cooper has high sputtering coefficient and its ionization potential is close to many sample elements ionization potentials, consequently such process is very probable. If our assumption is correct, it is very promising, because varying operating conditions one can influence on RSFs.

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