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Does asymmetric charge transfer play an important role as an ionization mode in low power–low pressure glow discharge mass spectrometry?☆

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ABSTRACT

We report results of comprehensive studies using the Nu Instruments Astrum high-resolution glow discharge mass spectrometer (GD-MS) and optical emission spectrometry (OES) to investigate the relative importance of discharge mechanisms, such as Penning ionization (PI) and asymmetric charge transfer (ACT), at low-power/low-pressure discharge conditions. Comparison of the ratios of the ion signals of each constituent element to that of the plasma gas shows that for oxygen, the ratio in krypton is more than ten times higher than in argon (oxygen ground state ions are produced by Kr–ACT). For many elements, the ratios are very similar but that for tungsten is higher with krypton, while for iron, the reverse holds. These effects are linked to the arrangement of ionic energy levels of the elements concerned and the resulting relative importance of ACT and PI. The GD-MS and GD-OES results have shown that the ACT process can play an important role as the ionization mode in low-power/low-pressure discharges. However, OES results have shown that the magnitude of change in spectral intensities of elements studied are dependent on the discharge conditions.

1. Introduction

Glow discharge mass spectrometry (GD-MS) is a highly sensitive analytical technique used for the investigation of high purity materials [1–6]. The ability to analyse and quantify, elemental composition from matrix to sub-ppb (parts per billion, nanogram/gram) levels, accurately and precisely is unique to this technique. The presence of trace level elements as impurities can have serious consequences for the properties of the ultra pure materials used in semiconductor and electronic industry and for high-tech products in aerospace, automotive, and other manufacturing industries. For this reason, GD-MS is broadly used for the elemental analysis in these fields.

For routine elemental analysis by GD-MS, nowadays, different types of commercial instruments, e.g. VG Elemental VG9000, Thermo-Fisher Scientific Element GD, and Nu Instruments Astrum GD-MS, are commonly used. Recently, the Plasma Profiling GD-TOFMS from Horiba Scientific and GD90 from Mass Spectrometry Instruments (MSI) were launched. These commercial GD instruments are operated at different discharge powers; the Element GD and GD-TOFMS run in a low-pressure noble gas, usually argon, with ~40 W, 5 hPa. On the other hand, the VG9000, Astrum, and GD90 are operated in lower-power/lower-pressure (~3 W, 1 hPa) conditions. This paper does not cover the general aspects and analytical merits of these instruments but focuses on the investigation of discharge mechanisms, such as electron ionization (EI), Penning ionization (PI), and asymmetric charge transfer (ACT), at low discharge power conditions. The ion currents produced in the ion source by the various abovementioned processes are proportional to the concentration of the elements in the sample. As the whole technique of GD-MS is based on the ions of the elements analysed, it is important to understand the discharge mechanisms involved.

ACT (see Eq. (1)) is a very important mechanism for the production of ground and, more usually, excited ions of the elements analysed in analytical glow discharges such as Grimm-type and fast-flow sources running in low-pressure noble gases (~15–40 W, ~5 hPa) [7–11].

$$\mathrm{ACT:}\ \mathrm{M_o} + \mathrm{I^+} \rightarrow \mathrm{M^+} + \mathrm{I_o} + \Delta\mathrm{E} \qquad (\mathrm{M_o^+}\ \mathrm{or}\ \mathrm{M^{+*}}) \tag{1}$$

where the subscript o and superscript * represent the ground and an excited state, respectively, and superscript + an ionized atom. M is a metallic atom and I a noble gas atom, and ΔE is the small kinetic energy release in the collision which can be either positive (exoergic) or negative (endoergic). The majority of excited ions decay very rapidly (~10^{-8} s) to ground or metastable state ions. Steers et al. [7,8] have shown the clear occurrence of ACT for a variety of sample elements in the Grimm-type GD (700 V, 20 mA) with argon as the plasma gas and

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also with other plasma gases [12]. On the other hand, it has been suggested that in low-power/low-pressure (~3 W, 1 hPa) analytical GD (e.g. VG9000 type sources), EI (Eq. (2)) and PI (Eq. (3)) are the main ionization pathways for the sputtered atoms [13],

$$\text{EI}: M_o + e^- \rightarrow M^+ + e^- + e^- + \Delta E \qquad (M_o^+ \text{or } M^{+*}) \tag{2}$$

$$\text{PI}: M_o + I_m \rightarrow M^+ + I_o + e^- + \Delta E \qquad ({M_o}^+ \text{or } M^{+*}) \tag{3}$$

where m is a metastable atom and that although ACT may occur in such sources, it only plays a minor role [14]. However, this study on ACT using the low-power discharge conditions involves investigation of only copper, which has a single energy level at 15.96 eV suitable for ACT and therefore results cannot be generalized from this limited study. On the other hand, Bogaerts and Gijbels have shown that deviations from the regular pattern of relative sensitivity factors (RSF) which cannot be explained by transport phenomena and PI only, most likely can be attributed to ACT [15].

In this paper, we report results of comprehensive studies using GD-MS and glow discharge optical emission spectrometry (GD-OES) to investigate the relative importance of discharge mechanisms, such as ACT and PI, at low-power/low-pressure discharge conditions. Information on total ion population (MS studies) and on radiative population and depopulation transitions (OES studies) linked to the arrangement of the ionic energy levels of the element concerned can help to identify selective (Penning excitation and ACT) and less selective (EI and PI) discharge processes in the plasma. Details of these processes which are mainly dependent on the nature of the plasma gas and analyte material have been reported previously by Mushtaq et al. [16] using a Grimm-type source with 4 mm diam. anode tube and discharge conditions ~15 W, 5 hPa. In the current work, the relative importance of ACT and PI processes in a low-power/low-pressure discharge (~5 W, 1 hPa) have been investigated by measuring the ion currents of constituent elements relative to that of the plasma using an Astrum GD-MS. The integrated ion current from both the constituent element and plasma gas are adjusted for the natural abundance of the isotope measured. The differences in the ratios using argon and krypton are shown to be linked to the arrangement of the ionic energy levels of the elements concerned and hence to the possibility of ACT.

2. Experimental details

The mass spectra generated in various plasma gases were recorded using the Nu Instruments Astrum high-resolution GD-MS [17] at Evans Analytical Group, Syracuse, USA. The instrument is similar to the first commercial GD-MS, the VG9000 (1984–2004) and joins a low-pressure GD source consisting of a tantalum cell allowing both pin and flat sample configurations with a double-focusing, high-resolution GD sector field MS. The measurements presented in this study were carried out using a dc discharge with constant voltage, constant current conditions (~1 kV and ~3 mA) and a pin sample (2 mm square). More details about the use of pin and flat cathodes and its implications for mass spectrometric analysis are reported by Bogaerts and Gijbels [18]. In our study, a Brammer Standard B.S. T-2 pure titanium sample (Brammer Standard Company, Inc., Houston, TX, USA) was used. The details of the elements present in the sample are given in Table 1. Prior to measurements, the sample was polished, washed with water, and then cleaned with ethanol and dried thoroughly with hot air. Before the start of the actual measurements, the sample was run in a pre-burning phase for few minutes under the discharge conditions used for this experiment. For the optical emission spectrometry studies, the GDA650 (Spectruma Analytik GmbH, Hof, Germany) [19] at IFW Dresden was used with a 4 mm diam. anode tube and conditions, 1000 V, 5 mA, and 700 V, 20 mA. Details of the instrument including the excitation source have been given previously [20]. Iron (purity 99.5%) and tungsten (purity 99.95%) samples, both from Goodfellow, Cambridge, UK, were used for OES measurements. Where necessary, to confirm the line identifications, we have also carried out high-resolution OES experiments using the Fourier transform spectrometer [21] at Imperial College London as previously described [22].

Table 1
Constituent elements present in B.S. T-2 pure titanium as percent by weight.

B.S. T-2 pure titanium			
Carbon	0.010	Iron	0.19
Nitrogen	0.017	Nickel	0.005
Oxygen	0.182	Copper	0.003
Aluminium	0.019	Zirconium	0.002
Silicon	0.007	Niobium	<0.01
Sulphur	0.002	Molybdenum	0.002
Vanadium	0.006	Tin	0.005
Chromium	0.003	Tungsten	<0.002
Manganese	<0.002		

3. Results and discussion

The first ionization energy of each element present in the B.S. T-2 sample is shown in Fig. 1 along with the metastable and ionic states of krypton and argon. Preliminary information about the likelihood of the PI and ACT processes can be obtained from this plot by comparing the first ionization energy of each element in the sample with the energies of metastable and ionic states of the plasma gas. It can be seen that, apart from nitrogen and oxygen, all the elements other than carbon have a first ionization energy lower than the metastable states of krypton (9.915 and 10.562 eV) and argon (11.548 and 11.723 eV). All those elements with ionization energy below the energy of the excited metastable states (Ar_m or Kr_m) are mainly ionized by the PI process. Due to the fairly close energies of the krypton and argon metastable states, it is expected that the ratios (i.e. the ion current of the element relative to that of the plasma gas) of many constituent elements which are mainly excited by PI would be similar to those excited by electronic excitation. On the other hand, the difference in ratios of constituent elements will increase when there is an additional contribution from a selective process, e.g. ACT. Modelling studies by Bogaerts and Gijbels [23] have shown that among the main discharge processes in GD plasmas, such as EI, PI, and ACT, to produce ground state and excited ions of elements analysed, EI accounts for only about 1% of the total ionization of sputtered atoms at the typical discharge conditions (~3 mA, 1000 V) of low-power GD-MS, and therefore, EI is less effective than the PI and ACT processes.

3.1. Glow discharge mass spectrometry results

In Fig. 2, the ratios I_E/I_G are shown where I_E is the ion current of a particular constituent element, E, in the sample measured, when a particular plasma gas is used and I_G is the current of the plasma gas ion, both corrected for isotopic abundance. These ratios are calculated and plotted for the trace, minor and major elements present in the sample and shown for argon (□) and krypton (○) as the plasma gases. The higher value of intensity ratio for a particular element, e.g. carbon in Fig. 2, reflects that the carbon atoms are probably ionized by a particular mechanism which may occur in the presence of argon but not in krypton. In the following section, by taking into account the ionization energies of each element comparatively with the metastable states of plasma gas and the schematic diagrams of ionic energy levels, we will interpret the discharge mechanisms responsible for individual elements in the sample.

Specific observations from GD-MS experimental data are

- the noticeable differences in the ion signal ratios for carbon, nitrogen, and oxygen for krypton and argon;
- the order of magnitude higher values of the ratio for oxygen when krypton is used;