Spectrochimica Acta Part B 133 (2017) 72–80

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Emission characteristics of 6.78-MHz radio-frequency glow discharge plasma in a pulsed mode

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ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form 2 May 2017
Accepted 8 May 2017
Available online 10 May 2017

Keywords:
Glow discharge optical emission spectrometry
Boltzmann plot
Excitation process
6.78 MHZ radio frequency
Pulsed discharge

ABSTRACT

This paper investigated Boltzmann plots for both atomic and ionic emission lines of iron in an argon glow discharge plasma driven by 6.78-MHz radio-frequency (RF) voltage in a pulsed operation, in order to discuss how the excitation/ionization process was affected by the pulsation. For this purpose, a pulse frequency as well as a duty ratio of the pulsed RF voltage was selected as the experimenter parameters. A Grimm-style radiation source was employed at a forward RF power of 70 W and at an argon pressures of 670 Pa. The Boltzmann plot for low-lying excited levels of iron atom was on a linear relationship, which was probably attributed to thermal collisions with ultimate electrons in the negative glow region; in this case, the excitation temperature was obtained in a narrow range of 3300–3400 K, which was hardly affected by the duty ratio as well as the pulse frequency of the pulsed RF glow discharge plasma. This observation suggested that the RF plasma could be supported by a self-stabilized negative glow region, where the kinetic energy distribution of the electrons would be changed to a lesser extent. Additional non-thermal excitation processes, such as a Penning-type collision and a charge-transfer collision, led to deviations (overpopulation) of particular energy levels of iron atom or iron ion from the normal Boltzmann distribution. However, their contributions to the overall excitation/ionization were not altered so greatly, when the pulse frequency or the duty ratio was varied in the pulsed RF glow discharge plasma.

1. Introduction

Glow discharge optical emission spectrometry (GD-OES) is extensively employed for direct analysis of solid samples because the glow discharge plasma is self-sustained under a stable condition, which can provide the emission spectra with small intensity variations as well as with low background levels. GD-OES can be operated using both direct-current (DC) and radio-frequency (RF) power supplies; especially, the latter can contribute to wider analytical applications of GD-OES principally because it enables non-conductive samples to be analyzed [1,2]. Nowadays, commercialized apparatuses for GD-OES have normally had a pulsed discharge mode, in order to reduce the sputtering rate and/or to minimize thermal damage of the sample surface [1]. Many scientific papers were published with respect to actual applications of the pulsed GD-OES; for instance, Sánchez et al. reported on depth profiling of a thin film for silicon solar cell [3] and Schwaller et al. indicated a GD-OES study of lead zirconate titanate thin films which were commercially employed for microelectronic devices [4]. Furthermore, the pulsed RF glow discharge was investigated with respect to variations in the emission intensity within the pulse cycles; Alberts et al. discussed the reason for a pre-peak which appeared at the beginning of the emission profile in a pulsed RF GD-OES [5] and Valledor et al. reported variations in the spatial distribution of argon and copper emission intensities when the pulse frequency was varied [6]. Our previous studies revealed that the pulsed discharge could be employed for phase-sensitive detection using a lock-in amplifier to improve a signal-to-noise ratio of the emission signal [7,8].

The concept of local thermodynamic equilibrium (LTE) is described as follows: a plasma in the LTE state is characterized by a unique temperature which can be determined by Maxwell-like distribution of collision partners in a dominant thermal collision of first kind, such as collisions with energetic electrons [9]. In this case, excitation and ionization processes occurring in the LTE plasma, resulting in the emission spectrum, could be predicted from the Boltzmann distribution among the corresponding excited energy levels [9]. However, glow discharge plasma is not in a LTE condition and thus the excitation/ionization phenomena in GD-OES cannot be explained from the Boltzmann distribution [10,11]. Our previous papers indicated that deviations from the Boltzmann distribution, which were observed in both atomic and ionic emission lines of iron, gave useful information on the excitation/ionization processes in argon GD-OES [12,13]. In the analysis of the iron atomic lines, it was found that excited energy levels of iron atom above ca. 6 eV were more populated than a Boltzmann distribution over excitation energies of 3.4–4.6 eV, probably through stepwise de-excitation processes from higher energy levels [12]. In the Boltzmann

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http://dx.doi.org/10.1016/j.sab.2017.05.003
0584-8547/

plot of singly-ionized iron, a large positive deviation from the normal distribution appeared in the excitation-energy range of 7.7 eV, which would be attributed to a charge-transfer collision with argon ion [13].

In present study, we selected a driving frequency of 6.78 MHz for an RF excitation source in GD-OES, mainly because it has larger self-bias voltage than that of 13.56 MHz [14] and thus may provide larger amounts of samples sputtered into the plasma. This paper discusses on Boltzmann plots for both atomic and ionic emission lines of iron, when a pulsed 6.78-MHz glow discharge plasma is employed, in comparison to the continuous RF mode. Several papers dealt with the plasma diagnostics of pulsed glow discharges in GD-OES. Jackson et al. indicated temporal and spatial distribution of argon emission lines from a millisecond pulsed glow discharge to investigate the behavior of argon metastable atoms [15], and Isola et al. reported on the electron temperature and density in a pulsed nitrogen glow discharge plasma [16]. However, few studies have been published regarding the plasma diagnostics of 6.78-MHz RF glow discharge in a pulsed mode. The objective of this paper is to consider the Boltzmann distribution of iron emission lines in order to understand how their characteristics can be explained by the excitation mechanism of iron species in the pulsed RF glow discharge plasma.

2. Experimental

A Grimm-style glow discharge lamp, as described in our previous paper [17], was employed for the excitation source. According to the original Grimm model [18], the lamp was in-house made, whose hollow-anode had a diameter of 8.0 mm and inter-electrode distance was adjusted to be ca. 0.3 mm. The RF power was conducted from a matching circuit (MB-300, Yamamoto Vinita Co. Ltd., Japan) to the back of the sample electrode, while the hollow-anode as well as the lamp body were grounded [19]. The matching circuit was connected with a 6.78-MHz RF power generator (RF-300, Yamamoto Vinita Co. Ltd., Japan) with a coaxial cable. The forward power was fixed to be 70 W in the continuous mode and the power of 70 W was controlled on a directional wattmeter in the pulsed mode, while the reflected power was able to be controlled to be less than 0.2 W in all the measurements. The pulsed mode was conducted with a function generator (AFG-2005, TEXIO Technology Corp., Japan), where the frequency ranges from 0 (continuous) to 617 Hz at a duty ratio of 50%, and further, the duty ratio of square wave was varied from 10 to 50% at a pulse frequency of 77 Hz. In the pulsed discharge, a time-averaged value of the self-bias voltage (effective value) was measured on a digital voltmeter (DME1500, Kikusui Electronics Corp., Japan) at a time constant of about 1 s, after the RF component was separated through a low-pass filter circuit having a cut-off frequency of 80 kHz [19].

An iron plate (99.8% purity) was prepared as the sample. It was polished with water-proof emery papers (No.180 - No.600) and then rinsed with ethanol. Before the measurement, pre-discharge was carried out for 5–10 min to remove the surface contaminants. After evacuating down to 1.3 Pa in the discharge chamber, high-purity argon was introduced with a gas pressure maintained during the measurement. The pressure of the plasma gas was measured with a Pirani gauge, whose readings had been corrected for argon gas, at the vacuum port of the discharge chamber.

A monochromator-based spectrometer equipped with a photomultiplier (P-5200, Hitachi Ltd., Japan) was employed for the emission measurement [20]. The focal length is 0.75 m and the grating has 3600 grooves/mm at a blaze wavelength of 200 nm, yielding a reciprocal linear dispersion of 0.29 nm/mm. The emission signal was averaged through a low-pass filter circuit having a time constant of ca. 1 s. Emission lines for analysis of Boltzmann distribution, the atomic lines (Fe I) [12] and the ionic lines (Fe II) [13], have already been listed in our previous papers. 42 emission lines of the Fe I, whose excitation energies range from 3.3 to 6.9 eV, were chosen in the wavelength range of 368–385 nm [21]. These Fe I lines are classified into three groups: $3d^74p$ - $3d^74s$, $3d^64s4p$ - $3d^74s$ ($3d^64s^2$), and $3d^64s4d$ - $3d^64s4p$ optical transitions [22]. The ground state of iron atom is the energy level of $^5\mathbf{D}_4$ (0.00 eV) in the $3d^64s^2$ electron configuration. In the Fe II lines, we selected a set of the ionic lines in the wavelength range of 234–264 nm, comprising 88 emission lines having excitation energies from 4.7 to 9.0 eV [21]. These Fe II lines are classified into three groups: $3d^64p$ - $3d^64s$, $3d^64p$ - $3d^7$, and $3d^54s4p$ - $3d^54s^2$ optical transitions [22]. The $3d^64s$ electron configuration gives the ground state of iron ion, including the lowest energy level of $^6\mathbf{D}_{9/2}$ (0.00 eV). Any correction for the wavelength-dependent sensitivity of the spectrometer system was not needed within each narrow wavelength range of the Fe I and Fe II lines.

For comparison, our previous papers regarding a DC glow discharge plasma are cited [12,13], where the analysis of the Boltzmann plots has been carried out at an argon pressure of 530 Pa in a DC voltage range of 500–900 V. The Boltzmann analysis in the DC plasma had been carried out using the same experimental setup for the excitation source as well as spectrometer system as in the 6.78-MHz RF plasma.

3. Results and discussion

3.1. Structure of the glow discharge plasma and the excitation phenomena

A glow discharge lamp working under the obstructed glow conditions [23] is generally employed as an excitation source for atomic emission spectrometry; the Grimm-style glow discharge lamp, comprising a hollow anode and a planar cathode, is a typical instance [19]. The obstructed glow plasma can be represented a simplified structure model, which includes only a negative glow region, a cathode dark space region, and an anode dark space region, as illustrated in Fig. 1 [23,24]. In this model, the negative glow occupies a great part of the discharge body and very narrow dark spaces are adjacent to each electrode. The lower diagram of Fig. 1 indicates the potential distribution schematically when a negative DC voltage is applied to the discharge lamp with the anode electrode grounded. A uniform potential distribution appears in the negative glow region, having a constant voltage called a plasma potential (typically 10 V), whereas most of the applied voltage appears in the cathode dark space, called a cathode drop (almost equal to the supplied voltage) [23]. This distribution means that, when an ambipolar diffusion takes place in the plasma body, a large difference in the mobility between electron and ion leaves a slightly positive plasma potential against the anode; therefore, electrons having low kinetic energies cannot move into the anode electrode through the anode dark space region. The effect eventually contributes to a self-stabilized plasma body [23].

Glow discharge produces a so-called 'cold plasma', which means that the kinetic energy of gas species in the plasma is fairly low and thus the gas temperature is much lower than the electron temperature, being not in the LTE condition. This effect is principally because the glow discharge is generally generated under reduced pressures; therefore, while electrons can receive the kinetic energy from the electric field directly, collisions with the energetic electrons do not occur to cause the energy transfer to the gas particles sufficiently. It is important to understand the behavior of electrons in the glow discharge plasma. Capman classified the electrons into three groups: primary electron (gamma electrons), secondary electrons, and ultimate electrons (glow electrons) [25]. Since a negative potential corresponding to the cathode drop is applied to the cathode, an strong electric field is produced in the cathode dark space region; therefore, electrons emanated from the cathode, called gamma electrons, are accelerated by the electric field in the cathode dark space and subsequently the electrons having larger kinetic energy are introduced into the negative glow region. Then, the energetic electrons collide with gas atoms to cause their ionization and eventually to produce secondary electrons. As a result of collision cascade with various kinds of electrons, a large number of electrons having relatively low kinetic energies are produced in the negative glow region. Low-energy electrons insufficient to overcome the plasma potential become repelled back towards the negative glow region not only by the cathode