Improvement in Signal Response of In-depth Elemental Profiles in Radio-frequency Glow Discharge Optical Emission Spectrometry by Using a Bias-current Introduction Method

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The objective of this paper is to suggest a new method for obtaining an in-depth profile with better precision in 13.56-MHz radio-frequency (RF) glow discharge - optical emission spectrometry. For this purpose, a phenomenon regarding self-bias voltage in the RF plasma is focused on. The self-bias voltage is induced near the RF-loaded electrode, enabling sample atoms to be sputtered from it into the plasma. A bias current can be introduced through the electric circuit including the plasma body, by connecting an external electric device with the glow discharge lamp. The amount of the bias current would change the characteristics of the plasma for atomic emission spectrometry. When higher bias current flows, the resulting plasma extended in the whole area of the glow discharge lamp, including both the electrodes and grounded housing of the lamp, thus making the plasma unstable. However, an exposure to such a plasma could remove gaseous species, which would be entrained when the sample was exchanged, from interior parts of the lamp. This effect contributed to better response of the emission signal just after the discharge was ignited. Depth profiles of a nickel-electroplated steel plate were measured in RF-GD-OES, to investigate the effect of the bias-current introduction.

KEY WORDS: glow discharge optical emission spectrometry; 13.56-MHz radio frequency plasma; bias current; depth profiling; Ni-electroplated steel plate.

1. Introduction

Glow discharge plasma - optical emission spectrometry (GD-OES) has extensively been employed as an analytical method for elemental quantification of various solid samples.\textsuperscript{1,2) The glow discharge plasma, in which sample atoms are atomized and excited, can be maintained under a stable condition; therefore, the resulting emission intensity has a small variance and thus can give the analytical result with good precision. Furthermore, in-depth elemental profiling of solid samples is the most important application of GD-OES,\textsuperscript{3)} because the sampling is conducted through the cathode sputtering against the sample surface.\textsuperscript{4)}

It is sometimes observed in the in-depth profiling that the emission intensity becomes unstable during an initial period of the glow discharge. This effect is considered to result from gas species adsorbed on the sample surface as well as the wall of the hollow anode, which must be exposed under ambient atmosphere when the sample is exchanged. In most cases, such variations in the emission intensity are to an extent that the analytical result is hardly affected; however, this problem should be overcome to further improve the analytical precision in the depth profiling of GD-OES.

This paper suggests a new method for stabilization of a glow discharge when it is ignited, which can provide a depth profile more precisely. For this purpose, a bias-current introduction method, which had been developed to enhance the emission intensity and thus to better the analytical performance,\textsuperscript{5–7)} was applied in GD-OES using a radio-frequency (RF)-driven glow discharge plasma. Purging of the glow discharge lamp could be carried out to improve the signal response of depth profiles, by flowing higher bias currents as a pretreating procedure before the measurement.

2. Experimental

2.1. Apparatus

Figure 1 schematically illustrates the experimental system, comprising an excitation source, an RF power supply, and a measuring system, employed in this study. A Grimm-style glow discharge lamp,\textsuperscript{8)} which consisted of a planar electrode (sample) and a grounded hollow electrode, was in-house made of brass except several parts of insulator, whose hollow-anode had a diameter of 8.0 mm and the inter-electrode distance was adjusted to be ca. 0.3 mm.\textsuperscript{9)} The emitted radiation was observed from the cylinder-axis direction of the hollow-anode with a convex lens having a
focal distance of 100 mm on a monochromator-based spectrometer (Model302, McPherson Inc., USA) equipped with a photomultiplier (R955, Hamamatsu Photonics, Japan), where the focal position was the plasma position close to the sample surface; in this optical alignment, all over the emitting zone could be taken into observation. The RF power was conducted from a matching circuit (MTH-50, ASTEC Corp., Japan) to the back of the sample electrode, while the hollow-anode as well as the lamp body were grounded.5) The matching circuit was connected with a 13.56-MHz RF power generator (Cesar133, ASTEC Corp., Japan) with a coaxial cable. The forward power was fixed to be 40 W at a pulse frequency of 72 Hz (a duty ratio of 50%), while the reflected power was adjusted to be less than 0.5 W. Values of the self-bias voltage and the bias current were measured on digital voltmeters (DME1500, Kikusui Electronics Corp., Japan) after the RF component was separated through a low-pass filter circuit.5)

2.2. Samples
A pure nickel plate (99.9% purity) and a nickel-electroplated steel plate were prepared as the test specimens. The as-received nickel plate was cleaned with ethanol before the measurement, and the electroplated steel plate was cleaned with a degreasing agent and then rinsed with ethanol. The average thickness of the nickel layer was estimated to be $0.35 \times 10^{-6}$ m, as a result of ICP measurement after dissolving the specimen with nitric acid totally. After evacuating down to 2.6 Pa in the discharge chamber, high-purity argon was kept flowing at a pressure of 210 Pa 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 lamp.

An emission line of Ni I 341.45 nm was monitored to actively.5,6) The bias current may also change the energy distribution of electrons in the plasma and thus would affect the excitation efficiency to each energy level of sample atom depending on the excitation energy.12) The bias current may also change the energy distribution of electrons in the plasma and thus would affect the excitation efficiency to each energy level of sample atom depending on the excitation energy.12) As illustrated in Fig. 2(c), some of the self-bias voltage is consumed by introducing the bias current. The wave forms are symbolized by introducing the bias current. The wave forms are symbolized by introducing the bias current.

2.3. Bias-current Introduction Method
The principle of the bias-current introduction5,6,10 and the figure of merit in the analytical application6,7,10 have already been described elsewhere, so this method is briefly explained here.

An RF glow discharge induces a direct-current (DC) potential, called a self-bias voltage,11 in the cathode sheath region between the powered electrode (sample) and the plasma body (negative glow). The magnitude of the self-bias voltage is determined by various experimental parameters such as RF frequency, RF power, the pressure of plasma gas, and the electrode arrangement. This effect is because of a large difference in the mobility between positive ions and electrons in the plasma, and most of the DC potential appears to be negative near the powered electrode, because there becomes the development of an impedance sheath near the powered electrode.11) The self-bias voltage causes sample atoms to be ejected by ion bombardment, just similar to cathode sputtering in a DC glow discharge plasma.2,11) In a conventional RF discharge, no DC current is generated by the self-bias voltage.

As shown in Fig. 1, the self-bias voltage can be separated through a low-pass filter circuit, and further, a DC current can be conducted by connecting a variable load resistor. We call this current a bias current.5) The bias current can induce higher electron flows into the plasma; therefore, more electrons in the plasma cause various collision processes with analyte species and eventually their excitations occur more actively.5,6) The bias current may also change the energy distribution of electrons in the plasma and thus would affect the excitation efficiency to each energy level of sample atom depending on the excitation energy.12)
RF voltage turns to positive in a part of the RF waveform (see Fig. 2(d)); in this case, the plasma extends to the whole area of the glow discharge lamp, because electrons in the plasma move towards both of the electrodes alternately, eventually making the discharge to become unstable. Such a plasma condition is not suitable for the excitation source for atomic emission spectrometry; however, it is useful to clean the inner wall of the lamp through plasma-gas bombardment. The method suggested in this paper is based upon this phenomenon.

3. Results and Discussion

3.1. Bias Voltage-current Characteristics

Figure 3 shows variations in the emission intensity of Ni I 341.45 nm (a) and the bias voltage (b) as a function of the bias current, when a pure nickel plate is employed as a test sample. The emission intensity increases with the bias currents from 18 to 40 mA and reaches a maximum value. In the analytical application, the bias-current condition of 40 mA should be selected. As shown in Fig. 3(b), the bias voltage monotonically decreases with increasing bias current and then drops down to 50 V or less. It can be considered that such variations would be caused by the potential distribution of the plasma through the bias-current introduction, such that the model is described in Fig. 2.

Figure 4 represents photographic images of the plasma, which are observed from the axial direction of the hollow electrode, at several different bias currents. The plasma was restricted in the hollow electrode in the conventional RF discharge (Fig. 4(a)), and then it looked to be brighter along with increasing the bias current. At a bias current of 50 mA, the plasma began to be unstable and extended in the whole area of the glow discharge lamp including the wall of the grounded electrode, which was not suitable for the excitation source but useful for removal of adsorbed gases on the interior of the lamp. Higher bias currents might work more effectively for the pre-discharge but the value of 50 mA was a maximum in this equipment; therefore, we selected this condition (50-mA bias current) in a pre-discharge stage before the measurement.

3.2. Evaluation of Emission Signal Response

In order to evaluate the signal response when the discharge is ignited, we defined $\Delta t$ as follows: an elapsed time for which the emission signal is elevated from 12% to 88% of the steady-state intensity just after breakdown of the discharge, meaning that the response becomes better at smaller $\Delta t$. In this experiment, pure nickel plates were employed just after the lamp was exposed to air when they were exchanged. Figure 5 indicates a variation of $\Delta t$ at different pre-treatment times, for which the bias current of 50 mA is introduced before the measurement. It is clear to say that the bias-current introduction could improve the signal response at an initial stage of the discharge, probably because adsorbed gas species on the electrodes as well as the body of the discharge lamp would be removed. Our previous studies have reported that small amounts of nitrogen and oxygen gases cause their collisions with excited species of argon and thus quench the argon plasma in a Grimm-style glow discharge excitation source;\textsuperscript{13,14} therefore, entrainment of these impurity gases would suppress the emission intensity of the nickel line, especially at the initial stage of the discharge. $\Delta t$ was gradually reduced at longer pre-treatment time; however, the prolonged pre-discharge might exert any damage on the outermost surface of samples. Therefore, the pre-treatment time at a bias current of 50 mA was deter-

![Fig. 3. Variations in the emission intensity of Ni I 341.45 nm (a) and the negative bias-voltage (b) as a function of the bias current.](a) (b)

![Fig. 4. Photos of the plasma observed through the hollow electrode at bias currents of 0.0 mA (a), 20 mA (b), 40 mA (c), and 50 mA (d).](a) (b) (c) (d)

![Fig. 5. Variation in $\Delta t$ as a function of the pre-treatment time when a bias-current of 50 mA is introduced before the measurement. $\Delta t$ is defined as an elapsed time for which the emission signal is raised from 12% to 88% of the steady-state intensity at an initial stage of the discharge.](a) (b) (c) (d)
mined to be 20 s for the following measurements.

3.3. Effect of Bias-current Introduction

Figure 6 shows a typical example of variations in the emission intensity of Ni I 341.45 nm along with a duration time after ignition of the discharge plasma, for a pure nickel sample after introducing the 50-mA bias current for 20 s and without introducing the 50-mA bias current. In this case, both of the temporal profiles were measured at a bias current of 0 mA (conventional RF plasma). The effect of the bias-current introduction clearly appears in Fig. 6; the emission signal reaches a steady-state intensity more rapidly, such that $\Delta t$ is 5 s with the bias-current treatment, while it is 20 s without the bias current.

Figure 7 indicates a comparison of a depth profile in a nickel-electroplated steel plate having a thickness of $0.35 \times 10^{-6}$ m. In this case, the pretreatment by a bias current of 50 mA was conducted for 20 s. This operation could improve the signal response at an initial stage of the discharge, where $\Delta t$ was 7 s and 20 s when the bias current was introduced or not, respectively. On the other hand, the depth profile itself, which was derived from the nickel coating, was hardly affected by the pretreatment, as compared to the profile obtained by the conventional method. They were very similar to each other except for the initial response of the emission signal, implying that any damage of the sample surface was negligible through the pre-discharge. The etching rate in these profiles was estimated to be $0.12 \times 10^{-6}$ m/min.

4. Conclusions

A bias current, driven by the self-bias voltage in a 13.56-MHz RF glow discharge, can be controlled to change the characteristics of the plasma for atomic emission spectrometry. At higher bias currents, the resulting plasma spread in the whole area of the glow discharge lamp, including both the electrodes and the wall of the lamp, thus making the plasma unstable. However, such an operation enabled gaseous species, which were adsorbed on interior parts of the lamp when the sample was exchanged, to be removed. This effect improved the rising-response of the emission signal just after the discharge was ignited, and thus contributed to a precise depth profile in RF-GD-OES.

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