Enhancement Factor in the Emission Intensities Excited by Radiofrequency-powered Glow Discharge Plasma Associated with Bias-current Introduction

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The introduction of a d.c. bias current to an r.f. glow discharge plasma led to enhancement in the intensities of particular emission lines. Atomic emission lines having the excitation energy of 3–4 eV were commonly enhanced 10–20 times by conducting the bias current of 20–30 mA. The enhancement factor strongly depended upon both the pressure of the plasma gas and the r.f. applied power. The intensities of atomic emission lines having the excitation energy of c.a. 5.7 eV were much more elevated and their enhancement factors exceeded 50. However, little increases for emission lines having the excitation energy more than 7 eV were observed regardless of the plasma conditions.

KEY WORDS: glow discharge optical emission spectrometry; d.c. bias current; r.f. plasma; enhancement factor; excitation energy; copper.

1. Introduction

In a radiofrequency-powered glow discharge plasma, the self-bias potential plays an important role in sustaining the stable plasma as well as continuous ion bombardment against the powered electrode.1) We have reported that the self-bias voltage enables a d.c. current to be conducted through the plasma and that the conduction of the d.c. bias current can modify the characteristics of the plasma drastically, leading to an increase in the emission intensities by a factor of 10–20.2,3) We have also indicated that this effect contributes to improvement in the detection sensitivity for direct determination of impurities in steels.4) It is expected that glow discharge optical emission spectrometry (GD-OES) with such modified plasmas would be employed as an analytical tool for the production control of manufactured steels, because of the rapid response as well as the capability of multi-element and minor-element analysis.

The d.c. bias current induces an actual flow of electrons along the electric circuit including the plasma body from the grounded electrode to the powered electrode (sample).2,3) Therefore, a large number of electrons are introduced into the plasma not from the powered electrode but from the grounded electrode. It is considered that the driving force for the introduction of such electrons can be the plasma potential, because the plasma body is floated positively against not only the powered electrode but the grounded electrode.1) The introduced electrons have kinetic energies of a certain range which are relatively small since the plasma potential is only several 10 V. The electrons could contribute to the emission excitations through various collisional processes; however, their kinetic energies are not large enough for higher energy levels to be excited. Indeed, it was found that atomic emission lines having lower excitation energies (3–4 eV) were predominantly enhanced by the electron introduction.2,3) Furthermore, the introduced electrons are also consumed in recombination processes occurring in the plasma, which leads to any changes in the plasma itself. The decreased intensities of ionic argon lines were observed,2,3) probably resulting from recombination processes in which ionic argon species are involved.

When the bias-current conduction method is applied to the routine analysis, it is very important to determine the degree of enhancement for each analytical line. Enhancement factors strongly depend on the excitation energy of the emission lines. It is further expected that the enhancement factors are varied by several experimental parameters such as the bias current, the pressure of the plasma gas, and the r.f. power. Accordingly, the experimental conditions should be optimized for each analytical line. No systematic experiments were performed to investigate the effect of these parameters on the bias-current introduction. In this paper, in order to find the optimum experimental conditions for the bias-current introduction, we studied variations in the emission intensities of copper atomic lines (Cu I) having different excitation energies when the bias current is conducted. The enhancement factors were estimated for these Cu I lines.

2. Experimental

The principle of the bias-current controlled r.f. glow dis-
charge excitation source and the experimental system have already been described.\textsuperscript{2–4) Table 1 summarizes the apparatus, which consists of a Grimm-style glow discharge lamp\textsuperscript{5,6)}, an r.f. power supply system, and a d.c./r.f. separator unit, and the experimental conditions in detail. A \textit{P-type} electric circuit comprising capacitors and coils is utilized as a component to remove signals having frequencies higher than the cut-off frequency. The d.c./r.f. separator, comprising a blocking capacitor and the \textit{P-type} low-pass filter circuit, was designed and made in our laboratory. The self-bias voltage is monitored through the d.c./r.f. separator, and a d.c. current can be conducted by connecting a load resistor with the separator. The d.c. bias current can be controlled by varying the resistance.

Plates of pure copper were employed as the test sample. Ten atomic copper emission lines having excitation energies of 3.79–7.24 eV were measured. The assignment\textsuperscript{7)} for these Cu I lines is indicated in Table 2.

3. Results and Discussion

3.1. Dependence on Excitation Energy

Figure 1 shows the intensity variations of the Cu I lines as a function of the d.c. bias current conducted at an Ar pressure of 430 Pa. By introducing bias currents of 20–30 mA, the intensities of the Cu I 510.55-nm line became about 10 times greater than those without the bias current (open circle in Fig. 1). The intensities of the Cu I 327.40-nm line were varied similarly (the data are not indicated in Fig. 1 because it is difficult to estimate the intensities precisely due to the self-absorption\textsuperscript{8}). As listed in Table 2, the excitation energy of these Cu I lines is about 3.8 eV. It has been discussed in our previous reports\textsuperscript{2–4)} that the conduction of the bias current leads to intensity enhancement of particular emission lines having excitation energy.

Table 1. Instrumentation (a) and the experimental conditions (b).

| (a) | (b) |
| --- | --- |
| Glow discharge excitation source | Grimm-style structure\textsuperscript{3}) (Laboratory-made)\textsuperscript{4}) |
| hollow electrode | 8 mm in inner diameter |
| distance between the electrodes | 0.2–0.3 mm |
| plasma gas | Argon (99.9999%) |
| Spectrometer | P-5200 (Hitachi Corp., Japan) |
| Mounting | Czerny-Turner |
| focal length | 0.75 m |
| grating | 3600 grooves/mm |
| blaze wavelength | 200 nm |
| slit width | 30 μm |
| RF linear amplifier | Model HL-2K (Tokyo High Power Co. Ltd., Japan) |
| available forward power | 0–200 W |
| frequency range | 3–27 MHz |
| RF driver amplifier | Model WL-2000HF (World System Eng. Co. Ltd., Japan) |
| available frequency range | 0.1–30 MHz |
| Function generator | Laboratory-made |
| Roller-inductor tuner | Model MFJ-989C (MFJ Enterprises Inc., USA) |
| DC/RF separator (low-pass filter) | Laboratory-made |
| cut-off frequency | ca. 100 kHz |
| time constant | more than 12 dB/dec |
| Sample | Copper plate (99.99 %) |
| Analytical lines | see Table 2 |
| Ar pressure | 230–80 Pa |
| RF driving frequency | 13.56 MHz |
| RF forward power | 50–100 W |
| Reflected power | less than 1 W |

| Table 2. Observed emission lines and their assignment. |
| --- |
| Wavelength (nm) | Upper (eV) | Assignment\textsuperscript{7)} | Lower (eV) |
| Cu I 2317.90 | 4s4p \textsuperscript{4}P_1/2 (5.6882) | --- | 4s \textsuperscript{4}S_3/2 (0.0000) |
| Cu I 2121.46 | 4s4p \textsuperscript{4}P_1/2 (6.9858) | --- | 4s \textsuperscript{4}S_3/2 (1.3889) |
| Cu I 2211.57 | 4s4p \textsuperscript{4}P_1/2 (7.2361) | --- | 4s \textsuperscript{4}S_3/2 (1.6422) |
| Cu I 2222.78 | 4s4p \textsuperscript{4}P_1/2 (7.2057) | --- | 4s \textsuperscript{4}S_3/2 (1.6422) |
| Cu I 2822.44 | 4s4p \textsuperscript{4}D_3/2 (7.5773) | --- | 4s \textsuperscript{4}S_3/2 (1.3889) |
| Cu I 2962.16 | 4s4p \textsuperscript{4}P_1/2 (7.5746) | --- | 4s \textsuperscript{4}S_3/2 (1.3889) |
| Cu I 3242.40 | 4p \textsuperscript{4}P_3/2 (3.7858) | --- | 4s \textsuperscript{4}S_3/2 (0.0000) |
| Cu I 5105.55 | 4p \textsuperscript{4}P_3/2 (3.8166) | --- | 4s \textsuperscript{4}S_3/2 (1.3889) |
| Cu I 5155.32 | 4d \textsuperscript{4}D_5/2 (6.1910) | --- | 4p \textsuperscript{4}P_3/2 (3.7858) |
| Cu I 5211.82 | 4d \textsuperscript{4}D_3/2 (6.1919) | --- | 4p \textsuperscript{4}P_3/2 (3.8166) |

Fig. 1. Changes in the emission intensities of several Cu I lines as a function of the bias current. Ar pressure: 430 Pa; r.f. forward power: 80 W.
energies of 3–4 eV and that this technique can be applied to measurement of atomic resonance lines which are usually employed as analytical lines in GD-OES. The data of the Cu I 510.55-nm line well follow this previous conclusion. Figure 1 also shows that some of the Cu I lines such as the Cu I 282.44 nm, whose excitation energy is 5.6–5.8 eV, were enhanced more largely, whereas little intensity increase was observed in the other Cu I lines such as the Cu I 221.57 nm. The Cu I lines where the intensity increases are not observed have excitation energies of more than 6.2 eV, as shown in Table 2. It is a noticeable feature that the intensity enhancement occurs selectively depending on the excitation energy of the Cu I lines. While the intensities of the Cu I 282.44-nm line increased 33-fold and the Cu I 296.12-nm line 58-fold, those of the Cu I 221.57-nm decreased with increasing bias currents.

The flow of the bias current should introduce a great many electrons into the plasma from the grounded electrode; in this case, the plasma potential may work as a driving force for the injection of electrons. The introduced electrons can excite particles in the plasma through various collisions and then their kinetic energies principally determine possible excited species. The results in Fig. 1 are probably because the kinetic energies of the introduced electrons are relatively uniform as well as not so large, which might result from acceleration of the electrons by the plasma potential only when they pass through a thin sheath region near the grounded electrode. In a conventional glow discharge plasma (without the bias current), excitations to copper excited species occur in the negative glow region by various collisions in which electrons and excited species like argon metastables are involved. Of course, the introduced electrons also cause recombination reactions with charged particles like argon ion in the plasma, which possibly exerts positive or negative effects on the emission excitation in the plasma. Simultaneously when the introduced electrons enable copper atoms to be excited with their kinetic energies, they indirectly influence other channels of the copper excitation caused by excited species in the glow region since the population of the excited species is varied by introducing the bias current. These effects may be investigated by changing the pressure of the plasma gases because the mean free path of electrons and the probability of these collisions are closely related to the gas pressure.

3.2. Influence of Ar Pressure

Figure 2 shows changes in the emission intensities of 6 Cu I lines as a function of the Ar pressure when the bias current is not conducted (circles) and the bias currents of 20–30 mA are conducted (square). These variations are very different for each Cu I line. It is clear from the upper 3 graphs of Fig. 2 that the emission intensities of Cu I 510.55 nm, Cu I 296.12 nm, and Cu I 282.44 nm are greatly enhanced by conducting the bias current. The intensity of Cu I 510.55 nm gives a maximum peak at an Ar pressure of 450 Pa, and that of Cu I 296.12 nm or Cu I 282.44 nm reaches a maximum at 330–400 Pa. On the other hand, the intensity of Cu I 221.46 nm or Cu I 221.57 nm gives a small peak at 300–340 Pa; however, their peaks are meaningless for the analytical application because larger intensities can be obtained at greater Ar pressures. Further, when the Ar pressure exceeds 450 Pa, their intensities are smaller than those.
obtained without the current introduction. In the case of Cu I 521.82 nm, the enhancement is less prominent compared to that of Cu I 296.12 nm, even though a clear peak appears at 430 Pa when conducting the bias current. It is found from Fig. 2 that the Cu I lines having higher excitation energy are not enhanced and in some cases are declined by the introduction of the bias current, regardless of the Ar pressure in the plasma. The conduction of the bias current is less effective for the emission excitation for all of the Cu I lines at larger pressures of Ar.

Figure 3 shows a dependence of the bias voltage on the Ar pressure. It indicates a decrease in the bias voltage with increasing Ar pressure, possibly implying that the plasma potential also decreases. As a result, it is likely to say that the kinetic energies of the introduced electrons decrease at greater Ar pressures, corresponding to the decrease in the plasma potential loaded between the plasma body and the grounded electrode. Also, the probability of collisions in the plasma is raised with increasing Ar pressures, directly leading to a decrease in the mean free path of the electrons. Further, recombination reactions with the introduced electrons result in loss of excited particles like argon ion. Such plasma modifications are generally unfavorable for excitations of species requiring higher excitation energies close to the ionization potential.

An enhancement factor (EF) is defined as the ratio between the maximum intensities obtained with the bias current and the intensities without the bias current. Figure 4 indicates an dependence of EF for three Cu I lines on the pressures of Ar. Different optimum conditions of the Ar pressure are found between the Cu I 296.12-nm line and the Cu I 510.55-nm line. In the Cu I 221.57-nm line, the EF of about 10 is obtained at the Ar pressure of 230 Pa; however, this condition is not available for the analytical application because the absolute value of the intensities is fairly small. It should be noted that the intensities of the Cu I 296.12-nm line (the excitation energy is 5.57 eV) have a very large EF. Similarly, EFs of the Cu I 217.90 nm (5.69 eV) and the Cu I 282.44 nm (5.78 eV) are predominantly large. It is expected that, also for other elements, the EF of emission lines having the excitation energy of c.a. 5.7 eV may be selectively elevated. This effect gives useful information for the line selection when the bias-current conduction method is employed.

3.3. Influence of RF Forward Power

Figure 5 shows plots of the emission intensities of 6 Cu I lines as a function of the RF forward power when the bias current is not conducted (circles) and the bias currents are conducted (square). The bias current conducted is shown in Fig. 6(a) and variations in the bias voltage for each RF power are shown in Fig. 6(b). Larger bias currents can be introduced into the plasma at larger RF forward powers, while the bias voltages decrease with the bias current. Our previous studies reported on similar results.2,4) The emission intensities of Cu I 510.55 nm, Cu I 296.12 nm, and Cu I 282.44 nm are always enhanced by conducting the bias current at all the r.f. powers applied. The intensities of Cu I 221.46 nm and Cu I 221.57 nm slightly increase with the bias-current introduction; however, the changes strongly depend on the r.f. power. At r.f. powers of more than 80 W, their intensities become smaller if the bias current is introduced.

Figure 7 shows variations in the intensity ratio, Cu I 221.57/Cu I 510.55, as a function of the r.f. power. If the bias current was not conducted (circles), the intensity ratio increases with the r.f. power. The excitation of the Cu I 221.57 nm requires larger energies (7.24 eV), compared to that of the Cu I 510.55 nm. In the normal r.f. plasma (without the bias current), the increase in the r.f. powers can lead to the increased population in the corresponding energy level. However, the introduction of the bias current never promote these excitations even though the r. f. powers in-
crease, as indicated in Fig. 7 (squares). This effect is probably because the introduced electrons cannot contribute to such excitations and further de-excite highly-excited species (ionic species) through recombination processes.

4. Conclusions

The introduction of the bias current leads to enhancement in the emission intensities excited by the r.f. glow discharge plasma. It is the most important standpoint that particular emission lines are selectively enhanced, which is principally determined by the excitation energy of the corresponding upper energy level. The EFs are also dependent on the pressure of Ar as well as the r.f. forward power; therefore, the optimization for these parameters is required. The intensities of emission lines having the excitation energy of 3–4 eV: in most cases, atomic resonance lines, are el-
evated 10–20 times. This is absolutely effective for analytical application of GD-OES, because atomic resonance lines are usually employed as the analytical lines in GD-OES. In addition, the data presented in this paper show that the emission lines having the excitation energy of c.a. 5.8 eV are much more enhanced by the bias-current conduction: the resulting EF is more than 50.

In steel-making processes, direct determination of minor elements provides useful information for the process and the quality control of manufactured steels. Rapid analysis of impurity elements in steels such as Cu, Pb, Bi, Sb, Sn, called ‘tramp’ elements, is recently required so that used commercial materials can be recycled and reused. It is expected that the r.f. GD-OES can be employed as a powerful tool for this purpose. If the bias-current introduction method is applied to the r.f. excitation source, the ‘tramp’ elements would be detected more sensitively because their analytical lines have the excitation energy of 5–6 eV; for example, Si I 288.16 nm (5.08 eV), Sb I 287.79 nm (5.36 eV), Cd I 228.80 nm (5.42 eV), Zn I 213.86 nm (5.80 eV), Te I 238.58 nm (5.78 eV), Pb I 217.00 nm (5.71 eV), Bi I 289.80 nm (5.69 eV), and Sn I 326.23 nm (4.88 eV).

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