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Application of a Bias-Current Modulation Technique to Radio-Frequency Glow Discharge Optical Emission Spectrometry

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A 13.56-MHz Grimm-style glow discharge plasma in which pulsated bias currents are introduced was investigated concerning the analytical applications. The d.c. bias currents driven by a self-bias potential are conducted through the r.f. plasma body by using a low-pass filter circuit and a variable resistor. Excitation by a modified r.f. plasma can yield larger emission intensities. By modulating the bias current associated with phase-sensitive detection, the emission intensities can be measured at very low noise levels, enabling the detection limit to be improved more. A detection limit of 3×10^{-4} mass % was obtained for Mn determination in Fe-based binary alloy samples, whereas 1.4×10^{-2} mass % Mn was obtained in the conventional excitation of an 80-W r.f. discharge plasma.

Keywords Radio-frequency Grimm glow discharge plasma, conduction of the bias current, current modulation, self-bias potential, detection limit, Fe-based alloys

Glow discharge optical emission spectrometry (GD-OES) is now an important analytical method for the direct determination of solid samples, and a powerful tool for the quality control of various manufactured materials.[1] Radio-frequency (r.f.) glow discharge plasmas[1,2] as well as conventional d.c. ones are employed in analytical applications.[3–6] The use of r.f. plasmas enables non-conductive samples, such as polymer coatings, to be analyzed by using a similar handling for the analysis of conductive samples. Several workers have reported on the emission characteristics of r.f. glow discharge plasmas: the effects of the discharge power, the discharge gas pressure, r.f.-driving frequency, and the structure of the discharge tube.[3–9] The self-bias phenomena of r.f. glow discharges[2] play an important role in sustaining stable plasmas as well as continuous ion bombardment against the powered electrode. It was reported that control of the self-bias d.c. voltage could result in an improvement of the analytical performance in the r.f. GD-OES.[10–12] We investigated the effect of externally applied bias voltages on the emission intensity from a 13.56-MHz Grimm-style glow discharge plasma source, and indicated that the d.c. voltages superimposed on the r.f. plasma led to an enhancement in the emission intensities.[11]

Our previous studies have also revealed that the conduction of a d.c. bias current could boost the emission excitation in the r.f. GD-OES.[13,14] The self-bias voltage is monitored by separating the d.c. voltage component with the use of a low-pass filter circuit; further, it is possible to conduct a d.c. current through the plasma body by connecting a load resistor with the low-pass filter circuit. It was observed that atomic emission lines resulting from lower energy levels were predominantly enhanced, and that their intensities were 10 – 20 times larger than those emitted by the r.f. plasma alone.[14]

In this paper, we report on a combined technique in where a pulsated flow of a d.c. bias current is introduced into the 13.56-MHz r.f. plasmas with the aid of a switching circuit. As a result, the emission signals can be modulated at the frequency of the pulsated d.c. current. The resulting modulated components can be selectively detected with a lock-in amplifier at low noise levels, which might better the detection power of the r.f. GD-OES. In the determination of minor elements in Fe-based alloys, the detection limits with the lock-in detection are described.

Experimental

Principle of measurement

The principle of a bias-current controlled r.f. glow discharge excitation source has been described elsewhere.[13] It is well known that an r.f. glow discharge induces a d.c. potential, which is called a self-bias voltage[1], between the powered electrode (sample) and the plasma. Low-pressure glow discharges have relatively large self-bias voltages (several hundred volts)[8,9], because a sheath electric field at the electrodes is generated due to the much greater mobility of electrons in the discharges. As illustrated in Fig. 1, the self-bias voltage can be monitored with a low-pass filter circuit comprising L_1 and C_2; further, it is possible to conduct a d.c. current through the overall circuit including the plasma body by connecting a load resistor (R). The low-pass filter was made with a cut-off frequency of approximately 300 kHz, and the resistance values of

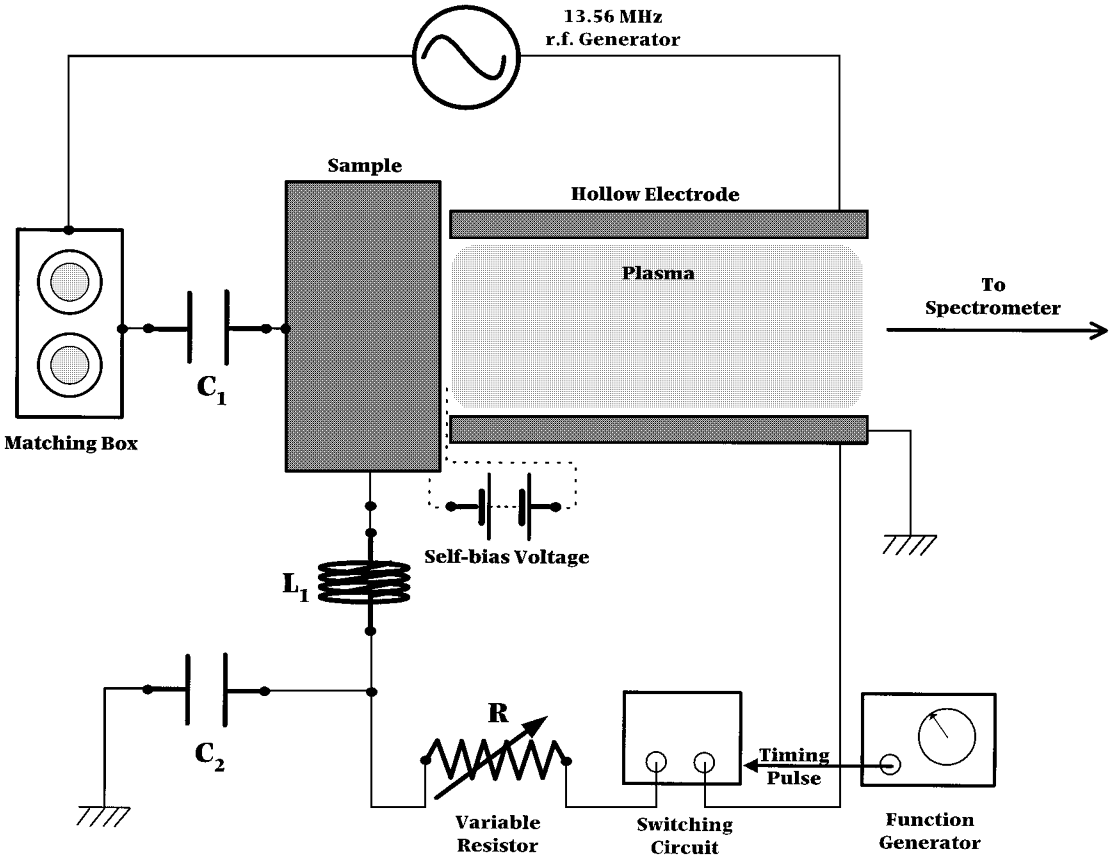

Fig. 1 Switching of the bias-current in a Grimm-style r.f. glow discharge lamp.

the load resistor varied over the range from 2.2 to 76 kΩ. An appropriate adjustment of the resistance enables a d.c. bias current to flow in maintaining stable r.f. discharges. D.c. bias currents as large as 50 mA could be conducted at a self-bias voltage of about 300 V.[13] As a result of the d.c. bias current, a large number of electrons are injected not from the sample electrode but from the hollow electrode into the r.f. plasma; thus, the characteristics of the plasma could be varied drastically. A noticeable increase in the intensities of the atomic emission lines of which excitation energies are less than 4 eV is observed. This effect is probably because collisions caused by the injected electrons are favorable for excitations of such atomic emission lines.

With a switching circuit shown in Fig. 1, the flow of a d.c. bias current can be modulated at a specified frequency determined by a function generator. A lock-in amplifier is commonly used to selectively detect signals having an alternating component. Recently, a DSP (digital signal processor) technique has also been applied to the lock-in amplifier, which contributes to a larger dynamic reserve compared to that of the analogous one.[15] Detection with the DSP lock-in amplifier enables the emission intensities to be obtained at very low noise levels, and thus gives accurate data regarding the spectrometric determination, especially for faint emission signals. It is therefore expected that the bias current modulation technique associated with the lock-in amplifier detection is very advantageous for the determination of trace elements.

Instrumentation

Figure 2 illustrates a block diagram of the apparatus used in this work, consisting of a Grimm-style glow discharge lamp[16], a discharge power supply system, and a light detection system. The structure of the glow lamp[17], the power supply[13,14], and the spectrometer[7] have been already described.

The TTL-level signal of the function generator was employed as a timing pulse for regulating the pulsated glow discharge. The average bias current was recorded on a digital multimeter (DME1401, Kikusui Electronics Corp., Japan), which enabled the RMS values of the current to be directly measured at frequencies of up to 20 kHz.

The dispersed emission signals were detected with a DSP lock-in amplifier (SR-830, Stanford Research System, USA) associated with a bandpass filter (FV-651, NF Circuit Design Block Corp., Japan). The time constant was set to be 0.1 s with synchronous filtering.[15] The resulting lock-in output was recorded with an analogous pen recorder (R-50, Rikadenki Kogyo Corp. Japan), or with a personal computer (PC-486SR, Epson, Japan) *via* the RS-232C interface of the lock-in amplifier. In addition, digital data of the emission signal were recorded on a personal computer (PC-286VS,

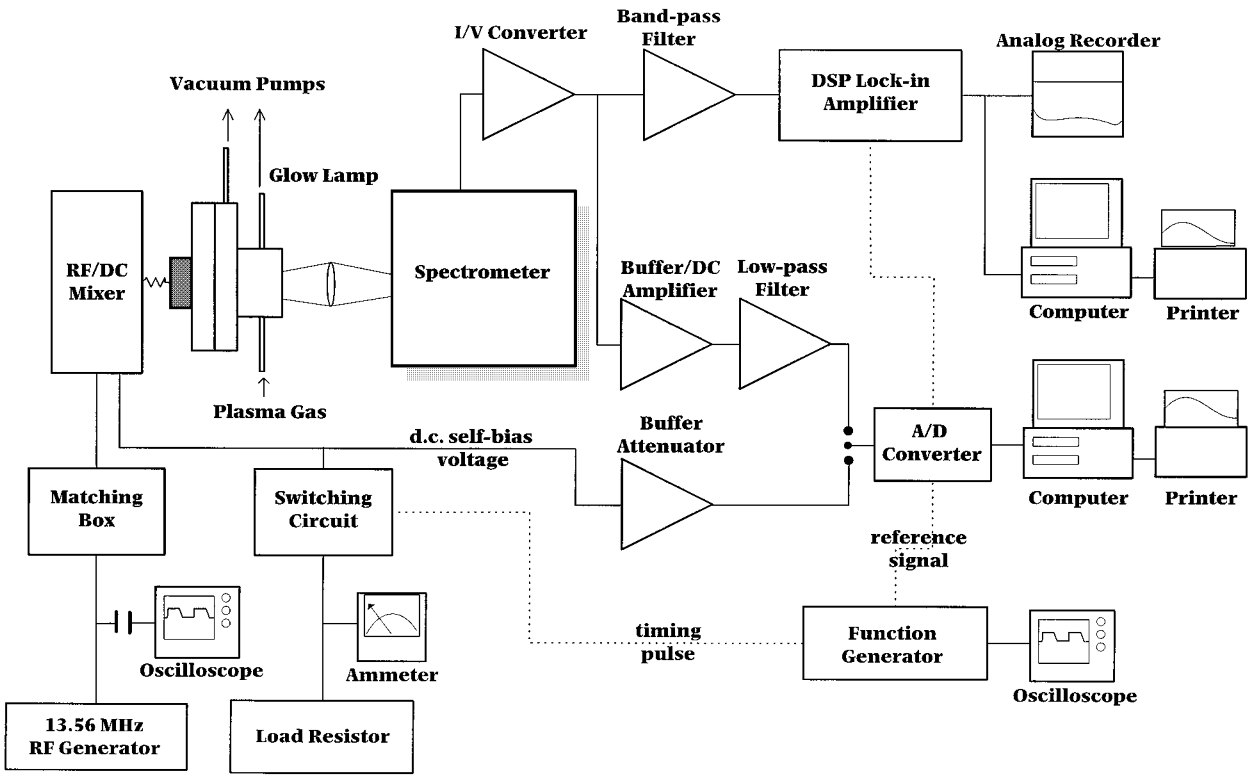

Fig. 2 Schematic block diagram of the experimental apparatus.

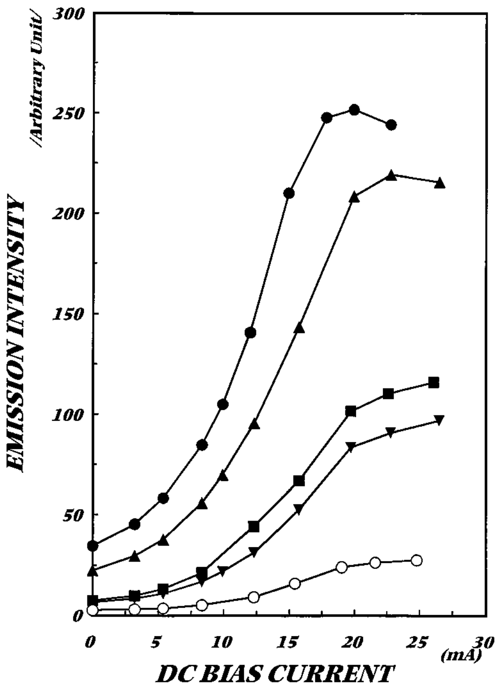

Fig. 3 Variations in the emission intensities of atomic nickel emission lines: Ni I 352.45 nm (●), Ni I 346.17 nm (▲), Ni I 305.08 nm (■), Ni I 301.20 nm (○), and Ni I 300.36 nm (▼), as a function of d.c. bias current. Sample: nickel plate; r.f. forward power: 60 W; Ar pressure: 400 Pa.

Epson, Japan) equipped with an analogous-to-digital converter board (ADM-5498BPC, Microscience Corp., Japan). The time dependence of the emission intensities as well as the self-bias voltage could be *in-situ* observed.

Procedures

High-purity argon (>99.99995%) was employed as the plasma gas at pressures ranging from 320 Pa (2.5 Torr) to 400 Pa (3 Torr) to obtain larger emission intensities.[13] The lamp was evacuated to less than 1.3 Pa by two oil rotary pumps and then the plasma gas was introduced to flow continuously during the measurements. The pressure of argon gas was regulated by a needle valve with the use of a calibrated Pirani gauge (GP-2T, ULVAC, Japan).

Nickel plates (purity >99.8%) were prepared for investigating the emission characteristics, and three series of Fe-based binary alloys (standard sample for an X-ray fluorescence analysis, The Iron and Steel Institute of Japan) containing 0.2, 0.5, 1.0 mass % Cu, 0.5, 0.98 mass % Cr, and 0.2, 0.49, 0.97 mass % Mn for obtaining the calibration parameters as well as the detection limits. The surfaces were mechanically polished with water-proof emery papers and then rinsed with ethanol. Pre-discharges for about 20 min were carried out to remove any surface contamination and oxides.

Results and Discussion

Figure 3 shows the intensity changes of the atomic

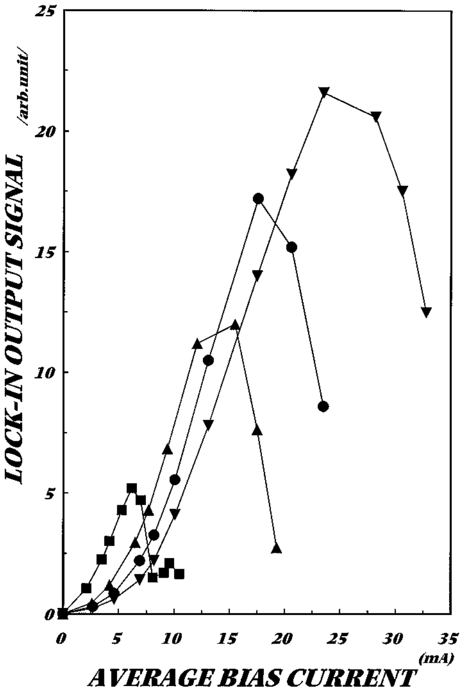

Fig. 4 Variations in the lock-in output at the Ni I 352.45-nm line as a function of the average bias current at several r.f. forward powers: 80 W (▼), 70 W (●), 60 W (▲), and 50 W (■). Sample: nickel plate; Ar pressure: 400 Pa; modulation frequency: 250 Hz.

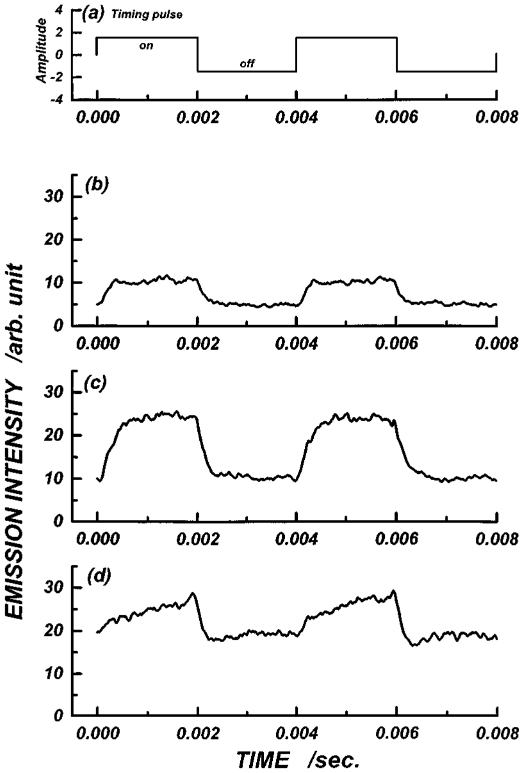

Fig. 5 Time dependence of the emission intensity of Ni I 352.45 nm when pulsated bias currents are conducted at average values of 9.0 mA (b), 14.8 mA (c), and 19.3 mA (d). Sample: nickel plate; Ar pressure: 400 Pa; r.f. forward power: 60 W; modulation frequency: 250 Hz; a/d sampling interval: 5 μs; a/d sampling number: 1600; cut-off frequency of low-pass filter: 10 kHz.

nickel emission lines: Ni I 300.36 nm (4.24 eV), Ni I 301.20 nm (4.54 eV), Ni I 305.08 nm (4.09 eV), Ni I 346.17 nm (3.61 eV), and Ni I 352.45 nm (3.54 eV)[18,19], as a function of the d.c. bias current conducted. This measurement was carried out in a non-pulsated current mode. By introducing bias currents of 20 – 24 mA, these Ni I intensities became 10 – 15 times greater than those obtained without the bias current. A d.c. bias current introduces a large number of electrons into the r.f. plasma, which could help to promote these excitations.[13] Because conduction of the bias current is maintained by a self-bias voltage induced in the r.f. plasma, large bias currents result in a great consumption of the self-bias potential. It was observed in a previous report[14] that the bias voltages gradually decreased with increasing bias currents and that the r.f. plasmas became unstable when the bias voltage was reduced down to about 100 V. This effect might be because the cathode sheath for maintaining a stable discharge is prominently destroyed when larger bias currents are conducted, which determines the optimum experimental conditions regarding the d.c. bias current.

Figure 4 shows the variations in the lock-in output measured at the Ni I 352.45 nm line as a function of the bias current when the current flow is pulsated at a frequency of 250 Hz. The shape of these curves is very similar for several different r.f. forward powers; the lock-in signals of the Ni I intensities increase with the bias currents and then give maximum values. At higher r.f. discharge powers, larger d.c. bias currents flow and larger lock-in output signals are obtained up to each maximum value. It can be seen from Fig. 4 that the d.c. bias current should be selected strictly so that larger lock-in signals can be obtained. An 80-W discharge gives the largest emission intensity at average bias currents of 25 – 30 mA.

Figure 5 shows the time dependence of the emission intensities of the Ni I 352.45 nm line at three different average bias currents (b) – (d) in a 60-W r.f. discharge plasma, together with a reference signal of 250 Hz (a). According to the switching of the bias current, the Ni I intensities can be varied periodically at the reference frequency. The Ni I intensity variations obtained at 9.0 mA (b) and 14.8 mA (c) follow the square-wave form of the 250-Hz reference, whereas those at 19.3 mA (d) are somewhat distorted. It seems that, up to a bias current of 14.8 mA, the intensity differences between the on- and off-switching periods increase with the average bias current, while following the frequency as well as the phase of the reference. This is favorable for phase-sensitive detection[15], which could result in an increase in the lock-in output signal, as shown in Fig. 4. However, at a bias current of 19.3 mA, the intensity component modulated at the reference frequency is clearly reduced compared to that at 14.8 mA, thus lead-

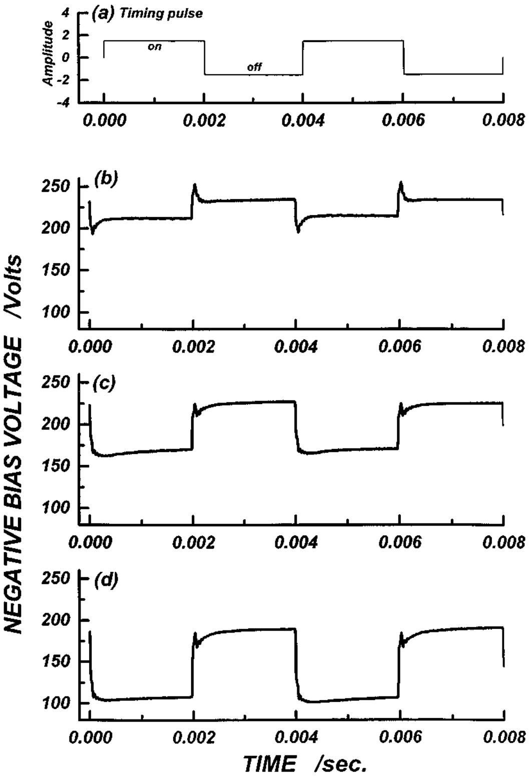

Fig. 6 Time dependence of the d.c. bias voltage when pulsated bias currents are conducted. The experimental conditions are the same as in Fig. 5.

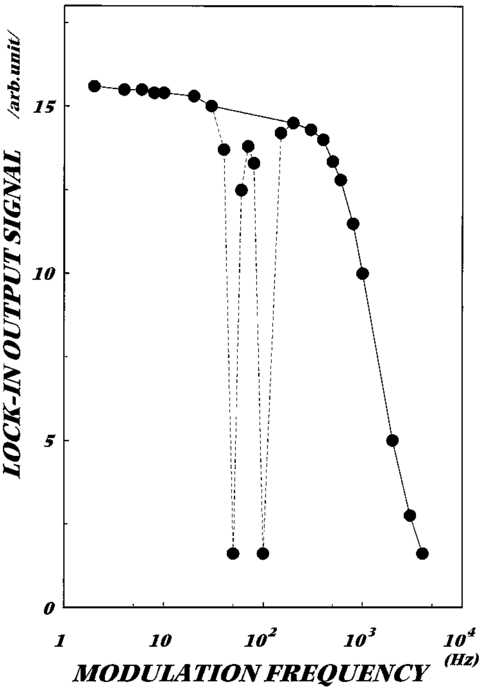

Fig. 7 Frequency dependence of the lock-in output at the Ni I 352.45-nm line when a pulsated bias current is conducted at the average value of 9.1 mA. Sample: nickel plate; Ar pressure: 400 Pa; r.f. forward power: 70 W.

ing to an decrease in the lock-in output signals at the bias currents of more than 15 mA. Figure 6 shows the time dependence of the d.c. bias voltages monitored under the same discharge conditions as in Fig. 5. The 60-W r.f. discharge alone induced a negative self-bias voltage of 260 V. The apparent d.c. bias voltages decrease when the bias current is conducted through the plasma body. It is clear from Fig. 6 that the apparent bias voltages do not return to 260 V (the self-bias voltage in the 60-W r.f. discharge alone) when the switching circuit is turned off. This effect results from an electric performance of the switching circuit; its resistance does not become infinity during the off-switching periods. Therefore, smaller d.c. bias currents can be conducted even when the switching circuit is turned off. It can be seen in Fig. 5 that the emission intensities in the off-switching period are gradually elevated with increasing bias currents. This is also due to leakage of the d.c. bias current. At a bias current of 19.3 mA (Fig. 6(d)), the voltage changes exceed 150 V in each pulse period, and the bias voltage in the on-switching period is reduced down to about 100 V. It is probable that the large voltage drop down to 100 V causes the r.f. discharges to be partly unstable, and therefore, the emission intensities might be modulated insufficiently, as shown in Fig. 5(d).

Figure 7 shows the variations in the lock-in output of the Ni I 352.45 nm line as a function of the modulation frequency in a 70-W r.f. discharge plasma. The lock-in output signals are slightly dependent on the modulation frequencies ranging from 2 Hz to 500 Hz; however, they are reduced adruptly at frequencies of more than 1 kHz. Sudden drops at both 50 Hz and 100 Hz are due to band elimination filters of the lock-in amplifier which remove any noise of the 50-Hz power line. Figure 8 shows the time dependence of the Ni I emission intensities at three different modulation frequencies at an average bias current of 9.1 mA. At the 2-kHz modulation (Fig. 8(a)), the resulting variation in the Ni I intensities is seriously distorted; accordingly, its phase differs from the phase of the reference signal and the modulated component becomes much smaller. If the modulation frequency increases up to 5 kHz, the modulated component was less observed and the intensity pattern was similar to that with the corresponding bias current being non-pulsated. It seems that the emission processes occurring in the r.f. plasma cannot respond to any variations in the d.c. bias current at relatively higher modulation frequencies; however, the detailed mechanism has not been specified at the present stage. On the other hand, the intensity variations obtained at frequencies of 20 Hz (b) and 200 Hz (c) follow a square-wave form as well as the phase of the reference signal. These effects well explain the modulation frequency dependence of Fig. 7.

The calibration parameters for Cr, Mn, and Cu determination in Fe-based binary alloy samples were estimated using the bias current conduction technique associated with lock-in detection. The experimental parameters employed are as follows: an r.f. forward

Table 1 Statistical data on the calibration curves Cr, Mn, and Cu in Fe-based binary alloys

Emission line/nm	D.C. bias current conducted/mA	Detection method	Calibaration curve			Detection limit[a] (mass %)
			Slope	RSD,%	R^2	
Cr I 425.43	0	conventional	107	0.9 – 1.3	0.9981	1.7×10^{-2}
	27.8 (245 Hz)	lock-in	1689	0.2 – 0.5	0.9979	8×10^{-4}
Mn I 403.10	0	conventional	84	1.0 – 1.9	0.9989	1.4×10^{-2}
	27.8 (245 Hz)	lock-in	2239	0.1 – 0.5	0.9993	3×10^{-4}
Cu I 327.40	0	conventional	30	1.1– 2.2	0.9999	2.9×10^{-2}
	28.1 (245 Hz)	lock-in	881	0.2 – 0.3	0.9997	7×10^{-4}

a. Content corresponding to three times the standard deviation of background fluctuations measured at 424.5 nm(Cr), 402.8 nm(Mn), and 327.7 nm(Cu).

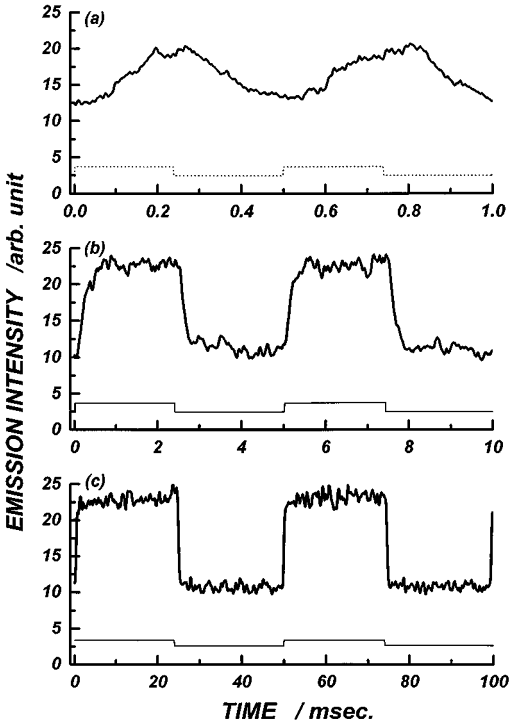

Fig. 8 Time dependence of the emission intensity of Ni I 352.45 nm when pulsated bias currents are conducted at the modulation frequencies of 2 kHz (a), 200 Hz (b), and 20 Hz (c). Sample: nickel plate; Ar pressure: 400 Pa; r.f. forward power: 60 W; average bias current: 9.1 mA; a/d sampling interval: 1 µs (a) , 10 µs (b), and 100 µs (c); a/d sampling number: 1600; cut-off frequency of low-pass filter: 100 kHz (a), 10 kHz (b), and 1 kHz (c).

power of 80 W, an Ar pressure of 320 Pa, a modulation frequency of 245 Hz, and an average bias current of 27.8 – 28.2 mA. These conditions were determined so that largest lock-in output signals could be obtained under stable glow discharges. Table 1 gives calibration data as well as the detection limits for Cr I 425.43 nm, Mn I 403.10 nm, and Cu I 327.40 nm. The detection limit was based on three-times the standard deviation of the corresponding background fluctuation. In the Mn determination, for example, the results are 7×10^{-4} mass % Mn in the conventional detection and 3×10^{-4} mass % Mn in the lock-in detection. Low noise levels obtained with the lock-in amplifier can contribute to better detection limits by a factor of 2.3 – 4.5. For a comparison, detection limits with the 80-W r.f. discharge alone were also estimated. The detection limits in the lock-in detection were 22 – 47 times better than those obtained with the conventional excitation method. It is expected that the proposed method can be successfully applied to the direct determination of trace elements.

The data presented in this paper demonstrate that conduction of the pulsated d.c. bias current in the r.f. glow discharge excitation source is an effective technique to better the detection limits in the r.f. GD-OES. The flow of a d.c. bias current introduces a great many electrons into the plasma, and thus the injected electrons could promote the emission excitations. The bias current therefore results in an enhancement of the emission intensities; furthermore, the pulsated bias current is available for phase-sensitive detection to select the emission signals at low noise levels. The analogous-to-digital converted data demonstrate that the modulated components in the emission signals determine the analytical performance of the detection method suggested in this paper. Leakage of the bias current when the switching circuit is turned off exerts a negative effect on the performance, because the intensity differences between the on- and the off-switching periods are limited. It is desirable to employ a switching circuit having the leakage current as small as possible, so that the detection limit can be further improved.

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