Application of Pulsed Voltage to d.c. Glow Discharge Plasma for Controlling the Sputtering Rate in Glow Discharge Optical Emission Spectrometry

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The application of a pulsed voltage to a Grimm-style glow discharge lamp was investigated to control the sputtering rate in d.c. glow discharge optical emission spectrometry. This purpose is to reduce the sampling depth so that thin film-like samples can be measured with a better spatial resolution and a better analytical precision. While the sputtering rate decreases by using a pulsed voltage due to the reduction in the effective discharge power, the emission signals from the glow discharge plasma are modulated by a cyclic variation of the discharge voltage so that only the desired signals can be detected without any noises with a lock-in amplifier. Whereas the sputtering rate could be more than 50 % reduced when the duty ratio of the pulsed voltage was down to 20 % compared to the rate in the corresponding continuous discharge, the emission intensities could be estimated with much better signal-to-noise ratios.

KEY WORDS: glow discharge optical emission spectrometry; sputtering rate; pulsed voltage; light modulation; chromium; steel.

1. Introduction

The Grimm-style glow discharge emission source\(^1\) has been extensively employed for in-depth analysis of various materials.\(^2,3\) This technique is especially suitable for the process control of manufactured materials such as electroplated films because it does not require an operation under ultra-high vacuum conditions and thus gives a rapid analytical response. The sputtering occurring in the glow discharge plasma is relatively severe (the sputtering rate can be typically 1 \(\mu\)m min\(^{-1}\)); therefore, relatively thick layers were major samples in glow discharge optical emission spectrometry (GD-OES).\(^4\) On the other hand, various materials comprising thin films have been recently developed for electric and magnetic devices, and therefore, an analytical method is required for the process control of such film-like materials having the thickness of several 10 nm. Several researchers reported on the application of GD-OES to thin-film analysis using conventional glow discharge spectrometers and yielded some interesting information on the composition and the structure of thin-film samples.\(^5,6\) However, a sampling depth of the order of 1 nm needs to be analyzed to obtain the accurate elemental composition of these thin-film samples. One must reduce the sampling depth, i.e. the minimum detectable amount of sample atom, in order to get the elemental composition in depth profiling more accurately.

Lower discharge powers decrease the sputtering rate in GD-OES, but this generally degrades the analytical performance because the resultant decrease in the sampling amount leads to a reduction in the signal-to-noise ratio as well as the net intensity of emission lines. Therefore, reducing the discharge power is not necessarily a good choice for controlling the sputtering rate. Changing the plasma gas was a possible option for this. It is well known in the glow discharge plasma that the plasma gas plays an essential role in the characteristics of the discharge and in the excitation of sample atoms.\(^7,12\) Compared with argon discharges, argon–helium mixed gas plasmas yield a suppression in the sputtering rate without degrading the analytical performance as well as the discharge stability.\(^12\) In addition, because helium atom has larger excitation energies, a better detection sensitivity was reported in the determination of some elements by use of an argon–helium mixed gas glow discharge plasma.\(^13\) Another approach is to adopt a new detection method of the emission signals. Modulation spectroscopy could be a suitable option because the plasma is easily modulated by changing the discharge voltage periodically.\(^14,15\) In this method, the effective discharge power is reduced and thus the resulting sputtering rate also decreases. However, the modulated component of the emission intensity can be selectively detected without any noises by using phase-sensitive detection with a lock-in amplifier, leading to an improvement in the signal-to-noise ratio even though the overall amount of sample atoms is reduced and conversely contributing to get more precise analytical values.\(^15,16\)

I have reported on a modulation technique in radiofre-
quency-powered GD-OES in which the radiofrequency voltage is cyclically varied, in order to improve depth profiling of thin-film samples.\(^{17}\) In the present study, a pulsed discharge voltage is applied to control the sputtering rate in d.c. GD-OES and the modulation detection technique is also employed to get good analytical performance. For this purpose, the most important experimental parameter is the duty ratio of the pulsed voltage. In order to get analytical information with good accuracy and precision, experimental parameters regarding the voltage modulation should be optimized so that a larger signal-to-noise ratio as well as a larger signal-to-background ratio can be obtained. Related to the sputtering rate, experimental parameters such as the duty ratio, the bias voltage, and the amplitude of the pulsed voltage are investigated.

2. Experimental

The principle of the discharge voltage modulation\(^{14}\) and the experimental system\(^{16}\) have been already described. A schematic diagram of the voltage pattern is illustrated in Fig. 1. Whereas a conventional glow discharge in GD-OES is usually operated in a direct voltage mode, an alternating voltage \((\Delta V)\) is superimposed on a d.c. bias voltage \((V_0)\) for the purpose of modulation so that the radiation excited by the plasma can be varied according to the frequency of the alternating voltage. The wave pattern of the applied voltage is fully regulated with a function generator or a personal computer so that the wave form, the duty ratio, the alternating voltage, and the d.c. bias voltage can be pre-determined individually. The modulated components are selectively detected with a lock-in amplifier tuned to the modulation frequency. The lock-in amplifier has an ability to detect only the signals corresponding to the frequency and phase of the reference and to remove any noises at frequencies other than the reference frequency. The effect of the modulation frequency on the emission characteristics has already been investigated\(^{14}\) and it was predetermined at 217 Hz to get larger emission intensities. Table 1 summarizes the apparatus employed and the experimental conditions in detail.

In this work, chromium in steel samples was investigated by using the Cr I 425.43-nm line as the analytical line. Standard reference materials of low-alloyed steel (No. 150-1 to No. 155-1, The Iron and Steel Institute of Japan) containing 3.0 to 0.11 mass% Cr were employed to investigate the analytical characteristics as well as to get a calibration curve. They were polished with waterproof emery papers and then rinsed with ethanol. Before the measurement, pre-discharges were carried out for about 10 min to measure the emission intensities under a steady discharge condition. The average sputtering rate was estimated from weighing the samples after a 30 to 40-min discharge.

3. Results and discussion

3.1. Waveform of Emission Signal Under Pulsed Discharge

Figure 2(a) shows waveforms of the discharge voltage loaded to the glow discharge lamp, together with reference signals for controlling the a.c. power amplifier which produces an alternating component in the voltage waveform.

These data were in-situ recorded on a personal computer equipped with an analog-to-digital converter board. According to the wave pattern of the reference signal, the discharge voltage could be periodically varied in both the cases of 50% and 20% duty ratio, although a little delay was observed at the upward and downward edges. This indicates that the resulting glow discharge plasmas would be also periodically varied by the applied voltage. As shown in Fig. 2(b), the variation in the emission intensities of the Cr I 425.43-nm line well follows the square-wave from the reference; the duty ratio as well as the phase of the reference signal. It is essential that the emission intensity can be
modulated with little distortion even though it includes dominant noises. This is favorable for phase-sensitive detection with a lock-in amplifier, which works as a very narrow bandpass filter and thus selects only the component modulated at the same frequency as the reference from the overall emission signal. In this case, the lock-in amplifier gives a signal proportional to the intensity difference between the high-voltage and low-voltage periods.

It is found in Fig. 2(b) that the emission intensities decrease drastically at the lower-voltage periods. In this experiment, the bias voltage ($V_0$), which corresponds to the lower voltage, was set at 350 V. The emission intensities emanated from a glow discharge plasma are generally elevated with increasing discharge voltage; however, their variations are different depending on the emitting species. It is known that the cathode sputtering occurs above a certain threshold voltage which depends on the chemical composition of the target material. One cannot observe emissions from sputtered species if discharge voltages are less than the threshold voltage; therefore, the modulated component would be relatively reduced when the discharge voltage is changed close to or less than the threshold voltage, leading to smaller intensities in the lock-in detection. It is supposed that the threshold voltage of steel samples is ca. 350 V under this experimental conditions. Because the background level as well as the emission intensities of gas species are observed even below this threshold voltage, it is desirable that the bias voltage is optimized at about 350 V to obtain larger signal-to-background ratio (SBR).

3.2. Sputtering Rate

Figure 3 shows a variation in the sputtering rate as a function of the duty ratio. Sample: iron (99.8%); bias voltage: 350 V; alternating voltage: 200 V; frequency: 217 Hz (square wave); plasma gas: Ar at 530 Pa.
function of the duty ratio \( t_1/t_2 \) when the dc bias voltage \( (V_0) \) and the alternating voltage \( (\Delta V) \) is kept at 350 and 200 V, respectively. The sputtering rate in a normal glow discharge is also plotted in Fig. 3. The average sputtering rate was estimated from triplicate measurements for each discharge condition. The rate at the duty ratio of 50 and 20% is reduced by a factor of 0.65 and 0.45, respectively, compared to that in a continuous discharge at the discharge voltage of 550 V. It is further clear that the sputtering rate is more reduced with a decrease in the duty ratio. This effect can be explained principally from the decrease in the effective discharge power caused by the pulsed voltages. Figure 4 shows a variation in the sputtering rate as a function of the alternation voltage in the case of the 50% duty ratio. In this case, the bias voltage is fixed at 350 V. The sputtering rate gradually increases along with the alternating voltage; however, the rates are always smaller than that at a continuous discharge voltage of 550 V. When the alternating voltage decreases down to 100 V, the rate becomes 0.36 times lower than the rate in the 550-V continuous discharge.

Figures 3 and 4 imply that the sputtering rate can be well controlled by using the pulsed discharge voltages. However, the reduction in the overall sputtering rate must lead to a decrease in the emission intensities due to smaller sampling amounts, and, in a conventional detection, the quality of the emission signals should be degraded. Therefore, one should apply a modulation detection technique with a lock-in amplifier so that the emission intensities can be evaluated under low-noise conditions.

### 3.3. Stability of Emission Intensity

Figure 5 shows intensity fluctuations of the Cr I 425.43-
nm line as well as background fluctuations measured at 425.52 nm at the duty ratio of 20 and 50%, when recorded with the conventional d.c. amplification method (a) and the lock-in detection method (b). A lowpass filter having the cut-off frequency of 0.4 Hz (24 dB/oct) was employed to obtain the average emission intensity (d.c. amplification method), and the lock-in intensity was measured at a time constant of 10 s which corresponds to a bandpass filter having the cut-off frequency of 0.02 Hz (6 dB/oct). The lock-in intensities are much less fluctuated than the emission intensities measured with the d.c. amplification method, leading to an improvement in the signal-to-noise ratio and thus the data precision. The relative standard deviation (RSD) is estimated to be 0.03% in the lock-in detection and 0.8% in the d.c. amplification method, when the duty ratio is 50%. If the cut-off frequency of the lowpass filter is lowered in the d.c. amplification method, the RSD might be improved. However, there is a limitation because the capacitor for the lowpass filter is prohibitively large in capacitance as well as in size. It is further noted in Fig. 5 that the background intensities are obviously smaller in the lock-in detection, giving larger SBRs. In this case, the SBR for the lock-in detection is 163 and 161, while that for the d.c. detection is 20 and 14, at the duty ratio of 50 and 20%, respectively. The modulated component in overall emissions, which is detectable with the lock-in detection method, is related to periodic variations in the sputtering as well as the excitation processes in the plasma. Whereas the Cr emission line is influenced by both of these processes, the background emission would be less sensitive to the sputtering process. Therefore, the Cr line intensities could be modulated more strongly than the background emission, enabling the SBR to be larger than in the d.c. amplification. It is obvious from Fig. 5 that the lock-in detection method can greatly improve the analytical performance under the pulsed discharge conditions.

3.4. Discharge Parameters

Figure 6 shows variations in the RSD (a) and the SBR (b) for the Cr I 425.43-nm line as a function of the duty ratio, when measured with the d.c. amplification method and the lock-in detection method. In this case, the d.c. bias voltage and the alternating voltage is fixed at 350 and 200 V, respectively. Regarding the RSD as well as the SBR, the lock-in detection method gives better analytical performance even though the duty ratio decreases down to 10%. The noise figure is expected to be much improved in the lock-in detection, leading to the RSDs to be less than 0.1% at the duty ratio of 20–50%, as shown in Fig. 6(a). The net emission intensities increase with the duty ratio due to larger sputtering amounts, which would yield the gradual increase in the SBR including the background level to be simultaneously elevated, as shown in Fig. 6(b). It is thus possible to control the sputtering rate by changing the duty ratio, without degradation in the analytical performance, when the lock-in detection method is employed.

Figure 7 shows variations in the RSD (a) and the SBR (b) for the Cr I 425.43-nm line as a function of the alternating voltage ($\Delta V$) at the duty ratio of 20 and 50%, In this case, the dc bias voltage is fixed at 350 V. The observed RSD values always indicate better analytical performance in the lock-in detection regardless of the alternating voltage and the duty ratio, and the RSDs decrease along with the alternating voltage. The RSD value in the lock-in detection is down to 0.06% at the alternating voltage of 250 V. This is because the intensities are elevated with the alternating voltage while the fluctuation is kept to be very small. The SBR values in the lock-in detection are much larger than those in the d.c. amplification method, and give little difference between the 50 and the 20% duty ratio, as indicated in Fig. 7(b). This is principally due to the smaller background levels relative to the Cr I intensities in the case of the lock-in detection (see Fig. 5).
3.5. Quantitative Analysis

Using the standard reference materials (No. 150-1 to 155-1, The Iron and Steel Institute of Japan), calibration curves of the Cr I 425.43-nm line were estimated for various discharge conditions (see Table 2). A linear relationship passing through the origin point was obtained for each calibration. The chromium contents in three low-alloyed steel samples (The Iron and Steel Institute of Japan) were determined by using these calibration curves. The analytical results are listed in Table 2. The Cr content and the corresponding RSD were estimated from 11 replicates. For each experimental condition, two individual measurements were performed to give a pair of the analytical value. The analytical values of all the pairs well agree with each other. The RSD tends to become slightly large as the duty ratio is smaller and the alternating voltage decreases; however, the resultant RSDs would guarantee the precision of all the analytical results (the average RSD is 0.21%). This is advantageous characteristics for quantitative analysis of thin-film samples.

4. Conclusions

The data presented in this paper demonstrate that the voltage modulation method applied to the d.c. glow discharge lamp is very effective for controlling the sputtering rate with keeping good analytical conditions. With the lock-in detection method, the emission intensities can be estimated with better RSD and SBR, despite the sputtering rate to be reduced by loading the alternating voltage at smaller duty ratios. This technique would be applied to in-depth analysis of thin-film samples having several 10-nm thickness as a rapid and accurate analytical method, because the sputtering rate can be reduced down to 100 nm/min or less. However, further studies on the sputtering regulation would be required to determine the elemental distribution of ultra-
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