Two-dimensional Observation of Emission Image of a Copper Chip Excited in a Glow Discharge Plasma

Munehiko MATSUURA and Kazuaki WAGATSUMA*

Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai, 980-8577 Japan.

(Received on February 13, 2013; accepted on July 25, 2013)

A two-dimensionally imaging spectrometer system was employed to obtain an emission image of a test specimen and to estimate the lateral resolution, when it was excited from a glow discharge plasma at a pulsed direct-current voltage. The specimen was a square-shaped copper chip having a dimension of 1.0 × 1.0 mm stuck on a nickel substrate. A Grimm-style glow discharge excitation source, whose hollow anode had an inner diameter of 8 mm, was employed as the excitation source. A conventional discharge condition did not give good lateral resolution being suitable for the actual application, because the emitting zone extended broadly over the size of the copper chip. The gate width of the charge-coupled device (CCD) detector and the on/off-periods of the discharge were investigated to improve the lateral resolution. Degradation of the resolution would be caused by the fact that a sample atom emits at different portions of the plasma body repeatedly, even during a single pulse of the discharge. Therefore, it is suggested that the gate width of the CCD detector should be reduced as small as possible, so that the emission of a sample atom can be detected instantaneously after ejected from the original position in the sample surface.

KEY WORDS: optical emission spectrometry; glow discharge plasma; spatially-resolved measurement; lateral resolution; copper chip.

1. Introduction

In the rolling process for the production of steel materials, relatively large inclusions, such as alumina and magnesia, in some cases degrade the quality of the final products. It is thus necessary to employ an analytical method in the process control, so that the distribution as well as the composition of such inclusions can be determined easily and rapidly.

Glow discharge optical emission spectrometry (GD-OES) has extensively been employed for the direct analysis of solid samples, because sample atoms are directly introduced into the plasma through cathode sputtering.\textsuperscript{1,2} Depth profiling of the chemical composition now becomes the most important application in GD-OES for various kinds of film-like samples, because it is a simple and rapid analytical method without complicated sample pretreatment and without an ultra-high vacuum condition.\textsuperscript{3} Furthermore, there is a possibility in GD-OES that the analytical information can be obtained not only along the depth direction but in the lateral direction over a sample surface, because sputtered atoms emit the characteristic radiation in the negative glow region just above the surface and thus a spatial image of the radiation may correspond to the lateral distribution of the sample atoms. In a conventional measurement system for GD-OES, the emission signal is observed from the axial direction of the plasma when it is collected onto an entrance slit of the spectrometer with a point-focused lens. Therefore, the intensity of an emission line is fully integrated over a certain area of the plasma, which is suitable for the general analytical application because the radiation can be averaged to be larger emission intensities with good precision; however, it cannot give any information on the spatial distribution of the emission intensity at different portions of the plasma.

A spatially-resolved spectral image of glow discharge plasma can be obtained with a particular spectrometer system, where the emitted radiation is directly collimated on the grating of the spectrometer and the plasma image after dispersion is projected on a position-sensitive detector.\textsuperscript{4} Gamez et al. first conducted spatially-resolved elemental analysis in GD-OES by using an imaging spectrometer system with a pulsed radio-frequency power supply, indicating that small particles embedded in an organic sample could be separately detected in the elemental mapping.\textsuperscript{5} More recently, his research group published a review article on the image measurement in GD-OES, discussing on the lateral resolution related to several experimental parameters for operating glow discharges.\textsuperscript{6} We have been interested in spatial variations in the emission intensity over the whole region of glow discharge plasma.\textsuperscript{5} Our previous papers reported on spectral images of zinc and copper samples by using a two-dimensionally imaging spectrometer having a spectral resolution of less than 1 nm, indicating that the intensities of their emission lines were not uniform over the plasma area, but were drastically reduced along the radial...
direction of the plasma. This effect was because the number density of the analyte species was inhomogeneous in the plasma.

In the present work, we investigate an emission image of a relatively large specimen on a sample surface when a direct-current discharge voltage is applied to the plasma with a pulsed operation, in order to obtain basic data for optimizing the measuring parameters, such as the pulse width and the duty ratio of the pulsed voltage, for a clear image with good resolution.

2. Experimental

2.1. Test Specimen

The specimen was a square-shaped copper chip having a dimension of 1.0 × 1.0 mm stuck on a pure nickel plate. The copper chip was made of a conductive copper tape with a thickness of 0.035 mm (CUS-13T, Takachi Ltd., Japan). The nickel plate was set to a glow discharge source so that the copper specimen could be at the center position of the plasma.

A resonance atomic line of copper, Cu I 324.7 nm, was measured, because this line has the largest emission intensity without overlapping with any nickel lines.

2.2. Apparatus

A glow discharge excitation source was made in our laboratory according to an original model of Grimm,7) where the inner diameter of the hollow anode was 8.0 mm and the distance between the anode and a cathode sample was adjusted to be 0.2–0.4 mm. The emitted radiation was observed from the axial direction of the plasma to a two-dimensionally (2D) imaging spectrometer, as a block diagram of the whole measuring system is shown in Fig. 1. The imaging spectrometer system comprised a collimator apparatus, an imaging spectrograph, and a charge-coupled device (CCD) detector.5,8) The emission signal from the excitation source was introduced through the collimator onto the entrance slit of the spectrograph (Model 12580, BunkoKeiki Corp., Japan), where the image could be directly projected on the diffraction grating by the collimator apparatus, and then the emission image dispersed at a certain wavelength was detected on the CCD detector (SensiCam QE Model, PCO Imaging Corp., Germany); as a result, a 2D image of a particular emission line could be observed in the radial direction of the plasma. The optical alignment between the glow discharge excitation source and the spectrometer was adjusted by using zero-order diffraction light, so that an image of the source could be observed most clearly. The Grimm-style excitation source produces obstructed glow discharge plasma, where the emission zone, called a negative glow, is localized just above the sample surface having a thickness as thin as the mean free path of sputtered sample atoms.9) It was thus considered that the emission image was obtained from the negative glow zone, itself. It was determined by measuring an image of a scale that a 2D image obtained by 10 × 10 pixels approximately corresponded to an actual sample area of 0.21 × 0.21 mm². The actual spectral resolution was ca. 0.4 nm (half width at half-maximum) when adjusting the slit width to be 0.02 mm. The data were accumulated and averaged on a personal computer to improve the spatial resolution and the plasma image was finally recorded.

A pulsed direct-current voltage loaded to the plasma source was generated with a power amplifier (HEOPT-1B60-L1, Matsusada Precision Ltd., Japan) controlled with a function generator (4502, Kikusui Electric Corp., Japan). Several discharge parameters, such as a peak value of the voltage, the frequency, and the duty ratio could be varied individually. The waveform of the applied voltage was monitored on a digital oscilloscope (TDS-1002B, Tektronix Corp., Japan).

High-purity argon (>99.999%) was introduced as the plasma gas after evacuating the chamber to below 10 Pa. A Pirani vacuum gauge (GP-2, ULVAC Corp., Japan), which had been corrected for pure argon, was placed between the evacuation port and a rotary vacuum pump (GLD-166, ULVAC Engineering Inc., Japan). The plasma gas was introduced during the measurement while keeping a predetermined chamber pressure.

3. Results and Discussion

3.1. Emission Image of Copper Chip

Figure 2 shows a typical emission image of the copper chip for the Cu I 324.7-nm line, when the glow discharge plasma is maintained at a peak voltage of 400 V and an argon pressure of 530 Pa. In this case, the emission intensity was varied from 50 to 1000 in an arbitrary unit, where the lowest value was comparable to the background level. The slit width of the spectrometer was set to be 1.5 mm. A pulsed voltage was conducted to the glow discharge source at a frequency of 10 Hz and a duty ratio of 10%, which corresponded to pulsed discharges with a width of 10 ms, and...
the emission from each pulsed discharge was measured on the CCD detector at a gate width of 1 ms. The emission signal was stored in the CCD detector during 32 timing pulses, and this accumulation was 900-times replicated and averaged on a personal computer. In this image, 100 pixels corresponded to 2.12 mm in the actual plasma size. Our previous paper had already represented an emission image of a pure copper plate covering over the whole emitting zone of glow discharge plasma, indicating that the emission of the sample was not irradiated uniformly over the plasma zone but the central portion, having a diameter of about 2 mm, gave the most intense emission and then the intensity was largely reduced towards the surrounding zone of the plasma.\textsuperscript{5,6} It should be thus noted that the intensity map in Fig. 2 was overlapped with the intensity variation of the plasma itself. Even with this effect considered, a surrounding zone of the emission image extended over the size of the copper chip (1.0 × 1.0 mm) and thus the copper image could not be resolved completely. The lateral resolution became degraded for any reason in the discharge conditions and/or the measuring parameters. The resolution power was estimated by using a half width at a half-maximum of the intensity (HWHM), as expressed in Fig. 3 showing the intensity variation along the axial direction.

### 3.2. Factors for Determining the Lateral Resolution

Figure 4 schematically illustrates a pathway of Cu atoms from the sputtering from a chip sample to the negative glow region in which their excitation and diffusion occur. The degradation in the lateral resolution, which is expressed as an emission zone more extended than the size of the Cu chip in Fig. 4, would be caused by re-emission of Cu atoms at plasma portions apart from their original positions on the sample surface, resulting from diffusion of the Cu atoms in the plasma body. Two probable mechanisms for this can be considered as follows: (1) a Cu atom remains in the plasma during several discharge pulses to emit the radiation repeatedly at different plasma portions, (2) a Cu atom moves in the plasma within a single discharge pulse with emitting the radiation repeatedly. The mechanism would be clarified through measurements where parameters of the pulsed discharge as well as the detector are appropriately controlled.

Figure 5 illustrates the waveform of a pulsed voltage for switching on/off a glow discharge, together with the gate timing of a CCD detector for determining the sampling period of the emission. The timing pulse of the gate is strictly synchronized with the pulse of the discharge voltage. On/ off-periods of the plasma can be widely changed by adjusting the frequency and the duty ratio of a pulsed discharge, to estimate the re-emission effect of a sample atom during a pulse train for the discharge. Furthermore, the gate width of a CCD detector can be adjusted to be narrower so that the re-emission effect of a sample atom within a single discharge would be less affected, although the intensity becomes much more reduced.

### 3.3. Parameter for Pulsed Discharge

Table 1 indicates HWHM values of emission images for Cu I 324.7 nm, together with each parameter of the pulsed discharge, when the off-period of the plasma is largely varied from 90 to 9990 ms. In these measurements, the glow discharge plasma was maintained at a peak voltage of 400 V and an argon pressure of 530 Pa. The gate width of the CCD detector was fixed to be 1.0 ms. The HWHM values almost become unchanged independent of the off-period of the plasma. The longest off-period in Table 1 (9990 ms) is a time enough for sputtered atoms to be removed from the plasma body, and the decrease in the off-period does not worsen the lateral resolution, implying that the atoms ejected from the sample surface can move in the plasma rapidly.
This result would indicate that it is not the reason for the blurred emission image, as shown in Fig. 2, that a sample atom emits the radiation at different plasma portions during successive on-periods of the pulsed discharge.

Table 2 indicates HWHM values of the emission images, when the gate width of the CCD detector is changed at 10, 1.0 and 0.1 ms. In this case, the frequency and the duty ratio were fixed to be 10 Hz and 10%, thus making the on/off-periods of the plasma to be kept constant. The discharge voltage and the pressure of argon were the same as those in Table 1. The HWHM values are almost the same at gate widths of 10 and 1.0 ms, which indicates that the sample atoms can diffuse in the plasma rapidly and re-emit the radiation at different plasma portions even when the observation is restricted for 1.0 ms. The effect would make the lateral resolution of the emission image to be worse. Also denoted in Table 2, the HWHM value could not be estimated when the gate width was reduced to be 0.1 ms, because the emission intensity became very faint. Narrower width of the gate is expected to improve the lateral resolution in spatially-resolved GD-OES, although the effect could not be confirmed using our present experimental apparatus, due to insufficient sensitivity of the CCD detector.

4. Conclusions

In spatially-resolved GD-OES, emission images of a copper chip, prepared as a test specimen, were observed to estimate the lateral resolution when the plasma is generated at a pulsed direct-current voltage. The lateral resolution could not be obtained to be suitable for the actual application because the emitting zone extended broadly over the size of the copper chip. The gate width of the CCD detector as well as the on/off-periods of the discharge was varied to improve the lateral resolution. As a result, defocusing of the emission image would be because a sample atom diffuses in the plasma rapidly and emits repeatedly during a single pulse of the discharge. Therefore, it is suggested that the gate width of the CCD detector should be reduced as small as possible, so that it can detect only the emission signal of a sample atom immediately after ejected from the original position.

Acknowledgment

The authors gratefully acknowledge Grant-in-Aids from the Iron and Steel Institute of Japan.

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