

# Depth Profiling of Metallic Coatings Evaluated from Spatially-resolved Measurement in Glow Discharge Optical Emission Spectrometry

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A two-dimensionally imaging spectrometer system was employed to measure spatial emission images of a glow discharge plasma in atomic emission spectrometry. The emission intensities were not uniform in the radial direction of the plasma region, but yielded a characteristic distribution from the central portion towards the surrounding zone in the plasma. Temporal variations in the emission images were observed when a zinc-coated steel plate and a thermally-deposited copper film were employed as the sample. Depth profiles of these surface layers, estimated from the emission images, were compared among different integration areas of the emission intensities.

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## Introduction

Glow discharge optical emission spectrometry (GD-OES) is extensively employed as a direct analytical method of solid samples because sample atoms are directly introduced into the glow discharge plasma through cathode sputtering.<sup>1</sup> The sputtering process enables GD-OES to be a rapid analytical method for obtaining a depth profile of the sample composition, because it requires no ultra-high vacuum conditions with a little sample pretreatment.<sup>1,2</sup> The depth profiling of various surface layers, such as electroplated coatings and oxide films, is now the most important application field in GD-OES.<sup>3-6</sup> In a conventional measurement system for GD-OES, the emission signal is observed from the axial direction of the glow discharge plasma, and is thus collected onto the entrance slit of the spectrometer with a point-focused lens. Therefore, this optical alignment allows the intensity of an emission line to be integrated over a certain region of the plasma; however, it cannot yield information on the spatial distribution of the emission intensity in the radial direction of the plasma.

The two-dimensional (2D) plasma image for each analytical line can help to find the optimum measuring conditions for depth profiling in GD-OES, because the depth resolution of the elemental profiles might be varied at different observation portion/area of the plasma. For such a spatially-resolved measurement, an interference filter may be employed to disperse the emission signals; however, it is not suitable for measuring emission spectra comprising many spectral lines, because of its bad spectral resolution of more than 10 nm. Few papers have reported on the 2D spectral image of the glow discharge plasma, principally due to a lack of spectrometers enabling 2D observation having a good spectral resolution.

Our previous paper reported on 2D spectral images of pure 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 towards the radial direction of the plasma.<sup>7</sup> In the present work, spatial and temporal intensity variations of zinc and iron emission lines were observed from their 2D spectral images while the zinc layer was removed by cathode sputtering in the case of a zinc-coated steel sample. Several depth profiles of the zinc coating were measured and compared at different positions/areas of the plasma. In addition, the sputtering process of a copper film which was thermally-deposited on a silicon substrate was observed with the imaging spectrometer system.

## Experimental

A glow discharge lamp was made in our laboratory according to an original model of Grimm,<sup>8,9</sup> where the inner diameter of the hollow anode was 8.0 mm and the distance between the anode and cathode sample was adjusted to be 0.2 - 0.4 mm. The imaging spectrometer system comprised collimator optics, an image spectrograph, and a charge-coupled device (CCD) detector.<sup>7,10</sup> Emission signals from the glow discharge lamp, which were observed from the axial direction of the plasma, were conducted through the collimator onto the entrance slit of the spectrograph (Model 12580, BunkoKeiki Corp., Japan), and the emission image was then dispersed and detected on the CCD detector (SensiCam QE Model, PCO Imaging Corp., Germany), where the 2D image of a particular emission line could be observed in the radial direction of the plasma. A 2D image obtained by 5 × 5 pixels corresponded to an actual sample area of 0.1 × 0.1 mm<sup>2</sup>. The spectral resolution was 0.1 - 1.0 nm, depending on the slit width. The emission signals were accumulated and averaged on a personal computer by using appropriate discharge and measuring conditions for each sample. The analytical lines were Zn I 334.50 nm (7.78 eV), Cu I 324.75 nm (3.82 eV), and Fe I 344.06 nm (3.60 eV).<sup>11</sup>

Pulsated discharge voltages were applied to the glow discharge

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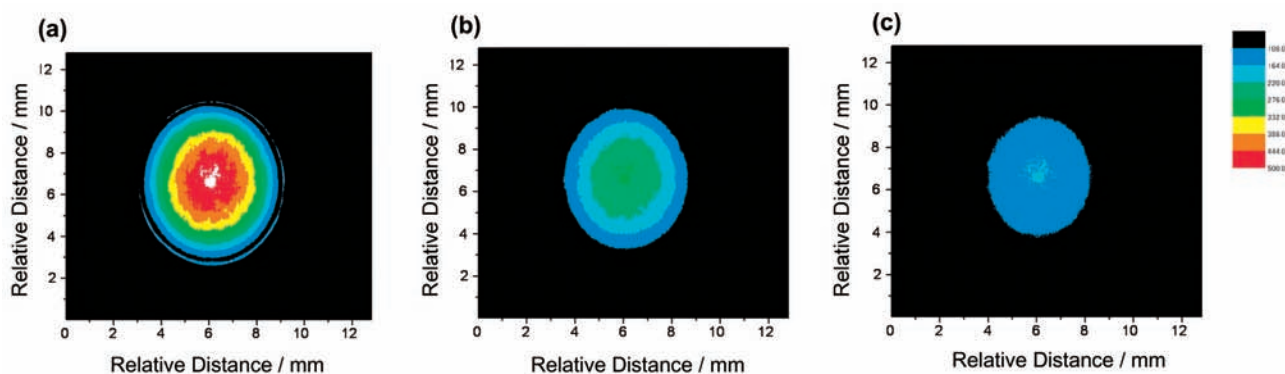


Fig. 1 Two-dimensional emission image of the Zn I 334.50-nm line observed from the axial direction of a glow discharge plasma when the sputtering time is 260 s (a), 520 s (b), and 910 s (c).

lamp with a high-voltage amplifier (HEOPT-B60-L1, Matsusada Precision Inc., Japan), which was controlled with a function generator (Model 4502, Kikusui Corp., Japan). The discharge parameters are described later. The elemental distribution of the resulting craters after sputtering was determined by an X-ray fluorescence spectrometer with a Rh-target X-ray source (ZSX Primus II, Rigaku Corp., Japan).

High-purity argon (>99.999%) was introduced as the plasma gas after evacuating the chamber to below 10 Pa. The pressure was monitored with a Pirani gauge (GP-2, ULVAC Corp., Japan), which had been corrected for pure argon, which was placed between the evacuation port and a rotary vacuum pump (GLD-166, ULVAC Engineering Inc., Japan). The plasma gas was flowed during the measurement while keeping a chamber pressure of  $5.3 \times 10^2$  Pa.

A commercially-available zinc-coated steel plate was prepared as the sample. The average thickness of the zinc coating was  $3.2 \times 10^{-6}$  m, where the coating weight was determined after acid dissolution by ICP emission spectrometry. The sample surface was cleaned with acetone and then fixed at the sample port of the chamber. A copper film on an optically-flat silicon substrate was produced with electro-thermal deposition in a vacuum chamber at  $2.7 \times 10^{-5}$  Pa. The thickness was controlled to be  $0.5 \times 10^{-6}$  m, which was measured with a deposition monitor (XTM/2, Inficon Corp., USA).

## Results and Discussion

### Zinc coating

Figure 1 shows 2D emission images of the Zn I line, whose intensities are expressed by mapping with several colors, when the surface layer of the zinc-coated steel sample is being removed through sputtering. These images indicate a spatial variation of the emission intensity as well as its temporal variation during progress of the sputtering. For this measurement, a pulsed voltage was applied to the glow discharge lamp,<sup>12,13</sup> where the frequency of the discharge was 100 Hz, the duty ratio was 10%, the maximum voltage was 500 V, and the minimum voltage (offset voltage) was 100 V. The pulsed discharge is required to accumulate the emission image in the CCD detector, and it is also useful to control the sputtering rate appropriately.<sup>12</sup> The slit width of the spectrometer was 4.0 mm and the gate width of the CCD detector was 1 ms. The emission signal was stored in the CCD detector during 32 discharge pulses, and this accumulation was 100-times replicated and averaged on a personal computer.

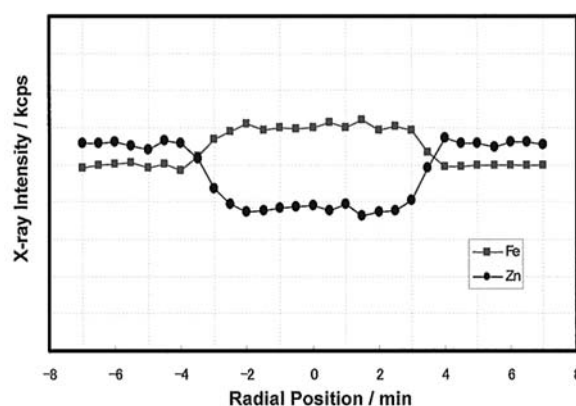


Fig. 2 Profiles of the X-ray fluorescence intensity of zinc  $K_{\alpha}$  (circle) and iron  $K_{\alpha}$  (square) along the cross-section of the resulting crater after a sputtering time of 300 s.

Figure 1(a) shows a 2D emission image at the sputtering time of 260 s when the sputtering is being developed inside the zinc coating. Note that the diameter of the hollow cathode is 8.0 mm; therefore, this diameter restricts the plasma zone. This image demonstrates that the emission from the zinc layer is not irradiated uniformly over the possible plasma zone, but has a large variation in the intensities along the radial distance. The central portion having a diameter of about 2 mm gives the most intense emission. The concentric-circles pattern means that the emission intensity gradually becomes faint at larger diameters.

As shown in Figs. 1(a) – 1(c), the overall intensities of the images are reduced with removing the zinc coating; however, such an intensity distribution remains. Similar patterns were reported when a pure zinc plate and a pure copper plate were employed as the sample.<sup>7</sup> Figure 2 shows variations in the X-ray fluorescence intensities of zinc  $K_{\alpha}$  and iron  $K_{\alpha}$  lines along the cross-section of a sputtering crater after a sputtering time of 300 s. This X-ray profile implies that the sputtering takes place uniformly over the central portion of the crater having a diameter of about 6 mm, although a zinc layer remains at the edge of the crater, which does not correspond to the intensity variation of the emission image (see Fig. 1(a)). Therefore, the reason for the emission image is a variation in the excitation efficiency appearing in the negative glow region. The plasma region should reach a boundary near the hollow anode (anode dark space),<sup>14</sup> and thus the resulting emission is extinguished there. As the result, the plasma parameters determining the

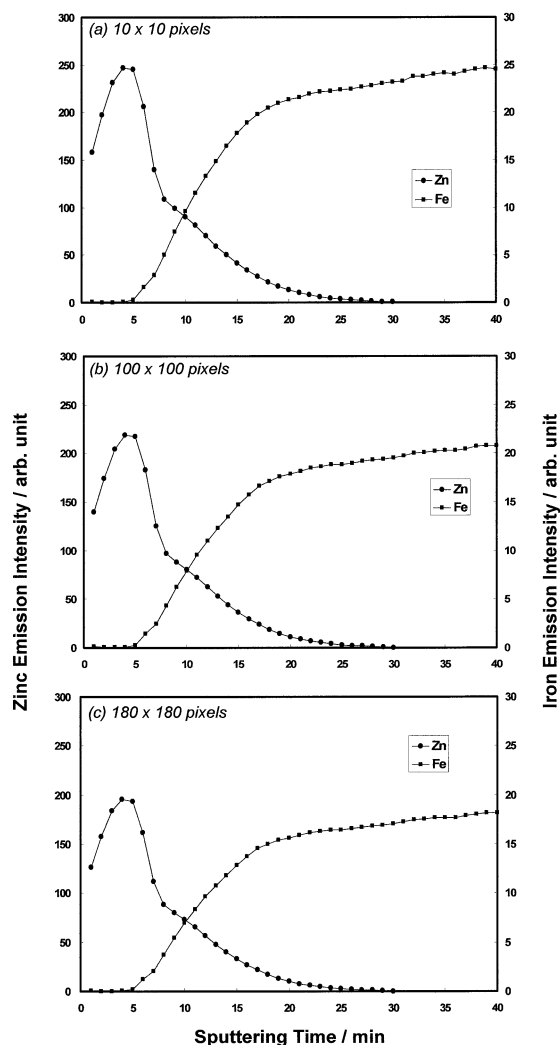


Fig. 3 Depth profiles of the Zn I 334.50-nm (circle) and the Fe I 344.06-nm (square) intensities in a zinc coating when the integration area in the plasma image is fixed at  $10 \times 10$  pixels (a),  $100 \times 100$  pixels (b), and  $180 \times 180$  pixels (c).

excitation processes, such as electron density and electron temperature, might be changed in the radial direction of the glow discharge plasma. On the other hand, the crater shape is principally determined by the number density as well as the kinetic energy of argon ions, working as bombarding ions for sputtering, in the cathode sheath region. It is therefore considered that the spatial distribution of these charged particles would be different between the negative glow region and the cathode sheath region. It is interesting to investigate which portion/area of the plasma gives better depth resolution in the depth profiling by analyzing the intensity distribution of the 2D emission image in detail.

Figure 3 shows depth profiles of the zinc and the iron emission lines estimated for different integration areas in the corresponding 2D images of the emission intensities. As illustrated in Fig. 3, their integration areas were determined as follows: (a) the central portion having  $10 \times 10$  pixels ( $0.2 \times 0.2 \text{ mm}^2$ ), (b)  $100 \times 100$  pixels ( $2.0 \times 2.0 \text{ mm}^2$ ), and (c)  $180 \times 180$  pixels ( $3.6 \times 3.6 \text{ mm}^2$ ). These depth profiles indicate that the zinc-coated steel sample comprises an outmost zinc layer, a transient layer containing both zinc and iron, and the iron substrate. The transient layer is considered to be zinc-iron inter-

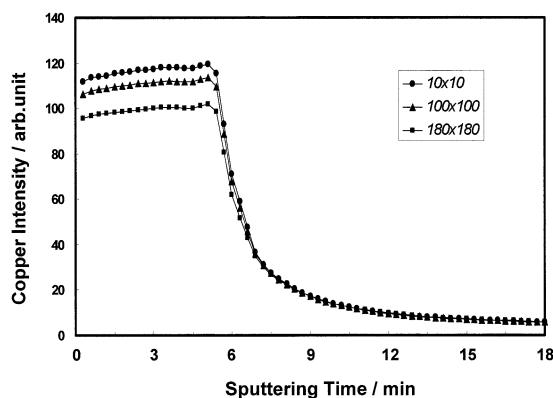


Fig. 4 Depth profiles of the Cu I 324.75-nm intensity in a copper film when the integration area in the plasma image is fixed at  $10 \times 10$  pixels (circle),  $100 \times 100$  pixels (triangle), and  $180 \times 180$  pixels (square).

metallic compounds, which are produced with heat treatment in a manufacturing process of commercial zinc-coated steels. It is found that these depth profiles are similar, being less dependent on the integration area of the plasma, which indicates that their depth resolutions are not varied at different plasma positions. This result is probably because the number density of zinc becomes almost uniform over a large part of the plasma, which can be confirmed from the line profile of X-ray fluorescence analysis (see Fig. 2). Furthermore, spatial information directly corresponding to the sample surface would be lost due to diffusion of the sputtered atoms in the plasma while the emission intensities are accumulated during lots of discharge pulses. A single-pulse discharge might be the most suitable for obtaining information on the sample surface; however, our imaging spectrometer system cannot be operated in this discharge mode, due to its very faint emission intensity. On the other hand, the precision for the intensity data is drastically varied depending on the integration area of the plasma. When estimating the relative standard deviation (RSD) of the intensity data over different integration areas, smaller RSD values could be always obtained in the  $10 \times 10$ -pixels integration because the central portion of the plasma gives the most intense and constant emissions. Accordingly, a spatially-resolved observation not including the surrounding area of the plasma is recommended for analytical application, if the optimum observation position can be determined from the 2D emission images.

#### Copper film

We also observed a variation in the 2D emission image for the copper film during the progress of sputtering. The following pulsed discharge conditions were employed: a maximum voltage of 500 V and a minimum voltage of 100 V, a frequency of 100 Hz, and a duty ratio of 10%. In this case, the slit width was 4.0 mm, the CCD gate width was 1 ms, and the accumulation times were set to be 50. Figure 4 shows depth profiles of the copper emission line estimated for three different integration areas in the 2D emission image, where the conditions for the integration area are the same as in the zinc-coated steel. As similar to the result of the zinc-coated steel sample, the shape of the profile and hence the depth resolution are very little varied among these integration areas. Also in this case, the RSD value of the emission intensity was the smallest in the most concentrated view. These results also imply that the sputtered copper atoms are uniformly distributed over a large area of the plasma during repetition of the pulsed discharges, whereas the

emission yield has a large variation in the radial direction of the plasma: the emission yield decreases gradually from the central portion towards the surrounding portion in the hollow-shaped plasma. Hence, the depth profiles could appear similarly at different plasma portions, even if the net intensities are varied depending on the integration area.

## Conclusion

Two-dimensional emission images for analytical lines in a zinc-coated steel sample and a copper film on a silicon substrate are observed to obtain information on the depth profiling. The emission images are not uniform in the radial direction of the plasma, but has a large variation in the intensities along the radial distance. The temporal variation of their emission images is measured to obtain the intensity changes with the progress of the cathode sputtering, which are integrated over the central portions of the plasma having different areas of  $0.2 \times 0.2$ ,  $2.0 \times 2.0$ , and  $3.6 \times 3.6$  mm<sup>2</sup>. The shape of the depth profiles and thus the depth resolution are less changed among these integration areas; however, the integration for the most concentrated area ( $0.2 \times 0.2$  mm<sup>2</sup>) always provides smaller RSDs of the integrated intensities due to the larger emission intensities with small deviations. Therefore, the integration area should be focused on the central portion of the plasma to obtain intensity data with good precision.

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