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# Surface elemental mapping using glow discharge—optical emission spectrometry

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# ABSTRACT

A glow discharge optical-emission spectrometry source was evaluated for use in imaging elemental surface distributions. A 1.8 cm<sup>2</sup> area of a nickel–chromium alloy was sampled and copper emission was observed directly above the surface of a copper inclusion. By pulsing the glow discharge, the resolution was improved greatly over measurements using direct-current powering. Ranges of gas flows, pulse frequencies, pulse potentials, pulse widths, and pressures were explored to determine their effects on spatial resolution and were related to atom transport in the glow discharge cell. Pressure, pulse width, and pulse frequency were all found to have a significant effect on resolution.

## **3.1 INTRODUCTION**

The glow discharge (GD) is a versatile source, useful for elemental analysis of liquids<sup>1-4</sup> and solids, as well as molecular, structural, and elemental analysis of gases.<sup>5-6</sup> Even within applications to elemental analysis of solids, it shows great flexibility in that it can be used for bulk analysis or for depth profiling on scales ranging from several nanometers to hundreds of micrometers,<sup>7-8</sup> can be used over a broad concentration range,<sup>8</sup> and can be used as a source for optical emission, atomic absorption, atomic fluorescence, or mass spectrometry. Alternative powering schemes to direct current (dc) have contributed to the utility of the glow discharge. Radio frequency powering has a number of desirable features, most notably the ability to analyze non-conductive samples.<sup>9</sup> A pulsed powering scheme offers its own advantages, including enhanced signals, reduced sample heating, and more flexible control of sputtering rate.<sup>7</sup>

One area in which GD spectrometry is lacking, however, is lateral resolution. Spatial resolution within the plane of the sample surface is usually no better than the size of the sputtered area. For a Grimm or similar type of GD source, this sputtered area is typically a circle at least 4 mm in diameter, limiting resolution to this scale. To analyze more than one spot with a typical glow discharge cell, the discharge must be terminated, the sample moved, and the discharge reignited and allowed to stabilize, increasing the potential for error and extending the analysis time. This problem is not unique to glow discharges. In laser ablation, spatial profiling is limited by shot-to-shot reproducibility,<sup>10</sup> but laser ablation does not require

breaking vacuum to examine different positions. Moreover, laser ablation samples smaller areas.

Resolution on the scale of several millimeters to several centimeters is useful in assessing the homogeneity of Standard Reference Materials at the National Institute of Standards and Technology and the sputtering targets used in the microelectronics industry.<sup>11</sup> Inclusions (inhomogeneous impurities) in steel samples can affect the properties of steel.<sup>12-15</sup> It is the macro inclusions, which can reach hundreds of micrometers, that are the most harmful.<sup>14-15</sup> In fact, failure can be caused by just one large inclusion.<sup>15</sup> A rapid technique covering a large sample area is needed for determination and characterization of these impurities.<sup>13</sup>

In 1995, Winchester and Salit<sup>11</sup> demonstrated a novel GD cell with multiple independent discharges running simultaneously over different spots, which enabled simultaneous analysis with a multiplex (Hadamard transform) detection scheme. The lateral resolution was limited to 4.75 mm along rows and columns and 6.7 mm along diagonals, and there were gaps of several millimeters that were not sampled between the discharges, but these sizes are limits of the specific design of the prototype rather than the technique. In the same year, Hoffmann and Ehrlich<sup>16</sup> showed that the lateral distribution of GD emission above the plasma surface is influenced by the lateral distributions of elements within the sample, but the resolution was too poor at that time to be of much analytical use. An implication of this study was that, when laterally heterogeneous samples are analyzed, different emission intensities might be observed (and therefore different concentrations calculated) depending on the orientation of a sample even if the same portion was sputtered. Winchester<sup>17</sup> verified this for a typical optical arrangement and demonstrated that the effect could be overcome with a different optical arrangement.

In the present work, a microsecond-pulsed glow discharge was used to greatly improve the resolution, and a 15-mm diameter area was sputtered at once. Ranges of gas flows, pulse frequencies, pulse potentials, pulse widths, and pressures were evaluated. Their effects on spatial resolution and relationships to atom transport were explored.

## **3.2 EXPERIMENTAL**

A home-built Grimm-type glow discharge cell with a floating restrictor, shown in Figure 3-1, was used. The floating restrictor had a 15.0 mm inner diameter, which confined both the sputtering and viewing to an area of approximately that size  $(1.8 \text{ cm}^2)$ . The sample was tightened against the cathode by an aluminum plate, which was held against the cathode with aluminum bolts. The cell was cooled to 10 to 15 °C by a Neslab Coolflow CFT-33 Refrigerated Recirculator (Newington, NH). Argon of 99.998% purity was used (Air Products, Allentown, PA). The argon flow was regulated by an MKS Instruments type 1159A-010005V flow regulator (Burlington, MA). An Edwards E2M2 High Vacuum Pump (Crawley, Sussex, England), was used to maintain low pressure and remove sputtered material. A valve between the cell and the vacuum pump was employed in combination with the flow regulator to adjust the pressure, which was monitored in the cell body with an MKS Instruments Baratron 122AA pressure gauge. For pulsed measurements, the discharge was powered by an Instrument Research Company model no. M3K-20-N Pulsed Power Supply (Columbia, MD). For dc measurements, a Hewlett Packard 6525 DC Power Supply was utilized.

The emission was monitored with a monochromatic imaging spectrometer of the kind described by Olesik and Hieftje.<sup>18</sup> The source was placed at the focal point of a 25 cm focal length plano-convex fused-silica lens. This lens collimated the light from the source and directed it into a (Model EU-700) 0.35 Heath m Czerny-Turner monochromator fitted with a 1200 lines/mm grating. After exiting the monochromator, the light was refocused onto a Photometrics CH350A CCD camera (Roper Scientific. Trenton, NJ) by means of a 15 cm focal length planoconvex fused-silica lens. The result is a monochromatic (1.5 nm bandpass) image with a magnification of 0.6. In the vertical direction, the image is good enough that a 56 µm valley between 56 µm lines on 1951 USAF glass-slide resolution target (Edmund Optics) backlit by a tungsten lamp are 30% as intense as the centers of the lines.

A nickel-chromium alloy sample (NIMONIC alloy 105 E3918 containing 75.2% Ni, 19.4% Cr, 5.4% other) with 0% to 0.01% Cu from Inco Europe Limited (Birmingham,

England) was used as the bulk material. A 1.0 mm diameter copper plug in the form of a piece of copper wire inserted into the alloy was used as the inclusion.

# **3.3 RESULTS AND DISCUSSION**

To allow the implications of each study to be better appreciated, our basic model is presented here; results will then be offered to support the model and to develop it. In a glow discharge, atoms are sputtered from the surface of the sample and then travel away from it by both diffusion and convective transport (with the gas flow). When those atoms reach certain regions, particularly the negative glow, they can be excited and emit light. The farther the atoms have been allowed to drift, the more smeared their distribution and the worse the spatial resolution will be. As a result, the spatial resolution will depend on the time between sputtering and emission as well as the speed at which the atoms move.

An image obtained with the imaging GD instrument is shown in Figure 3-2. The bright spot is above the copper pin and the dark area is over the nickel-chromium alloy. A dashed ring has been overlain to show the limits of the discharge cell. A distortion in the horizontal direction is seen when this type of imaging system is used.<sup>19</sup> To avoid this distortion, only vertical slices of the image were used in the subsequent evaluation. This is not a fundamental limitation of glow discharge imaging because other detection configurations could be used or the distortion could be corrected.

Emission from the same pin was imaged under a wide range of conditions (that is, a large number of combinations of the parameters discussed in the sections that follow), which produced a large data set. For each condition, 5 images of the Cu 327.4 nm emission and 5 images of the background (at 328.9 nm) were taken. To extract trends from the data, two numbers were necessary for each condition: a measure of the lateral width of the emission from the pin and a measure of the error in this width. To simplify the analysis, the 10 images were first reduced to a single vertical profile. A program written in house averaged the 5 images at 327.4 nm, averaged the 5 images at 328.9 nm, subtracted the latter from the former, and exported a one-dimensional slice along the y-axis of the resulting image. With Origin (OriginLab Corporation, Natick, MA), a Lorentzian function was fit to the observed profile (vertical slice) in order to determine its full width at half maximum (FWHM).

Although this process is an efficient way to arrive at widths for a large data set, it necessarily eliminates direct calculation of the error in these widths because only one width is returned for each condition. One might expect there to be a relationship between the intensity of a profile and the uncertainty in the fitting of that profile (that is, weaker signals will have lower signal-to-noise ratios than stronger signals, so there will be more uncertainty in the fit for weaker signals than for stronger signals).

For 14 conditions, which varied widely to ensure that the results would be applicable to the entire range of data, uncertainty in the width was calculated directly. That is, the 5 images (after background correction) were individually fit with Lorentzians, and the standard deviation among the 5 widths was calculated. Along with the width, the Lorentzian fit returns a peak area, which can be used as a measure of signal strength. These 14 sets were chosen to represent a range of emission intensities (and therefore a range of peak areas). The relative standard deviation (RSD) in FWHM was then plotted as a function of peak area (Figure 3-3) and a power curve was fit to the plot. The resulting curve had a power of -0.66. Although imperfect, errors estimated from this fit were judged to be adequate reflections of directly calculated purposes errors for our and are used throughout the remainder of the paper wherever an estimated error in profile width is given.

#### 3.3.1 Pulsed vs. dc operation of the GD

By using pulsed rather than dc powering, the resolution was improved significantly. At approximately 400 V dc (not pulsed) and 3 torr, the measured FWHM of the image from the 1 mm Cu inclusion was 2.3 mm. As will be shown later, the FWHM of the same pin when pulsed powering was used could be as narrow as 1.0 mm (the width of the pin itself). In a dc GD, energy is continuously being introduced into the system, so atoms that have traveled far from their original locations on the sample surface can still be excited and emit light. In a pulsed GD, the energy is available for a limited time, so the distance atoms can travel before emitting is correspondingly limited. Indeed, modeling predicts that the sputtered atom concentration is (axially, at least) relatively narrowly distributed and close to the cathode for the first few microseconds of a pulse<sup>20</sup> compared to the case of a dc Consequently, pulsed operation produces a GD. <sup>21</sup> narrower distribution and better resolution.

#### 3.3.2 Convection

The glow discharge cell has a single argon inlet, the flow through which is regulated by a mass flow controller. The argon is directed towards the quartz window and then to the main cell body. The cell also has two outlets that connect outside the cell and lead to a vacuum pump. Flow through these outlets is restricted by a valve between the connection and the pump. One outlet resides in the main cell body while the second surrounds the floating anode close to the sample. This arrangement creates forced convection (flow) from the main cell towards the sputtering crater then out to the perimeter of the sputtering crater. If this convection has a significant effect on the distribution of emission in a microsecond-pulsed glow discharge, it would be expected to spread the atoms and therefore their emission towards the perimeter of the sputtering crater. This spreading would result in broader lateral profiles at higher flow rates. In order to exclude pressure as a controlling variable, the outlet valve was adjusted to maintain a constant pressure of 2.75 torr while the inlet mass flow controller was used to vary the Ar flow from 41 mL/min to 105 mL/min. Pulses of 2.75 kV and 4 us duration, applied at a frequency of 100 Hz were used to sputter a nickel-chromium alloy with a 1.0 mm copper-pin insert. Five images of the Cu 327.4 nm emission and 5 measurements of the background (at 328.9 nm) were taken at each flow rate. As is shown in Figure 3-4, the FWHM of the Cu emission peak averaged 1.44 mm and varied by less (8 µm or 0.5% from the widest to the narrowest) than the smallest individual estimated standard deviation (10 µm). This variation was well below what was seen with other parameters, and no trend was observed. It can therefore be concluded that convection does not play a significant role under the conditions studied.

#### 3.3.3 Pulse frequency

The pulse frequency or, more pertinently, the separation between pulses had a marked effect on the shape of the spatial emission profile. Figure 3-5 shows the distortion in peak shape that arises at short pulse separation times. To quantify this change, Fig. 3-6 shows the ratio of the width at 25% of the peak height to that at 75% of the peak height as a function of the temporal separation between pulses. There is a transition at pulse separation intervals around 800 µs from peaks with broad bases to peaks with narrower bases. This behavior can be explained as a sort of flushing time of the region of the cell where excitation occurs. At longer inter-pulse spacings, atoms have time to be almost entirely removed from the negative glow region (where most excitation and emission occurs) before the next pulse occurs. At shorter delays, there are two atom populations, one of which is from the prior sputtering pulse. This population has had time to diffuse somewhat, but not to drift out of the negative glow entirely. Differences in cell geometries and gas flows certainly affect the flushing time, but it is interesting that the time apparent in Figure 3-6 is on the same order as those found optimal by Pisonero et al.<sup>22</sup> (10-130 µs) in double-pulse experiments, where sputtering occurs on the first pulse and ionization is enhanced by a second pulse.

# 3.3.4 Potential

Figure 3-7 shows typical trends in FWHM when pulse potential was varied and pressure, pulse width, and frequency were held constant. Pulse potential does not appear to have an appreciable impact. If there is any trend, it is towards slightly improved resolution at higher potentials. Consequently, it is best to use high potentials to maximize signal.

#### 3.3.5 Pressure

Figure 3-8 shows how FWHM varies with pressure while pulse width, frequency, and potential are held constant.

The FWHM narrows significantly as pressure is raised from 1.25 to 2.5 torr, but declines only slightly between 2.5 and 3.0 torr. The trend fits well to a 1/p dependence. This behavior likely has two related causes: diffusion and stopping distance. The exact contribution of diffusion to the relationship between pressure and profile width is complicated by the geometry of the cell and the relationship between intensities (summed perpendicular to the sample surface and over time) and actual Further, the local gas density and concentrations. temperature vary over the course of a discharge pulse.<sup>23</sup> Nonetheless, we can safely say that, because the diffusion coefficient is inversely proportional to pressure, the profile width should be greater at lower pressure, which is what is observed. Before moving by diffusion, however, the sputtered atoms travel a finite distance because of the momentum they receive during sputtering.<sup>24</sup> This distance is inversely proportional to number density in the ambient atmosphere, so it should be inversely proportional to pressure under otherwise fixed conditions. Again, the exact effect of this on profile width is difficult to establish. but it should be in the same direction as is observed. Whatever the relative contributions of the two causes, the results suggest that pressure should be kept above 2.5 torr to optimize resolution, but that above this point pressure has a diminishing impact on resolution.

#### 3.3.6 Pulse width

The FWHM was found to broaden with applied pulse width. As Figure 3-9 shows, the trend is well fit by a  $t^{\frac{1}{2}}$  dependence. With shorter pulses, atoms do not have time to travel far before the pulse terminates, so their distribution during the time that they can be excited and emit is narrow. When longer pulses are employed, the sputtered atoms can travel farther during the time when energy is available for excitation, so their distribution during the time when they can emit is broader. Because average diffusion distance follows a  $t^{\frac{1}{2}}$  dependence, the FWHM would be expected to have a similar dependence if the emission occurs throughout and even after the pulse, a  $t^{\frac{1}{2}}$  dependence still fits the data well.

Short pulse widths mean that there is a correspondingly brief amount of time that energy is being put into the glow discharge, but emission can continue a short time after the pulse. Gated detection might further improve resolution by limiting observation of the emission to a selected period.

# 3.3.7 Evaluation of optimized conditions and potential for improvement

Pulses of 1  $\mu$ s, 100 Hz, 4.0 kV, and a pressure of 3.5 torr, were chosen based on the results of the experiments above.

The Cu pin itself was measured under magnification to be  $1.02 \pm 0.03$  mm (FWHM) in diameter. This uncertainty results mainly from the fact that the pin is not perfectly circular. The emission peak over the pin was measured to be  $1.00 \pm 0.01$  mm. Given the resolution of the optical system and the slight asymmetry of the pin, better results cannot be expected. Further refinements in the technique would first require a higher-resolution optical system and a smaller, more regularly shaped inclusion.

# **3.4 CONCLUSIONS**

Glow discharge-optical emission spectrometry has been successfully used to image an inhomogeneity in elemental distribution. Using pulsed powering rather than dc greatly improved the resolution. Pulse width, pulse repetition rate, and pressure were found to have a significant impact on the resolution obtainable by the system. The effect of these parameters was traced to atom transport. Under optimized conditions, the width of a 1 mm copper insertion corresponded to the FWHM of the emission above it to better than 100  $\mu$ m accuracy. Limitations that are not inherent to the technique prevented resolution better than this level.

The obvious use of this technique is to add two dimensions to the analysis of conductive solids. With depth profiling, this capability would allow 3-dimensional analysis of elemental distributions. Other uses may not be as obvious. One factor that limits attainable depth resolution in glow discharge spectrometry is the shape of the sputtering crater. Although the center of the crater might be flat, its edges can curve upwards or downwards.<sup>8-9</sup> When this is the case, worse depth resolution results because different depths are being sputtered at the edges than at the center. By using short pulses and observing only emission from the central portion of the discharge, the depth resolution might be improved. The technique could also be expanded to non-conductive samples by applying radio-frequency energy gated with µs-pulses. Research into this avenue is ongoing in our laboratory, with promising results.

Particularly if gated detection were used, this technique could be used to further examine analyte transport in a glow discharge. A small insertion would limit the initial position, a brief pulse would limit the initial time, gated detection would limit the final time, and spatially resolved detection (either of emission or another signal such as fluorescence) would establish the final position.

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#### **FIGURES**



Figure 3-1. Cross section of the glow discharge cell (not to scale). Black areas are insulators, the window is fused silica, and the remainder of the cell body is brass. Inner diameter of the floating restrictor is 15.0 mm.



Figure 3-2. Background-corrected monochromatic image of the Cu I 327.4 nm line above a primarily Ni-Cr sample with a 1.0 mm diameter Cu insertion. The dashed ring shows the 15 mm diameter area sputtered by the discharge. Discharge Conditions: pulses of 1µs, 100 Hz, and 4.0 kV, and a pressure of 3.5 torr.



Figure 3-3. Relationship between uncertainty in peak FWHM (as percent RSD) and peak area. Glow discharge conditions were varied in order to encompass a wide range of peak areas.



Figure 3-4. Effect of Ar flow on spatial resolution. 4.0 µs pulse, 2.75 kV, 2.75 torr, 100 Hz.



Figure 3-5. Effect of pulse separation on profile shape. Solid line shows 2.0 ms separation. Dashed line shows 0.3 ms separation. 1.0 µs pulse, 4.0 kV, 4.0 torr.



Figure 3-6. Effect of pulse separation on profile shape. 1.0 µs pulse, 4.0 kV, 4.0 torr.



Figure 3-7. Effect of applied pulse potential on spatial resolution. 2.0 µs pulse, 2.5 torr, 100 Hz.



Figure 3-8. Effect of pressure on spatial resolution. Solid line is a 1/x fit to the data. 3.0-µs pulse, 3.0 kV, 100 Hz.



