Articles

Emission Characteristics of the Gas Jet Assisted Glow Discharge for Direct Solid Analysis : Preliminary Studies I

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The gas jet enhanced glow discharge system for direct solid analysis has been designed and constructed in our laboratory. Contrary to the conventional glow discharge, the laminar flow of argon gas through the 0.5 mm gap impacts a surface of solid sample. In addition, a needle valve is placed between a glow discharge cell and a vacuum pump to control the pressure of a glow discharge cell. As a result, the pressure could be precisely controlled without changing the flow rate of argon gas. Due to the presence of laminar flow of argon gas onto the surface of the sample, the analytical performances are quite different from those observed in a conventional glow discharge system. Emission behaviors of resonance and non-resonance lines for Cu, Zn and Ar are mainly discussed. In this report, the preliminary experimental results including emission characteristics and sputtering efficiency are presented.

Introduction

A glow discharge source (GDS) with a flat cathode was first introduced by Grimm[1] and soon regarded to be a powerful radiation source for the emission spectrometric analysis of conducting samples.[2~3] Due to sample ablation by cathodic sputtering, matrix effects resulting from selective volatilization are absent; also, as a result of the dynamic equilibrium between sample ablation and analyte redeposition, stable analytical signals are obtained.[4]

Gough[5] first described gas jet assisted glow discharge (GJGD) with a six-jet, which uses the principle of directed support gas flows. The six-high-velocity gas jets increase the amount of material atomized as well as change the electrical characteristics, as is apparent from the craters produced in the sample where the jets strike the surface. Compared with the cell designed by Grimm, it is probable that a resultant flow away from the cathode is established near the sample surface. Therefore, the six-high-velocity gas jets minimize the loss of atoms and retard the sample redeposition.[5~6] In recent years, GJGD for spectroscopic elemental analysis was studied by Blades[7,9,10] and others.[8,11,12] Blades[7,9,10] reported that the jet-gas flow increased the sample loss rate by a factor of three times comparing to a GD system with no flow. In general, the intensities of the emission lines were enhanced. However, slight self-absorption effects were observed for some resonance lines which have relatively large absorption coefficients. Chakbrabarti[11,12] investigated the effects of current, pressure, flow rate, and sample loss rate on atomic absorption and emission intensities with a jet-assisted cathodic sputtering atomizer. The enhancement on both absorption and emission intensities were observed.

The present paper describes a modification of a conventional Grimm-type GD that enables jet-assisted sputtering to be performed. Contrary to the other GJGD systems described above, a radial cone shaped gap was used instead of a six-jet nozzle. Therefore, its fundamental electrical characteristics and operating conditions are slightly different from those observed by the other GJGD using a six-jet nozzle. In this preliminary paper, the geometry of the GJGD and the effect of the several experimental variables on the emission intensity are mainly discussed. Effects of pressure change, flow rate, current, and sample loss rate on emission behavior in the GJGD with the radial cone shaped gap will be presented. In addition, the sample surfaces sputtered have been examined using SEM.

Experimental

The schematic diagram of the GJGD system constructed in our lab is shown in Figure 1. A single-stage oil rotary pump was used to attain gas flows of 0-600 L/min at 1.4-4.0 torr. The flow of argon gas through the jet was controlled and measured by a MKS 247C mass flow controller (MKS, Andover, MA, USA). A Balzers TPG 300 pressure gauge (Balzers, Furstentum, Liechtenstein, Switzerland) was used for measuring the gas pressure. A 1 kV, 200 mA DC power supply (IMACE, Seoul, Korea) was used. A 3-way solenoid valve (CKD normal close, AG43-02-5) operated by a 110V AC was used to change the flow direction. The solenoid valve was automatically operated by Solid State Relay and Relay Driver Board (PCLD-786, Advantech Ltd., Taiwan). The sputtering gas was passed through the mass flow controller when the power of a 3-way solenoid valve was on. Because of the

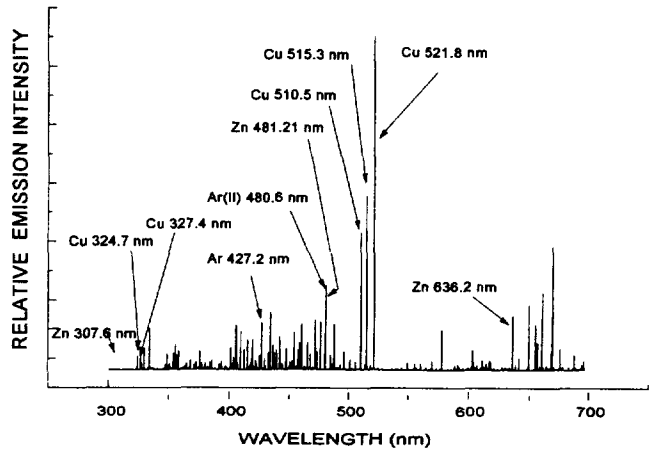

Figure 4. Emission Spectrum of brass.

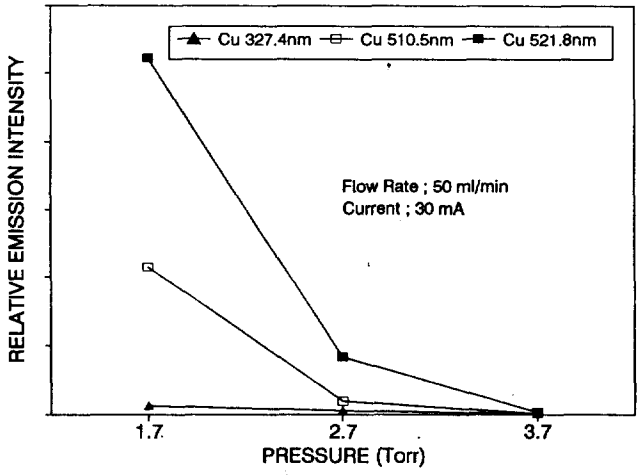

Figure 5. Effect of pressure on Cu emission intensity.

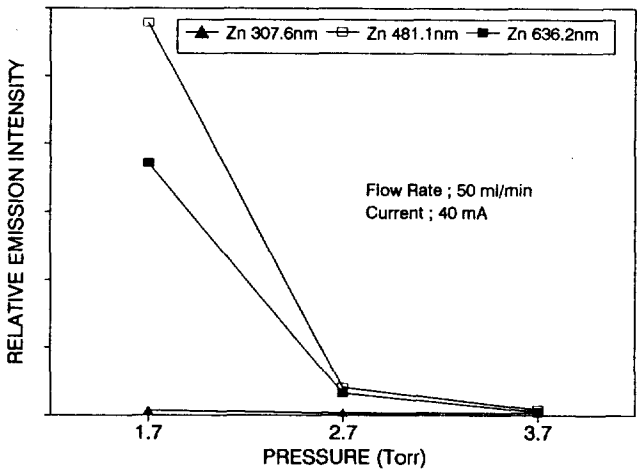

Figure 6. Effect of pressure on Zn emission intensity.

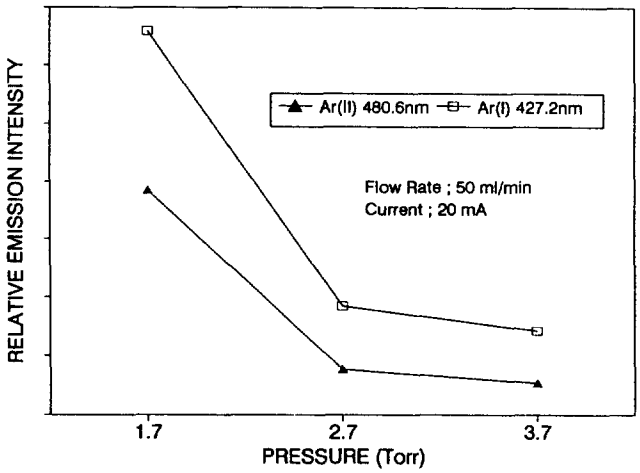

Figure 7. Effect of pressure on Ar emission intensity.

torr to 3.7 torr, the voltage decreases to keep the source discharge current. The discharge voltage rises considerably as the current increases at 1.7 torr, but is relatively invariant at 2.7 and 3.7 torr. It is found that the abnormal glow region plasma where cathodic sputtering is most active is produced. From the comparison of the slopes, it is apparent that the pressure is critical factor to affect the voltage change in the cell.

The typical emission spectrum of brass from 300 nm to 700 nm with the GJGD with a radial cone shaped gap is shown in Figure 4. The emission intensities of the Cu resonance lines at 324.7 and 327.4 nm are relatively less than those of the non-resonance line at 510.5 and 521.8 nm. It is apparent that self-absorption of the resonance line with the axial-viewed GD system is severe comparing to a side-viewed GD system, and reported by M. W. Blades.[12]

Figure 5 shows the plot of relative emission intensity of copper vs pressure at 50 mL/min and 30 mA. The copper resonance line at 327.4 nm (0-30535 cm^{-1}), the non-resonance line of lower energy level at 510.5 nm (11203-30784 cm^{-1}) and that of high energy level at 521.8 nm (30784-49942 cm^{-1}) were chosen. For the copper non-resonance lines at both 510.5 and 521.8 nm, the emission intensities decrease rapidly as the pressure increases from 1.7 to 3.7 torr. The emission intensity at higher energy level is more susceptible to change than that of at lower energy level. However, the pressure sensitivity of the copper resonance line is less than that of the non-resonance lines. This pattern is also observed at both 20 and 40 mA of current. In general, this result can possibly be explained by the shortened effective mean free path. That is, the effective mean free path in the negative glow region is shortened with increasing pressure. Therefore, the kinetic energy of argon ions which bombards the cathode surface is significantly reduced. From this reason, the lowering of cathodic sputtering rates may result in a decrease of emission intensities.

Figure 6 shows the pressure effect of the resonance line and the non-resonance lines for zinc. The zinc resonance line at 307.6 nm (0-32502 cm^{-1}), the non-resonance line of lower energy level at 481.1 nm (32890-53672 cm^{-1}), and that of high energy level at 636.2 nm (46745-62458 cm^{-1}) were investigated. The pressure sensitivity of zinc emission intensity is quite similar to that of copper. For the zinc non-resonance lines, the emission intensities decrease rapidly as the pressure increases from 1.7 to 3.7 torr, especially at lower energy level. Also, Figure 7 shows the pressure sensitivity

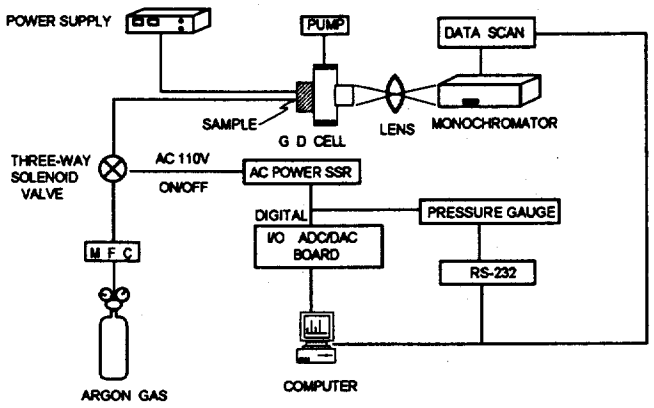

Figure 1. Schematic diagram of the gas jet-assisted glow discharge system.

Table 1. Specifications of the Instruments

Instruments	Specification
DC Power Supply	IMACE 1000V, 200 mA
DAC/ADC Board	PCLAB 812-PG (Advantech Ltd.)
	16 analog/digital input
	3 analog output
	12 bit ADC/DAC
Solid State Relay	PCLD 786 (Advantech Ltd.)
	AC Power: 110-240 V
Solenoid Valve	CKD AG31-02-1
	Three way valve
Mass Flow Controller	MKS 247C, 4 channel
Pressure Gauge	Balzers TGP 300
Monochromator	ARC VM-507
	Focal length : 50 cm

importance of excluding water vapor from the sputtering discharge and the purity of the inlet argon gas supply to the discharge cell, a molecular sieve filter was used for the argon inlet gas. In addition, a cold trap was used for the elimination of the back diffusion of pump oil vapor into the sputter cell.

A 0.5 m Czerny-Turner monochromator (ARC VM-507, USA) was used for emission intensity measurements. The emission intensity measured by a photomultiplier tube (Model R928P, Hamamatsu, Japan) was amplified by a current amplifier, and stored in an IBM compatible computer for data manipulation. The specifications of instruments used in this study are summarized in Table 1.

The schematic diagram of the GJGD cell used in this study is shown in Figure 2. The GD cell consists of a teflon chamber with a demountable quartz window at each end. The copper cathode plate is cooled by water in order to keep the sample temperature constant. A flat sample is sealed over the 0.8 cm diameter hole in the cathode plate with a silicon rubber O-ring. The 0.5-mm gap nozzle is located 1 mm away from the front of the sample, and pointed so that high velocity jets of gas are directed toward the sample surface at the angle of 60°. As shown in Figure 2, the argon gas flow transports the atoms away from the cathode, and

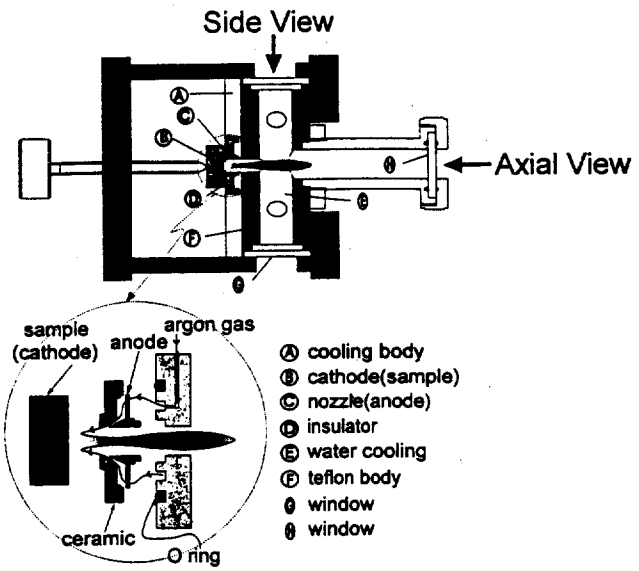

Figure 2. Schematic diagram of the gas jet-assisted glow discharge (GJGD) cell.

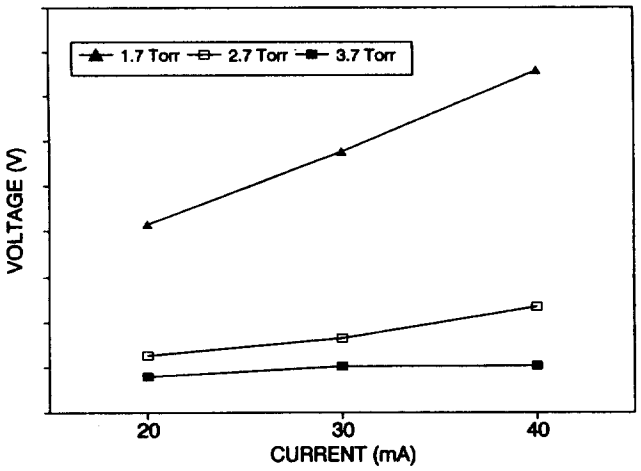

Figure 3. Effect of pressure on the voltage-current relationship.

hence the sampling efficiency increases.

Results and Discussion

There are three variables in this system which can be directly manipulated to affect emission intensities; argon flow rate through the jets, the pressure in the cell, and the source current. Among them, the voltage-current relationship at a constant pressure is very important on the cathodic sputtering. In order to keep the gas pressure constant while the gas flow rate is changed, the gas pressure in the cell is controlled by a needle valve between the pump and the cell.

The voltage-current characteristics of the discharge at the several pressures are shown in Figure 3. Because the power supply used in this experiment was operated in the current control mode, the voltage-current characteristics were obtained by measuring voltages at different argon gas pressures for each current setting. As the pressure increases from 1.7

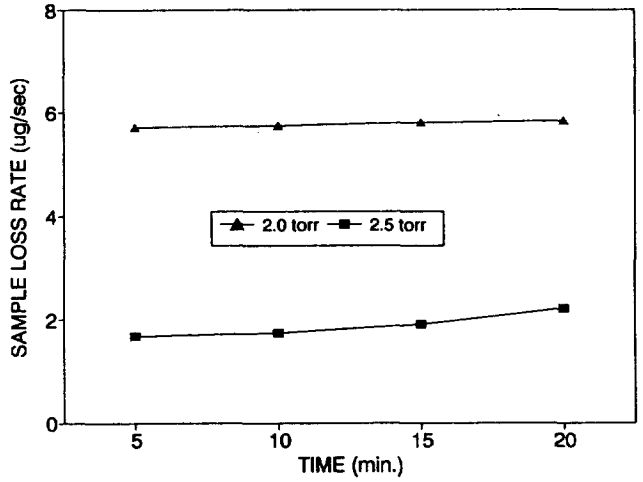

Figure 8. Plot of Sample loss rate vs sputtering time at 2.0 and 2.5 torr.

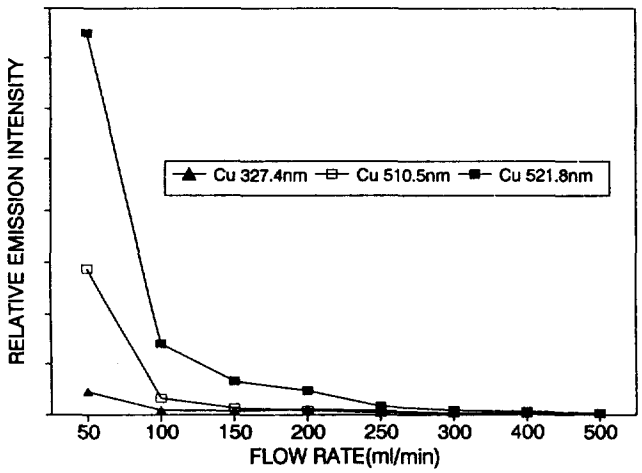

Figure 9. Dependency of Ar gas flow rate on Cu emission intensity.

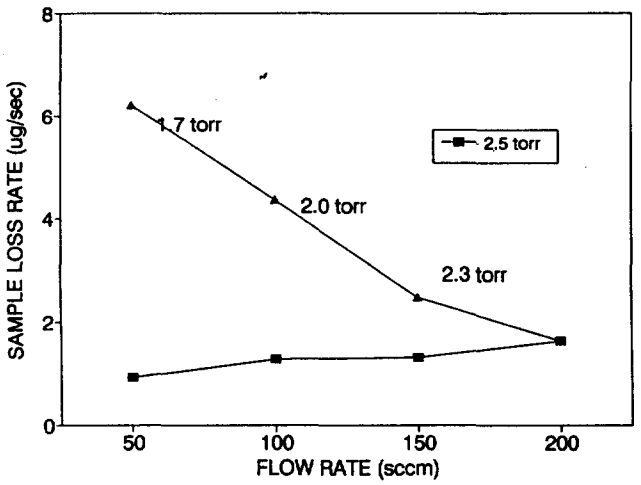

Figure 10. Dependency of gas flow rate on sample loss rate.

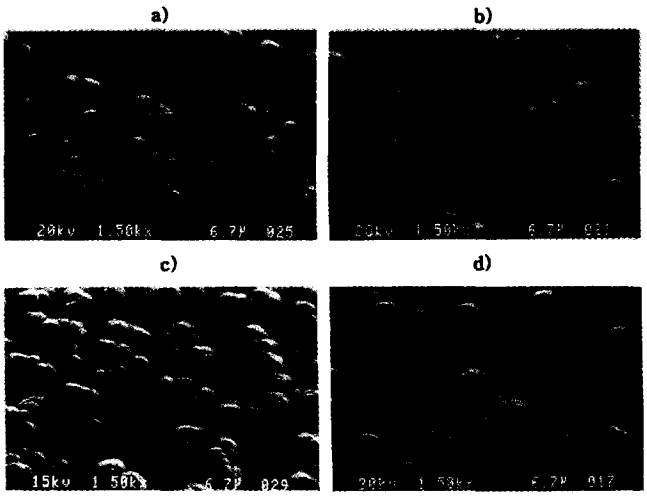

Figure 11. SEM photographs of brass sample with respect to gas flow rate at a constant pressure of 2.5 torr; a) 50 mL/min, b) 100 mL/min, c) 150 mL/min, d) 200 mL/min.

of emission intensities for a argon. It is found that the emission intensities for both neutral atom line at 427.2 nm and ionic line at 480.6 nm are decreased rapidly by the increasing pressure.

Figure 8 shows the sample loss rate as a function of sputtering time at the gas pressures of 2.0 and 2.5 torr. The argon flow rate of 100 mL/min and the discharge current of 23 mA were used. The average sample loss rate from 5 to 20 min of the sputtering time was studied for the pressures of 2.0 and 2.5 torr. The average sample loss rates are found to be 5.7 and 1.9 μg/sec at 2.0 and 2.5 torr, respectively. As described above, at the lower pressure, the greater sample loss rate becomes. It is found that the sample loss rate is generally constant during the entire sputtering time.

As the argon flow rate plays a key role in sputtering process, the argon flow rate was measured using a mass flow controller operated precisely by the IBM compatible computer. The variation in copper emission intensities as a function of argon flow rate is shown in Figure 9. The argon flow rate through the jets are varied from 50 mL/min to 500 mL/min. The intensities of both resonance and non-resonance lines tend to decrease. As the argon flow rate is increased through the jet, the pressure inside the source increases. As a result, the emission intensity decreases. This can be explained by two factors. First, this is mainly due to the pressure effect. As the gas flow rate increases, the cell pressure increases. Hence, it is obvious that the emission intensities of copper, zinc, and argon are decreased. Second, when the higher gas flow rate is used, the cooling of the negative glow is expected. It seems likely that the jet also causes a physical disruption of the glow discharge, perhaps making the negative glow more diffuse leading to a reduction in excitation ability. Some degree of visual proof is apparent by the increase in the size of the emission plume formed inside the hollow anode at higher argon flow rates.

In order to investigate the effect of argon gas-jet impact itself, the pressure of the cell was kept constant at 2.5 torr by adjusting the needle valve between the cell and the vacuum pump while the gas flow rates are varied. The aim is to elucidate the effect of argon gas-jet impact at a constant pressure. Figure 10 shows that the plot of the sample loss

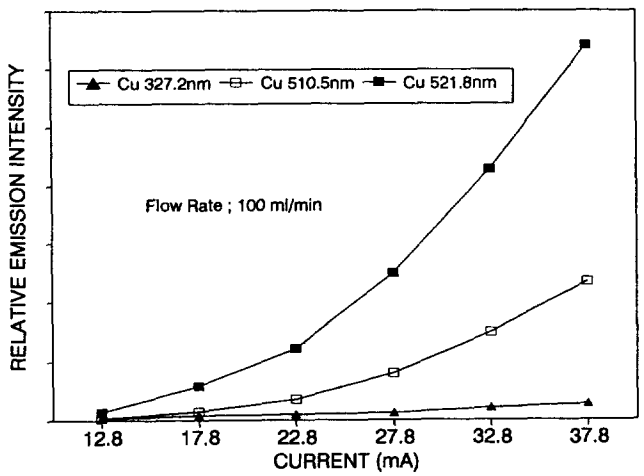

Figure 12. Effect of current on Cu emission intensity at 100 mL/min of flow rate and 1.7 torr of pressure.

rate *vs* the gas flow rate for the cases of the constant and varied pressures. As shown in Figure 10, when the gas flow rate is increased from 50 to 200 mL/min, the sample loss rate is significantly decreased from 6.2 to 2.0 g/sec due to apparent increase of the pressure from 1.7 to 2.5 torr. Contrary to the case of the varied pressure, when the pressure is kept constant at 2.5 torr while the gas flow rate is varied from 50 to 200 mL/min, the sample loss rate is rather increased from 1.0 to 2.0 g/sec. In the gas-jet system, the argon gas flow transports the atoms away from the cathode more rapidly than they can diffuse back to the cathode sample, so the sampling efficiency increases.

The SEM photographs of the sample surface observed at the constant pressure is shown in Figure 11. Figure 11 a), b), c), and d) represent the SEM photographs for 50, 100, 150, and 200 mL/min of a gas flow rate at a constant pressure of 2.5 torr, respectively. As it was seen earlier, the sample loss rate increases with increasing gas flow rate at a constant pressure. At the higher gas flow rate, the sizes of cones and hillock increase due to the great sample weight loss. Further experimental results related to the subject on the morphology, redeposition, and sample loss rate will be reported in a subsequent paper.

Figure 12 shows the current sensitivity on emission intensity for copper lines. This indicates that the emission intensities of copper rapidly increase as the current increases from 12.8 to 37.8 mA. A constant gas flow rate of 100 mL/min and a pressure of 1.7 torr are used. As mentioned in Figure 3, a voltage is generally increased by increasing a current. Therefore, the enhanced sputtering is observed by increasing a power. Because the electron number density in the discharge is directly proportional to the plasma current, the emission intensities are increased due to the activated sputtering.

Conclusion

The analytical characterization of a new laboratory-constructed glow discharge cell for direct solid analysis in atomic emission spectrometry has been done. In this system, three variables affecting emission intensities, argon flow rate through the jets, pressure in the source, and the source voltage, were thoroughly investigated.

According to this preliminary study, it is found that pressure in the source is the important parameter which determines the magnitude of emission intensity. For copper and zinc, the emission intensities of the non-resonance lines are greatly varied by operating parameters, but the resonance lines are less sensitive than the non-resonance lines due to a self-absorption effect. Self-absorption of the resonance line is observed with the axial-viewed GJGD system. Further investigations including the continued development of this system is undergoing. In particular, future designs should incorporate improved jet-gas flow characteristics in order to minimize problems associated with self-absorption.

As a pressure is increased at a constant gas flow rate, the emission intensities of copper, zinc, and argon are significantly decreased due to the shortened mean free path of the particulates. It is found that the emission intensity at higher energy level is more susceptible to change than that of at lower energy level. In the GJGD system studied here, the argon flow rate plays a key role in sputtering process. As the argon flow rate is increased through the jet, the pressure inside the source also is increased. Hence, the emission intensity decreases due to the pressure increase. However, when the pressure is kept constant while the gas flow rate is varied, the emission intensity and sample loss rate are enhanced. It suggests that the use of jets increases sampling efficiency. Further investigations are undergoing.

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