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Microwave-induced Plasma Boosted Microsecond-pulse Glow Discharge Optical Emission Spectrometry

YONGXUAN SU, PENGYUAN YANG*, DENGYUN CHEN, ZHIGANG ZHANG, ZHEN ZHOU, XIAORU WANG AND BENLI HUANG

Department of Chemistry, Laboratory of Analytical Science, Xiamen University, Xiamen 361005, China

A microsecond-pulse (μs-pulse) glow discharge (GD) source boosted by a microwave-induced plasma (MIP) has been developed and studied for optical emission spectrometry (OES). The excitation processes of the tandem GD source were investigated. The analytical characteristics of the GD-OES source in the presence and absence of the MIP were compared, including the operating parameters, signal-to-background ratios (S/B) and relative standard deviation (RSD). The results show that under a relatively low discharge pressure (<180 Pa), the μs-pulse GD can couple fairly well with the MIP and emit intense analytical lines. When the GD source is operated under a pressure higher than 200 Pa, two emission peaks appear, independent in time, for a given resonance atomic line, because sample atoms are independently structurally excited, first by the μs-pulse GD and then by the MIP. The time interval between the two peaks for Zn I 213.8 nm is longer than that for Cu I 324.7 nm, which is believed to be due to the faster diffusing velocity of copper atoms. When the μs-pulse GD lamp is operated under a gas pressure higher than 220 Pa, the ion population is so high that Cu II ionic line at 224.7 nm 'becomes' two peaks because of a possible self-absorption. The results show that the supplementary use of an MIP can eliminate the self-absorption of ionic and atomic lines. When the μs-pulse GD source is coupled with the MIP, S/Bs are improved by a factor of more than one order of magnitude for several analytical lines. A short-term RSD of 0.2% is achieved for the 'μs-pulse GD+MIP' configuration compared with that of 1.0% for 'μs-pulse GD only' mode. The experimental results show that the MIP boosted μs-pulse GD is a promising technique for solid sample and surface analysis.

Keywords: *Microsecond-pulse glow discharge; microwave-induced plasma; optical emission spectrometry; tandem source; excitation process*

Glow discharge (GD) has been widely used in optical emission spectrometry (OES), atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) for analytical applications, and also has served extensively as an ion source for mass spectrometry (MS).[1] Various techniques have been used to obtain high intensity without losing the advantage of narrow spectral lines. Leis and Steers have reviewed articles on boosted GD sources.[2] The use of an MIP to enhance the performance of a GD has attracted increased interest since the 1980s.[3–5] The advantage of a microwave-boosted GD lamp is that the atomization of a solid sample is performed by the process of cathode-sputtering in the GD while highly efficient excitation of analytical lines can be carried out in an MIP at low pressure.

A GD source with microwave boosting has been presented by Leis *et al.*[3] They combined a conventional Grimm-type GD source with an MIP sustained in a tunable Beenakker TM_{010} resonator. It is known that an MIP shows good excitation properties but is not particularly suitable for atomization. When in combination with a GD source, free sample atoms produced by cathode-sputtering in the GD enter the MIP by diffusion and convection. However, most previous studies on MIP boosted GDs operated under the dc GD mode.

As a new member type of GD, μs-pulse GD has recently been paid more attention in analytical areas, including OES, AAS, AFS and MS techniques.[6–9] Experimental results have shown that the μs-pulse GD mode has an analytical performance that is much better than the dc GD mode.[7,8] The pulsing technique is also a useful diagnostic tool for the excitation and ionization processes in a GD plasma.[6,10–12] In order to evaluate the possibility of using μs-pulse GD as an ion source for solid sample analysis as well as depth profile analysis on a solid surface, experiments on μs-pulse GD time of flight mass spectrometry (TOFMS), with some interesting results have been carried out.[8,9] One of the most significant characteristics of μs-pulse GD is that the sputtering rate of μs-pulse GD is more than two orders of magnitude higher than in dc GD during the pulse-on regime, and that the average discharge power is relatively low.[9] Therefore, the number of sample atoms produced in the very short pulse time is significantly high.

In the present work, an MIP plume is superimposed on the sputtered sample atom–ion cloud in order to obtain atomic and ionic lines of high intensity. Based on the work of μs-pulse GD-TOFMS, an MIP boosted μs-pulse GD source has been designed in which the MIP is sustained in a tunable Beenakker TM_{010} resonator. The excitation processes of the OES source were studied. The effects of the operating parameters on μs-pulse GD in the presence and absence of the MIP were investigated. A comparison of analytical characteristics for the μs-pulse GD alone and the μs-pulse GD-MIP tandem source is presented, in terms of the signal-to-background (S/B) ratios and relative standard deviation (RSD).

EXPERIMENTAL

MIP Boosted μs-Pulse GD-OES Source

A schematic diagram of the MIP boosted GD source is shown in Fig. 1. The structure of the GD source is similar to the one used as an ion source for TOFMS and has been described in detail previously.[9] Both the GD source and the resonator are made of brass. The discharge gap in GD lamp is designed to be relatively thin, such that the distance between the microwave cavity and the sample cathode is only 7 mm. Water cooling is used directly to cool the sample cathode. The anode body and the microwave cavity are earthed. A quartz tube with an id of 8 mm, separates the inner low pressure region from the outer atmospheric pressure. Two tuning screws are used to adjust the minimum reflected power.

The lamp is evacuated by a two-stage mechanical pump (4 dm^3 s^{-1}, Shanghai Vacuum Plant, Shanghai, China) and the working carrier gas is pumped continuously through the lamp. The working gas pressure is regulated by an inlet needle

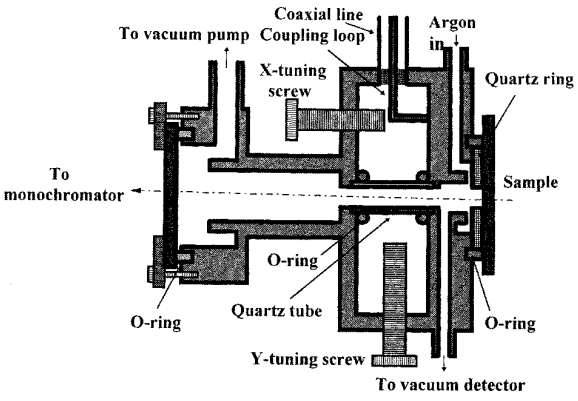

Fig. 1 Structure of the MIP boosted μs-pulse GD source. The solid sample is sputtered and atomized in the GD, and the excitation occurs in the MIP tandem μs-pulse GD discharge.

valve and monitored with a thermocouple gauge (ZDO-54, Chengdu Instrument Factory, Chengdu, China).

The μs-pulse GD power supply is laboratory built with the following adjustable parameters: discharge frequency (10–5000 Hz); discharge duration (0.2–5 μs); and discharge current (0.03 mA–3.1 A). The voltage output of the μs-pulse GD power supply is kept at −750 V.

The microwave generator produces a maximum power of 200 W at a frequency of 2450 MHz (Hai Guang Instruments, Beijing, China). It is connected to the resonator *via* a 2 m length of coaxial cable with 50 Ω impedance. Two meters indicate the forward and reflected microwave powers.

Experimental Set-up

Investigation of the excitation processes in the GD source

A block diagram of the experimental set-up used for investigating of the excitation processes is shown in Fig. 2. The radiation source is imaged by a quartz lens onto the entrance slit of a 0.5 m Czerny–Turner monochromator (Acton Research, Acton, MA, USA), with 1800 grooves mm^{-1} and a blaze wavelength of 500 nm. Both the entrance and exit slit-widths are 20 μm. Signals from the preamplifier were observed with a 40 MHz oscilloscope (Model BS-5504, Aron, Korea), they can also be integrated with a boxcar integrator (laboratory made) and then recorded with a recorder (Model 9176, Varian, Palo Alto, CA, USA) or a compatible PC-386 computer with a 20 MPS analogue to digital converter.

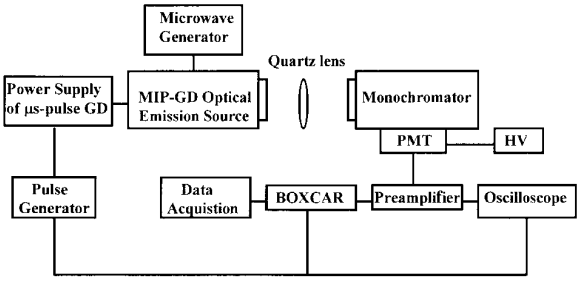

Fig. 2 Schematic diagram of the MIP boosted μs-pulse GD-OES system. A commercial ICP-AES is utilized to replace the monochromator and the signal processing system, when the analytical characteristics of this tandem GD source are evaluated. See text for details.

Comparison of the analytical characteristics of the GD source in the presence and absence of the MIP

An ICP-AES instrument (sequential ICP-AES, Model 2070, Baird, Bedford, MA, USA) was utilized, with a built-in 1 m Czerny–Turner monochromator with a grating of 3600 grooves mm^{-1} and a blaze wavelength of 400 nm. The ICP torch was removed and replaced by the GD–MIP tandem source. The slit-widths of both the entrance and the exit are 17 μm. Signals are integrated for 0.2 s, and then digitized with a OS-2 microcomputer. The signal processing part of this ICP-AES instrument is designed for continuous emission rather than signal pulses, such as a microsecond wide signal obtained in the present study. Thus, the signal pulse has to be averaged against a background signal of about 500 μs for a pulse rate of 2 kHz that is used in this study. Therefore, the S/B obtained in this experiment can only be used as reference values for a comparison of some of the results obtained for a μs-pulse GD in the absence and presence of the MIP.

Experimental Considerations

The lamp can be operated in two optical configurations: 'μs-pulse GD only' and 'μs-pulse GD + MIP'. The current was regulated for μs-pulse GD and argon was used as the carrier gas. A dc voltage (−750 V, with a current of several tens of μA) was utilized to pre-burn the sample cathode. After several days operation, the reflected microwave power could increase owing to the redeposition of sputtered material on the inner surface of the quartz tube. In the case of brass samples, the quartz tube should be cleaned frequently because of the high sputtering rate and the thin metallic film hampers the efficient coupling of the microwave energy.

RESULTS AND DISCUSSION

Study of the Excitation Processes of the GD-OES Source

Superimposition of an MIP on a GD

When sufficient microwave power (50 W forward power in the present experiment) is superimposed on a running GD plasma, a microwave discharge in the quartz tube can be ignited, and forms a plasma extention to the positive column of the GD. No boundary between the microwave discharge and the μs-pulse GD can be observed visually. A minimum reflected power of about 5 W can be obtained by adjusting the two tuning screws. Because charged particles are also produced by the MIP, the transient pulse voltage drop between the anode and cathode decreases significantly, and the radiation of the lamp is obviously enhanced when the microwave generator is switched on.

Effect of Discharge Parameters on Excitation Processes

Dependence of discharge pressure on the coupling of an MIP with μs-pulse GD

The argon pressure can clearly affect the coupling of an MIP with μs-pulse GD. As shown in Fig. 3, the sample atoms emit a strong radiation peak when the MIP boosted μs-pulse GD lamp is operated at a discharge pressure lower than 180 Pa. However, if this GD lamp is operated at a pressure higher than 200 Pa, two emission peaks appear independently in time for a given resonance atomic line (see Fig. 3). Depending on the increase in argon pressure, the MIP plume tends to shrink away from the GD region. The sample atoms are excited first by μs-pulse GD and then by the MIP when atoms move from the GD region to the MIP region. As shown in Fig. 3(*a*), the first peaks (peak I) correspond to the emission excited by μs-pulse GD and the second peaks (peak II) by the MIP. The

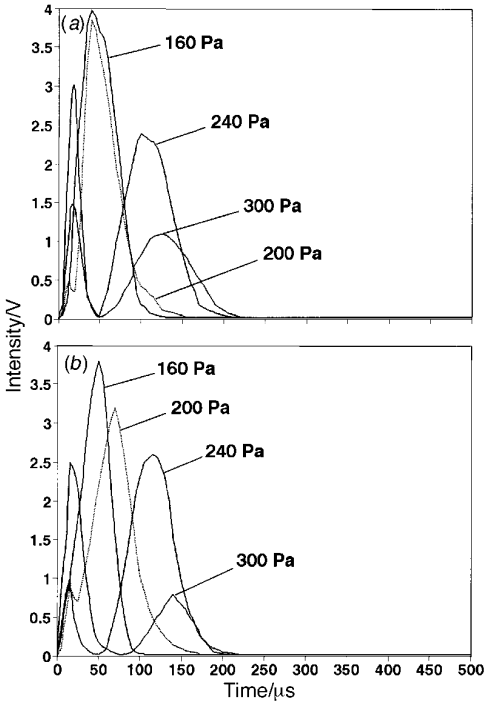

Fig. 3 Effect of discharge pressure on the time-resolved resonance atomic lines for a brass sample: (*a*) Cu I 324.7 nm; (*b*) Zn I 213.8 nm.

sputtering rate increases in accordance with discharge pressure, and the high pressure may also tend to slow the loss of sputtered atoms owing to diffusion, and as a result peak I increases. However, because the gap between the sample and the MIP plume lengthens, the density of the atom cloud decreases when the atom cloud passes through the MIP excited region. For ionic lines with high energy transition radiation, only the first peak appears with the superimposition of the MIP. In general, the radiation emitted by the microwave boosted lamp can be characterized by those spectral lines with low and mean excitation energies.

The time duration for peak I at its maximum value is 15 μs after the discharge pulse starts and is almost the same for both Zn I 213.8 nm and Cu I 324.7 nm. This time value hardly varies with the change in discharge pressure because the shift of the most excited region in μs-pulse GD is insignificant. However, the duration of peak II at its peak value changes according to the discharge pressure, because the MIP plume shrinks further away from the GD excited area with an increase in argon pressure.

The relationship between time interval of the two emission peaks and discharge pressure is illustrated in Fig. 4. It can be seen that the higher the discharge pressure, the longer the time interval, and that the time interval between the two peaks for Zn I 213.856 nm is longer than that of Cu I 324.7 nm under identical operating parameters, which is believed to be due to the faster diffusing velocity of the copper atoms. When the discharge pressure is 300 Pa, the times for peak II at the peak values are about 120 and 140 μs for Cu I 324.7 nm and Zn I 213.8 nm, respectively. The distance between the sample and the central part of the quartz tube is about 18 mm (the thickness of the quartz restrictor ring is 3 mm). Therefore, the average diffusing velocities of copper and zinc atoms can be estimated to be 150 and 129 m s^{-1}, respectively, and the most reactive region for excitation in this μs-pulse GD is 1.94–2.25 mm (estimated from the diffusing velocity multiplied by the time interval between the falling edge of the discharge pulse and peak I at its maximum value) from the sputtering

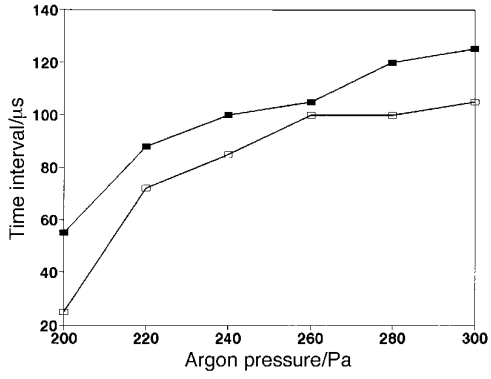

Fig. 4 Effect of discharge pressure on the time interval between peak I and peak II for different resonance atomic lines: ■, Zn I 213.8 nm; and □, Cu I 324.7 nm.

surface of the sample cathode under the operating conditions used.

Effect of discharge frequency and pulse duration on emission intensities

The effect of discharge frequency on the intensities of peaks I and II for Zn I 213.8 nm and Cu I 324.7 nm are illustrated in Fig. 5. It can be seen that the peak height for peak I reduces with an increase in discharge frequency. If the discharge frequency is operated between 800 and 1200 Hz, peak II can reach a maximum value. Above this frequency range, the higher the frequency, the lower the peak height will be. It could be supposed that a very high discharge frequency would eliminate the sputtered and excited processes because the laboratory made power supply is unable to recover for the next discharge pulse owing to its limited power capacity.[9] This finite capacity of the discharge power could also limit operation of the GD pulse to a relatively wide pulse duration. Walden *et al.* have found such results in their experiments on μs-pulse GD-OES.[7] The present work also indicated that intensities of both peak I and peak II increased according to the duration of the discharge pulse, although not obviously (the maximum pulse duration can be adjusted only to within 5 μs in the pulse generator).

Effect of discharge current on emission intensities

The relationship between the transient current and the radiation intensities of peak I and peak II is given in Fig. 6. Visual observation through the quartz window showed that the glow

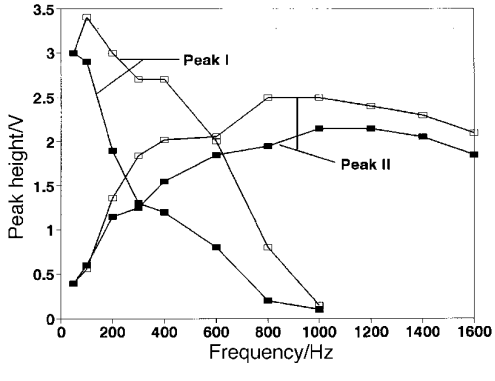

Fig. 5 Dependence of emission intensities of peak I and peak II on discharge frequency: ■, Zn I 213.8 nm; and □, Cu I 324.7 nm.

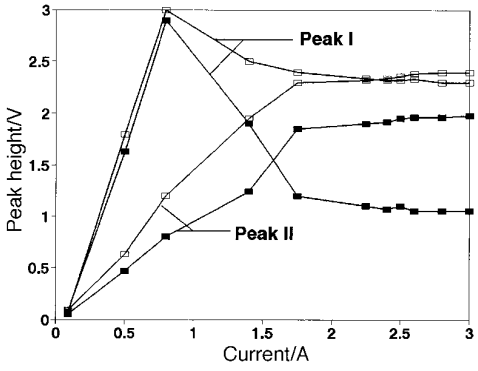

Fig. 6 Effect of discharge current on the intensities of peak I and peak II: ■, Zn I 213.8 nm; and □, Cu I 324.7 nm.

turns white and then green with an increase in discharge current, indicating very intensive sputtering and excitation processes. Peak I increases sharply correspondingly with discharge current and reaches its peak when the transient current is about 0.8 A, then the emission intensity tends to decrease. In this experiment, it was observed that when the discharge current increases, the line profile of peak I widens with hardly any increase in peak intensity. It could be that a self-absorption occurs, which is a result of the high density of 'cool' atoms surrounding the 'hot' atoms in the center of the plasma. However, peak II increases steadily and tends to saturation only when the current is higher than 2 A. The high current can result in an increase in the sputtering rate, and more sample atoms can be excited by the MIP. The self-absorption in the MIP excited region is not severe because of a relatively low density of 'cool' atoms.

Effect of microwave power on emission intensities

The forward microwave power was optimized at 50 W throughout the experiment. The microwave power has a minor effect on emission peaks when the power is varied between 50 and 80 W. When the forward power is high, the reflected power will increase accordingly, and is rather difficult to tune unless the discharge gas pressure is lowered for improved coupling. However, a low discharge pressure can eliminate sputtering. The experimental results are also supported by previous reports from Li *et al.*[5] They found that the MIP and dc GD can be optimized to an ideal coupling by adjusting the relationship between discharge voltage, microwave power and discharge pressure under different discharge conditions. In their experiments, the maximum S/B levels could also be achieved with a microwave power of 50 W, if the GD lamp is operated under a low discharge pressure.[5]

Effect of MIP on the Excitation of Ionic Lines

The excitation and ionization processes are very intensive when the μs-pulse GD lamp works under a high transient current and relatively high pressure (>220 Pa). Owing to its high ion populations, the ionic line of Cu II 224.7 nm appears to become two peaks because of a possible self-absorption. Supplementing with the MIP affects the excitation of sample ions and results in the alleviation of this self-absorption of Cu II 224.7 nm. Steers and Leis have reviewed many examples of charge exchange (CE) excitation between sample atoms and argon ions in a GD source,[13] which has been believed to be a very important process for the excitation of ionic lines in a GD with inert gases. The change in the ion density of argon can be observed by a mass analyser coupled with an MIP boosted μs-pulse GD for a better understanding of the excitation mechanism. Such an experiment is currently in progress in this laboratory.

Effects of MIP on Sputtering Rate and Sputtered Surface

The addition of an MIP has an obvious effect on sputtering rate as well as on the topography of the sputtered surface. The sputtering rate of μs-pulse GD has been studied previously[9]. The transient sputtering rate (9.5 μg s^{-1} mm^{-2}) for 'μs-pulse GD+MIP' is only about half of that of 'μs-pulse GD only' (21 μg s^{-1} mm^{-2}) under the same operating conditions for a brass sample, with a discharge frequency of 1.8 kHz, pulse duration of 3 μs, current of 2 A and pressure of 180 Pa. The crater on the surface of the erosion area also becomes finer, when observed with a scanning electron microscope (Hitachi S-300, Tokyo, Japan). The decrease in sputtering rate and the improvement in crater shape are believed to be due to the lower voltage drop between the anode and cathode.[14] For more details of the results of the sputtering rate and on the sputtered surface for μs-pulse GD, see ref. 9.

Comparison of the Analytical Characteristics of the OES Source in the Presence and Absence of the MIP

Dependence of emission intensities on discharge parameters

As described above, an MIP can couple well with μs-pulse GD if the discharge pressure is maintained at less than 200 Pa. In order to evaluate the analytical characteristics of the boosted GD source, the argon pressure in the discharge chamber was kept relatively low throughout the following experiments.

Effect of discharge frequency on spectral intensity. As shown in Fig. 7, emission intensities of the integrated signals increase steadily in accordance with the increase in discharge frequency without an MIP, and increase sharply (especially for Cu I

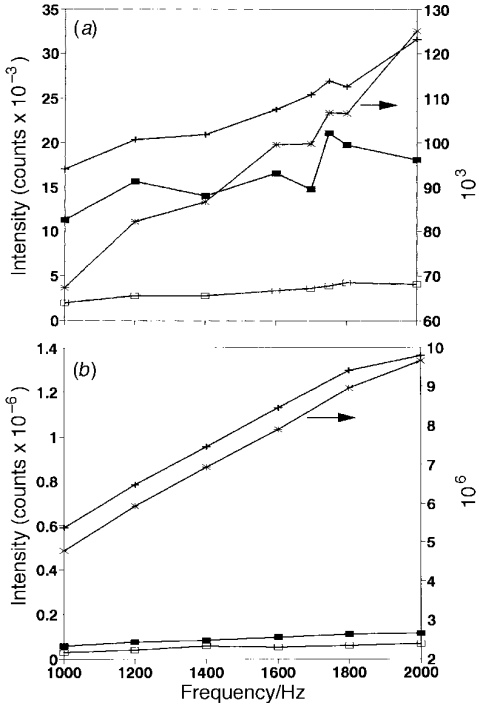

Fig. 7 Relationship between discharge frequency and line intensities of sputtered atoms, (*a*) in the absence of the MIP and (*b*) in the presence of the MIP: ∗, Cu I 324.7 nm, see right *y*-scale; ■, Cu II 224.7 nm; +, Zn I 213.8 nm; and □, Zn II 202.5 nm.

324.7 nm) when the microwave generator is switched on. Owing to the relatively low discharge pressure, self-absorption of emitted radiation by a cloud of 'cool' atoms in the outer region of the discharge is fairly serious when the discharge frequency is increased to as high as 2 kHz. The emission intensities decrease when the discharge frequency is adjusted to higher than 2 kHz. Two possible reasons account for the results: one is the possible self-absorption of radiation owing to an increase in the surrounding cold atoms, and the other results from the limited power capacity of the laboratory made μs-pulse power supply, as discussed previously.[9]

Effect of discharge pressure on spectral intensity. The effect of discharge gas pressure on the line intensity is shown in Fig. 8. The working carrier gas pressure is an important factor for it has a clear effect on the GD. As shown in Fig. 8(*a*), with the 'μs-pulse GD only' mode, the intensity of Cu I 324.7 nm rises rapidly in accordance with the gas pressure. The relationship between the argon gas pressure and the line intensities for Cu II 224.7 nm and Zn II 202.5 nm are similar in the two discharge configurations. However, self-absorption of spectral line Cu I 324.7 nm occurs in the μs-pulse GD + MIP mode when the argon pressure is higher than 180 Pa. As a result, the emission intensity decreases. It is interesting to note that the intensity of the Zn I 213.8 nm line is about four orders of magnitude lower than the intensity of the Cu I 324.7 nm line when the 'μs-pulse GD only' mode is utilized, while it is eight times lower when the 'μs-pulse GD + MIP' configuration is used, because the line transition for Zn I 213.8 nm originates from a higher energy state. Similar results can be seen in Figs. 7 and 9.

Effect of discharge current on spectral intensity. The dependence of emission intensities on discharge current is depicted in Fig. 9. As shown in Fig. 9(*a*), a possible self-absorption of selected spectral lines occurs when the discharge current is higher than 1.5 A, which is believed to be due to the high

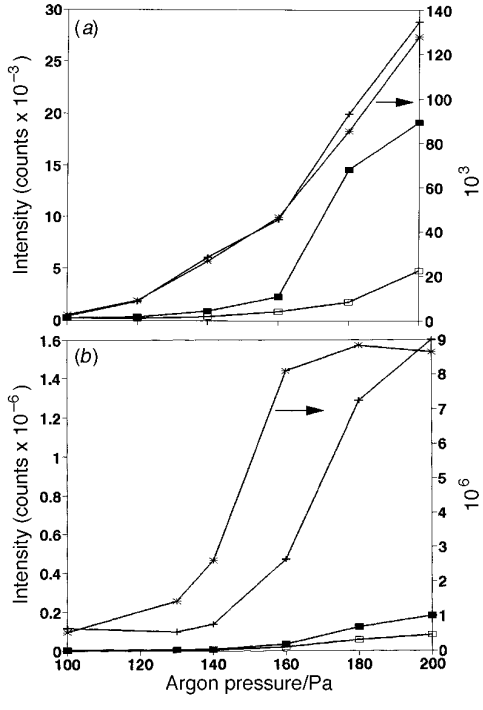

Fig. 8 Effect of discharge pressure on signal intensities, (*a*) in the absence of the MIP and (*b*) in the presence of the MIP: ∗, Cu I 324.7 nm, see right *y*-scale; ■, Cu II 224.7 nm; +, Zn I 213.8 nm; and □, Zn II 202.5 nm.

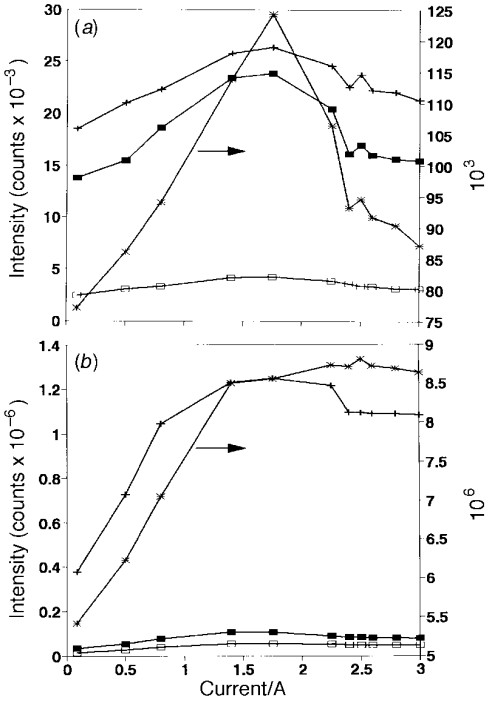

Fig. 9 Relationship between discharge current and signal intensities, (*a*) in the absence of the MIP (*b*) in the presence of the MIP: ∗, Cu I 324.7 nm, see right *y*-scale; ■, Cu II 224.7 nm; +, Zn I 213.8 nm and □, Zn II 202.5 nm.

sputtering rate. Coupling with the MIP results in a decrease in the sputtering rate and particularly enhances the excitation processes of the low energy lines. As a result, the self-absorption of Cu I 324.7 nm and Zn I 213.8 nm decrease because of the smaller number of 'cool' atoms and the intensities of Cu II 224.7 nm and Zn II 202.5 nm become lower with the increase in discharge current.

Signal-to-background Ratios and the Relative Standard Deviation

Signal-to-background ratios

As shown in Table 1, the S/B are enhanced for the selected lines when the microwave generator is coupled to the μs-pulse GD. As the generator is turned on, the emission intensities increase sharply but the background level rises only slightly. Therefore, detection power can be improved by using a μs-pulse GD–MIP source. Leis *et al.* have also shown that detection powers can be significantly increased by supplementing a dc GD with an MIP discharge.[3,14] Shown in Fig. 10 is the spectral profile for Cu I 324.7 nm (brass sample, 69.4% Cu), obtained with both the 'μs-pulse GD only mode' and 'μs-pulse GD + MIP' mode. It was found that the profile is still very narrow in the presence of the MIP and the S/B is fairly good with a relatively strong line intensity.

Relative standard deviation

The short-term stability of the lamp operated under 'μs-pulse GD only' and 'μs-pulse GD + MIP' modes was studied by measuring the intensity of the Mn I 257.610 nm line for a low alloy steel sample containing 0.122% Mn. About 2 min after ignition, the intensity of Mn I 257.610 nm becomes constant and then the RSD measurements were carried out. The RSDs of the 'μs-pulse GD only' and 'μs-pulse GD + MIP' configuration were 1.0 and 0.2%, respectively, obtained from line

Table 1 Comparison of the S/Bs of the GD source in the absence and presence of the MIP

Mode	Parameter	Spectral line/nm			
		Cu I 324.7	Cu II 224.7	Zn I 213.8	Zn II 202.5
μs-pulse GD only	Signal (count)	113071	20987	27908	4479
	Background (count)	1910	191	185	176
	S/B ratio	59	110	151	25
μs-pulse GD + MIP	Signal (count)	8096826	96030	1430311	96821
	Background (count)	4212	331	752	234
	S/B ratio	1922	290	1902	414

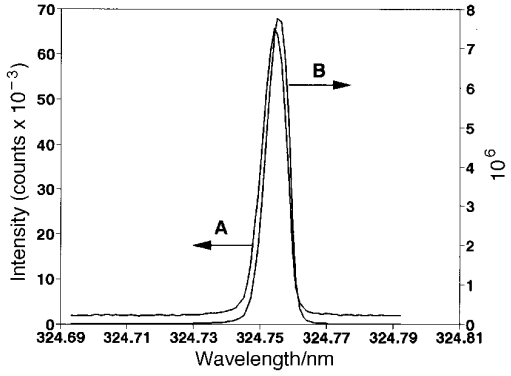

Fig. 10 Spectral profile of Cu I 324.7 nm: discharge frequency 1.7 kHz; pulse width of 2 μs; current 1.5 A; argon pressure 180 Pa; and microwave forward power 50 W. Signals were integrated for 0.2 s, recorded with a 3600 groves mm^{-1} high-resolution monochromator. A, In the absence of the MIP, see left *y*-scale; and B, in the presence of the MIP, see right *y*-scale.

intensities (ten measurements) with a 0.2 integration time for a 3 min interval. The application of microwaves could lead to an improvement in the background equivalent concentration, because the RSD and S/B of the analytical emission lines are enhanced in the MIP boosted μs-pulse GD lamp.

CONCLUSION

Results of the study on an MIP boosted μs-pulse GD-OES instrument show that an MIP can couple fairly well with μs-pulse GD when the discharge pressure is less than 200 Pa, and that this hyphenated discharge can produce strong emission intensities from sample atoms. However, under a relatively high discharge pressure (>240 Pa), the μs-pulse GD and MIP tend to excite the sputtered atoms separately and produce two emission peaks, independent in time, for a given resonance atomic line.

The effects of the discharge parameters on the emission intensities of the analytical lines of interest have been studied and optimized as 1.8 kHz for discharge frequency, 200 Pa for argon pressure and 1.5 A for discharge current. Spectral self-absorption appears to exist in the GD and can be reduced when the microwave generator is switched on, especially for low energy emission lines.

The net intensities of the spectral radiation increase sharply when the lamp is coupled with the MIP. Compared with operation of the lamp under 'μs-pulse GD only' mode, the S/B ratios of 'μs-pulse GD + MIP' mode have been enhanced several to several tens of times for selected lines. The RSD of the level of emission intensity for the GD lamp has also been improved from 1.0 to 0.2% in the presence of MIP boosting.

Further work will focus on the determination of detection limits for the boosted source and on investigating the excitation processes using TOFMS. The application of the technique to surface analysis of solid samples is also an attractive area.

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