Excitation Behavior of Copper Ionic Emission Lines During the $3d^94p - 3d^94s$ Transition in the Glow Discharge Plasma with Xenon in Comparison to Using Argon and Krypton

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ABSTRACT: The emission spectrum of copper in the wavelength range of 200–230 nm was investigated when xenon, instead of argon or krypton, was employed as the plasma gas in glow discharge plasma (GDP). The Cu II emission lines, which were assigned to the $3d^94p - 3d^94s$ transition of the copper ion, were observed, but their emission intensities were different depending on the plasma gas employed. The Cu II 224.700-nm line was studied intensively in an argon GDP. As was previously reported, the excitation mechanism of this line is an asymmetric charge-transfer collision with the argon ion. Here, a coincidence in the total excitation energy enables the corresponding energy level of the $3d^94p \ ^3P_2$ to be selectively populated through the charge-transfer collision. On the other hand, in a xenon GDP, the emission intensities of the Cu II 224.700-nm line as well as the other Cu II lines were not so strong, but a statistical relationship was found in the plots of the reduced emission intensity of these Cu II lines versus the excitation energy. This result implies that these Cu II lines are not emitted by a non-thermal process, such as charge-transfer collision, but by a thermal excitation process, such as electron collision in the xenon GDP. The first ionization potential of xenon is more than 3 eV lower than that of argon; therefore, it is almost impossible to excite the $3d^94p$ levels of the copper ion by the charge-transfer collision with xenon ion. A similar result to the xenon GDP was obtained with the krypton GDP because the ionization potential of krypton was still insufficient to obtain these high-lying excited levels.

INTRODUCTION

Glow discharge plasma have been utilized for one of the excitation sources in optical emission spectrometry, known as glow discharge optical emission spectrometry (GD-OES). GD-OES is employed for the direct analysis of solid samples because this excitation source has several benefits for the analytical application, such as rapid sampling through cathode sputtering, minimal sample pretreatment, and a wide concentration range in the quantification.^{1–3}

The emission characteristics of the glow discharge plasma (GDP) vary greatly and depend on the type of plasma gas employed which is little affected by the substrate material of the

analyte atom. The nature of the plasma gas plays a very important role in determining the excitation/ionization processes^{4,5} and thus the analytical performance in GD-OES.^{6,7} Unlike other plasma sources, the GDP is easily maintained without any instrumental modification when several gases, such as argon, neon, krypton, helium, and their mixtures, are used as the plasma gas, while argon is mostly used in conventional GD-OES. Many studies have been published regarding the features of the GDP using different plasma gases and their mixtures, indicating that the plasma gas dominantly determines the spectrum pattern of the analyte elements excited by the GDP.^{8–13} Only few studies on the xenon plasma have been published not only in scientific papers but analytical notes in GD-OES. The probable reason is that xenon gas

is very expensive and its benefits have not yet been established, especially for analytical applications. However, in comparison to other plasma gases, use of xenon GDP may give new interesting information on the excitation mechanism of emission lines. Thus, this paper focuses on the excitation of the $3d^9 4p$ excited levels of the copper ion in a xenon GDP.

Previous studies have shown that selective excitation to a particular excited level occurs in the excitation of an emission spectrum in GDP.¹⁴ This effect is caused by an energy transfer from the gas species, called a collision of the second kind, whereas a collision of the first kind means a transfer of kinetic energy like a collision with a fast electron.¹⁵ An asymmetric charge-transfer process¹⁶ is a typical second-kind collision and a major excitation channel for causing the emission spectra excited by GDPs. The $3d^9 4p - 3d^9 4s$ transition of singly ionized copper contributes to an abnormal spectral pattern through the charge-transfer process in Ar GDP. Steers et al. first reported that the Cu II 224.70-nm line has a very high emission intensity in the Ar GDP.¹⁷ This effect can be caused by selective excitation to a particular excited level of the copper ion, $3d^9 4p \ ^3P_2$ (8.23 eV), through an asymmetric charge-transfer collision between an Ar ion and a Cu atom.¹⁷ In this collision, the ground-state levels of the argon ion, the $3p^5 \ ^2P_{3/2}$ (15.76 eV) and the $3p^5 \ ^2P_{1/2}$ (15.90 eV),¹⁸ work as an energy donor as well as an electron acceptor. This type of collision is generally represented by the following equation: $M^g + Ar^+ \rightarrow M^{*+} + Ar^g + \Delta E$, where the superscripts g , $+$, and $*$ mean a ground state, an ionic state, and an excited state, respectively, and ΔE is the energy

difference before and after the collision.¹⁶ The charge transfer collision most likely takes place when the surplus energy, ΔE , is very small; in other words, an energy resonance is needed.¹⁶ In such a case, a particular excited level can be ionized/excited selectively because the gas species have to provide the internal energy to be corresponding to the sum of the excitation energy and the ionization potential of the colliding partner. Therefore, an appropriate combination between the emission line and the plasma gas can improve the detection sensitivity in GD-OES when the resonance condition is fulfilled for the corresponding excited energy level. The charge-transfer process was also found in excitations of other metallic elements in GDPs.¹⁴ My previous studies indicated that different emission lines in iron, cobalt and nickel were observed between argon and krypton plasmas, which can be caused by charge transfer collisions to particular $3d^8 4p$ excited levels of these singly ionized atoms.^{19,20}

In this paper, the Cu II emission lines assigned to the $3d^9 4p - 3d^9 4s$ transition were measured in detail when xenon was employed as the plasma gas in GD-OES. The spectrum pattern is analyzed using the transition probability for each Cu II line in comparison to the argon and krypton plasmas. It will also be investigated to what extent the charge-transfer process works for excitation of the Cu II lines because the ionization potential of xenon is more than 2 eV lower than that of argon. The main objective of this study was to suggest the probable excitation mechanism for the Cu II lines in the xenon GDP.

Table 1. Assignment and Transition Probability of Cu II Lines Employed in This Study

Wavelength (nm)	Assignment ²³		Transition probability ²⁴ ($\times 10^8 \text{ sec}^{-1}$)
	Upper (eV)	Lower (eV)	
Cu II 201.558	$3d^9 4p \ ^1P_1$ (9.1245)	$3d^9 4s \ ^3D_1$ (2.9754)	0.23
Cu II 202.548	$3d^9 4p \ ^1D_2$ (9.0944)	$3d^9 4s \ ^3D_1$ (2.9753)	0.84
Cu II 203.585	$3d^9 4p \ ^3D_1$ (9.0633)	$3d^9 4s \ ^3D_1$ (2.9753)	3.96
Cu II 203.713	$3d^9 4p \ ^1F_3$ (8.9167)	$3d^9 4s \ ^3D_2$ (2.8326)	1.39
Cu II 204.379	$3d^9 4p \ ^3D_3$ (8.7830)	$3d^9 4s \ ^3D_3$ (2.7187)	1.92
Cu II 205.498	$3d^9 4p \ ^3D_2$ (8.8634)	$3d^9 4s \ ^3D_2$ (2.8326)	1.72
Cu II 208.530	$3d^9 4p \ ^3F_2$ (8.6623)	$3d^9 4s \ ^3D_3$ (2.7187)	0.057
Cu II 210.479	$3d^9 4p \ ^3D_2$ (8.8639)	$3d^9 4s \ ^3D_1$ (2.9753)	0.98
Cu II 211.212	$3d^9 4p \ ^1P_1$ (9.1245)	$3d^9 4s \ ^1D_2$ (3.2563)	4.09
Cu II 212.297	$3d^9 4p \ ^1D_2$ (9.0944)	$3d^9 4s \ ^1D_2$ (3.2563)	2.52
Cu II 212.604	$3d^9 4p \ ^3F_2$ (8.6623)	$3d^9 4s \ ^3D_2$ (2.8326)	1.64
Cu II 213.437	$3d^9 4p \ ^3D_1$ (9.0633)	$3d^9 4s \ ^1D_2$ (3.2563)	0.017
Cu II 213.598	$3d^9 4p \ ^3F_4$ (8.5213)	$3d^9 4s \ ^3D_3$ (2.7187)	4.19
Cu II 214.897	$3d^9 4p \ ^3F_3$ (8.4862)	$3d^9 4s \ ^3D_3$ (2.7187)	0.64
Cu II 217.941	$3d^9 4p \ ^3F_2$ (8.6623)	$3d^9 4s \ ^3D_1$ (2.9753)	2.37
Cu II 218.963	$3d^9 4p \ ^1F_3$ (8.9167)	$3d^9 4s \ ^1D_2$ (3.2563)	1.10
Cu II 219.226	$3d^9 4p \ ^3F_3$ (8.4862)	$3d^9 4s \ ^3D_2$ (2.8326)	2.83
Cu II 221.026	$3d^9 4p \ ^3D_2$ (8.8639)	$3d^9 4s \ ^1D_2$ (5.2563)	1.48
Cu II 221.810	$3d^9 4p \ ^3P_1$ (8.4204)	$3d^9 4s \ ^3D_2$ (2.8326)	3.08
Cu II 222.887	$3d^9 4p \ ^3P_0$ (8.5361)	$3d^9 4s \ ^3D_1$ (2.9753)	3.69
Cu II 224.262	$3d^9 4p \ ^3D_3$ (8.7830)	$3d^9 4s \ ^1D_2$ (3.2563)	2.17
Cu II 224.700	$3d^9 4p \ ^3P_2$ (8.2347)	$3d^9 4s \ ^3D_3$ (2.7187)	3.34
Cu II 227.626	$3d^9 4p \ ^3P_1$ (8.4204)	$3d^9 4s \ ^3D_1$ (2.9754)	0.54
Cu II 229.437	$3d^9 4p \ ^3P_2$ (8.2347)	$3d^9 4s \ ^3D_2$ (2.8326)	0.21

EXPERIMENTAL

The Grimm-style glow discharge lamp employed in this study has been described in my previous paper.²¹ Based on the original Grimm model,²² the lamp comprised a hollow anode of 8.0 mm in diameter and a planar cathode (sample), and the distance between the electrodes was adjusted to 0.3 - 0.5 mm. High-purity xenon (99.999 %), argon (99.99995 %), and krypton (99.9995%) were employed as the plasma gas. The lamp was evacuated to less than 2.0 Pa with two oil rotary pumps, and then any one of these plasma gases was introduced to flow continuously during the measurements. The flow control of the plasma gas was carried out with a set of gas valves consisting of a ball (on/off) valve and a needle valve, which were inserted into each gas line. The pressure of the plasma gas was measured with a Pirani gauge, whose readings had been corrected for each gas by using a Baratron-type capacitance manometer, at the vacuum port of the lamp.

The emission spectra were measured with a Czerny-Turner mounting spectrometer (P-5200, Hitachi Corp., Japan), equipped with a photomultiplier (R-955, Hamamatsu Photonics, Japan). The discharge power was supplied with a dc power supply device (HEOPT-1B60-L1, Matsusada Precision Ltd., Japan). All of the measurements were conducted in constant voltage mode. A pure copper plate (purity, 99.99 %) was prepared as the sample, which was polished with waterproof emery paper (No. 600) and then rinsed with ethanol. Before measurement, pre-discharge was carried out for a few minutes to remove the surface contaminants.

RESULTS AND DISCUSSION

Wavelength table of analyzed Cu II lines

The optical transitions between the $3d^94p$ and $3d^94s$ electron configurations of singly ionized copper²³ give rise to many emission lines of Cu II in the wavelength range of 195 - 250 nm. The ground state is the $3d^{10}$ comprising a singlet level of $^1S_0$, and the $3d^94s$ and the $3d^94p$ are the second and the third excited configurations, respectively.²³ In this study, 24 Cu II lines ranging from 201.6 - 229.5 nm were measured, as listed in Table 1. Their excitation energies of the upper energy level range from 8.23 to 9.12 eV. The electron configuration and the energy levels of the copper ion are cited in a data book compiled by Moore.²³ Kono and Hattori measured relative lifetimes of the $3d^94p$ excited levels of the copper ion using a delayed-coincidence technique, then estimated the transition probabilities of the Cu II lines from these excited levels with an accuracy of 10 %, ²⁴ as cited in the fourth column of Table 1. In this study, this set of the transition probability was employed as a standard for the sensitivity correction between the different Cu II lines.

Correlation of excited energy levels between singly ionized copper and plasma gases

Figure 1 illustrates a correlation diagram between the ground and

Fig. 1 Correlation in the excitation energy between energy levels of singly ionized copper and the ionization levels of xenon, argon, and krypton.

excited energy levels of copper and the first ionization level as well as the metastable levels of the plasma gases employed: xenon, krypton, and argon. The energy levels are drawn based on the database compiled by Moore.^{18,23,25} The energy scale is represented by 'total excitation energy' that sums the excitation energy in the copper ion and the first ionization potential (7.73 eV).²³ As shown in Fig. 1, the excited energy levels of the $3d^94s$ and the $3d^94p$ electron configuration²³ are located in the total excitation energies of 10.4 - 11.0 eV and 15.9 - 16.8 eV, respectively. Copper ionic lines, which are assigned to optical transitions from the $3d^94p$ to $3d^94s$ energy levels, are observed in the GDP-excited spectra; however, their relative intensities are drastically dependent on the plasma gas employed, as described later.

A charge-transfer collision for an excited level of copper ion is shown using the following general equation:

where G is a plasma gas and the superscripts ^g, ⁺, ^{*}, and ^m indicate ground, ionic, excited, and metastable states, respectively, and ΔE corresponds to the energy difference before and after the collision. As pointed out by Steers,¹⁷ the Cu II 224.700-nm line has very high intensity in an Ar GDP, which is well explained by an asymmetric charge-transfer collision with the argon ion. Fig. 1 includes the ground state levels of the argon ion, e.g., $3p^5\ ^2P_{1/2}$ (15.93 eV) and $^2P_{3/2}$ (15.76 eV) on the scale of total excitation energy.¹⁸ The reason for the excitation for the Cu II 224.700-nm line is that there is a similarity in the total excitation energy between the corresponding upper level of the $3d^94p\ ^3P_2$ (8.2347 eV) and the $3p^5\ ^2P_{1/2}$ of argon ion. Such a correspondence of their excitation energies can be graphically understood in Fig. 1. In my

previous study it was reported that a different group of Cu II lines, which was assigned to the $3d^95s - 3d^94p$ transition of the copper ion, was intensively observed in a Ne GDP by the charge transfer collision with the neon ion.²⁶ Furthermore, previous researchers found very intense emission lines of other metallic elements using various plasma gases, such as argon, neon, krypton, and helium, in which a charge-transfer process with the plasma gas was involved.^{27,28} However, the first ionization potential of xenon, e.g., the $5p^5\ ^2P_{1/2}$ (13.43 eV) and $\ ^2P_{3/2}$ (12.13 eV),²⁵ is more than 3 eV lower than that of argon, as shown in Fig. 1. This study shows the keen interest taken to establish the effect of plasma gases used for the excitation of the Cu II lines.

Normalized intensity of copper emission lines for different plasma gases

The net emission intensity of 24 Cu II lines (as listed in Table 1) was measured for three different plasma gases. Each discharge condition was fixed in a voltage constant mode: 27 mA/650 V at 600-Pa Xe, 34 mA/600 V at 600-Pa Kr, and 28 mA/500 V at 670-Pa Ar. These conditions were selected so that the sputtering rate could be similar to each other. Their actual sputtering rates were estimated from the weight loss before and after the 10-min discharges, resulting in a relative value of 0.87 : 1.0 : 0.85 for Xe : Kr : Ar. The net intensities of the Cu II lines were averaged from triplicate measurements and their relative standard deviations were within 5%, except for several weak lines. The intensity data of the Cu II 213.437-nm line was excluded for the subsequent analysis because it overlapped with a neighboring atomic line of copper at Cu I 213.428 nm. Moreover, the net intensities were normalized with the intensity of the Cu II 201.558-nm line (9.1245 eV) for each plasma gas, and the normalized intensities were finally corrected by the difference of the sputtering rate.

Reduction of the normalized intensity by transition probability

The normalized intensity of the Cu II lines was divided by the corresponding transition probability (gA) to compensate for the different frequencies for each optical transition. A value of (Intensity / gA), defined as ‘reduced emission intensity’, will be discussed in relation to the excitation energy.

First, the result of the Ar GDP, which has already been recognized to include the selective excitation of the Cu II lines, is represented in Fig. 2. This excitation-energy dependence of the reduced emission intensity clearly indicates an abnormal enhanced population of the $3d^94p\ ^3P_2$ (8.2347 eV) and a normal population of the energy levels having excitation energies of more than 8.8 eV. A charge-transfer process, in which a collision with the $3p^5\ ^2P_{1/2}$ (15.93 eV) of the argon ion is involved, well explains this selective excitation because of a good match in the total excitation energy between the colliding partners. In this reaction, the difference in the total excitation energy is estimated to be -0.035 eV, thus realizing an energy resonance condition. Further, the

Fig. 2 Dependence of the reduced emission intensity (the normalized intensity divided by the transition probability) of Cu II lines on the excitation energy in an argon GDP. Discharge condition: 28 mA/500 V at 670-Pa Ar.

Fig. 3 Dependence of the reduced emission intensity (the normalized intensity divided by the transition probability) of Cu II lines on the excitation energy in a xenon GDP. Discharge condition: 27 mA/650 V at 600-Pa Xe.

charge-transfer process would work insufficiently for excitations of other $3d^94p$ excited levels requiring larger energies due to a lack of the total excitation energy. For instance, there appears an energy shortage of 0.93 eV to excite the $4p\ ^1P_1$ level for the Cu II 201.558-nm and the Cu II 211.212-nm lines. Therefore, assuming that their excitations are caused by a thermal process, such as electron collision, the charge-transfer collision additionally contributes to the excitation of the $4p\ ^3P_2$ level by a factor of 200-300, as seen in Fig. 2.

A similar analysis to the Ar GDP was carried out in a Xe GDP. Fig. 3 shows a variation in the reduced emission intensity of the Cu II lines as a function of the excitation energy in the Xe GDP. Differing from the result of the Ar GDP (see Fig. 2), the plots seem to be slightly varied with an increase in the excitation energy along with a negative linear relationship (a dotted line in Fig. 2), although their deviations are somewhat large. This result implies that the Cu II lines would be mainly excited by any thermal collision (transfer of the kinetic energy) in the Xe GDP and that there are no particular channels for their excitations as in the Ar GDP. As

Fig. 4 Dependence of the reduced emission intensity (the normalized intensity divided by the transition probability) of Cu II lines on the excitation energy in a krypton GDP. Discharge condition: 34 mA/600 V at 600-Pa Kr.

illustrated in Fig. 1, it is not possible to cause the charge-transfer process from the Xe ion to reach the $3d^94p$ excited levels of the copper ion. In this case, there is much less excitation energy (2.5 - 3.4 eV) in the charge-transfer collision for their excitations. In addition, other Cu II lines, which were assigned to the $3d^95s$ (13.39 - 13.68 eV) - $3d^94p$ transition and assigned to further high-lying excited states, were very faint or were not able to be observed in the Xe GDP. Accordingly, few Cu II lines with strong intensity were not found in the Xe-GDP spectra, principally because there were no effective excitation channels for the charge-transfer collision with the xenon ion.

Finally, the excitation behavior of the Cu II lines was investigated when krypton was employed as the plasma gas. Fig. 4 shows a dependence of their reduced intensities on the excitation energy in a Kr GDP. This variation is analogous to that of the Xe GDP (see Fig. 3), implying that a similar excitation mechanism would work for excitations of the Cu II lines. The first ionization potential of krypton, e.g., $4p^5\ ^2P_{1/2}$ (14.00 eV) and $\ ^2P_{3/2}$ (14.66 eV),²³ is more than 1 eV higher than that of xenon; however, they cannot work as energy donors in the charge-transfer collision to produce the $3d^94p$ excited levels of the copper ion. Fig. 1 shows that the internal energy of the krypton ion is short for this collisional reaction by 1 - 2 eV. On the other hand, the first excited state of the copper atom, comprising $3d^94s^2\ ^2D_{5/2}$ (1.389 eV) and $\ ^2D_{3/2}$ (1.642 eV), is located more than 1 eV above the ground-state level.²³ They might act as metastable energy levels for any collision process in GDPs, because they belong to the same even parity as the ground state of the copper atom, the $3d^94s\ ^2S_{1/2}$ (0.00 eV). In such a case, the metastable levels may take part in a charge-transfer collision as given in the following general equation:

If krypton is employed as G, it is possible to cause a charge-transfer collision to produce the $3d^94p$ excited levels of the copper ion due to a good matching in the total excitation energy. In some

combinations with the excited levels in the range of 8.3-8.6 eV, ΔE becomes almost zero and energy resonance is expected. As compared to the result with Xe GDP (see Fig. 3), the reduced intensity of the Cu II lines in the lower excitation energy look to be slightly elevated in the Kr GDP graph. However, there is no clear evidence in Fig. 4 that any selective excitation among these Cu II lines may occur. A reason for this is that these metastable levels might be less populated than the ground-state level in the plasma.

CONCLUSIONS

This paper represents the excitation feature of the Cu II lines derived from the $3d^94p$ - $3d^94s$ transition in a Xe GDP, in comparison to Ar and Kr GDPs. As pointed out in previous studies, a very intense emission line, the Cu II 224.700-nm line, was observed in the Ar GDP. The major excitation mechanism is an asymmetric charge transfer collision with the argon ion, in which there is a coincidence in the excitation energy between the corresponding energy level of the $3d^94p\ ^3P_2$ and the ground-state level of the argon ion. However, when the plasma gas was changed from argon to xenon, no intense Cu II lines were found in the GDP spectra, but a linear relationship among the reduced intensities of the Cu II line was found. In the Xe GDP, they were not emitted by a non-thermal process, such as charge-transfer collision, but by a thermal excitation process, such as electron collision. The major reason for this is that the first ionization potential of xenon is more than 3 eV lower than that of argon, thus not enabling the $3d^94p$ excited levels to be populated through the charge-transfer collision with the xenon ion. The results obtained with the Kr GDP was similar to that with the Xe GDP, because the ionization potential of krypton was still insufficient to obtain the excited levels. Such large differences of the intensity plots imply that the charge transfer process mainly determines the emission spectrum from high-lying excited energy levels, like the $3d^94p$ energy levels of the copper ion, so also in other metallic elements.

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Notes

The authors declare no competing financial interest.

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