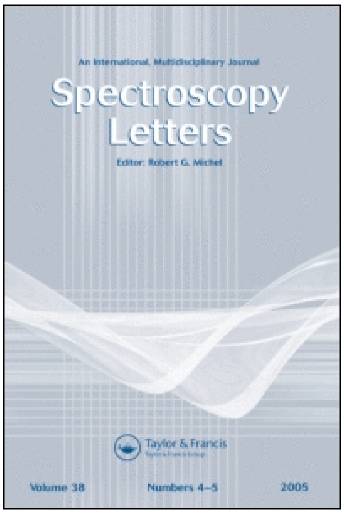

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Excitation of Doubly-Charged Ion Emission Lines from a Grimm-Style Glow Discharge Plasma—Comparison Between Yttrium and Zirconium

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ABSTRACT

Spectra of yttrium and zirconium emitted from a Grimm-style glow discharge plasma were investigated to elucidate the excitation mechanism of doubly-charged ionic lines when using argon–helium mixed gas as well as argon gas alone. The energy sum for exciting doubly-charged ion species of yttrium is slightly smaller compared to the case of zirconium, which yields an interesting correlation in the excitation energy between their ionic species and excited species of helium or argon. The Y III emission lines which were assigned to the $4p^6 5p$–$4p^6 5s(4p^6 4d)$ transitions could be observed in the argon–helium mixed gas plasma, but

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those were hardly excited with argon gas only. The Zr III emission lines did not appear in the spectra emitted by the argon gas plasma nor by the mixed gas plasma. A possible explanation for these phenomena is that the excitation of these ionic species is caused principally by collisional energy transfer from helium species to the analyte atoms.

Key Words: Doubly-ionized emission lines; Yttrium; Zirconium; Glow discharge plasma; Argon; Argon–helium mixed gas; Excitation and ionization mechanism; Collision of the second kind.

INTRODUCTION

Analytical spectrometry in which the excitation/ionization source is a glow discharge plasma has been extensively employed for the elemental analysis of various manufactured materials, because it has the ability to analyze solid samples without any troublesome dissolution procedures.[1] The glow discharge source has several benefits for analytical applications such as rapid sampling rate and minimal sample pretreatment. Also, this technique has the ability to yield depth profiles of the elemental composition due to the sampling process by cathode sputtering.[2]

Since a glow discharge is sustained under reduced pressure conditions, exchange of the kinetic energy among particles does not occur so effectively due to large mean free paths between their collisions. As a result, the glow discharge produces a so-called cold plasma of which the kinetic gas temperature is low (less than 1000 K).[3] The gas temperature is considered to be too low for excitation through collisions of the first kind,[4] i.e., kinetic energy transfer from fast atoms and ions. On the other hand, electrons emitted from the cathode should be accelerated by a voltage applied to the glow discharge lamp; however, collisions with these energetic electrons do not play a major role in excitation of analyte atoms, probably because their kinetic energies are too large for these species to be excited effectively.[5] The collisions with the electrons that are produced secondarily in the negative glow region can act as an alternative excitation channel, because such electrons are a large part of the overall number of electrons, but the kinetic energies are relatively small (only a few electron volts).[6] In addition, particles having large internal energies; for example, rare gas atoms in metastable levels or rare gas ions, can contribute to excitation of analyte atoms through collisional processes, i.e., collisions of the second kind.[4]

The first-kind of collisions with electrons could contribute to all excitation phenomena occurring in the glow discharge plasma. However, in

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Grimm-style glow discharge spectrometry, the intensities of spectral lines emitted from singly-ionized atoms of the analytes are determined primarily by the kind of the plasma gas employed, rather than the discharge parameters such as the voltage/current.[7] It is difficult to explain this effect through thermal collisions with energetic electrons, although the excitation schemes are very complex and thus are not fully understood. Alternatively, two types of the second-kind of collision are considered to be responsible for this observation. Penning ionization/excitation, which is caused by a collision between a metastable state atom of the plasma gas (G^m) and a ground state atom of the sample (M), that is, $G^m + MC \rightarrow G^g + (M^+)^* + e^-$, produces an excited state of the sample ion $(M^+)^*$. Due to the difference in metastable energies, excitation of sample species may be plasma gas dependent. It has been reported that particular excited levels are selectively populated through a (quasi-)resonance process resulting from a charge-transfer collision involving a ground state ion of the plasma gas (G^+), that is, $G^+ + MC \rightarrow G^g + (M^+)^*$.[8–12] This reaction also produces an excited state of the sample ion, $(M^+)^*$, and its efficiency increases exponentially with decreasing energy difference between the G^+ and the $(M^+)^*$.[8] This excitation scheme can well explain that, in some cases, extremely intense ionic lines are emitted from a particular plasma gas but are hardly excited with other gases.[9,10]

I have reported on the characteristics of a Grimm-style glow discharge plasma with argon–helium mixed gases.[9,13] The ionization potential of the helium atom (24.580 eV) is considerably higher than that of the argon atom (15.755 eV).[14] It is therefore possible to provide analyte atoms with more energy through charge transfer collisions with helium ions than with argon ions. In fact, it was found that higher energy excitations occurred only in the argon–helium mixed gas plasma.[13]

In some elements, one can observe emission lines of doubly-charged ions in the Grimm-style glow discharge plasma with argon–helium mixed gases. It is assumed that helium species provide sufficient energy to an analyte atom so that an excited state of the doubly-charged ion can be occupied. A spark spectrum of iron includes strong emission lines identified as doubly-ionized iron in the vacuum ultraviolet wavelength region, whose excitation energies range from 10 to 18 eV.[15] However, I have not found these iron lines in the glow discharge spectrum even when an argon–helium mixed gas is employed as the plasma gas. A possible reason for this is that the energy of the helium ion is not enough for excitation of the emission lines of doubly-ionized iron. It is characteristic of yttrium that both the first and the second ionization potentials are relatively small compared to the corresponding value of iron.[16] In the case of yttrium, some emission lines of the doubly-charged ion appear in the glow discharge

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spectrum when using argon–helium mixed gases, whereas those are not excited with argon alone.

In this paper, I discuss the excitation mechanism of emission lines of doubly-ionized yttrium (Y III) in a Grimm-style glow discharge plasma using argon–helium mixed gases. Furthermore, a spectrum of zirconium, which has slightly higher ionization potentials compared to yttrium, is analyzed concerning the excitation of doubly-charged ionic lines (Zr III).

EXPERIMENTAL

The glow discharge lamp was in-house made according to the original model by Grimm.[17] The structure of the lamp has been described in our previous paper.[18] The inner diameter of the hollow anode was 8.0 mm and the gap between the electrodes was adjusted to be c.a. 0.3 mm. The discharge lamp was evacuated down to ca. 1.3 Pa (1×10^{-2} Torr) and then the plasma gas was introduced. High-purity argon (99.9995 %) and helium (99.9999 %) were used. Flow control of the plasma gas was carried out with a ball (on/off) valve and a needle valve that were inserted in each gas line. The partial pressure of each gas was regulated with the corresponding needle valve and read on a Pirani gauge at the gas inlet of the lamp when the other ball valve was closed. The partial pressure of the argon gas was fixed at 3.3×10^2 Pa (2.5 Torr) and the partial pressure of the helium gas was varied from 0 to 6.7×10^2 Pa (5 Torr). All the measurements were conducted in a constant voltage mode.

A Fastie–Ebert mounting spectrograph (Simadzu GE-340 model) equipped with a photomultiplier tube (Hamamatsu Photonics R-955 model) was employed. The focal length was 3.4 m. The grating has 1200-grooves/mm and the blaze wavelength was 300 nm.

A yttrium plate (99.9%, purity) and a zirconium plate (99.7%, purity) were prepared as the cathode samples. They were polished with waterproof emery papers and then rinsed with ethanol. Before the measurement, predischarges for 20 min were needed to obtain steady emission intensities, probably due to the surface oxide layer.

RESULTS AND DISCUSSION

Meggers and Russell analyzed a spark spectrum of yttrium and found Y III emission lines which were assigned to the $4p^65d(4p^66s)$–$4p^65p$ or the $4p^65p$–$4p^65s(4p^64d)$ transitions.[19] Table 1 indicates the wavelength of

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Table 1. Observed emission lines of doubly-ionized yttrium and their relative intensities.

Wavelength (nm) in air	Assignment		Relative intensity		
	Upper (eV)	Lower (eV)	Ar†	Ar/He‡	Ref. [19]
212.800	5d $^2D_{3/2}$ (10.957)	5p $^2P_{1/2}$ (5.1329)	<1	<1	100
219.122	5d $^2D_{5/2}$ (10.987)	5p $^2P_{3/2}$ (5.3256)	<1	<1	200
220.078	5d $^2D_{3/2}$ (10.957)	5p $^2P_{3/2}$ (5.3256)	<1	<1	50
220.620	6s $^2S_{1/2}$ (10.751)	5p $^2P_{1/2}$ (5.1329)	<1	<1	30
228.453	6s $^2S_{1/2}$ (10.751)	5p $^2P_{3/2}$ (5.3256)	<1	<1	100
232.732	5p $^2P_{3/2}$ (5.3256)	4d $^2D_{3/2}$ (0.0000)	<1	8	20
236.727	5p $^2P_{3/2}$ (5.3256)	4d $^2D_{5/2}$ (0.0899)	<1	60	200
241.466	5p $^2P_{1/2}$ (5.1330)	4d $^2D_{3/2}$ (0.0000)	<1	40	100
281.699	5p $^2P_{3/2}$ (5.3256)	5s $^2S_{1/2}$ (0.9257)	<1	140	200
294.595	5p $^2P_{1/2}$ (5.1330)	5s $^2S_{1/2}$ (0.9257)	<1	65	150
Standard line for estimating the relative intensities					
Y I 410.239	5p $^2F_{7/2}$ (3.0871)	5s $^2D_{5/2}$ (0.0655)	4300	1000¶	–
Y II 285.450	5p^2 $^3P_2$ (7.3979)	5s5p $^3P_2$ (3.0558)	280	150	–

†Discharge conditions: Ar 3.5×10^2 Pa(2.6 Torr)/310 V.
‡Discharge conditions: Ar 3.5×10^2 Pa + He 4.0×10^2 Pa (3.0 Torr)/310 V.
¶Standard value for determining the relative intensities.

these Y III lines and the relative intensities in this work when the intensity of the Y I 410.239 nm is the standard, and the relative intensities from Ref. [19]. The $4p^65p$ electron configuration gives the lowest excited energy levels of doubly-ionized yttrium, thus leading to the resonance transitions. The $4p^65d$ and the $4p^66s$ configurations require more energies for the excitations.

As shown in Table 1, all of the Y III emission lines are extremely weak in an argon glow discharge plasma. However, it is possible to excite only the Y III lines which are identified as the $4p^65p$–$4p^65s(4p^64d)$ transitions in an argon–helium mixed gas plasma. One should notice that the lines resulting from the $4p^65d(4p^66s)$–$4p^65p$ transitions cannot be observed even in the argon–helium plasma. Figure 1 shows spectral scans for yttrium when using argon alone (a) and an argon–helium mixture (b) as the plasma gas in the wavelength range between 281 and 283 nm. Several emission lines of singly-ionized yttrium (Y II) appear in the argon-excited spectrum; in addition, the Y III 281.699 nm line clearly appears when using the argon–helium mixed gas, but not in pure argon. Further, spectral scans in the 219–222 nm wavelength range are also shown in Figure 1. There are several Y II lines and Ar II lines in both the spectra, but the Y III lines that should be in this wavelength region (see Table 1) at 219.122 nm,

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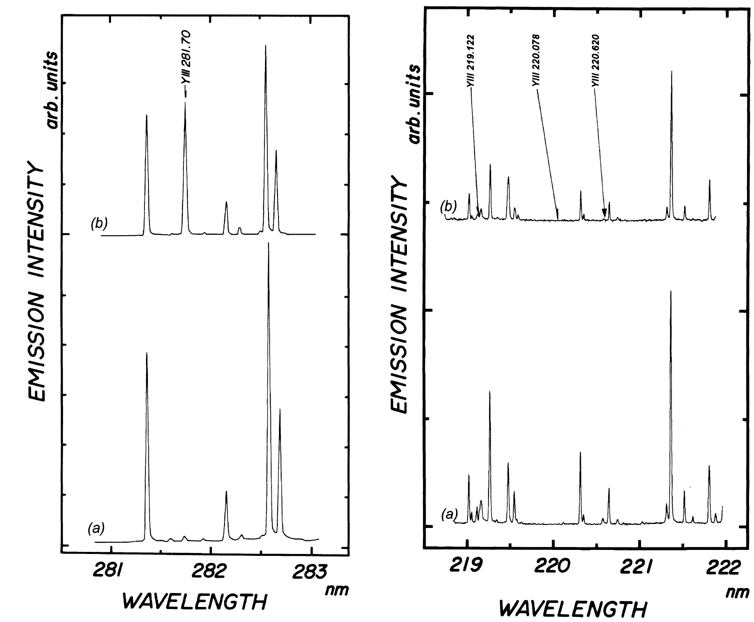

Figure 1. Spectral lines of yttrium excited by Grimm-style glow discharge plasmas using an argon gas alone (a) and an argon–helium mixed gas (b). Discharge conditions: (a) Ar 3.5×10^2 Pa (2.6 Torr)/310 V and (b) Ar 3.5×10^2 Pa (2.6 Torr) + He 4.0×10^2 Pa (3.0 Torr)/310 V.

220.078 nm, and 220.620 nm do not appear even with the argon–helium mixture.

Figure 2 shows variations in the discharge current (a) and the sputtering rate (b) when helium gas is added to an argon plasma. In this measurement, the argon pressure was kept constant. It is found that the sputtering rate as well as the discharge current decreases with increasing the amount of helium in the plasma. In the argon–helium mixed gas plasmas, such a decline in the discharge conditions can explain the decrease in the emission intensities of the Y II lines, as found in Figure 1, but it is the helium addition to the argon plasma that enables some of the Y III lines to be excited. This effect implies that helium species in the plasma principally contributes to ionization and excitation of the $4p^65p$ levels of doubly-ionized yttrium. Figure 3(a) shows variations in the net emission intensities of some yttrium lines as a function of the helium partial pressure added. Whereas the intensity of the Y II 285.450 nm line decreases with an increase in the partial pressure of helium, those of the Y III lines gradually

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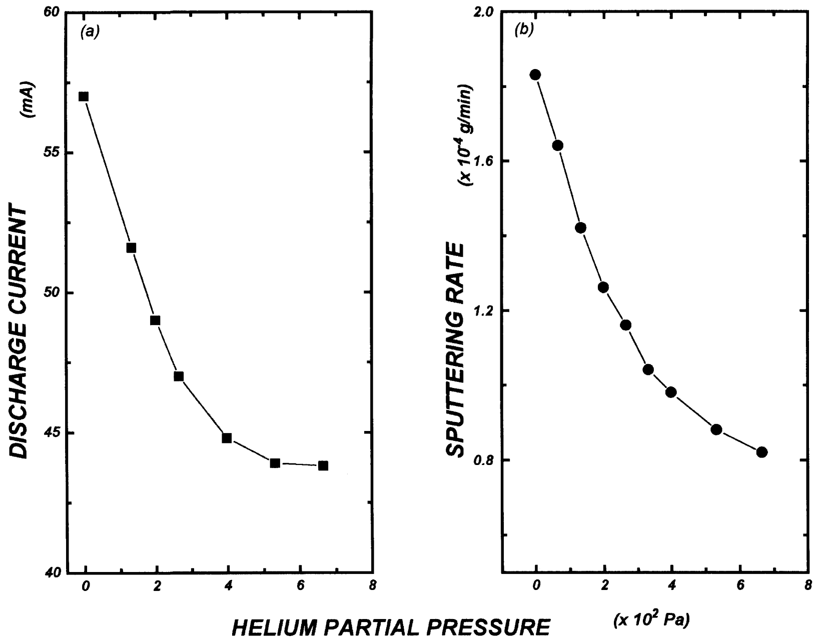

Figure 2. Dependence of the discharge current (a) and the sputtering rate (b) on the partial pressure of helium added to an argon plasma. Discharge conditions: Ar 3.3×10^2 Pa (2.5 Torr)/400 V.

increase, except for the Y III 219.122 nm line which is hardly observed at any helium pressure. As shown in Figure 3(b), I also calculated the reduced emission intensities of the Y III lines per unit of the sputtering rate in order to correct for changes in the number density of yttrium in the plasma. These results suggest that, while the $4p^6 5p$ excited state can be populated through excitation processes in which helium species are involved, the $4p^6 5d$ excited state is less populated even in the helium-containing plasma.

Kiess and Lang analyzed a spark spectrum of zirconium and found Zr III emission lines which are assigned to the $4p^6 4d5p$–$4p^6 4d^2$ transitions.[20] Table 2 indicates the wavelengths of some intense Zr III lines and the relative intensities observed in this work, together with the relative intensities which are extracted from a wavelength table.[21] The $4p^6 4d5p$ electron configuration gives the lowest excited levels from which the resonance transitions result. Unlike in yttrium, these Zr III emission lines cannot be observed when using either pure argon gas or argon–helium mixed gases. The first and the second ionization potential of zirconium is greater than the

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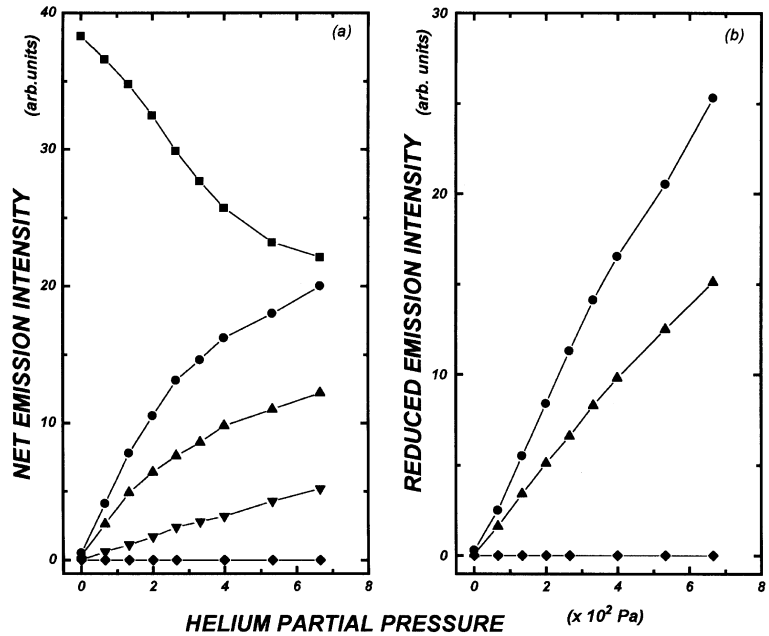

Figure 3. Variations in the net emission intensities (a) and the reduced intensities (b) as a function of the helium partial pressure added. The reduced intensity is estimated per unit of the sputtering rate indicated in Figure 2(b). Emission lines: Y III 219.122 nm(◆), Y III 281.699 nm(●), Y III 294.595 nm(▲), Y II 285.450 nm(■), and He I 282.907 nm (▼). Discharge conditions: Ar 3.3×10^2 Pa(2.5 Torr)/400 V.

corresponding one of yttrium;[16] thus, the behavior of the Zr III lines would be explained from the energy difference in the first and second ionization between zirconium and yttrium.

Figure 4 illustrates a simplified energy diagram of yttrium and zirconium in which only the relevant energy levels are drawn, together with the metastable levels and the ionization levels of argon and helium. As can be understood from Figure 4, it is possible to ionize a neutral atom of both yttrium and zirconium, to the singly-charged ion, through a Penning-type collision with the metastable argon: 4s $^3P_2$ (11.548 eV) and 4s $^3P_0$ (11.828 eV),[14] such as Y (or Zr) + $Ar^m \rightarrow Y^+$ (or Zr^+) + $Ar^g + e^-$, where Ar^m and Ar^g represents the metastable state and the ground state, respectively. It is thus considered that excited states of singly-ionized yttrium as well as singly-ionized zirconium can be easily populated because their excited

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Table 2. Major emission lines of doubly-ionized zirconium and their relative intensities.

Wavelength (nm) in air	Assignment		Relative intensity		
	Upper (eV)	Lower (eV)	Ar†	Ar/He‡	Ref. [21]
200.682	5p $^3F_2$ (6.8878)	4d $^1D_2$ (0.7118)	<1	<1	75
208.678	5p $^1D_2$ (6.6512)	4d $^1D_2$ (0.7118)	<1	<1	200
259.365	5p $^3D_3$ (7.1099)	5s $^3D_2$ (2.3312)	<1	<1	100
262.056	5p $^3F_4$ (7.1514)	5s $^3D_3$ (2.4218)	<1	<1	150
264.379	5p $^3D_3$ (7.1099)	5s $^3D_3$ (2.4218)	<1	<1	125
265.646	5p $^3D_2$ (6.9970)	5s $^3D_2$ (2.3312)	<1	<1	75
Standard line for estimating the relative intensities					
Zr I 351.958	5p $^3G_3$ (3.5216)	5s $^3F_2$ (0.0000)		1000¶	–

†Discharge conditions: Ar 3.5×10^2 Pa(2.6 Torr)/400 V.

‡Discharge conditions: Ar 3.5×10^2 Pa + He 4.0×10^2 Pa (3.0 Torr)/400 V.

¶Standard value for determining the relative intensities.

levels are in the 3–4 eV range above the first ionization potential of yttrium and zirconium, respectively. In fact, intense Y II and Zr II emission lines are found in the spectra emitted by an argon glow discharge plasma. Similarly, a Penning-type collision with the metastable helium: 2s $^3S_1$ (19.818 eV) and 2s $^1S_0$ (20.615 eV),[14] may occurs in the argon–helium mixed gas plasma, which produces ionic species of yttrium and zirconium. One should notice the difference in the sum of the first and the second ionization potential between yttrium and zirconium, i.e., 18.9 eV for yttrium and 20.98 eV for zirconium,[16] as shown in Figure 4. Only in the case of yttrium, the Penning-type collision with the metastable helium possibly produces the doubly-charged ion, according to the following reaction: $Y + He^m \rightarrow Y^{2+} + He^g + 2e^-$, where He^m and He^g represents the metastable state and the ground state, respectively, which leads to subsequent excitation of the doubly-ionized yttrium.

Another possible mechanism for obtaining doubly-ionized yttrium is a charge-transfer-like collision with the helium ion in the ground state: 1s $^2S_{1/2}$ (24.580 eV),[14] such as $Y + He^+ \rightarrow (Y^{2+})^* + He^g + e^-$. A charge-transfer collision between the helium ion and the yttrium atom leaves surplus energy enough to cause further ionization of the resultant singly-charged yttrium ion. As show in Figure 4, it is possible to excite the $4p^65p$ levels of doubly-ionized yttrium through such a collision, but it is difficult to populate the $4p^65d(4p^66s)$ levels of doubly-ionized yttrium and the $4p^64d5p$ levels of doubly-ionized zirconium. Though the probability of

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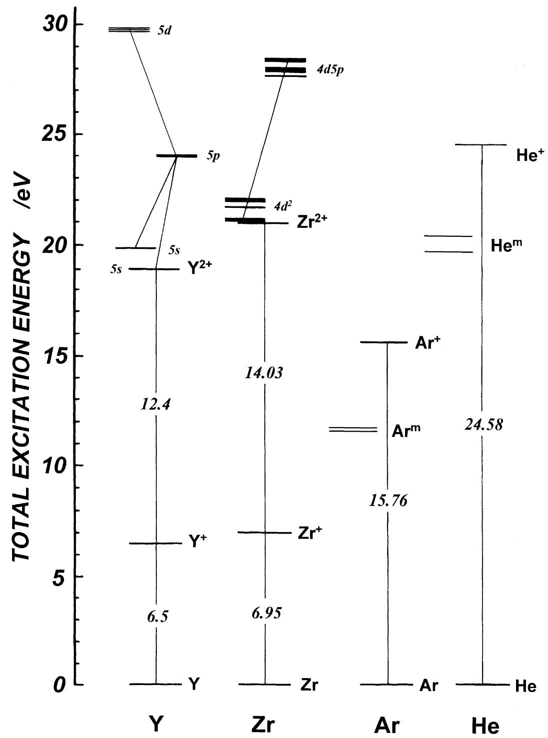

Figure 4. Schematic energy correlation diagram between excited levels of doubly-ionized yttrium and zirconium, and the metastable and ionization levels of argon and helium.

the collision is not known exactly, the experimental results can be well explained from the energy balance between the relevant species.

CONCLUSIONS

The data in this study demonstrate that helium gas plays an important role in excitation of doubly-charged ions in a Grimm-style glow discharge plasma. The Y III lines assigned not to the $4p^6 5d(4p^6 6s)-4p^6 5p$ transition but to the $4p^6 5p-4p^6 5s(4p^6 4d)$ transition could be emitted from the argon–helium mixed gas plasma, while neither of them appeared in the pure argon plasma. Furthermore, no Zr III lines could be found even by using the argon–helium mixed gases. These results are explained from correlation in the total excitation energy between helium excited species and the doubly-ionized ions.

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REFERENCES

1. *Glow Discharge Optical Emission Spectrometry*; Payling, R., Jones, D., Bengtson, A., Eds.; John Wily & Sons: Chichester, 1997; 352–462.
2. *Glow Discharge Plasmas in Analytical Spectroscopy*; Marcus, R.K., Broekaert, J.A.C., Eds.; John Wily & Sons: Chichester, 2003; 231–252.
3. Uzelac, N.I.; Leis, F. Measurement of gas temperatures and metastable state densities in a microwave boosted glow-discharge using a diode-laser. Spectrochim. Acta **1992**, *47B*, 877–887.
4. Von Engel, A. *Ionized Gases*; Clarendon Press: Oxford, 1965.
5. Wagatsuma, K. Some observations of an anomalous excitation behavior of chromium emission lines in an argon radio-frequency powered glow discharge plasma. Spectrochim. Acta **2003**, *58B*, 565–573.
6. Chapman, B. *Glow Discharge Processes*; John Wily & Sons: New York, 1980; 115–138.
7. Wagatsuma, K.; Hirokawa, K. Characterization of atomic emission lines from argon, neon, and nitrogen glow discharge plasmas. Anal. Chem. **1985**, *57*, 2901–2907.
8. Steers, E.B.M.; Fielding, R.J. Charge-transfer excitation processes in the Grimm lamp. J. Anal. At. Spectrom. **1987**, *2*, 239–244.
9. Wagatsuma, K.; Hirokawa, K. Spectrometric studies of excitation mechanisms on singly-ionized copper emission lines in Grimm-type discharge plasmas with helium mixture technique. Spectrochim. Acta **1991**, *46B*, 269–281.
10. Wagatsuma, K.; Hirokawa, K. Selective excitation of singly-ionized silver emission lines by Grimm glow discharge plasmas using several different plasma gases. Z. Phys., D **1996**, *37*, 231–239.
11. Steers, E.B.M.; Thorne, A.P. Application of high-resolution Fourier transform spectrometry to the study of glow discharge sources. J. Anal. At. Spectrom. **1993**, *8*, 309–315.
12. Steers, E.B.M. Charge transfer excitation in glow discharge sources: the

spectra of titanium and copper with neon, argon and krypton as the plasma gas. J. Anal. At. Spectrom. **1997**, *12*, 1033–1040.
13. Wagatsuma, K.; Hirokawa, K. Excitation of singly-ionized argon species in helium-matrix glow discharge plasma—role of the energy transfer from helium metastables. Spectrochim. Acta **1995**, *50B*, 109–125.
14. Moore, C.E. *Atomic Energy Levels, Vol. 1*, N.B.S. Stand. Circular 467; U.S. Government Printing Office: Washington, DC, 1949.
15. Kelly, R.L. Atomic and ionic spectrum lines below 2000 angstroms: hydrogen through krypton. Part II. J. Phys. Chem. Ref. Data **1987**, *16* (Suppl. 2), 769–786.
16. Moore, C.E. *Atomic Energy Levels, Vol. 2*, N.B.S. Stand. Circular 467; U.S. Government Printing Office: Washington, DC, 1956; 196–202.
17. Grimm, W. Eine Neue Glimmentladungslampe für die Optische Emissionsspktralanalyse. Spectrochim. Acta **1968**, *23B*, 443–454.
18. Wagatsuma, K.; Hirokawa, K. Observation of Cu–Ni alloy surfaces by low wattage glow discharge emission spectrometry. Surf. Interface Anal. **1984**, *6*, 167–170.
19. Meggers, W.F.; Russell, H.N. An analysis of the arc and spark spectra of yttrium. Bur. Std. J. Research **1929**, *2*, 733–769.
20. Kiess, C.C.; Lang, R.J. Structure of the spectra of doubly and trebly ionized zirconium. Bur. Std. J. Research **1930**, *5*, 305–324.
21. Moore, C.E. *Ultraviolet Multiplet Table, Section 2*, N.B.S. Stand. Circular 488; U.S. Government Printing Office: Washington, DC, 1952.

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