Emission and Sputtering Characteristics of Ne-Ar Mixed Gas Glow Discharge Plasmas

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The emission characteristics of several Cu lines emitted from a Ne-Ar mixed gas glow discharge plasma were investigated. The addition of small amounts of Ar to a Ne plasma increases the sputtering rate of a Cu sample because Ar ions, which work as the impinging ions for cathode sputtering, are predominantly produced through Penning ionization collisions between Ne metastables and Ar atoms. Ar addition also elevates the number density of electrons in the plasma. These changes occurring in the Ne-Ar mixed gas plasma result in enhanced emission intensities of the Cu lines. The Cu II 270.10-nm and the Cu II 224.70-nm lines yield different intensity dependence on the Ar partial pressure added. This phenomenon is because these Cu II lines are excited principally through different charge transfer processes: collisions with Ne ions for the Cu II 270.10-nm line and collisions with Ar ions for the Cu II 224.70-nm line. The shape of sputtered craters in the Ne-Ar glow discharge plasma was measured. The depth resolution was improved when Ar was added to a Ne plasma because the crater bottoms were flatter with larger Ar partial pressures.

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Introduction

The hollow anode glow discharge lamp, as first developed by Grimm,[1] has been extensively employed in optical emission spectrometry (GD-OES). This analytical technique has an advantage for the direct analysis of solid samples because the sample atoms are directly introduced into the plasma through cathode sputtering.[2] GD-OES can also be employed for surface analysis because the sampling process gives in-depth variations of the sample composition.[3,4]

Several papers have pointed out that spectral patterns emitted from a glow discharge plasma (GDP) depend principally on the kind of the plasma gas,[5,6] which helps to explain the excitation mechanisms occurring in GDP. Differing from other plasma sources, such as ICP, it is possible for GDP to be easily initiated and maintained by using various gases.[5,6] Although the resulting spectral patterns are different from each other, the emission characteristics of rare gases such as He, Ne, Ar, and Kr can be suitable for an excitation source in optical emission spectrometry. The intensities of particular ionic lines are enhanced selectively depending on the combination between the plasma gas and the sample species; for example, Cu ionic lines in Ar or Ne,[7,8] Ag ionic lines in He,[9] Al ionic lines in Ne,[10,11] and Ni ionic lines in Ar or Kr plasma gas.[12] Detailed investigations of GDP have indicated that these intense emission lines are excited through charge-transfer collisions between gas ions (G) and sample atoms (M) as follows:[13] $G^+ + M^g \rightarrow G^g + (M^+)^* + \Delta E$, where the superscript +, ∗, or g represents an ionic, excited, or ground state, respectively. When the difference in their internal energies, ΔE, is almost zero, a highly populated excited state of the sample, $(M^+)^*$, can be produced through resonance energy transfer collisions,[13] which leads to strong emission of the corresponding ionic lines. Such selectively-excited ionic lines could be employed as an analytical line which should be observed in analytical applications. Furthermore, gas mixing for the plasma gas would improve the detection sensitivity as well as the data precision in GD-OES. A mixture of Ar and He is potentially interesting because He has larger internal energies that are sufficient to excite high-lying energy states;[9,14,15] however, the other gas mixtures have been less investigated compared to the Ar-He mixed gases.

The authors reported on intensity changes of Bi and Pb emission lines with a mixture of Ne and Ar, which indicated that their atomic lines were more enhanced by adding Ar to the Ne matrix gas.[16] This paper describes the emission and sputtering features of Ne-Ar mixed gas GDP when Cu spectral lines having different excitation energies are measured. In addition to Cu atomic lines, several intense ionic lines of Cu are emitted from the Ne plasma through charge-transfer collisions between Ne ions and Cu atoms. Furthermore, the sputtering rate as well as the intensities of Cu emission lines can be elevated in the Ne-Ar mixtures. This effect can be derived from the increased population of Ar ions which are produced through the Penning ionization process[17] between Ne 3s metastables and Ar atoms. Mixing Ar gas with matrix Ne gas could improve both the crater shape and the detection sensitivity in Cu determination compared to pure Ne GDP.

Experimental

The structure of the glow discharge lamp[18] and the measuring system,[19] comprising a spectrometer and a direct-current power supply, have been described elsewhere. The discharge lamp

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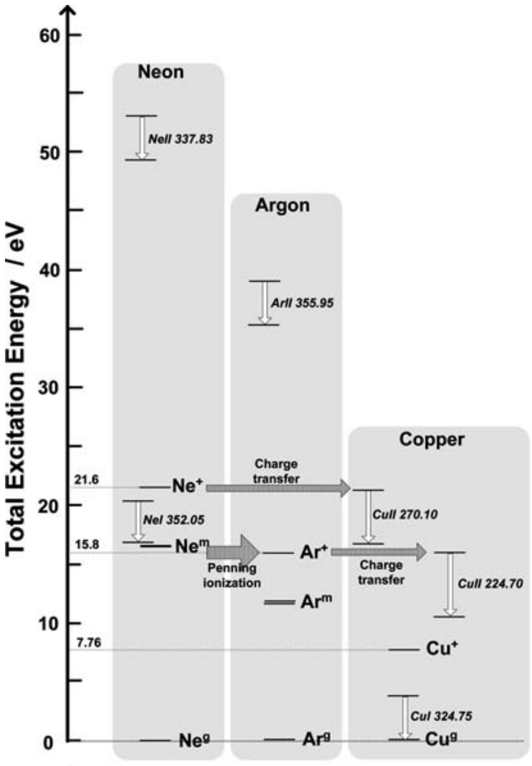

Fig. 1 Simplified energy level diagram of Cu together with the metastable and ionization levels of Ar and Ne.

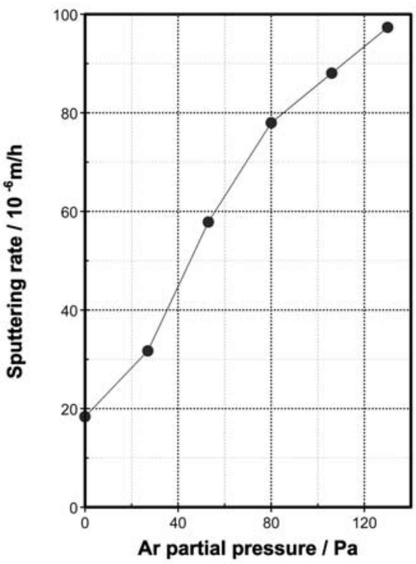

Fig. 2 Variation in the sputtering rate as a function of the Ar partial pressure added to a Ne plasma. Discharge voltage, 850 V; matrix plasma gas, Ne at 670 Pa.

was made according to the original model published by Grimm.[1] The inner diameter of the hollow anode was 8.0 mm and the distance between the anode and cathode was adjusted to be 0.2 – 0.3 mm. The lamp was evacuated down to *ca*. 2.6 Pa, and then the plasma gas was introduced and was flowed during the measurement. High-purity Ne (> 99.99%) and Ar (> 99.9995%) were employed as the plasma gas. The partial pressures of each gas were regulated with needle valves and read on Pirani gauges (corrected to pure Ne or Ar) at the gas inlet of the lamp. Pure Cu plates (99.99% purity) were employed as the sample. They were polished with waterproof emery papers and then finished to mirror faces. Before the emission measurement, pre-discharges were carried out for about 10 min to remove any surface contaminants. A depth profiling meter (Surfcom 1500DX, Tokyo Seimitsu Co. Ltd., Japan) was employed for the measurement of crater shapes after 60-min sputtering.

Table 1 Observed emission lines and the assignment[a]

Wavelength/nm	Upper level/eV	Lower level/eV
Cu I 324.753	4p $^2P_{3/2}$ (3.8166)	4s $^2S_{1/2}$ (0.0000)
Cu II 224.699	4p $^3P_2$ (8.2347)	4s $^3D_3$ (2.7187)
Cu II 270.097	5s $^1D_2$ (13.6834)	4p $^1D_2$ (9.0945)
Ne I 352.049	4p $[1/2]_0$ (20.3686)	3s $[1/2]_1$ (16.8479)
Ne II 337.830	3p $^2P_{1/2}$ (31.5277)	3s $^2P_{1/2}$ (27.8588)
Ar II 355.952	4d $^2F_{7/2}$ (23.1617)	4p $^2D_{5/2}$ (19.6796)

a. Refs. 21 and 22.

Results and Discussion

Emission characteristics in Ne-Ar GDP

There is a well-known effect, called Penning ionization, where a Ne glow discharge can be maintained at lower discharge voltages when a small amount of Ar is added to the matrix Ne gas.[20] Figure 1 illustrates a simplified energy level diagram of Ar and Ne, where the metastable and the ionization levels of each gas are shown together with excitation levels related to the observed emission lines of Cu, Ar, and Ne. One should notice that the first ionization level of Ar (15.76 eV) is slightly lower than the excitation energies of the Ne 3s metastables: 3s $[3/2]_2$ (16.62 eV) and 3s $[1/2]_0$ (16.72 eV).[21] This little difference in their internal energies enables an energy transfer process from the Ne metastable to the Ar ground-state atom to be caused more efficiently to enhance the ionization rate of the plasma gas, as indicated by the following equation:

$$Ne^m + Ar^g \longrightarrow Ne^g + Ar^+ + e^-, \quad (1)$$

where the superscript +, m, or g represents an ionic, metastable, or ground state, respectively. This reaction could increase both the number density of electrons and the population of Ar ions in the plasma; accordingly, sputtered amounts of sample atoms would be elevated because the resultant Ar ions also contribute to cathode sputtering.

Figure 2 shows a variation in the sputtering rate as a function of the Ar partial pressure introduced into a Ne plasma in the case where the pressure of Ne as well as the discharge voltage are kept constant. The crater shape after a 60-min discharge was measured with a surface profiler, and the resulting crater bottom was smoothed and converted to the average depth. The sputtering rate of a Cu sample was monotonically elevated along with increasing Ar partial pressures.

Because Ar addition makes the amounts of Cu atoms to be more introduced into the plasma, it is highly interesting to investigate the intensities of Cu emission lines in the Ne-Ar GDP, where two different types of Cu ionic lines and an atomic resonance line are observed. Table 1 summarizes the Cu emission lines and their assignment, together with Ne and Ar

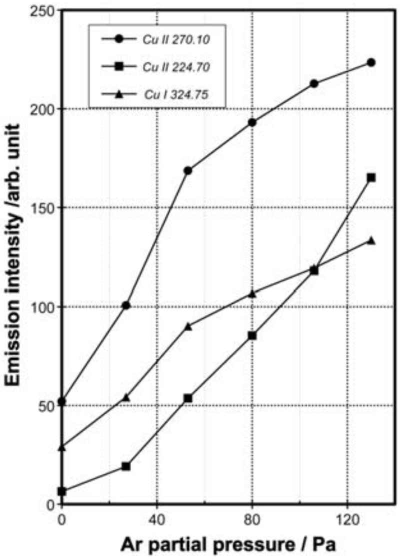

Fig. 3 Variations in the emission iniensities of Cu I 324.75 nm (triangle), Cu II 224.70 nm (square), and Cu II 270.10 nm (circle) as a function of the Ar partial pressure added to a Ne plasma. Discharge voltage, 850 V; matrix plasma gas, Ne at 670 Pa.

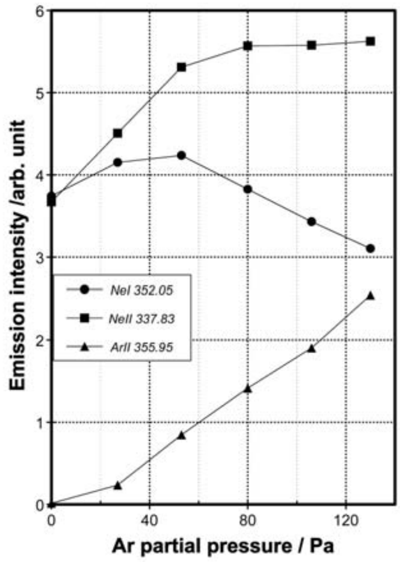

Fig. 4 Variations in the emission iniensities of Ne I 352.50 nm (circle), Ne II 337.83 nm (square), and Ar II 355.95 nm (triangle) as a function of the Ar partial pressure added to a Ne plasma. Discharge voltage, 850 V; matrix plasma gas, Ne at 670 Pa.

emission lines observed.[21,22]

Figure 3 shows variations in the net emission intensities of the Cu lines as a function of the Ar partial pressures added. The emission intensities generally increase with the Ar partial pressure; however, the pressure dependence is different from that of the sputtering rate, which is indicated in Fig. 2, especially at larger Ar pressures. The intensities of the Cu I 324.75-nm line and the Cu II 270.10-nm line seem to become saturated when the Ar pressure is more than 100 Pa, while the intensity of the Cu II 224.70-nm line is greatly elevated even at larger Ar pressures.

Previous studies have revealed the excitation mechanism concerning Cu ionic emission lines in the GDP; the most important characteristic is that the Cu II 270.10-nm line is selectively emitted form the Ne plasma, whereas the Cu II 224.70-nm line is dominantly from the Ar plasma.[7,8] These phenomena can be explained from resonance charge transfer collisions between Cu atoms and Ar (or Ne) ions, where the total excitation energy of the corresponding excited levels when considering the first ionization potential of Cu (7.76 eV): 4p $^2P_3$ (8.23 + 7.76 eV) for the Cu II 224.70-nm line or 5s $^1D_2$ (13.52 + 7.76 eV) for the Cu II 270.10-nm line is very close to the ionization potential of Ar or Ne,[21,22] respectively. Therefore, the population of Ne or Ar ions is considered to become a determining factor in exciting these excited levels, rather than the number density of electrons. The Penning ionization process (Eq. (1)) elevates the number density of Ar ions which work as impinging ions for cathode sputtering as well as an energy doner for the excitation of the Cu II 224.70-nm line. This effect would characterize the Ne-Ar mixed gas GDP. The Penning process also reduces the number density of the Ne metastables. The Ne metastables become an intermediate stage for ionization through a cumulative/stepwise ionization process as follows:

$$Ne^m + e^- \text{ (fast)} \longrightarrow Ne^+ + e^- + e^- \text{ (slow)}, \qquad (2)$$

where superscript m means a metastable state. Therefore, the ionization rate of the Ne ion may also be suppressed when Ar is added to the Ne plasma. This effect leads to a decrease in the collision probability between Cu atoms and Ne ions and thus the saturation in the emission intensity of the Cu II 270.10-nm line at larger Ar pressures. On the other hand, the collision probability between Cu atoms and Ar ions can be more elevated with larger partial pressures of Ar added, which explains the dominant increase in the emission intensity of the Cu II 224.70-nm line. As shown in Fig. 3, the intensities of the resonance atomic line, the Cu I 324.75 nm, become less elevated when the Ar partial pressure is larger. This dependence would be caused by self-absorption, which is frequently observed in GDP when sputtered amounts of Cu increase.

Figure 4 shows variations in the net emission intensities of plasma gas emission lines: the Ne II 337.83-nm, the Ne I 352.05-nm, and the Ar II 355.95-nm lines, as a function of Ar partial pressures added. The emission intensities of the Ne lines initially increase until the Ar partial pressure increases up to 50 Pa probably because the addition of Ar elevates the number density of electrons in the plasma; however, the intensity of the Ne II 337.83-nm line becomes unchanged and that of the Ne I 352.05-nm line decreases when the Ar partial pressures exceeds 50 Pa. The intensity change of the Ne II line could be derived from a slow-down of the ionization rate of Ne due to the Penning ionization collisions with Ar, and the intensity variation of the Ne I line could be strongly affected by a decrease in the population of the Ne metastables. On the other hand, the intensity variation of the Ar II 355.95-nm line can be explained by an increasing population of Ar ions with the partial pressure, which is evidence that the Penning ionization process enhances the ionization rate in the Ne-Ar GDP.

Crater shape in Ne-Ar GDP

GD-OES using pure Ne gas have a disadvantage feature such that it is difficult to get a flat-bottom crater in the depth profiling, which worsens the in-depth resolution. Figure 5 shows the shapes of the resulting crater after a 60-min sputtering, which was performed for different plasma gas compositions. In pure Ne GDP (Fig. 5a), a round-shaped crater was obtained and it is not suitable for in-depth analysis with

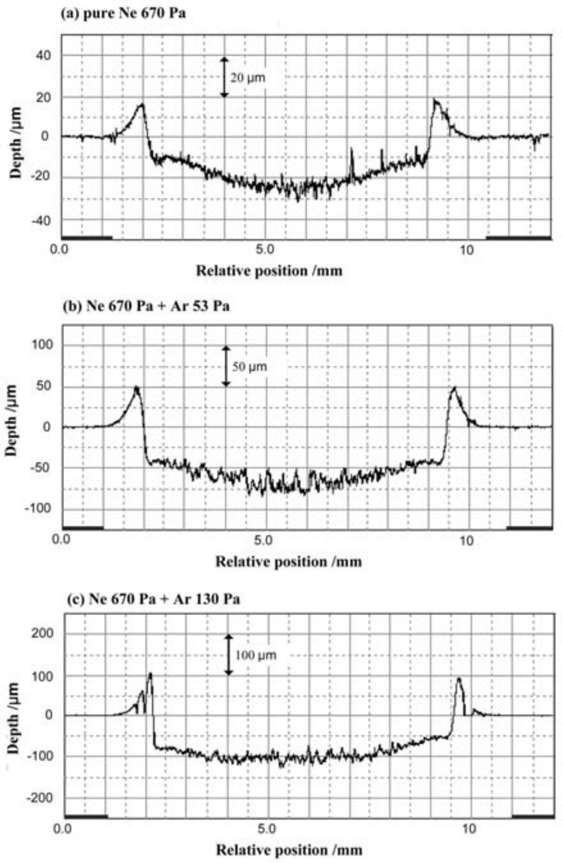

Fig. 5 Changes in the crater shape for different plasma gas compositions. Discharge voltage, 850 V. Plasma gas: (a) 670-Pa Ne pure, (b) 670-Pa Ne + 53-Pa Ar, (c) 670-Pa Ne + 130-Pa Ar.

good resolution. The average sputtering rate is estimated to be 18 ± 8 µm/h whose relative variation is 45%. It may be possible to obtain a better discharge condition by adjusting both the pressure of Ne and the discharge voltage; however, it includes a troublesome procedure. We could find that the bottom shape of the crater was improved along with increasing the sputtering rate when Ar gas was added to the Ne plasma. When mixed gas containing 130-Pa Ar was employed (Fig. 5c), the sputtering rate was estimated to be 97 ± 18 µm/h even if the contribution from both edges of the crater was considered. In this case, the relative variation was 18% which was better than that of the pure Ne plasma. This result is because a flat face having about 110 µm in depth occupies larger parts of the crater bottom. The reason for this is not clear in the present study; however, we suppose that the voltage distribution across the cathode sheath can be more uniform in the Ne-Ar GDP, due to an increase in charged particles such as Ar ions and electrons. This effect regarding the sputtering can be useful for surface analysis in the Ne-Ar GD-OES.

Conclusions

The addition of small amounts of Ar to a Ne plasma generally enhances the emission intensities of Cu lines, because the sputtering rate is elevated by Ar ions, which are produced through Penning ionization collision between Ne metastable and Ar atom. Their variations with the Ar partial pressures added are different from each other, because these Cu lines are emitted through each particular excitation mechanism. The depth resolution for surface analysis is expected to be better when Ar is added to a Ne plasma because the bottom face of the sputtering crater becomes flatter with larger Ar partial pressures.

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