Time-resolved optical emission spectroscopy on three-dimensionally integrated micro solution plasma in He/H$_2$O mixture

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Abstract. We have performed time-averaged and time-resolved optical emission spectroscopy (OES) on three-dimensionally integrated micro solution plasma (3D IMSP) in He/H$_2$O mixture. The results of time-resolved OES on 3D IMSP in He/H$_2$O mixture have shown that duration of the optical emission of OH($A^2\Sigma^+ \rightarrow X^2\Pi$ around 309 nm) is shorter than that in Ar/H$_2$O mixture. Possible causes of this difference are discussed by means of difference in the energy of metastable states of Ar and He.

1. Introduction
Nonthermal atmospheric pressure plasmas in contact with liquid is widely studied for variety of plasma application, such as nano-material synthesis, surface modification, water treatment, sterilization, recycling of rare materials, and decomposition of toxic compound [1-5]. Various plasma generation methods are used for these purposes, which include glow discharge [6], dielectric barrier discharge [7-9], radio-frequency discharge [10, 11] and microwave discharge [12, 13].

In our previous works, we have developed three-dimensionally integrated micro solution plasma (3D IMSP), in which a large amount of tiny plasma (microplasma [14]) is generated in a porous dielectric material filled with a gas/liquid mixed medium. 3D IMSP can be applied to gold nanoparticle synthesis [15, 16] and to decomposition of organic substances in water [17, 18]. Moreover, 3D IMSP have shown superior performance in the case of decomposition of methylene blue molecules in comparison to conventional solution plasma [19 - 21].

Recently, we have reported the results of time-resolved optical emission spectroscopy (OES) on 3D IMSP in Ar/H$_2$O mixture [22], in which we have observed that relatively high optical emission intensity of OH($A^2\Sigma^+ \rightarrow X^2\Pi$ around 309 nm) is kept even after the main peak pulse discharge has finished. In this paper, we report the results of time-resolved OES on 3D IMSP in He/H$_2$O mixture in order to compare to that in Ar/H$_2$O mixture.

2. Experimental set up
Figure 1 shows schematic illustration of the experimental set up, which is the same to that in our previous on 3D IMSP in Ar/H$_2$O mixture [22]. Table 1 is the experimental conditions for time-resolved OES in this and previous work. These conditions are the same to that in our previous report, expect that the feed gas is He [22]. The details are described in elsewhere [22]. Here after, 3D IMSP in
Ar/H₂O mixture and that in He/H₂O mixture are referred to as simply Ar/H₂O and He/H₂O, respectively.

3. Results and discussion

3.1 Time-averaged wide-range OES

Before starting the time-resolved OES, we performed OES in the wide range of 280 to 800 nm in order to see which emissive species can be detected in the case of He/H₂O. Figure 2 shows the result. A series of atomic He emission lines (e.g. 388, 501, 587, 706 nm etc.) is observed, because He is used for generating gas bubbles in porous dielectric material. Furthermore, OH (\(A^2\Sigma^+ \rightarrow X^2\Pi\) around 309 nm), H\(\beta\) (4d → 2p at 486 nm), H\(\alpha\) (3d → 2p at 656 nm) and O (3p → 3s at 777 nm) emission lines are observed. Hereafter, OH (\(A^2\Sigma^+\)) and OH (\(X^2\Pi\)) are represented as OH (A) and OH (X), respectively.

A series of peaks observed at 315, 337, 353, 357, 375, 380 nm etc. corresponds to the emission of second positive-system band (SPB; \(C^3\Pi \rightarrow B^3\Pi\)) of N\(_2\). One of the causes of the N\(_2\) SPB is the discharge of air, in the isolated pores that is incorporated in the porous dielectric material during its fabrication. Another is the parasitic air discharge between outer surface of the glass tube and grounded electrode surrounding it. Since these discharges are isolated from liquid medium, they do not contribute to treatment of liquid.

In comparison to our previous report on the wide-range OES in case of Ar/H₂O [22], the result of He/H₂O exhibit stronger optical emission intensity of H\(\alpha\) relative to that of OH(A). This can be

| Table 1. Experimental conditions for time-resolved OES on 3D IMSP in He/H₂O mixture (this work) and Ar/H₂O mixture (previous work). |
|----------------------------------------------------------|
| Liquid medium | Deionized Water |
| Electrical conductivity (µS/cm) | 0.77 |
| pH | 5.94 |
| Volume of liquid (mL) | 150 |
| Temperature (°C) | 25 |
| Voltage amplitude (kV) | 5 |
| Frequency (kHz) | 20 |
| Pulse width (µs) | 2.0 |
| He or Ar flow rate (L/min) | 1.1 |

Figure 1. Schematic illustration of the experimental set up for time-resolved optical emission spectroscopy on 3D IMSP.
explained by difference in energy level of metastable states of Ar and He. In order to emit Hα lines, H atoms should be once excited to the energy level of 3d (12.1 eV) or 4d (12.7 eV). The energy 19.8 eV of metastable state of He is high enough to excite H atoms to 3d or 4d levels, while the energy 11.5 eV of metastable of Ar is not high enough.

3.2 Time-resolved OES

After OH(A) emission has been confirmed in wide-range OES, we have investigated temporal behavior of OH(A) because it is believed to be the important reactant in water purification processes [4, 23]. Figure 3 (a) shows time-resolved OES spectra in the range of 300-325 nm in the case of He/H2O, which correspond to OH(A) emission band and are acquired after triggering pulse voltage of the power source. In the case of Ar/H2O, OH(A) emission spectra are observed for 500 ns after triggering the discharge [22]. In case of He/H2O, on the other hand, OH(A) emission spectra are not observed after 300 ns. In order to discuss in details, temporal variation of OH(A) intensity is compared the other parameters of voltage, current and emission intensity of He (388 nm).

Figure 3-(b) shows temporal variation of voltage, current, emission intensity of He (388 nm) and OH(A) (309 nm). After a trigger signal is send to the power source, voltage increases up to 5 kV and current peak is observed during voltage rise time during 0 to 200 ns. After that, weak current is observed during 200 to 500 ns. Intensity of optical emission of He is observed only during the voltage rise time during 0 to 200 ns, and is not observed during 200 to 500 ns. These characteristics are different from those in the case of Ar/H2O mixture [22].

Regarding the intensity of optical emission of OH(A), the main peak is observed during 0 to 200 ns, and weak emission of OH(A) is observed during 200 to 300 ns. These characteristics are slightly different from those in the case of Ar/H2O [22]. The first difference is the fact that intensity of OH(A) after the main peak in the case of He/H2O is relatively lower than that in the case of Ar/H2O. The second difference is the fact that duration (200-300 ns) of the weak emission is shorter than that (200-500 ns) in the case of Ar/H2O.

These differences are considered to be attributed to the differences in the contribution of metastable state of Ar(3P0 and 3P2, (Arm, hereafter)) and He(23S and 21S, (He m, hereafter). In the plasma containing H2O vapor with Ar or He, OH(A) can be generated mainly through following reactions [24 - 26];

\[
\begin{align*}
\text{H}_2\text{O} + e (> 9.1 \text{ eV}) & \rightarrow \text{H}(n = 1) + \text{OH}(A) + e \\
\text{H}_2\text{O} + \text{Ar} & \rightarrow \text{OH}(A) + \text{H} + \text{Ar}
\end{align*}
\]
In both cases of Ar/H₂O and He/H₂O, the OH(A) peak observed during 0 to 200 ns is considered to be caused mainly by the reaction (1) because energetic electrons exist during this period, which can be confirmed from the fact that the peak discharge current is also observed at the same time.

Regarding the time after 200 ns, energetic electrons does not exist, but low energy electrons and ions are considered to exist because weak current and Ar or He emission is observed. In this period, contribution of electron impact dissociation (1) is regarded as a minor reaction path to produce OH(A). Instead of reaction (1), following reaction may be expected [26, 27].

\[
\text{H}_2\text{O} + \text{e}(> 5.1 \text{ eV}) \rightarrow \text{OH}(X) + \text{H}(n=1) + \text{e}
\]  

(3)

And metastable Ar_m assisted H₂O dissociation (2) may be dominant.

Figure 3. (a) Time-resolved OES for the wavelength region of 300-325 nm, which corresponds to OH emission band \( \text{A}^2 \Sigma^+ \rightarrow \text{X}^2 \Pi \). (b) Temporal variation of (I) voltage (II) current and optical emission intensity of (III) He (388 nm), (IV) OH (A) (309 nm).
On the other hand, in the case of He/H$_2$O mixture, contribution of electron impact dissociation (1) and (3) is similar in Ar/H$_2$O mixture. But, unlike Ar/H$_2$O mixture, metastable He$_m$ assisted H$_2$O dissociation is not expected. Instead, following penning ionization reaction is expected because energy of He$_m$ (approximately 20 eV) is sufficient for ionizing H$_2$O molecules [28];

$$\text{H}_2\text{O} + \text{He}_m \rightarrow \text{H}_2\text{O}^+ + \text{He} \tag{4}$$

Thus, one of the cause of relatively lower OH(A) intensity after 200 ns in the case of He/H$_2$O than in the case of Ar/H$_2$O is considered to be due to the difference in the effects of metastable excited He and Ar. Although dissociative recombination reactions of H$_2$O$^+$ and/or H$_3$O$^+$ ions with electrons to produce OH(A) are also known to occur [4, 24, 29, 30], especially when electron energy is low as in the case of the period after 200 ns in this study, this will be discussed elsewhere using numerical simulation.

4. Conclusion
Time-averaged and time-resolved OES have been performed on the 3D IMSP in He/H$_2$O in order to compare to the OES results on Ar/H$_2$O. From the result of wide-range OES on 3D IMSP in He/H$_2$O mixture, optical emission of H$\alpha$ is stronger than that in Ar/H$_2$O mixture. This is due to difference in contribution of metastable Ar$_m$ (11.5 eV) and He$_m$ (19.8 eV). Because of this difference, He$_m$ contributes to generate H$\alpha$ line, while Ar$_m$ does not.

The results of time-resolved OES on 3D IMSP in He/H$_2$O has also been different from those in Ar/H$_2$O. Duration of optical emission of OH(A) in the case of He/H$_2$O is shorter than that in the case of Ar/H$_2$O. Intensity of OH(A) emission in the case of He/H$_2$O is lower than that in the case of Ar/H$_2$O. The cause of these differences can be attributed to the difference in the reactions of Ar$_m$ and He$_m$ with H$_2$O, in which Ar$_m$ can directly produce OH(A) while He$_m$ can produce H$_2$O$^+$ instead of OH(A). These qualitative conclusion will be verified quantitatively by using numerical simulation of reactions including the other OH(A) production reaction paths.

Acknowledgement
This work has been partly supported by the Grant-in-Aid for Scientific Research on Innovative Areas “Frontier Science of Interaction between Plasmas and Nano-Interfaces” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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