# Behaviors of optical emission from a dielectric barrier discharge in a He gas flow with small-fraction H<sub>2</sub>O impurity

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**Abstract:** In high-pressure plasmas generated in a rare-gas flow, presence of molecular impurities has critical influence on discharge characteristics even in a ppm order as indicated by various simulation studies. In this study, we experimentally investigate behaviors of optical emission from a dielectric barrier discharge in a He gas flow with H<sub>2</sub>O impurity in a fraction range between 2 and 600 ppm. Emission intensities of OH, H, and O radicals varied independently with variation of the water fraction and the voltage frequency. **Keywords:** Dielectric barrier discharge, He, H<sub>2</sub>O, Optical emission spectroscopy

## 1. Introduction

In high-pressure low-temperature plasmas in rare-gas flows, such as atmospheric-pressure plasma jets generated in dielectric tubes, presence of impurities has critical influence on various discharge characteristics. Previous experimental and simulation studies have indicated that propagation velocity of ionization front [1], He metastable (He<sup>m</sup>) atom density [2], breakdown voltage [3], and ionization level [4] are varied by changing a N<sub>2</sub> impurity fraction in He plasmas. Figure 1 summarizes ranges of the N<sub>2</sub> impurity fraction covered in previous studies. One can notice from Fig. 1 that experimental investigation of the impurity effects in a range below 10 ppm has not been conducted yet. It is due to difficulty of impurity control in the small-fraction range. To establish a way to precisely control the discharge characteristics, such as reactivespecies generation, it is indispensable to understand the influence of sub-10-ppm molecular impurities in more details.



Fig. 1. Ranges of  $N_2$  impurity fraction in He highpressure plasmas investigated by previous experimental and simulation studies.

In our previous studies, we found that water vapor (H<sub>2</sub>O) is a major impurity species in a high-purity He gas flow, and the H<sub>2</sub>O fraction varies with gas flowrate and pressure [5,6]. A source of the H<sub>2</sub>O impurity is detachment from the inner surface of gas tubing. The H<sub>2</sub>O is decomposed by the discharge, and we observe OH, H, and O emissions by an optical emission spectroscopy (OES). Also, density and lifetime of the He<sup>m</sup> atoms measured by a laser absorption

spectroscopy (LAS) are significantly affected by the  $H_2O$  fraction.

From these backgrounds, in this study, we investigated behaviors of optical emission intensities from the species related to H<sub>2</sub>O impurity in a He dielectric barrier discharge (DBD) mainly by the OES method. Optical emission intensities of OH, H and O radicals, normalized by a He emission intensity, are analyzed as a function of the H<sub>2</sub>Oimpurity fraction in a glass tube flowing the He gas. We calculated the H<sub>2</sub>O fraction in each discharge condition from the lifetime of He<sup>m</sup> atoms measured by the LAS method. We also measured dependence of the normalized emission intensities on a frequency of applied voltage. The applied-voltage frequency affects the H<sub>2</sub>O decomposition from the upstream edge of discharge region to the measurement spot at the center between two electrodes. Variation of the OH, H, and O emission intensities by the change of voltage frequency are analyzed with discussion of the H<sub>2</sub>O decomposition estimated from the variation of He<sub>m</sub> lifetime.

## 2. Experimental setup

Figure 2 shows an experimental setup used in this study. The He gas flow, in a flowrate range between 14 to 280 sccm, was fed into a glass tube with inner and outer diameters of 3 and 6 mm. The pressure in the tube was controlled at 40 kPa by a needle valve and a pump installed in the downstream. We used two types of gas tubing between a He cylinder and a mass flow controller (MFC), a 1/4-inch flexible tube and a 1/8-inch straight tube, to change a range of H<sub>2</sub>O fraction by changing the inner surface area of gas tubing. In addition to the He flowrate and gas tubing, a He gas purifier was used to control the H<sub>2</sub>O fraction in a ppm range. Two Cu electrodes were attached around the glass tube with a discharge gap at 10mm. Pulsed high voltages were applied to the electrode with a frequency range from 1 to 20 kHz. Photographs of the DBD configuration and the discharge emission are shown in Figure 3.

In the OES diagnostics, optical emission at the center between the electrodes was collected to an optical fiber by a quartz lens. A multi-channel spectrometer (Ocean optics, HR4000) recorded the emission spectra in a wavelength range from 200 to 900 nm.

The LAS diagnostics was performed to measure the lifetimes of  $He^m$  atoms generated in the DBD [7]. A



Fig. 2. Experimental setup of the He gas flow, DBD generation, and OES/LAS diagnostics used in this study.



Fig. 3. Photograph of the DBD configuration (left) and the discharge emission (right).

distributed feedback (DFB) laser beam (Toptica photonics, LD-1083-0070-DFB-1) at a wavelength of 1083 nm was focused on the same position as the OES. The transmitted laser intensity was measured by a photodetector (Thorlabs, PDA10CS2). From temporal decays of the absorbance by He  $2^{3}S_{1}-2^{3}P_{J}$  transition after the discharge pulse, we obtained the He<sup>m</sup> lifetimes in each discharge condition. The H<sub>2</sub>O fraction in the He gas flow was calculated from the He<sup>m</sup> lifetime considering collisional quenching reactions of He<sup>m</sup> with He, He<sup>m</sup>, N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O [6,8]. Densities of He, He<sup>m</sup>, and N<sub>2</sub>/O<sub>2</sub> (air) were estimated from the He pressure, the peak He<sup>m</sup> absorbance, and a leak rate of the gas tubing, respectively. Decomposition of H<sub>2</sub>O molecules in the discharge was not considered in the calculation of H<sub>2</sub>O fraction.

#### 3. Results and discussion

Figure 4 shows optical emission spectra of the DBD at the highest, middle, and lowest H<sub>2</sub>O-fraction conditions obtained in this study. Each spectrum is normalized by a He I ( $3^{3}S-2^{3}P$ ) peak intensity at 707 nm. The measured H<sub>2</sub>O fractions were from 200 to 600 ppm in the discharge experiments using the 1/4-inch flexible tube between the He cylinder and the MFC, from 3.5 to 11 ppm with the 1/8-inch straight tube, and at 2.5 ppm with the 1/8-inch tube and the He purifier. We observed emission peaks of He, He<sub>2</sub>, OH, H and O in the spectra after a procedure of cycle purge eliminating the air impurities.

The relative intensity of He<sub>2</sub> emission at 640 nm is higher in lower H<sub>2</sub>O-fraction conditions. This is because the He<sub>2</sub> molecules are generated by collisional reactions of He<sup>m</sup> + 2He and He<sup>m</sup> + He<sup>m</sup> promoted in high-purity conditions.

The OH (A-X) emission at 309 nm was weaker at 2.5 ppm than that at two other conditions. The peak intensity of  $H_{\alpha}$  emission at 656 nm increased with the decrease of H<sub>2</sub>O fraction. At 2.5 ppm, the H emission intensity becomes higher than the He emission. No significant variation was observed in the intensities of O I (3<sup>5</sup>P-3<sup>5</sup>S) emission at 777 nm in the three H<sub>2</sub>O-fraction conditions.



Fig. 4. Optical emission spectra of the DBD measured in three discharge conditions with different  $H_2O$  fractions.

Figure 5 shows the emission intensities of OH, H, and O normalized by the He emission intensity plotted against the H<sub>2</sub>O-fraction in ranges of 100~1000 ppm (Fig.5 (a)) and  $1\sim20$  ppm (Fig.5 (b)). In Fig. 5(b), data measured with and without the He purifier are plotted with square and triangle symbols, respectively.

With the decrease of  $H_2O$  fraction, the H and O emission intensities increase, and the OH intensity decreases in both ranges of  $H_2O$  fraction. Variation rate of the H and O emission intensities is higher in the lower  $H_2O$  fraction. Impact of  $H_2O$  decomposition on the optical emission is larger in the lower  $H_2O$ -fraction conditions. Comparing the data of Figs. 5(a) and 5(b), there is a gap in the emission intensities between 11 and 245 ppm conditions. It probably suggests that discharge characteristics, such as electron temperature and/or major reaction pathways, are considerably different between >100 ppm and <10ppm of



Fig. 5. Emission intensities of OH, H and O normalized by the He emission intensity measured with the  $H_2O$  fraction from 200 to 600 ppm (a) and from 2 to 11 ppm (b).

 $H_2O$ -fraction. The results indicates that the emission intensities of impurity-related species are not always positively correlated to the impurity fraction. In the case of DBD in He flow with  $H_2O$  impurity, only the OH emission intensity shows the positive correlation to the  $H_2O$  fraction.

Figure 6 shows dependences of the normalized OH, H, and O emission intensity and the He<sup>m</sup> lifetimes on the applied-voltage frequency. When the H<sub>2</sub>O fraction is at 6.6 ppm (Fig. 6 (a)), all intensities decrease with the increase of voltage frequency in the range of 1 to 7 kHz. When the voltage frequency is >7 kHz, the H and O intensities increase whereas the OH intensity decreases with the increase of voltage frequency. In 4.3 ppm of the H<sub>2</sub>O fraction (Fig. 6 (b)), the H and O intensity becomes minimum values at 3 kHz, and the OH emission monotonically decreases with the increase of voltage frequency. In the case of 2.2 ppm (Fig. 6 (c)), the H and O intensities both increase from 1 to 10 kHz. And only H intensity turns to decrease in the higher frequency range. The He<sup>m</sup> lifetime decreases with the increase of voltage frequency in all discharge conditions. The difference of the  $He^m$  lifetime between 1 and 20 kHz is larger in lower  $H_2O$ -fraction conditions.

Comparing the voltage-frequency dependences measured in three different H<sub>2</sub>O-fraction conditions, the OH intensity decreases toward higher voltage frequency in



Fig. 6. Dependences of the normalized OH, H and O intensities and He<sup>m</sup> lifetimes on the applied-voltage frequency in a range from 1 to 20 kHz. The H<sub>2</sub>O fractions are (a) 6.6 ppm, (b) 4.3 ppm, and (c) 2.2 ppm, respectively. The emission intensities plotted here shows relative variation of the emission intensity per voltage pulse.

all conditions. The H and O emissions showed similar intensity variation in 6.6 ppm (Fig. 6 (a)) and different behaviors in lower H<sub>2</sub>O-fraction conditions. When the voltage frequency increases, H<sub>2</sub>O decomposition is promoted. For the OH A-X emission, the correlation of OH emission intensity to the H<sub>2</sub>O fraction suggests that dissociative Penning ionization reactions between H<sub>2</sub>O and He<sup>m</sup> [9] shown below are major ways to generate OH(A) species in the DBD.

$$H_2O + He^m \rightarrow He + OH + H + e^-$$
  
 
$$H_2O + He^m \rightarrow He + OH + H^+ + e^-$$

In the similar process, a certain part of H and O emission source is the dissociative Penning ionization of H<sub>2</sub>O. When the ratio of H and O radicals to the H<sub>2</sub>O molecules increases by the H<sub>2</sub>O decomposition in the DBD, collisional reaction rates of  $H + He^m$  and  $O + He^m$  become comparable to H<sub>2</sub>O + He<sup>m</sup>. It increases H and O emission intensities in higher frequency range in Figs. 6(a) and 6(b) and all range in Fig. 6(c). The frequency showing minimum of H and O emission intensities becomes lower in lower-H2O-fraction conditions. The increase of O emission intensity is higher than that of H intensity in higher voltage-frequency range. It is probably because that the O-radical generation requires two-step decomposition processes of the H<sub>2</sub>O molecules. From these results, we revealed that the OH emission intensity correlates to a H<sub>2</sub>O dissociation degree in a same original-H2O-fraction condition, and emission intensities of H and O radicals shows various dependences on the H2O dissociation degree in different H<sub>2</sub>O-fraction conditions.

## 4. Conclusions

We investigated the emission intensity of OH, H, and O radicals for better understandings of the influence of sub-10-ppm molecular impurities on high-pressure discharge characteristics. We analyzed the relative emission intensities of OH, H and O normalized by the He emission intensity as a function of the H<sub>2</sub>O fraction in the ranges of 200 to 600 ppm and 2 to 11 ppm. With a decrease of H<sub>2</sub>O fraction, the OH intensity decreases, and the H and O intensities increase in both ranges of the H<sub>2</sub>O fraction. We also measured dependences of the normalized emission intensities on the applied-voltage frequency. The H<sub>2</sub>O decomposition is promoted at higher voltage frequency. The OH intensity decreases toward higher voltage frequency in all H<sub>2</sub>O fraction conditions in this study. The dependence of H and O intensity on voltage frequency varied with the original H2O fractions. These results suggest that, in the case of high-pressure DBD in He flow with small-fraction H<sub>2</sub>O impurity, the OH emission intensity has a potential to evaluate the H<sub>2</sub>O impurity fraction and correlates to a H<sub>2</sub>O dissociation degree in the same H<sub>2</sub>O-fraction condition.

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