Fluid Density Dependence of Electrical Discharges Generated Using Carbon Nanotubes as Electrode in Liquid, Supercritical, and Gaseous Nitrogen and Argon

Hitoshi Muneoka, Tomoki Kuroda, Tsuyohito Ito, Kazuo Terashima

Department of Advanced Materials Science, The University of Tokyo,Chiba, Japan.

Abstract: Plasmas in high-density media, including liquids and supercritical fluids (SCFs), have been attracting attention. In the discharge using carbon nanotube electrodes in supercritical and liquid N_2 and Ar, the auroral green emission related to the forbidden transition of O atom surrounded by fluid molecules was observed. In this study, we discuss the fluid density dependence of optical emissions at the density in the range of two to three orders of magnitude from gases, SCFs, and liquids at cryogenic temperatures.

Keywords: SCF plasma, supercritical fluid, plasma in liquid, carbon nanotube

1. Introduction

Plasmas in high-density media, including liquids and supercritical fluids (SCFs), have been studied extensively in recent years because of their wide range of applications [1]. In such high-density fluids, there is a wide choice of materials and media to be processed, and in addition, reaction fields can be formed by taking advantage of the thermal properties of the high-density media. Although low-voltage discharges are difficult in the dense media, field-emission driven discharges with relatively low voltages have been reported [2-4]. However, the emission of these discharge was only electron bremsstrahlung and no evidence of reactivity has been obtained.

The selection of cathode material is important to enhance the field emission. So far, generation of stable discharges in nitrogen and argon at low voltages by using carbon nanotubes (CNTs) as electrodes have been succeeded [5]. The discharge in N_2 and Ar is particularly remarkable for its density dependence. The strong auroral green emission, which is the transition related to a metastable oxygen atom ($O(^1S) \rightarrow O(^1D)$) surrounded by fluid molecules, can be confirmed at high-density N_2 and Ar. Here, we refer to the emission from the O atoms surrounded by fluid Y (N_2 or Ar) as OY_x^*. O atom was thought to be provided from the adsorbed O_2 on CNT electrodes. However, little is known about the details of the plasma chemistry of discharges with CNT electrodes, since no detailed measurements have been made so far.

As for nitrogen plasma, valious applications, such as N_2 fixation [6] and nitridation of various materials [7], have been still active. The auroral emission of O atom in ON_2 excimer in atmospheric pressure plasmas have been studied to contribute auroral physics [9,10] and similar emission was also reported in liquid Ar environments [8]. Therefore, it would be interesting to study electrical discharges in high density N_2 and Ar, not only as reactive environments but also as environments emitting strong auroral emissions.

In this study, we measured the dependence of the emission spectrum of high-density nitrogen and argon on the fluid density for further understanding of high-density discharges using a CNT electrode.

2. Experimental Setup

Figure 1 shows the schematic of experimental setup. Dielectric barrier discharge (DBD) electrodes using CNT were placed in a high-pressure cryostat, and an AC voltage (frequency: 5 kHz, amplitude: 1.60-3.25 kV) was applied to generate discharges. The electrodes were made of a glass plate of dielectric barrier with CNTs in contact on one side and Ag paste on the opposite side. Measurements were performed at a constant temperature conditions with continuously changing density by introducing a constant flow of N_2 gas (purity: >99.99995%) into the high-pressure cryostat using a mass flow controller. Stable discharges were successfully generated over a density range of two to three orders of magnitude from gases, SCFs, and liquids, with the constant AC voltage. The optical emission spectra were measured through a sapphire window and an optical fiber with Czerny-Turner spectrometer (SpectraPro-500i, Acton Research Corp.) and a charged-coupled device camera (Spec-10, Princeton Instruments Inc.). More than several thousand spectra were obtained at each temperature condition.

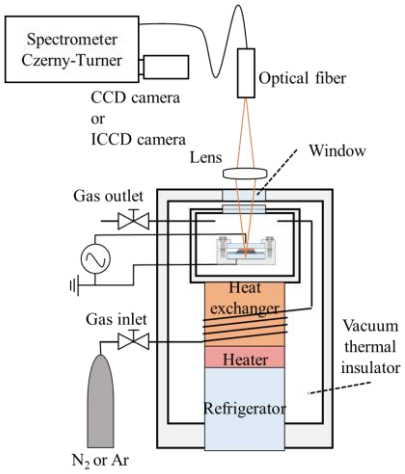

Fig. 1. Schematic of experimental setup.

3. Results and Discussion

In gaseous N_2 at relatively lower pressure near atmospheric pressure, the emission peaks corresponding to second positive system of N_2 (300 – 400 nm) and ON_x^* (557 nm)

were mainly observed. On the other hand, only the emission peak of ON_x^* was observed at high-pressure gaseous N_2, supercritical N_2, and liquid N_2. In Ar, the emission peaks corresponding to Ar I (690 – 820 nm) were mainly observed in gas phase. On the other hand, in addition to Ar I peaks, the emission peak of OAr_x^* (557 nm) and continuum emission were observed at higher pressure than 2 MPa. These are the similar tendency at the previously reported spectra [5].

The N_2 density dependence of the emission intensity of SPS of N_2 (336-340 nm) and ON_x^* (536-590 nm) at 122 ± 2 K was observed. Since the temperature is below the critical temperature (126.2 K) of N_2, there is a jump of the fluid density at gas/liquid phase transition. Focusing on the density dependence of the emission intensity of the N_2 SPS and ON_x^*, at least two emission modes were found. In the low-density N_2 near the atmospheric pressure, the emission intensities of both SPS of N_2 and ON_x^* became weaker as the pressure increased (mode I). We attribute these decreases in intensities to decrease in ionization coefficient with increase in fluid density in this density region. At the higher density than approximately 10^{21} cm^{-3}, only ON_x^* emission was observed (mode II). The emission intensity of ON_x^* and discharge area tended to increase as the density increases. The reason for the positive correlation between emission intensity and fluid density may be that the formation reaction of ON_2 excimer, which is reported as the source of O atom emission at atmospheric pressure gases [9,10], is dominated by the three-body collision reaction described below [11].

$$O(^1S) + N_2 + N_2 \rightarrow O(^1S)N_2 + N_2$$

The frequency of three-body collision reactions should increase with increasing N_2 density. However, the plasma chemistry of the discharge using CNT electrodes in N_2, such as the O atom production mechanism, has not been fully understood yet and further study is required.

The emission of ON_x^* is based on transition of oxygen atom ($O(^1S)\rightarrow O(^1D)$) and its spectral shape is reported to be different in vacuum [12], atmospheric pressure gas [13], and liquid N_2 [8], respectively. This implies that O atom can be utilized as density probe of surrounding fluid molecule. The broadening width of ON_x^* was continuously changed as increase in N_2 density from gas to supercritical fluid to liquid. In addition, the density dependence of broadening widths of ON_x^* measured at several temperatures were all consistent. This result suggests that the density of N_2 at the discharge space is almost the same as ambient density even in supercritical and liquid N_2.

While there were differences between N_2 and Ar, similar continuous change in OAr emission was observed with high-density Ar discharges. Additiinally, the continuum emission of bremsstrahlung was observed in high-density Ar discharges. The density and temperature of electrons could be estimated by the analysis of the continuum emission.

4. Summary

The emission spectra of discharges in high-density nitrogen and argon at cryogenic temperatures using CNT electrodes were obtained while continuously changing the density. It was clarified that at least two emission modes can be classified by the transition of ON_x^* intensity. At higher density, the emission of ON_x^* and discharge area gradually increased as the density increased. These were clearly different from the density dependence of emission intensity of normal discharges. In addition, the fluid density in the discharge space was estimated by the broadening widths of ON_x^*. Similar tendensies, though not completely same, was obaserved also with OAr in high-density Ar discharges. Further studies on the plasma chemistry of discharges with CNT electrodes are desired for plasma process utilization in high-density N_2 and Ar.

Acknowledgements

This work was financially supported in part by Grants-in-Aid for Scientific Research (A) (Grant No. 21H04450) from the Japan Society for the Promotion of Science.

References

[1] S. Stauss, H. Muneoka, and K. Terashima. Plasma Sources Sci. Technol. **27**, 023003 (2018).

[2] D. Z. Pai, S. Stauss, and K. Terashima. Plasma Sources Sci. Technol. **23**, 025019 (2014).

[3] T. Kawamura, M. Kanno, S. Stauss, K. Kuribara, D. Z. Pai, T. Ito, and K. Terashima. J. Appl. Phys. **123**, 043301 (2018).

[4] M. Kanno, R. Tanaka, S. Stauss, T. Ito, and K. Terashima. AIP Advances **9**, 055111 (2019).

[5] H. Muneoka R. Ohta, S. Stauss, and K. Terashima, Plasma Sources Sci. Technol. **28**, 075014 (2019).

[6] V. Hessel, D. B. Graves, and H. H. Kim, J. Phys. D: Appl. Phys. **53**, 420201 (2020).

[7] T. Czerwiec, N. Revevier, and H. Michel, Surf. Coat. Technol. **131**, 267 (2000).

[8] G. Black, R. L. Sharpless, and D. C. Lorents, J. Chem. Phys. **72**, 484 (1980).

[9] K. Sasaki, S. Nishiyama, and N. Shirai, Contrib. Plasma Phys. **60**, e202000061 (2020).

[10] S. Jaiswal, E. M. Aguirre, and G. V. Prakash, Sci. Rep. **11**, 1893 (2021).

[11] H. V. Lee, L. M. Rosario, R. B. Tumlos, H. J. Ramos, L. M. Bo-ot, and M. N. Soriano, Jpn. J. Appl. Phys. **57**, 066102 (2018).

[12] K. Henriksen and A. Egeland. Eos **69**, 721 (1988).

[13] K. Sasaki, S. Nishiyama, and N. Shirai, Contrib. Plasma Phys. **60**, e202000061 (2020).