# 論文内容の要旨

# 論文題目 Diagnosis on gas-temperature-dependent generation of cryoplasma

## （クライオプラズマ生成の温度依存性に関する診断）

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## 【1.　Introduction】

To achieve desirable plasma conditions for various applications such as material processing, the gas temperature might be one of the most important parameters. Generally, plasma with a gas temperature of a few thousand to millions of Kelvin is called thermal plasma, and it is used for light emission and material processing such as plasma spraying and welding. If the gas temperature is a few hundred to thousands of Kelvin, the plasma is called low-temperature plasma, and it is used for fluorescent lamps, ozonizers, and the surface fabrication of semiconductors such as deposition.

However, up to now, there have been few studies on plasmas with a gas temperature between room temperature (RT) and cryogenic temperature, or on their application. Generally, as shown in the following equation, the gas temperature decrease is equal to particle (atoms and molecules) kinetic energy decrease.

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}\mathrm{k_B}T_g \qquad (1)$$

Here, $m$ is the mass of the gas particle, $\bar{v}$ is the average velocity of the gas particle, $\mathrm{k_B}$ is Boltzmann constant and $T_g$ is the gas temperature. Relating to it, below RT, phenomenon such as phase transitions in many gas occurs due to the decrease in particle kinetic energy, and it remains to be studied how this decrease in particle kinetic energy below RT would or may affect plasmas and applications using those plasmas. Therefore, in this work, 'cryoplasma' with a gas temperature below RT ($T_\mathrm{g} \leq 300$ K) including plasma gas temperature below freezing point was developed and studied. The final goal in this work is generate cryoplasma, and to study the effect of decrease in particle kinetic energy to plasma by continuously decreasing its gas temperature below the room temperature, and contribute in developing the basics of new research field in plasma processing field through its study.

## 【2. Preparatory experiments】

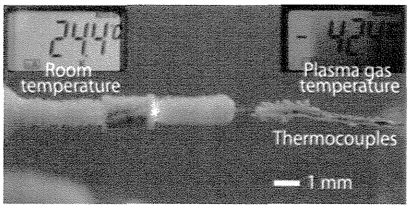

**Fig. 1.** Generation of helium cryoplasma in open air.

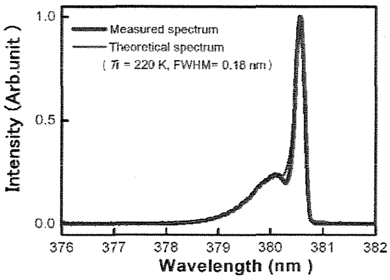

**Fig. 2.** Emission spectra of $N_2$ second positive system at $T$ = 200 K and theoretical fitting at 220 K.

Cryoplasma in open air was generated as a preparatory experiment (Fig. 1). To cool the plasma gas temperature, the gas temperature of operating gas was decreased by liquid nitrogen before introducing into electrodes part. DBD electrodes were employed for the generation method to prohibit excessive plasma gas temperature increase. The helium cryoplasma generated in open air accompanied the frost formation on the plasma generating part although, the generation was stable. It was confirmed by thermocouples and CFD-ACE+ simulation that the plasma gas temperature is below the freezing point of the water. Moreover, the plasma gas temperature was estimated from rotational temperature of $N_2$ second positive system emission measured by optical emission spectroscopy (OES) (Fig. 2), and it was confirmed that the gas temperature almost matches with the gas temperature measurement by thermocouples. Therefore, it was confirmed that $N_2$ rotational temperature measurement using OES spectra is also considered as an effective way of estimating plasma gas temperature of cryoplasma besides thermocouples. The results of these preparatory experiments had shown the possibility of generation of cryoplasma in further low temperatures and measurements of the effect of change in particle kinetic energy on the plasma by continuously changing its gas temperature.

## 【3. Generation and diagnosis of helium cryoplasma (296 - 5 K)】

Cryoplasma was generated under continuous gas temperature control between RT and 5 K. To avoid the frost formation at electrodes part, the apparatus which can separate generating chamber from the outer chamber by vacuumed layer zone was employed. Two types of DBD electrodes were used to observe the generation appearance of cryoplasma. One was ac-planer DBD' electrodes (Fig. 3) and the other was jet-type DBD electrodes (Fig. 4). In ac-planer DBD electrodes case, the discharge pattern changed upon decreasing gas temperature of inner chamber. Comparing with reaction-diffusion (RD) model which is used for explaining patterns forming in nature, it is assumed that gas temperature change is inducing the change in the spreading manner of activator and inhibitor, which results in pattern transitions. Due to the gas density increase upon decreasing the gas temperature, breakdown voltage of cryoplasma increased. From the stability of the generation, jet-type DBD electrodes were used for further measurements.

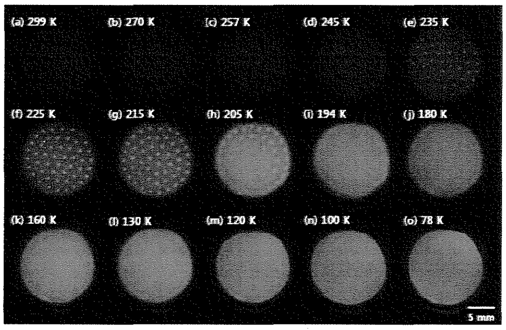

**Fig. 3.** Generation of AC-planer DBD helium cryoplasma in chamber (RT to 78 K).

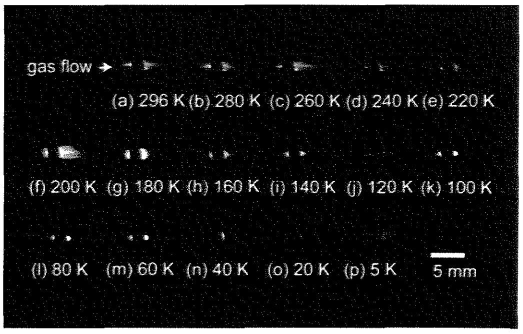

**Fig. 4.** Generation of jet-type DBD helium cryoplasma (RT to 5 K).

As the gas temperature decreases, emission spectra from $N_2$ second positive system starts to diverge from theoretical spectra and rotational temperature cannot be estimated. So the gas temperature of the plasma is not also obtained. Since invalidity of estimation of plasma gas temperature using optical emission spectroscopy was verified at lower temperatures, plasma gas temperature of cryoplasma was calculated using heat transfer equation, assuming a simple model. Thus, it turned out that the maximum difference of the gas temperature at the plasma generating part and the temperature measured at thermal sensor is 1 K (Fig. 5). So, the temperature measured in the inner chamber by thermal sensor was regarded as the gas temperature of helium cryoplasma. Moreover, from the calculation, it was confirmed that under the certain condition, the smaller plasma, the better controllability of the cryoplasma gas temperature can be gained (Fig. 5).

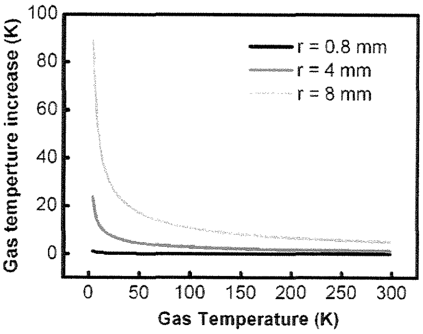

**Fig. 5.** Estimation of the plasma gas temperature increase depending on plasma sphere size with the same power consumption density (48 mW/cm$^{-3}$).

Then the effect of change in particle kinetic energy on the plasma by continuously changing its gas temperature between RT and 5 K was measured electronically and optically. Below around 50 K, the tendency of the electron density and temperature change is similar to the gas density change (Fig. 6(a) and (b)). So macroscopically, these changes are related to the gas density increase. Besides that, the tendency of the change in electron density and temperature below around 50 K is also similar to the second virial coefficient decrease upon decreasing gas temperature, which is indicating the increase of Van der Waals force between the particles. Furthermore, since the electron coupling parameter of helium cryoplasma below $T_g$ = 60 K increases, the effect of Coulomb force is increasing between electrons. Thus, considering the results from microscopic view, it can be assumed that helium cryoplasma is not just the plasma with an increased gas density but also

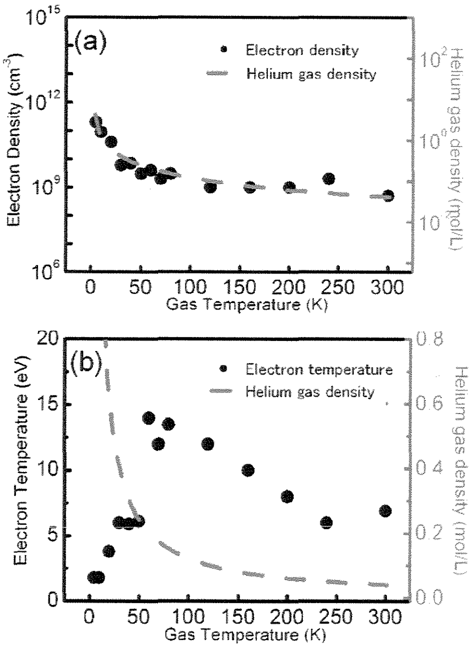

**Fig. 6.** Gas-temperature-dependent (a) electron density and (b) electron temperature of helium cryoplasma jet co-plotted with helium gas density.

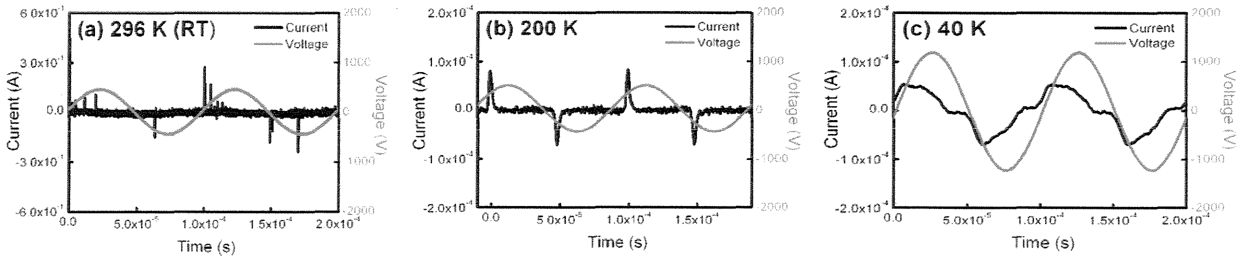

**Fig. 7.** Current and voltage (*I-V*) measurement results of helium cryoplasma jet; (a) RT, (b) 200 K and (c) 40 K.

the plasma under the effect of interparticle forces at lower temperatures. Under those circumstances, discharge mode changed from atmospheric glow (Fig. 7(b)) to atmospheric Townsend discharge (Fig. 7(c)) mode upon decreasing plasma gas temperature from 50 K. It is assumed that the generation of electrons due to collisions of helium metastables increased in the bulk gas upon decreasing plasma gas temperature. Finally, considering the result from both macroscopic and microscopic view at plasma gas temperature below 50 K, it can be assumed that plasma operation under three-body reaction due to high gas density and interparticle force due to less thermal heat favored the formation of $He_2$* (Fig. 8). Therefore it can be also assumed that not only $He_2$* but also larger helium clusters may exist in cryoplasma at plasma gas temperature below 50 K.

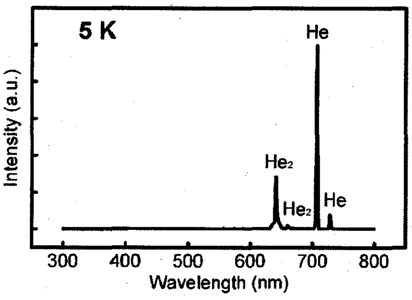

**Fig. 8.** OES spectra of helium cryoplasma at 5 K.

## 【4. Conclusion】

In this study, continuing to thermal plasma and low-temperature plasma, ‘cryoplasma’ with a third range of gas temperatures ($T_g \leq 300$ K) including plasma gas temperature below freezing point was focused. The appearance, electron density and temperature, discharge mode and excited species of cryoplasma at various gas temperatures below RT all showed $T_g$ dependent results. Therefore, through this study, it can be said that the plasma transitions were seen through the continuous particle kinetic energy decrease, which was expected at the beginning of this study in the motivation from pure science point of view. Especially at the gas temperatures below around 50 K, cryoplasma not only increases gas density but also interparticle forces start to affect the particles due to the decrease in particle kinetic energy. Bounding around that temperature, the results changed drastically compared with higher gas temperatures. Specifically, $T_e$ decreased whereas $N_e$ increased, discharge mode changed into atmospheric Townsend mode and $He_2$* appeared. On the other hand, from an application point of view, this study showed that reactions in bulk plasma changes as the gas temperature decrease, which results in the generation of different kind and amount of activated species. Therefore, cryoplasma may be utilized for controlling the reaction to gain expected species for material processing. Moreover, cryoplasma could be the source for cluster plasma application or even be an effective tool for material processing if optimum $T_e$ and $N_e$ are gained by changing the generation methods. Pattern change and discharge mode change upon changing the plasma gas temperature may also be utilized in material processing in low temperature environment below RT.

This study is the starting point of study on cryoplasma. Results and discussions obtained through this study opens up the possibility of not only further basic studies of cryoplasma, but also many other underlying cryoplasma application studies in this gas temperature range, such as generation of cryoplasma for applications and actual application of cryoplasma, which will further contribute in the developing new research field in plasma processing field.