MICROMETER-SCALE D.C. DISCHARGE PLASMA GENERATION UNDER A VERY HIGH-PRESSURE ENVIRONMENT

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ABSTRACT
Micrometer-scale discharge plasma under a very high-pressure carbon dioxide environment, up to a supercritical fluid environment, has been generated in this study. A novel sharp trough of breakdown voltage near the critical point has been discovered. The breakdown voltage near the critical point was almost one-fourth of the value for normal gaseous (non-supercritical) carbon dioxide estimated from Paschen’s law. This trough might result from the fluctuation of the structure and energy of clusters in supercritical fluid. Moreover, this indicates that the necessary power for discharge plasma generation under a supercritical fluid environment may be very low.

INTRODUCTION
Recently, the study of micro/nanometer-scale plasma has become a new field in plasma science and technology. The miniaturized plasma has high potential for applications due to its unique characteristics such as compactness, low energy and high density. Moreover, the miniaturization of plasma might also yield interesting phenomena, such as the quantum effect. However, thus far, there exists only almost normal state plasma followed by $P_d$ (Paschen’s) law. Therefore, we have studied micrometer-scale plasma not only for applications, but also for basic science in order to explore exotic plasma with the scanning probe microscopy technique [1] and coplanar film electrodes (CFE) [2-4].

In general, generating micrometer-scale plasma requires a high-pressure environment to allow sufficient ionization in a small space. It has been confirmed experimentally that micrometer-scale plasma has higher electron density than conventional macroscale plasma due to the higher density of particles. For example, the density of $1\mu m$ micrometer-scale plasma (1 atm, 10-$\mu m$-gap CFE, applied voltage 450 V) was estimated to be of the $10^{21} m^{-3}$ order and it was glow type discharge [3].

In this study, we have performed a plasma generation trial under a higher pressure condition up to a supercritical fluid (SCF) environment (fig. 1). SCF, which is an intermediate
state of matter between liquid and gas, has also attracted much interest in science and engineering fields, due to its unique characteristics such as high solubility [5-8]. The high potentials for extractions [9,10] or use as a catalyst have been proved in many engineering fields. In particular, near the critical point, large density fluctuation [11,12] results in some marked changes of the characteristics, such as thermal conductivity [13,14]. From the microscopic viewpoints, SCF consists of various-sized clusters, and may be called a “cluster fluid”. Therefore, SCF has also received much interest in cluster science, which has been one of the most attractive field of nanotechnology, motivated by its exotic characteristics [15] and requirements such as the necessity to control the characteristics of the atoms group. Thus, it is highly anticipated that the “plasma state” under the SCF condition may yield unique characteristics and reactions, unlike those of the normal plasma in the gas state. However, to the best of our knowledge, there have been few reports thus far.

Initially, carbon dioxide (CO₂), whose critical pressure is 7.38 MPa and critical temperature is 304 K, was employed. The discharge was able to be generated near the critical point with approximately fourfold lower voltage than that for conventional gas state. First, the breakdown voltage (£V_b$) was measured as a basic study, and the novel breakdown voltage’s trough was identified.

**EXPERIMENTAL**

Figure 2 shows a schematic diagram of the apparatus in this study. The cell for SCF discharge (a) made of stainless-steel can withstand up to 25 MPa and 373 K. Liquid CO₂ condensed in the condenser (m) was pumped to the cell and heated by four heaters controlled by a controller (h). The pressure and temperature in the cell were measured by a sensor (g) and a thermocouple (e), which were monitored with the controller (h). Micrometer-scale
discharge plasma was generated with CFE (n) and a d.c. power source (i). A CFE made of platinum on SiO$_2$ (n) was produced with lithography technology [2], which can easily fabricate a narrow gap with high reproducibility. The pressure and temperature were controlled within the range of 0.1 MPa and 1 K, respectively.

We have generated micrometer-scale discharge plasma under supercritical CO$_2$ with 1- and 2- m-gap CFE. In addition, breakdown voltages have been measured under 0.1-9.0 MPa CO$_2$ environments with a 2- m-gap CFE at 313 K. Moreover, for comparison with Paschen's curve of normal CO$_2$ gas, breakdown voltages with 0.5-mm-gap electrodes at room temperature, 296 K, were measured.

![Diagram](image)

**Fig. 2 Schematic diagram of the apparatus for SCF discharge.**


**RESULTS AND DISCUSSION**

Discharge plasmas under a SCF CO$_2$ environment have been generated. These micrometer-gap electrodes allow us to generate discharge plasma near the critical point, which is probably the most interesting issue, with low voltage of $< 1$ kV, which would be difficult with conventional macroscale-gap electrodes. Figure 3 presents an example of micrometer-scale discharge plasma under a SCF environment (1- m-gap CFE, CO$_2$-7.6 MPa, 313 K, applied voltage 230V). Generation was confirmed around the electrodes-gap. In addition, the generation was induced with lower voltage compared with estimated voltage from Paschen's law.

The breakdown voltages for platinum electrodes for CO$_2$ have been measured. Figure 4 shows the results of the measurements with 2- m-gap electrodes at 313 K. For comparison with Paschen's curve of normal CO$_2$ gas, the result of measurement with 0.5-mm-gap
Fig. 3 Micrometer-scale discharge plasma under SCF environment (1-μm-gap CFE, CO₂-7.6 MPa, 313 K, applied voltage 230V).

electrodes at room temperature, 296 K, is shown in fig. 5. The curves of breakdown voltages as a function of pressure (P) x interelectrode distance (d) are usually similar, and follow Paschen's law. However, in fig. 4, there are two main characteristics of the curves in the case of high-pressure environments. One is an inflection near 2.5 MPa, and the other is a trough near the critical point, 7.5 MPa.

Unstable clusters in SCF might cause the breakdown voltage trough near the critical point, which can be analogous to a drastic change of thermal conductivity.

In SCF, the mean free path of electrons (λ) is estimated to be shorter than that in gas state due to the larger electron-to-particle cross section. This shorter increases the breakdown voltage in a high-pressure environment because it becomes more difficult for electrons to gain sufficient energy for ionization. Therefore, lower breakdown voltage (Vₘₐₓ) such as 300 V (near Pd-15 MPa) shown in fig. 4, compared to 1100 V (near Pd-15 MPa) shown in fig. 5, should be due to factors such as a lower ionization potential (Vₘₐₓ) or a higher second Townsend coefficient (λ).

For a solid cluster, which is slightly different from that in a SCF environment, it is well known that clustering causes lower [16-18]. Moreover, a higher can be easily estimated, due to the higher mass of the cluster. For (CO₂)n, it was confirmed that the ionization potentials for n = 1, 2, 3 and 4 are 13.77, 13.32, 13.24 and 13.18 eV, respectively [17]. However, this novel trough existing near the critical point cannot be fully explained on the basis of the solid cluster.

To explain the phenomena, there must exist a unique ionization process for the cluster fluid. Large decrease of ionization potential, increase of secondary electron emission under unstable and highly reactive cluster fluid, particularly near the critical point, or a specific ionization mechanism such as Penning ionization due to various clusters are possible causes. However, a high alone is not enough to cause the troughs. If a specific ionization mechanism does not exist and is 1, approximately 35% of , compared with the molecule is needed for the low breakdown voltage. Moreover, even if is 10, approximately 50% is needed. There probably exists even lower , because estimated with normal gas, which is
probably longer and gives lower $v_0$ is employed in these estimations. These lower values of $v$ are different from those of the solid cluster, and can probably be yielded with the cluster existing under the cluster fluid. Additionally, the marked structure change of the cluster may yield a dielectric constant change and an increase in the effective electric field, which results in lower $v_0$.

The reasons for the inflection near 2.5 MPa are still not clear. We could not find any

![Graph](image1)

*Fig. 4 Breakdown voltages for high pressure CO₂ as a function of pressure ($P$) x interelectrode distance ($d$) for Pt coplanar film electrodes (CTE), whose thickness and width were 1 µm and 50 µm respectively, $d = 2$ µm, 313 K.*

![Graph](image2)

*Fig. 5 Breakdown voltages for normal CO₂ as a function of pressure ($P$) x interelectrode distance ($d$) for Pt coplanar electrodes. $d = 0.5$ mm, 296 K. The electrodes were fixed platinum plates, whose thickness and width were 0.1 mm and 5 mm, respectively.*

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reports on the state transitions in CO$_2$ caused by high pressure near the region of 2.5 MPa thus far. Therefore, it seems to be reasonable that the transition could result from both high pressure and strong electric field, applied simultaneously. Further investigations of the inflection are now in progress.

Although the mechanism of the breakdown voltage decrease remains to be unidentified, the inflection near 2.5 MPa and the trough near the critical point have been observed. Also, it has been demonstrated that the trough is a unique phenomenon occurred under the cluster fluid, which cannot be explained in terms of solid clusters. The details regarding this trough are discussed in reference [19].

CONCLUSIONS

The generation of micrometer-scale discharge plasma under a very high-pressure CO$_2$ environment up to SCF has been performed. It has been demonstrated that the plasma state under SCF, which might have very high reactivity, supported by both the plasma state under the gas environment and the recent study of SCF, can be generated with very low voltage. A trial for more stable plasma generation in SCF with very high-frequency power is also in progress. We hope that the number of studies on this new phenomenon of “discharge plasma in a SCF environment” will increase rapidly and widely.

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