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Carbon materials syntheses using dielectric barrier discharge microplasma in supercritical carbon dioxide environments

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Abstract

In this study, carbon materials syntheses using a dielectric barrier discharge (DBD) microplasma in supercritical carbon dioxide ($scCO_2$) environments are reported. The dependencies of the carbon materials synthesis processing on the environmental temperature, environmental pressure and power frequency were investigated. In contrast to atmospheric-pressure CO_2 environments, in which no carbon materials could be fabricated, it was possible to fabricate various carbon materials, such as amorphous carbon, graphite and nanostructured carbon materials, using $scCO_2$ as a processing medium and a raw starting material. In particular, in the vicinity of the critical point of CO_2, the quantity of carbon nanostructured materials, such as carbon nanotubes and carbon nanohorns, was larger than under other $scCO_2$ conditions. It is supposed that the high density and molecular clustering caused by supercritical conditions may affect the formation of such carbon nanostructured materials. In addition, we found that by varying the power frequency, the form of the synthesized carbon materials could be changed.

Keywords: Materials processing; Microplasma; Dielectric barrier discharge (DBD); Supercritical fluids; Carbon nanomaterials; Carbon nanotube

1. Introduction

Supercritical fluid (SCF) designates the intermediate state between gas and liquid. It has liquid-like high density, high solubility, gas-like low viscosity, zero surface tension and a diffusivity much higher than that of its liquid [1]. From a microscopic point of view, it is known that molecular clustering occurs in SCF [2]. In particular, molecular clustering is very frequent in the vicinity of the critical point, and reactants are surrounded by a number of molecules, which accelerate the reaction rates relative to that in the gas phase. Moreover, molecular clustering brings about a decrease in the ionization potential of molecules [3], and it is expected that the molecular clustering might affect the ionization process and the ionized state of SCF.

Recently, it has been found [4,5] that the breakdown voltage of direct current (dc) discharges generated in CO_2 near the critical point decreases drastically. Since, this discovery of the unique characteristics of the breakdown voltage near the critical point, plasmas generated in SCFs have attracted much attention [6,7,8]. In addition, plasma processing, which usually has been performed in a gaseous environment, may yield a high efficiency by applying SCF conditions owing to a combination of their advantages, such as the high activity of plasmas and the superior transport properties of SCF. It is anticipated that using this type of reactive plasma, the material synthesis processings using SCF, such as the processing of metallic conformal coating of high-aspect-ratio nanometer-scale trenches [9], might be carried out in a shorter time than conventional processings. Moreover, SCF plasma supposedly contains radical and ion clusters in SCF, which may lead to novel phenomena and reactions for producing new materials.

Among SCFs, supercritical CO_2 ($scCO_2$, the critical point: 304.2 K and 7.38 MPa) is used as a solvent in the studies of surface engineering for semiconductors, such as in the removal of photoresist from nanometer-scale patterned structures [10] and the metallic conformal coating of high-aspect-ratio nanometer-

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scale trenches [9], because CO_2 is very common and the critical pressure and temperature of CO_2 are relatively moderate.

On the other hand, various techniques, such as chemical vapor deposition (CVD) and plasma-enhanced CVD (PECVD) have been developed for producing carbon nanostructured materials [11]. Recently, thermal-equilibrium processing for carbon nanostructured materials synthesis from CO_2, as a raw starting material in $scCO_2$ environments has also been reported [12,13]. However, the thermal-equilibrium processings were performed under severe conditions with various catalysts, such as at 1273 K and 1000 MPa with melted metallic magnesium [12] and at 823 K and 70 MPa with melted metallic lithium [13].

In our previous work [14], we proposed applying a SCF plasma to carbon nanostructured materials synthesis. We succeeded in fabricating carbon materials, including carbon nanotubes (CNTs), using pulsed discharge microplasma (pulse duration: 400 μs) under relatively mild conditions (343 K, 12 MPa) with $scCO_2$ as a processing medium and a raw starting material without any catalyst. However, in that work [14], the pulsed discharge microplasma was an arc-like plasma, which might raise the gas temperature intensively and inactivate molecular clustering in $scCO_2$. To make good use of the unique characteristics of SCF in plasma processing, its gas temperature should be kept low and the molecular clusters in SCF should be prevented from breaking. Accordingly, we have applied a dielectric barrier discharge (DBD) to the generation of a SCF plasma, and succeeded in generating a micrometer-scale plasma by DBD (DBD microplasma) in a $scCO_2$ environment [15]. A DBD plasma is well known to be a low-temperature plasma operated even in a high-pressure environment (i.e., atmospheric-pressure environment) and employed in applications for materials processing, such as film deposition [16], surface treatment [17] and carbon nanostructured materials synthesis with catalyst [18].

The gas temperature of DBD microplasma was estimated to be approximately 400 K in a high-pressure N_2 environment up to supercritical conditions (313 K, 1–5 MPa) (critical point of N_2: 126 K and 3.39 MPa) [15]. On the other hand, for the case of a pulsed discharge microplasma (gap distance: approximately 100 μm), the discharge current of which was restricted below 0.7 mA, the gas temperature was estimated to be approximately 800 K in a supercritical N_2 environment (313 K, 4.0 MPa). Fig. 1 shows a schematic representation of the gas temperature of plasmas at environmental pressures. It was found that compared with conventional methods [19–23], using our DBD microplasma [15], the gap distance of which was reduced to approximately 100 μm, the generation of a low-temperature plasma in a higher-pressure environment could be realized.

It is anticipated that applying the DBD microplasma, which is a low-temperature plasma, might reduce the damage to the electrode inflicted by the plasma, compared with applying the pulsed discharge microplasma as in our previous study. This might make it possible to deposit material onto the electrode, which is also used as a substrate. Therefore, in this study, we used the electrode as the substrate, and fabricated carbon material on the substrate from $scCO_2$ using the DBD microplasma, the temperature of which was relatively close to the environmental temperature, compared with that of an arc-like plasma. We also analyzed the charge density of the DBD microplasma generated in a $scCO_2$ environment.

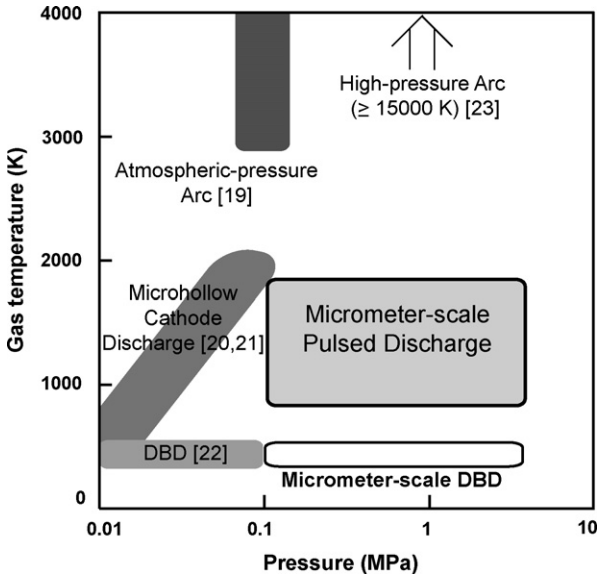

Fig. 1. Schematic representation of gas temperature in various types of plasmas at various environmental pressures [19–23].

2. Experimental

Fig. 2 shows a schematic diagram of the apparatus used for the generation of DBD microplasmas in $scCO_2$ environments. A stainless-steel cell (TSC-WC-0096, Taiatsu Techno Corp., Japan), which had internal dimensions of approximately 100 ml and could withstand conditions of up to 25 MPa and 373 K, was employed. Liquid CO_2 condensed in a condenser was pumped up to the cell, heated by four heaters (300 W × 4), and stirred by a stirrer (300 rpm) to achieve a more uniform state of temperature. Pressure and temperature in the cell were monitored using a sensor and a thermocouple within the accuracies of ± 0.1 MPa and ± 0.1 K, respectively.

We generated a DBD microplasma using an ac power source, with the electrodes fixed in the cell. Fig. 3 shows a schematic diagram of the electrodes for the DBD microplasma. The high-voltage electrode was a W-needle, and the grounded electrode consisted of conductive paste covered with a thin quartz glass plate. The W-needle was fabricated from a W-wire (diameter: 250 μm) by electro-polishing to enhance the electric field, and its top curvature and apex angle were about 100 nm and about 20°, respectively. A thin quartz glass plate (thickness: 120–170 μm) was employed for the dielectric barrier. The tip of the W-needle was placed into contact with the glass surface. A discharge was generated in the vicinity of the tip of the W-needle with an ac power (power frequency: 1–10 kHz, magnitude of voltage: 9–15 kV_{p-p}). Upon applying the voltage to the W-needle, a surface discharge was generated at first. Then, the type of discharge changed from surface discharge to volume discharge, because the tip of the W-needle became dull (top curvature: ∼1 μm) and the discharge gap was broadened to approximately 100 μm. Thereafter, the DBD microplasma was maintained stably. Fig. 4