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SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES IN DUSTY GLOW-DISCHARGE PLASMA

Carbon fine particles including single-walled carbon nanotubes (SWNTs) are synthesized by the hot-filament and plasma-assisted chemical vapor depositions, and their specific surface area is evaluated. Discharge was unstable with electrons depleted in plasma during the growth of fine particles because of the attachment of most electrons on them. The electron density and the dust charge decrease simultaneously in plasma with high dust density. The absolute dust potential is calculated, and the result indicates that a higher dust potential $|V_D|$ is realized in a higher density plasma, especially, under certain conditions of high density and large size for dusts. Carbon fine particles of larger surface areas are expected to be synthesized in higher density plasma owing to the defect induction in SWNTs by the energetic ion bombardment.

Keywords: carbon nanotube, ion bombardment, dusty plasma, plasma-enhanced chemical vapor deposition.

1. Introduction

Nanocarbons, particularly single-walled carbon nanotubes (SWNTs), are expected to be used for the hydrogen storage, supercapacitors, and fuel-cell electrodes, because they have a large surface area per unit weight or volume [1–3]. SWNTs are usually synthesized by arc discharge [4], laser ablation [5], and chemical vapor deposition (CVD) [6]. SWNTs were synthesized by CVD also in glow-discharge plasma, however, on the surface of substrate [7].

A new gas phase method of SWNT synthesis was developed applying a radio-frequency (RF) glow discharge plasma for the suspension of negatively charged fine particles containing catalytic metal and carbon nanotubes along with hot-filaments [8, 9]. Longer SWNTs are expected to grow being suspended in the reaction region for a longer time by the method than those obtained by the conventional thermal CVD. Furthermore, the surface area of SWNTs increases if they grow curved and kinked owing to the effect of ion bombardment in glow discharge plasma. Ions with much higher energy than the binding energy of C–C and C=C bombard SWNTs during the growth and make defects in them. In this paper, the results of synthesis of carbon fine particles including SWNTs by the method is presented, and the relation between the defect induction in SWNTs and the potential energy of fine particles is discussed.

2. Experiment

The schematic diagram of the RF glow discharge plasma system with hot-filaments is shown in Fig. 1. RF plasma was generated between grounded filaments and an RF-induced copper plate. Filaments were heated up to 1800–2000. 40–60% ethylene diluted in hydrogen containing the vapor of ferrocene ($Fe(C_5H_5)_2$) was allowed to flow toward the hot filaments. The pressure in the chamber was maintained at 2.7–5.3 kPa (20–40 Torr). The plate of the RF electrode was set 20 mm downstream from the hot filaments and placed perpendicularly to the reaction gas flow. The power up to 50 W was applied to the RF plate with the filaments heated for about one hour. Prepared carbon fine particles were collected on an upper-plate, which also serves as the RF electrode, and a bottom-plate. They were analyzed by the transmission electron microscopy (TEM) and Raman spectroscopy. The specific surface area was evaluated with the measurement of the adsorption isotherm for nitrogen molecules by the volumetric method. The self-bias voltage (V_{DC}) of RF plasma was measured during the synthesis of carbon fine particles.

3. Results and Discussion

The deposition quantity of CNTs on each plate was compared by measuring the weight density. The ratio of the weight density on the bottom-plate to that on the upper-plate increased with the RF power. The

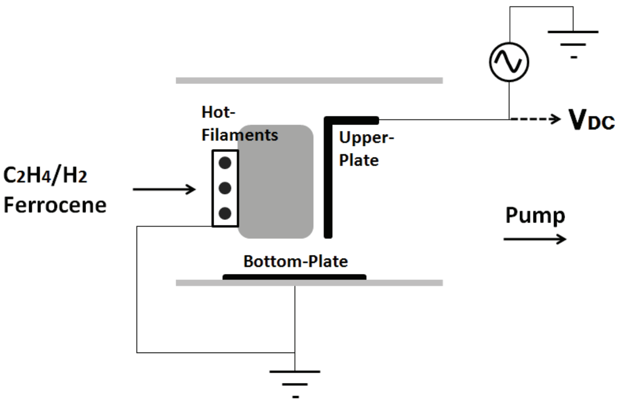

Fig. 1. Schematic diagram of the RF glow discharge plasma system with hot-filaments

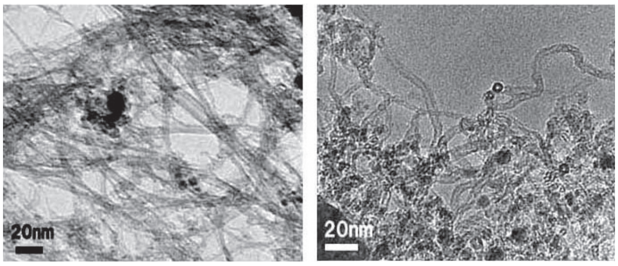

Fig. 2. Transmission electron micrographs of synthesized carbon fine particles

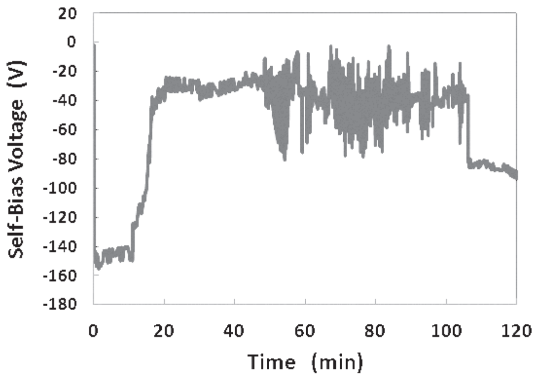

Fig. 3. Variation of the self-bias voltage during the fine-particle growth

result suggests that carbon fine-particles were suspended for a long time in RF and dropped on the bottom-plate after the growth to a considerable weight without transport by the gas flow on the upper-plate. The streams of fine particles were observed from a side view-port by scattered light emitted from hot-filaments. Streams became dimmer with

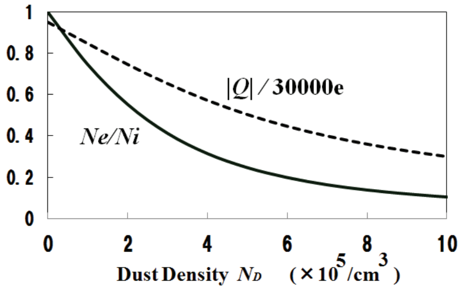

Fig. 4. Dust density dependence of Q and N_e/N_i under the conditions of $N_i = 10^{10}/cm^3$ and a spherical dust size of 10 microns. The electron and ion temperatures are assumed 5 eV and 0.1 eV, respectively

the increase of the RF power. The result also implies that negatively charged fine particles were confined and dispersed in plasma. TEM images of synthesized carbon fine-particles are shown in Fig. 2. Slightly curled nanotubes, as well as intricately-intertwined ones, are observed in the images. They were confirmed to be SWNTs by the Raman spectroscopy. The specific surface area evaluated for the synthesized carbon fine particles without purification was 120 m^2/g [9].

The RF self-bias voltage, V_{DC}, varied during the growth of fine-particles as shown Fig. 3. In Fig. 3, the voltage V_{DC} is generated about –150 V just after the ignition of plasma and gradually increases after the start of the sublimation of ferrocene at 10 min to become about –30 V around 20 min. It decreases again about –90 V in about 105 min after the depletion of ferrocene. The change of the self-bias voltage is understood by the transition between the α and γ regimes of RF discharge [10–14]. The α discharge regime shows a resistive behavior because of the lower electron density in plasma, while the γ discharge regime is capacitive, since the RF voltage is mainly applied in the sheath.

During the growth of carbon fine-particles, V_{DC} changes in an unstable manner, especially after about 45 min. The charge neutrality in dusty plasma is expressed as

$$eN_e + Q\,N_D = eN_i, \quad (1)$$

where N_e, N_D, N_i, and Q are the densities of electrons, dust, positive ions, and average dust charge, respectively. Relation (1) makes known that, when too many carbon fine-particles containing SWNTs exist

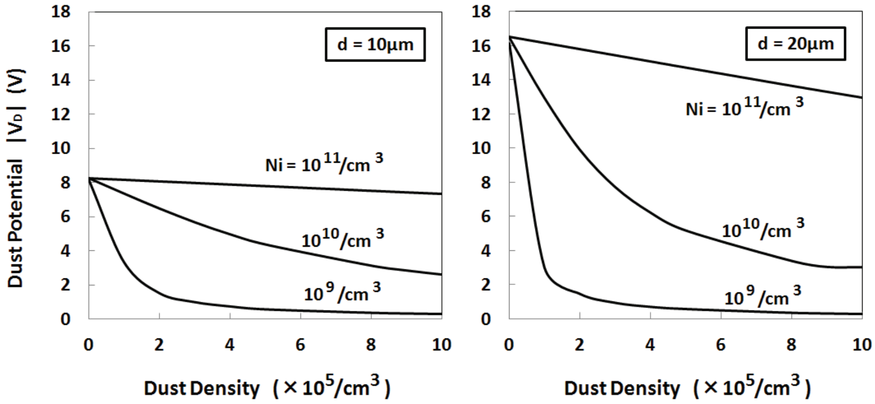

Fig. 5. Dust density dependence of the dust floating potential in plasma with ion densities of $10^{11}/\mathrm{cm}^3$, $10^{10}/\mathrm{cm}^3$, and $10^9/\mathrm{cm}^3$ for spherical dusts of 10 and 20 microns in diameter. The electron temperature and ion temperatures are assumed 5 eV and 0.1 eV, respectively

in plasma, electrons are left in a much lower density, because most electrons attach to dusts, i.e., to carbon fine particles. Thus, glow discharge should become unstable from 45 min to 105 min.

Figure 4 shows the result of calculations of the dust density dependence of Q and $N_\mathrm{e}/N_\mathrm{i}$ under the conditions of N_i of $10^{10}/\mathrm{cm}^3$, spherical dust size of 10 microns, electron temperature of 5 eV, and ion temperature of 0.1 eV. With the dust density, $N_\mathrm{e}/N_\mathrm{i}$, as well as Q, decreases under a certain plasma density, i.e., ion density. Thus, the electron density and the dust charge are lowered simultaneously in the plasma of high dust density, as is understood by Eq. (1).

The energy of ion impinging on a dust is calculated from the floating potential of a dust, V_D, where the reference potential is that of plasma, to be $e|V_\mathrm{D}|$ for a singly-charged ion under collisionless condition. V_D is calculated from Q as

$$V_\mathrm{D} = Q/(2\pi\epsilon_0 d), \qquad (2)$$

where d is the dust size. Q and N_e are calculated through the simultaneous equations, which are Eq. (1) and the equation of the orbital-motion-limited probe theory.

Figure 5 shows the dust density dependence of the dust floating potential for spherical dusts of 10 and 20 microns in diameter under the same conditions of the electron and ion temperatures of 5 eV and 0.1 eV, respectively. The absolute value of potential $|V_\mathrm{D}|$ decreases faster with the increase of the dust density for a lower plasma density, i.e., ion density, because the particle charge decreases mainly according to Eq. (1). Meanwhile, for a higher plasma density, the absolute potential decreases slower, and the particle charge is determined mainly by the equation of the probe theory. Under the same plasma density, the potential decrease is faster for larger size particles. These results means that a higher dust potential $|V_\mathrm{D}|$ is realized by a higher density plasma, especially, under certain conditions of a higher density and a larger size for dusts.

Under the conditions of gas pressure in this experiment, ions are subjected to the collision with neutral molecules several times in the sheath around dusts before the bombardment. The energy to induce defects in SWNTs should far exceed the binding energy of C–C or C=C, considering carbons are in the network of six-membered ring. Because of these reasons, threshold energy of ion bombardment to induce defects in a SWNT is much higher than C–C or C=C binding energy, which are 3.4 eV and 6.1 eV, respectively. Furthermore, carbon fine particles including SWNTs are not spherical. Therefore, the quantitative evaluation of the dust density and the plasma density for the induction of defects in SWNTs is difficult. However, in any case, a higher density plasma tends to make the dust potential higher and to induce defects in SWNTs, especially for dusts of large size and high density, as is shown in Fig. 5. Under such conditions, synthesized SWNTs are expected to include defects forming curled and intricately intertwined structures, which have larger surface areas.

4. Conclusions

Carbon fine particles including SWNTs were synthesized by the hot-filament and plasma assisted

CVD. Electrons in plasma were depleted during the growth of fine particles because of the attachment of most electrons on them. The electron density and the dust charge decrease simultaneously in the plasma with high dust density. The dust potential was calculated with the variable of dust density and the parameters of dust size and plasma density. The result indicates that a higher dust potential $|V_D|$ is realized by a higher density plasma, especially, under certain conditions of high density and large size for dusts. In other words, the higher density plasma tends to make dust potential higher and to induce defects in SWNTs, especially for dusts of large size and high density. Under such conditions, the synthesized SWNTs are expected to include defects forming curled and intricately intertwined structures, which make the surface area of SWNTs larger.

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СИНТЕЗ ОДНОСТІННИХ
ВУГЛЕЦЕВИХ НАНОТРУБОК У ЗАПИЛЕНІЙ
ПЛАЗМІ ТЛІЮЧОГО РОЗРЯДУ

Р е з ю м е

Синтезовано малі частинки вуглецю, у тому числі одностінні вуглецеві нанотрубки (ОВНТ) напиленням методом гарячої нитки і методом хімічного осадження з пари за участю плазми. Визначено їх питомі площі поверхні. Розряд нестабільний через зменшення кількості електронів у плазмі за рахунок приєднання їх до зростаючих малих частинок. У плазмі з високою густиною пилу густина електронів і заряд пилу зменшуються синхронно. Розрахунок абсолютного потенціалу пилу показав, що більш високий потенціал $|V_D|$ реалізується у плазмі з більшою густиною особливо в умовах високої густини і пилинок великих розмірів. Очікується, що малі частинки вуглецю з високими площами поверхні будуть синтезовані в плазмі з високою густиною завдяки генерації дефектів в ОВНТ при іонному бомбардуванні.

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СИНТЕЗ ОДНОСТЕННЫХ
УГЛЕРОДНЫХ НАНОТРУБОК В ЗАПЫЛЕННОЙ
ПЛАЗМЕ ТЛЕЮЩЕГО РАЗРЯДА

Р е з ю м е

Синтезированы малые частички углерода, в том числе одностенные углеродные нанотрубки (ОУНТ) напылением методом горячей нити и методом химического осаждения из пара с участием плазмы. Определены их удельные площади поверхности. Разряд нестабилен из-за уменьшения количества электронов в плазме за счет присоединения их к растущим малым частичкам. В плазме с высокой плотностью пыли плотность электронов и заряд пыли уменьшаются синхронно. Расчет абсолютного потенциала пыли показал, что более высокий потенциал $|V_D|$ реализуется в плазме с большей плотностью особенно в условиях высокой плотности и пылинок больших размеров. Ожидается, что малые частички углерода с высокими площадями поверхности будут синтезированы в плазме с высокой плотностью благодаря генерации дефектов в ОУНТ при ионной бомбардировке.