Significant Superiority of Plasma CVD in Cloning Growth of Carbon Nanotubes

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Nanocarbons including carbon nanotubes have attracted a great deal of attention in various kinds of scientific and technological fields, where the processing method of chemical vapor deposition (CVD) has played a major role in their production and structure control [1]. The perfectly structure-controlled growth of single-walled carbon nanotubes (SWNTs) has been a long-standing challenge in the field concerned, where the concept of cloning without using metal catalysts is expected to be a key method for its realization [2]. Here, we for the first time clarifies that plasma-enhanced CVD (PECVD) is much more effective compared with thermal CVD (TCVD) in the cloning growth of SWNTs.

Our experiments are performed using a diffusion PECVD system [1] consisting of an RF-discharge quartz tube and an electric furnace surrounding its center neighborhood, where plasmas of low n_e (~10^8 cm^{-3}) and T_e (~0.3 eV) are provided to a SWNT-growth substrate placed within the furnace site. Hence, the TCVD process can be carried out by switching off the RF power. After a solvent solution of shortly-segmented SWNTs as a molecular seed is sprayed on a Si substrate, two kinds of pretreatment processes are applied to the sprayed substrate for end-cap opening of the seed SWNTs leading to a successful start of the cloning growth. One is an air annealing at 420 °C (substrate temperature) for 20 min (Pre.A), while the other is a H_2O-filled annealing at 420 °C for 5 min following the above (Pre.B). The latter is expected to be more effective for oxidation of the end caps. Concerning the CVD process, C_2H_5OH is used as the feed carbon source, (1.3~6.7)x10^3 Pa, and an effect of introducing H_2 is investigated by comparison with introducing Ar. The H_2 introduction into the ethanol plasma is predicted to potentiate an organic chemical reaction to sprout six-membered ring structures for sustaining the cloning growth.

Atomic force microscopy (AFM) is adopted to substrates for obtaining distribution graphs of length vs number of SWNTs. The distribution of pristine (before the CVD processes) SWNTs yields a peak around 0.3 µm and a upper limit around 1.8 µm as shown in Fig. 1 (blue vertical bars). In the following paragraph we describe experimental results for the CVD time of 15 min in combination with processes of the pretreatment and the mixing-gas introduction, and focuse on the length distribution.

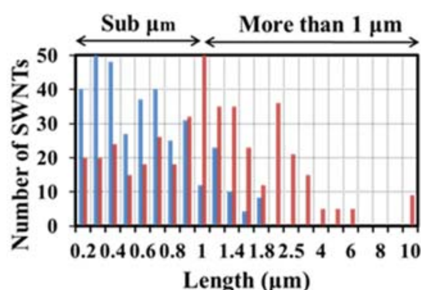

Fig. 1. Distribution graphs of length vs number of SWNTs. Blue: pristine, red: (4).

(1) Pre.A / Ar of 1.3x10^3 Pa : The peak around 0.3µm does not change, more than 1.8 µm length of SWNTs appears, and the upper limit approaches 3µm in the case of TCVD at 900 °C. When the PECVD process is performed, on the other hand, the peak-yielding length increases up to 1.2 µm and more than 4.0 µm length of SWNTs is found even at low temperature of 700 °C.

(2) Pre.A / H_2 of (1.6~8.5)x10^2 Pa : After performing the TCVD process at 900 °C, the number of SWNTs in the range of 1.0 µm to 2.0 µm increases in comparison with the TCVD result of Ar introduction mentioned above in (1). Furthermore, more than 2.0 µm length of SWNTs stands out and the upper limit reaches 6µm for the PECVD process at 700 °C.

(3) Pre.B / Ar of 1.3x10^3 Pa : The length-distribution aspect for the case of TCVD at 900 °C does not make much difference compared to the above-mentioned result of TCVD in (2). In the case of PECVD at 700 °C, on the contrary, the number of SWNTs in the range of 1.3 µm to 3.0 µm largely increases and besides SWNTs in the range of 4.0 µm to 10 µm is found to grow.

(4) Pre.B / H_2 of (1.6~8.5)x10^2 Pa : The result of TCVD/900 °C is not so different from that of TCVD noted above in (3). In contrast, a remarkable decrease of the number of SWNTs shorter than 1.0 µm and an increase in longer SWNTs are observed in the PECVD /700 °C process (red bars in Fig. 1). As a result, the number ratio of longer SWNTs in the range of 1.0 to 10 µm to SWNTs shorter than 1.0 µm attains to the maximum (Fig.2). Thus, PECVD is significantly superior to TCVD in the cloning growth of SWNTs due to active H and O species in plasmas, which are generated from H_2 mixed into H_2O_5OH and H_2O remained on SWNT walls even after pre-annealing.

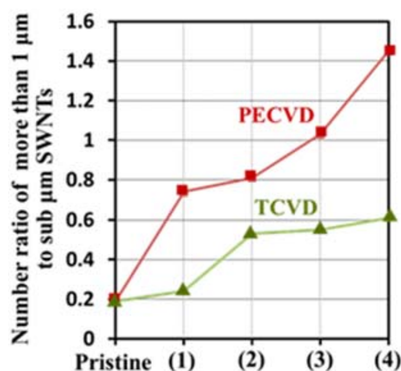

Fig.2. Number ratio of more than 1 µm to sub µm SWNTs for TCVD and PECVD processes.

References

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