THE SIMULATION STUDY ON THE BEHAVIOR OF CARBON ATOMS DURING INTERACTION WITH METAL CATALYST

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Introduction

Based on the catalytic chemical vapor deposition (CCVD) method [1,2], it is now possible to obtain a wide range of carbon nanotubes from single-walled, double-walled to multi-walled with various diameters (Figure 1). The CCVD method is now considered to be the most promising method for producing carbon nanotubes in quantity, which enables the lower-cost production of carbon nanotube. The study of the CCVD process is now moving toward the development of a way to control the quality, diameter, growth direction, and chirality of the nanotubes. There are some attempts to control the growth direction of the tubes [3,4] that has either grown aligned tubes or grown single walled tubes between the patterned pillars. Although not fully controllable, the studies have paved the way to the real control of the growth direction. Not much progress has been made for the control of quality, diameter and chirality control. The main reason for this is the lack of knowledge on the growth mechanism of the carbon nanotube and the empirical nature of the nanotube growth experiments.

It is well known that the critical factor for the growth of the tube in a CCVD process is the behavior of the catalytic particle, because the tube nucleation is considered to occur at the catalyst. There exist some studies treating the nucleation behavior in an empirical way [5], and in a more advanced way [6]. Both studies have treated a catalyst already formed in a crystalline shape.

In the present study, we will try to simulate the catalyst formation in the floating CCVD method, and observe the motion of carbon atoms during the catalyst formation.

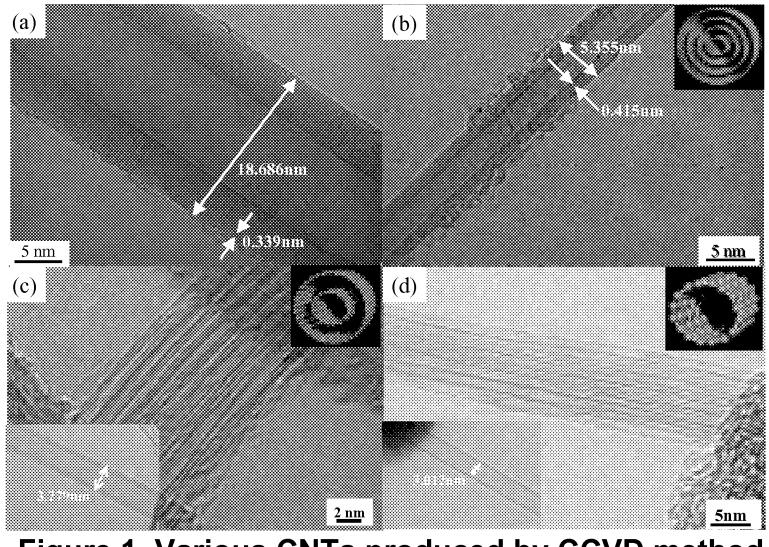

Figure 1 Various CNTs produced by CCVD method.

Experimental

To investigate the clustering behavior of catalytic particles in the floating CCVD method, we made a small model consisting of 6 ferrocene molecules. Vanderbilt ultra-soft pseudopotentials [7] were used in the CPMD code [8] to perform the MD simulation. The temperature was set to 2273K, and the simulation time was 250 fs. The motion of ferrocene molecules interacting with a Fe cluster was simulated in the same manner.

Results and Discussion

Figure 2 shows the snapshots during the MD simulation of the ferrocenes. In some molecules, pentagonal rings became into pieces and Fe atoms started to gather, showing the very early stage of catalyst particle formation. Carbon fragments were staying around the Fe atoms, forming a carbon-rich phase around the catalyst.

Figure 3 shows the snapshots of the interaction of ferrocenes with the Fe catalyst. It was found that there is an orientational dependence in the reactivity of ferrocene with the catalyst. When the side-edge of the ferrocene is exposed to the surface of the catalyst, pentagonal rings dissociate from the Fe atom, which become part of the catalyst.

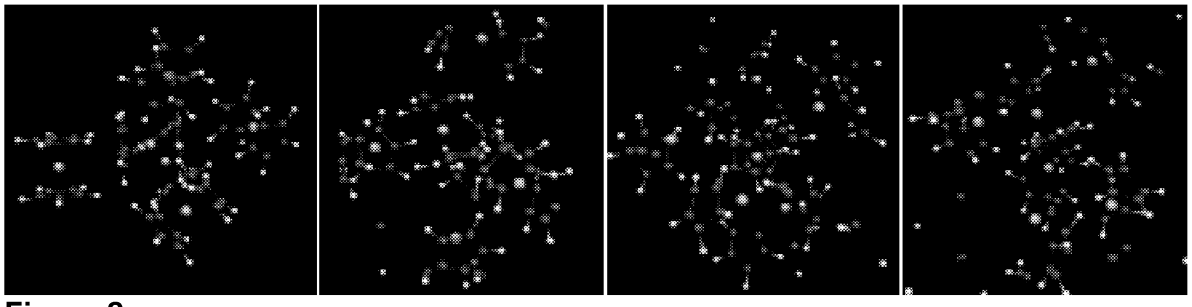

Figure 2
Snapshot of ferrocene MD simulation. Fragmentation of pentagonal rings and the aggregation of Fe atoms are found. (Viewpoint is rotated for the ease of understanding the movement of the particles)

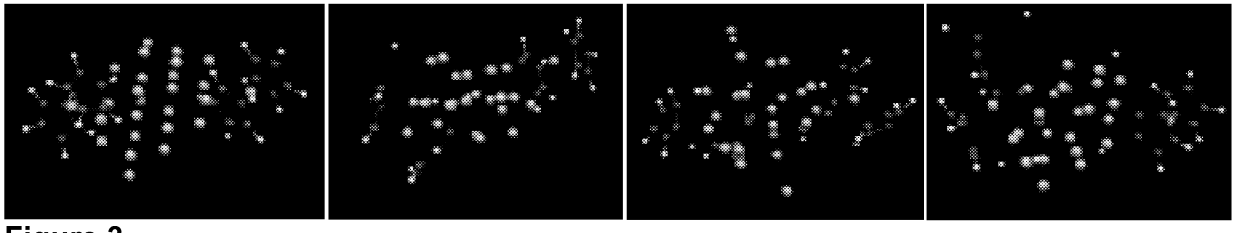

Figure 3
Snapshot of ferrocenes interacting with Fe cluster. Orientational dependence of the reactivity of ferrocene can be seen. Less reactive ferrocene at the right side rotates to reach the reactive position, and starts fragmenting. (Viewpoint is rotated for the ease of understanding the movement of the particles)

Conclusions

We have simulated several stages of catalyst formation, where the nucleation of carbon starts. We found that the fragmentation of pentagonal rings resulting in a carbon-rich

phase occurs during the catalyst formation. We can imagine that when more carbon species reach the catalyst, clustering of carbon species will start, resulting in a carbon nanotube.

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