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Cross-sectional transmission electron microscopic study on the initial stage growth of carbon nanotubes

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Abstract

The information about interface structure of carbon nanotubes/catalyst/substrate is investigated by cross-sectional transmission electron microscopy. At the initial stage growth of carbon nanotubes in chemical vapor deposition, driving force for the separation of graphite caps from catalytic metal results from stress energy due to the mismatch piled up at the edge side of the graphite cap.

Keywords: Nanotubes; Chemical vapor deposition; High resolutions electron microscopy; Interface structure

1. Introduction

Since their discovery by Iijima [1], carbon nanotubes (CNTs) have attracted great attention due to their scientific interest and potential applications of technological importance [2,3]. Aligned CNTs have attracted great attention due to their potential application to tip materials for a next generation field emission display (FED) [3–5]. For this purpose, thermal and plasma-enhanced chemical vapor deposition (CVD) methods are the first candidate for the synthesis of CNTs due to the capability of uniform growth on a large area [3,6–8]. Considering the FED fabrication process, a few requirements such as selective and vertically aligned growth may have to be satisfied [9]. Thus far, the CVD techniques have used catalytic-metal-coated plane substrates [10–15] or catalytic-metal embedded porous substrates [16–19].

The formation mechanisms of CNTs have been proposed through from theoretical to experimental results by several research groups. Growth mechanism of CNTs is based on the theory about the growth mode of carbon fiber. It is theoretically established that carbon atoms are diffused through vapor–liquid–solid (VLS) mechanism in the growth of carbon fiber [20,21]. The growth of carbon fiber with CVD method is elucidated as following theoretical approaches.

(1) Decomposition of hydrocarbon into nanosized catalytic metal.
(2) Diffusion and saturation of carbon atoms into catalytic metal particles.
(3) Upward growth of carbon fiber by a separation of the saturated carbon atoms in catalytic particles with the catalytic metal.

Based on this theory, growth mode of CNTs using CVD method can be classified into two categories. One is tip growth mode [22], in which catalytic metal particles are detached from a substrate during growth and the detached particles migrate upward as playing a role of catalyst in the process of growth, resulting in the existence of the particles at the tip of tube. The other is base growth mode [7,23], in which metal particles play a role of catalyst at the bottom of tube as staying on a substrate after the metal particles are formed on the substrate.

The initial stage of growth of CNTs is a key factor to determine the growth mode of CNTs. Therefore, it is required that the information on the interface between CNTs and catalyst deposited on the substrate should be sufficiently obtained at the initial growth stage. In the present work, we report that the interface structure between CNTs and catalyst

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particles and the driving force for CNT growth from catalyst at the initial stage of CNT growth in CVD method are analyzed using cross-sectional transmission electron microscopy (TEM).

2. Experimental

2.1. Carbon nanotube growth using chemical vapor deposition

To investigate the initial stage growth of CNTs in CVD method, CNTs were grown using thermal CVD. Fe thin film was deposited onto a SiO_2(100 nm)/Si substrate in the evaporator of 10^{-6} Torr at room temperature. The substrates were placed in a 60 mm-diameter quartz tube furnace and heated up to the growth temperature of 950 °C at a rate of 20 °C/min while introducing Ar gas. When the temperature was stabilized, NH_3 gas was introduced at a flow rate of 100 sccm for 5 min. Generally, NH_3 gas etches Fe film at a high temperature, resulting in nano-sized Fe particles which serve as a catalyst for CNT synthesis [6,9,24]. For CNT growth, C_2H_2 gas was supplied at 30 sccm. CNTs were grown as an only function of time (30 s, 1 min, 30 min, and 40 min), but other growth conditions were fixed. After reaction, furnace was cooled down to room temperature in Ar ambient.

2.2. Cross-sectional specimen preparation of carbon nanotubes for transmission electron microscopy

So far most microstructural investigations on CNTs using TEM or high resolution TEM (HRTEM) have been carried out in the longitudinal projection direction after ultrasonic treatment by dissolving the CNTs in ethanol/acetone. Feng et al. [25] prepared a cross-sectional specimen for TEM observations, but it was necessary to cut the sample using an ultramicrotomy after complete hardening of the nanotube-bundles in an epoxy matrix. Another TEM specimen preparation method for anodic alumina template samples was reported, based on a focused ion beam technique [26]. However, this approach involved a complicate process such as coating of Cr films on the CNTs for the purpose of protection, and resulted in poor images at high resolution.

There have been rare reports on the cross-sectional TEM observation of the interface structure of a CNTs–catalyst–substrate. This may be due to the weak adhesion of the CNTs to the substrate, and thus the typically used ion polishing method is difficult to apply. To develop a better understanding of the growth mechanism and the actual structures of CNTs, TEM/HRTEM observations in the cross-sectional direction for the unaffected integrity of CNTs–catalyst–substrate structure are required. This procedure is a direct and clear method for understanding the actual structure and growth mode or mechanism of CNTs.

For a direct observation of the cross-section of the grown CNTs, cross-sectional TEM specimens were prepared in which the CNTs were preserved as they were grown on the substrate. The steps involved in the cross-sectional preparation are described in Fig. 1.

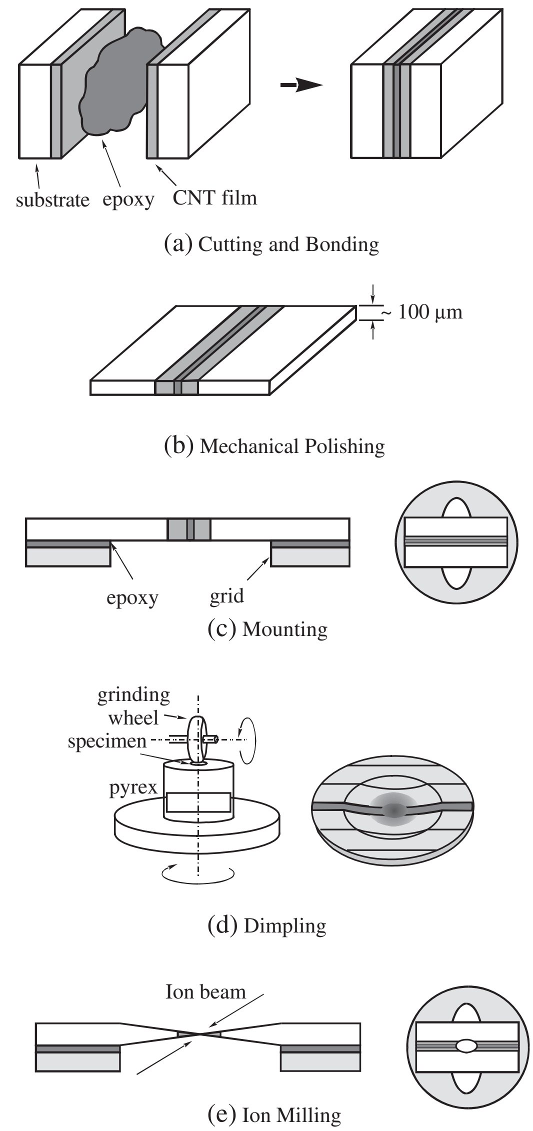

Fig. 1. Schematic illustration of processes for the preparation of the cross-sectional TEM specimens.

Some advantages using this method include;

(1) distinguishing the top and the bottom of the tube, and relevant morphologies
(2) direct inspection of the behavior of the catalysts relevant to the morphology of CNTs and to the interface during CNT growth
(3) defect analysis of CNTs, not through projection, but through genuine cross-sections.

These features offer significant advantages in terms of developing a better understanding of the growth mechanism and the actual structures of CNTs through imaging, diffraction, and high-resolution observations.

3. Results and discussion

Fig. 2 shows the cross-sectional scanning electron microscopy (SEM, Hitachi S600) results of CNTs. It was observed