論文の内容の要旨
Abstract of Dissertation

Title of Dissertation:　Controlled Growth of Vertically Aligned Single-Walled Carbon Nanotubes for Devices

（デバイス応用に向けた垂直配向単層 CNT の合成制御）

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A single-walled carbon nanotube (SWNT) is a novel one-dimensional material possessing attractive electric, mechanical, and thermal properties. Driven by the potential applications of SWNTs, many methods have been proposed to synthesize SWNTs. Among these, alcohol catalytic chemical vapor deposition (ACCVD) can yield high-quality SWNTs at moderate temperatures. It is also the first method by which vertically aligned SWNT arrays were obtained. However, the incomplete understanding of the growth mechanism in this process, such as insufficient information about the catalyst status and position during growth, hinders the full control over the final product.

Isotope labeling is a powerful technique for identifying the reaction pathway in chemical reactions. By feeding of two types of isotope-labeled ethanol in sequence and therefore forming ^{12}C-^{13}C SWNT junctions, we confirmed the root growth mechanism of SWNTs synthesized by ACCVD. This result is consistent with TEM observation, where catalyst particles are found only in one end of an array. Clarification of the root growth model is critical in understanding the growth and catalyst deactivation mechanisms in ACCVD. The no-flow condition we introduced is also able to produce high-quality SWNT arrays effectively.

In root growth mode, the feedstock molecules have to diffuse through the thick CNT array, reach the substrate where catalysts are located, and then contribute to the CNT growth. In this bottom-up growth process, the diffusion resistance of the feedstock from the top to the root arises as an obstruction, and can act as a unique decelerating growth mechanism. Existence of a feedstock diffusion resistance means that concentration of the carbon source at the CNT root should be lower than the bulk concentration. We proposed a method of using a non-dimensional modulus to quantitatively evaluate the degree of feedstock diffusion resistance (no diffusion resistance regime, transient regime, and strong diffusion limit regime). Five of the most frequently used systems are also discussed. The results show that, for mm-scale SWNT arrays, the feedstock concentration at the root of the array is much lower than the bulk concentration, while for mm-scale MWNTs the decreasing growth can not be

attributed to a diffusion limit, which agrees well with the currently available experimental results.

Recent investigations have also improved our understanding of SWNT growth behavior. We previously developed an *in situ* optical absorption measurement that allows for convenient real-time measurement of the film thickness. This technique revealed, for the first time, *in situ* growth kinetics of a VA-SWNT array. It provided sub-second resolution and much more direct information to the previously black-box approach to studying the growth process. We investigate the influence of various species on ACCVD synthesis of VA-SWNTs. A small amount of acetylene (approximately 1% partial pressure) was found to accelerate the growth rate by almost ten times, as revealed by a distinct change in the growth rate determined from *in situ* optical absorption. This accelerated growth, however, only occurred in the presence of ethanol, whereas pure acetylene at the same partial pressure resulted in negligible growth and quickly deactivated the catalyst. The dormant catalyst could be revived by reintroduction of ethanol, indicating that catalyst deactivation is divided into reversible and irreversible stages. Since the thermal decomposition of ethanol also yields some amount of acetylene, we calculated theoretically and also measure experimentally the concentration of different species. Contribution of such gases to the formation of SWNTs is quantified.

The diameter of a SWNT affects its mechanical, chemical and especially electronic or optical properties. SWNTs with smaller diameters (approximately 1 nm) have a larger band gap and are more mechanically stable than larger SWNTs (e.g. dia. >2 nm). Furthermore, they are also more easily measurable by spectroscopic methods such as resonance Raman spectroscopy and photoluminescence excitation. However, most vertically-aligned SWNT arrays produce SWNTs synthesized to date have the average diameter of ~ 2 nm, or even larger (~ 3 nm). The difficulty of diameter control lies not only in the synthesis but also the characterization. By extensive study on the CVD parameter and catalyst recipe, we show that the average diameter of vertically aligned SWNTs can be arbitrarily tuned between 1.4 and 2.5 nm. The average diameter was determined by optical absorption spectra as well as high-resolution TEM observations. We also show that the diameter of SWNTs along the growth direction is not uniform, as evidenced by carefully decomposed optical absorption spectra. TEM observations and Raman spectra obtained from different locations along the height of the array are consistent with the absorption results. These results provide insight into the SWNT growth mechanism and catalyst behavior on a flat substrate.

Localizing the growth of CNTs, therefore, has attracted much attention, since it is a

critical step for the fabrication of on-substrate devices. The conventional way is to pattern catalyst by sputtering or evaporation of metal through a physical mask or a pre-exposed photoresist layer. This conventional MEMS technique is, although effective, normally complicated and expensive. By identifying the role of the surface wettability in the deposition of catalyst by dip-coating, we demonstrate a method realize site-controlled SWNT growth. Hydrophilic/hydrophobic patterns were fabricated on a silicon substrate by self-assembled monolayer (SAM) surface functionalizaiton. Catalyst is found deposited only in the regions where surface is highly hydrophilic. Therefore the growth is successfully localized. The all-liquid-based procedure allows us to bypass conventional complicated fabrications and yield controlled patterns consisting of high-quality as-grown SWNTs. More importantly, when electron beam was utilized to destroy the SAM, sub-10-nm resolution may be obtained by this method. The ability of using commercial scanning electron microscope also facilitate the fabrication of SWNT based devices.