

# Oxygen contaminants affecting on the electronic structures of the carbon nano tubes grown by rapid thermal chemical vapor deposition

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## Abstract

Oxygen-related electronic structures of CNTs (carbon nanotubes) grown by rapid thermal chemical vapor deposition (RT-CVD) have been investigated by using partial electron yield near edge X-ray absorption spectroscopy (PEY-NEXAFS) and X-ray photoelectron spectroscopy (XPS). On the CNT surface with increased oxygen resulting from e-beam irradiation under the O<sub>2</sub> gas environment, C k-edge NEXAFS spectra showed an increase of the oxygen-related resonance peaks ranging from 287 to 289 eV whereas the sp<sup>2</sup> related peak at 285.4 eV was nearly unchanged. After the complete removal process of the oxygen atom on the surface by annealing the sample at 500 °C for 30 min, C K-edge spectra showed an abrupt decrease of the oxygen-related resonance peaks in 287–289 eV and an increase of the sp<sup>2</sup> related peak at 285.4 eV, indicating that the degree of crystallinity in the CNT sample was improved.

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## 1. Introduction

Carbon nanotubes have been attracting great interest for their unique physical and chemical properties and their potential applications in nano-devices, fuel cells, and field emitters [1–4]. High quality single-walled carbon nanotubes and multi-walled carbon nanotubes have been obtained using arc discharge, laser ablation, pyrolysis of hydrocarbon, and chemical vapor deposition [5–10]. Multi-walled carbon nanotubes are easily grown using thermal chemical vapor deposition on the catalytic metal thin film such as Fe, Co and Ni. Vertically aligned and various size of the carbon nanotubes can be obtained by controlling the size of the catalytic metal. The setup of thermal chemical vapor

deposition is simple, and uniform carbon nanotubes on the large area can be obtained if the temperature of the large substrate is uniformly controlled. These are the merit of the thermal chemical vapor deposition method.

Although the basis of the nanotubes synthesis is now well established, control of their fabrication is faced with many challenging problems. One of the main problems is their purification, involving separation from the byproducts from the synthesis such as other carbon materials, metal particles, and oxygen contaminants. For their purification, several methods have been used [11–14]. Unfortunately, in most cases, purification has resulted not just in elimination of impurities, but also in alteration or even destruction of nanotubes[15].

Previous research has found that the electronic properties of the carbon nanotube depend strongly on the adsorbed oxidizing molecules [16]. Oxygen contaminants as

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a side product during the fabrication process form defects on the nanotubes wall, and the defect sites act as a continuous oxidation center, resulting in the degradation of electronic properties of carbon nanotube [17].

This paper presents the investigation results of the electronic structures related to oxygen contaminants on the CNT sample grown by rapid thermal chemical vapor deposition (RT-CVD). The e-beam bombardment in an O<sub>2</sub> gas environment enhanced the adsorption of oxygen on the CNT surface without any sign of the degradation of the CNTs wall. Annealing at 500 °C for 30 min completely removed the oxygen on the CNT surface contaminated in air and healed the defects.

## 2. Experimental

To fabricate the CNT using rapid thermal chemical vapor deposition (RT CVD), 80 nm of Ni catalyst layer was deposited on the TiN/Si (100) surface. 100 nm of TiN was used as a buffer layer on the Si (100) cleaned by Ar<sup>+</sup> sputtering. The substrate was loaded in the vacuum chamber of which pressure was maintained at 6.5 m torr. The substrate was cleaned again by flowing the Ar gas at 800 sccm and NH<sub>3</sub> at 30 sccm for 5 min. Immediately after closing the flow of the NH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub> gas at 250 sccm was supplied to the chamber for 10 min, which resulted in the growth of multi-walled CNTs. During the growth process, the pressure and temperature of the substrate were maintained at 4.5 torr and 750 °C, respectively.

SEM (secondary electron microscopy, JEOL, JSM-6700F) was employed to observe the microstructures of the morphology of the CNTs.

Spectroscopic experiments were conducted at 4B1 PEEM (Photoemission electron microscopy) Beamline at Pohang Accelerator Laboratory (PAL) in Korea [18]. The resolving power ( $E/\Delta E$ ) of the beamline is 1200. The CNT samples prepared as 5 × 10 mm<sup>2</sup> were characterized by NEXAFS and XPS measurements. Then, the sample was irradiated by e-beam (2 kV, 0.65 mJ/s/cm<sup>2</sup>) in the O<sub>2</sub> gas environment in a separately connected UHV preparation chamber. The CNT sample was characterized by NEXAFS and XPS after every 20 min irradiation, and it showed no changes after 1 h irradiation. For another treatment of CNT sample, it was annealed at 500 °C after characterization of the newly inserted CNT sample. Spectroscopic data were taken after every 10 min annealing, and they showed no changes after annealing for 30 min. The base pressure of both measurement and preparation chamber were 4 × 10<sup>-10</sup> torr. During the e-beam irradiation, O<sub>2</sub> gas was flowed into the preparation chamber until the pressure of the chamber was maintained at 1 × 10<sup>-6</sup> torr. During the annealing process, the pressure of the preparation chamber reached 2 × 10<sup>-7</sup> torr owing to degassing. The destruction of CNT wall was observed after Ar<sup>+</sup> ion sputtering at 2 keV for 30 min.

NEXAFS measurements in total and partial electron yield mode were taken at the C K-edge by measuring the

sample current and by counting the electrons in the range of the kinetic energy of C KLL Auger electron. The spectra were recorded at an incidence angle of 45° to the surface normal and normalized to a gold-mesh signal ( $I_0$ ) measured concurrently to remove beam fluctuations. O 1s core level spectra were taken at a normal take-off angle to the analyzer (VSW125 with 5 channeltron) at the photon energy of 650 eV. The NEXAFS spectra after removing the influence of beam flux fluctuation are normalized following the procedure as below. To set the background level to zero the intensities at 270 eV far before the carbon K-edge subtracted from the spectra. Then, the spectra are multiplied by specific constant to set the intensities at 330 eV, which is far after carbon K-edge and it contains no peaks originated from carbon species, to 1. Through this procedure the peaks in the near edge region in the NEXAFS spectra were normalized [23].

## 3. Results and discussions

Fig. 1 represents the SEM (scanning electron microscopy) image of the side view of the as-grown CNTs (carbon nanotubes) using the RT-CVD method. The diameter and the length of the nanotubes were estimated by about 20–30 nm and 13 μm, respectively.

Fig. 2 shows O 1s core level, total electron yield (TEY) NEXAFS, and partial electron yield (PEY) NEXAFS spectra at carbon K-edge. The spectra represented by filled squares and empty circles in Fig. 2 were acquired on the as introduced CNT sample and on the CNT sample after irradiation by e-beam at 2 keV for 1 h under the O<sub>2</sub> gas environment. The NEXAFS spectra represented by open stars in Fig. 2(b) and (c) were acquired after Ar<sup>+</sup> ion sputtering at 2 keV for 30 min.

In Fig. 2(a), O 1s spectrum shows that the as introduced CNT sample is already containing oxygen species. After e-beam irradiation of CNT sample in the O<sub>2</sub> gas environment, the intensity of O 1s peak doubled although molecular oxygen is much less reactive because of its low sticking coefficient [17,22].

In Fig. 2(b), the first resonance peak at 285.4 eV originated mainly from the excitation to the π\* antibonding orbital at sp<sup>2</sup> (C=C bond) site from C 1s level. This peak was used as an index of degree of crystallinity of the CNTs sample. The amount of this peak can be partially overestimated since a certain proportion of C≡C bonds seems to be present on the defect site, and the resonance peak can contribute to the same energy position with the 1s → π\* resonance of C=C bond [19]. The peaks located at 291.8 and 282.8 eV are structure sensitive features of the graphite, and they have been reported to have σ symmetry [20]. The resonance peaks located at 286.8, 287.8 and 288.8 eV were assigned to originate from C 1s → π\* (C=O), C 1s → σ\* (C-H) and C 1s → π\* (O=C-OH species) by Lenardi et al. [19]. The overall feature of the NEXAFS spectrum at C K-edge is consistent with the previous report [21]. The NEXAFS spectrum on the CNTs surface after

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