# EFFECT OF BORON DOPING ON THE GROWTH AND MICROSTRUCTURE OF CARBON NANOTUBES GROWN BY PECVD

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## Introduction

Boron-doped carbon nanotubes (BCNTs) are of particular interest because of the expected modification of their electronic properties[1]. The substitution of boron in the carbon lattice is expected to increase the hole-type charge carriers, thereby influencing the electrical conductivity. BCNTs were reported as by-products when $BC_2N$ nanotubes were prepared by an arc discharge method[2]. They were also synthesized by a pyrolysis of acetylene-diborane mixtures[3] and a partial substitution of boron for carbon in CNTs[4].

Recently we have synthesized CNTs from acetylene and hydrogen gas directly on stainless substrates by RF-powered PECVD[5]. Therefore we have attempted to prepare BCNTs directly on stainless substrates using a metal-organic precursor as a boron source by RF-powered PECVD in this study.

## Experimental

Stainless steel plates were used as substrates for the synthesis of BCNTs. They were polished with sandpaper, and then cleaned in an ultrasonic bath with acetone and methanol sequentially. Afterwards they were dipped into a HF solution for a few minutes to etch the surface. Following a rinse with distilled water, they were put onto the heating block of the PECVD reactor. Then the reactor was evacuated to $10^{-3}$ Torr and the temperature of the heating block was raised to 700°C before the introduction of hydrogen and plasma treatment. After hydrogen plasma treatment for a few minutes, the mixture of acetylene, hydrogen gas and triethylboron (TEB) were simultaneously fed into the reactor to synthesize BCNTs. Typical conditions of PECVD for BCNTs growth were as follow: Pressure 7 Torr, temperature 700°C, RF plasma power 60 W, acetylene flow rate 10 sccm, hydrogen flow rate 40 sccm and TEB flow rate 0.01~1.0 sccm. SEM, TEM, and XPS were used to investigate structural and chemical changes of the synthesized BCNTs.

**Results and Discussion**

Figure 1 shows the change in morphology of the synthesized tubes with increasing the TEB flow rate. Tubes synthesized in this study were not straight. One of the reasons for the curly growth might be a rough surface of the stainless steel substrates by HF etching. Another possibility is that the tubes are not crowded enough to have van der Waals effects that make the aligned growth of tubes possible. When the TEB was not supplied, the tubes had smooth surfaces with average diameter of 40 nm, which was comparable to the catalyst grain size of the substrate[5]. When the TEB flow rate was 0.05 sccm, the average diameter of tubes was nearly the same as that of undoped, although their surfaces became rough. However, when the TEB flow rate was 0.5 sccm, the average diameter of tubes was drastically increased and such a high growth rate resulted in a very rough surface as shown in Figure 1(c).



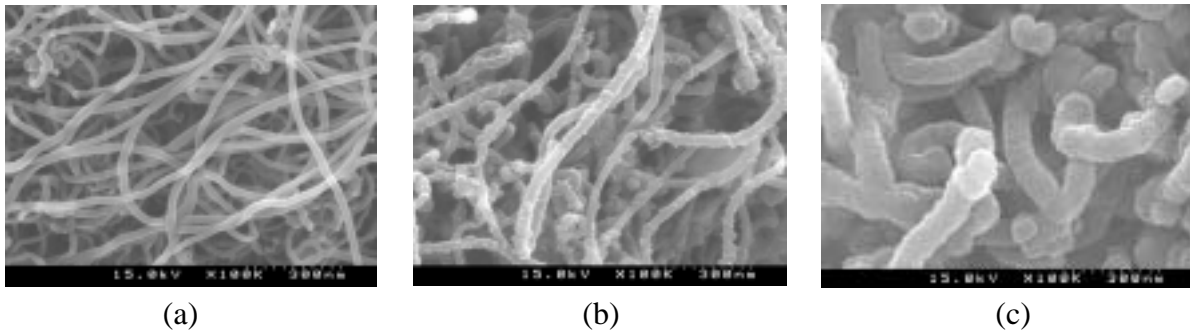(a)                              (b)                              (c)

Figure 1. Scanning electron micrographs of tubes synthesized in the TEB flow rate of (a) 0 sccm, (b) 0.05 sccm, and (c) 0.1 sccm.

The change of tube diameter is shown in Figure 2(a) as a function of the TEB flow rate. The tube diameter increases with the TEB flow rate. The tube diameter of the TEB flow rate of 1.0 sccm sample is 7 times larger than that of 0.05 sccm one. The length of tubes was not able to measure because they were curly in shape. But the length of tube might decrease with increasing the TEB flow rate because an amorphous layer was observed under the tubes and the thickness of the layer increased with the TEB flow rate. These results indicate that boron raises the growth rate of the tubes only in a radial direction. Figure 2(b) shows the change of tube diameter as a function of reaction time when the TEB flow rate is 0.1 sccm. The diameter increases until 40 nm on a constant growth rate of 4 nm/min, which is almost equal to catalyst grain size of the substrate.

Figure 3 shows the TEM micrographs of the tubes. Typical multi-walled structure is observed in undoped and 0.05 sccm sample, but the angles between the axis of graphite basal planes and the tube axis are not exactly zero resulting in the bamboo structure. In the 0.1 sccm sample, a narrow core is covered with a thick amorphous phase which makes the tube surface rough.
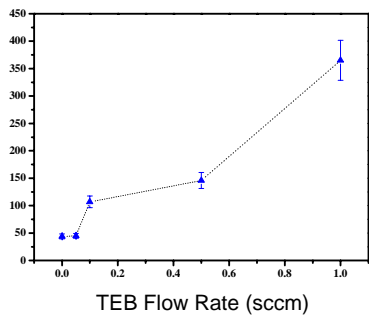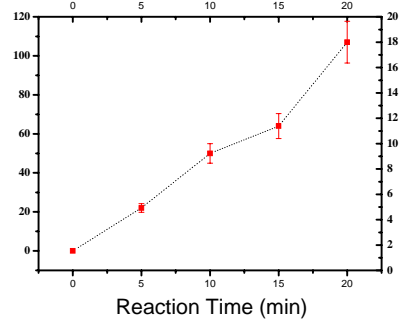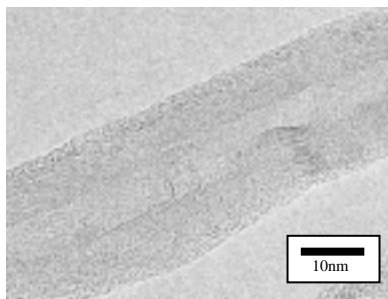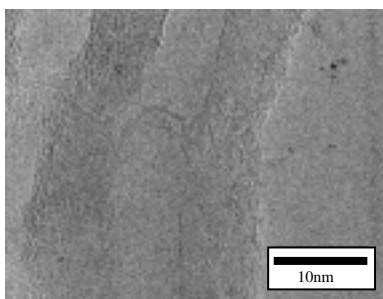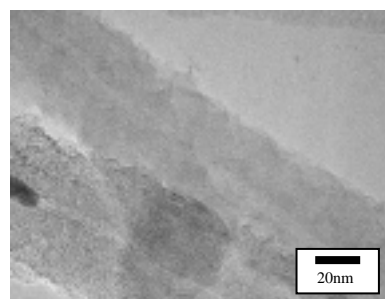
(a)  (b)

Figure 4. Change of the tube diameter as a function of (a) TEB flow rate and (b) reaction time under the TEB flow rate of 0.5 sccm.
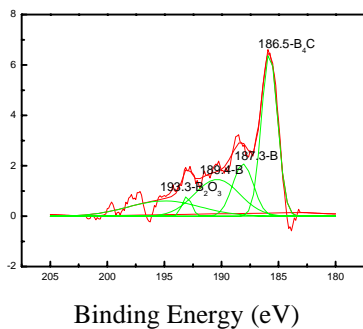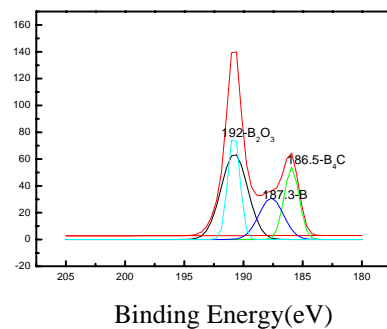


**(a)**  **(b)**  **(c)**

Figure 3. Transmission electron micrographs of (a) undoped, (b) 0.05 sccm, and (c) 0.1 sccm sample.



(a)  (b)

Figure 4. XPS spectra of B1s of the tubes with TEB flow rate of (a) 0.05 sccm and (b) 1.0 sccm.

XPS was used to investigate the chemical bonding of the tubes, and Fig. 4 shows the B1s peaks of 0.05 and 1.0 sccm sample. Peaks around 188 eV are assigned to boron atoms substituted in the graphite sheet[6] those around 192 eV to some oxide or mixed B-C and B-O bonding, and those around 186 eV to $B_4C$[7]. From the XPS results, it is believed that very small amount of boron is substituted in the graphite sheet forming in-plane $BC_3$ structure. However, boron atoms are found to prefer to form $B_4C$ or $B_2O_3$ rather than to be substituted in the graphite sheet even under the TEB flow rate of 0.05 sccm.

## Conclusions

Boron doped carbon nanotubes were synthesized directly on stainless steel substrates from acetylene and hydrogen, and triethylboron gas mixtures by RF plasma enhanced CVD. Synthesized tubes had a multi-walled structure with bamboo type when the boron concentration was low. At higher boron concentration, boron preferred to form $B_4C$ or $B_2O_3$ rather than to be substituted in the graphite sheet, resulting in tubes covered with amorphous phase.

## References

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