MULTIPLE COAXIAL CARBON NANOTUBES OF NITROGEN-DOPED AND BORON-DOPED MULTIWALLS PREPARED BY THE TEMPLATE TECHNIQUE

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Introduction

With the miniaturization of silicon devices used as semi-conducting devices now appearing its limits, development of other kinds of devices in smaller size (nanodevices) become an urgent task for next generation of electronics devices. Low dimensional carbon materials, especially carbon nanotubes (CNTs), are believed to be one of the most potential candidates for silicon. Constituting carbon based nanoscale diodes and transistors becomes one of main topics in CNTs–based nanoelectronics. Doping of some kinds of foreign elements into CNTs may lead to electron-excess *n*-type (e.g. N-doped CNTs) or electron-deficient *p*-type (e.g. B-doped CNTs) semiconducting nanotubes [1]. Provided one can control at nanometer level the position and distribution of such heteroatoms as N and B in CNTs, various types of nano-structured junctions with controlled electronic properties will be possibly prepared. Our group first reported the successful preparation of the double coaxial CNTs of N-doped and undoped multiwalls by the template technique [2]. In this study, we first succeed in the preparation of double and triple coaxial CNTs composed of N-doped and B-doped multiwalls using the template technique.

Experimental

The double and triple coaxial CNTs were, respectively, prepared by bi- and tri-step template CVD processes using an array of parallel and straight nanochannels of an anodic aluminum oxide (AAO) film as a template (schematically illustrated by Fig.1). The first acetonitrile CVD (CH_3CN: 21.0 cc/min, N_2: 500 cc/min) was conducted at 800 °C for 2 h, leading to the uniform coating of N-doped carbon layer on the inner walls of the AAO nanochannels, and a second-step CVD was carried out on the N-doped carbon coated AAO film using benzene as carbon source and boron trichloride as boron source (C_6H_6: 4.8 cc/min, N_2: 150 cc/min, BCl_3: 4.8 cc/min) at 725 °C for 20 min. The second CVD step gave rise to B-containing carbon deposition on the N-doped carbon layer. The as-prepared sample was then heat-treated in N_2 gas flow (300 cc/min) at 950°C. By

removing the AAO template with NaOH treatment, the double coaxial CNTs were liberated. If we conducted another acetonitrile CVD on the double carbon coated AAO film under the same condition as the first one, the triple coaxial CNTs will be prepared. The obtained samples were characterized with TEM (JEOL JEM-2010), XPS (PE PHI 5600 ESCA system) and XRD (Shimadzu XD-D1 XRD apparatus).

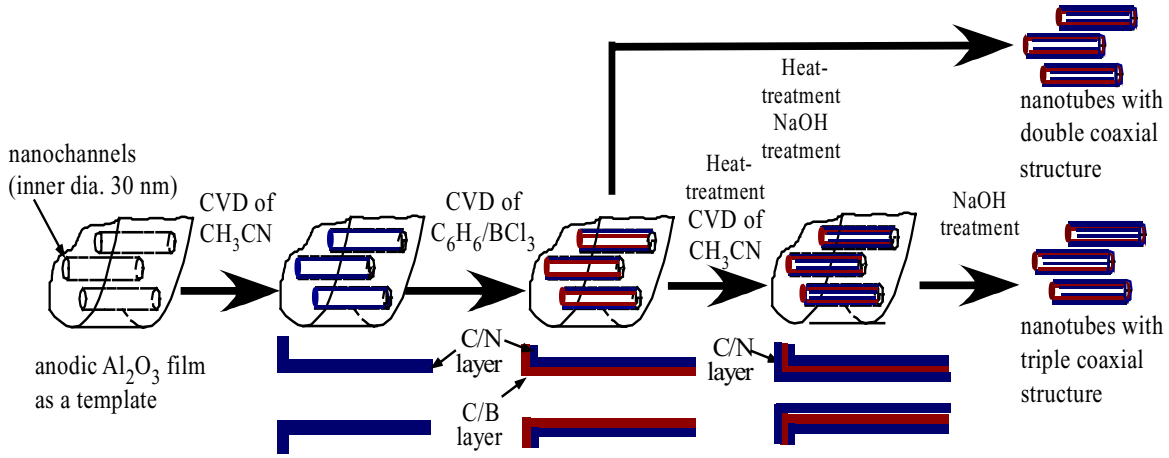

Fig. 1 Formation of double (bi-stage CVD) and triple (tri-stage CVD) coaxial CNTs composed with N-doped and B-doped multiwalls

Results and discussion

1. Double coaxial CNTs with outer N-doped and inner B-doped multiwalls

Fig. 2 shows the TEM images of single stack N-doped CNTs (prepared by the single–step CVD) and double coaxial CNTs (prepared by the bi-step CVD). It is apparent

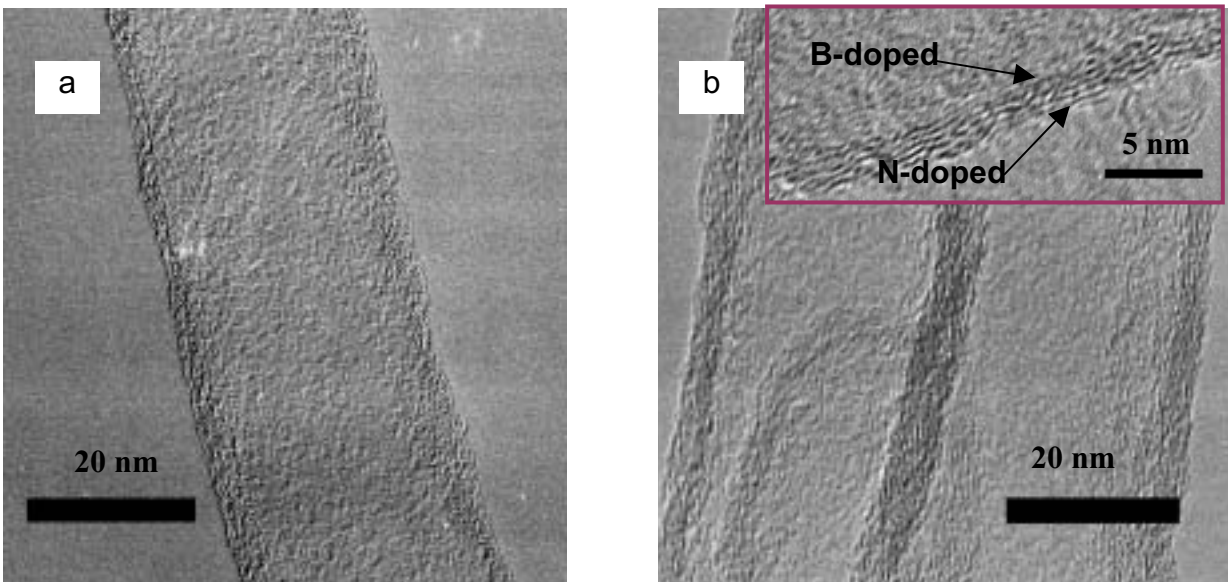

Fig. 2 TEM images of the N-doped single-stack (a) and the N, B doped double coaxial (b) CNTs. The inset of (b) shows a HRTEM image of the tube wall of a double coaxial CNT.

that the second CVD resulted in the uniform increase of the wall thickness (the single stack CNTs: 1.5 nm, the coaxial CNTs: 3.5 nm). It is seen from Fig.2 (b) that three nanotubes adjoin one another. Either single-stack or double coaxial CNTs has uniform diameter and thickness, which is one of the advantages of the template technique. The HRTEM image (the inset of Fig. 2 (b)) reveals that the coaxial CNTs contain roughly parallel graphene planes with many defects, and there is no visible difference between the outer and inner layers prepared by the different CVD steps.

Table 1 presents the surface chemical composition of a double carbon-coated AAO film and the resultant CNTs, respectively. As revealed in Fig. 1 (also referring to ref. [2]), the outer surface structure of a coated film is believed to be the same as the inner surface structure of CNTs and, therefore, we can regard an XPS spectrum of a coated film as that of the inner surface of the resultant CNTs. According to Table 1, the inner layer of CNTs (the outer layer of the coated film) is of a high B/C atomic ratio together with a relatively low N/C ratio, and on the contrary, a lower B/C ratio and a higher N/C ratio are found for the outer layer of CNTs. Note that the thickness of the carbon layer deposited in each CVD step is a little lower than the escape depth of photoelectrons (about 2.5 nm), and thus XPS provides the information of the outer layer together with a small portion of the inner layer. Therefore, it is believed that the N-doped layer is free form B while the B-doped one is free from N. In summary, the XPS results confirm the formation of double coaxial CNTs of N-doped outer and B-doped inner multiwalls.

Table 1 Atomic composition (by XPS) of outer and inner layers of the double coaxial CNTs

Sample	N/C	B/C
Coated film (CNT inner layer)	0.022	0.125
CNT (CNT outer layer)	0.060	0.025

2. Triple coaxial CNTs------sandwich structure

By performing another acetonitrile CVD using the double carbon coated AAO film as a template, we obtained the triple coaxial CNTs with inner and outer layers doped by N and the middle one doped by B. By the TEM observation, we can see that the third CVD increases the wall thickness uniformly, as we observed in the cases of the first two CVD steps, and the wall thickness of the triple CNTs is 5.5 nm.

The chemical composition of carbon layer coated on the AAO film prepared by the first CVD is believed to be the same as that of the outer layer of triple coaxial CNTs, and also should the compositions of carbon layers, deposited in the second and third CVD, be corresponding to those of the middle and inner layers of the triple CNTs, respectively. Table 2 presents the chemical composition of the carbon layer deposited on the AAO film by each CVD step, that is, accordingly, the composition of the outer, middle and inner layers of the triple CNTs. Thus, it is concluded that the outer and inner layers of the triple CNTs are doped by N and the middle one is doped by B.

Table 3 presents the structural parameters of the CNTs prepared by single-, bi-, and tri-step CVD. Among the three samples, the single stack N-doped CNTs, prepared by the first CVD, has the largest d_{002}. With the deposition of B-doped carbon layer by the second CVD, d_{002} is reduced for the double coaxial CNTs of N-doped and B-doped multiwalls. With another CVD of N-doped carbon, the triple CNTs have the larger d_{002} than the double CNTs. The above results imply that the B-doped layer has better crystallinity than the N-doped layers. Moreover, among the three samples, the single stack CNTs have the smallest and the triple CNTs have the largest Lc, which accords with the finding that the wall thickness of CNTs increases with each CVD step.

Table 2 Surface atomic composition (by XPS) of carbon coated AAO films prepared by single-, bi-, or tri-step CVD

CVD sequence	1st CVD	2nd CVD	3rd CVD
N/C	0.076	0.022	0.059
B/C	0	0.125	0.021

Table 3 Structural parameters of the single-stack N-doped (single CVD), double coaxial (bi-CVD), and triple coaxial (tri-CVD) CNTs

Sample	Single stack	Double coaxial	Triple coaxial
d_{002}(nm)	0.359	0.350	0.353
Lc (nm)	2.0	3.2	4.5
Thickness by TEM (nm)	1.5	4.0	5.5

Conclusions

Double and triple coaxial CNTs of N-doped and B-doped multiwalls have been prepared by the template technique for the first time. The novel materials with uniform diameter are possibly the prototypes of p-n and n-p-n nanojunctions, and possess great importance in future nanoelectronic application of CNTs.

Acknowledgment

This work was partly supported by the Japan Society of Promotion of Science (JSPS) postdoctoral fellowship (P 03282) for foreign researchers.

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