Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp151-152

Single Wall Carbon Nanotube Growth from Boron- and Nitrogen-Containing Feedstocks

Satoru Suzuki[1] and Hiroki Hibino[1]

[1]NTT Basic Research Laboratories, NTT Corporation,
3-1 Morinosato- Wakamiya, Atsugi, Kanagawa 243-0198, Japan

1. Introduction

The excellent electronic and mechanical properties and chemical stability of single wall carbon nanotubes (SWCNTs) make them attractive as a constituent of future nanoelectronics. For electric device applications, controlling the conduction type (namely, n or p) of SWCNTs is crucial. So far, the conduction type of semiconducting SWCNT devices has mainly been controlled by chemical functionalization of the SWCNT channel [1]. Alternatively, the conduction type can be controlled by the choice of electrode metal because barrier heights for electrons and holes at the contact depend on the metal work function [2]. The carrier type control could be more simply achieved by direct growth of doped SWCNTs. For example, boron and nitrogen doping to SWCNTs is expected to result in p- and n-type conduction, respectively. However, there have been a limited number of studies on the direct growth of doped SWCNTs. Especially, only a few attempts at thermal chemical vapor deposition (CVD) of doped SWCNTs have been reported [3-6], although the CVD technique has a great potential for highly controlled doped SWCNT growth, such as precise tuning of the carrier concentration and p-n junction formation.

More interestingly, co-doping of boron and nitrogen into SWCNTs may lead to bandgap tuning by means of composition control. As is well known, the bandgap of a SWCNT strongly depends on its chirality, which is still difficult to control. This is essentially because the π bands cross the Fermi level in graphene. If a nanotube could be formed from a semiconducting $B_xC_{1-x-y}N_y$ sheet, its electronic structure would be mostly determined by its composition, rather than by its chirality. In fact, the bandgap of BN nanotubes is reported to be almost independent of chirality [7].

In this study, we grew B- and N-doped SWCNTs directly on a substrate by the CVD method using boron or nitrogen containing feedstock. We also successfully synthesized BN-doped SWCNTs by supplying both boron and nitrogen containing feedstocks. The doped SWCNTs showed systematic spectral shifts of Raman peaks, which are considered to be direct indications of carrier doping.

2. Experimental Procedures

B- and N-doped SWCNTs were grown on an oxidized Si substrate by using the thermal CVD technique. Triisopropyl borate ($C_9H_{21}BO_3$) and benzylamine (C_7H_9N) were the boron and nitrogen feedstocks, respectively. Both materials also served as a carbon feedstock, and we did not use any other carbon feedstock. That is, B- or N-doped SWCNTs were grown by using 100 % triisopropyl borate or benzylamine. For the growth of BN-doped SWCNTs, triisopropyl borate and benzylamine were supplied at a rate of approximately 1:1.

Scanning electron microscopy (SEM: Zeiss, Ultra55) observation was performed at an acceleration voltage of ~1 kV. Resonance Raman measurements (Renishaw, inVia) were performed at the excitation wavelength of either 532 or 785 nm.

3. Results and Discussion

Figures 1(a) and (b) show SEM images of B- and N-doped SWCNTs, respectively. SWCNT growth from triisopropyl borate [5] and benzylamine [6] with MgO powders as a catalyst support have recently been reported. In contrast, in this study, high density SWCNTs were grown directly on the substrate without any catalyst support. CVD growth of SWCNTs from benzylamine diluted by ethanol was also reported [4]. In that work, it was reported that SWCNT growth is hindered when the benzylamine content is larger than 33 weight percent. We observed no such hindrance of SWCNT growth, although we used non-diluted feedstocks. Moreover, we were able to synthesize SWCNTs by supplying both triisopropyl borate and benzylamine, as shown in Fig. 1(c). Atomic force microscopy (AFM) and transmission electron microscopy (TEM) observations showed that the diameter of those SWCNTs is 1-2 nm.

The Raman spectrum of G and D band regions of SWCNTs grown from both triisopropyl borate and benzylamine is shown in Fig. 2. SWCNTs grown from either triisopropyl borate or benzylamine also showed a similar spectrum (not shown). For reference, the spectrum of undoped SWCNTs grown from ethanol is also shown in the figure. We can see that the D band intensity of the BN-doped SWCNTs is considerably small. This is in marked contrast to a previous study on N-doped SWCNTs [3], in which the D band intensity was comparable to or even larger than that of the G band. The so-called D' band, which is observed in highly disordered graphitic materials, is not visible, although it was observed in the previous study [3]. These results mean that the crystallinity of the doped SWCNTs is fairly good.

Figure 2 also shows that the G band position in the BN-doped SWCNTs is shifted to the higher wavenumber side by 4 cm^{-1}. A hardening of the G band has been observed in field-induced doping experiments and has been

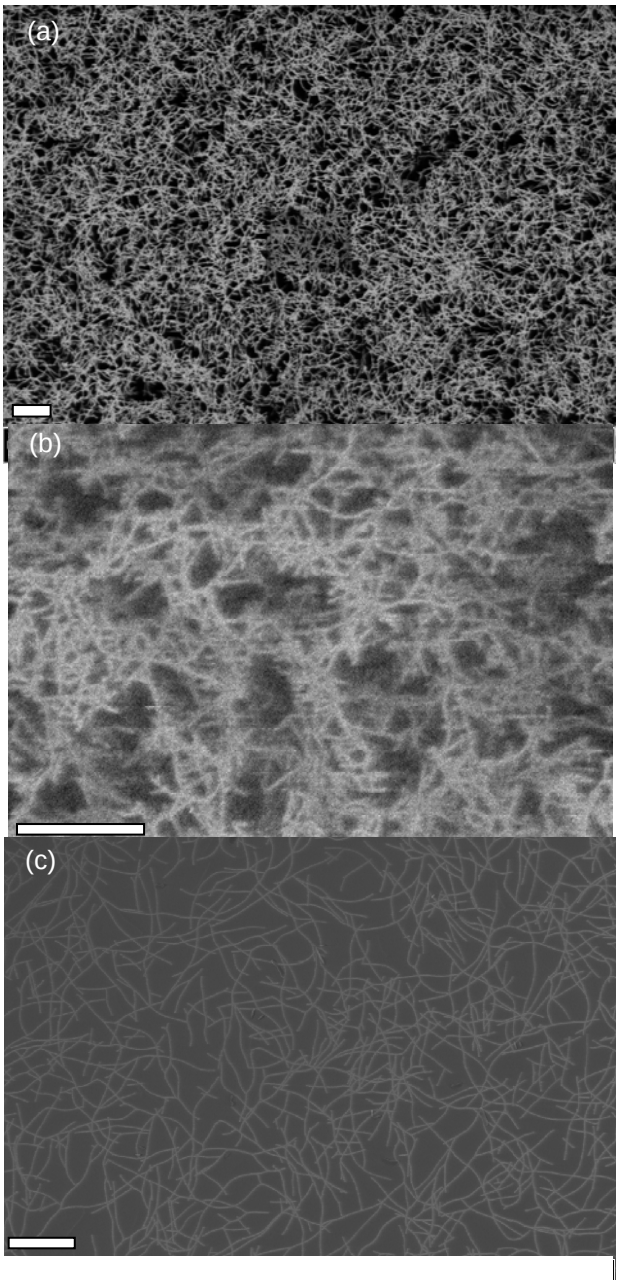

Fig. 1 SEM images of SWCNTs grown from (a) triisopropyl borate, (b) benzylamine, and (c) triisopropyl borate (50 %) and benzylamine (50 %). Scale bar: 1 μm.

interpreted as renormalization of phonon energy through electron-phonon coupling induced by a field-induced Fermi level shift [8]. We therefore think that the hardening of the G band in the BN-doped SWCNTs is due to a Fermi level shift from the neutral position and thus to carrier doping into the SWCNTs. Assuming that the SWCNTs are semi-conducting ones of 1.5-nm diameter, the carrier density is estimated to be significantly large, ~0.5 %. Similarly, a hardening of D band by about 10 cm^{-1} is also observed in Fig. 2. We think that the D band shift can also be regarded as a consequence of the carrier doping. In fact, a field-induced hardening of the G' (2D) band has been observed [9]. We think that the carrier doping into the

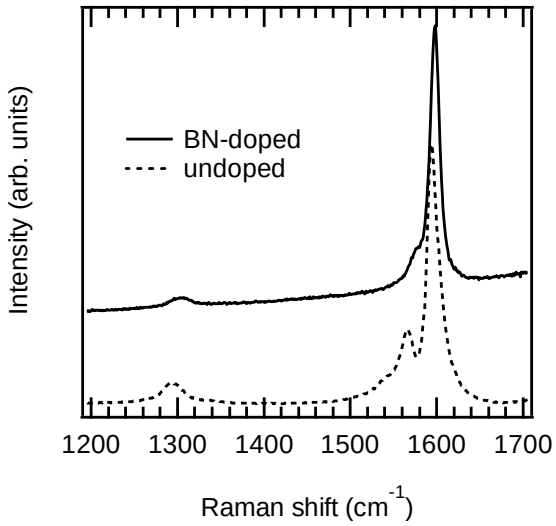

Fig. 2 Raman spectra of BN-doped and undoped SWCNTs. The excitation wavelength is 785 nm.

BN-doped SWCNTs is due to slight difference in the amounts of B and N. The results also show the possibility of carrier doping of bandgap-tuned $B_xC_{1-x-y}N_y$ SWNTs.

4. Conclusion

B-, N-, and BN-doped SWCNTs were successfully grown by using thermal CVD method from triisopropyl borate and benzylamine. Blueshifts of the G and D bands in Raman spectra were clearly observed for the doped SWCNTs, which is an indication of considerable carrier doping. Our results indicate the possibility of both bandgap tuning and carrier doping of SWNTs.

Acknowledgements

We would like to express sincere thanks to Dr. K. Ajito of NTT Microsystem Integration Laboratories for his support on the Raman measurements. We also thank Y. Sakai for preliminary experiments.

References

[1] C. Klinke, J. Chen, A. Afzali, and Ph. Avouris, Nano Lett. **5** (2005) 555.
[2] Z. Zhang et al, Nano Lett. **8** (2008) 3696.
[3] G. Keskar, R. Rao, J. Luo, J. Hudson, J. Chen, and A. M. Rao, Chem. Phys. Lett. **412** (2000) 14.
[4] F. Villalpando-Paez et al., Chem. Phys. Lett. **424** (2006) 345.
[5] P. Ayala, M. H. Rummeli, T. Gemming, E. Kauppinen, H. Kuzmany, and T. Pichler, Physica Stat. Sol. B **245** (2008) 1935.
[6] P. Ayala et al., J. Phys. Chem. C **111** (2007) 2879.
[7] A. Rubio, J. L. Corkill, and M. L. Cohen, Phys. Rev. B **49** (1994) 5081.
[8] J. C. Tsang, M. Freitag, V. Perebeinos, J. Liu, and Ph. Avouris, Nat. Nanotechnol. **2** (2007) 725.
[9] P. M. Rafailov, J. Maultzsch, C. Thomsen, U. Dettlaff-Weglikowska, and S. Roth, Nano Lett. **9** (2009) 3343.