Pressure-induced superconductivity in boron-doped Buckypapers

J. Nakamura,[1] M. Matsudaira,[1] J. Haruyama,[1,2,a)] H. Sugiura,[3] M. Tachibana,[3] J. Reppert,[4] A. Rao,[4] T. Nishio,[2] Y. Hasegawa,[2] H. Sano,[2] and Y. Iye[2]
[1]*School of Science and Engineerings, Material Science Course, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8581, Japan*
[3]*International Graduate School of Arts and Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama, Kanagawa 236-0027, Japan*
[4]*Department of Physics and Astronomy, Center for Optical Materials Science and Engineering Technologies, Clemson University, Clemson, South Carolina 29634, USA*

(Received 14 July 2009; accepted 8 September 2009; published online 6 October 2009)

We show creation of paperlike thin film (Buckypaper) consisting of pseudo-two-dimensional network of boron-doped single-walled carbon nanotubes (B-SWNTs) within weakly intertube van der Waals coupling (IVDWC) state. It was formed by sufficiently dissolving as-grown ropes of B-SWNTs and densely assembling them on silicon substrate. We find that superconducting transition temperature (T_c) of 8 K under absent pressure can be induced up to 19 K by applying a small pressure to the film and that a frequency in the radial breathing phonon drastically increases with applying pressure. Discussion about IVDWC and distribution of B-SWNTs diameter imply the strong correlation. © *2009 American Institute of Physics*. [doi:10.1063/1.3242016]

Recently, thin films consisting of assembled single-walled carbon nanotubes (SWNTs) are attracting considerable attention for application to electrically conductive transparent films, flexible display, and high-mobility flexible electronics using carbon nanotubes (CNTs)-field effect transistors.[1] It is opening up a door for new possibility of CNTs as well as graphene because it requires no exact positioning of individual CNTs on substrates for fabricating electronic circuits and is also easily fabricated even on a plastic substrate. If the thin films are highly conductive, they are much more valuable for any applications.

It is well known that ultimately conductive material is superconductors. Indeed, we reported that uniform thin films of boron-doped SWNTs (B-SWNTs) could exhibit Meissner effect at a transition temperature (T_c) of 12 K.[2] However, the obtained T_c was still low, inspite that one expects higher T_c for the carbon-based Bardeen–Cooper–Schrieffer-type superconductors due to the high phonon frequency and Debye temperature originating from small mass of carbon atoms. In CNTs,[2–5] one can expect even much higher T_c because (1) the curvature resulting from a small tube diameter (e.g., 0.5 nm) can yield sp^3 hybrid orbitals and also a strong coupling between the σ-π electrons and radial breathing mode (RBM) in phonon[6] and (2) the alignment of the Fermi level (E_F) to a van Hove singularity in the one-dimensional electronic density of states (EDOS) can lead to an extremely high EDOS.[6,7]

Here, in Ref. 2, we proposed the following methods for increasing T_c: (1) employing boron concentration (N_B) $\leqslant 1$ at. %, (2) using B-SWNTs with diameter $\leqslant 1$ nm, (3) forming a dense assembly of thin films, and (4) applying pressure to the films. Based on these, in the present study, we report that the onset T_c can be enhanced up to 19 K by applying a small pressure to the Buckypapers.

a)Author to whom correspondence should be addressed. Electronic mail: j-haru@ee.aoyama.ac.jp.

B-SWNTs were synthesized by the pulsed laser vaporization technique,[2] in which N_B was controlled by the amount of elemental B mixed with the Co/Ni-catalyst-impregnated targets. Substitutional B doping was confirmed by nuclear magnetic resonance (NMR) (JNM-ECX400) and Raman spectra measurements.[2] Here, structural difference between conventional B-SWNT film reported in Ref. 2 and the present Buckypaper is whether ropes of B-SWNTs with diameters of ~10 nm are included or not. Conventional film consists of ropes of B-SWNTs with diameters of ~10 nm, while Buckypaper does not include such thick ropes and consists of assembled individual B-SWNTs or very thin ropes. In order to realize this difference, Buckypaper was prepared using times for centrifuge and ultrasonication, which are much longer than those for conventional film (see supplemental material).[8]

Figure 1(a) shows the top-view field-emission scanning electron microscope (FESEM) images of the B-SWNTs thin films prepared by our previous method mentioned above. Figure 1(a) reveals that the film still consists of as-grown thin ropes of B-SWNTs with ~10 nm diameter, which are bundles of SWNTs within strongly intertube van der Waals coupling (IVDWC) triangular lattice in an orderly manner like a graphite.

On the other hand, Fig. 1(b) shows the FESEM image of the present novel thin film consisting of B-SWNTs fabricated by the above-mentioned method. This figure is clearly different from Fig. 1(a). It implies the absence of as-grown B-SWNTs ropes with 10 nm-order diameter and indicates that the dispersed SWNTs are assembled into continuous and spread thin film of individual B-SWNTs. The film can be a pseudo two-dimensional network of IVDWC SWNTs deposited in the form of paper fibers, the so-called Buckypaper.[1]

It is known that the strength of the IVDWC in the Buckypaper is weaker than that in as-grown ropes of SWNTs, because the Buckypaper was formed by assembling SWNTs in disordered manner once after sufficient dissolving

 © 2009 American Institute of Physics

Downloaded 08 Oct 2009 to 133.2.251.40. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

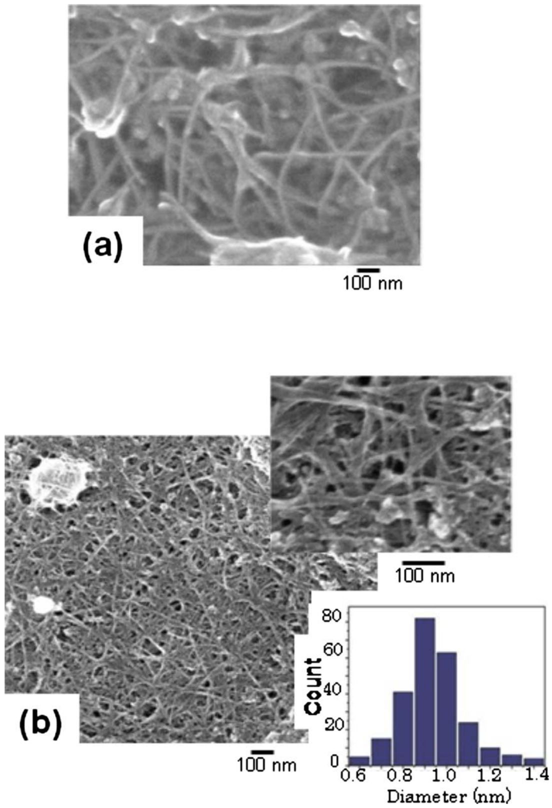

FIG. 1. (Color online) Top-view FESEM images of (a) the conventional B-SWNT films consisting of as-grown thin ropes (Ref. 2) and (b) the present thin film (i.e., Buckypaper) consisting of B-SWNTs without ropes [see supplemental material (Ref. 8)]. Upper inset: High-resolution image. Lower inset: Distribution of diameters confirmed by TEM observation of individual B-SWNTs.

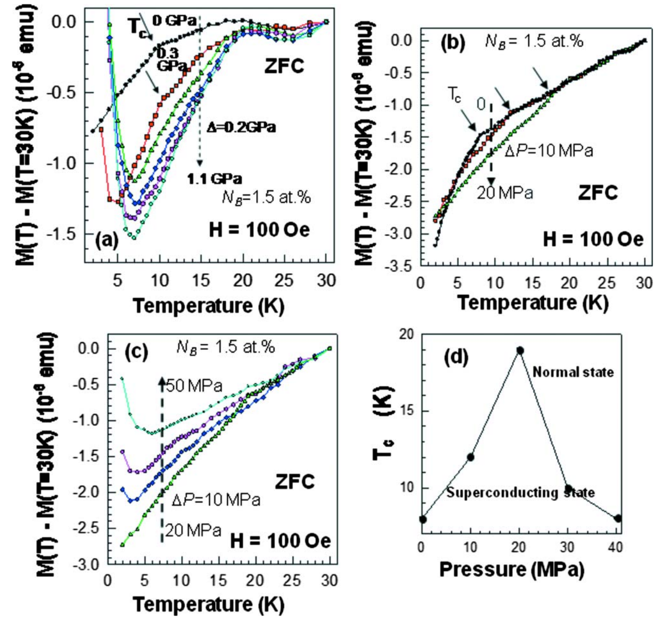

FIG. 2. (Color online) Pressure dependence of normalized magnetization vs temperature relationships for samples shown (a) in Fig. 1(a) (conventional B-SWNT film) and (b) in Fig. 1(b) (B-Buckypaper) at $P \leq 20$ MPa and (c) $P \geq 20$ MPa in zero-field cooled regime. They were measured using a superconducting quantum interference device (Quantum Design, MPMS) and by embedding the samples in an oil-filled cell for applying pressure. Arrows in [(a) and (b)] mean the T_c. (d) Pressure dependence of T_c confirmed from [(b) and (c)].

of the as-grown SWNT ropes. SWNTs are not closely-packed together into a triangle lattice and some parts of carbon atoms are even within incommensurate state in the Buckypaper.

We carried out magnetization measurements on the samples shown in Fig. 1. Figure 2(a) shows the normalized magnetization $[M_N = M(T) - M(T=30\text{ K})]$ of the sample shown in Fig. 1(a) as a function of temperature (T) and pressure (P) at a magnetic field (H) of 100 Oe. An evident T_c of $\sim$8 K as shown by an arrow is observed at $P=0$. We have confirmed that diamagnetism observed at $T < T_c$ is attributed to Meissner diamagnetism for type-II superconductivity (SC) on the basis of the magnetic field dependence of M_N (i.e., $M_N - H$ relationship) at each temperature following Ref. 2 while the diamagnetism at $T > T_c$ that appears gradually from high temperatures is due to the graphitic structure of the B-SWNT ropes.[2]

Figure 2(a) indicates that the T_c value of 8 K does not change even at P as large as 3000 MPa. As P increases further, the graphitic diamagnetism becomes well pronounced. Then, T_c corresponding to Meissner diamagnetism becomes no longer apparent. This tendency is also consistent with Fig. 1(a) showing presence of many ropes of B-SWNTs that produce a large graphitic diamagnetism by the strong IVDWC because applied pressure drastically induces this coupling.

Figures 2(b) and 2(c) show the $M_N - T$ relationships for the B-Buckypaper shown in Fig. 1(b) at $P \leq 20$ MPa [Fig. 2(b)] and $P \geq 20$ MPa [Fig. 2(c)]. At $P=0$, T_c is evident at $T = \sim 8$ K in Figs. 2(b). Meissner diamagnetism at $T \leq T_c = 8$ K and graphitic diamagnetism at $T \geq T_c = 8$ K could be identified from the $M_N - H$ relationships, as in the case of Fig. 2.[2]

In contradiction to Fig. 2(a), as P slightly increases, T_c shifts to higher temperatures over two times as apparently shown in Fig. 2(b). In contrast, in Fig. 2(c), as P exceeds 20 MPa, M_N increases almost over the entire temperature region, and the T_c becomes unclear. The overall $T_c - P$ relationship is summarized in Fig. 2(d). These behaviors are very different from those shown in Fig. 2(a) and suggest that the pressure dependence of the Meissner effect is highly sensitive to the structure of the B-SWNT assembly.

Moreover, Fig. 2(c) indicates that graphitic diamagnetism appearing at $T > T_c$ does not become stronger with an increase in $P > 20$ MPa in contradiction to that shown in Fig. 2(a). This behavior is consistent with the absence of the B-SWNT ropes in the B-Buckypaper as shown in Fig. 1(b) and supports the weak IVDWC among the B-SWNTs. Furthermore, in Fig. 2(c), amplitude of magnetization drops decreases with increasing pressure. Drastic increase in magnetization values below about 4 K is also observable. These behaviors are very similar to magnetic-field dependence of M-T curves, which were observed in the samples including a large-volume ferromagnetic catalyst. Thus, it might be due to residual Co/Ni catalyst. When pressure is applied, the residual catalyst in the Buckypaper may accidentally get together to near parts, resulting in formation of a large catalyst. It may cause the increase in magnetization values below 4 K even under a constant field value of 100 Oe and also eliminate Meissner diamagnetism.

Here, we clarify the origin for the pressure-induced T_c in the Buckypaper. Occurrence of the increase in phonon frequency can be at least considered by applying pressure. In

Downloaded 08 Oct 2009 to 133.2.251.40. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

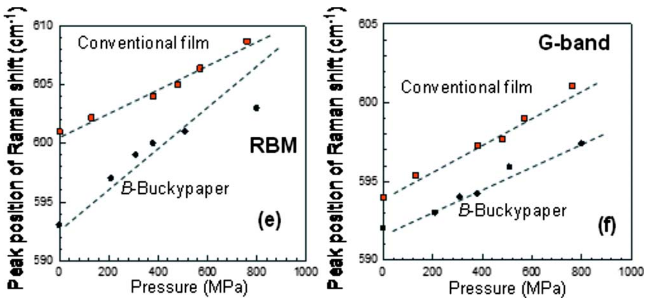

FIG. 3. (Color online) Relationship of peak positions of Raman spectra vs pressure for samples shown in Fig. 1; (a) RBM and (b) G-band mode. Spectra were measured by an irradiating Ar laser of 488 nm wavelength at room temperature. The peak positions were determined from the fitting peaks.

order to reveal this presence, we explored the pressure dependence of the Raman spectra for the sample shown in Fig. 1. The results are summarized in Fig. 3. The RBM reflects the out-of-plane phonon along tube-diameter direction, and the G-band mode does the in-plane phonon along tube longitudinal direction.

From Fig. 3, it is evident that at $P=0$, all the peak positions observed for the *B*-Buckypaper are lower than those observed for the conventional film in both the RBM and the G-band mode. This trend is consistent with the observation in Fig. 1 [i.e., presence of as-grown ropes in Fig. 1(a) and its absence in Fig. 1(b)] and proves that strength of IVDWC in the Buckypaper is weaker than that in the as-grown ropes of SWNTs. This is because it is known that strong IVDWC makes the phonon frequency increase in ensembles of SWNTs due to reduction of free vibration of lattices in individual SWNTs.[9,10]

With an increase in P, all the peak positions show a monotonic upshift for ratios of $\sim 1\ \mathrm{cm}^{-1}/100$ MPa and $\sim 2\ \mathrm{cm}^{-1}/100$ MPa in the RBM [Fig. 3(a)] and $\sim 0.7\ \mathrm{cm}^{-1}/100$ MPa and $\sim 0.6\ \mathrm{cm}^{-1}/100$ MPa in the G-band mode [Fig. 3(b)]. Only the RBM shows phonon softening above $P=400$ MPa. The RBM peak position for the B-Buckypaper shows the significantly high upshift ratio, which is twice the upshift in RBM observed for the conventional film and three-times larger than those for G-band modes.

This is also because the IVDWC in the B-Buckypaper is weaker than that in the as-grown ropes of SWNTs at $P=0$ as mentioned above and, thus, free lattice vibration for the RBM in individual SWNTs is not strongly restricted by IVDWC. Hence, as applied pressure increases, intertube spacing decreases and the IVDWC drastically increases only in the B-Buckypaper. Consequently, the RBM phonon frequency significantly upshifts in the B-Buckypaper because the free lattice vibration is suppressed particularly for the RBM, which is the out-of-plane phonon mode along tube-diameter direction.

Existence of the strong correlation of the increase in this RBM phonon frequency with the observed pressure-induced T_c in the B-Buckypaper is obvious between Figs. 2 and 3. However, the applied pressure in Figs. 2(b) is as small as 20 MPa, which corresponds to only an the RBM frequency increase of 0.4 cm^{-1} in Fig. 3(a). Thus, in order to conclude the increase in the RBM phonon frequency as the origin for the pressure-induced T_c, strong electron-phonon interaction must be identified in the B-SWNTs of the Buckypaper based on lower inset of Fig. 1(b) (see supplemental materials).[8]

In contrast, although phonon modes slightly increased with applying pressure also in the conventional thin films in Fig. 3, the T_c did not change in Fig. 2(a). This is due to reduction in the electron-phonon interactions in the rope structure. It is known that strong IVDWC in the rope structure weakens the electron-phonon coupling.[6]

The successful fabrication of the B-Buckypaper studied herein shows the feasibility of producing flexible superconducting films useful for application to transparent films and electronics.

The authors thank H. Fukuyama, J. Akimitsu, M. Dresselhaus, H. Shinohara, S. Saito, S. Maruyama, R. Saito, T. Ando, S. Bandow, J. Gonzalez, H. Bouchiat, and T. Koretsine for the encouragement provided and for fruitful discussions.

[1] J. A. Fagan, M. L. Becker, J. Chun, and E. K. Hobbie, Adv. Mater. **20**, 1609 (2008) and APS Homepage (http://www.aps.org /about/physics-images/buckypaper.cfm); T. Takenobu, N. Miura, S.-Y. Lu, H. Okimoto, T. Asano, M. Shiraishi, and Y. Iwasa, Appl. Phys. Express **2**, 025005 (2009); Q. Cao, H. Kim, N. Pimparkar, J. P. Kulkarni, C. Wang, M. Shim, K. Roy, M. A. Alam, and J. A. Rogers, Nature (London) **454**, 495 (2008).
[2] N. Murata, J. Haruyama, J. Reppert, A. M. Rao, T. Koretsune, S. Saito, M. Matsudaira,and Y. Yagi, Phys. Rev. Lett. **101**, 027002 (2008).
[3] I. Takesue, J. Haruyama, H. Shinohara, S. Maruyama, N. Kobayashi, S. Chiashi, and S. T. Sugai, Phys. Rev. Lett. **96**, 057001 (2006).
[4] N. Murata, J. Haruyama, Y. Ueda, M. Matsudaira, H. Karino, Y. Yagi, E. Einarsson, S. Chiashi, S. Maruyama, T. Sugai, N. Kishi, and H. Shinohara, Phys. Rev. B **76**, 245424 (2007).
[5] M. Matsudaira, J. Haruyama, S. Maruyama, H. Shinohara, N. Murataa, Y. Yagid, E. Einarssonb, and T. Sugaic, Physica E (Amsterdam) **40**, 2299 (2008).
[6] R. Barnett, E. Demler, and E. Kaxiras, Phys. Rev. B **71**, 035429 (2005).
[7] T. Koretsune and S. Saito, Phys. Rev. B **77**, 165417 (2008).
[8] See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3242016 for (1) film preparation, (2) difference in pressure ranges for magnetization and Raman measurements, (3) possibility of strong electron-phonon coupling in very thin SWNTs, and (4) resistance measurement.
[9] U. D. Venkateswaran, A. M. Rao, E. Richter, M. Menon, A. Rinzler, R. E. Smalley, and P. C. Eklund, Phys. Rev. B **59**, 10928 (1999).
[10] U. D. Venkateswaran, A. M. Rao, P. C. Eklund, E. A. Brandsen, U. Schlecht, E. Richter, I. Loa, and K. Syassen, Phys. Status Solidi B **223**, 225 (2001).

Downloaded 08 Oct 2009 to 133.2.251.40. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp