Meissner effect in films of ropes of boron-doped single-walled carbon nanotubes; Correlation with applied pressure and boron-doped multi-walled nanotubes

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Abstract

Superconductivity in carbon nanotubes (CNTs) is attracting considerable attention. Recently, we have reported successful boron doping into single-walled CNTs (SWNTs) and also revealed its correlation with superconductivity. In the present study, we report results of pressure-applied magnetization measurements in films consisting of ropes of boron-doped SWNTs. It reveals that Tc and magnitude for Meissner effect is mostly independent of applied pressure, while magnitude of graphite diamagnetism drastically increases as pressure increases. We also report result of resistance measurements in the samples and also correlation of boron doped SWNTs with multi-walled CNTs, in which we reported superconductivity previously.

1. Introduction

It is known that the small mass of carbon can promote high transition temperature (Tc) in Bardeen-Cooper-Schrieffer (BCS) -type superconductivity (SC) and novel behaviors of SC can also be expected. Recently, new carbon-based superconductors with order of Tc of ~10K (calcium- intercalated graphite (C₆Ca) and highly boron (B)- doped diamond [1-3]) have been discovered and higher Tc has been expected. In particular, the SC in a carbon nanotube (CNT), which is a rolled-up graphene sheet and a typical one-dimensional (1D) carbon conductor, is attracting considerable attention [4-8] for the following reasons: (1) The curvature resulting from a small diameter (~1 nm) can lead to formation of sp³ hybrid orbitals and σ-π mixed bands. Coupling of this σ-π electrons with radial breathing mode of phonon might bring high Tc [9]. (2) The alignment of the Fermi level (E_F) to a van Hove singularity (VHS) can also lead to high Tc due to the presence of an extremely large density of states (DOS) [9]. (3) It can provide an insight into the 1D electron correlation [7, 10-14]. Indeed, we have reported Tc as high as 12K in entirely end-bonded multi-walled CNTs (MWNTs) from viewpoint of an abrupt resistance drop.

Here, effective carrier doping is crucial for realizing high-Tc SC in any material. In fact, SCs in C₆Ca and B-diamond have been associated with it. Carrier doping into CNTs has also been studied in many previous works [15-17], including our present methods [15]. Nevertheless, correlation with carrier-doping has been never reported. Indeed, even in our previous finding of SC, presence of carriers in the MWNTs has not been clarified to date [7].
Only possibility of non-intentional boron doping through catalyst during CVD process has been discussed [7,8]. On the other hand, we have reported successful boron doping into single-walled CNTs (SWNTs) by mixing elemental boron into catalyst and realized Meissner effect with $T_c$ of 12K by assembling the boron-doped SWNTs ($B$-SWNTs) to thin film structures [18]. We found that 1. Boron concentration of the catalyst ($N_B > 4$ at.%) destroyed tube structure, 2. Lower $N_B$ values are favorable to occurrence of evident and higher $T_c$, and 3. High uniformity of the thin film is necessary for the SC.

Here, in this study, we report results of some new experiments of the $B$-SWNT thin films, i.e., high pressure magnetic measurement of the thin films consisting of ropes of $B$-SWNTs, electrical measurement of the films by fabricating FET structure on them, and also nuclear magnetic resonance (NMR) measurements of the MWNTs, in which we reported SC [7]. In particular, it is well known that applying high pressure drastically changes behaviors of SC. In the present thin films consisting of $B$-SWNTs, applying pressure enhances interaction among neighboring B-SWNTs. If loop current for Meissner effect flows across assembled $B$-SWNTs, this enhancement makes magnitude of the current flow stronger. Thus, it is expected that it changes behaviors of Meissner effect.

2. Sample preparation and characterization

We have used mostly the same high-uniformity $B$-SWNT thin films with $N_B = 1.5$ at. %, which were reported in ref.[18], for the present experiments. $B$-SWNT bundles(ropes) were synthesized using the pulsed laser vaporization technique [15]. Elemental boron and Co:Ni catalysts (0.5:0.5 at. %) were homogenously mixed with carbon paste and hot-pressed into 1” diameter targets. The YAG laser-generated products were characterized by high resolution transmission electron microscopy, NMR, and Raman spectroscopy as well as those in ref.[18].

Thin films consisting of these $B$-SWNTs were prepared by solubilizing the $B$-SWNTs in 5 mg/mL dichloroethane. Then, the solution was centrifuged for 48 h by Tomy, low-speed centrifuge in order to purify the SWNTs, and ultrasonication (As One, US cleaner) was carried out also for 20 h to separate the bundles (ropes) into individual $B$-SWNTs. Next, the solution was spin-coated at 500 rpm on a Si substrate to produce a highly homogeneous film consisting of assembled $B$-SWNTs. Finally, the thin films were annealed at 1600 °C for 1 h in order to entirely remove the residual catalyst.

Figure 1 shows AFM image of the film. It exhibits that the film consists of closely assembled ropes of the $B$-SWNTs with a rope diameter of about 10nm. This result is different from previous case in ref.[18], in which ropes were sufficiently dispersed to individual SWNTs. This is due to four-times shorter ultrasonication time (i.e., it was 80 h in [18]). However, because the sample also showed Meissner effect, we have used this condition in the present measurements.

3. Measurement results and discussions

3.1. High-pressure magnetization measurement

The magnetization measurements of the thin films consisting of $B$-SWNTs were performed using a superconducting quantum interference device (Quantum Design, MPMS), applying pressure between 0.3 – 1.1 GPa. At first, Fig. 2 shows normalized magnetization ($M_N = M(T) - M(T=40K)$) as a function of the temperature ($T$) ($M_N$-$T$ relationship) under zero-pressure in field-cooled (FC) and zero-field-cooled (ZFC) regimes in the highly uniform film with $N_B ~ 1.5$ at. % reported in ref. [18]. Evident drop in $M_N$ with a large slope value is
observed below \( T_c = 12 \text{ K} \) in the ZFC regime, and below \( T = \sim 8 \text{ K} \) in the FC regime. Interestingly, this value of \( T_c = 12 \text{ K} \) exactly agrees with the \( T_c \) value for an abrupt resistance drop observed in the array of entirely end-bonded MWNTs [7, 8].

In contrast, the small and gradual \( M_N \) drop observable at \( T_c > 12 \text{ K} \) in the ZFC regime is due to diamagnetism of graphite structure of assembled SWNTs and not associated with Meissner effect. Graphite diamagnetism in ensemble of SWNTs very gradually appears in \( M-T \) curves from high temperatures (e.g., \( > 50 \text{ K} \)) even in undoped samples and the amplitude does not decrease in \( M-H \) features even at high magnetic fields (e.g., \( > 2000 \text{ Oe} \)). They are very different from those in Meissner effect observed here. However, because the component is very small as the background (i.e., magnetization at \( T > 12 \text{ K} \) in Fig.2) in the samples shown here and different by respective samples, we could not entirely delete it in this study.

It is found that the magnitude of the drops observed in the \( M_N-T \) relationship becomes considerable at magnetic field \( (H) < \sim 1400 \text{ Oe} \) as \( H \) values increase. In contrast, it decreases for \( H > \sim 1400 \text{ Oe} \), and at \( H = \sim 3500 \text{ Oe} \), the magnitude becomes almost zero. This is typical behavior of type II SC as reported in refs.[8, 18]

In order to apply pressure, the thin films were immersed into oil-filled cells.

Here, Fig. 3(a) shows pressure dependence of \( M-T \) curves in ZFC regime in a thin film consisting of ropes of the \( B \)-SWNTs as shown in Fig.1. The \( M-T \) feature similar to Fig.2 is observable at zero-pressure and \( T_c \) is mostly \( 10 \text{ K} \) in this sample. As magnitude of pressure increases, positive \( M \) value itself increases in the entire temperature range. It should be noticed that magnetization drop in low temperature regime becomes significant with increasing pressure. Figure 3(b) shows pressure dependence of the \( M_N-T \) relationship of Fig.3 (a). It is found that amplitude of magnetization drops drastically increases at entire temperatures \(< 20\text{K} \) and \( T_c \) of \( \sim 10\text{K} \) for Meissner effect.
becomes ambiguous, as pressure increases. In particular, change in the $M_N-T$ relationship is significant under 0.3 GPa pressure. Although the $T_c$ becomes unclear, it still remains $T_c \approx \sim 10$K even under this high pressure. The $T_c$ entirely disappears under 0.7 GPa. On the other hand, magnetization drop at $T > 10$K becomes significant, as magnetic field increases. It eliminates Meissner effect at $T < \sim 10$K under pressure > 0.7 GPa. As mentioned above, this magnetization drop at $T > 10$K is attributed to graphite diamagnetism. These results imply the following pressure dependence of magnetization and that interpretation.

Amplitude for Meissner effect at $T < 10$ K is mostly independent of applied pressure, while amplitude of graphite diamagnetism at $T < 20$ K drastically increases as magnitude of the pressure increases. Here, interaction among neighboring SWNTs in the film increases with increasing pressure magnitude, when individual SWNTs are well dispersed. It should lead to enhancement of Meissner effect around ensemble of SWNTs including boron, while it should result in enhancement of graphite diamagnetism in ensemble of SWNTs without boron. However, as shown in Fig.2, amplitude of Meissner diamagnetism (volume fraction of SC) is very small in the present $B$-SWNT film (i.e., $10^{-5}$ emu). This is four order smaller than those for conventional Meissner effect (i.e., $10^{-2}$ emu). Indeed, we estimate superconducting coherence length of $\sim 10$ nm [18].

These two things suggest a possibility that the loop current for Meissner effect is confirmed in one rope of $B$-SWNT, because the present film consist of ropes with the diameter of $\sim 10$nm as shown in Fig.1. Because interaction among neighboring $B$-SWNTs in a rope is conventionally very strong as it was synthesized, it does not mostly change even under high pressure. This well explains the present result (i.e., mostly constant amplitude of Meissner effect at $T < 10$K as mentioned above).

In contrast, loop current for graphite diamagnetism can occur even among neighboring ropes of no-boron-doped SWNTs within a large volume fraction. Interaction among these ropes in a thin film should drastically increase as magnitude of the pressure increases. This is consistent with drastic increase in graphite diamagnetism at $T < 20$ K. On the other hand, the critical temperature of 20 K for the graphite diamagnetism is mostly constant even with the increase in magnitude. This implies that magnitude of loop current both for graphite diamagnetism has correlation with only magnitude of those diamagnetisms.

In order to clarify correlation of Meissner diamagnetism with applying pressure more evidently, thin films consisting of further dispersed SWNTs (e.g., in rope with diameter < 5nm) and also increase in volume fraction of $B$-SWNTs are required.

### 3.2. Resistance measurements

![Figure 4](image-url)

**Figure 4.** Result of zero-voltage resistance measurements of FETs fabricated on $B$-SWNT thin films with $N_B=1.5$ at.% used for Fig.3 (a) and the other sample (b). Resistance was measured three times at each temperature and noted by different symbols in (a). **Inset of (a):** SEM top view of Au/Ti electrode pattern of a FET fabricated on the film. In order to detect very small superconducting area, many source and drain electrode fingers were patterned within 300nm spacing.
Here, it is indispensable to detect resistance drop down to zero ohm as well as detecting Meissner effect for identification of SC. However, the volume fraction of superconducting region is extremely small as mentioned above. This suggests that the area of SC might be only a few μm scales. Thus, in order to detect this SC region, we patterned source and drain finger electrodes (Ti/Au) within 300 nm spacing on the B-SWNT film as many as possible and investigated electrical features. Figure 4 shows two examples of the resistance measurement results in the sample used for Fig. 3 (Fig.4(a)) and the other sample(Fig.4(b)).

In Fig.4(a), the resistance slightly drops at T = 10 K and becomes unstable (i.e., it shows different values for three-times measurements). Then, it drastically and abruptly drops to zero ohm at Tc = 5 K. This implies possibility of superconducting transition, because T = 10 K is in good agreement with Tc of Meissner effect in Fig.3 and also the magnitude of the drop is as large as ~1/5. The instability might originate from poor contact between electrodes and the B-SWNTs. Also in Fig.4(b), we can confirm an abrupt resistance drop starting from Tc = 3K with the magnitude of the drop as large as ~1/3. Only SC can be an origin for such a large and abrupt resistance drop in our system.

However, when we repeated measurements with applying further voltages or magnetic fields, the resistance drops disappeared and only high resistance at T > Tc remained in both samples. This might mean that small superconducting region was destroyed by applied high energy or concentration of superconducting current. At present stage, most of samples are very weak for repeated measurements with applying electrical and magnetic fields. Thus, increase of superconducting volume fraction and improvement of FET structures are indispensable for detecting resistance drops.

### 3.3. Correlation with superconductivity in MWNTs

As mentioned above, importantly the observed highest Tc of 12K for Fig.2 is exactly the same as that in the entirely end-bonded MWNTs, which we reported SC previously [7]. But we could not show evidence of carrier doping in ref.[7] and suggested only a possibility of boron doping via catalyst during CVD process [8]. “The Tc = 12K” is also in good agreement with that in C6Ca [1, 2]. Moreover, Ishii et al. have recently reported a resistance drop at Tc = 12K in a FET using an isolated B-MWNT as the current channel. Hence, it can be a “Magic Number”.

![Figure 5. Results of NMR measurement of B-MWNTs synthesized with N_B = 1 ~ 3 at. % catalyst (upper three) reported in ref. [7, 8] and H3BO3 (lowest) as a reference. The Fe/Co catalyst was electrochemically deposited into the bottom ends of alumina membrane. H3BO3 was occasionally used for only activation of chemical reaction for Fe/Co catalyst.](image)

Here, Fig.5 shows result of NMR measurement of the MWNTs, which were synthesized from catalyst with different N_B values, reported in Ref.[7, 8]. It evidently shows NMR peaks, which are similar to those in the B-SWNTs reported in ref.[18] and implies presence of boron-carbon chemical bonds in the MWNTs. In particular, the MWNTs with N_B = ~2 at.%, which showed the most evident SC with the highest possibility, exhibited the highest peak height. This is mostly consistent with the result reported in ref[18], which implied that lower N_B value was favorable to appearance of evident SC. Thus, the common Tc = 12K for the present SC in B-SWNT films and the previous SC in B-MWNTs [7, 8] implies presence of common origins for ensemble of B-CNTs. One of the candidates for the mechanism can be the best alignment of E_F to a VHS under such lows N_B values [18, 20] and suppression of one-dimensional quantum effect (e.g., repulsive Coulomb interaction in Tomonaga-Luttinger liquid) [19], which tends to obstruct occurrence of SC, by assembled structures. In contrast, because C6Ca has a different electronic structure (e.g.,difference in sp² and sp³ orbitals), the agreement of Tc may be occasional.
5. Conclusion

We have shown the results of high-pressure magnetization measurements in the films consisting of the ropes of boron-doped SWNTs. It revealed that $T_c$ and magnitude for Meissner effect was mostly independent of applied pressure, while magnitude of graphite diamagnetism drastically increased as pressure increases. We have also reported the result of resistance measurement and correlation of boron doping with SC in MWNTs. Consequently, we suggested that assembling of well dispersed $B$-CNTs was important.

The present results assure that applying high pressure to thin films consisting of sufficiently dispersed $B$-SWNTs with a larger volume fraction could lead to considerably high $T_c$. Homogeneously assembled $B$-CNTs are promising as a novel structure which is expected to open doors to the fields of carbon-based SC.

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