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Realization of high-temperature superconductivity in carbon-nanotubes and its low power applications

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14. ABSTRACT

Superconductivity (SC) is a hot topic in condensed matter physics and also key factor for applications to zero-emission energy system. In particular, SC in carbon nanotubes (CNTs) has been expected to have high transition temperature (Tc), because of its high phonon frequency due to the small mass, extremely high one-dimensional (1D) electronic density of state (EDOS) due to van Hove singularity, and strong electron-phonon coupling between a radial breathing phonon mode and hybrid orbital electrons. Previously, I tried to realize high-Tc SC in thin films consisting of randomly placed CNTs based on such advantages. Moreover, I applied ionic-gel(liquid) gating to the CNT thin films in order to cause extremely high EDOS on the surface and obtained Tc as high as 38K, however its reproducibility was too poor. Here, in the present work, I use novel solution (i.e., hexadecyltrimethylammonium bromide (CTAB)) to chemically modify CNT surface and create thin films consisting of highly oriented (aligned) CNTs with flat and homogeneous surface, which should resolve the problem of poor reproducibility and realize high-Tc SC. High reproducibility is obtained in partially oriented CNTs with the ionic-liquid gate by this approach, while the observed Tc is low (< 20K). On the other hand, possibly high-oriented MWNTs with CTAB solution confined into micro-trenches on substrate demonstrate high Tc (> 40K), while the reproducibility is poor. Further optimization based on this approach may realize higher Tc with high reproducibility.

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"Realization of high-temperature superconductivity in carbon nanotubes"

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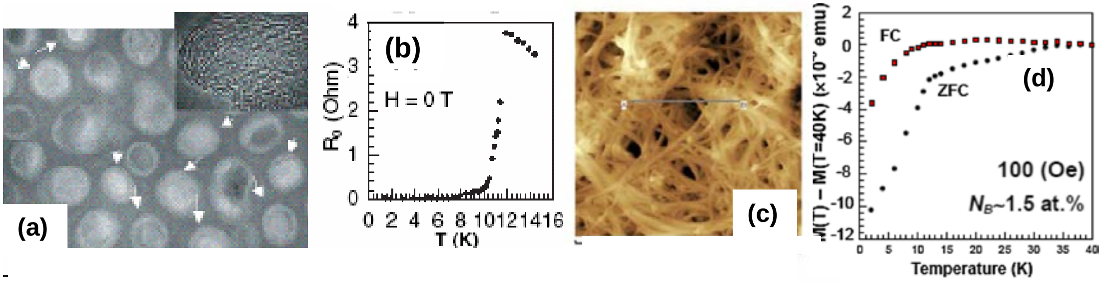
Abstract: Superconductivity (SC) is a hot topic in condensed matter physics and also key factor for applications to zero-emission energy system. In particular, SC in carbon nanotubes (CNTs) has been expected to have high transition temperature (T_c), because of its high phonon frequency due to the small mass, extremely high one-dimensional (1D) electronic density of state (EDOS) due to van Hove singularity, and strong electron-phonon coupling between a radial breathing phonon mode and $\sigma \cdot \pi$ hybrid orbital electrons. Previously, I tried to realize high-T_c SC in thin films consisting of randomly placed CNTs based on such advantages. Moreover, I applied ionic-gel(liquid) gating to the CNT thin films in order to cause extremely high EDOS on the surface and obtained Tc as high as 38K, however its reproducibility was too poor. Here, in the present work, I use novel solution (i.e., hexadecyltrimethylammonium bromide (CTAB)) to chemically modify CNT surface and create thin films consisting of highly oriented (aligned) CNTs with flat and homogeneous surface, which should resolve the problem of poor reproducibility and realize high-Tc SC. High reproducibility is obtained in partially oriented CNTs with the ionic-liquid gate by this approach, while the observed T_c is low (< 20K). On the other hand, possibly high-oriented MWNTs with CTAB solution confined into micro-trenches on substrate demonstrate high T_c (> 40K), while the reproducibility is poor. Further optimization based on this approach may realize higher T_c with high reproducibility.

1. Introduction:

(1) SC in carbon-based materials and CNTs

Carbon-based superconductors have attracted strong attention for high-T_c, because the small mass of carbon leads to high phonon frequency and high Tc. Nevertheless, the observed Tc were basically below 1K before 2004. On the other hand, significant advancement in carbon-based superconductors suddenly occurred for 2004 - 2008 materials, which enabled T_c > 10K [1]; e.g., highly boron-doped diamond with the highest $T_c \sim 10$K [2], calcium (Ca)-intercalated graphite (CaC_{60}) with the highest $T_c \sim 15$K [3], our two-different types of CNTs with the highest $T_c \sim 19$K [4-6], and pressure-applied cesium(Cs)-doped fullerene (Cs_3C_{60}) with the highest T_c ~38K which originates from Mott-transition caused by applied high pressure [6].

In particular, the SC in two different-typed CNTs were realized by my group as follows; (1) SC in entirely end-bonded multi-walled CNTs (MWNTs) with the world-highest T_c of 12K (Fig.1a) [4] and (2) SC in thin films consisting of boron-doped single-walled CNTs (SWNTs) with T_c = 19 K (Fig.1b) [5,6]. Both SCs were strongly associated with 1D electronic properties of CNTs. For the former one [4], we eliminated 1D repulsive Coulomb interaction (the so-called Luttinger liquid (LL)), which tends to destroy Cooper pair and BCS-type SC, by making current flow through all layers of MWNTs by entirely end-bonding by metal electrodes. Interlayer electrostatic-coupling resulted in suppression of the individual layer's LL. Then, I obtained SC with Tc of 12K. For the latter [5], very small amount of boron (< 2%) was doped into the SWNTs from catalyst during its synthesis. That led to the better alignment of Fermi level (E_F) to van Hove singularities (VHSs) in 1D EDOS ad produced Tc as high as 19K [6].



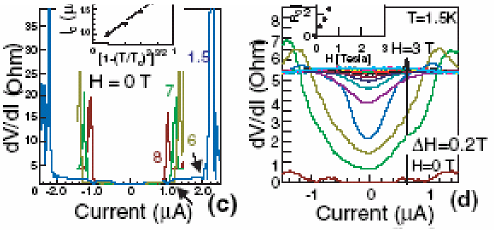


Fig.1 : **(a)** Planer transm f MWNTs synthesized in nanopores of alumina templat **(b)** Resistance drop caused by superconductivity in (a) at scope image of thin film of boron-doped SWNTs. **(d)** Ma ivity in (c).

However, much high t alignment of E_F to VHSs would be obtair pling between radial breathing phonon mode and σ-π electrons would be utilized in much thinner SWNTs (diameter < 1nm). Indeed, based on these factors, even T_c as high as 64K was theoretically predicted by Harvard group [8].

(2) High-Tc SC in CNT thin films with ionic-gel (liquid) gates

On the other hand, how to highly dope carriers is also another nontrivial factor to obtain high-T_c SC. Hence, I have applied ionic-gel (liquid) gating to the surface of CNT thin films.

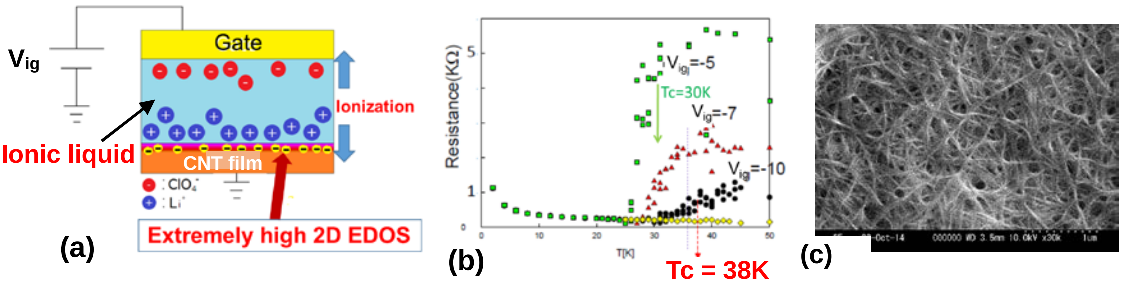


Fig.2 **(a)** Schematic cross sectional view of a CNT film with ionic-liquid gate voltage (V_{ig}). **(b)** High-T_c SC (38K in black symbol at V_{ig} = -10V) observed in novel ensemble of random-placed CNTs **(c)** under structure (a). The reproducibility is still poor and improvement has been expected.

An ionic-gel (liquid) gating method is actively used in recent some materials [9]. Because applying ionic-gel (liquid) gating voltages causes extremely high EDOS (i.e., carriers) on the sample surface through its easy ionization and subsequently formation of electrical double layer (EDL; Fig. 2a), the high EDOS has caused SC even in insulators. Previously, I tried to realize high-T_c SC in thin films consisting of randomly placed SWNTs (Fig. 2c), employing this ionic-gel gating method. As a result, I found a high possibility of high-T_c SC with T_c as high as 38 K, depending on the ionic-gel gate voltages (Fig. 2b). However, the reproducibility, which is one of the most important scientific factors for SC, was quite poor. Only a few samples showed this high T_c. In order to improve this problem, I optimized the component uniformity of ionic gel ($LiClO_4$) and also used ionic liquid (DEME-TFSI) in previous experiments. Nevertheless, this poor reproducibility was not resolved.

Hence, I have tried to reveal the further origin for this poor reproducibility and obtain high reproducibility of the high-T_c SC in the present research. One of the possible origins can be in the tube-shape of CNT. Ionic liquid gating is highly effective to very flat and homogeneous sample surface like pure 2D structure, because EDL is sufficiently formed only at such an interface. In contrast, a CNT has 1D tube shape (Figs.3c,d). Ionic liquid gating is not effective to such a non-flat surface (or interface). When such CNTs are placed at random and form thin film, ionic liquid placed on it works ineffectively because the tube shape of individual CNTs directly make non-flat interface to the ionic liquid. Only when some portions of CNTs in a film may be accidentally connected in parallel and form ensembles of CNTs, ionic liquid gating well works to such a portion with relatively flat surface (Figs.3c,d), resulting in the observed high T_c with the poor reproducibility. Therefore, thin films consisting of highly oriented and tightly connected CNTs with extremely small space between neighboring are indispensable to produce effective ionic liquid gating (like the case of flat and homogeneous sample surfaces) and realize high T_c with high reproducibility.

2.Experimental results

(1)Thin films consisting of partially oriented CNTs with CTAB solution

In order to create such thin films with highly oriented (aligned) CNTs and flat surface, in the present experiments, I have used CTAB solution and multi-walled CNTs (MWNTs) with diameter ~10 nm, which can eliminate LL states of pure 1D structure of CNTs with small diameter. It is known that chemical modifying nanowires with CTAB solution makes them closely connected within highly oriented state, when the nanowires are immersed into the CTAB solution and the solution is confined into close space like a trench (Fig. 3a) [10]. Moreover, CTAB solution includes brome (Br), which can cause SC via. electron charge doping.

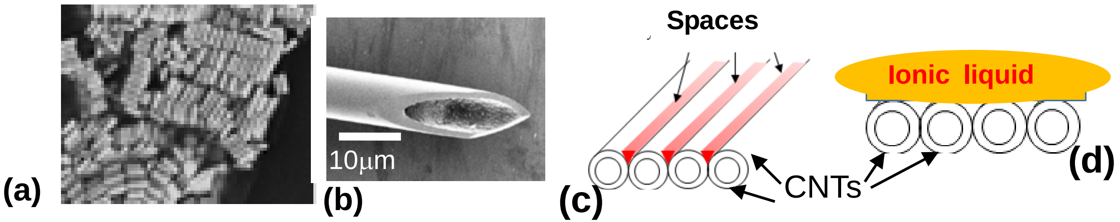


Fig. 3: **(a)** Example of SEM top-view image for highly oriented (aligned) nanowires, which are chemically functionalized with hexadecyltri-methylammonium bromide (CATB) solution, placed and confined in a trench of substrate. This method has been applied to the present experiment. **(b)** FESEM image of a nanoneedle, which was used to drop and absorb CTAB solution including CNTs. **(c,d)** Schematic cross sections of oriented CNTs **(c)** with and **(d)** without ionic liquid.

First, I formed MWNT thin films by dropping a droplet of CTAB solution including MWNTs on Si substrate without any trenches. In order to drop very small amount of solution on the expected position in a precisely controlled way, I used nano-needle with inner diameters of 10- 50 μm, which is our original method (Fig.3b). After dropping it, the droplet was dried by two different methods (i.e., (1) by annealing under high vacuum at high temperature (Type 1) or (2) by applying air blow with optimized power and angle at room temperature (Type 2)). The results are shown in Fig.4. The drying method (1) results in Fig.4a, in which the MWNTs are connected like thin ropes due to CTAB solution and randomly placed on substrate. On the other hand, the drying method (2) leads to Fig.4b, which demonstrates that the MWNTs are partially and closely connected with the same orientation, resulting in formation of those partial ensemble within a large number. This is due to the air blowing applied from various angles during the drying process and also CTAB solution.

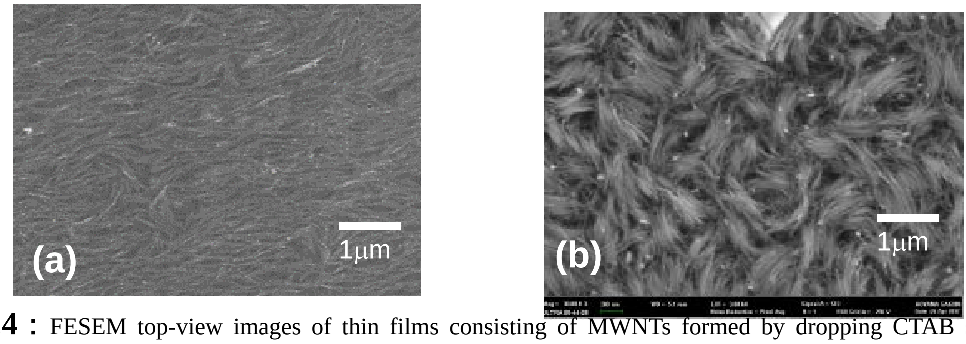


Fig.4 : FESEM top-view images of thin films consisting of MWNTs formed by dropping CTAB solution including MWNTs and dried by **(a)** high-temperature annealing under high vacuum (Type 1; random orientation) and by **(b)** applying air blow with the optimized power and angle at room temperature (Type 2; partial orientation).

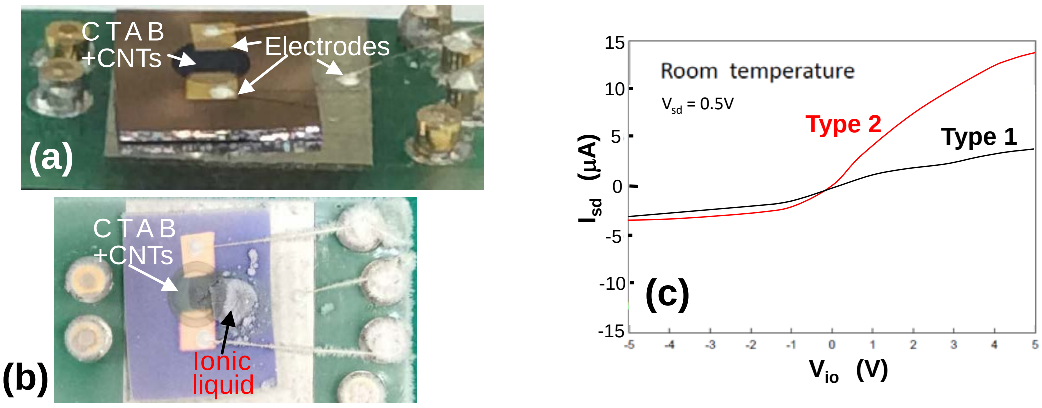


Fig.5 : **(a,b)** Optical microscope images of Fig.4b-sample with source, drain, and ionic-liquid gate electrodes. **(a)** without ionic liquid and **(b)** with frozen ionic liquid. **(c)** Result of measurement of source-drain current (I_{sd}) as a function of ionic-liquid gate (V_{io}) for Fig.4-samples a (Type 1) and b (Type 2).

Ionic liquid is dropped on these two-type thin films so as to connect the ionic-liquid gate electrode (Fig.5b). Figure 5c shows a typical result of electrical measurement of the two-type samples (i.e. source-drain current (I_{sd}) as a function of ionic liquid gate voltage (V_{io})). As a positive Vio increases, I_{sd} is drastically induced in Type 2 with the partially oriented MWNTs, while I_{sd} is almost constant in $-V_{io}$ region. This suggests formation of an EDL at the interface of the MWNT film/ionic liquid junction and accumulation of electron charge on the most surface of the film. This I_{sd} increase on V_{io} increase is larger than those in the samples using conventional ethanol solution to form CNT films, which I reported previously. Moreover, reproducibility of this electrical property is also higher than those in previous case. Four of six samples exhibited such large I_{sd} increase. On the other hand, the sample (Type 2) shows much lower I_{sd} increase with increasing V_{io} (Fig.5c). These results imply that the oriented MWNTs is highly effective to the robust formation of EDL on the film surface, even though they are partial with small area.

Temperature dependence of resistance (*R*) of Fig.4b–sample (Type 2) as a function of V_{io} is shown in Fig.6a. Evident *R* decrease is observed for T = 4 – 18 K, depending on V_{io}. T_c increases from 4 K to 18 K with increasing $+V_{io}$ with high reproducibility, while the highest T_c of 18 K is much lower than the highest T_c of 38 K in previous samples (Fig.2b). On the other hand, Fig.6b shows temperature dependence *R* of Fig.4a–sample (Type 1). T_c is much lower than those in Fig.4a. This is consistent with the lower I_{sd} increase on V_{io} increase (Fig.5c).

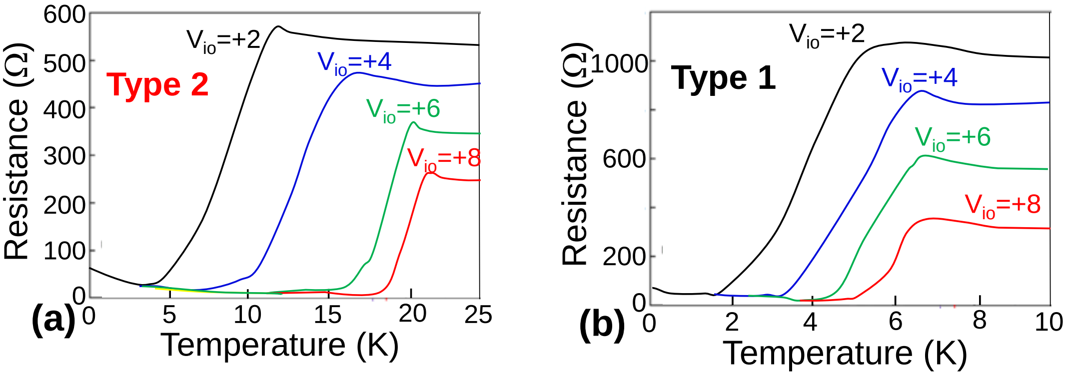


Fig.6 : **(a)** Temperature dependence of resistance (*R*) of Fig.4–sample as a function of V_{io}; **(a)** for Fig.4b (partially oriented MWNTs) and **(b)** for Fig.4a (random oriented MWNTs) samples.

This lower T_c should be associated with the thin films consisting of partially oriented MWNTs (Fig.4b), because SC current paths are disconnected among the partial ensemble of the oriented MWNTs and the high-T_c SC is suppressed.

(2)CNTs confined into micro-trenches on Si substrate with CTAB solution

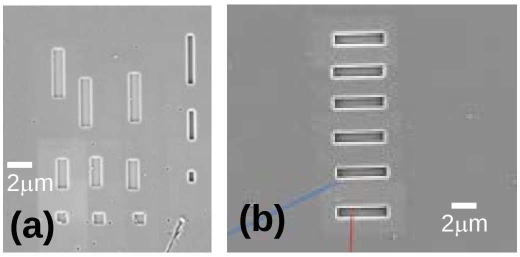
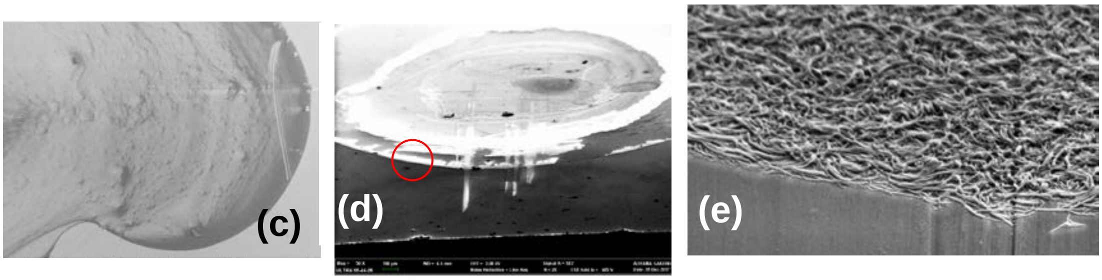


Fig.7 : **(a,b)** FESEM top-view image of various micro-trenches (0.5 – 1μm width, 1- 5μm length, and 0.5 μm depth) formed by focus ion beam on SiO_2/Si substrate. **(c,d)** SEM top-view images of CTAB solution with MWNTs **(c)** after dropping on (a) and **(d)** after absorption of the droplet of (c) by nanoneedle (Fig.3b). **(e)** Expansion of a local edge of (d) (shown by a red circle).



Thus, as a next step, I have dropped CTAB solution including MWNTs on various micro-trenches formed on SiO_2/Si substrate (Fig.7a) and tried to confine the solution into the trenches. As explained above, it is expected that this results in a thin films with highly oriented MWNTs along the inner wall of the trenches like Fig. 3a. However, I have been noticed that it is very difficult to observe the MWNTs confined into the trenches, because the droplet of CTAB solution cannot be confined only into the trenches and covers over the trenches on the substrate surface (Fig.7b). In order to resolve this problem, I have tried the following methods; (1) Etching out the CTAB solution covering the trenches, (2) Shift of the droplet covering the trenches from the trench surfaces by using sharp corners of a flake of glass or nanoneedle, (3) Absorption of the excess droplet covering the trenches by nanonedle, and (4) Evaporation of the droplet by high-temperature annealing under high vacuum. As a result, I have found that the method (3) is the most effective.

In spite of these trials, very thin CTAB solution with MWNTs still covers over the trenches (Fig.7c-e) and it is difficult to observe the inside of trenches with the confined MWNTs. Because this problem made formation of the electrode contacts to the MWNTs existing in the trenches difficult, it is impossible to carry out resistance measurements with ionic liquid gate.

Thus, I have measured Meissner effect in these samples with the trenches confining the MWNTs covered by very thin film of MWNTs. Figure 8 shows the result. In zero-field cooling (ZFC), diamagnetism with the gradual decrease in a magnetization appears below 80K and an abrupt drop is observed below 15K. In FC, very small decrease in a magnetization appears below 20K and a small abrupt drop is observed below 10K. These can be typical properties of Meissner effect. Because the T_c of 15K is comparable to that in Fig. 6(a) with ionic-liquid gate, this suggests effectiveness of the present ensemble of MWNTs confined into the trenches, which can be possibly oriented along the inner wall of trench. Moreover, if the T_c of 80K for the gradual decrease in magnetization would originate from Meissner effect, this strongly suggests a possibility of high-T_c SC. On the other hand, reproducibility of this high T_c is poor, while the T_c of 15K is reproducible. Thus, further research is indispensable. If I could control the confinement of the CTAB droplet including MWNTs only into trenches on SiO_2/Si substrate and directly observe the high alignment of MWNTs in the trenches, this can make electrical contacts to the MWNTs and form ionic-liquid gate. This may cause the high-T_c SC with high reproducibility.

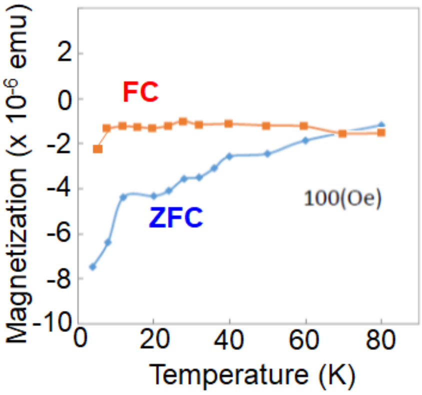


Fig.8：Magnetization measurement of the samples with some trenches confining the MWNTs by CTAB solution and covered by very thin film of MWNTs (Fig. 7e-samples with MWNTs highly oriented in the trenches but covered by thin CTAB solution with MWNTs). Applied in-plane magnetic field is 100 Oe. ZFC and FC mean zero-field and filed cooling, respectively.

Conclusion

Novel solution (CTAB) was used to chemically modify CNT surface and create the thin films consisting of highly oriented (aligned) CNTs with flat and homogeneous surface. High reproducibility of SC was obtained by this approach in the partially oriented MWNTs thin films with the ionic-liquid gate, while the observed T_c was low (< 20K). On the other hand, the samples with the MWNTs, which were confined into various trenches on substrate and possibly high-oriented along the inner walls of the trenches, demonstrated a possibility of the high T_c (> 40K), while the reproducibility was still poor. If I could control the confinement of the CTAB droplet including MWNTs only into the micro-trenches on SiO_2/Si substrate and directly observe the highly oriented MWNTs in the trenches, this can make electrical contacts to the MWNTs and form ionic-liquid gate. This may realize the high-T_c SC with high reproducibility. Further improvement is still indispensable to cause higher T_c with higher reproducibility in CNTs.

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