Studies of electronic distribution in potassium-doped mats of single-walled carbon nanotubes, double-walled carbon nanotubes, and peapods

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In this work, we have performed a systematic study of the electrical transport properties (both the resistivity and the thermoelectric power) on bundles of single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), and peapods (derived from the same batch of initial SWNTs) during in situ doping with potassium (donor). The charge transfer effects in K-doping are similar in SWNTs and DWNTs, but drastically different in C$_{60}$ at SWNTs. An impurity level associated with the chain of C$_{60}$ in the band gap of the tube with the Fermi level pinned near the top of the valence band, leading to the $p$-type behavior for the peapod. Significant charge transfer is found to occur only in the case of very low coverage of these nanostructures. © 2008 American Institute of Physics. [DOI: 10.1063/1.2952049]

I. INTRODUCTION

In recent years, there has been an intense research activity in the study of the functionalization of carbon nanotube (CNT)-based structures since the functionalization provides the means to endow these nanostructures with desired properties for innovative and useful applications.$^{1-3}$ The key effect in the functionalization of CNTs is the redistribution of the charge in the resulting nanostructure. Charge transfers in the doping of single-walled CNTs have been studied intensively.$^{4,5}$ However, there have only been a few attempts to study the charge transfer for other CNT-based structures.$^{6,7}$ Single-walled CNTs (SWCNTs) not only have extremely interesting and unique intrinsic physical and chemical properties, the interior space of SWCNTs can also be utilized for interesting applications such as one-dimensional array materials, drug delivery, and fluids.$^8$ C$_{60}$ molecules have been inserted with high efficiency in the interior of SWCNTs by vapor phase reaction of C$_{60}$ with SWCNTs to form peapods (C$_{60}$ at SWNT).$^9$ It has also been found that high temperature annealing of peapods at 1200 °C result in the coalescence of the C$_{60}$’s within the host SWCNT into an interior SWCNT, thus forming a double-walled CNT (DWCNT).$^{10}$ Recently, Chen et al. have reported the charge transfer properties between bromine and DWCNTs using resonant Raman scattering.$^5$ They have found that most of the charge resides on the outer wall of the DWNT, indicating a molecular Faraday cage effect. Doping of CNTs with alkali metals has drawn the attention of the scientific community from various perspectives. One is the possibility of superconductivity in potassium intercalated compounds. In particular, potassium intercalated graphite is a superconductor.$^{11,12}$ So is the C$_{60}$-crystal with potassium atoms in the interstitial sites of the buckyballs.$^{12}$ In this paper, we report the result of our systematic study of the change in electrical transport properties, specifically the resistance and the thermoelectric power (TEP), of mats of SWCNTs, DWCNTs, and peapods during in situ doping with potassium. The samples of SWCNTs, DWCNTs, and peapods used in the experimental measurements were derived from the same batch of initial SWCNTs. We found that upon doping of the bundles of CNT-based structures with potassium, a significant difference was observed in the transport properties between those of SWCNTs and DWCNTs and those of peapods. Specifically, mats of SWCNTs and DWCNTs exhibit switching from the $p$-type conductance to the $n$-type upon doping, while mats of peapods remain $p$-type conductors.

II. EXPERIMENTAL STUDIES

A. Sample preparation

The SWCNTs used in this study were prepared using high temperature pulsed laser vaporization (PLV) of a graphite target containing Fe/Ni (0.6%-0.6% atomic) catalysts. The chemical purification of the PLV derived material was carried out by refluxing in 70% HNO$_3$ for 8 h at 160 °C. The suspension was neutralized by centrifugal decantation with distilled water and finally with ethanol. Then the purified SWCNTs were dried and heated in dry air at 420 °C for 20 min. This last treatment was found to be necessary for opening the tube ends to allow the dopants to easily creep into the nanotubes. The doping of C$_{60}$ into the inner hollow space of SWCNTs was carried out in a sealed glass ampoule at 400 °C for 24 h by vapor phase reaction of C$_{60}$ with SWCNTs. The DWNTs were synthesized by annealing the peapods at 1200 °C in a vacuum better than 10$^{-6}$ Torr. During the high temperature annealing in vacuum, the C$_{60}$ molecules were found to coalesce between adjacent molecules within the host SWCNT. The fully packed C$_{60}$ molecules inside the SWCNTs are completely transformed into a tubular structure forming DWCNTs.

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FIG. 1. A typical in situ variation of four-probe dc resistance $R$ of K-doped SWNT mats normalized to the $T=400$ K resistance of the pristine SWNT mat as a function of exposure time to K vapor. The arrows indicate the time at which the temperature was increased to 410 and 412 K.

B. In situ measurements of transport properties

Each sample was vacuum degassed in situ in the TEP apparatus at 500 K before exposing to potassium. The doping-induced change of the thermopower, or Seebeck coefficient $S$, and the four-probe resistance $R$ were studied in a quartz reactor with 20 mm inner diameter and ~25 cm in length equipped with a 2.3/4 in. knife-edge flange sealed via a Cu gasket to a standard multipin feedthrough flange. For in situ transport measurements, two chromel-alumel thermocouples and two additional Cu leads were attached with small amounts of silver epoxy to four corners of the 4 × 4 mm$^2$ sample to measure the TEP and the dc four-probe electrical resistance simultaneously. The sample holder with the sample attached to the electrical leads was loaded into the glass reactor together with a small, break-seal ampoule containing potassium. The reactor was evacuated to 10$^{-7}$ Torr using a turbo molecular pump and degassed at 500 K while the temperature was increased to 410 and 412 K.

The reactor was cooled down to room temperature and isolated through a high vacuum valve. The potassium was then released by shaking the reactor and breaking the break seal on the alkali metal containing ampoule. The surface of the potassium remained shiny throughout the experiment indicating the absence of any significant amount of oxygen or water in the reactor. The reactor was positioned in a temperature gradient in a horizontal furnace and heated to vaporize the potassium. The temperature gradient was chosen to provide efficient transport of potassium atoms from the ampoule to the reactor. The reactor was positioned in a temperature gradient at which the temperature was increased to 410 and 412 K. Further sharp drops in $R$ indicated with arrows in Fig. 1 were observed when the furnace temperature was stepped up by another 10 K. We have increased the furnace temperature in steps in order to be able to observe the diffusion kinetics.

Figure 2 shows the K-doping effects of the resistance (normalized to the resistance $\Delta R/R$ of the undoped sample at $T=412$ K) of the three samples, mats of SWCNTs, DWCNTs, and peapods. They all show drastic drop of resistance. Interestingly mats of SWCNT and DWCNT show almost the same change in resistance, while the change for the mat of peapods is somewhat less. After saturation coverage of potassium atoms on these bundles, our studies on the individual SWCNTs, DWCNTs, and peapods indicate that a potassium metallic shell will be formed on the surface of these bundles. The SWCNTs, or DWCNTs, or peapods on the surface of the respective bundles adjacent to the potassium shell will also become weakly metallic. This metallic shell formed on the surface of these bundles thus provides an additional conduction channel of the $n$-type for the K-covered bundles in parallel with the conduction channels provided by the SWCNT-based structure underneath. Denoting $R_1$ as the resistance associated with the metallic shell and $R_0$ as the resistance of the SWCNT-based nanostructure underneath, we have $\Delta R/R = (R-R_0)/R - R_0/R_1$. Since both $R_0$ and $R_1$ are about the same for bundles of SWCNTs and DWCNTs of similar sizes, their corresponding $\Delta R/R$ should be similar, as shown in Fig. 2. On the other hand, for the bundle of peapods, $R_1$ should still be similar to those of covered bundles of SWCNTs and DWCNTs of similar sizes while $R_0$ is smaller because of the additional $p$-type conduction channel associated with the peapods due to the presence of C$_{60}$ inside the peapods. Hence the value of $[\Delta R/R]$ for the bundle of peapods under the saturation coverage by the potassium should be smaller compared to the corresponding values for bundles of SWCNTs and bundles of DWCNTs of similar sizes, as clearly seen in Fig. 2.\textsuperscript{13}

Figure 3 shows the concomitant results of the TEP ($S$) for the three samples during the K-doping. Again, mats of SWCNTs and DWCNTs show very similar changes in TEP, starting ~40 $\mu$V/K, decreasing in magnitude, reversing the sign, and eventually saturating at ~20 $\mu$V/K. Most interestingly, the TEP of the peapod sample saturates only at $R_0$ with exposure time to the potassium (K) vapor. An initial drop in $R$ was observed when the alkali-metal temperature reached 400 K. Further sharp drops in $R$ indicated with arrows in Fig. 1 were observed when the furnace temperature was stepped up by another 10 K. We have increased the furnace temperature in steps in order to be able to observe the diffusion kinetics.

III. EXPERIMENTAL RESULTS

Figure 1 shows a typical in situ variation of the resistance $R$ normalized to the resistance of a pristine SWCNT mat $R_0$ as a function of exposure time to K vapor. An initial drop in $R$ was observed when the alkali-metal temperature reached 400 K. Further sharp drops in $R$ indicated with arrows in Fig. 1 were observed when the furnace temperature was stepped up by another 10 K. We have increased the furnace temperature in steps in order to be able to observe the diffusion kinetics.
The trapped O$_2$ molecules were not only adsorbed on the surface of the bundles but were also trapped deep into the interior of these bundles. Therefore, it is expected to remove oxygen molecules. However, it should be noted that the SWCNT materials used in this study are heated in dry air at 420 °C. Oxygen molecules are trapped well into the interior of the mats of these materials. Hence there will be oxygen molecules left in the interior of the mats of these materials even after degassing at 500 K, leading to the persistent $p$-type behavior during degassing.

Doping effects on both the resistance and the TEP suggest that the electronic properties for K-doped SWCNT and DWCNT materials are very similar, consistent with the observations on charge transfer properties on Raman spectra of SWNTs and DWCNTs.\cite{15} However, mats of peapods show entirely different behavior. This behavior is not very well understood but it is expected to be related to the presence of C$_{60}$ in the peapod.

The samples used in the experimental measurement were bundles of SWCNTs, DWCNTs, and peapods, all derived from the same batch of initial SWCNTs. Since these samples were prepared at high temperature (~1200 °C), O$_2$ molecules were not only adsorbed on the surface of the bundles but were also trapped deep into the interior of these bundles. Even after annealing with most of the O$_2$ molecules desorbed from the surface of the bundles, a certain amount of O$_2$ remained trapped in the interior of the bundles. The trapped O$_2$ molecules had been shown\cite{14,15} to give rise to an impurity level in the gap of the semiconducting SWCNT. Therefore, these O$_2$ molecules are apparently responsible for the $p$-type behavior observed for bundles of SWCNTs and DWCNTs before potassium doping. For bundles of peapods, in addition to the trapped O$_2$ molecules, the impurity level associated with the C$_{60}$ peas in the gap of SWCNT pod also contributes to the $p$-type behavior. Hence, the resistance of the bundles of peapods that are synthesized from the same batch of initial SWCNTs will be smaller compared to those of the bundle of SWCNTs or DWCNTs of similar sizes. The TEP behavior of the bundle of peapods versus those of bundles of SWCNTs or DWCNTs after doping with K atoms, as shown in Fig. 3, can also be understood in terms of the scenario of multiconducting channels. Let $\sigma_i$ and $S_i$ be the conductivity and the TEP for the conduction channel $i$, with $i=1, 2,$ and $3$ referring to the $n$-type channel associated with the metallic shell, the $p$-type channel associated with the oxygen molecules trapped in the interior of the bundle, and the $p$-type channel due to the peapods, respectively. For the cases of bundles of SWCNTs and DWCNTs (prepared from the same batch of initial bundles of SWCNTs) before K-doping, there is only the $p$-type channel 2 associated with oxygen molecules trapped in the interior of the respective bundle. Therefore, the magnitude of the TEP of the bundle of SWCNTs is similar to that of the bundle of DWCNTs as observed in the experiment (shown in Fig. 3). For the bundle of peapods before K-doping, there is the additional $p$-type channel 3 associated with the presence of C$_{60}$ chain inside the SWCNT for each peapod. While $\sigma_1$ is expected to be greater than $\sigma_2$ because of the large number of peapods in the bundle of peapods, the magnitude of $S_3$ should be similar to that of $S_2$ because both are due to the $p$-type conduction associated with impurity states in the gap of the same batch of semiconducting SWCNTs. The effective TEP of the bundle of peapods before K-doping is therefore given by $S=(\sigma_2S_2+\sigma_3S_3)/(\sigma_1+\sigma_2)$, similar to the TEP of the bundle of SWCNTs or DWCNTs, as shown in Fig. 3. After saturated K-doping, the effective TEP $S$ of the bundle of SWCNTs or DWCNTs is given by $S=(\sigma_1S_1+\sigma_2S_2)/(\sigma_1+\sigma_2)$. Since the conducting channel 1 is $n$-type in nature, the corresponding TEP $S_1$ is negative. On the other hand, the conducting channel 2 is $p$-type and it leads to a positive $S_2$. For the bundle of SWCNTs or DWCNTs, the $p$-type behavior of the channel 2 is due to the limited amount of O$_2$ molecules trapped in the interior of the bundle. Therefore, $\sigma_2S_2$ will be dominated by $\sigma_1S_1$ associated with the $n$-type metallic shell due to the K-coverage. Hence, after the saturation coverage by the potassium atoms, the effective $S$ becomes $n$-type (negative), as shown in Fig. 3. For the bundle of peapods, in addition to the contribution to the $p$-type behavior due to the O$_2$ molecules trapped in the interior of the bundle, every interior peapod is itself a $p$-type conductor. The effective TEP is then given by $S=(\sigma_1S_1+\sigma_2S_2+\sigma_3S_3)/(\sigma_1+\sigma_2+\sigma_3)$. Since there is a large number of peapods in the bundle, $\sigma_1$ is large. Therefore, $\sigma_1S_1$ does not dominate over the sum of $\sigma_2S_2+\sigma_3S_3$ and the effective TEP of the K-covered bundle of peapods remains positive but much smaller.

Figure 4 shows the temperature dependence of the resistance and the TEP of the three samples before and after K-doping. It is clearly seen in Fig. 4(a) that all three samples show typical nonmetallic temperature dependence of resistance inherent to pristine SWNTs before doping (solid symbols). After saturation doping, they all show obvious metallic behavior of the resistance (open symbols). As seen in the temperature dependence of the TEP depicted in Fig. 4(b), before doping TEP stays positive and decreases with temperature as due to the percolated networks of metallic nanotubes consistent with previous results.\cite{15} After saturation dop-
corresponding isolated SWCNTs, respectively, suggesting no resistance and TEP. All three samples show monitoring their $p$-type behavior for the peapod. Significant charge transfer occurs only in the case of very low coverage of these nano-structures. At the saturation coverage by potassium, the charge transfer per potassium atom to the underlying CNT-based structures is reduced drastically, leading to the formation of a metallic potassium shell with 4$s$ electrons being mostly shared among potassium atoms rather than transferred to the nanostructures.

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**IV. CONCLUSIONS**

We carried out a detailed study of K-doping of bundles of SWNTs, DWNTs, and peapods by in situ monitoring their resistance and TEP. All three samples show $p$-type behavior before K-doping due to the oxygen molecules trapped on the surface of the bundles and in the interior. Degassing at 500 K under high vacuum is not sufficient to desorb oxygen molecules in the interior of the bundles. The experimental results seem to suggest that the charge transfer effects in K-doping are similar in SWNTs and DWNTs, but drastically different in $C_{60}$ at SWNTs. SWCNTs are essentially the same as the corresponding isolated SWCNTs, respectively, suggesting no appreciable interaction between the component-SWCNTs in the DWCNT. An impurity level associated with the chain of $C_{60}$ in the band gap of the tube with the Fermi level pinned near the top of the valence band, leading to the $p$-type behavior for the peapod.