Thermoelectric properties of single-wall carbon nanotube films: Effects of diameter and wet environment

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Received December 8, 2015; accepted December 21, 2015; published online January 19, 2016

Effects of diameter and wet environment

Single-wall carbon nanotubes (SWCNTs) have many advantageous properties from the thermoelectric engineering viewpoint, including flexibility, relatively low weight, high abundance, and non-toxicity. Despite these properties, the reported thermoelectric performance of bulk SWCNTs has remained unsatisfactory. Recently, however, the strong potential of these structures for use as flexible thermoelectric materials has been reported and has generated significant interest. In light of the significant recent developments in the field of large-scale purification and separation of SWCNTs, it is important to investigate strategies for achieving higher-performance SWCNTs.

Bulk SWCNT films usually consist of metallic (m-) and semiconducting (s-) SWCNTs of various diameters D. The effect of mixing m- and s-SWCNTs on the thermoelectric performance of a mixture has been reported, and the performance of these structures was remarkably improved by s-SWCNT enrichment. For example, the Seebeck coefficient S increased to 170 µV/K in an s-SWCNT film from 50–60 µV/K in “natural-abundance” (natural) films with a nominal m/s ratio of 1:2. In the present study, we investigated the effects of the nanotube diameter D, which is inversely proportional to the semiconducting gap, in natural SWCNT films. Because the thermoelectric performance of SWCNTs is sensitive to the carrier concentration (the Fermi level), we employed a technique based on the effect of a wet environment on the electronic properties of SWCNTs in air and in low-vacuum conditions.

Five SWCNT films with different mean diameters D were investigated: D = 1.44 (±0.1), 1.68 (±0.17), 1.91 (±0.2), 2.18 (±0.2), and 2.7 (±0.3) nm, where the numbers in the parentheses indicate the nominal values of the D distributions. The 1.44-nm-diameter film (a flake of ArcSO grade), which consisted of purified SWCNTs prepared by the arc-discharge method, was purchased from Meijyo Nanocarbon. The 1.68-, 1.91-, and 2.18-nm-diameter films were prepared by using the eDIPS method, and the as-grown SWCNT mats were gently pressed into the films by hand. The thickness of the as-grown powder was dispersed in ethanol and then transformed into a film by filtration. Before performing the measurements, each film was heated to 770 K under a dynamic vacuum (where the pressure reached 10⁻³ Pa) for removing adsorbed molecules. The bulk density values of the heat-treated films were calculated from the films’ weights and dimensions. The thickness t, measured by using a micrometer gauge, was in the 0.04–0.19 mm range. Standard four-probe measurements of the electrical resistance and Seebeck coefficient were conducted by using home-made systems. The resistivity ρ was calculated from the film dimensions and the measured resistances. Because the bulk density m varied widely from film to film and was in the 0.09–0.34 g/cm³ range, we also used the quantity ρ₀ to perform a comparison; this quantity was calculated by using the converted thickness t₀. This thickness corresponded to the bulk density of 0.5 g/cm³ by assuming that the films were compressed along the surface normal: t₀ = t × m/m₀ and ρ₀ = ρ × m/m₀, where m₀ = 0.5 g/cm³. Ultrahigh-purity water was delivered by using a Petri dish or clean tissue, as shown in Fig. 1(b). The highly enriched s-SWCNT films doped with HNO₃, which were reported in the previous paper, were also re-measured in detail.

The Seebeck coefficient S and the electrical conductance G were calculated for discussing the experimental results. The details will be reported elsewhere. Here, we considered two cases of parallel networks of s-SWCNTs and m-SWCNTs, as in the previous report: a network of (8,0) s-SWCNTs with the diameters of 0.63 nm and (5,5) m-SWCNTs with the diameters of 0.68 nm, and a network of (22,0) s-SWCNTs with the diameters of 1.72 nm and (13,13) m-SWCNTs with the diameters of 1.78 nm. The C–C bond length in the SWCNTs was set to 0.142 nm. The electronic states were calculated by using the semi-empirical (extended Hückel) theory with a Hoffmann carbon potential. The calculated semiconducting gaps were 0.79 and 0.38 eV for (8,0) and (22,0) SWCNTs.
SWCNTs, respectively. The transport calculation details were essentially the same as those reported previously for graphene nanoribbons (GNRs). The transmission function $\zeta(\epsilon)$ of a carrier with energy $\epsilon$ was calculated based on the non-equilibrium Green’s function method (NEGF). In this work, we used the Atomistix ToolKit (ATK 12.2.0) to calculate $\zeta(\epsilon)$.

The Seebeck coefficient $S$ and the electrical conductance $G$ are given by

$$S = \frac{1}{qT} \frac{K_1}{K_0}$$

and

$$G = q^2 K_0.$$

Here, $q$ is the charge of a carrier and $K_0$ is the intermediate function:

$$K_0 = \frac{2}{\hbar} \int_{-\infty}^{\infty} \zeta(\epsilon) \left( -\frac{df}{d\epsilon} \right) (\epsilon - \mu)^2 d\epsilon,$$

where $\hbar$ is Planck’s constant, $f$ is the Fermi–Dirac distribution function, and $\mu$ is the chemical potential.

Figure 1 shows the representative time charts of $S$ and $\rho$, measured following a heat treatment at 770 K. It is well known that as-grown SWCNTs have usually been p-doped, and can be de-doped by heating under vacuum. Thus, $\rho$ was highest immediately after heating at 770 K, and then decreased over time owing to the humidity and/or oxygen in the air. Water was delivered successively a few times, as indicated by arrows in Fig. 1. We found that $\rho$ decreased for more than several hours in humid air at room temperature after adding the water. Drying, which resulted from the shortage of water in the open system [see Fig. 1(b)], led to the increases in $\rho$ as shown by the asterisks (*) in Fig. 1(a). In contrast, the $S$ value of the SG film with a mean diameter of 2.7 nm, for example, increased or remained nearly unchanged after the first delivery, and then decreased after the next three. Similar behavior was observed in the other films, which had different diameters and/or quality, such as the number and nature of contacts among SWCNTs, the length of the SWCNTs and SWCNT bundles, and the presence or absence of defects. These imperfections dominate the observed bulk resistivity. In particular, the 1.44-nm-diameter SWCNTs had a distinctly larger $\rho_0$ than the films that were synthesized by using the eDIPS and SG methods. This most likely occurred owing to the purification process that was applied to the 1.44-nm-diameter SWCNTs, because the purification process likely introduces many defects into SWCNTs and shortens them. On the other hand, in addition to the fact that the SWCNTs that were synthesized by using the eDIPS and SG methods did not undergo any purification process, these as-grown SWCNTs have been reported to be high-quality and long. Thus, the resistivity of the presently studied 1.44-nm-diameter SWCNT films was higher than that of the other, non-purified films.
On the other hand, $S$, and in particular its maximal value $S_{\text{max}}$, appeared to be relatively independent of the film quality (Fig. 2), and there was no correlation between $S_{\text{max}}$ and $\mu_{\text{max}}$. This behavior can be qualitatively understood by considering a junction model. Because the film consists of many SWCNTs and bundles of finite length, there are many inter-SWCNT and inter-bundle contacts that could significantly affect the bulk properties. For example, consider a serial model of $N$ segments with contacts. In this model, the temperature difference at each segment may be given by $-\Delta T/N$, where $\Delta T$ is an applied bulk temperature difference. Assuming the same Seebeck coefficient $s$ and resistance $r$ for each segment, it follows that the total Seebeck coefficient $S$ is independent of $N$, whereas the bulk resistance $R$ is proportional to $N$: $S\Delta T = Ns(\Delta T/N) = s\Delta T$ and $R = nR$.

A similar qualitative explanation is possible by using a parallel model, in which the conductivity is dominated by the number (fraction) of conducting paths, while the Seebeck coefficient is nearly independent of that number. Therefore, it is generally believed that the bulk resistivity is sensitive to the film quality but that the bulk Seebeck coefficient may not be.

From a theoretical viewpoint, however, the observed weak $D$-dependence of $S_{\text{max}}$ or the lack of a clear correlation between $S_{\text{max}}$ and $D$, is of significant interest because the s-SWCNTs are expected to exhibit $S_{\text{max}} \sim E_g/2 - E_0$, where $E_0$ is on the order of a few $k_B T$ and $E_g$ is the SWCNT energy gap. Similar behavior has been reported in GNRs, and is also true for s-SWCNTs, as will be shown later in Fig. 3. Thus, we expect that $S_{\text{max}}$ will double with reducing the diameter $D$ from 2.7 to 1.44 nm, because $E_g$ is nearly proportional to $1/D$.

The discrepancy between the above prediction and the observed weak $D$-dependence could result from m-SWCNT mixing in the films. Note that the m-SWCNTs exhibit much smaller $S$ values and much larger $1/R$ values than s-SWCNTs. In the present work, we examined this effect by using calculations with a parallel network model, because the presence of parallel networks drastically changes the film thermoelectric properties. (The results for a serial network model are shown in Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/9/025102/mmedia.) This model is a parallel network of semiconducting chains with $S_s$ and $\sigma_s$, and metallic chains with $S_m$ and $\sigma_m$, where $\sigma(S_s)$ and $\sigma_m(S_m)$ are the electrical conductance values (Seebeck coefficients) of the semiconducting and metallic chains, respectively. Given a fraction $\beta$ of metallic chains, the observed $S$ is given by the electrical conductance-weighted average, $S = [S_s(1-\beta)\sigma_s + S_m\sigma_m\beta]/[\sigma_s(1-\beta) + \sigma_m\beta]$, and the conductance $1/R$ is given by $1/R = \sigma_s(1-\beta) + \sigma_m\beta$. In the following, we used the values for s-SWCNTs and m-SWCNTs as $\sigma_s(S_s)$ and $\sigma_m(S_m)$, where $\sigma_s \ll \sigma_m$ and $S_s \gg S_m$ for simplicity.

The calculated results are shown in Fig. 3(a). We focused on the structures in the gap region [$|\mu| < 0.53$ eV for the (8,0) SWCNT and $|\mu| < 0.26$ eV for the (22,0) SWCNT] because the others mainly consist of contributions from sub-bands other than the highest valence and lowest conduction bands of the s-SWCNTs. The $S$ value of a pure s-SWCNT exhibits a linear dependence on $\mu$. However, adding m-SWCNTs strongly modifies this linear relationship. In particular, $S$ is significantly reduced around $\mu \approx 0$ (the central region of the semiconducting gap) owing to the electrical shortening of the s-SWCNTs by the m-SWCNTs with higher $\sigma_m (\gg \sigma_s)$. As a result, $\{S\}$ exhibits a peak above $\mu = -E_g/2$ (or below $\mu = E_g/2$). These peaks shift toward the gap edges with increasing the metallic content, as shown in Fig. 3(a), because the central region of the gap, which is shortened by the m-SWCNTs, is broadened with increasing the metallic content.

Next, we discuss the effects of the semiconducting gap width $E_g$ (or the diameter $D$) on the thermoelectric performance of the parallel model. The calculated results for $E_g = 0.79$ and 0.38 eV can be compared in Fig. 3. The maxima of $S_{\text{max}}$ for pure s-SWCNTs are proportional to the energy gap, $S_{\text{max}} \propto E_g/2 - E_0$. However, even a slight mixing with m-SWCNTs, ca. >0.1%, made the $\mu$-dependence almost identical. Thus, $S_{\text{max}}$ is independent of $D$ in the mixed films, reproducing the observed results shown in Fig. 3(a). This is because the semiconducting chains are significantly short-circuited by the metallic chains in the central region of $\mu \sim 0$ where $\sigma_m \gg \sigma_s$, and because $\sigma_s$ and $S_s$ around the band edges behave almost in the same way, irrespective of the energy gap. It is worthwhile to note that $\sigma_s$ is basically independent of the density of states (DOS), even at the band edges, and is therefore also independent of the $D$, owing to the mutual cancelation of contributions by the DOS and the group velocity originating from the one-dimensional nature of SWCNTs. Another important feature in Fig. 3(b) is that $R (=R_{\text{max}})$ at $S_{\text{max}}$ decreases with increasing the metallic content. This also captures the behavior shown in Fig. 2(b), in which the results for the natural film are compared with those for an enriched film of s-SWCNTs. The s-SWCNT film had a mass density of $m = 0.65-1.0$ g/cm$^3$, was doped with HNO$_3$, and...
was de-doped by heating.\textsuperscript{5}) Assuming that the resistance scales as $R = rN$ or $\log r = \log R - \log N = \log(R/N)$, the data for the natural film were shifted in the semi-logarithmic plot so that the $S$ at small $\rho$ was equal to that of the s-SWCNT film. From this plot, we find that Fig. 2(b) is consistent with the calculated $s_{\text{max}}$, which appears at a higher $R_{\text{max}}$ with s-SWCNT enrichment [Fig. 3(b)].

Figure 4 summarizes the measured power factor $P = S^2/\rho_0$. The natural films exhibit larger $P$ at smaller $\rho_0$ because $S$ has nearly the same magnitude and $P$ is inversely proportional to $\rho_0$. Such behavior sharply contrasts the theoretical predictions for pure SWCNTs, for which the maximal power factor $P_{\text{max}}$ for an s-SWCNT remains constant, irrespective of $D$ (semiconducting gap $E_g$), as shown in Fig. 3. This is because $P_{\text{max}}$ appears when $\mu$ is located just above (or below) the edge of the valance (or conduction) band top (or bottom), where $S$ and $\rho_0$ behave in the same way regardless of the band gap.

The effect of the m-SWCNT mixing on $P$ is crucial. The calculated $P_{\text{max}}$ substantially decreases with increasing the metallic content, and is independent of the diameter and of the semiconducting gap [see Fig. 3(b)]. For example, a mixing of 30% m-SWCNTs reduces $P_{\text{max}}$ to one-third of the value for pure s-SWCNTs, in agreement with the experimental results for 1.44-nm-diameter SWCNTs shown in Fig. 4.

Finally, we evaluated a possible enhancement of $P_{\text{max}}$. Because it demonstrated the highest performance we had yet obtained, we considered a high-purity s-SWCNT film with a bulk density of $\sim 0.8 \text{ g/cm}^3$, $S_{\text{max}} = 170 \mu\text{V/K}$, and $P_{\text{max}} = 0.125 \text{ mW/(m-K)}^2$ as the starting film for this evaluation. The film was prepared from ArcSO grade SWCNTs, and its resistivity was nearly equal to that of the presently considered natural film of 1.44-nm-diameter SWCNTs, so we anticipated the possibility of improving the film resistivity to obtain even higher $P$. In reality, this should be achievable by making s-SWCNTs and/or s-SWCNT bundles with the same degree of length and defects as those of the non-purified eDIPS samples. This should decrease the resistivity by a factor of $\sim 10$ (see Fig. 4), leading to $P_{\text{max}} = 1.25 \text{ mW/(m-K)}^2$. Furthermore, if the SWCNT density is increased to $1.3 \text{ g/cm}^3$, we can expect further enhancement of $P_{\text{max}}$. Assuming the conductivity to be proportional to the density, we obtain $P_{\text{max}} = 2.0 \text{ mW/(m-K)}^2$.

Further improvement can be expected from aligning the SWCNTs in the films. We note that the bulk resistivity, even in high-quality SWCNT mats, in which the contact contributions can be ignored, may be 20 times larger than that of an individual bundle owing to the tortuosity effect of the bundles.\textsuperscript{21}) Therefore, aligned high-quality s-SWCNT films, in which the tortuosity effect is weaker, are likely to yield $P = 40 \text{ mW/(m-K)}^2$. This is much larger than the typical values for commercial BiTe materials. On the other hand, the figure of merit $ZT = S^2T/(\rho\kappa)$ would not substantially depend on the sample morphology or on the SWCNT length because both the electrical and thermal conductivity, $1/\rho$ and $\kappa$, may vary in a manner similar to the film quality, so that the product $\rho\kappa$ remains nearly constant. Actually, $\rho$ and $\kappa$ have been demonstrated to be independent of the sample morphology in aligned and non-aligned SWCNTs.\textsuperscript{22})

In conclusion, the present experiments and theoretical simulations strongly suggest that the maximal power factor based on carrier doping can be improved threefold through the enrichment of semiconducting SWCNTs, but changing the SWCNT diameter has little effect. Furthermore, it is suggested that the improvement of film resistivity critically affects the ability to achieve higher performance. Furthermore, we found that environmental humidity causes p-type doping by a mechanism that will be clarified in future systematic investigations.

Acknowledgments

Experiments with the s-SWCNT films were conducted by Mr. K. Honda. This work was supported in part by JSPS KAKENHI Grant Numbers 24681021, 25800201, 25104722, 25246006, 15K04601, 15K13523, and 15K17738. This research was also supported by the Murata Science Foundation and the Foundation Advanced Technology Institute.

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