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Temperature dependence of the Seebeck coefficient for mixed semiconducting and metallic single-wall carbon nanotube bundles

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The temperature (T) dependence of the Seebeck coefficient (S) for single-wall carbon nanotube (SWCNT) bundles was systematically investigated as a function of the chemical potential (μ) through theoretical simulations employing non-equilibrium Green's function theory. The bundles were modeled as laterally aligned parallel circuits of semiconducting and metallic SWCNTs. The T dependence of S varied substantially with μ and with metallic SWCNT content. The calculated results semi-quantitatively reproduced the typical behavior observed experimentally for SWCNT films with chemical doping reported previously. © 2019 The Japan Society of Applied Physics

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Single-wall carbon nanotubes (SWCNTs) are flexible and lightweight thermoelectric materials that exhibit high thermoelectric performance.^{1–18} In bulk SWCNTs, a thermoelectric power factor (P) of as much as $2000 \mu\text{W m}^{-1} \text{K}^{-2}$ has been reported,⁴ which is almost the same magnitude as that for commercial Bi–Te systems. However, the non-dimensional figure of merit ZT values are much smaller than those for Bi–Te systems. The thermoelectric properties may be enhanced by improving the hierarchic structures of the SWCNT films because bulk SWCNT films are usually composed of many randomly entangled bundles.^{1,2,19} Each bundle consists of many SWCNTs with different structures, characterized by the chiral index (n, m) with integers n and m . Therefore, the macroscopic thermoelectric properties of the bulk are expected to be determined not only by the intrinsic properties of individual SWCNTs but also by such hierarchic structures.

A previous study¹⁸ has suggested that the Seebeck coefficient (S) for SWCNT films is almost entirely determined by the bundles in the films, where each bundle was modeled as laterally aligned parallel circuits of semiconducting (s-) and metallic (m-)SWCNTs. The absolute value of S obtained from experiments conducted at room temperature was reproduced well by calculations. In this study, we examined the temperature (T) dependence of S for bundles in order to obtain a deeper understanding of S in SWCNT films.

The intrinsic conductance (G) and S for individual SWCNTs were calculated for the same model as described in previous reports.^{11,12,18} Rolled-up structures of graphene ribbons with a carbon–carbon bond length of 0.142 nm were used as SWCNT structures without any geometry optimization. As in previous studies,^{18,20} we calculated the transmission function for carriers with an energy ε , $\zeta(\varepsilon)$, by the non-equilibrium Green's function method and extended Hückel theory, using the software Atomistix ToolKit (ATK) developed by Quantum Wise Ltd. (www.quantumwise.com). The empirical potentials, so-called Cerda.Carbon [graphite] in the ATK software (<http://quantumwise.com/documents/manuals/ATK-2014/ReferenceManual/index.html>), were used in the Hückel basis set with a 0 eV vacuum level. The calculations were carried out for several electron temperatures (T) between 50 K and 500 K.

It is known that S has two contributions: (i) a ballistic contribution, which is related to the energy dependence of the electron density of states (DOS) and (ii) a diffusive contribution, which is related to the energy dependence of the diffusion coefficient.^{14,21,22} We assumed that in the present calculations the ballistic contribution dominates the observed values. This assumption may be suitably applied to s-SWCNTs at high temperatures because a relatively large contribution from the ballistic term is expected in the present doping regime. Indeed, the S values for SWCNT films at ~ 300 K were well reproduced by the ballistic term.¹⁸

In the Landauer theory of electronic transport,^{23,24} G and S are given by

$$G = K_0, \text{ and } S = \frac{1}{qT} \frac{K_1}{K_0}, \quad (1)$$

where K_n is defined as

$$K_n = q^2 \frac{2}{h} \int (\varepsilon - \mu)^n \zeta(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon} \right) d\varepsilon. \quad (2)$$

Here, q , h , and f are charge of the carriers, Planck's constant, and the Fermi-Dirac distribution function, respectively μ , which is the chemical potential of the system, can be experimentally controlled by carrier doping.^{6,7,11–13} In the present paper, we focus on the “lightly hole-doped” regime of $-0.8 < \mu < -0.2$ eV. However, it should be noted that the behavior in the “lightly electron-doped” regime would be essentially the same owing to the nearly symmetric band structures of SWCNTs for hole and electron doping.

The power factor (P) is usually defined as

$$P = S^2 \sigma, \quad (3)$$

where σ is the electrical conductivity. However, P in the present paper is defined instead as

$$P = S^2 G, \quad (4)$$

where S and G are the Seebeck coefficient and the electrical conductance G for individual SWCNTs, respectively. This is the power factor per SWCNT.



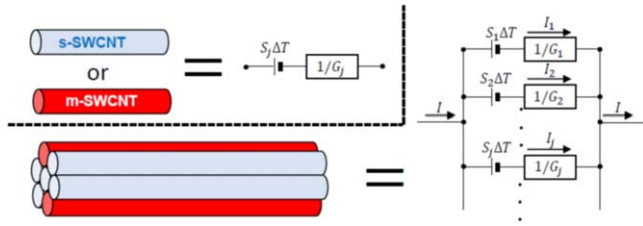


Fig. 1. (Color online) Illustration of an SWCNT bundle and its equivalent parallel circuit. S_j and G_j are the Seebeck coefficient and electrical conductance of the j th SWCNT in the bundle, respectively, and ΔT is a temperature difference applied to the bundle.¹⁸⁾

Next, using the results for the individual SWCNTs, laterally aligned parallel circuits of SWCNTs¹⁸⁾ as illustrated in Fig. 1, with an m-SWCNT content β , were calculated. When there are two channels in parallel due to s-SWCNTs and m-SWCNTs, the K_n ($n = 0$ or 1) value for the circuit is given by $K_n = \beta K_n^m + (1 - \beta) K_n^s$, where the superscripts m and s denote the contributions from m-SWCNTs and s-SWCNTs, respectively. Thus, the corresponding Seebeck coefficient for the circuit can be expressed as

$$S = \frac{1}{qT} \frac{\beta K_1^m + (1 - \beta) K_1^s}{\beta K_0^m + (1 - \beta) K_0^s} = \frac{\beta S_m (G_m/G_s) + (1 - \beta) S_s}{\beta (G_m/G_s) + (1 - \beta)}, \quad (5)$$

where $S_{m(s)}$ and $G_{m(s)}$ are the Seebeck coefficient and the electrical conductance for the individual intrinsic m(s)-SWCNT, respectively. The power factor P for the circuit is defined by Eq. (4) in the present paper. β is given by $\beta \equiv N_m/(N_m + N_s)$ where N_m and N_s are the numbers of m- and s-SWCNTs in the circuit, respectively.

First, we present the T dependence of S and G for an s-SWCNT with a chiral index (8, 0) and for an m-SWCNT with a chiral index (5, 5) in the lightly hole-doped region, $-0.8 < \mu < -0.2$ eV, for several temperatures between 50 K and 500 K.

The results for the individual (8, 0) s-SWCNT are shown in Fig. 2(a). The top of the valence band is located at $\mu = \mu_0 \approx -0.526$ eV. It is found that G and S exhibit metallic and semiconducting behavior for $\mu < \mu_0$ and $\mu > \mu_0$, respectively. For example, S and $1/G$ increase with decreasing T when μ is located in the semiconducting band gap, $-(\sim k_B T) > \mu > \mu_0$. More specifically, the T dependence of S varies as $S \approx S_0 - (\mu - \mu_0)/(qT)$, where S_0 is a constant depending on $\zeta(\varepsilon)$ around the band edge, $\varepsilon \approx \mu_0$. This is a well-known behavior established in previous studies.^{17,18,21,22)} On the other hand, S and G become metallic when μ is located within the valence band, $\mu < \mu_0$; S decreases and G approaches the value for m-SWCNTs with decreasing temperature.

The results for the individual (5, 5) m-SWCNTs are shown in Fig. 2(b). G is almost independent of T because the present calculation was performed in the ballistic regime. G is also independent of μ in the present μ region because of the assumption of ballistic transport. S decreases monotonically with decreasing T , i.e., it shows metallic behavior. However, its magnitude is substantially smaller than that for s-SWCNTs. This is expected on the basis of the Mott formula, which can be applied to metals: $S = \frac{\pi^2 k_B^2 T}{3q} \frac{d \ln G(\mu)}{d\mu} \approx 0$. Thus, in the case of m-SWCNTs, the diffusive contribution to S might be important.

Next, we present the results for parallel circuits consisting of (8, 0) s-SWCNTs and (5, 5) m-SWCNTs. The results for $\beta = 5\%$ and 30% are presented in Fig. 3(a). (The results for thick SWCNT circuits consisting of (22, 0) s-SWCNTs and (13, 13) m-SWCNTs are shown in Supplementary Data is available online at stacks.iop.org/APEX/13/015001/mmedia.) The results for $\beta = 0\%$ and 100% are essentially the same as those for the individual (8,0) s-SWCNTs and (5, 5) m-SWCNTs, respectively, which are shown in Fig. 2.

As expected, G for $\beta = 5\%$ and 30% increases with decreasing temperature for $\mu < \mu_0$ within the valence bands and decreases for μ within the band gap $-(\sim k_B T) > \mu > \mu_0$ because it is dominated by the T dependence for the s-SWCNTs. However, the values at the lowest temperatures remain finite in all cases because G is limited by the metallic value for the s- and m-SWCNTs.

On the other hand, the $S(T)$ of the mixed parallel circuits is quite different from those of the pure s-SWCNT circuits. While the $S(T)$ of individual s-SWCNTs monotonically increases with decreasing temperature for $-(\sim k_B T) > \mu > \mu_0$, as shown by the dashed lines in Fig. 2(a), those in the mixed circuits are seen to show different behaviors depending on μ , and to exhibit a peak. The $S(T)$ of the mixed circuits monotonically decreases with decreasing temperature at low temperatures, as explained by Eq. 5 for S of the mixed circuits. Because G_s steeply decreases with decreasing temperature while G_m and S_m are nearly constant, $S(T \rightarrow 0) \sim S_m$ for $\beta \neq 0$.

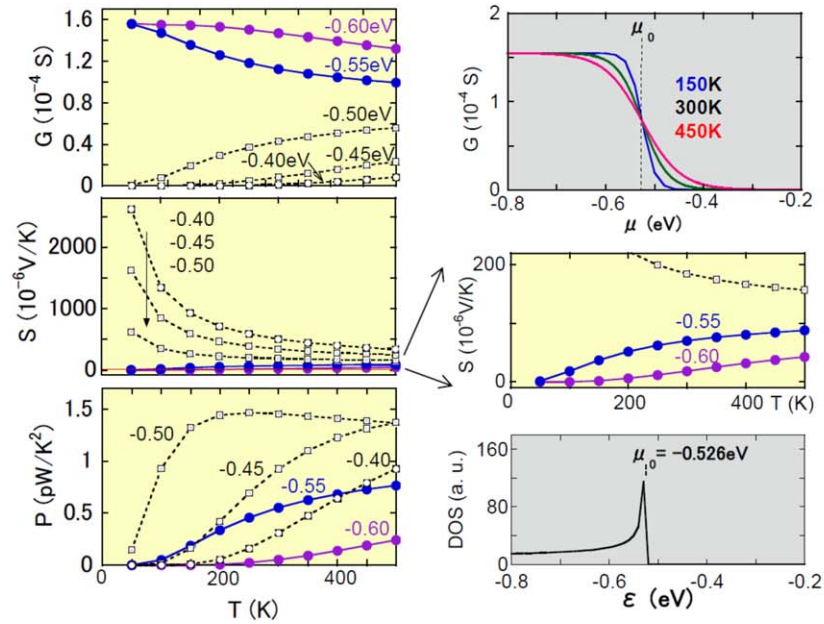
The peak seen in the S - T relationship moves to higher temperature as μ is reduced to the top of the valence band, $\mu = \mu_0$. The peak also moves to higher temperature with increasing m-SWCNT content, β . Such behavior is easily deduced from Fig. 3(b), where S is plotted as a function of μ for T values of 100 K, 300 K, and 500 K, and is seen to exhibit a peak. This can be inferred from the approximate form for $S(\mu)$: $S(\mu) \approx [(1 - \beta)/\beta] S_s (G_s/G_m)$, which can be obtained for $G_s/G_m \ll 1$ and $S_m \approx 0$ in Eq. (5). Because $S_s(\mu) \approx S_0 - (\mu - \mu_0)/(qT)$, and $G_s/G_m \propto G_s \propto \exp[-(\mu - \mu_0)/(k_B T)]$, it is found that the $S(\mu)$ peak moves to higher μ values with increasing T . Thus, for appropriate μ values, $S(T)$ exhibits a peak in the specific T range we examine. In Fig. 3(b), for example, a peak appears around 300 K for $\mu = \mu_2$.

Figure 3(b) also shows the power factor, $P(\mu)$. It is seen that the $P(\mu)$ and $S(\mu)$ maxima are both independent of temperature. However, the μ values where the maxima appear increase with temperature.

The calculation results can be compared with the experimental results for SWCNT films with chemical doping.⁶⁾ Figure 4(a) shows the T dependence of S for films enriched with s-SWCNTs. The nominal m-SWCNT content, β , was lower than 5%. It is well known that pristine films are already p-type. Further p-type doping was achieved chemically using HCl, H₂SO₃, and HNO₃, whereas annealing in vacuum led to de-doping, as shown in Fig. 4(d). Upon p-type doping, the film resistivity (ρ) decreases and S exhibits a peak corresponding to the change in μ . The S - ρ relationship has been well established in previous studies.^{11,18)}

The calculation results are shown by solid lines in Fig. 4(b) for fixed μ values. We found that the typical behavior observed for the annealed and pristine films in the upper panels is semi-quantitatively reproduced by calculation with

(a) (8,0) s-SWCNT



(b) (5,5) m-SWCNT

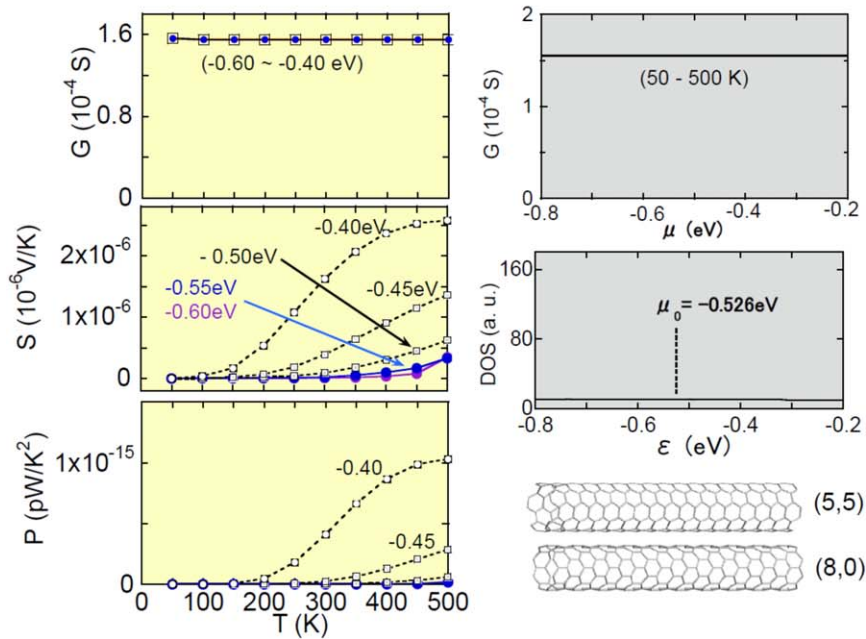


Fig. 2. (Color online) The T dependence of G , S , and P for individual SWCNTs for μ values between -0.8 and -0.2 eV. Squares with dashed lines and circles with solid lines are for $\mu > \mu_0$ and $\mu < \mu_0$, respectively, where the top of the valence band for (8, 0) s-SWCNTs is located at $\mu = \mu_0 = -0.526$ eV. (a) shows results for (8, 0) s-SWCNTs, and (b) for (5, 5) m-SWCNTs. The G of (5, 5) m-SWCNTs is almost independent of T and μ in (b). The third and second panels on the right of (a) and (b), respectively, show the electron DOS as a function of ϵ . The bottom panel on the right of (b) shows schematics of (5, 5) and (8, 0) SWCNTs.

$\mu = -0.40$ eV and $\mu = -0.45$ eV, respectively. The results for the chemically doped films are also semi-quantitatively reproduced by calculation using $\mu = -0.55$ eV for the HCl film and $\mu = -0.60$ eV for the H_2SO_4 film (and the HNO_3 film). It is important to note that the μ value used in the calculations consistently decreases with additional p-type doping or decreasing ρ , as shown in Fig. 4(d). Similarly, the β dependence is reproduced well by the calculations (see Fig. 5). Therefore, the overall behaviors observed experimentally, such as the absolute values for S at room temperature and qualitative T dependence of S for different μ and β values, were reproduced well by the present calculations.

Recently, it was reported that $S(T)$ decreases with decreasing temperature irrespective of the carrier density or the Fermi level examined in high purity s-SWCNT samples.²⁵⁾ It might have failed to reproduce observations of the intrinsic behaviors for $S_s(T)$ as shown by the dashed lines in Fig. 2(a) for $\mu > \mu_0$. This suggests the possibility of substantial effects which are related to impurity states and low metallic component inclusion in the samples.

Further inspection of Figs. 4 and 5, however, reveals that the experimental S values are substantially larger than the calculated values at low temperatures. This implies that S may be enhanced at low temperatures. There are several

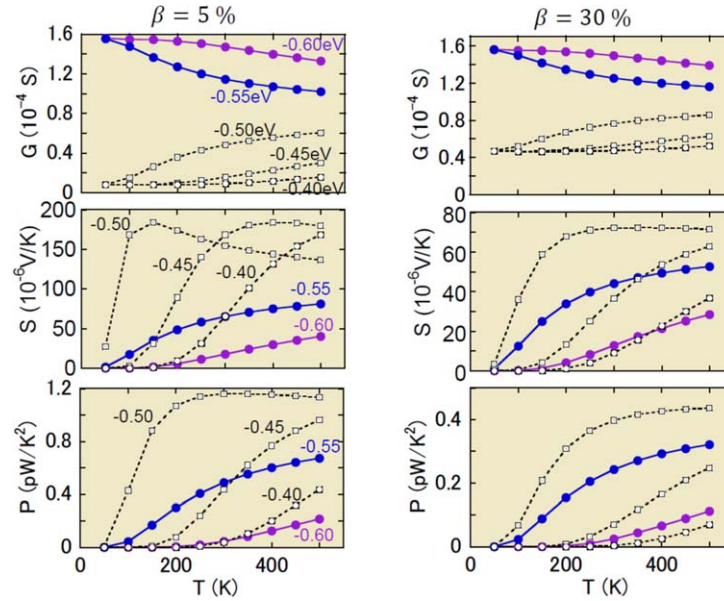
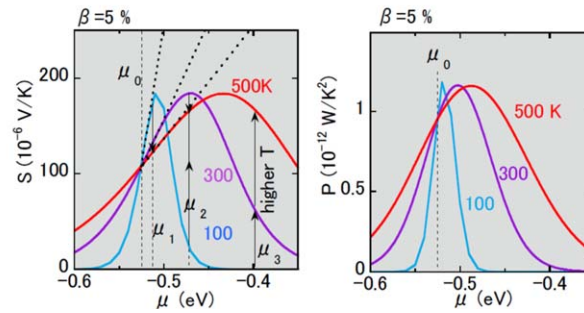
(a) T dependence of the mixed circuits(b) μ dependence of the mixed circuits

Fig. 3. (Color online) (a) T dependence of G , S , and P for mixed parallel circuits of (8, 0) s-SWCNTs and (5, 5) m-SWCNTs with μ values between -0.60 and -0.40 eV. Left: $\beta = 5\%$. Right: $\beta = 30\%$. (b) μ dependence of S and P for $T = 100$ K, 300 K, and 500 K. The thick dotted lines indicate $S(\mu) \propto S_0 - (\mu - \mu_0)/qT$. It is found that S shows a different T dependence below 500 K for $\mu = \mu_0$, μ_1 , μ_2 , and μ_3 : S is T -independent for μ_0 , decreases monotonically for μ_1 , attains a maximum at 300 K for μ_2 , and increases monotonically for μ_3 with rising temperature from 100 K to 500 K.

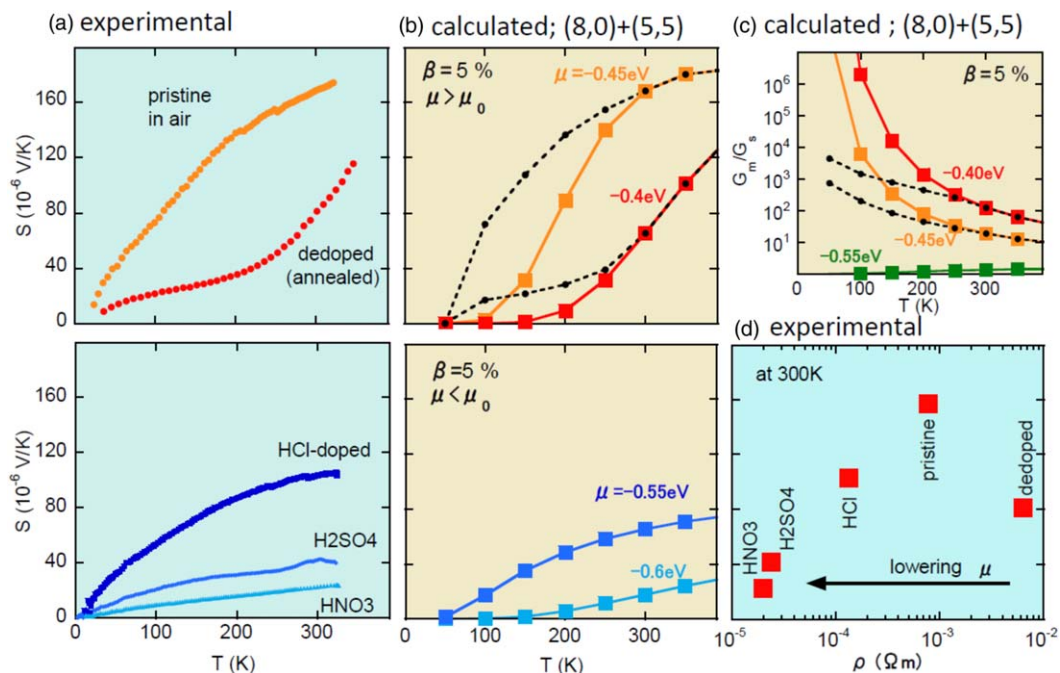


Fig. 4. (Color online) Comparison of (a) experimental results from Ref. 6 and (b) calculation results. Experiments were performed on s-SWCNT-enriched films. (c) G_m/G_s as a function of T . Solid lines are calculated values; dashed lines were used in order to reproduce experimental results. (d) S versus ρ at 300 K from the experiments.⁶⁾ With p-type doping or decreasing μ , ρ decreases monotonically while S exhibits a peak. In the calculations, (b) and (c), β was assumed to be 5% .

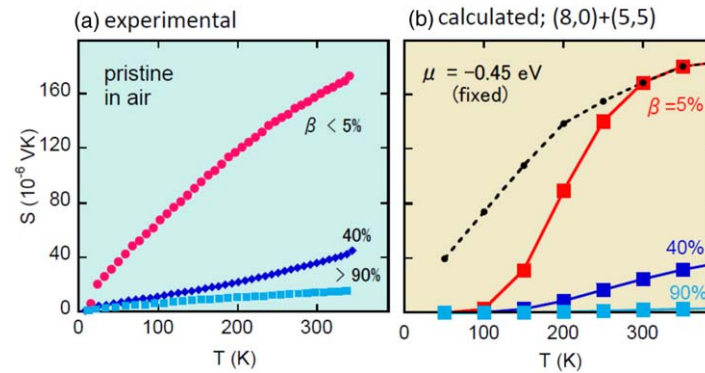


Fig. 5. (Color online) Comparison of experimental results taken from Ref. 6 (a) and calculated results (b). The dashed line in (b) shows S corrected by G_m/G_s , as represented by the dashed line in Fig. 4(c).

possible causes for this. Equation (5) indicates that S depends on the ratio G_m/G_s . Thus, the deviation in G_m/G_s from the calculations at low temperatures may be one possible cause. If it is assumed that the T dependence of G_m/G_s is much weaker than that for the calculated results, as suggested by the dashed lines in Fig. 4(c), the observed S is reproduced well by the calculations using the corrected values for G_m/G_s , as shown by the dashed lines in Fig. 4(b). The deviation of G_m/G_s from the calculated values may also be due to significant elastic and inelastic electron scattering,^{26,27} electron localization effects,²⁸ or the SWCNT–SWCNT junctions. It appeared that the corrected G_m/G_s obtained from the present analysis may be much lower than the values for the ballistic regime at low temperatures.

The enhancement of S at low temperatures may also stem from a diffusive contribution to S , a phonon drag effect,²⁹ inhomogeneity of the SWCNT diameter and the doping level, and a bundle effect or deviation from the one-dimensionality of the electronic states in SWCNTs. Further discussion on this issue, including T dependence of μ , is left for future study.

In conclusion, it was found that the T dependence of S in mixed s- and m-SWCNT films could be semi-quantitatively explained by a bundle model of parallel circuits of s- and m-SWCNTs. Calculations for the parallel model demonstrated that a low proportion of m-SWCNTs modifies substantially the T dependence of S from that of ideal pure s-SWCNT bundles. The highest values for S and P in a mixed film appeared at different doping levels, μ , depending on the temperature, while the maximum values showed little dependence on temperature. It also appeared that S is greatly enhanced at low temperatures.

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